

Ring-Opening Polymerization of Unsaturated Alicyclic Compounds

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Synopsis

The ring-opening polymerizations of cyclooctene, cyclododecene, 1,5-cyclooctadiene, 1,5,9-cyclododecatriene, 3-methylcyclooctene, and 3-phenylcyclooctene have been carried out by using a two-component catalyst system composed of ethylaluminum dichloride and tungsten hexachloride. NMR and infrared analyses of the respective polymers indicate structures which are consistent with a ring-cleavage mode of propagation. No evidence for double-bond shifts or transannular reactions during the polymerizations of 1,5-cyclooctadiene, 1,5,9-cyclododecatriene, 3-methylcyclooctene, and 3-phenylcyclooctene was found. The polymerizability of substituted, unsaturated, medium-sized alicyclic monomers suggests a convenient method for synthesis of certain perfectly alternating terpolymers. Since polymerizations occurred rapidly with little evolution of heat, it was concluded that entropy is a substantial contributor to the free energy of the ring-opening polymerization of medium-sized, unsaturated alicyclic monomers.

INTRODUCTION

The polymerization of cyclopentene by a ring-opening mechanism, leading to the formation of a solid, elastomeric polymer, was first disclosed by Eleuterio.¹ A linear, unsaturated repeat unit having the formula $[-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-]$ was suggested, where all the unsaturation is either *cis*- or *trans*-vinylene. The ring-opening polymerization of norbornylene (bicyclo-[2,2,1]-2-heptene), a highly strained, unsaturated alicyclic compound, has been reported in several publications.²⁻⁶ Catalysts such as lithium aluminum tetraalkyl in combination with titanium tetrachloride, trialkylaluminum complexed with a Lewis base in combination with titanium tetrachloride, or metal oxides of group VIb have all been claimed to be capable of causing ring-opening polymerization of norbornylene.

The use of organoaluminum compounds in combination with the chlorides of tungsten and molybdenum for the polymerization of cyclopentene, forming highly *trans*- or *cis*-polypentenamer, respectively, was unveiled recently by Natta et al.^{7,8} More recently, Natta et al.⁹ demonstrated that unsubstituted, unsaturated alicyclics of medium-sized rings, i.e., cycloheptene, cyclooctene, and cyclododecene, may undergo ring-opening polymerization forming linear unsaturated polymers with skeletal structures

homologous to polypentamer. The configuration of the vinylene double bonds in polyheptamer, polyoctamer, and polydodecener, prepared under the polymerization conditions described by Natta and co-workers,⁹ was found to be mostly *trans*-, and their polymers exhibited high degrees of crystallinity.

The work reported in the present paper concerns the ring-opening polymerization of unsaturated alicyclic monomers possessing medium-sized rings of eight or twelve carbon atoms. Included are rings possessing two and three double bonds and substituted rings. In particular, it was anticipated that polymers obtained from simple ring-opening of 1,5-cyclooctadiene and 1,5,9-cyclododecatriene would be identical to a polybutadiene of all-1,4 structure. Therefore, it was of interest to establish whether transannular reactions would interfere with the ring-opening process, since these reactions occur frequently in medium-sized rings. The polymerization catalyst system employed throughout the work presented in this paper was a combination of tungsten hexachloride and ethylaluminum dichloride.

EXPERIMENTAL

Materials

Cyclooctene, cyclododecene, *cis,cis*-1,5-cyclooctadiene and a nominally 40/60 mixture of *cis,trans,trans*- and *trans,trans,trans*-1,5,9-cyclododecatriene were supplied by Columbian Carbon Company. Prior to polymerization, cyclooctene and 1,5-cyclooctadiene were purified by distillation from metallic sodium under an atmosphere of dry nitrogen. Cyclododecene and 1,5,9-cyclododecatriene were distilled under reduced pressure from metallic sodium.

Standard Grignard procedures were used to prepare 3-methylcyclooctene and 3-phenylcyclooctene from 3-bromocyclooctene. Careful fractionation of 3-methylcyclooctene under nitrogen atmosphere yielded material indicated to be 99% pure by gas chromatography, b.p. 159–160°C., n_D^{30} 1.4605 (reported¹⁰ b.p. 77–78°C./56 mm., n_D^{25} 1.4622). Fractionation of 3-phenylcyclooctene under reduced pressure afforded material indicated to be 99% pure by gas chromatography, b.p. 95°C./1.1 mm., n_D^{30} 1.5403. Structures of these monomers were confirmed by their NMR spectra, which were obtained with a Varian A-60 spectrometer. Prior to polymerization, solutions of the various monomers in benzene were dried by passing them through a silica-gel column under an atmosphere of dry nitrogen.

Reagent-grade, thiophene-free benzene was dried by passing it through a silica-gel column. Tungsten hexachloride, supplied by Climax Molybdenum Company, was purified by sublimation of the more volatile impurity tungsten oxytetrachloride at 200°C. in a stream of dry nitrogen. Ethylaluminum dichloride, supplied by Texas Alkyls, Inc., as a 25% solution in hexane, was used without further purification. The catalyst components were employed as solutions in benzene. Benzene solutions of tungsten hexachloride (0.05*M*) and ethylaluminum dichloride (0.2*M*) were freshly prepared before being used.

Polymerizations

Polymerizations were conducted in dry, 4-oz. screw-cap bottles fitted with punctured caps and self-sealing gaskets lined with Teflon, and filled with dry nitrogen. For all of these polymerizations, monomer concentrations were 20% by volume in benzene. Each solution was sparged for 1 min. with dry nitrogen before the bottle was sealed. Catalyst solutions were introduced by hypodermic syringes. All polymerizations were conducted at ambient temperature, with the exception of cyclododecatriene polymerization which was carried out at 50°C., and were terminated with approximately 4 ml. of a 6% solution of 2,6-di-*tert*-butyl-*p*-cresol in an 80/20 mixture of benzene and methanol. Evolution of heat during polymerization was always slight, in contrast to conventional addition polymerizations, so that thermostatic control of temperature was unnecessary. The relevant data from these polymerizations are presented in Table I.

TABLE I
Polymerization of Unsaturated Alicyclic Monomers

Expt. no.	Monomer	Monomer ^a		Reaction time, min.	Yield, % ^b	Inherent viscosity, dl./g. ^c	Gel, %	Extractables, % ^d
		WCl ₆	Al ^a W					
1	Cyclooctene	6400	4	30	84	3.54	4	14
2	"	6400	6	30	84	3.38	0	16
3	"	6400	10	30	73	2.72	2	16
4	Cyclododecene	4200	6	30	87	n.d. ^e	n.d.	13
5	"	4200	8	30	94	n.d.	n.d.	10
6	1,5-Cyclooctadiene	3200	4	30	61	1.42	6	21
7	"	3200	6	30	87	1.43	4	19
8	"	3200	8	30	98	1.43	3	18
9	"	3200	10	30	47	1.60	3	23
10	1,5,9-Cyclododecatriene ^f	1450	2	240	46	0.34	14	44
11	"	1450	4	240	73	0.46	50	20
12	"	1450	6	240	35	0.32	10	42
13	"	2900	4	240	68	0.52	17	33
14	"	2900	6	240	62	1.12	5	19
15	3-Methylcyclooctene	1650	1	30	21	1.41	0	23
16	"	1650	2	30	24	1.27	0	22
17	"	1650	3	30	27	1.22	0	20
18	"	1650	4	30	90	2.30	5	21
19	"	1650	6	30	8	1.08	0	17
20	3-Phenylcyclooctene	1300	1	15	1	1.83	0	n.d.
21	"	1300	2	15	23	2.26	0	n.d.
22	"	1300	3	15	17	1.72	0	n.d.
23	"	1300	4	15	30	1.27	0	n.d.
24	"	1300	6	15	12	1.07	0	n.d.

^a Molar ratio.

^b For poly(3-phenyl)octenamer, yields were based on polymer recovered after extraction of monomer and low molecular weight extractables fraction with a 50/50 benzene-isopropanol mixture.

^c Values for poly(3-methyl)- and (3-phenyl)octenamers are for polymers after removal of extractables. All values determined in benzene at 30°C.

^d Per cent of low molecular weight material in the polymer (see Analyses).

^e Not determined.

^f Polymerizations were carried out at 50°C.

Analyses

Low Molecular Weight Extractables. Preweighed polymer samples (~10 g.) were placed in 100 ml. of a 50/50 hexane-isopropanol mixture

TABLE II
Relative Areas from NMR Analyses of Polymers Obtained by
Ring-Opening Polymerization

Polymer	Vinylene protons		Allyl protons		Other protons	
	Theory	Observed	Theory	Observed	Theory	Observed
Polyoctenamer	2	1.80	4	4.00	8	8.20
Polydodecenamer	2	1.80	4	4.22	16	15.98
Poly-1,5-octadienamer	4	3.92	8	8.08	—	—
Poly-1,5,9-dodecatrienamer	6	6.06	12	11.94	—	—
Poly(3-methyl)-octenamer	2	1.87	3	3.22	11	10.91
Poly(3-phenyl)-octenamer	2	1.75	1 ^a	0.82	15 ^b	15.37

^a Benzylic proton only.

^b Comprised of methylene and aromatic protons; respective observed relative areas: 10.37 and 5.00 (theory: 10 and 5).

[benzene-isopropanol for poly(3-methyl)octenamer] for 72 hr. at ambient temperature. The extracting mixtures were replaced with fresh mixtures every 24 hr. After extraction, the residual polymers were dried, weighed, and the low molecular weight extractable fractions were determined by difference. The pertinent data are included in Table I.

NMR and Infrared Spectra. Carbon tetrachloride solutions of polymers obtained by ring-opening polymerization (~5% concentration) were examined with a Varian A60 NMR spectrometer at room temperature. Table II contains data for the relative peak areas corresponding to the various protons in these polymers, as well as the predicted area ratios.

The infrared spectra of carbon disulfide solutions of the polyalkenamers were obtained with a Perkin-Elmer Model 521 spectrometer. Quantitative estimations of *trans*-vinylene content were based on a molar absorptivity value determined from a high *trans*-polybutadiene standard: $\epsilon_{10.35}(\text{CS}_2) = 125.2 \text{ mole}^{-1} \text{ cm.}^{-1}$. For all polyalkenamers the amount of *trans*-vinylene structures fell in the 40–70% range, and since NMR analyses indicated only vinylene type unsaturation it was assumed that the rest was *cis*-vinylene.

RESULTS AND DISCUSSION

The ring-opening polymerizations of unsaturated alicyclic compounds of medium-sized rings, with the use of a two-component catalyst system comprising ethylaluminum dichloride and tungsten hexachloride, proceeded rapidly to high conversions yielding polymers of high molecular weight. Increasing ring size of the alicyclics did not appear to reduce significantly the yield of polymer, contrary to the results of Natta and co-workers.⁹ A general comparison of the results obtained in the present work with those

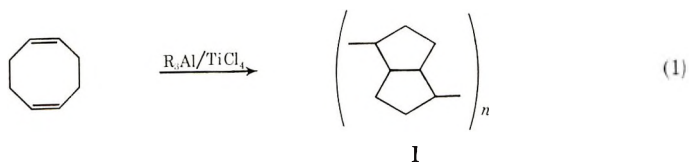
TABLE III
Comparison Between Alkylaluminum Chlorides in the
Polymerization of Cyclooctene with Tungsten Hexachloride

Aluminum compound	Al	Monomer	Monomer, vol.-%	Conditions	Yield, %
	W	WCl ₆			
(C ₂ H ₅) ₃ Al ^a	5	300	100	1 hr. -20°C.; then 69 hr./30°C.	60
C ₂ H ₅ AlCl ₂	4	6400	20	0.5 hr./25°C.	84

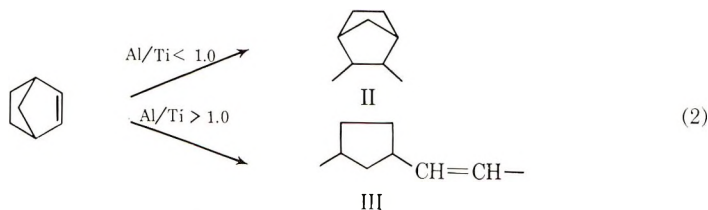
^a Data of Natta et al.⁹

of Natta and co-workers⁹ indicates ethylaluminum dichloride to be much more active, in combination with tungsten hexachloride, than the trialkylaluminum catalyst system towards the ring-opening polymerization of cyclooctene and cyclododecene. This may be seen from the rather typical examples given in Table III.

The ring-opening polymerization of unsaturated alicyclic compounds of medium-sized rings containing more than one double bond in the ring is an interesting feature of the present work. Experiments 6-9 and 10-14 in Table I contain data for the polymerization of 1,5-cyclooctadiene and 1,5,9-cyclododecatriene, respectively. It has been reported by Reichel et al.¹¹ that 1,5-cyclooctadiene, in the presence of a Ziegler-type catalyst formed by reacting triisobutylaluminum and titanium tetrachloride in a molar ratio of 1:2, yields a substantially saturated polymer through a transannular polymerization. Reichel et al. suggested a repeat unit with a structure (I) corresponding to bicyclo[3,3,0]octane [eq. (1)].

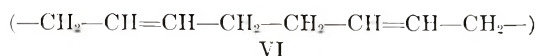
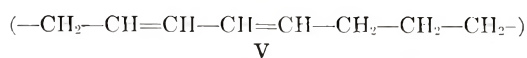
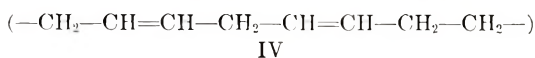


The polymers from 1,5-cyclooctadiene and 1,5,9-cyclododecatriene, as reported in Table I, prepared in the presence of ethylaluminum dichloride and tungsten hexachloride, are products of ring-opening polymerization. This is evident from the NMR analyses which are presented in Table II. The ability of an unsaturated alicyclic compound to undergo two modes of polymerization, depending on the catalyst employed, had been demonstrated earlier on bicyclo[2,2,1]-2-heptene.^{2,3,12} With a molar ratio of lithium aluminum tetraheptyl to titanium tetrachloride smaller than one, a low yield of a stiff, brittle, completely saturated polymer is produced. However, with an excess of lithium aluminum tetraheptyl a polymer containing one double bond per repeat unit is obtained. Thus, the structures II and III have been suggested for the polymers obtained from bicyclo[2,2,1]-2-heptene:



Transannular polymerization of 1,5-cyclooctadiene leads to a stiff material, as a consequence of the rigid structure of the repeat unit, bicyclo[3,3,0]-octane.¹¹ On the other hand, the polymer obtained by ring-opening polymerization of 1,5-cyclooctadiene, poly-1,5-octadienamer, is typically rubbery with a low glass transformation temperature, since its structure is equivalent to polybutadiene with all of its repeat units in the 1,4-configuration. In addition, the polymer obtained by ring-opening polymerization of 1,5,9-cyclododecatriene must possess the same skeletal structure as the polymers obtained by the ring opening of 1,5-cyclooctadiene. The NMR results presented in Table II show that this is the case indeed, since the ratio of allylic to vinylic protons is essentially constant.

Figure 1 illustrates a comparison of the NMR spectra of 1,5-cyclooctadiene and poly-1,5-octadienamer.¹³ Except for some shift of peak positions, the NMR spectrum of poly-1,5-octadienamer is essentially the same as the spectrum of the monomer, 1,5-cyclooctadiene. The spectra indicate the presence of two types of hydrogens, vinylic and allylic, and the theoretical ratio of the peak areas is 1:2. The fact that this ratio remains unchanged when 1,5-cyclooctadiene is polymerized to poly-1,5-octadienamer, and no new peaks appear in the NMR spectrum of the polymer, suggests that double bond shifts do not occur during the ring-opening polymerization of 1,5-cyclooctadiene. Structures IV and V, having hydrogens in more than two positions in relation to the carbon-carbon double bonds, should lead to more than two distinct peaks in the NMR spectra:



Structure VI, equivalent to 1,4-polybutadiene, has hydrogens in only two different positions in relation to the carbon-carbon double bond and, thus, should yield only two distinct peaks in the NMR. Figure 1 indicates that no shift of double bonds occurs during the ring-opening polymerization of 1,5-cyclooctadiene.

The presence of a hydrocarbon substituent at the allylic position of the cyclooctene double bond did not interfere with the normal mode of ring-opening polymerization, as indicated from the structures of the polymers obtained from 3-methylcyclooctene and 3-phenylcyclooctene. Infrared spectra of these polymers indicated approximately one-half of the vinylic

unsaturation to have the *trans* configuration. The NMR results presented in Table II confirm the fact that the double bonds of the monomers were preserved in the polymers. The vinylic proton contents of poly(3-methyl)octenamer and poly(3-phenyl)octenamer were approximately 96% and 88% of theory, respectively. The above results also indicated the absence of double bond migration in the system. For example, there is a

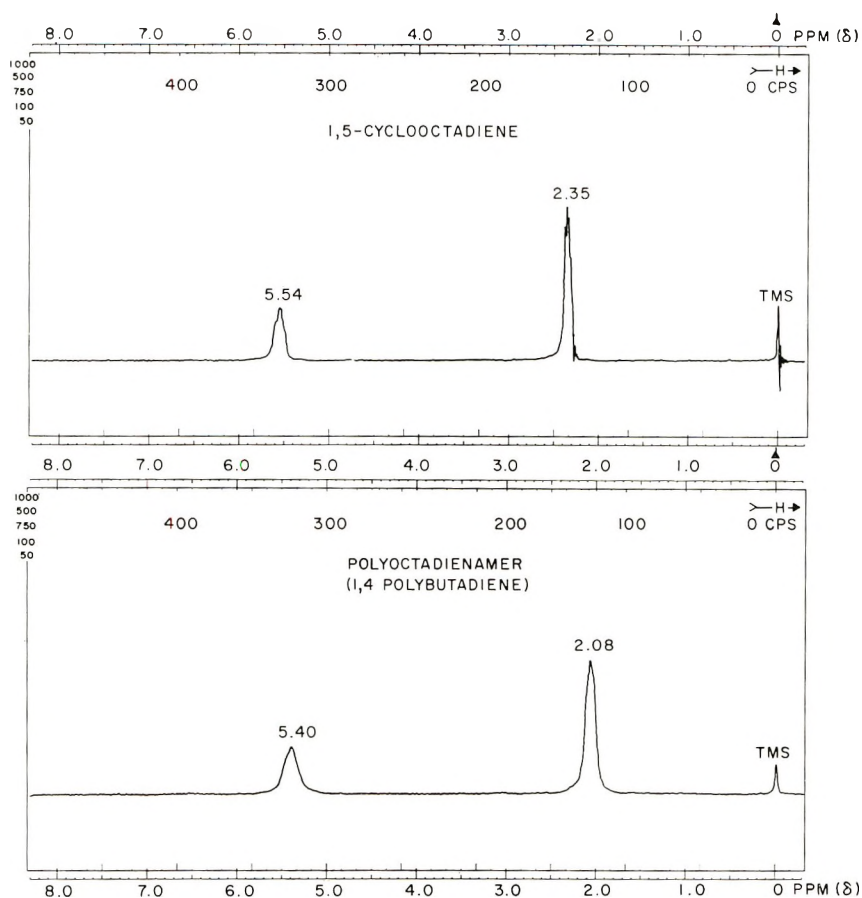
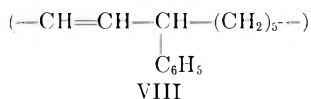
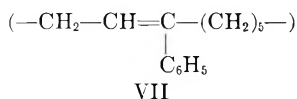
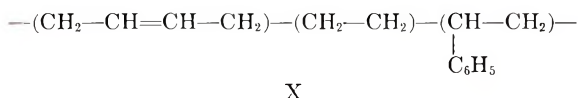
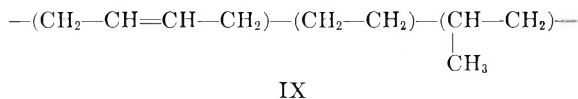


Fig. 1. Comparison of the NMR spectra of 1,5-cyclooctadiene and poly-1,5-octadienamer.¹³

substantial driving force for rearrangement of the double bond in 3-phenylcyclooctene to the conjugated structure VII. The NMR spectrum of such a structure would indicate only one vinylic proton in the repeat unit, and no benzylic protons. Instead, the observed spectrum was consistent with the proposed structure VIII. Although the catalyst system clearly possesses a certain Lewis acid character, catalyst concentration, time, and temperature tended to minimize rearrangement processes.



The feasibility of polymerizing substituted, medium ring-size, unsaturated alicyclics via ring opening, in the absence of secondary reactions, is of utmost importance as it should provide a convenient route to several perfectly alternating interpolymers. For example, the polymers obtained by ring-opening polymerizations of 5-methylcyclooctene and 5-phenylcyclooctene will have structures IX and X, respectively. These are equivalent to perfectly alternating terpolymers of butadiene-ethylene-propylene (IX) and butadiene-ethylene-styrene (X).



The occurrence of gel during the ring-opening polymerization of cyclooctene and 1,5-cyclooctadiene is a problem of only minor importance, when a combination of ethylaluminum dichloride and tungsten hexachloride is employed as the catalyst and polymerization conditions are maintained as specified in the experimental section. However, the presence of a low molecular weight, oily, extractable fraction appears to be a general feature which accompanies the ring-opening polymerization of unsaturated alicyclic monomers. The quantitative measurement of this low molecular weight fraction is based on a separation process arbitrarily chosen for convenience, and presumably other extracting systems would give somewhat different values.

The formation of extractables and the characteristic structure of the various components in these extractables, which contribute substantially to the understanding of these ring-opening polymerization systems, will be treated extensively in a forthcoming paper.

Throughout the course of the present work it was observed that unsaturated alicyclic monomers of medium-sized rings polymerized rapidly with very little evolution of heat. One is led to the conclusion that entropy is a substantial contributor to the free energy of the ring-opening process.

The authors are indebted to R. M. Pierson and Dr. K. W. Scott for their interest and helpful discussions, and to J. K. Clark for the infrared analyses.

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Résumé

Les polymérisations avec ouverture de cycle de cyclooctène, cyclododécène, 1,5-cyclooctadiène, 1,5,9-cyclododécatriène, 3-méthylcyclooctène et 3-phénylcyclooctène ont été effectuées en utilisant un système catalyseur à deux composants contenant du dichlorure d'éthylaluminium et de l'hexachlorure de tungstène. Les analyses NMR et infrarouges des polymères respectifs indiquaient des structures qui s'accordaient avec une rupture du cycle en cours de propagation. Aucune évidence pour des glissements de doubles soudures ou de réactions transannulaires en cours de polymérisation de 1,5-cyclooctadiène, 1,5,9-cyclododécatriène, 3-méthyl- et 3-phénylcyclooctène n'a été trouvée. La polymérisabilité de monomères substitués insaturés alicycliques de grandeur moyenne suggère une méthode convenable de synthèse de certains terpolymères parfaitement alternant. Puisque les polymérisations de passent rapidement avec faible dégagement de chaleur, on en conclut que l'entropie est un facteur de contribution substantiel à l'énergie libre de la polymérisation par ouverture de cycle de monomères alicycliques insaturés de grandeur moyenne.

Zusammenfassung

Die Ringöffnungspolymerisation von Cycloocten, Cyclododecen, 1,5-Cyclooctadien, 1,5,9-Cyclododekatrien, 3-Methylcycloocten und 3-Phenylcycloocten wurde mit einem aus Äthylaluminiumdichlorid und Wolframhexachlorid aufgebauten Zweikomponenten-Katalysatorsystem durchgeführt. NMR- und IR-Analysen der betreffenden Polymeren ergeben Strukturen, die einem Wachstum durch Ringspaltung entsprechen. Es wurden keine Hinweise auf Doppelbindungsverschiebungen oder transannuläre Reaktionen während der Polymerisation von 1,5-Cyclooctadien, 1,5,9-Cyclododekatrien, 3-Methyl- und 3-Phenylcycloocten gefunden. Die Polymerisierbarkeit substituierter, ungesättigter alicyclischer Monomere mittlerer Größe liefert eine bequeme Methode zur Synthese gewisser, vollkommen alternierender Terpolymerer. Da die Polymerisationen mit geringer Wärmeentwicklung rasch vor sich gingen, wird der Schluss gezogen, dass die Entropie einem wesentlichen Beitrag zur freien Energie der Ringöffnungspolymerisation ungesättigter alicyclischer Monomere mittlerer Größe bildet.

Received September 12, 1966

Revised November 28, 1966

Prod. No. 5336A

Aminobutadienes. V. Polymers of 1-Phthalimido-1,3-butadiene and 1-Succinimido-1,3-butadiene*

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Synopsis

The radical polymerizations of 1-phthalimido-1,3-butadiene (1-PB) and 1-succinimido-1,3-butadiene (1-SB) were carried out in bulk and in solution. The polymers obtained had reduced viscosities in the ranges of 1.0-4.0 (1-PB) and 0.2-0.6 (1-SB). Both polymers had a similar softening point of 190-200°C. The radical polymerization of 1-phthalimido-1,3-butadiene clearly showed a tendency to give crosslinked polymer. Steric arguments about these polymer structures as a result of the infrared and ozonolysis data led to the conclusion that these polymers contained approximately 20% of the 3,4 form but no 1,2 configuration, and, therefore, that the 1,4 addition was preferred.

INTRODUCTION

Some reports from this laboratory on the syntheses and reactivities of aminobutadiene monomers and related compounds, have been previously published.¹⁻⁷ An earlier study² indicated that on electrophilic addition the imido group of such monomers acts as an electrodonative group and allows for formation of the 1,4 adducts. For instance, 1-chloro-1-phthalimido-2-butene and 1-chloro-3-phthalimido-2-butene were obtained on hydrogen chloride addition to 1-phthalimido-1,3-butadiene and 2-phthalimido-1,3-butadiene, respectively.

The present paper deals with the radical polymerizations of 1-phthalimido-1,3-butadiene (1-PB) and 1-succinimido-1,3-butadiene (1-SB) in bulk and in solution. Some properties of the polymers and modes of monomer arrangement in the polymer chains will be discussed.

RESULTS AND DISCUSSION

Bulk Polymerization

Figure 1 shows the relationships between the polymerization time, the polymer yield, and the reduced viscosity of the polymer which results during bulk polymerizations in the absence of initiator. 1-Phthalimido-1,3-butadiene polymerized easily at the melting point, 116°C., and the yield

* For the preceding papers in this series, see Terada and Murata.^{1,2}

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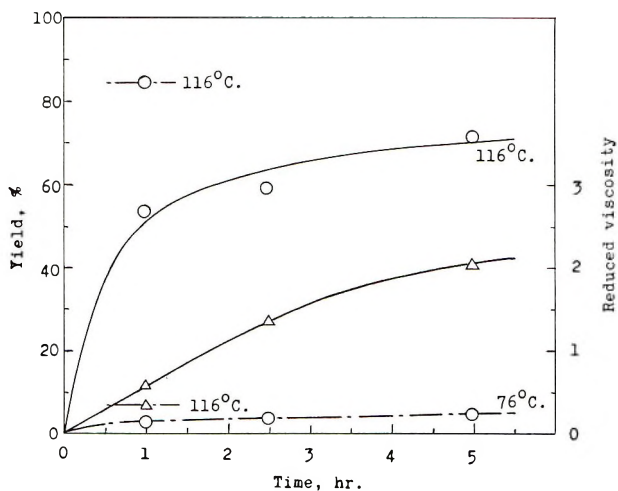


Fig. 1. Bulk polymerization of (—) 1-PB and (---) 1-SB in the absence of benzoyl peroxide: (O) polymer yield; (Δ) viscosity.

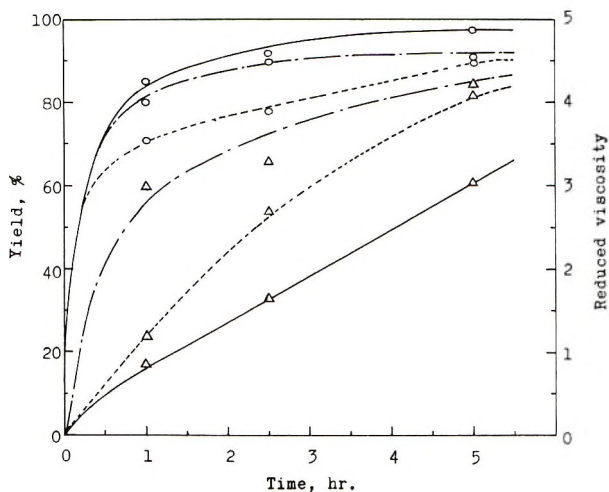


Fig. 2. Bulk polymerization at 116°C. of 1-phthalimido-1,3-butadiene in the presence of (—) 1.0 mole-% benzoyl peroxide (BPO), (---) 0.5 mole-% BPO, and (- - -) 0.1 mole-% BPO: (O) polymer yield; (Δ) viscosity.

and viscosity increased with an increase of the polymerization time. On the other hand, 1-succinimido-1,3-butadiene cannot polymerize at 76°C., but after 1 hr. at 116°C. gave a high polymer yield of 84%. Therefore, the polymerizability of 1-succinimido-1,3-butadiene is larger than that of 1-phthalimido-1,3-butadiene. This difference may be due to the higher steric requirement of the phthalimido monomer for undergoing polymerization.

Figures 2 and 3 illustrate the results of the bulk polymerization of 1-phthalimido-1,3-butadiene in the presence of benzoyl peroxide at 116°C. A homogeneous gel formation was observed on polymerization for 5 hr. in

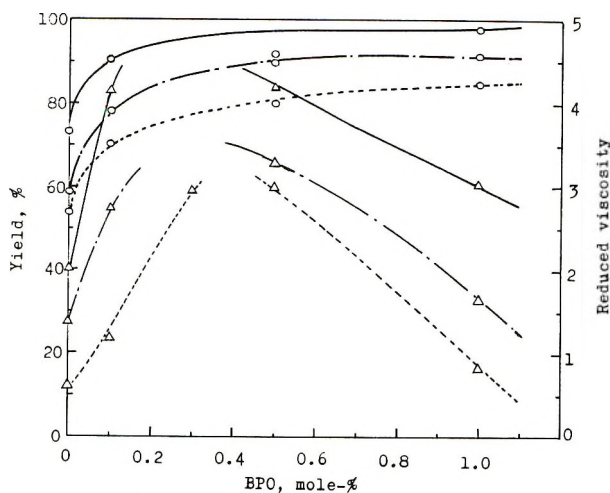


Fig. 3. Bulk polymerization of 1-phthalimido-1,3-butadiene in the presence of benzoyl peroxide at 116°C., reaction for (—) 5 hr., (---) 2.5 hr., and (- - -) 1 hr.: (O) polymer yield; (Δ) viscosity.

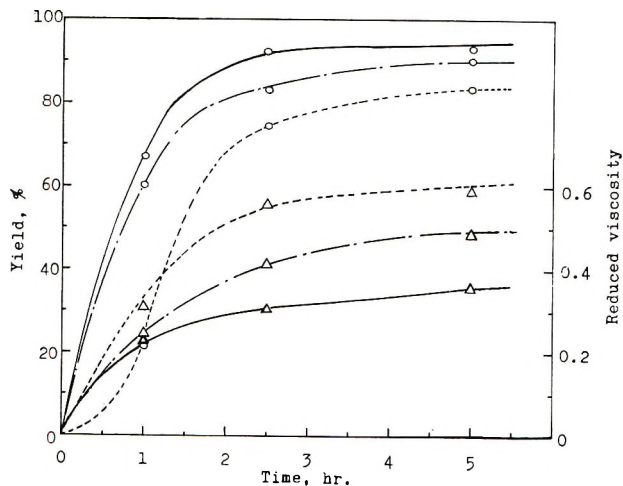


Fig. 4. Bulk polymerization at 76°C. of 1-succinimido-1,3-butadiene in the presence of (—) 1.0 mole-% BPO, (---) 0.5 mole-% BPO, and (- - -) 0.1 mole-% BPO: (O) polymer yield; (Δ) viscosity.

the presence of 0.3 mole-% of benzoyl peroxide, while under other conditions no insoluble polymer was obtained. The viscosity continued to increase with the longer reaction time as less monomer remained in the polymerization system (Fig. 2). These observations can be explained by the occurrence of intermolecular crosslinking between the polymers formed originally by the normal polymerization course.

Each of the viscosity curves in Figure 3 seems to have a maximum in the region of catalyst concentrations of 0.1–0.3 mole-%, and extreme gelation

was observed in the case of the 5-hr. polymerization as was described above. It is well known that the molecular weight of polymer in a vinyl polymerization system generally remains constant and therefore is not affected so much by the monomer conversion, and also that the increase of the initiator concentration usually results in a decrease in polymer viscosity. The appearance of these maxima should be due to the two competitive effects of the catalyst concentration on polymer growth, one is acceleration of crosslinking to raise the molecular weight and the other a decrease in viscosity. If a small amount of the catalyst is used, a polymer of higher molecular weight results, and consequently the crosslinking effect to such a higher polymer must be operative. That is, a further increase of the catalyst concentration over the maximum point results in the usual viscosity decrease, the crosslinking effect which tends to increase the molecular weight being cancelled out. The tendency of the maximum point to shift toward the upper left hand in Figure 3 with increasing polymerization time also supports these explanations.

A sample of this soluble polymer is changed into an insoluble polymer on storing over several months.

Figures 4 and 5 show the results of the polymerization of 1-succinimido-1,3-butadiene, in which the polymer yield is greatly increased by the use of benzoyl peroxide, while in its absence there is no polymerization at 76°C. No maximum viscosity is observed in this case.

Solution Polymerization

Table I shows the effects of solvent in the solution polymerization of 1-phthalimido-1,3-butadiene. *sym*-Tetrachloroethane and 1,2-dichloroethane were chosen as solvents since they gave better polymer yields. Reduced viscosities of the resulting polymers were comparable to those of polymer obtained by bulk polymerization of 1-succinimido-1,3-butadiene, but considerably lower than those obtained in the bulk process for 1-phthalimido-1,3-butadiene. Figure 6 summarizes the results of solution polymerization.

TABLE I
Solution Polymerization of 1-Phthalimido-1,3-butadiene in Various Solvents
in the Presence of 1.0 mole-% of Benzoyl Peroxide at 60°C.

Wt. monomer, mg.	Solvent	Vol. solvent, ml.	Time, hr.	Yield, wt.-%	Solubility of polymer
300	Benzene	3.00	6	3.7	Insoluble
300	Carbon tetrachloride	3.00	6	3.3	Insoluble
300	1,2-Dichloroethane	3.00	6	5.9	Soluble
300	1,2-Dibromoethane	3.00	6	6.3	Soluble
300	<i>sym</i> -Tetrachloroethane	3.00	6	8.8	Soluble
300	<i>sym</i> -Tetrachloroethane	2.00	6	8.6	Soluble
300	<i>sym</i> -Tetrachloroethane	1.00	6	11.0	Soluble

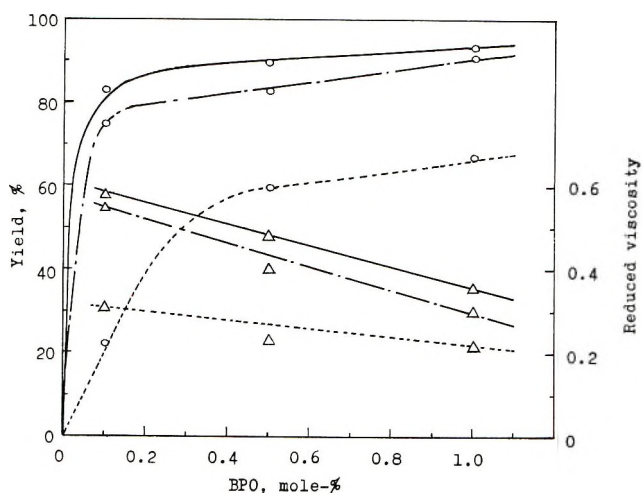


Fig. 5. Bulk polymerization at 76°C. of 1-succinimido-1,3-butadiene in the presence of benzoyl peroxide, reaction for (—) 5 hr., (— · —) 2.5 hr., and (- - -) 1 hr.: (O) polymer yield; (Δ) viscosity.

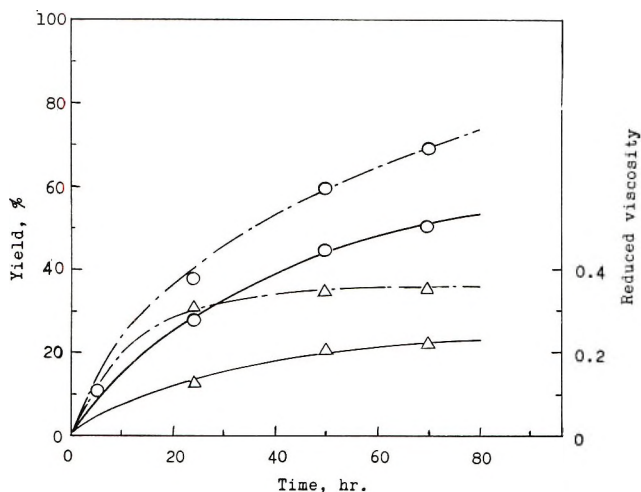


Fig. 6. Solution polymerization of (—) 1-PB and (— · —) 1-SB: (O) polymer yield; (Δ) viscosity. Monomer, 0.300 g.; BPO, 1 mole-%; in 1.00 ml. of *sym*-tetrachloroethane at 60°C.

Polymer Properties

The polymer of 1-phthalimido-1,3-butadiene obtained from bulk polymerization was a light yellow mass, which might be contaminated by residual monomer. 1-Succinimido-1,3-butadiene polymer was a colorless solid. After fractional precipitation, both the samples were obtained as white powder having softening points (measured by the capillary tube method) in the range of 190–200°C. Both are soluble in chloroform,

chlorobenzene, 1,2-dibromoethane, 1,2-dichloroethane, *sym*-tetrachloroethane, phenol, anisole, dioxane, dimethylformamide, nitrobenzene, pyridine, and benzene-methanol, but insoluble in acetone, carbon disulfide, carbon tetrachloride, diethyl ether, ethyl acetate, hydrocarbons, and carbinols.

Chemical Structures of the Polymers

The infrared spectrum of 1-phthalimido-1,3-butadiene polymer (Fig. 7) has a very strong absorption band at 964 cm^{-1} assignable to the internal *trans* disubstituted ethylenic linkage in the main chain of the polymer. This band is too intense to be attributed to the external double bond which would result from 3,4-addition polymerization. The absorption intensity by the 3,4 polymer can be estimated by comparison with the intensity of the same 1,2-double bond in the original monomer.

The ozonolysis study of this polymer structure indicated that it has approximately 20% of the 3,4 configuration. The 1,2 configuration can be excluded by the lack of formaldehyde formation and vinyl absorption in the above infrared spectrum. Although the isolation of α -phthalimido-

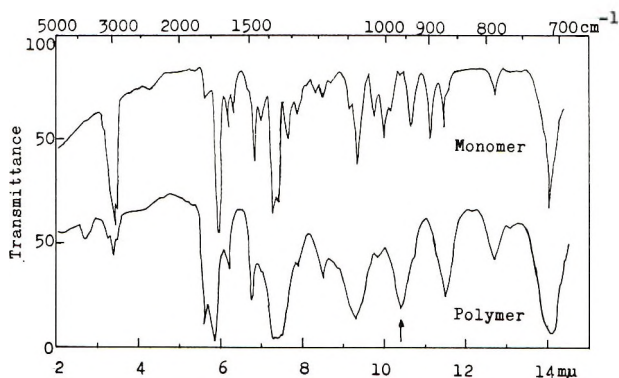


Fig. 7. Infrared spectra of 1-phthalimido-1,3-butadiene monomer and polymer.

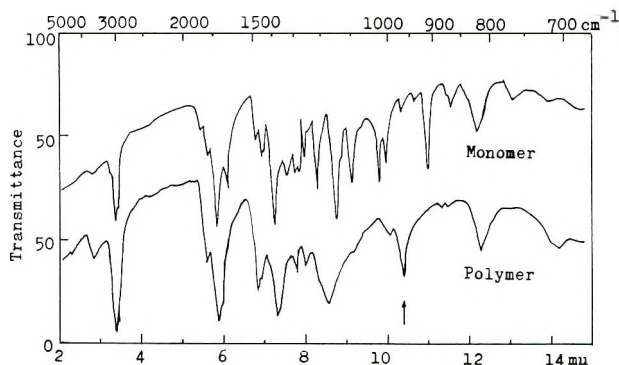
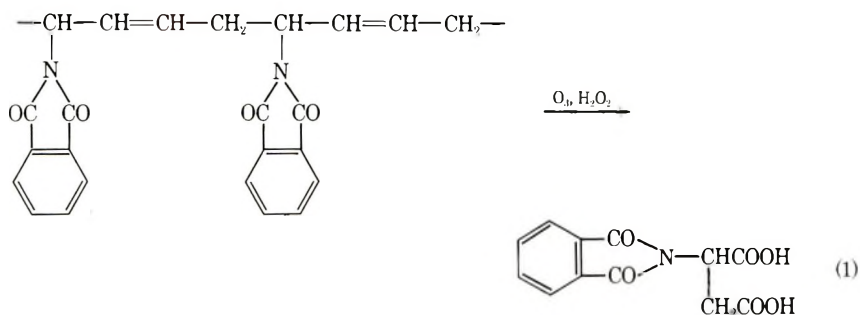


Fig. 8. Infrared spectra of 1-succinimido-1,3-butadiene monomer and polymer.

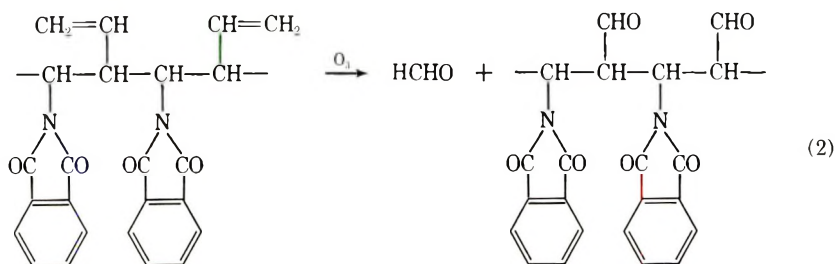
succinic acid from the degradation product has not been accomplished yet, the above results lead us to conclude that the configuration obtained as a result of 4,1 addition should be preferred, and this product should therefore constitute the remainder. The true 1,4-addition mode initiating at C₁ may be excluded by reason of the orientation of electrophilic additions to the monomers² and for steric reasons.

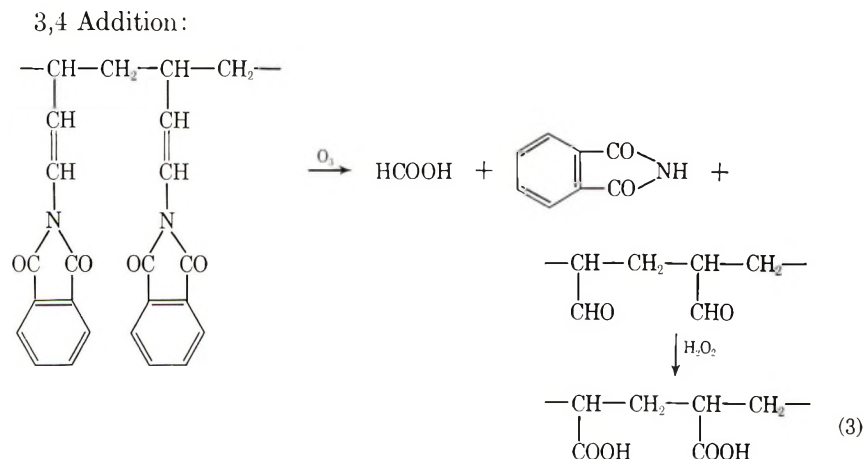
The same structure argument can be used for the infrared spectral data for the 1-succinimido-1,3-butadiene (Fig. 8), proving primarily 1,4 configuration. The ozonolysis study showed approximately 20% of the 3,4 configuration and no 1,2 configuration. Although a small amount of α -succinimidosuccinic acid was isolated as the diethyl ester from the degradation product after oxidation with hydrogen peroxide and esterification, attempts to determine the extent of 1,4 configuration by this method were unsuccessful. On the other hand, a small amount of succinic acid was isolated as a crude diethyl ester in addition to the ethyl α -succinimidosuccinate. This, however, does not mean a tail-to-tail monomer arrangement on 1,4-addition polymerization, because this monomer arrangement must be accompanied by succinic aldehyde formation. If such aldehyde formation was actual, it might be detected during the volatile aldehyde test, and also would be absent in the benzene-insoluble residue which was used for the above esterification as the sample. Therefore, this succinic acid must be produced by hydrolysis of such compounds as α -succinimidosuccinic acid during the esterification procedure. The ozonolysis reactions and expected products are given in eqs. (1)–(3).

1,4 Addition:



1,2 Addition:





EXPERIMENTAL

Materials

1-Phthalimido-1,3-butadiene and 1-succinimido-1,3-butadiene were prepared according to the procedures described previously¹ and obtained as yellow needles with a melting point of 114.5–116°C. and as white crystals with a melting point of 75–76°C., respectively. Benzoyl peroxide as an initiator was purified by repeated precipitation into methanol from a chloroform solution and then dried under vacuum, m.p. 104°C. The solvents were purified by the usual manners according to Kuwata.⁸

Procedures

The polymerization procedures were carried out as reported previously.⁵ The solution polymerization was almost the same as in the bulk process, and 0.300 g. of each of the monomers was polymerized in a solvent at 60 ± 1°C. in the presence of the 1.0 mole-% equivalent of benzoyl peroxide.

The relative viscosity of the polymers was determined in 0.50% *sym*-tetrachloroethane solution at 30 ± 0.01°C. with the use of an Ostwald viscometer.

Infrared Spectra

The infrared spectra were taken in a Nujol mull with a Perkin-Elmer infrared spectrometer, Model 21 (NaCl) (Figs. 7 and 8). Each of the polymer samples was also used in the ozonolysis study.

Ozonolysis

1-Phthalimido-1,3-butadiene Polymer. Dilute ozone prepared from air was passed for 5 hr. at -15°C. into a solution of the sample (1.30 g., 6.53 mmole, in 75 ml. of chloroform) obtained from the catalyst-initiated bulk polymerization of 1-PB at 116°C. After the removal of the solvent under

reduced pressure at room temperature, 40 ml. of water was added, and the temperature of the system was gradually raised to a boil. The water was distilled off to steam distill any of the volatile products, and this procedure was repeated. The distillate showed 8.68×10^{-4} mole of formic acid, and no formaldehyde-dimeton or any 2,4-dinitrophenylhydrazones. This amount of formic acid corresponds to 13.5 mole-% of the original polymer sample and should therefore be equivalent to the percentage of the 3,4 configuration.

The residue obtained from the above distillation procedure was immersed in 100 ml. of 3% hydrogen peroxide in order to oxidize and convert the remaining aldehyde compounds to the corresponding acids. The system was heated and allowed to boil to complete the reaction, and, after evaporation under reduced pressure, was boiled with a large amount of hot water and separated into two parts, an aqueous solution and a water-insoluble residue. The washings of the latter residue were combined with the former aqueous solution and concentrated. On standing, 0.20 g. of white crystals were obtained which melted at 230°C. and were proved to be identical with an authentic sample of phthalimide on admixture. This amount of phthalimide corresponds to approximately 21 mole-% of the original polymer sample used and shows the same percentage of the 3,4 configuration.

1-Succinimido-1,3-butadiene Polymer. The same procedure as above was carried out with the use of 1.30 g. (8.59 mmole) of the polymer sample obtained by the bulk polymerization of 1-SB at 76°C. with benzoyl peroxide and gave 26 mole-% of formic acid and 10.58 mole-% of succinimide from a benzene extract of the residue obtained after steam distillation; no volatile aldehyde was obtained.

The benzene-insoluble residue, from which succinimide was extracted, was immersed in absolute ethanol, saturated with hydrogen chloride gas, and refluxed for 5 hr. for esterification. After working up as usual, vacuum distillation of the product gave the two following fractions: (1) b.p. 29–64°C./0.025 mm., 0.10 g. yield; (2) b.p. 64–84°C./0.01 mm., 0.45 g. yield. The first fraction was confirmed to be a crude sample of ethyl succinate by a comparison of the infrared spectrum with that of an authentic sample.⁹

The second was concluded to be a crude diethyl α -succinimidosuccinate by its infrared spectrum. Therefore, further chromatographic purification by the use of silica gel (Mallinckrodt) was carried out on 0.340 g. of the sample; this yielded 0.165 g. (48.6%) of an analytical sample of ethyl α -succinimidosuccinate as a water-white liquid (eluted by benzene-ether 1:4, and ether).

ANAL. Calcd. for $C_{12}H_{17}NO_6$: C, 53.13%; H, 6.32%; N, 5.16%. Found: C, 53.35%; H, 7.01%; N, 4.87%.

Hydrolysis to DL-Aspartic Acid. A sample of the succinimidosuccinate (50 mg.) was refluxed with 3 ml. of 10% hydrochloric acid for 7 hr., and concentrated to dryness under reduced pressure. The residue (the hydro-

chloride form) was confirmed to be DL-aspartic acid by the usual paper chromatography¹⁰ and by the use of an amino acid autoanalyzer (Mitamura Riken Kogyo Co., Tokyo).

The authors wish to thank Dr. Isao Shiihara of this Institute for his excellent support of this work and Dr. Yoshiaki Oda of the University of Osaka Prefecture for the use of the amino acid autoanalyzer.

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Résumé

Les polymérisations radicalaires du 1-phthalamido-1,3-butadiène (1-PB) et du 1-succinimido-1,3-butadiène (1-SB) ont été effectuées en bloc et en solution. Les polymères obtenus ont des viscosités réduites de l'ordre de 1,0 à 4,0 (1-PB) et de 0,2 à 0,6 (1-SB). Les deux polymères ont des points de ramolissement similaires de 190 à 200°C. La polymérisation radicalaire du 1-phthalamido-1,3-butadiène montrait clairement la tendance à fournir des produits pontés. Des arguments stériques concernant ces structures polymériques au moyen des analyses par l'infrarouge et par ozonolyse permettent de conclure que ces polymères contiennent environ 20% de configuration 3,4 mais pas de configuration 1,2 et que dès lors l'addition 1,4 est la structure préférentielle.

Zusammenfassung

Die radikalische Polymerisation von 1-Phthalamido-1,3-butadien (1-PB) und 1-Succinimido-1,3-butadien (1-SB) wurde in Substanz und in Lösung durchgeführt. Die erhaltenen Polymeren besaßen Werte der reduzierten Viskosität im Bereich von 1,0 ~ 4,0 (1-PB) und 0,2 ~ 0,6 (1-SB). Beide Polymeren hatten einen ähnlichen Erweichungspunkt von 190 ~ 200°C. Die radikalische Polymerisation von 1-Phthalamido-1,3-butadien zeigte eine Tendenz zur Bildung vernetzter Polymerer. Infrarot- und Ozonolyseergebnisse bezüglich der sterischen Struktur der Polymeren führten zu dem Schluss, dass sie etwa 20% an 3,4- aber keine 1,2-Konfiguration enthalten und dass daher die 1,4-Addition bevorzugt ist.

Received October 10, 1966

Revised December 14, 1966

Prod. No. 5351A

Mechanism of Thermal Stabilizers for Poly(vinyl Chloride). II. Synergistic Effect of Combination of Metal Soaps

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Synopsis

The esterification of metal soaps, in the combination of zinc and calcium soaps, on poly(vinyl chloride) (PVC) has been carried out both in liquid and solid phase to determine why the reactivity of zinc soap decreases on addition of calcium soap, improving the long-run heat stability of PVC and causing the well-known synergism. It is suggested as the mechanism of synergism that metal soaps having low ionization-potential values, such as calcium soap, act as ester-exchangers of metal chlorides, such as zinc chloride, which is generated after the stabilization of PVC, and also decrease the reactivity of the zinc soap by forming a complex, as that of zinc soap-calcium soap. If a third material, such as organic ester silane, reacting as ester-exchanger on zinc chloride and preventing the formation of a zinc-calcium soap complex, is added to the system, these compounds have an excellent synergistic effect.

INTRODUCTION

According to the results of the reaction of metal salts on the model compounds and alkali-treated poly(vinyl chloride), the mechanism of metal soap stabilizers suggested by Frey and Horst¹ is acceptable as a reasonable one. The action of an epoxy compound in combination with metal soaps has been reported by Bengough and Onozuka² already.

It is well known that metal salts of certain carboxylic acids are seldom used alone, but generally in combination both with each other and with other stabilizing additives. Zinc and calcium soap as the nontoxic stabilizer are commonly used in combination, because the stabilization period of zinc soap alone with epoxy compound is too short to allow processing before the rapid dehydrochlorination begins. Zinc chloride generated from zinc soap accelerates¹ the dehydrochlorination of poly(vinyl chloride) as a catalyst of the Friedel-Crafts type.

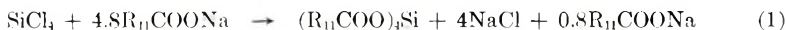
Therefore, it is very important that a third component is added as a deactivator of zinc chloride, such as calcium soap, mannitol, triphenylphosphite, and mercaptans. However, these compounding techniques have not yet been found completely practical, because the reactivity of esterification of zinc soap and epoxy compound on labile chlorine in poly(vinyl chloride) decreases on account of the addition of the third component.

Considering the above-mentioned phenomena, the synergistic action of stabilizers when used in combination with metal soaps seems to be unknown. In this paper a new explanation of the synergistic action is offered over some generally accepted thoughts³ that each component of the stabilizer combination has a different rate of reaction with the hydrogen chloride liberated from the poly(vinyl chloride).

EXPERIMENTAL

Preparation of Organic Silane Compounds

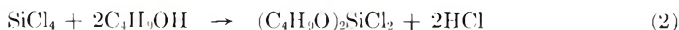
Tetralaurylsilane. A 2.61-mole amount of dried sodium laurate was placed in 1 liter of dry toluene, and 0.55 mole of distilled tetrachlorosilane (b.p. 57.3°C.) was added dropwise with vigorous stirring. The reaction mixture was then heated for 2 hr. over the temperature range 100–120°C., until the suspension of sodium laurate in toluene disappeared.



After reaction the mixture was filtered with ultracentrifuge, to take off the sodium chloride and excess sodium laurate produced, and then toluene was removed under reduced pressure. Tetralaurylsilane, which was identified by elementary analysis and absorption spectra, was prepared in crude yield of 85–95%.

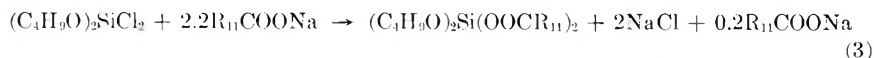
ANAL. Calcd. for $\text{C}_{48}\text{H}_{92}\text{O}_8\text{Si}$: C, 69.85%; H, 11.56%. Found: C, 70.87%; H, 11.56%.

Dibutoxydilaurylsilane. A 2-mole amount of *n*-butyl alcohol (b.p. 117–118.5°C.) was added to 1 mole of tetrachlorosilane (b.p. 57.3°C.) dropwise with vigorous stirring at room temperature for 30 min. The hydrogen chloride evolved in the reaction was continuously removed from the system under reduced pressure.



After stirring for 30 min. at room temperature the product was rapidly distilled under reduced pressure, and dibutoxydichlorosilane (b.p. 100–120°C. at 10 mm. Hg found) was obtained nearly quantitatively. This was identified as the desired substance by elementary analysis and absorption spectra.

Dibutoxydilaurylsilane was obtained in crude yield of 85–90% by a similar procedure, with the use of dibutoxydichlorosilane and sodium laurate.



This material, containing some impurities, was used without further purification.

ANAL. Calcd. for $\text{C}_{32}\text{H}_{64}\text{O}_6\text{Si}$: C, 67.08%; H, 11.26%. Found: C, 61.94%; H, 10.17%.

Butyl Dilauryl Silane. There are several ways^{4,5} of preparing organo-halosilanes: for instance, with Grignard reagents, alkyl lithium reagents, and direct synthesis. In these experiments the last method was applied for the synthesis of butyldichlorosilane. Powdered silane was mixed with 10% copper as cuprous chloride and packed in a reaction vessel with a glass tube. The mixture was heated for 3 hr. at 260–270°C. in a current of nitrogen, to reduce the cuprous chloride to copper. Powdered silane in 85 g. amount, containing reduced copper as promoter, is treated at 300–340°C. by passing butyl chloride over a mixture of Cu and Si. The product was collected in a trap of solid carbon dioxide and acetone, placed at the condenser exit, and then distilled. Butyldichlorosilane, b.p. 129–132°C. (found) (lit.⁶ 129°C.) was synthesized in yield of about 10%. This liquid was identified as butyldichlorosilane by elementary analysis and absorption spectra.

ANAL. Calcd. for $C_4H_{10}Cl_2Si$: H, 6.37%; Cl, 45.2%. Found: H, 6.40%; Cl, 44.36%.
 $C_4H_9SiHCl_2 + 2.2R_{11}COONa \rightarrow C_4H_9SiH(OOCR_{11})_2 + 2NaCl + 0.2R_{11}COONa$ (4)

Butyldilaurylsilane was obtained in crude yield, about 90%, by the same procedure. This material was identified as butyldilaurylsilane by elementary analysis and molecular weight measurement.

ANAL. Calcd. for $C_{28}H_{56}O_4Si$: C, 69.37%; H, 11.64%; mol. wt. 484.5. Found: C, 66.76%; H, 10.97%; mol. wt. 479.9 (in benzene).

Materials Used for Esterification with Metal Soap

Special grades of zinc, calcium, and sodium acetates and laurates were used without further purification.

4-Chlorohexene-2 was prepared as reported previously.⁷

Commercial poly(vinyl chloride) (Kureha S-901) was precipitated from tetrahydrofuran solution with methanol, to remove residual catalysts used in the polymerization process.

Alkali-treated poly(vinyl chloride) (chlorine contents 55.3 wt.-%) was prepared by treating a 3% solution of commercial poly(vinyl chloride) (chlorine contents 56.5 wt.-%) in tetrahydrofuran with 0.1 its volume of 0.1M potassium hydroxide in methanol for 1.5 hr. at room temperature. The polymer was finally precipitated and washed with water, then dried before use.

Quantitative Analysis of Zinc Chloride in Molded PVC

When zinc soap is used as stabilizer, poly(vinyl chloride) is rapidly decomposed⁸ owing to a catalytic effect of zinc chloride even at lower temperature, so it is very important to analyze the zinc chloride produced during processing. An analytical method⁹ with dithizone reagents was used for quantitative measurement of the zinc chloride generated as soon as the zinc soap began to be consumed.

Stabilizers added to PVC were thoroughly dispersed by a dry blending method before processing and then milled for 2 min. at a roll tempera-

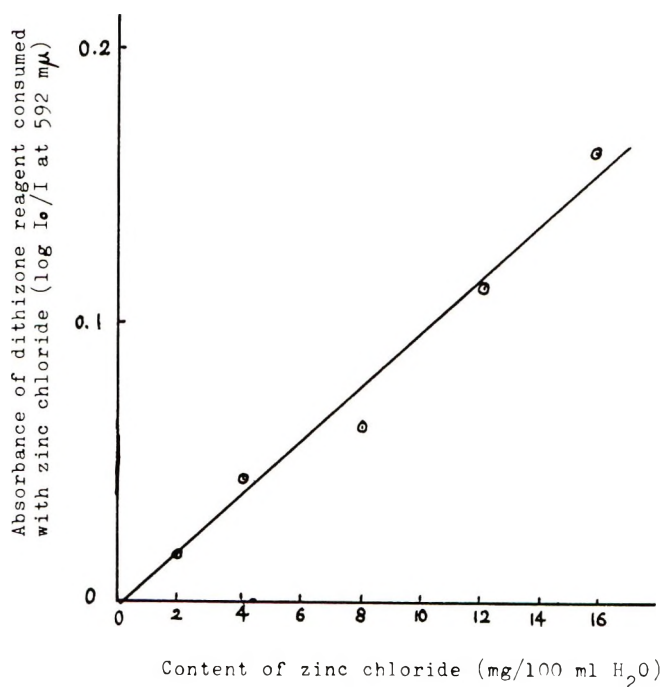


Fig. 1. Working curve relating zinc chloride content to absorbance of dithizone reagent consumed with zinc chloride.

TABLE I
Relationship Between Zinc Chloride Contents and Absorbance^a of
Dithizone Reagent Consumed in Reaction with Zinc Chloride^b

Concn. ZnCl ₂ , mg. per 100 ml. of H ₂ O	Absorbance of dithizone reagent consumed ^c in reaction with zinc chloride (592 mμ)
2	0.016
4	0.046
8	0.060
12	0.112
16	0.161

^a Absorption of zinc dithizoate at 510 mμ in aqueous methyl Cellosolve in superimposed on that of dithizone reagent, so that of the residual dithizone reagent at 592 mμ, which is not affected at all, is used as key band of measurements of zinc chloride generated from zinc soap.

^b The calculated value of zinc chloride generated from zinc laurate (0.1 g. per 5 g. of PVC) used in this experiment corresponds to 11 mg. per 100 ml. of H₂O. Ultraviolet absorptions were measured by Shimazu Model SV-50A UV-Spectrophotometer with 1-cm. quartz cell without reference cell.

^c Absorbance of consumed dithizone is calculated from the difference between that of added dithizone reagent and that of residual dithizone reagent after reaction on zinc chloride, and the amount of zinc chloride can be obtained by absorbance of consumed dithizone reagent.

ture of 150°C. and sheeted at a thickness of about 1 mm. by roll mill. This milled sheet was pressed for various time periods at 180°C. between ferro-type plates under a load of 1 kg./cm.² of pressed sheet with a laboratory hot press. Samples of 5 g. in weight were cut from pressed sheets and dissolved with tetrahydrofuran. After removal of the precipitated polymer by the addition of distilled water to the solution, the aqueous solution was condensed by distillation to 25 ml. The zinc chloride dissolved in this aqueous solution was analyzed with the use of 0.5 ml. of 0.01% dithizone reagents, reported by Vallee, by ultraviolet spectrophotometer. The working curve and data for the analysis of zinc chloride with dithizone reagents is given in Figure 1 and Table I. The amount of zinc chloride found in the pressed sheet can be calculated from the absorption of consumed dithizone reagent with zinc chloride at 592 m μ , because absorption spectrum of zinc dithizonate complex at 510 m μ overlaps with that of unreacted dithizone reagent at 475 m μ , but that of dithizone reagent at 592 m μ does not at all overlap with that of zinc dithizonate complex at 510 m μ .

RESULTS

Esterification of Metal Soaps and Model Compounds of Poly(vinyl Chloride)

Because allylic chlorine is the most unstable of all chlorines in poly(vinyl chloride), 4-chlorohexene-2 model compounds were used in the esterification with metal soap stabilizers. It has been reported,² that to use an epoxy compound together with metal soaps is inevitable, but esterification can be done successfully with different combinations of metal soaps, even if an epoxy compound is not used with a metal soap, as is shown in eqs. (8) and (9) below.

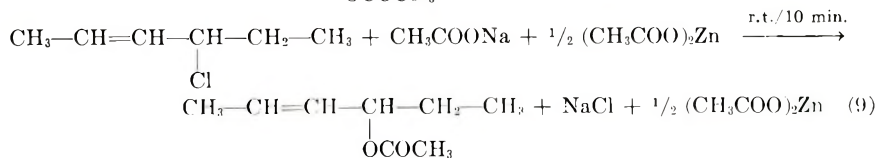
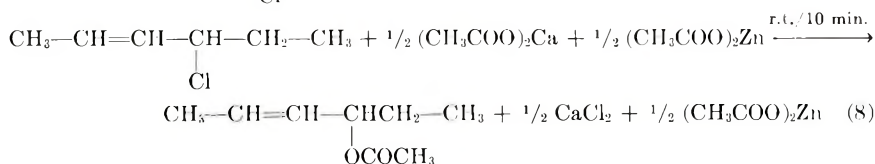
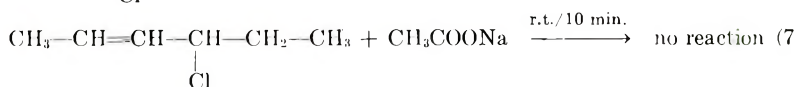
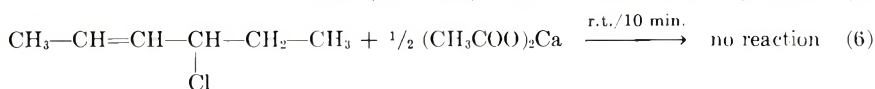
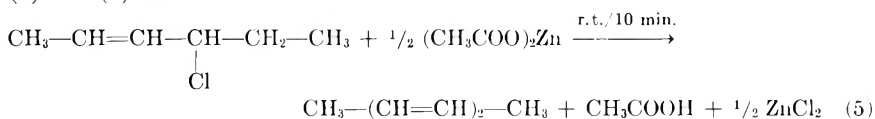


TABLE II
Yield of Esterification on Model Compound 4-Chlorohexene-2

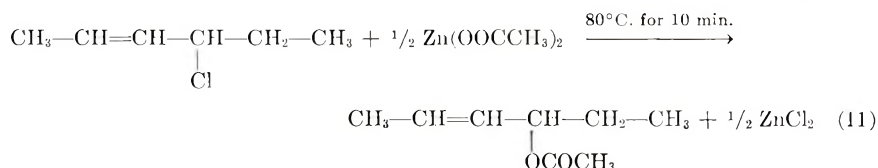
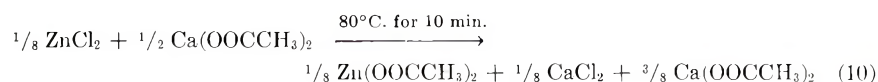
Run no.	Additive	Mole ratio model compound to additive	Yield of 4-acetoxy- hexene-2, %	Degree of conversion, %
1	ZnCl ₂	1:8	0	76.5 ^a
2	Ca(OOCCH ₃) ₂	1:2	0	0
3	ZnCl ₂	1:8		
	Ca(OOCCH ₃) ₂	1:2	36.5 ^b	93.7

^a Degree of conversion means the changed amount based on 4-Cl-hexene-2 and main product is 2,4-hexadiene which can be analyzed by gas chromatography. (Condition, DOP column 3 m. × 18 mm., temperature 100°C., He flow rate 75 ml./min., retention time of 2,4-hexadiene is 3 min.)

^b Yield of 4-acetoxyhexene-2 can be obtained by infrared spectrophotometry.

These reactions occur easily, even at room temperature, in yields of nearly 100%. However, they are prohibited in case of mixtures that are blended above their melting points. This unexpected phenomenon may be observed in the case of combinations of metal soaps with strong ionic bonds between the ester group and the zinc soap, and generally these metal soaps have excellent ester-exchanging property to zinc chloride as shown in Table II.

4-Chlorohexene-2 can be esterified with calcium acetate and zinc chloride, and 4-acetoxyhexene-2 can be obtained in 36.5% yield when more zinc chloride is added to the reaction system of 4-chlorohexene-2 plus calcium acetate, but neither component reacts on 4-chlorohexene-2 as esterifier. Therefore, esterification in this case can probably be explained by an ester-exchange reaction between zinc chloride and calcium acetate as follows:



Esterification Reaction of Metal Soaps and Alkali-Treated Poly(vinyl Chloride)

The same experiments have been carried out with alkali-treated poly(vinyl chloride) and repeated in detail, a situation analogous to the studies of model compounds. Alkali-treated poly(vinyl chloride) was used in this reaction to obtain more exact results. The conditions of esterification are given in Table III; note especially 3-(2-xynoxy)-1,2-epoxy-propane, used

TABLE III
Results of Esterification^a of Various Metal Soaps on Alkali-Treated PVC

Metal soap	Concn. metal soap, moles ($\times 10^3$)	ZnCl ₂ , moles ($\times 10^3$)	Optical density of ester carbonyl	
			Obsd. ^b	Cor. ^c
Zn(OOCC ₃ H ₇) ₂	1	0	0.016	—
Zn(OOC ₁₁ H ₂₃) ₂	1	0	0.033	—
Ca(OOCC ₃ H ₇) ₂	1	0	trace	—
	5	1	0.009	0.009
Ca(OOCC ₁₇ H ₃₅) ₂	1	0	0.002	—
	5	1	0.014	0.009
(C ₄ H ₉ O) ₂ Si(OOCC ₃ H ₇) ₂	1	0	trace	—
	5	1	trace	trace
(C ₄ H ₉ O) ₂ Si(OOCC ₂ H ₅ Cl) ₂	1	0	trace	—
	5	1	0.002	0.002
(C ₄ H ₉ O) ₂ Si(OOCC ₂ H ₅ Cl) ₂	1	0	trace	—
	5	1	0.006	0.004
(C ₄ H ₉ O) ₂ Si(OOCCCl ₃) ₂	1	0	trace	—
	5	1	0.011	0.006
C ₄ H ₉ SiH(OOCC ₁₁ H ₂₃) ₂	5	1	0.026	0.026
(C ₄ H ₉) ₂ Si(OOCC ₁₁ H ₂₃) ₂	5	1	0.019	0.019
(C ₄ H ₉ O) ₂ Si(OOCC ₁₁ H ₂₃) ₂	5	1	0.009	0.009
Si(OOCC ₁₁ H ₂₃) ₄	5	1	0.008	0.008

^a Condition of reaction of metal soaps on alkali-treated PVC: Alkali-treated PVC (Cl, 55.3%) 0.2 g.; THF, 30 ml.; H₂O, 2 ml.; 3-(2-xynoxyl)-1,2-epoxypropane, 2 g.; metal soap, shown in table; reaction temperature, 67°C.; reaction time, 2 hr.

^b Optical density was obtained by KBr (1.22 g.) disk containing esterified PVC (20 mg.).

^c Value, corrected by using the relative absorption coefficient in Table IV, corresponds with degree of esterification.

as epoxy compound, which has no ester groups in the molecule. Esterified poly(vinyl chloride) was dissolved with tetrahydrofuran and again precipitated with methanol twice, until residual reagents were taken off. This polymer was dried under reduced pressure, and the yield of esterification was measured by infrared spectrophotometer with a KBr disk.

As shown in Table III, esterification hardly occurs with calcium salt only. However, if zinc chloride is further added to the reaction system, the yield of esterification obviously increases. This experimental evidence also shows that with zinc soap the esterification proceeds after the ester-exchange reaction between zinc chloride and calcium salt. Such ester exchange can also be recognized in the case of silane ester compounds.

The degree of esterification with metal salts of different ester substituents should be compared after correction, as shown in Table III and Figure 2, because the absorption coefficients of esters (Table IV) are a bit different, depending on the structure of the ester groups. Figure 2 shows that when X is the silane ester substituent, the ester-exchange reactivity with zinc

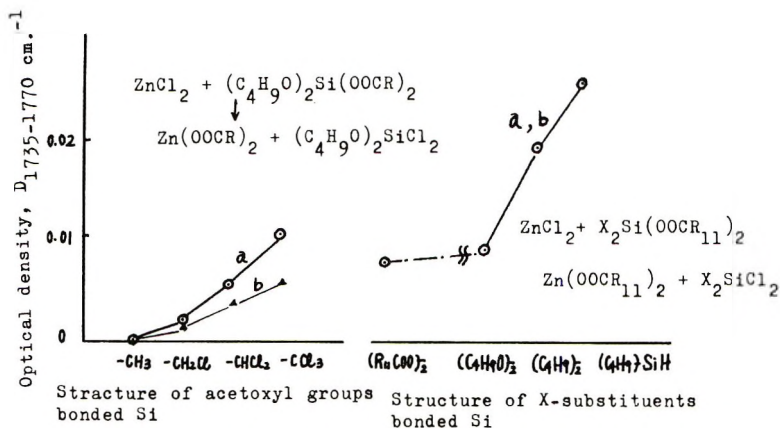


Fig. 2. Correlation optical density of esterified PVC and ester-exchange reactivity of silane compounds on zinc chloride, plotted as a function of electronegativity of substituents: (a) observed values of esterified PVC; (b) values, corrected by using relative absorption coefficient, show the conversion of esterification of PVC compared with the results from metal soaps consisting of the same metal.

chloride depends on the electronegativities of X, except when the ester group is the X substituent.

TABLE IV
Absorption Coefficient Ratio of Metal Ester Groups and Wavenumber of Various Ester Substituents

Metal soap	Absorption coefficient ratio of ester carbonyl in metal soap ^a	Wavenumber ^b of ester carbonyl, cm. ⁻¹	
		Metal soap	Esterified PVC
Ca(OOCR ₁) ₂	K	1540	1735
Ca(OOCR ₁₇) ₂	1.66 K	1540	1735
(C ₄ H ₉ O) ₂ Si(OOCCH ₃) ₂	K'	1720	1725
(C ₄ H ₉ O) ₂ Si(OOCCH ₂ Cl) ₂	1.02 K'	1740	1760
(C ₄ H ₉ O) ₂ Si(OOCCHCl ₂) ₂	1.52 K'	1750	1765
(C ₄ H ₉ O) ₂ Si(OOCCCl ₃) ₂	1.77 K'	1770	1770

^a The values for calcium soaps were obtained by KBr (1.2 g.) disk containing 2.5×10^{-4} mole of calcium salt; the values for silane soaps were obtained by CCl₄ solution (5×10^{-2} mole/l. of CCl₄) with 0.1 mm.

^b Measurements were made with Nihon-bunko Co. Ltd. Model 402 G. infrared spectrophotometer.

Esterification of Metal Soap Stabilizers and Poly(vinyl Chloride) in Actual Processing

Results obtained with the liquid phase have been described, but the actual esterification of metal soaps on poly(vinyl chloride) in practical processing are discussed herein.

TABLE V
Degree of Esterification by Metal Soap on PVC Under Various Milling Conditions

Run no.	PVC, part	Stabilizer, part		Mannitol, part	3-(2-Xyloxy)-1,2-epoxy propane, part	Ester wave-number, cm.^{-1}	Optical density of ester carbonyl ($D^{C=O}$ /mm.) under given milling condition (temp. and time in minutes)							
		Zn-(OOCR) _{11/2}	Ca-(OOCR) _{17/2}				130°, 1	130°, 2	130°, 3	150°, 1	150°, 1	150°, 4	150°, 10	
1	100	0.2	0	0	3	1730 ^a	0	0	0	0	0	0	0.07	0.13
						1540 ^b	0.33	0.38	0.33	0.28	0.30	0.13	0.02	
2	100	0.2	0.2	0	3	1730 ^a	—	—	—	0	0	0	0	0
						1540 ^b	—	—	—	0.36	0.37	0.37	0.36	0.36
3	100	0.2	0	0.2	3	1730 ^a	—	—	—	—	0	0.02	0.04	0.01
						1540 ^b	—	—	—	0.22	0.16	0.17	0.13	0.13

^a Carbonyl absorptions at 1730 cm.^{-1} are those of esterified PVC that have been corrected by the value of carbonyl contained in original PVC ($D^{C=O}/\text{mm.}$, 0.39).

^b Carbonyl absorptions at 1540 cm.^{-1} are those of metal soaps.

TABLE VI
Degree of Esterification by Metal Soap on PVC Under Various Press Conditions

Run no.	PVC, part	Stabilizer, part		Mannitol, part	3-(2-Xynoxy)-1,2-epoxy propane, part	Ester wavenumber, cm^{-1}	Optical density of ester carbonyl ($D^{C=O}/\text{mm.}$) at given temp. and time (min.)							
		Zn-(OOCR ₁₇) ₂	Ca-(OOCR _{17/2})				Milling		Hot-press condition					
							150°, 2	180°, 1	180°, 2	180°, 3	150°, 2	180°, 1	180°, 2	180°, 3
1	100	0.1	0	0	3	1730 ^a	0.13	0.10	0.14	0.14	0.03	0.03	0	
2	100	0.1	0.05	0	3	1540 ^b	0.14	0.05	0.03	0.03	0	0	0	
3	100	0	0.10	0	3	1730 ^a	0	0.09	0.07	0.07	0.07	0.04	0.04	
4	100	0.1	0	0.1	3	1540 ^b	0.16	0.13	0.08	0.08	0.08	0.04	0.04	
						1730 ^a	0	0.04	0.04	0.04	0.04	0.04	0.04	
						1540 ^b	0.09	0.09	0.09	0.09	0.09	0.09	0.08	

^a Carbonyl absorptions at 1730 cm^{-1} are those of esterified PVC that have been corrected by the value of carbonyl contained in original PVC ($D^{C=O}/\text{mm.}$, 0.39).

^b Carbonyl absorptions at 1540 cm^{-1} are those of metal soaps.

Milling sheets were prepared with the use of the compounds listed in Table V. Samples milled for various periods of time at different milling temperatures were taken off and measured by infrared spectrophotometer with the use of milled sheet without further treatment. The yield of esterification of poly(vinyl chloride) by zinc laurate is given in optical density of ester groups per sample thickness in millimeters versus various milling conditions.

The results of the second and third runs in Table V lead to the conclusion that esterification hardly occurs, contrary to our expectation, when calcium soap or mannitol is used with zinc soap.

As shown in Table VI, the same experiments were carried out with the pressed sheets, which were prepared by press at 180°C. under loads of 1 kg./cm.² of sample between ferro-type plates, which were placed at the electrically heated plates of a laboratory manual press. The temperature of the hot press was controlled by Slidac to a tolerance of +2°C. The optical densities per unit thickness of pressed sheet versus various press conditions is given in Table VI.

The absorption band at 1730 cm.⁻¹ corresponds with ester groups in poly(vinyl chloride), and that at 1540 cm.⁻¹ corresponds with ionic ester groups of metal soap. As in the results of milling sheet, the esterification hardly occurs when calcium soap or mannitol, to improve the long-run stability, are added to the zinc soap and epoxy compound.

Amount of Zinc Chloride Produced from Zinc Soap During Processing

Metal soaps having high reactivities with labile chloride in poly(vinyl chloride) possess at the same time the undesirable property of catalyzer of thermal dehydrochlorination after changing into metal chloride, so a third component, such as an ester-exchanger or a deactivator of metal chloride, is commonly used. The suggested synergism mechanism should be ascertained by measurement of the amount of zinc chloride generated during

TABLE VII
Correlation Between Type of Stabilizer and Amount of Zinc Chloride
Generated from Zinc Laurate During Hot Pressing at 180°C. for Various Times

Run no.	Amount of stabilizer, part			Additive, part	ZnCl ₂ (based on added zinc laurate) at given time min.,				
	PVC	EP-5 ^a	Zn-(OOCR ₁₁) ₂		0 ^b	5	10	15	
1	100	5	0.2	—	—	14	78	89	99
2	100	5	0.2	(C ₄ H ₉ O) ₂ Si(OOCR ₁₁) ₂	1.0	—	73	81	88
3	100	5	0.2	C ₄ H ₉ SiH(OOCR ₁₁) ₂	0.5	8	82	90	59
4	100	5	0.2	Ca(OOCR ₁₇) ₂	0.2	8	16	36	67

^a Trade name of epoxied linseed oil.

^b This value corresponds to the content of zinc chloride generated from zinc soap during milling at 150°C. for 2 min.

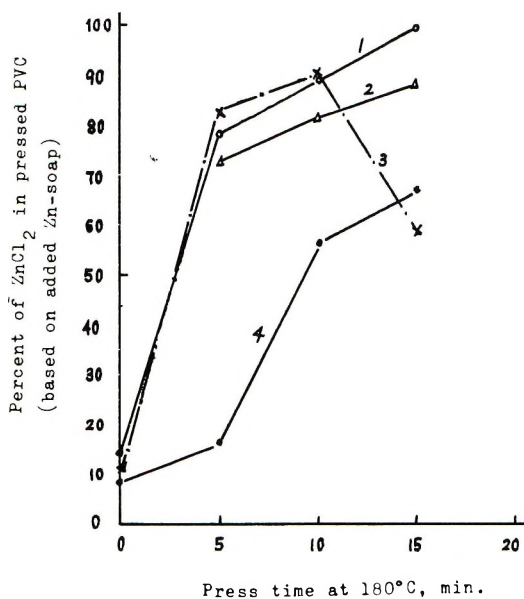


Fig. 3. Correlation of contents of zinc chloride generated from zinc soap with press time of PVC at 180°C.: (1) PVC(100)-EP-5(5)-Zn(OOCR₁₁)₂, 0.2; (2) (run 1) + (C₄H₉O)₂Si(OOCR₁₁)₂, 1.0; (3) (run 1) + C₄H₉SiH(OOCR₁₁)₂, 0.5; (4) (run 1) + Ca(OOCR₁₇)₂, 0.2.

processing. Therefore, determinations have been carried out with the compounds listed in Table VII for analysis of the percentage of zinc chloride formed under processing by hot-press; the results are given in Figure 3. The percentage of zinc chloride formed from zinc soap, based on the added original zinc soap, is plotted against time of heating with the hot press.

The remarkable facts in Figure 3 are that 8% zinc chloride is already present in milled poly(vinyl chloride), and in run 4 the content of that obviously can be decreased by the addition of calcium soap. The type of curve is assumed to depend on the reactivity of the ester exchangers used with zinc chloride. Comparing a blank run with other runs, the amounts of zinc chloride in each run are completely different from the others. From these results some possibilities of ester-exchange reaction may be proposed, and these mechanisms explain the synergistic action of the stabilizers.

DISCUSSION

Synergism in Combination of Metal Soaps

The explanation of the synergistic effect of the combination of metal soaps, as reported hitherto, is that it essentially depends on this combination. On the basis of the experimental data, however, we present a new explanation of the synergism effected by the combination of zinc soap and calcium soap that calcium soap reconverts zinc chloride into zinc soap by

TABLE VIII
Ionization Potentials^a of Various Metals

Metal	Ionization potential, e.v.	Transition
K	4.32	4'S[4]
Na	5.12	2'S[3 _i]
Ba	5.19	6'S[6 _i]
Ca	6.09	4'S[4 _i]
Cd	8.95	5'S[5 _i]
Zn	9.35	4'S[4 _i]

^a *International Critical Tables*, Vol. 6, p. 69.

an ester-exchange reaction. Considering the combination of metal soaps showing excellent synergistic effects it seems to be a necessary condition of synergism that there be certain differences in ionization potential¹⁰ between the group II metals in the periodic table; see Table VIII.

The observable peculiarity of the combination of zinc soap and calcium soap having excellent reactivity with zinc chloride as ester-exchange is the decrease in the reactivity of zinc soap as stabilizer. This unexpected phenomenon is, however, fully understood to be caused by complex formation between zinc soap and calcium soap.

The reactivity of organoester silane to zinc chloride as ester-exchanger seems to have an analogous correlation with calcium soap, especially in liquid-phase reaction, which has strongly ionic ester substituents. The inferior reactivities of silane ester compounds with metal chlorides, compared with calcium soap, can be improved when substituents of organic silane compounds are changed by some groups having more electron-accepting groups. As the alkyl chain length of the ester groups attached to silane increases, those reactivities become better, too, when the remaining structures of the silane compounds are the same. Then it may be assumed that the strain by bulky substituents affects these reactivities. Each silane compound has a different compatibility with the epoxy compound used and also a different lubricating power in the processing, so some explanation in regard to physical effectiveness should be done from the standpoint of dynamic heat stability, too.

Complex Formation in Combination of Calcium and Zinc Soap

When the melting points of the mixture of zinc stearate and calcium stearate at various concentrations are plotted against the compositions of these binary systems, the eutectic point P_1 between zinc stearate and compound regions is found as shown in Figure 4a. However, the melting-point curve of the mixture of zinc stearate and tetralaurylsilane or of calcium stearate and tetralaurylsilane shows typical binary-system behavior, as shown in Figures 4b and 4c. The ternary-mixture curve is given in Figure 5; see also Table IX. The oblique line shows the existence of a complex, but this complex disappears with increasing ester silane compound. That the mixture of zinc soap (65 mole-%) and calcium soap (35 mole-%) makes

TABLE IX
Melting Point^a of Binary and Ternary Mixtures of Zinc Soap, Calcium Soap, and Silane Soap

Binary mixtures, mole-% and melting point								
Zn(OOCR ₁₇) ₂	Ca(OOCR ₁₇) ₂	°C.	Zn(OOCR ₁₇) ₂	Si(OOCR ₁₁) ₄	°C.	Ca(OOCR ₁₇) ₂	Si(OOCR ₁₁) ₄	°C.
100	0	122	100	0	122	100	0	157
90	10	120	80	20	115	80	20	95
80	20	118	60	40	108	60	40	74
75	25	118	40	60	105	40	60	64
70	30	119	20	80	98	20	80	51
65	35	119	10	90	94	0	100	41
60	40	115	0	100	41			
50	50	120						
45	55	123						
0	100	157						

Ternary mixtures, mole-% and melting point							
Si(OOCR ₁₁) ₄	Zn(OOCR ₁₇) ₂	Ca(OOCR ₁₇) ₂	°C.	Si(OOCR ₁₁) ₄	Zn(OOCR ₁₇) ₂	Ca(OOCR ₁₇) ₂	°C.
45	55	0	109	30	70	0	112
45	44	11	108	30	63	7	111
45	38.5	16.5	107	30	56	14	110
45	33	22	98	30	49	21	111
45	27.5	27.5	86	30	42	28	101
45	22	33	76.5	30	35	35	92
45	16.5	38.5	73	30	28	42	87
45	11	44	68	30	24.5	45.5	81
45	5.5	49.5	76	30	21	49	78
45	0	55	78	30	14	56	86
				30	7	63	91
				30	0	70	83

^a Measured with Yanagimoto Co. Ltd. Micro Melting Apparatus.

a complex has been proved by measurement of x-ray diffraction patterns, as illustrated in Figure 6. This complex may be considered to have a poor coordination with labile chlorine in poly(vinyl chloride), because the coordination sites of zinc may be filled with carboxylate anion of calcium soap, but when organic ester silane is added as a third component of the

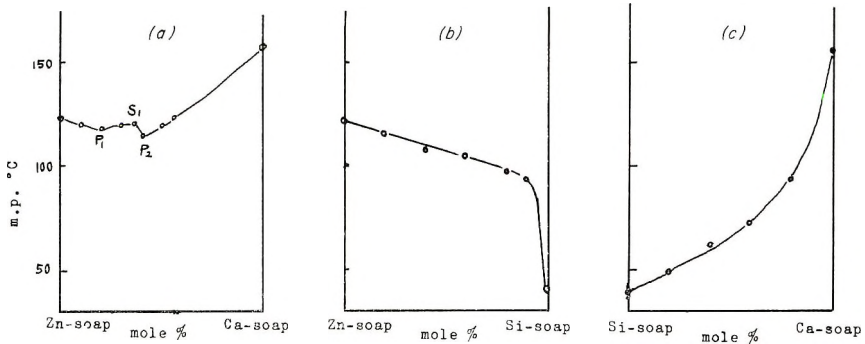


Fig. 4. Melting points of mixtures plotted against composition for binary systems of metal soaps.

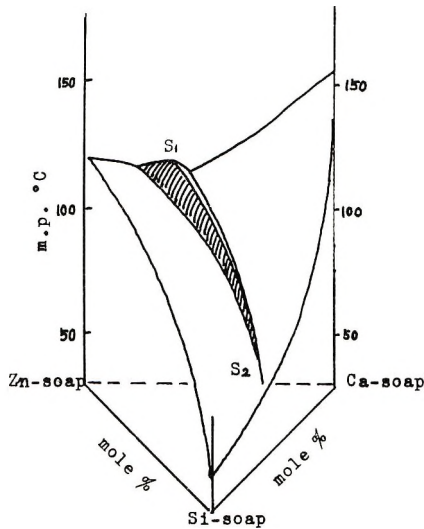


Fig. 5. Melting points of mixtures plotted against composition for ternary systems of metal soaps; $S_1 = \text{Zn}(\text{OOCR}_{17})_2$ (65 mole-%) and $\text{Ca}(\text{OOCR}_{17})_2$ (35 mole-%); $S_2 = \text{Zn}(\text{OOCR}_{17})_2$ (7 mole-%) $\text{Ca}(\text{OOCR}_{17})_2$ (48 mole-%) and $\text{Si}(\text{OOCR}_{11})_4$ (45 mole-%).

mixture; the reactivity of the zinc soap revises and leads to a noticeable improvement in heat stability; it may be considered to act as peptizer of the complex formation. The ability of the third component to prevent the formation of a stable complex correlates with the effectiveness of the stabilizer in removing the initial discoloration.

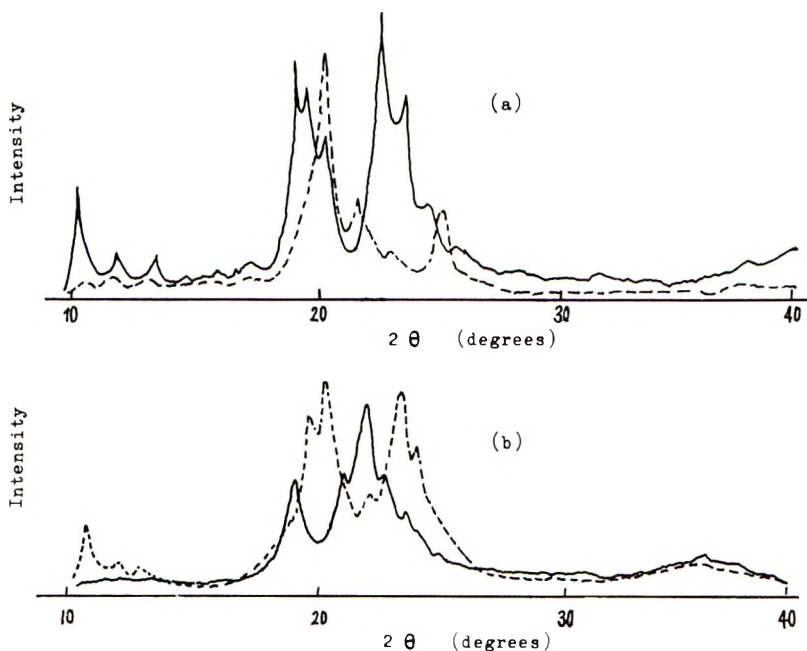


Fig. 6. X-ray diffraction curves of metal soaps: (a) zinc stearate (—), calcium stearate (---); (b) complex of zinc stearate, 65 mole-%, (—) and calcium stearate, 35 mole-% (—); mixture of above components mechanically blended (---). Measured by $\text{CuK}\alpha$ ray at room temperature with nickel filter.

Each of these stabilizers plays a particular, independent role in the stabilization of poly(vinyl chloride), and the ideal synergistic action can be obtained only by careful choice of a ratio and combination of stabilizers.

The author wishes to thank K. Iida and T. Nakamura, who have participated in this work; he is also greatly indebted to M. Asahina of Tokyo Research Laboratory, Kureha Chemical Industry Co. Ltd., for his encouraging help and advice. The author wishes to thank the directors of Kureha Chemical Industry Co. Ltd. for their permission to publish this paper.

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Résumé

L'estérification de savons métalliques en combinaison avec des savons zinciques et calciques sur le chlorure de polyvinyle a été effectuée à la fois en phase liquide et en phase solide afin de connaître la raison pour laquelle la réactivité d'un savon zincique diminue par addition d'un savon calcique qui améliore la stabilité thermique à longue durée du PVC et qui manifeste un synergisme dans ces combinaisons. Un mécanisme de synergisme peut être suggéré suivant lequel les savons métalliques ayant de basses valeurs potentielles d'ionisation, par exemple le savon calcique, agissant comme échangeur d'ester du chlorure métallique, par exemple, le chlorure zincique, engendré après stabilisation du PVC, de plus ils diminuent la réactivité du savon zincique en formant un complexe entre le savon zincique et le savon calcique. Si un troisième matériau réagissant comme échangeur d'ester sur le chlorure de zinc et empêchant la formation du complexe savon-zinc-calcium, par exemple un silane ester organique, est additionné en outre à ces systèmes, ces composés montreront un effet synergique excellent.

Zusammenfassung

Die Veresterung von Metallseifen in der Kombination von Zink- und Calciumseifen auf PVC wurde in flüssiger und fester Phase durchgeführt, um den Grund für den Rückgang der Reaktivität von Zinkseife beim Zusatz von Calciumseife, welche die Langzeit-Hitzeständigkeit von PVC verbessert und in dieser Kombination synergistisch wirkt, kennen zu lernen. Als Mechanismus für die synergistische Wirkung wird angenommen, dass Metallseifen mit niedrigen Werten des Ionisierungspotentials, z.B. Calciumseife, einen Esteraustausch mit Metallchlorid, z.B. Zinkchlorid, bewirken, welches nach Stabilisierung von PVC gebildet wurde, und dass sie auch die Reaktivität der Zinkseife durch Komplexbildung zwischen Zinkseife und Calciumseife beeinträchtigen. Wenn ein dritter Stoff, der als Esteraustauscher für Zinkchlorid wirkt und die Bildung eines Zink-Calciumseifenkomplexes verhindert, z.B. organische Ester-Silane, diesen Systemen zugesetzt wird, so zeigen die Verbindungen eine ausgezeichnete synergistische Wirkung.

Received November 15, 1966

Revised January 23, 1967

Prod. No. 5367A

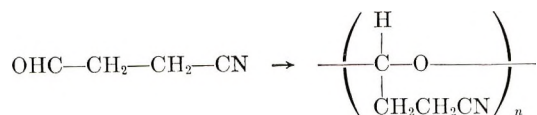
Polymerization of β -Cyanopropionaldehyde. II. Crystalline Poly(cyanoethyl)oxymethylene

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Synopsis

Additional investigation was made on the polymerization of β -cyanopropionaldehyde at -78°C . with triethylaluminum and triethylaluminum-titanium tetrachloride complexes as initiators. The complexes give a higher polymer yield than triethylaluminum alone. The yield-Ti/Al plot also has a maximum at a Ti/Al mole ratio of about 0.2 at constant $\text{Al}(\text{C}_2\text{H}_5)_3$ concentration. The rate of polymerization seems to be increased in the following order: toluene < methylene chloride < tetrahydrofuran. This order is reversed with regard to the content of DMF-insoluble fraction mentioned below. The polymer obtained consists of two fractions: one is soluble in dimethylformamide (DMF) and the other is not. The former consists of an amorphous polymer and the latter of crystalline polymer. It was found that the infrared absorption bands at 790, 1258, and 1375 cm^{-1} were characteristic of crystalline polymer and were assigned to crystalline bands. Those at 1270 and 1345 cm^{-1} are characteristic of amorphous bands. The crystalline bands and C—O—C bands show very intense infrared dichroism, whereas the nitrile band does not. The crystal data obtained from the analysis of the x-ray diffraction pattern, including the fiber repeat distance of 4.95 Å and other unit cell dimensions in a triclinic system, were compared with those reported for various aldehyde polymers. The unit cell dimension a' or the maximum interplanar distance is somewhat smaller, suggesting that the molecules are more tightly packed than poly(*n*-butyraldehyde), in which the side chain has the same carbon number as that of poly(cyanoethyl)oxymethylene. Internal rotation angles and a radius of helix were calculated for an isotactic fourfold helical model of the polymer. Some other characterizations of the polymer were also made.

In a previous paper¹ a new class of polyacetals, high molecular weight poly(cyanoethyl)oxymethylene, was obtained by the low-temperature polymerization of β -cyanopropionaldehyde (CPA) with the use of ionic initiators, including boron trifluoride etherate, diethylzinc, triethylaluminum, and triethylaluminum-titanium tetrachloride complexes.



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The present investigation was undertaken to study the formation of crystalline poly(cyanoethyl)oxymethylene. The influences of polymerization conditions on the yields, molecular weights, and crystallinity were determined. Some characterizations of the polymer were also made.

EXPERIMENTAL

Polymerization

The preparation of CPA and purification of solvents were previously described.¹

Triethylaluminum (Ethyl Corp.) was distilled under reduced pressure. Titanium tetrachloride (commercial origin) was purified by distillation after refluxing with about 1% copper powder.

Triethylaluminum and titanium tetrachloride diluted with a solvent were placed in a glass ampule in a nitrogen-filled dry box. After aging for 30 min. at room temperature the CPA solution was slowly added on cooling with Dry Ice. The ampule was evacuated at the liquid-nitrogen temperature, sealed under vacuum, and placed in a Dewar flask filled with Dry Ice.

Polymerization was stopped by pouring the reaction mixture into a large amount of cold methanol (at -78°C). The product was crushed to a fine powder with a Waring Blender and washed repeatedly with methanol. The polymer thus obtained was dried under reduced pressure at room temperature and weighed.

In this work all polymer samples were used for analyses and measurements without any after-treatment such as end-capping.

Fractional Extraction of Polymer

The polymer obtained as outlined above was separated into two fractions by extraction with dimethylformamide (DMF) at room temperature: one was soluble and the other was insoluble in DMF.

It was found from the results of elementary and x-ray analyses that a small amount of catalyst residue was still included in the DMF-insoluble fraction.

X-Ray Analysis

X-ray diffraction experiments were performed on the powder or hot-pressed film samples with nickel-filtered CuK_{α} radiation.

Melting Point Measurements

Measurements of the crystalline melting point were carried out for polymer films by means of a melting point measurement apparatus with a polarizing microscope; the disappearance of strong birefringence was observed at a temperature rising rate of $1^{\circ}\text{C}/\text{min}$.

Differential thermal analysis of samples of the DMF-soluble fraction showed very weak birefringence in a nitrogen atmosphere with α -alumina as reference substance.

Viscosity Measurements

Reduced viscosities, η_{sp}/c , of polymer samples were measured in DMF at $25 \pm 0.05^\circ\text{C}$. with an Ostwald viscometer.

RESULTS AND DISCUSSION

Polymerization

It was pointed out by Vogl and Bryant² that special methods would be required for the polymerization of carbonyl compounds with a frequency of less than 1725 cm.^{-1} , whereas aldehydes with a carbonyl frequency higher than 1750 cm.^{-1} (chloral, formaldehyde) polymerized readily, and saturated aldehydes ($1750\text{--}1725\text{ cm.}^{-1}$) could also polymerize with alkali alkoxides. CPA having a carbonyl frequency of 1720 cm.^{-1} (obtained in liquid state) has been found in our investigation to be easily polymerized and to form high molecular weight poly(cyanoethyl)oxymethylene.

It has been known that triethylaluminum is effective for polymerizing aliphatic aldehydes,^{3,4} but we have as yet very little information on the polymerization initiated by organoaluminum-transition metal complex catalysts.⁵ Triethylaluminum-titanium tetrachloride was found in the present investigation to work more effectively in polymerizing CPA than triethylaluminum alone, as is described below.

In Tables I and II are presented additional data on the polymerization of CPA at -78°C . for 1 day, when triethylaluminum and triethylaluminum-titanium tetrachloride were used as initiators and methylene chloride, toluene, and tetrahydrofuran (THF) as solvents. The tables also contain the results of the fractionation, reduced viscosities, and crystalline melting points of the resulting polymers.

The effects of variation in the Ti/Al mole ratio on the polymer yield are shown in Figure 1. It can be seen that the total polymer yield shows a maximum at a Ti/Al mole ratio of around 0.2 at constant triethylaluminum

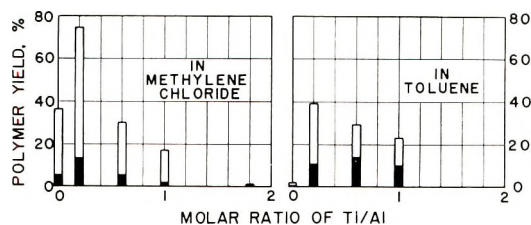


Fig. 1. Influence of molar ratio of Ti/Al in $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_4$ complex catalyst on the yield of polymer: (white bars) DMF-soluble fraction, (black bars) DMF-insoluble fraction; $\text{Al}(\text{C}_2\text{H}_5)_3$; 1 mole-% per mole of monomer; weight ratio of solvent to monomer, 2; polymerization temperature, -78°C .; time, 1 day.

TABLE I
 Polymerization of β -Cyanopropionaldehyde Initiated by Triethylaluminum^a

Run no.	CPA, g.	Al(C ₂ H ₅) ₃ , mole-% to monomer	Solvent	Wt. ratio of solvent to monomer	Polymer yield, %	DMF-insoluble fraction, %	M.p., °C.	η_{sp}/c of DMF-soluble fraction ^b
93	10	0.7	Methylene chloride	1	20.5	71.6	—	—
138	"	1.0	"	2	38.4	14.5	163-176	0.73
94	"	0.7	Toluene	1	1.8	74.5	—	—
154	50	1.0	"	2	0.2	42.6	160-168	—
153	10	"	THF	2	61.7	3.3	162-172	—

^a Temp., -78°C.; time, 1 day.

^b In DMF $c = 0.2$ g./100 ml. at 25°C.

TABLE II
 Polymerization of β -Cyanopropionaldehyde with
 Triethylaluminum-Titanium Tetrachloride Complexes^a

Run no.	CPA, g.	Molar ratio of Ti/Al	Solvent	Polymer yield, %	DMF-insoluble fraction, %	M.p., °C.	η_{sp}/c of DMF-soluble fraction ^b
155	20	0.2	Methylene chloride	74.7	1.8	152-159	—
160	10	0.6	"	30.2	18.5	145-148	—
156	20	1.0	"	17.2	11.6	— ^c	0.28
141	10	1.8	"	0.5	—	—	—
142	20	3.0	"	0	—	—	—
157	20	0.2	Toluene	39.1	27.5	153-158	—
161	10	0.6	"	29.5	47.6	148-151	0.05
158	20	1.0	"	23.1	43.3	151-154	0.13
108	10	5.0	"	0	—	—	—

^a $\text{Al}(\text{C}_2\text{H}_5)_3$, 1 mole-% to monomer; weight ratio of solvent to monomer, 2; temp., -78°C .; time, 1 day.

^b In DMF $c = 0.2$ g./100 ml., at 25°C .

^c DMF-soluble fraction was found to melt at 108 - 114°C . (differential thermal analysis).

concentration (1 mole-% of initiator with regard to monomer) and also that very little polymer can be obtained in the region of a Ti/Al mole ratio of more than 2.

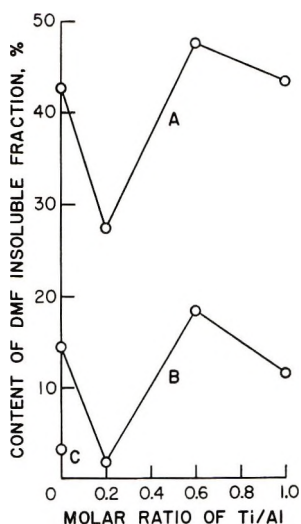


Fig. 2. Dependence of per cent content of DMF-insoluble fraction in polymerization product on molar ratio of Ti/Al: lines A and B and point C represent respectively toluene, methylene chloride, and tetrahydrofuran, used as solvents in the polymerization; $\text{Al}(\text{C}_2\text{H}_5)_3$, 1 mole-% per mole of monomer; weight ratio of solvent to monomer, 2; polymerization temperature, -78°C .; time, 1 day.

The rate of polymerization seems to be increased in the following order: toluene < methylene chloride < THF. This order, on the other hand, should be reversed with respect to the content of DMF-insoluble polymer, as shown in Figure 2. It also appears in Figure 2 that the content of DMF-insoluble fraction gives a minimum at a Ti/Al mole ratio of 0.2.

It was observed that polymer prepared with $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_4$ showed a lower melting point, narrower melting temperature range, and lower solution viscosity than that prepared with $\text{Al}(\text{C}_2\text{H}_5)_3$ alone.

Solubility

The solubilities of each of the two fractions are listed in Table III. It is interesting to note that poly(cyanoethyl)oxymethylene is insoluble in some solvents, such as naphthalene and tetrahydronaphthalene, in which poly(*n*-butyraldehyde) is soluble. It is, however, soluble in DMF, γ -butyrolactone, and concentrated aqueous solution of zinc chloride, which are good solvents for polyacrylonitrile.

TABLE III
Solubilities of Poly(cyanoethyl)oxymethylene
(about 1 g. of polymer in 100 g. of solvent)

DMF-soluble fraction	
1.	Soluble at room temperature in: acetonitrile, dimethylformamide, dimethylacetamide, dimethylsulfoxide, and γ -butyrolactone.
2.	Partially soluble at room temperature in: acetone.
3.	Soluble at higher temperature (100°C.) in: concentrated aqueous solution of zinc chloride, cyclohexanone, phenol, and <i>m</i> -cresol.
4.	Insoluble at even higher temperature in: water, methyl alcohol, carbon tetrachloride, chloroform, methylene chloride, tetrachloroethylene, <i>n</i> -hexane, benzene, toluene, tetrahydronaphthalene, tetrahydrofuran, and dioxane.
DMF-insoluble fraction	
1.	Soluble at higher temperature in: concentrated aqueous solution of zinc chloride (100°C.), dimethylformamide (170–180°C.), dimethylsulfoxide (160–170°C.), and γ -butyrolactone (160–165°C.).
2.	Insoluble at even higher temperature in: tetrachloroethane, tetrachloroethylene, ethylene carbonate, <i>p</i> -xylene, benzyl alcohol, aniline, nitrobenzene, phenol, cyclohexanol, naphthalene, and tetrahydronaphthalene.

The specific gravities of the DMF-soluble fraction and the DMF-insoluble one, determined by the floatation method, were, respectively, 1.16 and 1.22 at 25°C.

Infrared Absorption Spectra

In Figure 3 are illustrated infrared absorption spectra of the DMF-soluble and DMF insoluble fraction obtained from the polymer initiated

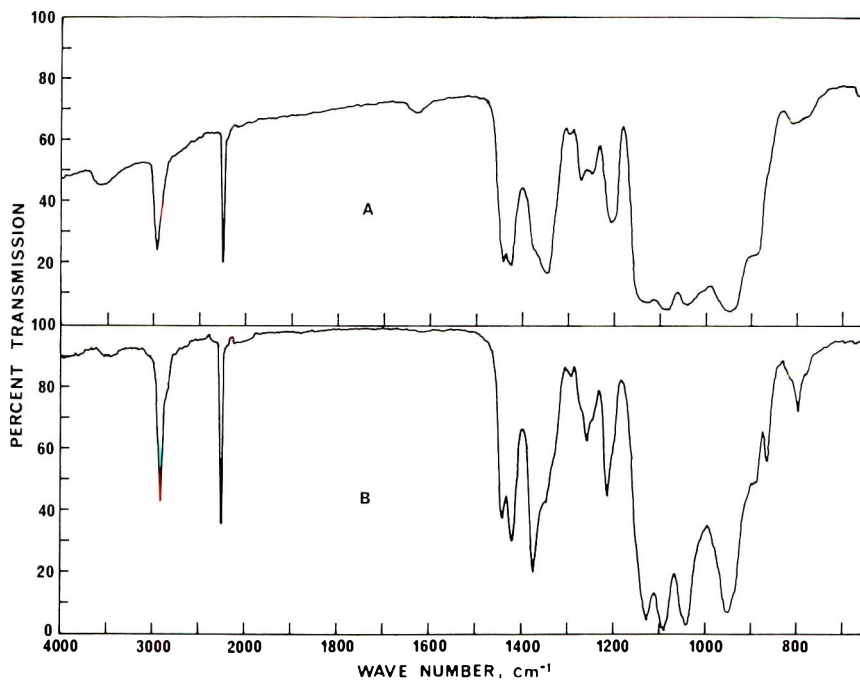


Fig. 3. Infrared absorption spectra of poly(cyanoethyl)oxymethylene prepared with $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_4$ (films): (A) DMF-soluble fraction; (B) DMF-insoluble fraction.

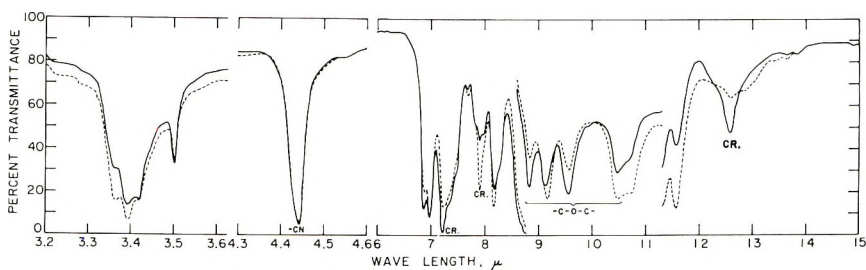


Fig. 4. Polarized infrared spectra of oriented film of crystalline poly(cyanoethyl)oxymethylene: electric vector (—) perpendicular and (---) parallel to the direction of orientation; CR denotes crystalline band.

with $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_4$. As mentioned previously, four strong bands assigned to the ether linkage appear in the region of $950\text{--}1140\text{ cm}^{-1}$ instead of the carbonyl band at 1720 cm^{-1} in the spectrum of the CPA monomer, although the frequency of the nitrile band at 2250 cm^{-1} does not change.

From a comparison with our results of x-ray diffraction measurements it was found that the absorption bands at 790 , 1258 , and 1375 cm^{-1} , etc. were characteristic of the DMF-insoluble fraction; this enabled us to assign them to crystalline bands. Bands at 1270 and 1345 cm^{-1} are characteristic of the DMF-soluble fraction and were assigned to the amorphous

bands. (Further investigation is in the progress on the relationship between the crystalline bands mentioned here and stereoregularity.)

Very strong birefringence for an oriented film prepared from the DMF-insoluble fraction was also observed with a polarized microscope.

The polarized infrared spectra were recorded with a Perkin-Elmer Model 221 infrared spectrophotometer in the range of 3.0–4.7 μ with a LiF prism and in the range of 6.0–15.0 μ with a NaCl prism. The infrared dichroism can be observed in Figure 4. It is of interest that the three crystalline bands show very intense dichroism, i.e., a parallel band at 1258 cm^{-1} and very intense dichroism, i.e., a parallel band at 1258 cm^{-1} and perpendicular bands at 790 and 1375 cm^{-1} . It can also be noted that two of the four bands due to the ether linkage are perpendicular bands at 1040 and 1127 cm^{-1} , and another two are parallel bands at 950 and 1090 cm^{-1} . There appears to be no infrared dichroism on the nitrile absorption at 2250 cm^{-1} .

Further detailed investigation of the spectral data will probably give more useful information on the physical structure of poly(cyanoethyl)oxymethylene.

X-Ray Diffraction

X-ray diffraction diagrams of both the DMF-soluble fraction and the DMF-insoluble fraction are shown in Figure 5. Diffuse amorphous halos appear in the regions of about 10° and 23° for the former, but crystalline-like peaks for the latter, the diffraction data of which are presented in Table IV.

It can be seen from these results that the DMF-soluble fraction consists of an amorphous polymer and the DMF-insoluble one of a crystalline polymer. Considerable molecular orientation when the polymer is repeatedly

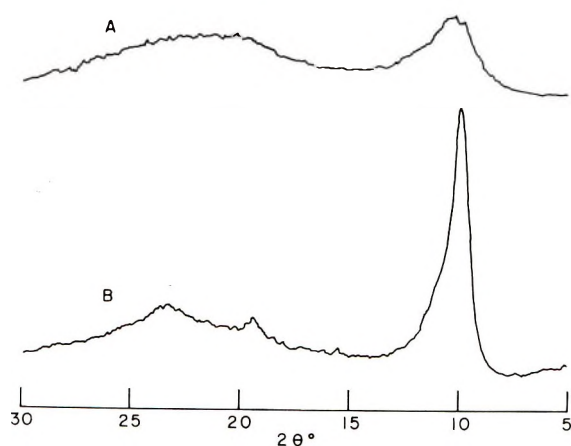


Fig. 5. X-ray diffraction diagrams of poly(cyanoethyl)oxymethylene prepared with $\text{Al}(\text{C}_2\text{H}_5)_2\text{-TiCl}_4$ ($\text{CuK}\alpha$, Ni filter): (A) DMF-soluble fraction, (B) DMF-insoluble fraction.

TABLE IV
 X-Ray Diffraction Data of DMF-Insoluble Fraction

Diffraction angle (2θ), degree	Relative intensity	Spacing (d), A.
9.8	100	9.03
19.4	32	4.57
23.3	38	3.77

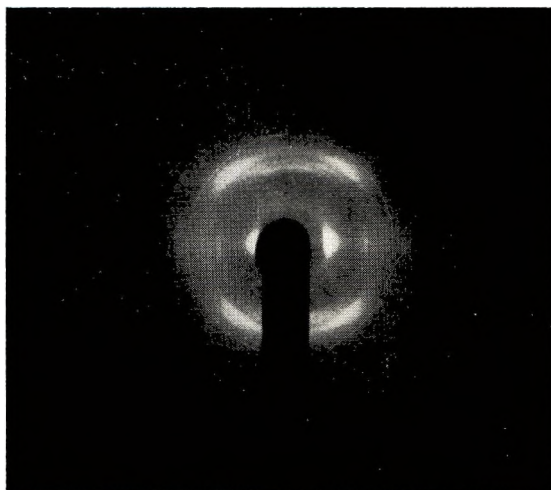

 Fig. 6. X-ray diffraction photograph of oriented film of crystalline poly(cyanoethyl)-oxymethylene (CuK α , Ni filter).

 TABLE V
 Crystal Data of Some Polyaldehydes

Side group of polyaldehyde	Maximum interplanar distance, A.	Unit cell dimension, A.				Ref.
		Sys-tem ^a	a	b	c , identity period	
CH ₃	7.30	TG	14.63	14.63	4.79	6
CH ₂ Cl	7.76	"	15.52	15.52	4.80	7
CHCl ₂	8.33	"	16.66	16.66	5.22	7
CCl ₃	8.69	"	17.38	17.38	6.45	7
CH ₂ CH ₃	8.76	"	17.50	17.50	4.78	6
CH ₂ CH ₂ CH ₃	10.01	"	20.01	20.01	4.78	6
CH ₂ CH ₂ CN	9.03	TC	9.44 (a') ^b	5.32 (b') ^b	4.95	This paper
CH ₂ CH ₂ CH ₂ CH ₃	11.8	—	—	—	—	9

^a TG = tetragonal system, TC = triclinic system.

^b The conventional values of a' and b' are given instead of the true dimensions.

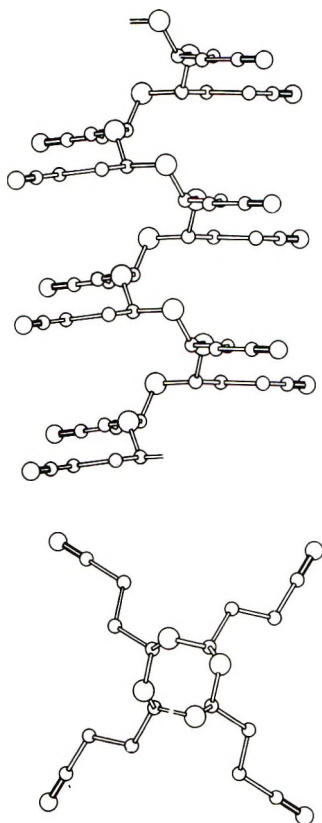


Fig. 7. Conformation of the molecule of poly(cyanoethyl)oxymethylene in crystal-line phase; internal-rotation angles $\tau_{12} = 138^\circ$ and $\tau_{21} = -83^\circ$; radius of helix, $\rho = 1.40$ A.

subjected to stress and an increase of crystallinity on heating were also observed.

The fiber repeat distance was estimated to be 4.95 A. from the x-ray diffraction pattern of an oriented polymer film, shown in Figure 6. This value is similar to that given for several substituted polyoxymethylenes for which fourfold helical structures had been proposed^{6,7} (cf. Table V).

In Figure 7 is shown an isotactic fourfold helical molecular model constructed for poly(cyanoethyl)oxymethylene, for which internal rotation angles of $\tau_{12} = 138^\circ$ and $\tau_{21} = -83^\circ$ and a radius of helix of $\rho = 1.40$ A. were calculated by means of Miyazawa's treatment.⁸ The basal plane of the reciprocal lattice was found from the equatorial diffraction to be $a^* = 0.167$, $b^* = 0.297$, and $\gamma^* = 78^\circ$. The unit cell dimensions obtained by assuming a monoclinic system are $a' = 9.44$, $b' = 5.32$, $c = 4.95$ A. (fiber axis), and $\gamma = 180^\circ - \gamma^* = 102^\circ$. On the other hand, the interplanar distance along the c axis was also observed to be 4.62 A., which is smaller than the value of the fiber repeat distance. Therefore it may be reasonable

to consider that the crystalline poly(cyanoethyl)oxymethylene belongs to a triclinic system. The crystal data of poly(cyanoethyl)oxymethylene are compared with those reported for various aldehyde polymers in Table V.

It is interesting to note that crystalline poly(cyanoethyl)oxymethylene is considered to have a triclinic symmetry, whereas many other aldehyde polymers are reported to have a tetragonal one,^{6,7} and also that the unit cell dimension a' or the maximum interplanar distance is somewhat smaller than that of poly(*n*-butyraldehyde), having the side group with the same carbon numbers as poly(cyanoethyl)oxymethylene. This fact suggests that poly(cyanoethyl)oxymethylene chains are more closely packed in the crystalline regions than those of poly(*n*-butyraldehyde). This might be attributed to the effect of the polar cyanoethyl side chains.

The stability¹⁰ of poly(cyanoethyl)oxymethylene to thermal degradation and to acid hydrolysis may be caused by compact chain packing, some interaction between polymer molecules, and the electrostatic effect of the polar side group.

The authors wish to express their gratitude to T. Miyazawa and N. Kasai for their assistance and valuable advice in carrying out the infrared dichroic and x-ray measurements, respectively. Thanks are also due H. Mikawa and O. Vogl for their active interest and helpful discussions.

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Résumé

Une nouvelle étude de la polymérisation de β -cyanopropionaldéhyde à -78°C à été effectuée en utilisant le triéthylaluminium et les complexes triéthylaluminium-tétrachlorure de titane, comme initiateurs. Les complexes fournissent un rendement plus élevé en polymères que le triéthylaluminium seul. Si l'on porte en diagramme le rendement en fonction du rapport Ti/Al, le diagramme manifeste un maximum pour un rapport molaire Ti/Al environ de 0.2 pour une concentration constante en triéthylaluminium. La vitesse de polymérisation semble croître dans l'ordre suivant: toluène < chlorure de méthylène < tétrahydrofurane. Cet ordre est renversé si l'on considère la teneur en fractions insolubles dans le DMF mentionné plus bas. Le polymère obtenu est formé de deux fractions dont l'une est soluble dans le diméthylformamide (DMF) et l'autre ne l'est pas. La première fraction consiste en un polymère amorphe et la dernière en un polymère cristallin. On a trouvé que les bandes d'absorption infrarouge à 790,

1258 et 1375 cm^{-1} étaient caractéristiques du polymère cristallin et devaient être attribuées à des bandes cristallines. Celles à 1270 et 1345 cm^{-1} sont caractéristiques des bandes amorphes. Les bandes cristallines et les bandes C—O—C montrent un dichroïsme infrarouge très intense, tandis que la bande nitrile ne le montre pas. Les résultats cristallographiques obtenus au départ de l'analyse des réseaux de diffraction aux rayons-X supposent une distance périodique de la fibre de 4,95 Å et d'autres dimensions de la cellule unitaire dans un système triclinique; ces résultats cristallographiques ont été comparés à ceux rapportés pour les polymères d'autres aldéhydes. La dimension de la cellule unitaire a' ou la distance interplanaire maximum est quelque peu plus petite, ce qui suggère que les molécules sont plus fortement entassées que dans le cas du polybutyraldéhyde où la chaîne latérale a la même nombre d'atomes de carbone que celle du poly(cyanoéthyle)oxyméthylène. Les angles de rotation interne et le rayon de l'hélice ont été calculés pour un modèle hélicoïdal isotactique quadruple du polymère. D'autres caractérisations du polymère ont également été effectuées.

Zusammenfassung

Eine zusätzliche Untersuchung der Polymerisation von β -Cyanpropionaldehyd bei -78°C mit Triäthylaluminium und Triäthylaluminium-Titantetrachlorid-Komplexen als Initiatoren wurde durchgeführt. Die Komplexe liefern eine höhere Polymerausbeute als Triäthylaluminium allein. Auch im Diagramm Ausbeute-Ti/Al-Verhältnis besteht ein Maximum bei einem Molverhältnis Ti/Al um 0,2 bei konstanter $\text{Al}(\text{C}_2\text{H}_5)_3$ -Konzentration. Die Polymerisationsgeschwindigkeit scheint in folgender Reihenfolge erhöht zu werden: Toluol < Methylenchlorid < Tetrahydrofuran. In Bezug auf den Gehalt an der unten erwähnten DMF-unlöslichen Fraktion wird diese Reihenfolge umgekehrt. Das erhaltene Polymere besteht aus zwei Fraktionen: eine ist in Dimethylformamid löslich (DMF) und die andere nicht. Erstere besteht aus amorphem Polymeren und letztere aus kristallinem. Die Infrarotabsorptionsbanden bei 790, 1258 und 1375 cm^{-1} waren für kristallines Polymeres charakteristisch und wurden kristallinen Banden zugeordnet. Diejenigen bei 1270 und 1345 cm^{-1} sind für amorphe Banden charakteristisch. Die kristallinen Banden und C—O—C-Banden zeigen sehr intensiven Infrarotdichroismus, dagegen die Nitrilbande nicht. Aus der Analyse des Röntgenbeugungsdiagrammes wurden als Kristalldaten die Faserperiode von 4,95 Å und andere Elementarzeldimensionen im triklinen System erhalten und mit den Literaturangaben für verschiedene Aldehydpolymeren verglichen. Die Elementarzeldimension a' oder der maximale Netzebenenabstand ist etwas kleiner, was dafür spricht, dass die Moleküle dichter gepackt sind, als Poly-*n*-butyraldehyd, bei welchem die Seitenkette dieselbe Kohlenstoffanzahl besitzt, wie bei Poly(cyanoäthyl)oxymethylen. Innere Rotationswinkel und ein Helixradius wurden für ein isotaktisches Vierfach-Helixmodell des Polymeren berechnet. Schliesslich wurden auch einige andere Polymercharakteristika bestimmt.

Received December 21, 1966

Revised February 20, 1967

Prod. No. 5383A

The Determination of Randomness in Copolyesters by High Resolution Nuclear Magnetic Resonance

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Synopsis

High-resolution nuclear magnetic resonance (NMR) spectra of several kinds of polyesters were measured. Proton signals due to heterolinkages could be observed in some copolyesters, and the average sequence length and the degree of randomness in the copolyester were calculated from the intensities of their signals. A process in the transesterification reaction between two kinds of homopolyester was pursued with the NMR spectra. Random copolyester is formed by the ordinary molten-state copolycondensation and also during the transesterification reaction between two kinds of homopolyester.

Introduction

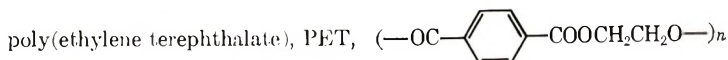
In the study of copolymerization it is necessary to know whether the product is actually a copolymer or a mixture of homopolymers and sometimes to have a knowledge of the degree of randomness in the copolymer chains.

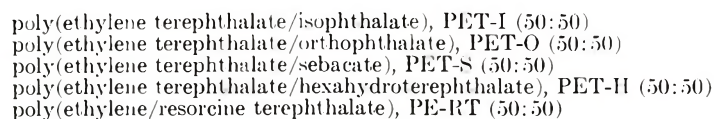
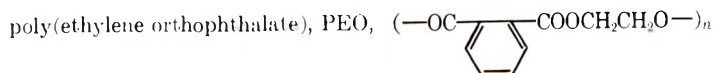
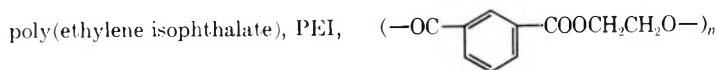
The average sequence length in vinyl copolymers and the stereosequence length in stereoregular polymers have been studied extensively with high-resolution nuclear magnetic resonance (NMR) spectroscopy.¹ There have been, however, few reports on the determination of sequence length in condensation copolymers.² Copolyester prepared by molten-state polycondensation has been generally considered to have a random distribution of the structural units along the polymer chain, because of the almost equal reactivities of the monomers and the random transesterification reaction during the polycondensation process.

In the present paper the NMR spectra of various kinds of copolyester were measured, and the determination of the average sequence length of the structural units was carried out on the copolyesters prepared by ordinary molten-state polycondensation and by transesterification between two kinds of homopolyester.

Experimental

The polyesters used in the experiment were as follows:





These samples were prepared from glycols and dimethyl esters of the acids by ordinary molten-state polycondensation under reduced pressure.

The transesterification reaction was carried out between PET and PES, which were mixed in various proportions at intervals of 10% and stirred under nitrogen atmosphere at 276°C. for the times 10, 30, 60, 120, and 180 min.

The NMR spectra were measured in a trifluoroacetic acid solution (0.05 g./ml.) at 70°C. with a Varian A-60 Spectrometer.

Results and Discussion

The NMR spectra of the homopolyesters are shown in Figure 1, and the assignments of the proton signals are listed in Table I. The chemical shifts of methylene protons in ethylene glycol residue have different values among these polyesters, although the signals are sharp singlets. Correspondingly, the methyl proton signals in dimethyl esters of each of the

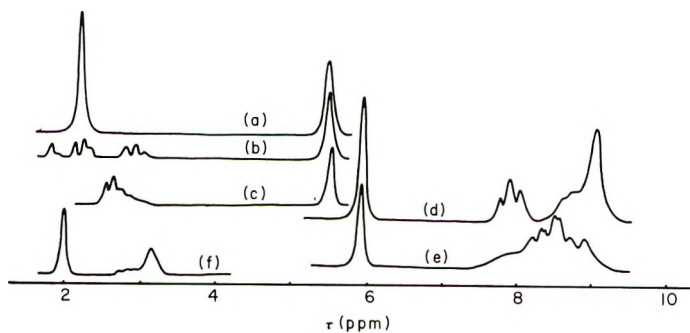


Fig. 1. NMR spectra of homopolyesters: (a) PET, (b) PEI, (c) PEO, (d) PES, (e) PEH, and (f) PRT.

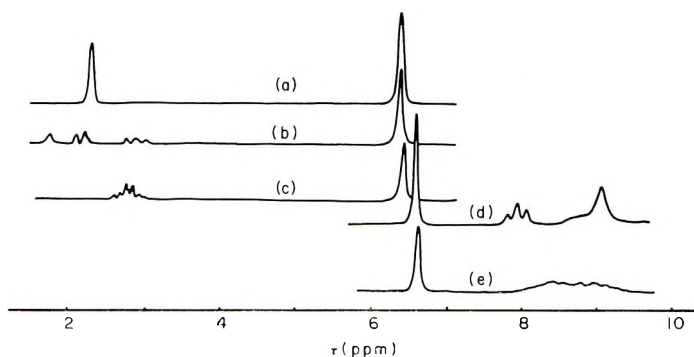


Fig. 2. NMR spectra of dimethyl esters: (a) DMT, (b) DMI, (c) DMO, (d) DMS, and (e) DMH.

acids dimethyl terephthalate (DMT), isophthalate (DMI), orthophthalate (DMO), sebacate (DMS), and hexahydroterephthalate (DMH) are also sharp singlets and have different values of chemical shifts, as shown in Figure 2 and Table II. This fact may be attributed to the electronegativities of those carboxyl groups, namely, the acidities of the original carboxylic acids.

TABLE I
Assignments of Proton Signals and Their Chemical Shifts
in the NMR Spectra of Homopolyesters

	Protons attached to benzene nucleus, ppm	Protons of glycol residue, ppm	Protons of aliphatic chain, ppm
PET	2.23	5.53	—
PEI	1.7–3.0	5.53	—
PEO	2.4–2.9	5.65	—
PES	—	5.93	7.7–9.2
PEH	—	5.95	7.5–9.2
PRT	2.05	3.0–3.3 (resorsine)	—

TABLE II
Assignments of Proton Signals and Their Chemical Shifts in
the NMR Spectra of Dimethyl Esters

	Protons attached to benzene nucleus, ppm	Protons of methyl groups, ppm	Protons of aliphatic chain, ppm
DMT	2.32	6.42	—
DMI	1.7–3.0	6.43	—
DMO	2.6–3.0	6.47	—
DMS	—	6.62	7.7–9.2
DMH	—	6.65	7.6–9.2

TABLE III
Sequence Distributions in PET-S with Various Copolymerization Ratios

No.	S-G-S, %	T-G-S, %	T-G-T, %	S, %	T, %	P_{ST}	P_{TS}	\bar{L}_{nT}	\bar{L}_{nS}	B
1	58.6	33.6	7.8	75.4	24.6	0.223	0.683	1.464	4.484	0.906
2	49.5	38.8	11.7	68.9	31.1	0.282	0.624	0.603	3.546	0.906
3	23.7	51.6	24.7	49.5	50.5	0.322	0.511	1.957	1.916	1.033
4	10.6	42.6	46.8	51.9	68.1	0.667	0.312	3.205	1.499	0.979
5	5.0	33.8	61.2	21.9	78.1	0.771	0.216	4.630	1.297	0.987
6	2.3	18.1	79.6	11.4	88.6	0.798	0.103	9.709	1.253	0.901

TABLE IV
Changes of Sequence Distribution During Transesterification
Between PET and PES at Various Feed Ratios

PET/PES	Time, min.	\bar{L}_{nS}	\bar{L}_{nT}	B
1/9	10	45.455	4.484	0.245
	30	15.140	1.880	0.598
	60	12.195	1.580	0.715
	120	9.709	1.222	0.912
	180	9.346	1.139	0.995
2/8	10	19.608	4.630	0.267
	30	7.752	1.805	0.683
	60	5.780	1.548	0.819
	120	5.618	1.372	0.907
	180	5.495	1.357	0.919
3/7	10	18.182	8.197	0.177
	30	6.494	2.882	0.501
	60	3.623	1.672	0.874
	120	3.584	1.590	0.908
	180	3.610	1.580	0.910
4/6	10	12.500	8.772	0.194
	30	4.425	3.086	0.550
	60	3.175	2.262	0.757
	120	2.890	2.070	0.829
	180	2.777	1.988	0.863
5/5	10	10.905	10.638	0.186
	30	3.289	3.236	0.613
	60	2.404	2.353	0.841
	120	2.222	2.165	0.912
	180	2.141	2.092	0.945
6/4	10	9.615	14.286	0.174
	30	3.344	4.950	0.501
	60	2.028	3.155	0.810
	120	1.855	2.865	0.888
	180	1.894	2.833	0.881
7/3	10	8.130	18.180	0.178
	30	2.817	6.944	0.499
	60	2.283	5.155	0.632
	120	1.672	3.802	0.861
	180	1.520	3.690	0.929
8/2	10	5.102	20.000	0.246
	30	1.842	7.752	0.672
	60	1.488	5.988	0.839
	120	1.445	5.618	0.870
	180	1.385	5.618	0.900
9/1	10	4.444	45.455	0.247
	30	2.000	17.544	0.557
	60	1.658	14.493	0.672
	120	1.202	8.929	0.944
	180	1.195	8.850	0.950

On the other hand, in the NMR spectra of copolyesters such as PET-O, PET-S, and PET-H three peaks are observed in the region of 5.5–6.0 ppm, as shown in Figure 3. Two peaks at both sides are assigned to the ethylene groups placed between the same acid groups, because they coincide with the ethylene proton signals of the homopolyesters. A central peak, which is not observed in the spectra of the corresponding homopolyesters, is due to the ethylene glycol residue bonded to the different acid groups at both sides. The intensity of this peak represents the amount of the "heterolinkage."

For instance, PET-S has three kinds of ethylene glycol residue ($-G-$), one of which is adjacent to terephthalate (T) at both sides, $T-G-T$, one to sebacate at both sides, $S-G-S$, and the other to terephthalate and sebacate, $T-G-S$. Their proton signals appear at 5.53, 5.93, and 5.73

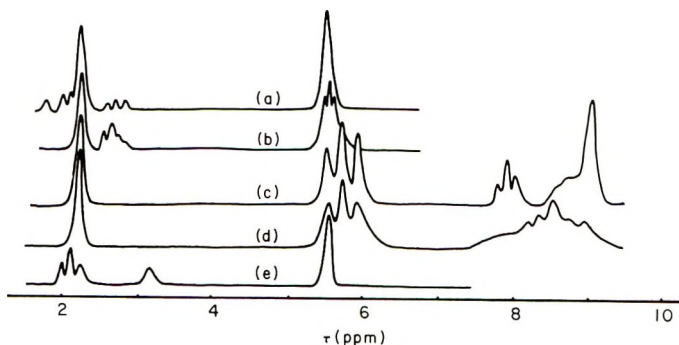


Fig. 3. NMR spectra of copolyesters having copolymerization ratio of 50/50: (a) PET-I, (b) PET-O, (c) PET-S, (d) PET-H, and (e) PE-RT.

ppm, respectively. No fine splitting was observed in the proton signal of the ethylene glycol residue in the heterolinkage because of the small difference in the chemical shifts between the two methylene protons.

The splitting of phenyl proton signals of terephthalate residue in PE-RT is interpreted in the same manner.

In the case of PET-I the chemical shifts of ethylene protons in PET or that of methyl protons in DMT have almost the same values as those of PEI or DMI, and the heterolinkage in PET-I cannot be detected by the NMR spectroscopy at 60 Mc. The possibility of detecting the existence of heterolinkage or of confirming the copolymerization may be predicted by the differences in chemical shifts of the ethylene glycol residue between the corresponding homopolyesters and those of the methyl groups between the corresponding dimethyl esters.

If the three kinds of signals due to homolinkages and heterolinkages are observed in the NMR spectrum of a copolymer, one can determine the average sequence length and the degree of randomness of the copolymer by the known procedure,³ as shown in the following.

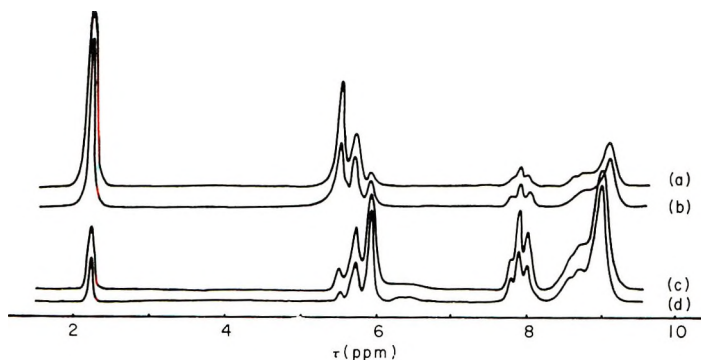


Fig. 4. NMR spectra of PET-S with various copolymerization ratios; (a) 80/20, (b) 70/30, (c) 30/70, and (d) 20/80.

PET-S is taken as an example. Molar fractions of terephthalate (P_T) and sebacate (P_S) are obtained from the intensities of the three kinds of signals in the NMR spectrum; that is,

$$P_T = P_{T-G-S}/2 + P_{T-G-T} \quad (1)$$

$$P_S = P_{T-G-S}/2 + P_{S-G-S} \quad (2)$$

where P_{T-G-T} , P_{S-G-S} , and P_{T-G-S} represent the proportion of the integrated intensities of T—G—T, S—G—S, and T—G—S signals, respectively, to the total intensity of the ethylene glycol residues.

If one could inspect the units along the PET-S copolymer chain from one end to the other, the probability of finding a T unit next to an S unit would be

$$P_{ST} = P_{T-G-S}/2P_S \quad (3)$$

Similarly, an S unit exists next to a T unit with a probability of

$$P_{TS} = P_{T-G-S}/2P_T \quad (4)$$

The degree of randomness is defined by

$$B = P_{ST} + P_{TS} \quad (5)$$

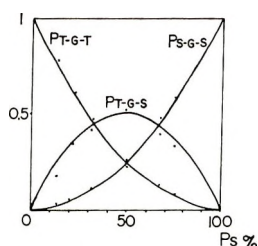


Fig. 5. Relationship between molar fraction of sebacate and proportions of three kinds of ethylene glycol residue in PET-S.

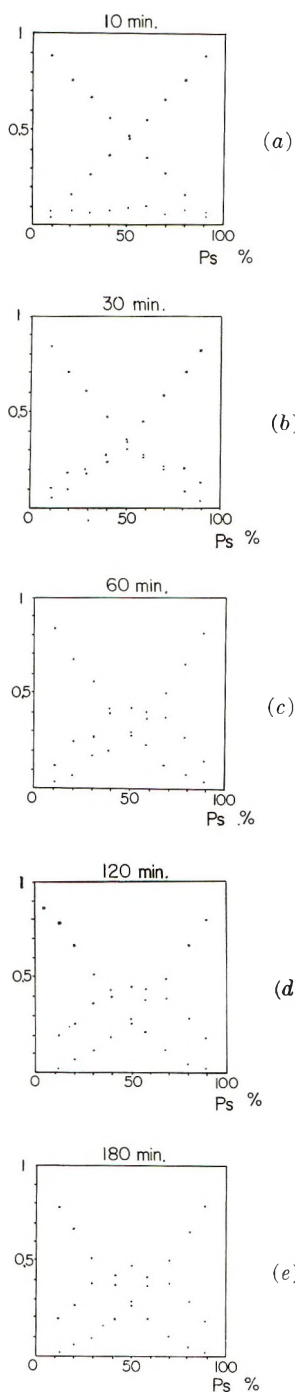


Fig. 6. Relationship between molar fraction of sebacate and proportion of the three kinds of ethylene glycol residue at time of transesterification between PET and PES: (a) 10 min., (b) 30 min., (c) 60 min., (d) 120 min., and (e) 180 min.

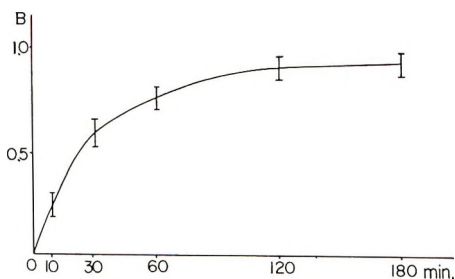


Fig. 7. Changes of degree of randomness (B) during transesterification between PET and PES.

When $B = 1$, the T and S units take a random distribution, and the probability of finding a copolymer unit belongs to Bernoulli statistics. If $B < 1$, these units tend to cluster in blocks of each units, and finally $B = 0$ in a homopolymer mixture, whereas if $B > 1$, the sequence length becomes shorter, and $B = 2$ in an alternative copolymer.

The number-average sequence length of a T unit (\bar{L}_{nT}) and an S unit (\bar{L}_{nS}) are given by

$$\bar{L}_{nT} = 2P_T/P_{T-G-S} = 1/P_{TS} \quad (6)$$

$$\bar{L}_{nS} = 2P_S/P_{T-G-S} = 1/P_{ST} \quad (7)$$

The fractions of the S—G—S, T—G—T, and T—G—S linkages, which are shown in the first three columns of Table III, were obtained from the NMR spectra of the PET-S copolyesters having several kinds of copolymerization ratio (Fig. 4). The parameters P_T , P_S , P_{ST} , P_{TS} , \bar{L}_{nS} , \bar{L}_{nT} , and B shown in Table III were calculated with eqs. (1)–(7). From the value of B , which is almost 1, the copolyester can be recognized to have a random distribution of two units.

Figure 5 is a diagram representing a relationship between the molar fraction of sebacate and the proportions of three kinds of linkage. This diagram follows theoretical curves based on Bernoulli statistics.

It has been reported that a mixture of two kinds of homopolyester changes gradually to a random copolyester by transesterification reaction for several hours at higher temperature than the melting points.⁴ This transesterification between two homopolyesters can be followed by the above-mentioned method, from a polymer mixture in which $B = 0$ to a random copolymer, $B = 1$.

Table IV shows the result of transesterification between PET and PES. For all feed ratios examined the values of B become almost 1 and the number-average sequence lengths \bar{L}_{nS} and \bar{L}_{nT} approach the theoretical values of a random copolymer after transesterification for 3 hr. In Figure 6 the values of P_{T-G-T} , P_{S-G-S} , and P_{T-G-S} are plotted against P_S . At earlier stage of transesterification, as shown in Figure 6a, the copolyester has small amounts of heterolinkage, or it is a block copolymer. The change to a random copolymer from a block copolymer with lapse of time

is seen in the Figures 6a to 6e. Almost all the points in Figure 6e fall on the theoretical curves obtained from Bernoulli statistics.

The increase in the value of B with transesterification time is shown in Figure 7. A random copolymer of PET-S is obtained from PET and PES after 3 hr.

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Résumé

Des spectres de résonance magnétique nucléaire à haute résolution, de nombreuses espèces de polyesters ont été mesurés. Les signaux protoniques dus à des liaisons hétérocycliques peuvent être observés dans certains copolyesters, et alors la longueur de la séquence moyenne et le degré de répartition statistique dans les copolyesters peuvent être calculés au départ des intensités de leurs signaux. Un processus de réaction de transestérification entre deux sortes de homopolyesters a été suivi par spectrométrie NMR. Un copolymère statistique est formé par copolycondensation ordinaire à l'état fondu; il est également formé en course de la transestérification entre deux sortes de homopolyesters.

Zusammenfassung

Hochauflösungs-kernmagnetische Resonanzspektren einiger Arten von Polyestern wurden gemessen. Auf Heteroverknüpfungen zurückzuführende Protonensignale konnten an manchen Copolyestern beobachtet werden; es werden dann die mittlere Sequenzlänge und der Unordnungsgrad in den Copolyestern aus der Intensität ihrer Signale berechnet. Die Umesterungsreaktion zwischen zwei Arten von Homopolyestern wurde an Hand der NMR-Spektren verfolgt. Ein statistischer Copolyester wird sowohl durch die gewöhnliche Copolykondensation in der Schmelze als auch während der Umesterungsreaktion zwischen zwei Arten von Homopolyestern gebildet.

Received December 28, 1966

Prod. No. 5384A

Effect of Impurities and the Initiation and Transfer Rate Constants on the Statistical Character of Anionic Polymers

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Synopsis

The simultaneous effect of impurities, finite rate of initiation, and chain transfer through the monomer on the size distribution in anionic polymers is investigated. It is assumed that monomer is added to the system containing monofunctional initiators in small doses so that there is no accumulation of the monomer or the impurities at any stage of the reaction. Firstly, by using the continuum approach, expressions for the size distribution and the averages are derived for the case when initiation is infinitely fast and chain transfer is absent. These results are compared with those obtained by Orofino and Wenger by a more rigorous analysis, and the adequacy of the simpler results is established. The complexities arising from the finite rate of initiation and chain transfer are considered subsequently. Finally, we describe a procedure for the determination of the initiation and transfer rate constants in terms of propagation rate constant and the fraction of impurities in the monomer supply.

Introduction

In an earlier paper,¹ we studied the effect of initiation and propagation rate constant ratio on the size distribution in anionic polymerization for the case in which an active chain is capable of indefinite growth. In general, however, some termination mechanism would be operative, e.g., a growing chain may undergo chain transfer through the monomer. This leads to the cessation of growth of the chain while the active monomer gives rise to another growing chain. The resulting polymer will thus consist of "active" and "dead" chains. The effect of chain transfer in anionic polymers was studied theoretically by Kyner et al.,² who derived expressions for the size distribution for the active and the dead chains, by solving a set of differential rate equations. These results are in the form of a number of series for which convergence, in general, is so poor that the numerical computations become very tedious for long chains. This problem has also been discussed recently by one of us³ making use of the approximate continuum approach.⁴ Here the expression for the size distribution is obtained in a closed form which is adapted for numerical computations. The number-average chain length and the weight-average chain length results are found to be in excellent agreement with the exact ones when the "modified" time

$\tau \gg 1$. This provides justification for the use of the simplified approach whenever the foregoing condition is satisfied.

In certain cases of anionic polymerizations, the preparation of monomer sufficiently free of deactivating impurities can not be achieved. The effect of impurities on the size distribution of the polymerization in which monomer is added slowly, was first studied by Szwarc and Litt⁵ and later investigated more rigorously for both monofunctional and bifunctional initiators by Orofino and Wenger.⁶ Recently, a general mathematical treatment has been given by Coleman et al.⁷ for batch polymerization. All these authors assumed an infinite rate of initiation of the active centers and the absence of chain transfer. The present communication aims at giving a formulation of this problem for the systems where monomer is added gradually to monofunctional initiators under conditions more general than those considered by earlier authors. Here, the continuum approach⁴ is employed in order to deduce the expressions for the size distribution and the averages of interest. First, the results of Orofino and Wenger's case⁶ are derived by using the continuum approach, and comparisons are made with their exact expressions in order to show the adequacy of our simpler results. The complications arising from the finite rate of initiation and chain transfer are considered subsequently. We have also indicated a procedure of obtaining the impurity ratio in the monomer supply and the ratios of the initiation and transfer rate constants with respect to the propagation rate constant.

Orofino and Wenger's Case

It is assumed throughout in this paper that the impure monomer is added in small doses to the initiator such that the reaction of the propagation centers with impurities is essentially completed within the time interval between the consecutive doses. Thus there would be no accumulation of the monomer or the impurities, even though the rate constants for two processes are different. In the present section, we also assume that the initiation of propagation centers is instantaneous. According to the continuum approach, a small amount dM of monomer consumed increases the chain length by dl , which is given by

$$dl = dM/N^*(l) \quad (1)$$

where $N^*(l)$ represents the number of growing chains (i.e., the number of centers still active) all having the same length l . Consider the stage of the reaction when the maximum chain length is L . The total amount of monomer consumed is then

$$M = \int dM = \int_0^L N^*(l)dl \quad (2)$$

The parameter γ , representing the mole fraction of impurities, may also be regarded as the probability that at any stage of polymerization a growing chain reacts with an impurity; $(1 - \gamma)$ is then the probability for reac-

tion with a monomer. During the increment dM of monomer, the number of active chains terminated is given by

$$dN^* = -\gamma dM \quad (3)$$

Now

$$\begin{aligned} L &= \int_0^M dM/N^*(l) \\ &= -1/\gamma \int_{I_0}^{N^*} dN^*/N^* \\ &= -1/\gamma \ln (N^*/I_0) \end{aligned}$$

where I_0 denotes the number of active centers at the start of polymerization process. This gives

$$N^*(L) = I_0 e^{-\gamma L} \quad (4)$$

Substituting from eq. (4) in eq. (2) we get †

$$\begin{aligned} M &= \int_0^L N^*(l) dl + I_0 \\ &= I_0 \{1 + [(1 - e^{-\gamma L})/\gamma]\} \end{aligned} \quad (5)$$

Thus the number-average chain length is

$$i_n = M/I_0 = (1 + \gamma - e^{-\gamma L})/\gamma \quad (6)$$

With these preliminaries we proceed to deduce the expressions for the size distributions and the averages. The number of dead chains having length ‡ between l and $l + dl$ is given by

$$N_l dl = \gamma N^*(l) dl \quad l \leq L$$

and the number fraction is

$$n_l dl = \gamma e^{-\gamma l} dl \quad l \leq L \quad (7)$$

The number of chains free of impurities, (i.e., still active) is

$$N_L^* = I_0 e^{-\gamma L}$$

The corresponding number fraction is

$$n_L^* = e^{-\gamma L} \quad (8)$$

† I_0 is added on the right-hand side of eq. (5) to take account of the monomer consumed during initiation.

‡ The term length here refers to the number of monomers added by propagation alone. In the calculation of averages, however, due account will be taken of the first monomer added during initiation.

The number-average chain length is then

$$\begin{aligned} \bar{i}_n &= \frac{\int_0^L (l+1)n_l dl + (L+1)e^{-\gamma L}}{\int_0^L n_l dl + e^{-\gamma L}} \\ &= \frac{(1 + \gamma - e^{-\gamma L})}{\gamma} \end{aligned} \quad (9)$$

while the weight-average chain length is

$$\begin{aligned} \bar{i}_w &= \frac{\int_0^L (l+1)^2 n_l dl + (L+1)^2 e^{-\gamma L}}{\int_0^L (l+1)n_l dl + (L+1)e^{-\gamma L}} \\ &= \frac{2 + \gamma}{\gamma} - \frac{2Le^{-\gamma L} + 2 - (1 - e^{-\gamma L})}{(1 + \gamma - e^{-\gamma L})} \end{aligned} \quad (10)$$

We shall now compare the results of our simplified analysis with those obtained by Orofino and Wenger and show that the differences are unimportant for long chains. In their treatment these authors consider first a hypothetical polymerization process in which impurities are assumed not to cause a chain termination. Since they have assumed the initiation to be infinitely fast this obviously gives rise to a Poisson distribution of chain lengths. The size distribution in the actual polymer then is obtained by determining the distribution of first monomer sequence lengths i.e., the total length of the first uninterrupted sequence of monomer units, starting from the initiator unit and ending at the terminus of the chain or at first impurity unit, whichever occurs first. Orofino and Wenger have shown that the average chain length θ_I in the hypothetical material is linked with the average chain length \bar{i}_n in actual polymer (arising from the monomer with impurity level γ) by the relation

$$\bar{i}_n = [1 + \gamma - e^{-\gamma(\theta_I - 1)}] / \gamma \quad (9a)$$

Further, for weight-average chain length they have obtained the expression

$$\bar{i}_w = \frac{2 + \gamma}{\gamma} - \frac{2}{\gamma} \cdot \frac{1}{\bar{i}_n} \{1 - (\theta_I - 1)(\gamma - 1)e^{-(\theta_I - 1)}\} \quad (10a)$$

If we make use of continuum approach, the hypothetical material of Orofino and Wenger would be monodisperse with a chain length $(L + 1)$, L units being added by propagation to each chain. For comparison, parameter θ_I is thus to be equated with $(L + 1)$. Equations (9a) and (10a) can now be written in the form

$$\bar{i}_n = (1 + \gamma - e^{-\gamma L}) / \gamma \quad (9b)$$

and

$$i_w = \frac{2 + \gamma}{\gamma} - \frac{2(1 - \gamma)e^{-\gamma L} + 2}{(1 + \gamma - e^{-\gamma L})} \quad (10b)$$

The expression (9b) is identical with the corresponding eq. (9) of the continuum approach while the expressions (10b) and (10) for i_w differ by $[(1 - 2\gamma L e^{-\gamma L} - e^{-\gamma L})/(1 + \gamma - e^{-\gamma L})]$. This, it may be verified, varies from (-1) for $\gamma L \ll 1$ to 1 for $\gamma L \gg 1$. Such a difference can be ignored for long chains.

Effect of Finite Rate of Initiation

With a finite initiation rate constant, the initiation gives rise to new chains during the polymerization process, while some of the growing chains are terminated by reaction with impurities.

Let δM denote the monomer added in a dose after an amount M of the monomer has already polymerized. Then

$$\delta M = k_p(I_0 - I - \gamma M) \int M' dt + \delta I \quad (11)$$

and for the initiator consumed is

$$\delta I = -k_i I (1 - \gamma) \int M' dt \quad (12)$$

where M' denotes the instantaneous monomer concentration. Obviously, $(I_0 - I - \gamma M)$ is the total number of active chains in the system at that instant, I being the initiator concentration. It is assumed here that initiation is slow so that I does not change appreciably during the consumption of a monomer dose. Thus,

$$\delta I / (\delta M + \delta I) = -(k_i/k_p)(1 - \gamma)I / (I_0 - I - \gamma M) \quad (13)$$

Increase in chain length δl by propagation is given by

$$\delta l = (\delta M + \delta I) / (I_0 - I - \gamma M) \quad (14)$$

Hence,

$$\begin{aligned} \delta I / \delta l &= -(k_i/k_p)(1 - \gamma)I \\ &= -\alpha(1 - \gamma)I \end{aligned} \quad (15a)$$

For infinitesimal doses of monomer, the deltas δ can be replaced by differentials so that

$$dI/dl = -\alpha(1 - \gamma)I \quad (15b)$$

which for $\gamma \ll 1$ leads to

$$I = I_0 e^{-\alpha l} \quad (16)$$

Similarly from eq. (14) integration gives

$$M = I_0 \left\{ [(1 - e^{-\gamma l})/\gamma] - [(e^{-\alpha l} - e^{-\gamma l})/(\gamma - \alpha)] + (1 - e^{-\alpha l}) \right\} \quad (17)$$

We now make use of the continuum approach⁴ to deduce an expression for the size distribution at the stage when the maximum chain length is L . The number $N_l dl$ of chains with length between l and $l + dl$ consists of two types: (1) active chains which have not reacted with the impurities, and (2) dead chains which have been terminated by reaction with the impurities. The first type arises from initiators which entered the reaction when the maximum chain length was $(L - l)$ and did not react with an impurity, the probability for which is $e^{-\gamma l}$. This number is given by

$$\alpha(I)_{L-l} \cdot e^{-\gamma l} dl = \alpha I_0 e^{-\gamma(L-l)} dl$$

The probability that a chain is terminated on attaining the length l is $\gamma e^{-\gamma l}$. Such chains can arise from the initiators entering the reaction in the interval 0 to $(L - l)$ whose number is given by

$$\alpha \int_0^{L-l} I_0 e^{-\alpha l'} dl' = I_0 [1 - e^{-\alpha(L-l)}]$$

Thus the number of chains of the second type with length between l and $l + dl$ is

$$\gamma I_0 e^{-\gamma l} [1 - e^{-\alpha(L-l)}] dl$$

Hence the total number of chains with length between l and $l + dl$ is given by

$$n_l dl = \alpha I_0 e^{-\alpha L} e^{(\alpha-\gamma)l} dl + \gamma I_0 e^{-\gamma l} [1 - e^{-\alpha(L-l)}] dl \quad (18)$$

The corresponding number fraction is

$$n_l dl = (1 - e^{-\alpha L})^{-1} \left\{ (\alpha - \gamma) e^{-\alpha L} \cdot e^{(\alpha-\gamma)l} + \gamma e^{-\gamma l} \right\} dl \quad (19)$$

The expressions for the averages are easily obtained. We find

$$i_n = (1 - e^{-\alpha L})^{-1} \left\{ [(1 - e^{-\gamma L})/\gamma] - [(e^{-\gamma L} - e^{-\alpha L})/(\alpha - \gamma)] \right\} + 1 \quad (20)$$

and

$$i_w = \frac{1}{i_n} \left\{ \frac{2(1 - e^{-\alpha L})^{-1}}{\gamma} \times \left[\frac{1 - e^{-\gamma L}}{\gamma} - L e^{-\gamma L} - \frac{L e^{-\gamma L}}{(\alpha - \gamma)} + \frac{e^{-\gamma L} - e^{-\alpha L}}{(\gamma - \alpha)^2} \right] + 1 \right\} + 2 \quad (21)$$

It can be verified that the results of the previous section are obtainable from eqs. (19), (20), and (21) when $\alpha \rightarrow \infty$.

Combined Effect of Chain Transfer and Finite Rate of Initiation

In the earlier paper,³ the problem of chain transfer through the monomer in the absence of impurities is treated as a two-stage process. In the

first stage the polymer is assumed to grow in the absence of transfer, while in the second one this hypothetical material is made to yield the actual polymer through degradation. It is found that this degradation can be treated as random while the degree of degradation

$$\sigma = k_t / (k_p + k_t)$$

We shall now make use of the two-stage procedure to deduce the expression for the size distribution when impurities are also present in the monomer supply. In absence of chain transfer, the number fraction for the hypothetical material is given by the eq. (19) derived in the preceding section.* For the second-stage process, the number fraction in the degraded material is given by the expression⁸

$$n_i = \frac{(1 - \sigma)^{i-1}}{1 + \sigma(P - 1)} \left\{ \phi(i) + \sigma \sum_{t>i} \phi(t) [2 + (t + i - 1) \sigma] \right\} \quad i \leq L$$

where $\phi(i)$ is the number fraction of the initial (first-stage) material with average chain length P . Substituting for the initial size distribution from eq. (19) and replacing summation by integration, we obtain for the final size distribution:

$$n_i = \frac{(1 - \sigma)^{i-1} (1 - e^{-\alpha L})^{-1}}{1 + \sigma(P - 1)} \left\{ (\alpha - \gamma) e^{-\alpha L} \cdot e^{(\alpha - \gamma)i} + \gamma e^{-\gamma i} + \sigma \left(2 + \frac{\sigma}{\gamma} \right) (e^{-\gamma i} - e^{-\gamma L}) + \sigma \left(2 - \frac{\sigma}{\alpha - \gamma} \right) \times [e^{-\gamma L} - e^{-\alpha L} \cdot e^{(\alpha - \gamma)i}] \right\} \quad i \leq L \quad (22)$$

The number-average chain length for the initial material according to eq. (20) is given by

$$P = (1 - e^{-\alpha L})^{-1} \left\{ \frac{1 - e^{-\gamma L}}{\gamma} - \frac{e^{-\gamma L} - e^{-\alpha L}}{\alpha - \gamma} \right\} + 1$$

Since $\sigma(P - 1)$ gives the average number of cuts per chain of the first-stage material, the number-average chain length i_n in the final polymer is given by

$$i_n = \frac{P}{1 + \sigma(P - 1)} = \frac{(1 - e^{-\alpha L}) + \left[\frac{1 - e^{-\gamma L}}{\gamma} + \frac{e^{-\gamma L} - e^{-\alpha L}}{\alpha - \gamma} \right]}{(1 - e^{-\alpha L}) + \sigma \left[\frac{1 - e^{-\gamma L}}{\gamma} - \frac{e^{-\gamma L} - e^{-\alpha L}}{\alpha - \gamma} \right]} \quad (23)$$

* Strictly a formal change in various expressions of the preceding section is called for since, in the presence of chain transfer, monomer is incorporated into the first-stage polymer according to the rate constant $(k_p + k_t)$ instead of k_p . All the results of the previous section apply in the present case by replacing k_p by $(k_p + k_t)$.

The weight-average chain length i_w in the degraded (second-stage) material is given by⁸

$$i_w = \frac{2 - \sigma}{\sigma} - \frac{2(1 - \sigma)}{\sigma^2(P - 1)} [1 - \Sigma_t \phi(t) \cdot (1 - \sigma)^t] \quad (24)$$

Substituting for $\phi(t)$ from eq. (19), we obtain, on simplification,*

$$i_w = \frac{2 - \sigma}{\sigma} - \frac{2(1 - \sigma)}{\sigma^2(P - 1)} \left\{ 1 - \left(\frac{\alpha - \gamma}{\alpha - \gamma - \sigma} \right) \times \left[\frac{e^{-(\gamma + \sigma)L} - e^{-\alpha L}}{1 - e^{-\alpha L}} \right] - \left(\frac{\gamma}{\gamma + \sigma} \right) \left[\frac{1 - e^{-(\gamma + \sigma)L}}{1 - e^{-\alpha L}} \right] \right\} \quad (25)$$

Discussion of Results

In this section we first examine some interesting statistical features of the polymer. For the case when αL , σL , and $\gamma L \ll 1$, the expressions for the number-average chain length and the weight-average chain length can be written in a simplified manner. Equation (23) takes the form

$$i_n = (L/2) \{ 1 + (\alpha L/6) [1 - (2\gamma/\alpha) - (3\sigma/\alpha)] \dots \} \quad (25)$$

To derive the corresponding expression for weight-average chain length, it is more convenient to use the result (24) instead of the final eq. (25) for i_w . The summation in eq. (24) on expansion in terms of σ as a parameter involves the moments of the initial distribution. One finds on simplification,

$$i_w = 1/\Sigma_t \phi(t) [\Sigma_t^2 \phi(t) - (\sigma/3) \Sigma_t^3 \phi(t) + \dots] \quad (26)$$

Substituting for $\Sigma_t \phi(t)$, $\Sigma_t^2 \phi(t)$, and $\Sigma_t^3 \phi(t)$, one gets

$$i_w = (2L/3) \{ 1 + (\alpha L/12) [1 - (2\gamma/\alpha) - (3\sigma/\alpha)] - \dots \} \quad (27)$$

Thus

$$R = i_w/i_n = 4/3 \{ 1 - (\alpha L/12) [1 - (2\gamma/\alpha) - (3\sigma/\alpha)] + \dots \} \quad (28)$$

which shows that for the limiting case $\alpha L \rightarrow 0$, the inhomogeneity ζ ($= R - 1$) would have a value $1/3$, characteristic of the rectangular distribution. It may also be noted that for nonnegligible values of αL , the impurities and chain transfer counteract the effect of finite rate of initiation.

For the case when $(2\gamma + 3\sigma) > \alpha$, the inhomogeneity ζ would increase monotonically with increasing L . It would finally attain the most probable value equal to unity in the limit $(\gamma + \sigma)L \gg 1$, as may be easily verified by the help of eqs. (23) and (24). On the other hand, when $(2\gamma + 3\sigma) < \alpha$, ζ would decrease with increasing L so long as the condition $(\gamma + \sigma)L \ll 1$ is applicable. Since eventually when $(\alpha + \sigma)L \gg 1$, it again attains

* Since we are using continuum distribution for $\phi(t)$, summations have been replaced by integrations in the evaluation of moments.

the most probable value, there must occur a minimum in the inhomogeneity as function of L (or M). It seems of some interest to locate the position of this minimum.

From eqs. (23) and (25), for $\alpha L \gg 1$ and $(\gamma + \sigma)L \ll 1$, we obtain

$$\frac{1}{i_n} = \sigma + \frac{1}{L} \left\{ 1 + \frac{\gamma L}{2} + \frac{\gamma^2 L^2}{12} + \frac{1}{\alpha L} + \frac{1}{\alpha^2 L^2} + \left(\frac{\gamma}{2\alpha} \right) \frac{1}{\alpha L} - \left(\frac{\gamma}{\alpha} \right) \frac{\gamma L}{12} + \dots \right\} \quad (29)$$

and

$$i_w = L \left\{ 1 - \frac{\sigma L}{3} - \frac{\gamma L}{6} - \frac{1}{\alpha L} + \frac{\sigma^2 L^2}{12} + \frac{\gamma \sigma L^2}{12} + \frac{(\gamma + 2\sigma)}{3\alpha} + \frac{1}{\alpha^2 L^2} - \dots \right\} \quad (30)$$

where

$$\frac{i_w}{i_n} = 1 + (\gamma + 2\sigma) \frac{L}{3} - \sigma(\gamma + \sigma) \frac{L^2}{4} - \frac{(\gamma + 2\sigma)}{3\alpha} + \frac{1}{\alpha^2 L^2} - \dots \quad (31)$$

The position of the minimum in ζ versus L curve is given by the solution of the approximate equation

$$L_{\min}^4 - \frac{2(\gamma + 2\sigma)}{3(\gamma + \sigma)} L_{\min}^3 + \frac{4}{\sigma \alpha^2} \cdot \frac{1}{(\gamma + \sigma)} = 0 \quad (32)$$

which gives

$$L_{\min} \simeq \left[\frac{6}{\alpha^2} \cdot \frac{1}{(\gamma + 2\sigma)} \right]^{1/3} \left\{ 1 + \frac{\sigma(\gamma + \sigma)}{2(\gamma + 2\sigma)} \left[\frac{6}{\alpha^2} \cdot \frac{1}{(\gamma + 2\sigma)} \right]^{1/3} \right\} \quad (33)$$

This result may have some practical importance in connection with attempts to make polymers with low polydispersity.

The problem of determination of the ratios α , σ , and γ will now be considered. In the previous section we have obtained expressions for the various statistical quantities when, besides the complications treated above, chain transfer through the monomer is also operative. Since this additional feature does not alter the number of active centers, eq. (17) for monomer consumed applies, provided we take $\alpha = k_i/(k_p + k_t)$. Making use of eqs. (17) and (23) we may write

$$1/i_n = [I_0(1 - e^{-\alpha L})/M] + \sigma \quad (34)$$

Since the fraction of impurities γ in the monomer in general will be very small, we may assume that $\alpha \gg \gamma$. When the reaction has sufficiently advanced, this gives the simple relation

$$1/i_n \simeq (I_0/M) + \sigma \quad (34a)$$

A plot of $1/i_n$ versus $1/M$ will thus be a straight line, which on extrapolation will give an intercept σ on the y axis. For the earlier stages of the reaction characterized by $\alpha L \ll 1$, eq. (34) with the help of eq. (17) takes the form

$$1/i_n \simeq (2\alpha I_0)^{1/2} (1/M)^{1/2} + \sigma \quad (34b)$$

Thus a plot of $1/i_n$ versus $1/M^{1/2}$ should give a straight line whose slope would make the determination of α possible. From a knowledge of σ and α , value of γ can be obtained from eq. (23), most simply from the number-average chain length values for sufficiently advanced stage of the reaction characterized by $\gamma L \gg 1$.

One of us (R. K. J.) is thankful to the Counsel of Scientific and Industrial Research, India, for a fellowship.

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Résumé

L'effet simultané des impuretés, de la vitesse limitée de l'initiation et du transfert de chaîne sur monomères sur la distribution de grandeur dans des polymères anioniques a été étudié. On admet que le monomère soit additionné à un système contenant des initiateurs monofonctionnels en petites quantités de telle sorte qu'il n'y a pas d'accumulation de monomère, ni d'impuretés à n'importe quel stade de la réaction. Premièrement, en utilisant une approche continue, les expressions pour la distribution de grandeurs et des moyennes ont été déduites dans le cas où l'initiation est infiniment rapide et le transfert de chaîne absent. Ces résultats sont comparés à ceux obtenus par Orofino et Wenger par des analyses plus rigoureuses et on prouve que les résultats plus simples sont parfaitement adéquats. Les complexités résultant d'une vitesse d'initiation finie et du transfert de chaîne sont considérées ensuite. Finalement nous décrivons un procédé pour la détermination des constantes de vitesse d'initiation et de transfert sur la base de la constante de vitesse de propagation et de la fraction d'impuretés dans le monomère.

Zusammenfassung

Der gleichzeitige Einfluss von Verunreinigungen sowie einer endlichen Start- und Übertragungsgeschwindigkeit durch das Monomere auf die Grössenverteilung bei anionischen Polymeren wird untersucht. Es wird angenommen, dass das Monomere dem einen monofunktionellen Initiator enthaltenden System in kleinen Dosen zugesetzt wird, so dass in keinem Reaktionsstadium eine Anhäufung von Monomerem oder der Verunreinigungen auftritt. Zunächst werden unter Annahme von Kontinuitätsbedingungen die Ausdrücke für die Grössenverteilung und die Mittelwerte für den Fall einer unendlich raschen Initiierung und des Fehlens einer Kettenübertragung abgeleitet. Die Ergebnisse werden mit den von Orofino und Wenger nach einem strengeren Verfahren erhaltenen verglichen und die Angemessenheit der einfacheren Ergebnisse nachge-

wiesen. Dann werden die durch die endliche Initiierungs- und Kettenübertragungsgeschwindigkeit bedingten Komplikationen einer Betrachtung unterzogen. Schliesslich wird ein Verfahren zur Bestimmung der Initiierungs- und Übertragungsgeschwindigkeitskonstanten mit Hilfe der Wachstums geschwindigkeitskonstanten und des Anteils an Verunreinigungen im Monomervorrat beschrieben.

Received January 4, 1967

Revised February 20, 1967

Prod. No. 5390A

Kinetics of Emulsion Polymerization

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Synopsis

The quantitative theory of the free-radical mechanism in emulsion polymerization is re-examined. A mechanism involving desorption and reabsorption of radicals is discussed. The average number of radicals per particle has been calculated as a function of three parameters. A simplified, approximate solution for the average number of radicals per particle is given for cases where this number is low.

A kinetic description of emulsion polymerization necessitates the knowledge of the stationary-state distribution of growing molecules in the latex particles, i.e., the average number of radicals per particle. This number may be evaluated from a probabilistic analysis. Such analyses have been provided by Stockmayer¹ and O'Toole.² The latter author has shown that the solution given by Stockmayer, although mathematically correct, is physically unacceptable for small but finite rates of radical desorption. The recurrence relation used by O'Toole for the case that the radicals are liberated in the water phase is:

$$(\rho_A/N^w)P_n = [k_d + nk_{tp}/v](n+1)P_{n+1} + (k_{tp}/v)(n+1)(n+2)P_{n+2} \quad (1)$$

where ρ_A is the rate of absorption of radicals per unit volume of H₂O, N^w is the total number of particles per unit volume of H₂O, k_d is the rate constant of desorption of radicals from a particle. (The rate of desorption from a particle containing n radicals is expressed as $r_d = nk_d$.) Also, P_n is the probability of n -fold occupancy in a particle, v is the volume of a polymer particle, and k_{tp} is the rate constant of mutual termination of radicals in the particles.

The solution of this equation, as given by O'Toole, for the average number of radicals per particle is

$$\bar{n} = (a/4)I_m(a)/I_{m-1}(a) \quad (2)$$

where I_m and I_{m-1} denote modified Bessel functions,

$$a = (8\alpha)^{1/2} = (8\rho_A v/N^w k_{tp})^{1/2}$$

$$m = k_d(v/k_{tp})$$

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By numerical methods this expression allows \bar{n} to be calculated as a function of α and m .

If the desorption of a radical involves a destruction of the activity of this radical, ρ_A may, as has been done by O'Toole, be treated as an independent variable, and may be set equal to the rate of production of radicals. This is kinetically equivalent to a case where, in addition to a second-order termination by mutual reaction of radicals, a first-order termination reaction takes place in the particles.

However, in discussing a case involving desorption of radicals from the particles, reabsorption of radicals into the particles should be taken into account. Recently, Ley et al.³ investigated the emulsion polymerization of several monomers by means of intermittent radiation. The interparticle termination observed by these authors may be taken to indicate the existence of desorption and reabsorption of radicals. Such a mechanism has earlier been advanced by Romatowski and Schultz⁴ for the emulsion polymerization of styrene, based on experiments with intermittent ultraviolet radiation.

In a mechanism involving desorption and reabsorption of radicals, ρ_A and thereby α are not independent variables. It would clearly be desirable to express \bar{n} as a function of a parameter which is determined by the rate of production of radicals in the water phase. The rate of absorption of radicals into the particles may be expressed as

$$\rho_A = \rho^w + k_d \sum_{n=1}^{\infty} nN_n - 2k_{tw}(C_R^w)^2 \quad (3)$$

where ρ^w is the rate of radical production in the water phase per unit volume of water, N_n is the number of particles per unit volume of water, containing n radicals, k_{tw} is the rate constant for mutual termination of radicals in the water phase, and C_R^w is the stationary state concentration of radicals in the water phase (molecules/unit volume water).

The rate of absorption of radicals into the particles may be expected to be proportional to the concentration of radicals in the water phase, i.e., $\rho_A = k_a C_R^w$. By inserting $C_R^w = \rho_A/k_a$ in eq. (3) and multiplying each term by $v/k_{tp} N^w$, one obtains:

$$\alpha = \alpha' + m\bar{n} - Y\alpha^2 \quad (4)$$

where

$$\alpha = \rho_A v / N^w k_{tp} = \rho_A V_p / (N^w)^2 k_{tp}$$

$$\alpha' = \rho^w v / N^w k_{tp} = \rho^w V_p / (N^w)^2 k_{tp}$$

$$m = k_d v / k_{tp} = k_d V_p / N^w k_{tp}$$

and

$$Y = 2N^w k_{tp} k_{tw} / k_a^2 v = 2(N^w)^2 k_{tp} k_{tw} / k_a^2 V_p$$

where V_p is the total volume of latex particles per unit volume of water.

By means of eqs. (2) and (4), \bar{n} may be evaluated as a function of α' , m , and Y in the manner described in the Appendix.

In Figure 1 $\log \bar{n}$ is given as a function of $\log \alpha'$ over a wide range of m values for the case that $Y = 0$. It follows from eqs. (3) and (4) that $Y = 0$ involves that the water-phase termination is completely negligible compared to the termination in the particles for all values of α' and m . It may be seen from Figure 1 that at low values of \bar{n} , $\log \bar{n}$ is proportional to $\log \alpha'$ with a slope of approximately $1/2$. This means that in this region \bar{n} , and consequently the rate of polymerization, should be half-order with respect to the concentration of initiator in the water phase. At low values of m , the order of \bar{n} with respect to α' decreases with increasing values of α'

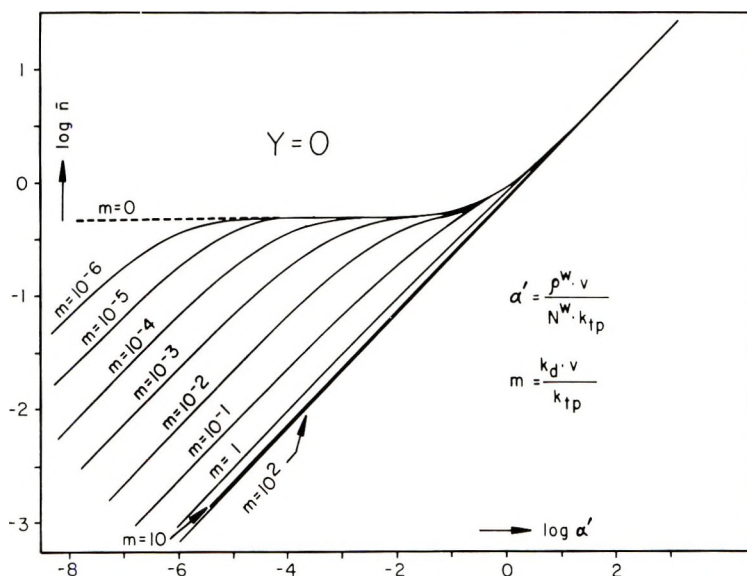


Fig. 1. Average number of radicals per particle \bar{n} as a function of the parameters α' and m for $Y = 2k_{tp}k_{tw}N^w/k_a^2v = 0$.

and passes through an approximately zero-order range. The decrease in order appears at a lower value of α' the lower the value of m . The limiting case, given by $m = 0$, is represented by the dashed line in Figure 1. At still higher values of α' , the order again increases to $1/2$, and the value of \bar{n} becomes independent of m . In the case that $Y = 0$, it is furthermore seen that at high values of m , \bar{n} is independent of m in the entire range of α' , and is half-order with respect to α' .

Figures 2, 3, and 4 give $\log \bar{n}$ as a function of $\log \alpha'$ for different values of m for $Y = 10^{-4}$, 10^{-2} , and 1, respectively.

The difference between a value of \bar{n} as obtained from one of these curves for a given set of values of α' and m , and the value of \bar{n} given by Figure 1 for the same set of α' and m , may be taken to indicate the relative contribution of water-phase termination to the overall rate of termination.

Termination in the water phase ($Y > 0$) will tend to reduce the value of \bar{n} as compared to the value of \bar{n} for $Y = 0$ (no water-phase termination).

When $Y = 10^{-4}$, the curves for $\log \bar{n}$ as a function of $\log \alpha'$ coincide with the curves of Figure 1 if $\alpha' < \sim 10^3$ and $m < \sim 10$. The upper limits of α'

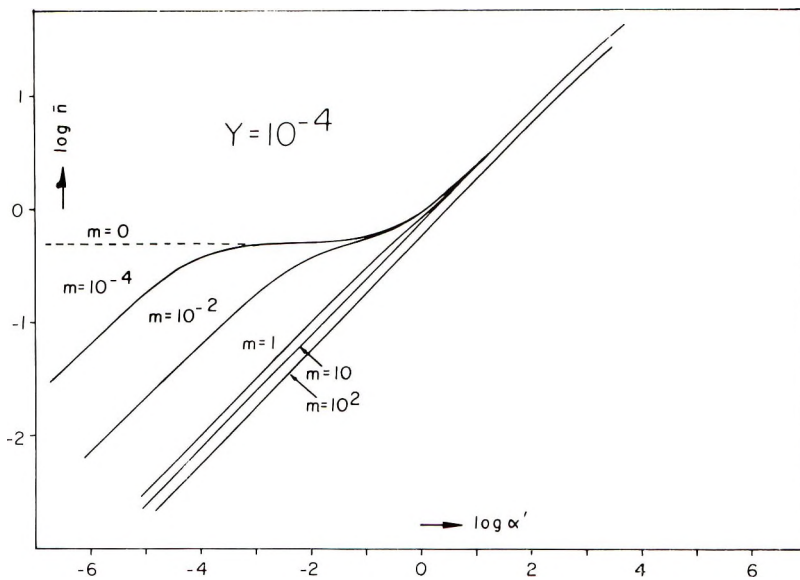


Fig. 2. Average number of radicals per particle \bar{n} as a function of the parameters α' and m for $Y = 10^{-4}$.

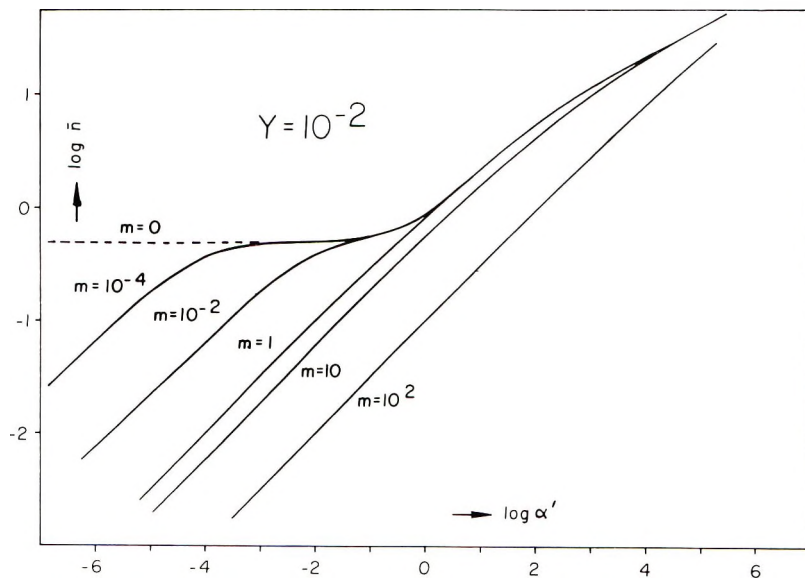


Fig. 3. Average number of radicals per particle \bar{n} as a function of the parameters α' and m for $Y = 10^{-2}$.

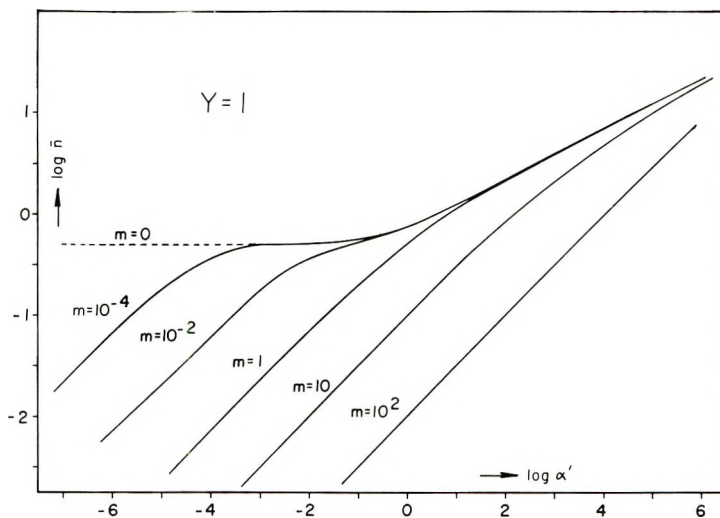


Fig. 4. Average number of radicals per particle \bar{n} as a function of the parameters α' and m for $Y = 1$.

and m below which the water-phase termination approximately may be neglected, decrease as the value of Y increases. For $Y = 10^{-2}$, the water-phase termination may be neglected if $\alpha' < \sim 10$ and $m < \sim 1$, for $Y = 1$ the necessary condition is $\alpha' < \sim 10^{-1}$ and $m < \sim 10^{-2}$.

It is difficult to estimate the value of Y with certainty. If the rate of absorption is simply a diffusion process, k_a is given⁵ by: $k_a = 4\pi DN^w r$, where D is the diffusion constant of the free radical through the water and r is the particle radius. Y is then given by:

$$\begin{aligned}
 Y &= k_{tp}k_{tw}/8\pi^2D^2r^2V_p \\
 &= k_{tp}k_{tw}/30D^2V_p^{5/3}N^{w-2/3}
 \end{aligned}
 \tag{5}$$

For an estimation of the actual values of Y by emulsion polymerization, we may consider a case where the total volume of latex particles per unit volume of water $V_p = 0.1$. Let $D = 10^{-5}$ cm.²/sec.,⁵ and as an example the number of particles $N^w = 10^{14}$ /cm.³ of water, then the value of the denominator in eq. (5) will be 3×10^{-20} . The appropriate units for the termination constants in the nominator are cubic centimeters per molecule-second. If as a further approximation, the product $k_{tp}k_{tw}$ is set equal to k_t^2 , where k_t is the rate constant of termination obtained in solution, Y values for different monomers may be estimated. For most monomers the value of Y obtained in this way is found to be less than 10^{-4} at the chosen value of N^w . As stated above, the water-phase termination may in this case be neglected up to relatively high values of α' and m .

It may be noted that a tendency towards an increase in the water phase termination brought about by an increase in the number of particles, and thereby in the value of Y , will be counteracted by a simultaneous decrease

in the values of α' and m . Similarly, a decrease in the value of Y due to a lowering of the value k_{tp} will be more than outweighed by the increase in both α' and m .

Recently, Ugelstad et al.⁶ have evaluated an approximate expression for the rate of polymerization, valid at low values of \bar{n} , in the case that desorption and reabsorption of radicals into the particles take place. This was done by assuming that at low values of \bar{n} , only particles containing 0, 1, and 2 radicals need be considered. The following steady-state equations may be formulated:

$$dN_1/dt = (\rho_A/N^w)[N^w - (N_1 + N_2)] + 2k_dN_2 - k_dN_1 - \rho_A(N_1/N^w) = 0 \quad (6)$$

$$dN_2/dt = \rho_A(N_1/N^w) - 2k_dN_2 - 2(k_{tp}/v)N_2 = 0 \quad (7)$$

$$dn_t/dt = \rho^w - (4k_{tp}/v)N_2 - 2k_{tw}(C_R^w)^2 = 0 \quad (8)$$

where N_1 and N_2 denote the number of particles containing one and two radicals, respectively, and n_t is the total number of radicals in the system. Assuming that $N^w \gg N_1 \gg N_2$, eqs. (6), (7), and (8) give:

$$\begin{aligned} \bar{n} = \frac{N_1}{N^w} &= \left\{ \frac{\rho^w k_a^2 (vk_d + k_{tp})}{2N^w [k_{tp}k_dk_a^2 + k_{tw}k_d^2N^w(vk_d + k_{tp})]} \right\}^{1/2} \\ &= \left\{ \frac{\alpha'}{m} \left[\frac{1+m}{2+Ym(1+m)} \right] \right\}^{1/2} \end{aligned} \quad (9)$$

By comparison with Figures 1-4 it is easily verified that eq. (9) is generally valid for values of $\bar{n} \ll 1$. If $Y \ll 2/m(1+m)$, eq. (9) reduces to

$$\bar{n} = \{(\alpha/2)[1 + (1/m)]\}^{1/2} \quad (10)$$

This equation may be obtained directly from the stationary-state equations by neglecting the term involving water-phase termination in eq. (8). Equation (10) appeared to be consistent with the experimental results obtained in the emulsion polymerization of vinyl chloride.⁶

APPENDIX

Computation of \bar{n}

O'Toole has computed \bar{n} as a function of α at the values 0, $1/3$, $1/2$, $2/3$, and 1 of m . To compute \bar{n} at all non-negative values of m , the following procedure may be used.

The recursion formula for modified Bessel functions,

$$I_{m-1}(a) - I_{m+1}(a) = (2m/a)I_m(a)$$

may be written:

$$\frac{I_m(a)}{I_{m-1}(a)} = \frac{1}{(2m/a) + [I_{m+1}(a)/I_m(a)]} \quad (11)$$

leading to the following continued fraction for $I_m(a)/I_{m-1}(a)$:

$$\begin{aligned} \frac{I_m(a)}{I_{m-1}(a)} &= \frac{1}{2m/a + \frac{1}{2(m+1)/a + \frac{1}{2(m+2)/a + \dots}}} \\ &= \frac{a/2}{m} + \frac{a^2/4}{m+1} + \frac{a^2/4}{m+2} + \dots \end{aligned} \quad (12)$$

From eqs. (2) and (12):

$$\begin{aligned} \bar{n} &= (a/4) \frac{I_m(a)}{I_{m-1}(a)} \\ &= 1/2 \frac{a^2/4}{m} + \frac{a^2/4}{m+1} + \frac{a^2/4}{m+2} + \dots \end{aligned} \quad (13)$$

and, since $a^2/4 = 2\alpha$,

$$\bar{n} = 1/2 \frac{2\alpha}{m} + \frac{2\alpha}{m+1} + \frac{2\alpha}{m+2} + \dots \quad (14)$$

The continued fraction converges for all $\alpha \geq 0$, $m \geq 0$, and convergence is usually very fast.

A graph of \bar{n} as a function of α' at a given value of m may be obtained by choosing a set of points α , computing \bar{n} at those points, and then calculating the corresponding values of α' from the equation:

$$\alpha' = \alpha - m\bar{n} + Y\alpha^2$$

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Résumé

La théorie quantitative du mécanisme radicalaire de la polymérisation en émulsion a été réexaminée. Un mécanisme comportant la désorption et la réabsorption des radicaux est discuté. Le nombre moyen de radicaux par particules a été calculé en fonction de trois paramètres. Une solution simplifiée approchée pour le nombre moyen de radicaux par particule est donnée pour les cas où ce nombre est faible.

Zusammenfassung

Die quantitative Theorie des Radikalmechanismus der Emulsionspolymerisation wird überprüft. Ein Mechanismus mit Desorption und Reabsorption von Radikalen wird diskutiert. Die mittlere Anzahl von Radikalen pro Partikel wurde als Funktion von drei Parametern berechnet. Eine vereinfachte Näherungslösung für die mittlere Anzahl von Radikalen pro Partikel wird für solche Fälle angegeben, in welchen diese Anzahl klein ist.

Received November 11, 1966

Revised March 2, 1967

Prod. No. 5392A

Aromatic Polyhydantoins from Bisiminoacetate and Diisocyanates*

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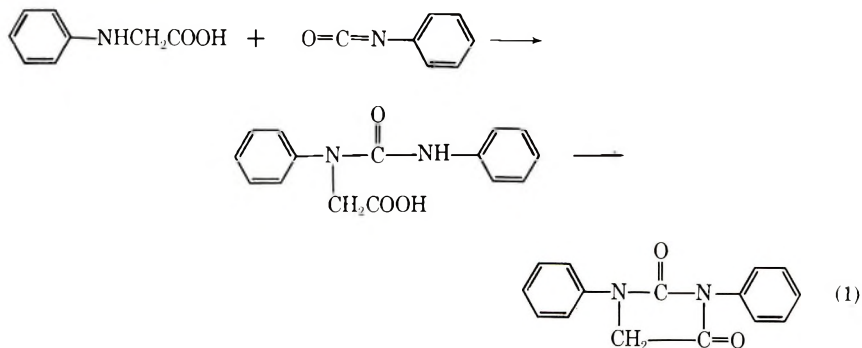
Synopsis

Aromatic polyhydantoins of high molecular weight have been prepared by a polyaddition-cyclocondensation reaction of diethyl *m*-phenylenebisiminoacetate with aromatic diisocyanates in *m*-cresol. The polyhydantoin obtained from methylenebis(4-phenyl isocyanate) showed good thermal stability up to 400°C. in air. A transparent and tough film could be cast from a *m*-cresol solution of the polymer.

INTRODUCTION

Recently many polymers containing recurring heterocyclic units have been investigated. Polyhydantoins and their analogs have been prepared by the polycycloaddition reaction of diisocyanates with hydrogen cyanide¹ and by the polycondensation of bishydantoins with formaldehyde.²

In the field of synthetic organic chemistry, it is well known^{3,4} that the reaction of amino acids or their esters with isocyanates is one of the most efficient routes to substituted hydantoins; the reaction of phenyliminoacetic acid with phenyl isocyanate has been reported by Wheeler and Hoffman⁵ to give 1,3-diphenyl hydantoin [eq. (1)].



Also, it has been shown in extensive studies by Mouneyrat⁶ and Bailey⁷ that intermediate hydantoic acids or their esters are readily converted

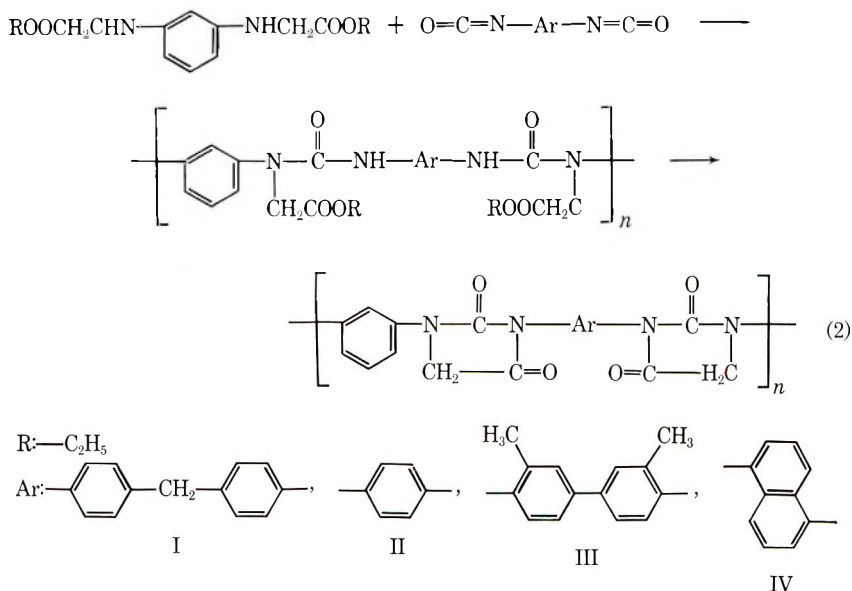
* Paper presented at the IUPAC Symposium on Macromolecular Chemistry, Tokyo-Kyoto, Japan, September-October 1966.

into the corresponding hydantoin in high yield by a thermal conversion at elevated temperatures or by a chemical conversion in solution with the use of a mineral acid as a condensing catalyst.

Those monomeric model reactions have been applied to a reaction with bifunctional compounds to obtain polymeric hydantoin, which would be expected to show a fair degree of thermal stability. The present paper is concerned with a successful synthesis of polyhydantoin by the reaction of bisiminoacetate with aromatic diisocyanates.* The properties of the polymers are also described.

RESULTS AND DISCUSSION

Aromatic polyhydantoin were synthesized in two steps. The polyaddition reaction of diethyl *m*-phenylenebisiminoacetate with an aromatic diisocyanate first gave a ureide-type polymer. A subsequent cyclocondensation reaction of this intermediate, either by heat or by chemical means, produced a polyhydantoin [eq. (2)].



The following compounds were used as the aromatic diisocyanate components: methylenebis(4-phenyl isocyanate) (MDI), *p*-phenylene diisocyanate (PDI), 3,3'-dimethyl-4,4'-biphenylene diisocyanate (BTDI), and 1,5-naphthylene diisocyanate (NDI).

Details of the preparation of polyhydantoin are summarized in Table I.

The first stage, polyaddition of the bisiminoacetate with a diisocyanate, proceeded smoothly in *m*-cresol at 50°C. to give a ureide-type polymer.

* After this work had been completed, the author learned that polyhydantoin similar to those described here were prepared independently by Prof. Iwakura at the University of Tokyo,⁸ and by Sallé, Sillion, and de Gaudemaris.⁹

TABLE I
 Preparation of Polyhydantoins

No.	Reaction intermediates		First stage		Second stage		Polymer		
	Bisimino- acetate, g.	Diisocy- anate, g.	<i>m</i> -Cresol, ml. ^a	Temp.,	Time,	Catalyst ^b	Temp.,	Yield, %	η_{inh}^c
				°C.	hr.		°C.		
1	2.80	MDI 2.52	10 + 10	80	4	HCl	80	99	0.38
2			10 + 10	50	4	HCl	80	99	0.53
3			20 + 0	50	4	HCl	80	99	0.47
4			10 + 10	50	4	HCl	50	100	0.60
5			10 + 10	50	4	—	150	70	0.12
6			10 + 10	50	4	H ₃ PO ₄	80	95	0.23
7			10 + 10	50	4	PPA	80	99	0.37
8	2.80	PDI 1.63	10 + 10	50	4	HCl	50	99	0.40
9	2.80	BTDI 2.66	10 + 10	50	4	HCl	80	94	0.28
10	2.80	NDI 2.12	10 + 20	50	4	HCl	80	87	0.15

^a The amount (10 + 10) indicates the volume added before first stage and second stage, respectively.

^b The amount of catalyst used was as follows: HCl, 1 ml.; H₃PO₄, 0.5 ml.; PPA [116% poly(phosphoric acid)], 0.8 g.

^c Measured at a concentration of 0.5 g./100 ml. in concentrated sulfuric acid at 30°C.

^d During the second-stage cyclocondensation, gelation of the solution occurred.

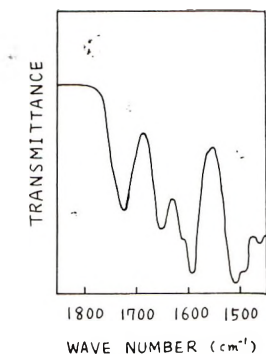


Fig. 1. Infrared spectrum of the ureide-type polymer from MDI in *m*-cresol.

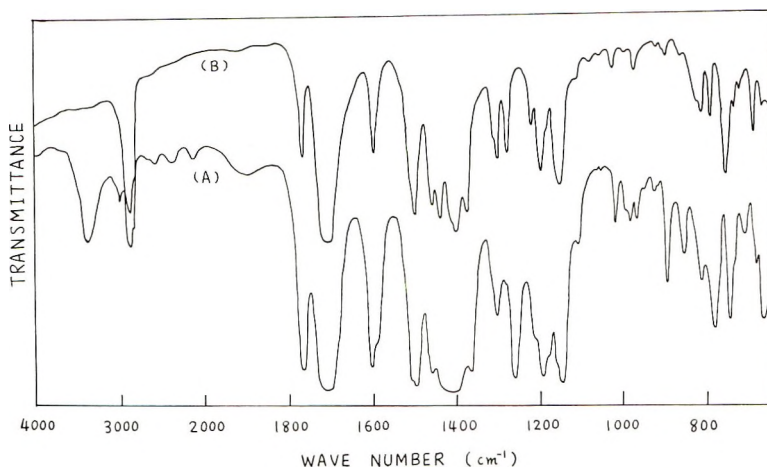


Fig. 2. Infrared spectra of (A) polyhydantoin from MDI (film); (B) the model compound (Nujol mull).

When the reaction temperature was raised to 80°C., the molecular weight of the polymer seemed to decrease (runs 1 and 2, Table I). This is probably due to enhanced, interfering side reactions and depolymerization of the ureide-type polymer.

The preparation of a high molecular weight polymer also required a higher monomer concentration and a longer reaction time as compared with those in the general syntheses of polyureas from diamines and diisocyanates. This appears to be due to poor reactivity of the imino groups of the monomer.

The second stage, thermal cyclocondensation, was carried out at an elevated temperature in a *m*-cresol solution. No reaction occurred at 80°C. within 6 hrs., as evidenced by the virtually unchanged infrared spectra of the reaction mixture. The thermal conversion to polyhydantoin proceeded at 150°C. with simultaneous degradation of the ureide-type polymer (run 5, Table I). Thus, the thermal conversion was inadequate to obtain a high molecular weight polyhydantoin.

The best method for the second-stage reaction was chemical cyclocondensation, which was performed in a *m*-cresol solution with a condensing catalyst at a rather low temperature. When concentrated hydrochloric acid was used as the catalyst, the conversion was completed readily at 50°C. (run 4, Table I). Other condensing catalysts, such as phosphoric acid and poly(phosphoric acid), were less effective than concentrated hydrochloric acid (runs 6 and 7).

As described above, the polyhydantoin having the highest viscosity was obtained from the bisiminoacetate and MDI in *m*-cresol in the presence of concentrated hydrochloric acid. When PDI, BTDI, and NDI were used as the diisocyanate, they gave inferior results; their inherent viscosities were lower than 0.4 (runs 8, 9, and 10, Table I).

One-step cyclopolycondensation reaction of the bisiminoacetate with MDI was further studied by melt polymerization. However, all attempts to prepare high molecular weight polyhydantoin were unsuccessful; only a polymer with inherent viscosity below 0.1 was obtained.

The above-mentioned polyaddition-cyclocondensation reaction was followed spectrophotometrically. The infrared spectrum of the intermediate polymer in *m*-cresol, given in Figure 1, showed two absorption bands at around 1720 and 1655 cm^{-1} , corresponding to bands of ester and ureide

TABLE II
Tensile Properties of a Film of Polyhydantoin from MDI^a

Property	
Tensile strength, kg./cm. ²	9.0×10^2
Elongation, %	5.3
Tensile modulus, kg./cm. ²	2.5×10^4

^a Measured by ASTM method D882-61T.

carbonyl groups, respectively. Figure 2 shows the infrared spectra of the final polymer and a model compound, 3,3'-(4,4'-methylenediphenylene)-bis(1-phenylhydantoin), which was synthesized from phenyliminoacetic acid and MDI. The infrared spectrum of the polymer was essentially identical with that of the model compound. The ester and ureide carbonyl bands disappeared from the first spectrum, and two new absorptions appeared at about 1770 and 1710 cm^{-1} , characteristic of the hydantoin ring. It has been reported¹⁰ that hydantoin compounds show two carbonyl bands, one at 1776–1728 cm^{-1} (4-oxo group) and the other at 1712–1698 cm^{-1} (2-oxo). The final polymer was thus proved to be the expected polyhydantoin; this was also supported by elemental analysis.

Polyhydantoin were soluble in concentrated sulfuric acid and *m*-cresol, and partially soluble or swollen in dimethyl sulfoxide, *N,N*-dimethylformamide, and *N*-methyl-2-pyrrolidone. A transparent, stiff and tough film was cast from a *m*-cresol solution of the polyhydantoin from MDI. Typical tensile properties of the film are listed in Table II.

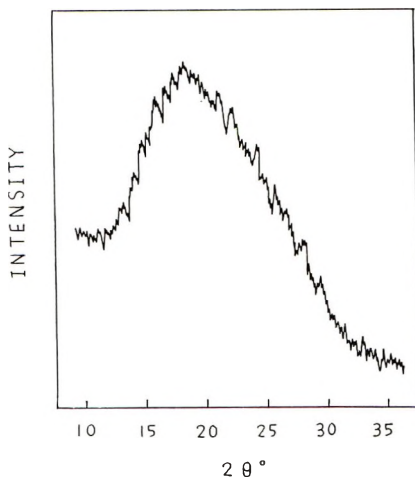


Fig. 3. X-ray diffraction diagram of polyhydantoin from MDI.

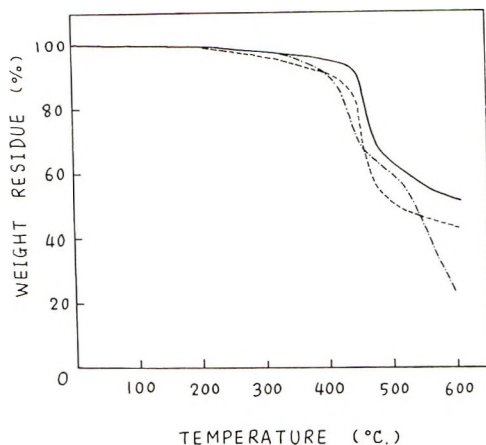


Fig. 4. Thermogravimetric analysis of polyhydantoin: (—) polyhydantoin from MDI, in N_2 ; (---) polyhydantoin from MDI, in air; (- -) polyhydantoin from PDI, in N_2 .

Figure 3 indicates the crystallinity of the polyhydantoin. This x-ray diffraction diagram was obtained by the use of nickel-filtered $CuK\alpha$ radiation. It appears from this evidence that the polyhydantoin from MDI was amorphous.

These aromatic polyhydantoin were infusible at temperatures above $400^\circ C$. in air and apparently thermally stable, as expected. Their thermal stability was further studied by thermogravimetric analysis (TGA), and the TGA curves are given in Figure 4. The analysis was carried out by heating a sample in a nitrogen atmosphere or in air at a rate of $5^\circ C./min$. The polyhydantoin from MDI showed only a minor weight loss up to $400^\circ C$. in air, despite the fact that it contains methylene groups in

its main chain; its decomposition occurred above this temperature, finally leaving a black residue.

EXPERIMENTAL

Materials

Methylenebis(4-phenyl isocyanate), *p*-phenylene diisocyanate, and 3,3'-dimethyl-4,4'-biphenylene diisocyanate were purified by vacuum distillation, and 1,5-naphthylene diisocyanate was purified by recrystallization from anhydrous benzene.

m-Cresol was also purified by distillation under reduced pressure.

Diethyl *m*-phenylenebisiminoacetate was synthesized from *m*-phenylenediamine and ethyl monochloroacetate in approximately 30% yield by the method of Gregor and his co-workers.¹¹

Synthesis of Model Compound, 3,3'-(4,4'-Methylenediphenylene)bis(1-phenylhydantoin)

To a solution of 500 mg. of methylenebis(4-phenyl isocyanate) in 10 ml. of methylene dichloride there was added 630 mg. of phenyliminoacetic acid with stirring at 50°C. Ethanol (20 ml.) and concentrated hydrochloric acid (0.5 ml.) were added to the reaction mixture at reaction times of 30 min. and 1.5 hr. The reaction was continued for additional 1 hr. at that temperature. The white precipitate formed was collected by filtration, washed with acetone, and dried. The yield was 570 mg. The crude product was purified by recrystallization from *N*-methyl-2-pyrrolidone and ethanol. The compound was obtained as a white powder melting at 222–223°C.

ANAL. Calcd. for $C_{31}H_{24}N_4O_4$: C, 72.08%; H, 4.68%; N, 10.85%. Found: C, 72.02%; H, 4.76%; N, 10.65%.

Preparation of Polyhydantoin from MDI

A mixture of 2.80 g. of diethyl *m*-phenylenebisiminoacetate and 2.52 g. of methylenebis(4-phenyl isocyanate) was added to 10 ml. of *m*-cresol all at one time at 50°C. The reaction mixture was stirred at that temperature for 4 hr. It became very viscous as the reaction proceeded. Then, to this was added another 10 ml. of *m*-cresol and 1 ml. of concentrated hydrochloric acid. Stirring was continued at 50°C. for additional 3 hr., and a clear solution of polyhydantoin was obtained. (In the case in which the cyclocondensation reaction was carried out at 80°C. for 3 hr., the solution became cloudy.) The solution was poured into 700 ml. of acetone and the polymer was separated by filtration. The solid was washed repeatedly with acetone and dried *in vacuo* at 120°C. for 4 hr. The inherent viscosity in concentrated sulfuric acid was 0.60 ($C = 0.5$ g./100 ml., at 30°C.). The yield was 4.38 g.

ANAL. Calcd. for $(C_{25}H_{18}N_4O_4)_n$: C, 68.49%; H, 4.14%; N, 12.78%. Found: C, 66.88%; H, 4.41%; N, 12.06%.

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Résumé

Des polyhydantoïnes aromatiques de poids moléculaire élevé ont été préparées par réaction de polyaddition-cyclocondensation du bis-iminoacétate de diéthyle méta-phénylène avec des diisocyanates aromatiques dans le *m*-crésol. La polyhydantoïne obtenue au départ de méthylène-bis(4-phényl isocyanate) montrait une stabilité thermique jusque 400°C à l'air. Un film transparent et dur a pu être coulé au départ d'une solution de polymère dans le *m*-crésol.

Zusammenfassung

Aromatische Polyhydantoine hohen Molekulargewichts wurden durch eine Polyadditions-Cyclocondensationsreaktion von Diäthyl-*m*-phenylen-bis(iminoacetat) mit aromatischen Diisocyanaten in *m*-Kresol hergestellt. Das aus Methylen-bis(4-phenylisocyanat) erhaltene Polyhydantoin wies in Luft gute thermische Stabilität bis hinauf zu 400°C auf. Aus einer Lösung des Polymeren in *m*-Kresol liess sich ein transparenter und zäher Film giessen.

Received January 10, 1967

Revised March 13, 1967

Prod. No. 5395A

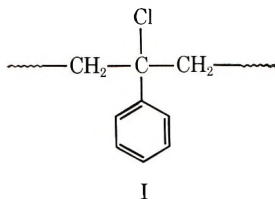
Dehydrochlorination Reactions in Polymers. Part II. Chlorinated Polystyrene*

R. A. HALDON, *Chemistry Department, University of Southern California, Los Angeles, California*, and J. N. HAY, *Chemistry Department, University of Birmingham, Birmingham, England*

Synopsis

The dehydrochlorination of chlorinated polystyrene was studied in the temperature range 120–220°C., when HCl was the sole volatile product. The dehydrochlorination was accompanied by the slow development of color and chain scission. The elimination rate fell too rapidly with reaction extent to be accounted for by reduction of reagent. Solution studies in *o*-dichlorobenzene indicated that the reaction was initially first-order in polymer concentration but was retarded by the polyene reaction products. The overall elimination was interpreted as a radical process in which the product was an active retarder. These observations are also valid for the elimination of HBr from brominated polystyrene.

The thermal behavior of poly(vinyl chloride) and poly(vinylidene chloride) has received considerable study from the standpoint of mechanism of the dehydrochlorination reaction.² A radical reaction initiated at a number of weak links, i.e., terminal unsaturation, and proceeding stepwise along the chain by allylic activation of the chlorine atoms in turn, has been invoked to explain the characteristics of the elimination process. In order to test the validity of this mechanism the present paper describes the dehydrochlorination reactions of chlorinated polystyrene. A product of the chlorination was poly- α -chlorostyrene which contained an allylic activated chlorine atom (I).



This ought to have considerable effect on the elimination reaction.

* For Part I of this series, see Burnett et al.¹

EXPERIMENTAL

Polystyrene was prepared by bulk thermal polymerization from purified monomer at 60°C. The polymerizations were taken to 10% conversion. The molecular weight calculated from the intrinsic viscosity, 3.49 dl./g. in toluene at 25°C., was 1.43×10^6 .³

The dehydrochlorination procedure has been described elsewhere.¹ The reproducibility of each rate determination was greater than 2%, when 50–100 mg. samples were used.

Chlorination of Polystyrene

Photochlorination. Teyssie and Smets⁴ have shown that chain substitution by chlorine on the α position is favored by high temperature and low chlorine concentration. Accordingly, chlorine gas was bubbled through a dilute solution of polystyrene in carbon tetrachloride (0.1 monomeric unit mole./l.) at reflux temperature, and the solution was kept just colored with chlorine. The reaction vessel was irradiated with a 300-w. tungsten lamp.

The substitution was followed by analyses of the samples withdrawn at intervals (Table I). Substitution occurred preferentially on the α position to about 20% chlorine content, when β -substitution became increasingly important. A 25% chlorine content corresponds to one chlorine atom per monomer unit.

TABLE I
Chlorination of Polystyrene

Sample	Time, min.	Chlorine in polymer, %	Flow temperature, °C.	Intrinsic viscosity, dl./g.
Photochemical, at 78°C.				
S0	0	0.0	223	3.49
C1	10	13.0	215	0.81
C2	20	18.0	230	
C3	30	20.0	224	0.70
C4	40	22.0	226	
C5	60	25.5	245	0.63
C6	90	27.0		0.58
C7	120	30.0	265	0.52
Ionic at 20°C.				
I1	120	35.5	275	0.26
I2	180	50.6		0.23

The chlorinations were accompanied by a very rapid reduction in molecular weight, representing a random radical attack on the polymer chain.

Ionic Chlorination. Polystyrene chlorinated in the presence of ferric chloride, aluminum trichloride, or iodine results in preferential substitution

on the aromatic nucleus.⁵ The total chlorine content of the polymer, however, cannot be completely attributed to ring substitution, as HCl is evolved on heating.

Ionically chlorinated polystyrene was prepared in the dark at 20°C. by passing chlorine gas through a dilute solution in carbon tetrachloride (0.1 monomeric unit mole/l.). The substitution was followed by withdrawing samples (Table I). The intrinsic viscosity changed on chlorination in a manner analogous to the photochlorination, indicating the presence of considerable radical substitution.

RESULTS

Polymer Characterization

There was little difference between the infrared spectra of the chlorinated products and polystyrene, but the bands at 2920, 2850, and 1370 cm.^{-1} progressively decreased in intensity on substitution. The reduction in intensity at 1370 cm.^{-1} was consistent with the substitution occurring on the α position only, since there was no corresponding decrease in the methylene band at 1450 cm.^{-1} .

A flow point temperature, defined as the point at which the polymer particles had sufficient mobility to coalesce when packed in a thin wall capillary and heated at a standard rate, was measured for each sample. After an initial drop it increased regularly with chlorine content (Table I), suggesting a regular substitution of chlorine atoms along the chain.

In an attempt to elucidate the structure, the chlorinated products were treated with (1) activated zinc dust in 0.1M dioxane solution, and (2) 5% sodium hydroxide in 2-ethoxyethanol solution under reflux for 24 hr. The second of these reactions, however, proved to be highly irreproducible, and the final loss of chlorine in treatment with Zn dust was very much less than expected.

The reddish-brown insoluble crosslinked products of the dehydrochlorinated C5 with NaOH contained small amounts of chlorine (about 5%) from unreacted groups. Lower chlorine-containing polymers, however, could be totally dehydrochlorinated if they remained in solution, and these products had ultraviolet spectra identical to those of thermally dehydrohalogenated polymers.

Photochlorination of the polymer appeared to occur exclusively on the α position at low extents of chlorination.

Ionically chlorinated polymer (II), on treatment with NaOH, gave a soluble, pale yellow product which contained about 30% unreacted chlorine. This is in agreement with aromatic substitution and a small amount of chain substitution.

Thermal Dehydrochlorination

General Characteristics. Polymer samples were degraded as thin films, about 10^{-3} cm. thick. Initial experiments established a linear dependence

TABLE II
 Color Development

Reaction, %	Color	
	Sample C5	PVdC
1	White	Yellow
10	Pale yellow	Brown
20	Yellow	Dark brown
30	Orange	Black
45	Brown	—
50	Brown	—

of the HCl elimination rate and sample size beyond the range used, i.e., 50–100 mg. The degradation reactions were studied in the temperature range 120–220°C. when the only volatile product was HCl. Above 220°C. a colored low molecular weight condensate appeared on the walls of the reaction vessel. The condensate had an infrared spectrum identical to that of the colored solid residue of the dehydrohalogenate.

Poly- α -chlorostyrene, i.e., sample C5, on dehydrochlorination, progressively colored from white, to yellow, orange, and finally brown. The development of color, however, was slower than that observed previously³ with poly(vinylidene chloride) (PVdC), which was distinctly yellow after 1% reaction (Table II).

The ultraviolet spectra of these colored products also exhibited the low tendency of chlorinated polystyrene to produce extended conjugated sequences, early in the dehydrochlorination reaction. The basic polystyrene chromophore at 260 m μ does not extend appreciably to higher frequencies but instead broadens and increases in intensity with dehydrochlorination (Fig. 1).

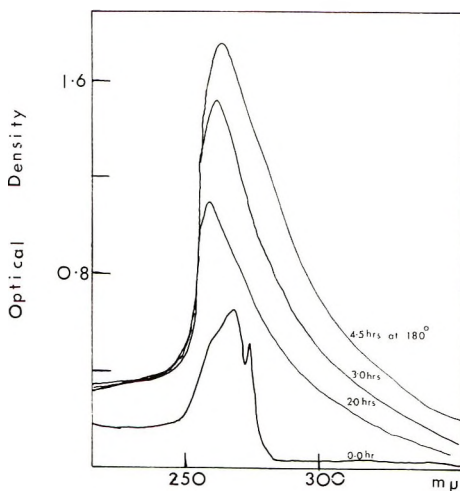


Fig. 1. Ultraviolet spectra of the dehydrochlorination products.

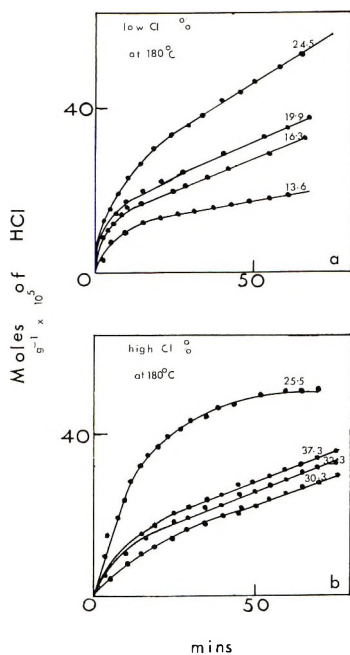


Fig. 2. Extent-time curves for dehydrochlorination: (a) low chlorine samples; (b) high chlorine samples.

The infrared spectra of the dehydrochlorinated residues also showed bands consistent with the appearance of conjugated double bonds at 1625 and 1580 cm.^{-1} . The intensities of these bands increased progressively with extent of degradation.

The dehydrochlorination reaction, unlike that of PVC and PVdC, was not followed by the development of crosslinks; instead there was a progressive decrease in viscosity, the decrease being too great to be explained

TABLE III
Intrinsic Viscosity Changes on Dehydrochlorination

Sample	Time, hr.	Dehydrochlorination, %	Intrinsic viscosity, dl./g.
C5, degradation at 204°C.	0	0	0.63
	1.0	13.5	0.28
	3.5	27.0	0.18
	12.0	38.5	0.09
	80.0	81.0	0.05
32% VdC-styrene copolymer		0	0.23
		13.0	0.17
		33.0	0.12
		40.0	0.21
		72.0	Gel

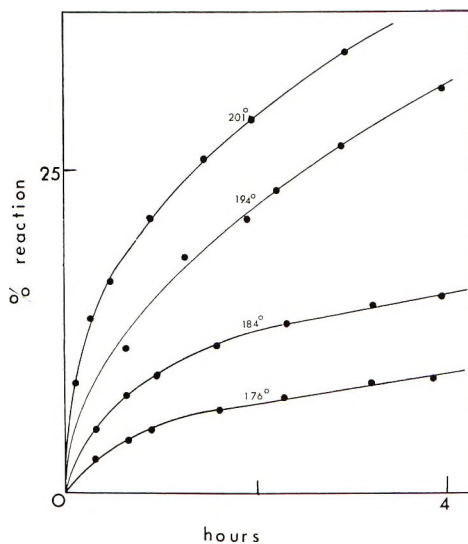


Fig. 3. Temperature dependence of the reaction (sample C5).

solely in terms of changes in functional groups. The decrease in viscosity did not fall off with conversion, and there was no evidence of a competing crosslinking reaction, as found in the dehydrochlorination of styrene-VdC copolymers (Table III).

The absence of color in the early stages of the reaction, of long conjugated sequences, and of crosslinking, clearly reflects some differences in the elimination mechanism of chlorinated polystyrene compared with PVdC.

Kinetics of Bulk Dehydrochlorination. The dehydrochlorination reactions were measured isothermally by the volume of volatiles produced. The HCl gas was condensed and measured separate from the reaction vessel so that it could take no further part in the reaction.

Figures 2a and 2b show typical reaction conversion-time plots for low and high chlorine-containing polymers, while Figure 3 shows the effect of temperature on the dehydrochlorination of sample C5. All the eliminations exhibited a linear decrease in rate with conversion. This can very readily be seen in Figure 4, where the reaction rates of sample C5 are plotted against reaction extent. This initial decrease is greater than can be accounted for in terms of changing reagent concentration.

Initial rates were obtained by extrapolation to zero conversion, and these were found to vary linearly with chlorine content of the polymer sample up to 25%, corresponding to one chlorine atom per monomer unit. Above this, the rate fell off rapidly with chlorine content. An activation energy of 20 ± 4 kcal./mole was obtained for the initial elimination rates from all samples of less than 25% chlorine content.

The reaction extent-time curves (Figs. 2a and 2b) were analyzed in terms of two concurrent first-order reactions, i.e., a fast reaction from a

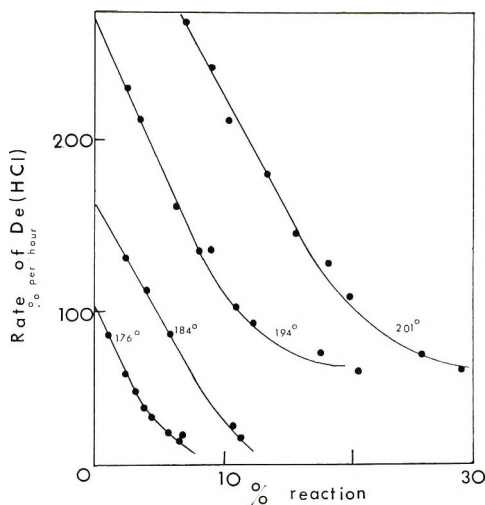


Fig. 4. Rate-conversion curves for dehydrochlorination (sample C5).

small number of labile units (mole fraction a_0), together with a slow reaction from the remainder (mole fraction $1 - a_0$). The conversion-time curves could be fitted exactly, and at first sight this seemed a possible interpretation, particularly since a_0 increased regularly with increasing chlorine substitution in the polymer (Table IV). However, for each polymer a_0 also increased regularly and significantly with temperature, which was not possible if the original assumption of a fixed concentration of labile units was correct. The other assumption of first-order rate expressions was not important as attempts to fit different orders to the concurrent reactions

TABLE IVA
Concentration of Labile Units a_0 at 180°C.

Chlorine, %	Mole fraction a_0
9.3	0.014
16.3	0.017
19.9	0.024
23.5	0.035
24.5	0.042
25.5	0.088

TABLE IIB
Concentration of Labile Units a_0 for Sample C5 (25.5% Cl)

Temperature, °C.	Mole fraction a_0
201	0.170
194	0.113
184	0.088
175	0.047

TABLE VA
Solution Dehydrochlorination of Sample C5 at 177°C.

Polymer concn., monomeric mole/l.	Initial rate, mole/min. $\times 10^6$	a_0 , mole fraction	Rate constant, min. ⁻¹ $\times 10^3$
0.151	6.15	0.30	8.1
0.070	3.00	0.29	8.6
0.039	1.70	0.31	8.7

TABLE VB
Temperature Dependence of Solution Dehydrochlorination of Sample C5

Temperature, °C.	Initial rate mole/min. $\times 10^3$	Activation energy, kcal./mole
177	8.1-8.7	19.8 \pm 2.0
156	2.75	
138	1.02	

were equally unsuccessful. A reaction scheme involving a single overall elimination process was considered to be present.

Solution Kinetics. In order to determine the equilibrium nature of the elimination reaction, sample C5 was degraded in solutions of *o*-dichlorobenzene by sweeping the evolved gas in a stream of nitrogen into standard sodium hydroxide solution and titrating with phenolphthalein as indicator. The conversion-time curves (Fig. 5) showed the same general features as before, except that the decrease in rate with conversion was not quite so marked, i.e., a_0 varied between 0.25 and 0.29 at 177°C. in solution, while it was 0.04 for bulk at 180°C.

The extrapolated initial rate of elimination showed a first-power dependence on concentration and a temperature dependence of 20 ± 2 kcal./mole (Table V).

The soluble colored product of the solution dehydrochlorination of C5 at 177°C. after 8 hr. was isolated by precipitation from *n*-heptane, then filtered and dried. This product still eliminated HCl but at a greatly reduced rate. Portions of it were added to a standard solution of C5 and the dehydrochlorination characteristics of the mixture examined. Marked retardation of the initial fast rates was observed, the rate decreasing by

TABLE VI
Retardation at 177°C. of Solution Dehydrochlorination of Sample C5^a

Added product <i>W</i> , g./l.	Initial rate <i>R</i> , mole/min. $\times 10^6$	a_0 , mole fraction	<i>RW</i> $\times 10^6$, mole-g./l.-min.
0.00	3.00	0.29	—
0.74	1.80	0.20	1.33
1.10	1.33	0.14	1.46
1.50	0.95	0.10	1.42

^a Polymer concentration = 0.070 monomeric mole/l.

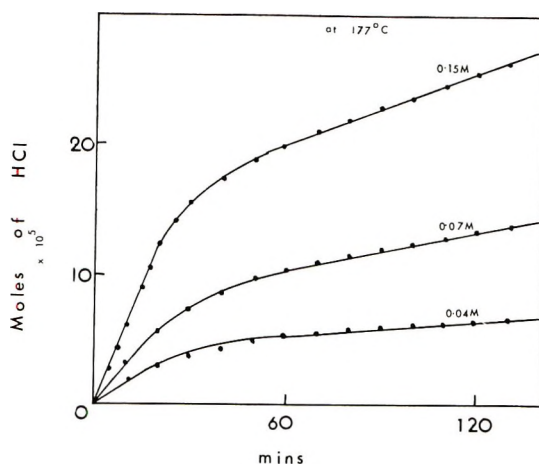


Fig. 5. Extent-time curves for solution dehydrochlorination (sample C5).

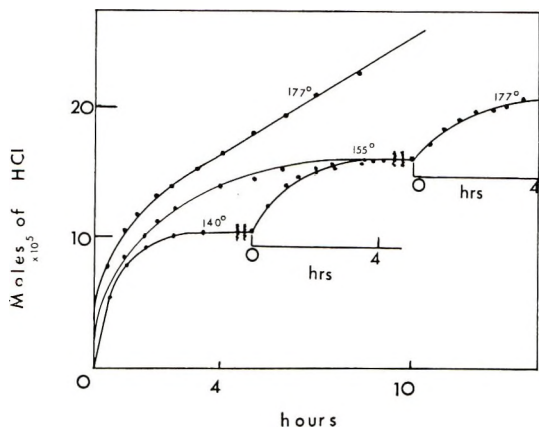


Fig. 6. Temperature dependence of dehydrochlorination limit in solution.

two for equal amounts of polymer and product (Table VI). These initial rates varied inversely with the concentration of added product; the product obviously retarded the reaction, and the decreasing rate with conversion must in turn be due to retardation by the polyene products of the elimination.

The efficiency of the reaction products to retard decreased with increasing temperature, and a sample degraded to almost zero rate could be induced to undergo a series of further fast eliminations by raising the temperature (Fig. 6).

Ionically Chlorinated Polystyrene

The decrease in molecular weight of polystyrene on ionic chlorination suggested the presence of some competing radical chain substitution. Accordingly, the thermal dehydrochlorination of I2 was measured. The

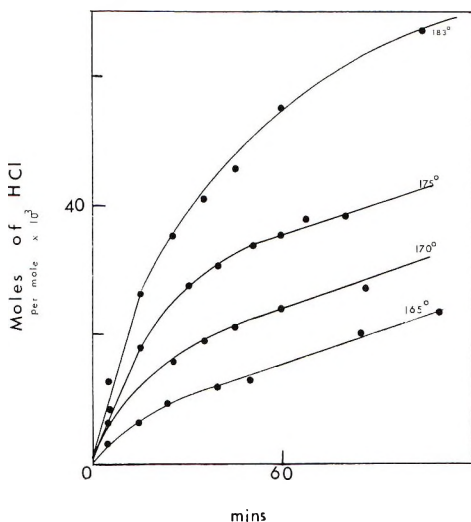


Fig. 7. Extent-time curves for dehydrochlorination of sample I2.

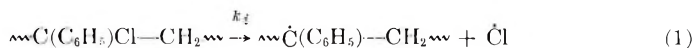
dehydrochlorination conversion-time plots for various temperatures are shown in Figure 7. They followed the same general trend as observed previously with photochlorinated samples. An activation energy was determined from the initial rates as 23 ± 2 kcal./mole. The rate curves were consistent with some 20–30% of the chlorine atoms labile, which is appreciably greater than the 15% estimated from the dehydrochlorination on sodium hydroxide treatment.

DISCUSSION

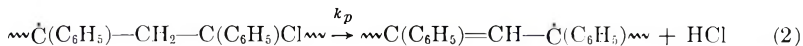
The slow development of color, chain scission, and retardation characteristics of the kinetics are all consistent with a radical elimination process in which the polyene product is an active retarder for the reaction. A similar conjugated product, triphenylmethane, has been found also to be active in retarding the dehydrochlorination of PVdC.¹ The slow development of color and chain scission also indicate the presence of considerable transfer, and so reduction of the average kinetic zip length.

The mechanism shown in eqs. (1)–(4) would seem to be operative.

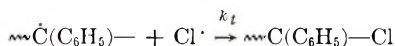
Initiation:



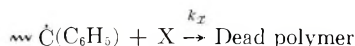
Propagation:



Termination:



Retardation:



where X denotes polyene residue.

Initiation is random as there is no observed dependence of the elimination rate on the degree of polymerization and no increase in rate with chain scission. Each monomer unit is activated by a phenyl group, and thus potentially capable of initiating. Accordingly, the rate of initiation R_i is,

$$R_i = k_i[M] \quad (5)$$

where [M] is the concentration of HCl-containing unit.

The bulk and solution reactions exhibit first-order dependence of rate on concentration of monomeric unit, and the termination step must also be first-order. Two reaction mechanisms can be invoked involving first-order termination; (a) loss of volatile radicals from the reaction system, e.g., Cl; and (b) termination predominately by geminate radical pairs.⁶ In a viscous polymer melt, a low stationary concentration of radicals will develop on degradation. Because of the viscosity and low radical concentration, pairs of kinetic chains produced from radicals created together ought preferentially to terminate.

Both are kinetically identical, and the rate of termination R_t is,

$$R_t = k_t[R^*] \quad (6)$$

On the development of a stationary state, the rate of dehydrochlorination R is,

$$R = (k_p k_i / k_t) [M] \quad (7)$$

Beyond the initial states of the elimination, retardation by the polyene product X becomes increasingly important and finally predominates; the rate of termination is then given by,

$$R_t = k_x [R^*] [X] \quad (8)$$

and on the development of a stationary state,

$$R = (k_p k_i / k_x) [M] [X]^{-1} \quad (9)$$

A negative first-order dependence of rate on polyene concentration was observed in solution.

The rate of dehydrochlorination at time t and reaction extent x is given by,

$$R = \frac{k_p k_i [a_0 - x]}{k_x (x)} \quad (9')$$

where a_0 is the initial concentration of eliminating units. A plot of rate R against $[a_0 - x]/[x]$ was made for all the polymer samples studied, and a linear relationship was obtained after an initial period of 1-2% conversion

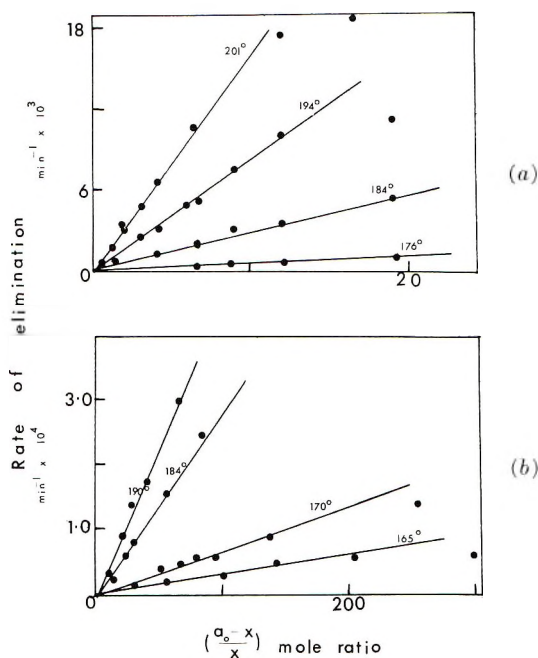


Fig. 8. Rate vs. $[a_0 - x]/[x]$ for (a) sample C5 and (b) sample I2.

for all the samples (Fig. 8). The temperature dependence of the relationship (9'), i.e., $(E_p + E_d - E_T)$, was observed to be 50 ± 5 kcal./mole.

A radical elimination reaction, retarded by the polyene products of the reaction, can exactly explain the peculiar characteristics of the dehydrochlorination of chlorinated polystyrene.

Dehydrobromination of Brominated Polystyrene

The conclusions arrived at in the previous section were applied to the interpretation of the elimination processes in brominated polystyrene.

Polystyrene was brominated by: (a) bromodan, (b) *N*-bromosuccinimide, and (c) liquid Br_2 , with benzoyl peroxide or ultraviolet, but all three methods gave very similar products which were brown or dark brown, de-

TABLE VII
Brominated Polystyrene

Bromine content, %	Viscosity, dl./g.	Color
0	3.49	White
4±2	2.38	White
5	0.35	White
6	0.21	White
10	0.10	Light brown
11	0.10	Light brown
18	0.07	Brown

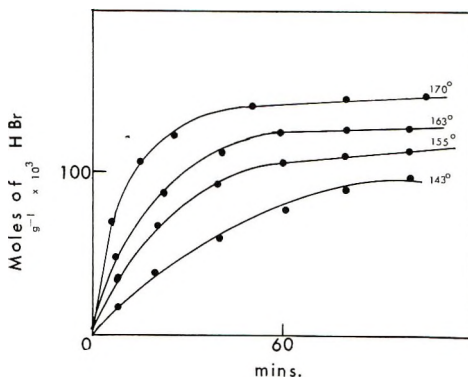


Fig. 9. Dehydrochlorination characteristics of brominated polystyrene.

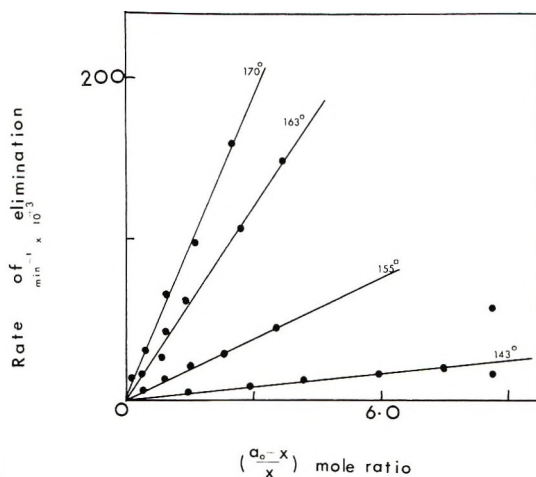


Fig. 10. Rate vs. $[a_0 - x]/[x]$ plots for brominated polystyrene.

pending on the bromine content, and which had greatly reduced molecular weights (Table VII).

The elimination extent-time curves of a sample containing 11% bromine are shown in Figure 9 for the temperature range 140–170°C. Hydrogen bromide was eliminated much more readily than hydrogen chloride from the corresponding chlorinated polystyrene. A marked decrease in rate of elimination with conversion was also present, and the reaction curves were also capable of being interpreted in terms of retardation by the polyene products (Fig. 10). All other brominated samples behaved in the same way, and the relative rates varied linearly with bromine content up to about 40% bromine in the polymer.

The initial unretarded elimination rate had a temperature dependence of 22 kcal./mole, and the retarded rate was 46 kcal./mole. These values compare favorably with those observed for chlorinated polystyrene, considering the relative strengths of the C—Br and C—Cl bonds, which would

suggest that a similar mechanism of radical elimination and retardation is operative in both systems.

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Résumé

La déshydrohalogénéation du polystyrène chloré a été étudiée dans un domaine de températures de 120 à 220°C lorsque HCl est le seul produit volatil. La déshydrohalogénéation était accompagnée d'un lent développement de couleur et de rupture de chaîne. La vitesse d'élimination tombait trop rapidement avec le degré de réaction pour résulter de la réduction des réactifs. Des études en solution dans l'*o*-dichlorobenzène indiquent que la réaction était initialement de premier ordre par rapport à la concentration en polymère mais était ensuite retardée par des produits de réaction polyéniques. Ces éliminations globales étaient interprétées comme un processus radicalaire dans lequel le produit était un retardateur actif. Ces observations sont également valables pour l'élimination d'acide bromidrique au départ de polystyrène bromé.

Zusammenfassung

Die Chlorwasserstoffabspaltung (De-HCl) aus chloriertem Polystyrol wurde im Temperaturbereich von 120–220° untersucht, wobei HCl als einziges flüchtiges Produkt auftrat. Die De-HCl war von einer langsamen Farbentwicklung und Kettenspaltung begleitet. Die Abspaltungsgeschwindigkeit fiel zu rasch mit dem Fortschreiten der Reaktion ab, als sich durch den Reaktantenverbrauch erklären liesse. Untersuchungen in *o*-Dichlorbenzollösung zeigten, dass die Reaktion anfangs erster Ordnung bezüglich der Polymerkonzentration ist, aber durch die als Reaktionsprodukte gebildeten Polyene eine Verzögerung erfährt. Die Eliminierung wurde in ihrer Gesamtheit als radikalischer Prozess aufgefasst, bei dem das Reaktionsprodukt ein aktiver Verzögerer ist. Diese Beobachtungen gelten auch für die Eliminierung von HBr aus bromiertem Polystyrol.

Received December 27, 1966

Revised March 6, 1967

Prod. No. 5396A

Syntheses of Polymerizable Dyes and Their Graft Copolymerization to Cellulose and Polypropylene Fibers

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Synopsis

Various methacrylic ester derivatives were synthesized from glycidyl methacrylate and aromatic amines or phenol. The homopolymerization and graft copolymerization of these compounds were carried out using azobisisobutyronitrile. These methacrylic derivatives reacted with diazonium salts to give azo compounds which have a double bond. These vinyl azo compounds gave homopolymer and graft copolymer with cellulose or polypropylene fibers.

In our laboratory, reactive polymers have been studied extensively.^{1,2} It was previously found that the acrylic fiber from a copolymer of acrylonitrile and glycidyl methacrylate (GMA) and the cellulose fiber grafted with GMA are dyeable by chemical bonding with dyes which have an amino or phenolic hydroxy group.³ In the course of this study, dyes were synthesized with a vinyl group from GMA and then graft copolymerized to various fibers. Up to the present time, several dyes which are polymerizable have been reported in patents,^{4,5} but few details are known about them.

This paper describes the novel synthesis of azo dyes with a vinyl group. Glycidyl methacrylate and aromatic amines or phenol gave addition compounds by the ring-opening reaction of epoxy group. These compounds obtained here coupled easily with diazonium salts to give azo dyes with a vinyl group. The addition products were grafted to cellulose and polypropylene fibers. The grafted fibers gave color by a treatment with diazonium salts. These procedures offer a novel method of dyeing by graft copolymerization.

RESULTS AND DISCUSSION

Reaction of GMA with *p*-Aminoazobenzene

The reaction of GMA with *p*-aminoazobenzene was carried out in tetrahydrofuran, dioxane, or *sec*-butanol in the presence of tertiary amines such as pyridine, dimethylaniline, and triethylamine to give an azo compound which has a vinyl group, as shown in eq. (1).

TABLE I
 Results of Syntheses of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}(\text{CH}_2-\text{R})\text{OH}$


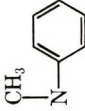
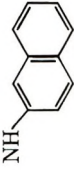



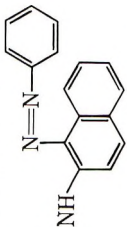
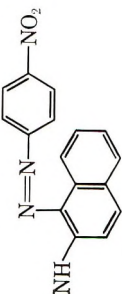
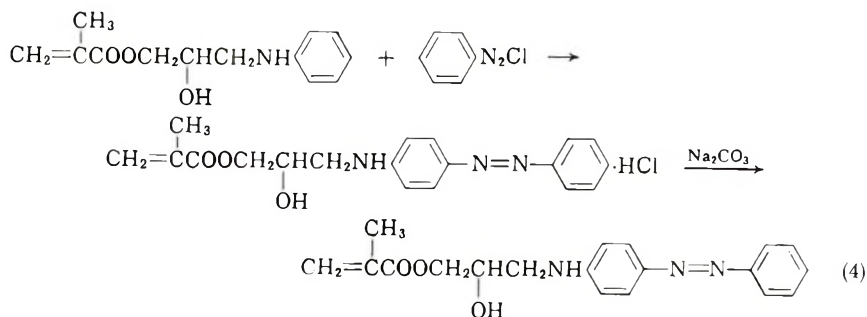
R	Reaction medium	Reaction		Yield, %	M.p., °C. (b.p., °C./mm.)	n_D^{25}	Product		N, %	
		temp., °C.	time, hr.				Calcd.	Found	Calcd.	Found
	CH ₃ OH	60	2	55	42.0		66.36	66.48	5.95	6.01
	—	95	8	60	(162-165/2)	1.5473	67.44	67.09	5.62	5.69
	CH ₃ OH	60	2	37	85-85.5		71.56	71.66	4.91	4.90
	—	95	10	42	(185-188/5)	1.5208	71.31	71.24		

TABLE II
Appearance and Analytical Data of Azo Compounds

R	M.p., °C.	Appearance	N, %	
			Calcd.	Found
$\text{CH}_2=\overset{\text{CH}_3}{\text{C}}\text{COOCH}_2\text{CHCH}_2-\text{R}$ OH				
 NH	111-112	Yellow needles	12.33	12.20
HCl salt of V	—	Needles	11.17	11.12
 NH	157-158	Red powder	14.58	14.35
HCl salt of VI	—	Needles	13.30	13.25
 NH	137-138	Orange needles	10.79	10.78
 NH	—	Violet	12.90	12.75

Coupling Reactions of I and III with Benzenediazonium Chlorides

Azo compounds with a vinyl group were obtained by the coupling reaction of I and III with benzenediazonium chlorides in acidic aqueous alcohol. The yields of these azo compounds were almost quantitative. In the case of I, hydrogen chloride salts of azo compounds were obtained at first, and hydrogen chloride was taken off by adding sodium carbonate [eq (4)].



On the contrary, pure azo compounds were obtained from III without hydrogen chloride salt formation. The appearances and the analytical data on these azo compounds are summarized in Table II.

Graft Copolymerization of I, II, III, and IV to Cellulose and I and III to Polypropylene Fiber (PP Fiber)

The graft copolymerizations of I, II, III, and IV to cellulose fiber were studied. As cellulose fiber Bemberg rayon was selected and the grafting

TABLE III
Graft Copolymerization of Vinyl Compounds (I, II, III, and IV) to Cellulose Fiber by Using Ferrous Ion and Hydrogen Peroxide^{a,b}

No.	Monomer	pH	Degree of graft copolymerization, %
1	I	5.2	2.0
2	I	3.7	9.0
3	I	3.1	29.0
4	III	5.2	6.3
5	III	3.7	7.1
6	III	3.5	13.2
7	II	3.7	3.5
8	IV	3.7	4.1

^a Pretreatment of the fiber: cellulose fiber (2 g.) was dipped in 100 ml. of aqueous solution containing 0.1–0.5% of Mohr's salt which was adjusted to pH 3.0 by oxalic acid, at room temperature for 60 min. The fiber was then dried at 70°C. for 30 min.

^b Polymerization: the pretreated fiber (2 g.) was added to 100 ml. of aqueous acetone (50:50) which contained 2 g. of vinyl compound and 1 ml. of 35% hydrogen peroxide. The mixture was heated at 40°C. for 120 min. under nitrogen.

TABLE IV
Graft Copolymerization of Vinyl Compound (I and III) to Polypropylene Fiber^a

No.	Monomer concn., g./100 ml.	Monomer	Solvent	Ratio of fiber/solvent, g./ml.	Reaction temp., °C.	Reaction time, min.	Degree of grafting, % ^b
1	3.3	I	Benzene	1:37	75	300	3.2
2	5.0	I	"	"	"	"	5.7
3	4.0	I	Water ^c	1:50	95	60	27.6
4	2.0	III	Benzene	1:37	75	300	10.2
5	3.3	III	"	"	"	"	28.6
6	5.0	III	"	"	"	"	29.1
7	4.0	III	Water ^c	1:50	95	60	22.5
8 ^d	4.0	III	"	"	"	"	0
9	3.3	MMA	Benzene	1:37	75	180	27.6
10	5.0	GMA	"	"	"	"	48.9

^a Pretreatment of the fiber: the polypropylene fiber (3 g.) was heated at 80°C. for 30 min. in 180 ml. of benzene which contained 3% of BPO. The fiber was washed with benzene and heated at 110°C. for 60 min. in air.

^b Degree of grafting was obtained by weight increase after extracting the fiber with acetone by ordinary methods.

^c 0.5% of non-ionic emulsifier was used.

^d In the pretreatment, the fiber was immersed in benzene solution of BPO, but heating was not applied. On heating the pretreated fiber in the water dispersion of III, no weight gain of the fiber was observed, but homopolymer of III was obtained.

TABLE V
 Color of the Fiber Grafted to Diazo Compounds

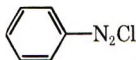
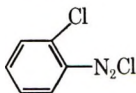
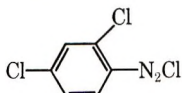

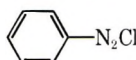
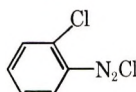
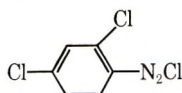
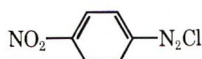
Compound	Diazonium salt	Color of the fiber
I		Yellow
I		Yellow
I		Yellow
I		Red
III		Red
III		Red
III		Red
III		Violet

 TABLE VI
 Graft Copolymerization of Dyes (V and VII) to Polypropylene Fiber^{a,b}

No.	Dye	Dye concn., g./100 ml.	Emulsifier concn., g./100 ml.	Carrier and concn., ml./100 ml.	Degree of absorption, % ^c
1	V	0.1	0.5	Benzyl alcohol, 1.0	99
2	V	"	"	—	43
3	VII	0.2	1.0	Xylene, 0.2	99
4	VII	"	"	—	55

^a Pretreatment of the fiber: propylene fiber (3 g.) was immersed in 100 ml. of aqueous emulsion containing 0.1% BPO and 0.5% non-ionic emulsifier at 70°C. for 30 min. After squeezing and washing, the fiber was dried at 110°C. for 60 min. in air.

^b Polymerization: pretreated fiber (2 g.) was dipped in 100 ml. of aqueous emulsion of the composition shown in the table and heated at 95°C. for 60 min. under nitrogen.

^c Degree of absorption was obtained by measuring the amount of unabsorbed dye by spectrophotometer. Decoloration was not observed after extraction treatment with acetone.

TABLE VII
Graft Copolymerization of Dyes (V and VII) to Polypropylene Fiber^{a,b}

No.	Dye	Emulsifier concn., g./100 ml.	Carrier and concn., g./100 ml.	Degree of absorption, % ^c	Degree of dye fixing, % ^d
1	V	0.5	Xylene, 0.1	99	75
2	V	"	<i>o</i> -Phenylphenol, 0.1	99	73
3	V	"	Phenol, 0.5	99	77
4	V	"	—	33	13
5	VII	"	<i>o</i> -Phenylphenol, 0.1	99	72
6	VII	"	Phenol, 0.2	99	78
7	VII	"	Benzyl alcohol, 0.5	99	74
8	VII	"	—	35	18

^a Pretreatment of the fiber: this was by the procedure described in Table VI, except that the concentration of BPO was 0.01%.

^b Polymerization: similar to that in Table VI.

^c Unabsorbed dye was measured by spectrophotometer.

^d The fiber was extracted with acetone. The extracted dye was measured and then the degree of dye-fixing was estimated.

Graft Copolymerization of V and VII to PP Fiber

The results of the graft copolymerization of BPO-pretreated PP fiber with dyes (V and VII) are summarized in Tables VI and VII. The concentrations of BPO in the benzene solution for pretreatment are 0.1% in Table VI and 0.01% in Table VII. In both series, the dyes used were absorbed completely when carriers of dyes, such as xylene or phenol were used in the grafting step. In the former series all of the absorbed dyes appeared to be grafted to fiber. However, in latter series, a part of the dyes absorbed was not combined chemically to fiber. This would be caused by the lower amount of active centers on the fiber compared with the former series. The propylene fiber which was not treated with BPO scarcely absorbed the dyes. Moreover, the small amount of dye absorbed was extracted completely with acetone. The dyes which have a vinyl group gave homopolymer by the usual polymerization methods. Therefore, these dyes might be called polymerizable dyes.

EXPERIMENTAL

Reaction of GMA with *p*-Aminoazobenzene

A typical reaction of GMA with *p*-aminoazobenzene is described below.

p-Aminoazobenzene (134 g., 0.7 mole), GMA (99 g., 0.7 mole), and triethylamine (141 g., 1.4 mole) were mixed in 420 ml. of dioxane containing 2.5 g. of phenyl- α -naphthylamine as an inhibitor of polymerization. The

mixture was heated at 97°C. for 17 hr. with stirring. Solvent and triethylamine were removed by distillation below 50°C. under reduced pressure.

Separation of the residual red oil was carried out by chromatography with a column (2.5 cm. in diameter and 150 cm. long) packed with 200-mesh active alumina and a mixture of chloroform-ether (100:1) as a solvent. The original oil was divided into three parts, pale yellow, deep yellow, and red. The deep yellow part was extracted with ethanol. Removal of the ethanol gave a red oil, 70 g. The second chromatographing of the oil gave only one fraction.

ANAL. Calcd. for $C_{19}H_{21}O_3N_3$: C, 67.24%; H, 6.24%; N, 12.38%. Found: C, 67.12%; H, 6.30%; N, 13.28%.

The analytical data shows the presence of an impurity, but further purification of the product was not successful.

Reaction of GMA with Aniline

Glycidyl methacrylate (142 g., 1.0 mole), aniline (93 g., 1.0 mole), and a small amount of hydroquinone were mixed in 125 ml. of methanol and heated under reflux for 5 hr. After cooling the reaction mixture, 200 ml. of ether was added and the ethereal solution was chilled to -40°C. The product was isolated by filtration, and recrystallization from ether gave white crystals, m.p. 42°C., 109 g. (55%).

A similar procedure was used for naphthylamine.

Reaction of GMA with *N*-Methylaniline

Glycidyl methacrylate (170 g., 1.2 mole), *N*-methylaniline (107 g., 1.0 mole), and a small amount of hydroquinone were mixed and heated at 95°C. for 14 hr. Fractional distillation of the reaction mixture under reduced pressure gave a viscous, colorless liquid, b.p. 162-165°C./2 mm., 119 g. (60%).

Reaction of GMA with Phenol

Glycidyl methacrylate (142 g., 1.0 mole), phenol (94 g., 1.0 mole), potassium hydroxide (4 g.), and a small amount of hydroquinone were mixed and heated at 95°C. for 10 hr. After cooling, ether was added to the reaction mixture. The ethereal solution was washed with dilute aqueous potassium hydroxide. Fractionation of the product under reduced pressure gave a colorless oil, b.p. 185-188°C./3 mm., 100 g. (42%).

Reaction of GMA with *N*-Methylaniline and *p*-Aminoazobenzene in Methanol

Glycidyl methacrylate (14.2 g., 0.1 mole) and *N*-methylaniline (10.7 g., 0.1 mole) were mixed in 50 ml. of methanol and heated at 60°C. for 2 hr. The fractional distillation of the reaction mixture by using a column of 60

cm. height gave 7.5 g. of methyl methacrylate. Recrystallization of the residue from ether gave white crystals, m.p. 73.5–74°C., 16.8 g., 3-(*N,N*-methyl phenyl)aminopropanediol-1,2.

ANAL. Calcd. for $C_{10}H_{13}O_2N$: C, 66.27%; H, 8.34%; N, 7.73%. Found: C, 66.40%; H, 7.99%; N, 7.74%.

The reaction of GMA with *p*-aminoazobenzene was carried out similarly, and methyl methacrylate and diol were obtained. The melting point of 3-(*N,N*-methyl 4-phenylazophenyl)aminopropanediol-1,2 was 121.5–122°C.

ANAL. Calcd. for $C_{15}H_{16}ON_3$: C, 66.40%; H, 6.32%; N, 15.49%. Found: C, 66.32%; H, 6.25%; N, 15.73%.

Coupling Reaction of I with Benzenediazonium Chloride

Aqueous benzenediazonium chloride solution was prepared from 4.65 g. (0.05 mole) of aniline. A solution of 11.7 g. (0.05 mole) of I 2 ml. of concentrated hydrochloric acid, and 50 ml. of methanol was added to the diazonium solution at below 10°C. dropwise with stirring. During stirring of the mixture for more than 2 hr. a large amount of crystals (*V'*) precipitated. The crystalline product was gathered and washed with cold water; it weighed 15 g. (90%).

Neutralization of *V'* with sodium carbonate in aqueous methanol gave yellow needles (*V*), m.p. 111–112°C. 13 g.

Coupling Reaction of III with Benzenediazonium Chloride

By a process similar to that used for I, 14.3 g. (0.05 mole) of III was reacted with benzenediazonium chloride from 4.65 g. of aniline. Recrystallization of the crystalline product from benzene gave orange needles (*VII*), m.p. 137–138°C., 17 g.

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Résumé

Différents dérivés d'ester méthacrylique ont été synthétisés au départ de méthacrylate de glycidyle avec des amines aromatiques ou du phénol. L'homopolymérisation et la copolymérisation greffée de ces composés ont été effectuées en utilisant l'asobisisobutyronitrile. Ces dérivés méthacryliques réagissent avec des sels de diazonium pour former des dérivés azoïques possédant une double liaison. Ces dérivés vinyliques-azoïques fournissaient des homopolymères et des copolymères greffés avec la cellulose et des fibres de polypropylène.

Zusammenfassung

Verschiedene Methacrylester-Abkömmlinge wurden aus Glycidylmethacrylat und aromatischen Aminen oder Phenolen hergestellt. Die Homopolymerisation und die Pfropfcopolymerisation dieser Verbindungen wurde unter Verwendung von Azobisisobutyronitril ausgeführt. Die Methacrylverbindungen reagierten mit Diazoniumsalzen unter Bildung von Azoverbindungen, die eine Doppelbindung besitzen. Diese Vinylazoverbindungen lieferten Homopolymere und mit Cellulose oder Polypropylenfasern auch Pfropfcopolymere.

Received December 5, 1966

Revised March 10, 1967

Prod. No. 5398A

Stereoregular Polymerization of 1-Vinylnaphthalene, 2-Vinylnaphthalene, and 4-Vinylbiphenyl

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Synopsis

1-Vinylnaphthalene, 2-vinylnaphthalene, 4-vinylbiphenyl, and styrene were polymerized with $\text{Et}_3\text{Al-TiCl}_4$, $\text{Et}_2\text{AlCl-TiCl}_3$, and $\text{Et}_3\text{Al-TiCl}_3$ catalyst systems. The latter catalyst system gave polymers in 75-95% conversion which were at least 90% isotactic. Extraction with 2-butanone (MEK) separated the atactic from the isotactic fractions. The polymers were characterized by infrared and nuclear magnetic resonance spectroscopy.

INTRODUCTION

Though a number of papers describe the stereoregular polymerization of styrene,¹ very little has been reported on the stereoregular polymerization of other vinylaromatics. In fact, the only major study is that by Natta et al.,² who surveyed the stereoregular polymerization of over 20 vinylaromatic monomers.

These polymerizations² were reported to give products which were not separable by solvent extraction into fractions of different steric order. Also, despite the fact that in the polymerization of vinylalkanes, catalyst systems based on TiCl_3 are known to give higher isotaxy than those based on TiCl_4 , with vinylaromatics both catalyst systems were reported to behave similarly. No detailed characterizations of the polymers were given; however, stereoregularity in some polymers was clearly demonstrated by their crystallinity. Noncrystalline stereoregular polyvinylaromatics reportedly differed from their atactic analogs in their infrared spectra.²

As part of a study of the synthesis and characterization of vinylaromatic polymers, we have prepared isotactic poly-1-vinylnaphthalene (PIVN), poly-2-vinylnaphthalene (P2VN), poly-4-vinylbiphenyl (P4VB), and, for comparison, polystyrene (PS). In the present paper we describe the synthesis of these polymers and their characterization by infrared and nuclear magnetic resonance spectroscopy.

RESULTS AND DISCUSSION

Preliminary experiments indicated that of the catalyst systems $\text{Et}_3\text{Al-TiCl}_4$, $\text{Et}_2\text{AlCl-TiCl}_3$, and $\text{Et}_3\text{Al-TiCl}_3$, the latter was clearly superior for

polymerization of vinylaromatics. With the first two systems conversions were below 65%, and polymer isotaxias as measured by MEK extraction were below 55%. The $\text{Et}_2\text{AlCl-TiCl}_3$ catalyst, which is an outstanding catalyst for the stereoregulated polymerization of propene, apparently polymerizes vinylaromatics so slowly that cationic polymerization, catalyzed by the Et_2AlCl , becomes important. In a control run, Et_2AlCl alone caused 2-vinylnaphthalene to polymerize. The $\text{Et}_3\text{Al-TiCl}_3$ system, on the other hand, consistently gave polymers that were >90% isotactic in conversions of >90% for 2VN, 4VB, and styrene, and about 75% for 1VN. These results are a distinct improvement over those previously reported.^{1,2}

The $\text{Et}_3\text{Al-TiCl}_3$ catalyst functioned best at Al/Ti ratios between 1 and 2. Higher Al/Ti ratios gave lower conversions. Benzene was the preferred solvent for stereoregular polymerizations of vinylaromatics; for styrene polymerizations cyclohexane was also satisfactory, but conversions of the other monomers in the latter solvent were low.

Extraction with 2-butanone (MEK) is known to remove atactic polystyrene from the insoluble isotactic polymer.³ Similar behavior was observed for the vinylaromatic polymers investigated during this study. Atactic P2VN and P4VB were readily extracted with refluxing MEK, but atactic P1VN was somewhat peculiar, in that extraction with hot MEK soon rendered it a fluid viscous mass, and long extraction periods were necessary to dissolve the atactic polymer.

The solubility behavior displayed by the isotactic polyvinylaromatics is both interesting and puzzling. P1VN was soluble during polymerization (in benzene at 60°C.) but the polymerization mixture gelled when cooled; subsequent warming at 75°C. did not dissipate the gel. Isolated P1VN, however, was largely (60–80%) extractable by hot toluene, and the resulting solutions were stable when cooled. Isotactic P2VN varied from entirely soluble to largely insoluble in hot toluene. While the cause of the partial insolubility of P2VN is not clear, there were indications that the insolubility was influenced by the particular batch of TiCl_3 used in the polymerization.* Isotactic P2VN precipitated from toluene at about 60°C. and from benzene at 35–40°C., but was soluble in tetrahydrofuran, chloroform, and dichloromethane at room temperature. Isotactic P4VB was only slightly swollen in its polymerization mixtures and was not dissolved by refluxing toluene. Further study showed that isotactic P4VB was also insoluble in decalin at 160°C. and insoluble in diglyme and 1,4-dichlorobutane at 140°C. However, it dissolved reversibly in the following solvents at the indicated approximate temperatures: tetralin, 145°C.; 1,2-dibromomethane, 135°C.; 1,3-dibromopropane, 130°C.; tetrahydrofuran, 125°C.; naphthalene, 120°C.; and dibromomethane, 95°C.

In view of these results, the viscosity datum for isotactic P4VB in tetralin at 100°C. which was reported by Natta et al.² is somewhat puzzling.

* The solubility behavior of isotactic P2VN is reminiscent of that of isotactic PS which has been variously reported to be soluble,⁴ insoluble,⁵ and partially soluble⁶ in toluene. Isotactic PS which we prepared was 60–90% soluble in hot toluene, and the resulting solutions were stable on cooling.

Since extremely high molecular weights could account for the insolubility of some of the polymers, a number of polymerizations were run in the presence of vinyl chloride, a molecular weight regulator for Ziegler-Natta polymerizations. Large amounts of vinyl chloride seriously reduced the polymerization rates and the isotaxy of the resulting polymers; small amounts gave acceptable conversions to isotactic P2VN which was largely soluble in toluene.

When heated at 300°C., atactic PS gradually decreases in molecular weight with only minimal volatilization or carbonization.⁷ We found that the proportion of toluene soluble polymer was significantly increased when isotactic PS and isotactic P2VN were heated 4 hr. at 300°C. (Table I),

TABLE I
Solubility of Stereoregular Polyvinylaromatics Before and After
Heating *in vacuo* 4 hr. at 300°C.

	PS		P4VB		P2VN	
	Before heating	After heating	Before heating	After heating	Before heating	After heating
Insoluble in 2-butanone, %	93	69	96	100	97	92
Insoluble in toluene, %	41	8.5	94	100	^a	11

^a Large, but could not be measured due to swelling.

and that the toluene-soluble, MEK-insoluble, extracts of the recovered polymers had IR spectra characteristic of the isotactic polymers. The solubility of isotactic P4VB was not altered after 15 hr. at 300°C. or 1 hr. at 350°C. At the latter conditions there was some volatilization, partly to monomer and partly to a high-boiling liquid. The fact that the polymer melt flowed fairly readily at 350°C. suggests that the polymer is not crosslinked and that the molecular weight is now relatively low.

The stereoregular polymers could be distinguished from their atactic analogs not only by their insolubility in MEK but also by their infrared and

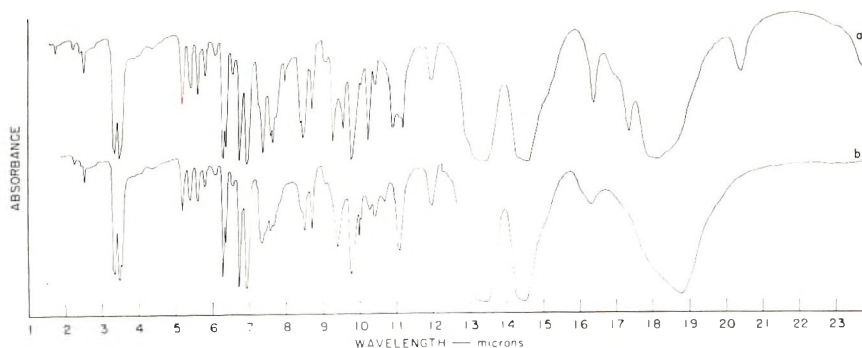


Fig. 1. Infrared spectra of (a) isotactic and (b) atactic polystyrene.

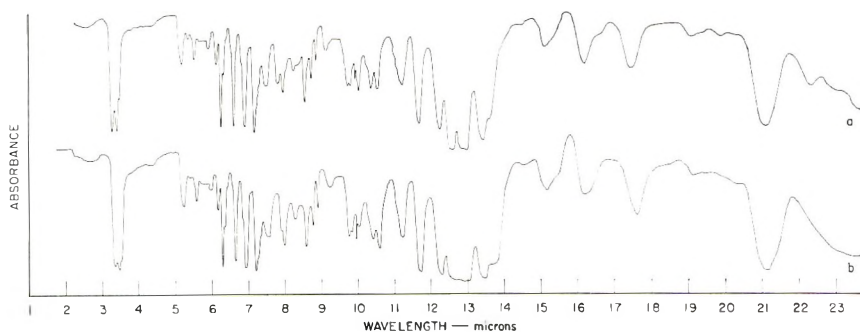


Fig. 2. Infrared spectra of (a) isotactic and (b) atactic poly-1-vinylnaphthalene.

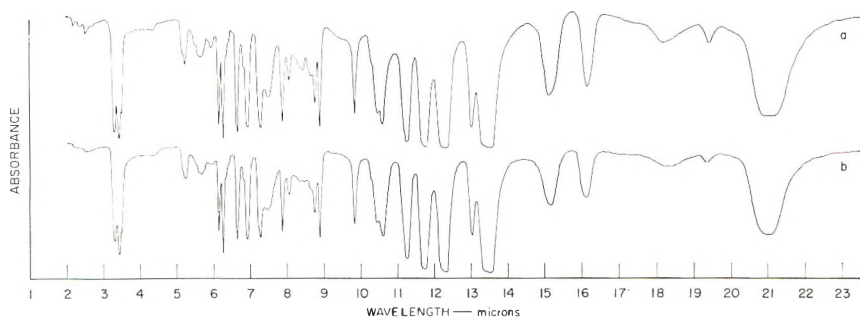


Fig. 3. Infrared spectra of (a) isotactic and (b) atactic poly-2-vinylnaphthalene.

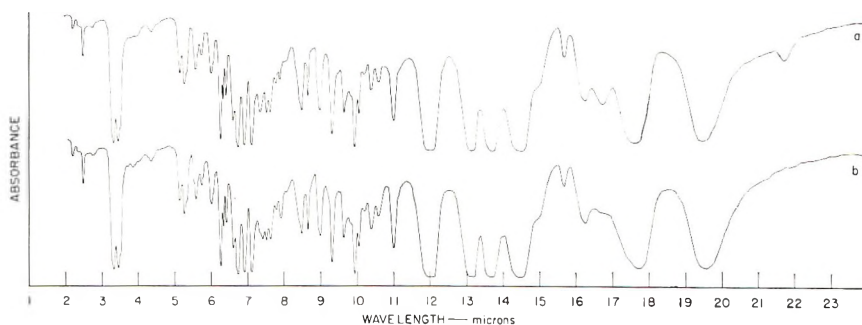


Fig. 4. Infrared spectra of (a) isotactic and (b) atactic poly-4-vinylbiphenyl.

NMR spectra. The infrared spectra of isotactic P1VN, P2VN, P4VB, and (for comparison) PS were obtained from pressed films and compared with the spectra of the atactic polymers prepared by anionic polymerization in benzene (Figs. 1-4). While there are major differences between the infrared spectra of isotactic and atactic PS, the differences between the spectra of the other isotactic and atactic polymers, though real, were relatively minor. Figure 5 shows portions of the spectra of isotactic and atactic P2VN obtained from relatively thick films; the difference now is clearly evident.

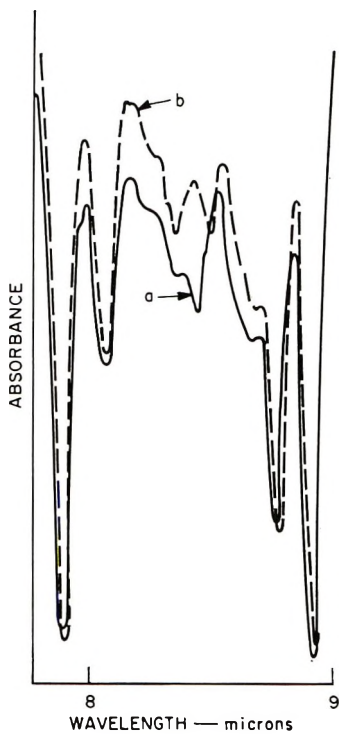


Fig. 5. Detail of infrared spectra of (a) isotactic and (b) atactic poly-2-vinylnaphthalene.

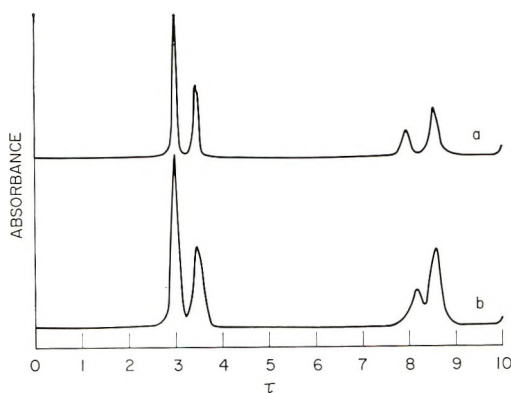


Fig. 6. NMR spectra of (a) isotactic and (b) atactic polystyrene.

NMR spectra of the isotactic and atactic polymers are shown in Figures 6-9. Two major differences could be noted between the NMR spectra of the isotactic polyvinylaromatics and their atactic analogs. These were in the position of the aliphatic protons and in the resolution of the aromatic protons.

Except for polystyrene, it was found that the aromatic H signals of isotactic P1VN, P2VN, and P4VB show considerably greater resolution than

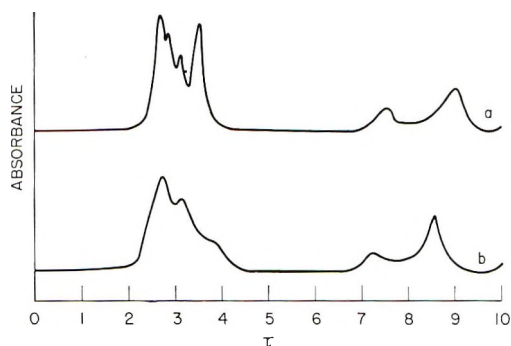


Fig. 7. NMR spectra of (a) isotactic and (b) atactic poly-1-vinylnaphthalene.

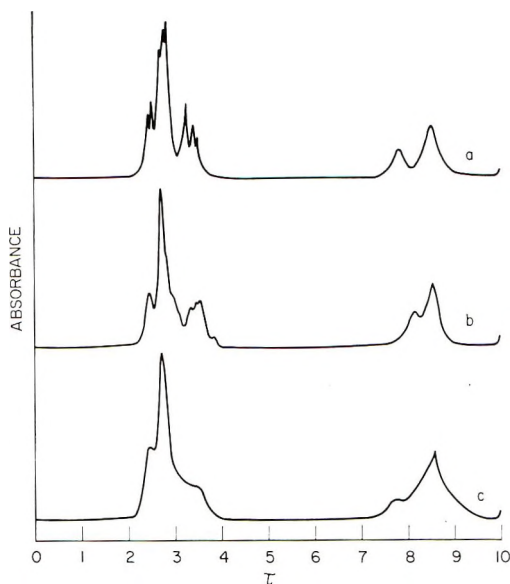


Fig. 8. NMR spectra of (a) isotactic, (b) atactic, and (c) sterically intermediate poly-2-vinylnaphthalene.

the aromatic H signals of the atactic polymers. It was shown that this difference is real and not due to different viscosities of the solution, so that it must be attributed to differences in configuration.

The aliphatic H signals of the HCH and ArCH groups of the polymer chains were rather broad (Figs. 6-9). The chemical shifts exhibited by the hydrogens showed some interesting trends and anomalies (Table II).

The HCH signals were influenced very little by the tacticity of the polymers, and, except for isotactic P1VN, all displayed HCH signals near 8.5-8.6 τ . The greatly increased shielding of the HCH in isotactic P1VN probably signifies an unusually close proximity or different orientation between the methylene group and the π cloud of the ring system.

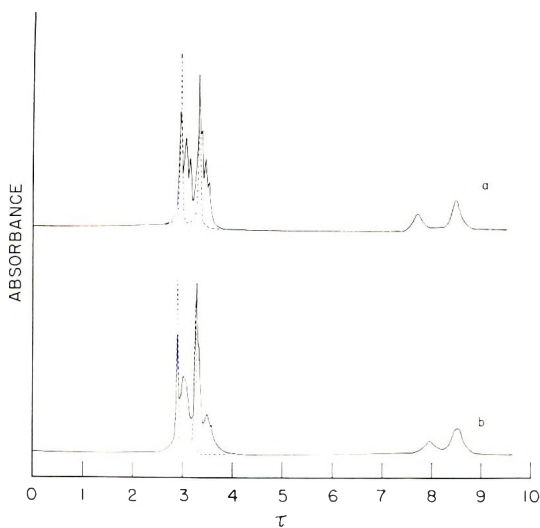


Fig. 9. NMR spectra of (a) isotactic and (b) atactic poly-4-vinylbiphenyl superimposed on spectra of naphthalene- d_8 (dotted line).

Isotactic PS, P2VN, and P4VB show ArCH signals that are somewhat downfield from the signals of the atactic polymers. The ArCH signal of isotactic P1VN, however, lies upfield from the atactic signal. The cause of these shifts and their lack of uniformity is not clear.

The reliability of the previously discussed characterizations of isotactic polyvinylaromatics by extraction with MEK was verified by infrared and NMR studies. In all cases, the MEK-insoluble products exhibited the spectra of isotactic polymers. The spectra of the MEK-soluble fractions isolated from stereoregular polymerizations sometimes resembled the atactic polymer spectra and sometimes were intermediate between the atactic and isotactic spectra. An example of the latter type is the NMR spectrum of MEK soluble fraction of P2VN from a stereoregular polymerization (Fig. 8c).

Finally, Natta et al. have found P1VN to be crystallizable, while P2VN and P4VB did not crystallize. Our findings agree: P1VN crystallized

TABLE II
NMR Signals of Chain Protons in Isotactic and Atactic Polyvinylaromatics^a

Polymer	ArCH, τ		HCH, τ	
	Isotactic	Atactic	Isotactic	Atactic
PS	7.96	8.17	8.54	8.59
P1VN	7.52	7.24	9.02	8.57
P2VN	7.84	8.16	8.54	8.55
P4VB	—	8.13	—	8.49
P4VB ^b	7.68	7.98	8.45	8.54

^a 100 Mc./sec. in deuteriochloroform with tetramethylsilane as internal standard.

^b In naphthalene- d_8 .

without difficulty, but P2VN and P4VB were found to be amorphous by x-ray and optical birefringence examination.

EXPERIMENTAL

Materials

1-Vinylnaphthalene (from J. T. Baker Co. or synthesized⁸), 2-vinylnaphthalene, and 4-vinylbiphenyl (from Research Organic Chemical Co. or Aldrich Chemical Co.) were purified by passing solutions of the monomers in benzene-hexane through columns of alumina and silicic acid. Alkylaluminums (Texas Alkyls Co.) were used as received; TiCl_3 AA (Stauffer Chemical Co.) and TiCl_4 (Matheson Chemical Co.) were used as a 1M suspension and a 1M solution, respectively, in cyclohexane.

Polymerizations

A typical procedure for a small-scale polymerization is as follows. To an argon-flushed pop bottle containing a Teflon-covered stirring bar was added 50 ml. of dry benzene, 0.41 ml. (3.0 mmole) of triethylaluminum, 3.0 ml. (ca. 2.0 mmole) of a 1M suspension of TiCl_3 in cyclohexane, and 5.0 g. (33 mmole) of 2-vinylnaphthalene. The bottle was capped with a Buna-N septum, then placed in a 60°C. water bath and stirred magnetically. After 1 day the partially gelled polymerization mixture was transferred to a blender, washed twice with isopropanol and, if not yet colorless, once or twice with MEK and then dried *in vacuo* at 80°C. The isolated polymer (91% conversion) was 96% insoluble in MEK and 58% insoluble in toluene. Since the polymerizations of 1-vinylnaphthalene and 4-vinylbiphenyl were rather slow, these were continued 2-4 days under conditions identical to those described above.

The quantities used in larger-scale polymerizations were 100 ml. benzene, 10 mmole triethylaluminum, 7-10 mmole TiCl_3 , and 20-35 g. monomer. The procedure was the same as that already given. The conversions to P1VN and P2VN (about 75 and 90%, respectively) were not changed in the larger-scale runs, but the conversion to P4VB decreased from 95 to about 70%.

Characterization

Infrared spectra were obtained from pressed films by using a Perkin-Elmer 221 spectrophotometer equipped with NaCl or KBr optics. Films of isotactic P2VN, isotactic P4VB, and the atactic polymers were pressed at about 200°C. Isotactic PS was pressed at 230°C. and annealed 30 min. at 180°C. Isotactic P1VN was pressed at 330°C. and annealed by slow cooling in the press. It showed a sharp x-ray diffraction pattern and optical birefringence which disappeared at 330-335°C. (lit.² $T_m = 360^\circ\text{C}.$).

Nuclear magnetic resonance spectra were obtained at 100 Mc./sec. by using a Varian AR-100 instrument. The spectra of isotactic and atactic

PS, P1VN, and P2VN and atactic P4VB were measured in deuteriochloroform at 25°C. with tetramethylsilane as internal standard. Spectra of isotactic P4VB and, for comparison, atactic P4VB were determined in naphthalene- d_8 at 130°C.

We wish to acknowledge experimental assistance of Mr. F. J. Martinelli and C. B. Kingsley who carried out the synthesis of 1-vinylnaphthalene and that of Mr. W. R. Anderson who measured the NMR spectra. X-ray diffraction work was carried out by Dr. M. Barlow.

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS 7-100.

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Résumé

Le 1-vinylnaphthalène, le 2-vinylnaphthalène, le 4-vinylbiphényle et le styrène ont été polymérisés avec des systèmes catalytiques à base de $\text{Et}_3\text{Al-TiCl}_4$, $\text{Et}_3\text{Al-TiCl}_3$, et $\text{Et}_2\text{AlCl-TiCl}_3$. Le dernier système catalytique fournit des polymères à conversion de 75 à 95% qui sont au moins pour 90% isotactique. L'extraction avec la 2-butanone (MEK) permet de séparer les fractions atactiques des isotactiques. Les polymères sont caractérisés par spectroscopie infrarouge et de résonance nucléaire magnétique.

Zusammenfassung

1-Vinylnaphthalin, 2-Vinylnaphthalin, 4-Vinylbiphenyl und Styrol wurden mit $\text{Et}_3\text{Al-TiCl}_4$, $\text{Et}_2\text{AlCl-TiCl}_3$ und $\text{Et}_3\text{Al-TiCl}_3$ als Katalysatorsysteme polymerisiert. Das letztgenannte System lieferte in 75 bis 95% Ausbeute Polymere, welche zumindest zu 90% isotaktisch waren. Durch Extraktion mit 2-Butanon (MEK) wurde die ataktische von der isotaktischen Fraktion getrennt. Die Polymeren wurden durch Infrarotspektroskopie und kernmagnetische Resonanzspektroskopie charakterisiert.

Received January 27, 1967

Revised March 1, 1967

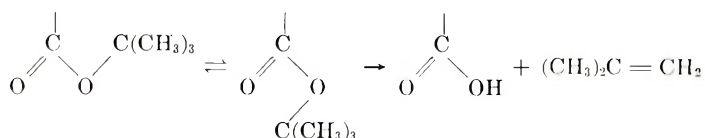
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Photochemistry of Poly(*tert*-butyl Acrylate). Effect of Ester Spatial Conformation on the Cycloelimination Process

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Synopsis

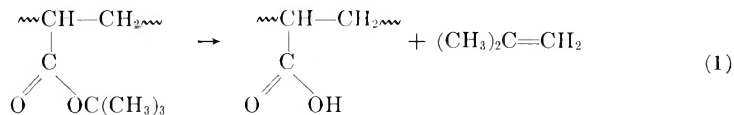
A preferred geometric isomer was found to exist for the Norrish type II photocycloelimination of isobutene from poly(*tert*-butyl acrylate). A detailed analysis of infrared spectroscopic and kinetic data under thin film conditions is consistent with the mechanism:



i.e., a photoinduced rotational equilibrium is established between the *cis* and *trans* ester spatial conformations, with isobutene elimination occurring from the *cis* form. In the glassy state of the polymer, an activation energy of 3.0 kcal./mole was obtained for the elimination step. Energy transfer experiments with naphthalene, benzophenone, and oxygen resulted in a significant decrease in the isobutene yield. This indicates that reaction occurs at least in part from a triplet state of the carbonyl group in the polymer.

INTRODUCTION

It is well established that esters containing one or more β hydrogens in the alkyl group may undergo an intramolecular photocycloelimination reaction to form an olefin and the corresponding acid.¹⁻³ Recently,⁴ it has been shown that polymeric esters undergo a similar reaction. For example, poly(*tert*-butyl acrylate) (PTBA) undergoes a photochemical elimination [eq. (1)]



to form isobutene and poly(acrylic acid). However, the question of a preferred geometric isomer for the process was not considered. It has been verified experimentally⁵ that the ester side chain can be found in two rotational sites and that these sites are not thermally accessible to each other

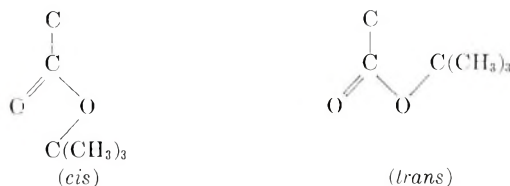
below the glass transition temperature (T_g) of the polymer. The present study implies a preferred geometric isomer for the elimination process as well as a photoinduced rotational isomerization occurring about the C—O bond.

EXPERIMENTAL

The polymerization and characterization of poly(*tert*-butyl acrylate) have been previously described.⁴

Uniform thin polymer films, 0.4–1 μ thick, were obtained by dip-coating KBr windows from solutions containing 0.5–1 g. of polymer per 100 cm.³ of toluene. The films were dried under vacuum at 50°C. for 24 hr. Film thickness measurements were carried out with a Watson 16-mm. interference objective. Chloroform and cyclohexane were also used as dip-coating solvents in order to determine whether any residual solvent was sensitizing the decomposition. No measurable effect was found.

The photochemical rates of disappearance of the two ester group conformations, *cis* and *trans*,



were carried out with a Beckman IR-10 infrared spectrophotometer and a Limit Research J-1 electrically heated cell. Polymer films on KBr substrates were used in all experiments. The film temperature was controlled to $\pm 0.2^\circ\text{C}$. with a Variac. The cell was continuously flushed with helium at a flow rate of 5 cm.³/min.

Isobutene rate measurements have been described elsewhere,⁴ as well as the techniques employed.⁶

The light source was a Hanovia 83A-1 mercury arc. The 2537 Å. line was isolated with a Corning 7-54 filter. Spectral purity of the light transmitted was previously reported.⁴ The output of the light source at 2537 Å. was measured with an Eppley Thermopile and was found to be 1.33×10^{15} quanta/sec.-cm.².

RESULTS

Isomer Characterization

Characterization of the rotational *cis*–*trans* isomers of poly(*tert*-butylacrylate) shown above was accomplished with a high degree of confidence by comparison of infrared spectral data with known systems. Table I gives a comparison of the C—O—R absorption bands, where R is either CH₃ or C(CH₃)₃. These are indicative of each arrangement in known alkyl⁷ and polymeric⁵ ester systems.

TABLE I
Infrared Spectral Data for the Isomeric Esters

Compound	Absorption band, cm. ⁻¹	
	<i>cis</i> isomer	<i>trans</i> isomer
Methyl acetate ^a	1245	1260 ^b
<i>tert</i> -Butyl acetate	1245	1260 ^b
Poly(methyl methacrylate) ^c	1242	1264
Poly(<i>tert</i> -butyl acrylate)	1238	1268

^a Data of Thompson and Torkington.⁷

^b Shoulder and very weak.

^c Data of Havrilak and Roman.⁵

The temperature dependence of the *cis* to *trans* molar absorbance ratio ($[C]/[T]$) for solid phase polymeric esters is markedly different from that of liquid esters. The $[C]/[T]$ ratio of PTBA remains constant at 1.54 from 20°C. to its T_g of 70°C. The ratio then approximates a linear decrease to 1.29 at a film temperature of 120°C. and remains constant. On the other hand, the absorbance ratio of PTBA in solution is 1.29 and invariant throughout the entire temperature range, i.e., 20°C. to >100°C. The above results agree with previous studies on liquid polymer⁵ and monomeric^{8,9} ester systems. These results suggest that the nature of the forces restricting thermal population of the two sites are in large part intermolecular.

Several films were sealed in glass ampules after pressurization with dry nitrogen. By quenching the films in liquid N₂ after heating to various temperatures above the T_g (70–120°C.), it was possible to maintain the high temperature conformations ($[C]/[T] < 1.54$) for several weeks at room temperatures. This agrees with the above results in that the isomers are not thermally accessible to each other below the T_g . Cracking of the polymer films or KBr substrates did not occur either during or after the annealing process.

The annealed samples were subsequently photolyzed at 24.4°C. and the initial isobutene formation rate was found to be directly proportional to the number of *cis* sites.

Kinetics

The rate of formation of isobutene from PTBA under 2537 Å. radiation was previously reported⁴ for polymer films ~0.60 μ thick and sample weights of 6.7×10^{-2} mg./cm.².

In this work, the rate of disappearance of the *cis* (1238 cm.⁻¹) and *trans* (1268 cm.⁻¹) infrared absorption bands was monitored as a function of temperature.

The molar extinction coefficient for each isomer band was found to be 107 ± 3 l./mole-cm. Evidence for the equivalence of the absorption coefficients was gained from the fact that the sum of the integrated intensities for the two isomer absorptions was independent of the relative amount of

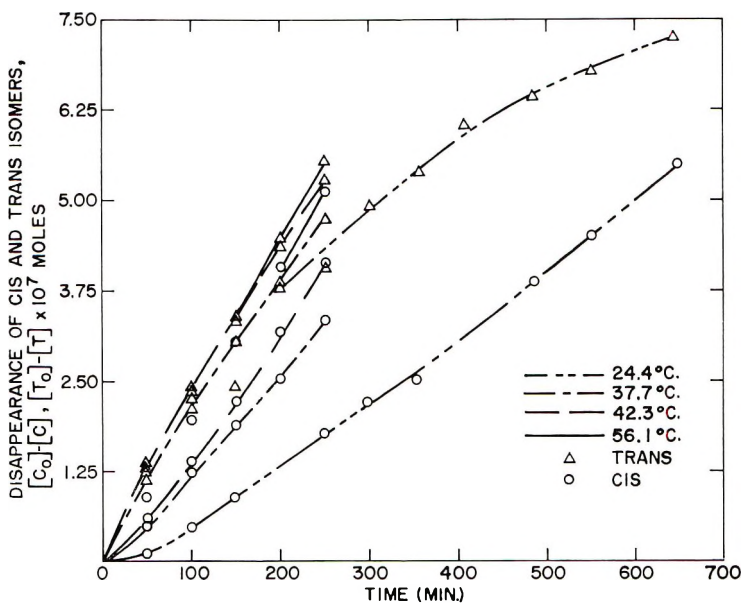


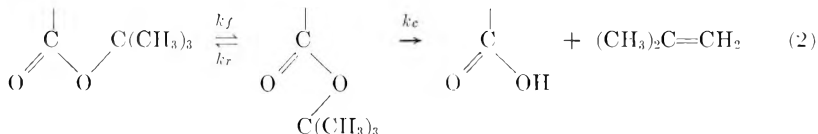
Fig. 1. Normalized rates of disappearance of the *cis* and *trans* rotational isomers.

each conformation present in the sample. By annealing the samples the relative amount of each could be varied while conserving the total number of rotational positions. Identical absorbances per ester group have recently been found for the analogous two transitions in poly(methyl methacrylate).⁵ Furthermore, the half band widths of the two peaks were identical and devoid of any appreciable broadening over the temperature range of the kinetic experiments. Hence, the concentration of each isomer ($[C]$, $[T]$) could be found from the isomer absorbance ratio, film volume, and polymer density. Therefore, from the absorbance data, the integral disappearance of each isomer in moles was calculated after normalizing for variations in sample thickness, light intensity, and polymer area. The normalized data are plotted in Figure 1. From these graphs, isomer disappearance rates were determined which could be correlated with the isobutene rate data. First-order decomposition kinetics was observed for the depletion of each conformation, consistent with the overall reaction order.⁴

Strong support that the infrared spectroscopic measurements would reflect only the cycloelimination process was previously reported⁴. That is, the sum of the quantum yields for free-radical (Norrish type I) processes producing *tert*-butyl alcohol, carbon dioxide, isobutane, etc., were found to be at least an order of magnitude lower than the cycloelimination quantum yield. Also, the interference of acrylic acid units in the 1200–1300 cm^{-1} region could be excluded due to the low photochemical conversions (<1%) and larger extinction coefficient for the ester bands.

DISCUSSION

A detailed analysis of the kinetic data gives good agreement with a mechanism based on photorotational isomerization about the C—O bond with isobutene elimination from the *cis* ester spatial form [eq. (2)]:



Alternative mechanisms include photoelimination from the *trans* form and/or one or more of the processes shown above. These mechanisms will be considered below. Strong evidence to support reaction from the *cis* form is gained from the room temperature photolysis of annealed samples. In the annealed samples, the initial rate of formation of isobutene is directly proportional to the concentration of *cis* ester sites.

The analysis of kinetic data plotted in Figures 2 and 3 in terms of rate laws [eqs. (3), (4)] is consistent with the above mechanism.

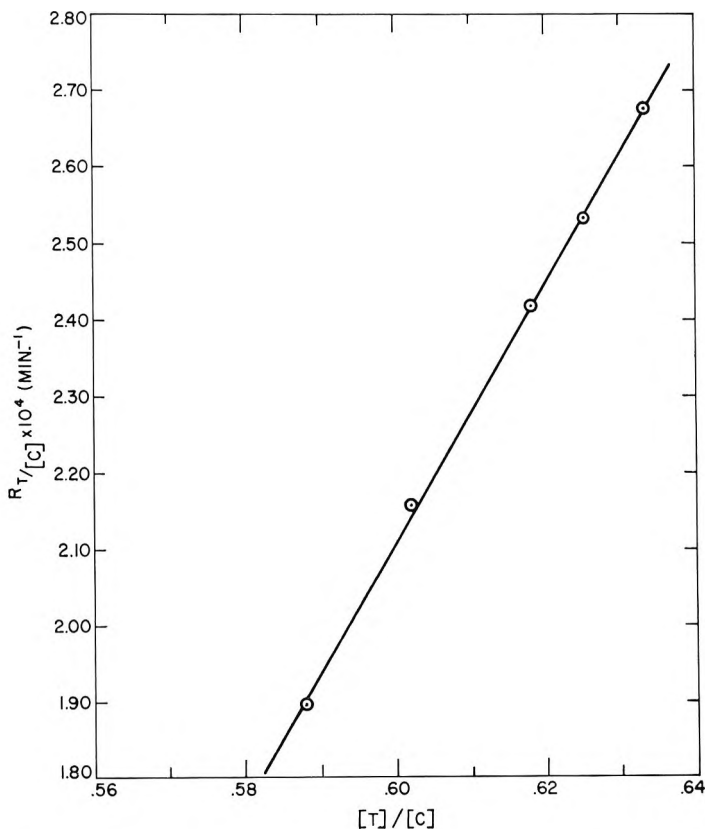


Fig. 2. A plot of $R_T/[C]$ vs. $[T]/[C]$ for the photolysis of PTBA at 24.4°C.

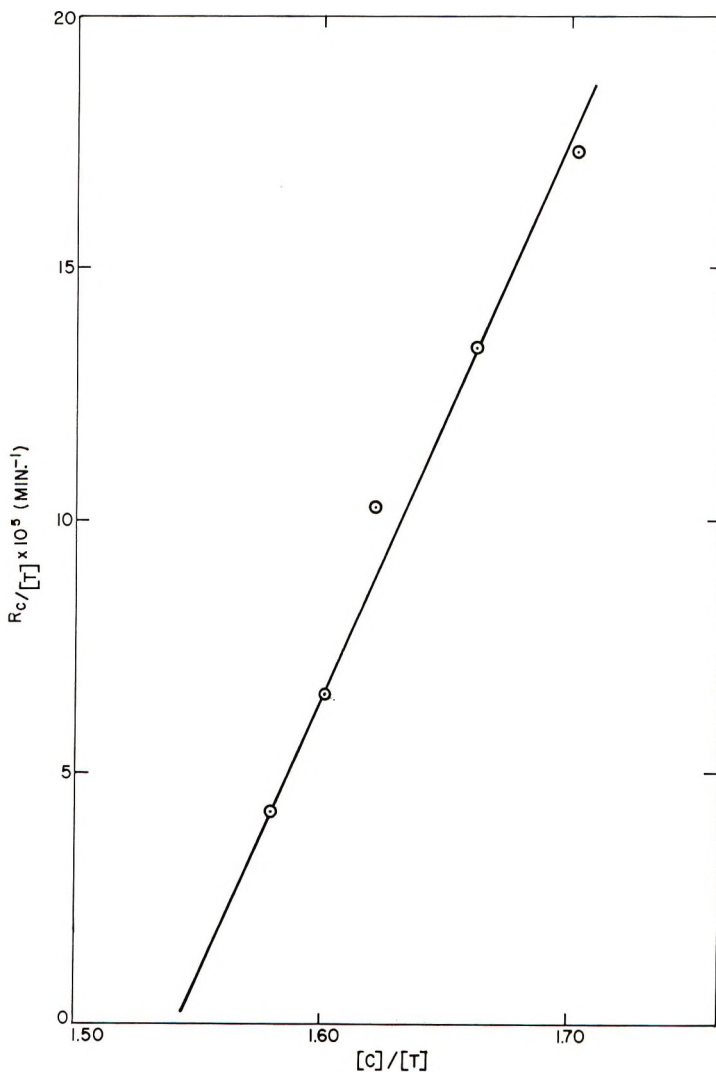


Fig. 3. A plot of $R_C/[T]$ vs. $[C]/[T]$ for the photolysis of PTBA at 24.4°C.

$$-d[T]/dt = -R_T = -k_r[C] + k_f[T] \quad (3)$$

$$-d[C]/dt = -R_C = (k_r + k_c)[C] - k_f[T] \quad (4)$$

$-R_T$ and $-R_C$ are defined as the rates of disappearance of the *trans* and *cis* isomers, respectively, and $[T]$ and $[C]$ are corresponding isomer concentrations. Nonlinear graphs of $-R_T$ versus $[T]$ and $-R_C$ versus $[C]$ eliminate all possible alternative mechanisms mentioned above. Thus, a plot of $R_T/[C]$ versus $[T]/[C]$ from eq. (3) yields the rate constants k_f and k_r . The rate constant k_c can be obtained from the plot of $R_C/[T]$ versus $[C]/[T]$ [eq. (4)] or a graph of $-(R_T + R_C)$ versus $[C]$. The former is shown in Figure 3. The rate constants obtained from a series of runs at

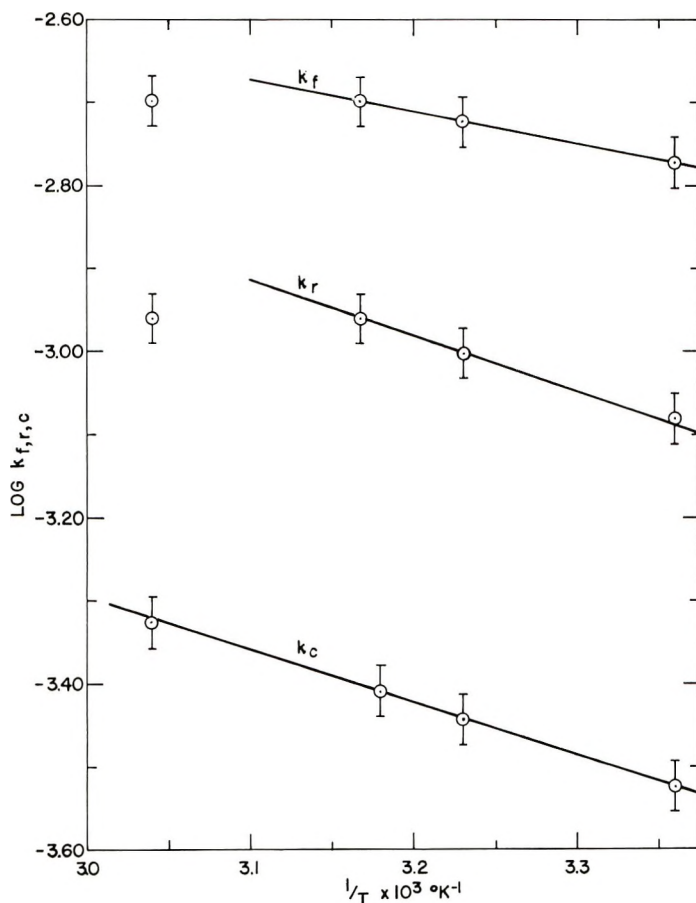


Fig. 4. Arrhenius plots for the three rate processes.

four temperatures are presented in Table II. The above mechanism also predicts $d[\text{isobutene}]/dt = -(R_T + R_C)$. This relationship was found to be verified experimentally and is shown in Table III. Table III also shows that agreement between the previously reported³ isobutene rate measurements and the isomer data is within 10%. It is therefore difficult to ascertain whether the proposed mechanism should include the photolysis of *trans* ester directly to isobutene. Within the limits of experimental error, the rate constant for this process, if it does occur is $<10^{-7} \text{ sec.}^{-1}$. However, it is reasonable to rule out reaction from the *trans* form due to the strong evidence in favor of a six-membered ring intermediate.¹⁰ The estimated *trans* rate constant is to be compared with $\sim 10^{-5} \text{ sec.}^{-1}$ for the isomerization processes and $\sim 10^{-6} \text{ sec.}^{-1}$ for the cycloelimination step.

From Figure 4, an Arrhenius activation energy of 3.0 kcal./mole was obtained for the photocycloelimination process. While a precise interpretation of this result is not yet possible, it probably represents, in part, the energy barrier for passage to the six-membered cyclic transition state.¹¹

TABLE II
 Tabulation of Rate Constants

Temperature, °C.	$k_c \times 10^6$, sec. ⁻¹	$k_f \times 10^5$, sec. ⁻¹	$k_r \times 10^5$, sec. ⁻¹
24.4	5.0	2.8	1.4
37.7	6.0	3.2	1.6
42.3	6.5	3.3	1.8
56.1	7.8	3.3	1.8

 TABLE III
 Comparison of Isobutene Evolution and Isomer Disappearance Rates

Temperature, °C.	$d[\text{isobutene}]/dt$ $\times 10^9$, mole/min. ^a	$-(R_T + R_C) \times$ 10^9 , mole/min.
24.4	2.86	2.75
37.7	3.30	3.00
42.3	3.86	3.50
56.1	4.25	4.25

^a Data of Monahan.⁴

Poly(*tert*-butyl acrylate) appears to undergo the photocycloelimination process at least partly through a triplet state. This is supported in quenching experiments with benzophenone, naphthalene, and oxygen. Thus, the rate of isobutene elimination is decreased by 11–14 mole-% when benzophenone or naphthalene is incorporated in the thin films. The ratio of polymer to acceptor was chosen to assure that 99% of the chemically active light was absorbed by the former. Similarly, 1 atm. of oxygen in the decomposition cell quenches the reaction by ~30%. These results are consistent with those of similar studies,¹⁻³ in that photocycloelimination of olefins from liquid phase esters also proceeds via a triplet state.

Since ultraviolet extinction coefficients of each isomer are not known, quantum yields for the respective steps in the process cannot be determined. Also, above 60°C. the measurement of photochemical rates is rendered uncertain by comparable rates of thermal isomerization and a change in the polymer state above the T_g .

The author would like to thank Dr. John B. Flannery, Jr. for critical comments during the course of this work.

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Résumé

L'isomère géométriquement préférentiel existe dans le cas de la photocycloélimination du type II de Norrish dans le cas de l'isobutène au départ de polyacrylate de *tert* butyle. Une analyse détaillée des résultats spectroscopiques infrarouges et cinétiques sous forme de films fins s'accordent avec le mécanisme dans le texte anglais, c'est-à-dire, un rapide équilibre rotationnel induit par la lumière a été établi entre les conformations spatiales ester *cis*- et *trans*-avec élimination d'isobutène au départ de la forme *cis*. Dans l'état vitreux du polymère, une énergie d'activation de 3.0 Kcal/mole a été obtenue pour l'étape d'élimination. L'effet du naphthalène, de la benzophénone et de l'oxygène sur le rendement en isobutène indique que la réaction se passe du moins en partie au départ de l'état triplet du groupe ester au sein du polymère.

Zusammenfassung

Es wurde gefunden, dass bei der "Norrish Type II"-Photocycloelimierung von Isobuten aus Poly-*t*-butylacrylat vorzugsweise ein bestimmtes geometrisches Isomeres vorliegt. Eine ausführliche Analyse der IR-spektroskopischen Daten und der Kinetik des Reaktionsablaufs in dünnen Filmen steht mit dem folgenden Mechanismus (Bzgl. Struktur vgl. englische Zusammenfassung) d. h. es bildet sich unter Lichteinfluss rasch ein Rotationsgleichgewicht zwischen den räumlichen *cis*- und *trans*-Esterkonformationen aus, wobei die Isobuteneliminierung von der *cis*-Form aus erfolgt. Für den Eliminierungsschritt in dem Polymeren im Glaszustand wurde eine Aktivierungsenergie von 3,0 kcal/Mol erhalten. Der Einfluss von Naphthalin, Benzophenon und Sauerstoff auf die Isobutenausbeute zeigt, dass die Reaktion zumindest teilweise von einem Tripletzustand der Estergruppe im Polymeren aus erfolgt.

Received January 11, 1967

Revised March 13, 1967

Prod. No. 5400A

Preparation of Fluorine-Containing Polyethers

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Synopsis

Polyethers were prepared from 3,3,3-trifluoro-1,2-epoxypropane by using both cationic and anionic initiators. Aluminum chloride and boron trifluoride were the two cationic initiators investigated. The polymer obtained with the use of aluminum chloride contained no functional endgroups other than hydroxyl, while the polymer prepared with boron trifluoride contained some terminal unsaturation. Potassium hydroxide and the monosodium salt of hexafluoropentane-1,2-diol were investigated as anionic initiators. The polymer obtained by using potassium hydroxide also contained terminal unsaturation, while the polymer prepared with the monosodium salt of hexafluoropentane-1,2-diol was terminated with primary hydroxyl groups capable of being used in polyurethanes. All polymers had molecular weights in the range from 970 to 4300. A fluorine-containing polyformal was prepared in high yield by the reaction of hexafluoropentane-1,2-diol with trioxane. The same polymer was obtained in poor yield by the reaction of hexafluoropentane-1,2-diol with dibutyl formal. Ring-opening polymerizations were attempted on two fluorinated cyclic ethers, 2,2,3,3,4,4-hexafluoropentamethylene oxide and 3,3,4,4-tetrafluorotetramethylene oxide. There was no reaction with anionic initiators. With most of the cationic initiators, there was no reaction. Boron trifluoride and phosphorus pentafluoride formed complexes with the ether, but would not cause ring opening.

INTRODUCTION

Polyurethanes are normally prepared from diisocyanates and hydroxyl-terminated polyethers or polyesters having molecular weights in the range from 500 to 2000.

The synthesis of highly fluorinated diisocyanates¹ led to the preparation of highly fluorinated polyurethanes.² The principal shortcoming of these fluorinated polyurethanes is their lack of flexibility due to the use of short-chain diols, as no fluorinated hydroxyl-terminated polyesters or polyethers were available.

The synthesis of fluorine-containing polyethers is a recent development, primarily because suitable monomers have been available only since 1957. However, research into the utilization of these polyethers in polyurethanes has been limited because of the lack of reactivity and the difficulty in obtaining hydroxyl termination. It is essential that these fluorinated polyethers contain terminal hydroxyl groups if they are to provide usable polyurethanes.

EXPERIMENTAL

Polymerization of 3,3,3-Trifluoro-1,2-epoxypropane

With Boron Trifluoride Catalysis. 3,3,3-Trifluoro-1,2-epoxypropane (3.0 g., 0.0267 mole) and hexane (3 ml.) were placed into a vial which had been cooled in Dry Ice-acetone. Boron trifluoride gas was then passed slowly into the epoxide for 1½ min. while being cooled in a Dry Ice-acetone bath. The mixture was left standing for ½ hr., during which time the product became frozen. After the slurry was warmed to just above its freezing point, boron trifluoride was passed through the viscous material for 1 min., then was left standing for 1 hr. The polymer was dissolved in ether, then washed with dilute sodium bicarbonate solution. The ether solution was dried and evaporated to yield 1.7 g. (57%) of a viscous, light-tan polymer. The molecular weight by vapor-pressure osmometry (VPO) was 1150 ± 70 . The hydroxyl value, obtained by using 3,5-dinitrobenzoyl chloride, was 1013 g./hydroxyl group. It was found that 3,5-dinitrobenzoyl chloride did not react with the secondary hydroxyl groups.

Two drops of an impurity, immiscible with the principal product, were also noted. The infrared spectrum of this product indicated unsaturation.

With Aluminum Chloride Catalysis. 3,3,3-Trifluoro-1,2-epoxypropane (45.0 g., 0.4 mole) was placed into a test tube and cooled to -78°C . Aluminum chloride (1.3 g., 0.01 mole) was then added slowly with cooling. The mixture was kept at -78°C . for 1 hr., and an additional 22.5 g. (0.2 mole) of the epoxide added, and the mixture allowed to come to room temperature over a period of 24 hr. The tube was then shaken for 120 hr. at room temperature, the polymer dissolved in isopropyl ether and washed with water. The ether was dried and evaporated to yield 35.0 g. (78%) of a clear, viscous oil having a molecular weight of 2800 ± 70 , as determined by VPO.

With Potassium Hydroxide Catalysis. 3,3,3-Trifluoro-1,2-epoxypropane (3.4 g., 0.03 mole) and potassium hydroxide (0.15 g., 0.0027 mole) were charged into a Carius tube, which was then sealed. The polymerization was conducted at $90-95^{\circ}\text{C}$. for 84 hr. The polymer was dissolved in ether and washed with dilute acid. The ether was dried and removed to yield 2.1 g. (62%) of a colorless, viscous oil. The infrared spectrum indicated hydroxyl termination with some unsaturation. The molecular weight by VPO was 4300 ± 300 .

With the Monosodium Salt of Hexafluoropentane-1,2-diol as Initiator. The monosodium salt of hexafluoropentane-1,2-diol (11.7 g., 0.05 mole) was placed in a bomb, to which 3,3,3-trifluoro-1,2-epoxypropane (45.0 g., 0.4 mole) was then added at -78°C . The tube was sealed and the polymerization conducted at $85-90^{\circ}\text{C}$. for 88 hr. The product was dissolved in ether and washed with water. The ether was dried and removed to yield 41.0 g. (72%) of a clear, slightly yellow polyether. The molecular weight by VPO was 970 ± 25 . The hydroxyl equivalent was 500 g./hydroxyl group, indicating primary hydroxyl termination on both ends of the polymer.

Preparation of Poly(hexafluoropentamethylene Formal)

From Dibutoxymethane. Dibutoxymethane (11.2 g., 0.07 mole), hexafluoropentanediol (16.3 g., 0.077 mole), and a trace of ferric chloride were mixed at 160–170°C. for 3 hr., during which time 2 ml. of butanol was removed (16% of theory). The black solution was heated an additional 12 hr. at 160–170°C., followed by 24 hr. at 230–240°C. The low-boiling fractions were distilled and the residue dissolved in ether. The ether was washed with dilute ammonium hydroxide, followed by water, and the ether was dried and then removed to yield 1.2 g. (6%) of black polyformal which was identified by its infrared spectrum.

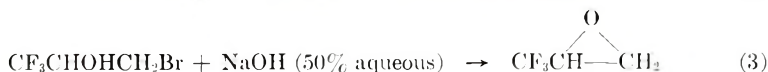
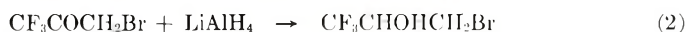
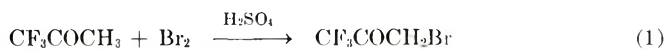
From Trioxane. Hexafluoropentanediol (53.0 g., 0.25 mole), *sym*-trioxane (7.5 g., 0.083 mole) and *p*-toluenesulfonic acid (1.5 g.) were mixed at 110–120°C. for 17 hr. Benzene was added and 3.8 ml. (85%) of water was removed by azeotropic distillation. The crude product was dissolved in ether, washed with 5% hydrogen peroxide solution containing 10% sodium carbonate, then washed with water. The ether was dried and removed, leaving a colorless oil which was distilled to yield 12.6 g. (57%) of clear, colorless poly(hexafluoropentamethylene formal). The infrared spectrum was identical to that of the product obtained using dibutoxy methane. The molecular weight by VPO was 835 ± 20 , and by endgroup analysis was 950.

ANAL. Calcd. for $C_6H_6F_6O_2$: C, 31.3%; H, 2.7%; F, 51.6%. Found: C, 31.30%; H, 2.76%; F, 51.34%.

RESULTS AND DISCUSSION

Polyethers of 3,3,3-Trifluoro-1,2-epoxypropane

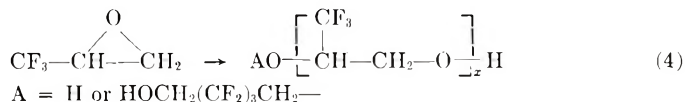
The monomer 3,3,3-trifluoro-1,2-epoxypropane was prepared previously;³ the reaction scheme is shown in eqs. (1)–(3).



Smith and co-workers⁴ described the polymerization of this monomer using Friedel-Crafts catalysts such as aluminum chloride and ferric chloride. The polymer obtained by using ferric chloride was a solid of 230,000 molecular weight, while that from aluminum chloride was a viscous liquid. No attempt was made to determine the type of endgroup present, and no anionic polymerization was attempted.

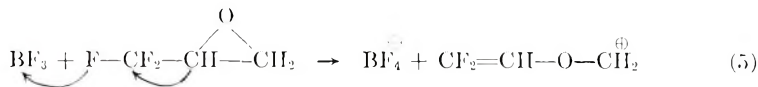
Jones and co-workers⁵ investigated the polymerization of 1,1,1-trifluoro-2,3-epoxybutane from which viscous liquid polymers resulted. With potassium hydroxide as an initiator, a yield of only 10% was obtained. Again, no attempt was made to determine the type of endgroups present in these polyethers.

This paper describes the preparation of liquid hydroxyl-terminated polyethers of 3,3,3-trifluoro-1,2-epoxypropane [eq. (4)] which contain over 50% fluorine by weight. The molecular weights of these polyethers, as determined by VPO, were in the range of 970–4300.

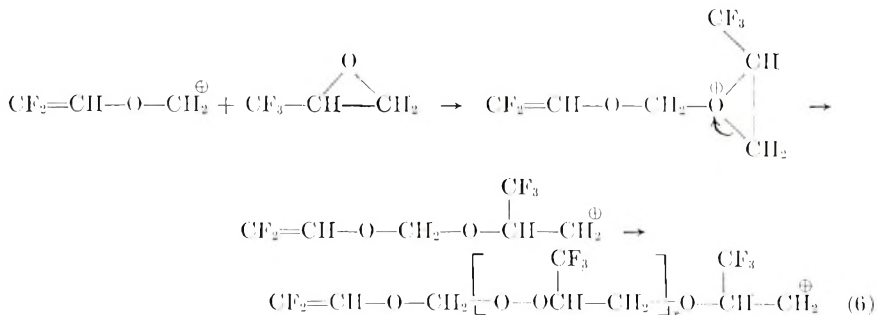


Cationic polymerization of this monomer was carried out by use of two Friedel-Crafts catalysts, boron trifluoride (gas) and aluminum chloride. The infrared spectrum of the polymer obtained with aluminum chloride catalysis indicated no functional groups other than hydroxyl. The boron trifluoride-initiated polyether was identical to the aforementioned polyether, with a trace of impurity containing unsaturation. This polymer impurity is believed to be a result of initiation by a carbonium ion formed by fluoride ion abstraction, as shown in eqs. (5)–(7).

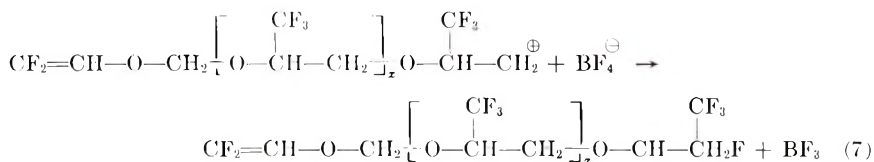
Initiation:



Propagation:



Termination:

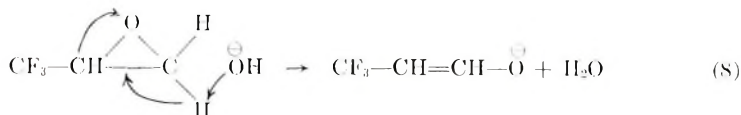


Polyethers have also been prepared successfully by anionic polymerization using potassium hydroxide and the monosodium salt of hexafluoropentandiol.

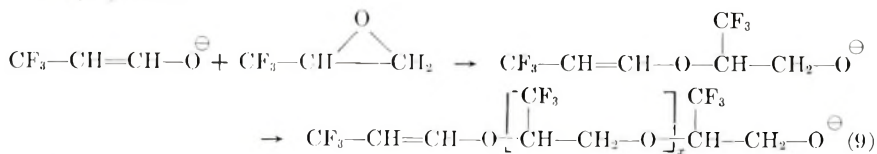
In contrast to the 10% yield of the polyether of 3,3,3-trifluoro-2,3-epoxybutane with potassium hydroxide catalysis,⁵ a colorless polyether of 3,3,3-trifluoro-1,2-epoxypropane was prepared in 61% yield with an unexpectedly high molecular weight of 4300. According to the infrared spectrum, the polymer contains some hydroxyl termination with some unsaturation.

It is believed that this unsaturation arises from the abstraction of a proton from the epoxide by hydroxyl, as illustrated in eqs. (8)–(10).

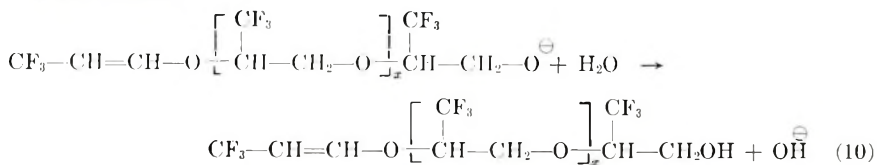
Initiation:



Propagation:



Termination:

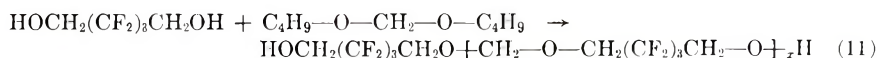


The monosodium salt of hexafluoropentenediol, prepared by reaction of hexafluoropentenediol with sodium hydride, was used as an anionic initiator for the polymerization of this epoxide so that primary hydroxyl termination could be obtained on both ends of the polymer. The polyether obtained in 72% yield was a clear, viscous liquid whose molecular weight was 970 as determined by VPO, and 1000 by endgroup analysis. Polyurethanes prepared from this hydroxyl-terminated polyether will be reported in a forthcoming paper.

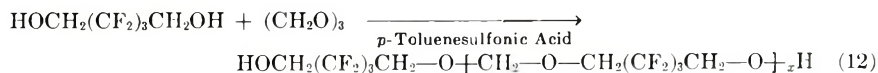
Polyformals of Hexafluoropentenediol

Smith⁴ attempted the preparation of a fluorine-containing polyglycol formal by reaction of dibutyl formal with hexafluoropentenediol. The product obtained was a high-boiling liquid that decomposed when allowed to stand or when heated at atmospheric pressure, which liberated formaldehyde and the original glycol.

The desired polyglycol, identified by its infrared spectrum, was obtained when this reaction was repeated [eq. (11)]. The yield, however, was extremely low.



The same hydroxyl-terminated polyformal was obtained as a nearly colorless oil in 57% yield by the reaction of hexafluoropentenediol with trioxane in the presence of *p*-toluenesulfonic acid [eq. (12)]. The molecular weight was 835.



The preparation of fluorinated polyurethanes from this polyformal is also the subject of a future paper.

Attempted Polymerization of Cyclic Fluorinated Ethers

The preparation of the cyclic ether, 2,2,3,3,4,4-hexafluoropentamethylene oxide was reported previously.⁶

Numerous attempts to initiate ring opening, both cationically and anionically, were unsuccessful.

In separate experiments, the cyclic ether was treated with triethylamine, solid potassium hydroxide, aqueous potassium hydroxide, rubidium fluoride, phosphorus pentafluoride, and phosphorus pentafluoride-tetrahydrofuran complex. None of these catalysts caused polymerization in 30 days at room temperature.

An attempt to polymerize this cyclic ether by extended refluxing in the presence of aluminum chloride was also unsuccessful.

Boron trifluoride was also investigated as a catalyst. A solid which formed on reaction with the cyclic ether at 0°C. may have been a complex of the oxide and boron trifluoride, similar to that formed between tetrahydrofuran and phosphorus pentafluoride. It did not, however, cause polymerization of a fresh sample of hexafluoropentamethylene oxide over a 2-week period at a temperature of 10°C. Passing boron trifluoride into a sample of the cyclic oxide at room temperature for 1 hr., then allowing the solution to stand for 2 days, resulted in the formation of a small amount of dense, dark oil. Workup of this oil indicated that it, too, is probably a complex of the oxide and boron trifluoride.

The preparation of 3,3,4,4-tetrafluorotetramethylene oxide has also been reported.⁶ Since tetrahydrofuran can be polymerized, attempts were made to polymerize this cyclic ether by using aluminum chloride, phosphorus pentafluoride-tetrahydrofuran complex, phosphorus pentafluoride, or boron trifluoride as catalysts. No noticeable reaction occurred with the first three catalysts. With phosphorus pentafluoride, a small amount of liquid formed which is probably a complex of the cyclic ether and phosphorus pentafluoride. Similarly, the crystalline solid formed with boron trifluoride catalysis is believed to be a complex of the cyclic ether and boron trifluoride.

This work was performed under Contract No. NAS 8-11068 for the George C. Marshall Space Flight Center, National Aeronautics and Space Administration. It was administered under the direction of the Propulsion and Engineering Division, Engineering Materials Branch, with J. M. Stuckey and W. E. Hill acting as project officers.

The authors would like to thank Mr. R. E. Empey for the physical properties data.

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Résumé

Des polyéthers ont été préparés au départ de 3,3,3-trifluoro-1,2-époxy propane en utilisant des initiateurs cationiques et anioniques. Le chlorure d'aluminium et le trifluorure de bore sont les deux initiateurs cationiques utilisés. Le polymère obtenu en utilisant le chlorure d'aluminium ne contenait pas de groupes terminaux fonctionnels autres que des groupes hydroxyles alors que le polymère préparé en utilisant le trifluorure de bore contenait quelques groupes terminaux insaturés. L'hydroxyde de potassium et le sel monosodé de l'hexafluoro-pentane-1,2-diol ont été étudiés comme initiateurs anioniques. Le polymère obtenu en utilisant l'hydroxyde de potassium contenait également une insaturation terminale alors que le polymère préparé avec le sel monosodé de l'hexafluoro-pentane-1,2-diol se terminait par des groupes hydroxyles primaires capables d'être utilisés pour la fabrication de polyuréthanes. Tous les polymères avaient des poids moléculaires du domaine de 970 à 4300. Un polyformal contenant du fluor a été préparé avec un rendement élevé par réaction de l'hexafluoro-pentane-1,2-diol avec le trioxane. Ce même polymère a été obtenu avec un rendement faible par la réaction de l'hexafluoro-pentane-1,2-diol avec le formal dibutylque. Les polymérisations avec ouverture de cycle ont été essayées sur deux éthers cycliques fluorés, à savoir, l'oxyde de 2,2,3,3,4,4-hexafluoro-pentaméthylène et l'oxyde de 3,3,4,4-tétrafluorotétraméthylène. Il n'y a pas de réaction avec les initiateurs anioniques. Avec la plupart des initiateurs cationiques, il n'y a pas de réaction non plus. Le trifluorure de bore et le pentafluorure de phosphore forment des complexes avec l'éther mais n'entraînent pas d'ouverture de cycle.

Zusammenfassung

Unter Verwendung sowohl kationischer als auch anionischer Starter wurden Polyäther aus 3,3,3-Trifluor-1,2-epoxypropan hergestellt. Als kationische Starter wurden Aluminiumchlorid und Bortrifluorid untersucht. Das Polymere, das mittels Aluminiumchlorid hergestellt wurde, enthielt ausser Hydroxylgruppen keine funktionellen Endgruppen, während das mit Bortrifluorid erhaltene Polymere einige endständige Doppelbindungen aufwies. Als anionische Starter wurden Kaliumhydroxyd und das Mononatriumsalz des Hexafluorpentandiols untersucht. Das mit Kaliumhydroxyd hergestellte Polymere enthielt ebenfalls endständige Doppelbindungen, während das Polymere, das mit dem Mononatriumsalz des Hexafluorpentandiols dargestellt wurde, an seinen Enden primäre Hydroxylgruppen besass, die zur Herstellung von Polyurethanen geeignet waren. Alle Polymeren hatten Molekulargewichte im Bereich zwischen 970 und 4300. Ein fluorhaltiges Polyformal wurde durch Reaktion von Hexafluorpentandiol mit Trioxan hergestellt. Dasselbe Polymere erhielt man in schlechter Ausbeute durch Reaktion von Hexafluorpentandiol mit Dibutylformal. An zwei fluorierten cyclischen Äthern, 2,2,3,3,4,4-Hexafluorpentamethylenoxyd und 3,3,4,4-Tetrafluortetramethylenoxyd, wurde eine Ringöffnungspolymerisation versucht. Mit anionischen Startern und den meisten kationischen Startern trat keine Reaktion ein. Bortrifluorid und Phosphorpentafluorid bildeten mit dem Äther Komplexe, brachten jedoch keine Ringöffnung zustande.

Received January 4, 1967

Revised March 14, 1967

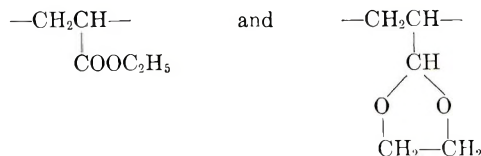
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Isomerization Polymerization of 2-Vinyl-1,3-dioxolane by α,α' -Azobisisobutyronitrile or by γ -Ray Irradiation

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Synopsis

2-Vinyl-1,3-dioxolane was polymerized by use of α,α' -azobisisobutyronitrile (AIBN) or by γ -ray irradiation. The polymer obtained was white amorphous powder which melted at ca. 70°C. and was soluble in chloroform, acetone, and *p*-dioxane. The infrared spectrum of the polymer indicated peaks at 1735 cm^{-1} characteristic of the carbonyl group, and at 1200–1000 cm^{-1} characteristic of the acetal group, while no absorption at 990 and 3100 cm^{-1} due to the vinyl group was observed. The spectra of the polymers obtained by AIBN and by γ -ray irradiation were essentially identical. The saponified product of the polymer was white powder and its reduced viscosity was a little larger than that of the original polymer. These results indicate that the polymer has no ester unit in the main chain. The results of gas chromatographic analysis of the saponified product of the polymer, indicate the presence of a small amount of ethyl alcohol. The results of the saponification showed that the ester content in the polymer varied from 7 to 25% depending upon the polymerization temperature. These results indicate that 2-vinyl-1,3-dioxolane polymerized by AIBN or by γ -irradiation with two modes of vinyl and hydrogen migration, yielding a copolymer having the unit structures



INTRODUCTION

A number of studies on the ring-opening polymerization of 1,3-dioxolanes with cationic catalyst have been reported.¹⁻⁴ The polymerization of dioxolanes having an unsaturated group was also reported: 2-methylene-1,3-dioxolane was polymerized by the carbon-carbon double bond addition route,⁵⁻⁷ while 4-methylene-1,3-dioxolanes⁸⁻¹⁰ and 2-vinyl-1,3-dioxolane¹¹ were polymerized by the carbon-carbon double bond opening coupled with a ring rearrangement route with the use of a cationic catalyst. Most of the work on the polymerization of dioxolanes has dealt with the cationic polymerization; little attention has been paid to the radical polymerization of these monomers.

The present work was concerned with a radical and γ -ray irradiation polymerization of 2-vinyl-1,3-dioxolane. The purpose of this paper is to report that the hydrogen migration occurred during the course of polymerization and that the polymer has two unit structures.

EXPERIMENTAL

Synthesis of Monomer

The monomer was prepared by dehydrohalogenation of 2-(β -chloroethyl)-1,3-dioxolane as follows.

2-(β -Chloroethyl)-1,3-dioxolane. Hydrogen chloride (240 g., 6.6 mole) was bubbled into a mixture of acrolein (300 g., 5.3 mole) and ethylene glycol (500 g., 8.1 mole) at -10°C . to -15°C . for 2 hr. The reaction mixture was neutralized with sodium bicarbonate. The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate overnight. 2-(β -Chloroethyl)-1,3-dioxolane was thus obtained: 450 g. (60% yield) b.p. $58-62^{\circ}\text{C}/8$ mm. Hg.

2-Vinyl-1,3-dioxolane. 2-(β -Chloroethyl)-1,3-dioxolane (164 g., 1.2 mole) was refluxed over potassium hydroxide powder (336 g., 6 mole) for 30 min. The reaction mixture was distilled at atmospheric pressure, and then under reduced pressure (20 mm. Hg). The product was dried over anhydrous magnesium sulfate overnight. The desired product was obtained by distilling twice over calcium hydride; the yield was 100 g. (80%); d_4^{20} 1.00, b.p. $115-116^{\circ}\text{C}$. (lit.¹² $114-116^{\circ}\text{C}$.).

Syntheses of Related Compounds

Acrolein Diethyl Acetal. Acrolein acetal was prepared from acrolein and ethyl orthoformate as described by Schmidt;¹³ b.p. 124°C . (lit.¹³ $120-125^{\circ}\text{C}$.).

2-Ethyl-1,3-dioxolane. This acetal was obtained by the condensation of propionaldehyde and ethylene glycol according to Astle's method;¹⁴ b.p. 104°C . (lit.¹⁴ $105-107^{\circ}\text{C}$.).

Poly(ethyl Acrylate). Ethyl acrylate was polymerized by AIBN in bulk, and the polymer was precipitated from benzene solution with ether.

Polymerization

Polymerization by α, α' -Azobisisobutyronitrile (AIBN). Definite amounts of the monomer and AIBN (G.R. Grade) were fed into glass ampules which were dried and swept with dry nitrogen before use. Polymerizations were carried out at temperature of $40-100^{\circ}\text{C}$. in bulk. After evaporating unreacted monomer, the polymer was precipitated from chloroform solution with ether.

Polymerization by γ -Ray Irradiation. Glass ampules containing measured amounts of the monomer were degassed and sealed *in vacuo*. Ampules

were exposed to γ -radiation from a ^{60}Co source without agitation. After the irradiation, polymers were treated as described above.

Characterization of the Polymer

Viscosity measurements were carried out with the use of an Ubbelohde-type viscometer at 35°C . in chloroform. Melting points were measured visually in a nitrogen atmosphere. Infrared spectra were obtained with the use of a Shimadzu infrared spectrophotometer, Model IR-27, with sodium chloride prism. The x-ray diffraction diagrams were recorded with a powder camera on a Shimadzu x-ray diffractometer, Model GX-3B, employing Ni-filtered $\text{CuK}\alpha$ radiation by the use of standard techniques.

Saponification of Polymer

A 100-mg. portion of polymer was saponified with 10 ml. of 0.1*N* NaOH/EtOH under reflux for 20 hr. The content of ester units in the polymer chain were determined by titration with 0.1*N* HCl solution. The results obtained by this method were identical to those calculated from the intensity at 1735 cm^{-1} in the infrared spectrum of the polymer. The saponified product was precipitated with water, and its infrared spectrum obtained. A mixture of 60 mg. of the polymer, 300 mg. of NaOH and 5 ml. of dioxane was refluxed for 8 hr. Gas-liquid chromatographic analysis of the saponified product was carried out with a Yanagimoto gas chromatograph, Model GCG-2.

RESULTS AND DISCUSSION

The results of the polymerization obtained by AIBN and by γ -ray irradiation are shown in Table I. Both of the polymers were white pow-

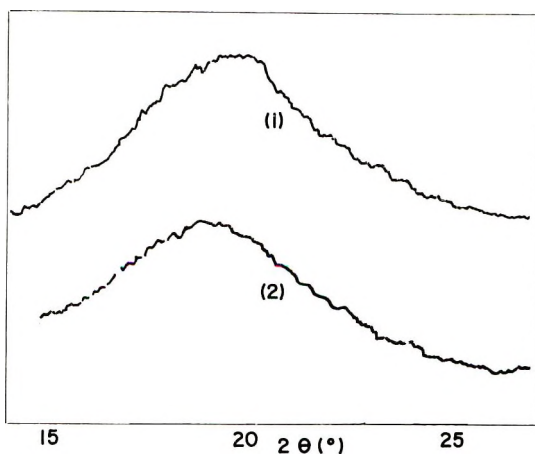


Fig. 1. X-ray diffraction diagrams of: (1) poly-2-vinyl-1,3-dioxolane and (2) saponified product of poly-2-vinyl-1,3-dioxolane.

TABLE I
 Polymerizations of 2-Vinyl-1,3-dioxolane by AIBN or by γ -Ray Irradiation^a

Expt. no.	Reaction temp., °C.	Initiator, mg.	Reaction time, hr.	Polymer yield, mg.	Ester content, %	Reduced viscosity ^b	Melting point, °C.
A-1	40	100	48	48	—	—	—
A-2 ^c	60	100	40	345	8.7	0.06	70-75
A-3	80	100	24	336	9.7	0.06	68-73
A-4	100	100	24	225	11.0	0.06	63-70
B-1	60	50	40	186	7.5	0.07	65-72
B-2	60	100	40	290	8.3	0.06	68
B-3	60	200	40	471	7.3	0.06	68-70
B-4 ^d	60	400	40	817	8.5	0.06	70-73
C-1	-78	—	27.5	84	15.0	—	—
C-2	35	—	27.5	100	25.0	—	—

^a Conditions A, B (polymerized by AIBN), monomer 5 g.; C (polymerized by γ -ray irradiation), dose rate 3.6×10^5 rad/hr.; monomer 3 g.

^b Measured in chloroform at 35°C., $c = 1.2$ mg./cc.

^c ANAL. Calcd. for $C_5H_8O_2$: C, 60.01%; H, 8.06%. Found: C, 59.25%; H, 8.36%.

^d ANAL. Found: C, 59.63%; H, 8.21%.

ders which melted at ca. 70°C., and were soluble in chloroform, acetone, and *p*-dioxane. The x-ray diffraction diagram showed that the polymer was partially crystalline (Fig. 1).

Infrared spectra of the polymer, the monomer, and related compounds are shown in Figures 2 and 3. The spectra of the polymers obtained by

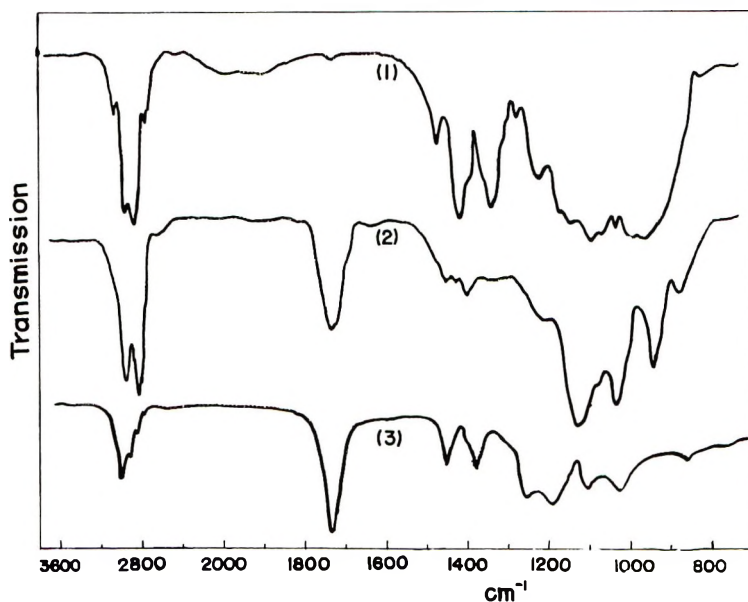


Fig. 2. Infrared spectra of: (1) 2-vinyl-1,3-dioxolane; (2) poly-2-vinyl-1,3-dioxolane; (3) poly(ethyl acrylate).

AIBN and by γ -ray irradiation are essentially identical. The characteristic peaks of the polymer are listed in Table II. The infrared spectrum of the polymer indicated that the polymer had absorption peaks assigned to ring acetal and carbonyl group, but did not have those assigned to the vinyl group.

The fact that the absorptions in the ether region were identical to those of the dioxolanes, especially of 2-ethyl-1,3-dioxolane (Fig. 3), may suggest that this monomer polymerized mainly at the carbon-carbon double bond. As shown in Figure 3, the absorption peaks at 3100 cm^{-1} and 990 cm^{-1} due to the vinyl group were observed in the spectra of the monomer and acrolein acetal, but not in the polymer. These facts lead to the conclusion that the ring-opening polymerization which gives the structure

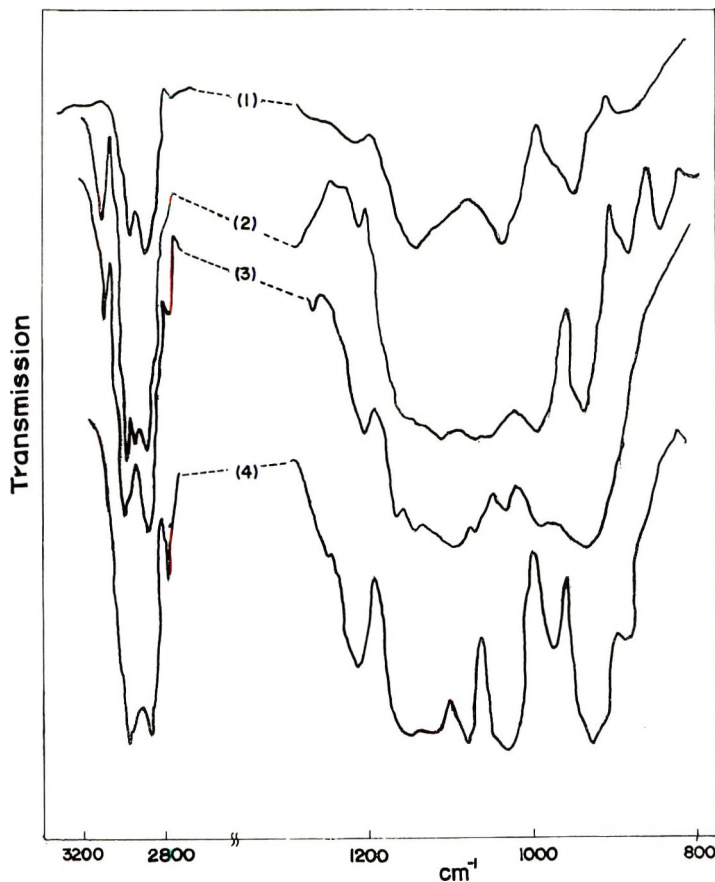
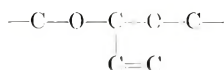
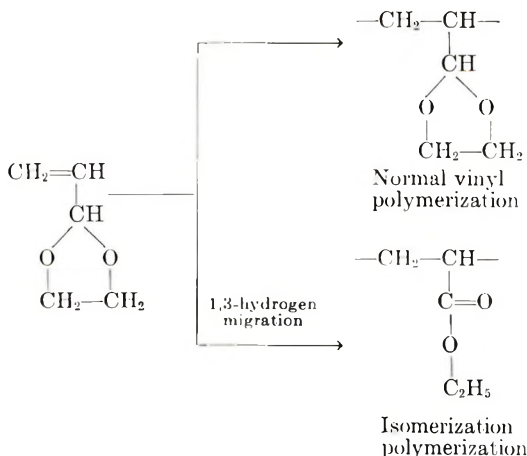


Fig. 3. Infrared spectra of: (1) poly-2-vinyl-1,3-dioxolane; (2) 2-vinyl-1,3-dioxolane; (3) acrolein diethyl acetal; (4) 2-ethyl-1,3-dioxolane.

did not occur in these polymerizations. Absence of a network structure in the polymer is consistent with this conclusion. As shown in Figure 2, the spectrum of the polymer showed a characteristic peak at 1735 cm.^{-1} . On the basis of the fact that this peak is identical to that of the ester group of poly(ethyl acrylate) (Fig. 2), it was concluded that the peak was ascribed to ester group.

In order to determine the position of this ester unit, saponifications of the polymer were carried out in comparison with the copolymer of β -propiolactone and ethylenimine which contains the same amount of ester units (ca. 15 mole-%).¹⁵ The infrared spectrum of the saponified polymer indicated a peak at 1710 cm.^{-1} characteristic of the carboxyl group. The gas chromatographic analysis also showed that a small amount of ethanol was present in the saponified product of the polymer. Furthermore, on saponification, the intrinsic viscosity of poly-2-vinyl-1,3-dioxolane increased a little, while that of the copolymer of β -propiolactone decreased to one-tenth of the original value. These results lead to the conclusion that the polymer did not contain the unit structure of $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-$ but contained a $-\text{CH}_2-\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)-$ structure. This means that 1,3-hydrogen migration occurred during the course of polymerization.

From these results, it was concluded that polymerization of 2-vinyl-1,3-dioxolane in the presence of AIBN or by γ -ray irradiation follows two modes of vinyl and isomerization polymerization:



and gives a copolymer containing two unit structures. Detailed study on the mechanism of this isomerization polymerization will be reported in a subsequent paper.

TABLE II
Characteristic Peaks in the Infrared Spectrum of Poly-2-vinyl-1,3-dioxolane

Wavenumber, cm^{-1}	Intensity	Assignment
2960	vs	$\nu_{\text{as}}\text{CH}$
2900	vs	$\nu_{\text{as}}\text{CH}_2$ OR $\nu_{\text{s}}\text{CH}_2$
1735	m	$\nu\text{C}=\text{O}$
1400-1500	w	δCH_2 scissoring
1140	vs	$\text{C}-\text{O}-\text{C}$
1050	vs	$\text{C}-\text{O}-\text{C}$
950	s	
890	w	

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Résumé

Le 2-vinyl-1,3-dioxolane a été polymérisé au moyen d' α,α' -azobisisobutyronitrile (AIBN) par irradiation aux rayons- γ . Le polymère obtenu était une poudre amorphe blanche fondant à environ 710°C et était soluble dans le chloroforme, l'acétone et le *p*-dioxane. Le spectre infrarouge du polymère indiquait des pics caractéristiques à 1735 cm^{-1} pour le groupe carbonyle et à 1200-1000 cm^{-1} pour le groupe acétalique, alors qu'il n'y a pas d'absorption à 990 et 3100 cm^{-1} due au groupe vinylique. Le spectre des polymères obtenus par AIBN et par radiation aux rayons- γ sont essentiellement les mêmes. Le produit saponifié du polymère était une poudre blanche et la viscosité réduite de celui-ci était quelque peu plus grande que celle du polymère de départ. Ce résultat indique que le polymère n'a pas d'unités esters dans la chaîne principale. Au départ des résultats d'analyse par chromatographie gazeuse du produit saponifié, on a trouvé de petites quantités d'alcool éthylique étaient contenues dans celui-ci. Ces résultats de saponification montraient que la teneur en ester dans le polymère variait de 7 à 25% suivant la température de polymérisation. Au départ de ces résultats on conclut que le 2-vinyl-1,3-dioxolane polymérise par AIBN ou par irradiation aux rayons- γ suivant deux modes de migrations vinylique et d'hydrogène et fournit un polymère ayant des unités structurales (voir les structures dans le texte anglais).

Zusammenfassung

2-Vinyl-1,3-dioxolan wurde mittels α, α' -Azobisisobutyronitril (AIBN) oder durch γ -Strahlung polymerisiert. Das erhaltene Polymere stellte ein weisses, amorphes Pulver dar, das bei ca. 70°C schmolz und in Chloroform, Aceton und *p*-Dioxan löslich war. Das Infrarotspektrum des Polymeren zeigte bei 1735 cm^{-1} die charakteristischen Absorptionsmaxima für die Carbonylgruppe und bei 1200–1000 cm^{-1} für die Acetalgruppe, während bei 990 und 3100 cm^{-1} keine einer Vinylgruppe entsprechende Absorption beobachtet wurde. Die Spektren der mit AIBN und durch γ -Bestrahlung erhaltenen Polymeren waren im wesentlichen identisch. Das Verseifungsprodukt des Polymeren war ein weisses Pulver; seine reduzierte Viskosität war etwas höher als die des Originalpolymeren. Diese Ergebnisse weisen darauf hin, dass das Polymere keine Estereinheiten in der Hauptkette besitzt. Aus den Resultaten der gaschromatographischen Analyse des Verseifungsproduktes des Polymeren ging hervor, dass in ihm eine kleine Menge Äthylalkohol enthalten war. Verseifungsergebnisse zeigten, dass der Estergehalt im Polymeren je nach der Polymerisationstemperatur zwischen 7 und 25% schwankt. Auf Grund dieser Resultate wurde der Schluss gezogen, dass die Polymerisation von 2-Vinyl-1,3-dioxolan mit AIBN oder durch γ -Strahlen auf den beiden Wegen der Vinyl- und der Wasserstoffmigrationspolymerisation erfolgt und zu einem Copolymeren führt, dessen Struktureinheiten (vgl. englische Zusammenfassung).

Received January 30, 1967

Revised March 29, 1967

Prod. No. 5404A

Cyclopolycondensations. VI. Fully Aromatic Polybenzoxazinones from Aromatic Poly(amic Acids)*

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Synopsis

New high temperature aromatic polybenzoxazinones of high molecular weight have been prepared by the cyclopolycondensation of 4,4'-diaminobiphenyl-3,3'-dicarboxylic acid (I) with aromatic dicarboxylic acid halides (II). The low temperature solution polymerization techniques afforded poly(amic acid) (III) of high molecular weight in the first step. An open-chain precursor subsequently underwent thermal cyclodehydration along the polymer chain at 200–350°C. in the second step, to give in quantitative yield a fully aromatic polybenzoxazinone (IV) of outstanding heat stability both in nitrogen and in air. The poly(amic acid) is soluble in *N*-methyl-2-pyrrolidone, and tough, transparent films can be cast from solution. Insoluble aromatic polybenzoxazinone films which possess excellent oxidative and thermal stability were obtained by the heat treatment of the polyamic acid. A detailed account of polymerization conditions in the low temperature solution polymerization of polybenzoxazinones is given, and the reaction mechanisms of cyclopolycondensation of poly(amic acids) and the formation of polybenzoxazinones are discussed.

INTRODUCTION

The interest in thermally stable heterocyclic polymers has generated a variety of new synthetic approaches to cyclopolycondensation reactions, which afford new, fully aromatic or pseudoaromatic polymers. The characteristic features of cyclopolycondensations for these aromatic heterocyclic polymers involve in the first step, the formation of a soluble, open-chain poly(amic acid) of high molecular weight by polycondensation or polyaddition reactions, followed by thermal cyclodehydration along the polymer chain to obtain unusually high-melting, insoluble aromatic polymers of outstanding thermal stability. We proposed to term these new classes of polymerization reactions cyclopolycondensation reactions.^{2,3}

In previous publications,^{1,3-7} it was shown that polymers containing quinazolinedione or benzoxazinone nuclei of high molecular weight could be

* Presented in part at the IUPAC International Symposium on Macromolecular Chemistry, Kyoto, October 1966. For part V of this series see Kurihara and Yoda.¹

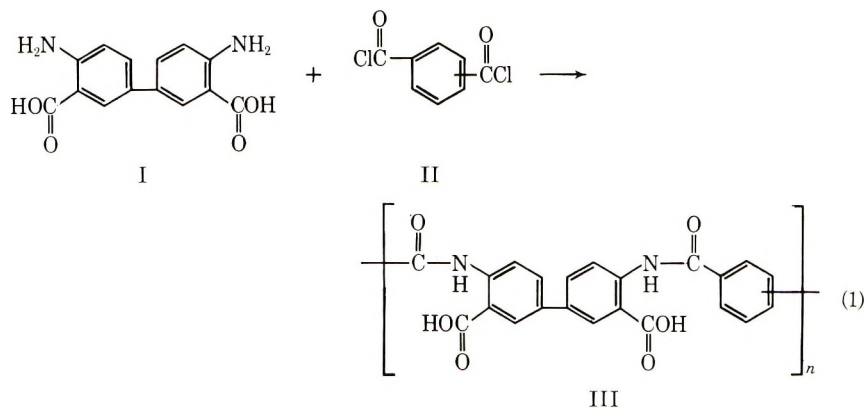
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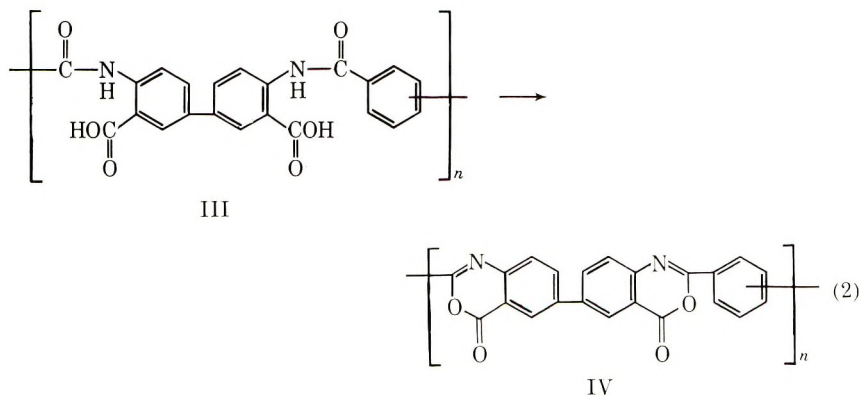
prepared by the melt and low temperature solution polymerizations of suitable aromatic diaminodicarboxylic acid with aromatic diisocyanate or dicarboxylic acid derivatives. In the present paper, we wish to report details of the low temperature solution polymerization of fully aromatic polymers with benzoxazinone structure units within the polymer backbone as a new class of thermally stable polymers.

A new aromatic polybenzoxazinone was prepared by the cyclopolycondensation of 4,4'-diaminobiphenyl-3,3'-dicarboxylic acid (BDC) with an aromatic dicarboxylic acid halide in two successive steps as shown in eqs. (1) and (2).

Low temperature solution polymerization process.



Thermal cyclodehydration process.



The cyclopolycondensation proceeds through the formation of a high molecular weight poly(amic acid) (III) in the first step, an open-chain, tractable precursor, which subsequently undergoes thermal cyclodehydration along the polymer chain, in the second step, to yield a fully aromatic polybenzoxazinone (IV) of outstanding thermal stability. The present paper deals with the reaction variables of the low temperature solution polymerization of polybenzoxazinones. The reaction mechanisms of

cyclopolycondensation of poly(amic acids) and the formation of poly-benzoxazinone are discussed.

EXPERIMENTAL

Reagents

***N*-Methyl-2-pyrrolidone.** This was obtained from Kishida Chemical, C. P. grade, and was distilled from calcium hydride at 3 mm. Hg.

***N*-Methyl- ϵ -caprolactam.** A 113-g. (1.0 mole) portion of ϵ -caprolactam is dissolved in 335 ml. of benzene and heated at 80°C. Into the flask is added dropwise 126 g. (1.0 mole) of dimethyl sulfate through a dropping funnel over a period of 1.5 hr. The mixture is refluxed for 16.5 hr., after which it is washed thoroughly with 50% aqueous potassium carbonate until alkaline. The organic layer is separated, dried with phosphorus pentoxide. Benzene is removed, and the residue is distilled under vacuum; the product is the fraction boiling at 81.0–82.0°C./3.5 mm. Hg (lit.⁸ b.p. 120°C./19 mm. Hg).

***N,N'*-Dimethylacetamide.** This was obtained from Kishida Chemical, C. P. grade, and was distilled from calcium hydride at 3 mm. Hg.

***N,N'*-Dimethylformamide.** This was obtained from Kishida Chemical, C. P. grade, and was distilled from calcium hydride at 3 mm. Hg.

Dimethyl Sulfoxide. This was obtained from Kishida Chemical, C. P. grade, and was distilled from calcium hydride at 3 mm. Hg.

4,4'-Diaminobiphenyl-3,3'-dicarboxylic Acid (BDC) and Its Dihydrochloride dihydrate (BDC·2HCl·2H₂O)(I). BDC was prepared in 92% yield from *o*-nitrobenzoic acid by benzidine rearrangement.⁹ The monomer was carefully purified by recrystallization followed by vigorous vacuum drying.

ANAL. Calcd. for free BDC, C₁₄H₁₂O₄N₂: C, 61.76%; H, 4.44%; N, 10.29%. Found: C, 61.53%; H, 4.53%; N, 10.12%.

Dihydrochloride dihydrate of BDC was obtained by the treatment of free BDC with concentrated hydrochloric acid at room temperature, and the colorless needles were precipitated out in 20 min.

ANAL. Calcd. for BDC·2HCl·2H₂O, C₁₄H₁₆O₆N₂Cl₂: C, 44.13%; H, 4.76%; N, 7.35%; Cl, 18.60%. Found: C, 44.22%; H, 4.88%; N, 7.28%; Cl, 18.27%.

Isophthaloyl Chloride (II). This was prepared by refluxing isophthalic acid with thionyl chloride, the fraction boiling at 116°C./3 mm. Hg being collected.

***N*-Benzoylanthranilic Acid (V_a).** A mixture consisting of 3.4 g. (0.024 mole) of anthranilic acid and 3.5 g. (0.025 mole) of benzoyl chloride was mixed with 115 g. of poly(phosphoric acid) (PPA). The reaction mixture was heated at 120–140°C. with mechanical stirring for 12 hr. and the reaction product was poured into water. White crystals were obtained in 92% yield by filtration, followed by washing with sufficient distilled water and recrystallization from ethanol three times; m.p. 179–183°C. (lit.^{10,11} 181–182°C.).

2-Phenyl-4H-3,1-benzoxazine-4-one (V_b). A 3.60-g. (0.015 mole) portion of *N*-benzoylanthranilic acid was added to 60 g. of PPA and the mixture heated at 200°C. for 30 min. After the reaction, the mixture was poured into 900 ml. of distilled water. The solid was filtered and washed successively with 10% aqueous sodium carbonate solution and distilled water. Recrystallization from ethanol yields white needles, in 92.5% yield, melting at 120.5°C. (lit.^{12,13} 123–124°C.).

***N,N'*-Dibenzoyl-3,3'-benzidinedicarboxylic Acid (VI).** A mixture of 1.36 g. (0.005 mole) of BDC and 2.0 g. (0.014 mole) of benzoyl chloride in 40 g. of PPA was heated at 140–150°C. for 5 hr. with vigorous mechanical stirring. The reaction products were poured into 500 ml. of distilled water to obtain a white precipitate, which was treated with 200 ml. of 10% aqueous sodium carbonate solution. An insoluble product (VII) removed. The acidic fraction (VI) was precipitated out from the filtrate by acidifying the solution with dilute hydrochloric acid. The recrystallization of product (VI) from aqueous *N,N'*-dimethylformamide solution afforded crystals in 87.5% yield. m.p. > 360°C. The infrared spectrum shows carbonyl stretching bands at 1690 cm.⁻¹ (strong) for the carboxyl group, and at 1670 cm.⁻¹ (strong) for amide I.

ANAL. Calcd. for C₂₈H₂₀N₂O₆: C, 69.99%; H, 4.20%; N, 5.83%. Found: C, 69.67%; H, 4.76%; N, 5.91%.

2,2'-Diphenyl-[6,6'-bi-4H-3,1-benzoxazine]-4,4'-dione (VII). From the neutral fraction of the above-described procedure, the product (VII) was obtained in 12% yield. Recrystallization from *N,N'*-dimethylacetamide afforded crystals melting above 360°C. The infrared spectrum shows the ester carbonyl band of carbonyl band of benzoxazinone ring system at 1760 cm.⁻¹ (strong), and $\nu_{C=N}$ at 1620 cm.⁻¹ (shoulder).

ANAL. Calcd. for C₂₈H₁₆N₂O₄: C, 75.67%; H, 3.63%; N, 6.30%. Found: C, 74.83%; H, 3.75%; N, 6.48%.

2,2'-Di-*p*-tolyl-[6,6'-bi-4H-benzoxazine]4,4'-dione (VIII). A mixture of 0.70 g. (0.0025 mole) of BDC and 0.83 g. of *p*-toluic acid in 45 g. of PPA was heated at 150°C. for 22 hr., and then at 220–230°C. for 2 hr. The product was treated as described above to afford the product. After recrystallization from *N,N'*-dimethylacetamide crystals with m.p. 360°C. (dec.) were obtained in 86% yield. The infrared spectrum shows an ester carbonyl band at 1760 cm.⁻¹, $\nu_{C=N}$ at 1650 cm.⁻¹, and ν_{C-O-C} at 1064 cm.⁻¹. Elemental analyses and the infrared spectrum support the structures, which are summarized in Table I.

ANAL. Calcd. for C₃₀H₂₀O₄N₂: C, 76.26%; H, 4.27%; N, 5.93%. Found: C, 76.12%; H, 4.40%; N, 6.08%.

Polymerizations

Typical Preparation of a Poly(amic Acid). The low temperature solution polymerization was carried out by the reaction of 4,4'-diaminobiphenyl-

TABLE I
Infrared Spectra of Benzoxazinone Model Compounds

Compounds	Structure	Infrared absorption band, cm^{-1} ^a	Melting point, °C.	Nitrogen, %	
				Calcd.	Found
V ^a		1670 1644	179-183	5.80	5.30
V ^b		1760 1260 1060	130	6.28	6.21
VI ^b		1690 1670	>360	5.83	5.91
VII ^b		1760 1620 1260 1060	>360	6.30	6.48
VIII ^b		1760 1650 1258 1064	360 dec.	5.93	6.20

^a KBr disk.

^b New compounds.

3,3'-dicarboxylic acid (I) with terephthaloyl chloride or isophthaloyl chloride (II) in organic polar solvents such as dimethylacetamide (DMAc), *N*-methylpyrrolidone (NMP), hexamethylphosphoramide (HMP), and poly(phosphoric acid) (PPA).⁶ To a solution of purified 4,4'-diaminobiphenyl-3,3'-dicarboxylic acid (0.100 mole) in *N*-methylpyrrolidone (780 ml.) containing lithium chloride (0.20 mole) was added freshly distilled isophthaloyl chloride (0.102 mole) as a solid at 5–20°C. in a heterogeneous system with rapid stirring in an inert atmosphere. An exothermic reaction took place after a few minutes, and a viscous polymer solution was obtained. After it was heated at 120°C. with mechanical stirring for 20 min., the viscous polymer solution was quenched by pouring into an aqueous methanol solution. The fibrous polymer was filtered, washed thoroughly with water and methanol, and dried under vacuum at 78°C. The yield of polymer was nearly quantitative (in 96% yield) and the inherent viscosity was 1.51 in concentrated sulfuric acid (0.5% concentration, 25°C.). The polyamide-acid (III) thus obtained was dissolved in *N*-methyl-2-pyrrolidone, and the resultant solution poured onto a glass plate and dried at 120°C. for 30 min. to afford a transparent, tough film.

ANAL. Calcd. for $(C_{22}H_{14}O_6N_2)_n$: C, 65.67%; H, 3.51%; N, 6.96%. Found: C, 65.39%; H, 3.50%; N, 6.78%.

The infrared spectrum of polyamide-acid film shows amide carbonyl band at 1670 cm.^{-1} , and the NH stretching band appears at 3400 cm.^{-1} . The polyamide-acid is soluble in dimethylacetamide, *N*-methyl-2-pyrrolidone, dimethylformamide, and dimethyl sulfoxide containing lithium chloride. It is also soluble in concentrated sulfuric acid.

Conversion to Polybenzoxazinone. The polyamide-acid film was heated on a frame in an oven at 180–360°C. under vacuum (0.1 mm. Hg). The dehydration was initiated at 200°C., followed by cyclization to form a benzoxazinone (IV) of high molecular weight.

ANAL. Calcd. for $(C_{22}H_{10}O_4N_2)_n$: C, 72.13%; H, 2.75%; N, 7.65%. Found: C, 72.16%; H, 2.71%; N, 7.62%.

The dehydration was also effected by treating polyamide-acid film with a solvent pair of acetic anhydride and pyridine (1:1), followed by heating the film at 130–180°C. under vacuum for 20 min.

The formation of the benzoxazinone ring by the intramolecular thermal dehydration of polyamide-acid was confirmed by the comparison of infrared spectra of model compounds. The appearance of a new characteristic carbonyl absorption band for the benzoxazinone ring at 1760 cm.^{-1} supports the hypothesis of the formation of the benzoxazinone ring along the polymer chain. The dehydration process was followed by the disappearance of a broad absorption band at 3400–3100 cm.^{-1} (ν_{NH}) and a strong band at 1670 cm.^{-1} (amide I) in infrared spectra, as shown in Figure 1, which were taken for poly(3,3'-dicarboxybenzidine isophthalamide) film heated in vacuum at 180, 250, 300, 370, and 450°C. successively for 0.5 hr. at each

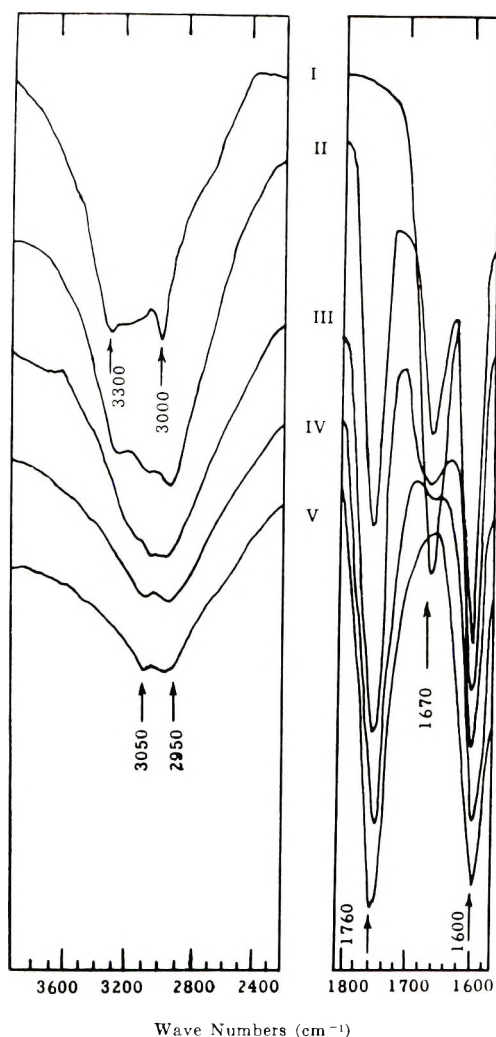


Fig. 1. Infrared spectra of a film of poly(amic acid) (III) heated in vacuum for consecutive 30 min. periods: (I) at 180°C.; (II) at 250°C.; (III) at 300°C.; (IV) at 370°C.; (V) at 450°C.

temperature. The infrared spectral changes for the polymer are closely related to those found for the reaction of the model amide-acid to the corresponding 2-aryl benzoxazinone.

RESULTS AND DISCUSSION

Syntheses of Model Compounds

Model compounds were prepared as described in the experimental section, and the physical properties and infrared absorption bands (C=O) of these model compounds are summarized in Table I.

The direct reaction of benzoyl chloride with anthranilic acid without solvent was first described by Friedländer and Wleügel,¹⁰ but this method is not suitable for general application owing to the instability of the reaction intermediate and the lack of a satisfactory method for its preparation. Although 2-methyl-3,1-benzoxazin-4-one is labile to hydrolysis,^{11,12} it was shown that the higher 2-alkyl benzoxazinones are increasingly stable,¹³ and we found that 2-aryl benzoxazinones can be handled without special precautions.² In the infrared spectra, an open-chain precursor (VI) shows strong carbonyl stretching bands of carboxyl and amide groups at 1670–1700 cm^{-1} , whereas the cyclized bisbenzoxazinone derivative (VII) has a sharp ester carbonyl absorption band of the benzoxazinone ring at 1760 cm^{-1} and it is quite stable to hydrolysis. The thermal cyclodehydration reaction along the polymer chain was followed by the determination of new carbonyl intensities at 1760 cm^{-1} of the ring system (Fig. 1).

Optimum Polymerization Conditions for Low Temperature Solution Preparation of Polybenzoxazinones

The optimum polymerization conditions were determined for the preparation of polyamic acid (III) by measuring the variation in the extent of polymerization with reaction variables. The data in Table II show that

TABLE II
Effect of Reactant Ratio on the Extent of Polymerization
in *N*-Methylpyrrolidone at 15.0°C.^a

Reactant mole ratio BDC/IPCl	Inherent viscosity of polymer η_{inh} (H_2SO_4 , 0.5%, 25°C.)
0.60	0.39
0.80	0.52
0.90	0.68
0.96	1.12
1.00	1.06
1.10	0.38
1.40	0.20

^a Initial monomer concentration, 5–10%; LiCl/BDC mole ratio, 1.3–5.0.

the reactant equivalence is critical, and a slight excess of dibasic acid chloride is beneficial. It is presumed that the excess may counteract losses from hydrolysis and other side reactions. This is supported by the experimental evidence in Table III that a trace of moisture affects seriously the decrease of molecular weight of the resulting poly(amic acid). When the moisture content increases from 0.001% to 0.5%, the inherent viscosity of the polymer (0.5% in concentrated sulfuric acid at 25°C.) drops sharply from 1.28 to 0.70. The optimum polymerization temperature was found to be in the range of 20–40°C. as shown in Figure 2, in which the maximum molecular weights were reached in the polymerization periods of 2.5 hr. at specific temperatures.

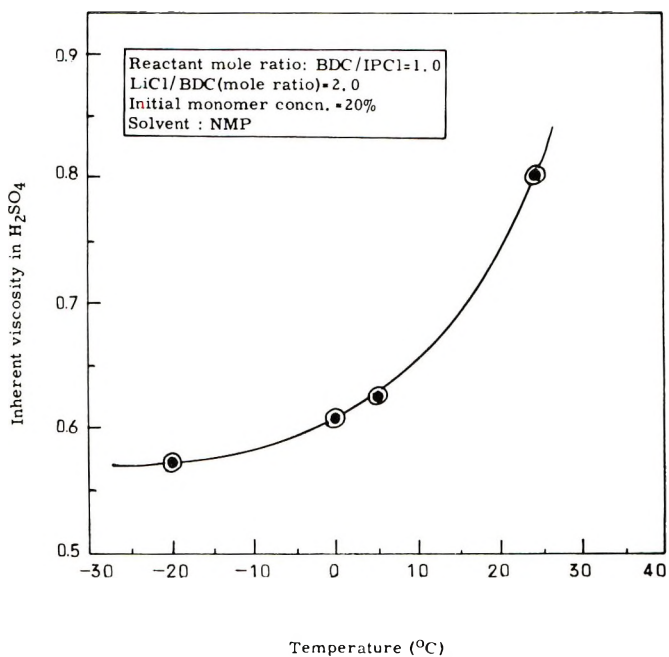


Fig. 2. Effect of temperature on the extent of polymerization.

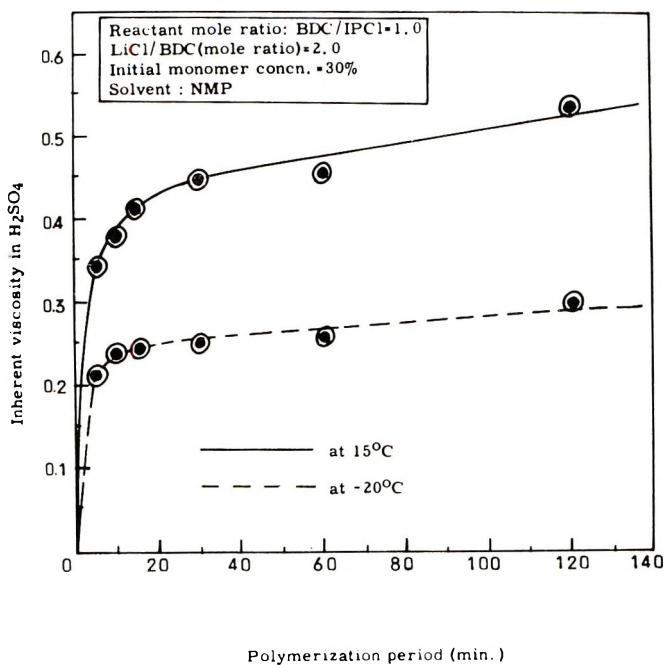


Fig. 3. Rate of polymerization of BDC with IPC1 at different temperatures.

The rate of polymerization increases with increasing temperature at -20 to $+15^{\circ}\text{C}$. as described in Figure 3. The initial monomer concentration is also important (Fig. 4), and a high monomer concentration favors formation of poly(amic acid) of high molecular weight. In order to increase

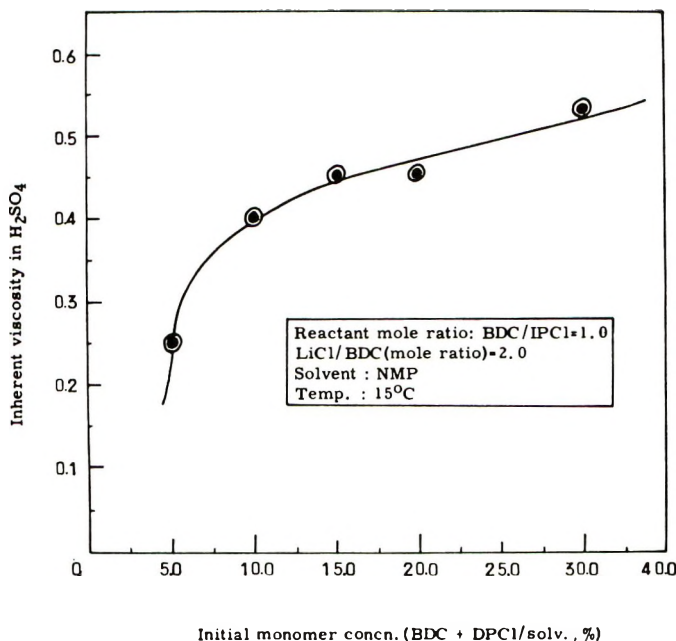


Fig. 4. Variation in the extent of polymerization with initial monomer concentration.

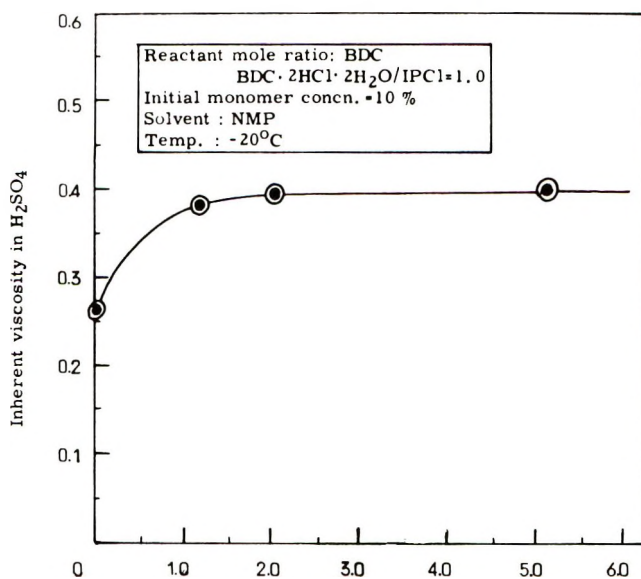


Fig. 5. Effect of lithium chloride concentration on the extent of polymerization.

TABLE III
Effect of Moisture on the Extent of Polymerization in NMP at 24°C.^a

Moisture content, %	Inherent viscosity of polymer $\eta_{inh}(\text{H}_2\text{SO}_4, 0.5\%, 25^\circ\text{C}.)$
0	1.28
0.5	0.70
2.0	0.38
3.0	0.35

^a BDC/IPCl mole ratio, 1.01; LiCl/BDC mole ratio, 2.0; initial monomer concentration, 7.0%.

solubility of the resulting poly(amic acid), the effect of lithium chloride concentration on the extent of polymerization was studied. The inherent viscosity of the poly(amic acid) (III) becomes constant (Fig. 5) when a mole ratio of LiCl/BDC·2HCl·2H₂O greater than 1.0 is employed. The effect of solvents on the low temperature solution polymerization of poly(amic acid) was studied at 24°C. in a homogeneous system. The results in Table IV indicate that dry *N*-methyl-2-pyrrolidone and *N*-methyl- ϵ -caprolactam are the most effective polar solvents for the polymerization.

TABLE IV
Effect of Solvents on the Low Temperature Solution Polymerization of Poly(amic Acid) at 24°C. in a Homogeneous System

No.	Monomer		Solvent ^b	Solvent, ml.	Initial mono- mer concn., %	LiCl/ BDC mole ratio	η_{inh}^c
	BDC, g. ^a	IPCl, g.					
1	2.78	2.05	NMP	100	7	2	1.51
2	1.45	1.16	NMCL	50	13	2	1.05
3	0.68	0.51	DMAC	24	24	2	0.41
4	1.36	1.02	DMF	38	10	2	0.09
5	1.35	1.02	DMSO	41	7	—	—

^a Carefully purified and dried 4,4'-diaminobiphenyl-3,3'-dicarboxylic acid derived from BDC dihydrochloride dihydrate was used as a monomer.

^b NMP = *N*-methylpyrrolidone; NMCL = *N*-methyl- ϵ -caprolactam; DMAC = *N,N*-dimethylacetamide; DMF = *N,N'*-dimethylformamide; DMSO = dimethyl sulfoxide.

^c 0.5% concn. in concd. H₂SO₄ at 25°C.

In an attempt to prepare a linear tractable poly(amic acid) (III) and polybenzoxazinone (IV) of good thermal stability, a copolymer was prepared from the dihydrochloride dihydrate of BDC and dibasic acid chlorides, and the resulting polymer was compared with the BDC homopolymer as described in Table V. The thermal stabilities of copolymers are found to be excellent, and the TGA curves are the same as those of the homopolymers (Fig. 6).

TABLE V
 Low Temperature Solution Polymerization of Equimolar Amounts of 4,4'-Diaminobiphenyl-3,3'-dicarboxylic Acid Dihydrochloride Dihydrate (BDC·2HCl·2H₂O) with Aromatic Dicarboxylic Acid Chlorides in a Homogeneous System

Expt. no.	Monomer		Solvent (NMP), ml.	Initial monomer concn., % ^b	LiCl/BDC·2HCl·2H ₂ O mole ratio	Temp., °C.	η_{inh}^c
	BDC·2HCl·2H ₂ O, g.	Diacid chloride, g. ^a					
1	2.67	IPCl, 1.41	60	8	—	-20	0.25
2	2.67	IPCl, 1.41	80	8	1.3	-20	0.38
3	4.57	IPCl, 2.44	60	14	2.0	-10	0.52
4	2.86	IPCl, 1.52	30	12	2.0	-15	0.38
5	2.28	IPCl, 1.22	40	13	2.0	-20	0.29
6	2.67	TPCl, 1.41	70	8	1.3	-20	0.63
7	1.91	TPCl, 1.02	40	16	5.3	-30	0.45
8	5.11	IPCl/TPCl, 2.18/0.54 (8:2)	60	16	2.0	-30	0.25
9	1.91	IPCl/TPCl, 0.10/0.92 (1:9)	40	16	2.0	-25	0.12

^a IPCl = isophthaloyl chloride; TPCl = terephthaloyl chloride.

^b BDC·2HCl·2H₂O + acid chloride/solvent.

^c 25.0°C, 0.5% in concentrated H₂SO₄.

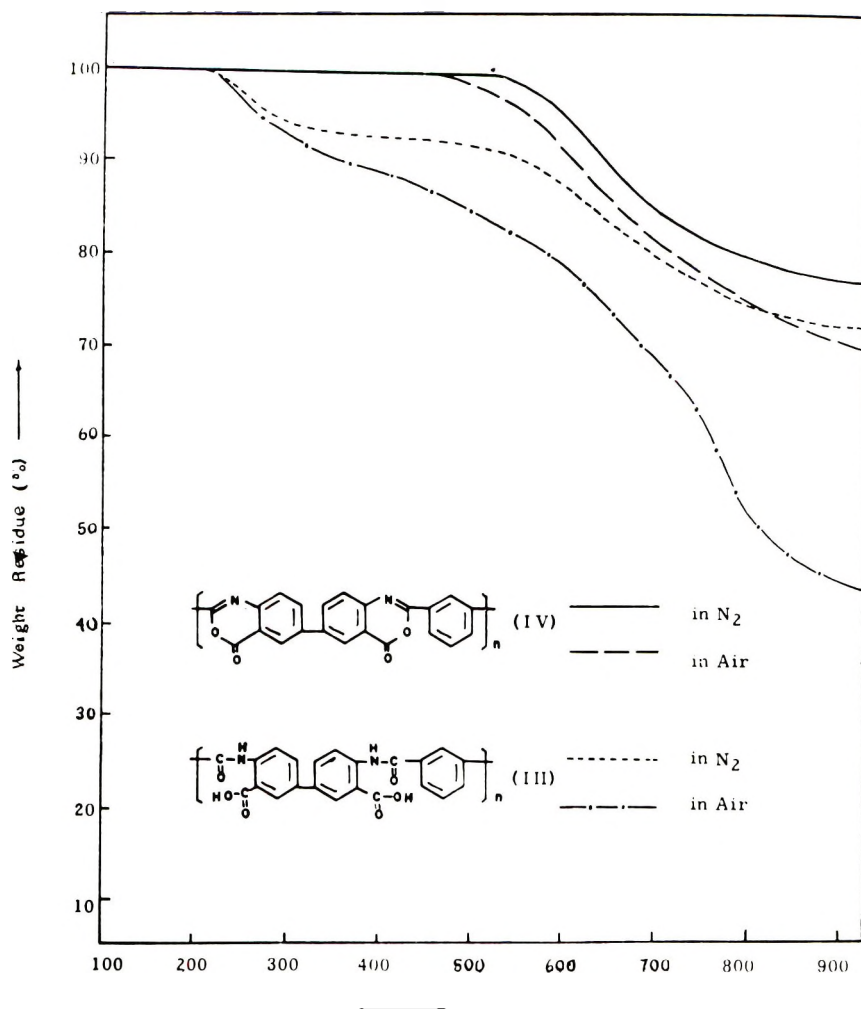


Fig. 6. Thermal gravimetric analysis curves for poly(amic acid) (III) and polybenzoxazinone (IV) in nitrogen and in air.

Properties of Polybenzoxazinones

Poly(amic Acids). The poly(amic acids) (III) are soluble in a variety of solvents such as dimethylacetamide, dimethylformamide, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone and *N*-methyl- ϵ -caprolactam. The poly(amic acid) in solution is quite stable to hydrolysis as shown in Figure 7, and the inherent viscosity does not decrease even in dilute polymer solutions of *N*-methyl-2-pyrrolidone and concentrated sulfuric acid.

Hydrolytic Stability. The polybenzoxazinone (IV) is highly resistant to hydrolytic degradation by strong acid or alkali and is insoluble in most organic solvents; it is soluble in fuming nitric acid and concentrated sulfuric acid. Data are summarized in Table VI.

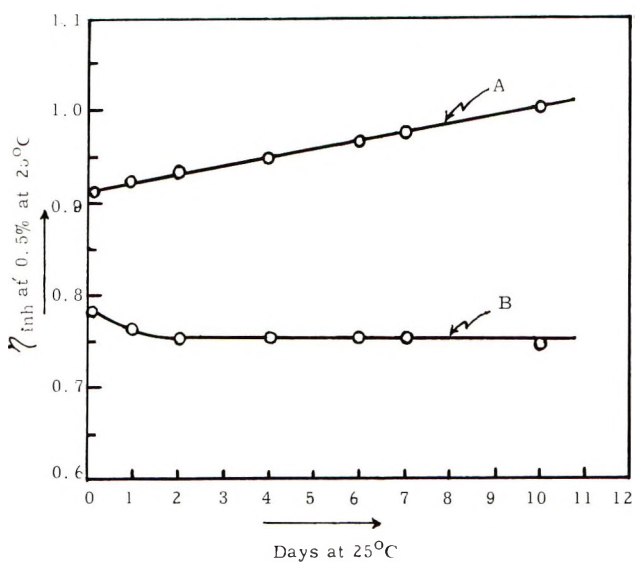


Fig. 7. Stability of poly(amic acid): (A) in *N*-methyl-2-pyrrolidone and (B) in concentrated sulfuric acid; polymer concentration, 0.5%.

TABLE VI
Stability of Aromatic Polybenzoxazinone Film (50 μ) in Organic and Inorganic Reagents^a

Reagents	Temp., °C.	Time	Infrared spectrum (ε ₁ /ε ₂) ^b	Weight change	Appearance
Methyl ethyl ketone	80	1 hr.	No change	None	No change
DMF	153	"	"	"	"
DMAc	163	"	"	"	"
NMP	202	"	"	"	"
DMSO	189	"	"	"	"
<i>m</i> -Cresol	202	"	"	"	"
10% Aqueous NaOH	25	1 week	No change	None	No change
10% Aqueous NH ₄ OH	"	"	"	"	"
10% Aqueous NaCl	"	"	"	"	"
Acetic acid	"	"	"	"	"
3% Sulfuric acid	"	"	"	"	"
10% HCl	"	"	"	"	"
Concentrated H ₂ SO ₄	"	"	Partially hydrolyzed	Increase	Swollen
Fuming HNO ₃	"	"	Completely hydrolyzed	"	Dissolved

^a Film (1.0 g.) was treated in 200 ml. of each solvent at specific temperature for certain period of time.

^b ε₁/ε₂ refers to the intensity ratio of ν_{C=O} = 1760 cm.⁻¹ and ν_{C-N} = 1680 cm.⁻¹



Thermal Stability. The thermal stability of the resulting fully aromatic polybenzoxazinone (IV) was measured either in nitrogen or in air by the thermogravimetric method, (Fig. 6). These benzoxazinone polymers have excellent thermal stabilities, and decomposition started at about 550°C. in nitrogen. When the polymers were heated to 900°C. in nitrogen, the weight loss was about 24%, compared with 30% in air. The elemental analysis of poly-2,2'-(*m*-phenylene)-6,6'-bibenzoxazinone film heated to 900°C. in nitrogen atmosphere contains about 6% of nitrogen (C, 53.78%; H, 1.71%; N, 5.97%).

The authors gratefully acknowledge the support and interest of Dr. T. Hoshino, the Director of Basic Research Laboratories, Toyo Rayon Company, Ltd. Messrs Y. Ebata and T. Mizushima directed the analytical support for this work and contributed much valuable advice. Numerous helpful discussions were held with Mr. T. Kubota of Central Research Laboratories, Toyo Rayon Company, Ltd. The technical assistance of Messrs. A. Kobayashi and N. Fujisawa are also acknowledged.

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Résumé

Des nouvelles polybenzoxazinones aromatiques résistant aux hautes températures et de haut poids moléculaire ont été préparées par cyclopolycondensation d'acide 3,3'-dicarboxylique-4,4'-diaminobiphényle avec des halogénures d'acide dicarboxylé aromatique. La technique de polymérisation en solution à basse température fournissait un acide polyamique (III) de poids moléculaire élevé dans une première étape. Un pré-curseur à chaîne ouverte subissait ultérieurement la cyclodéhydratation thermique le long de la chaîne à 200–350°C, en une seconde étape, en vue d'obtenir avec un rendement quantitatif des polybenzoxazinones (IV) complètement aromatiques, de stabilité thermique excellente à la fois sous azote et à l'air. L'acide polyamique est soluble dans la *N*-méthyl-2-pyrrolidone et fournit au départ de ces solutions des films durs et transparents. Des films de polybenzoxazinone aromatique insoluble ont été obtenus par traitement thermique de l'acide polyamique qui possède une excellente stabilité à l'oxydation de à la température. Les détails des conditions de polymérisation à basse température en solution des polybenzoxazinones sont décrits et le mécanisme de réaction de cyclopolyc-

condensation des acides polyamiques et la formation de polybenzoxazinones sont discutés.

Zusammenfassung

Neue temperaturbeständige aromatische Polybenzoxazinone hohen Molekulargewichts wurden durch Cyclopolykondensation von 4,4'-Diaminobiphenyl-3,3'-dicarbonsäure (I) mit aromatischen Disäurehalogeniden (II) hergestellt. Ein bei niedriger Temperatur durchgeführtes Lösungspolymerisationsverfahren lieferte im ersten Schritt eine Polyamidsäure (III) hohen Molekulargewichts. Diese offenkettige Vorstufe erlitt in der Folge bei 200–350°C im zweiten Schritt eine Cyclodehydratisierung entlang der Polymerkette, wobei in quantitativer Ausbeute ein vollaromatisches Polybenzoxazinon (IV) von hervorragender Hitzebeständigkeit sowohl in Stickstoff als auch in Luft entstand. Die Polyamidsäure ist in *N*-Methyl-2-pyrrolidon löslich; aus dieser Lösung können zähe, transparente Filme gegossen werden. Durch Hitzebehandlung der Polyamidsäure liessen sich unlösliche Filme aus aromatischen Polybenzoxazinonen mit ausgezeichneter Oxydations- und Hitzestabilität herstellen. Die Polymerisationsbedingungen bei der Tieftemperatur-Lösungspolymerisation der Polybenzoxazinone werden ausführlich beschrieben und die Reaktionsmechanismen für die Cyclopolykondensation der Polyamidsäuren und die Polybenzoxazinonbildung einer Diskussion unterzogen.

Received January 10, 1967

Revised March 17, 1967

Prod. No. 5405A

Poly(aryl Ethers) by Nucleophilic Aromatic Substitution. I. Synthesis and Properties*

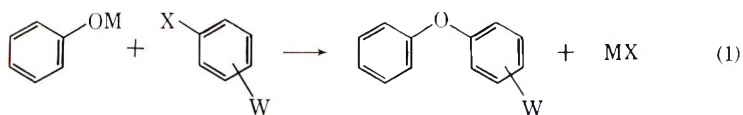
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Synopsis

A series of new aromatic polyethers have been prepared by solution condensation polymerization. The synthesis involves the condensation of a dialkali metal salt of a dihydric phenol with an "activated" or negatively substituted aromatic dihalide in an anhydrous dipolar aprotic solvent at elevated temperatures. The reaction is rapid, free of side reactions, and yields polymers of excellent color. Bakelite polysulfone can be prepared in this manner by reaction of the disodium salt of bisphenol A with 4,4'-dichlorodiphenyl sulfone in dimethyl sulfoxide (DMSO). Only dipolar aprotic solvents are useful for conducting the polymerization. Of these, DMSO and Sulfolane (tetrahydrothiophene 1,1-dioxide) are the most effective. Water or other competing nucleophiles must be absent if high molecular weight is to be obtained. Besides providing the necessary solubility, this highly polar solvent is believed to be essential in providing the rapid polymerization rates observed. The rates are further found to depend on the basicity of the bisphenol salt and upon the electron-withdrawing power of the activating group in the dihalide. As is usual for this type of reaction, the difluorides are found to be more reactive than the corresponding dichlorides. Most of the polyethers are amorphous, rigid, tough thermoplastics with high second-order transitions (T_g). Thermal stability and electrical properties are noteworthy. These and other properties are described for polysulfone, and glass transitions are given for a selected list of the other polyethers.

INTRODUCTION

It is known that reaction of alkali metal phenates with certain "activated" aromatic halides in suitable solvents results in high yields of the corresponding aryl ethers.¹ The reaction may be summarized as in eq. (1).

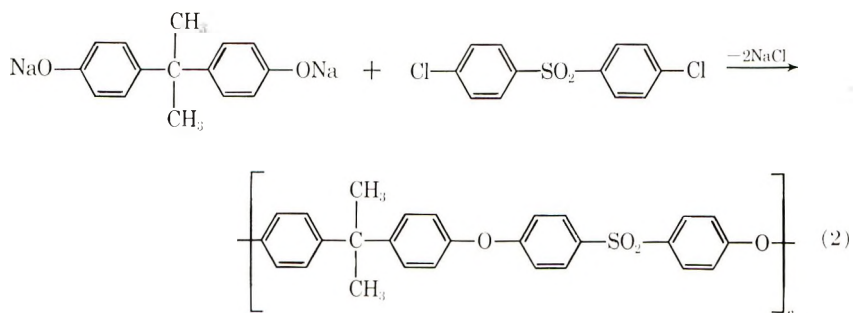


where $M = \text{Na}, \text{K}, \text{etc.}$; $X = \textit{ortho}$ or \textit{para} halogen, etc.; $W = \text{negative group, i.e., } -\text{NO}_2, -\text{SO}_2\text{R, etc.}$

* Paper presented in part at the 3rd Biennial American Chemical Society Polymer Symposium, Case Institute of Technology, Cleveland, Ohio, June 22-24, 1966.

As this reaction is distinguished from other nucleophilic processes generally and other aryl etherifications specifically, i.e., the copper-catalyzed condensation of phenates with aryl halides (the Ullman reaction), it is the nature and position of the activating group in the aryl halide that is focused upon. This group is electron-withdrawing and may occupy a position either *ortho* or *para* to the halogen being displaced.

We have been investigating for some time now the preparation of aryl polymers via the nucleophilic aromatic substitution reaction. Among other things, we have discovered a unique method for preparing a variety of linear, high molecular weight aryl polyethers by the condensation of bisphenates with activated aromatic dihalides. Thus, for example, Bakelite polysulfone can be prepared as shown in eq. (2).



This paper will cover the details of this synthesis with particular emphasis on the preparation of polysulfone. Additional chemical and physical properties of polysulfone will be presented, along with a list of glass transition temperatures for a variety of other new polyethers prepared by this method.

EXPERIMENTAL

Starting Materials

The various bisphenol, dichloro, and difluoro monomers used in this study were prepared in accordance with the literature directions or obtained from laboratory supply houses or other commercial sources. When necessary, samples were recrystallized from appropriate solvents to constant melting points before use. All solvents used were obtained from commercial sources and were distilled at least once before use.

Preparation of Polysulfone in DMSO

Into a 1-liter stainless steel resin kettle, fitted with an inert gas sparge tube, thermocouple, mechanical stirrer, dropping funnel, and take-off to a six-plate (glass helix) fractionating column connected to a moisture trap and condenser, is placed 51.36 g. (0.225 mole) of high purity bisphenol A [2,2-bis(4-hydroxyphenyl)propane], such as the UCAR HP grade sold by

Union Carbide, 115 g. of dimethyl sulfoxide (DMSO), and 330 g. of chlorobenzene. The mixture is heated to 60–80°C., whereupon a clear solution is obtained. Air is displaced from the system by flushing with nitrogen or argon and exactly 0.450 mole of 50.00% aqueous sodium hydroxide (35.86 g. of a 50.20% solution) is added with good stirring over about 10 min. In so doing, two liquid phases appear: one predominantly chlorobenzene, the other disodium salt dissolved in aqueous DMSO. The system is brought to reflux with inert gas sparging through the reaction mixture. Water is removed from the system, the chlorobenzene that codistills being returned continuously. In so doing the temperature of the contents rises from about 120°C. initially to 140°C. at the conclusion of this step. When this point is reached, most of the water originally present has distilled, and the disodium salt of bisphenol A appears as a precipitate.

Excess azeotrope solvent is distilled from the system until the temperature of the contents reaches 155–160°C. At this point the precipitate will redissolve with the formation of a very viscous solution. It is believed that at this point only traces of water remain.

A 50% solution of 64.61 g. (0.225 mole) of 4,4'-dichlorodiphenyl sulfone (DCDPS) in dry chlorobenzene maintained at 110°C. is added over a period of about 10 min., the excess solvent being allowed to distil at a rate sufficient to hold the material temperature at about 160°C. When all the sulfone has been added, polymerization is continued until the desired degree of polymerization is reached. A reduced viscosity as measured in chloroform solution (0.2 g./100 ml.) at 25°C. of about 1.0 or higher is reached in about 1 hr. at 160°C. after addition of all the sulfone.

The temperature must not drop below about 150°C. until the polymerization is well along, as sodium-ended low polymer may precipitate on the walls of the vessel. This material, which is polymeric, is very difficult to redissolve upon heating owing to the familiar problem of solvent migration. Too high a temperature during addition of the sulfone and subsequent polymerization is to be avoided, as the reaction is mildly exothermic, extremely rapid above 160°C., and excessive solvent decomposition and/or discoloration or even gelation of the reaction mass may occur. To prevent the danger of excessive overheating of the reaction mass, use of oil baths for heating is recommended. Upon addition of the sulfone, the reaction mixture becomes vividly colored, generally orange to yellow, but often deep greens are observed. The color is believed due to the formation of the Meisenheimer type σ -complex or possibly a charge-transfer complex composed of the reactants and the DMSO solvent.

The polymerization may be terminated in a variety of ways; one of which is to pass methyl chloride into the polymerizing mixture when the desired degree of polymerization is reached. The color of the reaction mixture fades in so doing to a light amber, signalling the completion of the termination. The methyl chloride reaction, which is very rapid and efficient, involves the conversion of aryl oxide ends to their respective methyl ethers, thus preventing further polymerization.

The color change is usually complete within about 5 min. when gaseous methyl chloride is passed through the polymerizing mixture at about 120–160°C. That termination has occurred is indicated not only by arrest of the viscosity rise but also by the appearance of a peak in the NMR at 211.3 cps (relative to tetramethylsilane in chlorobenzene solution) not found in polymer terminated by treatment with acids. The dimethyl ether of bisphenol A also gives a peak at 211.3 cps not found in the spectrum of bisphenol A.

The viscous polymer solution is then cooled and diluted with about 700 g. of chlorobenzene which provides a solution convenient for workup. The by-product sodium chloride is removed by simple pressure or vacuum filtration, and the clear light amber solution is coagulated in three or four volumes of ethanol. The resulting fluff is dried in a vacuum oven at 135°C. for several hours. The yield is about 90% of theory or higher depending on the severity of losses during the workup.

Films may be obtained by casting or by pressing at about 280°C.; the polymer softens at about 200°C. Fibers may be obtained by pulling from the melt. The polymer is soluble in dipolar aprotic solvents, cyclic ethers such as THF, polar aromatic solvents, most chlorinated hydrocarbons, and some carbonyls such as cyclohexanone. Hazy solutions may be noted upon dissolving in certain of these solvents. The haze which may not develop immediately is due to the precipitation of cyclic oligomers which are crystalline; the polymer is amorphous.

Preparation of the Other Polyethers

Most of the polyethers reported herein can be prepared in DMSO. In some cases, however, reaction in DMSO, where the more weakly activated dichlorides or the more acidic bisphenols are used, is too sluggish and in this event Sulfolane (tetrahydrothiophene 1,1-dioxide) is used more successfully as solvent. In all cases examined, reaction with the activated difluorides proceeds readily in DMSO. In some cases, it is very difficult to obtain high polymer owing to extensive crystallization before high conversion is realized. In one case, where the monomer pair is hydroquinone and DCDPS, the crystallization interferes in DMSO but not in Sulfolane. In another example, where the monomer pair is 4,4'-dihydroxybenzophenone and the corresponding difluoro compound, high polymer cannot be obtained, owing to the premature crystallization, even in Sulfolane.

RESULTS AND DISCUSSION

Selection of Solvent

We have found that very few solvents are useful for preparing poly(aryl ethers) by reaction of alkali bisphenates with activated aromatic dihalides. Generally only the so-called dipolar aprotic solvents show any effectiveness. Of these, dimethyl sulfoxide (DMSO) is best.

TABLE I
 Preparation of Polysulfone in Different Solvents

Salt of bisphenol A	Solvent ^a	Time, hr.	Temp., °C.	R.V. (CHCl ₃) ^b	Per cent reaction ^c
Na	DMSO	1	160-165	1.0	>99
K	DMSO	4.5	135-140	0.70	>99
K	DMSO ₂	4	195-200	0.65	>99
Na	TMSO ₂	3	200-210	0.75	>99
Na	Ph ₂ SO ₂	11	230-250	0.40	—
Na	DPSO	3.5	200-210	0.08	97.6
K	Ph ₂ CO	7.5	200-230	—	82
Na	Ph ₂ CO	8.5	220-230	—	53

^a TMSO₂ = Sulfolane; DPSO = di-*n*-propyl sulfoxide; Ph₂SO₂ = diphenylsulfone; Ph₂CO = benzophenone.

^b Reduced viscosity measured in chloroform at 25°C. at a concentration of 0.20 g. polymer/100 ml. solvent.

^c Per cent reaction based on per cent sodium phenolates consumed.

Certain sulfone solvents, i.e., dimethyl sulfone and Sulfolane, are particularly useful when higher reaction temperatures are required. The more common, less polar organic solvents by themselves generally fail to promote any reaction at all.

Some of the solvents we have examined with typical results obtained for the preparation of the polysulfone of bisphenol A are listed in Table I.

As can be seen from Table I, relatively high reaction temperatures are required. This is primarily to effect complete solution of the alkali bisphenate. At these higher temperatures the polymerization rates are quite rapid, in the more favorable cases, as with DMSO. Dimethyl sulfone (DMSO₂) is inferior to DMSO in solubilizing the growing polymer chains. Sulfolane gives good results, but contact times must be kept short owing to its involvement in a slow base-consuming side reaction. A similar side reaction is so severe with propyl sulfoxide as to completely preclude the formation of high polymer. Benzophenone, a reasonably polar solvent, even at high temperatures and long reaction times proves quite ineffective.

The use of Sulfolane permits the preparation of high molecular weight polyethers from the more acidic, and therefore, less reactive, bisphenols.

 TABLE II
 Reaction of 4,4'-Dihydroxydiphenyl Sulfone Dipotassium Salt
 with 4,4'-Dichlorodiphenyl Sulfone

Solvent	Time, hr.	Temperature, °C.	R.V.(NMP) ^a
DMSO	4.5	175-180	0.29
Sulfolane	6	235	0.97

^a Reduced viscosity measured in *N*-methyl-2-pyrrolidone at 25°C. at a concentration of 0.200 g. polymer/100 ml. solvent.

The much higher boiling point allows a considerably higher reaction temperature. This effect is shown in Table II for the reaction of the dipotassium salt of 4,4'-dihydroxydiphenyl sulfone with 4,4'-dichlorodiphenyl sulfone (DCDPS).

Probably the greatest single factor that limits solvent choice is the difficulty that is experienced in dissolving the alkali bisphenate under anhydrous conditions in solvents which are also suitable for the organic halide and growing polymer chains.

DMSO is known² to be an excellent solvent for a diverse variety of inorganic as well as organic compounds and for certain difficultly soluble polar polymers such as polyacrylonitrile.

No less important is the solvent effect upon reaction rate which accrues uniquely by use of dipolar aprotic solvents. Thus rates of bimolecular nucleophilic substitution reactions of the type considered here are known to be vastly greater in DMSO,^{2,3} etc. The attainment of convenient polymerization rates is probably a result of this catalysis.

Thus, in summary, the ability to dissolve both reactants under anhydrous conditions, to promote a facile reaction, and to solubilize the growing polymer chains are requirements which apparently only the dipolar aprotic solvents can satisfy altogether.

Reaction Stoichiometry

The preparation of polysulfone by nucleophilic displacement is consistent with the principles of condensation polymerization. As such, reaction stoichiometry is critical if high molecular weight is to obtain. This is borne out by the results of experiments summarized in Figure 1.

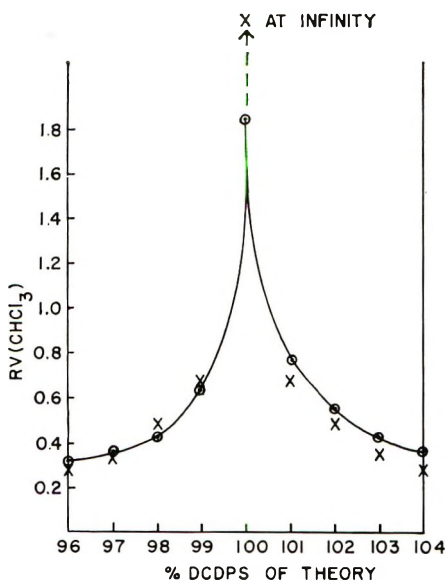


Fig. 1. Preparation of polysulfone with varying amounts of DCDPS.

Reduced viscosities are plotted against the ratio of DCDPS/disodium salt of bisphenol A, expressed here as the per cent DCDPS of theory. The polymerizations were carried out in DMSO-chlorobenzene at 160–165°C. for 3 hr. As expected, a reasonably symmetrical curve (experimental points \odot) results with the highest molecular weight obtained at a mole ratio of unity. Furthermore, the R.V. rises increasingly rapidly as this ideal ratio is approached.

The theoretical points were calculated by using the relationship⁴ between degree of polymerization and reactive group ratio at 100% efficiency and the relationship derived in our laboratories* for R.V. and \bar{M}_n . The agreement is reasonable.

Finally, measurements on polysulfone yield a value of 2.1–2.2 for the \bar{M}_w/\bar{M}_n ratio, very close to the predicted value of 2.0 for a condensation polymer.

Reaction Mechanism

Both the infrared and NMR spectra are consistent with an all 1,4-product, i.e., no *meta* or *ortho* linkages are formed. It is expected that, if a benzyne mechanism were in operation, some *meta* linkages would result. It is highly likely that the formation of polysulfone by chloride ion displacement occurs exclusively by a bimolecular process.¹ That DCDPS shows no reaction with dimethyl sulfoxide at elevated temperatures would seem to rule out any process involving prior dissociation of halide. The dimethyl sulfoxide, no doubt, greatly accelerates the rate, however, as observed in similar nucleophilic substitutions, most probably via preferential cation solvation. As Parker³ has pointed out, such solvation renders the anion or nucleophile in an unsolvated or highly active (or reactive) state.

Hydrolysis Side Reaction

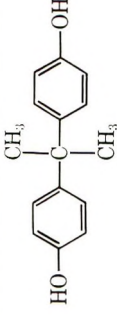

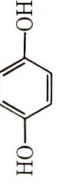
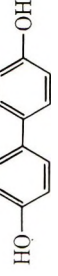
Moisture and, presumably, other protic contaminants such as alcohols, even if present in relatively small quantities, promote a devastating side reaction which precludes the formation of high polymer. The data in Figure 2 clearly illustrate that as the amount of water in a typical polysulfone reaction run in DMSO is decreased, the molecular weight increases, but the effect is most pronounced at rather low water concentrations.

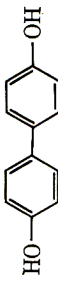
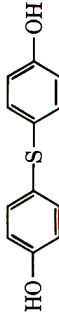

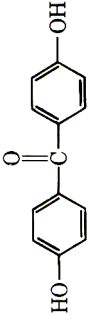

The effect is most certainly not the result of rate retardation via a solvent interaction. This is supported by the observation that a polymerization which had essentially ceased at the low molecular weight stage in the presence of water was not reactivated by removal of this water followed by continued, heating.

It is believed that water prevents the attainment of high molecular weight owing to its tendency to partake indirectly in two side reactions,

* Mr. John Dagon of our laboratories has kindly consented to the publication of part of his data here. For example, for an R.V. = 1, $\bar{M}_n \cong 90,000$; for R.V. = 0.5, $\bar{M}_n \cong 25,000$.

TABLE III
 Reactivity of 4,4'-Dichlorodiphenyl Sulfone with Alkali Metal Salts of Various Bisphenols in DMSO

Alkali metal	Bisphenol	Reaction conditions			R.V. (solvent) ^a
		Dilution, %	Time, hr.	Temp., °C.	
Na		43	1	160	1.4(CHCl ₃)
K		20	3.5	130	0.5(CHCl ₃)
K		20	6	135	0.4(PCP)
K		25	4	165	0.7(NMP)

Na		33	20	170	0.9(NMP)
Na		43	1.5	155	0.4(CHCl ₃)
Na		43	6	160	0.6(CHCl ₃)
K		43	10	165	0.4(CHCl ₃) 0.5(NMP)
K		20 43	29 10	150 165	0.2(TCE) 0.3(NMP)

^a Solvents: PCP = *p*-chlorophenol; NMP = *N*-methyl-2-pyrrolidone; TCE = *sym*-tetrachloroethane.

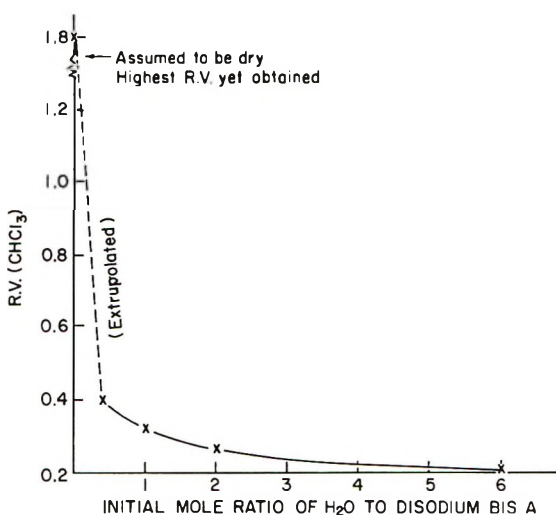


Fig. 2. Preparation of polysulfone in aqueous DMSO.

one with the activated dihalide, the other with the polymer itself. These side reactions are believed to involve sodium hydroxide, formed by hydrolysis of the sodium phenolate groups. Destruction of the active chloro groups then results upon attack by the caustic. This not only results in the formation of inactive endgroups but also, at the same time, in an upset in the stoichiometry. To a lesser extent, chain cleavage may also occur by attack of the caustic at the activated ether linkages being formed via the polymerization.

Other Side Reactions

Gross contamination with air must also be avoided as is generally the rule when handling readily oxidizable compounds such as alkali phenates. While this point has not been investigated in detail there is little doubt that besides the gross discoloration of the polymer that results, the ability to reach the highest molecular weights would certainly be impaired.

Scope of the Reaction

Bisphenate Reactivity. A wide assortment of polyethers can be prepared by nucleophilic substitution by using various combinations of bisphenates and activated dihalides. The reactivity of the various bisphenols that we have examined appears to vary inversely with their respective acidities and therefore in a direct manner to the basicity or nucleophilicity of their respective bisphenates. Thus the alkali metal salts of dihydroxydiphenyl sulfone, a relatively acidic bisphenol, react considerably more slowly with LCDPS than the corresponding bisphenol A salts.

Some of the bisphenols that we have examined are listed in Table III. (The reduced viscosities listed are typical but probably not optimal.)

While the data are largely qualitative in nature it is obvious that the bisphenols with the electron-withdrawing groups connecting the benzene rings react much slower. The results obtained for bisphenol A are typical of the many bisphenols with alkyl type connectors that we have examined.

Choice of Cation. The only generally useful cations are sodium or potassium. The dilithium, calcium, or magnesium salts of bisphenol A are insoluble in DMSO and therefore cannot be used.

Reactivity of Halides. The reactivity of the aromatic dihalide is dependent upon both the activating group and the halide to be displaced. The reported order of ease of displacement in activated aromatic halides is usually $F \gg Cl \sim Br \sim I$ or $F \gg Cl > Br > I$.⁵ This is in agreement with our results with dichloro and difluoro derivatives of the compounds shown in Table IV.

Polymer Characterization

Glass Transition Temperatures. The glass transition temperatures for a wide variety of poly(aryl ethers) prepared from dihydric phenols and activated aromatic dihalides have been measured. As was found for polycarbonates^{6,7} and polyhydroxyethers,⁸ there are apparently two glassy state transitions. The minor glass transitions are approximately at -100°C ., while the major glass transitions are considerably above room temperature. The major glass transitions were obtained by measuring the 1% secant modulus as a function of temperature as shown in Figure 3 for polysulfone. The minor transitions were obtained from mechanical loss measurements using the torsional pendulum.

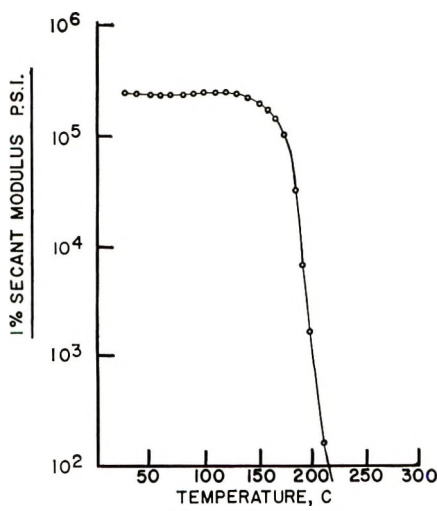
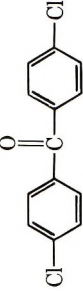
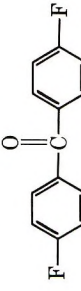


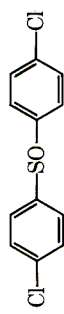
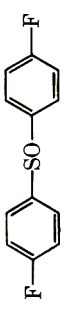
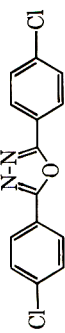
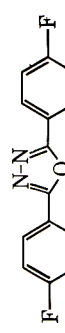
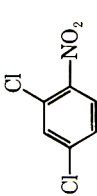


Fig. 3. Polysulfone 1% secant modulus vs. temperature.

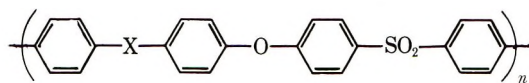
TABLE IV
 Reactivity of Activated Aromatic Dihalides with Alkali Metal Salts of Bisphenol A in DMSO

Alkali metal	Dihalide	Reaction conditions			R.V. (solvent) ^a
		Dilution (approx.), %	Time, hr.	Temp., °C.	
Na	DCDPS	40	1	160	1.35(CHCl ₃)
Na		20	4	135	0.71(CHCl ₃)
K		20	0.5	25-145	0.94(CHCl ₃)
K		10	18	135	0.16(CHCl ₃)
K		20	0.5	135	1.0(CHCl ₃)
Na		40	6	160	0.26(ODCB)
Na		40	<1	25-160	1.5(ODCB)

Na		30	10.5	163-168	0.35(CHCl ₃)
Na		35	3	160	0.57(CHCl ₃)
Na		25	3	160-165	0.13(CHCl ₃)
Na		30	1	155-160	0.50(CHCl ₃)
K		17	3.5	80	0.49(CHCl ₃)

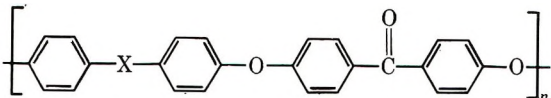
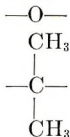
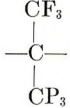
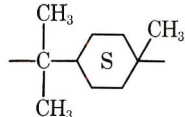
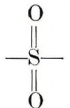
^a Solvents: ODCB = *o*-dichlorobenzene.

TABLE V
Influence of the Connecting Link in the Bisphenol on T_g of
Polyethers Containing Diphenyl Sulfone Units



X	T_g , °C.
—CH ₂ —	180
—CH— CH ₃ CHICH ₃	200
—C— CH ₃ CF ₃	195
—C— CF ₃ CH ₃	205
—C— C ₆ H ₅ C ₆ H ₅	200
—C— C ₆ H ₅	230
	205
CH ₃ —CH— 	230
	250
—O—	180
—S—	175
—C— O	205
—S— O O	245

TABLE VI
Influence of the Connecting Link in the Bisphenol on T_g
of Polyethers Containing Benzophenone Units

X	T_g , °C.
	150
	155
	175
	200
	205

The nature of the connecting link in the various bisphenols and in the activated dihalide appears to be related to the major glass transition temperature.

In Table V are listed a number of polyethers derived from dichlorodiphenyl sulfone and a variety of bisphenols in which the connecting link between the phenol rings of the bisphenol has been varied. By using the methylene link as a base, it can be seen that substitution of the hydrogens results in an increase in the glass transition. The larger the substituting group, the greater the increase. Substitution of hydrogen by methyl, phenyl, or alkyl appears to raise the glass transition by about 20°C. Substitution by two phenyl groups gives a more rigid system and the glass transition temperature is raised still further to 230°C. Cycloaliphatic groups also cause an increase in the T_g culminating in the case of the bisphenol derived from norcamphor with a T_g of 250°C. Similar results have been found by Jackson and Caldwell⁹ for the polycarbonates derived from bisphenols based on norcamphor-like connecting links.

Use of non-carbon-containing links results again in predictable variations. The flexible ether and thioether links reduce the glass transition to a level about that of the unsubstituted methylene link. The highly polar sulfone and carbonyl group again increase the T_g , the sulfone far more than the carbonyl group. Connecting the two phenyl rings directly by the use of

p,p'-biphenol (not shown in Tables) results in a very rigid system with a high T_g of 230°C.

In Table VI we have listed several polyethers derived from difluorobenzophenone and several different bisphenols. The first observation to be made is that the T_g for the benzophenone polyether is about 30–40°C. lower than that for the corresponding sulfone polyether. Within the benzophenone family, the same general relationships hold that were found for the sulfone family. The presence of cycloaliphatic groups or highly polar

TABLE VII
Influence of the Connecting Link in the Activated Dihalide
on T_g of Polyethers Containing Bisphenol A Units

X	$T_g, ^\circ\text{C.}$
	120
	155
	165
	165
	175
	180
	195

groups like the sulfone cause an increase of about 50°C. in the glass transition.

A series of bisphenol A polyethers are shown in Table VII in which the connecting link of the activated halide is varied. Again the polarity of the connecting link plays a major role in the glass transition with sulfone giving the highest T_g . Somewhat surprising is the observation that use of two carbonyl groups separated by a benzene ring gives only a minor increase in T_g over a single carbonyl group. The oxydiazole ring and the azo link

are somewhat higher than the carbonyl group but not as high as the sulfone. Use of the disulfonamide group separated by a methylene chain lowers the T_g considerably, presumably because of the flexible methylene chain.

In Table VIII are collected several polyethers which do not fit in the preceding tables. The first two, based on hydroquinone, again show the lowering of the T_g by substitution of a carbonyl group in place of a sulfone group. The third example, from 2,4-dichloronitrobenzene has a somewhat lower T_g than other polyethers presumably because the chain is kinked somewhat by the *meta* link and also by the bulky nitro group. The next two polyethers show the result of substitution on the benzene ring of the bisphenol A unit. The T_g is raised over that of polysulfone, considerably so in the case of the tetrasubstituted polyether. In the sixth example, the presence of a linear four-carbon chain exhibits its expected flexibilizing influence.

Most of the polyethers prepared to date are noncrystalline and are not easily crystallizable by solvent or annealing techniques. In Table IX are listed the polyethers that are crystalline as prepared or that are crystallizable by using the solvent or annealing technique. Generally, the sulfone polyethers appear to be less crystalline than do the benzophenone polyethers with the exception of the hexafluorobisphenol A polyethers, where the order is reversed.

Mechanical Properties. Typical of the polyethers reported here are the room temperature mechanical properties listed for polysulfone in Table X.* The polyethers derived from bis-*p*-hydroxyphenyldiphenylmethane and DCDPS and bisphenol A and 2,4-dichloronitrobenzene exhibit brittle behavior. In each case the absence of the usual low temperature transition was noted. As would be expected, the crystallizable polyethers tend to be brittle (unstretched) unless obtained in the amorphous form.

In general the tensile modulus, impact strength, and elongation do not vary substantially between the low temperature transition and the ASTM heat distortion, which for polysulfone itself would be over the range of -100 to $+175^\circ\text{C}$. Over the same range the tensile strength varies from 20,000 to 3000 psi at 175°C .

As indicated in the appropriate Tables V–IX, the glass transition varies with the structure of the polyether. The heat distortion temperature (ASTM D648) likewise varies with T_g and generally is about 20°C . below the glass transition temperature for each polyether.

Electrical Properties. The polyethers, in general, exhibit good electrical properties. Table XI lists some typical properties for polysulfone and for bis S polyether.†

Solubility Characteristics. The general solubility characteristics for polysulfone and bis S polyether are listed in Table XII.

The polyethers, in general, are not soluble in nor affected by either aque-

* For a more complete compilation of mechanical properties see Bugel and Walton.¹⁰

† For a more complete compilation of electrical properties see Bugel and Walton.¹⁰

TABLE VIII
Miscellaneous Polyethers Prepared via Activated Nucleophilic Aromatic Substitution with Their T_g 's

Structure	Diol	Dihalide	T_g , °C.
	Hydroquinone	DCDPS	210
	"	4,4'-Difluoro- benzophenone	160
	Bisphenol A	2,4-Dichloro- nitrobenzene	150
	2,2'-Dichloro- bisphenol A	DCDPS	205

	DCDPS	235
2,6,2',6'- Tetramethyl- bisphenol A		
	DCDPS	140
	Bisphenol A	180
	3,6-Dichloro- pyridine	

TABLE IX
 T_g and T_m of Crystallizable Polyethers

Structure	T_g , °C.	T_m , °C.
	210	310
	160	350
	205	255
	150	315
	155	248
	180	250

TABLE X
Mechanical Properties of Polysulfone

Property	Value	ASTM method
Tensile strength (yield), psi	10,200	D638
Tensile modulus, psi	360,000	D638
Tensile elongation to break, %	50-100	D638
Tensile impact strength, ft.-lb./in. ³	250-500	D1822
Density, g./cc.	1.24	D1505

ous inorganic acids or bases.* They are generally soluble in polar organic solvents as shown in Table XII. It is interesting that DMSO and Sulfolane, which are solvents in which the polyethers are made, are rather poor solvents for the polymers in the cold.

* Polysulfone dissolves in and is sulfonated by concentrated sulfuric acid. In addition, chain scission appears to occur as evidenced by a drop in viscosity with time. The presence of strong mineral acids in the melt also appears to result in severe molecular weight degradation. Bis S polyether or the polyethers derived from hydroquinone appear to be largely unaffected by such treatment, indicating the instability to derive from the bisphenol portion of the molecule.

TABLE XI
Some Electrical Properties of Bis-S Polyether and Polysulfone

Property	Bis S polyether ^a	Polysulfone
Dielectric constant		
60 cps, 23°C.	3.92	3.07
5 mc. 23°C.	3.62	—
60 cps, 150°C.	3.45	2.98
60 cps, 225°C.	3.39	—
Power factor		
60 cps, 23°C.	0.00092	0.0003
60 cps, 225°C.	0.0050	
60 cps, 225°C.	0.0204	
5 mc. 23°C.	0.0257	
Volume resistivity		
23°C.	8.9×10^{16}	9.1×10^{14}
50°C.	3.1×10^{16}	2.2×10^{14}
225°C.	1.3×10^{12}	—

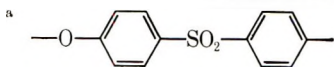


TABLE XII
Solubility Characteristics of Poly(aryl Ethers)
at Room Temperature

Solvent or class of solvent	Solubility ^a	
	Polysulfone	Bis S polyether
Inorganic acids	N	N
Alkalies	N	N
Aliphatic alcohols	N	N
Aliphatic esters	PS	N
Aliphatic ketones	PS	N
Aliphatic hydrocarbons	N	N
Aromatic hydrocarbons	PS	N
Polar aromatic compounds	S-PS	N-PS
Chlorinated hydrocarbons	S	N
DMF, DMAc	S	S
N-Methylpyrrolidone	S	S
DMSO, Sulfolane	PS	PS

^a N = not soluble; PS = partly soluble or swells; S = soluble.

Thermal Properties. Many of the polyethers possess excellent thermal stability up to 400°C. and, in some cases, somewhat beyond. This is not unexpected where the diphenyl ether, benzophenone, or diphenyl sulfone units are present in the polymer backbone, since the parent compounds are well known for this property.

Polysulfone, while, perhaps not at the top of this list, possesses remarkable thermal stability in the absence of oxidizers in spite of the presence of a relatively large number of methyl groups along the chains. In the

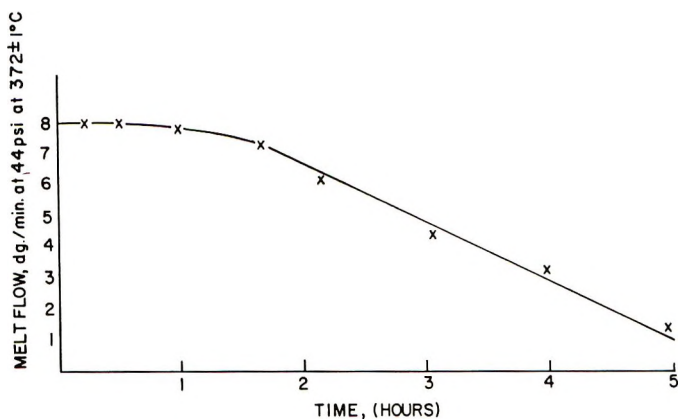


Fig. 4. Effect on melt flow of heat aging of polysulfone at 360–370°C. with limited air exposure.

presence of air at elevated temperatures, polysulfone is attacked, presumably at the methyl groups, resulting ultimately in crosslinking, (as evidenced by increasing pressure sensitivity to flow, increase in the \bar{M}_w/\bar{M}_n ratio, and the isolation of noncharred insoluble residues). This is never serious below the glass transition of 195°C.; samples aged at this temperature in air for several months show discoloration but only very minor changes in molecular weight. At 400°C. in air, attack is rapid, and crosslinking occurs within a few minutes. In the complete absence of air at 400°C., polysulfone shows no change in color or molecular weight up to at least 30 min. aging.

The excellent thermal stability of polysulfone is indicated by the plot in Figure 4. The melt flow was measured on successive portions of a given sample after increasingly greater heat aging times. Measurements were made by use of a Tinius-Olsen melt plasticometer in which the sample could be held reasonably free from air contact, but not completely so.* The spread in the aging temperature arises owing to the fact that a large sample was employed, necessitating initially filling the heated chamber to near the top. With this particular cell about a 10°C. gradient was found from the top to about halfway down. The temperature of the melt flow measurement is believed accurate to within 1°C. and was measured near the middle of the cell.

Up to about 1 hr. aging, the flow remains unchanged; thereafter the flow drops steadily but not precipitously. No change in reduced viscosity for this sample ($R.V. = 0.58 \pm 0.02$) was observed up to about 2 hr. Thereafter the extrudates were found to contain some gel. Over the entire 5-hr. period, the change in flow corresponds to a change in reduced viscosity of 0.2 units (i.e., ca. 0.6–0.8), if indeed the soluble portion changes in a

* Similar to melt index test (ASTM D 1238) for lower-melting thermoplastics. The number indicates rate of flow from a 0.0825 in. diameter orifice under 44 psi at the indicated temperature.

simple manner. The chemical change occurring during heat aging is an open question. Presently work is proceeding towards the elucidation of the mechanisms involved.

The authors wish to acknowledge the following members of our Research Staff: Mr. J. Dagon for molecular weight data on polysulfone; Dr. F. J. Karol for supply of the dichloro- and difluoroazobenzene, Dr. R. D. Swigert for 4,4'-dihydroxydiphenyl sulfide, and Dr. W. F. Beach for the NMR data on polysulfone.

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Résumé

Une série de nouveaux polyéthers aromatiques ont été préparés par condensation en solution. La synthèse comporte la condensation d'un sel métallique alcalin d'un bisphénol, avec un dihalogénure aromatique substitué, activité ou négativé dans un solvant aprotique dipolaire anhydre à température élevée. La réaction est rapide, dépourvue de réactions secondaires et fournit des polymères de couleurs excellentes. Une polysulfone du type bakélite peut être préparée de cette façon par réaction du sel disodé et du bisphénol-A avec la sulfone 4,4'-dichlorodiphénylée dans le diméthyl sulfoxyde (DMSO). Uniquement des solvants aprotiques dipolaires sont utilisables pour effectuer la polymérisation. Parmi ceux-ci, le DMSO et le Sulfolane (dioxyde de tétrahydrothiophène-1,1) sont les plus effectifs. L'eau et d'autres nucléophiles doivent être absents si l'on désire obtenir des poids moléculaires élevés. Outre le fait d'assurer la solubilité indispensable, ce solvant hautement polaire, est essentiel pour permettre une polymérisation rapide. Les vitesses dépendent de la basicité du sel de bisphénol et du pouvoir électrocapteur du groupe activant dans le dihalogénure. Comme d'habitude pour ces types de réactions, les difluorures sont plus réactifs que les dichlorures correspondants. La plupart des polyéthers sont des thermoplastiques amorphes, rigides et durs avec des transitions vitreuses élevées. La stabilité thermique et les propriétés électriques sont notables. Celles-ci et d'autres propriétés sont décrites pour la polysulfone et des transitions vitreuses sont indiquées pour une liste choisie d'autres polyéthers.

Zusammenfassung

Eine Reihe neuer aromatischer Polyäther wurde durch Kondensationspolymerisation in Lösung hergestellt. Die Synthese besteht in einer Kondensation eines Dialkalisalzes eines Diphenols mit einem "aktivierten" oder negativ substituierten aromatischen Dihalogenid in einem wasserfreien, polaren aprotischen Lösungsmittel bei hoher Tem-

peratur. Die Reaktion verläuft rasch und ohne Nebenreaktionen und liefert Polymere von hervorragender Farbqualität. Auf diesem Weg kann Bakelit-Polysulfon durch Reaktion des Dinatriumsalzes von Bisphenol A mit 4,4'-Dichlordiphenylsulfon in Dimethylsulfoxyd (DMSO) hergestellt werden. Ausschliesslich dipolhaltige, aprotische Lösungsmittel sind zur Ausführung der Polymerisation geeignet. Unter ihnen sind DMSO und Sulfolan (Tetrahydrothiophen-1,1-dioxyd) die wirkungsvollsten. Wasser oder andere nukleophile Konkurrenz-Agentien müssen abwesend sein, wenn hohe Molekulargewichte erreicht werden sollen. Die hochpolaren Lösungsmittel sorgen nicht nur für die notwendige Löslichkeit, sondern sind auch, wie angenommen wird, wesentlich für die Gewährleistung der beobachteten hohen Polymerisationsgeschwindigkeiten. Die Geschwindigkeiten hängen weiters, wie gefunden wurde, von der Basizität des Bisphenolsalzes und dem Elektronenanziehungsvermögen der aktivierenden Gruppe im Dihalogenid ab. Wie es für diesen Reaktionstyp üblich ist, erweisen sich Difluoride im Vergleich zu den entsprechenden Dichloriden als reaktionsfähiger. Die meisten Polyäther sind amorphe, steife und zähe Thermoplasten mit einer sehr hochliegenden Umwandlung zweiter Art (T_g). Ihre thermische Stabilität und ihre elektrischen Eigenschaften sind bemerkenswert. Diese und andere Eigenschaften werden für das Polysulfon beschrieben. Für eine ausgewählte Reihe anderer Polyäther werden die Glasumwandlungen angegeben.

Received January 27, 1967

Revised March 20, 1967

Prod. No. 5407A

Poly(aryl Ethers) by Nucleophilic Aromatic Substitution. II. Thermal Stability*

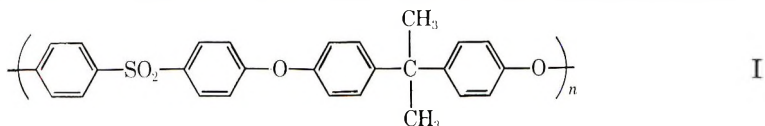
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Synopsis

The thermal stability and degradation process for a specific poly(aryl ether) system have been studied. In particular, the polymer which is available from Union Carbide Corporation as Bakelite polysulfone has been examined in detail. Polysulfone can be prepared from 2,2-bis(4-hydroxyphenyl)propane and 4,4'-dichlorodiphenyl sulfone by nucleophilic aromatic substitution. Because of a low-temperature transition at -100°C . and a glass transition at 195°C ., polysulfone retains useful mechanical properties from -100°C . to 175°C . A number of experimental methods were utilized to study the thermal decomposition process for this polymer system. Polysulfone gradually degraded in vacuum above 400°C . as demonstrated by mass spectrometry. Thermogravimetric analysis in argon, air, or high vacuum indicated that rapid decomposition began above 460°C . From gas chromatography, mass spectrometry and repeated laboratory pyrolyses, a number of products from polymer decompositions were identified. The most important degradation process in vacuum or inert atmosphere was loss of sulfur dioxide. Several model compounds representative of portions of poly(aryl ether) molecules were synthesized and the relative thermal stabilities determined. Possible mechanisms for pure thermal decomposition of polysulfone were derived from the product analyses, model studies, and consideration of bond dissociation energies.

INTRODUCTION

Utilization¹ of nucleophilic substitution on activated aromatic dihalides in polar aprotic solvents has made available a new class of high molecular weight poly(aryl ethers). The previous paper¹ has discussed the chemistry of polymer preparation and the effect of structural changes on physical properties. In addition, we have been concerned with the thermal properties of this polymeric system and this paper summarizes our investigations of thermal stability and degradation with particular emphasis on repeat unit I. Available from Union Carbide Corporation as Bakelite



* Paper presented in part at the 152nd American Chemical Society Meeting, New York, September 11-16, 1966.

polysulfone, I can be prepared from 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and 4,4'-dichlorodiphenylsulfone. This poly(aryl ether) is identified as polysulfone throughout this paper.

During the physical and mechanical property evaluation of these polymers, it became evident that softening temperatures approaching 400°C. were a general characteristic. It was of interest, therefore, to investigate the limits of thermal stability and to attempt to elucidate the important degradation processes.

Aromatic polyethers^{2,3} and polythioethers⁴ have been previously examined for thermal behavior in several independent studies. These studies support the general observation that aromatic ethers usually exhibit good thermal stability. A few early reports⁵⁻⁷ have indicated that aromatic sulfone polymers might also have good stability. The minimum temperature for noticeable decomposition of diphenyl sulfone has been given⁸ as 470°C., and di(*p*-tolyl) sulfone can be distilled⁹ at 450°C. without decomposition. More recently, Lancaster et al.¹⁰ have indicated that a mixed aromatic sulfone-ether polymer is more stable than an aromatic sulfone polymer but not as stable as a simple aromatic polyether. The stability of aromatic sulfone systems is in marked contrast to the observed¹¹⁻¹³ rapid decomposition of aliphatic sulfone polymers at about 250°C.

EXPERIMENTAL

Measurement of Physical and Mechanical Properties

Several different samples of the commercially available poly(aryl ether) (Union Carbide Corp., P1700 grade, Bakelite polysulfone) were used for the determination of mechanical and physical properties listed in Table I.

TABLE I
Common Thermal and Physical Properties of Polysulfone

Property	Value	ASTM method
Glass transition temperature, °C.	195	—
Deflection temperature (66 psi), °C.	181	D648
Deflection temperature (264 psi), °C.	174	D648
Tensile strength (yield), psi	10,200	D638
Tensile modulus, psi	360,000	D638
Tensile elongation to break, %	50-100	D638
Tensile impact strength, ft.-lb./in. ³	250-530	D1822
Density, g./cc.	1.24	D1505
Low-temperature transition, °C.	-100	—

Most of the data represent average values. The glass transition temperature was determined by measuring resiliency as a function of temperature.¹⁴ The low temperature transition was measured by mechanical loss.¹⁵

TABLE II
Analysis of the Thermal Decomposition of Polysulfone by Mass Spectrometry

Product	Mass	Product, moles $\times 10^{-6}$											Total product, moles ^b			
		200°C.	300°C.	300°C.	400°C.	400°C.	400°C.	450°C.	450°C.	450°C.	500°C.	500°C.		550°C.	600°C.	
Hydrogen	2	S ^a	S	ND	S	S	S	0.1	0.1	0.1	0.1	2.4	3.5	5.0	57.0	68.2
Methane	16	ND*	ND	ND	ND	ND	ND	0.6	0.6	0.6	0.6	21.7	22.9	17.1	17.1	81.2
Carbon monoxide	28	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.4	2.4	3.1	23.2	31.1
Hydrogen sulfide	34	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.6	0.8	4.9	21.1	27.4
Carbon dioxide	44	S	S	S	S	S	S	S	S	S	S	S	S	0.2	1.4	1.8
Sulfur dioxide	64	ND	S	S	0.7	0.7	0.7	8.2	6.8	7.6	127.5	127.5	127.5	97.0	5.0	383.8
Benzene	78	ND	ND	ND	ND	ND	ND	S	S	S	0.4	0.6	0.6	1.2	16.5	18.7
Toluene	92	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.2	1.1	1.0	1.0	10.0	12.3
Phenol	94	ND	ND	ND	S	S	S	0.3	0.2	0.5	6.9	7.7	7.7	1.0	2.9	19.5
Unknown	95	ND	ND	ND	S	S	S	0.4	0.3	0.6	5.2	4.7	4.7	0.3	1.0	12.5
Xylenes	106	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.1	0.1	0.1	0.1	0.6	0.9
Unknown	107	ND	S	S	S	S	S	S	S	S	0.1	S	0.1	S	1.0	1.2

^a S = less than 0.1×10^{-6} moles; ND = not detected.

^b Initial moles of polymer = 1130×10^{-6} .

Degradation Studies

Poly(aryl ether) samples were vacuum-dried for 24 hr. at 100°C. just prior to use.

Thermogravimetric Analyses (TGA).* Data were obtained on a Chevenard thermobalance with the use of a porcelain crucible. About 0.2 g. of sample was employed in each run.

Mass Spectrometer Analyses.† Polysulfone (I) (0.5 g.) was placed in a ceramic combustion boat which was inserted into a quartz tube. The tube was sealed directly to the mass spectrometer, and after maintaining the sample at 10^{-6} mm. at 100°C. for 16 hr. the system was closed to the vacuum source for 20 min. The volatiles evolved during the 20-min. period were analyzed. The temperature was adjusted as shown in Table II, the system evacuated again and sealed, and after 20 min. the volatiles were analyzed. This was repeated at each temperature interval.

Gas Chromatography (GLC). Injection port pyrolyses, analyses and isolation of volatiles from laboratory pyrolyses were run in a F & M Scientific Corp., Model 720, gas chromatograph with helium as carrier gas. A 1 m. column of 10% silicone rubber on 80×100 mesh Chromosorb P was used at a column heating program of 2 min. at 75°C. and then to 325°C. at 11°C./min. Spectral studies of the fractions isolated from bench-scale pyrolyses by GLC were carried out with a Beckman IR-5 spectrophotometer and a Varian Associates A-60 spectrometer.

Laboratory-Scale Pyrolyses. In a typical experiment, 25 g. of polysulfone (I) was placed in a round-bottomed Pyrex flask which was connected to a vacuum source by Dry Ice and liquid nitrogen traps in sequence. After evacuating the flask several times and refilling with argon, a pressure of 0.05 mm. was maintained, and the flask was immersed in a molten salt bath at 350°C. The temperature of the bath was raised to 460°C. at the rate of 0.5°C./min. and then maintained at 460°C. for 1 hr. The work-up of the residue and trapped volatiles is described later.

Preparation of Model Compounds


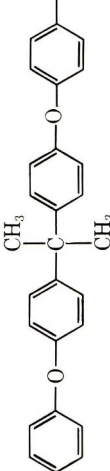

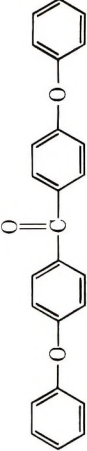

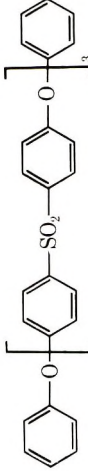
The model compounds listed in Table III were all prepared by reaction schemes which were similar to the previously described poly(aryl ether) preparation.¹ Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

4,4'-Diphenoxydiphenyl Sulfone (IV). A three-necked, round-bottomed flask equipped with a stirrer, dropping funnel, thermometer, condenser and modified Dean-Stark trap was charged with 94.11 g. (1.00 mole) of phenol, 150 ml. of dimethyl sulfoxide, and 100 ml. of toluene. After stirring to dissolve the phenol, 80.70 g. of a 49.56% aqueous sodium hydroxide solution (1.00 mole NaOH) was added and the mixture heated to reflux under argon.

* Thermogravimetric analyses by Prof. S. Gordon, Department of Chemistry, Fairleigh-Dickinson University, Madison, New Jersey.

† Mass spectrometry by Gollob Analytical Service, Inc., Berkeley Heights, New Jersey.

TABLE III
Stability of Model Compound at 400°C.

Model	Time, hr.	Atmosphere	Wt. loss, %	Color ^a	M.p., °C. ^b	Original m.p., °C.
	5 5	N ₂ Air	0.19 4.04	White Amber	140-141-142 115-121-133	141-142 "
	5 2.5	N ₂ Air	0.74 4.7	Lt. yellow Brown	55-58-60 Liquid	62-63 "
	5 5	N ₂ Air	0.37 11.1	White Brown	107-109-110 85-87-105	108-109-110 "
	5 2.5	N ₂ Air	0.32 1.89	Lt. yellow Brown	145-146-147 135-140-144	146-147 "
	5	N ₂	5.1	Amber	278-280-285	309-311-312
	5	N ₂	0.2	Lt. yellow	215-219-230	225-229-233

^a All compounds were initially white, crystalline solids.

^b Three-point melting points indicate shrinking, initial liquid, and complete liquid temperatures, respectively.

Reflux was continued for about 2 hr. with the water retained in the Dean-Stark trap and the toluene returned to the reaction flask. When the temperature of the reaction medium reached 160°C., a solution of 143.5 g. (0.50 mole) of 4,4'-dichlorodiphenyl sulfone in 150 ml. of toluene was added. Most of the toluene and additional water were removed by distillation and the reaction continued at 170°C. for 1 hr. After the mass had cooled somewhat, it was poured into 4 liters of water, the suspended solid was collected by filtration, and the solid was recrystallized from a 1:1 toluene-ethanol solution to give 174 g. (87% yield) of IV, m.p. 140–142°C. The sample was purified further by distillation at 260–272°C./0.10 mm. Hg followed by recrystallization from 1:1 monochlorobenzene-ethanol. The final melting point was 141–142°C. and the infrared spectrum was consistent with 4,4'-diphenoxydiphenyl sulfone.

ANAL. Calcd. for $C_{24}H_{18}O_2S$: C, 71.62%; H, 4.51%; S, 7.97%. Found: C, 71.87%; H, 4.60%; S, 8.10%.

2,2-Bis(4,4'-diphenoxydiphenyl)propane (V). To a round-bottomed flask was added 50.0 g. (0.219 mole) of bisphenol A [2,2-bis(4-hydroxyphenyl)propane], 300 ml. of dimethyl sulfoxide, and 85 ml. of benzene. The mixture was stirred and warmed to dissolve the bisphenol A and 46.33 g. of a 53.28% aqueous potassium hydroxide solution (0.438 mole KOH) was added. Under an argon blanket, water from the reaction mixture was collected in a Dean-Stark trap during 6 hr. of azeotropic distillation. Benzene was distilled off to bring the reaction temperature to 136°C. After cooling to 100°C., 10 ml. of a solution of anhydrous cuprous chloride in dry pyridine (20 g. $CuCl$ in 100 ml. pyridine) and 71.0 g. (0.452 mole) of bromobenzene was added. The temperature of the reaction mass was maintained at 133–137°C. for 12 hr., and after cooling the mixture was poured into excess water. The brown oil was taken up in benzene, filtered to remove copper salts, washed with dilute acetic acid, 5% aqueous potassium hydroxide solution, again with dilute acetic acid, and dried over anhydrous $MgSO_4$. After the benzene was removed by fractional distillation, the oily residue (74.9 g.) was distilled to give 53.5 g. (64% crude yield) of a pale yellow oil, b.p. 196–218°C./0.09 mm. Hg, which did not absorb in the hydroxyl region of the infrared. A lower-boiling fraction, 183–193°C./0.09 mm., 11.4 g., did absorb at 2.9 μ . The crude product was recrystallized three times from 1:1 toluene-ethanol and then redistilled to give a center cut, b.p. 210–220°C./0.12 mm. Hg, m.p. 62–63°C., 27.8 g. (33%).

ANAL. Calcd. for $C_{27}H_{24}O_2$: C, 85.23%; H, 6.36%. Found: C, 85.33%; H, 6.35%.

Bis(4-phenoxyphenyl) Ether (VI). By a procedure similar to that described for V, potassium phenate was reacted with bis(4-bromophenyl) ether for 12 hr. After two crystallizations from toluene-ethanol, fractional distillation, and further recrystallization, a 64% yield of VI, m.p. 108–110°C. (lit.¹⁶ 111°C.), was obtained.

4,4'-Diphenoxybenzophenone (VII). By a procedure similar to that described for IV, potassium phenate was reacted with 4,4'-dichlorobenzophenone for 12 hr. After repeated crystallizations from toluene-ethanol, distillation at high vacuum, and an additional crystallization, a 60% yield of VII, m.p. 146–147°C. (lit.¹⁷ 147–148°C.), was obtained.

(4,4'-Diphenylsulfonyl)diphenyl Sulfone (VIII). By a procedure similar to that described for IV, the sodium salt of benzenesulfinic acid was reacted with 4,4'-difluorodiphenyl sulfone for 2 hr. at 130°C. and for 1 hr. at 160°C. After pouring into water, filtering, and recrystallizing from dimethylformamide, an 85% yield of VIII, m.p. 309–312°C., was obtained.

ANAL. Calcd. for $C_{24}H_{18}O_6S_3$: S, 19.31%. Found: S, 19.25%.

[(4,4'-Diphenoxy)-4,4'-diphenylsulfonyl]-4,4'-diphenoxydiphenyl Sulfone (IX). By a procedure similar to that described for V, the potassium salt of 4-hydroxy-4'-phenoxydiphenyl sulfone was reacted with 4,4'-difluorodiphenyl sulfone for 2 hr. at 135°C. and for 2 hr. at 155°C. After pouring into water and filtering, the solid was crystallized once from acetone and twice from chlorobenzene to yield 83% of IX, m.p. 227–232°C., softening at 220°C. A sample which was chromatographed on alumina as a chloroform solution and then recrystallized again from chlorobenzene melted at 229–233°C. and softened at 225°C.

ANAL. Calcd. for $C_{48}H_{34}S_3O_{10}$: C, 66.50%; H, 3.95%; S, 11.10%. Found: C, 66.33%; H, 3.93%; S, 10.93%.

RESULTS AND DISCUSSION

Effect of Temperature on Physical Properties

Some thermal properties and the room temperature physical properties of polysulfone are listed in Table I. Transitions at 195°C. and –100°C. are indicative of the temperature range over which the polymer might be expected to exhibit useful thermoplastic properties. The existence of a low-temperature loss peak at –100°C. also predicts^{18,19} that “toughness” or impact strength should be observed in this system and this is indeed the case.

It has been pointed out²⁰ that the term “thermal stability” as applied to thermoplastics can be related to the quite different phenomena of melting or softening (a reversible process) and the time-temperature-atmosphere-dependent decomposition process (irreversible). From a practical viewpoint, the usefulness of a plastic depends on retention of mechanical properties over a reasonably wide temperature range under a variety of in-use conditions and also on the ability of the material to be processed or fabricated without affecting properties. From actual experience, the in-use temperature limits for polysulfone within which useful physical properties are retained indefinitely are –100°C. to 175°C. However, the maximum temperature at which the polymer may be repeatedly melt processed is approximately 440°C. This relatively high temperature is

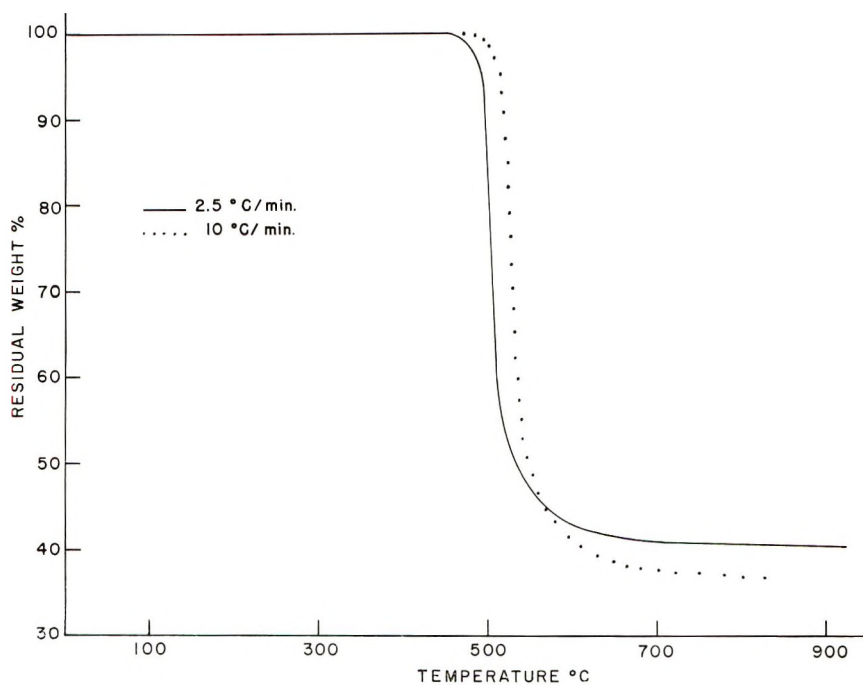


Fig. 1. Thermogravimetric curves of polysulfone in argon.

permitted by the short exposure times of most melt fabrication processes. Usually, a temperature²¹ in the range of 300–400°C. is satisfactory for ordinary molding or extrusion processes.

As a result of these relatively high fabrication temperatures and the long-term utility of polysulfone at temperatures approaching the glass transition of 195°C., it was of interest to determine the nature of the irreversible decomposition which would be expected under sufficiently severe combinations of temperature, time and environment. In addition, knowledge of the degradation mechanisms (more than one pathway might be predicted) might provide clues as to the best methods for polymer stabilization. Therefore, the study of this degradative process was initiated.

Thermogravimetric Analysis

Thermogravimetric traces for polysulfone are reproduced in Figures 1 and 2. Rapid weight loss occurred in the neighborhood of 500–550°C. regardless of heating rate or environment (air, argon, or vacuum). Except in air, 30–40% by weight of the initial samples was retained up to 800°C. No attempt was made to establish accurate kinetic constants²² for the decomposition since, as will be seen later, it can be reasonably assumed that several different degradative mechanisms are proceeding simultaneously and also since it was recognized that inherent difficulties²³ arise in the determination of kinetic constants for polymer degradation reactions

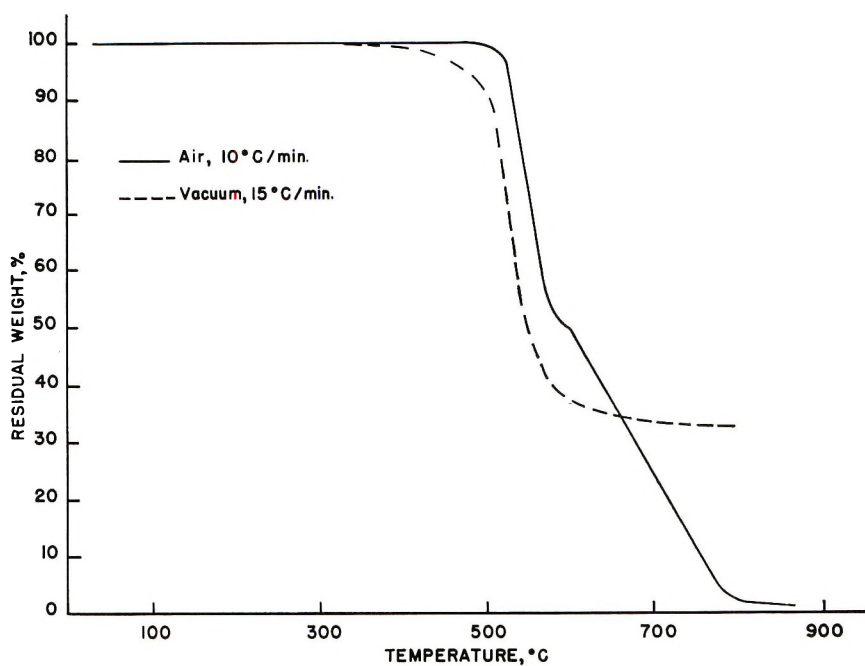


Fig. 2. Thermogravimetric curves of polysulfone in air and vacuum.

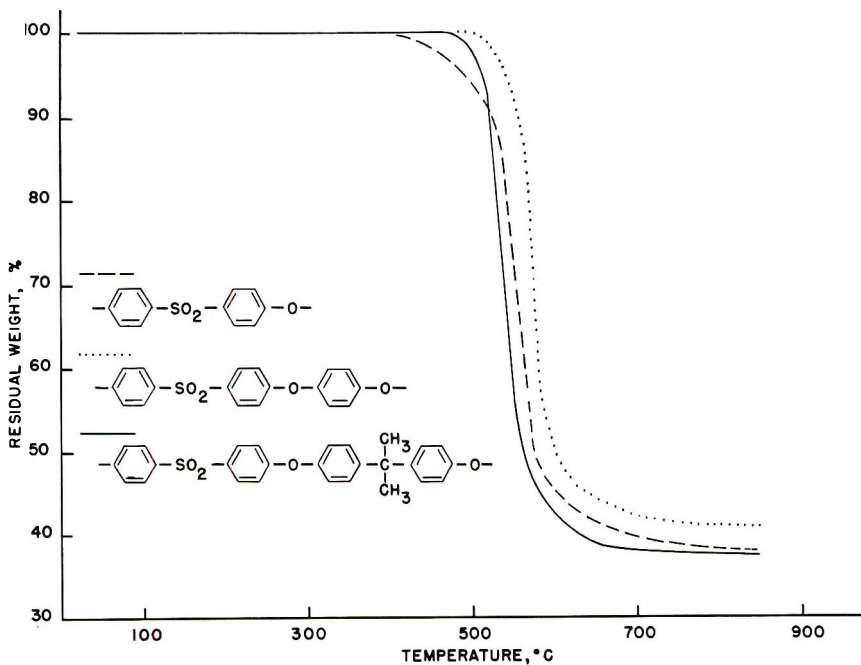


Fig. 3. Thermogravimetric curves of three poly(aryl ethers) in argon at 10°C./min.

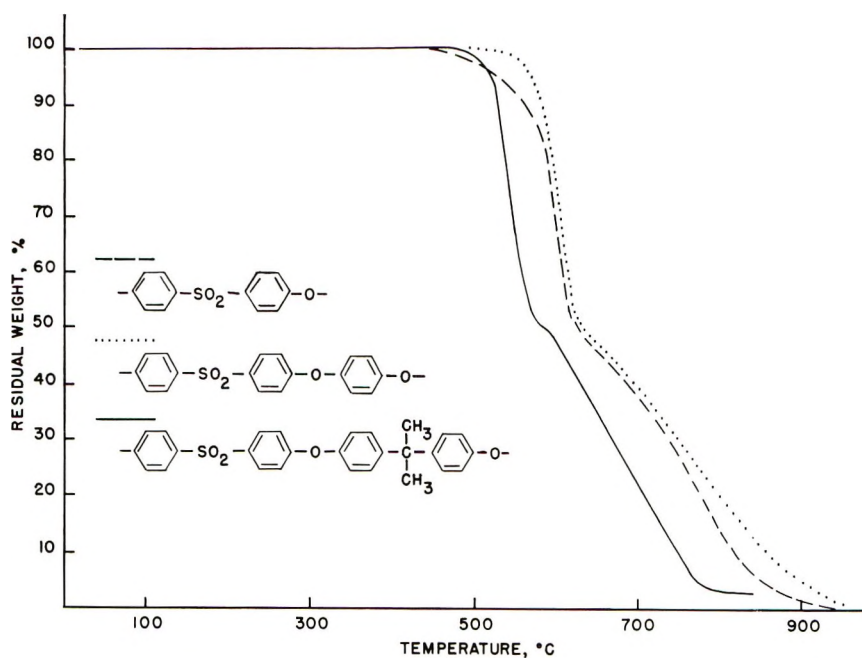


Fig. 4. Thermogravimetric curves of three poly(aryl ethers) in air at 10°C./min.

from weight loss data alone. However, an estimate of 70 kcal./mole for the activation energy of the overall degradation process was obtained by the method of Reich.²⁴ The temperature range of 500–600°C. on the 10°C./min. argon trace was used, and the overall reaction was assumed to be first order.

Thermogravimetric curves for two other poly(aryl ether) systems are compared with those for polysulfone in Figures 3 and 4. In argon, the three polymers give quite similar curves, whereas in air, the isopropylidene link appears to reduce the initial rapid decomposition temperature by about 50°C. when compared with the other repeat units. All three polymers show a change in slope at approximately 600°C. in air, which probably is indicative of a change in the dominant degradation mechanism at that temperature.

Thermal Decomposition Products

Mass Spectral Analysis. The products volatilized from a sample of polysulfone which was exposed to increasing temperatures for 20-min. intervals were analyzed in a mass spectrometer. The identity and number of moles of products at the various temperature–time intervals are shown in Table II. The polymer sample was maintained at 300°C. and 500°C. for two 20-min. periods and at 400 and 450°C. for three 20-min. periods as indicated in Table II. The combustion chamber was evacuated to 10^{-6} mm. Hg at the beginning of each constant temperature interval. From

Table II, the major product and also the one which is detected in significant amounts at the lowest temperature (400°C.) was sulfur dioxide. The total number of moles of sulfur dioxide collected up to 600°C. was 34% of the theoretical. Other products evolved in significant amounts up to 500°C. included methane, the mass 95 species (possibly protonated phenol), and phenol. Above 500°C., hydrogen, carbon monoxide, hydrogen sulfide, benzene, and toluene became significant, and sulfur dioxide, the mass 95 product, and phenol decreased.

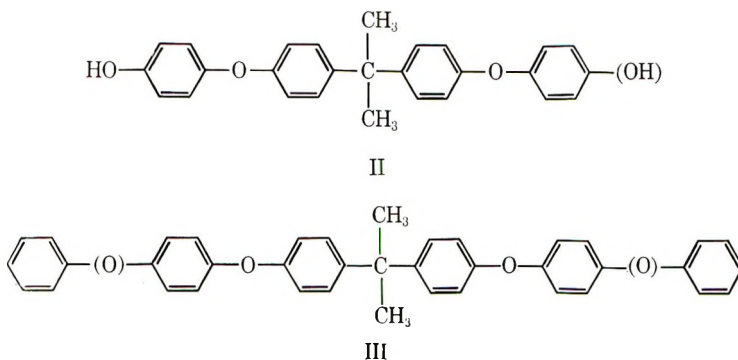
Decomposition in a Gas-Liquid Chromatographic Apparatus. By injection of a methylene chloride solution of the polyether into the heated port of a gas chromatography unit, the effect of injection port temperature on the number and kind of volatile products was studied. All runs were made with the same heating program with a silicone rubber column. At an injection port temperature of 350°C., no volatile products were detected. At 425°C., at least eight compounds were observed in small but detectable quantities. At 450°C., a similar chromatogram to the 425°C. case was obtained, except that a new compound with the same retention time as phenol appeared. As would be expected, the amounts of several components increased from 425 to 450°C.

Laboratory-Scale Pyrolyses. Several polymer pyrolyses were conducted with a sufficiently large sample so that some of the volatile products could be characterized by conventional techniques. In a typical experiment, polysulfone was heated in a Pyrex flask from 350 to 450°C. at a rate of 0.5°C./min. and then kept at 460°C. for 1 hr. at high vacuum. The sample was found to lose 53.8% of its weight under these conditions and the volatiles collected either in a -70°C. trap or in a -196°C. trap connected in series. The warmer trap contained 33.5% by weight of the initial sample and the colder trap retained 10.5%.

The -196°C. trap contained a red-brown liquid and a yellow solid. The odors of sulfur dioxide and hydrogen sulfide were quite apparent. An aqueous solution of the red liquid gave a strong, positive test for sulfite indicative of the presence of sulfur dioxide. The yellow solid was soluble in carbon disulfide and appeared to be sulfur. Although the odor of hydrogen sulfide was apparent, a positive sulfide test was not obtained.

The -70°C. trap contained a dark, red oil with the strong odor of hydrogen sulfide and sulfur dioxide. Gas chromatography of the oil indicated that 10 major components and another 12 constituents present in smaller quantities contributed to the mixture. By treatment of a sample of the oil with diazomethane and comparison of chromatograms, it was estimated that 41% of the mixture consisted of phenolic compounds and 59% of nonphenolic. From the retention times of known (not methylated), a large amount of phenol, a small amount of bisphenol A (ratio of phenol/bisphenol A, 372/1) and a trace of *p*-isopropenylphenol were observed. Fractional distillation of the oil provided a pure sample of phenol. by infrared and melting point, confirming the gas chromatographic identification. From the distillation residue (the fraction boiling above 55°C./

0.12 mm., pot temperature of 190°C.), two compounds, II and III, which totaled 7% of the Dry Ice trap condensate, were isolated via gas chromatographic (GLC) separation. Compound II was known to be phenolic and III nonphenolic from the GLC-diazomethane study. Nuclear magnetic resonance spectra analysis showed that both II and III retained a bisphenol A-derived isopropylidene link. However, aromatic protons *ortho* to a sulfone group were completely absent. Also, aliphatic protons from a methoxyphenyl group were not detected. The ratio of aromatic to aliphatic protons was 16.7/6 in II and 24/6 in III. Infrared confirmed the observation of a phenolic function in II and no phenolic function in III. Infrared also showed that both compounds had no sulfone groups but did have *p*-disubstituted phenyl links and aromatic ether absorptions. No chlorine was found in either compound. Based on the assumption that the GLC retention times were proportional to molecular weight on the nonpolar column and considering the other evidence, the structures shown were proposed for II and III, where the groups in parentheses may or may not be present and III may also be a macrocycle connected covalently at the 4-positions of the terminal phenyl groups. From a comparison of chromatograms, the same two compounds were observed in polymer decompositions run in the injection port of the GLC unit.



The carbonaceous residue (46.2% of the original sample) was found to be completely insoluble. Elemental analysis of the residue supported the observation that sulfur dioxide is an important degradation product, since a high carbon and low sulfur content was obtained in comparison with unpyrolyzed polymer.

Stability of Model Compounds

As further evidence in support of the observations on the thermal stability of polyaryl ethers, several model compounds representative of some possible combinations of functional groups in this system were synthesized. From a 5-hr. exposure at 400°C. in air and nitrogen, the extent of decomposition of the models was measured in terms of weight loss, color change, and melting point lowering. The results are summarized in Table III. In an inert atmosphere, the results are in general agreement

with the data on aromatic polymers of Lancaster et al.,¹⁰ which indicated that a mixed —O— and —SO₂— linked material would be more stable than a material linked by —SO₂— alone. In fact, 4,4'-diphenoxydiphenyl sulfone (IV) was at least equivalent to the simple aromatic ether model (VI) and the mixed carbonyl ether (VII) in an inert atmosphere. The diphenyl ether of bisphenol A (V) was quite unstable in air at 400°C. as was the simple ether (VI). Apparently, electron-withdrawing groups, such as carbonyl and sulfonyl, have a stabilizing influence toward oxidative degradation in these systems.

Thermal Degradation Mechanisms and Conclusions

This polymer degradation study has been almost exclusively concerned with a purely thermal decomposition. It is assumed that in an inert atmosphere or at high vacuum that oxidative or acid-catalyzed degradation is of secondary importance in interpreting the experimental results.

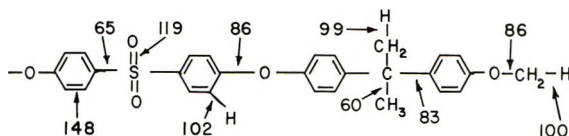
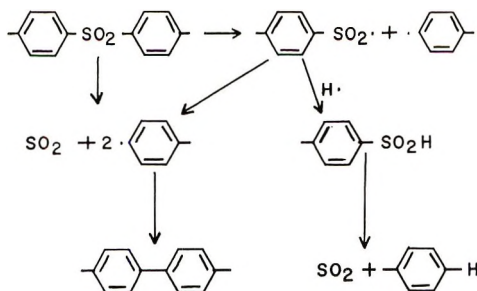


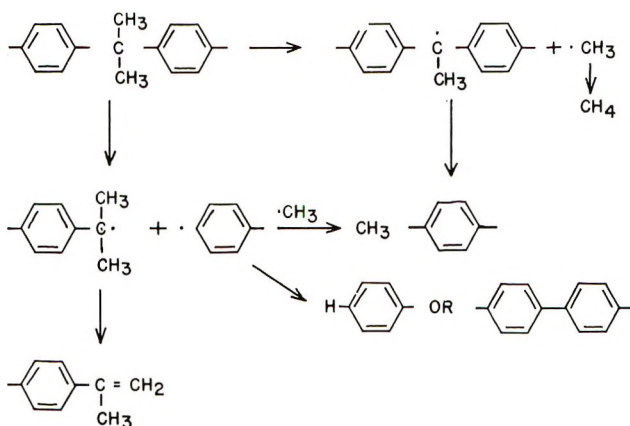
Fig. 5. Bond dissociation energies (in kcal./mole) for polysulfone.

From the mass spectrometer studies, sulfur dioxide was found to be the first measurable decomposition product as the temperature of the polymer reached 400°C. From these results and the supporting GLC and bench-scale pyrolyses, it is clear that scheme I offers a reasonable rationalization for thermal decomposition of the diphenyl sulfone moiety. In scheme I, the sulfinic acid shown is suggested as a possible intermediate and was not isolated. Eventual formation of 4,4'-diphenylene linkages can be assumed to follow loss of sulfur dioxide from the polymer. The isolation of compounds II and III from a pyrolysis at 460°C. supports these conclusions.

SCHEME I



SCHEME II



Another important product of thermal decomposition which appears at relatively low temperatures is methane. As shown in scheme II, methane is probably formed primarily by homolytic cleavage at the isopropylidene link of the bisphenol A moiety via initial formation of methyl radical and a relatively stable benzyl-type radical. Other reactions which can occur at the benzyl carbon are outlined in scheme II.

Other products at temperatures below 500°C. include phenol, bisphenol A, and *p*-isopropenyl phenol. Phenol has been known^{25,26} for many years to be a thermolysis product of aromatic ethers. Phenol, bisphenol A, and *p*-isopropenyl phenol can be generated from the bisphenol-A portion of polymers as has been shown for bisphenol A polycarbonate.²⁷ At temperatures over 500°C., the products are indicative of further, more complex fragmentation processes, which undoubtedly include further decomposition of the initial degradation products.

The initial products of degradation and the proposed mechanisms are supported by bond dissociation energy values²⁸ shown in Figure 5. Thus, the weakest links in the polysulfone repeat unit would be expected to be the carbon-sulfur bond between the aromatic ring and the sulfone group and the carbon-carbon bond between the methyl group and the center carbon of the isopropylidene moiety.

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Résumé

La stabilité thermique et le processus de dégradation pour un système polyaryléther ont été étudiés. En particulier le polymère qui est disponible à la Union Carbide Corporation comme polysulfone du type bakélite a été examiné en détail. La polysulfone peut être préparée au départ de 2,2-bis(4-hydroxyphényl)propane et de 4,4'-dichlorodiphényl sulfone par substitution nucléophile aromatique. Par suite d'une transition basse à -100°C et d'une transition vitreuse à 195°C , la polysulfone garde des propriétés mécaniques utiles de -100 à 175°C . Uncertain nombre de méthodes expérimentales ont été utilisées pour étudier le processus de décomposition thermique de ce système polymérique. La polysulfone se dégrade graduellement sous vide au-dessus de 400°C comme il a été démontré par spectrométrie de masse. L'analyse thermogravimétrique dans l'argon, l'air et sous vide indique une décomposition rapide débutant au-dessus de 460°C . Au départ des résultats de chromatographie gazeuse, de spectrométrie de masse et d'analyses de laboratoire un certain nombre de produits de décomposition des polymères ont été identifiés. Le processus de dégradation le plus important sous vide ou sous atmosphère inerte consiste dans la perte de SO_2 . On a synthétisé de nombreux composés modèles représentant des parties des molécules de polyaryléther, et leur stabilité thermique relative a été déterminée. Les mécanismes possibles pour la décomposition thermique pure de la polysulfone ont été déduits au départ des produits d'analyse des modèles d'étude et de considérations concernant les énergies de dissociation de liaisons.

Zusammenfassung

Die thermische Stabilität und der Abbauvorgang wurde an einem spezifischen Polyaryläther-System untersucht. Im besonderen, wurde das Polymere, das als Bakelit-Polysulfon von der Union Carbide Corporation erhältlich ist, einer detaillierten Untersuchung unterzogen. Das Polysulfon kann aus 2,2-Bis(4-hydroxyphenyl)propan und 4,4'-Dichlordiphenylsulfon durch nukleophile aromatische Substitution hergestellt werden. Wegen einer Tieftemperaturumwandlung bei -100°C und einer Glasumwandlung bei $+195^{\circ}\text{C}$ bewahrt sich das Polysulfon im Bereich von -100°C bis 175°C seine wertvollen mechanischen Eigenschaften. Eine Reihe experimenteller Methoden wurden dazu verwendet, den thermischen Zersetzungsprozess in diesem Polymersystem zu untersuchen. Wie durch Massenspektrometrie gezeigt wurde, unterliegt das Polysulfon im Vakuum über 400°C einem allmählichen Abbau. Eine thermogravimetrische Analyse in Argon, Luft oder Hochvakuum zeigte, dass über 460°C eine rasche Zersetzung beginnt. Durch Gaschromatographie, Massenspektrometrie und wiederholte Pyrolyse im Laboratoriumsmassstab konnte eine Reihe der Polymerzersetzungprodukte identifiziert werden. Den wichtigsten Abbauvorgang im Vakuum oder in inerte Atmosphäre stellt die Abspaltung von Schwefeldioxyd dar. Mehrere Modellverbindungen, die für Teile des Polyaryläthermoleküls repräsentativ sind, wurden hergestellt und ihre relativen thermischen Stabilitäten bestimmt. Aus Produktenanalysen, aus Untersuchungen an Modellschubstanzen und der Betrachtung der Bindungsspaltungsenergien wurden die möglichen Mechanismen für die rein thermische Zersetzung des Polysulfons abgeleitet.

Received January 27, 1967

Revised March 20, 1967

Prod. No. 5408A

Poly(aryl Ethers) by Nucleophilic Aromatic Substitution. III. Hydrolytic Side Reactions*

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Synopsis

The molecular weight of polysulfone, i.e., the aryl polyether that is prepared by the reaction of the disodium salt of bisphenol A with 4,4'-dichlorodiphenyl sulfone in dimethyl sulfoxide (DMSO) solvent is shown to depend, among other things, on the moisture content of the polymerizing system. In the presence of water, hydrolysis of the sulfone monomer occurs concomitant with the polymerization. This leads to a deviation from the desired 1:1 ratio of coreactant groupings and therefore in attendant reduction in possible molecular weight. The hydrolysis is shown to lead to the formation of the sodium salt of 4-chloro-4'-hydroxydiphenyl sulfone and to a lesser extent polymer derived from self-condensation of this salt. At low levels this salt is essentially inert towards the principal polymerization at hand but in somewhat greater amounts functions as an effective chain terminator. Similar hydrolysis of polysulfone chloro endgroups is believed to occur under the aqueous conditions of polymerization but to a lesser extent than for the sulfone monomer. It is shown that polysulfone or similar polyethers are subject to chain cleavage by bases in DMSO solvent. The base attacks the activated position *para* to the sulfonyl group with the formation of a chain terminating in a bisphenol A type phenolic group and a chain terminating in a phenolic group of the bisphenol S (*p*-hydroxyphenyl sulfonyl) type. It is shown that cleavage is probably not important under normal conditions of polymer formation. The effect of these hydrolytic side reactions on the attainment of high molecular weight under conditions of imperfect reaction stoichiometry is shown to be consistent with the above conclusions.

INTRODUCTION

In previous papers the preparation of certain poly(aryl ethers) by activated nucleophilic aromatic substitution, notably the polysulfone of bisphenol A,¹ and their thermal stability² were discussed. It was pointed out that successful polymerization by this method depended, among other things, upon the use of a suitable solvent, i.e., dimethyl sulfoxide (DMSO), and the need for anhydrous conditions. In aqueous DMSO, molecular weight is limited owing to the intervention of hydrolytic side reactions involving the activated halo monomer, i.e., 4,4'-dichlorodiphenyl sulfone, (DCDPS) and to a lesser extent hydrolysis of the polymers themselves.

* Paper presented at the 3rd Biennial American Chemical Society Polymer Symposium, Case Institute of Technology, Cleveland, Ohio, June 22-24, 1966.

Very little has been reported on the hydrolysis of DCDPS. Huissman³ indicated that hydrolysis by caustic at high temperatures and pressures leads to replacement of both active chlorines with the formation of 4,4'-dihydroxydiphenyl sulfone (bisphenol S). Upon fusion with sodium hydroxide, however, only one of the chlorines appears to be replaced,³ indicating that substitution of the second chlorine is considerably more difficult. Treatment of 4,4'-difluorodiphenyl sulfone with 1.1 equiv. of potassium methoxide is reported⁵ to yield the monomethyl ether; no mention is made of other products. That replacement of the second fluorine is more difficult is possibly indicated by the fact that treatment with 2.4 equiv. ammonia yields the monoamine in 70% yield.

Basic cleavage of activated aryl ethers is a well known reaction,⁶ and it is not surprising that similar poly(aryl ethers) suffer such reaction.

It is the purpose of this paper to present our findings with regard to the hydrolysis of DCDPS, particularly as it relates to the polymerization with alkali bisphenates and the cleavage of polysulfone and similar polyethers by strong bases in DMSO solvent.

EXPERIMENTAL

Polymerization Method

The procedure used to prepare polymers is the same as that reported previously.¹

Preparation of Polysulfone in Aqueous DMSO

The usual procedure¹ was used, except that a weighed quantity of water was added along with the sulfone. The water content of the "dry" polymerization was estimated by Karl Fischer titration on the last 5% of the chlorobenzene distillate.

Reduced Viscosity Measurement

Reduced viscosities were measured in chloroform at $25.00 \pm 0.01^\circ\text{C}$. and at a concentration of 0.2000 g. polymer/100.00 ml. solvent. The time taken for the polymer solution to flow in an Ostwald-type viscometer was compared with the time taken for the pure solvent. Reduced viscosity was calculated from the equation:

$$\text{R.V.} = [(\text{S.T.} - \text{B.T.})/\text{B.T.}](1/C)$$

where S.T. is sample time (in seconds), B.T. is blank time (in seconds), and C is concentration (in deciliters/gram).

Preparation of Polysulfone in the Presence of the Sodium Salt of 4-Chloro-4'-hydroxydiphenyl Sulfone (CHDS)

In the usual equipment,¹ 30.00 g. (0.1314 mole) of bisphenol A, 37.74 g. (0.1314 mole) of 4,4'-dichlorodiphenyl sulfone, 1.76 g. (0.0065 mole) of

4-chloro-4'-hydroxydiphenyl sulfone, 200 ml. of chlorobenzene, and 65 ml. of DMSO were charged and heated to 75°C. To the homogeneous solution was added 20.65 g. of 52.18% (0.2694 mole) of sodium hydroxide. The two-phase liquid mixture was rapidly heated to 172°C., whereupon most of the chlorobenzene and virtually all the water was distilled from the system over about 30 min. The viscous solution was held an additional 30 min. at 165–170°C., whereupon it was worked up in the usual fashion. A quantitative yield of polymer was obtained with a reduced viscosity (R.V.) of 0.79. A control experiment, i.e., with no CHDS added, gave an R.V. of 0.95. In another experiment where 7.06 g. of CHDS was used with 22.16 g. of 50.18% alkali, the R.V. was 0.43. Evaporation of the coagulation mother liquor to dryness yielded 6.47 g. of the methyl ether of CHDS (87% yield, theoretical for the ether 7.43 g., m.p. 101–104°C. (lit.⁷ 103–104°C.).

Effect of Incremental Addition of Excess Base and Excess Base Plus Excess DCDPS to a Polysulfone Reaction Mixture Under Hydrolysis Conditions

Excess Base. In the usual equipment,¹ 30.00 g. (0.1314 mole) of bisphenol A, 130 ml. chlorobenzene and 65 ml. DMSO were charged. At 75°C., 21.40 g. (0.2628 mole) of 49.17% sodium hydroxide was added. The mixture was heated to 155°C. with removal of water and excess chlorobenzene followed by the gradual addition and distillation of 40 ml. of dry chlorobenzene. (The extra chlorobenzene is added to further the dehydration.)

After some cooling, 37.74 g. (0.1314 mole) of DCDPS and 0.95 g. (0.0528 mole) of water were added. After 1 hr. at 160°C., a sample was extracted, coagulated in alcohol, washed with water, and dried. The R.V. was 0.35. Then 0.55 g. (0.00523 mole) of 53.2% potassium hydroxide was added and the mixture heated for 1 hr. more at 160°C. The R.V. of a sample extracted at this point was 0.51. Addition of 0.28 g. more (0.00261 mole) of 53.2% potassium hydroxide followed by further heating for 1 hr. at 160°C. resulted in a R.V. of 0.45. Addition again of 0.27 g. (0.00263 mole) of 53.2% potassium hydroxide followed by 1 hr. heating at 160°C. yielded an R.V. of 0.38.

Excess Base Plus Excess DCDPS. The same procedure as that used for excess base was employed; the initial R.V. was 0.41. The first incremental addition consisted of 0.75 g. (0.00261 mole) of DCDPS and 0.55 g. (0.00523 mole) of 53.2% potassium hydroxide. After 1 hr. at 160°C., a sample showed an R.V. of 0.66. A second addition consisting of 0.37 g. (0.001314 mole) of DCDPS and 0.27 g. (0.00257 mole) of the potassium hydroxide was made. After 1 hr. at 160°C., the R.V. was 0.59.

The same procedures (except that no water was added) were followed when studying the effect of addition of extra caustic and/or extra DCDPS to reaction mixtures which were initially short in Bis A or which initially had excesses of caustic and/or DCDPS charged.

Effect of the Addition of Sodium Phenate at the Conclusion of a Polysulfone Polymerization

To the usual batch polymerization¹ mixture just prior to addition of methyl chloride a solution of 2.1 g. (0.018 mole) of sodium phenate in dry DMSO was added after the reduced viscosity reached about 0.6–0.7. Further heating for 60 min. at 140°C. followed by the alcohol coagulation yielded polymer with a R.V. of 0.22 in quantitative yield.

Cleavage of Polysulfone with Sodium Hydroxide

A solution of 25 g. polysulfone, R.V.(CHCl₃) = 0.85 (methyl chloride-terminated)¹ in 65 ml. DMSO, and 35 ml. chlorobenzene contained in a metal (Monel) flask was heated to 165°C., a part of the chlorobenzene being distilled off to attain this temperature. Aqueous 52.5% NaOH (1.67 g., 21.9 mmole) was added, and heating and stirring continued for 1 hr. at 165°. Some water was distilled off with chlorobenzene after adding the NaOH (total distillates 14 ml.). Methyl chloride was bubbled in to terminate any sodium ended polymer chains. The solution was amber and very low viscosity as compared to the original. The product was diluted with 100 ml. chlorobenzene, centrifuged, and the clear solution precipitated in alcohol; 23 g. polymer having R.V. (CHCl₃) = 0.19 was isolated. The residual alkali was titrated and was equivalent to 2.9 mmole.

Cleavage of the Condensation Product of the Disodium Salt of Bisphenol A and 4,4'-Difluoroazobenzene with Sodium Phenate in Dry DMSO

The above polymer, 13.1 g. of R.V. 1.4 (*o*-dichlorobenzene), was dissolved in 137 ml. *o*-dichlorobenzene and 137 ml. of dry (by distillation) DMSO. Sodium phenate, 0.45 g. was added and the bright red solution heated to 150°C. After about 1 hr., the mixture was cooled and poured into ethanol. After drying, 12.6 g. product of R.V. 0.56 was obtained.

Effect of Added Potassium Fluoride on a Polysulfone Reaction in Dry DMSO

The usual procedure¹ was followed, except that 1.41 g. (0.015 mole) of potassium fluoride dihydrate was added and potassium hydroxide was the added base. After 3 hr. at 140°C. an R.V. of 0.80 resulted. In a control experiment (no KF), the R.V. was 0.72.

Hydrolysis of 4,4'-Dichlorodiphenyl Sulfone in Aqueous Alkaline DMSO

With KOH. Into a stainless steel flask equipped as usual¹ were placed 57.44 g. (0.200 mole) of 4,4'-dichlorodiphenyl sulfone and 200 ml. of DMSO. After heating to obtain homogeneity, 42.20 g. of 53.20% (0.400 mole) potassium hydroxide and then 7 ml. water (used to rinse the dropping funnel) were added. The mixture was heated to reflux, initially 128°C., for 4 hr., to

a final temperature of 140°C. The hot solution was poured into 600 ml. water, whereupon a small amount (1.6 g.) of solid, m.p. 120–148°C. (impure DCDPS), was collected by filtration. The filtrate was acidified to pH 6 by addition of 190 ml. of 1.03*N* HCl, whereupon 49.6 g. (53.6 g. theory for 4-chloro-4'-hydroxydiphenyl sulfone), m.p. 139–144°C. was collected by filtration. After recrystallization from 200 ml. 50/50 MeOH-toluene, the yield was 47.4 g., m.p. 142–147°C. and finally from 200 ml. toluene, 44.3 g., m.p. 146–146.5°C. (lit.⁷ m.p. 147.5–149°C.).

With NaOH. The procedure was the same for KOH except that 30.67 g. of 52.18% (0.400 mole) NaOH and 3 hr. at 130–140°C. was used. The recovered impure dichlorodiphenyl sulfone amounted to 2.2 g. (3.8%), and 50.1 theory) (93.3%) of 4-chloro-4'-hydroxydiphenyl sulfone, m.p. 143–145°C. was obtained.

ANAL. Calcd. for C₁₂H₉ClO₃S: C, 53.63%; H, 3.39%; Cl, 13.20%; S, 11.94%. Found: C, 53.68, 53.54%; H, 3.30, 3.31%; Cl, 13.44%; S, 12.08, 12.23%.

Cleavage of 4,4'-Diphenoxydiphenyl Sulfone

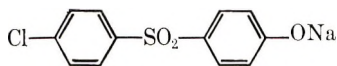
The diphenyl ether of bisphenol S² 40.25 g. (0.100 mole) and 150 ml. of DMSO were combined and heated 6 hr. at 130–140°C. with 20.9 g. (0.201 mole) of 53.16% potassium hydroxide. The reaction mixture was cooled and poured into 600 ml. water, whereupon 4.1 g. (10%), m.p. 135–138°C. (probably contaminated with DMSO), of recovered starting ether (authentic m.p. 141–143°C.)² was recovered by filtration and drying. The filtrate was acidified to the bromocresol purple color change (ph = 6), whereupon 29 g. (89%) of 4-hydroxy-4'-phenoxydiphenyl sulfone was isolated after filtering and drying. After one recrystallization from methanol and careful drying, material with m.p. 166–167°C. was obtained.

ANAL. Calcd. for C₁₆H₁₄O₄S: C, 66.24%; H, 4.32%; S, 9.83%. Found: C, 66.08%; H, 4.42%; S, 9.91%.

RESULTS AND DISCUSSION

Basic Hydrolysis of 4,4'-Dichlorodiphenyl Sulfone in DMSO

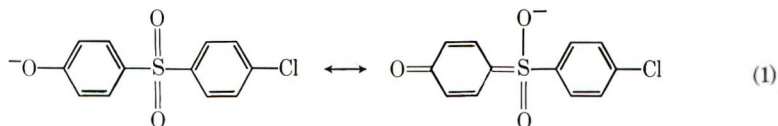
We have found that 4,4'-dichlorodiphenyl sulfone reacts smoothly with 2 equiv. of sodium hydroxide in aqueous DMSO to yield the sodium salt of 4-chloro-4'-hydroxydiphenyl sulfone, i.e., compound I, in about 95% yield. When somewhat larger amounts of base are employed, low



I

polymer, probably formed by self-condensation of I, results in addition to this salt.⁸ No dihydroxydiphenyl sulfones appear to be formed when 2 equiv. of base are used. This may indicate that the remaining chlorine in compound I is much less susceptible to hydrolysis than those in DCDPS.

This result might be expected in view of the reduced activating influence predicted for a sulfone group in conjugation with an aryloxy moiety [eq. (1)].



Molecular Weight of Polysulfone Prepared in Moist DMSO

In the reaction of the disodium salt of bisphenol A with 4,4'-dichlorodiphenyl sulfone in DMSO the deleterious effect of minor amounts of water on the attainment of truly high molecular weight is indicated by the data in Table I.

TABLE I
Preparation of Polysulfone in Aqueous DMSO

DCDPS/water mole ratio	R.V. (CHCl ₃)	\bar{M}_n^a
6	0.22	7,000
2	0.28	10,500
1	0.35	15,000
0.5	0.40	19,000
0.001 ^b	1.82	230,000

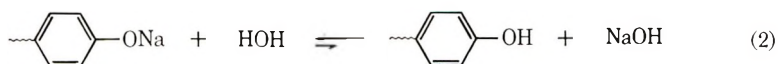
^a Osmotic molecular weight data of Mr. J. Dagon of our staff.

^b Estimated by Karl Fischer titration.

The very rapid drop-off in molecular weight attainable with rising water concentration suggests that a side reaction is occurring that upsets the necessary polymerization reaction stoichiometry. Rate retardation via a solvent effect* cannot be the principal problem, as polymerizations run initially in the presence of water which have stagnated do not proceed further after subsequent dehydration.

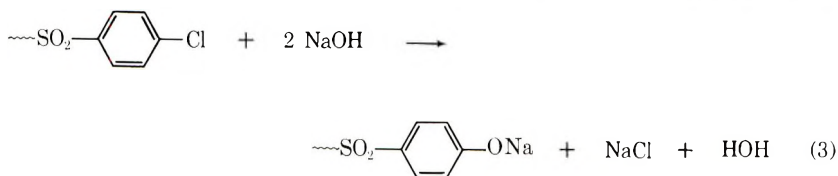
Chloro Group Hydrolysis During Polymerization

Water does not react with DCDPS in DMSO nor does it affect the polymer in any way under similar conditions. The sodium salt of bisphenol A is a salt of a weak acid and as such would be expected to undergo hydrolysis in aqueous media, as shown in eq. (2) for sodium phenolate polymer end-groups. The sodium hydroxide that is formed would be expected to react



* Nucleophilic reactions generally proceed more rapidly in anhydrous DMSO. It has been suggested that water solvates and thus reduces the reactivity of phenates in aqueous DMSO.⁹

irreversibly with DCDPS or polymer chloro endgroups as shown in eq. (3). (A bisphenol A sodium group may supply the second sodium in this reaction.) The net result of these reactions is the consumption of up to



twice as many equivalents of sodium bisphenol A groups as of the active chloro variety. The desirable reaction stoichiometry becomes upset, and therefore a limitation on molecular weight results.

In addition, the sodium bisphenol S type groups formed in eq. (3) are ineffective at furthering the polymerization in DMSO. At 150°C. for example, reaction of the dipotassium salt of bisphenol S with DCDPS is extremely slow; approximately 96% reaction is observed to occur in 17 hr. (Condensation at 240°C. in Sulfolane leads to high polymer, however.¹)

Preparation of Polysulfone in the Presence of the Sodium Salt of 4-Chloro-4'-hydroxydiphenyl Sulfone

Since the basic hydrolysis of DCDPS at low concentrations of sodium hydroxide should afford compound I as the only product, it was of interest to determine how its presence might affect an otherwise normal polysulfone preparation. The data are given in Table II. In addition, where 5 or 20 mole-% was added, unchanged salt was isolated in about 90% yield at the conclusion of the polymerization. It appears that the main effect of inclusion of this salt in the polymerization is one of termination. It is likely that reaction of bisphenol A sodium groups with the chloro end of I occurs resulting in chains capped with bisphenol S type sodium groups. Little contribution to chain growth would be expected in DMSO by the presence of such groups.

TABLE II
Preparation of Polysulfone in the Presence of Sodium Salt I

Compound I added, mole-%	R.V. (CHCl ₃)
0	1.82
1	0.92
5	0.79
20	0.42

Revival of Polymerizations Stopped Short by Hydrolysis

In a situation where molecular weight growth has been arrested by hydrolysis, it can be shown qualitatively that addition of a small amount

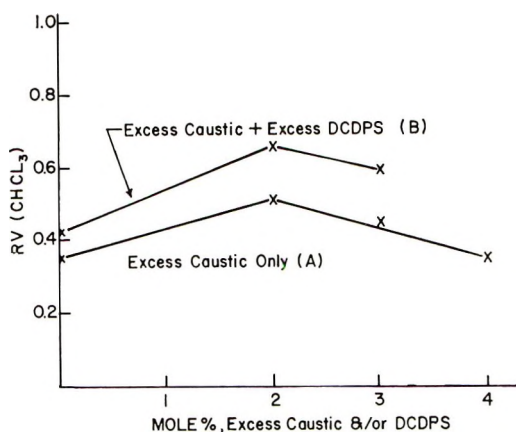


Fig. 1. Preparation of polysulfone in aqueous DMSO.

of sodium hydroxide or sodium hydroxide plus DCDPS will result in a nominal rejuvenation of the reaction. The results are shown in Figure 1.

The divergence of the initial reduced viscosities in Figure 1 is believed the result of the inability to exactly duplicate the degree of hydrolysis between experiments. Note, however, that in each case, the R.V. increased for an arbitrary addition of 2% excess reagent(s); further additions led to decreasing values. Where 2% DCDPS was added as well (curve B), the initial increase appears to be somewhat more pronounced.

The results are readily accommodated by the hydrolysis scheme. Thus, the extra added alkali serves to reconstitute the reactive bisphenol A phenates converted to the free phenol form by the hydrolysis. Subsequent reaction with remaining halide groups or with added DCDPS would be expected to lead to an increase in molecular weight.

Were the degree of hydrolysis known with certainty and if only DCDPS monomer were hydrolyzed, then the only deterrent to the formation of higher molecular weights by post addition of reagents would be the unavoidable reaction that takes place with sodium salt I.

It does appear that hydrolysis of DCDPS monomer largely predominates over that of polymer chloro endgroups. Thus, if polysulfone is prepared in the usual manner but with exactly 2 mole-% of free sodium hydroxide in the system, polymerization stops as expected at low R.V. (ca. 0.4) due to the hydrolysis by the free caustic. Now if extra DCDPS is added in an amount exactly equivalent to the amount of free caustic originally added, polymerization begins anew. We have obtained R.V.'s as high as 1.1 in this manner.

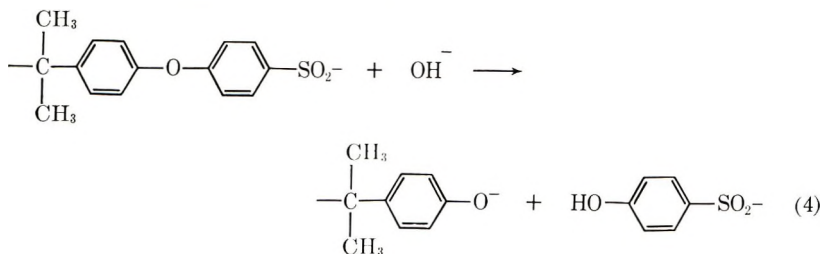
It is possible that hydroxide ion reacts faster with activated halogen than does bisphenol A phenate in anhydrous DMSO. Since hydroxide is the smaller anion, phenate would perhaps be less highly desolvated. Hydroxide ion then would have the higher activity and therefore the higher reactivity. If this were so, then hydrolysis in the cases under consideration

would be completed before appreciable polymerization could occur, and therefore before an appreciable number of polymer chloro endgroups would be formed.

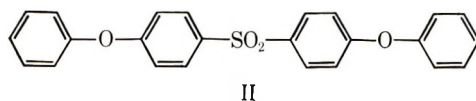
Polymer Hydrolysis

The drop in the R.V. that is observed in Figure 1, after the arbitrary addition of 3% (total) sodium hydroxide in each case is believed due to a base-induced chain cleavage reaction.

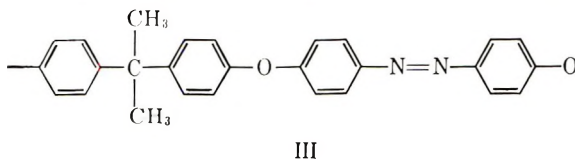
Cleavage is pictured to occur as shown in eq. (4),



followed by equilibration of the phenolic fragments. Nucleophilic displacements on activated aryl ethers are, of course, well known.⁶ We have found, for example, that bis(4-phenoxyphenyl)sulfone (II) is readily cleaved by 2 moles of aqueous alkali in DMSO to give a 90% yield of the sodium salt of monohydroxyphenoxydiphenyl sulfone and 10% unreacted starting material. (As is true with DCDPS, hydrolysis proceeds readily to the monohydroxy stage; further reaction is quite slow.)



We have further found that polysulfone is readily cleaved in DMSO at elevated temperatures by strong bases such as anhydrous sodium phenate or aqueous sodium hydroxide. Analogously, the polyether prepared from the disodium salt of bisphenol A and 4,4'-difluoroazobenzene (III) has



been cleaved with sodium phenate under anhydrous conditions. The results are given in Table III.

As would be expected, the degree of reaction is a function of the amount of sodium phenate used.

Polymer chain cleavage probably is relatively unimportant under normal conditions of polymer formation, as the fastest reaction that occurs with caustic is very likely with DCDPS monomer. The rapid and substantial

TABLE III
Cleavage of Bis A-Azobenzene Polyether (III)
by Treatment with Sodium Phenate (DMSO)

Wt. ratio polymer/phenate	Cleavage conditions	R.V. (<i>o</i> -dichlorobenzene)
Initial polymer	—	1.5
33/1	1 hr., 145–150°C.	0.78
30/1	1 hr., 145–150°C.	0.65
29/1	1 hr., 145–155°C.	0.56

increase in molecular weight observed when 2% excess DCDPS is subsequently added where the equivalent amount of excess base was initially employed (see above) is difficult to rationalize with cleavage as the major side reaction. The bisphenol S type phenates that result from cleavage would not be expected to contribute much (in DMSO) towards further molecular weight buildup, contrary to what is observed.

Preferential reaction of DCDPS with the sodium hydroxide might be expected even under conditions where appreciable polymerization has resulted, i.e., after a relatively large number of activated ether links have been formed. Kinetic data where methoxide^{10,11} is the nucleophile indicate that chloride is displaced more readily from 2,4-dinitrochlorobenzene than *p*-cresylate is from 2,4-dinitro-*p*-cresyl ether; similarly¹² for the attack of piperidine upon *p*-dinitrochlorobenzene versus *p*-nitrophenyl ether.

Effect of Halide Ions on the Polymerization

It has been reported¹³ that halides, in particular, fluoride ion, show enhanced reactivity in aromatic nucleophilic substitution in DMSO. Cleavage by by-product halide ion, however, is not considered too likely during polymerization, even when the concentration of reactive phenates has dropped to a very low value, since NaCl, KCl, and Na or KF appear to be quite insoluble in anhydrous DMSO. A polysulfone reaction run in the presence of anhydrous KF showed no significant difference in R.V. over a control experiment. This also shows that attack by fluoride ion on DCDPS is too slow to be of any consequence during polymerization. Were appreciable formation of fluorophenylsulfonyl groups to occur, it would be expected¹ that much faster rates and higher reduced viscosities would result.

Monomer Hydrolysis and Reaction Stoichiometry

Were the polymerization free of hydrolytic effects one might expect that if reduced viscosity were plotted (experimental points ⊙) against sodium hydroxide concentration, molecular weight would steadily rise to a maximum as the ratio to bisphenol A approached unity. Beyond this no change would be expected. The facts are, of course, otherwise, as the plot of Figure 2 shows.

A second point illustrated by the plot is that molecular weights are always higher on the excess side than on the corresponding deficiency, i.e., the R.V. at 101% is observed to be 0.76 and at 99% the value is 0.68. This teaches that the loss of DCDPS monomer by hydrolysis is slightly less

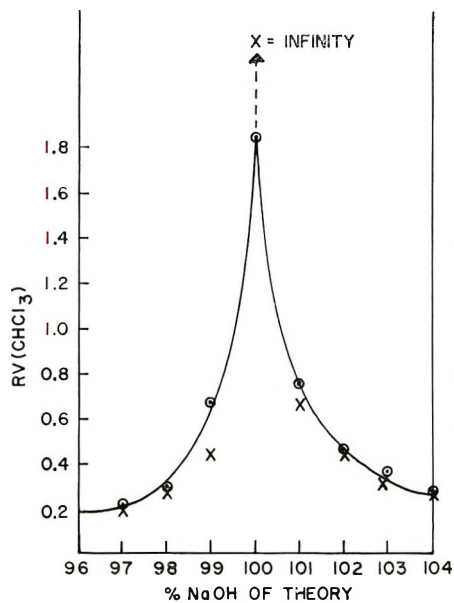


Fig. 2. Preparation of polysulfone with varying amounts of caustic.

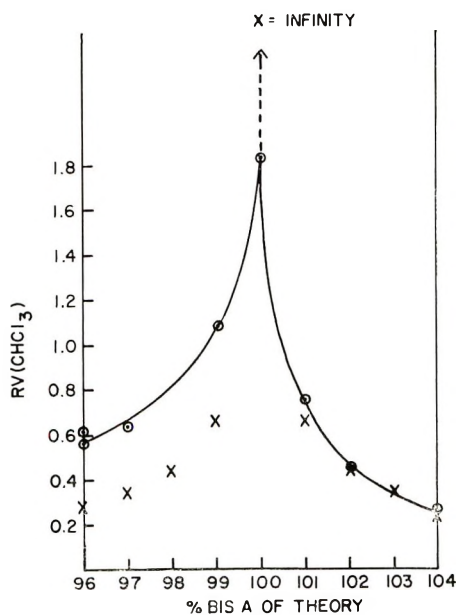


Fig. 3. Preparation of polysulfone with varying amounts of bisphenol A.

serious than being deficient in bisphenol A sodium phenates to begin with. The large discrepancy between theory and experiment at 99% is not understood.

The effect of monomer hydrolysis on the polymerization is strikingly evident when reduced viscosity is plotted against the per cent bisphenol A of theory (relative to DCDPS) as indicated in Figure 3 (experimental points \odot). A totally lopsided curve results with molecular weight much in excess of theory on the deficient side. Under these conditions it is also true that sodium hydroxide is in excess in amounts equivalent to DCDPS. Reaction to form the relatively unreactive compound I gives rise to stoichiometry closer to ideal than otherwise might be apparent.

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Résumé

Le poids moléculaire de la polysulfone c'est-à-dire du polyéther aryle préparé par réaction du sel disodé de bisphénol-A avec la sulfone 4,4'-dichlorodiphénylène dans le DMSO comme solvant, dépend entre autre de la teneur en humidité du système polymérisant. En présence d'eau, l'hydrolyse de la sulfone monomérique se passe en même temps que la polymérisation. Ceci amène à une déviation du rapport 1/1 souhaité des groupes coréactifs et dès lors entraîne une réduction possible du poids moléculaire. L'hydrolyse forme le sel sodé de la sulfone 4-chloro-4'-hydroxydiphénylée et à un moins grand degré, un polymère dérivé par auto-condensation de ce sel. A niveau faible, ce sel est essentiellement inerte à l'égard de la polymérisation principale mais peut fonctionner comme rupteur de chaîne effectif. Une hydrolyse similaire des groupes terminaux chlorés de la polysulfone se passe dans les conditions aqueuses de polymérisation mais à un degré moindre qu'avec la sulfone monomérique. On montre que la polysulfone ou des polyéthers semblables sont sujets à la rupture de chaîne par des bases dans le solvant DMSO. La base attaque la position *para* activée par rapport au groupe sulfonyle avec formation d'un groupe phénolique du type bisphénol A et d'un groupe phénolique du type bisphénol-S (*p*-hydroxyphénylène). On montre que la rupture est probablement peu importante dans des conditions normales de formation de polymères. L'effet de ces réactions secondaires hydrolytiques pour l'obtention d'un poids moléculaire élevé dans des conditions d'une stoechiométrie de réaction imparfaite est consistante avec les conditions ci-dessus.

Zusammenfassung

Das Molekulargewicht von Polysulfon, dem Arylpolyäther, der durch Reaktion des Dinatriumsalzes von Bisphenol A mit 4,4'-Dichlordiphenylsulfon in Dimethylsulfoxyd (DMSO) als Lösungsmittel hergestellt wird, hängt, wie gezeigt wird, unter anderem vom Feuchtigkeitsgehalt des polymerisierenden Systems ab. In Gegenwart von Wasser findet als Begleiterscheinung der Polymerisation eine Hydrolyse des Sulfonmonomeren statt. Dies führt zu einer Abweichung vom erwünschten 1:1-Verhältnis der miteinander reagierenden Gruppierungen und damit zu einer Verringerung des möglichen Molekulargewichts. Die Hydrolyse führt, wie gezeigt wird, zur Bildung des Natriumsalzes des 4-Chlor-4'-hydroxydiphenylsulfons und in geringerem Ausmass zu einem Polymeren, das durch Selbstkondensation dieses Salzes entsteht. In geringen Konzentrationen verhält sich dieses Salz im wesentlichen inert gegenüber der stattfindenden Hauptpolymerisation, in etwas höheren Mengen führt es zu einem wirksamen Kettenabbruch. Eine ähnliche Hydrolyse erleiden, wie angenommen wird, auch die Polysulfon-Chlorendgruppen, wenn die Polymerisation in Gegenwart von Wasser durchgeführt wird; diese erfolgt aber in geringerem Ausmass als bei dem monomeren Sulfon. Es wurde gezeigt, dass Polysulfon oder ähnliche Polyäther in DMSO-Lösung einer Kettenspaltung durch Basen unterliegen. Die Base greift die aktivierte, zur Sulfonylgruppe paraständige Position unter Bildung einer Kette, die am Ende eine Phenolgruppe vom Bisphenol A-Typ trägt, und einer Kette, die in einer Phenolgruppe vom Bisphenol S- (*p*-Hydroxyphenylsulfonyl-) Typ endet, an. Es wird gezeigt, dass die Spaltung unter den normalen Bedingungen der Polymerbildung wahrscheinlich nicht von Bedeutung ist. Die Auswirkungen dieser hydrolytischen Nebenreaktionen auf die Erreichung hoher Molekulargewichte unter den Bedingungen einer unvollkommenen Reaktionsstöchiometrie stehen, wie gezeigt wird, in Übereinstimmung mit den zuvor angeführten Folgerungen.

Received February 20, 1967

Prod. No. 5409A

New High Temperature Polymers. VI. Ordered Heterocycle Copolymers*

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Synopsis

A new class of linear, thermostable polymers is reported. The compositions are ordered heterocycle copolymers in which two different heterocycles alternate regularly along the polymer chain. Examples of combinations studied are: oxadiazole-benzimidazole, oxadiazole-pyromellitimide, and thiazole-pyromellitimide. The heterocycle copolymers, or alternatively, the corresponding precursor polymers, were prepared by condensing preformed di- or tetrafunctional blocks which contain one type of heterocycle with a second di- or tetrafunctional monomer under such conditions that no rearrangement of bonds occurred. The polymers are characterized in general by neither melting nor decomposing below 500°C. when heated in an inert atmosphere at a rate of about 10°C./min. Some of the copolymers are readily soluble in organic solvents; many, however, are soluble only in solvents such as concentrated sulfuric acid. In the case of the more intractable polymers, soluble precursor polymers can usually be prepared. In such precursor polymers only one of the heterocycles is preformed; the second heterocycle is formed by post-treatment after the polymer has been fabricated into an end product. All of the polymers yielded self-supporting films, some having very high strength; films of several of the polymers were hot-drawable. Drawn film of an ordered oxadiazole-imide copolymer was shown to be well oriented and moderately crystalline.

INTRODUCTION

Modern technology has demanded polymers which will perform well at temperatures greatly in excess of those at which present commercial materials are useful. Several routes to temperature-resistant polymers have been probed, but the most successful approach to high molecular weight polymers which can be fabricated into films or fibers has been the synthesis of wholly aromatic heterocycle polymers. Polymers of excellent thermal stability have been reported which contain heterocycles such as: benzimidazole,¹ 1,3,4-oxadiazole,² imide,^{3,4} quinoxaline,⁵ benzothiazole,⁶ and benzoxazole.⁷ Wallenberger⁸ has summarized our knowledge of those compositions reported which have been shaped into thermally stable films or fibers.

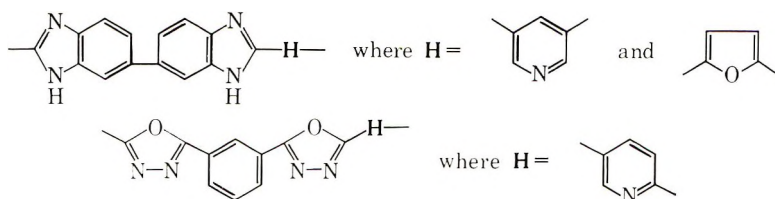
In this paper we wish to report the preparation of some high molecular weight, thermally stable, film-forming ordered heterocycle copolymers.⁹

* Presented in part at the 150th National Meeting, American Chemical Society, Atlantic City, N.J., September 1965.

This work is a continuation of our efforts to prepare thermally stable linear polymers by the ordered copolymer approach,^{10,11} an approach to polymerization which permits a very great degree of flexibility in tailoring polymers to meet specific needs. Such copolymerization is accomplished by first preparing a di- or tetrafunctional block into which units are incorporated in a predetermined way (in the present case one type of heterocycle and selected aromatic hydrocarbon units). This block is then condensed with another di- or tetrafunctional monomer (or another block of the type described) under such conditions that no rearrangement of bonds occurs.

Each of the polymers reported contains two different heterocycles which occur in a regularly alternating or ordered sequence, and further, each heterocycle is separated from the next one in the chain by an aromatic hydrocarbon unit (the benzene ring of a fused heterocycle, such as benzimidazole, is viewed as a separating aromatic hydrocarbon unit the same as a *m*- or *p*-phenylene unit). Regular alternation of different types of aromatic hydrocarbon units or regular alternation of isomeric hydrocarbon units, such as *m*-phenylene and *p*-phenylene rings, results in additional order in these polymers over that attained by alternation of the two heterocycles. By judicious selection of the two heterocycles and the aromatic hydrocarbon units one can make polymers having the desired balance of properties—thermal stability, tractability, crystallinity, modulus, glass transition temperature, and drawability. The use of two different heterocycles permits the construction of a much wider range of compositions than the use of only one. This approach, far more so than would a random copolymer approach, makes possible the preparation of thermostable polymers which are sufficiently tractable to be useful, but which at the same time have high glass transition temperatures and are high melting and crystalline.

Examples of a few other polymers with two alternating heterocycles have appeared in the literature;^{1,2} in each of the reported cases, however, the heterocycles were adjoining.



The regular alternation of *m*-phenylene and *p*-phenylene rings between the heterocyclic units of polyheterocycles has also been reported: the alternation of these units between the 1,3,4-oxadiazoles of a poly-1,3,4-oxadiazole¹² and the 4-phenyl-1,2,4-triazoles of a poly-4-phenyl-1,2,4-triazole¹³ was advantageous with regard to polymer properties.

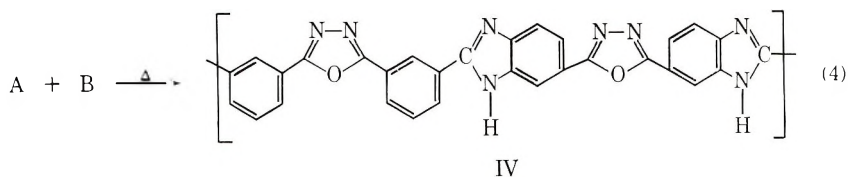
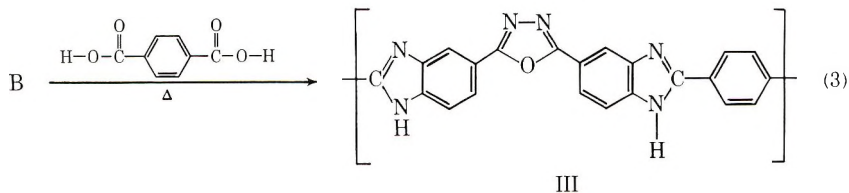
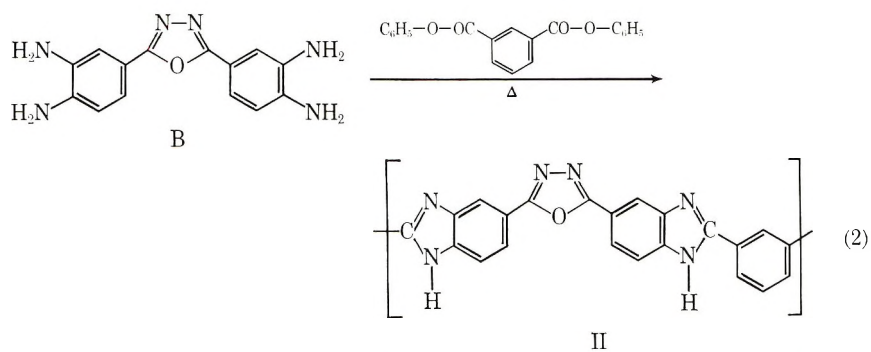
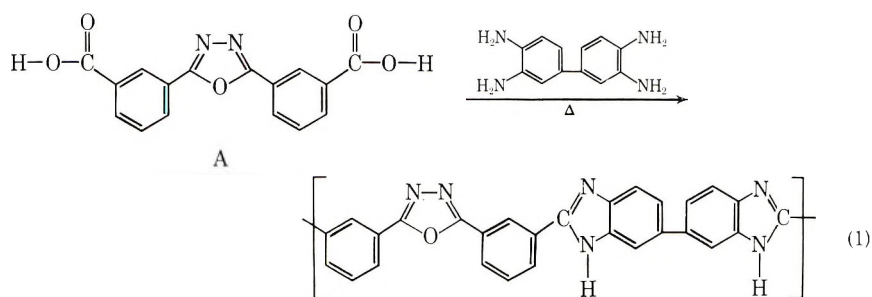
The preparative routes to several ordered heterocycle copolymers are illustrated with structural formulas in eqs. (1)–(10).

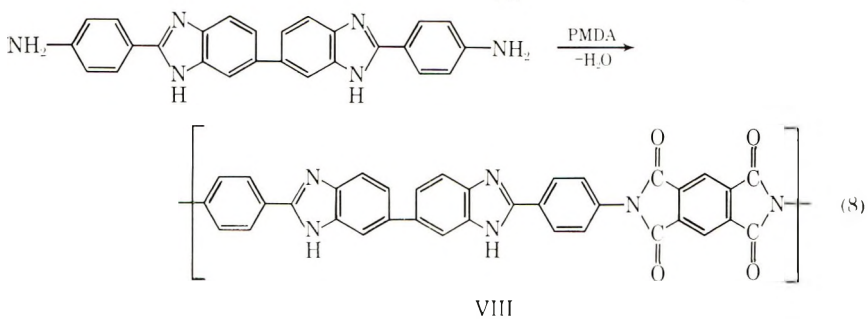
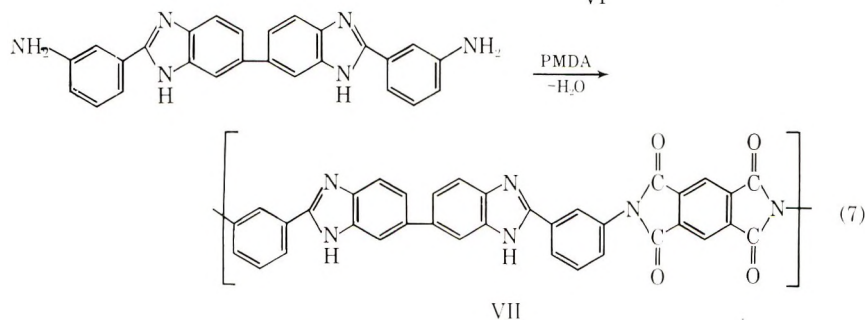
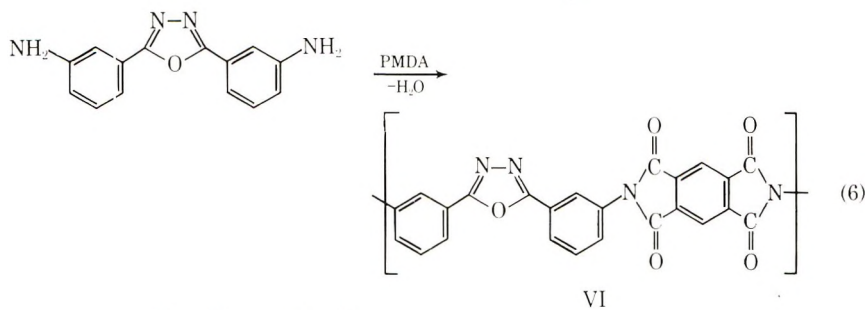
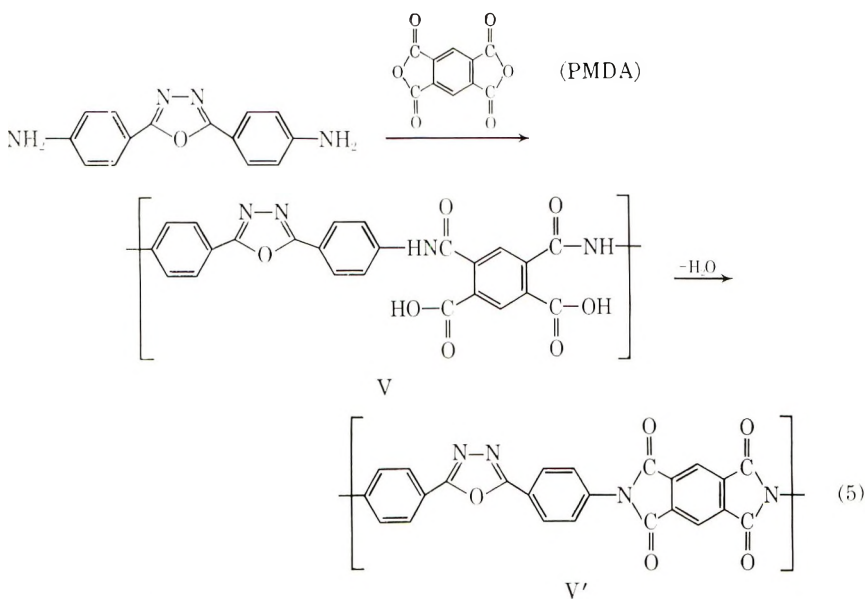
EXPERIMENTAL

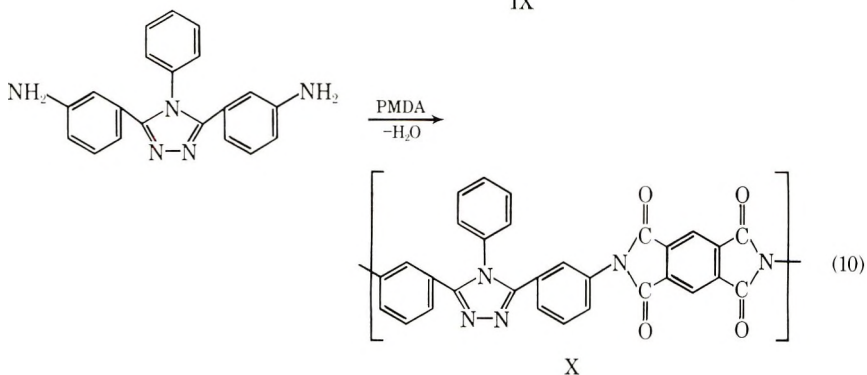
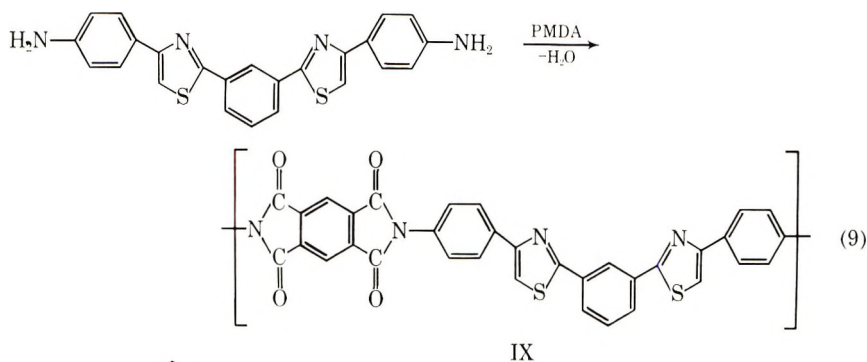
The preparation of the di- and tetrafunctional heteroaromatic monomers is described elsewhere.¹⁴ Pyromellitic dianhydride was purified by recrystallization from acetic anhydride followed by sublimation. Inherent viscosities were determined at 30°C. on solutions of 0.5 g. of polymer dissolved in 100 ml. of solvent.

Polymerizations

Polymerizations were carried out as solid-state thermal polycondensations or as low temperature solution polycondensations.¹⁵







Preparation of Polymers I and II. The appropriate diacid or derivative thereof was heated with the appropriate tetraamine at 220°C. under a nitrogen atmosphere for 10 min., then at 265°C. for 30 min., and finally at 400°C. under 0.1 mm. pressure for 3 hr. Films were cast from dimethyl sulfoxide solutions of the polymers.

Alternatively, the polymers were prepared as described in the following section. Polymer of apparently higher molecular weight was obtained which was soluble only in concentrated sulfuric acid.

Preparation of Polymers III and IV. Equimolar quantities of reactants were heated in polyphosphoric acid (PPA) at 220–220°C. under inert atmosphere for 3 hr. The PPA solution was cooled to 100°C. and the polymer was precipitated in water and allowed to soak overnight. These polymers had inherent viscosities in concentrated sulfuric acid of 0.93 and 0.44, respectively.

Preparation of Polymers V–X. The heteroaromatic diamines were placed in dimethylformamide (DMF) or dimethylacetamide (DMAc), cooled to 0°C., and equivalent amounts of pyromellitic dianhydride (PMDA) were added. The solutions were stirred for 1 hr. at 0°C. then for approximately 20 hr. at room temperature. An aliquot of the solution of polymer was removed, diluted and the inherent viscosity (η_{inh}) of the polymer determined. Thus, the η_{inh} of V was found to be 1.92. Films of the amic-acid polymers were spread onto glass plates, baked at 140°C. for 1 hr. to expel the solvent, and then heated at 300°C. for 1–3 hr. to effect

cyclodehydration to the corresponding imide; the η_{inh} of film of V' in concentrated sulfuric acid was 0.5.

Chemical cyclodehydration also was applied in some cases; it proved advantageous for preparing the thiazole-imide copolymer, IX. As a typical example, films of the amic-acid precursor to IX were soaked in a mixture¹⁶ of three parts acetic anhydride and two parts pyridine for 48 hr., placed in dioxane for 1 hr., air-dried, and finally dried at 110°C. for 1 hr.

Structural Characterization

The analyses of the polymers (Table I) support the assignments of structure. Furthermore, the infrared spectra of the polymers were in agreement with the proposed structures. The presence of the heterocycle

TABLE I
Nitrogen Analyses for Ordered Heterocycle Copolymers

Polymer	N, %	
	Calculated	Found
I	18.50	16.7
II	22.33	19.2
III	22.33	20.8
IV	21.53	18.1
V'	12.96	12.7
VI	12.96	12.7
VII	13.98	13.1
VIII	13.98	12.6
IX	9.21	9.0
X	13.75	13.4

formed by the polycondensation reaction was shown by absorption peaks as follows: polymers I-IV, benzimidazole, absorption peaks¹ at 1620 and 1530 cm.^{-1} ; polymers V'-X, imide absorption peaks⁴ at 1770 and 717 cm.^{-1} . The presence of the heterocycle preformed prior to polymerization was determined by elemental analysis of the intermediates.¹⁴

RESULTS AND DISCUSSION

Fabrication of Polymers

All of the polymers were soluble as such or in the form of a polymeric precursor, and could be fabricated to films of high strength. Polymers V'-X were prepared stepwise; first, a soluble, isolable poly(amic acid) precursor, as exemplified by V, was made; this was then converted to the desired ordered heterocycle copolymer by cyclodehydration.

Films of several of the polymers were hot-drawn; examination of the drawn film of the ordered oxadiazole-imide copolymer V' by x-ray diffraction showed it to be well oriented and moderately crystalline (Fig. 1).

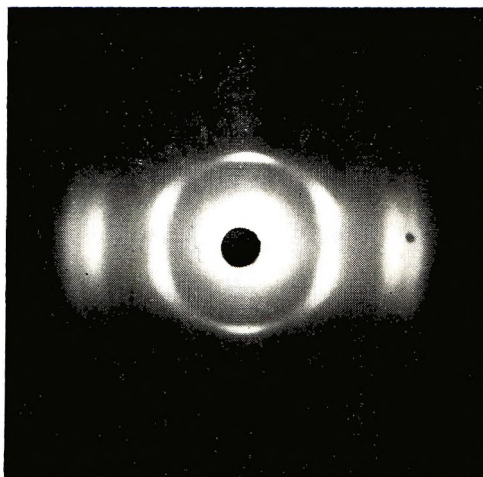


Fig. 1. X-ray diagram of an ordered heterocycle copolymer film (V').

Thermal Stability

All of the polymers were very thermally stable and high melting as indicated by the data obtained from differential thermal analysis (DTA) in nitrogen, thermogravimetric analysis (TGA) in nitrogen, and visual observation of films placed on hot surfaces. The TGA and DTA data for all the polymers are summarized in Table II; selected DTA and TGA plots are given in Figures 2-4. Polymer melt temperatures were determined by differential thermal analysis (Table II).

TABLE II
Thermal Properties of Ordered Heterocycle Copolymers

Polymer	Melt transition temperature, °C. ^a	Decomposition temperature, °C. ^b
I	530	585
II	525	520
III	>400 ^c	500
IV	480 ^c	480
V'	520 ^c	525
VI	500	500
VII	530	510
VIII	575 ^c	575
IX	565 ^d	550
X	450 ^e	510

^a Endothermic transition observed by differential thermal analysis (DTA) in nitrogen (rate = 10°C./min.).

^b Decomposition temperature observed by thermogravimetric analysis (TGA) in nitrogen (rate = 15°C./min.).

^c Rate = 20°C./min.

^d Sample was a film which was hot drawn at 350°C. and again at 425°C. prior to testing.

^e The softening point of the film on a hot surface in air was 350°C.

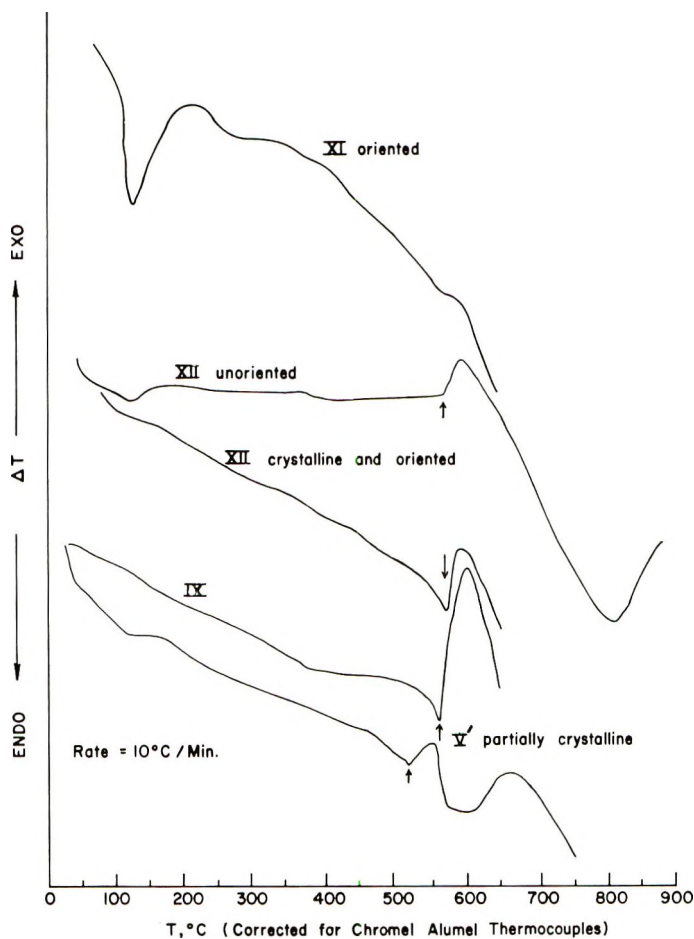


Fig. 2. Programmed DTA (in nitrogen) of some polymers containing heterocycles.

Although the ordered heterocycle copolymers do not melt in the conventional sense, an endothermic transition (which is followed closely by an exothermic transition) is observed for most, which is indicative of an incipient melting phenomenon (Fig. 2). Films which are well oriented or are oriented and crystalline usually exhibit such an endotherm. Unoriented films of polymers which crystallize readily, e.g. XII, may not show the endotherm, but only the exotherm which occurs at or near the same temperature for the oriented and crystalline film. Although films of polymers which are exceedingly difficult to crystallize, e.g. XI, may be well oriented by hot drawing, they nevertheless show neither an exothermic nor an endothermic transition, even at the temperature at which severe weight loss begins.

The polymer decomposition points were obtained by continuous thermogravimetric analysis (Table II). The values given are the tempera-

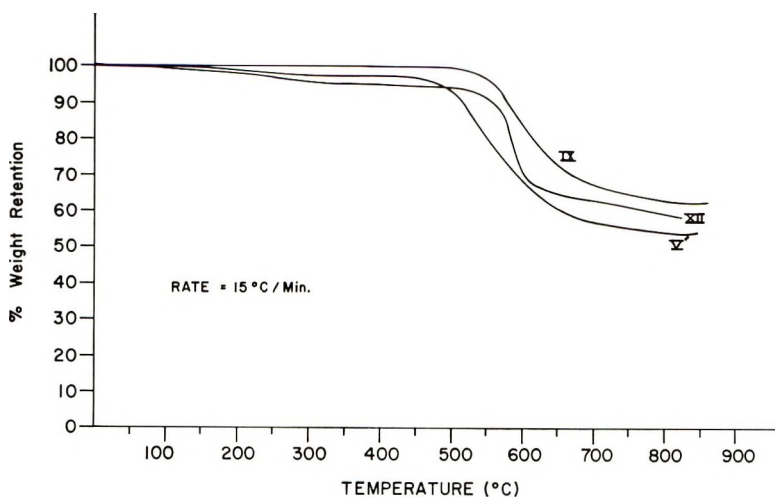


Fig. 3. Programmed TGA (in nitrogen) of polymers containing heterocycles.

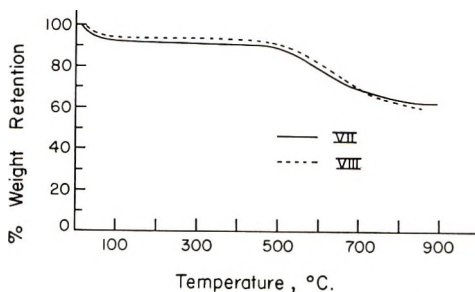


Fig. 4. Programmed TGA (in nitrogen, rate = 15°C./min.) of ordered benzimidazole-imide copolymers (VII and VIII).

tures at which the onset of rapid loss of weight began; these values are also the temperatures at which the weight loss was approximately 10% of the original weight after correction for loss of absorbed solvent or water. The decomposition temperature for a given heterocyclic ring of an ordered heterocycle copolymer can be readily detected when the decomposition temperature of the other ring is higher and is known independently. Figure 3 shows TGA plots of a polyimide homopolymer (XII), an ordered thiazole-imide copolymer (IX), and an oxadiazole-imide ordered copolymer (V'). The break in the TGA plot for V' is due to decomposition of the oxadiazole ring of V'; the plot for IX shows that the thiazole ring is approximately as thermally stable as is the imide ring.

With the exception of polymer X, the melting points and decomposition temperatures were remarkably alike for the various polymers. For example, the TGA thermograms (Fig. 4) of the two polyimides, VII and VIII, are essentially identical, even though one polymer has *m*-phenylene units whereas the other *para* units. This observation contrasts sharply with

that made for aromatic ordered copolyamides where thermal stability increases as *p*-phenylene content increases.¹¹

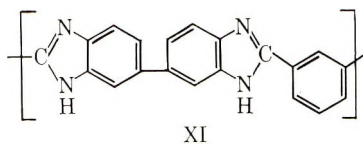
The order of thermal stability based on DTA and TGA data obtained in an inert atmosphere for the various heterocycles incorporated in the polymers reported here appears to be: imide > benzimidazole > thiazole > 1,3,4-oxadiazole > 4-phenyl-1,2,4-triazole. Possibly more important than thermal stability as gauged by melting point and decomposition temperature is long-term oxidative stability at moderately elevated temperatures. Quite another order of stability was observed when films were heated at 300°C. in air for long periods of time: 1,3,4-oxadiazole > imide > 4-phenyl-1,2,4-triazole > benzimidazole ≫ thiazole.

The oxidative thermostability of film of V', the pyromellitimide of 2,5-bis(*p*-aminophenyl)-1,3,4-oxadiazole, was compared (Table III) with that

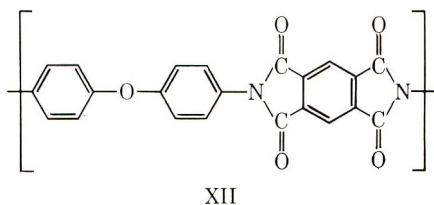
TABLE III
Heat-Aging of Films of Some Polyheterocycles in Air

Polymer	Aging	Remarks
V'	(Polyoxadiazole-imide)	300 35 Relatively unaffected
XII	(Polypyromellitimide)	300 35 Relatively unaffected
XI	(Polybenzimidazole)	300 2 Badly embrittled
V'	(Polyoxadiazole-imide)	350 4 Still flexible
XII	(Polypyromellitimide)	350 4 Failed
XI	(Polybenzimidazole)	350 4 Disappeared

of film of two thermostable polymers that have received considerable attention by others: poly-2,2'-*m*-phenylene-5,5'-bibenzimidazole (PBI)¹ (XI, prepared by a modification of a procedure reported by Iwakura¹⁷ et al.)



and of film of the pyromellitimide of 4,4'-oxydianiline (XII, prepared by the method of Sroog¹ et al.).



The films were heated in a muffle furnace at 300°C. in air; the ability of the films to be flexed after exposure was taken as the primary measure of

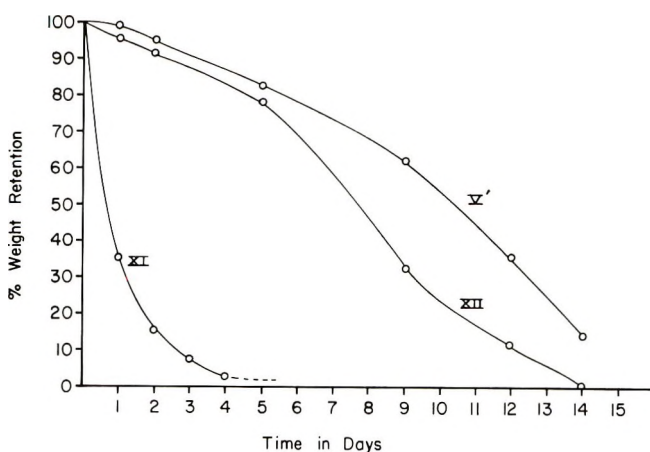


Fig. 5. Weight retention at 350°C. in air for films of polymers containing heterocycles.

stability. Films of V' and XII were relatively unaffected after 5 weeks at 300°C., but film of XI (PBI) was severely embrittled after only 48 hr. Upon accelerated heat-aging at 350°C. in air, film of V' was still flexible after 4 days whereas film of XII had failed. Figure 5 shows the retention of weight for films V', XI, and XII during this test.

The authors wish to express their appreciation to Mr. R. W. Smith for the preparation of one of the intermediates used, and to Messrs. W. L. Hofferbert, Jr. and M. T. Bryant for their excellent technical assistance.

The suggestions and criticisms of Dr. H. C. Bach and Dr. W. F. DeWinter are gratefully acknowledged.

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Résumé

Une nouvelle classe de polymères linéaires thermostables est rapportée. Les compositions se rapportent à des copolymères hétérocycliques coordonnés dans lesquels deux hétérocycles différents alternaient régulièrement le long de la chaîne principale. Les exemples de combinaisons étudiées sont: oxadiazole-benzimidazole, oxadiazole-pyromellitimide, et thiazole-pyromellitimide. Les copolymères hétérocycliques, ou alternativement, les polymères précurseurs correspondants ont été préparés par condensation de blocs di- ou tétrafonctionnels préformés qui contiennent un type d'hétérocycle avec un monomère di- ou tétrafonctionnel secondaire dans des conditions telles qu'il n'y ait pas de réarrangement de liaisons. Les polymères sont caractérisés en général par le fait qu'ils ne fondent, ni se décomposent en-dessous de 500°C lorsqu'ils sont chauffés sous atmosphère inerte à une vitesse d'environ 10°C par minute. Certains des copolymères sont facilement solubles dans les solvants organiques; beaucoup, toutefois, sont solubles uniquement dans des solvants tel que l'acide sulfurique concentré. Dans le cas des polymères plus solubles, des polymères précurseurs solubles peuvent être usuellement préparés. Dans de tels polymères précurseurs uniquement un des hétérocycles a été formé; le second hétérocycle est formé par post-traitement après que le polymère ait été transformé en son produit final. Tous les polymères fournissaient des films autoporteurs, certains ayant une force très élevée; des films de la plupart des polymères sont étirables à chaud. Les films étirés du copolymère ordonné oxadiazole-imide étaient bien orientés et modérément cristallins.

Zusammenfassung

Es wird über eine neue Klasse linearer, thermostabiler Polymerer berichtet, die geordnete, aus heterocyclischen Einheiten aufgebaute Copolymere darstellen, bei denen zwei verschiedene Heterocyclen regelmässig entlang der Polymerkette alternieren. Beispiele für die untersuchten Kombinationen sind: Oxadiazol-Benzimidazol, Oxadiazol-Pyromellithimid, und Thiazol-Pyromellithimid. Die heterocyclischen Copolymeren oder anderenfalls die ihnen entsprechenden polymeren Vorstufen wurden durch Kondensation vorgebildeter di- oder tetrafunktioneller Blöcke, die den einen Typus der Heterocyclen enthalten, mit einem zweiten di- oder tetrafunktionellen Monomeren unter solchen Bedingungen hergestellt, unter denen keine Umlagerung erfolgt. Die Polymeren sind im allgemeinen dadurch ausgezeichnet, dass sie in einer inerten Atmosphäre unterhalb von 500°C bei einer Erhitzungsgeschwindigkeit von etwa 10°C pro Minute weder schmelzen noch eine Zersetzung erleiden. Einige Copolymere sind leicht in organischen Lösungsmitteln löslich; viele lösen sich jedoch nur in Lösungsmitteln wie konzentrierter Schwefelsäure. Im Falle der schlechter verarbeitbaren Polymeren können gewöhnlich lösliche Polymervorstufen hergestellt werden. In diesen Vorstufen ist nur einer der Heterocyclen vorgebildet, der zweite Heterocyclus wird durch eine Nachbehandlung gebildet, nachdem das Polymere bereits zu seiner endgültigen Form verarbeitet wurde. Alle Polymeren lieferten freitragende Filme, von denen einige sehr hohe Festigkeit besitzen; die Filme mehrerer Polymerer konnten im heissen Zustand gestreckt werden. Wie gezeigt wurde, ist ein gestreckter Film eines geordneten Oxadiazol-Imid-Copolymeren gut orientiert und etwas kristallin.

Received March 17, 1967

Prod. No. 5410A

Syntheses of Optically Active Polymers by Condensation Polymerization of *d*-Tartaric Acid with Some Diamines

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Synopsis

In order to synthesize optically active polymers which have asymmetric carbon atoms in the polymer main chain, polyamides were synthesized at high temperatures by the condensation of the salt prepared from *d*-tartaric acid with diamines, such as hexamethylenediamine, *o*-, *m*-, and *p*-phenylenediamine. Effects of the solvent, polymerization time, intrinsic viscosity, and pH on the degree of the specific rotation of polyhexamethylene-*d*-tartaramide, were investigated. From the results of hydrolyses of the polymers, it was found that *d*-tartaric acid is not racemized during condensation polymerization.

INTRODUCTION

Recently, attention has begun to be focused on the stereoregular polymerization of vinyl monomers, and investigations of optically active polymers have been widely carried out.

The polymerization of the vinyl monomers having optically active groups as substituents has been widely investigated. It was found by many investigations^{1,2} that the optical activity of the optically active homopolymers disappear when optically active carbon atoms were removed from the side chain of the polymer. On the contrary, in the case of copolymers of maleic anhydride with *l*- α -methyl benzyl methacrylate³ or *l*- α -methyl benzyl vinyl ether,⁴ the copolymer retained some optical activity after removal of the side chain containing original asymmetric centers. Therefore, asymmetric induction in the free-radical-catalyzed polymerization of optically active vinyl monomers is possible by the defect of pseudoasymmetric carbon atoms which do not contribute to optical activity.

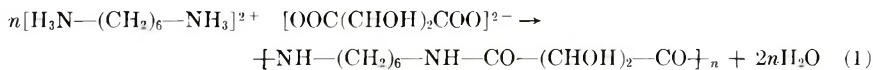
Recently, Natta and Farina reported that the optically active polymers could be obtained by ionic polymerization of optically inactive monomers, such as sorbic acid methyl ester⁵ or benzofuran.⁶ In this case it was expected that asymmetric induction was due to the breaking of pseudo-asymmetry. The ring-opening polymerization of *l*-lactide,⁷ optically active propylene oxide^{8,9} and propylenimine¹⁰ have also been studied.

In this work we have chosen polymers of alkylene- or arylene-*d*-tartaramide for investigation of optically active polymers containing asymmetric

centers in the backbone. The polyamide syntheses were carried out by high temperature condensation of the salts obtained from *d*-tartaric acid with some diamines such as hexamethylenediamine or *o*-, *m*-, or *p*-phenylenediamine. The salts were prepared by the usual method. The general structures are:



When the salts of hexamethylenediamine and *d*-tartaric acid is condensed, a polymer is formed, as shown in eq. (1).



The polyamide is fiber-forming, hygroscopic, and optically active. In the final step the polyamide was hydrolyzed to determine whether *d*-tartaric acid was racemized during the condensation polymerization.

EXPERIMENTAL

Materials

Commercially available *d*-tartaric acid which has $[\alpha]_{\text{D}}^{20} = +15.0^\circ$ in water was used without further purification. Hexamethylenediamine supplied by Toyo Rayon Co., Ltd., was distilled at a reduced pressure over potassium hydroxide. Commercially supplied *o*-, *m*-, and *p*-phenylenediamines were used without further purification.

Preparation of Diamine-*d*-tartaric Acid Salt

A typical preparation of the hexamethylenediamine-*d*-tartaric acid salt used in this work, is described below:

d-Tartaric acid (0.7 g., 0.1 mole) dissolved in hot absolute ethanol to saturation was added to hot absolute ethanol saturated with 11.6 g. (0.1 mole) of hexamethylenediamine. Precipitation soon occurred on mixing. After standing overnight, the salt was filtered off, washed with cold absolute ethanol, and dried *in vacuo* to constant weight. Similar reactions were carried out for preparation of other diamine-*d*-tartaric acid salts. Table I shows the yields, melting points, specific rotations, and analyses of the salts; all of them are white powders.

Preparation of Polyhexamethylene-*d*-tartaramide

The hexamethylenediamine-*d*-tartaric acid salt was placed in a polymerization tube.

The atmosphere in the reaction tube was completely replaced with nitrogen by repeated freeze-heat cycles. The tube was then placed in an oil bath, and the reaction was carried out at 140–145°C. for required times. After the reaction the oil bath was removed and the reaction mixture was cooled to room temperature. The pressure was then increased to atmos-

TABLE I
Salts of *d*-Tartaric Acid with Some Diamines

Diamine	Yield, %	M.p., °C.	$[\alpha]_D^{25}$ ^a	Anal.					
				Calculated			Found		
				C, %	H, %	N, %	C, %	H, %	N, %
Hexamethylenediamine	92	143-5	+29.5° (<i>t</i> = 12°C.)	45.11	8.72	10.50	44.74	7.91	9.80
<i>o</i> -Phenylenediamine	85	157	+18.2° (<i>t</i> = 18°C.)	46.51	5.43	10.85	46.27	5.83	10.22
<i>m</i> -Phenylenediamine	98	161-2	+17.7° (<i>t</i> = 18°C.)	46.51	5.43	10.85	45.91	5.49	10.66
<i>p</i> -Phenylenediamine	90	165	+12.0° (<i>t</i> = 18°C.)	46.51	5.43	10.85	46.62	5.51	10.66

^a *c* = 0.5-1 in water.

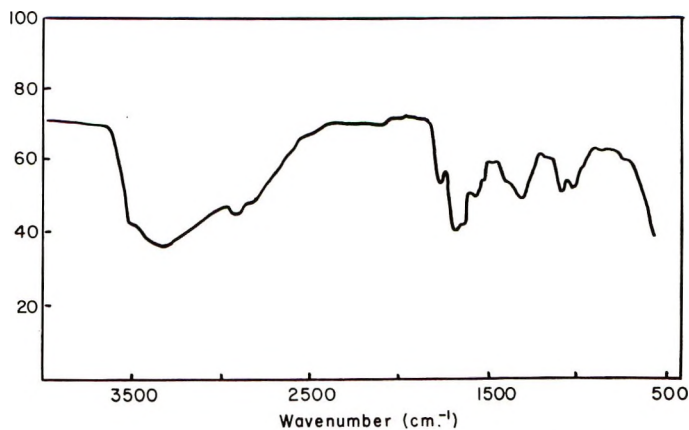


Fig. 1. Infrared spectrum of polyhexamethylene-*d*-tartaramide.

pheric pressure with nitrogen. A brown, opaque, hygroscopic, optically active polyamide was obtained.

As shown in Figure 1, the infrared spectrum of this polymer had absorption bands at 1650 and 1550 cm^{-1} due to $-\text{CONH}-$ group, at 3600–3200 cm^{-1} due to $-\text{OH}$ and $-\text{NH}$ group, and at 2925, 2850, 1350, 1100, and 1065 cm^{-1} due to the $-\text{CH}_2-$ group.

Fiber was obtained by the melt method. The results obtained are shown in Table II.

TABLE II
Data for Polyhexamethylene-*d*-tartaramide

Expt. no.	Polymerization time at 140–145°C., hr.	$[\eta]$, dl./g. ^a	$[\alpha]_D^{18}$ ^b	Yield, %	Anal., found ^c		
					C, %	H, %	N, %
1	3.8	0.0261	+47.6°	77	—	—	—
2	8	0.0264	+35.7°	90	—	—	—
3	16	0.0308	+31.8°	90	—	—	—
4	21	0.0340	+28.3°	83	—	—	—
3p ^d	—	0.0326	+29.5°	—	46.97	8.02	10.28
3f ^d	—	0.0280	+34.1°	—	45.72	7.82	10.21
4p ^d	—	0.0326	+28.3°	—	45.78	8.31	10.02
4f ^d	—	0.0321	+30.9°	—	46.45	8.15	9.35

^a Measured at 30°C. in water solution.

^b $c = 0.32\text{--}0.5$ g./100 ml. in water.

^c Calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{N}_2$: C, 52.17%; H, 7.83%; N, 12.17%. It seems that the degree of polymerization is low and both endgroups of the polymer main chain are carboxyl groups.

^d Fractional precipitation of samples 3 and 4 with ethanol from water was carried; 3p and 4p indicate precipitates and 3f and 4f indicate ethanol-soluble portions of samples 3 and 4, respectively.

Preparation of Poly-*o*-Phenylene-*d*-tartaramide

The high temperature condensation polymerization of the salt was carried out by the method described above at 145°C. for 2 hr. *in vacuo*. The polyamide obtained was dark green and was insoluble in water and soluble in formic acid, sulfuric acid, and *N,N*-dimethylformamide.

The polymer was purified by reprecipitation from formic acid with water; yield, 78%. The specific rotation of the polymer could not be measured due to the dark green color of the polymer. The softening temperature was 255°C., and $[\eta]$ in concentrated H₂SO₄ was 0.025.

ANAL. Calcd. for C₁₀H₁₂O₄N₂: C, 54.05%; H, 4.54%; N, 12.61%. Found: C, 53.04%; H, 4.63%; N, 11.22%.

Preparation of Poly-*m*-phenylene-*d*-tartaramide

High temperature condensation polymerization was carried out by the same method as described above. The salt was melted at 160°C.; after 1/2 hr. at this temperature, the viscous liquid became a solid which did not melt at higher temperature.

The polymer was a dark yellow-green powder, soluble in concentrated sulfuric acid and insoluble in water. The polymer was purified by reprecipitation from sulfuric acid with water. The specific rotation of the polymer could not be measured due to the dark yellow color of the polymer. The softening temperature was 275°C., and $[\eta]$ in concentrated H₂SO₄ was 0.0285.

ANAL. Calcd. for C₁₀H₁₂O₄N₂: C, 54.05%; H, 4.54%; N, 12.61%. Found: C, 58.93%; H, 4.08%; N, 11.79%.

Preparation of Poly-*p*-phenylene-*d*-tartaramide

High temperature condensation polymerization was carried out by the same method as described above.

When the salt, which melts at 165°C., was heated *in vacuo*, a gradual decomposition occurred, and a yellow powder was obtained. Little change occurred on further heating at higher temperature. The yellow powder was soluble in concentrated sulfuric acid and *N,N*-dimethylformamide.

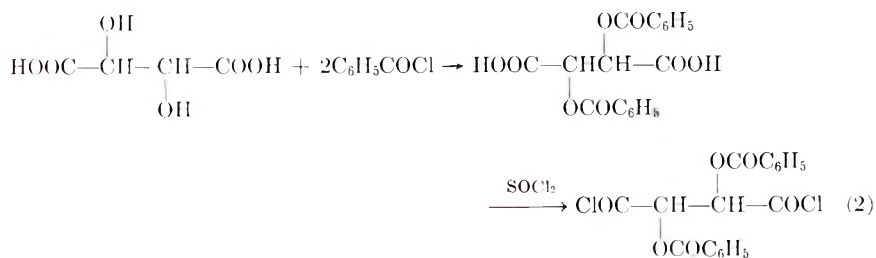
Interfacial Polycondensation of Diamines with *d*-Tartaric Acid Derivatives

d-Tartaric acid was esterified by benzoyl chloride and chlorinated with thionyl chloride to obtain dibenzoyl-*d*-tartaric acid chloride, which was used for the interfacial polycondensations with some diamines.

The product I had $[\alpha]_D^{25} = -101.4^\circ$ ($c = 1.0$ in methanol); m.p. 87–89°C.

The interfacial polycondensation of acid chloride I with hexamethylenediamine was attempted out by the following method.

Hexamethylenediamine (5.7 g., 0.049 mole), sodium carbonate (10.6 g., 0.10 mole), and sodium lauryl sulfate (2 g.) (surface active agent) were



I

dissolved in 250 ml. of water. To this was added rapidly, with vigorous stirring, 150 ml. of benzene containing 20.3 g. (0.051 mole) of dibenzoyl-*d*-tartaric acid dichloride. Polymerization of the acid chloride with diamine on the water-benzene interface was not observed at room temperature. The reaction mixture was heated at 60°C. on a water bath for 1/2 hr. but polymerization did not occur.

A similar procedure was used for *o*-, *m*-, and *p*-phenylene-diamines; however, no polymerization took place.

Hydrolysis of Polyhexamethylene-*d*-tartaramide

A 2-g. portion polyamide (Table II, expt. 4p) was dissolved in 14 g. of 10% hydrochloric acid. After the reaction mixture was refluxed at 120–125°C. for 5 hr., it was cooled to room temperature, and 2 g. of solid potassium hydroxide was added to the reaction mixture. A white precipitate rapidly appeared, but when more solid potassium hydroxide was added, the white precipitate gradually dissolved. Therefore, hydrochloric acid was gradually added to the solution until the amount of the white precipitate appeared to reach a maximum.

The precipitate was filtered, washed several times with water, and recrystallized two times from water; it had $[\alpha]_{\text{D}}^{20.5} = +27.7^\circ$ ($c = 0.324$ in water).

ANAL. Calcd. for $\text{C}_4\text{H}_3\text{O}_6\text{K}$: C, 25.50%; H, 2.68%. Found: C, 25.48%; H, 2.61%

Preparation of Potassium Hydrogen *d*-Tartarate

Potassium hydroxide powder was added to an aqueous solution of *d*-tartaric acid until the amount of the precipitate formed appeared to be a maximum. The precipitate was filtered off and washed several times with water. The white precipitate was recrystallized twice from water. Both infrared spectrum (Fig. 2) and elemental analysis of the potassium salt were in agreement with those of the salt obtained by hydrolysis of the polymer described above; $[\alpha]_{\text{D}}^{20.3} = +27.0^\circ$ ($c = 0.315$ in water).

ANAL. Calcd. for $\text{C}_4\text{H}_3\text{O}_6\text{K}$: C, 25.50%; H, 2.68%. Found: C, 25.51%; H, 2.62%.

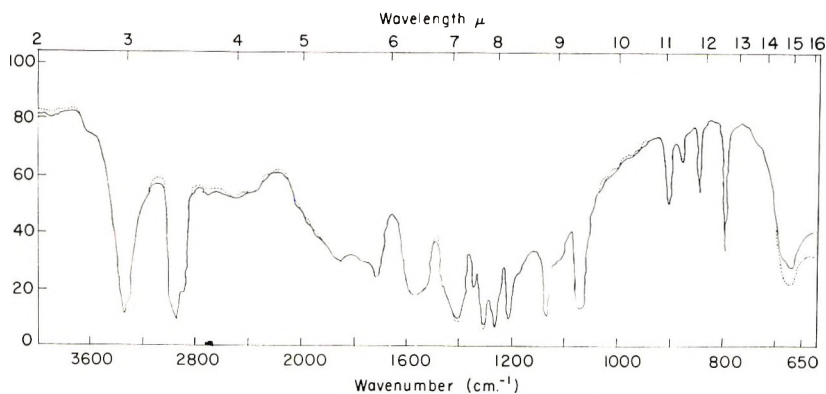


Fig. 2. Infrared spectrum of potassium salt of *d*-tartaric acid.

Measurements of Optical Activity

The optical rotatory powers of 0.32–1% solutions in water were measured at room temperature by use of a 1-dm. tube and a PO-B type Hitachi polarimeter with a 589 $m\mu$ light source. The optical rotatory powers of polymers and salts were measured for constant concentration.

Infrared Spectra of Potassium Acid-*d*-Tartarates

The infrared spectra of potassium acid-*d*-tartarates obtained from the result of hydrolysis of polyamide and the neutralization of *d*-tartaric acid with potassium hydroxide are shown in Figure 2. The two infrared spectra are closely similar.

RESULTS AND DISCUSSION

Solubility of Salts

All salts were insoluble in cyclohexane, benzene, toluene, *p*-xylene, methanol, ethanol, chloroform, carbon tetrachloride, and petroleum ether, and soluble in polar solvents such as dioxane, acetaldehyde, benzaldehyde, acetone, formic acid formamide, and water. The *o*-, *m*-, and *p*-phenylenediamine-*d*-tartaric acid salts were soluble in methyl acetate, aniline, pyridine and ethyl acetate, and the hexamethylenediamine-*d*-tartaric acid salt was insoluble in the above solvents.

Specific Rotation of Salt

It is interesting to note the specific rotations of the nylon salts of the three isomers, *o*-, *m*-, and *p*-phenylenediamine, tend to decrease with increase in the symmetry between two amino groups of phenylenediamine.

Solubilities of Polymers

All polymers were soluble in sulfuric acid. Polyhexamethylene-*d*-tartaramide was soluble in water and poly-*o*- and *m*-phenylene-*d*-tartaramide were insoluble in water. Polyhexamethylene-*d*-tartaramide and poly-*o*-phenylene-*d*-tartaramide were soluble in phenol, formic acid, and formamide, and poly-*o*- and *m*-phenylene-*d*-tartaramide were soluble in dimethyl sulfoxide. All polyamides were insoluble in cyclohexane, benzene, toluene, methanol, ethanol, *n*-butanol, dioxane, acetone, methyl

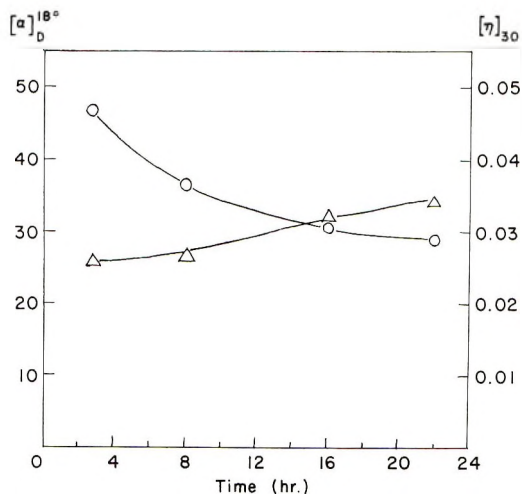


Fig. 3. Relation of (○) the specific rotation $[\alpha]_D$ and (Δ) polymer viscosity with the polymerization time.

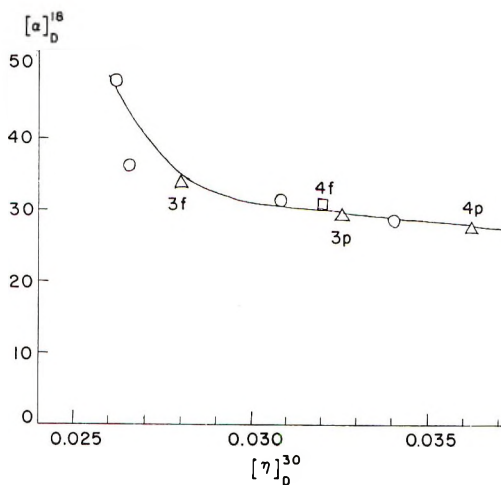


Fig. 4. Relation of the specific rotation with $[\eta]$ of the polymer.

acetate, carbon tetrachloride, aniline, pyridine, benzoyl chloride, petroleum ether, dichloroethane, and benzonitrile.

Specific Rotation

Figure 3 shows the plot of specific rotation and intrinsic viscosity versus polymerization time; the data are summarized in Table II. The intrinsic viscosity increases and the specific rotation decreases with increasing polymerization time.

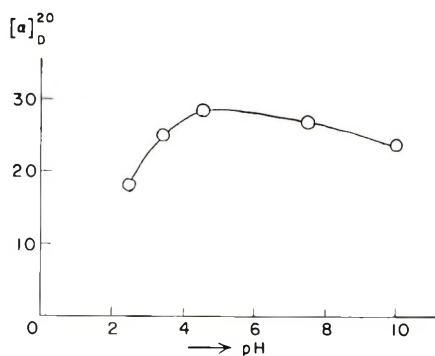


Fig. 5. Relation of specific rotation $[\alpha]_D$ with pH.

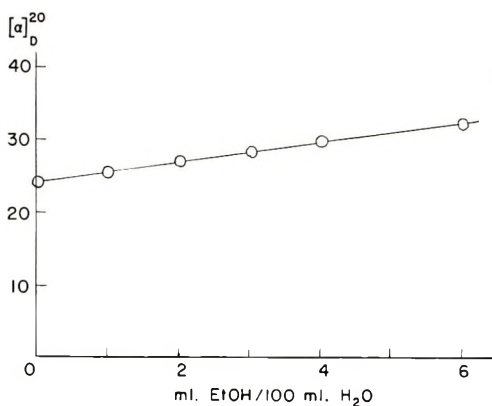


Fig. 6. Relation of the specific rotation to amount of poor solvent added.

Figure 4 shows the relation of specific rotation and intrinsic viscosity. The specific rotation decreases with increasing of the intrinsic viscosity, but it is interesting that the specific rotation reached constant value which is identical with the specific rotation of the salt, $+29.5^\circ$.

The relationship between the specific rotation of polyamide and the pH values is shown in Figure 5. The specific rotation showed a maximum

value on variation of pH. Because of the very low molecular weight of the polymer, the ionization of the free amino group and carboxyl group are probably the significant factor. pH values were measured by a pH meter with normal hydrochloric acid and sodium hydroxide solution.

The linear relationship between the amount of precipitant (EtOH) in polymer solution and $[\alpha]_D$ of the polymer (3p in Table II) is shown in Figure 6. The specific rotation increased with the addition of a precipitant such as ethyl alcohol.

Hydrolysis of Polymer

The polymer shown in Table II was hydrolyzed with hydrochloric acid, and the *d*-tartaric acid formed was precipitated as potassium acid-*d*-tartarate.

The potassium acid-*d*-tartarate obtained was compared with the potassium acid-*d*-tartarate which was prepared from *d*-tartaric acid by the same method described above. From the fact that infrared spectra and elemental analyses of both products are identical, it seems that *d*-tartaric acid was not racemized during polymerization.

We wish to thank Dr. Y. Shinohara of Toyo Rayon Co., Ltd. who supplied hexamethylenediamine for this work.

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Résumé

En vue de synthétiser des polymères optiquement actifs contenant des atomes de carbone assymétriques dans la chaîne polymérique principale, des polyamides ont été synthétisés à température élevée par condensation du sel préparé au départ d'acide tartarique-*d* avec des diamines, telles que l'hexaméthylènediamine, l'*o*-, *p*- et *m*-phénylènediamine. Les effets du solvant, de la durée de polymérisation, de la viscosité intrinsèque et du pH sur le degré de rotation spécifique du polyhexaméthylène-*d*-tartramide ont été étudiés. Au départ de résultats d'hydrolyse de ces polymères, on a trouvé que l'acide tartarique-*d* n'était pas racémisé au cours de la polymérisation par condensation.

Zusammenfassung

Zur Herstellung optisch aktiver Polymerer mit asymmetrischen Kohlenstoffatomen in der Hauptkette des Polymeren wurden bei hohen Temperaturen Polyamide durch

Kondensation des aus *d*-Weinsäure mit Diaminen, wie Hexamethyldiamin, *o*-, *m*- und *p*-Phenylendiamin dargestellten Salzes synthetisiert. Einflüsse von Lösungsmittel, Polymerisationsdauer, Viskositätszahl und pH auf die Grösse der spezifischen Drehung von Polyhexamethylen-*d*-weinsäureamid wurden untersucht. Die Ergebnisse der Hydrolyse der Polymeren zeigte, dass *d*-Weinsäure während der Kondensationspolymerisation nicht racemisiert wird.

Received March 8, 1966

Revised January 25, 1967

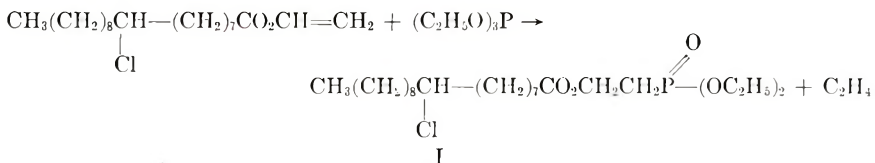
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NOTES

Reaction of Triethyl Phosphite with Vinyl Esters

During the course of some work on the polymers of the vinyl esters of the perchloro-cyclopentadiene adducts of petroselinic and oleic acids,¹ we attempted to carry out the Michaelis-Arbuzov reaction² to introduce a phosphonate group in place of some chlorine atoms and thus increase the flame resistance. The reaction proved to be quite complex, and a mixture of products resulted. None was completely characterized, but there was good evidence that one reaction was addition of triethyl phosphite to the vinyl ester groups.

The addition of triethyl phosphite to a variety of double bonds has been reported,² but there does not appear to be a report of its addition to a vinyl ester group. In order to simplify the reactions which we obtained with the above vinyl esters, we used vinyl 9-chlorostearate as a model compound. This ester reacted with triethyl phosphite to give a 27% yield of the addition product (I).



Evidence of the addition product's structure is its analysis: the infrared absorption at 1730 cm^{-1} for the carbonyl group; at 1185 cm^{-1} for the C—O— bond; at 1245 cm^{-1} for P—O stretching; at 1025 cm^{-1} for P—O—C in-phase stretching; at 1050 cm^{-1} for P—O—C out-of-phase stretching, and at 970 cm^{-1} for P^v—O— bonds. These absorptions have been reported for 2-diethylphosphonate ethyl groups by Overberger and Sarlo,³ McConnell and Coover,⁴ and by Sasin et al.⁵ There was no band at 850 cm^{-1} which has been recorded by McConnell and Coover⁴ for a 1-diethylphosphonate ethyl group.

We did not attempt to isolate and identify the ethylene but its formation in the addition reaction of trialkyl phosphite to nonactivated acetylenes has been reported by Griffin and Mitchell.⁶

Triethyl Phosphite Reaction with Vinyl 9-Chlorostearate

Vinyl 9-chlorostearate (3.3 g., 0.01 mole) was combined with triethyl phosphite (3.5 g., 0.02 mole, 95% pure) in a 25-ml. round-bottomed flask fitted with a magnetic stirrer, condenser, and a thermometer. The contents were heated at 145–150°C. for 8 hr. At the end of this period, excess phosphite was removed in a vacuum oven at 45°C. The re-

TABLE I

	C, %	H, %	Cl, %	P, %
Calcd. (for C ₂₀ H ₃₇ O ₂ Cl)	69.63	10.81	10.28	—
Found				
First fraction	70.42	10.84	10.26	—
Second fraction	69.66	11.02	12.00	—
Calcd. (for C ₂₄ H ₄₈ O ₅ PCl)	59.66	10.01	7.34	6.41
Found (third fraction)	58.81	9.94	8.15	6.10

action product was chromatographed on a silica gel (Baker Analyzed, Reagent) column (1 × 12 in.) with 2% ether-hexane as eluent followed by 4% ether-hexane and tetrahydrofuran. The analytical data on the various fractions are given in Table I.

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.

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**Aspects of Cationic Polymerization of Isobutene
with Butadiene and Isoprene**

The effects of solvent and relative monomer concentration upon the molecular weights and composition of isobutene–diene copolymers prepared in the presence of AlEtCl_2 catalyst were investigated. Reactivity ratios were calculated and compared with literature values for copolymerizations with an AlCl_3 catalyst.

In the first series of experiments we investigated the copolymerization of 30 vol.-% isobutene ($i\text{-C}_4^-$) with 70 vol.-% butadiene (C_4^-) using an AlEtCl_2 catalyst in a solvent of 90 vol.-% *n*-pentane and 10 vol.-% methyl chloride at -100°C . The polymerization is homogeneous under these conditions. At various time intervals aliquot samples were withdrawn, quenched in methanol, and the conversion, viscosity-average molecular weight, and butadiene incorporation (i.e., mole per cent unsaturation by the drastic iodine–mercuric acetate method¹) determined. The viscosity-average molecular weights increased during the run from about 25,000 to about 35,000. The unsaturation increased linearly with conversion, and a straight line was extrapolated to 10 mole-% unsaturation at zero conversion. These results are displayed in Table I. From the data we calcu-

TABLE I
Isobutene–Diene Copolymerizations at -100°C . with AlEtCl_2 Catalyst

Diene	$F = \frac{[i\text{-C}_4^-]}{[\text{Diene}]}$	$\bar{M}_v \times 10^{-3}$	C=C at 0 conversion, %	Fraction diene chain length
Butadiene (homogeneous)	30/70	~30	10.0	2.6×10^{-4}
Butadiene (heterogeneous)	30/70	~130	6.8	2.9×10^{-5}
	50/50	~680	1.9	1.6×10^{-6}
	70/30	~1,300	0.9	2.9×10^{-7}
Isoprene (heterogeneous)	84/16	~260	6.9	1.5×10^{-5}
	92/8	~500	3.1	3.4×10^{-6}

lated the number of butadiene units per given viscosity-average chain length. The amount of diene incorporation per given length of chain changes little with conversion. For this case, we obtained relatively low molecular weights coupled with relatively high levels of butadiene incorporation. It could be that the growing polyisobutylene carbonium ion in this system is preferentially solvated with butadiene monomer. Such a situation would result in depressed molecular weights (since butadiene is an efficient chain transfer agent) and high unsaturation levels. Preferential solvation by the diene is reasonable because the molar concentration of butadiene is about twice that of methyl chloride in this medium of low polarity.

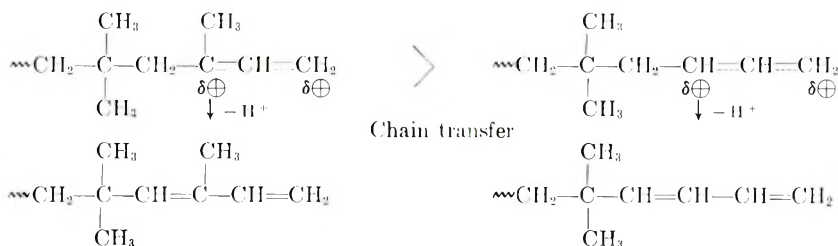
In the next series of experiments we used pure methyl chloride as the solvent at -100°C . and three feed ratios: $[i\text{-C}_4^-]/[\text{C}_4^-]$ (in volume per cent) = 30/70, 50/50, and 70/30. Here, the polymer is insoluble in methyl chloride at -100°C . (heterogeneous polymerization). A summary of the experimental results for the various feed ratios is given in Table I.

In these runs, polymerization started immediately upon introduction of the AlEtCl_2 catalyst. The molecular weights (although somewhat scattered) changed little with conversion, and, after reaching a certain level at low conversions ($\sim 1\%$), remained constant throughout the run. The final level of molecular weights was strongly affected by the amount of diene in the feed and decreased with increasing amounts of butadiene (Table I). As a result, the fraction of diene per given chain length of polymer decreased by an order of magnitude as the feed ratio F increased. The amount of butadiene incorporated

was linear with conversion. Zero conversion incorporations of butadiene (Table I) were obtained by back extrapolating of the straight lines.

To elucidate the effect of different solvent systems on the mechanism we compared (in Table I) the results of the homogeneous run carried out in a medium of low bulk polarity with those of a heterogeneous run in pure methyl chloride at a feed ratio of $f' = [i-C_4^-]/[C_4^-] = 30/70$. Evidently, higher molecular weights and lower butadiene incorporations are obtained when pure methyl chloride is the solvent. It could be that in the polar methyl chloride the chain carriers are "free ions." Free ions could produce higher molecular weights than ions associated with gegenions. It has been postulated that associated ion-gegenion pairs are involved in chain-transfer steps, the most important molecular weight determining event.² Associated ion-gegenion pairs probably prevail in the medium of much lower polarity (i.e., the homogeneous run of Table I).

Table I also contains results obtained with isobutene-isoprene systems. Experimentally, the copolymerization behaves similarly to that with butadiene. Obviously, isoprene is a much stronger molecular weight depressor (chain-transfer agent) than butadiene. This fact may be due to the higher stability of the ion formed from isoprene as compared to that obtained from butadiene.



Zero conversion unsaturations obtained in the course of the investigations were used to calculate reactivity ratios by the Fineman-Ross method³ for the isobutene-butadiene and isobutene-isoprene systems (cf. Table II). We compare in Table II our reactivity

TABLE II
Reactivity Ratios of Isobutene-Diene Copolymerizations at -100°C .

Copolymer	$r_1 = k_{11}/k_{12}$	$r_2 = k_{22}/k_{21}$	Catalyst	Reference
Isobutene-butadiene	43	~ 0	AlEtCl ₂	This work
Isobutene-butadiene	11.5 ± 1.5	~ 0.01	AlCl ₃	Lewis ⁴
Isobutene-isoprene	2.17	0.5	AlEtCl ₂	This work
Isobutene-isoprene	2.5 ± 0.5	0.4 ± 0.1	AlCl ₃	Lewis ⁴

ratios with those calculated by previous workers.⁴ These workers employed results from the patent literature concerning the isobutene-diene-AlCl₃ in methyl chloride system at -100°C .⁵ and made the arbitrary assumption that $r_1 r_2 = 1$ to calculate their reactivity ratios. Nevertheless, the reactivity ratios obtained for the AlEtCl₂ catalyst agree in magnitude with those for the AlCl₃ catalyst.

The results indicate that it is highly unlikely that isobutene-butadiene copolymers prepared with AlEtCl₂ or AlCl₃ catalysts at -100°C . contain blocks of butadiene in the chain. For the isobutene-isoprene systems the product of the individual reactivity ratios ($r_1 r_2$) in Table II is approximately 1.0, suggesting that both catalysts give completely random copolymers and that the polymerization mechanisms are quite similar.

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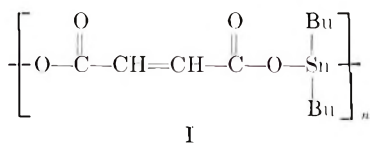
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Received February 15, 1967

Volatile Degradation Products of Organotin Polyesters

In a previous publication the thermal stability and glass transition of poly(di-*n*-butyltin adipate), poly(di-*n*-butyltin fumarate), and poly(di-*n*-butyltin terephthalate) were discussed. Infrared absorption data suggested that the butyl side groups of these polymers are vulnerable to oxidative cleavage when the materials are pyrolyzed in air. This was indicated by a progressive decrease in the absorbance of the CH-stretching bands of the alkyl groups between 2800 and 2950 cm^{-1} as well as the CH-bending bands at around 1460 cm^{-1} .

In the present study, mass spectrometric analyses of the volatile degradation products of poly(di-*n*-butyltin fumarate) (I) and poly(di-*n*-butyltin adipate) (II) were



carried out after the polymers had been pyrolyzed at 400°C. for 1 hr. *in vacuo*. Approximately 30-mg. samples were first preheated at 100°C. for 30 min. under a vacuum of $\sim 10^{-6}$ mm. of mercury with continuous pumping to remove absorbed gases and moisture; while maintaining this vacuum, the system was sealed for the actual pyrolysis. The col-

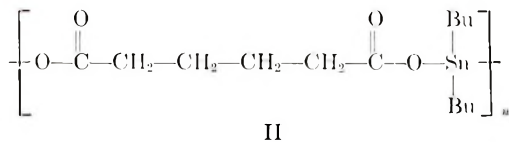


TABLE I
Mass Spectrometric Analysis of the Volatile Degradation Products of
Poly(di-*n*-butyltin Fumarate) and Poly(di-*n*-butyltin Adipate) after
Pyrolysis in Vacuum
($\sim 10^{-6}$ mm. Hg, 400°C., 1 hr.)

Component	Products, mole-%	
	From poly(di- <i>n</i> -butyltin fumarate)	From poly(di- <i>n</i> -butyltin adipate)
Hydrogen	<0.1	0.7
Methane	0.2	0.1
Water	3.7	3.8
Carbon monoxide	<0.1	<0.1
Carbon dioxide	42.5	21.3
Propane	3.4	3.3
Butene	16.5	4.5
Butane	31.4	38.0
Cyclopentanone	—	28.2
C ₅ H ₁₀	<0.1	0.1
C ₆ H ₁₀	~ 0.05	—
C ₇ H ₈	~ 0.05	—
C ₈ H ₁₀	~ 0.05	—
C ₉ H ₁₂	0.1	—

lection part of the pyrolysis cell was cooled in liquid nitrogen during the pyrolysis to facilitate rapid diffusion of the gaseous degradation products from the hot zone and thereby diminish the possibility of secondary reactions. A fractionation technique was employed (liquid nitrogen, Dry Ice-acetone) in admitting the degradation products (volatile at room temperature) into the mass spectrometer.

The composition of the two samples is tabulated in Table I. The main volatile degradation products of poly(di-*n*-butyltin fumarate) are carbon dioxide, butene, and butane, which constitute approximately 90% of the total volatiles. The remaining components include smaller amounts of water, propane, and methane. In addition, trace quantities of higher hydrocarbon ions were detected but no structural assignment could be made of these. The major volatile degradation products of poly(di-*n*-butyltin adipate) were carbon dioxide, butane, and cyclopentanone; however, only 4.5 mole-% butene was observed, and the mole per cent carbon dioxide was about one-half of that shown by poly(di-*n*-butyltin fumarate). This sharply reduced production of carbon dioxide indicates the participation of one of the carboxyl groups of the polymer in the formation of cyclopentanone. The appearance of cyclopentanone in the volatile degradation products of poly(di-*n*-butyltin adipate) is interesting because it has also been reported^{2,3} to be present in lesser amounts among the degradation products of nylon 66 [poly(hexamethylene adipamide)], but not in those of nylon 6 (polycaprolactam). The presence of cyclopentanone in the degradation products of poly(di-*n*-butyltin adipate) as well as in poly(hexamethylene adipamide) supports the view that this material originates from the adipic acid rather than the hexamethylene diamine moiety of nylons 66.³ Only trace amounts of carbon monoxide were found in both samples of organotin polyesters in contrast to the situation with other polyesters, including poly(ethylene terephthalate), where both carbon monoxide and carbon dioxide are produced in larger and about equal amounts.⁴

Butane most likely originates from the cleavage of the butyl side groups of both organotin polyesters. Carbon dioxide arises from the scission of the carboxyl links, except in the case of poly(di-*n*-butyltin adipate), where one of the carboxyl groups of the repeat unit participates in the formation of cyclopentanone. The surprisingly much higher yield of butene in the case of poly(di-*n*-butyltin fumarate) suggests that it may originate from both the main chain and the butyl side groups by the recombination of fragments rather than from the butyl side groups alone, as the latter are common to both samples. The presence of trace amounts of higher hydrocarbons in the degradation products of poly(di-*n*-butyltin fumarate) but not in those of poly(di-*n*-butyltin adipate), seems to lend some support to this view.

The author thanks Dr. Rodger L. Foltz of the Battelle Memorial Institute for his assistance in the mass spectrometric analyses.

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Received February 11, 1967

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BOOK REVIEWS

Organoboron Chemistry, Vol. II. HOWARD STEINBERG and ROBERT J. BROTHERTON. Interscience, New York, 1966. xx + 568 pp. \$25.00.

The progress of boron chemistry in relation to the possible development of materials having inorganic chains and rings in polymer structures has been so rapid in recent years as to require frequent new efforts to bring the bibliography up to date. This new volume from the U. S. Borax Research Corporation serves very well as a guide to the literature of organic derivatives of B—N, B—P, B—As, and B—Sb prototype compounds and polymers, with enough comment for the reader to select what he wishes to study more fully in the original papers. There is no apparent effort to develop any general rationale of the subject, but sometimes discrepancies between original-author opinions are noticed without decision. For example, the art of infrared assignment has made great progress since the misconstrued P—B frequency on page 481, but the authors only vaguely sense a disagreement with B—N frequencies. What has been accomplished very well indeed is a literal record of the literature.

The book is quite systematically organized, making it possible to find a subject by its proper place in the main sequence. About half of the space is devoted to the borazine ring, the chemistry of which has developed such broad variety that its potential rivalry with benzene is no fantasy. As long as practical polymers involving this flat (BN)₃ ring continue to be sought, this aspect may well grow even more rapidly. However, the authors are also thorough in their treatment of P—B polymers, about which far less is known; they find still less to say about B—As compounds; and they describe only one of the two known B—Sb compounds, apparently missing the very unstable Me₂SbBH₃.

In sum, this book introduces the reader to exciting new chemistry having polymer interest, and greatly aids the study of the original literature.

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Macromolecular Reviews, Vol. I. A. PETERLIN, M. GOODMAN, S. OKAMURA, B. H. ZIMM, and H. F. MARK, Eds. Interscience, New York, 1967, ix + 302 pp. \$12.00.

Macromolecular Reviews, Volume I, is the first in a new series. The field of polymer science has in recent years brought together the work of organic chemists, physical chemists, electrochemists, biochemists, chemical physicists, analytical chemists, etc., related to synthesis and properties of large molecules. Polymer science has grown rapidly because of the many disciplines involved in the study of macromolecules and its wide interest to both academic and industrial research workers. With such rapid growth, the need for short review articles which are easier to digest than full treatises has greatly increased. These review articles fill this need, introduce new fields to the researcher, who may have been working in only one discipline, and are a source of stimulation to those working in related fields.

The editors, A. Peterlin, M. Goodman, S. Okamura, B. H. Zimm, and H. F. Mark, rep-

resent a broad spectrum of interest in polymer science. They have chosen reviews that cover this broad range of interest and yet focus on major current polymer problems.

The six reviews are: (1) "Optically Active Polymers," by M. Goodman, A. Abe, and Y.-L. Fan; (2) "Electrolytically Controlled Polymerizations," by B. L. Funt; (3) "Poly-9-Vinylanthracene," by A. Rembaum and A. Eisenberg; (4) "Relationship of Catalyst Composition to Catalytic Activity for the Polymerization of α -Olefins," by H. W. Coover, Jr., R. L. McConnell, and F. B. Joyner; (5) "Structure of Crystalline Polyethers," by H. Tadokoro; (6) "Dynamic Thermogravimetric Analysis in Polymer Degradation," by L. Reich and D. W. Levi.

The review on optically active polymers covers recent work on stereoregular polymerization in relation to asymmetric induction of optically active monomers. There is considerable discussion of the optical rotatory properties as they relate to conformation and configuration. The review includes a brief description of condensation polymers from optically active monomers. Here we find in 30 pages a critical survey of all the available information on the preparation and optical properties of optically active polymers.

The article on electrolytically controlled polymerizations also reviews in 20 pages all recent work in this field. Free-radical, anionic, and cationic polymerization initiated at anodes or cathodes is covered. Funt, who has initiated much of the work with anionic systems himself, is ideally suited for making this critical review. The electrolytically initiated anionic systems bear close relationship to other living polymer systems.

The review on poly-9-vinylanthracene, in contrast, covers a single polymer which has been produced by a number of new techniques, the most interesting of which is cationic polymerization. However, the major interest in this polymer, besides the unique aspects of its polymerization, is the relationship between the structure of the polymer and its electrical properties. Poly-9-vinylanthracene is expected to have semiconducting properties, and indeed it exhibits in charge transfer complexes some of the interesting characteristics of polyradical anions. This is a field of recent research activity and the review is timely.

The article on relationship of catalyst composition to catalytic activity for the polymerization of α -olefins is of particular interest, in that it compares some specific data developed at the Tennessee Eastman Company with some of the recent literature in this field. The review is largely phenomenological in its approach, describing the effects on catalyst activity and stereospecificity of the polymer in relation to changes in the concentration and type of reactants used to make the heterogeneous coordination catalysts. The article is perhaps of greatest interest in that it confirms data from a number of laboratories with those obtained in a consistent fashion in a single laboratory. However, it is perhaps the least timely of the reviews in this volume, since it covers a field in which the peak in interest was a few years ago.

The review on structure of crystalline polyethers covers the extensive work on polyethers that has been carried out primarily in Japan. The review is written from the point of view of the structural information available on the crystalline polyethers by an outstanding practitioner of the Japanese school, H. Tadokoro. Physical properties, x-ray structure, and detailed crystal habits for all of these materials are covered in considerable detail. The review serves as a complete compilation of the physical data available on polyethers.

The last review in this volume, and the longest, is on dynamic thermogravimetric analysis in polymer degradation. It covers thoroughly the most important technique for studying the thermal behavior of polymers. This technique has been most valuable in developing high temperature-resistant materials and in understanding better the properties of polymers subject to degradation at relatively low temperatures. The review will be particularly valuable for anyone interested in thermal degradation of polymers, especially if they wish to develop the thermogravimetric technique as a tool for studying polymer degradation.

The only major criticism of this volume is the apparent delay between the preparation of the reviews and the final publication of the volume. Despite the fact that the book

is published in 1967, three of the reviews have no references to articles in 1966, and the other three have two or less references to 1966 articles, all of which refer to articles by an author of the review. Furthermore, the number of references to 1965 articles was limited in almost all cases. In the review on thermogravimetric analysis, for example, the 1965 references were either authored or co-authored by the author of the review. I would judge, therefore, that the review articles were written in 1965, with a few additional references inserted in 1966 during the proofing of the book. The great value of a review book of this type is timeliness, and greater speed in publication would seem desirable.

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Chemiefasern nach dem Viscoseverfahren, 3rd Ed. (2 Volumes). KURT GÖTZE. Springer-Verlag, Berlin, 1967. 1282 pp. \$62.00.

This is a monumental work! Since the publication of the second edition in 1951, polymer chemistry as a whole, cellulose chemistry in particular and, most of all, the technology of viscose rayon production has made such enormous progress that a completely new plan had to be developed for the third edition. No single man could possibly cope with this tremendous task alone. Thus, Dr. Götze had to look for co-workers and in doing so he was successful in assembling a list of most competent and prominent contributors for the fundamental and applied chapters for this new work. After a relatively short historical and general orientation on the subject there is presented a comprehensive and detailed description of the raw materials for the viscose process with special emphasis on wood pulp and its importance for the viscose process. Next, the reader is given a very thorough orientation on the fundamentals of each individual step of the transformation of the original cellulosic material into the final fiber beginning with the structure of cellulose, its relation to water and alkali, and continuing to the washing and drying of the final fibers, yarns, and fabrics. The next part discusses special spinning methods, fiber properties, and structure-property relationships with particular emphasis on high wet modulus staple fibers and on tire yarns and cords and with very educational chapters on the x-ray investigation of cellulose and on other physical fiber analysis. There follows in Part V the detailed description of the single processing steps as they are carried out in viscose rayon plants and as Part VI a comprehensive and complete survey on existing chemical, mechanical, and other physical test methods.

Each contribution is provided by an outstanding authority in the particular area, yet Dr. Götze has succeeded in molding all these individual chapters in a unified pattern which is complete but still manageable and highly educational. No other fiber field, natural or man-made, possesses an equally impressive cross-section through all phases of its activities.

The two volumes are true "Springer Books"—excellently printed, organized, and very attractively made up. The "Götze" is indispensable for anyone who is interested not only in cellulose but in textiles in general, and every user will draw profit and much pleasure from its use.

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