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Homopolymers and Copolymers of Acrylates and Methacrylates of Homoterpenylmethyl Carbinol and α-Campholenol

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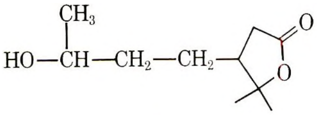
Synopsis

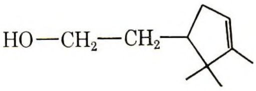
Acrylates and methacrylates of homoterpenylmethyl carbinol and α-campholenol were homopolymerized. Copolymers with each other and acrylonitrile were studied. Terpolymers of the acrylate of homoterpenylmethyl carbinol and the acrylate of α-campholenol with butadiene and styrene or acrylonitrile were also prepared. The lactone ring in the homopolymer of methacrylate of homoterpenylmethyl carbinol was opened up under basic conditions at room temperature, yielding a water-soluble polymer. Films of this polymer were cast from a water solution. The acrylate of homoterpenylmethyl carbinol gave a high molecular weight copolymer with acrylonitrile which could be molded into a transparent, extremely tough, film. The terpolymers of the acrylate of homoterpenylmethyl carbinol with butadiene and styrene or acrylonitrile were obtained in high yield and could be molded into strong, rubbery films. Several polymers were epoxidized and cured with *p*-phenylenediamine.

INTRODUCTION

In continuation of the studies on the preparation of polymers containing terpenes and various terpene derivatives,[1–6] two new derivatives from α-pinine have been investigated: (*1*) homoterpenylmethyl carbinol, 6-hydroxy-2-(1-hydroxy-1-methylethyl)heptanoic acid γ-lactone (I), and (*2*) α-campholenol, 2-(2,2,3-trimethyl-3-cyclopentenyl)ethyl alcohol (II). I was prepared by Howell and Hedrick by the platinum oxide reduction of homoterpenylmethyl ketone in sodium hydroxide solution;[7] II was obtained by reduction of the corresponding aldehyde, α-campholene aldehyde.[8] The properties and reactions of II and α-campholene aldehyde have been described.[8] Synthesis of various esters of II, conversion of the esters to epoxides, and evaluation of the epoxides as plasticizer-stabilizers for poly(vinyl chloride) have also been described.[9]



I



II

The work here describes the preparation and polymerization of the acrylates and methacrylates of I and II. In addition, studies on the epoxidation, curing, and hydrolysis of some of the polymers of II were conducted. Polymers containing the unit I would be expected to undergo the lactone ring opening to yield water-soluble polymers. Polymers of II would be expected to undergo an epoxidation readily. The reaction products of epoxidized polymers with, for example, fatty acids could find applications in the coatings field.

RESULTS AND DISCUSSION

Monomers

Samples of α-campholene aldehyde, I and II, were provided by Dr. G. W. Hedrick of the Naval Stores Laboratory of the Southern Utilization Research and Development Divisions, Agricultural Research Service. In the preparation of additional II, α-campholene aldehyde was reduced with lithium aluminum hydride.[8] The physical constants of the three materials are given in Table I.

TABLE I
Physical Constants of Terpene Derivatives

Derivative	B.p., °C./ mm. Hg	n_D^{20}	Remarks
α-Campholene aldehyde	86/14	1.4645	$[\alpha]_D^{22.5}$ −3.71 (10 cm., neat)
α-Campholenol, II	92/1.5	1.4700	H_2 absorption: 96% of one mole
Homoterpenylmethyl carbinol, I	140/0.4	1.4675	

The acrylates and methacrylates of I and II were prepared according to the procedure of Marvel and Schwen.[10] However, instead of distilling the products, chromatography on silicic acid with diethyl ether–hexane mixtures as eluent was used for purification of the monomers. Physical characteristics of the monomers and their analytical data are given in Table II. Infrared analysis showed the presence of a trace of hydroxyl-containing

TABLE II
Physical Characteristics and Analytical Data of Acrylates and Methacrylates of I and II

Monomer	n_D^{27}	Appearance	Calculated C, %	Calculated H, %	Found C, %	Found H, %
Acrylate of I	1.4630	Very light yellow, viscous oil	64.62	8.40	64.68	8.18
Methacrylate of I	1.4634	Yellow, very viscous oil	66.11	8.72	65.71	8.55
Acrylate of II	1.4659	Water-clear liquid	74.94	9.70	75.26	9.72
Methacrylate of II	1.4658	Yellow oil	75.63	10.00	74.77[a]	10.25[a]

[a] A 0.68% residue was found in the analysis of this monomer.

material in the acrylate and methacrylate of I. Although there was a good agreement in analytical data between the calculated and experimental values, it is possible that a minor amount of the hydrolyzed lactone was still present in the derivatives of I or the hydroxyl band may have been due to absorbed moisture. The residue found in the analysis of the methacrylate of II was probably due to colloidal silicic acid introduced inadvertently during the chromatography of the monomer.

Homopolymerization

The experimental conditions and polymerization results for the various polymers are given in Table III.

Homopolymerizations were conducted in an emulsion system with the use of a detergent (Siponate DS-10) rather than a soap as the emulsifier. The detergent gave better latices and conversions. The low inherent viscosities for the homopolymers of methacrylate of I and acrylate of II were unexpected. The polymers were isolated as white powders which could be molded (at about 150°C.) into water-clear, brittle films. On one occasion the acrylate of I gave a material which could be molded into a strong film. In the homopolymerization of the acrylate of II, whenever the conversion exceeded 35%, some insoluble polymer began to form. Similarly, long drying periods insolubilized the material, probably by oxidative coupling at the allylic position. The polyacrylates of I were soluble in ethyl methyl ketone and chloroform. The polyacrylates of II were soluble in tetrahydrofuran, ethyl methyl ketone, and methylene chloride. Whereas only a trace of a hydroxyl-containing material was indicated in the acrylate and methacrylate of I monomers the corresponding homopolymers appeared to contain more of the hydroxy acid despite the fact that their analytical data agreed with the calculated. A tightly bound water of hydration cannot be ruled out, as the infrared analysis is not conclusive on this point.

Copolymerization

Copolymers of the Acrylate of I. The acrylate of I was copolymerized with the acrylate and methacrylate of II, and with acrylonitrile. The acrylate copolymers were isolated as white, hard solids, soluble in ethyl methyl ketone, whereas the acrylonitrile copolymer was a yellow solid, soluble in *N*-methylpyrrolidone. The acrylate copolymers had inherent viscosities below 1.0; the acrylonitrile copolymer had the exceptionally high viscosity of 4.4. The acrylates could be molded (at about 150°C.) into water-clear, brittle films, whereas the acrylonitrile copolymer gave an extremely tough, somewhat soft film.

The properties of all the copolymer films are given in Table IV. All of the copolymers gave transparent films.

Prolonged drying of the copolymers of the acrylate and methacrylate of II insolubilized them. In general, the copolymers of acrylate of I exhibited adhesion to a copper foil in varying degrees. This may have been due to the hydroxy acid component present in the polymers.

TABLE
Polymers of Acrylates and Methacrylates of

Composition charged, wt.-%								Catalyst, parts/100 parts monomers	Polymerization time, hr.	Conversion, %	η_{inh}
HMCA[c]	HMCM[d]	TCEA[e]	TCEM[f]	AN[g]	FN[h]	Sty[i]	BD[j]				
100	—	—	—	—	—	—	—	1	20	94	1.06
—	100	—	—	—	—	—	—	1	20	99	0.28
—	—	100	—	—	—	—	—	0.4	18	90^{l}	0.48^{m}
—	—	—	100	—	—	—	—	0.5	20	85	1.21^{m}
50	—	50	—	—	—	—	—	2	20	85^{l}	—
60	—	40	—	—	—	—	—	1	16	98	0.25
50	—	—	50	—	—	—	—	1	20	90	0.83
60	—	—	40	—	—	—	—	0.5	16	83	0.56
50	—	—	—	50	—	—	—	1	20	~100	4.40^{n}
—	50	50	—	—	—	—	—	2	20	95^{l}	0.60
—	50	—	50	—	—	—	—	1	20	90	0.60
—	50	—	—	50	—	—	—	1	20	~100	1.11^{n}
—	—	50	—	50	—	—	—	2	20	95^{p}	0.31^{n}
—	—	—	50	50	—	—	—	1	20	$\sim 100^{q}$	0.65^{n}
—	—	—	50	—	50	—	—	2^{r}	20	14	0.29^{n}
40	—	—	—	9	—	—	51	1	16	~100	—
60	—	—	—	6	—	—	34	1	16	90^{s}	0.98^{t}
80	—	—	—	3	—	—	17	1	16	85	0.63^{t}
40	—	—	—	—	—	18	42	2	16	90	—
60	—	—	—	—	—	12	28	2	16	85	—
70	—	—	—	—	—	9	21	1	14	92	0.98
80	—	—	—	—	—	6	14	2	16	90	0.52
—	—	40	—	9	—	—	51	0.5	16	9	—
—	—	60	—	6	—	—	34	0.5	16	12	0.98^{m}
—	—	80	—	3	—	—	17	0.5	16	33	1.26^{m}
—	—	40	—	—	—	18	42	0.5	16	5	—
—	—	60	—	—	—	12	28	0.5	16	10	—
—	—	80	—	—	—	6	14	0.5	16	8	—

[a] All of the polymerizations were conducted at 60 ± 2°C. by tumbling the tubes end-over-end; Siponate DS-10 (alkyl-substituted benzene sodium sulfonate) was used as emulsifier in about 1–2% amounts; potassium persulfate was used as catalyst.

[b] Determined on solutions of 0.019–0.219 g./100 ml. of ethyl methyl ketone.

[c] Acrylate of homoterpenylmethyl carbinol.

[d] Methacrylate of homoterpenylmethyl carbinol.

[e] Acrylate of α-campholenol.

[f] Methacrylate of α-campholenol.

[g] Acrylonitrile.

[h] Fumaronitrile.

[i] Styrene.

[j] Butadiene.

Copolymers of the Methacrylate of I. The methacrylate and acrylate copolymers were isolated as white, hard solids soluble in ethyl methyl ketone; the acrylonitrile copolymer was a yellow solid, soluble in *N*-methylpyrrolidone. None of the methacrylate of I copolymers possessed adhesive properties.

Copolymers of the Acrylate and Methacrylate of II. The acrylate/acrylonitrile copolymer was isolated as a yellow solid in a 95% yield of which only 30% was soluble in *N*-methylpyrrolidone. The insolubility was probably due to the crosslinking of the acrylate portion.

The methacrylate/acrylonitrile copolymer was isolated in a quantitative yield; however, only about 20% of it was soluble in *N*-methylpyrrolidone.

III[a]
Homoterpenylmethyl Carbinol and α-Campholenol

Composition found wt.-%						Calculated			Found		
TCEA	TCEM	AN	FN	Sty	BD[j]	C, %	H, %	N, %	C, %	H, %	N, %
—	—	—	—	—	—	64.62	8.40	—	64.81	8.66	—
—	—	—	—	—	—	64.36	8.78[k]	—	64.19	8.65	—
—	—	—	—	—	—	74.94	9.70	—	74.78	9.65	—
—	—	—	—	—	—	75.63	10.00	—	75.29	10.10	—
45	—	—	—	—	—	69.26	8.98	—	69.04	9.05	—
40	—	—	—	—	—	68.74	8.92	—	68.44	8.91	—
—	48	—	—	—	—	69.90	9.17	—	69.62	9.58	—
—	34	—	—	—	—	68.35	8.94	—	68.47	8.92	—
—	—	44	—	—	—	66.05	7.20	11.62	65.32	7.35	12.18
60	—	—	—	—	—	70.70	9.32[o]	—	70.60	9.15	—
—	50	—	—	—	—	70.00	9.39[o]	—	70.17	9.30	—
—	—	39	—	—	—	65.73	7.56[o]	10.30	64.86	7.46	10.83
—	—	40	—	—	—	72.10	8.10	10.56	69.67	8.22	10.11
—	—	44	—	—	—	72.22	8.10	11.62	70.03	8.10	11.02
—	—	—	13	—	—	73.78	9.03	4.66	73.53	9.18	4.17
—	—	9	—	—	61	79.59	9.92	2.38	79.61	9.93	2.40
—	—	7	—	—	33	72.44	9.29	1.85	72.62	9.14	1.75
—	—	5	—	—	17	68.86	8.76	1.32	68.69	8.86	1.20
—	—	—	—	18	42	79.73	9.49[u]	—	79.98	9.46	—
—	—	—	—	10	27	72.64	8.98[u]	—	72.79	8.94	—
—	—	—	—	10	24	73.16	9.01[u]	—	73.03	8.96	—
—	—	—	—	6	14	69.64	8.76[u]	—	69.35	8.70	—
—	—	11	—	—	39	79.51	9.88	2.91	79.88	9.82	2.97
—	—	8	—	—	34	79.03	9.93	2.11	79.37	9.97	2.08
—	—	5	—	—	20	77.32	9.82	1.32	77.69	9.99	1.21
—	—	—	—	13	32	81.59	9.92[u]	—	81.32	9.81	—
—	—	—	—	13	32	81.59	9.92[u]	—	81.78	10.06	—
—	—	—	—	9	21	79.36	9.85[u]	—	79.19	9.90	—

[k] Calculated for a 60/40 mixture of the lactone methacrylate/hydroxy acid methacrylate.
[l] Includes 5% gel.
[m] Determined in tetrahydrofuran.
[n] Determined in N-methylpyrrolidone.
[o] Calculated for a 60/40 ratio of lactone/hydroxy acid for the methacrylate of I.
[p] Only 30% of the total polymer isolated was soluble.
[q] Only 20% of the total polymer isolated was soluble.
[r] Polymerized in benzene solution at 80°C. with the use of azobisisobutyronitrile.
[s] Includes 8% gel.
[t] Determined in chloroform.
[u] Calculation done assuming 70/30 BD/Sty ratio in the terpolymer.

The solution methacrylate/fumaronitrile copolymer was isolated as a dark tan solid, soluble in tetrahydrofuran.

Terpolymerization

Terpolymers of the Acrylate of I. Two series of terpolymers involving the acrylate of I have been prepared. One of the series involved BD/AN comonomers. The terpolymers were isolated as water-clear to white rubbery masses which could be molded (at about 130°C.) into clear tough films. Whereas the 30/61/9 acrylate/BD/AN terpolymer was essentially insoluble in hot tetrahydrofuran and chloroform, only 10% of the 60/33/7 acrylate/BD/AN terpolymer was not soluble and the 78/17/5 acrylate/BD/AN terpolymer was soluble in chloroform and tetrahydrofuran.

TABLE IV
Properties of Films of Various Copolymers

Composition, wt.-%						
HMCA	HMCM	TCEA	TCEM	AN	FN	Properties of films
55	—	45	—	—	—	Brittle, adheres to copper foil
60	—	40	—	—	—	Brittle, adheres to copper foil
52	—	—	48	—	—	Brittle
66	—	—	34	—	—	Brittle, adheres to copper foil
56	—	—	—	44	—	Light tan, extremely tough, soft
—	40	60	—	—	—	Brittle
—	50	—	50	—	—	Brittle
—	61	—	—	39	—	Light tan, very tough
—	—	60	—	40	—	Tan, weak
—	—	—	56	44	—	Light tan, weak
—	—	—	87	—	13	Dark tan, brittle

The other series involved BD/Sty comonomers. These materials again were isolated as water-clear to white rubbery masses which could be molded (at about 130°C.) into clear, tough films. A film prepared on copper foil of the 80/14/6 acrylate/BD/Sty terpolymer adhered strongly to the foil. Of the four compositions only the 80/14/6 and 66/24/10 acrylate/BD/Sty terpolymers were partially ($\sim$70%) soluble in hot ethyl methyl ketone.

Terpolymers of the Acrylate of II. Another terpolymer series identical to the one described but with the acrylate of II was attempted. However, with both, the BD/AN and BD/Sty comonomers only low conversions were realized. The best yield (33%) was obtained with the 75/20/5 acrylate/BD/AN terpolymer. The two terpolymers, 75/20/5 and 58/34/8, on which inherent viscosities were run, were soluble in tetrahydrofuran and had good viscosity values. The films pressed (at about 130°C.) from these materials were clear, rubbery, and strong.

Epoxidation

Epoxidation of several polymers was explored to increase their functionality. Development of adhesive properties was also sought. The following polymers were investigated: (*1*) polyacrylate of II, (*2*) 60/40 acrylate of I/acrylate of II copolymer, and (*3*) 66/24/10 acrylate of I/BD/Sty terpolymer. The *in-situ* method[11] with hydrogen peroxide/glacial acetic acid with a resin catalyst (Amerlite IR-120) was explored. This method was preferred over the ones involving use of preformed peracids because it gave higher oxirane oxygen content in a shorter time and less contamination in the final product. Ethyl methyl ketone was used as a solvent for the polymers. Normally, in epoxidations of polymers, secondary reactions products, such as glycol derivatives, ketones and ether derivatives, would be expected.

According to the infrared analysis of the epoxidized materials, only a trace amount of unsaturation was observed in the epoxidized homopolymer of acrylate of II and no unsaturation was detected in the other two materials. Furthermore, absorption bands attributed to epoxides[12] (1250, 840 cm.$^{-1}$) were observed in the epoxidized polymers.

Analytical data, calculated on the basis of one oxygen atom addition across the double bond, indicated that for the polyacrylate of II only 10% of the theoretical addition had taken place, for the copolymer 38%, and for the terpolymer 25%. A more accurate determination could be probably achieved by the ether–HCl method.[13]

Although the epoxidized copolymer was isolated as a soluble product from the reaction mixture, drying it at 39°C. for 26 hr. insolubilized it completely.

In the epoxidation of the terpolymer (66/24/10 acrylate of I/BD/Sty), two products were produced in about equal amounts. One of the materials was water-soluble, the other was water-insoluble. The water-soluble material was also insoluble in hot ethyl methyl ketone, was extremely tough, and a good film could not be molded. Hence an infrared spectrum could not be obtained. The water-soluble material was pressed into a film; the infrared spectrum showed it to be the hydroxy acid and contained absorption bands characteristic of epoxides. Analytical data on the water-soluble material could also be accounted for by assuming opening of the lactone ring. It is surprising that the lactone ring was opened under these acidic conditions.

Curing

Epoxypolybutadienes cured with polyamines or anhydrides are good adhesives to metallic substrates.[14] Accordingly, the epoxidized polyacrylate of II and the acrylate of I/acrylate of II copolymer were mixed with *p*-phenylenediamine, placed between copper foil, and compressed and heated at 160°C. for 2 min. The film from the polyacrylate of II was extremely hard and completely nonadhesive; the copolymer film was partially adhesive.

Hydrolysis of Polymethacrylate of I

The lactone ring in polymers of I should be susceptible to basic hydrolysis. A sample of the methacrylate homopolymer was hydrolyzed with 3.5% ethanolic potassium hydroxide at room temperature. After a period of about 2 hr. the infrared spectrum showed that most of the lactone ring had been opened; the product was soluble in ethanol and water. In water the hydrolyzed polymer formed a light blue, very viscous solution. Evaporation of water yielded a transparent, strong film. Infrared analysis on the film showed the presence of a strong absorption band for the carboxylate anion at 1565 and 1390 cm.$^{-1}$ and only a minor absorption band at 1775 cm.$^{-1}$, indicative of the lactone carbonyl. Thus, the potassium hydroxide-treated polymer is essentially all potassium salt of the polycarboxylate. The extremely facile opening of the lactone ring suggests an easy preparation of water-soluble polymers.

EXPERIMENTAL

Reduction of α-Campholene Aldehyde

α-Campholene aldehyde (397 g., 2.6 mole) was reduced with lithium aluminum hydride (25.7 g., 95% pure) in 3500 ml. of dry diethyl ether (distilled over lithium aluminum hydride). The aldehyde was added just fast enough to maintain a gentle boil. Good agitation was maintained during the addition. The reaction mixture was allowed to stand for one day, then water was added dropwise (5–6 drops/min.) while agitating until a granular precipitate was obtained. The solids were removed by filtration and the filter cake washed with ether. The ether solution was washed and dried over sodium sulfate. After stripping the ether and distilling the product, 386 g. (96%) of the alcohol was obtained.

Typical Preparation of a Monomer: Methacrylate of II

II (23.7 g., 0.154 mole), dimethylaniline (21.2 g., 0.175 mole, distilled, and ether (50 ml.) were combined in a 500 ml. flask and then methacrylyl chloride (18.8 g., 0.180 mole) was added dropwise. After all of the methacrylyl chloride was added, the reaction mixture was heated to 78°C. and kept at this temperature for 2 hr. after the white dimethylaniline hydrochloride salt had settled out. At the end of this period a 100-ml. portion of benzene was added to the reaction mixture followed by 200 ml. of water. The organic layer was separated and washed with 100 ml. of 10% sulfuric acid solution, followed by 100 ml. of saturated sodium bicarbonate solution and 100 ml. of water. The benzene solution was then dried over anhydrous magnesium sulfate, the solvent stripped in a Rotovac, and the isolated yellow oil chromatographed on silicic acid (Mallinckrodt, AR, 100 mesh) column with 4% anhydrous ethyl ether–hexane (99.3% pure) mixture as eluent. A light-yellow oil was isolated in 30 g. yield (87%).

Typical Homopolymerization Recipe: Homopolymer Methacrylate of II

The methacrylate of II (2.0 g.), Siponate DS-10 (0.02 g.), potassium persulfate (0.01 g.), and air-free, distilled water (6.0 ml.) were placed under nitrogen in a pressure tube (1 × 7 in.), emulsified at room temperature for 10 min. and polymerized at 60 ± 2°C. by tumbling end over end for 20 hr. A white latex was obtained. The latex was poured into 400 ml. of methanol and 20 drops of 17% hydrochloric acid was added to speed up the settling out of the polymer. The precipitated material was filtered and dissolved in 40 ml. of tetrahydrofuran and reprecipitated in 400 ml. of methanol. The yield was 1.7 g. (85%) of vacuum oven-dried (40°C./16 hr.) white powder. The infrared spectrum showed no characteristic absorption bands for the monomer.

Typical Copolymerization Recipe: Copolymer of the Methacrylate of II and Acrylate of I

The methacrylate of II (1.0 g.), the acrylate of I (1.0 g.), Siponate DS-10 (0.04 g.), potassium persulfate, and air-free, distilled water (8.0 ml.) were placed (under nitrogen) in a pressure tube (1 × 7 in.), emulsified at room temperature for 5 min., and polymerized at 60 ± 2°C. for 20 hr. A blue latex with few polymer particles was obtained. The latex was poured into 400 ml. of methanol, the precipitated material was next dissolved in 50 ml. of ethyl methyl ketone, and reprecipitated in 400 ml. of methanol. The yield was 1.8 g. (90%) of vacuum oven-dried (38°C./26 hr.) white powder. The infrared spectrum showed no characteristic absorption bands for the monomers.

Solution Copolymer of the Methacrylate of II and Fumaronitrile

The methacrylate of II (1.0 g.), fumaronitrile (1.0 g.), benzene (10 ml. dry, thiophene free), and azobisisobutyronitrile (0.04 g.) were charged under nitrogen in a pressure tube (1 × 7 in.) and polymerized at 80 ± 1°C. by tumbling end over end for 20 hr. A viscous solution was obtained. It was poured in 400 ml. of methanol, and 10 drops of 17% hydrochloric acid were added to speed up the settling out of the polymer. The precipitated material was dissolved in 40 ml. of tetrahydrofuran and reprecipitated in 250 ml. of methanol. The yield was 0.28 g. (14%) of vacuum-oven dried yellow solid. The infrared spectrum showed no characteristic absorption bands for the monomers.

Typical Terpolymerization Recipe:
Terpolymer of the Acrylate of I, Acrylonitrile, and Butadiene

The acrylate of I (0.80 g.), and acrylonitrile (0.18 g.), Siponate DS-10 (0.04 g.), $K_2S_2O_8$ (0.02 g.), and air-free distilled water (8.0 ml.) were charged under nitrogen in a pressure tube (1 × 7 in.). The tube was cooled to about −10°C., and butadiene (1.02 g., high purity) was added. An excess of butadiene was used to purge the tube before capping. The charge was emulsified at room temperature for 30 min. and polymerized at 60 ± 2°C. by tumbling end over end for 16 hr. A milky suspension was obtained. It was poured into 400 ml. of methanol to which 40 drops of 17% hydrochloric acid was added to speed up the settling out of the polymer. The filtered material was suspended in 100 ml. of refluxing tetrahydrofuran. Only a few per cent of the polymer was soluble. The suspension was next poured into 400 ml. of methanol. The yield was 2 g. (~100%) of vacuum oven-dried (40°C./16 hr.) water-clear, rubbery solid.

Typical Epoxidation Procedure

The acrylate of I/acrylate of II copolymer (3.0 g., 0.013 mole), methyl ethyl ketone (30 ml.), glacial acetic acid (0.42 g., 0.007 mole) and Amberlite IR-120 (0.19 g.) were all combined in a three-necked flask equipped with a reflux condenser, thermometer, mechanical stirrer, and a dropping funnel. The bath was then heated to 65°C., and 30% hydrogen peroxide (3.4 g., 0.016 mole) was added dropwise. After the addition of hydrogen peroxide, the temperature was raised to 79°C. and maintained there for 6 hr. The reaction mixture was then filtered through a sintered glass funnel and poured into 400 ml. of methanol. The collected precipitate was washed with warm water and dried in a vacuum oven (39°C./26 hr.). A white powder (2 g.) was isolated. The infrared spectrum showed absorption bands characteristic of epoxides and no trace of unsaturation. Analytical data on the epoxidized materials are as follows.

Anal. Acrylate of II Homopolymer. Calcd. for 10% of theoretical epoxidation C, 74.41%; H, 9.63%. Found: C, 74.85%; H, 9.82%.

Acrylate of I/Acrylate of II Copolymer. Calcd. for 38% of theoretical epoxidation: C, 67.95%; H, 8.82%. Found: C, 68.35%; H, 9.06%.

Acrylate of I/BD/Sty Terpolymer. Calcd. for 25% of theoretical epoxidation: C, 71.93%; H, 8.89%. Found: C, 72.01%; H, 9.21%.

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Résumé

On a homopolymérisé des acrylates et méthacrylates des carbinols de homoterpénylméthyle et de α-campholénol. Leurs copolymères avec l'acrylonitrile ont également été étudiés. Les terpolymères d'acrylate de homoterpénylméthyl-carbinol et de l'acrylate de α-campholénol avec le butadiène et le styrène ou l'acrylonitrile ont également été préparés. L'anneau lactonique du homopolymère de méthacrylate de homoterpénylmethyl-carbinol a été ouvert dans des conditions basiques à température de chambre, fournissant un polymère soluble dans l'eau. Les films de ce polymère ont été coulés au départ d'une solution aqueuse. L'acrylate de homoterpénylméthyl carbinol donnait un copolymère de poids moléculaire élevé avec l'acrylonitrile qui peut être fondu en un film transparent extrêmement tenace. Les terpolymères d'acrylate d'homoterpénylméthyl carbinol avec le butadiène et le styrène ou l'acrylonitrile ont été obtenus en rendement élevé et pouvaient être fondus en des films fort caoutchouteux. De nombreux polymères ont été époxydés et ensuite traités à la p-phénylène diamine.

Zusammenfassung

Acrylate und Methacrylate von Homoterpenylmethylcarbinol und α-Campholenol wurden homopolymerisiert. Copolymere der Monomeren untereinander und mit Acrylnitril wurden untersucht. Auch Terpolymere der Homoterpenylmethylcarbinol- und α-Campholenolacrylate mit Butadien und Styrol oder Acrylnitril wurden dargestellt. Der Lactonring des Homoterpenylmethylcarbinolmethacrylates wurde unter basischen Bedingungen bei Raumtemperatur unter Bildung eines wasserlöslichen Polymeren geöffnet. Filme dieses Polymeren wurden aus Wasserlösung gewonnen. Das Homoterpenylmethylcarbinolacrylat lieferte mit Acrylnitril ein hochpolymeres Copolymeres, aus welchem ein transparenter, extrem zäher Film hergestellt werden konnte. Die Terpolymeren aus Homoterpenylmethylcarbinolacrylat, Butadien und Styrol oder Acrylnitril wurden in hoher Ausbeute erhalten une konnten zu festen, kautschukartigen Filmen verarbeitet werden. Einige Polymer wurden epoxydiert und mit p-Phenylendiamin gehärtet.

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Polymerization of Methyl 12-Acryloxystearate, *N*,*N*-Dimethyl 12-Acryloxystearamide, and Methyl 14-Acryloxyeicosanoate

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Synopsis

Several homopolymers and copolymers of the title compounds have been prepared by radical initiation with potassium persulfate or diethyl azobisisobutyrate. The copolymers exhibit a combination of the properties of the homopolymers of the monomers. The homopolymers are adhesive, very slightly elastic, and show cold flow. Several of the copolymers show possible promise for use as adhesives.

INTRODUCTION

The work reported herein was undertaken in an effort to find useful polymers and copolymers derived from the fatty acids in oil seeds which are produced in this country. In particular, it was believed that these polymeric products might prove useful in the formulation of the adhesive mixtures.

The monomers were prepared in our laboratory and at the Western Utilization and Development Division of the United States Department of Agriculture. Methyl 12-acryloxystearate (MAS) and *N*,*N*-dimethyl 12-acryloxysteramide (DMMA) are derived from ricinoleic acid, and methyl 14-acryloxyeicosanoate (MAE) is derived from lesquerolic acid. They were prepared by reduction of the acid, esterification, or amidation, followed by introduction of the acryl group. Although poly(hexydecyl acrylate) is a solid, the homopolymers of the title compounds are tacky, soft, slightly elastic, and show cold flow.

RESULTS AND DISCUSSION

Monomers

The monomers which were studied were of different qualities as described in Table I. Methyl 12-acryloxystearate was supplied in two batches. The first batch was colored but was easily decolorized by treatment with Norite in petroleum ether or Skellysolve B (IA). Because 10–20% of it was lost during purification and the color could be removed from the polymer by stirring it in petroleum ether, most of the polymerizations were

TABLE I
Monomers Studied

Monomer	Code	Origin	B.p., °C. (mm.)	n_D (T)
Methyl 12-acryloxystearate[a]	MAS-I	USDA, batch 1	—	—
	IA	USDA, batch 1, decolorized	—	—
	IB-1	USDA, batch 2, distilled fraction 2[b]	170–177(0.05)	1.4511(24°)
	IB-2	USDA, batch 2, distilled fraction 3	177–182(0.05)	1.4524(24°)
	IC	Our laboratories, batch 1, distilled	170–180(0.05)	1.4516(24.5°), 1.4504(28°)
	ID	Our laboratories, batch 2, distilled	152–160(0.35)	1.4535(28°)
	IC-D1	Mixture IC-ID, distilled, fraction 1	155–159(0.005)	1.4486(28°)
	IC-D2	Mixture IC-ID, distilled, fraction 2+3	159–165(0.005)	1.4520(28°)
N,*N*-Dimethyl 12-acryloxystearamide[c]	DMAA-II	USDA	—	—
	IIA	II distilled	200–210(0.025)	1.4660 (24.5°)
Methyl 14-acryloxyeicosanoate	MAE-II	USDA	—	1.4520(27.2°)
	IIIA	III distilled, fraction 2	238–245(0.04)	1.4536(23°)

[a] n_D^{25} 1.4518, b.p. 140 at 1 μ Hg.[1]

[b] Undistilled, n_D^{28} 1.4520.[2]

[c] n_D^{25} 1.4652, b.p. 155/4 μ Hg.[1]

TABLE II
Bulk Polymerization of Methyl 12-Acryloxystearate (MAS) at 60°C. with Diethyl Azobisisobutyrate

Code[a]	Initiator, %	Time, hr.	η_{inh}[b]
I	2	46	0.81
IA	2	46	0.92
IB-1	1	64	0.76
IB-1	2	48	0.87
IB-2	2	48	0.57
IC	1	64	0.51
IC	2	64	0.60
ID	1	64	0.54
IC-D1	1	86	0.26
IC-D2	1	86	0.61

[a] See Table I.

[b] Inherent viscosities measured on about 0.2% tetrahydrofuran solution at 30°C.

run on the unpurified monomer (MAS I). Table II compares polymerization of I and IA. The second batch of MAS contained a crosslinking agent which was removed by distillation (IB).

Some monomer prepared in our laboratory formed crosslinked polymer. It was noted that the methyl 12-hydroxystearate from which the monomer is derived contained about 1% of the dihydroxy derivative.[3] Prior distillation of the ester removed the impurity. Nevertheless the preparations (IC, ID) contained an unidentified chain transfer agent. Distillation proved to be the best method for purification and resulted in removal of all but a trace of this material.

Polymerization of methyl 14-acryloxyeicosanoate (MAE) yielded polymers whose inherent viscosities approached 1.0. Efforts to increase the molecular weights by further purification of monomer by distillation were not successful.

It is difficult to prepare *N*,*N*-dimethyl 12-acryloxystearamide (DMAA) without the formation of several side products. The monomer as received gave either very low molecular weight or crosslinked polymers. It was found that pure monomer could be obtained by distillation. Table I gives the physical properties of these monomers.

Polymers

In general the properties of the homopolymers of these monomers are much alike. They are clear, soft, very slightly elastic, adhesive, slightly tacky polymers which are soluble in tetrahydrofuran, benzene, and acetone. *N*,*N*-Dimethyl 12-acryloxystearamide is different, in that it does not cold flow and is soluble in methanol. Although initial indications suggest that poly(methyl 12-acryloxystearate) would act as a tackifier for ethylene–propylene rubber more extensive testing showed that it was not of practical value.

Several copolymers were prepared with MAS. The properties of these copolymers appeared to be an addition of the properties of the homopolymers of the comonomers. This is illustrated by the vinylidene chloride copolymers shown in Table III. The copolymers which contain about 50% MAS show promise for use as adhesive tapes. It appears that for any extensive adhesiveness the copolymers should contain at least 50% MAS.

TABLE III
Bulk Copolymerization of Methyl 12-Acryloxystearate (MAS) with Diethyl Azobisisobutyrate at 60°C., 95 Hr.

Comonomer, %[a]	η_{inh}[b]	Properties
20 VA[c]	Crosslinked	Soft, elastic, very sticky
50 VA	Crosslinked	Rubbery, elastic, somewhat sticky
50 VA	0.86	Elastic, sticky
80 VA	Crosslinked	Clear, nonsticky
95 VA	Crosslinked	Clear, nonelastic, hard
20 VCl_2[d,e]	1.03	Elastic, very sticky, bonds well to metal
50 VCl_2	0.49	Very sticky, sol. tetrahydrofuran
80 VCl_2	—	Soluble dioxane, insoluble tetrahydrofuran
95 VCl_2	—	Soluble dioxane, brittle film

[a] Per cent of total monomer.
[b] Measured on 0.2% tetrahydrofuran solution at 30°C.
[c] VA = vinyl acetate.
[d] Initiator was 2% benzoyl peroxide, 4.5 hr., 1% dimethylaniline.
[e] VCl_2 = vinylidene chloride.

The vinyl acetate copolymers were also elastic adhesives. Crosslinked polymer was obtained by polymerization at 60°C. To prepare the uncrosslinked copolymer the polymerization was run at room temperature in the presence of an activator.

Although the preceding discussion about copolymers deals mainly with copolymers with MAS, the same general results were obtained with MAE. The notable exception was that MAE was even more adhesive than MAS. Apparently at least part of the properties are due to the length of the chain of the acrylate ester.

Copolymers of MAS with vinyl maleopimarate acid anhydride, a polar molecule, were more difficult to stretch than the homopolymers of MAS with the same viscosity. Polymers containing monomer DMAA are slightly more elastic than polymers containing monomers MAS and MAE. This is probably due to the polar character of the anhydride and amide functions. The amide group also improves heat stability of vinyl chloride copolymers, thus a film pressed at 150°C. was clear and flexible.

Tables II–VII show the effects of varying conditions on the molecular weight of the different polymers. As might be expected, emulsion polymerization gives polymers of higher molecular weight than those obtained

TABLE IV
Emulsion Polymerization of Methyl 12-Acryloxystearate (MAS) at 60°C.

Code	Soap, %[a]	Initiator, %[b]	Time, hr.	Conversion, %	η_{inh}[c]
I[d]	0.47 S	2.0 P	50	—	0.75
I	0.47 S	2.0 P	50	—	0.76
I	0.95 S	2.0 P	50	—	0.61
I	2.0 X	2.0 P	44	84	0.87
I	1.0 X	2.0 P	44	60	0.96
I	0.5 X	2.0 P	44	70	1.05
I	2.0 X	1.0 D	93	94	0.81
I	1.0 X	1.0 D	93	96	1.05
I	1.0 X	2.0 D	93	98	0.96
I	0.5 X	1.0 D	93	90	1.22
I	1.0 X	1.0 B	93	10	Very low
IB-1	0.5 X	1.0 D	62	75	1.20
IB-1	2.0 X	1.0 D	64	—	0.76
IC	2.0 X	1.0 D	64	—	0.64
IC	2.0 X	2.0 D	64	—	0.65
IC[e]	0.5 X	1.0 D	93	—	0.70
ID	2.0 X	1.0 D	66	—	0.52
IC-D1[f]	2.0 G	1.0 D	72	—	0.70
IC-D1[g]	2.0 X	1.0 D	72	Very low	0.58

[a] S = Siponate DS10, X = Triton X-400 (based on active ingredients), G = ORR soap.

[b] P = $K_2S_2O_8$, D = diethyl azobisisobutyrate, B = benzoyl peroxide.

[c] Measured on about 0.2% tetrahydrofuran solution at 30°C.

[d] This run with 3 parts of water per part of monomer; all others with 6 parts of water.

[e] IC distilled, $n^{24.5}_{D}$ 1.4516.

[f] IC-D1 after treatment with NaH, filtration, and distillation.

[g] IC-D1 after treatment with NaH, CH_3I, and distillation.

by bulk polymerization. It can also be seen that the initiator and surfactant as well as their concentrations are important. ORR soap proved to be the best surfactant and had several desirable properties; its emulsions were not only stable in the presence of salts and at elevated temperatures but the polymers did not come out on the sides of the polymerization tube. The choice of the initiator depends on the system.

EXPERIMENTAL

Polymerization Procedure

Water was deoxygenated by boiling it for 15 min. and then bubbling nitrogen through it while cooling in an ice bath.

Polymerizations were run in pressure tubes (Ace Glass, Inc., 4 in., T-1506). The polymerization mixture was placed in the tubes and nitrogen was used to flush out the oxygen. The tube was capped and tumbled end-over-end in a 60°C., constant temperature bath. When polymers were prepared with vinyl chloride, the tube was cooled in a Dry Ice–acetone

TABLE V

Emulsion Copolymerization of Methyl 12-Acryloxystearate (MAS) at 60°C.

Comonomer, %[a]	Soap, %[b]	Initiator, %[c]	Time, hr.	Conversion, %	MAS in polymer, %	C, %	η_{inh}[d]	Properties
33 MA	0.5 X	1 D	41.5	65	—	—		Crosslinked, adhesive
75 MA	0.5 X	1 D	41.5	71	26.44	60.00		Crosslinked, tough, rubbery
75 MA	0.5 X	1 P	41.5	73	—	—		Crosslinked
50 S	0.5 X	1 D	45	78	46.06	82.78		Sol. hot DMF
80 S	0.5 X	1 D	45	84	16.05	88.95	3.35	Foggy, brittle film
80 MM	0.5 X	1 D	45	82	15.80	61.83	2.94	Clear, brittle film
95 MM	0.5 X	1 D	45	84	5.64	60.60	3.39	Clear, brittle film
33 BD	0.5 X	1 D	106	83	—	—		Crosslinked, crumbly, very tacky
75 BD	0.5 X	1 D	106	90	—	—		Crosslinked, brittle
50 VA	0.95 Y	2 P	48.5	—	—	—		Crosslinked
50 VCl	0.95 Y	2 P	48.5	—	—	—	0.36	Partially crosslinked
50 VMPA	1.0 X	2 P	44	51	—	—	0.91	

[a] Per cent is of total monomer; MA = methyl acrylate, S = styrene, MM = methyl methacrylate, BD = butadiene, VA = vinyl acetate, VCl = vinyl chloride, VMPA = vinyl maleopimerate acid anhydride. All runs with 6 parts of water per part total monomer.

[b] X = Triton X-400 (based on active ingredients), Y = Siponate DS 10.

[c] D = diethylazobisisobutyrate, P = $K_2S_2O_8$.

[d] Measured on about 0.2% tetrahydrofuran solution at 30°C.

TABLE VI
Polymerization of Methyl 14-Acryloxyeicosanoate (MAE) at 60°C.

Soap, %[a]	Initiator, %[b]	Time, hr.	Comonomer, %	η_{inh}[c]	Properties
0.5 X	1 D	95	—	0.69	
0.5 X	2 D	70	—	0.76	
0.5 X	3 D	70	—	0.78	
3.0 G	1 D	54	—	No polymer	
3.0 G	1 P	54	—	0.64	
3.0 G	2 P	54	—	1.01	
3.0 G	3 P	70	—	0.82	
6.0 G	1 P	54	—	0.57	
3.0 G[d]	2 P	93	—	0.64	
—	1 D	86	—	0.85	
—	2 D	86	—	0.86	
—	1 D	95	20 VA		Crosslinked, sticky, elastic
—	1 D	95	50 VA		Crosslinked, sticky, sl. elastic
—	1 D	95	80 VA		Crosslinked, sl. sticky, sl. elastic
—	1 D	95	95 VA		Crosslinked, very sl. sticky

[a] Per cent is of total monomer; X = Triton X-400 (based on active ingredients), G = ORR soap.

[b] D = Diethylbisazoisobutyrate; P = $K_2S_2O_8$.

[c] Measured on about 0.2% tetrahydrofuran solutions at 30°C.

[d] Run on IIIA.

TABLE VII
Bulk Polymerization of *N*,*N*-Dimethyl 12-Acryloxystearamide (DMAA) with Diethyl Azobisisobutyrate at 60°C.

Code	Initiator, %[a]	Time, hr.	Comonomer, %	η_{inh}[b]	Properties
II	1	45	80 MM	0.29	
II	1	44	—	Extremely low	
II	2	44	—		Crosslinked, sticky
IIA	2	12	—	0.39	Tacky, sol. methanol, tetrahydrofuran
IIA	2	27	80 VCl	0.76	Clear, nontacky film, softening pt. 67–175°C., dec. 162°C.

[a] Per cent is of total monomer.

[b] Measured on about 0.2% tetrahydrofuran solution at 30°C.

bath. An excess of vinyl chloride was added and allowed to evaporate to the desired weight, and the tube was capped. The cap was lined with a neoprene seal. Nitrogen was not required because the vinyl chloride excluded the oxygen. When an activator was used the polymerizations were run at room temperature.

Methyl 12-Acryloxystearate (MAS)

Purification

By Charcoal. Several grams of I were dissolved in petroleum ether or Skellysolve B. To this solution was added Norite. The mixture was filtered and treated again with Norite until the solution was clear. The solvent was removed under vacuum. Approximately 10–20% of the monomer was lost during purification.

By Distillation. The following Labglass Inc. Micro-distillation equipment was used: 15-ml. or 50-ml. round-bottomed distillation flask (ML 1110, 14/20), distilling head (jacket length 100 mm., 14/20 joints, column length 82 mm., ML-850), and multiple fraction collector equipped with 3 15-ml. flasks.

A porous boiling chip and a piece of copper wire extending from the bottom of the distillation flask to the condenser junction were added. The apparatus was wrapped with an asbestos heating tape from the exposed portion of the distillation flask to the condenser. Table I gives the results of distillation.

By Column Chromatography. The thin layer chromatogram (TLC) of the monomer IC (see Table I) had two spots at R_f 0.8 and 0.2 [20% diethyl ether in petroleum ether (30–75°C.), plain silica gel for TLC]. The monomer was eluted through a 230-ml. silica gel column with 20% diethyl ether in petroleum ether (30–75°C.). The final fraction had broad OH and acrylate absorptions in the infrared, suggesting that it is 12-acryloxystearic acid.

Testing for an Emulsifying Agent

Samples made from 600 parts water, 100 parts monomer, and 8 parts soap were placed in a 4-in. polymerization tube and capped. The contents were shaken for 70 min. The following soaps were tested: Siponate DS10 (sodium dodecylbenzene sulfonate), Maprofix WAC (sodium lauryl sulfonate), ORR (Office Rubber Research soap, sodium stearate, sodium palmitate, and sodium oleate), Triton X-202 (sodium alkylaryl polyether sulfonate), Triton X-400 (stearyldimethylbenzylammonium chloride), Triton N-57 (alkylaryl polyether alcohol), Triton QS-15 (sodium salt of amphoteric surfactant). Only ORR and Tritons X-400 and N-57 gave stable emulsions at room temperature. These emulsions were heated in a water bath. The Triton N-57 emulsion was stable up to 92°C. The emulsion from ORR was the only one stable in the presence of salt and at elevated temperatures.

Hydrolysis of Poly(methyl 12-Acryloxystearate)

Poly(methyl 12-acryloxystearate) was heated to dryness with an excess of aqueous sodium hydroxide. The tough, nontacky film was washed with water until its pH was neutral. Acidification of this polymer produced poly(12-acryloxystearic acid). The infrared spectrum showed broad peaks at 3000 and 1730 cm.$^{-1}$.

Preparation of Methyl 12-Hydroxystearate

12-Hydroxystearic acid (Matheson, Coleman and Bell, practical) was esterified in methanol with a trace of sulfuric acid and a small amount of 2,2-dimethoxypropane. The ester was precipitated from a methanol solution by water. It was dried and distilled twice through a Vigreaux column heated by an infrared lamp; b.p. 180–187°C. 0.025 mm. Hg.

Methyl 14-Acryloxyeicosanoate (MAE)

Distillation

The same procedure was used as described for MAS. Compound III ($n_D^{27.2}$ = 1.4520) was distilled and three fractions were collected: fraction 1, b.p. 225–238°C./0.04 mm. Hg, n_D^{23} = 1.4539; fraction 2, b.p. 238–245°C./0.04 mm. Hg, n_D^{23} = 1.4536; fraction 3, b.p. 245–255°C./0.04 mm. Hg, n_D^{23} = 1.4540. The infrared spectrum showed absorptions at 1750, 1730, 1640, 1625, 1440, and 1410 cm.$^{-1}$. Each fraction had the same spectrum but the peak ratios of the 1440 and 1410 cm.$^{-1}$ absorptions were different.

By Thin-Layer Chromatography

A plain silica gel was used for TLC. With petroleum ether (b.p. 30–75°C.), three spots were observed; R_f 0.87 (faint), 0.833 (half-moon shape), 0.833 (major spot). The half-moon line was a hair line just above the major spot.

Emulsion Tests

Emulsion tests were carried out similarly to those for MAS. Only the ORR emulsion was stable in the presence of 2% $K_2S_2O_8$. The Triton X-400 emulsion was stable in the absence of salts.

***N*,*N*-Dimethyl 12-Acryloxystearamide (DMAA)**

Thin-Layer Chromatography

A plain silica gel was used for TLC. With 1% methanol in petroleum ether (30–75°C.), three spots were observed; R_f 0.35 (major), 0.60, 0.85.

Column Chromatography

A 300-ml. column containing a silica gel bed wet with petroleum ether (30–75°C.) was prepared. About 10 ml. of DMAA was put on the column, and eluted with 1% methanol in petroleum ether (30–75°C.). Aliquots were collected and checked for impurities and DMAA by TLC. Fractions were separated. These refractive indices varied irregularly between 1.4641 and 1.4659 at 25°C. Each fraction was polymerized in bulk and gave crosslinked polymer.

Distillation

The same procedure was used as described for MAS; b.p. 200–205°C./0.013 mm. Hg, $n_{\mathrm{D}}^{24.5}$ 1.4660. The infrared spectrum showed adsorption at 1730 (s), 1615 (s), 1600 (s), 1200 (s), 1190 (m), 1050 (m), 988 (s), and 813 (m) cm.$^{-1}$. The infrared spectrum of poly(*N*,*N*-dimethyl 12-acryloxystearamide) below 1200 cm.$^{-1}$ absorbed at 1125 (s), 856 (w) cm.$^{-1}$.

Preparation of Diethyl Azobisisobutyrate

The method used was generally that of Mortimer,[4] who prepared the methyl ester.

Into a 500-ml., three-necked, round-bottomed flask equipped with a stirrer, gas inlet and exit tube, and thermometer was added 300 ml. of absolute ethanol and 30 g. of 2,2′-azobis-2-methylpropionitrile (Eastman Organic Chemicals). The flask was placed in an ice–acetone bath. Anhydrous hydrogen chloride was passed into the stirred solution and the temperature was kept below 10°C. When the temperature no longer showed a tendency to rise the addition was stopped and the inlet-outlet tubes were replaced by a drying tube. The stirring was continued overnight and the temperature was kept between −10 and 0°C. During this time the reaction mixture became homogeneous and then the diimino ester precipitated. The reaction mixture was cooled to −75°C. in a Dry Ice–acetone bath and filtered. The solid was decomposed in ice water. Sodium carbonate was added until the solution was almost neutral. It was placed in a separatory funnel and washed several times with distilled water. The product was dried as an azeotrope with benzene under vacuum; yield, 15.5 g. (32.8%); m.p. about −9°C.; NMR, quartet 6.05 τ (2), triplet 9.10 τ (3), singlet 8.89 τ (6); infrared absorptions at 1750 (s, complex), no C═N or C≡N absorptions; n_{D}^{29} 1.4259. When the reaction was run at higher temperatures the yield is increased substantially but a shoulder appeared at 1700 cm.$^{-1}$, and new absorptions at 1600 and 3475 cm.$^{-1}$. The area of these peaks was reduced by repeated aqueous sodium carbonate washes but the last traces were difficult to remove.

The purity of the azo compound was checked by running a polymerization and comparing the results with a previous run.

Reference to a company or product name does not imply approval or recommendation of the product by the U.S. Department of Agriculture to the exclusion of others that may be suitable.

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Résumé

De nombreux homopolymères et copolyméres des composés cités si-dessus (voir le titre) ont été préparés par initiation radicalaire avec du persulfate de potassium ou de l'asobisisobutyrate de diéthyle. Les copolymères montrent une combinaison de propriétés de homopolymères et de monomères. Les homopolymères sont des adhésifs très faiblement élastiques et montrent un écoulement à froid. De nombreux copolymères montrent des possibilités prometteuses dans leur usage comme adhésif.

Zusammenfassung

Einige Homopolymere und Copolymere der im Titel genannten Verbindungen wurden durch Radikalstart mit Kaliumpersulfat oder Diäthylazobisisobutyrate dargestellt. Die Copolymeren zeigen eine Kombination der Eigenschaften der Homopolymeren der entsprechenden Monomeren. Die Homopolymeren sind klebrig, sehr wenig elastisch und zeigen kaltes Fliessen. Einige Copolymere könnten als Klebestoffe verwendbar sein.

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Pyrolysis of Polyaromatic Heterocyclics

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Synopsis

The oxidative and thermal degradation of some polyaromatic heterocyclics in air and helium has been studied by dynamic thermogravimetry to 1400°C. Decomposition characteristics are the result of polymer structure, molecular weight, and method of preparation. Decomposition in air follows first-order rate laws, while degradation under inert conditions does not appear to follow simple rate laws. The activation energies for the decomposition in air are between 30 and 35 kcal./mole for most polymers investigated. Carbonaceous polymer residues at 1400°C. are present in varying quantities.

INTRODUCTION

In recent years, the search for new high molecular weight polymers with superior thermal stabilities has led researchers to investigate a new family of macromolecules known as polyaromatic heterocyclics. Vogel and Marvel[1] published their findings on wholly aromatic polybenzimidazoles and reported that these polymers are remarkably stable compounds. The preparation of fully aromatic benzoxazole polymers was recently reported by Moyer, Cole, and Anyos.[2] The results of our experiments on polybenzoxazoles indicated excellent oxidative and thermal stability.

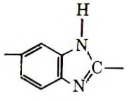
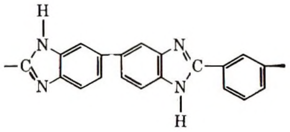
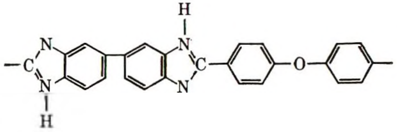
Completely aromatic polybenzothiazoles possessing superior oxidative and thermal characteristics have been prepared from bis(*o*-mercaptophenylamines) and aromatic dicarboxylic acids and their benzothiazole-forming derivatives by Hergenrother, Wrasidlo, and Levine.[3]

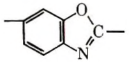
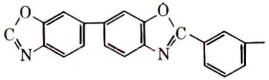
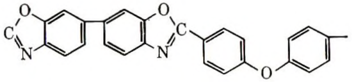
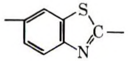
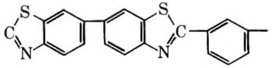
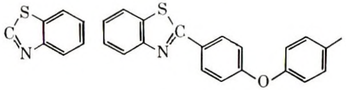
Although the majority of investigators evaluated the thermal stability of their polymers by dynamic thermogravimetry, a comparative evaluation of the polymers is not possible because the experimental conditions used by various investigators were significantly different. Thermogravimetric measurements are subject to errors which are often overlooked. These include the effect of air buoyancy and convection, the measurement of temperature, the effect of sample particle size, and the effect of atmosphere, heating rate, and heat of reaction.

The object of our work was to examine the thermal decomposition of several aromatic polyheterocyclics—polybenzimidazoles, polybenzoxazoles and polybenzothiazoles—by dynamic thermogravimetry under identical thermal environments, to study the effect of structure, method of prepara-

TABLE I

Pyrolysis of Polyaromatic Heterocyclics in Air

		Method of preparation							
Polymer	Structure	Reagents and reaction medium[a]	Poly-mer No.	Inher-ent viscos-ity	Temp. of initial wt. loss, °C.	Temp. of maxi-mum rate of wt. loss, °C.	Rate of maxi-mum wt. loss, % min.$^{-1}$	Activa-tion energy, kcal.-mole^{-1}	Fre-quency factor, min.$^{-1}$
Polybenzimidazoles Poly(2,5-benzimidazole)		3,4-Diaminobenzamide in poly(phosphoric acid)	1	—	510	620	4.00	30	10^7
		3,4-Diaminobenzamide in melt	2	0.45	(1) 520 (2) 525	625 625	3.40 3.40	29.5	10^6
Poly-2,2′-(*m*-phenylene)-5,5′-bibenzimidazole		3,3′-Diaminobenzidine + isophthalamide in melt	3	0.65	535	635	4.13	38, 40[b]	10^8
		DAB + diphenyl isophthalate	4	0.75	525	605	4.00	34	10^7
Poly-2,2′-(*p*,*p*′-oxydiphenylene)-5,5′-bibenzimidazole		DAB + 4,4′-diamino phenyl ether in melt	5	0.74	510	620	3.31	27.4	10^6
		DAB + DAPE in PPA	6	1.27	470	530	4.50	—	—

Polybenzoxazoles									
Poly(2,6-benzoxazole)		2-Amino-4-cyanophenol in PPA	7	1.54	575	660	4.4	33.6	10^{6}
		2-Amino-4-cyanophenol in melt	8	0.90	(1) 595 (2) 590	670 660	4.6 4.4	34.5	10^{6}
Poly-2,2′-(*m*-phenylene)-6,6′-bibenzoxazole)		3,3′-dihydroxybenzidine + IPAM in melt	9	0.75	550	650	3.6	36.1	10^{6}
		DHB + IPAM in PPA	10	0.65	490	560	4.5	37.2	10^{8}
Poly-2,2′-(*p*,*p*′-oxydiphenylene)-6,6′-bibenzoxazole		DHB + 4,4′-diphenyl ether dicarboxylic acid in PPA	11	0.32	505	580	3.8	34.5	10^{8}
Polybenzothiazoles									
Poly(2,6-benzothiazole)		3-Mercapto-4-amino benzoic acid in PPA	12	1.08	535	680	2.80	28.4	10^{4}
Poly-2,2′-(*m*-phenylene)-6,6′-bibenzothiazole		3,3′-dimercaptobenzidine + isophthalic acid in PPA	13	1.51	570	690	3.22	35.2	10^{8}
		DMB + IPAM in diethylaniline	14	0.48	(1) 535 (2) 525	610 610	2.80 2.80	—	—
Poly-2,2′-(*p*,*p*′-oxydiphenylene)-6,6′-bibenzothiazole		DMB + diphenyl ether diphenyl carboxylate in DEA	15	0.50	545	615	4.10	37.2	11^{10}

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[a] Abbreviations: DAB = 3,3′-diaminobenzidine; IPAM = isophthalamide; DPIP = diphenyl isophthalate; PPA = poly(phosphoric acid); DAPE = 4,4′-diamino pheny ether; DHB = 3,3′-dihydroxybenzidine; DMB = 3,3′-dimercaptobenzidine; IPA = isophthalic acid; DEA = diethylaniline; DMAC = *N*,*N*-dimethyl acetamide.

[b] 40 by the method of Freeman and Carroll.[6]

tion, and variations in molecular weight on the thermal properties, and to compare thermal degradation of these polymers on a quantitative basis.

EXPERIMENTAL

Materials

All polymers investigated were prepared in our laboratory and are listed in Table I. Two conventional synthetic routes were chosen. The first involved reaction in poly(phosphoric acid) (PPA) for several hours between 200 and 240°C. in an inert atmosphere. The second route involved melt condensations at 200–260°C. until the reaction mass solidified, followed by solid-state polymerization cycles for 1–2 hr. at 400°C. under reduced pressure. Polymer identity was confirmed by infrared spectroscopy and elemental analysis. The inherent viscosities of all polymers were measured as 0.5% solutions in concentrated sulfuric acid.

Apparatus and Procedure

Thermogravimetric experiments were carried out on an automatic Stanton (Model HT) recording thermobalance. Measurements were accurate to ±0.2 mg. Samples were ground in a mortar and pestle, screened with a microsieve, and fractions between 140 and 240 mesh selected for thermal analysis. One hundred milligram samples were placed loosely in #000 Coors glazed porcelain crucibles and heated at a rate of 6.3°C. min. from ambient temperature to 1400°C. or until 0% residue was recorded. Temperature measurements were made with a 28-gage platinum–13% rhodium–platinum thermocouple located $^1/_4$ in. above and $^1/_4$ in. from the furnace wall. Recordings were made both in air and with a constant stream of helium to maintain an inert atmosphere and to remove the volatile products.

RESULTS AND DISCUSSION

Dynamic Thermogravimetry

The thermal behavior of all polymers examined in air was characterized by a relatively slow rate of initial weight loss followed by a rapid increase with maximum rates depending on the temperature of pyrolysis. In all cases, 100% volatilization was achieved in air. Comparative weight loss curves of those polymers having similar chemical structures are shown in Figures 1–6. Figures 1 and 4 are the curves in air and helium, respectively, for three polyheterocyclics of the A-B type. Figures 2 and 5 are those of their AA-BB type analogs containing the *m*-phenylene moiety, and Figures 3 and 6 are weight loss curves of three AA-BB type polymers containing a diphenyl ether group in the polymer chain in place of the *m*-phenylene group.

In general, the rates of maximum weight loss in air were three to five times greater than those in helium; the temperature at which these maxima occurred were between 50 and 100°C. lower in air, and the temperatures of initial weight loss in helium were approximately 50–100°C. higher.

A total of 92 weight loss curves were examined and the quantitative data derived from those we considered most representative are listed in Tables I and II. Duplicate weight loss curves were obtained for several polymers with excellent reproducibility as also shown in Tables I and II. Temperatures are reported to ±10°C.

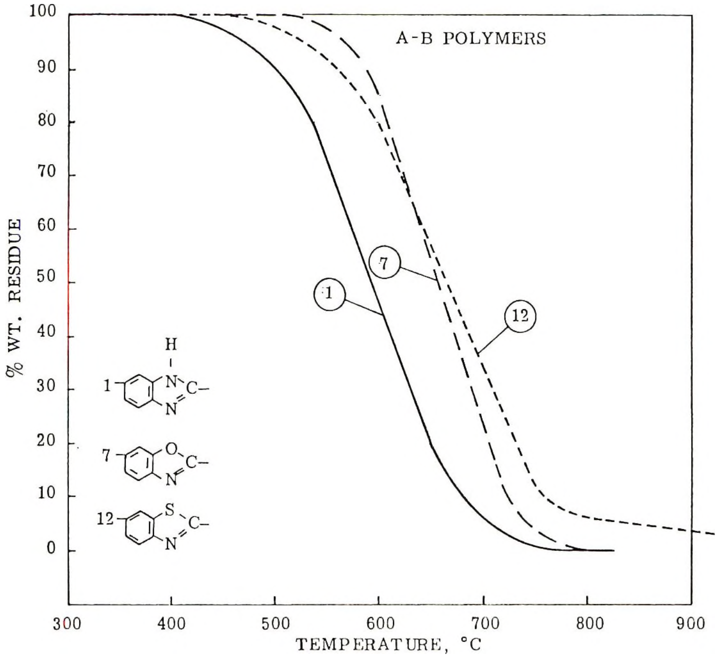
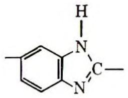
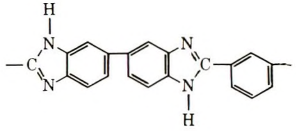
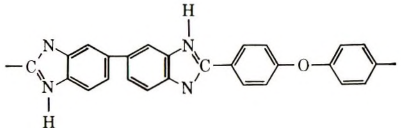


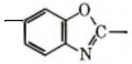
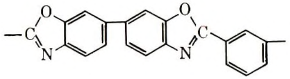
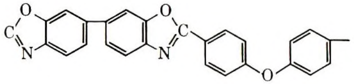
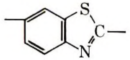
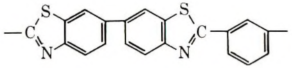
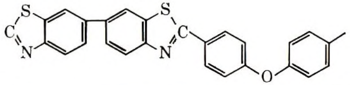
Fig. 1. Thermograms of polyaromatic heterocyclics in air.

The data given in Table I also contain information concerning the methods of preparation and the inherent viscosities of the polymers evaluated. Elemental analyses were obtained in some cases and showed that the residues were essentially carbon. Generally, the form of the weight loss curves in helium were extremely complex and indicated that a complicated degradation mechanism had taken place.

Duplicate weight loss curves obtained in helium gave essentially no differences in temperatures of initial weight loss, rates of maximum weight loss, and temperatures of maximum rates of weight loss, but the form of the curves were different, again indicating complicated degradation mechanisms.

TABLE II
Pyrolysis of Polyaromatic Heterocyclics in Helium Atmosphere

Polymer	Structure	Polymer No.	Temp. of initial wt. loss, °C.	Temp. of maximum rate of wt. loss, °C.	Rate of maximum wt. loss, %-min.$^{-1}$
Polybenzimidazoles Poly(2,5-benzimidazole)		1	650	760	0.70
		2	(1) 640	780	0.70
			(2) 640	780	0.75
Poly-2,2′-(*m*-phenylene)-5,5′-bibenzimidazole		3	560	700	0.47
		4	575	700	0.50
Poly-2,2′-(*p*-*p*′-oxydiphenylene)-5,5′-bibenzimidazole		5	560	600	1.70
		6	525	650	0.70

Benzoxazoles Poly(2,6-benzoxazole)		7	640	700	2.10
		8	(1) 660	700	2.90
			(2) 660	680	3.00
Poly-2,2′-(*m*-phenylene)-6,6′-bibenzoxazole		9	550	650	1.30
		10	500	670	1.10
Poly-2,2′-(*p,p*′-oxydiphenylene)-6,6′-bibenzoxazole		11	545	700	0.83
Polybenzothiazoles Poly(2,6-benzothiazole)		12	690	900	1.40
Poly-2,2′-(*m*-phenylene)-6,6′-bibenzothiazole		13	635	750	1.13
		14	(1) 660	750	1.30
			(2) 650	730	1.50
Poly-2,2′-(*p,p*′-oxydiphenylene)-6,6′-bibenzothiazole		15	550	750	1.00

Effect of Structure, Preparation, and Molecular Weight on the Thermal Decomposition

The relative stabilities of different polymers were compared by inspection of weight loss curves, which involved calculation of the rates of maximum weight loss, the temperatures of initial weight loss, and the temperature of maximum rates of weight loss. Results for the decomposition in air indicated the relative order of oxidative stability to be polybenzothiazoles > polybenzoxazoles > polybenzimidazoles.

Results for the decomposition in helium indicated the relative order of thermal stability to be polybenzothiazoles > polybenzimidazoles > polybenzoxazoles. However, the rate of maximum weight loss was found to be less for polybenzimidazoles than for either polybenzothiazoles or polybenzoxazoles.

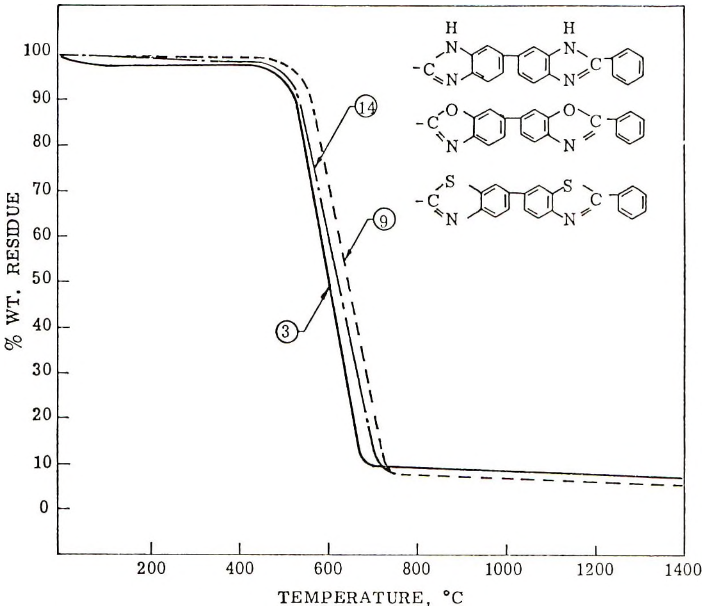


Fig. 2. Thermograms of polyaromatic heterocyclics in air.

Melt preparations gave higher initial temperatures of weight loss values in air than those prepared in PPA. This is particularly evident with polymers 5 and 6 (Table I) where the inherent viscosity of the polymer prepared in PPA is much higher than the melt polymer but is less stable. Even when the inherent viscosities are similar (polymers 9 and 10, Table I), polymers synthesized in PPA are less stable.

Again, values for the temperature of maximum rate of weight loss were greater for those of melt preparations than those of PPA preparations. Examination of rate of maximum weight loss values shows that melt preparations gave lower or same values as PPA preparations. Therefore, the method of preparation appears to influence oxidative and thermal stability, and an increase in molecular weight does not enhance oxidative or thermal stability except where the molecular weight is increased significantly from an initial low value.

The lower initial weight loss temperature exhibited by polymers synthesized in PPA does not necessarily indicate poorer stability inherent in the molecule because the presence of phosphorous containing materials is known to adversely effect stability. Also Marvel has just recently reported[4] that impurities present in commercial PPA adversely effect stability.

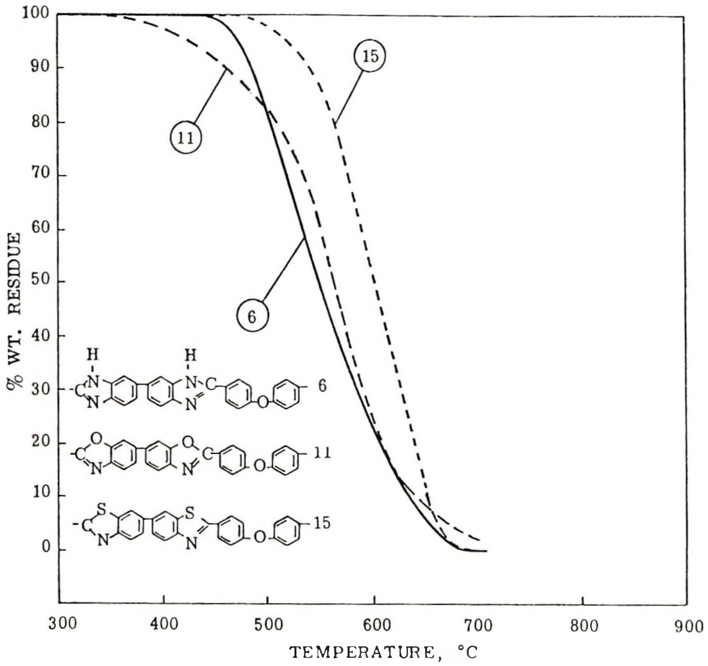


Fig. 3. Thermograms of polyaromatic heterocyclics in air.

Structural modification of mer unit structure, by use of different monomers, has a noticeable effect on both thermal and oxidative stability. This can be seen in Tables I and II.

It must be recognized that the presence of impurities can produce significant effects on polymer stability. This parameter was not examined in this work; however, the polymers were synthesized under rigorously controlled conditions such as inert atmosphere, deaerated solvents, and highest purity monomers to either minimize or preclude impurities.

Overall Activation Energies

The expressions developed by Reich[5] were used to determine the overall activation energies and frequency factors for the decomposition of the most

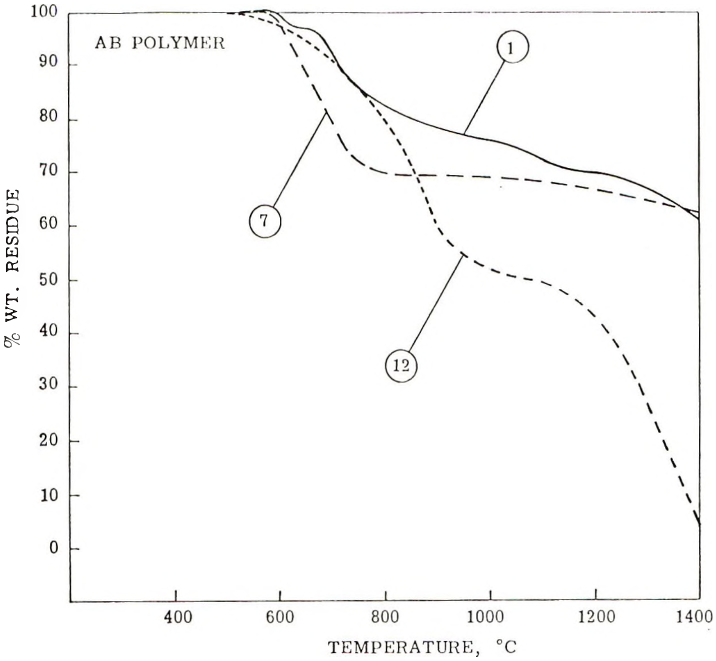


Fig. 4. Thermograms of polyaromatic heterocyclics in helium.

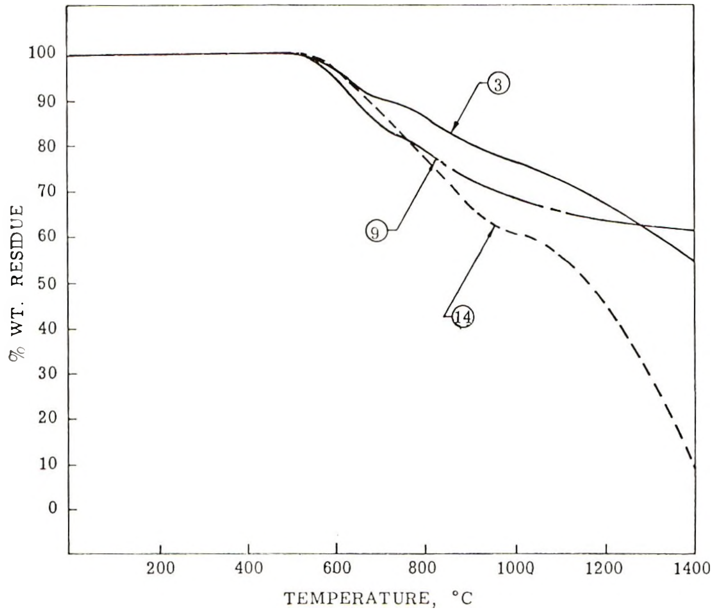


Fig. 5. Thermograms of polyaromatic heterocyclics in helium.

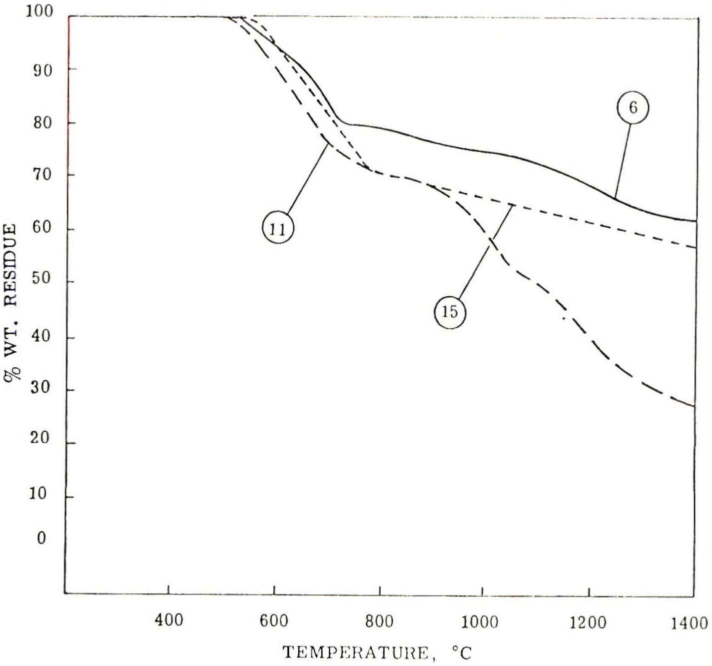


Fig. 6. Thermograms of polyaromatic heterocyclics in helium.

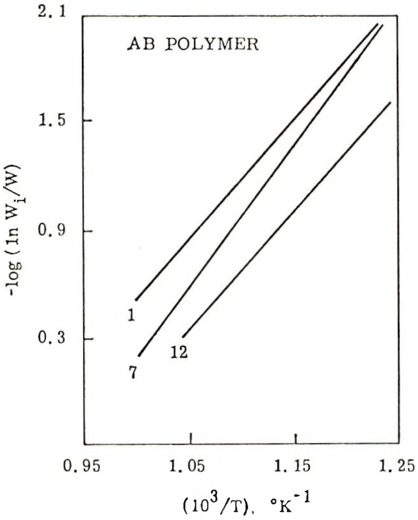


Fig. 7. Arrhenius plots for thermal degradation of polyaromatic heterocyclic in air (AB polymer).

representative polymers in air. The portions of the weight loss curves between approximately 90% and 10% weight residue were found to follow first-order kinetics. For first-order kinetics, the following equation may be written:

$$\ln\left[\ln\left(\frac{W_i}{W}\right)\right] = \frac{-E^*}{RT} + \ln\left(\frac{A\ \Delta T}{(RH)}\right)$$

where RH = constant heating rate (maintained throughout the polymer pyrolysis); ΔT = small and equal temperature intervals; E^* = energy of activation; W_i and W = weights of residues at temperatures T_i and T, respectively; A = first-order frequency factor.

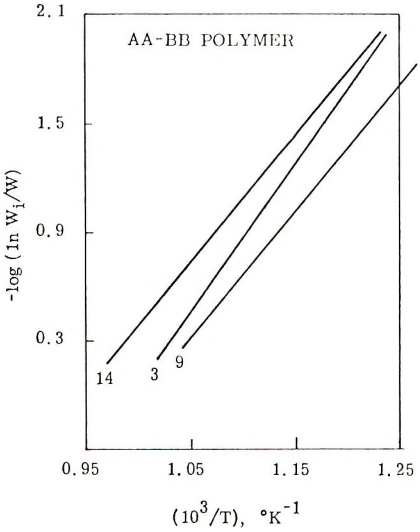


Fig. 8. Arrhenius plots for thermal degradation of polyaromatic heterocyclic in air (AA-BB polymer).

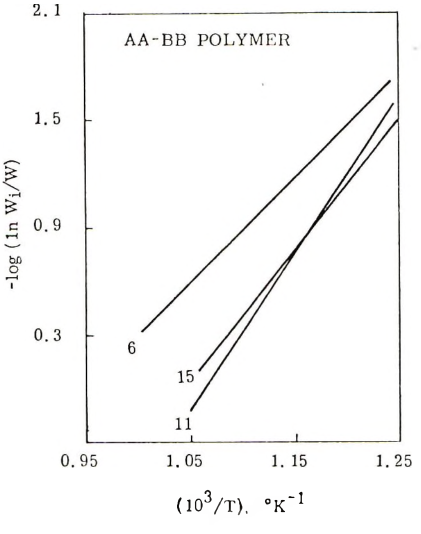


Fig. 9. Arrhenius plots for thermal degradation of polyaromatic heterocyclic in air (AA-BB polymer).

The values for W_t/W were taken at intervals of $1/T$ of $1.5 \times 10^{-5}K^{-1}$. The kinetic plots for the weight loss curves in Figures 1 to 3 are shown in Figures 7 through 9. The activation energies and frequency factors were calculated from the slopes and intercepts of the lines in Figures 7 through 9 and are listed in Table I. In view of the abnormally low frequency factor, the authors do not regard the observed activation energies for the pyrolysis as a measure of the dissociation energies of the polymers and suggest that the reactions were probably heterogeneous.

CONCLUSION

In general the pyrolytic behavior and thermal and oxidative stability of the three polyheterocyclic types studied is a result of their basic structure, method of preparation, molecular weight when large, and variation of structure. Methods of preparation and structural variations can favorably or adversely affect thermal and/or oxidative stability. Initial degradation in air, at a heat rise of 6.3°C./min., occurs between 500 and 600°C. with rates of maximum weight loss between approximately 3 and 4.5%/min. at temperatures between 550 and 680°C. Oxygen appears to enhance degradation, giving rise to higher rates and a decomposition mechanism different from that in helium. Degradation under inert conditions is extremely complex and does not follow simple kinetic rate laws. The polybenzimidazoles, polybenzoxazoles, and polybenzothiazoles show thermal stabilities superior to other organic polymers studied in the past.

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Résumé

La dégradation thermique à l'air et à l'atmosphère d'hélium de polymères aromatiques hétérocycliques a été étudiée par gravimétrie dynamique à 1400°C. La plupart des caractéristiques de décomposition thermique sont le résultat de la structure du polymère de base plutôt que des variations de poids moléculaires et des méthodes de préparation. Les vitesses de dégradation sont toutefois sensibles aux méthodes de préparation du polymère. Les décompositions à l'air suivent des lois de réaction de premier ordre. Les énergies d'activation des décompositions à l'air étaient entre 30 et 35 Kcal/mole pour la plupart des polymères étudiés. La dégradation dans des conditions inertes ne suit pas des lois cinétiques simples. Les résidus polymériques charbonnés à 1400°C sont formés dans des capacités variables.

Zusammenfassung

Der thermische Abbau von polyaromatischen Heterocyclen in Luft und Heliumatmosphäre wurde mittels dynamischer Thermogravimetrie bis 1400°C untersucht. Die Charakteristik der thermischer Zersetzung ist grössten Teils bedingt durch die Grundstuktur des Polymeren und nicht durch Variierung des Molekulargewichts und der Darstellungsmethode. Die Abbaugeschwindigkeit ist dagegen von der Darstellungsmethode abhängig. Die Zersetzung in Luft folgt dem Geschwindigkeitsgesetz erster Ordnung. Die Aktivierungsenergie der Zersetzung in Luft liegt bei den meisten untersuchten Polymeren zwischen 30 und 35 Kcal/Mol. Der Abbau unter inerten Bedingungen scheint nicht einfachen Geschwindigkeitsgesetzen zu folgen. Bei 1400°C treten kohleartige Polymerreste in wechselnder Menge auf.

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Colored Electrically Conducting Polymers from Furan, Pyrrole, and Thiophene

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Synopsis

Furan, pyrrole, and thiophene were polymerized under catalysis by trichloro- and trifluoroacetic acid to produce colored polymers which were characterized by various methods, including electronic and proton magnetic resonance spectra and electrical conductances of deeply colored trichloroacetic acid adducts. The predominant repeat units of these polymers are of the same type as those of deeply colored cyclopentadiene polymers, except that a CH_2 group is replaced by O, NH, or S.

The polymerization of furan, pyrrole, and thiophene by acidic catalysts has been described before,[1–4] but it could not be decided whether the repeat units of the products were cyclic, as in polymerized cyclopentadiene[5–8] or dihydrofuran,[9] or whether ring opening, as in polytetrahydrofuran,[10] occurs. We show that the polymers now to be described are predominantly cyclic and that hydrogen migration produces a short sequence of conjugated double bonds, which are responsible for color, proton acceptor properties, and electrical conductance.

EXPERIMENTAL

Molecular weight determinations,[6] brominations,[11] and alkaline hydrolyses[8] were carried out, respectively, in benzene or methylene chloride at 25.0°C., in carbon tetrachloride or chloroform, and in benzene–ethanol. The methods of measuring electronic, infrared, and proton magnetic resonance spectra, viscosities, proton transfer equilibria, and electrical conductance have been described.[5–7] Optical densitites, d_∞, [see eq. (4)] were estimated by plotting the observed optical densities d against the reciprocal acid concentrations, $1/[\mathrm{HB}]$; smooth graphs were obtained which could be extrapolated to $(1/[\mathrm{HB}])_{[\mathrm{HB}]\rightarrow 0}$. These optical densities were measured in nitrogen: the optical cells were fitted with rubber caps and the solutions, from which air had been removed, were introduced with the help of hypodermic syringes.

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The monomers were dried over calcium chloride or sodium sulfate, shaken with chromatographic aluminum oxide, and redistilled before use. Trichloroacetic and trifluoroacetic acid, benzene, and methylene chloride were purified as described before.[5,6,8] In polymerizing furan or pyrrole at 20°C. the acid catalyst was slowly added to the monomers. If a temperature rise occurs, if the specified concentration and time conditions are altered, or if air is freely admitted, infusible polymers, insoluble in all solvents listed in Table II, are obtained. Such materials are also formed during storage unless the products are kept in the dark in carefully evacuated, sealed-off containers.

RESULTS

Preparation of Polymers; Oxidation

The monomers were polymerized without diluent. Under condition I the reaction mixture was $10^{-4}M$ with respect to the antioxidant (α-tocopherol); under condition II the solution was refluxed with exclusion of moisture. Condition III, mentioned in Table I, refers to the removal of trichloroacetate groupings from polymers G and H, by alkaline hydrolysis,[8] benzene–ethanol and ethanol being used as solvent. The methods of isolation referred to in Table I were as follows. Method a involved precipitation of the polymer with ethanol and neutralization of traces of free acid by potassium bicarbonate under conditions which have been described.[5,6] Method b was like method a, except that pentane was the precipitant. In isolation method c, the reaction mixture was added to ethanol (40 volumes) which produced a precipitate. This was extracted with pentane, dried, dissolved in benzene (5–10%), and shaken for several hours with solid potassium bicarbonate to remove acid; the filtrate was added to pentane (10 volumes) and the precipitate was dried. In method d, the alkaline reaction mixture was filtered and added to pentane (10 volumes); the precipitate was dried, extracted with water, and redried. In method e, the alkaline reaction mixture was added to pentane (10 volumes), a precipitate was centrifuged off and discarded; the centrifugate was concentrated to a small volume and the residual solution repeatedly washed with water, thereby giving a viscous precipitate, which was separated by decantation. The precipitate solidified on drying.

A suspension of polymers G, H, or J (10 g.) in concentrated aqueous nitric acid (600 ml.) was heated to 100°C., evaporated to dryness, redissolved, and evaporated. The water-soluble product was dried and twice sublimed (100°C., 0.2 mm.), when oxalic acid (0.1–0.5 g.), identified by melting point and mixed melting point was obtained.*

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* When a deeply colored cyclopentadiene polymer[5] was oxidized under these conditions oxalic acid was obtained in similar yield.

TABLE I
Preparation of Polymers

Starting material	Catalyst	Initial concn., mole/l. Starting material	Initial concn., mole/l. Catalyst	Temp., °C.	Time, hr.	Conditions of polymerization[a]	Method of isolation[b]	Yield, %	Product designation
Furan	Cl_3COOH	11.0	2.00	20	170	I	a	20	G
Pyrrole	Cl_3CCOOH	12.0	2.00	20	190	I	b	20	H
Thiophene	F_3CCOOH	5.3	4.9	80	12	II	c	60	J
Polymer G	—	0.01–0.03	—	20	12	III	d	20	G′
Polymer H	—	0.1	—	20	1/2	III	e	20	H′

[a] I: with $10^{-4}M$ antioxidant; II: refluxed with exclusion of moisture; II: alkaline hydrolysis to remove trichloroacetate groups (see text).

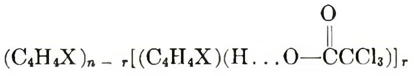
[b] Method a: precipitation with ethanol; method b; precipitation with pentane; method c: precipitation with ethanol, extraction with pentane, neutralization and precipitation with pentane; method d: alkaline filtrate precipitated with pentane; method e: alkaline solution precipitated with pentane and centrifugation (see text).

TABLE II
Solubilities of Polymers (20°C.)

Polymer	C_6H_6	CCl_4	$CHCl_3$	CH_2Cl_2	Me_2CO	Pyridine	$C_6H_5NO_2$	Dioxane	Pentane	EtOH	H_2O
G	+	+	+	+	−	+	+	+	−	−	−
G′	−	−	+	+	+			+	−	−	−
H	+		+	+				+	−	+	−
H′	−	−	+	+	+		+	+		+	−
J	+	+	+	+			+	+	−	−	−

Properties of Polymers; Analytical Data

These are in Tables II–IV. The chlorine content of polymers G and H and the results of alkaline hydrolysis (Table IV) indicate the presence of trichloroacetate groupings. This is confirmed by infrared tests (see below) and by the fact that the hydrolyzed polymers G′ and H′ contain no significant amount of chlorine. Elimination reactions, involving the loss of atoms X in each repeat unit* or uptake of oxygen may play a minor role during the polymerization of these monomers. If such side reactions are disregarded, as a first approximation, polymers G and H can be represented by the structure I,



$$(C_4H_4X)_{n-r}[(C_4H_4X)(H\ldots O-\overset{\overset{O}{\|}}{C}CCl_3)]_r$$

I

where X is O or NH, n is the number-average degree of polymerization, and r is the number of repeat units combined with the catalyst to form an ester or a salt. In the former case the acid adds to a double bond of the repeat unit, while in the latter case charge separation occurs and an acid proton is taken up by X; this is not indicated by structure I, which refers to both types of reaction.

Infrared Spectra

Table V, relating to the infrared spectra of these polymers (which were measured in potassium bromide disks within the range 2.5–20 μ) shows the total number of observed peaks and those which could be assigned to specified modes of vibration. Polymer G appears to be a trichloroacetic acid ester because of the typical ester carbonyl peak at 5.70 μ. The spectrum of polymer H contains instead a sharp and strong peak at 6.01 μ. As the same peak occurs in the spectrum of pyridinium trichloroacetate, it appears that polymer H is a salt, the proton of the trichloroacetic acid being taken up by a nitrogen of one of the repeat units. The spectra of the "hydrolyzed" polymers G′ and H′ showed no peaks between 3.5 and 6.1 μ.

Proton Magnetic Resonance Spectra

A typical spectrum is shown in Figure 1 and the peak positions of these polymers (τ values) are listed in Table VI. The τ values in columns II–IV in the range 2.50–3.84 are assigned to hydrogens bound to olefinic carbons, and the other τ values in columns V–XIV in the range 5.3–9.30, to hydrogens bound to nonolefinic carbons.[14] No assignment is made of the τ values in column I. Previous workers[14] observed that the τ values of hydrogens bound to α carbons of furan were lower than those of hydrogens bound to β carbons. For this reason we assign the τ values of polymers G and G′ in

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* Such reactions are comparable to those occurring in the addition of maleic anhydride to substituted thiophenes.[12,13]

TABLE III
Properties of Polymers

Polymer	Color of solid polymer[a]	Molecular weight $\times 10^{-3}$	No. C_4H_4X units (n)/mole	No. double bonds (m)/mole[b]	λ_{max}, mμ	$\epsilon_{max} \times 10^{-3}$, l./mole-cm.	No. conjugated double bonds/mole[c]	$[\eta]$ (25°C., C_6H_6 soln.), dl./g.	Decomposition temp., °C.
G	Red-brown	6.5 ± 0.6	76 ± 7	70 ± 7	280	24	3–4	0.055+ 0.001	>180
G′	Red-brown	5.3 ± 0.5	76 ± 7	74 ± 4	280	34	3–4	—	>180
H	Yellow-brown	0.416 ± 0.020	5.0 ± 0.5	4.0 ± 0.6	280	0.28	3–4	—	60–80
H′	Yellow-brown	0.250 ± 0.010	4.0 ± 0.5	4.9 ± 0.5	290,[d] 350[d]	0.76, 0.29	3–6	—	40–50
J	Yellowish	0.354 ± 0.020	4.0 ± 0.5	3.5 ± 0.5	310	0.090	4–5	0.028 ± 0.001	60–80

[a] All polymers are amorphous powders: the color is due to tailing of the peak in the ultraviolet into the visible range.

[b] Estimated from bromine uptake.

[c] Estimated from λ_{max} (see ref. 5).

[d] Shoulder.

TABLE IV
Analytical Composition and Alkali Consumption of Polymers

Polymer	Analysis					Equivalent weight × 10^{-3}		No. trichloroacetate residues per mole polymer
	C, %	H, %	Cl, %	N, %	S, %	From halogen content	From alkali consumption	
G	62.1	4.85	12.5			0.85 ± 0.06	0.85 ± 0.05	8.0 ± 0.8
G′	71.3	5.49	<1					
H	51.3	4.77	23.5	12.1		0.46 ± 0.03	0.43 ± 0.03	1.0 ± 0.1
H′	71.0	6.95	<1	18.1				
J	59.0	4.71			36.5			

TABLE VI
Proton Magnetic Resonance Signals (τ Values) of Polymers; Solvent: Deuterochloroform

	τ														
Polymer	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	α (obs.)	β (obs.)
G		2.50	3.58	3.78					6.2	7.7	8.41			9.18	1.9 ± 0.2	2.5 ± 0.2
G′		2.54	3.60	3.84					6.25	7.70	8.40			9.30	1.5 ± 0.2	2.4 ± 0.1
H		3.24	3.34	3.38	5.3	5.94	6.54		7.49	8.04	8.49	8.74		9.12	1.2 ± 0.1	
H′	1.84	3.18		3.79		5.78				7.87	8.57	8.68	8.80	8.92	1.5 ± 0.2	
J		2.83	2.98	3.17		5.14	6.71	6.87	7.57	7.97	8.77			9.15	2.1 ± 0.2	

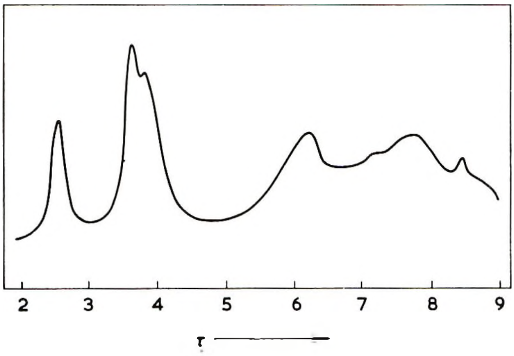


Fig. 1. Proton magnetic resonance spectrum of furan polymer G′ in deuterochloroform.

column II of Table VI to hydrogens bound to α-carbons, while the τ values in columns III and IV are assigned to hydrogens bound to olefinic carbons not in α positions. The figures in the last two columns of Table VI are defined by eqs. (1) and (2):

$$\alpha = \frac{\text{No. hydrogens of polymers bound to nonolefinic carbons}}{\text{No. hydrogens of polymers bound to olefinic carbons}} \tag{1}$$

$$\beta = \frac{\begin{array}{c}\text{No. hydrogens of furan polymers bound to}\\ \text{olefinic carbons in positions other than } \alpha\end{array}}{\begin{array}{c}\text{No. hydrogens of furan polymers bound}\\ \text{to olefinic carbons in } \alpha \text{ position}\end{array}} \tag{2}$$

and were obtained from the integrated signal areas.

TABLE V
Infrared Absorption of Polymers

Peaks[a]	Polymer G	Polymer G′	Polymer H	Polymer H′	Polymer J
No. peaks observed	26	29	19	14	24
O—H (*s*), μ	2.82	2.93	—	—	2.90
N—H (*s*), μ	—	—	2.97	3.0–3.1	—
C—H (*s*), μ	3.41, 3.50	3.40, 3.47	3.20, 3.47	3.2–3.5	3.43, 3.53
C═O, ester (*s*), μ	5.70		—	—	—
C═O, carboxylate (*s*), μ	—		6.01	—	—
C═C (*s*), μ	6.30	6.10, 6.19	6.30	6.20	6.10
C—H (d_1), μ	8.10	7.21, 8.25	7.53	7.50	8.10
C—O—C (*s*), μ	9.94	9.90	—	—	—
C—H (d_2), μ	11.35	11.32	10.80	10.90	12.0
C—Cl (*s*), μ	12.15		12.0	—	—
C—H (d_2), μ		14.75	14.8	13.5	14.7
C—S (*s*), μ				—	14.2

[a] *s* = stretching mode; d_1 = C—H in-plane deformation mode; d_2 = C—H out-of-plane deformation mode.

Proton Acceptor Properties and Electrical Conductance

On addition of trichloroacetic acid to solutions of these polymers in aprotic solvents deeply colored adducts are formed. In benzene, for instance, the electronic spectra are characterized by the peak positions and intensities listed in Table VII. The adduct formation is reversible, because by reaction with bicarbonate or other proton acceptors (e.g., ethanol) the original polymers are quantitatively recovered from the adducts. The reaction between polymer, P, and acid, HB, is formulated[5,6,8] as shown in eq. (3)

$$\mathrm{P} + \mathrm{HB} \overset{K}{\rightleftharpoons} \overset{+}{\mathrm{PH}}\ldots\overset{-}{\mathrm{B}} \tag{3}$$

where K is the equilibrium constant of proton transfer and $\overset{+}{\mathrm{PH}}\ldots\overset{-}{\mathrm{B}}$ is the deeply colored adduct; this is regarded as an ion pair containing the protonated polymer cation and the trichloroacetate anion. The K values, listed in Table VIII, were measured by the previously described technique.[5,6,8] The ratio

$$\Delta = (d - d_0)/(d_\infty - d) \tag{4}$$

where d, d_0, and d_∞ are optical densities of equilibrium solutions containing, respectively, P and $\overset{+}{\mathrm{PH}}\ldots\overset{-}{\mathrm{B}}$, P without $\overset{+}{\mathrm{PH}}\ldots\overset{-}{\mathrm{B}}$, and $\overset{+}{\mathrm{PH}}\ldots\overset{-}{\mathrm{B}}$ without P. The wavelengths of the light was near to the relevant $\lambda_{\max}$ value (see Table VII). The functional relationship between the concentration of the acid and the Δ value was similar to that shown by Figure 4 of reference 3. All log Δ–log HB plots were linear with slope 1.0 ± 0.1.

If these polymers, together with trichloroacetic acid, are dissolved in methylene chloride, the specific electrical conductance κ, is an order of magnitude larger than the κ values of solutions containing either the polymer or the acid. The effect is due to the dissociation of the ion pairs formed in reaction (3). In the concentration range, specified below, the formation of the carriers of the current is

$$\overset{+}{\mathrm{PH}}\ldots\overset{-}{\mathrm{B}} \overset{K_d}{\rightleftharpoons} \overset{+}{\mathrm{PH}} + \overset{-}{\mathrm{B}} \tag{5}$$

TABLE VII
Electronic Spectra of Trichloroacetic Acid Adducts of Polymers in Benzene at 20°C.[a,b]

Polymer	$\lambda_{\max}$, mμ	$\epsilon_{\max} \times 10^{-3}$, l./mole-cm.
G	600	4.0
G′	600	4.3
H	480	1.0
H′	460	2.1
J	520	0.10

[a] Trichloroacetic acid concentration: 1–2 mole/l.

[b] Similar $\lambda_{\max}$ and ϵ values were observed in methylene dichloride as solvent.

TABLE VIII
Equilibrium Constants of Proton Transfer K (20°C.), Limiting Molar Conductances Λ_0 (25.0°C.), and Ion-Pair Dissociation Constants K_d (25.0°C.) in Methylene Chloride

Polymer	log K	Λ_0, cm.^{2}/ohm-mole	log K_d
G	1.36 ± 0.05	15 ± 2	4.2 ± 0.2
G′	1.6 ± 0.1	20 ± 2	4.1 ± 0.2
H	1.7 ± 0.2	23 ± 2	5.4 ± 0.2
H′	1.6 ± 0.2	33 ± 3	5.4 ± 0.2
J	0.24 ± 0.03	1.1 ± 0.1	2.8 ± 0.3

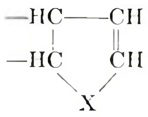
where K_d is the ion-pair dissociation constant. To estimate K_d we calculated molar electrical conductances of the ion pairs from eq. (6):

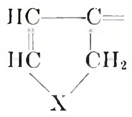
$$\Lambda = [\kappa_{\overset{+}{\mathrm{P}}\mathrm{H}\ldots\overset{-}{\mathrm{B}}} - (\kappa_{\mathrm{P}} + \kappa_{\mathrm{HB}})]/c \qquad (6)$$

where the κ's are the specific electrical conductances of the species indicated by subscripts (corrected for κ of the solvent) and c is the concentration of the ion pairs calculated from stoichiometric concentrations with the help of the known equilibrium constants of proton transfer. These Λ values were treated by Shedlovsky's method (as in ref. 8), thereby obtaining the limiting conductances Λ_0 and the K_d values in the last two lines of Table VIII. In these experiments the concentration of trichloroacetic acid was 0.100 mole/l. and the polymer concentration was varied from 10^{-2} to 10^{-5} mole/l.; at least five concentrations of each polymer were tested.

DISCUSSION

Possible structures of repeat units of these polymers are II–IV, where X is O, NH, or S. The observed unsaturation, as shown the data of Table III


IIa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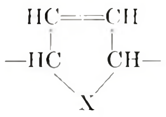
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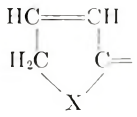
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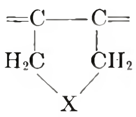
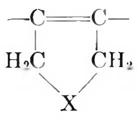
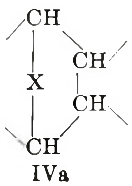

III


III


IVa

—CH=CH—CH=CH—X—

IVb

and the oxidative degradation into oxalic acid, are compatible with structures of types II or III. The nuclear magnetic resonance spectra should be a more powerful diagnostic tool, because the calculated ratios α and β, defined by eqs. (1) and (2), are as shown in Table IX.

TABLE IX
Calculated α and β Values

	IIa	IIb	III
α	1	1	∞
β	1	∞	—

The observed ratios α and β in Table VI on the other hand, are in the range 1.2–2.5; it is concluded, therefore, that these polymers are built up of both repeat units II and III and that the furan polymers contain repeat units IIa and IIb. An estimate of the proportion of the various structures can be obtained from Figure 2, in which calculated α and β values are plotted against ratios γ and δ, defined by γ = Number of repeat units (II)/Number of repeat units (III); δ = Number of repeat units (IIa)/Number of repeat units (IIb). The numerical values of γ and δ, listed in Table X were obtained from these graphs, in conjunction with the observed α and β values.

TABLE X
Proportion of Repeat Units

Polymer	γ	δ
G, G′	3 ± 1	1.5 ± 0.3
H, H′	7 ± 4	
J	2 ± 0.5	

The unsaturation of these polymers and the formation of oxalic acid on oxidation could be explained by the assumption that the polymers contain repeat units of types IVa and IVb in the ratio 1:1. This would require an α value of 1.0, which is at variance with the observed results. It follows that stepwise Diels-Alder reactions or ring-opening play no significant role, and that the predominant repeat units are of the same type as in deeply colored cyclopentadiene polymers.[5–7] In all these polymers the repeat units are cyclic, but the formation of new σ bonds at the expense of π bonds in the monomer is accompanied by migration of hydrogens.

The latter reaction appears to be responsible for the formation of conjugated double bonds, the occurrence of which is shown by the electronic spectra of the polymers (see Tables III and VII). The marked shift of the peak positions on addition of trichloroacetic acid must be due to a proton transfer to the conjugated double bonds, as in previously investigated systems.[5,6,8] This conclusion is in accordance with the numerical values of the equilibrium constants of proton transfer, listed in Table VIII. Under the conditions of these experiments protonation of the atoms X in

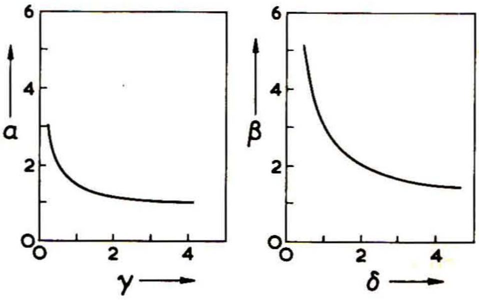


Fig. 2. Graphs for estimating proportion of different types of repeat units in polymers. For significance of symbols see text.

each repeat unit and of oxygen atoms in trichloroacetate residues attached to some of these polymers will also occur. One would expect, therefore, the addition of $(n + r)$ acid molecules to one molecule of polymer (n and r are defined as above, structure I), rather then the simple reaction (3). The participation of more than one acid molecule is incompatible, however, with the observation that the slopes of all the log Δ–log [HB] plots are unity. It appears, therefore, that the numerical values of the observed optical densities, d and d_∞, in ratio (4), at the specified wave lengths are mainly due to proton transfer to conjugated double bonds and that the contributions of those optical densities, which are due to protonation of oxygen, nitrogen, or sulfur are not significant.

Confirmatory evidence for proton uptake by conjugated double bonds are the ion pair dissociation constants, K_d, of reaction (5), which are given in Table VIII. Like the K_d values of the previously[5,6,8] investigated polycyclopentadiene–trichloroacetic acid adducts, they are larger than those of salts[15,16] containing cations with localized charge.

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Résumé

Le furane, le pyrrole et le thiophène ont été polymérisés catalytiquement par l'acide trichloro-et trifluoroacétique avec production de polymères colorés qui ont été caractérisés par différentes méthodes y compris les spectres de résonance magnétique nucléaire et électronique et les conductivités électriques des produits d'addition fortement colorés de l'acide trichloroacétique. Les unités périodiques de ces polymères sont du même type que celles des polymères cyclopentadiéniques fortement colorés, sauf que les groupes CH_2 sont remplacés par O, NH, ou S.

Zusammenfassung

Furan, Pyrrole und Thiophen wurden unter der katalytischen Einwirkung von Trichlor-und Trifluoressigsäure unter Bildung gefärbter Polymerer polymerisiert, welche mit verschiedenen Methoden wie protonmagnetische Resonanzspektroskopie und elektrische Leitfähigkeit der tiefgefärbten Trichloressigsäureaddukte charakterisiert wurden. Die vorherrschenden Kettenbausteine dieser Polymeren sind vom gleichen Typ wie diejenigen der tiefgefärbten Cyclopentadienpolymeren, ausgenommen, dass eine CH_2-Gruppe durch O, NH oder S ersetzt wird.

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Grafting in Reaction of Polyethylene and Poly(maleic Anhydride)

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Synopsis

Polyethylene has been grafted in a reaction with poly(maleic anhydride) in the presence of radical initiators. The role of oxygen, the comparison of the effectiveness of benzoyl peroxide and AIBN, and the kinetics of the reaction suggest that side chains are formed via a combination of the macroradicals of both polymers.

INTRODUCTION

In investigations of maleic anhydride homopolymerization Joshi[1,2] proved that the process is characterized by a high value of the constant for chain transfer to monomer. The cause of this phenomenon Joshi considered to be the presence of hydrogen atoms neighboring on an anhydride group. The same structure is also preserved in poly(maleic anhydride). The goal of our work was to examine whether this structure of poly(maleic anhydride) allows grafting on polyethylene in a reaction of two polymers in the presence of radical initiators.

It has already been found that grafting of maleic anhydride on polyethylene takes place readily when polyethylene is simultaneously oxidized. Oxidation causes the formation of peroxide and hydroperoxide groups.[3] Therefore the reaction of two homopolymers was conducted under the conditions described[3] elsewhere.

EXPERIMENTAL

Grafting was conducted on a low-density polyethylene (molecular weight 17,000) in the form of 0.03 mm. film, which was previously extracted with benzene for 90 hr. at 50°C. to remove substances added during manufacturing.

Poly(maleic anhydride) was obtained by the heating of a 50% solution of maleic anhydride in acetic anhydride in the presence of benzoyl peroxide (concentration of 5 g./100 g. of solution) at 100°C. for 48 hr. The polymer was precipitated in benzene and purified by dissolving in acetone and precipitation in benzene. The precipitate was washed with benzene and dried at 50°C. *in vacuo*.

Grafting was carried out in a 50-ml. conical flask with a ground-glass stopper. The poly(maleic anhydride) and the initiator were dissolved in acetic anhydride (20 g.); subsequently the film was immersed in the solution. Acetic anhydride was used as a solvent because of its influence toward increasing the rate of polyethylene oxidation.[4] The reaction was effected by heating the film in solution in air at temperatures of 90–110°C. The temperature was maintained to an accuracy of ±0.5°C. After reaction the film was extracted with boiling acetone to constant weight and subsequently the film was dried at 50°C.

The degree of grafting was determined as the percentage of increase in film weight. The method of purifying the copolymer and the method of determining the percentage of grafting were tested in our previous work.[3]

RESULTS AND DISCUSSION

Properties of Grafted Film

Under these conditions the obtained weight increase was up to 10%. The properties of grafted films were similar to those of films grafted in reaction with maleic anhydride.[3] The films were brown and insoluble and only swelled in solvents for polyethylene and poly(maleic anhydride). They did not melt, but decomposed at high temperatures.

Mechanism of Reaction

Side chains in a reaction of two polymers are formed by combination of the macroradicals of both polymers. Thus, we attempted to find the reactions which led to the formation of these macroradicals.

A comparison of the course of the reaction in air and under nitrogen showed that the presence of oxygen is of great importance. At concentration of benzoyl peroxide of 0.1 g./100 g. of solution and of poly(maleic anhydride) of 1.5 g./100 g. at 100°C. and after 20 hr. reaction, the percentage of grafting obtained in air was 4.4%, and in nitrogen 1.0%. Thus, as in the case of grafting in the reaction with a monomer,[3] polyethylene macroradicals are formed mainly by the decomposition of hydroperoxide and peroxide groups, which result from oxidation of polyethylene. The radical mechanism of the reaction, as well as the fact that the increase of the film mass is not due to diffusion of poly(maleic anhydride) into the film, were confirmed by the influence of *p*-benzoquinone on the percentage of grafting (Table I). Reactions were conducted under the above given conditions.

Poly(maleic anhydride) macroradicals resulted from the reaction between the polymer and radicals formed from the initiator. In this situation the results obtained with azobisisobutyronitrile (AIBN) should be lower than those obtained with benzoyl peroxide. The results obtained for a reaction carried out for 20 hr. at 100°C. and at a poly(maleic anhydride) concentration of 1.5 g./100 g. of solution are given in Table II.

TABLE I
Influence of *p*-Benzoquinone on Grafting

Inhibitor concentration, g./100 g.	Grafting, %
0	4.4
0.1850	2.6
0.5040	0.8

TABLE II
Grafting in the Presence of AIBN and Benzoyl Peroxide (BP)

Initiator	Initiator concentration, mole/100 g. × 10^4	Grafting, %
AIBN	4.05	1.4
BP	4.11	4.4
AIBN	8.81	2.2
BP	8.30	3.3
AIBN	12.50	2.3
BP	12.27	0.4

The results in Table II show that the percentages of grafting obtained with AIBN are lower than those with benzoyl peroxide. Moreover, the maximum grafting in the presence of AIBN appears at a higher initiator concentration than in the case of benzoyl peroxide. Such differences were not observed when the monomer was grafted on a polyethylene film,[3] but the percentages of grafting obtained with these initiators were clearly differentiated when maleic anhydride was grafted on polyethylene in a homogeneous medium, via the chain transfer reaction.[6]

Thus, it seems that the formation of polyethylene macroradicals is due to polyethylene oxidation, and that poly(maleic anhydride) macroradicals are formed in the chain transfer reaction.

Kinetics of the Reaction

This mechanism of grafting should be reflected in the kinetics of the reaction.

Figure 1 gives the curves of interdependence of the percentage of grafting and initiator concentration for different temperatures. All the curves pass through maxima. The initial increase of the percentage of grafting is most probably due to an increase of the rate of polyethylene oxidation, and consequently to the increase of the concentration of polyethylene macroradicals. The increase of initiator concentration causes an increase in the concentration of poly(maleic anhydride) macroradicals also.

At the same time, competitive reactions occur within the investigated system, among them mainly the mutual combination and disproportiona-

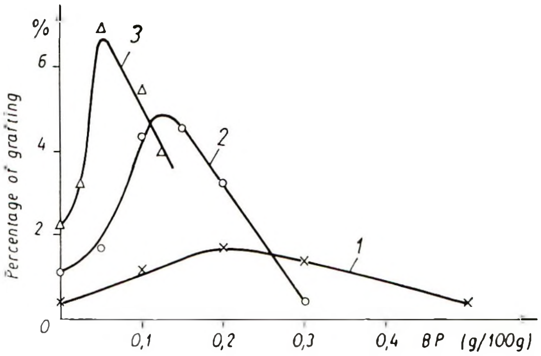

Fig. 1. Percentage of grafting vs. benzoyl peroxide concentration: (*1*) 90°C.; (*2*) 100°C.; (*3*) 110°C. Poly(maleic anhydride) concentration, 1.5 g./100 g.; time of reaction, 20 hr.

tion of poly(maleic anhydride) macroradicals. The rates of these reactions may be represented by eqs. (1)–(3).

$$R_g = k_g\,[\mathrm{PE}\cdot][\mathrm{PMA}\cdot] \tag{1}$$

$$R_c = k_c\,[\mathrm{PMA}\cdot]^2 \tag{2}$$

$$R_d = k_d[\mathrm{PMA}\cdot]^2 \tag{3}$$

Here R_g is the rate of grafting, R_d is the rate of disproportionation, and R_c is the rate of combination, and [PE·] and [PMA·] are the concentration of polyethylene and poly(maleic anhydride) macroradicals, respectively.

As clearly shown in eqs. (1)–(3), a high concentration of poly(maleic anhydride) macroradicals favors their mutual combination and disproportionation rather than grafting. The competitive reactions cause the appearance of the maximum.

The character of the curves does not change with increasing temperature, but the rate of reactions responsible for grafting and that of competitive reactions increases; this causes shifting of the maximum to lower initiator concentrations.

The situation is similar when the concentration of poly(maleic anhydride) changes. The increase of poly(maleic anhydride) concentration increases the probability of reaction with radicals formed from the initiator, and thus the concentration of poly(maleic anhydride) macroradicals increases. The appearance of a maximum on the curve of the influence of poly(maleic anhydride) concentration on the percentage of grafting (Fig. 2) is also caused by the above-described competitive reactions.

Since side chains are formed as a result of combination of polyethylene macroradicals with poly(maleic anhydride) macroradicals, the molecular weight of poly(maleic anhydride) should have a significant influence on the percentage of grafting. Results shown in Figure 3 indicate that the higher the molecular weight, the higher the percentage of grafting. Moreover, a change in the molecular weight of poly(maleic anhydride) causes a dis-

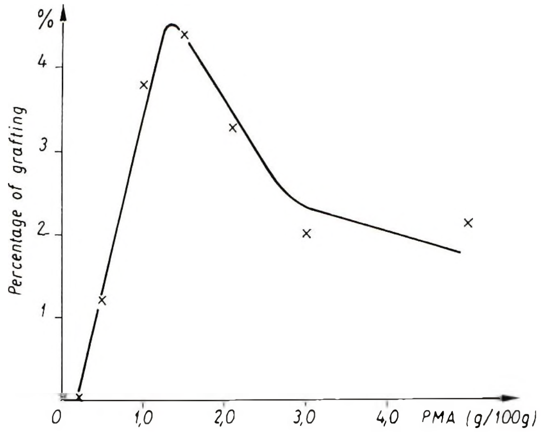

Fig. 2. Percentage of grafting vs. poly(maleic anhydride) concentration. Benzoyl peroxide concentration, 0.1 g./100 g.; temperature, 100°C.; time of reaction, 20 hr.

placement of the maximum on the curve of dependence between the percentage of grafting and the polymer concentration. This is probably due to the fact that the rate of combination and disproportionation of poly(maleic anhydride) macroradicals is related to their molar rather than their mass concentration.

If the proposed mechanism is correct, the mass of film ought to influence the percentage of grafting, as is the case in the grafting of monomer on polyethylene.[3] Because the percentage of grafting was small, it was impossible to study the reaction when the mass of film was smaller than 0.03 g. With smaller films the change of weight during reaction was within the range of the experimental error. But even in this limited range of film mass, the percentage of grafting decreased with increasing mass of film (Fig. 4).

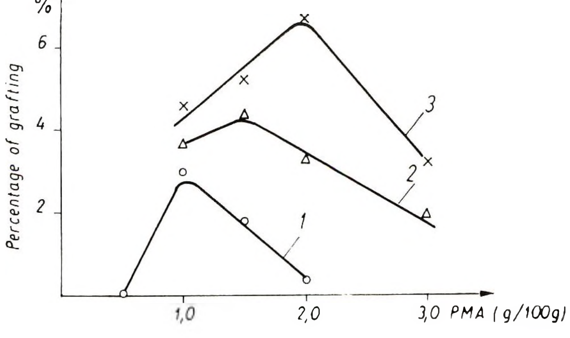

Fig. 3. Percentage of grafting vs. poly(maleic anhydride) concentration: (*1*) η_{red} = 4.66 ml./g.; (*2*) η_{red} = 5.38 ml./g.; (*3*) η_{red} = 8.99 ml./g. Benzoyl peroxide concentration, 0.1 g./100 g.; temperature, 100°C.; time of reaction, 20 hr.

The reasons for this phenomenon are most probably the same as those discussed in the paper dealing with the grafting of the maleic anhydride on polyethylene.[3] When the amount of film increases and the amount of solution is constant, the ratio of oxygen to polyethylene decreases. (The amount of oxygen in a reaction medium is limited and small because the reaction is carried out in closed flasks and at a high temperature.) This in turn brings about a lower concentration of peroxide and hydroperoxide groups formed on polyethylene, and consequently a lower percentage of grafting.

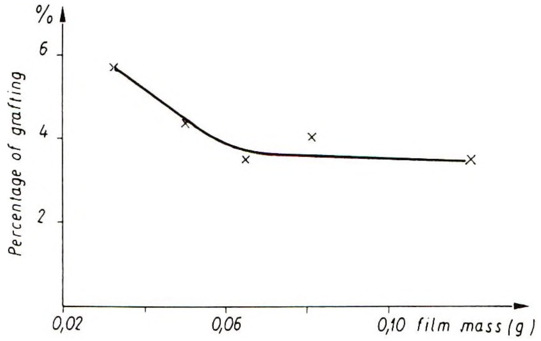

Fig. 4. Percentage of grafting vs. film mass. Temperature, 100°C.; poly(maleic anhydride) concentration, 1.5 g./100 g.; benzoyl peroxide concentration, 0.1 g./100 g.; total solution, 20 g.; time of reaction, 20 hr.

CONCLUSIONS

Graft copolymer was obtained in a reaction of poly(maleic anhydride) with polyethylene in the presence of radical initiators. Its properties were found to be similar to those obtained in the reaction of maleic anhydride with polyethylene.

Grafting in this system is due to the combination of macroradicals of both polymers. The macroradicals of polyethylene are formed mainly as a result of oxidation of polyethylene, while those of poly(maleic anhydride) are formed via a chain transfer reaction from radicals.

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Résumé

Le polyéthylène a été greffé au cours d'une réaction avec le poly(anhydride maléique) en présence d'initiateurs radicalaires. Le rôle de l'oxygène, l'efficacité relative du peroxyde de benzoyle et de l'azobisisobutyronitrile et la cinétique de la réaction elle-même suggèrent que les chaînes latérales sont formées par suite de la recombinaison de macroradicaux des deux polymères.

Zusammenfassung

Es wurde ein Propfpolymer von Polymaleinsäureanhydrid auf Polyäthylen in Gegenwart von Radikal-Initiierungsmittel erhalten. Der Einfluss von Sauerstoff, der Vergleich des Reaktionsverlaufes in Gegenwart von Benzoylperoxyd und Azodiisobuttersäuredinitril, wie auch die Reaktionskinetik suggerieren dass sich die Seitenketten infolge der Rekombination der Makroradikalen beider Polymeren bilden.

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Grafting of Maleic Anhydride on Polyethylene. I. Mechanism of Grafting in a Heterogeneous Medium in the Presence of Radical Initiators

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Synopsis

Polyethylene has been grafted with maleic anhydride, as proved by the infrared spectra and the properties of the grafted films. The influence of oxygen and a comparison of the effectiveness of benzoyl peroxide and AIBN showed that polyethylene macroradicals are formed through the decomposition of hydroperoxide and peroxide groups. Side chains of poly(maleic anhydride) are formed by a combination of polyethylene macroradicals with those of poly(maleic anhydride). This mechanism of reaction was confirmed by the influence of the amount of film, the initiator and monomer concentrations, and temperature on the percentage of grafting.

INTRODUCTION

For several years it was thought that 1,2 disubstituted ethylenes, among them maleic anhydride, do not undergo homopolymerization. Steric hindrance was considered to be the major reason for this phenomenon. Just recently, Lang and his co-workers[1–3] and also Joshi[4,5] published papers in which they described conditions under which the homopolymerization of maleic anhydride takes place. Joshi[4] found that high values of chain transfer constants to the monomer and initiator are characteristic of the polymerization of maleic anhydride. This fact he considered to be the cause of difficulty in polymerization.

There are few data, and those mainly in patent literature,[6–8] about the use of maleic anhydride as an agent to modify the properties of polyolefins. The data indicate only the possibility of grafting but do not offer any suggestion concerning the mechanism of the reaction.

The goal of this work was to study the mechanism of grafting of maleic anhydride on polyethylene.

EXPERIMENTAL

Grafting was carried out with a low-density polyethylene (molecular weight 17,000) in the form of a 0.03-mm. film. To remove substances added during manufacturing, the film was extracted with benzene at 50°C.

for 90 hr. before grafting. After this time its weight was constant. Subsequently the film was dried at 50°C. Elementary analysis and the infrared spectrum confirmed the purity of polyethylene treated in this way.

The maleic anhydride (produced by British Drug Houses Ltd.), benzoyl peroxide, azobisisobutyronitrile (AIBN) and acetic anhydride used were chemically pure and were not additionally purified before the reaction.

The reaction was carried out in a 50-ml. conical flask with a ground-glass stopper. In this flask were placed the film, benzoyl peroxide, and 20 g. of a solution of maleic anhydride in acetic anhydride. Copolymerization was effected by heating in air at temperatures of 80–110°C. The temperature was maintained to an accuracy of ±0.5°C. After reaction the film was extracted with boiling acetone to constant weight and was subsequently dried at 50°C.

The degree of grafting was measured by the percentage of weight increase. Results obtained by weighing were in accord with those from elementary analysis. Under the described conditions the obtained weight increase was up to 130%.

In all the reactions described below the concentration of the initiator is given in grams per 100 g. of solution, and the monomer concentration in weight per cent.

RESULTS AND DISCUSSION

Properties and Structure of Grafted Film

There are several lines of evidence which prove that the product of reaction is a graft copolymer.

The films with a percentage of grafting exceeding 10% are brown, similar to poly(maleic anhydride). They are insoluble in both boiling benzene and boiling Tetralin. In these solvents the films only swell. They also swell in good solvents for poly(maleic anhydride) (acetone, water, solutions of bases) at higher temperatures. Since the films, even those with a low percentage (more than 5%) of grafting, do not melt, they probably have a crosslinked structure.

The infrared spectra (Fig. 1) of the grafted film confirms the presence of poly(maleic anhydride). In comparison with the infrared spectrum of pure polyethylene, that of the graft copolymer shows very strong bands at 1779 and 1859 cm.$^{-1}$ which are characteristic of cyclic anhydrides. The band at 918 cm.$^{-1}$ is also associated with the presence of an anhydride group, and the band at 1221 cm.$^{-1}$ corresponds to the C—O stretching vibrations in the cyclic anhydride. Interesting in this spectrum is the occurrence of a strong band at 1057 cm.$^{-1}$. This band appears also in the spectrum of the monomer, but not in the spectrum of the homopolymer. These last results are in line with those reported by Joshi.[4] To verify that the appearance of this band in the spectrum of the graft copolymer is not due to the presence of traces of monomer, a number of spectra of grafted

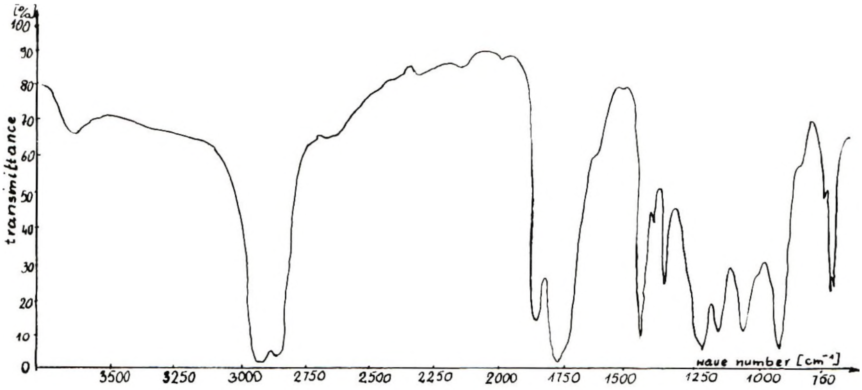

Fig. 1. Infrared spectrum of grafted film.

film were taken after prolonged extraction with boiling benzene. Maleic anhydride dissolves easily in boiling benzene, and the films swell in it a great deal. Thus, there is little probability that after extraction the monomer would still appear in the film. The infrared spectra of these samples remained the same even after extraction. Since this band does not appear in the spectrum of the hydrolyzed copolymer (Fig. 2), it is undoubtedly related to the anhydride group. So far we have not determined the reasons for the appearance of this band. It seems that Joshi's hypothesis about symmetrical conjugation imparting some aromatic character to the monomer structure, which causes the appearance of the band at 1060 cm.$^{-1}$, is not certain because in the graft copolymer there is no double C=C bond.

The analysis of further changes in the infrared spectrum of the hydrolyzed copolymer confirms the structure of the copolymer. On heating the films in boiling water, the band at 1057 cm.$^{-1}$ and other strong bands at 1859, 1779, and 918 cm.$^{-1}$, related to the anhydride group disappear. On the other hand, a broad band at 3133 cm.$^{-1}$ characteristic of the O—H group in COOH and the strong band at 1707 cm.$^{-1}$ characteristic of the C=

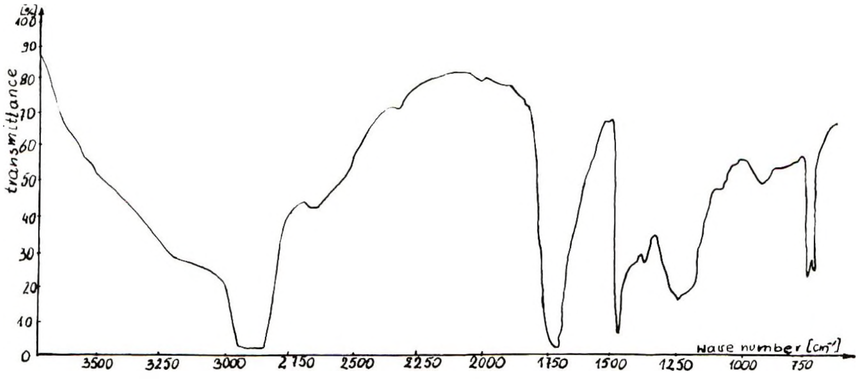

Fig. 2. Infrared spectrum of the hydrolyzed graft copolymer.

O group in COOH appear. The infrared spectrum of the hydrolyzed graft copolymer, the fact that on hydrolysis for 2 hr. in boiling water the weight of the films did not change, and the results of the elementary analysis confirm that the obtained product is not a mixture of homopolymers, and that this way of purifying the product is sufficiently effective.

Mechanism of Grafting

During the heating of polyethylene in a solution of maleic anhydride with radical initiators in air, the formation of macroradicals of polyethylene may be due to two reactions: (*1*) chain transfer from radicals formed by decomposition of the initiator or from growing chains of poly(maleic anhydride) or (*2*) decomposition of peroxide and hydroperoxide groups formed during the oxidation of polyethylene.

Macroradicals of polyethylene formed in these reactions can initiate the polymerization of maleic anhydride or combine with the growing chains of poly(maleic anhydride). Both reactions may, of course, occur simultaneously.

To determine which mechanism more closely corresponds with reality, reactions in air and nitrogen atmosphere were compared. Oxygen was removed by alternate degassing under vacuum and passing oxygen-free nitrogen through the reaction mixture. The operation was repeated three times. Grafting was conducted in a 30% solution of maleic anhydride in acetic anhydride at 100°C. (Table I).

Clearly the percentage of grafting is much higher in the presence of oxygen. The fact that oxygen is a decisive agent was confirmed by the agreement of the results from Table I (positions 4, 5, 6) with the results obtained when, upon removing the oxygen, air was passed through the solution for 6 hr. This great difference in the percentage of grafting does not result from different positions of the maximum on the curve of interdependence of the percentage of grafting and the initiator concentration. The reaction in nitrogen was studied for concentrations of benzoyl peroxide

TABLE I
Comparison of Grafting in Air and in Nitrogen

No.	Atmosphere	Time of reaction, hr.	Benzoyl peroxide concn., g./100 g.	Mass of film, g.	Mass of grafted film, g.	Percentage of grafting, %
1	N_2	20	0.1	0.0365	0.0387	6.0
2	N_2	20	0.1	0.0363	0.0386	6.3
3	N_2	20	0.1	0.0357	0.0378	5.8
4	Air	20	0.1	0.0362	0.0570	57.4
5	Air	20	0.1	0.0360	0.0562	56.1
6	Air	20	0.1	0.0364	0.0556	52.7
7	N_2	48	0	0.0364	0.0366	0.5
8	Air	48	0	0.0364	0.0445	22.2

up to 5 g./100 g. of solution; the percentage of grafting did not exceed 10%.

These results suggest that the formation of polyethylene macroradicals is due to the oxidation of the polymer.

A comparison of results obtained when grafting was conducted with benzoyl peroxide and with AIBN indicates that grafting is not based on a chain transfer reaction to polyethylene. In investigations conducted to date[9] it was found that in grafting via the chain transfer reaction AIBN is less active than benzoyl peroxide. In our work, though, we found that the results obtained with both initiators are of the same order, and even that the percentages of grafting in the presence of AIBN are a little higher. Table II includes the results of reactions conducted at 100°C. in a 30% solution of maleic anhydride in acetic anhydride with an initiator concentration of 8.3×10^{-4} mole/100 g. of solution. The reactions were conducted for 20 hr.

TABLE II
Grafting with Benzoyl Peroxide (BP) and AIBN

Initiator	Mass of film, g.	Mass of grafted film, g.	Percentage of grafting, %
AIBN	0.0362	0.0474	30.9
AIBN	0.0360	0.0452	25.5
BP	0.0357	0.0455	27.4
BP	0.0364	0.0449	23.3

Thus, polyethylene macroradicals are formed mainly through the decomposition of hydroperoxide and peroxide groups which result from the oxidation of the polymer.

It is much more difficult to decide whether the formation of the graft copolymer is due to the initiation of polymerization by the polyethylene macroradicals or to their combination with the growing chains of poly(maleic anhydride). To acquire some data on this subject, the influence of previous formation of hydroperoxide and peroxide groups on polyethylene was investigated. Since acetic anhydride accelerates oxidation of polyethylene,[10] heating of the film with benzoyl peroxide in acetic anhydride in air atmosphere was used as one method for the formation of those groups. The reaction was carried out at 100°C. for 20 hr. After oxidation the films were washed in acetone and dried at room temperature. The grafting was conducted both in air and nitrogen in a 30% solution of the monomer with benzoyl peroxide (concentration 0.1 g./100 g. of solution) for 20 hr. at 100°C. (Table III). The results in Table III point out that previous oxidation of polyethylene has no influence on the percentage of grafting.

The results of grafting on films irradiated with ultraviolet radiation in air lead to a similar conclusion. The irradiation was carried out with a

TABLE III
Grafting on Oxidized Films

Time of oxidation, hr.	Atmosphere during grafting	Percentage of grafting, %
20	Air	55.8
20	N_2	5.7
0	Air	55.8
0	N_2	6.0

S-300 lamp from a distance of 30 cm. Grafting was conducted without any initiator at 100°C. for 48 hr. in air (Table IV).

TABLE IV
Grafting on Ultraviolet-Irradiated Films

Time of irradiation, hr.	Monomer concn., %	Mass of film, g.	Mass of grafted film, g.	Percentage of grafting, %	Extinction
0	50	0.0578	0.0706	22.1	0.378
48	50	0.0610	0.0755	23.7	0.620
0	30	0.0364	0.0445	22.2	0.150
70	30	0.0409	0.0484	18.3	0.235

To determine whether this method of forming hydroperoxide and peroxide groups is effective, attempts were made to determine the quantity of the homopolymer formed during grafting. Since the quantities of homopolymer were small, precipitation could not be employed. It was decided to utilize the color of the homopolymer. Since it was found that the interdependence of extinction and concentration of the polymer changes with changing conditions of polymerization (concentration of initiator, concentration of monomer, temperature) preparation of standard curves was impossible. Therefore this method may be used only as a qualitative one, and only when the above-mentioned conditions are constant. Results from Table IV (last column) show that in the case of previous irradiation of the films, the quantity of homopolymer increases. This proves that during irradiation in the above-mentioned conditions hydroperoxide and peroxide groups are formed. The fact that those groups have no influence on the percentage of grafting is most probably related to a high constant of chain transfer to monomer during the polymerization of maleic anhydride.[4]

These investigations suggest that a combination of polyethylene macroradicals with the growing poly(maleic anhydride) chains is responsible for the formation of side chains.

To provide further proof, investigations were conducted on the influence of the length of time the solution was heated before the film was placed in it. A 30% solution of maleic anhydride, with benzoyl peroxide (0.1 g./

100 g.) was heated at 100°C. in air. After certain periods of time the film was introduced, and grafting was conducted for 20 hr. The results presented in Figure 3 are in accordance with the hypothesis that grafting is due to a combination of both kinds of macroradicals. With the increase of the time of previous heating the concentration of poly(maleic anhydride) macroradicals increases. Thus, the rate of combination of both kinds of macroradicals rises, and the percentage of grafting increases as well. But with a further rise in the concentration of poly(maleic anhydride) macroradicals their mutual combination outweighs their combination with polyethylene macroradicals. At the same time the concentration of radicals formed from benzoyl peroxide decreases but the presence of these radicals still accelerates the oxidation of polyethylene. As a result of these contrary tendencies the maximum appears at 0.5 hr. of previous heating.

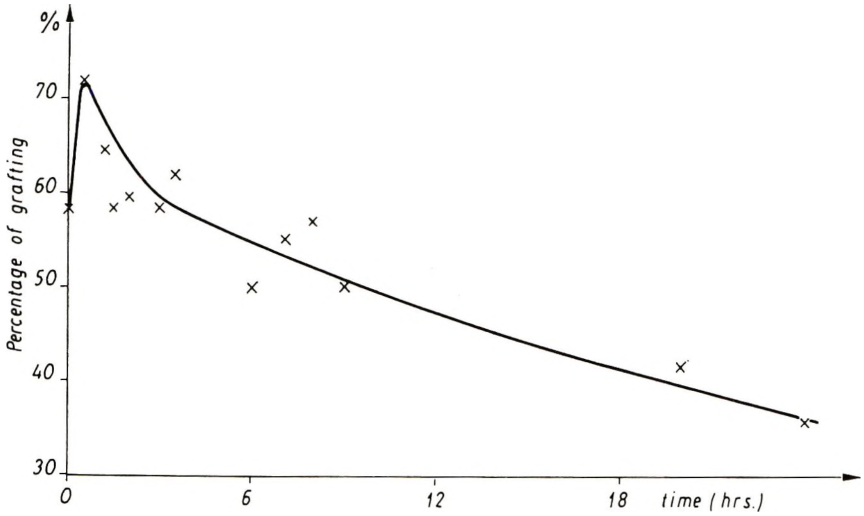

Fig. 3. Influence of time of previous heating of solution on the percentage of grafting. Temperature, 100°C.; maleic anhydride concentration, 30%; benzoyl peroxide concentration, 0.1 g./100 g. of solution; time of grafting, 20 hr.

If this mechanism of reaction is correct, then at least a number of side chains should be connected to the main chain by ether bonds. The hydrolysis of these bonds was carried out by using the method described by Houben-Weyl.[11] Grafted films were heated in a boiling mixture of NaI and 95% H_3PO_4 (weight ratio 4:5.9) for 7 hr., and subsequently were extracted with boiling acetone. After the reaction the loss of weight of the films corresponded to 40–50% of the grafted poly(maleic anhydride).

Thus, the formation of side chains is most probably due to the combination of both kinds of macroradicals. This reaction mechanism ought to be reflected in kinetic investigations.

Kinetics of Grafting

Influence of the Weight of Film. The important role of oxygen in the process of grafting suggested the need to study the influence of the weight ratio of the film and solution on the percentage of grafting. This ratio is indirectly related to that of oxygen to polyethylene.

As shown by the curves in Figure 4, when the mass of solution is constant, the percentages of grafting diminishes rapidly with increase in the film mass. This character of the curves is most probably a result of the way in which the reaction was conducted. Grafting was carried out in air but in closed flasks. Thus, the quantity of oxygen was limited and small, because the reaction took place at high temperatures (90–110°C.).

In this situation the smaller the amount of film, the higher the concentration of the hydroperoxide and peroxide groups formed, which subsequently causes a higher concentration of polyethylene macroradicals and a higher percentage of grafting. The character of curves for different concentrations of monomer (up to 75%) is the same.

As shown in Figure 4, the lower the temperature, the slower the decrease of the percentage of grafting with the increase of film weight. Most probably this is related to the decrease of the rate of polyethylene oxidation,

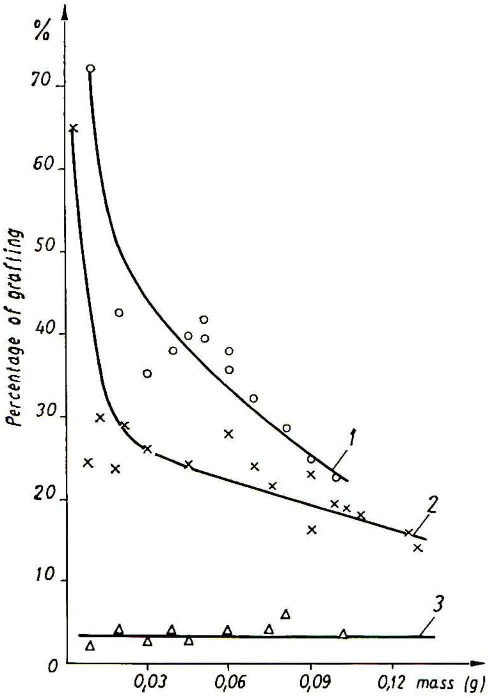

Fig. 4. Percentage of grafting vs. film weight: (*1*) 110°C.; (*2*) 100°C.; (*3*) 90°C. Benzoyl peroxide concentration, 0.1 g./100 g.; maleic anhydride concentration, 50%; time of reaction, 20 hr., weight of solution, 20 g.

which at 90°C. is so small that the amount of film was practically no influence on the percentage of grafting.

A similar situation was observed when the influence of the amount of film was investigated at a different initiator concentrations. An increase in initiator concentration causes more rapid consumption of oxygen, and thus the percentage of grafting decreases more rapidly with the increase of film mass.

To confirm that it is the oxygen which determines the character of the curves, the relative quantity of the homopolymer was established by measuring the extinction of reaction solutions.

Grafting was carried out without an initiator at 100°C. The concentration of maleic anhydride in acetic anhydride was 50% (Table V). Previously to the measuring of extinction, the solutions were diluted with acetone up to 50 ml. The measuring itself was carried out with an Electrophot I photometer at a wavelength 530 mμ.

TABLE V
Extinction of Reaction Solutions Versus the Film Weight

Film weight, g.	Extinction	Extinction: film weight ratio, g.$^{-1}$
0.0045	0.108	24.0
0.0112	0.204	21.4
0.0192	0.210	10.9
0.0504	0.258	5.1
0.0596	0.329	5.5
0.0823	0.349	4.2
0.1023	0.370	3.6

The results in Table V show that the higher the amount of film, the more homopolymer is formed. But at the same time, when the amount of film increases, the quantity of the homopolymer per unit of film mass decreases. This indicates that when the amount of oxygen is constant (the mass of solution being constant) and when the mass of film increases, the quantity of active groups also increases, but their concentration in the film diminishes because the amount of oxygen is limited and small.

Influence of Initiator Concentration. Studies were conducted over a range of maleic anhydride concentrations of 10–75% and at three temperatures: 90, 100, and 110°C. At 80°C. grafting took place at a very slow rate, and the percentage of grafting was so small that changes in the mass of film during the reaction were of the same magnitude as the error of weighing.

Figures 5 and 6 show that in all cases the curves of interdependence of percentage of grafting and initiator concentration pass through a maximum. The increase of the percentage of grafting in the first part of the curves is due to the increase of the rate of homopolymerization and of oxidation of polyethylene.

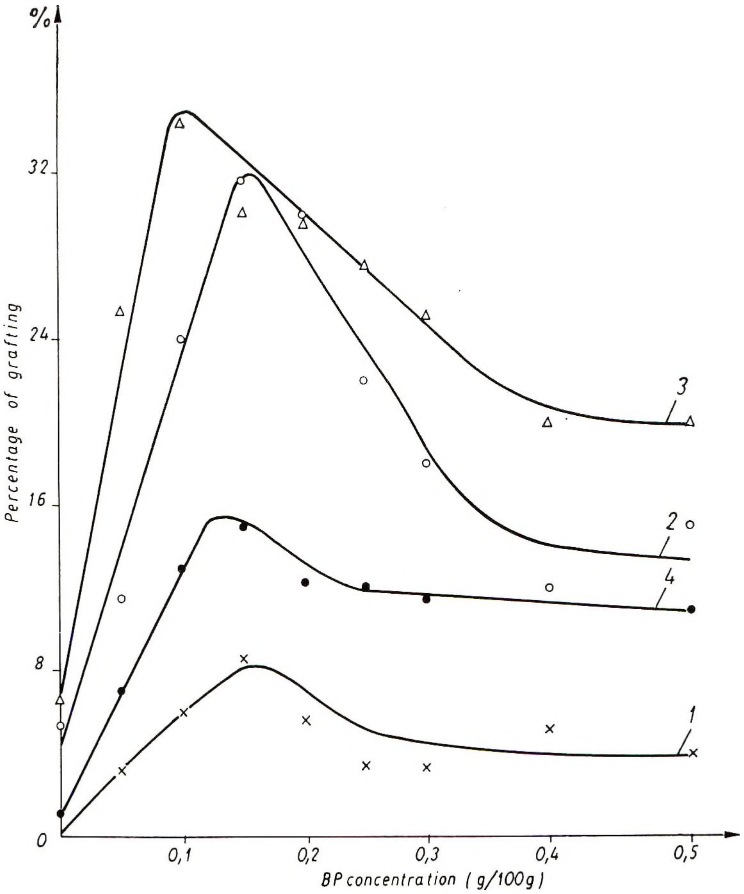

Fig. 5. Percentage of grafting vs. benzoyl peroxide concentration at various maleic anhydride concentrations: (*1*) 10%; (*2*) 30%; (*3*) 50%; (*4*) 75%. Temperature, 100°C.; time of reaction, 20 hr.

The percentage of grafting depends not only on the quantity of side chains but also on their molecular weight, which undoubtedly decreases with increasing initiator concentration. Beyond a certain point this causes a decrease in the percentage of grafting.

At the same time reactions which are competitive to grafting take place in the solution; i.e., combination and disproportionation of poly(maleic anhydride) macroradicals. When the concentration of poly(maleic anhydride) macroradicals increases, the rate of their combination and disproportionation increases faster than the rate of their combination with polyethylene macroradicals. These two factors are responsible for the decrease in the percentage of grafting.

The curves obtained at temperatures of 90 and 110°C. are analogous. The only important changes are in the positions of the maxima. With the increase of temperature the maximum shifts to lower initiator concentra-

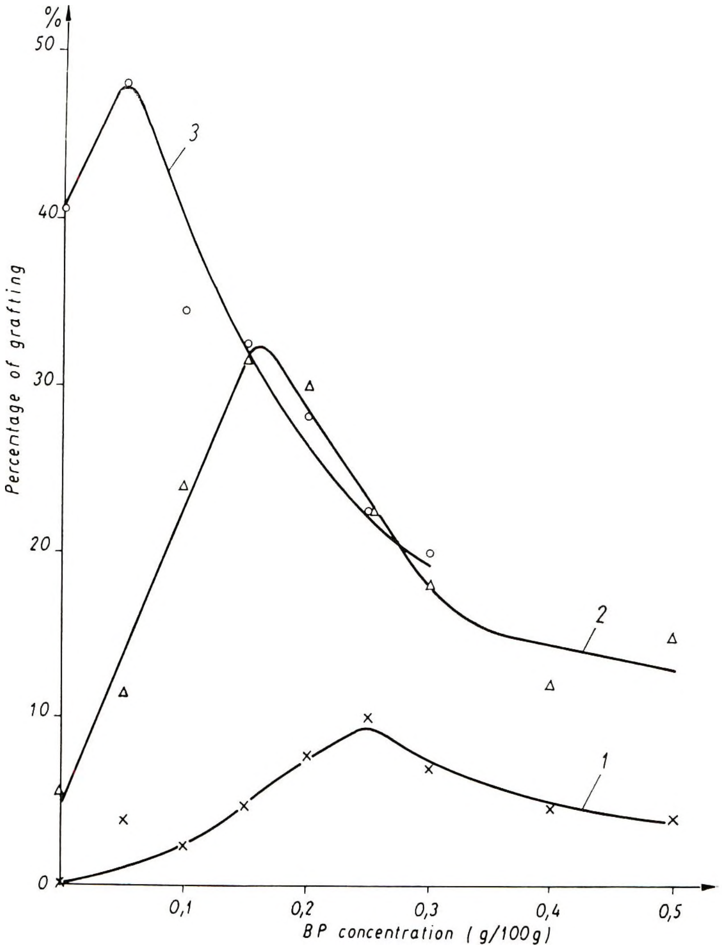

Fig. 6. Percentage of grafting vs. benzoyl peroxide concentration: (*1*) 90°C.; (*2*) 100°C.; (*3*) 110°C. Time of reaction, 20 hr.; maleic anhydride concentration, 30%.

tions, e.g., for 90°C. the maximum is at 0.15–0.25 g./100 g.; for 100°C. it is at 0.1–0.15 g./100 g., and for 110°C. it is 0–0.05 g./100 g. This is understandable because an increase of temperature causes an increase of the rates of both reactions responsible for grafting, and a more rapid decrease of the molecular weight of side chains as well.

Influence of Monomer Concentration. The curves of interdependence of the percentage of grafting and monomer concentration in Figure 7 also pass through maxima. In this case the initial increase of the percentage of grafting is due to an increase of the rate of homopolymerization. Its subsequent decrease is a result of the predominance of bimolecular termination reactions of growing chains of poly(maleic anhydride) over their combination with polyethylene macroradicals.

These curves have the same character at all three temperatures, but with

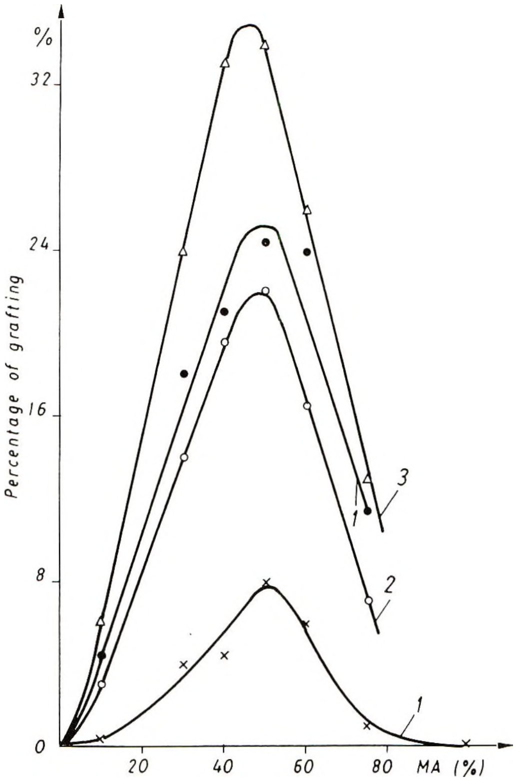

Fig. 7. Percentage of grafting vs. monomer concentration at various benzoyl peroxide concentrations: (*1*) 0; (*2*) 0.05 g./100 g.; (*3*) 0.1 g./100 g.; (*4*) 0.3 g./100 g. Temperature 100°C., time of reaction 20 hr.

increasing temperature the maximum shifts to lower monomer concentrations, e.g., for 90°C. it appears at a maleic anhydride concentration of 50%, for 100°C. at about 45%, and for 110°C. at about 30%. The reason for this shift is probably the same as in the case of the interdependence of percentage of grafting and initiator concentration. The higher the temperature, the lower the monomer concentration at which mutual reactions of poly(maleic anhydride) macroradicals predominate over their reaction with polyethylene macroradicals.

Influence of the Time of Reaction. The dependence is presented in Figure 8. After an initial rapid increase of the percentage of grafting, the curves for all monomer concentrations become parallel to the time axis. This is most probably related to the decrease in rate of polyethylene oxidation which takes place as the oxygen is consumed.

The character of the curves does not change with temperature. With increasing temperature the time in which the percentage of grafting rises rapidly decreases, e.g., for 90°C. it is over 100 hr., for 100°C. it is about 15 hr., and for 110°C. it is 6 hr.

The character of curves also does not change with initiator concentration.

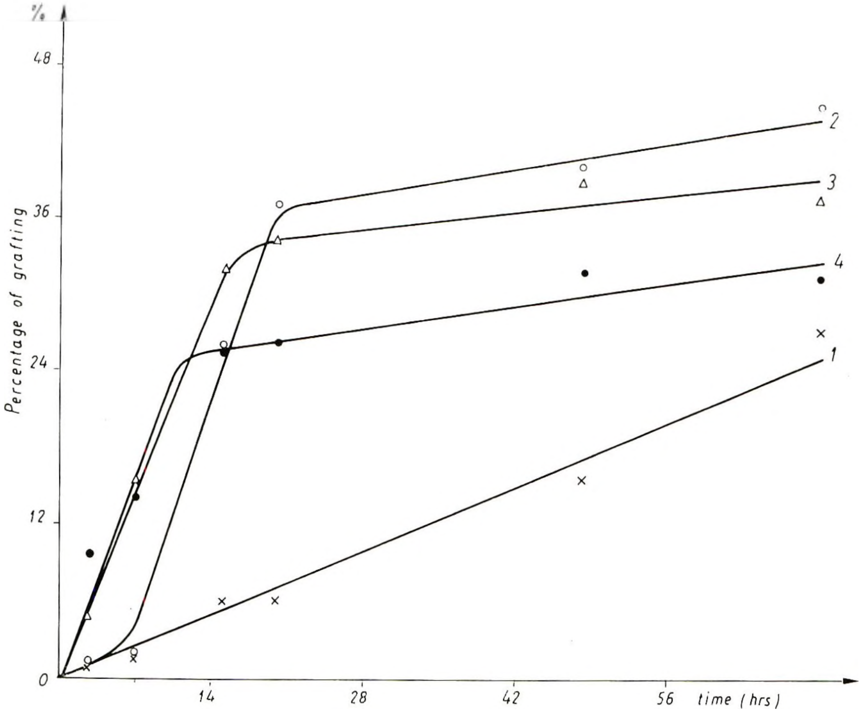

Fig. 8. Percentage of grafting vs. time of reaction at various maleic anhydride concentrations: (*1*) 10%; (*2*) 20%; (*3*) 30%; (*4*) 60%. Temperature, 100°C.; benzoyl peroxide concentration, 0.1 g./100 g.

The only difference is that the time after which the rise of the percentage of grafting is arrested is longer when the initiator concentration is smaller, e.g., at 100°C. for different maleic anhydride concentrations and at a benzoyl peroxide concentration of 0.1 g./100 g. this time is about 15 hr., while under the same conditions, but without an initiator, it is about 75–80 hr.

These phenomena are due to the fact that both higher temperature and higher initiator concentration increase the rate of polyethylene oxidation and maleic anhydride homopolymerization.

Influence of Temperature. As we could have predicted on the basis of the above-described data, the curve of interdependence of the percentage of grafting and temperature of reaction passes through a maximum. As shown in Figure 9, the curve for a maleic anhydride concentration of 50% has its maximum at 100°C. For lower monomer concentrations the maxima would appear at temperatures above 110°C. Unfortunately, the properties of the polyethylene film made experiments at higher temperatures impossible. Figure 10 shows that for higher initiator concentrations the maxima appeared at lower temperatures.

The reasons for this phenomenon are most probably the same as those described when the influence of initiator concentration on the percentage of grafting was discussed.

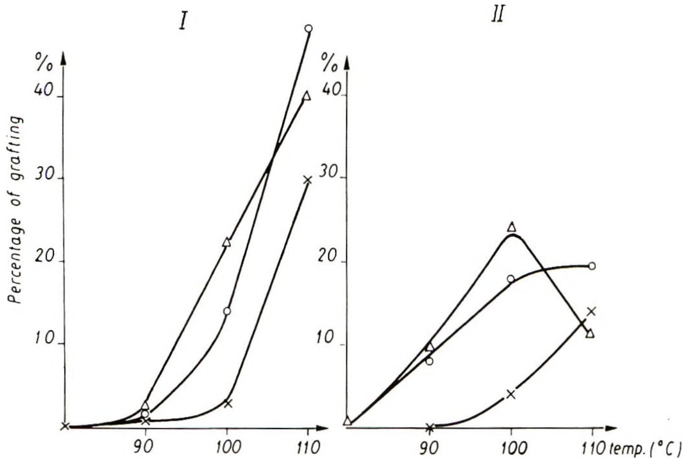

Fig. 9. Percentage of grafting vs. temperature at benzoyl peroxide concentrations of (*I*) 0.05 g./100 g. and (*II*) 0.3 g./100 g. and various maleic anhydride concentrations: (×) 10%; (○) 30%; (△) 50%. Reaction time, 20 hr.

Influence of Film Thickness. The above-described studies were conducted with films of 0.03 mm. of thickness. A comparison of the percentage of grafting obtained with films 0.03 and 0.06 mm. thick (Table VI) showed, that in this range of thickness grafting takes place not only on the surface, but throughout the film.

Thus, the kinetic dependences described in this paper are not changed by the influence of diffusion.

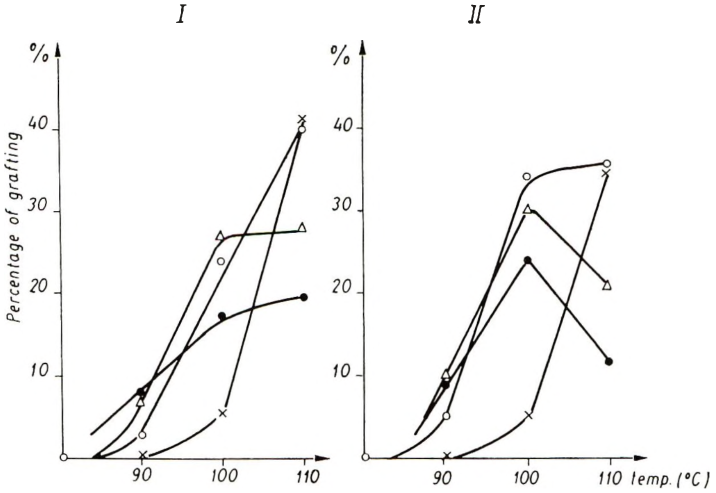

Fig. 10. Percentage of grafting vs. temperature at maleic anhydride concentrations of (*I*) 30% and (*II*) 50% and various benzoyl peroxide concentrations: (×) 0; (○) 0.1 g./100 g.; (△) 0.2 g./100 g., (●) 0.3 g./100 g. Reaction time, 20 hr.

TABLE VI
Influence of the Film Thickness

Benzoyl peroxide concn., g./100 g.	Temperature, °C.	Monomer concn., %	Time of reaction, hr.	Film thickness, mm.	Percentage of grafting, %
0	110	30	7	0.03	4.4
0	110	30	7	0.06	4.6
0	110	30	48	0.03	43.0
0	110	30	48	0.06	41.7
0.2	100	30	20	0.03	50.0
0.2	100	30	20	0.06	52.2
0.2	100	75	20	0.03	22.9
0.2	100	75	20	0.06	18.8

CONCLUSIONS

1. The studies proved that heterogeneous grafting of maleic anhydride on polyethylene is possible.

2. Comparisons of grafting in air and in nitrogen and of grafting in the presence of benzoyl peroxide and AIBN, indicate that polyethylene macroradicals are formed mainly during the decomposition of hydroperoxide and peroxide groups which in turn are a result of the oxidation of the polymer.

3. The formation of side chains is due to the combination of polyethylene macroradicals with those of poly(maleic anhydride). This conclusion is suggested by: (*a*) the lack of influence of previously formed hydroperoxide and peroxide groups on the percentage of grafting and (*b*) the appearance of a maximum on the curve of the interdependence of time of previous heating of solution and percentage of grafting.

4. Investigations on the influence of the mass of film, initiator and monomer concentrations, temperature, and reaction time on the percentage of grafting confirmed the mechanism of grafting.

5. The change of all factors which influence both reactions conditioning grafting (polyethylene oxidation and maleic anhydride homopolymerization) leads to the appearance of maxima in the dependence of the percentage of grafting on these factors. This is related to the occurrence of reactions competitive to grafting in the described system.

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Résumé

On a effectué la polymérisation greffée d'anhydride maléique sur un film de polyéthylène. La formation du copolymère greffé a été confirmé par des spectres infrarouges et par l'examen des propriétés des films greffés. L'influence de l'oxygène et la comparaison de l'efficacité du peroxyde de benzoyl de l'azobisisobutyronitrile ont demontré que les macroradicaux de polyéthylène sont formés par la décomposition des groupements peroxydiques. Des chaînes latérales sont formées à la suite de la recombinaison des macroradicaux de polyéthylène et de poly(anhydride maléique). Ce mécanisme de greffage a été confirmé par l'influence de la masse du film, de la concentration en initiateur et en monomère, et de la température sur la rendement du greffage.

Zusammenfassung

Es wurde ein Propfpolymer von Maleinsäureanhydrid auf Polyäthylen erhalten. Dies wurde auf Grund von UR-Spektraluntersuchungen und der Eigenschaften der erhaltenen Produktes festgestellt. Der Einfluss von Sauerstoff sowie der Vergleich des Reaktionsverlaufes in Gegenwart von Benzoylperoxyd und Azodiisobuttersäuredinitril bewiesen, dass die Makroradikale des Polyäthylens sich infolge der Zersetzung von Peroxyd- und Hydroperoxyd-Gruppen bilden. Die Seitenketten von Polymaleinsäureanhydrid entstehen infolge der Rekombination von Makroradikalen des Polyäthylens mit Makroradikalen des Polymaleinsäureanhydrid. Den Einfluss der Folienmasse, der Konzentration des Initiirungsmittels und des Monomers, sowie der Temperatur auf den Propfpolymerisationsprozess bestätigt der Reaktionsmechanismus.

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Grafting of Maleic Anhydride on Polyethylene. II. Mechanism of Grafting in a Homogeneous Medium in the Presence of Radical Initiators

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Synopsis

Grafting of maleic anhydride on polyethylene is found to take place also in a homogeneous medium. The course of reaction in nitrogen and in air and the influence of temperature of initiator and polymer concentrations suggest that grafting is due to the chain transfer reaction to polyethylene.

INTRODUCTION

In our previous paper[1] dealing with the grafting of maleic anhydride in a heterogeneous medium in the presence of radical initiators, it was reported that grafting is not due to a chain transfer reaction to the polymer. Under such conditions grafting is due to combination of poly(maleic anhydride) macroradicals with those of polyethylene. These latter result from oxidation of polyethylene and subsequent decomposition of hydroperoxide and peroxide groups so formed.

The goal of the present work was to examine whether the fact that the chain transfer reaction plays a negligible role in a heterogeneous grafting is due to the nature of the polyethylene–maleic anhydride system or to conditions unfavorable to this reaction at the time of interphase grafting. Thus, our efforts went in the direction of providing conditions most favorable to the chain transfer reaction.

EXPERIMENTAL

Grafting was carried out on a low-density polyethylene with a molecular weight of 15,600. Before reaction the polymer was purified by dissolving in benzene and precipitation in methanol. The reaction was conducted in xylene, in which neither benzoyl peroxide nor azobisisobutyronitrile (AIBN) influences the rate of polyethylene oxidation.[2]

The maleic anhydride, benzoyl peroxide, AIBN, and xylene used were chemically pure and were not additionally purified.

Grafting was carried out in a three-necked flask equipped with a stirrer, condenser, and thermometer. The temperature in the flask, which was heated in an oil bath, was maintained with an accuracy of ±0.5°C. In the flask were placed precisely determined amounts of polyethylene (about 0.7 g.) and xylene (about 72 g.). When the polymer was dissolved, maleic anhydride (weight concentration of 20%) and benzoyl peroxide were added. From this moment on the time of reaction was measured. After a determined time, the solution was poured into acetone and the precipitated product was centrifuged and washed in acetone until the solution over the precipitate was colorless. The product was subsequently dried at 50°C. *in vacuo* to constant weight.

To make possible a comparison of results obtained during heterogeneous and homogeneous grafting, the degree of grafting in the second instant was also determined on the basis of change in the polymer weight during reaction. Experiments conducted with pure polyethylene showed that during all operations the losses do not exceed 3–5%. This was confirmed by the agreement of the percentage of grafting determined by weighing with that from elementary analysis.

To find if this method of product purification is effective, the polymer was additionally dissolved in xylene and precipitated in acetone. The results of elementary analysis of the normally and additionally purified product were similar. Thus, the possible amounts of impurities (the monomer or homopolymer) were very small and did not influence the numerical value of the percentage of grafting.

Therefore, the applied method of polymer purification and of determining the percentage of grafting is sufficiently accurate.

RESULTS AND DISCUSSION

Properties of the Graft Copolymer

Like the copolymer obtained during heterogeneous grafting, the product with a higher percentage of grafting is brown, and the intensity of color increases with the increasing percentage of grafting. The copolymer does not dissolve in solvents of poly(maleic anhydride); at higher temperatures it only swells in water and base solutions. Since the copolymer is an anhydride, it undergoes the typical reactions of anhydrides with amines, alcohols, and water. In comparison with the properties of grafted films[1] there is one major difference. The copolymer is soluble, and it melts when heated. Solubility is clearly dependent on the percentage of grafting. Copolymer with a percentage of grafting of 8% is partially soluble in boiling benzene, while when the percentage of grafting reaches about 50% only negligible quantities of the copolymer dissolve in it. The copolymer is insoluble in CCl_4 but soluble in tetralin and xylene. When the percentage of grafting is high, the copolymer dissolves in xylene, though only after being heated for a long time at 130–140°C.

Viscosity of Graft Copolymer Solutions

The increase of molecular weight during grafting, the polymer degradation (high temperature of reaction and the presence of oxygen), as well as

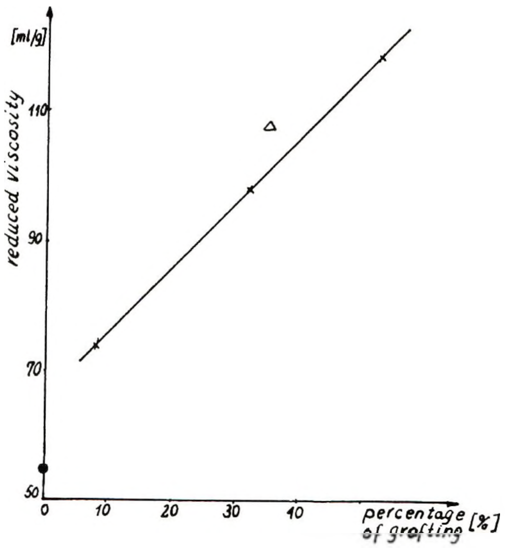

Fig. 1. Reduced viscosity vs. percentage of grafting: (●) pure polyethylene; (×) graft copolymers obtained in air; (△) graft copolymer obtained in nitrogen. Copolymer concentration, 0.0020 g./ml.; temperature, 125°C.

the formation of side chains undoubtedly influence the viscosity of solutions of the obtained graft copolymer. All these factors contribute to the complexity of the problem. Viscosity measurements were carried out solely with the aim of determining the predominant factors.

Measurements were carried out in tetralin solutions (concentration of copolymer of 0.0020 g./ml.) at 125°C. Before measurements all samples of the copolymer were purified by dissolving in boiling xylene and, after filtration, were precipitated in acetone. They were subsequently dried *in vacuo* at 50°C.

The results of measurements are presented in Figure 1. A clear increase of reduced viscosity confirms that the rise of molecular weight during grafting predominates over other factors. The very small difference between reduced viscosities of copolymers obtained in air and nitrogen shows that the extent of oxidative degradation is small.

Mechanism and Kinetics of Grafting

Influence of Oxygen and Initiator Concentration. The interdependence of the percentage of grafting and initiator concentration in air and nitrogen atmosphere is shown in Figure 2. Oxygen was removed by passing oxygen-free and dry nitrogen through the reaction mixture during the whole time of reaction. As Figure 2 shows, the percentages of grafting obtained in the reactions with low initiator concentrations in air are a little higher than those in nitrogen. The difference falls within the experimental error, but since the results in air are higher over the whole range of low initiator concentrations, it seems that oxygen increases the rate of grafting in this initiator concentration range. When the concentration of benzoyl peroxide exceeds 2.5 g./100 g. of solution, however, the percentage of grafting in nitrogen is clearly higher.

It seems that, unlike heterogeneous grafting, during the homogeneous reaction the chain transfer to polymer is responsible for the formation of polyethylene macroradicals. The formation of side chains may be due to the initiation of polymerization by these macroradicals or to their combination with those of poly(maleic anhydride). Since poly(maleic anhydride) is insoluble in xylene, it seems that it is rather the polymerization initiated by polyethylene macroradicals which is responsible for the formation of side chains.

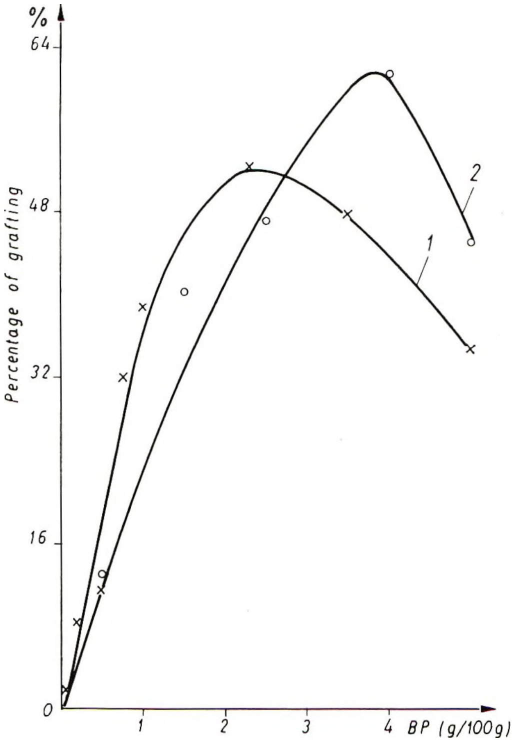

Fig. 2. Percentage of grafting vs. benzoyl peroxide concentration: (*1*) in air; (*2*) in nitrogen. Temperature, 110°C.; maleic anhydride concentration, 20%; polymer/monomer, 0.04 g./g.; time of reaction, 5 hr.

A comparison of results obtained with benzoyl peroxide and AIBN as initiators proves additionally that grafting is due to the chain transfer reaction to the polymer. The reactions were carried out with the same molar concentration of both initiators (0.0062 mole/100 g. of solution) at 110°C. for 5 hr. In the presence of benzoyl peroxide the percentage of grafting obtained was 46%, while with AIBN it was only 23.5%. Such a clear difference is caused by a much lower reactivity of radicals formed from

AIBN. Thus, it seems that the chain transfer reaction to the polymer in this system is due rather to the reaction with radicals formed from the initiator than with macroradicals of poly(maleic anhydride).

A slightly higher percentage of grafting in air than in nitrogen at the lower initiator concentrations is most probably due to the fact that polyethylene macroradicals formed during its oxidation take part in grafting.

The character of these two curves (Fig. 2) is typical for grafting resulting from the chain transfer reaction. The initial increase of the percentage of grafting is caused by an increase in the concentration of radicals formed through the decomposition of the initiator. The higher their concentration, the higher the rate of the chain transfer to the polymer. The presence of a maximum is the effect of decreasing molecular weight of the side chains and of greater consumption of monomer in the process of homopolymerization.

The shifting of this maximum to a lower initiator concentration range when grafting was conducted in air is most probably due to the inhibiting action of oxygen. The decrease of molecular weight with the increase of initiator concentration is much more pronounced in the presence of oxygen.

The fact that a maximum appears at much higher initiator concentrations than during heterogeneous grafting[1] (during a heterogeneous reaction conducted at 110°C. it appears at about 0.05 g./100 g. of solution, and during a homogeneous one at about 2.4 g./100 g.) also confirms that in the homogeneous process, the chain transfer reaction to the polymer is of major importance.

Influence of Polyethylene Concentration. To make possible a comparison with the heterogeneous reaction, the influence of polyethylene concentration was investigated in air. The reactions were carried out with different quantities of polymer, while the mass of solution was constant.

The character of the curve in this case is completely different from that for heterogeneous grafting. While the percentage of grafting during the heterogeneous reaction decreases with increasing quantity of polymer,[1] for homogeneous grafting the curve passes through a maximum (Fig. 3). This is typical for grafting via the chain transfer reaction. The increase of polyethylene concentration increases the probability of the reaction between radicals and the polymer taking place. On the other hand, the increase of polymer concentration increases the viscosity of the reaction mixture, which in turn changes the rate of the transfer reaction. These opposing tendencies result in the appearance of a maximum.

The course of the curve also explains the reasons why during heterogeneous grafting, even at high initiator concentrations, the chain transfer reaction to polyethylene does not play an important role.[1] The maximum ratio of polyethylene to maleic anhydride at which the film was completely immersed in the solution was below 0.01, while during homogeneous grafting the percentage of grafting at this ratio was only about 1%.

Influence of Time and Temperature. Figure 4 shows that the increase of the percentage of grafting in time is typical; the part parallel to the time axis is most probably a result of the consumption of radicals formed from the initiator.

The interdependence of the percentage of grafting and temperature (Fig. 5) is also in line with data published to date about other systems.[3] The appearance of a maximum is related to the fact that the increase of temperature, on one hand, increases the rates of transfer to the polymer and of monomer polymerization; on the other hand, it causes a decrease in the molecular weight of side chains.

Influence of Polyethylene Structure. To determine the influence of the structure of polyethylene, polymers with different molecular weights and different degrees of branching were used in the reaction.

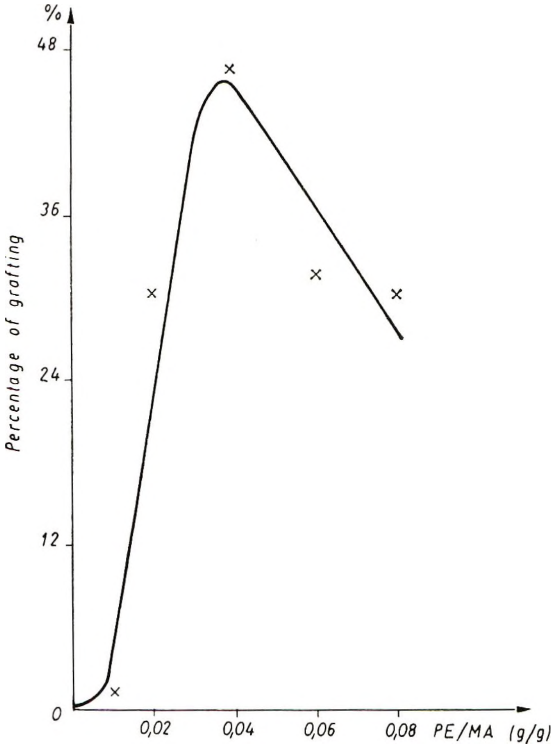

Fig. 3. Percentage of grafting vs. polyethylene–maleic anhydride ratio. Temperature, 110°C.; benzoyl peroxide concentration, 1.5 g./100 g.; maleic anhydride concentration, 20%; time of reaction, 5 hr.

The polyethylenes were purified before grafting; they were dissolved in xylene and precipitated in methanol. Grafting was carried out at 125°C. for 5 hr. at a benzoyl peroxide concentration of 1.5 g./100 g. of solution. The monomer concentration was 20%, and the weight ratio of the polymer to the monomer 0.03.

TABLE I
Grafting on Different Kinds of Polyethylene

Polyethylene	Type	Molecular weight	Degree of branching, CH_3/1000C	Percentage of grafting, %
Rigidex 50 (Phillips)	Linear	70,000	0	34.6
Rigidex 2 (Phillips)	Linear	137,400	0	46.7
Fertene D (Fawcett)	Branched	56,000	24.50	54.5
Fertene XX (Fawcett)	Branched	44,400	30.00	19.0
AC 617 (Fawcett)	Branched	5,160	47.24	21.0

The results given in Table I show that the reaction takes place also with linear polyethylene. The fact that with the increase of molecular weight the percentage of grafting also increases (compare results for Rigidex 50 with Rigidex 2), proves that endgroups do not play a decisive role in grafting. The increase of the percentage of grafting with increasing molecular weight may be due to the different courses of interdependence of the percentage of grafting and the polymer/monomer weight ratio. A similar situation is observed in the comparison of grafting on Fertene D and Fertene XX, in which the effect of the increase of molecular weight exceeds that of the increase of the degree of branching. A comparison of results for Fertene D and Rigidex 50 (close molecular weights) shows that the branched structure is favorable to grafting based on the chain transfer reaction to the polymer. Similarly, in the case of Fertene XX and AC 617, the influence of molecular weight is compensated by the diminishing of the degree of branching.

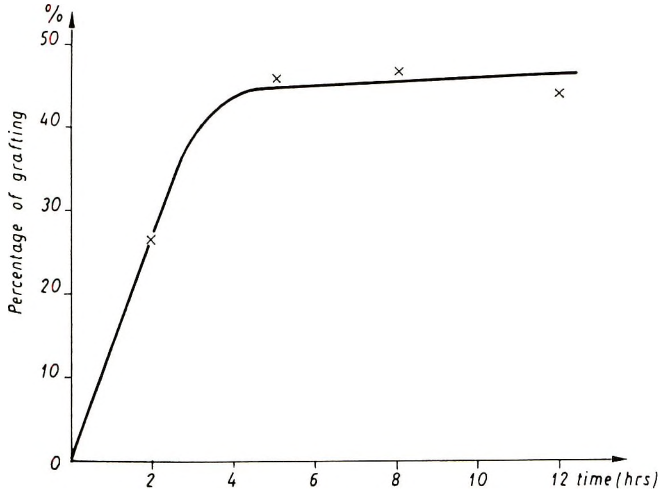

Fig. 4. Percentage of grafting vs. time of reaction. Temperature, 110°C.; benzoyl peroxide concentration, 1.5 g./100 g.; maleic anhydride concentration, 20%; polymer/monomer, 0.04 g./g.

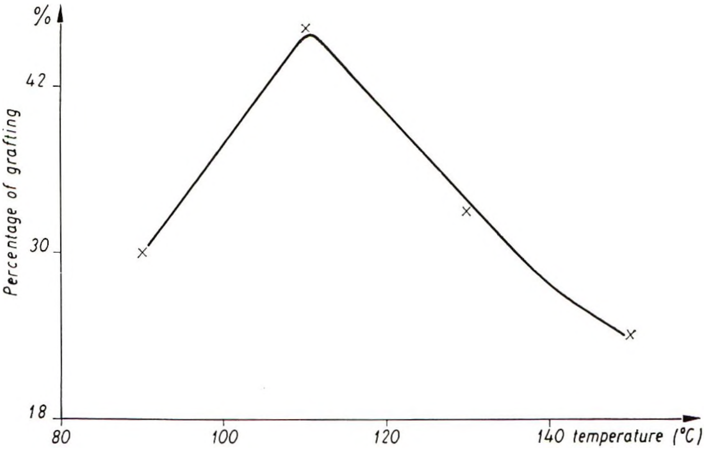

Fig. 5. Percentage of grafting vs. temperature. Benzoyl peroxide concentration, 1.5 g./100 g.; maleic anhydride concentration, 20%; polymer/monomer, 0.04 g./g.; time of reaction, 5 hr.

CONCLUSIONS

1. The studies conducted show that grafting of maleic anhydride on polyethylene, in a homogeneous medium, in the presence of radical initiators occurs mainly in effect of a chain transfer reaction to the polymer.

2. The presence of oxygen at low initiator concentrations leads to a slightly higher percentage of grafting as a result of additionally formed polyethylene macroradicals.

3. The influence of different parameters on the course of grafting of maleic anhydride is similar to that in other, already investigated, systems.

4. Grafting takes place on both linear and branched polyethylene.

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Résumé

Des études effectuées ont demontré que le greffage d'anhydride maléique sur le polyéthylène a lieu également en millieu homogène. L'allure de la réaction sous atmosphère d'azote et à l'air, l'influence des concentrations en initiateur et en polyéthylène, de même que l'influence de la température suggèrent que le greffage résulte d'une réaction de transfert de chaîne sur le polymère.

Zusammenfassung

Die in der vorliegenden Arbeit durchgeführten Untersuchungen bewiesen, dass auch im homogenem Medium in Gegenwart von Radikal-Initiierungsmittel dir Propfpolymerisation von Maleinsäureanhydrid auf Polyäthylen verläuft. Der Reaktionsverlauf

in Luft- und Stickstoff-Atmosphäre, der Einfluss der Konzentration des Initiierungsmittel und des Polyäthylens in der Lösung, sowie der Temperatur suggerieren dass es sich hier um eine Kettenübertragung auf Polyäthylen handelt.

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Theoretical Depolymerization Kinetics. IV. Effect of a Volatile Fraction on the Degradation of an Initial "Most Probable" Polymer*

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Synopsis

The effect of volatilization of molecules larger than monomer has been introduced into the solution of the Simha, Wall, and Blatz kinetic equations for the degradation of a high polymer with an initial "most probable" distribution. Equations describing the rate of sample weight and average molecular weight change result. They differ from the previous "most probable" equations primarily in the presence of an additive term representing the random splitting near the chain ends due to bond scission or transfer attack. Equations are also obtained for the rate of formation of each volatile species and hence the product distribution. The effect of volatilization of larger fragments is discussed in detail for the special case of random scission initiation. The product distribution is discussed for two special cases.

I. Introduction

The kinetic rate equations describing a general mechanism of thermal depolymerization have been derived by Simha, Wall, and Blatz.[2] The solution of the rate equations is difficult,[3-6] but it has been found possible[7,8] to find the general steady-state solution to the equations for an initial molecular weight distribution of wide interest, the so-called "most probable"[9] or exponential distribution. Simha and Wall[3,5,6,10] have emphasized that under certain conditions volatilization of molecules larger than monomer can be important and should be included in the kinetic treatment. This was not done in the original solution for the "most probable" distribution,[8] and it is the purpose of the present work to include this effect in that solution.

II. Inclusion of the Effects of Volatilization of Molecules Larger Than Monomer in the "Most Probable" Distribution Solution

The effect of volatilization will be included on the same basis as was done by Simha and Wall,[10] that is, molecules of degree of polymerization (DP) L or greater are not volatile, but those of DP of less than L are immediately removed by volatilization. The reactive intermediates (radicals) are assumed to react before volatilization regardless of DP.

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* For the preceding paper in this series see Boyd and Lin.[1]

A polymer whose molecular weight distribution is expressed by[9]

$$P_n = (M_1/x^2)[1 - (1/x)]^{n-1} \tag{1}$$

where P_n is the number of polymer molecules of DP n, $M_1 = \sum_{n=1}^{\infty} nP_n$, first moment of molecular weight distribution, $= W/m_0$, where W is sample weight and m_0 is molecular weight of a repeat unit, and x is the number-average degree of polymerization, on removal of molecules of DP $L - 1$ or less will still be characterized by a function of the form,

$$P_n = C[1 - (1/x')]^{n-1} \tag{2}$$

The physical significance of C and x' can be determined by the conditions

$$M_1 = \sum_{n=L}^{\infty} nP_n \tag{3}$$

and

$$x = \sum_{n=L}^{\infty} nP_n / \sum_{n=L}^{\infty} P_n \tag{4}$$

Substitution of eq. (2) in eqs. (3) and (4) and summing[11] results in

$$C = M_1/\{x'^2[1 - (1/x')]^{L-1}[1 + (L - 1)/x']\} \tag{5}$$

and

$$x = [1 + (L - 1)/x']x' \tag{6}$$

The rate equations, in the notation of paper I of this series,[8] under the above assumptions about volatility are as given in eqs. (7) and (8).

Nonvolatile polymer molecules:

$$\begin{gathered}\vdots\\ dP_n/dt = -(n - 1)(k_S + k_I\bar{R})P_n - k_E P_n + k_I\bar{R} \sum_{j=n+1}^{\infty} P_j + k_I(d_0/Im_0)R_n + k_T\alpha_n \\ \vdots \end{gathered} \tag{7a}$$

$$dP_L/dt = -(L - 1)(k_S + k_I\bar{R})P_L - k_E P_L + k_I\bar{R} \sum_{j=L+1}^{\infty} P_j + k_I(d_0/Im_0)R_L + k_T\alpha_L$$

Volatile polymer molecules:

$$\begin{gathered}\vdots\\ dP_m/dt = k_I\bar{R} \sum_{j=L+1}^{\infty} P_j + k_I(d_0/Im_0)R_m + k_T\alpha_m \qquad (1 < m < L) \\ \vdots \end{gathered} \tag{7b}$$

$$dP_1/dt = k_P(R - R_1) + [k_T\beta + (k_I d_0/m_0)]R_1$$

Radicals:

$$\frac{dR_n}{dt} = (2k_S + k_I\bar{R}) \sum_{=n+1}^{\infty} P_j + k_E P_{n+1} - \left(\frac{k_I d_0}{m_0} + k_P + k_T\beta\right) R_n + k_P R_{n+1} \qquad (L < n)$$

$$\vdots$$

$$\frac{dR_m}{dt} = (2k_S + k_I\bar{R}) \sum_{=L}^{\infty} P_j - \left(\frac{k_I d_0}{m_0} + k_P + k_T\beta\right) R_m + k_P R_{m+1} \qquad (1 < m < L) \qquad (8)$$

$$\vdots$$

$$\frac{dR_1}{dt} = (2k_S + k_I\bar{R}) \frac{M_1}{x} + k_E P_2 + k_E \frac{M_1}{x} - \left(\frac{k_I d_0}{m_0} + k_T\beta\right) R_1 + k_P R_2$$

The steady-state radical concentration R_n is given by the solution to eq. (8), with the left-hand side set equal to zero, in terms of P_n's as,[8]

$$R_n = (1 + \gamma)^n \sum_{k=n+1}^{\infty} \left[\frac{(2k_S + k_I\bar{R}) \sum_{j=k}^{\infty} P_j + k_E P_k}{k_P(1 + \gamma)^k}\right] \qquad n > L \qquad (9)$$

where $1/\gamma = 1/\gamma(x) = k_P/(k_T\beta + k_I d_0/m_0)$, the average zip length between initiation and transfer or termination,[8] and

$$\beta = \begin{cases} 1 & \text{first-order termination} \\ R/V = \bar{R}(x), & \text{total radical concentration, second-order termination} \end{cases}$$

where

$$\bar{R}(x) = [(2k_S d_0/k_T m_0) + (2k_E d_0/k_T m_0 x)]^{1/N}$$

$N = 1$ first-order termination
$N = 2$ second-order termination

The solution then proceeds in a manner similar to that used in Part I.[8] Substitution of eq. (2) in eq. (9) and performing the summations results in,

$$R_n = \{[(2k_S + k_I\bar{R})x'/k_P] + (k_E/k_P)\}[(x' - 1)/1 + x'\gamma(x)]P_n \qquad (10)$$

Differentiation of eq. (2) with C defined by eq. (5) results in,

$$\frac{dP_n}{dt} = \left\{\frac{1}{M_1}\frac{dM_1}{dt} - \left[\frac{2}{x'} + \frac{L(L-1)}{x'^2(x'-1)\left(1 + \left(\frac{L-1}{x'}\right)\right)}\right]\frac{dx'}{dt} + \frac{n-1}{x'(x'-1)}\frac{dx'}{dt}\right\} P_n \qquad (11)$$

Substitution of eqs. (2), (10), and (11) in the rate equations [eqs. (7a) and (7b)] and performing the summations gives eqs. (12) and (13).

First-order and disproportionation termination:

$$\frac{1}{M_1}\frac{dM_1}{dt} + \frac{n-1}{x'(x'-1)}\frac{dx'}{dt} - \left[\frac{2}{x'} + \frac{L(L-1)}{x'^2(x'-1)\left(1+\dfrac{L-1}{x'}\right)}\right]\frac{dx'}{dt}$$

$$= -(n-1)[k_S + k_I\bar{R}(x)] - k_E + k_I\bar{R}(x)(x'-1)$$

$$+ \left(\frac{k_I d_0}{m_0} + k_T\beta\right)\left\{\frac{[2k_S + k_I\bar{R}(x)]x' + k_E}{k_P}\right\}\frac{x'-1}{1+x'\gamma(x)} \tag{12}$$

Recombination termination:

$$\frac{1}{M_1}\frac{dM_1}{dt} + \frac{n-1}{x'(x'-1)}\frac{dx'}{dt}$$

$$- \left[\frac{2}{x'} + \frac{L(L-1)}{x'^2(x'-1)\left(1+\dfrac{L-1}{x'}\right)}\right]\frac{dx'}{dt} = -(n-1)[k_S + k_I\bar{R}(x)]$$

$$- k_E + k_I\bar{R}(x)(x'-1) + \frac{k_I d_0}{m_0}\left\{\frac{[2k_S + k_I\bar{R}(x)]x' + k_E}{k_P}\right\}\frac{x'-1}{1+x'\gamma(x)}$$

$$+ \frac{(n-1)d_0k_T}{2m_0x'^2}\left\{\frac{[2k_S + k_I\bar{R}(x)]x' + k_E}{k_P}\right\}^2\left(\frac{x'-1}{1+x'\gamma(x)}\right)^2 \tag{13}$$

Equations for x' alone can be determined from eqs. (12) and (13);[8] since they must be valid for any value of n, the coefficients of $n - 1$ may be equated leading to eqs. (14) and (15).

First-order and disproportionation termination:

$$[1/x'(x'-1)](dx'/dt) = -[k_S + k_I\bar{R}(x)] \tag{14}$$

Recombination termination:

$$[1/x'(x'-1)](dx'/dt) = -[k_S + k_I\bar{R}(x)]$$

$$+ (k_Td_0/2m_0x'^2)\{([2k_S + k_I\bar{R}(x)]x' + k_E)/k_P\}^2\{(x'-1)/[1+x'\gamma(x)]\}^2 \tag{15}$$

With the use of eq. (14) in eq. (12) or eq. (15) in eq. (13) there result eqs. (16) and (17), respectively.

First-order and disproportionation termination

$$\frac{1}{M_1}\frac{dM_1}{dt} = -\{[2k_S + k_I\bar{R}(x)]x' + k_E[1+\gamma(x)]\}/[1+x'\gamma(x)]$$

$$- \{(k_S + k_I\bar{R})[L(L-1)/(x'+L-1)]\} \tag{16}$$

Recombination termination:

$$\frac{1}{M_1}\frac{dM_1}{dt} = -\left\{[2k_S + k_I\bar{R}(x)]x' + k_E\right\}\left(1 - \frac{k_I d_0}{m_0 k_P}\left[\frac{x'}{1 + x'\gamma(x)}\right] - \frac{k_T d_0 x'}{m_0 k_P{}^2}\left\{[2k_S + k_I\bar{R}(x)]x' + k_E\right\}\left[\frac{1}{1 + x'\gamma(x)}\right]^2\right) - \left[(k_S + k_I\bar{R})\,\frac{L(L-1)}{x' + L - 1}\right] \tag{17}$$

The composition of the volatile fraction may be obtained from the equations for the volatile polymer molecules, P_m, eq. (7b). First, the steady-state solution for the radicals R_m is found[11] from eq. (8) to be,

$$R_m = C'(1+\gamma)^m - (1+\gamma)^m \sum_{k=0}^{m} \frac{(2k_S + k_I\bar{R})M_1}{k_P(1+\gamma)^k x} \tag{18}$$

where the identity $\sum_{j=L}^{\infty} P_j = M_1/x$ has been used. The constant C' can be determined from the boundary condition supplied by eq. (8) for the $L - 1$ radical,

$$0 = \left(\frac{2k_S + k_I\bar{R}}{k_P}\right)\frac{M_1}{\chi} - (1+\gamma)R_{L-1} + R_L \tag{19}$$

so that,

$$R_m = (1+\gamma)^m\left[\frac{R_L + \left(\dfrac{2k_S + k_I\bar{R}}{k_P}\right)\dfrac{M_1}{x}}{(1+\gamma)_L} + \left(\frac{2k_S + k_I\bar{R}}{k_P}\right)\frac{M_1}{x}\sum_{k=m+1}^{L-1}(1+\gamma)^{-k}\right] \tag{20}$$

where R_L is given by eqs. (10) and (2) as,

$$R_L = \left\{[(2k_S + k_I\bar{R})x' + k_E]/k_P\right\}\left(\frac{x' - 1}{1 + x'\gamma}\right)\frac{M_1}{x'^2\left(1 + \dfrac{L-1}{x'}\right)} \tag{21}$$

The sum in eq. (20), $\sum_{k=m+1}^{L-1}(1+\gamma)^{-k}$ is evaluated[11] as $= -[(1+\gamma)^{-L} - (1+\gamma)^{-m-1}]/[1 + (1/\gamma)]$. Thus eq. (7b), written as

$$\frac{dP_m}{dt} = k_I\bar{R}\frac{M_1}{x} + k_P\gamma R_m \qquad 1 < m < L - 1 \tag{22}$$

with R_m from eq. (20) determines the rate of volatile molecule formation.

III. Discussion

Inspection of eqs. (14) and (16) or (15) and (17) reveals that the principal effect of the volatile fraction is to contribute an additive term to the rate of weight loss, the form of the molecular weight change equation is unaltered. However, the number-average degree of polymerization x is replaced by the closely related variable, x', $(x = x' + L - 1)$, everywhere except in $\gamma(x)$ and $R(x)$. In the event the average DP remains much higher than $L - 1$, the largest volatile molecule, the distinction between x and x' becomes insignificant.

The additive term in the weight loss rate due to volatilization of molecules larger than monomer, $(k_S + k_I\bar{R})[L(L - 1)]/x$, is the same as the rate that would result from chain splitting within $L - 1$ units of the chain ends and the resultant volatilization of such fragments after their radicals have terminated without unzipping.[3]

The conditions under which the effects of volatilization are important may be investigated by means of eqs. (16) and (17). Equation (16), for example, shows that if $L/x[(L - 1)/x]$ is small compared to one (and usually it will be) volatilization of larger fragments will be important only in the short zip limit. In this limit $(1/\gamma \ll x')$, eq. (16) becomes,

$$\frac{1}{M_1}\frac{dM_1}{dt} = -k_S\left[2\frac{1}{\gamma} + \frac{L(L-1)}{x}\right] - k_I\bar{R}\left[\frac{1}{\gamma} + \frac{L(L-1)}{x}\right] - k_E\frac{1+\gamma}{\gamma x'} \tag{23}$$

If $(L - 1)/x \ll 1$, then volatilization effects will be negligible for zip lengths $1/\gamma$ of the order of L or larger. However, if $L - 1$ is not much smaller than x, then the effects of volatilization are important at larger values of the zip length $1/\gamma$ relative to L. Since at short zip lengths the molecular weight is rapidly degraded compared to conversion, the condition $L - 1 \ll x$ may not be maintained through the degradation and the effects of volatile fragments may be more important in the later stages than initially.

These effects have been investigated in more detail for the special case of random chain initiation (no transfer or endgroup initiation, $k_I = k_E = 0$). Equations (16) and (14) become

$$\frac{dM_1}{dt} = -k_S\left[\frac{2x'}{1+\gamma x'} + \frac{L(L-1)}{x' + L - 1}\right]M_1 \tag{24}$$

$$\frac{dx'}{dt} = -k_S x'^2 \tag{25}$$

where $x' \gg 1$ has been assumed. These equations can be combined and integrated to yield,

$$\ln\,(M_1/M_1{}^0) = 2\ln\left[\tilde{x}'\left(\frac{\gamma x'^0 + 1}{\tilde{x}'x'^0\gamma + 1}\right)\right] + \frac{L}{x'^0}\left[-\frac{1}{\tilde{x}'} + 1 + \frac{x'^0}{L-1}\ln\frac{\left(\tilde{x}' + \dfrac{L-1}{x'^0}\right)}{\tilde{x}'\left(1 + \dfrac{L-1}{x'^0}\right)}\right] \tag{26}$$

where $\tilde{x}' = x'/x'^0$ (the superscript zero indicates the initial value), $\tilde{x} = [\tilde{x}' + (L-1)/x'^0]/[1 + [L-1]/x'^0]$

and

$$\gamma x^0 = \gamma x'^0[1 + (L-1)/x'^0].$$

With the approximation $L \cong L - 1$, the results depend only on the ratios $(1/\gamma)x'^0$ and L/x'^0 and eq. (26) reduces to

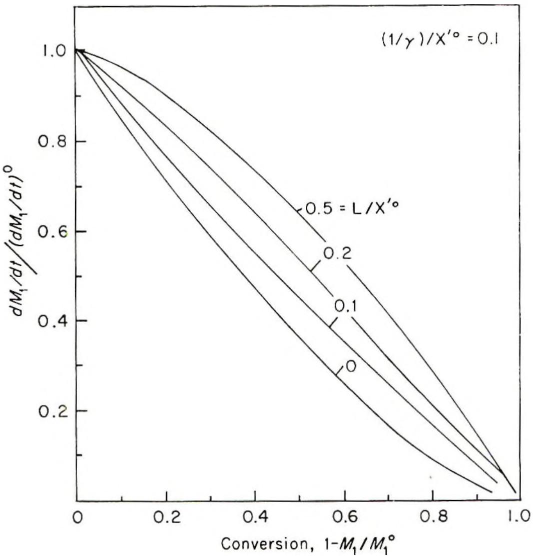

Fig. 1. Random chain scission initiation (no transfer). The relative rate of weight loss plotted vs. conversion for the ratio of zip length $(1/\gamma)$ to initial molecular weight parameter, $(1/\gamma)/x'^0 = 0.1$, at several ratios of the DP of the smallest nonvolatile molecule (L) to molecular weight parameter, L/x'^0. The number-average DP, $x = x' + L - 1$. From eq. (28) of text.

$$M_1/M_1{}^0 = \tilde{x}'^2\left(\frac{1 + \gamma x'^0}{1 + \tilde{x}\gamma x'^0}\right)^2\left[\frac{x' + L/x'^0}{\tilde{x}'(1 + L/x'^0)}\right]^{-(L/x'^0)\,[(1/x') - 1]} \tag{27}$$

The relative rate of weight loss is,

$$\frac{dM_1/dt}{(dM_1/dt)^0} = \frac{2\tilde{x}/(1 + x'\gamma\tilde{x}'^0) + (L/x'^0)^2[1/(\tilde{x}' + (L/x'^0))]M_1}{2/(1 + \gamma x'^0) + (L/x'^0)^2[1/(1 + (L/x'^0))]M_1{}^0} \tag{28}$$

Equations (27) and (28) have been used to calculate the average degree of polymerization and rate of weight loss as functions of conversion for several values of the ratio L/x'^0 at each of two ratios of zip length to molecular length parameter, $(1/\gamma)/x'^0$. These results are plotted in Figures 1–4. A retardation of molecular weight degradation (Figs. 2 and 4) in the later stages when volatilization is present is particularly noticeable and is similar to the behavior of curves calculated by Simha and Wall[3] for an initial monodisperse system.

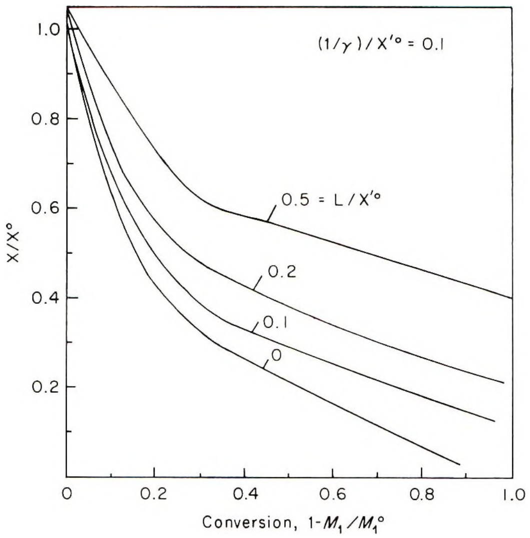

Fig. 2. Random chain scission initiation (no transfer). The relative degree of polymerization x/x^0 plotted vs. conversion for the same parameters as Fig. 1. From eq. (27) of text.

Equation (24) or (28) (see also Fig. 3) leads to a maximum in the rate, $-dM_1/dt$, against conversion at shorter values of the zip length, $1/\gamma$ compared to L. The rate, $-dM_1/dt$, from eq. (24) has a positive slope at $t = 0$ and hence a maximum for the case where the zip length is short compared to initial DP, $1/\gamma \ll x'^0$, when

$$\frac{2}{\gamma} < \sqrt{L(L-1)}\left(\frac{x'^0}{x'^0 + L - 1}\right) - \frac{L(L-1)}{x'^0 + L - 1} \qquad (29)$$

or if $x'^0 \gg L$, when

$$\frac{2}{\gamma} < \sqrt{L(L-1)} \qquad (30)$$

For the limit $1/\gamma \rightarrow 0$ and $L \cong L - 1$, the maximum occurs at 26% conversion, the same value found by Simha and Wall[3] for an initial monodisperse system.

Finally we may illustrate the use of eqs. (22), (20), and (21) for calcu-

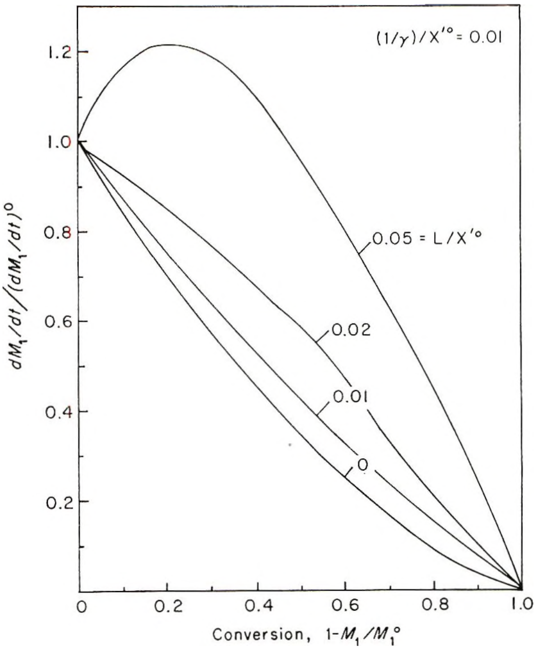

Fig. 3. Random chain scission initiation (no transfer). The relative rate of weight loss plotted vs. conversion for the ratio of zip length $(1/\gamma)$ to initial molecular weight parameter, $(1/\gamma)/x'^0 = 0.01$, at several ratios of the DP of the smallest nonvolatile molecule (L) to molecular weight parameter, L/x^0. The number-average DP, $x = x' + L - 1$. From eq. (28) of text.

lating the distribution of volatile products in two simple cases. First for no transfer or end initiation (k_I, $k_E = 0$), in the short zip limit, $1/\gamma \ll x$, and for $L - 1 \ll x$, eq. (21) reduces to

$$R_L = 2k_S M_1/k_P\gamma x \tag{31}$$

and eq. (20) becomes,

$$R_m = 2k_S M_1/k_P\gamma x \tag{32}$$

or from eq. (22),

$$\frac{dP_m}{dt} = 2k_S\frac{M_1}{x} \qquad 1 < m \leq L - 1 \tag{33}$$

Thus the rate of formation of weight of volatile molecules of DP m is proportional to,

$$\frac{dmP_m}{dt} = 2mk_S(M_1/x) \qquad 1 < m \leq L - 1 \tag{34}$$

and thus proportional to m up to the limit, $L - 1$. The total rate of weight accumulation (divided by the molecular weight of the repeat unit) due to volatilization of molecules of DP greater than one, obtained by summing eq. (34),

$$\frac{d}{dt}\left(\sum_{m=2}^{L-1} mP_m\right) = 2\left(\sum_{m=2}^{L-1} m\right) k_S M_1/x = k_S M_1 L(L-1)/x \qquad (35)$$

reproduces, as it should, the right-hand term in eq. (16) which represents the same quantity.

In the special case of endgroup initiation only ($k_S = 0$) in the presence of transfer in the short zip limit, $1/\gamma \ll x$, and $L - 1 \ll x$, eq. (21) becomes

$$R_L = k_E[(1 + \sigma x)/k_P](1/\gamma)(M_1/x^2) \qquad (36)$$

where[6]

$$\sigma \doteq k_I \bar{R} k_E$$

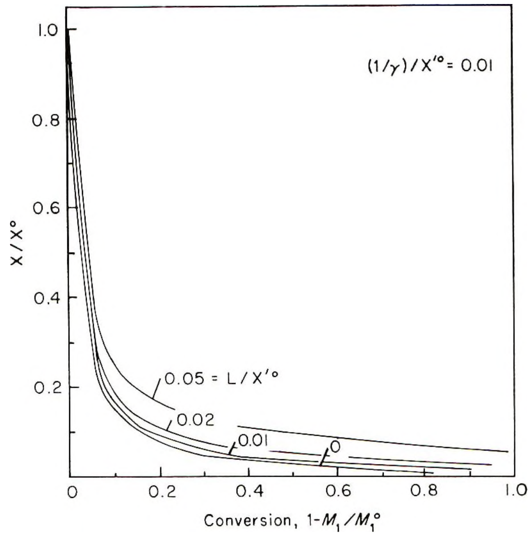

Fig. 4. Random chain scission initiation (no transfer). The relative degree of polymerization x/x^0 plotted vs. conversion for the same parameters as Fig. 4. From eq. (27) of text.

and eq. (20) reduces to,

$$R_m = (k_E M_1/k_P \gamma x^2)[\sigma x + (1 + \gamma)^{m-L}] \qquad (37)$$

Under conditions of short zip and $L - 1 \ll x$, L must be $\gg 1/\gamma$ or $L\gamma \gg 1$ if there is appreciable contribution from volatilization of larger fragments, in which case the $(1 + \gamma)^{m-L}$ term will contribute negligibly to the weight loss and may be dropped. Equation (22) becomes, then,

$$dP_m/dt = 2k_E \sigma M_1/x \qquad 1 < m \leq L - 1 \qquad (38)$$

Thus the rate of weight formation of volatile molecules is proportional to m up to the limit, $L - 1$. Summing eq. (38) over $m = 2$ to $L - 1$ reproduces the right-hand term in eq. (16).

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Résumé

L'effect de la volatilisation de molécules plus grandes que le monomère a été introduit dans la solution des équations cinétiques de Simha, Wall et Blatz pour expliquer la dégradation de hauts polymères avec une distribution initiale la plus plus probable. On indique des équations décrivant la vitesse de variation du poids de l'échantillon et de son poids moléculaire. Elles diffèrent des équations préalables les plus probables primairement par la présence d'un terme additionnel représentant la rupture statistique au voisinage des extrémités de chaînes due à la scission des liens ou attaque par transfert. Des équations sont également obtenues pour des vitesses de formation de chaque espèce volatile et partant de la distribution en produits. L'effet de la volatilisation de fragments plus grands est discuté en détail pour le cas particulier de l'initiation par scission statistique. La distribution de produits est discutée pour deux cas particuliers.

Zusammenfassung

Der Einfluss der Verflüchtigung von Molekülen grösser als das Monomere wurde in die Lösung der kinetischen Gleichungen von Simha, Wall und Blatz für den Abbau eines Hochpolymeren mit einer "wahrscheinlichsten" Anfangsverteilung eingeführt. Es ergeben sich Gleichungen für die Änderung des Gewichts und des Molekulargewichts der Probe. Sie unterscheiden sich von den früheren "wahrscheinlichsten" Gleichungen vor allem durch die Gegenwart eines additiven, die statistische Spaltung in der Nähe des Kettenendes durch Bindungsspaltung oder Übertragungsangriff darstellenden Terms. Weiters werden Beziehungen für die Bildungsgeschwindigkeit jeder flüchtigen Spezies und damit die Verteilung der Reaktionsprodukte erhalten. Der Einfluss der Verflüchtigung grösserer Bruchstücke wird genauer für den Spezialfall der statistischen Spaltungsinitiierung diskutiert. Die Verteilung der Reaktionsprodukte wird für zwei Spezialfälle diskutiert.

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Base-Catalyzed Polymerization of Acryloyl- and Methacryloyl-α-amino Acid Amides

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Synopsis

N-Acryloylglycinamide, *N*-methacryloylglycinamide, *N*-acryloyl-DL- and L-alaninamide, and *N*-methacryloyl-DL- and -L-alaninamide were polymerized by basic catalysts. Polymers with low viscosities were obtained. Automatic amino acid analyses of the hydrolyzates of these polymers indicated that a hydrogen transfer from the terminal amide group took place along with vinyl polymerization. Hydrogen transfer from the secondary amide group was also observed. The ratio of the hydrogen transfer and the vinyl polymerizations was determined by results of automatic amino acid analyses.

INTRODUCTION

Since the discovery of the hydrogen-transfer polymerization of acrylamide by Breslow et al.,[1] much work has been done in this field on methacrylamide,[2] crotonamide,[3] *p*-styrenesulfonamide,[4] maleimide,[5] and other monomers.[6-8] Murahashi et al.[8] have reported the hydrogen-transfer polymerization of β-acryloxypropionamide ($CH_2{=}CHCOOCH_2CH_2CONH_2$), which gave a copolymer with alternating ester and amide linkages. Such a transfer reaction is unique because the amide group is not conjugated with the double bond. If hydrogen transfer occurs from the terminal amide group of *N*-acryloylglycinamide ($CH_2{=}CHCONHCH_2CONH_2$),[9] an alternating copolymer of glycine and β-alanine should be obtained. This work was undertaken with the objective of examining the possibility of preparing such alternating copolymers of α- and β-amino acids from *N*-acryloyl- and *N*-methacryloylglycinamides and *N*-acryloyl- and *N*-methacryloylalaninamides by hydrogen-transfer polymerization.

RESULTS AND DISCUSSION

Monomers, *N*-acryloylglycinamide (I), *N*-methacryloylglycinamide (II), *N*-acryloyl-DL-alaninamide (III-DL), *N*-acryloyl-L-alaninamide (III-L), *N*-methacryloyl-DL-alaninamide (IV-DL), and *N*-methacryloyl-L-alaninamide (IV-L), were prepared by the condensation of acryloyl or methacryloyl chloride with the corresponding amino acid amide in the presence of hydroquinone as an inhibitor of polymerization.

TABLE I
Polymerization by Basic Catalyst[a]

Expt. no.	Monomer[b]	Solvent	Catalyst[c]	Monomer concn., g./ml.	Time, hr.	Temp., °C.	Conversion, %	Intrinsic viscosity [η], dl./g.[d]
PT-1	AGA	DMF	*n*-BuLi[e]	1	1.5	60	Trace	
PT-2	AGA	DMF	*n*-BuLi	1	1.5	100	73.1	0.04
PT-3	AGA	DMF	*n*-BuLi	1	1.5	140	81.9	0.05
PT-4	AGA	DMF	*n*-BuLi	0.2	1.5	100	55.5	0.03
PT-5	AGA	DMF	*n*-BuLi	0.2	3	100	63.8	0.07
PT-6	AGA	DMF	*n*-BuLi	0.2	44	100	65.1	0.05
PT-7	AGA	Pyridine	*n*-BuLi	0.2	8	100	62.0	0.08
PT-8	MGA	DMF	*n*-BuLi	0.5	20	100	31.7	
PT-9	DL-AAA	DMF	*n*-BuLi	1	20	100	93.8	0.04
PT-10	DL-AAA	DMF	*n*-BuLi	0.5	20	100	64.8	0.05
PT-11	DL-AAA	DMF	*n*-BuLi	0.2	20	100	44.0	0.03
PT-12	DL-AAA	Pyridine	*n*-BuLi	0.2	20	100	91.1	0.06
PT-13	L-AAA	DMF	*n*-BuLi	0.5	20	100	92.1	0.04

PT-14	L-AAA	Pyridine	*t*-BuONa	0.25	20	100	80.3	0.05
PT-15	DL-MAA	DMF	*n*-BuLi	0.5	20	100	35.1	0.04
PT-16	DL-MAA	Pyridine	*n*-BuLi	0.5	20	100	43.2	0.04
PT-17	DL-MAA	DMF	Na-dis.[f]	0.5	20	100	30.4	0.03
PT-18	DL-MAA	Pyridine	Na-dis.	0.5	20	100	79.9	0.04
PT-19	DL-MAA	DMF	*t*-BuONa	0.5	20	100	16.2	0.04
PT-20	DL-MAA	Pyridine	*t*-BuONa	0.5	20	100	36.9	0.03
PT-21	DL-MAA	DMSO	*t*-BuONa	0.5	20	100	24.3	0.06
PT-22	L-MAA	DMF	Na-dis.	1	20	100	32.9	0.05

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[a] Phenyl-β-naphthylamine (10 mg./g. monomer) was used as an inhibitor.

[b] AGA = *N*-acryloylglycinamide; MGA = *N*-methacryloylglycinamide; DL-AAA = *N*-acryloyl-DL-alaninamide; L-AAA = *N*-acryloyl-L-alaninamide; DL-MAA = *N*-methacryloyl-DL-alaninamide; L-MAA = *N*-methacryloyl-L-alaninamide.

[c] The quantity of a catalyst per gram of monomer was as follows: *n*-BuLi (concentration 0.99×10^{-3} mole/ml.) 0.5 ml., Na-dis. (concentration 40%) 0.05 g., *t*-BuONa, 0.05 g.

[d] In water at 30°C.

[e] *n*-BuLi 0.2 ml./g. monomer.

[f] Na-dis. = sodium dispersion.

$CH_2{=}CHCONHCH_2CONH_2$

I

$CH_2{=}C(CH_3)CONHCH_2CONH_2$

II

$CH_2{=}CHCONHCH(CH_3)CONH_2$

III-DL, III-L

$CH_2{=}C(CH_3)CONHCH(CH_3)CONH_2$

IV-DL, IV-L

These monomers were soluble in water, methanol, ethanol, acetone, dimethylformamide (DMF), pyridine, and dimethyl sulfoxide (DMSO), and insoluble in dimethylacetamide, tetrahydrofuran, dioxane, and hydrocarbons.

Polymerization reactions were carried out in DMF, pyridine, or DMSO with the use of a basic catalyst such as *n*-butyllithium, sodium *tert*-butoxide, or sodium dispersion. The results of the polymerization are summarized in Table I. The polymers were hygroscopic and soluble in water, hot DMF, and hot DMSO, and insoluble in acetone, benzene, chloroform, carbon tetrachloride. The polymer obtained from I was insoluble in methanol, while the polymers from the other monomers were soluble in this solvent. The polymers obtained from III-L and IV-L showed optical activities in water ($[\alpha]_D^{20} = -10.5°$ and $-2°$, respectively at $c = 2$g./dl.). The effects of various polymerization conditions such as temperature, reaction time, monomer concentration, solvent, and catalyst on the conversion and the intrinsic viscosity were studied. It was found that the polymerization hardly occurred below 100°C., that the conversion decreased with decreasing monomer concentration, and that pyridine gave higher conversions than DMF with each catalyst. The intrinsic viscosity of the polymers examined ranged from 0.03 to 0.08. The molecular weights of polymers were determined by vapor pressure osmometry or by a cryoscopic method in water. The results are shown in Table II. The molecular weights of the polymers obtained were low, the highest being 2050 for polymer PT-7.

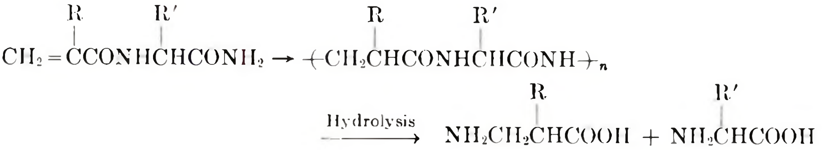
Since the monomers have a double bond and a primary and a secondary amide group, the following polymerizations are considered possible: hydrogen-transfer polymerization by the transfer of a hydrogen at the primary amide to the double bond [eq. (1)]; anionic vinyl polymerization

TABLE II

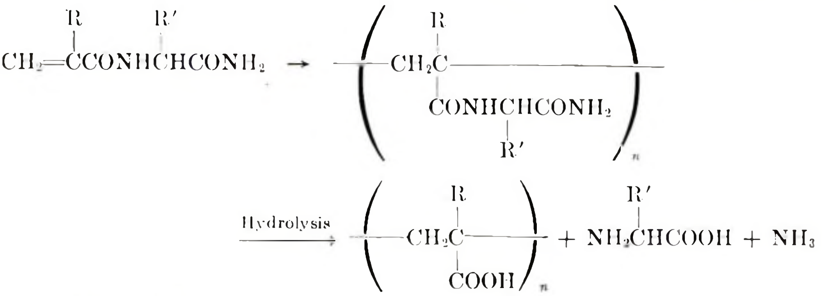
Molecular Weight of Polymers Obtained by Base-Catalyzed Polymerization

Polymer	Molecular weight	Method of measurement
PT-5	844	Cryoscopy in water
PT-7	2050	Vapor pressure osmometry
PT-12	750	Vapor pressure osmometry
PT-14	745	Vapor pressure osmometry

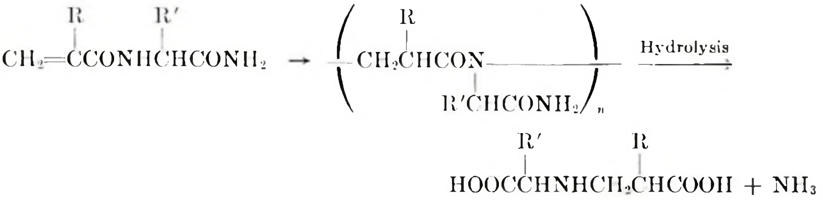
[eq. (2)]; hydrogen-transfer polymerization by the transfer of a hydrogen at the secondary amide to the double bond [eq. (3)]; and



$$\mathrm{CH_2{=}\overset{R}{C}CONH\overset{R'}{C}HCONH_2 \rightarrow -\!\!\left(CH_2\overset{R}{C}HCONH\overset{R'}{C}HCONH\right)\!\!-_n \xrightarrow{\text{Hydrolysis}} NH_2CH_2\overset{R}{C}HCOOH + NH_2\overset{R'}{C}HCOOH} \qquad (1)$$

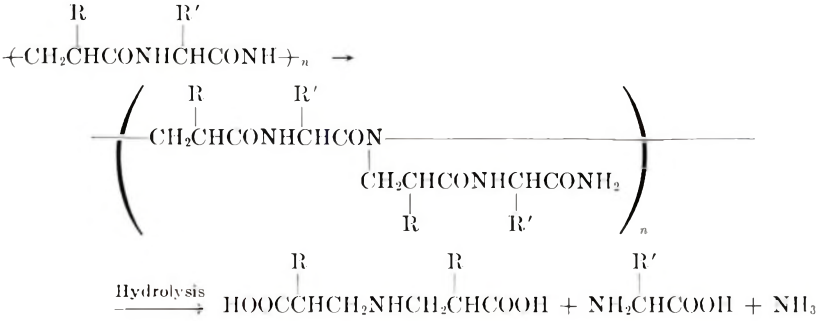


$$\mathrm{CH_2{=}\overset{R}{C}CONH\overset{R'}{C}HCONH_2 \rightarrow \left(CH_2\overset{R}{\underset{CONH\underset{R'}{C}HCONH_2}{C}}\right)_n \xrightarrow{\text{Hydrolysis}} \left(CH_2\overset{R}{\underset{COOH}{C}}\right)_n + NH_2\overset{R'}{C}HCOOH + NH_3} \qquad (2)$$



$$\mathrm{CH_2{=}\overset{R}{C}CONH\overset{R'}{C}HCONH_2 \rightarrow \left(CH_2\overset{R}{C}HCO\underset{R'CHCONH_2}{N}\right)_n \xrightarrow{\text{Hydrolysis}} HOOC\overset{R'}{C}HNHCH_2\overset{R}{C}HCOOH + NH_3} \qquad (3)$$

Michael addition [eq. (4)] of a monomer to the secondary amide formed from the primary amide through reaction (1).



$$\mathrm{-\!\!\left(CH_2\overset{R}{C}HCONH\overset{R'}{C}HCONH\right)\!\!-_n \rightarrow \left(CH_2\overset{R}{C}HCONH\overset{R'}{C}HCO\underset{CH_2\underset{R}{C}HCONH\underset{R'}{C}HCONH_2}{N}\right)_n \xrightarrow{\text{Hydrolysis}} HOOC\overset{R}{C}HCH_2NHCH_2\overset{R}{C}HCOOH + NH_2\overset{R'}{C}HCOOH + NH_3} \qquad (4)$$

There was little difference in the infrared and NMR spectra of base- and radical-catalyzed polymers, and it was impossible to distinguish these two types of polymers by spectral analysis. The polymer was hydrolyzed with concentrated hydrochloric acid, and the hydrolyzate was analyzed. If reaction (1) occurred, then only α- and β-amino acids should have resulted in a 1:1 molar ratio, while reaction (2) should result in the formation of poly(acrylic acid) or poly(methacrylic acid), an α-amino acid, and ammonia. By paper chromatography of the hydrolyzate of the polymer from I, β-alanine, glycine, and a third amino acid were detected. This third amino acid was found to be *N*-carboxymethyl-β-alanine, probably arising

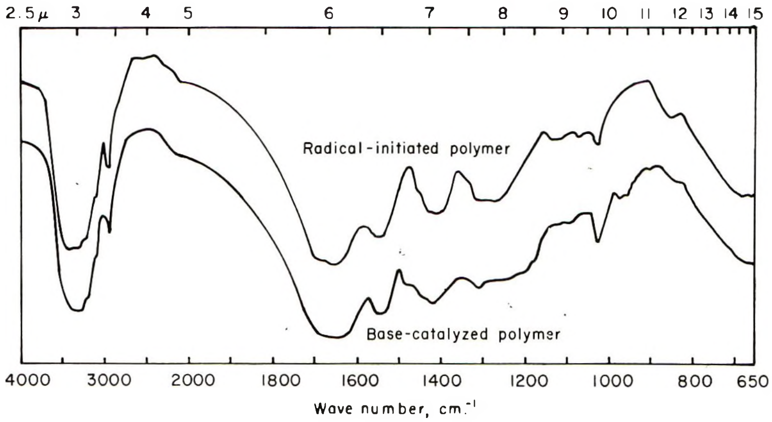


Fig. 1. Infrared spectra of the polymer obtained from *N*-acryloylglycinamide.

from reaction (3). The existence of β-alanine clearly showed that reaction (1) has occurred though not exclusively. Automatic amino acid analyses of the above hydrolyzate showed that it contained glycine in more than an equimolar amount to β-alanine. Analyses of the hydrolyzate of the radical-catalyzed polymer of I gave only glycine in an 89% yield. These facts would indicate that reactions (1) and (2) are taking place competitively.

TABLE III
Paper Chromatography of the Hydrolyzates of Polymers
Obtained by Base-Catalyzed Polymerization

Sample[a]	R_f value[b]		
PAGA			
Hydrolyzate	0.45	0.38	0.31
Standard	0.43	0.38	0.30
Assignment	β-Ala	*N*-Carboxy-methyl-β-ala	Gly
PMGA			
Hydrolyzate	0.60		0.31
Standard	0.59		0.31
Assignment	α-Methyl-β-ala		Gly
PAAA			
Hydrolyzate	0.45		0.40
Standard	0.42		0.39
Assignment	β-Ala		α-Ala
PMAA			
Hydrolyzate	0.63		0.50
Standard	0.63		0.48
Assignment	α-Methyl-β-ala		α-Ala

[a] PAGA = poly-*N*-acryloylglycinamide; PMGA = poly-*N*-methacryloylglycinamide; PAAA = poly-*N*-acryloylalaninamide; PMAA = poly-*N*-methacryloylalaninamide.

[b] Developing solvent: *n*-BuOH–CH_3COOH–H_2O (4:2:1); detecting reagent: 0.3% solution of ninhydrin in ethanol.

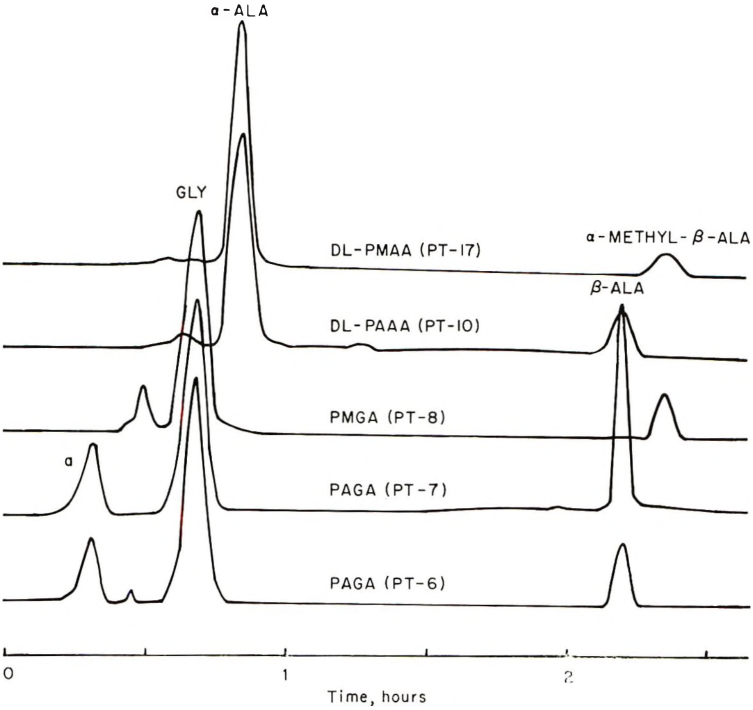


Fig. 2. Amino acid analytical charts of the hydrolyzates of base-catalyzed polymers. (*a* denotes the peak of *N*-carboxymethyl-β-alanine).

Similar results were obtained in the base-catalyzed polymerization of other monomers (Table IV). In all cases, one or two additional peaks appeared in the chart of the amino acid analyses. These peaks might probably be attributed to amino acids which result from reactions (3) or (4). In the case of PT-7, an additional peak was found to be due to *N*-carboxymethyl-β-alanine by comparison with an authentic sample, and the percentage content of the amino acid amounted to 52%. On the other hand, no appreciable amount of such amino acids were detected in the case of polymers from IV-DL and IV-L.

From the results summarized in Table IV, the ratio of reactions (1) and (2) was estimated on the assumption that the reaction (4) would be neglected. Such an assumption would be valid on account of the fact that the quantity of symmetrical amino acid was very small. From Table V, it is seen that the result with PT-7 is specific because the percentage ratio of the reaction (1) is very high compared with others. This may probably be due to the effect of the pyridine solvent.

As described thus far, in the base-catalyzed polymerization of *N*-acryloyl- and *N*-methacryloylglycinamides and *N*-acryloyl- and *N*-methacryloylalaninamides, hydrogen transfer from the terminal amide group has certainly occurred. However, at the same time, a substantial portion of anionic vinyl polymerization took place along with a small part of the hydrogen-transfer reaction from the secondary amide.

TABLE IV

Amino Acid Analyses of the Hydrolyzates of Polymers Obtained by Base-Catalyzed Polymerization[a]

Polymer	Detected amino acid and amount, μmole				Other small peaks
PAGA-R[b]	Gly	88.7			None
PAGA(PT-6)	Gly	35.8,	β-Ala	10.1	Two peaks before Gly
PAGA(PT-7)	Gly	27.1,	α-Ala	19.0	One peak before Gly[c]
PMGA(PT-8)	Gly	50.4,	α-Methyl-β-ala	15.1	Two peaks before Gly
DL-PAAA(PT-10)	α-Ala	41.9,	β-Ala	17.1	Each one peak before and after α-Ala
L-PAAA(PT-13)	α-Ala	55.6,	β-Ala	24.2	Each one peak before and after α-Ala
DL-PMAA(PT-17)	α-Ala	65.5,	α-Methyl-β-ala	22.2	Two peaks so small as to be neglected before α-Ala
L-PMAA(PT-22)	α-Ala	38.1,	α-Methyl-β-ala	9.6	Two peaks so small as to be neglected before α-Ala

[a] Sample: hydrolyzate of a polymer from 100 μmole monomer.

[b] PAGA-R = the polymer obtained by radical-induced polymerization of N-acryloylglycinamide.

[c] This peak is due to N-carboxymethyl-β-alanine; 28.7 μmole.

TABLE V

Ratio of the Polymer Units Resulting from the Reactions of the Vinyl Type and Hydrogen Transfer at a Primary Amide

Sample	Vinyl type units, %	Units from the hydrogen transfer at a primary amide
PT-6	72 (2.57[b])	28 (1[b])
PT-7[a]	29 (0.41)	71 (1)
PT-8	70 (2.33)	30 (1)
PT-10	59 (1.44)	41 (1)
PT-13	57 (1.32)	43 (1)
PT-17	66 (1.94)	34 (1)
PT-22	75 (3.00)	25 (1)

[a] Vinyl type units, 14%; units from the hydrogen-transfer polymerization at a primary amide, 34%; units from hydrogen-transfer polymerization at a secondary amide, 52%.

[b] Values in parentheses are the ratio of vinyl type units per units from the hydrogen transfer at a primary amide.

EXPERIMENTAL

Preparation of Monomers

Acryloyl Chloride and Methacryloyl Chloride. Acryloyl chloride and methacryloyl chloride were prepared from benzoyl chloride and acrylic or methacrylic acid, respectively, by the method reported by Stempel.[10]

Glycinamide Hydrochloride. This compound was prepared from α-chloroacetamide and 28% ammonium hydroxide by Bergell's method.[11]

***N*-Acryloylglycinamide** (I) **and *N*-Methacryloylglycinamide** (II). I and II were prepared from glycinamide hydrochloride and acryloyl chloride or methacryloyl chloride, respectively, by the method reported by Haas.[12] The yield of I was 40.5%, m.p. 135–136°C., and the yield of II was 32%, m.p. 135–137°C.

DL- and L-Alanine Ethyl Ester. DL- and L-alanine ethyl ester hydrochloride were prepared from DL- or L-alanine, respectively, by the procedure reported by McKenzie,[13] and without further purification, these hydrochlorides were converted to free esters by Fischer's method.[14]

DL- and L-Alaninamide. DL- and L-Alaninamide were prepared from DL or L-alanine ethyl ester, respectively, and ammonia by essentially the same method as reported by Yang.[15] This reaction could be accompanied by a side reaction giving 3,6-dimethyl-2,5-diketopiperazine which can be avoided by preventing the escape of NH_3 from the reaction.

***N*-Acryloyl-DL- and L-Alaninamide** (**III-DL and III-L**). III-DL and III-L were prepared from DL- or L-alaninamide, respectively, and acryloyl chloride by essentially the same method as described for I. The yield of III-DL was 66%, m.p. 150–151.5°C. The yield of III-L was 52%, m.p. 143–144°C. These compounds, III-DL and III-L, gave nearly identical infrared spectra. The characteristic absorption bands observed were: 3326, 3225, 3150 (ν_{NH}), 1690 (amide I band of a primary amide), 1655 (amide I band of a secondary amide), 1540 (amide II band of a secondary amide), 1628 ($\nu_{C=C}$), 1405 cm.$^{-1}$ (δ_{CH} of a vinyl group). The specific rotation of III-L was $[\alpha]_D^{20} = -50.8°$ ($c = 2$ g./dl., water).

ANAL. Calcd. for $C_6H_{10}O_2N_2$: C, 50.69; H, 7.09%; N, 19.71%. Found in III-DL: C, 50.41%; H, 7.26%; N, 19.76%. Found in III-L: C, 49.17%; H, 6.51%; N, 19.36%.

***N*-Methacryloyl-DL- and L-Alaninamide** (**IV-DL and IV-L**). IV-DL and IV-L were prepared from DL- or L-alaninamide, respectively, and methacryloyl chloride by essentially the same method as described for I. The yield of IV-DL was 90%, m.p. 147°C., and the yield of IV-L was 73%, m.p. 120.5–122°C. The infrared spectra of IV-DL and IV-L were nearly identical. The characteristic absorption bands observed were: 3375, 3275, 3175 (ν_{NH}), 1695 (amide I band of a primary amide), 1660 (amide I band of a secondary amide), 1534 (amide II band of a secondary amide), 1615 ($\nu_{C=C}$), 1425 cm.$^{-1}$ (δ_{CH} of a vinyl group). The specific rotation of IV-L was $[\alpha]_D^{20} = -6.8°$ ($c = 2$ g./dl., water).

ANAL. Calcd. for $C_7H_{12}O_2N_2$: C, 53.83%; H, 7.74%; N, 17.94%. Found in IV-DL: C, 53.80%; H, 7.42%; N, 17.97%. Found in IV-L: C, 53.54%; H, 7.64%; N, 17.59%.

These monomers were purified by recrystallization from acetone.

Solvents and Catalysts

The solvents (DMF,[16] pyridine,[17] and DMSO[18]) were purified by essentially the same method as described in the literature. *n*-Butyllithium in *n*-heptane (concentration 0.99 × 10^{-3} mole/ml.), and sodium dispersion in paraffin wax (concentration 40%) were obtained commercially. Sodium *tert*-butoxide was prepared by the usual method.

Polymerization

The general procedure of polymerization was as follows. Monomer, solvent, and phenyl-β-naphthylamine as an inhibitor were placed in a glass tube and heated to the point where all solid dissolved. After the tube was filled with dry nitrogen, a catalyst was added. The tube was sealed under atmosphere of nitrogen and allowed to stand in a silicone bath kept at a constant temperature. After the scheduled reaction time, the tube was opened. When the monomer was *N*-acryloylglycinamide, the solid polymer was dissolved in a small amount of water and precipitated into a large excess of methanol. With the other polymerized monomers, precipitation was carried out in a large excess of acetone, since these polymers were soluble in methanol. The precipitated polymer was filtered, and after another reprecipitation, the polymer was dried *in vacuo* at 80°C. for about 24 hr.

Model Compounds

The following amino and imino acids were used as the model compounds for the identification of the hydrolyzates of polymers in paper chromatography and amino acid analysis: glycine, α-alanine, β-alanine, α-methyl-β-alanine, *N*-carboxymethyl-β-alanine, and iminodipropionic acid. Glycine, α-alanine, and β-alanine were obtained commercially. The other compounds were synthesized by the following method.

3-Amino-2-Methylpropionitrile.[19] A mixture of 5.9 g. of methacrylonitrile and 70 ml. of 28% ammonium hydroxide was heated at about 100°C. for 7 hr. in an autoclave. The reaction mixture became homogeneous, though the mixture was separated in two layers before the reaction occurred. After removal of water and ammonia, the residue was distilled. 3-Amino-2-methylpropionitrile b.p. 62.5°C./3.5 mm. Hg, after rectification, was obtained in a yield of 4.2 g. (57%).

α-Methyl-β-Alanine. This compound was prepared by the hydrolysis of 3-amino-2-methylpropionitrile. The hydrolysis was carried out by essentially the same method as reported by Chodroff.[20] The product was purified by recrystallizing from aqueous methanol. The yield was 70%, m.p. 172–176°C. The infrared spectrum of this compound had representative bands at 3325 ($\nu_{NH_3^+}$), 1628, 1415 ($\nu_{C=C}$), and 1550 cm.$^{-1}$ ($\delta_{NH_3^+}$).

ANAL. Calcd. for $C_4H_9O_2N$: C, 46.59%; H, 8.80%; N, 13.51%. Found: C, 46.33%; H, 8.69%; N, 13.51%.

3-Aminopropionitrile and Iminodipropionitrile. Both compounds were prepared by the method given in the literature.[21] The mole ratio of ammonia to acrylonitrile was 0.53 : 1. The yield of iminodipropionitrile was 74%, b.p. 134–135°C./1 mm. Hg, and that of 3-aminopropionitrile was 17%, b.p. 79–81°C./16 mm. Hg.

***N*-(2-Cyanoethyl)glycine.**[22] To a solution of 33.7 g. (0.357 mole) of monochloroacetic acid in 30 ml. of water was added 28.6 g. (0.714 mole) of sodium hydroxide in 100 ml. of water, and the solution was added to 25 g. (0.357 mole) of 3-aminopropionitrile with stirring. After standing for 2 hr., the solution which became clear was neutralized with 30 ml. of concentrated hydrochloric acid. All above steps were carried out at a temperature below 30°C. On a water bath in which the temperature was kept below 50°C. the neutralized solution was evaporated under reduced pressure until a small quantity of water remained, and to the residue was added 200 ml. of methanol. After removal of precipitated sodium chloride by filtration, the half amount of the filtrate was distilled off. After cooling, the crystals were removed, and a second crop was recovered by distilling off the half amount of the filtrate and standing overnight in a refrigerator to give a total yield of 8.2 g. (18%). The product was recrystallized from aqueous methanol. The yield was 6.2 g. (9.4%), m.p. 197°C.

ANAL. Calcd. for $C_5H_8O_2N_2$: C, 46.87%; H, 6.29%; N, 21.87%. Found: C, 46.82%; H, 6.59%; N, 21.25%.

***N*-(Carboxymethyl)-β-Alanine.**[23] This compound was prepared by the hydrolysis of *N*-(2-cyanoethyl)glycine, and the hydrolysis was carried out according to the procedure reported by Chodroff.[20] The product was recrystallized from aqueous methanol. The yield was 25.6%, m.p. 184–185°C.

Iminodipropionic Acid. Iminodipropionitrile was hydrolyzed with barium hydroxide to give iminodipropionic acid, m.p. 140–145°C.[20] The product was recrystallized from aqueous methanol.

Paper Chromatography

In 1 ml. of hydrochloric acid was hydrolyzed 100 mg. of the polymer under reflux for 24 hr. to give a brown solution, and the solution was neutralized with sodium hydroxide. After having been diluted to a suitable concentration, the solution was developed on a 40 cm. × 8 cm. paper along with a standard sample, an aqueous solution of model compounds. The following solution system was used as a developing solvent: *n*-butanol–glacial acetic acid–water (4:2:1). A 0.3% solution of ninhydrin in ethanol was used as a detecting reagent. Identification and assignment of each spot was made by comparison with authentic compound.

Automatic Amino Acid Analysis

The polymer (50 mg.) was hydrolyzed in 1 ml. of hydrochloric acid under reflux for 24 hr., and the hydrolyzed solution was evaporated to dryness. This operation was carried out repeatedly so that the pH of the solution was about 3. Then the dry residue was dissolved in the buffer solution (pH 3.25) consisting of citric acid, sodium hydroxide, 2,2′-thiodiethanol, hydrochloric acid, BRIJ-35 (trade name for a non-ionic surface-active agent commercialized by Atlas Powder Co.), and *n*-caprylic acid. This solution and the standard solution obtained by dissolving the model compounds in the buffer solution were run in an automatic amino acid analyzer (Shibata Chemical App. Mfg. Co., Ltd. Tokyo, Model AA-600): 50 cm. column, Amberlite CG-120, 0.2*N* citrate buffer, pH 4.25, 5 ml./hr., 50°C.

Supplementary note: After this manuscript had been submitted to the *Journal of Polymer Science*, we found a paper [S. Tazuke and A. Nakamura, *Makromol. Chem.*, **95**, 92 (1966)], in which work rather similar to ours is described. That paper has referred to the anionic polymerization of *N*-acryloylbenzhydrazide ($CH_2{=}CH{-}CONHNHCO{-}C_6H_5$) and reported based on the infrared spectral data that a small amount of the hydrogen-transfer polymerization occurred along with vinyl polymerization.

The authors are indebted to Shibata Chemical App. Mfg. Co., Ltd. and Ajinomoto Co. Inc. for automatic amino acid analyses.

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Résumé

On a polymérisé en présence de catalyseurs basiques la *N*-acryloylglycinamide, la *N*-méthacryloylglycynamide, la *N*-acryloyl-DL- et L-alaninamide, la *N*-méthacryloyl-DL- et

L-alaninamide. Des polymères de basse viscosité ont été obtenus. Les analyses automatiques des amino-acides des hydrolysats de ces polymères ont indiqué que la réaction de transfert d'hydrogène au départ du groupe amide terminal a lieu tout le long de la polymérisation vinylique. La réaction de transfert d'hydrogène au départ du groupe amide secondaire a également été observée. Le rapport des polymérisations par transfert d'hydrogène et par polymérisations vinyliques a été déterminé par des résultats analytiques de dosages d'amino-acides.

Zusammenfassung

N-Acryloylglycinamid, *N*-Methacryloylglycinamid, *N*-Acryloyl-DL- und L-alaninamid wurden mit basischen Katalysatoren polymerisiert. Es wurden Polymere mit niedriger Viskosität erhalten. Automatische Aminosäureanalysen der Hydrolysate dieser Polymeren zeigten, dass gleichzeitig mit der Vinylpolymerisation eine Wasserstoffübertragungsreaktion von der endständigen Amidgruppe stattfindet. Auch eine Wasserstoffübertratungsreaktion von der sekundären Amidgruppe wurde beobachtet. Das Verhältnis von Wasserstoffübertragung zu Vinylpolymerisation wurde aus den Ergebnissen der automatischen Aminosäureanalyse bestimmt.

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Synthesis and Polymerization of *N*-[1-(1-Substituted-2-oxopropyl)]acrylamides and -methacrylamides. Copolymerization of These Monomers with Styrene and Substituent Effects

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Synopsis

The synthesis and polymerization of *N*-[1-(1-substituted-2-oxopropyl)]acrylamides and -methacrylamides are described. Seven new monomers were prepared by two kinds of synthetic procedure. The polymerization of these monomers was carried out. Monomer reactivity ratios in the polymerization of these monomers with styrene were determined and the Alfrey-Price Q and e values calculated. The effects of substituents on the reactivities in copolymerization were observed, and an interpretation of the results is given.

INTRODUCTION

A number of studies[1–7] have been made of the copolymerization of *N*-substituted acrylamides and methacrylamides with some reactive vinyl monomers. However, only a limited amount of information[1,2] about the substituent effect has been obtained. *N*-Oxoalkyl acrylamide derivatives have been studied only by Coleman and his co-workers.[7]

In this paper, in order to obtain more information about the reactivities of *N*-substituted acrylamide derivatives, the synthesis and polymerization of the new monomers, *N*-[1-(1-substituted-2-oxopropyl)]acrylamides and -methacrylamides, were accomplished. The effects of substituent on the reactivities of these monomers with a general type of radical in copolymerization reaction is discussed.

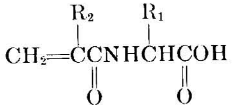
RESULTS AND DISCUSSION

Monomer Synthesis

New monomers, *N*-[1-(1-substituted-2-oxopropyl)]acrylamides and -methacrylamides (III) were prepared by two kinds of synthetic procedure. In the first method, α-amino acids were used as starting materials. The α-amino acids, DL-alanine, DL-leucine, and DL-phenylalanine, were acylated by acryloyl chloride and methacryloyl chloride. The melting points and elemental analyses of *N*-acyl-α-amino acids are shown in Table I.

TABLE I

N-Acyl-α-amino Acids (I)

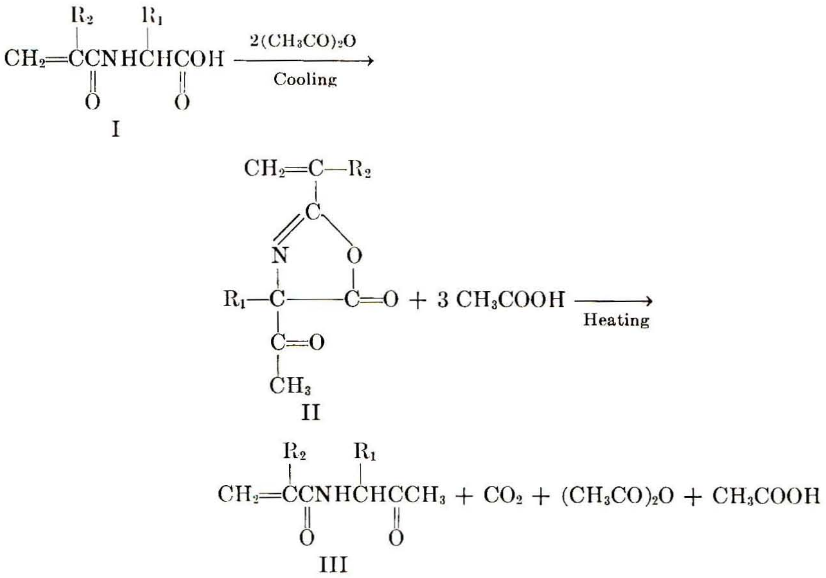


$$CH_2{=}\overset{R_2}{\overset{|}{C}}\underset{\underset{O}{\|}}{C}NH\overset{R_1}{\overset{|}{C}}H\underset{\underset{O}{\|}}{C}OH$$

Substituents					Calculated			Found		
R$_1$	R$_2$	Yield, %	M.p., °C.	Formula	C, %	H, %	N, %	C, %	H, %	N, %
CH_3	H	65	130	$C_6H_9NO_3$	50.34	6.34	9.79	50.23	6.40	9.59
CH_3	CH_3	70	118	$C_7H_{11}NO_3$	[a]					
$C_2H_3(CH_3)_2$	H	90	82	$C_9H_{15}NO_3$	58.36	8.16	7.56	58.12	7.95	7.54
$C_2H_3(CH_3)_2$	CH_3	90	106	$C_{10}H_{17}NO_3$	[a]					
$CH_2C_6H_5$	H	75	119	$C_{12}H_{13}NO_3$	65.74	5.98	6.39	65.62	6.10	6.22
$CH_2C_6H_5$	CH_3	80	104	$C_{13}H_{15}NO_3$	66.93	6.48	6.01	67.20	6.22	6.32

[a] Data of Iwakura et al.[8]

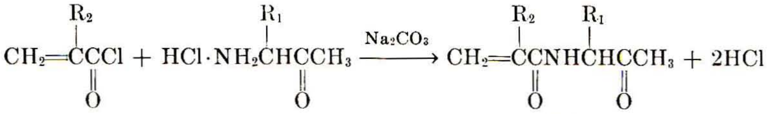
These *N*-acyl-α-amino acids (I) were treated with an excess of acetic anhydride in pyridine under cooling, and then the reaction mixture was heated on a steam bath.



(1)

This reaction [eq. (1)] is a variant of the Dakin-West reaction.[9] The compounds (III) were prepared by this reaction in high yields.

The second method [eq. (2)] was the reaction of α-aminoketone hydrochlorides with corresponding acid chlorides in the presence of alkali. This reaction is the Schotten-Baumann reaction. The yields by this method were generally low, but the method had merit in that compounds which could not be prepared by the former method were obtained. By the latter method, the compounds (III) with R_1 = H, CH_3, and $CH_2C_6H_5$ were prepared.



$$CH_2{=}\overset{\overset{R_2}{|}}{C}\underset{\underset{O}{\|}}{C}Cl + HCl\cdot NH_2\overset{\overset{R_1}{|}}{C}H\underset{\underset{O}{\|}}{C}CH_3 \xrightarrow{Na_2CO_3} CH_2{=}\overset{\overset{R_2}{|}}{C}\underset{\underset{O}{\|}}{C}NH\overset{\overset{R_1}{|}}{C}H\underset{\underset{O}{\|}}{C}CH_3 + 2HCl \qquad (2)$$

III

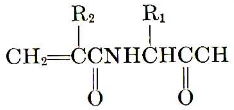
The structures of these new monomers were confirmed by elemental

TABLE II
Assignment of Infrared Spectra of New Monomers (III)

Absorption band, cm.$^{-1}$	Assignment
3300	N—H
1720	C=O (ketone)
1660	C=O (amide)
1620	C=C
1520	amide II

TABLE III

N-[1-(1-Substituted-2-oxopropyl)]acrylamides (III)



$$CH_2{=}\underset{\underset{O}{\|}}{\overset{\overset{R_2}{|}}{C}}CNH\overset{\overset{R_1}{|}}{C}H\underset{\underset{O}{\|}}{C}CH$$

Substituents		Yields, %[a]		B.p., °C./ mm. Hg.	M.p., °C.	Formula	Calculated			Found		
R_1	R_2	A	B				C, %	H, %	N, %	C, %	H, %	N, %
H	CH_3	0	18	110/2	—	$C_7H_{11}NO_2$	59.55	7.95	9.92	59.71	8.21	10.11
CH_3	H	50	45	115/4	64	$C_7H_{11}NO_2$	59.55	7.95	9.92	59.60	8.19	10.06
CH_3	CH_3	78	55	95/2	35	$C_8H_{13}NO_2$	62.20	7.85	9.08	61.92	8.08	9.08
$C_2H_3(CH_3)_2$	H	65		137/2	45	$C_{10}H_{17}NO_2$	65.54	9.35	7.64	65.50	9.18	7.44
$C_2H_3(CH_3)_2$	CH_3	72		121/2	43	$C_{11}H_{19}NO_2$	66.97	9.71	7.10	66.58	9.52	6.82
$CH_2C_6H_5$	H	60	75	—	130	$C_{13}H_{15}NO_2$	71.86	6.96	6.45	71.94	6.89	6.61
$CH_2C_6H_5$	CH_3	90	80	—	92	$C_{14}H_{17}NO_2$	72.70	7.41	6.06	72.75	7.28	6.31

[a] A: by the Dakin-West reaction, B: by the Schotten-Baumann reaction.

analyses and infrared spectra. The principal characteristics of the infrared spectra are given in Table II, and the yields, physical properties, and elemental analyses are summarized in Table III.

Homopolymerization

These monomers (III) were homopolymerized under heating at 60°C. with *α,α′*-azobisisobutyronitrile as an initiator. Polymerizations were carried out in benzene or dimethylformamide, and gave water-insoluble polymers, except for *N*-[1-(2-oxopropyl)]methacrylamide which swelled in water and was insoluble in ether. The polymers dissolved in benzene, dimethylformamide, and dioxane. The solubilities in methanol depended upon the substituent R_1; polymers for which R_1 was benzyl swelled in methanol; the others were all methanol-soluble polymers. *N*-[1-(2-oxopropyl)]-methacrylamide polymerized on storage at room temperature, but other monomers had good thermal stabilities.

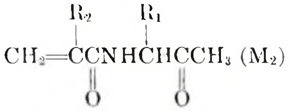
Copolymerization

Copolymerization of these monomers with styrene was carried out accomplished in benzene or in dimethylformamide. Monomer reactivity ratios were determined, and *Q* and *e* values were calculated by using the Alfrey-Price equations.[10] The results are summarized in Table IV, and composition curves for the copolymers are shown in Figure 1.

These results show some notable differences in the reactivities of the monomers, depending upon the bulkiness of the substituents. The more bulky the substituent R_1, the more reactive the monomer. It may seem unlikely that electrical effects of the substituent R_1 should play a significant role in the reactivities of vinyl and isopropenyl groups through —C—N—CO— bonds. Compared with the reactivities of vinyl and isopropenyl groups of similar type compounds, generally the vinyl group is more reactive because of its being free from the steric hindrance of the

TABLE IV

Copolymerization Data of New Monomers (M_2) with Styrene (M_1)



$$CH_2{=}\overset{R_2}{\overset{|}{C}}\underset{\underset{O}{\|}}{C}NH\overset{R_1}{\overset{|}{C}}H\underset{\underset{O}{\|}}{C}CH_3\ (M_2)$$

M_2					
R_1	R_2	r_1	r_2	Q_2	e_2
H	CH_3	1.15 ± 0.1	0.13 ± 0.1	0.29	+0.58
CH_3	H	1.83 ± 0.02	0.05 ± 0.02	0.16	+0.74
CH_3	CH_3	0.91 ± 0.02	0.01 ± 0.02	0.20	+1.35
$C_2H_3(CH_3)_2$	H	1.87 ± 0.1	0.25 ± 0.1	0.27	+0.07
$C_2H_3(CH_3)_2$	CH_3	1.07 ± 0.05	0.25 ± 0.05	0.38	+0.34
$CH_2C_6H_5$	H	2.06 ± 0.05	0.48 ± 0.05	0.44	−0.68
$CH_2C_6H_5$	CH_3	1.30 ± 0.1	0.57 ± 0.1	0.49	−0.26

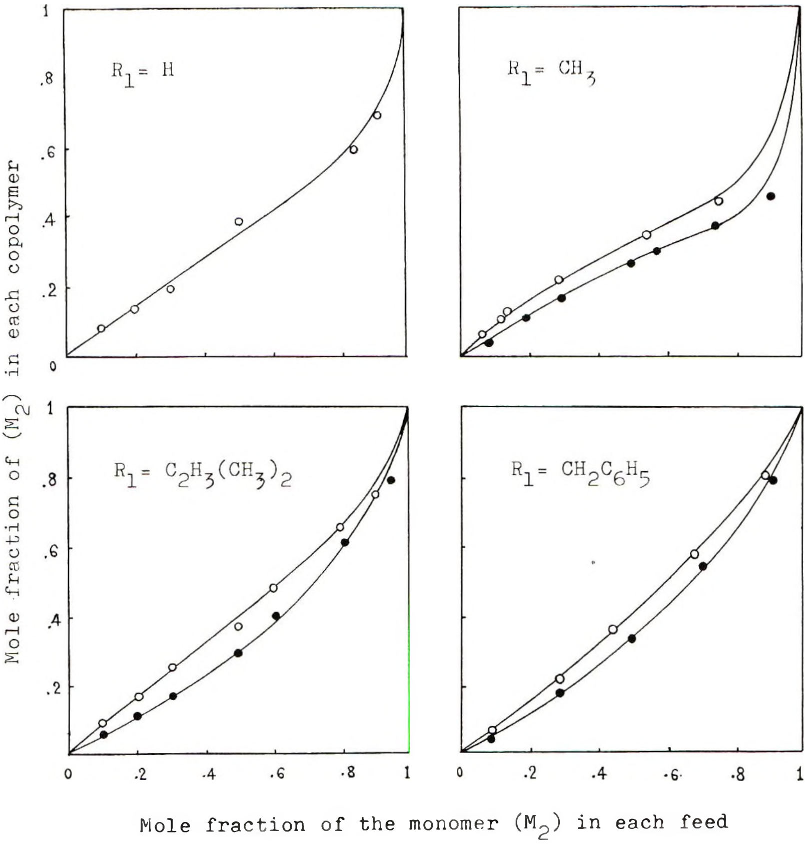


Fig. 1. Composition curves for copolymers: (●) acrylamide derivatives; (○) methacrylamide derivatives.

methyl group at the α-carbon atom of isopropenyl group. However, the monomer reactivity ratios r_1 for the styryl radical show higher reactivities for the methacrylamide derivatives than the acrylamides. Therefore, it would seem that the steric effects of the substituents R_1 and R_2 are significant in the reactivities of the monomers. These monomers would be forced to have limited conformations, because of the conjugation between the C–C double bond and the acid amide group and the formation of an intramolecular hydrogen bond as shown in Figure 2. This limited planar con-

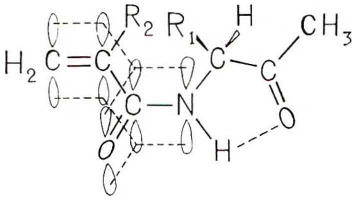


Fig. 2. Conformation of monomers (III).

formation gives rise to steric repulsion between substituents R_1 and R_2. As the steric repulsion becomes stronger, the plane of the molecule would be broken and the conjugation between the C–C double bond and the carbonyl group would become weak. The π electrons at the C–C double bond would then not be localized toward the strong electron-attracting carbonyl group, and radical polymerization reaction would give rise to a higher resonance stabilization energy in the transition state.[11] The Q and e values shown in Table IV tend to support this interpretation. Namely, the e values become negative and the Q values increase as the influence of the electron-attracting carbonyl group is weakened by the bulkiness of the substituent R_1.

Petrova and her co-workers[2] have reported the reactivities of *N*-substituted methacrylamide derivatives in the copolymerization with methyl methacrylate. They have found that the aryl-substituted derivatives were more reactive than aliphatic ones. Their results might also be explained by the steric effects of the substituents.

EXPERIMENTAL

Monomers

N-*Acyl-α-amino Acids (I)*

A 0.5-mole portion α-amino acid (DL-alanine, DL-leucine, or DL-phenylalanine) and 1 mole of sodium hydroxide were dissolved in 200 ml. of water. To the solution, 0.5 mole of acid chloride (acryloyl chloride and methacryloyl chloride) was added dropwise under cooling at 0–10°C. When the reaction was complete, the mixture was neutralized with 85 ml. of concentrated HCl. The precipitated product was filtered with suction and recrystallized from benzene (methacryloyl derivative) or water (acryloyl derivative). The melting points and elemental analyses are shown in Table I.

N-*[1-(1-Substituted-2-oxopropyl)]acrylamides and -methacrylamides (III)*

Dakin-West Reaction. A stirred solution of 0.25 mole of *N*-acyl-α-amino acid (I) in 200 ml. of pyridine was treated with 200 ml. of acetic anhydride under cooling in an ice bath. After the addition, stirring was continued for 6 hr. while the temperature was kept at 0–10°C., and then the reaction temperature was raised to 100°C. After the evolution of carbon dioxide ceased, pyridine, excess acetic anhydride, and acetic acid were removed under reduced pressure. The residual product was purified by distillation [$R_1 = CH_3$ and $C_2H_3(CH_3)_2$] or recrystallization from water ($R_1 = CH_2C_6H_5$).

Schotten-Baumann Reaction. To a vigorously stirred aqueous solution of α-aminoketone hydrochloride, equimolar amounts of corresponding acid chloride and aqueous solution of sodium carbonate were added dropwise under cooling. After the addition, stirring was continued for 1 hr. The product from aminoacetone hydrochloride[12] and 2-aminobutan-3-one hydrochloride[13] as starting materials, was extracted by three portions of ether, and the extracted mixture was dried over anhydrous sodium sulfate. After the removal of ether, the product was distilled under reduced pressure. In the reaction of 1-phenyl-2-aminobutan-3-one hydrochloride,[14] the precipitated product was filtered with suction and recrystallized from water.

The yields, physical properties, and elemental analyses of these new monomers prepared are summarized in Table III.

Polymerization

Polymerization experiments were carried out at 60°C. in sealed tubes under a nitrogen atmosphere. Solution polymerizations were carried out in benzene, except for *N*-[1-(1-benzyl-2-oxopropyl)]acrylamide which was not so soluble in benzene. The polymerization of this monomer was accomplished in dimethylformamide. All experiments were initiated by α,α'-azobisisobutyronitrile (0.01 wt.-% based on monomer). The experimental methods of copolymerization were essentially those described by Mayo and Lewis.[15] About 5 g. of a mixture of precisely weighed styrene (M_1) and the new monomer (M_2) was kept at 60°C. for 6–8 hr. Conversions were below 10%. The styrene-rich copolymers were precipitated by pouring the reaction solution into methanol, and styrene-poor copolymers were poured into petroleum ether. The copolymers obtained were reprecipitated three times, dioxane being used as a solvent and water as a nonsolvent. In the case of *N*-[1-(2-oxopropyl)]methacrylamide, methanol was added to dioxane in order to increase the solubility, and ether was used as a nonsolvent. The purified polymers were dried *in vacuo*, and the composition of the copolymers was determined by nitrogen analysis. Monomer reactivity ratios were determined from the general copolymerization equation by using both the method of intercepts[14] and the Fineman-Ross plots.[16]

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Résumé

La synthèse et la polymérisation d'acrylamides et méthacrylamides *N*-[1-(1-substitués-2-oxopropyliques)]- sont décrites. Sept nouveaux monomères ont été préparés au moyen de deux procédés de synthèse. La polymérisation de ces monomères a été effectuée. Les rapports de réactivité des monomères en copolymérisation avec le styrène ont été déterminés et leurs valeurs de Q et e suivant Alfrey-Price ont été calculées. Les effets des substituants sur les réactivités en cours de copolymérisation ont été observés et l'interprétation des résultats donnée.

Zusammenfassung

Synthese und Polymerisation von *N*-[1-(1-substituerten-2-oxypropyl)]-acrylamiden und -methacrylamiden werden beschrieben. Sieben neue Monomere werden nach zwei verschiedenen synthetischen Verfahren dargestellt. Die Polymerisation dieser Monomeren wird durchgeführt. Monomereaktivitätsverhältnisse dieser Monomeren mit Styrol werden bestimmt und die Alfrey-Price Q- und e-Werte berechnet. Die für die Reaktivität bei der Copolymerisation beobachteten Substituenteneffekte werden interpretiert.

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Mechanism of the Tertiary Amine-Catalyzed Dicyandiamide Cure of Epoxy Resins*

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Synopsis

Infrared and NMR data on tertiary amine-catalyzed, dicyandiamide–epoxy resin (and model compound) systems have been utilized to elucidate the mechanism of the curing process. The early exothermic curing reaction is shown to be ring opening of the resin epoxy groups by dicyandiamide imino and amino anionic species, giving rise to N-alkyl cyanoguanidines; a minor amount of polyether formation also occurs at this time. After the exothermic reaction is essentially complete at <90°C., a slow, high temperature (110–200°C.) addition of hydroxyl hydrogen across the nitrile triple bond occurs, giving rise to an imino ether which then rearranges to the guanyl urea.

Introduction

The mechanism of curing epoxy resins with dicyandiamide has been treated speculatively elsewhere.[1] However, no analytical evidence for a single predominant path has been presented. Instead, a number of possible routes and products have been proposed, and the reader has been expected to exercise his intuition in making a selection from among the offerings.

Discussion

Dicyandiamide is widely used as the curing agent in epoxy resin formulations for reinforced laminates. It offers many advantages in terms of the stability and shelf life of the prepreg, cost, and product uniformity.

It was assumed that profound changes in the infrared spectra, specifically a decrease of absorbance at 2180 cm.$^{-1}$ and an accompanying increase in absorbance at 1740 cm.$^{-1}$, were due to the reaction of resin hydroxyl groups with dicyandiamide nitrile groups. This reaction was believed to lead to the formation of substituted guanylurea groups as the final resin crosslinking reaction. Correlation of these infrared spectra of cured laminates with infrared spectra of the known unsubstituted guanylurea salt resulting from the acid hydrolysis of pure dicyandiamide formed the primary basis for this early assumption. Subsequently obtained NMR spectra of a model

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* Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

resin system incorporating a monofunctional epoxy compound has corroborated the most important aspect of the original assumption; namely, that the final observable crosslinking reaction results in the formation of the guanylurea group. Further corroboration of the originally proposed overall reaction leading to this species is also obtained from the NMR spectra of this model system in which a gradual reduction in alcoholic hydroxyl concentration also accompanies the increase in guanylurea —NH— concentration. The only uncertainty which still exists relative to the composition of this final curing reaction product is the absence of analytical evidence as to whether this species is linear or cyclic and our inability to react dicyandiamide with the model compound, 1,3-phenoxy-2-propanol in the presence of the amine catalyst. The reaction of alcohol functional groups with nitriles to form imino esters which are capable of rearranging at elevated temperatures to the corresponding guanylureas is known. The reaction being proposed here for the late-time resin cure has not been reported in the literature previously under these conditions. The published reactions[2-4] which were most nearly like the one described here occur under quite different conditions, leading to similar products, by what may be a very different mechanism.

Cyclic products have been reported[2] for some reactions of nitriles with alcoholic hydroxyls which have been shown to occur under conditions somewhat different from ours. The driving force for the formation of cyclic substituted guanylalkylureas under laminating conditions is not known. Though we have at present no valid, unambiguous analytical evidence upon which to base a preference for either the linear or cyclic form, the noncyclic form is considered more likely, since it does contribute to crosslinking and such increases are observed in the final stage of cure. Mechanical test data and solvent swelling studies indicate strongly that the crosslink density of the resin system does increase markedly during late cure. A further study will be required to resolve this uncertainty.

The NMR curves for nine samples of the model system, phenyl glycidyl ether–dicyanidiamide–TMBDA, model curing system samples taken at intervals over a 3-hr. period are given in detail in the Experimental section of this report. Interpretation of the NMR data yielded the significant information given in Table I.

Sampling was started immediately after complete solution of dicyandiamide in the liquid system had occurred. The composition and stoichiometry of this system were dictated by the following considerations: (*1*) the necessity for maintaining solubility of the products to the fully cured system, (required for NMR sample preparation); (*2*) the necessity for a liquid, solvent-free system, (required for high temperature reaction studies and highly desirable from the point of view of reducing the congestion in the infrared and NMR spectra to a minimum); (*3*) the desirability of duplicating as closely as possible the reactivity of the typical epoxy resins (Phenyl glycidyl ether undergoes all the chemical reactions of epoxy resins, and is of the same order of reactivity.); (*4*) the achievement of optimum conditions for

TABLE I
Relative Functional Group Concentrations Expressed as Normalized NMR Peak Areas[a]

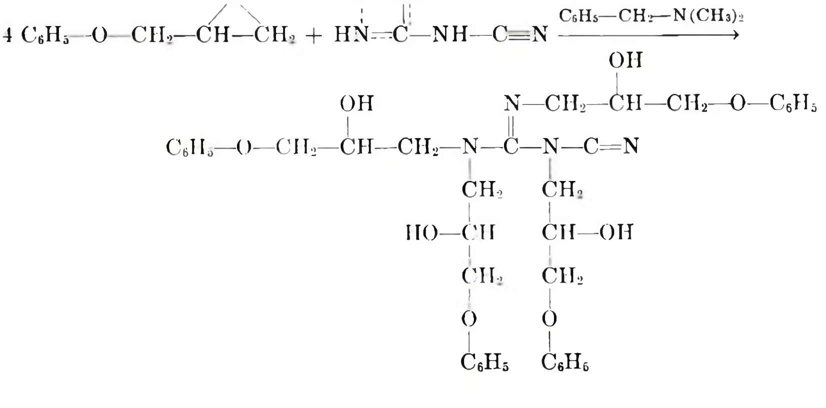
Sample no.	Temperature, °C.	$(\overset{\vert}{C}=HN)$	$(\overset{R}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-NH)$	$(\overset{OH}{\overset{\vert}{C}}H)$	Time, hr.
1	93	3.2	6.3	21.0	2:25
2	93	3.4	5.6	22.4	3:40
3	112	14.9	4.9	22.5	4:50
4	132	→ 11.4 ←		22.9	5:50
5	150		13.7	19.5	6:50
6	163		16.2	19.4	8:30
7	160		14.9	18.6	9:40
8	175		15.5	17.9	12:00
9	195		17.4	15.2	13:00

[a] Aromatic proton response peak areas were used as internal standard for the purpose of normalization. The corresponding data presented at the 151st National Meeting of the American Chemical Society were not presented in the normalized form.

analysis of the reaction products by using a stoichiometric equivalent of dicyandiamide, rather than one-half the stoichiometric equivalent, as is commonly used in the typical epoxy/dicyandiamide formulations. In this way, higher concentrations of epoxy/dicyandiamide reaction products were available, and small differences in concentration could be more readily detected by analysis. The equivalent weight of dicyandiamide with respect to replaceable amino and imino hydrogen atoms was independently determined to be one-fourth the molecular weight. Interpretation of the NMR curves and the corresponding relative concentrations listed in Table I indicate the following.

Most of the amino and imino —NH hydrogen atoms initially present in dicyandiamide had been replaced by reaction with phenyl glycidyl ether prior to the removal of sample 1 from the reaction flask.

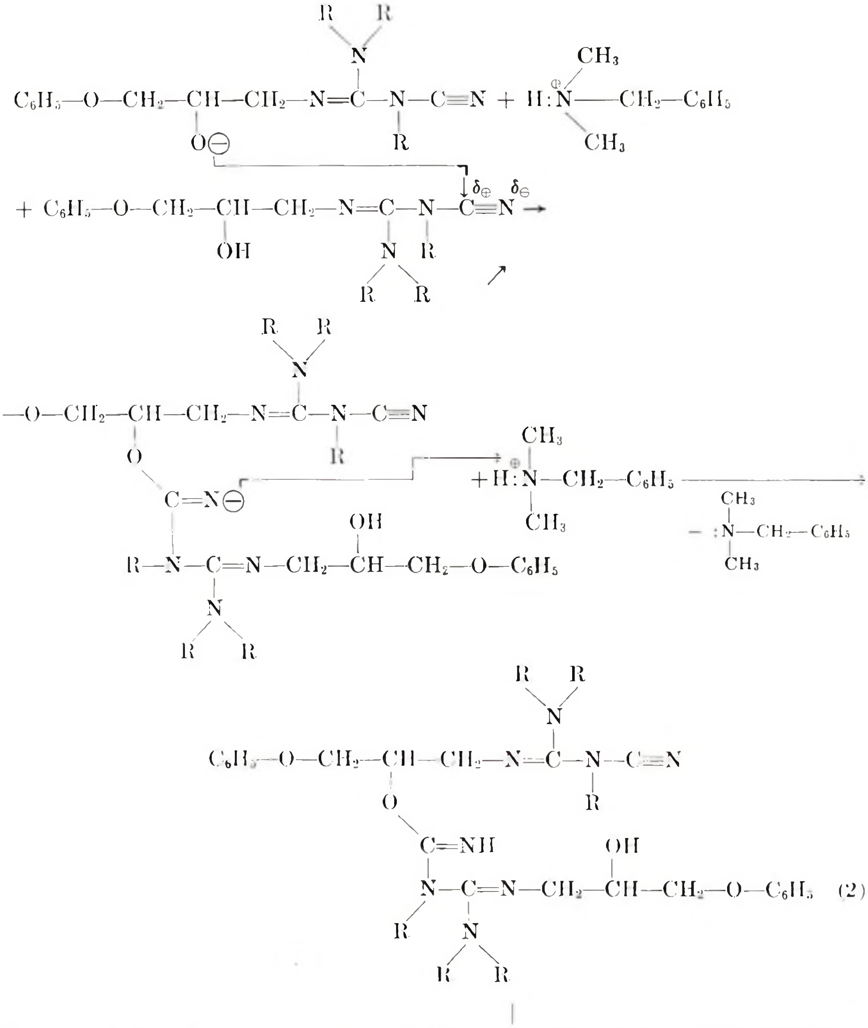
Sample 1 had a high alcoholic hydroxyl content, presumably produced by the reaction of the amino and imino groups of dicyandiamide, since there was a concurrent disappearance of this functionality, with the epoxy group in phenyl glycidyl ether to form α-hydroxy-*N*-alkyl cyanoguanidines [eq. (1)]



(1)

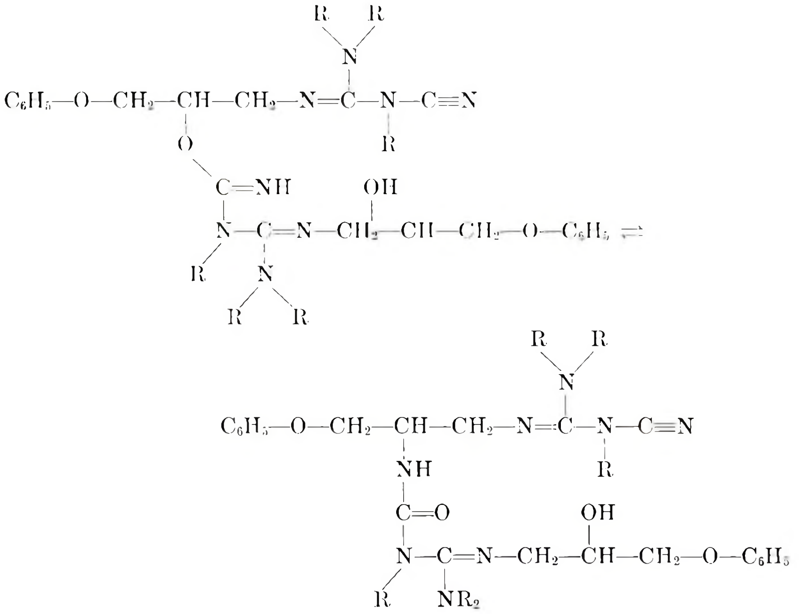
The consumption of most of the available oxirane functionality by reaction (1) is corroborated by the fact that the increase in intensity of the 1170 cm.$^{-1}$ (aliphatic ether) band in the infrared spectra of these model system samples was much less than in dicyandiamide-cured epoxy resin formulations. Polyether formation was greatly inhibited by this competitive and faster reaction of oxirane groups with dicyandiamide. The infrared spectra also showed that essentially all the available oxirane functionality had been consumed prior to the removal of sample 1.

Samples 1–3 show a rapid increase in imino functionality. This, we suggest, in the absence of any decrease in hydroxyl functionality is attributable to the mechanism shown in eq. (2).



(2)

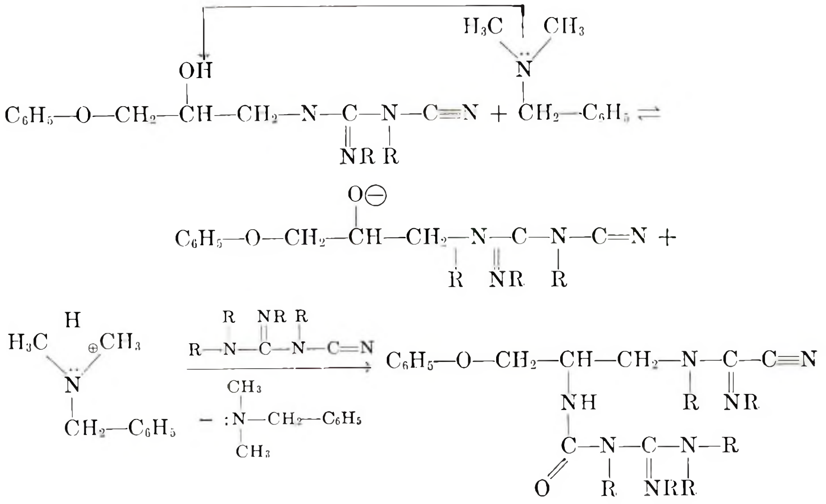
Sample 4 shows a broadening of the —C=NH and —NRC(O)NH— regions to such an extent that the two merge into one peak, indicating that this sample was taken as rearrangement of the imino ether (the formation of which was discussed above), was well under way. Subsequent samples showed no —C=NH functionality whatsoever. This rearrangement can be written[3] as shown in eq. (3).



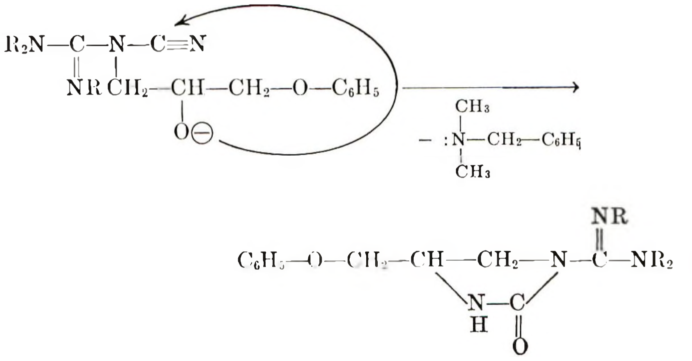
(3)

Samples 5–9 exhibit two significant trends in their NMR spectra: (*a*) an increase in $\overset{|}{\mathrm{R}}\mathrm{N}$—C(O)—NH— functionality and (*b*) a decrease in $>$CHOH functionality.

These trends are consistent with the mechanism shown in eqs. (4) and (5).



(4)



(5)

where R is C_6H_5—O—$CH_2CH(OH)CH_2$—.

As was stated previously, our basis for preferring eq. (4) to eq. (5) is the fact that the latter structure is inconsistent with the changes in properties which are observed to occur concurrently with a diminution of available nitrile functionality and the accompanying increases in both amide carbonyl functionality, as seen in the infrared spectra, and —NH functionality, as observed in the NMR spectra. However, an additional new band occurring in the spectra of the model system at 1700 cm.$^{-1}$ may very well be due to the formation of a significant quantity of the cyclic product. This band was noted in the model system only, and not in cured resin systems. The carbonyl absorbance in six-membered lactams, for example, is shifted down to 1650 cm.$^{-1}$ from the 1700 cm.$^{-1}$ of open chain amides. The reason for this additional product is probably the much higher initial concentration of dicyandiamide and the higher temperatures encountered. 1700 cm.$^{-1}$ is a reasonable absorbance frequency for a cyclic alkylguanylurea carbonyl group, in view of the effect of neighboring electronegative groups causing shifts to slightly higher frequencies.

Experimental

All infrared spectra were run on a Perkin-Elmer Model 521 grating infrared spectrophotometer. Samples for infrared analysis were prepared either as KBr dispersion pellets or as thin films sprayed on blank KBr pellets. Spectra of dicyandiamide hydrolysis products were obtained by using a heated cell. Several hundred spectra of resins in various stages of cure were run.

The phenyl glycidyl ether was Eastman 6377 and the 1,3-phenoxylpropanol Eastman 5012. Both were used without purification. The dicyandiamide was American Cyanamid's pulverized grade.

A mixture of 90.2 g. (0.6 mole) phenyl glycidyl ether, 12.6 g. (0.150 mole) dicyandiamide, and 1.0 g. benzyldimethylamine were heated on a Thermocap-controlled heating mantle under reflux condenser. The temperature was maintained at 85–96°C. for a period of $2^1/_3$ hr. at which time all of the dicyandiamide had gone into solution and sample 1 was taken. This portion of the reaction was very exothermic necessitating occasional removal of

TABLE II

Time from start, hr.	Temp., °C.	Sample no.	Remarks
2:25	93	1	All dicyandiamide in solution
3:40	93	2	
4:50	112	3	
5:50	132	4	Some NH_3 odor
6:50	150	5	CN in IR, NH_3 odor
8:30	163	6	NH_3 odor
9:40	160	7	CN in IR, NH_3 odor
12:00	175	8	
13:00	195	9	No CN in IR, off

the heating mantle and application of cooling bath. During the first half of this initial heating period the temperature was not allowed to rise above 90°C. Further heating is shown in Table II.

A mixture of 24.4 g. (0.1 mole) 1,3-diphenoxy-2-propanol, 4.2 g. (0.05 mole) dicyandiamide, and 0.20 g. benzyldimethylamine were heated as above. The temperature was gradually raised to 180°C. over 95 min. and samples were taken periodically. The final sample showed no peaks in the infrared spectrum over those found in the original starting materials.

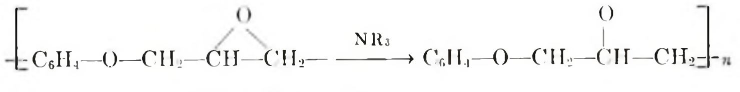
The above experiment was repeated in the presence of 0.1 ml. concentrated HCl with no difference in the result even though the heating period was extended to 265 min. All NMR spectra were obtained on a Varian A-60A NMR spectrometer using hexadeuteroacetone as the solvent and tetramethylsilane as the standard.

Conclusions

The most significant conclusions to be drawn from the work reported here are the following.

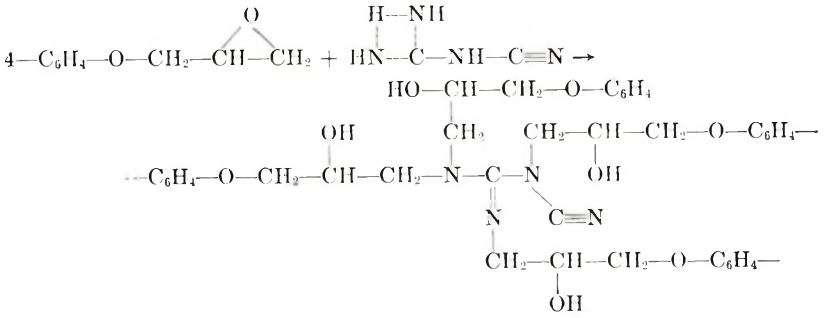
(*1*) The early, or primary cure of the dicyandiamide epoxy resin system can best be represented by two chemical reactions, eqs. (6) and (7):

Polyether Chain Propagation:



(6)

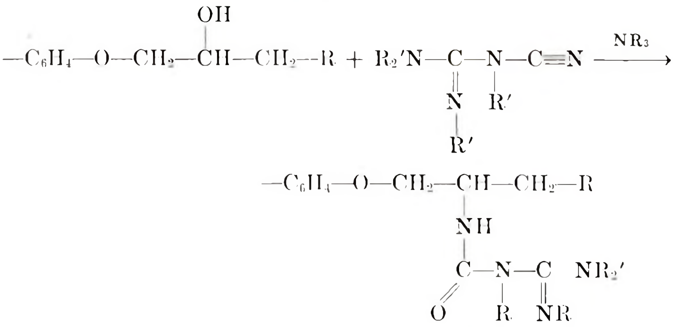
N-Alkyl Cyanoguanidine Formation:



(7)

Both reactions (6) and (7) occur during prepreg "B" staging and the short period of pressing prior to gelation. This primary cure is an exothermic process. It includes contributions from both reactions (6) and (7), both of which proceed until all available epoxy groups have been consumed. This process is not simply polyether chain propagation. The NMR data as well as the visual observation of gradual phase homogeneity being achieved indicate strongly that *N*-alkylcyanoguanidine production goes nearly to completion. However, in a system such as this, the production of significant traces of ammonia and aminotriazines (melamine, ammeline, etc.), as well as isocyanurates, cannot be overlooked. These compounds can, however, be correctly regarded as products of side reactions, such as the gradual thermal degradation of dicyandiamide and *N*-alkylcyanoguanidines, plus subsequent recombination of the reactive species thus formed to give a host of minor side products. These reactions, with the possible exception of *N*-alkylisocyanurate production and recombination, do not seem to contribute materially to the overall curing process.

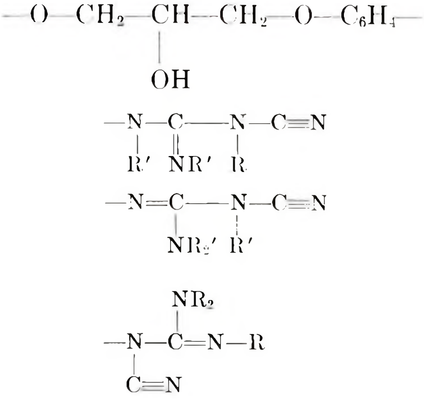
(*2*) The second and final stage of curing occurs almost entirely in the press, and can be adequately represented by the reaction (8):



$$-C_6H_4-O-CH_2-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2-R + R_2'N-\underset{\underset{\underset{\displaystyle R'}{|}}{\displaystyle N}}{\underset{\|}{C}}-\underset{\underset{\displaystyle R'}{|}}{N}-C\equiv N \xrightarrow{NR_3}$$

$$\begin{array}{l} -C_6H_4-O-CH_2-\underset{\underset{\displaystyle NH}{|}}{C}H-CH_2-R \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad \underset{\underset{\displaystyle O}{/\!/}}{C}-\underset{\underset{\displaystyle R}{|}}{N}-\underset{\underset{\displaystyle NR}{\|}}{C}\quad NR_2' \end{array} \qquad (8)$$

where R may be:



$$-O-CH_2-\underset{\underset{\displaystyle OH}{|}}{C}H-CH_2-O-C_6H_4-$$

$$-\underset{\underset{\displaystyle R'}{|}}{N}-\underset{\underset{\displaystyle NR'}{\|}}{C}-\underset{\underset{\displaystyle R}{|}}{N}-C\equiv N$$

$$-N=\underset{\underset{\displaystyle NR_2'}{|}}{C}-\underset{\underset{\displaystyle R'}{|}}{N}-C\equiv N$$

or

$$-\underset{\underset{\displaystyle C\equiv N}{|}}{N}-\overset{\overset{\displaystyle NR_2}{|}}{C}=N-R$$

and R′ may be —H or —CH_2—CH(OH)—CH_2—O—C_6H_4.

Since eq. (8) represents the principal late-cure crosslinking process, a good indication of properties and performance can be obtained by a quantitative determination of residual nitrile functionality in the fully cured resin and appropriate adjustments can be made in process variables in order to obtain optimum properties.

We gratefully acknowledge the valuable contributions of Mr. R. Angelo, Mr. O. Abolafia, and Mr. B. Serafin. We are particularly indebted to Mr. F. P. Ardito, who rendered yeoman service over a period of several months by performing virtually all the infrared laboratory work; and to the Varian Associates Pittsburgh Laboratory, where the NMR spectra of model samples were run.

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Résumé

On a utilisé la méthode infrarouge et de résonance nucléaire magnétique sur des résines époxy dicyane-diamide (et de composés modèles) catalysées par des résines tertiaires en vue d'élucider le mécanisme du processus de recuit. La réaction exothermique initiale au cours du recuit consiste dans l'ouverture du cycle des groupes de résines époxy par des espèces iminodicyane-diamide et amino-anioniques donnant lieu à la formation de *N*-alcoylcyanoguanidine; il se forme également une petite quantité de polyéther à ce moment. Lorsque la réaction exothermique est pratiquement complète à 90°C, une addition lente à température élevée (110–200°C.) des hydrogènes hydroxylés sur la triple liaison nitrilique se passe et donne lieu à la formation d'imino-éther qui ultérieurement se réarrange en guanylurée.

Zusammenfassung

Infrarot- und NMR- Daten an tertiär-amin-katalysierten Dicyandiamid-Epoxyharzsystemen (und Modellverbindungen) wurden auf Aufklärung des Härtungsmechanismus verwendet. Die exotherme Anfangsreaktion der Härtung besteht in einer Ringöffnung der Harzepoxygruppen durch anionische Dicyandiamid-Imino- und Aminospezies unter Bildung von *N*-Alkylcyanoguanidinen; gleichzeitig findet auch in geringer Menge Polyätherbildung statt. Nach im wesentlichen vollständigem Ablauf der exothermen Reaktion bei $<90°C$, tritt eine langsame Hochtemperaturaddition (110 bis 200°C) des Hydroxylwasserstoffes an die Nitril-Dreifachbindung unter Bildung eines Iminoäthers ein, der sich dann zum Guanylharnstoff umlagert.

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Radical and Anionic Homopolymerization of Maleimide and *N-n*-Butylmaleimide

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Synopsis

The rate of homopolymerization of maleimide has been measured in dimethylformamide solution at 60°C. in the presence of azobisisobutyronitrile; it has been compared to that of *N-n*-butylmaleimide. The overall rates of polymerization are equal to $R_p = k[\mathrm{M}]^{1.1-1.2}[\mathrm{In}]^{0.8}$ for maleimide, and $R_p = k'[\mathrm{M}][\mathrm{In}]^{0.5}$ for the *N*-substituted imide. The difference of behavior has been interpreted on the basis of an intramolecular tautomery of the terminal group of the maleimide growing chain and the formation of a resonance-stabilized succinimidyl radical. The relative ease of polymerization of these monomers and of maleic anhydride has been discussed. In the presence of sodium *tert*-butoxide at 20°C. in dimethylformamide solutions, maleimide polymerizes with hydrogen isomerization. The percentage of *N*-substituted isomerized units was evaluated at 70–75% by measurement of the rate of hydrolysis in 0.005*N* sodium hydroxide and comparison with succinimide and *N*-butylsuccinimide. *N-n*-butylmaleimide undergoes ring opening together with anionic polymerization in the presence of sodium *tert*-butoxide at 20°C. and butyllithium at −40°C. Unlike the radical-initiated polymerization, it was impossible to obtain anionic copolymers of maleimide and *N*-butylmaleimide with acrylonitrile and methyl methacrylate.

The homopolymerization of some unsaturated, symmetrically disubstituted cyclic monomers, such as vinylene carbonate,[1] maleic anhydride,[2,3] and maleimide[4–6] has been reported in the literature. The double bonds of these monomers are characterized by appreciable steric hindrance, taken as responsible for their low polymerization tendency, when compared to the corresponding vinyl monomers. On the other hand, the double bonds of maleic anhydride[7–9] maleimide,[10] and *N*-substituted maleimides[11] have strong electron-attracting properties, as demonstrated by their copolymerization behavior.

There is nevertheless a striking difference between maleic anhydride and the imides with respect to their polymerizability; indeed the anhydride, unlike the imides, polymerizes with considerable difficulty and necessitates large amounts of catalyst. It is evident that the differences in steric hindrance and polarity between these monomers cannot account for such differences in behavior. Recently Joshi[2] has shown that the homopolymerization of maleic anhydride is mainly characterized by high chain transfer constants with monomer and initiator, and that these transfer reactions are sufficient to account for its observed reluctance to polymerize, especially when initiator concentrations used are like those for the polymerization of vinyl monomers.

It is therefore interesting to examine the kinetics of polymerization of maleimides and *N*-*n*-butylmaleimide in the presence of azobisisobutyronitrile as initiator. A mechanism of polymerization will be presented, and the differences of behavior between the monomers discussed. The anionic polymerization will be examined in the last section.

Experimental

Maleimide was prepared by the method of Tawney et al.:[12] it was crystallized from ethyl acetate; before use it was purified by sublimation under vacuum (melting point 92°C.).

N-*n*-butylmaleimide was prepared by the method of Coleman et al.[13] and purified by repeated vacuum distillation (b.p. 210°C./30 mm. Hg). The degree of purity of both monomers was verified by elemental analysis.

Dimethylformamide and azobisisobutyronitrile were purified by classical methods. The water content of dimethylformamide never exceeds 0.08% (Karl Fischer titration).

Succinimide and phthalimide were analytical grade reagents; preliminary experiments demonstrated that these substances did not initiate the polymerization.

The radical polymerizations were followed dilatometrically at 60°C. in dimethylformamide as solvent in the presence of azobisisobutyronitrile. The solutions were prepared with the high vacuum technique. After polymerization polymaleimide was precipitated by pouring the solution into ethyl acetate; it is a slightly colored powder, that becomes red in alkaline solution. Poly-*N*-*n*-butylmaleimide was precipitated in methanol; it is a colorless substance, insoluble in alkaline medium and soluble in chloroform, carbon tetrachloride, and dimethylformamide. The radical-initiated polymaleimides were analyzed for their unsubstituted imide group content by titration with sodium methoxide in anhydrous dimethylformamide solution in the presence of *o*-nitroaniline as indicator. Although maleimide monomer and succinimide were found 100% by this method, polymaleimide contained only 80% groups with respect to the calculated value. This discrepancy was confirmed by the elemental analysis.

ANAL. Calcd.: C, 49.4%; H, 3.1%; O, 33.0%; N, 14.5%. Found: C, 46.13%; H, 4.99%; O, 28.97%; N, 14.2%; total: 94.29%.

Nevertheless, the infrared spectra of these polymers are identical with those described in the literature;[10,14] absorption bands at 3400–3600 cm.$^{-1}$ and 1620–1650 cm.$^{-1}$ correspond to O—H hydroxyl and C=N double bond, respectively. It must be pointed out that low molecular weight imides show no enolized tautomeric structure.[15] On the contrary, the elemental analysis of poly-*N*-*n*-butylmaleimide is very satisfactory.

ANAL. Calcd.: C, 62.7%; H, 7.2%; O, 20.9%; N, 9.2%. Found: C, 62.42%; H, 7.36%; O, 21.31%; N, 9.25%; total 100.34% (traces of water).

Its infrared spectrum corresponds to that of *N*-*n*-butylsuccinimide.

The anionic polymerization of maleimide was also carried out in dimethylformamide solution under vacuum at 20°C. in the presence of sodium *tert*-butoxide as initiator; the rate was followed dilatometrically. The polymer was precipitated in ethyl acetate; it is a pink powder, soluble in dimethylformamide and dimethyl sulfoxide. The polymerization of *N*-*n*-butylmaleimide at 20°C. in the presence of sodium *tert*-butoxide is violent and exothermic with formation of a polymer gel. The reaction was therefore carried out at −40°C. in toluene solution in the presence of *n*-butyllithium and was followed gravimetrically. The polymer was precipitated in petroleum ether: part of the reaction product is soluble in water and methanol; the other portion is soluble only in organic solvents, e.g., chloroform, carbon tetrachloride. The polymer is red, and the color fades on addition of acid.

The elemental analysis of polymaleimide shows, as for the radical-initiated polymer, a large discrepancy between the experimental and calculated values.

ANAL. Calcd.: C, 49.4%; H, 3.1%; O, 33.0%; N, 14.5%. Found: C, 49.3%; H, 4.74%; O, 33.39%; N, 13.35%; total: 95.77%.

For poly-*N*-*n*-butylmaleimide the results are very satisfactory.

ANAL. Calcd.: C, 62.7%; H, 7.2%; O, 20.9%; N, 9.2%. Found: C, 62.52%; H, 7.1%; O, 20.92%; N, 9.17%; total: 99.71%.

The infrared spectrum of base-catalyzed polymaleimide is identical with that described by Marvel and co-workers;[21] a much lower absorption band of the N—H band at 3350 cm.$^{-1}$ is observed when compared with the spectrum of the radical-initiated polymer. Contrarily, the spectra of both poly-*N*-*n*-butylmaleimides (anionic and radical initiated) are identical.

Anionic copolymerization experiments of maleimide and *N*-*n*-butylmaleimide were carried out with acrylonitrile and methyl methacrylate. All these experiments were unsuccessful, only maleimide homopolymers being formed. The experimental conditions are summarized in Table I.

Radical Polymerization

The kinetic results of the polymerization of maleimide and *N*-*n*-butylmaleimide are summarized in Tables II and III.

From logarithmic plots of the rate of polymerization versus initiator or monomer concentration, at constant monomer and initiator concentration respectively, the following overall rate expression can be calculated for maleimide: $R_p = k[M]^a[I]^{0.8}$, where $a = 1.1$–1.3; for *N*-*n*-butylmaleimide: $R_p = k'[M][I]^{0.5}$.

For the second monomer, plots of R_p against the square root of the initiator concentration and against the monomer concentration are linear and pass through the origin (Fig. 1).

TABLE I
Copolymerization Experiments with Acrylonitrile and Methyl Methacrylate

Maleimide, g.	*N*-*n*-Butylmaleimide, g.	Acrylonitrile, g.	Methyl methacrylate, g.	Dimethylformamide, ml.	Initiator, mmole[a]	Time, min.	Temp., °C.	Polymer, g.	Polymer composition[b]
1	—	—	3.84	5	BuONa 0.052	180	20°	0.376	PMI
1	—	—	0.936	2	SN 0.57	15	0°	0.096	PMI
—	1.047	—	0.936	2	SN 0.28	—	Exothermic	0.580	PBMI
1	—	0.828	—	2	SN 0.57	—	Exothermic	0.331	PMI
—	1.047	0.828	—	2	SN 0.57	—	Exothermic	0.641	PBMI
1	—	0.828	—	2	BuONa 0.26	5	20°	0.276	PMI

[a] BuONa = sodium *tert*-butoxide; SN = sodium naphthalene.

[b] PMI = polymaleimide; PBMI = poly-*N*-*n*-butylmaleimide.

TABLE II

Rate of Polymerization of Maleimide in Dimethylformamide at 60°C.

Maleimide, mole/l.	AIBN, mmole/l.	$R_p \times 10^5$, mole/l.-sec.	$[\eta]$ (25°C., DMF)
2.13	3.1	2.6	0.22
"	6.2	4.7	0.20
"	12.2	7.8	0.20
"	18.3	11.2	0.22
"	24.4	14	0.21
1.04	12.2	3	0.12
3.26	"	12	0.26
4.34	"	19	0.31
5.78	"	23.3	0.36
6.26	"		0.44

TABLE III

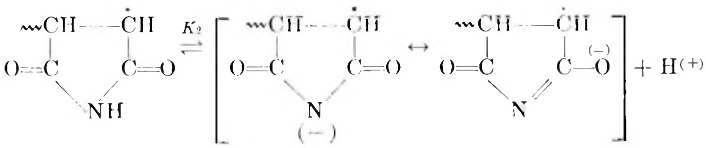
Rate of Polymerization of *N*-*n*-Butylmaleimide in Dimethylformamide at 60°C.

N,*n*-Butylmaleimide, mole/l.	AIBN, mmole/l.	$R_p \times 10^5$, mole/l.-sec.	$[\eta]$ (25°C., DMF)
1.368	6.1	1.76	0.11
"	12.2	2.53	0.10
"	24.4	3.6	0.09
0.342	12.2	0.7	0.07
0.684	"	1.25	0.08
1.368	"	2.38	0.1
2.052	"	3.42	0.11

From the last column of Tables II and III it can be seen that the intrinsic viscosities of the polymers are rather low, particularly in the case of poly-*N*-*n*-butylmaleimide.

The difference in behavior of the two monomers may be related to the presence of a mobile hydrogen atom in the unsubstituted maleimide. On this basis, however, different interpretations for an order of reaction higher than unity with respect to the monomer concentration can be presented.

Unsubstituted maleimide is a weak acid in dimethylformamide solution. The acid dissociation of the propagating radical deactivates it, as in the case of the polymerization of acrylic acid.[16,17]



If one assumes that the propagation results essentially from the addition of monomer to the undissociated imidyl radical (I), and that the proton con-

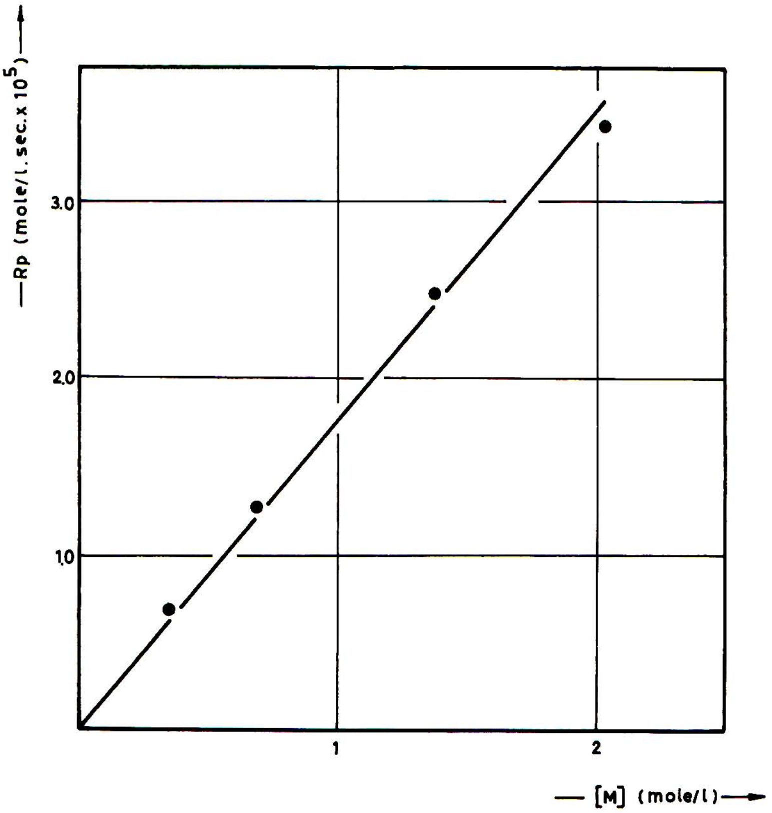


Fig. 1. Influence of the monomer concentration on polymerization of *N*-*n*-butylmaleimide in dimethylformamide at 60°C., [AIBN] = 12.2 mmole/l.

centration originates mainly from the monomer dissociation (i.e., $[M] \gg [M^{\cdot}]$), it can easily be shown that

$$R_p = [H^+]/(K_2 + [H^+])k_p[M^{\cdot}][M]$$

and considering the acid dissociation constant of the monomer

$$K_1 = [M^-][H^+]/[M]$$

we have

$$R_p = K_1^{1/2} k_p[M^{\cdot}][M]^{3/2}/\{K_2 + (K_1[M])^{1/2}\}$$

This interpretation based on the acidity of maleimide and on a decreased reactivity of the resonance-stabilized radical-anion (II) agrees also with the 0.8 exponent of the initiator concentration. It must, however, be pointed out, that the rate of polymerization is unaffected by the presence of succinimide (1 and 2*M*) or phthalimide (0.68*M*) as can be seen in Figure 2.

Monomer association, favored by hydrogen bond formation, can also account for a higher order; indeed, chain propagation should result from the addition of free (k_p) and associated (k_p') monomer molecules (e.g., dimers) to the reactive radicals.

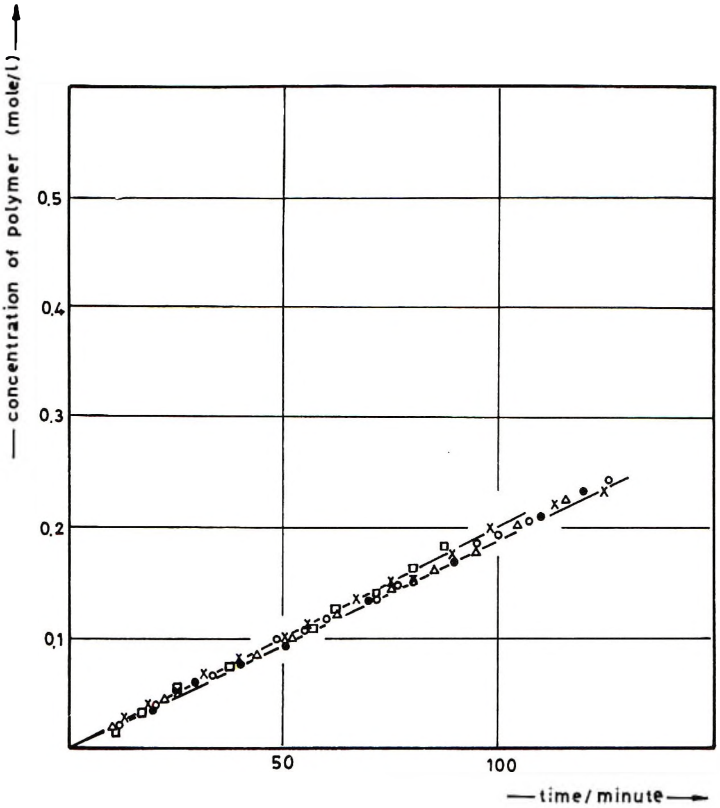


Fig. 2. Polymerization of maleimide in dimethylformamide solution at 60°C., [M] = 1.04 mole/l., [AIBN] = 12.2 mmole/l.: (●) pure dimethylformamide; (○) $1M$ succinimide; (×) $2M$ succinimide; (△) $0.68M$ phthalimide; (□) 30 vol.-% toluene.

Taking into account the dimerization equilibrium constant $K_D = [D]/[M]^2$ as well as the high polarity of the reaction medium, i.e. $[D] \ll [M]$, one obtains

$$R_p = [M^\cdot](k_p + 2k_p'K_D[M])[M]$$

Complex formation between the propagating radicals and a monomer molecule is another possibility; this complex formation would be enhanced by the presence of hydroxyl groups in the growing chain (see experimental, infrared spectra) and on this basis, the following rate expression can be deduced

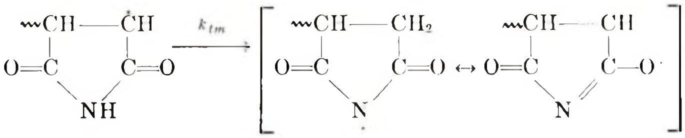
$$R_p = k_p[M^\cdot]\{K[M]/(1 + K[M])\}[M]$$

in which K corresponds to the complexation equilibrium constant.

An interpretation based on a cage effect with respect to the primary initiator radicals or on a chain transfer reaction with the solvent is valid only for less reactive monomers without conjugated double bonds, such as vinylene carbonate.[1] It would not explain the difference with respect to the

N-*n*-butylmaleimide. Moreover, rate and molecular weight measurements in the presence of succinimide, phthalimide, and toluene have shown that transfer reactions are negligible (Fig. 2).

Concerning the 0.8 order of initiator concentration, the formation of a resonance-stabilized succinimidyl radical (III) by intramolecular tautomerization can be admitted, in analogy with the formation of a glutarimidyl radical in the polymerization of acrylamide.[18]



III

This radical is unable to propagate further, and its formation is a monomolecular chain termination reaction. The intramolecular reaction of this tautomerization is demonstrated by the lack of influence of added succinimide on the rate and degree of polymerization ($[\eta] = 0.12$ in the absence and in the presence of $2M$ succinimide). The stationary state must therefore be written

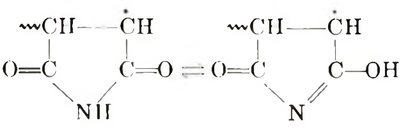
$$fk_i[\mathrm{In}] = k_{tm}[\mathrm{M}^\cdot] + k_t[\mathrm{M}^\cdot]^2$$

when f is the initiation efficiency, k_i, k_{tm}, and k_t the initiation, the monomolecular, and bimolecular termination rate constants, respectively. There results

$$[\mathrm{M}^\cdot] = \{-k_{tm} + [k_{tm}^2 + 4fk_i[\mathrm{In}]k_t]^{1/2}\}/2k_t$$

Depending on the relative importance of the intramolecular tautomerization rate constant k_{tm}^2 with respect to the bimolecular chain termination reaction $4fk_t[\mathrm{In}]k_t$, the order of reaction will vary from 0.5 to 1 for the initiator concentration.

The higher rate of polymerization of maleimide compared to that of *N*-*n*-butylmaleimide and that of maleic anhydride must be related with the enolization of the propagating radical, and the increased complexation possibility of the enolized radical with monomer through hydrogen bonding.



Moreover, the formation of an hydroxyl group rules out the repulsion between the carbonyl group of the growing chain and that of the next monomer molecule. This interpretation is in fact the same as that presented for the order of reaction with respect to the monomer.

The greater polymerizability of *N*-*n*-butylmaleimide as compared to that of maleic anhydride, results, at least partially, from the higher reactivity of the propagating *N*-*n*-butylmaleimide radical. The C=C double bonds of both monomers are similarly influenced by the two conjugated carbonyl groups; the electron pairs of the anhydride oxygen, however, participate more strongly to the delocalization of the C=O double bond than the imide nitrogen; consequently the growing maleic anhydride chain is less reactive.

Anionic Polymerization

The presence of imide hydrogen in maleimide makes it susceptible to polymerization by hydrogen-transfer reaction, as shown first in the case of acrylamide and *N*-substituted acrylamides by Breslow et al.[19] and Ishii and co-workers.[20]

Tawney et al.[5] and Cubbon[6] have already mentioned the anionic polymerization of maleimide and *N*-*n*-butylmaleimide, and the formation of red, low molecular weight polymers. Very recently Kojima et al.[21] described the base-catalyzed polymerization of maleimide and compared this polymer with the radical-initiated polymer. They demonstrated by hydrolysis and isolation of aspartic acid and ammonia that the polymer contained 75–85% $\overline{\mathrm{CO{-}CHCH_2{-}CO{-}N}}{-}$ recurring units as resulting from hydrogen-transfer polymerization. The kinetic results which will be described here confirm Marvel's data; they will be therefore briefly summarized.

The rate of polymerization of maleimide was examined at 20°C. in dimethylformamide solution as a function of the sodium *tert*-butoxide concentration, the monomer concentration being kept constant (1.04*M*); it is directly proportional to the initiator concentration (Table IV and Fig. 3). Contrarily, it is independent from the monomer concentration; it decreases strongly in the presence of toluene, and especially of succinimide.

The apparent zero-order with respect to the monomer concentration can be explained by assuming the rapid formation of a complex between the

TABLE IV
Anionic Polymerization of Maleimide in Dimethylformamide at 20°C.

[M], mole/l.	NaOBu, mole/l. × 10^3	Rate × 10^4, mole/l.-sec.	$[\eta]$ (25°C., DMF)
1.04	2.6	2.3	0.08
1.04	5.2	4.25	0.09
1.04	10.4	8.6	0.07
2.13	10.4	—	0.06
0.52	5.2	~4	—
2.13	5.2	4.3	0.08
3.26	5.2	4	0.14
1.04	5.2	4.1	
1.04[a]	5.2	1.8	
1.04[b]	5.2	0.85	

[a] 40 vol.-% toluene in dimethylformamide.

[b] 1 g. succinimide in 10 ml. dimethylformamide.

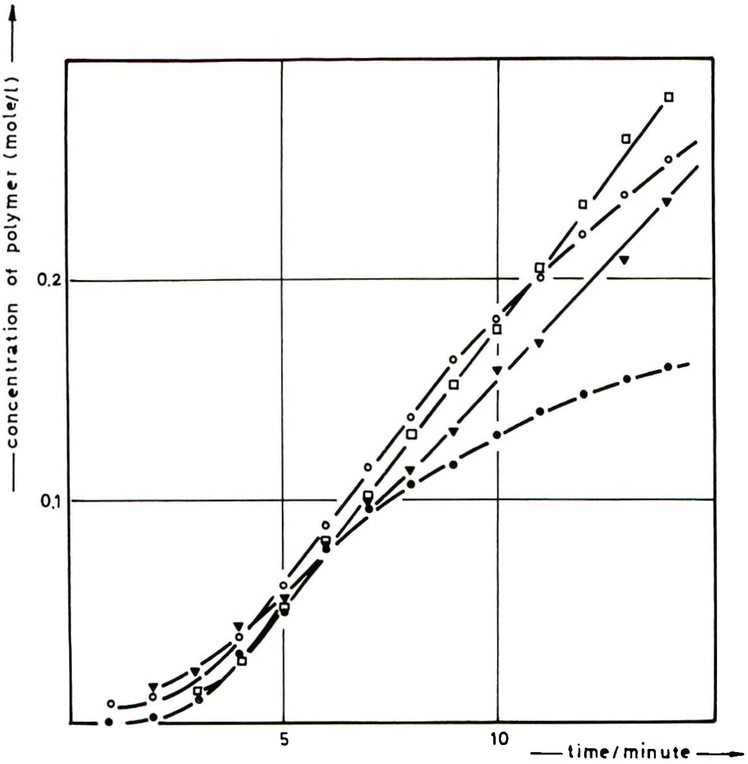
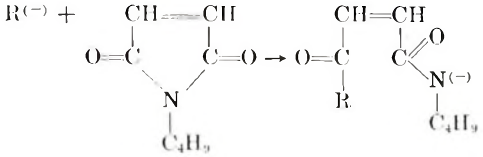


Fig. 3. Polymerization of maleimide in dimethylformamide at 20°C. and [sodium *tert*-butoxide] = 5.2 mmole/l. and various maleimide concentrations: (●) 0.52; (○) 1.04; (□) 2.13; (▽) 3.26 mole/l.

propagating anion and a monomer molecule, followed by the slow decomposition of this complex in a new propagating anion. The decrease of rate of anionic polymerization in the presence of toluene is likely due to a decrease of the dissociation of the ion pairs, while the influence of succinimide results from its competition with maleimide as well as for the initiation reaction with sodium butoxide as for the complex formation with the growing chain.

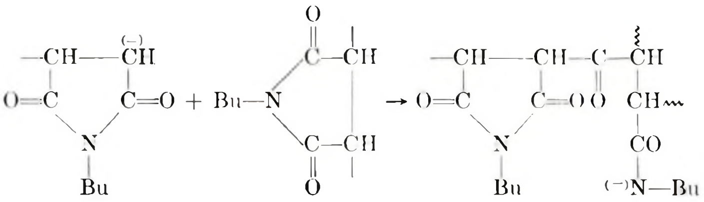
In the polymerization of *N*-*n*-butylmaleimide in toluene at −40°C. with butyllithium, the reaction is very rapid although the final yield of polymer remains relatively low (Table V) on account of a secondary termination reaction in which the ring *N*-butyl imide group opens up under the influence of a carbanion present in the medium (initiator or growing chain).



When this reaction occurs between a growing polymeric anion and an existing polymer molecule, chain branching and gel formation will result.

TABLE V
Polymerization of N-n-Butylmaleimide in
Toluene at −40°C. in Presence of n-Butyllithium

Monomer, mole/l.	Initiator, mmole/l.	Time of polymerization, min.	Yield of polymer, mole/l.
0.68	18.4	1	0.03
0.68	18.4	10	0.03
0.68	36.8	1	0.14
0.68	36.8	10	0.14
0.68	55.2	0.5	0.26
0.68	55.2	1.5	0.26
0.68	73.6	1.5	0.36
0.34	36.8	1	0.12
0.34	36.8	5	0.12
1.37	36.8	1	0.14



The importance of these secondary reactions influences strongly the composition of the reaction product and is responsible for the formation of very low molecular weights.

From structural point of view anionic poly-N-n-butylmaleimide shows the same infrared spectrum as the radical-initiated polymer; contrarily, the anionic polymaleimide is characterized by a low absorption N—H band, when compared to the radical-initiated polymer, in agreement with the data of Marvel and co-workers.[21] In order to evaluate the relative amount of $\underbrace{O{=}C{-}CHCH_2CON{-}}$ units with respect to the $\underbrace{O{=}C\overset{|}{C}H\overset{|}{C}H{-}CO{-}NH}$ units, rates of hydrolysis of the polymer were measured and compared to those of homologous substances.

Edward and Terry have shown that rate of hydrolysis of succinimide is proportional to the concentration of un-ionized succinimide, sodium succinimide being stable towards hydroxyl anion,[22] contrarily N-n-butylsuccinimide is hydrolyzed very rapidly. On this basis, it is possible to demonstrate the N-substituted structure of polymaleimide. As can be seen in Figure 4, where the degree of hydrolysis determined by potentiometric titration is plotted against the time of reaction, anionic polymaleimide hydrolyzes at 25°C. as fast as N-n-butylsuccinimide, while radical-initiated polymaleimide is practically stable toward $0.005N$ sodium hydroxide and much more stable than unsubstituted succinimide (electrostatic repulsion of the ionized macromolecule against the hydroxyl anion). The curve of anionic poly-

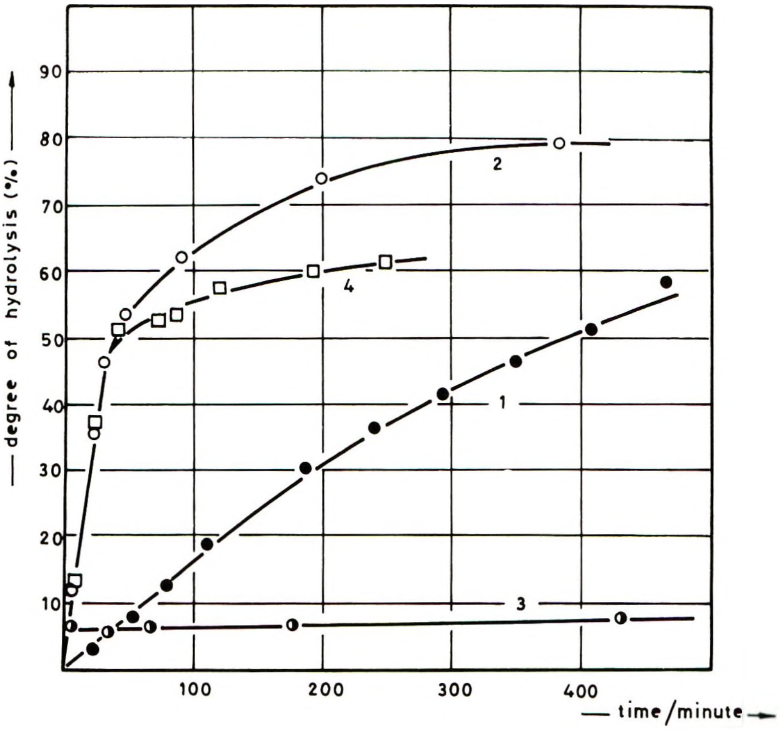


Fig. 4. Hydrolysis of (*1*) succinimide, (*2*) *N*-*n*-butyl succinimide, (*3*) radical-initiated polymaleimide; and (*4*) anionic polymaleimide in 0.005*N* NaOH solution; 25°C.

maleimide levels out at 50–55% hydrolysis because of the increasing charge of the macromolecule and some content of unsubstituted units.

By plotting the reciprocal of unhydrolyzed imides against the time and assuming a second-order reaction, the hydrolysis rate constants, respectively, 9.16×10^{-2} l./mole-sec. for *N*-*n*-butylsuccimide and anionic polymaleimide, 0.75×10^{-2} l./mole-sec. for succinimide, and 1.55×10^{-4} l./mole-sec. for radical-initiated polymer, may be determined.

In 0.05*N* sodium hydroxide at 25°C., radical-initiated polymaleimide 0.005*M* remains also unchanged, while the anionic polymer is directly hydrolyzed to 70%; progressively this increases to 79% after 100 min. In such an excess of sodium hydroxide, *N*-*n*-butyl succinimide hydrolyzes too fast to be measured. From these experiments it must be concluded that at least 70% of the units of the anionic polymer results from hydrogen-transfer polymerization. This has also been calculated from the absorbance of the ultraviolet absorption band of the ionized imide group, by comparing the spectra of succinimide and radical polymaleimide with that of the anionic polymer: it was found equal to about 20–25%. These results confirm Marvel's gas chromatography data.

It is worthwhile to point out that when radical-initiated polymaleimide is hydrolyzed at a temperature higher than 25°C. (50 and 80°C.), the degree of

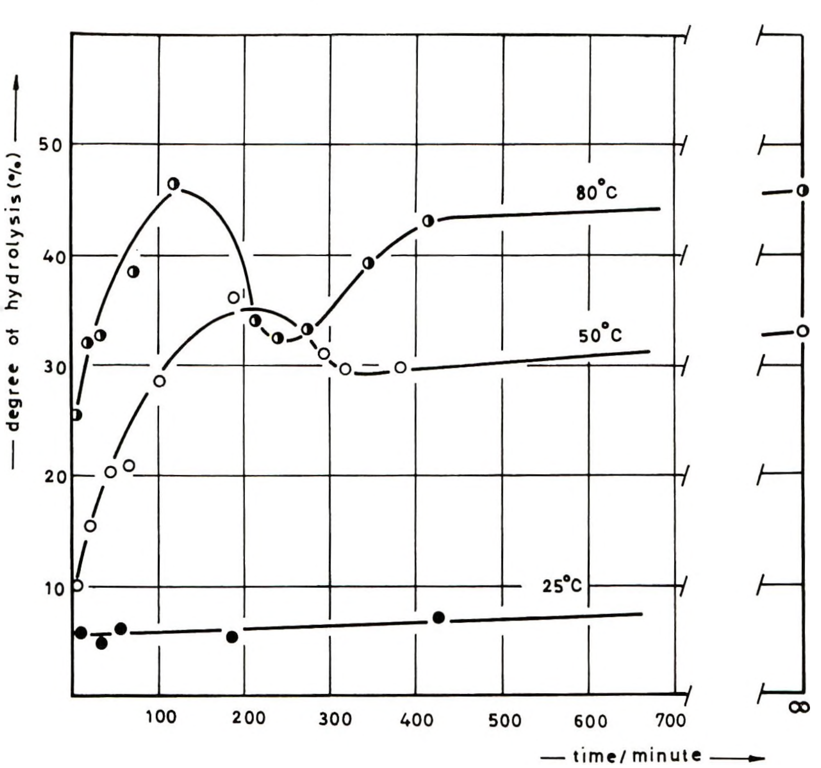
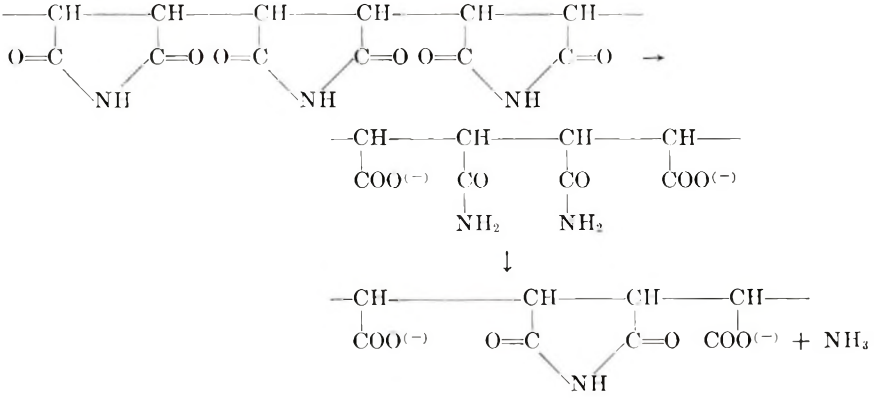


Fig. 5. Influence of the temperature on hydrolysis of radical-initiated polymaleimide in 0.005N NaOH; [polymaleimide] = 5×10^{-3} mole/l.

hydrolysis passes through a maximum, decreases to a minimum value, then reaches an asymptotic end value that is function of the reaction temperature (Fig. 5). This phenomenon can be explained on the basis of a liberation of ammonia resulting from two neighbor amide groups, and is analogous with the observations on phthalimide[23] and polyacrylamide.[24]



Concerning the lack of formation of any anionic copolymer with methyl methacrylate and acrylonitrile, it may be assumed that complex formation proceeds only with strong electron-attracting double bonds, and therefore homopolymerization is favored over any introduction of a foreign monomer.

Conclusion

The radical-initiated homopolymerization of maleimide is characterized by a partial monomolecular isomerization of the endgroup of the growing chain. This isomerization accounts for the main differences in the kinetics of polymerization between maleimide and *N*-*n*-butylmaleimide.

The anionic polymerization of maleimide proceeds with hydrogen transfer isomerization; 70–75% of *N*-substituted units has been evaluated from rate of hydrolysis measurements in agreement with Marvel's chromatography data.

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Résumé

La vitesse d'homopolymérisation du maléimide a été mesurée en solution dans le diméthylformamide à 60°C en présence d'azobisisobutyronitrile; elle a été comparée à celle du *N*-*n*-butyl-maléimide. Les vitesses globales s'expriment par la relation

$R_p = k[\mathrm{M}]^{1.1-1.2}$ $[\mathrm{In}]^{0.8}$ pour le maléimide, et par $R_p = k'[\mathrm{M}]$ $[\mathrm{In}]^{0.5}$ pour le dérivé substitué à l'azote. La différence de comportement est interprétée sur la base d'une tautomérie intramoléculaire du groupe terminal de la chaîne en croissance du maléimide et par la formation d'un radical succinimidyle stabilisé par résonance. La polymérisabilité relative des monomères et de l'anhydride maléique est soumise à discussion. En présence de tertiobutylate de sodium dans le diméthylformamide à 20°C le maléimide subit une polymérisation isomérisante par transfert d'hydrogène. Le pourcentage d'unités isomérisées N-substituées a été évalué à 70–75% par mesure de la vitesse d'hydrolyse en milieu NaOH $N/200$ et comparison avec le succinimide et le N-butylsuccinimide. Le N-n-butylmaléimide subit en présence de tertiobutylate de sodium à 20°C et de butyllithium à −40°C une polymérisation anionique en même temps qu'une ouverture du cycle penta-atomique. Contrairement au procesus radicalaire, il n'a pas été possible d'obenir de copolymères anioniques de maléimide et de N-butylmaléimide avec l'acrylonitrile et le méthacrylate de méthyle.

Zusammenfassung

Die Geschwindigkeit der Homopolymerisation von Maleinimid wurde in Dimethylformamidlösung bei 60°C in Gegenwart von Azobisisobutyronitrile gemessen; sie wurde mit derjenigen von N,n-Butylmalenimid verglichen. Die Bruttopolymerisationsgeschwindigkeit ist für Maleininimid $R_p = k[M]^{1,1-1,2}$ $[\mathrm{In}]^{0.8}$ und für das N- substituierte Imid $R_p = k'[\mathrm{M}]$ $[\mathrm{In}]^{0.5}$. Der Unterschied im Verhalten wurde auf Grundlage einer intramolekularen Tautomerie der Endgruppe der wachsenden Maleinimidkette und der Bildung eines resonanz-stabilisierten Succinimidylradikals erklärt. Die relative Polymerisationsfreudigkeit dieser Monomeren und von Maleinsäureanhydrid wurde diskutiert. In Gegenwart von Natrium-tert-butoxyd bei 20°C in dimethylformamidlösung polymerisiert Maleinimid unter Wasserstoffisomerisierung. Der Prozentgehalt an N-substituierten, isomerisierten Bausteinen wurde durch Messung der Hydrolysengeschwindigkeit in 0,005N Natronlauge und Vergleicht mit Succinimid und N-Butylsuccinimid zu 70–75% bestimmt. Zugleich mit der anionischen Polymerisation erfolgt bei N-n-Butylmaleinimid bei Gegenwart von Natrium-tert-butoxyd bei 20°C und Butyllithium bei −40°C eine Ringöffnung. Im Gegensatz zur radikalisch gestarteten Polymerisation konnten keine anionischen Copolymeren von Maleinimid oder N-Butylmaleinimid mit Acrylnitril und Methylmethacrylat erhalten werden.

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Oxidative Degradation of Polystyrene

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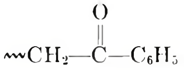
Synopsis

Nuclear magnetic resonance, infrared, and ultraviolet spectroscopy were used to elucidate the structure of oxidized polystyrene. To identify the nuclear magnetic resonance peaks of the degraded polystyrene, deuterated polystyrenes were synthesized and degraded. The primary structure present in the degraded polystyrene was found to be an aromatic carbonyl group. It was shown that this structure was formed regardless of the presence of ultraviolet light and was also present when polystyrene was degraded in carbon tetrachloride solution. When polystyrene was degraded in carbon tetrachloride solution, stable polymeric peroxides were formed in a concentration of 4 peroxide groups for every 1000 styrene units.

INTRODUCTION

The oxidative degradation of polystyrene has been extensively studied for more than a decade. It has been shown[1,2] that oxygen preferentially attacks the α-hydrogens found on the backbone of the polystyrene chain and that the initial product is hydroperoxide.[3] Positive proof of the structure of the final products resulting from the decomposition of this hydroperoxide has not, however, been shown.

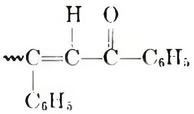
Several investigators[3,4] have postulated an acetophenone type structure (I),



$$\sim CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5$$

I

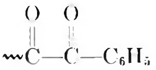
while others envision an aromatic carbonyl similar to benzal acetophenone[2] (II)



$$\sim\underset{\underset{\displaystyle C_6H_5}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5$$

II

or a dicarbonyl compound[5] (III)



$$\sim\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5$$

III

similar to 1,2-propanedione. It is believed that the present work will elucidate the structures present in oxidized polystyrene.

EXPERIMENTAL

Instrumentation

Nuclear magnetic resonance spectra were recorded on a Varian A60A high-resolution spectrometer equipped with a C1024 computer and a variable temperature probe. Polymer concentrations were 20% (w/v) in carbon tetrachloride and were referenced to tetramethylsilane.

Infrared spectra were recorded on a Perkin-Elmer Model 421 spectrophotometer. Thin films of the polymers were cast onto rock salt plates and were used directly. When polymers became too insoluble to be cast as films, KBr pellets were made.

Ultraviolet spectra were recorded on a Perkin-Elmer Model 350 spectrophotometer.

The molecular weights of the degraded polystyrenes were determined by using a Mechrolab, Model 301, vapor-pressure osmometer.

Preparation of Polymers

Poly-α-deuterostyrene, poly-β,β-dideuterostyrene, and poly-α,β,β-trideuterostyrene were prepared according to the procedure outlined by Beachell and Nemphos.[1]

Polystyrene was prepared by thermally polymerizing styrene (Eastman). A polystyrene with benzoate endgroups was prepared by polymerizing styrene with an excess of benzoyl peroxide at 80°C. Isotactic polystyrene was prepared by using a coordination catalyst according to the procedure outlined by Sorenson.[6] All polymers were freed from impurities by repeated precipitation in methyl alcohol.

Polymer Degradations

Three methods of degradation were used.

Polystyrene films (0.15 mm. thickness) were oxidized at 200°C. in a mechanical convection-type oven for periods up to 24 hr.

Polystyrene films were irradiated at 60°C. with an ultraviolet medium-pressure mercury lamp for periods up to 480 hr.

Oxygen was vigorously bubbled into a quartz flask containing a 2% solution of polystyrene in carbon tetrachloride. The solution was irradiated with ultraviolet light for periods up to 20 hr.

Reaction of Degraded Polymers with Sodium Borohydride and Lithium Aluminum Hydride

Oxidized polystyrenes were reacted with sodium borohydride in a dioxane–water mixture. The reactions with lithium aluminum hydride were done in tetrahydrofuran. The polymers were precipitated and hydrolyzed with dilute hydrochloric acid.

Tests for Functional Groups on the Degraded Polystyrene

The determination of the peroxide concentration of the degraded polystyrenes was done by measuring the increase in absorbance at 662 mμ of benzoyl leuco methylene blue after it had reacted with the oxidized polymers.[7] It has been shown that this method is capable of quantitatively detecting active oxygen down to 3 μg.

The oxidized polystyrenes were tested for (*1*) dioxo compounds with thiophene and sulfuric acid,[8a] (*2*) esters with hydroxylamine hydrochloride,[8b] and (*3*) anhydrides with an alcoholic acidified solution of hydroxylamine hydrochloride.[8c] The oxidized polystyrenes which had reacted with the lithium aluminum hydride were tested for 1,2-glycol with potassium periodate in a dioxane solution. The limit of sensitivity of these "spot tests" was approximately 10 μg.

RESULTS

Polystyrene which was oxidized at temperatures approaching 200°C. rapidly became yellow and increased in solubility. This was occasioned by a decrease in molecular weight which was found to fall rapidly from an initial 230,000 to 4,800 after 3 hr., to 2,800 after 6 hr. Polystyrene which was degraded at 60°C. with ultraviolet light, on the other hand, rapidly became insoluble in all solvents. The polystyrene degraded in carbon tetrachloride solution became insoluble after 10 hr. of degradation. Nuclear magnetic resonance, infrared, and ultraviolet spectra were able to be made of the products of polystyrene oxidized at 200°C. Only infrared spectra were made of the insoluble oxidized polystyrenes.

Spectra of Degraded Polystyrene

The infrared spectra of the polystyrenes oxidized thermally at 200°C., oxidized at 60°C. with ultraviolet light, and oxidized at 55°C. in carbon tetrachloride all showed changes in the carbonyl region of the infrared spectrum (Fig. 1). An intense, sharp band developed at 1685 cm.$^{-1}$ and continued to grow for the duration of the degradation. A much smaller band at 1720 cm.$^{-1}$ developed later. The isotactic polystyrene also showed these same changes in its infrared spectrum when heated above its crystalline melting point (230°C.). Below its crystalline melting point only surface yellowing occurred.

It was also found in this laboratory that when poly-2,3,4,5,6-pentafluorostyrene was degraded at 200°C., two carbonyl bands were found in the infrared spectra; one was at 1725 cm.$^{-1}$, the other at 1780 cm.$^{-1}$. It can be seen that these absorptions have been shifted 40 and 60 cm.$^{-1}$ when compared to the 1685 and 1720 cm.$^{-1}$ bands of degraded polystyrene noted above.

It is known that a fluorine on a carbon atom adjacent to a carbonyl will shift its carbonyl absorption to higher frequencies. The carbonyl of trifluoroacetone, for example, is found 40 cm.$^{-1}$ higher than acetone.[9] The

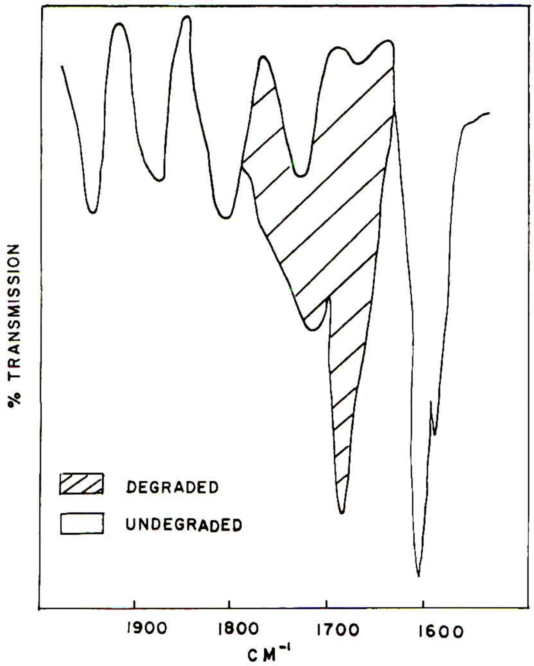


Fig. 1. Infrared spectra of degraded and undegraded polystyrenes.

carbonyl frequency of hexafluoroacetone is shifted 86 cm.$^{-1}$. However, it was found here that when the fluorine atoms are substituted on a benzene ring adjacent to a carbonyl group this effect is not as great. The carbonyl frequency of benzaldehyde, for instance, was found at 1695 cm.$^{-1}$ and that of pentafluorobenzaldehyde was at 1710 cm.$^{-1}$. A difference of 40 cm.$^{-1}$ in the polymer carbonyl, therefore, cannot be due to the fluorine atoms on the ring of a structure similar to that found in degraded polystyrene, i.e., an acetophenone type.

Considering the above evidence, there is a distinct possibility that a different mechanism exists for the degradation of poly-2,3,4,5,6-pentafluorostyrene, possibly an attack on the ring. Unfortunately, the polymer rapidly became completely insoluble in all solvents so no further study of the degradation products was possible.

The ultraviolet spectrum of the unsubstituted polystyrene oxidized at 200°C. is shown in Figure 2. It can be seen that a new maximum appeared at 241 mμ.

Figures 3 and 4 show the nuclear magnetic spectra of undegraded and degraded polystyrene, respectively. The identification and elucidation of the polystyrene NMR spectrum have been published elsewhere.[10] It can be seen in the spectrum of polystyrene which was degraded for 6 hr. that new resonances have appeared at 7.75, 7.35, and 2.90 ppm. Two extremely small peaks, which were resolved only with the help of the C1024 computer, were found at 4.80 and 5.05 ppm. With less drastic degradation, i.e., less

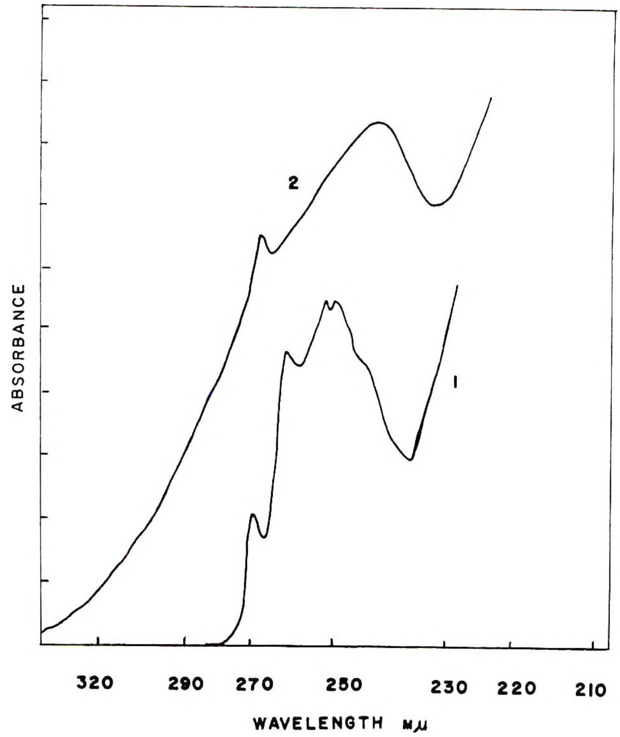


Fig. 2. Ultraviolet spectra of (*1*) undegraded and (*2*) degraded polystyrenes.

than 3 hr. at 200°C., the only change which occurred was the appearance of the 7.75 and 7.35 ppm resonances.

Since deuterium does not absorb in the same region of the NMR spectrum as protons, comparison of the spectra of the degraded deuteropolystyrenes with that of degraded polystyrene provided easy identification of the new peaks. The proton assignments for the new NMR resonances can be found in Table I.

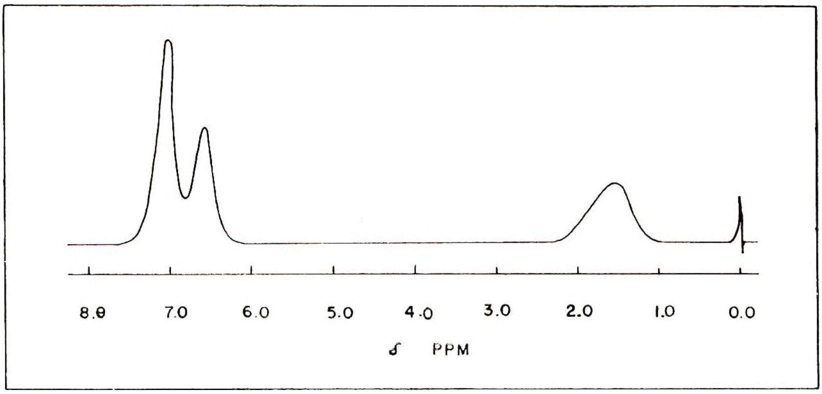


Fig. 3. Nuclear magnetic resonance spectrum of polystyrene.

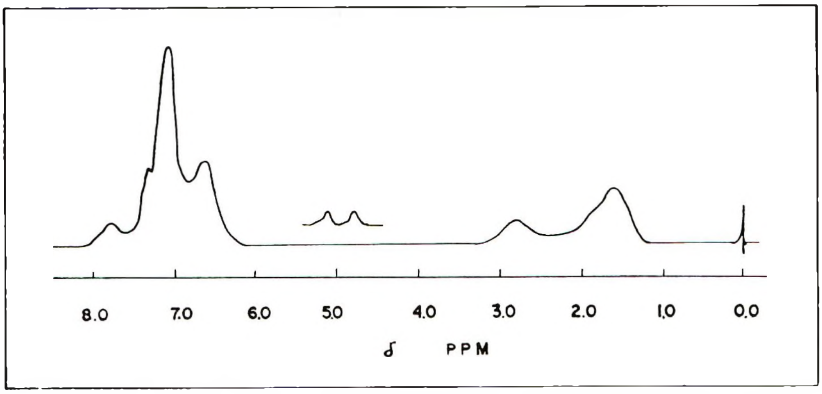


Fig. 4. Nuclear magnetic resonance spectrum of degraded polystyrene.

It was found that the polystyrene with benzoyl endgroups showed resonances at 7.85 and 7.35 ppm. These two NMR resonances showed the exact pattern as the new phenyl resonances of the oxidized polystyrene. Since it is known that the phenyl resonances of benzoate esters are in a 3/2 ratio,[11] it must be concluded that the 7.75 and 7.35 ppm peaks of oxidized polystyrene are in that same ratio.

Effect of Reaction with $LiAlH_4$ and $NaBH_4$ on Spectra

It was found that when polystyrene which was degraded at 200°C. for 3 hr. or less was reacted with lithium aluminum hydride or sodium borohydride, pronounced changes occurred in the spectra. The 241 mμ ultraviolet absorption, the 1685 cm.$^{-1}$ infrared band, and the 7.75 and 7.35 ppm NMR resonances were all removed, and the spectra returned to that of undegraded polystyrene. Treatment of more severely degraded polystyrene, i.e., polystyrene showing the 4.80, 5.05, and 2.90 ppm peaks, resulted in the shift of a portion of the 2.90 ppm resonance to 1.30 ppm. There was no effect on the 4.80 and 5.05 ppm resonances.

When polystyrene which had been degraded more drastically, i.e., more than 4 hr. at 200°C., was treated with lithium aluminum hydride or even sodium borohydride, the coloration in the polymer was greatly reduced. However, no amount of treatment could restore the polymer to its original white color.

TABLE I
Chemical Shifts of the New Peaks of the Degraded Polystyrene

Peak, ppm	Origin
7.75, 7.35	Phenyl protons
2.90	α-Hydrogen protons
5.05, 4.80	Methylene protons

Tests for Functional Groups

No hydroperoxides could be detected on the polystyrenes which were degraded at 200°C. or at 60°C. in the presence of ultraviolet light. Contrastingly, hydroperoxides in a concentration of 4 OOH units per 1000 polymeric styrene units were detected in the polystyrene degraded in carbon tetrachloride solution. Tests for 1,2-glycols, dioxo compounds, anhydrides, and esters on the degraded polymers all proved negative.

DISCUSSION OF RESULTS

The evidence as gathered from nuclear magnetic resonance spectra, infrared spectra, and ultraviolet spectra points conclusively to an aromatic carbonyl structure, similar to acetophenone, as a primary degradation product. The positive identification of this structure as a product of the degradation can be easily made when the corresponding infrared, ultraviolet, and nuclear magnetic resonance spectra of acetophenone are compared with those of the degraded polystyrene. The carbonyl frequency of acetophenone has been found at 1689 cm.$^{-1}$ compared to 1685 cm.$^{-1}$ for the degraded polystyrene. The ultraviolet spectrum of acetophenone shows the same maximum at 241 mμ as does the polystyrene. Furthermore, the NMR spectrum of acetophenone shows phenyl protons (found also in a 3/2 ratio) at the same chemical shift position as those found in the degraded polystyrene. That this one structure is responsible for the same peaks in the NMR spectrum, infrared spectrum, and ultraviolet spectrum was shown by the fact that the reduction of the carbonyl group with sodium borohydride resulted in the simultaneous removal of all spectral changes. Although solubility considerations prevented NMR and ultraviolet spectra from being made for all three types of degradation products, the presence of the same infrared bands indicates that this same aromatic carbonyl structure is present when polystyrene is oxidized by any method.

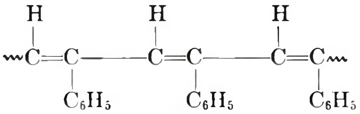
The combination of spectral changes in the ultraviolet, infrared, and NMR spectra of oxidized polystyrene refutes the existence of a benzal acetophenone type of carbonyl structure. Benzal acetophenone has an infrared carbonyl absorption at 1667 cm.$^{-1}$ and a maximum in its ultraviolet spectrum at 305 mμ. Its NMR spectrum does not show the 3 to 2 phenyl proton ratio but only a complicated mass of jagged peaks extending from 7.60 to 7.20 ppm.

Dicarbonyl structures similar to 1,2-propanedione must also be rejected on similar grounds. Although 1,2-propanedione showed infrared and NMR spectra similar to that found on degraded polystyrene, its ultraviolet spectrum shows a pronounced maximum at 260 mμ. Also, the exhaustive tests for dioxo compounds in the degraded polymer and tests for glycols in the polymer treated with sodium borohydride all proved negative.

The specific identification of other structures present, e.g., the 1720 cm.$^{-1}$ band in the infrared, is not as easily done. It was shown that sodium borohydride could reduce all carbonyl groups in oxidized polystyrene.

Brown has shown that sodium borohydride will reduce only aldehydes, ketones, lactones, and acid chlorides.[12] Chemical tests for esters and anhydrides were negative. Also, no aldehydic peaks were noted in any spectra. Thus, since all of the carbonyl groups were reduced by sodium borohydride, it must be concluded that all the carbonyl groups on degraded polystyrene are ketonic. The possibility of conjugation being associated with the 1720 cm.$^{-1}$ carbonyl band must not be ruled out. Protons associated with such a conjugated carbonyl could be masked in the NMR by the large phenyl resonances of the undegraded part of the polystyrene molecule.

Also, since some coloration of the oxidized polystyrene remained when degraded polystyrene had all the carbonyl groups removed, it is quite possible that conjugated structures of the type Grassie suggests[4] (IV) could be the cause of the 5.05 and 4.80 ppm peaks.



$$\sim\overset{H}{C}=\underset{C_6H_5}{C}-\overset{H}{C}=\underset{C_6H_5}{C}-\overset{H}{C}=\underset{C_6H_5}{C}\sim$$

IV

Their positions in the NMR spectrum would not be affected by any carbonyl reduction, as was observed.

The only other structures which were specifically identified were the polymeric peroxides found in a concentration of 4 peroxide units for every 1000 styrene units. It must be noted that others[13-15] have also had success in preparing polystyrene peroxides. The polymeric peroxides that were obtained, undoubtedly arose from a wide variety of reactions occurring in the carbon tetrachloride solution, including the reaction of the polymer with the solvent itself. The presence of approximately 12% chlorine found on the polystyrene attests to this. The fact that no peroxides were detected on the thermally oxidized polystyrenes is understandable when the relative instability of peroxides at elevated temperatures is considered.

A word must be said about the 2.90 ppm peak in the spectra of oxidized polystyrene. Bovey[10] has shown that at molecular weights of 2,000 or less the α-hydrogens of polystyrene become deshielded from the diamagnetic field of adjacent phenyl rings and appear at 2.90 ppm. The appearance of the 2.90 ppm resonances undoubtedly is due to low molecular weight fractions present in the degraded polymer. The anomalous shift of some of the α-proton resonances from 2.90 to 1.30 ppm when the carbonyl groups were reduced with sodium borohydride is quite difficult to explain. For a reason, as yet to be understood, when the carbonyl groups are removed these α-hydrogens are thrust more firmly than ever into the diamagnetic region of neighboring phenyl groups.

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Résumé

La résonance nucléaire magnétique, la spectroscopie infrarouge et ultraviolette ont été utilisées pour élucider la structure du polystyrène oxydés. Pour identifier les pics de résonance nucléaire magnétique des polystyrènes dégradés, des polystyrènes deutérés ont été synthétisés et dégradés. La structure primaire présente dans le polystyrène dégradé consiste dáns un groupe carbonylique aromatique. On a montré que cette structure était formée indépendamment de la présence de la lumière ultraviolette et était également présente lorsque le polystyrène était dégradé en solution dans le tétrachlorure de carbone. Lorsque le polystyrène était dégradé dans la solution de tétrachlorure de carbone, des peroxydes polymériques stables sont formés dans les concentrations de 4 peroxydes toutes les 1000 unités styréniques.

Zusammenfassung

Kernmagnetische Resonanz-, Infrarot- und Ultraviolettspektroskopie wurden zur Aufklärung der Struktur von oxydiertem Polystyrol herangezogen. Zur Identifizierung der kernmagnetischen Resonanzbanden von abgebautem Polystyrol wurden deuterierte Polystyrole synthetisiert und abgebaut. Die in dem abgebauten Polystyrol vorhandene Primärstruktur erwies sich als aromatische Carbonylgruppe. Es wurde gezeigt, dass sich diese Struktur unabhängig von der Anwesenheit von Ultraviolettlicht bildete und auch beim Abbau von Polystyrol in Tetrachlorkohlenstofflösung auftrat. Beim Abbau von Polystyrol in Tetrachlorkohlenstofflösung wurden stabile polymere Peroxyde in einer Konzentration von 4 Peroxydgruppen auf 1000 Styrolbausteine gebildet.

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Influence of Addition of Olefins on the Alternating Copolymerization of Carbon Monoxide and Ethylenimine by Azobisisobutyronitrile or by γ-Ray Irradiation

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Synopsis

The alternating copolymerization of carbon monoxide and ethylenimine to give poly-β-alanine could be initiated by γ-irradiation but hardly by α,α′-azobisisobutyronitrile (AIBN). It was found that in the case of the addition of olefin, this system could be copolymerized even by AIBN and that, in the γ-ray copolymerization of carbon monoxide and ethylenimine, the addition of olefin brought about an increase in the copolymer yield. No difference was observed between the nature of copolymers obtained by AIBN and those obtained by γ-irradiation, except in the system carbon monoxide–ethylenimine–ethylene. An increase in the amount of reacted olefin gave rise to an increase in copolymer yield. The melting points of the copolymers were in the range 295–335°C. The infrared spectra, x-ray diffraction diagrams, and NMR spectra of the copolymers were almost identical with that of poly-β-alanine obtained by the hydrogen-migration polymerization of acrylamide. Paper chromatographic analysis of the hydrolysis product of the copolymer showed the existence of β-alanine, ethylamine, and δ-aminovaleric acid homolog in the products. From these results, it was concluded that terpolymerization of carbon monoxide, ethylenimine, and olefin took place in the presence of AIBN or γ-irradiation which gave a crystalline solid copolymer containing the units of nylon 3 and nylon 5. A mechanism of this copolymerization was proposed on the basis of these results.

INTRODUCTION

Recently, the alternating copolymerization of carbon monoxide and ethylenimine to give a crystalline solid poly-β-alanine was reported.[1] In addition, a previous study showed that the copolymerization of carbon monoxide and ethylenimine in the presence of ethylene took place in the presence of γ-radiation and gave an amorphous polymer containing the units $\mathrm{-\!\!(CH_2CH_2NHCO)\!\!-}$, $\mathrm{-\!\!(CH_2CH_2CO)\!\!-}$, and $\mathrm{-\!\!(CH_2CH_2CH_2CH_2NHCO)\!\!-}$.[2]

During the course of an investigation of the copolymerization of carbon monoxide and ethylenimine, it was discovered that the copolymerization could be initiated with difficulty by AIBN and that a crystalline polyamide was obtained by the addition of olefin in this system.

The present investigation was undertaken to determine the influence of the addition of various olefins on the alternating copolymerization of carbon monoxide and ethylenimine with AIBN or γ-irradiation.

EXPERIMENTAL

Materials and Procedure

Commercial ethylenimine was dried over KOH pellets and NaH and then fractionated at 55.5–56°C. before use. Ethylene (99.9% purity, less than 5 ppm oxygen), propylene (99% purity), isobutylene (99% purity), and carbon monoxide (99.2% purity) were obtained commercially. Pentene-1 and dodecene-1 were fractionated at 30–31°C. and 96–97°C./15 mm. Hg, respectively. α,α'-Azobisisobutyronitrile (AIBN) was obtained commercially.

The copolymerization by AIBN was carried out as follows. Measured amounts of ethylenimine and AIBN were charged into a stainless steel autoclave of 30 ml. capacity. The vessel was evacuated twice under cooling with liquid nitrogen. Then, measured amounts of carbon monoxide and olefin were fed into the vessel from each reservoir. The vessel was immersed without agitation during the course of reaction in an oil bath. After the reaction stopped, the vessel was opened to purge the unreacted monomers. The product was washed thoroughly with a large amount of diethyl ether, dried *in vacuo*, and weighed.

In the experiment with γ-irradiation, the vessel was charged with ethylenimine, carbon monoxide, and olefin without AIBN according to the procedure described above. All irradiation was performed with γ-rays from a 5000 C. ^{60}Co source, and the reaction was carried out without agitation. After the reaction was stopped, the product was treated as described above.

Chemical Analysis of the Copolymer

The composition of the copolymer was determined from the contents of carbon, hydrogen, and nitrogen from elemental analysis. In order to determine the structure of copolymers, the hydrolysis product of the copolymers obtained was analyzed by a paper chromatographic method as follows. The copolymer was hydrolyzed in a sealed tube with 6*N* HCl at 110°C. for 20 hr. The hydrolysis product was compared with commercial β-alanine, δ-aminovaleric acid, and ethylamine by the usual one-dimensional ascending chromatography for amino acids.[3] Both samples were developed on Toyo Roshi No. 50 paper for chromatography with *n*-butanol–glacial acetic acid-water (4:1:5) as a solvent. Both spots were detected by using *n*-butanol solution of ninhydrin.

Physical Analysis of the Copolymer

The melting point of the copolymer was determined visually in a nitrogen atmosphere in a capillary on a Yanagimoto melting point measuring apparatus, Model MP-S2. The infrared spectrum was obtained by using a KBr pellet technique on a Shimadzu infrared spectrophotometer, Model IR-27, with NaCl prism. The x-ray diffraction diagram was recorded with a powder camera on a Shimadzu x-ray diffractometer, Model GX-3B, employing Ni-filtered CuKα radiation by the use of standard techniques. The NMR spectrum was run at 22°C. on a Japan Electron high resolution spectrometer, Model 4H-100, at 100 Mc./sec. in a formic acid solution with tetramethylsilane as a standard.

RESULTS AND DISCUSSION

The result of the copolymerization of carbon monoxide and ethylenimine in the presence of olefin by AIBN is shown in Table I. Very little copolymer could be obtained without the addition of olefin in this system (expt. 1). Figure 1 shows that the yield of copolymer is independent of olefin content and increases with the amount of reacted olefin. These results and the fact that the various polymers consist primarily of nylon 3 units indicate that the olefin in this copolymerization mainly acts as an initiator. If it is assumed that initiation proceeds in the gaseous phase, the rate of initiation increases with olefin concentration in gaseous phase, and this brings about the increase of copolymer yields. From this assumption, with the use of ethylene and propylene, high concentrations of these olefins in the gaseous phase result in higher yields. The melting point of the copolymer was about 280–312°C. and became lower with the olefin content in copolymers in all cases.

The result of copolymerization of carbon monoxide and ethylenimine by γ-irradiation in the presence of olefin is shown in Table II. Copolymer was obtained in this system without the addition of olefin, and the yield in-

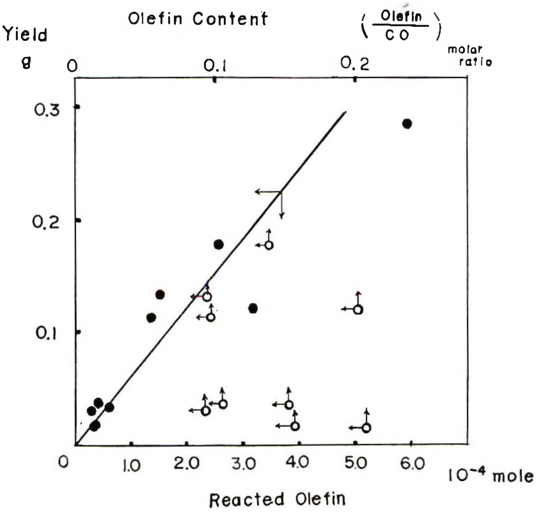


Fig. 1. Copolymer yield vs. (●) reacted olefin or (O) olefin content (AIBN initiation).

TABLE I

Influence of Olefins on the Copolymerization of Carbon Monoxide and Ethylenimine by Azobisisobutyronitrile[a]

Expt. no.	Olefin	Wt. olefin, g.	$\left(\frac{\text{Olefin}}{C_2H_5N}\right)$ molar ratio	Yield, g.	Melting point, °C.	Polymer composition (molar ratio)			Elementary analysis (found)		
						C_2H_5N	CO	Olefin	C, %	H, %	N, %
1	—	—	—	0.004	304–312	—	—	—	—	—	—
2	Ethylene	0.75	0.25	0.173	300–306	1.23	1.0	0.13	50.85	8.07	19.55
3	Ethylene	3.0	1.0	0.283	294–297	1.21	1.0	0.18	51.74	8.11	19.35
4	Propylene	1.14	0.25	0.133	290–297	1.13	1.0	0.09	50.91	7.91	18.99
5	Propylene	4.5	1.0	0.120	280–290	1.09	1.0	0.20	53.38	8.20	17.64
6	Isobutylene	1.5	0.25	0.111	297–310	1.12	1.0	0.09	52.44	7.96	18.89
7	Isobutylene	6.0	1.0	0.015	305–312	1.14	1.0	0.20	52.68	8.52	17.15
8	Pentene-1	1.9	0.25	0.035	290–303	1.15	1.0	0.15	53.29	8.40	17.86
9	Pentene-1	7.5	1.0	0.017	280–290	0.96	1.0	0.15	53.32	8.18	16.10
10	Dodecene-1	1.8	0.1	0.030	290–300	1.12	1.0	0.09	56.17	8.64	16.91
11	Dodecene-1	7.2	0.4	0.036	295–305	1.10	1.0	0.10	56.24	8.85	15.97

[a] Reaction conditions: ethylenimine, 4.6 g.; carbon monoxide, 3.0 g.; AIBN, 90 mg.; temperature, 60 ± 2°C.; time, 5 hr.; an autoclave of 30 ml. capacity was used.

TABLE II

Influence of Olefins on the Copolymerization of Carbon Monoxide and Ethylenimine by γ-Irradiation[a]

Expt. no.	Olefin	Wt. olefin, g.	$\left(\frac{\text{Olefin}}{C_2H_5N}\right)$ molar ratio	Yield, g.	Melting point, °C.	Polymer composition (molar ratio)			Elementary analysis (found)		
						C_2H_5N	CO	Olefin	C, %	H, %	N, %
1	—	—	0	0.449	305–317	1.25	1.0	—	48.35	7.86	20.23
2	Ethylene	3.5	1.0	1.212	325–335	1.35	1.0	0.48	54.38	8.91	18.36
3	Propylene	4.5	1.0	1.417	300–306	1.03	1.0	0.10	52.14	7.67	18.65
4	Isobutylene	6.5	1.1	0.635	285–296	1.07	1.0	0.10	51.61	7.83	18.16
5	Pentene-1	7.5	1.0	0.721	295–320	1.26	1.0	0.06	52.34	8.54	18.21
6	Dodecene-1	7.2	0.4	0.817	300–320	1.36	1.0	0.10	55.84	8.97	17.57

[a] Reaction conditions: ethylenimine, 4.6 g.; carbon monoxide, 3.0 g.; temperature, 12 ± 1°C.; dose rate, 4.0×10^5 rad/hr.; total dose, 1.88×10^7 rad; an autoclave of 30 ml. capacity was used.

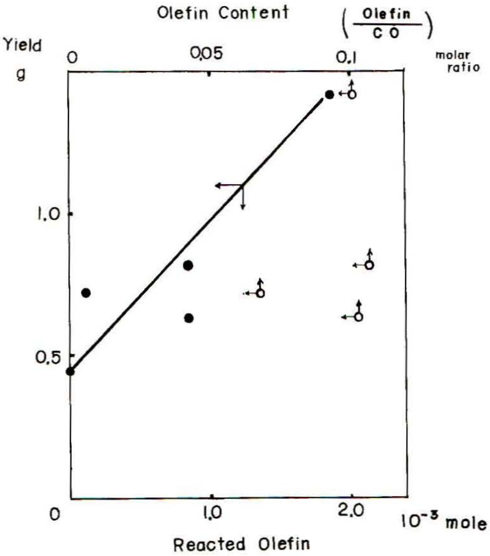


Fig. 2. Copolymer yield vs. (●) reacted olefin or (○) olefin content (γ-ray initiation).

creased markedly on addition of olefin. Similar to the result in the case of AIBN, copolymer yield did not depend on olefin content, but increased with the amount of reacted olefin as shown in Figure 2.

These results indicate that, in the case of the addition of olefin, the radiolysis product of olefin also acts as an initiator. Thus, the increase of copolymer yield in the presence of olefins is due to an increase in the amount of initiators.

Infrared Spectra of the Copolymers

Figures 3 and 4 show the infrared spectra of the copolymers obtained by AIBN and by γ-rays, respectively. All of the copolymer displayed major absorption peaks assigned to secondary amide at near 3300, 3080, 1635, and 1540 cm.$^{-1}$. And no peak at 1700 cm.$^{-1}$ attributable to ketone was observed, except in the system carbon monoxide–ethylenimine–ethylene and γ-ray.

γ-Ray Diffraction Diagrams of the Copolymers

Figures 5 and 6 show the x-ray diffraction diagrams of these copolymers. The data in Figure 5 and 6 indicate that, except the copolymer containing a large amount of ethylene (*2* in Figure 6), all copolymers were crystalline. Although no attempt was made to determine the per cent crystallinity, the result of a comparison of the relative half width corresponding to the crystallinity of the copolymers indicates that crystallinity decreased with increasing olefin content.

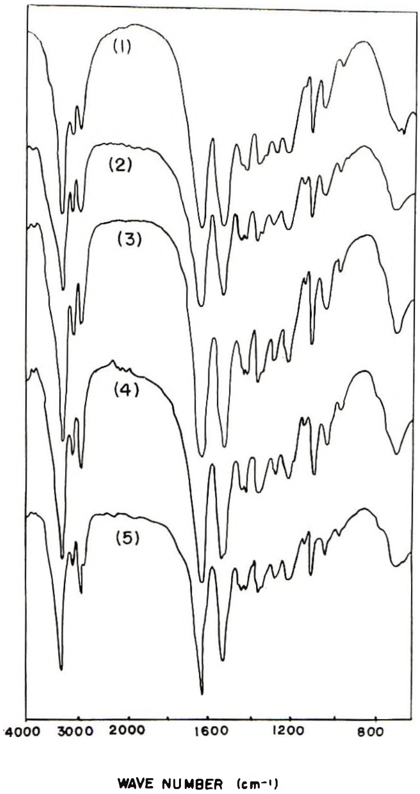


Fig. 3. Infrared spectra of the copolymers obtained by AIBN: (*1*) carbon monoxide–ethylenimine–ethylene; (*2*) carbon monoxide–ethylenimine–propylene; (*3*) carbon monoxide–ethylenimine–isobutylene; (*4*) carbon monoxide–ethylenimine–pentene-1; (*5*) carbon monoxide–ethylenimine–dodecene-1.

NMR Spectra of the Copolymers

As shown in Figure 7, the NMR spectra of the copolymers and poly-β-alanine obtained by hydrogen-migration polymerization of acrylamide are almost identical. The spectra of them showed three peaks at about $\tau = 7.35$ $-\!\!(CH_2CO)\!\!-$, 6.35 $-\!\!(NCH_2)\!\!-$, and 2.20 $-\!\!(CONH)\!\!-$. The molar ratio of —CH_2CO—/—NCH_2—/—CONH—, calculated from the ratio of integral values of the —CH_2CO—, —NCH_2—, and —CONH— peaks, was about 2:2:1 and agreed with the poly-β-alanine structure.

Paper Chromatograms of the Copolymers

Figure 8 shows the paper chromatograms of the hydrolysis product of the copolymers. The hydrolysis product of the copolymer obtained by γ-ray-induced copolymerization of carbon monoxide and ethylenimine showed only one spot, while those from the copolymers obtained in the presence of olefin showed three spots.

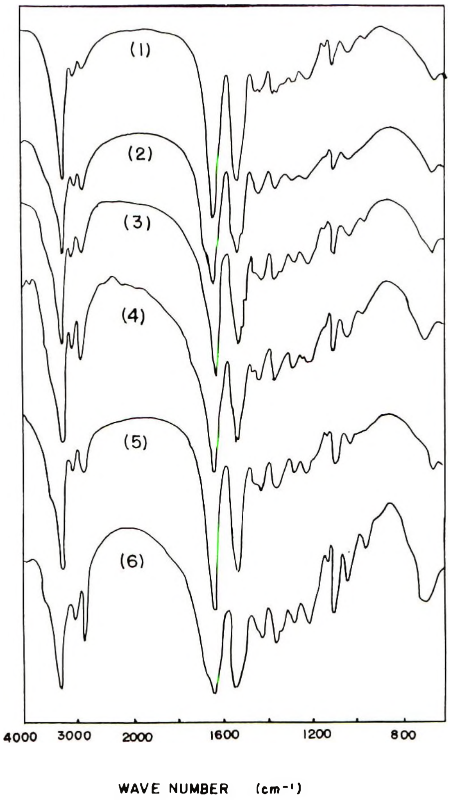


Fig. 4. Infrared spectra of the copolymers obtained by γ-irradiation: (*1*) carbon monoxide–ethylenimine; (*2*) carbon monoxide–ethylenimine–ethylene; (*3*) carbon monoxide–ethylenimine–propylene; (*4*) carbon monoxide–ethylenimine–isobutylene; (*5*) carbon monoxide–ethylenimine–pentene-1; (*6*) carbon monoxide–ethylenimine–dodecene-1.

The R_f value of the first spot (0.26–0.30) agreed closely with that of commercial β-alanine in the same solvent system. The R_f value of the second spot (0.41–0.45) agreed with that of ethylamine and that of δ-aminovaleric acid. This spot disappeared, except in the case of the copolymer obtained in carbon monoxide–ethylenimine–ethylene system, by heating the alkaline hydrolyzate of the copolymer for several minutes at 100°C., neutralizing, and chromatography as described before. In the case of the carbon monoxide–ethylenimine–ethylene system, the second spot did not disappear completely but the color diminished in intensity after the above treatment. This would indicate that the second spots (*2* and *7* in Fig. 8) (carbon monoxide–ethylenimine–ethylene system) show the existence of ethylamine and δ-aminovaleric acid, and the spot in the other copolymers (carbon monoxide–ethylenimine–α-olefin system) indicates the presence of ethylamine in the hydrolysis products. As the R_f value of the third spot increased with carbon number of the added olefin, this third spot is considered to be due to a δ-aminovaleric acid homolog con-

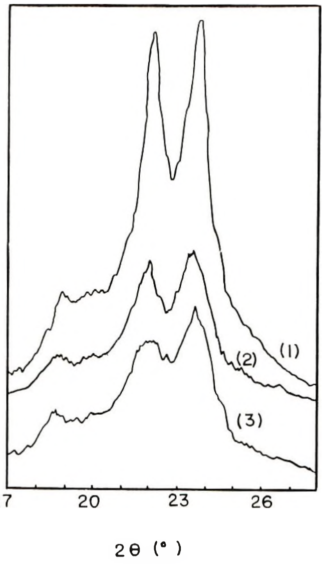
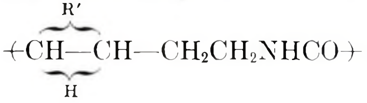
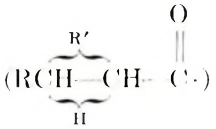


Fig. 5. X-ray diffraction diagrams of the copolymers obtained with AIBN: (*1*) carbon monoxide–ethylenimine–ethylene; (*2*) carbon monoxide–ethylenimine–propylene; (*3*) carbon monoxide–ethylenimine–isobutylene.

taining olefin unit. The evidence thus obtained supports the suggestion that the copolymer consists of nylon 3 $\left(\text{CH}_2\text{CH}_2\text{NHCO}\right)$, and nylon 5  $\left(\overbrace{\underbrace{\text{CH—CH}}_{\text{H}}}^{\text{R}'}\text{—CH}_2\text{CH}_2\text{NHCO}\right)$ units.

MECHANISM OF THE COPOLYMERIZATION OF CARBON MONOXIDE AND ETHYLENIMINE IN THE PRESENCE OF OLEFIN

Initiation of the Copolymerization Induced by AIBN

As described above, copolymerization of carbon monoxide and ethylenimine was initiated by AIBN only to a very small extent, while in the presence of olefin, a crystalline copolymer was obtained. This indicates that initiation reaction of the copolymerization by AIBN consists of two elementary reactions: the reaction of olefin and radical R· produced by the decomposition of AIBN, and the formation of initiating radical  $\left(\text{R}\overbrace{\underbrace{\text{CH—CH}}_{\text{H}}}^{\text{R}'}\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\cdot\right)$ by the reaction of carbon monoxide and the radical formed in reaction (1b).

$$\text{I} \rightarrow 2\text{R}\cdot \tag{1a}$$

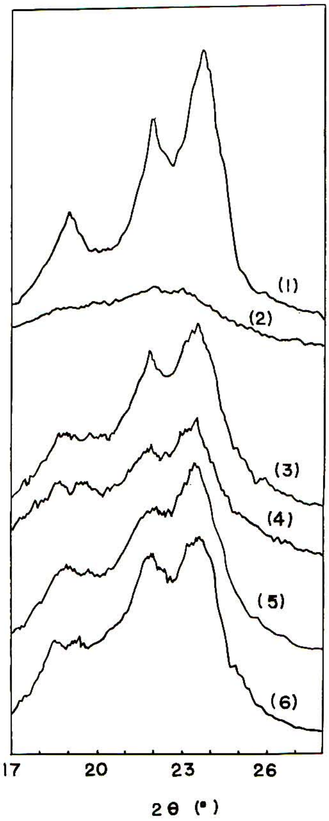
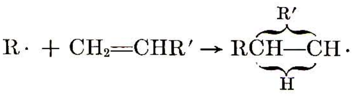
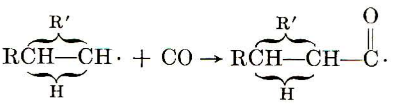


Fig. 6. X-ray diffraction diagrams of the copolymers obtained by γ-irradiation: (*1*) carbon monoxide–ethylenimine; (*2*) carbon monoxide–ethylenimine–ethylene; (*3*) carbon monoxide–ethylenimine–propylene; (*4*) carbon monoxide–ethylenimine–isobutylene; (*5*) carbon monoxide–ethylenimine–pentene-1; (*6*) carbon monoxide–ethylenimine–dodecene-1.



$$R\cdot + CH_2{=}CHR' \rightarrow R\overbrace{\underbrace{CH{-}CH}_{H}}^{R'}\cdot \qquad (1b)$$



$$R\overbrace{\underbrace{CH{-}CH}_{H}}^{R'}\cdot + CO \rightarrow R\overbrace{\underbrace{CH{-}CH}_{H}}^{R'}{-}\overset{\overset{O}{\|}}{C}\cdot \qquad (1c)$$

It may be that dimethyl cyanomethyl radical does not react with carbon monoxide because of the electronic nature of this radical.

Initiation by γ-Radiation

As described above, copolymerization of carbon monoxide and ethylenimine induced by γ-rays took place in the absence of olefin, and the olefins could copolymerize with carbon monoxide[4–8] but not with ethylenimine.[2]

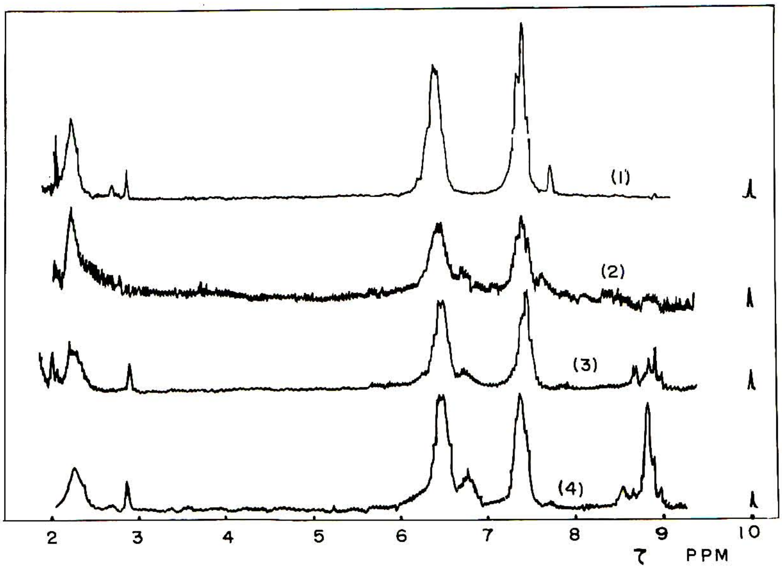
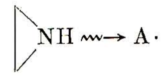
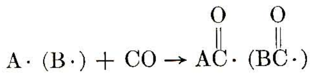


Fig. 7. NMR spectra of various substances: (*1*) poly-β-alanine obtained by the hydrogen-migration polymerization of acrylamide; (*2*) copolymer of carbon monoxide, ethylenimine, and ethylene (γ-ray initiation); (*3*) copolymer of carbon monoxide, ethylenimine, and propylene (AIBN initiation); (*4*) copolymer of carbon monoxide, ethylenimine, and isobutylene (γ-ray initiation).

These results suggest that the initiation reaction in the γ-ray-induced copolymerization is the formation of carbonyl radicals by the reaction of carbon monoxide and radicals produced by the radiolysis from ethylenimine (A·) or olefin (B·) as shown in eqs. (2).

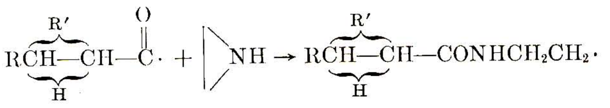

(2a)

$$CH_2{=}CHR' \rightsquigarrow B\cdot \qquad (2b)$$


$$A\cdot\ (B\cdot) + CO \rightarrow A\overset{\overset{\displaystyle O}{\|}}{C}\cdot\ (B\overset{\overset{\displaystyle O}{\|}}{C}\cdot) \qquad (2c)$$

Propagation

The main structure of the copolymers obtained by AIBN and that by γ-irradiation was poly-β-alanine, so the propagation reaction in both systems is considered to be the same. Since the carbonyl radical is highly electrophilic, the addition of ethylenimine having a high nucleophilicity to the carbonyl radical is considered to occur exclusively. The main propagation reaction, therefore, is proposed as shown in eqs. (3) and (4).


(3)

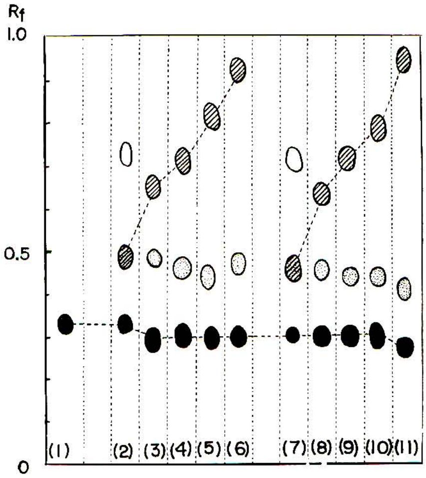
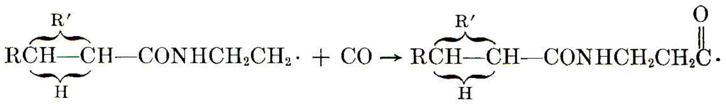


Fig. 8. Paper chromatograms of the hydrolysis product of the copolymers: (*1*) carbon monoxide–ethylenimine (γ-ray initiation); (*2*) carbon monoxide–ethylenimine–ethylene (AIBN initiation); (*3*) carbon monoxide–ethylenimine–propylene (AIBN); (*4*) carbon monoxide–ethylenimine–isobutylene (AIBN); (*5*) carbon monoxide–ethylenimine–pentene-1 (AIBN); (*6*) carbon monoxide–ethylenimine–dodecene-1 (AIBN); (*7*) carbon monoxide–ethylenimine–ethylene (γ-ray); (*8*) carbon monoxide–ethylenimine–propylene (γ-ray); (*9*) carbon monoxide–ethylenimine–isobutylene (γ-ray); (*10*) carbon monoxide–ethylenimine–pentene-1 (γ-ray); (*11*) carbon monoxide–ethylenimine–dodecene-1 (γ-ray).

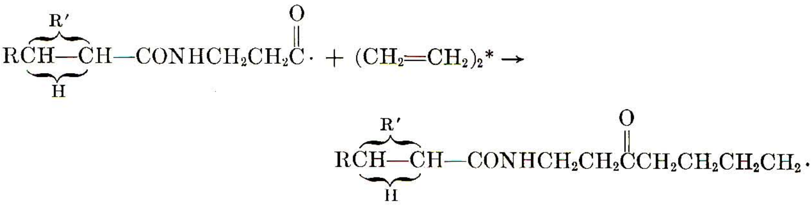


$$\mathrm{R}\overbrace{\underbrace{\mathrm{CH{-}CH}}_{\mathrm{H}}}^{\mathrm{R'}}\mathrm{{-}CONHCH_2CH_2\cdot} + \mathrm{CO} \rightarrow \mathrm{R}\overbrace{\underbrace{\mathrm{CH{-}CH}}_{\mathrm{H}}}^{\mathrm{R'}}\mathrm{{-}CONHCH_2CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\cdot \qquad (4)$$

The alternate occurrence of two selective addition reactions (3) and (4) gives the polymer with nylon 3.

For the propagation in the copolymerization in the carbon monoxide–ethylenimine–ethylene system by γ-irradiation, steps (5) of ethylene excitation[9] and (6) are proposed in view of the fact that polyketone was observed in this system.

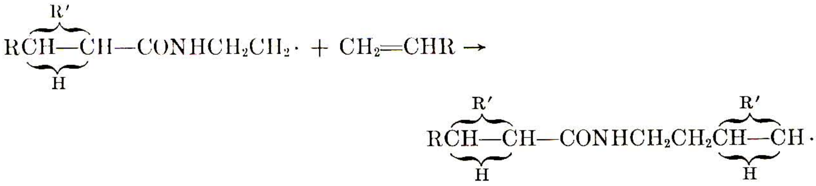
$$2\mathrm{CH_2{=}CH_2} \rightsquigarrow (\mathrm{CH_2{=}CH_2})_2^* \qquad (5)$$



$$\mathrm{R}\overbrace{\underbrace{\mathrm{CH{-}CH}}_{\mathrm{H}}}^{\mathrm{R'}}\mathrm{{-}CONHCH_2CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\cdot + (\mathrm{CH_2{=}CH_2})_2^* \rightarrow$$

$$\mathrm{R}\overbrace{\underbrace{\mathrm{CH{-}CH}}_{\mathrm{H}}}^{\mathrm{R'}}\mathrm{{-}CONHCH_2CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2CH_2CH_2\cdot} \qquad (6)$$

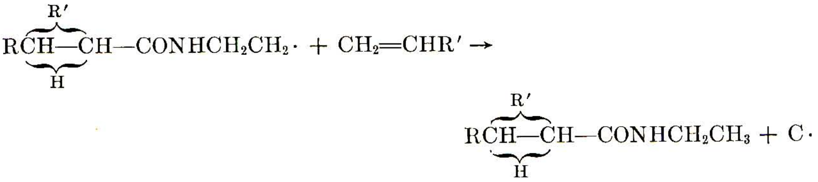
On the basis of the results of the changes in melting point, x-ray diffraction diagrams, and paper chromatographic analysis of the copolymer with the use of olefin, it was concluded that a small amount of the copolymer with nylon 5 was also formed. The reaction (7), therefore, should be considered as another propagation reaction of slow rate.



$$\underbrace{\overbrace{\mathrm{RCH{-}CH}}^{R'}}_{H}\mathrm{{-}CONHCH_2CH_2\cdot} + \mathrm{CH_2{=}CHR} \rightarrow \underbrace{\overbrace{\mathrm{RCH{-}CH}}^{R'}}_{H}\mathrm{{-}CONHCH_2CH_2}\underbrace{\overbrace{\mathrm{CH{-}CH}}^{R'}}_{H}\cdot \quad (7)$$

Transfer

Because ethylamine was observed in the hydrolysis product of the copolymer obtained in the presence of olefin, it is considered that a compound having an *N*-ethyl amide group is contained in the copolymer. Then, the transfer reaction (8) is proposed.



$$\underbrace{\overbrace{\mathrm{RCH{-}CH}}^{R'}}_{H}\mathrm{{-}CONHCH_2CH_2\cdot} + \mathrm{CH_2{=}CHR'} \rightarrow \underbrace{\overbrace{\mathrm{RCH{-}CH}}^{R'}}_{H}\mathrm{{-}CONHCH_2CH_3} + \mathrm{C\cdot} \quad (8)$$

The radical formed in reaction (3) abstracts the hydrogen atom from the olefin and gives a transfer radical (C·) and an *N*-ethyl amide endgroup on the copolymer.

A quantitative study of the copolymerization of carbon monoxide and ethylenimine in the presence of olefin by AIBN will be reported in a subsequent paper.

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Résumé

La copolymérisation alternante de l'oxyde de carbone et de l'éthylèneimine pour fournir de la β-polyalanine peut être initiée par irradiation aux rayons-γ mais est difficilement obtenable au moyen de l'α,α'-azobisisobutyronitrile (AIBN). On a trouvé que dans le cas de l'addition d'oléfine, ce système peut être copolymérisé même par l'AIBN, et que dans la copolymérisation aux rayons-γ de l'oxyde de carbone et de l'éthylèneimine, l'addition d'oléfine entraîne une augmentation du rendement en copolymères. Aucune différence entre la nature des copolymères obtenus au moyen de l'AIBN et obtenus par irradiation aux rayons-γ n'a pu être obseervée, sauf dans les systèmes monoxyde de carbone-éthylèneimine. Un accroissement de la quantité d'oléfine entraîne une augmentation du rendement en copolymères. Le point de fusion des copolymères allait de 295 à 335°C. Les spectres infrarouges, les diagrammes de diffraction aux rayons-X, les spectres NMR des copolymères étaient pratiquement identiques à ceux de la poly-β-alanine obtenus par polymérisation isomérisante de l'acrylamide. L'analyse chromatographique sur papier du produit d'hydrolyse du copolymère montrait l'existence de β-alanine, éthylamine et d'acide δ-aminovalérique dans les produits. Au départ de ces résultats on conclu que la terpolymérisation de l'oxyde de carbone, de l'éthylèneimine et d'oléfine a lieu soit par AIBN, soit par irradiation aux rayons-γ et fournit un copolymère cristallin contenant des unités de nylon-γ et nylon-5. Un mécanisme pour cette copolymérisation est proposé sur la base de ces résultats.

Zusammenfassung

Die alternierende Copolymerisation von Kohlenmonoxyd und Äthylenimin zu Poly-β-alanin konnte durch γ-Bestrahlung, kaum aber mit α,α'-Azobisisobutyronitril (AIBN) angeregt werden. Bie Zusatz von Olefinen konnte dieses System auch mit AIBN copolymerisiert werden und bei der γ-Strahlen-Copolymerisation von Kohlenmonoxyd und Äthylenimin führte der Olefinzusatz zu einer Erhöhung der Copolymerausbeute. Mit Ausnahme des Systems Kohlenmonoxyd–Äthylenimin–Äthylen konnte kein Unterschied in der Natur der mit AIBN und mit γ-Bestrahlung erhaltenen Copolymeren beobachtet werden. Eine Zunahme der Menge des umgestzten Olefins führte zu einer Zunahme der Copolymerausbeute. Der Schmelzpunkt der Copolymeren lag bei 295–335°C. Die Infrarotspektren, Röntgenbeugungsdiagramme und NMR-Spektren der Copolymeren waren fast mit denjenigen des durch Wasserstoffverschiebungspolymerisation von Acrylamid erhaltenen Poly-β-alanins identisch. Die papier-chromatographische Analyse der Hydrolysenprodukte des Copolymeren zeigte das Vorhandensein von β-Alanine, Äthylamin und eines δ-Aminovaleriansäurehomologen. Diese Ergebnisse führten zu dem Schluss, dass durch AIBN oder γ-Bestrahlung eine Terpolymerisation von Kohlenmonoxyd, Äthylenimin und Olefin angeregt wird, die ein kristallines, festes, aus Nylon-3- und Nylon-5-bausteinen bestehendes Copolymeres liefert. Auf Grundlage der Ergebnisse wurde ein Mechanismus für diese Copolymerisation vorgeschlagen.

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Preparation of Polymeric Amines from Poly(Schiff Bases)

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Synopsis

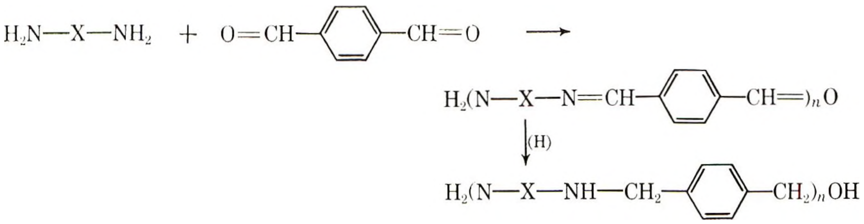
A study was made of the preparation of aromatic polymeric amines in order to test their thermal stability. The most useful method was the hydrogenation of polymeric Schiff bases by the dimethylamine-borane reagent or the borane-tetrahydrofuran reagent. The Schiff bases were prepared by the solution polymerization of terephthalaldehyde with various aromatic diamines, including 4,4′-methylenedianiline, benzidine, and *p*-phenylenediamine, and for comparison, 1,6-hexanediamine. The Schiff bases and the polyamines from the aromatic diamines were found to be dimers or trimers, not high polymers; the polymers from the aliphatic diamine had a degree of polymerization of about 14. Thermogravimetric analyses of the aromatic polyamines under nitrogen showed that the initial temperatures of marked degradation were 350-400°C.

INTRODUCTION

The thermal degradation of model *N*-phenylcarbamates gave considerable quantities of secondary and tertiary amines.[1] Hence it was of interest to attempt to prepare thermally stable polymers containing secondary or tertiary amine units and aromatic rings.

There are relatively few reports of polyamines in which the nitrogen atom is in the main chain, other than the polymers obtained by opening the ring of certain nitrogen-containing heterocycles.[2] The condensation of aliphatic diamines with alkylene dichlorides was studied by Suen et al.[3] Aliphatic polyamines of low molecular weight were also obtained by Zahn and co-workers[4,5] by hydrogenation of polyamide oligomers. Polyamines of high molecular weight, poly(xylylenyl piperazines), were ingeniously prepared by Klebe[6] through the reaction of xylylene dichloride with a bis-trialkylsilyl derivative of a piperazine.

In the current work unsuccessful attempts were made to prepare tractable polyamines (*a*) by condensation of the reactive halide α,α'-dibromo-*p*-xylene with piperazine or with *N,N′*-disubstituted-1,6-hexanediamines and (*b*) by the base-catalyzed melt polymerization of *p*-xylene-α,α'-diol with various aromatic diamines. The best route to polyamines of analytical purity was the condensation of a diamine with a dialdehyde (terephthalaldehyde) followed by hydrogenation of the resulting Schiff base.



POLY(SCHIFF BASES)

The condensation products from the reactions of diamines, such as *p*-phenylenediamine with various difunctional carbonyl compounds such as terephthalaldehyde have been studied as semiconductors.[7-9] Since most of these polymers are colored, insoluble substances, they have rarely been obtained pure and there has been relatively little information on molecular weights. Somewhat more tractable polyazines were obtained from phenolic dialdehydes.[10,11] While the current work was in progress, Popov and co-workers described[12] thirteen* polymeric Schiff bases derived from 2,6-diaminopyridine and *p*-phenylenediamine and showed that the degrees of polymerization of these polymers, with one exception, were from 2 to 6.

In the current work terephthalaldehyde was condensed with various diamines (Table I) in dimethyl sulfoxide or *N*-methyl-2-pyrrolidinone solution. The yields of products, which varied from 75–95%, were not appreciably affected by prolonging the reaction times nor by increasing the temperature. The use of glacial acetic acid as solvent for polymer III greatly speeded the reaction (an effect noted by Marvel and Tarköy[10] for salicylaldehyde derivatives). All of the polymers from aromatic diamines (I–V) were colored and had no true melting points, showing discoloration above certain temperatures, while the polymers from strictly aliphatic diamines (VII and VIII) were white and had true melting points.

Polymer I was reported in 1963 by Topchiev and co-workers[7] to have analyses very close to those in Table I. In 1965 Popov and co-workers[12] showed by endgroup analysis for carbonyl that this polymer was a trimer. Our analytical values would fit either a trimer or a dimer.

Polymer II, prepared in 1923 by Adams et al.[13] was then postulated to be a cyclic dimer, based on analytical data. Our polymer II, like all the others in Table I clearly shows carbonyl absorption in the infrared (at 1680 cm.$^{-1}$), which excludes the cyclic structure.

Polymers III and IV gave low analytical values for nitrogen, in spite of reprecipitations. This has been a common difficulty with polyazines; nine of the polymers described by Popov and co-workers[12] were low in nitrogen by 0.9% or more. [However, the polyamines from reduction of polymers III and IV (Table III) had suitable analyses for all elements.]

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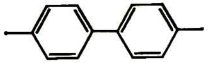
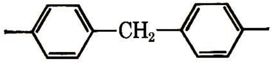
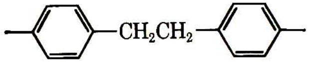
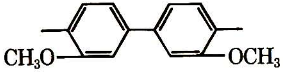
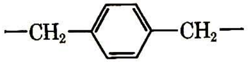
* One of these compounds was the same as ours.

TABLE I

Schiff Bases from Polymerization of Terephthalaldehyde with Various Diamines $H_2[N{-}X{-}N{=}CHC_6H_4CH{=}]_nO$

Polymer no.	—X—	Color	Dec. temp., °C.[a]	Solvents[b]	η_{inh}[c]	MW[d]	Analyses, (calcd.[e]) and found C, %	H, %	N, %
I		Brown	>350	F	0.089		(78.11) 78.45	(5.15) 5.17	(13.02) 12.75
II		Brown	>350	F	0.088		(82.45) 82.69	(5.20) 5.08	(9.62) 9.96
III		Tan	300	F, P, C	0.054	620	(83.41) 83.45	(5.56) 5.39	(9.27) 8.32
IV		Yellow	280	F	0.046		(85.12) 84.97	(5.84) 5.95	(9.03) 8.27
V		Brown	320	F	0.052		(77.07) 76.57	(5.30) 5.60	(8.18) 8.05
VI		Tan	210	F			Hydrogenated before analysis		
VII	$-(CH_2)_6-$	White	142[f]	B, N, F	0.062	3000	(78.46) 78.34	(8.46) 8.31	(13.08) 13.04
VIII		White	235[f]	B, N, F		1250	(79.95) 79.75	(8.39) 8.55	(11.66) 11.43

[a] Temperature of discoloration when heated at the rate of 8°C./min.

[b] F, formic acid; P, *N*-methyl-2-pyrrolidinone; B, benzyl alcohol; N, nitrobenzene; C, *o*-chlorophenol.

[c] Inherent viscosities at 30°C. in formic acid at a concentration of 1 g./100 ml.

[d] Ebullioscopic, III in NMP; VII in N; VIII in B.

[e] Calculated values for dimers (using the title formula with $n = 2$) except for VII and VIII, calculated for high polymers, ignoring the endgroups.

[f] True melting point.

The molecular weights of the polyazines from the aliphatic diamines were higher than those from the aromatic diamines. Polymers VII and VIII, from 1,6-diaminohexane and from cyclohexane 1,4-bismethylamine were shown by ebullioscopic determination of the molecular weights to have degrees of polymerization of 14 and 5, respectively, whereas polymer III, from methylenebisaniline was shown to be a dimer by this method. In addition, the elementary analyses for polymers I–V were in agreement with dimers or trimers, and for VII and VIII with higher polymers. Polymer VII was first prepared by Krässig and Greber,[14] who were unable to use colligative properties for molecular weight determination, but estimated a DP of 8–10 from analyses. The low molecular weights of the aromatic polymers are probably caused by their insolubility; they precipitate from the reaction mixtures at early stages of polymerization.

Attempts were made to increase the molecular weights of the poly(Schiff base) III by the use of better solvents for the polymerization of terephthalaldehyde with methylenedianiline. Only minor improvements were obtained, indicated by the following inherent viscosities of the products from reactions in the solvents specified: *N*-methyl-2-pyrrolidinone, 0.071; naphthalene, 0.088; glacial acetic acid, 0.091.

POLYMERIC AMINES

The Schiff bases were effectively hydrogenated by dimethylamine–borane in glacial acetic acid, the reagent used by Billman and McDowell[15] for reduction of monomeric azomethines. A more convenient reductant which often gave better yields (as shown in Table II) was the borane–

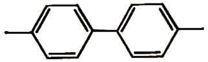
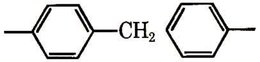
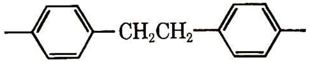
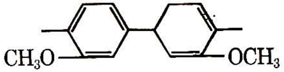
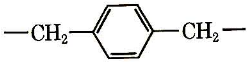
TABLE II
Preparation of Polymeric Amines by the Reduction of Polymeric Schiff Bases

Schiff base[a]	Reducing agent	Time, hr.[b]	Yield, %
I	BH_3–THF	8	95
I	DMAB[c]	4	90
II	BH_3–THF	8	90
II	DMAB	6	90
III	BH_3–THF	8	95
III	DMAB	0.25	95
IV	DMAB	4	90
V	BH_3–THF	8	90
V	DMAB	4	85
VI	DMAB	4	63
VII	BH_3–THF	8	90
VII	DMAB	4	55
VIII	DMAB	4	60

[a] Samples of 1.0 or 1.5 g.
[b] Of reflux.
[c] Dimethylamine–borane in glacial acetic acid.

TABLE III

Polymeric Amines from Reduction of Schiff Bases $H_2[N—X—NH—CH_2C_6H_4CH_2]_nOH$

Polymer no.[a]	—X—	Color	Dec. temp., °C.[b]	η_{inh}[c]	Analyses (calcd.[d]) and found		
					C, %	H, %	N, %
1		Orange	350	0.102	(77.03) 77.02	(6.46) 6.62	(12.84) 12.72
2		Brown	350	0.116	(81.33) 81.79	(6.45) 6.20	
3		Tan	(145)[e] 350	0.078	(81.52) 81.68	(6.84) 6.86	(9.06) 9.16
4		Yellow	250	0.061	(82.63) 82.83	(6.94) 6.31	(8.76) 8.63
5		Red	225	0.119	(74.16) 74.26	(6.74) 6.51	(7.87) 8.05
6		White	195[f]	0.208	(80.63) 80.28	(7.55) 6.96	
7	$—(CH_2)_6—$	White	210[f]	0.419	(77.00) 76.96	(10.11) 9.24	(12.83) 12.76

[a] Arabic numbers for polyamines correspond to Roman numerals for parent Schiff bases (Table I).

[b] Temperature of discoloration at a heating rate of 8°C./min.

[c] Inherent viscosities in formic acid at 30°C. with a concentration of 1 g./100 ml.

[d] Calculated for dimers except for compounds 6 and 7, calculated for high polymers.

[e] Slight discoloration; no marked decomposition below 350°C.

[f] True melting point.

tetrahydrofuran reagent, developed by Brown[16] for reduction of amides. The progress of the hydrogenation could be followed by the disappearance of the carbonyl band at 1680–1700 cm.$^{-1}$ and of the azomethine band at 1620 cm.$^{-1}$.

The properties of the polymeric amines formed by hydrogenation of the corresponding Schiff bases are shown in Table III. The reduced products were sparingly soluble in organic solvents except for formic acid; polymer 7 was soluble in nitrobenzene also. These polyamines had no true melting temperatures except for 6 and 7, derived from aliphatic amines. The reduced products were similar to the poly(Schiff bases) in most properties; however, the polymeric amines were stable to acidic and basic solutions.

In order to check the molecular weights of the polyamines, acetylation analyses were performed on polymer 3, derived from an aromatic diamine and on polymer 7, derived from an aliphatic diamine. The data of Table IV show that polymer 3 is close to a dimer and that polymer 7 has at least 14 units in the chain. These results confirm the assignments of molecular weights to the parent Schiff bases, and show that further degradation did not occur during the hydrogenation.

TABLE IV

Data on Molecular Size of Polyamines from Acetylation

$H_2[N—X—NH—CH_2C_6H_4CH_2—]_nOH$

Polyamine no.	—X—	n	Acetylatable groups, meq./g. Calcd.	Found
3	$—C_6H_4CH_2C_6H_4—$	1	9.43	8.05 ± 0.14
		2	8.09	
		3	7.62	
7	$—(CH_2)_6—$	10	9.54	9.32 ± 0.014
		12	9.50	
		14	9.45	

THERMAL STABILITY

The polyamines, when heated under nitrogen at a rate of 6°C./min., all showed a rapid loss in weight between 350 and 400°C. as shown in Figure 1. Based on the initial temperature of rapid decomposition, the most stable polyamines were those derived from benzidine (polymer 2) and from *p*-phenylenediamine (polymer 1), while the least stable was the one from *p*-xylene-α,α'-diamine (polymer 6). A rough order of decreasing thermal stability of the polymers is represented by the following list of groups in the diamine units: p,p'-C_6H_4 — C_6H_4 > p-C_6H_4 > p,p'-$C_6H_4CH_2CH_2C_6H_4$ > p,p'-$C_6H_4CH_2C_6H_4$ > o,p,o',p'-$(CH_3O)C_6H_4$ — $C_6H_4(OCH_3)$ > p-$CH_2C_6H_4$-CH_2.

The thermal stability of the polyamine 2 is less than that of the corresponding poly(Schiff base) II, given in Figure 2, as shown by the fact that II lost 5% of its weight by 475°C., whereas the polyamine 2 lost 5% of its

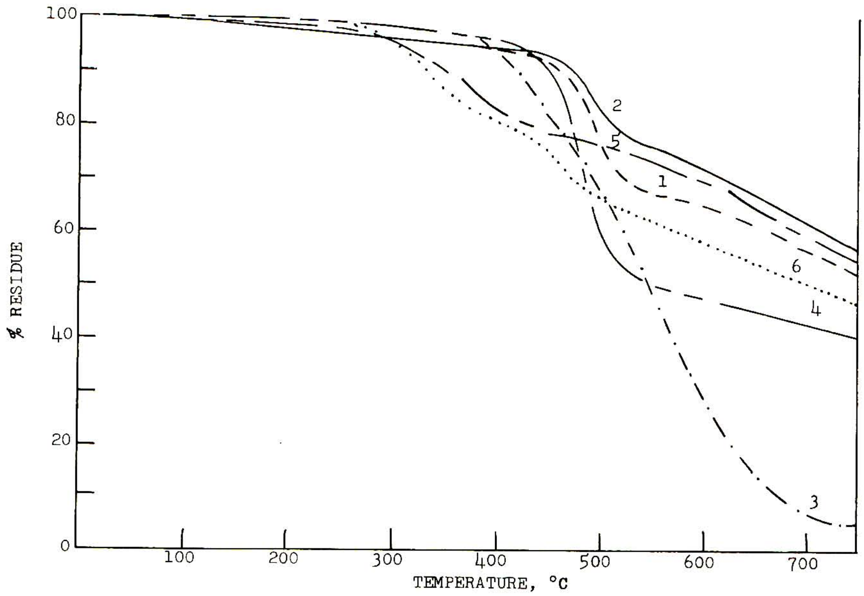


Fig. 1. Thermogravimetric analyses of polyamines, H[NH—X—NH—$CH_2C_6H_4CH_2$]$_n$ OH: (*1*) X = *p*-C_6H_4; (*2*) X = *p,p'*-C_6H_4—C_6H_4; (*3*) X = *p,p'*-$C_6H_4CH_2C_6H_4$; (*4*) X = *p,p'*-$C_6H_4CH_2CH_2C_6H_4$; (*5*) X = *o,p,o',p'*-(CH_3O)C_6H_4—C_6H_4(OCH_3); (*6*) X = *p*-$CH_2C_6H_4CH_2$.

weight by 400°C. (both heated under nitrogen at the same programmed rate). This difference is probably caused by the presence of an unbroken system of conjugated double bonds in II and not in 2. The original hope that the deleterious effect on thermal stability of interrupting the conjugation would be insignificant because of high molecular weights was not realized. No high molecular weight polyamines were obtained because of the limiting size of the precursor Schiff bases.

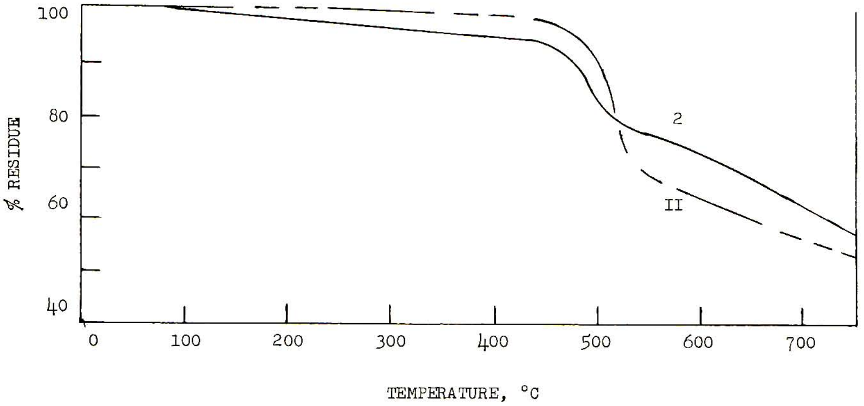


Fig. 2. Thermogravimetric analysis of poly(Schiff base) II and polyamine 2: (II) H_2[NC_6H_4—C_6H_4—N=CH—C_6H_4—CH=]$_n$O; (*2*) H[NHC_6H_4—C_6H_4—$NHCH_2C_6H_4$-CH_2]$_n$OH.

EXPERIMENTAL

Reagents

Commercial grades of terephthalaldehyde, *p*-phenylenediamine, benzidine, and *o*-dianisidine, purified by recrystallization from hot water, melted, respectively, at 115–116°C., 139–140°C., 125–126°C., and 130–131° C. 1,6-Hexanediamine, purified by distillation under reduced pressure, boiled at 80–84°C./10 mm. *p*-Xylene-α,α'-diamine boiled at 172–174°C./ 27 mm.

Commercial 4,4′-methylenedianiline dihydrochloride was dissolved in water, treated with 20% sodium hydroxide, and the free amine distilled at 195–197°C./0.04 mm.

4,4′-Diaminobibenzyl was prepared by oxidation of *p*-nitrotoluene,[17] followed by hydrogenation with a platinum oxide catalyst. The diamine melted at 133°C. (lit.[18] 134–135°C.)

All solvents were dried and distilled.

Preparation of Poly(Schiff Bases)

For a typical polymerization a solution of 0.025 mole (3.35 g.) of terephthalaldehyde in 200 ml. of dry dimethyl sulfoxide was placed in a one-liter, three-necked reaction flask carrying a reflux condenser, mechanical stirrer, and addition funnel. To this solution was added dropwise a solution of 0.025 mole (4.95 g.) of 4,4′-methylenedianiline dissolved in 300 ml. of dimethyl sulfoxide. During stirring for 24 hr. a yellow precipitate formed, which was filtered and washed with ethanol. The dried product weighed 7.9 g. (95% yield), and did not melt below 350°C. The product was purified by continuous extraction with ethanol and water. Properties and analyses are given in Table I.

Reduction of Schiff Bases

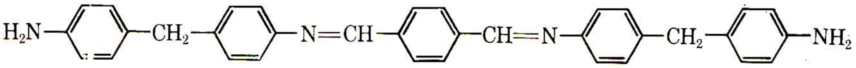
By Dimethylamine Borane.[15] In a 250-ml. three-necked, round-bottomed flask equipped with reflux condenser, addition funnel, and a magnetic stirrer were placed a slurry of 1.5 g. of polymer III (Table I) in 10 ml. of glacial acetic acid. To this mixture was added dropwise 0.5 g. of dimethylamine–borane dissolved in 8 ml. of glacial acetic acid. During the addition of reducing agent the reaction mixture was kept at approximately 20°C. by a water bath. After the reducing agent had been added, the mixture was refluxed for 15 min. The cooled mixture was filtered. The precipitate was washed with a 20% solution of potassium hydroxide. The product, after purification by continuous extraction with water, weighed 1.4 g. (95%). It did not melt below 350°C. The product had no carbonyl absorption and no azomethine absorption in the infrared.

Variations in the procedure with yields are given in Table II.

By Borane in Tetrahydrofuran.[16] In a 500-ml. three-necked round-bottomed flask equipped with a nitrogen sweep, stirrer, and reflux condenser was placed a suspension of 1 g. of polymer III in 200 ml. of dry tetrahydrofuran. Into this mixture was slowly poured 50 ml. of a 1*M* solution of borane–tetrahydrofuran reagent (0.05 mole of reagent). The mixture was refluxed for 8 hr., cooled, and treated with 6*M* hydrochloric acid until there was no further evolution of gas. The mixture was filtered and the light tan product was washed with a 20% solution of potassium hydroxide. The product was purified by continuous extraction with water and dried. The absence of the carbonyl absorption at 1680–1700 cm.$^{-1}$ and of the azomethine absorption at 1620 cm.$^{-1}$ indicated that reduction had taken place. The product, unmelted below 350°C., weighed 0.95 g. (95%).

Model Bisazine from 4,4′-Methylenedianiline and Terephthalaldehyde

To a solution of 7.92 g. (0.04 mole) of 4,4′-methylenedianiline in 200 ml. of dry methylene chloride was added dropwise with stirring a solution of 2.68 g. (0.02 mole) of terephthalaldehyde in 50 ml. of methylene chloride. The mixture was stirred for about 12 hr. at room temperature. The yellow precipitate was filtered, and purified by continuous extraction with acetone. The product was insoluble in the common organic solvents and did not melt below 350°C. The infrared spectrum showed no carbonyl absorption. This experiment indicated that even a small molecule with two azine groups has the insolubility and infusibility characteristics of the poly(Schiff bases):



ANAL. Calcd. for $C_{34}H_{30}N_4$: C, 82.55%; H, 6.08%. Found: C, 82.68%; H, 5.89%.

Attempted Preparation of Polyamines by Reaction of Diamines with Dihalides or with Diols

Treatment of α,α'-dibromo-*p*-xylene with piperazine in dimethyl sulfoxide gave products which were insoluble in all common solvents and which had incompatible analyses. Condensation of the disodium derivative of piperazine (prepared with sodium hydride) and the same dihalide gave a product soluble in formic acid, but of unexplained composition.

By an adaptation of Sprinzak's reaction for benzylation of aromatic amines[19] several aromatic diamines were melt-polymerized with *p*-xylene-α,α'-diol in the presence of potassium hydroxide. For example, 4,4′-methylenedianiline gave by this procedure a tan polymer melting at 220°C., from which brittle fibers and films could be obtained. The molecular weight by vapor pressure osmometry was 21,700 in dimethylformamide, using methylene–dianiline as standard. However, since repeated analyses were not in agreement with the expected formula,[20] further work on this reaction was abandoned.

Analytical Methods

Thermogravimetric Analyses. These analyses were carried out on a du Pont 950 instrument at a programmed rate of 6°C./min. with a flow rate of nitrogen of 40 ml./min.

Molecular Weights by Boiling Point Elevations. In a Cottrell apparatus *N*-methyl-2-pyrrolidinone, benzyl alcohol, or nitrobenzene was used as the solvent. The K_b for the first solvent was determined by using as standards 4,4′-methylenedianiline, *N*,*N*′-dibenzylidine-4,4′-methylenedianiline, and α,α'-*p*-xylenediol.

Determination of Total Acetylatable Groups. Essentially the standard procedure[21] was used to determine the sum of the equivalents of NH, NH_2, and OH groups per gram of polyamine. The sample was 0.02 g.; the acetylating mixture consisted of 1 ml. of acetic anhydride mixed with 3 ml. of pure pyridine.

This paper is abstracted from the Ph.D. dissertation of C. Clement Anderson, University of Delaware, 1965.

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Résumé

Une étude a été effectuée concernant la préparation d'amines polymériques aromatiques en vue de tester leur stabilité thermique. La méthode la plus utile était l'hydrogénation de la base de Schiff polymérique par le réactif diméthylamine-borane ou le réactif borane–tétrahydrofurane. Les bases de Schiff étaient préparées par polymérisation en solution du téréphthaldéhyde avec différentes diamines aromatiques comprenant la 4,4′-méthylènedianiline, la benzidine, la paraphénylène diamine et à titre de comparaison la 1,6-hexanediamine. Les bases de Schiff et las polyamines au départ des diamines aromatiques ont été trouvées être des dimères ou des trimères, mais pas des hauts polymères; les polymères au départ des diamines aliphatiques avaient un degré de polymérisation d'environ 14. Les analyses thermogravimétriques des polyamines aromatiques effectuées sous azote montraient des températures initiales de dégradation prononcée de 350 à 400°C.

Zusammenfassung

Die Darstellung aromatischer polymerer Amine wurde zur Untersuchung ihrer thermischen Stabilität durchgeführt. Die brauchbarste Methode war die Hydrierung polymerer Schiff'scher Basen mit dem Dimethylamin–Boranreagens oder mit dem Boran–Tetrahydrofuranreagens. Die Schiff'schen Basen wurden durch Lösungspolymerisation von Terephthalaldehyd mit verschiedenen aromatischen Diaminen, wie 4,4′-Methylendianilin, Benzidin und *p*-Phenylendiamin und zum Vergleich mit 1,6-Hexandiamin dargestellt. Die Schiff'schen Basen und die Polyamine aus den aromatischen Diaminen erwiesen sich als Dimere oder Trimere und nicht als Hochpolymere; die Polymeren aus dem aliphatischen Diamin besassen einen Polymerisationsgrad von etwa 14. Die thermogravimetrische Analyse der aromatischen Polyamine unter Stickstoff zeigte, dass die Temperatur eines deutlichen beginnenden Abbaus 350–400°C beträgt.

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Cohesive Energy Densities of Polymers from Turbidimetric Titrations

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Synopsis

Turbidimetric titrations have been made on polystyrene and poly-*o*-chlorostyrene in a series of solvents to deduce the solubility parameters of polymers from the Flory-Huggins interaction parameter χ. The assigned solubility parameter for polystyrene agrees well with the reported values obtained from swelling measurements. Brief discussion of the exceptional behavior in the solvent powers of paraffins is given.

Introduction

The solubility parameters of substances describe the relation between the energy of mixing and the mutual solubility of the substances. A knowledge of the solubility parameter of a polymer is necessary in obtaining valuable information for the solubility behavior of a polymer. The solubility parameter as defined by Hildebrand is the square root of the cohesive energy density, the energy of vaporization per unit volume. It is the energy required to completely vaporize 1 cc. of a liquid against the intermolecular forces between molecules.

The solubility parameters of polymers can not be determined directly from the heat of vaporization because of their nonvolatility. At the present time, the most widely used experimental method is based on the study of solvent-polymer interactions in a spectrum of solvents of known solubility parameter. Gee[1] studied the swelling of crosslinked polymers and found that the swelling is greatest in solvents having the same cohesive energy density as that of the polymer. Since Gee's early work, the Flory-Huggins interaction parameter χ (or μ) has been applied to describe the polymer swelling.[2–5] The solubility parameters of polymers can be also determined by intrinsic viscosity measurements in a series of solvents. The polymer solubility parameter is assumed to be equal to the solvent solubility parameter where the intrinsic viscosity has a maximum value. Bristow and Watson[6] derived the solubility parameters of polymers from viscosity measurements by an application of the interaction parameter χ. Small[7] has derived additive molar attraction constants for various molecular groups from vapor pressure measurements on volatile substances and used these values to estimate the solubility parameters for polymers. The purpose of this paper is to present a new method for the determination of polymer solubility parameters by turbidimetric titrations.

Experimental

Solutions of polystyrene ($\bar{M}_w = 295{,}000$) and poly-*o*-chlorostyrene ($\bar{M}_w = 200{,}000$) were prepared by dissolving 0.3 g. of polymer in 100 ml. of reagent-grade solvents. To a 25-ml. aliquot (10 ml. in the case of acetone as a nonsolvent) of polymer solution, a nonsolvent was slowly added until a standard turbidity (cloud point) was reached. The standard turbidity or cloud point was the threshold of precipitation at which a printed page could not be read looking through the solution.[8] Two different nonsolvents, one of lower solubility parameter and one of higher solubility parameter, were used to titrate the polymer solutions at 25°C.

Discussion

The Flory-Huggins interaction parameter χ is given by:

$$\chi = \frac{1}{z} + \frac{V_1(\delta_1 - \delta_3)^2}{RT} \tag{1}$$

where z is the coordination number, V_1 is the molar volume of the solvent (component 1), and δ_1 and δ_3 are the solubility parameters of solvent and polymer (component 3), respectively. The values of χ at the cloud points obtained from titrations with two different nonsolvents (component 2), one of lower δ value (χ_{cl}) and one of higher δ value (χ_{ch}), are represented by:

$$\chi_{cl} = \left(\frac{1}{z}\right)_{cl} + \frac{V_{ml}\,(\delta_3 - \delta_{ml})^2{}_{cl}}{RT} \tag{2}$$

$$\chi_{ch} = \left(\frac{1}{z}\right)_{ch} + \frac{V_{mh}(\delta_{mh} - \delta_3)^2{}_{ch}}{RT} \tag{3}$$

where subscripts *ml* and *mh* represent the mixtures of solvent and nonsolvent of lower solubility parameter and of solvent and nonsolvent of higher solubility parameter at the cloud points, respectively. Equating the above two expressions, assuming that $(1/z)_{cl} \cong (1/z)_{ch}$ for a small concentration difference in dilute solutions, we obtain

$$\sqrt{V_{ml}}(\delta_3 - \delta_{ml})_{cl} = \sqrt{V_{mh}}(\delta_{mh} - \delta_3)_{ch} \tag{4}$$

where

$$V_m = V_1V_2/(\Phi_1V_2 + \Phi_2V_1) \tag{5}$$

$$\delta_m = \Phi_1\delta_1 + \Phi_2\delta_2 \tag{6}$$

Φ_1 and Φ_2 represent the volume fractions of solvent and nonsolvent in the solution. Simplifying eq. (4), the solubility parameter of a polymer can be obtained by the relation:

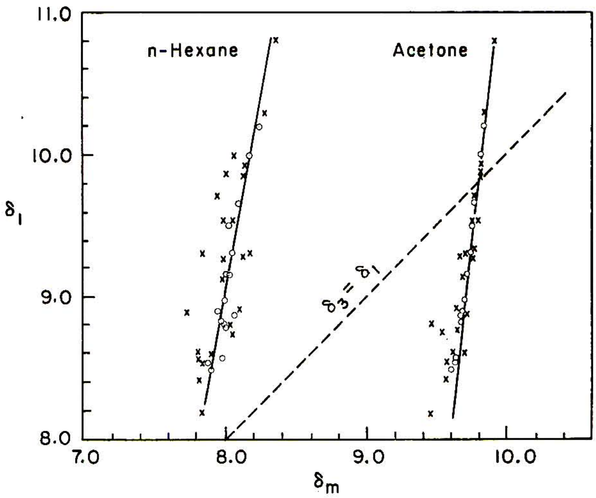

Fig. 1. Turbidimetric titration of polystyrene with acetone and n-hexane: (O) aromatic solvents; (×) aliphatic solvents.

$$\delta_3 = (\sqrt{V_{ml}}\delta_{ml} + \sqrt{V_{mh}}\delta_{mh})/(\sqrt{V_{ml}} + \sqrt{V_{mh}}) \tag{7}$$

Here Scott's "single liquid" approximation[9] was used in evaluating δ_m and V_m values. This is a good approximation if the interaction of solvents with the polymer is very small in comparison with the interaction between the two solvents. When $V_{ml} = V_{mh}$, the polymer solubility parameter can be obtained from the midpoints between the two cloud point δ values. Equation (7) then reduces to

$$\delta_3 = (\delta_{ml} + \delta_{mh})/2 \tag{8}$$

The relative magnitude of V_{ml} to V_{mh} is, however, approximately 3 to 2 in most cases.

Tables I and II show the experimental data obtained from turbidimetric titrations of polystyrene and poly-o-chlorostyrene in a series of solvents with methanol, acetone, n-hexane, and n-heptane. The cloud point δ values obtained from the turbidimetric titration of polystyrene in several solvents with acetone and n-hexane yielded almost vertical lines as shown in Figure 1. These small deviations from the vertical lines may be attributed to the inadequacy of eq. (6) due to the polarity of the solvents and nonsolvent. The solubility parameter of polystyrene was determined from the intersection of δ_1 versus δ_3 from eq. (7) with $\delta_3 = \delta_1$ line (45° line) as illustrated in Figure 2 and tabulated in Table IV. Equation (7) reduces to $\delta_3 = \delta_1$ when the composition of nonsolvent Φ_2 becomes zero.

Experimental data for polystyrene seem to indicate that if the solubility parameter of the nonsolvent is close to the critical solubility limit, $(\Delta\delta)_{\max}$, for polystyrene, two vertical lines will be obtained. In this case, the solubility parameters for polymers can be determined from the extrapola-

TABLE I

Turbidimetric Titration of Polystyrene at 25°C.

Solvent	δ_1	V_1	n-Hexane added to 25 cc. of solvent, cc.	Methanol added to 25 cc. of solvent, cc.	Acetone added to 10 cc. of solvent, cc.
Aromatic solvents					
tert-Butylbenzene	8.48	155.6	22.5	6.40	56.1
Isopropylbenzene	8.53	140.2	27.3	6.95	64.0
p-Cymene	8.56	157.3	20.6	6.45	61.7
Mesitylene	8.78	139.6	26.0	6.70	59.5
m-Xylene	8.80	123.5	26.8	7.50	67.0
p-Xylene	8.83	123.9	29.4	7.40	65.5
o-Diethylbenzene	8.87	153.1	25.1	6.70	60.5
Toluene	8.90	106.9	33.7	8.10	60.5
o-Xylene	8.98	121.2	33.4	7.80	70.5
Benzene	9.15	89.4	37.2	8.40	68.4
α-Methylstyrene	9.16	130.4	38.8	8.15	73.9
Styrene	9.30	115.6	40.1	8.80	63.5
Chlorobenzene	9.50	102.3	48.5	9.10	66.5
p-Bromotoluene	9.66	122.8	47.7	8.80	77.4
Bromobenzene	10.00	105.5	50.1	9.40	88.0
Iodobenzene	10.20	111.9	50.3	8.90	91.7
Aliphatic solvents					
tert-Butyl bromide	8.17	113.2	15.0	4.62	37.5
sec-Butyl bromide	8.40	109.3	26.1	6.60	51.0
Isopropyl bromide	8.53	93.9	30.0	6.72	45.2
n-Butyl bromide	8.54	107.3	33.0	6.90	55.1
Carbon tetrachloride	8.59	97.1	26.7	6.40	136.0
n-Propyl bromide	8.60	90.9	36.4	7.53	53.5
Amyl acetate	8.74	148.1	22.2	5.06	31.6
Ethyl bromide	8.80	75.2	41.0	7.75	50.0
Propyl acetate	8.81	115.7	25.0	4.40	19.9
Methylene chlorobromide	8.88	67.3	64.0	10.75	82.4
Isoamyl bromide	8.91	123.8	24.6	5.68	47.6
Isophorone	9.12	149.7	40.2	9.30	51.7
1,2-Propylene oxide	9.28	69.9	33.3	7.05	25.0
Chloroform	9.30	80.7	64.6	9.30	38.2
Perchloroethylene	9.30	102.1	30.8	6.00	72.8
1,3-dibromobutane	9.53	119.5	52.6	8.30	78.3
Propylene dibromide	9.53	105.0	48.4	9.40	112.5
Methylene chloride	9.71	63.6	65.3	7.20	26.8
Ethylene dichloride	9.85	79.4	50.0	9.15	42.4
Trichloroethane	9.87	93.2	59.4	11.70	55.0
Methyl iodide	9.93	62.3	51.6	9.50	69.5
Ethylene dibromide	10.30	86.6	50.0	10.00	87.8
Trimethylene chlorobromide	10.80	99.1	55.3	9.70	73.8
n-Hexane	7.29	131.6			
Acetone	9.81	74.0			
Methanol	14.54	40.7			

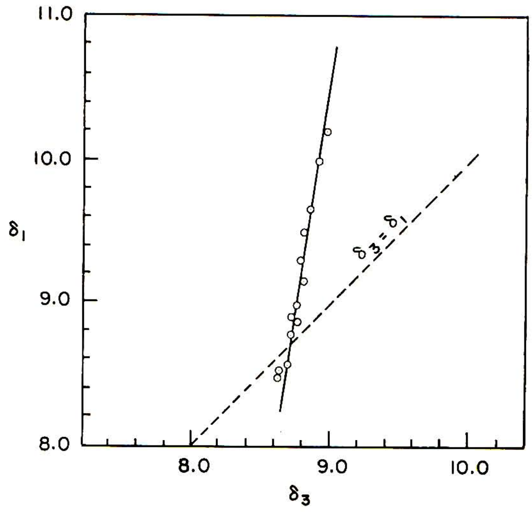

Fig. 2. Determination of the solubility parameter for polystyrene from the turbidimetric titration with acetone and *n*-hexane: (⊙) aromatic solvents.

tion of eq. (7) to $\Phi_2 = 0$. Since the polymer solubility parameter values are practically constant, only a few good solvents whose molecular structure and polarity are similar to those of the polymer could be chosen. To choose such a set of nonsolvents and good solvents, the preliminary solubility data should be taken for each polymer.

Figures 3 and 4 show the cloud point δ values for polystyrene and poly-*o*-chlorostyrene obtained from the titrations with methanol and *n*-hexane or *n*-heptane. It will be noted that the best straight line through the meth-

TABLE II
Turbidimetric Titration of Poly-*o*-chlorostyrene at 25°C.

Solvent	δ_1	V_1	*n*-Heptane added to 25 cc. of solvent, cc.	Methanol added to 25 cc. of solvent, cc.
Aromatic solvents				
Ethylbenzene	8.80	123.1	17.6	7.10
m-Xylene	8.80	123.5	12.3	6.90
Toluene	8.90	106.9	18.6	7.40
Benzene	9.15	89.4	21.6	7.65
Styrene	9.30	115.6	24.1	8.05
Chlorobenzene	9.50	102.3	27.3	7.90
Aliphatic solvents				
Methyl chloroform	8.50	100.0	13.8	4.80
Chloroform	9.30	80.7	26.2	6.70
Methylene chloride	9.71	65.0	30.0	5.95
Dioxane	10.00	86.0	25.4	13.00
Bromoform	10.50	88.0	30.3	8.55
n-Heptane	7.45	147.5		

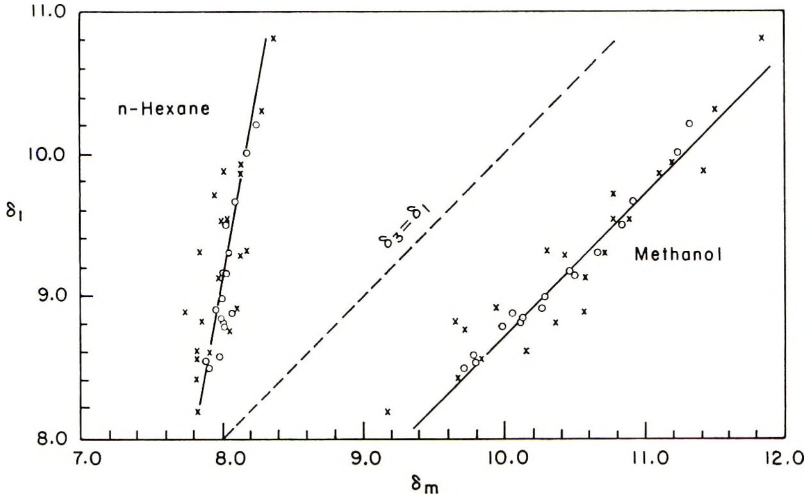

Fig. 3. Turbidimetric titration of polystyrene with methanol and *n*-hexane: (⊙) aromatic solvents; (×) aliphatic solvents.

anol cloud point δ values is parallel to the $\delta_3 = \delta_1$ line (45° line). These two lines are separated by a distance corresponding to the critical solubility limit (the largest difference between polymer and solvent solubility parameters, $(\Delta\delta)_{\max}$, where the polymer is soluble) on the solvent spectrum for polystyrene and poly-*o*-chlorostyrene. Namely,

$$(\delta_{mh} - \delta_3)_{\text{exp}} = (\delta_{mh} - \delta_1)_{\text{exp}} \cong (\delta_{mh} - \delta_3)_{ch} \tag{9}$$

It would appear that the polymer molecule is surrounded by the good solvent molecules and behaves as if its chemical composition were that

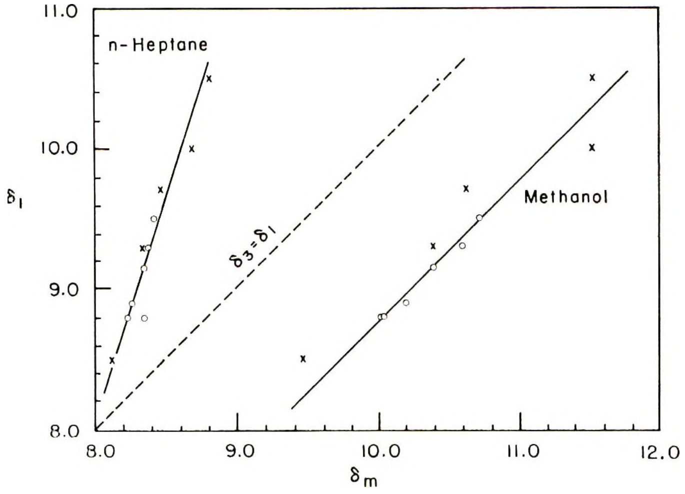

Fig. 4. Turbidimetric titration of poly-*o*-chlorostyrene with methanol and *n*-heptane: (⊙) aromatic solvents; (×) aliphatic solvents.

TABLE III
Compositions of Mixed Solvents at the Cloud Point for Polystyrene System

Solvent	Φ_2 (exptl.)	$\frac{\Phi_2'}{\Phi_1' + \Phi_2'}$ (calc. at $\Phi_3' = 0.1$)[a]
Solvent–methanol system		
Isopropylbenzene	0.215	0.114
Toluene	0.245	0.120
Benzene	0.252	0.174
Chlorobenzene	0.268	0.204
Bromobenzene	0.273	0.216
sec-Butyl bromide	0.209	0.128
Chloroform	0.271	0.178
Methylene chloride	0.224	0.186
Ethylene dibromide	0.285	0.233
Solvent–*n*-hexane system		
Isopropylbenzene	0.516	0.498
Toluene	0.584	0.559
Bromobenzene	0.668	0.612
sec-Butyl bromide	0.514	0.505
1,3-Dibromobutane	0.679	0.640
Ethylene dibromide	0.668	0.607
Solvent–acetone system		
Isopropylbenzene	0.862	0.865
Toluene	0.870	0.871
Benzene	0.872	0.872
Bromobenzene	0.898	0.901

[a] The prime represents the polymer phase.

of the good solvent with respect to the solvent–nonsolvent mixture. This may be attributed to the fact that the interaction of good solvents with the polymer is very large in comparison with the interaction between two solvents due to the high polarity of the methanol. This means that the solvent–nonsolvent mixture reacts with the cluster as with a compatible solution.

In general, with two very powerful nonsolvents, the precipitation data will yield parallel lines to the $\delta_3 = \delta_1$ line, one on the low edge of the solubility parameter spectrum and the other on the high edge of the spectrum. In this case, the polymer solubility parameter can not be determined because the two lines are essentially the same for all polymers regardless of their chemical composition and the polymer seems to be precipitating as if its composition were that of the good solvent. The thermodynamic calculations do show that a part of the good solvent is associated with the polymer as shown in Table III. The compositions of the nonsolvents in the polymer phase were obtained from the composition ratio relationship derived by Krigbaum and Carpenter.[10]

Substituting eq. (9) into eq. (4) and solving for the polymer solubility parameter, we obtain

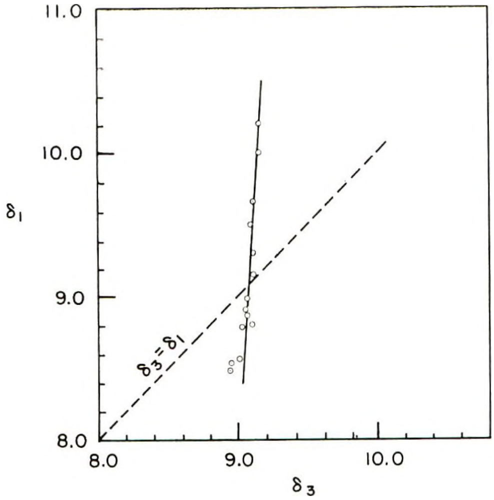

Fig. 5. Determination of the solubility parameter for polystyrene from the turbidimetric titration with methanol and *n*-hexane: (⊙) aromatic solvents.

$$\delta_3 = \delta_{ml} + \sqrt{(V_{mh}/V_{ml})}(\delta_{mh} - \delta_1) \tag{10}$$

The solubility parameters for the polystyrene and poly-*o*-chlorostyrene were also determined from the titrations with methanol and *n*-hexane or *n*-heptane by using eq. (10) as shown in Figures 5 and 6.

In most cases, the δ_3 values obtained from the titration data in aliphatic solvents are more widely scattered and consistently lower than the values obtained from the titration data in aromatic solvents as shown in Tables IV and V. This may be due to the irregularity in solvent powers of paraffins in aliphatic solvents. This irregular behavior of hydrocarbons in aliphatic solvents have been studied by Simons and Dunlap[11] and also by Hildebrand.[12] Hildebrand has suggested that a good agreement with the experimental data may be obtained by assigning to the hydrocarbons δ

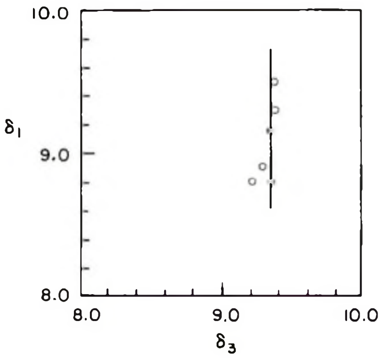

Fig. 6. Determination of the solubility parameter for poly-*o*-chlorostyrene from the turbidimetric titration with methanol and *n*-heptane: (⊙) aromatic solvents.

TABLE IV
Determination of the Solubility Parameter for Polystyrene

Solvent	δ_3 from methanol and *n*-hexane titrations	δ_3 from acetone and *n*-hexane titrations
Aromatic solvents		
tert-Butylbenzene	8.94	8.64
Isopropylbenzene	8.95	8.65
p-Cymene	9.01	8.70
Mesitylene	9.03	8.74
o-Diethylbenzene	9.07	8.77
Toluene	9.06	8.73
o-Xylene	9.07	8.76
Benzene	9.11	8.81
Styrene	9.11	8.79
Chlorobenzene	9.09	8.81
p-Bromotoluene	9.11	8.85
Bromobenzene	9.15	8.91
Iodobenzene	9.15	8.96
Aliphatic solvents		
sec-Butyl bromide	8.88	8.62
Carbon tetrachloride	8.91	8.74
Ethyl bromide	9.07	8.68
Chloroform	8.92	8.68
1,3-Dibromobutane	9.00	8.78
Methylene chloride	8.77	8.80
Methyl iodide	9.10	8.92

value about 0.6 higher than those calculated from the energies of vaporization per cubic centimeter. The adjusted δ values of 7.52 instead of 7.29 for *n*-hexane and 7.72 instead of 7.45 for *n*-heptane in aliphatic solvents will give the same δ_3 values for polystyrene and poly-*o*-chlorostyrene as those obtained from the titration of these polymers in aromatic solvents.

The solubility parameter of poly-*o*-chlorostyrene is found to be 9.35. The solubility parameter for polystyrene is compared with reported values

TABLE V
Determination of the Solubility Parameter for Poly-o-chlorostyrene from Titration with Methanol and *n*-Heptane

Solvent	δ_3
Aromatic solvents	
Ethylbenzene	9.22
m-Xylene	9.36
Toluene	9.30
Benzene	9.35
Styrene	9.39
Chlorobenzene	9.38
Aliphatic solvents	
Chloroform	9.22
Methylene chloride	9.20

TABLE VI
Comparison of the Solubility Parameter for Polystyrene

Source	Method	δ_3
Scott and Magat[4]	Swelling measurements	9.1
Boyer and Spencer[13]	Swelling measurements	9.05
Mangaraj et al.[14]	Swelling measurements	9.1
	Viscosity measurements	9.1
Bristow and Watson[6]	Viscosity measurements	8.56
Small[7]	Molar attraction constants	9.12
This work	Turbidimetric titration (acetone)	8.72
	Turbidimetric titration (methanol)	9.07

obtained from different methods in Table VI. The value of 9.07 for polystyrene obtained from methanol titration data agrees fairly well with other values. The value of 8.72 for polystyrene obtained from acetone titration data seems to be too low, considering the fact that the solubility range of polystyrene on the solvent spectrum is approximately $8.1 < \delta_1 < 10.8$ as shown in Tables I, II, and VII.

TABLE VII

Solvent	δ_1	Gross solubility of polystyrene, g. polymer/100 g. solvent[a]
n-Heptane	7.45	0.016
Methyl cyclohexane	7.82	0.312
Cyclohexane	8.20	4.58
Carbon tetrachloride	8.59	>50
Ethyl benzene	8.80	>100
Toluene	8.90	>90
Ethyl acetate	9.03	>90
Benzene	9.15	>90
Methyl ethyl ketone	9.30	>90
Chloroform	9.30	>70
Tetrahydrofuran	9.32	>90
Methyl isobutyl ketone	9.58	>100
Methylene chloride	9.71	>80
Acetone	9.81	0.30
Isoamyl alcohol	10.00	0.006
o-Dichlorobenzene	10.21	>50
Pyridine	10.70	>70
Nitroethane	11.10	0.736
Acetonitrile	11.80	0.056
Ethyl alcohol	12.80	0.000
Methyl alcohol	14.54	0.000

[a] Determined by dissolving as much polymer as possible in 100 g. of solvent until the solution became very viscous within a reasonable time[15] (about 1 week). A thermally polymerized polystyrene of 250,000 weight-average molecular weight was used in this experiment.

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Résumé

Des titrations turbidimétriques ont été effectuées sur du polystyrène et du poly-orthochlorostyrène dans une série de solvants afin de déduite les paramètres de solubilité des polymères au départ des paramètres d'interaction de Flory-Huggins χ. Le paramètre de solubilité pour le styrène s'accorde bien avec les valeurs rapportées, obtenues au départ de mesures de gonflement. Une brève discussion du comportement exceptionnel des pouvoirs solvants des paraffines est également donnée.

Zusammenfassung

Trübungstitrationen wurden an Polystyrol und Poly-*o*-chlorstyrol in einer Reihe von Lösungsmitteln zur Ableitung der Löslichkeitsparameter aus dem Flory-Huggins-Wechselwirkungsparameter χ durchgeführt. Der für Polystyrol bestimmte Löslichkeitsparameter stimmt gut mit den aus Quellungsmessungen erhaltenen Literaturwerten überein. Eine kurze Diskussion des exzeptionellen Verhaltens der Lösungsmittelgüte von Paraffinen wird gegeben.

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Polymer Reactions. VI. Inhibited Autoxidation of Polypropylene

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Synopsis

The autoxidation of polypropylene inhibited by 2,6-di-*tert*-butyl-*p*-cresol (AH) and dilauryl thiodipropionate (S) was studied by the combined methods of electron spin resonance, oxygen absorption, and chemical analysis. With AH alone, there is a critical concentration of about 6×10^{-3} mole/l. below which there is no inhibition. This critical concentration agrees with that determined for inhibited squalane autoxidation and that calculated from known rate constants. Above the critical concentration there is a well-defined induction period during which the ROO· concentration is estimated to be 10^{-8} mole/l. [ROOH] decreased rapidly as did [A·] and [AH]; the latter are kinetically related. The rate constant for the reaction between A· and ROO· is estimated to be 7×10^7 l./mole-sec. at 130°C. At the end of the induction period, [ROOH], [ROO·], and $-d[O_2]/dt$ increased rapidly until steady-state values were attained for all of them. With S alone, there are only retarded oxidation but no well-defined induction periods. [ROOH] is greatly reduced by S. In all systems where the oxidation rates were appreciably suppressed there was formed a very stable paramagnetic species, S·, which was inert toward AH and I_2 but reactive toward triethyl phosphite. Because of its similarity with spin centers in carbon black, S· is postulated to be a delocalized polysulfide spin center. With both S and AH present, the combined effect of stabilization is synergistic. The observed time-dependent variations of [ROOH], [ROO·], and [A·] follow familiar mechanisms. Mathematical relationships describing each of these three systems are included.

INTRODUCTION

Absolute rate constants for autoxidation are usually measured by the rotating sector method. The results of these measurements on hydrocarbon autoxidation have been reviewed by Howard and Ingold.[1] Because the rotating sector method cannot be readily adapted for the investigation of autoxidation of polymeric materials, we recently developed a method[2] which consists of determinations of hydroperoxide concentration, of radical concentrations by ESR, and of rate of oxidation. This method was used to obtain absolute rate constants for polypropylene autoxidation[2] and has been extended to study inhibited autoxidation of polypropylene. The results of that study are presented in this paper.

EXPERIMENTAL

Materials

The stabilizers used in this work were 2,6-di-*tert*-butyl-*p*-cresol (AH) and dilauryl thiodipropionate (S), obtained from Hercules Incorporated and American Cyanamid Company, respectively.

The stabilizers were introduced into polypropylene by the following procedure. The polymer was mixed with a benzene solution of the stabilizer and allowed to stand overnight. The solvent was subsequently removed from the swollen polymer at room temperature on a rotary evaporator. Analysis showed complete removal of the solvent. The amount of AH contained in such polymer samples was determined spectroscopically; the amount of S incorporated was analyzed chemically. Under the experimental conditions, there was no loss of the stabilizer due to either volatilization or other processes when the samples were heated under a nitrogen atmosphere.

Stabilized commercial polypropylene is very resistant to thermal oxidative degradation. Studies of this material are impractical. Instead, two types of modified polypropylene were used: polypropylene hydroperoxide (PPH) and preoxidized polypropylene (OPP). They differ in the method of preparation, hydroperoxide content, and crystallinity.

PPH was prepared from a chlorobenzene-soluble fraction of commercial polypropylene. This chlorobenzene solution was air-oxidized at 100°C. and was initiated by α,α'-azobisisobutyronitrile. Detailed discussions on the preparation, analysis, and structures of PPH have been described elsewhere.[3] The hydroperoxide contents in the two samples used in this work were 0.156 and 0.485 mmole/g.

OPP was prepared by heating commercial polypropylene at 140°C. and a pressure of 1 atm. of oxygen until the sample had absorbed about 7 ml. O_2/g. at S.T.P. The hydroperoxide contents of OPP were usually less than 0.2 mmole/g.

Both PPH and OPP were stored in the dark at 0°C.

Autoxidation Procedure

A sample containing stabilizer was introduced into a preheated ESR cavity. The sample tube was connected to an automatically regulated, recording oxygen-absorption apparatus.[4] The rate of oxidation and the radical concentration were monitored continuously.

A Varian V-4500 spectrometer with 100 kc./sec. modulation and a 12-in. electromagnet were used throughout. A Varian variable temperature assembly was modified to improve temperature control. A thermocouple, placed in the Dewar holder immediately below the sample tube, was connected to a Gardsman regulator which controlled the heating elements. A second thermocouple was placed next to the section of the sample tube where the polymers were located. The output of this thermocouple was either recorded continuously or read with a potentiometer.

Autoxidation was terminated by quenching of the tube containing the sample in a Dry Ice–trichloroethylene mixture. A section of Tygon tubing connecting the sample tube with the remaining equipment provided sufficient flexibility for rapid transfer of the ESR sample tube from the cavity to the quenching bath without opening the sample to air. The polymer was subsequently analyzed for either hydroperoxide or stabilizers.

ESR Spectra

The method used to calculate radical concentrations from the ESR spectra is the same as that given previously.[5] The same reference also gives an account of the variation of *g*-anisotropy and of linewidth of peroxy radicals and of radicals derived from AH.

RESULTS AND DISCUSSION

Systems Containing Phenolic Stabilizer

PPH with added AH, contained in an ESR sample tube under 1 atm. of oxygen, was heated in the ESR cavity. At low concentrations of radical scavenger, peroxy radical signals were observed immediately. The steady-state concentration of ROO· was reached within seconds. There were no detectable amounts of the phenoxy radical (A·) during 4 hr. of heating under these conditions. The results are presented in Table I.

At very high concentration, [AH] = 0.17 mole/l., an intense signal for A· was observed (Fig. 1) which decreased rapidly with time (Fig. 2). After 9 min. a signal from ROO· was superimposed on the A· signal (Fig. 3). The two radicals coexist in detectable amounts for the next 10 min., after which time the spectra were simply those of the ROO· radical. The steady-state [ROO·] is approximately equal to that found in the experiments with no stabilizer. The results of experiments with [AH] = 1.3×10^{-2}, 4.2×10^{-2}, and 8.3×10^{-2} mole/l. are qualitatively similar to the above description.

TABLE I
Reaction at 1 Atm. O_2 Between PPH and AH[a]

[AH], mole/l.	Temp., °C.	ESR signal intensity[b]	
		ROO·	A·
3.1×10^{-3}	110	80	—
3.1×10^{-3}	120	102	—
1.3×10^{-2}	120	100	300–0
1.3×10^{-2}	130	140	300–0
4.2×10^{-2}	110	80	330–0
8.3×10^{-2}	120	85	300–0
1.7×10^{-1}	120	80	115–0[c]

[a] $[ROOH]_0$ in PPH = 0.156 mmole/g.

[b] Intensity in arbitrary units.

[c] See Figure 1.

Fig. 1. ESR spectrum obtained during autoxidation of PPH containing AH early stage of reaction.

This series of experiments clearly shows that a critical inhibitor concentration, somewhere between 3.1×10^{-3} and 1.3×10^{-2} mole/l., is required to prevent chain branching reactions. At $[AH] \leq 3.1 \times 10^{-3}$ mole/l., an autocatalytic condition prevails.

The critical concentration found above may be compared with that calculated from the known rate constants. As shown in the Appendix, the critical stabilizer concentration is

$$[AH]_c = 2k_2[RH]/k_4 \tag{1}$$

The value of k_2 at 120°C. is determined[2] to be 3.3 l./mole-sec. The value of k_4 is 7.95×10^3 l./mole-sec.[6a] at 65°C. with an activation energy of 1.7 kcal./mole,[6b] from which we obtained a value of 1.14×10^4 l./mole sec. at 120°C. Substitution of these constants into eq. (1) gives a critical AH concentration of 6×10^{-3} mole/l. at 120°C. This value lies within the range found by the ESR experiments.

Further verification of the above results was obtained from the experiments on autoxidations of squalane at 120°C. in the presence of AH. The

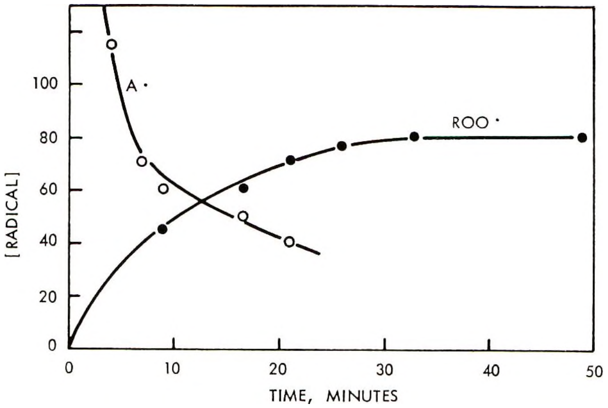

Fig. 2. Reaction between PPH and AH. Radical concentrations are in arbitrary units.

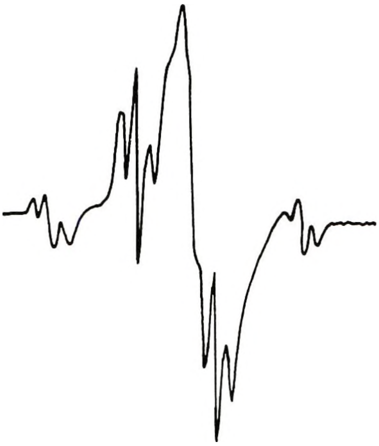

Fig. 3. ESR spectrum obtained during autoxidation of PPH containing AH. Intermediate stage of reaction.

results are shown graphically in Figure 4, where the observed induction periods are plotted against [AH]. The $[AH]_c$, obtained by extrapolating to zero induction period is 4×10^{-3} mole/l. The agreement found for the value of $[AH]_c$ estimated by different methods establishes its validity.

The fact that the critical inhibitor concentrations for autoxidations of squalane and of polypropylene are nearly the same has further implications. Earlier we suggested[2] that the propagation reaction in polypropylene autoxidation proceeds via an intramolecular mechanism and that the rate of this reaction is independent of phase changes. If this postulate is true, the above results imply that the reaction between AH and the polymeric radical is not diffusion-controlled and thus rather insensitive to phase and viscosity changes. Apparently the relatively small AH can diffuse sufficiently rapidly in the amorphous phase of the polymer so that its reaction with ROO· is kinetically controlled. Additional support for the postulated rapid diffusion is furnished by the fact that A· cannot be trapped by

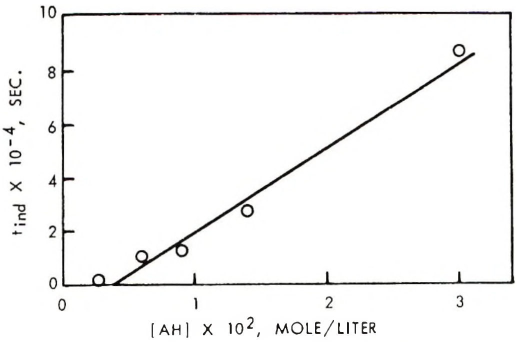

Fig. 4. Critical inhibitor concentration in squalane autoxidation at 120°C. and oxygen pressure of 1 atm.

TABLE II
Inhibited Autoxidation of OPP[a]

Time, min.	[ROOH], mole/l.	[AH] × 10^2, mole/l.	[A·] × 10^6, mole/l.	[ROO·] × 10^6, mole/l.
0	0.152	1.3	0	0
5	0.152	1.3	2.3	—
50	0.087	1.0	1.7	—
120	0.055	0.64	1.2	—
240	0.038	0.31	0.5	—
350[c]				0.1
400	0.033	—[b]	—[b]	1.0
550	0.223	—	—	2.0

[a] Temperature 130°C.; p_{O_2}, 1 atm.

[b] Not detected; the limits of detection for [radical] and for [AH] are about 1×10^{-7} and 1×10^{-3} mole/l., respectively.

[c] End of induction period, followed by oxidation at a rate of 1 ml. of O_2/min.-g.

rapid quenching of the polymer sample, whereas the corresponding phenoxy radical derived from 1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxytolyl) mesitylene can be trapped in polypropylene by quenching and is relatively stable at room temperature, having a half life of about 7 days.

A series of 12 experiments was performed where samples of OPP ($[ROOH]_0$ = 0.152 mole/l.) containing 0.013 mole/l. of AH were heated at 130°C. in an atmosphere of oxygen for various lengths of time. The samples after quenching were analyzed for unreacted AH as well as for hydroperoxide concentration. The results are shown in Table II and Figure 5.

The concentrations of AH and A· decrease steadily with time of reaction. Analysis of the results show that both species decay with approximately equal halflives of 2 hr. (Fig. 6). The fact that A· is a kinetically significant species here allows us to reject the mechanism of inhibition pro-

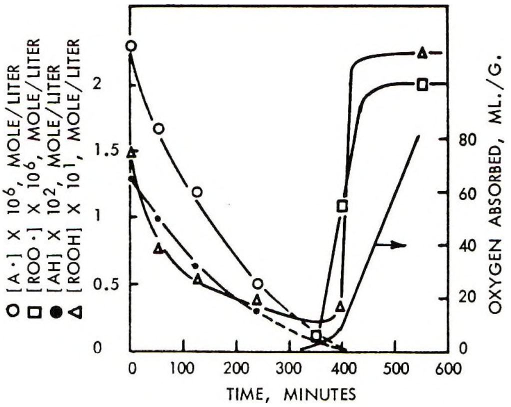

Fig. 5. Inhibited autoxidation of polypropylene at 130°C.: (○) [A·]; (□) [ROO·]; (●) [AH]; (△) [ROOH].

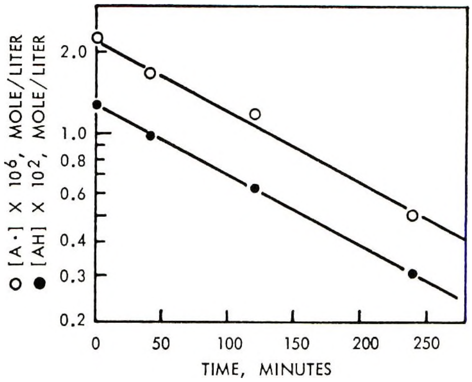

Fig. 6. Rate of disappearance of AH and A·: (O) [A·]; [AH].

posed by Hammond et al.[8] Kinetic and other arguments against this mechanism have been discussed by Howard and Ingold.[9] We prefer the well-accepted mechanism based on kinetic isotopic effects,[9,10] to describe our results [eqs. (2)].

$$\mathrm{ROO\cdot} + \mathrm{AH} \xrightarrow{k_4} \mathrm{ROOH} + \mathrm{A\cdot} \tag{2a}$$

$$\mathrm{ROO\cdot} + \mathrm{A\cdot} \xrightarrow{k_5} \text{products} \tag{2b}$$

According to this mechanism, the first-order disappearances of AH and of A· imply a constant concentration of ROO·. The kinetics become the same as that for isotopic parent–daughter decay,[11] and

$$[\mathrm{A\cdot}] = [\lambda_1/(\lambda_2 - \lambda_1)]\,[\mathrm{AH}] \tag{3}$$

where $\lambda_1 = k_4[\mathrm{ROO\cdot}]$, and $\lambda_2 = k_5[\mathrm{ROO\cdot}]$. From the known value of k_4 (*vide supra*), we estimate that, at 130°C., $k_5 = 7.0 \times 10^7$ l./mole-sec. This is believed to be the first published estimate of k_5, and the value shows that the reaction between A· and ROO· is only moderately fast. There is accumulated evidence that this is true; e.g., for some substituted phenols, a reversible equilibrium [eq. (4)]

$$\mathrm{ROO\cdot} + \mathrm{AH} \rightleftharpoons \mathrm{ROOH} + \mathrm{A\cdot} \tag{4}$$

has been shown[12] to exist, that is, the reverse reaction is competitive with that of eq. (5).

$$\mathrm{ROO\cdot} + \mathrm{A\cdot} \xrightarrow{k_5} \text{products} \tag{5}$$

The postulated steady-state concentration of ROO· during the induction period can now be estimated. Using a halflife of 2 hr. for AH, we obtain $[\mathrm{ROO\cdot}] = 0.85 \times 10^{-8}$ mole/l. This is well below the sensitivity limit of the spectrometer; [ROO·] was not observed experimentally during this period (Table II, Fig. 5). The ROO· signal was observed toward the end of the induction period, and increased rapidly thereafter until a steady-state concentration was attained.

The concentration of ROOH initially decreased with time until a minimum value of ~3 × 10^{-2} mole/l. was reached toward the end of the induction period. The time-dependent equation for ROOH concentration is

$$-d[\mathrm{ROOH}]/dt = k_i[\mathrm{ROOH}] - k_2[\mathrm{RO_2\cdot}][\mathrm{RH}] - k_4[\mathrm{RO_2\cdot}][\mathrm{AH}] \quad (6)$$

where the k_i and k_2 are the rate constants of initiation and propagation, respectively. At the minimum, eq. (6) may be set equal to zero. Using known values of rate constants[2] and assuming $[\mathrm{AH}] = [\mathrm{AH}]_c$, we calculate a value of $[\mathrm{ROO\cdot}] = 4.3 \times 10^{-7}$ mole/l. This estimate appears to be substantiated in Figure 5. In general, one should expect ROO· to become detectable by ESR when [ROOH] begins to increase.

Shortly after the induction period, [ROO·], [ROOH], and $-d[\mathrm{O_2}]dt$ attained steady-state values. The reaction is for most practical purposes the same as that of uninhibited autoxidation.[2]

It is of interest to note in Figure 5 that whereas at least 0.12 mole/l. of hydroperoxide has decomposed, only 0.013 mole/l. of AH was consumed during the same period. Therefore, the amount of ROOH decomposed and the amount of AH reacted differs by a factor of at least 10, not counting the ROOH produced during the reaction. Further experimental results and possible explanations are given elsewhere.[15]

Systems Containing Sulfide Stabilizer

At $[\mathrm{S}] = 8.7 \times 10^{-3}$ mole/l., OPP with a hydroperoxide content of 0.195 mole/l. consumes oxygen at a rate of 6.1 × 10^{-4} mole/l.-sec. at 130°C. There is no induction period. The only radical species discernable was that of ROO·, the intensity of which remained constant throughout the reaction. This rate of oxidation is not appreciably different from the uninhibited rate[2] of about 9 × 10^{-4} mole/l. sec., but the difference is a significant one. The presence of S at this level already reduced the [ROOH] of the reaction to 0.065 mole/l.; it is about 0.2 mole/l. for the uninhibited autoxidation.

More pronounced effects were seen when [S] was increased to 2.6 × 10^{-2} mole/l. under otherwise the same conditions. There was still no induction period. The rate of oxidation was constant at 1.25 × 10^{-5} mole/l. sec., or a factor of 70 slower than the uninhibited rate. The [ROOH] was only about 0.01 mole/l. Both the ROOH and the ROO· radical disappeared rapidly; the latter was replaced by a new and intense signal which was characterized by a very narrow linewidth of about 7.0 gauss and a $\bar{g}$ value of 2.0074. The line shape is symmetric and Gaussian. More will be said about this paramagnetic species (S·) in a later section. The changes of these radical concentrations are shown in Figure 7.

A simplified reaction sequence for the polypropylene autoxidation is given in eqs. (7) where S, or some active intermediates derived from S, are assumed to decompose ROOH via a heterolytic mechanism.

$$\mathrm{ROOH} \xrightarrow{k_i} \mathrm{RO\cdot} + \mathrm{OH\cdot}$$

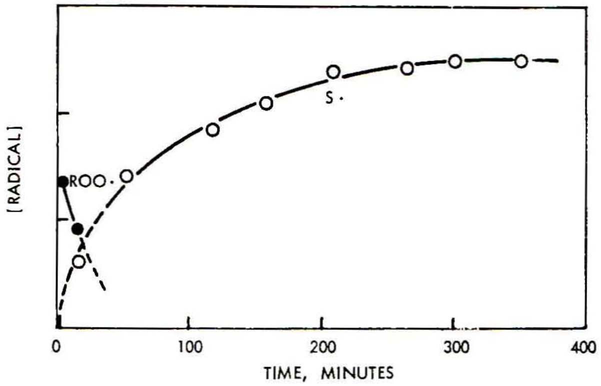

Fig. 7. Radicals in autoxidizing polypropylene containing S. Concentrations in arbitrary units.

$$
\begin{aligned}
\mathrm{RO\cdot(OH\cdot) + RH} &\rightarrow \mathrm{ROH(H_2O) + R\cdot} \\
\mathrm{R\cdot + O_2} &\xrightarrow{k_1} \mathrm{ROO\cdot} \\
\mathrm{ROO\cdot + RH} &\xrightarrow{k_2} \mathrm{ROOH + R\cdot} \\
\mathrm{2ROO\cdot} &\xrightarrow{k_3} \mathrm{products + O_2} \\
\mathrm{ROOH + S} &\xrightarrow{k_6} \mathrm{product + S\cdot}
\end{aligned}
\tag{7}
$$

Assuming steady states for RO·, OH·, and R·, we obtain,

$$-d[\mathrm{O_2}]/dt = 2k_i[\mathrm{ROOH}] + k_2[\mathrm{ROO\cdot}][\mathrm{RH}] - k_3[\mathrm{ROO\cdot}]^2 \tag{8}$$

Substituting the values of $-d[\mathrm{O_2}]dt$ and [ROOH] given above and the known values for the rate constants,[2] we estimate a concentration of ROO· under these conditions of 4.6×10^{-7} mole/l. Therefore, S is very effective in reducing both the [ROOH] and [ROO·] to about 1/20 of their respective uninhibited values.[2] This is understandable as ROO· is derived directly from ROOH.

The paramagnetic species S· has interesting characteristics. Its line width (7.0 gauss) and line shape do not change with temperature within the range of 140°C. to −150°C., whereas the linewidth and line shape of ROO· radical is quite temperature-dependent.[5] The species S· is apparently stable indefinitely. These characteristics resemble those of carbon blacks,[14] e.g., acetylene black. The ESR linewidths of acetylene black and S· are nearly the same, both being unaffected by oxygen. Their intensities are reduced by oxygen. Thus the intensities of S· signal at 0, 160, and 760 mm. of oxygen pressure are 3.0, 2.0, and 1.0, respectively.

The species S· is also inert to several radical scavengers. Thus, when a sample of polypropylene containing S· was swollen in a saturated benzene solution of AH, the ESR signal was undiminished in intensity and unchanged in spectral parameters after 23 hr. Similar treatment with iodine resulted in no change in intensity and a slight increase of linewidth to 7.8

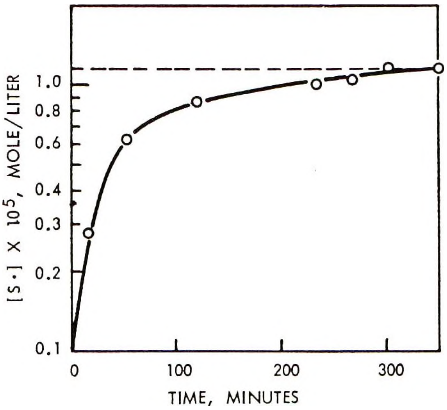

Fig. 8. Growth of paramagnetic species S·.

gauss after 48 hr. The only reagent tried which has noticeable effect on S· is triethyl phosphite. Reaction with neat triethyl phosphite causes, after 45 min., a reduction of spin concentration to one-third of the initial value.

The spin concentration appears to be related to the color of the sample; oxidized polymer, which is dark in color, gives a strong S· signal.

The S· spin center and the free spins in carbon black share several common properties, i.e., long life-times, inertness toward radical scavengers, and reversible interaction with oxygen. The free spins in carbon black are usually thought of as either mobile delocalized π electrons or immobile σ electrons.[14] It appears that the S· observed here may be polysulfides containing delocalized electrons. Spin centers have been observed previously for sulfur.[15] However, in those experiments elemental sulfur was heated at least above 180°C. and the complicated signal was attributed to more than one type of spin centers.

Figure 8 shows the rate at which S· was formed at 130°C. Its concentration increases rather slowly with time until a maximum value was attained. This rate was only slightly dependent upon temperature (*vide infra*). The semilog plot of Figure 8 is reminiscent of the growth curve of a long-life radioactive isotope from the decay of a much more rapidly decaying parent isotope.[11] Computer analysis shows that S· is the product of a reaction which has an apparent first-order rate of 52.5 min.$^{-1}$; the nature of this reaction is, however, unknown. The halflife of S· is estimated from the isotopic decay law to be 85.1 days. The paramagnetic species S· is always present when the rate of oxidation is appreciably retarded, it is absent when the system absorbs oxygen rapidly. S· is not believed to be the species which is initially responsible for the decomposition of hydroperoxide. Most of the hydroperoxide is destroyed during the first 5 or 10 min. of reaction, at which time S· is barely detectable. Its inertness toward AH and I_2 has already been cited. Therefore, it is unlikely that S· is the species responsible for the decomposition of hydroperoxides or scavenging of radicals during the early stage of the reactions. The fact

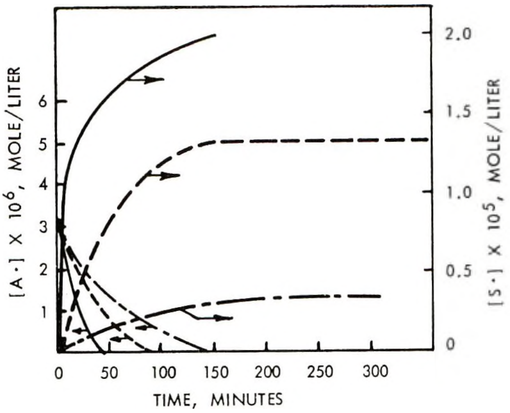

Fig. 9. Inhibition by synergistic stabilizers: (——) 140°C.; (- -) 130°C.; (- · -) 120°C.

that S· reacts with triethyl phosphite indicates that it is a reducible species. Now if S· is an oxidizing agent, one certainly does not expect it to be able to reduce hydroperoxides, as most hydroperoxide decomposers are compounds in their low and intermediate oxidation states.[16-18] Hawkins and Sautter[19] pointed out the importance of acid catalysis in heterolytic hydroperoxide decompositions. The possibility that S· may catalyze such reaction via an electron transfer process is, however, remote because the spin centers in carbon black are not known to be active in this respect.

Systems Containing Both S and AH

To demonstrate and understand the "synergistic" effect in the stabilization of polypropylene against autoxidation by a combination of AH and S stabilizers, we chose to use 2×10^{-2} mole/l. of the former and 8.7×10^{-3} mole/l. of the latter. At 2×10^{-2} mole/l. the amount of AH would be barely over the critical concentration. In the absence of S·, this system would have a very short induction period. Polypropylene containing 8.7×10^{-3} mole/l. of S alone would oxidize with a rate not appreciably different from the uninhibited rate.

When both AH and S were present in amounts given above, there was no oxygen consumed up to 350 min. at 120, 130, or 140°C. Numerous experiments were carried out at these temperatures; the ESR results are shown in Figure 9. At the beginning of a reaction the only radical seen was that of A·. Shortly thereafter, the ESR signal became that of an admixture of two paramagnetic species. For a long reaction time, only S· was observed. At no time during all the experiments were there definite indications of ROO· being present in detectable amounts.

The decay of A· was more rapid at 140°C. than at the lower temperatures. However, even at 120°C. the A· signal intensity decreased to one-third of its initial value after 60 min. Earlier we showed that A· and AH disappear with about the same halflives. Thus, after 60 min. the [AH] is probably less than $[\mathrm{AH}]_c$. It is unfortunate that spectroscopic analysis of [AH] was not possible because the samples became colored. In any event, rapid autoxidation would have started if S was not present.

Earlier in the paper, we noted that S· was not observed in autoxidizing polypropylene containing 8.7×10^{-3} mole/l. of S, the only radical detected being ROO·; at 2.3×10^{-2} mole/l., only S· was found. The spin concentration of S· was 10^{-5} mole/l. The same spin concentration of S· was obtained in the "synergistic" experiments. This spin concentration increases with the increase of temperature.

The hydroperoxide concentrations in all the experiments were about 0.01–0.02 mole/l. as compared to values of 0.2 to 0.3 mole/l. for uninhibited reactions.

The results presented here describe in detail the system inhibited by synergistic stabilizers. The S lowers the hydroperoxide content so that less ROO· radicals are produced. This lowers the critical concentration requirement for AH (Appendix). Thus, even at the very low concentration of AH remaining, there was no autoxidation. On the other hand, AH destroys ROO· to lower the chain length of oxidative reactions and effectively reduces the amount of ROOH which S has to react with.

APPENDIX

We use a simplified reaction sequence to define the critical stabilizer concentrations.

$$\begin{array}{rcl}
\mathrm{ROOH} & \xrightarrow{k_i} & \mathrm{RO\cdot} + \mathrm{OH\cdot} \\
\mathrm{RO\cdot(OH\cdot)} + \mathrm{RH} & \rightarrow & \mathrm{ROH(H_2O)} + \mathrm{R\cdot} \\
\mathrm{R\cdot} + \mathrm{O_2} & \xrightarrow{k_1} & \mathrm{ROO\cdot} \\
\mathrm{ROO\cdot} + \mathrm{RH} & \xrightarrow{k_2} & \mathrm{ROOH} + \mathrm{R\cdot} \\
\mathrm{ROO\cdot} + \mathrm{AH} & \xrightarrow{k_4} & \text{products} \\
\mathrm{ROOH} + \mathrm{S} & \xrightarrow{k_6} & \text{product}
\end{array} \tag{9}$$

Assuming steady states for RO·, OH·, and R·, we obtain

$$Dx = 2k_1y - k_4[\mathrm{AH}]x \tag{10}$$

$$Dy = k_2[\mathrm{RH}]x - (k_i + k_6[\mathrm{S}])y \tag{11}$$

where D is the differential operator, and x and y designate [ROO·] and [ROOH], respectively. Solving the simultaneous equation gives,

$$D^2 + (k_4[\mathrm{AH}] + k_i + k_6[\mathrm{S}])D + k_4[\mathrm{AH}](k_i + k_6[\mathrm{S}]) - 2k_ik_2[\mathrm{RH}] = 0 \tag{12}$$

Because the coefficient of D is positive, according to the theory of equations, the sum of the roots of eq. (12) is negative. Thus, if the term not containing operator D is negative, then one of the roots is positive. This implies an increase of [ROO·] and of [ROOH] with time and the reaction becomes autocatalytic. To keep the reaction stationary, both roots of eq. (12) must be negative, that is

$$k_4[\mathrm{AH}](k_i + k_6[\mathrm{S}]) > 2k_ik_2[\mathrm{RH}] \tag{13}$$

The critical concentration for AH is defined as that where the inequality becomes

$$k_4[\mathrm{AH}]_c(k_i + k_6[\mathrm{S}]c) = 2k_ik_2[\mathrm{RH}] \tag{14}$$

For the system containing only AH, then

$$[\mathrm{AH}]_c = 2k_2[\mathrm{RH}]/k_4 \tag{15}$$

Neiman[20] has derived a similar relationship.

For systems containing only sulfides, the oxidation is always in the autocatalytic region. However, the hydroperoxide concentration is greatly reduced by S. The rate of oxidation is retarded but not inhibited, and is in agreement with all known experimental observations.

A combination of AH and S is commonly referred to as a synergistic system. Mathematically, S serves to reduce the level for $[\mathrm{AH}]_c$ according to eq. (14). Therefore, in the presence of S, a given amount of AH gives a longer induction period. The retarded condition may also continue after all the AH has been consumed. However, AH is also consumed at a slower rate in the presence of S which effectively reduces [ROOH] and [ROO·].

To predict the optimum composition of such a mixture, it is perhaps correct to assume the condition of $k_4[\mathrm{AH}](k_1 + k_6[\mathrm{C}])$ to be maximum. We obtain

$$[\mathrm{AH}]^0 - [\mathrm{S}]^0 = k_i/k_6 \tag{16}$$

where the superscripts designate optimum composition for a given total concentration. Because k_i/k_6 is positive, the optimum composition is for [AH] to exceed [S]. In real applications, however, such factors as relative volatilities of AH, S, low molecular weight hydroperoxides, and oxidation products all have a pronounced effect on the optimum composition.

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Résumé

L'autooxydation du polypropylène inhibé par le 2,6-di-*t*-butyl-*p*-crésol (AH) et le thiodipropionate de dilauryl (S) a été étudiée par les méthode combinées de résonance de spin électronique, par absorption d'oxygène et analyse chimique. Avec AH seul il y a une concentration critique à environ 6 × 10^{-3} mole/litre en-dessous de laquelle il n'y a pas d'inhibition. Cette concentration critique s'accorde avec celle déterminée pour l'autooxydation du squalène inhibé et celle calculée au départ des constantes de vitesse connues. Au-dessus de la concentration critique, il y a une période d'induction bien définie au courant de laquelle la concentration en ROO· est estimée être égale à 10^{-8} mole/l. [ROOH] décroissait rapidement comme la faisait [A·] et [AH]; ces derniers sont liés cinétiquement. La constante de vitesse pour la réaction entre A· et ROO· était estimée égale à 7 × 10^7 l/mole sec. à 130°C. A la fin de la période d'induction, la concentration en [ROOH], [ROO·] et la vitesse de disparition de l'oxygène croît assez rapidement jusqu'à des valeurs stationnaires pour chacun d'entre eux. Avec S seul, il y a uniquement des oxydations retardées mais pas de périodes d'induction bien définies. La concentration en [ROOH] est grandement réduite par S. Dans tous les systèmes où les vitesses d'oxydation sont considérablement supprimées, il y a formation d'une espèce paramagnétique S· qui était inerte à l'égard de AH et I_2 mais réactionnel à l'égard dun phosphite de triéthyle. A cause de sa similitude avec les centres de spin dans le noir de carbone, S· est attribué à des centres polysulfures localisés. Avec S et AH simultanément présents, l'effet combiné de la stabilisation est synergétique. Les variations en fonction du temps de [ROOH], [ROO·] et [A·] suivent des mécanismes habituels. Les relations mathématiques décrivant chacun de ces trois systèmes sont également renseignés.

Zusammenfassung

Die durch 2,6-Di-*t*-butyl-*p*-kresol (AH) und Dilaurylthiodipropionat (S) inhibierte Autooxydation von Polypropylen wurde mittels Elektronspinresonanz, Sauerstoffabsorption und chemischer Analyse untersucht. Bei Verwendung von AH allein besteht eine kritische Konzentration von etwa 6 × 10^{-3} Mol/l, unterhalb welcher keine Inhibierung eintritt. Diese kritische Konzentration stimmt mit der für die inhibierte Squalanautooxydation bestimmten und mit der aus den bekannten Geschwindigkeitskonstanten berechneten überein. Oberhalb der kritischen Konzentration bseteht eine wohl definierte Induktionsperiode, während welcher die ROO·-Konzentration zu 10^{-8} Mol/l bestimmt wird. [ROOH] sowie [A·] und [AH] nahmen rasch ab; letztere sind kinetisch verknüpft. Die Geschwindigkeitskonstante der Reaktion zwischen A· und ROO· wird bei 130°C zu 7 × 10^7 l/Mol sec bestimmt. Am Ende der Induktionsperiode nahmen [ROOH], [ROO·] und $-d[O_2]/dt$ rasch bis zur Erreichung stationärer Werte für alle diese Grössen zu. Mit S allein tritt nur eine verzögerte Oxydation aber keine woh definierte Induktionsperiode auf. [ROOH] wird durch S stark herabgesetzt. In allen Systemen, in welchen die Oxydationsgeschwindigkeit stärker vermindert wurde, trat die Bildung einer sehr stabilen paramagnetischen Spezies ein, die gegen AH und I_2 unempfindlich war, mit Triäthylphosphit jedoch reagierte. Wegen seiner Ahnlichkeit mit Spinzentren in Russ, wird angenommen, dass S· ein delokalisiertes Polysulfid-Spinzentrum ist. Bei gemeinsamer Anwesenheit von S und AH besteht ein synergistischer Stabilisationseffekt. Die beobachtete Änderung von [ROOH] [ROO·] [A·] in Abhängigkeit von der Zeit folgt dem gewöhnlichen Mechanismus. Mathematische Beziehungen zur Beschreibung jedes der drei Systeme werden angegeben.

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Organic Photoconductors. VIII. Photoconductors Obtained from the Reaction Products of Poly(9-vinyl Anthracene)

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Synopsis

9-Vinyl anthracene has been polymerized by three methods in cationic systems to obtain organic photoconductors. Cationic polymerization catalysts used were titanium tetrachloride and aluminum chloride anhydride. According to the degree of conversion from poly(9-vinyl anthracene) to poly(9,10-dimethylene anthracene) the photosensitivity increased.

INTRODUCTION

Electrophotography is a copying method which combines electrostatic and a photoconductive phenomena. There are two electrophotographic processes now in practical use: Xerography, which employs a selenium photosensitive plate, and Electrofax, utilizing a resin dispersion of zinc oxide. Other known photosensitive materials for use in electrophotography include inorganic substances such as zinc sulfide and cadmium sulfide, and organic substances such as anthracene, anthraquinone, carbazole, and perylene.

Recently, a few series of heterocyclic compounds,[1] poly(*N*-vinyl carbazole),[2] and polymers of multinuclear aromatic compounds substituted by a vinyl group,[3] for example poly(9-vinyl anthracene), have been set forth from the Kalle Aktiegengesellschaft in Germany. The sensitivity of these substances, however, is not sufficient to allow use in practical copying fields.

The present authors, in studying the photoconductive behavior of poly(9-vinyl anthracene), have noticed that the reaction products of poly(9-vinyl anthracene) have much superior sensitivity in electrophotography.

EXPERIMENTAL

Materials Used

Poly(9-vinyl Anthracene)(Polymer A). 9-Vinyl anthracene was prepared by the method of Hawkins.[4] It is well known that 9-vinyl anthracene is possible from ionic polymerization[5,6] and radical polymerization.[7] For example, in a glass tube was dissolved 10 g. of 9-vinyl anthracene into 100 ml. of dry toluene, adding thereinto at −70°C. 2 mole-% titanium tetrachloride based on the amount of 9-vinyl anthracene, then the tube was sealed after reducing the pressure and was left for 2 hr. at −70°C. for polymerization. The pale yellow precipitate was obtained by pouring the solution into methanol. This polymer has a molecular weight of 2400 and a melting point of 210–220°C. and is soluble in benzene, methyl ethyl ketone, tetrahydrofuran, and methylene chloride. The similar polymer could also be prepared by radical polymerization, employing di-*tert*-butyl peroxide (yield 64%).

The product obtained as stated above is referred to herein as "polymer A."

Polymer B. Ten grams of 9-vinyl anthracene was dissolved in 50 ml. of dry toluene and 2 mole-% of titanium tetrachloride was added at −70°C. The mixture was then left for 2 hr. at −70°C. in a sealed glass tube and was heated gradually thereafter to room temperature over a period of 1 hr. The yellow polymer was obtained in 47% yield and was soluble in benzene and tetrahydrofuran. The residue was insoluble. A similar polymer could also be obtained by cationic polymerization in the presence of Friedel-Crafts type catalysts such as boron trifluoride, aluminum chloride anhydride, or sulfuric acid.

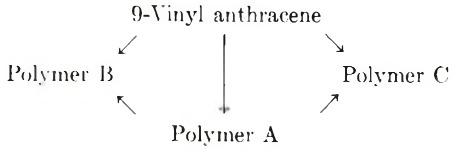
Furthermore, a similar polymer could be obtained by the following process; 2 g. of poly(9-vinyl anthracene) (polymer A) was dissolved in 40 ml. of nitrobenzene and added to 0.26 g. of aluminum chloride anhydride in a glass tube which was sealed after reducing the pressure and then left for 2 hr. at 20°C. The mixture was poured into dilute hydrochloric acid to decompose the catalyst. The yellow polymer was twice reprecipitated from a tetrahydrofuran solution by pouring it into methanol. The yield was 12.5%.

The polymer obtained as stated above is referred as "polymer B."

Polymer C. Ten grams of 9-vinyl anthracene were dissolved into 50 ml. of dry benzene, and 2 mole-% of titanium tetrachloride was added based on the amount of 9-vinyl anthracene. Then the mixture was reacted for 24 hr. at a temperature of 70°C. Light-brown polymer insoluble to solvents was obtained in 90% yield. A similar polymer could also be prepared according to the following process: 20 g. of poly(9-vinyl anthracene) (polymer A) was dissolved in 50 ml. of benzene, and a 2 mole-% of titanium tetrachloride was added thereinto and the mixture was reacted at 25°C. in a sealed glass tube under a reduced pressure. The viscosity increased gradually, then a precipitate began to be formed 1 or 2 hr. afterward and finally it was solidified. After leaving it for 24 hr.; it was poured into methanol–hydrochloric acid, washed sufficiently with methanol and water and then dried. It was washed again with benzene to remove a benzene-soluble product and dried to obtain a yellow polymer in 95% yield.

The polymer as discussed above is referred as "polymer C."

The relation among polymers A, B, and C described above is shown as follows:



in which arrows show flow of preparation.

Experimental Technique

Relative Surface Potential. The photosensitivity of the electrophotographic conduction layers is determined by a method of relative surface potential.[8] As has been stated in detail in another paper,[9,10] a thin specimen film 3 ~ 5 μ thick was formed on an aluminum plate. The top surface of a plate was sensitized in the dark to a potential of 200 ~ 400 v. (V_d) by positive corona-charging. Actinic light produces electron hole pairs which, under the influence of the electric field, are separated; the electron moves to the surface to neutralize a positive charge and the positive hole is accelerated to the induced negative charge. Therefore, the surface potential decreases with illuminated time to V_1, and so the exposure in which V_1/V_d is reduced to one-half represents the half-decay exposure E_{50}, which serves as an index of photoconductivity.

Specimen Plate. A thin film (3~5 μ) on an aluminum plate of polymer A or B was prepared from a solution of the polymer. In the case of polymer C a thin film (5 μ) was prepared from a dispersion of finely powdered polymer C 1 g., butyral resin (trade name: Esrex BMS) 0.5 g. and toluene 2 ml., which was mixed well in a bowl.

Infrared Spectra. In the case of polymer A or B, its solution is spread on a NaCl plate. The spectrum of polymer C was examined by the KBr method.

RESULTS AND DISCUSSION

Infrared Spectra

The infrared spectra of three polymers are shown in Figure 1.

Michel[5] reported cationic polymerization on 9-vinyl anthracene that its polymer was aside from the normal vinyl polymerization and it might

TABLE I
Index of Photosensitivity

Material	Half-decay exposure (E_{50}) lux sec.
Polymer A	12,500
Polymer B	200
Polymer C	8.1
Zinc oxide	280 (negatively charged)
Selenium	7

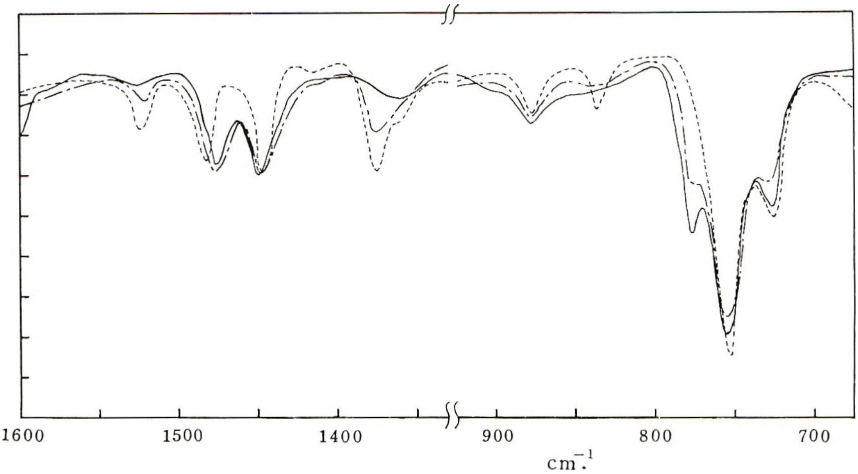


Fig. 1. Infrared spectra of reaction products of poly(9-vinyl anthracene): (——) polymer A; (– · –) polymer B; (- - -) polymer C.

polymerize by repeated addition of vinyl groups across the 9-10 positions of successive anthracene units and it was converted to poly(9,10-dimethylene anthracene). In our experiments polymer C may exhibit poly (9,10-dimethylene anthracene) and the structure of polymer B appears to be intermediate in degree of conversion between polymers A and C. It is characteristic that the absorption band at 777 cm.$^{-1}$ disappears and the solubilities change according to degree of conversion.

Figure 2 shows the light decay curves of polymers obtained; the surface of the specimen plates were illuminated with an incandescent light.

In Table I are shown the values of the half-decay exposure (E_{50}) comparing the conventional electrophotographic plate.

In the previous patent[3] some of dyestuffs increase the photosensitivity.

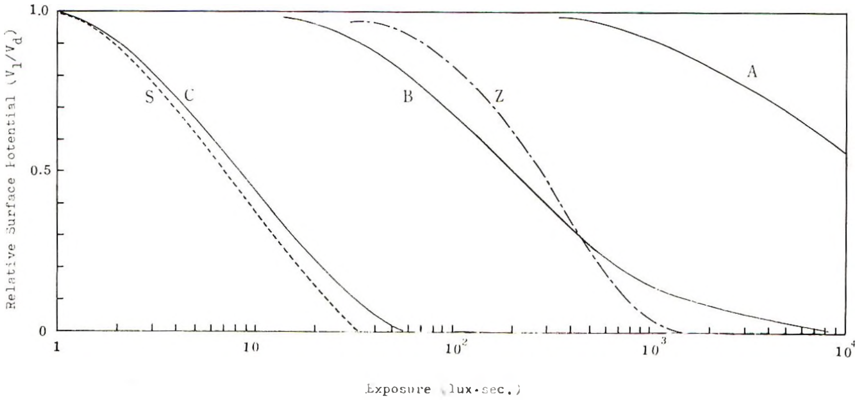


Fig. 2. Light decay curves. Relative surface potential (RSP) vs. exposure (Exp): (*A*) polymer A; (*B*) polymer B, (*C*) polymer C; (*Z*) zinc oxide; (*S*) selenium.

TABLE II
Index of Photosensitivity Containing Sensitizer

Material	Half-decay exposure (E_{50}) lux sec.
Polymer A	3,200
Polymer B	70
Polymer C	4.8
Zinc oxide (sensitized by rose bengal)	19

The results of the sensitized plate by 0.1% crystal violet are shown in Table II.

In the case of polymer C the relation of the ratio of the polymer and the butyral resin is examined, which is shown in Figure 3.

In the polymer C (sensitized) the value of E_{50} is 4.8 lux sec. when the plate is charged positively, but when charged negatively the value decreased to 24.5 lux sec. Other polymers show the same tendency according to the sign of the corona charging. This result shows that the majority charge carriers of these photoconductors are positive-hole.[11]

The increase of the photoconductivity according to degree of conversion suggests that the structure of 9,10-dimethylene anthracene is effective to the photosensitivity and one direction may be shown to prepare more sensitive photoconductors.

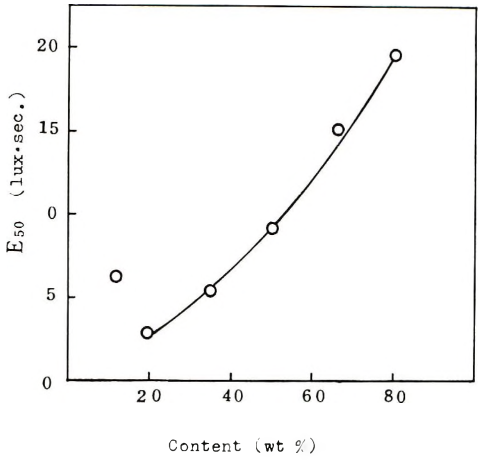


Fig. 3. Photosensitivity (E_{50}) vs. photoconductor content (Cont.) for polymer C.

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Résumé

Le 9-vinylanthracène a été polymérisé par trois méthodes de systèmes cationiques en vue d'obtenir des photoconducteurs organiques. Les catalyseurs de polymérisations cationiques, utilisés étaient le tétrachlorure de titane et le chlorure d'aluminium anhydride. De même que en ce qui concerne le degré de conversion, la photosensitivité, s'accroît de la poly-9-vinyle anthracène au poly-9,10-diméthylanthracène.

Zusammenfassung

9-Vinylanthracen wurde in drei kationischen Systemen polymerisiert, um organische Photoleiter zu erhalten. Als kationische Polymerisationskatalysatoren wurden Titantetrachlorid und wasserfreies Aluminiumchlorid verwendet. Entsprechend dem Umlungsgrad von Poly-9-vinylanthracen zu Poly-9,10-dimethylenanthracen nahm die Lichtempfindlichkeit zu.

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Kinetics of Polymerization of Gaseous Formaldehyde

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Synopsis

The polymerization of gaseous monomeric formaldehyde has been studied. The effects of the following variables have been investigated: temperature, initial monomer pressure, surface-to-volume ratio of reaction vessel, thickness of polymer deposit, and partial pressure of added oxygen. A three-step mechanism is proposed which successfully accounts for the results of experiments in which monomer is allowed to deposit on the bare wall of the reaction vessel. When a sufficient amount of polymer has been laid down, the termination reaction becomes negligible and a limiting two-step mechanism holds. The present results combined with literature values from work done on the depolymerization reaction give the activation energy of the propagation and termination reactions to be 14.2 ± 0.6 and 7.8 ± 0.9 kcal./mole, respectively. Although the reaction is heterogeneous, the activation energies are independent of surface-to-volume ratios within the experimental error. The nature of the polymer active sites is considered and these are thought to be hydroxyl groups. The results of work done with added oxygen show a small inhibitory effect.

INTRODUCTION

Formaldehyde is a highly important chemical, and its properties have been extensively investigated and documented.[1,2] It is well established that the polymerization of the anhydrous monomer yields a polymer of high number-average molecular weight (15,000–150,000). The properties of the high molecular weight polymer have been studied in detail.[1] However the kinetics of the polymerization of pure gaseous monomeric formaldehyde have received little attention, and the mechanism for this reaction has remained unknown up to the present. This lack of attention is surprising in view of the fact that monomeric formaldehyde is one of the simplest stable monomers known.

Early attempts to characterize this reaction met with scant success,[3,4] and the attainment of reproducible results was first reported by Toby and Rutz[5] in 1962. None of the investigators proposed a mechanism for this polymerization reaction, and their results must be held as mainly qualitative. The first quantitative characterization of the polymerization from the gaseous phase of monomeric formaldehyde has been recently given by us in brief.[6] This paper is a more detailed account; in addition, the effect on the polymerization of surface and of oxygen is discussed.

EXPERIMENTAL

A detailed description of the apparatus and procedures has been given elsewhere.[7] Formaldehyde monomer was prepared and purified as follows. Alkali-precipitated α-polyoxymethylene was prepared by the method of Staudinger et al.[8] This polymer (99.7–99.9% formaldehyde) was depolymerized in the temperature range 50–100°C. under vacuum, and the monomeric product was condensed at −196°C. This monomer was then subjected to three successive distillations, each from −86°C. (methyl ethyl ketone slush) to a receiver at −196°C. with head and tail fractions liberally discarded. The resulting pure monomer was stored at −196°C. under vacuum.

Gas chromatography based on a method developed by Bombaugh and Bull[9] was employed to check the monomer for the most abundant impurities: water, methanol, and methyl formate. Identification of these impurities was straightforward, since they eluted before the large formaldehyde peak. Samples of the monomer after each distillation during the preparation and of the monomer supply after three months of storage were taken and analyzed. The results of these analyses are shown in Table I.

A conventional high-vacuum system was employed, and all reaction vessels and associated tubing were made of virgin quartz which was untreated except for being flamed *in vacuo*. Quartz which had been in contact with tap water or cleaning solution was found to give erratic polymerization rates and was discarded. Greaseless conditions were maintained in the reaction section. Since no appreciably volatile polymer was formed, the decrease in monomer concentration within the reaction vessel was followed via mercury manometer made of sufficiently narrow tubing so that volume changes were negligible. The reaction section was thermostatted to within ±0.05°C. over the entire temperature range employed (0–60°C.). The surface-to-volume ratio S/V was varied by using a spherical reaction vessel, a cylindrical reaction vessel with an inner concentric tube, and a

TABLE I

Percentage Composition of Monomer Supply after Each of Several Successive Distillations and after 3 Months of Use

Distillation	Methyl formate, %	Methanol, %	Water, %	Formaldehyde, %
1 Direct from polymer (50–100°C.)	0.35	1.39	2.68	92.81[a]
2 From monomer at −86°C.	0.04	0.04	0.06	99.86
3 From monomer at −86°C.	0.03	0.04	0.44[b]	99.49
4 From monomer at −86°C.	0.01	0.05	0.04	99.90
From monomer supply after 3 months	0.01	0.02	0.02	99.95

[a] An unidentified peak accounted for 2.77% of sample.

[b] Unreliable due to air leak.

reaction vessel consisting of a spiral of tubing. The values of overall S/V were 1.0, 2.6, and 5.0 cm.$^{-1}$, respectively.

Two general types of polymerization experiments were performed: one in which monomer was allowed to polymerize on the bare wall of a reaction vessel which previously had been flamed red-hot under vacuum and another in which the polymer deposit was not removed between experiments and the coating was allowed to build up from run to run.

RESULTS

The effects of changes in the following variables were investigated: initial pressure, temperature, ratio S/V ratio of the reaction vessel, the age and thickness of the polymer deposit, and the presence of oxygen.

Qualitative Aspects

Over the entire temperature range employed, formaldehyde monomer polymerizes on the walls of the reaction vessel as a white solid polymer. At a given temperature, the rate of polymerization increases with increasing monomer pressure for both bare-wall and coated-wall experiments.

The polymerization rate at a given initial pressure and temperature increases with an increase in S/V of the reaction vessel, as shown in Figure 1.

In a series of experiments, each at the same temperature and initial pressure and where the polymer deposit is allowed to accumulate, the polymerization rate progressively decreases from one run to the next. However, the rate does not seem to approach a limiting value, but rather approaches a state where it exhibits a slow decrease from run to run.

All runs where the initial monomer pressure is appreciably above the equilibrium vapor pressure of the polymer exhibit an initial polymerization rate which increases with temperature. This initially relatively fast rate gradually decreases to a very slow and almost constant rate as the equilibrium vapor pressure is approached. In practice, equilibrium is seldom achieved, months being required in the approach from either direction.[10]

Oxygen, when present during the reaction, was found to have a slight inhibiting effect. This is illustrated in Figure 2, where a series of bare-wall experiments at 30°C. with 100 mm. Hg initial formaldehyde pressure was carried out in the presence of varying amounts of oxygen. The partial pressure of the oxygen was varied from 4×10^{-4} to 14.3 mm. Hg.

Mechanism

The results are explained in terms of the mechanism of eqs. (1)–(5):

$$\mathrm{F} + \mathrm{W} \xrightarrow{k_1} \mathrm{WF} \tag{1}$$

$$\mathrm{F} + \mathrm{WF} \xrightarrow{k_2} \mathrm{WF}_2 \tag{2}$$

$$\mathrm{F} + \mathrm{WF}_n \xrightarrow{k_p} \mathrm{WF}_{n+1} \tag{3}$$

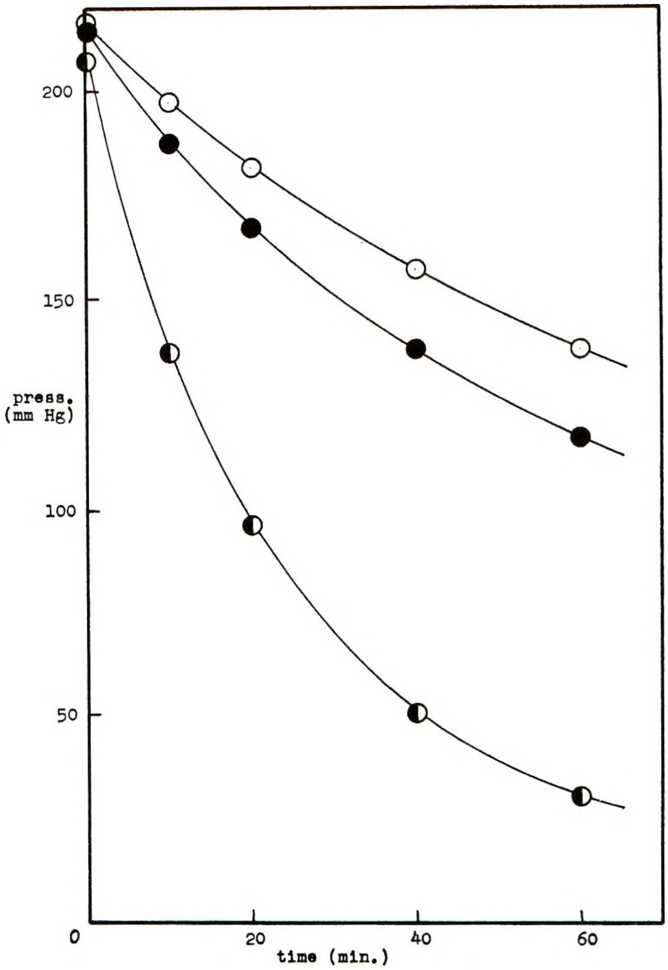

Fig. 1. Pressure–time curves showing the effect of S/V for bare-wall runs at 30°C. and constant initial monomer pressure: (○) $S/V = 1.0$ cm.$^{-1}$; (●) $S/V = 2.6$ cm.$^{-1}$; (◐) $S/V = 5.0$ cm.$^{-1}$.

$$WF_n \xrightarrow{k_d} WF_{n-1} + F \tag{4}$$

$$WF_n + WF_n \xrightarrow{k_t} \text{product} \tag{5}$$

where F represents formaldehyde monomer, W represents active sites on the wall, and WF_n represents polymer.

Since all W must be covered in an extremely short time and assuming the reactivity of WF_n to be independent of chain length, the mechanism can be simplified to the three-step sequence:

$$F + A \xrightarrow{k_p} A$$

$$A \xrightarrow{k_d} A + F$$

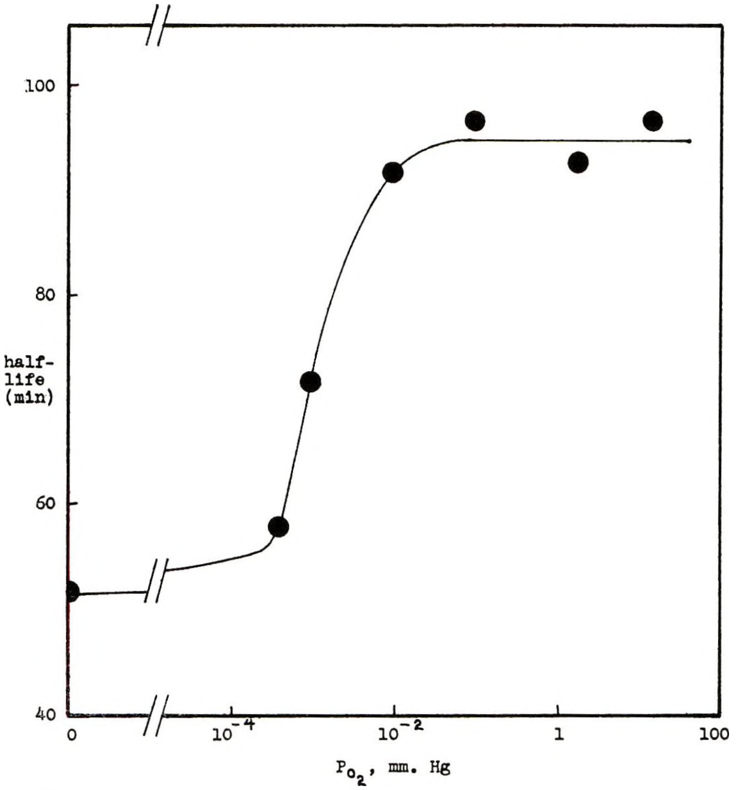

Fig. 2. Plot of reaction half-life against pressure of added oxygen for an initial monomer pressure of 100 mm. Hg at 30°C. (bare-wall runs).

$$A + A \xrightarrow{k_t} \text{product}$$

where A represents all active sites regardless of chain length.

This mechanism differs from a typical free-radical polymerization mechanism by the absence of an initiation step. This implies that the growing-polymer active sites A were all originally potentially present in the form of wall active sites, W.

Since the polymer is a solid phase, any active sites on the ends of growing polymer chains must become progressively less mobile as the chains become entangled and incorporated into the structure of the solid. However, there is always a residual mobility inherent in the growth of the chains. This implies that as time advances and more polymer is laid down, the termination rate constant k_t will decrease until eventually the termination reaction will be negligible with respect to the other two. The polymerization rate constant k_p might also be expected to decrease for the same reason but not to the same extent.

This is an extreme example of the gel effect. However, it should be noted that in this system, as k_t decreases, the concentration of active sites continues to decrease, although at a slower rate than previously. This

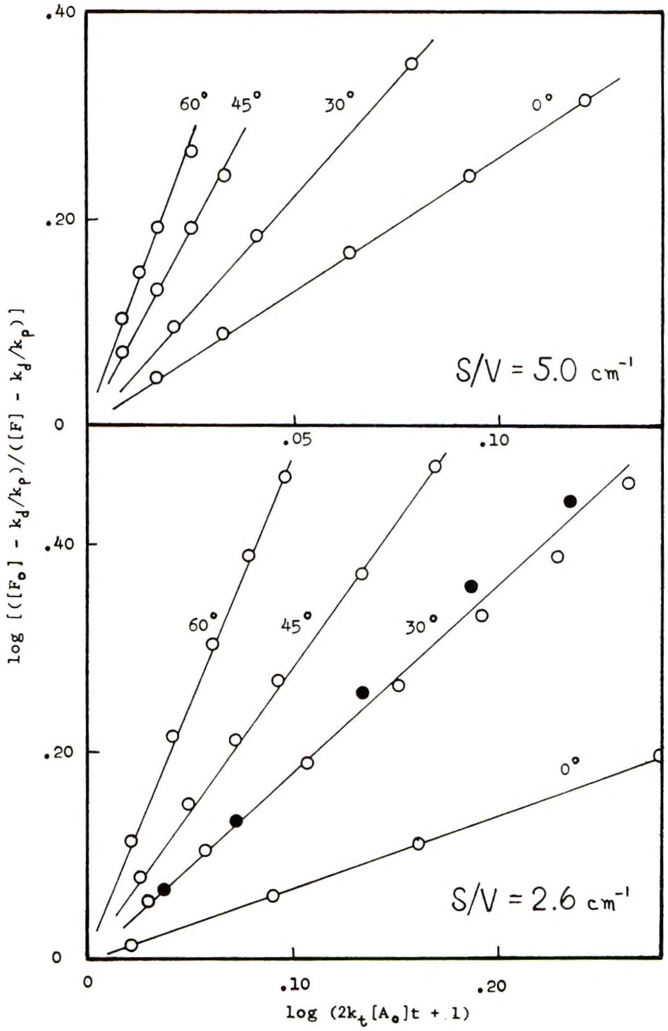

Fig. 3. Test of rate law for bare-wall runs at S/V = 2.6 and 5.0 cm.$^{-1}$. Initial monomer pressures are approximately 200 mm. Hg in all cases except filled circles, where $[F_0]$ = 17 mm. Hg.

contrasts with the gel effect in typical free-radical polymerization reactions, where a decrease in k_t causes an increase in the concentration of reactive intermediates, since their rate of initiation is essentially unaffected by a change in k_t.

We therefore characterize three identifiable stages during the polymerization reaction: initial, intermediate, and limiting stages.

Initial Stage. For bare-wall runs when polymer active sites are in high concentration and still relatively mobile, the three-step mechanism holds.

Intermediate Stage. As time advances and more polymer is laid down, the termination rate constant begins to decrease, since the concentration and mobility of the active sites are no longer such as to allow every site the possibility of terminating. The rate law from the three-step mechanism does not hold because k_t is decreasing during a given experiment.

Limiting Stage. After a sufficient amount of polymer has been laid down, the active sites are all effectively trapped. The termination rate constant will have fallen to a low and almost constant value, and only the first two steps of the mechanism hold, the concentration of active sites being now essentially a constant.

Kinetic Parameters

The initial stage where the total mechanism is operative leads to the integrated equation, eq. (6):

$$\ln\{([F_0] - k_d/k_p)/([F] - k_d/k_p)\} = (k_pS/2k_tV)\ \ln\ (2k_t[A_0]t + 1) \quad (6)$$

where $[F_0]$ and $[A_0]$ are the monomer and active site concentrations at zero time, respectively, and S and V are the reaction-vessel surface (square centimeter) and volume (cubic centimeters), respectively. Equation (6) differs slightly from that previously given,[6] in that $2k_t$ is conventionally used instead of k_t, and S/V has been introduced to allow for heterogeneity.

Examination of eq. (6) reveals that the ratio k_d/k_p must be equal to the equilibrium vapor pressure, and values have been taken from the work of Dainton et al.[10]

A plot of the left-hand side of eq. (6) versus $\ln\ (2k_t[A_0]t + 1)$ should be linear with a slope of $k_pS/2k_tV$. For each run there is one unknown constant, $2k_t[A_0]$, which must be determined graphically. The nature of eq. (6), however, is such that a choice of values too high or too low quickly results in noticeable curvature. The values of $2k_t[A_0]$ thus obtained were approximately independent of $[F_0]$ for each temperature but could not be separated further.

A plot showing the test of eq. (6) for bare-wall runs in a vessel with a S/V of 1.0 cm.$^{-1}$ at temperatures between 0 and 60°C. and with a 12-fold change in initial monomer pressure has already been given.[6] Figure 3 is a similar plot of runs in vessels with a S/V of 2.6 and 5.0 cm.$^{-1}$ and again shows good linearity with a slope essentially independent of $[F_0]$ over a 12-fold range.

The slopes of the eq. (6) plots, $k_p/S/2k_tV$, are plotted in Figure 4 according to the Arrhenius equation. The slopes of these plots yield $E_p - E_t$, and the intercepts yield $A_pS/2A_tV$, where E_p and E_t are the activation energies for the polymerization and termination reactions, respectively, and A_p and A_t are the Arrhenius A factors for these same reactions.

Table II lists data derived from the Arrhenius plots. On combining these results with those of previous investigators, the individual activation energies shown in Table III are obtained.

No analytical expression governing the intermediate stage of the reaction can be derived from the mechanism. This is because during the intermediate stage k_t is decreasing during a given experiment.

Considering the limiting stage, where all active sites are effectively

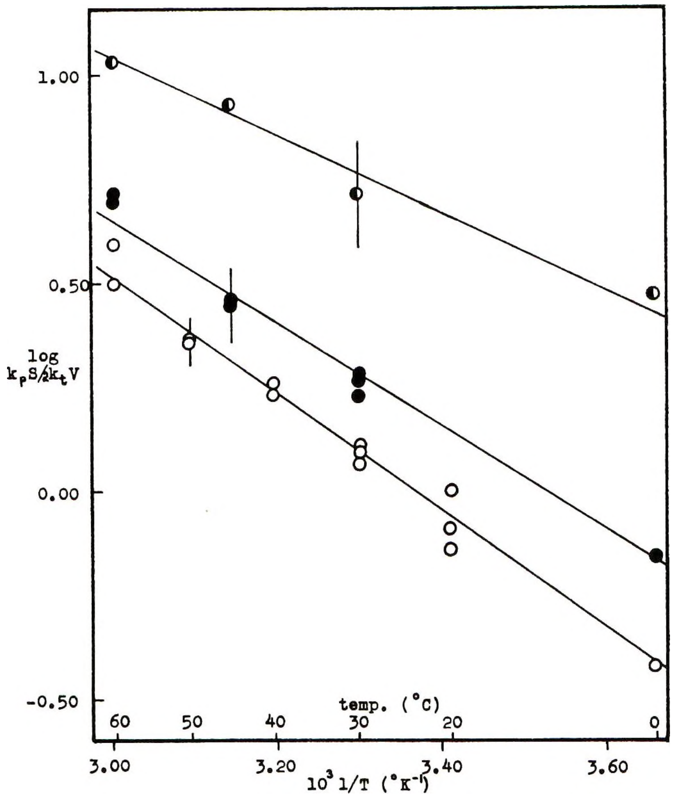

Fig. 4. Arrhenius plot of log ($k_pS/2k_tV$) vs. $1/T$: (○) $S/V = 1.0$ cm.$^{-1}$, (●) $S/V = 2.6$ cm.$^{-1}$, (◐) $S/V = 5.0$ cm.$^{-1}$. Error limits shown are typical.

trapped and at constant concentration, the termination step in the mechanism can be neglected. The integrated equation, eq. (7), can then be derived:

$$\ln\{([F_0] - k_d/k_p)/([F] - k_d/k_p)\} = k_p[A_0]St/V \qquad (7)$$

As before, k_d/k_p must equal the equilibrium vapor pressure. A plot of the left-hand side [which is the same as in eq. (6)] versus time should be linear with a slope of $k_p[A_0]S/V$. Such a plot has been shown previously[6] for a series at 30°C. which started with a bare-wall run and in which the

TABLE II

Activation-Energy Differences and A Factor Ratios Derived from Arrhenius Plots

S/V, cm.$^{-1}$	$E_p - E_t$, kcal./mole	$A_pS/2A_tV \times 10^{-4}$ (dimensionless)
1.0	6.4 ± 0.7	5.2 ± 0.7
2.6	5.7 ± 0.8	7.4 ± 1.4
5.0	4.4 ± 1.9	20 ± 9

TABLE III
Activation Energies Derived from This Work and Literature

Parameter	kcal./mole	Reference
$E_p - E_t$	6.4 ± 0.7	This work
$E_p - E_d$	−12.35 ± 0.05	10
$E_d - E_t$	18.8 ± 0.7	—
E_d	27.1	11
E_d	26	12
E_p	14.2 ± 0.6	—
E_t	7.8 ± 0.9	—

polymer deposit from succeeding runs, at the same initial monomer pressure, was allowed to build up on the walls of the reaction vessel. The same behavior was apparent at all temperatures studied: bare-wall runs obeyed eq. (6), but when a sufficiently thick polymer layer was allowed to build up, eq. (7) was obeyed.

DISCUSSION

Effect of S/V

Plots such as those in Figure 1 show that this polymerization reaction is very sensitive to the surface-to-volume ratio of the reaction vessel. This is typical of heterogeneous reactions, and was observed by several early investigators of this reaction. In the proposed mechanism, both the polymerization and depolymerization steps are heterogeneous, and the S/V term in the kinetic equations arises in a nonempirical manner.

In the Arrhenius plots of Figure 4, the slopes and hence the activation-energy differences are independent of the surface-to-volume ratio within the experimenal error. However, the intercepts, $A_pS/2A_tV$, are a strong function of the $S/V$and lie approximately in the ratio of the S/V values.

Diffusion

A modified mechanism designed to account for diffusion by postulating a "collision volume" analogous to the "cage" in liquid-phase work may be given:

$$\mathrm{F} + \mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mathrm{F} + \mathrm{A}) \tag{8}$$

$$(\mathrm{F} + \mathrm{A}) \underset{k_d}{\overset{k_p}{\rightleftharpoons}} \mathrm{A} \tag{9}$$

$$\mathrm{A} + \mathrm{A} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (\mathrm{A} + \mathrm{A}) \tag{10}$$

$$(\mathrm{A} + \mathrm{A}) \xrightarrow{k_t} \text{products} \tag{11}$$

Where reaction (8) represents the diffusion of a monomer unit and an active site into a collision volume and the reverse reaction represents diffusion out of this collision volume; reaction (10) represents the diffusion of two active sites into a collision volume and the reverse reaction represents diffusion out of this collision volume; and reactions (9) and (11) are to be interpreted as before.

The resulting kinetic equations have the same form as equations (6) and (7), the only differences being the interpretations placed on various constants. Regardless of the extent of diffusion, the rate law is formally unaffected. However, present data do not allow the role of diffusion to be unambiguously evaluated.

Nature of Active Sites

The exact nature of the wall active sites, W, is unknown. They may be lattice defects in the silica or impurities from the monomer which are adsorbed.

If the impurities in the formaldehyde initiate polymerization we may estimate a rough value for the molecular weight of the resulting polymer as follows. We assume a linear polymer since agreement of number-average molecular weight determinations in the range 20,000–100,000 measured by both osmometry and by endgroup analysis indicates little or no chain branching.[13] Our chromatographic analysis gave the impurity level as 0.05–0.1 mole-%. If each molecule of impurity produced a chain, then the degree of polymerization would be in the range 100/0.1 to 100/0.05, and the expected molecular weight would be 30,000–60,000 which is in agreement with reported values[1,2,13] for polymer obtained from the pure monomer.

If hydroxylic impurities initiate polymerization, then the most likely mechanism which gives rise to the observed rate law is

$$(CH_2O)_nCH_2OH + CH_2O \underset{k_d}{\overset{k_p}{\rightleftharpoons}} (CH_2O)_{n+1}CH_2OH$$

$$(CH_2O)_nCH_2OH + (CH_2O)_mCH_2OH \xrightarrow{k_t} (CH_2O)_nCH_2OCH_2(CH_2O)_m + H_2O$$

This mechanism is a modified version of that proposed by Bevington and Norrish[14] for the catalyst-initiated polymerization of gaseous formaldehyde.

It should be noted that one of the products of the mechanism is water, a known polymerization catalyst for formaldehyde. However, if an additional step is introduced in which water is adsorbed on the polymer to produce a new active site, the overall rate law remains unchanged when steady-state conditions are assumed for the water concentration.

It is interesting to note that Furukawa et al.[2,15] found that acetaldehyde vapor polymerized heterogeneously on a solid catalyst at −78°C. Under similar conditions formaldehyde did not polymerize.

Effect of Added Oxygen

Monomer was allowed to polymerize in a bare-wall vessel in the presence of varying amounts of oxygen, a radical scavenger. The effect on the reaction half-life is shown in Figure 2. The half-life is almost doubled as the oxygen partial pressure is increased from zero to 1.0×10^{-2} mm., but pressures above this value have apparently no further effect on the reaction rate.

Thus the presence of oxygen causes only a slight inhibition of the reaction, and this suggests that although the reaction is predominantly cationic in nature, there may be a small free-radical component. To check whether the effect of oxygen was merely due to adsorption and subsequent deactivation of active sites, a single run was carried out in the same vessel in the presence of 2.4 mm. of carbon dioxide. No effect was seen, and thus the effect seems not likely to be due to mere adsorption. Any interpretation of the effect of added oxygen is complicated by the fact that the decomposition of polyoxymethylene can be accelerated by its presence,[16] and a definitive interpretation must await further results.

We wish to express our gratitude to the National Science Foundation and to the Rutgers University Research Council for their support of this work.

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Résumé

La polymérisation de formaldéhyde monomérique gazeux a été étudiée. Les effets des variables suivantes ont été étudiés: la température, la pression monomérique initiale, le rapport surface–volume du récipient, l'épaisseur du dépôt de polymère et la pression partielle d'oxygène additionné. Un mécanisme en trois étapes est proposé qui rend compte avec succés du résultat des expériences dans lesquelles le monomère peut se déposer sur les paroîs découvertes du récipient de réaction. Quand une quantité suffisante de polymère est déposée, la réaction de terminaison devient négligeable et un mécanisme à deux étapes est valable. Les résultats présents combinés avec les valeurs de la littérature au départ d'un travail effectué sur la réaction de dépolymérisation, fournissent l'énergie d'activation de la propagation et des réactions de terminaison s'élevant à 14.2 ± 0.6 et 7.8 ± 0.9 Kcal/mole^{-1} respectivement. Bien que la réaction soit hétérogène, des énergies d'activation sont indépendantes du rapport surface–volume dans les limites de l'erreur expérimentale. La nature des sites actifs de polymères est considérée et on admet qu'il s'agit de groupes hydroxylés. Les résultats du travail effectué avec de l'oxygène additionné suggèrent qu'une contribution par radicaux libres faibles existe dans ce mécanisme.

Zusammenfassung

Die Polymerisation von gasförmigem monomeren Formaldehyd wurde untersucht. Der Einfluss folgender Variablen wurde gemessen: Temperatur, Anfangsdruck des Monomeren, Oberflächen–Volumsverhältnis des Reaktionsgefässes, Dicke der Polymerablagerung und Partialdruck des zugesetzten Sauerstoffes. Ein Dreistufenmechanismus wird vorgeschlagen, der erfolgreich die Ergebnisse von Versuchen, bei welchen das Polymere sich an den nackten Wänden des Reaktionsgefässes absetzen kann, wiedergeben kann. Nach Ansammlung einer genügenden Polymermenge wird die Abbruchsreaktion vernachlässigbar und ein zweistufiger Mechanismus wird als Grenze erreicht. Die vorliegenden Ergebnisse liefern zusammen mit Literaturwerten für die Depolymerisation für die Aktivierungsenergie der Wachstumsreaktion 14,2 ± 0,6 kcal Mol^{-1} und für diejenige der Abbruchsreaktion 7,8 ± 0,9 kcal Mol^{-1}. Obgleich die Reaktion heterogen verläuft, sind die Aktivierungsenergien innerhalb der Versuchsfehler vom Oberflächen–Volumenverhältnis unabhängig. Bei den aktiven Stellen des Polymeren scheint es sich um Hydroxylgruppen zu handeln. Die Ergebnisse von Versuchen mit zugesetztem Sauerstoff lassen einen kleinen Beitrag freier Radikale zum Mechanismus erkennen.

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Dielectric Properties of Vinylidene Chloride–Vinyl Chloride Copolymers

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Synopsis

The dielectric properties of vinylidene chloride–vinyl chloride copolymers prepared at conversions of less than 5% were studied. The magnitude of dielectric α absorption (absorption at high temperature) is not a linear function of the composition on account of the effect of the copolymer's crystallinity. On the other hand, a nearly linear relationship was observed between the dielectric glass transition temperature (T_g) of low-conversion polymer and its composition, while the relationship in a high-conversion copolymer system, observed by Boyer and Narita et al., is sigmoid. The differences in the temperature–composition relationship between low-conversion and high-conversion copolymer systems are illustrated in terms of the distribution of molecular composition. The dielectric β absorption observed in the copolymer whose vinyl chloride molar fraction is more than 0.5 was interpreted as the local motion of vinyl chloride sequences, and the vinyl chloride sequence of 2 or 3 units is sufficient to participate in the β absorption of the copolymer.

INTRODUCTION

The object of this paper is to describe the dielectric properties of vinylidene chloride–vinyl chloride copolymers (VDC–VC copolymers) and to find the relation between dielectric properties and the copolymer composition.

Boyer[1] has reported that the glass transition temperature T_g of VDC–VC copolymer, measured by a dilatometric method, varied with composition along a sigmoid line. A similar relation has been observed by Narita and Tabata[2] in a study of the dielectric properties of the same copolymer system. This relation has been a subject of our interests.

The peculiar behavior of the VDC–VC copolymer system is probably due to the wide distribution of its molecular composition and its crystallinity. For detailed information on the glass transition temperature and other dielectric properties of this copolymer it is necessary to eliminate the complexity arising from the distribution of the molecular composition. The studies presented in this paper aimed at avoiding the source of that complexity by using copolymers obtained at low conversion.

EXPERIMENTAL

Materials

The copolymers were prepared by suspension polymerization, and attention was paid to limiting the conversion to below 5%. The details of the materials are given in Table I.

Preparation of Films

Films of copolymers were prepared by solution-casting. Copolymer solutions of 5% *o*-dichlorobenzene were dried on a flat glass plate at about 180°C. for 5 min., while most of the solvent was removed. After the films were stripped from the glass plate, they were immersed in methanol and were kept for a day or more. Then they were dried again *in vacuo* and submitted to the experiments. Some of the films obtained are slightly colored.

Dielectric Measurement

Round specimens 25 mm. in diameter were cut from the films, and thin tin leaves as electrodes were applied on both sides of the specimens.

The measurement of the complex dielectric constant $\epsilon = \epsilon' - i\epsilon''$ were run at frequencies ranging from 30 cps to 3 Mc./sec. and at temperatures ranging from −70 to 60°C. on an Ando Electric Co. Model 1B Tan δ Meter.

RESULTS AND DISCUSSION

Figure 1 shows the plots for sample 5 of ϵ'' as a function of frequency at given temperatures. The absorption observed at higher temperatures,

TABLE I
Copolymers Studied and Summary of Results

Sample no.	Monomer feed ratio (VDC/VC)	VDC molar fraction in copolymer	Activation energy E^*, kcal./mole		T_g, °C.	Crystallinity,[a] %
			α	β		
1	100/0	1.00	34		−16	25
2	95/5	0.90				22
3	85/15	0.82	35		−11	—
4	80/20	0.75				22
5	60/40	0.70	40	7	4	—
6	50/50	0.69				16
7	30/70	0.60	58	11	7	13
8	25/75	0.56				10
9	20/80	0.46	62	11	20	Amorph.
10	5/95	0.14	88	12	46	Amorph.
11	0/100	0	92	13	81	Slightly crystalline

[a] These data are taken from the study of Okuda.[12]

due to the segmental motion of backbone chains, and that observed at lower temperatures are called α and β absorption, respectively. The former is observed in all samples treated in this study; the latter, only in samples whose VC molar fractions are more than 0.3.

α Absorption and Glass Transition Temperature

The ϵ'' of each sample at fixed frequency (110 cps) are plotted as a function of temperature in Figure 2. The temperature of ϵ'' maximum of α absorption shifts to higher temperature from 10 to 90°C. as the content of vinyl chloride increases.

In Figure 3 the products of the absolute temperature T and the magnitude of the α absorption $(\epsilon_0 - \epsilon_\infty)_\alpha$ are plotted as a function of composition.

The magnitude of the α absorption as related to the dipole moment μ and the number N of the dipoles per unit volume is given by the following equation,[3]

$$\epsilon_0 - \epsilon_\infty = [3\epsilon_0/(2\epsilon_0 + \epsilon_\infty)][(\epsilon_\infty + 2)/3]^2(4\pi Ng\mu^2/3kT)$$

where g is a parameter relating to dipole–dipole interaction, k is the Boltzmann factor, T is the absolute temperature, and ϵ_0 and ϵ_∞ are the limiting values of the dielectric constant at the low and high frequency ends of the dielectric dispersion, which are decided by Cole's circular-arc law.

The value $T(\epsilon_0 - \epsilon_\infty)_\alpha$ is independent of the temperature, as is easily understood from the equation, and essentially constant values are obtained above the glass transition temperatures.[4]

In the case of the copolymer system both N and μ are dependent upon the composition and the crystallinity.

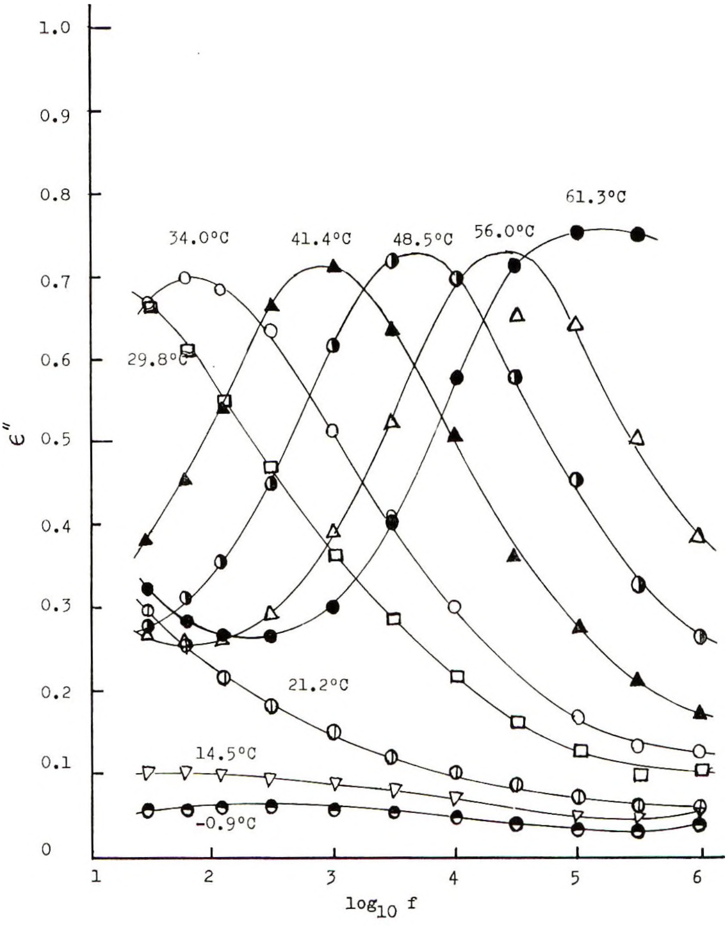
Accordingly, the observed relation is difficult to discuss quantitatively.

Since the molecular motion of α absorption is related to the motion in the amorphous region, the magnitude of α absorption is a linear function of crystallinity, and the extrapolated value of $(\epsilon_0 - \epsilon_\infty)_\alpha$ at 100% crystallinity is nearly zero.[5] Thus, assuming that the crystallinity and dipole moment depend linearly upon the composition, the linear relation between $T(\epsilon_0 - \epsilon_\infty)_\alpha$ and composition can be imagined.

The discrepancy between the observed relation and the linear relation may be explained as follows.

As shown in Table I, the copolymers whose VDC molar fraction is from 0.14 to 0.46 are noncrystalline. The discrepancy in the vicinity of the VC end of Figure 3 may be due to the crystallinity of the poly(vinyl chloride) sequence.

The steep decrease in $T(\epsilon_0 - \epsilon_\infty)_\alpha$ observed in the region of intermediate composition is due to the appearance of crystallinity of VDC sequences. When the VDC molar fraction exceeds 0.75, the crystallinity no longer increases and keeps an almost constant value that is independent of composition, as shown in Table I. Accordingly, the observed values of $T(\epsilon_0 - \epsilon_\infty)_\alpha$ deviate from the imagined relation toward higher values.



(a)

Furthermore, the variation of g with composition may affect the shape of the line in a similar way.

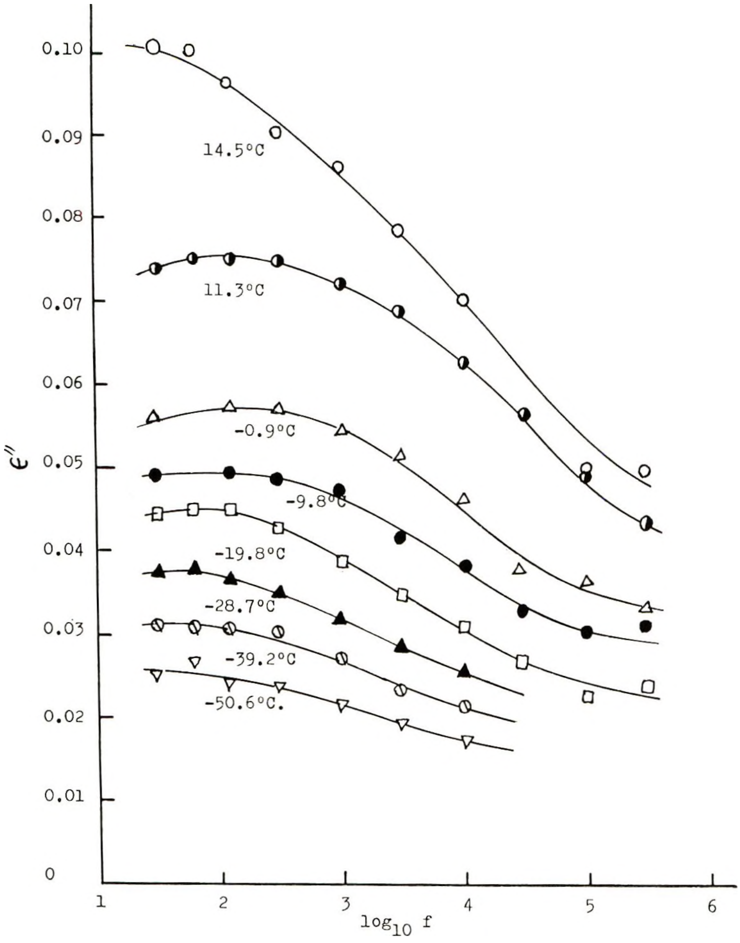
On the other hand, the glass transition temperature T_g changes almost linearly with copolymer composition, as shown by the solid line in Figure 4. The T_g plotted in the figure are calculated by following the W-L-F formula,[6] as was done by Saitoh et al.:[7]

$$\log \tau(T)/\tau(T_g) = -17.44(T - T_g)/(51.6 + T - T_g)$$

Here $\tau(T_g)$ is the relaxation time at T_g. The relation between T_g and the composition of this system can be understood by current theories.[8,9,10]

The broken line in Figure 4 is the result obtained by Boyer.[1] The deviation of this curve from the linear relationship may be interpreted on the basis of the distribution of copolymer composition as follows.

Considering the monomer reactivity ratios ($r_1 = 3.15$, $r_2 = 0.23$) of the VDC–VC copolymerization system, it may safely be said that the copoly-



(*b*)

Fig. 1. Sample 5, ε″ versus frequency: (*a*) high-temperature region; (*b*) low-temperature region.

mer has a relatively wide distribution of composition when the polymerization is carried out up to relatively high conversion.

Infrared analysis of the structure distribution in VDC–VC copolymer, reported by Enomoto,[11] shows that in the case of low-conversion polymer the existence of such structures as VDC–VC–VC and VC–VC–VC is negligible as long as the VDC molar composition is above 0.7. On the other hand, in the case of high-conversion polymer the VC chain units are a considerable part of the polymer whose VDC molar fraction is 0.8.

In the morphological study of VDC–VC copolymer series[12] Okuda suggested that VC monomer units are included as a fault in copolymer crystallites isomorphous to poly(vinylidene chloride). However, it seems unlikely that the VC units in VDC–VC–VC or VC–VC–VC structures have enough

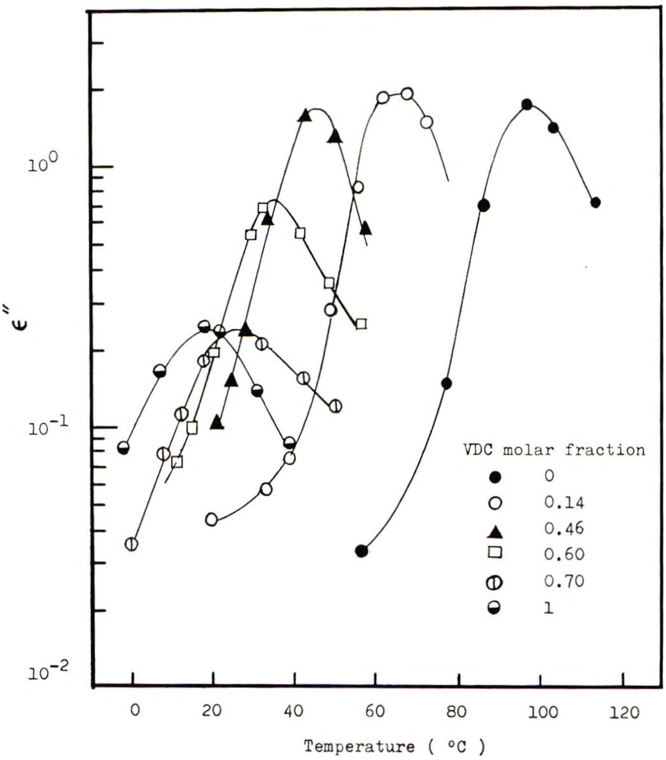


Fig. 2. ε″ versus temperature at 120 cps in high-temperature region; VDC molar fraction (●) 0, (○) 0.14, (▲) 0.46, (□) 0.60, (⦶) 0.70, (◒) 1.

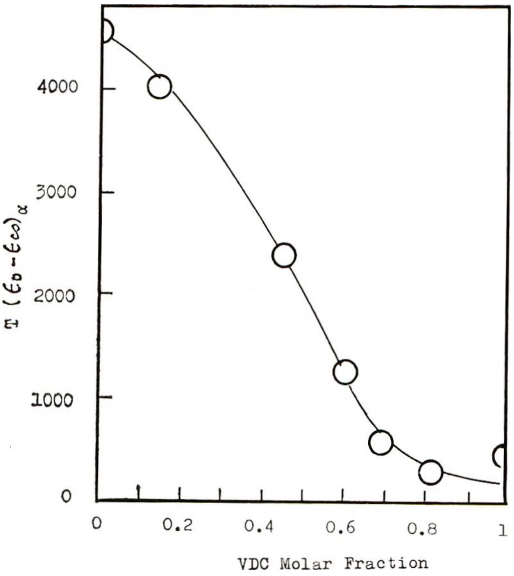


Fig. 3. $T(\epsilon_0 - \epsilon_\infty)_\alpha$ versus VDC molar fraction of copolymer.

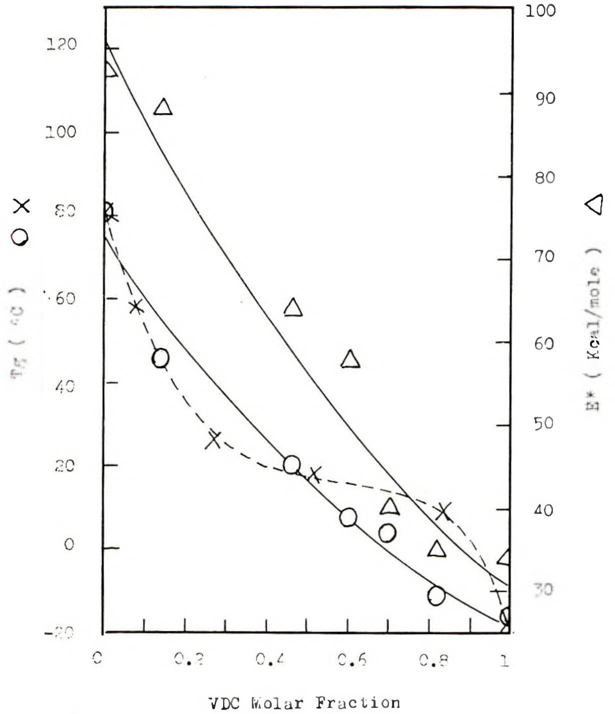


Fig. 4. T_g and E^* versus VDC molar fraction of copolymer: (△) E^*; (○) T_g; (×) T_g reported by Boyer.[1]

room in crystallites isomorphous to poly(vinylidene chloride). Therefore the VC units may be concentrated in amorphous phases.

As far as the glass transition phenomena are concerned, it seems reasonable that only the molecular movement in the amorphous phase should be considered.

The rise in T_g, obtained by Boyer[1] and Narita,[2] with the increase in VC molar content at both ends of the composition range in Figure 4, a rise steeper than is expected from the overall composition of the copolymer, and the roughly linear relation obtained in this study are well understood by considering the molecular composition in the amorphous domain.

The apparent activation energies of the dielectric relaxation process, E^*, obtained from Arrhenius plots, are plotted in the same figure. It is seen that E^* varies with composition much as does T_g.

β Absorption

In Figure 5 the dielectric loss at various compositions are plotted against temperature. It is seen that the temperature of β absorption has little dependence on the composition of the copolymer and lies at about −20°C., while the temperature of α absorption, as mentioned already, becomes lower and covers the β absorption at the foot of the curve with increase in

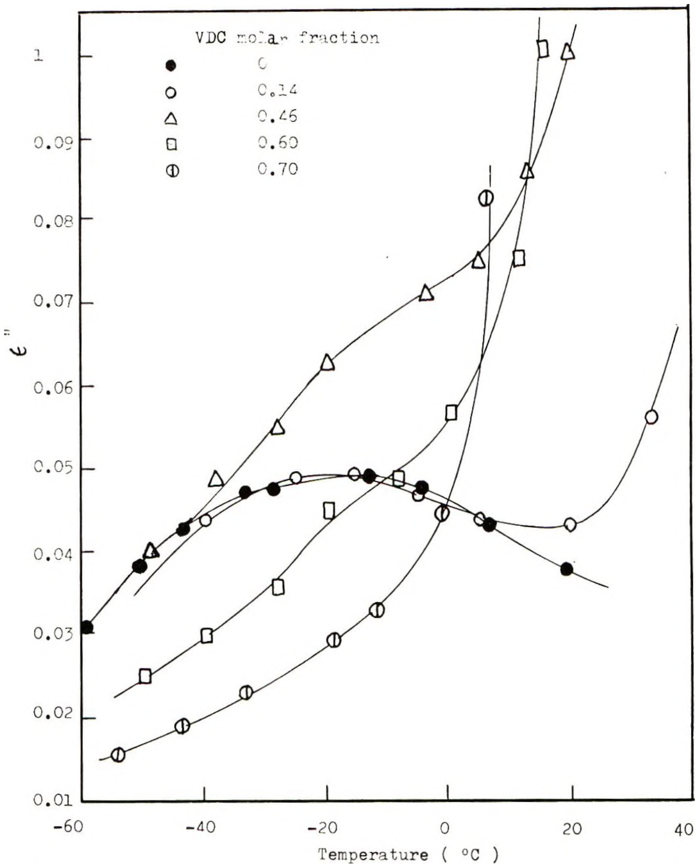


Fig. 5. ϵ'' versus temperature at 120 cps in low-temperature region; VDC molar fraction (●) 0, (○) 0.14, (△) 0.46, (□) 0.60, (⦶) 0.70.

the VDC content. Therefore, β absorption can be observed only in the copolymers whose VC molar fraction are more than 0.3.

Figure 6 shows the relation between the magnitude of β absorption $(\epsilon_0 - \epsilon_\infty)_\beta$, obtained by Cole's circular-arc law, and the composition. The values of $(\epsilon_0 - \epsilon_\infty)_\beta$ are taken at −25°C. to avoid the effect of α absorption. The magnitude of β absorption becomes smaller with the increase of VDC content, as is shown in the figure.

In the case of poly(vinyl chloride) the β absorption is considered due to the local movement of small chain sequences of molecules, probably consisting of two or three monomer units.

As mentioned above, the chain sequence of two or more VC units exists only in the copolymer whose VC fraction is more than 0.3. It coincides with the VC molar fraction at which the β absorption disappears.

From the facts described above it is considered that the β absorption of this copolymer series is due to the motion of VC chain sequences and that its intensity decreases with the decrease in the number of VC chain sequences.

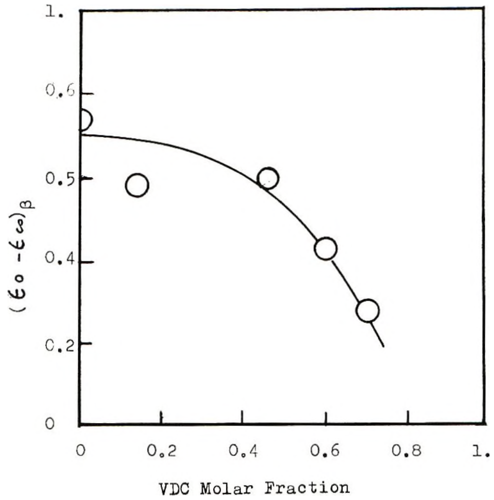


Fig. 6. $(\epsilon_0 - \epsilon_\infty)_\beta$ at −25°C. versus VDC molar fraction of copolymer.

In Table I it is seen that the apparent activation energy of β absorption shows the same tendency as the intensity of the absorption does, decreasing with the decrease in the number of VC chain sequences.

We are now carrying out studies on the β absorption of poly(vinyl chloride) and its copolymer systems; these will be discussed in a future paper.

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Résumé

Les propriétés diélectriques des copolymères de chlorure de vinylidène et chlorure de vinyle préparés à des degrés de conversion inférieurs à 5% ont été étudiées. La grandeur de l'absorption α-diélectrique n'est pas une fonction linéaire de la composition vu l'effet de la cristallinité du copolymère. Par ailleurs, une relation pratiquement linéaire a été observée entre la température de transition vitreuse diélectrique (T_g) du polymère de basse conversion et sa composition, tandis qu'une relation sigmoïde est observée pour un système obtenu à haute conversion tel que l'ont observé Boyer et Narita et coll. La différence dans la relation T_g–composition entre les systèmes copolymériques de basse et haute conversion a été illustrée sur la base d'une distribution de la composition moléculaire. L'absorption β-diélectrique observée dans le copolymère dont la fraction molaire en chlorure de vinyle est supérieure à 5 a été interprétée comme résultant de mouvements locaux des séquences de chlorure de vinyle et de longueurs de séquences de chlorure de vinyle de 2 à 3 unités, celles-ci étant suffisantes pour participer à l'absorption β du copolymère.

Zusammenfassung

Die dielektrischen Eigenschaften von Vinylidenchlorid–Vinylchloridcopolymeren, erhalten bei Umsätzen unter 5%, wurden untersucht. Die Grösse der dielektrischen α-Absorption ist wegen des Einflusses der Copolymerkristallinität keine lineare Funktion der Zusammensetzung. Andrerseits wurde zwischen der dielektrischen Glasumwandlungstemperatur (T_g) von Polymeren bei niedrigem Umsatz und ihrer Zusammensetzung eine lineare Beziehung erhalten, während von Boyer und Narita et al. für Copolymersysteme bei hohem Umsatz die beobachtete Beziehung eine sigmoide Gestalt hat. Der Unterschied in der T_g–Zusammensetzungsbeziehung zwischen Copolymeren bei hohem und niedrigem Umsatz wurde anhand der molekularen Zusammensetzungsverteilung erläutert. Die beim Copolymeren mit einem Molenbruch an VC höher als 0,5 beobachtete dielektrische β-Absorption wurde als lokale Bewegung von Vinylchloridsequenzen interpretiert, wobei eine VC-Sequenzlänge von 2 oder 3 Bausteinen genügt, um an der β-Absorption des Copolymeren teilzunehmen.

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Cationic Polymerization of α,β-Disubstituted Olefins. Part II. Cationic Polymerization of Propenyl *n*-Butyl Ether

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Synopsis

The cationic polymerization of propenyl *n*-butyl ether (PBE) in methylene chloride with boron fluoride etherate at −78°C. has been studied. The copolymerization of PBE with vinyl *n*-butyl ether (VBE) showed that both the isomers are more reactive than VBE, and their monomer reactivity ratios were found to be:

cis-PBE(M_1)/VBE(M_2): $r_1 = 4.0 \pm 1.0$, $r_2 = 0.5 \pm 0.2$
trans-PBE(M_1)/VBE(M_2): $r_1 = 2.3 \pm 1.0$, $r_2 = 0.8 \pm 0.3$

It was found in the copolymerization of the *trans* and *cis* isomers of PBE that the *cis* isomer is 1.5 to 1.6 times more reactive than the *trans* isomer. The different effects of the β-methyl group in PBE from the β substituent in propenyl benzene in the cationic polymerization have been discussed.

INTRODUCTION

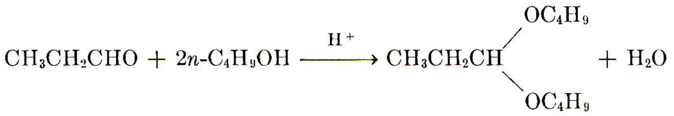
In Part I of this series of investigations of the cationic polymerization of α,β-disubstituted olefins β-methylstyrenes as aromatic olefins were investigated with reference to the steric and electronic effect of the β-methyl group.[1] It has been known that the polymerization reactivity of α,β-substituted olefins is much smaller than that of vinyl compounds.[2] The reactivity of β-methylstyrene in a homopolymerization was in fact small. However, the reactivity of β-methylstyrene itself—that is, the reactivity of the olefinic double bond of β-methylstyrene—was about the same as, or only a little smaller than, that of styrene. This means that the steric hindrance of the β-methyl substituent is important at the transition state. It was also found that the β-methyl group lowered the reactivity of the olefinic double bond electronically.[1]

In the present paper the effect of the β-methyl substituent in the cationic polymerization of vinyl ether, as compared with the styrene derivatives, will be reported. The reactivity difference between the geometric isomers of propenyl *n*-butyl ether will also be discussed.

EXPERIMENTAL

Synthesis of Propenyl *n*-Butyl Ether

Propenyl *n*-butyl ether was synthesized by dealcohol reaction of the acetal, which was synthesized from propionaldehyde and *n*-butyl alcohol:



$$CH_3CH_2CHO + 2n\text{-}C_4H_9OH \xrightarrow{H^+} CH_3CH_2CH(OC_4H_9)_2 + H_2O$$

$$CH_3CH_2CH(OC_4H_9)_2 \xrightarrow{H^+} CH_3CH{=}CH{-}OC_4H_9 + C_4H_9OH$$

Synthesis of Acetal.[3] A mixture of 4 moles of propionaldehyde and 16 moles of *n*-butyl alcohol was refluxed with 10 ml. of concentrated hydrochloric acid in 250 ml. of methylene chloride, the reaction being continued until no water was produced. The reaction mixture being cooled, 10-g. of sodium acetate was added, and the acetal was distilled: b.p. 202–203°C., yield 95%.

Synthesis of Propenyl Ether.[4] The acetal was distilled slowly with *p*-toluenesulfonic acid (about 0.5%), and the fraction of boiling point below 125°C. was collected. The distillate was a mixture of propenyl ether and butyl alcohol. The butyl alcohol was removed by shaking with saturated aqueous sodium bicarbonate. The organic layer was dried with potassium hydroxide and distilled over sodium: b.p. 119–125°C., yield 75%.

Separation of Isomers. The trans propenyl ether was separated from the *cis* isomer by distillation (45 plates) with a reflux ratio of 30:1. The physical constants of propenyl *n*-butyl ether are listed in Table I. By the synthetic route described above an isomeric mixture of the propenyl ether containing 75% of the *cis* isomer was obtained.

TABLE I
Physical Properties of Geometric Isomers of Propenyl *n*-Butyl Ether

	B.p., °C.		n_D	
	cis	*trans*	*cis*	*trans*
Observed	119	126	1.4122	1.4132
			(21.5°C.)	
Literature[a]	50	56.5	1.4131	1.4143
	(60 mm. Hg)		(20°C.)	

[a] See Reference 4 of this paper.

Purity of Isomer. The *trans* and *cis* isomers, which were separated by the distillation, were identified by infrared spectroscopy and gas chromatography. The conditions of the gas chromatographic measurement were as follows: [C-22 (30–60 mesh), 25% polyethylene glycol, 1 m., 6 mm.] + [Celite 545 (60–80 mesh), 30% dinonylphthalate, 1 m., 6 mm.], 90°C.,

H_2 at 90 ml./min. It was found that the *cis* isomer thus obtained had a purity of more than 98% and the *trans* isomer a purity of more than 95%.

n-Butyl Vinyl Ether

Commercial *n*-butyl vinyl ether was washed with saturated aqueous sodium bicarbonate, dried with potassium hydroxide, and distilled twice over sodium.

Catalyst and Solvent

Commercial $BF_3 \cdot O(C_2H_5)_2$ was distilled into a small glass ampule. Methylene chloride was washed with sodium carbonate aqueous solution and water, dried with calcium chloride, and distilled twice over phosphorus pentoxide just before use.

Polymerization Technique

Solvent and monomer were put in a 100 ml. flask through a self-sealing rubber cap, and the mixture was brought to the polymerization temperature in a bath of solid carbon dioxide and methanol under a slight pressure of dry nitrogen. The polymerizations were started by adding the catalyst through the rubber cap.

Determination of Polymerization Conversion

The conversion was determined gravimetrically or by measuring the residual monomer. The polymerizations were stopped by the addition of a small amount of methanol. The resultant solution was analyzed by gas chromatography with monochlorobenzene as internal standard under the above-mentioned conditions. The conversion was calculated from the amount of residual monomer. Under these polymerization conditions the amount of methanol-soluble oligomers was negligible within the experimental error.

Degree of Polymerization

The degree of polymerization was expressed by the intrinsic viscosity determined in benzene at 30°C.

Determination of Copolymer Composition

The copolymer composition was calculated from the composition of residual monomer analyzed by gas chromatography. The monomer reactivity ratios were calculated by means of the Walling-Mayo equation or the Fineman-Ross-Sakurada equation.

RESULTS

Copolymerization of *n*-Butyl Vinyl Ether and Propenyl *n*-Butyl Ether

For an estimate of its reactivity propenyl *n*-butyl ether was copolymerized with *n*-butyl vinyl ether, and the monomer reactivity ratios were determined. The choice of comonomer was made so as to have the propa-

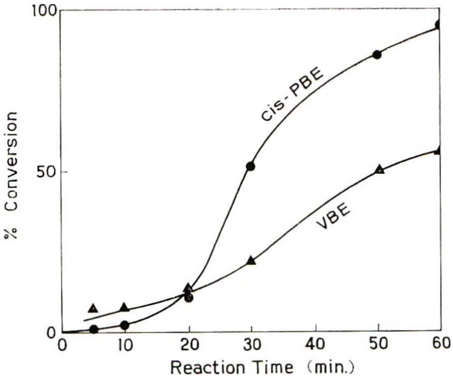


Fig. 1. Time–conversion curves for copolymerization of *cis*-propenyl *n*-butyl ether and vinyl *n*-butyl ether: monomer mole ratio *cis*-PBE/*n*-BVE, 0.47:0.53; solvent CH_2Cl_2, 90 vol.-%; catalyst BF_3OEt_2, 4 mmole/liter; temp. −78°C.

gating species of electronically the same structure, as was done for the β-methylstyrenes in Part I.[1] The steric and electronic effects of the β-substituent were thus estimated.

In Figure 1 are shown the time–conversion curves for the copolymerization of an approximately equimolar mixture of *n*-butyl vinyl ether and *cis*-propenyl *n*-butyl ether, which were obtained by following the residual amount of each monomer gas-chromatographically. As is seen in the figure, *cis*-propenyl *n*-butyl ether was polymerized faster than *n*-butyl vinyl ether. The polymerization had an induction period. During the induction period *n*-butyl vinyl ether was consumed faster; this was followed by a fast polymerization of *cis*-propenyl *n*-butyl ether. From these curves the monomer reactivity ratios were calculated according to the Fineman-Ross-Sakurada equation,

$$[M_1]/[M_2] - 1/\alpha = r_1(1/\alpha, [M_1]/[M_2]) - r_2 \qquad (1)$$

where α is given by the equation

$$\alpha = (d[M_1]/d[M_2])/([M_1]/[M_2]) \qquad (2)$$

By plotting $[M_1]/[M_2] - 1/\alpha$ against $[M_1]/\alpha[M_2]$ the reactivity ratios r_1 and r_2 are obtained from the slope and the intercept of the straight line, respectively. This is shown in Figure 2, where M_1 and M_2 represent *cis*-propenyl *n*-butyl ether and *n*-butyl vinyl ether, respectively. It was found that r_1 was 4.0 ± 1.0 and r_2 was 0.5 ± 0.2.

The same procedure was applied to the copolymerization of *n*-butyl vinyl ether and *trans*-propenyl *n*-butyl ether. Figure 3 shows the time–conversion curves, and Figure 2 is a plot of the data from Figure 3, made by using equation (1). It was found that r_1 was 2.3 ± 1.0 and r_2 was 0.8 ± 0.3, where M_1 is *trans*-propenyl *n*-butyl ether and M_2 is *n*-butyl vinyl ether.

In the two sets of copolymerization described above the reproducibility of the overall rate was not satisfactory, but it was good enough for a dis-

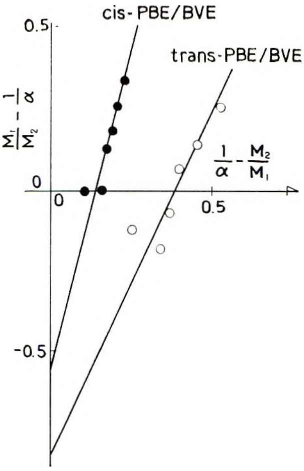


Fig. 2. Fineman-Ross-Sakurada plot for copolymerization of propenyl *n*-butyl ether and vinyl *n*-butyl ether, from Figures 1 and 3; catalyst $BF_3 \cdot OEt_2$, solvent CH_2Cl_2, at −78°C.

cussion of monomer reactivity. It was found that, regardless of the nature of isomers, propenyl *n*-butyl ethers were more reactive than *n*-butyl vinyl ether and that when *n*-butyl vinyl ether was comonomer, *cis*-propenyl *n*-butyl ether was more reactive than the *trans* isomer.

Estimation of the Reactivities of *cis* and *trans* Isomers

Little investigation has been made into the cationic polymerization of the geometric isomers of α,β-substituted olefins.[5,6] In the present research the difference in reactivity between the *cis*- and *trans*-propenyl *n*-butyl ethers was investigated as follows.

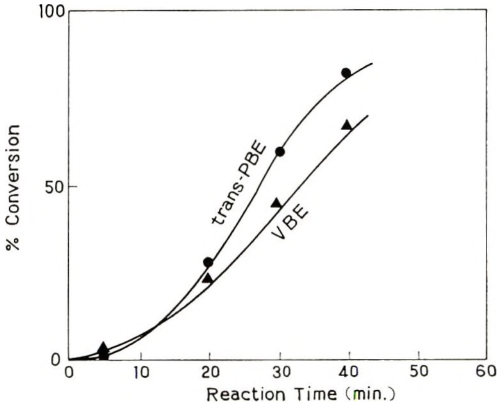


Fig. 3. Time–conversion curves for copolymerization of *trans*-propenyl *n*-butyl ether and vinyl *n*-butyl ether: monomer mole ratio *trans*-PBE/*n*-BVE, 0.47:0.53; solvent CH_2Cl_2, 90 vol.-%; catalyst $BF_3 \cdot OEt_2$, 4 mmole/liter; temp. −78°C.

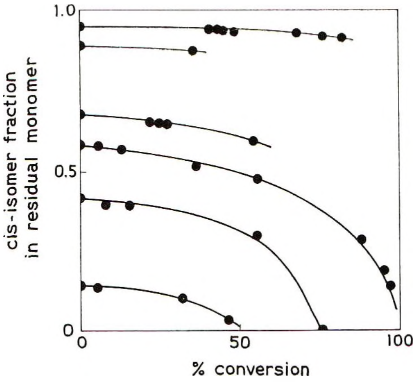


Fig. 4. Relation between conversion and *cis* isomer fraction in a residual monomer in the polymerization of *cis*- and *trans*-propenyl *n*-butyl ether mixture: monomer, 10 vol.-%; solvent CH_2Cl_2, 90 vol.-%; catalyst $BF_3 \cdot OEt_2$; temp. −78°C.

Propenyl *n*-butyl ether of varying molar ratios of isomers was polymerized in methylene chloride with $BF_3 \cdot O(C_2H_5)_2$ at −78°C., and the change in the molar ratio of residual isomers with time was followed by gas chromatography. Figure 4 shows the change in the molar ratio of the *cis* isomer with conversion. It was found that the *cis* isomer was consumed faster than the *trans* isomer.

The *cis–trans* mixture was polymerized in methylene chloride with $BF_3 \cdot O(C_2H_5)_2$ at −78°C., and the conversion–time curves for the *cis* and the *trans* isomers are shown in Figure 5. Figure 6 is the first-order plot of the experimental data given in Figure 5. It was confirmed that the steady state was attained except during the induction period. Hence *cis–trans* isomerization during polymerization did not seem to take place. In fact, the isomerization was found not to occur in the polymerization of pure *trans* isomer or pure *cis* isomer in analysis of the residual monomer in the polymerization systems.

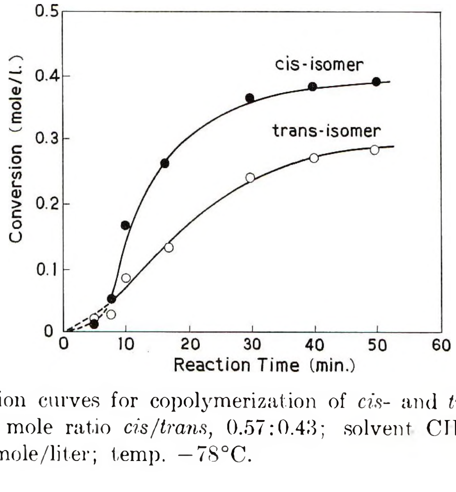


Fig. 5. Time–conversion curves for copolymerization of *cis*- and *trans*-propenyl *n*-butyl ether: monomer mole ratio *cis*/*trans*, 0.57:0.43; solvent CH_2Cl_2, 90 vol.-%; catalyst $BF_3 \cdot OEt_2$, 4 mmole/liter; temp. −78°C.

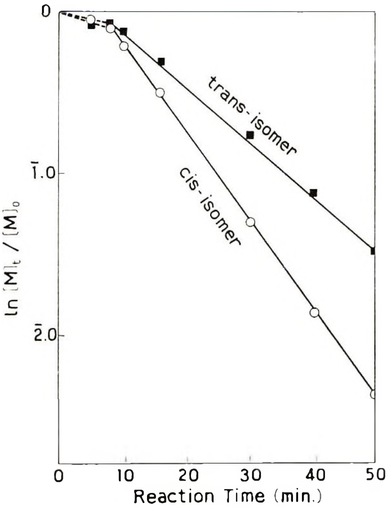


Fig. 6. First-order plot of copolymerization of *cis*- and *trans*-propenyl ether: monomer mole ratio, *cis/trans*, 0.57:0.43; catalyst $BF_3 \cdot OEt_2$; solvent CH_2Cl.

The straight line of the first-order plot in Figure 6 means that eq. (3) holds for both isomers:

$$\ln [M]_t/[M]_0 = -k_p[P^*]t \tag{3}$$

If the growing end consisting of a *trans* isomer is the same as that of a *cis* isomer in the polymerization of a mixture of both isomers, then [P*] is simply expressed by the equation

$$[P^*] = [P^*_{cis}] + [P^*_{trans}] \tag{4}$$

Thus the ratio of the slopes of the straight lines in Figure 6 gives the k_p ratio:

$$\text{Ratio of slope} = k_{p,cis}[P^*]/k_{p,trans}[P^*] = k_{p,cis}/k_{p,trans} = 1.63$$

The *cis* isomer is about 1.6 times as reactive as the *trans* isomer.

The polymerization of the mixture of both isomers is regarded as a copolymerization. A mixture of varying *cis/trans* ratios was polymerized and after a conversion of a few hundredths the *cis/trans* ratio in the residual monomer was analyzed. The "copolymer composition" thus determined was plotted against the *cis/trans* ratio of the feed, Figure 7.

Figure 7 shows that the *cis* isomer is more reactive than the *trans* isomer. By the intersection method,

M_1, *cis* isomer: $r_1 = 1.35 \pm 0.1$

M_2, *trans* isomer: $r_2 = 0.74 \pm 0.1$

The assumption that the end growing from the *cis* isomer is same as that from the *trans* isomer requires the relation $r_1 = 1/r_2$ in the copolymerization of both isomers, which was satisfied experimentally ($r_1r_2 \approx 1.0$). This

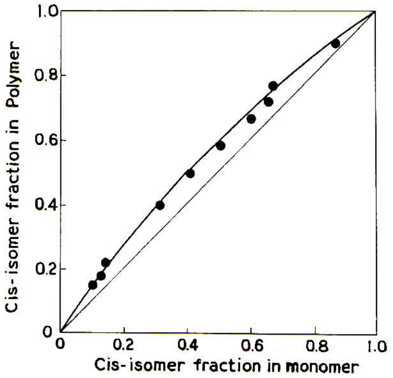


Fig. 7. Composition curve for copolymerization of *cis*- and *trans*-propenyl *n*-butyl ether: monomer, 10 vol.-%; solvent CH_2Cl_2, 90 vol.-%; catalyst $BF_3 \cdot OEt_2$, 4 mmole/liter; temp. −78°C.

means that the assumption is reasonable. Hence, $k_{11}/k_{12} = k_{11}/k_{22}$, leading to a modified copolymer composition equation:

$$d[M_1]/d[M_2] = k_{11}[M_1]/k_{22}[M_2]$$

When $d[M_1]/d[M_2]$ was plotted against $[M_1]/[M_2]$, a straight line was drawn experimentally, as shown in Figure 8. The slope gives $k_{p,cis}/k_{p,trans} = 1.5$, which is in good agreement with the k_p ratio given in the previous section.

Intrinsic viscosity $[\eta]$ is plotted against conversion for the polymerizations of *cis*-propenyl *n*-butyl ether in methylene chloride and toluene with

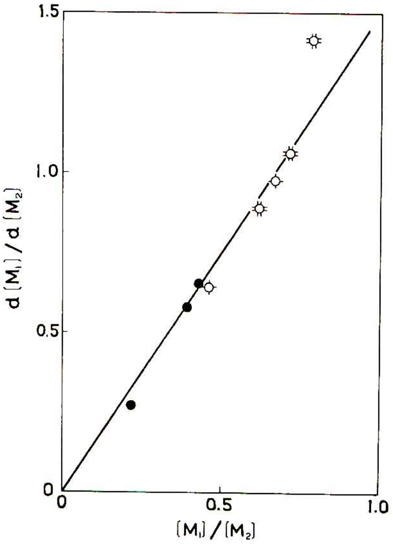


Fig. 8. Plot of copolymer composition of *cis*(M_1) and *trans*(M_2)-propenyl *n*-butyl ether as the ideal copolymerization, from Fig. 7: (●) both axes enlarged 5 times; (☼) both axes reduced 1/5 time.

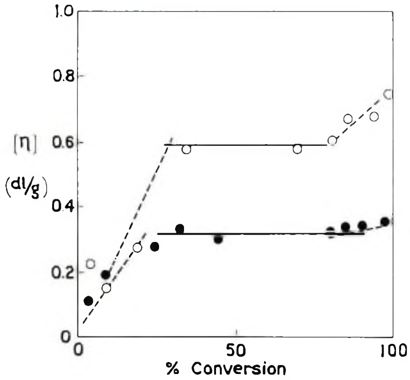


Fig. 9. Relationship between conversion and intrinsic viscosity [η] of poly-*cis*-propenyl *n*-butyl ether: monomer, 0.69 mole/liter, 10 vol.-%; solvent, 90 vol.-%, toluene (○) and methylene chloride (●); catalyst $BF_3 \cdot OEt_2$, 4 mmole/liter; temp. −78°C.

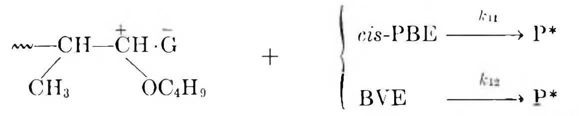
$BF_3 \cdot O(C_2H_5)_2$ at −78°C. in Figure 9. Polymers produced during the induction period had low molecular weights, but after the induction period the [η] of the polymer increased quickly with conversion. The increase in molecular weight slowed down after about 20% conversion. Polymers produced in toluene were of higher molecular weight than those in methylene chloride, a fact which agrees with the experimental results observed with alkyl vinyl ethers.

DISCUSSION

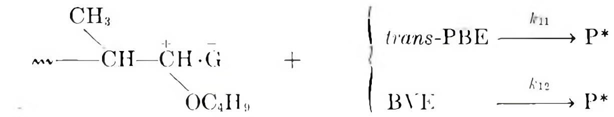
Comparison of the Reactivities Between Propenyl *n*-Butyl Ethers and *n*-Butyl Vinyl Ether

It has generally been considered that α,β-substituted ethylenes are much less reactive than corresponding vinyl compounds. In the present investigation, however, propenyl *n*-butyl ethers were found to be more reactive than *n*-butyl vinyl ether.

In the copolymerization of propenyl *n*-butyl ethers and *n*-butyl vinyl ether the relative reactivities of *cis*- and *trans*-propenyl *n*-butyl ethers and of *n*-butyl vinyl ether to the propenyl *n*-butyl ether cations are as follows, where G^- is a counter-ion:

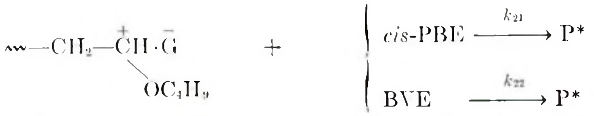


(growing end from *cis* isomer) $r_1 = k_{11}/k_{12} = 4.0 \pm 1.0$



(growing ends from *trans* isomer) $r_1 = k_{11}/k_{12} = 2.3 \pm 1.0$

The growing ends of both the *trans* and *cis* isomers of the propenyl *n*-butyl ethers are more reactive than those of the *n*-butyl vinyl ether. If a comparison is made of the relative reactivities to the *n*-butyl vinyl ether cations, one obtains:



$$\sim\mathrm{CH_2{-}\underset{\displaystyle \diagdown OC_4H_9}{\overset{+}{C}H}\cdot\overset{-}{G}} \quad + \quad \left|\begin{array}{l} cis\text{-PBE} \xrightarrow{k_{21}} \mathrm{P^*} \\ \mathrm{BVE} \xrightarrow{k_{22}} \mathrm{P^*} \end{array}\right.$$

(growing end from BVE) $1/r_2 = k_{21}/k_{22} = 2.2 \pm 0.8$

$$\sim\mathrm{CH_2{-}\underset{\displaystyle \diagdown OC_4H_9}{\overset{+}{C}H}\cdot\overset{-}{G}} \quad + \quad \left|\begin{array}{l} trans\text{-PBE} \xrightarrow{k_{21}} \mathrm{P^*} \\ \mathrm{BVE} \xrightarrow{k_{22}} \mathrm{P^*} \end{array}\right.$$

(growing end from BVE) $1/r_2 = k_{21}/k_{22} = 1.45 \pm 0.55$

The same conclusion as in the case of the growing chain ends and propenyl *n*-butyl ether can be drawn here. As was made clear in the copolymerization of β-methylstyrene and styrene,[1] the β-methyl group exerts an important steric hindrance, making the polymerization of β-methylstyrene difficult. However, this sort of steric hindrance was not observed in the cationic polymerization of propenyl *n*-butyl ether. It was expected that the steric interaction between two methyl groups is important when propenyl *n*-butyl ether adds to the propenyl *n*-butyl ether cation and that it is not important when propenyl *n*-butyl ether adds to the *n*-butyl vinyl ether cation. It was experimentally observed, however, that $r_1 > 1/r_2$ when M_1 is propenyl *n*-butyl ether and M_2 is *n*-butyl vinyl ether. This implies that in the cationic copolymerization of *cis*- or *trans*-propenyl *n*-butyl ether and *n*-butyl vinyl ether the reaction between propenyl *n*-butyl ether and its cation, which is thought to be sterically hindered, proceeds more easily than the reaction between propenyl *n*-butyl ether and *n*-butyl vinyl ether cation, which is thought to be sterically less hindered.

These results are not in agreement with the results found with β-methylstyrene, which was less reactive than styrene. The reason why the effect of the β-methyl group is different with the vinyl ether derivative and with the styrene derivative is not known. The experimental fact that propenyl *n*-butyl ether was more reactive than *n*-butyl vinyl ether might be explained by assuming that the β-methyl group stabilizes the cation at the transition state and lowers the activation energy of the propagation reaction. A similar phenomenon was observed with β-phenyl alkyl vinyl ethers,[7] which were more reactive than the corresponding alkyl vinyl ethers. A similar effect of β-methyl group may also be expected with β-methylstyrene, but in fact β-methylstyrene was less reactive than styrene. The steric and the electronic effects of the β-methyl group in the transition state were thus found to be different with vinyl ethers and with styrenes. The reason is not clear, but the difference in the nature of the transition state of propagation reaction between vinyl ethers and styrenes may have something to do with it.

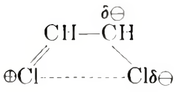
Comparison of the Reactivities Between *cis* and *trans* Isomers

The reactivity difference between *cis* and *trans* isomers in the polymerization reaction of α,β-substituted ethylenes has been investigated mainly with radical polymerization. With fumaric ester and maleic ester the trans isomer was more reactive than the *cis* isomer.[8] With 1,2-dichloroethylene, fumaronitrile, and malenitrile the *trans* isomer was more reactive than the *cis* isomer.[9] These experimental facts were explained in terms of the greater resonance stabilization of the propagating radical from the *trans* isomer at the transition state.

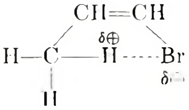
On the other hand, little investigation has been made into the cationic polymerization of geometric isomers. Overberger et al.[5] reported that in the cationic copolymerization of β-methylstyrenes and *p*-chlorostyrene the *trans* isomer was a little more reactive than the *cis* isomer. This was explained in terms of the distortion of the planary ethylenic double bond of the *cis* isomer due to the steric repulsion between ortho hydrogen of the phenyl group and the β-methyl group. The deviation of the monomer double bond from planarity causes a steric hindrance when the *cis* isomer attacks the propagating cation and, hence, makes for a less reactive *cis* isomer.

Brackmann and Plesch[6] observed that the less stable *cis*-stilbene was more reactive than the *trans* isomer. On the assumption of the same transition states for the propagation of the *cis* and *trans* isomers, the *cis* isomer, which is energetically less stable in the ground state, is more reactive. Recently Fueno et al.[10] studied the reactivities of some α,β-unsaturated ethers, including propenyl isobutyl ether, by hydrolysis, silver ion complexation, and copolymerization. They suggested, from the data on the activation parameters in the hydrolysis reaction at 25°C., that the *trans* isomer is more stable than the *cis* isomer. Thus, various sorts of explanation have been proposed for the reactivity difference between the isomers.

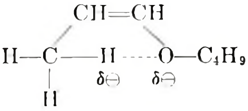
In the copolymerization of propenyl *n*-butyl ethers and *n*-butyl vinyl ether and of *cis*-propenyl *n*-butyl ethers and the *trans* isomer it was found that the *cis* isomer was 1.5 times as reactive as the *trans* isomer. Since the *cis* isomer does not isomerize into the *trans* isomer during polymerization or when heated with benzoyl peroxide, and since a mixture rich in *cis* isomer was obtained when propenyl *n*-butyl ether was synthesized, the *cis* isomer seems to be more stable than the *trans* isomer. The molecular model of the *cis* isomer showed no steric interaction between the two substituents. In fact, *cis* isomers of 1,2-dichloroethylene[11] and β-bromopropylene[12] are more stable in solution because of the polarized structures (I) and (II):



(I)



(II)



(III)

Therefore, a possible explanation of the greater reactivity of the *cis* isomer would be as follows. With regard to *cis*-propenyl *n*-butyl ether structure

(III) may stabilize the compound. Structure (III) is impossible with the *trans* isomer. The entropy of the *cis* isomer (III) in the ground state is therefore less than that of the *trans* isomer. If the entropy at the transition state is the same for both isomers, polymerization of the *cis* isomer may be facilitated by the entropy term.

At present, however, there cannot be found a very satisfactory interpretation that will explain exclusively the difference between the effects of the β-methyl group on the monomer reactivities of styrene derivatives and of vinyl ether derivatives, and the different reactivities of the geometrical isomers. The polymers from isomers of some propenyl alkyl ethers have been found to have different structures. Such lines of study might make clear the transition state of the polymerization of geometrical isomers.

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Résumé

La polymérisation cationique de l'éther propényl-*n*-butylique (PBE) a été étudiée dans le chlorure de méthylène avec l'éthérate de fluorure de bore à −78°C. La copolymérisation du PBE avec l'éther vinyle-*n*-butylique (VBE) montrait que les isomères sont plus réactionnels que VBE et leur rapport de réactivité monomérique a été trouvé comme suit: *cis*-PBE(M_1)/VBE(M_2): $r_1 = 4.0 \pm 1.0$, $r_2 = 0.5 \pm 0.2$; *trans*-PBE(M_1)/VBE(M_2): $r_1 = 2.3 \pm 1.0$, $r_2 = 0.8 \pm 0.3$. On a trouvé au cours de la copolymérisation des isomères *trans*- et *cis*- de PBE que l'isomère *cis* est environ 1.5 à 1.6 fois plus réactionnel que l'isomère *trans*. Les effets différents du groupe méthyle-β dans le PBE au départ du substituant-β dans le propényle benzène dans la polymérisation cationique ont été soumis à discussion.

Zusammenfassung

Die kationische Polymerisation von Propenyl-*n*-butyläther (PBE) mit Borfluoridätherat wurde in Methylenchlorid bei −78°C untersucht. Copolymerisation von PBE mit Vinyl-*n*-butyläther (VBE) zeigte, dass beide Isomere reaktionsfähiger als VBE sind;

ihre Monomer-Reaktivitätsverhältnisse wurden bestimmt zu: *cis*-PBE (M_1)/VBE (M_2) $r_1 = 4{,}0 \pm 1{,}0$, $r_2 = 0{,}5 \pm 0{,}2$; *trans*-PBE (M_1)/VBE (M_2) $r_1 = 2{,}3 \pm 1$, $r_2 = 0{,}8 \pm 0{,}3$. Bei der Copolymerisation der *trans*- und *cis*- Isomeren von PBE erwies sich das *cis*-Isomere als 1,5 bis 1,6 mal reaktiver als das *trans*-Isomere. Die verschiedenartige Wirkung der β-Methylgruppe in PBE im Vergleich zum β-Substituenten in Propenylbenzol bei der kationischen Polymerisation wurde diskutiert.

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Photopolymerization Initiated by Triphenylphosphine*

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Synopsis

The triphenylphosphine-initiated photopolymerization of acrylic monomers was studied. Only those monomers containing an α,β-unsaturated carbonyl group could be photoinitiated by triphenylphosphine, styrene being unaffected at the level of initiator employed. Kinetic studies with methyl methacrylate showed that the propagation was free radical in nature. Analysis of the resulting polymer indicated that it contained one phosphorus atom per chain. Ultraviolet spectral data suggested the formation of complexes between the triphenylphosphine and each monomer for which it is initiator. A relationship between the complex and the polymerization was shown to exist. A mechanism is proposed, involving a light-activated dipole interaction between the carbonyl oxygen and the phosphorus atom with the ultimate formation of a methacrylate type of free radical.

I. INTRODUCTION

The triphenyl derivatives of antimony, arsenic, and bismuth have been reported to be effective initiators for crosslinking elastomeric polymers.[1] They were used as a source of phenyl radicals when heated at 200°C.

It has been found in this laboratory that these compounds and triphenylphosphine are capable of initiating photopolymerization. Experiments on the polymerization of various monomers with the use of the triphenyl derivatives of phosphorus, arsenic, antimony, and bismuth as photoinitiators indicated that these compounds did not all initiate photopolymerization by the same mechanism. The bismuthine, stibine, and arsine initiated the photopolymerization of monomers that normally could be polymerized by a free-radical mechanism induced by peroxide or an azo type of catalyst. For example, triphenylbismuthine decomposed upon irradiation to give phenyl radicals and bismuth, as evidenced by the deposition of the free element on the sides of the reaction vessel. Triphenylphosphine, on the other hand, was quite selective. It initiated the photopolymerization of only acrylic types of monomer (under the experimental conditions given in this work), styrene being completely unaffected. Because of this selectivity triphenylphosphine was chosen as the subject of a more extensive study.

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II. EXPERIMENTAL

Materials

Methyl methacrylate, methyl acrylate, and styrene were washed with sodium hydroxide solution, passed through an alumina column, and distilled under reduced pressure. Immediately prior to use the monomers were redistilled under vacuum from partially polymerized monomer,[2] in order to insure the absence of any inhibitor. The triphenylphosphine (Eastman) was recrystallized to constant melting point (m.p. 79.5–80°C.) from absolute alcohol. Spectroquality-reagent benzene, ethyl acetate, and heptane (Matheson, Coleman and Bell) were used without further purification.

Procedure

The reaction mixtures were prepared by dilution and placed in Vycor No. 7900 test tubes. These samples were then deoxygenated by the freeze-melt method with nitrogen, which had been purified by being scrubbed with chromyl sulfate solution and passed through a series of drying tubes and finally through heated copper turnings. The polymerizations were carried out at the specified temperatures to within 0.1°C. Ultraviolet light was provided by a 450-w. Hanovia medium-pressure lamp set through the center of a rotating plate (16 rpm), which held the samples 7.6 cm. (center to center) from the lamp in the constant-temperature bath. After polymerization (up to 7% conversion) the samples were diluted with acetone and the polymer precipitated with heptane. The rate of disappearance of monomer was followed by gravimetric determination of the precipitated polymer dried in a vacuum oven at 60°C. to constant weight.

The molecular weights of poly(methyl methacrylate) were determined by solution-viscosity measurements in methyl ethyl ketone at 25°C. with the equation[3]

$$[\eta] = 6.8 \times 10^{-5} M^{0.72}$$

Phosphorus analyses on polymer that had been precipitated ten times with heptane were made by the spectrophotometric molybdenum-blue method.[4] A similarly treated physical mixture of polymer and triphenylphosphine was used as a blank.

The composition of the styrene–methyl methacrylate copolymers was determined by gas chromatography of the residual monomers on a Perkin-Elmer Model 154D Vapor Fractometer.

Ultraviolet spectra were obtained on a Cary 14 recording spectrophotometer with cells having a 1 cm. optical path. Infrared spectra were obtained on a Perkin-Elmer 337 grating infrared spectrophotometer.

III. RESULTS AND DISCUSSION

Triphenylphosphine-Initiated Polymerization

A typical example showing the effect of triphenylphosphine on the photopolymerization of methyl methacrylate at 20°C. is shown in Figure 1. Although there is a considerable amount of polymer formed that is due to the ultraviolet light alone, it is obvious that the phosphine does have an initiating effect. The resulting poly(methyl methacrylate) was found to contain phosphorus even after ten times of reprecipitation. A physical mixture containing triphenylphosphine and poly(methyl methacrylate), which had been initiated by benzoyl peroxide showed no phosphorus after one reprecipitation. Under thermal conditions (at 60°C. for 2 hr.) triphenylphosphine did not initiate polymerization.

The effect of temperature on the rate of the triphenylphosphine-initiated photopolymerization of methyl methacrylate is shown in Figure 2, which indicates a positive temperature coefficient. The overall energy of activation was found to be 4.5 kcal./mole; this value is in good agreement with that reported by Matheson[5] (4.9 kcal./mole) for the photopolymerization of methyl methacrylate with biacetyl as initiator. The triphenylphosphine-initiated copolymerization of methyl methacrylate and styrene yielded 1:1 copolymers. These results point to a free-radical mechanism, although triphenylphosphine is a known catalyst for the ionic polymerization of formaldehyde.[6]

The phosphine-initiated photopolymerization gave a linear rate curve

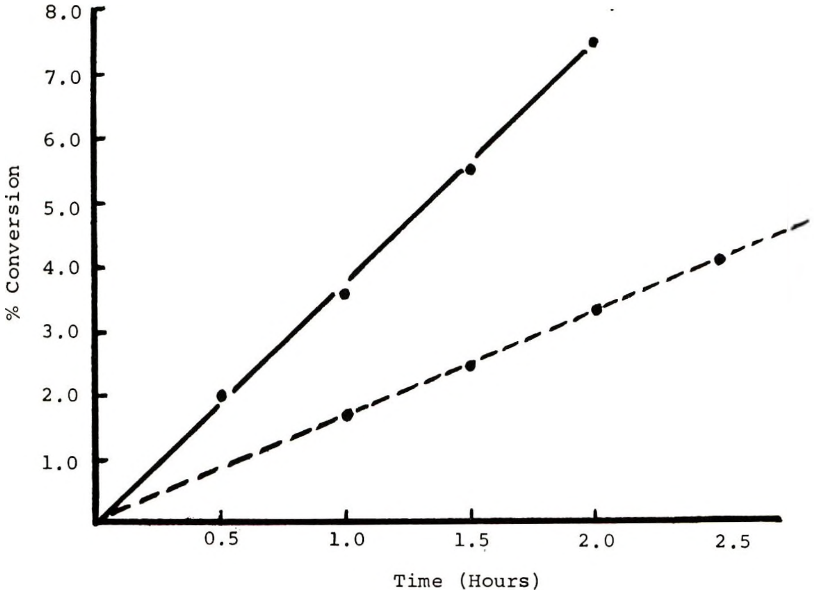


Fig. 1. Photopolymerization of methyl methacrylate at 20°C.: (——) 4×10^{-4} mole/liter of triphenylphosphine; (- - -) no initiator added.

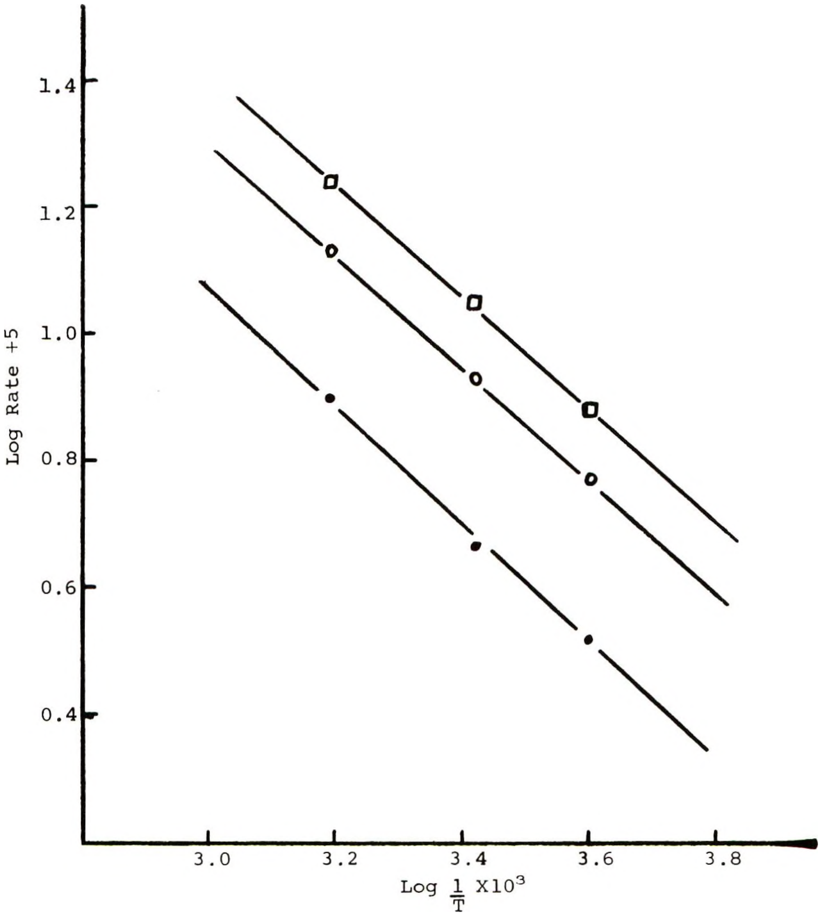


Fig. 2. Arrhenius plot for triphenylphosphine-initiated photopolymerization of methyl methacrylate: (●) no initiator; (○) 2 × 10^{-4} mole/liter of triphenylphosphine; (□) 4 × 10^{-4} mole/liter of triphenylphosphine.

up to at least 10% conversion, most data having been obtained from between 1 to 7% conversion. The effect of a changing triphenylphosphine concentration on the rate of polymerization at 20°C. is given in Figure 3. From this graph it may be seen that at a concentration of about 10^{-3} mole/liter of initiator the rate of polymerization reaches a maximum. This break in the curve is probably due to a self-quenching effect similar to that observed with anthracene.[7] Increasing the triphenylphosphine concentration above 1 × 10^{-2} mole/liter leads to an increase in the rate. This phenomenon can probably be explained on the basis of the work reported by Kaufman and Griffin.[8] At relatively high phosphine concentration the effect of photolytic decomposition of triphenylphosphine becomes important and introduces an additional reaction into the photoinitiation mechanism. In most of our experiments a phosphine concentration of about 4 × 10^{-4} mole/liter was chosen.

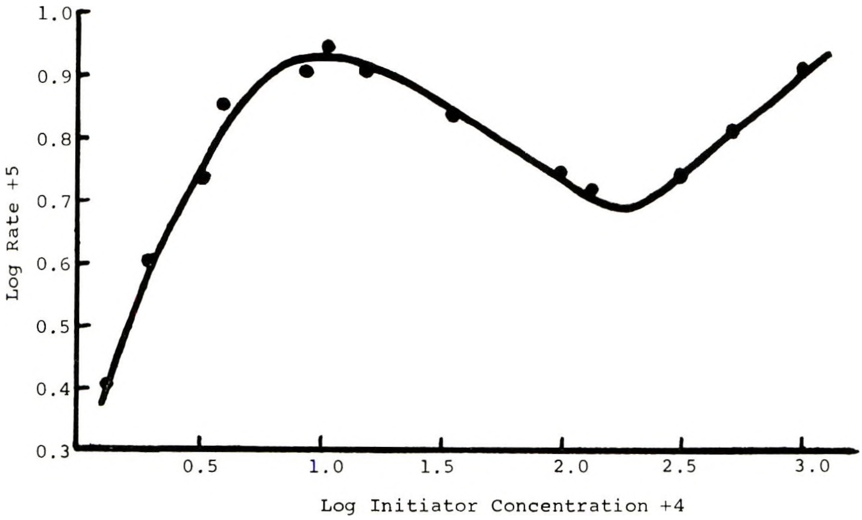


Fig. 3. Effect of triphenylphosphine concentration on rate of polymerization of methyl methacrylate.

When these experiments were repeated in the presence of air, no polymerization occurred until the phosphine concentration exceeded about 3 × 10^{-3} mole/liter. The rate then rapidly approached that obtained in a nitrogen atmosphere. (It was determined spectrophotometrically that triphenylphosphine could be quantitatively converted to triphenylphosphine oxide upon ultraviolet irradiation in the presence of dissolved oxygen. Triphenylphosphine oxide, however, showed no effect upon the photopolymerization process.) It appeared that the dissolved oxygen simply prevented initiation by conversion of the phosphine to the oxide until all the oxygen had been exhausted.

Selectivity of Triphenylphosphine

To determine why triphenylphosphine was a selective photoinitiator the effect of ultraviolet irradiation upon this compound in heptane solution was investigated. Figure 4 shows an initial ultraviolet spectrum of triphenylphosphine with an absorption peak at 260 mμ, a value in agreement with that reported by Rao et al.[9] In the presence of air triphenylphosphine underwent photo-oxidation, giving triphenylphosphine oxide very rapidly. The decrease of the 260 mμ peak was observed after only 5 sec. of irradiation. The decay was logarithmic in character. At the end of 100 sec. practically all the phosphine was converted to the oxide, as shown in Figure 4. The evidence of the formation of the oxide came from ultraviolet and infrared spectral analyses as well as from the mixed melting-point data. In the absence of air the irradiation at low concentrations used in these studies had no discernible effect on the triphenylphosphine.

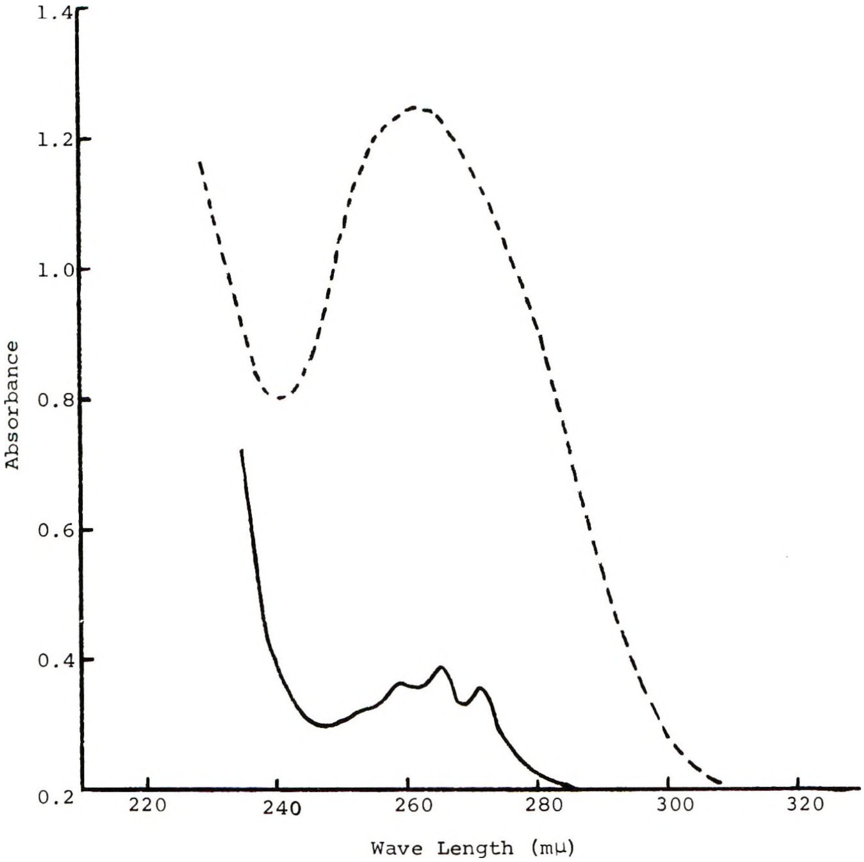


Fig. 4. Effect of irradiation on triphenylphosphine (1×10^{-4} mole/liter) in heptane: (- - -) initial; (——) after 100 sec. of exposure in the presence of air.

In Figure 5 is given a comparison of the ultraviolet spectra of triphenylphosphine in heptane, of methyl methacrylate in heptane, and of a typical reaction mixture containing triphenylphosphine and methyl methacrylate. These spectra show the existence of a new peak at 292 mμ in the reaction mixture. This new peak is believed to be due to the formation of a complex between methyl methacrylate and triphenylphosphine. Other vinyl monomers, such as styrene and vinyl acetate, do not show an absorption peak. Interestingly, triphenylphosphine has no effect upon the photopolymerization of these monomers.

Complex Formation

For further evidence of complex formation the ultraviolet spectra for all the triphenyl derivatives of the Group VB elements in heptane and in methyl methacrylate were obtained as shown in Tables I and II. It is seen that the methyl methacrylate solution of triphenylphosphine follows Beer's law, giving a constant value of extinction

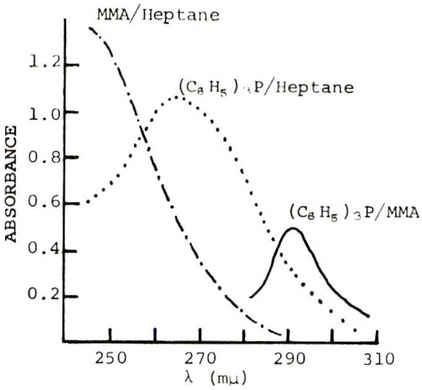


Fig. 5. Ultraviolet spectra: (- · · -) 1×10^{-4} mole/liter of methyl methacrylate in heptane; (· · ·) 1×10^{-4} moles/liter of triphenylphosphine in heptane; (——) 1×10^{-4} mole/liter of triphenylphosphine in methyl methacrylate.

coefficient (ϵ_{max} 7,300). With the exception of triphenylamine all the triphenyl derivatives in methyl methacrylate have an absorption peak at the same wavelength, 292 mμ, whereas the heptane solutions of these compounds show different absorptions. Significantly, all these compounds except triphenylamine are found to initiate the photopolymerization of methyl methacrylate (in the case of triphenylbismuthine, for example, a dual mechanism, involving both complex formation and photolytic decomposition, is believed to be possible).

Other efforts in isolating and characterizing the complex, including infrared, electron spin resonance, and nuclear magnetic resonance techniques, were unsuccessful. One possible explanation is that the complex between triphenylphosphine and methyl methacrylate is a rather weak one. To substantiate this point the following experiments were performed. At a constant triphenylphosphine concentration the ultraviolet spectra of successive dilutions of the phosphine–monomer mixture were obtained. The λ_{max} and ϵ_{max} were determined after each dilution. In Figure 6 are shown the results as the concentration of methyl methacrylate was decreased and replaced by heptane. As the monomer concentration was reduced to 0.1%, the λ_{max} approached the value (262 mμ) for triphenylphosphine in heptane.

TABLE I
Spectral Data for the Triphenyl Derivatives of Group VB Elements in Heptane

Compound	Concn., moles/liter	λ_{max}, mμ	ϵ_{max}
$(C_6H_5)_3P$	1.0×10^{-4}	262	10,880
$(C_6H_5)_3Bi$	1.0×10^{-4}	280	3,600
		250	13,000
$(C_6H_5)_3Sb$	6.4×10^{-5}	255	13,670
$(C_6H_5)_3As$	8.0×10^{-5}	248	13,750
$(C_6H_5)_3N$	3.65×10^{-5}	299	24,400

TABLE II
Spectral Data for the Triphenyl Derivatives of Group VB Elements in Methyl Methacrylate

Compound	Concn., moles/liter	λ_{max}, mμ	ϵ_{max}
$(C_6H_5)_3P$	4.0×10^{-5}	292	7,300
$(C_6H_5)_3P$	1.0×10^{-4}	292	7,300
$(C_6H_5)_3P$	2.0×10^{-4}	292	7,300
$(C_6H_5)_3Bi$	4.0×10^{-4}	292	1,910
$(C_6H_5)_3Sb$	8.0×10^{-4}	292	459
$(C_6H_5)_3As$	4.0×10^{-3}	292	71
$(C_6H_5)_3N$	4.0×10^{-5}	300	25,700

At this point the system contains essentially pure phosphine in the inert solvent. The graph actually represents a composite of the complexed and noncomplexed triphenylphosphine, which have some area of overlap, as seen in Figure 5, thereby giving an impression of a shift in the wavelength. This equilibrium behavior is quite typical of weak complexes[10] and suggests that the complex is solvent-sensitive.

Complex and Initiation

To relate the complex formation to photoinitiation another experiment was carried out, in which methyl acrylate was used as the monomer, because it polymerizes more rapidly than methyl methacrylate. The photopolymerization of methyl acrylate in the presence of triphenylphosphine

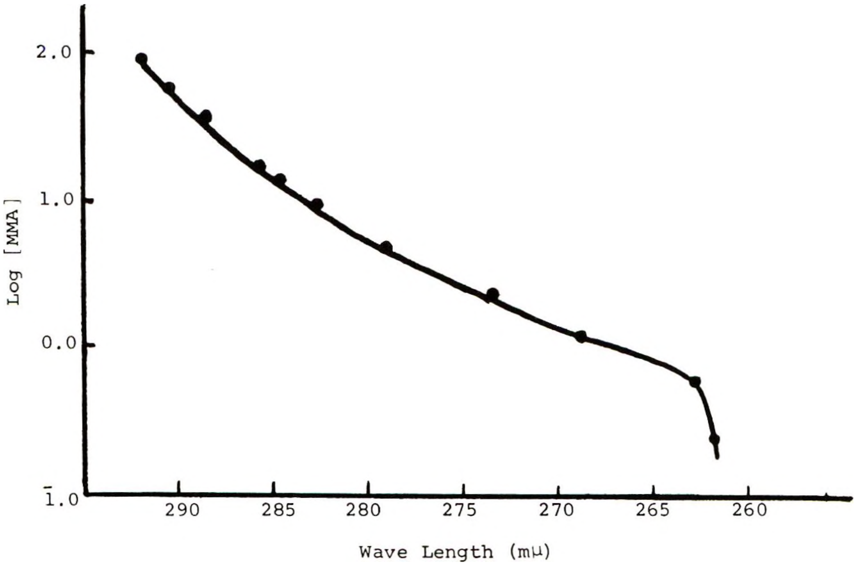


Fig. 6. Change in wavelength of complex peak of triphenylphosphine (1×10^{-4} mole/liter) in methyl methacrylate upon dilution with a solution of 1×10^{-4} mole/liter of triphenylphosphine in heptane.

was monitored spectrophotometrically. The reaction mixture, containing the acrylate and the initiator in the absence of oxygen, was irradiated at short intervals, and the ultraviolet spectrum was determined after each exposure to ultraviolet light. Figure 7 shows that the complex peak at 292 mμ decreased in intensity linearly with time of irradiation. This decrease in intensity was not caused by any reaction of a polymer radical with the phosphine, since no decay of the complex peak was observed when the reaction mixture was allowed to stand in the dark for prolonged periods while polymerization continued. At the end of the experiment a precipitation of polymer was observed when the reaction mixture was poured into heptane. These results support the concept that the absorption of the light energy by the complex is responsible for the initiation of polymerization. This view is further strengthened by the fact that in the spectra of those monomers for which triphenylphosphine is not an initiator no complex peak can be found. On the other hand, all those monomers for which triphenylphosphine is an initiator exhibit a complex peak in their spectra.

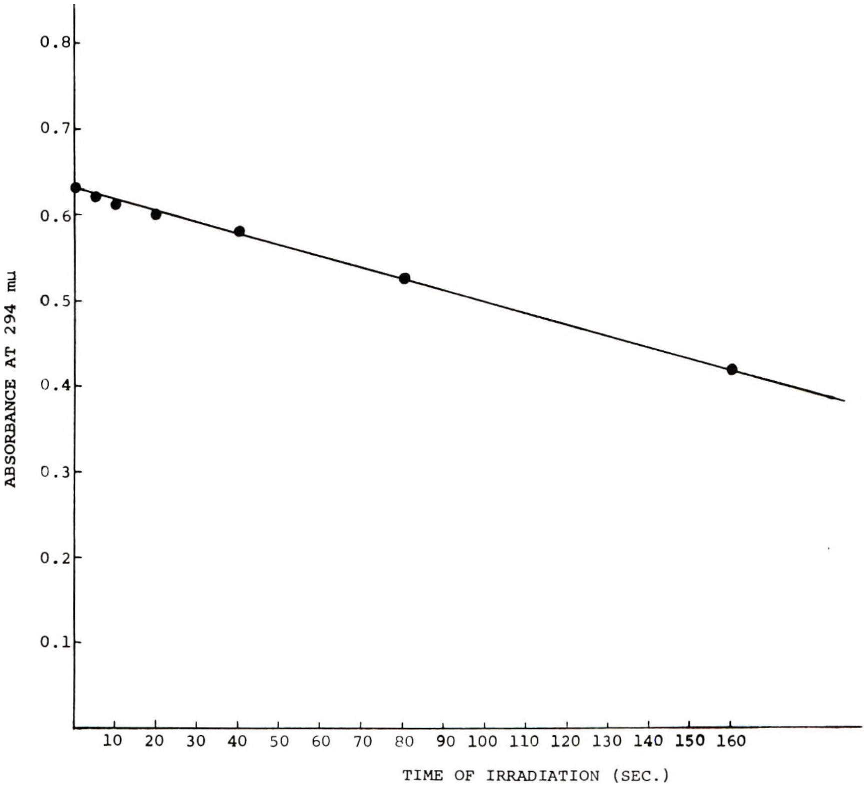
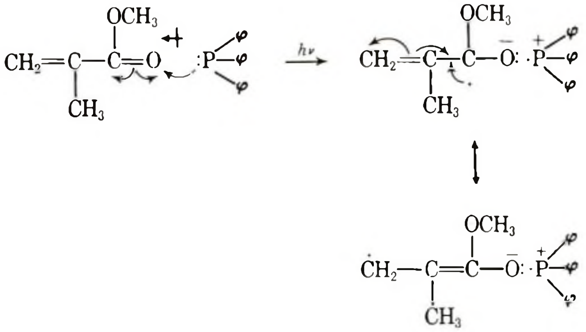


Fig. 7. Decay of complex peak of triphenylphosphine (4 × 10^{-4} mole/liter) in methyl acrylate during photopolymerization.

Nature of Complex

The first choice for the site of complex formation in methyl methacrylate would be the double bond. However, failure of other vinyl compounds, such as styrene, to be initiated by the phosphine rules out this possibility. Alternatively it is proposed that there is a dipole interaction between the carbonyl oxygen and the phosphorus. Upon irradiation phosphorus donates one of its unpaired electrons to the oxygen, resulting in an intermolecular charge-transfer complex. A rearrangement of electrons throughout the system, as shown in the following scheme, produces a methyl methacrylate radical, which can proceed to propagate the reaction.



Similar complexes can be formed between the monomer and other triphenyl derivatives except triphenylamine. This can be explained by the fact that the nitrogen atom, unlike phosphorus or other members of Group VB elements, does not have any *d* orbital and, therefore, it is difficult to participate in this type of complex formation.

The proposed mechanism is also consistent with the results obtained from a solvent study. Experiments with ethyl acetate and benzene, representing a polar and a nonpolar system, were performed. The data shown in Table III indicate that ethyl acetate molecules could interfere with the dipole formation between the monomer and triphenylphosphine. If the ethyl acetate forms a dipole with triphenylphosphine, the effective initiator concentration would be reduced, thereby giving a decreased rate of polymerization.

TABLE III
Effect of Solvent on Triphenylphosphine-Initiated Polymerization

Solvent	Rate without $(C_6H_5)_3P$, mole/liter/sec.	Rate with $(C_6H_5)_3P$, mole/liter/sec.	[M], moles/liter
C_6H_6	1.11×10^{-5}	6.44×10^{-5}	5.66
EtOAc	2.22×10^{-5}	5.81×10^{-5}	5.66

The authors wish to thank Dr. P. Weiss for his helpful discussions, Prof. N. C. Yang of the University of Chicago, and Prof. J. E. Mulvaney of the University of Arizona for their suggestions concerning the nature of the initiation reaction.

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Résumé

La photopolymérisation initiée par la triphényl phosphine de monomères acryliques a été étudiée. Uniquement les monomères contenant des groupes carbonyles α,β-insaturés peuvent être photoinitiés par la triphénylphosphine. Le styrène ne subit pas l'influence de cet initiateur. Des études cinétiques utilisant le méthacrylate de méthyle ont montré que la propagation était de nature radicalaire. L'analyse du polymère résultant indique qu'il contient un atome de phosphore par chaîne. Les résultats d'analyse spectrale ultraviolette suggèrent la formation de complexes entre la triphénylphosphine et chaque monomère pour lequel la phosphine est un initiateur. Un rapport entre le complexe et la polymérisation existe. Un mécanisme est proposé; il comporte une interaction dipolaire activée par la lumière entre l'oxygène carbonylique et l'atome de phosphore avec la formation finale de radicaux libres du type méthacrylate de méthyle.

Zusammenfassung

Die mit Triphenylphosphin initiierte Photopolymerisation von Acrylmonomeren wurde untersucht. Nur bei Monomeren mit einer α,β-ungesättigten Carbonylgruppe war eine Photoinitierung möglich; Styrol blieb bei dem verwendeten Initiatorniveau unverändert. Kinetische Untersuchungen an Methylmethacrylat zeigten, dass es sich um ein radikalisches Wachstum handelt. Die Analyse der entstandenen Polymeren ergab einen Phosphorgehalt von einem Atom pro Kette. Ultraviolettspektren sprechen für die Bildung von Komplexen zwischen Triphenylphosphin und dem Monomeren, welches es startet. Es wurde gezeigt, dass der Komplex zur Polymerisation in Beziehung steht. Ein Mechanismus mit einer light-aktivierten Dipolwechselwirkung zwischen dem Carbonylsauerstoff und dem Phosphoratom unter schliesslicher Bildung eines freien Radikals vom Methacrylattyp wird vorgeschlagen.

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Studies on the Charge-Transfer Complex and Polymerization. Part XIII. Dilution and Solvent Effects in Radical Terpolymerization*

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Synopsis

In the terpolymerization of 2-chloroethyl vinyl ether–maleic anhydride–acrylonitrile and *p*-dioxene–maleic anhydride–acrylonitrile systems the compositions of the terpolymers obtained from feed of the same mole fraction were found to be changed beyond the limit of error for the given amounts and kinds of solvent. This change was considered to be divided into two parts. The first part, discussed quantitatively, was due to a dilution effect on the equilibrium complex formation between donor and acceptor monomer, and the second, as tentatively proposed, was due to a solvent effect on the reactivity of the complex.

INTRODUCTION

Bartlett and Nozaki[2] proposed in 1946 that the molecular complex formed between styrene and maleic anhydride (MAnh) might participate in their free-radical alternating copolymerization, but Mayo and Walling and their associate's[3,4] stood against this proposal, offering instead a charge-transfer interaction between the growing radical and monomer in a transition state of the cross-propagating steps, based on the following three experimental facts: no evidence of physical association in every mixture of monomers showing high or moderate alternation,[4] no change of monomer reactivity ratios on dilution,[4-6] and no unequivocal kinetic evidence in alternating systems. In certain systems containing sulfur dioxide, however, the molecular complex formed between the sulfur dioxide and the comonomer has often been considered to play an important role in the alternating copolymerization.[7] The writers have studied the alternating copolymerization of *p*-dioxene (PD) or vinyl ethers with MAnh and found evidence of a physical association[8,9] (formation of a charge-transfer complex between them) and kinetic evidence of participation of the complex.[10] Especially in the terpolymerization of these alternating copolymerizable monomer pairs with the third monomer, which had little or no interaction

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* For Part XII of this paper see reference 1.

with either monomer of the pairs for, example, in the systems PD–MAnh–AN (where AN = acrylontrile),[9,11] PD–MAnh–2-chloroethyl acrylate,[12] CEVE–MAnh–AN (where CEVE = 2-chloroethyl vinyl ether[13]), dodecyl vinyl ether–fumaronitrile–2-chloroethyl acrylate[14]—it was quite apparent from the relation between the monomer feed and the terpolymer composition that an interaction between donor and acceptor monomer played an important role in the alternating copolymerization, and this, it was concluded, supported the complex mechanism, in which the complex between these two monomers polymerizes by itself through a radical intermediate to give an alternating copolymer. However, there has been no evidence of change of monomer reactivity ratios with amount of dilution in copolymerization or the polymerization of more than two monomers, although some studies[15–18] on the change of monomer reactivity ratios with kind of solvent in radical copolymerization have been reported.

In this study successive experiments on terpolymerization involving an alternating copolymerizable monomer pair permitted an observation of the change of monomer reactivity ratios both with amount of dilution and with kind of solvent and, moreover, a quantitative examination of the equilibrium formation of the complex between the alternating copolymerizable monomers. These experiments also supported the complex mechanism in alternating copolymerization.

The two terpolymerization systems used in this study were CEVE–MAnh–AN and PD–MAnh–AN.

EXPERIMENTAL

Materials

According to the method of Cretcher et al.[19] CEVE (b.p. 108°C.) was prepared by dehydrochlorination of 2,2′-dichloroethyl ether. PD was prepared from *p*-dioxane according to the method of Summerbell and his co-workers,[20,21] in which *p*-dioxane was converted to 2,3-dichloro-*p*-dioxane (m.p. 28–30°C., n_D^{30} 1.4960) by chlorination and dichloro-*p*-dioxane reacted with magnesium iodide in ethyl ether to yield PD (b.p. 93–95.5°C., 74% yield). MAnh was purified by recrystallization and vacuum distillation of the commercial product. AN was used soon after distillation of the commercial product. Benzene (Bz), toluene (Tol), chlorobenzene (ClB), *m*-xylene (*m*-Xyl), chloroform, and acetone as solvents were purified by the conventional method and by fractional distillation.

Polymerization Procedure

Into a 30 ml. glass ampule was put an appropriate mixture of monomers totalling 0.02 mole, a definite amount of solvent, and 4.6 mg. of azobisisobutyronitrile. After being well flushed with nitrogen the ampule was sealed and placed, without stirring, in an oil bath at 60 ± 0.2°C. for the time necessary to give conversion, which was no more than 10%. It was

TABLE I
Terpolymerization Results for CEVE–MAnh–AN System[a]

								Terpolymers					
	Monomer feed				Total vol.,	Time of polymn.,	Convsn.,	Element anal., %		Compn., mole-%			η_{sp}/C,[b]
Exp. no.	g.	ml.	Solvent, ml.		ml.	min.	%	Cl	N	CEVE	MAnh	AN	dl./g.
CE-36	1.5633	1.61	—	—	1.61	25	7.58	15.8	3.04	47.2	38.4	14.4	
37	1.5633	1.61	Bz	0.5	2.11	15	3.12	16.4	3.14	42.8	36.5	20.7	
38	1.5433	1.59	"	1.0	2.59	20	1.83	16.0	3.65	41.0	34.5	23.6	
39	1.5851	1.63	"	2.0	3.63	30	3.75	16.2	4.43	40.6	31.3	28.1	
40	1.5578	1.60	"	3.0	4.63	32	7.06	15.3	5.08	37.6	30.8	31.6	0.333
41	1.5502	1.60	"	5.0	6.60	41	7.10	15.7	5.41	38.2	28.5	33.3	
42	1.5698	1.61	"	10.0	11.61	55	2.34	16.1	4.04	40.8	33.2	26.0	0.176
43	1.5461	1.61	Tol	1.0	2.59	20	5.15	16.7	4.05	42.3	31.7	26.0	0.242
44	1.5414	1.59	"	2.0	3.59	45	4.16	15.6	5.15	38.3	29.7	32.0	0.351
45	1.5626	1.61	"	5.0	6.61	50	2.69	15.8	5.55	38.3	27.6	34.1	0.198
46	1.5853	1.63	"	10.0	11.63	125	5.90	16.4	4.59	40.8	30.3	28.9	0.176
53	1.5096	1.55	$CHCl_3$	1.0	2.55	28	3.16	16.9	2.53	45.0	38.0	17.0	0.371
52	1.5886	1.63	"	2.0	3.63	38	2.01	17.6	2.66	46.6	35.5	17.9	0.243
54	1.5894	1.63	"	5.0	6.63	37	6.63	16.7	3.27	43.4	35.1	21.5	0.156
55	1.5711	1.62	"	10.0	11.62	44	3.42	17.3	2.22	46.4	38.5	15.1	

[a] Total monomers in feed, 0.02 mole. Mole percentages in feed: CEVE, 24.8; MAnh, 24.7; AN, 50.5. Temperature of polymerization, 60°C. AIBN, 4.6 mg.

[b] Measurement by Ostwald viscometer at 30°C. with *N*,*N*-dimethylformamide containing 0.1 wt.-% LiCl as solvent.

TABLE II
Terpolymerization Results for PD–MAnh–An System[a]

Exp. no.	Solvent, ml.		Time of polymn., hr.	Convsn., %	Element anal., %			AN, wt.-%	PD–MAnh part, anal.,[b] %		η_{sp}/C,[c] dl./g.
					H	C	N		C	H	
Monomer mole percentages in feed: PD, 24.77; MAnh, 24.85; AN, 50.38											
115	—	—	6	21.14	4.78	55.87	9.94	35.12	49.35	4.28	0.418
95	Bz	1.0	6	15.28	5.04	57.12	11.06	41.90	49.35	4.56	0.373
96	"	2.0	6	10.51	4.93	56.26	11.64	44.10	47.07	4.33	0.315
97	"	5.0	8	6.32	5.04	55.56	11.42	43.26	46.14	4.53	0.221
98	"	10.0	12	7.77	4.86	56.02	11.05	41.86	47.47	4.25	0.133
99	Tol	1.0	6	15.90	5.11	57.07	11.70	44.32	48.44	4.63	0.398
100	"	2.0	6	10.09	5.19	57.36	11.31	42.85	49.45	4.81	0.314
101	"	5.0	8	7.42	4.99	56.41	11.76	44.55	47.18	4.42	0.186
102	"	10.0	12	5.52	5.32	56.60	10.57	40.03	49.06	5.12	
103	ClB^{*3}	1.0	6	8.55	4.89	56.41	10.57	40.03	48.74	4.35	0.355
104	"	2.0	6	5.37	5.00	55.82	9.94	37.66	48.52	4.57	0.298
105	"	5.0	8	7.15	4.93	55.97	10.88	41.22	47.60	4.39	
106	"	10.0	12	5.48	4.58	54.97	9.87	37.39	47.24	3.91	

107	*m*-Xyl	1.0	6	19.38	5.19	57.43	11.55	43.76	49.29	4.80	0.399
108	"	2.0	6	9.56	4.92	57.33	11.79	44.67	48.80	4.28	0.313
109	"	5.0	8	7.13	5.33	57.62	10.96	41.52	50.32	5.06	
112	Acet.	2.0	6	4.44	5.00	58.31	10.73	40.65	51.74	4.52	
113	"	5.0	8	2.07	4.93	56.51	11.75	44.51	47.39	4.31	
114	"	10.0	12	3.87	5.06	49.07	11.24	42.58	35.11	4.58	

Monomer mole percentages in feed: PD, 22.64; MAnh, 22.46; AN, 54.90.

77	—	—	4	6.73	5.22	56.86	10.08	38.22	50.06	4.92	0.312
78	$CHCl_3$[d]	1.0	4	2.74	5.07	55.59	7.99	30.27	50.25	4.79	
79	"	2.0	4	1.99	5.06	54.81	7.39	27.99	49.85	4.80	
80	"	3.0	4	1.99	4.94	53.64	6.30	23.86	49.17	4.70	
81	"	4.0	4	1.99	4.66	52.75	6.23	23.60	48.08	4.33	
82	"	6.0	10	3.03	4.79	54.07	7.17	27.16	48.92	4.55	
83	"	10.0	10	1.49	4.77	52.33	4.99	18.90	48.71	4.55	
84	"	20.0	10	1.22	4.74	51.47	5.01	18.98	47.62	4.52	

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[a] Total monomers in feed, 0.02 mole. Temperature of polymerization, 60°C. AIBN, 4.6 mg.

[b] Calculated composition of 1:1 PD and MAnh part: C, 52.40%; H, 4.38%; O, 43.06%.

[c] See footnote, Table I.

[d] The Beilstein test results with these terpolymers were negative.

opened, and an excess of ethyl ether was added so as to precipitate a terpolymer, which was dissolved with a small amount of acetone or *N*,*N*-dimethylformamide, reprecipitated with ethyl ether, rewashed very well with ethyl ether repeatedly, and dried under reduced pressure.

The composition of the CEVE–MAnh–AN terpolymer was determined from the nitrogen content by the semimicro-Kjeldahl method and from the chlorine content by the Schöniger method;[22] that of a PD–MAnh–AN terpolymer, by elementary analysis.

RESULTS

CEVE–MAnh–AN System

The solvents used in this system were Bz, Tol, and $CHCl_3$. The results are shown in Table I and the composition diagram of this system in Figure 1. It was found from Figure 1 that the composition of the terpolymers obtained from monomer feeds of the same concentration, in mole fraction, changed very much with the amount and kind of solvent used and the mole ratios of the CEVE and the MAnh, in unit content, remained always at about unity.

PD–MAnh–AN System

The solvents used in this system were Bz, Tol, *m*-Xyl, ClB, $CHCl_3$, and acetone. The results are shown in Table II, which shows that the compositions of terpolymers obtained from monomer feeds of the same concentration changed with the amount and kind of solvent similarly to those cited above. Although the mole ratios of the PD and the MAnh unit contents in the terpolymers could not be precisely determined by examination of the content of carbon and hydrogen in the PD–MAnh part, calculated by deducing the AN unit content from the total content of carbon and hydrogen in the terpolymers, they were assumed to be equal to unity from the correction made for water absorbed and from previous results.[9,11] In the following discussion it will be seen that this assumption is considered to be substantiated.

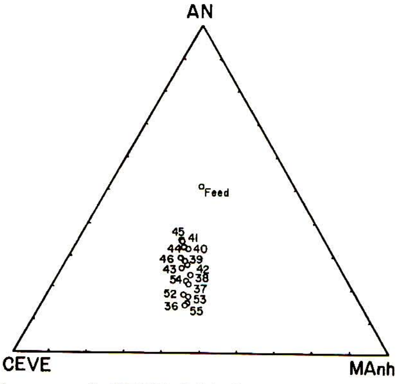

Fig. 1. Composition diagram of CEVE–MAnh–AN system; numbers refer to experiment numbers given in Table I of text.

DISCUSSION

In the terpolymerizations described above the composition of the terpolymers obtained with the same mole fraction in feed changed much beyond the limit of error according to the amounts and kinds of solvent. In other words, the apparent monomer reactivity ratios changed remarkably with dilution and with the nature of the solvent.

Since the donor and acceptor monomer unit contents in the terpolymers could be considered to be the same at any feed, these terpolymerizations were regarded as copolymerizations of AN and the complex between donor and acceptor monomer, and an estimation of their composition could be carried out only from the AN content in the terpolymers. In Figures 2 and 3 are shown the relationships between AN content and amount and kind of solvent in the CEVE–MAnh–AN and PD–MAnh–AN systems, respectively. Except for the run with $CHCl_3$ as solvent in the PD–MAnh–AN system, the tendency was for the AN content in the terpolymers to increase, reach a maximum, and then decrease, as the amount of solvent increased. Therefore, the change in AN content on dilution could be divided into two parts. The first was the part before the maximum, in which the AN content increased with amount of solvent, and the second was the part after the maximum, in which the AN content decreased as the amount of solvent increased. These behaviors were considered to conflict with each other and to be due to different causes.

The first part could be explained by a dilution effect as follows. As has already been pointed out,[9,11,14] these terpolymerizations could not be examined with the composition equation of Alfrey and Goldfinger,[23] which is applied to the usual terpolymerization, in which three monomers have no interaction each other in the monomer state, but had to be treated as a copolymerization of AN and a complex between donor and acceptor monomer. In this treatment the equilibrium formation of the complex between them could be given as

$$\text{donor} + \text{acceptor} \overset{K}{\rightleftharpoons} \text{complex} \tag{1}$$

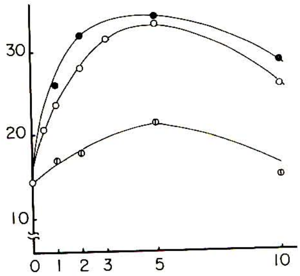

Fig. 2. Dependence of composition of terpolymers from same feed on amount and kind of solvent in CEVE–MAnh–AN system. Abscissa, volume of solvent, in milliliters; ordinate, AN content in terpolymer, in mole percentage; (○) Bz, (●) Tol, (⦶) $CHCl_3$.

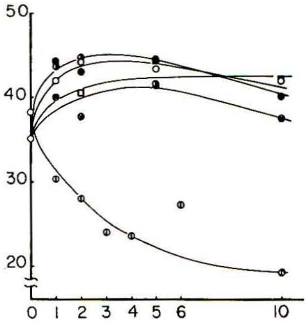

Fig. 3. Dependence of composition of terpolymers from same feed on amount and kind of solvents in PD–MAnh–AN system. Abscissa, volume of solvent, in milliliters; ordinate, AN content in terpolymer, in weight percentage; (○) Bz, (●) Tol, (◑) *m*-Xyl, (□) acetone, (⊗) ClB, (⦶) $CHCl_3$.

where K is the equilibrium constant of the complex formation. Therefore, the concentration of the complex considering K to be very small,[8] is given as

$$[\text{complex}] = K\,[\text{donor}][\text{acceptor}] \tag{2}$$

Since AN and the complex may be considered to copolymerize at random with each other, the copolymerization composition equation is given as follows, where the conventional copolymerization composition equation of Mayo and Lewis[24] and eq. (2) are used:

$$-\frac{d[\text{complex}]}{d[\text{AN}]} = \left(-\frac{d[\text{donors}]}{d[\text{AN}]} = -\frac{d[\text{acceptor}]}{d[\text{AN}]}\right) = \frac{[\text{donor}][\text{acceptor}]}{[\text{AN}]}\left(\frac{r_1K[\text{donor}][\text{acceptor}] + [\text{AN}]}{[\text{donor}][\text{acceptor}] + (r_2/K)[\text{AN}]}\right) \tag{3}$$

where r_1 and r_2 are the monomer reactivity ratios of the complex and of AN, respectively. The validity of eq. (3) was previously examined in the systems PD–MAnh–AN,[11] vinyl ether–MAnh–AN,[13] PD–MAnh–acrylate,[12] and others. Hereupon, the concentration in moles per liter was changed into that in mole fraction, in order to calculate easily the change of composition on dilution, and the whole concentration, in moles per liter, of the monomer mixture was taken as M. Then eq. (3) could be converted into

$$\frac{d[\text{complex}]}{d[\text{AN}]} = \frac{(\text{donor})(\text{acceptor})}{(\text{AN})}\left(\frac{r_1K(\text{donor})(\text{acceptor})M + (\text{AN})}{(\text{donor})(\text{acceptor}) + (r_2/K)(\text{AN})(1/M)}\right) \tag{4}$$

where (monomer$_i$) was the concentration, in mole fraction, of monomer. In Figure 4 is shown the application of eq. (4) to the benzene solution terpolymerization of the CEVE–MAnh–AN system with the use of the monomer reactivity ratios $r_1K = 1.52$ and $r_2/K = 0.385$, which were recalculated from the values in the previous paper[13] by adjusting the concentration unit. The open circles show points calculated from eq. (4), and the closed circles

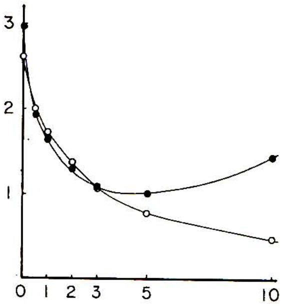

Fig. 4. Theoretical and experimental relationships between composition ratios in terpolymers and amounts of benzene. Abscissa, volume of benzene, in milliliters ordinate, composition ratios in terpolymers, complex/AN; (○) theoretical value, from eq. (4); (●) experimental value.

show the experimental points. A good agreement between calculated and experimental points is observed in the first part of the curve. This was considered to be the first observation of a dilution effect on the radical polymerization and to support strongly the proposal that a complex formed between donor and acceptor monomers polymerizes by itself and gives an alternating copolymer.

The second part of the curves, in which the AN content in the terpolymers decreases as the amount of solvent increases, cannot be unequivocally explained at present. However, the reactivity of the complex was imagined to be increased owing to solvation on the complex, since the complex content in the terpolymers increased with the amount of solvent. In addition, as a whole, a dependency of the reactivity of the complex on the kind of solvent was observed. As shown in Figures 2 and 3, the height of the maxima and the magnitude of the dependency of the reactivity change on the kinds of solvent permitted the following order of solvents to be given: *m*-xylene $\geqslant$ toluene $\geqslant$ benzene $\geqslant$ acetone $>$ chlorobenzene $\gg$ chloroform. This order disagreed with that of the dipole moments. Peculiarly, chloroform was found to have so abnormal a solvent behavior that there was found no first part in the curve of change of reactivity ratios in PD–MAnh–AN and a very small first part in that of CEVE–MAnh–AN. These abnormalities were hardly considered to be due to the solvent transfer reaction, because of the negative result given in the Beilstein test on the terpolymers of PD–MAnh–AN and the equal CEVE and MAnh unit contents in the terpolymers of CEVE–MAnh–AN, as shown in Figure 1, but it was considered that one of reasons was that, of those solvents, chloroform has no π electron and the others do. Moreover, the π-electron density of the other solvents was considered to play some role in the change of reactivity ratios, since the order of π-electron densities in that series of aromatic solvents agreed with that of the change of reactivity ratios. Therefore, it was proposed tentatively that, when a π-electron-rich solvent solvated on the complex, the complex was very stable to any free-radical attack.

Alternatively, these changes in reactivity ratios with solvent might be considered due to the heterogeneity of the systems during terpolymerization, since in these system all the terpolymers produced were precipitated. However, in PD–MAnh–AN with acetone as solvent, which had a partial solubility toward these terpolymers, the solvent did not affect the terpolymerization exceptionally, and this fact was considered to permit exclusion of the concept of heterogeneity in this case.

One of the reasons why the dilution effect on alternating copolymerization could be observed for the first time was considered to lie in the terpolymerization technique, in which the equilibrium formation of the complex must be developed in relation to the third monomer. In the copolymerization of donor and acceptor monomers the equilibrium formation of their complex might be considered difficult to estimate, since such a copolymerization might be regarded as a homopolymerization of the complex.

At this time only two alternating copolymerizable monomer pairs, vinyl ether–MAnh and PD–MAnh, are concluded to polymerize through a complex mechanism to give the alternating copolymers, but the problem still remains whether every alternating copolymerizable monomer pair polymerizes through the complex mechanism.

Further studies of the other pairs are now going on and will be reported subsequently.

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Résumé

On a prouvé que la composition de terpolymères obtenus au départ d'une même fraction molaire des monomères changeait appréciablement plus au delà des limites d'erruer avec la quantité et la nature des solvants: cette constatation a été faite dans le cas des systèmes éther 2-chloroéthyle vinylique–anhydride maléique–acrylonitrile et *p*-dioxène–anhydride maléique–acrylonitrile. Cette variation de composition peut être divisée en deux parties. La première partie est discutée quantitativement comme provenant d'un effet de dilution sur l'équilibre de formation des complexes entre monomères donneur et accepteur et la seconde partie, de l'effet du solvant sur la réactivité du complexe lui-même.

Zusammenfassung

Bei der Terpolymerisation in System 2-Chloräthylvinyläther–Maleinsäureanhydrid–Acrylnitril und *p*-Dioxen–Maleinsäureanhydrid–Acrylnitril hängt die Zusammensetzung der aus Ansätzen mit gleichem Molverhältnis erhaltenen Terpolymeren weit ausserhalb der Versuchsfehler von Menge und Art der Lösungsmittel ab. Diese Abhängigkeit wurde in zwei Anteile zerlegt. Der erste Anteil wurde quantitativ als Verdünnungseffekt beim Komplexbildungsgleichgewicht zwischen Donor- und Akzeptormonomerem diskutiert, der zweite als Lösungsmitteleffekt für die Reaktivität des Komplexes.

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Cyclopolycondensations.* V. New High-Temperature Aromatic Polyquinazolinediones by Solution Polymerization in Poly(phosphoric Acid)

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Synopsis

Fully aromatic polyquinazolinediones of high molecular weight were prepared by the cyclopolycondensation reaction of 4,4′-diamino-3,3′-biphenyldicarboxylic acid with aromatic diisocyanates. The poly(phosphoric acid) solution polymerization techniques yielded tractable poly(urea acid), which was converted to polyquinazolinediones by thermal cyclodehydration at 300–400°C. under reduced pressure. The polyquinazolinediones thus obtained have excellent thermal stability both in nitrogen and in air. The poly(urea acid) is soluble in dimethyl sulfoxide, and films can be cast from the polymer solution of poly(urea acid) (η_{inh} = 0.8 to 1.8). The films are made tough by being heated in nitrogen or under reduced pressure at 300–400°C. The polymerization mechanism of the cyclopolycondensation reaction was studied, and it was established that the polymerization proceeded through the formation of tractable poly(urea acid), Structure (I), of high molecular weight, followed by cyclodehydration, yielding poly(1,2-dihydro-2-imino-4H-3,1-benzoxazin-4-one), Structure (II). On subsequently being heated this undergoes intramolecular rearrangement along the polymer chain, giving the thermodynamically stable polyquinazolinedione, Structure (III).

INTRODUCTION

In earlier publications[1–5] it was demonstrated that polymers containing quinazolinedione or benzoxazinone nuclei of high molecular weight could be prepared by the reaction of suitable aromatic diaminodicarboxylic acid with aromatic diisocyanate or dicarboxylic acid derivatives by using both melt and low-temperature solution polymerization techniques in addition to the poly(phosphoric acid) solution polymerization method. These polymers showed remarkable thermal stability and were soluble in a variety of organic and inorganic solvents.

During the course of our studies of cyclopolycondensation reactions[1–5] several new polyquinazolinediones were prepared by the reaction of 4,4′-diamino-3,3′-biphenyldicarboxylic acid (BDC) with such aromatic diisocyanates as *p*-phenylene diisocyanate, methylenedi-*p*-phenylene diisocyanate, 1,5-naphthylene diisocyanate, 3,3′-dimethyl-4,4′-biphenylylene diisocyanate, 3,3′-dimethoxy-4,4′-biphenylylene diisocyanate, and tolylene

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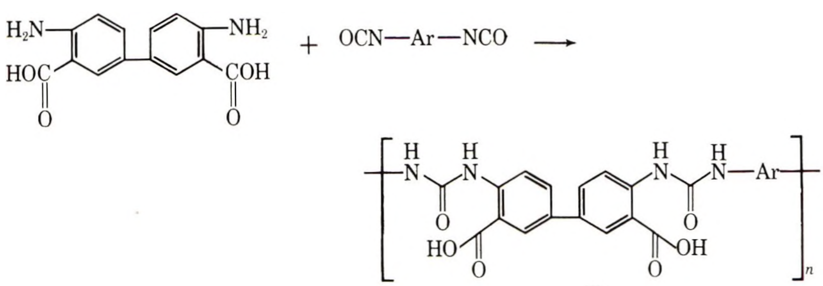
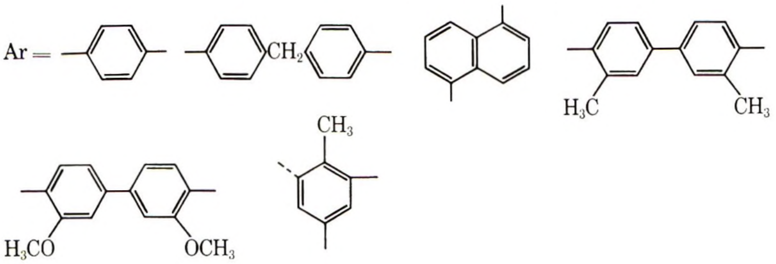
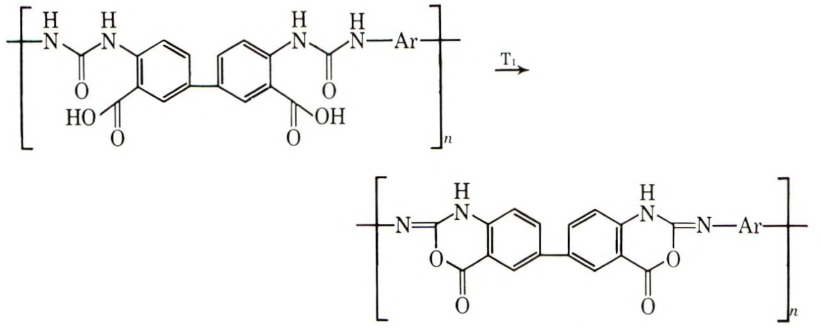
* For Part IV of this series see reference 1.



(1)

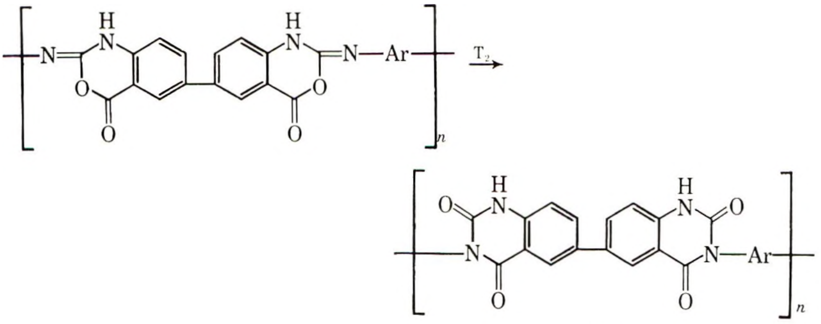
(I)





(2)

(II)



(3)

(III)

diisocyanate by means of the poly(phosphoric acid) solution polymerization technique.

The present paper deals with the preparation and the study of the properties of new aromatic polyquinazolinediones. A detailed account of the experimental work concerning the optimum polymerization conditions for poly(urea acid) formation and the cyclodehydration of polyquinazolinedione of high molecular weight is given; see the above equations.

EXPERIMENTAL

All the melting points were taken on a Büchi melting point apparatus and were uncorrected. The microanalyses were carried out by the Microanalytical Section of this laboratory. The infrared spectra were recorded with Hitachi Model EPI-S recording spectrophotometers in a potassium bromide disk, Nujol, or film.

The molecular weight was determined with a Mechrolab Model 310A vapor-pressure osmometer in benzene and methyl ethyl ketone. Thermal gravimetric analyses in nitrogen and air were recorded with an Oyorika Type ORK-IBB with 100 mg. of sample at $\Delta T = 3$°C./min. The x-ray diffraction diagrams were taken by the powder method using nickel filtered CuK_α radiation by a Norelco x-ray diffraction analyzer.

Materials

4,4′-Diamino-3,3′-biphenyl Dicarboxyl Acid.[6,7] This was prepared in 92% yield from *o*-nitrobenzoic acid by reduction with zinc and sodium hydroxide, followed by the benzidine rearrangement with hydrochloric acid. The product was recrystallized from aqueous hydrochloric acid and neutralized with aqueous sodium acetate to give light yellow crystals, m.p. 300°C. (decomp.).

ANAL. Found: C, 61.53%; H, 4.53%; N, 10.12%. Calcd. for $C_{14}H_{12}O_4N_2$: C, 61.76%; H, 4.44%; N, 10.29%.

Diisocyanate

Commercially available isocyanates (C.P. grade) were recrystallized from *n*-hexane or benzene, and each structure was confirmed by the infrared spectra, elemental analyses, melting points, and boiling points.

***p*-Phenylene Diisocyanate.** *p*-Phenylene diisocyanate (Kishida Kagaku Co.) was recrystallized three times from *n*-hexane in the presence of decolorizing charcoal; m.p. 95.5°C.

Methylene Di-*p*-phenylene Diisocyanate. The commercially available compound (Hodogaya Kagaku Co.) was recrystallized three times from *n*-hexane; m.p. 42°C., b.p. 190°C. at 5 mm. Hg.

1,5-Naphthylene Diisocyanate. The commercially available compound (Mitsui Chemical Co.) was recrystallized several times from diethyl ether or *n*-hexane; m.p. 130°C.

3,3′-Dimethyl-4,4′-biphenylylene Diisocyanate. This compound (Carwin Co.) was recrystallized twice from boiling *n*-hexane; m.p. 75°C.

3,3′-Dimethoxy-4,4′-biphenylylene Diisocyanate. This compound (Carwin Co.) was recrystallized three times from benzene; m.p. 141°C.

Tolylene Diisocyanate. This compound (2.4:2.6 = 80:20) (Hodogaya Kagaku Co.) was distilled at 127.5°C. at 14 mm. Hg.

ANAL. Found: C, 61.92%; H, 3.51%; N, 16.16%: Calcd. for $C_9H_6O_2N_2$: C, 62.07%; H, 3.47%; N, 16.09%.

Poly(phosphoric Acid)

Poly(phosphoric acid) (orthophosphoric acid) content 116%) of C. P. grade reagent (Yoneyama Kagaku Co.) was employed.

Model Compounds

***N*-(Phenylcarbamoyl)anthranilic Acid,**[8,9] **Structure (IV).** A 3.5 g. portion (0.03 mole) of phenyl isocyanate was made to react with a 2.74 g. portion (0.01 mole) of anthranilic acid in benzene at 80°C. for 1 hr. After removal of benzene the product was filtered and recrystallized from ethanol, yielding colorless needles, melted at 185–186°C. (lit.[8] m.p. 183°C.) in 97% yield. The infrared spectrum (KBr), Figure 1, showed a band at 3320 cm.$^{-1}$ (N—H stretching). The carbonyl stretching bands fall at 1673 cm.$^{-1}$ (carboxyl) and at 1666 cm.$^{-1}$ (ureido carbonyl). Ultraviolet spectrum: λ_{max} were 265 (ϵ: 37,500) and 306 mμ (ϵ: 9,149).

ANAL. Found: C, 65.70%; H, 4.72%; N, 10.93%. Calcd. for $C_{14}H_{12}O_3N_2$: C, 65.62%; H, 4.72%; N, 10.93%.

3-Phenyl-2,4(1H, 3H)quinazolinedione, Structure (VI).[8,9] A 3.00 g. portion of *N*-(phenylcarbamoyl)anthranilic acid was dissolved in 200 g. of poly(phosphoric acid) (PPA) at 60°C. and heated at 150°C. for 5 hr., and the reaction mixture was poured into 200 ml. of distilled water. After filtration the colorless crystals, melting at 280°C., were obtained quantitatively. The infrared spectrum (KBr), Figure 1, showed absorption bands at 3200 (bonded N—H), 1730 (4-carbonyl), 1650 (2-carbonyl), and 1600 cm.$^{-1}$ (phenyl). The ultraviolet spectrum exhibited absorption maxima at λ_{max} of 243 (ϵ: 11,200) and 312 mμ (ϵ: 3,490).

ANAL. Found: C, 70.33%; H, 4.38%; N, 11.76%; mol. wt. 241. Calcd. for $C_{14}H_{10}O_2N_2$: C, 70.58%; H, 4.23%; N, 11.48%; mol. wt. 238.

1,2-Dihydro-2-phenylimino-4H-3,1-benzoxazin-4-one, Structure (V).[8,9] A 0.300 g. portion of *N*-(phenylcarbamoyl)anthranilic acid was heated with 20 g. of PPA at 80–100°C. for 1 hr., and the reaction mixture was poured into 100 ml. of distilled water and the product filtered. The recrystallization from chloroform yielded colorless crystals; m.p. 193°C. in 95% yield. The infrared spectrum (Nujol), Figure 1, shows absorption bands at 3300 (N—H), 1747 (lactone carbonyl), 1644 ($>$C=N—), and 1240 and 1060 cm.$^{-1}$ (C—O—C). The ultraviolet spectrum had absorption maxima at λ_{max} of 244 (ϵ: 8,160), 282 (ϵ: 9,200), 292 (ϵ: 8,600), and 332 mμ (ϵ: 2,665).

ANAL. Found: C, 70.28%; H, 4.25%; N, 11.25%; mol. wt. 237. Calcd. for $C_{14}H_{10}O_2N_2$: C, 70.58%; H, 4.28%; N, 11.48%; mol. wt. 238.

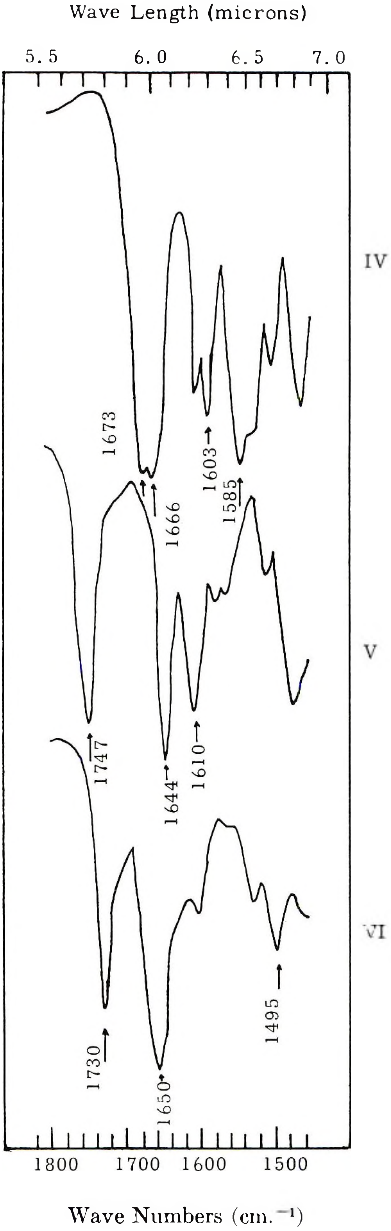


Fig. 1. Infrared spectra of *N*-(phenylcarbamoyl)anthranilic acid (IV), 1,2-dihydro-2-phenylimino-4H-3,1-benzoxazin-4-one (V), and 3-phenyl-2,4(1H,3H)quinazolinedione (VI).

Intramolecular Rearrangement of 1,2-Dihydro-2-phenylimino-4H-3,1-benzoxazin-4-one(V) to 3-Phenyl-2,4(1H,3H)quinazolinedione, Structure (VI).[8,9] A 0.200 g. (0.0084 mole) portion of (IV) was heated with 20.0 g. of (PPA) at 150°C. for 5 hr. The colorless needles (m.p. 282°C.) were obtained in 70% yield, and the structure was confirmed by the comparison of its infrared spectrum (KBr) with those of an authentic sample of (VI) prepared directly from *N*-(phenylcarbamoyl)anthranilic acid in PPA. It was confirmed in the infrared spectra that absorption bands at 1240 (N=C—O—C) and 1060 cm.$^{-1}$ (C—O—C) disappeared and that new carbonyl bands appeared at 1730 and 1650 cm.$^{-1}$ in the quinazolinedione ring system.

A. Polycondensation in Poly(phosphoric Acid) (First-Stage Polymerization): General Procedure[10]

In a three-necked flask equipped with nitrogen inlet and outlet tubes, a stirrer, and an apparatus to introduce the reagent under inert atmosphere the 116% PPA was added and then heated at 60°C.

The calculated amount of aromatic diisocyanate was then added slowly under a thin stream of nitrogen and heated at 80–100°C. When this compound was completely dissolved, powdered 4,4′-diamino-3,3′-biphenyl dicarboxylic acid was added gradually. The reaction mixture was heated under nitrogen at 140–160°C. Usually after 4 or 5 hr. of heating the reaction mixture becomes very viscous. The polymer was isolated by pouring the hot reaction mixture into distilled water; the solution was centrifuged or filtered, and the precipitate washed thoroughly with distilled water. The solid was then dipped into 5% aqueous sodium carbonate solution and allowed to stand overnight at room temperature. Finally, the polymer was washed with dilute hydrochloric acid, water, and methanol, successively, and dried at 50°C. under reduced pressure at 1 mm. Hg. If not noted otherwise, the inherent viscosities were measured at 0.5% concentration in concentrated sulfuric acid at 25°C. Typical examples for the preparation of the poly(urea acid) are described below.

B. Cyclodehydration[11] (Second-Stage Polymerization): General Procedure[11]

The polymers obtained by the first-stage polymerization were pulverized and heated at 250°C. under reduced pressure at 0.1 mm. Hg and then gradually heated up to 400°C. by means of a Wood's metal bath for 1 hr. in a rotating flask containing two steel ball bearings 8 mm. in diameter, to facilitate mixing. In the second-stage polymerization a trace (5–6%) of hydrolyzed diamine from the corresponding diisocyanate and the low molecular weight polymer were discarded by sublimation, and the polymer was obtained as a brown or black powder. It was found that the elemental analyses of the resultant polymer were in good agreement with the theoretical values. The solubility of the polymer in concentrated sulfuric acid decreased, owing to the cyclization and crosslinking, whereas the hydrolytic stability against the acidic or alkaline degradation increased. The experimental results are summarized in Table I.

Polymer from BDC and *p*-Phenylene Diisocyanate

A 1.6 g. portion of purified *p*-phenylene diisocyanate was dissolved in 80 g. of PPA with vigorous mechanical stirring, and the polymerization vessel

TABLE I

Preparation of Poly(urea Acid) (I)

Expt. no.	Monomer: BDC, g.	Monomer: Diisocyanate, g.	Solvent PPA, g.	Init. monomer concn., %	Polymn. temp., °C.	Hours	Yield, %	η_{inh}[a]	Solubility[b] in H_2SO_4, %	Comment
1	2.720	*p*-Phenylene diisocyanate, 1.6	86	5.0	140–150	5	92.2	1.79	97	Tough, flexible film
2	1.36	Methylene di-*p*-phenylene diisocyanate, 1.4	110	2.5	150–155	5	84.4	0.50	97	Tough, flexible film
3	2.72	1,5-Naphthylene diisocyanate, 2.10	96	5.0	150–160	3	100	0.61	96.2	Tough, flexible film
4	1.36	3,3′-Dimethyl-4,4′-biphenylylene diisocyanate, 1.32	54	5.0	150–160	2.5	91.5	0.61	100	Transparent tan film
5	1.36	3,3′-Dimethoxy 4,4′-biphenylylene diisocyanate, 1.48	57	5.0	150–160 200	5 5	72.7	0.78	95.4	Tough, flexible film
6	1.36	Tolylene diisocyanate (2.4:2.6 = 80:20), 1.0	44	5.4	150 200	4 0.5	70.0	—	0	Gelation

[a] Obtained from 0.5% concentration in H_2SO_4 at 25°C.

[b] At 25.0°C., 0.5% concentration.

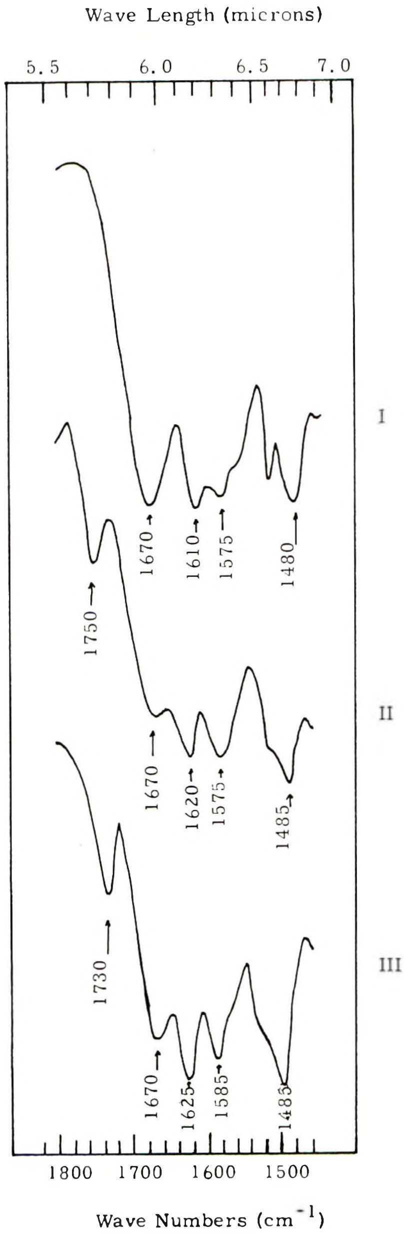


Fig. 2. Infrared spectra of poly(urea acid) (I), iminobenzoxazinone polymer (II), and polyquinazolinedione (III).

was heated at 130°C. Then a 2.72 g. portion of BDC was added under nitrogen, and the heating was continued at 140–150°C. for 5 hr. The yield of polymer was 2.7 g. (90%), and the inherent viscosity measured in concentrated sulfuric acid was 1.29. The resultant polymer was partially soluble in *N*-methylpyrrolidone, dimethylacetamide, and dimethyl sulfoxide containing 5–10% of lithium chloride. It was also soluble in concentrated sulfuric acid. The polymer solution of dimethyl sulfoxide was poured onto a glass plate and dried at 110°C. for 2 hr., giving a tough film.

ANAL. Found: C, 64.60%; H, 4.03%; N, 10.89%.

Polymer from BDC and Methylene Di-*p*-phenylene Diisocyanate

A 1.4 g. portion of methylene di-*p*-phenylene diisocyanate was dissolved in 110 g. of PPA at 100°C., and a 1.36 g. portion of BDC was added under nitrogen to the solution at 140°C. The reaction mixture was stirred vigorously at 150–155°C. for 5 hr. [polymer (I)], and then half of this reaction mixture was heated further at 250–250°C. for 2 hr. [polymer (II)]. The infrared spectra of the resultant polymers (I) and (II) are shown in Figure 2. The inherent viscosity of polymer (I) was 0.51.

Polymer from BDC and 1,5-Naphthylene Diisocyanate

A 2.10 g. portion of 1,5-naphthylene diisocyanate and a 2.7 g. portion of BDC were dissolved in 97 g. of PPA at 160°C. under nitrogen. The reaction mixture was heated at 150–160°C. for 3 hr. The resultant polymer was yellowish brown, and the inherent viscosity was 0.61. The second-stage polymerization, with polymer at 300°C. for 1 hr. and at 360°C. for 1 hr. under reduced pressure, 0.1 mm. Hg, gave a cyclized polymer as a black powder.

ANAL. Found: C, 70.14%; H, 4.06%; N, 12.53%. Calcd. for $C_{26}H_{14}O_4N_4$: C, 69.95%; H, 3.16%; N, 12.55%.

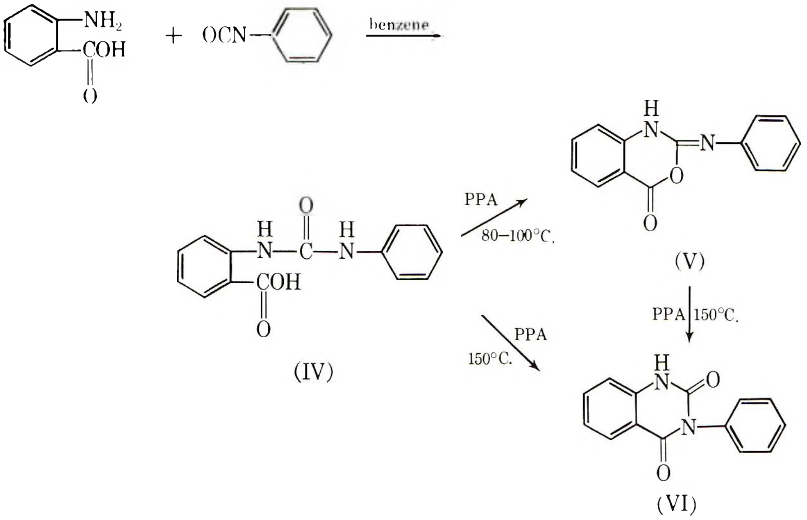
The resultant polymer is insoluble in concentrated sulfuric acid. The infrared spectrum of the polymer is shown in Figure 2. A trace of prepolymer was obtained by sublimation, and the elemental analysis was in good agreement with the poly(urea acid), which was soluble in concentrated sulfuric acid.

ANAL. Found: C, 65.64%; H, 4.49%; N, 11.88%. Calcd. for $C_{28}H_{18}O_6N_4$: C, 64.73%; H, 3.76%; N, 11.61%.

In the cyclopolycondensation stage 1,5-naphthylenediamine was obtained by sublimation and its structure confirmed by elemental analysis, melting point, and infrared spectrum.

RESULTS AND DISCUSSIONS

Model compounds were prepared as described in the previous papers[8,9] in connection with the intramolecular rearrangement in PPA:



(4)

The physical properties and infrared absorption bands of the model compounds were compared with those of the polymers in the region of 1500–1800 cm.$^{-1}$ as shown in Figures 1 and 2. From the data on the infrared spectra of these model compounds, given in Table II and Figure 1, the car-

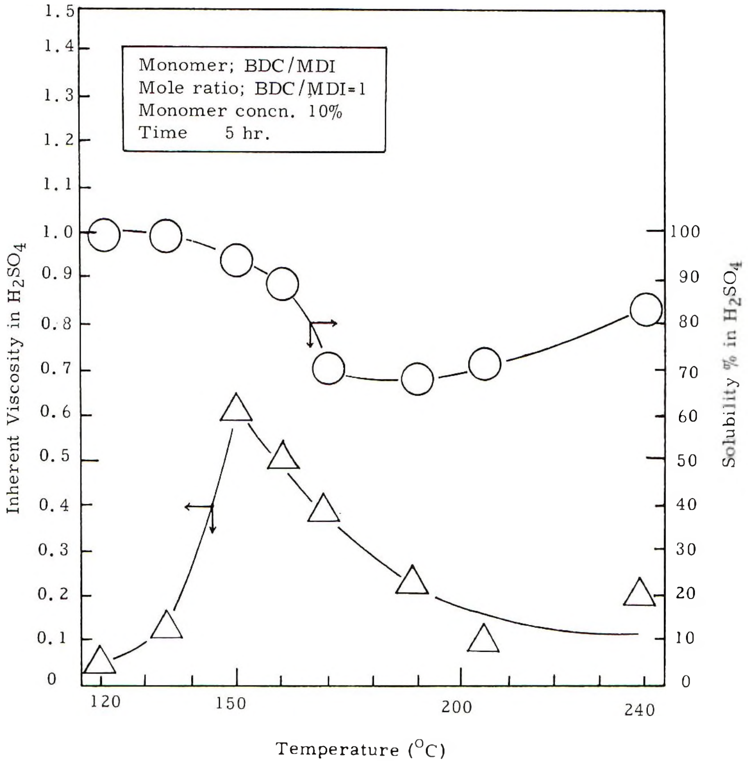
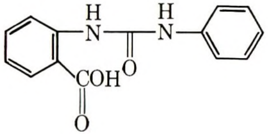
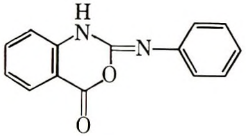
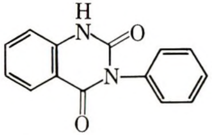


Fig. 3. Effect of temperature on extent of polymerization and solubility of polymer.

TABLE II
Infrared Spectra Data and Physical Properties of Model Compound

Compound	Structure		M.p., expt. and lit.[8,9]	IR,[a] cm.$^{-1}$	Mol. wt.[b] expt. and calc.	Elemental analysis, %
N-(Phenylcarbamoyl)-anthranilic acid		(IV)	186; 183	3320 1673	255; 256	Calcd.: C, 65.62; H, 4.72; N, 10.93 Found: C, 65.70; H, 4.72; N, 10.89
1,2-Dihydro-2-phenylimino-4H-3,1-benzoxazin-4-one		(V)	193; 192–193	3300[c] 1747 1644 1244 1065	237; 238	Calcd.: C, 70.58; H, 4.23; N, 11.48 Found: C, 70.28; H, 4.25; N, 11.25
3-Phenyl-2,4(1H,3H)-quinazolinedione		(VI)	284; 280	3225 1730 1650	241; 238	Calcd.: C, 70.58; H, 4.23; N, 11.48 Found: C, 70.33; H, 4.38; N, 11.76

[a] KBr disk.
[b] Methyl ethyl ketone and benzene.
[c] Nujol.

bonyl absorption of (IV) fell at 1673 and 1666 cm.$^{-1}$, and the carbonyl group of (V) showed an absorption band at 1747 cm.$^{-1}$ corresponding to the lactone carbonyl group and the C=N group at 1644 cm.$^{-1}$. The carbonyl absorption bands of (VI) appeared at 1730 and 1650 cm.$^{-1}$, which were assigned to 4-carbonyl and 2-carbonyl groups of quinazolinedione, respectively. The infrared spectrum of the resultant polymer (I), given in Figure 2, showed the absorption band at 1670 cm.$^{-1}$ for carbonyl groups, which was closely related to the carbonyl absorption band of the model compound (IV) in Figure 1. Consequently, the structure of the resultant polymer (I) was confirmed as the poly(urea acid). Polymer (II) showed the characteristic carbonyl absorption band of the benzoxazinone ring at 1750 cm.$^{-1}$, which was identical with the carbonyl absorption of model compound (V). The carbonyl absorption band at 1670 cm.$^{-1}$ indicated that the polymer contained appreciable amounts of the uncyclized poly(urea acid) structure.

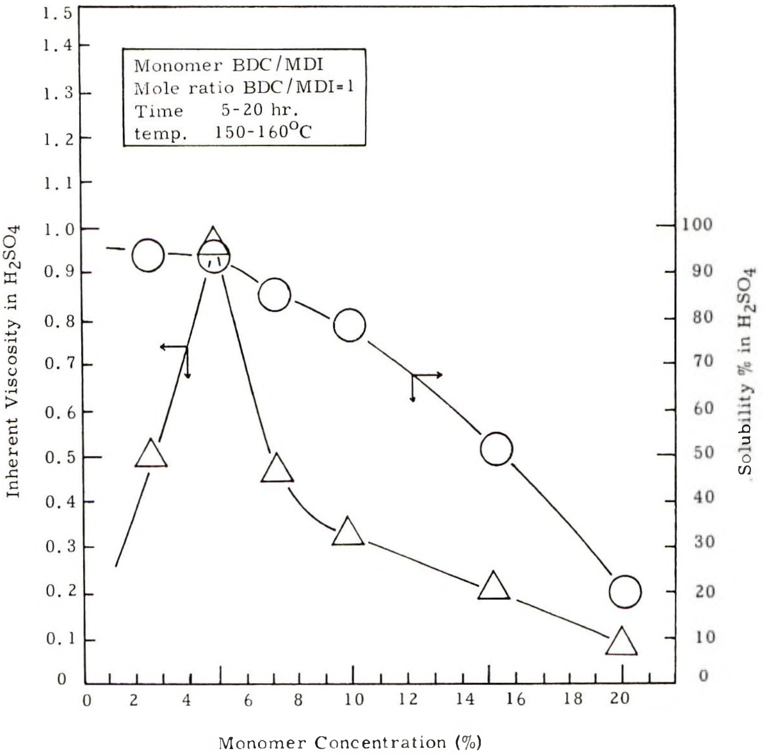


Fig. 4. Effect of monomer concentration on extent of polymerization and solubility of polymer; mole ratio of 4,4′-diamino-3,3′-biphenyldicarboxylic acid to methylene di-*p*-phenylene diisocyanate, 1:1; time, 5–20 hr.; temperature, 150–160°C.

The resultant polymer (III) obtained by the second-stage polymerization showed the carbonyl absorption band at 1730 cm.$^{-1}$, which was identical with the absorption of model compound (VI). The carbonyl absorption band of polymer (III) at 1670 cm.$^{-1}$ suggested that the polymer contained an appreciable amount of the uncyclized poly(urea acid) structure. The elemental analyses and the infrared characteristic absorption band of the resultant polymers (II) and (III) were in good agreement with the copolymer structure of poly(1,2-dihydro-2-imino-4H-3,1-benzoxazin-4-one), polyqinazolinedione, and poly(urea acid). On the basis of the infrared spectra of the polymer and several of the model reactions described above, the cyclopolycondensation of poly(urea acid) (I) was confirmed by the formation of poly(1,2-dihydro-2-imino-4H-3,1-benzoxazin-4-one), structure (II). Intramolecular rearrangement along the polymer chain occurred upon heating, to form the thermodynamically stable polyquinazolinedione (III). In an attempt to prepare a linear tractable poly(urea acid) (I), which was soluble in sulfuric acid, the optimum polymerization conditions in PPA were determined by measuring the variation of the extent of polymerization and the solubility in sulfuric acid with temperature. The plots in Figure 3 show that the optimum polymerization temperature was in the range of 140–160°C. It was reasonably presumed, on the basis of the reactivity differences between isocyanate groups and amino and carbonyl groups, that

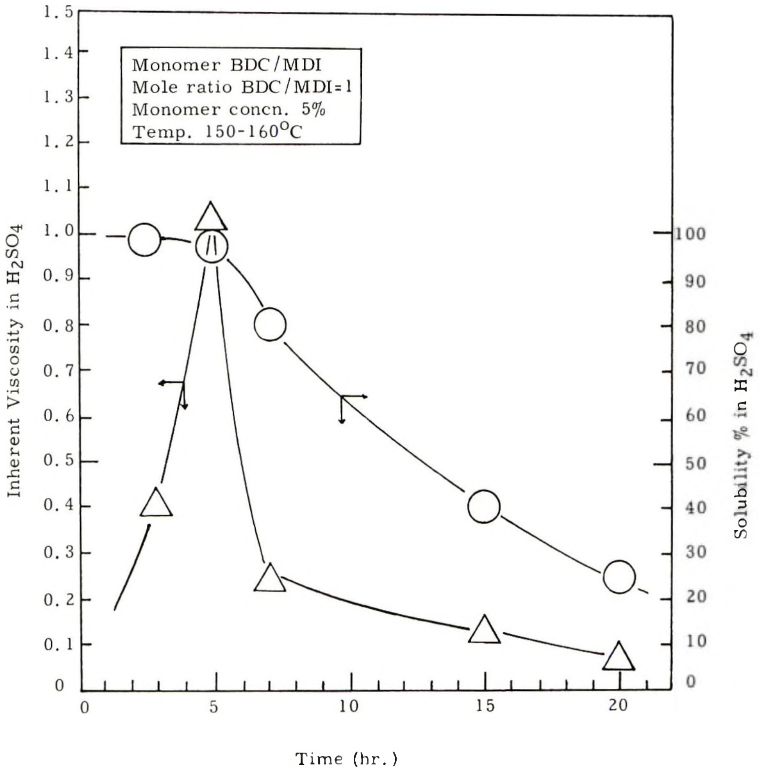


Fig. 5. Rate of polymerization and solubility of polymer: mole ratio of 4,4′-diamino-3,3′-biphenyldicarboxylic acid to methyl di-*p*-phenyl diisocyanate, 1:1; monomer concentration, 5%; temperature, 150–160°C.

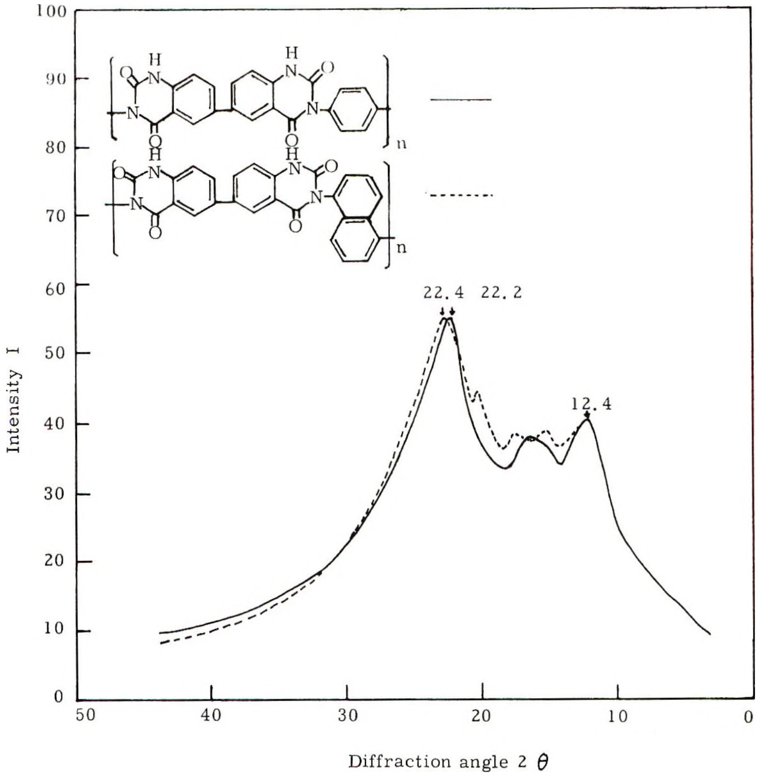


Fig. 6. X-ray diffraction diagrams of polyquinazolinedione.

the comparatively mild reaction conditions at lower temperature were necessary to give linear poly(urea acid). The optimum total monomer concentration for obtaining linear soluble polymers was found to be 5 wt.-% at 150–160°C., as shown in Figure 4. Gelation was observed in a short time by using more than 5% monomer concentration at 150–160°C. The data in Figure 5 indicate that the polymerization period should be less than 5 hr. at 150–160°C. in PPA for a tractable open-chain precursor. Longer heating after gelation gave infusible polymer by crosslinking; thus, it was necessary to stop the reaction system before the gelation.

Properties of Poly(urea Acid) and Polyquinazolinedione. The crystallinity of the resulting polymer was investigated by the powder method with a nickel-filtered CuK_α radiation. The x-ray diffraction diagrams in Figure 6 indicate that the polymer has a low degree of crystallinity. The thermal stability of the resultant polymer was measured either in nitrogen or in air by the thermogravimetric method; see Figure 7. The thermogravimetric analyses, Figure 7, show that these quinazolinedione polymers had excellent thermal stability and were stable up to 550°C. in nitrogen. The solubility behavior of poly(urea acid) in a variety of organic polar solvents and in concentrated sulfuric acid was studied. The polymers were fairly

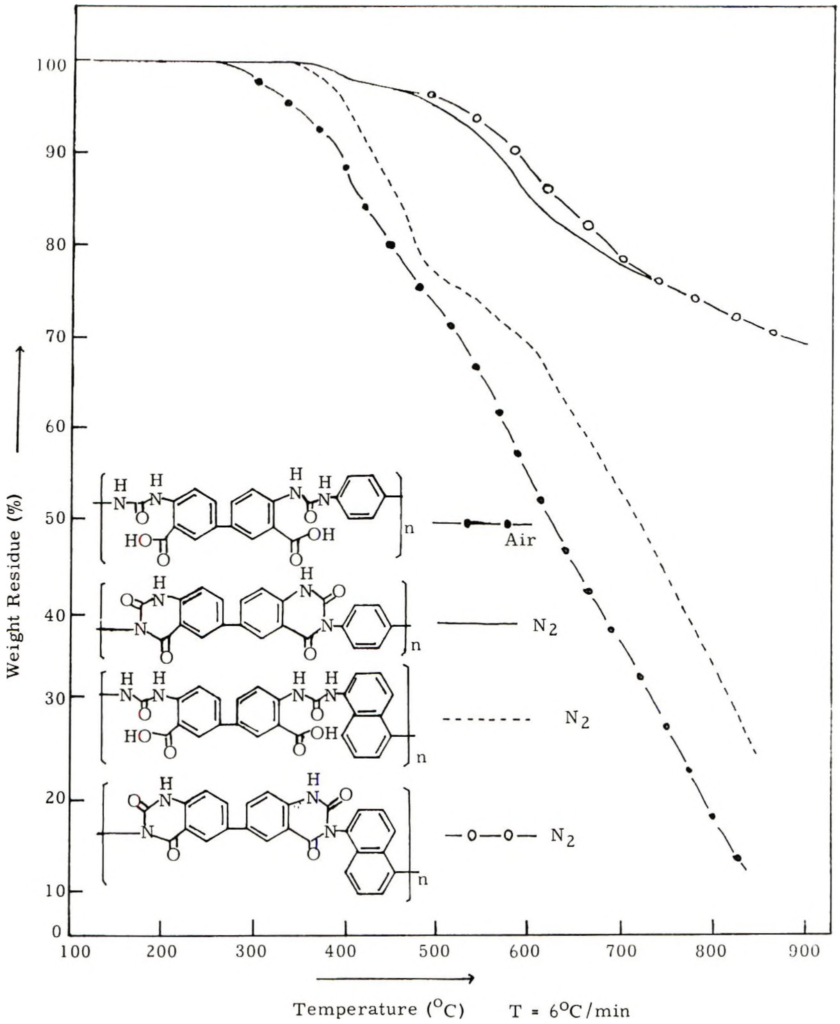


Fig. 7. Thermogravimetric analysis of poly(urea acid) (I) and polyquinazolinedione (III) in nitrogen and in air.

soluble in *N*-methylpyrrolidone, *N*,*N'*-dimethylacetamide, and dimethyl sulfoxide containing 5–10% lithium chloride, and the polymer could be cast into a tough film from these polymer solutions. It was also soluble in concentrated sulfuric acid, as shown in Table I. It was reasonably presumed from the solubility behavior given in Table I that the resultant polyurea acid was partially cyclized by intramolecular dehydration, and was crosslinked by intermolecular amide linkage formed by the reaction of pendant carboxyl groups and isocyanate terminal groups from the polyureide main chain.[9] The polyquinazolinedione was insoluble in most organic solvents and cold concentrated sulfuric acid, whereas it was soluble in fuming nitric acid.

The hydrolytic stability of the poly(urea acid) (I) and the polyquinazolinedione (III) toward acid and alkali was tested. The pulverized polymers were boiled either in 35% sulfuric acid or in 28% aqueous potassium hydroxide solution at 120°C. for 5 hr. The inherent viscosity of the poly(urea acid) (I) decreased from 1.07 to 0.27 in 91% yield in the case of the acidic treatment, and the viscosity decreased to 0.06 in 46.5% yield in the case of the basic treatment. The polymer of polyquinazolinedione (III) obtained by the second-stage polymerization was 62.5% in yield in the case of the acidic treatment and 76.5% in yield in the case of the basic treatment. It was insoluble in concentrated sulfuric acid.

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Résumé

Des polyquinazolinediones aromatiques de poids moléculaire élevé ont été préparées par cyclopolycondensation d'acide 4,4′-diamino-3,3′-biphényldicarboxylique avec des diisocyanates aromatiques. Les techniques de polymérisation en solution d'acide polyphosphorique fournissent l'acide polyureique, et celui-ci est converti en polyquinazolinedione par cyclodéhydratation thermique à 300–400°C sous pression réduite. Les polyquinazolinediones ainsi obtenues avaient une stabilité thermique excellente à la fois sous azote et à l'air. L'acide polyuréique est soluble dans le diméthylsulfoxyde et des films peuvent être coulés au départ de la solution du polymère de d'acide polyuréique (η_{inh} = 0.8–1.8). Des films résistants ont été obtenus par chauffage du film sous azote ou sous pression réduite à 300–400°C. Le mécanisme de polymérisation de la cyclopolycondensation a été étudié et on a établi que la polymérisation résulte de la formation d'un acide polyuréique de haut poids moléculaire suivi de sa cyclodéhydradation poly(1,2-dihydro-2-imino-4H-3,1-benzoxazine-4-one) (II). Ce polymère subit ultérieurement un réarrangement intramoléculaire le long de la chaîne principale par chauffage pour obtenir la polyquinazolinedione (III) thermodynamiquement stable.

Zusammenfassung

Vollaromatische hochmolekulare Polychinazolindione wurden durch die Cyclopolykondensationsreaktion von 4,4'-Diamino-3,3'-biphenyldicarbonsäure mit aromatischen Diisocyanaten dargestellt. Das Polymerisationsverfahren in Polyphosphorsäurelösung lieferte die Polyharnstoffsäure, die durch thermische Cyclodehydratisierung bei 300–400°C unter reduziertem Druck in die Polychinazolindione umgewandelt wurde. Die so erhaltenen Polychinazolindione besitzen in Stickstoff und in Luft eine ausgezeichnete thermische Stabilität. Die Polyharnstoffsäure ist in Dimethylsulfoxyd löslich und aus der Polyharnstoffsäurelösung (η_{inh} = 0,8–1,8) können Filme gegossen werden. Durch Erhitzen des Filmes unter stickstoff oder unter reduziertem Druck auf 300–400°C werden zähe Filme erhalten. Der Polymerisationsmechanismus der Cyclopolykondensationsreaktion wurde untersucht und es wurde gefunden, dass die Polymerisation über die Bildung der hochmolekularen Polyharnstoffsäure (I) verläuft, worauf Cyclodehydratisierung zum Poly-(1,2-dihydro-2-imino-4H-3,1-benzoazin-4-on) (II) erfolgt. Beim Erhitzen kommt es schliesslich zur intramolekularen Umlagerung entlang der Polymerkette und das thermodynamisch stabile Polychinazolindion (III) wird gebildet.

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Analysis of the Negative Peaks in Gel Permeation Chromatography

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Synopsis

The negative peak usually encountered in gel permeation chromatography has been resolved into three distinct peaks through selection of appropriate columns. The three peaks are associated with water, nitrogen, and oxygen. Separation of these simple molecules was found to follow the fundamental theory of gel permeation chromatography, that is, separation according to straight-chain length.

INTRODUCTION

Gel permeation chromatography (GPC) is a relatively new technique, which fractionates polymers and permits determination of their molecular weight distribution. The technique separates materials according to molecular size, based on the depth to which each molecular specie is able to diffuse into the gel network.[1] Control of the separation is exerted through control of the porosity existing in the gel. Volume elution curves, called chromatograms, are produced as a representation of the fractionation taking place within the GPC columns.

The appearance of a negative peak at the end of the volume elution chromatogram is a common occurrence. These have been reported in the literature,[2,3] but no attention has been devoted to their generation. The cause of these peaks has been attributed to water,[2,3] and in one instance soap[3] was suspected of contributing to such peak formation. It was found that with a column arrangement capable of fractionating low molecular weight materials this negative peak had the dissymmetry associated with a mixture of materials. The work conducted in this investigation was conducted in an effort to elucidate the nature of the materials contributing to the negative peak and to assess the potential of the technique for the separation of low molecular weight materials.

EXPERIMENTAL

A Model 100 Waters Associates GPC was used for this investigation utilizing a four-column series of crosslinked polystyrene gels of 900, 400, 400, and 250 A. porosity. An excellent description of the basic equipment has been given by Maley.[3] Eastman Kodak tetrahydrofuran (THF) was used as the carrier solvent for the GPC system and was degassed before

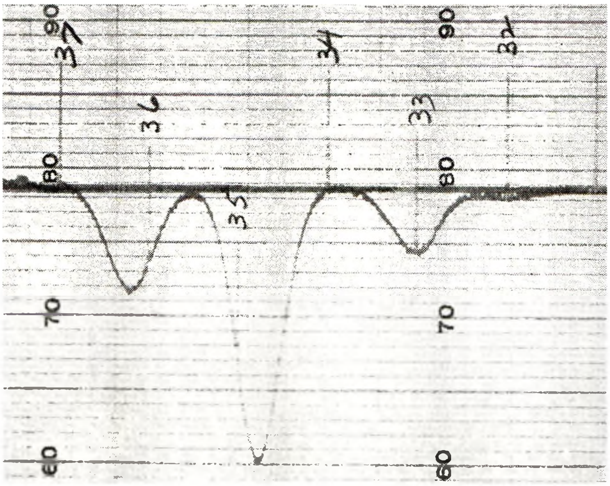

Fig. 1. Tetrahydrofuran reference chromatogram.

entering the columns. The analyses were carried out at ambient temperatures with a solvent flow rate regulated at 1 cc./min. Under these experimental conditions the single negative peak was resolved into three distinct peaks.

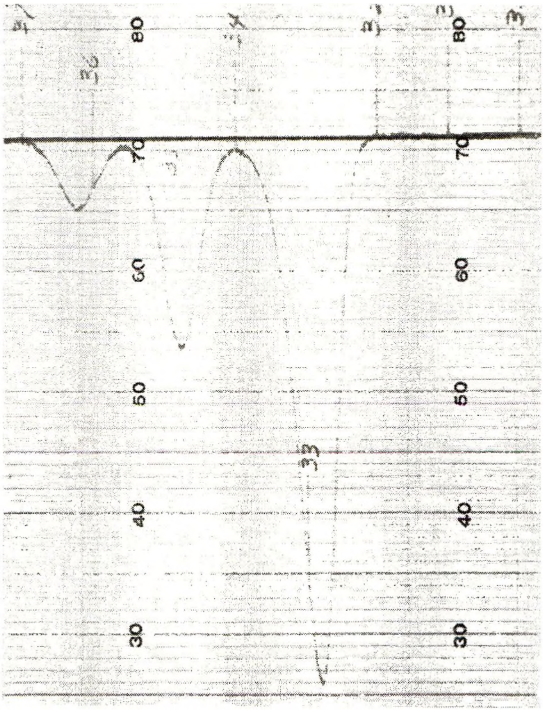

Fig. 2. Chromatogram obtained from 10 cc. of tetrahydrofuran with 1 drop of H_2O added.

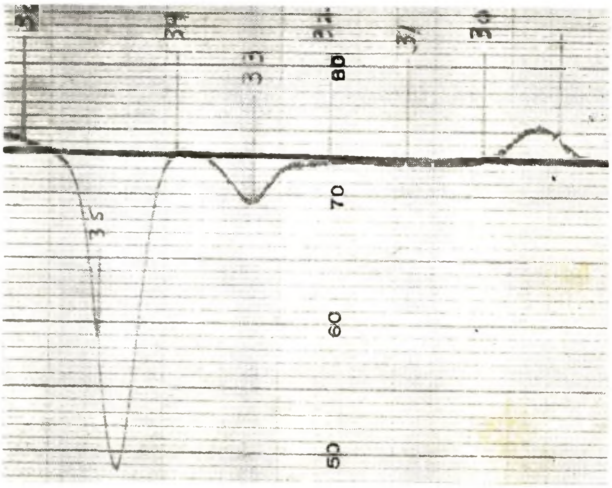

Fig. 3. Chromatogram obtained from nitrogen-saturated tetrahydrofuran.

Several analyses were carried out in an effort to identify the materials responsible for the generation of these three negative peaks. Injections of 10 cc. of the THF carrier solvent were made into the column system, to establish a reference chromatogram for the negative peaks, and it gave the chromatogram shown in Figure 1. A solution was injected into the columns with a concentration of 1 drop of distilled water in 10 cc. of THF, producing the chromatogram shown in Figure 2. Finally, a 10 cc. sample of THF carrier solvent, saturated with nitrogen gas, was injected into the system, resulting in the chromatogram reproduced in Figure 3. The GPC chromatograms were obtained for each analysis with 2-min. injection periods at 2× attenuation.

RESULTS AND DISCUSSION

The chromatogram represented by Figure 1 was obtained for all injections of THF carrier solvent into the GPC system. Three distinct negative peaks were obtained for each analysis at elution volume counts of 32 to 37. Each elution count interval represents 5 ml. of THF carrier solvent submitted to the refractometer from the GPC columns. The water peak was eluted between the count intervals 32 and 34, as shown in Figure 2. This peak coincides with the first unknown peak observed in the carrier solvent injection shown in Figure 1. These results indicate that the first of three negative peaks obtained with THF is caused by water in the carrier solvent.

Figure 3 shows the chromatogram obtained from the THF carrier solvent saturated with nitrogen gas. A sharp negative peak was observed between elution interval 34 and 35. This corresponds identically to the second unknown peak obtained from the carrier solvent injection shown in Figure 1.

From the data obtained—that is, identification of negative peaks associated with water and nitrogen—it was obvious that the third peak must result from oxygen in the system. Undoubtedly, the presence of the last material results from incorporation of air into the sample during the injection operation.

According to gel permeation chromatography theory, the largest molecular species should penetrate the crosslinked polymer gel the least and be eluted first.[2]

Table I shows the straight-chain lengths in angstrom units for each of the simple molecules encountered in this work. In accordance with GPC theory these angstrom values indicate that water should be eluted first and nitrogen and oxygen should follow according to their decreasing chain length. Results in this study show that the three negative peaks obtained from THF injections are in the order of the straight-chain lengths for water, nitrogen, and oxygen. These data indicate that GPC theory is applicable to very small molecules and that separation of such materials can occur with the proper column selection.

TABLE I
Straight-Chain Lengths For Simple Molecules[4]

Substance	Straight-chain length, A.
H_2O	1.92
N_2	1.09
O_2	0.55

Conclusions

The results of this investigation have shown that the negative peak reported by other investigators may be resolved into three distinct peaks by a proper column selection. These peaks have been associated with water, nitrogen, and oxygen and are artifacts resulting from injection. A most significant fact is that the separation of these three simple molecules still follows the fundamental theory of GPC, that is, separation by virtue of straight-chain length.

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Résumé

Le pic négatif rencontré généralement dans la chromatographie par perméation sur gel a été résolu en trois pics distincts par sélection de colonnes appropriées. Les trois pics sont associés à l'eau, à l'azote et à l'oxygène. La séparation de ces molécules simples suit le théorie fondamentale de la chromatographie par perméation sur gel c'est-à-dire séparation conformément à la longueur de la chaîne rectiligne.

Zusammenfassung

Die üblicherweise bei der Gelpermeationschromatographie gefundene negative Spitze wurde durch Wahl geeigneter Säulen in drei deutliche Spitzen aufgelöst. Die drei Spitzen entsprechen Wasser, Stickstoff und Sauerstoff. Die Trennung dieser einfachen Moleküle gehorcht der grundlegenden Theorie der Gelpermeationschromatographie und erfolgt gemäss der geraden Kettenlänge.

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Kinetics of Polymerization of Styrene Initiated by Substituted Benzoyl Peroxides. IV. Decomposition Induced by Substituted Diethylanilines

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Synopsis

Equilibrium complex formation between symmetrically substituted benzoyl peroxides and ring-substituted *N,N*-diethylanilines has been quantitatively measured. From the results the rate constant for the unimolecular decomposition of the complexes, producing an initiating free radical, is found to be approximately $10^{12} \exp \{(-25 \times 10^3)/RT\}$. The data obtained are consistent with a previously postulated mechanism for radical production in the presence of vinyl monomers.

Introduction

In the previous paper[1] it was shown that the rate constants for the decomposition of substituted benzoyl peroxides induced by ring-substituted *N,N*-diethylanilines could be determined in styrene polymerization and represented by the equation

$$\log (k_{d(X,Y)}/k_{d(H,H)}) = 1.6(2\sigma_X) - 2.7(\sigma_Y) \tag{1}$$

where σ is the Hammett factor for the substituent X on the peroxide or the substituent Y on the amine. Earlier work had established that there existed a true equilibrium between the amine (A) and peroxide (B), yielding a complex (C), which could be determined spectrophotometrically.[2] It was postulated that C decomposed to yield free radical R·, which can initiate polymerization:

$$\mathrm{A} + \mathrm{B} \overset{K}{\rightleftarrows} \mathrm{C} \xrightarrow{k} \mathrm{R}\cdot \tag{2}$$

The rate for induced decomposition would then be given by

$$d[\mathrm{R}\cdot]/dt = kK[\mathrm{A}][\mathrm{B}] \tag{3}$$

where k_d, the apparent decomposition rate constant, is equal to the product of Kk. Such an equilibrium is consistent with the mechanism [eq. (2a)]

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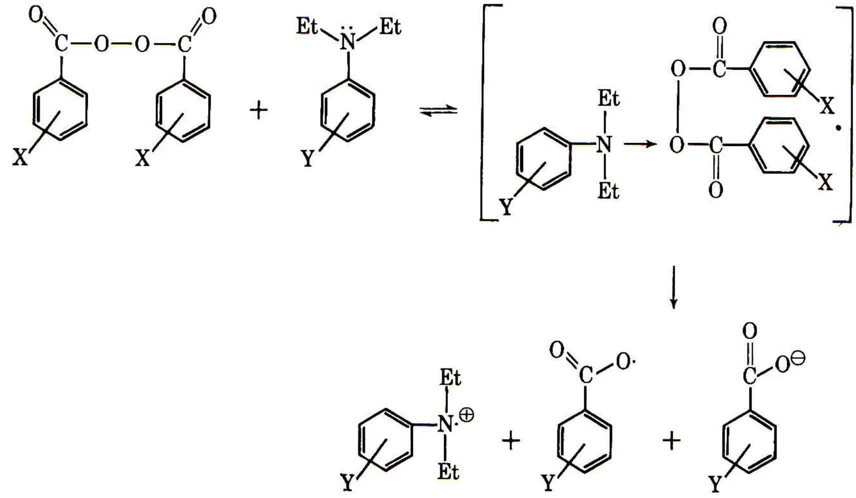
originally postulated by Imoto and his co-workers[3] in an attempt to explain the observed products of the reaction. Note that this mechanism is not consistent with the series of reactions proposed by Graham and Mesrobian[4] who carried out their studies in the absence of a radical trap such as styrene. However, it is consistent with the recent study by Imoto and Choe[5] on initiation by the system benzoic anhydride plus dimethylaniline *N*-oxide.



(2a)

In this paper we report further quantitative studies on complex formation between symmetrically substituted benzoyl peroxides and ring-substituted diethylaniline, which enable us to calculate the value of k in eq. (2).

Experimental

The procedure for determining the equilibrium constant has been described.[2] Peroxides[6] and amines[7] were obtained and purified immediately before use as previously reported. Dilute solutions (10^{-4} to $10^{-5}M$) of amine and peroxide in reagent-grade chloroform were prepared, and the absorbance of mixtures of varying mole ratios were then measured in ultraviolet light.

Results

Figure 1 presents the chloroform solution spectra of *N,N*-diethylaniline, benzoyl peroxide, and the complex formed between them. The last spectrum (C) was obtained by difference at 0°C. The occurrence of a maximum for the complex near 260 mμ justifies the subsequent use of that wavelength for absorbance measurements.

At low temperatures the equilibrium shown in eq. (2) is shifted completely to the right.[2] Therefore, absorbances of mixtures of amine and

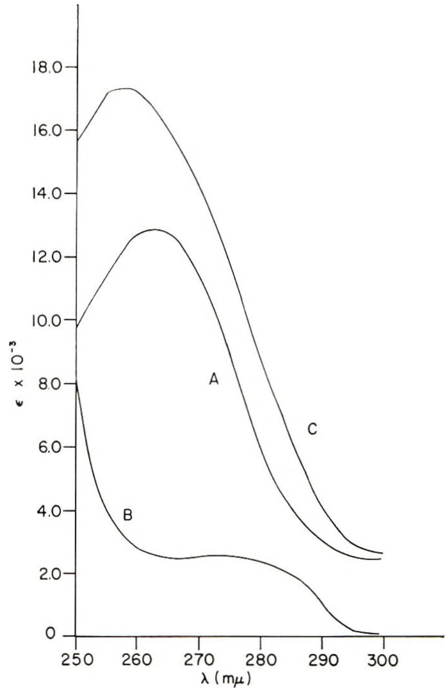


Fig. 1. Molar extinction coefficient for chloroform solution of (*A*) diethylaniline, (*B*) benzoyl peroxide, and (*C*) the complex formed between them.

peroxide at 0°C. and at a particular wavelength can be described by either of the equations

$$A/C_A^\circ = \epsilon_A + C_B^\circ/C_A^\circ(\epsilon_C - \epsilon_B) \tag{4a}$$

$$A/C_B^\circ = \epsilon_B + C_A^\circ/C_B^\circ(\epsilon_C - \epsilon_B) \tag{4b}$$

where A is the absorbance of a solution originally containing concentration C_A° of the amine and C_B° of the peroxide, which, respectively, have extinc-

TABLE I

Extinction Coefficients[a] at 260 mμ

Benzoyl peroxide substituent	Diethylaniline substituent	$\epsilon_A \times 10^{-3}$	$\epsilon_B \times 10^{-3}$	$\epsilon_C \times 10^{-3}$
p-Methyl	None	12.71	17.19	32.08
None	"	12.71	2.78	17.22
3,4-Dichloro	"	12.71	32.16	46.39
p-Cyano	"	12.71	10.50	25.15
3,5-Dinitro	"	12.71	14.29	27.48
None	*p*-Nitroso	5.09	2.78	9.82
None	*p*-Acetamide	9.15	2.78	13.49
None	*m*-Methyl	12.40	2.78	16.54

[a] Estimated errors in ϵ_A and ϵ_B are less than ±1%; in ϵ_C they are less than ±5%.

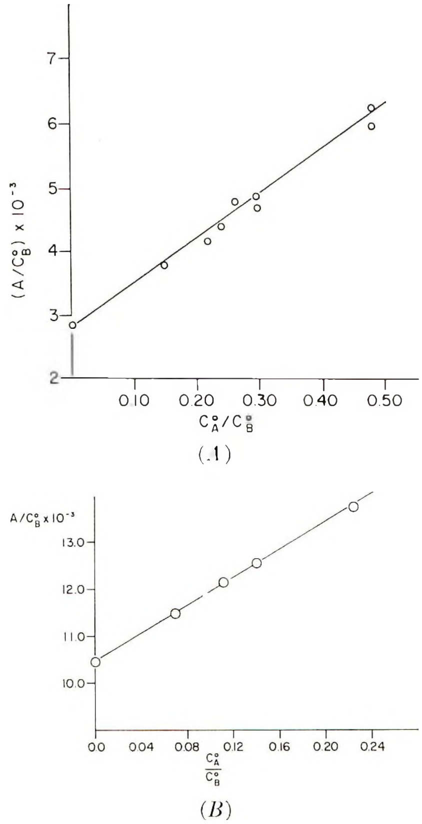


Fig. 2. Determination of ϵ_C at 260 mμ for complex formation (*A*) between *p*-nitroso diethylaniline and benzoyl peroxide and (*B*) between *p*-cyano benzoyl peroxide and diethylaniline.

tion coefficient ϵ_A and ϵ_B. The complex formed has extinction coefficients ϵ_C. Equation (4a) is to be used with an excess of amine over peroxide and (4b) with an excess of peroxide over amine. Figure 2 shows typical plots of eqs. (4), from which ϵ_C can be evaluated. Table I lists values of extinction coefficients measured in this work.

From the variation of absorbance with temperature and the value of ϵ_C obtained at low temperatures it is possible to determine the value of the equilibrium constant K of eq. (2) over a wide range of temperature. Figure 3 shows typical plots, which also permit determination of the standard enthalpy and entropy changes accompanying the equilibrium. Values of K, ΔH°, and ΔS° for complex formation are tabulated for 30°C. in Table II.

Hammett plots for symmetrically substituted benzoyl peroxides with diethylaniline and for substituted diethylanilines with benzoyl peroxide are given in Figure 4. The combined Hammett equation for K analogous to eq. (1) for k_d is given by

$$\log K_{(\mathrm{X,Y})}/K_{(\mathrm{H,H})} = 0.83(2\sigma_{\mathrm{X}}) - 1.52\sigma_{\mathrm{Y}} \qquad (5)$$

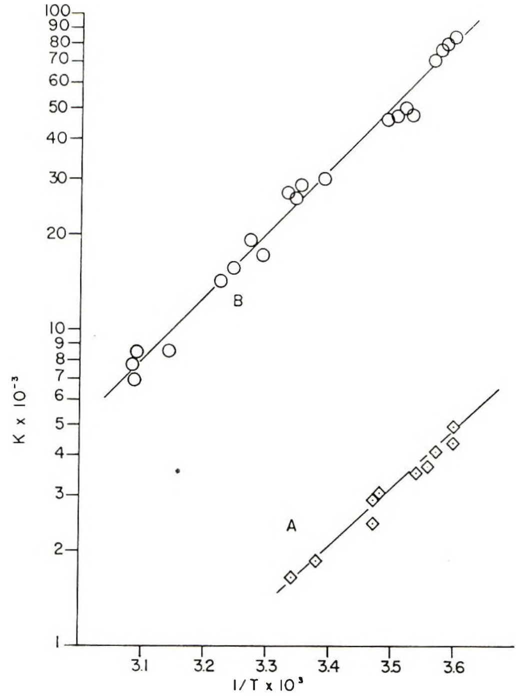


Fig. 3. Variation of K with temperature for complex formation (A) between *p*-nitroso diethylaniline and benzoyl peroxide and (B) between *p*-cyano benzoyl peroxide and diethylaniline.

Discussion

Combining eqs. (1) and (5) we obtain for the decomposition of the complex formed between Y-substituted diethylanilines and X-substituted benzoyl peroxides the equation

$$\log (k_{XY}/k_{HH}) = 0.77(2\sigma_X) - 1.2\sigma_Y$$

TABLE II

Thermodynamic Values[a] at 30°C. for Complex Formation Between Substituted Benzoyl Peroxides and Diethylanilines

Benzoyl peroxide substituent	Diethylaniline substituent	$K \times 10^{-3}$, liter/mole	$\Delta H°$, kcal./mole	$\Delta S°$, e.u.
p-Methyl	None	1.17	−8.5	−13.9
None	"	2.05	−8.4	−12.6
3,4-Dichloro	"	16.1	−9.4	−11.8
p-Cyano	"	20.1	−9.2	−10.6
None	*p*-Nitroso	1.40	−8.0	−11.7
None	*p*-Acetamide	2.15	−8.6	−12.6
None	*m*-Methyl	2.70	−9.0	−13.5

[a] Estimated errors K, ±5%; $\Delta H°$, ±0.5 kcal.; $\Delta S°$, ±1 e.u.

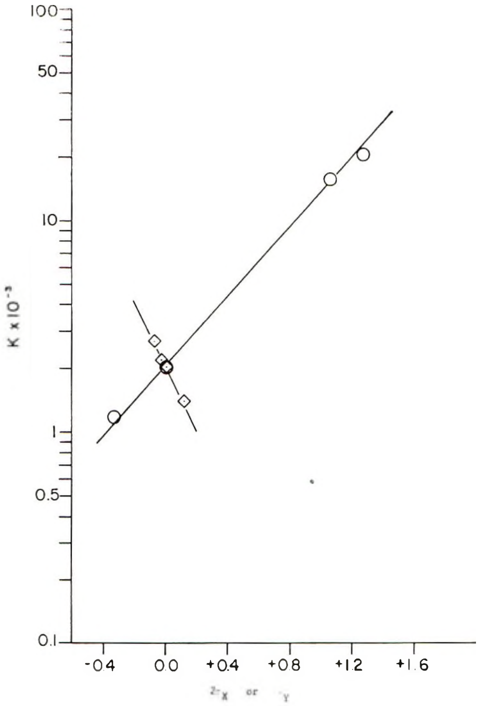


Fig. 4. Variation of K at 30°C. with Hammett substituent for complex formation (□) between substituted diethylanilines and benzoyl peroxide and (O) between substituted benzoyl peroxides and diethylaniline.

The absolute magnitude of k_{XY} from the observed values of K and k_d is of the order of 10^{-6} sec.$^{-1}$. Since the activation energy for benzoyl peroxide decomposition induced by dimethylaniline is approximately 13 kcal./mole, and the heat of complex formation as given in Table II is approxi-

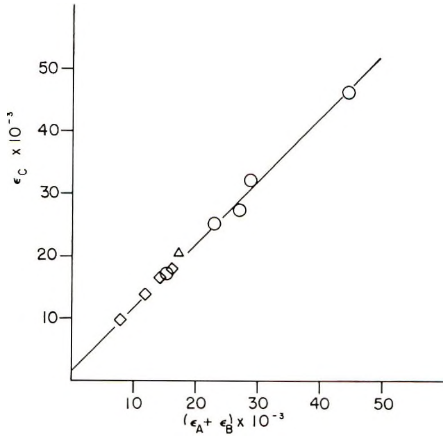


Fig. 5. Correlation between ϵ_C and $\epsilon_A + \epsilon_B$ for (□) substituted diethylanilines with benzoyl peroxide, (O) substituted benzoyl peroxides with diethylaniline, and (△) benzoyl peroxide with dimethylaniline (see ref. 2 of the paper).

mately -12 kcal./mole, the activation energy for k can be estimated as 25 kcal./mole. Therefore the frequency factor for k has a value of 10^{12} sec.$^{-1}$, which is quite normal[8] for unimolecular decompositions into free radicals. The 25 kcal./mole activation energy is considerably less than the >30 kcal./mole value for the non-induced benzoyl peroxide decomposition.

It is interesting to note that at 260 mμ the value of ϵ_C is simply the sum $\epsilon_A + \epsilon_B + (2 \times 10^3)$, since a plot (Fig. 5) of ϵ_C versus $\epsilon_A + \epsilon_B$ is extremely linear and gives a least-squares slope of 0.99 ± 0.02. This indicates that the absorbance maximum near 260 mμ for the complex represents very little more than the addition of the two molecules. It may also be taken to mean that in the complex formation there is no conjugation between the phenyl rings of the amine and peroxide. These data are then seen to be consistent with Imoto's proposed mechanism, eq. (2a).

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Résumé

On a mesuré la formation d'un complexe à l'équilibre entre des peroxydes de benzoyle substitués symmétriquement et des diéthylaniline-N,N' substituées dans l'anneau. Au départ de ces résultats, on a trouvé que la constante de vitesse pour une décomposition unimoléculaire des complexes en vue de produire des radicaux primaires, a été trouvée être approximativement égale à $10^{12} \exp\{-25 \times 10^3/RT\}$. Les résultats obtenus sont en accord avec le mécanisme postulé précédemment pour la production de radicaux en présence de monomères vinyliques.

Zusammenfassung

Das Komplexbildungsgleichgewicht zwischen symmetrisch substituierten Benzoylperoxyden und ring-substituierten N,N-Diäthylanilinen wurde quantitativ bestimmt. Die Ergebnisse liefern für die Geschwindigkeitskonstante der monomolekularen Zersetzung des Komplexes unter Bildung initiierender freier Radikale etwa $10^{12} \exp\{-25000/RT\}$. Die erhaltenen Daten entsprechen einem früher aufgestellten Mechanismus für die Radikalerzeugung in Gegenwart von Vinylmonomeren.

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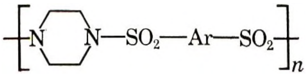
NOTES

Preparation and Thermal Properties of Some Piperazine Polysulfonamides

A number of investigators have studied the polymerization of piperazines with a variety of difunctional aromatic compounds.[1-10] Among these investigations was the preparation of polyamides from piperazines and aromatic diacid chlorides.[7,8] These polymers were of high molecular weight and exhibited appreciable thermal stability, i.e., thermogravimetric studies *in vacuo* showed breakdown in the region of 420–480°C.[11,12] An analogous system which has been only summarily investigated is that of the aromatic piperazine polysulfonamides:



The polycondensation of piperazine and *m*-benzenedisulfonyl chloride has been reported by Kwolek.[9] However, no information was given regarding the thermal properties of the resulting low molecular weight polymer.

In order to determine the thermal behavior of the aromatic piperazine sulfonamides, it was necessary to prepare some representative polymers and to subject them to softening range determinations, thermogravimetric analysis (TGA), and differential thermal analysis (DTA).

Preparation of Polymers

Piperazine was reacted with *m*-benzenedisulfonyl chloride, diphenyl ether-4,4′-disulfonyl chloride, and diphenylmethane-4,4′-disulfonyl chloride using interfacial or solution polymerization methods. In all cases, the products were soluble only in cold sulfuric acid and exhibited low inherent viscosities in that solvent.

In order to obtain a more soluble polymer, *trans*-2,5-dimethylpiperazine was used as a monomer. The polycondensation of this compound with *m*-benzenedisulfonyl chloride was performed by using methods similar to those used above. The products were soluble in a number of organic solvents (DMSO, DMF, *m*-cresol) but also were of low inherent viscosities.

Either a chloroform–water or a toluene–water solvent system was used in the interfacial polymerizations. The solution polymerizations were performed in a chloroform medium in a manner similar to that used for the corresponding polyamides.[7,8] However, the polysulfonamides were insoluble in this solvent and precipitated during the course of the polymerization. It was considered that this, in part, was responsible for the low inherent viscosities of the polymers. An attempt was made to increase the molecular weight of the products by using a reaction medium in which the polymer was soluble. Dimethyl sulfoxide, pyridine, and *N*-methyl-2-pyrrolidone were used as solvents in the polymerization of *trans*-2,5-dimethylpiperazine and *m*-benzenedisulfonyl chloride. In the case of dimethyl sulfoxide, the infrared spectrum, elemental analysis, and physical characteristics of the product indicated that the solvent had entered into or altered the course of the reaction. With pyridine and *N*-methyl-2-pyrrolidone, the products obtained were similar to those obtained when chloroform was used as a reaction medium. No appreciable increase in inherent viscosity was noted.

An attempt to prepare the above polymer by the melt polycondensation of *trans*-2,5-dimethylpiperazine and *m*-benzenedisulfonyl chloride was unsuccessful. Exten-

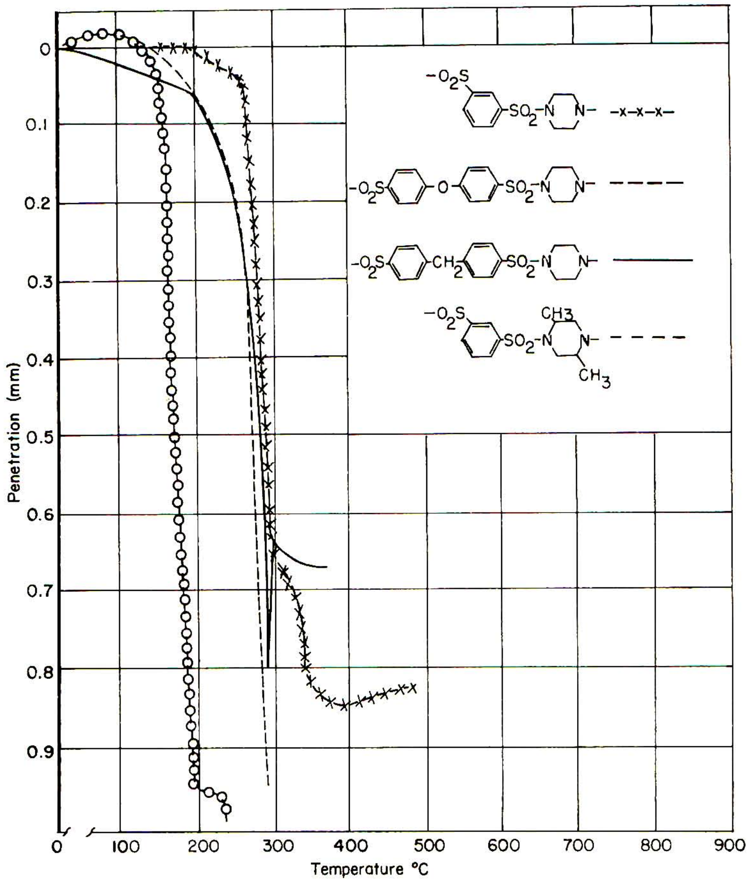


Fig. 1. Composite softening curves (ΔT = 150°C./hr.).

sive decomposition occurred during the prolonged reaction times and high temperatures (~200°C.) necessary to effect the evolution of HCl.

Properties of the Polymers

In general, the polymers were white or cream-colored powdery materials. They exhibited inherent viscosities ranging from 0.05 to 0.12. Molecular weight determinations by vapor-pressure osmometry in dimethylformamide gave values ranging from 1630 to 2290 for several of the *trans*-2,5-dimethylpiperazine polymer samples. These values would correspond to approximately 5 to 7 repeating units in the molecule.

The elemental analysis and infrared spectra of the polymers were consistent with the proposed structures. In all cases, the spectra exhibited bands at 1320–1380 and 1140–1180 cm.$^{-1}$, indicative of a sulfonamide group. Also present were bands at 2800–3000 cm.$^{-1}$, attributable to aliphatic carbon–hydrogen bonds, and bands at 1450 and 1600 cm.$^{-1}$, indicative of the phenyl nucleus.[13]

The softening range of the samples was obtained through use of a modified Vicat apparatus with the softening range being determined from a plot of temperature versus penetration (Fig. 1). The piperazine polymers were found to soften in the range of

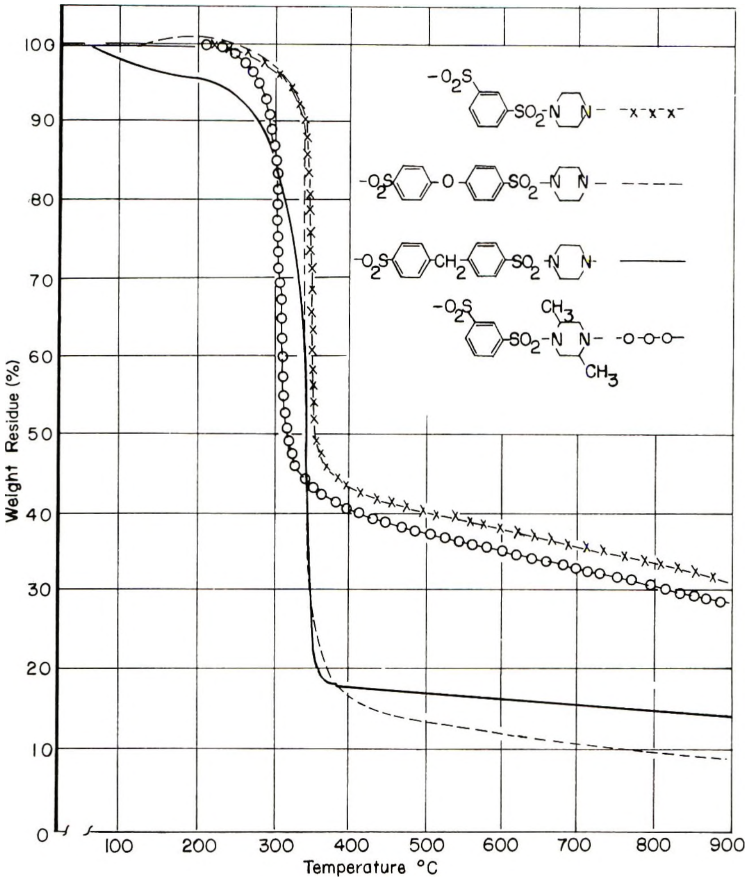


Fig. 2. Composite TGA plot ($\Delta T = 150$°C./hr.).

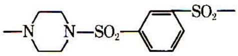
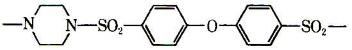
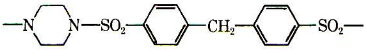
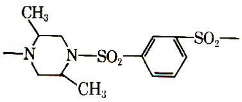
250–280°C. while the *trans*-2,5-dimethylpiperazine polymer softened in the range of 150–200°C. The thermal stability of the polymers was evaluated by thermogravimetric analysis under a nitrogen atmosphere with a plot of per cent weight residue versus temperature (Fig. 2) being made for each polymer. All of the polymers show a breakdown in the region of 300–350°C. with the polymer from the polycondensation of piperazine and *m*-benzenedisulfonyl chloride exhibiting the best stability. Differential thermal analysis of three of the polymers revealed decomposition endotherms between 324 and 370°C. The polymer from piperazine and diphenylmethane-4,4′-disulfonyl chloride had two additional endotherms at 55 and 190°C. The latter possibly can be attributed to the melting point.

A summary of the thermal behavior data is given in Table I. As can be seen, these piperazine polysulfonamides are of considerably lower molecular weight and are appreciably less stable than the aromatic piperazine polyamides reported in the literature.[7,8,11,12]

Experimental

Interfacial Polycondensation. A solution of the piperazine (0.01 mole) in 60 ml. of water was placed in a Waring Blendor. Sodium hydroxide (0.02 mole) was added as an

TABLE I

		Inversion points, °C.		
Polymer	η_{inh} (solvent; concn., g./dl.)	Softening curve	TGA curve	DTA transitions, °C.
	0.07 (H_2SO_4; 0.3)	285	350	360
	0.12 (H_2SO_4; 0.4)	275	355	—
	0.06 (H_2SO_4; 0.4)	285	355	55, 190, 324, 370
	0.07 (DMSO; 0.4)	180	310	235, 360

acid acceptor and sodium lauryl sulfate (0.1 g.) as a surface-active agent. A solution of the disulfonyl chloride (0.01 mole) in 45 ml. of alcohol-free chloroform was prepared. With the blender being run at a moderate speed, the chloroform solution was added rapidly and the blender then run at full speed for 30 min. The polymer was precipitated by the slow addition of the reaction mixture to 300 ml. of rapidly stirred acetone. After being washed with hot water, the polymer was isolated by filtration, dried in a vacuum oven, and ground into a fine powder. It was purified by extraction with methanol in a Soxhlet for 48 hr. and was then dried in a vacuum oven at 80°C. for 24 hr.

Solution Polymerization. To a solution of the disulfonyl chloride (0.01 mole) in 35 ml. of alcohol-free chloroform was slowly added a solution of the piperazine (0.02 mole) in 30 ml. of chloroform. Vigorous stirring was maintained and the solution heated to reflux. A precipitate formed almost immediately. This reaction was allowed to continue for several hours, at which time the reaction mixture was poured into petroleum ether and the precipitate isolated by filtration. It was washed well with methanol and hot water. The finely crushed polymer was extracted with methanol in a Soxhlet for 50 hr. and the product dried in a vacuum oven at 110°C. for 24 hr.

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Poly(arylene Sulfones) *Prepared by Friedel-Crafts Reactions*

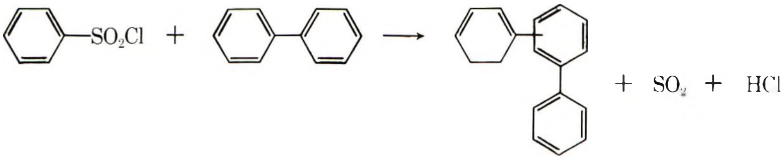
The preparation of poly(arylene sulfones) by the Friedel-Crafts reaction has been described recently. Cudby et al.[1] prepared polysulfones by homocondensation of monomers such as *p*-phenoxybenzenesulfonyl chloride, or by cocondensation of disulfonyl chlorides with dinuclear aromatic compounds such as diphenyl ether. The authors used small (up to 4%) amounts of ferric chloride and temperatures up to 260°C. Reduced specific viscosities of up to 2.0 were obtained for the homopolymer from *p*-phenoxybenzenesulfonyl chloride while values not greater than 0.6 were obtained from the two-component systems. Detailed structural examination by NMR indicated that the polymers are essentially linear and showed how the substitution depends upon the structure of the monomer. Analytical results were not shown.

Cohen and Young[2] prepared a polysulfone from diphenyl ether 4,4′-disulfonyl chloride and diphenyl ether in nitrobenzene at temperatures of up to 120°C. Equivalent amounts of aluminum chloride were present. Inherent viscosities of up to 0.35 have been obtained. The authors point out that the elemental analysis shows carbon to be 1–2% high and sulfur 1–2% low. The polymer contains varying amounts of ash, indicating that the catalyst was chemically combined with the polymer.

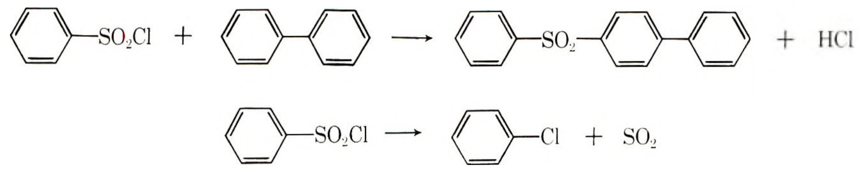
Earlier work performed in this laboratory supplements the above results. *m*-benzenedisulfonyl chloride and 4,4′-diphenyldisulfonyl chloride have been reacted with diphenyl, diphenyl ether, and diphenyl carbonate in the presence of ferric chloride, zinc dust, or aluminum chloride. The latter was used in connection with carbon disulfide or nitrobenzene as a solvent. A ratio of 2 moles of ferric chloride or aluminum chloride or 1 mole of zinc dust per mole of disulfonyl chloride was used. Reaction temperatures up to 300°C. were applied for the melt reactions and the reactions in carbon disulfide and nitrobenzene were run at 45 and 120–180°C., respectively. The reactions were performed under nitrogen.

The polymers prepared in carbon disulfide or in a melt varied from light to dark brown in color while those prepared in nitrobenzene were black. Between 60 to 80% of the polymers from the melt reactions were soluble in tetrahydrofuran or dimethylformamide while those from the solution reactions were completely soluble. Inherent viscosities between 0.07 and 0.11 (0.3% in DMF) have been obtained. Empirical viscosity–molecular weight relationships (on the basis of inherent viscosities of model compounds) suggest molecular weights of at least 3000–4000.

Elemental analyses revealed that the sulfur content was too low for polymers with a 1:1 ratio of the two components and the chlorine content much too high to be attributed to sulfonyl chloride endgroups. Extensive work by Kovacic et al.[3–9] shows that benzene and other aromatic hydrocarbons in the presence of a Lewis acid and an oxidizing agent ($FeCl_3$ or $AlCl_3$–$CuCl_2$) form polyphenylenes. It has also been found[10] that aromatic sulfonyl chlorides or disulfonyl chlorides, under pyrolysis conditions (for example, in boiling biphenyl), can react in the following manner:



with side reactions such as:



The side reactions are minimized when the solution is kept dilute in sulfonyl chloride and in the presence of copper and some other metal salts, but are catalyzed by even trace amounts of aluminum and iron.

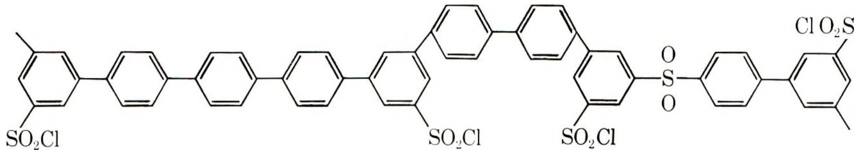
From the foregoing it is evident that carbon–carbon coupling has occurred as part of the condensation mechanism, either by the same cationic oxidative mechanism Kovacic found for aromatic hydrocarbons or by loss of SO_2 from the sulfonyl chloride. The former mechanism should lead to pendent sulfonylchloride groups. The Cl:S ratio determines the number of pendent sulfonyl chloride groups vs. the number of sulfone linkages. Alkaline fusion also has been used on selected polymers to determine the number of pendent groups. This reaction did not go to completion in several instances (based on the chlorine still present) but it showed that 54–64% or more of the sulfur was present in the form of pendent groups. The structure of several polysulfones has been calculated from the analysis data (Table I).

TABLE I

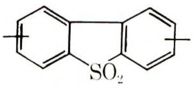
Structure of Polysulfones from *m*-Benzene Disulfonyl Chloride and Biphenyl

No.	Catalyst	Solvent	1—SO_2— linkage every.... rings	1—SO_2Cl group every.... rings	1—SO_3H group every.... rings
1	$FeCl_3$	—	6	6	—
2	Zn	—	$3^{1}/_{3}$	—	$3^{1}/_{3}$
3	$AlCl_3$	Carbon disulfide	10	$2^{1}/_{2}$	—
4	“	Nitrobenzene	—	$2^{1}/_{2}$	—

Polymer 3, for example may be represented by the following structure:

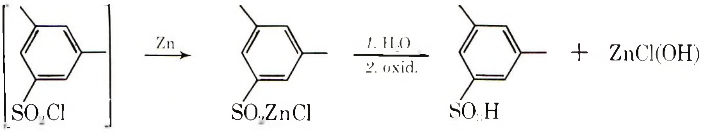


The question may arise whether dibenzothiophene dioxide type structures may form



instead of sulfone linkages. It is believed that this will not be the case. The *meta*-directing influence of the sulfonyl chloride group probably will not allow carbon–carbon coupling in *o*-position to this group. Coupling of this kind *after* a sulfone linkage has formed, appears to be even less likely.

Chlorine is practically absent in polymer 2. Since alkaline fusion indicates that 50%



or more of the sulfur is present in the form of pendent groups, these must be sulfonic acid rather than sulfonyl chloride groups. Probably a zinc salt of sulfinic acid forms first and is hydrolyzed and oxidized during the work-up (washing with water).

The sulfonyl chloride group itself is relatively stable to hydrolysis. The analysis of this polymer also suggests the presence of water bound to the sulfonic acid group as is the case with benzene sulfonic acid. The IR spectrum of this polymer (while otherwise identical to those of the other polymers) has an additional absorption at 715 cm.$^{-1}$. Thermal stability of polymer 2 is considerably lower than others. It seems feasible that the polymers with pendent sulfonyl chloride groups crosslink at higher temperatures with evolution of hydrogen chloride and form a stable network, while the one with sulfonic acid groups cleaves.

DTA shows melting point endotherms of 105°C. for polymer 1 and 126°C. for polymer 2. However, an endotherm of 224°C. was obtained for polymer 4 which is essentially a polyphenylene with high rigidity and aromaticity (black color).

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1,2,4- and 1,3,5-Trivinylbenzenes. Vapor-Phase Chromatographic and Nuclear Magnetic Resonance Characterization

The mixture of 1,2,4- and 1,3,5-trivinylbenzenes prepared as previously described[1] has been obtained in 25% yields at reaction temperatures of −10 to 10°C. The ratio of the 1,2,4- and 1,3,5-isomers in the crude reaction mixture, as determined by gas–liquid chromatography, is 90 to 10. The isomeric mixture has been separated with preparative gas chromatographic techniques similar to those used for divinylbenzene.[2] Both Perkin Elmer "R" column and a column prepared with 15% Bentone-34 and 5% polypropylene glycol (Ucon LB 550-X) on 60 mesh Chromosorb-W (80%) have been used in the Perkin Elmer Model D 154 Fractometer with thermistor detectors and six 1 in. by 0.5 m. column tubes. The injection block was maintained at 250°C., the column at 165°C., and pressure at 10 psi (97 cc./min.). At these temperatures and flow rates there is considerable loss of liquid phase into the helium carrier gas. The columns are conditioned under operating conditions prior to use to bring the loss of liquid phase to a uniform level. In operation the trivinylbenzene (2 ml.) was injected slowly as a 50% solution in xylene with 1,6-di-*tert*-butyl-*p*-cresol and quinone as inhibitors. There is considerable loss (up to 50%) due to polymerization and rapid sample injection results in almost complete polymerization in the injection block. Samples with over 10% 1,3,5-isomer are especially prone to polymerize. The retention times of the two isomers are at about 26 and 29 min. The trivinylbenzene "peak" was divided into two fractions. The first is an 83% 1,2,4- and 17% 1,3,5-mixture as determined by peak height-width at half height products. The second is a 29% 1,2,4- and 71% 1,3,5-mixture. A second separation of the first fraction gave a principal fraction over 99% pure 1,2,4-trivinylbenzene, b.p. 57°C./2 mm., n_D^{25} 1.6052. The second fraction was separated into two distinct fractions, the first 94% 1,2,4- and the second 98% 1,3,5-trivinylbenzene, b.p. 60°C./2 mm., n_D^{25} 1.5930. On a pure Bentone column the separation was better but the loss due to polymerization was increased.

The nuclear magnetic resonance spectra (Varian 4320, 60 Mc.) of the two isomers are shown in Figures 1 and 2. The 1,3,5-isomer shows the same absorption maxima seen with styrene and *m*-divinylbenzene.[3] The 60 Mc. pattern for the 1,2,4-isomer is a com-

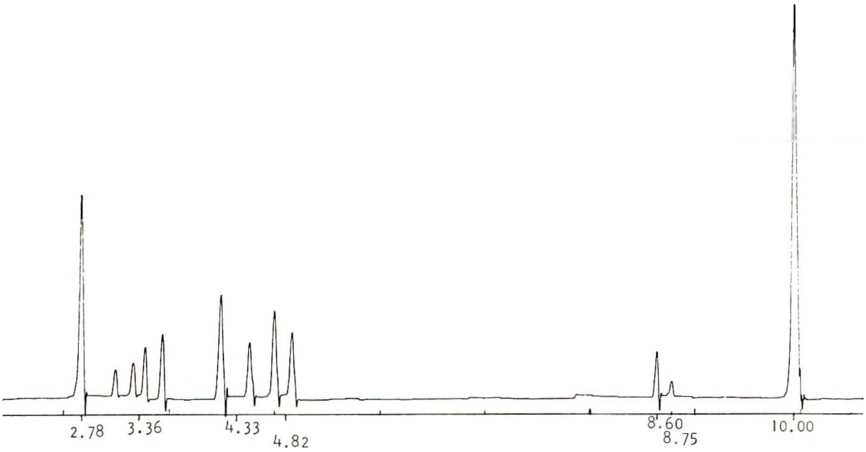

Figure 1. Nuclear magnetic resonance spectrum of 1,3,5-trivinylbenzene. Tau values from tetramethylsilane (TMS); 33% in carbon tetrachloride; extrapolated to infinite dilution. Absorption at 2.78 τ (aromatic H); 3.36 τ (J 17.4; 10.6) H_a; 4.33 τ (J 17.4) H_c; 4.82 τ (J 10.6) H_b; 8.60–8.75 τ (inhibitor).

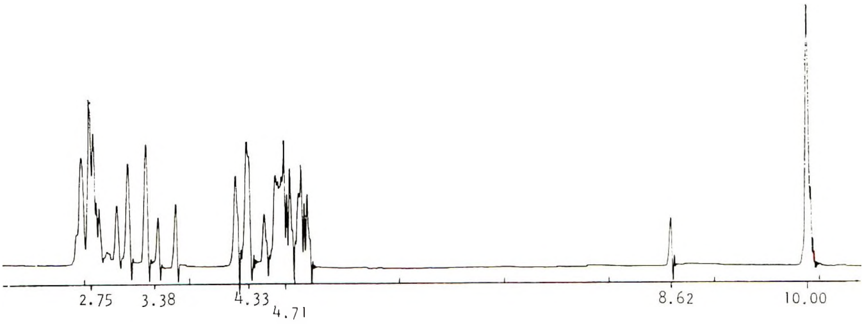

Figure 2. Nuclear magnetic resonance spectrum of 1,2,4-trivinylbenzene. Tau values from tetramethylsilane (TMS); 20% by volume in carbon tetrachloride extrapolated to infinite dilution. Absorption at 2.75 τ (aromatic H), 3.38 τ (J 18.2; 10.8) H_a; 4.33; 4.71 τ H_b and H_c; 8.62 τ (inhibitor).

plicated combination of the *o*-, *m*-, and *p*-divinylbenzene absorption characteristics. Further study with spin decoupling and at 100 Mc. is planned to clarify the assignments.

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BOOK REVIEWS

An Atomistic Approach to the Nature and Properties of Materials. J. A. PASK, Ed. Wiley, New York, 1966. 477. $19.95.

This is an excellent educational book for high school and college graduates who want to familiarize themselves with the principles of the atomic and molecular approach for the understanding of the properties of matter.

The individual chapters (17) are, on the average, 30 pages long and are surprisingly homogeneous if one considers that each of them was written by a different author. Obviously the editor succeeded to exercise a beneficial activity of bringing the different chapters to the same level.

Each chapter starts with an explanation of the basic aspects of the subject matter, proceeds to the treatment of increasingly complicated conditions, and winds up with relationships between properties and structure. There is a carefully selected and, in most cases, rather elaborate text of references at the end of each chapter.

In respect to the origin of the individual contributor the book has a distinct Western touch which does not hurt its content and usefulness at all. I liked it very much and can recommend it with good conscience as a source of useful and reliable knowledge.

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Polymerization by Organometallic Compounds. L. REICH and A. SCHINDLER. Interscience, New York, 1966. x + 740. $25.00.

This is Volume 12 of *Polymer Reviews*, the Interscience series edited by H. F. Mark and E. H. Immergut.

Workers in the field of organometallic-initiated polymerizations have been so proliferous in the last 15 years that their research efforts have resulted in a voluminous journal and patent literature. It is a formidable task for the new worker to collect and assess this vast literature. Because they wanted to do something about this problem the authors set out "to present, in a single volume and in an organized and categorized sequence, pertinent information derived from the literature (scattered and often confusing) on organometallic-initiated polymerizations." They suggest that the book should be useful mainly to research workers and graduate students who have already been introduced to polymer chemistry and who desire to broaden their knowledge in the field of organometallic-catalyzed polymerizations.

I believe that this volume meets this objective. The chapters are well organized and highly informative. The authors have been diligent in collecting leading references and in reporting faithfully the pertinent data and the interpretations of the original publications.

This volume offers many examples which demonstrate convincingly that organometallic compounds have found wide application in the polymerization of monomers by most of the presently conceived modes or catalysis. Chapters III and IV describe mainly polymerizations by the Ziegler type catalysts; Chapter V is concerned with the Alfin catalyst while Chapters VI, VII, and VIII describe polymerizations by free-radical, anionic, and cationic mechanisms, respectively.

The authors have chosen to restrict the discussions to (*a*) catalysts in which at least one of the components contains a metal–carbon bond and (*b*) linear monomers which contain a single double bond or two conjugated double bonds.

Some of the chapters, however, are overburdened with detail which make their reading difficult for those who are seeking a general insight into the subject matter. Also, parts of Chapter II (entitled "General Theoretical Concepts of Polymerization") could have been condensed or omitted since this information can be generally found in texts on polymerization chemistry.

In summary, this book is timely and extremely useful in a field which shows no sign of slowing down in the generation of new information.

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