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Polymers of the Vinyl Esters of Perchlorocyclopentadiene Adducts of Petroselinic and Oleic Acids

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Synopsis

Homopolymers of vinyl 5-(1,4,5,6,7,7-hexachloro-3-undecylbicyclo[2.2.1]5-hepten-2-yl)-pentanoate and vinyl 8-(1,4,5,6,7,7-hexachloro-3-octylbicyclo[2.2.1]5-hepten-2-yl)-octanoate were prepared, as well as their copolymers with a vinyl tetrahydroabietate–tetrahydropimarate mixture, vinyl 12-hydroxystearate, and vinyl chloride. The vinyl octanoate–12-hydroxystearate copolymer gave light-weight urethane foams with practically no volume change upon humid aging. The vinyl pentanoate and vinyl octanoate monomers lose hydrogen chloride during polymerization. The vinyl pentanoate homopolymer was hydrolyzed in an attempt to establish the position of the loss of hydrogen chloride. Fractionation of vinyl chloride copolymers of the vinyl petanoate and the vinyl octanoate derivatives showed that they possessed a rather homogeneous composition. Incorporation of the vinyl pentanoate monomer in a poly(vinyl chloride) copolymer imparted some internal plasticization with serious loss of tensile strength.

INTRODUCTION

The Agricultural Research Service of the U.S. Department of Agriculture has been sponsoring research at the University of Arizona for several years aimed at extending the utilization of agricultural commodities. One phase of this program has involved new oilseed crops. The work described here is based on the acid obtained from the oilseed of a family of plants known as *Umbelliferae*. A unique feature of the oilseed of these plants is that it is, with very few exceptions, the only known large-scale (30–75%) source of petroselinic acid (*cis*-6-octadecenoic acid).[1] The isolation of petroselinic acid, the preparation of its adduct with perchlorocyclopentadiene, and the preparation of the vinyl ester of the acid adduct has been described elsewhere.[1,2] Although oleic acid is also found in the oilseeds of these plants, the oleic acid used in this work did not come from this source.

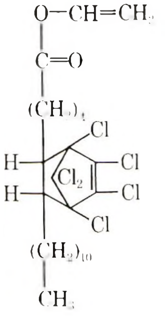
In the work undertaken to prepare polymers with useful properties from the vinyl esters of the perchlorocyclopentadiene adducts of petroselinic and oleic acids, two specific objectives were pursued. One involved the extention of earlier studies[3,4] of the effect of the type, number, and location of chlorine atoms in the fatty acid portion of vinyl ester, upon the plasticization efficiency in internally plasticized poly(vinyl chloride). The other involved preparation of chlorine-containing polyols for subsequent rigid polyurethane foam work.

RESULTS AND DISCUSSION

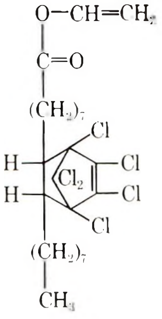
Monomers

Samples of the monomers were provided by the Oilseed Crops Laboratory of the Southern Utilization Research and Development Division of the Agricultural Research Service. The vinyl ester of perchlorocyclopentadiene adducts of petroselinic acid, vinyl 5-(1,4,5,6,7,7-hexachloro-3-undecylbicyclo[2.2.1]5-hepten-2-yl)-pentanoate (VSP), and of oleic acid, vinyl 8-(1,4,5,6,7,7-hexachloro-3-octylbicyclo[2.2.1]5-hepten-2-yl)-octanoate (VSO), were supplied as hydroquinone-stabilized oils. Both materials were chromatographed on a silica gel (Silica Gel, plain; Research Specialties Co.; Richmond, Calif.) column with 4% anhydrous ethyl ether–hexane (Phillips, 99.3% pure) mixture as eluent before use. Some of the physical properties on the chromatographed materials are listed in Table I.

The chromatographed VSP was obtained as a translucent (hazy) liquid. The hazy appearance could not be dissipated by heating the liquid up to 160°C. in an open test tube. Thin-layer chromatography (TLC) on silica gel with 2% ethyl ether–hexane as eluent showed only one spot. TLC on



VSP



VSO

TABLE I
Physical Properties of VSP and VSO

	VSP	VSO
Appearance	Hazy, very light yellow-colored oil	Light yellow-green-colored oil
B.P.	>210°C./0.05 mm.	—
n_D^{29}	1.5025	1.5108
d_4^{24}	1.216	—
δ (solubility parameter)	9.6	—

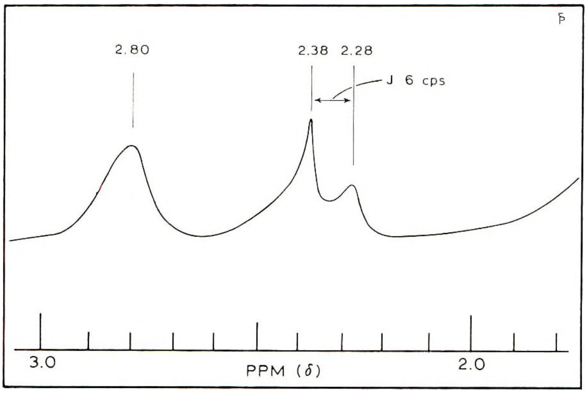


Fig. 1. Portion of NMR spectrum of VSP.

silver nitrate-treated silica gel[5,6] also produced only one spot, but it was more elongated than on the plain silica gel. A portion of the observed NMR spectrum is given in Figure 1. The vinyl, methyl, and methylene proton resonances appeared at the expected places (quartets at 7.16–7.50 and 4.48–4.97; doublet at 0.90–1.00, and a large peak at —1.25–1.80 ppm, respectively). A peak at 2.80 ppm was due to *cis*-$\overset{|}{\mathrm{C}}\mathrm{H}—\overset{|}{\mathrm{C}}\mathrm{H}—$ in the bicyclic ring. The large downfield shift for this type of protons was due to the deshielding effect of $>\mathrm{C}—\mathrm{Cl}_2$ and the double bond in the bicyclic ring. The doublet ($J = 6$ cps) at 2.28 and 2.38 is due to the two protons α to the carbonyl. Absence of other absorptions indicates the presence of very little if any other isomeric materials.

As VSP was intended to be used in internal plasticization of poly(vinyl chloride) (PVC) it was of interest to know its solubility parameter σ for compatibility considerations. The estimation of σ was done according to the proposal of Small from the molar-attraction constants, structural formula, and density. The σ of VSP turned out to be 9.6, which is about the same as that for PVC (9.5).

The chromatographed VSO did not have the hazy appearance, and TLC on silica gel showed only one spot. However, the monomer was dark tan in color.

Homopolymerization

VSP Homopolymers. Homopolymerization was conducted in three systems: bulk, solution, and emulsion. The experimental data are given in Table II. The polymers from the three systems were obtained as semiglassy yellow-green solids possessing no noteworthy adhesive properties. The low inherent viscosities, even for a vinyl ester, are probably due to the chain-transfer activity of the tertiary hydrogen atoms and/or chlorine atoms.

TABLE II

VSP and VSO Homopolymers and Copolymers[a]

System	Comonomer[b]	Comonomer charged, wt.-%	Catalyst, phm[c]	Polymerization time, hr.	Conversion, %	Ester, %[d]	η_{inh}[e]	Calculated			Found		
								C, %	H, %	Cl, %	C, %	H, %	Cl, %
VSP homopolymerization													
Bulk	—	—	10	48	55	—	0.05	53.27	6.36	34.62[f]	53.14	6.71	34.60
17% solution, benzene	—	—	10	48	83	—	0.04	52.90	6.33	35.02[g]	52.80	6.49	34.64
Emulsion[h]	—	—	10	48	45	—	0.05	—	—	—	—	—	—
Emulsion[i]	—	—	10	48	~100	—	0.11	52.24	6.33	35.81[j]	52.47	6.49	35.45
VSP copolymerization													
Emulsion[i]	VCl	90	5	48	96	14	0.56	40.39	5.06	53.75	40.18	5.03	53.62
"	"	80	5	48	95	21	0.57	41.37	5.17	52.27	41.51	5.27	52.12
"	"	70	5	48	86	31	0.52	42.68	5.34	50.14	42.83	5.46	50.03
"	"	60	5	48	80	41	0.42	44.18	5.51	48.00	44.07	5.59	47.91
"	"	50	5	48	75	53	0.36	45.87	5.70	45.46	46.17	5.72	45.58
Emulsion[i]	VTA	78	5	53	74	21	0.10	74.03	9.94	7.69	74.37	10.03	8.18
"	"	63	5	53	60	36	0.07	69.94	9.29	12.76	70.12	9.31	12.87
"	"	47	5	53	34	46	0.06	67.21	8.85	16.31	67.37	8.89	16.06
29% solution, benzene	VHS	10	5	48	70	11	0.09	71.29	11.14	3.81	71.41	10.95	3.94
"	"	20	5	48	53	23	0.08	68.79	10.52	7.97	68.58	10.45	7.70
"	"	40	5	48	50	43	0.05	64.64	9.48	14.89	64.81	9.50	14.81

VSO homopolymerization												
Bulk	—	—	7.5	48	25	—	0.05	51.78	6.23	35.43[j]	51.54	6.16	35.18
25% solution, benzene	—	—	7.5	48	20	—	0.04	51.57	6.21	35.60[k]	51.17	6.02	35.06
Emulsion[i]	—	—	8.0	48	25	—	0.04	50.96	6.18	36.15	51.21	6.05	36.37
Emulsion[i,l]	—	—	10.0	48	62	—	0.07	—	—	—	—	—	—
VSO copolymerization												
Emulsion[i]	VCl	80	8	25	84	21	0.45	41.11	5.09	52.46	41.15	5.18	52.83
"	"	70	8	25	88	30	0.37	42.26	5.19	50.62	41.85	5.18	50.19
"	"	60	8	25	82	35	0.31	42.90	5.26	49.61	43.04	5.34	49.62
20% solution, benzene	VHS	60	10[m]	48	19	35	0.05	59.03	8.04	23.64	58.73	8.25	23.81
Emulsion[i]	"	60	10[m]	48	55	41	0.09	64.40	9.40	14.91	64.76	9.34	15.34

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[a] All of the polymerizations were conducted at 60 ± 2°C. by tumbling the tubes end-over-end.

[b] Comonomers: VCl = vinyl chloride; VTA = vinyl tetrahydroabiate–vinyl hydropimarate; VHS = vinyl 12-hydroxystearate.

[c] Diethyl azobisisobutyrate (DEABIB), parts per 100 parts monomer (phm).

[d] By weight, based on %C, %H, and %Cl in the copolymer.

[e] Determined on solutions from 0.187 to 0.483 g./100 ml. of tetrahydrofuran at 30.3°C.

[f] Calculated for a repeating unit which has lost 50% of HCl.

[g] Calculated for a repeating unit which has lost 40% of HCl.

[h] ORR soap (a mixture of sodium salts of stearic, palmitic, and oleic acids); no conjugated dienes and silicates present; batch was buffered to pH 7.0.

[i] Siponate DS-10 (alkyl-substituted benzene sodium sulfonate); the batch was buffered to pH 7.0.

[j] Calculated for a repeating unit which has lost 20% of HCl.

[k] Calculated for a repeating unit which has lost 15% of HCl.

[l] Used twice-chromatographed monomer.

[m] Azobisisobutyronitrile (AIBN) was the catalyst.

Buffering of the batch to pH 7.0 improved the conversion considerably. Because of the bulky size and the hydrophobic nature of the monomer, soaps gave poor emulsions. An alkyl-substituted benzene sulfonate detergent was a much better emulsifier in this particular case. Use of a water-soluble initiator, or a mercaptan-water-soluble initiator combination gave only a trace of the polymer. Of the four oil-soluble initiators investigated, diethyl azobisisobutyrate gave the best results. A relatively high initiator level (10%) was necessary to obtain reasonable conversions. Lower levels gave lower conversions.

The solubility characteristics of the homopolymers were as shown in Table III. The σ for tetrahydrofuran was calculated by using the method of Small;[7] the other values were obtained from Burrell.[8] Except for tetrahydrofuran, the solubilities were what one would expect from the compatibility σ relationship.[9]

TABLE III

Solvent	δ	Solubility of homopolymers
Tetrahydrofuran	7.4	Soluble
Benzene	9.2	Soluble
Cyclohexanone	9.9	Soluble
Nitrobenzene	10.0	Insoluble
N,N-Dimethylacetamide	10.8	Insoluble
Acetonitrile	11.9	Insoluble

Analytical data on the polymers were unexpected. The chlorine content in bulk and solution homopolymers was about 2.0% lower than calculated and in emulsion homopolymer 1.15% lower. The lower chlorine content in the emulsion homopolymer was not due to unremoved emulsifier or buffer salts as the polymer was checked for these and no sulfur or residue was found. Furthermore, the greater chlorine loss occurred in the bulk and solution runs.

The NMR spectra on the homopolymers showed a minor peak around 2.00 ppm, indicating the presence of $-CH_2-\overset{|}{C}=\overset{|}{C}-$. The relevant portions of the spectra of the monomer and emulsion homopolymer are given in Figure 2. The doublet at *a* is due to protons α to the carbonyl, shifted to higher field in the homopolymer because of the loss of the deshielding effect of the vinyl ester double bond. The minor peak at *b* indicates the presence of $-CH_2-\overset{|}{C}=\overset{|}{C}-$. Unfortunately the integration curve in the area of this peak was smooth, and thus no quantitative estimate of the amount of this structure could be made.

Acid Hydrolysis of VSP Homopolymer. In an attempt to learn more about the structure of the low chlorine content material, a sample of the emulsion homopolymer was submitted to hydrolysis. To minimize side

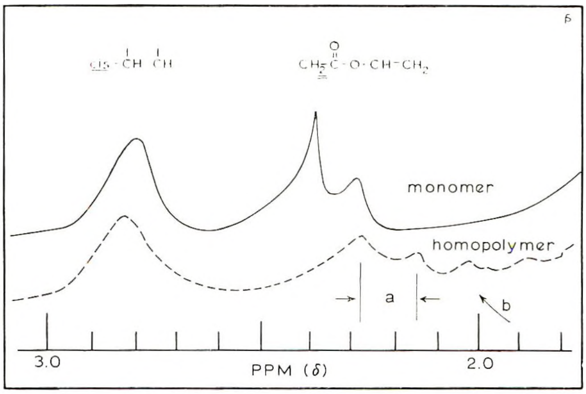

Fig. 2. Portions of NMR spectra of VSP and its homopolymer.

reactions during hydrolysis, we resorted to acidic (anhydrous hydrogen chloride in absolute methanol) hydrolysis conditions. The hydrolysis reaction mixture was chromatographed on silica gel and a fraction which, by infrared (carbonyl at 1740 cm.$^{-1}$ indicated saturated ester absorption; absorption at 1600 cm.$^{-1}$ indicated internal unsaturation) and NMR (the signal at 3.6 indicated $COOCH_3$ and integration showed 3 protons), appeared to be the methyl ester, was isolated. TLC of the ester on silica gel showed only one spot. Vapor-phase chromatography also showed only one peak, which, however, was quite broad. Analysis of the ester gave a chlorine content which was 1.4% low; this was expected because the parent polymer was 1.2% low in chlorine content. Mass spectral examination of the hydrolysis product, however, has not been conclusive as to its composition.

VSO Homopolymers. The polymers from the three systems were isolated as brown-colored viscous masses with no noteworthy adhesive properties. The conversions and inherent viscosities were much lower than for the VSP polymers. Although a chromatographed material was used, it is still possible that some impurity active in chain transfer was present. The analytical data on the once-chromatographed monomer showed a chlorine content only 0.45% lower than the calculated value. The solubility characteristics of the VSO homopolymers were the same as those of VSP homopolymers.

The analytical data on the three homopolymers again indicated a chlorine loss upon polymerization, however, smaller than with VSP (bulk 1.42% lower; 2.0% for VSP). The bicyclo ring is three methylene units further away from the carbonyl in VSO than in VSP. Assistance from another point in the VSP molecule may then be responsible for the higher chlorine loss in VSP.

Thermal Stability of VSP and VSO Homopolymers. Heating a film of the homopolymers on a hot plate above 300°C. produced a steady loss in the weight of the films. When the homopolymers were placed in refluxing

N,N-dimethylacetamide (b.p. 166°C.) for 1 hr., examination of the reaction mixtures (infrared, NMR, analytical data) showed the presence of reverse Diels-Alder reaction products. New infrared absorption at 1625, 1650, and 1665 cm.$^{-1}$ indicated internal unsaturation. NMR showed a broad signal at 1.9–2.0 ppm. due to unsaturation of the —CH_2—CH=CH_2— type and a weak signal at 5.30 ppm indicated the —CH=CH— structure. Analytical values for chlorine dropped from 36.60% for the monomer to 33.33% in this sample. Interestingly, it was noticed that the partially reverse Diels-Alder degraded homopolymers possessed a slightly higher inherent viscosity than the original materials. Apparently the perchlorinated cyclopentadiene component, due to its high mass value and bulk, contributes to decreased inherent viscosity values when incorporated in the polymer chain.

Curing of VSP Homopolymer. Because the repeating unit contained tertiary hydrogens and chlorines (potential curing sites), curing of the solution VSP homopolymer was investigated. The curing composition was prepared in tetrahydrofuran solution containing 20% of dicumyl peroxide (Di-Cup, Hercules Powder Co., 96–99% pure) and the cure itself was done on a cast, dried film at 160°C. for 30 min. A completely insolubilized material was obtained.

Chlorination of VSP Homopolymer. Chlorination of the homopolymer at 2 ± 1°C. and in the dark resulted in chlorine substituted α to the carbonyl as well as elsewhere in the molecule. The infrared carbonyl absorption was shifted from 1730 to 1750 cm.$^{-1}$ by the α-chlorine substitution. A higher chlorine incorporation can be achieved at room temperature and in presence of ultraviolet light. The increased chlorine content materials became increasingly rigid.

Copolymerization

VSP/Vinyl Chloride Copolymers. In the evaluation of VSP as internal plasticizer for poly(vinyl chloride), a set of emulsion VSP/vinyl chloride copolymers was prepared. The copolymers were isolated as white powders soluble in tetrahydrofuran and which could be molded (at about 160°C.) into transparent, tan-colored films. The films were tough until all of the solvent was removed, then they became brittle. The material for physical properties evaluation was prepared by using a 70/30 (by weight, charged) ratio of vinyl chloride/VSP and using azobisisobutyronitrile as the initiator.

VSP/Vinyl Tetrahydroabietate–Tetrahydropimarate Copolymers.[9] The VSP homopolymer is nonflammable. It was of interest to evaluate VSP flame-retarding effect in other materials. A set of VSP copolymers with vinyl tetrahydroabietate–tetrahydropimarate mixture (VTA) was prepared. Because both monomers individually gave low inherent viscosity homopolymers, the low inherent viscosities for the copolymers were not unexpected. The 21% and 36% VSP copolymers were isolated as white powders while the 46% VSP copolymer as a dark tan-colored material. The copolymers could be molded (at about 100°C.) into very brittle films. The flammability of the copolymers was tested by placing a piece of the film in a Bunsen flame. While the VTA homopolymer supports combustion readily, increasing incorporation of VSP decreased this characteristic until the 46% VSP copolymer did not support combustion.

VSP/Vinyl 12-Hydroxystearate Copolymers. The work with the VSP/VTA copolymers demonstrated that if more than 16% of alicyclic chlorine was incorporated in the copolymer, the material did not support combustion. Incorporation of chlorine in a polyol would be expected to produce a less flammable polyurethane composition. Thus, three VSP/VHS copolymers were prepared in solution. The 11% and 23% VSP copolymers were isolated as white powders, while the 43% VSP copolymer was a dark tan-colored soft mass. All formed brittle films and none possessed noteworthy adhesive properties. While the 11% and 23% VSP copolymers supported combustion, the 43% VSP copolymer did not.

VSO/Vinyl Chloride Copolymers. A set of three different vinyl chloride/VSO copolymers was prepared. The copolymers were isolated as white powders soluble in tetrahydrofuran. All could be molded (at about 120°C.) into brittle, tan-colored films. The low inherent viscosities for the copolymers are due to the poor polymerization quality of the VSO itself.

VSO/Vinyl 12-Hydroxystearate Copolymers. In the work with VSP/vinyl 12-hydroxystearate copolymers, it was found that the 43% VSP composition did not support combustion. For the preparation of a flame-retarding polyol for polyurethanes the 60/40 vinyl 12-hydroxystearate/VSO composition was chosen. The solution copolymer was isolated as a dark-

TABLE IV
Analytical and Inherent Viscosity Data on Fractionated Copolymers of VSP and VSO with Vinyl Chloride

Samples	Wt., g.	Cl, %	η_{inh}[a]
VSP/vinyl chloride			
Entire sample	3.00	50.03[b]	0.52
Fraction 1	0.60	48.07	0.88
Fraction 2	0.90	50.03	0.65
Fraction 3	0.64	50.60	0.37
Fraction 4	0.76	51.86	0.35
Recovered	2.90 (97%)		
VSO/vinyl chloride			
Entire sample	3.00	51.32	0.37
Fraction 1	0.60	50.32	0.61
Fraction 2	0.25	50.80	0.52
Fraction 3	0.45	50.90	0.45
Fraction 4	0.30	51.18	0.39
Fraction 5	0.40	53.94	0.30
Fraction 6	0.80	55.53	0.26
Recovered	2.80 (93%)		

[a] Determined on solutions of 0.101–0.345 g./100 ml. of tetrahydrofuran at 30.3°C.

[b] Chlorine content of poly(vinyl chloride) is 56.74%.

tan-colored soft mass. The composition had only a borderline flammability. The emulsion copolymer was isolated as a tan-colored soft solid which did not support combustion. The emulsion copolymer was used in the subsequent polyurethane work.

Fractionation of Vinyl Chloride Copolymers of VSP and VSO. As the differences in r_1r_2 values between the vinyl chloride and vinyl esters is quite considerable,[10] it was of interest to learn more about the homogeneity, as well as molecular weight distribution, in the VSP and VSO copolymers with vinyl chloride. The copolymers fractionated were: the 31/69 VSP/vinyl chloride and the 30/70 VSO/vinyl chloride. Fractionations were done on 3.0-g. samples in 300 ml. of tetrahydrofuran. The analytical and inherent viscosity data are given in Table IV.

No significant amount of homopolymer was found in either the VSP/vinyl chloride or VSO/vinyl chloride copolymers. Both VSP and VSO are very efficient molecular weight modifiers, as judged from the low inherent viscosities (0.6–0.9). Of the two comonomers, the VSO would seem to have given a less homogeneous copolymer, as the last fraction isolated (0.80 g., 29%) should be predominantly poly(vinyl chloride) and, surprisingly, of very low molecular weight. The VSP copolymer would seem to have a rather uniform comonomer distribution.

Evaluation

VSO/Vinyl 12-Hydroxystearate Copolymer in Urethane Formation. Because the copolymer was too high-melting and incompatible with the other polyol components to be incorporated conveniently with the polyol portion of a one-shot urethane foam formulation, a prepolymer had to be prepared. The prepolymer was prepared by adding the melt slowly with rapid stirring to an excess of toluene diisocyanate (80/20) maintained at 80°C. Stirring was continued for 1 hr. at 80°C. after addition was complete.

Foams were prepared by reacting a 5% excess of the prepolymer with Quadrol (tetrahydroxypropylethylenediamine) in the presence of fluorotrichloromethane blowing agent, dibutyltin dilaurate catalysts, and Dow Corning 199 silicone. In another formulation Sb_2O_3 was added to improve the flame resistance of the foam.

A polyurethane foam was also prepared by an identical procedure from poly(vinyl 12-hydroxystearate)[11] for comparison.

The foam compositions and prepolymer and foam properties are listed in Table V.

A light-weight foam with practically no volume change upon humid aging can be obtained. A higher chlorine content is necessary, as the foams were flammable.

VSP as Internal Plasticizer for PVC. The following formulation was used in all evaluations of the VCl–VSP 70/30 copolymer: copolymer 100 parts, stearic acid 0.5 parts, tin mercaptide stabilizer (Advastab T-360) 4 parts. This composition milled and molded satisfactorily at 100–106°C.

TABLE V
Urethane Foam from Poly(vinyl 12-Hydroxystearate) and VSO/Vinyl 12-Hydroxystearate Copolymers

	Formulation		
	1	2	3
Foam composition, parts/100			
Poly(vinyl 12-hydroxystearate), η = 0.06	27.2	—	—
VSO/vinyl 12-hydroxystearate	—	29.1	29.1
TDI (80/20)	44.2	44.1	44.1
Quadrol	28.6	29.8	29.8
CCl_3F	16.0	16.0	16.0
Dibutyltin dilaurate	0.05	0.05	0.05
DC-199 silicone	1.5	1.5	1.5
Sb_2O_3	—	—	5.0
Prepolymer properties			
NCO, %	24.3	24.9	24.9
η^{25}, cp.	2,200	2,580	2,580
Foam properties			
Density, lb./ft.^{3}	2.28	2.36	2.09
Comp. strength, psi (d = 2.0)	33	37	20
Closed cells, %	78	77	90
Humid aging, % volume increase (14 days, 70°C., 100% R.H.)	+7	−3	—
Flammability (ASTM D1692-59T)	Burns	Burns	Burns

The resulting dark tan molded sheet (0.076 in. thick) was brittle and exhibited poor flexibility. Specimens used in the evaluations of the physical characteristics of the copolymer were not prepared from the thermally molded sheet but were die-cast from a 0.034-in. thick sheet cast from a tetrahydrofuran solution of the copolymer. They were cut from the cast sheet while it was still plasticized with residual solvent to facilitate cutting and to minimize imperfections in the specimens. They as well as the remaining uncut portion of the cast sheet were then heated for 24 hr. in a 70°C. forced draft oven to remove the residual solvent. Although the desolventized cast sheet appeared more flexible as would be expected, than the thicker thermally molded sheet, it was just as brittle.

Tensile strength, yield point, elastic modulus under tension, and elongation were determined in accordance with ASTM method D638-64T. The testing rate used was 0.2 in./min., and the gauge length was 2 in. No extensiometer was used. The T_f and T_4 torsional stiffnesses were determined in accordance with ASTM method D1043-61T.

The lower modulus, strength, and T_f and T_4 values of this copolymer when compared to those for a similar vinyl chloride–vinyl acetate copolymer (Table VI) show that the VSP component has imparted some measure of internal plasticization to the polymer. However, the degree of plasticization attained, as reflected by the torsional stiffness measurements, T_f and T_4, is far short of the desired goal and not at all comparable to that of the externally plasticized poly(vinyl chloride) composition. Recourse to higher levels of VSP comonomer incorporation as a means of improving low-temperature performance would hardly be desirable as this would very likely exert a concomitant deterioration of tensile strength which is already low at the present level of incorporation. The mediocre low-temperature performance and poor balance between it and tensile strength exhibited by this experimental 70/30 VCl–VSP copolymer presages a dim future for the VSP monomer as an internal plasticizing component for poly(vinyl chloride).

TABLE VI
Comparison of Physical Characteristics of VCl–VSP Copolymer with Those of a Vinyl Chloride–Vinyl Acetate Copolymer and an Externally Plasticized Poly(vinyl Chloride) Composition

Test	70/30 VCl–VSP copolymer	66.3/33.7 VCl–VA copolymer[a]	PVC with 25% DOP external plasticizer[a]
Elastic modulus tension, psi	38,800	420,000	—
100% modulus tension, psi	—	—	3120
Yield point, psi	1,200	—	—
Tensile strength, psi	1,620	7,900	3720
Elongation, %	120	—	210
T_f, °C.	19	40	1
T_4, °C.	39	—	—
Milling temp., °F.	212–220	300	340

[a] Data of Port et al.[12]

EXPERIMENTAL

Homopolymerization of VSP

Bulk. VSP (4.0 g.) and DEABIB (0.4 g.) were charged under nitrogen in a pressure tube (1 × 4 in.) and capped with an aluminum-lined cap. Polymerization was continued at 60 ± 2°C. for 48 hr., and a very viscous and dark red-brown-colored material was obtained. It was dissolved in 25 ml. of benzene and then poured into 100 ml. of methanol. About 0.2 g. of hot benzene- and tetrahydrofuran-insoluble material was also obtained. The precipitated material was redissolved in 25 ml. of benzene and reprecipitated in 100 ml. of methanol; 2 g. (50%) of vacuum-oven-dried (48°C./7 hr.) light-yellow-green-colored semiglassy material was isolated. The infrared spectrum showed no absorption bands characteristic for the monomer, (such as 1650 cm.$^{-1}$ characteristic of vinyl ester).

Solution. VSP (4.0 g.), DEABIB (0.4 g.), and dry, thiophene-free benzene (20 ml.) were charged under nitrogen into a pressure tube (1 × 7 in.)

and capped with an aluminum-lined cap. Polymerization was continued at 60 ± 2°C. for 48 hr. The light yellow solution was then poured into 200 ml. of methanol. The precipitated material was dissolved in 25 ml. of benzene and reprecipitated into methanol (100 ml.) twice. A 3.3-g. yield (83%) of vacuum-oven-dried (48°C./7 hr.) light yellow-colored viscous mass was obtained. The infrared spectrum showed no absorption bands characteristic for the monomer, (such as 1650 cm.$^{-1}$ characteristic of vinyl ester).

Emulsion. VSP (4.0 g.), DEABIB (0.4 g.), Siponate DS-10 (0.24 g.), and 12 ml. of a 1:1 mixture of air-free distilled water and Beckman pH 7.0 solution were charged under nitrogen in the above order in a pressure tube (1 × 7 in.). The materials were emulsified at room temperature for 15 min. and then polymerized at 60 ± 2°C. for 48 hr. A good latex was formed. The latex was poured into 200 ml. of methanol and the isolated material dissolved and reprecipitated from benzene (35 ml.) into methanol (150 ml.) twice; 4 g. of vacuum-oven-dried (48°C./7 hr.) light yellow-green-colored semiglassy material was isolated. The infrared spectrum showed no absorption bands characteristic for the monomer (such as 1650 cm.$^{-1}$ characteristic of vinyl ester).

The procedure for the VSO homopolymers was similar to that for the VSP homopolymers.

Hydrolysis of Emulsion VSP Homopolymer

Poly(VSP) (1.5 g.) was dissolved in thiophene-free, dry benzene (30 ml.), placed in a 250 ml. round-bottomed flask, and heated to 120°C. Next, anhydrous methanol (90 ml.) was added to the heated solution and dry HCl bubbled through for 7 hr. The HCl was passed through concentrated H_2SO_4 before entering the reaction mixture. At the end of the heating period the reaction mixture was purged with nitrogen for about 30 min. Next, the reaction mixture was extracted with 200 ml. of benzene and the combined benzene extracts were washed, first with 2% sodium bicarbonate solution (200 ml.) and then water (200 ml.). The benzene solution was then dried over anhydrous sodium sulfate. The dried benzene solution was placed in a Rotavac at 75°C., and a dark-brown viscous oil was obtained. The oil was next chromatographed on a silica gel (TLC, plain, Research Specialties Co.) column with 4% ether–hexene followed by chloroform and finally tetrahydrofuran. The first major fraction isolated (0.55 g., about 37%) was the methyl ester according to the infrared, NMR, and analytical data.

ANAL. Calcd. for 35% loss of one of the chlorine atoms in the monomer (1.4% of the total chlorine): C, 51.84%; H, 6.46%; Cl, 35.92%. Found: C, 51.49%; H, 6.65%; Cl, 35.50%.

Copolymerization of VCl with VSP

VSP (1.0 g.), diethyl azobisisobutyrate (0.5 g.), Siponate DS-10 (0.3 g.), and air-free, distilled water (30 ml.) were charged under nitrogen in a pressure tube (1.5 × 7 in.). The tube was then cooled to about −15°C., and VCl (9.0 g.) was added. An excess was added to purge the tube of air before capping. The materials were emulsified at room temperature for about 15 min. and then polymerized at 60 ± 2°C. for 48 hr. A thick latex was produced. It was poured into methanol (300 ml.) and the isolated material was dissolved in tetrahydrofuran (150 ml.) and reprecipitated in 400 g. of methanol; 9.6 g. (96%) of vacuum-oven-dried (50°C./24 hr.) material was isolated. The infrared spectrum showed no characteristic absorption bands for the monomers.

Copolymerization of VSP with VTA

VSP (1.0 g.), VTA (3.5 g.), diethyl azobisisobutyrate (0.225 g.), Siponate DS-10 (0.135 g.), and air-free, distilled water (12 ml.) were charged under nitrogen in a pressure tube (1 × 7 in.), emulsified at room temperature for about 5 min. and polymerized at 60 ± 2°C. for 53 hr. The charge had formed a tan-colored plug. It was broken up in 300 ml. of methanol in a Waring Blendor. The isolated material was dissolved in 80 ml. of tetrahydrofuran and reprecipitated in 300 ml. of methanol. A 3.3-g. yield grams (74%) of vacuum-oven-dried (55°C./28 hr.) of white powder was obtained. The infrared spectrum showed no characteristic absorption bands for the monomers.

Copolymerization of VSP with Vinyl 12-Hydroxystearate (VHS)

VSP (0.4 g.), VHS (3.6 g.), diethyl azobisisobutyrate (0.2 g.) and thiophene-free benzene (10 ml.) were charged under nitrogen in a pressure tube (1 × 7 in.) and polymerized at 60 ± 2°C. for 48 hr. The charge had formed a very viscous solution. It was poured into 300 ml. of methanol, and the isolated material was then dissolved in 50 ml. of tetrahydrofuran and reprecipitated in 400 ml. of methanol. The suspension was allowed to stand for 2 days before centrifuging and filtering, yielding 2.8 g. (70%) of vacuum-oven-dried (58°C./22 hr.) white powder. The infrared spectrum showed no characteristic absorption bands for the monomers.

Copolymerization of VSO with Vinyl Chloride

VSO (1.0 g.), diethyl azobisisobutyrate (0.4 g.), Siponate DS-10 (0.25 g.), and air-free, distilled water (20 ml.) were charged under nitrogen into a pressure tube (1.5 × 7 in.). The tube was then cooled to about −15°C., and vinyl chloride (4.0 g.) was added. An excess of vinyl chloride was used to purge the tube of air before capping. The contents were emulsified at room temperature for about 15 min. and then polymerized at 60 ± 2°C. for 25 hr. The latex was poured into 250 ml. of methanol, and the precipitated material was dissolved in 75 ml. of tetrahydrofuran and reprecipitated in 400 ml. of methanol. The suspension was allowed to stand for 1 day, then 2 ml. of 9% hydrochloric acid was added to speed up the settling out; 4.2 g. (84%) of vacuum-oven-dried (60°C./18 hr.) white powder was isolated. The infrared spectrum showed no characteristic absorption bands for the monomers.

Copolymerization of VSO with Vinyl 12-Hydroxystearate

Solution. Vinyl 12-hydroxystearate (15.0 g.), VSO (10.0 g.), AIBN (2.50 g.), and dry, thiophene-free benzene (100 ml.) were charged under nitrogen in a pressure tube (2 × 9 in.) and polymerized at 60 ± 2°C. for 48 hr. The dark-tan-colored obtained solution was poured into 2 liters of stirred methanol to which 10 ml. of concentrated HCl was added to speed up the settling out of the polymer. The oil that settled out was separated and 10 ml. of concentrated hydrochloric acid in 400 ml. of water was added to the decanted methanol layer. Additional oil had settled and was separated. Finally, 500 ml. of water was added to the methanolic aqueous layer from the previous separation to yield an additional small amount of oil. The combined oil fractions were then dissolved in 60 ml. of tetrahydrofuran, filtered, and reprecipitated in 250 ml. of methanol. The suspension was allowed to stand for 1 day before separating the oil. A 4.8-g. yield (19%) of vacuum-oven-dried (45°C./20 hr.) dark-tan-colored soft solid was isolated. The infrared spectrum showed no characteristic absorption bands for the monomers.

Emulsion. Vinyl 12-hydroxystearate (12.0 g.), VSO (8.0 g.), Siponate DS-10 (1.0 g.), AIBN (2.0 g.), and air-free, distilled water (100 ml.) were charged under nitrogen into a pressure tube (2 × 9 in.), emulsified at room temperature for 10 min. and polymerized at 60 ± 2°C. for 48 hr. A dark-tan-colored latex was obtained which tended to settle out with time. The latex was then poured into 1 liter of methanol and the suspension allowed to stand for 1 day. The viscous oil layer was separated and 250 ml. of water added to the methanol layer. Additional viscous oil was isolated. The oil fractions were combined and dissolved in 100 ml. of tetrahydrofuran, filtered, and reprecipitated in 1 liter of methanol. Concentrated HCl (2 ml.) was added to the suspension to speed up the settling out of the semisolid. The methanol–tetrahydrofuran layer was separated and 300 ml. of water was added to it, yielding additional viscous oil. The oil fractions were combined for drying purposes. The yield was 11 g. (55%) of vacuum-oven-dried (55°C./24 hr.) dark-tan-colored, soft solid. The infrared spectrum showed no characteristic absorption bands for the monomers. The material was completely nonflammable.

Fractionation of 69/31 Vinyl Chloride/VSP Copolymer

A 3.0-g. sample of the copolymer was dissolved in 300 ml. of tetrahydrofuran. A precipitate (1.50 g.) was obtained by adding 320 ml. of methanol. It was allowed to stand at room temperature for 4 hr. before filtering and drying in a vacuum oven (55°C./20 hr.). The dried precipitate was next dissolved in 150 ml. of tetrahydrofuran and 106 ml. of methanol was slowly added to the stirred solution. The fine precipitate was allowed to stand for 1 day, and then the liquid phase was decanted and the precipitate dried in a vacuum oven (60°C./48 hr.) yielding the first fraction (0.60 g.). The second fraction (0.90 g.) was isolated by adding 5 ml. of 17% hydrochloric acid to the decanted phase from isolation of the first fraction. The third fraction (0.64 g.) was obtained by adding 200 ml. of methanol to the first liquid phase from filtering. The suspension was allowed to stand overnight before centrifuging and filtering. The last fraction (0.76 g.) was obtained by adding 40 ml. of water. The isolation was done as before.

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Résumé

Des homopolymères de (1,4,5,6,7,7-hexachloro-3-undécylbicyclo (-2,2,1)5-heptène-2-yl)pentanoate de vinyle 5 et de (1,4,5,6,7,7-hexachloro-3-octylbicyclo(2,2,1)5-hepténvl-2)octanoate de vinyle 8, ont été préparés, aussi bien que leurs copolymères avec le tétrahydroabiétate et tétrahydropimarate de vinyle en mélange, le 12-hydroxystéarate de vinyle et le chlorure de vinyle. Le copolymère d'octanoate de vinyle 12-hydroxystéarate donnait des mousses d'uréthane légères avec pratiquement aucune modification de volume par vieillissement humide. Les monomères pentanoate de vinyle et octanoate de vinyle perdent de l'acide chlorhydrique au cours de leur polymérisation. L'homopolymère de pentoate de vinyle a été hydrolysé en vue d'établir la position de l'élimination de l'acide chlorhydrique. Le fractionnement des copolymères de chlorure de vinyle et du pentanoate de vinyle et de l'octanoate de vinyle montraient qu'ils possèdent une composition plutot homogène. L'incorporation de monomère de pentanoate de vinyle à un copolymère de chlorure de polyvinyle apporte à celui-ci une plastification interne mais avec une considérable perte de force de tension.

Zusammenfassung

Homopolymere von Vinyl-5-(1,4,5,6,7,7-hexachlor-3-undecyl-bicyclo[2.2.1.]-5-hepten-2-yl)-pentanoat und Vinyl-8-(1,4,5,6,7,7-hexachlor-3-octylbicyclo[2.2.1.]-5-hepten-2-yl)-octanoat sowie Copolymere mit einer Vinyltetrahydroabietat-tetrahydropimarat-Mischung, mit Vinyl-12-hydroxystearat und Vinylchlorid wurden dargestellt. Das Vinyloctanoat-12-Hydroxystearat-Copolymere liefferte Leichtgewichts-Polyurethanschaumstoffe, die bei der Alterung in feuchtem Milieu praktisch keine Volumns-änderung zeigten. Monomeres Vinylpentanoat und Vinyloctanoat verlieren während der Polymerisation Chlorwasserstoff. Zur Bestimmung des Ortes des Chlorwasserstoffverlustes wurde das Homopolymere des Vinylpentanoates hydrolysiert. Fraktionierung der Vinylchloridcopolymeren der Vinylpentanoat- und Vinyloctanoatderivate zeigte, dass sie eine recht homogene Zusammensetzung besitzen. Einbau des Vinylpentanoatmonomeren in ein Polyvinylchloridcopolymeres führte zu einer gewissen inneren Weichmachung mit ernstlichem Verlust an Zugfestigkeit.

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Cyclocopolymerization of Bicyclopentene and Other Dicyclic Dienes with Sulfur Dioxide to Fused Ring Systems

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Synopsis

The synthesis and cyclocopolymerization with sulfur dioxide of four 1,5- and 1,6-dienes (bicyclopentene, bicyclohexene, dicyclopentenyl ether, and dicyclohexenyl ether) and one tetraene (quartercyclopentene) is described. Under optimum conditions, completely soluble copolymers are obtained from bicyclopentene in high conversions at temperatures down to −39°C. Bicyclohexene also gave soluble copolymers, but in a by far slower reaction and in low conversion. Quartercyclopentene does copolymerize, but as expected, gives only insoluble polymers. The two compounds with 1,6-diallyl ether structure, dicyclopentenyl ether and dicyclohexenyl ether, failed to polymerize. The influence of initiator, temperature, reaction medium, diene concentration, etc., on the properties of the polymers was studied in detail for copolymerizations of bicyclopentene. Only a very limited number of peroxides in unusual large quantities was found to be effective in initiating this copolymerization. The reaction is further limited to a narrow choice of solvents, e.g,. diethyl ether and tetrahydrofuran, in order to obtain soluble products. Polymerization could not be achieved in ethanol, benzene, methylene chloride, dimethyl sulfoxide, and tetramethylene sulfone; excess sulfur dioxide yields only dark and insoluble products. Diene concentrations of below 0.3 wt.-% are normally required to obtain poly(bicyclopentene sulfones) which are soluble in dimethyl sulfoxide, tetramethylene sulfone, or sulfuric acid. Polymerization can be carried out from room temperatures down to −39°C.; optimum results are generally obtained around 0°C. Inherent viscosities of 1.72 (0.5 g./100 ml. dimethyl sulfoxide) have been measured. X-ray diffractions are those of amorphous polymers.

INTRODUCTION

Numerous examples of copolymerizations of olefins and sulfur dioxide are known,[1,2] which with three exceptions, namely, styrene and derivatives, vinyl chloride, and vinyl bromide, give strictly alternating 1:1 copolymers. Recent developments have shown that alternating cyclocopolymerization can be achieved when nonconjugated dienes such as 1,5-hexadiene[3] or diallyl compounds[4] are used. Bicyclocopolymerization occurs when *cis,cis*-1,5-cyclooctadiene is polymerized in the presence of sulfur dioxide.[5] These polymers exhibit a composition ratio of diene to sulfur dioxide of 1:2, indicative of alternating copolymerization in the

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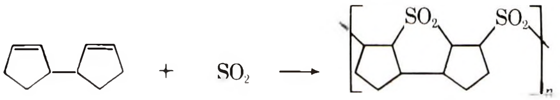
inter- as well as the intramolecular polymerization step. The one known exception is diallylamine hydrochloride,[4] where sulfur dioxide is presumably incorporated only in the intermolecular propagation step.

The purpose of our investigation was to achieve the cyclocopolymerization of dicyclic dienes and sulfur dioxide to form fused three-ring systems, as shown in eq. (1).



(1)

I

This is, to our knowledge, the first attempt to prepare fused ring systems by a cyclocopolymerization.

Two five-membered dicyclic dienes and two six-membered dicyclic dienes with 1,5-diene-(diallyl) and 1,6-diene-(diallyl ether) structures were selected for this investigation, but only two of these were found to undergo cyclocopolymerization resulting in soluble polymers in high yields. One five-membered tetraene could also be copolymerized; however, only insoluble products were obtained. The results are presented in this paper.

EXPERIMENTAL

Reagents

Dibenzoyl peroxide, *tert*-butyl hydroperoxide, methyl ethyl ketone peroxide (Luperzol DDM, 60% in dimethyl phthalate), 1,1′-bishydroxycyclohexyl peroxide (all Wallace and Tiernan, Lucidol Division); di-*p*-chlorobenzoyl peroxide, lauroyl peroxide, ketone peroxides (Cadox HDP-85, 85% in dibutyl phthalate) (all Cadet Chemical Corporation); *tert*-butyl peroxide, cumene hydroperoxide (both U.S. Peroxygen Corporation); ascaridol (K & K Laboratories); hydrogen peroxide (94% DuPont, Electrochemical Division) were all used as obtained. Their active oxygen content was determined iodometrically where possible.

Sulfur dioxide (anhydrous; Matheson, Coleman and Bell) was either used as obtained or dried further over P_2O_5. The additional drying, however, had no apparent influence on the properties of the products.

Diethyl ether (anhydrous; Baker Analyzed Reagent Grade) was stored over sodium wire and freshly distilled under nitrogen. Tetrahydrofuran (Eastman) was distilled from sodium benzophenone under nitrogen shortly before use, a forerun of approximately 25% being discarded. Benzene (Baker Analyzed Reagent Grade) was stored over sodium wire and distilled. Petroleum ether was extracted with sulfuric acid, washed, dried, distilled from sodium wire. Ethanol (absolute, Commercial Solvent Corp.) was used as obtained. Dimethyl sulfoxide (Fisher Certified Reagent Grade) and tetramethylene sulfone (Beacon Chemical Industries) were redistilled in vacuum; a middle fraction of approximately 50% of the material was used. Dicyclopentadiene (95%, practical; Matheson, Coleman and Bell) was used as obtained.

Instruments and Analyses

The spectroscopic investigations were performed with a Perkin-Elmer Infracord infrared spectrometer and Varian A60 nuclear magnetic resonance spectrometer. Elemental analyses were carried out by Alfred Bernhardt, Mikroanalytisches Laboratorium, Mühlheim (Ruhr), Germany, and by Galbraith Laboratories, Inc., Knoxville, Tennessee. Gas chromatographic analyses and x-ray diffraction were obtained from the Physical Measurement Laboratory of Mellon Institute.

Polymerization Procedure

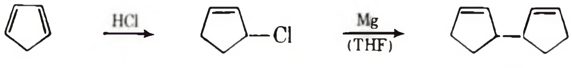
The polymerizations were carried out in an argon atmosphere in ampules sealed with rubber serum caps. Reaction conditions are listed in Tables I–V. In a typical example, 25 g. diethyl ether was transferred from a storage bottle into a 100-ml. ampule by means of hypodermic wire by applying a slightly positive argon pressure in the storage bottle. Bicyclopentene, 0.21 g. (1.5×10^{-3} mole), was added by means of a hypodermic syringe and the mixture was cooled to −78°C. To the cooled solution 97.4 mg. of methyl ethyl ketone peroxide (60% in dimethyl phthalate), in 2 ml. ether was added, which represents 60 mole-% (0.9×10^{-3} mole) peroxide based on diene (determined by iodometric titration). From a storage ampule containing 6.4 g. (10^{-2} mole) of sulfur dioxide in 45 g. diethyl ether, approximately 1.0 g. solution, amounting to about 2×10^{-3} mole SO_2, was transferred into the polymerization ampule. The mixture was then allowed to warm to 0°C. in about 15 min. while being shaken. At this temperature, the rest of the sulfur dioxide solution in ether was added. The onset of the polymerization was apparent from the cloudy appearance of the solution. The ampule was kept at the polymerization temperature for 24 hr. with occasional shaking. The polymer was more or less suspended and formed a precipitate with a clear supernatant solution at the late stage of the polymerization. To terminate the polymerization at early stages, hydroquinone was added. In the work-up, the content of the ampule was poured into a tenfold volume of methanol, filtered, and washed several times with methanol, and dried at room temperature in vacuum; 0.366 g. poly(bicyclopentene sulfone) corresponding to 87.6% conversion (based on diene) was obtained. The polymer was soluble in DMSO, TMS, and sulfuric acid and had an inherent viscosity (0.5 g./100 ml. DMSO) of 1.72.

ANAL. Calcd. for I, $C_{10}H_{14}S_2O_4$: C, 45.80%; H, 5.34%; S, 24.42%. Found: C, 45.61%; H, 5.46%; S, 24.87%.

Soluble polymers were generally purified by reprecipitation (DMSO/methanol).

Monomer Syntheses

1,1′-Bicyclopent-2,2′-ene. This monomer (II) was obtained by the reactions shown in eq. (2).



(2)

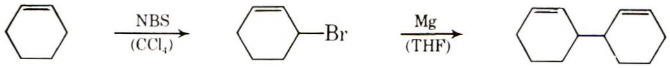
II

Cyclopentadiene (CPD) was obtained from thermal degradation of dicyclopentadiene (DCPD). Its purity was determined by NMR. Only freshly distilled CPD containing less than 1% DCPD was used in the synthesis of 3-chlorocyclopentene by addition of HCl[8] at −30 to −78°C. and distillation of the mixture at room temperature in vacuum. 3-Chlorocyclopentene was stored at −78°C. and used within a few hours after preparation. 1,1′-Bicyclopent-2,2′-ene was synthesized by a modified biallyl synthesis.[9] In an argon atmosphere, 274 g. of 3-chlorocyclopentene was diluted with 300 ml. THF and added to 36 g. of magnesium in 150 ml. THF over a period of 75 min. at a rate fast enough to maintain gentle reflux. After the addition was complete, another 100 ml. THF was added to facilitate stirring and the mixture was stirred for 3 hr. The contents were then cooled to 0°C.; 350 ml. of 5% hydrochloric acid was added, followed by 200 ml. H_2O. The organic layer was washed with dilute $NaHCO_3$ and then with water until neutral and dried over sodium sulfate. Evaporation of solvents and fractionation under argon yielded 130 g. of 1,1′-bicyclopent-2,2′-ene (72.2%), b.p. 43°C./1.4 mm.; n_D^{30} 1.4859.

ANAL. Calcd. for $C_{10}H_{14}$: C, 89.55%; H, 10.45%. Found: C, 89.46%; H, 10.50%.

From gas chromatography the product was determined to be +99.8% pure, with benzene as the major impurity. NMR gave $H_{\text{olefinic}}:H_{\text{aliphatic}}$ = 4:10.7 (4:10 theor.).

1,1′-Bicyclohex-2,2′-ene. This monomer (II) was synthesized from cyclohexene according to eq. (3).



(3)

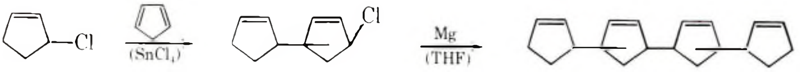
III

3-Bromocyclohexene was synthesized by allylic bromination of cyclohexene with *N*-bromosuccinimide[10] (NBS) in 80% yield. For the synthesis of 1,1′-bicyclohex-2,2′-ene, the same procedure as given for the synthesis of 1,1′-bicyclopent-2,2′-ene was followed, except that the Grignard mixture was heated under reflux for 2 hr. after the addition of 3-bromocyclohexene was completed. 1,1′-Bicyclohex-2,2′-ene was obtained in 87% yield; b.p. 50°C./0.2 mm. (argon bleeding); n_D^{30} = 1.5264.

ANAL. Calcd. for $C_{12}H_{18}$: C, 88.88%; H, 11.12%. Found: C, 88.72%; H, 11.14%.

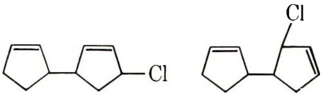
From gas chromatography the product was determined to be +99.8% pure, with benzene as major impurity. NMR gave $H_{olefinic}:H_{aliphatic}$ = 4 : 14 (4 : 14 theor.).

Quatercyclopentene. This was prepared from 3-chlorocyclopentene as shown in eq. (4).



(4)

Cyclopentenylcyclopentenyl chloride was synthesized by addition of 3-chlorocyclopentene to cyclopentadiene following the procedure of Fitzpatrick.[11,12] Since both 1,4- and 1,2-addition is possible, the mixture will consist of at least two isomers:



1-chloro-4-(cyclopent-2-enyl)-cyclopent-2-ene and 1-chloro-2-(cyclopent-2-enyl)-cyclopent-4-ene. Quatercyclopentene (IV) was synthesized via Grignard reaction of cyclopentenylcyclopentenyl chloride by following the procedure given for 1,1′-bicyclopent-2,2′-ene, except that the mixture was heated to reflux for 2 hr. after addition of the chloride was complete.

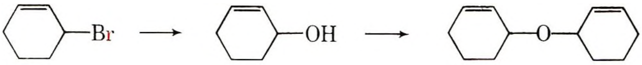
Quatercyclopentene was obtained in 72% yield; b.p. 139°C./0.42 mm. (argon bleeding); n_D^{30} 1.5279.

ANAL. Calcd. for $C_{20}C_{26}$: C, 90.23%; H, 9.77%. Found: C, 90.01%; H, 10.07%.

NMR gave $H_{olefinic}:H_{aliphatic}$ = 8 : 18.09 (8 : 18 theor.). Three major components with peak area ratio of 1 : 4.76 : 5.17 and respective retention times of 1.00, 1.07, and 1.11, were found by gas chromatography. They presumably represent the three expected isomers resulting from coupling of the two isomeric chlorides: 1,1′:4′,1″:4″,1‴-quatercyclopent-2,2′,2″,2‴-ene; 1,1′:4′,1″:5″,1‴-quatercyclopent-2,2′,3″,2‴-ene; and 1,1′: 5′1″:5″,1‴-quatercyclopent-2,2′,3″,2‴-ene. No attempt was made to isolate and identify the quatercyclopentene isomers.

1,1′-Dicyclopent-2,2′-enyl Ether. This (V) was synthesized from 3-chlorocyclopentene following the procedure of Alder and Flock.[8]

1,1′-Dicyclohex-2,2′-enyl Ether. This was prepared from 3-bromocyclohexene by variation of the procedure[8] for 1,1′-dicyclopent-2,2′-enyl ether [eq. (5)].



(5)

VI

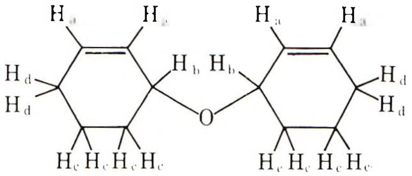
3-Bromocyclohexene (111 g., 0.69 moles) was slowly added to a stirred solution of 65 g. $NaHCO_3$ in 370 ml. water over a period of 1 hr. with external cooling by ice water. After the addition was completed, the mixture was stirred for 2 hr. at approx. 10°C. and then at room temperature for 2 hr. more. The water layer was then saturated with sodium chloride; the organic layer was separated, and the aqueous solution was extracted with ether four times. The combined organic layers were dried over Na_2SO_4 and fractionated.

3-Hydroxycyclohexene was obtained in 67% yield (44.5 g.), b.p. 61°C./2.9 mm. (argon bleeding); n_D^{30} 1.4837.

3-Hydroxycyclohexene (44.5 g.; 0.454 moles) and 2 ml. HCl were stirred for 24 hr. with no apparent sign of reaction. It was necessary to force the reaction by adding 100 ml. benzene and refluxing the mixture in the presence of 0.5 g. *p*-toluenesulfonic acid for 4 hr., after which the collection of water in the water separator ceased. The organic layer was separated, washed with dilute $NaHCO_3$ solution and water, and dried over Na_2SO_4. The solvents were stripped off and the residual oily liquid was fractionated.

1,1′-Dicyclohex-2,2′-enyl ether (VI) was obtained in 57% yield (23.2 g.); b.p. 80–89°C./0.5–0.6 mm. (argon bleeding).

ANAL. Calcd. for $C_{12}H_{18}$: C, 80.91%; H, 10.11%; O, 8.98%. Found: C, 80.4%; H, 9.93%; O, 9.78%.



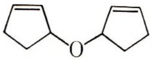
NMR gave $H_a : H_b : (H_c + H_d) = 2.0:0.9:6.0$ (theor. 2:1:6).

RESULTS AND DISCUSSION

Polymerization

The prime object of this paper was the establishment of optimum reaction conditions. This was necessary because of the incomplete and sometimes controversial information about suitable reaction media, effective catalytic systems, ceiling temperatures, etc., for even the relatively simple monoolefin–sulfur dioxide polymerizations.[1,2] The naturally more complicated behavior for copolymerizations of nonconjugated dienes,[3–5] and the unusual behavior sometimes observed in sulfur dioxide copolymerizations of cyclic olefins (e.g., high ceiling temperature of cyclopentene,[6] spontaneous copolymerization by a biradical coupling mechanism of bicyclo[2,2,1]-hept-2-ene)[7] made a search for optimum conditions in the complicated reactions of the cyclic dienes obligatory. It was anticipated furthermore that the dicyclic diene systems would be extremely sensitive not only to the diene structure, but to concentration and temperature, and would respond to changes of these parameters by forming more or less crosslinked, and hence, insoluble polymers.

The four dienes (and one tetraene) selected for this study included three compounds with five- and six-membered 1,5-diene ("diallyl") structures: 1,1′-bi-cyclopent-2,2′-ene (BCP) (II), 1,1′-bicyclohex-2,2′-ene (BCH) (III), quartercyclopentene (mixture of isomers) (QCP) (IV), and two compounds with five- and six-membered 1,6-diene (diallyl ether) structure: 1,1′-dicyclopent-2,2′-enyl ether (DCPE) V



V

and 1,1′-dicyclohex-2,2′-enyl ether (DCHE) VI.

Polysulfones were formed most easily, as expected, from the five-membered species with 1,5-diene structures. With polymerizations carried out at low diene concentration, high yields of a completely soluble poly(bicyclopentene sulfone) (I) could be obtained in a fast reaction at 0°C. and lower temperatures.

Quartercyclopentene does also react easily, but, as expected, yielded only completely insoluble material. The three intramolecular cyclization steps which would be required in this particular case to obtain linear polymers would only be favored in extremely dilute solutions. The situation was further complicated since due to the route of synthesis, quartercyclopentene consisted of a mixture of three positional isomers. Two of these would make complete intramolecular propagation very unlikely for steric reasons; they possess partial 1,6-diene structures. The generally lower probability of formation of cyclopolymers from these structures further enhances the chance of crosslinking by an independent noncyclic polymerization of isolated double bonds. The elaborate isolation of pure 1,5-isomers could not be undertaken.

Bicyclohexene also copolymerizes with sulfur dioxide, but at a far slower rate of reaction and to low conversion.

No polysulfones could be obtained from the 1,6-diene systems, dicyclopentenyl and dicyclohexenyl ether, even at temperatures as low as −40°C. This is somewhat surprising, since diallyl ether itself is known to copolymerize with sulfur dioxide up to a fairly high ceiling temperature of >85°C.[6]

For all the above-mentioned reasons, the emphasis of this investigation has been put on bicyclopentene, and the examples listed below refer to this system only.

The choice of solvents and diluents is limited to not too polar solvents (to minimize interference with the olefin–sulfur dioxide complex) and was further narrowed by the desire to allow polymerization down to −40°C. In preliminary tests, it was found that at temperatures of 0°C. and below, bicyclopentene can be polymerized in diethyl ether and tetrahydrofuran in high yields. The polymer precipitates in these media and, when soluble, was purified by washing with methanol and reprecipitation from dimethyl sulfoxide (DMSO), tetramethylene sulfone (TMS), or sulfuric acid solution. Polymerization also proceeds in excess sulfur dioxide as the diluent at 0°C. and below, but the resulting product is very dark and completely insoluble. Ethanol at 0°C., benzene at 0°C. and above, petroleum ether at room temperature, methylene chloride at 0°C. and below, dimethylsulfoxide and tetramethylene sulfone at room temperature, are not suitable media since either no polymerization occurs at all, or only traces of reaction products are formed; none of these solvents was extensively investigated.

The rather broad spectrum of free-radical sources usually effective in copolymerization of monoolefins and conjugated dienes[1,2] narrows down to a few peroxides which are able to initiate the copolymerization of bicyclopentene: methyl ethyl ketone peroxide, 1,1′-bishydroxycyclohexyl peroxide, a mixture of cyclohexanone peroxides, cumene hydroperoxide. Other peroxides such as dibenzoyl peroxide, di-*p*-chlorobenzoyl peroxide, lauroyl peroxide, *tert*-butyl hydroperoxide, and ascaridol, either alone or in combination with HCl or H_2SO_4, were found to be completely ineffective. This classification resembles the behavior found with cyclooctadiene.[5] Neither could polymerization be initiated by azobisisobutyronitrile or ultraviolet light; however, these initiating systems were not studied extensively. Oxygen, although claimed as an initiator for several olefin–sulfur dioxide copolymerizations,[1,2] was not investigated. Rather, an attempt was made to eliminate oxygen as far as possible in order to avoid complications caused by the extremely fast autoxidation of these dienes. Table I lists some of the catalytic systems.

It is assumed that the ineffectiveness of certain peroxides is caused by failure to produce active intermediates in the redox reaction with sulfur dioxide and/or by the extreme speed of the redox reaction. Furthermore, the yield of free radicals useful for initiation is very low, even with catalysts capable of initiating the polymerization, because of the low concentration of diene and the large excess of SO_2 always present which may further interact with the active species of the redox systems. Thus, unusually high concentrations of peroxides are required to promote polymerization. To enhance the probability of forming active radicals without interference from excess SO_2, the initiation was allowed to proceed with only equimolar amounts of peroxide and sulfur dioxide in the presence of the diene at low temperatures. The bulk of the sulfur dioxide was added later. Although this process gave more reproducible data with peroxides also effective in an excess of sulfur dioxide, it did not change the above-mentioned classification of effective and ineffective peroxides.

The unusually large amounts of peroxide needed to initiate the copolymerization of bicyclopentene and sulfur dioxide are shown in Table II for a typical example, methyl ethyl ketone peroxide (MEKPO) as initiator in diethyl ether at 0°C.

No polymerization was observed for initiator concentrations less than 5 mole-% MEKPO. Above 40 mole-%, the degree of conversion becomes virtually independent of the catalyst concentration, whereas the inherent

TABLE I

Influence of Catalyst on the Copolymerization of BCP and Sulfur Dioxide[a]

Reaction	Catalyst	Catalyst, mmole[b]	BCP, mmole	Conc., wt.-% BCP in THF	Yield, mole-%[c]	Analysis[d] C, %	H, %	S, %	{η}[e]	Solubility at 30°C. DMSO	TMS	H_2SO_4
88	Dibenzoyl peroxide	1.0	3	0.6	No polymerization							
89	Di-*p*-chlorobenzoyl peroxide	1.0	3	0.6	No polymerization							
90	1,1'-Bishydroxycyclopentyl peroxide	1.0	3	0.6	55.9	45.58	5.86	24.22	1.06	+	+	+
91	Cumene hydroperoxide	1.0	3	0.6	76.8	44.31	5.65	23.76	0.14	+	+	+
92	Methyl ethyl ketone peroxide[f]	1.0	3	0.6	79.8	44.47	5.45	23.74	0.27	+	+	+
63	Ketone peroxide[f]	0.6	2	0.3	72.6	44.49	5.40	23.79	0.30	+	+	+
65	Cyclohexanone peroxide[f]	0.5	2	0.3	80.8	44.48	5.71	23.89	0.28	+	−	+
36	Ascaridol	3 drops	2	0.5	No polymerization							

[a] Reaction conditions: solvent, THF; temperature, 0°C.; time, 24 hr.; atmosphere, argon in rubber-capped ampules; excess sulfur dioxide, 500 mole-%.

[b] Determined by iodometric titration.

[c] Based on BCP.

[d] Calculated for $C_{10}H_{14}S_2O_4$: C, 45.80%; H, 5.34%; S, 24.42%.

[e] 0.5 g./100 ml. DMSO at 30°C.

[f] Mixtures of various peroxides.

TABLE II

Variation of Catalyst Concentration in Copolymerization of BCP and Sulfur Dioxide in Diethyl Ether[a]

Reaction	BCP, mmole	Conc., wt.-% BCP in ether	MEKPO/BCP, mole-%	Yield, %[b]	Analysis[c]			$[\eta]$[d]	Solubility[e]		
					C, %	H, %	S, %		DMSO	TMS	H_2SO_4
93	1.5	0.3	0.1	No polymerization							
94	1.5	0.3	1	No polymerization							
95	1.5	0.3	5	No polymerization							
96	1.5	0.3	10	44.5					−	−	−
83	1.5	0.3	20	79.1			24.03		−	−	+
84	1.5	0.3	40	84.4			24.21		−	−	+
85	1.5	0.3	60	87.6	45.61	5.46	24.87	1.72	+	+	+
86	1.5	0.3	80	83.5	43.97	5.58	23.55	0.93	+	+	+
87	1.5	0.3	100	85.4	43.70	5.53	23.47	0.75	+	+	+

[a] Reaction conditions: solvent, 70 g. diethyl ether; catalyst, methyl ethyl ketone peroxide (MEKPO); sulfur dioxide, 10^{-2} mole; temperature, 0°C.; time: 24 hr.

[b] Based on BCP.

[c] Calculated for $C_{10}H_{14}S_2O_4$: C, 45.80%; H, 5.34%; S, 24.42%.

[d] 0.5 g./100 ml. DMSO at 30°C.

[e] At room temperature.

viscosity decreases with increasing catalyst concentration. Polymers obtained from experiments with less than ~50 mole-% peroxide are normally insoluble in DMSO but are still soluble in concentrated sulfuric acid (with degradation). For those obtained at minimum catalyst concentration, no solvent could be found. It must be left open whether the insolubility is due to an increase in molecular weight of linear polymers or to crosslinking.

Completely soluble poly(bicyclopentene sulfones) were obtained only at high dilutions naturally favorable to cyclopolymerization. A definite threshold in diene concentration can be observed. No attempts have been made to determine the percentage of soluble material in incompletely soluble polymers, since a wide enough range of diene concentration allowed the synthesis of entirely soluble polymers.

As shown in Table III, experiments carried out along the borderline of solubility suggest that the conversion is independent of the solubility of the polymers formed. The inherent viscosity is also independent of diene concentration as long as the polymers stay soluble. Solubility in sulfuric acid alone characterizes the solubility limit. Higher diene concentrations result in completely insoluble polymers. Lower concentrations than those shown in Table III give polymers soluble in DMSO and TMS.

Since the formation of soluble polymers also depends very strongly on other parameters, such as temperature and catalyst concentration, changes in these will also influence the range of diene concentrations suitable for obtaining soluble polymers. From our experience, bicyclopentene concentrations below 0.3 wt.-% normally give completely soluble poly(bicyclopentene sulfones) unless extremely low catalyst concentrations or temperatures above room temperatures are employed. A large excess of sulfur dioxide was provided in all experiments. The influence of variation of the sulfur dioxide concentration was not studied in order to avoid enhanced crosslinking caused by a deficiency of sulfur dioxide at low concentrations.

Table IV shows the influence of temperature in a typical example. Copolymerization was found feasible at temperatures down to −39°C., with optimum conditions near 0°C. Temperatures below 0°C. very often result in insoluble polymers, whereas temperatures above 0°C. give serious decreases in conversion and inherent viscosities, probably due to a reduction in the concentration of initiating species through a fast redox reaction or to side reactions before the initiation step. No polymerization occurred in 5 hr. at −78°C.; when the mixture was then allowed to warm to −39°C., polymerization began, and the obtained product was identical with the one obtained originally at −39°C. The presence of a definite ceiling temperature could not be observed in this and the other systems, although there seems to be a temperature threshold below which no polymerization of bicyclopentene occurs. This was not further investigated, since it was believed that these systems are too complicated and too sensitive as to allow such a study. The temperature effects around a possible ceiling temperature would be overshadowed by reactions leading to more or less

TABLE III

Variation of Diene Concentration in Copolymerization of BCP and Sulfur Dioxide at 0°C. in Diethyl Ether[a]

Reaction	BCP, mmole	Conc., wt.-% BCP in ether	Catalyst, mole-%[b]	Yield, %[b]	Analysis[c]			$\{\eta\}$[d]	Solubility[e]		
					C, %	H, %	S, %		DMSO	TMS	H_2SO_4
103	1.5	0.3	70	79.0	44.62	5.86	23.34	1.27	+	+	+
104	3.0	0.6	70	83.5	44.68	5.82	23.71	1.29	+	+	+
105	4.5	0.9	70	81.7					−	−	+

[a] Reaction conditions: solvent, 70 g. diethyl ether; catalyst, methyl ethyl ketone peroxide; sulfur dioxide, 0.07 mole; temperature, 0°C.; time, 24 hr.

[b] Based on BCP.

[c] Calculated for $C_{10}H_{14}S_2O_4$: C, 45.80%; H, 5.34%; S, 24.42%.

[d] 0.5 g./100 ml. DMSO at 30°C.

[e] At room temperature.

TABLE IV
Influence of Temperature in Copolymerization of BCP and Sulfur Dioxide in Diethyl Ether[a]

Reaction	BCP, mmole	Conc. wt.-% BCP in ether	MEKPO, mole-%[b]	Temperature, °C.	Yield, mole-%[b]	$\{\eta\}$[c]	Solubility[d]		
							DMSO	TMS	H_2SO_4
113	1.5	0.3	70	25	50.2	0.10	+	+	+
112	1.5	0.3	70	0	97.2	0.45	+	+	+
114	1.5	0.3	70	−39	100.0		−	−	−
115	1.5	0.3	70	−78[e]	No polymerization				
				−39	95.9		−	−	−

[a] Reaction conditions: solvent, 70 g. diethyl ether; catalyst: methyl ethyl ketone peroxide (MEKPO); sulfur dioxide, 0.05 mole; time, 24 hr.

[b] Based on BCP.

[c] 0.5 g./100 ml. DMSO at 30°C.

[d] At room temperature.

[e] No polymerization during 5 hr. at −78°C.; sample allowed to warm up to −39°C., 19 hr. at 39°C.

crosslinked products, as observed, for example, in the case of bicyclopentene copolymerizations (See expts. 114 and 115 in Table IV).

The reaction is fast even at very low temperatures and is virtually complete after 10 min. at 0°C. (Table V). Conversion data in these examples collected in Table V were obtained by terminating the reaction by addition of hydroquinone, contrary to all other reported examples in this paper where polymerization was allowed to reach completion or self-termination.

TABLE V
Conversion versus Time in Copolymerization of BCP and Sulfur Dioxide in Diethyl Ether[a]

Reaction	BCP, mmole	Conc., wt.-% BCP in ether	MEKPO, mole-%[b]	Time, sec.[c]	Yield, mole-%[b]	$\{\eta\}$[d]
108	2.78	0.53	80	15	17.4	0.11
109	2.78	0.53	80	30	26.4	0.20
107	2.78	0.53	80	60	46.1	1.15
110	2.78	0.53	80	600	83.1	1.21

[a] Reaction conditions: solvent, 70 g. diethyl ether; catalyst, methyl ethyl ketone peroxide (MEKPO); sulfur dioxide, 0.05 mole; temperature, 0°C.

[b] Based on BCP.

[c] 4×10^{-3} mole hydroquinone added at this time to terminate the reaction.

[d] 0.5 g./100 ml. DMSO at 30°C.

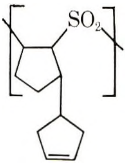
Polymer Structure and Properties

The polysulfones obtained from bicyclopentene are colorless powders, ranging from complete solubility in polar organic solvents, such as DMSO, TMS, *N*-methylpyrrolidone, hexamethyl phosphoric amide, etc., to complete insolubility in any solvent. Intermediate stages are characterized by solubility in concentrated sulfuric or methanesulfonic acid. However, as shown in Table VI, the viscosity is reduced drastically when a sample is

TABLE VI
Degradation of Poly(bicyclopentene Sulfone) Caused by Sulfuric Acid

		Inherent viscosity $\{\eta\}$			
Reaction	Reaction medium	Untreated, meas. in DMSO	Untreated, meas. in H_2SO_4	After 2 reppt. from DMSO, meas. in DMSO	After 1 reppt. from H_2SO_4, meas. in DMSO
61	THF	0.25	0.14		
85	Ether	1.72	0.19		
83	Ether	Insoluble	0.23		
90	THF	1.06		0.99	
92	THF	0.27		0.23	
104	Ether	1.30	0.12		0.15

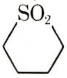
dissolved in strong acid, indicating a severe degradation, although the polymer does not decompose completely even in sulfuric acid. The inherent viscosity obtained immediately after dissolving, seems to be independent of the inherent viscosity in DMSO and remains constant over a period of several days. Qualitative comparisons show that a relationship exists between solubility and composition of the polymers. Polysulfones which approach the theoretical composition for I (C, 45.80%; H, 5.34%; S, 24.42%) are the most soluble in organic solvents. Whereas those with lower sulfur content (S, 22.0% and below) are generally insoluble, or at best, soluble in sulfuric acid, thus indicating also in this solubility behavior deviations from the ideal cyclocopolymerization. Pendant cyclopentenyl groups (VII)



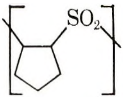
VII

barred from participating in the intramolecular cyclization lower the sulfur content and are potential sites for crosslinking through grafting, and hence may cause the insolubility.

The infrared spectrum is consistent with structure I. The SO_2 absorptions occur at 1125 and 1310 cm.$^{-1}$. Model compounds, tetramethylene sulfone (VIII) and the polysulfone of cyclopentene (IX),



VIII



IX

absorb at 1100 and 1300 cm.$^{-1}$ and 1140 and 1310 cm.$^{-1}$, respectively. Only very little, if any, residual unsaturation may be present in the polymers. An observed weak absorption at 1650 cm.$^{-1}$ is rather broad and suggests adsorbed or complexed water, since its intensity always corresponds to the intensity of a weak hydroxylic absorption; however, this does not rule out a covered weak C=C absorption. Very weak acidic hydroxyl absorptions occurring at 2950 cm.$^{-1}$ in some samples are probably due to sulfonic acid groups incorporated in the polymer.

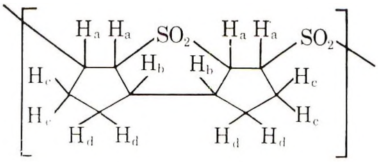
Lack of suitable solvents (deuterated dimethyl sulfoxide underwent quite rapid deuterium exchange) allowed only a semiquantitative NMR evaluation, and this only on completely soluble samples. No detectable amounts of residual unsaturation were found in those samples even at spectrum amplitudes of 40. (Bicyclopentene shows a multiplet centered at $\tau = 4.28$ with a half bandwidth of 3 cps.) The preliminary assignments are presented in Table VII.

Poly(bicyclopentene sulfones), soluble or insoluble, do not soften or melt up to 260°C., as determined on a Kofler hotbench in air. Thermogravimetric analysis (heating rate 5°C./min., in nitrogen) shows a weight loss of only 2.5% at 200°C., 11% at 250°C., and 52% at 300°C.

Owing to lack of suitable solvents, no absolute molecular weight determination could be undertaken. The viscosity behavior resembles that of polyelectrolytes; however, no consistent behavior was observed and there were variations from sample to sample. This can probably be attributed to the presence of various amounts of ionic groups, e.g., sulfonic acids, incorporated in the polymer by side reactions. No intrinsic viscosity could be determined for this reason. The inherent viscosities at 0.5 g./100 ml. solvent fall in the range of the concentration curves where the polyelectrolytic effect is negligible.

TABLE VII

NMR Assignments of Poly(bicyclopentene Sulfone)[a]



Protons	Chemical shifts τ, ppm	Half bandwidths, cps	Integrated areas	
			Found[b]	Theor.
H_a	5.85	22	4	4
H_b	7.10[c]	c	11.4	10
H_c	8.00[c]	c		
H_d		c		

[a] Measured at room temperature in 10% solution of d_6-dimethyl sulfoxide. TMS as internal reference.

[b] Deuterium exchange approximately 11% (integrated area of d_5-dimethyl sulfoxide).

[c] Overlapping, unresolved peaks.

Inherent viscosities (0.5 g./100 ml. dimethyl sulfoxide at 30°C.) of up to 1.7 have been measured on soluble poly(bicyclopentene sulfones) prepared in diethyl ether, the normal range being 0.75–1.4. Polymers prepared in THF show consistently lower inherent viscosities, normally in the range 0.14–0.34, with the highest value 1.05.

X-ray diagrams are those typical for amorphous polymers.

We are indebted to Dr. Thomas G Fox for his encouragement during the work and to Dr. S. S. Pollack for x-ray measurements and their interpretation. We also thank the Lucidol Division of Wallace and Tiernan, Inc., the Cadet Chemical Corporation and the U.S. Peroxygen Corporation for generously providing us with samples of various peroxides.

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Résumé

La synthèse et la cyclopolymérisation du dioxyde de soufre avec quatre diènes 1,5- et 1,6- le bicyclopentène, le bicyclohexène, l'éther dicyclopentènylique et l'éther dicyclohexénylique, et un tétraène, le quartercyclopentène, sont décrites. Dans des conditions optimums des copolymères complétement solubles ont été obtenus du départ de bicyclopentène à des degrés de conversion élevés à la température inférieure à $-39°C$. Le bicyclohexène également donne des copolymères solubles, mais par une réaction beaucoup plus lente et à des degrés de conversion faibles. Le quartercyclopentène copolymérise comme prévu et donne uniquement des polymères insolubles. Les deux composés avec une structure 1,6-diallyléther, le dicyclopentènyl éther et le cyclohexényl éther, ne donnent pas de polymérisation. L'influence de l'initiateur, de la température, du milieu de réaction, de la concentration en diène, etc., sur les propriétés des polymères a été étudiée en détail pour les copolymérisations du bicyclopentène. Uniquement un petit nombre très limité de peroxydes en quantités exceptionnellement elevées est efficace pour initier cette polymérisation. La réaction est en outre limitée par un choix limité de solvants, c'est-à-dire, léther diéthylique, et le tétrahydrofurane, en vue d'obtenir des produits solubles. La polymérisation ne peut être effectuée dans l'éthanol, le benzène, le chlorure de méthylène, le sulfoxyde de diméthyle et la tétraméthylène sulfone; un excès de dioxyde de soufre produit uniquement des produits sombres et insolubles. Des concentrations en diène inférieures à 0.3% en poids sont normalement requises pour obtenir, ne polydicyclopentène sulfome soluble dans le diméthylsulfoxyde, la tétraméthylènesulfone ou l'acide sulfurique. La polymérisation peut être effectuée depuis la température de chambre jusqu'à $-39°C$; les résultats optimums sont généralement obtenus vers 0°C. Des viscosités inhérentes de 1.72 (0.5 g/100 ml de diméthyl sulfoxyde) ont été mesurées. Des diffractions aux rayons-X montrent une structure de polymères amorphes.

Zusammenfassung

Die Synthese von vier 1,5- und 1,6-Dienen, nämlich Bicyclopenten, Bicyclohexen, Dicyclopentenyläther und Dicyclohexenyläther, und eines Tetraens, des Quartercyclopentens, sowie ihre Cyclo- Copolymerisation mit Schwefeldioxyd wird beschrieben. Bei optimalen Bedingungen werden aus Bicyclopenten bei Temperaturen bis hinunter zu $-39°C$ in hoher Ausbeute vollständig lösliche Copolymere erhalten. Bicyclohexen lie-

ferte ebenfalls lösliche Copolymere, wenn auch in weitaus langsamerer Reaktion und mit niedrigem Umsatz. Quartercyclopenten copolymerisiert zwar, ergibt aber, wie erwartet, nur unlösliche Polymere. Die beiden Verbindungen mit 1,6-Diallylätherstruktur, Dicyclopentenyläther und Dicyclohexenyläther, polymerisierten nicht. Der Einfluss von Initiator, Temperatur, Reaktionsmedium, Dienkonzentration etc. auf die Eigenschaften der Polymeren wurde eingehender an der Copolymerisation von Bicyclopenten untersucht. Nur eine sehr begrenzte Zahl von Peroxyden in umgewöhnlich grossen Mengen erwies sich zum Start dieser Copolymerisation als wirksam. Weiters ist die Reaktion zur Erzielung löslicher Produkte auf eineenge Auswahl von Lösungsmitteln, z.B. Diäthyläther und Tetrahydrofuran, beschränkt. Keine Polymerisation konnte in Äthanol, Benzol, Methylenchlorid, Dimethylsulfoxyd und Tetramethylensulfon beobachtet werden; überschüssiges Schwefeldioxyd als lösungsmittel liefert nur dunkle und unlösliche Produkte. Dienkonzentrationen unterhalb 0,3 Gew.% sind normalerweise erforderlich, um in Dimethylsulfoxyd, Tetramethylensulfon oder Schwefelsäure lösliche Polybicyclopentensulfone zu erhalten. Die Polymerisation kann bei Temperaturen von Raumtemperatur bis hinunter zu −39°C ausgeführt werden; optimale Ergebnisse werden im allgemeinen um 0°C erhalten. Inherent-Viscosity-Werte von 1,72 (0,5 g/100 ml Dimethylsulfoxyd) wurden gemessen. Die Röntgenbeugung entspricht derjenigen amorpher Polymerer.

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Cyclocopolymerization of Dicyclic Dienes and Maleic Anhydride to Fused Ring Systems

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Synopsis

The cyclocopolymerization of maleic anhydride and four 1,5- and 1,6-dienes (bicyclopentene, bicyclohexene, dicyclopentenyl ether, and dicyclohexenyl ether) and one tetraene (quartercyclopentene) is described. Soluble, low molecular weight copolymers were obtained from all five compounds. Their compositions approach 2:1 copolymer ratios. Fused ring structures are proposed as the main repeating units. Among the compounds listed, bicyclopentene copolymerized most easily and gave good conversions for monomer ratios of 2:1. Quartercyclopentene and dicyclopentyl ether, the other five-membered ring compounds, also polymerized to good-to-fair yields. However, a monomer ratio of about 4:1 was required to obtain conversions comparable to a 2:1 maleic anhydride–bicyclopentene polymerization. The six-membered systems, bicyclopentene and dicyclopentenyl ether, gave consistently low conversions, even with a 4:1 monomer ratio. The influence of the initiator system, initiator concentration, and reaction medium was studied on copolymerizations of bicyclopentene. Best results were obtained in acetic anhydride with azobisisobutyronitrile as the initiator.

INTRODUCTION

Copolymerization with *cis,cis*-1,5-cyclooctadiene is the only reported case of a cyclocopolymerization of maleic anhydride (MA).[1] This reaction, however, is not believed to be a strictly alternating copolymerization, since maleic anhydride seems only to be incorporated in the intermolecular step, the intramolecular step being a transannular reaction of the cyclooctadiene. This leads to a 1:1 copolymer.[1]

In a foregoing paper[2] we described the cyclocopolymerization of dicyclic dienes with sulfur dioxide to fused ring systems. In the present investigation, we used the same four dienes, namely bicyclopentene (BCP)(I), bicyclohexene (BCH), dicyclopentenyl ether (DCPE), dicyclohexenyl ether (DCHE), and one tetraene, quartercyclopentene (QCP), in attempts to achieve alternating cyclocopolymerization with maleic anhydride. The reaction leads to soluble, low molecular weight polymers approaching a 2:1 copolymer ratio, for which we propose fused ring structures (e.g., II) as the main repeating unit.

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TABLE I

Copolymerization of Maleic Anhydride (MA) with Bicyclopentene (BCP), Quartercyclopentene (QCP), Bicyclohexene (BCH), Dicyclopentenyl Ether (DCPE), and Dicyclohexenyl Ether (DCHE) in Acetic Anhydride[a]

Reaction	Monomers, mole × 10^{-3}		Conversion, mole-%[b]	Analyses			$\{\eta\}$[c]	Softening point, °C.[d]
	Diene	MA		C, %	H, %	O, %		
BCP/MA/18[e]	3.6	7.6	45.4	64.06	5.65	30.07[f]	0.037	200
QCP/MA/1	1.0	8.0	67.8	65.09	5.87	26.46[g]	0.063[h]	
BCH/MA/1	3.0	12.0	28.3	64.23	5.96	27.38[i]	0.033	194
DCPE/MA/1	3.0	12.0	54.4	60.21	5.17	32.31[j]	0.039	218
DCHE/MA/1	3.0	12.0	21.0	60.55	5.53	31.34[k]	0.029	198

[a] Reaction conditions: temperature, 70°C.; time, 40 hr.; solvent, 5.0 ml. Ac_2O; catalyst, 5 wt.-% azobisisobutyronitrile (AIBN) based on diene.

[b] Based on diene.

[c] 0.5 g./100 ml. tetrahydrofuran.

[d] Determined on a Kofler hot bench in air.

[e] Reaction conditions: 70°C.; 24 hr.; 8.0 ml. Ac_2O; 4.0 wt.-% AIBN.

[f] Calculated for $[C_{18}H_{18}O_6]$: C, 65.44%; H, 5.49%; O, 29.06%.

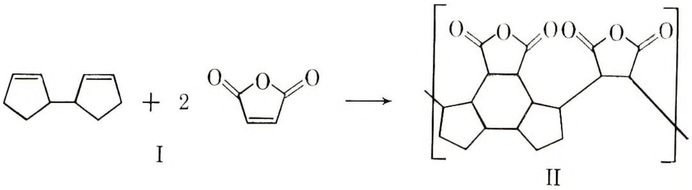
[g] Calculated for $[C_{36}H_{34}O_{12}]$: C, 65.55%; H, 5.16%; O, 29.29%.

[h] In dimethyl sulfoxide.

[i] Calculated for $[C_{10}H_{22}O_6]$: C, 67.02%; H, 6.19%; H, 26.29%.

[j] Calculated for $[C_{18}H_{18}O_7]$: C, 62.42%; H, 5.24%; O, 37.34%.

[k] Calculated for $[C_{20}H_{22}O_7]$: C, 64.16%; H, 5.92%; O, 29.92%.



EXPERIMENTAL

Reagents

Lauroyl peroxide (LPO), *p*-chlorobenzoyl peroxide (PCPBO) (Cadet Chemical Corp.), and cumene hydroperoxide (U.S. Peroxygen Corp.) were used as obtained. The active oxygen content of the peroxides was determined iodometrically.

Azobisisobutyronitrile (Eastman Organic Chemicals) was recrystallized twice from ethanol.

Maleic anhydride (Fisher Certified Reagent Grade) was recrystallized twice from equal volumes of chloroform and carbon tetrachloride with a small amount of petroleum ether added.

Benzene (Baker, analyzed reagent grade) was stored over sodium wire and distilled. Acetic anhydride (Baker, analyzed reagent grade) was purified by fractionation shortly before use. Tetrahydrofuran was stored over sodium benzophenone and redistilled shortly before use in viscosity measurements. Other solvents used were redistilled reagent grade materials.

Instruments and Analyses

Spectroscopic investigations were performed with Perkin-Elmer Infracord and Beckman IR 9 infrared spectrometers; NMR measurements were obtained with a Varian A60 nuclear magnetic resonance spectrometer.

TABLE II
Variation of Initiator System for Cyclocopolymerization of Maleic Anhydride (MA) and Bicyclopentene (BCP) in Benzene[a]

Reaction	Initiator	Initiator concentration, mole-%[b]	Solvent (benzene), g.	Conversion, mole-%[b]
BCP/MA/1	Azobisisobutyronitrile	2.32	22	19.0
/5	Azobisisobutyronitrile	2.37	42	2.0
/2	*p*-Chlorobenzoyl peroxide	2.55	22	36.0
/3	Cumene hydroperoxide	3.36	22	5.4
/4	Lauroyl peroxide	2.52	22	15.4

[a] Reaction conditions: molar ratio BCP: MA = 2.0: 4.02 (10^{-3} moles); time, 264 hr.; temperature, 73°C.

[b] Based on BCP.

TABLE III
Variation of Polymerization Medium in Cyclocopolymerization of Maleic Anhydride (MA) and Bicyclopentene (BCP) in Benzene and Acetic Anhydride (Ac_2O)[a]

	Solvent		Initiator				Analyses[c]		
Reaction	Type	Vol., ml.	Type	Concn., mole-%[b]	Time, days	Conversion, mole-%[b]	C, %	H, %	O, %
BCP/MA/6	Benzene	16	AIBN	4.5	5	32.4	63.83	5.38	28.75
/7	Benzene	16	PCBPO	3.7	5	34.3			
/8	Benzene	16	LPO	3.7	5	21.8			
/9	Ac_2O	8	AIBN	5.5	4	56.6	64.03	5.35	29.13
/10	Ac_2O	8	PCBPO	6.0	4	22.4			
/11	Ac_2O	8	LPO	6.0	4	26.2			

[a] Reaction conditions: temperature, 73°C.; ratio BCP/MA = 2.0/4.0 (10^{-3} moles).

[b] Based on BCP.

[c] Calculated for $C_{18}H_{18}O_6$: C, 65.44%; H, 5.49%; O, 29.06%.

Elemental analyses were carried out by Alfred Bernhardt, Mikroanalytisches Laboratorium, Mühlheim (Ruhr), Germany.

Diene and Tetraene Synthesis

The synthesis of the four dienes, bicyclopentene, bicyclohexene, dicyclopentenyl ether, dicyclohexenyl ether, and of quartercyclopentene has been described in the foregoing paper.[2]

Polymerization Procedure

The polymerizations were carried out in ampules sealed with rubber serum caps in an argon atmosphere. Reaction conditions are listed in Tables I–V.

In a typical example, 1.1 g. MA was dissolved in 6.5 ml. freshly distilled acetic anhydride (Ac_2O) in a 10-ml. ampule, which was cooled down to −78°C. and then evacuated; after the melting of the contents at room

TABLE IV

Time vs. Conversion for Cyclocopolymerization of Maleic Anhydride (MA) and Bicyclopentene (BCP) in Acetic Anhydride[a]

Reaction	Time, hr.	Conversion, mole-%[b]	Analyses[c]		
			C, %	H, %	O, %
BCP/MA/18	24	45.4	64.06	5.65	30.07
/19	48	52.7			
/20	72	57.0	64.11	5.56	30.08
/21	96	56.8			

[a] Reaction conditions: temperature, 70°C.; catalyst, 4.1 wt.-% AIBN; molar ratio BCP:MA: 3.6:7.6 (10^{-3} moles); solvent, 8 ml. Ac_2O.

[b] Based on BCP.

[c] Calculated for $C_{18}H_{18}O_6$: C, 65.44%; H, 5.49%; O, 29.06%.

TABLE V

Variation of Initiator Concentration in Cyclocopolymerization of Maleic Anhydride (MA) and Bicyclopentene (BCP) in Acetic Anhydride[a]

Reaction	Initiator (AIBN) concentration, wt.-%	Conversion, mole-%[b]	$[\eta]$[c]	Analyses[d]		
				C, %	H, %	O, %
BCP/MA/14	0.075	19.5	0.037	64.27	5.67	29.95
/15	0.378	29.4	0.036			
/16	1.0	39.8	0.037			
/17	2.63	67.3	0.037	64.37	5.59	30.01

[a] Reaction conditions: molar ratio BCP:MA, 5:11 (10^{-3} moles); temperature, 70°C.; time, 72 hr.; solvent, 7 ml. Ac_2O.

[b] Based on BCP.

[c] 0.5 g./100 ml. tetrahydrofuran.

[d] Calculated for $C_{18}H_{18}O_6$: C, 65.44%; H, 5.49%; O, 29.06%.

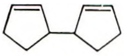
temperature, the ampule was filled with argon. The freezing–melting cycle was repeated five times. Before the last freezing, 0.60 g. BCP (BCP was stored in a bottle, sealed with a rubber serum cap, under a slight positive argon pressure) as well as a solution of 0.0527 g. azobisisobutyronitrile (AIBN) in 1 ml. Ac$_2$O were added by a hypodermic syringe. After warming to room temperature, the ampule was placed in an oil bath at 70 ± 0.5°C. and kept at this temperature for 72 hr. with occasional shaking. The contents were cooled to room temperature and precipitated by pouring into 300 ml. of a 1:1 mixture of petroleum ether and diethyl ether. After being filtered and dried at room temperature, the polymer was redissolved in tetrahydrofuran (THF) and reprecipitated twice in petroleum ether–diethyl ether. After isolation and drying to constant weight, 0.5128 g. (corresponding to 39.8% conversion) of a white polymer was obtained; $\{\eta\} = 0.037$ (0.5 g./100 ml. THF).

RESULTS AND DISCUSSION

Polymerization

Four dienes (and one tetraene) were selected for the study of cyclocopolymerization with maleic anhydride:

1,1′-Bicyclopent-2,2′-ene (BCP)

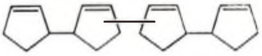


I

1,1′-Bicyclohex-2,2′-ene (BCH)

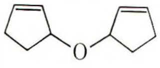
III

Quartercyclopentene (mixture) (QCP)



IV

1,1′-Dicyclopent-2,2′-enyl ether (DCPE)



V

1,1′-Dicyclohex-2,2′-enyl ether (DCHE)

VI

Copolymers were obtained from all five compounds. This is contrary to the findings in the copolymerization with sulfur dioxide,[2] where only the five-membered and six-membered 1,5-dienes gave copolymers; the compounds with 1,6-diallyl ether structure (V and VI), failed to polymerize. As in the case of cyclocopolymerization with sulfur dioxide, bicyclopentene gave copolymers most easily; and thus a large excess of maleic anhydride was unnecessary (Table I). Quartercyclopentene and dicyclopentenyl ether, the other five-membered ring compounds, also polymerized to good-to-fair conversions. However, in these cases, a twofold excess of maleic anhydride was required to obtain comparable conversion of 67.7 and 54.4 mole-%, respectively. The six-membered systems gave consistently lower conversions and reached only 28.3 mole-% for BCH and 21.0 mole-% for DCHE (Table I) under identical conditions.

Although it had been a dogma for many years that maleic anhydride does not homopolymerize, early studies of copolymerizations with allyl acetate[3] indicated and recent investigations proved[4] that homopolymerization does in fact occur. In our experiments, we, therefore, tried to stay as closely to equivalent ratios as reasonable to reduce any potential block-copolymerization of MA. Since all other dienes tested in this investigation required a larger excess of MA over diene to obtain reasonable conversion of the dienes —although the resulting copolymer compositions did not deviate seriously from the proposed structures—we restricted further studies to bicyclopentene where a slight excess of MA is sufficient to obtain conversions of 40–60%.

Various free-radical initiators such as peroxides and azodinitriles are found to be effective. Table II lists some of the systems tested. In benzene as the reaction medium, *p*-chlorobenzoyl peroxide (PCBPO) gives the highest conversion (38 mole-%), compared to 19% when initiated with azobisisobutyronitrile (AIBN).

Table III shows the influence of the reaction medium. Precipitation occurs in all cases during the polymerization in benzene. Acetic anhydride is therefore the solvent of choice, as this homogeneous system gives higher conversions. Particularly effective is the combination Ac_2O/AIBN.

A marked increase in conversion is observed for AIBN/Ac_2O as compared to AIBN/benzene, whereas the peroxide-initiated systems show only a slight increase in the case of lauroyl peroxide (LPO) (from 21.8 to 26.2%) or even drop (from 38.3 to 27.4%) for PCBPO when Ac_2O is used instead of benzene. This occurs despite the higher concentration in the Ac_2O reaction. Similar behavior was described for the homopolymerization of MA,[4] where no polymer was obtained in benzene while 15.98% was obtained in Ac_2O (^{60}Co-initiated).

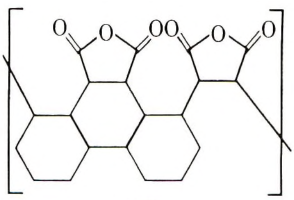
The reaction in Ac_2O initiated by AIBN requires about 70 hr. to reach optimum conversion at 70°C. (Table IV). The polymer composition is independent of the conversion as expected for an alternating copolymerization. The conversion itself strongly depends on the initiator concentration (Table V), whereas the inherent viscosity appears to be completely independent of the initiator concentration, and, hence, the conversion.

Polymer Structure and Properties

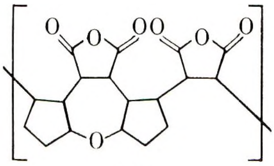
The copolymers obtained from maleic anhydride and BCP, BCH, DCPE, DCHE, and QCP are colorless powders, completely soluble in a variety of common organic solvents: acetone, acetic anhydride, tetrahydrofuran, ethyl acetate, pyridine, nitromethane, nitrobenzene, dimethylformamide, dimethyl sulfoxide, butyrolactone, etc., as well as in aqueous base solutions and concentrated mineral acids, such as sulfuric acid. Nonsolvents are aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons and aliphatic alcohols.

Softening points fall in the range of 190–220°C., depending on the type of olefinic compound used (Table I).

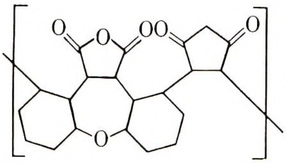
Infrared spectra are in agreement with the main structures proposed for cyclocopolymerization, e.g., II and VII–X.



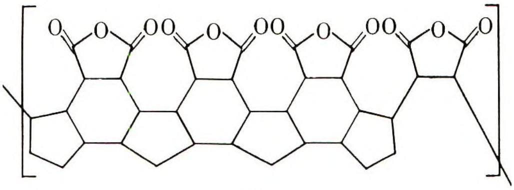
VII



VIII



IX



X

No residual unsaturation, or only a trace, could be observed in the copolymers of BCP, BCH, QCP, and DCHE; a very weak C=C-absorption at 1600 cm.$^{-1}$ is present in the spectra of DCPE/MA, which, however, is also present in maleic anhydride homopolymers.[4] The carbonyl doublet of the anhydride system is observed at 1860 and 1780 cm.$^{-1}$ in all five copolymers. Typical absorptions of poly(maleic anhydride)[4] at 1250, 1060, and 945 cm.$^{-1}$ also occur in all five copolymers of this series with slight shifts to 1225, 1065, and 920 cm.$^{-1}$. That hydrolysis to the carboxylic acid derivative during polymerization, work-up, and handling is negligible is indicated by barely noticeable OH— absorptions at 3600 and ~2500 cm.$^{-1}$.

Exact structure determinations on the basis of nuclear magnetic resonance measurements could not be carried out with these polymers, since only very broad unresolved peaks were obtained. However, nothing more than traces of residual unsaturation could be detected by NMR.

Inherent viscosities $\{\eta\}$ (η_{sp}/c at a concentration of 0.5 g./100 ml. solvent) indicate low molecular weight products; the values obtained for the diene (BCP, BCH, DCPE, and DCHE) copolymers fall in the range 0.029–0.039 (in tetrahydrofuran); QCP copolymers gave distinctively higher values of about 0.06. The neutralization equivalent of BCP-copolymers was found between 104 and 109.5 (calculated for tetraacid, based on II, 91.5), thus indicating a copolymer with a somewhat low MA content.

We are indebted to Dr. Thomas G Fox for his encouragement during the work. We also wish to thank the Lucidol Division of Wallace and Tiernan, Inc., the Cadet Chemical Corp., and the U. S. Peroxygen Corporation for generously providing us with samples of various peroxides.

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Résumé

La cyclo-copolymérisation de l'anhydride maléique et de quatre 1,5- et 1,6-diènes, le bicyclopentène, le bicyclohexène, l'éther dicyclopenténylique et l'éther dicyclohexénylique, et un tétraène, le quatercyclopentène, a été décrite. On a obtenu des copolymères de bas poids moléculaire soluble pour les cinq composés. Leur composition s'approchait d'un rapport 2/1 du copolymère. Des structures à anneaux fondus étaient proposées comme unités périodiques principales. Parmi les composés cités, le bicyclopentène, copolymérisait le plus facilement et donnait de bonnes conversion avec des rapports monomériques de 2/1. Le quatercyclopentène et l'éther dicyclopenténique, les autres composés à anneaux à cinq atomes, polymérisaient également avec des rendements suffisants. Toutefois, le rapport monomérique était d'environ 4/1 si l'on désire obtenir des degrés de conversion comparables à la polymérisation 2/1 de l'anhydride maléique bicyclopentène. Les systèmes à six atomes bicyclopentène et l'éther dicyclopenténylique donnaient des conversions basses même dans un rapport monomérique de 4/1. L'influence des systèmes initiateurs, de la concentration en initiateurs et du milieu de réaction a été étudiée sur les copolymérisations du bicyclopentène. Les meilleurs résultats ont été obtenus dans l'anhydride acétique avec l'azodiisobutyronitrile comme initiateur.

Zusammenfassung

Die Copolymerisation von Maleinsäureanhydrid mit vier 1,5-und 1,6-Dienen, Bicyclopenten, Bicyclohexen, Dicyclopentenyläther und Dicyclohexenyläther, sowie mit einem Tetraen, Quartercyclopenten, wird beschrieben. Mit allen fünf Verbindungen wurden lösliche, niedermolekulare Copolymere erhalten. Ihre Zusammensetzung nähert sich einem Copolymerverhältnis 2:1. Als Hauptbausteine werden annellierte Ringstrukturen vorgeschlagen. Von den angeführten Verbindungen copolymerisierte Bicyclopenten am leichtesten und lieferte bei einem Monomerenverhlätnis 2:1 gute Umsätze. Quartercyclopenten und Dicyclopentenyläther, die anderen Verbindungen mit fünfgliedrigen Ringen, polymerisierten elbenfalls mit guten Ausbeuten. Es war jedoch ein Monomerverhältnis von etwa 4:1 erforderlich, um Umsätze in vergleichbarer Höhe zu denjenigen einer 2:1 Maleinsäureanhydrid-Bicyclopentenpolymerisation zu erhalten. Die sechsgliedrigen Systeme, Bicyclopenten und Dicyclopentenyläther, lieferten durchwegs, auch bei einem Monomerverhältnis 4:1, niedrige Umsätze. Der Einfluss des Initiatorsystems, der Initiatorkonzentration und des Reaktionsmediums wurde bei der Copolymerization von Bicyclopenten untersucht. Die besten Ergebnisse wurden in Essigsäureanhydrid mit Azobisisobutyronitril als Initiator erhalten.

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Studies on Tacticity of Polyacrylonitrile. II. High-Resolution Nuclear Magnetic Resonance Spectra of 2,4-Dicyanopentanes

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Synopsis

The NMR spectra of 2,4-DCNP were measured in CCl_4, NaCNS–D_2O, DMSO-d_6, and other solutions. The spectra of the *meso* form show no significant change with the solvent, but the racemic form shows two kinds of spectra, one of which is observed in a solvent for PAN and the other in a nonsolvent. In the solution, the *meso* 2,4-DCNP is considered to have two equivalent conformations, TG and G'T, which are the mirror images with each other. The racemic 2,4-DCNP, however, might have predominantly either the TT or GG conformation in CCl_4, pyridine, and benzene, while it has the two conformers with almost equal probability in NaCNS–D_2O and DMSO-d_6. The results obtained from the calculation assuming appropriate constants are in fairly good agreements with the observed spectra of the 2,4-DCNP isomers. The values of chemical shifts and coupling constants used in the calculation correspond to those of PAN which were obtained previously from the analysis of the NMR spectra.

Introduction

As is well known, it is very important to study the high resolution nuclear magnetic resonance (NMR) spectra as well as the infrared spectra in order to determine the configuration and conformation of a polymer chain.

Previously, the authors have reported[1,2] that the tactic structure of polyacrylonitrile (PAN), which had been difficult to elucidate from the infrared and x-ray studies, could be determined approximately by the NMR spectra.

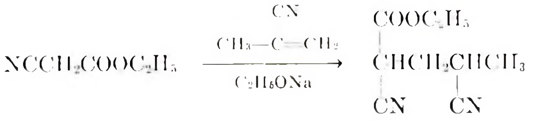
However, a study on low molecular weight model compounds may be necessary to permit discussion of the problem in more detail. In the case of poly(vinyl chloride) (PVC) and poly(vinyl alcohol) (PVA), there have been many reports on the structures of the model compounds, such as 2,4-dichloropentane,[3-6] 2,4,6-trichloroheptane,[5] 2,4-pentanediol,[7,8] and 2,4,6-heptanetriol.[9]

As for the model compounds of PAN, Takata et al.[10] have prepared 2,4-dicyanopentane (2,4-DCNP), 2,4,6-tricyanoheptane, and 2,4,6,8-tetracyanononane in their studies on the coloration of PAN. Clark[11] has prepared *meso* and racemic 2,4-DCNP and measured the infrared and NMR spectra. McMahon et al.[12] have studied the energy difference between two conformations of racemic 2,4-DCNP from the NMR spectra taken in CCl_4

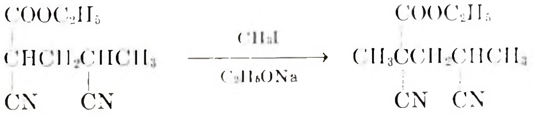
solution. In the present paper, the NMR spectra of the two isomers of 2,4-DCNP (*meso* and racemic) are explained by assuming chemical shifts and coupling constants of each proton and then discussed in comparison with the spectra of PAN.

Experimental

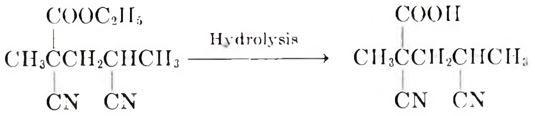
A mixture of stereoisomers of 2,4-DCNP was synthesized by the method reported by Takata et al.[10] [eqs. (1)–(4)].



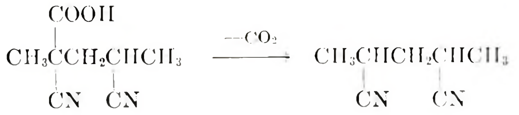
$$NCCH_2COOC_2H_5 \xrightarrow[C_2H_5ONa]{\overset{CN}{CH_3-C=CH_2}} \underset{CN}{\overset{COOC_2H_5}{CH}}CH_2\underset{CN}{CH}CH_3 \quad (1)$$



$$\underset{CN}{\overset{COOC_2H_5}{CH}}CH_2\underset{CN}{CH}CH_3 \xrightarrow[C_2H_5ONa]{CH_3I} CH_3\underset{CN}{\overset{COOC_2H_5}{C}}CH_2\underset{CN}{CH}CH_3 \quad (2)$$



$$CH_3\underset{CN}{\overset{COOC_2H_5}{C}}CH_2\underset{CN}{CH}CH_3 \xrightarrow{\text{Hydrolysis}} CH_3\underset{CN}{\overset{COOH}{C}}CH_2\underset{CN}{CH}CH_3 \quad (3)$$



$$CH_3\underset{CN}{\overset{COOH}{C}}CH_2\underset{CN}{CH}CH_3 \xrightarrow{-CO_2} CH_3\underset{CN}{CH}CH_2\underset{CN}{CH}CH_3 \quad (4)$$

The racemic form was separated by distillation and collected in fraction boiling at 105°C./7 mm. Hg. The other isomer, the *meso* form, was taken at 115–117°C./7 mm. Hg.

These stereoisomers of 2,4-DCNP were dissolved in various solvents, such as carbon tetrachloride, deuterium oxide solution of sodium thiocyanate (50% by weight), hexadeuterodimethyl sulfoxide (DMSO-d_6), pyridine, and benzene, at a concentration of 5 wt.-%, respectively.

The NMR spectra of these solutions were measured on Varian A-60 and V-4311 spectrometers operating at 60 Mc./sec. and a JNM-4H-100 spectrometer at 100 Mc./sec. The spin decoupling technique with the side band method was used.

Results and Discussion

In the previous paper,[1,2] the methylenic proton resonance spectrum of PAN in NaCNS–D_2O solution was explained as a superposition of two triplets; one of them centered at higher magnetic field is due to syndiotactic (racemic) methylene and the other at lower field due to isotactic (*meso*). On the other hand, the methylenic proton resonance measured in DMSO-d_6 was not separated into two triplets,[2,13] and a solvent effect was expected on the chemical shift of racemic and *meso* methylene groups of PAN.

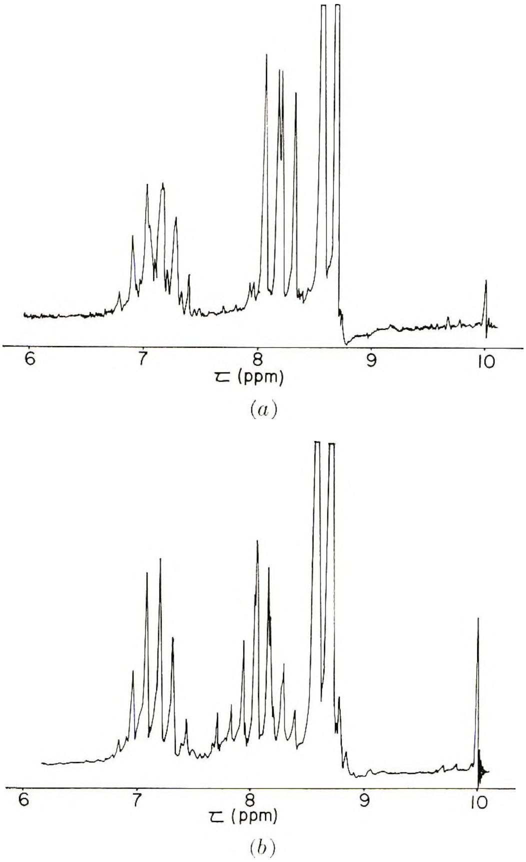
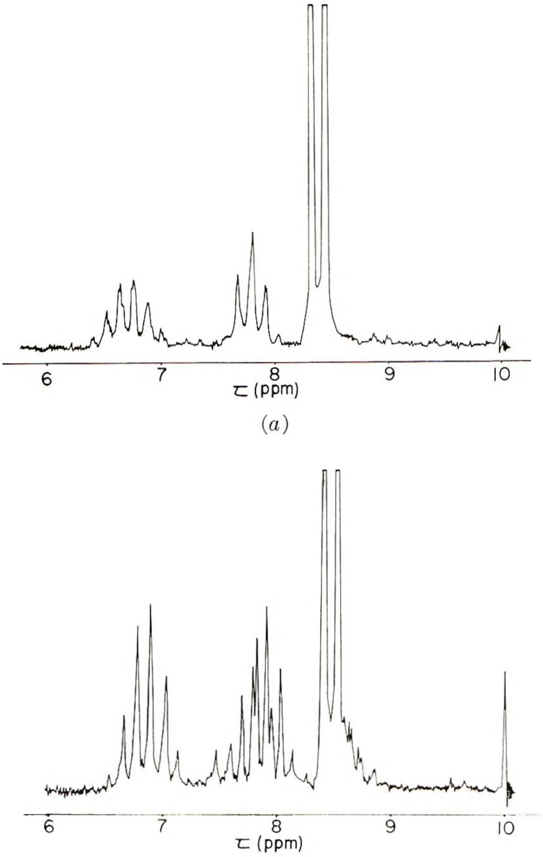


Fig. 1. NMR spectra of (a) racemic and (b) *meso* 2,4-DCNP in CCl_4 solution.

The methylene groups of racemic and *meso* 2,4-DCNP are considered to be simple models of syndiotactic and isotactic methylene groups in a PAN molecular chain, similar to poly(vinyl chloride), poly(vinyl alcohol), and other vinyl polymers. The NMR spectra of the 2,4-DCNP isomers were measured in carbon tetrachloride solution,[11] but not measured in a solvent for PAN, such as NaCNS–D_2O, DMSO, and DMF.

Figure 1 shows the NMR spectra of racemic and *meso* 2,4-DCNP in CCl_4; these are almost in agreement with the spectra reported by Clark. The NMR spectra in NaCNS–D_2O and DMSO-d_6 are shown in Figures 2 and 3. The methylenic resonance spectra of the racemic form in NaCNS–D_2O and DMSO-d_6 differ slightly from that in CCl_4. This fact suggests a difference in stability of the conformers in various solvents. The spectrum of the *meso* form has no remarkable change due to the kinds of solvent.

The analysis of the NMR spectra of the two-unit model compounds of vinyl polymers has been described by Fujiwara et al.[8,14] According to their calculation method, ten protons of 2,4-DCNP were reduced to two six-spin systems and one four-spin system. That is, the methylenic proton



(a)

(b)

Fig. 2. NMR spectra of (a) racemic and (b) *meso* 2,4-DCNP in NaCNS–D_2O solution.

resonance is associated with two methine protons (H_A and H_B in Figure 4), and is analyzed as the KL part of an $ABKL$ system. The methine protons interact with three protons of methyl group and the two protons of methylene group, and then they show a complicated spectrum due to A part of an $AKLX_3$ system.

TABLE I
Chemical Shifts and Coupling Constants of *meso*- and Racemic 2,4-DCNP

		Coupling constants, cps						
2.4-DCNP	Solvent	J_{AK}	J_{BL}	J_{AL}	J_{BK}	J_{KL}	J_{AX}	ν_{KL}
meso	CCl_4	7.2	7.2	7.2	7.2	14.0	7.2	15.0
Racemic	CCl_4	11.5	11.5	4.2	4.2		7.2	0
meso	NaCNS–D_2O	7.5	7.5	7.5	7.5	13.5	7.5	13.0
Racemic	NaCNS–D_2O	7.5	7.5	7.0	7.0		7.5	0
meso	$(CD_3)_2SO$	7.0	7.0	7.0	7.0	13.2	7.0	11.0
Racemic	$(CD_3)_2SO$	7.0	7.0	7.2	7.2		7.0	0

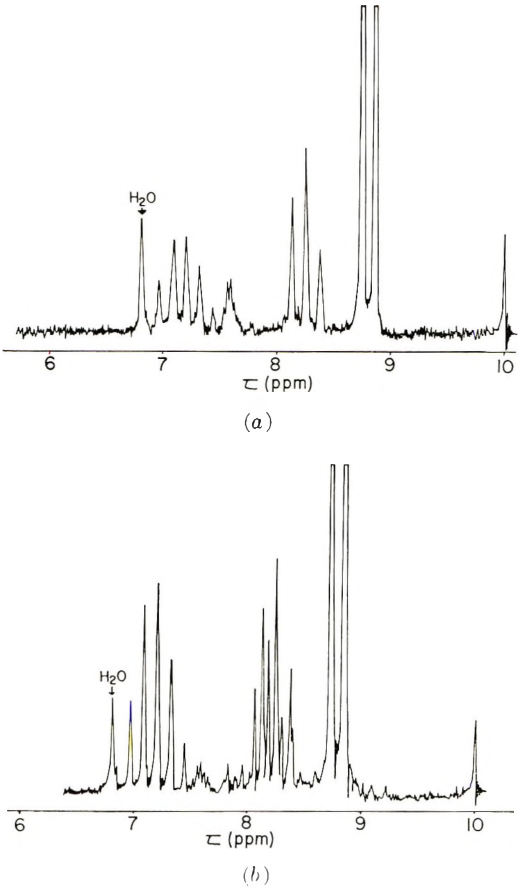


Fig. 3. NMR spectra of (*a*) racemic and (*b*) *meso* 2,4-DCNP in DMSO-d_6 solution.

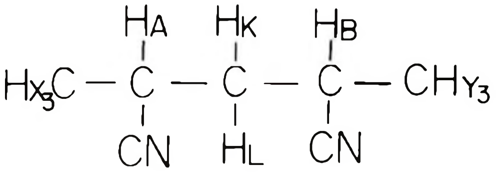


Fig. 4. Schematic representation of protons of 2,4-DCNP.

The values of the coupling constants (J_{AK}, J_{BL}, J_{AL}, J_{BK}, and J_{KL}), and the chemical shifts ν_{KL}, were estimated so as to obtain an agreement between the calculated and observed spectra. The calculated spectra are shown in Figures 5–8, and the values used in the calculation are summarized in Table I.

The methylenic proton resonance of *meso* 2,4-DCNP are treated as the KL part of an $ABKL$ ($A = B$) system where $J_{AK} = J_{BL} = J_{AL} = J_{BK}$. This fact can be confirmed by the methylenic proton spectrum decoupled

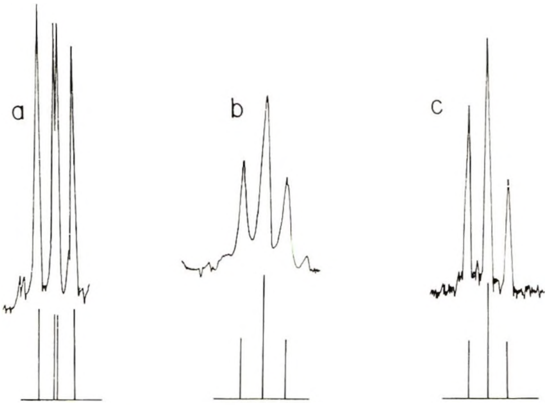


Fig. 5. Methylenic proton resonance spectra of racemic 2,4-DCNP: (*a*) in CCl_4; (*b*) in NaCNS–D_2O; (*c*) in DMSO-d_6; (top) observed spectra; (bottom) calculated.

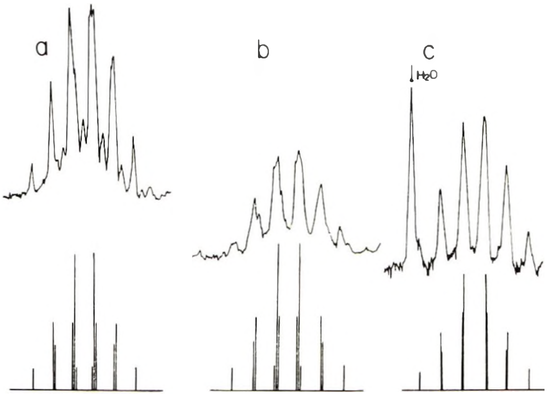


Fig. 6. Methinic proton resonance spectra of racemic 2,4-DCNP: (*a*) in CCl_4; (*b*) in NaCNS–D_2O; (*c*) in DMSO-d_6; (top) observed spectra; (bottom) calculated.

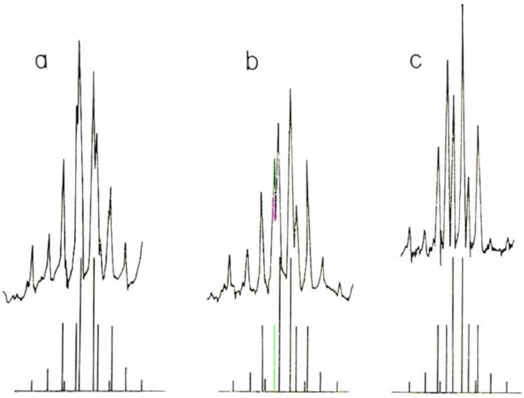


Fig. 7. Methylenic proton resonance spectra of *meso* 2,4-DCNP: (*a*) in CCl_4; (*b*) in NaCNS–D_2O; (*c*) in DMSO-d_6; (top) observed spectra; (bottom) calculated.

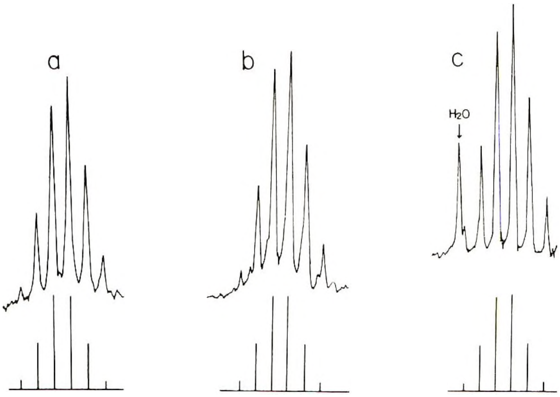


Fig. 8. Methinic proton resonance spectra of *meso* 2,4-DCNP: (*a*) in CCl_4; (*b*) in NaCNS–D_2O; (*c*) in DMSO-d_6; (top) observed spectra; (bottom) calculated.

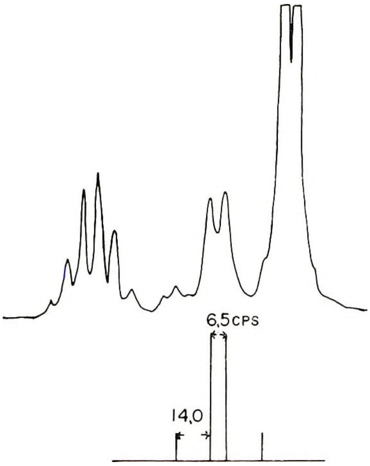


Fig. 9. Decoupled methylenic proton resonance spectra of *meso* 2,4-DCNP in CCl_4: (top) observed; (bottom) calculated.

from the methinic proton. A quartet of the KL system is observed in the decoupled spectrum as shown in Figure 9.

On the other hand, the methylenic proton resonance of the racemic form consists of four peaks in CCl_4 solution, and it can be analyzed as the KL part of an $ABKL$ ($A = B$, $K = L$) system, where $J_{AK} = J_{BL}$ and $J_{AL} = J_{BK}$. Whereas the methylenic resonance spectra in benzene and in pyridine show four peaks and can be treated in the same way as above, the spectra in NaCNS–D_2O, in $ZnCl_2$–D_2O, in DMSO-d_6 and in DMF show simple triplets which have an intensity ratio of 1:2:1. In the latter case, two couples of the values of coupling constants are almost equal ($J_{AK} = J_{BL} \approx J_{AL} = J_{BK}$), and then the J_{KL} value is not defined, because the separation of the central peaks in the β-proton spectra of the racemic 2,4-DCNP is about zero.

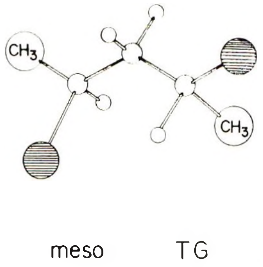


Fig. 10. Possible rotational isomer of *meso* 2,4-DCNP (TG).

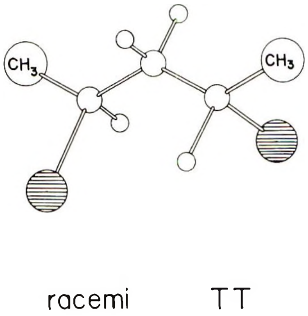


Fig. 11. Possible rotational isomer of racemic 2,4-DCNP (TT).

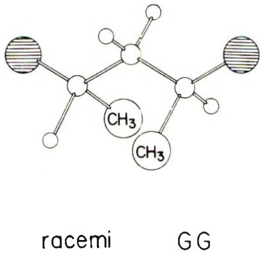


Fig. 12. Possible rotational isomer of racemic 2,4-DCNP (GG).

These results may suggest the chain conformation of 2,4-DCNP molecule. The coupling constants obtained from the spectra of molecules with rotational isomerism may be regarded as an averaged value of those isomers.[5] In the case of the *meso* form, the analysis of the NMR spectrum shows that $J_{AK} = J_{BL} = J_{AL} = J_{BK}$, while in the racemic form, $J_{AK} = J_{BL} \neq J_{AL} = J_{BK}$ in CCl_4, pyridine, and benzene, and $J_{AK} = J_{BL} \approx J_{AL} = J_{BK}$ in NaCNS–D_2O and DMSO-d_6. Such a result may be interpreted as follows. In solution, the *meso*-2,4-DCNP is considered to have two equivalent conformations, TG and G′T, which are the mirror images of each other. The racemic-2,4-DCNP, however, might have either a TT or GG conformation predominantly in CCl_4, pyridine, and benzene, while it has the two conformers with almost equal probability in NaCNS–D_2O and DMSO-d_6. (Figs. 10–12). This fact may be associated with the dipole moments of these solvents and suggests a relationship of the chain conformation of PAN and its solubility.

The values of the chemical shift and the coupling constant are listed in Table II, in which the values for PAN are also listed.

TABLE II
Comparison of Chemical Shifts and Coupling Constants of 2,4-DCNP and PAN

	τ, ppm		J_{CH_2-CH}, cps	
	D_2O + NaCNS	$(CD_3)_2SO$	D_2O + NaCNS	$(CD_3)_2SO$
2,4-DCNP				
meso	7.77	8.23	7.5	7.0
Racemic	7.82	8.25	7.5 7.0	7.2 7.0
PAN				
Iso CH_2	7.45	8.08	7.2	7.0
Syndio CH_2	7.50		6.6	

As shown in Table II, the *meso* methylene protons give a triplet in PAN but not in 2,4-DCNP. These facts correspond to data for the other vinyl polymers, such as PVC, and it has not been clarified why the value of ν_{KL} becomes small in high polymers. The spectrum of *meso* methylene protons should give a triplet, if one takes a small value for ν_{KL}. If the center of methylenic resonance shift can be taken for a comparison of the chemical shifts of 2,4-DCNP and PAN, the chemical shift of racemic methylene has a higher value than that of *meso* methylene in PAN (7.50 and 7.45 ppm) as well as 2,4-DCNP (7.82 and 7.77 ppm) in the solution of NaCNS–D_2O. In DMSO-d_6, the racemic methylene of 2,4-DCNP has slightly higher shift (8.25 ppm) than the *meso* methylene (8.23 ppm), and correspondingly, the methylenic resonance of PAN could not be separated.

The authors wish to express their sincere thanks to Dr. S. Satoh of this Institute for measurement of the decoupled spectrum and helpful advice.

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Résumé

Les spectres NMR de 2,4-DCNP ont été mesurés dans le CCl_4 NaCNS–D_2O, DMSO-d_6 et d'autres solutions. Les spectres de la forme méso ne subissent pas de modification par les solvants, mais la forme racémique montre deux sortes de spectres, un qui est trouvé dans un solvant pour la solution de PAN et l'autre dans un non-solvant. Dans la solution, le 2,4-DCNP méso est considéré avoir deux conformations équivalentes TG et G'T qui sont les images spéculaires de l'autre. Toutefois, le DCNP-2,4-racémique peut avoir soit une conformation TT ou GG prédominente dans le CCl_4, pyridine ou benzéne, tandis qu'il a les deux conformaires avec une probabilité presque égale dans NaCNS–D_2O and DMSO-d_6. Les résultats obtenus au départ de calculs admettant des constantes appropriées sont en bon accord avec les spectres observés du DCNP's-2,4. Les valeurs de glissements chimiques et des constantes de couplage utilisées dans ce calcul correspondent à celles pour le PAN qui étaient obtenues antérieurement au départ des spectres NMR.

Zusammenfassung

Das NMR-Spektrum von 2,4-DCNP wurde in CCl_4, NaCNS–D_2O, DMSO-d_6 und anderen Lösungen gemessen. Das Spektrum der meso-Form wird durch Wechsel des Lösungsmittels nicht wesentlich geändert, aber die Racem-Form zeigt zwei Arten von Spektren, von welchen das eine in einem Lösungsmittel für PAN und das andere in einem Fällungsmittel auftritt. Es wird angenommen, dass *meso*-2,4-DCNP in Lösung zwei äquivalente Konformationen, TG und *G'T*, besitzt, welche sich wie Bild und Spiegelbild verhalten. Racemisches 2,4-DCNP hingegen könnte in CCl_4, Pyridin und Benzol entweder vorwiegend *TT*- oder *GG*-Konformation besitzen, während in NaCNS–D_2O und DMSO-d_6 beide Konformationen etwa gleiche Wahrscheinlichkeit besitzen. Rechnungsergebnisse unter Annahme geeigneter Konstanten stimmen mit den beobachteten 2,4-DCNP-Spektren ziemlich gut überein. Die bei der Berechnung verwendeten Werte für chemische Verschiebung und Kopplungskonstanten entsprechen den früher für PAN aus der Analyse des NMR-Spektrums erhaltenen.

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Polyoxazolidones

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Synopsis

Polyurethans with chloromethyl side chains were prepared by the polyaddition reaction of bischlorohydrins and diisocyanates. The polyurethans had inherent viscosities in a range of 0.22–0.60 and gave transparent films by solution casting. These polyurethans were easily converted to the polyoxazolidones by treatment with sodium methoxide. The polyoxazolidones had inherent viscosities up to 0.51, and gave transparent films by solution casting.

INTRODUCTION

Polymers having oxazolidone rings in the main chain have been prepared from diisocyanates and bisepoxides.[1-3] However, these polyoxazolidones are reported to be insoluble in organic solvents and infusible, possibly because of the existence of crosslinking structures. In our previous paper,[4] it was shown that linear polyoxazolidones were obtained by the polyaddition–condensation reaction between bisepoxides and difunctional urethans. However, the degree of polymerization was low due to the low solubility of the growing polymer molecules in the solvents under the reaction conditions.

In continuation of the study of polymer syntheses, high molecular polyurethans with chloromethyl side chains were prepared from diisocyanates and bischlorohydrins. Such polyurethans were easily converted to polyoxazolidones by dehydrochlorination with bases.

RESULTS AND DISCUSSION

Monomers

The aromatic bischlorohydrins were prepared from bisepoxides* and hydrochloric acid, and purified by recrystallization from benzene or a

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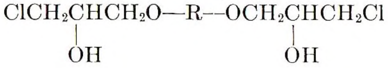
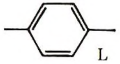
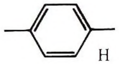
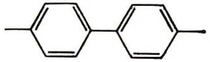
* Since these bisepoxides contain two equivalent asymmetric carbon atoms, there should be respective *meso*- and racemic isomers. With respect to 1,4-bis(1,2-epoxypropoxy)-benzene, such isomers were separated by fractional recrystallization from acetone and methanol. For simplicity, we wish to employ subscripts (or suffixes) H and L, standing for the higher melting bisepoxide and its derivatives and the lower melting one and its derivatives, respectively. Other bisepoxides were used without separation of the isomers.

TABLE I

Bischlorohydrins



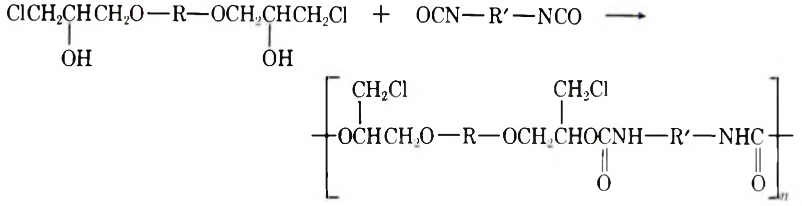
$$\underset{\mathrm{OH}}{\mathrm{ClCH_2CHCH_2O}}\text{—R—}\underset{\mathrm{OH}}{\mathrm{OCH_2CHCH_2Cl}}$$

R	Yield, %	Melting point, °C. (or boiling point, °C./mm. Hg)	Elemental analysis					
			Found			Calculated		
			C, %	H, %	Cl, %	C, %	H, %	Cl, %
$—(CH_2)_4—$	28	(176/0.05)	43.75	7.33	25.82	43.65	7.33	25.77
 L	89	77–84	48.32	5.48	24.00	48.83	5.46	24.02
 H	90	106–108	48.87	5.40	23.60	48.83	5.46	24.02
	76	139–145	58.37	5.46	18.87	58.23	5.43	19.10

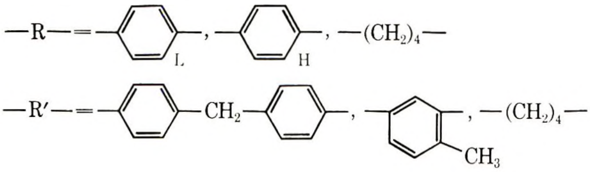
mixture of benzene and cyclohexane. 1,1′-Tetramethylenedioxybis(3-chloro-2-propanol) was prepared from tetramethylene glycol and epichlorohydrin and purified by distillation in a poor yield, since distillation at high temperatures always accompanied dehydrochlorination of the product. The yields, the melting points or boiling point, and the analytical data are listed in Table I.

Polyurethans

The bischlorohydrins prepared above were subjected to polyaddition reaction with diphenylmethane diisocyanate, 2,4-toluene diisocyanate, and tetramethylene diisocyanate to form polyurethans having chloromethyl groups.



$$\mathrm{ClCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2O{-}R{-}OCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2Cl} + \mathrm{OCN{-}R'{-}NCO} \longrightarrow \left[\mathrm{{-}O\overset{\displaystyle CH_2Cl}{\overset{|}{C}}HCH_2O{-}R{-}OCH_2\overset{\displaystyle CH_2Cl}{\overset{|}{C}}HO\underset{\displaystyle O}{\underset{\|}{C}}NH{-}R'{-}NH\underset{\displaystyle O}{\underset{\|}{C}}{-}} \right]_n \quad (1)$$



The polyaddition reaction was carried out in the usual manner, di-*n* butyltin dilaurate being used as a catalyst and anisole as a solvent.

These polyurethans were soluble in various organic solvents, such as acetone, tetrahydrofuran, dioxane, dimethylformamide, and *m*-cresol, and insoluble in methanol, *n*-hexane, toluene, and formic acid. Tough, transparent films were obtained by solution casting. Table II summarizes the yields, the inherent viscosities, the melting points, and the analytical data of the polyurethans.

Model Compounds

In order to make possible identification of the polymers and to investigate the oxazolidone formation from the polyurethans, difunctional *N*-aryl and alkyl urethans were prepared from bischlorohydrin and aromatic and aliphatic isocyanate [eq. (2)], where R′ is C_6H_5 or C_2H_5.

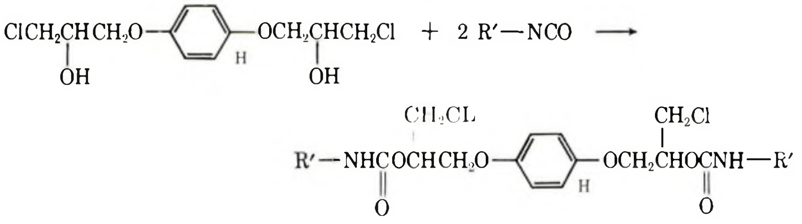
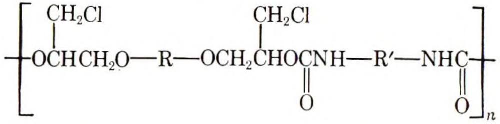
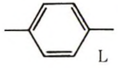
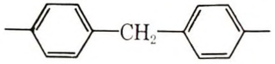
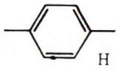


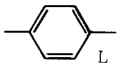
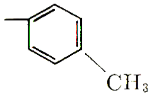
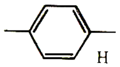
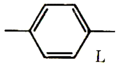
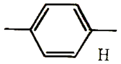
TABLE II

Polyurethans



$$\left[-\overset{\overset{\displaystyle CH_2Cl}{|}}{O\,CH}CH_2O-R-OCH_2\overset{\overset{\displaystyle CH_2Cl}{|}}{CH}O\underset{\underset{\displaystyle O}{\|}}{C}NH-R'-NH\underset{\underset{\displaystyle O}{\|}}{C}- \right]_n$$

No.	R	R′	Yield, %	η_{inh}, dl./g.[a]	PMT, °C.[b]	Elemental analysis: Found C, %	Found H, %	Found N, %	Found Cl, %	Calculated C, %	Calculated H, %	Calculated N, %	Calculated Cl, %
I			96	0.60	123	58.95	5.04	5.06	12.81	59.46	4.80	5.14	13.00
II		″	92	0.44	125	59.58	5.03	4.69	12.77	59.46	4.80	5.14	13.00
III	—$(CH_2)_4$—	″	96	0.41	80	57.36	5.86	5.07	12.78	57.15	5.76	5.33	13.50

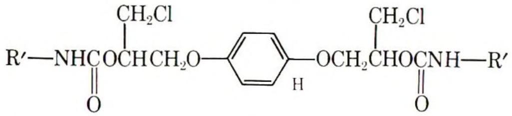
IV			97	0.35	104	53.78	5.11	5.99	14.49	53.74	4.72	5.97	15.11
V		"	98	0.41	100	54.02	5.13	5.84	14.74	53.74	4.72	5.97	15.11
VI	$-(CH_2)_4-$	"	89	0.22	83	51.67	6.04	6.20	14.85	50.79	5.83	6.23	15.78
VII		$-(CH_2)_4-$	93	0.58	70	51.13	5.89	6.39	15.74	49.66	5.56	6.44	16.29
VIII		"	92	0.34	87	49.93	5.78	6.19	15.67	49.66	5.56	6.44	16.29
IX	$-(CH_2)_4-$	"		Viscous oil									

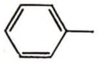
---

[a] Measured at a concentration of 0.5 g./100 ml. of *m*-cresol at 30°C.

[b] Polymer melt temperature.

TABLE III
Bisurethans



R′	Yield. %	Melting point, °C.	Elemental analysis							
			Found				Calculated			
			C, %	H, %	N, %	Cl, %	C, %	H, %	N, %	Cl, %
	89	160.5–162.5 (from ethanol)	58.02	4.98	5.21	13.02	58.54	4.91	5.25	13.27
C_2H_5—	82	132.5–133.5 (from benzene)	49.54	6.09	6.30	16.20	49.44	5.99	6.41	16.21

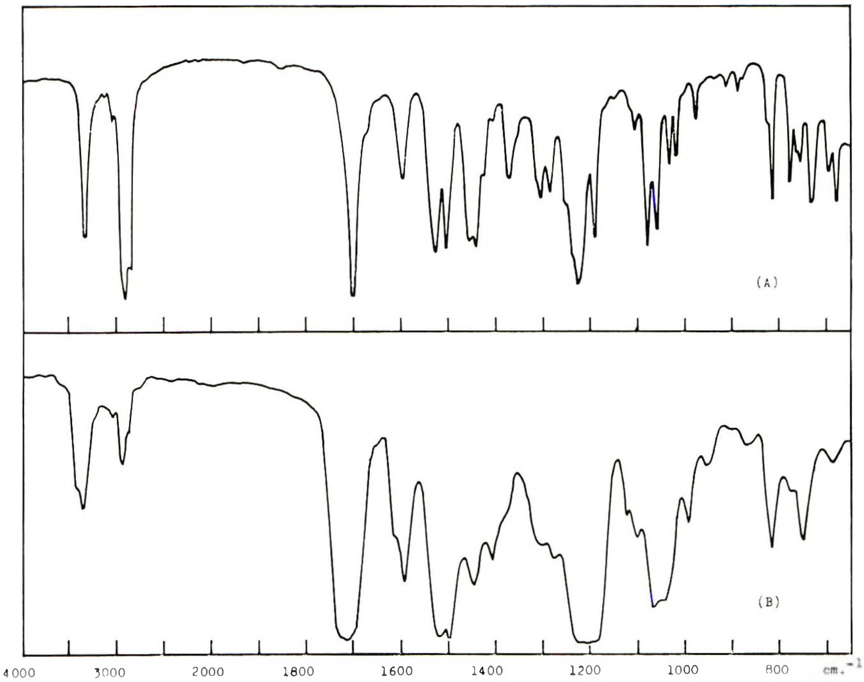
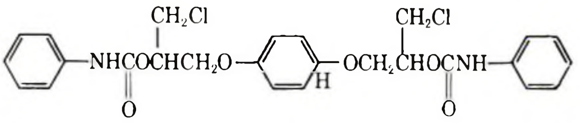


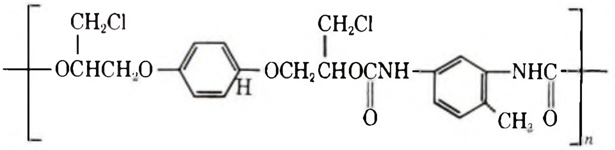
Fig. 1. Infrared spectra of the bisurethan and the polyurethan:

(A)



(Nujol);

(B)

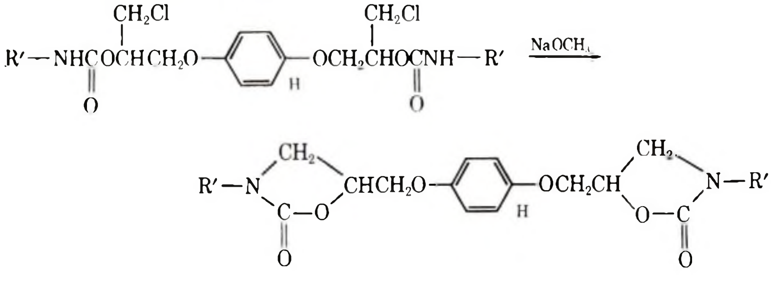


(film).

The yields, the melting points, and the analytical data of the bisurethans are listed in Table III.

Infrared spectra of the bisurethans and the polyurethans obtained above are shown in Figure 1. They are essentially identical, and the most characteristic absorption bands are found at 3350 (NH stretching), 1700–1710 (C=O stretching), and 1520–1530 cm.$^{-1}$ (NH bending).

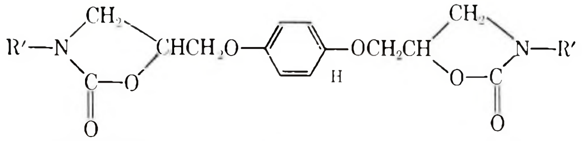
These bisurethans obtained above were treated with sodium methoxide to form bisoxazolidones under various conditions [eq. (3)].

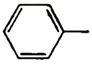


(3)

Results are summarized in Table IV. As seen in Table IV, when a large excess of sodium methoxide was used at higher temperatures, bisoxazolidones were obtained in almost quantitative yields.

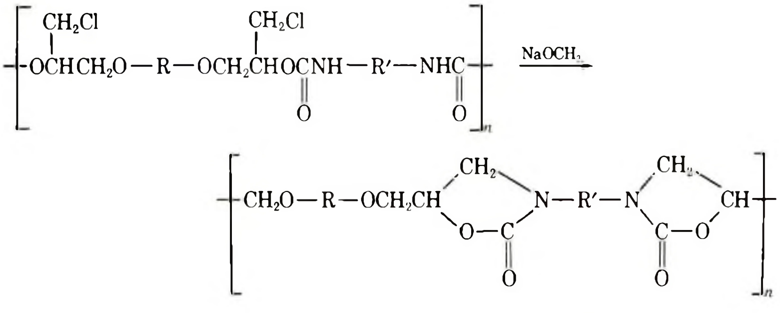
TABLE IV
Preparation of Bisoxazolidones from Bisurethans



R′	Molar equivalence of NaOCH₃	Temperature, °C.	Time, min.	Yield, %
	1.2	20	30	84
″	1.2	70	10	98
″	2	100	60	80
″	3	60	60	89
C_2H_5—	1.2	20	30	86
″	1.2	50	90	90
″	2	100	60	87
″	3	60	60	90

Polyoxazolidones

Treatment of the polyurethans obtained above in a similar manner with sodium methoxide resulted in the formation of polyoxazolidones [eq. (4)]. The reaction was carried out in dimethylformamide at room temperature for about 1 hr. The polymer reaction proceeded without the formation of precipitate.



(4)

Table V summarizes the yields, the inherent viscosities, the melting points, and the analytical data of the polyoxazolidones.

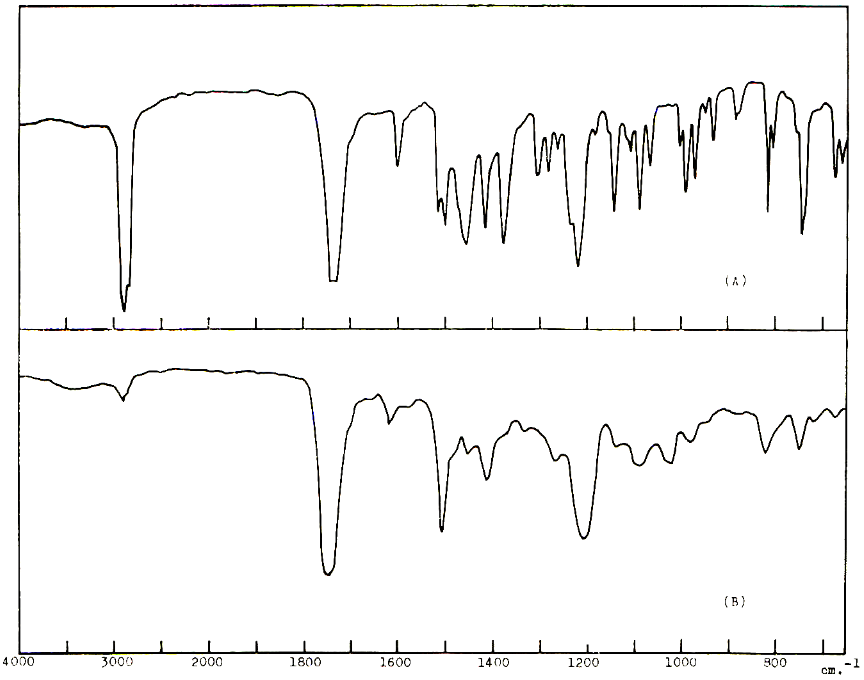
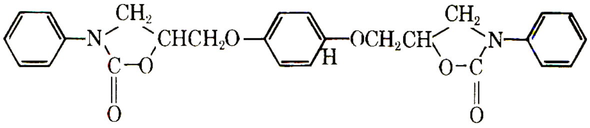
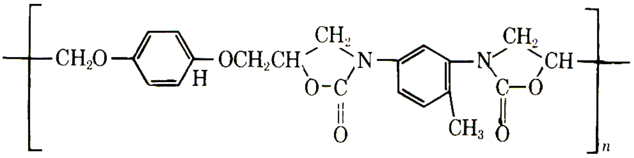


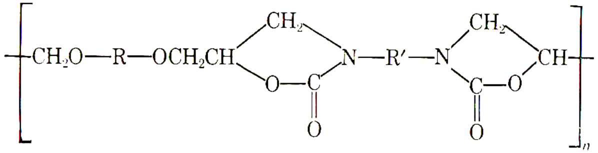
Fig. 2. Infrared spectra of the bisoxazolidone and the polyoxazolidone:

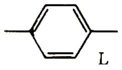
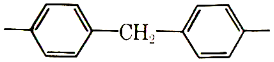
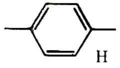
(*A*)

(Nujol);

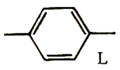
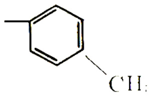
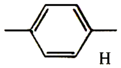
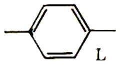
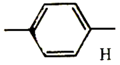
(*B*)

(film).

The rate of the ring closure reaction was affected by the structure of the *N*-substituent of the polyurethans. The polyurethans derived from diphenylmethane diisocyanate were dehydrochlorinated very rapidly, and the reaction was completed in a few minutes. However, in case of those derived from 2,4-toluene diisocyanate, the reaction was slower, presumably due to the steric hindrance by the *o*-methyl group. Accordingly, a little longer reaction time was necessary to complete the reaction. The polyurethans derived from tetramethylene diisocyanate underwent dehydrochlorination much more slowly. Moreover, in contrast to the results with *N*-aryl derivatives, the cyclization reaction of the *N*-tetramethylene polyurethans resulted in the marked reduction of the inherent viscosities of the polymers. The fact would indicate that the cleavage of the polymer main chain occurred to some extent. It is well known that

TABLE V
Polyoxazolidones



						Elemental analysis					
						Found			Calculated		
No.	R	R′	Yield, %	η_{inh}, dl./g.[a]	PMT, °C.[b]	C, %	H, %	N, %	C, %	H, %	N, %
I			88	0.51	188	67.19	4.98	5.70	68.63	5.12	5.93
II		″	95	0.41	196	67.68	4.95	5.91	68.63	5.12	5.93
III	$-(CH_2)_4-$	″	81	0.30	88	65.68	6.25	5.70	66.36	6.24	6.19

IV			79	0.24	178	62.73	5.17	7.09	63.63	5.09	7.07
V		"	82	0.39	177	62.53	5.49	7.12	63.63	5.09	7.07
VI	$-(CH_2)_4-$	"	83	0.20	86	60.16	6.54	7.60	60.62	6.43	7.44
VII		$-(CH_2)_4-$	61	0.11	68	57.24	6.48	7.36	59.66	6.12	7.73
VIII		"	61	0.10	75	58.89	6.86	7.04	59.63	6.12	7.73

---

[a] Measured at a concentration of 0.5 g./100 ml. of *m*-cresol at 30°C.

[b] Polymer melt temperature.

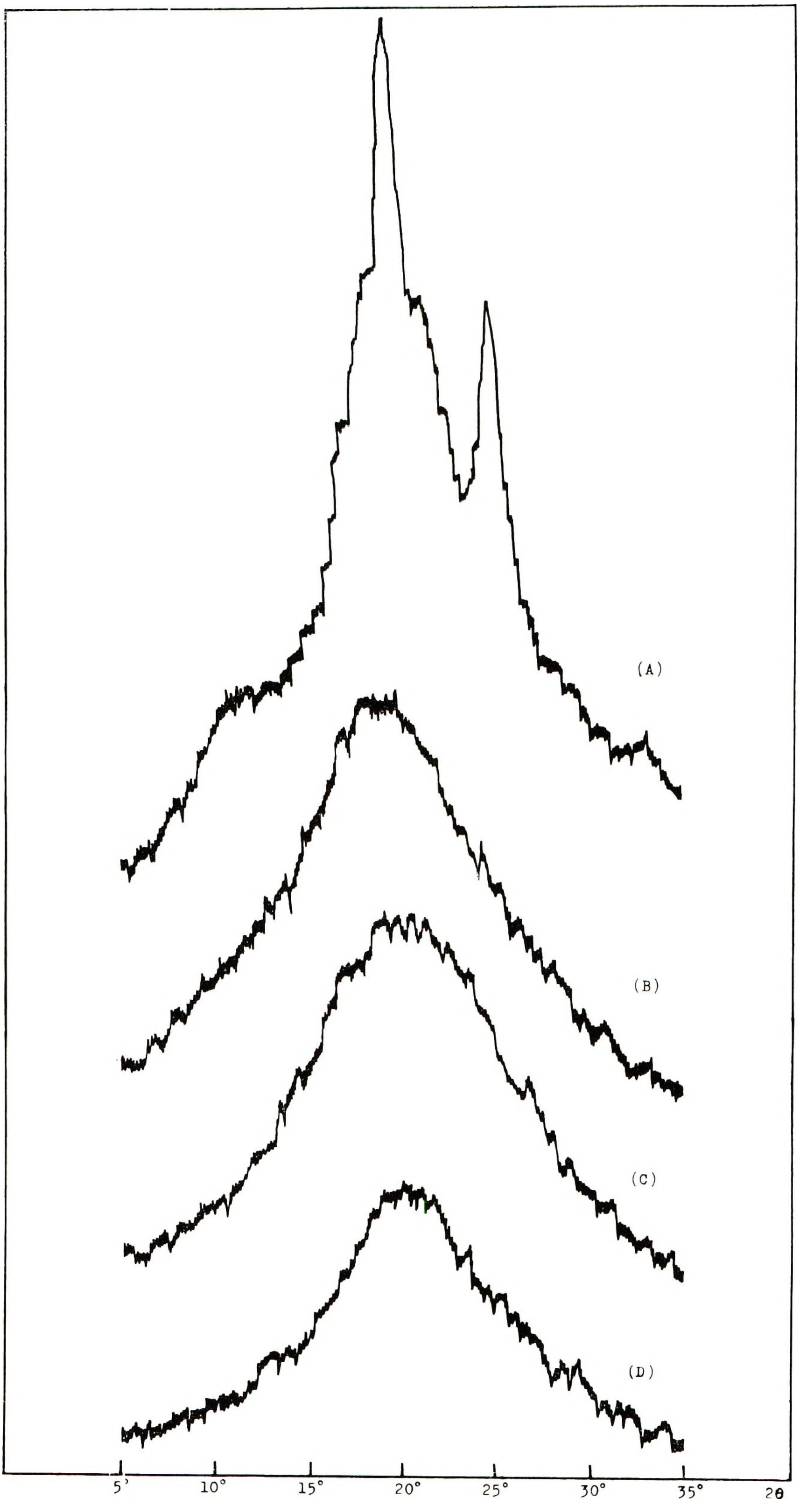
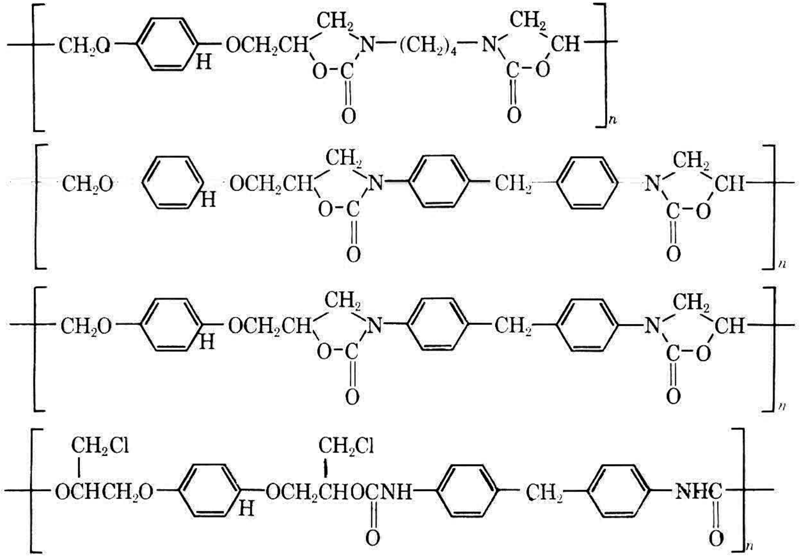

(A)
(B)
(C)
(D)
5°
10°
15°
20°
25°
30°
35°
2θ

Fig. 3. X-ray diffraction diagrams of the polyurethan and the polyoxazolidones:



(A) ($\eta_{inh} = 0.10$);

(B) ($\eta_{inh} = 0.12$);

(C) ($\eta_{inh} = 0.41$);

(D) ($\eta_{inh} = 0.44$).

N-monosubstituted or unsubstituted urethans are attacked by bases much more rapidly than the disubstituted ones.[5] The above results suggest that the cleavage of the urethan linkage in the starting *N*-tetramethylene polyurethans would have occurred partially before the slow cyclization reaction took place to give the oxazolidone ring, which is considered to be a disubstituted urethan.

The formation of the polyoxazolidones was confirmed by infrared spectra and the analytical data. Figure 2 shows the infrared spectra of the bisoxazolidone and the polyoxazolidone. The characteristic absorption bands of urethans at 3350 and 1520–1530 cm.$^{-1}$ entirely disappeared, and a band at 1700–1710 cm.$^{-1}$ shifted to 1740–1750 cm.$^{-1}$, showing that the ring closure reaction proceeded completely.

Polyoxazolidones obtained here were soluble in dimethylformamide (polyoxazolidones II and V were soluble on heating) and *m*-cresol, and insoluble in usual organic solvents such as acetone, methanol, *n*-hexane, tetrahydrofuran, dioxane, toluene, and formic acid.

Crystallinity

The x-ray diffraction diagrams show that all the polyurethans having chloromethyl groups were amorphous. The polyoxazolidones derived from aromatic diisocyanates were crystalline to some extent, while those derived from aliphatic diisocyanate were highly crystalline. The difference is not attributed to the lower molecular weight of the latter polymers, since low molecular weight polyoxazolidones from aromatic diisocyanate also showed a low crystallinity as those of the high molecular weight ones. The low crystallinity of the polyoxazolidones derived from aromatic diisocyanates as shown in Figure 3, might be due to the rigid all-ring structures and bent constitution along the nitrogen of oxazolidone and the carbon of aromatic ring, which added less chain mobility and disorder of orientation among the polymer chain. In *N*-polymethylene polyoxazolidones, on the other hand, the flexibility of the polymethylene chain would allow the polymer chain to arrange more regularly.

EXPERIMENTAL

Monomers

1,1′-*p*-Phenylenedioxybis(3-chloro-2-propanol) (H). To a large excess of concentrated hydrochloric acid (120 ml.) dissolved in 120 ml. of dioxane was added 15 g. of 1,4-bis(1,2-epoxypropoxy)benzene (H). The epoxide went into solution gradually in the course of the reaction. The mixture was allowed to stand at room temperature for 1 hr., and the solvent was evaporated under reduced pressure. The residual white solid was recrystallized from 90 ml. of benzene to give 18.0 g. (90%) of the product, m.p. 106–108°C.

The other aromatic bischlorohydrins were prepared by the same method. 1,1′-Tetramethylenedioxybis(3-chloro-2-propanol) was prepared by treating tetramethylene glycol with epichlorohydrin in the presence of stannic chloride.[6]

Polyaddition

Polyaddition was carried out at 120–155°C. for 1–6 hr. in anisole in the presence of a small amount of di-*n*-butyltin dilaurate as a catalyst. A typical example was as follows.

Polyurethan I. To a mixture of 1.496 g. of diphenylmethane diisocyanate and 1.765 g. of 1,1′-*p*-phenylenedioxybis(3-chloro-2-propanol) (I) dissolved in 20 ml. of dry anisole was added a few drops of di-*n*-butyltin dilaurate as a catalyst. The mixture was stirred at 120°C. for 1 hr. under an atmosphere of nitrogen and then poured into 500 ml. of *n*-hexane to precipitate the polymer. The polymer was obtained as white fibrous material and weighed 3.13 g. (96%). The inherent viscosity was 0.60 (determined at a concentration of 0.5 g./100 ml. of *m*-cresol at 30°C.).

Model Compounds

Bisurethans. The bisurethans were prepared from the bischlorohydrin and the monoisocyanates by using di-*n*-butyltin dilaurate as a catalyst.

***p*-Phenylenebis(3-ethyl-2-oxazolidinon-5-yl-methyl) Ether.** To a solution of 0.88 g. of 1,1′-*p*-phenylenedioxybis[3-chloro-2-(*N*-ethyl)carbamoylpropane] in 10 ml. of dimethylformamide was added a solution of 0.26 g. of sodium methoxide in 0.5 ml. of methanol. Soon sodium chloride and the bisoxazolidone precipitated out. The mixture was stirred at 20°C. for 30 min. and then poured into 200 ml. of water, and the crystals were collected on filter. The yield was 0.63 g. (86%). Recrystallization from 30 ml. of anisole gave white plates, m.p. 173.5–175°C.

ANAL. Calcd. for $C_{18}H_{24}N_2O_6$: C, 59.33%; H, 6.64%; N, 7.69%. Found: C, 59.24%; H, 6.44%; N, 7.59%.

p-Phenylenebis(3-phenyl-2-oxazolidinon-5-yl-methyl) ether was prepared in a similar manner as above. The yield was 84%. Recrystallization from anisole gave white plates, m.p. 215–216.5°C. (reported:[4] 216–217°C.).

Polyoxazolidones. An example of the synthesis of a polyoxazolidone was as follows. To a solution of 0.436 g. of polyurethan I in 10 ml. of dimethylformamide was added a slight excess of sodium methoxide (0.10 g.) dissolved in 0.5 ml. of methanol. After stirring for 50 min. at 20°C., the mixture was poured into 200 ml. of water. The polyoxazolidone was obtained as powdery material, which weighed 0.33 g. (88%) and gave tough, transparent films by solution casting. The inherent viscosity was 0.51 (determined at a concentration of 0.5 g./100 ml. of *m*-cresol at 30°C.).

Crystallinity

The x-ray diffraction diagrams of the polyurethans and the polyoxazolidones were obtained by the powder method with the use of nickel-filtered CuKα radiation.

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4. Y. Iwakura, S. Izawa, and F. Hayano, *J. Polymer Sci. A-1*, **4**, 751 (1966).
5. P. Adams and F. A. Baron, *Chem. Rev.*, **65**, 567 (1965).
6. S. G. Cohen and H. C. Haas, *J. Am. Chem. Soc.*, **75**, 1733 (1953).

Résumé

Par polyaddition de bis-chlorohydrines et de diisocyanates, on a préparé des polyuréthanes avec des chaînes latérales chlorométhylées. Les polyuréthanes ont des viscosités inhérentes de 0.22 à 0.60 et donnaient des films transparents au départ du coulage de leur solution. Ces polyuréthanes étaient facilement transformés en polyoxazolidones par traitement avec le méthylate de sodium. Les polyoxazolidones avaient des viscosités inhérentes allant jusque 0.51 et fournissaient des films transparents par coulage au départ de leur solution.

Zusammenfassung

Durch die Polyadditionsreaktion von Bischlorhydrinen und Diisocyanaten wurden Polyurethane mit Chlormethylseitenketten dargestellt. Die Polyurethane besassen Viskositätszahlen im Bereich von 0,22 bis 0,60 und liessen sich aus Lösung zu transparenten Filmen giessen. Diese Polyurethane konnten durch Behandlung mit Natriummethylat leicht in Polyoxazolidone umgewandelt werden. Die Polyoxazolidone hatten Viskositätszahlen bis zu 0,51 und lieferten durch Giessen aus Lösung transparente Filme.

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Kinetics of the Bulk Polymerization of Dioxolane in the Presence of Water

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Synopsis

The polymerization of dioxolane initiated by the $\sim Si^{\oplus}HSO_4^{\ominus}$ ion pair is greatly influenced by water which changes the overall polymerization rate. Particularly great changes are brought about at certain higher conversions (whose values are also a function of an initial concentration of water). The polymerization practically stops at these conversions and the system appears to be close to a monomer-polymer equilibrium. It is shown that the equation $v_{\text{overall}} = f([H_2O])$, which describes the dependence of the overall rate of polymerization on the concentration of water and which was originally derived for the polymerization of trioxane, holds also for the polymerization of dioxolane. The decrease of water concentration during the polymerization was measured and the observed equilibrium was shown to be a kinetic phenomenon.

INTRODUCTION

The polymerization of dioxolane has been studied in several laboratories[1-7] recently. Until now, however, there has been no interest in the sharp changes in the kinetics of the process which are brought about by water in the polymerizing medium. We also failed to observe the effect of water in our previous study.[5] At that time we used a dioxolane-solvent system containing a constant initial amount of water.

Detailed study has shown that the effect of water on the kinetics of the polymerization of dioxolane is so great that it cannot be neglected even in a medium with a constant amount of water but with a varying concentration of dioxolane. These problems are discussed in detail in this paper.

EXPERIMENTAL

Materials

Dioxolane was prepared by condensation of pure ethylene glycol with 75% formaldehyde in the presence of 2% (by weight of glycol) of analytically pure sulfuric acid. As soon as the reaction was over, a dioxolane-water azeotrope mixture was distilled off and freed from the main part of water by adding $CaCl_2$. The remaining dioxolane was dried by repeated distillation over sodium metal. The purity of dioxolane was checked chromatographically[8] in the first syntheses; it was no longer checked in subsequent work as no impurities had been found.

Initiator of the type $\sim Si^{\oplus}HSO_4^{\ominus}$ was used to initiate the polymerization of dioxolane. Its preparation and properties have already been described.[9]

Apparatus

As in the case of trioxane, an automatic recording dilatometer was used to study the polymerization of dioxolane.[10]

The concentration of water was measured by a modified Fischer coulometric method.[11]

Procedure

Dioxolane was kept in a thermostatted container. By adding a suitable amount of water (either in a monomer solution or directly) to the container before every experiment a polymerization mixture with the required initial concentration of water was obtained. The concentration of water was determined before the start of the polymerization.

In the course of polymerization it was determined by stopping the polymerization at different conversions and taking an aliquot of the polymerization mixture for analysis.

The conversion curves were obtained by evaluating data from the automatic recording dilatometer. The relation previously found between the conversion and the height of the graphical record was used to determine the conversion.

RESULTS

The enormous influence of water on the course of the polymerization of dioxolane is demonstrated by the conversion curves in Figure 1. The ion pair $\sim Si^{\oplus}HSO_4^{\ominus}$ was used as the initiator.[9] Detailed description of the conditions at which the different curves were obtained is given in the legend of Figure 1.

A few facts are immediately obvious from Figure 1. The rate of polymerization depends on water concentration. Also a monomer–polymer "equilibrium" depends on the concentration of water. Both the polymerization rate v and the "equilibrium" $x_{\infty} = (N_0 - N_{\infty})/N_0$, where N_{∞} is concentration of dioxolane at time $t \gg 200$ min.) are shown in Figure 2 to be a function of the water concentration. The rates were found by graphic differentiation, the equilibria by approximate extrapolation of the conversion curves to t_{∞}. The amount of free water (this term characterizes dissolved and solvated water which can be determined by the coulometric method[11]) does not remain constant over the course of the whole polymerization. This is shown in Figure 3; immediately after the start of the polymerization the amount of water decreases to a fraction of the original value but does not change in the subsequent phases of the reaction. In our opinion the

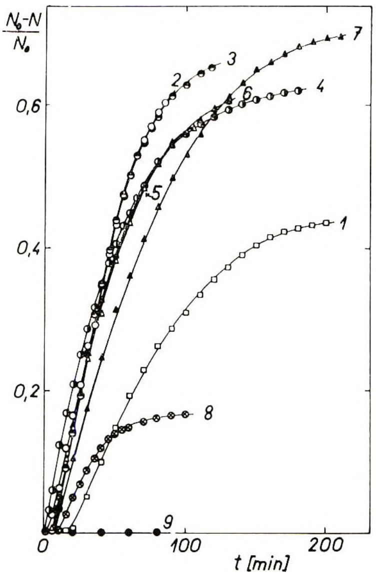

Fig. 1. Effect of water on the course of the bulk polymerization of dioxolane (13.5 mole/kg.) at 70°C.: (*1*) initial water concentration $[H_2O]_0$ = 20 ppm, final water concentration $[H_2O]_\infty$ = 12 ppm, $[H_2O]_\infty/[H_2O]_0$ = 0.6; (*2*) $[H_2O]_0$ = 320 ppm; (*3*) $[H_2O]_0$ = 1500 ppm, $[H_2O]_\infty$ = 30 ppm, $[H_2O]_\infty/[H_2O]_0$ = 0.02; (*4*) $[H_2O]_0$ = 2060 ppm, $[H_2O]_\infty$ = 56 ppm, $[H_2O]_\infty/[H_2O]_0$ = 0.015; (*5*) $[H_2O]_0$ = 3800 ppm, $[H_2O]_\infty$ = 165 ppm, $[H_2O]_\infty/[H_2O]_0$ = 0.043; (*6*) $[H_2O]_0$ = 8100 ppm, $[H_2O]_\infty$ = 274 ppm, $[H_2O]_\infty/[H_2O]_0$ = 0.034; (*7*) $[H_2O]_0$ = 22,800 ppm; (*8*) $[H_2O]_0$ = 39,200 ppm, $[H_2O]_\infty$ = 1460 ppm, $[H_2O]_\infty/[H_2O]_0$ = 0.037; (*9*) $[H_2O]_0$ = 200,000 ppm Initiator concentration, 114.0 mmole/kg. Conversion = $(N_0 - N)/N_0$, where N_0, N are the initial and instantaneous concentrations of the monomer.

phenomena examined are related to the effects observed in the polymerization of other heterocyclics.

DISCUSSION

The character of the dependence of the reaction rate on the concentration of water in the polymerization of dioxolane reminds us very much of the dependence found in the polymerization of trioxane.[12] There is no reason why we should not try to apply the same reaction scheme to the case of dioxolane, including assumptions of the reactivities of the single components.

According to this scheme the origin of the active center is due to hydration (generally solvation) as is shown in eqs. (1)–(3).

$$A^{\oplus}HSO_4^{\ominus} + mH_2O \overset{K_1}{\rightleftharpoons} A^{\oplus}\|HSO_4^{\ominus} \tag{1}$$

$$A^{\oplus}\|HSO_4^{\ominus} + nH_2O \overset{K_2}{\rightleftharpoons} A-OH + H_3O^{\oplus}HSO_4^{\ominus} \tag{2}$$

$$H_3O^{\oplus}HSO_4^{\ominus} \overset{K_3}{\rightleftharpoons} A^{\oplus}\|HSO_4^{\ominus} + rH_2O \tag{3}$$

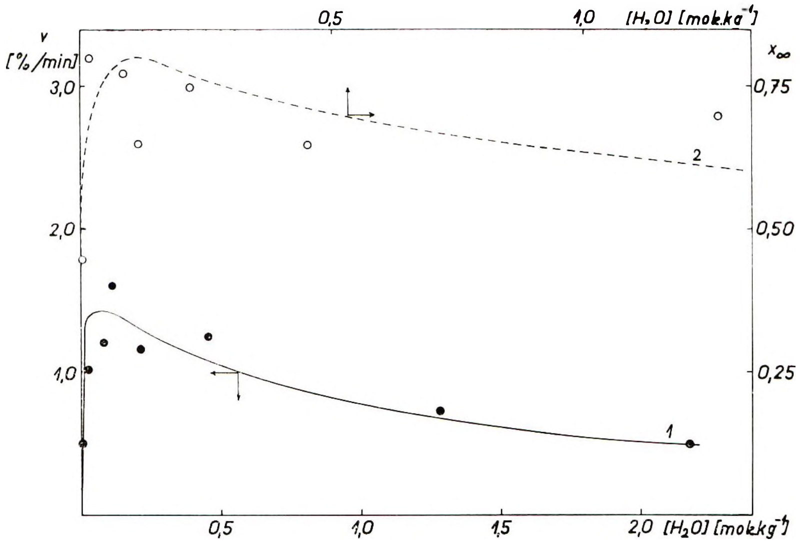

Fig. 2. Dependence of the rate v of bulk polymerization of dioxolane and of the maximum conversion x_∞ on the concentration of water at 70°C. The curve (*1*) is calculated from eq. (6), the points are experimental.

In eqs. (1)–(3) $A^{\oplus}HSO_4^{\ominus}$ indicates the molecule of the native initiator or of the ion pair formed by desolvation of the active center; $A^{\oplus}||HSO_4^{\ominus}$ is the solvated initiator, the active center proper; $H_3O^{\oplus}HSO_4^{\ominus}$ symbolizes the hydrolyzed active center; $A^{\oplus}$ represents the -onium part of the initiator (a short siloxane chain with the siliconium atom) or the polydioxolane chain with the carbonium atom. The reaction rate is controlled by the concentration of $A^{\oplus}||HSO_4^{\ominus}$; the other participants have so small a reactivity that their contribution to the rate of the loss of monomer can be neglected.

If the establishment of the equilibria is quick, a relation for the momentary concentration of active centers can be derived by using a simple method (described in detail elsewhere[12,13]).

$$[A^{\oplus}||HSO_4^{\ominus}] = \frac{K_1[H_2O]^m}{1 + K_1[H_2O]^m + (K_1/K_3)[H_2O]^{r+m}}[\text{init}] \tag{4}$$

As was shown previously,[5] the polymerization of dioxolane is a first-order reaction with respect to initiator. Then we can write for the overall rate:

$$-d[N]/dt = k[N]^{\alpha}[A^{\oplus}||HSO_4^{\ominus}] \tag{5}$$

where [N] represents the concentration of dioxolane and α is the reaction order with respect to monomer. As the reaction rates at the given concentration of the initiator were measured at constant conversion, it is possible to include [N] in the constant of eq. (5) and to write:

$$-\frac{d[N]}{dt} = k'\frac{K_1[H_2O]^m}{1 + K_1[H_2O]^m + (K_1/K_3)[H_2O]^{r+m}}[\text{init}] \tag{6}$$

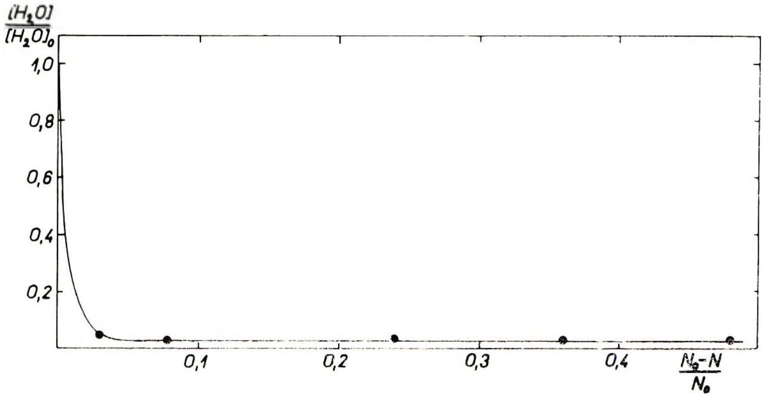

Fig. 3. Decrease of water in the bulk polymerization of dioxolane at 70°C. Initiator concentration, 110.0 mmole/kg.; initial water concentration, 23.9 mmole/kg.

There are three constants and two exponents in eq. (6). All of these can be derived from the experimental data with relatively good accuracy. The graphical form of eq. (6) is plotted as curve *1* in Figure 2; the points represent the experimental values. The values of the constants used to calculate the expression $v_{\text{overall}} = f([H_2O])$ are summarized in Table I.

TABLE I
Constants of the Initiator-Water Interaction at 70°C.

$k'K_1 \times 10^{-3}$, kg.^{2}/mole^2-min.	K_1, kg./mole	K_1/K_3	K_3	m	r
3.95	280	300	0.94	1	1

The question of a maximum conversion (x_∞) at which the polymerization stops remains open. The observed equilibria cannot be explained in terms of thermodynamics; the experiments were run under rigorously isothermal conditions. It is certain that the presence of a cocatalyst (of water) in different concentrations cannot influence the thermodynamic monomer-polymer equilibrium. An explanation of the observed processes must be sought in the kinetics of the process. It is interesting, however, that most of the water reacts in the initial stages of polymerization; the major part of the polymerization takes place in the presence of a constant amount of free water (Fig. 3). Then, in accordance with the legend of Figure 1, $[H_2O]_\infty = f([H_2O]_0)$. A detailed discussion of the equilibria will be possible after the course of the polymerization at various concentrations in solutions of dioxolane has been measured.

CONCLUSION

The rate of the dioxolane polymerization initiated by the $\sim Si^{\oplus}HSO_4^{\ominus}$ ion pair is a function of the initial concentration of water. An equation describing this dependence is practically identical with the equation which describes the same effect in the polymerization of trioxane. The observed agreement shows the analogy of the cocatalytical processes in the polymerizations of both monomers.

The initial concentration of free water determines also a conversion at which a sharp decrease of the reaction rate occurs. The loss in the rate of the monomer consumption is so great that we can be misled into supposing that a position close to a monomer–polymer equilibrium was reached.

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Résumé

La polymérisation de dioxolane initiée par la paire d'ions $\sim Si^+HSO_4^-$ est fortement influencée par la présence d'eau qui entraîne des modifications de vitesse de polymérisation globale. En particulier, des grands changements sont obtenus à des degrés de conversion plus élevés (dont les valeurs sont également fonction de la concentration initiale en eau). La polymérisation s'arrêt pratiquement à ces conversions et le système apparait être voisin d'un équilibre monomère–polymère. Les auteurs ont montré que l'équation de la vitesse globale est une fonction de H_2O qui décrit la dépendance de la vitesse globale de polymérisation en fonction de la concentration en eau et qui était initialement dérivée pour la polymérisation du trioxane et est également valable pour la polymérisation du dioxolane. Ils ont mesuré la diminution de concentration en eau au cours de la polymérisation et ont montrè que les équilibres observés sont en fait dus à un phénomène cinétique.

Zusammenfassung

Die durch das Ionenpaar $\sim Si^+HSO_4^-$ initiierte Polymerisation von Dioxolan wird durch Wasser stark beeinflusst, wobei die Bruttopolymerisationsgeschwindigkeit geändert wird. Besonders grosse Änderungen entstehen bei gewissen höheren Umsätzen, deren Werte ebenfalls eine Funktion der Anfangskonzentration an Wasser sind. Die Polymerisation kommt bei diesen Umsätzen praktisch zum Stillstand und das System scheint sich nahe bei einem Monomer-Polymergleichgewicht zu befinden. Die Autoren zeigten, dass die Gleichung $v_{\mathrm{Brutto}} = f[(H_2O)]$, die die Abhängigkeit der Bruttopolymerisationsgeschwindigkeit von der Wasserkonzentration beschreibt und die ursprünglich für die Polymerisation von Trioxan abgeleitet wurde, auch für die Dioxolanpolymerisation gilt. Sie massen die Abnahme der Wasserkonzentration während der Polymerisation und zeigten, dass die beobachteten "Gleichgewichte" ein kinetisches Phänomen darstellen.

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Kinetics of the Solution Polymerization of Dioxolane in the Presence of Water

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Synopsis

Water acts as a cocatalyst in the polymerization of dioxolane initiated by the ion pair $\sim Si^{\oplus}HSO_4^{\ominus}$. The dependence of the reaction rate on the water concentration exhibits a maximum, the width of which strongly depends on the concentration of dioxolane. The change of the coordinates of the maximum and its shape with the decrease of the monomer concentration causes the reaction rate to decrease with increasing conversion. The point at which the slope of the conversion curve changes is a function of initial concentration of water. There is a very fast decrease of the concentration of free water in the polymerizing system. The consumption of water is associated with some peculiarities. The amount of free water which remains in the system is a function of the concentration of the original initiator. The ratio $[H_2O]_e/[\text{initiator}]$ is constant over a rather broad range of initial concentration of water.

INTRODUCTION

The conversion curves of the bulk polymerization of dioxolane[1] change slope greatly after a certain amount of polymer has been formed. The point at which the polymerization rate decreases sharply is a function of the initial concentration of water brought into the system with the dioxolane. The sharp decrease of the rate from a certain conversion is similar to the behavior of a system approaching the equilibrium state. The change of the polymerization rate with concentration of water shows that water has a cocatalytic effect in the system studied.

While the effect of water on the polymerization rate can be explained by analogous reactions which are presumed to take place in the polymerization of trioxane,[2] the explanation of the "equilibria" remains open. This phenomenon, as far as we know, has not been mentioned in the literature. For this reason we have tried to find out whether there are any other factors influencing the equilibria and thus to contribute to their explanation.

EXPERIMENTAL

The preparation of dioxolane, the initiator used, and the experimental technique were described in the previous paper.[1]

A mixture of tetrachloroethane and *n*-heptane (tetrachloroethane: *n*-heptane = 90:10 by volume) was used as a solvent in the solution polymerization of dioxolane.

Commercial 1,1,2,2-tetrachloroethane was distilled twice before use and its purity was determined by measuring the index of refraction.

Concentrated sulfuric acid was added to commercial *n*-heptane and the mixture was stirred for 4 hr. After the sulfonated impurities had been removed, *n*-heptane was freed from water by adding KOH and finally distilled over sodium metal before each polymerization.

Solutions of dioxolane were prepared in a thermostatted container. The concentration of water was adjusted to the required value in the manner described in the previous paper.[1]

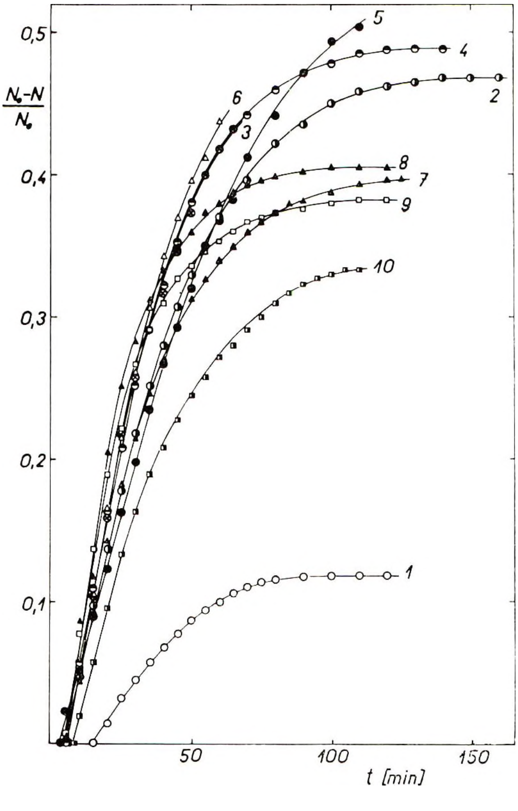

Fig. 1. Effect of water on the course of the polymerization of dioxolane at 70°C.: (*1*) initial water concentration $[H_2O]_0 = 10$ ppm; final water concentration $[H_2O]_\infty = 4$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.4$; (*2*) $[H_2O]_0 = 50$ ppm, $[H_2O]_\infty = 15$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.3$; (*3*) $[H_2O]_0 = 250$ ppm, $[H_2O]_\infty = 60$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.2$; (*4*) $[H_2O]_0 = 460$ ppm, $[H_2O]_\infty = 25$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.025$; (*5*) $[H_2O]_0 = 500$ ppm; (*6*) $[H_2O]_0 = 865$ ppm, $[H_2O]_\infty = 50$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.06$; (*7*) $[H_2O]_0 = 1040$ ppm, $[H_2O]_\infty = 40$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.04$; (*8*) $[H_2O]_0 = 1770$ ppm, $[H_2O]_\infty = 77$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.04$; (*9*) $[H_2O]_0 = 3200$ ppm; (*10*) $[H_2O]_0 = 14{,}700$ ppm, $[H_2O]_\infty = 2120$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.14$. Dioxolane concentration, 5.5 mole/kg.; initiator concentration, 110.0 mmole/kg. Conversion $= (N_0 - N)/N_0$, where N_0 and N are initial and instantaneous concentrations of the monomer.

RESULTS

The dielectric constant (DC) of the polymerizing medium is one of the factors complicating the kinetics of the process. In order to avoid this complication a 10:90 mixture of n-heptane and tetrachloroethane was used as solvent. The dielectric constant of this mixture is equal to that of dioxolane at 70°C., i.e., 5.52.

The course of the polymerization of dioxolane in solution in the presence of varying amounts of water is represented by the conversion curves in Figures 1–3. These plots give $(N_0 - N)/N_0$ versus time t, where N_0 and N are initial and instantaneous concentration of the monomer. It has been shown that both the overall rate of reaction and the point at which it decreases sharply depend on the concentration of water, even in the polymerization in solution. This dependence is more distinct at lower concentrations of the polymerized dioxolane. The changes of both parameters—

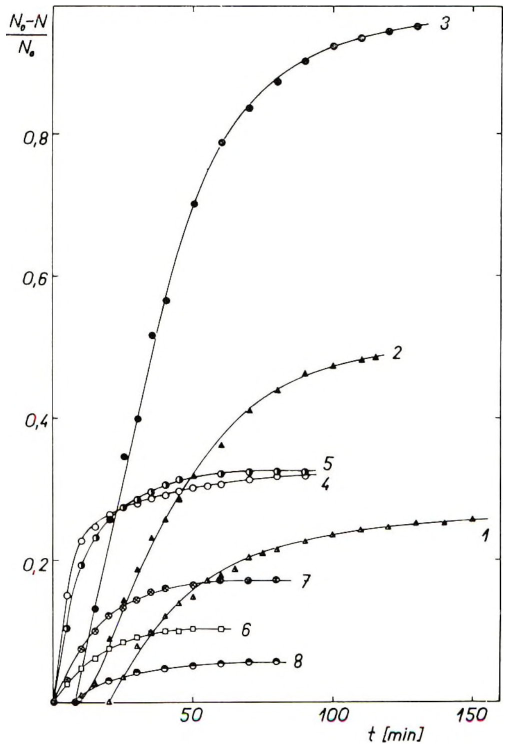

Fig. 2. Effect of water on the course of the polymerization of dioxolane at 70°C.: (*1*) $[H_2O]_0 = 5$ ppm; (*2*) $[H_2O]_0 = 22$ ppm, $[H_2O]_\infty = 9$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.4$; (*3*) $[H_2O]_0 = 50$ ppm, $[H_2O]_\infty = 22$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.4$; (*4*) $[H_2O]_0 = 80$ ppm, $[H_2O]_\infty = 32$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.4$; (*5*) $[H_2O]_0 = 180$ ppm, $[H_2O]_\infty = 76$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.4$; (*6*) $[H_2O]_0 = 300$ ppm; (*7*) $[H_2O]_0 = 390$ ppm, $[H_2O]_\infty = 48$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.1$; (*8*) $[H_2O]_0 = 1020$ ppm, $[H_2O]_\infty = 192$ ppm, $[H_2O]_\infty/[H_2O]_0 = 0.2$. Dioxolane concentration, 3.1 mole/kg.; initiator concentration, 107 mmole/kg.

the rate and the maximum conversion (x_∞)—with the water content can be seen more clearly in Figures 4 and 5.

The decrease of water concentration depends on its initial concentration ($[H_2O]_0$) and also on the concentration of the initiator, as is seen in Figures 6 and 7.

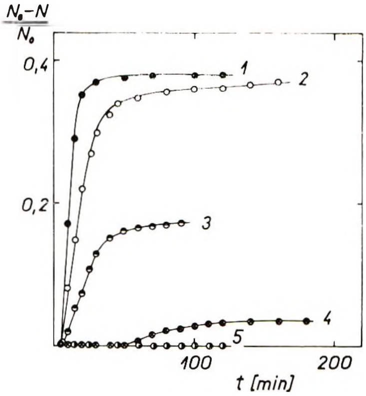

Fig. 3. Effect of water on the course of the polymerization of dioxolane at 70°C.: (*1*) $[H_2O]_0$ = 7 ppm, $[H_2O]_\infty$ = 7 ppm; (*2*) $[H_2O]_0$ = 37 ppm, $[H_2O]_\infty$ = 16 ppm; $[H_2O]_\infty/[H_2O]_0$ = 0.43; (*3*) $[H_2O]_0$ = 52 ppm, $[H_2O]_\infty$ = 41 ppm, $[H_2O]_\infty/[H_2O]_0$ = 0.80; (*4*) $[H_2O]_0$ = 216 ppm, $[H_2O]_\infty$ = 20 ppm, $[H_2O]_\infty/[H_2O]_0$ = 0.09; (*5*) $[H_2O]_0$ = 300 ppm, $[H_2O]_\infty$ = 33 ppm, $[H_2O]_\infty/[H_2O]_0$ = 0.11. Dioxolane concentration, 1.5 mole/kg.; initiator concentration, 105 mmole/kg.

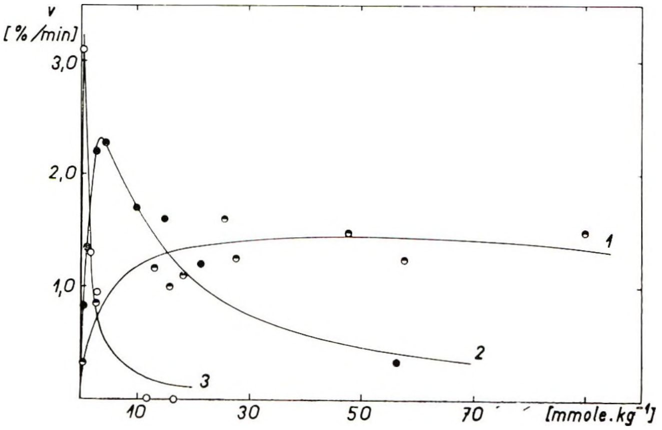

Fig. 4. Dependence of the rate of dioxolane polymerization at 70°C. on the concentration of water $[H_2O]_0$ at various dioxolane concentrations: (*1*) 5.5 mole/kg.; (*2*) 3.1 mole/kg.; (*3*) 1.5 mole/kg. The curves are calculated values and the points are experimental.

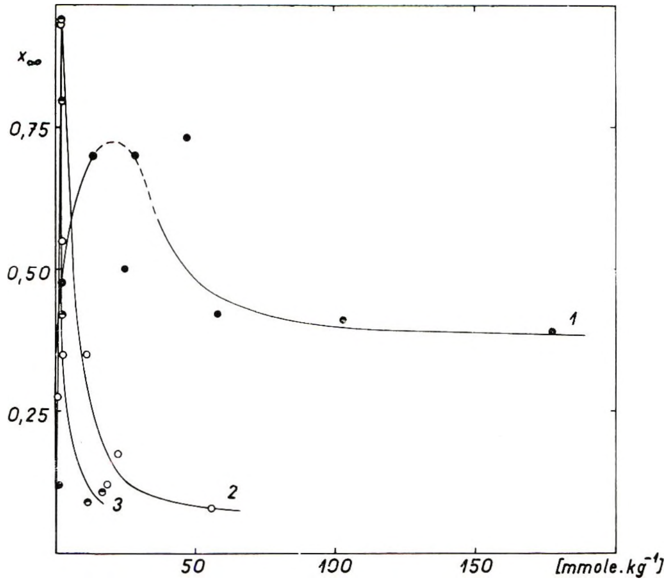

Fig. 5. Dependence of the maximum conversion x_∞ at 70°C. on the concentration of water $[H_2O]_0$ at various dioxolane concentrations: (*1*) 5.5 mole/kg.; (*2*) 3.1 mole/kg.; (*3*) 1.5 mole/kg.

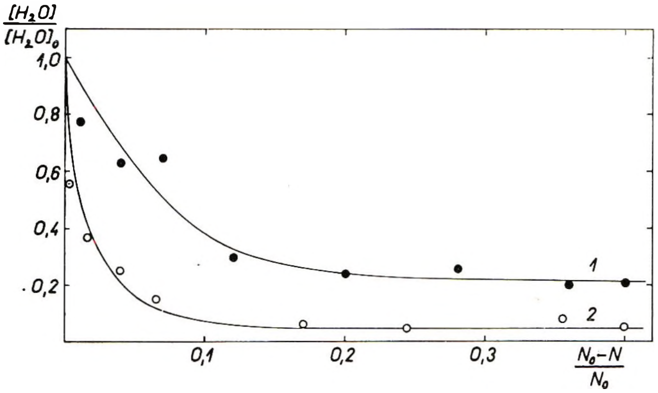

Fig. 6. Decrease of water concentration in the polymerization of dioxolane at 70°C.: (*1*) $[H_2O]_0$ = 570 mmole/kg.; (*2*) $[H_2O]_0$ = 22.2 mmole/kg. Dioxolane concentration, 5.5 mole/kg.; initiator concentration, 110 mmole/kg.

DISCUSSION

The curves in Figure 4 were calculated from eq. (6) of our preceding paper.[1] The constants for this equation were derived from the experimental data (see Table I). The solvation constant K_1 [see eq. (1) of the preceding paper[1]] is not altered by the change of the concentration of the monomer.

The concentration of free dioxolane decreases with increasing conversion. The change of K_3 with the concentration of dioxolane N is very abrupt; therefore the rate decreases sharply even at an already invarying concentration of water. This is the main factor determining x_∞. Another, less important, factor is the formation of oligomers; it can be shown by a simple calculation that linear dimers, trimers, and tetramers are formed as the concentration of water decreases. These oligomers can take part in solvation of the active centers, but their ability to activate the initiator probably decreases with increasing degree of polymerization. The fate of these oligomers now depends on $[H_2O]_0$. As the conversion increases they can be built into longer chains by transfer with the polymer; the consumption of the oligomers is faster if $[H_2O]_0$ is lower. On the contrary, at high $[H_2O]_0$ they can survive throughout the polymerization even up to x_∞.

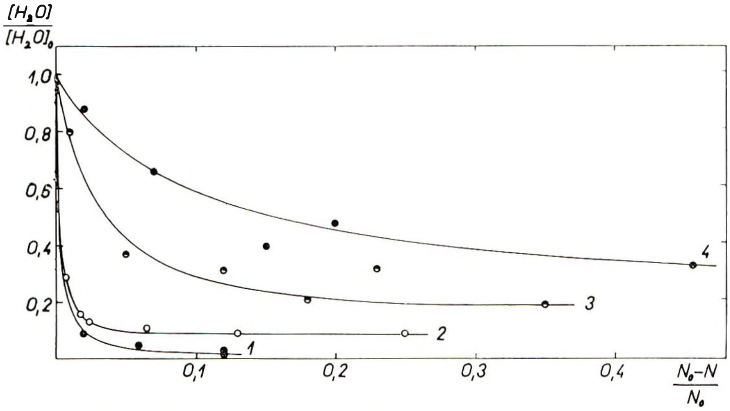

Fig. 7. Decrease of water concentration in the polymerization of dioxolane at 70°C. at various initiator (water) concentrations: (*1*) $[H_2O]_0 = 23.4$ mmole/kg., [initiator] = 21.0 mmole/kg.; (*2*) $[H_2O]_0 = 24.4$ mmole/kg., [initiator] = 107.0 mmole/kg.; (*3*) $[H_2O]_0 = 23.4$ mmole/kg.; [initiator] = 214.0 mmole/kg.; (*4*) $[H_2O]_0 = 2.3$ mmole/kg., [initiator] = 107.0 mmole/kg.

TABLE I

Constants of the Initiator-Water Interaction at 70°C.[a]

Dioxolane concn., mole/kg.	$k'K_1 \times 10^{-3}$, kg.^{2}/mole^2-min.	K_1, kg./mole	K_1/K_3	K_3	r	m
5.5	4.0	280	300	0.94	1	1
3.4	17.5	280	7×10^4	4.03×10^{-3}	1	1
1.5	124.0	280	5×10^5	5.70×10^{-5}	1	1

[a] Initiator concentration, 105–114 mmole/kg.

Now let us consider the polymerization processes at different $[H_2O]_0$ levels.

Polymerization at Very Low $[H_2O]_0$

Water decreases slowly (see Fig. 7) and a higher molecular weight polymer is formed which can activate the initiator to some extent. The reaction rate is low. As soon as the concentration of dioxolane is lower than a critical value, a rapid decrease of K_3 occurs with increasing conversion and the rate of reaction decreases sharply; the conversion–time curve has the shape it would if an equilibrium had been reached. These examples are illustrated by curves *1* in Figures 1–3.

Polymerization at High $[H_2O]_0$ (>50 ppm)

The water concentration decreases rapidly to $[H_2O]_\infty$ and oligomers are formed by transfer; depending on the initial water content the oligomers can activate the initiator in a shorter or longer interval of the polymerization, or take part in solvation equilibria. The explanation of these processes occurring during the polymerization is analogous to that at low $[H_2O]_0$, but there is a small difference, in that the contribution of the lowest molecular weight polymers in the solvation equilibria near x_∞ is higher. The change of K_3 in this case causes the system always to reach the decreasing part of the rate–$[H_2O]$ curve (Fig. 4). The rapid change of the reaction rate with decreasing N causes this alleged equilibrium to be attained sooner. The point of the rapid decrease of the rate changes with $[H_2O]_\infty$ and with activating oligomers. These conditions are characterized by curves *2–10* in Figure 1, curves *4–8* in Figure 2, and curves *2–5* in Figure 3.

Special Case

An extremely high conversion is reached in a special case. This occurs when the slow decrease of the water concentration (Figure 7) leaves as much free water in the medium as is necessary to reach a maximum rate. (In other words: the decrease of the concentration of free water with conversion parallels the shift of the maximum of the reaction rate with monomer concentration.) The rate of reaction does not decrease under these conditions. This is the case illustrated by curve *3* in Figure 2.

These special conditions can be fulfilled only in a very narrow range of water concentration. If the monomer concentration is higher than 5.5 mole/kg. it may not be possible to find the $[H_2O]_0$ which would fulfill the special conditions. At higher concentrations of monomer the change of K_3 with N is very small (we cannot detect it by using our method). However, water decreases irrespective of this circumstance. At higher conversions, when K_3 begins to change substantially, $[H_2O]_\infty$ already remains constant and the shift of the reaction rate maximum is not followed by the water decrease. Then, sooner or later, the reaction must stop according to the descending part of the rate–$[H_2O]$ curve (Fig. 5). Also, the presence of low molecular weight polymers can be a complicating factor.

Kinetics

The processes connected with the cocatalysis of the polymerization of dioxolane which lead to a rapid decrease of reaction rates at various conversions depending on $[H_2O]_0$ make the study of the thermodynamic parameters of the polymerization more difficult. From the results discussed hitherto it follows that it is almost impossible to determine the true monomer–polymer equilibrium and thereby also the ceiling temperature of the polymerization.

Let us consider more closely the effect of water from another point of view. The system with extremely high water concentrations (higher than 200 mmole/kg. at $N \geq 5.5$ mole/kg., and higher than 10 mmole/kg. at $N = 3.1$ mole/kg., will not be included in the following discussion.

As is shown in Figures 1–3, the overall rate of polymerization is directly proportional to the "equilibrium" concentration of water $[H_2O]_\infty$. By using eq. (6) from our previous paper[1] we can write:

$$r_{\text{overall}} = k' \frac{K_1 [H_2O]_0 [\text{init}]}{1 + K_1[H_2O]_0 + (K_1/K_3)[H_2O]_0^2} = k'K_1[H_2O]_\infty[\text{init}] \quad (1)$$

and for $1 + K_1[H_2O]_0 \gg (K_1/K_3)\ [H_2O]_0^2$, $[H_2O]_0 < 1$, we have

$$[H_2O]_0/(1 + K_1[H_2O]_0) = [H_2O]_\infty \quad (2)$$

Then

$$[H_2O]_\infty/[H_2O]_0 = 1/(1 + K_1[H_2O]_0) \quad (3)$$

Equation (3) is a quantitative expression for the ratio of the final and initial concentrations of water as a function of $[H_2O]_0$. Since we know the value of K_1 (Table I), we can plot $[H_2O]_\infty$ against $[H_2O]_0$ (Fig. 8). The curve has been completed by plotting of the values of $[H_2O]_\infty/[H_2O]_0$

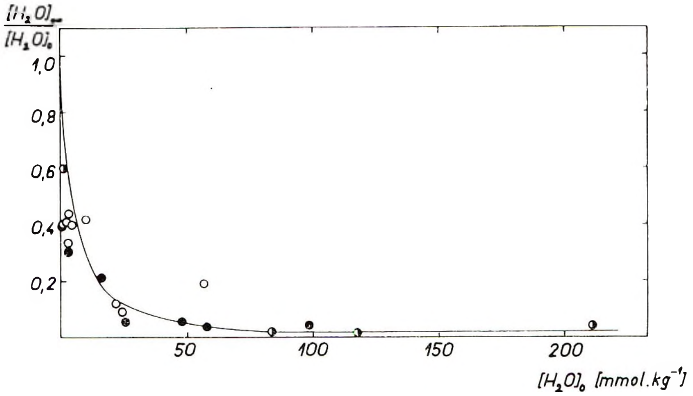

Fig. 8. Dependence of $[H_2O]_\infty/[H_2O]_0$ on $[H_2O]_0$ at various dioxolane concentrations: (◑) 13.5 mole/kg.; (●) 5.5 mole/kg.; (○) 3.1 mole/kg. The curve is calculated, the points are experimental.

found experimentally. The agreement of the experimental points with the curve calculated by using K_1 determined by other independent means shows that the previous hypothesis is correct.

If K_1 $[H_2O]_0 >> 1$, it follows from eq. (3) that $[H_2O]_\infty$ is constant. Then the amount of free water in the polymerization of dioxolane is practically constant over a rather wide range of $[H_2O]_0$. Free water then equals $1/K_1$, i.e., $[H_2O]_\infty = 3.6$ mmole/kg.

Under these conditions the concentration of free water is at least ten times lower than the concentration of the complex $\sim Si^{\oplus}HSO_4^{\ominus}$. $[H_2O]_\infty$ is a function of the initiator concentration as is seen in Figure 7. This fact is rather important. It may mean that a certain amount of water is bound by the initiator more firmly; that relatively stable units are formed in a definite stoichiometric ratio. The water bound in these units cannot be active as a transfer agent.

CONCLUSION

Some evidence for the cocatalysis by solvation has already been collected in the technical literature. However, there are only a few papers attempting to explain the complications of the polymerization processes caused by the decrease of the cocatalyst concentration in the course of the reaction. The polymerization of dioxolane is quite complicated because the reaction rate depends on the water and monomer concentrations. The relation between these variables and their effect on the reaction rate is not yet clear. The lower the dioxolane concentration N is the sharper is the decrease of the overall reaction rate. The change in slope of the conversion curve caused by a sharp decrease in the reaction rate is so great that the reaction seems to approach a thermodynamic equilibrium. But in fact, a loss of the active centers provides a kinetic reason for this. The reaction can reach higher conversions under different conditions. Therefore, ignorance of the kinetic factors can lead to a misinterpretation of the experimental results.

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Résumé

L'eau agit comme cocatalyseur de la polymérisation de dioxolane initiée par la paire d'ions $\sim Si^{+}HSO_4^{-}$. La dépendance de la vitesse de réaction en fonction de la concentration en eau manifeste un maximum dont la largeur dépend fortement de la concentration en dioxolane. Le changement des coordonnées du maximum et le changement de sa forme avec une diminution de concentration en monomère entraîne une diminution de la vitesse de réaction avec une conversion croissante. Le point auquel la tangente de la courbe de degré de conversion change est une fonction de la concentration initiale en eau. Il y a une diminution très rapide de la concentration d'eau libre dans le système en polymérisation. La consommation de l'eau est associée à certaines particularités. La quantité d'eau libre qui reste dans les systèmes est une fonction de la concentration de l'initiateur de départ. Le rapport $[H_2O]_\infty$/[initiateur] est constant sur un domaine plutôt large de concentration initiale en eau.

Zusammenfassung

Wasser wirkt bei der durch das Ionenpaar $\sim Si^+HSO_4^-$ initiierten Polymerisation von Dioxolan als Cokatalysator. Die Abhängigkeit der Reaktionsgeschwindigkeit von der Wasserkonzentration zeigt ein Maximum, dessen Breite sehr von der Dioxolankonzentration abhängt. Die Änderung der Koordinaten des Maximums und seiner Gestalt mit der Abnahme der Monomerkonzentration verursacht eine Abnahme der Reaktionsgeschwindigkeit mit steigendem Umsatz. Die Ordinate des Beginns der scharfen Biegung der Umsatzkurve ist eine Funktion der Anfangskonzentration des Wassers. Es findet eine sehr rasche Abnahme der Konzentration des freien Wassers im polymerisierenden System statt. Der Verbrauch des Wassers ist mit gewissen Besonderheiten verknüpft. Die Menge an freiem Wasser, welche im System verbleibt, ist eine Funktion der Konzentration des ursprünglichen Initiators. Das Verhältnis $[H_2O]_\infty/[\text{Initiator}]$ ist über einen breiten Bereich der Anfangskonzentration an Wasser konstant.

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Radiation-Induced Solid-State Polymerization in Binary Systems. IV. Solid-State Polymerization in the Glassy Phase

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Synopsis

The radiation-induced polymerization of glass-forming systems containing monomers has been investigated. It was found that irradiation below the second-order transition temperature T_g of the systems causes no in-source polymerization but causes a rapid post-polymerization on warming above the T_g after initial irradiation below the T_g. The post-polymerization was followed by differential thermal analysis and ESR spectra. It is caused above the T_g by the release of peroxy radicals trapped below the T_g, and its rate is proportional to the irradiation dose to some extent, often is explosively high, and brings about a remarkably large temperature rise by accumulation of polymerization heat. Irradiation above the T_g causes rapid in-source polymerization which is accelerated by the high viscosity of the monomeric system between T_g and T_s (WLF temperature) compared to crystal or ordinary solution polymerization. The temperature dependence of the in-source polymerization of glassy systems shows a peak between the T_g and T_s which may be the result of competing effects of the rate increase by the decreased termination near T_s and the rate decrease by the decreased propagation caused by the diffusion prevented near the T_g. The degree of polymerization was also investigated. The temperature dependence of the degree of polymerization of the polymers obtained by in-source polymerization shows a peak similar to that of the temperature dependence of conversion. Unusually large values of the Huggins constant k' are noted between T_g and T_s. The degree of polymerization of the polymer obtained by post-polymerized increases with the increase of irradiation dose and the polymerization rate; this may be the result of decreased chain transfer to nonpolymerizable components.

INTRODUCTION

In the previous studies,[1] some fundamental investigations about the mechanism of glass formation and properties of the glassy state in binary systems containing acrylic monomers were made. On the basis of these results, the radiation-induced polymerization of glassy systems containing acrylic monomers has been studied to obtain new information about low-temperature polymerization. It was found that rapid polymerization took place easily at very low temperature in these glassy systems and that this

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polymerization was sensitive to physical properties such as viscosity and transition temperature of the glassy systems. In the present paper, characteristics of the glassy polymerization of acrylic monomers are reported in detail.

EXPERIMENTAL

The materials were purified by the usual methods and mixed and melted homogeneously, if necessary, by heating.

Transition temperature and phase diagram were determined by the volume change and differential thermal analysis. The irradiations were with γ-rays from a ^{60}Co source. The polymerization rate was investigated in part by differential thermal analysis of the irradiated samples and in part by the usual gravimetric method. The degree of polymerization of acrylamide polymer was determined from the viscosity measurement in aqueous solution at 30°C. by using the equation:

$$[\eta] = 3.73 \times 10^{-4} M^{0.66}$$

RESULTS AND DISCUSSION

Polymerization of Glass-Forming Systems

Radiation-induced polymerization of glass-forming systems containing acrylamide and acrylic acid by γ-rays from ^{60}Co has been investigated in order to study the general aspects of glassy polymerization. Results are shown in Table I. The following conclusions are obtained from these results. Irradiation at temperatures below the T_g (second transition point) causes no in-source polymerization, but by warming above the T_g after irradiation, a violent, almost explosive post-polymerization occurs and is completed within a few minutes, the temperature rising to 80–160°C., due to the heat of polymerization.

Irradiation at temperatures above the T_g causes in-source polymerization to be completed at a high rate, almost to 100% conversion.

These results suggest that the transition point is the most important factor for the polymerization in the glassy state. The polymerization does not occur below the T_g, but does occur as a result of increased molecular diffusion above the T_g as well as crystal growth.

Transition points of glassy systems are much lower than those of crystalline systems in general and can be varied widely by selecting various combination of components. Thus, it should be possible to complete high polymerization at very low temperatures by a suitable choice of glass-forming systems. The distinction of in-source and post-polymerization is based on the following observations: (*1*) the polymerization heat peak of differential thermal analysis is small or non-existent for in-source polymerization with warming after irradiation; (*2*) on the other hand, a remarkable temperature rise is observed for the post-polymerization; (*3*) polymer obtained by in-source polymerization is closely crosslinked containing nonpolymerizable components, and shows gumlike elastic properties, while that obtained by post-polymerization is not so highly crosslinked as to show elasticity but does show plastic properties; (*4*) crystallization of nonpolymerizable components occurs rapidly, and half of the transparency of the samples is lost during post-polymerization. In in-source polymerization, no crystallization occurs, and a more transparent appearance is maintained due to the closely crosslinked structure including nonpolymerizable substances.

TABLE I
Polymerization of Glass-Forming Systems

System	Composition	Irradiation dose, Mr.	Irradiation temperature, °C.	Temperature of polymerization, °C.[a]		Second transition temperature, °C.
				In-source polymerization	Post-polymerization	
Acrylamide–itaconic acid	1:0.8	0.14	−78	—	−45 to −21	−39
		0.09	−78	—	−42 to −21	
		0.07	−78	—	−41 to −19	
		0.05	−78	—	−47 to −21	
Acrylamide–malonic acid	1:1	0.14	−45	−45	—	
		0.27	−78	—	−55 to −45	−60
		0.09	−78	—	−60 to −46	
		0.07	−78	—	−55 to −41	
Acrylamide–succinic acid–acetamide	1:0.5:1	0.14	−45	−45	—	−74
		0.14	−78	—	−60 to −55	
Acrylamide–propionic acid–acetamide	1:1:0.5	0.14	−45	−45	—	−110
		0.14	−78	—	—	
		0.14	−196	—	−90	
Acrylic acid–acetamide	1:0.5	0.14	−78	−78	—	−110 to −115
		0.14	−196	—	−114	
Acrylic acid–formamide	1:1	0.14	−78	−78	—	−135 to −145
		0.14	−196	—	−125	

[a] A dash (—) indicates no polymerization takes place.

Explosive post-polymerization in glassy systems containing acrylamide may be compared to the explosion polymerization achieved by Kargin[2] using the molecular beam method.

The crystallization caused by the rise in temperature may not be a necessary condition of this polymerization but an unconnected phenomenon. Because in-source polymerization can be conducted near the T_g without crystallization and post-polymerization occurs just above the T_g, the polymerization can be explained only by the release of molecular motion.[3-4]

In-Source Polymerization of Glass-Forming Systems

The polymerization behavior of some glassy systems in in-source polymerization at −78°C. is shown in Figure 1.

An induction period was observed in some systems, because oxygen is not completely excluded, in order to avoid the possibility of thermal polymerization.

The polymerization is accelerated from its initial stage because the viscosity of the monomeric systems is very high at the temperature between T_s and T_g.

Polymerization is completed rapidly even for very small dosage owing to the high viscosity of the system and the small termination rate. To clarify the effect of temperature on in-source polymerization, the polymer conversions for the irradiation at a definite dosage at different temperatures are compared in Figure 2.

The polymerization rate decreases with the decrease of temperature far above T_s as in the usual liquid-state polymerization, but it increases with decreasing temperature near T_s and decreases again near T_g, so a conversion peak as a function of temperature appears.

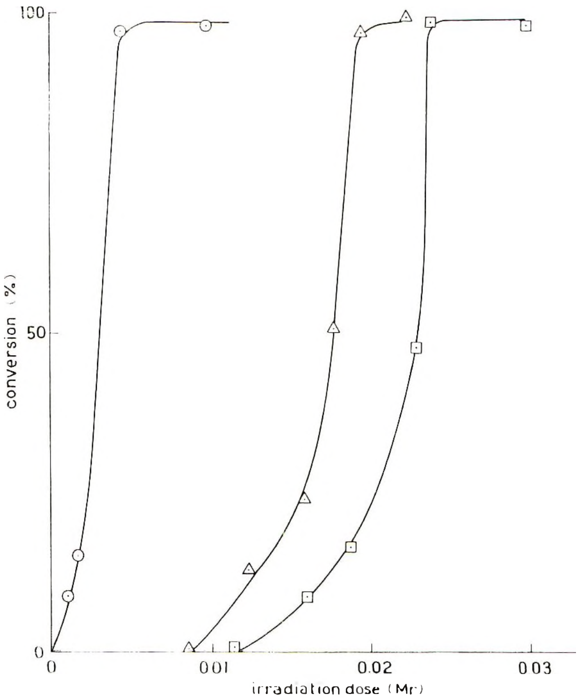

Fig. 1. In-source polymerization of glass-forming systems containing acrylamide and acrylic acid: (⊙) acrylamide–propionic acid–formamide (1.1:0.5); (△) acrylic acid–acetamide (1:0.5); (⊡) acrylic acid–formamide (1:1). Temperature, −78°C.; dose rate: 1.5 × 10^4 r./hr.

These results suggest the existence of some important relationship between polymerization and molecular diffusion in glassy systems. An increase of conversion in the range between T_s and T_g is attributed to the decrease of the termination rate owing to the prevention of diffusion of active polymer chains. A decrease of conversion near T_g is attributed to the decrease in the propagation rate owing to the prevention of monomer diffusion. It is obvious from Figure 2 that the in-source polymerization rate in glassy systems is much greater at low temperature than that of crystal or ordinary solution systems.

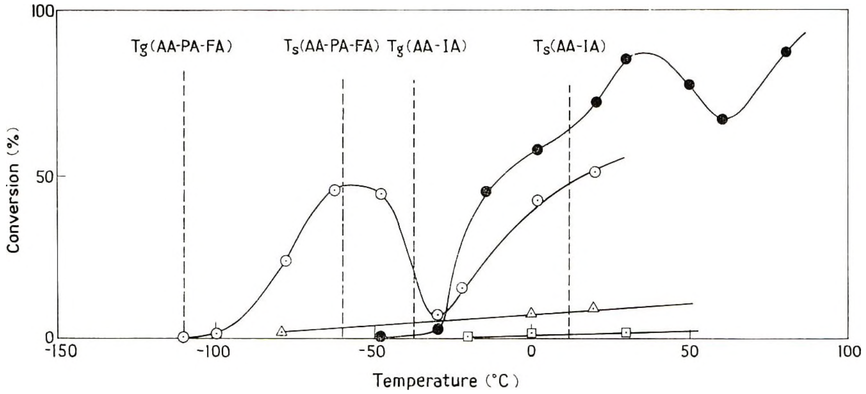

Fig. 2. Relationship between conversion and polymerization temperature for in-source polymerization of glass-forming systems containing acrylamide: (⊙) acrylamide (AA)–propionic acid (PA)–formamide (FA) system (1:1:0.5), glassy; (●) AA–itaconic acid (IA) system, (1:0.8), glassy; (△) 20% solution of AA in methanol;[6] (⊡) AA–IA system, (1:0.8), crystal. Dose, 0.003 Mr.; dose rate, 1.5×10^4 r./hr.

Post-Polymerization of Glass-Forming Systems

General aspects of the post-polymerization of some glassy systems are shown in Table II.

Almost 100% final conversions are obtained in the systems containing acrylamide after rapid post-polymerization. In the acrylamide–itaconic acid system, copolymerization occurs. The inner temperatures of the samples rise to 40–100°C. from the T_g as a result of the heat of post-polymerization which proceeds explosively, so that the polymerization rate can not be pursued by the usual weighing method. The possibility of a quantitative treatment of the post-polymerization rate by differential thermal analysis was investigated according to the relationship [eq. (1)] introduced by Borchardt and Daniels.[5]

$$R_p = -dn/dt = (N_0/kA)[C_p(d\Delta T/dt) + k\Delta T] \qquad (1)$$

where $-dn/dt$ is reaction rate; N_0 is the initial number of moles of monomer, K is the heat transfer coefficient, taken as 0.17 cal./deg.-sec.-cm. in a

TABLE II
Post-Polymerization of Glass-Forming Systems Containing Acrylamide

System	Composition	Irradiation dose, Mr.	Irradiation tempera-ture, °C.	Polymeri-zation beginning tempera-ture, °C.	Maximum inner tempera-ture reached, °C.	Time to reach maximum tempera-ture, min.	Final conversion, %	Itaconic acid content in polymer obtained, %
Acrylamide–malonic acid	1:1	0.14	−78	−60	115	2.5	91.5[a]	—
		0.09		−60	85	3.0	97.6	
		0.07		−55	80	3.3	95.1	
		0.04		−55	69	6.5	95.2	
Acrylamide–succinic acid–acetamide	1:0.5:1	0.23	−78	−60	78	3.6	96.4[a]	—
		0.14		−60	65	4.5	98.1	
		0.09		−60	60	4.9	95.0	
		0.03		−60	56	6.9	97.3	
Acrylamide–itaconic acid	1:0.8	0.09	−78	−45	40	4.0	68.8[b]	19.3
		0.07		−40	35	4.6	63.6	21.0
		0.04		−40	32	9.7	52.7	26.1

[a] The conversion is based on the amount of acrylamide used.

[b] The conversion is based on the amount of acrylamide and itaconic acid used.

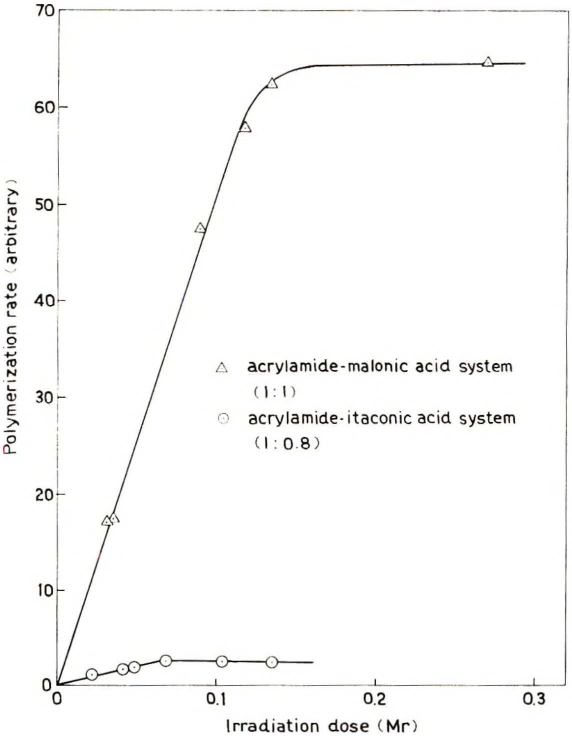

Fig. 3. Relationship between polymerization rate and irradiation dose in post-polymerization of glass-forming systems containing acrylamides: (△) acrylamide–malonic acid (1:1); (⊙) acrylamide–itaconic acid (1:0.8).

platinum cell; $A = \int_0^{\infty} \Delta T dt$ is taken as constant at definite conversion (100%); C_p is the heat capacity of the reference substance, taken as 0.24 cal./g.-deg. in air; ΔT is the observed height of the polymerization heat peak, and $d\Delta T/dt$ is the observed slope of the polymerization heat peak.

$d\Delta T/dt$ of some glassy systems containing acrylamide are plotted against the irradiation dose in Figure 3.

The results show a proportionality between polymerization rate and irradiation dose for a certain dose range. This suggests the lack of bimolecular termination and the possibility of inactivation by the occlusion of propagating chains. The higher rate in the acrylamide–malonic acid system than in the acrylamide–itaconic acid system may be attributed to an accelerative effect of malonic acid or a chain degradative effect of itaconic acid.

ESR Spectra of Post-Polymerization of Some Glassy Systems

In order to clarify the mechanism of post-polymerization in the glassy systems, ESR spectra were measured for some irradiated glassy systems (acrylamide–malonic acid, acrylamide–itaconic acid). ESR spectra of the acrylamide-malonic acid system irradiated at −196°C. in air are shown in Figure 4.

The spectrum consists mainly of a superposition of the quintet spectrum and the triplet spectrum with a coupling constant of about 24 gauss. They are assigned to $CH_3—\dot{C}H(CONH_2)$ and $\sim CH_2\dot{C}H(CONH_2)$, respectively. Another less intense spectrum was also observed, which may be attributed to free radicals from malonic acid.

When the temperature of the sample was raised to −129°C., there remained only the triplet spectrum. This spectrum completely changed to

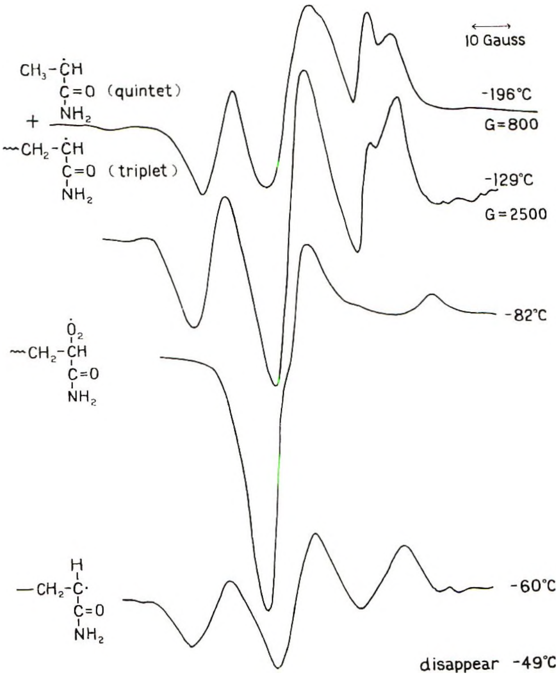

Fig. 4. Change with increasing temperature of ESR spectrum of acrylamide–malonic acid system irradiated at −196°C.

that of the peroxy radical at −82°C. This fact indicates that diffusion of oxygen molecules begins to take place near this temperature. The peroxy radical spectrum changed into the triplet spectrum responsible for the propagating radical at about −60°C., i.e., a little above the glass transition temperature (T_g). It is clear that post-polymerization began with the peroxy radical at this temperature; this is entirely in agreement with the results of differential thermal analysis and polymerization experiments. The propagating radical disappeared sharply at about −49°C.

The ESR spectrum of the irradiated acrylamide–itaconic acid system is shown in Figure 5. Almost the same feature was observed as in the acrylamide–malonic acid system.

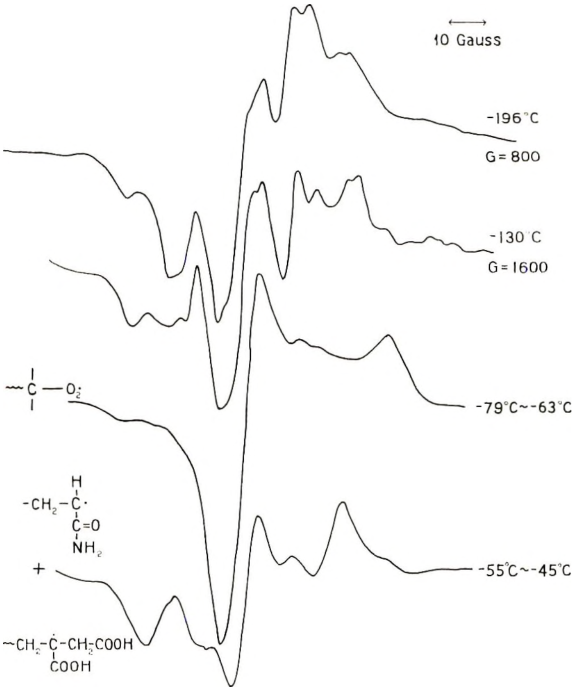

Fig. 5. Change with increasing temperature of the ESR spectrum of acrylamide–itaconic acid irradiated at −196°C.

In this case, the ESR spectrum due to the propagating radicals was a little different from that in the acrylamide–malonic acid system. It seems to be caused by superposition of the spectra of two kinds of propagating radicals, $\sim CH_2\dot{C}H(CONH_2)$ and $\sim CH_2\dot{C}(COOH)CH_2COOH$. They survived to a slightly higher temperature than in the acrylamide–malonic acid system. This difference in stability of the propagating radicals in these two systems corresponds to a difference in second transition temperature, polymerization rate, and temperature rise of the system due to the heat of polymerization.

Degree of Polymerization

The degree of polymerization is expected to be very high owing to the low termination in glassy systems. Table III shows the degree of polymerization and Huggins constant k' of the polymers formed by polymerization of some glassy systems containing acrylamide.

The degree of polymerization of polymers obtained by in-source polymerization varies with the polymerization temperature in correspondence with the dependency of conversion on temperature, though such a dependency is not so clear as in conversion.

It is surprising that k' of polymer between T_s and T_g is extremely large, while k' of polymer above T_s is the normal value. The reason may be that at a temperature between T_g and T_s active species are formed in the

TABLE III
Molecular Weight of Polymer Obtained in the Polymerization of Glass-Forming Systems Containing Acrylamide

In-source polymerization[a]			Post-polymerization[b]		
Irradiation temperature, °C.	$\overline{DP} \times 10^{-4}$	k'	Irradiation dose, Mr.	$\overline{DP} \times 10^{-4}$	k'
−78	2.1	3.40	0.23	7.0	0.22
−63	2.4	3.00	0.14	6.6	0.29
−48	1.6	0.52	0.09	5.9	0.48
−30	1.1	0.51	0.03	4.7	0.76
−20	1.3	0.48	0.02	4.4	0.78

[a] Acrylamide–propionic acid–formamide, 1:1:0.5; dose, 0.003 Mr.
[b] Acrylamide–succinic acid–acetamide, 1:0.5:1, temperature, −78°C.

polymer chain by irradiation and these begin to propagate at a very high rate owing to the high viscosity. So, the branching develops to an unusual degree.

The degree of polymerization of polymers formed by post-polymerization increases with dosage and polymerization rate. k' decreases with increasing dosage.

The reason may be that the chance of chain transfer to nonpolymerizable components increases with the decrease of polymerization rate.

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Résumé

La polymérisation induite par radiation de systèmes vitreux contenant des monomères a été étudiée. On a observé que l'irradiation en-dessous de la température de transition de second ordre T_g de ces systèmes n'entraîne pas de polymérisation immédiate mais occasionne une postpolymérisation rapide par chauffage au-dessus de T_g après une irradiation initiale en-dessous de ce même T_g. La postpolymérisation a été suivie par analyse thermique différentielle et par des spectres ESR. Elle est due, au-dessus de T_g, à la libération des radicaux peroxydés piégés en-dessous de T_g et sa vitesse est proportionnelle à la dose d'irradiation dans une certaine mesure, souvent elle est explosive et entraîne une augmentation de température vraiment appréciable par accumulation de la chaleur de polymérisation. L'irradiation au-dessus de T_g cause une polymérisation rapide immédiate et accélérée par la viscosité élevée du système monomérique entre T_g et T_s (température W.L.F.) comparée au cristal ou à la polymérisation en solution normale. La dépendance thermique de la polymérisation immédiate du système vitreux montre un pic apparent entre T_g et T_s; ce pic pourrait être le résultat d'effets compététifs dûs à l'accroissement de vitesse par diminution de la terminaison au voisinage de T_s et une diminution de vitesse due à la décroissance de la propagation par suite d'une diffusion freinée au voisinage de T_g. Les degrés de polymérisation ont également été étudiés. La dépendènce thermique du degré de polymérisation des polymères de polymérisation immédiate montre un pic semblable à la dépendance thermique du degré de conversion et montre des valeurs exceptionnellement élevées de la constante K' d'Huggins entre T_g et T_s. La degré de polymérisation des polymères de postpolymérisation croissait avec une augmentation de la dose d'irradiation et de la vitesse de polymérisation qui peut être le résultat d'une diminution de la réaction de transfert de chaîne sur des composants non-polymérisables.

Zusammenfassung

Die strahlungsinduzierte Polymerisation von glasbildenden, monomerhältigen Systemen wurde untersucht. Bestrahlung unterhalb der Umwandlungstemperatur zweiter Ordnung T_g der Systeme führt nicht zu einer unmittelbaren Polymerisation, verursacht aber eine schnelle Nachpolymerisation beim Erwärmen über T_g nach Bestrahlung unterhalb T_g. Die Nachpolymerisation wird mittels Differentialthermoanalyse und ESR-Spektroskopie verfolgt. Sie wird oberhalb T_g durch die Freisetzung der unterhalb T_g eingeschlossenen Peroxydradikale ausgelöst und ihre Geschwindigkeit ist in gewissem Ausmass der Bestrahlungsdosis proportional; sie erreicht oft eine explosive Höhe und führt durch Ansammlung der Polymerisationswärme zu einem bemerkenswert grossen Temperaturanstieg. Bestrahlung oberhalb von T_g führt zu einer raschen unmittelbaren Polymerisation, welche, im Vergleich zur Polymerisation im Kristall oder in normaler Lösung, durch die hohe Viskosität des Monomersystems zwischen T_g und T_s stark beschleunigt wird. Die Temperaturabhängigkeit der unmittelbaren Strahlungspolymerisation von Glassystemen besitzt zwischen T_g und T_s ein Maximum, das durch das Gegeneinanderspiel der Geschwindigkeitserhöhung durch den herabgesetzten Kettenabbruch in der Nähe von T_s und der Geschwindigkeitserniedrigung durch herabgesetztes Kettenwachstum infolge der Diffusionserschwerung in der Nähe von T_g verursacht werden kann. Polymerisationsgrade wurden ebenfalls untersucht. Die Temperaturabhängigkeit des Polymerisationsgrades besitzt bei der unmittelbaren Strahlungspolymerisation ähnlich wie die Temperaturabhängigkeit des Umsatzes ein Maximum; die Werte des Huggins k' sind zwischen T_g und T_s unbewöhnlich gross. Der Polymerisationsgrad des bei der Nachpolymerisation erhaltenen Polymeren nimmt mit steigender Bestrahlungsdosis und Polymerisationsgeschwindigkeit zu, was das Ergebnis einer verminderten Kettenübertragung an nicht polymerisierbare Komponenten sein kann.

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Effects of Metal Salts on Polymerization.* Part IV. Polymerization of *N*-Vinylcarbazole Initiated by Oxidizing Metal Nitrates

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Synopsis

The polymerization of *N*-vinylcarbazole (VCZ) in ethylene dichloride, acetone, benzene, and dioxane with cupric nitrate, ferric nitrate, and ceric ammonium nitrate as catalyst was studied. In all cases the polymerization seemed to be of a cationic nature, judged by copolymerization with styrene. Electron spin resonance (ESR) spectroscopy was made for the polymerization system and also for a system containing *N*-ethylcarbazole instead of VCZ. Singlet ESR spectra were observed for all systems containing ceric salt and for some systems containing ferric salt but not for systems containing cupric salt. The ESR spectra indicated the formation of an ion radical by electron transfer between the oxidizing metal salt and the carbazole derivatives. Mechanisms of initiation other than electron transfer were less likely, and it was concluded that the initiation process was most likely to be of the electron transfer type.

INTRODUCTION

The polymerization of *N*-vinylcarbazole (VCZ) has lately attracted the attention of many researchers. This monomer is peculiar with respect to its high reactivity to cationic polymerization and its strong tendency to form donor–acceptor complexes that can initiate polymerization. Such donor–acceptor complexes as an ether–acid anhydride system have been reported initiators for both radical[1] and cationic[2,3] polymerizations. It seems reasonable, therefore, to assume that the initiation by a donor-acceptor complex involves radical-ion formation by electron transfer. The polymerization of VCZ initiated by organic acceptors is similarly explained, by considering a charge transfer or polarization between VCZ and acceptors.[4-5]

Ellinger[4,5] considered that the polymerization is initiated through mesomeric polarization but not by complete charge transfer, since very weak acceptors, such as acrylonitrile or methyl methacrylate, could initiate the polymerization. He also considered the attacking monomer to be activated by complex formation. His original idea was extended to other systems as "activated monomer polymerization."[7] This would be a new category of polymerization, but confirmatory evidence in support of

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* For Part III see *J. Polymer Sci. A-1*, **5**, 1083 (1967).

Ellinger's proposal has not been obtained. Cation-radical formation would be another possible type of initiation. Pác and Plesch[8] considered that the slow dissociation of charge-transfer complex to radical ions is the initiation process for the polymerization initiated by tetranitromethane in nitrobenzene.

There is considerable confusion about the mechanism of polymerization of VCZ initiated by oxidizing metal salts. Such metal salts could accept electrons leading to oxidation of VCZ, during which radical ion might be formed as an intermediate. The actions of oxidizing metal salts might be considered to be the same as those of organic acceptors as a first approximation. All reported results on systems of VCZ and oxidizing metal salts have been therefore explained by assuming initial ion-radical formation similar to organic donor–acceptor systems. The interpretations of secondary reactions involving ion radicals widely differ among researchers. Wang[9] presented the first report on the polymerization of VCZ initiated by oxidizing nitrates in methanol. According to him, ceric ammonium nitrate, ferric nitrate, and cupric nitrate are capable of polymerizing VCZ in methanol solution and also of polymerizing completely the mixture of VCZ and styrene. He has postulated the polymerization to be of a radical nature like that of 4-vinylpyridine initiated by the same oxidizing metal salts. As has been pointed out by Bawn et al.,[10] the poly-VCZ that Wang claimed to obtain in methanol seems to be in fact dimeric VCZ, 1,2-dicarbazylcyclobutane. The present authors have reëxamined the experiment made by Wang and are critical of his report, since the reaction product of ferric nitrate and VCZ in methanol shows entirely different infrared spectra from those of poly-VCZ. Polymerization of VCZ was observed, however, when methanol was replaced with aprotic solvents such as dioxane, benzene, ethylene dichloride, tetrahydrofuran, or acetone. We have already reported[11] that the polymerization of VCZ initiated by cupric salts is cationic whereas that of vinylpyridine is radical. A kinetic study of the polymerization of 4-vinylpyridine initiated by cupric acetate[12] led to the conclusion that an electron-transfer process between monomer and cupric salt is the initial process of polymerization. The initiation process of VCZ by oxidizing metal salts might be a similar electron transfer. There is, however, another possibility, since these oxidizing metal salts are hydrolyzed rather easily and would produce nitric acid, which could initiate the cationic polymerization of highly reactive VCZ. The present study is consequently directed toward the initiation process in the polymerization.

EXPERIMENTAL

Materials

N-Vinylcarbazole (Koch-Light Laboratories Ltd.) was recrystallized twice from hot *n*-hexane and dried *in vacuo;* m.p., 64.2°C.

N-Ethylcarbazole (Tokyo Kasei Co. Chemical Pure Grade) was dissolved in benzene and purified by being passed through a column 17 mm. in diameter and 30 cm. in length, packed with activated alumina (200–300 mesh). The eluted *N*-ethylcarbazole was recrystallized three times from *n*-hexane; m.p., 66–67°C.

Styrene was dried over calcium chloride and distilled twice *in vacuo* after the stabilizer was removed by washing. The purified styrene was stored over calcium hydride and distilled again immediately before use.

Solvents were purified by fractional distillation from reagents of guaranteed reagent grade (G.R.) and finally dried over metallic sodium (for benzene and dioxane) or calcium hydride (for acetone and ethylene dichloride) and distilled before use.

All metal salts (G.R. grade) were used without further purification.

Polymerization

Polymerization was carried out in a reaction vessel equipped with a T-type three-way stopcock on the top. One of the sidearms of the stopcock was connected to a nitrogen line, through which a dry-nitrogen stream was supplied. Another sidearm was open to air, but the dry-nitrogen stream prevented the moisture from diffusing into the reaction vessel. A catalyst solution and then a monomer solution were introduced into the reaction vessel from the open end of the stopcock by means of an injector. These monomer and catalyst solutions were prepared in vessels similarly equipped with three-way stopcocks, so that contamination by moisture was avoided. When the metal salt had not enough solubility, it was directly weighed into the reaction vessel. The vessel containing the polymerization solution was placed in a thermostatted water bath, and the polymerization solution was taken out at appropriate intervals by means of an injector under the dry-nitrogen counterflow. The polymer, precipitated with a large excess of methanol, was filtered and weighed Contamination of the polymer with catalyst or with by-products, such as dimeric VCZ, could be avoided by using a large amount of the precipitant. The reaction products of the VCZ and the oxidizing metal salts in methanol were soluble in methanol, although the solubility was very small.

The viscosity measurement was made in a benzene solution of polymer at 25°C.

Copolymerization

The copolymer composition was analyzed by means of infrared spectroscopy. The absorptions at 988 cm.$^{-1}$ of poly-VCZ and at 1020 cm.$^{-1}$, which was common to poly-VCZ and polystyrene, were used as key bands.

Spectroscopy

A Varian Model V-4500 spectrometer and Shimazu SV50A spectrometer were used for electron spin resonance spectroscopy at liquid nitrogen temperature and electronic spectroscopy at room temperature, respectively.

RESULTS AND DISCUSSION

Polymerization of VCZ in Various Solvents, Initiated by Oxidizing Metal Nitrates

Polymerizations in different solvents are described in Figures 1 to 4. Among these solvents acetone has the highest dissolving power, and all three metal salts are soluble in acetone; dioxane does not dissolve cerium salts whereas benzene and ethylene dichloride dissolve none of the metal salts. It is therefore not possible to compare the catalytic activity of metal salts in different solvents. Polymerization in acetone is very fast during the initial stage but does not go to 100% conversion. This tendency of the saturation of polymer yield seems to be more or less a general feature of the polymerization of VCZ with metal salts, which effect reversible oxidation.[10] The polymerization of VCZ in ethylene dichloride or in dioxane, initiated by ferric nitrate, saturates at about 80%. Although ferric nitrate is soluble in acetone and dioxane, a brown, amorphous solid begins to precipitate, on standing, from the catalyst solution. The effects of solvent and metal salt on the polymerization are qualitatively shown in Tables I and II. The initial rate of polymerization is larger in a polar solvent, as judged from the limited amount of data.

It might seem strange that a cation-like polymerization proceeds rapidly in a strong Lewis base such as acetone. The high basicity of VCZ seems to enable the monomer to compete with Lewis bases for propagation. For example, water is a rather weak retarder of the polymerization of the

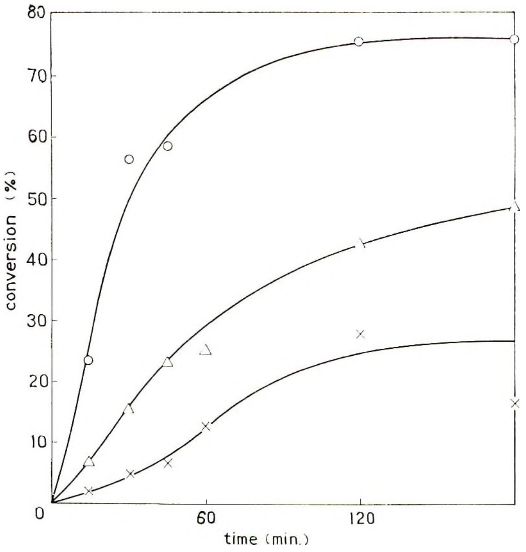

Fig. 1. Time–conversion curves for the polymerization of VCZ in $(CH_3Cl)_2$ at 40°C.; [VCZ] = 1.3M, [initiator] = $10^{-2}M$; (△) $Cu(NO_3)_2 \cdot 3H_2O$, (○) $Fe(NO_3)_3 \cdot 9H_2O$, (×) $Ce(NH_4)_2(NO_3)_6$.

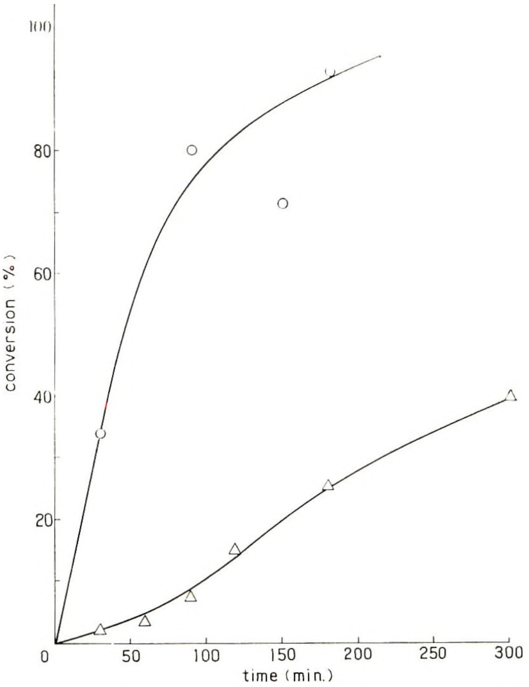

Fig. 2. Time–conversion curves for the polymerization of VCZ in benzene at 40°C.; [VCZ] = 1.3M, [initiator] = $10^{-2}M$. (○) $Fe(NO_3)_3 \cdot 9H_2O$, (△) $Cu(NO_3)_2 \cdot 3H_2O$.

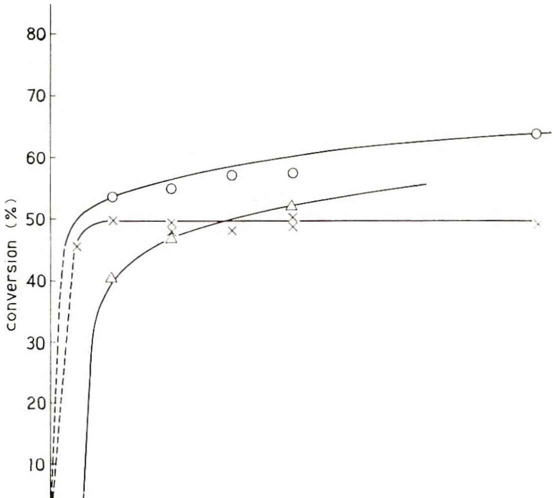

Fig. 3. Time–conversion curves for the polymerization of VCZ in acetone at 40°C.; [VCZ] = 1.3M, [initiator] = $10^{-2}M$; (△) $Cu(NO_3)_2 \cdot 3H_2O$, (○) $Fe(NO_3)_3 \cdot 9H_2O$, (×) $Ce(NH_4)_2(NO_3)_6$.

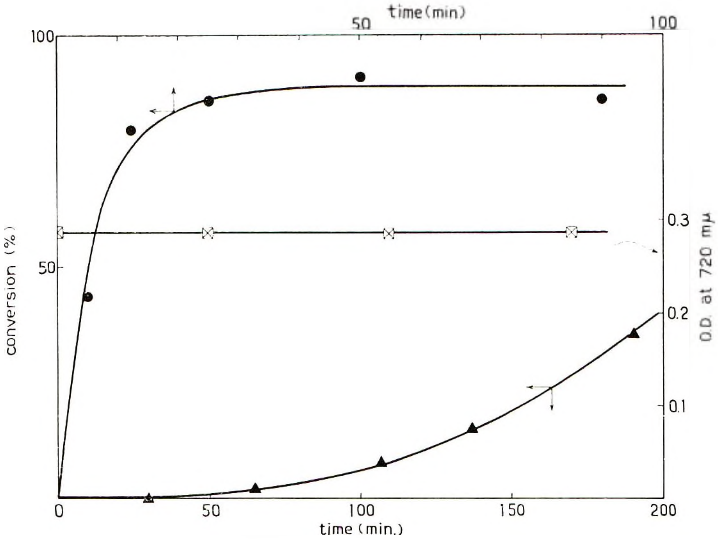

Fig. 4. Time–conversion curves for the polymerization of VCZ in dioxane at 40°C.; [VCZ] = 0.67M, [metal salt] = $10^{-2}M$: (●) Fe(NO_3)$_3$·9H_2O in dark, (▲) Cu(NO_3)$_3$·3H_2O in dark, (☒) [VCZ] = 0.2M, [Cu(NO_3)$_2$·3H_2O] = 2 × $10^{-2}M$.

TABLE I

Effect of Solvent

Solvent	Dielectric constant ϵ	Solubility of metal salt	Sequence of R_p	Intrinsic viscosity[a] [η]
Acetone	21.4	Good	1	0.02–0.04
Dioxane	2.23	Good	2	0.04–0.05
Ethylene dichloride	10.36	Poor	1	0.12–0.18
Benzene	2.28	Poor	2	0.04–0.08

[a] Benzene solution at 25°C.

TABLE II

Properties of Metal Salts and Their Catalytic Activities

Metal salt	Sequence of R_p				Intrinsic viscosity [η]	Oxidation potential, v.	log K_h* at 25°C.[a]
	Acetone	Dioxane	(CH_2Cl)$_2$	Benzene			
Cu(NO_3)$_2$·3H_2O	2	2	2	2	Differences	0.167	−7.34 ($\mu = 0$)[b]
Fe(NO_3)$_3$·9H_2O	1	1	1	1	are	0.772	−1.74 ($\mu = 0$)
Ce(NH_4)$_2$(NO_3)$_6$	1	—	3	—	small	1.6	0.72 ($\mu = 2$)

[a] $M^{n+} + H_2O \overset{K_h^*}{\rightleftharpoons} MOH^{(n-1)+} + H^+$.

[b] μ: ionic strength.

monomer when the process is initiated by tetranitromethane in nitrobenzene.[8] When the basic solvents do not interfere with the propagation step very much, the dielectric constant may be more important than the basicity. A high dielectric constant would facilitate not only the propagation step but also the initiation step, if the initiation step was of an electron-transfer type. An increase of the rate of electron-transfer initiation with increasing dielectric constant has been demonstrated in the polymerization of 4-vinylpyridine initiated by cupric acetate.[12]

The shape of the time–conversion curve may be compared with that of a polymerization catalyzed by organic oxidants. The initial acceleration period, which is particularly prominent for cupric nitrate in all solvents, has been reported also for the polymerization initiated by tetranitromethane[8] or chloranil.[4] This might indicate a slow process of formation of active species, possibly by charge-transfer interaction. As will be mentioned later, the polymerization initiated by nitric acid does not show any such acceleration period, indicating a different initiation mechanism.

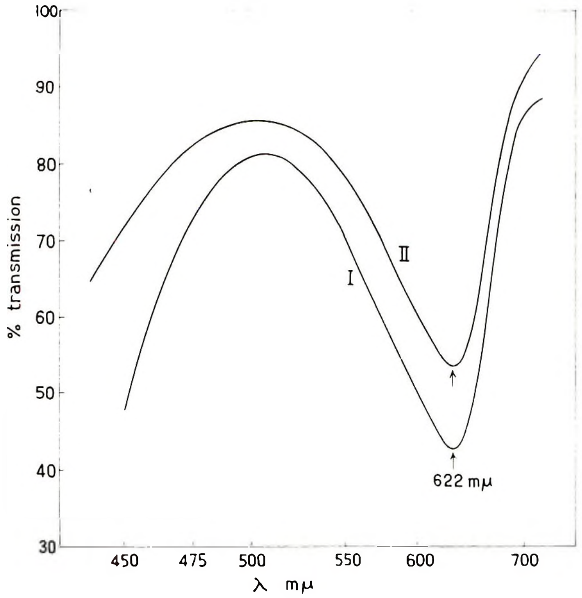

Fig. 5. Visible-wavelength absorption spectra: (I) VCZ–$Fe(NO_3)_3 \cdot 9H_2O$–$(CH_2Cl)_2$; (II) poly-VCZ–$Fe(NO_3)_3 \cdot 9H_2O$–$(CH_2Cl)_2$.

The viscosity of the polymer is shown in Table I. Although the viscosity is low, all methanol-precipitated products were confirmed as poly-VCZ by their infrared spectra. The fact that polymer of the highest molecular weight is obtained in ethylene dichloride indicates that the polymerization is of a cationic nature rather than a radical one. The dependence of the molecular weight of the polymer on the kind of metal salts or on the polymerization time is negligibly small.

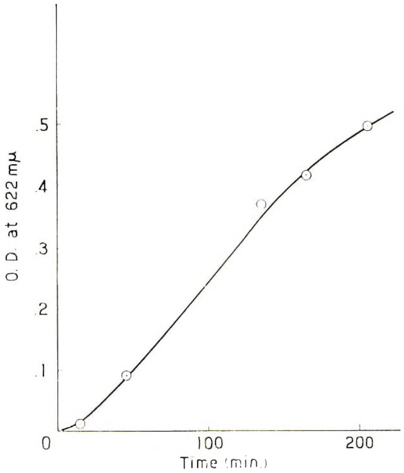

Fig. 6. Color development of VCZ–$Fe(NO_3)_3 \cdot 9H_2O$–$(CH_2Cl)_2$ system; reaction at 40°C. in air.

During the polymerization in ethylene dichloride, catalyzed by ferric nitrate, a distinct color change was observed. A yellowish color begins to develop from the surface of the metal salt and then slowly changes to a bluish green. Eventually the whole polymerization system becomes colored. The spectrum of the reaction system is shown in Figure 5, and the change in the intensity of the maximum absorption with polymerization time is shown in Figure 6. The color change of the polymerization system recalls the color of Wurster blue and might be considered a result of radical-ion formation. The colored species is, however, not likely to be the active species in the polymerization. Comparing Figures 4 and 6, the development of color is much slower than the formation of polymer and continues even after the time–conversion curve has reached its saturation value. Moreover, the same color could be produced when poly-VCZ dissolved in ethylene dichloride was treated with ferric nitrate (Fig. 5), and this colored polymer solution does not give an ESR signal. Such a brilliant color change is not observed in other systems.

Spectroscopic measurements of the polymerization systems were not attempted, except for the dioxane–cupric nitrate system, since solutions of ferric and ceric salts gave small amounts of precipitation during polymerization. No evidence of complex formation between the cupric salt and VCZ is obtained from the absorption spectra in the visible-wavelength region. The optical density of the polymerization system containing cupric nitrate does not change with polymerization time, as shown in Figure 4. Thus, the results of electronic spectroscopy do not provide evidence of irreversible electron transfer between VCZ and cupric salt. However, if the kinetic chain length of polymerization is very large (this is very likely for this extremely active monomer), we cannot neglect the possibility that an undetectable amount of cupric reduction species might produce sufficient amounts of active species for polymerization.

The question arises whether the polymerization is initiated by an electron-transfer process or by some other mechanism. Since the polymerization is apparently cationic, judged by the foregoing results and the following results on copolymerization, any polymerization other than one of the electron transfer type, if any, should be brought about by the direct interaction of metal salt and monomer, initiating a cationic polymerization, or by free acid, which might be formed as a result of the hydrolysis of metal salt. These metal nitrates have not hitherto been recognized as Friedel-Craft catalysts; consequently, this participation in the polymerization as conventional cationic catalysts could be ignored. The role of free acid in the polymerization will be discussed in the following section.

Polymerization of VCZ in Dioxane, Initiated by Nitric Acid

Nitric acid itself can also initiate polymerization, as shown in Figure 7. It is possible to make an approximate calculation of the amount of nitric acid produced by hydrolysis. For example, the hydrolysis of ferric nitrate may be estimated as follows. The hydrolysis constant K_h^* and stability constant K_1 for ferric nitrate complex have been obtained as follows:

$$\mathrm{Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+}, \quad K_h^* = [\mathrm{FeOH^{2+}}][\mathrm{H^+}]/[\mathrm{Fe^{3+}}] \tag{1}$$

$$\mathrm{Fe^{3+} + NO_3^- \rightleftharpoons FeNO_3^{2+}}, \quad K_1 = [\mathrm{FeNO_3^{2+}}]/[\mathrm{Fe^{3+}}][\mathrm{NO_3^-}] \tag{2}$$

Higher orders of hydrolysis or complex formation and the effect of the spontaneous dissociation of water molecules are neglected. The value of K_h^* at 40°C., when $\mu \rightarrow 0$, is calculated to be 1.55×10^{-2} from the value of $\log K_h^* = -2.17$ measured at 25°C., when $\mu \rightarrow 0$ and $\Delta H_\mathrm{h}^* = 10.4$

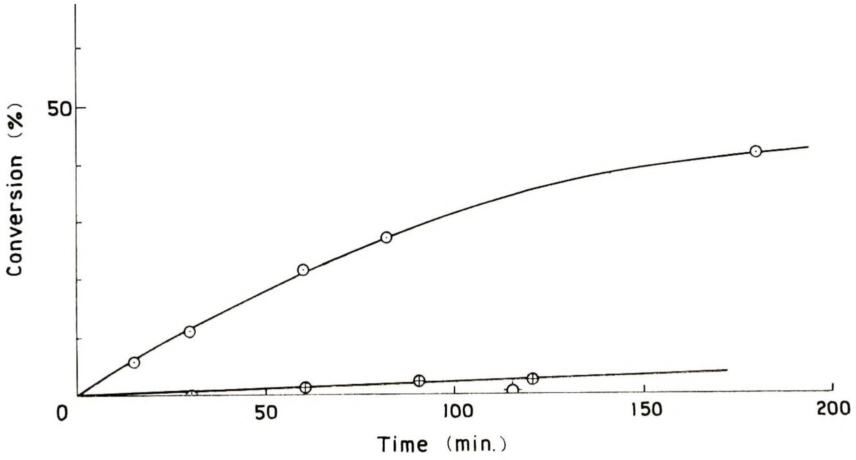

Fig. 7. Time-conversion curves for the polymerization of VCZ in dioxane at 40°C., initiated by nitric acid; [VCZ] = $0.67M$; (⊙) [$\mathrm{HNO_3}$] = $6.5 \times 10^{-3}M$, (⊕) [$\mathrm{HNO_3}$] = $6.5 \times 10^{-4}M$, (-ȯ-) [$\mathrm{HNO_3}$] = $6.5 \times 10^{-5}M$.

kcal./mole.[13] The value of K_1 at 40°C., when $\mu \rightarrow 0$, is estimated as 10.0 from the reported value at 25°C., neglecting the heat change of the complex formation, since the value of K_1 seems to be rather insensitive to temperature.[14] When the total ferric concentration is 10^{-2} mole/l., then $[FeOH^{2+}]$ and $[FeNO_3^{2+}]$ are calculated as 0.58×10^{-2} and 0.20×10^{-2} mole/l., respectively; then $[H^+]$ is also 0.58×10^{-2} mole/l.

These figures correspond, however, to the composition of ferric species in aqueous solution. Since the value of K_h^* is in fact the product of the real K_h^* and the concentration of water in dilute aqueous solution, it is not proper to apply eq. (1) to an organic system. The real K_h^* (distinguished by adding a prime) should be expressed as follows:

$$K_h^{*\prime} = \frac{[FeOH^{2+}][H^+]}{[Fe^{3+}][H_2O]} \tag{3}$$

The value of $K_h^{*\prime}$ is then reduced to 2.8×10^{-4} (that is, $K_h^*/[H_2O]$ in dilute aqueous solution). Using this figure and assuming the concentration of water in the system to be equal to crystalline water dissolved in ferric nitrate, one obtains $[FeOH^{2+}] = 4 \times 10^{-4}$ and $[FeNO_3^{2+}] = 3.6 \times 10^{-3}$ mole/l.

The real composition of the dioxane solution containing metal salt would be more complicated as a result of the interaction of metal salt with solvent molecules and, in addition, changes in the stability constants K_1 and $K_h^{*\prime}$, owing to the much smaller dielectric constant of dioxane than of water. In nonpolar solvents the ion-pair complexes would be stabilized, and the formation of $FeOH^{2+}$ would be very much facilitated. The formation of $FeNO_3^{2+}$ would be enhanced to the same extent as $FeOH^{2+}$ and, as a whole, the relative amounts of $FeOH^{2+}$ and $FeNO_3^{2+}$ would not be affected much. Now it is clear from the discussion above that the concentration of acid produced by the hydrolysis of ferric salt is much smaller, probably one order less than the initial total ferric concentration.

Cupric ion is less easily hydrolyzed than ferric ion (the K_h^* for cupric ion is 10^{-6} to 10^{-7}), and the amount of nitric acid formed would be very much smaller than in the case of ferric nitrate.

It has been reported that the polymerization of VCZ in the dry state could be catalyzed by a trace of protonic acid ($10^{-7}M$).[15] In the presence of water the polymerization was retarded but not inhibited. A low yield of low molecular weight polymer was reported to be produced within half an hour at room temperature when solid monomer was added to concentrated hydrochloric acid. The initiating activity of 62% nitric acid is in fact much weaker than that of the protonic acid in a completely dry system, as mentioned by Scott, since polymerization of VCZ was observed only when $[HNO_3] > 10^{-4}M$, as shown in Figure 7. The wet system was intentionally chosen so that the results could be compared with those of the systems initiated by metal nitrate. The ratio of water to nitric acid in 62%

nitric acid about 2, and this value corresponds to the completely hydrolyzed state of $Fe(NO_3)_3 \cdot 9H_2O$:

$$Fe(NO_3)_3 \cdot 9H_2O \rightarrow Fe(OH)_3 + 3HNO_3 + 6H_2O$$

The water-to-acid ratio in an actual ferric nitrate system that is incompletely hydrolyzed would be then larger than 2.0, and consequently its catalytic activity as a protonic acid would be weaker than would be anticipated from the model experiments with 62% nitric acid as initiator.

A comparison of Figures 7 and 4 leads to the conclusion that nitric acid would not be the main active species inducing polymerization when ferric nitrate and, probably, also cupric nitrate are used as catalyst in dioxane. The initial rate of polymerization initiated by nitric acid is only one-tenth of that initiated by ferric nitrate when the ratio of $[HNO_3]$ to $[Fe(NO_3)_3]$ is as high as 0.65.

Copolymerization of VCZ with Styrene

Copolymerization is one of the best methods of determining the mechanism of propagation. Although a cationic copolymerization of VCZ and styrene has not been reported, the high cationic reactivity of VCZ would bring about a copolymer rich in VCZ units.

In electron-transfer polymerization systems the formation of pure poly-VCZ was reported[6] to take place when VCZ was polymerized by using *p*-chloranil or tetracyanoquinodimethane in styrene. Scott mentioned that no absorptions other than those of poly-VCZ were detected in the infrared spectra of methanol-precipitated products. However, the infrared absorptions due to styrene units almost overlap with those of poly-VCZ, and it would be rather difficult to confirm the formation of any homopolymer of VCZ. Wang[9] reported that the mixture of VCZ and styrene was completely polymerized in the presence of 1% by weight of ferric nitrate at room temperature during a period of 24 hr., even though air was not excluded. A reexamination of his experiment gave sharply contrasting results. A saturated solution of VCZ made up with 1 g. of VCZ and styrene was added to 20 mg. of ferric nitrate, and the mixture was kept at room temperature. Complete polymerization was not observed, and the methanol-insoluble products after 9 days' reaction were only 0.80 g. The products were nearly pure poly-VCZ, judged by nitrogen analysis.

Copolymerization of VCZ (M_1) with styrene (M_2) in acetone, dioxane, benzene, or ethylene dichloride, with cupric nitrate, ceric ammonium nitrate, or ferric nitrate as catalyst at 40°C. always gave polymers very rich in VCZ. When the feed ratio of VCZ to styrene was 0.07, the polymer produced was at least 80% VCZ units. This result differs entirely from those of radical copolymerization.[16] Since the possibility of producing mixtures of homopolymers or mixtures of copolymers and homopolymer[5] was not examined, because of a lack of suitable solvent for extraction, further discussion could not be made.

Electron Spin Resonance Spectroscopy

The foregoing discussions indicate that the cationic polymerization of VCZ, initiated by oxidizing metal nitrates, is very likely to be caused by an electron-transfer process. When relatively stable ion radicals are formed thermally and can be trapped by cooling of the reaction system, ESR spectroscopy is a suitable method of detecting the species. Some of the ESR spectra are shown in Figure 8, and qualitative observations of other systems are tabulated in Table III. The ESR absorptions of metal salts alone in methanol, benzene, and ethylene dichloride were confirmed to be negligible, except that of cupric salt.

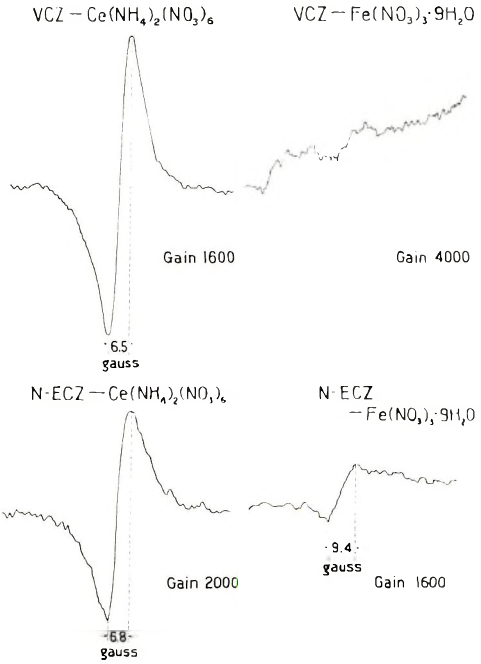

Fig. 8. ESR spectra of vinylcarbazole and *N*-ethylcarbazole in the presence of oxidizing metal salts in ethylene dichloride at 77°K.

The ESR spectrum, when it is observed, appears always as a singlet band that may be assigned to the delocalized ion radical. The behaviors of VCZ and *N*-ethylcarbazole are qualitatively the same according to the ESR spectroscopy, indicating that the presence of the vinyl group in forming the paramagnetic species is not the essential condition. At the present time it is not decided whether the π molecular orbitals or the pair of nonbonding electrons of the nitrogen atom would participate in the electron-transfer process. In organic donor–acceptor systems *N*-isopropylcarbazole is considered a π donor.[17] The free spins produced on the carbazole ring by either mechanism would conjugate with the vinyl group and activate the monomer. The high stability of the paramagnetic species would be an

TABLE III
ESR Spectrum of Vinylcarbazole and N-Ethylcarbazole in the Presence of Oxidizing Metal Salts, Measured at 77°K.[a]

Donor–acceptor pair	Solvent[b] Methanol	Benzene	Ethylene dichloride
VCZ–$Cu(NO_3)_2 \cdot 3H_2O$	□ (G = 80)[c]	□ (G = 80)	□ (G = 250)
VCZ–$Fe(NO_3)_3 \cdot 9H_2O$	□ (G = 2000)	△ (G = 1000)	△ (G = 4000)
VCZ–$Ce(NH_4)_2(NO_3)_6$	○ (G = 63) 8.8 gauss[d]	○ (G = 2000) 7.2 gauss	○ (G = 1600) 6.5 gauss
ECZ–$Cu(NO_3)_2 \cdot 3H_2O$	□ (G = 16)		□ (G = 2)
ECZ–$Fe(NO_3)_3 \cdot 9H_2O$	□ (G = 250)		○ (G = 1600) 9.4 gauss
ECZ–$Ce(NH_4)_2(NO_3)_6$	○ (G = 10) 9.6 gauss		○ (G = 2000) 6.8 gauss

[a] Sample: 0.5 ml. of solution containing 0.08 mmole of VCZ or ECZ was added to ≈0.03 mmole of metal salt.

[b] No signal, □; weak signal, △; strong and clear signal, ○.

[c] Gain.

[d] Values of ΔH_{msl} (peak-to-peak width).

indication of extensive delocalization of an unpaired electron over the carbazole ring. Its stability is so high that the ESR signal is still observable even after several cycles of freeze and thaw.

The intensity of the ESR signal depends on the catalyst used. No ESR signal was observed for the system containing cupric nitrate. This might be due partially to the fact that the strong background absorption caused by cupric species prevents ESR measurement at high sensitivity. The strength of the ESR signal seems to be correlated to the oxidizing power of the metal salts. This is a reasonable correlation, because stronger oxidants (i.e. stronger acceptors), such as Ce^{IV}, bring about a larger extent of electron transfer than do the weaker oxidants such as Fe^{III} and Cu^{II}.

No general correlation could be found between the strength of the ESR signal and the rate of polymerization. The strengths of ESR signals may be given in the order $Ce^{IV} > Fe^{III} > Cu^{II}$, whereas the strength of the catalytic activity of the ferric salt is always larger than that of the cupric salt, but the position of the ceric salt is uncertain. In homogeneous systems the ceric salt is as strong an initiator as the ferric salt (Fig. 3). In heterogeneous systems (Fig. 1) the initiating activity of the ceric salt is even weaker than that of the cupric salt. Complicating factors due to the insolubility of the initiator must be considered, and consequently a comparison of the catalytic activity of metal salts in this system seems to have little significance.

The production of paramagnetic species does not mean the initiation of polymerization, unless the reaction conditions, such as the solvent used, are favorable for the polymerization to proceed. For instance, the ESR signal was observed for the system VCZ–Ce^{IV}–methanol, but no polymer was formed.

CONCLUSION

The initiation process for the polymerization of VCZ catalyzed by oxidizing metal salts is most likely to be of an electron-transfer type. Confirmatory evidence of the formation of ion radicals through the reaction between carbazole derivatives and ceric or ferric salts has been obtained by ESR spectroscopy. Although there is still no direct evidence of the identity of the paramagnetic species and the active species in the initiation of the polymerization, initiation mechanisms other than one involving electron transfer are less likely. Concerning cupric nitrate systems, electron transfer could not be confirmed by ESR spectroscopy, for technical reasons. The catalytic activity of cupric nitrate is nevertheless difficult to explain on the assumption that the polymerization is initiated by free nitric acid produced by the hydrolysis of cupric nitrate. The probability of the formation of a weak donor–acceptor complex between VCZ and the metal salt is not discussed in this report. Very weak organic acceptors, such as methyl methacrylate and acrylonitrile, could initiate the polymerization of VCZ, which was regarded as a polymerization induced by mesomeric polarization.[4,5] If any charge-transfer complex is formed, it could be detected by electronic spectroscopy. As far as we have examined, no interaction between VCZ and the cupric salt has been found. Further study on this point is clearly required.

The VCZ would show peculiar behavior in conventional cationic polymerization systems because of its strong donor property. Interaction between VCZ and conventional cationic catalysts would often involve donor–acceptor complex formation. For example, a strong singlet ESR signal is observed for the system VCZ–anhydrous ferric chloride–ethylene dichloride, in which ferric chloride would act both as an electron acceptor and as a conventional cationic initiator.

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Résumé

La polymérisation du *N*-vinylcarbazole (VCZ) dans le dichlorure d'éthylène, l'acétone, le benzène, le dioxane, utilisant le nitrate de cuivre, le nitrate ferrique et le nitrate cérique ammonique comme catalyseurs, a été étudiée. Dans tous les cas la polymérisation semble être de nature cationique si l'on en juge par la copolymérisation avec le styrène. La spectroscopie ESR a été faite pour le système en polymérisation et également pour le système contenant du *N*-éthyl-carbazole au lieu de VCZ. Les spectres ESR singlets ont été observés pour tous les systèmes contenant le sel cérique et pour certains systèmes contenant un sel ferrique mais pas pour les systèmes contenant un sel cuivrique. Les spectres ESR indiquaient la formation d'un ion radical par transfert électronique entre le sel métallique oxydant et le dérivé carbazole. Les mécanismes possibles d'initiation autres que par initiation par transfert électronique sont moins probables et on conclut que le procesus d'initiation est très probablement du type transfert d'électrons.

Zusammenfassung

Die Polymerisation von *N*-Vinylcarbazol (VCZ) in Äthylendichlorid, Aceton, Benzol und Dioxan mit Kupfernitrat, Eisen-III-nitrat und Cerammonnitrat als Katalysator wurde untersucht. In allen Fällen handelte es sich, nach der Copolymerisation mit Styrol zu urteilen, um eine kationische Polymerisation. ESR-Spektren des Polymerisationssystems sowie des Systems mit *N*-Äthylcarbazol an Stelle von VCZ wurden gemessen. An allen Systemen mit Cersalz und an einigen mit Eisen-III-salz jedoch nicht an Systemen mit Kupfer-II-salzen wurden Singulett-ESR-Spektren beobachtet. Die ESR-Spektren sprachen für die Bildung eines Ionenradikals durch Elektronenübertragung zwischen oxydierendem Metallsalz und den Carbazolderivaten. Andere, an sich mögliche Mechanismen als Elektronenübertragung sind für die Initierung weniger wahrscheinlich und man kommt zu dem Schluss, dass der Initiierungsvorgang mit grosser Wahrscheinlichkeit in einer Elektronenübertragung besteht.

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Copolymerization of Trioxane with Styrene Catalyzed by $BF_3 \cdot O(C_2H_5)_2$

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Synopsis

It was determined whether trioxane, a cyclic formal, can copolymerize with styrene, a vinyl monomer, in the presence of $BF_3 \cdot O(C_2H_5)_2$ catalyst at 30°C. The methanol-insoluble fraction after extraction with benzene was found to contain the copolymer of styrene and trioxane, thus demonstrating that trioxane can copolymerize with styrene In this case the amount of the methanol-insoluble polymer was less than that of the total monomer consumed, as determined by gas chromatography. This was found to be caused partly by the formation of the cyclic oligomer, 4-phenyl-1,3-dioxane. The relative reactivity of styrene was qualitatively found to be larger than that of trioxane, not only from the rate of monomer consumption but also from the composition of the methanol-insoluble polymer obtained. In a nonpolar solvent the reactivity of trioxane increased, and the difference in reactivity between the two monomers decreased. Indeed, an apparent monomer reactivity ratio might be obtained from the relationship between the monomer composition and the monomer consumption rate or the composition of the methanol-insoluble polymer, but it did not have a quantitative meaning because of the complexity of the copolymerization reaction.

INTRODUCTION

Recent studies have been made to determine whether cyclic compounds such as cyclic formal,[1,2] cyclic ether,[3] and lactone[4] can copolymerize with vinyl monomers, which are quite different in chemical structure from the former. It was found that cyclic formal and lactone can react with styrene with formation of the copolymer. It was of interest to determine the reaction mechanism between these monomers having such differences in chemical structure and relative reactivities. In the published papers these points are discussed mainly on the basis of the analyses of the polymer obtained. These results would be valid only if substances other than copolymer were not formed during the copolymerization of the two monomers. If this were not so, these results may be invalid.

We have found that the cyclic oligomer is formed in the homopolymerization of cyclic formals such as trioxane,[5] tetraoxane,[5] and dioxolane.[6] Therefore, in the copolymerization of cyclic formals and vinyl monomers the formation of these or similar reaction products other than polymer may be expected. In such case the copolymerization reaction should be studied, not only on the basis of the analyses of the polymer obtained, but also on the basis of the consumption of each monomer and the formation of by-products.

The copolymerization of trioxane with styrene was studied kinetically from the above-mentioned point of view, since the formation of the copolymer had been previously reported by Höhr et al.[1] The cationic polymerizability of trioxane was found to be less than that of styrene. The yield of methanol-insoluble polymer did not coincide with the amount of total monomer consumption, the latter being larger than the former. This discrepancy was found to be caused partly by the formation of the cyclic oligomer, 4-phenyl-1,3-dioxane. The solvent effect on the reactivity of styrene and trioxane was also studied.

EXPERIMENTAL

Materials

Styrene was refined by washing commercial material with sodium hydroxide and sodium bisulfite aqueous solutions, drying over calcium chloride, and distilling over calcium hydride at reduced pressure. Other materials were purified as described in a previous paper.[7]

Procedures

The copolymerization was carried out in solution by using boron trifluoride etherate [$BF_3 \cdot O(C_2H_5)_2$] as catalyst. The reaction was initiated by adding the catalyst solution from a syringe through a rubber stopper into a flask containing the monomer solution. The effect of air was not considered, and the polymerization solution was not stirred. In a given period of time the polymerization was stopped by adding a certain quantity of ammoniated methanol. By use of the upper layer the concentration of residual monomers and cyclic oligomers (tetraoxane and 4-phenyl-1,3-dioxane) formed were measured by gas chromatography according to the internal-standard method. The conditions of the gas chromatographic measurement are as follows, where PEG is poly(ethylene glycol) and DNP is dinonyl phthalate.

For trioxane: PEG-4000 (1 m.) + DNP (1 m.), temp. 95°C., H_2, 60 ml./min., *m*-xylene as internal standard.

For styrene and tetraoxane: PEG-4000 (1 m.) + DNP (1 m.), temp. 130°-C., H_2, 70 ml./min., *p*-cymene as internal standard.

For 4-phenyl-1,3-dioxane: PEG-6000 (1 m.), temp. 170°C., H_2, 70 ml./min., nitrobenzene as internal standard.

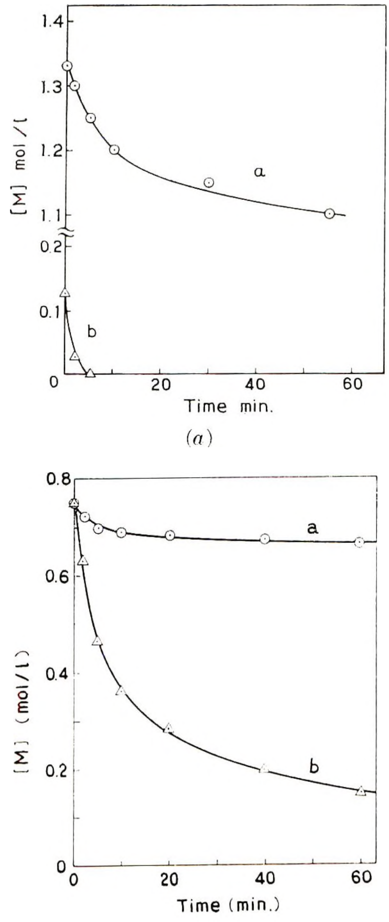
The peak area was measured by using a planimeter. The methanol-insoluble polymer was obtained by pouring the polymerizing system into a large quantity of methanol filtering the precipitate, washing with methanol, and drying in vacuum at room temperature.

The formation of the copolymer was confirmed by the extraction of the methanol-insoluble product with benzene; that is, the infrared spectra and the elemental analyses showed that both the parts soluble and insoluble in benzene contained oxymethylene and styrene units. The composition of the methanol-insoluble polymer was determined by elemental analysis. In the following results $[M]_0$ denotes *total* initial concentration of both monomers.

RESULTS AND DISCUSSION

Rates of Monomer Consumption and Polymer Formation

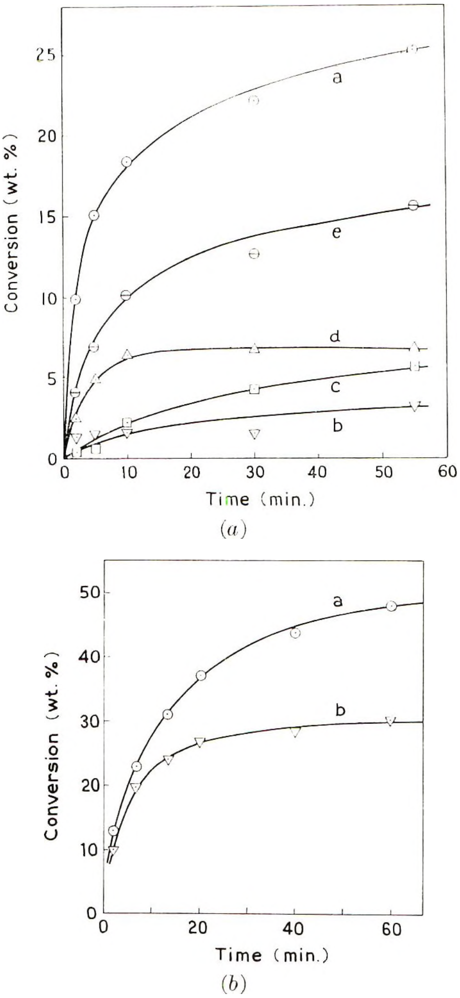
The rate of consumption of each monomer was measured by gas chromatography for the copolymerization of trioxane and styrene in ethylene



(*a*)

(*b*)

Fig. 1. (*a*) Change in concentration of each monomer with reaction time in copolymerization of trioxane and styrene catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in ethylene dichloride at 30°C. with $[M]_0 = 1.50$ moles/l.: (O) consumption of trioxane, (Δ) consumption of styrene (moles/l.). Monomer composition $[TO]_0/[St]_0$, 92:8; catalyst concentration, 20 mmoles/l. (*b*) Same as Figure 1*a*, except that $[TO]_0/[St]_0$ is 50:50 and catalyst concentration is 10 mmoles/l.



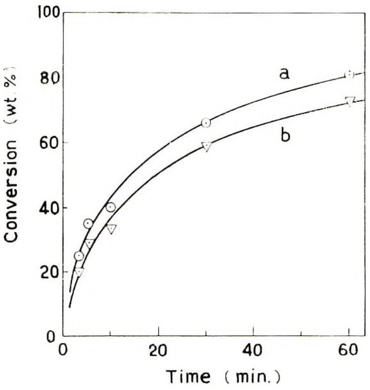
(*a*)

(*b*)

Fig. 2. See caption, p. 1931.

dichlorode at 30°C. The results for different monomer compositions, are shown in Figures 1*a* and 1*b*. Clearly, from these figures the consumption rate of styrene is larger than that of trioxane, regardless of the monomer composition. Therefore, it is concluded that the reactivity of trioxane in the presence of the cationic catalyst is smaller than that of styrene. In such a system a polymer which is rich in trioxane units cannot be expected.

It has been already found that in the homopolymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ the amount of methanol-insoluble polymer does not coincide with that of the monomer consumed, the former being smaller than the latter.[5] This point was also confirmed in the copolymerization of trioxane and styrene at various monomer compositions. The results are shown in Figures 2*a*, 2*b*, and 2*c*. As is seen in these figures, the amount of methanol-insoluble polymer does not coincide with that of the total mono-



(*c*)

Fig. 2. (*a*) Time–conversion curves in copolymerization of trioxane and styrene catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in ethylene dichloride at 30°C. with $[M]_0$ = 1.50 moles/l.: (○) total monomer consumption rate, (▽) methanol-insoluble polymer yield, (□) tetraoxane yield, (△) 4-phenyl-1,3-dioxane yield, (⊖) curves *b* + *c* + *d*. Monomer composition $[TO]_0/[St]_0$, 92:8; catalyst concentration, 20 mmoles/l. (*b*) Same as Figure 2*a*, except that $[TO]_0/[St]_0$ is 50:50 and catalyst concentration is 10 mmoles/l. (*c*) Same as Figure 2*a*, except that $[TO]_0/[St]_0$ is 5:95 and catalyst concentration is 5 mmoles/l.

mer consumed, the latter being larger than the former, as occurs in the homopolymerization of trioxane. On the other hand, in the homopolymerization of styrene catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in ethylene dichloride at 30°C. the amount of the methanol-insoluble polymer exactly coincided with that of the monomer consumed, as is shown in Figure 3.

Therefore, the difference between the amount of methanol-insoluble polymer and that of monomer consumed in the copolymerization of trioxane with styrene is caused by the presence of trioxane in the polymerizing system. This difference increased with an increase in the trioxane feed content, as is shown in Figure 4. It is also clear from Figure 4 that the

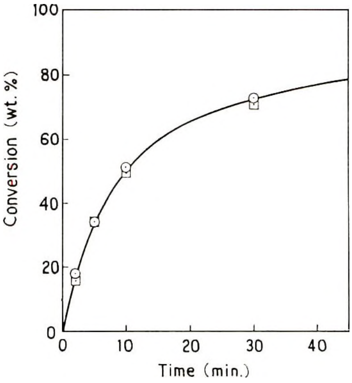


Fig. 3. Time–conversion curve in homopolymerization of styrene catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in ethylene dichloride at 30°C. with $[M]_0$ = 1.00 mole/l., $[BF_3 \cdot O(C_2H_5)_2]$ = 4.0 mmoles/l.: (○) monomer consumption rate, (□) polymer yield.

addition of a small amount of styrene decreased remarkably the formation of methanol-insoluble polymer as compared with the case of the trioxane homopolymerization under similar conditions, while the amount of the monomer consumption was almost the same in both cases. These facts suggest the occurrence of a side reaction other than polymer formation by the reaction of trioxane with styrene.

In the homopolymerization of trioxane the formation of tetraoxane has been found.[5] In the copolymerization of trioxane and styrene the formation of tetraoxane has been recognized by gas chromatography. Moreover, in the gas chromatogram of the trioxane–styrene copolymerized system a new substance was found in the high boiling-point region, besides the substances, charged and the tetraoxane formed. This new substance was collected by a fraction collector through gas chromatography and shown to be 4-phenyl-1,3-dioxane by its refractive index and infrared spectrum (Fig. 5). This spectrum is the same as reported for 4-phenyl-1,3-dioxane.[1] The refractive index of the fraction collected was $n_D^{21} = 1.5255$, while that of the commercial 4-phenyl-1,3-dioxane was $n_D^{21} = 1.5255$ (lit.[8]) $n_D^{20} = 1.5269$). Therefore during the copolymerization of trioxane and styrene the substances, polymer, tetraoxane, and 4-phenyl-1,3-dioxane are formed.

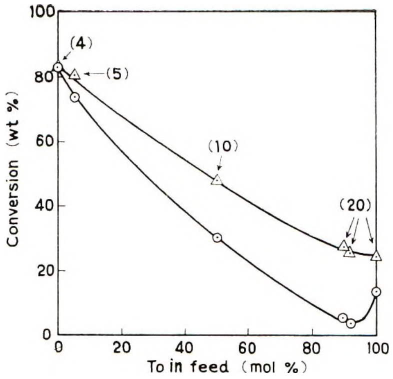


Fig. 4. Monomer composition dependence of conversion at a reaction time of 60 min. in copolymerization of trioxane and styrene catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in ethylene dichloride at 30°C. with $[M]_0 = 1.50$ moles/l.: (△) total monomer consumption, (○) methanol-insoluble polymer yield. Numbers in parentheses denote concentration of $BF_3 \cdot O(C_2H_5)_2$ in mmoles/l.

The formation of 4-phenyl-1,3-dioxane was confirmed in all systems investigated in this report, but the amount formed depends on the monomer composition. The time–conversion curves for each component, for example, was as shown in Figure 2*a* for the system in which the difference between the monomer consumption amount and the amount of the methanol-insoluble polymer was the largest. The total amount of monomer consumed still did not coincide with the total amount of the polymer, tetraoxane, and 4-phenyl-1,3-dioxane formed.

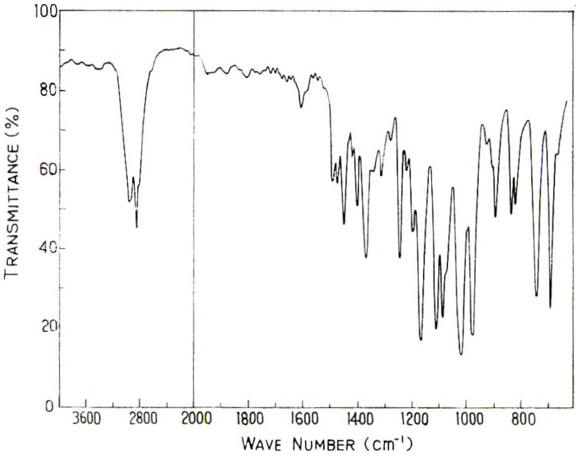


Fig. 5. Infrared spectrum of reaction product 4-phenyl-1,3-dioxane in copolymerization of trioxane and styrene by $BF_3 \cdot O(C_2H_5)_2$.

4-Phenyl-1,3-dioxane has little homopolymerizability with a cationic catalyst such as $BF_3 \cdot O(C_2H_5)_2$,[9] but it is not clear whether this compound can copolymerize with styrene, trioxane, or tetraoxane, which is produced during the copolymerization of trioxane with styrene. The formation of 4-phenyl-1,3-dioxane may be explained in terms of the back-biting reaction (or intramolecular transacetalization), as was reported with respect to tetraoxane formation in the homopolymerization of trioxane.[5]

Effect of Solvent

In the copolymerization of cyclic formal and vinyl monomer it is also possible to obtain the relationship between the monomer composition ratio and the ratio of each component in the product, as done for the copolymerization of vinyl monomers. In the copolymerization of trioxane with sty-

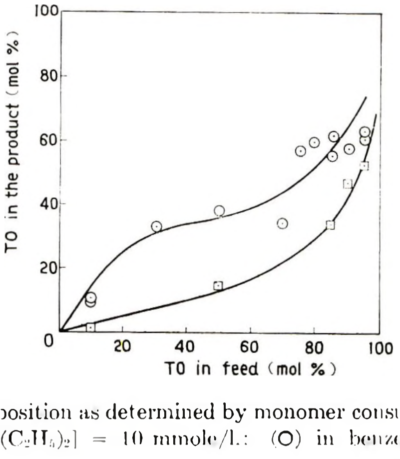


Fig. 6. Polymer composition as determined by monomer consumption rate, with $[M]_0 = 1.5$ mole/l., $[BF_3 \cdot O(C_2H_5)_2] = 10$ mmole/l.: (○) in benzene, (□) in ethylene dichloride.

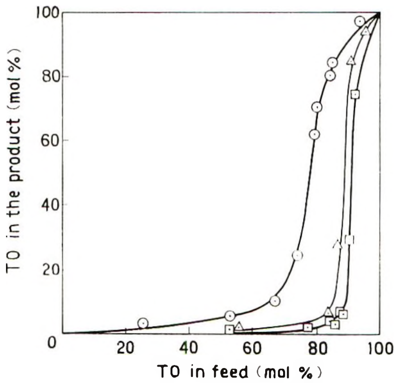


Fig. 7. Polymer composition as determined by elemental analysis of methanol-insoluble polymer obtained, with $[M]_0$ = 4.0 moles/l.: (○) in benzene, (□) in ethylene dichloride, (△) in nitrobenzene.

rene in various solvents the composition curves determined by monomer consumption are as shown in Figure 6, and those determined by elemental analysis of the polymer are as shown in Figure 7.

These curves, however, do not simply show the relative reactivity of the monomer as found in the copolymerization of vinyl monomers for the following reasons. Since reactions other than polymerization occur during the copolymerization of trioxane and styrene, the monomers are not always consumed just for formation of polymer. The polymer is also probably formed by the reaction of styrene, tetraoxane, and other by-products in addition to the reaction of styrene and trioxane. Therefore, it is meaningless in regards to this system to discuss the results quantitatively by determining the monomer reactivity ratios r_1 and r_2 according to the Lewis-Mayo equation.

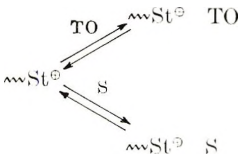
Speaking qualitatively, Figures 6 and 7 support the above-mentioned conclusion that styrene is more reactive than trioxane. The composition curves in Figure 6 are clearly different from those in Figure 7. This shows that the ratio of trioxane consumption to styrene consumption does not coincide with that of trioxane content to styrene content in the polymer formed. This is supported by the fact that 4-phenyl-1,3-dioxane and other by-products are formed in the copolymerization of trioxane and styrene.

As is seen in Figures 6 and 7, the apparent relative reactivity of monomer varies with the nature of the solvent used. At the present time, a quantitative discussion is impossible, since all the reaction products have not been confirmed yet. However, it can be qualitatively concluded that in the copolymerization of trioxane and styrene by cationic catalysis the reactivity of trioxane as compared with that of styrene increases with a decrease in the polarity of solvent.

As is shown in Figure 7, the composition of the polymer obtained in nitrobenzene is not very different from that obtained in ethylene dichloride.

Therefore, it seems that the reactivity of trioxane increases only in a nonpolar solvent such as a hydrocarbon compound. It has been reported by Minoura et al. that the trioxane content in the methanol-insoluble polymer increases with a decrease in the dielectric constant of the benzene–nitrobenzene mixture solvent.[10]

In the homopolymerization of trioxane by $BF_3 \cdot O(C_2H_5)_2$ at a low monomer concentration the polymerization rate (the polymer formation rate) in a nonpolar solvent was larger than that in a polar solvent.[11] This phenomenon was explained in terms of the selective solvation of the active end with monomer. Accordingly, the larger reactivity of trioxane in a nonpolar solvent during the copolymerization of trioxane and styrene may be explained by the same idea. It is assumed that the styryl carbonium ion is stabilized by solvation with trioxane and solvent molecules and that both processes proceed competitively, as is shown in the following scheme, where TO is the trioxane molecule and S is the solvent molecule:



If the solvation with trioxane occurs predominantly, the styryl carbonium ion may be easily transformed to a very stable oxonium ion, so that styrene monomer then adds to it with difficulty. Since the solvation power of solvent decreases with the decrease in the polarity of solvent, in a nonpolar solvent the styryl carbonium ion may be stabilized selectively by solvation with trioxane molecules rather than by solvent molecules, and thus the styrene monomer may be consumed with difficulty. A similar phenomenon may occur with respect to the active end composed of a trioxane unit at low concentrations of trioxane, as is mentioned above.[11]

As mentioned, trioxane reacts with styrene in the presence of $BF_3 \cdot O(C_2H_5)_2$ catalyst with the formation of the copolymer. In this case it was made clear that styrene is more reactive than trioxane and that appreciable amounts of by-products other than polymer are formed. Therefore, for this copolymerization system it is not correct to discuss the relative reactivities of the monomers only on the basis of the composition of the polymer obtained.

This investigation was reported at the Meeting on Polymer Chemistry at Kobe, Japan, July 9, 1966.

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Résumé

On a étudié la copolymérisation éventuelle du trioxane, un formal cyclique, avec le styrène, un monomère vinylique, en présence d'un catalyseur $BF_3{\cdot}O(C_2H_5)_2$ à 30°C. La fraction insoluble dans le méthanol après extraction au benzène contenait un copolymère de styrène et de trioxane, démontrant ainsi que le trioxane et le styrène copolymérisent effectivement. Dans ce cas, la quantité de polymère insoluble dans le méthanol est plus petite que la quantité totale de monomères consommés tel que cela a été déterminé par chromatographie gazeuse. Ceci est dû partiellement à la formation de l'oligomère cyclique, le 4-phényle-1,3-dioxane. La réactivité relative du styrène a été trouvée être qualitativement plus grande que celle du trioxane, non seulement par la vitesse de consommation du monomère, mais également par la composition du polymère obtenu insoluble dans le méthanol. Dans un solvant non-polaire, la réactivité du trioxane augmente et la différence de réactivité entre les deux monomères diminue. En effet, un rapport de réactivité monomérique apparent peut être obtenu par la relation entre la composition monomérique et la vitesse de consommation des monomères ou par la composition du polymère insoluble dans le méthanol, mais il n'a pas de signification quantitative par suite de la complexité de la réaction de copolymérisation.

Zusammenfassung

Die Möglichkeit, Trioxan, ein cyclisches Formal, mit Styrol, einem Vinylmonomeren, in Gegenwart von $BF_3{\cdot}O(C_2H_5)_2$ als Katalysator bei 30°C zu copolymerisieren, wurde untersucht. Durch Extraktion mit Benzol wurde festgestellt, dass der methanolunlösliche Anteil das Styrol-Trioxancopolymere enthält und so die Copolymerisation zwischen Trioxan und Styrol nachgewiesen. Die Menge des methanol-unlöslichen Polymeren war in diesem Fall geringer als diejenige des gesamten, gaschromatographisch bestimmten, umgesetzten Monomeren. Die Ursache dafür lag zum Teil in der Bildung des cyclischen Oligomeren, 4-Phenyl-1,3-dioxan. Die relative Reaktivität von Styrol erwies sich qualitativ als grösser als diejenige von Trioxan, nicht nur durch die Geschwindigkeit des Monomerverbrauches sondern auch durch die Zusammensetzung des erhaltenen, methanol-unlöslichen Polymeren. In einem nicht-polaren Lösungsmittel nahm die Reaktivität von Trioxan zu und der Reaktivitätsunterschied zwischen den beiden Monomeren verringerte sich. Aus der Beziehung zwischen Monomerzusammensetzung und Monomerumsatzgeschwindigkeit oder der Zusammensetzung des methanolunlöslichen Polymeren könnte man ein scheinbares Monomer-Reaktivitätsverhältnis erhalten; dieses besitzt aber wegen des komplexen Charakters der Copolymerisationsreaktion keine quantitative Bedeutung.

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Copolymerization of Tetraoxane with Styrene Catalyzed by $BF_3 \cdot O(C_2H_5)_2$

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Synopsis

The copolymerization of tetraoxane with styrene catalyzed by $BF_3 \cdot O(C_2H_5)_2$ was studied at 30°C. to determine whether a cyclic monomer can copolymerize with a vinyl monomer. The formation of the copolymer was confirmed by elementary analysis of both benzene-soluble and benzene-insoluble fractions of the polymer obtained. It was found by gas chromatography that a fairly large amount of 4-phenyl-1,3-dioxane and a small amount of trioxane were formed in the present system, in addition to polymers. Roughly a third of the total amount of the monomers reacted was consumed in the formation of methanol-insoluble polymer, a third for 4-phenyl-1,3-dioxane, and another third for trioxane and unknown products which could not be identified. The formation of these cyclic compounds during the copolymerization may be explained in terms of a back-biting (or intramolecular transacetalization) reaction. The cationic reactivity of tetraoxane was found to be similar to that of styrene on the basis of both the consumption rate of each monomer in the copolymerizing system and the composition of the methanol-insoluble polymer obtained.

INTRODUCTION

In a previous paper,[1] the copolymerization of trioxane with styrene by a cationic catalyst was studied to determine whether a cyclic monomer can copolymerize with a vinyl monomer having a chemical structure quite different from the former. It was found that the cationic polymerizability of trioxane is smaller than that of styrene. The copolymer containing many oxymethylene units was obtained with difficulty because of the predominant formation of by-products other than the polymer even at the high trioxane feed content. Therefore, a more reactive cyclic formal than trioxane should be used as a comonomer so as to readily obtain a copolymer containing many oxymethylene units. In this paper, the copolymerization of styrene with tetraoxane, which has a larger polymerizability than trioxane,[2] was studied in the presence of $BF_3 \cdot O(C_2H_5)_2$ as catalyst at 30°C.

The reactivity of tetraoxane was found to be similar to that of styrene during the copolymerization of tetraoxane with styrene. In this case, the formation of a large amount of 4-phenyl-1,3-dioxane was also observed, as in the copolymerization of trioxane with styrene.[1]

EXPERIMENTAL

Tetraoxane was supplied by Toyo Ko-atsu Co. Ltd. and recrystallized from acetone. Chloroform was washed with concentrated sulfuric acid, aqueous sodium hydroxide, and water, dried over calcium chloride, and distilled over phosphorus pentoxide. The purification of the other materials, the procedures of the copolymerization, and the determination of the concentration of each component in the reaction system by gas chromatography are the same as described in the previous paper.[1] The total initial monomer concentration $[M]_0$ was equal to 1.0 mole/l.

RESULTS AND DISCUSSION

Rate of Monomer Consumption During Polymer Formation

In the homopolymerization of tetraoxane, trioxane was formed.[2] In the copolymerization of trioxane with styrene, the formation of a cyclic oligomer, 4-phenyl-1,3-dioxane, was found.[1] In the copolymerization of tetraoxane with styrene, the formation of these cyclic compounds was also recognized by gas chromatography. Consequently the change in the concentration of each component with reaction time was measured by gas chromatography during the copolymerization of tetraoxane with styrene in ethylene dichloride. The results for various monomer compositions are shown in Figures 1–3. As is seen from curves *a* and *b* in Figure 2, tetraoxane and styrene are consumed at almost the same rate with $BF_3 \cdot O(C_2H_5)_2$ as catalyst. The reactivity of tetraoxane is similar to that of styrene, or strictly speaking, is slightly larger than that of styrene during the initial

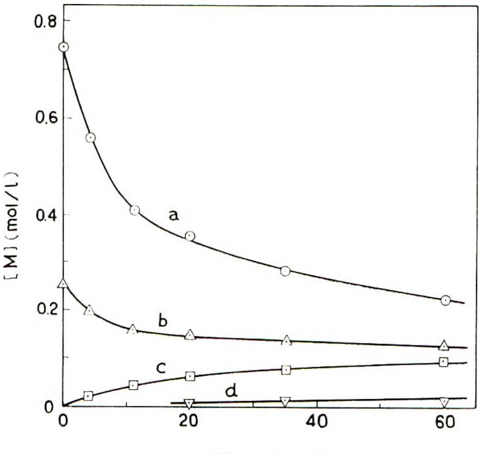


Fig. 1. Change in the concentration of each component with reaction time in the copolymerization of tetraoxane with styrene in ethylene dichloride at 30°C.: (*a*) consumption of styrene; (*b*) consumption of tetraoxane; (*c*) formation of 4-phenyl-1,3-dioxane; (*d*) formation of trioxane. Monomer composition [TeX]:[St] = 1:3; $[M]_0$, 1.0 mole/l.; $[BF_3 \cdot O(C_2H_5)_2]_0$, 4.0 mmole/l.; $[H_2O]_0$, 3.7 mmole/l.

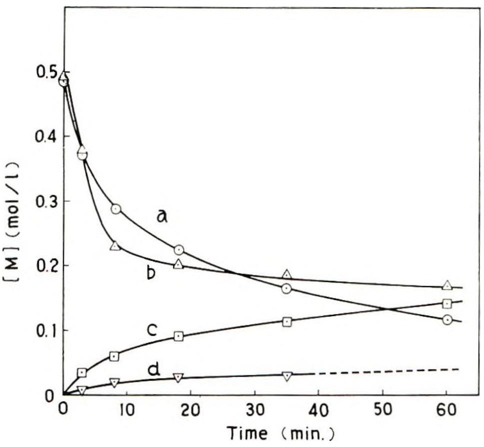


Fig. 2. Change in the concentration of each component with reaction time in the copolymerization of tetraoxane with styrene in ethylene dichloride at 30°C.: (*a*) consumption of styrene; (*b*) consumption of tetraoxane; (*c*) formation of 4-phenyl-1,3-dioxane; (*d*) formation of trioxane. [TeX]:[St] = 1:1; other conditions as in Fig. 1.

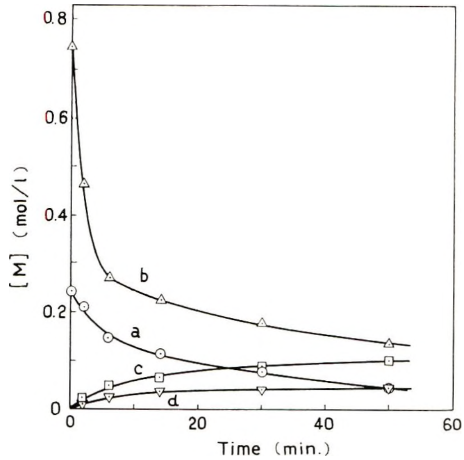


Fig. 3. Change in the concentration of each component with reaction time in the copolymerization to tetraoxane with styrene in ethylene dichloride at 30°C.: (*a*) consumption of styrene; (*b*) consumption of tetraoxane; (*c*) formation of 4-phenyl-1,3-dioxane; (*d*) formation of trioxane. [TeX]:[St] = 3:1; other conditions as in Fig. 1.

stage of the reaction. In the copolymerization of trioxane with styrene at low contents of styrene in the feed (8 mole-%), all of the styrene was consumed in a few minutes,[1] but during the copolymerization of tetraoxane with styrene at the low styrene feed content (Fig. 4), the styrene was consumed at a reasonable rate without disappearing suddenly, although the homopolymerizability of tetraoxane is much larger than that of trioxane. This fact suggests that the rates of monomer consumption

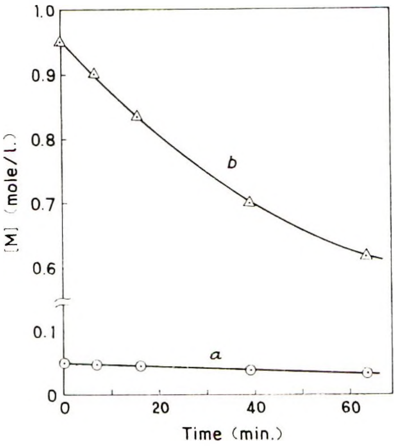


Fig. 4. Change in the concentration of each monomer with reaction time in the copolymerization of tetraoxane with styrene in ethylene dichloride at 30°C.: (*a*) consumption of styrene; (*b*) consumption of tetraoxane; $[M]_0$, 1.00 mole/l.; [TeX]:[St] = 95:5; $[BF_3 \cdot O(C_2H_5)_2]$; 6.0 mmole/l.

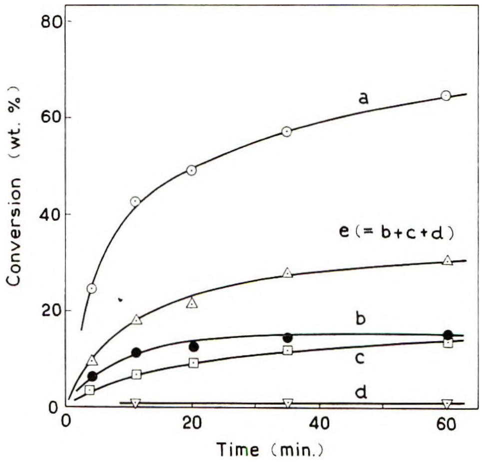


Fig. 5. Time–conversion curves for the copolymerization of tetraoxane with styrene in ethylene dichloride at 30°C.: (*a*) total monomer consumption; (*b*) polymer yield; (*c*) 4-phenyl-1,3-dioxane yield; (*d*) trioxane yield; (*e*) total products (*b* + *c* + *d*). [TeX]:[St] = 1:3. $[M]_0$, 1.0 mmole/l., $[BF_3 \cdot O(C_2H_5)_2]$, 4.0 mmole/l.; $[H_2O]_0$, 3.7 mmole/l.

during the copolymerization depend on the relative reactivities of the monomers towards the growing chain ends and not necessarily on their homopolymerizability.

In the copolymerization of trioxane with styrene, the amount of methanol-insoluble polymer did not coincide with that of the monomers consumed, the latter being larger than the former.[1] In the copolymerization of tetraoxane with styrene a similar phenomenon was observed. The total

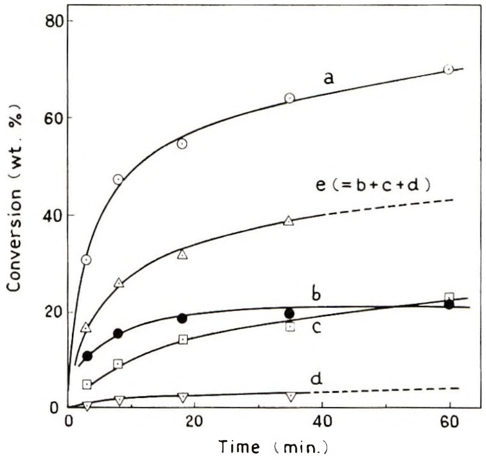


Fig. 6. Time-conversion curves for the copolymerization of tetraoxane with styrene in ethylene dichloride at 30°C.: (*a*) total monomer consumption; (*b*) polymer yield; (*c*) 4-phenyl-1,3-dioxane yield; (*d*) trioxane yield; (*e*) total products (*b* + *c* + *d*). [TeX]:[St] = 1:1; other conditions as in Fig. 5.

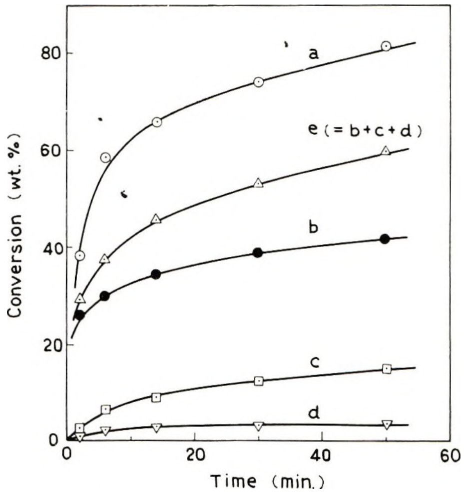


Fig. 7. Time-conversion curves for the copolymerization of tetraoxane and styrene in ethylene dichloride at 30°C.: (*a*) total monomer consumption; (*b*) polymer yield; (*c*) 4-phenyl-1,3-dioxane yield; (*d*) trioxane yield; (*e*) total products (*b* + *c* + *d*). [TeX]:[St] = 3:1; other conditions as in Fig. 5.

monomer consumption and the polymer yield in various monomer compositions are shown by curves *a* and *b* in Figures 5–7 in which the yields of trioxane and 4-phenyl-1,3-dioxane formed are also shown. In this case, the total amount of methanol-insoluble polymer and cyclic compounds (trioxane and 4-phenyl-1,3-dioxane) does not still coincide with the total amount of the monomers consumed and a fairly large amount of the methanol-soluble product, which has not yet been investigated, is present.

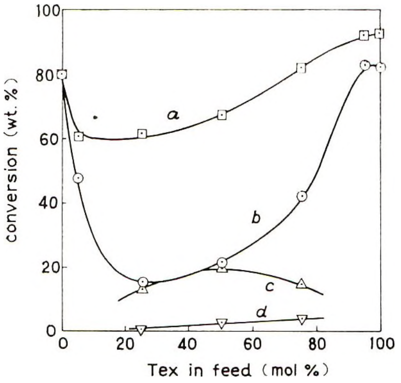


Fig. 8. Monomer-composition dependence of conversion at a reaction time of 50 min. in the copolymerization of tetraoxane with styrene in ethylene dichloride at 30°C.: (*a*) total monomer consumption; (*b*) polymer yield; (*c*) 4-phenyl-1,3-dioxane yield; (*d*) trioxane yield. $[M]_0$, 1.0 mole/l., $[BF_3 \cdot O(C_2H_5)_2]$, 4.0 mmole/l.

Figure 8 shows the amount of each component detected at a reaction time of 50 min. in the copolymerization of tetraoxane with styrene. The amount of each component produced clearly depends on the monomer composition. Roughly a third of the total amount of monomers reacted is consumed by formation of the methanol-insoluble polymer, and a third goes towards formation of 4-phenyl-1,3-dioxane, and another third towards formation of the unknown methanol-soluble product.

As is clear from Figure 8, in the copolymerization of tetraoxane with styrene the amount of methanol-insoluble polymer is decreased markedly by the addition of each comonomer while the amount of total monomer consumption does not decrease as much. The difference between the amount of monomer accounted for in polymer formation and the monomer consumption increases with an increase in the styrene content in feed up to high styrene content, and then decreases. That is, the amount of the methanol-soluble product has a maximum at a high styrene feed content. This is different from the copolymerization of trioxane with styrene in which addition of a small amount of styrene markedly increased the amount of methanol-soluble material.[1] It seems that during the copolymerization of styrene with trioxane or tetraoxane, the addition of a small amount of the more reactive comonomer tends to inhibit the formation of the methanol-insoluble polymer.

As is seen in Figures 5–8, the amount of methanol-insoluble polymer depends on the composition of the monomer mixture. It should be noticed (Figs. 5 and 6) that the formation of the methanol-insoluble polymer was suppressed or apparently interrupted at a certain yield, depending on the composition of the monomer mixture. Therefore it is clear from Figures 1 and 2 that styrene is consumed for the formation of compounds other than 4-phenyl-1,3-dioxane even after the apparent interruption of the formation of the methanol-insoluble polymer. One of the unknown products may be a very low molecular weight polymer which is soluble in methanol; a high molecular weight polymer is not to be expected because of the formation of 4-phenyl-1,3-dioxane, a cyclic ether having little cationic homopolymerizability.[4] This cyclic ether adds to the active end with the formation of a very stable oxonium ion, thereby retarding the copolymerization reaction between tetraoxane and styrene. In fact, it has been found that the addition of a small amount of ether decreased the molecular weight of polymer obtained in the homopolymerization of styrene by a cationic catalyst.[5] Another possible methanol-soluble product may be cyclic compounds larger than six-membered rings. The possibility for the formation of these compounds is likely on the basis of the considerations for the formation of 4-phenyl-1,3-dioxane, discussed below in detail.

Properties of the Methanol-Insoluble Product

The infrared spectrum of the methanol-insoluble product obtained in the copolymerization of tetraoxane with styrene with $BF_3 \cdot O(C_2H_5)_2$ was the same as that of the mixture of homopolystyrene and polyoxymethylene. The carbon and hydrogen contents of the product as determined by elementary analysis lie between those of polystyrene and polyoxymethylene. Subsequently, it was checked whether the product contained a true copolymer.

The polymer obtained was fractionated by extraction with benzene. A 200-mg. sample was added to 20 ml. of benzene at 30°C. with vigorous stirring, allowed to stand for one day, and the benzene-insoluble part filtered off. The benzene-insoluble fraction was extracted three additional times with benzene. The benzene-soluble part was obtained by evaporating benzene from the filtrate at reduced pressure. The polymer was genererally divided into two fractions, the benzene-soluble and -insoluble parts. Each fraction was found qualitatively by infrared spectroscopy to contain not only oxymethylene units but also styrene units. The composition of each fraction was quantitatively determined by elementary analysis. The results are shown in Table I. It is concluded from these results that a true copolymer was formed as in the case of the copolymerization of trioxane with styrene.[1,3]

TABLE I
Benzene Extraction of the Methanol-Insoluble Product Obtained in Copolymerization of Tetraoxane with Styrene in Ethylene Dichloride at 30°C.[a]

	Composition	
Fraction, wt.-%	TeX units, mole-%	St units, mole-%
Benzene-insoluble (56)	79.5	20.5
Benzene-soluble (33)	4.5	95.5

[a] Conditions: $[M]_0$, 1.0 mole/l. ([TeX]:[St] = 4:6); $[BF_3 \cdot O(C_2H_5)_2]$, 2.0 mmole/l., reaction time, 120 min.; polymer yield, 14% (weight).

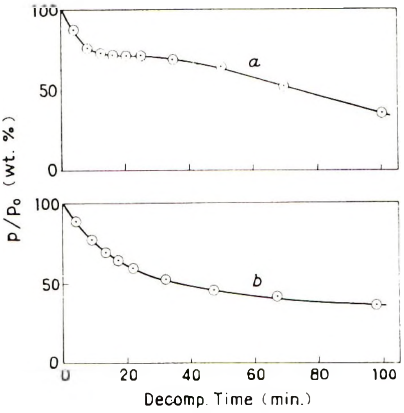


Fig. 9. Thermal decomposition rate (P/P_0) of the methanol-insoluble polymers obtained (*a*) in the copolymerization of tetraoxane with styrene and (*b*) in the homopolymerization of tetraoxane, catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in ethylene dichloride at 30°C. For (*a*) $[M]_0$, 1.0 mole/l. ([TeX]:[St] = 8:2); yield, 25%; η_{sp}/c, 0.54. For (*b*) $[M]_0$, 1.0 mole/l.; yield, 29%; η_{sp}/c, 0.87.

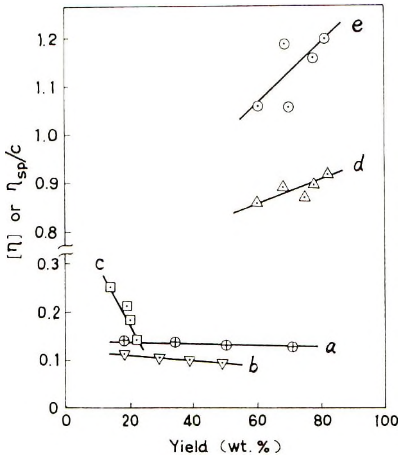


Fig. 10. Relationship between the viscosity of the polymer and the yield in the copolymerization of tetraoxane with styrene in ethylene dichloride at 30°C.: (*a*) [TeX]:[St] = 0:100; (*b*) [TeX]:[St] = 5:95; (*c*) [TeX]:[St] = 48:52; (*d*) [TeX]:[St] = 95:5; (*e*) [TeX]:[St] = 100:0.

The formation of the copolymer was also confirmed qualitatively by thermal decomposition of the polymer obtained. In Figure 9 is shown one of the results of the thermal decomposition in air at 220°C. of the copolymer and of end-untreated polyoxymethylene. The decomposition of the polymer obtained in the copolymerization was temporarily stopped near a decomposition rate of 70%, while that of polyoxymethylene or its mixture with polystyrene (the latter data are not shown here[13]) proceeded without interruption. Though the absolute value of the decomposition rate in the initial stage could not be compared for three kinds of samples be-

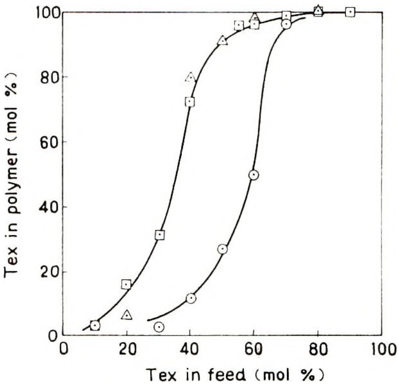


Fig. 11. Composition curves for the methanol-insoluble polymers obtained in the copolymerization of tetraoxane with styrene in various solvents at 30°C.: (○) chloroform; (□) ethylene dichloride; (△) nitrobenzene. $[M]_0$, 1.0 mole/l.; $[BF_3 \cdot O(C_2H_5)_2]$, 1.0 mmole/l. Polymer yield, 5–8 wt.-%.

cause of bad reproducibility, such a temporary interruption was deduced to be caused by the existence of styrene units combined chemically with oxymethylene units in the main chain, and this supports the formation of copolymer.

In Figure 10 is shown the relationship between the viscosity of the methanol-insoluble polymer and the polymer yield at various monomer compositions. Here the limiting viscosity number $[\eta]$ of the styrene-rich polymer was measured in benzene at 30°C. (Fig. 10, lines *a* and *b*) and the viscosity number (η_{sp}/c) of the tetraoxane-rich polymer was measured in *p*-chlorophenol including 2% α-pinene at a polymer concentration of 0.6 g./100 ml. solvent at 60°C. (Fig. 10, lines *c*, *d*, and *e*). Clearly the addition of a small amount of each comonomer decreased the molecular weight of the polymer as compared with the homopolymerization. This suggests that each comonomer serves as a transfer or terminating agent, as in the copolymerization of only vinyl monomers, or that 4-phenyl-1,3-dioxane formed during the copolymerization inhibits the formation of the high molecular weight polymer, as is mentioned above.

In Figure 11 is shown the composition curves for the methanol-insoluble polymer obtained in various solvents at yields of 5–8 wt.-%, as determined by elementary analysis. This figure may support the conclusion that the cationic reactivity of tetraoxane is similar to that of styrene. There was no difference in composition of the polymer obtained in ethylene dichloride and nitrobenzene solvents, as was also the case for the copolymerization of trioxane with styrene.[1] The composition of the polymer obtained in chloroform, however, was different from that obtained in the other two solvents, the content of styrene units in the polymer being increased in chloroform. It seems that the reactivity of each monomer is strongly affected by the nature of solvent, especially in a nonpolar solvent. The monomer reactivity ratio might be determined from Figure 11 according to a simple copolymerization equation or the Lewis-Mayo equation, but the results are not quantitative because of the complexity of the copolymerization reaction.

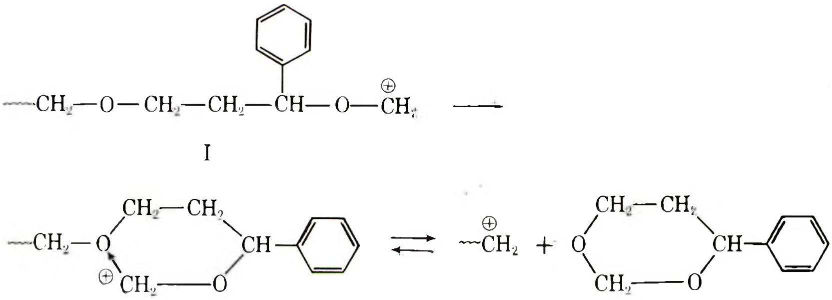
Mechanism of Formation of 4-Phenyl-1,3-Dioxane

The formation of trioxane during the polymerization of tetraoxane by the cationic catalyst has been reported and could be explained in terms of a "back-biting" reaction (intramolecular transacetalization).[2] In the copolymerization of tetraoxane with styrene, the rate of formation of trioxane depends markedly on the monomer composition and is larger, the higher the content of tetraoxane in the feed, as shown in Figures 1–3.

On the other hand, it has been reported that 4-phenyl-1,3-dioxane is formed by a reaction of formaldehyde with styrene in water or acetic acid by a strong acid catalyst such as perchloric acid at a high temperature (100°C.).[4,6–8] This reaction is generally called the Prins reaction. The formation of 4-phenyl-1,3-dioxane by a reaction of trioxane or tetraoxane with styrene in an organic solvent by a mild catalyst at room temperature has not been reported yet, however. Therefore, it is very interesting to consider the mechanism of 4-phenyl-1,3-dioxane formation.

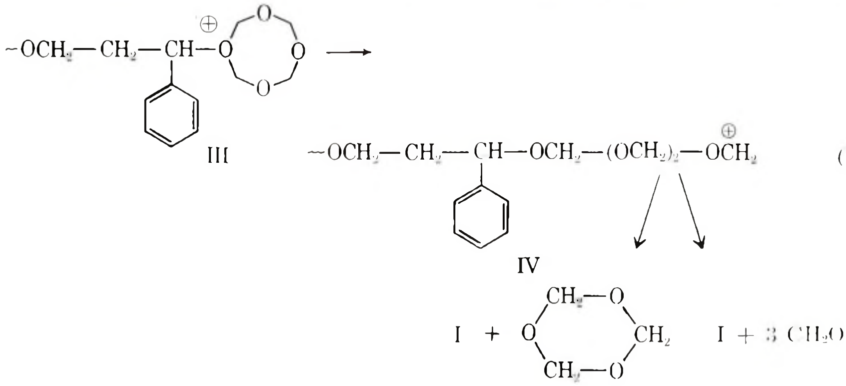
In the first place, it was supposed that 4-phenyl-1,3-dioxane is formed by the direct interaction of styrene with formaldehyde which may be derived from the decomposition of tetraoxane or trioxane, or from a depolymerization of the oxymethylene active end, by a Prins reaction. The amount of formaldehyde detected in the homopolymerization of trioxane by the cationic catalyst is very small at room temperature except for the particular case.[9,10] On the other hand, the rate of formation of 4-phenyl-1,3-dioxane in the present case is fairly large. Therefore, it was supposed that this compound is not formed mainly by the reaction of styrene with free, monomeric formaldehyde.

Thus the formation of 4-phenyl-1,3-dioxane may be also explained in the terms of a back-biting reaction. In this case, two different routes may be proposed. As is shown in eqs. (1), a carbonium ion (I) formed as an intermediate is, besides the propagation reaction, stabilized by

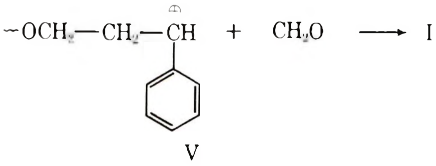


(1)

a self-cyclization in which the end of the ion I attacks an oxygen atom in its own chain with the formation of an oxonium ion (IIa) (back-biting reaction). Then the depolymerization of 4-phenyl-1,3-dioxane takes place. The formation of the ion (I) is possible according to eqs. (2) and (3).



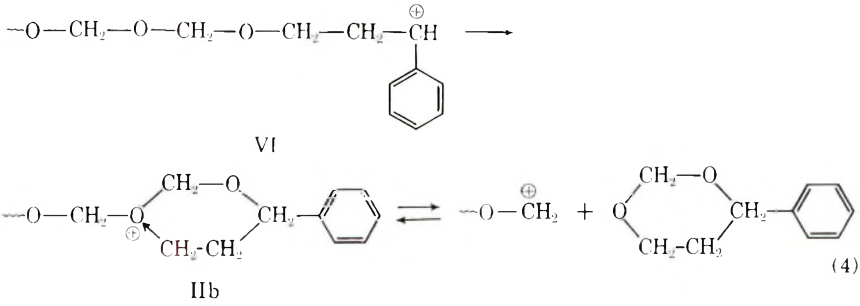
(2)



(3)

An active end composed of styrene and tetraoxane (III), which is inferred to exist on the basis of the formation of the copolymer, is transformed through a ring-opening to a carbonium ion (IV), from which the depolymerization of trioxane or formaldehyde takes place, leading to the formation of the ion (I), or a probable active end composed of a styrene unit (V) reacts directly with formaldehyde liberated in the system.

Another possible scheme is shown in eq. (4); the carbonium ion (VI) as an intermediate is, besides the propagation reaction, stabilized by self-cyclization and the oxonium ion formed (IIb) depolymerizes to 4-phenyl-1,3-dioxane.



(4)

In the copolymerization of tetraoxane with styrene, the formation of ion VI is much easier than that of ion I, because the latter is accompanied by the side reaction as is shown in eqs. (2) and (3). Therefore the formation of 4-phenyl-1,3-dioxane is deduced to be ascribed mainly to the mechanism shown in eq. (4). The same mechanism for the 4-phenyl-1,3-

dioxane formation may be applied to the trioxane–styrene copolymerization system.

According to the above-mentioned back-biting mechanism, the formation of cyclic compounds larger than six-membered rings, or macrocyclic species is also possible. Therefore, as mentioned earlier, they may partly compose the methanol-soluble product. But the detection of such macrocyclic species has not been attempted.

The reaction in which the active chain end (a carbonium or oxonium ion) attacks an oxygen atom in its own chain (back-biting reaction) possibly occurs during the homopolymerization or copolymerization of other cyclic ethers or formals. In fact, the formation of 1,4-dioxane in the homopolymerization of ethylene oxide[11] and the formation of 1,3-dioxolane, 1,3,5-trioxepane, and 1,4-dioxane in the copolymerization of trioxane with ethylene oxide[12] have been reported. We have also observed the occurrence of such a reaction in the polymerization of oxetane, propylene oxide, dioxolane, etc.[13] Therefore the formation of cyclic compounds must be generally taken into account during the polymerization and copolymerization of cyclic monomers.

Especially in the copolymerization of these monomers, it is very dangerous to discuss the reactivity of monomers only on the basis of polymer analyses obtained without checking the formation of any substances other than the polymer, and careful attention should be paid to results discussed in previously published papers.

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Résumé

La copolymérisation du tétraoxane avec le styrène catalysée avec $BF_3 \cdot O(C_2H_5)_2$ a été étudiée à 30° en vue de prouver si un monomère cyclique peut copolymériser avec un monomère vinylique. La formation du copolymère a été confirmée par analyse élémentaire à la fois des fractions solubles dans le benzène du polymère obtenu et insolubles dans ce solvant. On a trouvé par chromatographie gazeuse que une quantité appréciable de 4-phényle-1,3-dioxane et une petite quantité de trioxane étaient formé à côté du polymère dans ce système. Approximativement un tiers de la quantité totale des monomères qui ont réagi sont consommés et donnent lieu à la formation d'un polymère insoluble dans le méthanol, un tiers à la formation de 4-phényl-1,3-dioxane et un autre tiers à la formation de trioxane et de produits inconnus qui n'ont pas pu être identifiés jusqu'ici. La formation de ce composé cyclique en cours de copolymérisation peut être expliquée sur la base d'une réaction en retour (intramoléculaire de transacétylation). La réactivité cationique du tétraoxane a été trouvée semblable à celle du styrène sur la base à la fois de la vitesse de consommation de chaque monomère dans le système copolymérisant et de la composition du polymère obtenu insoluble dans le méthanol.

Zusammenfassung

Die Copolymerisation von Tetraoxan mit Styrol wurde mit $BF_3 \cdot O(C_2H_5)_2$ als Katalysator bei 30°C untersucht um zu sehen, ob ein cyclisches Monomeres zur Copolymerisation mit einem Vinylmonomeren fähig ist. Die Bildung des Copolymeren wurde durch Elementaranalyse der benzol-löslichen und -unlöslichen Fraktionen des erhaltenen Polymeren bestätigt. Gaschromatographisch wurde festgestellt, dass im vorliegenden System neben den Polymeren eine ziemlich grosse Menge 4-Phenyl-1,3-dioxan und eine kleine Menge Trioxan gebildet wurden. Etwa ein drittel der gesamt umgesetzten Monomermenge wurde zur Bildung des methanol-unlöslichen Polymeren verbraucht, ein drittel für 4-Phenyl-1,3-dioxan und das letzte drittel für Trioxan und unbekannte, bis jetzt noch nicht identifizierte Produkte. Die Bildung dieser cyclischen Produkte während der Copolymerisation kann durch eine "Back-biting"-reaction (oder intramolekulare Transacetalisierung) erklärt werden. Wie die Umsatzgeschwindigkeit jedes Monomeren im Copolymerisationssystem sowie die Zusammensetzung des erhaltenen methanol-unlöslichen Polymeren zeigt, ist die kationische Reaktivität von Trioxan ähnlich derjenigen von Styrol.

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Cyclopolymerization of Diallylamine Derivatives in Dimethyl Sulfoxide

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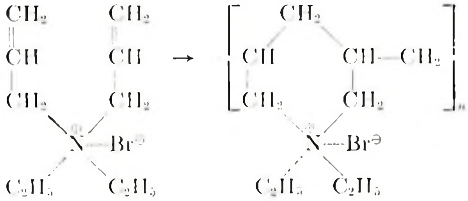
Synopsis

Diallyl quaternary ammonium chlorides, bromides and N-alkyldiallylamine hydrochlorides were polymerized with ammonium persulfate (APS) in dimethyl sulfoxide (DMSO). The dependences of yield and molecular weight of polymers on polymerization conditions were examined and quaternary ammonium chlorides were found to have better polymerizability than bromides. The poly(diallyl quaternary ammonium chlorides) obtained with APS-DMSO system are expected to have quite high molecular weights, as determined from the measurement of limiting viscosity numbers of the polymers in NaCl aqueous solution.

INTRODUCTION

In a series of studies of the radical-initiated polymerization of unsaturated quaternary ammonium salts,[1-9] Butler and his co-workers reported that diallyl quaternary ammonium salts polymerized in the presence of catalytic quantities of *tert*-butyl hydroperoxide (*t*-BHP) to form water-soluble, noncrosslinked polymers, and proposed intra-intermolecular polymerization mechanism for the polymerization of those containing two allyl groups, e.g., diallyldiethylammonium bromide:



In their work, dialkyldiallylammonium bromides and diallylamine hydrochloride as diallylamine derivatives were used, and polymerizations were carried out in aqueous phase by adding small amounts of water to those monomers and using *t*-BHP as catalyst. Attempts of polymerization in aqueous solutions with hydrogen peroxide, ammonium or potassium persulfate, benzoyl peroxide and di-*tert*-butyl peroxide as catalyst were reported to be unsuccessful.[1]

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In this paper, the ammonium persulfate (APS)-induced cyclopolymerization of some diallylamine derivatives in dimethyl sulfoxide (DMSO) is described and compared with the polymerization by the t-BHP–H_2O system. As monomers, not only quaternary ammonium bromides but also quaternary ammonium chlorides and *N*-alkyldiallylamine hydrochlorides were used. The dependence of degree of conversion and molecular weight of the polymers on polymerization condition is examined. Quaternary ammonium chlorides were found to polymerize more easily to give polymers having higher molecular weight than in the case of quaternary ammonium bromides.

As is well known, allyl compounds do not yield polymers of high molecular weight because of degradative chain transfer, and Butler et al. in their work estimated the degree of polymerization of poly(diallyldiethylammonium bromide) to be low (15–50),[8] but no physical determination such as limiting viscosity number measurement was made. In this paper, we carried out viscosity measurements on the polymers in 1*N* NaCl aqueous solution. From the limiting viscosity numbers thus determined, it is expected that some of the poly(diallyl quaternary ammonium chlorides) obtained in this work are polymers of quite high molecular weight. Molecular weight measurements on these polymers by the osmotic pressure method in methanol solution of LiCl was unsuccessful because of poor reproducibility.

EXPERIMENTAL

Materials

Preparation of Allyl Tertiary Amine. The preparation of dimethylallylamine described in the following will illustrate the general procedure. A portion of 40% aqueous solution of dimethylamine (90 g., 0.8 mole) was placed in a 500 ml. four-necked flask. Then 61.2 g. of allyl chloride (0.8 mole) and 80 g. of 50% aqueous sodium hydroxide (1.0 mole) were added dropwise separately from two dropping funnels with stirring in about $^1/_2$ hr. After the addition was completed, the mixture was heated for 4 hr. at 60°C. with stirring. After cooling, the oily layer was separated, dried overnight over sodium hydroxide pellets and fractionally distilled; yield 50.8 g.; b.p. 62–63°C.

Diethylallylamine (b.p. 109–111°C.), allylpiperidine (b.p. 84.5–85°C./90 mm.) and allylmorpholine (b.p. 90–90.5°C./80 mm.) were prepared from allyl chloride and diethylamine, piperidine, and morpholine, respectively.

Preparation of *N*-Alkyldiallylamine. The preparation of methyldiallylamine described below will illustrate the general procedure: 460 g. of allylchloride (6 mole) and 600 g. of 50% aqueous sodium hydroxide (7.5 mole) were added from two dropping funnels to 300 g. of 30% aqueous solution of methylamine (2.9 mole) with stirring in about an hour and heated for another 5 hr. at 70°C. After cooling, the oily layer was separated, dried over sodium hydroxide pellets and fractionally distilled; yield 150 g.; b.p. 109°C.

Ethyldiallylamine (b.p. 128–130°C.), isopropyldiallylamine (b.p. 146–148°C.), and *n*-butyldiallylamine (b.p. 63–64°C./22 mm.) were prepared from allyl chloride or allyl bromide and ethylamine, isopropylamine, and *n*-butylamine, respectively, by a method similar to that above.

Preparation of Diallyl Quaternary Ammonium Chloride. Diallyldimethylammonium chloride (DADMACl), diallyldiethylammonium chloride (DADEACl), diallylpiperidinium chloride (DAPipCl), and diallylmorpholinium chloride (DAMorCl) were prepared from allyl chloride and dimethylallylamine, diethylallylamine, allylpiperidine, and allylmorpholine with the following method, respectively. Analytical data are given in Table I.

TABLE I

		Found			Calculated		
Compound	Formula	C, %	H, %	N, %	C, %	H, %	N, %
DADMACl	$C_8H_{16}NCl$	59.20	10.49	8.61	59.43	9.98	8.66
DADEACl	$C_{10}H_{20}NCl$	62.96	10.43	7.57	63.30	10.63	7.38
DAPipCl	$C_{11}H_{20}NCl$	65.27	9.98	6.89	65.49	9.99	6.94
DAMorCl	$C_{10}H_{18}ONCl$	58.71	8.88	6.85	58.96	8.90	6.88

Allyl tertiaryamine, which was dried over sodium hydroxide pellets and distilled prior to use, was mixed with equivalent amount of freshly distilled allyl chloride (b.p. 44.5–45°C.) in dry acetone. The white crystalline solid of quaternary ammonium salt was gradually precipitated from the mixture at room temperature. The mixture was left for 2 days or more, and then the precipitated hygroscopic salt was collected quickly by filtration, washed several times with cold acetone, and dried in vacuum. The quaternization proceeds mildly except the case of the formation of DADMACl. These quaternary ammonium salts were recrystallized from hot acetone-absolute ethanol (10:1 by volume).

Preparation of Diallyl Quaternary Ammonium Bromide. Diallyldimethylammonium bromide (DADMABr), diallyldiethylammoniumbromide (DADEABr), diallylpiperidinium bromide (DAPipBr), and diallylmorpholinium bromide (DAMorBr) were prepared from allylbromide (b.p. 69.5–70°C.) and corresponding allyl tertiary amine by a method similar to that for the preparation of quaternary ammonium chloride. Analytical data are given in Table II.

TABLE II

		Found			Calculated		
Compound	Formula	C, %	H, %	N, %	C, %	H, %	N, %
DADMABr	$C_8H_{16}NBr$	46.27	7.69	6.77	46.61	7.82	6.80
DADEABr	$C_{10}H_{20}NBr$	51.14	8.82	5.45	51.29	8.61	5.98
DAPipBr	$C_{11}H_{20}NBr$	53.45	8.23	5.48	53.66	8.19	5.69
DAMorBr	$C_{10}H_{18}ONBr$	48.22	7.56	5.37	48.40	7.31	5.65

TABLE III

Compound	Formula	Found C, %	Found H, %	Found N, %	Calculated C, %	Calculated H, %	Calculated N, %
DAAHCl	$C_6H_{12}NCl$	54.09	9.19	10.22	53.93	9.05	10.48
DAMAHCl	$C_7H_{14}NCl$	56.69	9.48	9.04	56.94	9.56	9.49
DAEAHCl	$C_8H_{16}NCl$	59.16	10.03	8.59	59.43	9.98	8.66
DAPrAHCl	$C_9H_{18}NCl$	61.44	10.34	7.72	61.52	10.32	7.97
DABuAHCl	$C_{10}H_{20}NCl$	63.32	10.44	7.03	63.30	10.63	7.38

Generally, quaternizations by allyl bromide proceed more rapidly than with allyl chloride, and sometimes the reaction vessel must be cooled because of the heat of reaction. These quaternary ammonium bromides were also recrystallized from hot acetone–absolute ethanol (10:1 by volume).

Preparation of *N*-Alkyldiallylamine Hydrochloride. Diallylamine hydrochloride (DAAHCl), diallylmethylamine hydrochloride (DAMAHCl), diallylethylamine hydrochloride (DAEACHCl), diallylisopropylamine hydrochloride (DAPrAHCl), and diallyl-*n*-butylamine hydrochloride (DABuAHCl) were prepared from diallylamine or corresponding *N*-alkyldiallylamines and hydrogen chloride gas by the following method. Analytical data are given in Table III.

Dry hydrogen chloride gas (about mole equivalent to amine) was introduced into the ethereal solution of amine cooled in Dry Ice–acetone. The hygroscopic crystalline salt formed was collected by filtration, washed with ether and dried in vacuum. These salts were recrystallized from hot acetone or an ether–acetone mixture.

Solvent. Crown Zellerbach dimethyl sulfoxide (DMSO) was dried over sodium hydroxide pellets, then fractionally distilled under reduced pressure and the middle fraction was used.

Catalyst. Ammonium persulfate(APS) and *tert*-butyl hydroperoxide(*t*-BHP), the highest grade of commercial samples, were used without further purification.

Polymerization

The procedure was as follows. The solid monomer was weighed and dissolved in solvent. The solution was diluted with solvent in a volumetric flask. Then a definite amount was pipetted out from the solution, and transferred into a Pyrex test tube containing a definite amount of catalyst and frozen in a Dry Ice–acetone bath. After air in the test tube was replaced with nitrogen by repeated evacuation and introduction of N_2, the tube was sealed and put in the bath regulated at the desired temperature. After the frozen mass in the tube was melted and the catalyst was dissolved in the solution, the tube was left immersed in the bath at a constant temperature. After an appropriate time of polymerization the tube was opened, and the polymer was precipitated by pouring the solution into a large amount of acetone. When the polymer was not soluble in DMSO and the polymerizing solution had become hard mass, it was dissolved in a small amount of methanol, and the viscous solution obtained was poured into acetone. The precipitated polymer was collected by filtration washed repeatedly with acetone, and dried in vacuum at 50°C.

Viscosity Determination

The limiting viscosity numbers of all samples were determined in aqueous 1*N* NaCl solution at 30°C. by using an Ubbelohde type viscometer.

Infrared Spectra

The infrared spectra of the polymers were measured with a Shimadzu AR 275 IIs double-beam spectrometer (Shimadzu Manufacturing Co., Kyoto).

RESULTS AND DISCUSSION

Polymerization Induced with APS in DMSO

The results of the polymerization of diallyl quaternary ammonium chlorides are summarized in Table IV. Polymerizing solutions became turbid after about $^1/_2$ hr. polymerization and were not fluid after 1 hr. After about 50 hr., at the time of recovery of polymers, the polymerizing solutions have been converted entirely to hard masses. Generally, polymerization rates are fast, and polymers are obtained in high yields. The limiting viscosity numbers measured in 1*N* NaCl solution are high, and so the degree of polymerization is expected to be high compared with the reported value of poly(*n*-butylpyridinium bromide) in solution of added electrolytes in polar solvent.[10,11] The conversion and the limiting viscosity numbers of poly-DAMorCl were low, probably because the polymerizations were carried out at low monomer concentration due to the poor solubility in DMSO.

The polymerization data of diallyl quaternary ammonium bromides are shown in Table V. The polymerizing solutions became opaque and were not fluid at the end. Polymerizabilities of quaternary ammonium bromides are obviously inferior to those of quaternary ammonium chlorides of same class.

The polymerization data of *N*-alkyldiallylamine hydrochloride are shown in Table VI. The polymers of DAAHCl and DABuAHCl were soluble in DMSO, and polymerizations proceeded homogeneously until the end. The polymerizing solutions of DAMAHCl, DAEAHCl, or DAPrAHCl became opaque as polymerizations proceeded. All polymerizing solutions of this class were brown whereas those of quaternary ammonium salts were almost colorless or light yellow. Generally, the degree of conversion was low and limiting viscosity numbers were small.

TABLE IV
Polymerization of Quaternary Ammonium Chloride with APS in DMSO

Expt. no.	Compound	Monomer, g.	DMSO, g.	APS, mg.	Monomer concentration, %	Catalyst concentration, %	Time, hr.	Temp., °C.	Yield, g.	Conversion, %	$[\eta]$[a]
MCl-1	DADMACl	3.77	7.05	37.7	34.8	1.0	48	30	2.23	59.7	0.81
MCl-2	DADMACl	3.77	7.05	75.4	34.8	2.0	48	30	2.59	68.7	0.72
MCl-3	DADMACl	3.78	6.89	37.8	35.5	1.0	48	30	2.17	57.4	0.81
MCl-4	DADMACl	3.78	6.89	18.9	35.5	0.5	48	30	1.86	49.1	0.90
MCl-5	DADMACl	3.78	6.89	9.5	35.5	0.25	48	30	1.53	40.6	0.95
MCl-6	DADMACl	3.78	6.89	4.7	35.5	0.125	48	30	1.33	35.2	0.93
MCl-15	DADMACl	4.98	5.42	12.5	47.9	0.25	120	30	3.01	60.4	1.24
MCl-16	DADMACl	4.98	5.42	6.2	47.9	0.125	120	30	2.35	47.3	1.36
ECl-5	DADEACl	3.78	6.94	9.5	35.3	0.25	46	30	2.13	56.2	0.79
ECl-6	DADEACl	3.78	6.94	18.9	35.3	0.5	46	30	2.76	72.9	0.73
ECl-7	DADEACl	3.78	6.94	37.8	35.3	1.0	46	30	3.06	80.8	0.66
ECl-8	DADEACl	3.78	6.94	75.7	35.3	2.0	46	30	3.54	93.4	0.56
ECl-15	DADEACl	3.74	6.96	37.4	35.0	1.0	20	50	3.68	98.5	0.40
ECl-17[b]	DADEACl	3.92	6.89	39.2	36.3	1.0	96	30	—	—	0.60
ECl-18[b]	DADEACl	3.92	6.89	78.3	36.3	2.0	96	30	3.84	98.1	0.57
PipCl-3	DAPipCl	3.70	7.16	37.0	34.1	1.0	48	30	2.93	79.2	0.52
PipCl-4	DAPipCl	3.70	7.16	74.0	34.1	2.0	48	30	3.39	91.7	0.43
MorCl-1	DAMorCl	1.87	9.14	18.7	17.0	1.0	68	30	1.09	58.3	0.32
MorCl-2	DAMorCl	1.87	9.14	37.5	17.0	2.0	68	30	1.31	69.5	0.27
MorCl-4	DAMorCl	1.87	9.14	75.0	17.0	4.0	68	30	1.47	78.3	0.23

[a] Limiting viscosity number determined in 1N NaCl at 30°C. (c: g./100 ml.).

[b] Polymerization carried out in air.

TABLE V
Polymerization of Quaternary Ammonium Bromide with APS in DMSO

Expt. no.	Compound	Monomer, g.	DMSO, g.	APS, mg.	Monomer concentration, %	Catalyst concentration, %	Time, hr.	Temp., °C.	Yield, g.	Conversion, %	$[\eta]^a$
MBr-1	DADMABr	3.70	7.79	37.0	32.2	1.0	90	30	0.38	10.3	0.25
MBr-2	DADMABr	3.70	7.79	74.1	32.2	2.0	90	30	0.21	5.6	0.16
EBr-3	DADEABr	3.76	7.59	37.6	33.1	1.0	120	30	1.44	38.4	0.24
EBr-4	DADEABR	3.76	7.59	74.1	33.1	2.0	120	30	1.14	30.4	0.12
EBr-7	DADEABr	3.88	7.59	38.8	33.8	1.0	144	60	0.87	22.3	0.15
EBr-8	DADEABr	3.88	7.59	77.6	33.8	2.0	144	60	0.45	11.7	0.10
EBr-11	DADEABr	5.24	6.15	52.4	46.0	1.0	170	30	2.77	52.9	0.41
PipBr-3	DAPipBr	2.66	8.61	26.6	23.6	1.0	190	30	0.58	21.9	0.14
PipBr-4	DAPipBr	2.66	8.61	53.2	23.6	2.0	190	30	0.62	23.4	0.10
MorBr-1	DAMorBr	3.71	7.98	37.7	31.7	1.0	45	30	0.92	24.9	0.30
MorBr-2	DAMorBr	3.71	7.98	74.2	31.7	2.0	45	30	1.34	36.2	0.22
MorBr-3	DAMorBr	4.05	7.66	80.9	34.6	2.0	72	50	2.01	49.6	0.23
MorBr-4	DAMorBr	4.05	7.66	161.9	34.6	4.0	72	50	2.35	58.1	0.12

[a] Limiting viscosity number determined in 1N NaCl at 30°C. (c: g./100 ml.).

TABLE VI

Polymerization of *N*-Alkyldiallylamine Hydrochloride with APS in DMSO

Expt. no.	Compound	Monomer, g.	DMSO, g.	APS, mg.	Monomer concentration, %	Catalyst concentration, %	Time, hr.	Temp., °C.	Yield, g.	Conversion, %	$[\eta]^a$
HCl-1	DAAHCl	3.74	6.95	37.4	35.0	1.0	96	30	0.58	15.1	0.19
HCl-2	DAAHCl	3.74	6.95	74.9	35.0	2.0	96	30	1.00	26.7	0.18
MHCl-3	DAMAHCl	3.87	6.74	38.7	36.5	1.0	96	30	0.76	19.7	0.29
MHCl-4	DAMAHCl	3.87	6.74	77.4	36.5	2.0	96	30	1.08	27.8	0.29
EHCl-1	DAEAHCl	3.76	6.79	37.6	35.7	1.0	120	30	0.65	17.3	0.20
EHCl-2	DAEAHCl	3.76	6.79	75.2	35.7	2.0	120	30	0.98	26.1	0.20
PrHCl-1	DAPrAHCl	2.18	8.51	21.8	20.4	1.0	110	30	0.37	16.9	0.15
PrHCl-2	DAPrAHCl	2.18	8.51	43.6	20.4	2.0	110	30	0.67	30.8	0.15
PrHCl-3	DAPrHCl	2.18	8.51	87.2	20.4	4.0	110	30	0.58	26.9	0.10
BuHCl-1	DABuAHCl	3.82	6.58	38.2	36.8	1.0	120	30	0.95	24.9	0.18
BuHCl-2	DABuAHCl	3.82	6.58	76.4	36.8	2.0	120	30	1.14	29.9	0.18

[a] Limiting viscosity number determined in 1*N* NaCl at 30°C. (*c*: g./100 ml.).

Dependence of Degree of Conversion and Limiting Viscosity Number on Polymerization Conditions

Monomer Concentration. It is obvious that both the yields and the limiting viscosity numbers of polymers polymerized in higher monomer concentrations are higher, comparing MCl-15 and MCl-16 with MCl-5 and MCl-6, respectively, in Table IV or EBr-11 with EBr-3 in Table V. Monomer concentrations of 48% for DADMACl and 46% for DADEABr are saturated values of the monomers in DMSO at 30°C.

Catalyst Concentration Relative to Monomer. It is evident in the series of experiments from MCl-3 to MCl-6 or from ECl-5 to ECl-8 in Table IV, or also in the experiments of other compounds in Tables IV–VI that as catalyst concentration increases, degree of conversion increases and limiting viscosity number decreases. This is the general characteristics of radical-initiated polymerization. In the cases of DADMABr and DADEABr, however, anomalous behavior was observed; in both cases the conversions in the polymerization with 1% catalyst (based on monomer) were larger than those in the polymerization with 2% catalyst (compare MBr-1 with MBr-2, EBr-3 with EBr-4, and EBr-7 with EBr-8 in Table V).

Polymerization Time and Temperature. The polymerization rate of DADEACl is shown in Figure 1. Polymerization was carried out at a catalyst/monomer ratio of 1% at 30 and 50°C., and conversion was plotted against polymerization time. The conversion is almost 100% in about 20 hr. of polymerization at 50°C. The limiting viscosity numbers of the resulting polymers are independent of polymerization time and those of the polymers polymerized at 50°C. are all nearly equal to 0.4 and at 30°C. are 0.7.

From the results described above, it is concluded that higher yields are obtained at higher polymerization temperatures, but the degree of polymerization of the polymers is low. The conclusion is supported by this

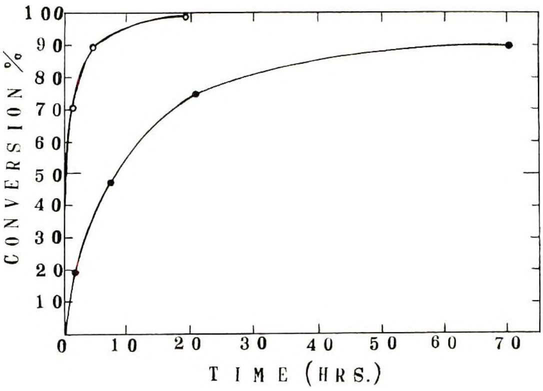

Fig. 1. Time–conversion curves of diallyldiethylammonium chloride (DADEACl) at (●) 30°C. and (○) 50°C. Monomer concentration in DMSO, 35%; catalyst concentration, 1.0% based on monomer.

result of polymerization of DAMorBr in Table V (compare MorBr-1 and MorBr-2 with MorBr-3 and MorBr-4). In the case of DADEABr, however, the result was contrary to this conclusion, and higher yield was obtained by the polymerization at lower temperature (compare EBr-3 and EBr-4 with EBr-7 and EBr-8).

Difference of Polymerizability Between Quaternary Ammonium Chloride and Bromide

Both the degree of conversion and the limiting viscosity numbers of poly(quaternary ammonium chlorides) in Table IV are obviously greater than those of poly(quaternary ammonium bromides) of same classes in Table V.

Rabinowitz and Marcus in their polymerization of vinyl phosphonium compounds observed the inferior polymerizability of tributylvinylphosphonium bromide in comparison with phosphonium chloride, and they attributed the cause to the ease of oxidation of bromide ion.[12]

The difference between polymerizabilities of quaternary ammonium chloride and bromide could also be explained by the same mechanism. Since the ease of oxidation of halide ions decreases in the order $I^- > Br^- > Cl^-$, bromide ion is probably oxidized more easily by catalytic persulfate to generate bromine, which can then act as an inhibitor.

$$R\cdot + Br^- \rightarrow R^- + Br\cdot$$
$$Br\cdot + Br\cdot \rightarrow Br_2$$
$$R\cdot + CH_2{=}CHCH_2X \rightarrow RCH_2{-}\dot{C}HCH_2X$$
$$RCH_2{-}\dot{C}HCH_2X + Br_2 \rightarrow Br\cdot + RCH_2CHBrCH_2X$$

Thus bromide ion inhibits the polymerization both by the consumption of starting radical and by the termination of growing chain.

Polymerization in H_2O

The results of the polymerization with *t*-BHP in water are shown in Table VII. Dependences of conversions and limiting viscosity numbers on polymerization conditions (catalyst concentration and temperature) are the same as observed with the APS–DMSO polymerization system. High conversions obtained in this case are probably due to the fact that the polymerization can be carried out at very high monomer concentration because of good solubility of monomers in H_2O. The difference between polymerizabilities of chloride and bromide is the same as observed with the APS–DMSO polymerization system. The molecular weights of the resulting polymers are lower than those with the APS–DMSO system (compare MCl-14 and EBr-9 in Table VII with MCl-1 in Table IV and EBr-11 in Table V).

Polymerization is found to be induced also with APS in H_2O, but polymerizability is not as great as with the APS–DMSO system (see EBr-10 in Table VII and EBr-11 in Table V).

TABLE VII
Polymerization with *tert*-Butyl Hydroperoxide in Water

Expt. no.	Compound	Monomer, g.	H_2O, g.	*t*-BHP, cc.[a]	Monomer concentration, %	Catalyst concentration, %	Time, hr.	Temp., °C.	Yield, g.	Conversion, %	[η][b]
MCl-11	DADMACl	3.35	1.94	0.1	64.8	1.7	45	60	3.24	95.7	0.20
MCl-12	DADMACl	3.35	1.94	0.05	64.8	0.85	45	60	3.31	98.8	0.30
MCl-13	DADMACl	3.35	1.94	0.1	64.8	1.7	240	30	2.42	72.1	0.45
MCl-14	DADMACl	3.35	1.94	0.05	64.8	0.85	240	30	2.76	82.5	0.59
EBr-5	DADEABr	7.24	4.13	0.2	63.5	1.54	140	60	6.18	85.5	0.11
EBr-6	DADEABr	7.24	4.13	0.4	63.5	3.08	140	60	6.04	83.5	0.08
EBr-9	DADEABr	7.86	3.60	0.2	68.7	1.42	170	30	1.80	22.9	0.26
EBr-10	DADEABr	7.86	3.60	52.4 mg.[c]	68.7	1.0	170	30	1.53	19.5	0.30

[a] *tert*-Butyl hydroperoxide (purity about 60%).

[b] Limiting viscosity number determined in 1*N* NaCl at 30°C. (*c*: g./100 ml.).

[c] Catalyst used was APS.

Properties of Polymers

The nitrogen analyses of the polymers are shown in Table VIII. The polymers of diallyl quaternary ammonium chlorides are obtained as white hygroscopic powders, which are soluble in water and methanol but insoluble in other organic solvents.

TABLE VIII
Nitrogen Analysis of the Polymers of Some Diallylamine Derivatives

Polymer	Nitrogen, % Found	Nitrogen, % Calculated
PDADMACl	8.82	8.66
PDADEACl	7.80	7.84
PDAPipCl	6.41	6.94
PDAMorCl	6.59	6.88
PDADMABr	6.24	6.80
PDADEABr	5.47	5.98
PDAPipBr	5.34	5.69
PDAMorBr	5.36	5.65
PDAAHCl	9.72	10.48
PDAMAHCl	8.99	9.49
PDAEAHCl	8.42	8.66
PDAPrAHCl	7.51	7.97
PDABuAHCl	7.32	7.38

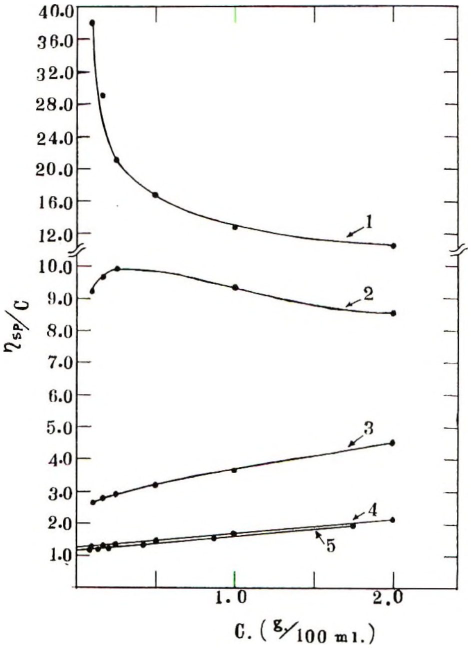

Fig. 2. Viscosity behavior of poly(diallyldimethylammonium chloride) (obtained by expt. MCl-15) in aqueous NaCl solutions at 30°C.: (*1*) pure water; (*2*) 0.01*N* NaCl; (*3*) 0.1*N* NaCl; (*4*) 1*N* NaCl; (*5*) 2*N* NaCl.

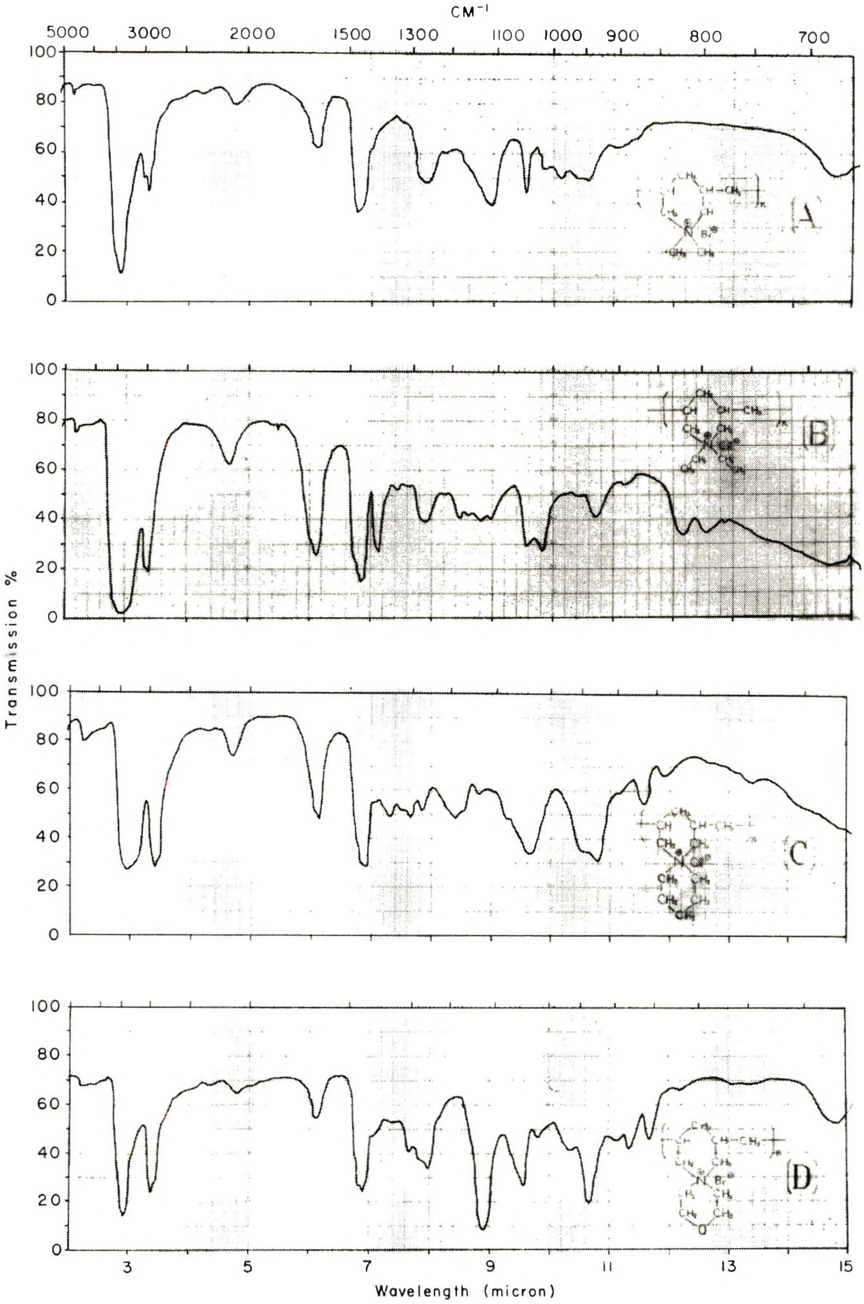

Fig. 3. See caption, p. 1964.

Polymers of the diallyl quaternary ammonium bromides are white powdery solids, and soluble in water. PDADEABr and PDAPipBr are soluble in methanol but insoluble in other organic solvents. PDADMABr and

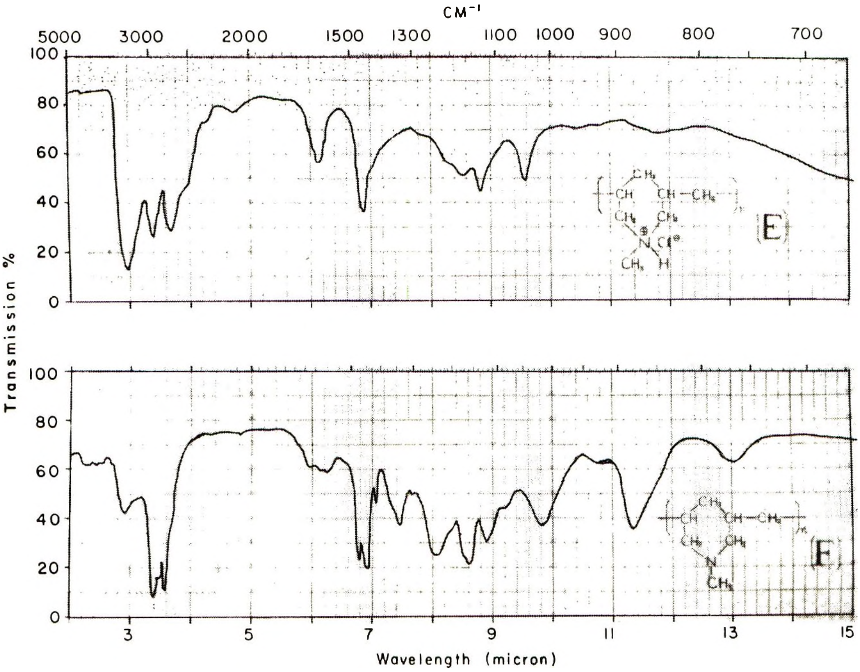

Fig. 3. Infrared spectra of the polymers of some diallylamine derivatives: (*A*) poly(diallyldimethylammonium bromide) (KBr disk); (*B*) poly(diallyldiethylammonium chloride) (film obtained from methanol solution); (*C*) poly(diallylpiperidinium chloride) (film); (*D*) poly(diallylmorpholinium bromide) (KBr disk); (*E*) poly(diallylmethylamine hydrochloride) (film); (*F*) polydiallylmethylamine (KBr disk).

PDAMorBr are soluble neither in methanol nor other organic solvents. These are not as hygroscopic as polymers of quaternary ammonium chlorides.

Polymers of *N*-alkyldiallylamine hydrochlorides are obtained as powdery or waxy masses, colored brown or yellow, soluble in water and methanol but insoluble in other organic solvents. PDAAHCl is very hygroscopic; however, the hygroscopic nature of its *N*-alkyl derivatives decreases as the number of carbon atoms of the *N*-alkyl substituent increase.

The viscosity curves (η_{sp}/c versus c) of PDADMACl in pure water and in NaCl aqueous solutions are shown in Figure 2. They exhibit the same characteristics as those observed very often with polyelectrolytes. Limiting viscosity numbers decrease with increasing added salt concentration and converge to a minimum at $2N$. The limiting viscosity numbers of all samples in Table IV–VII were determined in $1N$ NaCl aqueous solutions.

The infrared spectra of poly(diallyldimethylammonium bromide), poly(diallyldiethylammonium chloride), poly(diallylpiperidinium chloride), poly(diallylmorpholinium bromide), poly(diallylmethylamine hydrochloride), and polydiallylmethylamine are shown in Figure 3. The polydiallylmethylamine was obtained as water-insoluble precipitate by neutralization of poly(diallylmethylamine hydrochloride) by adding an aqueous solution of the latter to aqueous ammonia. These polymers, except the polydiallylmethylamine, are strongly hygroscopic and so the absorption bands of H_2O at 3.0, 4.7, and 6.1 μ could not be eliminated in these spectra. In the spectrum of polydiallylmethylamine, the absorption bands of H_2O are weak, and an absorption band for C═C stretching at 6.5 μ is not observed. The result that C═C double bond absorption bands are relatively weak in the spectra of these polymers, in conjunction with their solubility, supports the intramolecular–intermolecular cyclic polymerization mechanism.

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Résumé

Les chlorures d'ammonium diallyles quaternaires de bromure et de chlorhydrate de N-alcoyldiallylamine ont été polymérisés avec un persulfate d'ammonium (-APS) dans le diméthylsulfoxyde (DMSO). Les dépendances du rendement et du poids moléculaire des polymères en fonction des conditions de polymérisation ont été étudiées et les chlorures d'ammonium quaternaires ont été trouvés polymériser plus facilement que les bromures correspondants. Les chlorures de polydiallylammonium quaternaire obtenus avec le système APS–DMSO ont des poids moléculaires élevés ainsi qu'il résulte de la mesure de leur viscosité intrinsèque en solution aqueuse de chlorure de sodium.

Zusammenfassung

Quaternäre Diallylammoniumchloride und -bromide sowie N-Alkyldiallylaminhydrochloride wurden mit Ammoniumpersulfat (APS) in Dimethylsulfoxyd (DMSO) polymerisiert. Die Abhängigkeit von Polymerausbeute und -molekulargewicht von den Polymerisationsbedingungen wurde untersucht und es wurde festgestellt, dass quaternäre Ammoniumchloride besser polymerisierbar sind als Bromide. Die Messung der Grenzviskositätszahl der Polymeren in wässriger NaCl-Lösung lässt erwarten, dass die mit dem APS–DMSO-System erhaltenen quaternären Poly-diallylammoniumchloride Molekulargewichte von beträchtlicher Höhe besitzen.

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Effect of Reaction Medium on Copolymerization of Acrylonitrile and Methyl Acrylate

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Synopsis

The copolymerization of acrylonitrile (AN) with methyl acrylate (MEA) has been investigated in three types of polymerization, i.e., emulsion polymerization in water with a water-soluble initiator, suspension polymerization in water with an oil-soluble and water-insoluble initiator, and solution polymerization in dimethyl sulfoxide (DMSO). Monomer reactivity ratios at 50°C. for AN and MEA are found to be $r_1 = 0.78 \pm 0.02$, $r_2 = 1.04 \pm 0.02$ in emulsion polymerization; $r_1 = 1.02 \pm 0.02$, $r_2 = 0.70 \pm 0.02$ in DMSO solution polymerization; $r_1 = 0.75 \pm 0.05$, $r_2 = 1.54 \pm 0.05$ in suspension polymerization. The large differences found in the reactivity ratios may be attributed to the different ratio of concentration of two monomers in the loci of polymerization. Chemically, AN is somewhat more reactive than MEA as shown by the reactivity ratios in DMSO. In the case of the suspension polymerization, the MEA/AN ratio in the polymer particles in which polymerization occurs may be higher than that in the total phase. Experimental results of the emulsion polymerization show that the emulsion polymerization of AN occurs both in the particles and in water. In addition, rates of the copolymerization of AN with MEA have also been investigated.

INTRODUCTION

Only a few investigations have been conducted on the influence of the heterogeneity on the copolymer composition. Brandrup[1] examined the copolymerization of acrylonitrile (AN) with the short-chain acrylates and found a difference in the apparent reactivity ratios between solution polymerization and emulsion polymerization with a water-soluble initiator. He ascribed the difference to the adsorption of the monomers onto the precipitating particles. The major purpose of this work is to study the quantitative relationship between the copolymer composition and types of polymerization, and to obtain experimental evidence for the loci of emulsion polymerization of AN. In the present investigation, the reactivity ratios of copolymerization of AN and methyl acrylate (MEA) were studied in three types of polymerization: emulsion polymerization in water with a water-soluble initiator, suspension polymerization in water with an oil-soluble and water-insoluble initiator, and solution polymerization in dimethyl sulfoxide (DMSO).

EXPERIMENTAL

Materials

AN (supplied by Nitto Chemical Co.) was dried with calcium chloride and then twice distilled under nitrogen. A middle fraction having a refractive index 1.3914 at 20°C. was used; the absolute purity was ascertained by gas chromatography. MEA (supplied by Toa Chemical Co.) was purified by a similar method. A middle fraction having a refractive index 1.4040 at 20°C. was used; the absolute purity was ascertained by gas chromatography. Ammonium persulfate (APS) (supplied by Wako Chemical Co.) was purified by recrystallization from water, and then the solution, of which the concentration was determined iodometrically, was stored in a refrigerator to minimize thermal decomposition. *tert*-Butyl peroxypivalate (*t*-BPP)(supplied by Nihon Fats and Oils Co.) was used without further treatment. Azobisisobutyronitrile (AIBN)(supplied by Otsuka Chemical Co.) was recrystallized from anhydrous methanol. DMSO (supplied by Crown Zellerbach Co.) was dried by shaking with calcium oxide for at least 24 hr. The dried DMSO was twice distilled in a closed system under 3 mm. Hg pressure. The fraction boiling in the range 49.7 ± 0.2°C. was collected. This procedure gives a product whose refractive index was 1.4783 at 20°C. The absolute purity was ascertained by gas chromatography.

Copolymerization Technique

Copolymers for the determination of the monomer reactivity ratios were prepared in a sealed tube *in vacuo*. The polymerization was carried out in the dark under 10^{-4} mm. Hg pressure. Rates of copolymerization were obtained from the observed rates of volume contraction in the dilatometer which was used previously,[2] and the total mole fraction α consumed in the reaction is obtained from eq. (1) as expressed previously:[3]

$$\alpha = (1000/V)(Ah/[\mathrm{M}_1] + [\mathrm{M}_2])[(R + 1)/(\Delta_1 R + \Delta_2)] \qquad (1)$$

where h is the observed change in the height of the liquid in the dilatometer capillary at time t, A is the cross-sectional area of the capillary, V is the volume of the dilatometer bulb, $[\mathrm{M}_1]$ and $[\mathrm{M}_2]$ are the initial concentration of AN and MEA monomer, respectively, in the feed expressed in moles/liter. Δ_1 and Δ_2 are the changes in volume caused by complete polymerization of 1 mole of the respective monomer. R is the molar ratio of AN/MEA in the initial copolymer. The numerical values used here at 50°C. are: $V = 9.28$ cm.^{3}; $[\mathrm{M}_1] + [\mathrm{M}_2] = 0.50$ mole/l. in aqueous solution and 2.0 mole/l. in DMSO; $\Delta_1 = 14.21$ cm.^{3}/mole in aqueous solution and 20.52 cm.^{3}/mole in DMSO; $\Delta_2 = 9.78$ cm.^{3}/mole in aqueous solution and 19.05 cm.^{3}/mole in DMSO, $A = 3.967 \times 10^{-3}$ cm.^{2}. By inserting these values into eq. (1), eqs. (2) and (3) are obtained for DMSO solution and aqueous solution, respectively;

$$\alpha = [0.2137\,(R + 1)/(20.52R + 19.05)]h \tag{2}$$

$$\alpha = [0.8550\,(R + 1)/(14.21R + 9.78)]h \tag{3}$$

Initial rates of the copolymerization were obtained from tangents to the curve of α against t at low conversion.

The copolymer was recovered by precipitation twice in methanol from DMSO solution. The copolymer was filtered in a glass crucible and dried to constant weight in a vacuum oven kept at 50°C. under 1 mm. Hg for about 50 hr.

Several analytical methods were applied for the determination of the compositions of the copolymers. The compositions of AN–MEA copolymers containing over 10 mole-% MEA were determined from nitrogen contents obtained by the Kjeldahl method. Digestion was catalyzed by mixture of copper sulfate and anhydrous potassium sulfate, and 0.1% methyl red in 95% alcohol was used as an indicator. Analysis was conducted three times and its reproducibility was ascertained for the pure polyacrylonitrile. The copolymers with MEA contents less than 10 mole-% were analyzed by the infrared absorption method by using a mixture of AN–MEA (MEA 12.3 mole-%) copolymer and polyacrylonitrile as standards; here it was ascertained that the absorbance index of the copolymer follows Beer's law. The spectra were recorded with a Perkin-Elmer Model 125 double-beam spectrophotometer with a grating. As characteristic absorptions, the one at 2237 cm.$^{-1}$ for AN and another at 1730 cm.$^{-1}$ for MEA were chosen.

Furthermore, the nuclear magnetic resonance spectra (NMR) was used for the analysis of 10, 50, and 80 mole-% MEA in the monomer mixture in each solvent. The copolymers were all examined in dimethyl sulfoxide-d_6 (DMSO-d_6) in the temperature range 150–160°C. and at a concentration of 10%(w/v) copolymer. A fully equipped Varian A-60 spectrometer was employed. One typical spectrum is shown in Figure 1. The DMSO shown is present as an isotropic impurity of DMSO-d_6. DMSO-d_6 is very hygroscopic, and, hence, a resonance line due to H_2O is also observed. Other pertinent line assignments are given. The content of MEA in the copolymer is calculated from the ratio of a third of the area of the OCH_3 group to a half of the area of the CH_2 group.

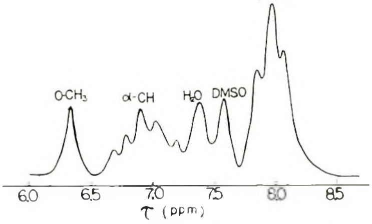

Fig. 1. NMR spectra for AN–MEA copolymers (feed MEA 10 mole-%) prepared from emulsion polymerization.

RESULTS AND DISCUSSION

Monomer Reactivity Ratios

In Table I are shown the copolymer compositions determined by the infrared absorption method in three types of polymerization: (*1*) emulsion

TABLE I
Acrylonitrile–Methyl Acrylate Feed and Copolymer Composition Determined by the Infrared Absorption Method

Polymerization system	MEA in the monomer feed M_2, mole-%	Monomer reacted, wt.-%	MEA in the copolymer m_2, mole-%
Emulsion[a]	1	3.60	1.23
"	2	3.93	2.50
"	5	4.15	6.10
Solution in DMSO[b]	1	5.03	0.96
"	2	3.90	1.90
"	5	4.11	4.80
Suspension[c]	1	3.5	1.40
"	2	5.3	2.92
"	5	3.2	6.90

[a] Copolymerization conditions: 0.50 mole/l. monomer, 0.005 mole/l. APS as initiator, 1 g./l. sodium lauryl sulfate as emulsifier at 50°C.

[b] Copolymerization conditions: 2.0 mole/l. monomer, 0.02 mole/l. AIBN as initiator at 50°C.

[c] Copolymerization conditions: 0.50 mole/l. monomer, 0.005 mole/l. *t*-BPP as initiator at 50°C.

TABLE II
Acrylonitrile–Methyl Acrylate Feed and Copolymer Composition Determined by the Kjeldahl Method

Polymerization system	MEA in the monomer feed M_2, mole-%	Monomer reacted, wt.-%	Nitrogen, %	MEA in the copolymer m_2, mole-%
Emulsion	10	4.66	21.49	12.3
"	20	4.56	17.54	23.7
"	50	4.62	8.57	56.2
"	80	3.69	3.34	80.9
"	90	3.64	1.54	90.9
Solution in DMSO	10	4.01	22.33	10.1
"	20	4.04	19.42	18.2
"	50	4.04	11.47	43.3
"	80	3.97	4.82	75.4
"	90	4.11	2.44	85.8
Suspension	10	3.5	21.4	12.6
"	20	4.1	17.9	24.6
"	50	3.9	8.08	58.3
"	80	4.7	2.77	84.0
"	90	9.0	1.15	93.1

TABLE III
Acrylonitrile–Methyl Acrylate Feed and Copolymer Composition Derived from the NMR Spectral Measurements

Polymerization system	MEA in the monomer feed M_2, mole-%	Monomer reacted, wt.-%	MEA in the copolymer m_2, mole-%
Emulsion	10	4.06	12.0
"	50	4.16	53.8
"	80	4.76	80.6
Solution in DMSO	10	3.90	9.44
"	50	4.85	38.8
"	80	6.02	75.1
Suspension	10	3.49	13.5
"	50	3.21	60.2
"	80	4.56	85.8

polymerization in aqueous solution with APS as initiator; *(2)* solution polymerization in DMSO solution with AIBN as initiator; *(3)* suspension polymerization in aqueous solution with *t*-BPP as initiator. In Tables II and III are shown the copolymer compositions determined by the Kjeldahl method and NMR spectral measurements, respectively. All polymerizations were carried out at 50°C. The concentration of MEA in the copolymer is plotted in Figure 2 against the mole per cent MEA in the monomer feed. There can be seen large differences between reactivity ratios in each type of the polymerization. All the data are plotted according to the method of Mayo and Lewis, as shown in Figure 3. The precision of the three analytical methods is obviously quite acceptable. The apparent reactivity ratios are listed in Table IV. This investigation may be the first one which treats the copolymerization reaction from the viewpoint of

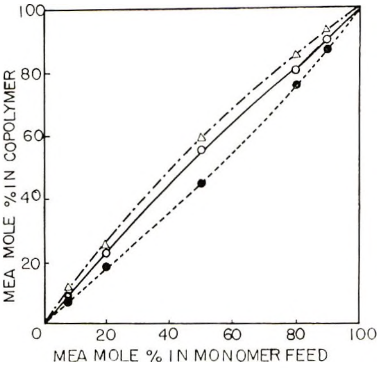

Fig. 2. Plot of MEA contents in the copolymer (m_2) vs. MEA in the monomer feed (M_2): (○) experimental points in the emulsion polymerization and (——) calculated for $r_1 = 0.78$ and $r_2 = 1.04$; (●) experimental points in DMSO and (- -) calculated for $r_1 = 1.02$ and $r_2 = 0.70$; (△) experimental points in suspension polymerization and (– · –) calculated for $r_1 = 0.75$ and $r_2 = 1.54$.

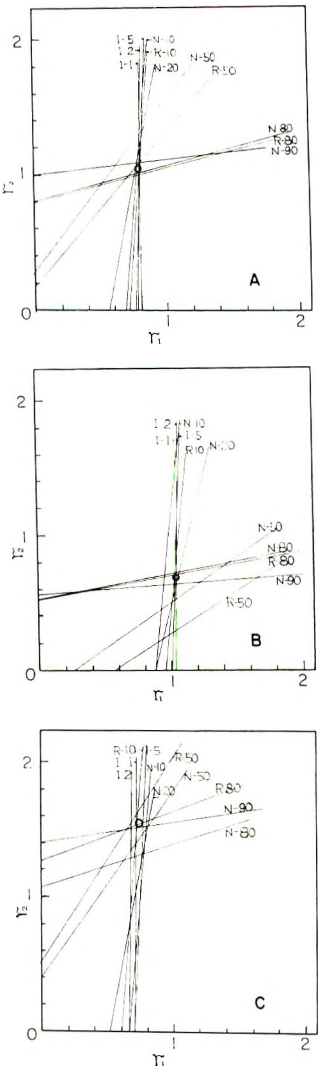

Fig. 3. Intersects for the copolymerization of AN and MEA for (*A*) emulsion polymerization in aqueous solution, (*B*) solution polymerization in DMSO solution, and (*C*) suspension polymerization in aqueous solution: (*I*) determined by the infrared absorption method; (*N*) determined by the Kjeldahl method; (*R*) derived from the NMR spectral measurements. The numerical values shown are MEA mole-% in the monomer feed.

the loci of polymerization. In the case of the solution polymerization, the polymerization occurs in a homogeneous system, and the difference of reactivity may be attributed to solely a chemical effect. In this case, AN is a little more reactive than MEA. From these reactivity ratios and the *Q* and *e* values for AN ($Q_1 = 0.60$, $e_1 = 1.2$), Price *Q* and *e* for MEA are calculated $Q_2 = 0.29$, $e_2 = 0.62$. In the case of the suspension polymerization, the loci of the polymerization are restricted to the polymer

TABLE IV
Copolymerization Parameters for AN and MEA in the Three Types of Polymerization at 50°C.

Polymerization type	r_1(AN)	r_2(MEA)	Q_2(MEA)	e_2(MEA)
Emulsion polymerization	0.78 ± 0.02	1.04 ± 0.02		
Solution polymerization in DMSO	1.02 ± 0.02	0.70 ± 0.02	0.29	0.62
Suspension polymerization	0.75 ± 0.05	1.54 ± 0.05		

particles since the initiator does not dissolve in water. It is reasonable to consider that the apparent increased reactivity of MEA compared with the case of the solution polymerization is attributed to the fact that MEA is more dissolved in the particles due to its smaller solubility in water. The MEA/AN ratio in the loci of polymerization to that in the total phase is calculated from Figure 2 and is shown in Figure 4. In the case of the emulsion polymerization, the apparent reactivity ratio of AN and MEA is found between that in the solution polymerization and the suspension polymerization. This may be caused by the fact that the loci of the emulsion polymerization exist both in the particles and in water. In other words, the experimental results obtained above may support that the emulsion polymerization occurs both in polymer particles and in water, which is in accord with other experimental results obtained previously.[4]

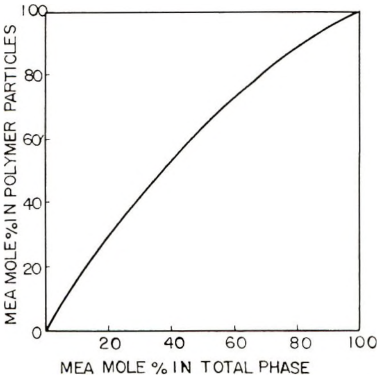

Fig. 4. MEA/AN ratio in the loci of polymerization vs. that in the total phase in suspension copolymerization.

Copolymerization Rate

The initial rates of copolymerization R_p at 50°C. for the three types of polymerization described above are shown in Figure 5. There can be seen a minimum at 1 mole-% MEA in the monomer feed in the emulsion poly-

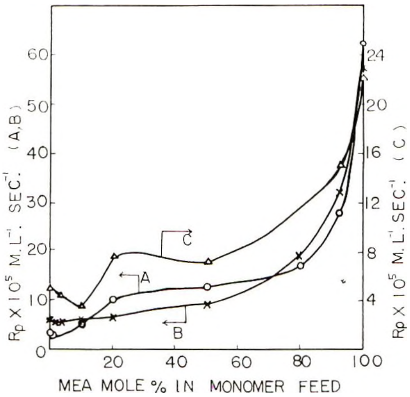

Fig. 5. Plot of initial rate of copolymerization R_p against MEA content in the monomer feed: (*A*) emulsion polymerization; (*B*) solution polymerization in DMSO; (*C*) suspension polymerization.

merization and at 1–2 mole-% MEA in the monomer feed in the solution polymerization. This difference may be attributed to the different apparent reactivity in the two cases. In the case of the suspension polymerization, there can be seen a large irregularity in the rate of copolymerization. The copolymers of 10 mole-% MEA and 50 mole-% MEA seem bulky, whereas that of 20 mole-% MEA is a finely dispersed particulate. The rate coincides with changes in appearance of the reaction mixture, but the reason can not be elucidated.

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Résumé

La copolymérisation de l'acrylonitrile (AN) avec l'acrylate de méthyle (MEA) a été étudiée dans trois types de polymérisation à savoir, la polymérisation en émulsion dans l'eau utilisant un initiateur soluble dans l'eau, la polymérisation en suspension dans l'eau utilisant un initiateur soluble dans la phase huileuse et insoluble dans l'eau, et la polymérisation en solution dans la diméthylsulfoxyde (DMSO). Les rapports de réactivité des monomères à 50°C pour AN et MEA ont été trouvés être $r_1 = 0.78 \pm 0.02$, $r_2 = 1.04 \pm 0.02$ pour la polymérisation en émulsion; $r_1 = 1.02 \pm 0.02$, $r_2 = 0.70 \pm 0.02$ dans DMSO et $r_1 = 0.75 \pm 0.05$, $r_2 = 1.54 \pm 0.05$ pour la polymérisation en suspension. Les grandes différences trouvées dans les rapports de réactivité peuvent être attribuées à des rapports différents de concentration des deux monomères dans les lieux de polymérisation mêmes. Chimiquement, l'acrylonitrile est quelque peu plus réactif que MEA ainsi qu'il résulte du rapport de réactivité dans le DMSO. Dans le cas de la polymérisation en suspension, le rapport MEA/AN dans les particules polymériques au sein desquelles la polymérisation se passe peut être plus élevé que dans la phase totale. Des résultats expérimentaux de la polymérisation en émulsion montraient que la polymérisation en émulsion de AN se passe à la fois dans les particules et dans l'eau. En outre, des vitesses de copolymérisation de AN avec MEA ont également été étudiées.

Zusammenfassung

Die Copolymerisation von Acrylnitril (AN) mit Methylacrylat (MEA) wurde in drei Polymerisationstypen untersucht, nämlich Emulsionspolymerisation in Wasser mit einem wasserlöslichen Starter, Suspensionspolymerisation in Wasser mit einem öllöslichen und wasser-unlöslichen Starter und Lösungspolymerisation in Dimethylsulfoxyd (DMSO). Die Monomereaktivitätsverhältnisse bei 50°C ergeben sich für AN und MEA zu $r_1 = 0{,}78 \pm 0{,}02$, $r_2 = 1{,}04 \pm 0{,}02$, bei der Emulsionspolymerisation, zu $r_1 = 1{,}02 \pm 0{,}02$, $r_2 = 0{,}70 \pm 0{,}02$ in DMSO und zu $r_1 = 0{,}75 \pm 0{,}05$, $r_2 = 1{,}54 \pm 0{,}05$ bei der Suspensionspolymerisation. Die bei den Reaktivitätsverhältnissen gefundenen grossen Unterschiede können auf das verschiedene Konzentrationsverhältnis der beiden Monomeren am Polymerisationsort zurückgeführt werden. Chemisch ist AN etwas reaktiver als MEA, wie das Reaktivitätsverhältnis in DMSO zeigt. Im Falle der Suspensionspolymerisation kann das Verhältnis MEA/AN in den Polymerteilchen, in welchen die Polymerisation stattfindet, höher als in der Gesamtphase sein. Die Versuchsergebnisse bei der Emulsionspolymerisation zeigen, dass die Emulsionspolymerisation von Acrylnitril sowohl in den Teilchen als auch in Wasser abläuft. Schliesslich wurde auch die Geschwindigkeit der Copolymerisation von AN mit MEA untersucht.

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Reactivity of Ester Groups on Insoluble Polymer Supports

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Synopsis

A study was made of the comparative rates of reaction of active ester functional groups (*p*-nitrophenyl and 2,4-dinitrophenyl esters) situated on three types of insoluble support polymers and on small, soluble analogs of the polymer molecules. The supports consisted of a styrene–divinylbenzene bead-type polymer (2% DVB), a styrene–divinylbenzene popcorn polymer (0.2% DVB), and a popcorn polymer with 2,3-dimethylbutadiene and substituted styrene units in the chain. *p*-Nitrophenyl benzoate and 2,4-dinitrophenyl *p*-isopropylbenzoate were used as soluble analogs. Rates of aminolysis by small molecules (2-aminoethanol and *n*-tetradecylamine) in pyridine and of solvolysis in alcohols catalyzed by both small (*N*-methylimidazole) and large (polyvinylimidazole) molecules were determined. With the small amines, finely divided particles of popcorn and bead type styrene polymers reacted at about the same rate, which was approximately $^1/_5$ the rate of reaction of the homogeneous analogs. With a high molecular weight reagent, polyvinylimidazole, the heterogeneous reactions were much slower and the popcorn polymer reacted faster than the bead polymer. In catalyzed solvolyses, the styrene popcorn derivative reacted faster in benzyl alcohol and slower in 1-hexanol than the dimethylbutadiene popcorn polymer derivatives.

INTRODUCTION

Two types of insoluble polymers have been used as supports in repetitive step synthetic work. One, a styrene bead polymer containing 2% divinylbenzene, has been used extensively in synthesizing polypeptides.* The active functional groups were introduced by substitution reactions on the preformed polymer. The other, a styrene based popcorn polymer containing 0.02–0.2% divinylbenzene, has been utilized in synthesizing oligonucleotide derivatives.[2] Active functional groups were introduced in this case by incorporating a substituted vinylbenzene in the copolymerization mixture with styrene and *p*-divinylbenzene.[3,4] These support polymers differ considerably in physical form as well as in the per cent divinylbenzene present. In addition, differences in the distribution of reactive functional groups through the polymers might be expected in view of the different methods employed to introduce these groups.

Since the rate of reaction of functional groups joined to the support is an important factor in determining the success of a synthesis on an insoluble

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* A review of this field, which has been developed by Merryfield and co-workers, is given in ref. 1.

polymer, we have prepared representative specimens of bead and popcorn polymers bearing the same active functional groups and have investigated the reactivity of the functional groups under identical conditions. It was of interest to see how the rate in the heterogeneous systems were related to the nature of the support polymer and how they compared to rates for soluble model compounds.

The reactions selected for study were aminolysis of a *p*-nitrophenyl ester by 2-aminoethanol or *n*-tetradecylamine in pyridine and solvolysis of a 2,4-dinitrophenyl ester in benzyl alcohol or 1-hexanol catalyzed by *N*-methylimidazole or poly-*N*-vinylimidazole. These reactions could be followed conveniently by the absorbance increase associated with liberation of *p*-nitrophenol or 2,4-dinitrophenol into solution. The bead polymer derivative was obtained by acetylating a commercially available styrene-divinylbenzene bead copolymer (200–400 mesh, 2% DVB, Dow Chemical Co.), oxidizing the acetyl derivative with hypobromite, and esterifying the resulting acid groups with *p*-nitrophenol or 2,4-dinitrophenol. The popcorn polymer was prepared by copolymerizing styrene (0.25 mole), *p*-vinylbenzoic acid (0.04 mole), and divinylbenzene (4.6×10^{-4} mole) as previously described[3] and then esterifying (via the acid chloride) the acid groups with the appropriate phenol. As soluble models for the ester portion of the polymer chains, 2,4-dinitrophenyl *p*-isopropyl benzoate and *p*-nitrophenyl benzoate were employed. For comparative purposes, an ester derivative of an insoluble support polymer with a structural backbone largely aliphatic in nature was also prepared and examined.

EXPERIMENTAL

Reagents

Liquid reagents and solvents were purified by distillation. The boiling points of the fractions collected were: 1-hexanol, 156°C., benzyl alcohol, 68°C./0.4 mm.; *N*-methylimidazole 69°C./3 mm.; 2-aminoethanol, 52.5–53°C./0.2–0.5 mm. Reagent-grade pyridine was distilled successively from *p*-toluenesulfonyl chloride and calcium hydride and stored over Linde molecular sieves. *n*-Tetradecylamine was recrystallized from acetonitrile; m.p. 37–38°C. Poly-*N*-vinylimidazole was washed thoroughly with ether and then dissolved in water, sealed in a cellulose dialysis bag, and dialyzed for 3 days in water; the polymer solution was then lyophilized and the resulting cake dried over phosphorus pentoxide at 60°C. for several hours. *p*-Vinylbenzoic acid[5] (m.p. 140–142°C.), *p*-nitrophenyl benzoate[6] (m.p. 143–144°C.), 2,4-dinitrophenyl *p*-isopropylbenzoate[7] (m.p. 116–117°C.), and 2,4-dinitrophenyl acetate[8] (m.p. 71–72°C.) were prepared by procedures described in the literature.

Carboxylated Styrene Bead Polymer

To a solution of 7.0 g. of aluminum chloride in 100 ml. of nitrobenzene was added 25.0 g. of styrene–divinylbenzene copolymer beads (200–400 mesh, 2% divinylbenzene, Lot 6075-42, Dow Chemical Company: purified as described by Merrifield[9]). The mixture was allowed to stand 10 min.; then 4.00 g. of acetyl chloride was added rapidly with stirring. Within seconds the reaction mixture thickened, and the temperature rose 10–15°C. Additional nitrobenzene was added (50 ml.) and the mixture was stirred 30 min. at room temperature, 90 min. at 70°C., and overnight at room temperature. The acetyl polymer ($\lambda = 5.96\ \mu$) was filtered from the solution, washed successively with nitrobenzene, dioxane, 1M hydrochloric acid, methanol, and ether, and then oxidized by addition, with stirring at 7°C., to a hypobromite solution (prepared by adding 50 g. of bromine slowly to 60 g. of potassium hydroxide in 90 ml. of water and 450 ml. of dioxane below 15°C.). After 5 hr. of stirring at 5°C. and standing overnight at room temperature, the polymer was filtered off and washed with dioxane, 1M sodium hydroxide, dioxane, methanol, and ether An infrared spectrum showed strong absorption attributable to the carboxylate anion (6.44 μ and 7.18 μ) and an absence of bands in the carbonyl range (5.6–6.0 μ). On the basis of the sodium chloride recovered from this reaction, 1.5 mmole of carboxyl groups was present per gram of polymer.

Dimethylbutadiene–Vinylbenzoic Acid Popcorn Copolymer

A mixture of 3.30 g. (22.3 mmole) of p-vinylbenzoic acid, 24.0 g. (292 mmole) of 2,3-dimethyl-1,3-butadiene, 0.07 g. (0.54 mmole) of p-divinylbenzene, and a few small pieces of growing 2,3-dimethyl-1,3-butadiene popcorn polymer[10] was warmed at 55°C. in a flask which had been purged with nitrogen and then evacuated. Within a few hours the presence of fresh popcorn polymer was apparent, and after 2 days the process was complete. The polymer was ground in a Waring Blendor with benzene and collected by filtration. The yield based on monomer weight was almost quantitative; therefore the polymer contained ~0.81 mmole of carboxyl groups per gram. The infrared spectrum showed a single band in the carbonyl region at 5.95 μ.

This polymer was insoluble, though it swelled somewhat, in pyridine, dimethylformamide, benzene, benzyl alcohol, and hexanol. On standing in air it slowly oxidized. After several days' exposure to air the polymer became tacky, and a band appeared in the infrared spectrum at 5.83 μ. Eventually the polymer degraded sufficiently to become soluble in common organic solvents. The polymer was stable, however, when stored under vacuum or as a suspension in benzene. It reacted readily with bromine in carbon tetrachloride, liberating hydrogen bromide, and it dissolved in concentrated sulfuric acid, giving a red-brown solution. On reaction with diazomethane in ether the carboxyl groups were converted quantitatively to carbomethoxyl groups.

Nitrophenyl and Dinitrophenyl Esters of the Insoluble Polymers

The carboxylated styrene polymers were converted to acid chlorides by heating in benzene with excess thionyl chloride for 5 hr. The polymers were collected by filtration, washed well with dry benzene, and stored in a vacuum desiccator over phosphorus pentoxide.

The dinitrophenyl ester of styrene–vinylbenzoic acid popcorn polymer was prepared by stirring 1.5 g. of the acid chloride polymer with 1.5 g. of 2,4-dinitrophenol in 25 ml. of dry pyridine for 3 hr. An infrared spectrum of the washed and dried polymer showed complete conversion to the ester ($\lambda = 5.72\ \mu$). A similar reaction with *p*-nitrophenol (12 hr.) afforded the *p*-nitrophenyl ester quantitatively ($\lambda = 5.75\ \mu$).

The dinitrophenyl ester of the carboxylated styrene bead polymer was prepared in the same way from 0.43 g. of the acid chloride polymer and 0.4 g. of 2,4-dinitrophenol in pyridine. The reaction in this case was essentially complete, though very weak absorption at 5.90–5.95 μ indicated ~3–5% of the carboxyl groups remained. For preparation of the *p*-nitrophenyl ester, 1.00 g. of the bead polymer in the carboxyl form was stirred with 1.00 g. of *p*-nitrophenyl trifluoroacetate and 0.50 g. of *p*-nitrophenol in 25 ml. of pyridine for 4.5 hr. At this stage a small portion of the polymer was removed and examined by infrared. The spectrum showed no acid (no bands at 5.79 or 5.90 μ for acid or at 6.44 and 7.18 μ for carboxylate anion); however, half of the carbonyl absorbance appeared at 5.75 μ, as expected for the desired ester, and the other half was split between 5.60 and 5.81 μ, indicative of a carboxylic acid anhydride. Accordingly, 2.0 ml. of triethylamine was added to the reaction mixture and the suspension was stirred for an additional 12 hr. An infrared spectrum of the resulting polymer showed complete conversion to the *p*-nitrophenyl ester ($\lambda = 5.75\ \mu$).

Since the dimethylbutadiene–vinylbenzoic acid popcorn polymer discolored in hot solutions of thionyl chloride, a very mild procedure was used for preparation of the ester of this polymer. Polymer in the acid from (1.5 g.) was stirred with 1.5 g. of 2,4-dinitrophenol and 1.5 g. of dicyclohexylcarbodiimide in 35 ml. of pyridine for 2 days; then the polymer was filtered off, washed, and dried. In addition to the usual washing solvents, acetic acid and ethanol were employed to remove precipitated dicyclohexylurea. An infrared spectrum showed complete conversion to the 2,4-dinitrophenyl ester ($\lambda = 5.72\ \mu$). That all dicyclohexylurea had been removed was shown by absence of absorption in the 5.95–6.05 μ region.

Kinetics

For rate measurements on polymer substrates, a suspension of 0.15–0.20 mg. of polymer particles in 1.00 ml. of solvent was prepared directly in a standard silica ultraviolet cell and stored for sufficient time in the thermostatted compartment of a Beckman Model DU spectrophotometer to allow the polymer to swell fully and thermal equilibrium to be established. The temperature was 25 ± 0.2°C. unless otherwise indicated. At zero time, 2.00 ml. of the amine solution, which had been brought to the same temperature as the polymer suspension, was added. The cell was agitated quickly and placed in the spectrophotometer. Appearance of *p*-nitrophenol was followed by the absorbance increase at 432 mμ. Formation of 2,4-dinitrophenol was similarly monitored at 410 mμ. Directly before an absorbance was read, the cell was agitated for 10 sec. and the polymer then allowed to settle for 10 sec. Infinity values, unless otherwise noted, were obtained by carrying the reactions to completion under the same reaction conditions. Visible spectra taken at the end of the reactions confirmed the fact that *p*-nitrophenol (or 2,4-dinitrophenol) was the absorbing species measured. Pseudo first-order rate constants (k_{obs}) were obtained from plots of $A_\infty - A$ versus time on semilogarithmic graph paper.

Infinity values for reactions of poly-*N*-vinylimidazole with the insoluble polymer substrates were not obtained directly since the reactions were quite slow. After the desired measurements had been made, *N*-methylimidazole was added to drive the reaction to completion. The infinity value was obtained from the absorbance of the resulting solution, corrected for the change in extinction coefficient of 2,4-dinitrophenol produced by *N*-methylimidazole in benzyl alcohol and the volume change accompanying addition of the methylimidazole solution. Reactions in 1-hexanol were driven to completion by warming the mixtures after the measurements at 25°C. had been made.

For reactions with *p*-nitrophenyl benzoate and 2,4-dinitrophenyl *p*-isopropyl benzoate, 3.00 ml. of a solution of the amine was added to an ultraviolet cell and brought to the desired temperature in the sample compartment of a Cary 14 spectrophotometer. At zero time, 0.025 ml. of stock solution of the ester ($2.58 \times 10^{-3}M$ *p*-nitrophenyl benzoate in dioxane or $6.77 \times 10^{-3}M$ 2,4-dinitrophenyl *p*-isopropylbenzoate in benzyl alcohol) was added, and the absorbance change was followed automatically at 410 mμ or 432 mμ. Reactions with 2,4-dinitrophenyl acetate were carried out in the same way, except that 0.1 ml. of $3.67 \times 10^{-3}M$ 2,4-dinitrophenyl acetate in benzyl alcohol was added to 2.9 ml. of a solution of the imidazole in benzyl alcohol. Rates of noncatalyzed solvolytic reactions in benzyl alcohol and 1-hexanol were negligibly small in all cases.

RESULTS AND DISCUSSION

Pyridine has been found to be a good solvent for synthetic work with styrene-based supports.[2-4] In Table I are collected pseudo first-order rate constants for reaction of the nitrophenyl esters derivatives of the popcorn and the bead polymers with solutions of 2-aminoethanol and *n*-tetradecylamine in pyridine. Data for *p*-nitrophenyl benzoate, a soluble model for the region of the polymers near the ester function, are also included. Three points of interest may be noted. (*1*) The appearance of *p*-nitrophenol follows first-order kinetics for the individual runs through more than 75% conversion for 2-aminoethanol and through 60–70% conversion for tetradecylamine. At higher conversions in the tetradecylamine reaction, the rate decreases below that predicted by the first-order rate equation. Accordingly, the bulk of the functional groups in the insoluble polymer appear to be equally accessible to these small molecules, though there may be some discrimination of sites by the larger of the amines, tetradecylamine. (*2*) The rates for the bead polymer and the popcorn polymer are about the same. This fact shows that the differences in physical form and divinylbenzene content for these polymers have very little effect on the rate of reaction of the adjoined functional groups with small molecules. (*3*) The rates of the heterogeneous reactions are about $^1/_5$ the rate of the homogeneous reaction of *p*-nitrophenyl benzoate. This result indicates that the polymer matrix has an influence on the effective rate of reaction of the ester groups joined to it.

TABLE I

Aminolysis of *p*-Nitrophenyl Esters in Pyridine[a]

	k_{obs}, min.$^{-1}$	
p-Nitrophenyl ester of:	2-Amino-ethanol	*n*-Tetra-decylamine
Carboxystyrene popcorn polymer	0.11	0.18
Carboxystyrene bead polymer	0.12	0.15
Benzoic acid[b]	0.60	0.92

[a] Reaction conditions: ~0.15 mg. of polymer particles (~30 pieces) in 3 ml. of pyridine 0.0223 *M* in amine at 25 ± 0.2°C.

[b] 2.07×10^{-5} *M*.

Additional experiments were carried out with *N*-substituted imidazoles in benzyl alcohol. Benzyl alcohol proved to be especially suitable for these reactions since it possesses both an OH group, which functions in a solvolytic reaction catalyzed by a tetriary amine, and an aromatic ring, which favors penetration and expansion of the support particles. Furthermore, it is a good solvent for poly-*N*-vinylimidazole, a high molecular weight amine useful for investigating reactivity of support derivatives with a high polymeric reagent. 2,4-Dinitrophenyl esters rather than *p*-nitrophenyl esters were used in these reactions since the rates of the catalyzed solvolysis of *p*-nitrophenyl esters in benzyl alcohol are inconveniently low. The soluble model ester employed in these studies was 2,4-dinitrophenyl *p*-isopropylbenzoate.

Rate data for reactions of *N*-methylimidazole are summarized in Table II. The results confirm the conclusions drawn from the aminolyses conducted in pyridine; namely, that the heterogeneous reactions are slower than the homogeneous reaction of a small model ester and that the bead polymer and the popcorn polymer derivatives react at about the same rate. In addition, the rate of reaction of the popcorn polymer was found to depend upon the state of subdivision. A single piece of polymer (0.2 mg.) suspended in 3 ml. of solution reacted at about $^2/_5$ the rate of the same amount of polymer which was divided into 30 pieces and at approximately $^1/_{10}$ the rate of an equal amount of ester in the soluble analog, 2,4-dinitrophenyl *p*-isopropylbenzoate.

TABLE II
Solvolysis of 2,4-Dinitrophenyl Esters in Benzyl Alcohol Catalyzed by 0.0265*M* *N*-Methylimidazole

	$10^3 \times k_{obs}$, min.$^{-1}$	
2,4-Dinitrophenyl ester of:	25°C.	45°C.
Carboxystyrene bead polymer[a]	3.8	7.8
Carboxystyrene popcorn polymer[b]	2.3	8.6
Carboxystyrene popcorn polymer[c]	—	3.5
p-Isopropylbenzoic acid[d]	9.15	33.6

[a] 0.15–0.2 mg. of 200–400 mesh particles; ~30 pieces.
[b] 0.15–0.2 mg. of N100 mesh particles; ~30 pieces.
[c] One particle, 0.2 mg.
[d] $5.6 \times 10^{-3}M$.

In syntheses with insoluble supports, cases may arise where it is desirable to carry out reactions between substituents on the support and high molecular weight reagents in solution. Certainly, if large polypeptides and polynucleotides are synthesized on insoluble supports, the problem of removing the polymeric products from the support particles will be encountered. As a test of the feasibility of utilizing supports in work with high polymeric, soluble materials, we investigated the rate of reaction of poly-*N*-vinylimidazole with suspensions of dinitrophenyl ester derivatives of the bead and popcorn polymers in benzyl alcohol. The poly-*N*-vinylimidazole had been dialyzed in water to insure absence of low molecular weight fragments. This system represents a stringent test, since the poly-*N*-vinylimidazole may bind to the surface of the partially hydrolyzed polymer particles thereby rendering diffusion through the particles difficult. In addition, the intrinsic reactivity of poly-*N*-vinylimidazole with a dinitrophenyl ester in solution in benzyl alcohol is considerably less than that of *N*-methyl-

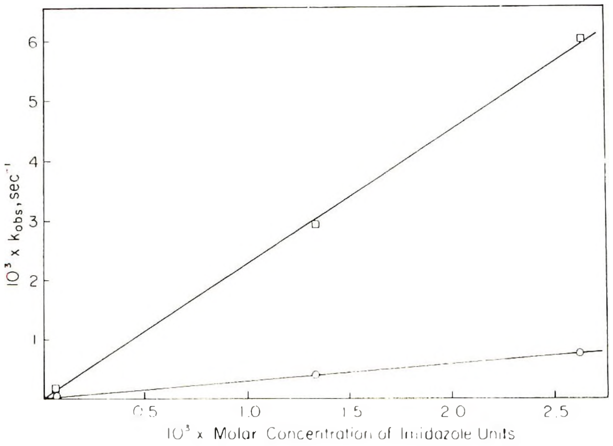

Fig. 1. Solvolysis of 2,4-dinitrophenyl acetate in benzyl alcohol catalyzed by (□) *N*-methylimidazole and (○) poly-*N*-vinylimidazole.

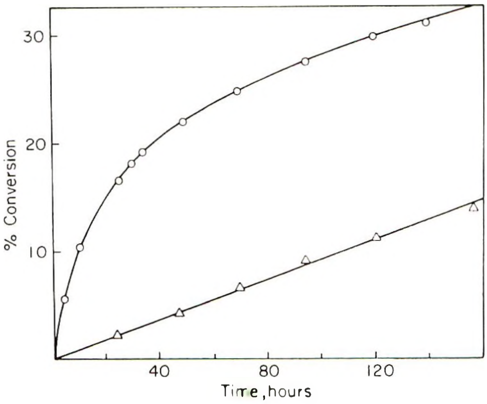

Fig. 2. Solvolysis of 2,4-dinitrophenyl esters of (O) carboxystyrene popcorn polymer and (△) carboxystyrene bead polymer in benzyl alcohol catalyzed by poly-*N*-vinylimidazole (0.0265*M* in imidazole units).

imidazole (see Fig. 1). As shown in Figure 2, poly-*N*-vinylimidazole does in fact react with the insoluble polymers. However, the reaction is not first-order with respect to the ester groups and the rate is much less than for *N*-methylimidazole. Indeed, the reactions do not go to completion within a reasonable time period. As measured with this polyamine, the functional groups on the popcorn polymer (0.2% DVB) are somewhat more accessible than those on the bead polymer (2% DVB). Accordingly, a popcorn type support may be preferable to a bead type support for synthetic work involving high molecular weight compounds. Difficulties may be expected with either type of support, however, when very large reagent molecules are used.

To see what effect a change in composition of the backbone of the support polymer might have on reactivity of pendant functional groups, we prepared a popcorn copolymer of 2,3-dimethyl-1,4-butadiene, *p*-vinylbenzoic acid, and *p*-divinylbenzene. Data for *N*-methylimidazole-catalyzed solvolysis of the 2,4-dinitrophenyl ester derivative of this polymer and the corresponding derivative of the styrene popcorn polymer are presented in Figure 3. Three differences in the reactions of the styrene and the dimethylbutadiene based polymers were found. (*1*) The dimethylbutadiene polymer reacts more slowly than the styrene polymer in benzyl alcohol. (*2*) In contrast to the case for the styrene polymer, plots of the log of the absorbance increase at 410 mμ versus time for reaction of the dimethylbutadiene polymer deviate markedly from a straight line above 30% conversion, suggesting that the ester groups in the polymer are not equally disposed for reaction with *N*-methylimidazole. (*3*) The two polymers respond differently to a change in solvent from benzyl alcohol to 1-hexanol. As shown in Figure 3, the rates of reaction of the ester groups in the dimethylbutadiene polymer are about the same in the two solvents whereas the ester groups on the styrene polymer react considerably more rapidly

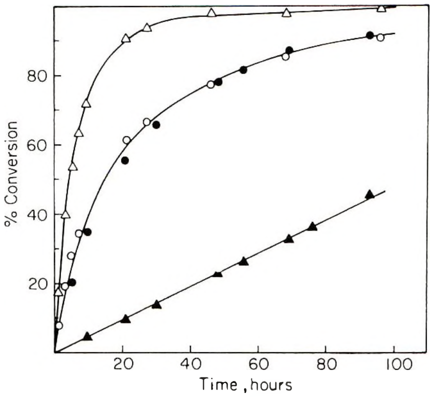

Fig. 3. Solvolysis of 2,4-dinitrophenyl esters catalyzed by 0.0265*M* *N*-methylimidazole: (△) styrene popcorn polymer derivative, in benzyl alcohol; (○) dimethylbutadiene popcorn derivative, in benzyl alcohol; (▲) styrene popcorn derivative, in 1-hexanol; (●) dimethylbutadiene popcorn derivative, in 1-hexanol.

in benzyl alcohol than in 1-hexanol. For comparison, k_{obs} for solvolysis of 2,4-dinitrophenyl *p*-isopropylbenzoate in the presence of 0.0265*M* *N*-methylimidazole in benzyl alcohol and in 1-hexanol at 25°C. is 0.009 and 0.016 min.$^{-1}$, respectively. The results with the polymer substrates accord with the concept that the styrene polymer, which is preponderantly aromatic in character, is penetrated more effectively by the aromatic solvent (benzyl alcohol) than by the aliphatic solvent (1-hexanol). The differential in penetration of the copolymer derivative of dimethylbutadiene and *p*-vinylbenzoic acid by the two solvents seems to be much less.

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Résumé

Une étude a été effectuée concernant les vitesses de réaction comparatives des groupes fonctionnels esters (*p*-nitrophényle et 2.4-dinitrophényle) situés sur trois types de polymères supports insolubles et sur des petites molécules solubles analogues des polymères. Les supports étaient des perles polymériques de styrène divinylbenzène à 2% de DVB, des perles gonflées de styrène–divinylbenzène à 0.2% de DVB et un polymère gonflé de 2,3-diméthylbutadiène et d'unités styréniques substituées dans la chaîne. Les benzoates de *para*-nitrophényle et l'isopropylbenzoaté de 2.4-dinitrophényle ont été utilisées comme analogues solubles. Les vitesses d'aminolyse par les petites molécules (les 2-aminoéthanol et *n*-tétradécylamine) dans la pyridine et la vitesse de solvolyse dans les alcools catalysée à la fois par le *m*-méthylimidazole et le polyvinylimidazole ont été déterminées. Avec les petites amines, les particules finement divisées des perles de polymères styréniques réagissaient environ à la même vitesse, c'est-à-dire environ 1.5 de la vitesse des réactions des analogues homogènes. Avec un réactif de poids moléculaire élevé le polyvinylimidazole, les réactions hétérogènes étaient beaucoup plus lentes et le polymère gonflé réagissait plus rapidement que le polymère en perle. Pour les solvolyses catalysées, les dérivés styréniques gonflés réagissaient plus rapidement dans l'alcool benzylique et plus lentement dans l'hexanol-1 que le polymère gonflé de diméthyl butadiène.

Zusammenfassung

Eine vergleichende Untersuchung der Reaktionsgeschwindigkeit funktioneller Gruppen aktiver Ester (*p*-Nitrophenyl- und 2,4-Dinitrophenylester) an drei Typen unlöslicher Trägerpolymerer und an einem kleinen, löslichen Analogon der Polymermoleküle wurde durchgeführt. Die Trägermaterialien bestanden aus einem Styrol-Divinylbenzolpolymeren vom Perltyp (2% DVB), einem Styrol–Divinylbenzolpopcornpolymeren (0,2% DVB) und einem Popcornpolymeren mit 2,3-Dimethylbutadien- und substituierten Styrolbausteinen in der Kette. Als lösliche Analoga wurden *p*-Nitrophenylbenzoat und 2,4-Dinitrophenyl-*p*-isopropylbenzoat verwendet. Die Geschwindigkeit der Aminolyse durch kleine Moleküle (2-Aminoäthanol und *n*-Tetradecylamin) in Pyridin und der Solvolyse in Alkoholen bei Katalyse mit kleinen (*N*-Methylimidazol) und grossen (Polyvinylimidazol) Molekülen wurde bestimmt. Mit den kleinen Aminen reagierten fein verteilte Popcornteilchen und Styrolpolymere vom Perltyp mit etwa der gleichen Geschwindigkeit und zwar etwa mit 1/5 der Geschwindigkeit der Reaktion der homogenen Analoga. Mit einem hochmolekularen Reagens, Polyvinylimidazol, waren die heterogenen Reaktionen viel langsamer und das Popcornpolymere reagierte rascher als das Perlpolymere. Bei der katalysierten Solvolyse reagierte das Popcornstyrolderivat in Benzylalkohol rascher und in 1-Hexanol langsamer als die Popcorndimethylbutadienpolymerderivate.

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Synthesis of 5(6)-Vinylbenzimidazole and of 2-Vinylbenzimidazole

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Synopsis

The syntheses of 2- and 5(6)-vinylbenzimidazole are described. These compounds were characterized by appropriate chemical reactions and physical properties. Incidental to this work, 3,4-diaminostyrene was also prepared.

Introduction

Of the four possible isomers of vinylbenzimidazole only *N*-vinylbenzimidazole has been well characterized.[1] 2-Vinylbenzimidazole has been reported in the patent literature but was not well characterized.[2,3] The 4(7)- and 5(6)-vinylbenzimidazoles have not been reported.

2-Vinylbenzimidazole has been prepared by the spontaneous dehydrohalogenation of 2-β-chloroethylbenzimidazole in a moist atmosphere and characterized by its melting point.[2] In another report,[3] the same compound was prepared by the pyrolysis of α- or β-acetoxyethylbenzimidazole; the product is described as an oil which did not crystallize. Bachman et al.[4] reported attempts to prepare 2-vinylbenzimidazole by conventional dehydrohalogenation, dehydration, and pyrolysis of the appropriate derivatives of 2-ethylbenzimidazole. These procedures at best led to poly-2-vinylbenzimidazole without isolation of the monomer.

The synthesis described here entails the oxidative condensation of acrolein and *o*-phenylenediamine catalyzed by cupric acetate according to the general procedure described by Weidenhagen.[5] The monomer, while produced in low yields, is stable and may be purified by sublimation or recrystallization from benzene. It is characterized by its physical properties.

In the preparation of 5(6)-vinylbenzimidazole, two routes were investigated (Fig. 1). The six-step sequence ending in the dehydrochlorination of 5(6)-β-chloroethylbenzimidazole gave the desired vinylbenzimidazole and its polymer. Nitration of (*p*-formamidophenyl)ethyl formate was accomplished at −30°C. At higher temperatures the dinitro derivative was the predominant product. The protective formyl group was not removed in

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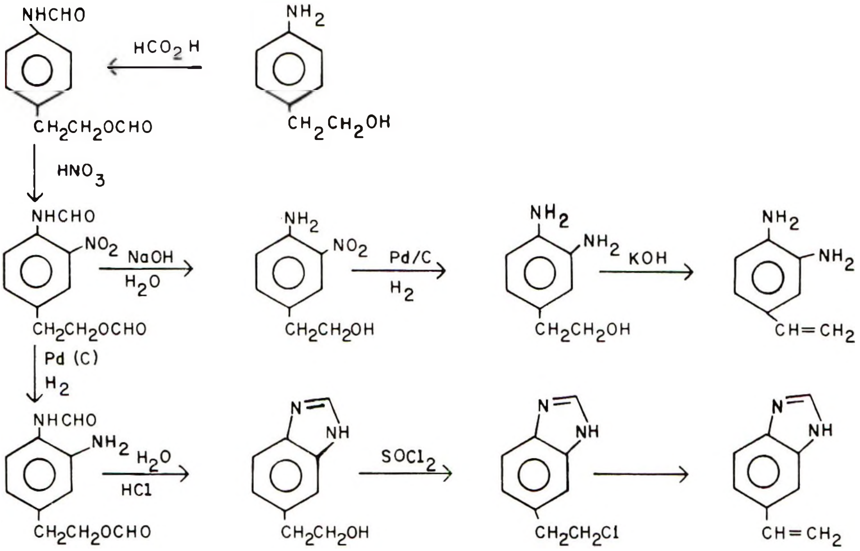

Fig. 1. Synthesis of 5 (or 6)-vinylbenzimidazole.

the next reaction because it serves to stabilize the sensitive diamine and is essential to the condensation which forms the heterocyclic ring. The last step in this sequence of reactions, dehydrochlorination, is not reproducible and gives yields of 0–67%. The alternative sequence ending in the condensation of 3,4-diaminostyrene with formic acid gave only polymer under the conditions investigated.

As proof of structure, the vinyl compound was oxidized to the known 5(6)-carboxylic acid derivative. Ozonolysis of the olefin gave formaldehyde, which was identified as the dimedone derivative. 5(6)-Vinylbenzimidazole was further characterized by its infrared spectrum, elemental analysis, and melting point.

The properties of poly-5(6)-vinylbenzimidazole and its catalytic effect on the hydrolyses of active esters is reported elsewhere.[6,7]

Melting points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Lab., Woodside, N. J., and Alfred A. Bernhardt, Mulheim (Ruhr) Germany.

Experimental

2-Vinylbenzimidazole. *o*-Phenylenediamine dihydrochloride (18.3 g., 0.1 mole) and cupric acetate (40 g., 0.2 mole) were dissolved in 500 ml. of water. Acrolein (5 g., 0.1 mole) in 50 ml. of methanol was added slowly to this solution with stirring. A brown precipitate was formed immediately. After 2 hr. of mixing, the precipitate was collected and suspended in hot water. The slurry was saturated with hydrogen sulfide and allowed to stand overnight. The cuprous sulfide was filtered and the filtrate, after neutralization, was extracted three times with equal volumes of ether. After drying, the ether was removed and the solid was recrystallized from benzene, 0.2 g. (2%), m.p. 187–189°C. 2-Vinylbenzimidazole sublimes at 120°C./0.1 mm. The infrared spectrum (KBr) showed vinyl absorptions at 930 and 980 cm.$^{-1}$. The proton NMR spectrum in dimethyl sulfoxide showed bands at 3.1 τ (quartet), 4.3 τ (doublet), and 3.7 τ (doublet).

ANAL. Calcd. for $C_9H_8N_2$: C, 75.0%; H, 5.6%; N, 19.4%. Found: C, 75.2%; H, 5.7%; N, 19.4%.

β-(4-Foramidophenyl)ethyl Formate. Recrystallized (ethanol) *p*-aminophenethanol (13.8 g., 0.1 mole) was dissolved in 250 ml. of 80% formic acid and the solution was refluxed for 30 min. The water and formic acid were then removed under reduced pressure. The viscous residue crystallized after several hours. The product was recrystallized from a chloroform–carbon tetrachloride solution, giving 13.7 g. (70%), m.p. 78.5–79°C.

ANAL. Calcd. for $C_{10}H_{11}NO_3$: C, 62.15%; H, 5.73%; N, 7.24%. Found: C, 61.94%; H, 5.74%; N, 7.50%.

β-(3-Nitro-4-formamidophenyl)ethyl Formate. The above compound (11.9 g., 0.061 mole) was nitrated in 100 ml. of fuming nitric acid (d = 1.5 g./cc.) by adding small portions of the solid to the acid over a period of 60 min., at a temperature maintained between −30 and −20°C. by partial immersion in a Dry Ice–acetone bath. The solution was kept at this temperature for an additional 30 min., and then poured onto ten times its volume of ice. The precipitate was filtered and washed with water until acid-free. The product was recrystallized from ethanol, giving 7.7 g. (56%) of long, yellow needles, m.p. 118–119°C.

ANAL. Calcd. for $C_{10}H_{10}N_2O_5$: C, 50.40%; H, 4.22%; N, 11.7%. Found: C, 50.36%; H, 4.20% N, 11.71%.

β-(3-Amino-4-formamidophenyl)ethyl Formate. The above compound (12 g., 0.05 mole) was partially dissolved in 200 ml. of dioxane-ethanol (50:50) and 0.5 g. of 10% palladium on charcoal was cautiously added to the mixture in a Parr hydrogenator. The slurry was degassed and placed under 41 psi of hydrogen. After shaking overnight the pressure was constant at 27 psi (calc. $\Delta P = 0.05 \times 3 \times 85 = 13$ psi). The catalyst was removed by filtration and the solvent was removed in a flash evaporator. The product may be recrystallized from methanol, m.p. 127–128°C., but was usually reacted further without additional purification.

ANAL. Calcd. for $C_{10}H_{12}N_2O_3$: C, 57.7%; H, 5.79%; N, 13.46%; Found: C, 57.78%; H, 5.78%; N, 13.49%.

5(6)-(β-Hydroxyethyl)benzimidazole. This compound was prepared by the intramolecular condensation of the aminoformate. The crude product from this reaction was dissolved in 100 ml. of water and refluxed with stirring for 1.5 hr., then treated with charcoal. After filtration the solution was neutralized with sodium bicarbonate. The product precipitated and was recrystallized from water to yield 5.6 g. of the desired compound (63% based on β-(3-nitro-4-formamidophenyl)ethyl formate), m.p. 140–142°C.

Anal. Calcd. for $C_9H_{10}N_2O$: C, 66.65%; H, 6.21%; N, 17.27%. Found: C, 66.47%; H, 6.18%; N, 17.39%.

5(6)-(β-Chloroethyl)benzimidazole. The above compound (16.2 g., 0.1 mole) was added in small portions to 100 ml. of thionyl chloride at 0°C. After the solid had completely dissolved, the mixture was heated for 30 min. on a water bath which resulted in the formation of a white precipitate. The thionyl chloride was removed *in vacuo*, and ice water was carefully added. The product, after removal by filtration, recrystallization from water, and decolorization with charcoal, was obtained in 51% yield, m.p. 126–128°C.

Anal. Calcd. for $C_9H_9N_2Cl$: C, 59.69%; H, 5.02%; N, 15.52%; Cl, 19.63%. Found: C, 60.01%; H, 5.27%; N, 15.36%; Cl, 19.51%.

5(6)-Vinylbenzimidazole. Potassium (2.6 g., 0.065 g.-atom) was dissolved in 100 ml. of *tert*-butanol. After cooling to 30°C., the above compound (3.6 g., 0.02 mole) was added with stirring. The solution gradually became turbid during the reaction time of 15 hr. The precipitated potassium chloride was removed by centrifugation, the solution was neutralized with acetic acid, and the potassium acetate which formed was removed by centrifugation. The *tert*-butanol was removed *in vacuo* at 30–35°C. The residue was extracted with boiling, anhydrous ether, leaving behind insoluble poly-5(6)-vinylbenzimidazole. The solution was filtered and the ether was allowed to evaporate. The remaining oil crystallized after several days at room temperature, 1.9 g. (67%) m.p. 115–116°C.

Anal. Calcd. for $C_9H_8N_2$: C, 74.91%; H, 5.59%; N, 19.43%. Found: C, 74.91%; H, 5.76%; N, 19.57%.

The infrared spectrum (Nujol) showed vinyl absorptions at 910 and 990 cm.$^{-1}$. Bromine and potassium permanganate solutions were decolorized by 5(6)-vinylbenzimidazole.

3-Nitro-4-aminophenethanol. The reaction product from 50 g., from β-(4-formamidophenyl)-ethyl formate and 300 ml. of red, fuming nitric acid was washed with water until neutral and then was added with stirring to a 10% aqueous sodium hydroxide solution. After standing for 15 hr. at room temperature the orange precipitate was collected and dried. The product was recrystallized from toluene to yield 20 g., 42.5% overall yield, of the desired product, m.p. 86–88°C. (lit.[8] m.p., 85–87°C.).

3,4-Diaminophenethanol. The above compound (16 g., 0.088 mole) was dissolved in 200 ml. of absolute ethanol to which was added 200–300 mg. of Pd/C. The solution was placed under 36 psi of hydrogen in a Parr hydrogenator. After 16 hr. at room temperature the pressure had dropped to 14 psi (calc. $\Delta P = 0.088 \times 3 \times 85 = 22$ psi). The catalyst was filtered from the solution and the ethanol was evaporated *in vacuo*. The crude product, which discolors rapidly on standing, was recrystallized from benzene to yield 6.5 g. (49%) of the desired product as a pale yellow solid, m.p. 93–94.5°C.

ANAL. Calcd. for $C_8H_{12}N_2O$: C, 63.1%; H, 8.0%; N, 18.4%. Found: C, 63.1%; H, 8.3%; N, 18.3%.

3,4-Diaminostyrene. In an apparatus suitable for the distillation of solids, the above compound (3 g., 0.02 mole) was mixed with 2 g. of potassium hydroxide pellets. The system was evacuated and heated slowly in an air bath. Product distilled at 180–200°C. /0.4 mm. Hg and crystallized in the receiver. After several recrystallizations from hexane, 0.74 g. (28%) of white plates were obtained, m.p. 53–54°C. The same reaction on a larger scale gave a lower yield.

ANAL. Calcd. for $C_8H_{10}N_2$: C, 71.6%; H, 7.5%. Found: C, 71.6%; H, 7.6%.

The infrared spectrum (KBr) contained vinyl absorptions at 905 and 990 cm.$^{-1}$ and the absorption characteristic of 1,2,4-phenyl substitution at 828 and 880 cm.$^{-1}$.

Attempted Ring Closure of Diaminostyrene. The above compound (1.3 mg., 10^{-3} mole) was combined with 88% formic acid (0.1 ml., about 1.5×10^{-3} mole) and one drop of concentrated hydrochloric acid. This mixture was refluxed in 20 ml. of water for 30 min. The solution, after cooling, was neutralized with ammonium hydroxide. The precipitate which formed was collected and dried and proved to be poly-5(6)-vinylbenzimidazole from which no monomer could be isolated by chloroform or ether extraction.

Ozonolysis and Oxidation of 5(6)-Vinylbenzimidazole. The monomer (0.43 g., 0.003 mole) was dissolved in 30 ml. of ethyl acetate and an oxygen stream containing 3% ozone was bubbled through the solution. After 30 min. the ozonide precipitated. The ethyl acetate was evaporated *in vacuo*, and 10 ml. of water was slowly added to the residue. The formaldehyde was steam-distilled and isolated as the dimedone derivative. The product had the same melting point, 191°C., and identical infrared spectrum as an authentic sample of formaldehyde dimedone. The melting point of a mixture of prepared and authentic samples was 191°C. To the undistilled aqueous solution was added 10 ml. of acetic acid to dissolve the product. The solvent was removed and the residue recrystallized from water, m.p. 333–336°C. (dec.). The infrared spectrum of the product was identical to 5(6)-carboxybenzimidazole prepared by the condensation of 3,4-diaminobenzoic acid and formic acid[9] or by the oxidation of 5(6)-vinylbenzimidazole with $KMnO_4$.

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Résumé

Les synthèses de 2- et 5(6)-vinylbenzimidazole sont décrites. Ces composés ont été caractérisés par des réactions chimiques appropriées et par leurs propriétés physiques. A l'occasion de ce travail, le 3,4-diaminostyrène a également été préparé.

Zusammenfassung

Die Synthese von 2- und 5(6)-Vinylbenzimidazol wird beschrieben. Diese Verbindungen wurden durch geeignete chemische Reaktionen und physikalische Eigenschaften charakterisiert. Im Zuge dieser Arbeit wurde auch 3,4-Diaminostyrol dargestellt.

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Analysis of Polyethylenimine by Spectrophotometry of Its Copper Chelate

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Synopsis

Polyethylenimine (PEI) forms a copper chelate with a N/Cu ratio of about 5 and with extinction coefficients of about 175 at 6350 A. and 4250 at 2694 A. Solutions of PEI–copper chelate obey Lambert's and Beer's laws and show increased optical density in the presence of chloride ion. Above pH 4.25, hydrogen ion has little effect. A comparison with the copper chelate of polyvinylamine suggests that PEI has a highly, branched structure. Analysis of PEI via its copper chelate is described.

RESULTS AND DISCUSSION

Polyethylenimine (PEI) is a water-soluble material prepared by polymerizing aziridine with an acid catalyst. It has the empirical composition C_2H_5N and is comprised of primary, secondary, and tertiary amino groups. Various investigations[1,2] of its structure indicate a high degree of branching.

Although the polymer is strongly basic (pH = 11 in 5% aqueous solution), it cannot be determined by titration because of the progressive increase in charge on the polymer chain as the nitrogens are protonated.[3,4] This effect is diminished but by no means eliminated by increasing the ionic strength of the solvent or by chelation of the nitrogen. Figures 1 and 2 show titration curves of PEI which illustrate these effects.

We have found that PEI forms a copper chelate which has a N/C ratio of approximately 5, and at this ratio in 0.1*M* (in terms of N) solution, about 96% of the reactants are in the form of the chelate (data determined graphically from Fig. 3). The chelate has the dark blue cuprammonium color and the large equilibrium constant to make it suitable for colorimetric analysis of PEI (and probably of copper as well). The visible and ultraviolet spectrum of the complex is shown in Figure 4. The maxima occur at 2940 and 6350 A. The latter is a very broad peak and is suitable for approximate analytical determinations of PEI, because the accuracy of the wavelength setting is not critical and because the absorption of $Cu(OAc)_2$ in this region is very low, so that errors in correcting for excess copper are less important than they would be in the ultraviolet region.

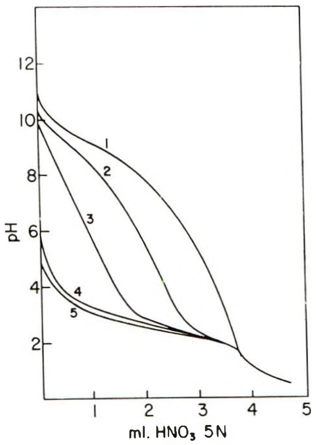

Fig. 1. Titration of 23.3 mmoles PEI with 5*N* HNO_3 in the presence of various amounts of copper: (*1*) no Cu^{++}; (*2*) 1.165 mmoles Cu^{++}; (*3*) 2.67 mmoles Cu^{++}; (*4*) 4.66 mmoles Cu^{++}; (*5*) 11.65 mmoles Cu^{++}. The curves reunite at 18.50 mmoles of HNO_3.

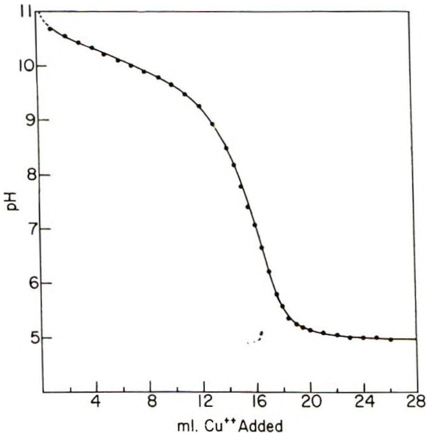

Fig. 2. Titration of 23.3 mmoles PEI in 20 ml. H_2O with 0.267*M* $Cu(NO_3)_2$. The inflection points correspond to N/Cu ratios of 6.66 and 4.72, and roughly would be consistent with 6:1 and 4:1 chelates with 15% of uncombined N.

Table I gives the molar extinction coefficients (*E*) which have been obtained over a period of time with various PEI samples, and Figure 3 shows a typical curve obtained at 6350 A. for the formation of the complex from various amounts of PEI and a standard amount of copper. In the region of excess copper, the curve is a straight line (i.e., quantitative formation of the chelate) with a slope which is determined by the concentration of the PEI added. In the region of PEI excess, the curve is a line of constant optical density, since PEI has negligible absorption in this region. The intersection of these two lines defines the N/Cu ratio in the chelate, and

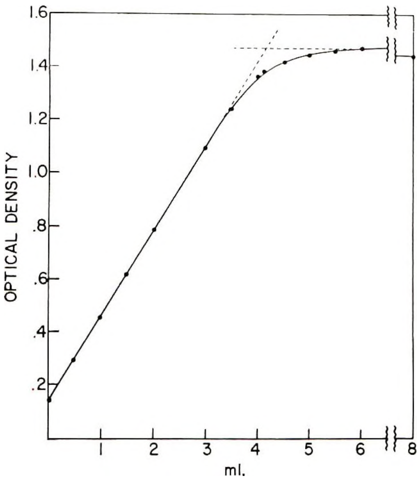

Fig. 3. Curve for the formation of PEI–copper chelate by adding 0.0954 merlar Chemirad PEI to 4.00 ml. of 0.0207M copper acetate. Volume of each sample, 10.0 ml. The equivalence point is at 4.17 ml. of PEI and OD = 1.47.

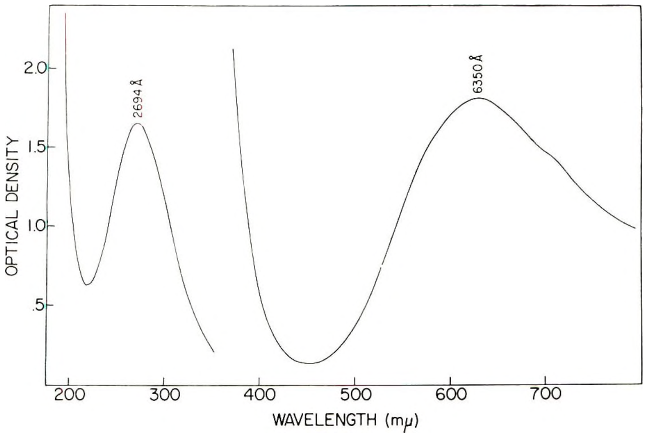

Fig. 4. Spectrum of PEI–copper chelate 0.5 merlar in PEI and 0.1M in $Cu(OAc)_2$. E_{6350} = 174, E_{2694} = 4242; cell thickness: visible, 1.04 mm., ultraviolet, 0.0295 mm.

the actual optical density at this ratio is a close approximation of the amount of chelate formed (95%), needing only to be corrected for the small amount of free Cu^{++}. Since the extinction coefficient of the latter is about 9% of that of the complex, neglecting the free copper causes an error of 0.5%.

Examination of the results reported in Table I shows that neither the N/Cu ratio nor the extinction coefficient is constant for all PEI samples examined. These variations may be due to differences in the branching of the polymer, and consequent differences in the steric availability of nitrogen for chelate formation. This speculation obtains some support

TABLE I

Extinction Coefficients of Copper Chelates of Various PEI Samples at 6350 A.

Source	Molarity[a]	E_{apparent}[b]	E_{ideal}[c]	N/Cu	Cl/N
Dow	0.00829	181	190	4.46	0
Chemirad	0.00829	168	176	4.74	0
Chemirad	0.00728	189	194	4.91	0.407
Chemirad	0.00428	188	—	5.15	0.389
PEI · HCl	0.00752	197	205	5.31	1.38
PEI · HCl	0.00762	196	203	5.25	1.38
Chemirad	0.00776	166	175	4.36	0
Chemirad	0.100	174	—	5.00	0
Acetyl PEI	0.00526	187	198	7.60	0
Average		183	192	4.90[d]	

[a] Based on Cu^{++}.
[b] Measured at the equivalence point.
[c] Measured in region of complete conversion.
[d] Excluding value for acetyl PEI.

from the data in Table II. If one plots the increase in extinction coefficient against the decrease in N/Cu, an approximate straight line is obtained. It is reasonable that increased ionic strength would open up the polymer chain and increase the ease of chelation. However, nitrate and acetate ions do not seem to exhibit this effect. We intend to study the matter further. For the purpose of the present communication it is sufficient to note that these effects occur, and that if an accuracy of greater than about ±5% is required, they must be corrected for. In this case, in using the chelate as an analytical tool, a reference curve should be prepared from the same batch of polymer whose portions are to be analyzed. It is of course also necessary to control the presence of other amines or materials which form colored chelates. We have not found interfering substances in PEI.

TABLE II

Numerical Values Derived from Figure 5

	Molarity		At equivalence point				
Curve no.	Cu^{++}	Cl^-	N/Cu	OD_{6350}	Maximum OD_{6350}	E_{copper}	OD ratio[a]
1	0.00776	0	4.91	1.29	1.36	175	1.05
2	0.00776	0.004	4.91	1.29	1.36	175	1.05
3	0.00776	0.02	4.81	1.33	1.40	180	1.05
4	0.00776	0.04	4.75	1.35	1.41	182	1.04
5	0.00776	0.08	4.75	1.40	1.47	189	1.05
6	0.00776	0.20	4.69	1.45	1.51	195	1.04
7	0.00776	0.40	4.67	1.49	1.55	200	1.04

[a] Ratio of true optical density of the chelate to the apparent optical density. Subtracting 1.00 from this ratio gives a close approximation to the degree of dissociation of the chelate.

The use of a high ionic strength solvent is desirable in many studies with charged polymers because it minimizes the charge effect. We have used 5% KOAC exclusively as a solvent system in this work so that we could relate PEI analytical determinations directly to other studies (i.e., viscosity determinations) in which this ionic strength was required. No effort has been made to determine the effect of ionic strength on the properties of the chelate other than to show that the extinction coefficient is not altered by moderate changes in acetate concentration.

Interference by Other Ions

Nitrate ion shows strong absorption in the ultraviolet. Chloride ion has a complicated effect, and in higher concentrations, may enhance the extinction coefficient at 635 mμ as much as 15%, as shown in Table III. Figure 5 illustrates the effect of various amounts of chloride ion on the optical density of PEI–copper mixtures, and Table II lists the critical numerical values. The effect of chloride ion is strongly concentration dependent.

TABLE III
Effect of Chloride Ion on the Extinction Coefficient of 0.01 Merlar PEI–Copper Complex

	5:1 N/Cu			6:1 N/Cu		
Cl/Cu	OD	Δ OD × 10^3	Increase, %	OD	Δ OD × 10^3	Increase, %
0	1.292	—	—	1.350	—	—
0.5	1.292	0	0	1.350	0	0
2.58	1.348	56	4.33	1.390	40	2.96
5.15	1.372	80	6.19	1.410	60	4.44
10.31	1.431	139	10.76	1.450	100	7.41
25.77	1.475	183	14.16	1.502	152	11.26
51.55	1.530	238	18.42	1.545	195	14.44

TABLE IV
Effect of pH on the Extinction Coefficient of 0.01*M* PEI–Copper Complex at N/Cu-5

pH	Cl/Cu	E_{6350}	$E_{\text{corrected}}$[a]
5.39	0	169	169
5.02	6	179	166
4.82	12	184	166
4.58	24	188	165
4.41	30	190	165
4.30	36	191	165
4.10	42	192	164
3.91	48	192	163
1.4	60	9	7.6

[a] Corrected for chloride ion effected by using data from Table III.

The effect of hydrogen ion is roughly depicted in Figure 6. Since the changes in pH were induced by adding concentrated hydrochloric acid to the complex, the chloride ion effect was corrected for Table IV gives uncorrected and corrected values. It is apparent that hydrogen ion *per se* has little effect above pH 4.2.

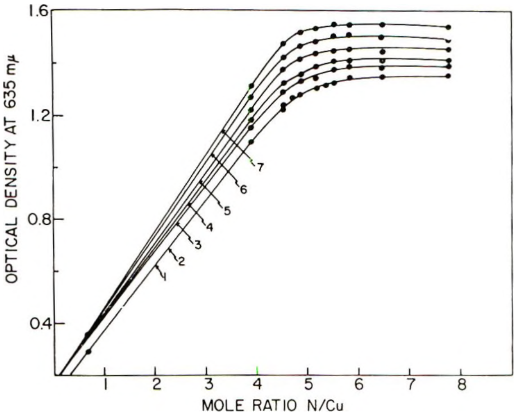

Fig. 5. Curves for the formation of PEI–copper chelate in the presence of chloride ion. (*1*) Cl/Cu = 0; (*2*) Cl/Cu = 0.52; (*3*) Cl/Cu = 2.58; (*4*) Cl/Cu = 5.15; (*5*) Cl/Cu = 10.31; (*6*) Cl/Cu = 25.77; (*7*) Cl/Cu = 51.55. All solutions are 0.00776*M* in Cu^{++}.

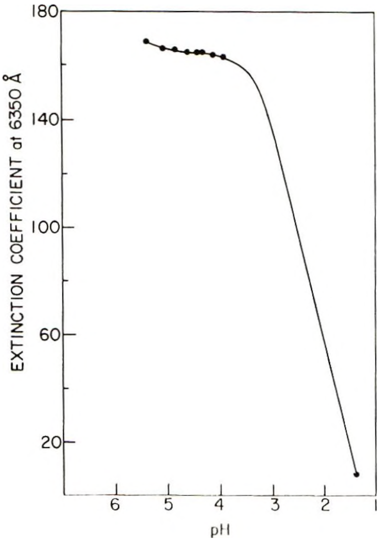

Fig. 6. Apparent effect of pH on the copper chelate of PEI. The pH change is induced by HCl, and the effect above pH 4.25 is due essentially to added chloride ion. Below this value, dissociation of the chelate becomes increasingly important.

Effect of Source and Treatment of PEI

Two samples of PEI were at our disposal. One was made by BASF, West Germany, and supplied as a 50% aqueous solution by the Chemirad Corporation. The molecular weight of this material is stated to be 30,000–40,000, determined by light scattering.[5] The other sample was supplied by the Dow Chemical Co., as a solution with 33% solids. The molecular weight is not stated, but appears to be higher than the BASF material as judged by its viscosity.

The concentration of both samples was confirmed by nitrogen analyses in our microanalytical department. The maximum error of these determinations is probably ±1%.

In addition, in order to get a standard PEI material which was free of carbonate, the Chemirad material was converted to the hydrochloride as described in the experimental section. A strongly basic polymer, 50% PEI does slowly absorb CO_2, but our analytical data suggests that the carbonate is eventually converted to urea crosslinks or large rings, since it appears that in the material we used there is about 1 extra carbon atom for every 20 nitrogens, and that one out of every 10 nitrogens is nonbasic.

The extinction coefficients and N/Cu ratios obtained with these materials are listed in Table I.

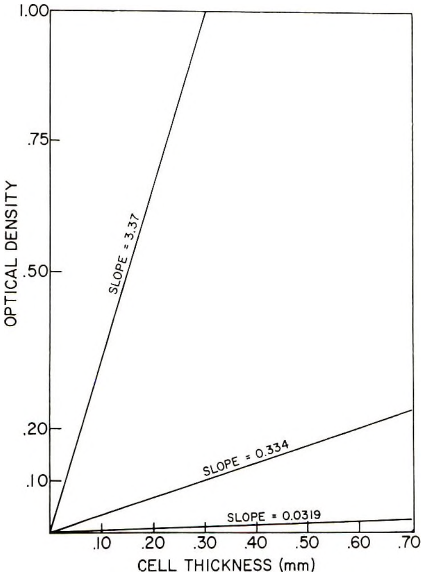

Fig. 7. Lambert's law plots of PEI–copper chelate, measured at 6350 A. The maximum deviation from Beers' law is less than 5%.

Effect of Dilution on the Chelate

In Figure 7 we show Lambert's law plots of the optical density of the chelate at three dilutions. These determinations were made with a calibrated variable path-length cell. Since the ratio of slope to concentration for these three curves is essentially constant, there is no appreciable deviation from Beer's law.

In some of the earlier work we did on this system, copper chloride was used as the source of copper ion. The chloride ion introduced in these cases causes only a moderate error in our results. It can be seen from Table III that chloride ion has less than 3% effect at a Cl/Cu molar ratio of 2:1.

In addition to PEI itself, the acetyl derivative (N:acetyl = 2:1) was also converted to the chelate. The N:Cu ratio found was 7.6, and the ideal and actual extinction coefficients 205 and 182, respectively.

Polyvinylamine

A sample of this material, made by the method of Reynolds and Kenyon[6] gave an entirely different sort of copper-binding curve (Fig. 8). This chelate has been described in detail by Teyssie et al.[7]

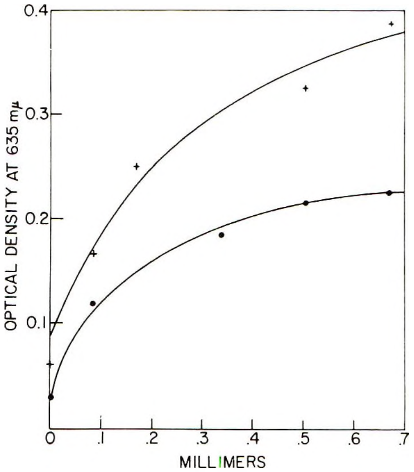

Fig. 8. Curves for the formation of polyvinylamine-copper chelate obtained under the same conditions as those used for Fig. 3: (×) 0.00364 mM Cu^{++}; (), 0.00182 mM Cu^{++}. Abscissa: mmers of polyvinylamine added.

EXPERIMENTAL

All solutions used in this work were 5% in potassium acetate and had pH 5.5 unless otherwise stated. Reagent grade chemicals of reputable manufacture were used thruout. Copper solutions were analyzed by thiosulfate titration, and PEI concentrations were obtained by Dumas nitrogen analyses on the working solutions used. The error on these determinations probably does not exceed 1%. Spectra were determined on a Carey model 15 spectrophotometer.

Preparation of PEI·HCl

A 50% solution of PEI was analyzed (Found: C, 29.23%; N, 16.13%; C/N ratio, 2.12/1). Based on N, the solution is 49.6 ± 0.9%.

This solution (9 g.) was strongly acidified with 25 ml. concentrated HCl and evaporated to dryness on the steam bath (Found: C, 26.23%; N, 14.70%; C/N ratio 2.11/1). The acid treatment was repeated, and the sample kept under high vacuum (0.5 μ) for 10 hr. (Found: C/N ratio 2.12/1; C/Cl ratio 1.975/1). The vacuum drying was continued 4 days at 0.1 μ (Found: C, 30.64%; H, 7.89%; N, 17.48%; Cl, 41.26, 41.25% (by precipitation), 41.49% (by combustion); C/N ratio 2.05; C/Cl ratio 2.19). C_2H_6NCl requires: C, 30.20%; H, 7.61%; N, 17.61%; Cl, 44.58%. If one carbonic acid is condensed with a 20-nitrogen unit of the polymer to form a carbamide linkage, the empirical formula, $C_{41}H_{116}N_{20}OCl_{18}$ requires: C,31.90%; H, 7.57%; N, 18.14%; Cl, 41.34%. The analysis is in reasonable agreement with this formulation. The slight reduction in C/N ratio upon prolonged acid treatment may signify a liberation of basic nitrogen. This hypothesis is consistent with the increased N/Cu ratio in the chelate of the acid-treated polymer (see Table I).

Determination of PEI as the Copper Complex

To 4.00 ml. of 0.02*M* copper acetate we added various amounts of 0.1 merlar PEI solution, diluted each mixture to 10.0 ml. (always using 5% KOAc at pH 5.5 as the solvent), and constructed a standard optical density–PEI content curve similar to that shown in Figure 9. Unknown samples,

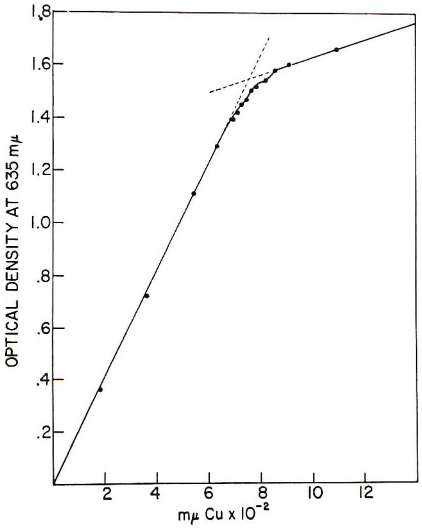

Fig. 9. Curve for the formation of PEI–copper chelate from 0.400 mmer PEI·HCl and $CuCl_2$ in a volume of 10.0 ml. The slopes are 20.5 and 3.4 OD units per mmole of Cu^{++}.

made in the same way, may then be read directly, as long as the optical density values are below 1.2 (linear slope).

Polyvinylamine

This was prepared by the method of Reynolds and Kenyon.[6] After hydrolysis with hydrazine hydrate, in which 30 g. of the dry polymer was added portionwise to a hot (100°C.), stirred mixture of 30 ml. of <95% hydrazine hydrate and 70 ml. of water, the mixture was acidified with acetic acid, clarified by centrifugation, and the supernate purified by dialysis against distilled water. Analysis of the dialyzate for C and N indicated that the concentration of the polymer solution was 0.042 merlar.

The dialyzate shows a very strong peak at 310 mμ, presumably due to residual phthalimido residues, but this peak is not diminished by repeating the hydrazinolysis. This final dialyzate gave the analysis: C, 5.94 mg./ml.; H, 1.16 mg./ml.; N, 1.89 mg./ml.; acetic acid, 5.02 mg./ml. Thus, the C/N ratio is 3.67 and the N/acetic acid ratio is 1.61. From these data, it can be calculated that there is a residual phthalimidyl residue for each $18^1/_2$ monomer units, corresponding to 94.6% hydrolysis. Kenyon[6] gives the value 95.8%.

The copper-binding curve was run on this material under the same conditions as that described for PEI. The binding is very weak compared to that of PEI.

Effect of Acetylation

The Chemirad Corporation was kind enough to supply us with a sample of acetylated PEI (made with acetyl chloride). Analysis indicated a 3:1 C/N ratio (50% acetylation). This material was dialyzed against KOAc solutions to remove chloride, then against distilled water, lyophillized, and made up to 0.85 merlar in 5% KOAc (concentration determined by N analysis). This was then diluted with 5% KOAc to 0.1 merlar and converted to the chelate. The N:Cu ratio is 7.60, and $E_{\text{apparent}} = 182$, $E_{\text{ideal}} = 205$, as determined from the graph of the optical density versus composition.

We wish to thank the Chemirad Corp. for their generosity in supplying us with some of the materials used in this work.

Microanalyses were made by B. Baer, P. M. Parisius, E. Peake, and A. L. Wong in our microanalytical laboratory under the direction of Dr. W. C. Alford.

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Résumé

La polyéthylènimine (PEI) forme un chélate cuivrique avec un rapport N/Cu d'environ 5 et avec des doefficients d'extinction d'environ 175 à 6350 Å et 4250 à 2694 Å. des solutions du chélate cuivrique PEI obéissent à la loi de Lambert et Beer et montrent une densité optique croissante en présence d'ions chlorures. Au-dessus du pH 4.25, la concentration en ions hydrogènes a peu d'effet. Une comparaison avec des chélates cuivriques de la polyvinylamine suggèren que PEI a une structure fortement ramifiée. L'analyse de PEI au moyen d'un chélate cuivrique est décrite.

Zusammenfassung

Polyäthylenimin (PEI) bildet ein Kupferchelat mit einem Verhältnis N/Cu von etwa 5 und mit Extinktionskoeffizienten von etwa 175 bei 6350 Å und 4250 bei 2694 Å. Lösungen von PEI–Kupferchelat gehorchen dem Lambert-Beer'schen Gesetz und zeigen in Gegenwart von Chloridion erhöhte optische Dichte. Oberhalb pH 4,25 besitzt Wasserstoffion wanig Einfluss. Ein Vergleich mit dem Kupferchelat von Polyvinylamin lässt erkennen, dass PEI eine stark verzweigte Struktur besitzt. Die Analyse von PEI über sein Kupferchelat wird beschrieben.

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Studies on the Polymerization of Ethyl Acrylate. I. Kinetic Studies

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Synopsis

Kinetic studies on the polymerization of ethyl acrylate have been carried out and the various rate constants and their corresponding activation energies determined.

Although the polymerization kinetics of methacrylic esters have been studied quite extensively,[1-5] there are less data available on similar studies on the acrylate series.[6-10] This prompted the present study with ethyl acrylate, as the available literature are very meager. This paper reports kinetic studies with this monomer to evaluate the different kinetic constants.

EXPERIMENTAL

Materials

Ethyl acrylate supplied by Eastman Kodak was freed from inhibitor by repeated washing with 5% aqueous caustic soda followed by washing with distilled water to remove any trace of alkali. After drying over calcium chloride it was distilled twice, the fraction boiling in the range 99–99.5°C. being collected.

Benzene was purified according to the standard method.[11]

2,2′-Azobisisobutyronitrile was recrystallized twice from absolute ethyl alcohol; m.p. 103–104°C.

Polymerization

The polymerization experiments were carried out in Pyrex glass ampules which were first thoroughly cleaned with hot chromic acid, washed with water, then with sulfurous acid solution, and finally washed with distilled water and dried. The required volumes of the monomer and solvent mixtures were placed in these ampules, frozen in liquid oxygen, degassed, and the ampules sealed. The tubes were then suspended in oil thermostats maintained at the required temperatures within an accuracy of ±0.01°C. After a specific time, when the conversion was less than 10%, the tubes were taken out, chilled, and broken open. The polymer was precipitated with

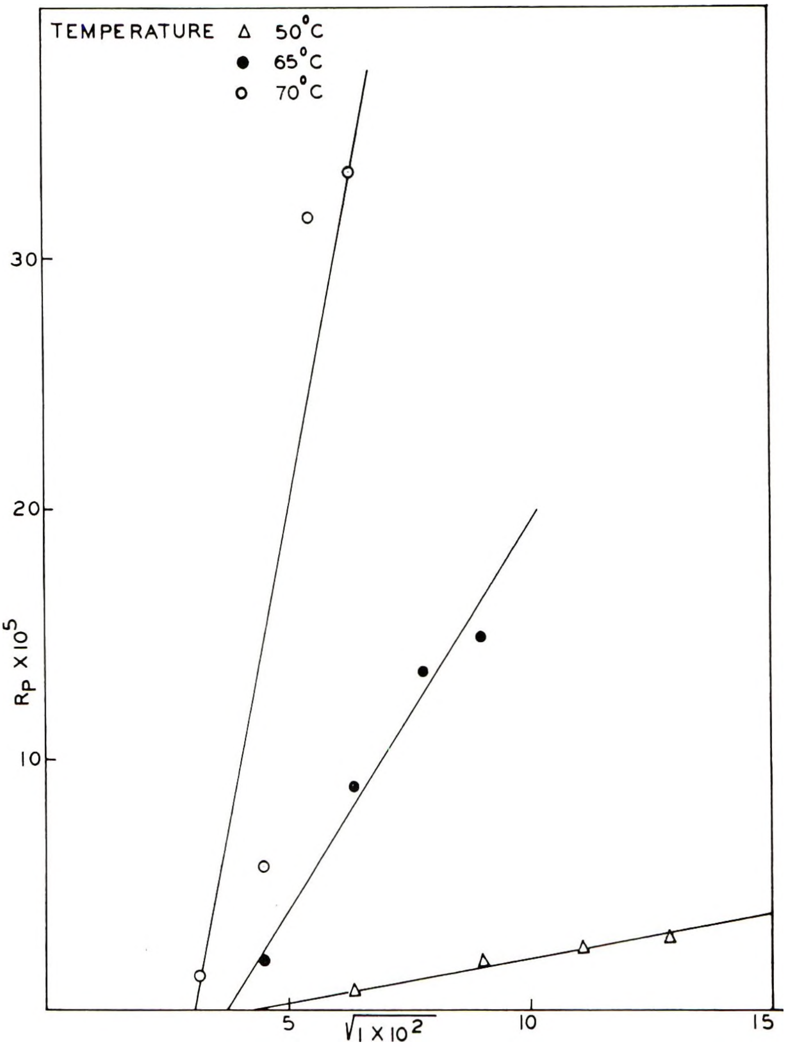

Fig. 1. Dependence of the rate of polymerization on the initiator (AIBN) concentration: (△) 50°C.; (●) 65°C.; (○) 70°C.

petroleum ether (boiling range 40–60°C.), reprecipitated from benzene solution, and finally dried at 50°C. to constant weight.

Degree of Polymerization

The degree of polymerization P was determined from viscosity measurements at 30 ± 0.05°C. in benzene solution from the relation $P = k[\eta]^{\alpha}$, where $[\eta]$ is the intrinsic viscosity of the solution and k and α are constants for each polymer system in benzene. The values used in the calculation of the present work were $k = 2.03 \times 10^3$; $\alpha = 1.492$.[6]

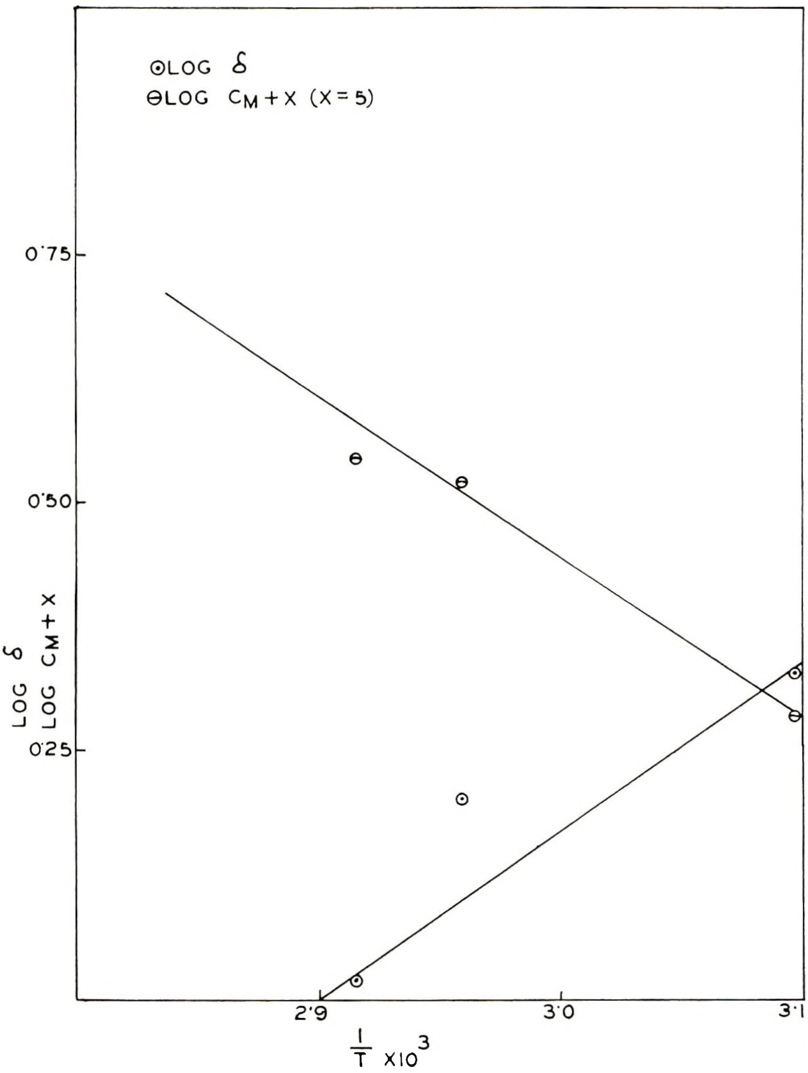

Fig. 2. Temperature effect of C_M and δ in the polymerization of ethyl acrylate: (⊙) log δ; (⊖) log $C_M + X$ ($X = 5$).

RESULTS AND DISCUSSION

Rate of Polymerization (R_p)

R_p in the case of ethyl acrylate is found to be quite fast in comparison to the rate for methacrylates under similar conditions. The kinetics were studied at 50, 65, and 70°C. in bulk and in solution. It is found that R_p is proportional to $[I]^{1/2}$ in agreement with the usual relationship.

$$R_p = K[I]^{1/2}[M]^n$$

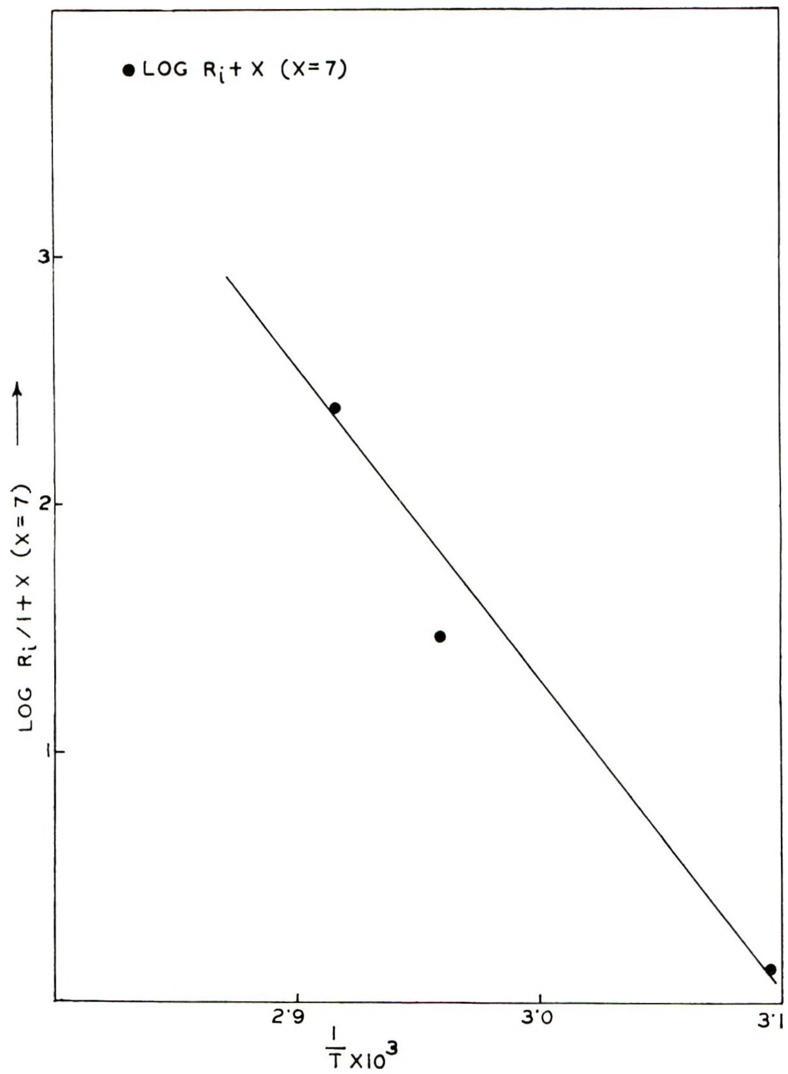

Fig. 3. Temperature effect of $R_i/[\mathrm{I}]$ in the polymerization of ethyl acrylate; log R_i + X (X = 7).

where [I] and [M] are the initiator and monomer concentrations, respectively, and K is a constant. The straight lines do not pass through the origin, showing the presence of an induction period, and termination is probably by a bimolecular free-radical interaction.

Value of δ ($k_t^{1/2}/k_p$)

The general equation for the degree of polymerization is

$$1/\bar{P} = \sum C_x[\mathrm{X}]/[\mathrm{M}] = C_\mathrm{M} + C_\mathrm{I}\,([\mathrm{I}]/[\mathrm{M}]) + C_\mathrm{S}([\mathrm{S}]/[\mathrm{M}]) + R_p(\delta^2/[\mathrm{M}]^2)$$

TABLE I

Polymerization of Ethyl Acrylate (3.08M) in Benzene Solution at Different Temperatures

Temp., °C.	$[I] \times 10^3$, mole/l.	$R_p \times 10^5$, mole/l.-sec.	$\frac{1}{P} \times 10^5$	δ, mole$^{1/2}$/l.$^{1/2}$-sec.$^{1/2}$	$(E_p - {}^1/_2E_t)$, kcal./mole	$C_M \times 10^5$	E_{C_M}, kcal./mole	$R_p^2/[I] \times 10^6$, mole/l.-sec.^{2}	$R_i/[I] \times 10^6$, sec.$^{-1}$	$E_{R_i}/[I]$, kcal./mole
50	16.64	2.98	4.49	2.13	6.8 ± 1	1.93	7.69 ± 1	0.113	0.11	35.2 ± 3
	12.20	2.47	4.15							
	8.13	1.97	3.81							
	4.06	0.75	3.34							
65	8.13	14.94	10.54	1.59		3.32		5.57	2.94	
	6.10	13.50	10.09							
	4.05	8.92	8.82							
	2.03	1.98	6.99							
70	4.06	33.37	13.34	1.04		3.51		9.75	25.0	
	3.05	31.63	12.51							
	2.03	5.70	10.10							
	1.02	1.38	9.27							

where C_M, C_I, and C_S are chain transfer constants for monomer, initiator, and solvent, respectively. With AIBN, C_I is consistently near zero, and

$$1/\bar{P} = C_M + C_S([S]/[M]) + R_p\,(\delta^2/[M]^2)$$

Hence a plot of $1/\bar{P}$ against R_p should be straight line from whose slope δ can be evaluated.

In the present work δ has been evaluated at three temperatures: 50, 65, and 70°C. Experiments at higher temperatures could not be carried out due to the explosive nature of the reaction. As observed in Table I, experiments were conducted in solutions of benzene. This is partly to control the rate of the reaction and partly to avoid high viscosity of the medium with progress of polymerization. We tried to determine the kinetic constant from results of bulk polymerization of ethyl acrylate. It was observed that in bulk the molecular weight of the polymer formed was very high, and the system becomes highly viscous even with very low percentage of conversion. This obviously resulted in diffusion-controlled reaction, and the value of δ at a particular temperature was found to vary with the monomer concentration. In order to avoid this, work was carried out in solution of benzene (benzene: monomer = 2:1 by volume; at this concentration the reaction was not diffusion-controlled), and the results have been reported in Table I. As is mentioned earlier, quite little literature exists on this, and whatever data are available give a value of δ from bulk experiments which is very low in comparison to our value. We think this to be due to the high viscosity in bulk experiments which causes a reduction in the termination rate and thus affects the value of δ.

The effect of temperature on δ and hence the energy of activation $E_p - E_t/2$ has been evaluated; the value of energy of activation found was 6.8 kcal./mole; this may be compared with the value of 8.42 kcal./mole obtained for methyl acrylate.[7]

TABLE II
Rate Constants for the Polymerization of Methacrylic and Acrylic Esters

Monomer	δ at 50°C., mole$^{1/2}$/l.$^{1/2}$sec.$^{1/2}$	$E_p - {}^1/_2E_t$, kcal./mole	$E_{R_i}/[I]$, kcal./mole	$C_M \times 10^5$ at 50°C.	E_{C_M}, kcal./mole
Methyl acrylate	2.49[a]	8.42[a]		1.30[a]	6.03[a]
Ethyl acrylate	2.13	6.80	35.2	1.93	7.69
Butyl acrylate	—	2.10[b]			
Methyl methacrylate	11.62[c]	4.40[c]	30.7[d]	0.80[c]	7.60[c]
Ethyl methacrylate	9.43[c]	4.22[c]	32.7[e]		4.12[c]
Butyl methacrylate	5.99[c]	4.00[c]	33.4[e]	1.79[c]	3.54[c]
Nonyl methacrylate	2.48[c]	2.59[c]	34.0[e]	—	—

[a] Data of Sen et al.[9]

[b] Data of Melville and Bickel.[10]

[c] Data of Nandi.[12]

[d] Data of Matyka et al.[8]

[e] Data of Khanna et al.[3]

Rate of Initiation

At a steady state during polymerization,

$$R_i = 2k_t\,[\mathrm{M}^*]^2 = (2k_t/k_p^2)\,R_p^2/[\mathrm{M}]^2$$
$$R_i/[\mathrm{I}] = (2\delta^2/[\mathrm{M}]^2)\,R_p^2/[\mathrm{I}]$$

Since $R_p^2/[\mathrm{I}]$ is a constant, $R_i/[\mathrm{I}]$ should be a constant at a particular monomer concentration.

The value of δ obtained was utilized and $R_i/[\mathrm{I}]$ determined at three temperatures. The results are reported in Table I and the energy of activation has been found to be 35.2 kcal./mole. This can be compared with a value of 30.7 kcal./mole for AIBN-initiated polymerization of methyl methacrylate (Table II) and other methacrylic esters.

Transfer to Monomer (C_{M})

C_{M} has been evaluated from the plot of $1/\bar{P}$ against R_p, where the intercept gives the value of $C_{\mathrm{M}} + C_{\mathrm{S}}\,[\mathrm{S}]/[\mathrm{M}]$. From a knowledge of the values of C_{S} and $[\mathrm{S}]/[\mathrm{M}]$, C_{M} can be evaluated easily. The results for C_{M} and the corresponding energy of activation are tabulated in Table I.

It might be observed from Table II that although the energies of activation for C_{M} are almost identical for methyl methacrylate and ethyl acrylate, the values of C_{M} at a certain temperature are quite different. C_{M} for methyl methacrylate is quite low in comparison to that for methyl or ethyl acrylate. This might be due to the fact that the presence of an α methylenic group would favor propagation rather than transfer, which is much easier in the case of the acrylates.

The authors are grateful to Professor Santi R. Palit for constant encouragement and helpful discussion during the course of the work.

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Résumé

Des études cinétiques de la polymérisation de l'acrylate d'éthyle ont été effectuées et les différentes constantes de vitesse et leurs énergies d'activation correspondantes déterminées.

Zusammenfassung

Eine kinetische Studie der Polymerisation von Äthylacrylat wurde ausgeführt und die verschiedenen Geschwindigkeitskonstanten sowie die entsprechenden Aktivierungsenergien bestimmt.

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Determination of Tacticity in Poly(vinyl Chloride) by Infrared Spectroscopy

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Synopsis

From the temperature dependence of infrared spectra of poly(vinyl chloride) samples prepared by different methods, the intensity of the band at 690 cm.[1] (proportional to the number of isotactic diads in the sample), as well as that of the tacticity-independent C—H stretching band, was found to be independent of the crystallinity of the sample. These lines were therefore applied for the tacticity determination in poly(vinyl chloride), measured in the form of KBr pellets. The numerical tacticity value was obtained from the known values of absorbance coefficients of S_{CH} and S_{HH} type C—Cl stretching bands in solution, and from the shape of the spectrum.

In the region of 600–700 cm.$^{-1}$, the infrared spectrum of poly(vinyl chloride) shows bands assigned to C—Cl stretching vibrations. The intensities of these bands depend on the conformational and configurational structure and on the crystallinity of the sample, and they have been used in the past for tacticity determination.[1–6]

In our previous communication,[7] the absorption around 690 cm.$^{-1}$ was shown to be proportional to the number of isotactic diads, and in the region of 600–640 cm.$^{-1}$ to syndiotactic diads. Based on this finding we proposed a method for determining the tacticity of amorphous samples of PVC.[7] As some samples cannot be easily transformed into an amorphous state, an infrared method of tacticity determination which is independent of the crystallinity of the samples was sought.

Experimental

The preparation of model polymers has been described in detail in previous communications.[8,9] Polymerizations were carried out in dilatometers up to 5% conversion. Polymerization conditions of the polymers investigated are summarized in Table I.

Samples 1, 2, and 3 were fractionated into 12–14 fractions. Samples 4 and 5 were polymerized at low temperature in heptane by block photopolymerization with methyl azobisisobutyrate as initiator. Polymer 6 was prepared by a copolymerization of vinyl chloride with a small amount of vinyl acetate, the latter monomer being used for a reduction of the

TABLE I
Polymerization Conditions

Sample no.	Vinyl chloride, mole/l.	Vinyl acetate, mole/l.	Solvent	Solvent concn., mole/l. × 10²	Initiator (methyl azobis-isobutyrate), mole/l. × 10²	Temp., °C.	Polymerization time, hr.	Conversion, %	Contents of syndiotactic diads		
1	13.2	—	Diethyl-oxalate	0.63	0.063	+25	15.5	2.16	0.56,	0.57,[a]	0.56[b]
2	4.95	—	2,4-Dichloro-pentane	4.95	1.85	+50	2.7	8.54	0.55,	0.56,[a]	0.55[b]
3	4.9	—	Isopropyl-chloride	7.3	1.9	+50	1.0	5.5	0.56,	0.58,[a]	0.56[b]
4	5.2	—	Heptane	4.4	1.8	−40	3.0	1.4	0.59[a]	—	—
5	14.1	—	—	—	0.064	−50	18.0	1.2	0.59	—	—
6	14.1	0.1	—	—	0.064[d]	+25	2.5	3.2	0.55	—	—
7[c]	—	—	—	—	—	+55	—	95.0	0.55,	0.57,[a]	0.53[b]
8	—	—	—	—	—	0	6.0	5.0	0.56	—	—
9	—	—	—	—	—	−25	6.0	25.0	0.57	—	—
10	—	—	—	—	—	−35	12.0	12.0	0.58	—	—

[a] Least soluble fraction.

[b] Most soluble fraction.

[c] Commercial suspension of Czechoslovak origin.

[d] 2,2-Azobis(2,4-dimethyl-4-methoxy)valeronitrile used as initiator instead of methyl azobisisobutyrate.

regularity of the structure. Sample 7 is a typical commercial suspension polymer, prepared under standard conditions at 55°C.; by extraction with benzene it was separated into two parts, a benzene-soluble part, 7a, and a benzene-insoluble part, 7b. Both parts were subjected to further fractionation. The series of samples 8, 9, 10 were prepared according to Germar[10] at 0, −25, and −35°C., respectively, but to low conversion.

The infrared spectra were measured on a Perkin-Elmer 421 spectrophotometer. For temperature-dependence measurements of infrared spectra, the samples were heated and cooled in KBr pellets containing 5 mg. of powdered polymer. The absorbance of the bands at the maximum was determined by the base-line method.

Results and Discussion

In order to determine the effect of crystallinity upon the intensities of various bands in the infrared spectra of the PVC samples, the spectra of polymers prepared by various procedures were measured over a broad temperature range. It was found that the intensities of all lines change with temperature. The intensities of the lines at 615, 690, 960, 1105, and 1438 cm.$^{-1}$ exhibit smooth temperature changes under all circumstances. On the other hand, the temperature changes of the lines at 635, 1258, 1338, and 1428 cm.$^{-1}$ indicate that these lines are influenced by the crystallinity of the sample (Figs. 1 and 2).

The reversible temperature changes of intensities (Fig. 2) in crystallinity-independent bands may be caused either by changes of conformational equilibrium or by changes of absorbance coefficients. In order to determine which of these factors is dominant, we analyzed the region of C—Cl stretching vibrations with respect to the findings of our previous communications.[7,11,12] By studies of model compounds, the syndiotactic parts of the chain were shown to contain TT and GG conformations, the relative amounts of these two forms depending on temperature. The TT

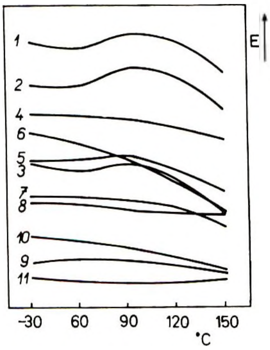

Fig. 1. Temperature dependence of the absorbances of various lines in the infrared spectrum of PVC sample 7b: (*1*) 1258 cm.$^{-1}$; (*2*) 1428 cm.$^{-1}$; (*3*) 635 cm.$^{-1}$; (*4*) 1438 cm.$^{-1}$; (*5*) 1338 cm.$^{-1}$; (*6*) 615 cm.$^{-1}$; (*7*) 960 cm.$^{-1}$; (*8*) 2910 cm.$^{-1}$; (*9*) 1105 cm.$^{-1}$; (*10*) 690 cm.$^{-1}$; (*11*) 2970 cm.$^{-1}$.

conformations are known to absorb in the region 600–640 cm.$^{-1}$. The GG form in a syndiotactic diad contains two S_{CH} chlorine atoms lying in the plane of the polymer chain. According to Colthup,[13] strong interaction between chlorine atoms can take place in this case. The infrared spectrum of *d,l*-2,4-dichloropentane, which from NMR spectra is known to contain GG forms, does not exhibit any bands in the region of S_{CH} type C—Cl stretching vibrations. For this reason, the S_{CH} band of GG forms expected to lie at 690 cm.$^{-1}$ was assumed to be split into two components, as a consequence of an interaction between the two Cl atoms.[12] We expected one of the components to lie above 700 cm.$^{-1}$ and the other between 600 and 640 cm.$^{-1}$. This assumption was confirmed by a normal vibration calculation of the GG form of *d,l*-2,4-dichloropentane by Krimm[14] and by our own measurements.[15]

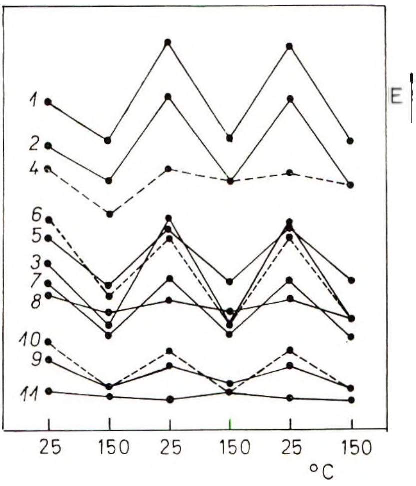

Fig. 2. Absorbance changes of various lines in the infrared spectrum of PVC sample 7b during repeated heating. Identification of curves as for Fig. 1.

In rapidly cooled samples of pure syndiotactic PVC which had previously been heated up to 200°C. under high pressure, Krimm[16] found a band in the region of 690 cm.$^{-1}$, assigned to TG conformations of syndiotactic diads. This band does not occur in syndiotactic samples of PVC subjected to simple heating only. As in model compounds of syndiotactic PVC, an appreciable band of the TG forms has not been observed; the 690 cm.$^{-1}$ band in the PVC samples presently investigated is assumed to correspond only to S_{CH} vibrations of isotactic diads and to be independent of the conformational structure of PVC. As this line is independent of crystallinity, the temperature changes of its intensity must be caused by a temperature dependence of absorbance coefficients, as in the 2,4-dichlorpentanes.[17] This conclusion is further supported by the fact that the intensity of the band at 690 cm.$^{-1}$ changes even at very low temperatures, where changes of conformational structure are highly improbable (Fig. 3).

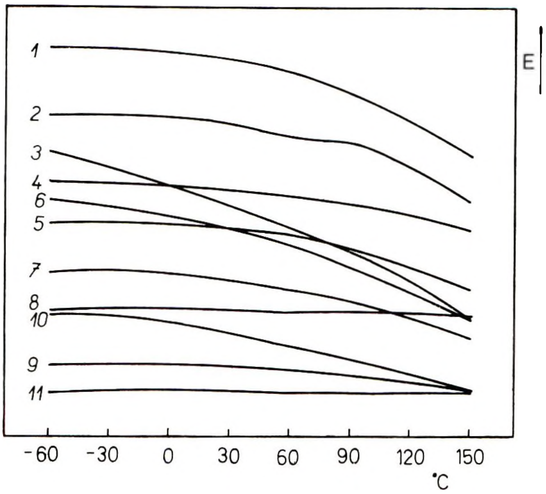

Fig. 3. Temperature dependence of the absorbance of various lines of PVC sample 7b crystallized at 150°C. Identification of curves as for Fig. 1.

The band at 690 cm.$^{-1}$ consists of two components, assigned by Tasumi[18] to the symmetrical and degenerate C—Cl stretching vibration of isotactic sequences. In our spectra these two components were not resolved. In measuring the absorbance of this band, both the integral and the peak absorbances were determined. Overlapping of the 690 cm.$^{-1}$ band with the S_{HH} (600–650 cm.$^{-1}$) C—Cl stretching band makes the measurement of integral absorbance less accurate. In spite of this, the ratio of the two absorbance values remained approximately constant in all the samples measured at all temperatures investigated. In all cases the observed differences remained within the limits of accuracy given by the measurement of integral absorbance. For this reason, even this composite band was further evaluated by means of peak absorbance.

In the region of 600–640 cm.$^{-1}$ a number of bands overlap; the frequencies and intensities of these bands depend on the length of syndiotactic sequences in TTTT conformations[7] and on crystallinity of the sample. Moreover, this region also contains bands of GG forms of syndiotactic sequences, and these may have absorbance coefficients differing from those of TT forms. Temperature changes in this region were also observed in model compounds.[12,15] No single band from this region is therefore suitable for tacticity determination.

From the bands in the region 600–700 cm.$^{-1}$, only the band at 690 cm.$^{-1}$ can therefore be used for determining tacticity. The bands of CH stretching vibrations are most suitable to be used as internal standard lines, as they are independent both of tacticity and of crystallinity of the sample (Fig. 1, curve *6*). Besides that, their intensity is comparable to that of the band at 690 cm.$^{-1}$, so that the influence of the mosaic effect is expected to be small.

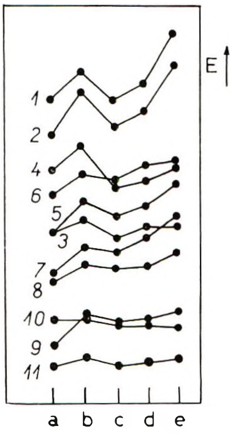

Fig. 4. Absorbance of various lines in the infrared spectra of PVC samples polymerized at different temperatures: (*a*) sample 7b; (*b*) sample 8; (*c*) sample 9; (*d*) sample 10; (*e*) sample 5. Identification at curves as for Fig. 1.

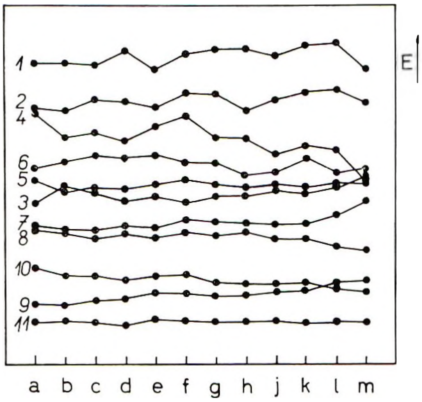

Fig. 5. Absorbance of various lines in the infrared spectra of PVC samples obtained by different polymerization procedures: (*a*) sample 7a; (*b*) sample 2; (*c*) sample 7b; (*d*) sample 6; (*e*) sample 3; (*f*) sample 7; (*g*) sample 1; (*h*) most insoluble fraction of sample 7b; (*j*) most insoluble fraction of sample 1; (*k*) most insoluble fraction of sample 1; (*l*) most insoluble fraction of sample 3; (*m*) most insoluble fraction of sample 4. Identification of curves as for Fig. 1.

For the determination of absolute tacticity (Table I), the ratio of absorbance coefficients A_{690}/A_{2970} must be known. This was determined in easily soluble samples of PVC of known tacticity[7] and found to be equal to 3.2.

We have also measured the ratio of integrated absorbances of the band at 690 cm.$^{-1}$ and of the sum of integrated absorbances of all the bands between 600 and 640 cm.$^{-1}$, recommended for tacticity determination by Shimanouchi.[16] We have found that this ratio depends on the crystallinity of PVC. For sample 7, the following values of $A_{600-640}/A_{690}$ were found:

2.5 for a film, 2.2 for a powder obtained by precipitation from solution, and 1.96 for PVC in solution.

Tacticity values given by Shimanouchi[19] are further based on the assumption of equal absorbance coefficients for both S_{CH} and S_{HH} CCl stretching vibrations. In model compounds,[12] the ratio of these absorbance coefficients $A_{S_{HH}}/A_{S_{CH}}$ was found to be 1.5.

Germar[6,10] determines tacticity from temperature changes of infrared spectra of PVC in solution. He assumes temperature-independent absorbance coefficients and therefore ascribes all temperature variations of line intensities to changes of chain conformation equilibria. The actual temperature dependence of absorbance coefficients renders Germar's procedure unsuitable and explains the highly improbable values of ΔE between GG and TT forms in syndiotactic sequences following from his measurements.

The tacticity of PVC samples polymerized in the temperature range +50 to −50°C. was evaluated by means of infrared spectra by using the intensity of the 690 cm.$^{-1}$ band referred to the CH stretching band (Fig. 4). Absorbances of all lines in the infrared spectra of PVC samples prepared under widely varying polymerization conditions are shown in Figure 5. In the temperature range investigated, tacticity varies by about 4% (Table I). This result indicates a small difference between the activation energies of formation of the two configurations, and the ratio of syndiotactic and isotactic diads must consequently be near to 50%. This is in agreement with the tacticity values of PVC found experimentally from infrared spectra.

For samples 1, 2, 3, and 7, the tacticity of fractions of different solubility was investigated. Tacticity is practically equal (Fig. 6) in all fractions,

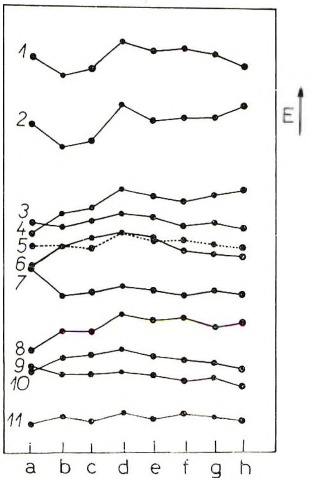

Fig. 6. Absorbance of various lines in the infrared spectra of fractions of sample PVC-3 annealed for 1 hr. at 150°C. Solubility of fractions increases from *a* to *h*. Identification of curves as for Fig. 1.

except for the first least soluble portion which is about 2% more syndiotactic. By fractionation of sample 7, extreme fractions differing by 4% in tacticity may be obtained, with the most soluble fraction enriched up to 2% by isotactic sequences. This result confirms the assumption that in the given polymer with sufficiently high molecular weight, the chains contain an approximately equal proportion of syndiotactic or isotactic diads.

The small difference in tacticity of samples prepared at widely differing temperatures, together with the large differences in physical properties, e.g., in solubility, indicate that tacticity is not the only factor determining physical properties. Solubility is known to depend on the contents of anomalous structures originating, e.g., in copolymerizations for example, in investigations of physical properties, the influence of anomalous structures originating by more complicated reactions during the polymerization of PVC must be considered. In these anomalous structures, a higher temperature factor may be expected compared to the stereoregular placements, and their contents should therefore be more sensitive to variations in polymerization conditions.

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Résumé

Au départ de la dépendance thermique des spectres infrarouges des échantillons de chlorure de polyvinyle préparés par différences méthodes, l'intensité de la band à 690 cm^{-1} (proportionnelle au nombre de diades isotactiques de l'échantillon) aussi bien que celle de la bande d'étirement C-H indépendante de la tacticités, ne sont pas fonction de la cristallinité de l'échantillon. Ces bandes sont dès lors appliquées à la détermination de la tacticité dans le chlorure de polyvinyle mesurée dans des pastilles de KBr. La valeur numérique de la tacticité a été obtenue au départ de valeurs connues des coefficients d'absorption des bandes d'étirement C-Cl du type S_{CH} et S_{HH} en solution et au départ de la forme du spectre.

Zusammenfassung

Aus der Temperaturabhängigkeit der Infrarotspektren von nach verschiedenen Methoden dargestellten Polyvinylchlorid-proben ergab sich die Intensität der Bande bei 690 cm^{-1} (proportional der Anzahl der isotaktischen Diaden in der Probe) sowie diejenige der taktizitäts-unabhängigen C-H-Valenzbande als unabhängig von der Kristallinität der Probe. Diese Linien wurden daher zur Taktizitätsbestimmung an Polyvinylchlorid, gemessen in Form von KBr-Pillen, verwendet. Der numerische Taktizitätswert wurde aus den bekannten Werten der Absorptionskoeffizienten von C-Cl-Valenzbanden vom S_{CH}- und S_{HH}-Typ in Lösung sowie aus der Gestalt des Spektrums erhalten.

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Quantitative Determination of Short Branches in High-Pressure Polyethylene by Gamma Radiolysis

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Synopsis

A careful study of the radiolysis products of a series of ethylene α-olefin copolymers and ethylene homopolymers has shown that if a correction is applied, to take into account the fragments arising from scission at chain ends, the remaining products can be quantitatively accounted for as entirely due to scission of side branches introduced onto the backbone chain by the α-olefin comonomer. The cleavage of branches takes place, for all practical purposes, exclusively at the branch points at which the branches are attached to the backbone chain. The same data together with similar radiolysis data of poly(3-methyl pentene-1) and poly(4-methyl pentene-1) have further shown that all branches cleave with equal efficiency, regardless of their length. Radiolysis does, therefore, provide a reliable and convenient tool for the quantitative characterization of high-pressure polyethylene with regard to the unique short-chain branching distribution that is characteristic of each.

A very intriguing structural feature of so-called high-pressure polyethylene is the complex nature of its short-chain branches. There are reasons for believing that a polyethylene resin prepared under a specific set of synthesis conditions is characterized by a unique short-chain branching distribution, and the latter in turn exerts a definite influence on the final resin properties. As such, there has been considerable practical interest, among research workers concerned with polyethylene, in investigating whether one can determine quantitatively the type and number of different branches in high-pressure polyethylene so that one may subsequently correlate this information with the synthesis conditions on the one hand and the resin properties on the other.

The total number of branches present in a polyethylene is generally determined by an infrared method via analysis of the number of methyl groups.[1] Experts in this technique have spent much effort in extending the use of the technique to the analysis of the number of different branch types, but with limited success.[2]

A literature survey has indicated that this problem might be solved satisfactorily by employing high-energy radiation[3,4] for cleaving the branches from the backbone chain, since the weakest bonds, involving tertiary carbon atoms,[5] should be broken preferentially under these condi-

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tions. The rationale here is that, should the branches break, as postulated, the alkyl radicals so formed would immediately react with any of the numerous, readily available hydrogen atoms (the most profuse product of radiolysis of polyethylene) and yield the corresponding alkane molecules, which may subsequently be analyzed in a quantitative fashion. However, the literature survey has also shown that, although the rationale of the method is quite straightforward, the investigators have not so far seemed to arrive at a definitive conclusion about the real practical merit of this method as an analytical tool for determining the various branch types in a quantitative fashion. This paper reports the results of some of our work on this point.

EXPERIMENTAL

Polymer Samples

The ethylene α-olefin copolymers employed in these studies were prepared with Phillips' catalyst. Poly(3-methyl pentene-1) and poly(4-methyl pentene-1) were obtained through the courtesy of California Chemical Co. The low-density polyethylenes were obtained from commerical sources.

Irradiation Procedure

The polymer was first converted into a finely divided form either by being ground in a mill or being dissolved and reprecipitated as a fibrous material which was then dried under vacuum. Approximately 1-g. quantities of the finely divided polymers were accurately weighed into break-seal tubes, which were subsequently evacuated to a pressure of 10^{-5} mm. Hg. The tubes containing the polymer were then flushed three times with dry nitrogen, to insure the complete removal of oxygen, thereafter kept under high vacuum for 15 hr., and finally sealed off.

The irradiations were carried out at ambient temperature with a spent-fuel element, consisting of ^{235}U as the radiation source. The dose received by each sample was about 100 Mrad.

Gas Chromatographic Analysis

After irradiation the break-seal tubes were joined to a gas-sampling system, which was then evacuated, and the seal was broken and the pressure in the system measured. The gases were then quantitatively analyzed on a Barber Coleman Model 20 instrument with a 12-ft. packed column containing 9% glutaronitrile and 21% propylene carbonate deposited on Chromosorb, 100–200 mesh, and maintained at 35°C. The column was calibrated immediately before and after each analysis by using known standard mixtures.

G Values

The *G* value is defined as the number of molecules of the particular product produced per gram of sample per 100 e.v. of incident radiation dose. This calculated, with 10% accuracy, from the gas chromatographic analysis data of the products, weight of the polymer sample irradiated, and radiation dose to which the sample had been subjected.

RESULTS AND DISCUSSION

The first question that arises in one's mind is: To what extent does the thesis postulated—that the alkyl branches on the polyethylene backbone chain will undergo preferential scission at the branch points on radiolysis—actually hold in practice? To answer this question a series of ethylene α-olefin copolymers were prepared by a low-pressure process (Phillips' catalyst system), in which the combined comonomer was in more or less the same mole amounts (approx. 4 mole-%). They were irradiated by the procedure described under "Experimental," and their volatile radiolysis products were analyzed for various hydrocarbons by means of a standard gas chromatographic method. The results are summarized as *G* values in Table I. The most profuse hydrocarbon detected in each case is unmistakably the paraffin corresponding to the branch introduced on the backbone chain by the particular comonomer. Thus, it is methane in the case of propylene copolymer, ethane in the case of butene copolymer, and so on. However, a rather disconcerting feature of these data is that in every instance there are also detected in the radiolysis products small but significant amounts of many other hydrocarbons that cannot be accounted for as readily.

In an attempt to trace the probable cause of these extraneous hydrocarbons a sample of pure homopolymer of ethylene, made by the same low-pressure method as that used in the synthesis of the copolymers, was irradiated under identical conditions and its volatile radiolysis products were analyzed in exactly the same manner as before. The results are presented also in Table I and are indeed very interesting, especially because this particular homopolymer of ethylene is well known to be, for all practical pur-

TABLE I
Radiolysis Products of Ethylene α-Olefin Copolymers

Copolymers	*G* value × 10^2						
	CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}	n-C_5H_{12}	n-C_6H_{14}
Ethylene–propylene	1.7	0.1	0.1	—	0.03	—	—
Ethylene–butene-1	0.2	1.5	0.1	0.1	0.2	0.03	—
Ethylene–pentene-1	0.2	0.3	2.1	0.02	0.05	—	—
Ethylene–hexene-1	0.4	0.3	0.2	0.03	1.2	0.02	—
Ethylene–octene-1	0.2	0.3	0.1	—	0.1	0.1	1.2
Linear polyethylene	0.2	0.3	0.2	0.03	0.06	0.05	—

TABLE II
Efficiency of Radiation Scission of Short Branches

		G value × 10^2					Average $G \times 10^2$
Copolymers	CH_3 per 1000 CH_2	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}	n-C_6H_{14}	CH_3 per 1000 CH_2
Ethylene–propylene	41.9	3.4					0.074
	26.4	1.7					
Ethylene–butene-1	28.7		2.0				
	21.6		1.5				0.072
	4.1		0.3				
Ethylene–pentene-1	25.6			2.1			0.072
	17.1			1.1			
Ethylene–hexene-1	23.5				1.2		0.073
	7.8				0.7		
Ethylene–octene-1	19.1					1.3	
	15.1					1.2	0.074
	11.6					0.9	

poses, a strictly linear polymer characterized by only two chain ends per chain molecule. Not only do we observe every one of the extraneous hydrocarbons in the case of this homopolymer, but, surprisingly enough, their G values are also of the same magnitude as that observed with the copolymers, indicating that the source of the extraneous hydrocarbons appearing in the radiolysis products of the homopolymer and in the copolymers must be one and the same.

We conclude, therefore, that during radiolysis of polyethylene there also takes place a certain amount of random scission at chain ends in addition to the cleavage of branches, and that the observed extraneous hydrocarbons are simply the products derived from this fragmentation at the chain ends. It is quite probable that a portion of the extraneous hydrocarbons is derived from scission of stray branches that might have been introduced on the chains by stray impurities during polymerization, but the fact that one also observes a consistent decrease in the total amount of these extraneous hydrocarbons derived from the homopolymer with an increase in its molecular weight leads us to conclude that the random scission at chain ends is their main cause. Obviously, then, if one makes an appropriate allowance for these radiolysis fragments derived from chain ends, then the only significant paraffin left in the radiolysis products of each copolymer is that corresponding to the branch introduced on the polyethylene backbone by the comonomer.

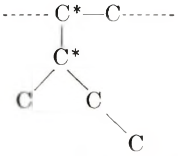
Since it is generally agreed that high-pressure polyethylene actually contains a variety of short branches and not just one type of branch, it is obvious that, if one wants to translate the hydrocarbon analysis of its radiolysis products into quantitative branch-type analysis, one will also need accurate information on the relative efficiency of the scission of different branch types. To obtain this information some additional ethylene α-olefin copolymers, differing significantly in their comonomer content, were irradiated, and the hydrocarbons in their radiolysis products were analyzed as before. Table II lists these results. The efficiency of scission is calculated from the known comonomer content (methyl group analysis) and the observed *G* values of the principal hydrocarbon after application of the appropriate correction against the small chain-end fragmentation. It is clear from the data that all branches of up to 6 carbon atoms or more break off with equal efficiency and that the branch length *per se* exerts little or no effect on the ease of scission.

An observation that is extremely interesting in connection with the conclusion given above is one that pertains to the radiolysis of poly(3-methyl pentene-1) and poly(4-methyl pentene-1); see Table III. The repeat units in these two isomeric polymers are shown below; the tertiary carbon atoms are marked with asterisks.

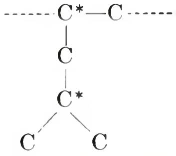
TABLE III

Radiolysis Products of Poly(3-methyl Pentene-1) and Poly(4-methyl Pentene-1)

	G value × 10^2					
Polymer	CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}	C_4H_8
Poly(3-methyl pentene-1)	14.5	14.0	0.6	2.5	16.0	1.1
Poly(4-methyl pentene-1)	24.7	1.0	9.9	11.2	0.7	1.1



Poly(3-methyl pentene-1)



Poly(4-methyl pentene-1)

One would predict that, if the efficiency of scission is the same for all branch types, poly(3-methyl pentene-1) would yield approximately equal amounts of methane, ethane, and *n*-butane, whereas poly(4-methyl pentene-1) would yield in like manner equal amounts of propane and *i*-butane but twice this amount of methane. The data in Table III are indeed in line with the prediction.

RADIOLYSIS OF HIGH-PRESSURE POLYETHYLENE

From the evidence thus far it is clear that radiolysis should provide a practical and direct answer to the long-sought question of the quantitative determination of branching in polyethylene. It was therefore thought most appropriate to irradiate some typical high-pressure polyethylene samples and find out what information of general interest the radiolysis

TABLE IV
Distribution of Short-Chain Branches in High-Pressure Polyethylene

Resin no.	Density, g./cc.	Branches per 1000 methylene units						Total branches per 1000 methylene	Methyl[a] group content per 1000 methylene
		$—CH_3$	$—C_2H_5$	$—C_3H_7$	i-C_4H_9	$—n$-C_4H_9	$—C_5H_{11}$		
A	0.934	2.9	11.8	1.7	0.3	5.9	1.6	24.2	18.8
B	0.929	2.5	15.2	2.1	0.3	8.5	2.0	30.6	24.0
C	0.924	3.8	16.7	2.2	—	9.9	1.8	34.4	30.9

[a] Determined by infrared analysis.

method would actually reveal about the short-chain branching distribution of high-pressure polyethylene as a group. The results observed with three arbitrarily selected resins are shown in Table IV. Since these resins were of commercial origin prior to radiation, each one was cleaned by being dissolved in hot xylene and precipitated with an ethanol–acetone mixture, to remove any impurities or additives that might interfere with the radiolysis mechanism. The number of various branches was calculated from the observed G value of the corresponding hydrocarbons isolated in the radiolysis products and by assuming the same scission efficiency of 0.073×10^{-2} G per branch per 1000 carbon atoms for each type of branch. Further, in view of the fact that in all these resins the short-chain branches outnumbered the chain ends by more than 30 to 1, it was deemed superfluous to try to apply any correction for the fragmentation products at chain ends, a correction which, on the other hand, was so very necessary in the case of α-olefin copolymers.

The most important observation revealed by Table IV is probably the disparity, which is greater than the limits of experimental error, between the total number of all branches, as determined from the radiolysis data, and the methyl group content, as derived by the infrared method. This may be attributed to the fact that the usual infrared method of determining the methyl group content, based on the absorbance at 7.25 μ, does not necessarily count all methyl groups. For example, if two methyl groups are attached to one carbon atom, as in polyisobutylene, the characteristic methyl absorption at 7.25 μ splits, giving two bands at 7.20 μ and 7.40 μ respectively,[2] which consequently are lost in the methyl group determination procedure.

In line with the observations reported by earlier workers, the two most populous branches, according to the radiolysis method, are ethyl and n butyl, which occur in the ratio 2:1, as observed by others.[3]

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Résumé

Une étude soignée des produits de radiolyse d'une série de copolymères d'éthylène et α-oléfine et d'homopolymères d'éthylène a montré que si une correction est appliquée pour tenir compte des fragments se produisant lors de la scission aux extrémités de chaîne, les produits résiduels peuvent être quantitativement évalués comme étant complètement dûs à la scission de branches latérales introduites sur la chaîne principale par le comonomère α-oléfinique. La rupture des branches a lieu, pour tous les buts pratiques, exclusivement au point de jonction auquel les branches sont attachées à la chaîne principale. Les mêmes résultats en même temps que les résultats de radiolyse similaires sur le poly-3-méthyle pentène et poly-4-méthyle pentène-1 ont montré en outre que toutes les branches cassent avec une égale efficacité indépendamment de leur longueur. La radiolyse constitute dès lors un outil reproductible et adapté pour caractériser quantitativement le polyéthylène de haute pression considérant la distribution à courte chaîne qui est caractéristique de chacun d'eux.

Zusammenfassung

Eine sorgfältige Untersuchung der Radiolyseprodukte einer Reihe von Äthylen-α-Olefincopolymeren und Äthylenhomopolymeren zeigte, dass bei Anwendung einer Korrektur zur Berücksichtigung der durch Abspaltung an den Kettenenden entstehenden Produkte, die übrigen Produkte quantitativ, als gänzlich durch Spaltung der durch das α-Olefincomonomere an der Hauptkette eingeführten Verzweigungen gebildet, erklärt werden können. Praktisch findet die Verzweigungsspaltung ausschliesslich an den Verzweigungspunkten statt, an welchen die Verzweigungen an der Hauptkette sitzen. Die gleichen Daten zeigten, gemeinsam mit ähnlichen Daten für die Radiolyse von Poly-3-methylpenten-1 und Poly-4-methylpenten-1, ausserdem, dass alle Verzweigungen unabhängig von ihrer Länge mit gleicher Häufigkeit abgespalten werden. Die Radiolyse liefert daher ein verlässliches und bequemes Mittel zur quantitativen Charakterisierung von Hochdruck-Polyäthylen, unabhängig von der für jede Probe charakteristischen, besonderen Verteilung der Kurzkettenverzweigung.

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Radical-Initiated Copolymerization of Carbon Monoxide and Ethylenimine in the Presence of Ethylene*

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Synopsis

The radical-initiated copolymerization of carbon monoxide and ethylenimine in the presence of ethylene was studied quantitatively. Carbon monoxide copolymerized with difficulty with ethylenimine with α,α'-azobisisobutyronitrile as radical initiator. In the presence of a small amount of ethylene, however, a remarkable amount of crystalline powdery poly-β-alanine (nylon 3) was obtained. The crystalline copolymer, which mainly consists of nylon 3 and contains a small amount of nylon 5 and other substances of higher homologous nylon structure, was obtained in the presence of a large amount of ethylene. This copolymer scarcely contained any ketone structure. Increasing the total feed of the equimolar mixture of the monomers increased the conversion of total monomer and nylon 3 content in the copolymer formed. The effect of increasing carbon monoxide content in this system was to increase both the conversion and the nylon 3 content in the copolymer. In both cases the copolymers were almost identical with nylon 3. Increased ethylene content in the monomer feed, however, increased the conversion and the content of higher homologous nylon structures, such as nylon 5 and 7. From the results it was concluded that ethylene was involved not only in the propagation reaction but also particularly in the initiation reaction.

INTRODUCTION

Recently some results on the gamma-ray-induced copolymerization of carbon monoxide and aziridines were reported by the present writers.[1,2] These results indicated that carbon monoxide copolymerized alternately with ethylenimine and gave a crystalline, powdery poly-β-alanine[1] and that it could copolymerize with ethylenimine and ethylene to yield a copolymer composed of β-alanine, δ-valeramides, and ketone structures.[2] The copolymerization of carbon monoxide and ethylenimine in the presence of various olefins by means of a radical initiator or gamma-ray irradiation was also reported by the writers.[3] In the study it was concluded that the crystalline powdery polyamides consist mainly of β-alanine units (nylon 3 structure) and also of higher homologous nylon structures, such as derivatives of nylon 5 and 7, which were formed in this radical-initiated system.

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To understand the relationship between copolymer structure and reaction conditions in this radical-initiated system, the radical-initiated copolymerization of carbon monoxide and ethylenimine in the presence of ethylene was studied quantitatively. In the present paper the results obtained in the copolymerization are described, and a possible mechanism of the copolymerization is proposed.

EXPERIMENTAL

Materials and Copolymerization

Ethylene (99.9% pure, and oxygen less than 5 ppm) and carbon monoxide (99.2% pure) were obtained commercially. Ethylenimine (EI), obtained commercially, was dried over potassium hydroxide and sodium hydride and then fractionated at 55.5 to 56.0°C. prior to use. α,α'-Azobisisobutyronitrile (AIBN) was obtained commercially.

The copolymerizations were carried out as follows. Measured amounts of EI and AIBN were placed in a stainless-steel high-pressure reaction vessel of 30 ml. capacity. The vessel was degassed twice in vacuo under cooling with liquid nitrogen. Then the measured amounts of ethylene and carbon monoxide were fed into the vessel from the reservoirs. All the copolymerizations were carried out in an oil bath at definite temperature without agitation. The copolymer formed was washed with ethyl ether, dried *in vacuo*, and weighed.

Chemical Analysis of the Copolymer

The composition of the copolymer was determined from the contents of carbon, hydrogen, and nitrogen by elementary analysis. To determine the structure of the copolymer the hydrolysis products of the copolymers obtained in experiments 19 and 15 were analyzed by paper chromatography.[1,2] The hydrolysis products were compared with a mixture of commercial β-alanine, δ-aminovaleric acid, and ζ-aminoenanthic acid by the usual one-way ascending chromatography for amino acids.[4] Both samples were developed on Toyo Roshi No. 50 paper for chromatography with *n*-butanol–glacial acetic acid–water (4:1:5) as solvent. The spots of the hydrolysis products and the standard sample were detected by using an *n*-butanol solution of ninhydrin. The R_f values of the hydrolysis products were assigned to the following amino acids:

Expt. no.	β-Alanine	δ-Aminovaleric acid	ζ-Aminoenanthic acid
19	0.33	—	—
15	0.32	0.46	0.65

Physical Analysis of the Copolymer

The melting point of the copolymer was measured in a nitrogen atmosphere on a Yanagimoto melting point measuring apparatus, Model

MP-S2. The infrared spectrum was obtained by using the potassium bromide pellet technique with a Shimadzu infrared spectrophotometer, Model IR-27, with a sodium chloride prism. The x-ray diffraction diagram was recorded with a powder camera on a Shimadzu x-ray diffractometer, Model GX-3B, and nickel-filtered CuK_α radiation by standard techniques.

RESULTS AND DISCUSSION

As shown in Table I, the polymer was hardly obtained in the case of ethylene (expt. 2), ethylenimine (expt. 1), and ethylene–ethylenimine mixture (expt. 3). A very small amount of the copolymer was obtained in the case of CO–ethylene (expt. 4) and the CO–EI (expt. 5). When a small amount of ethylene was added to the CO–EI system, a large amount of white, powdery copolymer was obtained (expt. 6). This copolymer was confirmed a polyamide containing a small amount of ethylene by the results of elementary analysis and the IR spectrum of the copolymer. A white, powdery copolymer with no ethylene units was obtained by increasing the total feed monomers having the same composition as that in expt. 6 (expt. 19). The hydrolysis product of this copolymer was confirmed β-alanine by means of paper chromatography. From the results of the paper-chromatographic analysis, the elementary analysis, and the IR spectrum the copolymer obtained in expt. 19 was concluded to be poly-β-alanine, i.e. nylon 3.

Further, the hydrolysis product of the copolymer (expt. 15) containing a large amount of ethylene was compared with commercial β-alanine, δ-aminovaleric acid, and ζ-aminoenanthic acid by means of paper chromatography. Thus, the definite spots corresponding to β-alanine and to δ-aminovaleric acid and the faint spot corresponding to ζ-aminoenanthic

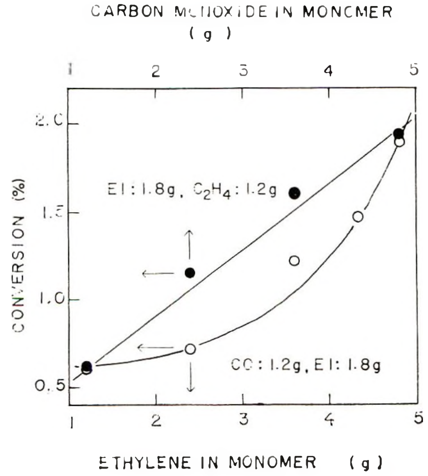


Fig. 1. Conversion versus amount of added monomer: AIBN, 0.090 g.; temp., 60°C.; time, 5 hr.

TABLE I

Radical-Initiated Copolymerization of Carbon Monoxide and Ethylenimine in the Presence of Ethylene[a]

Expt. no.	Monomers in feed, g.			Yield, g.	M.p., °C.	Polymer compn., mole ratio[b]			H_2O,[c] mole-%	Elem. anal., found, %		
	EI	CO	C_2H_4			EI	CO	C_2H_4		C	H	N
1	4.6	—	—	trace	—	—	—	—	—	—	—	—
2	—	—	3.0	trace	—	—	—	—	—	—	—	—
3	4.6	—	3.0	0	—	—	—	—	—	—	—	—
4	—	3.0	3.0	0.003	175–185	—	—	—	—	—	—	—
5	4.6	3.0	—	0.004	304–312	—	—	—	—	—	—	—
6	4.6	3.0	0.75	0.173	300–306	1.00	0.82	0.11	7.19	50.85	8.07	19.55
7	4.6	3.0	3.0	0.283	294–297	1.00	0.82	0.15	5.60	51.74	8.11	19.35
8	4.6	0.75	3.0	0.048	215–224	1.00	0.82	0.36	5.22	54.32	8.61	17.90
9	1.15	3.0	3.0	0.125	288–294	1.00	0.77	0.21	5.62	52.67	8.41	19.27
10	1.84	1.2	1.2	0.027	266–275	1.00	0.61	0.35	11.40	53.34	9.33	18.76
11	2.45	1.6	1.6	0.056	263–278	1.00	0.70	0.31	8.30	53.47	8.93	18.74
12	3.7	2.4	2.4	0.166	280–292	1.00	0.83	0.25	4.01	53.45	8.32	18.68
13	1.84	1.2	2.4	0.039	243–278	1.00	0.63	0.36	5.50	55.26	9.23	19.31
14	1.84	1.2	3.6	0.081	235–245	1.00	0.76	0.48	5.65	55.73	9.05	17.47
15	1.84	1.2	4.3	0.108	230–250	1.00	0.79	0.58	5.93	55.06	8.92	18.62
16	1.84	1.2	4.8	0.148	238–250	1.00	0.72	0.67	6.30	57.55	9.48	16.49
17	1.84	2.4	1.2	0.062	273–284	1.00	0.85	0.20	5.49	52.36	8.17	18.77
18	1.84	3.6	1.2	0.106	301–307	1.00	0.88	0.12	5.21	51.29	7.86	19.16
19	1.84	4.8	1.2	0.151	312–317	1.00	0.96	0	4.96	49.38	7.29	19.62

[a] A 30 ml. autoclave was used; AIBN, 0.090 g.; time, 5 hr.; temp., 60°C.

[b] Polymer composition was calculated with EI, CO, and C_2H_4.

[c] Absorbed water.

acid were detected. Accordingly, it was concluded that the copolymer is mainly composed of nylon 3 units and, moreover, contains nylon 5 and 7 structures. As was described above, the copolymer composition depends on the reaction conditions. Therefore a quantitative study was carried out over a wide range of reaction conditions, as shown in Table I.

As shown in Figure 1, the conversion increased with the increase of CO or ethylene content in a given monomer mixture and also in the case of total feed of equimolar monomer mixture.

Effect of Total Feed of Monomer on the Copolymerization

Figure 2 shows the relationship between the total feed of an equimolar monomer mixture and both the composition and the melting point of the copolymer. With increasing total feed of equimolar monomer mixture the ethylene content in the copolymer approached zero, the molar ratio of EI to CO approached unity, and the melting point of the copolymer increased and approached that of nylon 3.

From these results it is concluded that the structure of the copolymer approaches that of nylon 3 with an increase of total feed. The results also indicate that the dependence of copolymer composition on the initial pressure of the monomers is larger than that on the initial monomer composition. On the other hand, Brubaker and his co-workers[5] found the same result in their study of the radical-initiated copolymerization of CO and ethylene; that is, the CO content in the copolymer increased with

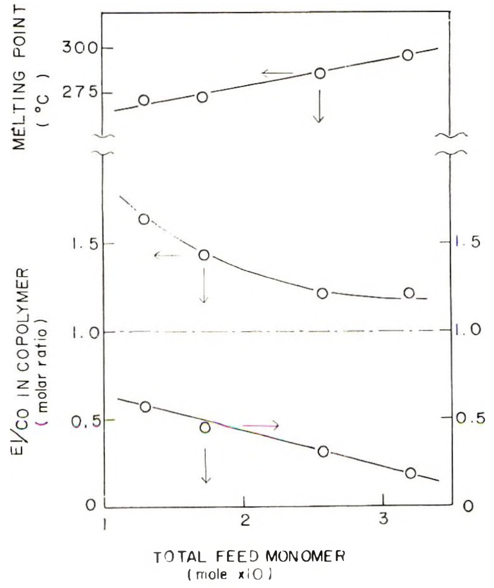


Fig. 2. Total feed monomer versus composition and melting point of copolymer: autoclave capacity, 30 ml.; molar ratio of monomers, CO/EI/C_2H_4, 1:1:1; AIBN, 0.090 g.; temperature, 60°C.; time, 5 hr.

increasing feed pressure of monomer mixture with a definite composition. These results can be explained on the basis of the fact that the ratio of the fugacity coefficient of ethylene to that of CO for the constant gas mixture (f_E/f_{CO}) decreases with increasing total pressure.

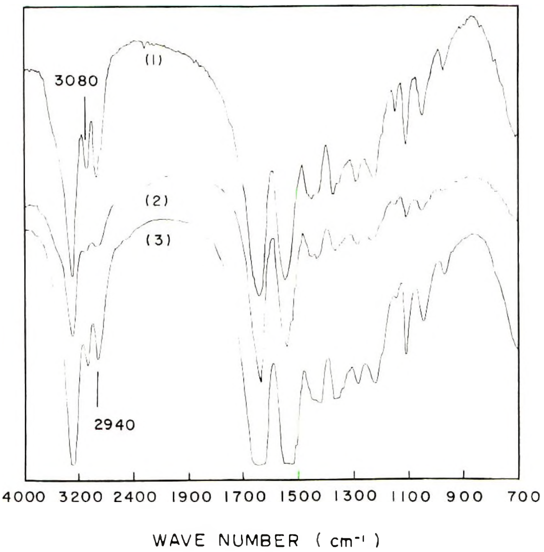


Fig. 3. Infrared spectra of copolymers obtained in (*1*) expt. 10, (*2*) expt. 12, and (*3*) expt. 7.

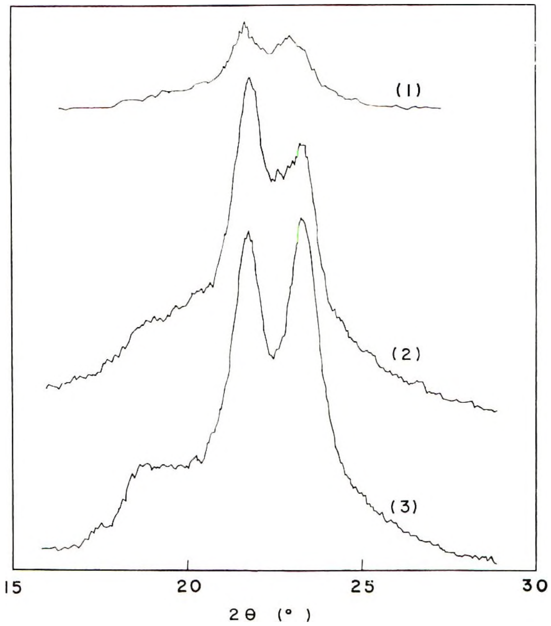


Fig. 4. X-ray diffraction diagrams of copolymers obtained in (*1*) expt. 10, (*2*) expt. 12, and (*3*) expt. 7.

The IR spectra and x-ray diffraction diagrams of the copolymers are shown in Figures 3 and 4, respectively.

All the copolymers displayed major absorption peaks assigned to secondary amide near 3300, 3080, 1640, and 1540 cm.$^{-1}$ but they did not give a ketonic band at about 1700 cm.$^{-1}$. The fact that no ketonic band appeared in the copolymer contradicts the result obtained by gamma-ray irradiation.[2] The IR spectral data in the experiment with constant monomer composition shows that decreasing the total feed of the equimolar mixture results in increasing the absorption ratio of the methylene band at 2940 cm.$^{-1}$ to NH the band of amide at 3080 cm.$^{-1}$ (ν_{2940}/ν_{3080}). These results suggest that the copolymer obtained with low monomer feed (expt. 10) contains nylon 5 or higher homologous nylon units.

As shown in Figure 4, the effect of increasing the total feed of monomer was to increase both the crystallinity of the copolymer and the intensity of the peak at about 23.75° (2θ), corresponding to the main peak of nylon 3.[1] Thus, the x-ray diffraction diagram of the copolymer becomes similar to that of nylon 3 with an increase of total feed of monomer. This fact is consistent with the melting point, elementary analysis, and the IR spectrum results for the copolymer.

Effect of Ethylene on the Copolymerization

The relationship between the ethylene content in the monomer mixture and the composition and melting point of the copolymer is shown in Figure 5.

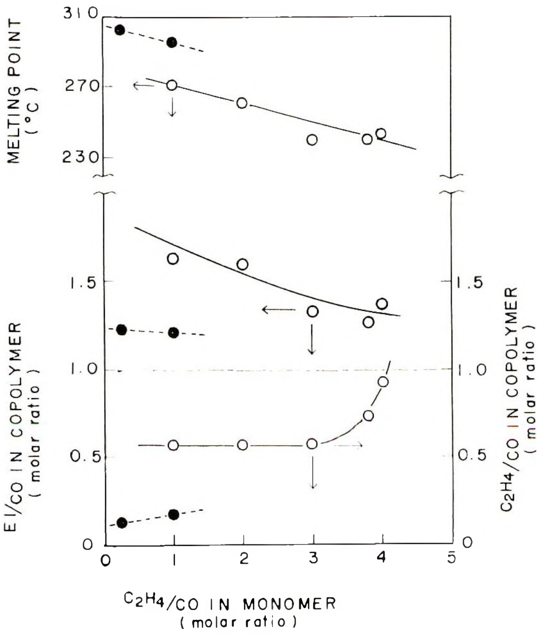


Fig. 5. Ethylene content in monomers versus composition and melting point of copolymer: (○) EI, 1.84 g., CO, 1.2 g.; (●) EI, 4.6 g., CO, 3.0 g.; molar ratio of monomers, EI/CO, is unity.

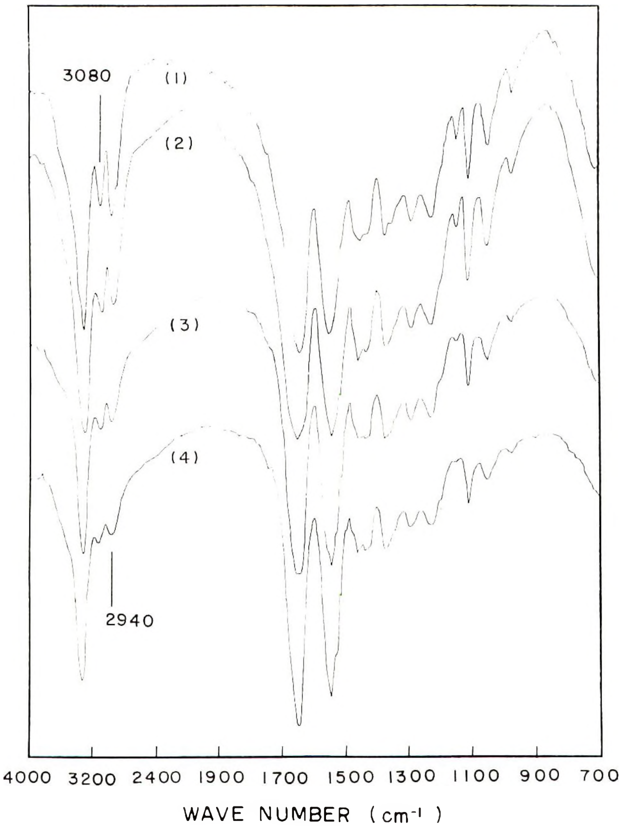


Fig. 6. The IR spectra of copolymers obtained (*1*) expt. 10, (*2*) expt. 13, (*3*) expt. 14, (*4*) expt. 15, and (*5*) expt. 16.

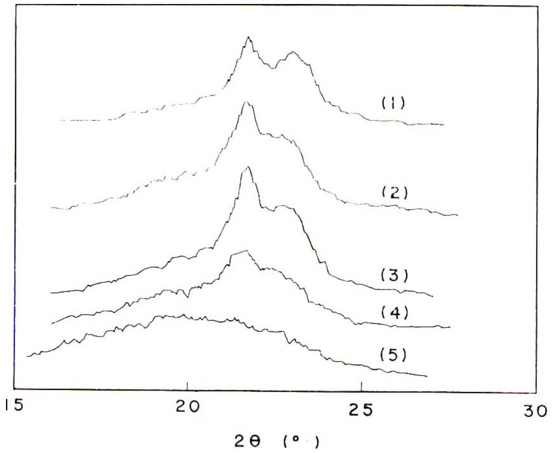


Fig. 7. X-ray diffraction diagrams of copolymers obtained in (*1*) expt. 10, (*2*) expt. 13, (*3*) expt. 14, (*4*) expt. 15, and (*5*) expt. 16.

The figure shows that increasing the amount of added ethylene in the equimolar CO–EI system resulted in a decrease of melting point and a decrease of the ratio EI/CO in the copolymer, approaching unity. The deviation of the molar ratio EI/CO from unity is not clear but may be ascribed to the addition of EI to the chain end of an ethyl group, yielding a small amount of polyamine. The molar ratio C_2H_4/CO in the copolymer increases rapidly from 0.57 to 0.93, as it increases from 3 to 4 in the monomer. The fact that C_2H_4/CO in the copolymer is almost constant when C_2H_4/CO in the monomer is varied from 3 to unity may be ascribed to the compensation effected by increasing the partial pressure of the ethylene and decreasing the fugacity coefficient of the ethylene with an increase of the partial pressure.

It was observed that in the IR spectra of the copolymers containing a large amount of ethylene (Fig. 6) no ketonic band at about 1700 cm.$^{-1}$ appeared, but there was an increase in the value of ν_{2940}/ν_{3080} with an increase of ethylene content in the monomer. These results indicate that ethylene did not attack the carbonyl end but the EI end, yielding the higher nylon structures, such as nylon 5 and 7. This consideration is consistent with the paper chromatographic analysis of the copolymer obtained in expt. 15 (C_2H_4/CO in monomers, 3.8). The difference between the white and black circles in Figure 5 is due to the difference in the total feed of monomer.

As shown in Figure 7, x-ray diffraction diagrams of the copolymer indicate that the effect of increasing the ethylene content in the monomer is to decrease both the crystallinity of the produced copolymer and the intensity of the peak near 23.75° of nylon 3. Furthermore, the melting point of the copolymer decreased with increasing ethylene content in the monomer (Fig. 5). From these results it is concluded that the higher nylon unit was contained in the main chain of nylon 3, not as a mixture but as the copolymer.

Effect of Carbon Monoxide on the Copolymerization

Figure 8 indicates that the composition and the melting point of the copolymer approach those of nylon 3 with an increase of the CO content in the monomer as well as in the case of an increase of the total feed of the monomer. As described previously, the amount of nylon 3 in the system CO–EI–C_2H_4 (expt. 19) was much larger than that in the system CO–EI (expt. 5); See Table I. This fact suggests that ethylene is not only the propagating monomer but also particularly a cocatalyst for the initiation reaction.

Figures 9 and 10 are the IR spectra and x-ray diffraction diagrams of the copolymers, respectively. As shown in these figures, the effect of increasing the CO content in the monomer was to decrease the intensity of the absorption peak of the methylene group at 2940 cm.$^{-1}$, increase the crystallinity of the copolymer, and increase the intensity of the peak (23.75°)

of nylon 3. The results are consistent with the composition and the melting point of the copolymer.

Mechanism of Radical-Initiated Copolymerization of Carbon Monoxide and Ethylenimine in the Presence of Ethylene

On the basis of these results a reaction mechanism for the copolymerization of carbon monoxide–ethylenimine–ethylene with AIBN was proposed as follows.

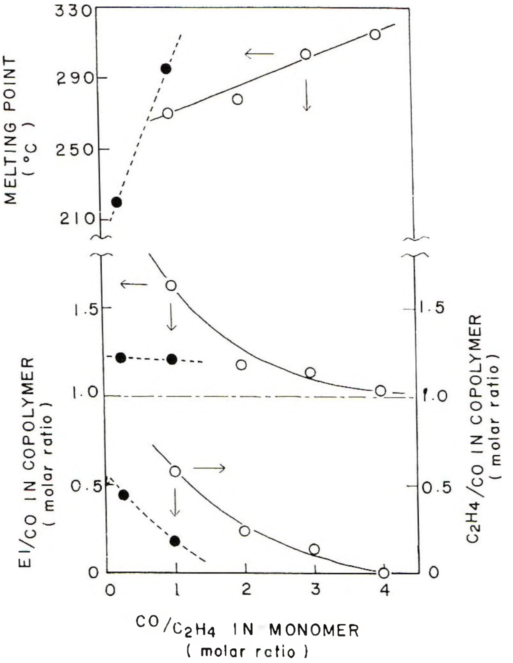
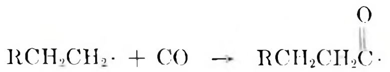


Fig. 8. CO content in monomers versus composition and melting point of copolymer: (○) EI, 1.84 g., C_2H_4, 1.2 g.; (●) EI, 4.6 g., C_2H_4, 3.0 g.; molar ratio of monomers, EI/C_2H_4, is unity.

Initiation. Only the ethylene in the three monomers can homopolymerize and also copolymerize with CO to yield polyketone by radical initiation. In addition, as was described above, the radical-initiated copolymerization of CO and EI was initiated only in the presence of ethylene. From these results a two-step initiation mechanism, which has already been reported,[3] was proposed as follows;

$$\mathrm{I} \rightarrow 2\,\mathrm{R}\cdot$$

$$\mathrm{R}\cdot + \mathrm{CH_2{=}CH_2} \rightarrow \mathrm{RCH_2CH_2}\cdot \qquad \text{(A)}$$



$$\mathrm{RCH_2CH_2}\cdot + \mathrm{CO} \rightarrow \mathrm{RCH_2CH_2}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\cdot \qquad \text{(B)} \qquad (1)$$

Reaction (A) is the reaction of ethylene and free radical ($R\cdot$) formed by the decomposition of AIBN. Reaction (B) is the formation of the initiating radical through the reaction of CO and $RCH_2CH_2\cdot$.

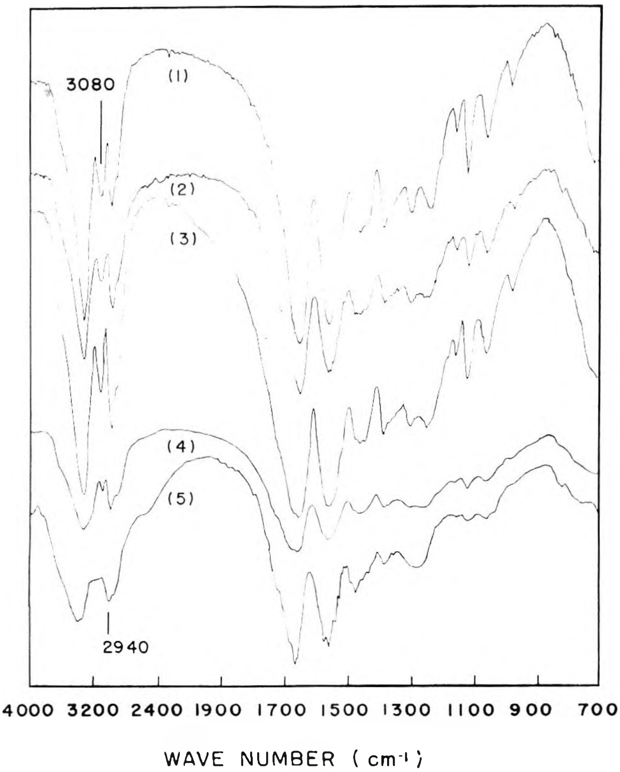
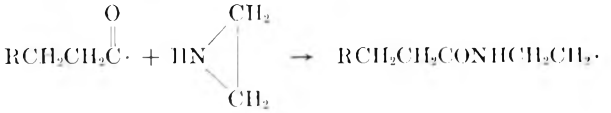


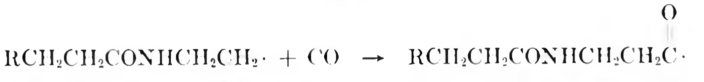
Fig. 9. IR spectra of copolymers obtained in (*1*) expt. 10, (*2*) expt. 17, (*3*) expt. 18, and (*4*) of nylon 3 in expt. 19.

Propagation. In view of the fact that the carbonyl radical produced by reaction (A) has a high electrophilicity the carbonyl radical was considered to react exclusively with nucleophilic ethylenimine as follows:



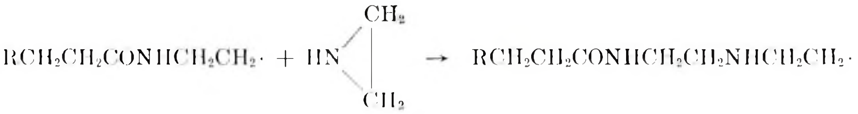
$$RCH_2CH_2\overset{\overset{O}{\|}}{C}\cdot + HN\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \rightarrow RCH_2CH_2CONHCH_2CH_2\cdot \qquad (2)$$

That no polyketone structure is in the copolymer may indicate that the reaction of the carbonyl radical with ethylene does not take place. The following three modes of propagation reaction are proposed:



$$RCH_2CH_2CONHCH_2CH_2\cdot + CO \rightarrow RCH_2CH_2CONHCH_2CH_2\overset{\overset{O}{\|}}{C}\cdot \qquad (3)$$

$$RCH_2CH_2CONHCH_2CH_2\cdot + CH_2{=}CH_2 \rightarrow RCH_2CH_2CONHCH_2CH_2CH_2CH_2\cdot \qquad (4)$$



$$\mathrm{RCH_2CH_2CONHCH_2CH_2\cdot + HN\left\langle\begin{array}{l}CH_2\\ \vert\\ CH_2\end{array}\right. \rightarrow RCH_2CH_2CONHCH_2CH_2NHCH_2CH_2\cdot} \quad (5)$$

The fact that the main structure of the copolymer is nylon 3 indicates that reactions (2) and (3) take place infrequently.

The fact that the content of nylon 5 or other higher homologous nylons in the copolymer depended on the ethylene content in the monomer mixture indicates that the rate of reaction (4) increased with the ethylene content. The fact that the content of higher homologous nylons is much smaller than that of nylon 3 in the copolymer leads to the conclusion that reaction (4) is much slower than reaction (3).

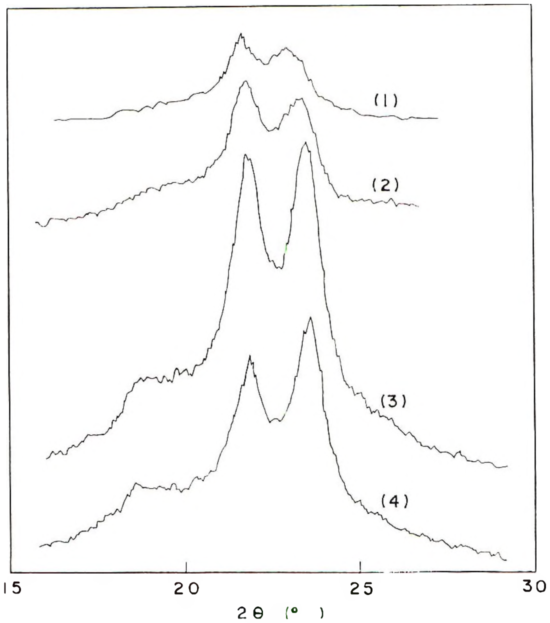


Fig. 10. X-ray diffraction diagrams of copolymer obtained in (*1*) expt. 10, (*2*) expt. 17, (*3*) expt. 18, and (*4*) of nylon 3 in expt. 19.

The decrease of the CO content or the total feed monomer in this system brought about a rise in the EI/CO ratio in the copolymer from unity, as shown in Figures 2 and 8. This also indicates that reaction (5) gives a polyamine unit as a side reaction, which takes place at a slow rate.

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Résumé

La copolymérisation radicalaire du monoxyde de carbone et de l'éthylènimine en présence d'éthylène a été étudiée quantitativement. L'oxyde de carbone copolymérise difficilement avec l'éthylènimine en présence d'α,α'-asobisisobutyronitrile comme initiateur radicalaire. En présence de petites quantités d'éthylène toutefois, une quantité remarquable de poly-β-alanine poudreuse et cristalline (nylon 3) a été obtenue. Le copolymère cristallin, qui est constitué principalement de nylon 3 et qui contient une faible quantité de nylon 5 et d'autres structures de nylons homologues supérieurs, a été obtenu en présence de grandes quantités d'éthylène. Ce copolymère contient quelques rares structures cétoniques. En augmentant la quantité totale du mélange équimoléculaire des monomères on augmente la conversion des monomères totaux et la teneur en nylon 3 au sein du copolymère formé. L'effet et l'augmentation de la teneur en monoxyde de carbone dans le système accroît à la fois la conversion et la teneur en nylon 3 des copolymères. Dans les deux cas décrits ci-dessus, les copolymères formés sont très similaires au nylon 3. Toutefois une augmentation de la teneur en éthylène dans le mélange de départ donnait une conversion accrue et des teneurs plus élevées en nylon supérieur tel que le nylon 5 et le nylon 7. Au départ de ces résultats, on peut conclure que l'éthylène est inclu non suelement dans la réaction de propagation mais également particulièrement dans la réaction d'initiation.

Zusammenfassung

Die radikalisch gestartete Copolymerisation von Kohlenmonoxyd und Äthylenimin in Gegenwart von Äthylen wurde quantitativ untersucht. Mit α,α'-Azobisisobutyronitril als radikalischem Starter trat kaum eine Copolymerisation zwischen Kohlenmonoxyd und Äthylenimin auf. In Gegenwart einer kleinen Menge Äthylen dagegen wurde eine bemerkenswerte Menge von kristallinem, pulvrigem Poly-β-alanin (Nylon-3) erhalten. Das kristalline Copolymere, das hauptsächlich aus Nylon-3 besteht und eine kleine Menge von Nylon-5 und anderen höher homologen Nylonstrukturen enthält, wurde in Gegenwart einer grossen Äthylenmenge erhalten. Dieses Copolymere enthielt kaum Ketonstrukturen. Eine Vergrösserung des Gesamtansatzes der äquimolaren Mischung der Monomeren führte zu einer Erhöhung des Umsatzes an Gesamtmonomeren und des Nylon-3-Gehaltes im gebildeten Copolymeren. Der Einfluss der Erhöhung des Kohlenmonoxydgehaltes in diesem System bestand in einer Erhöhung sowohl des Umsatzes als auch des Nylon-3-Gehaltes des Copolymeren. In beiden oben beschriebenen Fällen waren die gebildeten Copolymeren weitgehend mit Nylon-3 identisch. Eine Erhöhung des Äthylengehaltes im Monomeransatz jedoch lieferte erhöhten Umsatz und einen Gehalt an höher homologen Nylonstrukturen, wie Nylon-5 und 7. Aus den Ergebnissen wurde der Schluss gezogen, dass Äthylen nicht nur an der Wachstumsreaktion sondern besonders auch an des Startreaktion beteiligt ist.

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A Study of the Molecular Weights of Tetrahydrofuran–Propylene Oxide Copolymers by Gel Permeation Chromatography and Other Methods*

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Synopsis

The cationic copolymerization of tetrahydrofuran and propylene oxide was studied in a batch system. Boron fluoride ethyl ether and 1,2-propanediol were used as catalyst–cocatalyst system. Number-average molecular weights $\bar{M}_n$ of various copolymers were determined by vapor-pressure osmometry (VPO) and hydroxyl endgroup analysis (OH). The VPO and OH molecular weights differed considerably. To explain the differences, several copolymers were analyzed by gel permeation chromatography (GPC). The chromatograms obtained showed for each copolymer analyzed two peaks, one located in the high molecular weight region, the other in the low molecular weight region. An attempt is made to correlate the results and to show the usefulness of GPC in the characterization of THF–PO copolymers.

INTRODUCTION

The preparation of copolyether diols, as intermediates in the formation of polyurethane elastomers has been under investigation for some time now in this department. The work was initiated when a need arose for binder materials having reduced cold-hardening and improved molding properties. It is believed that such properties could be obtained by preparing the polyurethanes from diisocyanates and from low molecular weight copolyether diols made from straight-chain and branched-chain monomers.[1] Since little information is available in the literature on the preparation of such diols, it was decided to study the cationic copolymerization of alkylene oxides. The tetrahydrofuran–propylene oxide system was therefore investigated, with boron fluoride ethyl ether as catalyst and propanediol as the source of hydroxyl groups, to meet cocatalyst requirements.

Emphasis has been placed on the kinetics of this copolymerization reaction and on the characterization of the copolyether diols obtained. Kinetic results are reported elsewhere,[2,3] and results on the molecular weights are presented here.

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† Postdoctorate Fellow, National Research Council of Canada.

EXPERIMENTAL

Materials

The following chemicals were used for this study after appropriate purification.[4] (*a*) Comonomers: propylene oxide (Anachemia, polymerization grade, water content 30 ppm); tetrahydrofuran (Anachemia, b.p. 64 to 66°C., water content 300 ppm). (*b*) Solvent : ethylene chloride (Fisher certified reagent, water content 11 ppm). (*c*) Catalyst: boron fluoride ethyl ether (Eastman, purified). (*d*) Cocatalyst: 1,2-propanediol (Fisher, U.S.P., water content 387 ppm).

Methods and Equipment

In most of the experiments the solvent and comonomers were blended in equal molar ratios; that is, 0.4 mole of ethylene chloride (EC) was mixed with 0.4 mole of various tetrahydrofuran–propylene oxide (THF–PO) mixtures. To these mixtures catalyst and cocatalyst were added. The amount of catalyst added was 7×10^{-4} mole (except when the effect of catalyst concentration was being studied), and that of cocatalyst varied between 0 and 12 mole-% of the comonomers charged.

The glassware used for this study was thoroughly washed, dried, and finally purged with dry nitrogen gas before use. The reactions were carried out in an atmosphere of dry nitrogen gas, in a 150 ml. round-bottom Pyrex flask, as shown in Figure 1. Reactants were introduced, and samples were withdrawn for analysis through the lateral port on the right, which was covered with a rubber septum.

The disappearance of reactants was followed by vapor-phase chromatography with a Perkin-Elmer vapor fractometer (model 154-C) equipped with

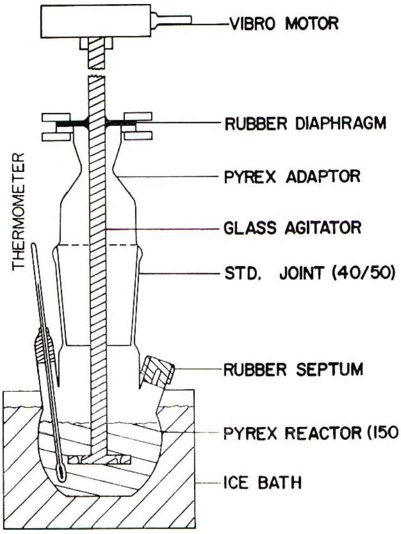

Fig. 1. Schematic diagram of reactor used for copolymerization reactions.

thermistor detectors and a type R column. The chromatograms were recorded on a Westronics two-pen recorder (model DU/11A), while areas under the peaks were evaluated with a Self-Organizing-Systems electronic integrator (model RI 220).

When no changes in the monomer concentrations were detected by gas chromatography, the reaction was presumed to be terminated. Residual reaction charge was then removed from the copolymer by evaporation under reduced pressure at 50°C. at first with a water aspirator and later with a high-vacuum mechanical pump.

The number-average molecular weights $\bar{M}_n$ of the copolymers were determined by vapor-pressure osmometry (VPO) and hydroxyl endgroup analysis (OH).

The Mechrolab vapor-pressure osmometer Model 301A was operated at 37°C., methyl ethyl ketone used as solvent. The calibration constant of the instrument (440 ohms/mole/liter) was obtained by using standard substances of known molecular weights, such as poly(propylene glycols) (PPG-425 and PPG-2025), poly(ethylene glycols) (PEG-200, PEG-600, PEG-1000), and benzil (210).

Hydroxyl endgroup analysis was carried out in a phthalation procedure. Experimentation showed that 40 mole-% excess phthalic anhydride in the phthalic anhydride–pyridine reagent is necessary to give complete esterification of the copolyether diols being analyzed.[5]

The distributions of molecular weight of the copolymers were determined by gel permeation chromatography (GPC) with the Waters Associates GPC instrument Model 100 at McMaster University. The conditions of analysis were temperature 25°C., solvent THF, sample concentration 0.5 wt.-%, sample size 1 ml. in solvent, flow rate 1 ml./min., columns 3×10^4, 1×10^3, 1×400 A., plate count 843. The calibration curve of angstroms versus counts was used as supplied by the McMaster University laboratory.

The procedure outlined by Waters Associates was followed in interpreting the GPC distribution curves.[6] Number-average molecular lengths $\bar{A}_n$ have been calculated for the total distribution curve, $\bar{A}_n$ (T) and for the distribution curves of each peak, $\bar{A}_n$ (A) and $\bar{A}_n$ (B), where (T), (A), and (B) refer to the total distribution curve, peak A, and peak B, respectively. (GPC technique has been described in a number of papers and reviews published in the past.[7–18])

Calculation of Comonomer Conversions, Copolymer Yields, and Determination of Reaction Times

The conversion was calculated by dividing the difference between the initial and the final concentrations of a monomer (as determined by vapor-phase chromatography) by its initial concentration. The yield of copolyether diol was calculated by dividing the weight of nonvolatile products obtained at the end of the reaction by the total weight of comonomers and diol charged to the reactor. The reaction time in a given experiment was the overall time required to obtain 100% consumption of propylene oxide. In a few instances the reaction was stopped before this point was reached.

RESULTS

A typical GPC chromatogram of THF–PO copolymer prepared in this laboratory is presented in Figure 2. Two peaks can be seen, one (A) located in the high molecular weight region and the other (B) in the low molecular weight region.

The number-average molecular lengths $\bar{A}_n$ were calculated for the total distribution curve $\bar{A}_n$(T) and for the distribution curves of each peak, $\bar{A}_n$(A) and $\bar{A}_n$(B).

The low molecular weight peak B always appeared in the same region, (16 A. < $\bar{A}_n$(B) < 18 A.) for all of the copolymers analyzed.

These results and others obtained from various experiments carried out under different operating conditions are reported in Table I and Figures 3, 4, and 5.

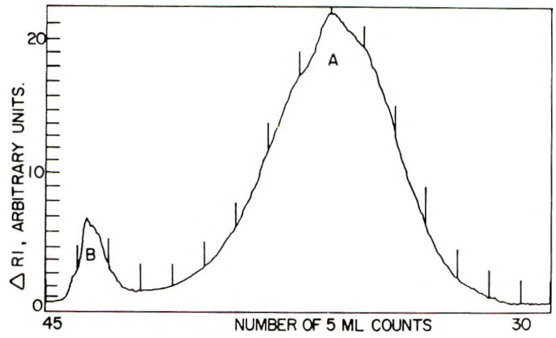

Fig. 2. Typical GPC chromatogram of a THF–PO copolymer.

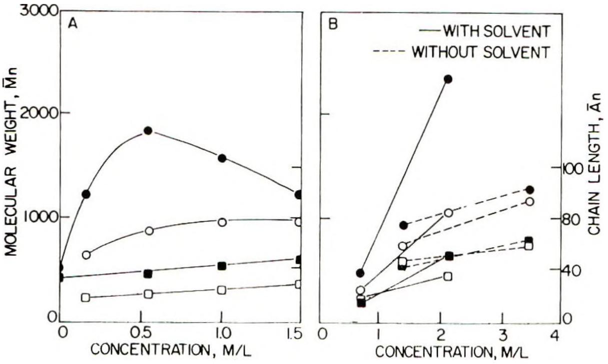

Fig. 3. Number-average molecular weight versus concentration of (A) THF and (B) PO: (●) $\bar{M}_n$(OH), (■) $\bar{M}_n$(VPO), (○) $\bar{A}_n$(A), (□) $\bar{A}_n$(T).

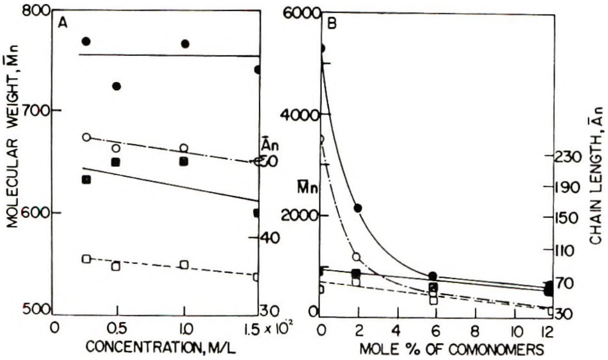

Fig. 4. Number-average molecular weight versus concentration of (A) catalyst and (B) cocatalyst: (●) $\bar{M}_n$(OH), (■) $\bar{M}_n$(VPO), (○) $\bar{A}_n$(A), (□) $\bar{A}_n$(T).

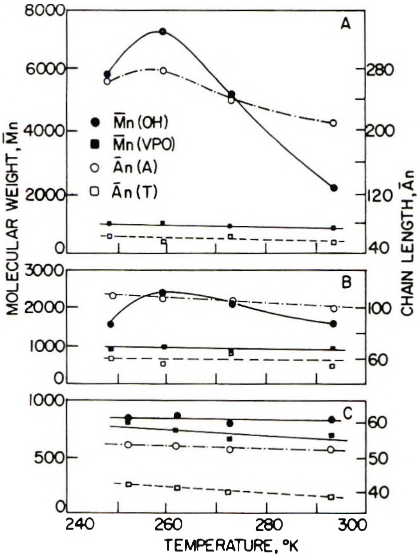

Fig. 5. Effect of copolymerization reaction temperature on number-average molecular weight: (A) 0% diol, (B) 2% diol, (C) 6% diol.

TABLE I

Molecular Weights and Experimental GPC Number-Average Molecular Lengths for Propylene oxide, 1,2-Propanediol, Dioxane, Ethylene Chloride, and the Secondary Product (Peak B, GPC Chromatogram)

Compound	Mol. wt.	No. of 5 ml. count	Number-average molecular length $\bar{A}_n$, A.
Propylene oxide	58.5	47.5	4.5
1,2-Propanediol	76.1	44.5	12.0
Dioxane	88.1	46.9	5.6
Ethylene chloride	97.0	46.5	7.5
Secondary product (peak B, GPC chromatogram)	116.0	43–44	16.0–18.0

DISCUSSION

The discrepancy between $\bar{M}_n$(VPO) and $\bar{M}_n$(OH) may be understood in the limitations of the two techniques employed. The vapor-pressure osmometry technique is sensitive to the total number of particles in solution, whereas the endgroup technique sees only those particles having hydroxyl endgroups. Should there be in the sample low molecular weight substance without hydroxyl endgroups, such as cyclic ethers, the hydroxyl endgroup analysis will yield molecular weights higher than those obtained by vapor-pressure osmometry.

In Figure 2 one sees that the copolymer samples contain two products. One of these is a long-chain high molecular weight material, indicated by peak A; the other is a short-chain low molecular weight material, indicated by peak B. In all the copolymers analyzed peak B was found in the 16 to 18 A. region, and peak A was found to be between 27.3 and 277.0 A., depending on the reaction conditions.

Figure 4*b* shows that with decreasing OH concentration in the copolymerization reaction mixture the $\bar{M}_n$(OH) increases, following an inverse-function law. Under the same conditions $\bar{M}_n$(VPO), however, undergoes little change. If only hydroxylated products were formed in this system, the number of particles would be proportional to the OH concentration, and $\bar{M}_n$(VPO) would vary in a manner similar to $\bar{M}_n$(OH). The $\bar{M}_n$(VPO) results indicate, however, that the total number of particles in the system remains essentially constant. This is evidence that the substance responsible for peak B has no OH endgroups. Therefore, this substance is not a copolyether diol but some other low molecular weight product.

In attempts to identify the product responsible for peak B the substances PO, EC, 1,2-propanediol, and dioxane were analyzed separately by GPC. The resulting chromatograms contained one peak each, appearing at chain-length values smaller than those obtained for peak B (Table I). As far as THF and any of its impurities are concerned, they were not responsible for peak B, because of the following considerations: THF was used as the GPC solvent, and the intensity of peak B varied with the operating reaction conditions, such as OH concentration. It is quite clear, therefore, that these materials as such were not responsible for peak B. Instead it is speculated that a cyclic dimer of propylene oxide was formed during the copolymerization reaction. Such dimers have been found in the products of the homopolymerization of ethylene oxide[19–21] and styrene oxide.[22]

To confirm this point of view, when a GPC instrument is available in this laboratory, the following experiments are planned: (*a*) fractionation of polymer, to separate the products of peak A and peak B, and their analysis by physical and chemical methods and (*b*). synthesis of dimethyl dioxane (because this product is not readily available commercially) and its GPC analysis.

These experiments will not only help identify the products present in the polymers but will also throw light on their composition and structure.

The influence of the initial concentration of THF on $\bar{M}_n$(OH), $\bar{M}_n$(VPO), $\bar{A}_n$(A) and $\bar{A}_n$(T) is shown in Figure 3*a*. The $\bar{M}_n$(VPO) and $\bar{A}_n$(T) are influenced in the same way, both increasing to the same extent with increasing concentration of THF. The $\bar{M}_n$(OH), however, goes through a maximum, and $\bar{A}_n$(A) rises toward an asymptotic value.

Limited data were available for Figure 3*b*. One can see, nevertheless, that the initial concentration of PO has the following effects: (*a*) when solvent was used in the reaction charge, all the four parameters $\bar{M}_n$(OH), $\bar{M}_n$(VPO), $\bar{A}_n$(A), and $\bar{A}_n$(T) increased proportionately with the concentration of PO, and (*b*) in the absence of solvent a similar effect was observed but to a lesser extent.

The initial concentration of the catalyst has no effect on the number-average molecular weights and number-average molecular chain lengths of the copolymers; see Figure 4*a*. The cocatalyst, on the contrary, has a marked influence on these values; see Figure 4*b*. Copolymers prepared with higher hydroxyl concentrations in the copolymerization reaction mixtures have lower number-average molecular weights and number-average molecular chain lengths.

The temperature of the copolymerization reaction has only a slight effect on $\bar{M}_n$(VPO) and $\bar{A}_n$(T) values, but both $\bar{M}_n$(OH) and $\bar{A}_n$(A) show slight variations, particularly at lower OH concentrations; see Figures 5*a*, 5*b*, and 5*c*.

In conclusion, (*a*) a correlation exists between $\bar{M}_n$(VPO) and $\bar{A}_n$(T) but none between $\bar{M}_n$(OH) and $\bar{A}_n$(A) and, furthermore, $\bar{M}_n$(OH) is the upper limit of the true molecular weight of the copolyether diols obtained, whereas the difference between $\bar{M}_n$(OH) and $\bar{M}_n$(VPO) is a result of the dilution effects of the low molecular weight product found in GPC analysis; (*b*) the polymers prepared are mixtures.

Confirmation of these findings should come from molecular weights $\bar{M}_n$ calculated for each peak (or for each product) appearing in the GPC chromatograms. Attempts are presently being made to calculate Q, the molecular weight per chain length (since $\bar{M}_n = Q \times \bar{A}_n$).

Progress in this direction is hampered because of the non-availability of a GPC instrument in this laboratory, because of the unverified composition and quantity of the low molecular weight product, and because of the complicated geometry of the THF-PO copolymer molecule.

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Résumé

La copolymérisation cationique du tétrahydrofurane avec l'oxyde de propylène a été étudiée en bloc. Le fluorure de bore complexé à l'éther éthylique et le 1,2-propane-diol ont été utilisés comme systèmes catalyseurs, co-catalyseurs. Les poids moléculaires moyens en nombre $\bar{M}_n$, des différents copolymères ont été déterminés par osmométrie de pression de vapeur (VPO) et par analyse des groupes terminaux (OH). Les poids moléculaires obtenus par VPO et OH diffèrent considérablement. Pour expliquer ces différences, de nombreux copolymères ont été analysés par chromatographie par perméation sur gel (G.P.C.). Les chromatogrammes obtenus ont pour chaque copolymère analysé, deux pics: un localisé dans la région de haut poids moléculaire, l'autre dans la région de bas poids moléculaire. Un essai est fait pour relier ces résultats et pour montrer l'utilité de la GPC pour la caractérisation des copolymères THF–PO.

Zusammenfassung

Die kationische Copolymerisation von Tetrahydrofuran mit Propylenoxyd wurde in einem diskontinuierlichem System untersucht. Als Katalysator–Cokatalysator-System wurden Borfluorid–Äthyläther und 1,2-Propandiol verwendet. Zahlenmittel-Molekulargewichte, $\bar{M}_n$, verschiedener Copolymerer wurden durch Dampfdruck-Osmometrie (VPO) und Hydroxylendgruppen-Analyse (OH) bestimmt. Die VPO- und OH-Molekulargewichte differierten beträchtlich. Zur Aufklärung der Differenzen wurden einige Copolymere mittels Gelpermeationschromatographie (GPC) analysiert. Die erhaltenen Chromatogramme zeigten bei jedem analysierten Copolymeren zwei Maxima, eines im Bereich hoher und das andere im Bereich niedriger Molekulargewichte. Es wird versucht, eine Korrelation zwischen den Ergebnissen herzustellen und die Brauchbarkeit der GPC zur Charakterisierung von THF–PO-Copolymeren nachzuweisen.

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The Polymerization of Styrene Oxide by the Triisobutylaluminum–Water System

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Synopsis

Styrene oxide has been polymerized by the triisobutylaluminum–water catalyst system. Kinetic studies of the effects of varying the monomer, triisobutylaluminum, and water concentrations in benzene solutions have been made. Styrene oxide was consumed in two reactions: an initial fast one producing trimer and a slower reaction forming higher molecular weight polymer.

INTRODUCTION

The polymerization of epoxides by organometallic systems can be explained in terms of either a coordinate anionic mechanism or a cationic mechanism. One of the first catalysts studied for the polymerization of epoxides with respect to mechanism was the ferric chloride complex catalyst. The coordinate anionic mechanism was proposed for the polymerization of propylene oxide by ferric chloride and water.[1] A detailed and exacting mechanistic study of the trimethylaluminum and water system formulated a cationic mechanism rather than the coordinate anionic mechanism for the polymerization of propylene oxide.[2] The cationic mechanism has been applied to the polymerization of various ethylene oxides by the closely related diethylzinc and water system.[3]

Although fundamental differences obviously exist between the partly hydrolyzed iron catalyst and the aluminum and zinc catalysts, they have two things in common. First, the polymerization proceeds in two stages, a primary (fast) reaction producing low molecular weight polymer and a secondary (slow) reaction producing high molecular weight, solid polymer. Second, the main effect of water was to increase the proportion of high molecular weight polymer formed. Without water no polymerization was observed in the diethylzinc system, and only the primary (fast) stage producing low molecular weight polymer occurred in the trimethylaluminum system.

In both the ferric chloride–water and diethylzinc–water systems it was established that the polymerization of styrene oxide shows characteristics other than those generally exhibited by epoxides. The anomalous behavior of styrene oxide has not been explained in either system. It was of value, therefore, to determine whether styrene oxide exhibited polymerization characteristics different from alkyl-substituted ethylene oxides in the trialkylaluminum system. Very little has been published on the polymerization of styrene oxide by partial hydrolysis of aluminum alkyls; the investigations were exploratory in nature, encompassing a range of catalysts, cocatalysts, and solvents.[4,5]

EXPERIMENTAL

Materials

Solvent. Purified benzene was refluxed over sodium, distilled, and stored over sodium ribbon.

Monomer. The styrene oxide (obtained from Eastman Organic Chemicals) was dried over anhydrous sodium sulfate and fractionally distilled at atmospheric pressure. The middle fraction, boiling at 188°C., was collected for use in the polymerization studies.

Catalysts. The catalyst triisobutylaluminum (purchased from the Hercules Powder Company) was used as received. The catalyst solution was prepared in a nitrogen-filled dry box by prereacting the triisobutylaluminum, in a specified molar ratio, with water in benzene in a volumetric flask.

Procedure

In the rate studies the monomer and catalyst solutions were transferred to a 0.5-cm. silica cell fitted with a ground-glass stopper with calibrated hypodermic syringes in a nitrogen-filled dry box. The polymerization reaction was followed by near-infrared analysis[6] of the change of absorbance at 2.223 μ with a Beckman DK2A spectrophotometer equipped with a thermostated carriage cell. The monomer absorbance followed Beer's law over the entire concentration range studied.

For the purpose of polymer characterization sufficient quantities of polymer were prepared by using suitable amounts of reactants under conditions similar to those in the kinetic studies. Polymer recovery was accomplished by decomposition of the catalyst with methanol and removal of the solvent and unpolymerized monomer under reduced pressure. The polymeric residue was washed with dilute acid and water and dried under reduced pressure. The low and higher molecular weight polymers were separated by precipitation from methanol.

Physical Properties

The number-average molecular weights were obtained on a Mechrolab 301A vapor-pressure osmometer. All intrinsic viscosities were calculated by means of a concentration scale in grams of solute per 100 ml. of toluene at 25°C.

RESULTS AND DISCUSSION

Kinetic Data

Kinetic Data, $[W]_0/[C]_0 = 0.50$. The notation [M], [C], and [W] will be used for the styrene oxide monomer, the triisobutylaluminum catalyst, and the water cocatalyst concentrations, respectively; subscript 0 refers to the initial concentration.

This catalyst system at 26°C. was chosen for a more detailed study early in the investigation because this ratio of water to aluminum alkyl has been studied previously[2] and gave the most active catalyst.

A typical first-order plot for the polymerization at 26°C. with $[W]_0/[C]_0 = 0.50$ is shown in Figure 1. After an initial rapid rate in the first hour the polymerization follows a first-order rate law for the disappearance of monomer. After 24 hr. the rate begins to decrease, possibly owing to catalyst decomposition. The first-order dependence of the rate of the secondary (slow) reaction on monomer concentration was confirmed by a series of experiments in which $[M]_0$ was varied (Table I). The rate of the secondary reaction is also dependent on the catalyst concentration, as is shown by the results of a series of experiments in which the catalyst concentration was varied (Table II). No well-defined initial rate of the secondary reaction was observed because of overlap with the end of the

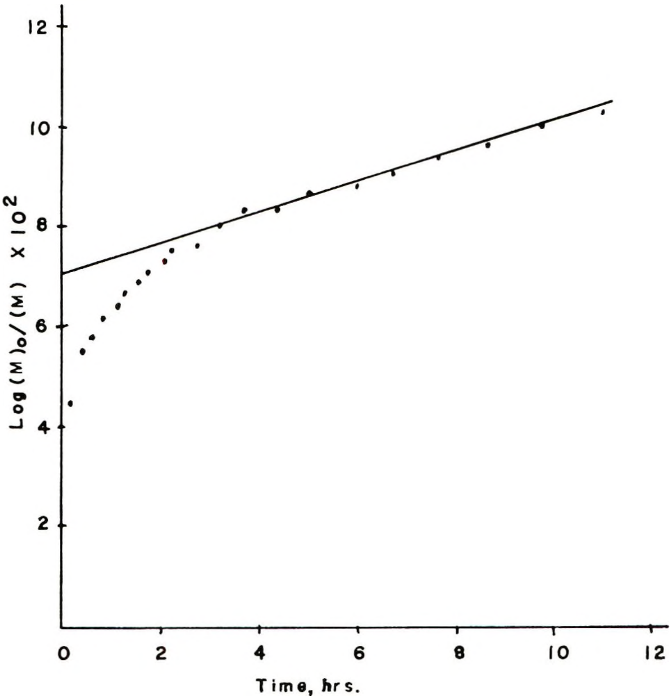


Fig. 1. Log $[M]_0/[M]$ versus time for the polymerization of styrene oxide at 26°C. with $[M]_0 = 1.5M$, $[C]_0 = 0.075M$, and $[W]_0/[C]_0 = 0.5$.

primary (fast) reaction. The values of the second-order rate constant and the amount of monomer per mole of catalyst consumed in the fast reaction were determined over a twofold range of monomer (1.125–1.875 moles/l.) and catalyst concentration (0.075–0.210 moles/l.), as indicated in Tables I and II. They were found to be constant within experimental error; k_2 was found to have an average value of 0.0157 l.-mole/hr. Three moles of monomer per mole of catalyst, M_1 were consumed in the fast reaction.

TABLE I
Effect of Varying Monomer Concentration: $[C]_0 = 0.075M$, $[W]_0/[C]_0 = 0.50$, $T = 26$°C.

$[M]_0$, moles/l.	10^2k_2, l./mole/hr.	Molar ratio,[a] M_1
1.875	1.37	3.27
1.500	1.51	3.23
1.125	1.51	3.09

[a] M_1 is the amount of monomer per mole of catalyst consumed during the primary (fast) reaction, estimated by extrapolating the linear portion of the first-order plot, corresponding to the secondary (slow) reaction, back to zero time.

TABLE II
Effect of Varying Catalyst Concentration: $[M]_0 = 1.50M$, $[W]_0/[C]_0 = 0.50$, $T = 26$°C.

$[C]_0$, moles/l.	10^2k_2, l./mole/hr.	Molar ratio M_1
0.075	1.51	3.23
0.120	1.43	3.29
0.165	1.68	2.92
0.210	1.94	3.05

The rate of the primary (fast) reaction was not studied in detail, but the amount of monomer per mole of catalyst, M_1 consumed during the primary (fast) reaction was estimated by extrapolating the linear portion of the first-order plot, corresponding to the secondary (slow) reaction, to zero time. The estimates of the amount of monomer consumed during the period of fast rate indicates that this quantity is dependent on the catalyst concentration but not on the monomer concentration. The consumption of 3 moles of monomer per 1 mole catalyst in the fast reaction was confirmed by the number-average molecular weight of 311 (c.a. trimer) for the low molecular weight polymer produced after $1^1/_2$ hr.

Effect of Water Concentration. The effect of the value of $[W]_0/[C]_0$ upon the overall rate of reaction has been investigated for the propylene oxide and trimethylaluminum system.[2] The kinetic data were interpreted as indicating that the catalyst formed from 2 moles of trimethylaluminum per 1 mole of water was more active than either trimethylaluminum alone or a species with a higher degree of oxygen substitution, that is $[W]_0/$

$[C]_0 > 0.50$. It was observed that in the presence of water the polymerization proceeded with a primary (fast) reaction, yielding low molecular weight oligomers, and a secondary (slow) reaction, yielding higher molecular weight polymer. In the absence of water only the fast reaction occurred to give low molecular weight oligomers.

Our experimental results confirmed that the molar ratio of water to trialkylaluminum is an important variable in the polymerization reaction. However, the value of $[W]_0/[C]_0$ does not change the kinetic features of the reaction. The polymerization reaction proceeded in two rates over a range of $[W]_0/[C]_0$ equal to 0–0.50. The secondary (slow) reaction differs only in the value of the rate constant. In the first hour there is a rapid rate of monomer consumption, after which the polymerization follows a first-order rate law for the disappearance of monomer. The kinetic data shown in Table III indicate that the catalyst involving 4 moles of triisobutylaluminum per mole of water is more active than triisobutylaluminum alone or a species with a greater degree of oxygen substitution, that is, $[W]_0/[C]_0 > 0.25$.

TABLE III

Effect of Varying Water Concentration: $[M]_0 = 0.75M$, $[C]_0 = 0.0375M$, $T = 26°C$.

$[W]_0/[C]_0$ mole ratio	10^2k_2 l./mole/hr.
0.50	2.07
0.25	3.18
0	1.01

Nature of the Polymer

Primary and Secondary Reaction Products, $[W]_0/[C]_0 = 0.50$. The characteristics of the polymers are given in Table IV. The polymerization reactions afforded a homogeneous mixture of low and higher molecular weight fractions. The addition of methanol gives a white solid and a solution of oligomers. The $\bar{M}$ suggests that the oligomers produced in the fast reaction consist of trimer. The infrared spectra of the polymer fractions from both fast and slow reactions were almost indistinguishable except for a slight increase of a very small carbonyl absorbance in the trimer as the

TABLE IV

Conversion and Molecular Weights of Poly(styrene Oxide): $[M]_0 = 1.33M$, $[C]_0 = 0.066M$, $[W]_0/[C]_0 = 0.5$, $T = 25°C$.

Time, hr.	Low molecular weight fraction		Higher molecular weight fraction		
	%	$\bar{M}_n$	%	$\bar{M}_n$	$[\eta]$, dl./g.
1.5	15.2	311	0.5	1450	0.20
240	30.0	395	5.2	850	0.14

polymerization progressed. Infrared spectra of the low molecular weight fractions show no absorption due to unsaturation but strong absorption due to hydroxyl. The higher molecular weight fractions show decreased absorption due to hydroxyl and no absorption due to unsaturation.

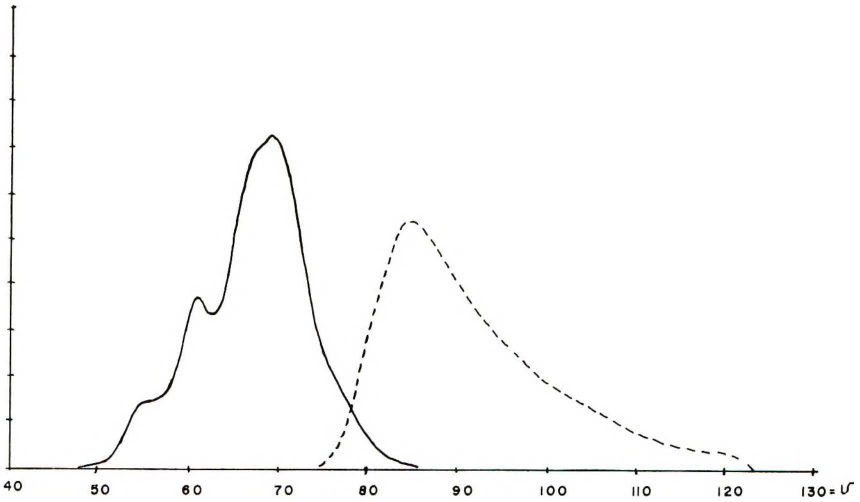


Fig. 2. Molecular weight distribution of poly(styrene oxide) after 1.5 hr. with $[M]_0 = 1.33M$, $[C]_0 = 0.066M$, $[W]_0/[C]_0 = 0.5$: (- - -) higher molecular weight; (——) trimer

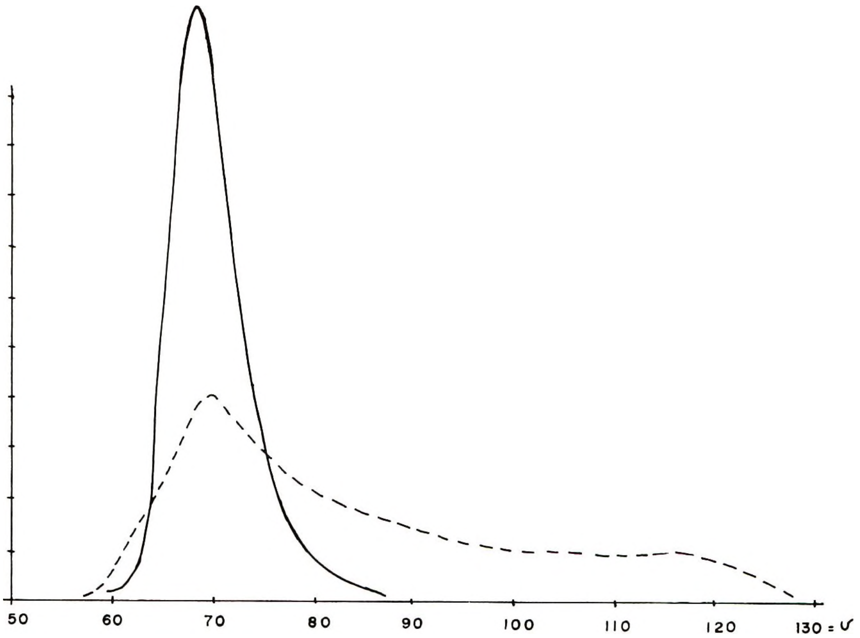


Fig. 3. Molecular weight distribution of poly(styrene oxide) after 240 hr. with $[M]_0 = 1.33M$, $[C]_0 = 0.066M$, $[W]_0/[C]_0 = 0.5$: (- - -) higher molecular weight; (——) trimer.

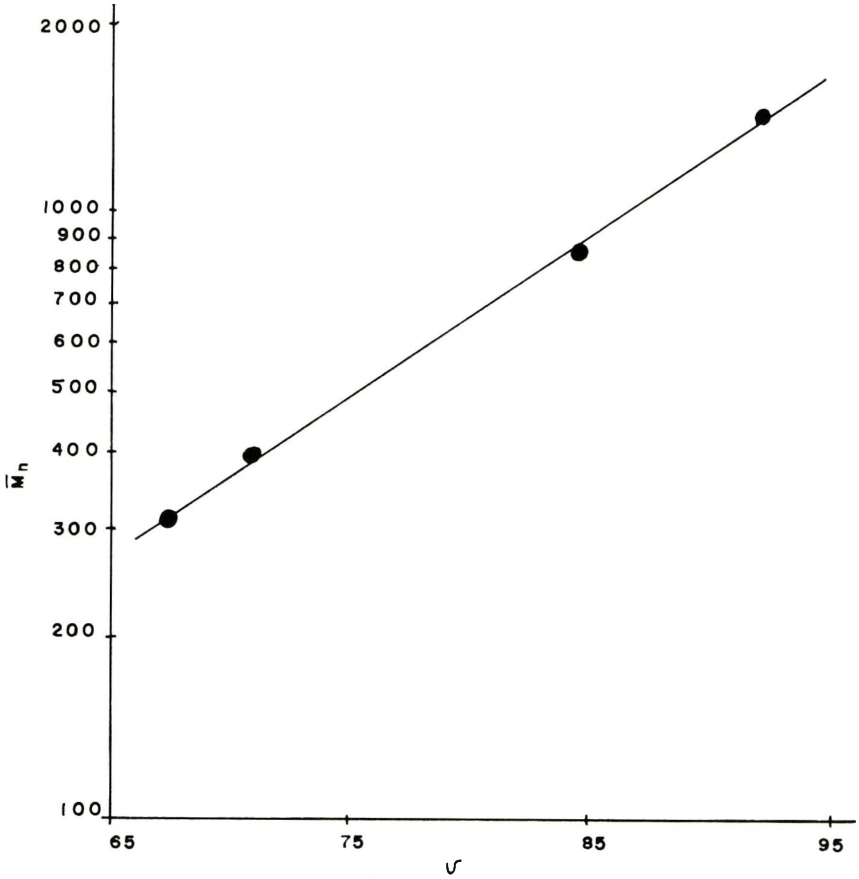


Fig. 4. Correlation of mean ν with $\overline{M}_n$ for the polymer samples illustrated in Figs. 2 and 3.

Although the trimer is formed rapidly until the consumption of 3 moles of monomer per mole of aluminum and is not produced rapidly during the next 24 hr. of the polymerization, a small amount of higher molecular weight solid polymer is produced early in the reaction, and the amount increases throughout the polymerization.

The molecular weight distributions of the low and higher molecular weight fractions were obtained by gel permeation chromatography (the GPC was carried out by R. L. Erickson, Lycra Technical Section, E. I. du Pont de Nemours and Co., Waynesboro, Va.); see Figures 2 and 3. Both of the higher molecular weight fractions have a broad distribution. The low molecular weight fraction obtained from a polymerization time of 240 hr. and both of the higher molecular weight fractions deviate significantly from a normal distribution. Figure 4 gives the correlation of the mean ν [volume of dimethylacetamide needed to purge the columns of polymer; related to elution count by the formula $\nu = 5$ (40-count)] with $\overline{M}_n$ for these polymer samples.

TABLE V
Effect of Water Concentration on Primary and Secondary Reaction Products: $[M]_0 = 1.02M$, $[C]_0 = 0.051M$, $T = 25°C$.

$[W]_0/[C]_0$ mole ratio	Conversion 1.5 hr., %		Conversion 240 hr., %		Solid, 240 hr., $[\eta]$, dl./g.
	Oil	Solid	Oil	Solid	
0.50	10.1	0.5	22.7	5.2	0.14
0.25	12.9	0.9	27.1	4.0	0.08
0	3.0	0.05	6.5	5.7	0.30

Effect of Water Concentration. The various effects of increasing $[W]_0/[C]_0$ on polymer characteristics were studied and are given in Table V. The main effect of water on the polymerization was to increase the production of low molecular weight polymer and to lower the molecular weight of the polymer produced in the secondary reaction.

Role of Triisobutylaluminum in Polymerization System, $[W]_0/[C]_0 = 0.5$

The role of the alkyl group attached to aluminum has been investigated in several polymerization systems. In the polymerization of acetaldehyde, a nonradioactive polymer was produced with labeled triethylaluminum.[7,8] Triphenylaluminum did not react with cyclohexene oxide to yield a polymer containing a phenyl unit.[9] In addition, it has been established that in the polymerization of propylene oxide with both the trimethylaluminum and the trimethylaluminum plus water (0.5 ratio) catalysts all the methyl groups originally attached to aluminum were evolved as methane after final hydrolysis of the polymerization products.[2]

Hydrolysis of triisobutylaluminum results in the liberation of 2 moles of isobutane per mole of water.[5] The trialkylaluminum is converted to the corresponding hydroxides, which are further converted to the oxides:

$$R_3Al + H_2O \xrightarrow{\text{fast}} R_2AlOH + RH$$

$$R_2AlOH + R_3Al \xrightarrow{\text{slow}} R_2AlOAlR_2 + RH$$

When $[W]_0/[C]_0 = 0.50$, the composition of the catalyst system used in the polymerization of styrene oxide is near $(i\text{-Bu})_2AlOAl(i\text{-Bu})_2$. At the end of the two polymerization reactions the quantity of gas evolved on hydrolysis was found by vapor-phase chromatography to correspond to two isobutyl groups per aluminum atom. Thus, all the isobutyl groups originally attached to the metal atom in the catalyst were evolved as isobutane, and none are transferred to the polymer chain.

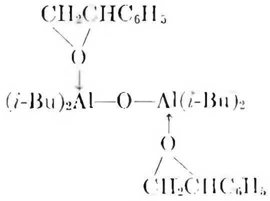
Mechanism

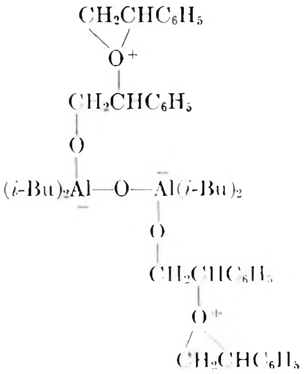
Only the polymerization carried out with a mole ratio of water to triisobutylaluminum of 0.50 can be discussed in detail. The polymerization of styrene oxide over the range of $[W]_0/[C]_0$ ratios involves essentially the same type of active centers. The water concentration does not affect the nature of the relatively simple kinetics, which differs only in the values of the rate constant.

The polymerization system was homogeneous throughout the reaction over the range of $[W]_0/[C]_0$ ratios studied. A yellow color developed instantaneously, when the catalyst solution was added to the monomer solution, and faded quickly. As the polymerization progressed, the color developed more deeply. Similar behavior in the polymerization of styrene oxide with diethylzinc and water[3] was attributed to optical properties of an intermediate or of a monomer-catalyst complex. In this study the formation of small amounts of colored materials might be accounted for by rearrangement of some of the monomer to a carbonyl compound, followed by aldol or related condensations. This explanation is favored because of the following observations: (*1*) the color is not completely destroyed when the polymerization is terminated with methanol and (*2*) the small carbonyl absorbance of the low molecular weight fraction in the infrared increases slightly as the polymerization progresses.

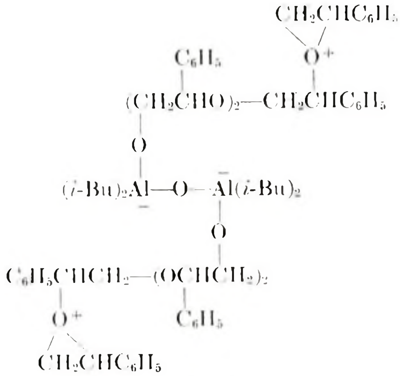
It is evident from the results that the polymerization of styrene oxide by triisobutylaluminum and water is a complicated process. Since our results and the results reported for the polymerization of propylene oxide by trimethylaluminum and water are very similar, the kinetic results may be discussed in terms of the cationic active-center mechanism outlined for this system. The composition $(i\text{-Bu})_2AlOAl(i\text{-Bu})_2$ is analogous to the species chosen as the catalyst for the initial reaction in the polymerization of propylene oxide by trimethylaluminum.

Initiation probably involves coordination of $(i\text{-Bu})_2AlOAl(i\text{-Bu})_2$ by monomer, followed by ring opening to an oxonium ion.


(I)

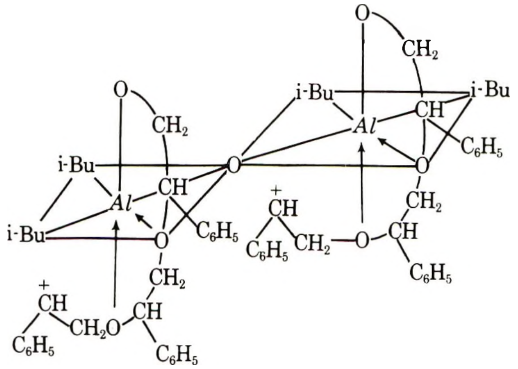

(II)

The addition of more monomer molecules to (II) would yield (III), containing one trimer molecule per aluminum atom.



(III)

Our data for the primary (fast) reaction can be explained by the formation of an intramolecular complex such as (IV). It is not unreasonable to suggest that the trimers formed in the primary reaction can act as tridentate ligands to form an octahedral complex.



(IV)

A complex such as (IV) could be destroyed either by rearrangement of an isobutyl group attached to aluminum, giving an addition reaction product, or by ring closure, giving a cyclic product. However, it has been established by others[2,9] and by our own data that the reaction with the aluminum alkyl catalyst does not give the addition reaction product. It has been proposed that the addition reaction between diethyl ketone and monomeric triethylaluminum does not occur, because of its steric hindrance in the complex.[10] Since steric hindrance would be greater in the reaction complex between $(i\text{-Bu})_2\text{AlOAl}(i\text{-Bu})_2$ and styrene oxide, the stability of the complex to a similar addition reaction is understandable. The destruction of complex (IV) by a cyclization reaction of the trimer would be sterically unfavorable, because a nine-membered ring would be formed.

Therefore, complex (IV), in which the carbonium ion is stabilized by the overall negative charge on the remainder of the complex or by combination with another base, is relatively inactive toward polymerization. Once it is formed, further addition is stopped, and aluminum sites are no longer available for the polymerization. This complex accounts for the trimer.

Although we have not been able to identify the catalyst for the secondary reaction, which produces higher molecular weight polymer, it is probably a catalyst of low oxygen content or triisobutylaluminum itself.

The authors are indebted to R. L. Erickson, of the Lycra Technical Section, E. I. du Pont de Nemours & Co., Inc., Waynesboro, Virginia, for the determination of the computer analysis of the polymers by gel permeation chromatography.

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Résumé

L'oxyde de styrène a été polymérisé au moyen d'un système catalyseur à base de triisobutyle-aluminium et d'eau. L'étude cinétique des effets de la variation des concentrations en monomère, en triisobutyle-aluminum et en eau dans des solutions benzéniques a été effectuée. L'oxyde de styrène est consommés par deux réactions: une réaction initiale rapide produisant le trimère, et une réaction plus lente formant un polymère de poids moléculaire plus élevé.

Zusammenfassung

Styroloxyd wurde mit dem Triisobutylaluminum–Wasser-Katalysatorsystem polymerisiert. Eine kinetische Untersuchung des Einflusses einer Variation der Monomer-, Triisobutyl-aluminum- und Wasserkonzentration in Benzollösung wurde durchgeführt. Styroloxyd wurde nach zwei Reaktionen umgesetzt: eine rasche, zu Trimerem führende Anfangsreaktion und eine langsamere, höhermolekulares Polymeres bildende Reaktion.

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Cyclopolymerization of Diastereomeric Diepoxides

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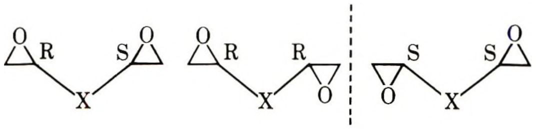
Synopsis

The *meso*- and *d,l*-diastereomers of *o*-bis(epoxyethyl)benzene have been synthesized and identified. The diastereomers were polymerized by a variety of catalysts to give a polymer which has mainly isochroman recurring units as a result of a cyclopolymerization mechanism. Some features of the polymerization with the triisobutylaluminum catalyst system have been studied. The rates of polymerization of the monomers and the transition temperatures of the resulting polymers have been determined. The results are explained on the basis of a controlled intramolecular propagation and a stereospecific polymerization.

INTRODUCTION

Although the cyclopolymerization of diepoxides is known,[1,2] no attention has been given to the stereochemical configuration of the monomer and the consequences on the intramolecular propagation. Diepoxides of the general formula given in the accompanying diagram should exist as *meso*-(I) and *d,l*-(II) diastereomers.



meso

(I)

d,l

(II)

The cyclopolymerization of diastereomers is of interest, because the *meso*-isomer would necessitate an intramolecular propagation involving the addition of S to the R or of R to the S carbon associated with the epoxide moiety, but the *d,l*-isomeric mixture would always involve an intramolecular R-to-R or S-to-S propagation, depending on the enantiomer involved. In both cases the intermolecular propagation could be random, unless some selectivity was shown by the asymmetric growing chain end.

Biallyl diepoxide, previously cyclopolymerized,[1] is a liquid monomer, and the isolation of the diastereomers was not possible. However, a crystalline solid monomer should lend itself to separation of the diastereomers. Such a monomer suitable for study is *o*-bis(epoxyethyl)benzene.

During the initial stages of investigation of this system the polymerization of *o*-bis(epoxyethyl)benzene was reported to proceed by intramolecular–intermolecular propagation to give the isochroman recurring unit.[2] However, only one of the isomers was reported and polymerized. We therefore pursued this study in an effort to demonstrate differences in the intramolecular propagation of the diastereomers as evidenced by the rates of polymerization and the properties of the polymers.

EXPERIMENTAL

Materials

Monomer. A mixture of the diastereomeric diepoxides was prepared in a 75% yield by epoxidizing *o*-divinylbenzene[3] in the following manner. A solution of 21.5 g. (0.165 mole) of *o*-divinylbenzene in 150 ml. of benzene was added to 1200 ml. of a benzene solution containing 85.5 g. (0.42 mole) of *m*-chloroperbenzoic acid.[4] The reaction mixture was kept in the dark at room temperature. The progress of the reaction was followed iodometrically. After the epoxidation reaction was complete (18 hr.), the solution was washed with 10% sodium sulfite solution, 10% sodium bicarbonate solution, and water and dried over anhydrous sodium sulfate. After flash evaporation of the solvent under reduced pressure at room temperature the residual oil was fractionally crystallized from redistilled pentane at −20°C. to yield 20.1 g. (75%) of the diepoxide mixture. Further recrystallization of the diepoxide afforded two fractions melting at 31–32°C. (85–90%) and 56°C. (10–15%).

The two fractions had identical infrared spectra, nearly identical ultraviolet spectra, and nuclear magnetic resonance solution spectra. The infrared spectra showed bands at 880 and 835 cm.$^{-1}$, which are attributed to the epoxy group. The nuclear magnetic resonance spectra show four principal regions of absorption with centers at 2.63, 3.08, 4.08, and 7.30 ppm with integration ratios of 2:2:2:4, respectively. The ultraviolet spectra showed absorption maxima at 215 and 264 mμ in both diastereomers.

ANAL. Calcd. for $C_{15}H_{10}O_2$: C, 74.05%; H, 6.21%. Found (56°C., m.p. isomer): C, 73.60%; H, 6.56%. Found (31 to 32°C., m.p. isomer): C, 73.86%; H, 6.58%.

The melting points of mixtures of the diastereomers in various proportions were determined. In every case the mixture melted over a range intermediate between the melting points of the separate diastereomers.

The establishment of the configuration of the diastereomers was based on the partial resolution of one isomer by means of *d*-amphetamine. In two simultaneous reactions samples of each isomer were added to a benzene solution containing enough *d*-amphetamine to destroy 20% of the monomer. After the reaction was allowed to continue for 2 weeks, the benzene solvent was removed, and the residual oil was extracted with pentane, to remove the monomer from the very slightly pentane-soluble reaction product. The recovered isomers were not washed with dilute acid, because of their high reactivity to acids and acid-catalyzed hydrolysis. However, *d*-amphetamine was removed from the monomer by recrystallizing the monomer six times from pentane. The purity of the recovered isomers was determined from their melting points and infrared spectra.

The recovered low melting monomer had a specific rotation of $[\alpha]_{3800}^{25°} = -3.50°$, and the recovered high-melting isomer was inactive. A duplicate reaction of the low-melting monomer with *d*-amphetamine afforded recovered monomer with a specific rotation of $[\alpha]_{3800}^{25°} = -3.40°$. It was also established that the observed rotation was not due to traces of *d*-amphetamine, since *d*-amphetamine, in the same solvent and at the same wavelength as utilized for the isomers, is dextrorotatory.

Solvents. Chloroform was purified just before the polymerization runs by removing the ethanol stabilizer, drying over calcium chloride, and distilling. Purified benzene was refluxed over sodium, distilled, and stored over sodium ribbon. Methylene dichloride was stored over phosphorus pentoxide and distilled therefrom just before use.

Catalysts. Phosphorus pentafluoride was obtained from the thermal decomposition (150–160°C.) of recrystallized benzenediazonium hexafluorophosphate (Ozark-Mahoning Company) and swept with dry, purified nitrogen into the reaction systems.

The catalyst triisobutylaluminum (purchased from the Hercules Powder Company) was used as received. The catalyst solution was prepared in a nitrogen-filled dry box by prereacting the triisobutylaluminum and the specified molar ratio of water in benzene in a volumetric flask.

Polymerizations

Phosphorus Pentafluoride. The polymerizations with phosphorus pentafluoride were run under nitrogen in side-armed flasks previously flamed out and fitted with ebullator tubes. The catalyst was swept with dry, purified nitrogen into the reaction systems. Solvent was added to the systems with standard calibrated hypodermic syringes. The solvent and monomer were added before the catalyst was bubbled in below the surface of the solutions. The catalyst was fed into the system, until foam appeared on the surface or a yellow color was detected in the solution. Polymerization was achieved in thermostated baths without agitation.

The polymerization reactions were terminated by the addition of methanol, to decompose the catalyst. After the solvent was evaporated under reduced pressure, the polymeric residue was washed with pentane, to remove unreacted monomer. The remaining polymeric residues were dissolved in chloroform and filtered. The volumes of the solutions were reduced and the solutions poured into stirred pentane, to precipitate the polymers. The resulting polymers were dried under reduced pressure.

Triisobutylaluminum. In the rate studies the monomer and catalyst solutions were transferred to a 0.5-cm. silica cell fitted with a ground-glass stopper with calibrated hypodermic syringes in a nitrogen-filled dry box.

The polymerization reaction was followed by near-infrared analysis[5] of the change of absorbance at 2.221 μ with a Beckman DK2A Spectrophotometer equipped with a thermostated carriage cell. The monomer absorbance followed Beer's law over the entire concentration range studied.

For purposes of polymer characterization sufficient quantities of polymer were prepared by using suitable amounts of reactants under conditions similar to those in the kinetic studies. Polymer recovery was accomplished by decomposition of the catalyst with methanol and removal of the solvent under reduced pressure. Unpolymerized monomer was removed by extraction with pentane. The solid polymeric residues were washed with dilute hydrochloric acid and water and dried under reduced pressure.

Physical Properties

The infrared spectra of the polymers prepared with phosphorus pentafluoride and the triisobutylaluminum catalyst systems were obtained as films and as chloroform solutions. The spectra showed an absorption maximum at 1100 cm.$^{-1}$ (unstrained ether). In a few polymer samples weak maxima were observed at 3500 (hydroxyl), 1715 (carbonyl), and 880 cm.$^{-1}$ (oxirane). The model compounds isochroman,[6] poly(styrene oxide), and tetrahydrofuran showed the ether absorption maxima at 1098, 1105, and 1075 cm.$^{-1}$, respectively.

The nuclear magnetic resonance spectra of the polymers prepared with phosphorus pentafluoride exhibited very broad principal absorption-band signals centers at 3.70, 4.40, and 7.17 ppm. The catalyst system triisobutylaluminum and water in 0.5 ratio yielded polymer which also contained broad regions of absorption in the NMR, particularly in the 3.9 and 4.2 ppm region.

Transition temperatures were measured with a Du Pont 900 differential thermal analyzer. Finely ground polymer samples were packed into the thermocouple well, and the analyses were run under dry nitrogen at a heating rate of 20°C./min. with alumina as reference material.

The number-average molecular weights were obtained on a Mechrolab 301A vapor-pressure osmometer. The inherent viscosities were calculated by means of a concentration scale in grams of solute per 10 ml. of solvent at 25°C.

DISCUSSION AND RESULTS

Configuration of the Diastereomers

The configuration of *o*-bis(epoxyethyl)benzene could be established by either determining the number of isomers formed after a chemical transformation of the diastereomers or resolving one of the diastereomers. Utilization of the former method is complicated by the orientation of ring opening, which may proceed in either one or both of two directions. It was previously established that the addition reaction of styrene oxide and

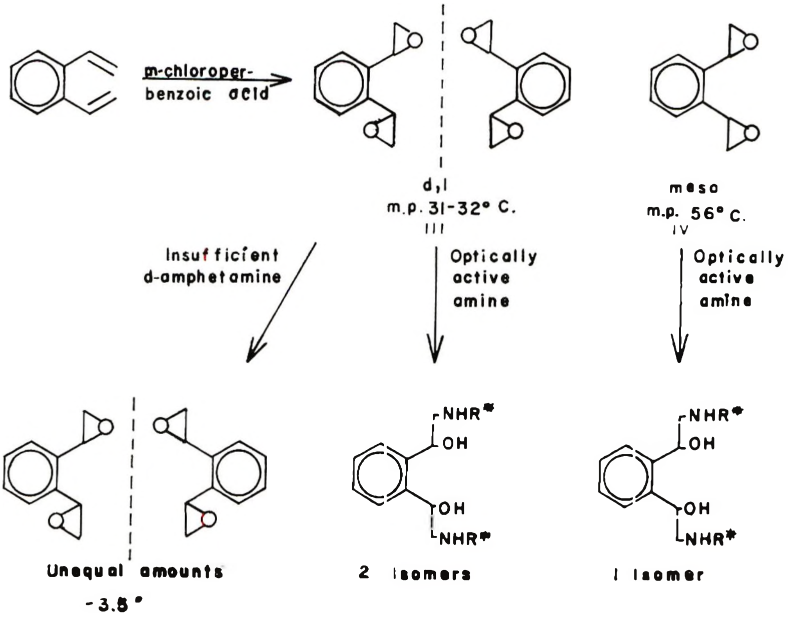


Figure 1.

benzyl amine yielded the secondary amino secondary alcohol in a 94% yield.[7] Therefore, the problem of ring-opening orientation would be eliminated by using a similar amine. The reaction of the diastereomers with excess (−) or (+) α-phenylethyl amine was studied. The *d,l*-isomer would be expected to form two diastereomeric hydroxy amines and the meso isomer only one hydroxy amine (Fig. 1). However, this method was found impracticable, because uncrystallizable products were formed.

It was also not possible to resolve readily the *d,l*-isomers of the diepoxides by conventional means. Resolution by elution chromatography, utilizing a lactose column, was unsuccessful. Although optically active styrene oxide has been prepared from optically active precursors[8,9] obtained by either kinetic or biochemical[10] asymmetric transformations, these methods did not yield the diepoxide under analogous reaction conditions.

The establishment of the configuration of the diastereomeric *o*-bis(epoxyethyl)benzenes having resolvable (*d,l*) and nonresolvable (*meso*) forms was based on the partial resolution of the *d,l*-isomer by means of *d*-amphetamine (Fig. 1). Since the low-melting isomer (31–32°C.) became partly active after reacting with an insufficient amount of *d*-amphetamine, this material must be the *d,l*-pair. Similarly, asymmetric destruction of *d,l*-propylene oxide occurred in its polymerization with the diethylzinc-*d*-borneol catalyst system.[11]

The same assignment of configuration would be obtained on the basis of physical evidence. In most instances the symmetry of the *meso* form results in the higher-melting crystals. Thus, the *meso* form is higher melting than the *d,l* in all known cases of compounds containing a dibenzyl-like structure.[12]

Polymerization

The phosphorus pentafluoride catalyst was effective for the conversion of both diastereomers to polymers in high yield. The results are given in Table I.

TABLE I
Polymerization of the Diastereomers with Phosphorus Pentafluoride[a]

Monomer form	Temp., °C.	Solvent	Conversion, %	Solubility,[b] %	Inherent viscosity[c] η_{inh}	Number-av. mol. wt.[d] M_n
meso	−30	$CHCl_3$	46	66	0.12	—
d,l	−30	$CHCl_3$	59	78	0.13	—
meso	−78	CH_2Cl_2	100	40	0.16	3,300
d,l	−78	CH_2Cl_2	100	70	0.22	5,510

[a] At −30 and −78°C. the monomers at concentrations of 0.8 g. (0.005 mole) and 0.5 g. (0.003 mole) per 10 ml. of solvent, respectively, were allowed to react for 24 hr.

[b] Solubilities were determined in the same solvent as used for measuring η_{inh}.

[c] Inherent viscosities on the soluble portion were determined in chloroform at concentrations of 0.10–0.40 g./100 ml.

[d] Soluble portion.

The polymer obtained from the *meso* isomer at −78°C. exhibited a sharp endotherm at 120°C. in the differential thermal analysis. The polymer produced from the *d,l*-isomer at −78°C. exhibited a broad endotherm at 120°C. and a sharp one at 176°C.

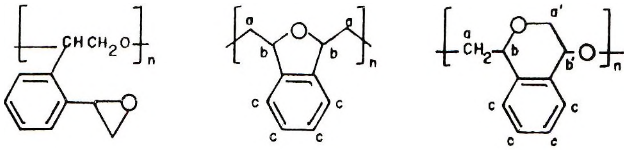
TABLE II
Polymerization of the Diastereomers with Triisobutylaluminum[a]

Monomer form	$[W]_0/[C]_0$ mole ratio[b]	Monomer/solvent, g./ml.	Time	Conversion, %	Inherent viscosity[c] η_{inh}
meso	0.5	0.243	2.5 hr.	12	—
meso	0.5	0.204	30 days	26	0.15
d,l	0.5	0.243	2.5 hr.	8	—
d,l	0.5	0.322	10 days	28	0.11
d,l	0.5	0.210	30 "	46	0.15
meso	0	0.203	30 "	26	0.22
d,l	0	0.206	30 "	50	0.24

[a] The polymerizations were run at 25°C. in benzene. The ratio of monomer to catalyst was 20:1 in all trials, based on the moles of monomer and triisobutylaluminum.

[b] $[C]_0$ and $[W]_0$ are the initial triisobutylaluminum catalyst and water cocatalyst concentrations, respectively.

[c] Inherent viscosities were determined in a mixture of phenol and *sym*-tetrachlorethane (100:66 by weight) at a concentration of 0.15–0.25 g./100 ml. These polymers were completely soluble in this solvent.



V VI VII

Figure 2.

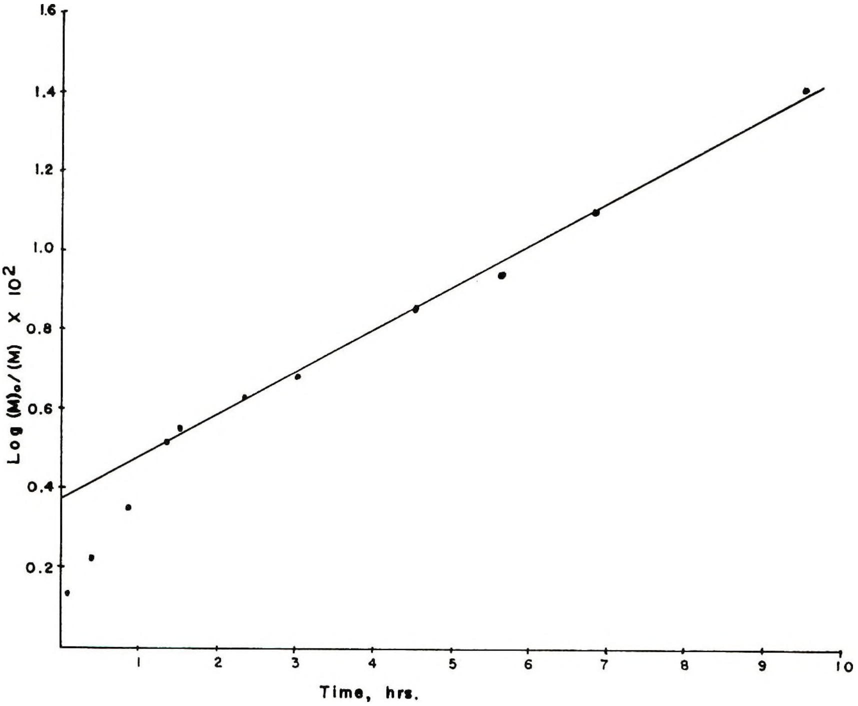


Fig. 3. Log $[M]_0/[M]$ versus time for the polymerization of the *d,l*-isomer at 27°C. with $[M]_0$ = 0.75 molar, $[C]_0$ = 0.0375 molar, and $[W]_0/[C]_0$ = 0.50.

Triisobutylaluminum, with and without a water cocatalyst, was also effective for the conversion of the diastereomers to polymers. However, the aluminum system is not as active a catalyst as phosphorus pentafluoride. As indicated in Table II, a long reaction time is required to convert monomer to polymer in quantity.

Differential thermal analyses were obtained for polymer samples from the catalyst systems triisobutylaluminum and triisobutylaluminum plus water in 0.5 ratio, after a reaction time of 30 days. The polymers prepared with the triisobutylaluminum catalyst from the *meso*- and *d,l*-isomer exhibited a broad endotherm at 125 and 85°C., respectively. The melting points of the polymers from both isomers were slightly lower when water was present as cocatalyst. These differences in melting points between the *d,l*- and the *meso*-polymers originate in the steric effects of the recurring unit, since melting point relates directly to the symmetry and interaction forces of the repeating unit.[13]

The polymerization of the diastereomers could yield recurring unit structures (V), (VI), or (VII) from either the phosphorus pentafluoride or the triisobutylaluminum catalyst systems; see Figure 2. However, structure (VII), containing the isochroman unit resulting from a cyclopolymerization, is assigned to the polymers from both diastereomers and from both catalyst systems on the basis of the following observations: (*1*) soluble polymers were obtained from the aluminum systems; partially soluble polymers were obtained from the PF_5 systems; (*2*) the polymers contained no or few residual epoxide moieties; (*3*) the infrared spectra of the polymer samples showed maxima (C–O–C stretching) characteristic of the strainless model compounds isochroman and poly(styrene oxide); and (*4*) the nuclear magnetic resonance studies of the polymer from the triisobutylaluminum and 0.5 water catalyst system gave evidence of five different protons, as would be expected in structure (VII). All polymer samples exhibited broad maxima in the region of absorption of protons of the type *a* and *b*. Unit (VI) should probably show a doublet for proton *a* and a triplet for *b*.

Kinetic studies of the effects of diastereomer and water concentration were made in the triisobutylaluminum catalyst system, which was homogeneous throughout the reaction. After an initial rapid reaction in the first hour monomer was consumed in a slow reaction. A typical first-order plot for the polymerization of the *d,l*-isomer with $[W]_0/[C]_0 = 0.50$ is shown in Figure 3. Since the nature of the kinetics was complex, it was necessary to determine the relative rates of the initial and slow reactions (Table III).

TABLE III

Effect of Diastereomer and Water Concentration: $[M]_0 = 0.75M$, $[C]_0 = 0.0375M$, and $T = 27°C$.

Monomer form	$[W]_0/[C]_0$ mole ratio	Relative rate[a] initial reaction	Relative rate[a] slow reaction
d,l	0.50	1.00	1.00
d,l	0.25	1.70	1.04
d,l	0	2.58	0.88
meso	0.50	3.21	0.80

[a] The relative rates were estimated by dividing the slope obtained from the linear portion of the first-order plot by the slope obtained in the first reaction listed.

The rates of polymerization of the monomer and the melting points of the resulting polymers produced by the triisobutylaluminum catalyst system furnish some information on the nature of the intramolecular propagation. The intramolecular propagation of *meso*- and *d,l*-diepoxides must proceed with predominant retention or inversion of configuration (Fig. 4);

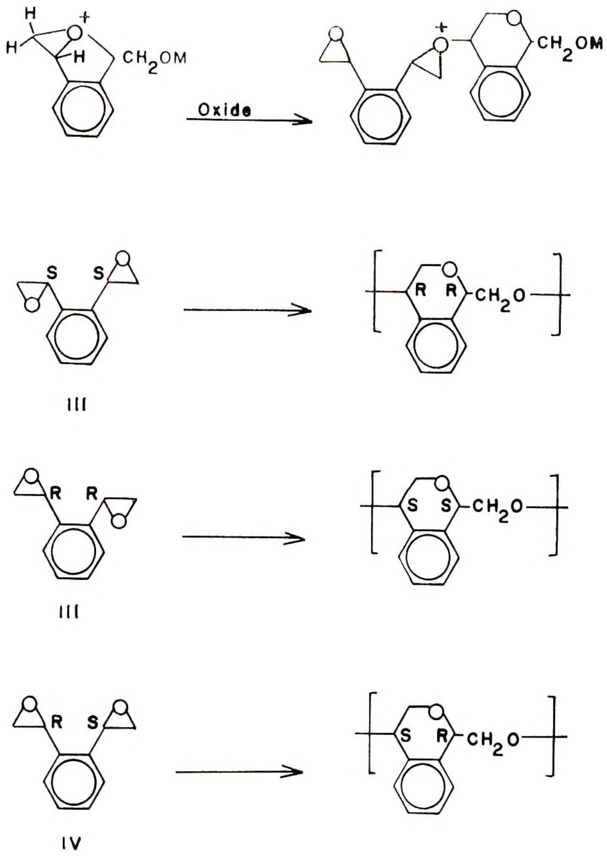


Figure 4.

otherwise, the same polymer would be obtained from either isomer. Previous studies established that the polymerization of *d,l*-2,3-epoxybutane with the catalyst system triisobutylaluminum plus water, 0.5 ratio, proceeded with inversion of configuration, involving nucleophilic attack of monomer at the carbon bearing the epoxide moiety.[14] Since other workers established that the polymerization of alicyclic epoxides with triethylaluminum follows known stereochemical principles for these compounds,[15] the intramolecular–intermolecular propagation of the diastereomers probably proceeds with double head-to-tail inversion through a cationic mechanism. The direction of ring opening (Fig. 4) has been depicted as such, since the cationic ring opening of styrene oxide affords products resulting predominantly from this direction of opening.[16]

A study of the rates show that the *meso*-isomer reacted much faster during the initial stages of the polymerization than the *d,l*-isomer but reacted slightly slower during the slow polymerization. These differences in rates must originate in steric effects, since the same groups are attached to the asymmetric atoms in the two starting materials. Hence, the different kinetic behavior of the diastereomers can be explained in terms of the different complexing abilities of the monomers and resulting polymers with the catalyst and growing chain.

It was proposed that in the polymerization of epoxides with the trialkylaluminum catalyst, with and without water, the initial reaction is preceded by coordination of the epoxide units to the metal and followed by formation of a complex capable of initiating polymerization in the subsequent slow reaction.[17] Hence, the complexing abilities of the monomer would be of primary importance. It is possible that the *meso*-isomer can coordinate with the aluminum atom better than the *d,l*-isomer, and a faster initial rate is observed. During the slow reaction the *meso*-isomer is consumed at a slightly slower rate than the *d,l*-isomer.

The Du Pont 900 DTA, on which the differential thermal analyses were carried out, was obtained in part through a gift of the Dunlop Research Centre, Sheridan Park, Ontario, Canada.

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Résumé

Les diastéréomères *méso*- et *d,l* du *o*-bis(époxyéthyle)benzène ont été synthétisés et identifiés. Les diastéréomères ont été polymérisés par une variété de catalyseurs en vue de former un polymère qui a en moyenne des unités isochromes qui se répetent suite à un mécanisme de cyclopolymérisation. Certaines caractéristiques de cette polymérisation par un système catalyseur à base de triisobutylaluminum ont été étudiées. Les vitesses de polymérisation de ces monomères et les températures de transition des polymères résultants ont été déterminées. Les résultats sont expliqués sur la base d'une propagation intramoléculaire contrôlée et d'une polymérisation stéréospécifique.

Zusammenfassung

Die *meso-* und *d,l*-Diastereomeren von *o*-Bis(epoxyäthyl)benzol wurden synthetisiert und identifiziert. Die Diastereomeren wurden mit einer Vielfalt von Katalysatoren unter Bildung eines Polymeren polymerisiert, welches hauptsächlich Isochromanbausteine als Ergebnis eines Cyclopolymerisationsmechanismus enthält. Die Polymerisation mit dem Triisobutyl-aluminium-Katalysatorsystem wurde untersucht. Die Polymerisationsgeschwindigkeit der Monomeren und die Umwandlungstemperaturen der gebildeten Polymeren wurden bestimmt. Die Ergebnisse werden auf Grundlage eines kontrollierten intramolekularen Wachstums und einer stereospezifischen Polymerisation erklärt.

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Polymerization of Styrene with $VOCl_3$–Aluminum Alkyls*

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Synopsis

The polymerization of styrene with $VOCl_3$ in combination with $AlEt_3$ and with $Al(i\text{-}Bu)_3$ in *n*-hexane at 40°C. has been investigated. The rate of polymerization was found to be second order with respect to monomer in both systems. With respect to catalyst the rate of polymerization was first order for $VOCl_3$–$AlEt_3$ and second order for $VOCl_3$–$Al(i\text{-}Bu)_3$ systems. The activation energies for $VOCl_3$–$AlEt_3$ and $VOCl_3$–$Al(i\text{-}Bu)_3$ systems were 7.37 and 11.25 kcal./mole, respectively. The molecular weight of polystyrene in the $AlEt_3$ system was considerably higher than that in the $Al(i\text{-}Bu)_3$ system. The valence of vanadium obtained by a potentiometric method showed that the catalyst sites in the $AlEt_3$ system are different in nature from those in the $Al(i\text{-}Bu)_3$ system. The effect of diethylzinc as a chain-transfer agent in the $AlEt_3$ system was also studied.

Stereospecific polymers of α-olefins are obtained with the use of catalysts prepared in reactions of metal alkyls with titanium halides. Similar studies with other transition metal halides such as vanadium halides, have also been carried out. The $VOCl_3$–$AlEt_3$ system[1] has been used for the polymerization of ethylene as well as for the copolymerization of ethylene with propylene and propylene with acrylonitrile,[1,2] but no detailed kinetic study with this catalyst has been so far reported. In this communication the results of our work on the polymerization of styrene with $VOCl_3$–aluminum alkyls in *n*-hexane at 40°C. are reported.

It has been observed that whereas the behavior of the $VOCl_3$–$AlEt_3$ system is similar to that of the $TiCl_4$–$AlEt_3$ system, the $VOCl_3$–$Al(i\text{-}Bu)_3$ system is very much different from the $TiCl_4$–$Al(i\text{-}Bu)_3$ system.

Experimental

$VOCl_3$ was prepared[3] by reacting 1 mole of V_2O_5 with 2 moles of anhydrous $AlCl_3$ at about 400°C. and distilling out the brown liquid. On redistillation under anhydrous condition a lemon-yellow liquid was obtained. Its stock solution (0.5*M*) was prepared in *n*-hexane.

$AlEt_3$ and $Al(i\text{-}Bu)_3$ were supplied by M/s. Ethyl Corporation, U. S. A, and were redistilled under reduced pressure and nitrogen atmosphere before

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* National Chemical Laboratory Communication No. 984.

use. A $2M$ solution of $AlEt_3$ and a $1M$ solution of $Al(i\text{-}Bu)_3$ in n-hexane were prepared prior to use.

Styrene (Dow Chemical Co.) was first washed with 5% alkali, to remove inhibitor, then with water, and stored over anhydrous Na_2CO_3. Prior to use it was distilled under reduced pressure (b.p. 56°C.) and nitrogen atmosphere in a flask containing activated silica gel.

n-Hexane was purified by shaking with concentrated H_2SO_4 several times and then washed with Na_2CO_3 solution and distilled water and left overnight over anhydrous $CaCl_2$. It was distilled and stored over sodium wire. It was refluxed under dry nitrogen on sodium for 12 hr., distilled, and kept in a brown, glass bottle over activated silica gel.

Polymerization

All the experiments were carried out inside a dry glove box, which was maintained anhydrous under oxygen-free nitrogen atmosphere. All the reagents were added with all-glass hypodermic syringes fitted wth stainless-steel needles.

In an Erlenmeyer flask (50 ml.) fitted with B_{19} cone joint the reagents were added in the following order: solvent, $VOCl_3$ solution, and aluminum alkyl solution. The catalyst complex formed was aged for a specific time, and then the monomer was introduced into the system. The flask was stoppered tightly with well-greased B_{19} socket joint and held in thermostat maintained at constant temperature. The reaction mixture was stirred vigorously with a specially fabricated magnetic stirrer.[4] After a specific time of reaction the polymer was precipitated with a large amount of methanol containing 5% HCl and left overnight to settle down well. It was washed thoroughly with methanol inside a weighed crucible provided with cintered disk and dried to constant weight.

The polymer obtained was refluxed with toluene for 6 hr., and the soluble portion was reprecipitated and dissolved in benzene for viscometric determination of the molecular weights with the following relationship:[5]

$$P_n = 1.770 \times [\eta]^{1.4}$$

Potentiometric Titration for Determination of Vanadium Valence

For further insight into the nature of the catalytic species responsible for the polymerization the valence distribution of vanadium in the catalytic complexes at various ratios of Al to V was studied potentiometrically. Redox titrations of acid solution of complex were carried out with saturated-calomel and Pt-indicator electrodes and $0.1N$ $KMnO_4$ solution as oxidant at 80°C.[6]

Results and Discussion

Both the catalyst systems instantaneously developed a dark brown color and a fine precipitate was formed on mixing of the two components,

TABLE I
Effect of Aging Time on Polymerization of Styrene with $VOCl_3$-$AlEt_3$ System[a]

Aging time, min.	Conversion, %	Intrinsic viscosity, dl./g.	Mol. wt.
10	2.13	0.5109	71,980
20	2.17	0.5628	81,350
30	2.18	0.6655	104,105
60	2.57	0.5335	75,385
1,440	2.26	0.6825	105,455

[a] $[VOCl_3] = 0.02M$, $[AlEt_3] = 0.04M$, Al/V molar ratio = 2, styrene = 10 ml., temperature = 40°C.

irrespective of the concentration of catalyst. The rate of polymerization and also the molecular weights of the polymer obtained remained unchanged with the variation of aging time from 10 min. to 24 hr. (Tables I and II), showing thereby that catalytic activity remained unchanged for a long time. All the experiments were therefore carried out after 20 min. of aging of the catalyst systems.

It is well known[7,8] that the nature of catalyst sites changes with the variation in ratio of the catalyst components. In the two systems under investigation the rate of polymerization was found to decrease with the increase in Al/V ratios (Fig. 1). In the case of the $VOCl_3$-$AlEt_3$ catalyst system a sharp decrease in the rate of polymerization was observed when the Al/V ratio was increased from 1 to 2, and a further increase in the ratio resulted in a gradual decrease in the rate of polymerization. The molecular weight of the polymer obtained showed a sharp increase as the ratio of Al/V was increased from 1 to 2, and it was maximum at the Al/V ratio of 2; thereafter it decreased rapidly up to a ratio of 4 and then remained almost steady. In the case of the $VOCl_3$-$Al(i\text{-}Bu)_3$ system the rate of polymerization decreased sharply between the Al/V ratios of 2 and 3, and a further increase in ratio showed a much slower decrease in the rate of polymerization. However, the molecular weight of the polymer increased steadily with increase in the Al/V ratio above 2 and up to the Al/V ratio of 6, the highest

TABLE II
Effect of Aging Time on Polymerization of Styrene with $VOCl_3$-$Al(i\text{-}Bu)_3$ System[a]

Aging time, min.	Conversion, %	Intrinsic viscosity, dl./g.	Mol. wt.
10	11.04	0.1631	14,540
20	10.60	0.1226	9,745
30	9.19	0.1236	9,860
60	13.11	0.1343	11,060
1,440	9.34	0.1595	14,100

[a] $[VOCl_3] = 0.01M$, $[Al(i\text{-}Bu)_3] = 0.03M$, Al/V molar ratio = 3, styrene = 5 ml., reaction time = 15 min., temperature = 40°C.

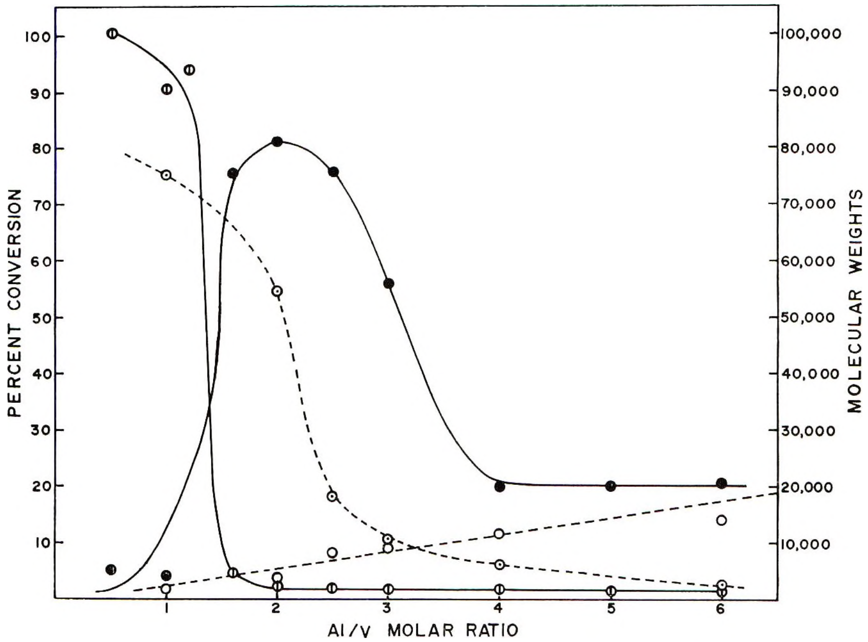

Fig. 1. Molar ratio versus conversion and molecular weight. $VOCl_3$–$AlEt_3$ system: $[VOCl_3] = 0.02M$, $[\text{styrene}] = 3.49M$, reaction time = 3 hr., aging time = 20 min., and temperature = 40°C.; (⦶) versus conversion, (●) versus molecular weight. $VOCl_3$–$Al(i\text{-}Bu)_3$ system: $[VOCl_3] = 0.01M$, $[\text{styrene}] = 1.74M$, reaction time = 15 min., aging time = 20 min., temperature = 40°C.; (⊙) versus conversion, (○) versus molecular weight.

investigated. The molecular weights of polymer obtained with the system $VOCl_3$–$Al(i\text{-}Bu)_3$ were considerably lower than those obtained with $VOCl_3$–$AlEt_3$. In the light of these observations a detailed kinetic study of the $VOCl_3$–$AlEt_3$ system was carried out at an Al/V ratio of 2, at which the molecular weight of the polymer was highest and the variation in the rate of polymerization with the Al/V ratio was least. In the case of $VOCl_3$–$Al(i\text{-}Bu)_3$ a ratio of 3.0 was arbitrarily chosen from the region where the rate variation with the Al/V ratio was least.

The rates of polymerization were constant in the early stages (for about 1 hr. in the $VOCl_3$–$AlEt_3$ system and about 30 min. in the $VOCl_3$–$Al(i\text{-}Bu)_3$ system) for both systems (Figs. 2 and 3), and with longer reaction times the rates of polymerization slowed down, probably owing to covering of catalyst sites by precipitated polymer in *n*-hexane. A similar covering of catalyst sites has been established in the polymerization of ethylene[9] with $TiCl_3$–$AlEt_2Cl$. Because of the faster reaction the precipitation in the case of $VOCl_3$–$Al(i\text{-}Bu)_3$ is earlier than that in the case of $VOCl_3$–$AlEt_3$. A recent study by Bushick and Stearns[10] has shown that the ionic character of the organometallic compound in the catalyst affects the rate of polymerization and also that the dissociation constant of $AlEt_3$ is about 30 times that of $Al(i\text{-}Bu)_3$. The highly ionic nature of $Al(i\text{-}Bu)_3$ may be

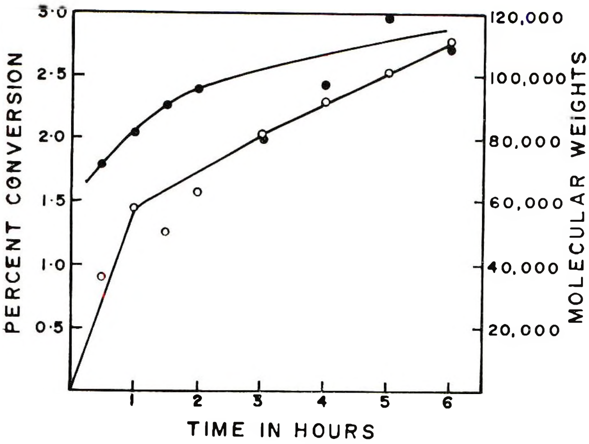

Fig. 2. Reaction time versus conversion and molecular weight. VOCl$_3$–AlEt$_3$ system: [VOCl$_3$] = 0.02M, [AlEt$_3$] = 0.04M, Al/V molar ratio = 2, [styrene] = 3.49M, aging time = 20 min., temperature = 40°C.; (○) versus conversion, (●) versus molecular weights.

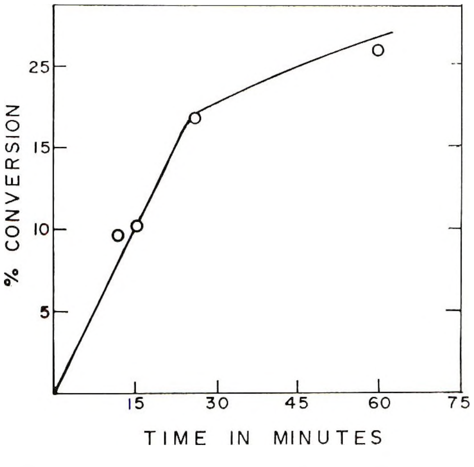

Fig. 3. Reaction time versus conversion. VOCl$_3$–Al(i-Bu)$_3$ system: [VOCl$_3$] = 0.01M, [Al(i-Bu)$_3$] = 0.03M, [styrene] = 1.74M, aging time = 20 min., temperature = 40°C.

responsible for the much higher rates of polymerization in the case of VOCl$_3$–Al(i-Bu)$_3$ than in the case of VOCl$_3$–AlEt$_3$.

Keeping in view the above findings, the variation of rate of polymerization with catalyst and monomer concentration was studied at an Al/V ratio of 2.0 and a reaction time of 60 min. in the case of VOCl$_3$–AlEt$_3$ and a reaction time of 15 min. in the case of VOCl$_3$–Al(i-Bu)$_3$ at an Al/V molar ratio of 3.0.

The rate of polymerization was observed to be second-order with respect to monomer in both the systems: $K = 4.831 \times 10^{-5}$ for VOCl$_3$–AlEt$_3$ and

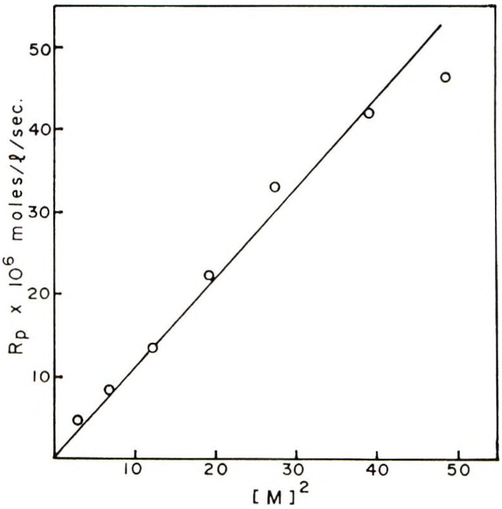

Fig. 4. Rate of polymerization versus monomer concentration. $VOCl_3$–$AlEt_3$ system: $[VOCl_3] = 0.02M$, $[AlEt_3] = 0.04M$, Al/V molar ratio = 2, reaction time = 1 hr., aging time = 20 min., temperature = 40°C.

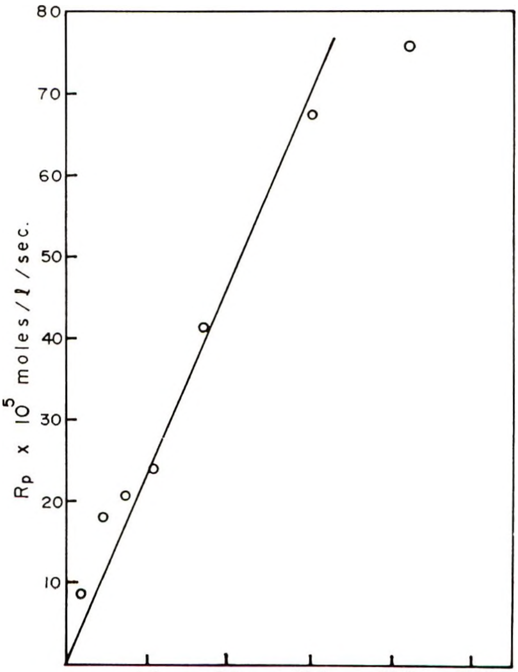

Fig. 5. Rate of polymerization versus monomer concentration. $VOCl_3$–$Al(i\text{-}Bu)_3$ system: $[VOCl_3] = 0.01M$, $[Al(i\text{-}Bu)_3] = 0.03M$, Al/V molar ratio = 3, reaction time = 15 min., aging time = 20 min., temperature = 40°C.

$K = 9.615 \times 10^{-1}$ for $VOCl_3$-$Al(i\text{-}Bu)_3$; see Figures 4 and 5. The values of the rate constants represent a high activity of catalyst for both systems, $VOCl_3$–$Al(i\text{-}Bu)_3$ being, however, much more active than $VOCl_3$–$AlEt_3$. A second order with respect to monomer can be rationalized by a Rideal or Hinshelwood mechanism, as has been done by Gaylord et al.[11]

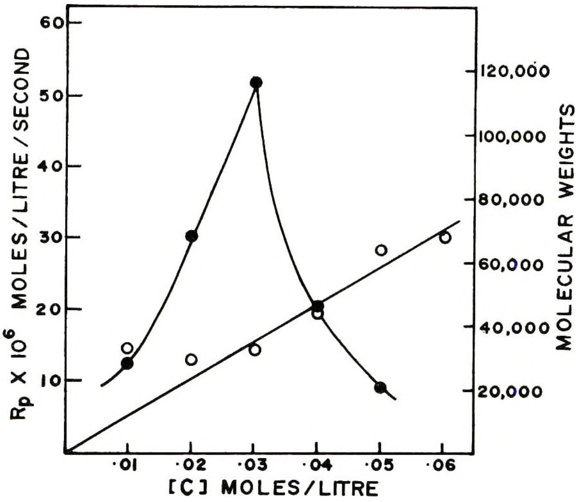

Fig. 6. Rate of polymerization and molecular weight versus catalyst concentration. $VOCl_3$–$AlEt_3$ system: [styrene] = 3.49*M*, Al/V molar ratio = 2, temperature = 40°C., reaction time = 1 hr., aging time = 20 min.; (○) R_p versus [C], (●) mol. wt. versus [C].

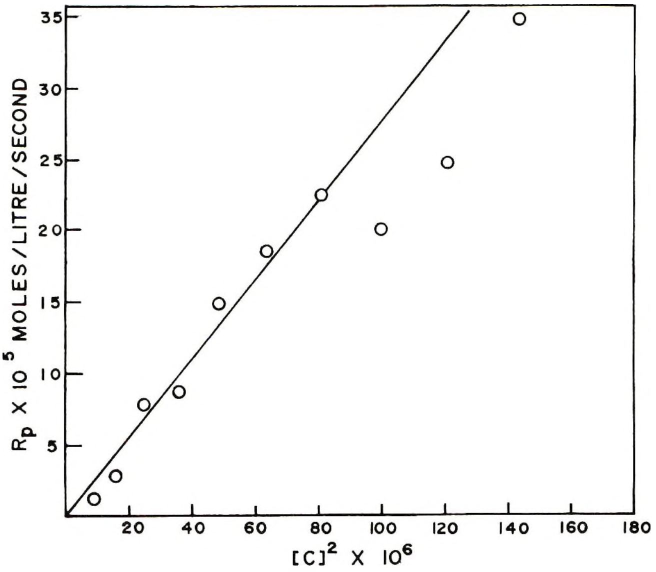

Fig. 7. Rate of polymerization versus catalyst concentration. $VOCl_3$–$Al(i\text{-}Bu)_3$ system: [styrene] = 1.74*M*, aging time = 20 min., reaction time = 15 min., temperature = 40°C.

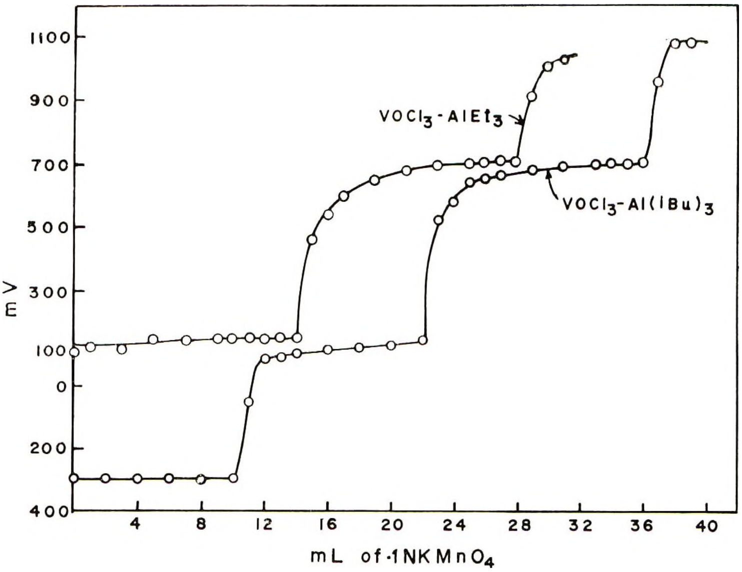

Fig. 8. Distribution of valence of vanadium at Al/V molar ratio 2 in $VOCl_3$–$AlEt_3$ and at Al/V molar ratio 3 in $VOCl_3$–Al(*i*-Bu)$_3$.

The rate of polymerization with respect to catalyst was first order in the case of $VOCl_3$–$AlEt_3$ and second order in the case of $VOCl_3$–Al(*i*-Bu)$_3$; see Figures 6 and 7. A second order with respect to catalyst has not been reported with Ziegler-type catalysts, but its occurrence in the case of $VOCl_3$–Al(*i*-Bu)$_3$ does not necessarily imply a departure from Ziegler-type behavior. It shows, however, the complexity of catalyst-forming reactions. It is postulated that the reaction between the catalyst components results in two types of species, one of which is active in the polymerization of styrene:

$$2C \rightleftharpoons C^{*1} + C^{*2}$$

where C^{*2} is not active in styrene polymerization. Thus, the reaction which is first order with respect to C^{*1} will be second order with respect to C, the total amount of catalyst present.

The rate constants with respect to catalyst, $K = 4.746 \times 10^{-5}$ for $VOCl_3$–$AlEt_3$ and $K = 6.006 \times 10^{-1}$ for $VOCl_3$–Al(*i*-Bu)$_3$, are comparable to those obtained with respect to monomer in both cases.

The molecular weights of the polymer obtained in the case of $VOCl_3$–$AlEt_3$ system are much higher than those obtained in the case of the $VOCl_3$–Al(*i*-Bu)$_3$ system. This may be attributed to the dissimilar natures of the catalyst sites formed in the two cases. The average valence of vanadium in the catalyst complex formed with $VOCl_3$–$AlEt_3$ is 3 and, further, all the vanadium present in the complex is in the trivalent form as shown in Figures 8 and 9. Only the trivalent form is known to give stereospecific polypropylene, in the case of VCl_4–$AlEt_3$ and V(AcAc)$_3$–$AlEt_2Cl$ systems.[12]

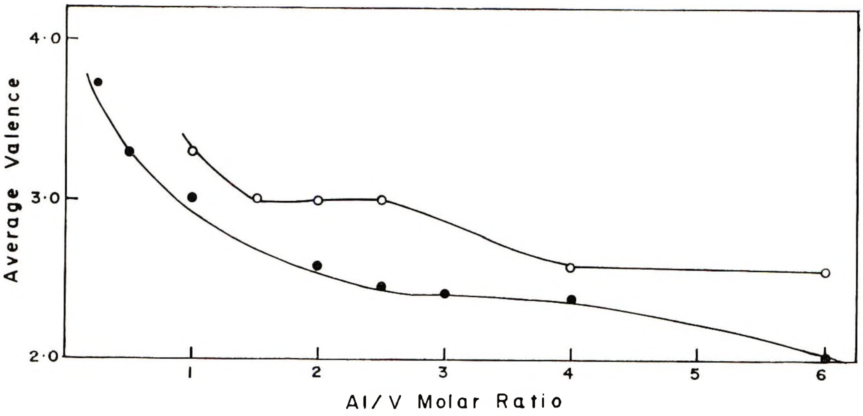

Fig. 9. Average valence versus Al/V molar ratio: (●) $VOCl_3$–$Al(i\text{-}Bu)_3$, (○) $VOCl_3$–$AlEt_3$.

On the other hand, the complex in the $VOCl_3$–$Al(i\text{-}Bu)_3$ system contains vanadium in bivalent as well as trivalent form, and the average valence of the vanadium in the complex is 2.54. Vanadium in the divalent form is known to be less active for isotactic polymerization.[12] The poor isotacticity obtained with catalysts containing $VOCl_3$ can be explained to a certain extent by the presence of oxygen in the transition-metal compound. Because of resonance between the structures,

$$M—\ddot{\underset{\cdot\cdot}{O}}—V—R \leftrightarrow M—\underset{\cdot\cdot}{O}^{\delta\oplus}{=\!=}V^{\delta\ominus}—R$$

the coordination of monomer to catalyst sites is weak and results in a poorer orientation of monomer before addition to the growing chain.

These observations indicate that for both the systems investigated, a coordinated anionic mechanism of polymerization essentially is operating.

Further support of the mechanism of polymerization can be obtained from the studies of activation energy and the effect of diethylzinc on polymerization (studied with $VOCl_3$–$AlEt_3$ only). The activation energy

TABLE III
Effect of Diethylzinc on Polymerization of Styrene with $VOCl_3$–$AlEt_3$ System[a]

$ZnEt_2$ concn., moles/l.	Yield, g.	Mol. wt.
0.00	0.1327	68,484
0.01	0.1730	12,865
0.02	0.1462	14,166
0.04	0.0942	15,392
0.06	0.0945	31,793
0.10	0.0944	15,724

[a] Styrene = 10 ml., reaction time = 1 hr., aging time = 20 min., $[VOCl_3] = 0.02M$; $[AlEt_3] = 0.04M$, temperature = 40°C., Al/V molar ratio = 2.

calculated from the plots of log R_p versus the reciprocal of the absolute temperature was 7.37 kcal./mole for $VOCl_3$–$AlEt_3$ and 11.25 kcal./mole for $VOCl_3$–$Al(i\text{-}Bu)_3$ both of which fall in the range of 5–12 kcal./mole obtained for most Ziegler-type catalysts, such as $TiCl_4$–$AlEt_3$ and $TiCl_3$–$AlEt_3$.[13,14] Diethylzinc acted as chain-transfer agent with the $VOCl_3$–$AlEt_3$ system (Table III), its action being similar to that with the classic Ziegler catalyst $TiCl_4$–$AlEt_3$,[15] where it has been observed that the polymerization reaction is terminated by chain transfer with diethylzinc. Because of the rather low molecular weight of the polymer obtained with $VOCl_3$–$Al(i\text{-}Bu)_3$ the effect of diethylzinc in this case was not undertaken.

The studies indicate that the formation of catalyst sites is greatly dependent on the organometallic compound used. Differences in kinetic behavior show that catalyst sites formed by the addition of $AlEt_3$ to $VOCl_3$ are entirely different from those formed by the addition of $Al(i\text{-}Bu)_3$ to $VOCl_3$. This is further manifested by the change in the valence of vanadium in the complexes of these catalyst systems.

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Résumé

La polymérisation du styrène avec $VOCl_3$ en combinaison avec $AlEt_3$ et $Al(i\text{-}Bu)_3$ dans l'hexane-*n* à 40°C a été étudiée. La vitesse de polymérisation a été trouvée être de second ordre par rapport au monomère dans les deux systèmes. Par rapport à la concentration en catalyseur la vitesse de polymérisation est de premier ordre pour le système $VOCl_3$–$AlEt_3$ et de second ordre dans le cas de $VOCl_3$–$Al(i\text{-}Bu)_3$. L'énergie d'activation pour $VOCl_3$–$AlEt_3$ et $VOCl_3$–$Al(i\text{-}Bu)_3$ était 7.37 Kcal/mole et de 11; 25 Kcal/mole respectivement. Le poids moléculaire du polystyrène pour le système $AlEt_3$ était considérablement plus élevé que pour le système $Al(i\text{-}Bu)_3$. La valence du vanadium obtenue par la méthode potentiométrique a montré que les sites catalytiques dans le système $AlEt_3$ étaient différents de nature de ceux dans $Al(i\text{-}Bu)_3$. L'effet du diéthylzinc comme agent de transfert de chaîne dans le système $AlEt_3$ a été étudié également.

Zusammenfassung

Die Polymerisation von Styrol mit VOCl$_3$ in Kombination mit AlEt$_3$ und Al(i-Bu)$_3$ in n-Hexan bei 40°C wurde untersucht. Die Polymerisationsgeschwindigkeit ist in Bezug auf das Monomere in beiden Systemen von zweiter Ordnung. In Bezug auf die Katalysatorkonzentration war die Polymerisationsgeschwindigkeit für VOCl$_3$–AlEt$_3$ von erster Ordnung und im Falle des VOCl$_3$–Al(i-Bu)$_3$-Systems von zweiter Ordnung. Die Aktivierungsenergie betrug für VOCl$_3$–AlEt$_3$ 7,37 kcal/Mol und für VOCl$_3$–Al(i-Bu)$_3$ 11,25 kcal/Mol. Das Molekulargewicht des Polystyrols war im AlEt$_3$-System bedeutend höher als im Al(i-Bu)$_3$-System. Die nach der potentiometrischen Methode erhaltene Wertigkeit des Vanadins zeigte, dass sich die Orte katalytischer Wirksamkeit im AlEt$_3$-System und im Al(i-Bu)$_3$-System ihrer Natur nach unterscheiden. Schliesslich wurde auch die Wirkung von Zinkdiäthyl als Kettenüberträger im AlEt$_3$-System untersucht.

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Free-Radical Polymerization of Vinyl Ferrocene

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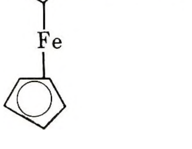
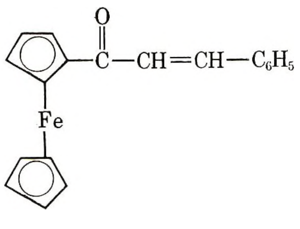
Synopsis

The results of quantitative studies of the rates of free-radical polymerization of vinyl ferrocene indicate that the latter has polymerization characteristics similar to those of styrene. The rates of homopolymerization of these two monomers in benzene at 70°C. were measured with the use of azobisisobutyronitrile as catalyst. The rate constants ($k = R_p/[M][I]^{1/2}$) are $k_{VF} = (1.1 - 1.8) \times 10^{-4}$, $k_{STY} = 1.65 \times 10^{-4}$. Small amounts of vinyl ferrocene and styrene have similar effects on the rates of polymerizations of methyl methacrylate and ethyl acrylate and on the molecular weights of the resulting polymer. Polystyrene and poly(vinyl ferrocene) with similar molecular weights are isolated from polymerizations carried out under identical conditions. The rates of copolymerization of vinyl ferrocene–methyl methacrylate, vinyl ferrocene–styrene, and styrene–methyl methacrylate were determined by following the disappearance of monomers by means of gas chromatographic analyses. The relative reactivity for vinyl ferrocene is slightly lower than that for styrene.

Many polymers that contain the ferrocene group have been studied in recent years.[1-8] These polymers are of interest because of their electrical and magnetic properties[9] and their redox, or electron-exchange, properties.[10] No quantitative descriptions of the free-radical polymerization of vinyl ferrocene (I) have been reported. Arimoto and Haven[2] made homopolymers and copolymers of vinyl ferrocene using azobisisobutyronitrile (AIBN) as initiator. Chen et al.[10] repeated this work, preparing bulk polymers of vinyl ferrocene with a number-average molecular weight, $\overline{M}_n$ of 48,600. Rausch and Coleman[6] found that *trans*-cinnamoylferrocene (II) did not homopolymerize, but it was copolymerized with a variety of vinyl monomers and dienes by conventional bulk and solution techniques with AIBN as initiator.



(I)



(II)

This paper describes the kinetics of the homopolymerization of vinyl ferrocene at 70°C., the effect of vinyl ferrocene on the rates of polymerization with some common monomers, the molecular weight of poly(vinyl ferrocene) and methyl methacrylate–vinyl ferrocene copolymers, and the relative copolymerization reactivities of vinyl ferrocene, methyl methacrylate, and styrene. The similarity in the polymerization characteristics of vinyl ferrocene and of styrene is emphasized.

EXPERIMENTAL

Materials

(*a*) Vinyl ferrocene was supplied through the courtesy of Thiokol Chemical Corporation and was purchased from Columbia Chemicals. It was sublimed in vacuum; m.p. 46.5–47.5°C. Repeated sublimation did not change the melting point.

(*b*) Other monomers were fractionally distilled at reduced pressures just prior to use.

(*c*) Solvents were reagent grade, distilled.

(*d*) (AIBN) was recrystallized from methanol; m.p. 102–103°C. with decomposition.

Techniques

(*a*) Dilatometric polymerization rate determinations have been described elsewhere.[11]

(*b*) The NMR technique for following polymerization has been described.[12] The peaks that arise from vinyl protons in vinyl ferrocene were used for following the disappearance of the monomer.

(*c*) Solution viscosities were determined in Ubbelohde-type viscometers at 30°C. Acetone or toluene was used as solvent, depending on the polymer solubilities.

(*d*) The Mechrolab Vapor Pressure Osmometer was used for determining the $\bar{M}_n$ of polymers when it is below 15,000. The solvent used was benzene, and the instrument was calibrated with a standard polymer (polystyrene, obtained from Arro Laboratories) having an $\bar{M}_n$ of 10,000.

The Hallikainen Automatic Membrane Osmometer was used for determining the $\bar{M}_n$ of polymers having $\bar{M}_n$ greater than 15,000. A gel cellophane 600 membrane was used with toluene as solvent.

(*e*) The copolymerizations of vinyl ferrocene with styrene and with methyl methacrylate were followed by observing the disappearance of the monomers by gas chromatographic (GC) analyses. The polymers were analyzed for iron to determine the amount of ferrocene in the copolymer, confirming the applicability of the GC analyses.

An Aerograph Model A-350-B Dual Column Chromatograph and a Leeds and Northrup Speedomax H Recorder with disk integrator were used for the GC Analyses. The column used was stainless steel (6 ft. by $^1/_8$

in. O.D.) packed with 20% by weight of General Electric SE-30 (methyl silicon gum rubber) on Anakrom A. Similar columns were found[13] to be very efficient for the separation of ferrocene compounds.

The monomers, initiator (AIBN), internal standard (*n*-butyl benzoate), and solvent (diethyl phthalate) were degassed by helium purge and weighed into a one-necked flask fitted with a stopcock with serum cap covering the section above the stopcock.

The flask was placed in a bath at 60°C., and samples were withdrawn at 15-min. intervals with a hypodermic needle. A pressure of 2 lb. of helium was kept in the flask and in the section above the stopcock, to permit sample withdrawals without letting air into the system. The samples were immediately added to a vial containing diphenylpicrylhydrazyl, to quench the polymerization. The samples were then put through the GC column, which was at 140°C. having a helium flow of 100 ml./min.

RESULTS

Homopolymerization

Dilatometric polymerization rate determinations were made with solutions of vinyl ferrocene and of styrene in benzene, with AIBN as the initiator at 70°C. The concentrations in both experiments were: monomer 1.6 moles/l., AIBN 0.0102 moles/l. After 2 hr. the shrinkage that had occurred for each monomer was noted, and the polymers were obtained by precipitation in methanol. The polymer samples were dried and weighed, and the shrinkage per mole of monomer converted to polymer was calculated. For vinyl ferrocene, ΔV/mole = 10.9 cc., and for styrene ΔV/mole = 18.7 cc. The ΔV/mole for styrene and other monomers can be calculated from polymer and monomer densities.[14] Several of these are shown in Table I. The apparent discrepancy in ΔV/mole for styrene probably reflects the difference between solution polymerization (18.7 cc./mole) and bulk polymerization (16.6 cc./mole). At any rate, the data indicate that ΔV/mole for vinyl ferrocene is similar to that for other bulky monomers.

Table II gives the homopolymerization data obtained at 70°C. The polymerization rate data were calculated on the assumption that the fraction polymerized is proportional to the shrinkage, with the molar shrinkage listed above. The quantity $R_p[\mathrm{M}][\mathrm{I}]^{1/2}$ gives a relative measure of the

TABLE I

Polymerization Shrinkage per Mole of Monomer (Ref. 14) Calculated from Densities of Monomer and Bulk Polymer at Ambient Temperature

Monomer	ΔV/mole, cc.
Styrene	16.6
N-Vinyl carbazole	14.3
Vinyl pyrene	9.1

TABLE II
Homopolymerization of Vinyl Ferrocene and Styrene at 70°C.

Monomer	[M], moles l.$^{-1}$	[AIBN], moles/l.	R_p, moles l.$^{-1}$ sec.$^{-1}$ ($\times 10^5$)	$R_p/$[M][I]$^{1/2}$, moles l.$^{-1}$ sec.$^{-1}$ ($\times$ 10^4)	Reduced specific viscosity	M_n
Styrene	1.6	0.0102	2.64	1.65	0.12	5,400
	1.6	0.0051	1.24	1.1	0.14	—
Vinyl ferrocene	1.6	0.0102	1.90	1.2	—	—
	1.6	0.0204	4.01	1.8	0.05	6,000

polymerization rates of monomers for a given initiator and temperature. It is seen that vinyl ferrocene resembles styrene in this quantity.

In addition to the dilatometric study, which could be carried to only relatively low conversion because of nitrogen evolution from the AIBN, the homopolymerization was studied by an NMR technique over a much longer time period. The purpose of the experiment was to discover the possible buildup of an inhibitor through a degradative-transfer reaction of some sort. A 50% solution of vinyl ferrocene in benzene containing 1% AIBN was heated in a sealed NMR tube at 60°C. for 4 days, and the NMR spectrum was obtained at intervals. The monomer had polymerized approximately 90% in this period, judging by the decrease in the vinyl proton absorption. The resulting solution was a clear, brown, very viscous liquid.

Several homopolymerizations were attempted with benzoyl peroxide as initiator. Very little polymerization was observed, even over long periods of time. It appears that the benzoyl peroxide is destroyed by a nonradical reaction with ferrocene, as was reported by Coleman and Rausch.[4]

Effect of Vinyl Ferrocene on the Polymerization of Other Monomers

As a means of ranking vinyl ferrocene qualitatively as to reactivity in free-radical polymerizations a series of experiments was run, in which a small amount of vinyl ferrocene was added to solutions of common monomers of known properties. The polymerization rates were then determined at given AIBN and monomer concentrations and compared with the rates obtained under the same conditions in the absence of vinyl ferrocene. The monomers used were styrene, methyl methacrylate, ethyl acrylate, and vinyl acetate. Where applicable the effect of styrene was also determined.

The data are shown in Table III, in which are given the rates of polymerization of the monomers both alone and in the presence of vinyl ferrocene and styrene and also the reduced specific viscosities of the polymers formed. It should be pointed out that no attempt was made in these experiments to follow the relative disappearance of vinyl ferrocene and the standard monomers but, rather, all polymerization was assumed to be of the standard

TABLE III
Relative Effects of Vinyl Ferrocene and Styrene on Polymerization of Methyl Methacrylate, Ethyl Acrylate, and Vinyl Acetate at 60°C.[a]

			Vinyl ferrocene		Styrene	
Monomer	Initial R_p %/min.	η_{sp}/c	Initial R_p	η_{sp}/c	Initial R_p	η_{sp}/c
Styrene	0.065	0.23	0.074	0.22	—	—
Methyl methacrylate	0.414	0.49	0.15	0.42	0.22	0.49
Ethyl acrylate	3.89	2.4	0.20	0.64	0.18	0.45
Vinyl acetate	0.17	—	0	—	0	—

[a] [AIBN] = 0.0203M; standard monomer concn., = 2.4M. Solvent, benzene; Added comonomer concn., 0.30M.

monomer. Since the amount of vinyl ferrocene was small in the experiments, this assumption should not affect the overall conclusions.

It is seen from Table III that vinyl ferrocene is very similar to styrene in its effect on the rates of polymerization of methyl methacrylate and ethyl acrylate and on the viscosity of the polymers produced. Vinyl ferrocene had essentially no effect on the rate of polymerization of styrene, and both vinyl ferrocene and styrene inhibit polymerization of vinyl acetate.

Number-average molecular weights were determined for the PMMA and the PMMA–VF copolymer described in Table III. The M_n for PMMA was 25,300; that for PMMA–VF, 22,000. This supports the conclusion that chain transfer activity of VF is low.

Copolymerization of Vinyl Ferrocene with Styrene and with Methyl Methacrylate

Approximately equimolar solutions of vinyl ferrocene–styrene and vinyl ferrocene–methyl methacrylate were copolymerized at 60°C. Styrene

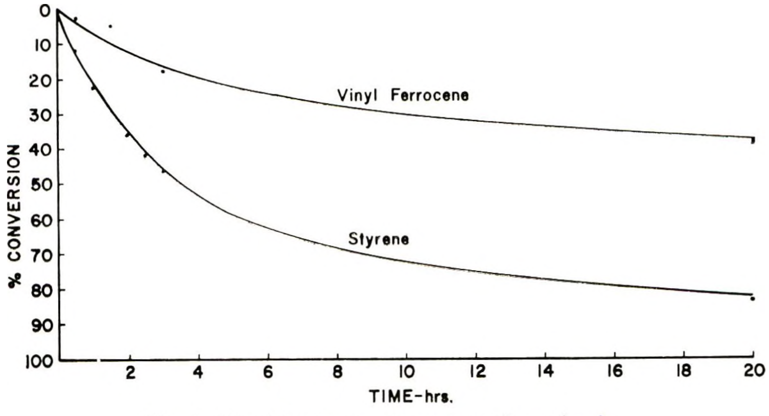


Fig. 1. Vinyl ferrocene–styrene copolymerization.

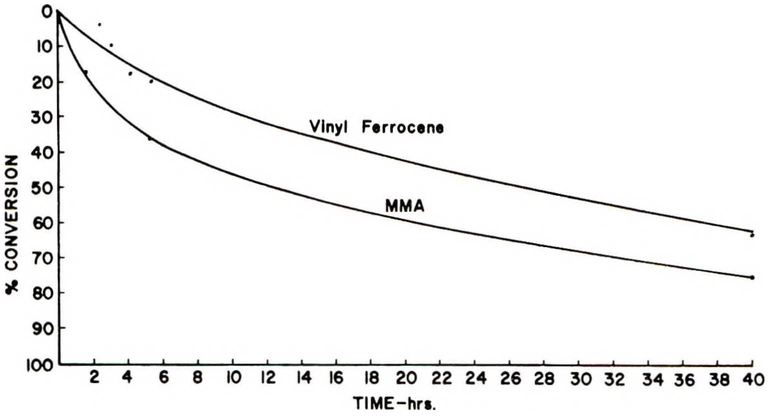


Fig. 2. Vinyl ferrocene–MMA copolymerization.

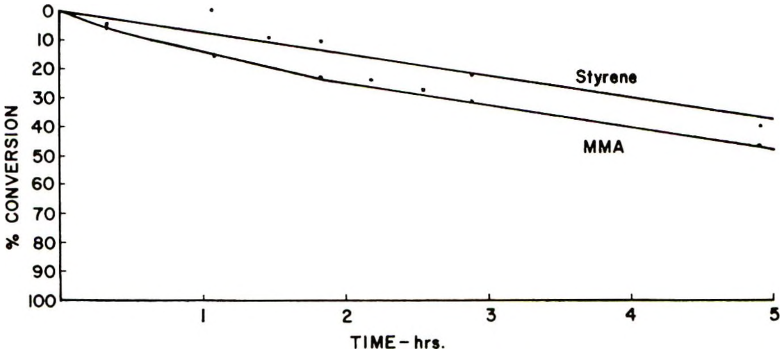


Fig. 3. MMA–styrene copolymerization.

and MMA are incorporated into the copolymers at a faster rate than is vinyl ferrocene. The total rate of polymerization is slightly faster in the VF–styrene copolymerization than with VF–MMA, but more vinyl ferrocene is incorporated into the VF–MMA copolymer during the early part of the polymerization (Figs. 1 and 2). The data obtained during the first 5–10% conversion were not precise enough for the determination of the relative reactivity ratios of vinyl ferrocene with MMA and styrene.

Approximations of the values for these VF–MMA ratios were obtained by comparing the rates of incorporation of monomers into PMMA–STY (Fig. 3) and PMMA–VF (Fig. 2). The reactivity ratios[15] of MMA–styrene are $r_1 = 0.46$ and $r_2 = 0.52$ (M_1 = MMA, M_2 = STY). The data indicate that r_1 and r_2 (M_1 = MMA, M_2 = VF) are both less than 1 and in the same range as those for MMA and styrene, but the values are reversed.

SUMMARY AND CONCLUSION

The free-radical polymerization characteristics of vinyl ferrocene and styrene in benzene are similar. The rate of homopolymerization of vinyl ferrocene is approximately 25% lower than that of styrene. Small amounts of vinyl ferrocene and styrene have similar effects on the rates of polymerization of methyl methacrylate and ethyl acrylate and on the molecular weights of the resulting copolymers. Both vinyl ferrocene and styrene inhibit polymerization of vinyl acetate.

Copolymerization data obtained from equimolar mixtures of vinyl ferrocene–methyl methacrylate, vinyl ferrocene–styrene, and methyl methacrylate–styrene indicate that vinyl ferrocene has a somewhat lower relative reactivity than does styrene or methyl methacrylate in the respective copolymerizations.

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Résumé

Les résultats d'études quantitatives de vitesses de polymérisation radicalaire de vinyl ferrocène indiquent que ce dernier a des caractéristiques de polymérisation similaires à celles du styrène. Les vitesses d'homopolymérisation de ces deux monomères dans le benzène à 70°C ont été mesurées en utilisant l'azobisisobutyronitrile comme catalyseur. Les constantes de vitesse ($k = R_p/[\mathrm{M}][\mathrm{I}]^{1/2}$) sont $k_{\mathrm{VF}} = (1.1\text{–}1.8) \times 10^{-4}$, $k_{\mathrm{STY}} = 1.65 \times 10^{-4}$. De faibles quantités de vinyl ferrocène et de styrène ont des effets semblables sur les vitesses de polymérisation du méthacrylate de méthyle et l'acrylates d'éthyle, et sur les poids moléculaires des polymères résultants. Du polyvinyl ferrocène et polystyrène avec des poids moléculaires semblables ont été isolés au départ des polymérisations effectuées dans des conditions identiques. Les vitesses de copolymérisation de vinyle ferrocène–méthacrylate de méthyle, vinyl ferrocène–styrène et styrène–méthacrylate de méthyle ont été déterminées en suivant la disparition des monomères au moyen de l'analyse par chromatographie gazeuse. Le rapport de réactivité relatif au vinyl ferrocène est légèrement plus bas que celui du styrène.

Zusammenfassung

Die Ergebnisse der quantitativen Untersuchung der Geschwindigkeit der radikalischen Polymerisation von Vinylferrocen zeigen, dass dieses ein ähnliches Polymerisationsverhalten wie Styrol zeigt. Die Geschwindigkeit der Homopolymerisation dieser beiden Monomeren in Benzol bei 70°C wurde mit Azobisisobutyronitril als Katalysator gemessen. Die Geschwindigkeitskonstanten ($k = R_p/[M][I]^{1/2}$) betragen $k_{VF} = (1,1-1,8) \times 10^{-4}$, $k_{STY} = 1,65 \times 10^{-4}$. Kleine Mengen von Vinylferrocen und Styrol besitzen einen ähnlichen Einfluss auf die Polymerisationsgeschwindigkeit von Methylmethacrylat und Äthylacrylat und auf das Molekulargewicht der entstehenden Polymeren. Polystyrol und Polyvinylferrocen mit ähnlichem Molekulargewicht werden bei Ausführung der Polymerisation unter identischen Bedingungen isoliert. Die Geschwindigkeit der Copolymerisation von Vinylferrocen–Methylmethacrylat, Vinylferrocen–Styrol und Styrol–Methylmethacrylat wurde durch gaschromatographische Verfolgung des Verschwindens der Monomeren bestimmt. Das relative Reaktivitätsverhältnis liegt für Vinylferrocen etwas niedriger als für Styrol.

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Catalysts for Asymmetric-Induction Polymerization of Benzofuran. II. Properties and Catalyses of Some Binary Systems Containing the Menthoxy Group

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Synopsis

It has been found that the equimolar binary system consisting of aluminum trichloride and (−)-menthoxytriethyltin, -germanium or -silicone is effective for the asymmetric-induction polymerization of benzofuran in toluene at −78°C. The specific rotation $[\alpha]_D$ of the resultant polybenzofuran ranged from +10° to +40°, depending on the polymerization conditions as well as the metal atoms constituting the menthoxy compounds. The 1:1 ethylaluminum dichloride–menthol system was also effective for the same polymerization. It was confirmed that these binary systems easily undergo an exchange reaction, giving a dimeric menthoxyaluminum dichloride, $(Men^*OAlCl_2)_2$, m.p. 72–75°C. A toluene solution of the crystalline dimer polymerized benzofuran into a high polymer having as large an $[\alpha]_D$ value as +79.4°, although polymerization with the dimer was much slower than that with the parent binary mixtures. All these results lead to the conclusion that the true catalytic species of our multicomponent systems is most probably the dimeric menthoxyaluminum dichloride.

INTRODUCTION

In a previous paper of this series[1] we reported that the binary homogeneous mixture of triethylaluminum and stannic chloride in toluene becomes capable of effecting the cationic asymmetric-induction polymerization of benzofuran when (−)-menthoxytriethyltin, Men^*OSnEt_3, is added as a third component. The binary mixture has been known to undergo easily an exchange reaction, giving aluminum chloride and triethyltin chloride,

$$AlEt_3 + SnCl_4 \rightarrow AlCl_3 + Et_3SnCl \qquad (1)$$

the products in turn forming multiple ions such as $(Et_3Sn^+ \cdots AlCl_4^-)_n$, as has been demonstrated in our still earlier communication.[2] Thus, the catalysis of the above-mentioned ternary system appeared to be ascribable to an optically active counterion, such as $Men^*OSnEt_3 \cdots AlCl_4^-$.

Continuation of the work along these lines has recently revealed to us that the optically active binary system consisting of $AlCl_3$ and Men^*OSnEt_3

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can also be effective for the asymmetric-induction polymerization, when the molar ratio of the two components is 1:1. The situation was much the same for analogous systems containing the germanium and silicone homologs of the menthoxytin compound. Further, the system of ethylaluminum dichloride plus menthol was also found to be useful for the same purpose.

It then seems that our catalyst systems containing the menthoxy group may be identical in nature with the binary systems comprising $AlCl_3$ or $EtAlCl_2$ and various optically active substances, which were first adopted by Natta and his colleagues for the benzofuran polymerization.[3-5] However, no decisive conclusion has yet been reached on the question of what the true catalytic species is, which no doubt would be very important in the elucidation of the mechanism of the asymmetric-induction process.

These situations have impelled us to look into the nature of our catalyst systems in more detail. Thus, in the present paper we have, first, compared the catalytic behaviors of various binary systems containing an aluminum component and the menthoxy group. Second, we have ascertained that these binary systems undergo an exchange reaction, to give a dimeric menthoxyaluminum dichloride, $(Men^*OAlCl_2)_2$, which can be isolated in crystalline form:

$$AlCl_3 + Men^*OSnEt_3 \rightarrow {}^1/_2(Men^*OAlCl_2)_2 + Et_3SnCl \quad (2)$$

$$EtAlCl_2 + Men^*OH \rightarrow {}^1/_2(Men^*OAlCl_2)_2 + EtH \quad (3)$$

Finally, it has been confirmed that a toluene solution of the crystalline dimer does effect the asymmetric-induction polymerization of benzofuran. The dimeric menthoxyaluminum compound has proved to be less effective for the polymerization in terms of the rate, yet more effective for the asymmetric induction than are the parent binary mixtures. All these results lead us to conclude that the true catalytic species of our multicomponent systems is $(Men^*OAlCl_2)_2$, necessitating some amendment of our earlier view[1] of the role of Men^*OSnEt_3 in controlling the asymmetric induction during the benzofuran polymerization.

EXPERIMENTAL

Materials

Toluene, benzene, isobutyl vinyl ether, triethylaluminum ($AlEt_3$), and stannic chloride ($SnCl_4$) were purified in the same manner as before.[2]

(−)-Menthol (Men*OH), which was used not only as the catalyst component but also for the syntheses of various menthoxy derivatives, was fractionally distilled on metallic sodium; the optical purity was 98.5%.

Ethylaluminum dichloride ($EtAlCl_2$), a product from the Ethyl Corporation, was fractionally distilled twice through a 40-cm. Vigreaux column under reduced pressure. The main fraction, boiling at 97.0–98.0°C. at 32 mm., was collected.

n-Hexane and *n*-heptane were dried by reflux on calcium hydride and then fractionally distilled.

Triethyltin chloride (Et_3SnCl), aluminum chloride ($AlCl_3$), (−)-menthoxytriethyltin (Men*OSnEt$_3$), (−)-menthyl ethyl ether (Men*OEt), and benzofuran were prepared by the methods described previously.[1,2]

(−)-Menthoxytriethyl silane (Men*OSiEt$_3$) was synthesized by refluxing a toluene solution of an equimolar mixture of triethylsilyl chloride (Et_3SiCl) and sodium menthylate (Men*ONa) for 3 hr.; b.p. 138.6–139.6°C. at 72 mm., $[\alpha]_D^{34} = -56.7°$ (in toluene).

ANAL. Calcd. for $C_{16}H_{34}SiO$: C, 71.04%; H, 12.67%. Found: C, 71.05%; H, 12.66%.

(−)-Menthoxytriethyl germane (Men*OGeEt$_3$) was prepared from triethylgermanium bromide (Et_3GeBr) and Men*ONa by the same method as used for Men*OSiEt$_3$; b.p. 105.0–105.7°C. at 1.0 mm., $[\alpha]_D^{34} = -56.30°$ (in toluene).

ANAL. Calcd. for $C_{16}H_{34}GeO$: C, 61.00%; H, 10.88%. Found: C, 60.90%; H, 11.33%.

(−)-Menthoxyaluminum dichloride (Men*OAlCl$_2$) was prepared in the following manner.

To 82.6 mmoles (9.9 g.) of $EtAlCl_2$ placed in a three-necked flask equipped with a magnetic stirrer, a dropping funnel, and a filling tube having a side arm for nitrogen inlet, 82.6 mmoles (12.8 g.) of menthol dissolved in 20 ml. of *n*-heptane was added gradually through the funnel under dry nitrogen at −78°C. The temperature of the mixture rose spontaneously on account of the heat of reaction. After the cessation of ethane gas evolution at room temperature the resulting white amorphous precipitates were isolated by decantation followed by evaporation of *n*-heptane. The precipitates were then dissolved in a 30-ml. portion of toluene at room temperature, and the solution was kept at −78°C. for a day. Crystals of Men*OAlCl$_2$ grew in the toluene solution. The crystalline product was further purified by repeating the cycles of decantation, redissolution, and recrystallization; yield 60.8%, m.p. 72–75°C., $[\alpha]_D^{20} = -39.1°$ (in toluene).

ANAL. Calcd. for $C_{10}H_{19}OAlCl_2$: C, 47.45%; H, 7.57%; Al, 10.66%; Cl, 28.01%. Found: C, 47.30%; H, 7.61%; Al, 10.84%; Cl, 27.76%.

The triethylsilyl chloride (Et_3SiCl) and triethylgermanium bromide (Et_3GeBr) used for the syntheses of the above-mentioned menthoxy compounds were prepared by the methods of Di Giorgio et al.[6] and Krausand et al.,[7] respectively. The boiling points of these halides were: Et_3SiCl, 145.0–147.5°C. at 755 mm. (lit.,[6] 144°C. at 735 mm.); Et_3GeBr, 76–77.5°C. at 22 mm. (lit.,[7] 176°C./760 mm.).

Procedures

The procedure for polymerization was the same as had been described previously,[1] except that the catalytic solutions were prepared and aged for half an hour in a separate flask and that a specified quantity of catalytic solution was transferred into a polymerization flask for each run. The crude polymer formed was washed with methanol, reprecipitated twice with toluene as solvent and methanol as precipitant, and finally dried *in vacuo* at 70°C.

The intrinsic viscosities of the polymers obtained were measured on toluene solutions at 30°C. with an Ubbelohde viscometer.

The cryoscopic determination of the molecular weights of the catalysts and the electric conductivity measurement of the catalyst solutions were performed in the manner described previously.[2]

The infrared absorption spectra of both polymers and catalysts were recorded under dry nitrogen on either a Japan Spectroscopic IR-S double-beam spectrometer or a Japan Spectroscopic 402-G grating-type spectrometer. Potassium bromide cells or plates of various thicknesses were used. All the observed spectra were corrected for wavenumber by means of a standard polystyrene film and by carbon dioxide.

The optical rotatory powers of the various organometallic compounds and the resulting polybenzofuran were measured in toluene with a Rex Photoelectric polarimeter Model NEP-2.

RESULTS AND DISCUSSION

Binary Catalysts Consisting of Aluminum Chloride and Menthoxytriethylmetals

As has already been reported,[2] the binary system prepared from equimolar amounts of $AlEt_3$ and $SnCl_4$ possibly produces a multi-ionic complex consisting of the $AlCl_4$ anion and the Et_3Sn cation in a solvent of low dielectric constant. However, it has been a question whether or not such a multi-

TABLE I

Polymerizations of Benzofuran by the $AlCl_3$-(−)-Men*$OMEt_3$ Systems (M = Si, Ge, Sn) with Toluene as Solvent at −75°C.

Catalytic system, molar ratio	Polymerization time, hr.	Conversion, %	$[\alpha]^{20}_D$ in toluene, deg.	Intrinsic viscosity $[\eta]$,[a] dl./g.
$AlCl_3$–Men*OEt, 1:1[b]	5	16.4	0	0.38
$AlCl_3$–Men*$OSiEt_3$, 1:1[b]	68	10.0	+10.4	1.22
$AlCl_3$–Men*$OGeEt_3$, 1:1[b]	63	12.0	+34.5	1.93
1:1[c]	2.5	26.4	+11.3	1.78
$AlCl_3$–Men*$OSnEt_3$, 1:1[b]	0.25	53.5	+25.1	1.60
1:1[c]	2.5	12.1	+38.8	1.60
1:1.5[b]	102	0	—	—
Et_3SnCl–Men*$OSnEt_3$, 1:1[d]	168	0	—	—

[a] In toluene at 30°C.

[b] Concn., mole/l.: benzofuran 750, $AlCl_3$ 37.5.

[c] Concn., mole/l., benzofuran 620, $AlCl_3$ 12.4.

[d] Concn., mole/l.: benzofuran 450, Et_3SnCl and Men*$OSnEt_3$ 22.5. At room temperature.

ionic complex would still exist in solutions when Men*$OSnEt_3$, an ethereal compound, is added. In fact, white precipitates were formed in this ternary system. Moreover, the remarkable decrease in the electric conductivity of the solution observed on addition of the ether implied the destruction of the multi-ionic complex, perhaps producing non-ionic species such as $AlCl_3$ and Et_3SnCl. Such non-ionic species may well be attacked by Men*$OSnEt_3$ and thereby transformed into a true catalytic species that is effective for the asymmetric-induction polymerization. The known reaction between $AlCl_3$ and $ROSiEt_3$, giving $ROAlCl_2$ and Et_3SnCl, where R is an alkyl group,[8] may have some bearing on this possibility.

With this in mind we have undertaken the polymerization of benzofuran, using equimolar mixtures of $AlCl_3$ and Men*$OMEt_3$, where M signifies the Sn, Ge, Si, and C atoms. The results are summarized in Table I.

From the data listed in Table I it can be seen that the catalytic solutions prepared from $AlCl_3$ and Men*$OMEt_3$, where M is Sn, Ge, or Si, are effective for the asymmetric-induction polymerization of benzofuran. On the other hand, the system of $AlCl_3$ and Men*OEt failed to give an optically active polymer, though it was able to polymerize benzofuran. The binary mixture of Et_3SnCl and Men*$OSnEt_3$ was entirely incapable of polymerizing the benzofuran monomer even at room temperature.

Table II shows the results of the electric conductivity measurements of the various binary mixtures. The most important feature of the results given in this table is that the combination of aluminum chloride and menthoxytriethylmetal leads to a very much smaller conductivity than that of the $AlCl_3$–Et_3SnCl system. The conductivity of the $AlCl_3$–Men*OEt is in between the two limits. These results suggest that the catalyses of the $AlCl_3$–Men*$OMEt_3$ and $AlCl_3$–EtSnCl systems in the polymerization of benzofuran are quite different in nature.

Measurements of the freezing-point depressions of benzene containing these binary systems have manifested an interesting correlation. Our previous result from the 1:1 $AlCl_3$–Et_3SnCl mixture showed that the mixture gives a product having an average molecular weight of 1800, which corresponds to the complex compound $(Et_3SnCl:AlCl_3)_n$ with a value of n

TABLE II

Electric Conductivities of the 1:1 $AlCl_3$–Men*$OMEt_3$ Systems, Measured in Toluene at 18°C.

Catalytic system	Concentration, mmole each/l.	Specific conductivity, 10^8 ohm^{-1} cm.$^{-1}$	Equivalent conductivity, 10^6 ohm^{-1} cm.^{2} mole^{-1}
$AlCl_3$–Men*OEt	114.045	2.986	261.8
$AlCl_3$–Men*$OSiEt_3$	29.240	0.028	9.6
$AlCl_3$–Men*$OGeEt_3$	14.620	0.014	9.6
$AlCl_3$–Men*$OSnEt_3$	33.086	0.024	7.3
$AlCl_3$–Et_3SnCl	376.5	3649	9.69×10^4

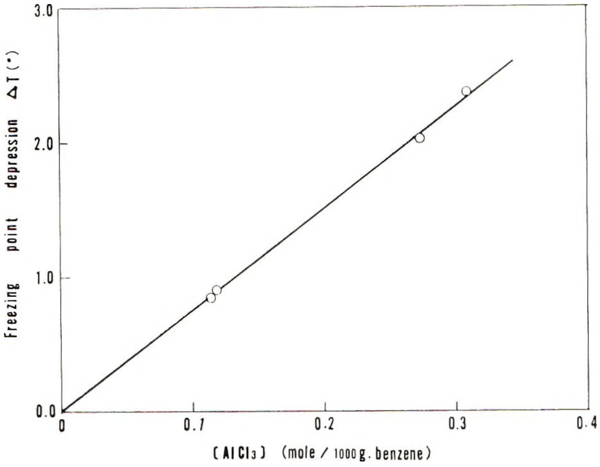

Fig. 1. Concentration dependence of the freezing point depression of benzene containing 1:1 $AlCl_3$–Men*OSnEt$_3$ mixture. The slope, 7.53° per mole per 1000 g. of benzene, of the straight line is exactly 1.5 times as large as the molar depression of benzene, indicative of the completion of the reaction (2) of the text.

as great as 4.8.[2] In the present $AlCl_3$–Men*OMEt$_3$ systems, however, no such trend was observed, as may be seen in Table III.

In the case of the 1:1 $AlCl_3$–Men*OSnEt$_3$ system the freezing point depression was measured with varying concentrations. A plot of the observed depression ΔT versus concentration gave a straight line in the concentration range studied, as is shown in Figure 1. This finding rules out the possibility that the mixture is in equilibrium with a molecular complex of the form $AlCl_3$:Men*OSnEt$_3$. The slope of the straight line, 7.53° per mole per 1000 g., gives a value of 1.48 when divided by the molar de-

TABLE III

Freezing Point Depressions of Benzene Solutions Containing 1:1 $AlCl_3$–Men*OMEt$_3$ Systems

Catalytic system	Concentration, mmole each per 1000 g. of benzene	Freezing point depressions, deg.			
			Calculated[a]		
		Observed	I	II	III
$AlCl_3$–Men*OEt	0.280	2.526	1.432	2.148	2.864
$AlCl_3$–Men*OSiEt$_3$	0.285	2.273	1.458	2.187	2.916
$AlCl_3$–Men*OSnEt$_3$	0.309	2.362	1.582	2.372	3.164
	0.273	2.03	1.398	2.097	2.796
	0.118	0.91	0.604	0.906	1.208
	0.116	0.86	0.593	0.890	1.186

[a] I, calculated by assuming that a complete molecular association takes place between the two components; II, calculated by assuming reaction (2); III, calculated by assuming that there occurs no change in the total number of molecules on mixing of the two components.

pression of benzene, i.e. 5.12° per mole per 1000 g. The quotient 1.48 is very close to the value 1.50, which must be attained when 1 mole each of two components are totally consumed by a mutual reaction to give 1.5 moles of product or products. This is consistent with reaction scheme (2). This argument receives further support from the results of the infrared spectroscopies of our catalytic systems, as will be discussed.

From the lines of evidence described above we may conclude that the exchange reaction (2) easily takes place at room temperature. The situation is probably the same in Men*OGeEt$_3$ and Men*OSiEt$_3$ but a bit more complicated in Men*OEt. The lack of asymmetric-induction ability of the AlCl$_3$–Men*OEt system may be connected with its difficulty in forming Men*OAlCl$_2$ through an exchange reaction.

The Ethylaluminum Dichloride–Menthol System

As has been described in the preceding section, the results of the cryoscopic determination led us to consider the dimeric menthoxyaluminum dichloride to be the main product of a reaction between aluminum chloride and menthoxytriethylmetals.

However, it may well be feared that the main product would not necessarily constitute a true catalytic species. Taking this subtle aspect of catalysis into account, we have chosen the ethylaluminum chloride–menthol system as an independent source of obtaining menthoxyaluminum dichloride [reaction (3)]. The product was then isolated in a crystalline form from its toluene solution. The results of the elemental analysis and the molecular weight determination have checked with the formula (Men*OAlCl$_2$)$_2$.

TABLE IV
Polymerization of Benzofuran with Various Catalysts Containing the Menthoxy Group[a]

Catalytic system[b]	Polymerization time	Conversion, %	$[\alpha]^{20}_{D}$, deg.
AlCl$_3$–Men*OH	4 days	0	—
EtAlCl$_2$–Men*OH	2 hr.	35.2	+30.74
Men*OAlCl$_2$[c]	1 day	3.8	+57.53
Men*OAlCl$_2$	3 days	6.2	+79.40
Men*OAlCl$_2$–Et$_3$SnCl	2 days	4.1	+77.25
Men*OAlCl$_2$–EtAlCl$_2$			
0:1[d]	5 sec.	100	0
1[d]:0.1	5 sec.	100	0
1[d]:0.05	5 sec.	100	0
1[d]:0.025	13 hr.	15.2	+27.46

[a] In toluene at −75°C.; [catalyst]/[benzofuran] = 0.05, [benzofuran] = 1.0 mole/l.

[b] Equimolar amounts unless otherwise indicated.

[c] Ratio [catalyst]/[benzofuran] = 0.037.

[d] One part corresponds to the catalyst/monomer ratio of 0.05.

Table IV lists the data of the asymmetric-induction polymerization of benzofuran with the binary $EtAlCl_2$–Men*OH system and the dimeric Men*$OAlCl_2$ as catalysts. It is seen in this table that the dimeric Men*$OAlCl_2$ does polymerize benzofuran into an enantiomorphic high polymer of sufficiently high optical activity. In general, the dimeric catalyst, once isolated in pure crystal, largely reduces its catalytic ability in terms of the polymerization rate but exhibits even greater efficiency for the induction of asymmetric carbons in polymer chains than do its parent binary mixtures.

Table IV further indicates that the addition of an equimolar amount of Et_3SnCl to Men*$OAlCl_2$ has no appreciable influence on the polymerization of benzofuran. On the other hand, the existence of an extremely small amount of $EtAlCl_2$ greatly affects the asymmetric-induction polymerization. Since $EtAlCl_2$ is an excellent cationic catalyst, the rate of benzofuran polymerization by $EtAlCl_2$ is far greater than that of the asymmetric-induction polymerization. This would at least partly explain the cause of the characteristic difference in catalytic ability between the (pure) dimeric Men*$OAlCl_2$ and its parent binary mixtures; the formation of the dimeric menthoxyaluminum compound in the latter catalysts may often be incomplete under the experimental conditions employed.

Infrared Absorption Studies of the Catalytic Systems

From the foregoing investigations we may conclude with some certainty that the true catalytic activity of the asymmetric-induction polymerization derives from (Men*$OAlCl_2)_2$ both in the $AlEt_3$–$SnCl_4$–Men*$OMEt_3$ and $AlCl_3$–Men*$OMEt_3$ systems.

To confirm the formation of (Men*$OAlCl_2)_2$ in the multicomponent systems mentioned above, we carried out infrared spectroscopic studies of the various catalysts. The spectra recorded in the wavenumber range of 400 – 1100 cm.$^{-1}$ are compared in Figure 2.

First of all, it is noticed that very strong bands appear at 633 and 573 cm.$^{-1}$ in the KBr region both in the binary system $AlCl_3$–Men*$OSnEt_3$ and in the ternary system $AlEt_3$–$SnCl_4$–Men*$OSnEt_3$. These bands are also characteristic in the spectrum of (Men*$OAlCl_2)_2$. In the NaCl region, moreover, the bands that are characteristic of (Men*$OAlCl_2)_2$ appear distinctly at 913 and 946 cm.$^{-1}$.

Next, both in the binary and ternary systems there appear medium to strong bands at 489, 520, and 673 cm.$^{-1}$, which are characteristic of Et_3SnCl. These bands were assigned by Okawara et al.[9] to the Sn—CH_2 rocking vibration, the Sn—C symmetric stretching, and the Sn—C degenerate stretching vibration, respectively.

These results lend confirmatory support to the belief that the $AlCl_3$–Men*$OSnEt_3$ system easily undergoes an exchange reaction to give (Men*$OAlCl_2)_2$ and Et_3SnCl. This confirmation, together with the polymerization data, renders it possible to conclude that in the case of our multicomponent catalysts the true active species in the asymmetric-induction polymerization of benzofuran is the dimeric menthoxyaluminum dichloride.

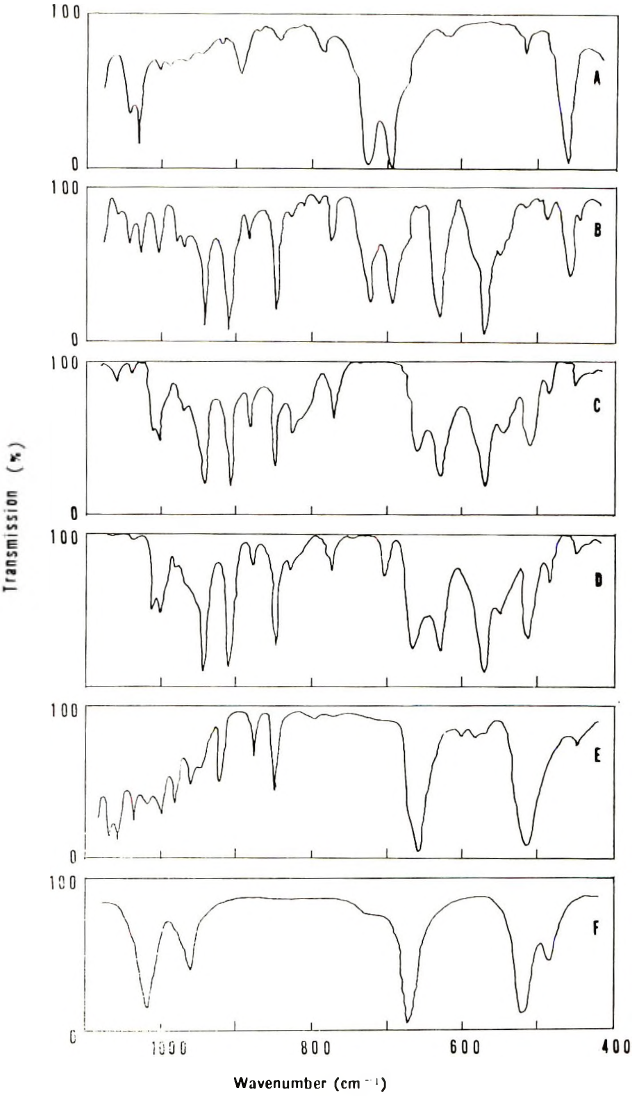

Fig. 2. Infrared absorption spectra of various catalytic systems studied: (*A*) toluene, (*B*) Men*OAlCl$_2$ in toluene, (*C*) AlCl$_3$–Men*OSnEt$_3$ in toluene, (*D*) AlEt$_3$–SnCl$_4$–Men*OSnEt$_3$ in toluene, (*E*) Men*OSnEt$_3$, (*F*) Et$_3$SnCl. The spectra of samples *A*, *B*, *C*, and *D* were measured in a 0.05-mm. KBr cell; those of *E* and *F*, on a KBr plate.

Polymerization of Isobutyl Vinyl Ether

Benzofuran may formally be regarded as belonging to a class of vinyl ethers. It is then interesting to inquire whether or not our catalysts would be capable of polymerizing vinyl ether into an isotactic polymer. Thus, several runs of polymerization of isobutyl vinyl ether were undertaken. The results are given in Table V.

TABLE V
Polymerization of Isobutyl Vinyl Ether[a]

Catalytic system	Polymerization time, sec.	Conversion, %	Precipitation temp.,[b] °C.	Intrinsic viscosity [η], dl./g.
$AlCl_3$–Men*OEt	260	54.1	−21.5	0.40
$AlCl_3$–Men*OSiEt$_3$	220	69.8	−8	0.64
$AlCl_3$–Men*OGeEt$_3$	140	78.8	−7	0.42
$AlCl_3$–Men*OSnEt$_3$	120	79.6	−6	0.64
$AlEt_3$–$SnCl_4$–Men*OSnEt$_3$	58	97.8	−6	0.37
Men*OAlCl$_2$[c]	60	94.3	−5	0.60

[a] In toluene at −75°C.; [catalyst] = 0.01 mole each/l., [monomer] = 0.50 mole/l.

[b] Measured for 0.5 g. of polymer dissolved in 100 ml. of methyl ethyl ketone.

[c] Concn. (mole/l.): catalyst 0.02, monomer 1.0.

As a conventional measure of relative isotacticity of the polymers formed we may use the precipitation temperature of a methyl ethyl ketone solution of the polymers.[10] Such temperatures are included in Table V. A comparison of Table V with Table I shows that a catalytic system that is more effective for the asymmetric-induction polymerization of benzofuran tends to give a poly(isobutyl vinyl ether) of higher isotacticity. This parallelism may be taken as an indication that the polymerizations of the two monomers proceed by essentially the same mechanism. However, to consolidate this stereochemical aspect of polymerization, we would of course have to await more detailed and quantitative analyses of the stereospecificity of the two polymers.

CONCLUDING REMARKS

All the results presented in the foregoing section converge to the conclusion that the catalytic ability of our various binary systems used for the asymmetric-induction polymerization of benzofuran is ascribable to the formation of (Men*OAlCl$_2$)$_2$, which is no doubt the very species responsible for the asymmetric induction. The different catalytic efficiencies of Men*OMEt$_3$, where M is C, Si, Ge, or Sn, used in conjunction with $AlCl_3$, may best be interpreted in terms of the relative easiness with which they form (Men*OAlCl$_2$)$_2$. The addition of Et_3SnCl to a toluene solution of (Men*OAlCl$_2$)$_2$ did not affect its catalytic efficiency at all. In this and many other ways the binary systems here investigated are different in nature from the previously studied $AlCl_3$–Et_3SnCl system, which was effective for the isotactic polymerization of isobutyl vinyl ether.

The mechanism of benzofuran polymerization with our asymmetric catalysts is not quite unambiguous yet. Although the polymerization is definitely of the cationic type, the initiation mechanism is still itself unraveled. For the propagation step, however, this much may be said with confidence: the dimeric Men*OAlCl$_2$ somehow carries a negative charge to form a counterion of the growing chain end and exists in its vicinity during the polymerization, playing an important role in controlling the configurations of the monomer units imbedded in the polymer chain end.

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Résumé

On a trouvé qu'un système binaire équimoléculaire formé de trichlorure d'aluminium et de menthoxytriéthyletin, germanium ou silicium est efficace pour la polymérisation par induction assymétrique du benzofuranne dans le toluène à −78°C. La rotation spécifique, $(\alpha)_D$, du polybensofuranne résultant s'élève de +10 à + 40°, suivant les conditiones de polymérisation aussi bien que suivant l'atome métallique constituant le dérivé menthoxy. Le système dichlorure d'éthylaluminium–menthol 1:1 est également eficace pour la même polymérisation. On a confirmé que ces systèmes binaires subissaient facilement une réaction d'échange pour former le dichlorure de menthoxyaluminium dimérique $(\text{Men*OAlCl}_2)_2$, m.p. 72–75°C). Une solution toluénique du dimère cristallin polymérise le bensofuranne en un haut polymère ayant une $(\alpha)_D$ appréciable de +79.4°, bien que la polymérisation avec le dimère soit beaucoup plus lente que celle avec les mélanges binaires parents. Tous ces résultats convergent vers une même conclusion suivant laquelle l'espèce catalytique vraie de nos systèmes à multicomposants sont plus que probablement les dichlorures de menthoxyaluminum dimériques.

Zusammenfassung

Das äquimolare binäre System aus Aluminiumtrichlorid und (−)-Menthoxytriäthylzinn, -germanium oder -silizium bewirkt die asymmetrisch induzierte Polymerisation von Benzofuran in Toluol bei −78°C. Die spezifische Drehung $[\alpha]_D$ der gebildeten Polymeren lag in Abhängigkeit von den Polymerisationsbedingungen und vom Metallatom in der Menthoxyverbindung im Bereich von +10 bis +40°. Auch das 1:1 Äthylaluminiumdichlorid–Menthol-System bewirkte die gleiche Polymerisation. Es wurde bestätigt, dass diese binären Systeme leicht eine Austauschreaktion unter Bildung eines dimeren Menthoxyaluminiumdichlorids, $(\text{Men*OAlCl}_2)_2$, M.P. 72–75°C, eingehen. Eine Toluollösung des kristallinen Dimeren polymerisiert Benzofuran zu einem Hochpolymeren mit dem hohen $[\alpha]_D$-Wert von +79,4°; allerdings war die Polymerisation mit dem Dimeren viel langsamer als mit der ursprünglichen binären Mischung. Alle diese Ergebnisse führen zu dem Schluss, dass der eigentliche Katalysator in unserem Vielkomponentensystem wahrscheinlich das dimere Menthoxyaluminiumdichlorid ist.

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Preparation and Polymerization of a Sugar Dithiol

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Synopsis

2,4-*O*-Benzylidene-1,6-dithiol-D-glucitol is prepared by nucleophilic displacement of tosyloxy groups from 3,5-di-*O*-acetyl-2,4-*O*-benzylidene-1,6-di-*O*-tosyl-D-glucitol with thioacetate in *N*,*N*-dimethylformamide and deacetylation of the product. Oxidative polymerization with oxygen and selenium dioxide produces film-forming disulfide polymers with intrinsic viscosities up to 0.41. Other oxidizing agents produce polymers of lower viscosity. Condensation of the dithiol with benzaldehyde also gives polymers of low viscosity.

INTRODUCTION

Although the oxidation of thiols to disulfides is well known, there have been only a few instances in which the reaction has been used to form disulfide polymers.[1,2] Marvel and Olson[3] found that oxygen was a more satisfactory reagent for oxidizing dithiols to polymer disulfides than bromine, nitric acid, or ferric chloride. Their unfractionated products had inherent viscosities up to 0.59.

In the present work a new type of sugar polymer is produced by oxidation of 2,4-*O*-benzylidene-1,6-dithiol-D-glucitol to the polydisulfide.

Oxygen,[3] hydrogen peroxide,[4] and ammonium persulfate[5] are used as oxidizing agents.

Condensation polymerization of the sugar dithiol with benzaldehyde with the use of an anhydrous dioxane–hydrogen fluoride solvent–catalyst system[6] is also attempted.

EXPERIMENTAL

3,5-Di-*O*-acetyl-2,4-*O*-benzylidene-1,6-*O*-*p*-tolylsulfonyl-D-glucitol

2,4-*O*-Benzylidene-1,6-di-*O*-*p*-tolylsulfonyl-D-glucitol, m.p. 147°C., was prepared according to the method of Stedehouder.[7]

To 46 g. of 2,4-*O*-benzylidene-1,6-di-*O*-*p*-tolylsulfonyl-D-glucitol in 700 ml. of dry pyridine at 0°C. was added 70 ml. of acetic anhydride. The reaction proceeded for 20 hr. at 25°C. The solution was poured into 6 liters of ice and water and extracted with 2 liters of chloroform. The chloroform extract was successively washed with dilute sulfuric acid (0.1%) and with sodium bicarbonate and water and then dried over anhydrous sodium

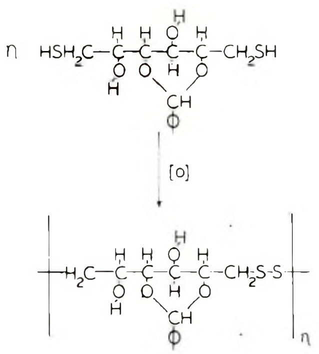

Figure 1.

sulfate. Crystals formed upon evaporation of the chloroform under reduced pressure. Recrystallization from 1.5 liters of ethanol, after treatment with Darco-G-60 charcoal, gave 31 g. (60%) of 3,5-di-*O*-acetyl-2,4,*O*-benzylidene-1,6-di-*O*-*p*-tolylsulfonyl-D-glucitol; m.p. 133–134°C., $[\alpha]_D^{25}$, 34.5° (c = 0.905 in chloroform).

ANAL. Calcd. for $C_{31}H_{34}O_{14}S_2$: S, 9.25%. Found: S, 9.29%.

3,5-Di-*O*-acetyl-1,6-di-*S*-acetyl-2,4-*O*-benzylidene-1,6-dithiol-D-glucitol

A 21.14 g. amount of 3,5-Di-*O*-acetyl-2,4-*O*-benzylidene-1,6-di-*O*-*p*-tolylsulfonyl-D-glucitol and 11.2 g. of potassium thioacetate were dissolved in 110 ml. of *N*,*N*-dimethylformamide. This mixture was heated at 125°C. in an oil bath for 3.5 hr., after which the *N*,*N*-dimethylformamide was removed under reduced pressure as its benzene azeotrope. The solid residue was taken up in 500 ml. of chloroform, and the chloroform mixture was successively washed with dilute sulfuric acid (0.1%) and 1% sodium bicarbonate solution and twice with water. After drying over anhydrous sodium sulfate, the chloroform was removed under reduced pressure. Crystallization was induced by the addition of 150 ml. of ethanol. Recrystallization from 150 ml. of ethanol, after treatment with Darco-G-60 charcoal, gave 8.5 g. (73.4%) of long white needles, m.p. 122–123°C., $[\alpha]_D^{25}$, 25.7° (c = 0.646 in chloroform).

ANAL. Calcd. for $C_{21}H_{26}O_8S_2$: S, 13.6%. Found: S, 13.5%.

2,4-*O*-Benzylidene-1,6-dithiol-D-glucitol

To 65.8 g. of 3,5-di-*O*-acetyl-1,6-di-*S*-acetyl-2,4-*O*-benzylidene-1,6-dithiol-D-glucitol dissolved in 1 liter of dry, oxygen-free methanol was added 40 ml. of 1.0*N* sodium methoxide in methanol. After 14 hr. at 25°C. 1 liter of water was added, and the mixture was neutralized to the phenolphthalein endpoint with 0.5*N* hydrochloric acid. The resulting precipitate was filtered, washed with cold water, and recrystallized from 1 liter of ethanol–methanol–water (1:1:3 v/v) to give long white needles; m.p. 186–187°C. An immediate positive-result thiol test was given with 2,3,5-

triphenyl-2*H*-tetrazolium chloride[8] and sodium nitroprusside.[9] Infrared spectra indicated the absence of *O*- and *S*-acetyl groups. The compound was shown to be pure by thin-layer chromatography, with an R_f of 0.24, with benzene–ethanol–water–ammonium hydroxide (200:40:19:1) as irrigant.

ANAL. Calcd. for $C_{13}H_{18}O_4S_2$: C, 51.5%; H, 5.99%; S, 21.2%. Found: C, 51.6%; H, 5.89%; S, 21.1%.

Polydisulfide Preparation

Solution polymerizations, with oxygen, were conducted in a constant-temperature apparatus similar to that described by Marvel et al.[10] In a typical experiment 1.0 g. of the sugar dithiol was dissolved in 5 ml. of pyridine containing 20 mg. of selenium dioxide and 0.5 ml. of 0.5*N* potassium hydroxide. After dissolution of the monomer by warming of the mixture, the solution was immediately placed in the constant-temperature apparatus and oxygen bubbled through for 24 hr. The viscous solution was then poured into 70% methanol, from which it precipitated. The polymer was collected by filtering on a tared sintered-glass funnel, washed well with water, and vacuum dried over anhydrous calcium chloride (0.85 g.).

Emulsion polymerization was conducted by the method of Marvel and Olson.[3] Oxygen was bubbled through an emulsion of 2.0 g. of the sugar dithiol, 4 g. of potassium hydroxide, 1.0 g. of lauric acid, and 20 mg. of selenium dioxide in 20 ml. of water. The reaction continued for 45 hr. at 35°C., after which the emulsion was broken with dilute hydrochloric acid. The mixture was filtered and the precipitate washed with water and dried under reduced pressure over anhydrous calcium chloride.

Polymerizations with the use of hydrogen peroxide or ammonium persulfate were done in a pyridine solution at 25°C. To 1.0 g. of the sugar dithiol in 10 ml. of pyridine were added and the desired equivalents of hydrogen peroxide or ammonium persulfate, and the reaction was continued for 20 hr. The pyridine solutions were dialyzed for 3 hr., precipitated in water, filtered, and dried over anhydrous calcium chloride.

All these polymers were soluble in pyridine, dimethyl sulfoxide, and *N*,*N*-dimethylformamide and were insoluble in water, acetone, chloroform, ether, ethanol, and benzene. Table I summarizes the results of these polymerizations.

Further analysis of the polydisulfides showed that no periodate[11] was consumed after 90 hr. at 5°C. and that 0.96 benzylidene groups per repeating unit were present.

The thiol endgroup was shown to be present by the positive-result test given by 2,3,5-triphenyl-2*H*-tetrazolium chloride. Assuming two thiol groups per molecule, the number-average molecular weights were determined by amperometric titration[12] with silver nitrate (Table II).

Acetylation was done by adding 2 ml. of acetic anhydride at 0°C. to 0.5 g. of polymer in 15 ml. of dry pyridine. After 20 hr. at room temperature the mixture was poured into 300 ml. of ice and water, from which the

TABLE I
Oxidative Polymerization of 2,4-*O*-Benzylidene-1,6-dithiol-D-glucitol

Oxidant	Time, hr.	Temp., °C.	Sulfur,[a] %	Melting range	Intrinsic viscosity
Oxygen	24	56	21.26	200–209	0.33
Oxygen	24	65	21.30	203–218	0.41
Oxygen	10	78	21.14	205–220	0.26
Oxygen[b]	24	78	21.22	195–211	0.23
Oxygen	24	78	21.31	208–224	0.30
Oxygen	24	100	21.10	150–185	0.18
Oxygen[c]	45	35	21.88	222–230	0.12
Persulfate[d]	20	25	21.35	152–175	0.067
Persulfate[e]	1	50	21.11	190–200	0.16
Persulfate[f]	4	30	21.17	165–188	0.31
Hydrogen peroxide	24	25	20.95	150–155	0.056
Hydrogen peroxide	20	40	21.03	152–163	0.076

[a] Calcd. for $C_{13}H_{16}O_4S_2$: S, 21.34%.
[b] Without selenium dioxide catalyst.
[c] All reactions in solution except this one, which was in emulsion.
[d] Equivalent amounts of monomer and persulfate.
[e] 100% excess of persulfate.
[f] 200% excess of persulfate.

TABLE II
Analysis of Disulfide Polymers

Oxident	Intrinsic viscosity	Benzylidenes per repeating unit	Acetyls per repeating unit	Molecular weight[a]	
				Vapor-phase osmometer	End-group
Oxygen	0.41	0.96	2.00	7630	7700
Oxygen	0.33	0.95	1.97	6310	6940
Oxygen	0.25	0.96	2.02	4840	5410
Oxygen	0.12	0.94	1.99	2460	2010
Persulfate	0.16	0.96	1.98	4110	5210
Persulfate	0.31	0.98	2.00	—	15600

[a] Number-average molecular weights of the acetylated polymers.

acetylated polymer precipitated. This was filtered, washed with water, then dried. The acetylated polymers were soluble in acetone, pyridine, dimethyl sulfoxide, *N*,*N*-dimethylformamide, and chloroform and insoluble in water, ether, ethanol, and benzene. Chloroform solutions of these polymers were used in the Mechrolab vapor-phase osmometer as another method of determining number-average molecular weights.

Acetyl determinations[13] of the acetylated polymers showed 2.0 acetyl groups per repeating unit (Table II). The presence of disulfide groups was shown by reduction with zinc in acetic acid. Amperometric titrations of reaction-mixture aliquots showed an increase in the concentration of thiol groups with time.

Polythioacetal Preparation[6]

Dry, crystalline sugar dithiol (1.0 g.) was placed in a 4-oz. wide-mouthed polyethylene bottle with 0.35 g. of benzaldehyde and 10 ml. of 50% hydrogen fluoride in anhydrous dioxane. The bottle was tightly capped and shaken at 25°C. for 24 hr. The contents were neutralized with 5% potassium carbonate. The precipitate was filtered and washed with water, dissolved in acetone, and dialyzed for 20 hr. against acetone and then against an increasing concentration of water, until all acetone was removed. The precipitate that formed in the dialysis bag was removed by filtration and dried in a desiccator. Intrinsic viscosities from several preparations are shown in Table III. Viscosity measurements were made in pyridine with a Ubbelohde viscometer at 25°C. Films were formed by allowing a 15% pyridine solution of polymer to evaporate from a clean mercury surface.

ANAL. Calcd. for polymer from benzaldehyde and the sugar dithiol, $C_{20}H_{22}O_4S_2$: S, 16.41%. Found: S, 16.72%.

TABLE III
Polymerization of Benzaldehyde and 1,4-*O*-Benzylidene-1,6-dithiol-D-glucitol

Concentration of HF, %	Time, hr.	Yield, %	Temp., °C.	S,[a] %	Melting range	Intrinsic viscosity
25	24	73	25	16.9	70–87	0.032
35	24	98	25	16.8	67–80	0.034
50	24	80	25	16.5	69–87	0.040

[a] Calcd. for $C_{20}H_{23}O_4S_2$: S, 16.4%.

RESULTS AND DISCUSSION

Polymerizations with the use of oxygen were performed both in emulsion and in pyridine solution with selenium dioxide catalyst. The solution polymerization with oxygen gave polymers with the highest intrinsic viscosities (Table I). The best polymerization conditions for 2,4-*O*-benzylidene-1,6-dithiol-D-glucitol were obtained by bubbling oxygen through a pyridine solution containing a selenium dioxide catalyst and made 0.05*N* in potassium hydroxide at 65°C.

Solution polymerization with ammonium persulfate gave polymers with intrinsic viscosities up to 0.31. Polymerization with hydrogen peroxide gave polymers of low intrinsic viscosity and low sulfur content, suggesting oxidation beyond the disulfide stage.

The polymers were soluble in pyridine, *N,N*-dimethylformamide, and dimethylsulfoxide. Since number-average molecular weights determined by endgroups agreed with molecular weights from vapor-phase osmometry (Table II), the polymers were assumed to be linear. Polymers with intrinsic viscosities above 0.20 gave clear but brittle films.

2,4-*O*-Benzylidene-1,6-dithiol-D-glucitol was chosen because of the strained conformational change it has to undergo in order to form an intramolecular cyclic disulfide:

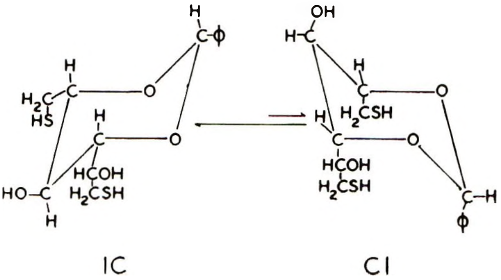

Figure 2.

The 1*C* conformation is more favorable than the *C*1 conformation because of the equatorial position of the bulky groups in the acetal ring.

Condensation of benzaldehyde and the sugar dithiol in an anhydrous hydrogen fluoride–dioxane catalyst–solvent system gave polymers of low intrinsic viscosities (Table III). All the polymers were soluble in acetone, chloroform, and pyridine. The low intrinsic viscosities are probably due to reactions competing with thioacetal formation. Under these conditions acetal formation between benzaldehyde and the two secondary hydroxyls of the sugar dithiol can occur.

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Résumé

Le glucitol-2,2,*O*-benzylidène-1,6-dithiol-D a été préparé par déplacement nucléophile de groupes tosyloxy au départ de 3,5-di-*O*-acétyl-2,4-*O*-benzylidène-1,6-di-*O*-tosyl-D-glucitol avec le thioacétate dans le diméthylformamide et par déacétylation du produit. La polymérisation oxydante à l'oxygène et au dioxyde de sélénium produit des polymères disulfurés filmogènes avec des viscosités intrinsèques allant jusque 0.41. Les autres agents d'oxydation produisent des polymères de viscosité plus basse. La condensation du dithiol avec le benzaldéhyde fournit également des polymères de basse viscosité.

Zusammenfassung

2,4-*O*-Benzyliden-1,6-dithiol-D-glucitol wird durch nukleophile Verdrängung der Tosyloxygruppen aus 3,5-Di-*O*-acetyl-2,4-*O*-benzyliden-1,6-di-*O*-tosyl-D-glucitol mit Thioacetat in *N*,*N*-Dimethylformamid und Deactylierung des Reaktionsprodukts dargestellt. Oxydative Polymerisation mit Sauerstoff und Selendioxyd liefert filmbildende Disulfidpolymere mit Intrinsic-viscosity-Werten bis hinauf zu 0,41. Andere Oxydationsmittel liefern Polymere mit niedrigerer Viskosität. Auch die Kondensation des Dithiols mit Benzaldehyd führt zu Polymeren mit niedriger Viskosität.

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On the Thermal Behavior of 4-(*o*-Carboranyl)-1-butylmethyl Siloxane–Dimethyl Siloxane Copolymers*

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Synopsis

Polysiloxanes containing carboranylbutyl and methyl pendant groups were investigated, to determine their resistance to thermal decomposition when heated in air. Results indicate that the copolymers degrade through Si—C as well as Si—O bond rupture. At 300°C. thermooxidative scission of pendant groups was the predominant reaction, whereas Si—O and Si—C bond rupture occurred at 500°C. Variations in the behavior of the copolymers studied suggest that the carborane nucleus provides some inhibiting influence on their thermal decomposition. This is mainly attributed to steric hindrance effects rather than polarity factors. Chain extension with tin octoate caused a reduction of thermal stability, probably because of the addition of Sn—O bonds to the molecules.

INTRODUCTION

The search for new, useful, heat-stable elastomers is being conducted by many investigators over a broad spectrum of research. Included in this work are recent efforts that have produced novel copolymers containing a pendant group having a polycyclic structure, in which a nucleus of ten boron atoms is bridged by two carbon atoms.[1] The original impetus for these studies resulted from the unusually good chemical and thermal resistance exhibited by more simple derivatives of 1,2-dicarbaclovododecaborane(12).[2-6]

This manuscript presents the results of our investigations of the heat stability of copolymers of 4-(*o*-carboranyl)-1-butylmethyl siloxane–dimethyl siloxane.

MATERIALS

Two types of 4-(*o*-carboranyl)-1-butylmethyl siloxane–dimethyl siloxane copolymers were examined as received (from the Thiokol Chemical Corp., Reaction Motors Division, Denville, N. J.). The recurring structures of the copolymers are as follows (see following page):

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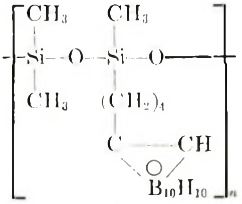
* Presented at the 2nd Western Regional Meeting of the American Chemical Society, San Francisco, California, October 16–21, 1966.



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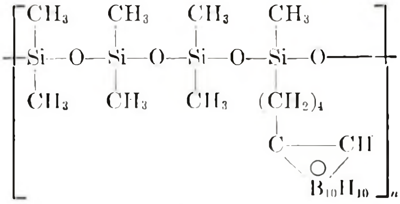

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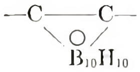

is used to represent the *o*-carborane nucleus.

Five specimens of copolymer (I) were examined. These products were different in so far as they were synthesized in the presence or absence of $FeCl_3$ catalyst, were or were not chain-extended with tin octoate, and had molecular weights of about 1500–13,000.

EXPERIMENTAL

Thermogravimetric Analysis (TGA)

About 200 mg. of sample was heated in air in a Kanthal wire-wound furnace[7] at the rate of 180°C./hr. Residual sample weights and furnace temperatures were recorded simultaneously on an Ainsworth semimicro recording balance, Model BYR-AU-A.

Differential Thermal Analysis (DTA)

A sandwich technique, similar to that described in the literature,[8] was employed for accommodating the test sample. A 20 mg. sample was placed on 200 mg. of alumina (Fisher Certified Reagent Grade, Catalogue No. A-591) in a 1-cc. platinum crucible and covered with 680 mg. of alumina. The sample container and a similar crucible holding 900 mg. of alumina as the reference material were heated together in air at a rate of 180°C./hr. The furnace temperature and the temperature difference between the sample and reference specimen were measured with a Pt/Pt-10%Rh differential thermocouple and recorded on a Honeywell X-Y function plotter.

Isothermogravimetric Analysis (IGA)

Weight changes of 200 mg. samples were recorded, as described, under TGA while the samples were heated in air for several hours at 300 or 500°C.

The furnace was preheated to the desired temperature prior to insertion of the test specimen.

Infrared Spectrophotometry

Infrared absorption data were obtained with Nujol mull suspension and attenuated total reflectance (ATR) techniques on a Perkin-Elmer Model 137 spectrophotometer equipped with sodium chloride optics. The spectra were recorded over the range of 2.5–15.0 μ.

RESULTS AND DISCUSSION

Figures 1–5 present the TGA and differential TGA thermograms obtained from different specimens of copolymer(I). These data show that the onset of the weight decrease for all of the samples of this copolymer occurred at about 250–280°C. It is interesting to note that the specimens composed of smaller chains began to decrease in weight at the lower end of the temperature range and exhibited slightly higher weight losses than the samples having a larger molecular size. This suggests that the thermal stability of this type of polymeric material may be influenced by molecular chain length, the larger molecules appearing to be slightly more heat-resistant than the smaller chains. Similar effects of molecular size on thermal behavior have been observed with conventional dimethylsiloxane polymers.[8] Infrared spectra of the unheated samples showed a weak Si—OH absorption mode at 3.12 μ, which may be attributed to end-group structures. Since the terminal-group content is higher in the smaller than in the larger molecular weight species, it seems reasonable to assume that the observed variations in initial weight loss may have been due to the

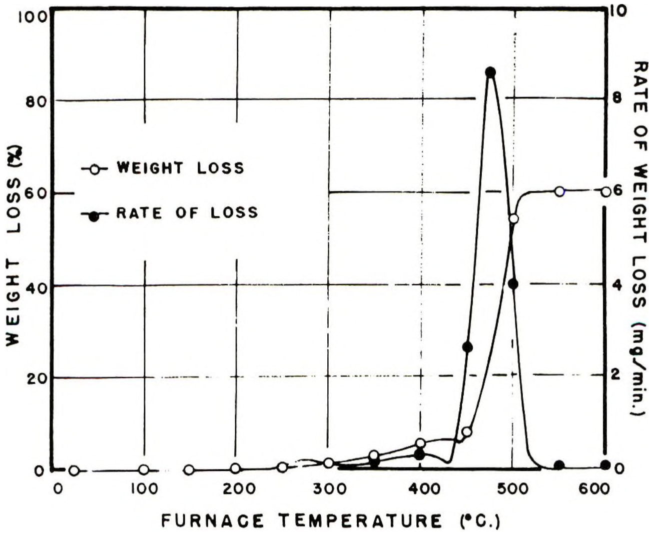

Fig. 1. TGA thermogram of copolymer(I), mol. wt. 1500–2000; no catalyst.

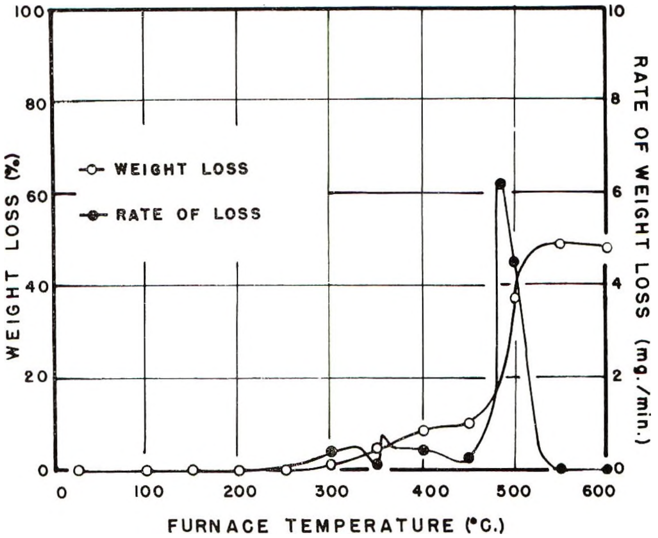

Fig. 2. TGA thermogram of copolymer(I) mol. wt. 1500–2000; $FeCl_3$ catalyst.

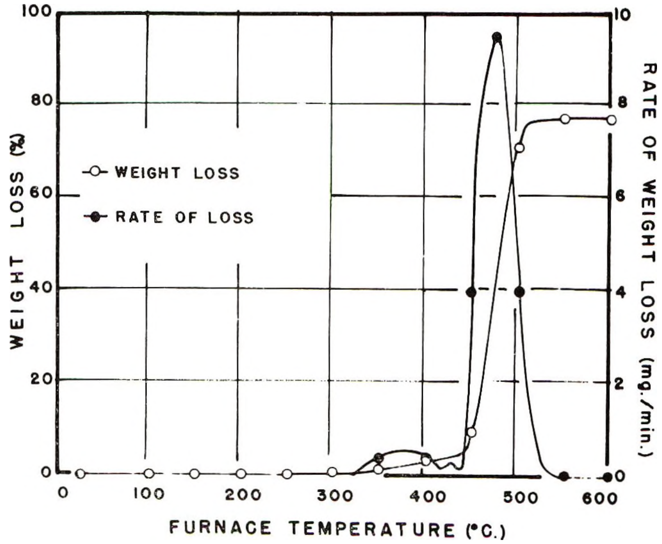

Fig. 3. TGA thermogram of copolymer(I); $FeCl_3$ catalyst, tin octoate chain-extended.

thermal condensation of hydroxyl groups rather than to the number of recurring units. Of course it is conceivable that the observed weight loss variations in this temperature range may have been caused by differences in the amount of contaminants,[9] such as cyclic siloxanes, which usually volatilize when heated above 200°C.[10]

On further heating the copolymer(I) samples continued to lose weight slowly until about 435–445°C., at which time the rate of decrease declined. In fact, each of the samples synthesized in the absence of $FeCl_3$

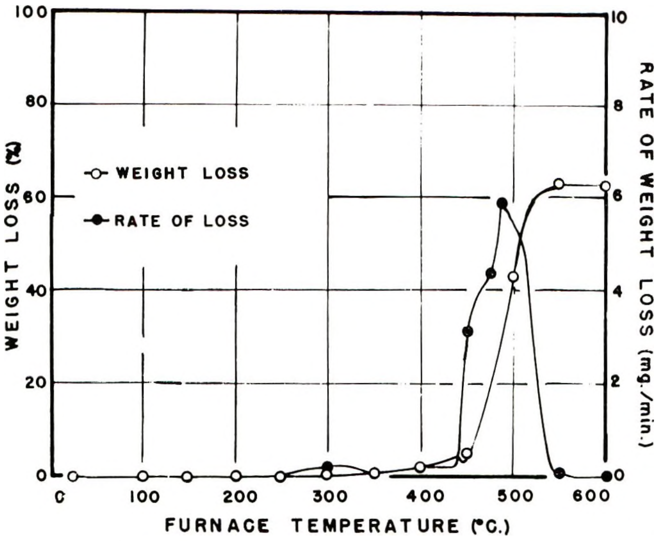

Fig. 4. TGA thermogram of copolymer(I), mol. wt. 13,000.

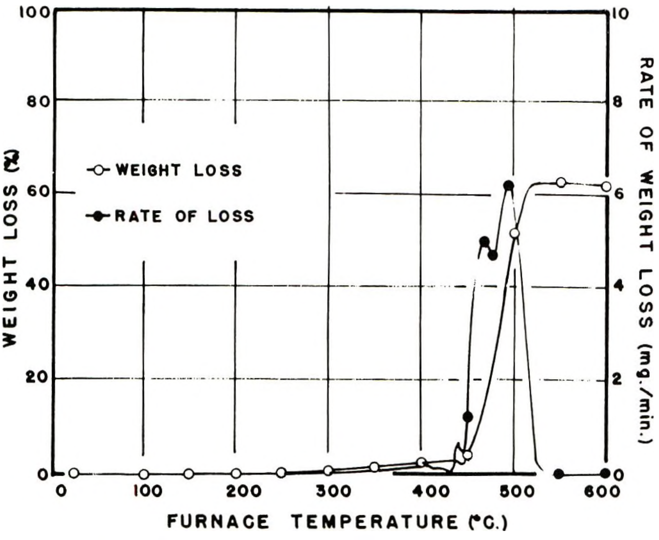

Fig. 5. TGA thermogram of copolymer(I), mol. wt. >13,000.

catalyst showed a small but definite weight increase in this temperature range, which probably was due to thermal-oxidation reactions.

Although both copolymer(I) and copolymer(II) are composed of recurring units that contain a polyhedral structure, they can be classified as modified alkyl polysiloxanes, because the carborane nucleus is attached through a 1,4-butylene group to a silicon atom. In this connection, it is generally known that alkyl pendant groups of polysiloxanes are subject to oxidation reactions. In fact, the higher molecular weight side chains tend to oxidize more readily than methyl groups. In addition, it has been reported in the literature that an accumulation of reaction groups is produced during the oxidation of pendant alkyl groups of polysiloxanes.[11] It is conceivable from this that the small weight increase shown in the TGA thermograms of most of the copolymer(I) samples at 435–445°C. were the result of methyl and carboranylbutyl group oxidation. It is also possible that the small weight gains observed at these temperatures were caused by some oxidation of the carborane nucleus.

As the furnace temperature rose above 435–445°C., the copolymer(I) specimens began to lose weight rapidly, reaching maximum rates of decrease of about 6.0–9.6 mg./min. in the region of 475–495°C. It seems reasonable at this time to assume that the loss of weight at these temperatures was due to the oxidation-induced rupture of side chains. In place of the organic groups siloxane bonds were probably formed and the molecules crosslinked.[12] The formation of the siloxane bonds tends to impede the admittance of oxygen into the polymer molecules, and thus the decomposition process after 475–495°C. then slows down.[13,14] It would seem from these studies that the behavior of copolymer(I) is similar to that of benzylmethyl polysiloxanes, which undergo methyl and benzyl group rupture when heated in air.[15]

Above 475–495°C. all the copolymer(I) samples gained weight slowly. This may have been the result of oxidation of residual carborane groups.

It should be noted that the largest weight loss and highest rate of decrease was obtained from the $FeCl_3$-catalyzed product that had been chain-extended with tin octoate. On this basis it would seem that the chain-extension process had an adverse effect on the thermal stability of the copolymer(I) material. This may have been the result of incorporating Si—O—Sn bonds in the polymer molecules.[16] Previous studies showed that the substitution of Sn—O bonds for some of the Si—O linkages in organosiloxanes caused a reduction in heat resistance.[17]

The TGA and differential TGA thermograms obtained from a sample of copolymer(II) are presented in Fig. 6. These data show that the material started to lose weight at about 100°C. The weight decreased at the average rate of 0.029 mg./min. up to about 340°C., when the observed loss was only 1.2%. Above this temperature the decrease of weight became quite rapid and attained a peak rate of about 1.6 mg./min. at 410°C. When the thermograms were compared, the temperature at which copolymer(II) underwent a maximum rate of weight loss was found to be substantially lower than that observed for the copolymer(I) specimens. This would seem to indicate that copolymer(I) is somewhat more heat-stable than copolymer(II). Since the carboranylbutyl/methyl group ratio of copolymer (I) is higher than that of copolymer(II), this may suggest that the carborane nucleus has a stabilizing influence over thermal decomposition.

The small weight increase shown by most of the copolymer(I) specimens just prior to the event of rapid weight decrease was not observed at this point on the TGA thermogram obtained from copolymer(II). Instead,

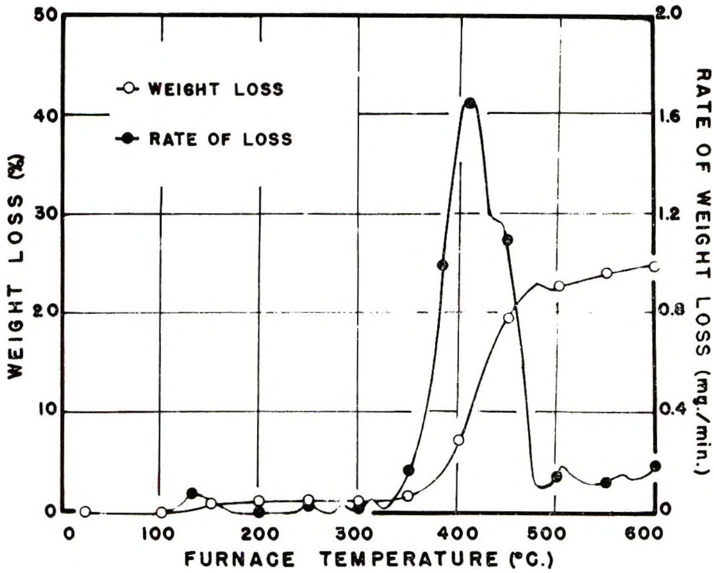

Fig. 6. TGA thermogram of copolymer(II).

this occurred at the end of the sharp rise in the rate of weight decrease at 480 to 490°C. Then the sample weight decreased again at an average rate of 0.13 mg./min. to about 600°C. Above this temperature the sample weight increased at the rate of 0.05 mg./min.

The variations observed between the behavior of the copolymer(I) specimens and copolymer(II) appear to suggest that the nature of the thermal decomposition processes differs somewhat among these materials. In this connection, the shapes of the TGA thermograms indicate that the degradation occurred in several steps. One of these stages, which appears to provide some insight into these differences, is the region on the thermograms showing a small weight increase. Just prior to this point the average weight loss for the copolymer(I) samples was 4.3%, compared to a 22.8% decrease exhibited by copolymer(II). These weight losses are appreciably lower than that predicted from the total rupture of the carboranylbutyl group. Instead, the average loss sustained by the copolymer(I) samples corresponds more closely with a net decrease produced by the scission of 2 methyl groups and gain of 1 oxygen atom. The rupture of a dimethyl siloxane unit plus the net loss obtained from the scission of 5 methyl groups and gain of 2.5 oxygen atoms would provide a weight loss equivalent to that shown by copolymer(II). Of course, the 22.8% decrease may have resulted from the partial cleavage of the carboranylbutyl group.

After going through the weight increase stage the copolymer(I) specimens showed rapid and large weight losses when heated at about 475–540°C. On the basis of the assumptions made above the weight decrease observed at this temperature range was due largely to carboranylbutyl group rupture. In almost all instances, however, the maximum weight

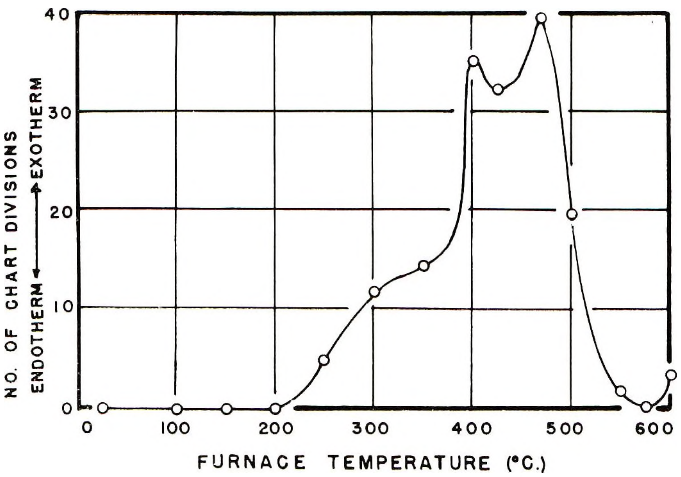

Fig. 7. DTA thermogram of copolymer(I), mol. wt. >13,000.

loss values recorded for the copolymer(I) samples were larger than that expected from only Si—C bond cleavage, and it is likely that some Si—O bond rupture also took place at these temperatures.

In contrast to the copolymer(I) specimens copolymer(II) only showed a small weight decrease after the weight increase stage at 480–490°C. It is reasonable to assume from previous observations that the weight loss was caused by the partial cleavage of carboranylbutyl groups. If all the pendant groups had ruptured, then an additional weight decrease of 22.2% would have occurred.

During the final phase of thermal decomposition the copolymers behaved alike, both types undergoing gradual weight gains. This may be attributed to the thermal oxidation of residual carboranylbutyl groups.

Figure 7 presents the DTA thermogram obtained from the sample of copolymer(I) having a molecular weight of 13,000. Similar thermograms were given by the other copolymer(I) specimens. These data show that a broad exothermic change was initiated at 220°C., which may be reasonably associated with oxidative decomposition. The exotherm displays a shoulder at about 325°C. and two peaks near 400 and 470°C. The shoulder probably indicates that an endothermic or another exothermic reaction was superimposed on the oxidation exotherm. Since TGA data showed that this material exhibited only a 1% weight loss at 325°C., it appears to be more reasonable to assume that the shoulder was primarily the result of exothermic reactions. The peak at 400°C. corresponds to the point on the TGA thermogram at which a small weight increase was observed, while the one at 470°C. occurred in the temperature range in which a high rate of weight loss was noted.

The DTA thermogram obtained from copolymer(II) is shown in Figure 8. The weak exothermic changes beginning at about 200 and 250°C. may denote the temperature at which oxidation reactions were initiated.

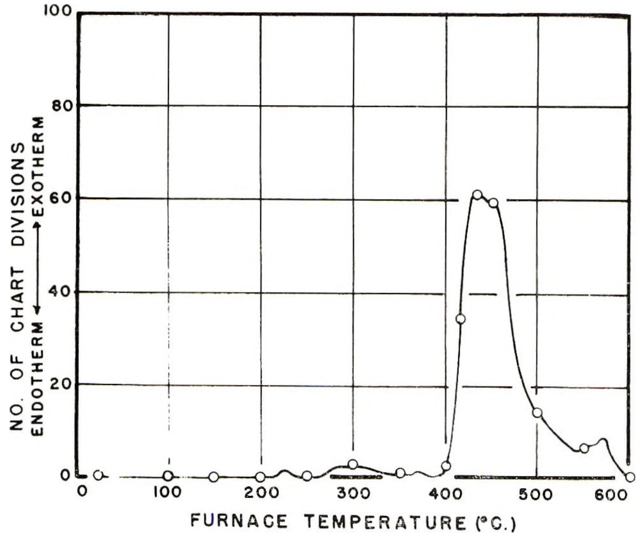

Fig. 8. DTA thermogram of copolymer(II).

The thermogram next displays a much stronger exothermic change having a peak at 425°C., which appears to be related to a shoulder following the main peak on the differential TGA thermogram of this material. This is reasonably assignable to a superposition on the oxidation exotherm of an endotherm produced by the volatilization of decomposition products. The peak at about 570°C. may be associated with the thermooxidative degradation of the carborane nucleus or of residual carbonaceous products.

Figure 9 shows the weight changes observed while samples of the copolymers were exposed for extended time intervals in a preheated furnace at 300°C. After 10 min. copolymers(I) and (II) exhibited weight losses of about 1.5 and 2.5%, respectively. These materials showed comparable weight decreases at this temperature during the TGA experiments.

Within the next 30 min. copolymer(I) continued to lose weight at a slower rate, in contrast to copolymer(II), which exhibited a small weight gain. On being further heated copolymer(I) continued to lose weight at a more rapid rate, whereas copolymer(II) sustained an additional small loss during the following hour and thereafter the sample weight increased slowly. At the end of the 6-hr. heating period visual examinations showed the residues to be darker in color and less flexible than the original copolymers. The loss in elasticity probably resulted from the formation of a number of crosslinks brought on by the thermal oxidation of pendant groups.

A comparison of the infrared absorption spectra of the residues and the original polymers gave additional evidence of the occurrence of such thermal oxidation reactions during the isothermal heating process. The spectra from the residues showed a well-defined peak at 3.12 μ, which was more intense than that in the spectra from the unheated copolymers. This

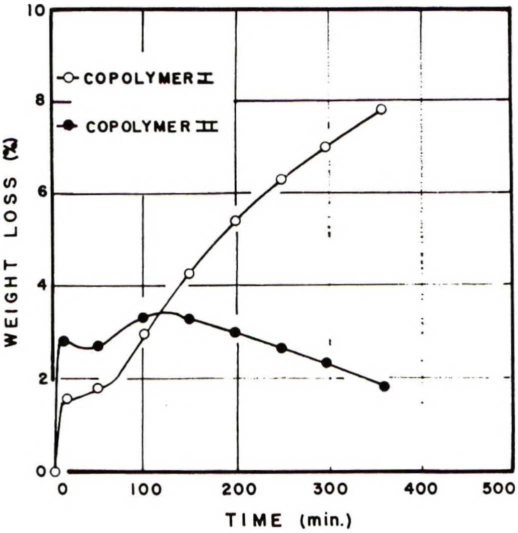

Fig. 9. IGA thermograms of copolymers at 300°C.

peak is usually associated with a stretching vibration from Si—OH linkages, which are known to form when alkylpolysiloxanes are heated in air. The infrared spectra from the residues also exhibited absorption modes at 3.90 and 7.98 μ, which were much less intense than those in the spectra from the original copolymers and are ascribed to B—H and Si—CH_3 vibrations, respectively. This indicates that pendant groups were removed through Si—C or Si—O bond cleavage when the copolymers were heated at 300°C. From the small weight losses observed at this temperature it is believed, however, that Si—C rather than Si—O bond rupture was the predominant decomposition reaction.

The thermograms obtained from isothermal studies at 500°C. are presented in Figure 10. These data show that within 10–20 min. after being inserted into the preheated furnace copolymers(I) and (II) underwent weight losses of 79.5 and 55.9%, respectively. Thereafter the weight of the sample residues remained virtually unchanged. It is evident from these data that the copolymers decomposed very rapidly when heated in air at 500°C.

Infrared absorption spectra of the residues showed a strong Si—OH vibration mode at 3.12 μ, as in the case of the IGA studies at 300°C. The spectrum from the copolymer(I) residue also exhibited weak B—H and Si—CH_3 absorption peaks at 3.90 and 7.98 μ, respectively. These vibration frequencies were not evident in the spectrum obtained from the copolymer(II) residue. These data indicate that the residue from copolymer(I) contained methyl and carboranylbutyl groups, whereas such chemical structures were completely ruptured from copolymer(II) during 6 hr. at 500°C. It is significant to note that the spectra from the residues of copolymers(I) and (II) did not exhibit a B—O bond vibration frequency at

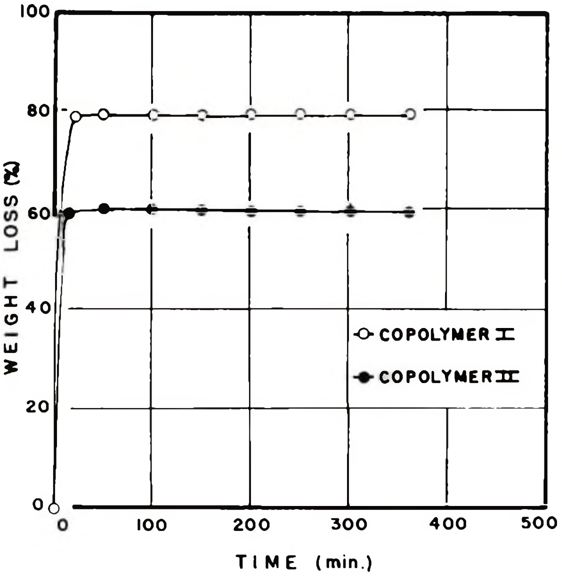

Fig. 10. TGA thermograms of copolymers at 500°C.

about 7.4 μ. It may be concluded from this that the carborane nucleus did not oxidize, even when the copolymers were subjected to 500°C. in air. It is believed, however, that the very rapid volatilization of the cleavage products produced at this temperature prevented the observation of such oxidation reactions.

On the basis of the weight decreases noted at 500°C. it would seem that copolymer(II) was more heat-stable than copolymer(I). This would appear to be contrary to conclusions made from other experimental data. It must be remembered, however, that copolymer(I) would undergo larger weight losses than copolymer(II) if all of the pendant groups ruptured and volatilized. Thus, the relative order of the weight losses from the copolymers at 500°C. is consistent with that predicted from the complete scission of Si—C bonds. Since the measured decreases were too large to have resulted only from pendant-group cleavage reactions, it is believed that some Si—O bond rupture also occurred at this temperature.

In general, the influence of the carboranylbutyl group on the heat stability of the copolymers may be associated with polar or steric factors or a combination of both. In this connection, it is well known that methyl radicals attached to silicon atoms are more resistant to thermal oxidation than butyl substituents.[15] Hinshelwood[18] has shown that electron-withdrawing groups usually cause an increase in the oxidation rate of such alkyl groups, whereas electron-donating structures generally produce an opposite effect. Since the carbon atoms in a butyl group attached to a silicon atom have partial charges that alternate along the chain,[15] it might be expected that the polarity of the Si—C bond would be enhanced when a strong electron-withdrawing group, such as the carborane nucleus,[19] is connected even to the terminal carbon atom. On this basis, then, the carboranylbutyl group should be even less stable than an unsubstituted butyl radical attached to a silicon atom. Copolymers(I) and (II) would be expected, therefore, to be less resistant to thermooxidative decomposition than conventional dimethylpolysiloxanes. This would appear to be in contradiction to our findings, however, which suggest that the carborane nucleus may have an inhibiting influence on the thermal oxidation of the copolymers studied. This suggests that, although decomposition of the copolymers may have been affected by polar factors, they were too small to account for the observed results. It is suspected that, instead, the bulky carborane nucleus stabilized the molecules by sterically hindering the access of oxygen to the methylene radicals of the butyl group. It is also considered possible, from these studies, that the carborane nucleus had some influence on the heat-resistance of the methyl pendant groups. Such effects, if they did occur, were probably greater on the methyl radical attached to the same silicon atom as the carboranylbutyl structure than on the other methyl groups. Additional studies of these materials would be necessary to confirm this assumption. In this connection, Papetti and co-workers,[20] reporting on a new series of siloxane polymers containing a *m*-carborane group in the main chain of the recurring units, are in general agreement with our findings concerning the stabilizing influence of the carborane nucleus. They found that methyl groups bonded to the silicon atom adjacent to the carborane nucleus were more resistant to thermooxidative decomposition than those further away. More recent results of our investigation of the same series of poly(*m*-carboranylenesiloxanes) indicate that the protective effects of the carborane nucleus decrease as the distance between the carborane group and the methyl units increases.[21]

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Résumé

Des polysiloxanes contenant des groupes latéraux carboranylbutyles et méthyles ont été étudiés en vue de déterminer leur résistance à la décomposition thermique lorsqu'ils sont chauffés à l'air. Les résultats indiquent que les copolymères se dégradent par rupture du lien Si—C aussi bien que du lien Si—O. A 300°C, la scission thermique oxydante des groupes latéraux, est la réaction prédominante tandis que les ruptures Si—O et Si—C se passent à 500°C. Les variations dans le comportement des copolymères étudiés, suggèrent que le noyau carboranique exerce une certaine influence inhibitrice à la décomposition thermique. Ceci est principalement attribué aux effets d'encombrement stérique, plutôt qu'à des effets polaires. L'extension de chaîne avec l'octoate d'étain causait une réduction de la stabilité thermique, probablement par suite de l'addition de liens Sn—O aux molécules.

Zusammenfassung

Polysiloxane mit einer anhängenden Carboranylbutyl- und Methylgruppe wurden auf ihre Beständigkeit gegen thermische Zersetzung beim Erhitzen unter Luft untersucht. Die Ergebnisse zeigen, dass die Copolymeren sowohl durch Sprengung der Si—C -Bindung als auch der Si—O-Bindung abgebaut werden. Bei 300°C war die thermisch-oxydative Spaltung der anhängenden Gruppen die Hauptreaktion, während bei 500°C Sprengung von Si—O- und Si—C-Bindungen auftrat. Die Variation des Verhaltens der untersuchten Copolymeren spricht dafür, dass der Carborankern einen gewissen inhibierenden Einfluss auf die thermische Zersetzung besitzt. Das wird hauptsächlich auf sterische Hinderung und nicht auf Polaritätseinflüsse zurückgeführt. Ketten-Erweiterung mit Zinnoctoat verursachte eine Herabsetzung der thermischen Stabilität, wahrscheinlich wegen der Anfügung von Sn—O-Bindungen an die Moleküle.

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Acid-Catalyzed Methanolysis of Tri-*O*-methylamylose and Tri-*O*-methylcellulose

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Synopsis

Past experimental evidence has indicated that the acid-catalyzed hydrolysis of polysaccharides does not proceed randomly, and it has been suggested that hydrolysis is more rapid for the glycosidic bonds by which the nonreducing endgroups are attached. To test this hypothesis, amylose and cellulose were permethylated and subjected to methanolysis. It was found that in both the methanolysis of tri-*O*-methylamylose and tri-*O*-methylcellulose the production of methyl 2,3,4,6-tetra-*O*-methyl-α,β-D-glucopyranoside was complete before the production of methyl 2,3,6-tri-*O*-methyl-α,β-D-glucoside was finished. Since the former compound could only come from the original nonreducing end units and the latter from all other units, these results were interpreted as giving support to the idea of a preferential scission of the bonds at the nonreducing ends, even though the release of original end units was not complete until 70–85% of the glycosidic bonds had been cleaved. It was concluded that methanolysis proceeds by a modification of the hydrolysis mechanism and that methanolysis is therefore a poor model for hydrolysis.

INTRODUCTION

Although one might expect that polymers such as homopolysaccharides, in which each unit is identical, would be degraded in a random fashion, experimental data do not uphold this assumption. Theoretical models have been proposed for the random hydrolysis of polysaccharides.[1–12] However, when the theoretically calculated amounts of D-glucose and maltooligosaccharides are compared with the actual amounts formed by the hydrolysis of starch, it is discovered that there are more products of low degree of polymerization (D.P.) and less intermediate-sized products than would be expected from a completely random hydrolysis,[13–15] assuming that the total reducing value by the Fehling reaction calculated as percentage of D-glucose (dextrose equivalent, D.E.) expresses the degree of hydrolysis.

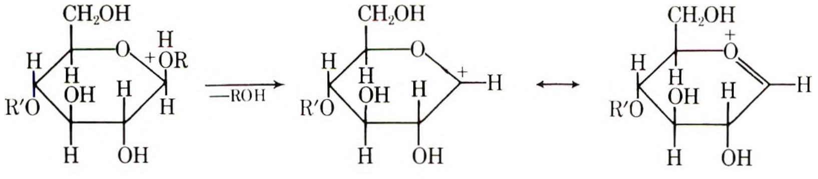
Simha[10,11] approached random degradation from a statistical kinetic point of view and derived an equation for the size distribution at time t for an initial material of a single molecular weight, assuming a first-order degradation with equal hydrolysis probability for all linkages regardless of their position in the chain. In a single test of his formula,[16] with cellulose, which was assumed to be an actual case of random degradation, it was found that the homogeneous acid-catalyzed hydrolysis of cellulose dissolved in phosphoric acid[17,18] followed closely his equation for long times of hydrolysis, but the error was large for short times of hydrolysis.

It has also been found[19] that starch hydrolysis starts slowly, then increases, with the first 10–20% of hydrolysis giving less depolymerization than demanded by the Kuhn equation.[1–5]

The very early products of hydrolysis can also be examined. It may be considered that monomers and oligomers can be formed only by cleavage near a chain end.[20] Therefore, for random depolymerization the rate of formation of each product would be proportional to the number of chain ends from which the particular product can be formed. Hence, in the early stages of the hydrolysis of starch the rates of formation of D-glucose maltose, and maltotriose should be identical, because the number of cleavage points that would form each of them is identical (regardless of D.P., if D.P. is large), and the mole fractions of each should be identical. With this model, too, experiments indicate that not all the glucosidic linkages are equally susceptible to hydrolysis and that hydrolysis does not occur by random scission, for in the acid-catalyzed hydrolysis of potato starch in dilute hydrochloric acid the D-glucose appeared first, then the maltose, then the maltotriose.[21] Moreover, in the hydrolysis of starch with cation-exchange resins the first product is D-glucose.[22] Thus, it appears that terminal linkages are more rapidly hydrolyzed.

Because the rate constant for hydrolysis (k) increases during the course of hydrolysis of cellulose and starch, and because the overall rate constant decreases with increasing D.P., it has previously been postulated that terminal linkages are hydrolyzed at a greater rate than internal linkages.[4,5,23–27] Various explanations of the differences in k for saccharides of various degrees of polymerization have been offered.[28]

Because of the mechanism of acid-catalyzed hydrolysis one of us[29] has suggested that hydrolysis of the glycosidic bond at the reducing end is more rapid. Acid-catalyzed hydrolysis of pyranosides is believed to proceed by protonation of the glycosidic oxygen atom to form a conjugate acid(I), followed by heterolysis of the acyclic O—C-1 bond to give a cyclic carbonium ion(II), which can be stabilized by resonance with an oxonium ion-(III). Reaction with water would then give the protonated reducing sugar and, thence, the reducing sugar.



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According to this mechanism conformations and intramolecular steric interactions would affect the relative rates of hydrolysis.[30–33] It has been postulated[34] that the rate-determining step is the formation of the carbonium-oxonium ion, which exists in a half-chair conformation. Its formation involves a small rotation about the C-2—C-3 and C-4—C-5 bonds, and it is believed that the rate is primarily dependent on the extent of interaction of substituents on C-2 relative to C-3 and on C-4 relative to C-5.[33] Therefore, internal bonds should be hydrolyzed slowly, compared to nonreducing end bonds, because the change of a D-glucopyranose unit from a C-1 conformation to the half-chair conformation of the carbonium-oxonium ion in a central portion of a chain [(I), R′ = polymer chain] would necessitate reorientation of an entire chain, whereas the change in conformation necessary to form this ion from a terminal nonreducing end unit [(I); R′ = OH] would not require chain-segment reorientation and, hence, hydrolysis at this point should be more facile.[29]

One way to test this hypothesis is to label the end of the polymer. Laszlo et al.[35,36] labeled both the reducing and nonreducing ends of amylose with D-glucopyranose–^{14}C and found that D-glucose was released from the nonreducing end at three times the rate at which it was released from the reducing end. Earlier it had been shown that the hydrolysis of starch was the resultant of two simultaneously occurring processes, namely the hydrolysis of terminal and of nonterminal bonds, and that the rate constant for the hydrolysis of terminal bonds is larger than that for nonterminal bonds and equal to that for the hydrolysis of maltose.[37] However, which end had this characteristic was not determined.

Another way to label the nonreducing end unit is to derivatize completely the polymer. In this work cellulose, a β-D-(1→4)-glucan, and amylose, an α-D-(1→4)-glucan, were permethylated, since these derivatives are well characterized. Because the completely methylated derivatives are insoluble in water, alcoholysis (methanolysis) was used in place of hydrolysis. The product of cleavage at the nonreducing end of these polymers is methyl 2,3,4,6-tetra-*O*-methyl-α,β-D-glucopyranoside, and the monomeric product from anywhere else in the molecule is methyl 2,3,6-tri-*O*-methyl-α,β-D-glucoside. (Any internal cleavages or removal of the original nonreducing end unit would expose new nonreducing ends, which would yield the trimethyl ether.) By determining at what extent of methanolysis are all the nonreducing end units released it can be determined whether this degree of methanolysis agrees with a random cleavage or a preferential cleavage at the nonreducing end, proceeding stepwise down the chain, releasing monosaccharide (with slow internal cleavages forming new ends), similarly to the mechanism proposed for the acid-catalyzed hydrolysis of protein.[38]

It should be noted that treatment of methylated starch with acetyl bromide resulted in selective removal of the nonreducing end units.[39]

MATERIALS

Tri-*O*-methylcellulose

Avicel Superfine microcrystalline cellulose, D.P. <300 (a product of Food Machinery Corp., American Viscose Division, Marcus Hook, Pa.), was acetylated.[40] Methylation was effected by a slight modification of published procedures. A 10-g. amount of the cellulose acetate was dissolved in 200 ml. of acetone, and the solution was kept at 55°C. during the gradual addition of dimethyl sulfate (120 ml.) and 30% sodium hydroxide (321 ml.).[41] The reagents were added at the rate of one-tenth of the total every 10 min. Methylation was done in air, to reduce the chain length.[42] The acetone, the volume of which was maintained at about 200 ml., was removed after 3 hr. by distillation. The temperature was raised to 85°C., to destroy excess dimethyl sulfate; the hot reaction mixture was filtered, and the product was washed several times with boiling water. The product was dissolved in chloroform, and this solution was dried with anhydrous sodium sulfate and evaporated to dryness.

A solution of this methylcellulose in 100 ml. of dry tetrahydrofuran was methylated with 84 ml. of dimethyl sulfate and 70 g. of pulverized solid sodium hydroxide, the reagents being added in 7 portions during 2 days.[43] When all the reagents had been added, the mixture was refluxed 1 hr., cooled, and filtered. The precipitate was suspended in water, and the mixture was extracted with chloroform. The methylated cellulose obtained after evaporation of the filtrate and washings was also dissolved in chloroform. The two chloroform solutions were combined, dried with anhydrous sodium sulfate, and evaporated to dryness. To insure complete methylation, the resulting product, soluble in methyl iodide, was methylated with the reagents of Purdie.[41]

The product obtained after methylation with Purdie reagents showed no infrared absorption at 3400–3800 cm.$^{-1}$ (benzene solution), and upon extended methanolysis only methyl 2,3,4,6-tetra-*O*-methyl- and 2,3,6-tri-*O*-methyl-α,β-D-glucopyranosides were indicated by thin-layer chromatography.

Tri-*O*-methylamylose

Nepol amylose, D.P. >300 (a product of the A. E. Staley Mfg. Co., Decatur, Ill.), was acetylated by the following procedure,[44] which probably effects some degradation. Amylose (60 g.) was refluxed and mechanically stirred for 2 hr. with 630 ml. of pyridine. After the addition of 13.95 g. of fused sodium acetate and 195 ml. of acetic anhydride the mixture was refluxed (125°C.) for 1 hr. The temperature was reduced to 100°C., and the mixture was heated overnight. The termperature was raised, and the mixture was refluxed for another hour, then cooled to 50–60°C. Portions of the homogeneous solution were poured into absolute ethanol in a Waring Blendor. The fine precipitate was washed three times with 95% ethanol in the blender, filtered out, and air-dried.

Amylose triacetate so prepared was used for preparing tri-*O*-methylamylose by the procedure described for the preparation of tri-*O*-methylcellulose. The product obtained showed no infrared absorption at 3400–3800 cm.$^{-1}$ (benzene solution) and, upon extended methanolysis, yielded only a trace of methyl 2,3-di-*O*-methyl-α,β-D-glucopyranoside, as indicated by thin-layer chromatography. This compound originates from amylopectin (<10%), which contaminates the starting compound.

Methyl Hepta-*O*-methylmaltoside

Pure maltose[45] (0.2 g.) was added to an ether solution of 1.5 g. of diazomethane. After standing overnight the solution was stirred for 1 hr. Dropwise addition of glacial acetic acid destroyed the excess diazomethane. Evaporation of the ether solution gave partially methylated maltose. Two more methylations with the reagents of Purdie gave completely methylated maltose.[46]

METHODS

Methanolysis and Isolation of Monomers

To a 2% solution of tri-*O*-methylcellulose, tri-*O*-methylamylose, or methyl hepta-*O*-methylmaltoside in chloroform (100 ml.) was added 100 ml. of a 20% (v/v) solution of concd. sulfuric acid in methanol, to give a final solution of 1.89*M* in sulfuric acid. The solution was refluxed (59°C.) over a steam cone. Aliquots of 10 ml. were taken at intervals; the aliquots were neutralized with 10 ml. of concd. ammonium hydroxide and evaporated to dryness.

The residue was extracted with three portions (100, 50, and 50 ml.) of boiling (2 min.), redistilled (over P_2O_5), 30–60°C. petroleum ether with frequent shaking, to remove the monomeric products.[47] Acetone (30 ml.) was then added to the remaining residue, and the mixture was stirred vigorously; then 50 ml. of petroleum ether was added, to precipitate any dissolved salts, polysaccharides, or oligosaccharides, which interfere in the determination of the methylated monomers. This solution was then filtered. The three extracts were combined, evaporated to dryness, and dissolved in acetone.

Thin-Layer Chromatography

Thin-layer chromatography (TLC) plates were prepared especially for quantitative work. Silica Gel G (Brinkmann Instruments, Inc., Westbury, New York), 30 g. was mixed in 70 ml. of water for 2 min. in a Waring Blendor. The slurry was applied to five 20- by 20-cm. double-strength window-glass plates with a Desaga applicator set at 300 μ. The plates were dried for 1 hr. at 130°C. After drying they were scraped with a straightedge, to remove silica gel from the edges.

Acetone solutions were spotted on a plate, which was then developed 45 min. with acetone–petroleum ether–benzene (2:4:4, v/v; petrol. ether, 30–60°); all solvents were redistilled and anhydrous.

After development the plates were sprayed with 50% sulfuric acid in absolute ethanol and then heated in an oven at 130°C. for 2 min. Plates were kept in the dark, to prevent fading. The density of the spots was determined with a Photovolt Model 530 TLC Densitometer with a Varicord Variable-Response Recorder Model 42 and an Integraph Automatic Integrator Model 49.

To determine methyl 2,3,6-tri-*O*-methyl-α,β-D-glucopyranoside from tri-*O*-methylcellulose, 6 μl. of a 2 ml. acetone solution was spotted; from tri-*O*-methylamylose, 2 μl. To determine methyl 2,3,4,6-tetra-*O*-methyl-α,β-D-glucopyranoside from tri-*O*-methylcellulose, 10 μl. of a 0.5 ml. acetone solution of each aliquot was spotted; from tri-*O*-methylamylose, 20 μl. of a 2 ml. acetone solution.

Methanolysis Rate Determinations

Solutions (0.5%) of the two methylated polysaccharides were methanolyzed as before. Aliquots were removed, diluted to 20 ml. with chloroform, and cooled rapidly to 25°C. Optical rotation was determined in a Bendix ETL-NPL Automatic Polarimeter with a 546 mμ interference filter. Rate constants were calculated by the Guggenheim method.

RESULTS

Figure 1 shows the standard curves prepared by complete methanolysis of methyl hepta-*O*-methylmaltoside, yielding equal molar proportions of methyl 2,3,4,6-tetra-*O*-methyl- and methyl 2,3,6-tri-*O*-methyl-α,β-D-gluco-

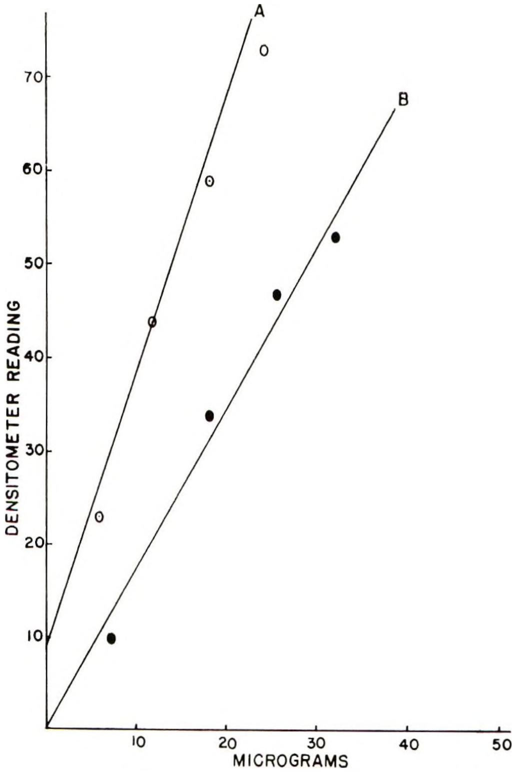


Fig. 1. Standard curves obtained by determination of methanolysis products of methyl hepta-*O*-methylmaltoside: (*A*) methyl 2,3,6-tri-*O*-methyl-α,β-D-glucoside; (*B*) methyl 2,3,4,6-tetra-*O*-methyl-α,β-D-glucopyranoside.

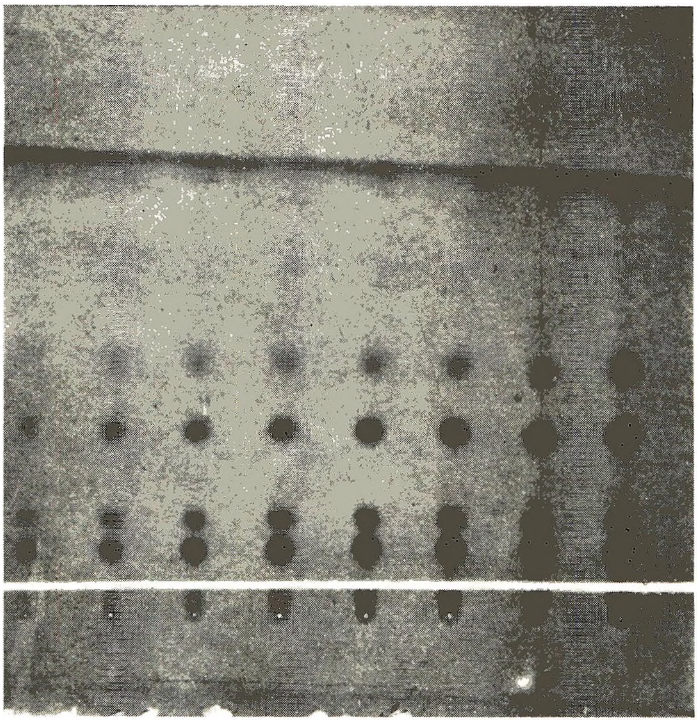


Fig. 2. Thin-layer chromatography plate from which standard curves were made. Lower two spots are 2,3,6-tri-*O*-methyl-α,β-D-glucoside. Upper two spots are 2,3,4,6-tetra-*O*-methyl-α,β-D-glucopyranoside. Distance from origin to solvent front is about 14 cm. Original picture was taken with a Polaroid camera.

pyranosides. Figure 2 shows the TLC plate from which the standard curves were made. A number of factors affect analysis by this method. The glass plates used were not of uniform thickness, and as a result the thickness of the adsorbent varied across the plates. Both curves of Figure 1 should pass through the origin; however, changes in adsorbent thickness affect the background readings and hence the intercepts. Further, when there is incomplete separation at higher concentrations, the total density of the two spots corresponding to the α-D and β-D anomers is not recorded.

Figure 3 gives typical results of the methanolysis of tri-*O*-methylcellulose. Figure 4 gives typical results of the methanolysis of tri-*O*-methylamylose. A typical TLC plate used for the determination of methyl tetra-*O*-methyl-α,β-D-glucopyranoside is shown in Figure 5; one for the determination of methyl 2,3,6-tri-*O*-methyl-α,β-D-glucopyranoside is shown in Figure 6.

A third source of error, one not present on the standard plates, is evident in Figures 5 and 6, namely background color. Background color appears as a streak through the spots and is the greatest source of error, especially in the determination of methyl tetra-*O*-methyl-α,β-D-glucopyranosides. Since this background color was not all of the same intensity, the density increase was not uniform for all spots.

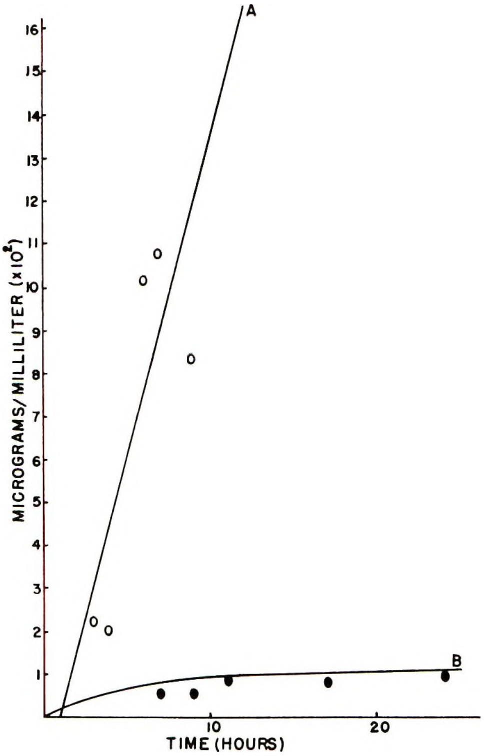


Fig. 3. Micrograms per milliliter of aliquot plotted against time of methanolysis of tri-*O*-methylcellulose: (*A*) methyl 2,3,6-tri-*O*-methyl-α,β-D-glucoside; (*B*) methyl 2,3,4,6-tetra-*O*-methyl-α,β-D-glucopyranoside.

Although there are experimental errors in the results, there is a definite trend in them. Figure 3 shows that, in the methanolysis of tri-*O*-methylcellulose, at approximately 11 hr. methyl 2,3,6-tri-*O*-methyl-α,β-D-glucoside is still increasing, while methyl tetra-*O*-methyl-α,β-D-glucoside has reached a constant value. Figure 4 shows that in the methanolysis of tri-*O*-methylamylose, again at approximately 11 hr., the original nonreducing endgroups have all been released, while internal units are still being released.

Figure 7 shows the changes in specific optical rotation with time during the methanolysis reaction. The first-order rate constant for acid-catalyzed methanolysis of tri-*O*-methylcellulose under the conditions used was found to be 3.12×10^{-3} min.$^{-1}$. The first-order rate constant for acid-catalyzed methanolysis of tri-*O*-methylamylose under the conditions used was found to be 1.91×10^{-3} min.$^{-1}$.

DISCUSSION

The evidence presented here does not unequivocally answer the question whether the acid-catalyzed hydrolysis of amylose and cellulose is somewhat specific for nonreducing end bonds. However, the fact that the amount of

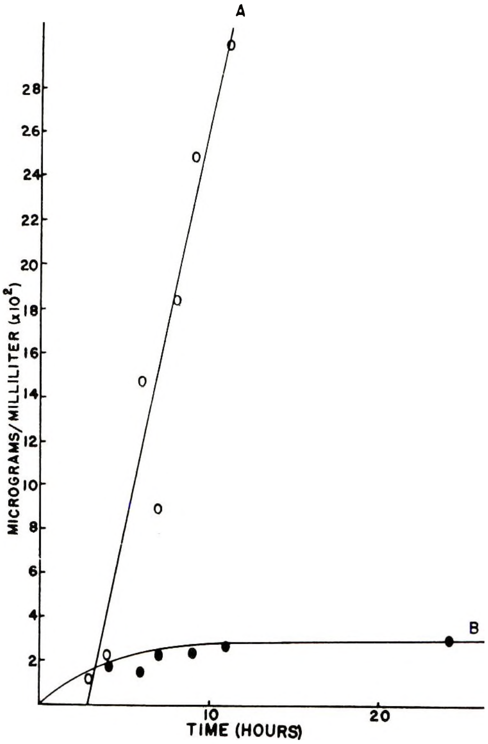


Fig. 4. Micrograms per milliliter of aliquot plotted against time of methanolysis of tri-*O*-methylamylose: (*A*) methyl tri-*O*-methyl-α,β-D-glucoside; (*B*) methyl tetra-*O*-methyl-α,β-D-glucopyranoside.

methyl tetra-*O*-methyl-α,β-D-glucopyranoside reaches a maximum while the concentration of methyl tri-*O*-methyl-D-glucoside was still increasing does support the hypothesis of preferential cleavage of the nonreducing end. Further indication of a preferential cleavage was the presence of oligosaccharides after the removal of tetra-*O*-methyl-D-glucoside units was complete, which shows that the formation of methyl 2,3,6-tri-*O*-methyl-α,β-D-glucopyranosides is continuing.

However, from the rate data presented in Figure 7 it can be calculated that at 11 hr., when the release of nonreducing end units is complete, 69% of the glucosidic bonds in tri-*O*-methylamylose and 87% of the bonds in tri-*O*-methylcellulose are broken. These values indicate that methanolysis is quite nonspecific for the nonreducing end. However, only methanolysis of the glucosidic bond at the original nonreducing end was measured. Since both the removal of tetra-*O*-methyl-D-glucose units and any internal cleavages would form new nonreducing ends, which would yield methyl 2,3,6-tri-*O*-methyl-α,β-D-glucopyranoside on methanolysis, the yields of methyl tri-*O*-methyl-D-glucosides at the times of maximum yield of methyl tetra-*O*-methyl-D-glucosides could be very high. Although the D.P. of the permethylated polysaccharides was not known, all evidence indicated that

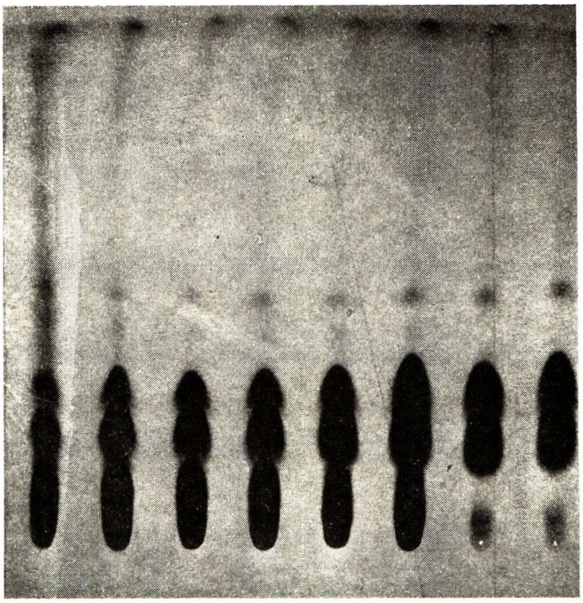


Fig. 5. Typical thin-layer chromatography plate used for determination of methyl tetra-*O*-methyl-α,β-D-glucopyranoside (upper two spots) obtained by methanolysis of tri-*O*-methylamylose. Distance from origin to solvent front is approximately 14 cm. Methanolysis times are 2, 4, 6, 7, 9, 11, 17, 24 hr., left to right, respectively. Original picture was taken with a Polaroid camera.

both had a D.P. of >10, so a maximum of 10% of the bonds would be at the original nonreducing end. Whether or not this is indicative of a "zip"[38] is not known.

Of the two polymers, tri-*O*-methylcellulose and tri-*O*-methylamylose, the latter had a slightly greater apparent specificity for methanolysis of the nonreducing end. This might be due to greater order (helix) in the tri-*O*-methylamylose molecule or to a higher molecular weight of the starting material.

The shapes of the methanolysis curves in Figure 7 suggest that, as methanolysis proceeds, the β-D-(1 → 4)-linked tri-*O*-methylcellulose yields predominantly the α-D anomeric form of the methyl D-glucosides, whereas the α-D-(1→4)-linked tri-*O*-methylamylose initially yields a mixture of methyl D-glucosides in which the β-D anomeric form probably predominates. However, as the latter reaction reaches thermodynamic equilibrium, the rotation increases and the α-D anomeric form predominates.

Although this apparent predominance of the inversion product has not been noticed in acid-catalyzed hydrolyses, it has been observed in the acid-catalyzed methanolysis of phenyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside and of phenyl α- and β-D-glucopyranoside.[48,49] The explanation given was that of a shielding effect of the departing alcohol. It is probable that because of the more negative oxygen atom in the methanol molecule the methanol molecule approaches the glucosyl unit before the carbonium ion

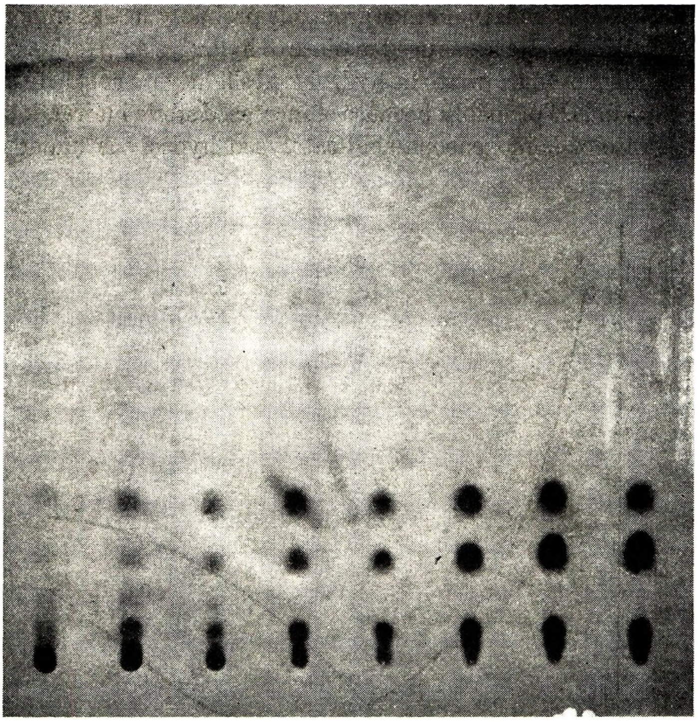
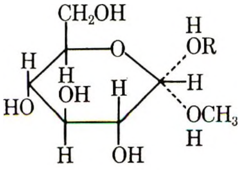


Fig. 6. Thin-layer chromatography plate used for determination of methyl tri-*O*-methyl-α,β-D-glucoside (upper two spots) obtained by methanolysis of tri-*O*-methylamylose. Distance from origin to solvent front is approximately 14 cm. Methanolysis times are 2, 3, 4, 6, 7, 8, 9, and 11 hr., left to right, respectively. Original picture was taken with a Polaroid Camera.

is actually formed and, in fact, helps the other alcohol to leave, so that a transition state such as (IV), for tri-*O*-methylamylose, would be found rather than a true carbonium–oxonium ion [(II), (III)].

If (IV) is the transition state, only the C-1 hydrogen would need to invert, and there would be no great change in ring conformation such as that needed to form the half-chair



IV

conformation of the carbonium-oxonium ion. Therefore, there would be much less specificity for nonreducing endgroup hydrolysis than for internal linkage hydrolysis. Hence, methanolysis cannot be used as a model for hydrolysis, a conclusion reached by others also.[48] Other models are now being investigated in our laboratories.

The presence of the methyl ether groups is probably not as important as the fact that methanolysis was used in place of hydrolysis. Methyl ethers of pyranosides have been shown to be hydrolyzed slightly more slowly than the parent compounds,[50] probably because of increased steric interactions. Although the rate of homogeneous acid-catalyzed hydrolysis under comparable conditions cannot be determined, it appears that acid-catalyzed methanolysis of the permethylated polysaccharides is as fast or slightly faster than hydrolysis, probably because of the difference in the mechanism which modifies the rate-determining heterolysis step.

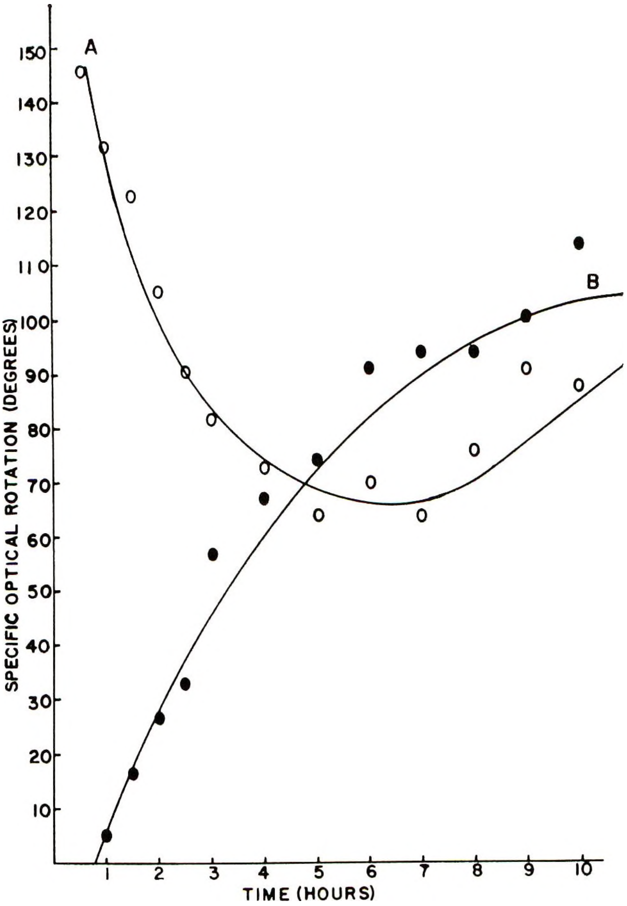


Fig. 7. Specific optical rotation plotted against the time for methanolysis of (*A*) tri-*O*-methylamylose and (*B*) tri-*O*-methylcellulose.

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Résumé

Des expériences antérieures ont indiqué que l'hydrolyse, catalysée par les acides, des polysaccharides nè progressent pas de façon statisque. On a suggéré que l'hydrolyse est plus rapide pour les liens glycosidiques auxquels sont attachés les groupes terminaux non-réducteurs. En vue de contrôler cette hypothèse, l'amylose et la cellulose ont été complètement méthylées et soumises à la méthanolyse. On a trouvé que dans le cas de la méthanolyse de la tri-*O*-méthylamylose et de la tri-*O*-méthylcellulose, la production du méthyle 2,3,4,6-tétra-*O*-méthyle-α,β-D-glucopyranoside était complète avant que la production de méthyle 2,3,6-tri-*O*-méthyle-α,β-D-glucoside ne soit achevée. Puisque le premier composé pouvait uniquement provenir des extrémités non réductrices originales et et le dernier de toutes les autres unités, ces résultats ont été interprétés pour confirmer l'idée d'une scission préférentielle des liens aux extrémités non réductrices bien que la scission des unités terminales originales ne soit complète que à 70–85% des liaisons glycosidiques étaient rompues. On en conclut que la méthanolyse progresse par une modification du mécanisme d'hydrolyse et que la méthanolyse est dès lors un modèle pauvre pour l'hydrolyse elle-même.

Zusammenfassung

Frühere Arbeiten haben Hinweise dafür geliefert, dass die säure-katalysierte Hydrolyse von Polysacchariden nicht statistisch verläuft und es wurde angenommen, dass die Hydrolyse für die glykosidischen Bindungen, durch welche die nichtreduzierenden Endgruppen gebunden werden, rascher ist. Zur Überprüfung dieser Hypothese wurden Amylose und Cellulose permethyliert und der Methanolyse unterworfen. Bei der Methanolyse von Tri-*O*-methylamylose und Tri-*O*-methylcellulose war die Bildung von Methyl-2,3,4,6-tetra-*O*-methyl-α,β-D-glucopyranosid vor Beendigung der Bildung von Methyl-2,3,6-tri-*O*-methyl-α,β-D-glukosid schon vollständig. Da erstere Verbindung nur aus den ursprünglichen nicht-reduzierenden Endgruppen und letztere aus allen anderen Bausteinen stammen konnte, wurden diese Ergebnisse als eine Stütze für die Vorstellung von einer präferentiellen Spaltung der Bindungen beim nichtreduzierenden Ende betrachtet, obzwar die Freisetzung der ursprünglichen Endgruppen nicht vor einer Spaltung von 70–85% der glycosidischen Bindungen vollständig war. Man kam zu dem Schluss, dass die Methanolyse nach einem modifizierten Hydrolysemechanismus verläuft und dass daher die Methanolyse nur ein unvollkommenes Modell für die Hydrolyse bildet.

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Differential Permeation and Absorption of Water Vapor in Polyacrylamide Film

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Synopsis

An investigation has been made of successive differential absorption and differential permeation of water vapor in polyacrylamide at 30°C. The successive differential absorptions showed two types of non-Fickian anomalies: sigmoid type and two-stage type curves. The experimental data have been analyzed in terms of the Fick diffusion equation assuming a time-dependent approach of the surface concentration. The calculated family of absorption curves agreed with the experimental results. The permeation curves in the region of high and low pressure increments were apparently normal, but at medium pressures they showed anomalous behavior. It was found that in the differential type of permeation experiment the stress effect induced by a concentration gradient between the surfaces of the film was eliminated. By assuming the time-dependent approach of the equilibrium surface concentration, we calculated the time lag as a function of film thickness and applied the theory to the data for permeation through polyacrylamide film with different film thicknesses at relatively small pressure intervals. The rate parameter calculated from permeation data was found to be in good agreement with that from successive differential absorption data.

INTRODUCTION

Recent studies[1-4] on the permeation of organic vapors through amorphous polymer solids have revealed that the nonstationary state of permeation at temperatures well above the glass transition T_g is controlled by purely Fickian diffusion mechanism, but when the temperature is slightly above or below T_g these processes exhibit various non-Fickian features. Park,[1] studying the permeation of methylene chloride through polystyrene membrane at 25°C., observed an anomalous behavior, in which a high initial permeation rate gradually decreased to the final steady value. He suggested the phenomenon was due to rapid permeation through cracks in the dry polymer which sealed up as the polymer absorbs vapor. Recently, Meares[2] made permeation measurements on allyl chloride through poly(vinyl acetate) films at 40°C. and observed complex behavior, in which an initial sharp increase in permeation rate decreased in a short time interval before appreciable permeation by the normal steady build-up started. Similar anomalous permeation curves were observed for the system poly-

(vinyl acetate)–methanol at temperatures slightly below and above T_g.[3] Such behavior could not be interpreted in terms of the time-dependent approach of the surface concentration,[5] the time dependence of the diffusion coefficient D,[6] and the presence of a convective flow through cracks or internal pores present in the dry polymer.[7] Meares has suggested that these anomalies are due to the stress effect induced by an appreciable concentration gradient between the surfaces of the film under conditions of usual permeation experiments. In order to eliminate the stress effect upon the permeation processes, it is hoped that the differential type of permeation experiment is to be done. The term "differential" refers to the experiment in which the pressure difference between the ingoing and outgoing sides of film is small. In this paper, data for differential permeation and absorption of water vapor in polyacrylamide (PAM) film at 30°C. are presented. This system is chosen because PAM is soluble in water and the permeation behavior of the system for water–water-soluble polymer is expected to be similar to that for organic solvent–polymer systems.

EXPERIMENTAL

Materials

The PAM used in the present study was furnished by the Department of Polymer Science, University of Osaka, through the courtesy of Dr. A. Teramoto. The polymer was used without further purification. Its intrinsic viscosity in 1.0M sodium nitrate solution at 30°C. was 1.128 dl./g., corresponding to a molecular weight of 1.9 × 10^5, according to the equation:[8]

$$[\eta] = 3.73 \times 10^{-4} M_w^{0.66}$$

Films of the polymer were cast from a 3% aqueous solution on a clean mercury surface and dried over P_2O_5 or various saturated salt solutions in a desiccator at room temperature. Prior to the permeation experiments, all the samples were stored over salt solutions in a desiccator for more than 1 week, which is maintained at corresponding relative humidities. The films used for the measurements varied from 7.7 × 10^{-3} to 1.43 × 10^{-2} cm. in thickness. A value of 1.092 g./ml. was used for the density of PAM in calculating these film thicknesses. This density value was determined in the usual Gay-Lussac type pycnometer at 30°C., n-hexane being used as the confining liquid.

Apparatus and Procedure

The transmission of water vapor through the film was determined by a modification of the well-known cup method. Film samples previously equilibrated with water vapor held at proper relative humidities were inserted in a cup, into which the corresponding salt solution was poured.

The cups equipped with the film and salt solution were suspended from the steel spiral spring in a desiccator over various salt solutions held at final relative humidities. The transmission of water vapor was determined from a decrease or increase in weight of the cups. The weight gain or weight loss of the cups was followed as a function of time by measuring the extension of the spring by means of a travelling microscope.

The sorption apparatus described previously[3] was used throughout this study. Successive differential absorption of water vapor in PAM was measured at 30°C.

The equilibrium sorption isotherms were obtained not only by means of the sorption balance but also by the weighing bottle method at various relative humidities controlled with saturated salt solutions. This experiment was undertaken to obtain data which serve to check the reliability of our permeability chamber when used as a constant humidity chamber.

RESULTS AND DISCUSSION

Permeation

In a typical example, the results of permeation of water through PAM films equilibrated at initial relative pressure $p_i/p_s = 0.446$ are shown in Figure 1 as a function of higher final relative pressures p_f/p_s than p_i/p_s. Here, p_i and p_f are initial and final water vapor pressures, respectively, and

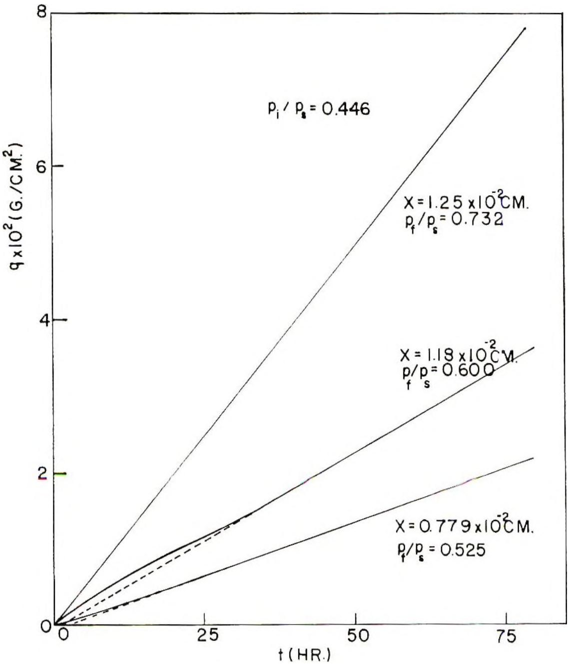

Fig. 1. Permeation curves of water for PAM at 30°C. as a function of higher final relative pressure than initial pressure.

p_s is the saturated pressure at 30°C. In the figure, the ordinate is the amount of water vapor, $q(t)$, which has passed through a unit area of the film. It is seen from the figure that the curves are apparently normal in the region of higher or lower final pressures, but at medium pressures they start with a low rate, increase their gradually decreasing rate, and then approach asymptotically a straight line. These curves are similar to the permeation curves for allyl chloride[2] and methanol[3] in PVAc. Similar anomalous permeation curves were found at other initial relative pressures of 0.360, 0.670, and 0.732.

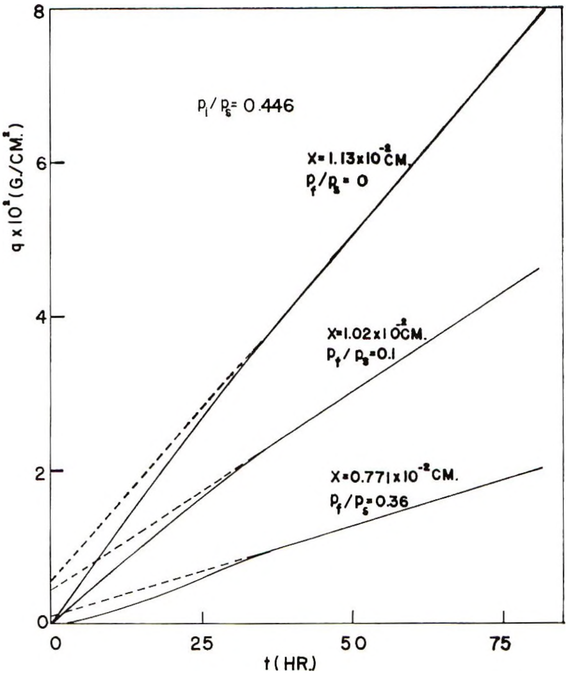

Fig. 2. Permeation curves of water for PAM at 30°C. as a function of lower final relative pressure than initial pressure.

Figure 2 gives results of permeation of the vapor from initial relative pressure $p_i/p_s = 0.446$ to various final pressures p_f/p_s less than p_i/p_s. It is seen that the curves are concave toward the time axis in the region of final pressures well below p_i and have negative values of time lags. These behaviors are the features expected from normal Fick diffusion mechanism, when the permeation experiment is started from p_i to p_f less than p_i. The absolute values of time lag observed are found to be larger than those calculated from the $D(C)$ data derived from steady-state permeability by using Frisch's equation.[9] This suggests that the permeation curves observed in Figure 2 are not strictly controlled by a purely Fickian diffusion mechanism. Permeation curve at a final pressure slightly below p_i is similar to the anomalous behavior observed in Figure 1.

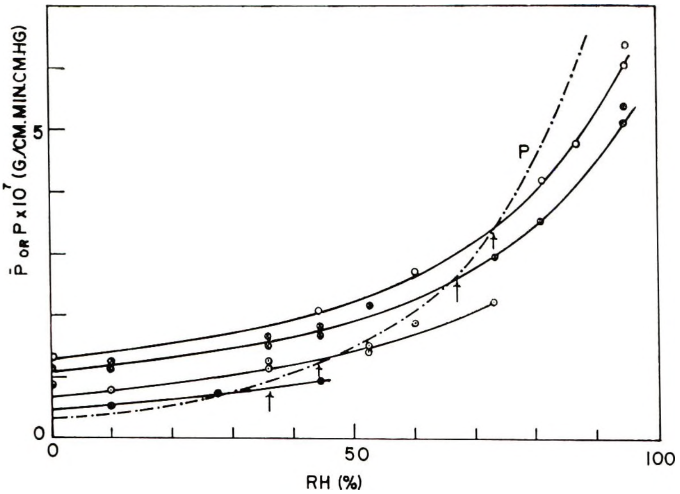

Fig. 3. Integral and differential permeability coefficient of water in PAM at 30°C.

The steady-state permeability coefficient $\bar{P}$ for the pressure gradient p_i to p_f is evaluated from the rate of permeation in the steady state as:

$$\bar{P} = [X/(p_f - p_i)] \lim_{t \to \infty} dq(t)/dt \tag{1}$$

in which X is the thickness of the film. In Figure 3 are shown the results of $\bar{P}$ data for the system PAM–water starting from various fixed initial pressures p_i. The arrows in the figure indicate the initial equilibrium relative pressures p_i/p_s. It is seen that at fixed initial pressure p_i, $\bar{P}$ increases with increase of relative humidity as is found in the system of hydrophilic polymer–water.[10] If the permeability coefficient is dependent upon the pressure, $\bar{P}$ is termed the integral permeability coefficient and is defined as:

$$\bar{P} = 1/(p_f - p_i) \int_{pi}^{pf} P(p)dp \tag{2}$$

where $P(p)$ is the differential permeability coefficient. This equation permits evaluation $P(p)$ by simple graphical differentiation when the curve for $\bar{P}$ at fixed p_i as a function of p_f is given.

Figure 3 includes P values so obtained. It is seen that the P values derived from $\bar{P}$ data agree quite well, irrespective of the values of p_i, and the curve for P intersects the $\bar{P}$ curves at the positions of the respective relative pressures.

Figure 4 shows the water sorption isotherm data for PAM at 30°C. The open circles are the results from the measurements with spring balances. The filled circles are the values obtained from the weighing bottle method. The two sets of data are seen to agree quite satisfactorily, demonstrating our permeability chamber served as a good constant humidity chamber.

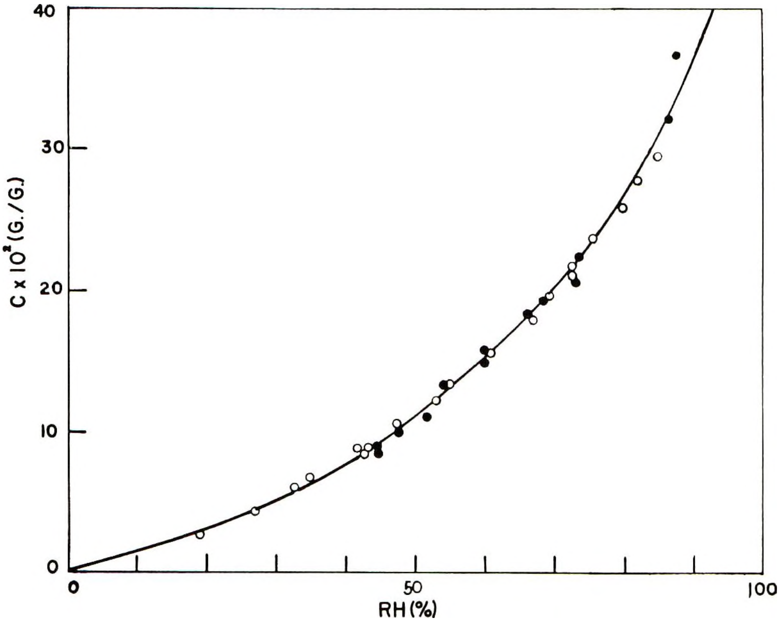

Fig. 4. Water vapor absorption isotherm of PAM at 30°C.: (○) data obtained with spring balance; (●) data obtained from weighing bottle method.

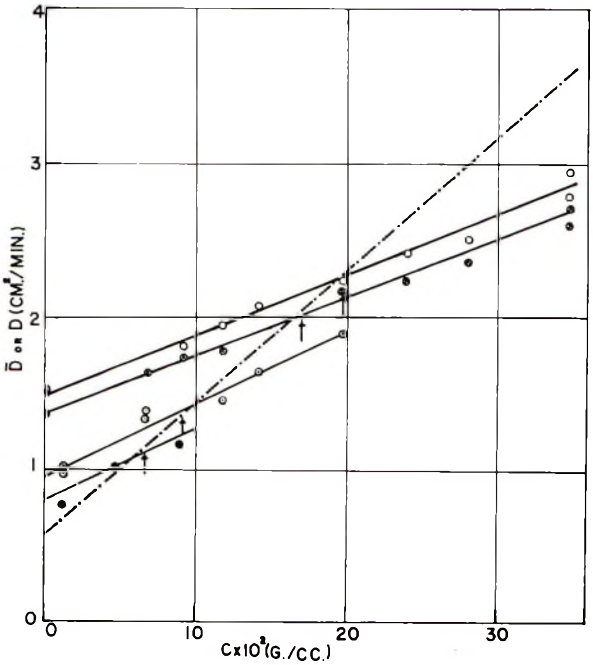

Fig. 5. Integral and differential diffusion coefficient as a function of water concentration for the system PAM–water at 30°C.

Combination of integral permeability coefficient for the pressure gradient p_i to p_f with equilibrium absorption isotherms enables us to calculate the integral diffusion coefficient $\bar{D}$ for the concentration interval C_i to C_f as a function of C_f. Plots of $\bar{D}$ versus water concentration at 30°C. are shown in Figure 5. It is seen that the $\bar{D}$ values increase linearly with the water concentration. From the $\bar{D}$ data the dependence of $D(C)$ on C can be estimated; this is included in Figure 5 (broken line). The D data derived from various concentrations C_i are found to agree with each other and are represented satisfactorily by a linear function of water concentration as:

$$D = 6 \times 10^{-7}(1 + 14.2C) \tag{3}$$

A similar dependence on C has been observed in the system rubber–benzene over a fairly wide range of concentration.[11]

Successive Differential Absorption

Figure 6 gives results of a series of successive differential absorption experiments for the system PAM–water at 30°C. The solid line is for the experimental data. The increments of water concentration in successive

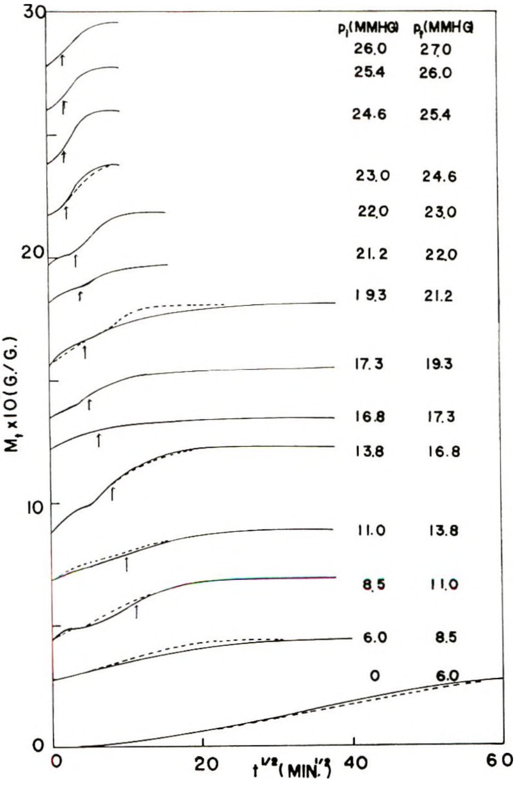

Fig. 6. Successive differential absorptions of the system PAM–water at 30°C.

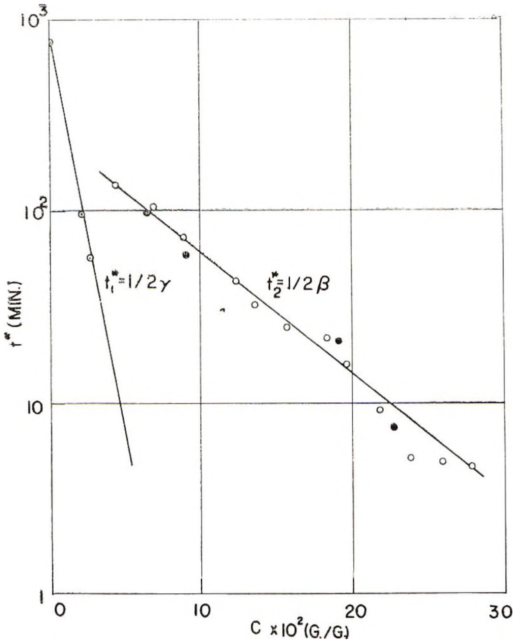

Fig. 7. Logarithmic correlation plots of t^* and initial concentration: (○) data obtained from absorption experiments; (●) data obtained from permeation experiments.

steps were approximately the same, about 2.5×10^{-2} g. water/g. dry polymer. The general character of this family of curves is similar to that reported for the sorption of organic vapors in semicrystalline polymers.[12]

For the first two steps the absorption starts at a low rate, increases rather rapidly in the intermediate stage, and then gradually approaches equilibrium. Thus, the behavior in this low-pressure region is of the sigmoid type. With increasing initial concentration the inflection point of the sigmoid curve shifts toward shorter times. When entering the third stage a two-stage process appears. With further increase of initial concentration the second stage portion shifts towards shorter times, the rate increases, and there is a greater contribution to the total concentration increment of each step. When a certain concentration is reached, the second stage portion predominates, and the two-stage process eventually changes to a sigmoid curve; a further increase of initial concentration merely gives rise to a vertical shift of this sigmoid curve without changing its shape. No definite evidence is observed in Figure 6 that the transition from non-Fickian to Fickian behavior occurs at the highest of the initial concentrations studied. The behavior appears to manifest features characteristic of partially crystalline polymer–solvent systems.[12]

From Figure 6 it was found that both the sigmoid curve in the regions of low initial concentration and the second-stage portion of the two-stage curve shift towards shorter times with increasing initial concentration. To characterize the positions of the sigmoid curve and the two-stage curve on the time axis we chose the times t_1^* and t_2^* corresponding to the inflection point of each curve (t_2^* is indicated by an arrow in the figure). In Figure 7 the values of t_1^* and t_2^* are plotted semilogarithmically against the initial concentration for each differential absorption. It is seen that plots for $\log t^*$ versus C are linear, and t_1^* rapidly approaches zero as C increases, but t_2^* decreases slowly with the concentration. The slope of the plot for t_2^* versus C is found to be slower than that reported for amorphous polymer–solvent systems.[2] This indicates that the processes responsible for second-stage behavior are sensitive to structural features of the polymer.

Recently, Long and Richman[5] showed that both sigmoid and two-stage absorption curves can be derived from the Fick diffusion equation if one assumes a boundary equation of the form:

$$C_s = C_q + (C_f - C_q)(1 - e^{-\beta t}) \tag{4}$$

where C_s is the surface concentration of the film, C_q is the surface concentration obtained instantaneously, and β is a rate parameter. Examination of the Long-Richman solution indicates that the value of t_2^* defined previously is nearly equal to $^1/_2\beta$, provided D/X^2 is not too small compared with β.

Fujita and Kishimoto[13] have found that eq. (4) was not capable of reproducing successive differential absorption curves and that this arose from the fact that eq. (4) involved a sudden increase of surface concentration at the start of an experiment. For glassy polymers[14,15] it is reasonable to assume that the initial increase of C_s to C_q is also time-dependent with a rate-determining parameter γ. Then the expanded form of eq. (4) is

$$C_s = C_i + (C_q - C_i)(1 - e^{-\gamma t}) + (C_f - C_q)(1 - e^{-\beta t}) \tag{5}$$

where $\gamma > \beta$ for all values of C. The analytic solution of the Fick diffusion equation with D independent of concentration subject to the boundary condition (5) and initial condition $C = C_i$ at $t = 0$ is given in eq. (6):

$$\frac{\Delta M}{\Delta M_\infty} = \delta\left[1 - 2\exp\{-\gamma t\}(\gamma X^2/D)^{-1/2}\tan(\gamma X^2/4D)^{1/2} - 8/\pi^2 \sum_{n=0}^{\infty} \frac{\exp\{-(2n+1)^2\pi^2 Dt/X^2\}}{(2n+1)^2[1 - (2n+1)^2\pi^2 D/\gamma X^2]}\right] + (1-\delta)\left[1 - 2\exp\{-\beta t\}(\beta X^2/D)^{-1/2}\tan(\beta X^2/4D)^{1/2} - 8/\pi^2 \sum_{n=0}^{\infty} \frac{\exp\{-(2n+1)^2\pi^2 Dt/X^2\}}{(2n+1)^2[1 - (2n+1)^2\pi^2 D/\beta X^2]}\right] \tag{6}$$

where ΔM is the weight of water vapor per unit volume of polymer + penetrant system, ΔM_∞ the value of ΔM at absorption equilibrium and δ is the ratio $(C_q - C_i)/(C_f - C_i)$. Equation (6) indicates that the values t_1^* and t_2^*, the times of the inflection point on the sigmoid curve and second-stage portion of the two-stage curve, are nearly equal to $^1/_2\gamma$ and $^1/_2\beta$, respectively. Equation (6) may be used to derive a theoretical system of successive differential absorption curves which may be compared with the experimental data given in Figure 6, if the functional form of D, γ, β and C_q with C is given.

As shown in Figure 5, the concentration dependence of diffusion coefficient for the PAM–water system is linear. Generally, Fick's diffusion equation could not be solved analytically for the general case of a diffusion coefficient which depends on concentration. It is, however, not a bad approximation to replace the known concentration-dependent diffusion coefficient by a constant D which will represent an average for the true $D(C)$ over the concentration interval concerned. By using the concentration dependences of D (Fig. 5), γ, β (Fig. 7) and C_q (Fig. 6), a family of successive differential absorption curves was calculated and is shown in Figure 6 as a dotted line. It is seen that, except for minor details, the calculated family of curves agrees with the experimental results for the system PAM–water. This suggests that non-Fickian features are caused by the slow relaxation of polymer chains leading to a time-dependent approach of the surface concentration.

Differential Permeation

From Figure 1 it was found that the permeation curves appear to be normal, provided the pressure difference between ingoing and outgoing sides of film is chosen sufficiently small. The time-lag values determined experimentally were found to be larger than those calculated from the $D(C)$ data in Figure 5 by using Frisch's equation.[7] For example permeability measurement from $p_i/p_s = 0.446$ to $p_f/p_s = 0.525$ for a film of thickness 7.79×10^{-3} cm. gives the time lag value of 84 min., while the theoretical one is 6.8 min. This means that the permeation curves, even at a small pressure increment, are not controlled by a purely Fickian diffusion mechanism, but may be interpreted as due to slow relaxation of polymer chain.

The solution of the Fick diffusion equation applicable to the permeation problem with the time-dependent approach of surface concentration gives the time lag θ as

$$\theta/X^2 = 1/6D + \delta/\gamma X^2 + (1 - \delta)/\beta X^2 \qquad (7)$$

This indicates that a plot of θ/X^2 against $1/X^2$ at a given concentration should be linear, and that the intercept at $1/X^2 = 0$ and the slope of the resulting straight line are $1/6D$ and $\delta/\gamma + (1 - \delta)/\beta$, respectively.

Differential permeation experiments with various film thicknesses were carried out at several initial vapor pressures. In Figure 8 are shown plots for θ/X^2 against $1/X^2$. It is seen that the data at each concentration follow a straight line, in agreement with the theoretical prediction from eq. (7). From the absorption experiment shown in Figure 6 it was found that the values of γ become infinite in the concentration region indicated in the figure. With the δ value found from the absorption experiment, the values

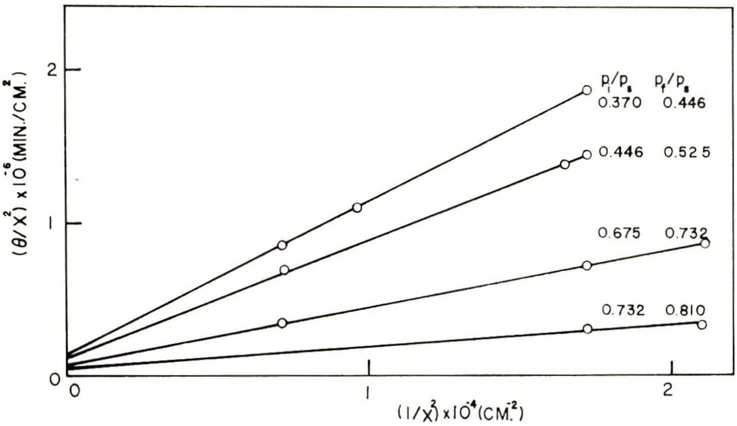

Fig. 8. Linear dependence of θ/X^2 on $1/X^2$ in the system PAM–water at 30°C.

of D and β are calculated as a function of concentration from the intercept and slope of the straight line.

The D thus obtained is a mean diffusion coefficient over the concentration interval between C_i and C_f and may be compared with the integral diffusion coefficient $\bar{D}$ for the corresponding concentration range, provided the concentration interval for the permeation experiment is rather small as in the present case. The values of D are found to be 1.2×10^{-6}, 1.4×10^{-6}, 2.1×10^{-6}, and 2.4×10^{-6} cm.^{2}/min., corresponding to pressure intervals 0.370–0.446, 0.446–0.525, 0.675–0.732, and 0.732–0.810, respectively, and agree with the data given in Figure 5.

The data of the rate parameter β, evaluated from permeation, is included in Figure 7 (filled circles). Both sets of data agree quite well. This suggests that differential permeation experiments in glassy polymers may be interpreted in terms of the time-dependent approach of surface concentration, as follows in the analysis of the differential absorption behavior.

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Résumé

Une étude de l'absorption différentielle successive et de la perméation différentielle de la vapeur d'eau a été faite dans le cas du polyacrylamide à 30°C. Les absorptions différentielles successives montraient deux types d'anomalies ne correspondant pas à la loi de Fick, c'est-à-dire des types sigmoides et des types à deux étapes. Les résultats expérimentaux ont été interprétés et analysés sur la base de l'équation de diffusion de Fick en admettant une approche de la concentration en surface dépendant du temps. La famille des courbes d'absorption calculées est en accord avec les résultats expérimentaux. Les courbes de perméation dans la région des incréments de prèssion plus élevée et plus base sont apparemment normales mais à pression moyenne, elles montrent un comportement anormal. On a trouvé que le type différentiel d'expérience de perméation est capable d'éliminer l'effet de tension induit par un gradient de concentration entre les surfaces du film. En admettant une approche de la concentration en surface à l'équilibre dépendante du temps, nous avons calculé le délai de temps en fonction de l'épaisseur du film et appliqué la théorie à ces résultats pour la perméation à travers un film de polyacrylamide avec différentes épaisseurs de film à des intervalles de pression relativement faibles. Le paramètre de vitesse calculé au départ des résultats de perméation est en bon accord avec celui calculé au départ des résultats d'absorption différentielle successive.

Zusammenfassung

Eine Untersuchung der sukzessiven differentiellen Absorption und Permeation von Wasserdampf in Polyacrylamid bei 30°C wurde durchgeführt. Die sukzessive differentielle Absorption zeigte zwei Typen von nicht-Fick'scher Anomalie, nämlich den sigmoiden Typ und den Zwei-Stufen-Typ. Die Versuchsergebnisse wurden mittels der Fick'schen Diffusionsgleichung unter Annahme einer zeitabhängigen Annäherung der Oberflächenkonzentration analysiert. Die berechnete Absorptionskurvenschar stimmte mit den Versuchsergebnissen überein. Die Permeationskurven waren im Bereich höherer und niedrigerer Druckinkremente offenbar normal, zeigten aber bei mittleren Drucken anomales Verhalten. Mit dem Differentialtyp des Permeationsexperiments konnten die durch einen Konzentrationsgradienten zwischen den Filmoberflächen induzierten Spannungseffekte beseitigt werden. Unter Annahme der zeitabhängigen Erreichung der Gleichgewichts-Oberflächenkonzentration berechneten wir die Durchbruchzeit als Funktion der Filmdicke und wandten die Theorie auf die Permeationsdaten für Polyacrylamidfilme mit verschiedener Dicke bei verhältnismässig kleinen Druckintervallen an. Der aus Permeationsdaten berechnete Geschwindigkeitsparameter stand mit demjenigen aus Daten über sukzessive differentielle Absorption in guter Übereinstimmung.

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Influence of Intrachain Interactions on the Kinetics of Styrene Polymerization and Copolymerization

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Synopsis

In the free-radical polymerization of styrene, it has been observed that the onset of an acceleration of the polymerization due to increased solution viscosity can be quantitatively measured as occurring at a critical point. The product of the degree of polymerization of the polymer in solution at the critical point times its volume fraction can be represented by a temperature-dependent constant ($\bar{P}_n V_c = K$). The value of the constant passes through a maximum between 60 and 90°C. The value of the constant is somewhat lower than that for the phenomenon called chain entanglement. It is postulated that the temperature-dependent behavior of K is due to a previously reported solution phase transition which is believed to be caused by interaction between phenyl groups on the polystyrene chain. Observations on the ultraviolet absorbance of styrene copolymers and calculations on the absolute rate of copolymerization of styrene with methyl methacrylate are presented to support the postulated intrachain interactions.

INTRODUCTION

For many years it has been recognized that the increased viscosity during the free-radical polymerization of some vinyl monomers causes a decrease in the termination rate constant and thereby an apparent autoacceleration of the rate of polymerization. This phenomenon is usually called the Trommsdorff[1] or Norrish-Smith[2] effect, but it has been occasionally referred to as the onset of diffusion control of termination. The latter terminology has become imprecise in view of the careful definition of diffusion-controlled reactions by Benson and North[3] and the subsequent experimental studies.[4] The termination reaction in free-radical polymerization is at least partially diffusion-controlled, even in an environment of low viscosity. Therefore, the Trommsdorff effect must be regarded as a phenomenon which occurs because there has been a *change* in the conditions which produce diffusion control. The microscopic nature of this change has not been elucidated as yet.

In copolymerization, absolute reaction rate data have frequently been interpreted in terms of ϕ^5, a parameter purporting to measure the increased rate of termination due to a heightened interaction between a chain ending in monomer 1 and a chain ending in monomer 2 compared to reactions between two monomer 1 or two monomer 2 units. Usage of this concept has continued in spite of the evidence for diffusion control of the termination reaction which cannot permit an acceleration of an order of magnitude because of chemical effects. A paper by North has put the problem of diffusion control of copolymerization kinetics in perspective,[6] but a general way of describing termination rate constants in copolymerization has not yet been found.

Recent work on determination of sequence distributions and their prediction in copolymerization offers the possibility of rigorously defining the concentration distribution function for the segment of the copolymer chain involved in determining the rate of the diffusion controlled termination step. What is lacking is necessary knowledge with respect to the physics of intramolecular chain interactions in solution. Such interactions can be quite subtle as revealed by the recent discovery of a solution phase transition for polystyrene, both atactic and isotactic.[7,8]

In this paper we report some observations on the temperature dependence of the Trommsdorff effect in styrene polymerization which appear to be related to the solution phase transition. These observations are then coupled with data on the spectral properties of styrene–methyl methacrylate copolymers in an attempt to explain existing data[5] on the rate of copolymerization.

EXPERIMENTAL

Styrene monomer was purified and its rate of polymerization measured dilatometrically as previously described.[9] Copolymers of styrene and methyl methacrylate were also prepared and their ultraviolet absorbance determined in a manner similar to that described earlier,[10] the major exception being that a Beckman DK-1 spectrophotometer equipped with a temperature-controlled cell was used. All absorbancies measured were corrected for the volume change of the solvent upon heating.

Results

Figure 1 shows a typical plot of the logarithm of instantaneous rate of polymerization divided by monomer concentration versus time for free-radical polymerization of styrene initiated by an initiator such as benzoyl peroxide or azobisisobutyronitrile which decomposes according to first-order kinetics with negligible induced decomposition. For such an initiator, the deviation from linearity of plots such as Figure 1 has been taken in this and earlier work[9] to be a quantitative measure of the onset of the Trommsdorff effect. The time of this occurrence t_c can be related to the conversion of monomer to polymer and thereby the volume fraction of polymer V_c at that time can be calculated. This has been done for 60, 75, and 90°C. and the results plotted against the number-average degree of polymerization $\bar{P}_n$ in Figure 2. The value of $\bar{P}_n$ can be calculated from known kinetic

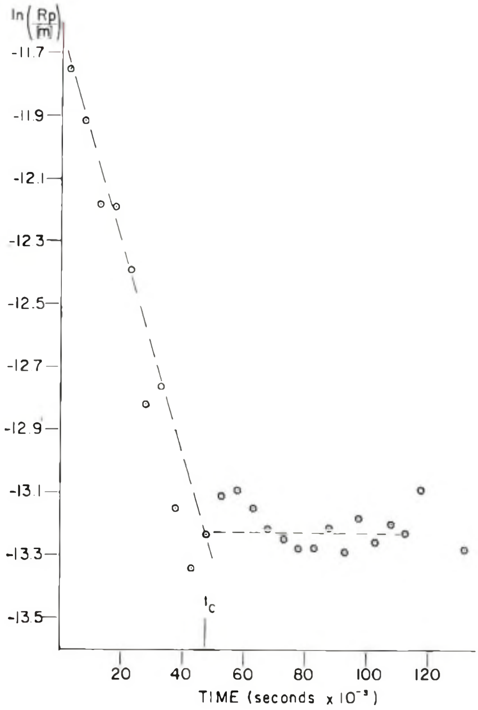

Fig. 1. Determination of the onset of the Trommsdorff effect, t_c. Bulk polymerization of styrene at 75°C. with [AIBN] = $4 \times 10^{-4}M$.

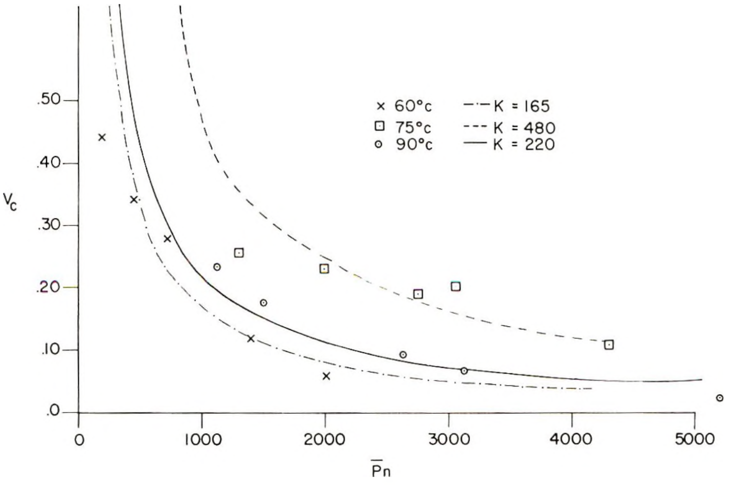

Fig. 2. Volume fraction of polystyrene at critical point vs. degree of polymerization: (×) 60°C.; (□) 75°C.; (○) 90°C.

constants of styrene by using the average value of R_p over the linear portion of plots such as Figure 1. The data in Figure 2 suggest a hyperbola and within the precision of the data fit the expression

$$V_c\bar{P}_n = K \tag{1}$$

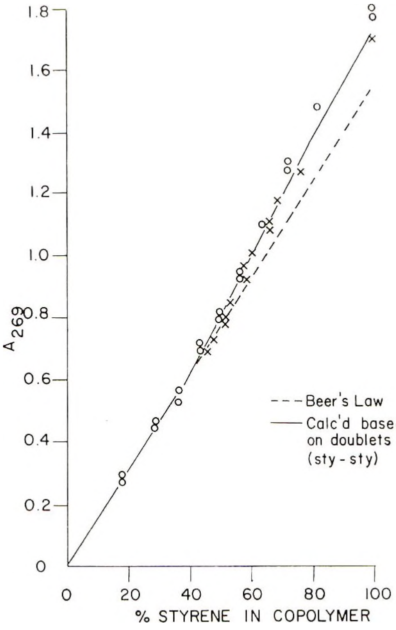

Fig. 3. Absorbance at 269 mμ of a 1 mg./ml. solution of styrene–methyl methacrylate copolymer in $CHCl_3$: (—) calculated; (O) data of O'Driscoll et al.;[10] (×) this work.

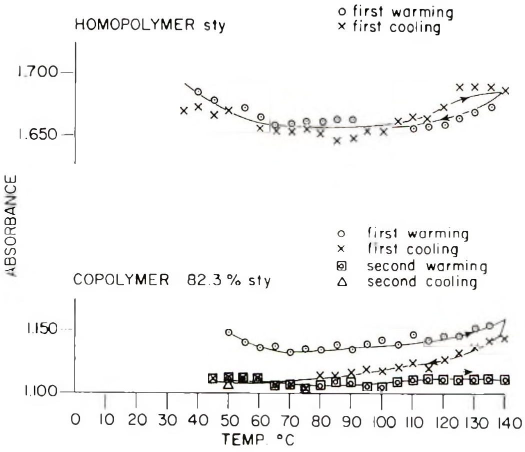

Fig. 4. Effect of temperature on the absorbance at 269 mμ for polystyrene homopolymer and copolymer solutions in decalin.

where K has the values 165, 480, and 220 at 60, 75, and 90°C., respectively.

Figure 3 shows the absorbance at 269 mμ of a 1 mg./ml. solution of styrene–methyl methacrylate copolymers in chloroform at 30°C. Figure 4 shows the absorbance at the same wavelength and concentration with the use of decalin as a solvent and on cycling the temperature between 40 and 140°C. Note that the homopolymer of styrene does not change its absorbance upon heating and cooling, but that the copolymer containing 82% styrene and 18% methyl methacrylate irreversibly (in the time scale of the experiment) loses some absorbance during the first heating cycle but none thereafter.

Discussion of Results

The concept of chain entanglement[11] has been invoked to explain discontinuities in the solution behavior of many polymers. The critical concentration at which the discontinuity occurs may perhaps be expressed by an equation of the form of eq. (1). The constant K for chain entanglements is somewhat larger than those we measure for the onset of the Trommsdorff effect. Therefore, at the present time we regard chain entanglement and the Trommsdorff effect as two separate phenomenological observations which happen to (approximately) obey the same equations. If one adopts a view of solution discontinuities such as that recently set forth by Cornet,[12] then perhaps the Trommsdorff effect can be regarded as a phenomenon which expresses crowding in the solution, and which shows itself sooner than do abrupt changes in solution viscosity.

Figure 5 compares the results of the kinetic measurements K of eq. (1), with the radius of gyration from the light-scattering results of Reiss and Benoit[7] on atactic polystyrene ($\bar{P}_n = 25 \times 10^3$) in decalin solution. It is obvious that the apparent collapse of the chain at about 75°C. is also influencing the free-radical termination process. Presuming that this transition might be due to interaction of the phenyl groups on adjacent monomer units, and therefore be noticed in the ultraviolet spectrum,[13,14] we have calculated the solid line in Figure 3. In the calculation of this line it was assumed that a styrene mer adjacent to another styrene mer had an absorption coefficient equal to that of homopolymer, while styrene mers isolated between methyl methacrylate mers would have an absorption coefficient given by the slope of the plot at low styrene content. Based on the reactivity ratios the sequence distribution is readily calculated. The agreement with the measurements supports the hypothesis strongly.

The temperature dependence of the absorbance of homopolymer may be interpreted as showing a small, reversible transition at about 70°C. also. However, the same treatment of a copolymer gives irreversible behavior. This is not thoroughly understood, but it might be due to a cooperative behavior which is possible in a homopolymer, but interrupted in a copolymer by the presence of methyl methacrylate between sequences of styrene mers.

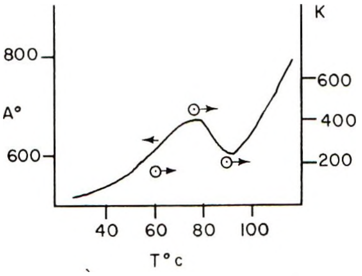

Fig. 5. Comparison of temperature effect on eq. (1) and Fig. 2 data with temperature effect on radius of gyration (solid curve) from light-scattering data of Reiss and Benoit.[7]

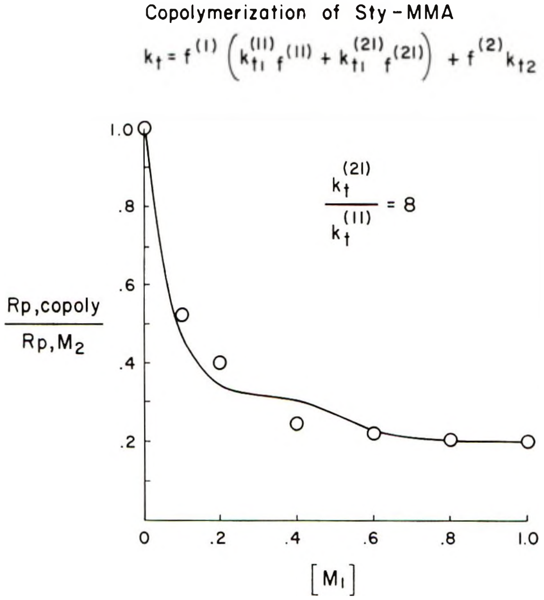

Fig. 6. Plot of expected effect of styrene on relative rate of copolymerization of styrene–methyl methacrylate at 60°C. by using eqs. (2)–(4) with $\alpha = 8$: Data of Walling.[5]

In copolymerization, North[4] has shown that, if the rate of termination is diffusion-controlled, then the rate of copolymerization is given by

$$\frac{-d([M_1] + [M_2])}{dt} = \frac{R_i^{1/2}(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)}{k_t^{1/2}\{(r_1[M_1]^2 k_{p1} + r_2[M_2]/k_{p2})\}} \tag{2}$$

where R_i is the rate of initiation, k_t is the composition-dependent termination rate constant and the other terms have their usual meaning. In the copolymerization of styrene (M_1) with methyl methacrylate (M_2) we postulate that the interaction between the phenyl rings on adjacent styrene units will tend to make the segmental motion slower because of hindered rotation about the chain axis. In the termination of a chain ending in $-M_1-M_1^*$ we further postulate that the rate constant of termination $k_t^{(1)}$ may therefore be slower than the rate constant $k_t^{(21)}$ for a unit $-M_2-M_1^*$; i.e.,

$$k_t^{(11)} = k_t^{(21)}\alpha \tag{3}$$

with $\alpha > 1$. The average k_t will then depend on the fraction of terminal diads, f_{11} or f_{21}, as well as the fraction of chains ending in M_1 or M_2, f_1 or f_2. This is given as:

$$k_t = f_1(k_t^{(11)}f_{11} + k_t^{(21)}f_{21}) + f_2k_t^{(2)} \tag{4}$$

where $k_t^{(11)}$ is taken to be the homopolymerization termination rate constant for styrene, $k_t^{(2)}$ is the homopolymerization termination rate constant for methyl methacrylate. The values of f_1, f_2 and f_{11} and f_{21} can be determined from reactivity ratios at given monomer feeds.

Equation (4) has been applied to existing data for a value of $\alpha = 8$. The results are shown in Figure (6), where, for comparison, the data of Walling[5] are also plotted. While the fit is imperfect, it is better than that obtainable with any single ϕ factor and perhaps suggests that effects larger than penultimate do exist in the termination step in copolymerization.

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Résumé

On a observé dans la polymérisation radicalaire du styrène, que le début de l'accélération de la polymérisation due à une augmentation de la viscosité de la solution peut être mesurée quantitativement et se présente à un point critique. Le produit du D.P. du polymère en solution à ce point critique multiplié par la fraction de volume peut être représenté par une constante dépendant de la température ($P_nV_c = K$). La valeur de la constante passe par un maximum entre 60 et 90°C. La valeur de la constante est quelque peu plus basse que celle observée pour le phénomène dénommé enlacement de chaîne. On admet que le comportement dépendant de la température de K est dû à une transition de phase en solution rapportée précédemment qui est causée par l'interaction entre les groupes phényles dans la chaîne polystyrénique. Des observations d'absorbance UV de copolymères styréniques et des calculs sur les vitesses absolues de copolymérisation du styrène avec le méthacrylate de méthyle sont présentés en vue de confirmer cette interaction intracaténaire postulée.

Zusammenfassung

Bei der radialischen Polymerisation von Styrol wurde beobachtet, dass das Einsetzen einer Polymerisationsbeschleunigung durch erhöhte Viskosität des Systems bei einem kritischen Punkt erfolgt und quantitativ gemessen werden kann. Das Produkt aus dem D.P. des Polymeren in Lösung beim kritischen Punkt und seinem Volumsbruchteil kann durch eine temperaturabhängige Konstante ($\bar{P}_n V_c = K$) dargestellt werden. Der Wert der Konstanten geht zwischen 60 und 90°C durch ein Maximum. Der Wert der Konstanten ist etwas niedriger als derjenige für die, Kettenverschlingung genannte, Erscheinung. Es wird angenommen, dass das Verhalten von K in Abhängigkeit von der Temperatur auf eine schon früher gefundene Phasenumwandlung in Lösung zurückzuführen ist, welche durch die Wechselwirkung zwischen Phenylgruppen an der Polystyrolkette verursacht zu sein scheint. Beobachtungen über die UV-Absorption von Styrolcopolymeren sowie Berechnungen der Absolutgeschwindigkeit der Copolymerisation von Styrol mit Methylmethacrylat werden zur Stütze der angenommenen Wechselwirkungen in den Ketten angeführt.

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Stereoregularity of Poly(methyl Acrylate)

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Synopsis

The stereoregularity of poly(methyl acrylate) and poly(methyl acrylate-α-d) was determined from the NMR spectra. A method of quantitative determination of stereoregularity of poly(methyl acrylate) proposed in this paper is based on the fact that in the 100 Mc./sec. NMR spectrum the absorption peaks due to methylene protons in syndiotactic configurations overlap absorptions due to only one of two methylene protons in isotactic configurations. The stereostructure of poly(methyl acrylates) polymerized with anionic catalysts such as Grignard reagents, n-butyllithium, and $LiAlH_4$ is generally richer in isotactic diads than in syndiotactic diads. For example, poly(methyl acrylate) polymerized with phenylmagnesium bromide as catalyst at -20°C. consists of 99% isotactic and 1% syndiotactic diads. In radical polymerization, the isotacticity of poly(methyl acrylate) is independent of polymerization temperature. Poly(methyl acrylates) polymerized with a Ziegler-Natta catalyst consisting of $Al(C_2H_5)_2Cl$ and VCl_4 have configurations similar to those polymerized by radical initiators. The stereoregularity of poly(methyl acrylate-α-d) resembled that of poly(methyl acrylate) polymerized under the same conditions.

INTRODUCTION

In the previous papers,[1-3] we reported on the preparation of poly(methyl acrylates) of different tacticities and qualitative measurement of their stereoregularity by NMR spectroscopy.

In this paper, a quantitative method for determining stereoregularity of poly(methyl acrylate) is proposed, based on the finding that in the 100 Mc./sec. NMR spectrum the absorption peaks due to methylene protons in syndiotactic configurations overlap absorptions due to only one of two methylene protons in isotactic configurations, while in the 60 Mc./sec. spectrum the absorption peaks due to syndiotactic methylene protons overlap absorption of both methylene protons in isotactic configurations. Polymerizations of methyl acrylate were carried out under various conditions in order to investigate effects of catalyst, temperature, and solvent on the stereoregularity of poly(methyl acrylate).

The stereoregularity of poly(methyl acrylate) determined by this method was compared with that of poly(methyl acrylate-α-d).

EXPERIMENTAL

Monomers

Methyl acrylate was purified by successive washing with dilute aqueous sodium hydroxide, water, dilute sulfuric acid, and water. After drying over calcium hydride or sodium sulfate, it was distilled *in vacuo* under nitrogen. Methyl acrylate-α-d was prepared by esterification of acrylic acid-α-d (obtained by hydrolysis of acrylonitrile-α-d in D_2O–D_2SO_4 with $FeSO_4 \cdot H_2O$ as a polymerization inhibitor) in a mixture of methanol and deuterium oxide. The yield of methyl acrylate-α-d based on the starting acrylonitrile-α-d was 14%. The deuterium content at the α-position of methyl acrylate-α-d was measured as 91% by means of a mass spectrometer.

Polymerization

Methyl acrylate was polymerized in 50% toluene solution by ultraviolet light of wavelength of 320–420 mμ or 400–600 mμ with benzoin (0.2–0.3 mole-% relative to monomer) as a photosensitizer at several temperatures from 0 to -90°C. A four-necked quartz or Pyrex glass flask, which was equipped with stirrer, thermometer, and nitrogen inlet and outlet, was the polymerization apparatus.

For polymerization by γ-radiation, methyl acrylate and methyl acrylate-α-d were sealed *in vacuo* in glass ampules together with solvent or in bulk, and were irradiated by γ-rays (ca. $10^4 \sim 10^5$ r./hr.) from a ^{60}Co source at various temperatures.

Polymerizations of methyl acrylate with phenylmagnesium bromide and *n*-butyllithium as catalysts were carried out in toluene at temperatures ranging from -20 to -78°C. under nitrogen with stirring. Phenylmagnesium bromide was prepared in diethyl ether, which was then removed by distillation after adding toluene to the solution. Since the content of ether in phenylmagnesium bromide solution in toluene was determined as 8.8 vol.-% by means of gas chromatography, the polymerization solution consisted of 3×10^{-3} mole phenylmagnesium bromide, 9×10^{-4} mole ether, 4.8 g. (5.6×10^{-2} mole) of the monomer, and 50 ml. of toluene. *n*-Butyllithium was prepared in *n*-hexane by reaction of lithium with *n*-butyl

TABLE I
Polymerization of Methyl Acrylate-α-d

PMA-α-d no.	Catalyst	Solvent	Temperature, °C.	Time, hr.	Yield, %
1	$LiAlH_4$	Toluene	-78	20	30
2	*n*-Butyllithium	Toluene + hexane(1:1)	-78	24	63
3	*n*-Butyllithium	Toluene + hexane(1.3:1)	-40	6	39
4	γ-Rays	Acetone	-78	6	12

TABLE II
Polymerization of Methyl Acrylate

PMA no.	Initiator	Solvent	Temperature, °C.	Time, hr.	Yield, %	[η], dl./g.
1	*n*-Butyllithium	Toluene	−20	3	1.1	—
2	*n*-Butyllithium	Toluene	−40	2	4.6	0.24
3	*n*-Butyllithium	Toluene	−78	21	17.8	0.25
4	Phenylmagnesium bromide	Toluene	−20	2	7.1	0.31
5	Phenylmagnesium bromide	Toluene	−78	3.5	30.0	0.52
6	$LiAlH_4$	Toluene	−78	19	28.0	—
7	Ultraviolet light	Toluene	0	1	35.9	—
8	Ultraviolet light	Toluene	−15	1.5	25.7	—
9	Ultraviolet light	Toluene	−55	2	22.1	0.67
10	Ultraviolet light	Toluene	−70	2.5	30.3	—
11	Ultraviolet light	Toluene	−90	4	4.2	0.31
12	γ-Rays	None	40	1.5	1.7	1.10
13	γ-Rays	None	24	4.2	1.9	—
14	γ-Rays	None	0	4.3	1.0	—
15	γ-Rays	None	−78	19.3	0.9	—
16	γ-Rays	Acetone	40	1.8	4.7	—
17	γ-Rays	Acetone	−40	5.4	30.8	1.22
18	$Al(C_2H_5)_2Cl–VCl_4$	Toluene	0	21	9.6	0.28
19	$Al(C_2H_5)_2Cl–VCl_4$	Toluene	−78	24	38.1	0.93
20	$Al(C_2H_5)_2Cl–VCl_4$–anisole	Toluene	−78	20	28.0	0.85

bromide. Polymerizations of methyl acrylate-α-*d* with *n*-butyllithium and $LiAlH_4$ as catalysts were conducted in glass ampules at low temperatures. Methyl acrylate also was polymerized with $LiAlH_4$ as catalyst under the same conditions.

Methyl acrylate was polymerized with diethylaluminum chloride–vanadium tetrachloride (5:1) complex and diethylaluminum chloride–vanadium tetrachloride–anisole (5:1:1) complex as catalysts in toluene at 0 and −78°C. in a nitrogen atmosphere.

All the polymers were purified by redissolving in acetone and reprecipitating with *n*-hexane.

Viscosities of poly(methyl acrylates) were measured on solutions in benzene at 25°C.

The results of polymerizations are shown in Tables I and II.

NMR Measurement

Poly(methyl acrylate) and poly(methyl acrylate-α-*d*) were dissolved in *o*-dichlorobenzene to give 5.5–7% solutions. NMR measurements were carried out at temperatures from 80 to 150°C. by means of a Japan Electron Optics Laboratory 100 Mc./sec. spectrometer.

RESULTS AND DISCUSSION

Stereoregularity of Poly(methyl Acrylate-α-d)

Stereoregularity can usually be determined by NMR spectra more easily in deuterated polymers than in nondeuterated polymers. Previously, we estimated that poly(methyl acrylate-*α-d*) derived from polyacrylonitrile-*α-d* consists of 53% isotactic and 47% syndiotactic diads.[3]

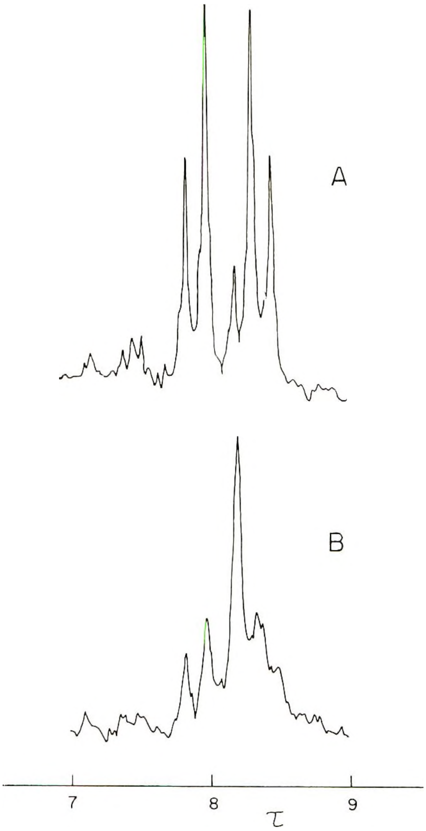

Fig. 1. NMR spectra (100 Mc.) of poly(methyl acrylate-*α-d*) polymerized (*A*) with $LiAlH_4$ catalyst at −78°C. and (*B*) by γ-rays at −78°C.

Now we have investigated the stereoregularity of poly(methyl acrylate-*α-d*) prepared directly from the monomer. Methyl acrylate-*α-d* was synthesized by esterification of acrylic acid-*α-d*, which was obtained by hydrolysis of acrylonitrile-*α-d* with D_2SO_4–D_2O.

In Figure 1, the 100 Mc./sec. NMR spectra of poly(methyl acrylate-*α-d*) (PMA-*α-d*) polymerized with $LiAlH_4$ as catalyst in toluene at −78°C. and by γ-radiation in acetone at −78°C. are shown. Backbone methylene protons in isotactic configurations give a quartet at 8.41, 8.27, 7.95, and 7.81 τ, while those in syndiotactic configurations give a singlet at

8.17 τ. Therefore, the ratio of the area under the quartet to that under the singlet will give the proportions of the two stereoregular diads.

The stereoregularity of PMA-α-d polymerized under various conditions given in Table III indicates that PMA-α-d polymerized with anionic catalysts is predominantly isotactic. In particular, PMA-α-d polymerized with $LiAlH_4$ catalyst is 93% isotactic diads. The polymers prepared with n-butyllithium catalyst had fewer isotactic diads than the one with $LiAlH_4$ catalyst. The reason may be the presence of hexane in the solvent, since poly(methyl acrylate) polymerized with n-butyllithium catalyst in toluene alone is very highly isotactic, as will be shown later. Poly(methyl acrylate-α-d) polymerized by γ-rays in acetone at −78°C. was 58% isotactic.

TABLE III
Stereoregularity of Poly(methyl Acrylate-α-d)

PMA-α-d no.	Polymerization conditions			Isotactic, %
	Catalyst	Solvent	Temperature, °C.	
1	$LiAlH_4$	Toluene	−78	93
2	n-Butyllithium	Toluene + hexane(1:1)	−78	71
3	n-Butyllithium	Toluene + hexane(1.3:1)	−40	80
4	γ-Rays	Acetone	−78	58

Stereoregularity of Poly(methyl Acrylate)

We have found that the stereoregularity of poly(methyl acrylate) can be determined from the 100 Mc./sec. NMR spectrum of the nondeuterated polymer. In Figure 2 are shown NMR spectra of isotactic poly(methyl acrylate) (PMA) prepared with phenylmagnesium bromide as catalyst in toluene at −20°C. and of PMA of random configuration prepared by γ-irradiation bulk at 40°C.

As is obvious from Figure 2*A*, methylene protons of isotactic PMA produce two quintets; one has peaks at 8.48, 8.41, 8.35, 8.27, and 8.22 τ and the other at 8.03, 7.96, 7.88, 7.82, and 7.75 τ. Backbone methine protons show a quintet centered at 7.43 τ. The analysis of the theoretical NMR spectrum[2,3] has shown that each of the methylene quintets corresponds to non-equivalent methylene protons and that they do not overlap each other. According to Yoshino et al.,[4] the absorption peaks ranging from 8.48 to 8.22 τ are due to isotactic methylene protons *trans* to carboxyl groups, and those from 8.03 to 7.75 τ are due to *gauche* conformations.

Figure 2*B* shows that a triplet at 8.23, 8.17, and 8.10 τ due to methylene protons in syndiotactic configurations overlaps only the quintet at high

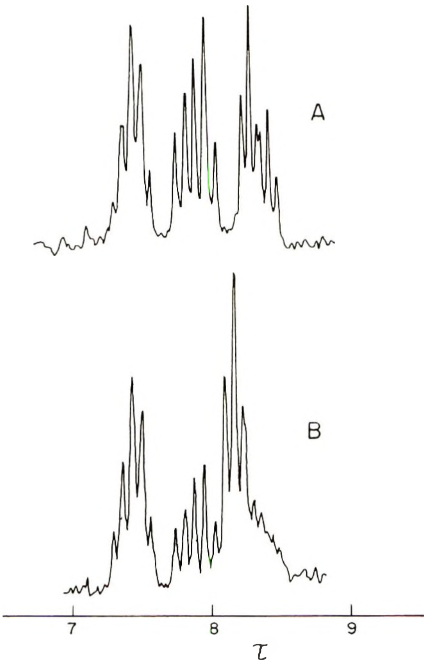

Fig. 2. NMR spectra (100 Mc.) of poly(methyl acrylates) polymerized (*A*) with phenylmagnesium bromide catalyst in toluene at −20°C. (isotactic configuration) and (*B*) by γ-rays in bulk at 40°C. (random configuration).

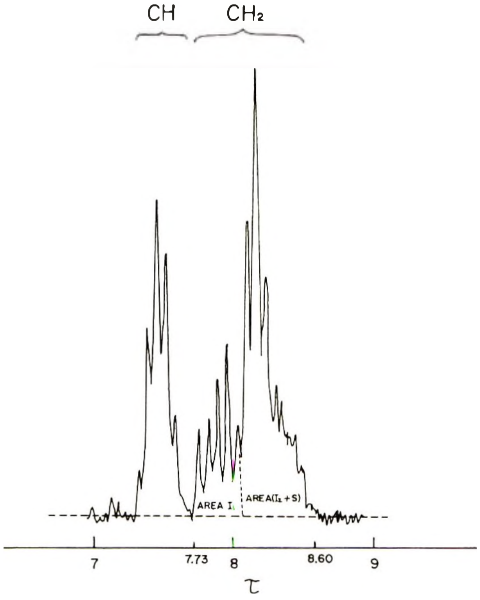

Fig. 3. Illustration of a determination of the stereoregularity of poly(methyl acrylate) from the 100 Mc. NMR spectrum.

magnetic field. Therefore, the area under the quintet ranging from 8.03 to 7.75 τ corresponds to half the area due to isotactic methylene protons.

The content of isotactic diads can be calculated from the equation:

$$\text{Isotacticity } (\%) = \frac{2 \times \text{Area } I_1}{\text{Area } I_1 + \text{Area } (I_2 + S)} \times 100$$

where Area I_1 and Area$(I_2 + S)$ are the areas due to half the isotactic methylene protons and to the other half of the isotactic methylene protons plus that due to the syndiotactic methylene protons, respectively, as shown in Figure 3.

The accuracy of this method was estimated as ±3% by carrying out NMR measurements several times on the same polymer sample.

No information on stereoregularity has been obtained from the methine proton spectrum.

Anionic Polymerization

In Table IV, the stereoregularity of PMA prepared with anionic catalysts is shown. In order to compare the stereoregularity determined by this method with that of the deuterated polymer, PMA No. 6 was polymerized with $LiAlH_4$ as catalyst under the same conditions as PMA-α-*d* No. 1 shown in Table III. The former contains 96% isotactic diads, while the latter is found to contain 93% isotactic diads. These values agree within experimental error. This shows that the determination of stereoregularity by means of the 100 Mc. spectrum is satisfactory. Yoshino et al.[5] observed tetrad signals for PMA, and Doskočilová et al.[6] also suggested their presence from the investigation of model compounds. Splitting of the signals in Figure 1*B* may be due to tetrad structures, but the effect, if any, on our determination would be slight.

TABLE IV
Stereoregularity of Poly(methyl Acrylates) Polymerized with Anionic Catalysts

PMA no.	Polymerization conditions: Catalyst	Solvent	Temperature, °C.	Isotactic, %
1	*n*-Butyllithium	Toluene	−20	98
2	*n*-Butyllithium	Toluene	−40	97
3	*n*-Butyllithium	Toluene	−78	97
4	Phenylmagnesium bromide	Toluene	−20	99
5	Phenylmagnesium bromide	Toluene	−78	69
6	$LiAlH_4$	Toluene	−78	96

When *n*-butyllithium was used as catalyst, the isotactic content was 97–98% and independent of polymerization temperature. When phenylmagnesium bromide is the catalyst, PMA polymerized at −20°C. consists of 99% isotactic diads, and the isotacticity decrease to 69% for polymerization at −78°C. This effect is probably attributable to solvation by a small amount of ether in the solution of phenylmagnesium bromide in toluene, since solvation can be expected to increase at lower temperature, thus hindering strong coordination between a growing polymer anion and a counterion.

Radical Polymerization

The stereoregularity of poly(methyl acrylates) polymerized by ultraviolet light in toluene and by γ-rays in bulk and in acetone is shown in Table V.

TABLE V
Stereoregularity of Poly(methyl Acrylates) Polymerized with Radical Initiators

PMA no.	Polymerization conditions			Isotactic, %
	Initiator	Solvent	Temperature, °C.	
7	Ultraviolet light	Toluene	0	53
8	Ultraviolet light	Toluene	−15	49
9	Ultraviolet light	Toluene	−55	56
10	Ultraviolet light	Toluene	−70	54
11	Ultraviolet light	Toluene	−90	51
12	γ-Rays	None	40	53
13	γ-Rays	None	24	53
14	γ-Rays	None	0	51
15	γ-Rays	None	−78	52
16	γ-Rays	Acetone	40	52
17	γ-Rays	Acetone	−40	53

It is indicated that the stereostructure of all the polymers consists of 49–56% isotactic diads; that is, the configuration is random and independent of polymerization temperature and solvent.

Enthalpy and entropy differences between syndiotactic and isotactic additions for PMA polymerized by a radical mechanism were calculated according to Fordham[7] to give the following values: $\Delta H^* = \Delta H_s^* - \Delta H_i^* = 0$ cal./mole. $\Delta S^* = \Delta S_s^* - \Delta S_i^* = -0.20$ e.u.

The tendency for the isotacticity of poly(methyl acrylate) prepared by radical polymerization to be independent of polymerization temperature is in contrast with the case for poly(methyl methacrylate), for which isotacticity decreases with decreasing temperature of radical polymerization, reaching a small value at very low temperature. For other polymethacrylates,[8] the temperature dependence of stereoregularity was found to be similar to that for poly(methyl methacrylate). Poly(vinyl chloride)[9,10] also exhibits decreasing isotacticity with decreasing polymerization temperature, though the effect is not large. Enthalpy and entropy differences between syndiotactic and isotactic additions for the polymers so far studied are shown in Table VI.

TABLE VI
Enthalpy and Entropy Differences Between Syndiotactic and Isotactic Additions for Polymethacrylates and Poly(vinyl Chloride)

Polymer	ΔH^* ($= \Delta H_s^* - \Delta H_i^*$), kcal./mole	ΔS^* ($= \Delta S_s^* - \Delta S_i^*$), e.u.
Poly(methyl methacrylate)[a]	−0.775	0
Poly(methylbenzyl methacrylate)[b]	−0.81	−0.41
Poly(cyclohexyl methacrylate)[b]	−0.31	1.12
Poly(vinyl chloride)[c]	−0.31	−0.6

[a] Data of Bovey.[11]
[b] Data of Matsuzaki et al.[8]
[c] Data of Bovey et al.[10]

Comparing the stereoregularity of poly(methyl acrylate) and of polymethacrylates formed by the radical mechanism, we conclude that *(1)* in poly(methyl acrylate), since no α-methyl groups are present, the effect of methyl ester groups alone is insufficient to give a highly stereoregular polymer and *(2)* in polymethacrylates, α-methyl groups have a greater effect on the stereoregularity than ester groups and lead to a predominance of syndiotactic diads. However, the effects of higher alkyl ester groups on the stereoregularity of polyacrylates are not yet known.

Polymerization with Ziegler-Natta Catalysts

The stereoregularity of poly(methyl acrylate) prepared with Ziegler-Natta catalysts is shown in Table VII. It is noted that the PMA obtained has almost the same configuration as PMA polymerized by ultraviolet light and γ-rays, that is, random configuration. On the other hand, the $Al(C_2H_5)_2Cl-VCl_4$-anisole catalyst system was used by Natta et al.[12] to prepare syndiotactic polypropylene, and Abe et al.[13] obtained syndiotactic polymethyl methacrylate by polymerization with Ziegler-Natta catalyst. Although the polymerization mechanism of methyl acrylate by the Ziegler-Natta catalysts used is not yet understood, it may be deduced from the stereoregularity of the product that the polymerization proceeds either by a free ion or radical mechanism.

TABLE VII
Stereoregularity of Poly(methyl Acrylates) Polymerized with Ziegler-Natta Catalysts in Toluene

	Polymerization conditions		
PMA no.	Catalyst	Temperature, °C.	Isotactic, %
18	$Al(C_2H_5)_2Cl-VCl_4$	0	53
19	$Al(C_2H_5)_2Cl-VCl_4$	−78	59
20	$Al(C_2H_5)_2Cl-VCl_4$-anisole	−78	58

It has been found that poly(ethyl acrylate) also gives a backbone proton spectrum similar to that of poly(methyl acrylate). An account will be published in the near future.

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Résumé

La stéréorégularité du polyacrylate de méthyle et du polyacrylate-α-d- de méthyle a été déterminée au départ de spectres NMR. Une méthode de détermination quantitative de la stéréorégularité du polyacrylate de méthyle proposée dans ce manuscrit est basée sur le fait que à 100 Mc, le spectre NMR des pics d'absorption dûs aux protons méthyléniques dans des configurations syndiotactiques de superpose aux absorptions dues uniquement à l'un des protons méthyléniques de la configuration isotactique. La structure stéréochimique du polyacrylate de méthyle polymérisé au moyen de catalyseurs anioniques tels que les réactifs de Grignard, le n-butyllithium et le $LiAlH_4$ est généralement plus riche en diades isotactiques que en diades syndiotactiques. Par exemple, le polyacrylate de méthyle, polymérisé avec le bromure de phénylmagnésium comme catalyseur à -20°C consiste pour 99% de diades isotactiques. Dans la polymérisation radicalaire, l'isotacticité du polyacrylate de méthyle est indépendante de la température de polymérisation. Le polyacrylate de méthyle polymérisé avec un catalyseur Ziegler-Natta constitué de $Al(C_2H_5)_2Cl$ et de VCl_4 ont des configurations semblables à celles polymérisées en présences de radicaux initiateurs radicalaires. La stéréorégularité du polyacrylate de méthyle-α-d ressemble à celle du polyacrylate de méthyle polymérisé dans les mêmes conditions.

Zusammenfassung

Die Stereoregularität von Polymethylacrylat und Polymethylacrylat-α-d wurde aus den NMR-Spektren bestimmt. Die in dieser Arbeit vorgeschlagene Methode zur quantitativen Bestimmung der Stereoregularität von Polymethylacrylat beruht auf der Tatsache, dass im 100 MHz-NMR-Spektrum die Absorptionsmaxima der Methylenprotonen in syndiotaktischen Konfigurationen sich mit Absorptionen nur eines der beiden Methylenprotonen in isotaktischen Konfiguration überlappen. Die Stereostruk-

tur des mit anionischen Katalysatoren wie Grignard-Reagentien, *n*-Butyllithium und $LiAlH_4$ erhaltenen Polymethylacrylates ist im allgemeinen reicher an isotaktischen Diaden als an syndiotaktischen. So besteht z.B. das mit Phenylmagnesiumbromid als Katalysator bei −20°C erhaltene Polymethylacrylat zu 99% aus isotaktischen Diaden. Bei der radikalischen Polymerisation ist die Isotaktizität des Polymethylacrylates unabhängig von der Polymerisationstemperatur. Mit Ziegler-Natta-Katalysatoren aus $Al(C_2H_5)_2Cl$ und VCl_4 gebildetes Polymethylacrylat besitzt eine ähnliche Konfiguration wie das mit Radikalstartern erhaltene. Die Stereoregularität von Polymethylacrylat-α-*d* entsprach derjenigen des unter gleichen Bedingungen gebildeten Polymethylacrylates.

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Polyethers. I. Polymerization of 2-Methyl-2-butene Oxide

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Synopsis

2-Methyl-2-butene oxide (2,3-epoxy-2-methylbutane) was polymerized with modified alkylaluminum initiators at low temperatures to a high-melting, crystalline, film-forming polymer. High yields and comparatively high molecular weights were obtained with $Al(i\text{-}Bu)_3$–xH_2O initiators in inert diluents. When such initiators were modified with acetylacetone they became ineffective. Ammonia could be substituted for water in formulating an active initiator. Attempts to prepare an active initiator in the presence of the monomer were unsuccessful indicating competition with the water for $Al(i\text{-}Bu)_3$. Thermal decomposition of the polymer produced methyl isopropyl ketone with some pivaldehyde.

INTRODUCTION

The polymerization of oxiranes with a variety of initiators has received considerable attention.[1,2] Among these initiators were the systems based on organometallic compounds.[3] Propylene oxide, as an example, was polymerized to high molecular weight by the diethylzinc–water[4,5] and by the trimethylaluminum–water[6] systems. The use of modified trialkylaluminum systems to polymerize 1,2-disubstituted ethylene oxides was demonstrated for the 2-butene epoxides.[7,8] It was of interest to evaluate the application of these initiators to the polymerization of a trisubstituted ethylene oxide. This paper is concerned with the polymerization of 2-methyl-2-butene oxide[9] (2,3-epoxy-2-methylbutane) and with a description of the resulting film-forming polymer. Previous studies had led only to low molecular weight oil.[9]

EXPERIMENTAL

2-Methyl-2-butene Oxide

The oxide was prepared from 2-methyl-2-butene via the bromohydrin.[10] Equimolar quantities of *N*-bromosuccinimide and olefin were reacted in water slurry at 18–22°C. by dropwise addition of olefin. Bromohydrin separated as a lower layer and was dehydrohalogenated with 20% aqueous

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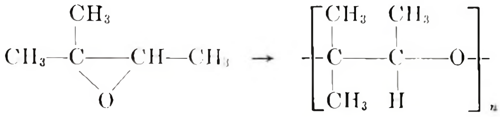

NaOH at 90°C. The epoxide was distilled from CaH_2 and rectified in a spinning band column to yield monomer boiling at 74.3°C. 760 mm.; n_D^{20} 1.3846; 86%.

Polymerization

Polymerizations were usually carried out in Pyrex glass reactors of 100 ml. capacity equipped with a stirrer and serum-stoppered inlet and exit ports. Additions were made by hypodermic syringe, and the reactors were maintained under a slightly positive nitrogen pressure. Initiator solutions were made externally to the reactor unless otherwise noted. Typically, distilled water was syringed dropwise into 1*M* solutions of $Al(i\text{-}Bu)_3$ in *n*-heptane or CH_2Cl_2 at 0°C. held in a serum-stoppered bottle containing a magnetic stirring bar and blanketed with N_2. The resulting solutions were employed after aging at room temperature for 1–24 hr. The 2-methyl-2-butene oxide, 5 ml., and dry solvent was charged to the reactor and cooled in a Dry Ice–acetone bath under a N_2 atmosphere. The initiator solution was syringed in rapidly while the system was vigorously agitated. After a given time a small amount of CH_3OH was added to terminate the polymerization and the polymer was isolated after digestion in acidified excess CH_3OH. In Table I are tabulated typical results of polymerization runs.

RESULTS AND DISCUSSION

Polymerization of 2-Methyl-2-butene Oxide

A variety of initiators was screened in attempts to prepare high molecular weight polymers. Those to be discussed have been tabulated in Table I. Classical cationic initiators, typified by BF_3, yielded products with inherent viscosities below 0.20, which in some instances took the form of viscous oils. Trialkylaluminum compounds, shown to be effective for the polymerization to high molecular weight of some alicyclic oxiranes,[11] yielded polymers with higher inherent viscosities, but conversions were not high even at high organometallic levels. The more acidic dialkyl- and monoalkylaluminum halides afforded products of lower molecular weight. Dialkylzinc systems, reported to be highly effective toward propylene oxide,[4] did not lead to methanol-insoluble polymers (expt. 4, Table I).

Triisobutylaluminum modified with either water[7,8] or ammonia proved to be most effective. Methylene chloride and *n*-heptane were the most suitable of the diluents screened. At Dry Ice–acetone temperatures polymer precipitated as a swollen gel in the former but remained in solution in the latter. Heptane led to more rapid rates of polymerization and methylene chloride to higher molecular weights. Blends of diluents led to intermediate results (expts. 9, 11, Table I). Under optimum conditions with methylene chloride as diluent, high yields of polymer of inherent viscosity of about 0.6 could be obtained (expts. 8, 12, Table I). Temperatures higher than −78°C. resulted in lowered molecular weights and reduced conversions (expt. 6, Table I). The technique of dropwise addition of initiator to a solution of the monomer, or its reverse sequence, proved to be as effective as batch addition of initiator when the latter was carried out with due regard for heat transfer (expt. 13, Table I).

Experimentally it was found desirable and indeed necessary to prepare the initiator in the absence of the monomer. *In situ* formulations by addition of "wet" 2-methyl-2-butene oxide to a solution of triisobutylaluminum at Dry Ice–acetone temperatures, or the reverse, led to no polymerization. The latter system remained homogeneous in methylene chloride for periods up to a tested 24-hr. reaction time, and rapid deposition of polymer resulted only when catalyst formulated outside of the polymerization zone was added to the latter. An active catalyst could be obtained when water was added to solution of triisobutylaluminum at Dry Ice–acetone temperatures, providing evidence for the availability of water under these conditions. The aforementioned inhibition was shown by NMR to be due to complexation of the trialkylaluminum by the monomer which effectively blocked the initiator forming reaction at the low temperature.

The preferred initiator was easily prepared by reaction of water with triisobutylaluminum[7] in heptane or in methylene chloride diluent at ice-water temperatures. When ammonia was employed, the most desirable initiator was obtained after aging for periods up to 25 hr. Further reaction of the water-modified alkylaluminum initiator with chelating agents,[7] such as acetylacetone, (expt. 14, Table I) led to inhibition under the experimental conditions. Reduced activity was also found when a number of complexing

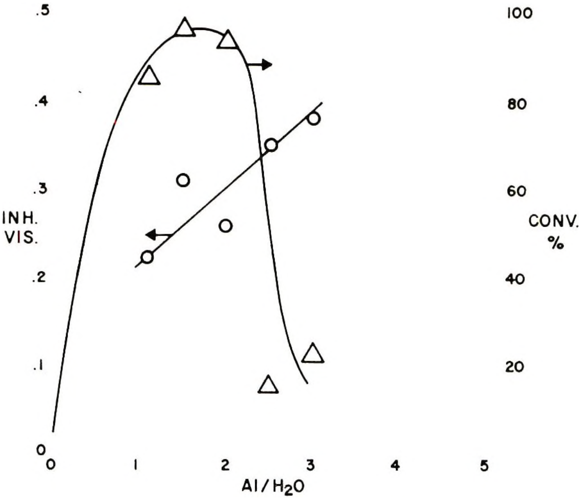

Fig. 1. Al(i-Bu)$_3$·αH$_2$O initiator; monomer/Al = 25 (m/m); monomer/heptane = 0.17 (v/v); temp. −78°C.; time 2.5–3.8 hr.; see Expt. 5, Table I.

TABLE I
Polymerization of 2-Methyl-2-butene Oxide

Expt.	Initiator[a]	Molar ratio monomer/initiator	Diluent	Volume ratio monomer/diluent	Temp., °C.	Time, hr.	Yield, %	Inherent viscosity[b]
1	BF_3		CH_2Cl_2	0.5	−78	0.1	12.5	0.19
2	$Al(i\text{-}Bu)_3$	10	C_7H_{16}	0.25	−78	22	59	0.35
	"	25	"	"	"	2.5	26.5	0.32
	"	50	"	"	"	"	10.5	0.34
3	Et_2AlCl	50	CH_2Cl_2	0.17	−78	1	14.4	0.13
	$Et_2AlCl/\cdot 5W$	50	"	"	"	"	5.6	0.21
	$Et_3Al_2Cl_3$	25	"	"	"	"	56	0.11
	$Et_3Al_2Cl_3\cdot 6W$	25	"	"	"	"	71	0.12
4	$Et_2Zn/\cdot 5W$	50	CH_2Cl_2	0.17	−78	2.6	0	—
	$Et_2Zn/\cdot 25W$	50	"	"	"	"	"	—
5	A·33W	25	C_7H_{16}	0.17	−78	3.8	22.2	0.38
	A·4W	25	"	"	"	3.8	15	0.37
	A·5W	25	"	"	"	2.5	92.5	0.26
	A·67W	25	"	"	"	3.5	96.5	0.31
	A·9W	25	"	"	"	3.5	86	0.22
	A·5W	100	C_7H_{16}	0.17	−78	3.5	58	0.37
	A·67W	100	"	"	"	3.5	86	0.30
	A·9W	100	"	"	"	3.5	71	0.35
6	A·5W	100	C_7H_{16}	0.17	0	5	37	0.11
	A·67W	100	"	"	"	5	42	0.11
7	A·33W	100	CH_2Cl_2	0.33	−78	3.8	Trace	—
	A·4W	100	"	"	"	3.8	Trace	—
	A·5W	100	"	"	"	3.8	25.2	0.48
	A·67W	100	"	"	"	3.8	23.9	0.37
	A·9W	100	"	"	"	3.8	4.3	0.40

8	A·5W	100	CH_2Cl_2	0.17	−78	2	27	0.55
	"	50	"	"	"	2	87	0.47
	"	25	"	"	"	2	89	0.52
9	A·5W	100	∞[c]	0.25	−78	5.8	84	0.24
	"	100	20	"	"	5.8	65	0.36
	"	100	3	"	"	5.8	25	0.42
	"	100	1	"	"	5.8	5	0.45
10	A·5W	100	C_7H_{16}	0.17	−78	3.3	58	0.37
	"	100	"	0.25	"	3.3	83.5	0.24
	"	100	"	0.50	"	3.3	78	0.20
	"	100	"	∞	"	3.3	27.5	0.10
11	A·5W	48	0.64[c]	0.17	−78	24	56	0.40
	"	24	"	"	"	24	82	0.33
	"	12	"	"	"	24	94	0.30
	"	6	"	"	"	24	89	0.21
	"	3	"	"	"	24	64	0.11
12	A·33N	25	CH_2Cl_2	0.17	−78	18	50	0.56
	A·33N	13	"	"	"	24	72	0.60
	A·5N	50	"	"	"	18	79	0.61
	A·5N	50	C_7H_{16}	"	"	18	91	0.49
	A·5CH_3NH_2	50	CH_2Cl_2	"	"	18	43	0.48
13	A·5W	50	CH_2Cl_2	0.17	−78	24	92	0.44
	A·5W[d]	50	"	"	"	24	91	0.45
14	A·5W·5AcAc[e]	25	C_7H_{16}	0.25	−78	5	0	—
	"	25	CH_2Cl_2	"	"	5	0	—

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[a] A·xW = Al(i-Bu)·$x$$H_2O$ (when $x = 33$, H_2O is $^1/_3$ of AlR_3 on a molar basis); A·xN = Al(i-Bu)$_3$·$x$$NH_3$.

[b] Inherent viscosity of 0.5% solution in benzene at 30°C.

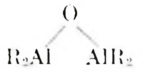
[c] Mixed diluent, heptane/CH_2Cl_2 = number given (v/v).

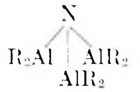
[d] Inverse dropwise addition of monomer to initiator solution.

[e] A·5W·5AcAc = Al(i-Bu)$_3$·0.5H_2O·0.5 acetylacetone on a molar basis.

agents, notably pyridine and tetrahydrofuran, added to change the possible heterogeneity of catalyst sites[12] were used. Inexplicably, thiophene appeared to have exerted only a small effect on conversion and inherent viscosity.

Conversion to methanol-insoluble polymer was maximized at triisobutylaluminum: water ratios greater than 1[2] in either methylene chloride or heptane (expts. 5, 7, Table I and Fig. 1). The value of the optimum ratios are in the region of 2, assuming reaction only between water and triisobutylaluminum, and 3 in the case of reaction with ammonia to give species of the types:





These reactions, however, may be quite complex[12] and a mixture of products, some of which are associated in solution[13] may have formed. A decrease in the triisobutylaluminum:water ratio corresponded with a decrease in molecular weight of the polymer as evidenced by the positive slope of the inherent viscosity curve in Figure 1. This may be ascribed to the proposed greater acid strength of the products formed at low Al/H_2O ratios,[14] since it was shown that classical cationic initiation resulted in lower degrees of polymerization.

The mechanism of this polymerization is not unequivocally established. It would appear to be a coordinate type of initiation with a large cationic contribution.[7,15,16] The latter is indicated by our observation of higher molecular weight in methylene chloride, the inverse temperature effect and an inverse monomer concentration–molecular weight effect (expt. 10, Table I). This is reminiscent of the inverse monomer concentration–

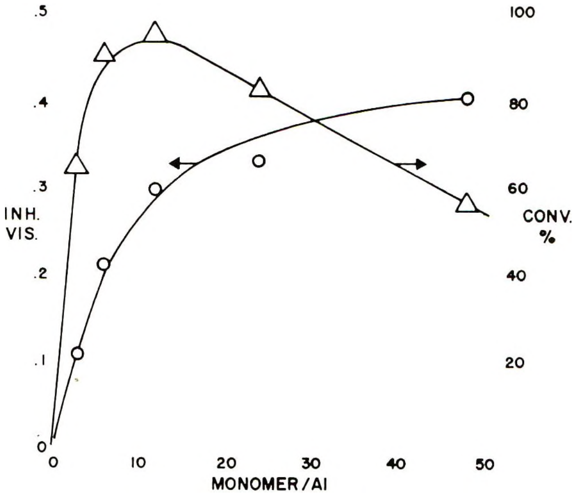


Fig. 2. Al(i-Bu)$_3\cdot$5H_2O initiator; heptane/CH_2Cl_2 = 0.67 (v/v); monomer/solvent = 0.17 (v/v); temp. −78°C.; time 24 hr.; Expt. 11, Table I.

molecular weight relationship observed by Kennedy[17] in his studies of the low-temperature cationic polymerization of isobutene. The mechanism is further complicated by a marked inverse dependence on initiator concentration (expt. 11, Table I, and Fig. 2). This strongly implies bimolecular termination reactions involving two growing chains or one growing chain and an initiator moiety.

Poly(2-methyl-2-butene Oxide)

The formation of methanol-insoluble polymers analyzing as high as 0.5–0.6 inherent viscosity with initiators of the type $AlR_3/0.5–0.7\ H_2O$ and $AlR_3/0.3–0.5\ NH_3$ was in sharp contrast to the previously reported polymerization of 2-methyl-2-butene oxide to low molecular weight oils.[9] Poly(2-methyl-2-butene oxide), a colorless solid, exhibited a melting range of 180–196°C. on a differential scanning calorimeter. Mechanical properties of material of 0.58 inherent viscosity (0.5% in benzene at 30°C.) included a tensile strength of 1700 psi, an elongation of 1.5%, an initial modulus of 116,000 psi, and a tensile yield of 1300 psi obtained at a 0.1 in./min. Instron extension rate on a 1-in. molded specimen.

Using powder diagram techniques, the polymers exhibited x-ray crystallinity with *d* spacings of 6.3, 5.9, and 5.5 A. A partially oriented film demonstrated two low-intensity layer lines with spacings at 3.5 and 7.0 A. This is reminiscent of data for poly(propylene oxide) and indicates a planar zigzag structure. NMR analysis was consistent with the expected structure except in fine detail. Spin-spin decoupling of methinyl hydrogen from adjoining methyl hydrogens suggested that equal quantities of two structures were present. The NMR procedures, analysis of the data, and interpretation of the result will be published separately.[18]

The polymer was subjected to destructive distillation. This was essentially complete at 300°C. and produced mainly methyl isopropyl ketone along with some pivaldehyde. When a sample of 0.41 inherent viscosity was thermally degraded about 20%, its inherent viscosity reduced to 0.26, indicating something more complicated than a simple unzipping.

Pivaldehyde was deliberately added back to the polymerization reaction as a check for possible causes for difficulties in raising molecular weight. It was found to act as a chain transfer agent at levels up to 5%. Incorporation of 25% pivaldehyde completely inhibited the polymerization of 2-methyl-2-butene oxide.

Poly(2-methyl-2-butene oxide) was cast and molded into films which were somewhat brittle. This was reduced by plasticization with a variety of materials, and samples of clear, flexible film were readily obtained.

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Résumé

L'oxyde de 2-méthyle-2-butène (2,3-époxy-2-méthylbutane) a été polymérisé avec des initiateurs à base d'alcoylaluminium modifié à basse température en vue d'obtenir un polymère filmogène cristallin, de point de fusion élevé. Des rendements élevés et des poids moléculaires comparativement élevés ont été obtenus avec un initiateur $Al(i\text{-}Bu)_3$–xH_2O dans des solvants inertes. Quand de tels initiateurs sont modifiés avec l'acétylacétone ils deviennent inefficaces. L'ammoniaque peut être substitué à l'eau en vue de la préparation d'un initiateur actif. Des essais de préparation d'un initiateur actif en présence de monomères ont été sans succès, ce qui était une compétition avec l'eau pour $Al(i\text{-}Bu)_3$. La décomposition thermique du polymère produisait de la acétone méthyle isopropylique avec une certaine quantité d'aldéhyde pivalique.

Zusammenfassung

2-Methyl-2-butenoxyd (2,3-Epoxy-2-methylbutan) wurde mit modifizierten Alkylaluminiuminitiatoren bei niedrigen Temperaturen zu einem hochschmelzenden, kristallinen, filmbildenden Polymeren polymerisiert. Mit $Al(i\text{-}Bu)_3$–xH_2O Initiatoren in inerten Lösungsmitteln wurden hohe Ausbeuten und verhältnismässig hohe Molekulargewichte erhalten. Durch Modifizierung mit Acetylaceton wurden solche Initiatoren unwirksam. Im Rezept eines aktiven Initiators konnte Wasser durch Ammoniak ersetzt werden. Versuche, einen aktiven Initiator in Gegenwart des Monomeren herzustellen, blieben ohne Erfolg, was für eine Kompetition mit dem Wasser um das $Al(i\text{-}Bu)_3$ spricht. Thermische Zersetzung des Polymeren führte zu Methylisopropylketon mit etwas Pivaldehyd.

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NOTES

Crystalline Poly-p-tert-*butylstyrene*

INTRODUCTION

Early studies by Natta[1] on the stereospecific polymerization of substituted styrenes indicated that *p*-alkyl- or aryl-substituted styrene gave amorphous noncrystallizable polymers. This work, however, did not include *p-tert* butylstyrene. More recently, Overberger[2] and co-workers have investigated the copolymerization of styrene and *p-tert*-butylstyrene and reported that a homopolymer of *p-tert*-butylstyrene showed low crystallinity after annealing at 200°C. A crystalline polymer of *p*-trimethylsilylstyrene having a melting point of 284°C. has been obtained by suitable heat treatment of the isotactic polymer obtained from a Ziegler-Natta polymerization.[3] Thus, it appears that certain isotactic polymers of *p*-alkyl-substituted styrene can crystallize.

In this laboratory crystallizable polymers of *p-tert*-butylstyrene have been prepared further to substantiate the above latter observations. These polymers exhibit a rather rapid crystallization rate under suitable thermal conditions. The polymerization, characterization, and crystallization of this polymer are described in the present article.

RESULTS AND DISCUSSION

Polymerization

Polymerization of *p-tert*-butylstyrene (95% *para* isomer) was carried out under nitrogen atmosphere with dry, redistilled monomer and solvent and with a Ziegler-Natta type catalyst. After a polymerization time of 6 hr. at 90°C., the catalyst was deactivated with isopropyl alcohol and the polymer filtered and washed with methanol. The results of the polymerizations are shown in Table I. With the $Al(Et)_3$–$TiCl_4$ catalyst, the maximum conversion was obtained at a Al/Ti ratio of about 3/1. A 1/1 ratio gave low molecular weight atactic polymer.

TABLE I
Polymerization of *p-tert*-Butylstyrene[a]

Catalyst	Al/Ti ratio	Conversion, %	$[\eta]$[b]	Crystalline m.p., °C.[c]
$AlEt_3$–$TiCl_4$	1/1	55	0.08	Amorphous
$AlEt_3$–$TiCl_4$	2/1	45	0.72	295
$AlEt_3$–$TiCl_4$	3/1	63	0.82	290
$AlEt_3$–$TiCl_4$	4/1	18	1.41	295
$AlEt_3$–VCl_3	1/1	48	0.77	300
$AlEt_3$–$TiCl_3$	1/1	17	0.67	300

[a] Polymerization was carried out with 50 ml. of monomer in 100 ml. of *n*-heptane at 90°C. for 6 hr., catalyst concentration, 15 mmole.

[b] Intrinsic viscosity in benzene at 25°C.

[c] Crystalline melting point observed under crossed polaroids in a hot stage microscope.

When VCl_3 or $TiCl_3$ was used with triethylaluminum at a 1/1 Al/metal ratio, crystallizable polymers were also obtained. The VCl_3 was more active than the $TiCl_3$ in this system. The 1/1 ratio was used based on other studies with styrene monomer which indicated this to be the optimum catalyst ratio.

Polymer Characterization

The polymer is amorphous when recovered from the polymerization and is soluble in benzene; therefore viscosity measurements were made in this solvent to obtain information on the relative molecular weight of the polymers prepared with the various catalyst systems given in Table I. The intrinsic viscosity appears to be considerably lower than obtained with polystyrene prepared under similar polymerization conditions.

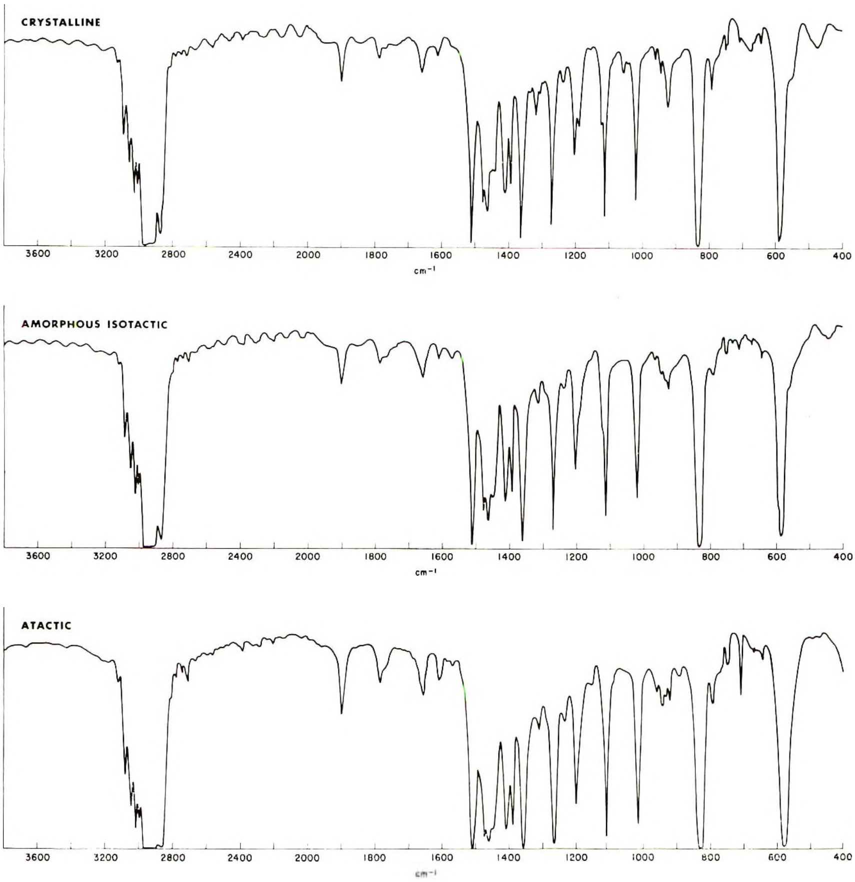

Fig. 1. Infrared spectra of poly-*p*-*tert*-butylstyrene.

The crystalline melting point was obtained by heating the polymer in a hot stage microscope and observing the melting point under crossed polaroids. As the amorphous polymer is heated slowly, the polymer particles fuse and crystalline birefringence develops at temperatures in the range 250–275°C. Upon further heating, the crystalline melting point of 300°C. is observed as the spherulites melt.

The infrared spectra were measured on thin films of crystalline, amorphous isotactic, and atactic polymer. These spectra are compared in Figure 1. While additional work is needed to assign the various peaks in the spectra, the isotactic crystalline polymer exhibits several absorption peaks not present in the atactic polymer. The most obvious ones are at 790, 1055, 1125, 1190, 1305, and 1335 cm.$^{-1}$.

Attempts were made to compare proton NMR spectra of the polymer in its various forms. The most significant variations were obtained in the high-resolution proton NMR spectra of the *tert*-butyl absorption, run in *o*-dichlorobenzene solution at 150–180°C. at 60 MHz on a Varian A-60 spectrometer. Chemical shifts are given as shielding relative to bistrimethylsilyl ether as the internal standard. The atactic polymer gave a peak at 1.21 ppm, with distinct shoulders at -1.13, -1.17, and -1.24 ppm, and possibly at -1.28 ppm. The amorphous isotactic polymer gave a single peak at -1.19 ppm, with a half-height width of 2.6 Hz. The crystalline polymer gave a single peak at 1.19 ppm with a width at half-height of 1.2 Hz. A high degree of tacticity of the isotactic polymer is indicated by these results.

Crystallization

As indicated in the previous section, the poly *p*-*tert*-butylstyrene prepared with the Ziegler-Natta catalyst is amorphous when recovered from the polymerization. However, upon heating or annealing the polymer, it crystallizes to give a typical spherulitic structure and crystalline melting point when observed in a polarizing microscope.

The relative overall rate of crystallization as a function of annealing temperature was determined from relative crystallinity–time plots by using the half-time of crystallization $t_{1/2}$ as the measure of the overall rate of crystallization. Small samples of the amorphous polymer were placed in a preheated constant temperature oven and after the desired annealing time they were removed and quenched. The relative crystallinity of the polymer was determined from x-ray diffraction measurements. The maximum

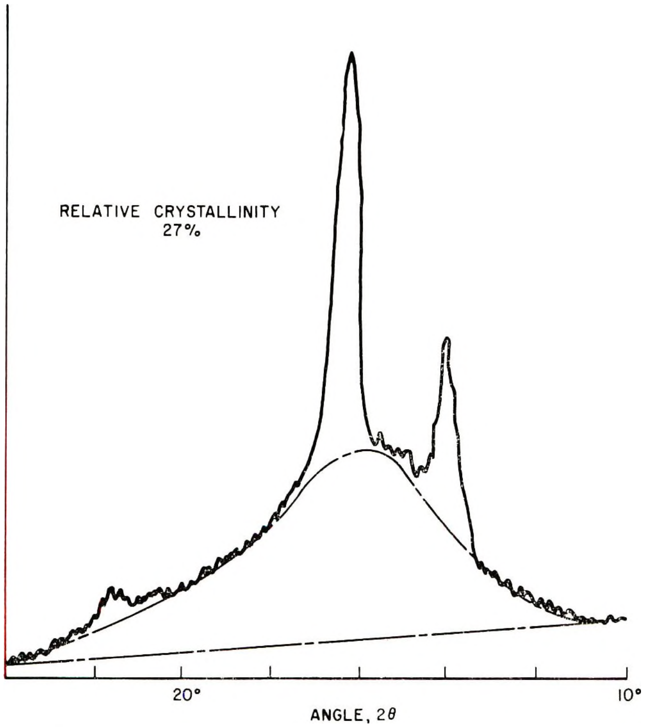

Fig. 2. X-ray diffraction pattern of crystalline poly-*p*-*tert*-butylstyrene.

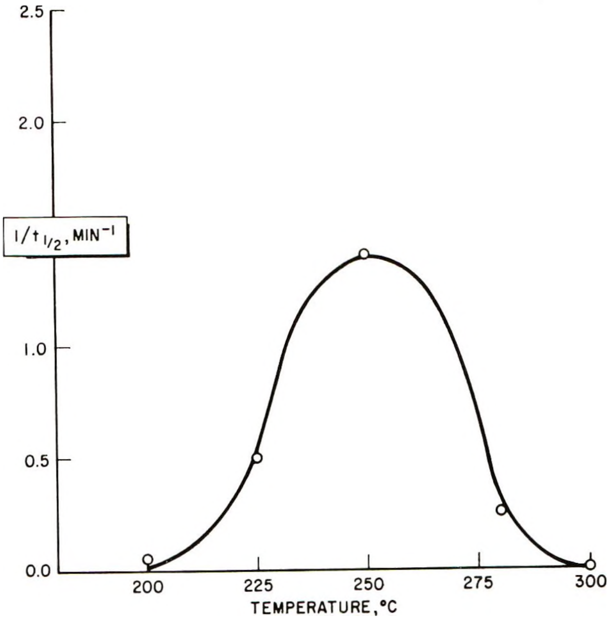

Fig. 3. Effect of temperature on crystallization rate of isotactic poly-*p*-*tert*-butylstyrene.

relative crystallinity obtained for the polymer was 30%. A typical x-ray diffraction pattern is shown in Figure 2.

The change in the overall rate of crystallization with annealing temperature is shown in Figure 3. The maximum rate of crystallization is observed at a temperature of about 250°C. It is to be noted that the polymer crystallized at a rapid rate at 250°C. where the value for $t_{1/2}$ is less than 1 min. Due to this rapid rate of crystallization there is some uncertainty in the rate data obtained by the experimental technique used. However, the data shown are a good first approximation of the crystallization behavior of this polymer.

The crystalline melting point of the annealed crystallized polymer as measured under crossed polaroids in a hot stage microscope is 295–300°C. Differential thermal analysis on the crystallized polymer also shows an endotherm at 300°C. The second-order transition temperature is estimated to be 154°C. by thermomechanical analyses techniques.

With the aid of a density gradient column, density determinations were made on polymer samples fabricated into thin sections under different molding conditions to obtain different degrees of crystallinity. These results are given in Table II.

TABLE II
Effect of Crystallinity on Density

Molding temperature, °C. (5 min.)	Relative crystallinity, %	Density, g./cc.
185	0	0.9496
250	30	0.9462
275	22	0.9479
300	~0	0.9497

The density data indicate a lower density for the crystallized polymer than for the amorphous isotactic polymer. While the difference in density between the two states is relatively small, it may indicate a situation similar to that observed in isotactic poly-4-methyl-1-pentene where the density of the crystalline polymer is less than that of the amorphous polymer at room temperature.[4,5] Crystallization of the bulky *p-tert*-butyl side groups may be a factor in producing a slight increase in the specific volume of the bulk polymer.

CONCLUSIONS

The polymerization of *p-tert*-butylstyrene with Ziegler-Natta type catalysts can give an isotactic crystallizable polymer. The isotactic polymer crystallizes rapidly with a maximum rate of crystallization observed at a temperature of 250°C. The crystalline polymer has a melting point of 300°C. and appears to have a density slightly lower than the amorphous polymer. Preliminary results obtained from infrared and NMR spectra indicate characteristic peaks associated with the structure of the crystalline polymer.

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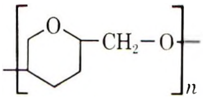
Linear Polymers from Diepoxides

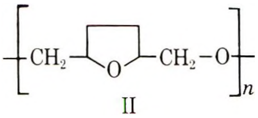
INTRODUCTION

The polymerization of 1,2,5,6-diepoxyhexane by cationic and heterogeneous anionic catalysts has been reported by Stille and Culbertson[1-3] to give soluble solid polyethers. Stille and Culbertson proposed that these soluble polymers arise from an intramolecular–intermolecular propagation mechanism which results in a linear polymer consisting of enchained tetrahydropyran moieties (I).



I

The results of the work reported here confirm the cyclopolymerization of this diepoxide with soluble anionic catalysts; however, strong evidence is given in support of a linear polymer structure composed of symmetrically substituted tetrahydrofuran rings (II).



II

The cyclopolymerization of N,N-diglycidylaniline has also been carried out, and an analogous structure consisting of symmetrically substituted enchained morpholine units has been proposed.

EXPERIMENTAL

Monomers

The method of Korach et al.[4] was used to epoxidize the 1,5-hexadiene. The pure 1,2,5,6-diepoxide was obtained by fractionation under reduced pressure; b.p. 67°C./8 mm. Hg, yield 37%.

To prepare N,N-diglycidylaniline, to 185 g. (2.0 moles) of refluxing epichlorohydrin in a 2-liter round-bottomed, four-necked flask fitted with a dropping funnel, condenser, stirrer, and thermometer was added dropwise 93 g. (1.0 mole) aniline. The aniline was added at ca. 25 drops/min.; as the reaction progressed, the heat to the kettle was decreased. Dehydrohalogenation of this chlorohydrin was carried out by adding a methyl ethyl ketone solution of the chlorohydrin to a 50% sodium hydroxide solution at 50°C.

The organic phase was separated, neutralized with solid carbon dioxide, and dried with anhydrous magnesium sulfate. The product was obtained by distilling through a short Vigreux column to yield a pale yellow oil; b.p. 113–116°C./0.5 mm. Hg.

ANAL. Calcd. for $C_{12}H_{15}NO_2$: C, 70.26%; H, 7.37%. Found: C, 69.72%; H, 7.37%.

Polymerizations

All polymerizations were carried out in sealed, heavy-walled glass ampules. The solvent, catalyst solution, and monomer were charged into the ampules with a hypodermic syringe under a nitrogen atmosphere. The tubes were then cooled in liquid nitrogen, evacuated, sealed, and then placed in a constant temperature bath. The polymers were worked up by precipitation in mixed hexanes and then dried *in vacuo*.

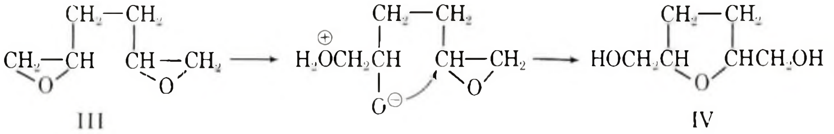
Characterization of Polymers

The nuclear magnetic resonance spectra were obtained by means of the Varian A-60 spectrometer, and the infrared analyses were carried out on a Beckman IR-7 high-resolution grating spectrophotometer.

RESULTS AND DISCUSSION

Polymers of 1,2,5,6-Diepoxyhexane

Wiggins and Woods[5] have described the preparation of 1,2,5,6-diepoxyhexane (III) by the oxidation of 1,5-hexadiene with perbenzoic acid. They have also shown that the diepoxide upon hydrolysis gives two distinct reaction products, depending upon the nature of the reagent used. These products are (*a*) derivatives of 2,5-hexanediol, and (*b*) 2,5-disubstituted derivatives of tetrahydrofuran. In particular, when III was treated with boiling water, tetrahydrofuran-2,5-dimethanol (IV) resulted. The reaction presumably proceeds as shown in eq. (1).


III IV (1)

However, it is not clear why the anion should attack the secondary carbon atom of the second epoxy group (contrary to the usual mode of anionic attack on a substituted epoxide). Possibly the driving force for the formation of a five-membered ring rather than a six-membered ring overrides the preference for S_N2 attack at the least substituted carbon atom.[6]

1,2,5,6-Diepoxyhexane was readily polymerized in benzene or tetrahydrofuran solution using potassium *tert*-butoxide as initiator to give completely soluble polymers which range from viscous oils to tacky semisolids. Table I lists a few typical polymerization conditions and the results. Sample 39-1 was the highest molecular weight polymer prepared [viscosity (I.V.) = 0.27 dl./g.] and was shown by ebullioscopic measurements to have a number-average molecular weight of about 5000. Efforts to prepare higher molecular weight materials with potassium *tert*-butoxide were not successful. Other catalyst systems that are known to give high molecular weight polyethers from epoxides, such as diethyl zinc–water[7] and magnesium aluminum isopropoxide,[8] gave essentially insoluble polymers in our hands.

The polymer is believed to have a cyclic structure because (*1*) it is completely soluble in polar organic solvents and (*2*) there is no evidence for pendant oxirane rings in the nuclear magnetic resonance spectrum (NMR) of the polymer. Thus, two structures are possible from a cyclic polymerization of this diepoxide. The first (V) would result

TABLE I
Polymerization of 1,2,5,6-Diepoxyhexane[a]

No.	Solvent (3.5 ml.)	Yield, %	I.V., dl./g.[b]
39-1	Benzene	72.8	0.23
39-2	"	97.1	0.15
39-5	THF	58.3	0.27
39-6	"	53.4	0.23

[a] Temperature, 50°C.; 64 hr.; 2.0 ml. 1,2,5,6-diepoxyhexane; catalyst, potassium *tert*-butoxide, 0.1 g.

[b] Toluene at 25°C.

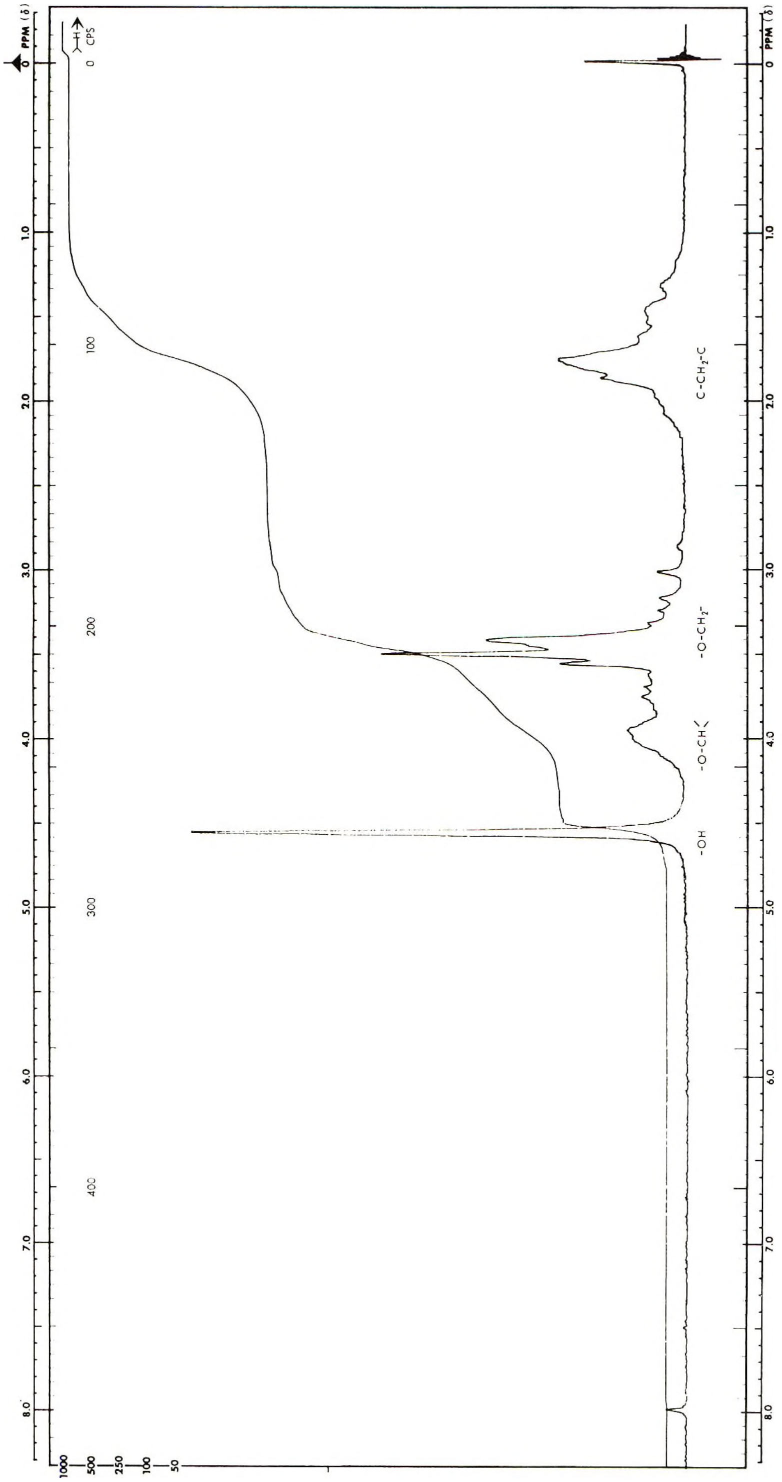


Fig. 1. NMR spectrum of poly-1,2,5,6-diepoxyhexane.

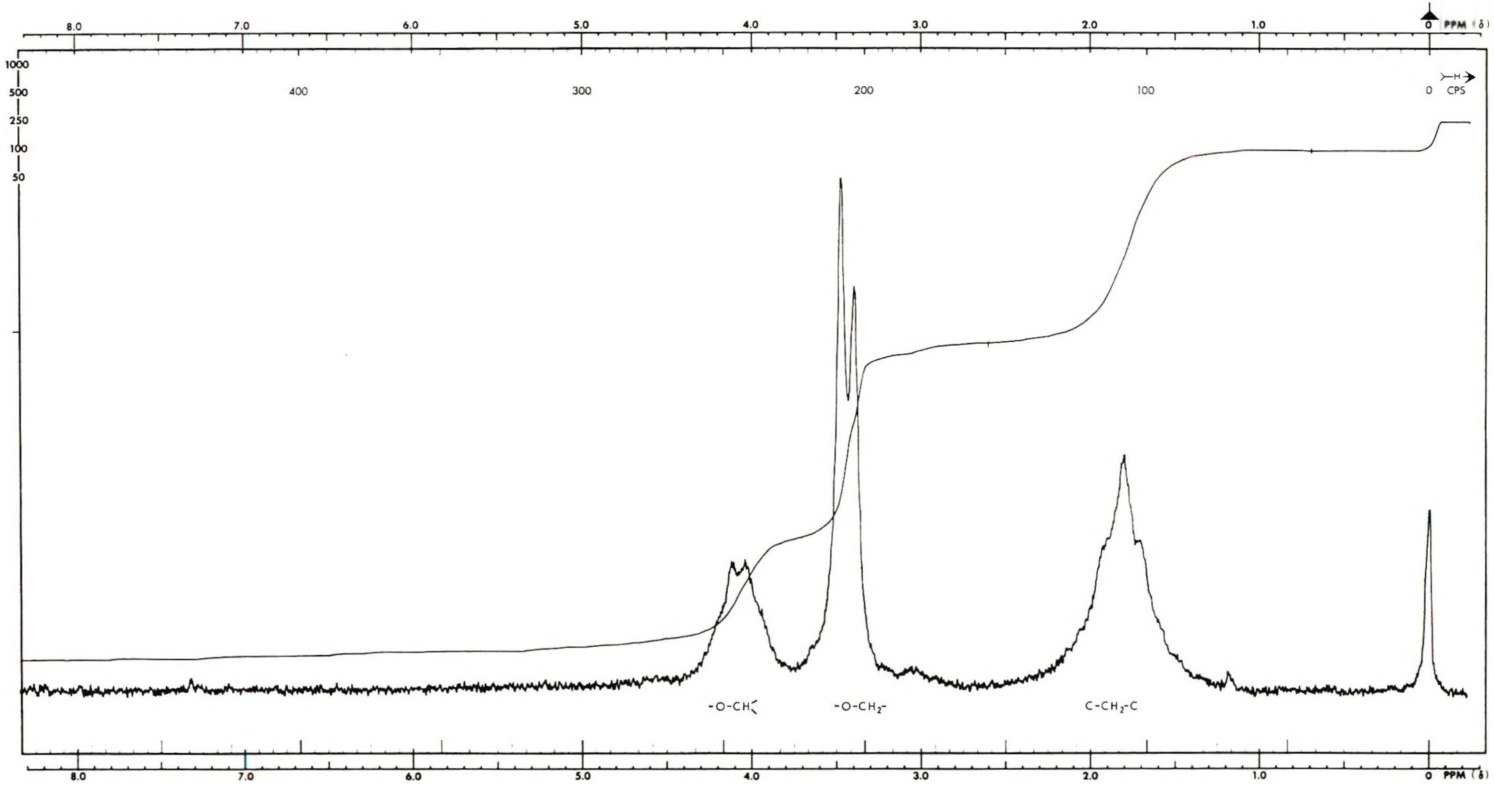
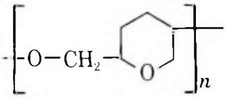
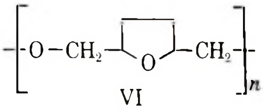


Fig. 2. NMR spectrum of the hydrolyzate of 1,2,5,6-diepoxyhexane.

from the usually observed mode of anionic attack on substituted epoxides. The second is the tetrahydrofuran structure (VI) which is analogous to the product observed when the diepoxide is hydrolyzed.



V



VI

Because of the preference for formation of a five-membered ring upon hydrolysis of III, structure VI would appear to be the favored one, and this seems to be consistent with the NMR analysis. The outstanding feature in the NMR spectrum (see Fig. 1) of the poly-1,2,5,6-diepoxyhexane is a sharp doublet centered at about 3.45 δ which also appears in the NMR spectrum of the hydrolyzate (Fig. 2) of the diepoxide. The doublet bands arise from the spin-spin coupling of the chain $—O—CH_2$ groups with the adjacent ring hydrogens. The two $—O—CH_2—$ groups (one being a ring $—O—CH_2—$, the other a chain $—O—CH_2—$ group) in structure V are not equivalent and would result in broadening of these lines. Also the similarities between the NMR of the polymer and the model compound favor the tetrahydrofuran structure. The small peaks at about 230 cps from TMS and these between 180 and 200 cps from TMS are believed to be impurities, since their intensities vary with the particular preparation of IV.

TABLE II
Infrared C—H Stretching Frequencies of Five- and Six-Membered Rings

Sample	Infrared C—H stretching	
	Frequency, cm.$^{-1}$	Wavelength, μ
Polymer (6549-39-1)	2950; 2874	3.39; 3.48
Tetrahydrofuran-2,5-dimethanol	2967; 2874	3.37; 3.48
Tetrahydrofuran	2976; 2874	3.36; 3.48
Cyclopentyl chloride[a]	2950; 2865	3.39; 3.49
Tetrahydropyran-2-methanol	2899; 2857	3.45; 3.50
Cyclohexyl chloride[a]	2915; 2841	2.43; 3.52

[a] Data of Roberts and Chambers.[9]

Stille and Culbertson[1-3] assign structure I to their poly(1,2,5,6-diepoxyhexane) on the basis that the infrared spectra of their polymer samples, which had an absorption at 1094 cm.$^{-1}$, showed maxima (C—O—C stretching) characteristic of their model compounds tetrahydropyran (1095 cm.$^{-1}$) and diethylcellosolve (1105 cm.$^{-1}$). In contrast, the infrared spectra of the polymers obtained in this laboratory with soluble anionic catalysis show a rather broad peak in the carbon–oxygen stretching region with a definite maximum at 1079 cm.$^{-1}$ which is more consistent with tetrahydrofuran structure (tetrahydrofuran has an absorption maxima at 1074 cm.$^{-1}$) rather than a tetrahydropyran structure for our polymer.

Further evidence in support of the tetrahydrofuran structure for these polymers is obtained from the comparison of the infrared C—H stretching frequencies of tetrahydrofuran, tetrahydrofuran-2,5-dimethanol (IV), and the polymer, on the one hand, with tetrahydropyran-2-methanol on the other. That is, the C—H stretching frequencies of the polymer were very similar to those of tetrahydrofuran-2,5-dimethanol and tetrahydrofuran, whereas the C—H stretch frequencies in tetrahydropyran-2-methanol are somewhat lower. Roberts and Chambers[9] have shown that the frequencies of the $—CH_2—$ bonds increase as the ring size becomes smaller. They found that the values for six-membered rings were normal and those for five-membered rings very nearly so.

Table II lists the frequencies observed for the polymer, the model compounds, and also those observed by Roberts for five- and six-membered rings. A direct comparison between the C—H stretching frequencies of carbocycles and oxygen heterocycles is probably not strictly valid. Thus the agreement between frequencies of the polymer and cyclopentyl chloride is probably fortuitous. A less controversial comparison is between the observed frequencies for the polymer and those for model oxygen heterocycles. The polymer frequencies are more consistent with a tetrahydrofuran rather than a tetrahydropyran ring structure assignment, in agreement with the NMR evidence.

Polymers of *N,N*-Diglycidylaniline

When *N,N*-diglycidylaniline is polymerized in the same manner as described for 1,2,5,6-diepoxyhexane, a completely soluble and fusible solid polymer is obtained. Table III lists a few typical polymerizations and the results. It is interesting to note that this diepoxide gave a soluble polymer with aluminum isopropoxide, whereas diepoxyhexane gave essentially insoluble polymers with this catalyst.

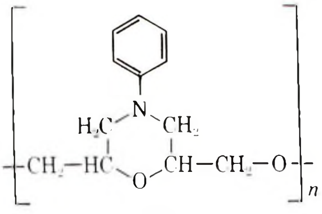
TABLE III
Polymerization of *N,N*-Diglycidylaniline[a]

No.	Vol. solvent (benzene), ml.	Catalyst	Wt. catalyst, g.	Time, hr.	Yield, %	I.V., dl./g.[b]
44-4	3.5	Potassium butoxide	0.05	48	79.0	0.08
46-8	3.0	Aluminum isopropoxide	0.10	64	63.0	0.08
47-1	6.0	Potassium *tert*-butoxide	0.25	144	79.0	0.22
47-3	4.0	Potassium *tert*-butoxide	0.25	144	—	0.22

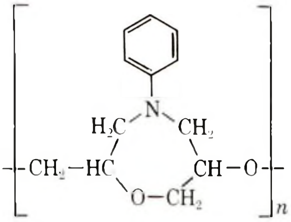
[a] 2.0 ml. *N,N*-diglycidylaniline, temperature 50°C.
[b] Chlorobenzene at 25°C.

Polymer samples 44–4 and 46–8 were found to have number-average molecular weights of 2100 determined by ebullioscopic measurements and NMR endgroup analysis. However, for the polymers of higher viscosity, the ebullioscopic and NMR methods did not agree. Molecular weights were very low (1400) by ebullioscopic measurements while NMR analysis gave molecular weights greater than 81,000. We favor the latter values since they are more in line with the viscosity measurements and especially since it is known that trace amounts of low molecular weight impurities can cause larger errors in ebullioscopic molecular weights.

As with the poly-1,2,5,6-diepoxyhexane, these polymers from *N,N*-digylcidylaniline are believed to have a cyclic structure. Unfortunately, the presence of both nitrogen and oxygen in this molecule makes the determination of the polymer structure by NMR and infrared impossible. However, because of the solubility of the polymer and the fact that there are essentially no pendant oxirane rings (this was shown by NMR) a cyclopolymer seems reasonable. The cyclopolymer could then be made up of six- (VII) or seven-membered (VIII) rings. On the basis that six-membered ring formation is favored over seven-ring formation, the morpholine structure (VII) appears more likely and is favored by the author.



VII



VIII

The assistance of Dr. C. A. Reily in interpreting the NMR data and of Mr. A. D. Jeong and Mr. C. T. Alwine in the experimental part of this work is gratefully acknowledged.

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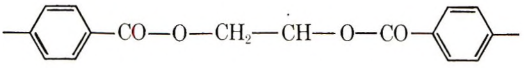
ESR Study of Radicals Trapped in Amorphous and Crystalline Samples of Poly(ethylene Terephthalate) After γ-Irradiation

Previously, a variety of samples of poly(ethylene terephthalate), PET, with varying levels of crystallinity (5–50%) have been exposed to γ-rays and the resulting ESR spectra compared. Only slight differences were noticed and the spectra were not assigned.[1] Subsequently, sufficiently well resolved spectra were obtained from an oriented sample to identify the radicals trapped in the crystalline regions as I (>90%) and, tentatively, II.[2]



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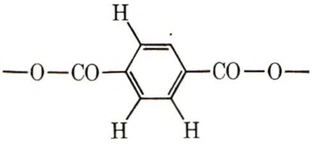


II

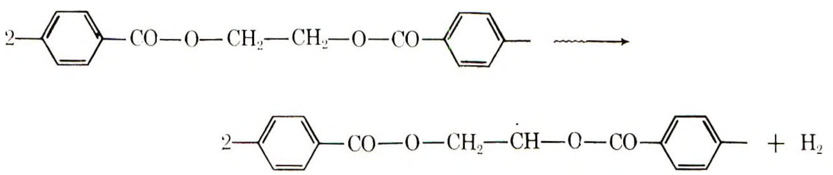
Against this background, a further comparison has been made of spectra obtained from completely amorphous and highly crystalline samples of PET following γ-irradiation.

A sample of pure amorphous PET, of thickness 0.3 mm., was kindly provided by Dr. C. J. Heffelfinger of E. I. du Pont de Nemours & Company, Inc., Circleville, Ohio. A part of this polymer was thoroughly degassed, sealed in a vacuum, and then heated for 48 hr. at 235–240°C. The x-ray diffraction patterns indicated that considerable crystallization occurred, consistent with the report that this treatment results in a sample with about 70% crystallinity.[3] It is to be expected that such rigorous annealing would result in some thermal degradation of the polymer.[4] The concentration of carboxyl endgroups was found, by Pohl's method,[5] to increase from an initial value of 0.42×10^{-4} to 0.69×10^{-4} mole/g. after annealing. Despite this increase in endgroups, the limiting viscosity number (determined in a 1:1 mixture, by weight, of tetrachloroethane and phenol at 25°C.) increased from an initial value of 57.4–64.6 ml./g. This observation was unexpected, since it would seem to indicate that some crosslinking occurred during annealing.[4]

Samples of the amorphous and crystalline PET were degassed and sealed in a vacuum in Suprasil quartz tubes at a pressure of 10^{-4} mm. Hg. The samples were irradiated in a ^{60}Co γ-source at a dose rate of 0.5 Mrad/hr. at room temperature. After irradiation the quartz was flame-annealed, and first and second derivatives of the absorption curve were recorded with a Varian V4502-10 spectrometer. The number of free radicals in the sample was estimated by double integration of the first derivative spectrum and by comparison with α,α'-diphenyl-β-picrylhydrazyl.

Quite different spectra were obtained from the crystalline and amorphous samples (Fig. 1). The spectrum obtained from the polycrystalline sample is complex due to the lack of preferred orientation of the radicals, but it is clear that the marked peaks correspond to the 6- and 8-line spectra previously assigned to radical I. Assignment of the spectrum from the amorphous sample can only be tentative, but it may be seen that there is one component which resembles the spectrum previously assigned to radical II, the spectrum of which is shown in Figure 1 as a dotted line. There is also a second, more stable component (radical III which is unassigned) with a singlet spectrum which remains in isolation after about one-half of the radicals have decayed at 70°C.

A reasonable explanation of the above findings would be that radical I is formed in both the amorphous and crystalline regions by reaction 1, which takes account of the similar initial G values for trapped radical (0.025) and hydrogen (0.015).[6] Radical I is trapped in the rigid crystalline regions, but in the amorphous regions is supposed to react further to yield an equal number of other radicals (II and III).



(1)

Evidence that radical I is, indeed, less stable than radical II in the crystalline regions was reported previously,[2] while evidence that radical II is less stable than radical III in the amorphous regions was mentioned above. Although the stabilities of the radicals are in line with the above explanation there are two further observations which seem to cast doubt on it. First, as reported previously,[2] radical I decays in the crystalline regions, without formation of II or III. Second, attempts to observe I by γ-irradiation of the amorphous polymer at 77°K. followed by careful heating or exposure to visible light to remove trapped electrons have not been successful. Therefore, the simple explanation proposed above remains open to question.

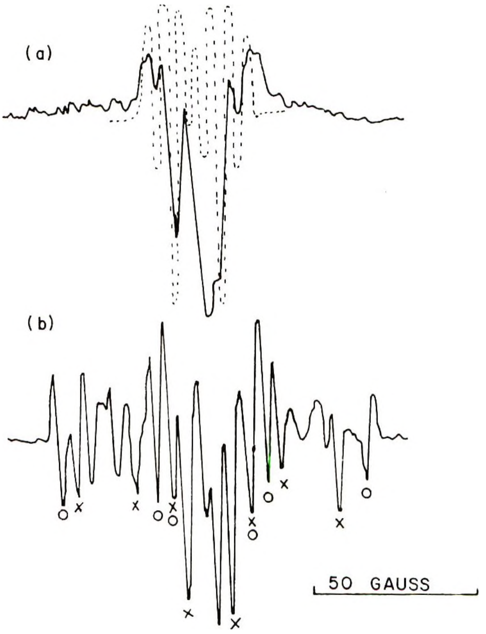


Fig. 1. Second derivative ESR spectra of γ-irradiated poly(ethylene terephthalate): (*a*) amorphous sample (dashed line shows spectrum of —$\dot{C}_6H_3$—); (*b*) highly crystalline sample, peaks corresponding to (×) 8-line spectra and (O) peaks corresponding to 6-line spectra of —O—CH—CH_2—O—.

Finally, it remains to mention apparently related findings on other polymers. It was suspected that a difference between the types of radicals trapped, following γ-irradiation, in highly crystalline monoamides and a sample of nylon 6 might be due to the high amorphous content of the polymer.[7] Recently, different spectra were reported for γ-irradiated amorphous and bulk-crystallized samples of isotactic polybutene-1 while, surprisingly, a sample of single crystals was found to give an ESR spectrum resembling that of the amorphous rather than the bulk-crystallized sample.[8] It seems important to elucidate the reason for these differences, as they seem to imply that the radiation chemistry of a polymer may be strongly influenced by its physical state, a matter which is also of current interest in connection with the radiation-induced gelation of polyethylene. In the case of PET, a comparison is being made of the general radiation chemistry of amorphous and crystalline samples, and it is hoped to report the findings in the near future.

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Thermal Stability of Imide-Crosslinked Poly(vinylphthalic Anhydride)

Extensive research since 1959 has produced several tough and thermally stable polymers. Among these, the aromatic polyimides prepared by the condensation of pyromellitic dianhydride and aromatic diamines were found to be quite impressive.[1] With this in mind poly(vinylphthalic anhydride) has been prepared and treated with a series of diamines. The thermal stabilities of the resulting polymers were determined by both thermogravimetric (TGA) and differential thermal analysis (DTA).

Vinylphthalic anhydride was prepared from vinylphthalic acid according to a modification of a procedure reported earlier.[2,3] Finely ground vinylphthalic acid was spread uniformly on the bottom surface of a 500-ml. suction flask. A cold finger containing liquid nitrogen was then attached and the flask immersed in a heated oil bath. The anhydride sublimed at a bath temperature of 180°C. and a pressure of 0.25 mm. The product was collected and stored over P_2O_5; m.p. 90–91°C., yield 55%. Both the melting point and infrared spectrum are consistent with that of the desired compound.

Vinylphthalic anhydride was found to be soluble in dimethylformamide, dimethylacetamide, and acetonitrile, partially soluble in aromatic solvents, and insoluble in aliphatic hydrocarbons.

The polymerization was effected by the addition of a trace of azobisisobutyronitrile to a solution of 1 g. of the monomer in dry acetonitrile and heating at gentle reflux for 24 hr. When the solvent was evaporated, a brittle amorphous solid with a yellow tint remained as residue. An infrared spectrum of this material shows bands at 1840(ms), 1750(s), 1260(s), and 900(s) cm.$^{-1}$. When this residue was subjected to thermogravimetric analysis rapid degradation was found to occur at 320–350°C. The monomer could be obtained from this residue by heating at 60–70°C. and 30 mm. pressure in a sublimation apparatus. The molecular weight of this polymer was determined by osmotic measurements made with a Zimm and Myerson[4] osmometer employing a No. 450 cellophane membrane. By this method a molecular weight of 44,000 was obtained.

Imide formation was effected by treating poly(vinylphthalic anhydride) with four aromatic diamines which included *p*-phenylenediamine, benzidine, *p,p'*-methylenedianiline, and 4,4'-oxydianiline.

In the general procedure used, polyanhydride (1 mole) was dissolved in dry dimethylacetamide to give about a 1% solution. Then 0.5 mole of the diamine was added rapidly with stirring until the solution became completely homogeneous. The solution was then allowed to stand for 2 hr. at room temperature, after which it was poured into a Petri dish and kept overnight in an oven at 105°C. The film which formed was placed in a furnace at 300°C. for 1 hr. to complete the imidation and to drive off any remaining solvent.

The infrared spectra of the films before heating showed, in general, a broad absorption band at about 2800 cm.$^{-1}$ attributable to the carboxyl group of the poly(amic acid) as well as several bands in the carbonyl region due to the C═O absorption of the carboxyl, amide, and imide groups present in the molecules. After the films were heated, the carboxyl and amide group absorption peaks had nearly disappeared, while peaks near 1780 (w), 1725 (s), and 1380 (ms) cm.$^{-1}$ remained and became more intense.

In order to determine the minimum time that was required for the complete formation of poly(amic acid), the viscosity of a solution of polyanhydride and the diamine was measured at frequent intervals. A constant viscosity was reached after 2 hr., which indicated that little if any additional reaction took place after that time.

The thermal stability of the polyimide films was evaluated by using both TGA and DTA. TGA curves were determined at a heating rate of 2.5°C./min. The three polyamides obtained from *p*-phenylenediamine, benzidine, and *p,p'*-methylenedianiline showed stabilities on the average up to 500°C. in air and rapidly degraded at temperatures of 500–520°C. In nitrogen atmosphere the degradation occurred at 540–560°C.

In the case of the polyimide from 4,4′-oxydianiline, the thermal stability was lowered by approximately 30°C. in air. In all the cases a black organic residue was obtained which weighed 15–20% of the original weight.

DTA measurements were in complete agreement with the results of TGA. A gradual exotherm appeared at 460°C., followed by a sharp exotherm at 520–540°C. No other peaks were evident in these curves.

Studies on thermal aging were carried out by exposing the polyimide films at 300°C. in air for one week. During this time, a 30% weight loss occurred. The films turned a deep brown in color but retained their flexibility.

Assuming that no carboxyl groups were present in the heated samples and that all the nitrogen was present in the form of imide, the degree of imidation in the polyimide films was estimated from the nitrogen content to vary between 65 and 75%. Since this figure could theoretically represent both intermolecular and intramolecular imidation, the thermal stability is indeed very impressive despite the presence of a polymethylene chain associated with poly(vinylphthalic anhydride). The number of free anhydride groups could not be estimated directly due to the insolubility of the polyimide.

In order to determine the stability of these polyamides to hydrolysis they were placed in boiling water for one week. At the end of this time they were found to have retained their physical properties and the water was found to be neutral. The films of polyimide also showed great stability toward acid in that they were found to be unaffected after one week in concentrated sulfuric acid.

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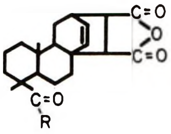
Some Polyimide-Amides from Maleopimaric Acid

Maleopimaric acid (Ia) is a readily obtainable compound, made by the reaction of maleic anhydride with pine gum, rosin, or the various pure conjugated dienic resin acids, namely, levopimaric, plaustric, neoabietic, and abietic acids.[1] The pure compound finds use in photographic processes while maleated rosin is used as a paper size and in varnishes and surface coatings.



I a, R = OH
b, R = Cl

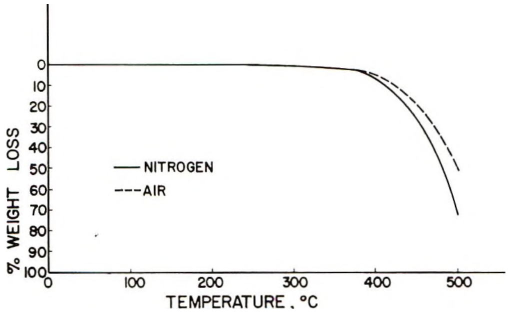


Fig. 1. TGA curves on polyimide-amide from the monoacid of maleopimaric and 4,4′-methylenedianiline.

Some representative types of polyimide-amides have been prepared to demonstrate the utility of maleopimaric acid as a starting material in this new area of heat resistant plastics, first described by Bower and Frost.[2] The monoacid chloride of maleopimaric acid (Ib)[3] was fused with a variety of diamines to give random-linked polyimide-amides. The polymer made from 1,6-hexanediamine gave the best film. The polymers made from 4,4′-oxydianiline and from *p*-phenylenediamine could be cold-drawn from a hot melt into fibers. The TGA curves (Fig. 1) on a typical polymer of this type made from 4,4′ methylenedianiline indicate about a 6% loss in weight on heating to 400°C. in nitrogen and about an 11% loss in weight on heating to 425°C. in air. This would seem to place these polymers in about the same class as the *meta* aromatic polyamides[4] with respect to thermal stability.

The monoacid chloride of maleopimaric acid (2 mole) was next reacted with the diamine (1 mole) either in pyridine or via a modified Schotten-Baumann reaction to give a dianhydride. These were fused with a variety of diamines to give head-to-tail, tail-to-tail linked polyimide-amides. Again, 1,6-hexanediamine as the amine in both steps resulted in a polymer which gave the best films.

Thirdly, the monoacid chloride of maleopimaric acid (1 mole) was reacted with 1,6-hexanediamine (1 mole) to give the amide-amine hydrochloride. On fusion, this gave a head-to-tail linked polyimide-amide, which gave a good film.

The monoacid chloride of maleopimaric acid was also reacted with 1,6-hexanediamine at room temperature in 1-methyl-2-pyrrolidone to give a polyamide-acid which on heating was converted to a polyimide-amide.

EXPERIMENTAL

Fusion of the Monoacid Chloride of Maleopimaric Acid with Diamines

An intimate mixture of 4.19 g. (0.01 mole) of the monoacid chloride of maleopimaric acid (Ib) and 1.98 g. (0.01 mole) of 4,4′-methylenedianiline was made, and a 2-g. portion fused over an open flame in a test tube equipped with a thermometer and a capillary tube reaching to the bottom of the test tube and through which passed a rapid stream of nitrogen. The temperature was held at 320°C. for 3 min. A hard glass was obtained. An infrared spectrum was determined in chloroform solution: λ_{max} 2.90 (amide), 5.63 μ (imide). A small portion of the product was fused at 320°C. for an additional 3 min. and the infrared spectrum determined in chloroform at the same concentration as before. A comparison of the spectra showed that imidization was essentially complete after the first period of fusion for 3 min. at 320°C.[5] TGA curves (Fig. 1) were run on finely divided solids at a heating rate of 20°C./min. A sample of the polyimide-amide was dissolved in chloroform and fractionated by the addition of benzene into five fractions representing 7.9%, 9.5%, 33.0%, 1.9%, and 47.8% of the starting material, respectively. Fraction 3 (33% of starting product) was found to exhibit η_{inh} 0.10 (c = 1.0, 30°C., DMF); molecular weight via vapor pressure osmometry 6070; capillary m.p. 392°C.; nitrogen analysis (Kjeldahl) 4.92% (theory for polyimide-amide is 4.98%). The polyimide-amide was insoluble in acetone, ethyl acetate, pentane, ethyl alcohol, water, acetonitrile, glacial acetic acid, dioxane, concentrated acid and alkali, benzene, carbon tetrachloride, and soluble in DMF, DMSO, and chloroform. The infrared spectrum (Nujol mull) exhibited bands at 3.0 (s) (amide), 5.65 (m) (imide), 5.88 (s) (imide), 6.11 (s) (amide), 6.62 (m) (amide), 13.92 (m) (imide) μ. The following amines were also fused with the acid chloride: 1,6-hexanediamine, *m*-phenylenediamine, *p*-phenylenediamine, 4,4′-oxydianiline. The polymer from 1,6-hexanediamine could be dissolved in chloroform and a film cast which was impervious to water. The polymers made from 4,4′-oxydianiline and from *p*-phenylenediamine could be cold-drawn from hot melt into fibers.

Reaction of the Monoacid Chloride of Maleopimaric Acid with a Diamine to Give a Diamide

Modified Schotten-Baumann Method. A solution of 4.19 g. (0.01 mole) of the monoacid chloride of maleopimaric acid (Ib) in 30 ml. of dioxane was added with cooling to a solution of 0.34 ml. (0.005 mole) of 1,2-ethanediamine in 30 ml. of dioxane and 18 ml. of 10% aqueous sodium hydroxide. After 1 hr. of stirring, 18 ml. of 3*N* hydrochloric acid was added with cooling, the supernatant poured off, and water added to the residual oil. A solid formed; yield 2.50 g.; neutralization equivalent 205, theory 206. Infrared spectrum (Nujol mull) 2.98 (m) (amide), 5.44 (m) (anhydride), 5.56 (s) (anhydride), 8.18 (s) (anhydride) μ. The following amines were reacted via this method: 1,6-hexanediamine, 1,3-propanediamine, and 4,4′-methylenedianiline.

Pyridine Method. A solution of 0.54 g. (0.005 mole) of *m*-phenylenediamine in 30 ml. of pyridine was added with cooling to a solution of 4.19 g. (0.01 mole) of the monoacid chloride of maleopimaric acid (Ib) in 35 ml. of pyridine. After 1 hr., 40 ml. of 5*N* hydrochloric acid added with cooling and excess water added. The precipitate was collected and was washed with water; yield 4.0 g.; neutralization equivalent 218, theory 218. The following amines were reacted via this method: *p*-phenylenediamine, 4,4′-methylenedianiline, 1,6-hexandiamine, 1,3-propanediamine, and 4,4′-oxydianiline.

Fusion of Bisamides with Diamines

An intimate mixture of the bisamide from 1,6-hexanediamine (0.881 g. 0.001 mole) and 1,6-hexanediamine (0.116 g., 0.001 mole) was fused at 320°C. for 3 min. as described previously. The hard glass exhibited the following infrared spectrum: λ_{max} (Nujol mull) 2.98 (w) (amide), 5.67 (m) (imide), 5.88 (s) (imide), 6.1 (m) shoulder (amide), 6.62 (m) (amide), 13.93 μ (w) imide. The product exhibited essentially the same properties as the product from the fusion of the monoacid chloride of maleopimaric acid and 1,6-hexanediamine. A water-impervious film could be cast from chloroform. The bisamides prepared above were fused with the same diamine used in their preparation and also with different diamines from the same group mentioned previously.

Preparation of Amide-Amine Salt

To solution of 11.6 g. (0.10 mole) of 1,6-hexanediamine in 40 ml. of dioxane and 18 ml. of 10% aqueous sodium hydroxide wxs added at 0–10°C. a solution of 4.19 g. (0.01 mole) of the monoacid chloride of maleopimaric acid (Ib) in 40 ml. of dioxane. After 1 hr. an excess of $3N$ hydrochloric acid was added with cooling. The precipitate was collected and washed; yield 1.67 g.; neutralization equivalent 182, theory 178; test for chloride ion positive.

Fusion of Amide-Amine Salt

The salt was fused at 290°C. for 2 min., 320°C. for 3 min., and 345°C. for 3 min. A good water-impermeable film of Sward hardness of 54 could be cast from chloroform.

Reaction of the Monoacid Chloride of Maleopimaric Acid with Diamine in a Solvent

A solution of 8.4 g. (0.02 mole) of the monoacid chloride of maleopimaric acid (Ib) in 36 ml. of dry 1-methyl-2-pyrrolidone was added slowly at 10–15°C. to a solution of 2.32 g. (0.02 mole) of 1,6-hexanediamine in 27 ml. of dry 1-methyl-2-pyrrolidone in which was dispersed 2.12 g. (0.02 mole) of finely divided anhydrous sodium carbonate, over a 35 min. period. Vigorous stirring was supplied for 40 min. at room temperature and the solution then filtered. A portion was diluted with water. A white precipitate formed which was insoluble in chloroform and DMF; λ_{max} 3.02 (m) (amide), 5.65 (w) (imide), 6.15 (m) (amide), 6.57 μ (m) (amide); molecular weight via vapor pressure osmometry 3753; nitrogen analysis (Kjeldahl) 5.83% (calculated for poly half amide, 5.62%). A portion of the 1-methyl-2-pyrrolidone solution was refluxed at 200°C. for 3 min. and a portion diluted with water to give a precipitate which was chloroform-soluble; λ_{max} (chloroform) 2.90 (s) (amide), 3.28 (amide), 5.67 μ (imide). The boiled solution was refluxed an additional 3 min., and precipitated with water. The infrared spectrum in chloroform at the same concentration as before indicated that essentially complete imidization had occurred during the first 3-min. boiling period.[6] A portion of the precipitate obtained after boiling for 3 min. was fractionated into 7 parts by adding ethyl ether to a chloroform solution of the polymer. Fraction 2 (33% of material fractionated) was of molecular weight 3263 via vapor pressure osmometry; nitrogen analysis (Kjeldahl) 5.34% (theory for polyimide-amide 5.83%). Fraction 3 (44%) was of molecular weight 3030; nitrogen analysis (Kjeldahl) 5.41%.

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