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Diels-Alder Polymers. III. Polymers Containing Phenylated Phenylene Units

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Synopsis

The Diels-Alder reaction of biscyclopentadieneones with diacetylenes produces colorless, soluble, phenylated polyphenylenes of high molecular weight ($\bar{M}_n \simeq 40{,}000$) in nearly quantitative conversions. The polymers are noncrystalline, form clear films, and are stable in air to 550°C. Under nitrogen, the polymers lost approximately half the phenyl groups attached to the phenylene main chain to give brown-black insoluble polyphenylenes of very low crystallinity.

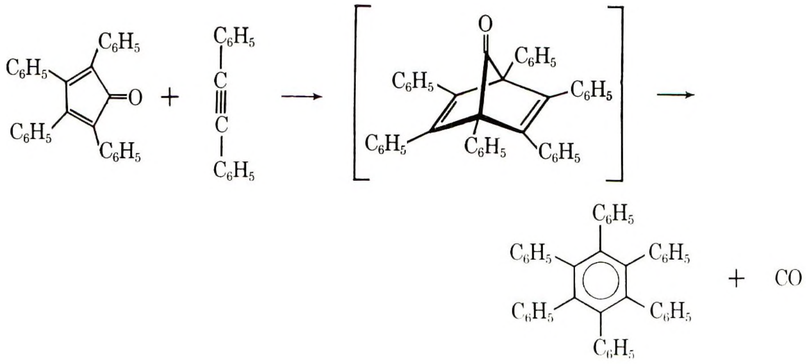
INTRODUCTION

The synthesis of polymers through utilization of the Diels-Alder reaction as a means of propagation, has been reviewed.[1] The majority of the Diels-Alder reactions that are employed as a propagation mode do not produce high molecular weight polymers because of the frequency of side reactions and the ease with which the reverse reactions take place. Therefore, in order to achieve a successful polymerization, a reaction for which a perfect stoichiometry can be maintained and which will suffer no reversal is highly desirable.

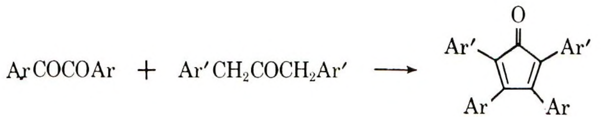
High molecular weight Diels-Alder polymers have been realized[2-4] by the reaction of such dienes as tetrasubstituted cyclopentadieneones, α-pyrones, and thiophene dioxides with double ethylenic dienophiles to produce adducts which eliminate carbon monoxide, carbon dioxide, and sulfur dioxide, respectively, at elevated temperatures. This reaction affords good monomer balance and prevents reversibility of the initial adduction.

The Diels-Alder addition of tetraphenylcyclopentadieneone (tetracyclone) to acetylenes affords substituted benzenes by the elimination of carbon monoxide from the intermediate adduct [eq. (1)]. The reaction is carried out at elevated temperatures (100–400°C.) with or without solvent. The yields are generally excellent and often quantitative.

The preferred route to the synthesis of tetraarylated cyclopentadieneones is the base-catalyzed condensation of benzils and benzyl ketones [eq. (2)].[5] Of particular interest to the formation of polymers is the fact that many bistetracyclones have been synthesized by this method.[5,6] The utilization of this Diels-Alder reaction in polymer synthesis requires the reaction of suitable diethynyl compounds with the appropriate bistetracy-

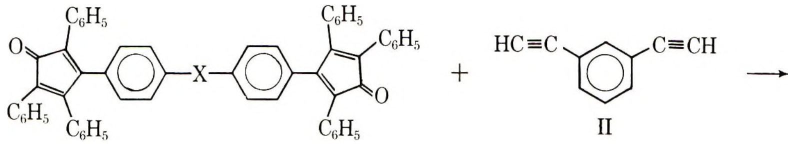


(1)

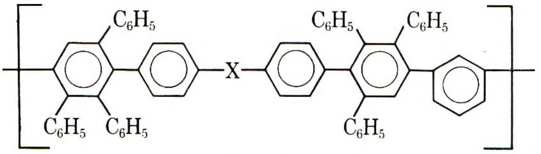


(2)

clones, and these requirements are met by the reaction of the bistetracyclones (Ia–c) with *m*- (II) or *p*-diethynylbenzene (III) to give phenyl-substituted polyphenylenes [eqs. (3),(4)].[7–9] Although the Diels-Alder reaction can take place to produce either *meta* or *para* attachments on the phenylated phenylene ring, only *para* links are depicted.



Ia. X = nil
b. X = O
c. X = S



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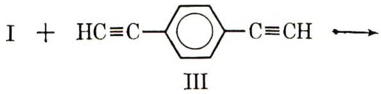
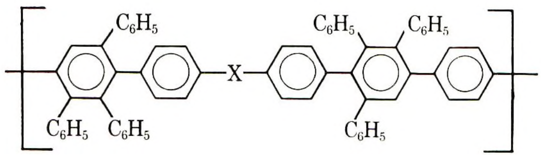
IVa. X = nil
b. X = O
c. X = S





(4)

Va. X = nil
b. X = O
c. X = S

EXPERIMENTAL

Monomers

Bistetracyclones. The bistetracyclones (I) were prepared by the condensations of the appropriate bisbenzils with dibenzyl ketone in refluxing ethanol.[6] The bistetracyclones were further purified by chromatography on Woelm neutral alumina with toluene–ether (9:1). A small sample was then rechromatographed to assure that only one compound was present.

Diacetylenes. The diacetylenes, *m*- (II) and *p*-diethynylbenzene (III), were synthesized by the bromination of divinylbenzenes, followed by dehydrobromination.[10] The *m*-diethynylbenzene was distilled and the *p*-diethynylbenzene was sublimed just prior to polymerization.

Solvent

The solvent used throughout for polymerization, membrane osmometry, and viscosity measurements was reagent-grade toluene. No attempt to purify it further was undertaken.

Polymerizations

All polymerizations were carried out by the same method (Table I); a typical polymerization to yield the poly(hexaphenylpentaphenylene oxide) (Vb) follows. A mixture of 0.1038 g. (0.823 mmole) of *p*-diethynylbenzene (III)[7,8,10] and 0.6448 g. (0.823 mmole) of 3,3′-oxydi-*p*-phenylene)bis-2,4,5-triphenylcyclopentadieneone (Ib)[6] was placed in a 20-ml. polymerization tube with 10 ml. of toluene. The contents of the tube were degassed by several freeze–thaw cycles at liquid nitrogen temperatures and then sealed *in vacuo*. Toluene (200 ml.) was added to a 600-ml. Paar pressure reactor, the tube was placed inside, and the reactor was closed and heated to 200°C. for 24 hr. After the reactor had cooled to room temperature, the contents of the tube were poured into 200 ml. of acetone. The precipitated polymer was filtered and dried *in vacuo* at 60°C. for 24 hr. The white polymer, 0.639 g. (91%) was reprecipitated from toluene by acetone, $[\eta] = 0.58$ (25°C. in toluene). Viscosities were obtained with a Cannon-Ubbelohde microdilution viscometer No. 75.

Thermal Analyses

Thermogravimetric analyses were carried out on a DuPont 950 thermogravimetric analyzer. Under an atmosphere of air, at a heating rate of 5°C./min., all polymers showed a major break near 550°C. and rapidly decomposed completely (Fig. 1). In a nitrogen atmosphere with the same heating rate, all the polymers rapidly lost about 30% by weight near 575°C. and then underwent a very slow weight loss above this temperature (Fig. 1).

Powdered samples of polymers Va and Vb were heated to 750°C. under a slow stream of nitrogen for 30 min., and the volatile product from the pyrolysis was caught in a liquid nitrogen trap. Vapor-phase chroma-

TABLE I
Polymerization Results

Bistetracyclones	Diacetylene	Polymer	$[\eta]_{sp}$, dl./g.[a]	DTA transition, °C.	Calculated C, %	Calculated H, %	Found C, %	Found H, %
Ia	III	IVa	0.26	120	94.7	5.30	94.2	5.15
Ia	III	Va	0.46	—	94.7	5.30	93.9	5.59
Ib	II	IVb	0.32	145	92.9	5.20	92.8	5.56
Ib	III	Vb	0.61	195	92.9	5.20	94.4	5.09
Ic	II	IVc	0.20	135	91.2	5.10	91.2	5.28
Ic	III	Vc	0.40	150	91.2	5.10	90.9	5.56

[a] In toluene at 25°C.

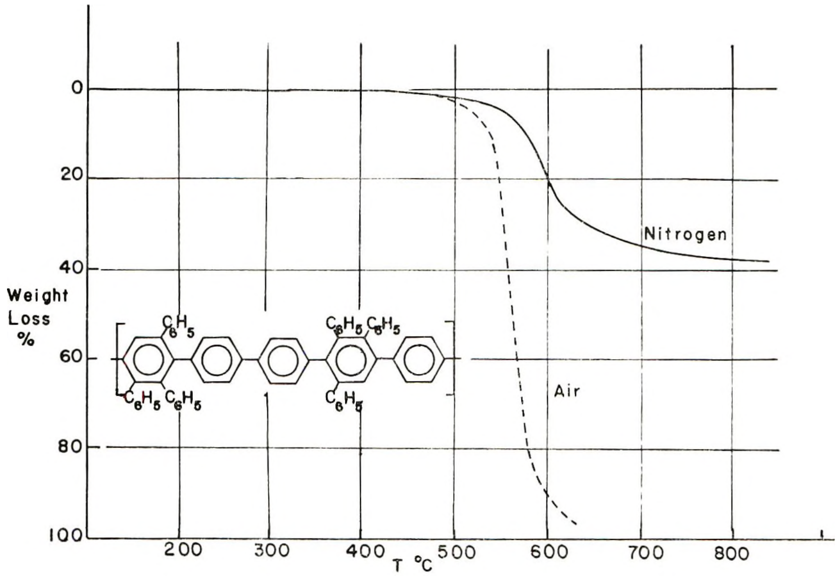


Figure 1.

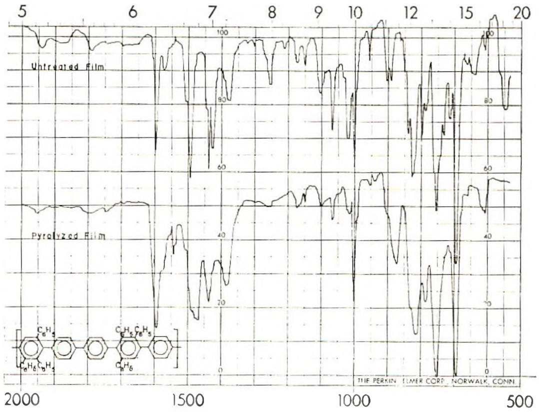


Figure 2.

tography of the liquid at 90°C. on a 2-ft. silicone-on-Chromasorb column revealed the presence of benzene which was identified by comparison with an authentic sample. Chromatography at 185°C. showed the presence of biphenyl which was similarly identified. Higher molecular weight fragments were not identified.

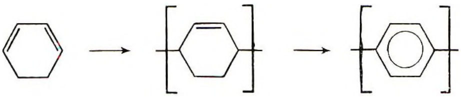
Polymers Va and Vb were not crystalline, as determined by x-ray powder patterns, and the infrared spectra (KBr pellet) showed maxima for hydrogens on the aromatic nuclei near 900 (isolated), 825 (2 adjacent), 755, and 695 cm.$^{-1}$ (5 adjacent).[11] Pyrolyzed samples of powdered Va and Vb showed a marked decrease in the intensity of the maximum at 695 cm.$^{-1}$. The spectra of a film of Vb before and after a partial pyrolysis under nitrogen at 750°C. for 10 min. are shown in Figure 2.

The differential thermal analyses of the polymers were carried out on a DuPont 900 differential thermal analyzer. The transitions reported are those at which the slight changes in the slopes of ΔH versus T were observed.

DISCUSSION

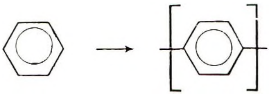
One of the most intriguing polymer structures, both with respect to physical properties and thermal stability, is the polyphenylene structure. Two major synthetic approaches to this structure have been explored previously.

The 1,4-addition polymerization of 1,3-cyclohexadiene to afford a polymer containing cyclohexene units, and the subsequent dehydrogenation, [eq. (5)] is one approach which has beem employed to obtain poly-*p*-phenylene.[12-15] This method has not been particularly successful since the polycyclohexadiene is a somewhat low molecular weight polymer


(5)

($[\eta] = 0.23$), the black polyphenylene polymers obtained therefrom are either insoluble or have very low solubility, the synthesis is difficult, and some of the polyphenylenes do not show quite the good thermal stability that would be expected.

The other major approach to the synthesis is the dehydrogenation (oxidation) of benzene[16-18] or other aromatics[19,20] to afford poly-*p*-phenylene and other aromatic polymers, respectively [eq. (6)].


(6)

The oxidation of benzene, although relatively easy to carry out, affords a brown polymer which is reported to have mainly *p*-phenylene recurring units with some branching or crosslinking. This polymer also suffers from insolubility, and a thermal stability that is not as good as might be expected. For example, this polyphenyl shows appreciable weight loss in air at 450°C., while other polyaromatic heterocyclics reveal breaks at 500–550°C.

The synthesis of polymers by the Diels-Alder reaction of the bistetracyclones (Ia–c) with the diethynylbenzenes (II, III) results in polymers (IV, V) containing either phenylated polyphenylene units or phenylene units linked by groups such as oxygen and sulfur. In addition to the fact that these polymers exhibit thermal stability associated with the polyaromatic structure, they are colorless and appreciably soluble in common organic solvents. Thus, the polymers were studied with respect to (*1*) the effect of monomer balance on molecular weight and other poly-

TABLE II
Effect of Monomer Balance on Molecular Weight (Polymer Vb)

Mole ratio Ib:III[a]	$[\eta]_{sp}$, dl./g.[b]	$\bar{M}_n \times 10^{-4}$ [c]
1.02	0.61	3.6
1.01	0.64	—
1.00	0.58[d]	2.9
0.98	0.38	1.9

[a] At a concentration of 0.08 mole/l. for each monomer.

[b] Taken at 25°C. in toluene.

[c] Obtained with a Hewlett-Packard high-speed membrane osmometer using a superdense membrane at 29.5°C. in toluene.

[d] When this reaction was run with a concentration of 0.01 mole/l. for each monomer the viscosity was 0.16.

merization conditions, *(2)* the relationship of structure to some of the more obvious physical properties, *(3)* the thermal stability, and *(4)* the mechanism of thermal degradation.

In order to achieve proper monomer balance, great care in the purification of the monomers was taken. The stoichiometry required to achieve the highest molecular weight polymer (Table II) required a 1% excess of bistetracyclone. This suggests either that there were impurities in the bistetracyclone that escaped detection in chromatography, or that some side reaction upset monomer balance.

Severe polymerization conditions (350°C., 48 hr.), in fact, gave lower molecular weight polymers ($[\eta] = 0.1$) and a small amount of black, insoluble precipitate. These results suggest that there was considerable degradation which interfered with monomer balance. Such degradation reactions at elevated temperatures are known for many tetracyclones.[5]

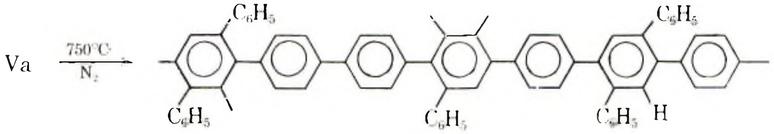
The unusual effect of concentration on the molecular weight has also been observed. An increase in the concentration of monomer from 0.01 to 0.08 mole/l. gave an increase in viscosity from 0.16 to 0.58 for polymer Vb. Although these results are somewhat difficult to explain, they are not without precedent for this type of polymerization.[3]

The different polymers (IVa–c and Va–c) obtained from these polymerizations showed very little differences in solubility. All the polymers were soluble to the extent of 10% in toluene, and clear films could be cast from chloroform. The differential thermal analyses of the polymers showed minimal changes in the slope of ΔH versus T lines, and no definite conclusions could be drawn as to the nature of the transition (Table I). Polymers Va and Vb showed no crystallinity.

Thermogravimetric analysis of the polymers reveals that the polymers rapidly lose weight near 550°C. in air. However, in nitrogen, all the polymers show breaks near 575°C., at which temperature the polymers lose approximately 30% of their total weight. Above 650°C., the decomposition was slow (Fig. 1). The fact that all of the polymers showed a nearly identical (30%) weight loss under nitrogen at exactly the same temperature led us to suspect that the one identical structural feature in all the polymers—the phenylated phenylene ring—was responsible.

Samples of the polymers Va and Vb were pyrolyzed at 750°C. under nitrogen to afford benzene, biphenyl, and other higher-boiling hydrocarbons as volatile products of 30% total weight. The pyrolyzed polymer, a black, noncrystalline insoluble material showed a marked decrease in the amount of monosubstituted phenyl groups compared to the starting polymer as observed by the infrared spectra (Fig. 2). These results substantiate the loss of phenyl groups from the phenylated phenylene ring.

From these results, several mechanisms for the pyrolysis and the structures of the pyrolyzed polymers can be postulated. The loss in weight of 29% the total weight of polymer is accounted for by the loss on the average of only three of the six phenyl substituents per recurring unit. It would be expected that because of steric effects, the phenyl group between the main chain attachment and the adjacent phenyl substituent would be most easily lost as a phenyl radical. This radical could then account for the presence of benzene by hydrogen abstraction or biphenyl by coupling. The radical thus generated on the chain could abstract hydrogen, serve as a crosslinking site, or enter into a series of reactions to afford a graphite-like structure at that site [eq. (7)]. It is also possible that two adjacent phenyl substituents could crack off to form biphenyl, leaving behind a reactive benzyne intermediate. Since the pyrolyzed polymer reveals very minimal crystallinity and yet is insoluble, crosslinking must have taken place during the pyrolysis.



(7)

It is particularly interesting that these polymers have much the same properties as those obtained from the oxidation of benzene.[16–18] The color developed by the polymer during pyrolysis indicates that enough phenyl groups have been lost to remove hindrance to phenyl coplanarity in the main chain. Yet the polymers are insoluble, apparently because of crosslinking and not because of crystallinity or some effect of chain stiffness.

A more extensive investigation of the mechanism of thermal degradation, polymerization, and the physical properties of other polymer structures which can be obtained from this reaction is in progress.

We wish to thank Professor N. C. Baenziger for the x-ray determinations.

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Résumé

La réaction de Diels-Alder des biscyclopentadiénones avec les diacétylènes produit des polyphénylènes phényles, incolores, solubles, de poids moléculaire élevé ($\bar{M}_n$ = 40.000) avec des degrés de conversion quasi quantitatifs. Les polymères ne sont pas cristallins, ils forment des films clairs et sont stables à l'air jusqu'à 550°C. Sous azote, les polymères perdent approximativement la moitié des groupes phényles attachés à la chaîne principale phénylénique et fournissent des polyphénylènes insolubles brun-noirs de cristallinité très basse.

Zusammenfassung

Die Diels-Alder Reaktion zwischen Biscyclopentadienonen und Diacetylenen führt in fast quantitativer Ausbeute zu farblosen, löslichen, hochmolekularen ($\bar{M}_n \simeq$ 40.000) phenylierten Polyphenylenen. Die Polymeren sind nicht kristallin, bilden klare Filme und sind in Luft bis 550°C. beständig. Unter Stickstoff verlor das Polymere etwa die Hälfte der an der Phenylen-Hauptkette befindlichen Phenylgruppen under Bildung schwarzbrauner, unlöslicher, sehr wenig kristalliner Polyphenylene.

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Effect of Oxygen on the γ-Radiation-Induced Polymerization of Ethylene

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Synopsis

The effects of oxygen on the γ-radiation-induced polymerization of ethylene were studied at a temperature of 30°C.; the pressure was 400 kg./cm.^{2}, the dose rate was 1.9×10^5 rad/hr.; and oxygen content was from 1-2000 ppm. The main product was solid polymer, and no liquid product was found. The gaseous products were hydrogen, acetylene, higher hydrocarbons, carbon dioxide, aldehydes, and acids. Several kinds of carbonyls similar to those formed in γ-ray oxidized polyethylene were observed in the polymer. The polymer yield and the degree of polymerization decreased markedly with increasing oxygen content, while the amount of carbonyls in the polymer increased. The number of moles of polymer chain and the amounts of hydrogen and acetylene were found to be almost independent of the oxygen content. The polymerization of pure ethylene was not affected by carbon dioxide and formic acid. On addition of acetaldehyde, the polymer yield and the degree of polymerization decreased markedly, while the number of moles of polymer chain increased. In the polymerization of ethylene containing oxygen, both the rate of oxygen consumption and the carbonyl content of the polymer increased, while the inhibition period decreased by the addition of acetaldehyde. It was found that the degree of polymerization after the inhibition period is almost independent of the reaction time in the presence of acetaldehyde, while it increases with the time in the absence of acetaldehyde.

INTRODUCTION

It has been reported by a few workers that a very small amount of oxygen inhibits the γ-radiation-induced polymerization of ethylene. Hayward et al.[1] pointed out that the inhibition period is roughly proportional to the amount of oxygen added. Steinberg et al.[2] reported the induction period is practically eliminated when the oxygen concentration is decreased less than 60 ppm. More recently, Munari et al.[3] found, however, that 10 ppm of oxygen lowers the yield, and proposed an inhibition mechanism in which a stable, long-lived peroxide radical is formed by the reaction of the growing radical with oxygen.

The present investigation was undertaken to determine the effect of oxygen on the polymerization in connection with the gaseous products and the polymer structure.

EXPERIMENTAL

The reaction apparatus, ethylene monomer, and molecular weight determination method were the same as described in previous papers.[4,5] Before the reaction vessel was filled with ethylene, the system was evacuated to less than 1 mm. Hg, and desired amount of air or oxygen (99.9% pure) was introduced. Commercially available acetaldehyde and formic acid of extra-pure reagent grade, and carbon dioxide (99.99% pure) were used. The γ-radiation was from a 5,000 curie ^{60}Co source and the method of dosimetry was the same as that reported previously.[5]

After the irradiation, about 25 liters of residual gas was passed at a rate of 200 ml./min. through about 70 ml. distilled water by use of a glass bubbler placed in an ice-water bath. The sample was diluted to 100 ml., and used for analysis for aldehydes, acids, ethylene oxide, and hydrogen peroxide. Total aldehyde content was determined by the silver oxide oxidation method of Mitchell and Smith,[6] formaldehyde by the phenylhydrazine hydrochloride–potassium ferricyanide method of Tannenbaum,[7] acids by direct titration with alcoholic sodium methylate,[6] and ethylene oxide by a colorimetric determination method by conversion to formaldehyde.[8] Hydrogen peroxide was analyzed qualitatively by a method involving decoloration of dichromate ion. The analytical method for oxygen, nitrogen, hydrogen, methane, ethane, acetylene, and hydrocarbons higher than C_3 was same as that reported previously.[5] Oxygen was also determined by using a micro oxygen analyzer, Model HRL (Horiba Co.). Carbon monoxide and carbon dioxide were determined by using a Shimadzu GC-1B gas chromatograph with a 2-m. activated charcoal column (50°C.). A 2-m. poly(ethylene glycol) column (100°C.) was used for alcohols and water.

The infrared spectra of the polymer produced were measured with a Nipponbunko Model DS 301 infrared spectrophotometer using NaCl optics.

RESULTS AND DISCUSSION

Oxygen Balance

As can be seen in Table I, ethylene containing 1838 ppm oxygen gave mainly solid polymer on γ-irradiation, while no liquid products were obtained. Results of analysis of the gaseous products are shown in Table II. The main products were found to be hydrogen, acetylene, higher hydrocarbons, carbon dioxide, aldehydes, and acids. Small amounts of carbon monoxide, alcohols, ethylene oxide, water, no hydrogen peroxide, and a relatively large amount of oxygen were also observed. The fact that the polymerization can take place in spite of the presence of oxygen (395 ppm) is very important in contrast with the result that no polymer was formed when this amount of oxygen is present at the initial stage.

TABLE I
Polymers Formed Under Various Conditions[a]

Polymer	Irradiated system	Pressure, kg./cm.^{2} Initial	Pressure, kg./cm.^{2} Final	Time, hr.	Temperature, °C.	Dose rate $\times 10^{-5}$, rad/hr.	Yield, g.	Degree of polymerization $\times 10^{-3}$
A	C_2H_4	399	366	1	30	1.9	2.12	6.321
B-1	C_2H_4	401	380	0.75	30	1.9		
B-2[b]	Polymer + O_2	1[c]	1[c]	63	30	1.9	1.36	4.286
C	C_2H_4 + 1838 ppm. O_2	395	363	63	30	1.9	1.66	0.196

[a] Reactor volume, 100 ml.

[b] After the polymerization of B-1, ethylene was purged and oxygen of 1 kg./cm.^{2} was charged and then the system was irradiated.

[c] Oxygen pressure.

TABLE II

Gaseous Products in the γ-Radiation-Induced Polymerization of Ethylene Containing Oxygen[a]

	Feed gas		Residual gas	
	ppm	$10^5 \times$ mole/l.	ppm	$10^5 \times$ mole/l.
Oxygen	1838	2966	395	617
Nitrogen	8	14	9	13
Hydrogen	0	0	433	676
Methane	87	140	94	146
Ethane	213	344	287	447
Acetylene	0	0	559	872
C_4 hydrocarbons	0	0	52	81
$>C_6$ hydrocarbons	0	0	672	1049
Carbon monoxide	0	0	5	7
Carbon dioxide	0	0	153	238
Alcohols	0	0	83	129
Methyl alcohol	0	0	55	85
Ethyl alcohol	0	0	28	45
Aldehydes	0	0	343	535
Formaldehyde	0	0	33	51
Acids	0	0	457	712
Ethylene oxide	0	0	41	64
Water	0	0	35	54
Hydrogen peroxide	0	0	0	0

[a] Reaction conditions: initial pressure, 395 kg./cm.^{2}; final pressure, 364 kg./cm.^{2}; temperature, 30°C.; time, 63 hr.; dose rate, 1.9×10^5 rad/hr.; reactor volume, 100 ml.

TABLE III

Oxygen Balance[a]

	O_2 in reactant		O_2 in product	
	$10^5 \times$ mole/l.[b]	%	$10^5 \times$ mole/l.[b]	%[c]
Oxygen	2966	100.0	617	20.8
Carbon monoxide			4	0.1
Carbon dioxide			238	8.0
Alcohols			64	2.2
Aldehydes			268	9.0
Acids			712	24.0
Ethylene oxide			32	1.1
Water			27	0.9
Polymer			982[d]	33.1
Total	2966	100.0	2944	99.2

[a] Reaction conditions: same as given for Table II.

[b] Amount given as moles oxygen per reactor volume of 1 liter.

[c] Per cent of the amount of oxygen in products to that in reactants.

[d] Estimated as the residual from the results of the elementary analysis of the polymer (C, 83.95%; H, 14.17%).

The material balance of oxygen between the reactants and the products is shown in Table III. The fact that more than 30% of the feed oxygen was found in the polymer indicates that oxidation of the polymer chain occurs. Oxygen in the gaseous products was mainly found as carbon dioxide, acids, and aldehydes. Since aldehydes are considered to be primary oxidation products of ethylene and growing radical, and acids and carbon dioxide are subsequent oxidation products of aldehydes, this result indicates that the mechanism of radiation oxidation of ethylene at a normal temperature is similar to that of thermal slow oxidation of ethylene at high temperature.[9,10]

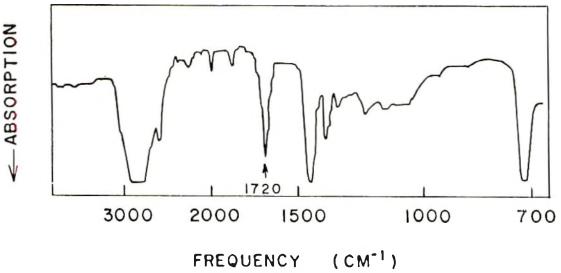


Fig. 1. Infrared spectrum of polymer C (described in Table I).

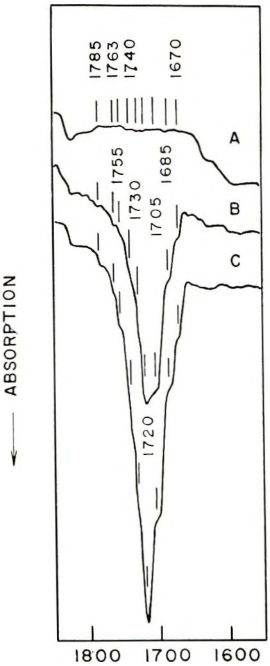
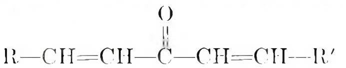
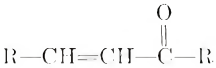
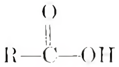
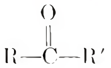
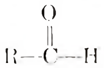
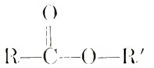
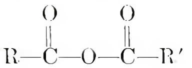
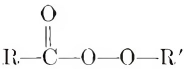
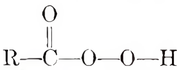


Fig. 2. Carbonyl-stretching region of infrared spectra of the polymers described in Table I.

TABLE IV
Characteristic Absorption Maxima for Various Types of Carbonyl Groups in Polyethylene[11,12]

Type of carbonyl group	Absorption maximum, cm.$^{-1}$
 $\mathrm{R{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH{-}R'}$	1670
 $\mathrm{R{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}R}$	1685
 $\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OH}$	1705
 $\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}R'}$	1720
 $\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}H}$	1730
 $\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}R'}$	1740
 $\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'}$	1755
 $\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}R'}$	1763
 $\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}H}$	1785

Polymer Structure

As is shown in Figure 1, the infrared spectrum of the polymer formed by the experiment described above displayed a strong absorption band at 1720 cm.$^{-1}$, assigned to the carbonyl group, in addition to typical polyethylene bands. Figure 2 shows the infrared spectra in the carbonyl stretching region of polymers obtained under the conditions shown in Table I. The characteristic absorption maxima for various types of carbonyl groups[11,12] are shown in Table IV. The carbonyls were scarcely observed in the polymer obtained by the polymerization of pure ethylene (polymer A), while several kinds of carbonyls were found in the γ-ray-oxidized polymer (polymer B) and the polymer obtained by the polymerization of ethylene containing oxygen (polymer C). Since the types of carbonyls in polymer C are similar to those in polymer B, it can be concluded that the oxidation of the polymer chain also occurs simultaneously in this polymerization.

Effects of Oxygen Content

The results of the polymerization of ethylene containing various concentrations of oxygen are shown in Table V. Table V shows that the amount ef carbonyls calculated from the peak at 1720 cm.$^{-1}$ by the method of Rugg et al.[11] increases with the oxygen content. As is shown in Figure 3, both the moles of polymerized monomer M_p (that is, polymer yield) and the de-

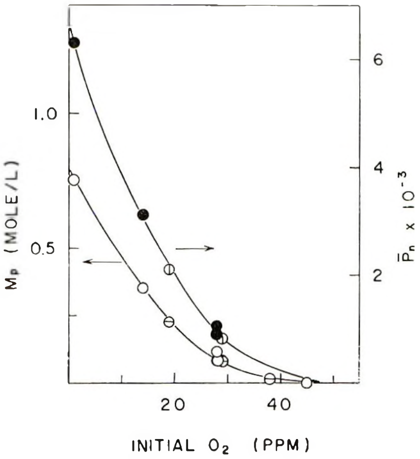


Fig. 3. Effect of initial oxygen content on the amount of polymerized monomer M_p and the degree of polymerization P_n with addition of (○), (●) air or (⊖), (⦶) oxygen. Initial pressure, 400 kg./cm.^{2}; temperature, 30°C.; time, 1 hr.; dose rate, 1.9 × 10^5 rad/hr.; reactor volume, 100 ml.

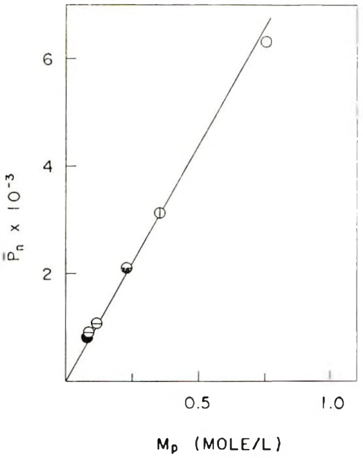


Fig. 4. Relation between the degee of polymerization $\bar{P}_n$ and the amount of polymerized monomer M_p for various additives and initial oxygen contents: (○) air, 1 ppm; (⦶) air 14 ppm; (⊖) air, 28 ppm; (◒) oxygen, 19 ppm; (●) oxygen, 29 ppm. Initial pressure, 400 kg./cm.^{2}; temperature, 30°C.; time, 1 hr.; dose rate, 1.9 × 10^5 rad/hr.; reactor volume, 100 ml.

gree of polymerization ($\bar{P}_n$) decrease rapidly with increasing the oxygen content. The plots of M_p versus $\bar{P}_n$ at various oxygen contents lie on a straight line passing through the origin (Fig. 4). Therefore, it is concluded that the number of moles of polymer chain N_p (defined by the ratio of the moles of polymerized monomer to the number-average degree of polymerization, i.e., $M_p/\bar{P}_n$) is independent of the oxygen content. Further, Figure 5 shows that the amounts of hydrogen and acetylene formed are independent of the oxygen content. The molar ratio of C_2H_2 to H_2 is found to be about 2. From these results (Figs. 4 and 5), it is concluded

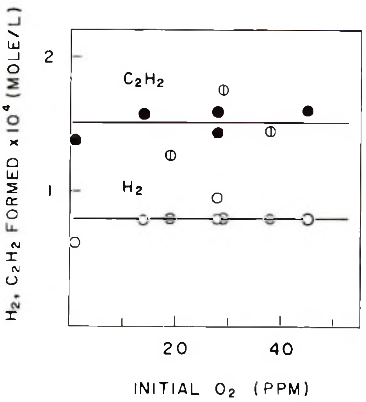


Fig. 5. Effect of initial oxygen content on the amounts of hydrogen and acetylene formed with addition of (O), (●) air and (⊖), (⦶) oxygen. Initial pressure, 400 kg./cm.²; temperature, 30°C.; time, 1 hr.; dose rate, 1.9 × 10⁵ rad/hr.; reactor volume, 100 ml.

that the initiation reaction with the mechanism proposed in the previous paper[5] is not inhibited by oxygen. The conclusion is consistent with the result that the carbonyl content in the polymer, which is indicative of the oxidation rate, increases with the oxygen content.

TABLE V
Effect of Oxygen on the Polymerization of Ethylene[a]

Additive	O_2 content, ppm		M_p, mole/l.	$\bar{P}_n$ $\times 10^{-3}$	Carbonyl content $\times 10^3$, %	Gaseous product $\times 10^4$, mole/l.	
	Initial	Final				H_2	C_2H_2
None	1	1	0.756	6.32	4.2	0.62	1.38
Air	14	4	0.354	3.14	8.6	0.79	1.58
Air	28	18	0.117	1.07	28.2	0.96	1.60
Air	28	15	0.087	0.91	—	0.80	1.44
Air	45	25	0.000	—	—	0.80	1.61
O_2	19	13	0.230	2.11	4.7	0.80	1.27
O_2	29	18	0.080	0.82	—	0.80	1.76
O_2	38	32	0.015	—	—	0.80	1.45

[a] Reaction conditions; initial pressure, 400 kg./cm.²; temperature, 30°C.; time, 1 hr.; dose rate, 1.9 × 10⁵ rad/hr.; reactor volume, 100 ml.

Effects of Carbon Dioxide, Acetaldehyde, and Formic Acid

As was described above, the main oxygen-containing by-products in the polymerization of ethylene containing oxygen were carbon dioxide, aldehydes, and acids. Several experiments were carried out in order to study the effects of carbon dioxide, acetaldehyde, and formic acid on the polymerization of pure ethylene. As shown in Table VI, the polymerization was little affected by the addition of carbon dioxide and formic acid. It is, therefore, considered that these compounds formed in the polymerization

TABLE VI
Effect of Additives on the Polymerization of Pure Ethylene[a]

Additive	Additive concn., mmole/l.[b]	M_p, mole/l.	$\bar{P}_n \times 10^{-3}$	$N_p \times 10^4$, mole/l.
None	—	0.666	6.07	1.10
CO_2	30	0.647	5.00	1.29
CH_3CHO	36	0.186	0.28	6.64
HCOOH	53	0.630	4.11	1.53

[a] Reaction conditions: initial pressure, 400 kg./cm.^{2}; temperature, 30°C.; time, 1 hr.; dose rate, 1.9×10^5 rad/hr.; initial oxygen content, 1 ppm; reactor volume, 100 ml.

[b] The amount of additive per reactor volume of 1 liter.

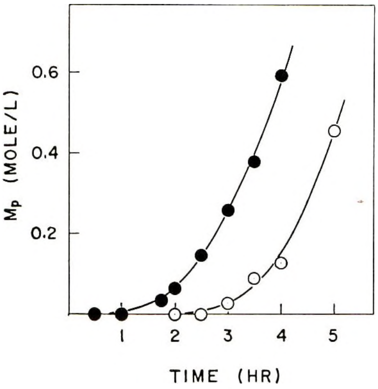


Fig. 6. Relation between the amount of polymerized monomer M_p and the reaction time: (●) in the presence of 36 mmole/l. acetaldehyde; (○) in the absence of acetaldehyde. Ethylene, containing 65 ppm oxygen; initial pressure, 400 kg./cm.^{2}; temperature, 30°C.; dose rate, 1.9×10^5 rad/hr.; reactor volume, 100 ml.

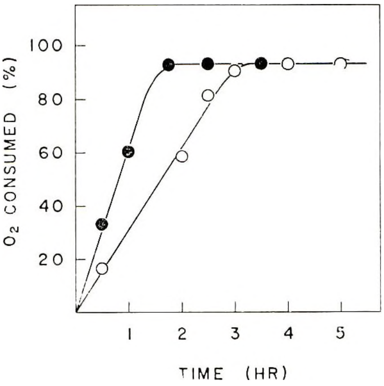


Fig. 7. Oxygen consumed vs. reaction time. Reaction conditions same as given for Figure 6.

TABLE VII
Effect of Acetaldehyde on the Polymerization of Ethylene Containing Oxygen[a]

Time, hr.	CH_3CHO addition, mmole/l.[b]	M_p, mole/l.	$\bar{P}_n \times 10^{-2}$	$N_p \times 10^4$, mole/l.	O_2 consumed, %
0.5	0	0.000	—	—	16.9
2.0	0	0.000	—	—	58.8
2.5	0	0.000	—	—	81.7
3.0	0	0.027	—	—	90.9
3.5	0	0.089	2.86	3.11	—
4.0	0	0.127	3.36	3.78	93.1
5.0	0	0.456	8.04	5.67	93.1
0.5	36	0.000	—	—	33.3
1.0	36	0.000	—	—	60.6
1.75	36	0.034	1.71	1.99	93.0
2.0	36	0.064	2.21	2.90	—
2.5	36	0.147	2.79	5.27	93.2
3.0	36	0.259	3.23	8.02	—
3.5	36	0.380	3.43	11.08	93.1
4.0	36	0.593	2.93	20.24	—
5.0	36	0.783	3.18	24.62	—

[a] Reaction conditions: initial pressure, 400 kg./cm.^{2}; temperature, 30°C.; dose rate, 1.9×10^5 rad/hr.; initial oxygen content, 65 ppm; reactor volume, 100 ml.

[b] The amount of acetaldehyde added per reactor volume of 1 liter.

of ethylene containing oxygen have no effect on the polymerization of pure ethylene. On the other hand, on the addition of acetaldehyde, the polymer yield and the degree of polymerization were markedly decreased, and the number of moles of polymer chain increased. The result indicates that the acetaldehyde formed has a marked effect on the polymerization.

Additional experiments were carried out in order to study the effects of acetaldehyde on the polymerization of ethylene containing oxygen. The results of the polymerization of ethylene containing 65 ppm oxygen (sys-

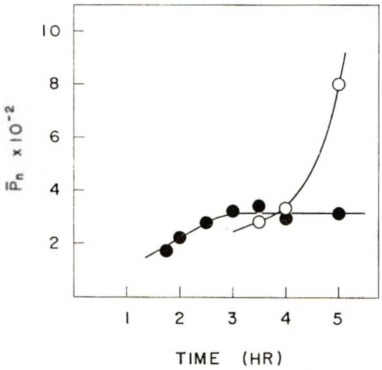


Fig. 8. Relation between the degree of polymerization $\bar{P}_n$ and the reaction time. Reaction conditions same as given for Figure 6.

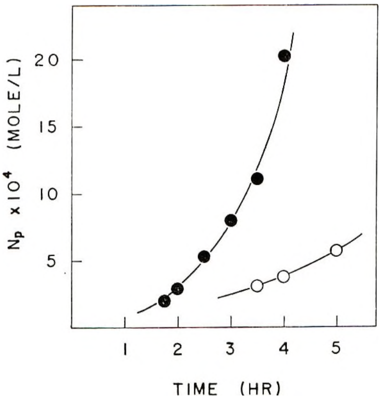


Fig. 9. Relation between the number of moles of polymer chain N_p and the reaction time. Reaction conditions same as given for Figure 6.

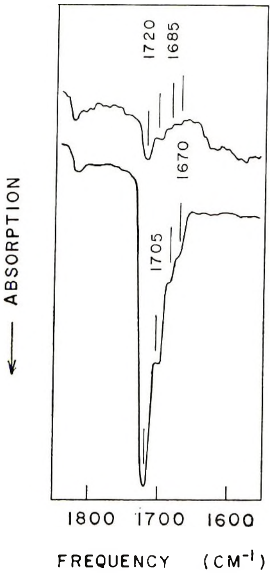


Fig. 10. Carbonyl-stretching region of infrared spectra of polymers formed by γ-radiation-induced polymerization of ethylene containing 65 ppm oxygen (upper spectrum) and ethylene containing 65 ppm oxygen and 36 mmole/l. acetaldehyde (lower spectrum). Initial pressure, 400 kg./cm.^{2}; temperature, 30°C.; time, 5 hr.; dose rate, 1.9×10^5 rad/hr.; reactor volume, 100 ml.

tem I), and the ethylene containing 65 ppm oxygen and 36 mmole/l. reactor acetaldehyde (system II) are shown in Table VII. Figure 6 shows that in both systems no polymer is observed in the early stage (inhibition period), that the inhibition period decreases on addition of acetaldehyde, and that after the inhibition period the polymer yield increases markedly with the reaction time. Figure 7 indicates that the rate of oxygen consumption in system II is larger than that in system I. Further, Figures 6 and 7 show that, in both systems, after the time when oxygen is almost consumed, the polymer yield begins to increase markedly. From these results, in the inhibition period, oxygen is considered to be consumed by the reaction with ethylene and initiating species to form oxidation products. In addition, the role of acetaldehyde is considered to consume predominantly the oxygen.

Figure 8 shows that the degree of polymerization increases with reaction time in system I, while it is almost constant in the system II. As is shown in Figure 9, the number of moles of polymer chain increased with time in both systems, and the rate of increase in system II was much larger than that in system I. From the facts that the polymer yield and the number of moles of polymer chain is increased and the degree of polymerization is reduced by the addition of acetaldehyde, the acetaldehyde is considered to act as an initiator and/or a chain-transfer agent. An increase of the amounts of carbonyls in the polymer formed in the presence of acetaldehyde (Figure 10) is consistent with those considerations.

On the basis of these results, it is considered that the aldehydes formed during the polymerization of ethylene containing oxygen act as an initiator and/or a chain-transfer agent after the inhibition period.

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Résumé

Les effets de l'oxygène sur la polymérisation, induite par radiation-γ, de l'éthylène ont été étudiés à une température de 30°C; la pression est de 400 kg/cm^2; la vitesse de dose était de 1.9×10^5 rad/h; et la teneur en oxygène variait de 1 à 2.000 ppm. Le produit principal était un polymère solide et il n'ya pas de produit liquide. Comme produit gazeux, il y de l'hydrogène, de l'acétylène, des hydrocarbures élevés, du dioxyde de carbone, des aldéhydes, et des acides. De nombreuxes sortes de groupes carbonyles semblables à ceux qu'on trouve dans le polyéthylène oxydé aux rayons-γ ont été observées dans le polymère. Le rendement en polymères, le degré de polymérisation décroissaient notablement par augmentation de la teneur en oxygène, alors que la quantité de groupes carbonyles dans le polymère formé croissait. Le nombre de moles de chaînes polymériques et les quantités d'hydrogène et d'acétylène étaient pratiquement indépendants de la teneur en oxygène. La polymérisation de l'éthylène n'était pas affectée par le CO_2 et par l'acide formique. Par addition d'acétaldéhyde, le rendement en polymère et le degré de polymérisation décroissaient considérablement alors que le nombre de moles de chaîne polymérique croissait. Pour la polymérisation de l'éthylène en présence d'oxygène, l'addition d'acétaldéhyde n'avait pas d'effet sur la période d'inhibition et sur la vitesse de consommation de l'oxygen. On a trouvé dans ce système, que la vitesse de polymérisation après la période d'inhibition et que le degré de polymérisation sont indépendants de la durée de la réaction et que le nombre de groupes carbonyles croissait notablement au sein du polymère.

Zusammenfassung

Der Einfluss von Sauerstoff auf die mit γ-Strahlen angeregte Polymerisation von Äthylen wurde bei einer Temperatur von 30°C und einem Druck von 400 kg/cm^2 untersucht. Die Dosisleistung betrug dabei 1,9 × 10^5 rad/h, der Sauerstoffgehalt lag zwischen 1 und 2.000 ppm. Hauptsächlich bildete sich festes Polymeres und kein flüssiges Produkt, als gasförmige Produkte entstanden Wasserstoff, Acetylen höhere Kohlenwasserstoffe, Kohlendioxyd, Aldehyde und Säuren. In den Polymeren wurde das Auftreten verschiedener Typen von Carbonylgruppen beobachtet, ähnlich denen, die bei der Oxydation von Polyäthylen mit γ-Strahlen auftreten. Die Polymerausbeute und der Polymerisationsgrad nahmen merklich mit steigendem Sauerstoffgehalt ab, während die Anzahl der Carbonylgruppen im gebildeten Polymeren zunahm. Die Molzahl der Polymerketten und die Wasserstoff- und Acetylenmengen waren, wie gefunden wurde, nahezu unabhängig vom Sauerstoffgehalt. Die Polymerisation des Äthylens wurde durch Kohlendioxyd und Ameisensäure nicht beeinflusst. Durch die Zugabe von Acetaldehyd wurde die Polymerausbeute und der Polymerisationsgrad auffällig verringert, während die molare Anzahl der Polymerketten zunahm. Bei der Polymerisation von Äthylen in Gegenwart von Sauerstoff war die Zugabe von Acetaldehyd ohne Einfluss auf die Inhibitionsperiode und die Geschwindigkeit des Sauerstoffverbrauchs. Darüberhinaus wurde gefunden, dass in diesem System die Geschwindigkeit der Polymerisation nach der Inhibitionsperiode und der Polymerisationsgrad von der Reaktionsdauer unabhängig waren und dass der Carbonylgehalt im Polymeren deutlich zunahm.

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Arylene-Modified Siloxanes

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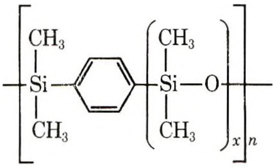
Synopsis

Polyarylenepolysiloxanes with varied structure can be obtained in condensation reactions of arylenedisilanols and N-methylsiloxazanes. Molecular weights, viscometric properties, glass transition temperatures, and thermogravimetric analysis data are reported.

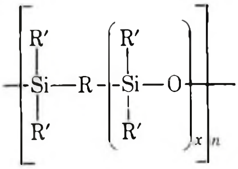
Introduction

Poly-*p*-phenylenetetramethyldisiloxane (structure I, $x = 1$),



I

which can be obtained by the dehydration of *p*-phenylenebis(dimethylsilanol), has been known for a considerable time,[1] and its properties have been described in detail.[2] Methods have also been reported for the synthesis of random and block copolymers of *p*-phenylenebis(dimethylsilanol) and α,ω-dihydroxypolydimethylsiloxanes.[3] In this work, a more general method of polymer synthesis has been adapted to the preparation of poly-*p*-phenylenepolydimethylsiloxanes (structure I, $x = 2$, 3, and 4). In addition, the properties of polyarylenesiloxanes with other structural modifications (structure II) have been investigated. As the length of the chain is increased between arylene groups, the polymer structure can be



II

$R = m\text{-}C_6H_4$, $p\text{-}C_6H_4$, or $p,p'\text{-}C_6H_6OC_6H_4$
$R' = CH_3$ or C_6H_5

TABLE I
Polymer Preparation

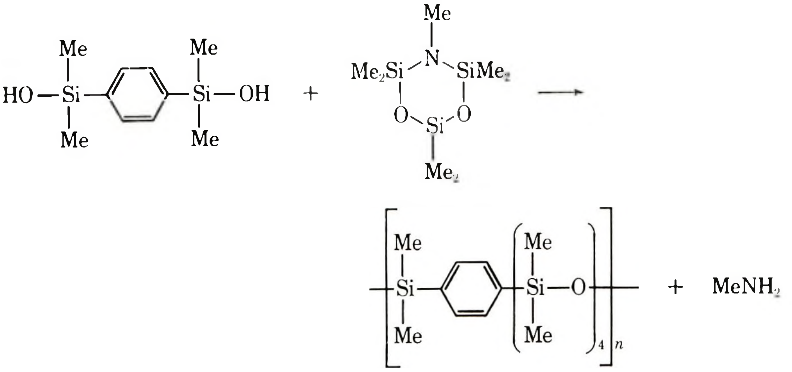
Polymer no.	Arylenedisilanol	Amt. silanol, mole	Cyclosiloxazane	Amt. siloxane, mole	Polymerization conditions	
					Temp., °C.	Time, hr.
1	Bis-*p*-dimethylhydroxysilylphenyl ether	0.0100	Decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane	0.0051	160	8
2	Bis-*p*-dimethylhydroxysilylphenyl ether	0.0100	Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane	0.0105	180	8
3	Bis-*p*-dimethylhydroxysilylphenyl ether	0.0100	Nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane	0.0105	160	8
4	*p*-Phenylenebisdimethylsilanol	0.0100	Decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane	0.00525	160	8
5	*p*-Phenylenebisdimethylsilanol	0.0100	Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane	0.0105	160	8
6	*p*-Phenylenebisdimethylsilanol	0.0100	Nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane	0.0105	160	8
7	*m*-Phenylenebisdimethylsilanol	0.0100	Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane	0.0105	160	8
8	*p*-Phenylenebismethylphenylsilanol	0.0100	Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane	0.0105	160	8
9	*m*-Phenylenebismethylphenylsilanol	0.0050	Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane	0.0105	160	8
10	*p*-Phenylenebisdiphenylsilanol	0.0050	Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane	0.00550	[a]	7
11	*m*-Phenylenebisdiphenylsilanol	0.0050	Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane	0.00550	155	0.75

[a] In 10 ml. of refluxing toluene.

regarded as a siloxane in which arylene groups replace oxygen atoms at regular intervals along the chain.

Method of Synthesis

It has been established that silylamines condense with silanols to form siloxanes under conditions in which there is no self-condensation of the silanol.[4] When applied to the condensation of arylenedisilanols with α,ω-bis(methylamino)polysiloxanes, this method affords a satisfactory approach to the synthesis of arylene-modified siloxanes. Because of their greater hydrolytic stability and ease of preparation, *N*-methylsiloxazanes were used in these polymerization reactions rather than α,ω-bis(methylamino)polysiloxanes [eq. (1)]

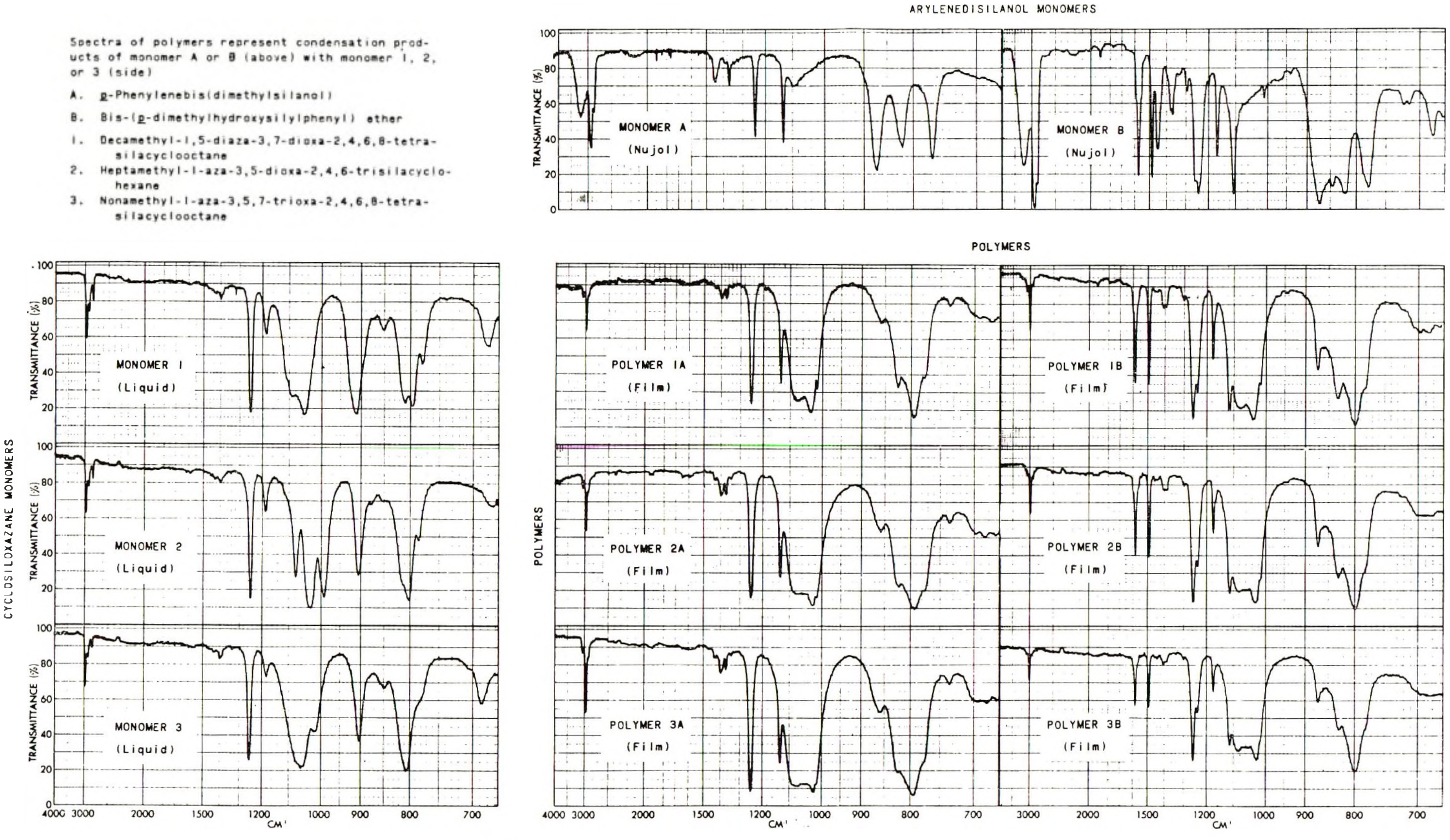


(1)

A series of high molecular weight polymers was obtained by heating mixtures of the disilanol and the cyclosiloxazane under the conditions described in Table I. No attempt was made to optimize polymerization conditions. Some difficulties were encountered in polymerizations involving *m*- and *p*-phenylenebisdiphenylsilanol, since an extended heating period rendered the polymers insoluble. Elemental analyses of the insoluble polymer suggested that the polymers had become insoluble as a result of the cleavage of silicon-phenyl bonds and consequent crosslinking.

The polymers were characterized by elemental analyses, which are reported in Table II, and infrared spectra. The excellent agreement between the calculated results of the analyses and experimental values for elemental content confirms that the polymerizations proceed in the proposed manner without randomization of groups along the chain.

Infrared spectra of selected monomers and polymers are compared in Figure 1. As would be predicted, the strong Si_2N asymmetric stretch at 900–910 cm.$^{-1}$ and the CN stretch at 1180–1185 cm.$^{-1}$, which are present in the siloxazanes[5,6] are absent in the polymers. Also, the silanol OH stretch at 3200 cm.$^{-1}$ disappears during polymer formation. Characteristic Si-methyl and Si-phenyl vibrations present in the monomers persist in the polymers, for example the characteristic Si-phenyl band at 1120–1130 cm.$^{-1}$ is present in all the polymers. The intensity ratio of



Spectra of polymers represent condensation products of monomer A or B (above) with monomer 1, 2, or 3 (side)

A. p-Phenylenebis(dimethylsilanol)

B. Bis-(p-dimethylhydroxysilylphenyl) ether

1. Decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane
2. Heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane
3. Nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane

Fig. 1. Infrared spectra of monomers and polymers.

the aryl ether band found at 1240 cm.$^{-1}$ in bis(p-dimethylhydroxysilylphenyl) ether to the dimethylsilyl band at 1259 cm.$^{-1}$ would be expected to decrease as the length of the dimethylsiloxy segment in the polymers increases. This change is easily observed in the spectra and provides additional confirmation for the proposed structures.

Polymer Properties

The heat stabilities of the polymers, determined by thermogravimetric analyses, are shown in Figures 2 and 3. It is readily apparent that both the identity of the arylene group present in the chain and the number of dimethylsiloxy groups in the chain segments affect the heat stability; however, the regular decrease in heat stability with increase in the number of siloxy groups illustrated in Figure 1 is particularly noteworthy. A typical commercial polydimethylsiloxane gum undergoes catastrophic decomposition under these conditions at 300°C. or below. It is apparent

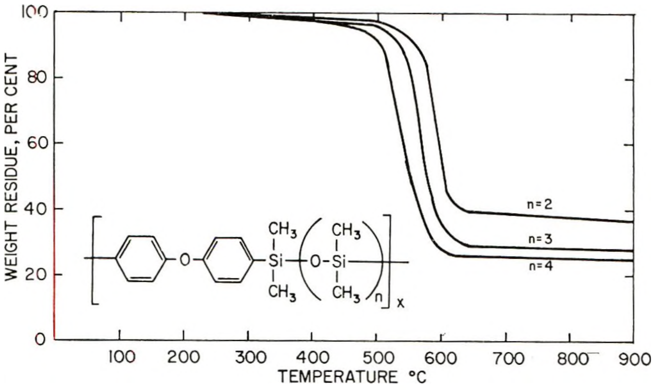


Fig. 2. Thermogravimetric analysis of polyarylenesiloxanes. Heating rate, 15°C./min.; N_2 atmosphere.

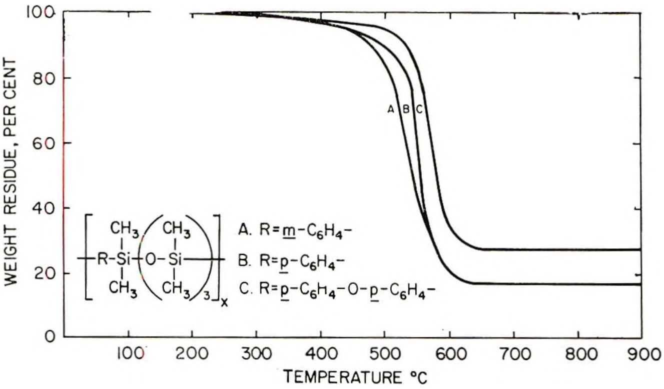
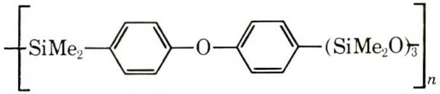
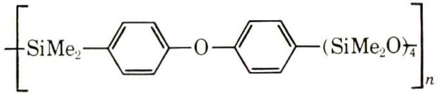
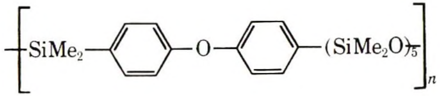
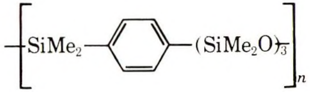
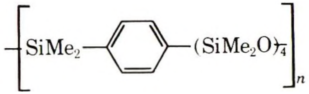
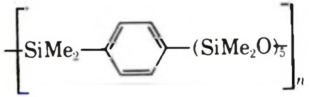
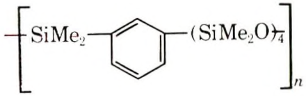
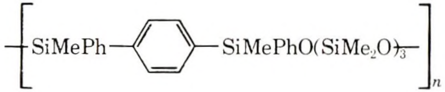
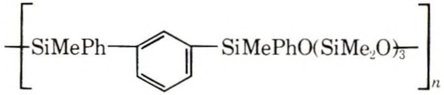
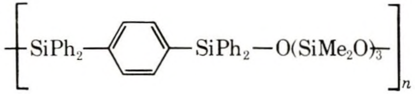
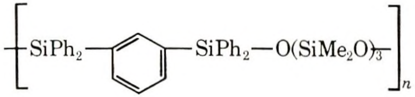


Fig. 3. Thermogravimetric analysis of polyarylenesiloxanes. Heating rate, 15°C./min.; N_2 atmosphere.

TABLE II
Polymer Properties

Polymer no.	Polymer structure	η_{inh} (0.5% solution in in toluene at 30°C.)	T_g, °C.	Empirical formula	Analyses (calcd.) and found		
					C, %	H, %	Si, %
1		2.48	−37°	$C_{20}H_{32}O_4Si_4$	(53.52) 53.74	(7.19) 7.27	(25.03) 25.08
2		2.72	−52°	$C_{22}H_{38}O_5Si_5$	(50.52) 50.62	(7.32) 7.35	(26.86) 26.70
3		3.83	−65°	$C_{24}H_{44}O_6Si_6$	(48.27) 48.02	(7.43) 7.34	(28.23) 28.11
4		0.73	−62°	$C_{14}H_{28}O_3Si_4$	(47.14) 46.97	(7.91) 7.81	(31.49) 30.90
5		2.77	−72°	$C_{16}H_{34}O_4Si_5$	(44.60) 44.40	(7.95) 7.93	(32.60) 30.20

6		2.48	−80°	$C_{18}H_{40}O_5Si_6$	(42.80) 42.76	(7.98) 7.99	(33.37) 33.19
7		1.60	−75°	$C_{16}H_{34}O_4Si_5$	(44.60) 44.49	(7.95) 7.90	(32.60) 32.51
8		0.15	—	$C_{26}H_{38}O_4Si_5$	(56.26) 56.00	(6.90) 6.97	(25.31) 25.02
9		1.62	−42°	$C_{26}H_{38}O_4Si_5$	(56.26) 56.23	(6.90) 6.83	(25.31) 25.08
10		0.21	—	$C_{36}H_{42}O_4Si_5$	(63.66) 63.75	(6.24) 6.25	(20.68) 20.29
11		0.66	—	$C_{36}H_{42}O_4Si_5$	(63.66) 64.08	(6.24) 6.07	(20.68) 20.45

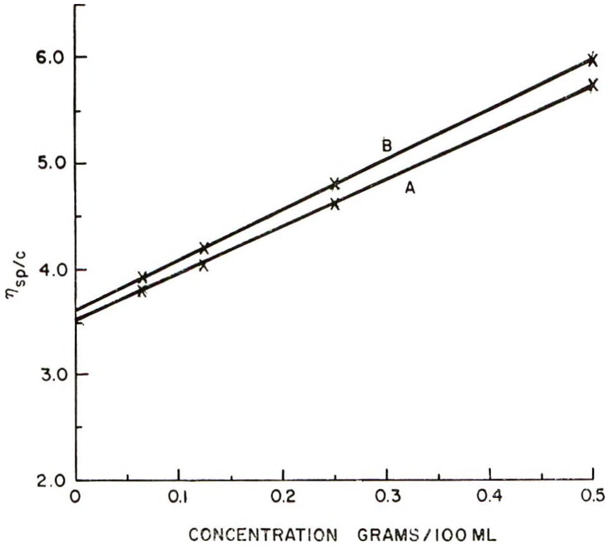


Fig. 4. Reduced viscosity–concentration curves: (*A*) polymer 2; (*B*) polymer 5. Polymer numbers refer to Table II.

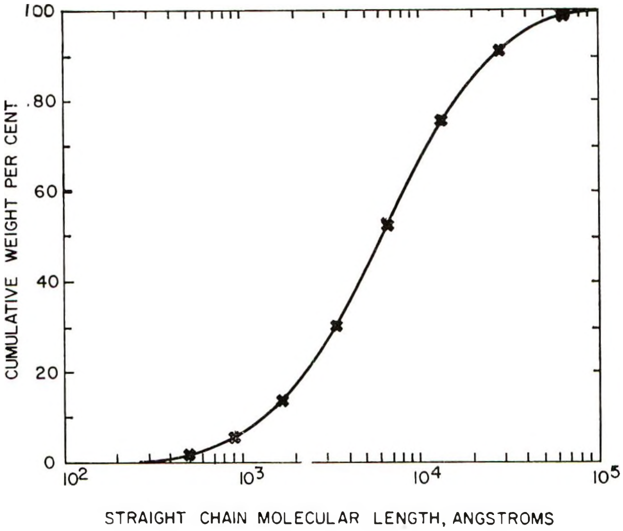


Fig. 5. Gel permeation chromatography of polymer 2 (Table II).

from Figure 2 that chain segments containing considerable numbers of dimethylsiloxy groups can be present before the decomposition mechanism effective in the polydimethylsiloxanes (randomization and volatilization of cyclics) limits the stability of the polymer.

Similarly, changes in the length of the siloxane chain segment could be correlated directly with changes in the glass transition temperatures of the polymers (Table II). The effect is apparent in the polymers prepared from *p*-phenylenebisdimethylsilanol and from bis-*p*-dimethylhydroxysilylphenyl ether. Glass transition temperatures were the only thermal changes that were observed on differential thermal analyses between −110 and 500°C.

Molecular weights, determined in the unfractionated polymers 2 and 5 by light scattering, were 905,000 and 820,000, respectively. These molecular weights and the intrinsic viscosities, 3.52 and 3.60 (Fig. 4), fit the molecular weight–intrinsic viscosity relationship established by Merker for poly-*p*-phenylenetetramethyldisiloxane, $\eta = 1.12 \times 10^{-4} \bar{M}_w^{0.75}$, reasonably well. The molecular weight distribution derived from results of gel permeation chromatography data (Fig. 5) was 3.7.

Experimental

In a typical preparation of a siloxazane monomer,[7] 100 ml. of methylamine was condensed and subsequently distilled into a mixture of 108 g. (0.39 mole) of 1,5-dichlorohexamethyltrisiloxane and 500 ml. petroleum ether, b.p. 60–90°C., which was heated to 50°C. prior to the addition. The temperature did not rise above 56°C. during the addition. After the addition was complete, the mixture was cooled, filtered, and the solids were washed with petroleum ether. Distillation of the solvents and fractional distillation of the residue through a spinning band column gave 56.7 g. (66%) of heptamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane, b.p. 60–61°C./17 mm., n_D^{20} 1.4100.

Decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane, was similarly prepared and purified, b.p. 87–88°C./5 mm., m.p. 27–28°C., n_D^{30} 1.4321; nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane had b.p. 84–85°C./8 mm., n_D^{20} 1.4202.

The difunctional silanols were prepared via organosodium or Grignard procedures. Details of the methods and characterization of the compounds will be reported in another publication.[8] In a typical procedure, a mixture of 43.0 g. (0.131 mole) of bis-*p*-bromophenyl ether, 39.0 g. (0.282 mole) of chlorodimethylethoxysilane, and 13.0 g. (0.564 g. atom) of 1-mm. diameter sodium wire in 500 ml. of ether was stirred at reflux for 24 hr. The mixture was filtered, and the filtrate was stripped of solvent. The residue was distilled on a spinning-band column to obtain 27.4 g. (56%) of bis-*p*-dimethylethoxysilylphenyl ether, b.p. 141–142°C./0.1 mm., n_D^{20} 1.5213.

A solution of 42.8 g. (0.11 mole) of bis-*p*-dimethylethoxysilylphenyl ether in 100 ml. of ethanol was added to a solution of 17.3 g. of sodium hydroxide in 12 ml. of water and 80 ml. of methanol. After a few minutes, the mixture was treated with a solution of 17.3 g. of sodium hydroxide in 80 ml. of water and stored 1 hr. The solution was added to 126 g. of potassium hydrogen phosphate in 2 liters of ice and water and stored overnight. When the crystallized product was filtered off and dried under reduced pressure, 32.5 g. (93%) of crude bis(*p*-dimethylhydroxysilyl)phenyl ether, m.p. 100–103°C., was obtained. The diol used in the polymerizations, m.p. 104–105°C., was obtained by recrystallizing the crude material from toluene and drying the product in a vacuum oven at 65°C. for 16 hr.

The following are the melting points of other arylenedisilanols used in the polymerization experiments: *p*-phenylenebisdimethylsilanol, 136–137°C; *m*-phenylenebisdimethylsilanol, 79–81°C.; *p*-phenylenebismethylphenylsilanol (mixture of isomers), 126–136°C.; *p*-phenylenebismethylphenylsilanol (high-melting isomer), 139–140°C.; *p*-phenylenebisdiphenylsilanol, 216–217°C.; and *m*-phenylenediphenylsilanol, m.p. 111–113°C.

The polymerizations followed essentially the same procedure. In a typical experiment, a mixture of 31.9 g. (0.1 mole) of bis-*p*-dimethylhydroxysilylphenyl ether and 32.5 g. (0.105 mole) of nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclooctane in a polymerization flask under a positive nitrogen pressure was immersed in a Wood's metal bath, which was preheated to 160°C. A small excess of the siloxazane was used in all the polymerizations to compensate for the loss of the more volatile monomer when the mixture was heated. While the monomers were being heated to the bath temperature, the mixture became homogeneous, and methylamine was evolved rapidly. The mixture was maintained at 160°C. and samples taken at time intervals had the following inherent viscosities: 1 hr. = 1.44; 2 hr., 2.10; 5 hr., 2.72; and 8 hr., 3.18. The polymeric product, heated at 55°C. under reduced pressure to constant weight (13 hr.), weighed 56.8 g. The yield was 95% and the final inherent viscosity of the polymer was 3.26.

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Résumé

Des polyarylènepolysiloxanes avec différentes structures peuvent être obtenus par réaction de condensation d'arylènedisilanols et de *N*-méthylsiloxazanes. Les poids moléculaires, les propriétés viscosimétriques, les températures de transition vitreuse et les résultats d'analyses thermo-gravimétriques sont rapportés.

Zusammenfassung

Polyarylenpolysiloxane mit variierter Struktur können durch Kondensationsreaktionen zwischen Arylendisilanolen und *N*-Methylsiloxazanen hergestellt werden. Molekulargewichte, Viskositätseigenschaften, Glasumwandlungstemperatur und thermogravimetrische Analysendaten werden angegeben.

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Synthesis of Polyurethanes from Fluorinated Diisocyanates

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Whittaker Corporation, San Diego, California 92123

Synopsis

A number of polyurethanes based on fluorinated aliphatic diisocyanates, perfluorinated aromatic diisocyanates, and chlorinated aromatic diisocyanates have been prepared. The polyurethane prepared from perfluorotrimethylene diisocyanate and hexafluoropentanediol was a rubbery solid which hydrolyzed readily in air to a liquid or sticky solid but was stable if protected from moisture. The products of hydrolysis were isolated and identified. Polyurethanes based on hexafluoropentamethylene diisocyanate were synthesized by reaction of hexafluoropentanediamine with hexafluoropentamethylene bischloroformate and with tetrafluoro-*p*-phenylene bischloroformate. Polyurethanes were synthesized by reaction of tetrafluoro-*p*-phenylene diisocyanate with hexafluoropentanediol and pentanediol. Other perfluoroaryl diisocyanate-based polyurethanes were synthesized by reaction of tetrafluoro-*m*-phenylene diisocyanate with hexafluoropentanediol and with tetrafluoro-*p*-hydroquinone. Polyurethanes were also synthesized by reaction of tetrachloro-*p*-phenylene diisocyanate and 2,3,5,6-tetrachloro-*p*-xylylene-α,α'-diisocyanate with hexafluoropentanediol.

INTRODUCTION

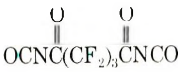
The synthesis of polyurethanes based on fluorinated diisocyanates had not been realized because these fluorinated diisocyanates were unavailable. A series of fluorinated diisocyanates have been synthesized by Narmco Research & Development, and the preparation of such polyurethanes has been accomplished. The syntheses of perfluorotrimethylene diisocyanate (I), hexafluoropentamethylene diisocyanate (II), perfluoroglutaryl diisocyanate (III), tetrafluoro-*p*-phenylene diisocyanate (IV), tetrafluoro-*m*-phenylene diisocyanate (V), and 4,4′-diisocyanatooctafluorobiphenyl (VI) were described in a recent paper.[1]

$OCN(CF_2)_3NCO$

I

$OCNCH_2(CF_2)_3CH_2NCO$

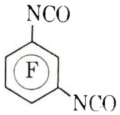
II



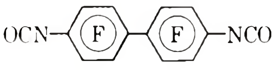
$$OCN\overset{\overset{O}{\|}}{C}(CF_2)_3\overset{\overset{O}{\|}}{C}NCO$$

III

IV



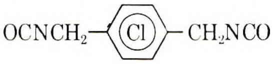
V



VI

Also described in that paper were two chlorinated diisocyanates, tetrachloro-*p*-phenylene diisocyanate (VII) and 2,3,5,6-tetrachloro-*p*-xylylene-α,α'-diisocyanate (VIII).

VII



VIII

We have prepared polyurethanes based on the reaction of these diisocyanates with simple fluorinated diols. These preparations will be the subject of this paper.[2]

EXPERIMENTAL

Poly(hexafluoropentamethylene Perfluorotrimethylene Dicarbamate)

Polymer Synthesis. The polymer was prepared by reaction of perfluorotrimethylene diisocyanate (3.2 g., 0.0137 mole) with hexafluoropentanediol (2.9 g., 0.0137 mole) in dry ethyl acetate with 1 drop of triethylamine as catalyst. The polymer solution was mixed at room temperature for 20 min. under nitrogen, then the temperature was slowly raised to reflux (87°C.). The solution was refluxed and stirred for 1 hr. under nitrogen, then cooled under nitrogen. The polymer solution was stripped at 125°C., under vacuum for $1\frac{1}{2}$ hr., resulting in a very rubbery opaque polymer. Infrared maxima (neat) were observed at 3.2 (m), 5.6 (s), 5.8 (s), 6.0 (s), 6.55 (s), 6.75 (m), 7.2 (m), 8.35 (m), 8.75 (s), 11.25 (m), 13.3 (w), and 14.75 (w) μ.

The polymer degraded to an oil on exposure to air overnight, while a sample stored under dry nitrogen remained unchanged. After the determination of the melting point, which was in excess of 300°C., the sample was observed to have improved hydrolytic stability and did not become liquid after 24 hr. in moist air. This improvement in hydrolytic stability was pursued as described in the following section.

Crosslinking of Polymer by Postcure. The polymer prepared above was subjected to various degrees of postcure, and the effect on hydrolytic stability is shown in Table I.

Polymer Degradation Products. The polymer prepared above was exposed to the atmosphere for 1 month in a glass crystallizing dish. During this period, the glass was attacked by hydrofluoric acid being formed in the hydrolysis. The polymer first became oily, then later became a white solid solid mass which could be recrystallized from water to yield a product melting at 135–136.5°C. Vapor-phase osmometry indicated a molecular weight of 315 ± 15 (calculated 298). By using infrared data and results

TABLE I
Effect of Postcure on Poly(hexafluoropentamethylene Perfluorotrimethylene Dicarbamate)

Postcure temp., °C.	Time, hr.	Melting point of postcured polymer, °C.	Softening temp. after 24 hr. in water, °C.	Remarks[a]
150–180	1	>300	70	All specimens lost HF at about 80–90°C.
200–230	1	>300	80	
250–280	1	>300	90	Polymer became brittle after postcure
280–330	1	>300	>300	Very brittle after postcure; 7 days in water gave a softening point of 165°C.

[a] All polymers showed degradation after 10 days atmospheric exposure.

of elemental analysis, the identity of the compound was established as the dicarbamate of hexafluoropentanediol.

ANAL. Calcd. for $C_7H_8F_6N_2O_4$: C, 28.2%; H, 2.68%; F, 38.3%; N, 9.40%. Found: C, 29.22%; H, 2.71%; F, 37.75%; N, 9.45%.

Poly(hexafluoropentamethylene Hexafluoropentamethylene Dicarbamate)

Solution Polymerization. Hexafluoropentamethylene bischloroformate (10.1 g., 0.03 mole) was added slowly with stirring to hexafluoropentanediamine (6.3 g., 0.03 mole), pyridine (5.2 g., 0.066 mole), and dry ethyl acetate (50 ml.) at 22–50°C. under nitrogen. After all the bischloroformate had been added, the slurry was a blood red. It was mixed for 1$^3/_4$ hr. at 30–50°C., followed by 4 hr. at 80°C., at which time the slurry had turned a dark green. When the reaction mixture was poured into 1 liter of rapidly stirred water, a black oil settled. The water was decanted and the black oil dried in a vacuum oven overnight at 90°C. A brown, brittle solid, 11.9 g. (84.0% yield), was obtained.

Interfacial Polymerization with Sodium Hydroxide. Into a 250-ml. three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and nitrogen inlet, was added hexafluoropentanediamine (4.20 g., 0.02 mole), sodium hydroxide (1.76 g., 0.044 mole) and 100 ml. of water. Hexafluoropentamethylene bischloroformate (6.74 g., 0.02 mole) in 50 ml. of methylene chloride was rapidly added to the diamine solution at 0–25°C. The methylene chloride solution was decanted and the polymer dried in a vacuum oven at 40–50°C. for 4 hr. to yield a viscous oil.

Interfacial Polymerization with Sodium Carbonate. Hexafluoropentamethylene bischloroformate (23.6 g., 0.07 mole) in methylene chloride (100 ml.) was rapidly added to hexafluoropentanediamine (14.7 g., 0.07 mole) and sodium carbonate (14.9 g., 0.14 mole) in 250 ml. of distilled water at 0–5°C. with vigorous stirring. The slurry was then stirred for 2$^1/_2$ hr. at 0–5°C. The water and methylene chloride were decanted and the oily residue dried overnight at 80–100°C. in a vacuum oven. A white opaque elastomeric polyurethane, weighing 21.4 g. (6% yield) was obtained. The above described polymer was a semisolid when prepared at 5–10°C. Infrared maxima (film) were observed at 3.1 (m), 5.8 (s), 6.6 (s), 7.0 (w), 7.85 (m), 8.75 (s), 10.4 (m), 11.25 (w), and 12.85 (w) μ.

Poly(tetrafluoro-*p*-phenylene Hexafluoropentamethylene Dicarbamate)

Tetrafluoro-*p*-phenylene bischloroformate (4.8 g., 0.016 mole) in THF (25 ml.) was slowly added to hexafluoropentanediamine (3.4 g., 0.016 mole) and pyridine (2.7 g., 0.034 mole) in THF (75 ml.) with rapid stirring. Pyridine hydrochloride precipitated as the bischloroformate was added. After the addition was completed, the mixture was stirred at 60°C. for 1 hr., then at room temperature overnight. It was then poured into dilute hydrochloric acid and boiled for $^1/_2$ hr. The orange-brown solid obtained was suspended in water, boiled for an additional $^1/_2$ hr., filtered, washed with additional water, and dried overnight in a vacuum oven at 60°C. The orange-brown product weighed 4.9 g. (69% yield) and had a softening point of 175–196°C. (with darkening). Infrared maxima (Nujol) were observed at 3.1 (m), 5.75 (w), 6.1 (s), 6.4 (s), 6.7 (s), 8.25 (m), 8.6 (s), 10.2 (s), 11.0 (w), 13.1 (w), and 14.8 (w) μ.

Poly(hexafluoropentamethylene Tetrafluoro-*p*-phenylene Dicarbamate)

Solution Polymerization. Hexafluoropentanediol (3.02 g., 0.0142 mole) was dissolved in 10 ml. of dry ethyl acetate and added to a 50-ml. three-necked flask equipped with a stirrer, condenser, dropping funnel, thermometer, and nitrogen inlet. Tetrafluoro-*p*-phenylene diisocyanate (0.0142 mole, 3.30 g.) in 12 mi. of dry ethyl acetate was added to the diol solution in 5 min. with mixing under nitrogen. The solution was mixed for 24 hr. at 80–82°C. under nitrogen, after which practically all of the diisocyanate had reacted. One drop of triethylamine was added and the solution stirred for one additional hour. The ethyl acetate was removed in a vacuum oven to yield 4.0 g. of a light-tan, waxy polymer, m.p. >340°C. Infrared maxima (Nujol) were observed at 3.1 (s), 5.75 (s), 6.4 (s), 6.6 (m), 6.75 (s), 7.65 (m), 7.8 (s), 8.2 (m), 8.6 (s), 9.2 (m), 9.75 (m), 10.5 (m), 12.3 (w), 13.2 (m), and 14.75 (w) μ.

Melt Polymerization. Tetrafluoro-*p*-phenylene diisocyanate (16.2 g., 0.07 mole) and hexafluoropentanediol (14.8 g., 0.07 mole) were heated to 140°C., at which time the temperature increased to 205°C. and the mixture solidified. The polymer was a strong, brittle solid.

Poly(pentamethylene Tetrafluoro-*p*-phenylene Dicarbamate)

Into a 100-ml. three-necked flask equipped with a stirrer, reflux condenser, and addition funnel with a nitrogen inlet was placed 1,5-pentanediol

(2.1 g., 0.02 mole) dissolved in 10 ml. of ethyl acetate. The system was flushed with nitrogen and the polymerization run under a nitrogen atmosphere. Tetrafluoro-*p*-phenylene diisocyanate (4.6 g., 0.02 mole) dissolved in 15 ml. of ethyl acetate was added slowly with stirring over a period of 25 min. Almost immediately, a white precipitate came out of solution. The mixture was stirred at room temperature for 1$^1/_2$ hr., then at reflux (77°C.) for 2$^1/_2$ hr. The white solid was filtered and dried in a vacuum oven at 70°C., yielding 6.1 g. (91%) of polyurethane melting at 280–281°C. Infrared maxima (Nujol) were observed at 3.2 (m), 5.85 (s), 6.6 (s), 7.65 (m), 8.2 (s), 9.15 (w), 9.8 (m), 10.5 (m), 13.0 (w), and 14.8 (w) μ.

Poly(hexafluoropentamethylene Tetrafluoro-*m*-phenylene Dicarbamate)

Tetrafluoro-*m*-phenylene diisocyanate (2.90 g., 0.0125 mole) and hexafluoropentanediol (2.65 g., 0.0125 mole) were mixed and warmed to 40°C.; at this temperature a clear solution was obtained. After stirring a few minutes, the stirrer was removed and the temperature raised to 90°C. After 1 hr. at 90°C., the polymeric mass solidified. This solid polymer could be pressed into thin film at 200°F. Infrared maxima (Nujol) were observed at 3.1 (m), 5.8 (s), 6.6 (s), 7.6 (m), 8.15 (s), 8.7 (s), 10.0 (m), 10.3 (m), 11.25 (w), and 13.15 (w) μ.

Poly(tetrafluoro-*p*-phenylene Tetrafluoro-*m*-phenylene Dicarbamate)

Tetrafluoro-*p*-hydroquinone (1.8 g., 0.01 mole) was added to tetrafluoro-*m*-phenylene diisocyanate (2.3 g., 0.01 mole) in dry xylene (20 ml.). The mixture was refluxed for 24 hr. Since the infrared spectrum of the solution showed a strong absorption at 4.5 μ indicating excess isocyanate, an additional 0.5 g. of tetrafluoro-*p*-hydroquinone was added and reflux continued for 6 hr. The resulting suspension was cooled to room temperature, filtered, and the solids washed with ether. After drying in a vacuum oven, the resultant white powder (4.0 g.) was found to be infusible below its decomposition point of 225°C. Infrared maxima (KBr) were observed at 3.05 (m), 5.7 (s), 6.15 (s), 7.55 (w), 7.9 (w), 8.25 (s), 8.6 (m), 9.35 (m), 9.9 (s), and 13.3 (w) μ.

Poly(hexafluoropentamethylene Tetrachloro-*p*-phenylene Dicarbamate)

To hexafluoropentanediol (10.6 g., 0.05 mole) in 25 ml. of ethyl acetate, tetrachloro-*p*-phenylene diisocyanate (14.9 g., 0.05 mole) in 35 ml. of ethyl acetate was added over a 5 min. period with mixing under nitrogen. The slurry was stirred for $^1/_2$ hr. at 30–35°C., then refluxed at 82°C. for 1$^1/_2$ hr. The ethyl acetate was removed and 40 ml. of *o*-dichlorobenzene was added. The slurry was mixed at 130–140°C. under nitrogen. Triethylamine (5 drops) was added and the slurry heated for 3 hr. at 100°C. The slurry was then filtered and the polymer residue dried in a vacuum oven at 130–140°C. for 4 hr. to yield 16.0 g. of brown polymer, m.p. 190–196°C. Infrared maxima (Nujol) were observed at 3.1 (m), 5.8 (s), 6.25 (w), 6.5 (m), 6.7 (m), 7.35 (m), 8.1 (s), 8.7 (s), 9.15 (m), 10.1 (w), 11.3 (w), and 13.15 (w) μ.

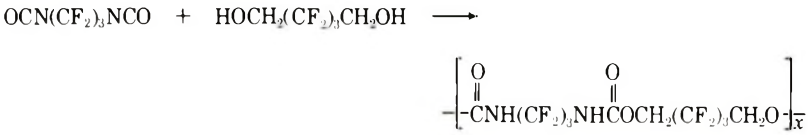
Poly(hexafluoropentamethylene Tetrachloro-*p*-xylylene Dicarbamate)

To a stirred melt of tetrachloro-*p*-xylylene α,α'-diisocyanate (8.7 g., 0.0267 mole) was added hexafluoropentanediol (5.65 g., 0.0267 mole) under a nitrogen atmosphere. Stirring was continued for 50 min. while the temperature of the mixture was maintained at 130–140°C. At the end of this time, the polyurethane hardened to a brittle solid. Infrared maxima (KBr) were observed at 3.1 (m), 5.8 (s), 6.7 (s), 6.9 (w), 7.25 (m), 7.5 (m), 8.1 (s), 8.9 (s), 9.65 (m), 10.5 (m), and 13.2 (m) μ.

RESULTS AND DISCUSSION

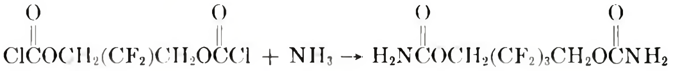
Polyurethanes from Aliphatic Diisocyanates

A polyurethane was prepared by reaction of perfluorotrimethylene diisocyanate with hexafluoropentanediol in refluxing ethyl acetate solution [eq. (1)]. Triethylamine was used as a catalyst.



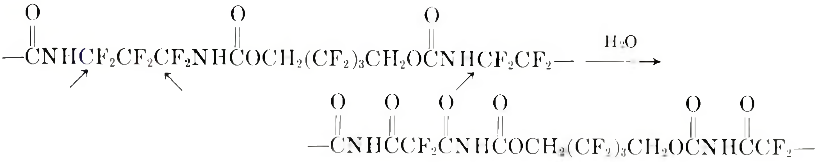
$$OCN(CF_2)_3NCO + HOCH_2(CF_2)_3CH_2OH \longrightarrow \left[-\overset{O}{\overset{\|}{C}}NH(CF_2)_3NH\overset{O}{\overset{\|}{C}}OCH_2(CF_2)_3CH_2O- \right]_x \qquad (1)$$

The polymer obtained was a rubbery solid which degraded to an oil on exposure to air overnight, but did not undergo any change when stored under dry nitrogen. A study was conducted to establish the nature of the hydrolytic degradation of this polymer. The polymer was exposed to atmospheric moisture for 1 month in a glass crystallizing dish. The dish was attacked by HF formed in the hydrolysis. The polymer first became oily, then later became a white solid mass which could be recrystallized from water to yield a crystalline solid melting at 135–136.5°C. This solid was identified as the dicarbamate of hexafluoropentanediol by its infrared spectrum, molecular weight (by vapor-phase osmometry), and by elemental analysis. It was identical to an authentic sample prepared by reaction of hexafluoropentamethylene bischloroformate with ammonia [eq. (2)].



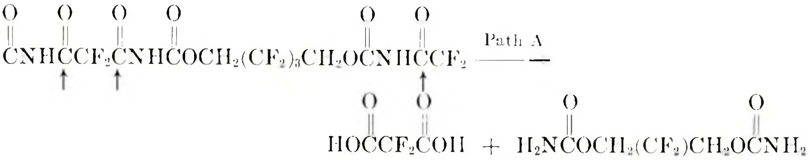
$$Cl\overset{O}{\overset{\|}{C}}OCH_2(CF_2)CH_2O\overset{O}{\overset{\|}{C}}Cl + NH_3 \rightarrow H_2N\overset{O}{\overset{\|}{C}}OCH_2(CF_2)_3CH_2O\overset{O}{\overset{\|}{C}}NH_2 \qquad (2)$$

A logical intermediate in this degradation is the polyacylurethane formed by hydrolysis of the difluoromethylene groups adjacent to the carbamate nitrogen atoms [eq. (3)]. This hydrolysis is analogous to that occurring in several synthetic routes which would be expected to result in perfluorinated amines.[3-9]

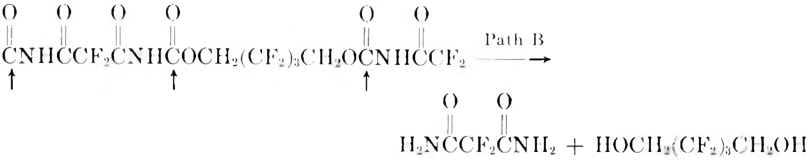


$$\mathrm{—\overset{O}{\overset{\|}{C}}NH\underset{\nearrow}{C}F_2\underset{\nwarrow}{C}F_2CF_2NH\overset{O}{\overset{\|}{C}}OCH_2(CF_2)_3CH_2O\overset{O}{\overset{\|}{C}}N\underset{\nearrow}{H}CF_2CF_2— \xrightarrow{H_2O} —\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}CF_2\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}OCH_2(CF_2)_3CH_2O\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}CF_2—} \quad (3)$$

Hydrolysis of the acylurethane could result in two sets of products, depending upon which bond to nitrogen proved to be more hydrolytically stable [eqs. (4a), (4b)].



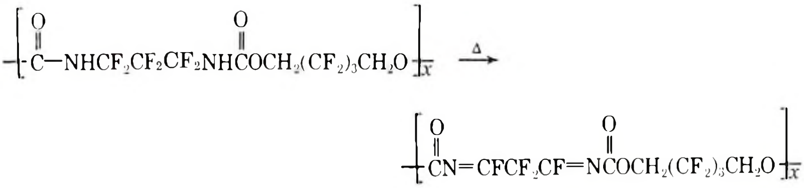
$$\mathrm{\overset{O}{\overset{\|}{C}}NH\underset{\uparrow}{\overset{O}{\overset{\|}{C}}}\underset{\uparrow}{\overset{O}{\overset{\|}{C}}F_2}\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}OCH_2(CF_2)_3CH_2O\overset{O}{\overset{\|}{C}}NH\underset{\uparrow}{\overset{O}{\overset{\|}{C}}}CF_2 \xrightarrow{Path\ A} HO\overset{O}{\overset{\|}{C}}CF_2\overset{O}{\overset{\|}{C}}OH + H_2N\overset{O}{\overset{\|}{C}}OCH_2(CF_2)CH_2O\overset{O}{\overset{\|}{C}}NH_2} \quad (4a)$$



$$\mathrm{\underset{\uparrow}{\overset{O}{\overset{\|}{C}}}NH\overset{O}{\overset{\|}{C}}CF_2\overset{O}{\overset{\|}{C}}NH\underset{\uparrow}{\overset{O}{\overset{\|}{C}}}OCH_2(CF_2)_3CH_2O\underset{\uparrow}{\overset{O}{\overset{\|}{C}}}NH\overset{O}{\overset{\|}{C}}CF_2 \xrightarrow{Path\ B} H_2N\overset{O}{\overset{\|}{C}}CF_2\overset{O}{\overset{\|}{C}}NH_2 + HOCH_2(CF_2)_3CH_2OH} \quad (4b)$$

As would be predicted, the carbonyl carbon atoms adjacent to the difluoromethylene groups were more susceptible to attack by water molecules due to the strong electron withdrawing effect of the difluoromethylenes resulting in hydrolysis by path A, reaction (4a). No evidence of the formation of difluoromalondiamide could be found. This compound has been reported to melt at 204–205°C., considerably higher than the melting point of 135–136.5°C. which was observed for the dicarbamate. This hydrolysis path is analogous to that described by Dannley[10] for the alcoholysis of urethanes prepared from perfluoroalkyl monoisocyanates.

It is interesting to note that this polyurethane exhibited good stability if protected from moisture. In fact, fresh polymer was subjected to considerable thermal exposures in an attempt to crosslink the system, with no serious degradation up to 280°C. However, it was observed that hydrogen fluoride was lost at 80–90°C., and it seems that the polymer was modified as shown in eq. (5):

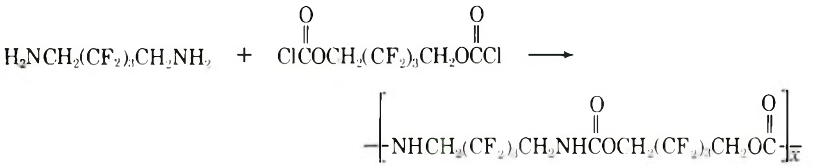


$$\mathrm{\left[\overset{O}{\overset{\|}{C}}—NHCF_2CF_2CF_2NH\overset{O}{\overset{\|}{C}}OCH_2(CF_2)_3CH_2O\right]_x \xrightarrow{\Delta} \left[\overset{O}{\overset{\|}{C}}N{=}CFCF_2CF{=}N\overset{O}{\overset{\|}{C}}OCH_2(CF_2)_3CH_2O\right]_x} \quad (5)$$

This treatment gives some improvement in hydrolytic stability, but the modified polymer also degrades to the dicarbamate, indicating that the remaining fluorine is still labile, much like an imino chloride.

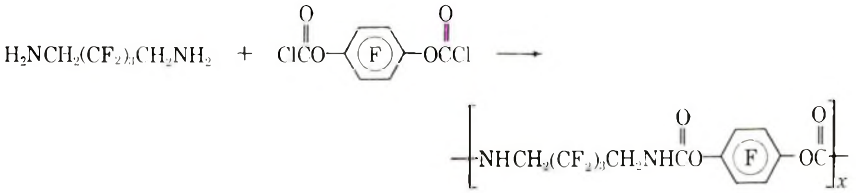
Fluorinated polyurethanes having a methylene group between the urethane nitrogen and the difluoromethylene groups should possess far better hydrolytic stability than the type of polyurethane just discussed. Due to difficulties encountered in the preparation of hexafluoropentamethylene diisocyanate, this type of polyurethane was prepared by the reaction of hexafluoropentanediamine with various bischloroformates.

Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate) was prepared by reaction of hexafluoropentanediamine with hexafluoropentamethylene bischloroformate, both in solution and interfacially [eq. (6)]. The polyurethane prepared in ethyl acetate solution was a brown, brittle solid. The polymer prepared interfacially with sodium hydroxide as the acid acceptor was a viscous oil. Apparently, the rate of hydrolysis of the bischloroformate by this base was much more rapid than the reaction of the bischloroformate with the diamine. The polyurethane prepared interfacially by using sodium carbonate, a weaker base, as the acid acceptor was a tan semisolid which solidified at room temperature.



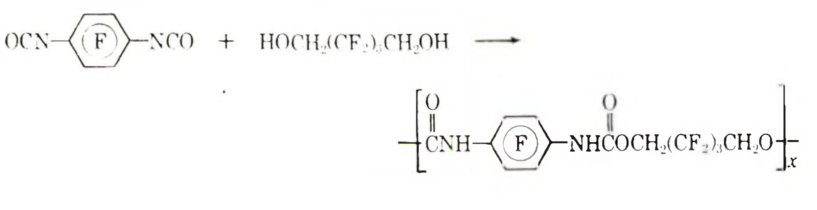
$$H_2NCH_2(CF_2)_3CH_2NH_2 + Cl\overset{\overset{O}{\|}}{C}OCH_2(CF_2)_3CH_2O\overset{\overset{O}{\|}}{C}Cl \longrightarrow \left[NHCH_2(CF_2)_3CH_2NH\overset{\overset{O}{\|}}{C}OCH_2(CF_2)_3CH_2O\overset{\overset{O}{\|}}{C}\right]_x \quad (6)$$

Poly(tetrafluoro-*p*-phenylene hexafluoropentamethylene dicarbamate) was prepared by reacting hexafluoropentanediamine with tetrafluoro-*p*-phenylene bischloroformate in tetrahydrofuran solution with pyridine as the acid acceptor. The polyurethane was a tan solid having a softening point of 175–179°C.



Polyurethanes from Aromatic Diisocyanates

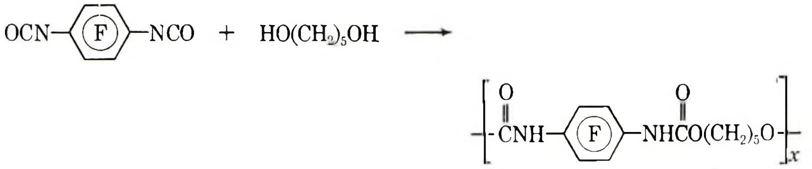
Poly(hexafluoropentamethylene tetrafluoro-*p*-phenylene dicarbamate) was prepared both in solution and in the melt according to eq. (7):



(7)

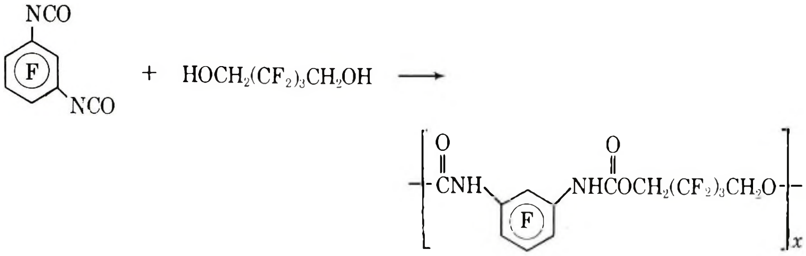
The polyurethane was a white, opaque, highly crystalline, polyurethane which melted at 262–265°C.

Poly(pentamethylene tetrafluoro-*p*-phenylene dicarbamate) was prepared by reaction of tetrafluoro-*p*-phenylene diisocyanate and 1,5-pentanediol in ethyl acetate solution [eq. (8)]. The polyurethane was a white crystalline solid, having a melting point of 280–281°C.



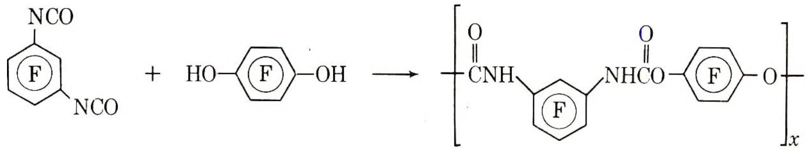
(8)

Poly(hexafluoropentamethylene tetrafluoro-*m*-phenylene dicarbamate) was prepared by reaction of tetrafluoro-*m*-phenylene diisocyanate with hexafluoropentanediol in the melt [eq. (9)]. The polyurethane obtained was a clear, colorless solid which could be molded to a clear, brittle sheet.



(9)

A fully fluorinated aromatic polyurethane was prepared by reaction of tetrafluoro-*m*-phenylene diisocyanate and tetrafluoro-*p*-hydroquinone in refluxing xylene solution [eq. (10)]:

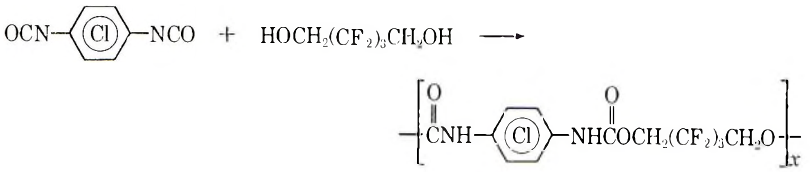


(10)

The reaction was extremely slow, indicating that the fluorinated phenolic hydroxyl groups were very unreactive. The polyurethane obtained was infusible below its decomposition point. Tetrafluoro-*p*-hydroquinone was recovered from the decomposition products.

Because of our interest in polyurethanes containing various amounts and types of halogens, polyurethanes were prepared from two chlorinated aromatic diisocyanates.

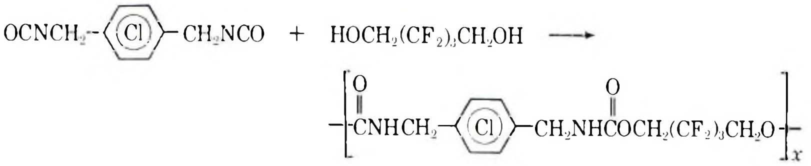
Poly(hexafluoropentamethylene tetrachloro-*p*-phenylene dicarbamate) was prepared by reaction of tetrachloro-*p*-phenylene diisocyanate with hexafluoropentanediol in ethyl acetate solution [eq. (11)].



(11)

The polymer obtained was a brown, brittle solid melting at 190–196°C.

Poly(hexafluoropentamethylene tetrachloro-*p*-xylylene dicarbamate) was prepared by reaction of tetrachloro-*p*-xylylene α,α'-diisocyanate with hexafluoropentanediol in the melt [eq. (12)]. The polyurethane obtained was a brittle solid.



(12)

The thermal stabilities of several of the polyurethanes described in this paper were studied briefly. The results of thermogravimetric analyses run on these polymers are shown in Table II. Also included for comparison is the polyurethane prepared from toluene 2,4-diisocyanate and poly(tetrahydrofuran). Only one of the fluorine-containing polyurethanes, poly(hexafluoropentamethylene tetrafluoro-*p*-phenylene dicarbamate), exhibited thermal stability as good as or slightly better than the nonfluorinated polyurethane.

TABLE II
Results of Thermogravimetric Analysis

	Polymer decomposition temperature, °C.	
Polyurethane	In air	In helium
Poly(hexafluoropentamethylene hexafluoropentamethylene dicarbamate)	215 ± 10	200 ± 10
Poly(tetrafluoro-*p*-phenylene hexafluoropentamethylene dicarbamate)	190 ± 10	200 ± 10
Poly(hexafluoropentamethylene tetrafluoro-*p*-phenylene dicarbamate)	300 ± 10	285 ± 10
Poly(tetrafluoro-*p*-phenylene tetrafluoro-*m*-phenylene dicarbamate)	225 ± 10	200 ± 10
Polyurethane from toluene 2,4-diisocyanate and polytetrahydrofuran	280 ± 10	280 ± 10

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Résumé

Plusieurs polyuréthanes à base de diisocyanates aliphatiques fluorés, de diisocyanates aromatiques perfluorés et de diisocyanates aromatiques chlorés ont été préparés. Le polyuréthane préparé au départ de diisocyanate de perfluorotriméthylène et de hexafluoropentanediol était un solide caoutchouteux qui s'hydrolysait facilement à l'air en un liquide ou un solide gommeux, mais il était stable s'il était protégé de l'humidité. Les produits d'hydrolyse ont été isolés et identifiés. Les polyuréthanes à base de diisocyanates hexafluoropentaméthyléniques ont été synthétisés par réaction de l'hexafluoropentanediamine avec le bis-chloroformiate d'hexafluoropentaméthylène et avec le bis-chloroformiate de tétrafluoro-*p*-phénylène. Le polyurét anes ont été synthétisés par réaction du diisocyanate de tétrafluoro-*p*-phénylène avec l'hexafluoropentanediol et pentanediol. D'autres polyuréthanes à base de perfluoroaryl diisocyanates ont été synthétisés par réaction du diisocyanate de tétrafluoro-*m*-phénylène avec l'hexafluoropentanediol et avec la tétrafluoro-*p*-hydroquinone. Des polyuréthanes ont été également synthétisés par réaction de diisocyanate de tétra-chloro-*p*-phénylène et du α,α'-diisocyanate de 2,3,5,6-tétrachloro-*p*-xylylène avec l'hexafluoropentanediol.

Zusammenfassung

Eine Reihe von Polyurethanen wurde auf Basis fluorierter aliphatischer Diisocyanate, perfluorierter aromatischer Diisocyanate und chlorierter aromatischer Diisocyanate hergestellt. Das aus Perfluortrimethylendiisocyanat und Hexafluorpentandiol hergestellte Polyurethan war ein kautschukartiger Festkörper, der an Luft sogleich zu einer Flüssigkeit oder einer klebrigen Festsubstanz hydrolysierte, vor Feuchtigkeit geschützt jedoch stabil war. Die Hydrolysenprodukte wurden isoliert und identifiziert. Polyurethane auf Grundlage von Hexafluorpentamethylendiisocyanat liessen sich durch Reaktion von Hexafluorpentandiamin mit dem Bis(chlorameisensäureester) des Hexafluorpentamethylendiols und des Tetrafluorhydrochinons herstellen. Auch durch Reaktion von Tetrafluor-*p*-phenylendiisocyanat mit Hexafluorpentandiol und mit Pentandiol wurden Polyurethane synthetisiert. Andere Polyurethane auf Basis perfluorierter Aryldiisocyanate wurden durch Reaktion von Tetrafluor-*m*-phenylendiisocyanat mit Hexafluorpentandiol und mit Tetrafluor-*p*-hydrochinon hergestellt. Auch durch Reaktion von Tetrachlor-*p*-phenylendiisocyanat und 2,3,5,6-Tetrachlor-*p*-xylylen-α,α'-diisocyanat mit Hexafluorpentandiol wurden Polyurethane synthetisiert.

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Polymerization Initiated by an Electron Donor–Acceptor Complex. Part I. Polymerization of Methyl Methacrylate Initiated by Liquid Sulfur Dioxide–Pyridine Complex in the Presence of Carbon Tetrachloride

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Synopsis

The polymerization of methyl methacrylate can be initiated by a charge-transfer complex of liquid sulfur dioxide and pyridine in the presence of carbon tetrachloride. The molar ratio of sulfur dioxide and pyridine which participated in the complex was found from a spectrophotometric study to be 2:1. The polymerization proceeds through free-radical intermediates. The overall rate of polymerization is proportional to the square root of the concentration of the complex, and the values of $k_p/k_t^{1/2}$ under the various polymerization conditions were satisfactorily consistent with the literature value. For the activation energy of the overall reaction, 8.2 kcal./mole was obtained, and for initiation, 9.7 kcal./mole was evaluated from the values of $k_p/k_t^{1/2}$. It was deduced from a kinetic mechanism for the initiation that a primary radical may be produced from the reduction of carbon tetrachloride by an associated complex consisting of liquid sulfur dioxide–pyridine complex and the monomer.

INTRODUCTION

It is well known that liquid sulfur dioxide behaves as an electron acceptor and forms charge-transfer type complexes with donors such as amines, ethers, aromatic hydrocarbons, and some of the olefins.[1-3] Pyridine and its derivatives also form complexes with liquid sulfur dioxide,[4-7] and it has been recently reported by the present authors[8] that the complex of liquid sulfur dioxide and pyridine can initiate the radical polymerization of vinyl monomers in the presence of an organic halogen compound such as carbon tetrachloride, chloroform, or bromoform. That the organic halides play an important role in the polymerization of *N*-vinylcarbazole in the absence of any initiator has also been reported.[9-11]

Some of the vinyl monomers also form complexes with liquid sulfur dioxide,[12,13] and radical polymerization with such complexes yielded polysulfones.[12-14] On the other hand, the radical polymerization of methyl methacrylate[15] and acrylonitrile[16] gave only poly(methyl methacrylate) and polyacrylonitrile, respectively. Matsuda et al.[15] proved that methyl methacrylate and acrylonitrile will not mutually interact with liquid sulfur dioxide.

It is the purpose of the present paper to examine the polymerization of methyl methacrylate initiated by the complex from liquid sulfur dioxide and pyridine in the presence of carbon tetrachloride without any initiator.

EXPERIMENTAL

Methyl methacrylate (MMA) was washed three times with 10% aqueous caustic soda and then three times with water. It was dried over anhydrous sodium sulfate and then twice distilled in a nitrogen atmosphere at reduced pressure (40 mm. Hg).

Carbon tetrachloride was washed with dilute aqueous sodium carbonate and then with water and was dried over magnesium sulfate; the fraction distilling at 78°C. was isolated. It yielded no precipitate when treated with aqueous silver nitrate.

Toluene was purified by successive shaking with sulfuric acid, sodium hydroxide, and mercury, followed by drying over phosphorus pentoxide and then fractional distillation.

Pyridine was distilled in nitrogen atmosphere at a reduced pressure in the presence of potassium hydroxide immediately before use, and its purity was checked by gas chromatography.

The purification of liquid sulfur dioxide was essentially the same as described in a previous report.[13]

The polymerization reaction was carried out in a sealed glass vessel. The required quantities of monomer, pyridine, carbon tetrachloride, and toluene were pipetted into the vessel. The reaction vessel was provided with a ground glass stopcock joint. The vessel, immersed in a cooled methanol bath (−78°C.) was attached to the liquid sulfur dioxide dropping apparatus. The oxygen in the reaction vessel was replaced as much as possible with purified dry nitrogen, the vacuum cock was closed, and liquid sulfur dioxide was fed into the reaction vessel. The rate of polymerization was measured gravimetrically, and the polymerization proceeds in a homogeneous system.

The electronic spectrum of the complex of liquid sulfur dioxide and pyridine was measured in methanol with a Cary Model 14 spectrophotometer in a pressure-resistant quartz photocell (2-mm. wide optical cell containing a 1.97 mm. spacer).

RESULTS

Charge-Transfer Type Complex of Liquid Sulfur Dioxide and Pyridine

The ultraviolet spectra of liquid sulfur dioxide, pyridine, and the complex in *n*-hexane are shown in Figure 1. The absorption maximum of the

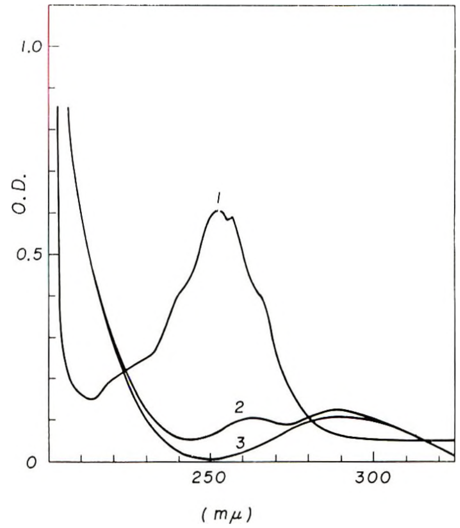
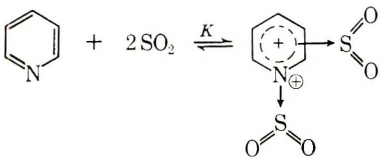


Fig. 1. Ultraviolet spectra of pyridine, SO_2, and pyridine–SO_2 complex at 20°C: (*1*) [Py] = 1.06×10^{-2} mole/l. in *n*-hexane (ref.: *n*-hexane); (*2*) [SO_2] = 1.08×10^{-2} mole/l., [Py] = 1.06×10^{-2} mole/l. in *n*-hexane (ref. 1.06×10^{-2} mole/l. pyridine in *n*-hexane); (*3*) [SO_2] = 1.19×10^{-2} mole/l. in *n*-hexane (ref.: *n*-hexane). Optical path length $d = 3.3 \times 10^{-2}$ cm.

complex lies at 263 mμ. The molar ratio of liquid sulfur dioxide and pyridine which participated in the complex was determined by the method of continuous variations.[17] As is shown in Figure 2, the maximum of the optical density (O.D.) due to the complex lies near 33 vol.-% pyridine solution at every wavelength measured. Therefore, it is clear that the complex consists of two moles of sulfur dioxide and 1 mole of pyridine, and the complex probably has a structure similar to that shown in eq. (1).



(1)

The equilibrium constant K can be written as shown in eq. (2):

$$K = \frac{[\mathrm{C}]}{([\mathrm{SO_2}]_0 - 2[\mathrm{C}])^2([\mathrm{Py}]_0 - [\mathrm{C}])} \tag{2}$$

where Py and C represent pyridine and complex, respectively, and the concentration of the complex [C] (in moles/liter) can be found from the following relation

$$[\mathrm{C}] = \mathrm{O.D.}_{\text{complex}}/\epsilon_c d \tag{3}$$

in which ϵ_c and d represent the molar extinction coefficient of the complex and the optical path length, respectively. Taking out the terms containing the third and second order of the complex concentration, eq. (4) is easily derived,

$$\frac{[\mathrm{Py}]_0[\mathrm{SO_2}]_0{}^2}{\mathrm{O.D.}} = \frac{1}{\epsilon_c K} + \frac{1}{\epsilon_c}\{4[\mathrm{SO_2}]_0[\mathrm{Py}]_0 + [\mathrm{SO_2}]_0{}^2\} \tag{4}$$

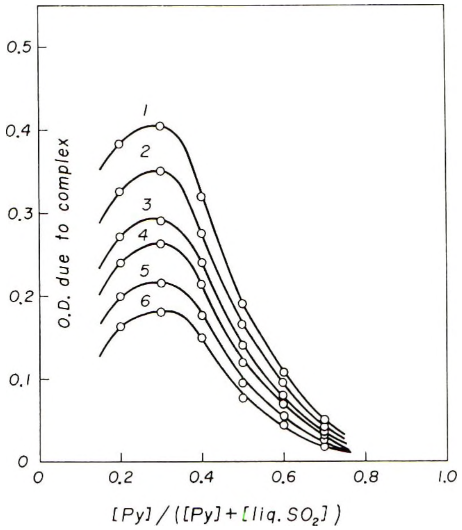


Fig. 2. Continuous variations in methanol at 20°C.: (*1*) 3275 A.; (*2*) 3300 A.; (*3*) 3325 A.; (*4*) 3350 A.; (*5*) 3375 A.; (*6*) 3400 A. [Py] + [liq. SO_2] = 3.0 mole/l.

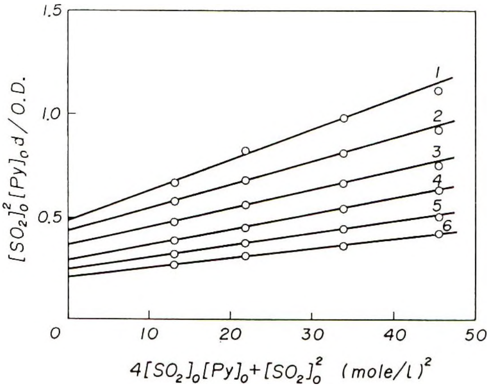


Fig. 3. Plots of eq. (4): (*1*) 3375 A.; (*2*) 3350 A.; (*3*) 3325 A.; (*4*) 3300 A.; (*5*) 3275 A.; (*6*) 3250 A. Optical path length $d = 3.3 \times 10^{-2}$ cm.; 20°C.

Plots of $[\mathrm{Py}]_0[\mathrm{SO_2}]_0{}^2/\mathrm{O.D.}$ against $(4[\mathrm{SO_2}]_0[\mathrm{Py}]_0 + [\mathrm{SO_2}]_0{}^2)$ should be linear; K may be obtained from the intercept of the line with the ordinate by using the value of ϵ_c from the slope. Figure 3 shows the plots of this relation; the equilibrium constant obtained was 0.028 l.^{2}/mole^2.

Effect of Halogen Compounds on the Polymerization of Methyl Methacrylate Initiated by the Complex of Liquid Sulfur Dioxide and Pyridine

Methyl methacrylate monomer at a constant concentration of 2.82 mole/l. was heated for 180 min. with 3.71 mole/l. pyridine and 10 vol.-% of liquid or 3.0 g. of solid halogen compound. Toluene was chosen as a diluent for all the experiments, since it dissolves the monomer, the polymer, and the complex, has a low dielectric constant (2.38 at 25°C.), and does not affect the overall rate of polymerization. The results of the polymerization are summarized in Table I.

From the data for experiments 41, 141, and 16, it is clear that no polymer is obtained when either the complex (that is, liquid sulfur dioxide and pyridine) or the organic halide is missing from the polymerization systems. The most effective system is a mixture of liquid sulfur dioxide, pyridine, and carbon tetrachloride.

Inhibitors were used to determine the active center (chain carrier) in this polymerization system. The results are shown in Table II.

TABLE I

Polymerization of Methyl Methacrylate Initiated by the Complex of Liquid Sulfur Dioxide and Pyridine with Different Organic Halide Systems (50°C.)

Expt. no.	Pyridine (donor), mole/l.	Liquid SO_2 (acceptor), mole/l.	Organic halide	Organic halide concn., mole/l.	Conversion, wt.-%/3 hr.
41	3.71	3.04	—	—	Trace
141	—	3.04	Carbon tetrachloride	1.03	Nil
16	3.71	—	Carbon tetrachloride	1.03	Nil
1	3.71	3.04	Carbon tetrachloride	1.03	17.0
519	3.71	3.04	Chloroform	3.21	Nil
520	3.71	3.04	Dichloromethane	1.55	Nil
523	3.71	3.04	Carbon tetrabromide	0.57	Nil
522	3.71	3.04	Bromoform	1.14	7.3
531	3.71	3.04	Dichloroacetic acid	1.21	5.1

TABLE II

Effect of Inhibitors on the Polymerization of Methyl Methacrylate Initiated by the Complex of Liquid Sulfur Dioxide and Pyridine with Carbon Tetrachloride System (50°C.)[a]

Expt. no.	Inhibitor	Inhibitor concn., mole/l.	Conversion, wt.-%/3 hr.
1	—	—	17.0
3	Hydroquinone	0.10	17.1
5	DPPH	0.08	4.3
7	DMF	1.96	57.8

[a] The concentrations of liquid sulfur dioxide, pyridine, MMA, and carbon tetrachloride were kept constant at 3.04, 3.71, 2.82 and 1.03 mole/l., respectively.

Dimethylformamide (DMF) was added as an inhibitor for the cationic polymerization. Tokura et al.[14] have previously reported that the cationic polymerization of styrene and its derivatives were completely inhibited when such bases as DMF and dimethyl sulfoxide were added. As shown in Table II, however, the addition of DMF accelerates the rate; this unanticipated effect of DMF will be discussed in a subsequent paper.[29] In another experiment, when DPPH was used at a much lower concentration (5×10^{-5} mole/l.), a solution of liquid sulfur dioxide and pyridine in carbon tetrachloride decolorized DPPH instantly at 50°C. These results indicate that the complex of liquid sulfur dioxide and pyridine acts as an initiator for the radical polymerization in the presence of carbon tetrachloride.

Effect of Complex Concentration on the Rate of Polymerization of MMA

The relationship between the overall rate of polymerization, R_p and the square root of the complex concentration which was calculated by using eq. (2) is shown in Figure 4. R_p is proportional to the square root of the concentration of complex, which indicates that the initiation of methyl methacrylate by a radical mechanism is probably involved in this polymerization.

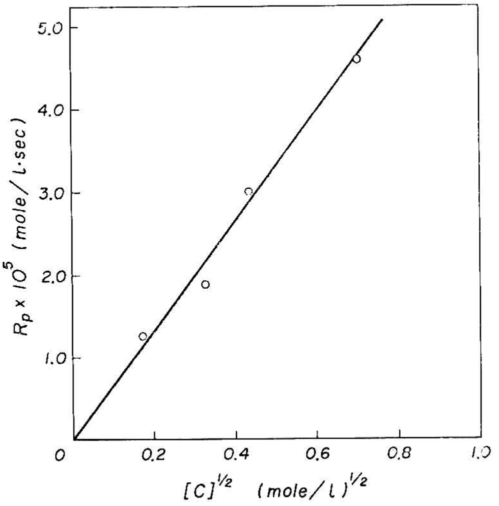


Fig. 4. Relationship between overall rate of polymerization R_p and the square root of the concentration of the complex. $[MMA]_0 = 3.29$ mole/l.; $[CCl_4] = 0.52$ mole/l.; 50°C.

Effect of MMA Concentration on the Rate of Polymerization

Figure 5 shows that the overall rate of polymerization can be represented by eq. (5):

$$R_p \propto [C]^{0.5}[M]^{1.5} \quad (5)$$

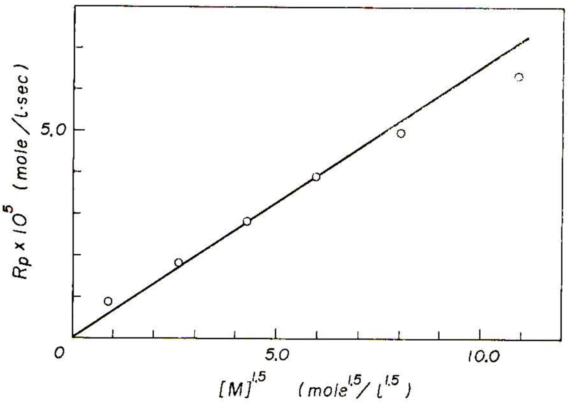


Fig. 5. Relationship between the overall rate of polymerization R_p and two-thirds order of the monomer concentration. $[CCl_4]$ = 0.52 mole/l.; [C] = 0.553 mole/l.; 50°C.

Effect of Carbon Tetrachloride Concentration on the Rate of Polymerization of MMA

The relationship between R_p and the concentration of carbon tetrachloride is shown in Figure 6; it can be seen from this plot that the rate increases rapidly with carbon tetrachloride up to a concentration of 0.15.

Overall Activation Energy of Polymerization

The Arrhenius plot is shown in Figure 7. The activation energy was evaluated as 8.2 kcal./mole.

Number-Average Degree of Polymerization

The number-average degree of polymerization $\bar{P}_n$, as determined viscometrically, is shown in Table III. The value of $k_p/k_t^{1/2}$ was cal-

TABLE III

Values of $k_p/k_t^{1/2}$ Obtained at Various Polymerization Conditions at 50°C.

$[MMA]_0$, mole/l.	[C], mole/l.	$[CCl_4]_0$, mole/l.	$10^{-3}\ \bar{P}_n$	$-10^5 d[M]/dt$, mole/l.-sec.	$k_p/k_t^{1/2}$, (l./mole-sec.)$^{1/2}$
0.94	0.553	0.52	3.72	0.783	0.182
4.00	0.553	0.52	5.78	4.883	0.134
3.29	0.031	0.52	13.80	1.285	0.128
3.29	0.117	0.52	7.71	1.894	0.116
3.29	0.224	0.52	9.26	3.028	0.161
3.29	0.725	0.52	3.91	4.602	0.129
2.82	0.553	0.13	9.59	3.220	0.197
2.82	0.553	0.19	9.39	3.213	0.195
2.82	0.553	0.32	9.56	3.213	0.199
					Avg. 0.160

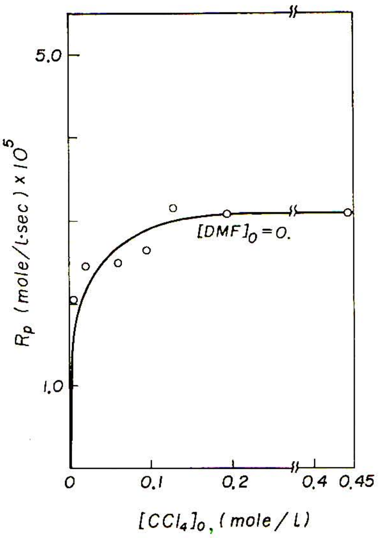


Fig. 6. Relationship between R_p and the concentration of carbon tetrachloride: $[MMA]_0 = 2.82$ mole/l.; $[C] = 0.553$ mole/l.; 50°C.

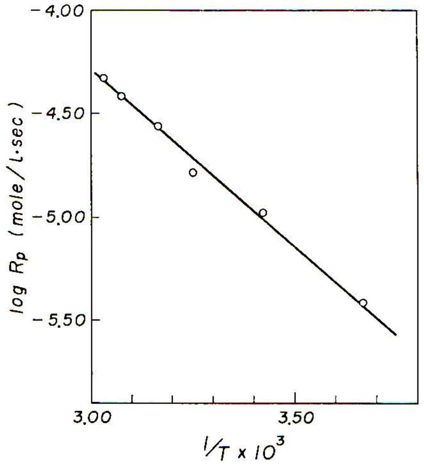


Fig. 7. Arrhenius plot for the overall rate of polymerization.

culated by using the conventional relationship,

$$-\bar{P}_n\, d[\mathrm{M}]/dt = (k_p^2/k_t)[\mathrm{M}]^2 \tag{6}$$

where k_p and k_t represent the rate constant of propagation and termination, respectively. The values of $k_p/k_t^{1/2}$ obtained here agree satisfactorily with the literature value, i.e. 0.125 (l./mole-sec.)$^{1/2}$ at 50°C.,[18] and it supports the radical polymerization.

Activation Energy of the Initiation

The Arrhenius plot of $k_p/k_t^{1/2}$ which was obtained at temperatures between 20 and 60°C. is shown in Figure 8. The activation energy of

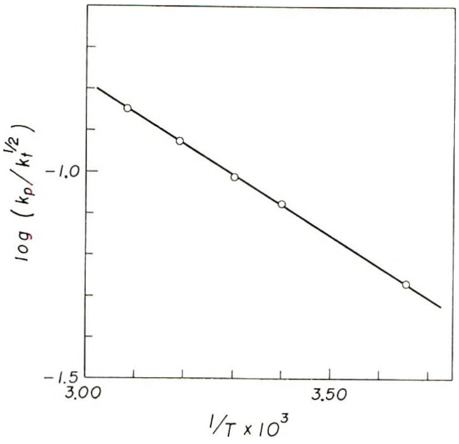


Fig. 8. Arrhenius plot for values of $k_p/k_t^{1/2}$.

$E_p - E_t/2$ can be evaluated as 3.4 kcal./mole, E_p and E_t being the activation energy of propagation and termination, respectively. Therefore, it follows that the activation energy of the initiation is 9.7 kcal./mole.

DISCUSSION

It has been reported[9-11] that the polymerization of *N*-vinylcarbazole by an organic electron acceptor can be initiated by using compounds which range widely in their electron affinity and is not limited only to such stronger acceptors as chloranil, tetranitromethane, and maleic anhydride.[19,20] Carbon tetrachloride can act as a weak electron acceptor molecule, and Davidson et al.[21] have shown the existence of solid complexes of carbon tetrachloride and various pyridines. Bamford and his co-workers[22-26] have examined extensively the effect of carbon tetrachloride on metal carbonyl-initiated polymerization of methyl methacrylate.

In the present polymerization system, pyridine can act as an electron donor for both liquid sulfur dioxide and carbon tetrachloride. The existence of the complex of liquid sulfur dioxide and pyridine is confirmed by the data of Figures 1 and 2, but a complex of carbon tetrachloride and pyridine was not detectable from the spectrophotometric study. It is reasonable to consider that the active complex for the initiation of the polymerization is the liquid sulfur dioxide–pyridine complex, since the electron affinity of liquid sulfur dioxide is much larger than that of carbon tetrachloride. From the relationship between the composition diagram and the freezing point of the mixture solutions of liquid sulfur dioxide and pyridine, Hoffman and Vanderwerf[27] have shown that liquid sulfur dioxide forms 1:1 addition compounds with pyridine. For 1:1 complex, the relation of Benesi and Hildebrand[28] can be adopted to determine an association constant, but its application for our spectrophotometric data did not give a linear relation. The molar ratio which is obtained from the cryoscopic data implies the molar ratio applies to the crystal state of the complex. Therefore, for the calculation of the concentration of the complex formed in the present polymerization system, the data obtained from the spectrophotometric study must be used.

It is reasonable to consider a radical intermediate in the present polymerization system, as the rate of polymerization is retarded by the addition of DPPH, the polymerization takes place even when DMF is added, and the rate is proportional to the square root of the concentration of the liquid sulfur dioxide and pyridine complex which may probably act as an initiator. The value of $k_p/k_t^{1/2}$ also supports the radical polymerization.

As shown in Table I, no polymer was obtained when either the complex or carbon tetrachloride was missing from the polymerization systems. The overall rate of polymerization is clearly very sensitive to the concentration of carbon tetrachloride at low concentrations of carbon tetrachloride, but for a carbon tetrachloride concentration more than 0.15 mole/l. it is practically independent of the CCl_4 concentration. On the other hand, the rate is proportional to the square root of the concentration of the complex and to two-thirds the monomer concentration. These kinetic results can be explained by the reaction scheme shown in eqs. (7) and (8).

$$\mathrm{C} + \mathrm{M} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (\mathrm{I}) \tag{7}$$

$$(\mathrm{I}) + \mathrm{CCl_4} \xrightarrow{k_3} \mathrm{Cl_3CM}\cdot + \overset{\ominus}{\mathrm{Cl}} + \overset{\oplus\,\cdot}{(\mathrm{II})} \tag{8}$$

The formation of an associated complex (I) consisting of liquid sulfur dioxide–pyridine complex and monomer is presumed to be reversible, but it could not be confirmed experimentally. The associated complex (I) enters into a reaction with carbon tetrachloride to (II), which is probably a radical cation. By assuming a stationary concentration of an associated complex (I) we may easily derive the following expression [eq. (9)] for the rate of initiation, v_i.

$$v_i = (k_1k_3[\mathrm{C}][\mathrm{M}][\mathrm{CCl_4}])/(k_2 + k_3[\mathrm{CCl_4}]) \tag{9}$$

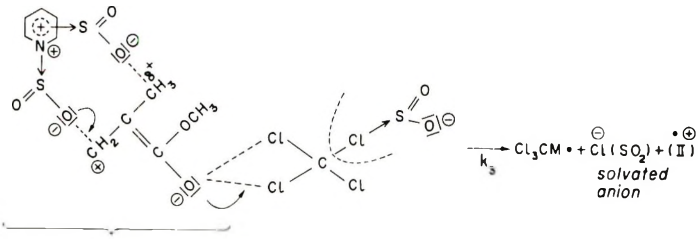
The overall rate of polymerization R_p can be represented by eq. (10):

$$R_p = -d[\mathrm{M}]/dt = k_p[\mathrm{M}\cdot][\mathrm{M}] \tag{10}$$

By assuming bimolecular termination and stationary concentration of radicals, the eq. (11) can be obtained:

$$\begin{aligned} R_p &= k_p[\mathrm{M}](v_i/k_t)^{1/2} \\ &= \frac{k_p}{k_t^{1/2}}[\mathrm{M}]\left(\frac{k_1k_3[\mathrm{C}][\mathrm{M}][\mathrm{CCl_4}]}{k_2 + k_3[\mathrm{CCl_4}]}\right)^{1/2} \end{aligned} \tag{11}$$

This type of expression is in qualitative agreement with the experimental results: the rate of polymerization is proportional to the square root of the concentration of the complex for constant concentration of monomer and carbon tetrachloride and to the monomer concentration to two-



Associated complex (I)

Fig. 9. Representation of the initiation mechanism.

thirds order for constant concentration of the complex and carbon tetrachloride. The relationship between the rate of polymerization and the concentration of carbon tetrachloride given in eq. (11) is also consistent with the experimental result shown in Figure 6, i.e., the rate initially increases with increasing concentration of carbon tetrachloride and finally becomes constant when $k_3[\mathrm{CCl_4}] \gg k_2$.

From the experimental result shown in Figure 6, the kinetic constant at 50°C. can be evaluated as follows: $k_1 = 4.61 \times 10^{-9}$ l./mole-sec.; $k_2/k_3 = 2.24 \times 10^{-2}$ mole/l. By using these numerical values, the complete rate equation can be obtained as:

$$R_p = 3.35 \times 10^{-5}\{[\mathrm{CCl_4}]/(2.24 \times 10^{-2} + [\mathrm{CCl_4}])\}^{1/2} \tag{12}$$

or

$$R_p = 1.09 \times 10^{-5}\{[\mathrm{M}]^3[\mathrm{C}][\mathrm{CCl_4}]/(2.24 \times 10^{-2} + [\mathrm{CCl_4}])\}^{1/2} \tag{13}$$

For the rate of initiation eq. (14) can be obtained:

$$v_i = 5.53 \times 10^{-9}[\mathrm{CCl_4}]/(2.24 \times 10^{-2} + [\mathrm{CCl_4}]) \tag{14}$$

These kinetics mentioned above involve essentially the same treatment as for polymerization of methyl methacrylate initiated by metal carbonyl, which was extensively examined by Bamford and co-workers.[22-26]

Figure 9 shows a representation of the initiation step for the polymerization of methyl methacrylate by an associated complex (I). The associated complex reduces carbon tetrachloride to give a primary radical in which liquid sulfur dioxide may assist in the reduction, since the solvation power of liquid sulfur dioxide for the anion stabilizes chloride anion.

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Résumé

On a trouvé que la polymérisation du polyméthacrylate de méthyle peut être initiée par des complexes du type transfert de charge obtenus dans le SO_2 liquide et la pyridine en présence de tétrachlorure de carbone. Le rapport molaire du dioxyde de soufre et de la pyridine qui participent à la formation du complexe était de 2:1 suite à des études spectrophotométriques. On a montré que la polymérisation résulte d'intermédiaires radicalaires. La vitesse globale de polymérisation est proportionnelle à la racine carrée de la concentration du complexe et les valeurs $k_p/(k_t)^{1/2}$ qui étaient obtenues dans diveres conditions de polymérisation s'accordaient avec les valeurs de la littérature. Une énergie d'activation globale de 8.2 kcal./mole a été obtenue, et pour l'initiation, 9.7 kcal./mole a été évaluée au départ des valeurs de $k_p/k_t^{1/2}$. On déduit, d'un mécanisme cinétique supposé pour l'initiation, que les radicaux primaires sont probablement produits par la réduction du tétrachlorure de carbone par un complexe associé formé par le complexe dioxyde de soufre–pyridine et le monomère.

Zusammenfassung

Es wurde gefunden, dass die Polymerisation von Methylmethacrylat in Gegenwart von Tetrachlorkohlenstoff durch einen Elektronendonor–Acceptorkomplex aus flüssigem Schwefeldioxyd und Pyridin angeregt werden kann. Das molare Verhältnis, in dem Schwefeldioxyd und Pyridin im Komplex vorliegen, beträgt nach spektrophotometrischen Untersuchungen 2:1. Es wurde gezeigt, dass die Polymerisation über radikalische Zwischenprodukte verläuft. Die Bruttogeschwindigkeit der Polymerisation ist der Quadratwurzel aus der Komplexkonzentration proportional. Die $k_p/k_t^{1/2}$-Werte, die unter den verschiedenen Polymerisationsbedingungen erhalten wurden, standen in befriedigender Ubereinstimmung mit dem Literaturwert. Für die Aktivierungsenergie der Bruttoreaktion ergaben sich 8,2 Kcal./Mol, aus den $k_p/k_t^{1/2}$-Werten wurde für den

Start eine Aktivierungsenergie von 7,9 Kcal./Mol ermittelt. Aus einem kinetischen Mechanismus für den Start wurde abgeleitet, dass sich wahrscheinlich ein Primärradikal durch Reduktion des Tetrachlorkohlenstoffs durch einen assoziierten Komplex bilden kann, der aus dem Monomeren und dem Komplex aus flüssigem Schwefeldioxyd und Pyridin besteht.

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Anionic Copolymerization of Styrene and Isoprene in Cyclohexane

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Synopsis

The copolymerization of isoprene with styrene initiated with *sec*-butyllithium in cyclohexane solution has been studied by kinetic methods. The rates of the homopolymerization have been measured by normal methods. The rates of the cross-propagation reactions were measured by the rate of appearance or disappearance of the ultraviolet absorption of polystyryllithium when the individual chain ends were reacted with the opposite monomer in the absence of the first. The rates of some of the reactions were also measured in the presence of the other monomer. It was found that polyisoprenyllithium reacted with both monomers with a one quarter-order dependence, and the polystyryllithium with a one half-order dependence. It was found possible to describe the copolymerization in terms of the four individual rate constants and to predict the initial copolymer composition. It was not found necessary to resort to explanations based on preferential absorption of isoprene around the chain ends to explain the high isoprene content of the copolymer.

Copolymerization of nonpolar monomers in anionic systems is particularly well suited to experimental investigation because of the long-lived nature of the propagating species.[1] It is possible to isolate and to measure the individual rates of reaction which constitute the copolymerization: the two homopolymerization rates and the two crossover rates. The systems of styrene and butadiene initiated with *n*-butyllithium in cyclohexane and in benzene solution have already been studied in this way.[2,3] It was possible to demonstrate that the unexpectedly high initial butadiene content in the copolymer, despite the low butadiene homopolymerization rate, is caused by kinetic factors and is not due to preferential absorption of butadiene at the active centers as has sometimes been suggested.[4]

The similar system of styrene and isoprene initiated with *sec*-butyllithium in cyclohexane has now been studied. Before, study has been restricted to copolymer compositions mostly for this monomer pair.[5-7] The homopolymerization propagation rates in this case are comparable, but again the copolymer initially formed contains mostly the diene. In the butadiene system it was not found possible to measure one of the crossover rates because of its great rapidity, although this did not impair the interpretation of the reaction scheme. Here all four rates are measurable, although the reaction of isoprene with polystyryllithium is still very fast.

Experimental

All the reactions were preinitiated with *sec*-butyllithium as it has been shown that with this isomer the initiation rate is far higher[8] than for the *n*-butyllithium used before. This enabled the reactions to be preinitiated far more readily and greatly facilitated the measurement of the propagation rates.

The *sec*-butyllithium was obtained as a 12% solution from Foote Mineral Co. Before use it was freed from solvent by pumping, and given a short path distillation onto a cold finger, under high vacuum in an all-glass apparatus. The distillation was quite rapid at 75°C. The clear, colorless viscous initiator was sealed off and diluted with cyclohexane into a number of fragile bulbs by techniques described before.[9] The bulbs were stored in a refrigerator and gave reproducible results over a period of weeks.

The homopolymerization rates were measured spectrophotometrically as before[2,10] under vacuum conditions with the vessels washed with butyllithium solution. The crossover rates were studied by taking preinitiated solutions of the polymer lithium salts that had been allowed to stand for at least 20 half lifetimes of the propagation reaction, to reduce the first monomer concentration to negligible amounts. After breaking a fragile bulb of the opposite monomer, the reaction was followed by measuring spectrophotometrically the appearance or disappearance of the polystyryllithium absorption peak at 328 mμ.

The reactions were all done at 40°C. to be above the Θ temperature of polystyrene. All rates are given in units of mole, liters, and seconds.

Results and Discussion

The rates of reaction of polyisoprenyllithium (PI) with isoprene and with styrene in the absence of the other monomer are shown in Figure 1. It is seen that for both monomers the rate is proportional to close to the one-quarter power of polyisoprenyllithium given by the lines drawn. The order of the propagation step in the homopolymerization is in accord with that found by most authors[11] at other temperatures and is attributed to the fourfold association of this salt in this solvent. It is thought that only a small equilibrium amount of the monomeric form is active in polymerization. This interpretation is strengthened by the similar order found when the polyisoprenyllithium is reacted with styrene in a much slower reaction.

The rates of reaction of polystyryllithium (PS) with both monomers are shown in Figure 2. The rate of the propagation reaction in the homopolymerization of styrene in cyclohexane is again half order in polystyryllithium, as found before with *n*-butyllithium as initiator.[10] The rates here are somewhat higher than those found before and are to be preferred, as the *sec*-butyllithium is far preferable as an initiator because of its higher activity and ease of purification. The reaction of the polystyryllithium with isoprene, a comparatively very fast reaction, is also half

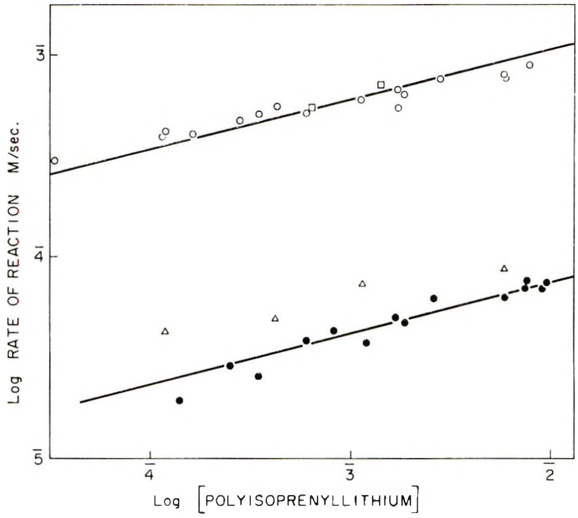

Fig. 1. Rates of reaction of polyisoprenyllithium at 40°C. in cyclohexane with: (⊙) isoprene; (⊡) isoprene in the presence of ca. 0.15 mole/l. styrene; (●) styrene; (◬) styrene in the presence of ca. 0.15 mole/l. isoprene.

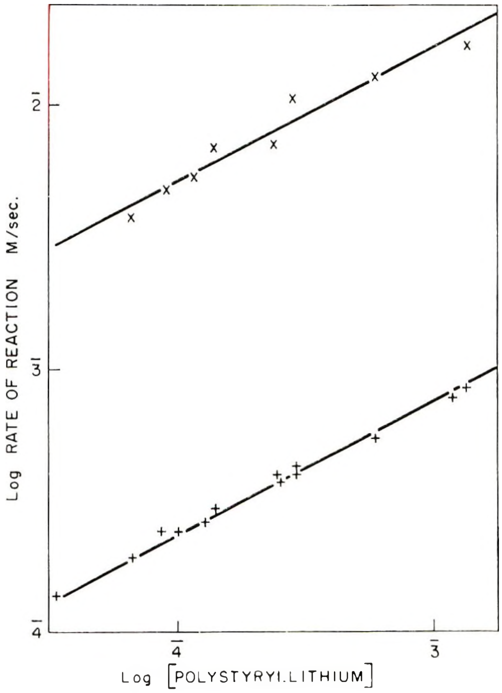

Fig. 2. Rates of reaction of polystyryllithium at 40°C. in cyclohexane with: (+) styrene; (×) isoprene.

TABLE I
Rate Constants for Copolymerization at 40°C.

Rate constant, sec.$^{-1}$ [a]
$k_{II}' = 3.41 \times 10^{-3} M^{1/4}$
$k_{SS}' = 2.29 \times 10^{-2} M^{1/2}$
$k_{IS}' = 2.37 \times 10^{-4} M^{1/4}$
$k_{SI}' = 5.13 \times 10^{-1} M^{1/2}$

[a] $k_{II}' = K_I^{1/4} k_{II}$ and $k_{SS}' = K_S^{1/2} k_{SS}$, etc.

order in the salt. Both half orders are in accordance with the dimeric nature of polystyryllithium found in hydrocarbon solvents. The four rate constants derived from the lines drawn through the experimental points are in Table I.

The dimerization of the *sec*-butyllithium-initiated polystyrenes was confirmed by light-scattering measurements on 1% solutions in cyclohexane at the Θ temperature on first the living polymer and then the dead polymer as was done before,[10] but with the use of a Sofica instrument. The greater association of the polyisoprenyllithium chain end was confirmed by adding sufficient isoprene to the polystyryllithium solutions in cyclohexane to add a few monomer units to each chain. In all cases the light scattering increased greatly, but the degree of association found was between 3 and 4, usually nearer 3. On killing with butanol the molecular weight fell to the calculated kinetic value, so the increase in apparent molecular weight of the associated living polymer was not due to cross-linking. There is a possibility of an equilibrium between a tetrameric and a dimeric form, but the experimental difficulties could well account for the found association being less than 4.

In preinitiated conventional copolymerization, with comparable amounts of both monomers initially present, there is no measurable ultraviolet absorption of the polystyryl carbanion in the early stages of reaction, and virtually all the chains end in polyisoprenyllithium. This is because of the slow rate of reaction of styrene with the polyisoprenyllithium chain end to give polystyryllithium (Fig. 1), and the very rapid reaction of isoprene with the polystyryllithium when it does form to give back polyisoprenyllithium (Fig. 2).

Under these conditions the major reaction is the reaction of isoprenyllithium with isoprene. The rate of consumption of isoprene in the presence of comparable amounts of styrene, as measured by vapor-phase chromatography is in fact close to the normal homopolymerization rate, as is shown by two points in Figure 1. The rate of incorporation of the styrene into the copolymer would be governed initially by the comparatively low rate of addition of styrene to the isoprenyllithium and accounts for the low styrene content in the copolymer. In the later stages of the reaction when the isoprene has been consumed, the rate becomes that of the homopolymerization of styrene.

The low styrene content of the initial copolymer has at times been attributed to the preferential absorption of isoprene around the active chain end.[4-6] If this were so, the rate of reaction of the isoprenyllithium with styrene would be lower in the presence of isoprene than in its absence. The rate in the absence of isoprene is given by the crossover rate measured above. The rate in its presence is closely given by the rate of consumption of styrene in the initial stages of an actual copolymerization, as the major chain end present is the polyisoprenyllithium. Some such rates of styrene consumption in the presence of severalfold excess of isoprene are shown in Figure 1, and are in fact somewhat higher than in the straight crossover reaction, and preclude the possibility of preferential absorption of isoprene. The higher rates are possibly due to the build up of a small amount of polystyryllithium. The presence of less than 0.1% of the chain ends in this form would account for this rate if the normal association occurred.

The possibility of absorption of monomers in large amounts around chain ends in homogeneous ionic polymerization has been suggested several times.[12] If this were true, the internal kinetic order of reaction of the monomer would tend toward zero at high monomer concentration, or deviate from first order when the monomer concentration fell below that of the initiator, according to the details of the schemes proposed. The close adherence to first-order kinetics is easily demonstrated for isoprene in its homopolymerization as the reaction may be followed spectrophotometrically for many half lifetimes. Several reactions were so followed, but none were found to deviate from first order. The two furthest followed were followed for twelve half lifetimes, and the rate constants measured over four successive periods of three half lifetimes are given in Table II.

The reactions are first-order in monomer from 250 times the chain-end concentration to $^1/_{25}$ of its concentration. Thus the number of chain ends with isoprene absorbed on them if any, must be very restricted and not kinetically significant.

From the knowledge of the four rate constants it is possible to calculate that the initial copolymer should contain 13% by weight of styrene if the initial concentrations of isoprene and styrene are equal. Literature values for hydrocarbon solvents are 12, 15, and 17%, and that found in cyclohexane was 15%.

TABLE II
Propagation Rate in the Polymerization of Isoprene

[PI], mole/l. × 10^3	[Isoprene] Initial, mole/l.	[Isoprene] Lowest measured, mole/l. × 10^4	$10^4 \times R_{11}$ for half-lifetime, sec.$^{-1}$ 1-3	4-6	7-9	10-12
4.13	1.03	1.6	7.42	7.49	7.56	7.56
3.26	1.22	3.5	7.15	7.09	7.02	6.82

Thus the early parts of the copolymerization can be described in terms of the four reactions and two equilibria:

$$[\mathrm{PI}]_4 \overset{K_\mathrm{I}}{\rightleftharpoons} 4\mathrm{PI} \tag{1}$$

$$\mathrm{PI} + \mathrm{I} \xrightarrow{k_\mathrm{II}} \mathrm{PI} \tag{2}$$

$$\mathrm{PI} + \mathrm{S} \xrightarrow{k_\mathrm{IS}} \mathrm{PS} \tag{3}$$

$$[\mathrm{PS}]_2 \overset{K_\mathrm{S}}{\rightleftharpoons} 2\mathrm{PS} \tag{4}$$

$$\mathrm{PS} + \mathrm{S} \xrightarrow{k_\mathrm{SS}} \mathrm{PS} \tag{5}$$

$$\mathrm{PS} + \mathrm{I} \xrightarrow{k_\mathrm{SI}} \mathrm{PI} \tag{6}$$

The reactions controlling the rate of consumption of monomer are those in the first half of the scheme. However this simple scheme is almost certain to fail somewhat later in the reaction as the isoprene concentration falls, because an appreciable fraction of the chains will begin to end in polystyryllithium, and cross-association between the two types of chain end may be important and complicate the association equilibria.

The reactivity ratios may be calculated from the found rate constants, and where styrene is M_1, $r_1 = 0.046$, and $r_2 = 16.6$, then $r_1r_2 = 0.76$. The product of the reactivity ratios is somewhat less than one, and suggests a slight tendency for the crossover reactions to be preferred over homopolymerization. This method might have its shortcomings, however, as penultimate effects could occur in true copolymerizations which are not measured here.

In reactions with both polystyryl and polyisoprenyl chain ends, isoprene is very much more reactive than styrene. This is a far truer reflection of the reactivities of these monomers under these conditions than is a comparison of the homopolymerization rates where the association effects are not cancelled. It is interesting to note that the reactivities of styrene and isoprene are the reverse of those found in ether solvents by copolymer composition[7] when lithium is the counterion.

The polyisoprenyllithium chain-end reaction rate is far less than that of polystyryllithium with either monomer in the range covered here, but since comparison of the rates of different chain ends incorporates consideration of the unknown equilibrium constants, it is not possible to say which unassociated chain end has the higher reactivity.

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Résumé

La copolymérisation de l'isoprène avec le styrène, initiée par le *sec*-butyllithium, en solution dans le cyclohexane a été étudiée par des méthodes cinétiques. Les vitesses d'homopolymérisation ont été mesurées par les méthodes habituelles. Les vitesses des réactions de propagation croisée ont été mesurées par la vitesse d'apparition ou de disparition de l'absorption ultraviolette du polystyrylithium lorsqu'on fait réagir chacune des fins de chaînes avec le monomère opposé en absence du premier monomère. Les vitesses de certaines réactions ont également été mesurées en présence de l'autre monomère. On a trouvé que le polyisoprényllithium réagissait avec les deux monomères suivant un ordre-0.25 et le polystyryllithium suivant un ordre-0.5. On a pu décrire la copolymérisation sur la base de quatre constantes de vitesse individuelles et prédire la composition du copolymère initial. Il n'est pas nécessaire de faire usage d'explications basées sur l'absorption préférentielle d'isoprène autour des fins de chaînes pour expliquer la teneur elevée en isoprène au sein du copolymère.

Zusammenfassung

Die mit sec-Butyllithium in Cyclohexanlösung gestartete Copolymerisation von Isopren und Styrol wurde mit kinetischen Methoden untersucht. Die Geschwindigkeiten der Homopolymerisation wurden mit den normalen Methoden gemessen. Die Geschwindigkeit der gekreuzten Wachstumsreaktion wurde durch die Geschwindigkeit des Auftretens oder Verschwindens der UV-Absorption von Polystyryllithium bei Reaktion der individuellen Kettenenden mit dem entgegegnesetzten Monomeren in Abwesenheit des gleichen bestimmt. Die Geschwindigkeiten einiger Reaktionen wurde auch in Gegenwart des anderen Monomeren gemessen. Es wurde gefunden, dass Polyisoprenyllithium mit beiden Monomeren mit der Ordnung ein viertel und Polystyryllithium mit der Ordnung ein halb reagiert. Es war möglich, die Copolymerisation mit den vier individuellen Geshwindigkeitskonstanten zu beschreiben und die Anfangs-Copolymerzusammensetzung vorherzusagen. Es war nicht notwendig zur Erklärung des hohen Isoprengehaltes des Copolymeren eine preferentielle Absorption des Isoprens um die Kettenenden anzunehmen.

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Effects of Carbonyl and Aldehyde Groups in the Graft Copolymerization of Methyl Methacrylate on Cellulose with a Ceric Salt

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Synopsis

Graft copolymerization of methyl methacrylate on cellulosic materials of various carbonyl and aldehyde contents with the use of a ceric salt as an initiator was studied. It was found that the concentration of the ceric salt which gives the maximum per cent grafting is in good agreement with the equivalent of total carbonyl content in the cellulosic material, and the number of grafted chains in copolymers is roughly proportional to it. However, the molar ratio of the number of grafted chains to total carbonyl content is quite small, being approximately 1:50, and the graft copolymerization can be explained kinetically on the assumption that the number of radicals produced on cellulose by the ceric salt leading to branching is very much smaller than the number of radicals destroyed by the ceric salt, and growing radicals can be stabilized by the termination reaction with the ceric salt or with a cellulose radical. Although both aldehyde and carbonyl groups contribute to the formation of grafted chains, the former are effective mainly at low concentrations of the ceric salt; both groups participate in the production of graft copolymers showing the maximum per cent grafting.

INTRODUCTION

Our previous report[1] dealt with a study on the graft copolymerization of methyl methacrylate on pulp with a ceric salt as an initiator, especially on factors affecting the formation of grafted chains. The copper number, one of the characteristic properties of pulp, was found to be an important factor: the larger this value becomes, the more grafted chains the polymers tend to have. The number of grafted chains showed a tendency to increase with the amount of the ceric salt used. There is a maximum per cent grafting at a certain catalyst concentration, and the ceric salt concentration which gives the highest per cent grafting corresponds approximately to the reduction equivalent calculable from the copper number of pulp. However, the number of grafted chains in this case was found to be only $^1/_{10}$ to $^1/_{50}$ of this value. In the present study the graft copolymerization of methyl methacrylate on pulps of different carbonyl and aldehyde contents, both groups representing the reducing properties of cellulose, was examined kinetically and the mechanism of the formation of grafted chains discussed.

EXPERIMENTAL

Cellulosic Materials

Commercial absorbent cotton (cotton), bleached kraft pulp (KP), bleached sulfite pulp (SP), and bleached semichemical pulp (SCP) were used untreated; SP was also treated as shown in Table I to prepare reduced as well as oxidized cellulosic materials.

TABLE I
Conditions of Oxidative and Reductive Treatment on Sulfite Pulp

Reagent	Concentration of reagent	Ratio of bath	pH of bath	Temperature, °C.	Time, hr.
Ceric salt	$0.01M$ in $0.035M$ nitric acid	70	1.7	25	24
Potassium dichromate	$0.05N$ in $2N$ sulfuric acid	40	—	25	5
Sodium hypochlorite	$0.02N$ in buffer solution	40	7.0	25	5
Sodium hypochlorite	$0.02N$ in buffer solution	40	10.0	25	5
Sodium borohydride	$0.05M$ in $1N$ sodium hydroxide	70	12.2	25	48

Analytical Methods

Carboxyl Groups.[2] The cellulosic material was washed with $0.1N$ hydrochloric acid, then with distilled water, and treated with a 0.3 mN calcium acetate solution. The cation adsorbed on the sample was determined from the calcium ion concentration in the filtrate and the carboxyl content calculated.

Aldehyde Groups.[3] The cellulosic material was oxidized with a $0.01M$ sodium chlorite solution (pH = 3.52) at 40°C. for 3 hr., the increase in carboxyl content due to the oxidation determined, and the aldehyde content calculated.

Total Carbonyl Groups.[4] The cellulosic material was allowed to react with a hydroxylamine hydrochloride solution (50 g./l.) whose pH was adjusted to 5.2 by $1N$ sodium hydroxide for 2 hr. at 55°C. and the liberated hydrochloric acid was determined. The pH for standardization was adjusted to 3.2.

Number of Grafted Chains. This was determined from the weight of grafted chains calculated from the per cent grafting B (in grams/100 g. cellulose) and the average molecular weight of grafted chains M according to the equation:

$$\text{Number of grafted chains (mmole/100 g. cellulose)} = B/M$$

Copper Number. This was determined by Tappi standard method T215m-50.

Weight-Average Molecular Weight of Grafted Chains. Grafted polymer was isolated with 72% sulfuric acid, dissolved in acetone, and the weight-average molecular weight determined from the viscosity of the acetone solution by using the same equation ($[\eta] = 0.96 \times 10^{-4}M^{0.69}$) as in the previous report.[1]

Graft Copolymerization

The polymerization procedures are the same manner as reported previously.[1] A 2.5-ml. portion of methyl methacrylate was emulsified with 25 ml. of distilled water and 0.127 g. of non-ionic emulsifier, and 0.5 g. of cellulosic material was placed in the reaction vessel together with the emulsified solution. A solution containing a known amount of ceric salt in 15 ml. of 0.1*N* nitric acid was then added.

The polymerization reaction was carried out at 45°C. for 60 min. in nitrogen atmosphere and stopped with hydroquinone solution.

RESULTS AND DISCUSSION

Copper Number and Carbonyl and Aldehyde Contents in Cellulosic Materials

The relationship between the copper number expressed as reduction equivalent and the total carbonyl content for various cellulosic materials is shown in Figure 1. Liedman-Safwat and Theander[5] reported that the relationship between copper number and carbonyl content is linear, but the slope of the line varies depending upon the degree of oxidation. Linear relationships are seen for the untreated samples in Figure 1, but no definite relationships are recognizable when oxidized or reduced samples are included.

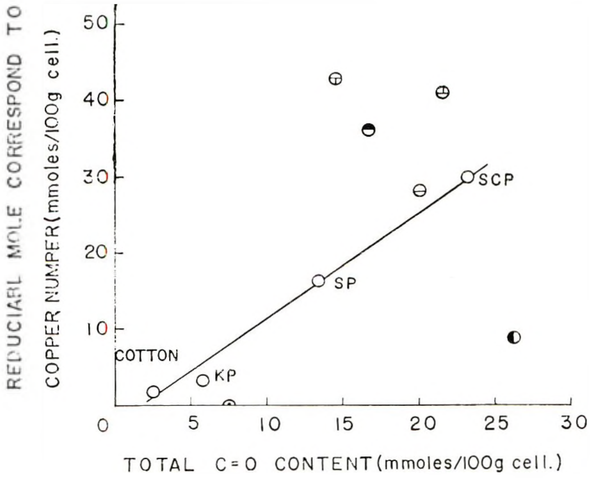

Figure 1.

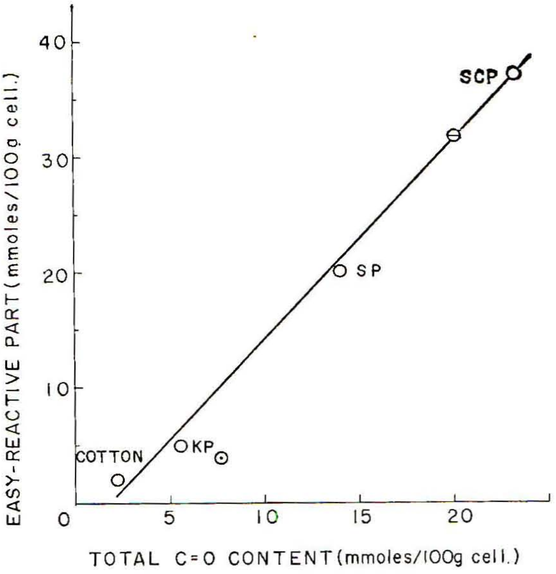

Figure 2.

The relationship between the total carbonyl content and the reactive portion,[1] which is determined from the rate of consumption of the ceric salt, is shown in Figure 2 for these samples. Linear relationships are obtained, and the molar ratio of the two is approximately 1:1.6. Samples reduced by sodium borohydride deviate from the linear relationship, and this is probably due to a low reactivity of carbonyl groups present in the samples towards the ceric salt.

TABLE II

Aldehyde and Total Carbonyl Group Content of Cellulosic Material

Cellulosic material	CHO, mmole/100 g. cellulose	Total C=O, mmole/100 g. cellulose
Cotton	0.11	2.50
KP	0.61	5.55
SP	0.73	14.0
SCP	2.95	23.2
SP oxidized with potassium dichromate	1.39	16.7
SP oxidized with sodium hypochlorite at pH 4, 4 hr.	0.95	21.5
SP oxidized with sodium hypochlorite at pH 4, 18 hr.	1.69	18.6
SP oxidized with sodium hypochlorite at pH 7	1.00	27.7
SP oxidized with sodium hypochlorite at pH 10	0.23	24.2

Aldehyde groups are more reactive than carbonyl groups towards an oxidizing agent and seem to exert more influence on the graft copolymerization. Morrow[3] determined aldehyde and carbonyl contents in commercial pulps and noticed an almost linear relationship between the two groups. The relationships between the total carbonyl content and the aldehyde content in various celluloses are shown in Table II. The aldehyde content is less than about $^1/_{10}$ the carbonyl content, and no well-defined relationship is seen between the ratio of the two groups and the conditions for treating pulps.

Relationship Between Maximum Grafting and the Carbonyl Content

The relationship between the ceric salt concentration and the per cent grafting is shown in Figure 3 for graft copolymers on various celluloses obtained under standard polymerization conditions.[1] As other investigators reported previously,[1,6–8] there is a maximum per cent grafting at a certain concentration of ceric salt for each sample. Ide and coworkers[7] explained this phenomenon as follows: a backbone polymer radical is oxidized secondarily by the free ceric ion, and this oxidation takes place with more ease at the ceric salt concentration which will show the maximum per cent grafting. However, as will be described below, the number of grafted chains keeps increasing with the ceric salt concentration, even beyond the concentration showing the maximum per cent grafting, and secondary oxidation alone appears insufficient to explain this phenomenon. We reported previously that the ceric salt concentration showing the maximum per cent grafting roughly agreed with the reduction equivalent corresponding to the copper number. For the samples examined in the present study, a definite correlation is seen

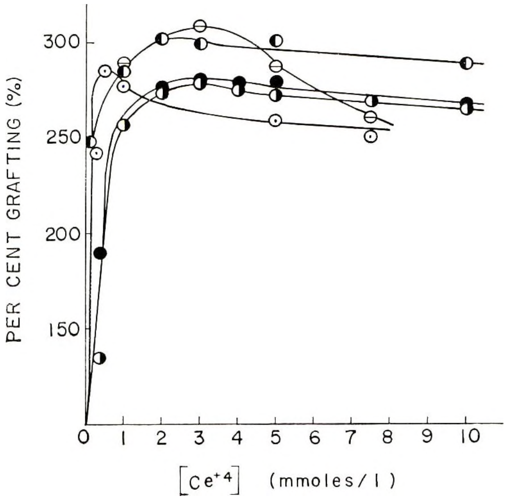

Figure 3.

TABLE III
Relationship of Total Carbonyl Group Content to Ceric Salt Concentration at Maximum Per Cent Grafting

Cellulosic material	Ceric salt concentration at maximum per cent grafting, mmole/l.	Ceric salt concentration at maximum per cent grafting, mmole/100 g. cellulose	Total C=O, mole/100 g. cellulose
Cotton	0.5–1.0	4.25–8.5	2.50
KP	0.5–1.0	4.25–8.5	5.55
SP	1.0–2.0	8.5–17.0	14.0
SCP	2.5–3.5	21.2–29.8	23.2
SP reduced with sodium borohydride	0.5–1.0	4.25–8.5	7.53
SP oxidized with ceric salt	2.0–3.0	17.0–25.5	20.0
SP oxidized with potassium dichromate	2.0–3.0	17.0–25.5	16.7
SP oxidized with sodium hypochlorite at pH 7	2.5–3.5	21.2–29.8	27.7
SP oxidized with sodium hypochlorite at pH 10	2.0–3.0	17.0–25.5	24.2

between the ceric salt concentration showing the maximum per cent grafting and the total carbonyl content in the cellulosic material, as shown in Table III. It is apparent here that the cellulosic material with a higher total carbonyl content requires a larger quantity of ceric salt, but the per cent grafting of the graft copolymer does not necessarily depend upon the total carbonyl content in the sample. A possible explanation for this is that, as Sihtola and Neimo[9] pointed out, carbonyl groups with varying degrees of reactivity are produced in cellulose, depending upon the method of oxidative treatment.

No definite quantitative relationship was found between the maximum per cent grafting and the aldehyde content.

Weight-Average Molecular Weight of Grafted Chains

It is widely recognized[1,10] that the average molecular weight of grafted chains increases with decreasing ceric salt concentration and increasing monomer concentration. The ceric salt concentration is plotted against the reciprocal of the average molecular weight for various cellulosic materials in Figure 4. Each sample gives a broken line composed of two lines of different slope in a certain region of ceric salt concentration, and the ceric salt concentration at the inflection point roughly agrees with that which gives the maximum per cent grafting.

It is inferred from the linear relationship between the ceric salt concentration and the average molecular weight of grafted chains that the termination of the graft copolymerization proceeds mainly by the reaction of ceric ion with a growing radical. A similar mechanism of ter-

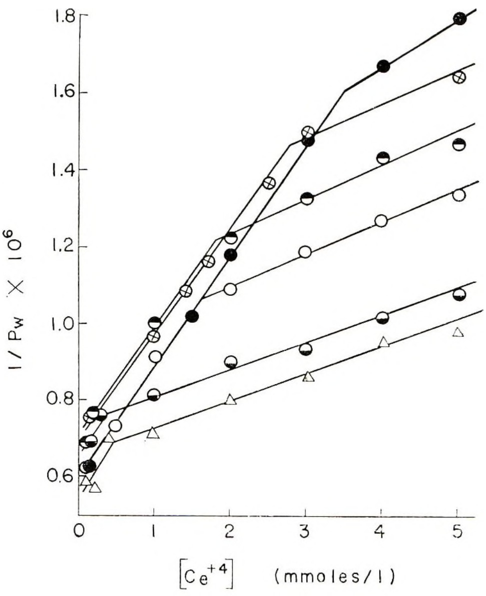

Figure 4.

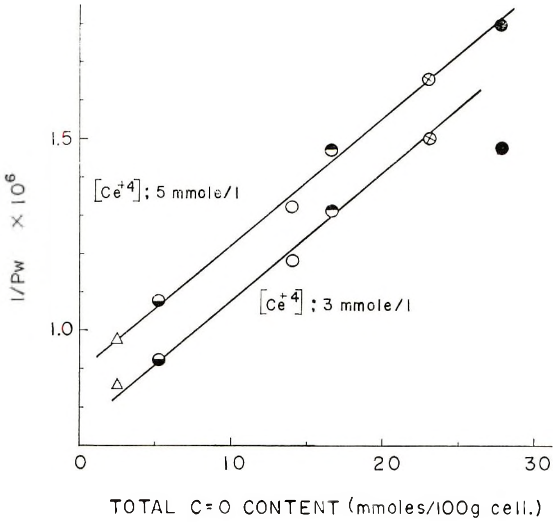

Figure 5.

mination is reported for the graft copolymerizations involving acrylamide and cellulose,[11] acrylonitrile and ethylene glycol,[12] and acrylamide and dextran.[13]

The effects of the ceric salt concentration on the average molecular weight of grafted chains are large in the region of the straight line with a steep slope in Figure 4. However, the differences among the various celluloses are slight, and this indicates that the total carbonyl content

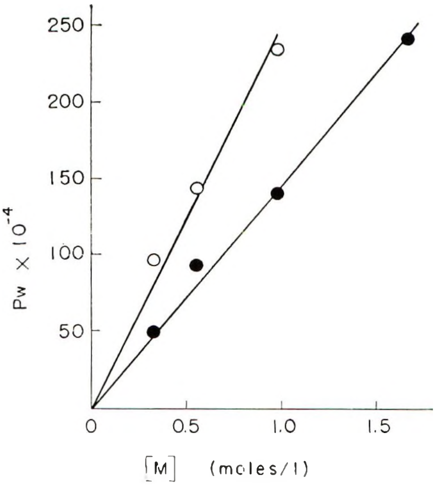

Figure 6.

does not appreciably influence the average molecular weight of grafted chains.

On the other hand, when the ceric salt concentration exceeds the point which gives the maximum per cent grafting, the slope of the line becomes less steep, and the differences among the cellulosic materials show up distinctly, although the effects of the ceric salt concentration on the average molecular weight of grafted chains are small.

When a ceric salt concentration which is slightly higher than the one giving the maximum per cent grafting was used, a linear relationship was noticed between the reciprocal of the average molecular weight of grafted chains and the total carbonyl content as shown in Figure 5. It is apparent that the average molecular weight of grafted chains formed tends to decrease as the total carbonyl content in cellulose and the ceric salt concentration increase. It is also seen from Figure 6 that there is a linear relationship between the average molecular weight of grafted chains and the monomer concentration.

Number of Grafted Chains

The number of grafted chains in graft copolymers increases with the ceric salt concentration, as shown in Figures 7 and 8. As was mentioned in our previous report, a plot of the logarithm of the ceric salt concentration against the number of grafted chains gave an inflected line which changed slope at the ceric salt concentration giving the maximum per cent grafting for each cellulosic material. Since the total carbonyl content is closely related to the ceric salt concentration giving the maximum per cent grafting, the relationship between the total carbonyl content and the number of grafted chains is shown in Figure 9.

The number of grafted chains shown in Figure 9 is obtained at a ceric salt concentration higher than the one giving the maximum per cent

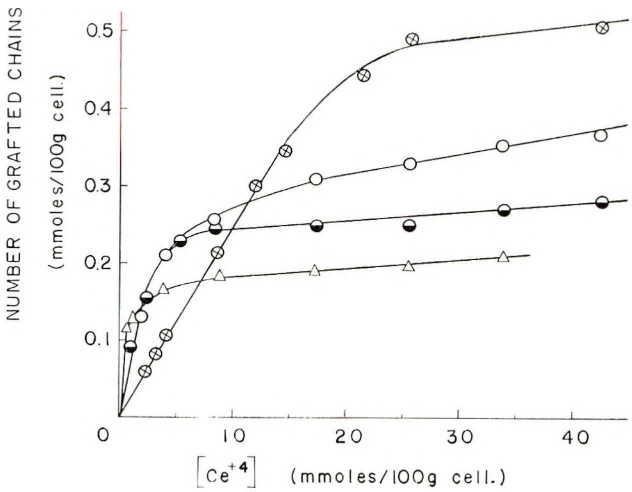

Figure 7.

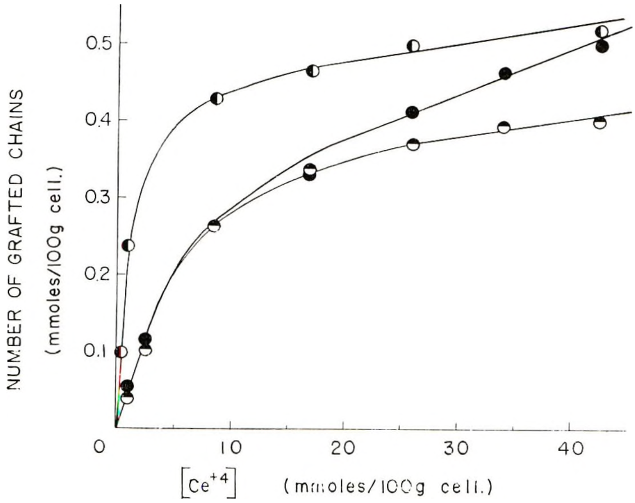

Figure 8.

grafting, and it is clear that a sample with a higher total carbonyl content shows a larger number of grafted chains. However, the number of grafted chains and the total carbonyl content differ greatly from each other as the molar ratio of about 1:50 indicates, and it is considered that some of the carbonyl groups participate in formation of grafted chains.

The aldehyde group is more reactive than the carbonyl group and it has been considered more closely related to the formation of grafted chains. However, a comparison of the aldehyde content with the number of grafted chains in graft copolymer with nearly maximum per cent grafting does not show the presence of a definite relationship, and there is no conclusive evidence indicating the aldehyde group is a main cause for the formation of grafted chains.

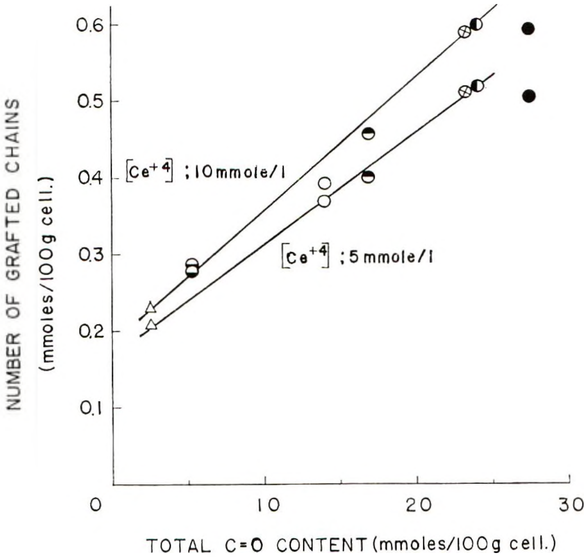

Figure 9.

Per Cent Formation of Grafted Chains

The number of grafted chains is proportional to the ceric salt concentration in the region of low concentrations (Figs. 7 and 8). It is conceivable that the straight line portion is the region where the reactive

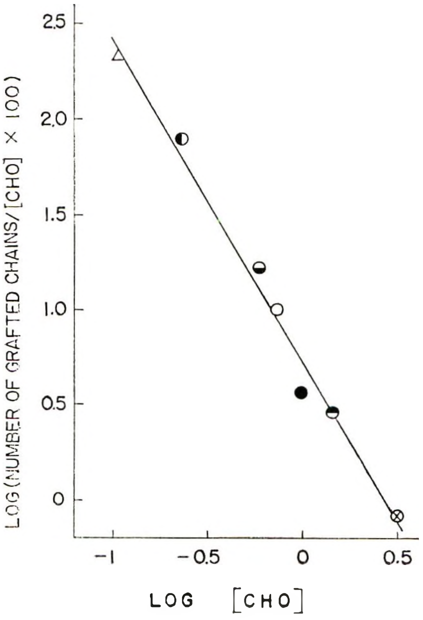

Figure 10.

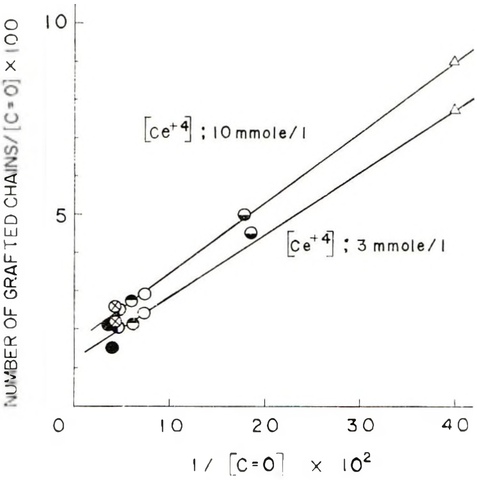

Figure 11.

aldehyde groups participate, and the slope of the line is different for each cellulosic material. The per cent ratio of the number of grafted chains formed (mmole/100 g. cellulose) to the aldehyde content in the cellulosic material (mmole/100 g. cellulose) when a unit amount of the ceric salt is used is defined as the per cent formation of grafted chains, and the relation of this value to the aldehyde content in the cellulosic material was studied. The results indicated that a sample with a higher aldehyde content shows a smaller per cent formation of grafted chains, that is, a good linear relationship was found between the logarithm of the per cent formation of grafted chains and the logarithm of the aldehyde content in the cellulosic material (Fig. 10).

As is apparent in Figure 9, the number of grafted chains in the graft copolymers varies considerably, depending upon the cellulosic material at ceric salt concentrations higher than the concentration giving the maximum per cent grafting. In this case as well, a linear relationship was obtained as shown in Figure 11 when the per cent formation of grafted chains based on the carbonyl content in the cellulosic material is plotted against the reciprocal of the carbonyl content at a given ceric salt concentration.

Mechanism of Graft Copolymerization

The reciprocal of the average molecular weight of grafted chains formed by graft copolymerization changes linearly with the ceric salt concentration and also with the total carbonyl content in the cellulosic material (Figs. 4 and 5). Furthermore, there is a linear relationship between the molecular weight and the monomer concentration (Fig. 6). Consequently the elementary reactions (1)–(6) were assumed for the graft copolymerization.

Initiation:

$$Ce^{+4} + Cell\text{—}H \overset{K}{\rightleftharpoons} Complex \xrightarrow{k_d} Cell\cdot + Ce^{+3} + H^{+} \tag{1}$$

$$Cell\cdot + M \xrightarrow{k_i} Cell\text{—}M\cdot \tag{2}$$

$$Ce^{+4} + M \xrightarrow{k_i'} M\cdot + Ce^{+3} + H^{+} \tag{3}$$

Propagation:

$$Cell\text{—}M_n\cdot + M \xrightarrow{k_p} Cell\text{—}M_{n+1}\cdot \tag{4}$$

$$M_m\cdot + M \xrightarrow{k_p'} M_{m+1}\cdot \tag{4'}$$

Termination:

$$Cell\text{—}M_n\cdot + Ce^{+4} \xrightarrow{k_t} Cell\text{—}M_n + Ce^{+3} + H^{+} \tag{5}$$

$$M_m\cdot + Ce^{+4} \xrightarrow{k_t'} M_m + Ce^{+3} + H^{+} \tag{5'}$$

$$Cell\cdot + Ce^{+4} \xrightarrow{k_0} \text{Oxidative products} + Ce^{+3} + H^{+} \tag{6}$$

Here, Cell—H denotes a reactive group in cellulose; M is monomer; K is the equilibrium constant; and k_i, k_i', k_p, k_p', k_t, k_t', and k_0 are rate constants.

Equations (4′) and (5′) are, respectively, propagation and termination reactions for homopolymers, and eq. (6) is the stabilization of a cellulose radical by ceric ion. It is assumed that the homopolymer and graft copolymer show the same rate constant, that is, $k_p = k_p'$ and $k_t = k_t'$.

By applying steady-state conditions to the concentrations [Cell·] and [Cell—M·] in reactions (1)–(6), the overall rate of polymerization can be expressed by eq. (7).

$$R_p = \frac{k_p}{k_t}[M]^2\left\{k_i' + \frac{k_d K\,[Cell\text{—}H]}{[M] + (k_0/k_i)\,[Ce^{+4}]}\right\} \tag{7}$$

Katai and co-workers[12] reported that eq. (7) can be applied to the ethylene glycol–acrylonitrile system. On the other hand, the number-average molecular weight of polymers,[1] P_n, can be represented by eq. (8). This equation treats the sum of grafted polymers and homopolymers, but in this paper only the grafted polymers are considered.

$$\frac{1}{P_n} = \frac{[Ce^{+4}]}{k_p[M]}\left[k_t + \frac{k_t''\,k_d\,K[Cell\text{—}H]}{k_i\{[M] + (k_0/k_i)[Ce^{+4}]\}}\right] \tag{8}$$

Equation (8) is derived by taking into account participation of a cellulose radical in the termination reaction, as is shown in eq. (5″).

$$Cell\text{—}M_n\cdot + Cell\cdot \xrightarrow{k_t''} \text{Stabilization} \tag{5''}$$

In their study of the ethylene glycol–acrylonitrile system using a ceric salt as an initiator, Katai and co-workers[12] estimated that $k_0/k_i = 50$, and reported that the rate constant for the oxidation of radicals formed is considerably larger than the rate constant for the initiation. Assuming that $(k_0/k_i)[\mathrm{Ce}^{+4}] \gg [\mathrm{M}]$, eq. (7′) and (8′) are obtained.

$$R_p = \frac{k_p}{k_t}[\mathrm{M}]^2\left\{k_i' + \frac{k_i k_d K[\mathrm{Cell{-}H}]}{k_0[\mathrm{Ce}^{+4}]}\right\} \tag{7′}$$

$$\frac{1}{P_n} = \frac{k_t[\mathrm{Ce}^{+4}]}{k_p[\mathrm{M}]} + \frac{k_t'' k_d K[\mathrm{Cell{-}H}]}{k_p k_0[\mathrm{M}]} \tag{8′}$$

Equation (8′) should hold approximately even when the weight-average (P_w) is used in place of P_n, and this equation explains quite well the linear relationship between the carbonyl content and the reciprocal of the average molecular weight of grafted chains (Fig. 5) and that between the monomer concentration and the average molecular weight of grafted chains.

In the graft copolymerization, the initiation reaction mainly proceeds via eq. (5). However, since the effect of the total carbonyl content in the cellulosic material on the molecular weight of grafted chains is apparent, the termination reaction (5″) does not seem negligible.

On the assumption that the number of grafted chains in graft copolymers is proportional to R_p/P_n, eq. (9) can be derived from eqs. (7′) and (8′).

$$\text{Number of grafted chains} \propto \frac{R_p}{P_n} = \frac{k_d K[\mathrm{M}]}{k_0}\left[\frac{k_0 k_i'[\mathrm{Ce}^{+4}]}{k_d K} + \left(\frac{k_i' k_t'' + k_i k_t}{k_t}\right)[\mathrm{Cell{-}H}] + \frac{k_i k_t'' k_d K[\mathrm{Cell{-}H}]^2}{k_t k_0[\mathrm{Ce}^{+4}]}\right] \tag{9}$$

As linear relationships are observed between the number of grafted chains and the ceric salt concentration as well as the total carbonyl content (Figs. 7–9), the third term in eq. (9) is negligibly small, which leads to eq. (9′).

$$\frac{R_p}{P_n} = \frac{k_d K[\mathrm{M}]}{k_0}\left[\frac{k_0 k_i'[\mathrm{Ce}^{+4}]}{k_d K} + \left(\frac{k_i' k_t'' + k_i k_t}{k_t}\right)[\mathrm{Cell{-}H}]\right] \tag{9′}$$

Division of both sides of eq. (9′) by [Cell—H] gives the per cent formation of grafted chains:

$$\text{Per cent formation of grafted chains} = \left\{\frac{k_i'[\mathrm{Ce}^{+4}][\mathrm{M}]}{[\mathrm{Cell{-}H}]} + \frac{k_d K(k_i' k_t'' + k_i k_t)}{k_0 k_t}\right\} \times 100 \tag{10}$$

The region where the number of grafted chains increases with the ceric salt concentration in Figures 7 and 8 is regarded as the region where aldehyde groups in cellulose participate in the reaction. The linear relationship in Figure 10 can be explained if [Cell—H] is replaced with the aldehyde content and the second term is negligibly small compared with the first term in eq. (10).

It is already clear that all the carbonyl groups in the cellulosic material participate in the reaction when the ceric salt concentration used is higher than that which gives the maximum per cent grafting. The molar concentration of total carbonyl groups is more than ten times that of aldehyde groups, and in this case the first term in eq. (10) may assume a slightly smaller value. When the second term is not negligible compared with the first, the per cent formation of grafted chains becomes proportional to the reciprocal of the total carbonyl content; this relationship is clearly shown in Figure 11.

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Résumé

La copolymérisation greffée du méthacrylate de méthyle sur des matériaux cellulosique à des teneurs variables en fonctions carbonyliques et aldéhydes en utilisant des sels cériques comme initiateurs a été étudiée. On a prouvé que la concentration de sels cériques qui donne le maximum de pourcentage de greffage est en accord avec un équivalent de la teneur totale en fonction carbonylique (I) du matériaux cellulosique, et le nombre de chaînes greffés dans le polymère, est approximativement proportionnel à (I). Toutefois, le rapport molaire du nombre de chaînes greffées à (I) est faible, étant approximativement égal à 1:50, et la copolymérisation greffée peut être expliquée cinétiquement en admettant que le nombre des radicaux produits sur la cellulose au moyen du sel cérique amenant à ramification est beaucoup plus petit que le nombre de radicaux détruits par le sel cérique; les radicaux en croissance peuvent être stabilisés par une réaction de terminaison entre le sel cérique et un radical cellulosique. Bien que les groupes aldéhydes et carbonyliques contribuent à la fois à la formation de chaînes greffées, le premier est en moyenne le plus effectif aux faibles concentrations en sel cérique; les deux groupes qui participent à la production de copolymères greffés montrent un maximum de pourcentage de greffage.

Zusammenfassung

Die unter Verwendung eines Cer(IV)-Salzes als Starter durchgeführte Pfropfcopolymerisation von Methylmethacrylat auf Cellulosematerialien verschiedenen Carbonyl- und Aldehydgehalts wurde untersucht. Es wurde gefunden, dass die Konzentration

des Cersalzes, die die maximale prozentuelle Pfropfausbeute ergibt, in guter Übereinstimmung mit dem Äquivalent an Gesamtcarbonylgehalt (I) im Cellulosematerial steht; die Zahl der aufgepfropften Ketten ist (I) ungefähr proportional. Das molare Verhältnis von gepfropften Ketten zu (I) ist jedoch ausnehmend niedrig und beträgt etwa 1:50. Die Pfropfcopolymerisation kann kinetisch auf Grund der Annahme erklärt werden, dass die Zahl der durch das Cersalz an der Cellulose produzierten Radikale, die zu einer Verzweigung führen, sehr viel kleiner als die Zahl der durch das Cersalz zerstörten Radikale ist, und dass wachsende Radikale durch Abbruchsreaktion mit dem Cersalz oder mit einem Celluloseradikal stabilisiert werden können. Obwohl sowohl Aldehyd- als auch Carbonylgruppen zur Bildung von gepfropften Ketten beitragen, sind bei niedrigen Cersalzkonzentrationen vornehmlich erstere wirksam. An der Bildung von Pfropfcopolymeren nehmen beide Gruppen teil, wobei sie die maximale prozentuelle Pfropfung zeigen.

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Role of *para*-Substituted Phenols in Curing Resole-Type Phenolic Resins*

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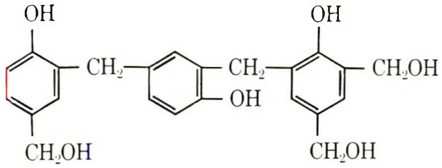
Synopsis

Certain *para*-substituted phenols, namely, those phenols without *ortho* substituents and containing an electron-attracting atom or group in the *para* position, e.g. *p*-nitro-, *p*-bromo-, and *p*-chlorophenol, hasten gelation of etherified phenolic resoles. A mechanism involving cleavage of dibenzyl ether linkages in these resins is proposed to explain gelation.

INTRODUCTION

It is known in the art of phenolic resin manufacture that resoles or the so-called one-stage resins contain methylol groups and require heat and/or acids, e.g. sulfuric phosphoric, hydrochloric, oxalic, and *p*-toluenesulfonic acid, for cure.[1] A typical resole is illustrated by the structure I.



I

Because the use of heat alone requires rather long curing cycles, strong acids generally have been employed to effect cure of these resins. However, Hoyt et al.[2] have demonstrated that such strong acids, particularly nonvolatile ones like sulfuric and phosphoric, cause degradation when left unneutralized in the resin.

EXPERIMENTAL

Chemicals used were commercial products of high purity.

Dianisyl Ether

This ether was prepared according to Pratt and Erickson[3] from *p*-methoxybenzyl alcohol with *p*-toluenesulfonic acid as a catalyst. Efforts to

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* Presented before the Polymer Division of the American Chemical Society, 140th National Meeting, Chicago, 1961.

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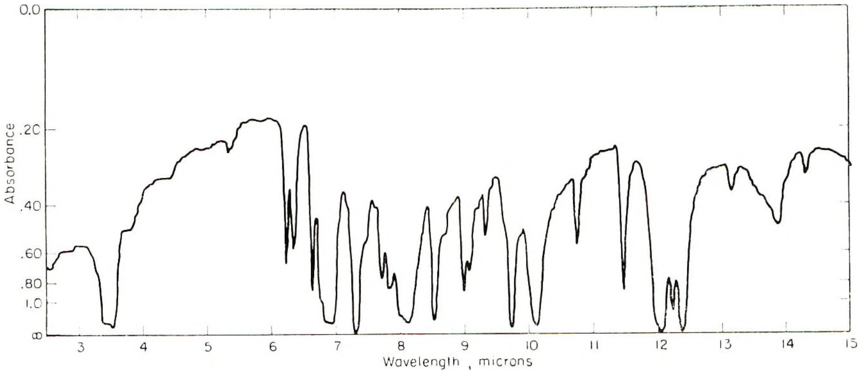


Figure 1.

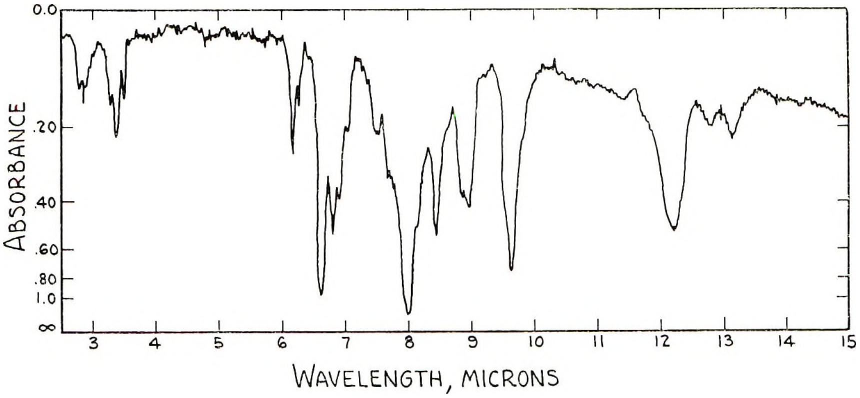


Figure 2.

distil under reduced pressure the crude ether after neutralization of the acid catalyst produced only two small fractions, (*1*) b.p. 90–92°C./1.5 mm. Hg and (*2*) b.p. 161–176°C./1.5 mm. Hg. The residue after distillation was a brittle solid whose infrared spectrum showed the absence of an absorption band at 9.2 μ which is characteristic of the —CH_2OCH_2— grouping. (Figs. 1 and 2). Fraction *1* was identified as anisaldehyde by its 2,4-dinitrophenylhydrazone derivative, m.p. 253.6–254.0°C.; fraction *2* after purification was characterized as bis(*p*-methoxyphenyl)-methane, m.p. 46–48°C., which showed no depression when mixed with an authentic sample and whose infrared spectrum was identical to that of a synthetic sample.

Reaction of Dianisyl Ether and *p*-Bromophenol

Dianisyl ether and *p*-bromophenol were reacted each in 0.1 molar quantities at 130–140°C. for 3 hr. Reaction set in at 80°C. with a splitting out of water. Subjecting the reaction mixture to distillation under reduced pressure yielded 0.05 mole of unreacted bromophenol and a brittle

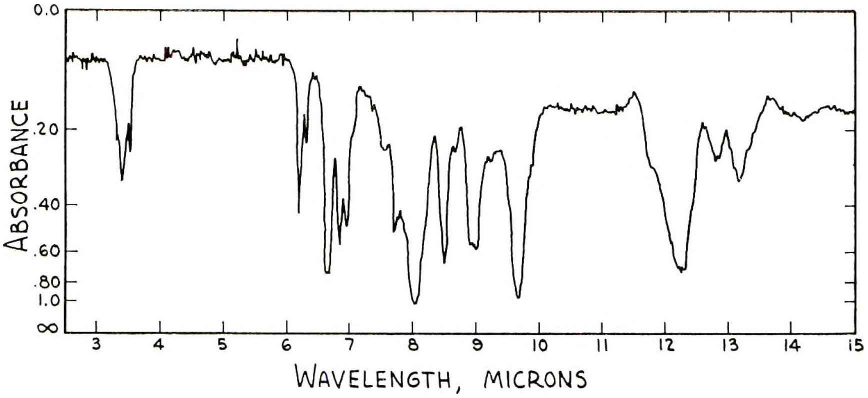


Figure 3.

polymeric material as a residue. This resin by chemical analysis contained 10.8% bromine; its infrared spectrum (Fig. 3) with a band in the 2.8 μ region indicated the presence of hydroxyl groups. The absence of a band in the 9.2 μ region indicated that dibenzyl ether linkages were destroyed in reaction.

Reaction of *p*-Methoxybenzyl Alcohol and *p*-Bromophenol

A charge of 0.8 mole of *p*-methoxybenzyl alcohol and 0.1 mole of *p*-bromophenol was heated at 140°C. for 3 hr. A slight vacuum was applied to the system which was set for distillation to remove water formed during reaction. Yield of water was 8.0 g. Extraction of the reaction mixture with 10% sodium hydroxide followed by neutralization with dilute hydrochloric acid failed to yield any unreacted *p*-bromophenol. Distillation under reduced pressure of the liquid reaction mixture produced a fraction, b.p. 159–160°C./0.2 mm. solid, m.p. 124–125°C. The yield was 7.8 g. A second recrystallization from *n*-hexane gave a product melting at 125.8–126.4°C.

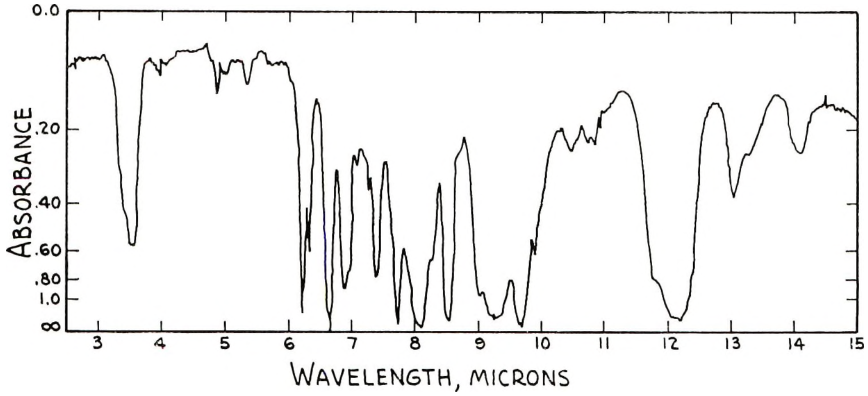


Figure 4.

ANAL. Calcd. for *p*-methoxybenzyl-*p*′-bromophenyl ether, $C_{14}H_{13}O_2Br$: Br, 27.3%. Found: Br, 27.5%.

Its infrared spectrum (Fig. 4) showed a strong *para*-substitution band in the 12 μ region and the absence of a hydroxyl band. A subsequent fraction distilling at 148–159°C./0.1 mm. Hg and weighing 35.3 g. was obtained which yielded additional phenyl ether when extracted with hot petroleum ether (40–60°C.).

RESULTS AND DISCUSSION

It has been found that phenols with electron-withdrawing groups in the *para* position are capable of curing resole-type phenolic resins; examples include *p*-nitrophenol, *p*-bromophenol, and *p*-chlorophenol. The use of such phenols has a distinct advantage over using strong acids, in that no base is required for neutralization to prevent degradation of the polymer, as the substituted phenols become part of the polymer chain by reaction with dibenzyl ethers in the resole.

Phenols without *ortho* substituents are essential for cure of these resins, as atoms or groups substituted *ortho* to the phenolic hydroxyl group, e.g., 2,6-dibromophenol, interfere with the curing ability of the phenol. The fact that only certain *para*-substituted phenols (*p*-nitro- and *p*-bromophenol, but not *p*-cresol, 2,4-dimethylphenol, and 2,6-dibromophenol) are effective suggested the importance of ionization constant and functionality of the phenols. A plot of pK_a of *para*-substituted phenols versus gelation time of resin reveals a direct relationship (Fig. 5). This, as will be seen, is in good agreement with the findings that gelation occurs through cleavage of dibenzyl ether linkages by the acidic phenols.

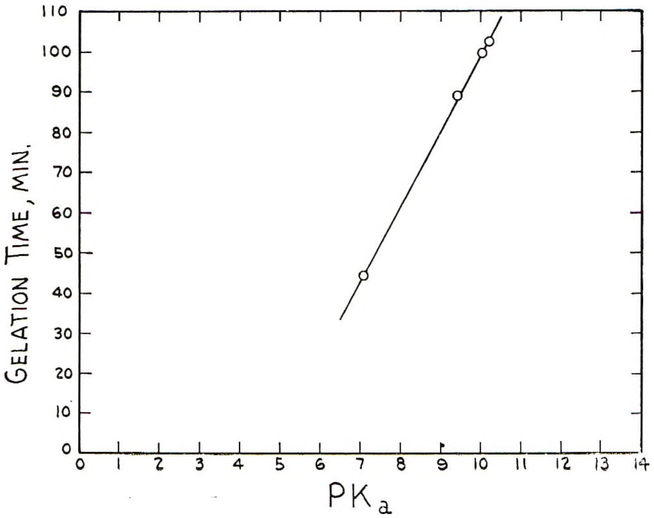
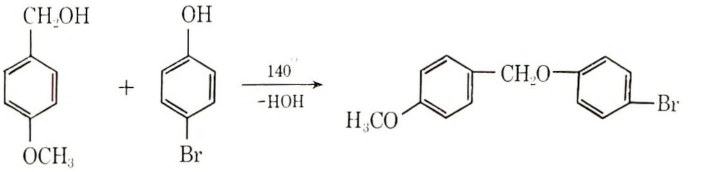


Figure 5.

In an effort to gain insight into the mechanism by which these phenols cure resole-type resins, model compounds similar in chemical structure and reactivity to those present in the resins were prepared and studied under similar experimental conditions. Since these modified phenolic resins contain an excess of methylol groups (formaldehyde:phenol ratio of 1.5:1), *p*-methoxybenzyl alcohol was chosen as a representative model and studied in its reaction with *p*-bromophenol. When reacted in a ratio of eight molecular equivalents of *p*-methoxybenzyl alcohol to one of *p*-bromophenol, a 25% yield of *p*-methoxybenzyl-*p*′-bromophenyl ether was obtained (see Experimental section).



(1)

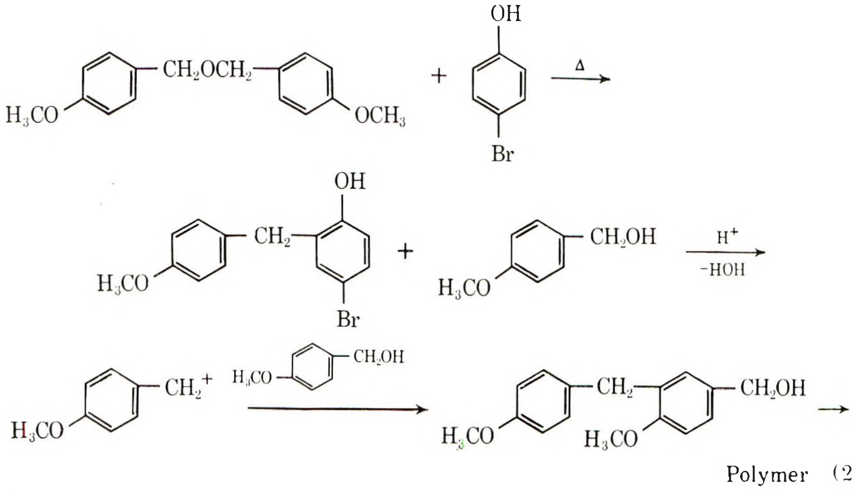
Because reaction between methylol groups and phenolic hydroxyls to form phenyl ethers could not possibly explain curing of the resins, the possibility of splitting dibenzyl ether linkages by *para*-substituted phenols was investigated. Additional impetus was given to this study when it was learned that methyl- and allyl-etherified phenolic resins contain the dibenzyl ether linkage as a principal bond (approximately 50%). The data[4] for an allyl etherified resin are shown in Table I.

TABLE I

Functional group	Functional groups/100 g. resin	Ratio functional groups/phenolic nucleus (155)
Total hydroxyl (A)	0.276	0.43 ± 0.01
Methylol and dibenzyl ethers (B)	0.372	0.58 ± 0.2
Phenolic hydroxyl (C)	0.172	0.29 ± 0.01
Methylol (D) = (A-C)		0.16 ± 0.02
Dibenzyl ethers (B-D)		0.42 ± 0.04

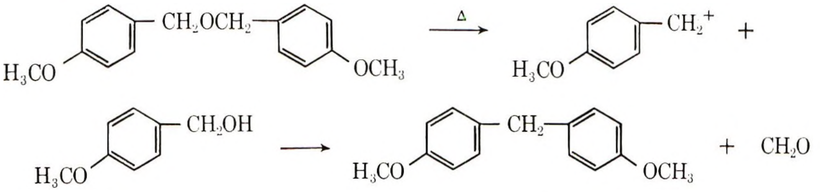
These analytical data coupled with the experimental finding that reaction between dianisyl ether and *p*-bromophenol gives a polymeric material indicate that these particular *para*-substituted phenols hasten the cure time of resole-type etherified phenolic resins by cleavage of dibenzyl ether linkages in the resin.

One explanation of the above data is that the particular phenol, either through association or hydrogen bonding with an electron pair of the ether oxygen atom, causes a weakening and ultimate cleavage of the carbon–oxygen bond of the ether into benzyl alcohol and a benzyl cation. The latter, because of its strong electrophilic nature, attacks the phenol at its position of high electron density (*ortho* and *para*) with formation of a methylene bridge. A second methylene linkage is formed by conversion of benzyl alcohol into another benzyl cation which then proceeds to attack another phenolic nucleus. These reactions can be depicted with dianisyl ether and *p*-bromophenol as shown in eq. (2).



(2)

Formation of bis(*p*-methoxyphenyl)methane by thermal decomposition of dianisyl ether also can be explained according to this mechanism. After decomposition of ether into benzyl cation and *p*-methoxybenzyl alcohol, attack by a benzyl cation at a methylol site with its displacement as formaldehyde would give the diphenylmethane [eq. (3)].



(3)

This process gains support from the work of Fraser et al.,[5] who found by paper chromatography that bis(2-hydroxybenzyl) ether when heated at 150°C. with phenol yielded *o*-hydroxybenzyl alcohol (saligenin), 2,2′- and 2,4′-dihydroxydiphenylmethane, and tri- and tetranuclear novolacs. In addition, displacement of a methylol group from methylol phenols is a well known process in phenolic resin chemistry.[6–8] The reaction of diazonium salts with phenol alcohols is an example of such an aromatic substitution. Considerable experimental evidence has been accumulated supporting an ionic-type mechanism in which the diazonium cation has been proposed as the reactive species.

Results of the effect of a number of phenols on gelation time of methyl- and allyl-etherified phenolics and ammonia-catalyzed resole-type phenolics are shown in Tables II, III, and IV, respectively. The methyl- and allyl-etherified resins were prepared by condensation of phenol and formalin having a molar ratio of formaldehyde to phenol between the limits 1.0–1.5 to 1.0 with one molecular equivalent to sodium hydroxide followed by etherification with dimethyl sulfate and allyl bromide.[9] In each experi-

TABLE II
Effect of Certain Phenols on Gelation Time of Methyl-Etherified Phenolic Resins

Phenol added	Resin (52.5% solids), wt.-%	Time to gel, min.
None		87
p-Nitrophenol	9.5	36
p-Bromophenol	9.5	68
2,4-Dimethylphenol	9.5	87
2,6-Dibromophenol	9.5	100

TABLE III
Effect of Certain Phenols on Allyl-Etherified Phenolic Resins

Phenol added	Resin (52.5% solids), wt.-%	Time to gel, min.	pK_a
None	Control	107	
p-Nitrophenol	14.25	44	7.16
p-Nitrophenol	9.5	44	
p-Nitrophenol	4.75	81	
p-Bromophenol	9.5	77	
p-Bromophenol	4.75	94	
2,4-Dimethylphenol	9.5	127	
2,6-Dibromophenol	9.5	107	
p-Chlorophenol	9.5	89	9.39
p-Hydroxyphenol	9.5	91	
Phenol	9.5	100	10.00
p-Methylphenol	9.5	103	10.17

TABLE IV
Effect of Certain Phenols on Ammonia-Catalyzed Phenolic Resins

Phenol added	Resin (56.0% solids) wt.-%	Time to gel, min.
None	Control	22
p-Nitrophenol	8.9	15
p-Bromophenol	8.9	24
p-Chlorophenol	8.9	23
o-Chlorophenol	8.9	30
Phenol	8.9	27

ment, 10 g. of resin solution (ca. 50% solids) and 0.5 g. (unless stated otherwise) of particular phenol were mixed in an aluminum foil dish and placed in an oven at 150°C. until gelation occurred. Gelation time was taken as the point where resin was no longer fluid but spongy and elastic.

The author is grateful to Dr. Harold Lady, formerly of the Technology Department, Westinghouse Research Laboratories, Pittsburgh 35, Pennsylvania, for his assistance with the infrared phase of this work.

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Résumé

On peut hâter la gélification de résoles phénoliques éthérifiés par l'utilisation de certains phénols *para*-substitutés, notamment les phénols ne portant pas de substituants en position *ortho*- et contenant un atome ou un groupe électro-capteur en position *para*- tel que paranitré, bromé et chloré. Un mécanisme comportant le clivage des liens éthers dibenzyliques dans ces résines est proposé pour expliquer la gélification.

Zusammenfassung

Gewisse parasubstituierte Phenole, nämlich jene, die keine ortho-Substituenten und in der para-Stellung ein elektronenanziehendes Atom oder eine elektronenanziehende Gruppe enthalten wie z.B. *p*-Nitro-, -Brom- und -Chlorphenol, beschleunigen die Gelierung verätherter phenolischer Resole. Zur Erklärung dieser Gelierung wird ein Mechanismus vorgeschlagen, der auf der Spaltung der Dibenzylätherbindungen in diesen Harzen beruht.

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Influence of $SeOCl_2$ on the Polymerization of Propylene by $TiCl_3$–$Al(C_2H_5)_3$

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Synopsis

The influence of $SeOCl_2$ on the polymerization of propylene by $TiCl_3$–$Al(C_2H_5)_3$, and the temperature dependence of the stereospecificity of the catalyst, $TiCl_3$–$Al(C_2H_5)_3$, have been investigated. $SeOCl_2$ decreases the rate of polymerization and increases the stereospecificity of the catalyst, which could be explained on the basis of a decrease of the concentration of $Al(C_2H_5)_3$ accompanied by a reaction between $Al(C_2H_5)_3$ and $SeOCl_2$. On the other hand, the stereospecificity of the catalyst, $TiCl_3$–$Al(C_2H_5)_3$, increases gradually with a decrease in polymerization temperature from 40 to 0°C. From these results, we conclude that $SeOCl_2$ exerts no essential influence on the polymerization of propylene by $TiCl_3$–$Al(C_2H_5)_3$, and that the stereospecificity of the catalyst is attributed mainly to the reducing ability of the organometallic compound.

INTRODUCTION

In the polymerization of propylene by Ziegler-Natta catalysts, it is generally recognized that some electron donors increase the stereospecificity of the catalysts. However, the detailed mechanism has remained relatively obscure, because most of the investigations have been made for a practical use.

In the present study, we have selected $SeOCl_2$ as an electron donor and kinetically examined the influence of it on the polymerization of propylene with $TiCl_3$–$Al(C_2H_5)_3$.[1] Then, with $TiCl_3$–$Al(C_2H_5)_3$ as a catalyst, the temperature dependence of the stereospecificity of the catalyst has been investigated to ascertain whether the stereospecificity of the catalyst depends upon the surface heterogeneity of $TiCl_3$ or upon the reducing ability of the organometallic compounds employed.

EXPERIMENTAL

Polymerizations were carried out with the same apparatus as reported previously.[2] Polymerization was quenched after 75 min. with a methanol–1*N* hydrochloric acid solution. After adequate washing with methanol and water, the polymers were dried overnight at room temperature in a vacuum oven. The intrinsic viscosity was measured at 135°C. in decalin containing 0.1% phenyl-β-naphthylamine under a nitrogen atmosphere. Molecular weight was calculated by Kinsinger's equation[3]:

$$\eta = 1.07 \times 10^{-4} \bar{M}_v^{0.8} \qquad (1)$$

For the determination of the isotacticity of the polymer, we used the method of infrared spectroscopy with a Shimadzu IR-27A infrared spectrometer at 36°C.[4] Propylene was from Mitsubishi Petrochemical Co., purity 99.5%. Toluene (Wako Pure Chemical Industries Co., C.P. grade) was purified by refluxing over sodium metal after distillation. $TiCl_3$ was from Stauffer, AA grade, and $Al(C_2H_5)_3$ was from Ethyl Corp. $SeOCl_2$ (Kishida Chemical Industries Co., C.P. grade) was used as a 10 wt.-% solution in toluene.

RESULTS

Since it is expected that the order of the addition of $TiCl_3$, $Al(C_2H_5)_3$, and $SeOCl_2$ exerts some influence on the kinetical behavior of the polymerization, polymerizations were carried out with the following two cases: case I: $\{SeOCl_2 + Al(C_2H_5)_3\} + TiCl_3$; case II: $\{SeOCl_2 + TiCl_3\} + Al(C_2H_5)_3$.

Case I

After 3.2 mmole of $Al(C_2H_5)_3$ and a given amount of $SeOCl_2$ were injected into a four-necked, 500-ml. glass flask containing 250 ml. of refined toluene, the mixture was agitated for 40 min. at the polymerization temperature under a nitrogen atmosphere. Then, 3.2 mmole of $TiCl_3$ was added, and propylene was introduced after the nitrogen in the flask was pumped out.

The rate of polymerization changes markedly at first, then it arrives at a steady-state value, the kinetic behavior of which is well expressed by eqs. (2) or (3).[5]

$$r_t = r_\infty(1 + fe^{-kt}) \qquad (2)$$

or

$$\ln (r_t - r_\infty) = \ln r_\infty f - kt \qquad (3)$$

where t is the polymerization time, r_t the rate of polymerization at t, r_∞ the stationary rate of polymerization which is determined by a trial-and-error method from the linearity of eq. (3), and f and k are constants. The stationary rates, r_∞, obtained with the various concentrations of $SeOCl_2$ at 31, 41, and 61°C. are shown in Figure 1. It can be seen from Figure 1 that polymerization can no longer proceed when the concentration of $SeOCl_2$ reaches 1.6 mmole, where it corresponds to half of the concentration of $Al(C_2H_5)_3$.

To explain these results, the reaction (4) has been assumed.

$$Al_2(C_2H_5)_6 + SeOCl_2 \rightleftharpoons X \qquad (4)$$

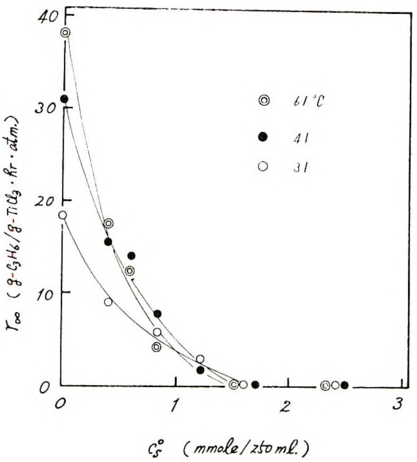

Fig. 1. Stationary rates of polymerization with various concentrations of $SeOCl_2$ and 3.2 mmole $TiCl_3$, 3.2 mmole $Al(C_2H_5)_3$, 250 ml. toluene at various temperatures.

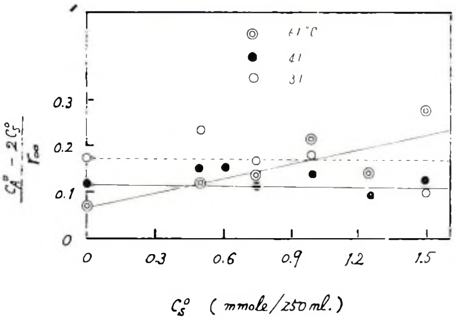

Fig. 2. Plots of $(C_A^0 - 2C_S^0)/r_\infty$ vs. C_S^0.

where X is an inactive complex. [The catalyst is written as $Al_2(C_2H_5)_6$ since $Al(C_2H_5)_3$ exists as a dimer under the experimental conditions.[6]] Then the stationary rate of polymerization may be expressed by eqs. (5) and (6) [or (7)].

$$r_\infty = \frac{k_p K_A C_A}{1 + K_A C_A + K_S C_S + K_X C_X} \tag{5}$$

$$\cong \frac{k_p K_A (C_A^0 - 2C_S^0)}{1 + K_A(C_A^0 - 2C_S^0) + K_X C_S^0} \tag{6}$$

or

$$\frac{C_A^0 - 2C_S^0}{r_\infty} = \frac{1}{k_p} \cdot \left(\frac{K_X}{K_A} - 2\right) \cdot C_S^0 + \frac{1}{k_p} \cdot \left(\frac{1}{K_A} + C_A^0\right) \tag{7}$$

TABLE I

Values of k_p, K_A, and K_X, and the Heats of Absorption

Temp., °C.	k_p, g. C_3H_6/g. $TiCl_3$, hr.-atm.	K_A, l./mmole[a]	K_X, l./mmole	E_A, kcal./mole	E_X, kcal./mole
31	18	3.70	4.5–6.5	12	2–3
41	32	2.04	4.1		
61	38	0.65	3.4		

[a] From the polymerizations of propylene by $TiCl_3$–$Al(C_2H_5)_3$.[16]

with

$$C_A = C_A^0 - 2C_S^0$$

$$C_S = 0$$

$$C_X = C_S^0$$

Here k_p is the polymerization rate constant, C_A, C_S, and C_X are the equilibrium concentrations of $Al(C_2H_5)_3$, $SeOCl_2$, X, respectively; and K_A, K_S, and K_X are the corresponding adsorption constants; and C_A^0 and C_S^0 are the initial concentrations of $Al(C_2H_5)_3$ and $SeOCl_2$, respectively.

Although there is some discrepancy in the case at 31°C., it may be said that the validity of eq. (7) is confirmed from the linearity in Figure 2.

The values of k_p (which are considered equal to the values of r_∞ at $C_S^0 = 0$ in Figure 1, because K_AC_A in eq. (5) is much greater than unity), K_A, and K_X (calculated from the slopes and the intersections in Figure 2) are given in Table I.

TABLE II
Dependence of Molecular Weight $\bar{M}_v$ on Initial Concentration of $SeOCl_2$; C_S^0, at 41°C.

C_S^0, mmole/250 ml.	$\bar{M}_v \times 10^{-5}$
0	4.7
0.50	5.0
0.75	5.2
1.25	5.0

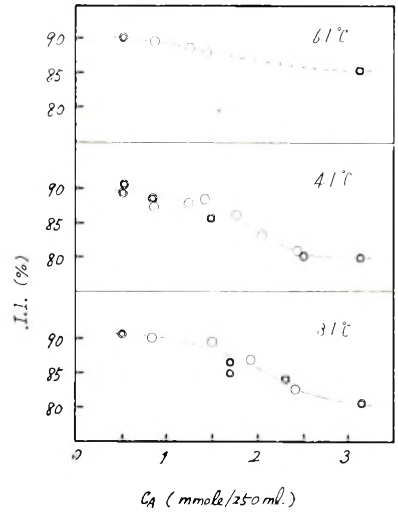

Fig. 3. Dependence of the isotacticity on the initial concentrations of $SeOCl_2$ and $Al(C_2H_5)_3$: (○) 3.2 mmole $TiCl_3$, 3.2 mmole $Al(C_2H_5)_3$, 250 ml. toluene in the presence of $SeOCl_2$; (◎) 3.2 mmole $TiCl_3$, 250 ml. toluene in the absence of $SeOCl_2$.

Table II shows the dependence of the molecular weight on the initial concentration of $SeOCl_2$; it is seen that $SeOCl_2$ exerts no influence on the molecular weight.

On the other hand, the dependence of the isotacticity on the initial concentration of $SeOCl_2$ is shown in Figure 3. The isotacticity increases with increasing concentration of $SeOCl_2$.

Case II

After 3.2 mmole of $TiCl_3$ and a given amount of $SeOCl_2$ were added to a flask containing 250 ml. of refined toluene, the mixture was agitated for 40 min. at the polymerization temperature under a nitrogen atmosphere. Then 3.2 mmole of $Al(C_2H_5)_3$ was injected, the flask was evacuated, and propylene was introduced. Polymerizations were carried out only at 41°C.

TABLE III
Results for Case II Polymerization at 41°C.

C_S^0, mmole/250 ml.	r_∞, g. C_3H_6/ g. $TiCl_3$-hr.-atm.	$\bar{M}_v \times 10^{-5}$	Isotacticity (I.I.), %
0	32	4.7	81
0.20	12	4.6	82
0.40	4.0	5.1	81
0.80	0	4.9	—

The rate of polymerization in this case is also well expressed by eq. (2) or (3). The results, for the stationary rate of polymerization, the molecular weight, and the isotacticity (I.I.) are summarized in Table III. The stationary rate in this case is very small as compared with that in Case I and neither the molecular weight nor the isotacticity is affected by $SeOCl_2$. The small rate in this case may be attributed to the strong adsorption of $SeOCl_2$.

DISCUSSION

As shown in Figure 3, the isotacticity increases with increasing concentration of $SeOCl_2$ in Case I. Ingberman[7] found with the polymerization of propylene by $TiCl_3$–$Al(C_2H_5)_3$ that the isotacticity of the polymer produced increases with decreasing concentration of $Al(C_2H_5)_3$. Soga and Keii also found a similar result with the polymerization of propylene by $TiCl_3$–$Zn(C_2H_5)_2$.[8]

Accordingly, the present results may be explained on the basis of the concentration change of $Al(C_2H_5)_3$ according to eq. (4). This view has been confirmed by the polymerization with lower concentrations of $Al(C_2H_5)_3$ in the absence of $SeOCl_2$ (see Fig. 3).

Concerning the differences in the isotacticity at 31, 41, and 61°C. in the absence of $SeOCl_2$ at $[Al(C_2H_5)_3]$ = 3.2 mmole, a proposal has been made in the previous paper.[9] From above, it may be concluded that $SeOCl_2$ exerts no significant effect except to act as a poison.

The question is now, why does the isotacticity increase with decreasing concentration of the organometallic compound.

Boor[10-14] concluded on the basis of his series of investigations with the catalytic system, $TiCl_3$–$Zn(C_2H_5)_2$ with some electron donors, that there exist various sites having different abilities to coordinate and orient the olefin on the crystal component of the catalyst. According to his conclusion, the present results will be grasped as follows: $Al(C_2H_5)_3$ adsorbs preferentially on the site which affords higher isotactic polymers.

However, we are somewhat doubtful of his conclusion, mainly because those electron donors which exert a significant influence on the isotacticity in the presence of $TiCl_3$–$Zn(C_2H_5)_2$ often do not exert any influence in the presence of $TiCl_3$–$Al(C_2H_5)_3$.[15] We have previously reported[9] that the lower isotacticity of a polypropylene produced by $TiCl_3$–$Al(C_2H_5)_3$ as compared with that produced by $TiCl_3$–$Al(C_2H_5)_2Cl$ is attributed to the stronger reducing ability of $Al(C_2H_5)_3$, i.e., the weaker the reducing ability of the organometallic compound, the higher the isotacticity of the polymer. The present results will be well explained on the basis of the concept that the lower the concentration of $Al(C_2H_5)_3$, the weaker the reducing ability and therefore the higher the isotacticity.

TABLE IV
Dependence of Isotacticity on Polymerization Temperature[a]

Temperature, °C.	Isotacticity (I.I.), %
0	90, 85[b]
10	87
20	86
30	84
40	80

[a] Conditions except as otherwise noted: 3.2 mmole $TiCl_3$; 3.2 mmole $Al(C_2H_5)_3$; 250 ml. toluene.

[b] With 7 mmole $Al(C_2H_5)_3$; 3.2 mmole $TiCl_3$; 250 ml. toluene. The stationary rate in this case is almost the same as that with 3.2 mmole $Al(C_2H_5)_3$, is support of our concept (see text).

To confirm the validity of this concept, polymerizations were carried out with a rather high concentration of $Al(C_2H_5)_3$ (i.e., 13 mmole/l.) and at varying polymerization temperatures from 40 to 0°C., and the isotacticity of the produced polymer was measured. The results are shown in Table IV. The isotacticity increases with decreasing polymerization temperature, although the coverage of $Al(C_2H_5)_3$ is almost unity under the experimental conditions.[16] This result strongly supports our idea. Concerning the reaction between $Al(C_2H_5)_3$ and $SeOCl_2$ [eq. (4)], further study must be done.

CONCLUSIONS

$SeOCl_2$ exerts no significant influence on the polymerization of propylene by $TiCl_3$–$Al(C_2H_5)_3$.

The isotacticity of polypropylene produced by Ziegler-Natta catalysts is mainly attributable to the reducing ability of the organometallic compound.

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Résumé

On a étudié à la fois l'influence de $SeOCl_2$ sur la polymérisation du propylène au moyen de $TiCl_3$–$Al(C_2H_5)_3$, et la dépendance thermique de la stéréospécificité du catalyseur, $TiCl_3$–$Al(C_2H_5)_3$·$SeOCl_2$ provoque une diminution de la vitesse de polymérisation et un accroissement de la stéréospécificité du catalyseur ce qui pourrait être expliqué sur la base d'une diminution de la concentration en $Al(C_2H_5)_3$ accompagnée par la réaction entre $Al(C_2H_5)_3$ et $SeOCl_2$. Par ailleurs, la stéréospécificité du catalyseur $TiCl_3$–$Al(C_2H_5)_3$ croît graduellement avec une diminution des températures de polymérisation entre 40 et 0°C. Au départ de ces résultats, on a trouvé que $SeOCl_2$ n'exerce pas d'influence essentielle sur la polymérisation du propylène an présence de $TiCl_3$–$Al(C_2H_5)_3$, et que la stéréospécificité du catalyseur doit être attribuée principalement au pouvoir réducteur du composé organo-métallique.

Zusammenfassung

Sowohl der Einfluss von $SeOCl_2$ auf die Polymerisation von Propylen mittels $TiCl_3$–$Al(C_2H_5)_3$, als auch die Temperaturabhängigkeit der Stereospezifität des Katalysators $TiCl_3$–$Al(C_2H_5)_3$ wurde untersucht. $SdOCl_2$ setzt die Polymerisations-geschwindigkeit herab und erhöht die Stereospezifität des Katalysators. Dies konnte auf der Basis einer Abnahme der Konzentration von $Al(C_2H_5)_3$erklärt werden, die im Gefolge der

Reaktion zwischen $Al(C_2H_5)_3$ und $SeOCl_2$ auftritt. Andererseits steigt die Stereospezifität des Katalysators, $TiCl_3$–$Al(C_2H_5)_3$, allmählich mit abnehmender Polymerisationstemperatur (von 40°C auf 0°C) an. Auf Grund dieser Ergebnisse haben wir geschlossen, dass $SeOCl_2$ keinen wesentlichen Einfluss auf die Polymerisation von Propylen mittels $TiCl_3$–$Al(C_2H_5)_3$ ausübt und dass die Stereospezifität des Katalysators hauptsächlich der Reduktionsfähigkeit der organometallischen Verbindung zuzuschreiben ist.

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Kinetics of γ-Ray Polymerization of Formaldehyde in the Presence of Carbon Dioxide*

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Synopsis

A kinetic study of the γ-ray polymerization of formaldehyde in toluene solution in the presence of carbon dioxide was carried out at temperatures of +13 to −17°C. Two modes of the polymerization, spontaneous and γ-ray polymerization, occur in this system. The γ-ray polymerization, experimentally separated from the spontaneous polymerization, was investigated. The rate of γ-ray polymerization increased slightly with the square root of carbon dioxide concentration. The rate of polymerization was also found to be proportional to the dose rate and the square of monomer concentration. The molecular weight of polymer formed was independent of the reaction condition. The apparent activation energy was estimated to be 10.3 kcal./mole. The kinetics of the γ-ray polymerization in the presence of carbon dioxide are explained quantitatively by a cationic mechanism, and the role of carbon dioxide is as an action of retardation for neutralization of the cationic initiating species, which was produced by γ-radiation, by means of a reverse reaction with an electron. Physical and mechanical properties of the polymer obtained by γ-ray polymerization were also investigated.

INTRODUCTION

Ionizing radiation may be used for the polymerization of formaldehyde monomer.[1-5] Okamura et al.[3] reported that whether the polymerization in organic solvent at −78°C. proceeds by an ionic or anionic mechanism depends on the solvent used. Chachaty et al.[5] suggested a radical contribution to the mechanism of this polymerization reaction at temperatures above −80°C. As described by Walker,[6] monomeric formaldehyde polymerizes easily and spontaneously without any catalyst or ionizing radiation, even at a low temperature such as −80°C. Most investigations on the radiation-induced polymerization of monomeric formaldehyde were carried out at a temperature below −50°C. in order to avoid spontaneous polymerization.

It has been already reported in our previous paper[7] that the spontaneous polymerization of formaldehyde proceeds by anionic initiation and the

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rate of polymerization is inversely proportional to the square root of the carbon dioxide concentration. The spontaneous polymerization has been also found to be substantially inhibited at 0°C. by addition of carbon dioxide at concentrations above 2 mole-%. Based upon this research, we have developed a new γ-ray polymerization process for forming high molecular weight polyoxymethylene at a higher temperature, such as 0°C., which is considered to be a more economical condition. The purpose of the present investigation is to determine the influence of carbon dioxide on the γ-ray polymerization of formaldehyde and to elucidate the kinetics of polymerization in the presence of carbon dioxide.

EXPERIMENTAL

Preparations of formaldehyde monomer and toluene and the viscosity study of the polymer followed the same procedure as described in the previous paper.[7]

The liquid monomer was distilled *in vacuo*, and a middle fraction (10–60%) was simultaneously condensed into a number of glass ampules. Dried toluene and carbon dioxide were introduced into the system by using syringes through a rubber stopper fitted into the ampule. The sealed ampules were kept in a temperature-controlled bath during the reaction. Irradiation was carried out by γ-rays from a 2000-curie ^{60}Co source. The intensity of the radiation was determined by Fricke dosimetry ($G = 15.5$). After the polymerization, the polymer was separated, washed with cold diethyl ether, and dried *in vacuo*.

Infrared spectra obtained by the film and KBr pellet methods were measured by using a Hitachi EPI-2 infrared spectrometer. Physical and mechanical properties such as impact and tensile strengths, elongation,

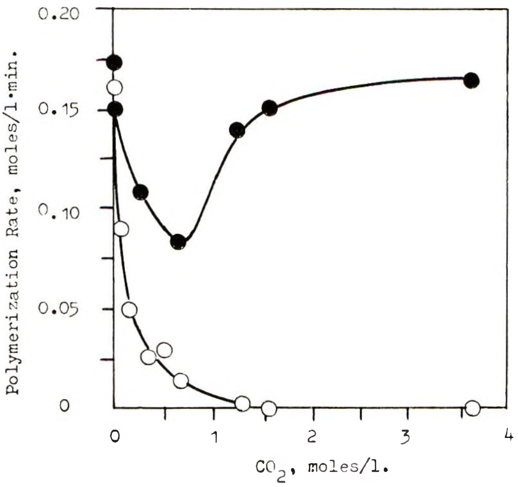

Fig. 1. Influence of carbon dioxide on the total and spontaneous polymerization: (●) total rate; (○) spontaneous rate. $[M_0] = 15.2$ mole/l. in toluene solution at 0°C.; $I = 1.6 \times 10^3$ r./hr.

heat distortion, folding endurance, and dielectric properties of the obtained polymer were also investigated by the usual methods. The thermal stability of the capped polymer was determined by measuring the first-order reaction rate constant, k_{222}, for thermal degradation in a nitrogen atmosphere under constant heating at 222°C. in a methyl salicylate vapor bath.

Gas-phase components of the reaction system were analyzed by using a Hitachi RMU-5B mass spectrometer. Two samples of 50% toluene solution of formaldehyde containing 0.1% carbon dioxide were prepared at −78°C. in reaction vessels which were equipped with stopcocks and magnetic stirrers. One of the samples was stirred for 10 min. at −78°C., and the gas-phase components of the system were analyzed by mass spectrography at a total pressure around 20 μm. Hg. The other was subjected to γ-irradiation at a dose rate of 2000 r./hr. at −78°C.; gas-phase components were analyzed under the same conditions. The degree of conversion of the monomer was approximately 16%.

RESULTS AND DISCUSSION

Effect of Carbon Dioxide on the Polymerization of Formaldehyde

The polymerization of formaldehyde in toluene solution at 0°C. was carried out under no irradiation (referred to as spontaneous polymerization) and with γ-irradiation, with increasing concentration of carbon dioxide in the system. The influence of carbon dioxide concentration on the polymer yield of both polymerizations is shown in Figure 1.

As shown in Figure 1, formaldehyde monomer which is kept at 0°C. and at a carbon dioxide concentration below 1.5 mole/l. undergoes spon-

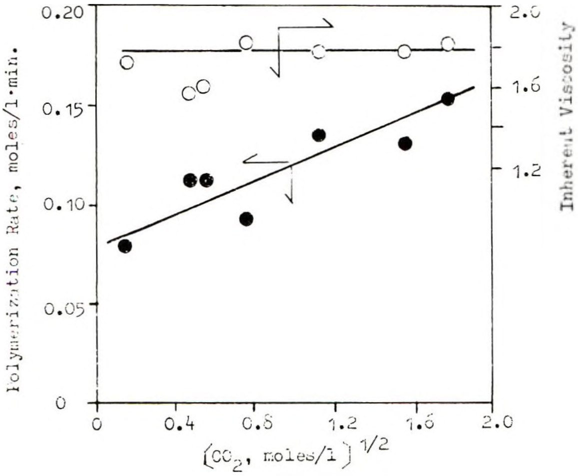

Fig. 2. Influence of carbon dioxide on (●) the rate of γ-ray polymerization and (○) inherent viscosity of the product. $[M_0]$ = 15.2 mole/l. in toluene solution at 0°C.; I = 1.3×10^3 r./hr.

taneous polymerization. The polymerization yield of true γ-ray polymerization must therefore be defined as the polymer yield calculated by subtracting the polymer yield of the spontaneous polymerization from the total yield obtained under irradiation. The polymer yield was thus determined as the difference between the yields of total and spontaneous polymerization which were simultaneously carried for each set of experimental conditions. By separating the γ-ray polymerization from the spontaneous polymerization, better reproducibility of experiment and a simple kinetic pattern were obtained.

Figure 2 shows the plots of the rate of γ-ray polymerization and of the inherent viscosity of polymer produced against the square root of carbon dioxide concentration. It was found that the initial rate of γ-ray polymerization increased with the square root of carbon dioxide concentration, but the molecular weight of polymer was not significantly changed.

In order to elucidate the role of carbon dioxide in the γ-ray polymerization of formaldehyde, the variation of the gaseous components in the reaction system was determined by mass spectrography before and after the polymerization. As shown in Table I, the greater part of the added carbon dioxide was dissolved in the liquid phase of the system and was not consumed during the polymerization reaction. A slight increase of hydrogen was also noted after polymerization. The infrared spectrum, as shown in Figure 3, shows no absorption band originating from the ester C=O bond in the range of 1650–1780 cm.$^{-1}$. It was, therefore, concluded that carbon dioxide does not copolymerize with formaldehyde monomer under the conditions used.

TABLE I

Gas-Phase Components of the Reaction System[a]

	Mole ratio components[b]	
Component	Initial	After polymerization[c]
H_2	0.1	0.4
O_2	1.7	1.0
CH_2O	3.4	30.8
CO_2	1.3	1.5
N_2	10.0	10.0

[a] $[M_0]$ = 50 vol.-% in toluene solution; 0.1% CO_2 added to the monomer.

[b] Standardized by calculating N_2 as 10.0.

[c] $I = 1.3 \times 10^3$ r./hr.; reaction time, 30 min.; temperature, −78°C.; conversion, ca. 16%.

From the results that the rate of γ-ray polymerization is proportional to the square root of carbon dioxide concentration and the molecular weight of the resulting polymer is not affected by carbon dioxide, the effect of carbon dioxide was considered to be attributable neither to a decrease in termination nor to an increase in propagation, but to an increase

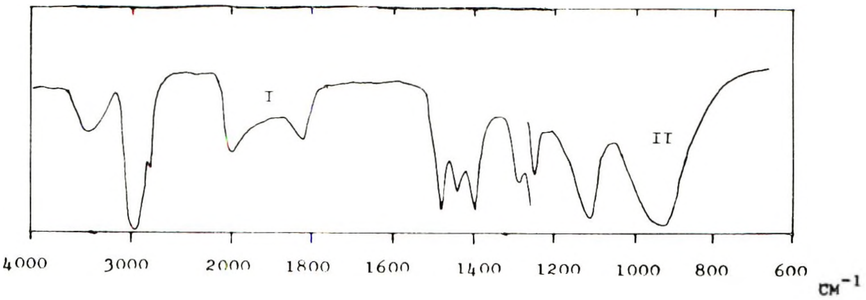

Fig. 3. Infrared spectra of polyoxymethylene obtained by γ-ray polymerization in the presence of carbon dioxide: (*I*) KBr pellet; (*II*) film specimen.

in initiation of polymerization. This was contrary to the results for the spontaneous polymerization of formaldehyde[7] in the presence of carbon dioxide.

Effect of Reaction Conditions on the Polymerization of Formaldehyde in the Presence of Carbon Dioxide

Influence of Monomer Concentration. The γ-ray polymerization at various monomer concentrations was carried out at constant carbon dioxide concentration. The results are shown in Figure 4. The rate of polymerization was proportional to the square of monomer concentration, while the

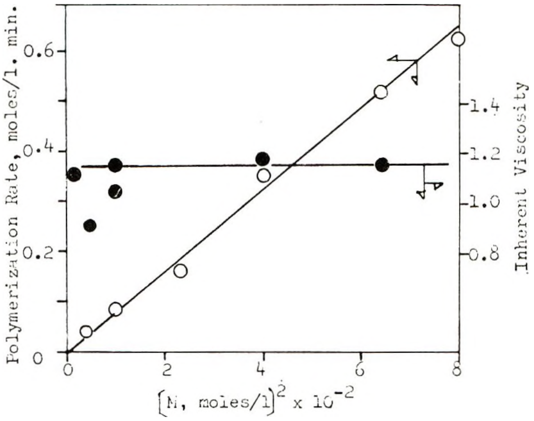

Fig. 4. Influence of monomer concentration on (○) the rate of γ-ray polymerization and (●) inherent viscosity of the product in toluene solution at 0°C.; $I = 1.3 \times 10^{3}$ r./hr.; $[CO]_2 = 0.1$ mole/l.

molecular weight of resulting polymer was independent of the monomer concentration.

Nakashio et al.[4] reported that a rate equation of third order with respect to monomer concentration was applicable to the γ-ray polymerization in toluene solution at −78°C. in the absence of carbon dioxide. The discrepancy between these two results is probably due to the presence of spontaneous polymerization, since an increase of the monomer concentration causes an increase in spontaneous polymerization.

The result that the molecular weight of polymer was independent of the monomer concentration seems to suggest that an increase in monomer concentration causes an increase in the initiation reaction.

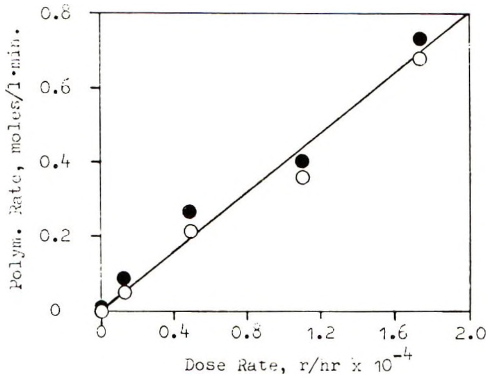

Fig. 5. Influence of dose rate on the rate of γ-ray polymerization: (○) $[CO_2]$ = 0.2 mole/l.; (●) $[CO_2]$ = 1.5 mole/l. $[M_0]$ = 15.2 mole/l. in toluene solution at 0°C.

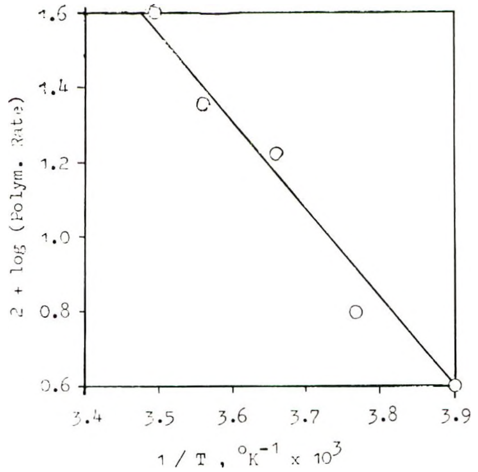

Fig. 6. Arrhenius plot of the rate of γ-ray polymerization. $[M_0]$ = 15.2 mole/l.; $[CO_2]$ = 1.5 mole/l.; I = 1.5×10^3 r./hr.

Influence of Dose Rate. The rate of γ-ray polymerization was proportional to the dose rate; the slope of the plot of polymerization rate versus dose rate was almost unity, as shown in Figure 5. Therefore, it is considered that the γ-ray polymerization proceeds according to an ionic mechanism.

Influence of Polymerization Temperature. Temperature dependency on the rate of polymerization was observed in the range of −17°C. to

+13°C. The Arrhenius plot is shown in Figure 6, from which an activation energy of 10.3 kcal./mole for the overall polymerization was obtained.

Kinetic Consideration on γ-Ray Polymerization in the Presence of Carbon Dioxide

Okamura et al.[3] studied kinetically the γ-ray polymerization of formaldehyde at −78°C. and concluded the reaction in toluene solution was cationic. We have also assumed cationic γ-ray polymerization of formaldehyde in the presence of carbon dioxide, the effect of carbon dioxide on the γ-ray polymerization also being explained by a cationic mechanism as follows.

The formaldehyde monomer is ionized by γ-ray irradiation to produce the cation, a part of which is neutralized immediately by recombination with an electron to produce the monomer. The amount of cation, that is, the initiating species of polymerization is, therefore, obtained as the difference between the reaction of ionization and recombination [eqs. (1) and (2)].

$$\mathrm{M} \overset{k_i}{\rightsquigarrow} \mathrm{M}^+ + e \tag{1}$$

$$\mathrm{M}^+ + e \rightarrow \mathrm{M} \tag{2}$$

On the other hand, carbon dioxide added reacts with water in the system to produce protons, the concentration of which is proportional to the square root of the concentration of carbon dioxide, as described in the previous paper.[7]

$$\mathrm{H_2O} + \mathrm{CO_2} \overset{K_1}{\rightleftharpoons} \mathrm{H_2CO_3} \overset{K_2}{\rightleftharpoons} \mathrm{H}^+ + \mathrm{HCO_3}^- \tag{3}$$

$$[\mathrm{H}^+] = K_1^{1/2}K_2^{1/2}[\mathrm{CO_2}]^{1/2}[\mathrm{H_2O}]^{1/2} \tag{4}$$

At a constant concentration of water,

$$[\mathrm{H}^+] = \alpha[\mathrm{CO_2}]^{1/2} \tag{5}$$

where α is equal to $K_1^{1/2}K_2^{1/2}[\mathrm{H_2O}]^{1/2}$. Assuming that the inorganic anion, HCO^{3-}, does not initiate the polymerization of formaldehyde monomer, the proton existing in the system retards reaction (2) by decreasing the concentration of electrons according to reaction (6):

$$e + \mathrm{H}^+ \rightarrow {}^1/_2\mathrm{H_2} \tag{6}$$

Therefore, the extent of retardation of reaction (2) by carbon dioxide is equal to $\beta[\mathrm{CO_2}]^{1/2}$, where β is a constant. According to the above assumption, the overall concentration of the initiating species M^+ produced by γ-ray irradiation becomes $k_i[\mathrm{M}]I(1 + \beta[\mathrm{CO_2}]^{1/2})$, where k_i is a rate constant of initiation by γ-ray irradiation in the case of no addition of carbon dioxide to the system and I is the dose rate of γ-rays. This assumption is supported by the increase of the concentration of hydrogen in the system, as shown in Table I.

TABLE II
Comparison of Physical and Mechanical Properties of Aceylated Polymer Obtained by γ-Ray Method with a Commercial Polymer

Property	ASTM	Measurement condition	Acetylated polymer	Delrin 500-NC-10
Impact strength, Charpy, kg.-cm./cm.^{2}	D 256-54T	23°C.	13.48	7.76
Tensile strength at break, kg./cm.^{2}	D 638-52T	"	650	657
Elongation at break, %	"	"	15	15
Heat distortion temperature, °C.	D 648-56T	18.6 kg./cm.^{2}	117	120
Tabor abrasion test, mg./1000 rotations	D 1044-56	1000 g., 33°C., 63% R.H. Cs-17 wheel	13.5	14.2
Volume resistivity	D 257-54	31°C., 61% R.H.	1.2×10^{13}	1.1×10^{14}
Dielectric constant	D 150-54	10^3 cps, 31°C., 61% R.H.	4.7	4.2
Dielectric loss	"	"	0.0092	0.0057
Test for folding endurance	D 643-43	Mean value of two measurements	226,360	20,877
Thermal decomposition constant at 222°C., k_{222}, %/min.	—	Nitrogen atmosphere	0.04	0.03

The elementary reactions (7)–(10) of the polymerization have been postulated.

Propagation
$$M^+ + M \xrightarrow{k_p} M_2^+ \tag{7}$$
$$\vdots$$
$$M_{n-1}^+ + M \rightarrow M_n^+ \tag{8}$$

Termination
$$M_n^+ \xrightarrow{k_t} P \tag{9}$$

Transfer
$$M_n^+ + M \xrightarrow{k_{tr}} P + M^+ \tag{10}$$

Here M_n^+ and P represent the active and "dead" polymers with the degree of polymerization of n, respectively, and k_p, k_t, and k_{tr} are the rate constants of propagation, termination, and chain transfer, respectively.

The rate of monomer consumption and the rate of concentration change of the active species, M^+, are given by eqs. (11) and (12).

$$-d[M]/dt = k_p[M][M^+] \tag{11}$$

$$d[M^+]/dt = k_i[M]I(1 + \beta[CO_2]^{1/2}) - k_t[M_n^+] \tag{12}$$

Using the steady-state assumption with respect to M^+, we have

$$-d[M]/dt = (k_ik_p/k_t)I[M]^2(1 + \beta[CO_2]^{1/2}) \tag{13}$$

Hence,

$$1/[M] - 1/[M_0] = (k_ik_p/k_t)I(1 + \beta[CO_2]^{1/2})t \tag{14}$$

where $[M_0]$ and t are the initial concentration of monomer and the reaction time, respectively. The values of the constant, k_ik_p/k_t, calculated from Figures 2 and 4, which were obtained in separate experiments, were 3.4×10^{-5} and 3.9×10^{-5} l./mole-r., respectively, and thus show good agreement. And the value of β was calculated as 1.9×10^{-5} l.$^{1/2}$/mole$^{1/2}$-r. from Figure 2.

Properties of the Polymer

Polymers obtained under various polymerization conditions were acetylated with acetic anhydride by means of a conventional procedure,[8] and the resultant polyoxymethylene diacetate was molded into film or sheet after mixing in 1% of 4,4′-butylidene-bis(3-methyl-6-*tert*-butylphenol) as antioxidant.[9] The physical and mechanical properties of one of these stabilized polymers is shown in Table II, compared with those of a commercial product (Delrin 500 NC-10). The result shows that the polymer obtained by the γ-ray polymerization at a temperature around 0°C. had the approximately similar properties to the commercial product, although the folding endurance was eleven times larger.

The authors wish to express their gratitude for the guidance and encouragement received from Dr. K. Fujimura, Director of Takarazuka Radiation Laboratory. This work was greatly assisted by the continued efforts of Mr. H. Sakai.

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Résumé

En présence de dioxyde de carbone une étude cinétique de la polymérisation par rayons-γ du formaldéhyde en solution toluénique a été effectuée à des températures de +13 à −17°C. Deux modes de polymérisation, à savoir la polymérisation spontanée et une polymérisation due aux rayons-γ se présentent dans ce système. La polymérisation aux rayons-γ a pu être séparée expérimentalement de la polymérisation spontanée et a été soumise à une investigation. La vitesse de la polymérisation par rayons-γ croissait lentement avec la racine carrée de la concentration en anhydride carbonique. La vitesse de polymérisation est également proportionnelle à la dose et au carré de la concentration en monomère. Le poids moléculaire du polymère formé était indépendant des conditions de reactions. L'énergie d'activation apparente était estimée à 10.3 kcal./mole. La cinétique de la polymérisation-γ en présence d'oxyde de carbone a été discutée quantitativement sur la base d'un mécanisme cationique. Le rôle du dioxyde de carbone a été expliqué comme une action de retardement de la neutralisation d'une espèce cationique initiante produite par irradiation aux rayons-γ au moyen de la réaction inverse avec un électron. Les propriétés physiques et mécaniques du polymère obtenu par polymérisation aux rayons-γ ont également été étudiées.

Zusammenfassung

Die Kinetik der γ-Strahlen-Polymerisation von Formaldehyd in Toluollösung in Gegenwart von Kohlendioxyd wurde bei Temperaturen von +13 bis −17°C untersucht. In diesem System verläuft die Polymerisation auf zwei Wegen, und zwar treten in diesem System eine spontane und eine durch γ-Strahlen ausgelöste Polymerisation auf. Die γ-Strahlen-Polymerisation wurde experimentell getrennt von der sponaten Polymerisation untersucht. Die Geschwindigkeit der γ-Strahlen-Polymerisation nahm geringfügig mit der Quadratwurzel der Kohlendioxydkonzentration zu. Ausserdem war die Polymerisationsgeschwindigkeit, wie gefunden wurde, der Dosisleistung und dem Quadrat der Monomerkonzentration proportional. Das Molekulargewicht des gebildeten Polymeren war von den Reaktionsbedingungen unabhängig. Die scheinbare Aktivierungsenergie wurde zu 10,3 kcal./Mol bestimmt. Die Kinetik der durch γ-Strahlen ausgelösten Polymerisation in Gegenwart von Kohlendioxyd wurde quantitativ auf Grundlage eines kationischen Mechanismus diskutiert. Der Einfluss des Kohlendioxyds wurde durch eine verlangsamende Wirkung auf die Neutralisation der kationischen startwirksamen Spezies durch Elektronen erklärt, die in Umkehrung zu ihrer Bildung bei der Bestrahlung mit γ-Strahlen erfolgt. Die physikalischen und mechanischen Eigenschaften des durch Polymerisation mit γ-Strahlen erhaltenen Polymeren wurden ebenfalls untersucht.

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Gel Permeation Chromatography: Effect of Pore-Size Distribution*

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Synopsis

The pore-size distributions of various grades of porous glass were determined by gas desorption and mercury porosimeter measurements. This allowed the calculation of elution volumes as a function of pore diameters. The coil sizes of polystyrenes in toluene were obtained for a series of molecular weights from hydrodynamic theory and matched with pore diameters. In this manner, expected calibration curves for gel permeation chromatography could be calculated. Good agreement was found with experimental data.

INTRODUCTION

The process of gel permeation chromatography has been shown to give useful separations of polymers permitting rapid determination of molecular weight distributions.[1] This procedure employs a column packed with small particles, usually of rigid gels, with pores of various sizes. The column is filled with a solvent that enters both the void spaces and the pores. The sample is added at the head of the column and transported through the column by the solvent. The larger molecules emerge first, followed by progressively smaller molecules, thus effecting separation. Applications and technique have been the subject of review articles.[2,3]

The exact mechanism of the separation is not well understood, although it is generally agreed that some measure of molecular size is primarily involved in the separation process.[4] In theory, the retention volume of any molecule is given by eq. (1).[5]

$$V_{Ri} = V_I + K_{Ri} V_p \tag{1}$$

Here, V_{Ri} is the elution volume of the ith species, V_i is the volume in the interstices of the column, V_p is the volume in the pores, and K_{Ri} is the fraction of accessible pores with sizes as big as, or bigger than, the size of the ith species. There appear to have been few, if any, experimental studies to attempt to confirm this equation by independent experimental techniques. This is because of the major difficulty in determination of K_{Ri}, the pore-size distribution, of gel particles.

Recently, glass packings covering a wide range of porosities have become available. Thus, independent pore-size distributions can be determined.

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* This paper is Part XII of a series on column fractionation of polymers.[6]

This report compares elution volumes on polystyrenes computed from molecular dimensions and experimental pore-size distributions with directly measured elution volumes.

EXPERIMENTAL

The porous glass, trade name Bio-Glas, was obtained from Bio-Rad Laboratories, Richmond, California, USA. Four grades were used, with nominal exclusion diameters of 200, 500, 1000, and 1500 A. The columns were 0.8 cm. inside diameter, 120 cm. in length. The polystyrene fractions were narrow molecular weight distributions obtained from Pressure Chemical Company, Pittsburgh, Pennsylvania, USA. The solvent used was toluene at room temperature. Flow rates were 1 ml./min. and were controlled by a constant-volume pulseless pump.[6] The detector was a differential refractometer, and the volume measuring syphon has been previously described.[7] Sample sizes were 1.7 mg. in all cases. Results of log molecular weight versus elution volume are shown as circles in Figures 1–4. Figures 1, 2, and 3 are for single 120-cm. columns; Figure 4 is for four 120-cm. columns in series.

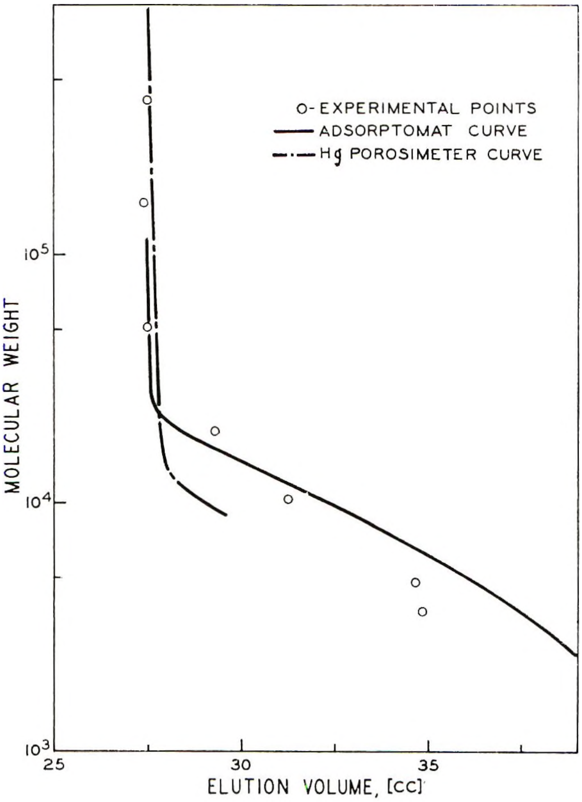

Fig. 1. Porous glass 200.

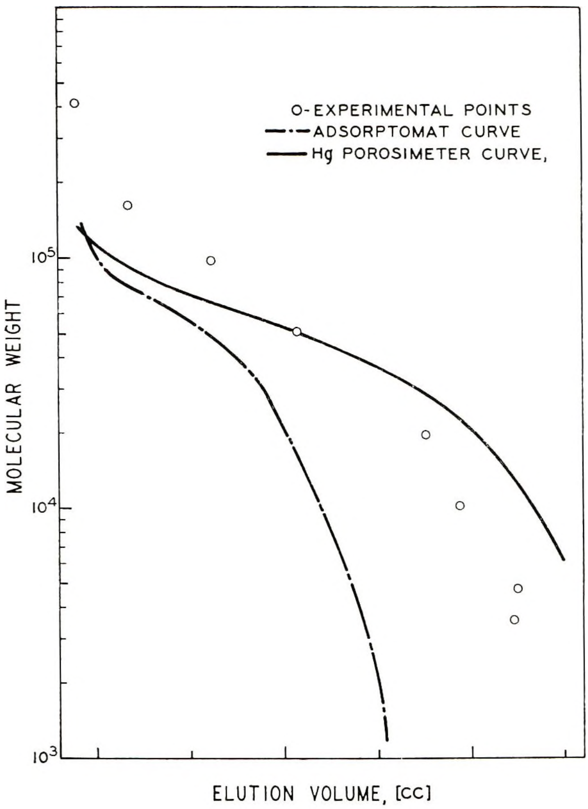

Fig. 2. Porous glass 500.

Determination of Pore-Size Distributions

Two standard methods of experimentally determining pore-size distributions in the porous glass were used: that involving gas desorption isotherms and mercury porosimetry. The gas desorption isotherms were measured by using an automated isotherm apparatus (American Instrument Company, Silver Springs, Maryland) based on a design of Ballou and Doolen.[8] Since the pioneering work of Wheeler,[9] an extensive literature devoted to the subject of calculation of pore size distributions from gas adsorption data has emerged.[10,11] This material is outside the scope of this paper, but it must be emphasized that various geometrical models of the pores may be selected and that film thickness expressions vary from author to author; hence, results cannot be considered to be exact. The cylindrical model and film thickness constants used by Lippens et al.[12] were used for the computations reported here.

The mercury porosimeter measurements were made using an Aminco-Winslow porosimeter, and results were furnished by Bio-Rad Laboratories. Again, results are not absolute because of assumptions including a circular cross-section geometry for the pores and a contact angle of 140° for mercury and glass.[13,14]

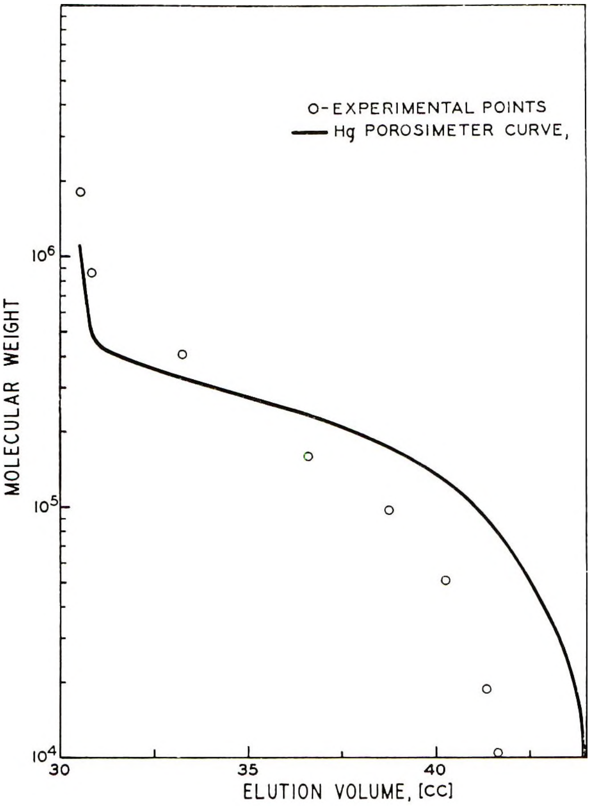

Fig. 3. Porous glass 1000.

Results from both techniques were computed as cumulative cubic centimeter per gram as a function of pore diameter.

Determination of Polymer Coil Size

The dimensions of the polymer molecules in solution were determined by using the hydrodynamic theory of Ptitsyn and Eizner.[15] These authors improved the model of Kirkwood and Riseman[16] by assuming a non-Gaussian distribution for the monomer units in the chain. This approach accounts for the rigidity of short segments within the chains and, more importantly, for excluded volume effects between remote portions of the chain. They arrive at the expression (2) for the intrinsic viscosity $[\eta]$ of a polymer solution:

$$[\eta] = \Phi(\epsilon)\ (\bar{h}^2)^{3/2}/M \tag{2}$$

Here $\bar{h}^2$ is the mean-square end-to-end distance of the polymer chains and M their molecular weight. The Flory coefficient, $\phi(\epsilon)$, can be approached by the following series:

$$\Phi(\epsilon) = 2.86 \times 10^{23}\ (1 - 2.63\epsilon + 2.86\epsilon^2) \tag{3}$$

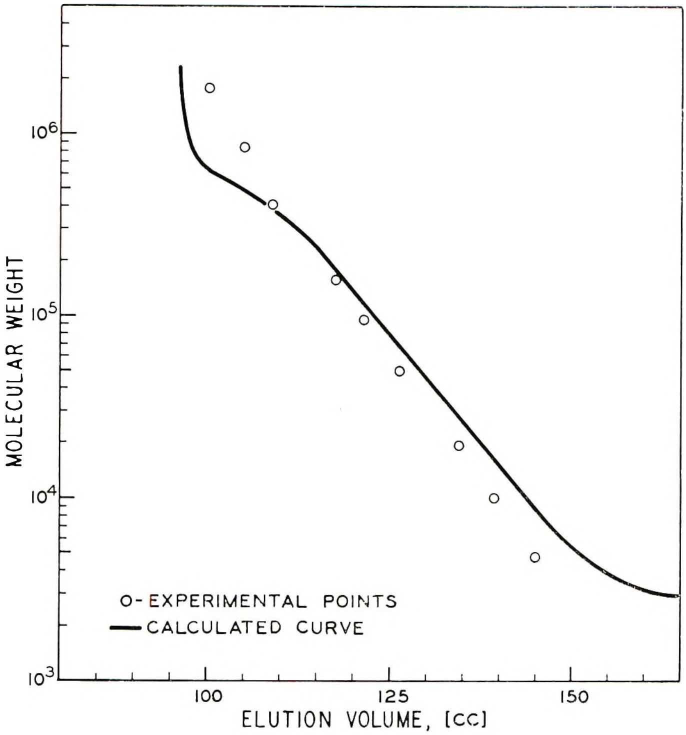

Fig. 4. Porous glass, multiple column.

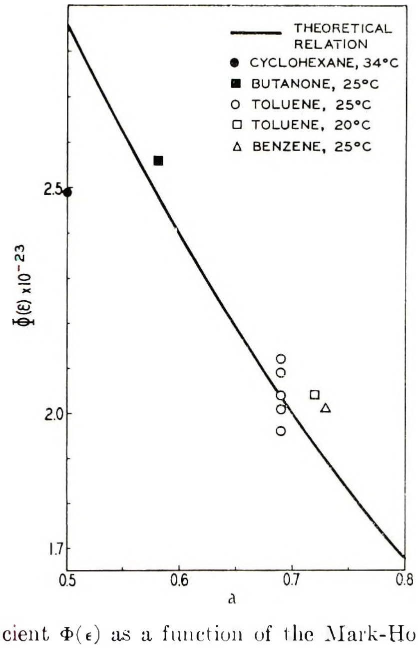

Fig. 5. Flory coefficient $\Phi(\epsilon)$ as a function of the Mark-Houwink exponent a.

with

$$\epsilon = (2a - 1)/3$$

where a is the exponent in the respective Mark-Houwink relation. Equation (2) expresses the fact that the polymer coil volume increases faster with increasing solvent power than the intrinsic viscosity. In Figure 5, the quantity $\Phi(\epsilon)$ as a function of a is given by the solid line. The points represent experimental values, obtained from light-scattering measurements of $\bar{h}^2$ and determination of $[\eta]$ for sharp polystyrene fractions of molecular weights ranging from 166,000 to 2,400,000 in the indicated solvents.[17] In case of polydisperse samples, the function $\Phi(\epsilon)$ should be divided by a factor, g, which can be approximated by[15]

$$g = (\bar{M}_z/\bar{M}_w)^{1.6 + 2\epsilon} \tag{4}$$

This correction has been neglected above because very sharp fractions were used.

RESULTS AND DISCUSSION

The experimentally determined cumulative pore volumes per gram of porous glass were multiplied with the known weight of glass per column, giving the available cumulative internal volume as a function of pore size. To this the experimentally determined interstitial volume was added, resulting in the total respective elution volumes. By trial and error, good agreement with the experiments was obtained by assigning to each pore size a polymer molecular weight with a calculated coil size of one-half of the pore diameter. In this manner, the solid lines in Figures 1–4 were arrived at. The above assumption allows all possible cases between the following two limits: Any polymer molecule can completely utilize the internal volume of all pores of diameters larger or equal than twice the polymer coil size; and it can, in the average, penetrate into 25% of the pore volume with a diameter equal to its own. This latter case might well be explained by the non-uniformity of the pores, which was observed on micrographs of the porous glass.

Figure 1 shows the expected calibration curve for porous glass 200 on the basis of gas desorption measurements. The high molecular weight cutoff point is well confirmed by the experimental points, while the expected lower limit is overestimated. The results from the porosimeter curve are not sensitive enough at the smaller pore sizes. In Figure 2 the porosimeter data on porous glass 500 were used for the calculation, since the gas desorption method is not optimal in this region. The same applies to Figure 3 on porous glass 1000. Again, the expected higher limit is in better agreement with the experimental values than the lower limit. Figure 4 shows the composite expected calibration curve for the column combination described in the experimental part. The agreement with the measured data is quite satisfactory.

The underlying simple model allows prediction of the experimental elution curve over a molecular weight range from 4000 to 2,000,000. The fact that an equivalence factor of two had to be used could be caused by assumptions made in calculating the pore size distribution. It has, however, no effect on the general shape of the calculated calibration curve, which is in good agreement with the experimental data.

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Résumé

Les distributions des grandeurs de pore de différents verres poreux ont été déterminées par désorption gazeuse et par mesures au porosimètre à mercure. Ceci permet le calcul du volume d'élution en fonction du diamètre des pores. Les grandeurs des pelottes de polystyrène dans le toluène ont été obtenues pour une série de poids moléculaires au départ de la théorie hydrodynamique et évaluées au moyen des diamètres des pores. De cette façon des courbes de calibrage attendues pour la chromatographie par perméation sur gel ont pu être calculées. Un bon accord a été trouvé avec les résultats expérimentaux.

Zusammenfassung

Die Porengrössenverteilungen in verschiedenen Sorten porösen Glases wurden durch Gasdesorption und durch Messungen mit dem Quecksilberporosimeter bestimmt. Dadurch war eine Berechnung der Elutionsvolumina als Funktion der Porendurchmesser möglich. Die Knäuelgrössen von Polystyrolen in Toluol wurden für eine Reihe von Molekulargewichten aus der hydrodynamischen Theorie ermittelt und mit den Porendurchmessern in Übereinstimmung gebracht. Auf diese Weise konnten die erwünschten Kalibrierungskurven für die Gelpermeationschromatographie berechnet werden. Es ergab sich gute Ubereinstimmung mit experimentellen Daten.

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Synthesis of Poly-3,3-bis(chloromethyl)-oxacyclobutane (Penton) Derivatives

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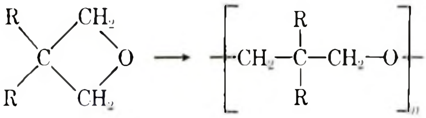
Synopsis

The derivatives of poly-3,3-bis(chloromethyl)oxacyclobutane were prepared by the reaction of the chloromethyl group with organic alkali salts at 100–130°C. in dimethyl sulfoxide. Various reagents were used, including sodium cyanide, sodium acetate, sodium thiophenolate, sodium phenolate, sodium methoxide, sodium diethyl malonate, and potassium phthalimide. For all the substitution reactions, the infrared spectra and elementary analyses substantiated the structures of the designated products. The intrinsic viscosities of the derivatives decreased with increasing the reaction time. It was found that the ions of these salts are strong nucleophiles in dimethyl sulfoxide.

INTRODUCTION

Polyoxacyclobutanes bearing various functional groups at the γ-position have been synthesized by the ring-opening polymerization of the corresponding monomers:



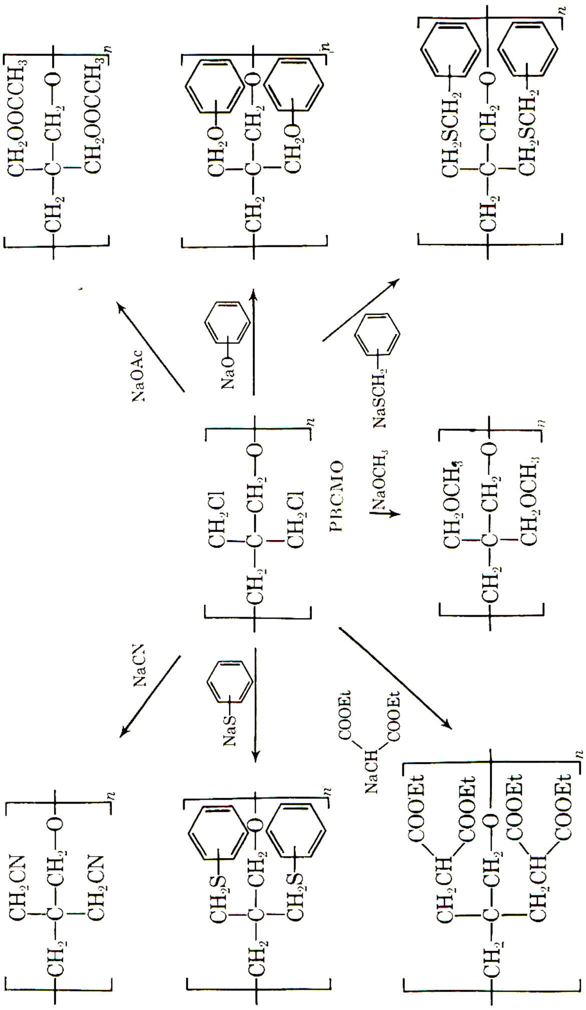
(1)

where R is H, CH_3, CH_2Cl, CH_2F, CH_2CN, CH_2OH, etc.[1-3]

In the course of the investigation of chemical reactions of the polymers in our laboratory, we expected that poly-3,3-bis(chloromethyl)oxacyclobutane (PBCMO) would undergo substitution reactions at the chloromethyl group with various reagents, e.g., organic alkali salts, because of the moderate reactivity of its primary chlorine atom towards several reagents.

$$\left[-CH_2-\overset{\displaystyle CH_2Cl}{\underset{\displaystyle CH_2Cl}{C}}-CH_2-O-\right]_n \xrightarrow[\text{in DMSO}]{M-R} \left[-CH_2-\overset{\displaystyle CH_2R}{\underset{\displaystyle CH_2R}{C}}-CH_2-O-\right]_n \qquad (2)$$

The organic alkali salts, M—R, in the eq. (2) may be sodium cyanide, sodium acetate, sodium thiophenolate, etc. In these reactions it was



Scheme 1.

expected that the corresponding derived polymer would be obtained through the elimination of the alkali metal halide. Many polar solvents, such as alcohols, acetic acid, dimethylformamide (DMF), and acetone have so far been used in this type of metathesis between organic halides and alkali salts. Although the synthesis of nitriles by the action of alkali cyanides on alkyl halides is most difficult even in a polar solvent, recent investigators[4,5] have shown dimethyl sulfoxide (DMSO) to be a suitable solvent for these reactions.

In this work therefore the seven reactions shown in Scheme 1 were carried out in DMSO.

EXPERIMENTAL

Materials

Poly-3,3-bis(chloromethyl)oxacyclobutane (PBCMO) supplied by the Hercules Co., was purified by dissolving it in cyclohexanone, precipitating with methanol, and drying. Analysis showed C, 38.73%; H, 5.20%; Cl, 45.74%. $[\eta]$ of this polymer in cyclohexanone at 30°C. was 1.07 dl./g.

Dimethyl sulfoxide (DMSO) was dried completely by heating to 150°C. with calcium hydride and then distilling under reduced pressure.

Commercially available sodium cyanide, potassium phthalimide, and sodium acetate were used without further purification, and sodium methoxide was prepared by dissolving metallic sodium in anhydrous methanol and removing the excess methanol. Sodium ethyl malonate, sodium thiophenoxide, and sodium phenoxide were obtained by the reactions of sodium methoxide with ethyl malonate, thiophenol, and phenol, respectively. Sodium benzylmercaptide was prepared by the direct reaction of metallic sodium with benzyl mercaptan in benzene.

Reaction of PBCMO with Sodium Cyanide

Sodium cyanide (1.9 g., 0.04 mole) was placed in a 100-ml. three-necked flask equipped with a stirrer, a thermometer, and a reflux condenser, under a nitrogen atmosphere. It was heated under nitrogen until the absorbed moisture in the sodium cyanide was completely removed. Then the contents were left to stand at room temperature, while flushing continuously with nitrogen. Anhydrous DMSO (80 ml.) was added, and the mixture was heated with stirring and maintained at 120–130°C. Then 1.5 g. of PBCMO was added, and a pale yellow solution was obtained after 1 hr., then a white precipitate appeared, indicating that the reaction of sodium cyanide was taking place. The contents became yellowish brown after 2 hr. and brown after 3 hr.; at this time the sodium chloride was completely deposited. The supernatant solution was cooled to room temperature and poured into 200 ml. of methanol. The precipitate at the bottom of the flask was dissolved immediately in a small amount of water and was thought to be NaCl.

The reprecipitated polymer was collected, washed with hot water repeatedly and then with methanol, and dried in vacuo. A hard, tough, brownish polymer was obtained which was soluble in DMSO, DMF, cyclohexanone, and THF, but insoluble in benzene, ether, chloroform, and carbon tetrachloride. The film deposited from a cyclohexanone solution on a glass plate adhered tightly and it was impossible to strip off. The infrared spectrum of a film on a salt plate was taken. The sharp band due to —C≡N was observed at 2250 cm.$^{-1}$ and a broad band due to the associated OH band at about 3550 cm.$^{-1}$. [η] in cyclohexanone at 30°C. was 0.622 dl./g. Analysis showed C, 62.67%; H, 6.08%; N, 14.75%; Cl, 4.68%. The extent of the reaction calculated from the Cl content was 90.9%.

Reaction of PBCMO with Sodium Acetate

Sodium acetate (3.3 g.), dried in an oven at 100–110°C. and ground quickly, was placed in a flask similar to that used in the reaction of sodium cyanide with PBCMO. DMSO (60 ml.) was added, and the mixture was heated with stirring. At 130°C., sodium acetate seemed to be insoluble in DMSO. Polymer (1.5 g.) was added to the mixture, and heating and stirring were continued for a further 24 hr. at 130–140°C. The mixture became yellowish brown and formed a gel at room temperature. The resulting polymer could not be precipitated with methanol or with water. The polymer was collected by salting out and washed well with hot water and methanol. When it was separated from DMSO and once it had coagulated, it was no longer soluble in methanol. After drying *in vacuo*, a brownish, slightly transparent, rubberlike polymer was obtained in 1.5 g. yield. Its infrared spectrum was taken with a film deposited on a salt plate. A strong band due to C=O at 1740 cm.$^{-1}$ and a band due to the associated OH at about 3500 cm.$^{-1}$ were present. [η] at 30°C. in cyclohexanone was 0.290 dl./g. Analysis showed C, 48.34%; H, 6.79%; Cl, 7.7%. The extent of the reaction calculated from the residual Cl content was 78.8%.

Reaction of PBCMO with Sodium Thiophenolate

The apparatus used was the same as that used in the above experiments. Sodium thiophenolate (3.2 g., 0.024 mole) and DMSO (50 ml.) were placed in the flask and heated with stirring. The mixture became transparent immediately. PBCMO (1.5 g.) was added at 110–120°C. The reaction occurred rapidly, as could be seen by the formation of sodium chloride. After 5 hr. heating and stirring, the mixture was cooled and poured into methanol. The polymer precipitated was collected, washed with hot water and methanol, and dried *in vacuo.*

A slightly soft and gray-colored polymer (3.0 g.) was obtained, and its absorption spectrum was taken with a film deposited on a salt plate. The absorptions due to the stretching and bending of an aromatic C—H at 3060 and 1583 cm.$^{-1}$ and of a monosubstituted benzene at 2200 and

1730 cm.$^{-1}$ were observed distinctly and an absorption due to S—C at 690 cm.$^{-1}$ was also present. Analysis showed C, 63.26%; H, 6.23%. [η] at 30°C. in cyclohexane was 0.688 dl./g.

Reaction of PBCMO with Sodium Phenolate

Sodium phenolate (4.6 g., 0.04 mole) was dissolved in 80 ml. of DMSO with stirring and heating. At 120–135°C. 1.5 g. of PBCMO was added. After 5 hr. the resulting mixture became dark and was poured into water after cooling. The polymer was collected by salting out with sodium chloride and washed with hot water and then with methanol, and dried. A 2.9-g. yield of a gray, rubberlike polymer was obtained. An infrared spectrum of the film was obtained which showed bands at 3060, 2200–1700, and 1595 cm.$^{-1}$, indicating the presence of an aromatic substituent. [η] in cyclohexane at 30°C. was 1.00 dl./g. Analysis gave C, 53.4%; H, 6.7%; Cl, 8.5%. The extent of reaction calculated from the residual Cl content was 71.2%.

Reactions with the use of 1 equiv. sodium phenolate to PBCMO were also carried out similarly.

Reaction of PBCMO with Potassium Phthalimide

Potassium phthalimide (4.4 g., 0.024 mole) and 70 ml. of DMSO were mixed and heated with stirring. To this transparent solution was added with stirring 1.5 g. of PBCMO. After 10 hr. heating at 130–140°C. the yellowish-brown mixture obtained was cooled and poured into water. The coagulated polymer was collected by salting out, and washed with hot water and then with methanol, and dried. A pale yellowish powder polymer, which was insoluble in most solvents and swelled only in cyclohexanone, dioxane, DMF, and DMSO, was obtained in 2.2 g. yield. Analysis showed C, 57.53%; H, 5.32%; N, 4.18%; Cl, 10.40%.

Reaction of PBMCO with Sodium Methoxide

Anhydrous DMSO (60 ml.) and 1.6 g. of sodium methoxide (0.03 mole) were mixed in a three-necked flask and heated with stirring. Sodium methoxide was insoluble. PBCMO (1.5 g.) was then added. The polymer seemed to dissolve in the mixture but deposited on the wall of the flask a few minutes later as a rubberlike material. After 1.5 hr. the mixture was treated with water and the resulting polymer was washed repeatedly with hot water and dried. A white polymer which was insoluble in all solvents was obtained in 1.9 g. yield. Analysis showed C, 39.16%; H, 6.93%; Cl, 19.41%.

Reaction of PBCMO with Benzylmercaptide

Anhydrous DMSO (80 ml.) and PBCMO (1.5 g.) were placed in a 100-ml. three-necked flask and heated at 120°C. with stirring. After the polymer was dissolved, the mixture was kept at 100°C. Sodium benzylmercaptide (5.9 g., 0.04 mole) was added rapidly, and the reaction was carried out for 5 hr. at 100–110°C. The mixture became dark after 5 hr. The cooled mixture was treated with water, and a sticky polymer coagulated. It was washed with hot water several times and with methanol and dried. A slightly elastic brown polymer was obtained in 1.9 g. yield. The infrared spectrum of its film on a salt plate, deposited from a cyclohexanone solution, showed absorption bands at 3050, 2000–1700, and 1603 cm.$^{-1}$ due to the aromatic substituents and a band at 690 cm.$^{-1}$ due to the C—S bond. The extent of the reaction calculated from the residual Cl content was 84.6%. $[\eta]$ in cyclohexanone at 30°C. was 0.56 dl./g. The resulting polymer was readily soluble in various solvents such as toluene, chloroform, THF, dioxane, anisole, MEK, and cyclohexanone, in contrast to the original polymer.

Reaction of PBCMO with Sodium Diethyl Malonate

Anhydrous DMSO (80 ml.) and sodium diethyl malonate (5.5 g., 0.03 mole) were mixed in a 100-ml. three-necked flask and heated at 120°C. with stirring. The sodium salt dissolved in DMSO. PBCMO (1.5 g.) was added to the mixture at 130–140°C. The polymer dissolved immediately and the mixture became brown. After 24 hr. the mixture was poured into water, and the polymer coagulated. It was washed well with hot water and with methanol and dried. The brownish polymer showed a band in its infrared absorption spectrum at 1740 cm.$^{-1}$ due to C=O. $[\eta]$ in cyclohexanone at 30°C. was 0.59 dl./g. Analysis showed C, 41.5%; H, 5.5%; Cl, 36.4%. The extent of the reaction calculated from the residual Cl content was 8.8%.

Saponification of Acetoxylated Polymer

The acetoxylated polymer (residual Cl 1.55%, extent of reaction 87.6%) was dissolved in a mixture of 50 ml. THF and 3 g. methanol, and 1–2 drops of 5% sodium methoxide solution in methanol were added to this solution from a dropping funnel with stirring. A white precipitate appeared immediately, and after 3 ml. of sodium methoxide solution had been added, the mixture was heated at 60°C. for 30 min., poured into four times the amount of methanol, and dried.

RESULTS AND DISCUSSION

Reaction of PBCMO with Sodium Cyanide

The reaction of PBCMO with NaCN in DMSO proceeded at a moderate velocity. The reaction mixture became brown, as reported by Friedman and Schechter[5] and Smiley and Arnold[4] even if completely anhydrous DMSO and NaCN were employed. In Table I the relation between the time required for the completion of the reaction, which was followed both by Beilstein's test on the supernatant solution and the extent of the increase in the amount of sodium chloride deposited, and some other factors, together with some results, are shown.

TABLE I
Reaction of PBCMO with NaCN

	NaCN		Reaction time, hr.	Yield, g.	Analysis				Extent of reaction, %		$[\eta]$, dl./g.
	g.	Equiv. based on Cl			C, %	H, %	N, %	Cl, %	From N	From Cl	
N-1	1.96	2	3.0	1.2	62.67	6.08	14.75	4.68	72.5	90.9	0.622
N-2	1.0	1	5.5	1.2	63.82	6.17	14.80	3.97	73.9	92.3	0.550
N-3	0.5	0.25	14.5	1.4	33.84	6.03	6.45	26.54	34.0	45.2	0.462
N-4	0.25	0.5	24.0	1.2	41.74	5.29	2.37	27.64	12.8	40.2	0.332

The infrared spectrum of each sample in Figure 1 showed the presence of an identical sharp band due to —C≡N at 2250 cm.$^{-1}$ and of an identical broad band due to associated —OH at 3580 cm.$^{-1}$ which also appeared in the spectra of the acetoxylated polymer described below.

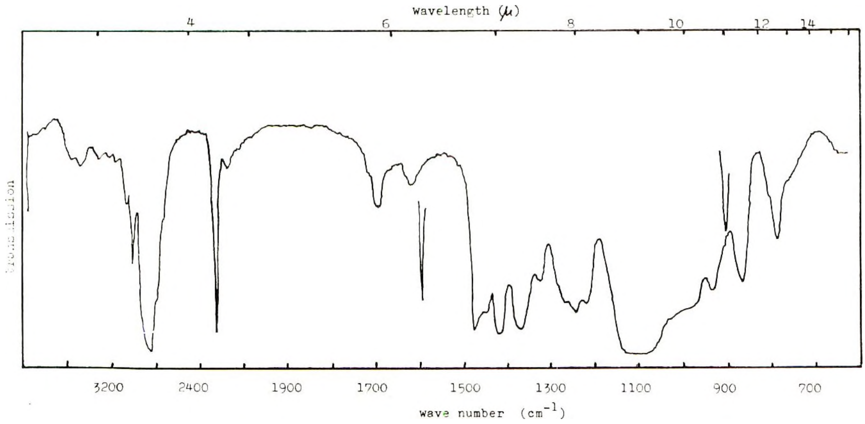


Fig. 1. Infrared spectrum of cyanomethyl-substituted polymer.

From elemental analysis it was found that the residual Cl contents decreased and the N contents increased with increasing amounts of NaCN. The residual Cl content of polymer N-4 in Table I, which was obtained by using a quarter equivalent of NaCN, implies an unexpected reaction, because the extent of the reaction of polymer N-4 calculated from its Cl content is 40.2%.

In general, this type of metathesis reaction can be expressed as follows:

$$\mathrm{R-Cl + MR' \rightarrow R-R' + MCl} \qquad (3)$$

The substitution reaction takes place on nucleophilic attack of the carbon atom carrying the Cl atom by the R′ anion. The high dielectric constant of DMSO can increase the solubility and facilitates the dissociation of the salts. However, the availability of DMSO as a solvent is restricted by its instability toward heat and basic reagent.

Investigations[6,7] of the behavior of DMSO show that metallation of DMSO by alkaline compounds and successive reaction of metallated or decomposed intermediates with main and side chain of polymer seem to occur. The difference in extent of reaction calculated from N content from that from Cl content may imply the presence of such side reactions. It appears that the extent of the reaction derived from the N content is more reliable. [η] decreases with increasing reaction time in spite of the decrease in the amounts of NaCN.

One of the side reactions at an ether linkage on the main chain would yield chain scission and terminal hydroxy group as detected by the [η] and the infrared spectrum, respectively. Isonitrile and other groups such as amide and carbonyl were not found in the infrared spectrum.

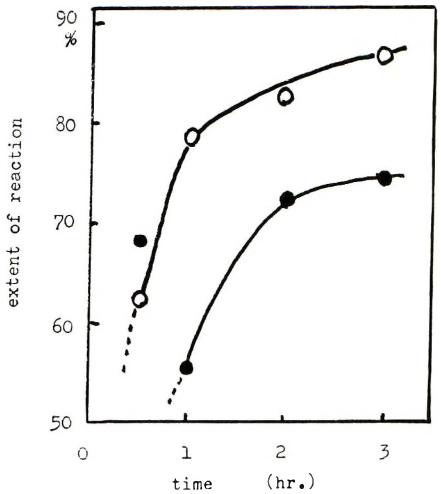


Fig. 2. Relation of extent of reaction to time: (○) from Cl content; (●) from N content.

The resulting polymer with a higher extent of reaction was a brownish hard solid, soluble in DMSO, DMF, cyclohexanone, and nitrobenzene like the original polymer and insoluble in benzene, methanol, and carbon tetrachloride. Polymer N-1, having the highest extent of reaction, was not perfectly soluble, even in THF.

In the second experiment we obtained a relationship between the time and other factors, when two equivalents of NaCN to Cl were used. The results are shown in Table II and Figure 2. The reaction reached 60% conversion in 30 min., but $[\eta]$ remained constant.

TABLE II
Relation of Time and Extent of Reaction

	Reaction time, hr.	Analysis				Extent of reaction, %		$[\eta]$, dl./g.	Softening point, °C.
		C, %	H, %	N, %	Cl, %	From N	From Cl		
N-5	0.5	60.7	6.39	13.5	18.4	68.5	62.4	0.81	210
N-6	1.0	56.0	6.10	10.8	10.5	55.5	79.0	0.87	215
N-7	2.0	61.8	6.7	14.3	8.7	72.7	82.6	0.75	135
N-8	3.0	62.7	6.4	14.8	6.3	74.5	87.5	0.81	175

Reaction of PBCMO with Sodium Acetate

Sodium acetate, unlike sodium cyanide, had a low solubility in DMSO, and under the conditions it dissolved insufficiently and gave a turbid solution. Its reactivity towards the polymer PBCMO was slightly lower than that of sodium cyanide, probably because of its low solubility. Table III shows the reaction time, the yield, and the extent of reaction and analysis for the acetoxylation with 2 equiv. sodium acetate to the

TABLE III
Acetoxylation by Sodium Acetate

	Reaction time, hr.	Yield, g.	Analysis			Extent of reaction, %	[η], dl./g.
			C, %	H, %	Cl, %		
A-1	2	1.8	39.83	5.34	40.62	8.7	0.98
A-2	8	1.8	43.67	5.88	20.57	48.3	0.74
A-3	16	1.1	45.46	6.31	15.51	59.8	0.50
A-4	24	1.5	48.34	6.99	7.7	83.6	0.29

chlorine in PBCMO. The extent of reaction is plotted against reaction time in Figure 3.

With increasing reaction time, the Cl content decreased. The most highly acetoxylated polymer was a rubbery, brown, and slightly sticky solid, and flowed on standing for 2 months. The absorption due to the carbonyl group at 1740 cm.$^{-1}$, was present in every acetoxylated polymer. A broad band due to the associated OH groups at 3500 cm.$^{-1}$, which was also seen with the polymer resulting from the cyanation, appeared. [η] decreased with increasing reaction time.

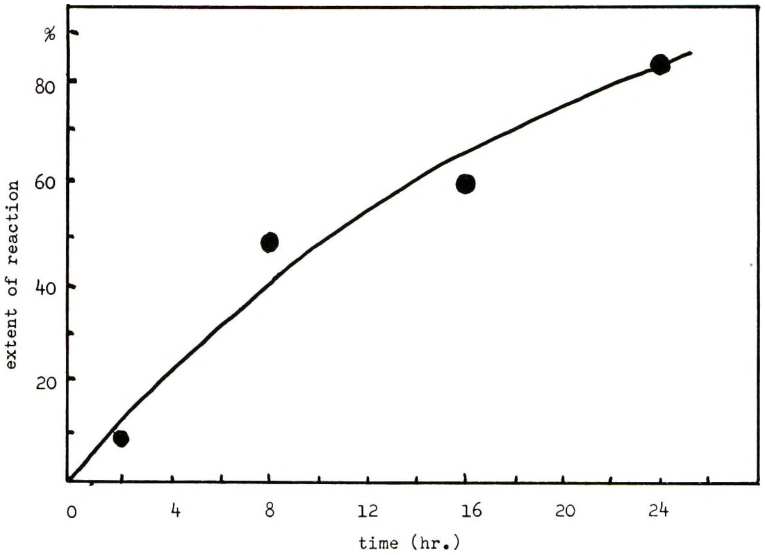


Fig. 3. Relation of extent of reaction to time.

Reaction of PBCMO with Sodium Thiophenolate

Sodium thiophenolate was most reactive towards the polymer PBCMO, which reacted with thiophenolate as soon as it was dissolved in DMSO, and the mixture became turbid with the appearance of sodium chloride at a very early stage of the reaction. The polymers obtained were white to gray in color and were slightly soft. In Table IV the results from the

TABLE IV
Reaction of PBCMO with Sodium Thiophenolate

	Reaction time, hr.	Yield, g.	Analysis			Extent of reaction, %	[η], dl./g.
			C, %	H, %	Cl, %		
S-1	0.5	3.1	61.82	6.57	1.68	97.0	0.687
S-2	1	3.6	57.57	6.28	2.68	92.7	0.699
S-3	2	3.8	57.57	6.41	2.60	92.6	0.757
S-4	3	4.0	54.96	6.77	1.21	97.2	0.752
S-5	5	3.0	63.26	6.23	1.11	97.8	0.688

reaction carried out by using 2 equiv. of sodium thiophenolate to Cl for various periods of time are shown.

Infrared spectra of these polymers (Fig. 4) showed aromatic bands at 3060, 1583, and 1700–2200 cm.$^{-1}$ and the S—C absorption band at 690 cm.$^{-1}$. The characteristic odor of SO_2, when these polymers were burned, suggested it contains considerable amounts of the thiophenoxy moiety.

The extent of reaction was also very high in all the reactions. The reaction was almost complete at an early stage. [η], which was lower than that of PBCMO, was not influenced by the reaction time.

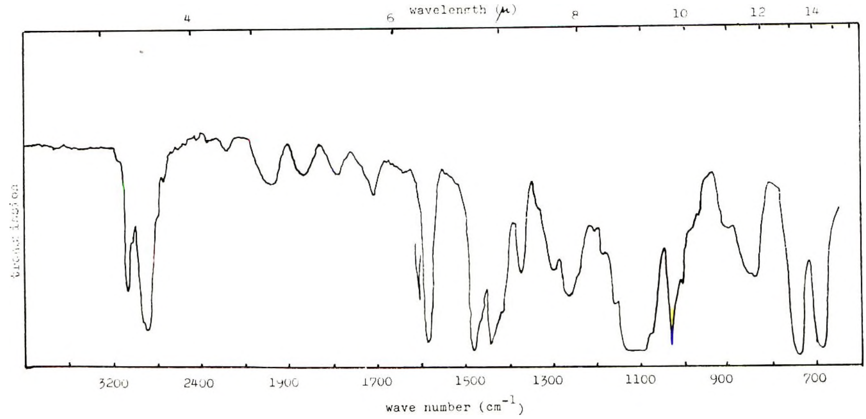


Fig. 4. Infrared spectrum of thiophenoxylated polymer.

Reaction of PBCMO with Sodium Phenoxide

The results of this reaction are summarized in Table V and Figure 5. Although the substitution at the chloromethyl group with sodium phenoxide was not faster than that with thiophenoxide, 2 equiv. of reagent gave a yield of 50% within 1 hr. The extents of three runs with 1 equiv. of the reagent were lower.

The polymers obtained could be cast to a film from cyclohexanone solution and their infrared spectra (Fig. 6) showed aromatic bands at 3060, 1600, 2200–1800 cm.$^{-1}$.

TABLE V
Reaction of PBCMO with Sodium Phenoxide

	Sodium phen- oxide, equiv.	Reac- tion time, hr.	Analysis			Extent of reaction, %	[η], dl./g.	Softening point, °C.
			C, %	H, %	Cl, %			
P-1	2	1	50.0	6.5	15.6	52.1	1.11	72
P-2	2	2	57.1	6.2	13.5	57.2	1.13	67
P-3		4	60.3	6.4	11.2	63.3	1.13	59
P-4	2	5	53.4	6.7	8.5	71.2	1.00	76
P-5	1	1	—	—	39.0	8.1	1.14	98
P-6	1	2	—	—	24.9	30.7	1.34	94
P-7	1	5	—	—	21.6	35.0	1.01	98

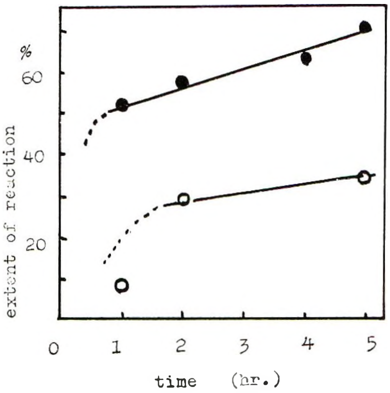


Fig. 5. Relation of extent of reaction to time: (●) 2 equiv. of sodium phenoxide; (○) 1 equiv. of sodium phenoxide.

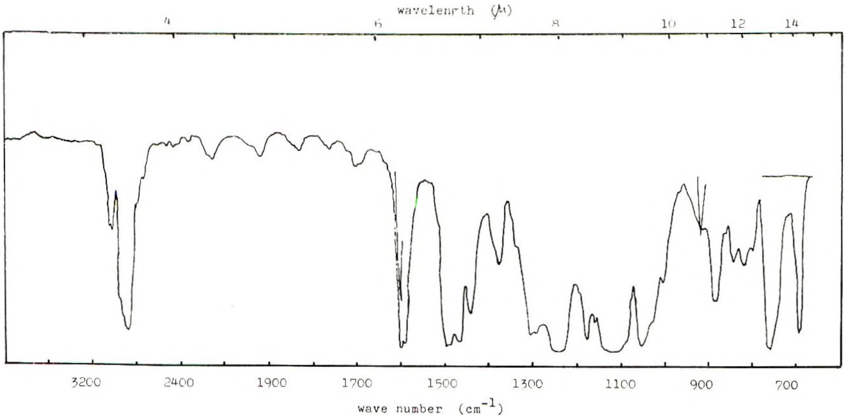


Fig. 6. Infrared spectrum of the polymer obtained from the reaction of sodium phenoxide and PBCMO.

Reaction of PBCMO with Potassium Phthalimide

Gabriel's[8] reaction was used in an attempt to obtain a polymer containing the aminomethyl group. Potassium phthalimide was soluble in hot DMSO, and the mixture with PBCMO was not turbid throughout the reaction, indicating that no reaction was taking place. The polymer obtained only swelled in cyclohexanone and DMSO and did not dissolve in any solvents. Quantitative and qualitative elemental analyses of this polymer showed the presence of nitrogen.

Reaction of PBCMO with Sodium Methoxide

One of the expected reactions of PBCMO was the formation of a methyl ether linkage in the polymer. This reaction was carried out by the action of sodium methoxide (Williams' synthesis). A polymeric gelled material deposited on the wall of the flask at an early stage of the reaction.

Reaction of PBCMO with Sodium Benzylmercaptide

The reaction of benzylmercaptide with PBCMO was very perplexing. The solvent decomposed at temperatures above 130°C. in the presence of sodium benzylmercaptide and the decomposition led to the crosslinking of the polymer. In order to avoid the decomposition of the solvent, it was necessary to add benzyl mercaptide to the mixture at temperatures below 100°C. after PBCMO was dissolved and to maintain the mixture at near 100°C. Under these conditions the expected soluble polymer was obtained. Its infrared spectrum and the residual chlorine content, from which the rate of the reaction seemed to be relatively high, showed the presence of the benzylmercapto moiety.

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Résumé

Les dérivés du poly-3,3-bis(chlorométhyl)oxacyclobutane ont été préparés par réaction du groupe chlorométhyle avec des sels organiques alcalins à 100–130°C dans le diméthylsulfoxyde. Les différents réactifs utilisés sont le cyanure de sodium, l'acétate de sodium, le thiophénolate de sodium, le phénolate de sodium, le méthylate de sodium, le diéthylmalonate de sodium et le phthalimide potassique, etc. Pour toutes les réactions de substitution, les spectres infrarouges et les analyses élémentaires confirment les structures proposées pour les produits. Les viscosités intrinsèques de ces dérivés décroissent

avec l'augmentation de la durée de réaction. On a trouvé que les ions de ces sels constituent des nucléophiles puissants dans le diméthylsulfoxyde.

Zusammenfassung

Durch Reaktion der Chlormethylgruppen mit organischen Alkalisalzen bei 100–130°C in Dimethylsulfoxyd wurden Derivate des Poly-3,3-bis(chlormethyl)oxacyclobutans hergestellt. Die verschiedenen verwendeten Reagenzien umfassten Natriumcyanid, Natriumacetat, Natriumthiophenolat, Natriumphenolat, Natriummethylat, Natriumdieäthylmalonat, Phthalimidkalium, u.s.w. Für alle Substitutionsreaktionen stellten Infrarotspektren und Elementaranalysen die Struktur der designierten Produkte sicher. Die Viskositätszahlen der Derivate nehmen bei Vergrösserung der Reaktionsdauer ab. Es wurde gefunden, dass die Ionen dieser Salze in Dimethylsulfoxyd stark nukleophilen Charakter besitzen.

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Endgroup Study of Chlorate–Sulfite-Initiated Acrylonitrile Copolymer

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Synopsis

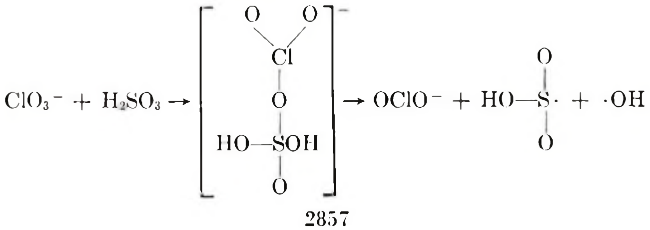
Quantitative determination of endgroups in an acrylonitrile–methyl acrylate (90:10) copolymer polymerized with $NaClO_3$–Na_2SO_3 redox system in aqueous solution was carried out by conductometric and dyeing methods for SO_3H incorporated into polymer, x-ray analysis for S in polymer, and polarography for Cl in polymer. The number-average molecular weight was measured by osmometry. Determination of endgroups was done on both unfractionated polymer and fractionated polymer. On the average, 0.95 mole S and 0.71 mole SO_3H per molecule were found in unfractionated polymer. For fractionated polymer, 0.68 mole S and 0.69 mole SO_3H per molecule were found. A small amount of Cl was also found in both unfractionated polymer and fractionated polymer. The difference between results for the two polymers and polymerization kinetics are discussed.

INTRODUCTION

It has commonly been accepted for a number of years that the residual fragments of polymerization catalysts are incorporated into polymer as endgroups in vinyl polymerization. The knowledge of amount and type of endgroups is available for studying polymerization kinetics and, especially in acrylic copolymers, dyeability of acrylic fiber produced from these copolymers.

Bamford[1] and Bevington[2] presented evidence that combination occurs in ethylene carbonate and dimethylformamide solution polymerization. On the other hand, Tsuda[3] presented evidence that in aqueous suspension polymerization with potassium persulfate initiator, termination is by disproportionation.

Gleason et al.[4] studied the aqueous suspension polymerization initiated by the $NaClO_3$–Na_2SO_3 redox system; they indicate that the exact nature of the free-radical intermediates is still in doubt, but that sulfoxy radical-ions and hydroxyl radicals are likely to be involved.



$$ClO_3^- + H_2SO_3 \rightarrow \left[\begin{array}{c} O\diagdown\ \diagup O \\ Cl \\ | \\ O \\ | \\ HO\text{—}SOH \\ | \\ O \end{array}\right]^- \rightarrow OClO^- + HO\text{—}\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{S}}\cdot + \cdot OH$$

$$HO\cdot + \text{monomer} \rightarrow \text{polymer}$$

$$HSO_3\cdot + \text{monomer} \rightarrow \text{polymer}$$

Palit and co-workers,[5] on the other hand, showed that the hydroxyl radical cannot exist in the presence of HSO_3 ion,

$$RHSO_3^- + \dot{O}H \rightarrow \dot{R}SO_3^- + H_2O$$

and therefore the hydroxyl radicals $\dot{O}H$ may be not involved. Yamadera[6] reported in his paper on infrared spectroscopic study of endgroups in polyacrylonitrile polymerized by $NaClO_3$–$NaHSO_3$ with that the band at 1043 cm.$^{-1}$ should be attributed to S—O symmetric stretching of the —SO_3H endgroup in the polymer, that the absorption intensities decrease proportionally with increasing degree of polymerization, and that the dyeability of the polymer for basic dyes increases with the increase of the absorption intensity.

The purpose of the work reported here is to determine the relative amount and types of endgroups in acrylonitrile–methyl acrylate copolymer polymerized with $NaClO_3$–Na_2SO_3 and to obtain some information about the polymerization mechanism and the dyeability of this acrylonitrile–methyl acrylate copolymer.

EXPERIMENTAL

Polymerization

A continuous polymerization system was used. Deionized water was used in the polymerization. The pH was maintained in the range of 1.7–2.0 by feeding an aqueous solution of nitric acid into the polymer reactor. The monomer mixture (acrylonitrile/methyl acrylate = 90/10 weight ratio) was also continuously fed into polymer reactor. $NaClO_3$–Na_2SO_3 was fed as aqueous solution. The molar ratio of $NaClO_3$–Na_2SO_3 was 1/3 or 1/4.75. Polymerization was stopped at about 80% conversion. Polymer was washed by deionized water.

Fractionation

Fractionation was carried out by using a dimethylformamide–diethylether–*n*-heptane system at 30°C. Dimethylformamide was the solvent and a 1:1 mixture (by volume) of ether and heptane was used as precipitant.

Measurement of Number-Average Molecular Weight

Measurement of number-average molecular weight by osmometry involved many difficult problems; details will be reported in another paper.[7] The measurement was made in γ-butyrolactone at 35°C. in a Stabin type osmometer. The membrane used was gel cellophane (Stabin), gage number 300.

Sulfur Analysis

An x-ray emission (fluorescence) technique was used to determine the sulfur content of the polymer. The preparation of polymer used as a standard for sulfur determination was as follows. Sulfurylamide (1 g.) was dissolved in 100 cc. methyl alcohol. The purity of the sulfurylamide used was checked by elementary analysis. This alcoholic solution was added to powder of polymer especially polymerized by azobisisobutyronitrile catalyst. After evaporation of methyl alcohol, the polymer powder was further dried and used as a standard.

Sulfonic Acid (SO_3H) Analysis (Conductometric Method)

Sulfonic acid (SO_3H) incorporation into polymer was measured by the conductometric method as described in a previous publication.[8] Polymer samples were dissolved in dimethylformamide and then the polymer solution was passed through an ion exchange resin (Amberlite IR-120 H type). By this operation, sulfonic acid salts were converted to free acid. The conductivity of the solution was measured by using a conductometer (Yanagimoto, Type MY-6) on titration with aqueous NaOH solution.

Dyeing Method for Determining SO_3H

Sulfonic acid (SO_3H) incorporated into polymer was also measured by the dyeing method.[9-12] Rhodamine 6-G was selected for use, it being a dye stable in solution for long periods at high temperature and high pH. The structure of this dye is given in the *Color Index*, Vol. 3, p. 3384 (Am. Assoc. Textile Chem. Colorists) and the molecular weight is 479. The dyeing of unfractionated polymer sample was carried out at 100°C. for about 2 hr. which was the time required to reach maximum adsorption. The dye concentration used was in excess of the concentration of SO_3H in the polymer and the dyeing solution was buffered, at pH 3.0 with buffer solution of Britton and Robinson.[13] After being dyed, the polymer was filtered and washed with 200 cc. of the buffer solution and then dried. To determine the amount of dye absorbed, the dyed polymer was dissolved in γ-butyrolactone and the dye concentration was determined spectrophotometrically.

Chlorine Analysis

In this experiment, a small amount of chlorine was quantitatively analyzed by an alternating current polarograph method. Polymer was burned in oxygen under pressure and the HCl evolved was absorbed into Na_2CO_3 aqueous solution. Then $HClO_4$ was added as a support electrolyte. An alternating current polarogram of Cl^- was recorded and the small amount of chlorine contained in the polymer was quantitatively analyzed from the peak of Cl^-.

RESULTS AND DISCUSSION

Experimental results are shown in Tables I–VI and Figures 1 and 2.

In the case of unfractionated polymer, the amount of S and SO_3H in polymer did not agree (Table I), S and SO_3H per polymer molecule being 0.95 and 0.71 mole, respectively (Table II).

TABLE I
Relationship between SO_3H and S of Unfractionated Polymer[a]

	SO_3H (by conductometry)		S (by x-ray analysis)	
Sample no.	wt.-%	10^5 mole/g.	wt.-%	10^5 mole/g.
M-10108	0.27	3.33	0.124	3.87
M-10114	0.18	2.22	0.098	3.06
M-10115	0.20	2.47	0.095	2.97
L-838	0.18	2.22	0.086	2.69
K-814	0.28	3.46	0.142	4.44
K-881	0.36	4.44	0.174	5.44

[a] $S = SO_3H + 0.70 \times 10^{-5}$ mole/g.

TABLE II
SO_3H and S per Molecule of Unfractionated Polymer

Sample no.	$\bar{M}_n \times 10^{-4}$	SO_3H (conductometry) $\times 10^5$, mole/g.	S (by x-ray analysis) $\times 10^5$, mole/g.	$(1/\bar{M}_n) \times 10^5$	SO_3H per molecule	S per molecule
N-1936	4.79	1.24	—	2.08	0.60	—
N-1938	3.83	1.85	—	2.61	0.71	—
2D-272	3.83	1.61	—	2.61	0.62	—
P-1921	3.58	1.73	—	2.80	0.62	—
M-10114	3.05	2.21	3.06	3.28	0.67	0.93
M-10115	2.97	2.47	2.97	3.36	0.73	0.88
M-10108	2.70	3.34	3.87	3.70	0.90	1.04
M-1932	1.12	7.53	—	8.93	0.84	—
				Avg.	0.71	0.95

In the case of fractionated polymer, the amount of S and SO_3H in polymer agreed, the S and SO_3H per polymer molecule being 0.68 and 0.69 mole, respectively (Table III).

The SO_3H groups per polymer molecule is almost same for fractionated polymer and unfractionated polymer, but, the S per polymer molecule in the case of unfractionated polymer differs from that in fractionated polymer.

For some reason it may be that only sulfur in polymer decreases during fractionation. The reason is not clear at present, but catalyst not linked to polymer or its decomposed fragments might be mixed in polymer and then removed during fractionation,[4,8] or a small amount of low molecular

TABLE III

SO_3H and S of Fractionated Polymer

Sample no.	$[\eta]$ (30°C., DMF)	$\bar{M}_n \times 10^{-4}$	$(1/\bar{M}_n) \times 10^5$	SO_3H (by conductometry)		S (by x-ray analysis)		SO_3H per molecule	S per molecule
				wt.-%	10^5 mole/g.	wt.-%	10^5 mole/g.		
3L-39-3	0.65	1.65	6.06	0.293	3.58	0.134	4.19	0.59	0.69
3L-39-4	0.96	2.49	4.02	0.191	2.35	0.070	2.19	0.58	0.54
3L-39-5	1.25	3.79	2.64	0.121	1.48	0.053	1.66	0.56	0.63
3L-39-6	1.51	4.65	2.15	0.105	1.36	0.042	1.31	0.63	0.61
3L-39-7	1.66	5.51	1.81	0.098	1.24	0.040	1.25	0.66	0.66
3L-39-11	2.47	7.22	1.38	0.110	1.36	0.034	1.06	0.99	0.77
3L-39-13	2.70	8.29	1.21	0.080	0.99	0.034	1.06	0.81	0.88
							Avg.	0.69	0.68

TABLE IV
Amount of SO_3H in Unfractionated Polymer by Dyeing Method

Sample no.	Amount of dye absorbed, mg./g.	$SO_3H \times 10^5$, mole/g. By dyeing method	$SO_3H \times 10^5$, mole/g. By conductometry
L-838	11.6	2.42	2.22
K-814	16.4	3.42	3.46
K-881	21.9	4.57	4.44

TABLE V
Amount of Chlorine (Cl) in Unfractionated Polymer

Sample no.	$\bar{M}_n \times 10^{-4}$	Cl wt.-%	Cl 10^5 mole/g.
N-1936	4.79	0.004	0.11
N-1938	3.83	0.004	0.11

TABLE VI
Amount of Chlorine (Cl) in Fractionated Polymer

Sample no.	$\bar{M}_n \times 10^{-4}$	Cl wt.-%	Cl 10^5 mole/g.
3L-39-3	1.65	0.003	0.08
3L-39-4	2.49	0.003	0.08
3L-39-5	3.79	0.003	0.08
3L-39-6	4.65	0.005	0.14
3L-39-7	5.51	0.004	0.11

weight polymer containing S which could not be measured by conductometric method might be removed.

In order to confirm the difference of SO_3H and S per polymer molecule, determination of the amount of SO_3H in polymer by the dyeing method was tried. The results are shown in Table IV. The amount of SO_3H as determined by the dyeing method agrees fairly well with the value obtained by conductometry.

The relationship of the difference between SO_3H and S of unfractionated polymer is represented by the equation (Fig. 1):

$$S = SO_3H + 0.70 \times 10^{-5} \text{ mole/g.}$$

A small amount of chlorine (about 0.003–0.005 wt.-%) was found in both unfractionated polymer and fractionated polymer (Tables V and VI).

Firsching and Rosen,[14] in a study of initiation of polymerization by the chlorine radical, found that, in the polymerization of vinyl chloride by radioactive $KClO_3$–$NaHSO_3$ catalyst, 0.3 atom of catalyst sulfur and 0.08 atom of catalyst chlorine were chemically bound per poly(vinyl chloride) molecule.

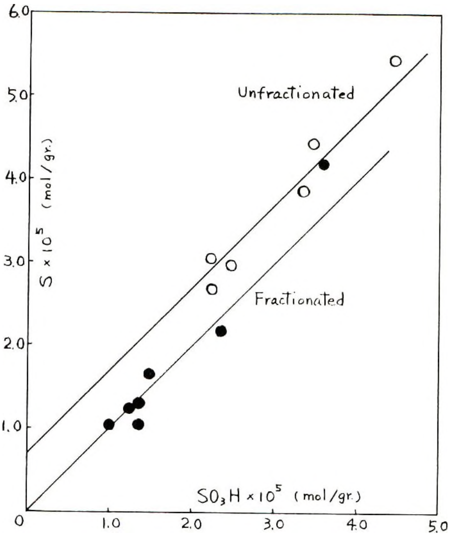


Fig. 1. Relationship between S in polymer as determined by x-ray and SO_3H in polymer by conductometry.

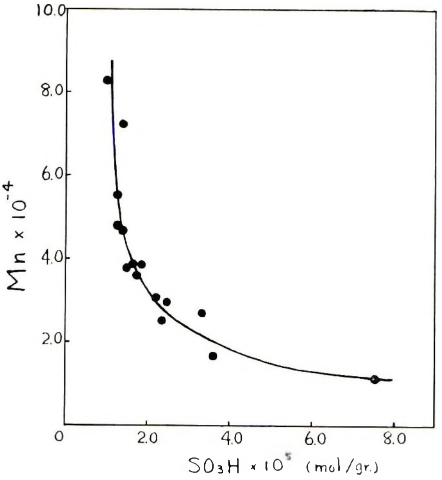


Fig. 2. Relationship between the content of SO_3H in the polymer and $\overline{M}_n$.

The amount of chlorine which we found in the polymer is quite small (0.003–0.005%). Accordingly this chlorine is probably not an incorporated endgroup but impurity originating from the catalyst.

As mentioned above, about 0.7 mole SO_3H or S in fractionated polymer and small amount of chlorine were found. We cannot, however, discuss the termination step of polymerization initiated by the chlorate–sulfite system on the basis of this fact alone, because there is a possibility of the existence of OH in polyacrylonitrile polymerized by $NaClO_3$–Na_2SO_3 redox system. Measurement of hydroxyl endgroups in the polymer has been attempted but no effective methods could be found. Recently, Palit and co-workers[15] reported that the hydroxyl endgroup is found in poly(methyl methacrylate) initiated by redox system of $KClO_3$–Na_2SO_3 in aqueous media, and the amount of OH group changes, depending on the $KClO_3/Na_2SO_3$ molar ratio. In addition, in the case of aqueous suspension polymerization of acrylonitrile initiated by the $NaClO_3$–Na_2SO_3 redox system, the polymerization is considered to occur both in aqueous solution and on the surface of the polymerized particle.[16] Therefore, the mechanism of termination is complicated and we can not conclude at present that termination in this aqueous suspension polymerization is simply by disproportionation or by combination.

Lastly, the relationship between the content of SO_3H in the polymer and number-average molecular weight is shown in Figure 2. This shows that the dyeability of the polymer for basic dyes increases markedly with decreasing number-average molecular weight.

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Résumé

La détermination quantitative des groupes terminaux dans le copolymère acrylonitrile–méthacrylate de méthyle (90:10) initié avec un système rédox $NaClO_3$–Na_2SO_3 en solution aqueuse, a été effectuée par application à la fois de la méthode conductimétrique et de la méthode aux colorants pour les groupes SO_3H incorporés dans le polymère, par analyses aux rayons-X du soufre contenu dans le polymère et par la méthode polarographique pour le chlore dans le polymère. Le poids moléculaire moyen en nombre a été déterminé par la méthode osmométrique. La détermination des groupes terminaux a été effectuée à la fois sur des polymères non-fractionnés et fractionnés. En moyenne 0.95 mole de soufre et 0.71 mole de SO_3H ont été trouvées par molécule dans le polymère non-fractionné. Considérant la polymère fractionné 0.68 mole de soufre et 0.69 mole de SO_3H par molécule ont été trouvées. Une faible quantité de Cl a également été trouvée dans les deux polymères. Cette différence du taux de soufre dans les deux polymères et les cinétiques de polymérisation ont été discutées.

Zusammenfassung

An einem mittels eines $NaClO-Na_2SO_3$-Redoxsystems in wässriger Lösung hergestellten Acrylnitril–Methacrylat-(90:10)-Copolymeren wurde eine quantitative Bestimmung der Endgruppen durchgeführt, wobei sowohl eine konduktometrische als auch eine Färbemethode zur Bestimmung der im Polymeren eingebauten SO_3H-Gruppen, Röntgenanalyse zur Erfassung des Schwefels im Polymeren und eine polarographische Methode zur Erfassung des Chlors im Polymeren angewandt wurden. Die Zahlenmittelwert des Molekulargewichts wurden osmotisch gemessen. Die Bestimmung der Endgruppen wurde sowohl an unfraktionierten als auch an fraktionierten Polymeren durchgeführt. Im Mittel wurden 0,95 Mol S und 0,71 Mol SO_3H pro Molekül im unfraktionierten Polymeren gefunden. In einer Fraktion des fraktionierten Polymeren wurden 0,68 Mol S und 0,69 Mol SO_3H gefunden. Sowohl im unfraktionierten als auch im fraktionierten Polymeren wurde auch eine kleine Menge Cl gefunden. Der Unterschied im S-Gehalt in beiden Polymeren und die Polymerisationskinetik wurden einer Diskussion unterzogen.

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Polymerization of DL-Alanine NCA and L-Alanine NCA

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Synopsis

The polymerization of *N*-carboxy-DL-alanine anhydride and *N*-carboxy-L-alanine anhydride were carried out in various solvents such as acetonitrile, dimethyl sulfoxide (DMSO), and nitrobenzene. The x-ray diffraction diagram and the infrared spectra of the polymers of DL- and L-alanine were obtained. The polypeptides obtained in acetonitrile and in nitrobenzene were in the α conformation, and the conformation of polypeptide obtained in acetonitrile was not influenced by its molecular weight. The polypeptide obtained in DMSO was essentially in the β conformation. It was observed that the α and β forms of polyalanine were altered on treatment of the polymer with *m*-cresol, dichloroacetic acid, or formic acid.

INTRODUCTION

It has been reported that the conformation of poly(γ-benzyl L-glutamate) depends on the conditions of polymer formation.[1–5] However, very little is known about poly-DL-alanine and poly-L-alanine.

The present study reports the relationship between the conformation of poly-DL- and poly-L-alanine and polymerization conditions. Poly-DL- and poly-L-alanine obtained in acetonitrile and nitrobenzene were in the α form but polyalanine obtained in DMSO or in the solid state was in the β form.

RESULTS AND DISCUSSION

Polymerization

The results of the polymerization of DL- and L-alanine NCA are shown in Tables I and II. For polymerization in acetonitrile, various initiators were used.

When water or triethylamine was used as an initiator, the rate of polymerization was slow, and high molecular weight polyalanine was obtained in spite of the low conversion (Table I). On the contrary, butylamine gave fast polymerization, and the molecular weight of the polymer obtained increased with the conversion of NCA (Table I). This may indicate that the

TABLE I

Conditions of Polymerization DL- and L-Alanine NCA

Polymer no.	Monomer	Solvent	Temp., °C.	Catalyst, mole-%	Time, hr.	Conversion, %	η_{sp}/c
A-1	DL-Alanine NCA	Acetonitrile	30	Water, 1.9	96	66	0.83
A-2	"	"	30	" 0.5	68	6.5	0.76
A-3	"	"	30	" 0.5	168	66	0.72
A-4	"	"	25	Butylamine, 1.0	0.5	4.0	0.05
A-5	"	"	25	" 1.0	20	67	0.38
A-6	"	"	0	Alcohol 4.8	163	96	0.31
A-7	"	"	25	Triethylamine, 0.1	23	13	0.21
A-8	"	"	30	Ammonia, 0.025	408	50	0.93
A-9	"	"	30	" 0.17	96	57	1.22
B-1	L-Alanine NCA	Acetonitrile	30	Water, 2.6	1000	99	0.80
B-2	"	"	30	" 1.6	333	35	4.12
B-3	"	"	30	" 2.6	40	15	0.79
B-4	"	"	30	Triethylamine, 0.5	5.5	6.9	0.93
B-5	"	Nitrobenzene	30	Water, 0.09	240	93	3.10
B-6	D-Alanine NCA	Acetonitrile	30	Water, 2.6	1000	99	0.81

TABLE II
Conditions of Polymerization of DL- and L-Alanine NCA

Polymer no.	Monomer	Solvent	Temp., °C.	Catalyst, mole-%	Time, hr.	Conversion, %	η_{sp}/c
C-1	DL-Alanine NCA	DMSO	30	Water, 3.8	0.1	20	0.21
C-2	"	"	30	" 3.8	96	64	0.38
D	L-Alanine NCA	DMSO	30	Water, 3.8	96	65	0.32
E	DL-Alanine NCA	solid state	0–10	—	>21 days	1–3[a]	1.0

[a] Yield of the water-insoluble poly-DL-alanine.

rate of initiation of water or triethylamine is comparatively small compared to that of propagation.

When crystals of DL-alanine NCA were allowed to stand for long time in dry isopropyl ether at 0–10°C., water-insoluble poly-DL-alanine was obtained in poor yield.

Conformation of Polyalanine

The x-ray diffraction diagrams of poly-DL- and poly-L-alanine obtained under the conditions described in Tables I and II are shown in Figure 1.

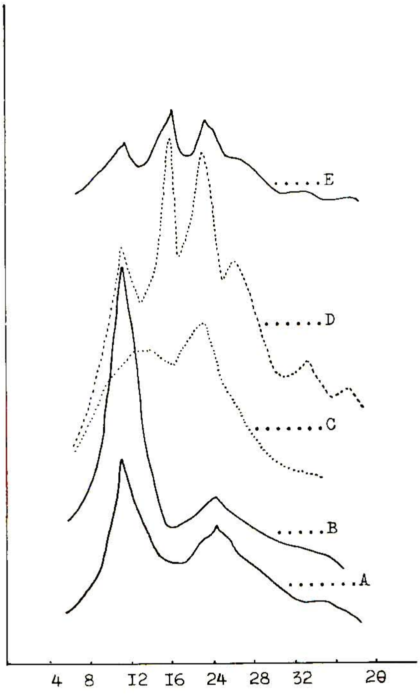

Fig. 1. X-ray diffraction diagram of poly-DL-alanine and poly-L-alanine polymerized under the conditions described in Table I.

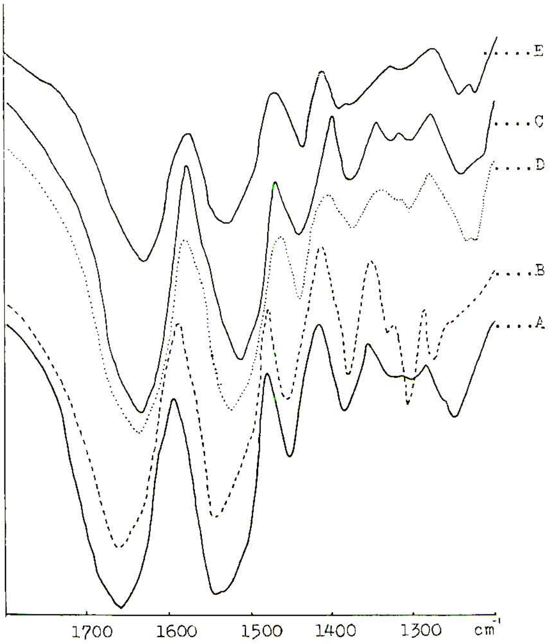

Fig. 2. Infrared spectra of poly-DL-alanine and poly-L-alanine polymerized under the conditions described in Table I.

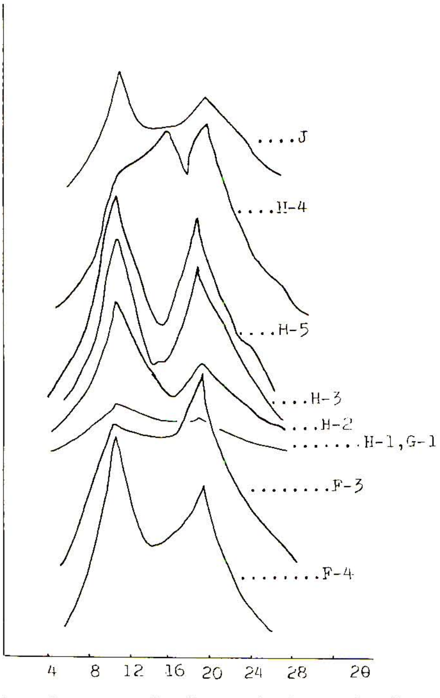

Fig. 3. X-ray diffraction diagrams of poly-DL-alanine and poly-L-alanine reprecipitated under the conditions described in Table III.

The x-ray diffraction diagrams of the polymers of each group in the tables were essentially the same.

The x-ray diffraction diagrams of poly-DL-alanine and poly-L-alanine obtained in acetonitrile and nitrobenzene (series A and B) show two peaks at $2\theta = 11.9°$ and $19.9°$, which are characteristic peaks of the α form of poly-L-alanine.[5] On the other hand, poly-DL- and poly-L-alanine obtained in DMSO and in the solid state (Table II) show another shape of x-ray diagram (Fig. 1, polymer series, C, D, E). Of these, pattern D is identical to that of β-poly-L-alanine.[5]

TABLE III
Reprecipitation Conditions of Polymers

Reprecipitated polymer no.	Original polymer	Solvent–nonsolvent	Temp., °C.	Time, hr.
F-1	A-1 (α form)	Dichloroacetic acid–ether	70	48
F-2	A-1 "	m-Cresol–ether	70	48
F-3	A-1 "	Formic acid–ether	70	48
F-4	A-1 "	Formic acid–ether	10–15	48
G	B-1 (α form)	Dichloroacetic acid–ether	70	48
H-1	C-2 (β form)	Dichloroacetic acid–ether	10	48
H-2	C-2 "	Dichloroacetic acid–ether	70	48
H-3	C-2 "	m-Cresol–ether	70	48
H-4	C-2 "	Formic acid–ether	70	48
H-5	C-2 "	Formic acid–ether	10	48
I	D (β form)	Dichloroacetic acid–ether	10–15	48
J	E (β form)	Dichloroacetic acid–ether	70	48
K[a]	B-6 (α form) + B-1 (α form), 1:1	Dichloroacetic acid–ether, acetone	20–40	48

[a] Mixture of poly-L- and poly-D-alanine reprecipitated from dichloroacetic acid solution.

The infrared absorption spectra (Fig. 2) of poly-DL- and poly-L-alanine obtained in acetonitrile and nitrobenzene gave absorption bands at 1661, and 1249 cm.$^{-1}$, and 1655, 1305, and 1275 cm.$^{-1}$, respectively. In the case of poly-DL-alanine, the absorption at 1305 cm.$^{-1}$ was observed when the polymerization was carried out at low temperature. But in the infrared spectra of polyalanines C, D, and E, the absorption bands around 1630 cm.$^{-1}$ were stronger than that at 1660 cm.$^{-1}$ The absorption band around 1660 cm.$^{-1}$ is characteristic of an α-polypeptide,[6] and absorption at 1305 cm.$^{-1}$ is considered to be characteristic of crystalline poly-L-alanine.[7] The absorption around 1630 cm.$^{-1}$ is characteristic of the β form of polypeptides.[6] Thus the infrared spectra coincided with the results of x-ray analysis.

The x-ray diagram of poly-DL-alanines A-4 and A-5 showed the same pattern. Moreover, the infrared spectra of these two polymers were quite similar. This would mean that the conformation of the poly-DL-alanine does not change from very low molecular weight up to high molecular weight during the propagation in acetonitrile.

It has been reported that the conformation of polypeptides changes from α to the β form on treatment in dichloroacetic acid and formic acid.[8]

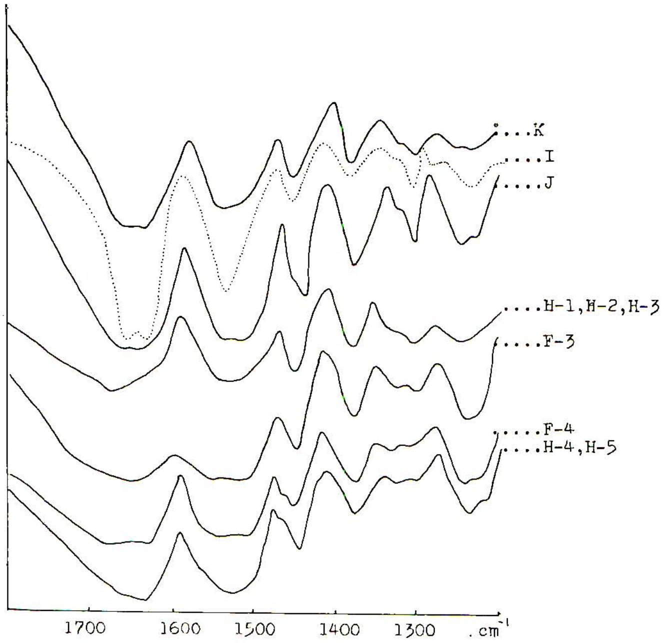

Fig. 4. Infrared spectra of poly-DL-alanine and poly-L-alanine reprecipitated under the conditions described in Table III.

The changes in conformation of poly-DL- and poly-L-alanine obtained here were examined under the conditions described in Table III. The x-ray diffraction diagrams and infrared spectra of the treated polymers are shown in Figures 3 and 4. These figures showed that the α-polyalanine did not change its conformation on treatment with dichloroacetic acid but changed from the α to β form on treatment with formic acid. On the other hand, β-polyalanine was converted to the α form by treatment with dichloroacetic acid or *m*-cresol. The temperature of the treatment strongly influenced the alteration of the conformation. When the α or β polyalanine was allowed to stand at room temperature, the change in conformation was not complete, but it was completed by the treatment at 70°C.

EXPERIMENTAL

Preparation of *N*-Carboxy-DL-alanine Anhydride and *N*-Carboxy-L-alanine Anhydride

DL-Alanine NCA and L-alanine NCA were prepared in high purity (chlorine content less than 0.02%) as reported previously.[9]

Polymerization

Poly-DL-, poly-L-, and poly-D-alanine were prepared by the method reported previously.[9]

Reprecipitation of the Polymer

After dissolving a polymer in dichloroacetic acid, formic acid, or *m*-cresol, the solution was allowed to stand at a constant temperature for a certain period, and the polymer was reprecipitated with ether or acetone and dried in vacuum at room temperature. The polypeptides thus obtained were subjected to x-ray diffraction and infrared absorption analysis.

Characterization of Polymers

X-ray diffraction diagrams were obtained by powder or film method by using a Rigaku Denki diffraction meter with nickel-filtered CuKα radiation. The infrared spectra of the polymers were obtained by a DS-301 Nihon Bunko infrared spectrometer on KBr disks or films of polymers.

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Résumé

La polymérisation de *N*-caroboxy-DL-alanine anhydride et de l'anhydride *N*-carboxy-L-alanine a été effectuée dans différents solvants tels que l'acétonitrile, le diméthylsulfoxyde (DMSO) et le nitrobenzène. Le diagramme de diffraction des rayons-X et les spectres infrarouges des poly-DL- et poly-L-alanines ont été rélevés. La conformation des polypeptides obtenus dans l'acétonitrile et le nitrobenzène étaient des formes α et la conformation du polypeptide obtenu dans l'acétonitrile n'était pas influencée par son poids moléculaire. La conformation des polypeptides obtenus dans le DMSO étaient essentiellement du type β. On a observé que les formes α et β de la polyalanine étaient modifiées par traitement des polymères avec le *m*-crésol, l'acide dichloroacétique ou l'acide formique.

Zusammenfassung

Die Polymerisation von *N*-Carboxy-DL-alaninanhydrid und *N*-Carboxy-L-alaninanhydrid wurde in verschiedenen Lösungsmitteln wie Acetonitril, Dimethylsulfoxyd (DMSO) Nitrobenzol ausgeführt. Das Röntgenbeugungsdiagramm und die Infrarotspektren des Poly-DL- und des Poly-L-alanins wurden aufgenommen. Die in Acetonitril und in Nitrobenzol erhaltenen Polypeptide wiesen α-Konfiguration auf; die Konformation des in Acetonitril hergestellten Polypeptids war von seinem Molekulargewicht unabhängig. Das in DMSO hergestellte Polypeptid besass im wesentlichen β-Konformation. Es wurde beobachtet, dass die α- und β-Form des Polyalanins durch Behandlung des Polymeren mit *m*-Kresol, Dichloressigsäure oder Ameisensäure ineinander übergeführt werden.

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Stereoregularity of Polyacrylonitrile Determined by NMR

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Synopsis

The NMR spectrum of polyacrylonitrile is interpreted and the tacticity of three polyacrylonitrile samples prepared at different temperatures in the range from −78 to 120°C. determined. The ratio between isotactic and syndiotactic units is about 50:50 for all the three samples examined.

Introduction

The steric structure of polyacrylonitrile (PAN) and the way in which polymerization conditions affect it have not yet been completely explained, even though various papers have recently appeared on the subject.

Some authors[1–4] state that some physical properties of commercial PAN are typical of a semicrystalline polymer; PAN therefore should have a high degree of stereoregularity. On the basis of x-ray measurements Stefani et al.[2] state that the PAN chain is 80% syndiotactic with a planar zigzag conformation in the crystalline regions. Yamadera et al.[4] found that the infrared vibrational frequencies of PAN and deuterated PAN are in agreement with those calculated by the GF matrix method assuming a planar zigzag syndiotactic structure for the polymeric chain. Inagaki et al.[5] recently determined the unperturbed dimensions in solution for seven fractions of a PAN sample obtained at −30°C. and for six fractions of a sample obtained at +60°C. These authors came to the conclusion that the syndiotactic fraction of a PAN chain increases on decreasing polymerization temperature.

Chiang[6] and Talamini and Vidotto[7] observed that samples of PAN prepared at different conditions exhibit marked differences in the dissolution and crystallization behavior. They believe that these differences depend probably on variations of the stereoregularity degree.

On the other hand, according to other authors, PAN is a practically atactic polymer.[8–10] Krigbaum and Tokita[11] have calculated theoretically the energy of the most probable conformations for a sequence of two polyacrylonitrile units having syndiotactic and isotactic configurations, respectively.

The energy is the same, and that seems to indicate that PAN stereoregularity is independent of the polymerization temperature. Moreover, these calculations indicate that the helical conformation is the most probable for the syndiotactic configuration.

Also the NMR data recently obtained on PAN stereoregularity show some disagreement. Yamadera and Murano[12] investigated the NMR spectrum of both normal and α-deuterated PAN in NaCNS–D_2O solution. The absorption of chain methylenes is the result of two overlapping triplets, the one at higher field being due to the syndiotactic methylenes.

From the spectrum of the α-deuterated polymer it appears that the syndiotactic configuration prevails and there is no difference between the PAN prepared at high temperatures (40 and 65°C.) and the PAN prepared at −190°C. with γ-ray initiation. Matsuzaki et al.[13] have studied both normal and α-deuterated PAN in dimethyl sulfoxide-d_6 (DMSO-d_6) and have come to the conclusion that stereoregularity cannot be determined in this solvent because of the strong overlapping between the triplets of syndiotactic and isotactic methylenes. Thereafter they found that the overlapping triplets observed in DMSO-d_6 resolve into two triplets in dimethylformamide-d_7,[14] thus allowing stereoregularity measurement. This interpretation is supported by the spectra of deuterated samples, which exhibit two peaks 0.03 ppm apart in the methylene absorption region. The ratio between isotactic and syndiotactic units is about 50:50 for all the samples examined independently of the initiation system used in the polymerization process (redox, *n*-buthyllithium, γ-rays).

This work reports the results of a NMR study of the stereoregularity of PAN samples prepared at different temperatures.

Experimental

The PAN samples were prepared by bulk polymerization with the system $B(C_4H_9)_3 + O_2$ as initiator at temperatures of −78 and 35°C. and *tert*-butyl peracetate at 120°C. High concentrations of initiator (1–2%) were used in order to obtain low molecular weight polymers.

The polymerization reactions were stopped by adding methanolic ammonia or quinone. The polymers were recovered by pouring the reaction mixture onto an excess of methanol.

The NMR spectra of PAN samples were measured in dimethylsulfoxide-d_6 (10% w/v) at 150°C. (thermostatted probe) by using a Varian A 56/60 and a Varian HR 100 spectrometer.

Results and Discussion

Figure 1 shows the spectrum at 60 Mc./sec. of the PAN sample prepared at 120°C. The spectrum is similar to the one reported by Matsuzaki et al.[13] and is characterized by a quintet at 6.85 τ corresponding to the α CH groups and by a strongly asymmetric triplet at 7.90 τ corresponding to the β CH_2 groups (the absorption near 7.5 τ is due to residual protons in the

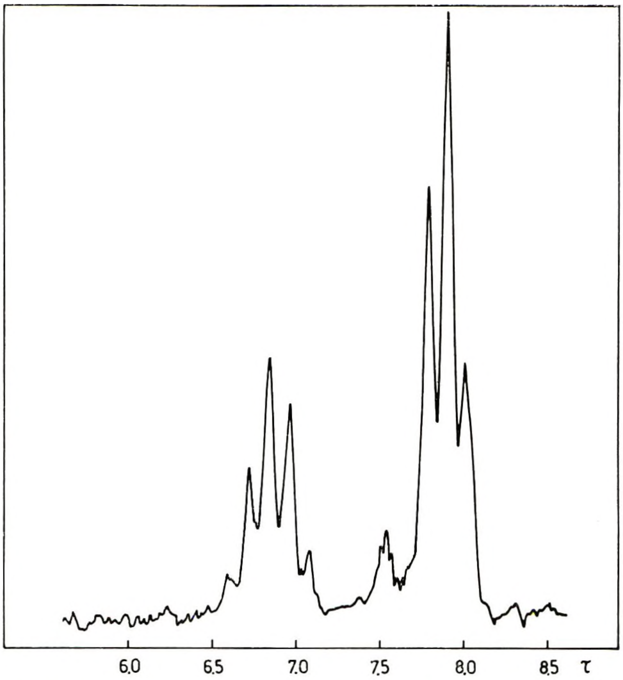

Fig. 1. NMR spectrum at 60 Mc./sec. of PAN prepared at 120°C.

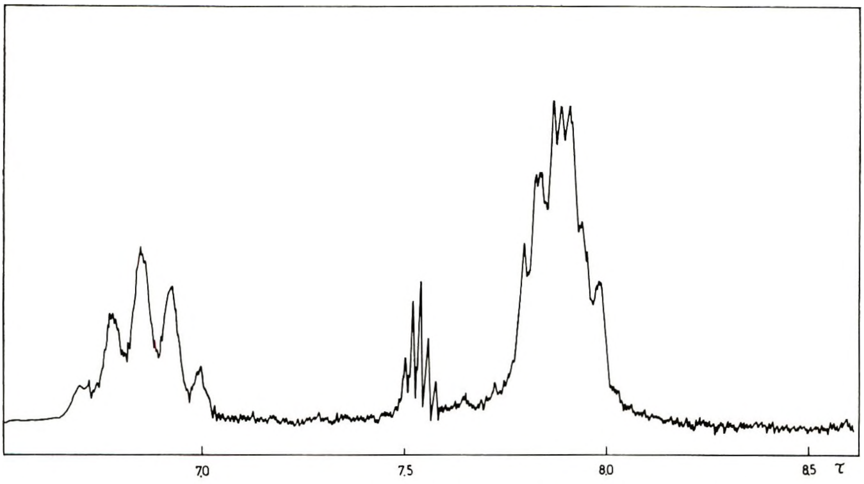

Fig. 2. NMR spectrum at 100 Mc./sec. of PAN prepared at 120°C.

solvent). This spectrum does not allow determination of the stereoregularity of the sample.

In the spectrum recorded at 100 Mc./sec. (Fig. 2) the α CH absorption is not altered, whereas the β CH_2 absorption becomes much more complex; a series of peaks can be recognized at 7.79_5, 7.83_5, 7.86_8, 7.88_7, 7.91_0, 7.93_9, 7.95_3, 7.98_3 τ.

This complex structure may result from the overlapping of a triplet at higher field at 7.83_7, 7.91_0, and 7.98_3 τ due to the methylenes in syndiotactic configurations and from a more complex absorption at lower field, which can be interpreted as the AB part of an ABX_2 system[15] due to the two protons of the methylenes in isotactic configurations.

From a theoretical point of view the magnetic non-equivalence of the methylene protons in isotactic configuration could be expected, and it has been experimentally detected in the NMR spectra of many polymers.[16–20] There are some cases, however, where the protons of isotactic methylenes seem to be equivalent.[21–23] Even though the low resolution generally obtained in the NMR spectra of polymers is not taken into account, this equivalence can occur when the difference in chemical shift between the methylene protons is rather small and, because of the geminal coupling, the absorption bands further converge toward the center of the single signals of the two protons. By increasing the resonance frequency, the conditions of the non-equivalence observation for the β protons are obviously improved.

Whereas at 60 Mc./sec. this non-equivalence is not detectable (the distance between the two central lines of the AB quartet should be 0.7 cps and the intensity of the external lines would be lost in the background), it actually appears at 100 Mc./sec. in our case. In the PAN spectra reported up to now,[12–14] the magnetic non-equivalence of isotactic methylene protons has not been observed. This can be ascribed to the different solvent used[12,14] and, in the particular case where the solvent was the same,[13] to the better resolution we obtained working with samples of low molecular weight.

The parameters for the isotactic and syndiotactic methylenes obtained from the 100 Mc./sec. spectrum in DMSO-d_6 at 150°C. are collected in Table I.

TABLE I
Parameters for the Isotactic and Syndiotactic Methylenes of PAN Obtained from the 100 Mc./sec. Spectrum

Methylene	$(\tau_A + \tau_B)/2$	$\nu_A - \nu_B$, cps	J_{AB}, cps	J_{AX}, cps	J_{BX}, cps	Half-band-width, cps
Isotactic	7.87_7	7.6	−14.4	7.6	6.5	2
Syndiotactic	7.91_0	0	—	7.3	7.3	3

In Figure 3 are reported the spectra for the isotactic and syndiotactic methylenes calculated* by using the parameters of Table I together with the experimental methylene absorption of the sample polymerized at

*The isotactic and syndiotactic methylene spectra were calculated by Prof. Rigatti of the Institute of Physical Chemistry at the University of Padua using the computer Olivetti ELEA 6000 of the Scientific Calculation Electronic Center.

120°C. From this interpretation the ratio between isotactic and syndiotactic methylenes is found to be about 50:50.

The spectra of other two samples of PAN polymerized at 35 and −78°C. have been analyzed.

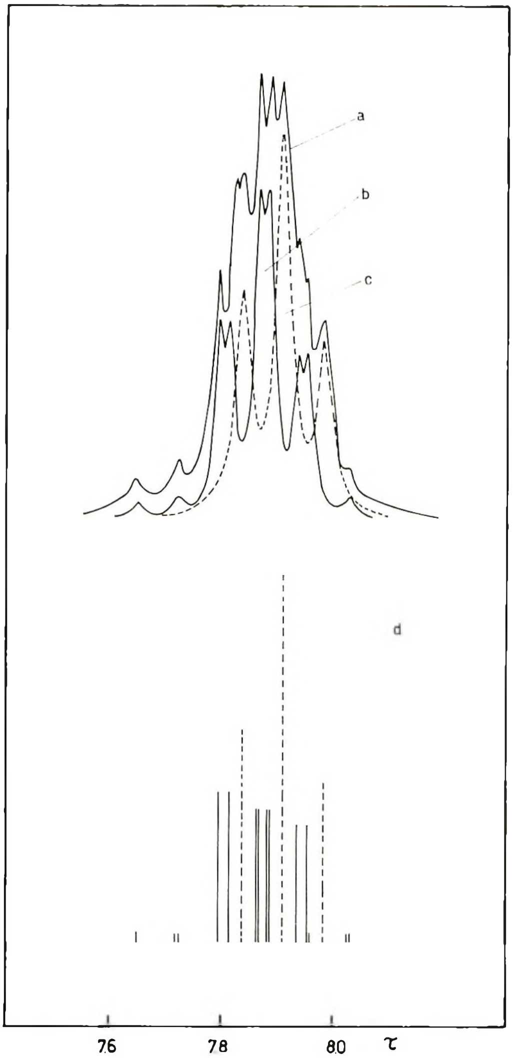

Fig. 3. NMR spectra of the methylene protons of PAN at 100 Mc./sec.: (*a*) observed spectrum of the sample prepared at 120°C.; (*b*) calculated isotactic component; (*c*) calculated syndiotactic component; (*d*) line spectra corresponding to *b* and *c*.

By resolving the methylene absorption in the isotactic and syndiotactic contribution according to the above-reported method, it appears that there is no substantial difference in the values of the ratio between isotactic and syndiotactic methylenes of the samples prepared at different temperatures.

The methylene absorption of the three samples examined is reported in Figure 4. We can therefore conclude that the degree of stereoregularity of PAN is independent of the polymerization temperature and that the polymer has 50% units with isotactic configuration and 50% units with syndiotactic configuration.

The independence of stereoregularity of the polymerization temperature is in agreement with the theoretical calculations of Krigbaum and Tokita.[11]

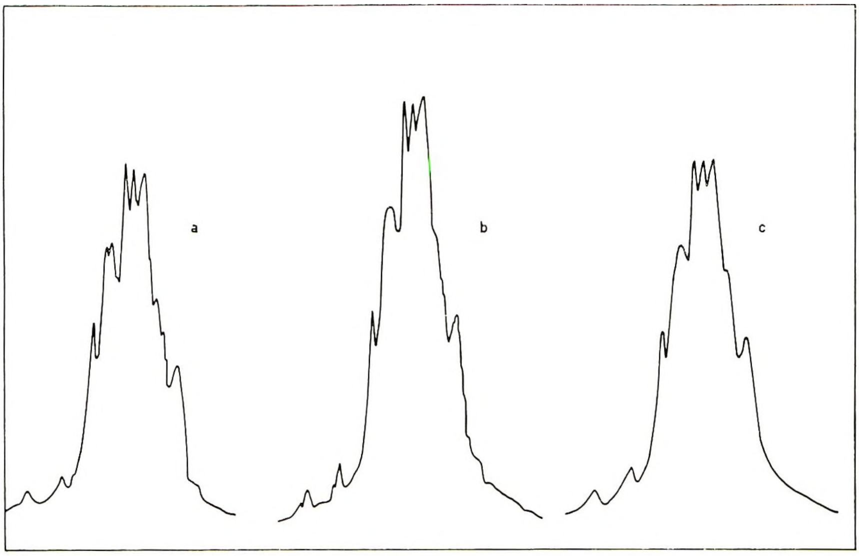

Fig. 4. Methylene absorption of PAN samples prepared at different temperatures: (*a*) 120°C.; (*b*) 35°C.; (*c*) −78°C.

The difference in the physicochemical properties of PAN samples prepared at different temperatures, found by Inagaki et al.[5] and Talamini and Vidotto[7] could be ascribed to variations in the number of irregularities of the polymer such as branching, head-to-head placement, cyanoethyl groups, etc., all of which are connected with the polymerization temperature. A 50:50 ratio between isotactic and syndiotactic units is in disagreement with the opinion of various authors[2,4,5,12] and could raise the doubt that PAN undergoes racemization in DMSO solution. It is to be noted, however, that DMSO has no racemizing action on the PAN model compounds *meso*- and *d,l*-2,4-dicyanopentanes.[14]

Note: After the completion of this work a paper by Bargon et al. [*Kolloid Z.*, **213**, 51 (1966)] appeared on the determination of PAN steric microstructure by NMR. Their results are in fairly good agreement with ours.

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Résumé

On donne une interprétation du spectre NMR du polyacrylonitrile. Sur la base de cette interprétation on détermine la tacticité de trois échantillons de polyacrylonitrile préparés aux differentes températures dans l'intervale de −78 à +120°C. Le rapport des unités iso- et syndiotattiques est environ 50:50 pour tous les trois échantillons étudiés.

Zusammenfassung

Man gibt eine Deutung des Polyacrylonitril NMR-Spectrums. Auf Grund dieser Deutung bestimmt man die Taktizität von drei Polyacrylonitril-Proben, die bei verschiedenen Temperaturen, −78 bis +120°C, hergestellt wurden. Das Verhältnis zwischen iso- und syndiotaktischen Monomereinheiten ist ungefähr 50:50 für die drei geprüften Proben.

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Comments on the Theories of the Intrinsic Viscosity of Chain Polymers

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Synopsis

The theory of intrinsic viscosity developed recently by the present author is examined and compared with experiments and the theories by Peterlin, Kirkwood and Riseman, Brinkman, and Debye and Bueche. The fundamental assumptions and essential approximations in the theories are criticized.

Introduction

Approximately twenty years have passed since Brinkman, Debye, and Bueche,[1,2] and Kirkwood and Riseman[3] (Hereafter, BDB and KR) published their well known papers on the intrinsic viscosity of chain polymers. During this period, Flory and others have found that these theories do not quite agree with experiments and the excluded volume effects which are neglected in these theories are of primary importance in explaining the molecular weight dependence of the intrinsic viscosity. Yet, it has also been found recently that a number of chain polymers have a stronger molecular weight dependence than the limit which one could expect from Flory's theory[4] even if the difficulties in the nonconstancy of the Φ constant are neglected. For this reason and since the KR theory involves various mathematical approximations, efforts have been made to achieve better results by using the basic approach.[5]

Recently, the present author developed a new viscosity theory[6] which did not require the replacement of the Oseen tensor by its average and allowed in principle to take the excluded volume effects of segments into consideration in a natural way.

It has been found that in the absence of the hydrodynamical interactions between the segments of a polymer this theory results in a formula which agrees in its general form with what Peterlin reported some time ago.[7] Comparison of these two theories shall be made in this note, as this has not been done. We shall also try to elucidate the relation between our theory and the KR and BDB theories. In so doing, it is hoped that the situation will be clarified for further development of our theory.

Intrinsic Viscosity and the Segment Distribution Function

The theory developed by the present author for a chain polymer of spherical configuration corresponds to the following situation.

(I) A chain polymer, when immersed in a laminar flow, acquires a rotational motion. The velocities of the segments are determined by the rotational motion. The viscosity arises from the difference in the rotational motion and the original laminar flow.

(II) The original flow is perturbed by the excluded volume and the motion of the segments. This perturbation can be expressed by a fluid dynamical force.

(III) The fluid dynamical force on a segment depends not only on its coordinates but also on those of the other segments. Thus, it is a many-body force, while in the evaluation of the intrinsic viscosity a one-body force comes in.

These observations are based on first principles and are in accord with BDB and KR. However, differences between the theories arise in the evaluation of the one-body force. The author has shown that (I,a) the one-body force may be determined in a self-consistent way as a function of the position from the center of a given polymer.

This statement has nothing to do with the excluded volume effects, and leads to a fundamental difference between our theory and the KR theory, as we shall discuss a little later. To proceed further, the author has then postulated (I,b) the pair segment distribution function is given by a product of singlet distribution functions.

Such an assumption is very common, even in the case of simple liquids. The present author has shown that the same product assumption made in the evaluation of the second virial coefficient of chain polymers yields very good results.[8,9] Actually, the assumption is consistent with the choice of segments coordinates as independent coordinates. The basic difference between the Rouse theory[10,11] and the Kirkwood theory[12] based on the description in a generalized Riemanian space is also in the choice of variables.

The general viscosity formula derived under the above consideration is characterized by a Fourier transform of the segment distribution function $w(k)$ as follows:

$$[\eta] = -\frac{(2\pi)^3\zeta}{2m\eta_0 N}\left\{\frac{\partial}{\partial k_x}\frac{\partial}{\partial k_x'}\left[\frac{w(\mathbf{k}+\mathbf{k}')}{1+(2\pi)^3\zeta\lambda(k)}\right]\right\}_{\mathbf{k}=\mathbf{k}'=0} \tag{1}$$

Here ζ is the frictional constant of a segment, η_0 the viscosity of solvent, N the number of segments in a polymer molecule, and $\lambda(k)$ is essentially the eigenvalue of the Oseen hydrodynamical interaction tensor in k-space.

The function $w(k)$ is independent of assumption (I,b) and represents that the viscosity of the entire molecule is the sum of the energy dissipation due to individual segments. Thus, it is a singlet distribution function referred to the center of gravity. The Fourier transform of a distribution function appears in the theory of Markoff chains as a natural step. Therefore, eq. (1) may be considered convenient from the theoretical point of view.

The eigenvalue $\lambda(k)$ is related to the assumption (I,b). Together with $w(k)$, it should be determined for the most realistic model of a polymer molecule. Yet, a rigorous theory has not been developed for even a pearl necklace model with excluded volume effects. Therefore, if one uses a perturbation method, he arrives at:

$$[\eta] = AN\,(1 + BN^{1/2})\,(1 + CN^{1/2} - DN)^{-1} \tag{2}$$

where the terms with the constants A and B represent the excluded volume effects.

As is seen, eq. (2) is rather involved to compare with experiments. In the absence of the excluded volume effects, it reduces to

$$[\eta] = [\eta]_0\,[1 + \gamma\,(a/b)\,N^{1/2}]^{-1} \tag{3}$$

$$[\eta]_0 = \zeta N b^2/36 m\eta_0 = \pi\,Nab^2/6m$$

where a is the radius of a segment, b the bond length when a pearl necklace model is adopted, m the mass of a segment, and γ is a constant which arises in connection with the assumption (I,b). If one assumes (I,b1) that the pair distribution function is given by a product of the singlet segment distribution functions referred to the center of gravity, γ is found in the first approximation to be

$$\gamma = 0.2863 \tag{4}$$

As an alternative approximation, one may assume (I,b2) the pair distribution function is replaced by a singlet distribution function referred to the center of gravity multiplied by the probability distribution function* of finding another segment around the first chosen segment. One finds in this case

$$\gamma = 3.6852 \tag{5}$$

To compare eq. (3) with experiments, it is convenient to rewrite it in the form:

$$M/[N] = A + BM^{1/2} \tag{6}$$

Here

$$A = 600 m_0^2/\pi\,N_0 ab^2$$

$$B = 600 m_0^{3/2}/\pi N_0 b^3 \tag{7}$$

m_0 is the molecular weight of a segment, N_0 is Avogadro's number, and the unit of the intrinsic viscosity corresponding to eq. (7) is deciliters per gram. Equation (6) agrees in its general form with what Peterlin[7] obtained by an intuitive method, as we shall discuss in the next section. However, since constants A and B are different we have determined them from the

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*This type of distribution function has been used in the theory of light scattering.[13,14]

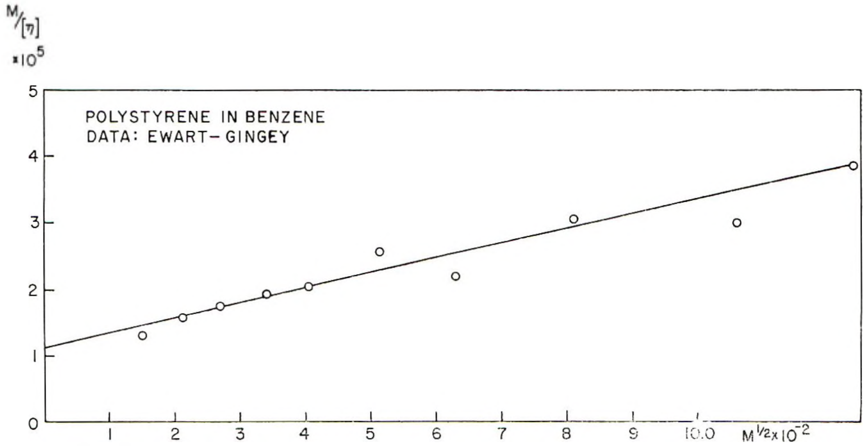

Fig. 1. Theoretical prediction (3) is tested for polystyrene in benzene.

plot illustrated in Figure 1. The data here are those on polystyrene obtained by Ewart and Gingey.[15] As a result we find $a = 0.12$ A., $b = 15.2$ A. for $\gamma = 3.6852$; $a = 0.64$ A., $b = 6.47$ A. for $\gamma = 0.2863$. These values have been obtained for $m_o = 100$. The a values are rather small, but they depend on m_o. Generally, a increases more rapidly than b with m_o.

From Figure 1 one might conclude that the general theoretical form of eq. (6) is satisfactory. However, it has been found that stiff molecules such as cellulose do not follow the theoretical prediction.[16] In any case, one can conclude from Figure 1 only that the theory is in the right direction. As we mentioned before, even in the case of no excluded volume effects, improvements upon the assumption (I,a) and related mathematics would yield different a and b values. Furthermore, whether or not such a theoretical improvement yields better a and b values, one should take excluded volume effects into consideration.

Nevertheless, within the framework of this theory, it is clear from the plot in Figure 1 that both A and B terms are important. Thus, it may not be appropriate to neglect the A term and use

$$\begin{aligned}[\eta] &= [\eta]_0(bN^{1/2}/\gamma a) \\ &= \Phi\langle r_0^2\rangle^{3/2}/M \qquad (8)\end{aligned}$$

to explain the molecular weight dependence of the intrinsic viscosity. Here, Φ represents a universal constant and $\langle r_0^2\rangle$ is the mean-square end-to-end distance. Equation (8) corresponds to $N \rightarrow \infty$ and for a finite N its functional form is not correct.

Comments on Peterlin's Work

As we mentioned before, eq. (6) agrees in form with what Peterlin obtained by an intuitive method. For comparison, and since his derivation is given in a paper which is not very accessible, we shall summarize his method.[7]

(P,a) One half of the segments of a polymer is assumed to move in one direction, while the other in opposite direction.

(P,b) The velocity of the jth segment is assumed to be related to that of the first segment by

$$v_j = [(N - 2Nj + 1)/(N - 1)]v_1 \tag{8}$$

In the absence of the hydrodynamical interactions the same relation is assumed to hold:

$$v_j' = [(N - 2Nj + 1)/(N - 1)]v_1' \tag{9}$$

(P,c) The force on the one half of the molecule:

$$\begin{aligned} F &= \sum_{j=1}^{N/2} F_j \\ &= \zeta \sum_{j=1}^{N/2} v_j' \end{aligned} \tag{10}$$

in the absence of the interactions is assumed to be equal to

$$F = \zeta_0 v_1 \tag{11}$$

where v_1 corresponds to the velocity of the first segment in the presence of the interaction, and the constant ζ_0 is somehow related to the total viscosity by

$$[\eta] = (Nb^2/6)(\zeta_0/\zeta_0 V_0) \tag{12}$$

(P,d) The velocities v_1 and v_1' are connected by the relation

$$\begin{aligned} v_1 &= v_1' + \sum_{k=1}^{\mathrm{N}} \psi_{1k}\, v_k' \\ &= \left\{1 + \sum \psi_{1k}\left(\frac{(N - 2k + 1)}{N - 1}\right)\right\} v_1' \end{aligned} \tag{13}$$

where ψ_{1k} is the average hydrodynamical interaction defined by

$$\psi_{1k} = \frac{a_0}{\langle|r_{1k}|\rangle} \tag{14}$$

Using the above relations one easily finds

$$[\eta]_p = (6\pi ab^2/24V_0)N[1 + 2.3(a_0/b)N^{1/2}]^{-1} \tag{15}$$

which is very close in form to eq. (3). This is not surprising, because Peterlin gave a correction to the Staudinger rule by evaluating an average hydrodynamical interaction, which is inversely proportional to $N^{1/2}$, through eq. (14). Therefore, the correction should be of the right order of magnitude.

However, irrespective of the similarity in the theoretical form, there are important differences between his theory and ours. The main differences are: (*1*) the motion of the chain molecule is entirely different; (*2*) the steps to the hydrodynamical interactions are entirely different; (*3*) the expressions for A and B are different. Especially, Peterlin's result does not reduce to Debye's expression $[\eta]_0$ in the limit of no hydrodynamical interaction.

Comments on the KR theory

Our theory may be understood better if compared with the KR theory. Their theory has been developed along the observations (I)–(III) discussed above. However, their steps corresponding to (I,a) and (I,b) are different and are as follows.

(KR,a) A one-body force is determined as a function of the ordering number of a segment irrespective of its location.

(KR,b) Because of (KR,a), the Oseen hydrodynamical interaction tensor is replaced by its average.

The result obtained by KR may be expressed as

$$[\eta]_{\mathrm{KR}} = [\eta]_0 F(x) \tag{16}$$

where $F(x)$ is a function of a variable

$$x = (6^{1/2}/\pi^{1/2})(a/b)N^{1/2} \tag{17}$$

Equation (16) may be written in the form:

$$[\eta]_{\mathrm{KR}} = 5.3654(\langle r_0^2\rangle^{3/2}/M)F(x) \tag{18}$$

From this expression Flory's Φ value can be evaluated from the limiting value of $F(x)$. Unfortunately, the limit depends on a numerical solution of their integral equation. Since the solution is very slowly convergent, efforts have been made to obtain better results. Accordingly, it is interesting to observe that improvements on the numerical solution have resulted in smaller Φ values: 3.62×10^{23} (Kirkwood and Riseman[3]); 3.36×10^{23} (Kirkwood, Zwanzig, Plock[17]); 2.86×10^{23} (Auer and Gardner[18]); 2.84×10^{23} (Zimm[11]).

It should be remarked that these Φ values correspond to $x \to \infty$. Actually x is not very big and is of order $0.1N^{1/2}$. Thus, if $M = 10^6$ and $m_0 = 100$, x is only of the order of 10. The values of Φ corresponding to x of this order of magnitude are less than that for $x \to \infty$, while Flory's original objection to the KR theory was based on the high Φ value in the KR result.[4]

In this respect, it is very interesting to observe that Hermans[19] reproduced the KR function $F(x)$ by a simpler function and reported an approximate formula:

$$[\eta]_{\mathrm{KR}} = [\eta]_0[1 + 1.078(a/b)N^{1/2}]^{-1} \tag{19}$$

The error involved in this approximation is a few per cent. We see that this expression is identical in form with that derived by Peterlin and Isihara.

Comments on the BDB Theory

The BDB theory has also been developed under I, II, III and (I,a) discussed above. Instead of (I,b) the BDB theory assumes (BDB,b) that the segment distribution is uniform inside a sphere. Because of this assumption they were able to solve a differential equation which has been shown by the author equivalent to the integral equation used by the author.[20] Therefore, their result is characterized by the radius R_s of a polymer molecule:

$$[\eta]_{\mathrm{DB}} = (4\pi/3)N_0(R_s^3/M)G(\sigma) \tag{20}$$

where σ^2 is defined by

$$\sigma^2 = 9Na/2R_s \tag{21}$$

In order to compare this result with ours it is necessary to introduce an assumption on R_s. We assume

$$R_s^2 = Nb^2/3.6 \tag{22}$$

so that eq. (20) for finite σ^2 is approximately given by

$$[\eta]_{\mathrm{DB}} = [\eta]_0[1 + 0.4150(a/b)N^{1/2}]^{-1} \tag{23}$$

As we see, the difference between this formula and eq. (3) with eq. (4) is again very small. This is, of course, for finite values of σ. The closeness in the final results of the KR and BDB theories has been illustrated by a graph in the DB paper. This suggests that a certain relation exists between the assumptions (KR,b) and (BDB,b). It seems that the averaging process corresponding to (KR,b) amounts to introducing a uniform segment distribution although locally the density is supposed to change. Furthermore, the assumption (I,b) is a consequence of small correlation. Thus, it seems that the author's assumption (Ib,1) which replaces the pair segment distribution by the two singlet distribution functions referred to the center of gravity is the most natural one. Unfortunately, the subsequent calculations are not simple compared with those for the alternative assumption. However, the very difficulty of the problem is clearly connected to the complexity of the calculation.

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Résumé

La théorie de la viscosité intrinsèque développée récemment par le présent auteur est examinée et comparée aux expériences et aux théories de Peterlin, Kirkwood et Riseman, Brinkam, et de Debye et Bueche; par là, les hypothèses fondamentales et les approximations essentielles intervenant dans ces théories sont soumises à la critique.

Zusammenfassung

Die kürzlich vom Verfasser dieser Arbeit entwickelte Theorie der Viskositätszahl wird untersucht und mit Experimenten und mit den Theorien von Peterlin, Kirkwood und Riseman, Brinkman sowie Debye und Bueche verglichen. Dabei wurden die grundlegenden Annahmen und wesentlichen Vereinfachungen in den Theorien kritisiert.

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Copolymerization of *trans*-2,6-Diazidohexaphenylcyclophosphonitrile Tetramer with 1,4-Bis(diphenylphosphino)butane or 4,4′-Bis(diphenylphosphino)biphenyl

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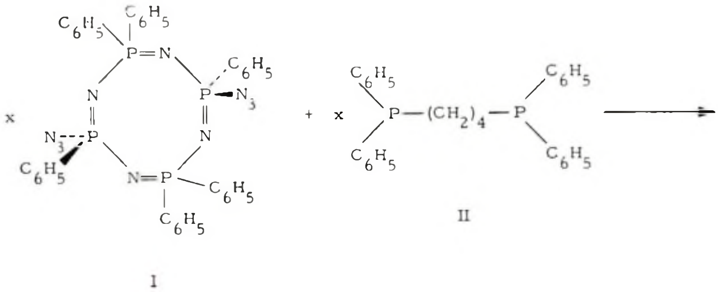
Synopsis

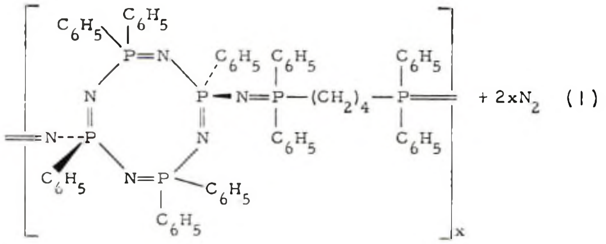
Polymers $[N(PN)_4(C_6H_5)_6N{=}P(C_6H_5)_2(CH_2)_4P(C_6H_5)_2]_x$ and $[N(PN)_4(C_6H_5)_6N{=}P(C_6H_5)_2C_6H_4C_6H_4P(C_6H_5)_2]_x$ have been formed by thermal copolymerization of *trans*-2,6-diazidohexaphenylcyclophosphonitrile $[N_3(PN)_4(C_6H_5)_6N_3]$ with either 1,4-bis(diphenylphosphino)butane $[(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2]$ or 4,4′-bis(diphenylphosphino)biphenyl $[(C_6H_5)_2C_6H_4C_6H_4P(C_6H_5)_2]$. The maximum molecular weights obtained were about 10,000. A polymer endcapped with triphenyl phosphine was stable to 400°C.

INTRODUCTION

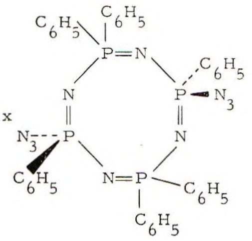
The reaction of triphenylphosphine with phenylazide to form $(C_6H_5)_3P{=}N{-}C_6H_5$ was reported by Staudinger and Hauser.[1]

This basic reaction was utilized by Herring[2] to form polymeric material from 1,4-bis(diphenylphosphino)benzene and 1,4-diazidobenzene. We prepared *trans*-2,6-diazidohexaphenylcyclophosphonitrile tetramer (I) and studied its properties, thermal decomposition, and reactions with arylphosphines.[3] In this paper we report the polymerization of (I) with 1,4-bis(diphenylphosphino)butane (II) and with 4,4′-bis(diphenylphosphino) biphenyl (IV) to give polymers III and V as shown in eqs. (1) and (2).

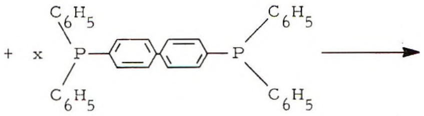




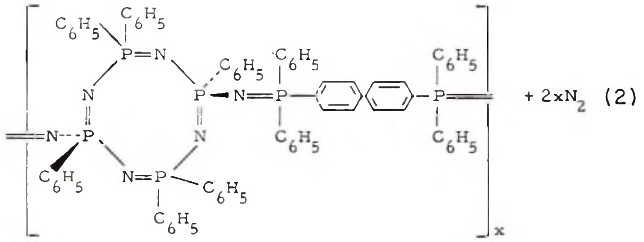
III



I



IV



V

EXPERIMENTAL

Materials

Diazide I, 2,6-diazidohexaphenylcyclophosphonitrile tetramer, was prepared by procedures described earlier[3] and recrystallized from acetonitrile; m.p. 207–208°C. (corr.). Diphosphine II, 1,4-bis(diphenylphosphinobutane, was prepared from 2 moles of lithium diphenylphosphide and 1 mole of 1,4-dibromobutane by a procedure similar to that reported by Aguiar et al.[4] Diphosphine II was purified by repeated crystallizations from the mixed solvent system tetrahydrofuran–methanol; m.p. 134.5–135.0°C. (corr.). Diphosphine II was prepared previously by reduction of tetramethylenebis(triphenylphosphonium)dibromide with lithium aluminum hydride; reported m.p. 135–136°C.[5] Diphosphine IV, 4,4′-bis-(diphenylphosphino)biphenyl was prepared from one mole 4,4′-dilithiobiphenyl and two moles of chlorodiphenylphosphine by a procedure furnished by Baldwin;[6] IV was recrystallized from tetrahydrofuran–methanol solvent; m.p. 191.4–191.7°C. (sealed capillary, corr.).

Solvents used in the work were the best commercial grades available, and were distilled under vacuum before use in polymerization.

Apparatus

Polymerizations were carried out in standard glassware on a standard vacuum line.

Procedure

Equimolar weights of diazide I and either the diphosphine II or IV were placed in a flask on the vacuum line. Appropriate solvent was added either directly and the system degassed, or added by vacuum line transfer bulb-to-bulb distillation. The polymerization reaction system was heated to the appropriate temperature and nitrogen evolution observed by the manometric technique appropriate to the solvent in use.

Details of preparation of polymers III and V are given in Tables I and II.

Thermal gravimetric analyses were carried out with a Stanton Model H. T. thermal balance. The thermal differential analysis was carried out with a Du Pont 900 DTA.

RESULTS AND DISCUSSION

Polymers III and V were obtained according to eqs. (1) and (2). Polymerizations could be achieved in aromatic solvents in the temperature range 130–160°C. Some decomposition of diazide I occurred at this temperature, as shown by discoloration of the polymer. From rate constants and activation energies of the first-order decomposition of diazide I reported earlier,[3] it is expected that decomposition will be significant enough at 150°C. to limit the polymerization reaction.

The white polymers III and V were formed in dibutyl phthalate solvent at 100–110°C. Alkyl esters such as butylacetate did not lead to polymers at the temperature of refluxing.

Polymer molecular weights were disappointing. Molecular weights at best were in the range 9000–10,000. Polymers were brittle and did not draw nicely into fibers when melted.

At higher temperatures (> 140°C) it is believed the chain length is limited by thermal decomposition of diazide I. At low temperature in dibutyl phthalate one of the limiting factors for polymerization is precipitation of the polymer from solution. A second limiting factor appears to be the second-order nature of the reaction. The importance of oxidation by oxygen to phosphine oxide linkages is not known. No phosphorus–oxygen impurity could be detected in diphosphines II and IV.

A sample of polymer V endcapped with triphenylphosphine had the thermal gravimetric analysis in helium and air as shown in Figures 1 and 2 and the differential thermal analysis as shown in Figure 3. In air and in helium the polymer did not lose weight at under 400°C.

TABLE I

Copolymerization of 1,4-Bis(diphenylphosphino)butane and *trans*-2,6-Diazidohexaphenylcyclophosphonitrile Tetramer

Run no.	1,4-Bis(diphenylphosphino)butane		2,6-Diazidohexaphenylcyclophosphonitrile tetramer		Solvent	Vol. solvent, ml.	Temp., °C.	Time, hr.	Procedure and work up	Comments[a]
	g.	mmole	g.	mmole						
1076-027	0.3407	0.7988	0.5786	0.7963	Xylene	100	Reflux	72	White residue after solvent removed and treated 150°C., 1 hr.	M.W. 2120, m.p. < 200°C.
1076-010	0.2639	0.6145	0.4429	0.6145	Dibutyl phthalate	10	132	24	Reaction 98% comp. in 3 hr. based on manometrically determined N_2; 100% in 24 hr. based on N_2	M.W. 7000, Calcd. for 1:1 copolymer $C_{64}H_{58}P_5N_6$: C, 70.06%; H, 5.33%; N, 7.66%. Found: C, 70.26%; H, 5.69%; N, 7.36%.
1076-023	0.2611	0.6122	0.4424	0.6086	Dibutyl phthalate	25	100–120	16	Precipitated polymer with heptane–benzene	M.W. 3350. Solvent in polymer as deduced from carbonyl absorption in infrared
1076-030	0.3583	0.8395	0.6100	0.8395	Dibutyl phthalate	52	110–115 160–170 185	16 4 2	Distilled solvent at 185°C. Dissolved in hot benzene and added hot hexane until 0.500 g. precipitated. Dried at 130°C./0.05 mm.	M.W. 9100; polymer slightly off-white

1076-034	0.3479	0.8149	0.5921	0.8149	Xylene	25	137	16	Removed solvent at reduced pressure. Heated at 140°C./0.1 mm. for 2 hr.	M.W. 8900 on entire 0.90 g. sample
871-068	0.5997	1.405	1.397	1.013	*o*-Dichlorobenzene	30	140 155	4 3	97% N_2 evolved in 4 hr. 99.5% in 7 hr.	Polymer light brown in color. When pyrolyzed at 280°C., remaining N_2 evolved. No addtl. decomp. until 420°C.
1025-11	0.8513	1.993	1.459	2.005	Chlorobenzene	50	132	120	72% N_2 in 2 hr., 95.8% in 6 hr., 12 mg. triphenylphosphine added after 120 hr. and heated another 24 hr. Polymer fractionated by adding heptane	Fraction 1, 1.2 g., m.p. 245–285°C., M.W. 10,000; Calcd. $C_{64}H_{58}P_6N_6$: C, 70.07%; H, 5.33%; P, 16.94%; N, 7.66%; Calcd. for $(C_6H_5)_3P$ terminated octamer of $C_{584}H_{524}P_{54}P_{44}$: C, 70.34%; H, 5.30%; P, 16.77%; N, 7.58%; Found: C, 70.68%; H, 5.31%; P, 16.7%; N, 7.87%. Fraction 2, 0.204 g., m.p. 175–200°C., M.W., 9890 and 10,000.

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[a] All molecular weights measured with a Mechrolab Osmometer, Model 301. Elemental analyses made by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

TABLE II

Copolymerization of 4,4′-Bis(diphenylphosphino)biphenyl and *trans*-2,6-Diazidohexaphenylcyclophosphonitrile Tetramer

Run no.	1,4-Bis(diphenyl phosphino)-butane g.	1,4-Bis(diphenyl phosphino)-butane mmole	2,6-Diazidohexa-phenylcyclo-phosphonitrile tetramer g.	2,6-Diazidohexa-phenylcyclo-phosphonitrile tetramer mmole	Solvent	Vol. solvent, ml.	Temp., °C.	Time, hr.	Procedure and work up	Comments
1142-025	1.5677	3.000	2.1798	3.000	Dibutyl phthalate	50	100–140	72	White residue after distillation of solvent; dissolved in hot benzene and fractionated with hot hexane	Fraction 1, M.W. 5350; 2, 4760; 3, 3350; 4, 2900. Infrared free of azide absorption.
1142-033	2.1805	4.1725	3.0317	4.1755	Dibutyl phthalate	50	100–110	72	Added addtl. diphosphine (0.20 g.) and distilled off solvent at 150–160°C. (1 mm.). Polymer purified by successively dissolving in hot benzene and precipitating with hot heptane 3 times	4.67 g. had M.W. 6500; small benzene-insoluble fraction had M.W. > 10,000 when $CHCl_3$ was solvent.
1076-040	1.0085	1.498	0.7827	1.498	Dibutyl phthalate	50	95–110	16	Add excess diazide (0.10 g.) and distilled off dibutyl phthalate rapidly at 160°C., < 1 mm. Added triphenylphosphine to endcap at 160°C.	50% of polymer estimated to have M.W. > 10,000 (very low solubility in benzene gave inaccurate M.W.)
1025-15	1.0394	1.98	1.4534	2.00	Chlorobenzene	50	132	120	Triphenylphosphine added after 120 hr. to endcap	Calcd. $C_{72}H_{58}P_6N_6$: C, 72.48%; H, 4.90%; P, 15.57%; N, 7.04%. Found: C, 72.44%; H, 4.57%; P, 15.83%; N, 7.58%. Sample not sufficiently soluble for M.W. with osmometer.

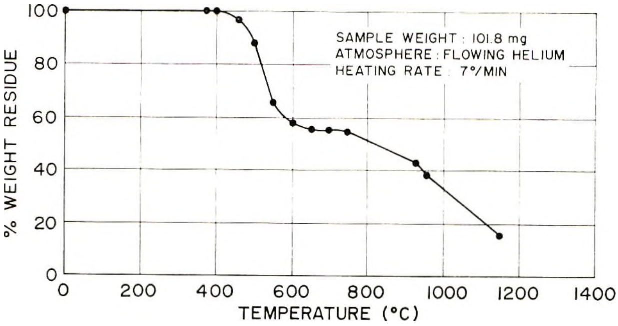

Fig. 1. Thermal gravimetric analysis of sample 1076-040 in helium.

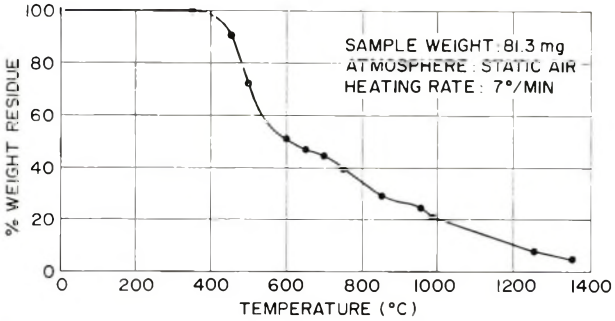

Fig. 2. Thermal gravimetric analysis of sample 1076-040 in air.

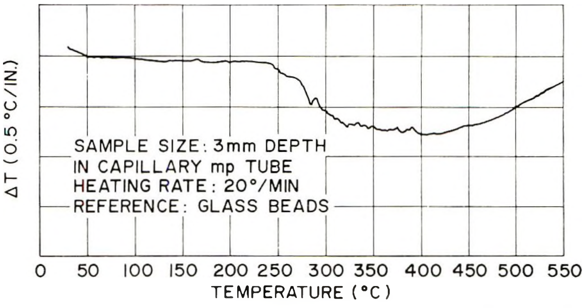

Fig. 3. Differential thermal analysis of sample 1076-040 in nitrogen.

Present work is directed to increasing the molecular weight of the polymer in a solvent that allows polymerization below 100°C. and that is significantly more volatile than dibutyl phthalate.

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Résumé

Des polymères $[N(PN)_4(C_6H_5)_6N{=}P(C_6H_5)_2(CH_2)_4P(C_6H_5)_2]_x$ et $[N(PN)_4(C_6H_5)_6N{=}P(C_6H_5)_2C_6H_4C_6H_4P(C_6H_6)_2]_x$ ont été obtenus par copolymérisation thermique du 2,6-diazidohexaphénylcyclophosphonitrile-*trans* $[N_3(PN)_4(C_6H_5)_6N_3]$ avec soit le 1,4-bis-(diphénylphosphino)butane $[(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2]$ ou le 4,4′-bis(diphénylphosphino)biphényl $[(C_6H_5)_2C_6H_4(C_6H_4P(C_6H_5)_2]$. Le poids moléculaire maximum obtenu est d'environ 10.000. Un polymère terminé avec un groupe triphénylphosphine est stable jusqu'à 400°C.

Zusammenfassung

Polymere der Formeln $[N(PN)_4(C_6H_5)_6N{=}P(C_6H_5)_2(CH_2)_4P(C_6H_5)_2]_x$ und $[N(PN)_4(C_6H_5)_6N{=}P(C_6H_5)_2C_6H_4C_6H_4P(C_6H_5)_2]_x$ wurden durch thermische Copolymerisation von *trans*-2,6-Diazidohexaphenylcyclophosphonitril $[N_3(PN)_4(C_6H_5)_6N_3]$ mit entweder 1,4-Bis(diphenylphosphino)butan $[(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2]$ oder 4,4′-Bis(diphenylphosphino)biphenyl $[(C_6H_5)_2C_6H_4C_6H_4P(C_6H_5)_2]$ hergestellt. Die höchsten erhaltenen Molekulargewichte lagen um etwa 10.000. Ein Polymeres mit Triphenylphosphin-Endgruppen war bis zu 400°C stabil.

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Homopolymers and Vinyl Chloride Copolymers of Vinyl Esters of Chlorinated Fatty Acids from *Umbelliferae* and *Limnanthes douglasii*

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Synopsis

Homopolymers and copolymers of vinyl esters of chlorinated C_{18}, C_{20}, and C_{22} fatty acids with vinyl chloride have been prepared and evaluated. The incorporation of the vinyl ester of chlorinated C_{18}, C_{20}, and C_{22} acids as comonomers with vinyl chloride produced more flexible copolymers than have other comonomers, yet none have imparted the plasticization that can be obtained by an equal amount of external plasticizer.

INTRODUCTION

In the study of internally plasticized poly(vinyl chloride), the effect of the number and location of chlorine atoms in the fatty acid portion of vinyl esters upon the plasticization efficiency has been reported.[1–3] The earlier studies involved the following vinyl esters: 9- and 12-chlorostearates, 9,10-dichlorostearate, 9,10,12,13-tetrachlorostearate, 14-chloroeicosanoate, 13,14-dichlorobehenate, and hexachlorocyclopentadiene adduct of petroselinic acid. In some cases, low brittle temperatures for the copolymer were obtained.[1]

To determine further the effect of the substituent position in the ester side chain upon the properties of the copolymer, additional chlorinated fatty acid esters have been investigated. Various homopolymers and copolymers have been prepared. Some copolymers were fractionated to gain an idea about their homogeneity as well as molecular weight distribution. All of the copolymers were evaluated for strength and low-temperature properties.

RESULTS AND DISCUSSION

Monomers

Samples of the various monomers were provided by the Oilseed Crops Laboratory of the Southern Utilization Research and Development Division of the Agricultural Research Service. A description of their composition and their abbreviations are given below. Their preparation and detailed analysis is fully described elsewhere.[4]

VLd. Vinyl esters of chlorinated C_{18} (~3%), C_{20} (~64%), and C_{22} (~31%) fatty acids with the chlorine substituted mainly in the 5,6 positions and a minor amount in 13,14 and 5,6,13,14 positions. The material was an orange-colored oil of n_D^{25} 1.4734 and boiling at 210°C./0.15 mm. and higher. The low-boiling fraction of the material had the following properties: n_D^{25} 1.4720, b.p. 210–13°C./0.15 mm., Cl, 15.59%. Infrared (no absorption at 1640–1500 cm.$^{-1}$) and NMR (no signal at 5.4 ppm) spectra indicated no internal unsaturation.

VCD. Vinyl esters of 33% of 5,6-dichlorodocosanoic acid and 67% of 13,14-dichlorodocosanoic acid. The material was a light yellow-colored oil of n_D^{25} 1.4740. Infrared and NMR spectra indicated no other unsaturation than the vinyl ester.

VCE. Vinyl esters of 96% of 5,6-dichloroeicosanoic acid and 2% of a mixture of 5,6- and 13,14-dichlorodocosanoic acids. The material was a light yellow-colored oil of n_D^{25} 1.4723. Infrared and NMR spectra indicated no internal unsaturation.

VCS. Vinyl esters of about 83% of 6,7-dichlorostearic acid and about 17% of 9,10-dichlorostearic acid. The material was an amber-colored oil of n_D^{25} 1.4682. The infrared spectrum indicated no unsaturation other than the vinyl ester and a minor amount of free hydroxyl (minor band at 3500–3300 cm.$^{-1}$ and at 1100 cm.$^{-1}$). No free carboxylic acid was indicated at 1700–1725 cm.$^{-1}$.

Homopolymerization

The four monomers were homopolymerized in an emulsion system. The experimental data are given in Table I. Early in the work it was noticed

TABLE I

Emulsion Homopolymers of Vinyl Esters of Chlorinated Fatty Acids[a]

Monomer	Amt initiator, (DEABIB[b]), phm[c]	Polymerization time, hr.	Conversion, %	η_{inh}[d]
VLd	10	50	20	0.08
VLd (distilled, low-boiling fraction)	10	48	55	0.08
VCD	10	48	55	0.15
VCE	10	48	70	0.13
VCS	7.5	48	48[e]	0.08

[a] Siponate DS-10 (alkyl-substituted benzene sodium sulfonate) used as emulsifier. All of the polymerizations were conducted at 60 ± 2°C. by tumbling the tubes end over end.

[b] Diethyl azobisisobutyrate.

[c] phm = parts per 100 parts monomer.

[d] Determined on solutions from 0.251 to 0.498 g./100 ml. of tetrahydrofuran.

[e] A small amount of gel present.

that the use of a buffered recipe increased not only the conversion but also the inherent viscosity of the homopolymers.

The buffer finally used was Beckman buffer solution, pH 7.00. The polymers were obtained as transparent light tan to dark tan-colored viscous masses. As the VCS material gave also some insoluble material, residual difunctionality is indicated. None of the homopolymers exhibited particular adhesive properties.

Since each monomer consisted of a number of related components, it was necessary to obtain analytical data on the purified homopolymers for the copolymerization work with vinyl chloride. The various homopolymers were reprecipitated in methanol from a dilute tetrahydrofuran solution until no characteristic absorptions for the monomer were shown by the infrared spectra (at 1645 cm.$^{-1}$) and then were analyzed for C, H, and Cl. The analytical data for the homopolymers and their monomers, for comparison, are given in Table II.

TABLE II
Analytical Data on Momomers and Homopolymers of Vinyl Esters of Chlorinated Fatty Acids

Material	Analyses C, %	Analyses H, %	Analyses Cl, %	Position of chlorines	Chain length of the acid
VLd					
Monomer	64.15	9.49	16.64	5,6	C_{18}, C_{20}, C_{22}
Homopolymer	64.37	9.66	17.46		
VCD					
Monomer	64.36	9.86	17.74	13,14 and 5,6	C_{22}
Homopolymer	64.10	9.46	17.39		
VCE					
Monomer	63.95	9.69	17.00	5,6	C_{20}
Homopolymer	64.68	9.71	17.52		
VCS					
Monomer	63.77	9.34	15.77	6,7 and 9,10	C_{18}
Homopolymer	64.25	9.46	15.14		

In the copolymer composition calculations, the homopolymer analytical data were used.

Copolymerization

A series of vinyl chloride copolymers with the various vinyl esters was prepared in an emulsion system. None of the recipes were buffered in this series. The experimental data are given in Table III.

Of the four monomers, the VLd and VCS possessed poorer polymerization qualities also in copolymerization with vinyl chloride. VCS gave a definite amount of insoluble copolymer. Since the soluble portion of the copolymer contained considerably less vinyl ester than charged, apparently the ester was responsible for the crosslinking reaction. Such a reaction may have resulted from some difunctional impurity in the ester or its formation during the polymerization.

All of the copolymers were isolated as white powders which were, except for the VCS copolymer, soluble in tetrahydrofuran. The materials could be molded (at about 160°C.) into transparent, tough films. The properties of the films are given in Table IV.

TABLE III

Emulsion Vinyl Chloride–Vinyl Ester of Chlorinated Fatty Acid Copolymers[a]

	Charged composition, wt.-%		Catalyst		Polymerization	Conversion,	Ester,	
Vinyl ester	VCl	Vinyl ester	Type[b]	Amt., phm	time, hr.	%	%[c]	η_{inh}[d]
VLd	90	10	DEABIB	4	45	88	9	0.66
	80	20	DEABIB	4	45	84	14	0.48
	70	30	AIBN	3	20	67	20	0.82
VCD	90	10	DEABIB	4	45	88	14	0.57
	80	20	DEABIB	4	45	80	23	0.61
	70	30	DEABIB	4	45	84	33	0.89
	60	40	DEABIB	4	45	84	42	0.75
VCE	90	10	DEABIB	5	21	96	14	0.63
	80	20	DEABIB	5	21	94	20	0.59
	70	30	AIBN	4	21	91	25	0.67
	60	40	DEABIB	5	21	84	38	0.61
VCS	90	10	DEABIB	5	21	72	7	0.58
	80	20	DEABIB	5	21	78[e]	12	0.60[f]
	70	30	DEABIB	5	21	84[e]	18	0.62[f]
	60	40	DEABIB	5	21	68[e]	21	0.52[f]

[a] Siponate DS-10 used as emulsifier. All polymerizations were conducted at 60 ± 2°C. by tumbling the tubes end over end.

[b] DEABIB = diethyl azobisisobutyrate; AIBN = azobisisobutyronitrile.

[c] By weight, based on analyses for C, H, Cl, in the copolymer (see Experimental section).

[d] Determined on solutions from 0.178 g. to 0.362 g./100 ml. of tetrahydrofuran.

[e] Includes about 24% of insoluble material.

[f] On the soluble fraction.

In general, increase in ester content to a certain level contributed to toughness of the films. However, the dependence upon molecular weight could also be noticed: copolymers with inherent viscosities below about 0.60 possessed poor strength properties. The 70/30 charged vinyl chloride–vinyl ester composition gave the toughest films. This was the composition chosen for physical and low-temperature properties evaluation.

Fractionation

Inherently, the vinyl ester has a low reactivity (Q value) in comparison to many monomers. In free-radical polymerizations with vinyl chloride, the difference in r_1r_2 values is considerable.[5,6] This being the case, the formation of a mixture of homopolymers can be expected in a great many systems. Two of the copolymers (VCl–VCD and VCl–VCE) were fractionated and analyzed for composition as well as molecular weight distribution. The VCl–VCD copolymer contained 33%, by weight, of the ester and the VCl–VCE contained 34%. The fractionations were conducted on 3.0 g. samples in 300 ml. of tetrahydrofuran. Methanol and aqueous

TABLE IV
Films of Vinyl Chloride/Vinyl Ester of Chlorinated Fatty Acid Copolymers

Vinyl ester	Composition Vinyl chloride, %	Vinyl ester, %	Properties of films
VLd	91	9	Tan, very tough
	86	14	Tan, not brittle
	80	20	Tan, very tough
VCD	86	14	Tan, tough
	77	23	Tan, very tough
	67	33	Tan, extremely tough
	58	42	Brown, tough
VCE	86	14	Tan, strong
	80	20	Tan, tough
	75	25	Tan, very tough
	62	38	Tan, very tough
VCS[a]	93	7	Tan, not brittle
	88	12	Tan, strong
	82	18	Tan, strong
	79	21	Tan, not brittle

[a] On the soluble fraction.

TABLE V
Analytical and Inherent Viscosity Data on Fractionated
VCl-VCD and VCl-VCE Copolymers

Sample	Wt., g.	Cl, %[a]	η_{inh}
VCl/VCD			
Entire sample	3.00	44.02	0.89
Fraction 1	0.60	41.19	2.33
Fraction 2	0.75	41.34	0.77
Fraction 3	0.85	45.38	0.46
Fraction 4	0.68	45.32	0.20
Recovered	2.88 (96%)		
VCl/VCE			
Entire sample	3.00	43.26	0.62
Fraction 1	0.65	41.15	2.56
Fraction 2	0.45	40.92	0.95
Fraction 3	0.70	42.98	0.48
Fraction 4	1.05	44.90	0.24
Recovered	2.85 (95%)		

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

hydrochloric acid were used as the nonsolvents. The analytical and inherent viscosity data are given in Table V.

Apparently, in both materials no significant amount of homopolymer formation of either kind had occurred as indicated by the analytical data. Considering both the analytical data and inherent viscosity data, i.e., a 4% variation in chlorine content and a tenfold variation in inherent viscosity between the first and last fractions, indicates a rather uniform comonomer distribution. The two vinyl esters were not very effective molecular weight modifiers, as the fatty acid-rich fractions had the very high inherent viscosities of 2.3 and 2.6. An interesting feature in these copolymerizations is the very wide average molecular weight distribution: from η_{inh} 0.2 to 2.61. These polymers should possess easy processing qualities because of their wide molecular weight distribution.

Evaluation

The following formulation was used in evaluating all the 70/30 (vinyl chloride–vinyl chloro-fatty acid ester) copolymers: copolymer 100 parts, stearic acid 0.5 parts, tin mercaptide stabilizer (Advastab T-360) 4 parts. These copolymers except for the insoluble fraction of the VCl–VCS copolymer could be readily milled and molded at 212–230°F. The insoluble fraction of the VCl–VCS copolymer required a somewhat higher temperature of 230°F. The milled sheets were, with one exception, light tan-colored sheets; that from the soluble fraction of the VCl–VCS copolymer was dark tan in color. Both the VCl–VCS milled sheet and that from the VCl–VCE copolymers were very brittle at room temperature. The sheeted insoluble fraction of the VCl–VCS copolymer was, on the other hand, not brittle, and it along with the VCl–VCD copolymer sheet were by far the most flexible of all the copolymer compositions and were the only ones from which test specimens could be die-cut without fracture at room temperature. Test specimens could not be die-cut from the other compositions at room temperature without inducing some fracturing in both specimen and sheet, and cutting at more elevated temperatures (70°C.) did not appear feasible because it introduced a dimensional stability problem. Dumbell test specimens, except in the case of the insoluble fraction of the VCl–VCS copolymer, were therefore die-cut from sheets 0.034 in. thick cast from tetrahydrofuran solutions of the respective copolymers, while they were still plasticized with residual solvent to facilitate cutting and to minimize imperfections in the specimen. They, as well as the remaining uncut portion of the cast sheets, were heated for 24 hr. in a 70°C. forced draft oven to remove residual solvents. The desolventized cast sheets of both the VCl–VCE copolymer and the soluble fraction of the VCl–VCS copolymer were just as brittle as the milled sheets of these copolymers.

Tensile strength, yield point, elastic modulus under tension, and elongation were determined in accordance with ASTM method D 638-64T. The stressing rate used was 0.2 in./min. for a gage length of 2 in. The T_f

TABLE VI
Comparison of Some Physical Characteristics of Experimental Copolymers with Those of a Plasticized and Nonplasticized Vinyl Chloride–Vinyl Acetate Copolymer

Physical property	Copolymer						
				VCl–VCS			
	VCl–VCE	VCl–VCD	VCl–VLd	Soluble fraction	Insoluble fraction	VCl–VA (66.3/33.7)[a]	VCl–VA (95/5) + 25% DOP[a]
Elastic modulus, psi (tension)	32,300	13,300	46,100	24,700	16,900	420,000	
100% Modulus, psi (tension)							3,120
Yield point, psi	920						
Tensile strength, psi	1,760	1,880	1,760	550	1,960	7,900	3,720
Elongation, %	130	200	100	1	120		210
T_f, °C.	11	8	13	[b]	12	40	1
T_4, °C.	25	27	30		29		
Milling temp., °F.	212–220	212–220	212–220	212–220	230	300	230

[a] Data of Port et al.[7]

[b] All test samples fractured in test $T_f > 25$°C.

and T_4 torsional stiffness were determined in accordance with ASTM method D 1043-61T.

The physical characteristics for each of these test compositions are given in Table VI. For comparative purposes Table VI also includes data from the literature for a 66.3/33.7 vinyl chloride–vinyl acetate copolymer (VCl–VA) and for an externally plasticized 95/5 vinyl chloride–vinyl acetate copolymer (with 25% di-2-ethylhexyl phthalate).

The experimental copolymers, with the exception of the soluble VCl–VCS copolymer fraction, exhibited torsional stiffness, T_f and T_4 values, well below that of the 66.3/33.7 VCl–VA copolymer, which is indicative of some measure of internal plasticization by the vinyl ester of the respective chlorinated fatty acid moieties.

The extremely brittle and almost friable character of the soluble VCl–VCS copolymer fraction precluded torsional stiffness measurements. Fracture occurred in every test specimen of this composition when torque was applied at environmental temperatures over the range of −10 to +25°C. The superior performance characteristics of the insoluble fraction of this copolymer, particularly in the areas of flexibility and torsional stiffness, are consistent with the reputedly higher level of fatty acid-derived monomer incorporated in the fraction but are, on the other hand, somewhat at odds with the solubility data-drawn concept of a crosslinked polymer. Performance and solubility characteristics in this instance seem far more consistent with a simple concept of a higher average molecular weight for the fraction.

None of the chlorinated fatty acid vinyl ester comonomer moieties impart sufficient plasticization, certainly not to any extent approaching that attainable with an equal amount of external plasticizer. Although none of these comonomers are outstanding internal plasticizers the data does show that the VCD and VCS comonomers produce more flexible copolymers and are to be preferred over the others including the previously reported[3] vinyl ester of the hexachlorocyclopentadiene–petroselinic acid adduct.

EXPERIMENTAL

Homopolymerization

VCE (4.0 g.), DEABIB (0.40 g.), Siponate DS-10 (0.24 g.), air-free distilled water (6 ml.), and air-free Beckman buffer solution, pH 7.00, (6 ml.) were combined under nitrogen in a pressure tube (1 × 7 in.). The contents were emulsified at room temperature for 10 min. and polymerized at 60 ± 2°C. by tumbling end over end for 48 hr. A lumpy latex was obtained. The latex was poured into 250 ml. of methanol, allowed to stand for one day and was then filtered. The isolated material was dissolved in 52 ml. of tetrahydrofuran, filtered from the buffer salts, and reprecipitated in 250 cc. of methanol. A yield of 2.8 g. of oven-dried (55–60°C./24 hr.) light tan-colored, soft mass was obtained. The infrared spectrum showed no characteristic absorption bands at 1645 cm.$^{-1}$ for the monomer. The procedure for the other monomers (VLd, VCD, and VCS) was similar to the one described.

Copolymerization of VCl with VCD

VCD (1.5 g.), DEABIB (0.2 g.), Siponate DS-10 (0.1 g.), air-free, distilled water (20 ml.) were combined under nitrogen in a pressure tube (1 × 7 in.). The tube was then cooled to about −15°C. and VCl (3.5 g.) was added. An excess of VCl was used to purge the tube of air before capping. The contents were emulsified at room temperature for 1 hr. and then polymerized at 60 ± 2°C. by tumbling end over end for 45 hr. A latex was obtained that settled out with time. The latex was poured into 200 ml. of methanol and the precipitated material was dissolved in 100 ml. of tetrahydrofuran and reprecipitated in 400 ml. of methanol; 4.2 g. (84%) of vacuum oven-dried (58°C./22 hr.) white powder was isolated. The infrared spectrum showed no characteristic absorption bands at 1645 cm.$^{-1}$ for the monomers. The other compositions were prepared similarly to the one described.

The VCS latex was of poor quality, containing agglomerated particles of polymer. Upon purification of the copolymer, by dissolving it in tetrahydrofuran, about 24% of the total isolated material was insoluble. The insoluble portion was then filtered off and dried under the same conditions as the purified, soluble copolymers.

TABLE VII
Analytical Data for Compositions Prepared

	Composition		Calculated			Found		
Vinyl ester	Vinyl chloride, %	Vinyl ester, %	C, %	H, %	Cl, %	C, %	H,	Cl, %
VLd	91	9	40.76	5.27	53.20	40.90	5.46	53.15
	86	14	42.06	5.50	51.24	41.88	5.49	50.75
	80	20	43.62	5.80	48.88	43.65	5.76	48.66
VCD	86	14	41.92	5.47	52.23	42.07	5.70	52.15
	77	23	44.33	5.90	47.77	44.50	6.04	47.83
	67	33	46.90	6.36	43.87	47.17	6.56	44.02
	58	42	49.20	6.77	40.20	49.27	6.98	39.84
VCE	86	14	42.10	5.51	51.24	41.88	5.74	50.86
	80	20	43.70	5.84	48.87	43.53	5.87	48.90
	75	25	45.04	6.10	46.91	45.20	6.10	47.21
	62	38	48.46	6.75	41.79	48.77	6.66	42.35
VCS[a]	93	7	40.19	5.14	53.86	39.68	5.23	53.58
	88	12	41.46	5.37	51.72	41.37	5.14	52.17
	82	18	42.90	5.68	49.35	42.17	5.49	48.83
	79	21	43.75	5.77	48.13	43.80	5.57	48.05

[a] On the soluble fraction.

The analytical data for all of the compositions prepared are given in Table VII.

Fractionation of 67/33 VCl–VCD Copolymer

A 3.0 g. sample of the copolymer was dissolved in 300 ml. of tetrahydrofuran. The first fraction was obtained by adding slowly 100 ml. of methanol. An extremely fine precipitate was obtained which was allowed to stand for one day. The liquid phase was then decanted and the precipitate dried in a vacuum oven (55°C./21 hr.); 1.35 g. of dried material was isolated. The dried material was dissolved in 135 ml. of tetrahydrofuran, and 95 ml. methanol was added. The fine precipitate was allowed to stand for one day and then the liquid phase was decanted and the precipitate dried in a vacuum oven (60°C./48 hr.). Fraction 1, 0.60 g., was isolated. Fraction 2, 0.75 g., was obtained by adding 2 ml. of 17% aqueous hydrochloric acid to the decanted liquid. Fraction 3, 0.85 g., was obtained by adding slowly 90 ml. of methanol to the decanted liquid from the first precipitation. Fraction 4, 0.68 g., was obtained by adding 140 ml. of methanol and 80 ml. of water to the liquid phase from fraction 3. This produced milky suspension which was allowed to stand for one day and then 2 ml. of 9% aqueous hydrochloric acid was added to speed up the settling out. The VCl–VCE copolymer was fractionated in the same general way with similar results.

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Résumé

Homopolymères et copolymères d'ester vinylique des acides gras chlores, C_{18}, C_{20} et C_{22} ont été préparés et évaluées. L'incorporation d'ester vinylique des acides gras chlorés C_{18}, C_{20} et C_{22} comme comonomères du chlorure de vinyle produit des copolymères plus flexibles qu'avec les autres comonomères; toutefois aucun n'a causé une plastification comparable à ce qué l'on peut obtenir par incorporation de quantités équivalentes de plastifiant externe.

Zusammenfassung

Homopolymere der Vinylester chlorierter C_{18}-, C_{20}- und C_{22}-Fettsäuren und ihre Copolymeren mit Vinylchlorid wurden hergestellt und untersucht. Der Einbau der Vinylester chlorierter C_{18}-, C_{20}- und C_{22}-Säuren als Comonomere des Vinylchlorids führt zu flexibleren Copolymeren, als mit anderen Comonomeren hergestellt werden können, doch wurde durch kein Comonomeres die Plastifizierung erreicht, die man mit der gleichen Menge eines äusseren Weichmachers erhalten hann.

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Polymerization of Vinylbenzamides*

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Synopsis

In the base-catalyzed polymerization of *p*-vinylbenzamide, hydrogen-transfer polymerization occurs. The structure of the new polymer was identified. Various effects on the hydrogen-transfer polymerization of *p*-vinylbenzamide were studied. The infrared spectrum of the oligomer has characteristic absorptions of secondary amide, as well as weak absorption of the vinyl group. The oligomer also gives a hydrogen-migrated polymer with anionic catalysts. From these facts a possible polymerization mechanism was proposed. The hydrogen-transfer polymerization occurred most readily with the *p*-vinylbenzamide, next and to a small extent with the *meta*-substituted isomer, and hardly with the *o*-substituted isomer. *o*-Vinylbenzamide gives 3,4-dihydroisocarbostyril.

INTRODUCTION

Breslow and co-workers[1] have reported that hydrogen-transfer polymerization occurs to give a polymer of poly-β-alanine structure in the alkoxide-catalyzed polymerization of acrylamide.

A similar polymerization has been postulated for the anionic polymerizations of acrylamide derivatives,[2-4] ethylene sulfonamide,[1] methyl vinyl ketone,[5] acetaldehyde,[6] maleimide,[9] *p*-styrene sulfonamide,[7] and its derivatives.[8]

Very few investigations of the anionic polymerization of vinylbenzamides have been reported. Kojima et al.,[9] reported that the alkoxide polymerization of *p*-vinylbenzamide gives the hydrogen-migrated polymer, but they showed no evidence for the hydrogen-transfer polymerization. On the other hand, Imoto et al.[10] reported that no hydrogen-transfer polymerization occurs in the anionic polymerization of *p*-vinylbenzamide.

In the present work, the anionic polymerization of vinylbenzamides is systematically studied and a possible polymerization mechanism is discussed.

EXPERIMENTAL

Materials

Vinylbenzamides were prepared by treating the corresponding cyanostyrenes with hydrogen peroxide in an alkaline solution.

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TABLE I
Preparation of Vinylbenzamides

Cyanostyrene	Boiling point, °C./mm. Hg	Vinylbenzamide	Melting point, °C.	N analysis, %	
				Calcd.	Found
o-Cyanostyrene	97/7	*o*-Vinylbenzamide	154	9.52	9.84
m-Cyanostyrene	78/3	*m*-Vinylbenzamide	133	9.52	9.38
p-Cyanostyrene	67/2	*p*-Vinylbenzamide	169	9.52	9.42

Crude products were purified by recrystallization three times. The melting points, yields, and the analytical data are shown in Table I.

p-Toluamide was prepared by the method of Noller;[11] m.p. 160°C. (lit.[11] m.p., 160.5°C.).

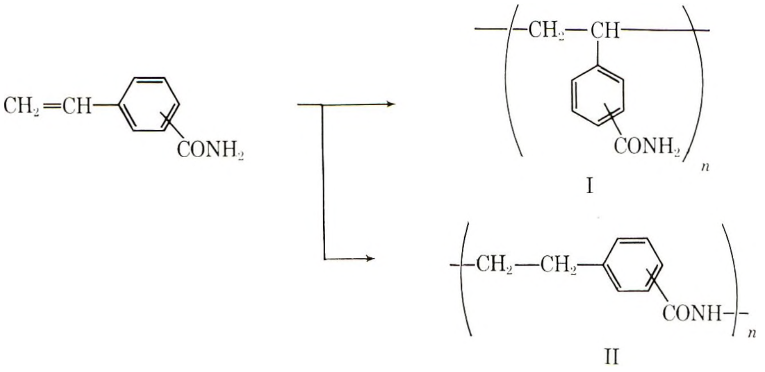
N-Methyl-*p*-toluamide was prepared from *p*-toluic chloride and methylamine according to the method of Wilds;[12] m.p. 145–146°C. (lit.[12] m.p., 146°C.).

Polymerization

Solution polymerization was carried out in a glass ampule with potassium *tert*-butoxide as catalyst. Phenyl-β-naphthylamine was added to inhibit the radical propagation. After the polymerization, the polymer was precipitated with methanol, filtered, and dried. The oligomer and the unreacted monomer were recovered separately from the filtrate by precipitation and extraction.

RESULTS AND DISCUSSION

Two types of propagation are possible in the polymerization of vinylbenzamides,



that is, conventional vinyl polymerization yielding (I) and hydrogen-transfer polymerization, giving a polyamide (II) with a secondary amide linkage in the main chain.

p-Vinylbenzamide

The polymer obtained with potassium *tert*-butoxide as catalyst in dimethylformamide is different from the polymer prepared with benzoyl peroxide. The radical-initiated polymer is completely soluble in dimethylformamide, while the polymer prepared with the use of potassium *tert*-butoxide is insoluble in dimethylformamide. The infrared absorption spectra of the two polymers are quite different.

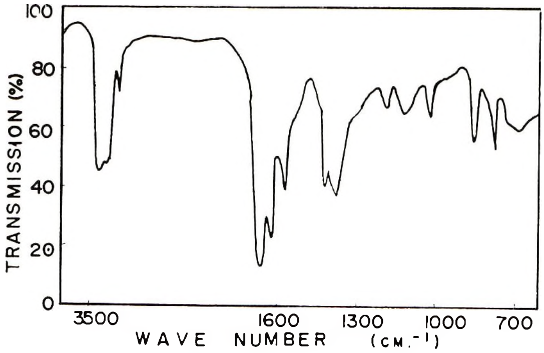


Fig. 1. Infrared spectrum of the polymer prepared with benzoyl peroxide.

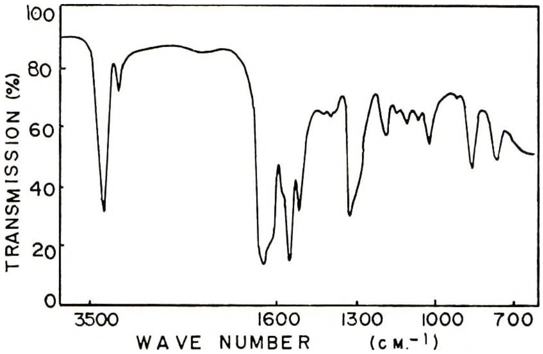


Fig. 2. Infrared spectrum of the polymer prepared with potassium *tert*-butoxide.

As shown in Figure 1, in the infrared absorption spectrum of the polymer prepared with benzoyl peroxide, the amide absorptions appear at 1650 cm.$^{-1}$, and two bands are distinct at 3350 and 3150 cm.$^{-1}$, assigned to the N—H stretching vibration, which are characteristic of a primary amide.

The polymer prepared with potassium *tert*-butoxide, however, has the amide absorptions at 1640, 1540, and 1300 cm.$^{-1}$ and one N—H absorption at 3250 cm.$^{-1}$ which are characteristic of a secondary amide (Fig. 2). Moreover, the alkoxide-catalyzed polymer has bands at 2925 and 760 cm.$^{-1}$ assigned to the $-(-CH_2)_2-$ group.

These results show that *p*-vinylbenzamide gives the polymer of type I by use of benzoyl peroxide catalyst and polyamide II by use of an alkoxide catalyst.

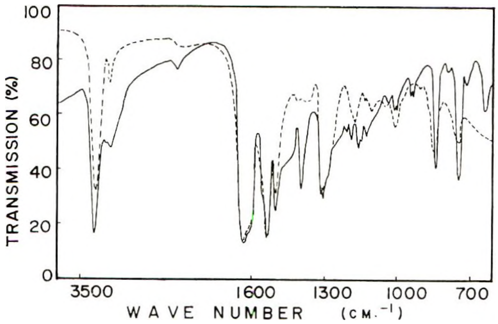


Fig. 3. Infrared spectra of (——) N-methyl-*p*-toluamide and (- - -) the polymer prepared with *tert*-BuOK.

The polyamide structure (II) is supported by the fact that the infrared spectrum of the polyamide is very similar to that of *N*-methyl-*p*-toluamide, has an authentic polyamide unit structure (Fig. 3).

The polymer obtained with potassium *tert*-butoxide catalyst was treated with dimethylformamide at 100°C., but essentially no soluble fraction was extracted. Since the vinyl type polymer is completely soluble in dimethylformamide the polymer prepared with the use of the alkoxide catalyst does not seem to contain a polymer having vinyl-type structure.

Various factors effecting the polymerization of *p*-vinylbenzamide were studied.

Effect of Monomer Concentration. *p*-Vinylbenzamide and potassium *tert*-butoxide were dissolved in dimethylformamide, and the solution was heated at 150°C. for 19 hr. The yield of the polymer was the highest at a monomer concentration of 0.033 g./ml. and decreases with increasing monomer concentration as shown in Figure 4.

At monomer concentrations higher than 0.16 g./ml., the vinyl-type polymerization predominates (Table II).

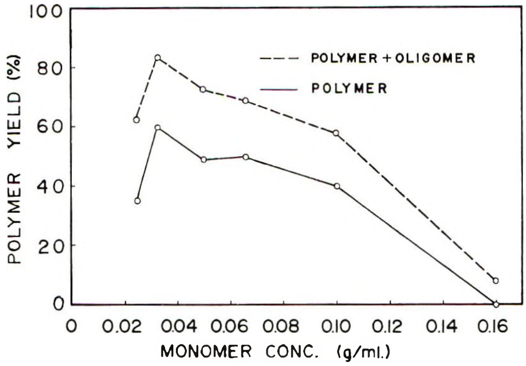


Fig. 4. Effect of monomer concentration on yield of (——) polymer and (- - -) polymer and oligomer. Catalyst, *tert*-BuOK, 7.85 mole-%; solvent, dimethylformamide; polymerization temperature, 150°C.; polymerization time, 19 hr.

TABLE II
Effect of Monomer Concentration in
Hydrogen-Transfer Polymerization of *p*-Vinylbenzamide[a]

Monomer concn., g./ml.	Catalyst concn., mole-%	Polymerization		Hydrogen migrated		Polymer
		Time, hr.	Temp., °C.	Polymer yield, %	Oligomer yield, %	η_{inh}[b]
0.160	7.85	25	150	0	7.8	
0.100	7.85	19	150	39.7	18.1	0.15
0.066	7.85	19	150	49.7	18.8	0.17
0.050	7.85	25	150	48.8	23.5	0.20
0.033	7.85	19	150	59.7	23.6	0.11
0.025	7.85	19	150	35.1	26.8	0.16

[a] Solvent, DMF, catalyst, *t*-BuOK.
[b] In *m*-cresol, $c = 0.5$ g./100 ml.

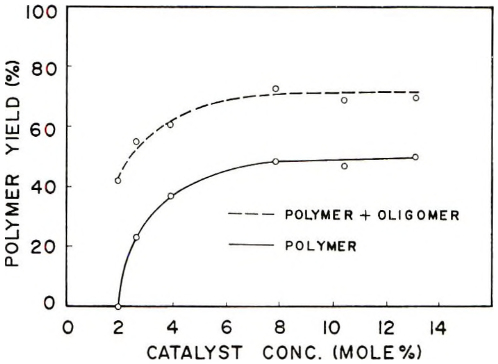


Fig. 5. Effect of catalyst concentration on yield of (—) polymer and (- - -) polymer and oligomer. Catalyst, *tert*-BuOK; monomer concentration, 0.05 g./ml.; solvent, dimethylformamide; polymerization temperature 150°C.; polymerization time, 19 hr.

TABLE III
Effect of Catalyst Concentration in
Hydrogen-Transfer Polymerization of *p*-Vinylbenzamide[a]

Monomer concn., g./ml.	Catalyst concn., mole-%	Polymerization		Hydrogen migrated		Polymer
		Time, hr.	Temp., °C.	Polymer yield, %	Oligomer yield, %	η_{inh}[b]
0.05	1.97	30	150	0	42.0	
0.05	2.62	19	150	23.8	31.5	0.09
0.05	3.92	19	150	37.1	23.0	0.13
0.05	7.85	25	150	48.8	23.5	0.20
0.05	10.45	19	150	47.0	21.3	0.18
0.05	13.10	19	150	50.0	19.4	0.15

[a] Solvent, DMF; catalyst, *tert*-BuOK.
[b] In *m*-cresol, $c = 0.5$ g./100 ml.

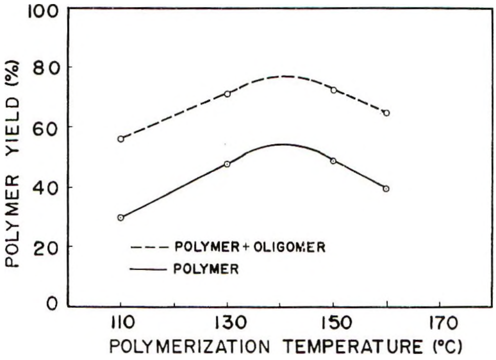


Fig. 6. Effect of polymerization temperature on yield of (——) polymer and (- - -) polymer and oligomer. Catalyst, *tert*-BuOK, 7.85 mole-%; monomer concentration, 0.05 g./ml.; solvent, dimethylformamide; polymerization time, 19 hr.

Effect of Catalyst Concentration. As shown in Figure 5, the polymer yield increases with increasing catalyst concentration until it reaches 8 mole-%. There is polymerization at catalyst concentrations less than 2 mole-% (Table III).

Effect of Polymerization Temperature. The optimum temperature range for the polymerization is between 130 and 150°C., as shown in Figure 6 and Table IV.

TABLE IV
Effect of Polymerization Temperature in Hydrogen-Transfer Polymerization of *p*-Vinylbenzamide[a]

Monomer concn., g./ml.	Catalyst concn., mole-%	Polymerization Time, hr.	Polymerization Temp., °C.	Hydrogen migrated Polymer yield, %	Hydrogen migrated Oligomer yield, %	Polymer η_{inh}[b]
0.05	7.85	19	110	30.0	26.3	0.07
0.05	7.85	19	130	47.9	23.0	0.17
0.05	7.85	25	150	48.9	23.5	0.20
0.05	7.85	19	160	39.5	25.0	0.22

[a] Solvent, DMF; catalyst, *tert*-BuOK.
[b] In *m*-cresol, $c = 0.5$ g./100 ml.

Rate of Polymerization. The rate of polymerization was determined in dimethylformamide at a monomer concentration of 0.05 g./ml. in the presence of 7.85 mole-% of potassium *tert*-butoxide (Fig. 7 and Table V).

Effect of Solvent. The effect of solvent on the polymerization was studied; the results are listed in Table VI. Dimethylformamide and dimethyl sulfoxide are the most effective solvents; in pyridine, dioxane, chlorobenzene, and *m*-cresol, no polymerization occurs.

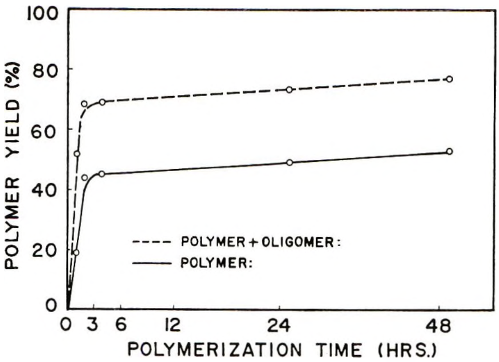


Fig. 7. Rate of polymerization vs. yield of (——) polymer and (- - -) polymer and oligomer. Catalyst, *tert*-BuOK, 7.85 mole-%; monomer concentration 0.05 g./ml.; solvent, dimethylformamide; polymerization temperature, 150°C.

TABLE V
Effect of Polymerization Time in Hydrogen-Transfer Polymerization of *p*-Vinylbenzamide[a]

Monomer concn., g./ml.	Catalyst concn., mole-%	Polymerization Time, hr.	Polymerization Temp., °C.	Hydrogen migrated Polymer yield, %	Hydrogen migrated Oligomer yield, %	Polymer η_{inh}[b]
0.05	7.85	1	150	18.8	33.0	0.07
0.05	7.85	2	150	44.1	24.2	0.14
0.05	7.85	4	150	44.5	23.9	0.14
0.05	7.85	25	150	48.9	23.5	0.20
0.05	7.85	43	150	52.5	24.4	0.17

[a] Solvent, dimethylformamide; catalyst, *tert*-BuOK.
[b] In *m*-cresol, $c = 0.5$ g./100 ml.

TABLE VI
Effect of Solvent on Hydrogen-Transfer Polymerization of *p*-Vinylbenzamide[a]

Monomer concn., g./ml.	Catalyst concn., mole-%	Solvent	Polymerization time, hr.	Hydrogen migrated Polymer yield, %	Hydrogen migrated Oligomer yield, %	Polymer η_{inh}[b]
0.05	7.85	DMF	25	48.8	23.5	0.20
0.05	7.85	Pyridine	19	—	—	—
0.05	7.85	Chlorobenzene	19	Trace	—	—
0.05	7.85	*m*-Cresol	19	—	—	—
0.05	7.85	DMAc	19	6.5	32.5	—
0.05		DMSO	19	44.0	11.5	0.15

[a] Polymerization temp., 150°C.; catalyst, *tert*-BuOK.
[b] In *m*-cresol, $c = 0.5$ g./100 ml.

TABLE VII
Effect of Catalyst on Hydrogen-Transfer Polymerization of *p*-Vinylbenzamide[a]

Monomer concn., g./ml.	Catalyst concn., °C.	Catalyst	Polymerization time, hr.	Hydrogen migrated Polymer yield, %	Hydrogen migrated Oligomer yield, %	Polymer η_{inh}[b]
0.05	7.85	*tert*-BuOK	25	49.8	23.5	0.20
0.05	7.80	*tert*-BuONa	19	14.1	21.7	0.19
0.05	—	K	19	50.0	20.3	0.17
0.05	—	Na	19	13.2	19.7	0.18
0.05	—	Li	19	Trace	Trace	—

[a] Polymerization temp., 150°C.; solvent, DMF.
[b] In *m*-cresol, $c = 0.5$ g./100 ml.

Effect of Catalyst. The catalytic activities of alkali metals and alkali metal *tert*-butoxides were investigated in dimethylformamide at a monomer concentration of 0.05 g./ml. The catalytic activity increases in the order Li < Na < K. (Table VII).

Properties of the Polymer. The hydrogen-migrated polymer of *p*-vinylbenzamide has a high melting point (>340°C.). The solubility of the polymer is very poor in usual organic solvents: slightly soluble in *m*-cresol and insoluble in dimethylformamide, chloroform, dioxane, pyridine, methanol, ethanol, dimethyl sulfoxide, dimethylacetamide, acetone.

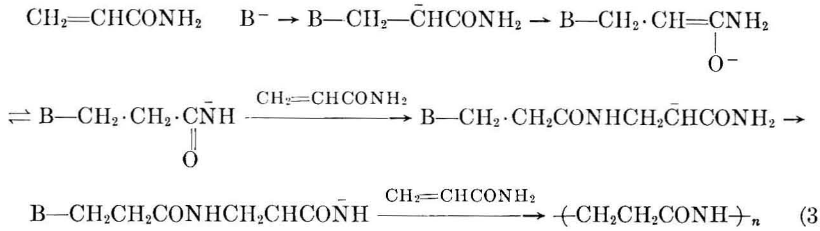
Mechanism of Polymerization. Two different mechanisms are proposed for the sodium alkoxide-initiated polymerization of acrylamide.

Breslow et al.[1] obtained a dimer containing a vinyl group and concluded that acrylamide reacts first with the alkoxide to give an *N*-alkali metal acrylamide and that the growth to a polymer occurs at the amide part of the molecule, according to the reaction scheme represented by eqs. (1) and (2).

$$\mathrm{CH_2{=}CHCONH_2 + B^- \rightarrow CH{=}CHCO\bar{N}H^- + BH}$$
$$\xrightarrow{\mathrm{CH_2=CHCONH_2}} \mathrm{CH_2{=}CHCONHCH_2CH\,\bar{C}ONH_2}$$
$$\xrightarrow{\mathrm{CH_2=CHCONH_2}} \mathrm{CH_2{=}CHCONHCH_2{-}CH_2{-}CONH_2 + CH_2{=}CHCO\bar{N}H} \quad (1)$$

$$\mathrm{CH_2{=}CH{(}CONHCH_2CH_2{)}_{\mathit{m}}CONH_2 + {-}{-}{-}\bar{C}HCONH_2 \rightarrow}$$
$$\mathrm{CH_2{=}CH{(}CONHCH_2CH_2{)}_{\mathit{m}}{-}CO\bar{N}H^- + {-}CH_2CONH_2}$$
$$\xrightarrow{\mathrm{CH_2=CHCONH_2}} \mathrm{CH_2{=}CH({-}CONHCH_2CH_2){-}CONHCH_2\bar{C}HCONH_2}$$
$$\xrightarrow{\mathrm{CH_2=CHCONH_2}} \mathrm{{(}CH_2CH_2CONH{)}_{\mathit{n}}} \quad (2)$$

The second mechanism was proposed by Ogata,[13] who followed the polymerization reaction by infrared spectroscopy and concluded that nucleophilic attack at the vinyl group must be the initiation step of the polymerization, as shown in scheme (3):



$$CH_2{=}CHCONH_2 \quad B^- \rightarrow B{-}CH_2{-}\overset{-}{C}HCONH_2 \rightarrow B{-}CH_2{\cdot}CH{=}\underset{\displaystyle O^-}{\underset{|}{C}}NH_2$$

$$\rightleftharpoons B{-}CH_2{\cdot}CH_2{\cdot}\underset{\displaystyle O}{\underset{\|}{C}}\overset{-}{N}H \xrightarrow{CH_2=CHCONH_2} B{-}CH_2{\cdot}CH_2CONHCH_2\overset{-}{C}HCONH_2 \rightarrow$$

$$B{-}CH_2CH_2CONHCH_2CHCO\overset{-}{N}H \xrightarrow{CH_2=CHCONH_2} {\leftarrow}CH_2CH_2CONH{\rightarrow}_n \qquad (3)$$

In the alkoxide-catalyzed polymerization of *p*-vinylbenzamide, a considerable amount of oligomer was also formed.

The infrared absorption spectrum of the oligomer has absorptions characteristic of a secondary amide at 1640, 1540, and 1300 cm.$^{-1}$, as well as weak absorptions at 990 and 915 cm.$^{-1}$ of a vinyl group and absorptions of medium intensity at 3350 and 3150 cm.$^{-1}$ ascribable to the N—H stretching vibration of a primary amide (Fig. 8).

These data seem to indicate that the polymer chain is terminated with a vinyl group at one end and with a primary amide group at the other.

The oligomer, potassium *tert*-butoxide, and phenyl-β-naphthylamine were dissolved in dimethylformamide and solution polymerization was carried out in a glass ampule as in the polymerization of *p*-vinylbenzamide.

A powdery product was obtained. Its infrared spectrum was identical with that of the polymer (Fig. 9).

This result indicates that the oligomer polymerizes with an alkoxide catalyst and gives the polyamide II.

These facts described above show that the initiation reaction of the anionic polymerization of *p*-vinylbenzamide is not nucleophilic attack at the vinyl group, but the abstraction of a proton from amide group, as proposed by Breslow et al. for the hydrogen-transfer polymerization of acrylamide. At the same time, it might be concluded from the above results that the anionic polymerization of *p*-vinylbenzamide proceeds stepwise.

The propagation mechanism of the oligomer might be assumed to follow the scheme shown in eq. (4) on p. 2920. Accordingly, as for the mechanism of the hydrogen-transfer polymerization of *p*-vinylbenzamide, the scheme shown on pp. 2921, 2922 is proposed.

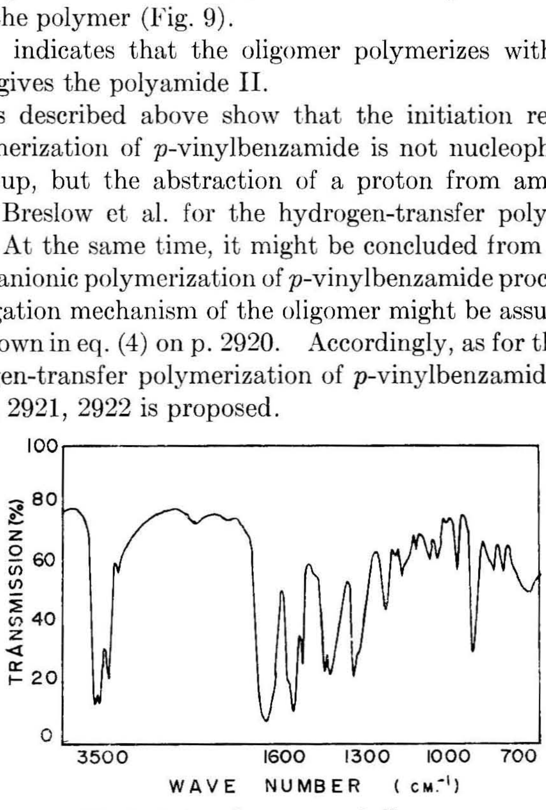
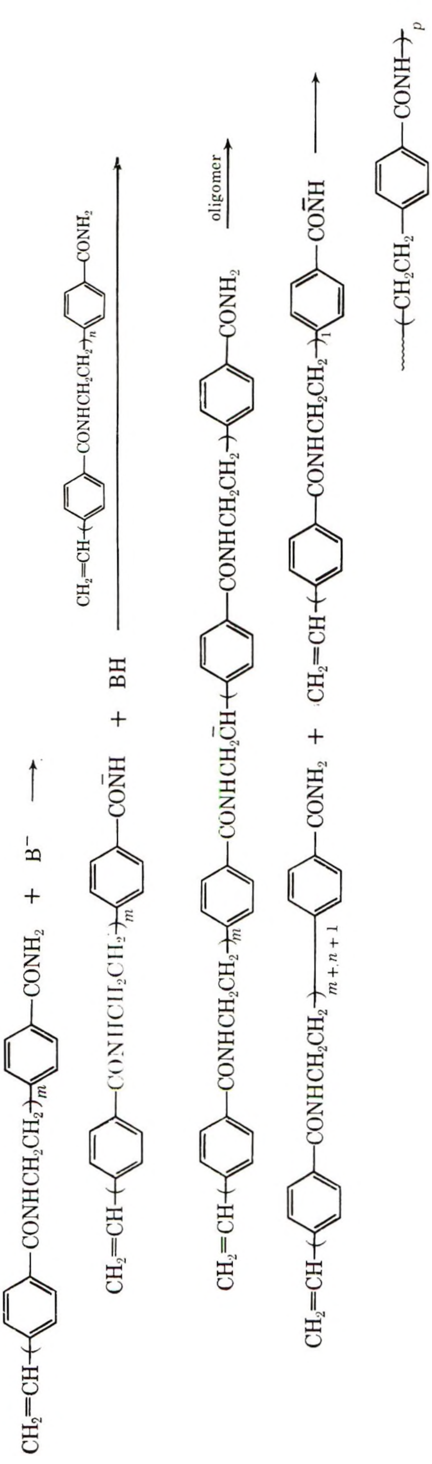


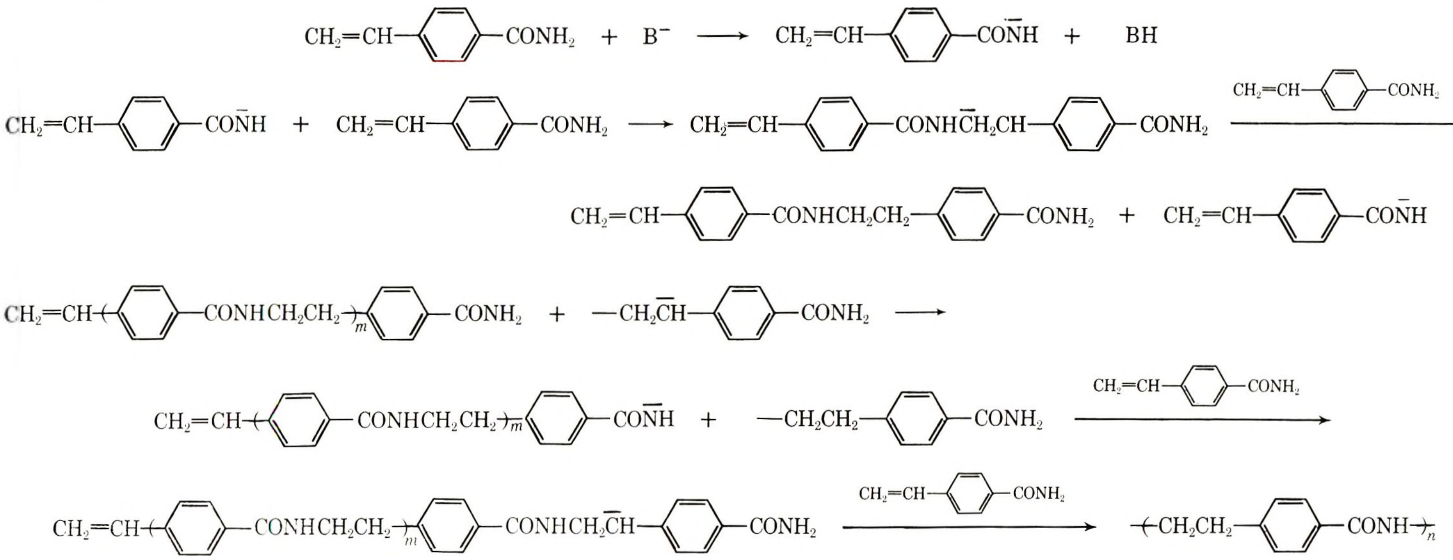
Fig. 8. Infrared spectrum of oligomer.

Initiation:



(4)

Initiation:



(5)

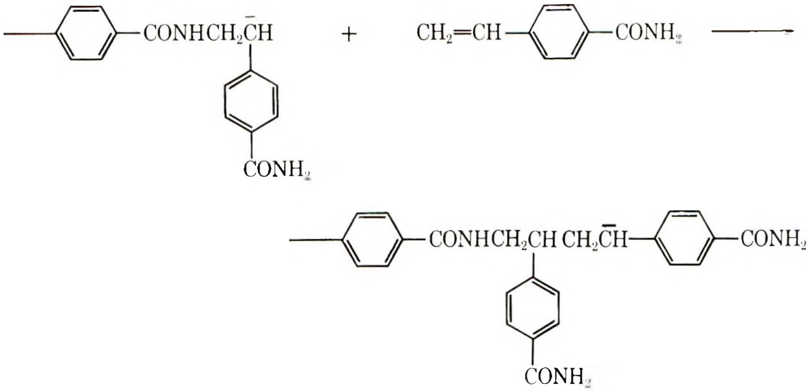
(6)

(7)

Termination:

(8)

When the infrared spectrum of the polymer was examined carefully (Fig. 10), two weak absorptions were found, one at 3350 cm.$^{-1}$ and the other at 3150 cm.$^{-1}$. They might be assigned to the N—H stretching absorptions of the primary amide. An explanation of this fact would be the vinyl-type propagation reaction which may be competitively involved in the alkoxide polymerization of *p*-vinylbenzamide. However, the primary amide absorptions are so weak that they might be assigned to the endgroups of the polymer.



(9)

A quantitative study of the polymer structure was based on the fact that a vinyl-type segment of the polymer chain should have no absorption at 1540 cm.$^{-1}$, the absorption of amide II. *N*-Methyl-*p*-toluamide and *p*-toluamide were chosen as model compounds for amide-type structure and the vinyl-type, respectively. The result shows that the content of the vinyl-type structure in the polymer chain is only 4–10%. In other

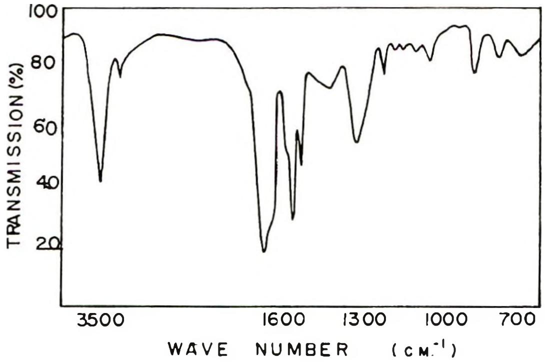


Fig. 9. Infrared spectrum of the polymer from the oligomer.

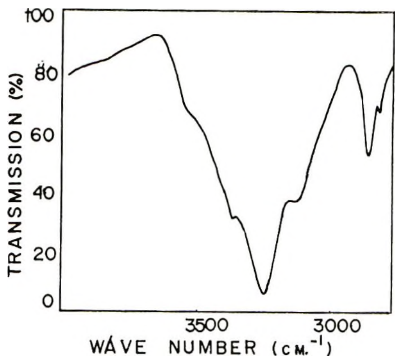


Fig. 10. Infrared spectrum of the polymer.

words, this indicates that, in the alkoxide polymerization of *p*-vinylbenzamide, the intermolecular proton transfer reaction predominates.

o-Vinylbenzamide

o-Vinylbenzamide, phenyl-β-naphthylamine, and potassium *tert*-butoxide were dissolved in dimethylformamide. The solution was heated at 150°C. for 19 hr. The reaction mixture was poured into methanol, but no precipitate was obtained. After removing the solvent, the residual viscous liquid was distilled under reduced pressure (100–105°C./1 mm. Hg). The infrared spectrum of the distillate was entirely different from that of the benzamide (Fig. 11).

Absorptions are at 3250 and 2925 cm.$^{-1}$, are assigned to the N—H and C—H (or methylene) stretching vibration, respectively.

The vinyl absorptions at 995 and 915 cm.$^{-1}$ are absent, and the C—N stretching absorption of a primary amide at 1390 cm.$^{-1}$ is very weak in the distillate. Moreover, no absorption[15] found at around 1540 cm.$^{-1}$, which is the amide II band, characteristic of a linear secondary amide, in this spectrum. Accordingly, it seems that the reaction product is neither a hydrogen-migrated polymer nor a vinyl-type polymer. However, it is

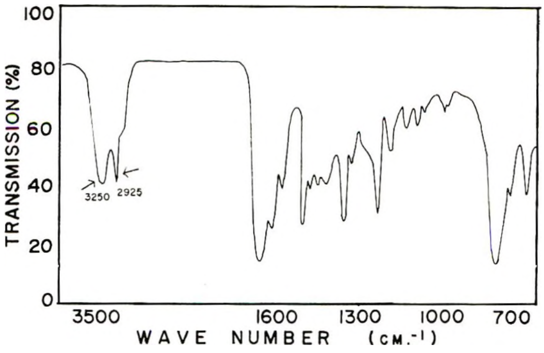


Fig. 11. Infrared spectrum of the product from *o*-vinylbenzamide.

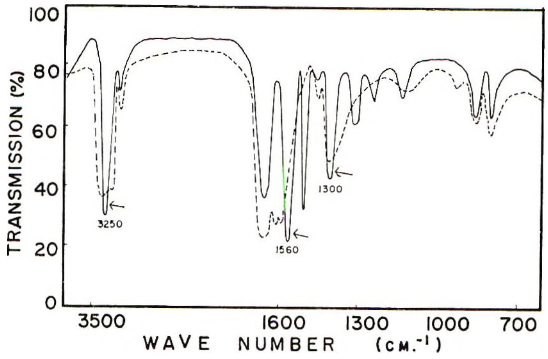
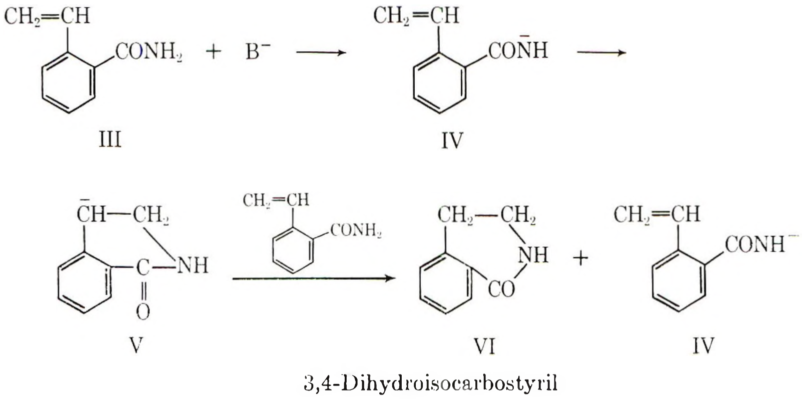


Fig. 12. Infrared spectra of the polymer of *m*-vinylbenzamide: (——) anionic catalyzed polymer; (- - -) radical-catalyzed polymer.

known that a five- or six-membered cyclic amide shows almost no amide II absorption. From the spectral data, therefore, the reaction product may be 3,4-dihydroisocarbostyril (lit. b.p. 300°C.).

A feasible mechanism for its formation is shown in eq. (10).



(10)

Anion IV, induced by the initiator, attacks at the *o*-vinyl group of the molecule to form anion V, which subsequently abstracts a proton from another vinylamide molecule to give 3,4-dihydroisocarbostyril (VI). The self-attacking of anion IV may be favored, because an intramolecular reaction is generally faster than an intermolecular one and the reaction produces a stable six-membered ring structure.

m-Vinylbenzamide

As shown in Figure 12, the infrared absorption spectrum indicates that the anionic polymerization of *m*-vinylbenzamide gives a polyamide as in the case of the *para*isomer.

However, the polymer yield is very low, and a large amount of the unreacted monomer is recovered (Table VIII).

TABLE VIII
Anionic Polymerization of *m*-Vinylbenzamide

Catalyst	Solvent	Polymerization Temp., °C.	Time, hr.	Hydrogen migrated Polymer yield, %	Oligomer yield, %	Unreacted monomer, %
tert-BuOK	DMF	150	19	Trace	Trace	78
K	DMF	150	19	Trace	Trace	63

The results show that the *m*-vinyl amide is rather inert to the anionic catalyst, which is explained in the following way. In the initiation reaction the abstraction of proton from the amide group may be easier with the decreasing electron density at amide group. The electron density of the amide group of *m*-vinylbenzamide is expected to be higher than that of the *para*isomer, due to the more efficient inductive effect of *m*-vinyl group. Therefore, the reactivity of the *meta* isomer may be poor.

Moreover, in the propagation, the addition of the amide anion to the vinyl group may be more difficult as a result of the inductive effect of the *meta* amide group.

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Résumé

La polymérisation catalysée par les bases du *para*-vinylbenzamide entraîne un transfert d'hydrogène en cours de réaction. La structure du nouveau polymère a été identifiée. L'effet de divers facteurs sur la polymérisation par transfert d'hydrogène du *p*-vinylbenzamide a été étudié. Les spectres infrarouges de l'oligomère présentent les absorptions caractéristques d'une amide secondaire ainsi que les absorptions faibles du groupe vinylique. L'oligomère fournit aussi le polymère par migration d'hydrogène en présence d'un catalyseur anionique. Au départ de ces faits, un mécanisme de polymérisation possible a été proposé. La polymérisation par transfert d'hydrogène se produit le plus facilement avec le *p*-vinylbenzamide, ensuite mais à un degré moindre, avec l'isomère *m*-substitué et difficilement avec l'isomère-*o*-substitué. L'*o*-vinylbenzamide fournit le 3,4-dihydroisocarbostyrile.

Zusammenfassung

Die basenkatalysierte Polymerisation von *p*-Vinylbenzamid erfolgt in Form einer Wasserstofftransferpolymerisation. Die Struktur der neuartigen Polymeren wurde aufgeklärt. Verschiedene Einflüsse auf die Wasserstofftransferpolymerisation von *p*-Vinylbenzamid wurden untersucht. Das Infrarot-Spektrum des Oligomeren weist sowohl die charakteristischen Absorptionen eines sekundären Amins als auch schwache Absorptionen von Vinylgruppen auf. Das Oligomere ergibt mit anionischen Katalysatoren ebenfalls das Wasserstoffmigrationspolymere. Auf Grund dieser Tatsachen wurde ein möglicher Polymerisationsmechanismus vorgeschlagen. Die Wasserstofftransferpolymerisation geht am leichtesten mit *p*-Vinylbezamid, danach und in geringem Ausmass mit dem *m*-substituierten Isomeren, sowie kaum mit dem *o*-substituierten Monomeren vor sich. *o*-Vinylbenzamid liefert 3,4-Dihydroisocarbostyril.

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Organometallic Polymers. I. Synthesis of Ferrocene-Containing Poly(phosphine Oxides) and Poly(phosphine Sulfides)

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Synopsis

Poly(phosphine oxides) and poly(phosphine sulfides) of ferrocene were synthesized in the melt phase. The resulting ferrocene polymers, linked by phosphorus bridges, were thermally stable and infusible solids, of low molecular weight ($\bar{M}_n < 4000$). Phenyldichlorophosphine, phenyldichlorophosphonate, and phenylphosphonothioic dichloride were copolymerized with ferrocene in the melt phase (80–110°C.) with $ZnCl_2$ as a catalyst. As the polymerization temperature was raised, cleavage of cyclopentadiene rings from iron became more pronounced, and cyclopentane-bridged polymers of ferrocene were produced in competition with the ferrocene–phosphorus polymers. The cleavage-polymerization process became predominant at 140°C. The structures of poly(phosphine oxides) (and sulfides) of ferrocene were verified by infrared and nuclear magnetic resonance spectroscopy.

INTRODUCTION

A wide variety of ferrocene polymers have been investigated. Methylene and other alkyl and cycloalkyl-bridged polymers,[1–7] polyferrocenyl (benzborimidazolines),[8] polyferrocenylenes,[9] silicon-containing ferrocene polymers,[10–12] ferrocene-containing polyurethanes,[13] polyesters,[14] and ferrocene polymers linked through conjugated double bonds and heteroatoms[15–17] represent the diversity of ferrocene polymers recently prepared.

Not previously reported, however, is the synthesis of ferrocene polymers with the ferrocene groups linked through a phosphorus atom. Sollott and co-workers reported the synthesis of diferrocenylphenylphosphine and ferrocenyldiphenylphosphine from phenyldichlorophosphine [$C_6H_5PCl_2$] and diphenylphosphinous chloride [$(C_6H_5)_2PCl$], respectively, in the presence of aluminum chloride and ferrocene.[18,19] This Friedel-Crafts alkylation of ferrocene by phosphorus derivatives suggested that polymers of ferrocene linked through a phosphorus atom could be synthesized through similar routes. The use of the melt phase with $ZnCl_2$ catalysis was suggested by the extensive work of Neuse et al.[1–7] and by the predominance of monomeric products obtained by the aluminum chloride Friedel-Crafts reactions in solution reported by Sollott.[18–20]

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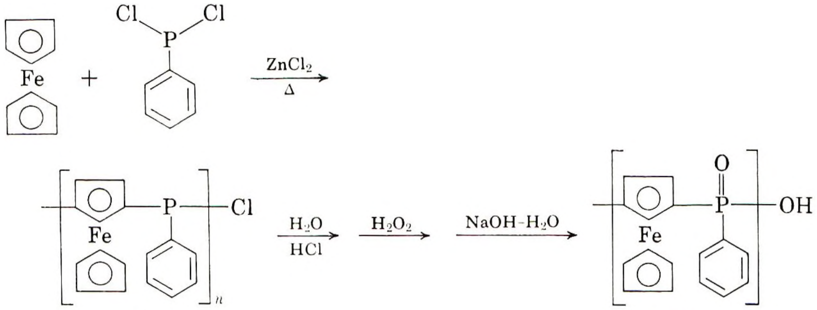
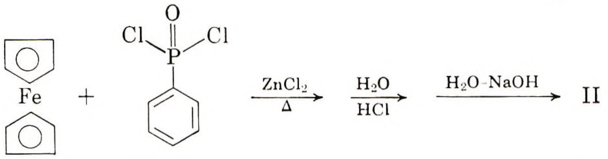
RESULTS AND DISCUSSION

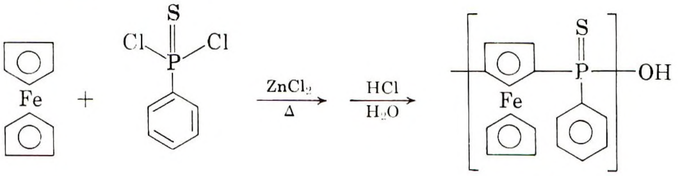
In a melt, in the presence of $ZnCl_2$, ferrocene reacted with phenyldichlorophosphine [eq. (1)], phenyldichlorophosphonate [eq. (2)], and phenylphosphonothioic dichloride [eq. (3)] to produce ferrocene phosphorus polymers I, II, and III.



I II (1)



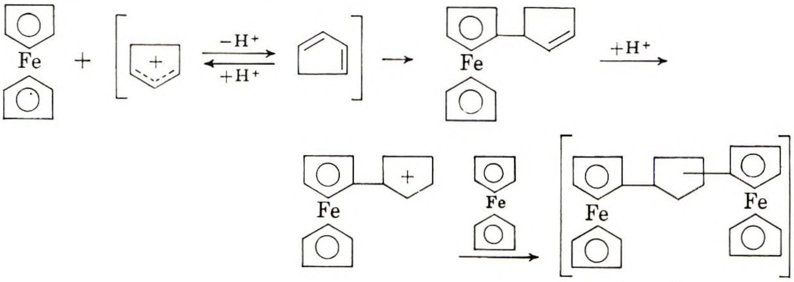
(2)



III (3)

Copolymerization of ferrocene with phenyldichlorophosphine [eq. (1)] and phenylphosphonothioic dichloride [eq. (3)] proceeded at approximately equal rates, while the polymerization with phenyldichlorophosphonate [eq. (2)] was much slower. Poly(phosphine oxides) II prepared by eq. (1) were soluble in dimethylformamide, chloroform, pyridine, dibromoethane, aniline, and dimethyl sulfoxide; however, polymers II and III, prepared according to eqs. (2) and (3), were far less soluble and were often difficult to dissolve in refluxing DMF. This lower solubility indicated a higher degree of branching in the polymer chains.

Polymerization according to eqs. (1), (2), and (3) was always accompanied by cleavage of the cyclopentadienyl ring from iron by the action of $ZnCl_2$ and HCl. (HCl is formed as a by-product during the polymerization, and the combination of Lewis acid and proton acid is known to promote cyclopentadienyl ring cleavage from iron.[7,21] The cleaved cyclopentadiene ring existed in equilibrium with its cyclopentadienyl carbonium ion, and this ion alkylated a second molecule of ferrocene to give a cyclopentene-substituted ferrocene. The cyclopentene-substituted ferrocene was then protonated and the resulting cycloalkyl carbonium ion alkylated a third molecule of ferrocene, resulting in a cycloalkyl-bridged ferrocene polymer IV [see eq. (4)].*



IV

(4)

The incorporation of cyclopentane units into the polymer was minimized at lower temperatures but became progressively more prevalent as the polymerization temperature was increased or the reaction time lengthened.

Copolymerization of Ferrocene and Phenyldichlorophosphine

Ferrocene, phenyldichlorophosphine, and $ZnCl_2$ in the mole ratios of 1.2, 1, and 0.5, respectively, were charged into a round-bottomed flask and heated in a thermostatted oil bath, and the resulting melt was vigorously stirred. As the polymerization proceeded the melt gradually became stiff. When stirring was no longer possible, sulfone solvents, such as tetramethylene sulfone (sulfolane), were added to make the melt fluid again, and the reaction was continued.† Some experiments were terminated only after the melt temperature was raised to 135–140°C. for 1 hr. and then cooled. In general, this heating resulted in higher polymer yields. In all cases, excess ferrocene was added to replace the small amounts lost from the melt by sublimation into the cooler portions of the flask. Exploratory experiments indicated yields were increased by the addition of a small excess of ferrocene. The amount of catalyst used, however, appeared to have little effect: preliminary experiments showed only slight change in polymer yield when the molar equivalent of $ZnCl_2$ was varied between 0.2 and 1 mole per mole of phosphorus derivative.

After being cooled, the resulting polymer I was analyzed before work-up. The first runs exhibited a small oxygen content indicating poly(phosphine oxide) II was produced to a slight extent during polymerization. This was prevented in subsequent runs by using a nitrogen atmosphere during polymerization. The crude polymer was suspended in a large excess of water and digested five times to remove $ZnCl_2$. This was followed by three digestions with excess 10% HCl (aqueous) to hydrolyze Cl endgroups.

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*If cleavage of cyclopentadiene rings had led to acyclic, ring-opened carbonium ions, these would have undergone rapid rearrangement to highly branched tertiary carbonium ions which on alkylation of the ferrocene ring would have left methyl groups in the bridges. Both NMR and infrared data rule out this behavior.

†The use of tetramethylene sulfone as an inert solvent in Friedel-Crafts reactions and its advantages and purification have been discussed by Olah et al.[22,23]

TABLE I
Poly(phosphine Oxides) (or Sulfides) of Ferrocene from the Reaction of Phosphorus Derivatives and Ferrocene in Presence of $ZnCl_2$[a]

Run	Temperature, °C.	Time, hr.	Polymer yield after work-up, %	Moles of sulfolane[b]
	Polymers of phenyldichlorophosphine and ferrocene			
1	80	30	5.1	1
2	80[c]	30	12.3	1
3	90	20	16.4	1
4	90[c]	20	19.4	1
5	100	20	18.2	1
6	100[c]	20	25.4	1
7	100[c]	20	28.1	0.5
8	105[c]	20	32.9	0.5
9	105[c]	50	35.9	0.5
10	110	10	24	0.5
11	135	20	53	0.5
	Polymers of phenyldichlorophosphonate and ferrocene			
12	80	30	2.3	0.5
13	90	60	9.3	0.5
14	100	60	11.6	0.5
15	100	80	12.9	0.5
16	100	300	18.9	0.5
17	120	30	25.5	0.5
18	130	30	33.2	0.5
19	140	30	45.8	0.5
20	160	30	61.4	0.5
	Polymers of phenylphosphonothioic dichloride and ferrocene			
21	80	20	7.3	0.5
22	80	100	13.2	0.5
23	80[c]	30	21.1	0.5
24	90	20	15.4	0.5
25	90	60	18.5	0.5
26	95	15	29.3	0.5
27	95	40	34.1	0.5
28	105	20	33.6	0.5
29	115	20	46.4	0.5
30	140	20	58	0.5

[a] All polymerizations contained a starting charge of 1.2 moles of ferrocene to 1 mole of phosphorus derivative, and 0.5 mole of $ZnCl_2$.

[b] Moles of sulfolane per mole of phosphorus derivative.

[c] After reaction proceeded to the time indicated, a 135°C. heating cycle was applied for 1–2 hr. before cooling.

Analysis of the polymers from all runs at this point indicated a large oxygen content, demonstrating conversion of polyphosphine I to poly(phosphine oxide) II by hydrolysis.* Subsequent treatment of the poly-

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*Sollott and co-workers have reported triferrocenylphosphine to be easily oxidized to triferrocenylphosphine oxide in solution.[18–20]

TABLE II
Molecular Weights and Elemental Analyses of Polymers

Run	Number-average molecular weight	P, %	Fe, %	C, %	H, %
1	1100	8.02	17.51	62.32	4.87
2	2200	8.31	16.43	62.13	4.90
3	1300	8.41	17.41	61.92	5.01
4	2300	9.21	14.26	63.21	5.43
5	1100	8.62	17.54	61.72	4.75
6	2900	9.11	15.10	62.88	5.31
9	2800	9.24	14.73	63.12	5.40
10	1300	8.50	17.59	61.23	4.81
11	3300	6.21	18.01	63.92	5.41
12	880	9.31	17.87	—	—
14	1200	9.91	17.23	65.81	5.21
16	1300	9.72	16.91	66.58	5.51
18	—	3.83	19.74	68.23	6.01
19	—	0.77	22.2	70.43	6.42
20	—	0.51	23.2	70.20	6.01
22	1700	9.38	17.31	60.60	4.22
26	—	9.31	17.15	60.83	4.31
28	2000	8.20	17.61	62.55	4.62
30	—	1.2	12.8	69.4	5.54

mer with 5% H_2O_2 in H_2O–DMF completed the oxidation of polymer I to II. The next step in the procedure consisted of extracting the crude polymer four times with excess benzene to remove unreacted ferrocene and low molecular weight compounds, and twice with aqueous NaOH to remove low molecular weight phosphinic acids. After these treatments, the polymer yield was never greater than 40%. The polymer was then reprecipitated from DMF with methanol. The yields and properties of the reprecipitated polymers obtained under varying conditions are summarized in Tables I and II (runs 1–11).

The effect of temperature on the production of poly(phosphine oxide) II by eq. (1) (Table I) was striking. The reaction was very slow below 90°C. and yielded only small amounts of polymer II. When the reaction was conducted entirely above 130°C., the polymers contained a large amount of aliphatic C—H (as analyzed by infrared and NMR), indicating that cleavage of the cyclopentadienyl ring from iron was occurring and the polymer was incorporating higher percentages of structure IV. This incorporation of repeating units of structure IV would lower the percentage of phosphorus in the polymer, and elemental analyses (Table II) clearly showed a reduced incorporation of phosphorus (only 6.21% in run 11) with higher polymerization temperatures. The increase in the percentage of iron in polymers obtained at higher temperatures also reflected the incorporation of repeating units of structure IV.

Higher polymerization temperatures, coupled with longer reaction times, also generally increased the molecular weights. For example, the molecular weight of poly(phosphine oxide) ($\overline{M}_n$ obtained on a Mechrolab vapor pressure osmometer in dibromoethane) from run 5 was 1100, but under identical conditions with an added 1-hr., 135°C. heating period the $\overline{M}_n$ increased to 2900. Finally, the runs at higher temperatures showed increasing amounts of heterobridged polymers, as deduced from the infrared spectra. This aspect is discussed more fully in succeeding sections.

Optimum yields of polymer II were obtained by eq. (1) at a melt temperature of 105°C. followed with a 1-hr., 135°C. treatment immediately before work-up. Under these conditions only a very small amount of aliphatic C—H was observed in the infrared spectra, and polymer yields of 30% were reproducibly obtained. When the melt was initially heated to 135–140°C. for 1–2 hr. and followed by 20 hr. at 105°C., incorporation of the cyclopentane-bridged structure IV into the resulting polymer was greatly increased. This behavior was expected, since earlier in the polymerization there is more unreacted ferrocene available to be cleaved by the action of HCl in the presence of $ZnCl_2$.

In several runs, fractionation of the final polymer by reprecipitation from DMF–pyridine with methanol indicated the presence of a wide range of molecular weights. Fractions obtained from the polymer in run 7 ranged in $\overline{M}_n$ from 880 to 6800.

Copolymerization of Ferrocene with Phenyldichlorophosphonate

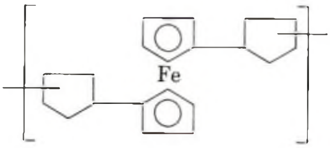
The copolymerization of ferrocene with phenyldichlorophosphonate to yield poly(phosphine oxide) II according to eq. (2) required reaction times on the order of 1 week to approach the degree of conversion obtained in 20 hr. with the method of eq. (1). The $ZnCl_2$ probably coordinates strongly with the phosphonate oxygen and is not as effective as removing chlorine (or complexing chlorine to weaken the P—Cl bond) as it is in phenyldichlorophosphine. Thus, the electrophilic phosphorus species which alkylates ferrocene is not as readily generated. Polymers from eq. (2) were insoluble in most organic solvents but could be dissolved in hot DMF. However, upon reprecipitation with methanol, the resulting polymers were very insoluble, and in cases where polymerization temperatures above 115°C. were used, the reprecipitated material was insoluble in hot DMF.

Ferrocene, phenyldichlorophosphonate, and $ZnCl_2$ were reacted, in a 1.2:1:0.5 mole ratio, as described previously for eq. (1). Results of some of these experiments are summarized in Table I (runs 12–20). On termination of heating, the crude polymer was, in turn, digested five times with excess water to remove $ZnCl_2$, digested three times with 10% aqueous HCl to hydrolyze P—Cl endgroups, washed in excess dilute NaOH to remove phosphinic acids, washed in benzene–petroleum ether to remove unreacted ferrocene and low molecular weight materials, dissolved in hot DMF, and reprecipitated with methanol.

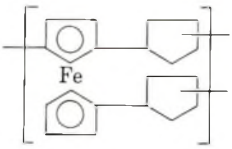
Optimum polymer yields were obtained at 100–105°C. after about

200–300 hr. Longer reaction times showed no further increase in polymer yield. Higher temperatures produced far higher polymer yields, but also resulted in cleavage of cyclopentadiene from iron and the consequent incorporation into the polymer of large amounts of repeating units of structure IV. Runs 16–20 showed a sharp drop in the percentage of phosphorus found in the polymer as structure IV became predominant. Polymerizing at 100°C. yielded a polymer II containing 9.72% P, which is close to the theoretical amount for this structure. With a polymerization temperature of 160°C., the incorporation of phosphorus dropped to 0.51%. The infrared spectra showed a corresponding increase in aliphatic C—H bands as the polymerization temperature was varied from 100 to 160°C. Because of this propensity to incorporate large amounts of cyclopentane-bridged ferrocene at higher temperatures, eq. (2) is not an attractive route to polymer II. Furthermore, higher yields of II can be obtained with shorter reaction times by eq. (1).

Heteroannular polymerization, resulting in structures represented in Va and Vb, became more prevalent with increasing temperatures and longer reaction periods. The decrease of homoannularity was followed in the infrared spectra by watching the decrease of a pair of bands at approximately 1110 and 1005 cm.$^{-1}$ which are always present in monosubstituted but not 1,1-disubstituted ferrocenes.[24,25]



Va



Vb

Quantitative estimates of the homoannularity percentage by using the 1110 and 1005 cm.$^{-1}$ bands have been made for polyferrocenylene polymers,[3] but application of this method to polymers I–Vb was not attempted because of the probable occurrence of phenyl C—H in-plane bending modes in the 1116–1120 cm.$^{-1}$ region which has already been demonstrated for ferrocenyldiphenylphosphine oxide and triphenylphosphine oxide.[18,19,26] In addition, the 1005 cm.$^{-1}$ band could be overlapped by a phenyl phosphorus absorption expected[27] to appear at 995 cm.$^{-1}$ However, as structures such as IV and V become predominant and less phosphorus is incorporated into the polymer, the 1110 and 1005 cm.$^{-1}$ absorptions can be unequivocally assigned to monosubstituted ferrocene.

Copolymerization of Ferrocene with Phenylphosphonothioic Dichloride

In the copolymerization of ferrocene with phenylphosphonothioic dichloride according to eq. (3), the procedure was the same as that used with phenyldichlorophosphonate [eq. (2)], and work-up of the polymers was identical. The results are summarized in Tables I and II (runs 21–30). Elemental analyses showed clearly that increasing the polymerization temperature to 140°C. results in polymeric material of structures IV and V. The percentage of phosphorus falls off to 1.2% in run 30. This is in accord with the large increase of aliphatic C—H stretching evident in the infrared spectra. Optimum yields of polymer III were obtained at about 110°C. and a reaction time of 30 hr. As the reaction time was lengthened, the contribution of structures such as IV became more pronounced. As in the case of the poly(phosphine oxides) (II) from eq. (2), the poly(phosphine sulfides) (III) were quite insoluble, and molecular weight measurements were difficult to perform and could not be reproduced.

Thermal Stability

The thermal stability of poly(phosphine oxide) II (run 7) and poly(phosphine sulfide) III (run 28) was measured by thermogravimetric analyses in first air and then nitrogen, at a heating rate of 5°C./min. at atmospheric pressure in an all-glass system housing a Cahn microbalance. Two fractions of II (run 7) ($\bar{M}_n$ = 1600 and 3200) showed essentially identical TGA curves. Both appeared stable in air to 285°C. and showed rapid weight loss around 440–480°C., with 20–30% residual weight remaining at 530°C. In nitrogen there was gradual weight loss, with a residual weight of about 75% at 500°C. Poly(phosphine sulfide) III was slightly less thermally stable than II in the nitrogen, exhibiting similarly shaped TGA curves with a residual weight of 60% at 500°C.

The polymer from run 19, which is largely cyclopentane-bridged polyferrocene (IV), had a rapid weight loss in air at 270°C., and only 35% residual weight remained at 350°C. Polymer from run 30 was more stable in air, and had a 35% residual weight at 460°C.

Structural Determination

NMR Spectra. The NMR spectra of poly(phosphine oxides) II and poly(phosphine sulfides) III were obtained in deuterated DMF solutions by using a Varian A60 spectrometer. All polymers exhibited aliphatic proton bands in the −2.5 to −1.3 ppm range relative to tetramethylsilane as an internal standard. These bands must be attributed to bridging cyclopentane rings; they roughly resembled the ring patterns of 1,3- and 1,2-dimethylcyclopentane, and the spectra reported for 1,1-diferrocenylcyclopentane[7] and 1,3-diferrocenylcyclopentane.[7] Additional absorption bands were found from −3.2 to −2.5 ppm, where methinyl protons were reported by Neuse.[7] No bands were observed above −1.2 ppm, which strongly indicated methyl groups were not present. These results all attest to the presence of cyclopentane bridging as represented in structures IV and V (see first footnote on p. 2929). Ferrocene ring hydrogens exhibited strong absorption bands in the −3.8 to −4.4 ppm region of the spectra, as expected, and phenyl protons were centered at −7.2 ppm.

The spectra obtained were not well resolved, and integrations provided only qualitative data. However, the spectra of the various polymers formed at temperatures from 90 to 150°C. did show a constant, and considerable, increase in cyclopentane proton absorption with each increase in temperature. This finding is in agreement with results of elemental analyses and infrared spectra—only tiny amounts of cyclopentane protons could be observed in structures II or III when polymerization was carried out at 90°C. As the cyclopentane NMR bands increased in intensity, a corresponding decrease in phenyl absorption was observed. This decrease indicated a progressively lower incorporation of the phosphorus monomer into the polymers, which was borne out by the elemental analyses. The NMR data clearly showed that increasing amounts of structures IV and V were produced as the polymerization temperature was increased.

Infrared Spectra. Infrared spectra of polymers II and III were taken in KBr pellets on a Perkin-Elmer 21 spectrometer equipped with sodium chloride optics. In both polymers, ferrocene C—H stretching bands of moderate intensity were observed at 3085 cm.$^{-1}$, and moderate phenyl C—H stretching bands at 3020 cm.$^{-1}$. The bands were not well resolved in most spectra. Phenyl C═C absorption bands were found at 1595 and 1490 cm.$^{-1}$. The 1490 cm.$^{-1}$ band could either be a phenyl C═C absorption or, as suggested previously,[18,19,27,28] a P—C band. A strong, broad band appearing at 825 cm.$^{-1}$ was assigned to ferrocene C—H out-of-plane bending mode. This band has been observed in over 40 ferrocene compounds studied in this laboratory. A weak to moderate band which appeared at 1310 cm.$^{-1}$ could be assigned to the ferrocenyl-phosphorus group, on the basis of Sollott's [18–20] assignment of this band for diferrocenylphenylphosphine oxide and triferrocenylphosphine oxide.

Polymer II exhibited a strong, broad band (in some cases two bands) from 1155 to 1190 cm.$^{-1}$ which was not present in polymer III. This absorption may be assigned to the P═O stretch. Triferrocenylphosphine oxide[18,19] and triphenylphosphine oxide[26] have bands in this region which have been assigned to the P═O stretch.

Two bands observed at 1008 and 1110 cm.$^{-1}$, respectively, for both II and III were assigned to C—H in-plane bending of a ferrocene ring and were indicative of monosubstituted ferrocene rings,[24,25] although other overlapping absorptions apparently occurred in this region. Bands at 1116–1120 cm.$^{-1}$ for similar compounds have been assigned to in-plane C—H bending modes.[18,19,26]

Both polymers II and III exhibited strong bands at 746 and 693 cm.$^{-1}$ typical of monosubstituted phenyl bands. Polymer III showed a third band in this region not observed in polymer II. This absoprtion of moderate intensity, appearing at 717 cm.$^{-1}$, was tentatively assigned to the P═S stretching vibration which is known to occur for a large number of compounds in the 750–600 cm.$^{-1}$ range.[27,29] Thomas [30] has predicted that phosphine sulfides would be observed at 770–750 cm.$^{-1}$, but both the intensity and location of the P═S stretch are found to be quite variable.[26,31] Polymers II and III exhibited broad bands centering at 3410 cm.$^{-1}$ due to the hydrogen-banded O—H stretching vibration of the O═P—OH end-groups. Thus the infrared spectra clearly indicated the presence of structures II and III, according to eqs. (2) and (3), respectively, for polymers formed at temperatures below 110°C.

It was equally clear from the spectra that increasing the polymerization temperature produced increasing proportions of structures IV and V. When polymerization temperatures of 100°C. or below were used, aliphatic C—H stretching at 2910 and 2860 cm.$^{-1}$ appeared as weak bands; however, as higher temperatures were employed these bands increased dramatically, and for runs 19, 20, 29, and 30 became, along with the 825 cm.$^{-1}$ ferrocene C—H out-of-plane bending absorption, the most intense bands in the spectra. As the aliphatic C—H stretching absorptions increased in intensity, there was a decrease in the monosubstituted phenyl bands at 746 and 693 cm.$^{-1}$ and in the phenyl C═C absorption at 1595 and 1490 cm.$^{-1}$. The P═O stretch (1155–1190 cm.$^{-1}$) also greatly decreased. The in-plane C—H bending bands at 1008 and 1110 cm.$^{-1}$ were more clearly resolved in polymers synthesized at higher temperatures, and their presence in polymers from runs 11, 18, 19, 20, 29, and 30 showed that a large amount of homoannular polymerization had occurred (structure IV). Another indication of the presence of cycloaliphatic bridges in polymers generated at high temperatures was the lack of CH_3 umbrella deformation around 1360 cm.$^{-1}$ and the strong CH_2 deformation bands at 1440–1475 cm.$^{-1}$ found in all polymers produced at temperatures of 115°C. or above.

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Résumé

Les oxydes de polyphosphine et les sulfures de polyphosphine de ferrocène ont été synthétisés à l'état fondu. Les polymères de ferrocène résultant liés par des liens phosphorés sont stables thermiquement et forment des solides infusibles de bas poids moléculaire ($\bar{M}_n$ plus bas que 4.000). La phényldichlorophosphine, le phényldichlorophosphonate et le dichlorure phénylphosphonothioique ont été copolymérisés avec le ferrocène à l'état fondu (entre 80 et 110°C), en utilisant le chloure de zinc comme catalyseur. Lorsque la température de polymérisation croît, la scission des anneaux cyclopentadiéniques et du fer devient plus prononcée et des polymères de ferrocène pontés par du cyclopentane sont produits en compétition avec des polymères phosphorés-ferrocéniques. Le processus de polymérisation par clivage devient prédominant à 140°C. Les structures des oxydes et sulfures de polyphosphine de ferrocène ont été vérifiées par spectroscopie infrarouge et spectroscopie de résonance nucléaire magnétique.

Zusammenfassung

Ferrocen-Polyphosphinoxyde und -Polyphosphinsulfide wurden in der Schmelzphase dargestellt. Die entstehenden Ferrocenpolymeren, die durch Phosphorbrücken verknüpft sind, waren thermostabile und unschmelzbare Feststoffe von niedrigem Molekulargewicht ($\bar{M}_n$ unter 4000). Unter Verwendung von $ZnCl_2$ als Katalysator wurden Phenyldichlorphosphin, Phenyldichlorphosphonat und Phenyldichlorthiophosphonat mit Ferrocen in der Schmelze (bei 80 bis 110°C) copolymerisiert. Bei Erhöhung der Polymerisationstemperatur trat die Abspaltung der Cyclopentadienylringe vom Eisen stärker hervor und es bildeten sich in Konkurrenz zu dem Ferrocen-Phosphor-Polymeren Ferrocenpolymere mit Cyclopentadienylbrücken. Bei 140°C gewann der Spaltungs-Polymerisationsprozess die Oberhand. Die Struktur der Ferrocen-Polyphosphinoxyde (und -sulfide) wurde durch Infrarot- und Kernresonanzspektroskopie bestätigt.

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NOTES

Polymerization of Maleic Anhydride by an Intense Shock Wave

The author[1] has found that maleic anhydride, which is reluctant to undergo homopolymerization,[2] polymerizes spontaneously and rapidly when it is heated to 100–170°C. at pressures above 20,000 atm. The pressures used in the experiments were approximately hydrostatic[1] and were sustained for the time needed to heat and cool the sample—usually about 1 hr. The results posed the question whether maleic anhydride might also be made to polymerize by subjecting it to transient high pressures and high temperatures, lasting only a few microseconds, in shock waves generated by explosions.

Experimental

The experiments were carried out in devices of the type described by Kiker.[3] Briefly, an explosive lens[4] was used to initiate a plane detonation wave at the upper surface of a block of cast composition B (60/40 RDX/TNT), 2 in. in diameter and 1 in. thick, whose bottom surface was in contact with a metal plate. The plate in turn was in contact with a pellet of maleic anhydride, cast in a support ring and held in a heavy steel recovery block.[3] The detonation drove a plane shock wave into the metal plate, and the wave later passed into the pellet of maleic anhydride, somewhat attenuated by its travel through the plate and by reflection at the metal–maleic anhydride interface. The intensity of the final shock was varied in different experiments by changing the thickness and material of the metal plate. The highest pressure was achieved by using only the $^1/_4$-in. thick steel plate that forms the closure plug in Kiker's assembly, and the lowest by using an additional $^1/_2$ in. of steel and $^1/_{16}$ in. of copper.

The recovery assembly failed to seal properly at the highest pressure and most of the sample was lost. However, enough was recovered to enable its infrared spectrum to be measured. It is hoped to overcome the problem of recovery in a more satisfactory way in future work.

Results and Discussion

Figure 1 curve (*1*) shows the infrared spectrum of material that had been subjected to the strongest shock wave. It is clearly that of a polymer of similar structure to the polymers formed by the solid-phase polymerization of maleic anhydride at high static pressures[1] (Figure 1, curve *2*) and by the liquid-phase polymerization initiated by benzoyl peroxide[1,5] (Fig. 1, curve *3*). It is characterized by the absence of the sharp C—H bands[6] of maleic anhydride (Fig. 1, curve *4*) at 840 and 1057 cm.$^{-1}$ and the C—C bands at 867 and 892 cm.$^{-1}$, and by the appearance of a broad absorption between 1150 and 1270 cm.$^{-1}$.

The instantaneous values of the pressure and temperature in the shock wave that caused polymerization are not known, as no measurements have yet been made of the shock propagation velocities or the thermodynamic properties of maleic anhydride at very high pressures, but by analogy with the behavior of other solids of similar density it may be guessed that the pressure was of the order of 100,000 atm. and the temperature several hundred degrees. Weaker shocks, attenuated by plates $^1/_2$-in. thick, or thicker, yielded no detectable amounts of polymer.

It is remarkable that a rather complex reaction of this kind, involving many molecules can occur in a few microseconds. The explanation could lie in the fact that shock compression is accompanied by a high shearing stress[7] which may help to arrange the molecules into a configuration that is more favorable to polymerization than the normal

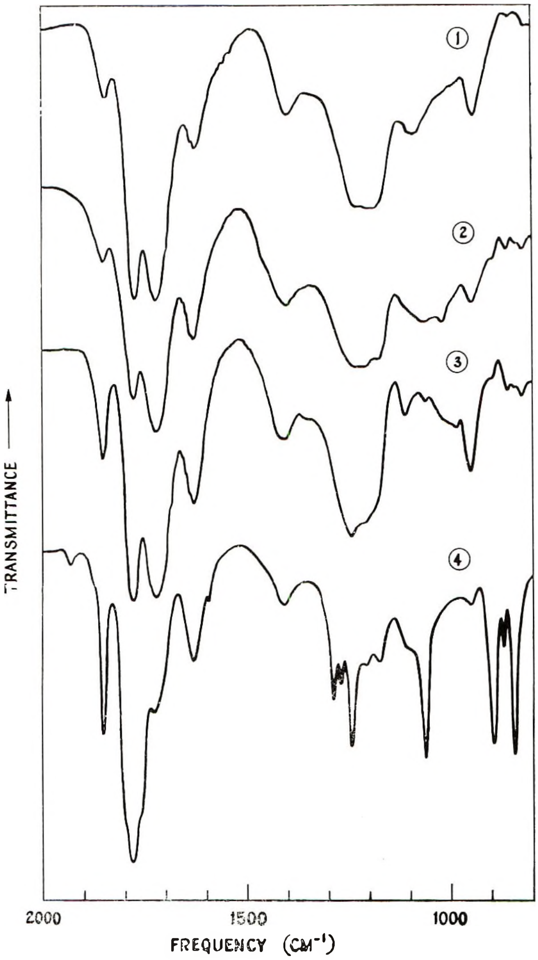

Fig. 1. Infrared spectra measured in KBr pellets: (*1*) shock-compressed maleic anhydride, (*2*) maleic anhydride polymerized under a hydrostatic pressure of 40,000 atm. at 160°C.; (*3*) maleic anhydride polymerized by benzoyl peroxide at 1 atm., 70°C.; (*4*) monomeric maleic anhydride.

arrangement. It is also possible that the chemical transformation is preceded by a physical phase change.[1] A few other organic compounds have shown signs of undergoing chemical changes in strong shocks,[8] and Alder[7] have found that white phosphorus polymerizes to black phosphorus at a shock pressure of 70,000 atm.

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Polymerization of N-*Vinylphthalimide by* γ-*Ray Radiation*

Introduction

Although polymerization and copolymerization of *N*-vinyl imides initiated by radical catalysts have been reported by many workers, radiation-initiated polymerizations of these compounds have been limited to the work of Hardy et al. on solid-state polymerization of *N*-vinylsuccinimide[1,2] and its copolymerization with *N*-vinyl pyrrolidone[3,4] by γ-radiation.

The present paper deals a study of the polymerization of *N*-vinylphthalimide in solid and in solution states by γ-radiation.

Experimental

***N*-Vinylphthalimide (VPI) and *N*-Vinylsuccinimide (VSI).** VPI was prepared via β-hydroxyethylphthalimide obtained by the condensation of monoethanolamine with phthalic acid and the subsequent pyrolysis of its acetate. The product consisted of pale yellow needles melting at 85–86°C. (lit. m.p. 86°C.,[5,6] 85.5–86°C.[7,8] VSI was prepared by the same method as of VPI; the product was in the form of colorless plates melting at 48–48.5°C. (lit. m.p. 48°C.,[9] 48–49[10]).

***N,N*-Dimethylformamide (DMF).** DMF was dried over anhydrous sodium sulfate and then purified by repeated distillation; b.p. 53–53.5°C./23 mm. Hg.

Radiation Source. The γ-rays were from a 1000-curie^{60} Co source and the dose rate was measured by a Toshiba dosimeter, Model RCD-43101.

Polymerization Procedure. In solid-state polymerization, required amounts of monomer crystals were irradiated in air by a ^{60}Co source for a given time at 5–10°C. The irradiated crystals were immersed in a large amount of methanol for a week at room temperature to extract the monomer. The resulting polymer crystals were filtered, washed with methanol, dried under vacuum, and then weighed.

In solution polymerization, the required amounts of VPI and DMF were weighed in a glass tube and the tube was sealed under nitrogen. Solution polymerization by γ-radiation was carried out for a given time at 25–28°C. After the polymerization, the contents of the tube were poured into a large amount of methanol to precipitate the polymer. The resulting polymer was filtered, washed with methanol, dried under vacuum, and then weighed.

Viscosity Measurement. The reduced viscosity of the obtained polymer was determined by viscosity measurements on a 0.50% solution in DMF by using an Ostwald viscometer at 30 ± 0.01°C.

X-Ray Diffraction Patterns. The finely powdered monomer, irradiated monomer, and polymer crystals were packed into glass capillaries and exposed to x-rays (Ni-filtered CuKα 1.542 A.) in a Debye-Scherrer camera for approximately 5 hr.

Results and Discussion

Solid-State Polymerization. The results of the solid-state polymerization of VPI and VSI are shown in Table I. The polymerization of VSI was carried out for comparison with that of VPI. VSI was easily polymerized by γ-radiation, and the resulting polymer crystals were insoluble or merely swollen by several solvents. However, VPI was comparatively difficult to polymerize, and the resulting polymer crystals were soluble in several solvents, including DMF, chloroform, acetylene tetrachloride, and ethylene dichloride. From the difference in stability to γ-radiation between phthalimido and succinimido groups in these polymers, it is reasonably expected that the polymer crystals of VPI are not crosslinked, unlike those of VSI.

The irradiated monomer and polymer crystals of VPI were similar in external appearance; both crystals were anisotropic as shown by observation with a polarized

TABLE I
Solid-State Polymerizations of VPI and VSI by γ-Radiation in Air at 5–10°C.

Monomer	Dose rate × 10^{-4}, r./hr.	Irradiation time, hr.	Polymer yield, %	Reduced viscosity, dl./g.
VPI	11	96	4.9	—
VPI	11	407	55.0	0.263
VSI	0.9	95	48.2	Gelled
VSI	11	121	93.1	Gelled

microscope. The results of the x-ray diffraction studies are given in Table II. Although the monomer crystals show many sharp Debye-Scherrer rings, the irradiated monomer crystals show few weaker bands than the monomer crystals without any new bands, but retain the original crystallinity. The polymer crystals which were obtained from the irradiated monomer crystals by extracting the residual monomer have only one halo near 3.5 A.

Also the crystallinities of the monomer, irradiated monomer, and polymer crystals from VSI were measured by the x-ray method; the results were identical with those for VPI.

TABLE II
X-Ray Diffraction Patterns of the Monomer, Irradiated Monomer, and Polymer Crystals of VPI

Monomer		Irradiated monomer[a]		Polymer[b]	
Lattice spacing, A.	Intensity[c]	Lattice spacing, A.	Intensity[c]	Lattice spacing, A.	Intensity[c]
1.66	w				
1.97	w				
2.14	w				
2.22	w				
2.35	w				
2.46	w				
2.63	w				
2.79	m	2.78	w		
3.21	m				
3.33	vs	3.33	w		
3.43	m	3.5	w	3.5	m
3.68	s	3.65	w		
3.87	s	3.85	w		
4.62	vs	4.66	m		
4.85	w				
5.70	w				
6.21	s	6.17	m		
7.34	s	7.34	w		

[a] The monomer was subjected to γ-irradiation in air for 407 hr. at 5–10°C.; dose rate 1.1 × 10^5 r./hr.

[b] Residual monomer was extracted from the irradiated monomer with methanol; the resulting polymer was obtained in 55% yield.

[c] Intensity; w, weak; m, medium; s, strong; vs, very strong.

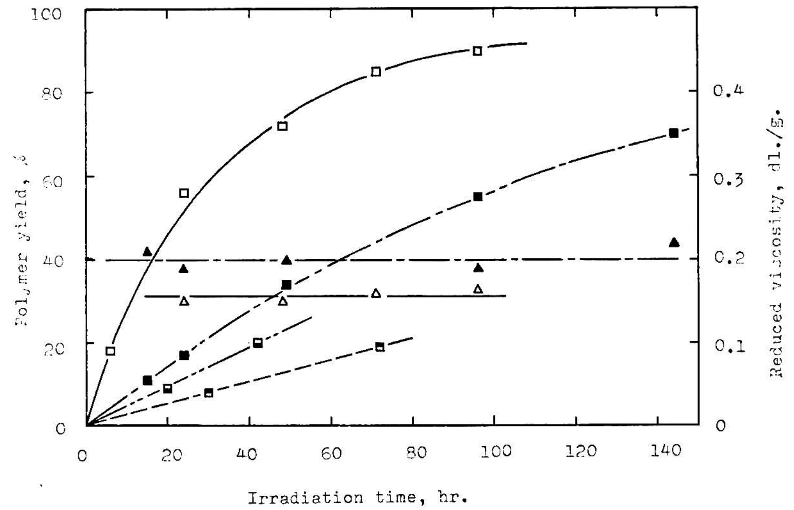

Fig. 1. Plots of (□,■,⊟,▣) polymer yield and (△,▲) reduced viscosity for solution polymerization of VPI in DMF at 25–28°C. at various dose rates: (——) 1.1×10^5 r./hr.; (- - -) 0.9×10^4 r./hr.; (–-–-) 5.4×10^3 r./hr.; (----) 2.4×10^3 r./hr. Monomer concentration, 1.21 mole/kg.

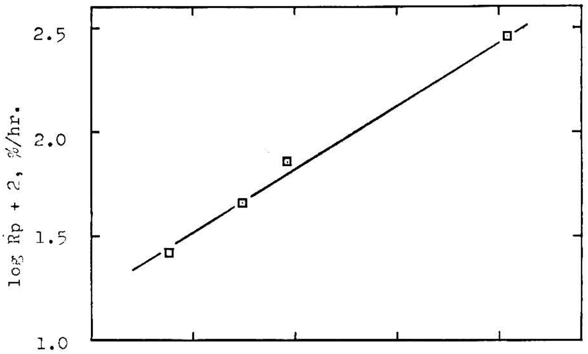

Fig. 2. Relationships between the dose rate I and the rate of polymerization R_p in DMF at 25–28°C.; monomer concentration 1.21 mole/kg.

These results showed the polymer crystals of VPI and VSI to be amorphous, although both were unchanged in external appearance.

Solution Polymerization. The results of the solution polymerization of VPI in DMF induced by γ-radiation are shown in Figure 1. VPI polymerized easily, quite unlike the case of the solid-state polymerization. As is seen in Figure 1, no induction period was observed in this polymerization system, and reduced viscosities of the resulting polymers were nearly constant regardless of the irradiation time, but decreased with increasing dose rate.

In order to investigate the effect of the dose rate on the rate of polymerization, the monomer concentration and temperature were kept constant, and the dose rate was changed in the range from 1.1×10^5 to 2.4×10^3 r./hr. The results are shown in Figure 2. From the slope of a straight line it is seen that the kinetic order of the dose rate to the rate of polymerization is 0.60. This indicates that the termination mechanism in this polymerization system is mainly bimolecular, essentially the same as the homogeneous radical polymerization of many vinyl compounds.

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Vinyl Chloride Acrylate of Methoxy Poly(ethylene Glycol) Copolymers

In our continuing work on preparation and evaluation of various vinyl chloride copolymers[1] for mechanical and low-temperature properties, we noticed that certain hydroxyl-containing comonomers (vinyl 9,10-dihydroxystearate, vinyl 9-hydroxystearate, and vinyl 14-hydroxystearate) gave copolymers with one of the lowest flex temperature points T_f observed (below +10°C.) for this type of material.[2] In a continuation of these studies, we prepared the acrylate of monomethyl ether of a poly(ethylene glycol) [Carbowax, methoxypoly(ethylene glycol) 750] and a number of its vinyl chloride copolymers. Experimental data and results on some of the copolymers are given in Table I.

The 78/22 VCl/acrylate copolymer was evaluated for mechanical and low-temperature properties, some of which are listed in Table II. The procedure for evaluation has been given in detail elsewhere.[1] The evaluation data show that incorporation of 22 parts of a poly(ether acrylate) in poly(vinyl chloride) produced low-temperature properties that are better than these obtained by external addition of 25 parts of dioctyl phthalate to a 95/5 VCl/VAc copolymer.[3]

Monomers

The methyl ether of the poly(ethylene glycol) [Carbowax, methoxypoly(ethylene glycol) 750] was obtained from the Union Carbide Chemical Co. It was used as received in the preparation of the acrylate. The analysis for the glycol monoether was as follows.

ANAL. Calcd. for $C_{33}H_{68}O_{17}$: C, 53.79%; H, 9.29%. Found: C, 53.98%; H, 9.33%.

The acrylate was prepared from acrylyl chloride and the glycol ether essentially according to the procedure of Marvel and Schwen.[4] The product was isolated by suspending the reaction mixture in benzene, centrifuging down the aniline salt, and stripping the benzene solution in a Rotovac at about 3 mm. and a temperature up to 60°C. Typically, a tan-colored oil was obtained in about 85% yield which solidified into a white solid upon cooling below room temperature.

ANAL. Calcd. for $C_{36}H_{70}O_{18}$: C, 54.66%; H, 8.92%. Found: C, 54.71%; H, 8.88%.

Copolymerization

The acrylate (4.6 g.), Siponate DS-10 (0.8 g.), AIBN (0.4 g.), and air-free, distilled water (80 ml.) were charged under nitrogen into a pressure tube (1.5 × 7 in.). The tube was then cooled to about −15°C. and vinyl chloride (15.4 g.) was added. An excess of vinyl chloride was used to purge the tube of air before capping. The contents were emulsified at room temperature for about 2 hr. and then polymerized at 60 ± 2°C. for 15 hr. Lumpy latex, containing polymer particles, was obtained. It was poured into 1 liter of methanol, the precipitated material dissolved in 180 ml. of tetrahydrofuran, filtered, and reprecipitated in 1 liter of methanol. The isolated material was dried in a vacuum oven at room temperature for about 20 hr. and then at 40°C. for 8 hr. Drying of these materials at increasing temperatures produces progressively greater discoloration. The yield was 14 g. (70%) of vacuum oven-dried white solid. The infrared spectrum showed no characteristic absorptions of the monomers.

This is a partial report of work done under contract with the Western and Southern Utilization Research and Development Divisions, Agricultural Research Service, U.S. Department of Agriculture and authorized by the Research and Marketing Act. The contract is supervised by Dr. Glenn Fuller of the Western Division.

TABLE I

Emulsion Vinyl Chloride/Acrylate Copolymers[a]

Charged composition		Polymerization time, hr.	Conversion, %	Acrylate, %[b]	η_{inh}[c]	Calculated			Found		
VCl, wt.-%	Acrylate, wt.-%					C, %	H, %	Cl, %	C, %	H, %	Cl, %
70	30	18	70	27	0.80	42.81	5.91	41.43	43.13	6.04	42.15
77	23	15	70	22	1.00	42.00	5.72	44.25	41.90	5.68	44.25
84	16	20	72	20	0.80	41.68	5.65	45.39	41.85	5.70	45.28

[a] Siponate DS-10 (alkyl-substituted benzene sodium sulfonate) used as emulsifier and about 2% of azobisisobutyronitrile as initiator; all of the polymerizations were conducted at 60 ± 2°C. by tumbling the tubes end over end.

[b] By weight, based on analysis for C, H, Cl, in the copolymers.

[c] Determined on solutions of 0.189–0.230 g./100 ml. of tetrahydrofuran.

TABLE II

Some Physical Properties of Vinyl Chloride Copolymers

Property	78/22 VCl/acrylate	95/5 VCl/VAc + 25% DOP
Elastic modulus (tension), psi	55,800	—
Yield point, psi	1,690	—
Tensile strength, psi	2,580	3,720
Elongation, %	200	210
T_f, °C.	−4	+1
T_4, °C.	+27	—
Milling temp., °F.	240	340

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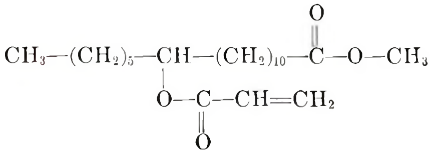
Copolymers of Methyl 12-Acryloxystearate and Vinyl Chloride

As a continuation of studies on internal plasticization of vinyl chloride polymers, it was undertaken to prepare copolymers of vinyl chloride with derivatives of fatty acids originated from agricultural commodities. In this communication, we report the preparation of copolymers of vinyl chloride and methyl 12-acryloxystearate (I, MAS).



$CH_3{-}(CH_2)_5{-}CH(O{-}CO{-}CH{=}CH_2){-}(CH_2)_{10}{-}CO{-}O{-}CH_3$

I

This monomer was supplied to us by Dr. T. H. Applewhite of the U. S. Department of Agriculture, Western Utilization Research and Development Division. MAS was prepared by treatment of methyl 12-hydroxystearate with β-chloropropionyl chloride in the presence of excess sodium bicarbonate in tetrahydrofuran, followed by dehydrohalogenation with anhydrous pyridine.[1]

Copolymerization of MAS and vinyl chloride initiated with diethyl α,α'-azobisisobutyrate at 60°C. gave partially crosslinked polymers. Similar results have been reported.[2] However, soluble, high molecular polymers can be obtained in a typical redox system containing ferrous ion, benzoyl peroxide, and sodium pyrophosphate. It was found that ferrous sulfate (FS, as the heptahydrate) gave better conversion than ferrous ammonium sulfate (FAS, is the hexahydrate) in the polymerization. Nevertheless, usually higher molecular weight materials were produced by the use of ferrous ammonium sulfate. The results are given in Table I. Copolymers thus obtained were fairly homogeneous except for a small amount of low molecular weight fraction which could be separated by fractional reprecipitations, as indicated in Table II.

Methyl 12-acryloxystearate at 50% level gave copolymers which were tough and showed good adhesiveness toward glass plates. They are suggested for use as adhesives. The copolymer of 80% MAS was soft snd sticky, and did not seem to have any practical usefulness. Films cast from the copolymers of some 30% MAS were rubbery and flexible, indicating that MAS may be a potential internal plasticizer for vinyl chloride polymers.

EXPERIMENTAL

Copolymerization

The monomer (MAS, sample no. 498-12) furnished by the U. S. Department of Agriculture, Western Utilization Research and Development Division had a refractive index of $n_D^{31} = 1.4497$ and exhibited the characteristic carbonyl absorptions at 1740s, 1720s, and vinylic absorptions at 1630s, 1615s, 985m, 810s, and 722m cm.$^{-1}$. Its purity was checked by thin layer chromatography. The polymerization was run in six parts of deaerated water following the procedure described previously.[3] The composition of the copolymers shown in Table III was calculated from the analytical data.

Fractionation of Copolymers of MAS and VCl

A sample of the copolymer (COMAS-34; 5.425 g.) was dissolved in 200 ml. of tetrahydrofuran. To this were added 200 ml. of methanol and a few drops of concentrated sulfuric acid to precipitate 4.684 g. (86.4%) of fraction A. An attempt was made unsuccessfully to further fractionate fraction A. A second fraction (B) of 0.410 g. (7.7%) was obtained upon the addition of 100 ml. of methanol to the filtrate. To this second

TABLE I

Emulsion Copolymerization of Methyl 12-Acryloxystearate and Vinyl Chloride at 27°C. with Redox Initiation[a]

Run no.	MAS charged, %	MAS in polymer, %	Ferrous compound, %[b]	Benzoyl peroxide, %	Time, hr.	Conversion, %	η_{inh}[b]	Softening point, °C.
COMAS-13	25	36.8	FAS, 1	2	37	32	2.23	150
COMAS-14	25	31.6	FS, 1	2	37	70	2.02	145
COMAS-34	25	28.0	FS, 1	2	21	79	1.75	125
COMAS-15	50	81.0	FS, 1	0.5	20	31	2.11	25
COMAS-17	50	53.3	FS, 1	2	20	74	2.82	140
COMAS-18	50	51.1	FS, 1	3	20	68	2.49	130

[a] The Office Rubber Research soap (1%), 10% sodium pyrophosphate decahydrate and 6 parts of deaerated water were used in each of the experiments.

[b] Viscosities were determined on ca. 0.2% tetrahydrofuran solutions at 30°C.

TABLE III

Elementary Analyses and Composition of Copolymers of MAS and VCl

Sample no.	Found			MAS in copolymer, %	Calculated		
	C, %	H, %	Cl, %		C, %	H, %	Cl, %
COMAS-13	49.68	7.23	36.07	36.8	50.70	7.03	35.97
COMAS-14	48.95	6.73	39.07	31.6	48.97	6.71	38.93
COMAS-15	65.31	9.71	10.56	81.0	65.43	9.71	10.81
COMAS-17	55.60	8.14	26.58	53.3	55.27	8.03	26.58
COMAS-18	55.04	7.91	27.27	51.1	55.42	7.90	27.83
COMAS-34	47.64	6.49	40.43	28.0	47.77	6.50	40.98
COMAS-34A	48.26	6.63	39.18	30.3	48.54	6.64	39.67
COMAS-34B	42.61	5.63	49.12	13.3	42.76	5.59	49.17
COMAS-34C	41.13	5.33	52.24	8.3	41.22	5.30	52.19

TABLE II
Fractional Precipitation of a Copolymer of Vinyl Chloride and Methyl 12-Acryloxystearate[a]

Fraction	Wt., g.	Wt.-%	η_{inh}[b]	MAS, %
A	4.684	86.4	1.80	30.3
B	0.410	7.7	0.436	13.3
C	0.051	0.9	0.014	8.3

[a] The copolymer (COMAS-34) consisted of 72.0% VCl and 28.0% MAS, and had an inherent viscosity of 1.75.

[b] Viscosities were determined on 0.2% tetrahydrofuran solutions at 30°C.

filtrate was again added 200 ml. of methanol to give 0.051 g. (0.9%) of fraction C upon standing for about 2 days. These fractions were dried and analyzed.

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Basic Consideration of Permeability of Polymer Membrane to Dissolved Oxygen

A number of questions have arisen concerning a recent note on permeability of polymer membranes to dissolved oxygen[1] and a mistake in the calculation of permeability constants has been pointed out. It therefore, seems appropriate to present a more general basic consideration of the subject and, by doing so, to present the correction of the mistake involved in the original article.

At first, it might be necessary to define the permeability constant in order to avoid possible misunderstanding of the subject. Permeability coefficients of membranes, in general, may be defined as the amount of permeant transported through a membrane of unit area in unit time by unit driving force gradient expressed in terms of a variable which is measured outside of the membrane, such as pressure or concentration, i.e.,

$$P = \frac{\text{(amount of permeant transported)}}{\text{(area of membrane)(time)(driving force gradient)}} \tag{1}$$

The difference between permeability constant and diffusion constant is in the way driving force is expressed, though permeability constants are much more general, in the sense that the transport does not necessarily involve a diffusion process. Because of the arbitrary way of expressing the driving force, permeability coefficient, in strict sense, is a phenomenological coefficient rather than a specific parameter of the membrane, while the diffusion constant can be considered to be of more specific nature.

Although a phenomenological permeability constant can be calculated with any arbitrarily chosen driving force, regardless of the actual mechanism, the proper selection of driving force gradient depends on the actual mechanism which governs the transport process. For instance, if transport takes place as a flow through porous medium, the pressure difference itself is the driving force. If the transport occurs as an activated diffusion process, the concentration gradient or, in more general terms, the chemical potential gradient of the penetrant within the membrane is the driving force gradient.

The proper choice of driving force gradient for a given transport process is important to obtain a specific permeability constant rather than a mere phenomenological coefficient, especially when two different phases are involved in both sides of the membrane.

The discussion, in this note, is primarily on the permeation of small molecules through a membrane by an activated diffusion process. In order to simplify the presentation, it will be limited to the permeability of oxygen, though the basic principle can be extended to the permeability of solute molecules in general.

Now we consider a generalized and simplified case of transport of oxygen molecules which can be represented by the schematic diagram in Figure 1, where C^{I}, p^{I}, and σ^{I} are concentration, partial pressure, and Henry's law constant, respectively, of oxygen in phase I; C^{II}, p^{II}, and σ^{II} are the corresponding parameters in phase II. C_1^{M} and C_2^{M} represent the concentration of oxygen in membrane at the surface in contact with the phase I and II, respectively.

Phase I and phase II can be either gas or liquid phases, independent of each other. In this situation, and considering in a classical way that the difference in the concentration of oxygen inside the membrane is the driving force of the transport process, the following relations can be derived.

$$\text{(driving force)} = \Delta C^{\text{M}} = C_1^{\text{M}} - C_2^{\text{M}} \tag{2}$$

At each of the two membrane surfaces, it can be assumed that the phases are in equilibrium with respect to the solute. In this case, this can be approximated by the relations

$$C_1^{\text{M}} = k_1 C^{\text{I}} \tag{3}$$

$$C_2^{\text{M}} = k_2 C^{\text{II}} \tag{4}$$

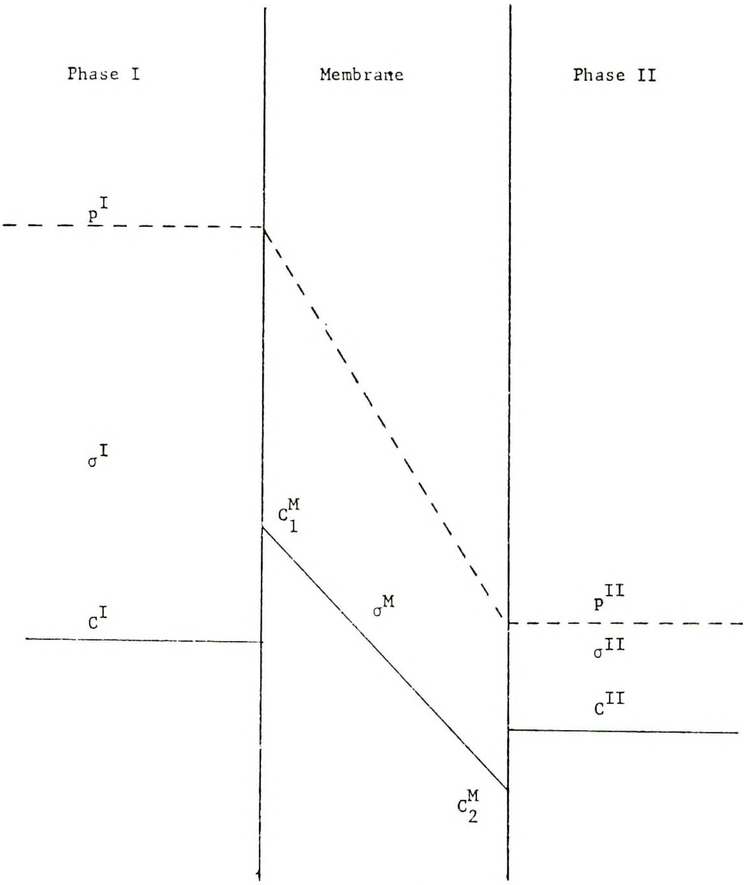

Figure 1.

where k is a constant which is the solute distribution coefficient between the membrane and the contacting phases.

Assuming a linear gradient of concentration within the membrane, eq. (2) can be written as

$$(\text{driving force gradient}) = (C^{I}k_1 - C^{II}k_2)/L \tag{5}$$

where L is the thickness of the membrane.

On the other hand, the amount of permeant transported through the membrane in time t is equal to $C^{II}V$, i.e.,

$$(\text{amount of permeant transported}) = C^{II}V \tag{6}$$

Therefore, permeability constant P can be generally given as

$$P = \frac{dC^{II}}{dt}\,\frac{1}{(C^{I}k_1 - C^{II}k_2)}\,\frac{VL}{A} \tag{7}$$

When the concentration of solute can be related to its partial pressure by Henry's law, i.e.,

$$p = (1/\sigma)C \tag{8}$$

then, eq. (7) can be expressed by the partial pressure,

$$P = \frac{dP^{\mathrm{II}}}{dt} \frac{\sigma^{\mathrm{II}}}{(p^{\mathrm{I}}k_1 - p^{\mathrm{II}}k_2)} \frac{VL}{A} \tag{9}$$

Equations (7) and (9) are essentially the same, differing only in the variable used and consequently in the units. Either one can be considered as a general equation with which permeability can be calculated in various combinations of phases.

However, only P given by eq. (9) is the specific gas permeability constant of the membrane, and P given by eq. (7) is not a specific permeability constant in the strict sense. This is shown by the following relationship.

When an equilibrium is maintained with respect to the solute at each membrane surface, the fugacity of the solute in each phase should be identical. In our case, the fugacity can be replaced by the partial pressure of the solute, therefore,

$$p^{\mathrm{I}} = p^{\mathrm{M}} = p^{\mathrm{II}} \tag{10}$$

where p^{M} is the partial pressure of the solute in the membrane phase. Then,

$$C^{\mathrm{I}}/\sigma^{\mathrm{I}} = C^{\mathrm{II}}/\sigma^{\mathrm{II}} = C^{\mathrm{M}}/\sigma^{\mathrm{M}} \tag{11}$$

where σ^{M} is Henry's law constant in the membrane phase. Therefore, the solute distribution coefficient defined in eqs. (3) and (4) can be given as

$$k_1 = \sigma^{\mathrm{M}}/\sigma^{\mathrm{I}} \tag{12}$$

$$k_2 = \sigma^{\mathrm{M}}/\sigma^{\mathrm{II}} \tag{13}$$

Therefore, the driving force, given by eq. (5) can be written as

$$(\text{driving force}) = \sigma^{\mathrm{M}}(p^{\mathrm{I}} - p^{\mathrm{II}}) \tag{14}$$

Equation (14) means that the driving force of the transport is identical, regardless of the phases which contact with the membrane, and consequently the flux will be identical as long as the partial pressure difference is maintained constant.

By using eq. (14), eq. (9) can be written as

$$P = \frac{dp^{\mathrm{II}}}{dt} \frac{\sigma^{\mathrm{II}}}{\sigma^{\mathrm{M}}(p^{\mathrm{I}} - p^{\mathrm{II}})} \frac{VL}{A} \tag{15}$$

Now, the relationship between the experimental variable and the resulting permeability constant is clear. Let us consider the situations for all possible combinations of phases. (The oxygen sensor is in the second phase.)

Gas–Gas: (in gas phase, $\sigma_g = 1/RT$) therefore:

$$P(\mathrm{G/G}) = \frac{dp^{\mathrm{II}}}{dt} \frac{(1/RT)}{\sigma^{\mathrm{M}}(p^{\mathrm{I}} - p^{\mathrm{II}})} \frac{VL}{A} \tag{16}$$

Water–Gas:

$$P(\mathrm{W/G}) = \frac{dp^{\mathrm{II}}}{dt} \frac{(1/RT)}{\sigma^{\mathrm{M}}(p^{\mathrm{I}} - p^{\mathrm{II}})} \frac{VL}{A} \tag{17}$$

Gas–Water:

$$P(\mathrm{G/W}) = \frac{dp^{\mathrm{II}}}{dt} \frac{\sigma^{\mathrm{II}}}{\sigma^{\mathrm{M}}(p^{\mathrm{I}} - p^{\mathrm{II}})} \frac{VL}{A} \tag{18}$$

Water–Water:

$$P(\mathrm{W/W}) = \frac{dp^{\mathrm{II}}}{dt} \frac{\sigma^{\mathrm{II}}}{\sigma^{\mathrm{M}}(p^{\mathrm{I}} - p^{\mathrm{II}})} \frac{VL}{A} \tag{19}$$

TABLE I
Permeability of Gas and Dissolved Oxygen in Polymers

Polymer	$P \times 10^{10}$, cm.³ STP (cm.)/cm.²-sec. (cm. Hg) G/G	W/W
Polydimethylsiloxane[a]	665	113
Polyethylene (low density)	2.34	1.52
Teflon FEP	3.86	2.97
Teflon TFE	2.37	2.58
(HEMA) Hydrogel[b]	—	5.10
Polyelectrolyte complex[c]	—	7.64

[a] Dow Corning Medical Silastic, with SiO_2 fillers.

[b] Crosslinked poly(hydroxyethyl methacrylate); water content 38%.

[c] Poly(vinyl trimethylammonium)–poly(styrene sulfonate); water content 35% (Amicon Inc., Cambridge, Massachusetts).

In the original article,[1] the permeabilities were calculated by the equation given for a gas phase experiment, in which the amount of gas is expressed in cubic centimeters (S.T.P.) and, therefore, the equation already included σ_g. As it is seen in eq. (19), the permeabilities measured by water–water experiment should have σ^{II} rather than σ_g. Therefore, to obtain specific gas permeability constants in the same units, numbers shown for the W/W column in Table I of the original note should have been multiplied by the solubility of oxygen at the temperature (25°C.), 2.83×10^{-2} cm.³ (STP)/cm.³-atm.

Accordingly, the revised data are given in Table I.

A great difference in O_2 permeability of silicone rubber may be due to the concentration polarization at the interface of membrane and water.

These considerations also point out the fundamental difficulty of defining the permeability constant of a solute, in general, beyond a phenomenological coefficient, unless the chemical potential difference of a solute is readily obtainable.

In order to see the nature of the difficulty, let us consider a general case which often appears in practical experiments. Both sides of the membrane contact an identical phase, e.g., water, and the transport of a solute, e.g., oxygen, is measured by creating a concentration gradient across a membrane of which detail of structure is unknown. In this situation, a proper expression of permeability constant can be given by eq. (7), i.e.,

$$P = \frac{dC^{II}}{dt} \frac{1}{(C^{I}k_1 - C^{II}k_2)} \frac{VL}{A} \tag{7}$$

Since the both phases are identical $k_1 = k_2$ and can be written simply as k, and C^{I} and C^{II} can be written as C_1 and C_2, respectively.

Then, in this particular case,

$$P = \frac{dC_2}{dt} \frac{1}{k(C_1 - C_2)} \frac{VL}{A} \tag{20}$$

Under such a situation, we can obtain the flux rate (dC_2/dt) at a given concentration difference ($C_1 - C_2$), and in the general case, we would conventionally calculate the permeability constant by simply dividing the flux rate by the concentration gradient, that is, without considering the factor k. Furthermore, k cannot be obtained by a simple flux measurement. Therefore, a permeability constant thus obtained is no longer the specific permeability constant of the membrane, but it is a phenomenological coefficient, and consequently it depends on the experimental conditions.

It can further be explained by the following hypothetical experiment, in which the water phase is replaced by a hypothetic fluid that does not interact with the membrane but changes the solubility of oxygen keeping the partial pressure of O_2 constant. In this new condition, the total flux of the solute does not change, as previously explained, but the concentration gradient of the solute is different. Thus, we will obtain a completely different permeability constant for the identical flux of the solute.

Permeability of gases in the gas phase is a particular case, where the permeability constants can be considered as specific parameters to the membrane without any further consideration. However, even a gas permeability constant becomes a phenomenological coefficient which can no longer be considered as specific to the membrane, when it is measured in dissolved phase without additional information on the solubility constant or without obtaining the partial pressure, rather than the concentration of the gas.

The author's acknowledgment is due to Miss L. C. Markley, Amicon Corporation, Cambridge, Massachusetts for her kindly pointing out the mistake involved in the original note.

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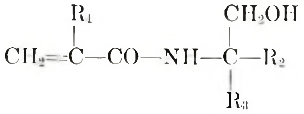
Synthesis and Polymerization Studies of Some N-Alkylolacrylamides. III. Polymerization of 2-Methacrylamido-2-methylpropanediol-1,3 and 2-Methacrylamido-2-methylpropanol-1

In our previous papers[1,2] we reported on the synthesis of some new *N*-alkylolacrylamides with the general formula:



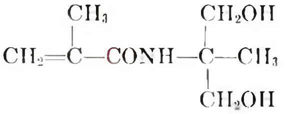
$$\mathrm{CH_2{=}\overset{\displaystyle R_1}{\overset{|}{C}}{-}CO{-}NH{-}\underset{\displaystyle R_3}{\underset{|}{\overset{\displaystyle CH_2OH}{\overset{|}{C}}}}{-}R_2}$$

where R_1 = H or CH_3; R_2 = CH_3, $-C_2H_5$ or $-CH_2OH$; R_3 = $-CH_3$ or $-CH_2OH$.

We found that these compounds with relatively large side chain substituents polymerized readily into high molecular weight products. Some of these monomers, when polymerized in bulk or in aqueous solutions to higher conversion, yielded partially cross-linked products.[3]

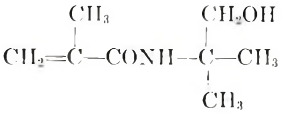
The object of this work was to investigate the polymerization rates of these monomers under homogeneous conditions and to compare some properties of the resulting polymers.

The two monomers selected for this work were the 2-methacrylamido-2-methylpropanediol-1,3 (I) and the 2-methacrylamido-2-methylpropanol-1 (II) synthesized by Luskin.[4]



$$\mathrm{CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CONH{-}\underset{\displaystyle CH_2OH}{\underset{|}{\overset{\displaystyle CH_2OH}{\overset{|}{C}}}}{-}CH_3}$$

I



$$\mathrm{CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CONH{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_2OH}{\overset{|}{C}}}}{-}CH_3}$$

II

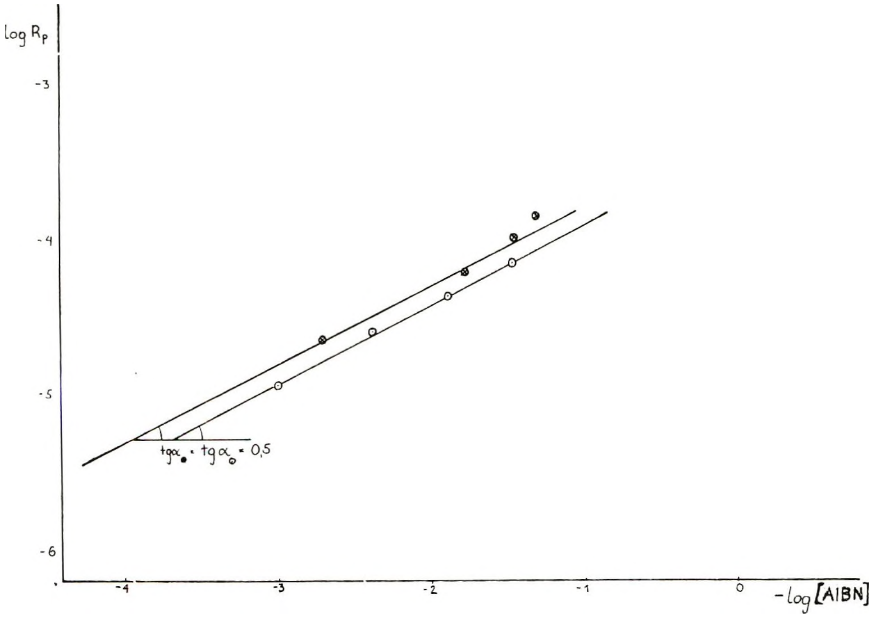


Fig. 1. Relationship between R_p and [AIBN] at 60°C. in DMF, [M] = 1.60 mole/l.: (⊘) for monomer I; (⊙) for monomer II.

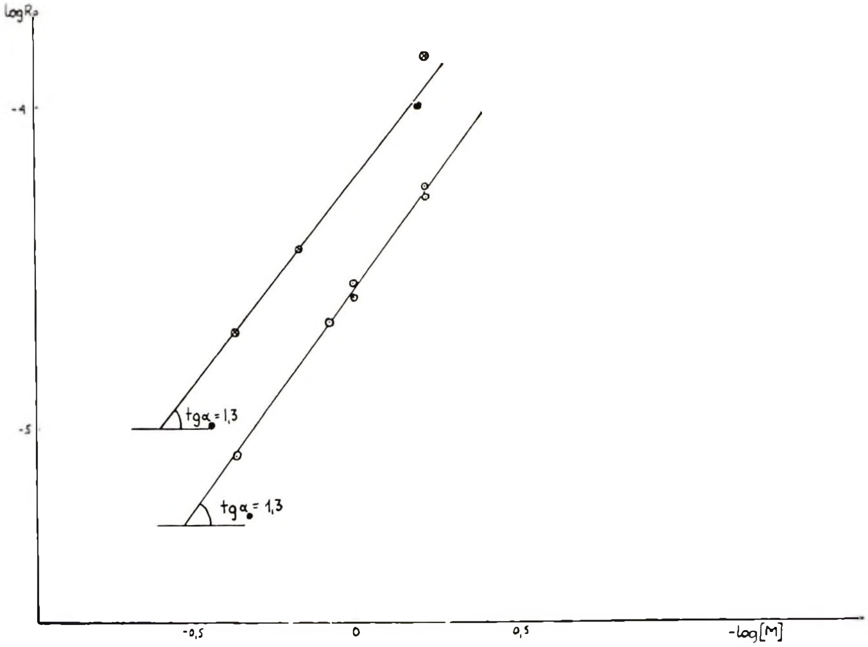


Fig. 2. Relationship between R_p and [M] at 60°C. in DMF, [AIBN] = 33.2 × 10^{-3} mole/l.: (⊗) for monomer I; (⊙) for monomer II.

RESULTS

Polymerization in DMF

First, the dependence of [AIBN] and [M] on the polymerization rate R_p was studied. We found that the R_p depends on the square root of [AIBN]. For both monomers this dependence is shown in Figure 1. Straight lines with a slope of 0.5 were found. The dependence of R_p on monomer concentration [M] was studied in the concentration range 0.42–1.68 mole/l. because of the limited solubility of monomer I in DMF. In this range R_p was proportional to $[M]^{1.3}$ The log-log plots of this dependence for both monomers are shown in Figure 2, with slopes of 1.3. For this system the rate of polymerization may be expressed as:

$$-\frac{dM}{dt} = R_p = k[\mathrm{AIBN}]^{0.5}[\mathrm{M}]^{1.3}$$

The polymerization rates determined for both monomers were found not to differ very much. This indicates that the second hydroxyl group present in monomer I does not exert much of an influence on the polymerization rate. The dependence of $[\mathrm{AIBN}]^{0.5}$ on $1/[\eta]$ for the polymer of I is shown in Figure 3.

Polymerization in DMSO

The polymerization conditions and results obtained for monomers I and II are given in Table I.

With polymerization in DMSO R_p was found to be greater, and the viscosities were lower than those obtained in DMF solution.

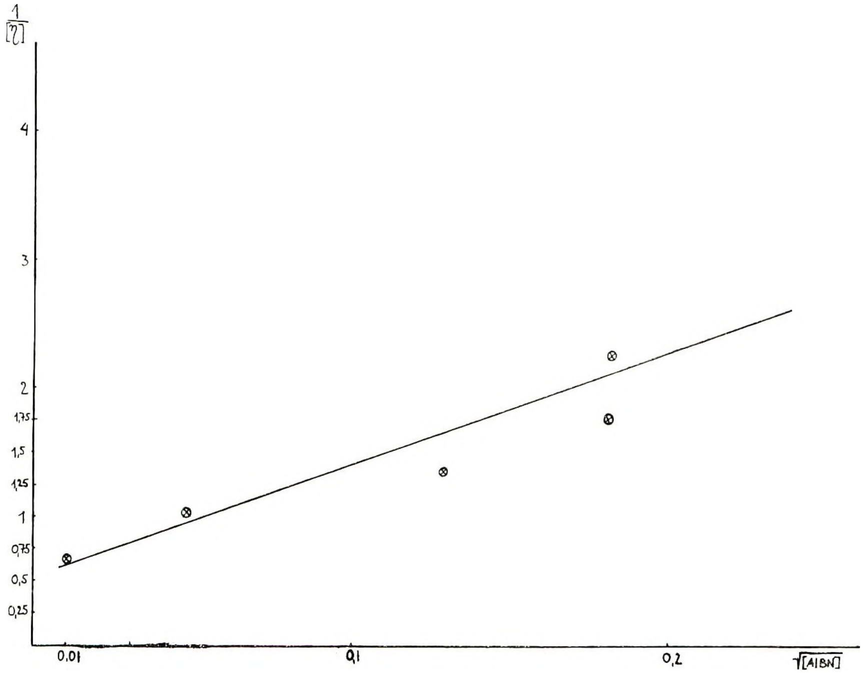


Fig. 3. Relationship between $1/[\eta]$ and $[AIBN]^{0.5}$ for polymer I.

TABLE I

	I	II
Polymerization temperature, °C.	60	60
[M], mole/l.	1.68	1.68
[AIBN], mole/l.	33.2×10^{-3}	33.2×10^{-3}
R_p, mole/l.-sec.		
In DMSO	4×10^{-4}	2.5×10^{-4}
In DMF	8.8×10^{-5}	6.8×10^{-5}
$[\eta]$, dl./g.		
In DMSO	0.58	0.6
In DMF	1.2	0.32

EXPERIMENTAL

Materials

The monomers were prepared according to the previously described method[1] and then carefully purified.

2-Methacrylamido-2-methylpropanediol-1,3 (I), m.p. 102–103°C., was purified by a threefold crystallization from acetonitrile. 2-Methacrylamido-2-methylpropanol-1 (II) was purified by a double distillation in a nitrogen atmosphere at 97–99°C./0.15 mm. Hg.

N,*N*′-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were both doubly distilled in a nitrogen atmosphere under vacuum. α,α′-Azobisisobutyronitrile was recrystallized twice from ethanol.

Polymerization Procedure

A homogeneous solution of the desired molar concentration of monomer in DMF or DMSO was charged into a thick-walled tube. Then the initiation solution was added.

In one series of experiments the monomer concentration was kept constant and the initiator concentration [AIBN] varied, while in another series the monomer concentration was varied and the initiator concentration kept constant.

The sample was degassed twice by freezing and thawing and sealed under 10^{-3} mm. of pure nitrogen. The tubes were placed in a thermostat at 60 ± 0.05°C. and shaken. After a given time the tubes were opened and the contents poured into a large amount of acetone and washed thoroughly with acetone. From the dry polymer obtained, the conversion was calculated.

The reaction rate R_p at given [M] and [AIBN] was computed from the slope of the time–conversion curves.

Viscosity Measurements

Relative viscosities were determined with a modified Ubbelohde viscometer at 20°C. in DMF. The intrinsic viscosity of the polymers were obtained by extrapolation to zero concentration by the usual method $(\eta_{sp}/c)_{c\rightarrow 0}$.

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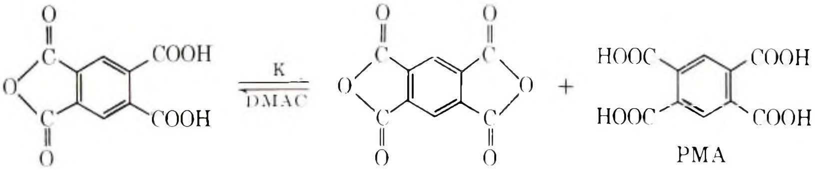
Hydrolysis of Some Aromatic Cyclic Anhydrides

In connection with our research with aromatic cyclic anhydrides in polymer syntheses, we have been interested in their rates of hydrolyses in polymerization solvents. Hydrolysis rates of some cyclic carboxylic anhydrides have been studied previously, especially in dioxane–water mixtures,[1–4] but hydrolysis rates of aromatic cyclic anhydrides have not been examined in dimethylacetamide (DMAC) as a solvent. Therefore, we are reporting our NMR and infrared results for the hydrolysis of pyromellitic dianhydride (PMDA), trimellitic anhydride (TMA), and phthalic anhydride (PA) in DMAC. We also report an equilibration of pyromellitic monoanhydride (PMMA) with pyromellitic acid (PMA) and PMDA [eq. (1)].



PMMA PMDA PMA (1)

Chemical shifts relative to tetramethylsilane of the aromatic protons of the anhydrides and their corresponding acids are given in Table I. Narrow singlet proton peaks were observed except for TMA and its acid, which had complex spectra, and *o*-phthalic acid, which had a doublet. Protons of the anhydrides and acids were accounted for separately and per cent of anhydride remaining or acid formed during hydrolysis was analyzed by repetitive scans and peak-height ratios of either aromatic acid or anhydride protons to total aromatic protons present.

TABLE I
H^1 Chemical Shifts and Hydrolysis Rate Constants of Aromatic Cyclic Anhydrides

Compound	δ, ppm	k_3 (25°C.), l./mole-sec.
PA	8.16	6×10^{-6}
Phthalic acid	7.69, 7.72	—
TMA	8.14, 8.26, 8.40, 8.46, 8.62	1×10^{-4}
Trimellitic acid	7.72, 7.84, 8.14, 8.26, 8.34	—
PMDA	8.53	1.3×10^{-2}
PMMA	8.18	6.8×10^{-4}[a]
PMA	7.95	—

[a] Data scattered badly beyond 40% hydrolysis because of PMA precipitation.

The complexity of the NMR spectra of TMA and its acid required an infrared study of its hydrolysis rate. The cyclic anhydride absorption at 1830 cm.$^{-1}$ was used to determine anhydride concentration. With PA, equivalent hydrolysis rates were found by NMR and infrared (1830 cm.$^{-1}$) analyses.

All anhydrides exhibited second-order hydrolysis rates; rate constants at 25°C. are listed in Table I. PMDA hydrolyzed essentially in a stepwise manner, first to PMMA and then to PMA [eq. (2)]. Rates increased as the number of electron-withdrawing substituents on the anhydride increased, and were in the order of PMDA > PMMA > TMA > PA. The greater reactivity of PMDA compared to PMMA (about 20:1) suggests that a cyclic anhydride group exerts a stronger electron-withdrawing effect than two *ortho* carboxyl groups. Autocatalysis due to generated acid was ruled out since (*1*) the hydrolyses were second-order over at least 80% of the reaction, and (*2*) the addition of phthalic acid in the case of phthalic anhydride did not change the hydrolysis rate.

$$\text{PMDA} \xrightarrow[\text{DMAC}]{H_2O} \text{PMMA} \xrightarrow[\text{DMAC}]{H_2O} \text{PMA}\cdot 4\text{DMAC}\downarrow \qquad (2)$$

PMMA was not isolated. We believe its presence is accounted for by the proton peak at 8.18 ppm, which formed at the expense of the PMDA proton peak at 8.53 ppm when one equivalent of water was added. Furthermore, the PMMA proton peak (8.18 ppm) degenerated with the formation of a PMA proton peak when a second equivalent of water was added. PMA dissolved as its DMAC tetrasolvate showed one kind of aromatic proton peak at 7.95 ppm.

PMMA also equilibrated on standing in DMAC to yield some PMDA and PMA [eq. (1)]. The PMA gradually precipitated from these solutions as a tetrasolvate. After the solutions remained at room temperature for 7–10 days, precipitation ceased. The content of dissolved PMA was determined by NMR and alkaline titration to be 1.3 mmole/50 ml., whereas independent solubility studies of saturated solutions of PMA in DMAC showed 1.08 mmole PMA/50 ml. NMR analyses of the percentages of PMDA, PMA, and PMMA in solution at this time gave an average equilibrium constant of 0.10 for reaction (1) (Table II).

TABLE II
Equilibration of PMMA in DMAC

Acid (titrimetry), mmole/ 50 ml.[a]	NMR analyses of supernatant			PMA precipitate as tetrasolvate, mmole	Sum of acid (by titrimetry) + PMA precipitate, % acct. for[b]
	PMA, %	PMMA, %	PMDA, %		
10.3	12.1	55.8	33.0	3.37	99.6
10.8	15.4	59.6	25.0	1.10	92.2
10.5	9.4	60.2	30.3	3.04	98.8
10.0	12.6	59.3	28.0	3.32	97.2

[a] After complete hydrolysis of supernatant.
[b] Theoretical sum is 13.75 mmole.

The PMA·DMAC tetrasolvate is similar to that isolated previously.[5] Infrared spectra confirmed PMA and DMAC as components of the precipitates; chemical analyses gave 9.47% nitrogen compared to 9.27% nitrogen, the theoretical value for a tetrasolvate; NMR analyses showed a composition of PMA·3.7 DMAC. Thermogravimetric analyses revealed DMAC was lost in two distinct steps. The first loss at 75–125°C. corresponded to slightly less than 2 moles DMAC and the second loss at 125–175°C. corresponded to another 2 moles DMAC. This suggests that PMA can solvate with DMAC to yield both the di- and tetrasolvate, or mixtures, depending on conditions. Possibly DMAC molecules of solvation are non-equivalent, since data showed two molecules of DMAC are more tightly bound than the other two.

Experimental

DMAC was purified by refluxing under nitrogen at atmospheric pressure for 24 hr. over calcium hydride and distilling onto 3A Molecular Sieves under nitrogen at 74°C./30 mm. Gas chromatographic analyses showed the only impurities to be traces of dimethylformamide and dimethylpropionamide. Water content was 20–30 ppm as determined with a KF-3 Aquameter. PMDA, TMA, and PA were sublimed before use at 200°C./

<0.05 mm., 170°C./<0.05 mm., and 100°C./<0.05 mm., respectively. Equipment was baked at 130°C. for at least 1/2 hr. before use, and solutions were prepared in a dry box.

The concentration of each anhydride solution was made up at 0.275*M* and total volumes of solutions were either 25 or 50 ml. Water was added in a molar equivalent to anhydride present. A 50 ml. solution required 0.25 ml. of water. Zero time for the hydrolyses was taken at the time of addition of water. Some PA runs were spiked with phthalic acid before hydrolyzing. Phthalic acid additions with phthalic anhydride were 0.228 g., 0.571 g., and 0.913 g. corresponding respectively to 25, 50, and 80 mole-% of the initial phthalic anhydride concentration.

High resolution NMR studies were done with a Varian DP spectrometer. An Infracord spectrophotometer was used. Quantitative infrared analyses for anhydride content were made in a 1 mil NaCl cell, and absorptions were compared to a standard curve. Thermogravimetric analyses were done with an Aminco Thermo-grav.

Titrimetric analyses were carried out on aliquots of DMAC–anhydride solutions after allowing them to hydrolyze in distilled water overnight at 25°C. They were titrated to a phenolphthalein endpoint.

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Aroyl Peroxides Containing Reactive Functional Groups

Although many free-radical-producing initiators are described in the literature, very few have been prepared that contain reactive functional groups. It seems to us that peroxides of this type should be very useful as polymerization initiators, as unique cross-linking agents, and for the preparation of "telechelic" polymers which in turn can be used for block copolymer synthesis.

The term telechelic has been proposed[1] for polymer molecules possessing two functional terminal groups. The concept of telechelic polymers is not new. The preparation of telechelic condensation polymers, for example, is readily accomplished by employing a calculated excess of one reactant or by employing a monofunctional reactant which contains the desired group.[2] If a free-radical-producing initiator containing a functional group is used in conjunction with a vinyl monomer that terminates predominantly by combination, telechelic polymers result. Several investigations[3-5] have shown that styrene chains terminate almost exclusively by combination. Bamford and Jenkins,[6] employing γ,γ'-azo-(γ-cyano-*n*-valeric acid) prepared telechelic polymers of styrene and by conversion of the carboxyl endgroups to acid chlorides and condensation with a diol were able to obtain a multifold increase in molecular weight.

In this note, we describe the preparation of two additional radical-producing catalysts containing reactive functional groups, *p,p'*-bischloromethylbenzoyl peroxide and *p,p'*-bisformylbenzoyl peroxide and the telechelic polymers of styrene derived therefrom.

p,p'-Bischloromethylbenzoyl Peroxide

To 25 ml. of 10% hydrogen peroxide, stirred and maintained at 0°C. were added 18 ml. of cold 15% sodium hydroxide and 7.5 g. (0.04 mole) of *p*-chloromethylbenzoyl chloride, b.p. 141°C./20 mm. The additions were made dropwise over a 10 min. period, the reaction mixture always being maintained slightly alkaline. Stirring was continued for an additional 3 min. and the product filtered off and washed with ethanol. The product was recrystallized once from benzene and reprecipitated three times from chloroform into absolute ethanol; m.p., 148.5°C. Iodometry gave a value of 95.7% peroxide. Analysis (C. K. Fitz, Needham Heights, Mass.) for Cl gave 20.7% (theory 20.7%).

Chloromethyl Telechelic Polystyrene

Distilled styrene (2 g.) and 4 ml. of dry benzene containing 60 mg. of *p,p'*-bischloromethylbenzoyl peroxide were sealed off under vacuum and heated at 70°C. for 20 hr. Polystyrene was isolated by precipitation into ethanol, purified by three additional reprecipitations into large quantities of ethanol, and dried under vacuum. The intrinsic viscosity, in benzene at 25°C. was determined to be 0.183 dl./g. Pepper's relationship[7] for unfractionated polystyrene

$$[\eta] = 4.7 \times 10^{-4} \bar{M}_n^{0.66}$$

led to a number-average molecular weight of 9390. Two terminal chloromethyl groups per chain should lead to a chlorine content of 0.755%. Analysis (S. Nagy, Microanalytical Lab, M.I.T., Cambridge, Mass.) gave a value of 0.736% Cl, confirming again that termination in this system is predominantly by combination and that polystyrene containing reactive terminal benzyl chloride type groups can be produced. The presence of —C—Cl stretching is not detectable by infrared but absorption at 1720 cm.$^{-1}$ shows that chain initiation is started by $ClCH_2C_6H_4COO\cdot$ radicals as well as $ClCH_2C_6H_4\cdot$ radicals.

p,p'-Bisformylbenzoyl Peroxide

To 5.04 g. (0.03 mole of *p*-formylbenzoylchloride, m.p., 41°C., b.p. 100°C./3 mm. in 6 ml of acetone, stirred and maintained at 0–15°C., were added dropwise 1.71 g. (0.015 mole) of 30% hydrogen peroxide and excess sodium bicarbonate in 6 ml. of water. The reaction mixture was stirred for 10 min. and the product filtered off. The peroxide was

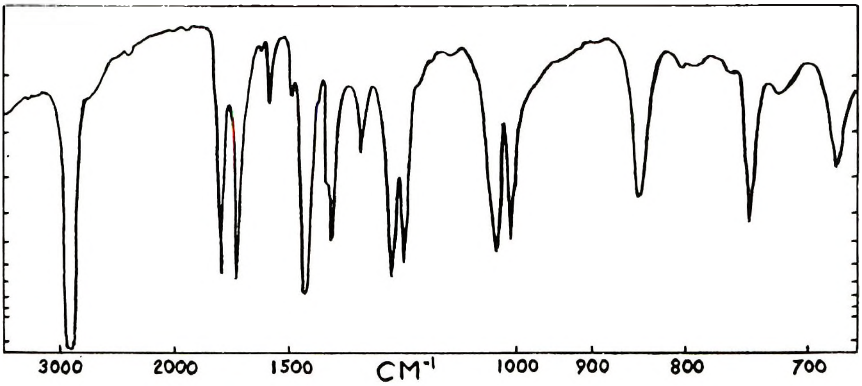

Fig. 1. Infrared spectrum of *p,p'*-bisformylbenzoyl peroxide (mineral oil mull).

purified by dissolving in acetone and precipitation into water, drying under vacuum, and reprecipitation from benzene into hexane. Many samples of this peroxide were prepared and iodometric analysis gave values ranging from 80 to 93%. The peroxide does not melt but explodes weakly on heating. We believe internal redox reactions explain the above. Analysis (C. K. Fitz, Needham Heights, Mass.) for C and H gave C, 63.8%, H, 3.40% (theory: C, 64.4%; H, 3.35%). The infrared spectrum (Fig. 1) is consistent with the structure of *p,p'*-bisformylbenzoyl peroxide.

Formyl Telechelic Polystyrene

Styrene monomer was polymerized with the use of *p,p'*-bis-formylbenzoyl peroxide and the polymer purified in the same manner as described above except that polymerization was carried out for 70 hr. The intrinsic viscosity in benzene of 0.173 corresponds to an $\bar{M}_n$ of 8600. The infrared spectrum (Fig. 2) of a film of this polystyrene (1.94×10^{-2} mm. in thickness) shows clearly discernible carbonyl stretching absorptions for aldehyde at 1700 cm.$^{-1}$ and ester at 1720 cm.$^{-1}$ By using the corrected optical density of 0.13 for the 1700 cm.$^{-1}$ band and a value of 300 for the extinction coefficient for carbonyl stretching, this sample is found to contain 0.224 mole of aldehyde per liter of polystyrene. Completely telechelic polystyrene of $\bar{M}_n = 8600$ (employing a density for polystyrene of 1.06 g./cm.^{3}) should be 0.246*M* in aldehyde so that here again a very large proportion of the polystyrene chains contain active aldehyde end groups. If the corrected optical density of 0.11 for ester carbonyl (1720 cm.$^{-1}$) is used to calculate the ester content

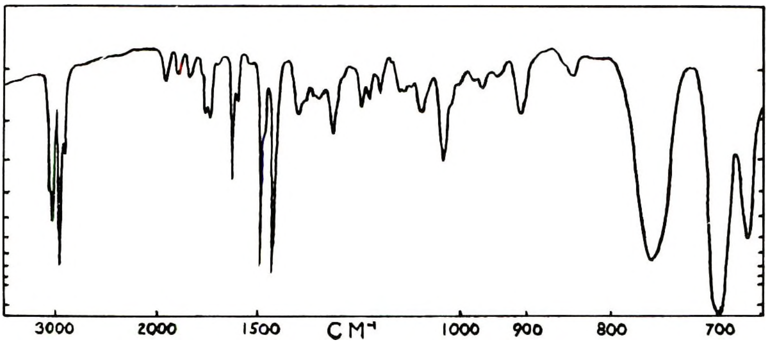

Fig. 2. Infrared spectrum of polystyrene containing aldehyde endgroups.

(employing a value of 600 for the ester carbonyl extinction coefficient) a value of about $0.095M$ is obtained. This value implies that about 42% of the initiating species is the $HOCC_4H_6COO\cdot$ radical and the remaining 58%, the $HOCC_4H_6\cdot$ radical.

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Grafting of Polyacrylonitrile to Granular Corn Starch by Initiation with Cerium

Prior publications from the A. E. Staley Laboratories on grafting to granular corn starch[1–5] have described the use of hydrogen peroxide as initiator. On the other hand, most of the other published work on grafting to starch via chemical initiation has involved ceric ion[6–10] as the initiator. Thus, no direct comparison of our results with those of others was possible. It was therefore desirable to compare cerium with hydrogen peroxide plus activator. This note presents the results of such work.

The general procedure was the same as that described in detail for runs using hydrogen peroxide.[1,2] Starches were A. E. Staley commercial grade, defatted prior to use as previously described. Acrylonitrile was freshly redistilled prior to use. Ceric ammonium nitrate reagent grade was used as received.

For polymerization, a slurry of 100 g. of starch and 500 ml. of distilled water was deaerated by repeated evacuation and flushing with nitrogen. Thereafter, the mixture was kept under slight positive nitrogen pressure. The acrylonitrile was added and the mixture blended by stirring for 15 min. At this point, temperature was adjusted to the desired level. At time zero, ceric ammonium nitrate, dissolved in the minimum amount of very dilute nitric acid (pH 2) was added. For most runs (4–9 in Table I), ice bath cooling was applied at time zero and maintained until the temperature had dropped back to near the starting temperature. After 4 hr. of total reaction time, the solid product was recovered by filtration, thoroughly washed with water, and air dried. PAN content, grafting efficiencies of PAN and of starch, and the frequency of grafting were determined as described previously.[4]

Table I summarizes the runs made with cerium initiation. The data illustrate that polymerization starts very promptly and goes rapidly. Judging by the extent and duration of the temperature peak, well over 50% of the monomer is converted during the first several minutes. Final conversions of 90% or more are realized in every instance. In all these respects, the results are very similar to those realized with peroxide initiation.

Table II summarizes data on efficiency and frequency of grafting. The table shows that PAN is grafted very efficiently to unmodified starch with cerium at the 5–25 mmole level. With oxidized starch, PAN grafts less efficiently at the lower level of cerium. With cerium at 10 mmole, PAN grafts to the oxidized starch less efficiently but more frequently than to unmodified starch.

Changing the cerium level produces the changes illustrated in runs 5–7. PAN grafting efficiency increases with increasing cerium level in the 5–25 mmole range. This is difficult to explain, since increasing the initiator concentration ought to increase, rather than decrease, opportunity for the initiation of homopolymer. At the same time, starch grafting efficiency increases with increasing cerium concentration. This suggests the higher level of initiator generates more frequent grafting sites. This conclusion is consistent with the remainder of the observations, namely that increasing initiator level: (*1*) reduces the $\bar{M}_n$ value of the grafted PAN chains; (*2*) reduces the number of glucose units (in total starch) per grafted PAN chain; (*3*) does not change the number of glucose units in the grafted starch per PAN chain.

Increasing the monomer level (run 9 versus run 6) apparently has little effect on grafting efficiencies. Other effects could not be determined because of the unexpected partia insolubility in dimethyl formamide of the PAN recovered from the graft. That the overall product is not itself crosslinked is illustrated by its ready and complete solubility in hot dimethyl sulfoxide. The product was given a second 6-hr. reflux in 1*N* HCl to remove any remaining starch. The product still showed considerable gel in DMF, even though the infrared spectrum did not indicate presence of starch fragments. Pellon et al.[11] have reported that PAN undergoes irreversible chemical change on heating above 80°C. Such change might account for limited crosslinking of this particular sample during heating at reflux in aqueous HCl. Removal of starch under milder conditions would be advisable in future work involving PAN; Fanta et al. have recently reported

TABLE I

Graft Polymerizations with Cerium Initiation[a]

Run	Starch	Acrylonitrile, g.	Ce^{+4}, mmole/mole glucose unit of starch	Temperature, °C.		Time to max. temp., min.	Product		Monomer conversion, %
				Initial	Maximum[b]		Weight, g.	Contained PAN, wt.-%	
1	Unmodified	50	5	30	53	8	142	32.7	93
2	Unmodified	50	25	30	55	3	145	34.0	99
3	Oxidized	50	5	30	50	8	139	32.4	90
4	Unmodified	50	10	30	45	4	146	33.5	98
5	Oxidized	50	5	30	34	3	141	32.6	92
6	Oxidized	50	10	30	43	2	142	33.9	96
7	Oxidized	50	25	23	38	1	142	33.8	96
8	Oxidized	100	10	23	61	4	[c]	[c]	[c]
9	Oxidized	100	10	2	34	140[d]	189	49.5	94

[a] 100 g. starch (dry basis), 500 ml. water; 4.0 hr. reaction time.

[b] Ice bath cooling applied at time zero in runs 4–9.

[c] Gelled at maximum temperature, not worked up.

[d] Cooling applied continuously up to this point.

TABLE II

Efficiency and Frequency of Grafting

Run	Initiator		AN, g.	Grafting efficiency, %		$\bar{M}_n$ of grafted PAN	Glucose units per grafted PAN chain	
	Type	mmoles/mole of glucose unit in starch		PAN	Starch		Total starch	Grafted starch
1	Ce^{4+}	5	50	99	—	—	—	—
2	"	25	50	99	—	—	—	—
3	"	5	50	63	—	—	—	—
4	"	10	50	96	—	66,000	840	—
5	"	5	50	63	13	96,800	1960	255
6	"	10	50	79	35	45,100	690	241
7	"	25	50	94	55	30,200	390	214
9	"	10	100	83	39	[b]	—	—
	H_2O_2/Fe^{+2}/ascorbic acid[a]	10/—/2	50	96	79	33,000	390	310
	"	10/1/—	50	92	32	89,000	1090	350
	"	100/1/10	50	89	30	17,000	250	75
	"	100/1/10	100	81	32	64,000	410	130

[a] Data from previous paper.[4]

[b] PAN recovered from graft not completely soluble in DMF.

good results by oxidation with periodic acid followed by treatment with methanolic sodium methoxide.[12]

Generally, similar molecular weights and grafting efficiencies and frequencies are realized when peroxide is used instead of cerium (Table II, lower part). The most striking difference is in the response to increased initiator level. This raises grafting efficiencies of both PAN and oxidized starch when cerium is used. The opposite effect occurs with peroxide. This could arise from the fact that peroxide/activator is a potent initiator of homopolymerization in the absence of starch, whereas cerium is a very poor one.

Previously published work most nearly comparable to that here reported was done by Reyes et al.[8] Table III lists pertinent data derived from the most closely analogous runs.

TABLE III

	Reyes et al.	Present work, run 6
Solvent type	50/50 DMF/water	Water
Starch, g.	100	100
Volume of solvent, ml.	1234	500
Acrylonitrile, g.	65.4	50
Ce^{+4}, mmole/mole of glucose unit	10	10
Temperature, °C.	30	30–43
Monomer conversion	ca. 30% in 60 min., no further conversion in 100 min.	ca. 90% in 60 min.
PAN, parts/100 parts starch in product	23.7	51.3
Grafting efficiency, PAN, %	87	79
$\bar{M}_n$ of grafted PAN	25,900	45,100
Anhydroglucose units/PAN side chain	690	690

Chief differences in reaction conditions are that Reyes et al. used wheat starch in a relatively larger volume of solvent consisting of equal volumes of dimethylformamide and water. The amount and nature of the solvent apparently account for the much slower and less complete polymerization of acrylonitrile realized by Reyes et al. The efficiency and frequency of grafting PAN and the length of the grafted chains, are generally similar for the two techniques, so far as can be judged from the single run for which Reyes et al. report such data.

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BOOK REVIEWS

Chemical Reactions at High Pressures. K. E. Weale. E. and F. Spon Ltd., London, 1967. 349 pp. $12.50.

Since the publication of Hamann's *Physico-Chemical Effects of Pressure* in 1957, there have appeared several volumes dealing with the physical, geophysical, chemical, and engineering aspects of high pressure research. Although, jointly, these works cover nearly all major recent research topics, they contain the contributions of many authors and lack the unity of a monograph. For this reason, and because it covers the field of high pressure chemistry in greater detail than do earlier works, the present volume fulfills a definite need.

Dr. Weale who has been associated for many years with Imperial College of Science and Technology, one of the oldest and most influential centers of high pressure research, reviews high pressure chemistry comprehensively with special emphasis on research done in the past ten years. The volume contains several introductory chapters dealing with experimental technique and with the thermodynamics of high pressure in single and multiphase systems. Here, much of the discussion follows lines similar to those of Hamann's book, but new experimental results are presented. The inclusion of these chapters is appropriate, not only because nearly all kinetic treatments of high pressure reactions are based on transition state theory, but also because rather unfamiliar types of phase equilibria sometimes control the course of such reactions.

The later chapters include an up-to-date review of organic reactions in liquids and in gases. Gas reactions, in particular, had received relatively scanty treatment in earlier reviews, especially their kinetics, which are more difficult to treat here than in less compressible systems.

Of particular interest to the polymer chemist will be the most comprehensive treatment yet published of polymerization and polymerizability at high pressures, including copolymerization, one of the author's major interests. There is a brief discussion of the high pressure polymerization of ethylene. Anyone interested in the commercial potential of other high pressure polymerizations will find Chapters 8 and 9 useful background material.

The book reads well. Analysis and criticism of experimental results seem to me to have been carried to a level of sophistication appropriate to the subject matter.

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Polymer Fractionation. Manfred J. R. Cantow, Ed. Academic Press, New York, 1967. 527 pp.

The continuing need to explore the relation of polymer structure with solution and solid state properties has provided the impetus for polymer scientists to investigate many methods of separation and analysis utilizing a variety of physical principles. In contending with such structural features as molecular weight, branching, isomerization, stereoregularity and chemical composition and their distribution in a given material, it is not surprising that polymer fractionation and analysis has become rich and complex.

The breadth of this discipline is effectively encompassed for the first time in this single volume. *Polymer Fractionation* consists of fifteen chapters contributed by twenty authors. The volume is effectively begun with an excellent chapter by Huggins and Okamoto outlining the thermodynamic principles of fractionation of amorphous polymers by precipitation from dilute solution; some brief attention to crystalline systems and to efficiency of separation is included. This is followed by five chapters dealing with large scale methods of separation, i.e., fractional precipitation and solution, chromatography, gel permeation techniques, and thermal diffusion. Additional chapters deal with analytical methods which include sedimentation, diffusion (isothermal), turbidimetric titration, and the relation of viscoelastic and rheological properties of polymers to polydispersity of molecular weight.

Several chapters follow on the analysis of fractionation data to derive molecular weight distributions; an interesting chapter by Goodrich includes a discussion of the relation of polydispersity to reaction kinetics. A useful compendium of polymers and fractionation techniques to be found in the literature complete the text.

While much of the material has appeared recently in other reviews, it is nevertheless of value to have a single source book in this area. Many of the chapters are authoritatively written with a balanced combination of theory, experiment, and critical analysis. The chapters on Fractional Solution (Elliot), Chromatographic Fractionation (Porter and Johnson), Gel Permeation Chromatography (Altgelt and Moore), and Turbidimetric Titration (Giesekus) may be cited as illustrations. There is, unfortunately, some unevenness of presentation; some chapters are of poorer caliber being little more than bibliographies and in this respect, deficient in references to current literature.

While the published literature in polymer science is especially rich in investigations of molecular weight fractionation of linear, amorphous polymers which reflects itself in the emphasis placed on this subject in the book, it is regretted that theoretical studies and experimental findings on grafted, branched, stereoregular, and crystallizable polymers did not receive more attention. Also, almost no mention is made of biological polymers. Finally, this reviewer feels that the extensive recent literature on molecular weight effects in adsorption and desorption from solids of high specific surface area might well have deserved a separate chapter.

Overall, *Polymer Fractionation* is definitely to be recommended to all practising polymer scientists.

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Proceedings of the Second Tihany Symposium on Radiation Chemistry

This book contains the collected papers of the "Second Tihany Symposium on Radiation Chemistry" held in Tihany, Hungary in May 1966. In addition to the presented papers, there is also included some of the limited discussion which followed some of the papers.

The papers are drawn from many of the major centers of radiation chemistry research in Japan, the United States, and Western Europe with about half of the contributions coming from laboratories in Eastern Europe.

The volume is about 800 pages long and is divided into four sections (*1*) General Problems, Inorganic and Biological Systems; (*2*) Aqueous Solutions; (*3*) Organic Compounds; and (*4*) Polymers through which run traces of most of the main topics of radiation chemistry interest. One will find isolated papers of ESR spectroscopy, pulse radiolysis, energy transfer and luminescence, with little emphasis on any aspect.

The sections on Organic Compounds and Polymers comprise almost three-quarters of the total. The section on Polymers is most heavily weighted with papers on solid state polymerization and graft copolymerization. Actually, however, much of what is contained in this volume has already appeared in technical journals, and there is little in it to recommend to the experienced follower of the field.

The main advantage of this volume is that it contains, in a single place, a good cross-section of the radiation chemistry effort of the Eastern European laboratories.

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