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Polyisonitriles. II. Heterophasic Catalytic Synthesis of Poly(α-phenylethylisonitrile) and of Poly(n-hexylisonitrile)

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Synopsis

A three-component catalytic system has been discovered, which successfully polymerizes α-phenylethylisonitrile to high polymer (DP = 200–900) and also polymerizes n-hexylisonitrile. The catalyst components are a strong acid, a free-radical source, and a heterophase and are all necessary in this system. The use of a liquid medium in which the polymer is insoluble promotes the rate of polymerization and total yield. Poly(α-phenylethylisonitrile), formed from monomer in a presence of oxygen and finely ground glass coated with sulfuric acid, can itself serve, in the presence of monomer and oxygen, as a catalyst for this polymerization. Preparative details and discussion of these synthesis factors are given.

INTRODUCTION

A meager though distinguished chemical literature is associated with organoisonitriles. Their discovery a century ago[1,2] was an early example of structural isomerism, and succeeding revivals of interest have included important contributions[3-5] to the justification of the octet rule and some pioneering work in unimolecular reactions.[6]

Little attention has been given the possibility of the addition homopolymerization of isonitriles through reaction of the $-\text{N}\equiv\text{C}:$ triple bond, despite the intensive search among compounds of various types of unsaturated bond. Not long ago[7] the successful homopolymerization of nitriles was achieved in solid-state reaction. It was therefore of some interest to investigate the chemical potentiality of the isonitrile group as a *bifunctional*, homopolymerizable moiety.

The chemical literature contains a limited number of citations of the occurrence of "tars" and "resins" and "polymers,"[8-14] but such products have never been characterized as high polymers nor has the chemical bonding been investigated. A few reports[10,15-17] mention that cryoscopy was performed and that the molecular weights of dimeric or trimeric compositions had been found.

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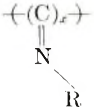
Isonitriles are sensitive to cationic attack. Much of the reported chemistry of organoisonitriles concerns ionic condensations of these compounds with compounds of different functional groups.[18] Such reactions have been used in two instances[19,20] with diisonitriles to achieve copolymerizations in which each isonitrilo group serves as a monofunctional agent in regard to forming a single link in the backbone chain of linear polymer. However, this functionality is distinct from that which must take place in the homopolymerization of monoisonitriles.

Liquid samples of aromatic and aliphatic isonitriles, $R{-}\ddot{N}{=}C{:} \leftrightarrow R{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}{:}$, stored at room temperature in amber bottles, were observed in our laboratories to deposit precipitates with time.[21] Aryl isonitriles are particularly prone to undergo this phenomenon; however, aliphatic isonitriles polymerize spontaneously at rates that may require many months. This is especially true in the cases in which the organic substituent R is bulky, as in those discussed in this paper. Isonitriles are readily available by synthesis through a number of methods.[22]

The product from α-phenylethylisonitrile proved to be soluble and of high molecular weight. Further study of the chemical structure of this polymer and of the chemistry of homopolymerization of this class of compounds posed the requirement of accelerating the slow rates of spontaneous formation. This paper reports the details of two catalytic systems that have been developed for the homopolymerization of α-phenylethylisonitrile, it reports the application of one of these catalysts with partial success to the polymerization of *n*-hexylisonitrile, and it presents some physical properties, including molecular weight averages, of the polymeric products.

A discussion of the chemical structure of poly(α-phenylethylisonitrile) has been presented recently,[23] where it was concluded that the repeating unit originally formed most probably has the structure



$$\left(\underset{\underset{\diagdown R}{\overset{\|}{N}}}{(C)_x}\right)$$

RESULTS AND DISCUSSION

Spontaneous Products

Samples of fractionally distilled liquid organoisonitriles, upon standing at room temperature in cork-stoppered amber bottles for several months to a year, where observed to deposit small amounts of sediment. Milligram amounts of colorless precipitate were isolated by filtration from samples of neopentyl, *t*-butyl, and cyclohexylisonitriles. A copious amount of canary yellow precipitate was recoverable from stored *o*-tolylisonitrile (which also contained a comparable quantity of a white, as yet unidentified, crystalline solid). These substances were tested for solubility to the extent that supply of the materials allowed. The product from neopentylisonitrile showed slight solubility in benzene and chloroform, and that from *t*-butylisonitrile was soluble in water. Other than this the samples were insoluble in water, methanol, ethanol, acetone, benzene, toluene, chloroform, and the original mother liquors. The samples from σ-tolyl-, cyclohexyl-, and α-phenylethylisonitrile were insoluble in several other media, including 85% phosphoric acid and cold, concentrated sulfuric acid, but all were attacked by the latter at elevated temperatures.

The yellow precipitate from α-phenylethylisonitrile was found to be soluble in benzene, toluene, chloroform, carbon tetrachloride, and carbon disulfide and partially soluble in nitrobenzene. Samples of this material were treated by several isolation techniques and characterized in solution. The results, summarized in Table I, prove the material to be high polymer, with the indicated molecular weight dispersity, and show an increase in average molecular weight with the extent of treatment. The data for the three characterization methods were treated in the conventional manner; that is, the physical property, normalized per unit concentration, in each case was plotted as a function of concentration, and the limiting value of the property was obtained by extrapolation to infinite dilution. The reduced variable in each of the three characterization techniques showed a smooth, positive concentration dependence typical of the solution behavior of high polymers in any of the solvents chloroform, benzene, and toluene.

TABLE I

Molecular Weight Determinations of Sample of Poly(α-phenylisonitrile) Isolated from Shelf-Stored Monomer by Several Techniques

Purification techniques	$\bar{M}_n$ ($\times 10^{-4}$)	$\bar{M}_w$ ($\times 10^{-5}$)[a]	$[\eta]$,[b] dl./g.
1[c]			0.533
2[c,d]	5.49[e]		0.760
3[c,f]	7.57[g]	1.20	
4[c,f,h]		1.50	0.780

[a] Light-scattering determination performed on toluene solutions at 35°C.

[b] Viscometry determination performed in benzene at 30°C.

[c] Product filtered from monomer and rinsed with ethyl ether.

[d] Lyophilized from benzene solution.

[e] Osmometry determination performed in benzene at 37°C.

[f] "Recrystallized" from nitrobenzene (80% return).

[g] Osmometry determination performed in toluene at 37°C.

[h] Washed benzene solution of polymer with dilute aqueous acid.

Initiation of Polymerization of α-Phenylethylisonitrile

The search for a catalyst for the polymerization of α-phenylethylisonitrile showed many classes of compounds to be inadequate. Chemical sources of radicals, such as benzoyl peroxide and azobisisobutyronitrile, failed to polymerize α-phenylethylisonitrile. Protonic acids, such as gaseous HCl and phosphoric, sulfuric and acetic acids, also failed, although they produced darkening in the monomer liquid. If such darkened liquid was transferred to the successful catalytic system, described below, it acted to inhibit polymerization. Currently some promising cationic catalysis is being accomplished with Lewis acids, such as boron trifluoride, and aluminum halide salts.

However, the observation of solid residue being formed at the ground-glass joints of quick-fit glassware during the distillation of monomer first led to the discovery of the heterophasic catalytic system that is described here. It consists of the necessary requirements of solid surface (e.g., fine-mesh ground glass), a strong acid (e.g., concentrated sulfuric acid coating applied to the ground glass), and a free-radical source (e.g., gaseous oxygen and benzoyl peroxide). None of these component elements, used alone or in combinations of two, suffices to polymerize α-phenylethylisonitrile. Thus, acid-coated powdered glass, when used in a helium atmosphere, fails to show activity. Powdered glass that has been scrupulously cleansed of cationic impurities or has been coated with sodium hydroxide, used in the presence or absence of oxygen, also lacks activity.

Substitutions of type can be made in the complete three-component system. It has been found that the monomer will polymerize in the presence of oxygen when some other acidic solid surface is substituted for the acid-coated powdered glass. Dowex-50 cation-exchange resin, acid-powdered quartz, anhydrous aluminum chloride, and aluminum oxide have served with at least partial success, although the optimal conditions for the use of these have not been developed. Even the small yields of polymer produced by the above are significant in comparison to the results obtained in efforts employing homogeneous liquid systems.

The requirement of both an acid and a free-radical source for the initiation of polymerization appears to be another example of a growing class of hybrid systems in which the free-radical and ionic stages are cooperatively involved, such as some Zeigler types of polymerization[24] and those recently described by Okamura et al.[25]

Another method of producing high polymer from α-phenylethylisonitrile was found to be accomplished by simply warming in air at 50°C. for several days monomer that which had been seeded with polymer produced by the ground-glass catalyst system. It is probably significant that the amount of polymer used as "seeding catalyst" always exceeds the very low solubility of polymer in its own monomer, thereby providing a heterophase. Also of probable significance is the fact that present polymer products suffer cleavage and a consequent drop in molecular weight during heating periods such as that used above. (The polymer samples produced in the presence of oxygen usually contain 0.5–1.8% oxygen, shown by elemental analysis, but this has not been conclusively linked to the thermal instability found in present samples.)

Uncatalyzed thermal polymerization of pure monomer has not been successful; monomer, heated at temperatures in the range of 50–200°C. with or without oxygen, was not observed to yield high polymer (at elevated temperatures isonitriles are known to isomerize to nitriles). Ultraviolet irradiation of monomer at 254 mμ at room temperature in the presence or absence of air failed to yield high polymer. Low-temperature storage of cooled liquid or frozen monomer at a temperature about that of its melting point for long periods had no detectable effects.

Catalyzed Polymerization of α-Phenylethylisonitrile

Parameters have been evaluated for the use of ground glass coated with sulfuric acid and developed for the conversion in good yields, of α-phenylethylisonitrile to high polymer. Some typical data are given in Table II, which shows that almost quantitative conversion is possible when a free-radical source is provided. The last two entries in the table indicate the importance of the latter.

TABLE II
Polymerization of α-Phenylethylisonitrile in Heptane at 50°C. with Powdered-Glass Catalyst Coated with Sulfuric Acid

Sample no.	Coating on catalyst[a]	Atmosphere[b]	Reaction time, hr.	Yield,[c] %	M_n ($\times 10^{-4}$)[d]	$[\eta]$,[d] dl./g.
13	0.0193	O_2	20	97	5.11	
				81[e]	3.38	0.486
15-1	0.0273	air	40	93		
				65[e]	2.92	
15-3	0.0143	air	48	86		
				63[e]	5.92	0.730
DBP-1	0.0252 plus 0.054 g. of dibenzoyl peroxide	He	26	63[f]	5.60	
He-2	0.0273	"	40	3[e]		
He-3	0.0273	"	40	0[e]		

[a] Grams of coating per gram of powdered glass (cf. "Experimental").

[b] Continuous passage of gas through reaction mixture at 10 cm.³/min.

[c] Yield not adjusted for unused, recoverable monomer; polymer isolated by complete lyophilization.

[d] In toluene at 30°C., dynamic membrane osmometry.

[e] Purified by complete lyophilization followed by precipitation in methanol from benzene solution and drying at 50°C.

[f] Purified by precipitation in methanol from benzene solution, followed by lyophilization from benzene solution.

Most of the polymerizations were performed at 50°C., but in two experiments they were carried out side by side in identical fashion, except that one was heated at 50°C. and the other at 90°C. Table III shows the results of this. A higher temperature produced a faster rate but a lower molecular weight. An old acid-coated powdered glass (less active) preparation was used in these experiments to slow down the rate, so that comparisons could be made of less than quantitative yields; otherwise, the preparation was standard.

TABLE III
Effect of Temperature on Catalytic Polymerization of α-Phenylethylisonitrile[a]

Preparation	Temp., °C.	Yield, %	$\bar{M}_n$ (× 10^{-4})
Monomer heated 15 hr. in both cases with same (aged) acid-coated powdered glass and O_2 bubbling, in hexane	50	8.9	6.29
	90	66	3.46
Monomer heated 9 hr. in both cases with same (aged) acid-coated powdered glass and O_2 bubbling, in hexane	50	13	4.77
	90	72	2.07

[a] Yields are not corrected for unused, recoverable monomer and are based on material isolated after purification by precipitation from benzene solution in tenfold excess of methanol, followed by lyophilization from benzene solution.

Some other experimental parameters that have been studied include the acidity and age of the acid-coated powdered glass and the nature of the reaction solvent. Table IV gives some data obtained for increasing amounts of acid coating on the powdered glass. The best yield of polymer was obtained with a value of 0.02 g. of acid coating per gram of powdered glass. Lower amounts of acid produced a slower rate, whereas higher amounts increased the formation of products other than polymer. In the case of α-phenylethylisonitrile the major by-product isolated after product work-up under aqueous conditions was *N*-formyl-α-phenylethylamine. This compound presumably results from hydrolysis of a predictable enolic half-ester of sulfuric acid, formed by 1,1 addition of the latter to the isonitrile group.

TABLE IV
Effect of Amount of Coating of Powdered-Glass Catalyst on Yield of Poly(α-phenylethylisonitrile) in *n*-Heptane Solvent at 50°C.

Sample no.	Acidity of powdered glass, g. coating per g. powdered glass	Time, hr.	Yield,[a] %
12	0.00278	120	0
15-3	0.0143	48	86 (63)
13	0.0193	20	97 (81)
15-1	0.0273	40	93 (65)
18	0.0798	24	64 —
11-1	0.0934	19	— (44)

[a] Yields are not adjusted for unused, recoverable monomer; the figures shown in parentheses give the yield after purification by precipitation in methanol from benzene solution, followed by lyophilization from benzene solution.

If the acid-coated powdered glass is not carefully stored it loses its activity (observed as diminished polymer yields) because of the absorption of water and, most probably, the vapors of neutralizing substances. Some of the effects upon the yield of poly(α-phenylethylisonitrile) produced by various treatments of a single catalyst preparation is shown in Table V.

TABLE V
Yields of Poly(α-phenylethylisonitrile) as a Function of Various Treatments of Acid-Coated Powdered-Glass Catalyst

Acid-coated powdered glass prepn. no.	Coating of powdered glass, g. coating per g. powdered glass	Time, hr., and temp., °C.	Polymer yield,[a] %	Remarks
13	0.0193	20, 50	81 (97)	Freshly prepd. powdered glass
13W	0.3964	48, 50	0	Same powdered glass used in 13, except originally not dried
13M	0.0333	24, 50	0–1	Same powdered glass exposed 2 days to moist room air
13R	0.0188	20, 50	2.8	Same powdered glass a in 13M after redrying

[a] Yields are not adjusted for unused, recoverable monomer and are given for product purified by precipitation in methanol from benzene solution, followed by lyophilization from benzene solution; the figure shown in parentheses was isolated by lyophilization from benzene solution only.

The most satisfactory solvent that has been used in the polymerization of α-phenylethylisonitrile is heptane, in which the monomer, but not the polymer, is soluble. As shown in Table VI, other solvents, such as toluene, benzene, chloroform, and methanol, in which the polymer is soluble or

TABLE VI
Solvent Effects on Yield of Poly(α-phenylethylisocyanide)

Sample no.	Acidity of powdered glass, g. coating per g. powdered glass	Solvent	Time, hr., and temp., °C.	Yield,[a] %
10–1	0.0231	None	37, 50	48
10–2	0.194	"	18, 30; 18, 50	0–1
10–T1	0.0231	Toluene	48, 50	7
10–T2	0.194	"	360, 50	7
10–T3	0.194	"	24, 50	0
10–T4	0.194	"	24, 100	1
10–M	0.194	Methanol	48, 50	1–6
15–3	0.0143	*n*-Heptane	48, 50	63 (86)
13	0.0193	"	20, 50	81 (97)
15–1	0.0273	"	40, 50	65 (93)

[a] Yields are not adjusted for unused, recoverable monomer and are given for product purified by precipitation in methanol from benzene solution, followed by lyophilization from benzene solution; the figures shown in parentheses give yields isolated by lyophilization from benzene solution only.

which interact with sulfuric acid, have been used in the polymerization without producing significant polymer yields.

The polymer is insoluble in the monomer from which it is derived and, as in the case of the use of *n*-heptane, polymer can be synthesized, in bulk. However, the omission of a diluent leads to a reaction mixture which becomes arrested. Moreover, in this procedure appreciable amounts of *N*-formyl-α-phenylethylamine can be isolated during the aqueous washes of the benzene solution filtrate.

In all of the catalytic syntheses of poly(α-phenylethylisonitrile) characterization of the polymer products has not revealed any dependence of molecular weight upon extent of conversion. This argues that the polymerization takes place by an addition chain reaction mechanism rather than by a step-wise propagation.

Polymerization of *n*-Hexylisonitrile

Some initial work on extending the polymerization method to other monomers has been attempted. Again it was found that more conventional initiator systems did not succeed in polymerizing *n*-hexylisonitrile. However, some success has been achieved in polymerizing *n*-hexylisonitrile by using the optimized experimental conditions derived from the polymerization studies of α-phenylethylisonitrile. The results are summarized in Table VII.

All of the spontaneous solid products, except that from *t*-butylisonitrile, and the catalytically synthesized polymers were observed on a melting-

TABLE VII

Polymerization of *n*-Hexylisonitrile in *n*-Heptane in the Presence of Oxygen and Acid-Coated Powder Glass (0.0209 g. of coating per g. of catalyst)

Sample no.	Time, hr.	Catalyst temp., °C.	Yield,[a] %	$\bar{M}_n$[b]
A-5-1	10	72	38[c]	1530 ± 50
A-5-2	96	90	5[d]	2400 ± 100[e]
A-5-3	"	"	"	3530 ± 10[f]
A-5-4[g]	72	55	1[d]	—
A-5-5[h]	120	80	34[i]	976

[a] Yields not corrected for unused, recoverable monomer.

[b] Determined by vapor-phase osmometry of toluene solutions.

[c] Product was lyophilized from benzene solution, and the solid was heated for 2 hr. at 70–110°C. at 0.2 mm.

[d] Product was isolated by precipitation from benzene solution in methanol.

[e] Benzene-soluble fraction.

[f] Fractional residue from benzene extraction, soluble in chloroform

[g] Benzoyl peroxide (0.10 g. per 2.0 g. of catalyst) also present.

[h] Monomer heated in a stream of oxygen at 80°C. for 21 hr. before introduction of catalyst.

[i] Product isolated by lyophilization from benzene solution.

point block to be stable up to temperatures below 225°C. At temperatures in the range of 224–300°C. for different samples the solids were observed to liquefy with resinification. Volatilization, accompanied by the apparent odor of the monomer, and weight losses of 50% were observed for synthetic poly(α-phenylethylisonitrile) and poly(σ-tolylisonitrile). The former showed no weight loss when heated at 92°C. at 0.5 torr pressure for 12 hr. but, when heated at 50°C. in the presence of air for 48 hr., showed a tenfold reduction in the number-average molecular weight.

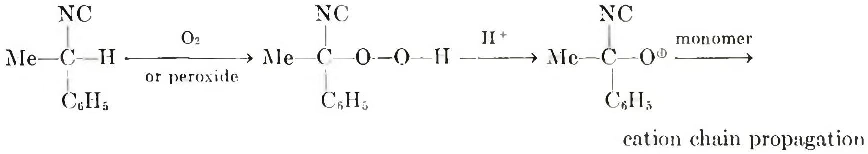
Synthetic poly(α-phenylethylisonitrile) is in every apparent way identical with the sample isolated from shelf-stored monomer, with the understandable allowance of variation in molecular weights and oxygen content among different samples. The polymer appears yellow and produces orange-brown solutions. Infrared spectra, ultraviolet absorption data, crystallographic data, and discussion of the molecular structure of this polymer are given in a previous publication.[23]

Mechanistic Considerations

At the present state of knowledge of the acid-coated powdered-glass catalysis of isonitriles only the barest discussion of facts that bear on the mechanism of reaction is justified. The necessary role of a heterophase in the polymerization is probably one of overcoming a very unfavorable loss of entropy during kinetic chain growth. Such a rationale was offered by Kargin et al.[7] to explain why polymerization succeeds when a nitrile is polymerized as a solid and fails otherwise; i.e., part of the loss of entropy of the system is overcome prior to chain propagation. Poly(α-phenylethylisonitrile), being substituted, as it is, by a bulky substituent on each backbone carbon atom, requires a high degree of positional localization and orientation of the entering monomer during chain propagation.[23] The promotion of the polymerization rate in n-hexane (in which the polymer is insoluble), in contrast to the inhibition in the presence of chloroform (in which the polymer dissolves), is consistent with this picture of the locus of polymerization dependent on a condensed environment on the catalyst surface. There may be other features of mechanism involved in the solvent effect, but the aspect of unfavorable entropy on monomer addition is undoubtedly one of them.

The fact that the strong-acid catalyst coating is effective in accelerating polymerization is not surprising in the light of the known acid sensitivity of isonitriles. However, the failure of strong acids to lead to high polymers in the absence of an associative solid surface suggests that the conjunct cationic reactions are competitive with polymerization only when the latter is inhibited by a large unfavorable entropy change. It is possible that the use of low temperature may alleviate the presently observed necessity of a heterogeneous associative.

The necessary corequisite role of a free-radical source such as oxygen or dibenzoyl peroxide is not as clear. The standard polymerizations, when conducted in the additional presence of 1,4-naphthoquinone or m-dinitrobenzene, showed no appreciable reduction in yield or molecular weight, and it is probable that the chain propagation step is mainly a cationic one. The free radical may be involved in initiation. However, the results of elemental analysis of oxygen indicate that oxygen is incorporated into the molecule at a frequency (e.g., 1 oxygen atom per 10–25 mer units) that is much in excess of that attributable to endgroups, since average degrees of polymerization range from 200 to 900 under the conditions used. A mechanism may be formulated for the oxidation of the benzylic C—H bond of the monomer yielding a hydroperoxide that could serve as an initiator. The decomposition of a hydroperoxide may be promoted[26,27] by cationic catalysis:



$$\mathrm{Me{-}\overset{NC}{\underset{C_6H_5}{C}}{-}H} \xrightarrow[\text{or peroxide}]{\mathrm{O_2}} \mathrm{Me{-}\overset{NC}{\underset{C_6H_5}{C}}{-}O{-}O{-}H} \xrightarrow{\mathrm{H^+}} \mathrm{Me{-}\overset{NC}{\underset{C_6H_5}{C}}{-}O^{\oplus}} \xrightarrow{\text{monomer}}$$

cation chain propagation

However, this alone does not explain the frequent incorporation of oxygen. The infrared spectra of currently available samples of the polymer do not reveal the nature of bonding of the 2% of oxygen, although the spectrum of one sample (cf. Millich and Sinclair,[23] Fig. 2A) is suggestive of amide functional groups. Further investigations with other selected free radicals incorporated into oligomeric isonitriles should yield additional information.

EXPERIMENTAL

Solution Characterization of Polymers

All conditions of solvent and temperature are given in the tables. Number-average molecular weight determinations of poly(α-phenylethylisonitrile) were conducted with a Mechrolab Membrane Dynamic Osmometer, Model 502, with grade 0-8 Schleicher and Schuell membranes. In this and the following solution methods determinations were made over a range of concentrations up to 15 g./l., and the limiting value, obtained by extrapolation of the conventional concentration-reduced property to infinite dilution, was used for computation. Number-average molecular weights for the oligomeric poly(n-hexylisonitrile) samples were estimated with a Mechrolab Vapor Phase Osmometer, Model 301A, previously standardized with β-glucosepentaacetate and with benzil.

Weight-average molecular weight determinations were conducted with a Phoenix-Brice Universal Light Scattering Photometer 2001-D, and Zimm-plots were constructed. The value of dn/dc for poly(α-phenylethylisonitrile) in toluene is 0.149.

Intrinsic viscosities were deduced from viscosity data obtained with a Cannon-Ubbelohde viscometer of 0.008 cstokes/sec. constant and thermostated in baths regulated to ±0.01°C.

The elemental analyses were performed in three different industrial laboratories.

Synthesis of *N*-Formyl α-Phenylethylamine

The Leuchart synthesis, essentially that of Ingersoll et al.[28] and Moore,[29] was used. A 2.1 three-necked flask is fitted with a thermometer, a short, wide reflux condenser, and a Claisen head arranged with an addition funnel and a condenser for downward distillation. Acetophenone (240 g., 2 moles), formamide (270 g., 6 moles), and formic acid (25 ml.) are placed in the flask and heated to reflux and maintained at about 175°C. for 20–30 min. Water of condensation is distilled in 30 min. with the application of slight suction as the reaction mixture temperature rises to 185°C. Any codistilled acetophenone is separated and returned to the reaction vessel. A 25 ml. portion of formic acid is added and, as water is formed, the temperature is observed to drop about 10°C. The process is repeated until 325 ml. of formic acid has been added (about 40 hr.). The product is collected by vacuum distillation through a Claisen head as a distinct fraction boiling at 189–192°C. at 26 mm.; yield 244 g. (1.6 moles, 80%, based on acetophenone), m.p. 37–42°C., infrared spectrum typical of substituted formamide, ultraviolet ϵ (max. 257 mμ) = 353.

Synthesis of *d,l*-α-Phenylethylisonitrile

The synthesis is essentially that of Ugi and his co-workers.[22,30] Into a 2.1 three-necked flask equipped with a reflux condenser, which is vented through a drying tube, is placed 68 g. (0.45 mole) of α-phenylethyl formamide dissolved in 300 ml. of dry triethylamine and 750 ml. of dry methylene chloride. Freshly distilled $POCl_3$, 77 g. (0.5 mole), is added dropwise with cooling and stirring. After 45 min. at room temperature the reaction solution is washed with cold water, then 100 ml. of concentrated NH_4OH solution, and finally with ice water. The methylene chloride is first removed by distillation, and then the product is distilled quickly through a 28-cm. packed Allyn column, to yield 37 g. (63%) of water-white α-phenylethylisonitrile b.p. 54°C. at 0.6 mm. An infrared spectrum shows no amide bands and has a strong band at 2150 cm.$^{-1}$ (4.7 μ). Ultraviolet ϵ (max. 257 mμ) = 208; n_D^{31} = 1.5041, density 0.952 g./ml. at 32°C., insoluble in water, soluble in *n*-heptane, methanol, acetone, chloroform, benzene, and toluene; concentrated hydrochloric acid yields a purple solution. The product is stored in a refrigerator in a brown bottle.

Preparation of Powdered-Glass Catalyst Coated with Sulfuric Acid

Powdered glass, approximately 200 mesh (Fisher Scientific Company), is washed with benzene, dried, soaked overnight in sulfuric acid–dichromate, washed clear with water, and then washed alternately on a porcelain fritted filtration disk with 5*N* sodium hydroxide, distilled water, and 6*N* sulfuric acid; the last wash is with the acid, the excess of which is thoroughly sucked down on the filter. The acid-coated powdered glass is spread out on a petri dish or in the flask of a rotary evaporator and dried at 50 ± 2°C. at 1 ± 0.5 mm. for 16 hr. Usually the weight loss is slow after 4 hr. Approximately 20 g. of powdered glass is handled in a batch. After drying, the amount of acid coating on the powdered glass is evaluated by washing a weighed portion of coated catalyst with water and then acetone and then drying and reweighing.

A calculation then shows approximately 0.02 g. of coating per gram of powdered glass. Replicate titration indicates the acid-coated powdered-glass preparations are coated with 80% sulfuric acid. The acid-coated powdered glass is white, free from visible debris, and has some tendency to form lumps. It is neither a rigid cake nor a freely flowing powder. It may be stored in a desiccator or well-stoppered flask. With slight changes occurring in temperature and pressure during drying, and also with drying time differences of 4–16 hr., the coating of the powdered glass could be reproducibly prepared under these conditions to contain 0.025 g. of coating per gram of powdered glass, respectively, for eight preparations, with an average deviation of ±0.002 g./g.

Polymerization of α-Phenylethylisonitrile

In a 100-ml. round-bottomed flask 2.0 g. of acid-coated powdered glass is quickly covered with 10 ml. of *n*-heptane (Mallinckrodt AR grade or equivalent). A magnetic stirrer is turned on, and 3.0 ml. of α-phenylethylisonitrile is pipetted into the reaction flask. A red-brown color appears immediately, if the reactants are prepared in sufficient purity. A vertical condenser is fitted onto the flask, and oxygen is passed through anhydrous calcium chloride, a flask of *n*-heptane, and thence by means of a fine-tipped bubbler into the solution of *n*-heptane and monomer at a rate of 10 ml. of gas per minute. The reaction flask is heated 40 hr. at 50°C. with stirring and oxygen bubbling. The powdered glass should now be coated with red-brown curds, and the solution is red-brown.

The *n*-heptane is decanted through coarse filter paper, leaving behind the powdered-glass–polymer matrix in the flask. Dissolution of the polymer may require 25–50 ml. of benzene to produce a viscosity that will allow flow through the filter paper. Gravity filtration is preferable, since suction tends to deposit polymer in the paper and clog the pores of the paper (a sintered-glass filter is useless except for solutions of approximately 2% concentration or less). The filter paper is washed with benzene until free from nearly all color; the latter may require cutting up of the paper, washing with benzene, and putting through fresh filter paper. The combined benzene phases are evaporated at room temperature, if necessary, to reduce the volume to 25–50 ml., which is then added dropwise to a tenfold excess of vigorously stirred methanol, precipitating polymer solute. The precipitate is collected on a Büchner funnel, air-dried somewhat, dissolved in approximately 30 ml. of benzene, and lyophilized at 0.5–1.0 mm. vacuum. Alternatively, the methanol precipitation may be omitted when rigorous elimination of monomer is not needed. The lyophilized product is a cream color, yellow to orange as a benzene solution, and can be evaporated from solvent to form slick, hard, transparent films, brown in color. The polymer decomposes on heating in air at 250–260°C.

Synthesis of *n*-Hexyl Formamide

The method of Moffat and his co-workers[31] is used to prepare *n*-hexyl formamide: 2.0 moles each of *n*-hexylamine and ethyl formate are mixed with cooling, refluxed 72 hr., and distilled. The fraction boiling at 127°C. at 5.5 mm. is collected and amounts to 188 g. (73%); $n_D^{25} = 1.4466$. The infrared spectrum is typical of an aliphatic formamide.

Synthesis of *n*-Hexylisonitrile

With the use of conditions of the Ugi method very similar to those given above 168 g. (1.46 moles) of *n*-hexyl formamide, dissolved in 750 ml. of methylene chloride and 485 ml. of triethylamine, reacts with 70 ml. (0.77 mole) of $POCl_3$. Yield was reduced by thermal decomposition during a slow distillation, and 42 g. (26%) was collected at 67°C. at 14 mm. and at 48°C. at 5 mm. The infrared spectrum shows an isonitrile absorption band at 4.68 μ (2150 cm.$^{-1}$); $n_D^{19} = 1.4165$, density at 25°C. 0.774 g./ml. The ultraviolet spectrum shows weak absorption at 210 mμ with a molar extinction coefficient of $\epsilon = 8$.

Preparation of Poly(*n*-hexylisonitrile)

With the procedure described above *n*-hexylisonitrile can be substituted as monomer to yield a polymer of lower molecular weight. Isolation is best accomplished by lyophilization from benzene followed by vacuum heating, since the low molecular weight polymer is soluble to an appreciable extent in methanol (Table VII). Polymerization temperatures of 70–90°C. are best. The typical polymer by this polymerization has the following properties: $\bar{M}_n$ (vapor-pressure osmometry), 2400 ± 100, the ultraviolet spectrum yields a molar extinction coefficient of ϵ (max. 239 mμ) = 759; the infrared spectrum shows a strong band at 1640 cm.$^{-1}$ (6.12 μ) and progressive series from 1375 to 1332 cm.$^{-1}$ (7.27–7.52 μ). The lyophilized product is either a dark syrup or a rich-brown crumb partially soluble in methanol or benzene and soluble in $CHCl_3$.

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This paper is taken in part from the dissertation of R. G. Sinclair, II, University of Missouri at Kansas City, June 1967.

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Radical Grafting on Lignin.
Part I. Radiation-Induced Grafting of Styrene onto Hydrochloric Acid Lignin

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Synopsis

By irradiation with gamma rays styrene was grafted onto hydrochloric acid lignin. When the graft polymers were subjected to nitrobenzene oxidation, the vanillin yields indicated two kinds of reaction occurring in the grafting. Polystyrene branches were separated from the graft polymers, and their $\bar{M}_n$ were determined osmometrically. At grafting ratios of up to 100 the vanillin yields diminished proportionately with increasing grafting, and the $\bar{M}_n$ of the branches, 5000, was unchanged. At grafting ratios of more than 100 the vanillin yields were constant, independent of the ratios, but the $\bar{M}_n$ values of the branches increased with grafting. Paper chromatography of the aromatic acids obtained by oxidation of methylated lignin and the graft polymer indicated that isohemipic and metahemipic acids were more abundant in the acid fraction of the graft polymer than in the lignin itself. A qualitative mass analysis of the gaseous products evolving from the irradiated lignin showed the presence of hydrogen molecules only. Gamma-ray radiation brought about no change in the yields of vanillin. It was therefore concluded that radiation grafting on lignin at grafting ratios of less than 100 proceeded through the addition of styrene polymer radicals to the aromatic nuclei of the lignin and that then branches propagated from the aliphatic part of the lignin, where C—H bond scission had been caused by the irradiation. The grafting sites of lignin would be C-5 and C-6 of the guaiacyl nucleus and, probably the β and γ carbon atoms of the aliphatic side chain of the lignin.

INTRODUCTION

Coniferous lignin is a tridimensional polymer consisting of 4-hydroxy-3-methoxyphenyl (guaiacyl) propane building units. One half of the guaiacyl propane units are joined by C—C bonds and the remaining units by C—O—C bonds. Lignin is insoluble in water, most organic solvents, and strong sulfuric or hydrochloric acid. It is readily oxidized and readily susceptible to sulfonation and halogenation. When it is oxidized with alkaline nitrobenzene, it gives substantial amounts of vanillin. In an attempt to use lignin as a polymeric material radiation-induced grafting was carried out with methyl methacrylate,[1] vinyl acetate,[1] and styrene.[2] The grafting was inhibited by the addition of hydroquinone[2] and retarded by the phenolic hydroxyl[1] of lignin, and its initial grafting rates were proportional to the square root of the radiation intensities.[2] Lignin is stable to gamma rays owing to the protective action of its aromatic nuclei, which are about half of the molecular weight; the G value for the radical production of lignin lies between 0.6 and 0.7.[1] It is interesting to know how the grafting onto lignin occurs. In this paper the radiation grafting process and the grafting sites of the lignin molecule were studied with styrene as monomer. Hydrochloric acid lignin prepared from pine wood was used as the lignin component, since a large amount of this comparatively pure lignin is readily obtained.

EXPERIMENTAL

Radiation-Induced Grafting of Styrene onto Lignin

As the lignin component hydrochloric acid lignin was used, which was prepared from pine wood (*Pinus densiflora*), as described earlier.[2] Grafting was carried out by gamma-ray irradiation of the mixture lignin–styrene–methanol (1:10:0.2) *in vacuo*.[2]

Nitrobenzene Oxidation of Lignin–Styrene Graft Polymers

An amount of graft polymer containing 0.7 g. of lignin component was heated electrically with $2N$ aqueous sodium hydroxide (120 ml.) and nitrobenzene (10 ml.) in a stainless-steel autoclave for 3 hr. at 160°C. After oxidation a precipitating, branched polystyrene as a white, adhesive sludge, was separated from the liquor and repeatedly extracted with hot water (300 ml.). The extracts were combined with the alkaline liquor part, and vanillin was isolated as its *m*-nitrobenzoyl hydrazone (90% purity). In Figure 1 the grafting ratios of the graft polymers are plotted against the amounts of vanillin expressed as percent of the lignin component.

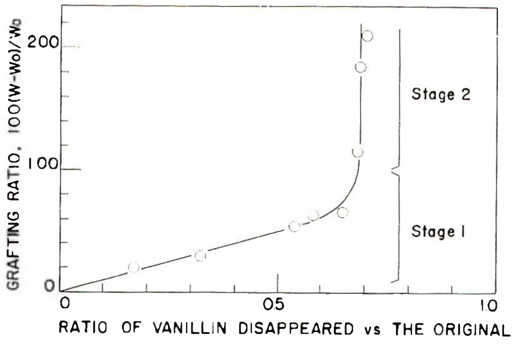


Fig. 1. Amount of vanillin disappearing in grafting vs. grafting ratio of lignin–styrene graft polymers.

Molecular Weight Determination of Branches of Graft Polymers

A vapor-pressure osmometer (Hitachi-Perkin-Elmer, Model 115) was used for the determination of the number-average molecular weights of the polystyrene branches, since the expected values were below 10,000. Measurements were carried out at 40.8°C. and a concentration of 8×10^{-4} mole per kilogram of benzene. For complete separation of the benzene-soluble branches from the lignin component at least 11 treatments with a sodium chlorite–acetic acid mixture at 75°C. necessary.[3] When the radiation-polymerized polystyrene was subjected to the same treatments, the observed values of $\lim_{c \to 0} \pi/c$ coincided completely, both before and after oxidation.

Synthesis of Lignin-Model Compounds

α-(3,4-Dimethoxyphenyl)–Ethylene Glycol–β-Guaiacyl Ether. This compound was prepared by the method of Gierer and Norton,[4] as follows: guaiacol → acetoguaiacone (42 g., m.p. 113–114°C.) → ω-bromoacetoveratrone (25 g., m.p. 78–79.5°C.) → ω-(2-methoxyphenoxy)-acetoveratrone (27 g., m.p. 90–91°C.) → α-(3,4-dimethoxyphenyl)-ethylene glycol-β-guaiacyl ether (19 g., m.p. 127–130°C.). Recrystallization from acetone raised the melting point to 132–134°C.

Veratryl Guaiacyl Ether.[5] To absolute ethanol (500 ml.) containing 2.8 g. of sodium metal were added guaiacol (18.3 g.) and veratryl chloride (20 g.) in benzene (92 ml.); this was refluxed for 1.5 hr. After being cooled the solution was evaporated to dryness *in vacuo,* the residue dissolved into ether, and the ether solution washed twice with 1% aqueous sodium hydroxide. When the ether solution was cooled, veratryl guaiacyl ether crystallized: 8 g., m.p. 75–76°C. After recrystallization from ethanol the melting point was raised to 77–78°C. The synthesis of veratryl chloride was carried out according to Tiffeneau's procedure.[6]

Veratryl Alcohol. Commercial reagent was distilled at 157–159°C. at 5 mm. Hg; n_D^{30}, 1.5495.

Dimethyl Homocatechol. Dimethyl sulfate (45 g.) was added to a solution of 2-methoxy-4-methylphenol (50 g.) in 99% ethanol (100 ml.) previously cooled at 3°C. At this temperature aqueous potassium hydroxide (90 g. in 210 ml.) was poured into the mixture portionwise, the reaction temperature being kept below 50°C. with external cooling. After the addition of alkali the mixture was refluxed for 1 hr., cooled, and then extracted with ether; yield 43 g. A portion with b.p. 216–217°C. (20 g.) was used for the following experiments.

Radiation-Induced Polymerization of Styrene in Presence of Lignin Model Compounds

The compound, 1 g., prepared as above, 10 g. of styrene, and 0.2 g. of methanol[2] were sealed *in vacuo* and irradiated with 0.8–4.8 Mrads of gamma rays at room temperature. After irradiation the reaction mixture was dissolved with benzene, the benzene solution and washings (20 ml.) being combined and precipitated with methanol (500 ml.). The methoxyl contents and number-average molecular weights were determined from the polymer purified by repeating this treatment. The methoxyl contents were calculated by weighing the silver iodide precipitate according to the Micro-Zeisel method.

Molecular Weight Determination of Polystyrene Containing Model Compound

The osmotic pressures of the benzene solutions were measured at 25°C. by a high-speed membrane osmometer (Mechrolab, Model 502). The $\bar{M}_n$ values are presented in Table I. For the case $f_1 = 0$ and $f_2 = 1$, in eq. (1) given below, the $\bar{M}_n$, calculated from their methoxyl contents on the assumption that one polymer molecule contains one model compound, are also shown in this table.

TABLE I
Radiation-Induced Polymerization of Styrene in the Presence of Lignin Model Compounds

Model compd.[a]	Convsn., %	Methoxyl, %	f_1	f_2	$\bar{M}_n$	
					Calcd.	Found
(I)	9.49	0.099	0.25	0.75	—	70,000
(II)	14.7	0.149	0.18	0.82	—	51,000
(III)	30.4	0.135	0	1	46,000	46,000
(IV)	21.0	0.140	0	1	44,000	44,000

[a] (I), α-(3,4-dimethoxyphenyl)-ethylene glycol-β-guaiacyl ether; (II), veratryl guaiacyl ether; (III), veratryl alcohol; (IV), dimethyl homocatechol.

Paper Chromatography of Acid Fractions Resulting from Oxidation of Methylated Lignin and Graft Lignin

According to Freudenberg's procedure,[7] methylated lignin and methylated lignin–styrene graft polymer having a grafting ratio of 197 were heated with 70% potassium hydroxide at 170–175°C., methylated again, and oxidized with potassium permanganate at pH 6–7. The acid fraction was obtained by extracting the solution part with ether at pH 2 after extraction of the neutral fraction. The yields were 9.46% (methylated lignin) and 11.1% (methylated graft lignin), respectively. Paper chromatography was carried out on each of the acid fractions, with the use of the solvent systems (A) benzene–acetic acid–water (8:11:4 v/v, organic phase), (B) *n*-butanol–morpholine–water (5:1:4 v/v, organic phase), and (C) *n*-butanol–acetic acid–water (5:1:4 v/v, organic phase). The paper (Toyo-Roshi, No. 50) was exposed for 3–4 hr. in saturated solvent vapor before use. After development the chromatograms were revealed by spraying Rhodamine B in methanol (20 mg. in 250 ml.). Solvent A gave the most distinct chromatograms. Table II gives the R_f values observed. Two acid fractions showed the same kind of spots, except one (R_f 0.10 in solvent C) that appeared only in graft lignin. It was observed, however, that isohemipic acid appeared at R_f 0.59 in solvent A and at 0.12 in solvent

TABLE I
Paper Chromatogram of Acid Fractions Obtained by Oxidation of Methylated Graft Polymer and Lignin

R_f		
Found[a]	Lit.[7]	Acid
Benzene–acetic acid–water:		
0.84	0.85	Veratric acid Trimethyl gallic acid Anisic acid
0.78	—	—
0.69	—	—
0.59	0.58	Isohemipic acid
0.37E	0.34	Metahemipic acid
0.24–0.25*E*	0.27	Succinic acid
0.15–0.16*E*	—	—
0.10*E*	0.11	Methoxytrimesic acid
n-Butanol–morpholine–water:		
0.60*E*	0.61	Anisic acid
0.36*E*	—	—
0.24*E*	0.27	Dehydrodiveratric acid
0.12E	0.11	Isohemipic acid
n-Butanol–acetic acid–water:		
0.90	0.90	Veratric acid
0.71	0.73	Succinic acid
0.10	—	—

[a] Italics indicate acids more abundant in oxidation product of graft polymer; *E* indicates an elongate spot.

C, and probably metahemipic acid, at R_f 0.37 in solvent A, was richer in the acid fraction of the graft lignin.

Nitrobenzene Oxidation of Irradiated Lignin

Hydrochloric acid lignin prepared as described above was irradiated *in vacuo* by gamma rays of 0.1 Mrads/hr. and then subjected to nitrobenzene oxidation. Vanillin yields: 17.7 (original), 17.4 (25 hr.), 17.2 (42 hr.), and 17.6% (162 hr.).

Qualitative Mass Analysis of Gases Evolved from Irradiated Lignin

Diazomethane-methylated hydrochloric acid lignin was used for the present experiment, since it has been used throughout the graft copolymerization experiment series[1–3] as lignin component. Before analysis the lignin was dried over phosphopentoxide for 8 hr. at 75°C. at 2 mm. Hg and then 5 hr. at 5×10^{-3} mm. Hg in the sample tube, which was directly attachable to the mass spectrometer by opening of the glass stopper. The tubes, containing 1 g. of dry lignin *in vacuo*, were put in the middle of a protective cylinder containing cobalt-60 (700 curies) and irradiated for 24 and 144 hr.; the total dose amounts were 1.9 and 11.5 Mrads, respectively. After irradiation each tube was connected to the mass spectrometer

(Atlas, Model CH-3) and analyzed at room temperature *in vacuo* (10^{-6} mm. Hg). Only the hydrogen molecule was detected, except for a small amount of air, but no methanol or its fragmentation products were detected in any of the cases.

Determination of Primary and Secondary Alcohol Groups in Graft Polymers

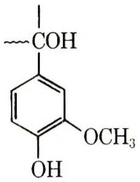
Phenolic hydroxyls of lignin had been methylated with diazomethane before grafting.[1,2] Lignin–styrene graft polymer (1 g.) was acetylated with acetic anhydride (50 ml.) and pyridine (60 ml.) at 100°C. for 2 hr. The amounts of primary and secondary hydroxyl groups were calculated from the amounts of acetyl introduced, which were determined by the method of Whistler and Jeanes.[8] The results are presented in Table III.

TABLE III
Amounts of Primary and Secondary Alcohol Groups in Lignin–Styrene Graft Polymers

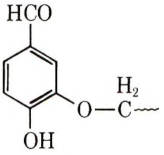
Grafting ratio, $100(W - W_0)/W_0$	OH, %	
	Found	Calcd.
0	8.55	—
41	5.65	5.70
104	4.05	3.95
113	3.76	3.76
242	2.50	2.35
332	2.08	1.87
343	2.05	1.82

RESULTS AND DISCUSSION

In the grafting of styrene onto the lignin molecule there seem to be two kinds of process, which are distinguished by the vanillin yields on nitrobenzene oxidation. *The one represents the grafting stage of up to a grafting ratio of about 100,* and the vanillin yields in this stage are diminished in proportion to the increase in grafting. This grafting stage is called stage 1 in Figure 1. *At grafting ratios of more than 100 the grafting reaction proceeds independently of the vanillin yields, which keep a constant value of 30% of the original; this is the other process, which represents the later stage of grafting, referred to as stage 2.* The reduction of vanillin yields is not ascribed to a formation of structure (I) or (II) in lignin molecules, due to the grafting of styrene, since the total methoxyl[3] and primary and secondary hydroxyls of lignin are retained after grafting; see Table III.



(I)



(II)

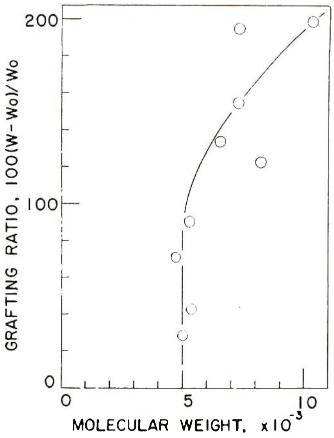
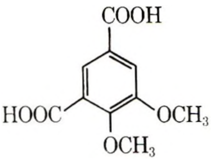


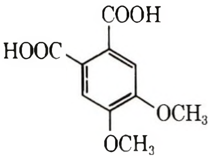
Fig. 2. Molecular weights of branches separated from graft polymers.

The number-average molecular weights of the polystyrene branches separated from the lignin–styrene graft polymers are plotted against the grafting ratios of the corresponding graft polymers in Figure 2. At grafting ratios up to 100 the molecular weights of the branches, 5000, are invariable despite the increased grafting. It is, therefore, reasonable to conclude that radical grafting on lignin proceeds, in stage 1, via addition of styrene polymer radicals to the aromatic nuclei of lignin molecules. That is, the grafting would proceed in such a way that polymer radicals would add one by one to the aromatic nuclei. A polymer radical would be expected to suffer a restriction in going into the inner part of the tridimensional structure of hydrochloric acid lignin because of steric hindrance. Accordingly, it is possible to conjecture that polymer radicals have a tendency to react with noncondensed guaiacyl residues, particularly with "pendant" guaiacyls, both of which give vanillin upon nitrobenzene oxidation. Figure 2 also indicates that, at grafting ratios greater than 100 the molecular weights of the polystyrene branches increase with the grafting ratio. *This fact implies that the propagation of polystyrene branches takes place from the aliphatic part of the lignin molecule and also from the polystyrene, already grafted to the lignin.* This type of grafting process seems to be predominant in stage 2, owing to the increased diffusion rate of styrene into "polystyrene-swollen" lignin. It became apparent also from Figure 2 that the lower molecular weights of the branches separated by nitrobenzene oxidation of the graft polymers, as described earlier,[3] were due to thermal degradation of the branches.

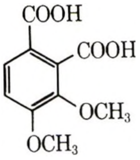
Freudenberg has oxidized methylated lignin by permanganate and identified almost all of the isolated aromatic acids, which afforded important information concerning the amount and sites of C—C bond in relation to the aromatic nuclei of lignin molecules.[7] This procedure was applied to the present grafted lignin and the original lignin, and the resultant acid fractions were investigated by paper chromatography. Although two acid fractions gave almost the same kind of chromatograms, isohemipic and, probably, metahemipic acids are distinctly observed to be more in the acid fraction of grafted lignin. It was difficult to distinguish metahemipic from hemipic acid by a spot of R_f 0.37, but a reaction of polymer radicals with the C-2 of guaiacyl nuclei seems to be unlikely. From the results of paper chromatography the grafting sites of the aromatic part of the lignin might be assigned to the C-5 and C-6.



Isohemipic acid



Metahemipic acid



Hemipic acid

Model compounds of lignin, (I), (II), (III) and (IV), were irradiated by 0.8–4.8 Mrads of gamma rays in the presence of styrene, and the resultant polymers were analyzed (Table I). In all cases the polystyrene contains methoxyl, whose amount is expressed by

$$31Nf_2/(M_1f_1 + M_2f_2) = (\%\ \text{methoxyl})/100 \qquad (1)$$

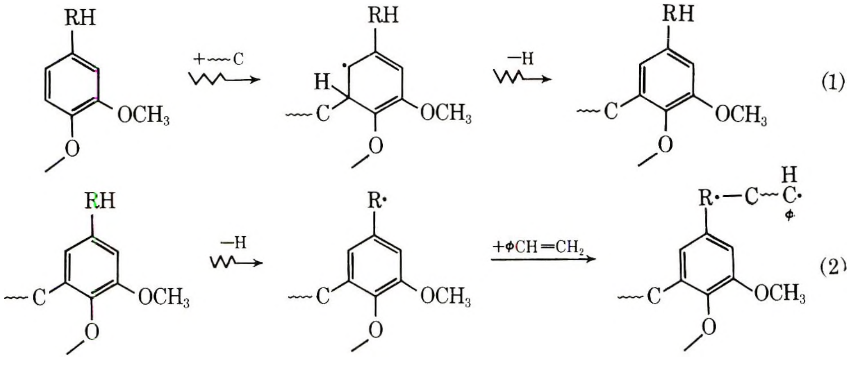
$$f_1 + f_2 = 1 \qquad (2)$$

where N is the number of methoxyl groups in the model compounds, M_1 is the $\overline{M}_n$ of the polystyrene molecules, M_2 is the $\overline{M}_n$ of the polystyrene molecules containing one model compound, f_1 is the ratio of polystyrene molecules, and f_2 is the ratio of polystyrene molecules containing one model compound. The sum $M_1f_1 + M_2f_2$ is equal to the number-average molecular weights ($\overline{M}_n$) of the polymer mixtures. Accordingly, f_1 and f_2 can be calculated by measuring the $\overline{M}_n$ of the resultant polymers. The value of f_2 means a reactivity of model compound to styrene or styrene polymer radical, or both, under irradiation (Table I). Model (I) most closely resembles the structure of actual lignin. It is interesting that the f_2 of (I) is 0.75, since it corresponds to the fact that only 70% of the vanillin-yielding guaiacyls join in a reaction with polymer radicals, as indicated in Figure 1. In general, the reactivities of the model compounds decrease with increasing bulk of the substituents at C-1 of the aromatic nucleus.

It is correct to predict that lignin is more or less subjected to degeneration by irradiation; nevertheless, it is resistant to ionizing radiation. In the case of hydrochloric acid lignin, no degradation takes place on the guaiacyl residues, since the rates of vanillin yields are constant before and after irradiation (see under "Experimental"). On the other hand, scission of the C—H bond undoubtedly occurs at the side chain of the lignin molecule, but scission of the C—C never occurs, because carbon-containing fragments are not detected by mass analysis of the evolving gaseous product. Therefore, grafting must occur at the radical site on the carbon atom through C—H bond scission. It could take place at a primary carbon, through scission of the C—H bond of the primary alcohol group, usually locating at the γ position with respect to the guaiacyl nucleus. It has been clear, however, from the results of primary and secondary hydroxyl analysis, presented in Table III, that radiation grafting on lignin has never taken place at the carbon of a secondary alcohol group, which is usually located at the α position with respect to the guaiacyl nucleus and, probably, of the corresponding ether group. The grafting also could occur at the secondary carbon of the ether linkage and the tertiary carbon, respectively, which are at the β position with respect to the guaiacyl. Thus, the hydrogen atom is supposed to be liberated from almost all kinds of C—H bonds in lignin side chains, but grafting would occur at the β and γ carbons.

CONCLUSION

At least two kinds of reaction are believed to take place in the radiation grafting of styrene or other vinyl monomers onto a lignin molecule:



Here RH is the lignin side chain or grafted side chain already present.

Reaction (1) takes place at grafting ratios of less than 100 (stage 1 in Fig. 1), and reaction (2) becomes predominant at grafting ratios of more than 100 (stage 2 in Fig. 1). In the initial stage reaction (1) takes place exclusively on the guaiacyl nuclei located at the outermost part of the lignin molecule. At grafting ratios greater than 100 reaction (2) proceeds on the aliphatic parts and also on grafted polystyrene branches already present, owing to the increased rate of diffusion of styrene monomer into the inner part of the "polystyrene-swollen" lignin macromolecule. The grafting sites of lignin are C-5 and C-6 of the aromatic nuclei and, probably, the β and γ carbons of the lignin aliphatic parts. As is usual in radiation-induced graft copolymerization, repeated homografting would lead to a more complicated tridimensional structure of the lignin molecule.

The authors express their sincere thanks to S. Mima, of the Government Industrial Research Institute, for analyzing the evolving gaseous products by mass spectrometry.

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Polymerization Initiated by the Charge-Transfer Complex of Styrene and Maleic Anhydride in the Presence of Cumene and of Cumene and Liquid Sulfur Dioxide

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Synopsis

A polymerization was induced with a charge-transfer type of complex consisting of styrene and maleic anhydride in the presence a solvent such as ethyl benzene, cumene, or *p*-cymene. No polymer was obtained either when the solvent was missing from the polymerization system or when benzene, toluene, or xylene, which are relatively stable to hydrogen abstraction, was added to the polymerization system. An effective initiation, however, took place when cumene or *p*-cymene, each of which has a labile hydrogen on an α carbon, was added. On the basis of elementary analysis and infrared spectroscopy the formation of copolymer containing substantially equimolar amounts of styrene and maleic anhydride was ascertained. This polymerization was inhibited by the addition of DPPH, suggesting that the system styrene–maleic anhydride–cumene functions much as a conventional free-radical initiator. On the other hand, when a solution of cumene and liquid sulfur dioxide was added to the polymerization system, polystyrene was obtained. This polymerization was inhibited by the addition of a base such as dimethylformamide or dimethyl sulfoxide, indicating that the polymerization proceeds through carbonium ion intermediates. The addition of ethyl benzene or of *p*-cymene brought about the same result as cumene. It is conceivable that the polymerization is induced by the abstraction of hydrogen attached at the α position of cumene by means of the charge-transfer complex of styrene and maleic anhydride.

Numerous papers in the past twenty years or so have dealt with the radical copolymerization of styrene and maleic anhydride, and it is well known that a copolymer containing equimolar amounts of styrene and maleic anhydride can be obtained. In the absence of radical initiator, however, initiation cannot take place at all. Bawn and his co-workers[1] found that the tetrahydrofuran–maleic anhydride complex irradiated with a mercury lamp initiates the polymerization of methyl methacrylate. In another paper[2] it was reported that a heated solution of trioxane, maleic anhydride, and a small amount of benzoyl peroxide can initiate the cationic polymerization of trioxane. The present paper is concerned with a polymerization induced by a charge-transfer complex consisting of styrene and maleic anhydride in the presence of ethyl benzene, cumene, or *p*-cymene.

TABLE I
Effect of Added Solvent on System Styrene–Maleic Anhydride (50°C.)

Expt. no.	Monomer, moles/l.			Added solvent, moles/l.		Convsn.,[a] wt.-%/3 hr.	Remarks
	Liq. SO_2	MAnh	St				
36		0.91	8.22			trace	
124		1.03	1.74	Benzene,	8.25	0.9	
125		1.03	1.74	Toluene,	6.93	0.9	
126		1.03	1.74	*m*-Xylene,	5.98	0.6	
134		1.03	1.74	Cumene,	5.26	19.0	Conversion at 110 min.
71		1.03	1.74	"	5.26	29.4	
129		1.03	1.74	"	5.26	nil	DPPH (0.097 mole/l.) added
123		1.03	1.74	*p*-Cymene,	4.68	15.4	
122		1.03	1.74	Chloroform,	9.19	3.2	
73	7.21		1.68	Cumene,	3.22	0.3	
72			1.74	"	5.74	1.1	
48	17.11	1.33				nil	
49	6.98		5.70			trace	
36		0.91	8.22			trace	

[a] Conversions estimated from total monomer weight.

Table I shows the effect of the added solvents on the solution of styrene and maleic anhydride in the absence of any initiator. As may be seen from the table, no polymer was obtained without solvent or in solvents such as benzene, toluene, or xylene, which are relatively stable to the hydrogen abstraction. On the other hand, an effective result was obtained on the addition of cumene or *p*-cymene, each of which has a labile hydrogen on the α carbon, but in the case of either styrene or a mixture of styrene and liquid sulfur dioxide the effect of cumene could not be observed. On the basis of elemental analysis and infrared spectroscopy of the polymer obtained from the system styrene–maleic anhydride–cumene the authors have ascertained the formation of copolymer containing equimolar amounts of styrene and maleic anhydride. The polymerization was inhibited by the addition of DPPH, suggesting that the system styrene–maleic anhydride–cumene functions in a manner similar to that of a conventional free-radical initiator. It is well known that styrene forms a charge-transfer type of complex with maleic anhydride,[3] and it is conceivable that the polymerization is induced by the abstraction of hydrogen attached at the α-position of cumene by the charge-transfer complex of styrene and maleic anhydride, as shown in eqs. (1) and (2).

Two courses must be considered: eq. (1) represents the abstraction of the proton by maleic anhydride radical anion, and eq. (2) represents that of hydride ion by the styrene radical cation.

Various types of solvent were added to the system styrene–maleic anhydride–liquid sulfur dioxide, as is shown in Table II. Effective results also were obtained when ethyl benzene, cumene, and *p*-cymene, respec-

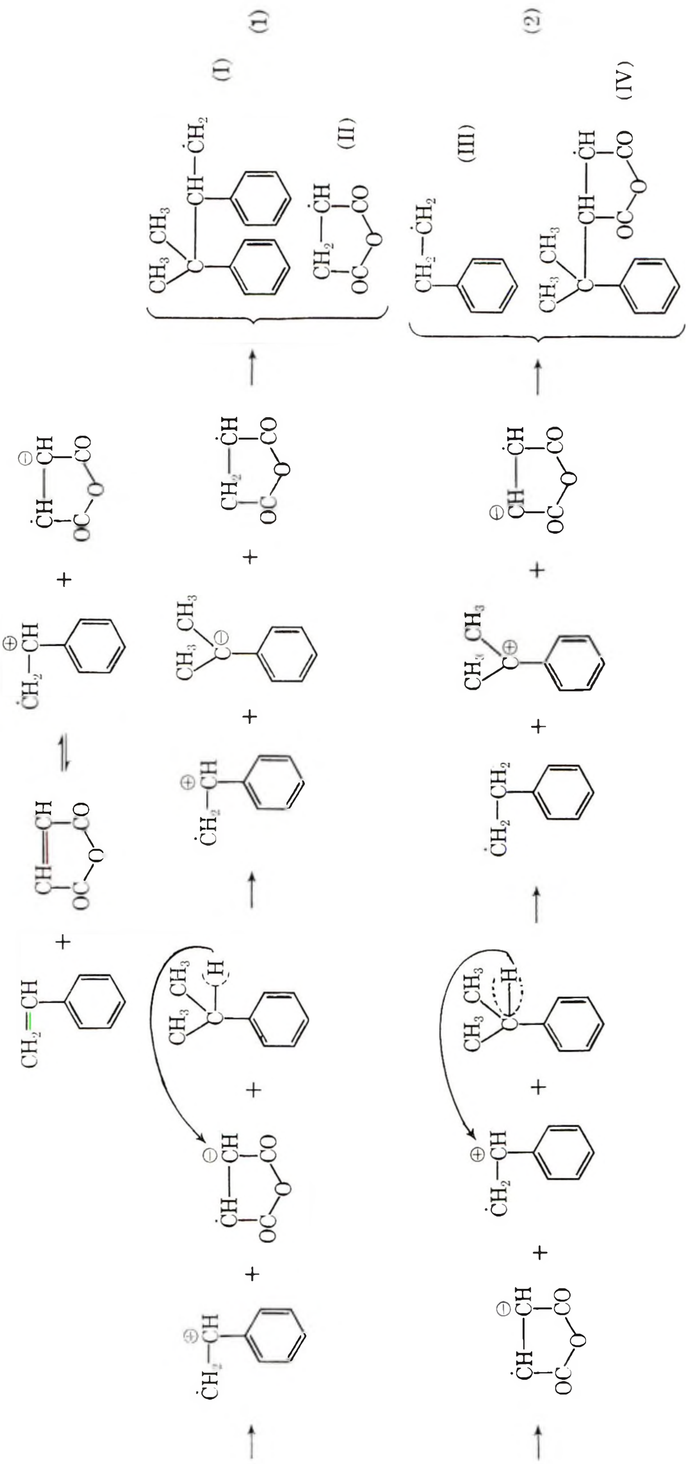

(I)
(II)
(III)
(IV)
(1)
(2)

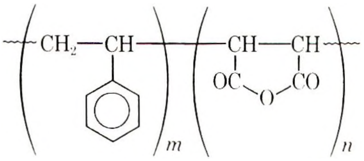
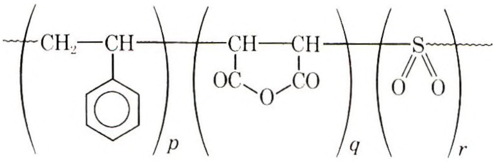
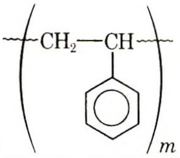
TABLE II
Effect of Added Solvents on System Styrene–Maleic Anhydride–Liquid Sulfur Dioxide (50°C.).

Expt. no.	Monomer, moles/l. Liq. SO_2	MAnh	St	Added solvent, moles/l.		Convsn.,[a] wt.-%/3 hr.	Remarks
96	11.22	0.43	3.64			0.6	Styrene–maleic anhydride copolysulfone
76	6.64	0.31	2.06	Carbon tetrachloride,	4.30	0.3	
112	6.64	0.31	2.06	Chloroform,	5.47	0.5	
83	6.64	0.31	2.06	Benzene,	4.66	0.4	
78	6.64	0.31	2.06	Toluene,	3.93	0.3	
79	6.64	0.31	2.06	*m*-Xylene,	3.39	0.3	
80	6.64	0.31	2.06	Cumene,	2.98	29.5	Polystyrene
81	6.64	0.31	2.06	*p*-Cymene,	2.50	40.1	
213	6.64	0.31	2.06	Ethyl benzene,	3.38	79.3	
214	6.64	0.31	2.06	*tert*-Butyl benzene,	2.68	0.3	Styrene–maleic anhydride copolysulfone
98	6.64	0.31	2.06	Dimethylformamide,	5.36	nil	
99	6.64	0.31	2.06	Dimethyl sulfoxide,	6.14	nil	
93	6.64	0.31	2.06	*n*-Hexane,	1.89	0.3	
94	6.64	0.31	2.06	Cyclohexane,	2.22	0.3	
82	6.64	0.31	2.06	Acetonitrile,	7.94	0.9	

[a] Conversions estimated from weight of styrene monomer, except for styrene–maleic anhydride copolysulfone.

tively, were added. The polymers were polystyrene, which was characterized by infrared spectroscopy and by qualitative analysis of sulfur in the polymer, and the polymerizations were inhibited by the addition of such bases

TABLE III
Relationship between Reaction Intermediates and Polymer Composition Obtained from Present Work

Polymer compositions obtainable from systems of present work	Remarks
	Styrene–maleic anhydride copolymer, which can be obtained from radical polymerization of styrene and maleic anhydride
	Styrene–maleic anhydride copolysulfone, which can be obtained from radical terpolymerization of styrene, maleic anhydride, and liquid sulfur dioxide
	Polystyrene, which can be obtained from cationic polymerization of styrene in liquid sulfur dioxide

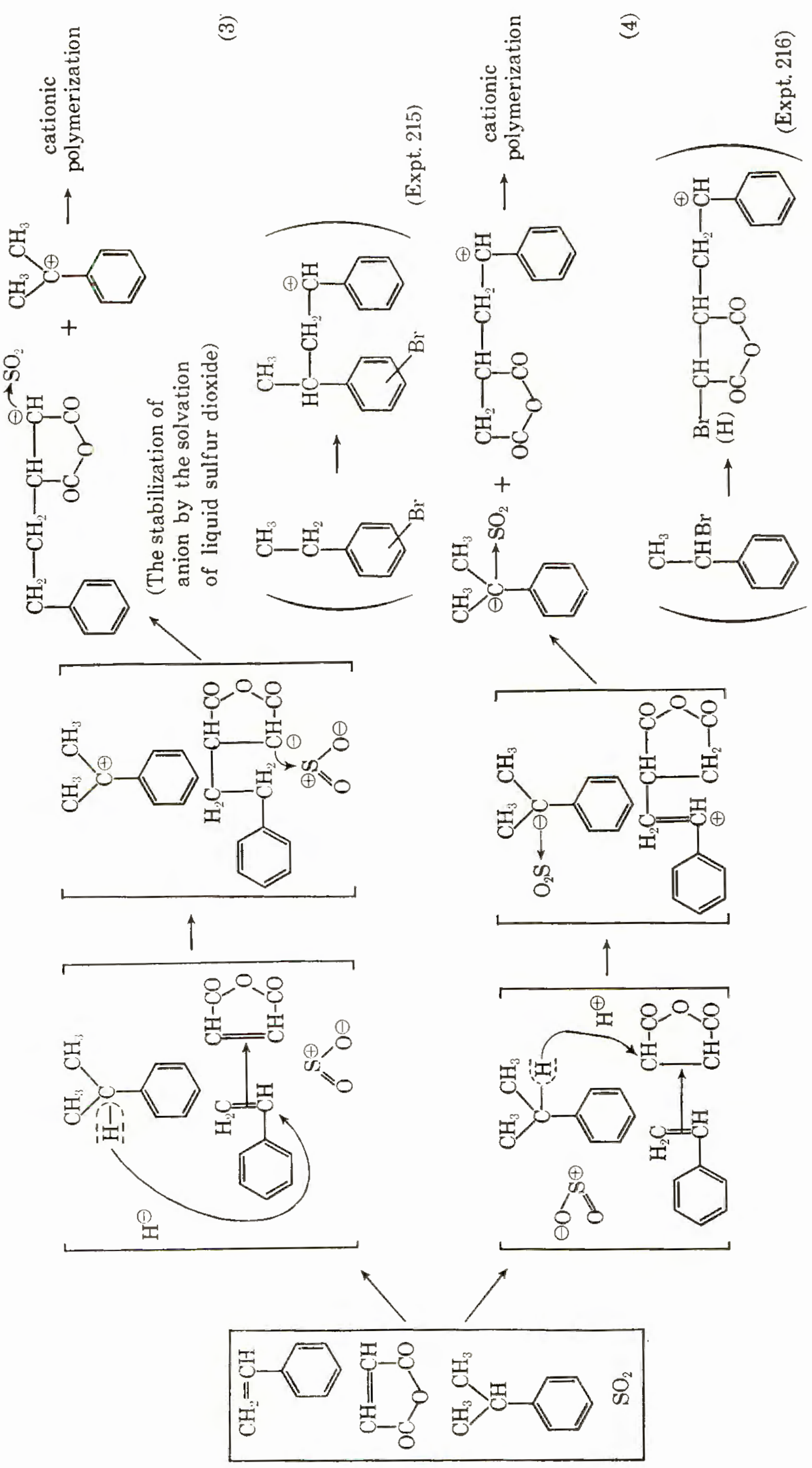

cationic polymerization
(3)
(The stabilization of anion by the solvation of liquid sulfur dioxide)
(Expt. 215)
cationic polymerization
(4)
(Expt. 216)
SO₂

TABLE IV
Result of Polymerization Obtained from System Styrene–Maleic Anhydride–Cumene–Liquid Sulfur Dioxide (50°C.)

Expt. no.	Monomer, moles/l.			Added solvent, moles/l.		Polymer			
						Convsn., wt.-%/5 hr.	Elem. anal., %		
	Liq. SO_2	MAnh	St				C	H	Br
215	6.64	0.31	2.06	*o*- and *p*-bromoethyl benzene mixture	1.94	81.1	87.48	7.17	3.79
216	8.08	0.37	2.51	α-bromoethyl benzene	1.35	32.2	86.78	6.97	6.58

as dimethylformamide and dimethyl sulfoxide, suggesting that they proceed through carbonium ion intermediates. The cationic and radical polymerizations of styrene in the system including liquid sulfur dioxide give polystyrene[4,5] and styrene polysulfone,[6,7] respectively; therefore, the composition of the polymers may be used for characterization of the reaction intermediates (Table III). When *tert*-butyl benzene rather than ethyl benzene, cumene, or *p*-cymene was used, no polymer was obtained except for the thermal polymerization product, which was characterized by infrared spectroscopy, showing the formation of styrene–maleic anhydride copolysulfone; see Table III. The initiation mechanism may probably be written as eqs. (3) and (4), in which liquid sulfur dioxide solvates to stabilize cabanion [the maleic anhydride anion, eq. (3), and the cumene anion, eq. (4)]. This mechanism was confirmed by using bromo-substituted ethyl benzenes. As shown in Table IV, polymers containing bromine were obtained from both a mixture of *o*- and *p*-bromoethyl benzenes and α-bromoethyl benzene.

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Linear Polyhydrazides

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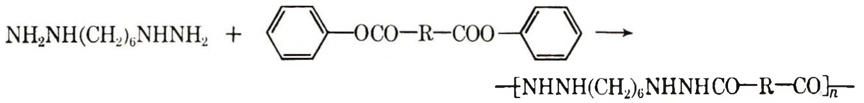
Synopsis

Linear polyhydrazides have been obtained successfully by heating diphenyl dicarboxylate with 1,6-dihydrazino hexane. The structure of the polymers was established by the *N*-deuteration method. The resulting polymers have many remarkable characteristics, such as high water-absorption ratio (20–100%), basic character ($pK_a = 3.15$), the ability to form a metal complex, and the power to initiate vinyl polymerization as a cocatalyst with ferric ion.

INTRODUCTION

A new type of linear polyhydrazide was prepared from 1,6-dihydrazinohexane and some diphenyl dicarboxylates, as briefly reported in a previous paper:[1]



where R is 1,4-tetramethylene, 1,4-phenylene, 1,3-phenylene, or 2,6-pyridine.

It is remarkable in this study that linear high molecular weight polymers result without any crosslinking reaction, although dihydrazine might be expected to behave as a tetrafunctional monomer in reaction with the electrophilic reagents.

There are only a few reports on the preparation of polymer from alkyl dihydrazines,[2,3] and a preliminary study of the reactivity of alkyl hydrazine was necessary before the study could proceed.

In our previous study[3] it was generalized that a relatively highly electrophilic reagent would attack the alkyl hydrazine predominantly at the alkyl group bearing nitrogen (α-nitrogen), whereas the milder electrophilic reagent would produce β-*N*-substituted *n*-alkylhydrazine in high yield (β-nitrogen attack). A similar tendency in the reaction of methylhydrazine with methyl carboxylates and carboxylic anhydrides had been reported.

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In the present model reaction of *n*-butylhydrazine with phenyl butyrate, carried out in *N*,*N*-dimethylformamide, only 30% pure β-*N*-*n*-butyryl-*n*-butylhydrazine was obtained, and a much smaller amount of α-*N*-*n*-butyryl-*n*-butylhydrazine was identified in the residue.

From all results of monomeric reactions it is naturally expected that there exists a smaller amount of the α type of linkage with β type of linkage in polyhydrazides. In this work the structure of the polymer was therefore examined in detail by the *N*-deuteration method; the spectra of the original polymer and model compounds were compared with those of *N*-deuterated derivatives and the characteristic absorption band of the α type of linkage was determined. From this study the chemical structure of the polymer was established: it is made up mostly of the β type of linkage, with a small portion of α type of linkage.

The new polyhydrazides have many interesting characteristics, chiefly originating in the uncommon hydrazide linkage, —NHNHCO—. To evaluate the relationship between the properties and the structure of the polymers, measurements of the basicity (pH titration) and of the water-absorption ratio were made and, in addition, of the abilities to produce metal complex and to initiate vinyl polymerization as cocatalyst with ferric ion.

As was expected, the polymers show relatively low basicity and high water absorption ratio, and act as ligand of metal complex and cocatalyst for redox polymerization.

RESULTS AND DISCUSSION

Preparation and Properties of Polyhydrazides

The polyhydrazides were prepared by solution polymerization, which was successively followed by melt polymerization. 1,6-Dihydrazinohexane was dissolved in a very small amount of solvent, such as *N*,*N*-dimethylformamide or *m*-cresol, and to this solution an equimolar amount of diphenyl dicarboxylate was added. The resulting mixture was heated at about 100°C. for 7–15 hr. After the solvent and phenol eliminated were distilled

TABLE I
Polymerization Conditions

	Diphenyl ester component	Solution polymerization		Melt polymerization	
		Temp., °C.	Time, hr.	Temp., °C.	Time, hr.
I	Adipic acid	100	8.0	120 (150–180)[a]	8.0 (3.0)[b]
II	Terephthalic acid	100	8.0	120 (150–200)	10.0 (2.0)
III	Isophthalic acid	100–110	15.0	120 (150–180)	8.0 (2.0)
IV	Dipicolinic acid	100–110	7.0	120 (150–160)	3.0 (5.5)

[a] Figures in parentheses: to remove the eliminated phenol completely, temperature raised to this temperature at final stage of reaction.

[b] Figures in parentheses: the period that the temperature was raised higher than 150°C.

TABLE II
Properties of Polyhydrazides

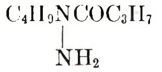
	Polymer no.			
	I	II	III	IV
Intrinsic viscosity (30°C., *m*-cresol):	2.02	0.55	0.40	1.37
Softening temp., °C.	105–110	192–200	116–126	113–120
Solubility:[a]				
Hexamethylphosphoramide	+[a]	+	+	+
m-Cresol	+	+	+	+
Dimethylformamide	±[b]	−	+	+
Ethylene chlorohydrine	+	+	+	+
Chloroform	−[c]	±	±	+
Methanol	±	±	±	±
HCl, concd.	+	+	+	+
H_2O	±	−	−	±
Water-absorption ratio, %:	98.2	19.2	20.6	47.2

[a] Soluble, +; [b]swollen, ±; [c]insoluble, −.

off under reduced pressure, melt polymerization was continued for 2–5 hr. under reduced pressure. It was necessary to keep the reaction temperature well below 150°C. so as to avoid crosslinking reaction. The polymerization was finished when the theoretical amount of phenol was distilled off. The polymerization conditions are shown in Table I. The resulting polymers are extremely hygroscopic, much more so than ordinary polymers, and show rubbery characteristics. These characteristics are probably caused by the existence of nonacylated NH bonding. The melting temperature, solubility character, and water-absorption ratio of the resulting polymers are summarized in Table II.

Structure of Polyhydrazide

For the purpose of discussing the fine structure of the polyhydrazide, α-*N*-*n*-butyryl-*n*-butylhydrazine was prepared in a reaction of *n*-butylhydrazine with *n*-butyric anhydride at low temperature (−40°C.), and β-*N*-*n*-butyryl-*n*-butylhydrazine was prepared in the reaction of *n*-butylhydrazine with phenyl butylate. The former model compound has no amide II peak at about 1550 cm.$^{-1}$, which is characteristic of the NH vibration of the amide bonding, and has two peaks at about 3300 and 3200 cm.$^{-1}$, which correspond to primary amine peaks. The NH deformation vibration of the primary amine peak appears at 1630 cm.$^{-1}$ as the shoulder of the carbonyl absorption peak only when the compound is in solution (CCl_4). Moreover, this compound reacted easily with *p*-nitrobenzaldehyde in water–alcohol (1:1) solution at room temperature and gave the corresponding hydrazone, α-*N*-*n*-butyryl-*n*-butylhydrazone of *p*-nitrobenzaldehyde, m.p. 55–56°C. The latter model compound has an amide II peak at 1555 cm.$^{-1}$ and did not react with *p*-nitrobenzaldehyde. From these results the structures of the two model compounds are deduced:[4]



$C_4H_9N(NH_2)COC_3H_7$

α-*N*-*n*-Butyryl-*n*-butylhydrazine
b.p. 102–104°C. at 1 mm. Hg

$C_4H_9NHNHCOC_3H_7$

β-*N*-*n*-Butyryl-*n*-butylhydrazine
m.p. 61–62°C.

ANAL. Calcd. for $C_{15}H_{21}N_3O_3$ (α-*N*-*n*-butyryl-*n*-butylhydrazone of *p*-nitrobenzaldehyde): C 61.84%, H 7.27%, N 14.42%. Found: C 61.52%, H 7.18%, N 14.17%. Calcd. for $C_8H_{18}N_2O$ (β-*N*-*n*-butyryl-*n*-butylhydrazine): C 60.72%, H 11.47%, N 17.70%. Found: C 61.01%, H 11.84%, N 16.85%.

As mentioned above, the split peak at 3200–3300 cm.$^{-1}$ and the shoulder of the carbonyl stretching at 1630 cm.$^{-1}$ are the α type of absorption bands.

When the strong β type of NH stretching coexists with the split peak, the splitting of the band cannot be detected, and when the sample is measured in neat liquid, the shoulder cannot be found. Therefore, the absorption characteristic of the α type of linkage cannot be detected if it exists in only a very small portion of the polymer.

To avoid this difficulty the *N*-deuteration method was applied to the polymer and to the two model compounds. The infrared spectra of *N*-deuterated polyhydrazide from diphenyl adipate and two model compounds are shown in Figure 1, together with those of the original compounds for comparison. From this study the characteristic absorption band of the α type of linkage was confirmed.

The frequency shifts due to *N*-deuteration are given in Table III. For *N*-deuterated α-*N*-*n*-butyryl-*n*-butylhydrazine the ND deformation absorption that corresponds to the NH deformation absorption of the primary amino group (1630 cm.$^{-1}$) occurs at 1520 cm.$^{-1}$, which is characteristic of the α type of linkage. On the other hand, the ND deformation absorption band that corresponds to the amide II band of the original compound is recognized at 1425 cm.$^{-1}$ for *N*-deuterated β-*N*-*n*-butyryl-*n*-butylhydrazine. The infrared spectrum of *N*-deuterated polyhydrazide shows a strong ND deformation absorption band at 1425 cm.$^{-1}$ and a decreased absorption band at 1540 cm.$^{-1}$, which is due to the residual NH linkage in the polymer.

The shifts of the characteristic absorption bands in polyhydrazide show the same tendency as those of the β type *N*-deuterated model compound. But it is not difficult to see, if careful observation is made, that the residual amide II peak in the spectrum is not as symmetrical in shape as that of β type of model compound, suggesting the existence of an α type of ND deformation vibration.

So it is reasonably concluded that there are some α linkages in polyhydrazide, insofar as they may be detected in the region of 1520 cm.$^{-1}$ when *N*-deuterium exchange is carried out.

The other three polymers are considered to have the same structure as the polymer from diphenyl adipate, though they are somewhat different in this content of α linkages. Elemental analyses of the resulting polymers are shown in Table IV.

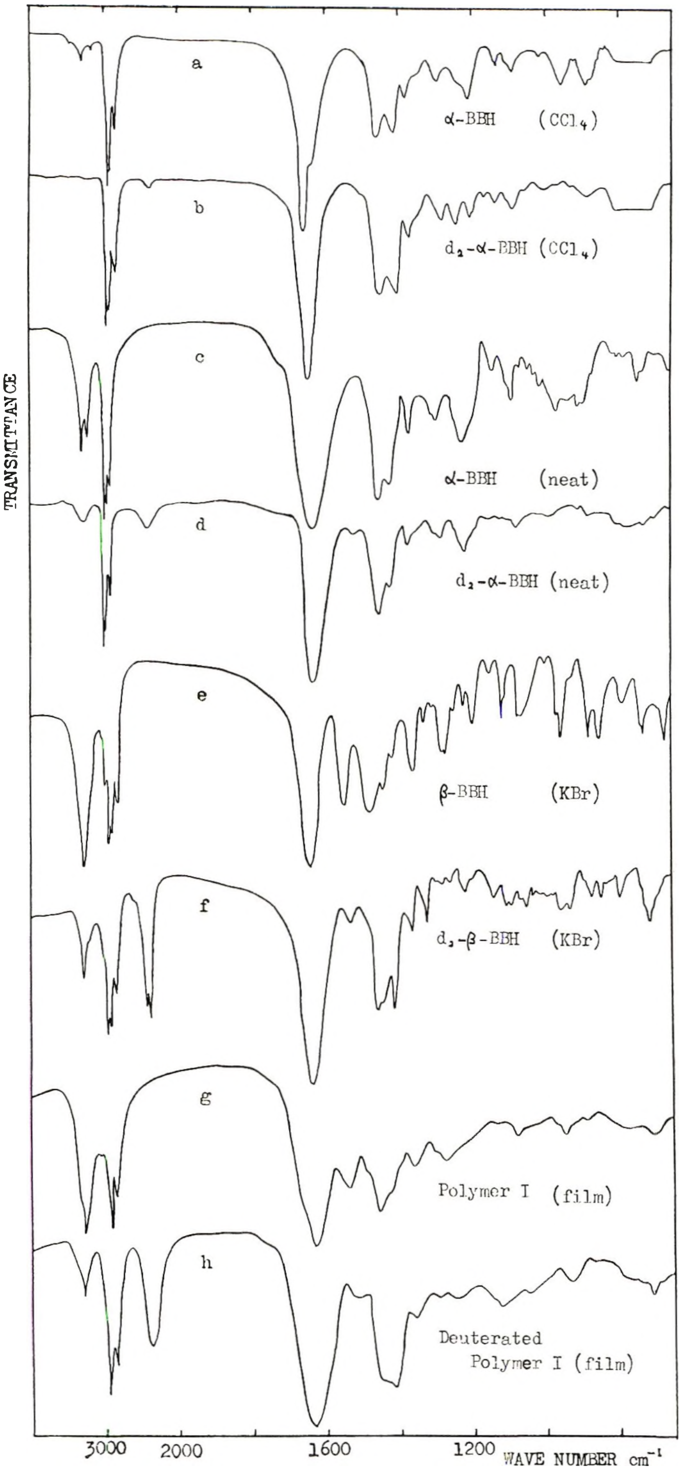


Fig. 1. Infrared spectra of *N*-*n*-butyryl-*n*-butylhydrazine (BBH). Polymer I is polyhydrazide from diphenyl adipate.

TABLE III
Frequency Shifts of Bands in *N*-Deuteration

	Original				*N*-deuterated			
	νNH	νCO	δNH (amide II)	δNH	νND	νCO	δND (amide II′)	δND
α-*N*-*n*-Butyryl-*n*-butylhydrazine in neat liquid[a]	3200 3300	1640		—[b]	2350 2400	1630		1520 (weak, broad)
α-*N*-*n*-Butyryl-*n*-butylhydrazine in CCl_4 solution	3200 3300	1650		1630 (shoulder)	2350 2400	1640		—[b]
β-*N*-*n*-Butyryl-*n*-butylhydrazine in KBr disk	3250	1645	1555		2425	1640	1425	
Polyhydrazide from diphenyl adipate in film	3300	1645	1555		2400	1630	1425	1520 (very weak shoulder)

[a] Neat liquid examined between NaCl plates.
[b] Not observed in this procedure.

TABLE IV
Polyhydrazides

		Calculated, %			Found, %		
		C	H	N	C	H	N
I	$C_{12}H_{24}N_4O_2$	56.23	9.44	21.86	55.98	9.22	20.52
II	$C_{14}H_{20}N_4O_2$	60.85	7.30	20.27	61.23	6.93	18.89
III	$C_{14}H_{20}N_4O_2$	60.85	7.30	20.27	60.48	6.92	19.03
IV	$C_{13}H_{19}N_5O_2$	56.30	6.91	25.25	55.83	6.52	24.21

Basicity of Polyhydrazide

To determine quantitatively the basicity of polyhydrazide the pH titration method (pK_a' method) was applied to the polymer prepared from

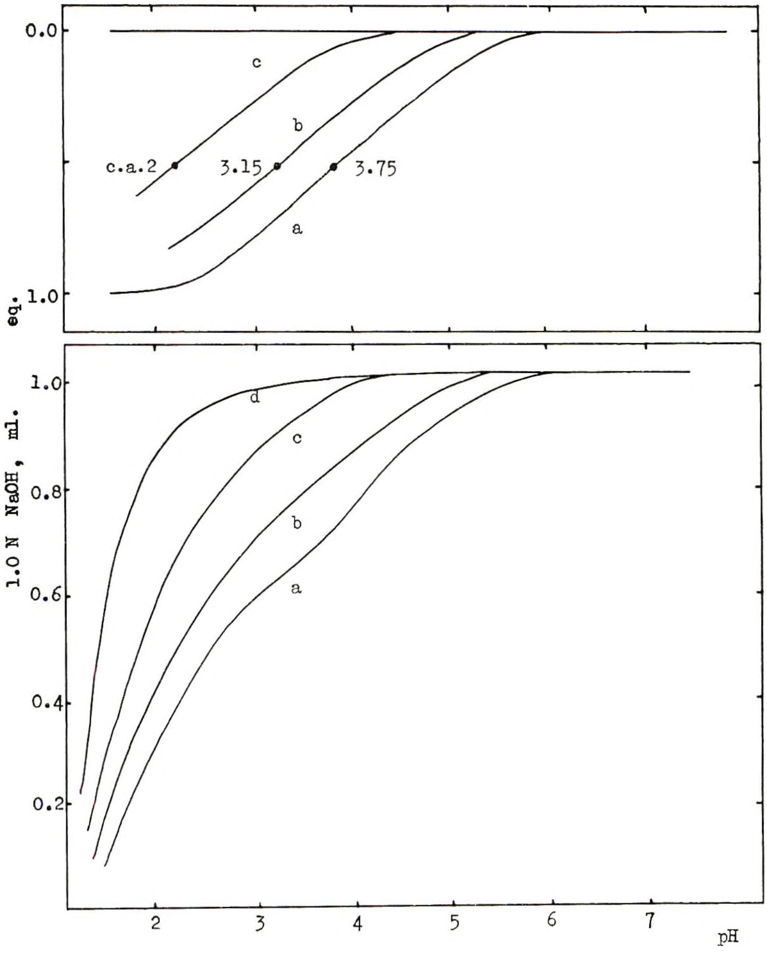


Fig. 2. Titration curves (pH) and dissociation curves: (a) β-*N*-*n*-butyryl-*n*-butylhydrazine; (b) polyhydrazide from diphenyl adipate; (c) α-*N*-*n*-butyryl-*n*-butylhydrazine; (d) standard line.

diphenyl adipate and two model compounds; the titration curves are shown in Figure 2. The pK_a' values of the polyhydrazide and the α and β types of model compound are 3.15, >2, and 3.75, respectively. The polymer shows a lower pK_a' value than does the β model compound. This might be caused, not by the existence of an α linkage in the polymer, but by the effect of the polymer's chain entanglement in solution. It is reasonable that the basicity of the outer nitrogen in the hydrazide linkage is not as high as was expected but, if a parallel relationship is maintained between the basicity and the nucleophilicity among these alkyl hydrazines, these values would explain the fact that the alkyl-bearing nitrogen in polyhydrazide reacts with isocyanate easily but scarcely at all with phenyl esters and that therefore no crosslinking reactions were observed during the polymerization.

It is an interesting fact that there still remain such basic reactive sites in the polymer prepared by melt polymerization at high temperature.

Preparation of Metal-Complexed Polyhydrazide

Linear aliphatic polyhydrazide from diphenyl adipate was also investigated with respect to its ability to form metal chelate or metal-complexed polymer.

The polyhydrazide was dissolved in dried *m*-cresol, and to this solution an equimolar amount of cupric chloride was added. Gradually a dark-

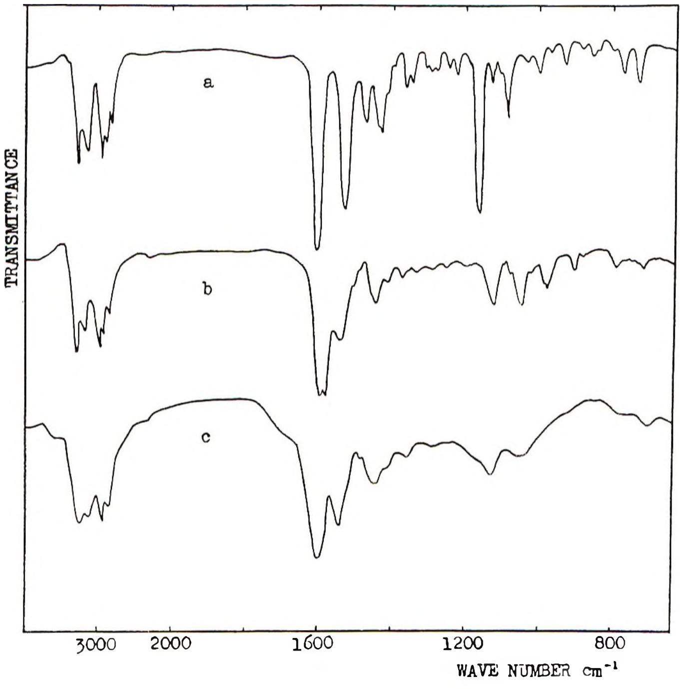
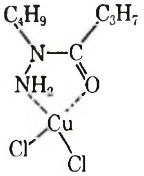


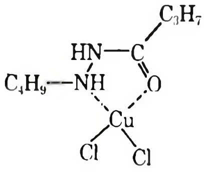
Fig. 3. Infrared spectra: (a) α-*n*-butyryl-*n*-butylhydrazine–Cu(I)); (b) β-*N*-*n*-butyryl-*n*-butylhydrazine–Cu(II); (c) metal-complexed polyhydrazide.

green precipitate was obtained. This compound is less stable than the original polymer and is very intractable; it is insoluble in dimethyl sulfoxide, concentrated sulfuric acid, and other common polymer solvents: it degrades and becomes soluble in concentrated sulfuric acid a few days later; it also changes gradually into a brownish-green compound in the atmosphere, unless moisture is excluded, and easily decomposes at about 180°C.

The copper complex formation was also attempted with the two model compounds in order to confirm the structure of the polymer. The infrared spectra of these complexed compounds are shown in Figure 3. Considerably small shifts of the carbonyl stretching vibration to a lower wavenumber are observed with the formation of metal complex and suggest that these compounds are not deprotonated complexes but merely addition complexes according to Nagano's report;[5] among the metal-complexed acid hydrazides deprotonated complexes show a larger frequency shift (300–500 cm.$^{-1}$) than addition complexes (20–100 cm.$^{-1}$). From these considerations the structures of the complexed compounds are taken to be



α-*N*-*n*-Butyryl-*n*-butylhydrazine–Cu(II)



β-*N*-*n*-Butyryl-*n*-butylhydrazine–Cu(II)

Elemental analysis of these complexes showed good agreement with these structures.

The infrared spectra of the complexed polymer and of β-*N*-*n*-butyryl-*n*-butylhydrazine–Cu(II) resemble each other (Fig. 3). Therefore the polymer is considered to have almost the same structure as the complexed β type of model compound; that is, the complexed polymer consists of merely addition complex. The analysis of copper content also supports this structure.

ANAL. Calcd.: Cu 24.20%. Found: Cu 22.20%.

In an attempt to obtain a deprotonated complex the complex formation was carried out in an alkaline medium, but cupric ion was reduced by the hydrazide group, and no complex was obtained. Consequently, a deprotonated complex was not derived from this type of polyhydrazide, but an unstable complex was produced.

Graft Copolymerization

As the hydrazide group reduces cupric ion in alkaline medium and also reduces silver ammonium ion, a $\mathrm{—NH\dot{N}CO—}$ type of radical is probably produced in the reaction medium, if the hydrazide is treated with a suitable oxidant.

TABLE V
Graft Copolymerization Conditions

		Catalyst			
	Acrylonitrile, g.	Polyhydrazide, g.	Fe^{3+} (0.17*N*), ml.	Aqueous acetic acid solution (1.0*N*), ml.	Polymer solvent
Graft copolymer I	5.2113	0.6300	6.1	30	Insoluble
Graft copolymer II	2.0111	0.2494	0.55	15	DMSO, concd. H_2SO_4
Graft copolymer III	0.9994	0.5103	17.0	30	Insoluble
Polyacrylonitrile[a]	7.8570	1.2417[b]	9.7	45	DMSO, DMF, concd. H_2SO_4

[a] Polyacrylonitrile initiated by the redox catalyst of β-*N*-*n*-butyryl-*n*-butylhydrazine and ferric ion.

[b] Weight of β-*N*-*n*-butyryl-*n*-butylhydrazine.

It has been reported that the redox catalyst of acetyl hydrazine and ferric ion can induce the polymerization of acrylonitrile.[6] Therefore the redox catalyst of β-*N*-*n*-butyryl-*n*-butylhydrazine (*N*-alkyl-substituted hydrazide) with ferric ion was applied to the polymerization of acrylonitrile, and positive results were obtained. During the reaction no evolution of nitrogen gas was observed. This indicates that ferric ion acted effectively as oxidant, originating free radicals.

According to these results, the preparation of graft copolymer from polyhydrazide and acrylonitrile was examined. A certain amount of polyhydrazide from diphenyl adipate and acrylonitrile were dissolved in 1.0 *N*

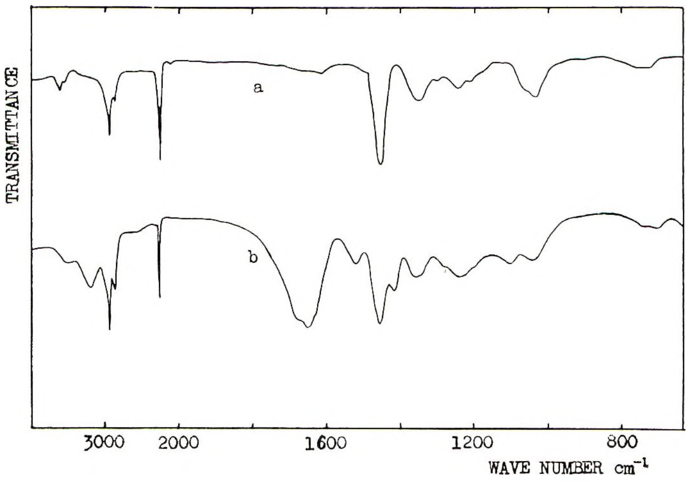


Fig. 4. Infrared spectra: (a) polyacrylonitrile initiated by β-*N*-*n*-butyryl-*n*-butyl-*n*-hydrazine and ferric ion; (c) graft copolymer III.

aqueous acetic acid solution. To this solution $0.17N$ aqueous ferric sulfate solution was added at 30°C. The polymerization started immediately after ferric ion was added into the mixture. Without ferric ion no polymerization was observed. The resulting polymer was insoluble in common polymer solvents, unless very small amounts of polyhydrazide and ferric ion, relative to the acrylonitrile, were used.

But when the insoluble graft copolymer was hydrolyzed with acid catalyst, it became soluble, suggesting the hydrolysis of polyhydrazide in the main chain; the graft copolymerization was successfully initiated without degradation of the main chain, and the expected graft copolymer was produced. Typical polymerization conditions are given in Table V.

The infrared spectra of polyacrylonitrile initiated by a redox system consisting of β-*N*-*n*-butyryl-*n*-butylhydrazine and ferric ion and of graft copolymer initiated by a redox system consisting of polyhydrazide and ferric ion are shown in Figure 4.

Experimental

n-Butylhydrazine, 1,6-dihydrazinohexane, and the phenyl esters were prepared according to the literature; the alkyl hydrazides were prepared from the amines passing through the intermediate sydnons, and the phenyl esters were obtained from phenol and the acid chlorides.

Preparation of Polymers

All the polyhydrazides were prepared in a combination of solution and melt polymerization. A typical example, the preparation of polyhydrazide from diphenyl adipate, is described. The other three polymers were prepared by the same procedure, and the individual conditions are tabulated in Table I.

Preparation of Polymer I. 1,6-Dihydrazinohexane (2.2190 g.) was dissolved in 10 ml. of dried dimethyl formamide, and to this solution an equimolar amount of diphenyl adipate (4.5369 g.) was added. The mixture was kept at about 100°C. for 8 hr. Then the solvent and the phenol eliminated were removed under reduced pressure, and the remaining polyhydrazide was continuously heated at about 120°C. for an additional 8 hr. under reduced pressure (1 mm. Hg). It was then held at 170–180°C. for 3 hr. under reduced pressure (1 mm. Hg). The polymer thus prepared had an intrinsic viscosity of 2.02 (30°C., *m*-cresol).

About 0.5 g. of completely dried specimen was placed in a small container with distilled water maintained at 30°C. for 24 hr. Then the water was removed, and the swollen specimen was washed with ethanol and ether successively, dried at 60°C. for 15 min., and weighed immediately. The water-absorption ratio was calculated as follows:

$$\text{Water absorption ratio, \%} = \frac{(\text{wet weight}) - (\text{dried weight})}{\text{dried weight}} \times 100$$

When nylon 6 tip (Nichiray A 1030) was used as sample, the water absorption ratio was 8.1%.

pH Titration Curves

The pH measurements were made with a Tokyo Rikagaku GAS-2. To keep the junction potentials constant throughout the titration the standard calomel electrode was dipped into a saturated KCl solution and connected through a saturated KCl salt bridge to the solution to be examined.

The sample, 0.10 mole, was dissolved in 30 ml. of 0.1*N* hydrochloric acid solution, and 10 ml. of this solution was titrated with 1.0*N* sodium hydroxide solution.

Preparation of Metal-Complexed Compounds

Polyhydrazide–Cu(II). A 1.5207 g. amount of polyhydrazide was dissolved in 50 ml. of dried *m*-cresol; to this solution 2.066 g. of cupric chloride dihydrate was added, and the mixture was stirred vigorously. The copper salt was gradually dissolved, and finally a dark-green substance precipitated. This was collected on a glass filter, washed with ether, and dried. The softening temperature was 120–130°C.; decomposition was at ≈180°C.

α-*N*-*n*-Butyryl-*n*-butylhydrazine–Cu(II). A solution of 0.2855 mg. of α-*N*-*n*-butyryl-*n*-butylhydrazine in 3 ml. of ethanol was added to a solution of 0.3075 g. of cupric chloride dihydrate in 3 ml. of ethanol. A light-blue precipitate appeared instantly. This was collected on a glass filter, washed with ether, and dried; m.p. 155–156°C. (decompn.).

ANAL. Calcd. for $C_8H_{18}N_2OCuCl_2$: C 32.83%, H 6.20%, N 9.57%, Cu 21.71%, Cl 24.23%. Found: C 33.24%, H 6.28%, N 9.61%, Cu 21.20%, Cl 23.58%.

β-*N*-*n*-Butyryl-*n*-butylhydrazine–Cu(II). A solution of 0.3030 g. of β-*N*-*n*-butyryl-*n*-butylhydrazine in 3 ml. of ethanol was added to a solution of 0.3338 mg. of cupric chloride dihydrate in 30 ml. of an ether–ethanol (10:1) mixture. A light-green substance precipitated instantly. This was collected on a glass filter, washed with petroleum ether, and dried; m.p. 101–102°C. (decompn.).

ANAL. Calcd. for $C_8H_{18}N_2OCuCl_2$: C 32.83%, H 6.20%, N 9.57%, Cu 21.71%, Cl 24.23%. Found: C 31.49%, H 6.10%, N 9.34%, Cu 20.20%, Cl 23.57%.

Preparation of Graft Copolymer

Polymer I (0.6300 g.) and acrylonitrile (5.2113 g.) were dissolved in 30 ml. of 1.0*N* acetic acid solution; this mixture was frozen in solid carbon dioxide and acetone and subjected to freezing and thawing operations five times *in vacuo*. Then 6.1 ml. of 0.17*N* ferric sulfate solution was added to this mixture and kept at 30°C. for 20 hr. The white precipitate obtained was washed with water and dried.

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Cationic Polymerization of α-Methylstyrene Catalyzed by Boron Trifluoride Etherate in 1,2-Dichloroethane under an Electric Field*

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Synopsis

The cationic polymerization of α-methylstyrene with boron trifluoride etherate was studied in 1,2-dichloroethane under an electric field. The electric field was again found to increase the polymerization rate. This field effect was independent of monomer concentration, as was found previously. The effect, however, became greater as the catalyst concentration was lowered, unlike previous findings with various cationic systems. Furthermore, the field effect became smaller with rising temperature, whereas it had been practically independent of temperature in previous studies. The field effect increased linearly with the field strength. At 2.7 kv./cm. the rate was almost tripled. The field effect was small at lower dielectric constants, as had been observed previously. The large field effects observed and their "exceptional" behavior led to the interpretation that "partial" desolvation of free, growing chain ends, in addition to the field-facilitated dissociation, was responsible for the effect. Specific conductivities of polymerizing solutions and catalyst solutions were measured and are discussed.

Introduction

In a previous paper[1] the influence of a high-intensity electric field on the cationic polymerization of α-methylstyrene catalyzed by iodine in 1,2-dichloroethane has been studied. The results show that the polymerization rate was increased by 30% in the presence of an electric field of 1 kv./cm. Subsequently, the work has been extended to other solvents. In nitrobenzene the accelerating effect amounted to 150% at a rather low electric field of 0.11 kv./cm., whereas in toluene no effect was shown at 1.0 kv./cm.[2] In other words, the field effect increased with the dielectric constant of the solvent for the combination of α-methylstyrene and iodine. This paper presents the results of experiments carried out on α-methylstyrene in 1,2-dichloroethane with boron trifluoride etherate instead of iodine. The purpose of the work was to investigate the effect of the catalyst on the field effect.

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Experimental

The α-methylstyrene, a gift of the Kurashiki Rayon Company, Kurashiki, Japan, was very carefully purified as previously described.[1] 1,2-Dichloroethane (DCE) and toluene were washed by standard methods, dried over Drierite for 2 wk. or so, heated over calcium hydride under reflux for at least 20 hr., and fractionally distilled both over and through calcium hydride in a dry nitrogen atmosphere. A commercial sample of boron trifluoride etherate (BF_3OEt_2) was distilled at atmospheric pressure under nitrogen. The water content of toluene and DCE was below 1.0×10^{-3} mole/l.

The polymerization was carried out in a glass vessel described previously.[2] The polymerization procedures have also been described.[1]

RESULTS

Field Effect and Catalyst Concentration. The rate of polymerization is given as a function of the catalyst concentration in Figure 1. The filled circles denote the rates under electric field (R_{pE}) and the blank ones those in the absence of the field (R_{p0}). The polymerization rate was determined from the slope of the linear relation between the logarithm of the ratio of initial monomer concentration and concentration of monomer unconsumed and polymerization time. The field strength was 2.2 kv./cm., the temperature −12.0°C., and the initial monomer concentration 0.80 mole/l. The polymerization rate is seen to increase with application of the field, and the relative increase appears to get smaller as the initial catalyst concentration becomes lower. We note here that the system studied at present is an exception to the so far usually observed insensitivity of the field effect to the catalyst concentration.[1,2]

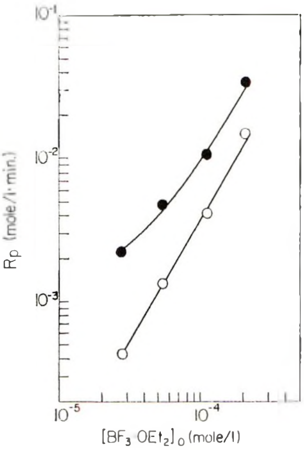

Fig. 1. Catalyst concentration dependence of polymerization rate, $[M]_0 = 0.80$ mole/l., −12°C.: (○) $E = 0$; (●) $E = 2.2$ kv./cm.

As was often previously the case, the application of the field resulted in a temperature rise in the present systems. Thus, a temperature correction was introduced for the observed polymerization rates, to give the true value, by a method mentioned in a previous paper.[3] The R_{pE}'s reported in the present work are the corrected values.

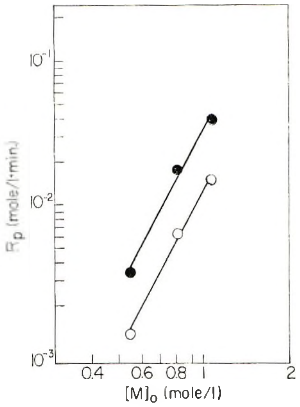

Fig. 2. Monomer concentration dependence of polymerization rate, $[BF_3OEt_2]_0 = 1.1 \times 10^{-4}$ mole/l., −12°C.: (○) $E = 0$; (●) $E = 2.2$ kv./cm.

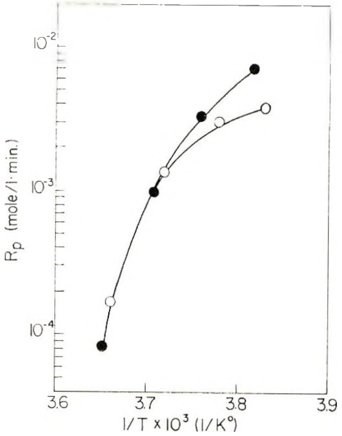

Fig. 3. Temperature dependence of polymerization rate, $[M]_0 = 0.55$ mole/l. $[BF_3OEt_2]_0 = 1.1 \times 10^{-4}$ mole/l.: (○) $E = 0$; (●) $E = 1.1$ kv./cm.

Field Effect and Monomer Concentration. Figure 2 represents the polymerization rates as a function of the initial monomer concentration. The field strength was 2.2 kv./cm., the temperature −12.0°C., and the initial catalyst concentration 1.1×10^{-4} mole/l. The dielectric constant of the polymerizing solutions was kept constant by substituting toluene for the monomer, the sum of volume fractions being approximately constant. As seen from Figure 2, the R_{pE} is larger than R_{p0}. The relative increase of

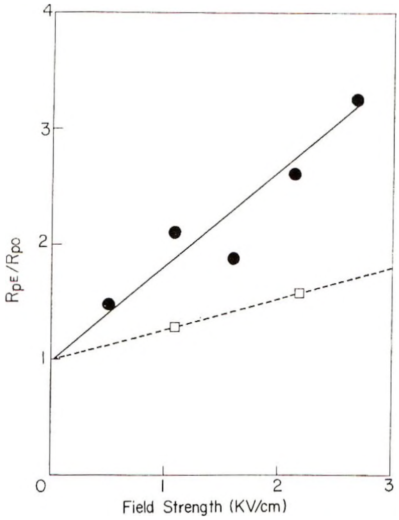

Fig. 4. Field effect and field strength, $[M]_0$ = 0.80 mole/l., $[BF_3OEt_2]_0$ = 1.1 × 10^{-4} mole/l., −12°C.: (●) present system; (□) α-methylstyrene–iodine–DCE.

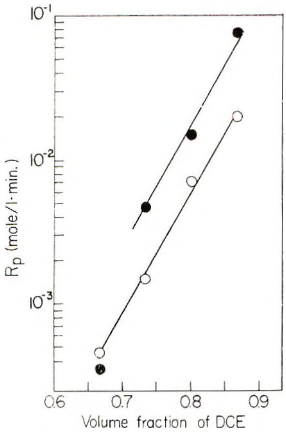

Fig. 5. Polymerization rate and solvent composition, $[M]_0$ = 1.07 mole/l., $[BF_3OEt_2]_0$ = 2.2 × 10^{-4} mole/l., −12°C.: (○) E = 0; (●) E = 2.2 kv./cm.

the rate due to the field may be regarded as constant with respect to the monomer concentration, as was often the case.

Field Effect and Temperature. The polymerization rate is plotted against the polymerization temperature in Figure 3. The field strength was 1.1 kv./cm., and the concentrations of monomer and catalyst were 0.55 and 1.1 × 10^{-4} mole/l., respectively. The field's accelerating effect is seen to decrease with increasing temperature: no field effect is observable above 0°C. For systems previously studied the field effect was practically independent of the temperature.[1,2] Thus the present system is again "exceptional."

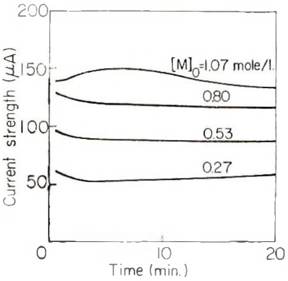

Fig. 6. Current strength and polymerization time, $[BF_3OEt_2]_0 = 1.1 \times 10^{-4}$ mole/l., −12°C., $E = 2.2$ kv./cm.

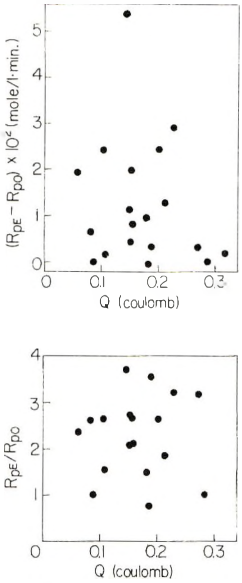

Fig. 7. Field effect and quantity of electricity.

Field Effect and Field Strength. The R_{pE}/R_{p0} value obtained at −12°C. is plotted against the field strength in Figure 4. A linear relation appears to hold up to 3 kv./cm. For comparison, the field effects on α-methylstyrene–iodine–DCE are given.

Field Effect and Solvent Composition. Figure 5 gives the polymerization rates in a series of mixtures of DCE and toluene. The temperature was −12.0°C., the field strength 2.2 kv./cm., the monomer concentration 1.07 mole/l., and the catalyst concentration 2.2×10^{-4} mole/l. It is seen that the R_{pE}/R_{p0} value is 3.0 in the range of 0.73 and 0.87, whereas it is almost unity at a low DCE fraction of 0.67 (i.e., at low dielectric constant). This tendency is in agreement with our previous finding and interpretation.[2]

Field Effect and Quantity of Electricity. In Figure 6 current strength is plotted against time. The time variation was rather small in the present

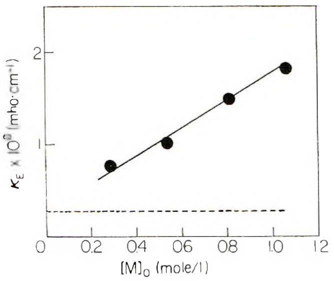

Fig. 8. Specific conductivity and monomer concentration, $[BF_3OEt_2]_0 = 1.1 \times 10^{-4}$ mole/l., −12°C., E = 2.2 kv./cm.: (●) polymerizing solution; (- - -) catalyst solution.

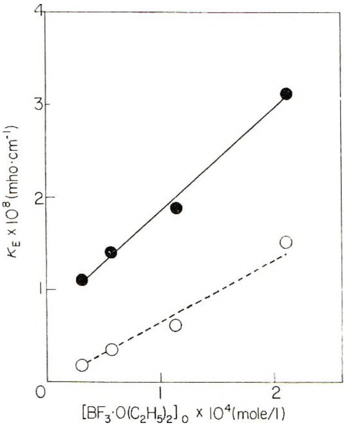

Fig. 9. Specific conductivity and catalyst concentration, $[M]_0$ = 0.80 mole/l., −12°C., E = 2.2 kv./cm.: (●) polymerizing solution; (○) catalyst solution.

system. From the data it was possible to calculate the quantity of electricity by graphical integration. In Figure 7 the field effect is plotted against the quantity of electricity. Whether $R_{pE} - R_{p0}$ or R_{pE}/R_{p0} was chosen as a measure of the field effect, no simple correlation was detectable.

Specific Conductivity and Catalyst and Monomer Concentrations. Figure 8 gives the monomer concentration dependence of the specific conductivity of the polymerizing solution which was determined from the measured field and current strengths. The dotted line denotes the conductivity of the catalyst solution determined in the same manner. The dielectric constants of the two solutions were so adjusted as to be practically the same by adding an appropriate quantity of toluene into the catalyst solutions. No temperature correction on the conductivity value was effected, because the temperature rise at most was 2.6°C., which appears to be negligible in the light of the temperature dependence of conductivity (Fig. 10). It is seen from Figure 8 that κ_E is a linear function of the monomer concentration. Figure 9 shows that the conductivity is a linear function of catalyst concentration both in the polymerizing solutions and the catalyst solutions in the concentration range studied.

NOTE: We note that the conductivity data in Figures 8 and 9 are not consistent. The κ_E value of the catalyst solution at $[BF_3OEt_2] = 1.1 \times 10^{-4}$ mole/l. and $[M]_0 = 0.80$ mole/l. is 0.63×10^{-8} mho cm.$^{-1}$ according to Figure 9, whereas it is 0.25×10^{-8} mho cm.$^{-1}$ in Figure 8 at the same

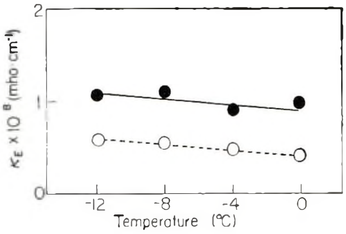

Fig. 10. Specific conductivity and temperature, $[M]_0 = 0.55$ mole/l., $[BF_3OEt_2]_0 = 1.1 \times 10^{-4}$ mole/l., $E = 1.1$ kv./cm.: (●) polymerizing solution (O) catalyst solution

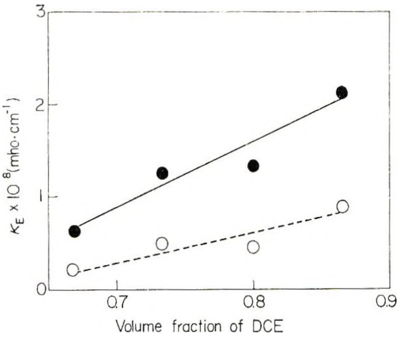

Fig. 11. Specific conductivity and solvent composition (DCE–toluene), $[M]_0 = 1.07$ mole/l., $[BF_3OEt_2]_0 = 2.2 \times 10^{-4}$ mole/l., −12°C., $E = 2.2$ kv./cm.: (●) polymerizing solution; (O) catalyst solution.

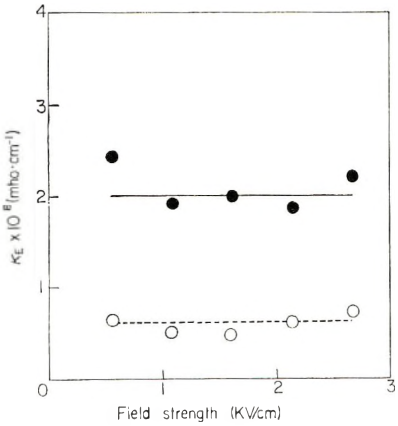

Fig. 12. Specific conductivity and field strength, $[M]_0 = 0.80$ mole/l., $[BF_3OEt_2]_0 = 1.1 \times 10^{-4}$ mole/l., −12°C.: (●) polymerizing solution; (O) catalyst solution.

concentrations. This is due to the difference in the volume fraction of DCE (and, hence, the dielectric constant) in the mixed solvent.

Specific Conductivity and Temperature. Figure 10 shows that the specific conductivity slightly decreases with increasing temperature, both for the polymerizing solutions and the catalyst solutions. This would be due to the decrease in the dielectric constant of the solvent with increasing temperature.

Specific Conductivity and Solvent Composition. Figure 11 presents the specific conductivity data as a function of the volume fraction of DCE in the mixed solvents of DCE and toluene. The conductivity is seen to increase with rising volume fraction of DCE.

Specific Conductivity and Field Strength. As is shown in Figure 12, the conductivity is practically independent of the field strength both for polymerizing and catalyst solutions.

Discussion

From the foregoing results we note distinct field accelerating effects on α-methylstyrene–BF_3OEt_2–DCE. The magnitudes of the effects, $(R_{pE} - R_{p0})/R_{p0}$, are about three times larger than those found for α-methylstyrene–iodine–DCE reported previously[1] (see Fig. 4).

The field accelerating effects are easily seen not to be due to the Joule heat effect, because the apparent overall activation energy is negative, as is shown in Figure 3. Furthermore, it would be most likely that the electrolytical initiation is not responsible for the effects in view of the data given in Figure 7, showing no correlation between the field effect and the quantity of electricity passed.

NOTE: Most recently we have successfully found the field accelerating effects on a living anionic system. The results show further that the concentration of the active chain ends was practically independent of polymerization time both with and without an electric field. Thus we are led to the conclusion that the field accelerating effects have not resulted from the electrolytical initiation or production of living active ends. These experimental data appear to constitute a more conclusive denial of the electroinitiation mechanism than any other argument presented previously and at present. Detailed data will be published elsewhere.[4]

Before a discussion of the field effects it seems desirable to comment on the electric conductivity of the solutions. It is reasonable to conclude from the dotted line in Figure 9 that the conducting species in the catalyst solutions are free ions such as $C_2H_5^+$ and BF_3O–C_2H_5, since the specific conductivity is proportional to the catalyst concentration. Furthermore, the conductivities of polymerizing solutions (κ_{Ep}) are always larger than those of catalyst solutions (κ_{Ec}). Accordingly, it is possible to conclude that a portion of the active chain ends is free ions.

As will be easily accepted, the overall propagation rate constant k_p may be represented as

$$k_p = \alpha k''_p + (1 - \alpha)k'_p \tag{1}$$

where k''_p and k'_p are the propagation rate constants of free ions and ion pairs, respectively, and α is the degree of dissociation of the ion pairs. If we assume that the total polymerization rate R_p is equal to the propagation rate, we have

$$R_p = [\alpha k''_p + (1 - \alpha)k'_p][\mathrm{M}^*][\mathrm{M}] \tag{2}$$

where [M*] and [M] are concentrations of the growing active end and the monomer, respectively. In order to represent quantities in the presence and absence of the electric field, we use the subscripts E and 0. Then

$$R_{pE}/R_{p0} = [\alpha_E k''_{pE} + (1 - \alpha_E)k'_{pE}]\ [\mathrm{M}^*]_E/ [\alpha_0 k''_{p0} + (1 - \alpha_0)\ k'_{p0}]\ [\mathrm{M}^*]_0 \tag{3}$$

Figure 12 implies that $[\mathrm{M}^*]_E \approx [\mathrm{M}^*]_0$, because $\kappa_{Ep} - \kappa_{Ec}$ is practically constant with field intensity. Then

$$R_{pE}/R_{p0} = \frac{\alpha_E k''_{pE} + (1 - \alpha_E)\ k'_{pE}}{\alpha_0 k''_{p0} + (1 - \alpha_0)\ k'_{p0}} \tag{4}$$

As was shown in previous papers,[1-3] eq. (4) can account for the observed field effect, that is, $R_{pE}/R_{p0} > 1$, in a qualitative manner on the assumption that $k''_{pE} = k''_{p0}$ and $k'_{pE} = k'_{p0}$. As far as these assumptions are valid, however, eq. (4) requires

$$R_{pE}/R_{p0} \leqslant \alpha_E/\alpha_0 \tag{5}$$

as was first pointed out in our previous work.[5] According to the data given in Figure 4, then, $\alpha_E/\alpha_0 > 3.2$ at 2.7 kv./cm. Since conductivity is a measure of the degree of dissociation, we have

$$(\kappa_{Ep} - \kappa_{Ec})/(\kappa_{0p} - \kappa_{0c}) > 3.2 \tag{6}$$

where the subscript 0 denotes the absence of a high electric field. On the other hand, Figure 12 shows that the κ's are independent of the field strength; in other words, $(\kappa_{Ep} - \kappa_{Ec})/(\kappa_{0p} - \kappa_{0c}) = 1$. Thus our observation disagrees with eq. (6).

At present we are inclined to regard this disagreement as due to a defect in our simplifying assumptions that $k''_{pE} = k''_{p0}$ and $k'_{pE} = k'_{p0}$.

NOTE: Besides the propagation constants, the ratio of the initiation constant and termination constant (k_i/k_t) might vary with field strength, giving rise to the observed field accelerating effects. Figure 12 shows, however, that [M*] does not change with field strength, so that k_i/k_t would be interpreted as field-independent.

It is well recognized that the solvation of free ions results in a lowering of their reactivity.[6] We believe that the solvation of growing chain ends is an important factor in determining the polymerization rate, and the application of a high-intensity electric field results in "partial" desolvation. Then it may be admitted that the field can accelerate the polymerization. In other words, $k''_{pE} > k''_{p0}$. Although the situation for the ion pairs is not clear, it is felt that the presence of gegenions in the vicinity of the growing chain ends would make it difficult for the monomer molecules to approach the chain ends, whether or not some of the solvent molecules around the chain ends could be taken away by the field. Therefore, $k'_{pE} \approx k'_{p0}$. Then by using eq. (4) we would be able to account at least qualitatively, for the large field effects, which are not explainable in terms of the second Wien effect alone.

By using this desolvation theory the catalyst concentration dependence of the field effect (Fig. 1) may be accounted for as follows. To the chain ends, which are "partially" desolvated by the electric field, more polar molecules can easily approach. In the present system the dipole moment of BF_3OEt_2 is 4.96 ± 0.14D,[7] much larger than that of α-methylstyrene, 0.17D (the latter value was obtained by using the dielectric constant and refractive index).[8] The catalyst molecules, then, would prevent the monomer molecules from reacting with the "partially" desolvated chain ends. This tendency would be enhanced as the catalyst concentration became high. R_{pE}/R_{p0} therefore should become smaller with increasing concentration of the catalyst, as was observed in Figure 1.

In a similar manner, the observed insensitivity of R_{pE}/R_{p0} to monomer concentration (Fig. 2) could be explained by taking into consideration that a large portion of the catalyst molecules remained unconsumed in our experimental condition.

Figure 3 indicates that R_{pE}/R_{p0} decreases with rising temperature. From this result it is possible, if not necessary, to conclude that the desolvation can take place through thermal agitation at higher temperatures rather than through an electric field. Furthermore, we note that temperature has practically no influence on $\kappa_{Ep} - \kappa_{Ec}$ and possibly none on $[M^*]$. This allows us to conclude that the initiation and termination processes are not influenced by temperature. The observed temperature dependence of the polymerization rate thus could be ascribed to the variation of the propagation rate constant with temperature.

At present, our study is being extended to the effect of the field on the degree of polymerization; the results will be published.

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The Stereoregularity of Polyacrylonitrile and Its Dependence on Polymerization Temperature

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Synopsis

The stereoregularity of polyacrylonitrile was studied by NMR spectroscopy. The methylene protons in isotactic configuration are equivalent in dimethylformamide-d_7 solution and are nonequivalent in dimethylsulfoxide-d_6 solution. In the case of the latter solution the difference in chemical shift between the isotactic methylene protons is 6.6 cps. The stereoregularity of polyacrylonitrile-α-d instead of polyacrylonitrile was determined on the dimethylformamide-d_7 solution. In the radical polymerization all the polyacrylonitrile-α-d's that polymerized at temperatures between 80 and −78°C. have a configuration consisting of about 50% of isotactic diads and, accordingly, the stereoregularity of polyacrylonitrile does not depend upon the polymerization temperature. Analysis of the NMR spectra of isotactic polyacrylonitrile prepared from acrylonitrile–urea canal complex was also carried out. The NMR spectra of *meso*- and *dl*-2,4-dicyanopentanes, dimer models of isotactic and syndiotactic polyacrylonitriles, respectively, were analyzed by a computer program proposed by Bothner-By.

INTRODUCTION

Many discussions[1–7] of the stereoregularity of polyacrylonitrile have been published. Recently several works on the stereoregularity of the polymer have given rise to confusion. We reported[8] that by NMR spectroscopy all the polyacrylonitriles polymerized with a redox catalyst at 40°C., with *n*-butyllithium as catalyst at −20°C., and by gamma-ray irradiation at −196°C. have a random configuration consisting of about 50% of isotactic diads. Yamadera and Murano[9] have reported that polyacrylonitrile, polymerized with a redox catalyst at 40°C., consists of 25% isotactic diads and that in the radical polymerization the syndiotacticity tends to increase with decreasing polymerization temperature. According to Bargon and his co-workers,[10] polyacrylonitrile polymerized by radical mechanism has a configuration of 60% isotactic diads, independent of the polymerization temperature from −78 to 70°C. Yoshino and his co-workers[11] have reported that polyacrylonitrile-α,β-d_2 polymerized with a radical catalyst has a random configuration, in agreement with our results.

In this paper we wish to report our further experiments on the stereoregularity of polyacrylonitrile, which support our previous results, that is, detailed analysis of NMR spectra of polyacrylonitrile dissolved in dimethylformamide-d_7. In addition, we shall reveal that the stereoregularity of polyacrylonitrile can also qualitatively be examined in the 100 Mc./sec. NMR spectrum taken from its solution in dimethylsulfoxide-d_6.

EXPERIMENTAL

Monomers

Acrylonitrile was purified by successive washings with 5% sulfuric acid, 5% sodium carbonate solution, and water. After being dried on anhydrous calcium chloride it was distilled at atmospheric pressure and then dried over calcium chloride. Then it was distilled *in vacuo* under nitrogen.

Acrylonitrile-α-d was prepared from acrylonitrile by H–D exchange in D_2O with CaO as catalyst.[12] The exchange reaction was repeated twice, and the overall yield of acrylonitrile-α-d was 10%, based on the starting acrylonitrile. The deuterium content at the α position was estimated as 98% by a mass spectrometer.

Polymerization

Acrylonitrile-α-d was polymerized by gamma rays from a ^{60}Co source in toluene at −78 and 0°C. The polymerization of acrylonitrile-α-d at −40°C. was conducted in toluene by ultraviolet light of wavelength 320 to 420 mμ with benzoin as photosensitizer. Polymerizations of acrylonitrile and acrylonitrile-α-d were carried out by a redox catalyst consisting of potassium persulfate and sodium bisulfite in water at 40°C. In the case of polymerization at 80°C. benzoyl peroxide was used as an initiator. Polymers obtained were purified by being dissolved in dimethylformamide, reprecipitated from methanol, and then thoroughly dried *in vacuo*.

Urea canal complexes of acrylonitrile and acrylonitrile-α-d were prepared from 1 ml. of monomer, 1 g. of urea, and a trace of methanol, according to the method of White.[13] The urea complexes were polymerized by gamma-ray irradiation at −78°C. After gamma-ray irradiation of 3.5 Mr. a mixture of polymer and urea was washed with water and then Soxhlet-extracted with methanol, to separate the polymer from the urea. The separated polymer was thoroughly dried *in vacuo*.

Preparation of 2,4-Dicyanopentane

meso- and *dl*-2,4-dicyanopentanes were prepared according to the method of Takata et al.[14] and separated by means of gas chromatography. The purities of the *meso*- and *dl*-isomers were 97.6 and 99.6%, respectively.

NMR Measurements

The NMR spectra of polyacrylonitrile and polyacrylonitrile-α-d were measured in dimethylformamide-d_7 (*D*, 99%; Merck Sharp & Dohme) and dimethylsulfoxide-d_6 (*D*, 99%; E. Merck AG) solutions at 120°C. by means of a Japan Electron Optics Laboratory 100 Mc./sec. spectrometer. The NMR spectra of 2,4-dicyanopentanes were measured at 140°C. Tetramethylsilane was used as reference.

RESULTS AND DISCUSSION

Analysis of NMR Spectrum of Polyacrylonitrile in Dimethylformamide-d_7 Solution

Several solvents of polyacrylonitrile for high-resolution NMR measurements have been discovered. We have reported[8] that dimethylformamide-d_7 is a suitable solvent for the determination of the stereoregularity of polyacrylonitrile, and in this solution the stereoregularity (in diads) of polyacrylonitrile-α-d can be evaluated. Yamadera and Murano[9] used NaSCN–D_2O, and Bargon used CD_3NO_2–$(CH_2O)_2CO$ as solvents. Recently Yoshino et al.[11] has found that the NMR spectrum of polyacrylonitrile-α,β-d_2 can be measured in $HClO_4$–H_2O solution at room temperature.

The NMR spectra measured by each investigator have resulted in different analyses of methylene proton signals of polyacrylonitrile. We

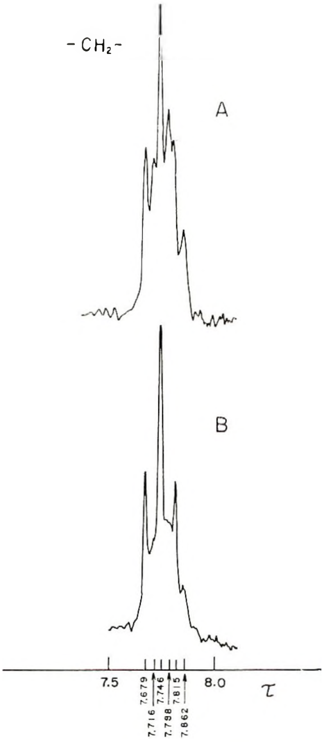

Fig. 1. Methylene proton spectra of polyacrylonitriles polymerized (*A*) with a redox catalyst and (*B*) by gamma-ray irradiation of the urea canal complex, in dimethylformamide-d_7 solutions.

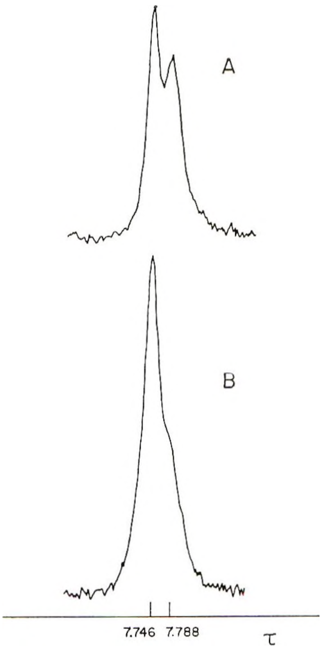

Fig. 2. Methylene proton spectra of polyacrylonitrile-α-*d*'s polymerized (*A*) with a redox catalyst at 40°C. and (*B*) by gamma-ray irradiation of the urea canal complex, in dimethylformamide-d_7 solutions.

have reported that the methylene protons in isotactic configuration are equivalent and so are those in syndiotactic configuration, and both Yamadera[9] and Bargon[10] have also interpreted that the isotactic methylene protons are equivalent. However, Yoshino has found the isotactic methylene protons are nonequivalent in the $HClO_4$–H_2O solution and also in the NaSCN–D_2O solution.

As the first step in determining the stereoregularity of polyacrylonitrile we shall show that the isotactic methylene protons of polyacrylonitrile are equivalent in the dimethylformamide-d_7 solution.

In Figure 1*A* the 100 Mc./sec. NMR spectrum of polyacrylonitrile polymerized with a redox catalyst at 40°C. is shown. The spectrum indicates six peaks at 7.862, 7.815, 7.788, 7.746, 7.716, and 7.679 τ. It is obvious from the NMR theory that methylene protons in syndiotactic configuration, which are equivalent, show a triplet signal by coupling with two adjacent methine protons, while those in isotactic configuration show a triplet, if they are equivalent, and a more complicated spectrum if they are nonequivalent.

The NMR spectrum of polyacrylonitrile obtained by gamma-ray irradiation of the acrylonitrile–urea canal complex is shown in Figure 1*B*. White[13] found by x-ray diffractometry that the stereostructure of the polyacrylonitrile obtained from the urea complex was different from that of polyacrylonitrile polymerized with a radical initiator. Yoshino et al.[11]

have revealed that the polyacrylonitrile-α,β-d_2 prepared by x-ray irradiation of the urea complex has a configuration with a ratio of isotactic to syndiotactic diads of 10:1.

In Figure 1*B* three peaks at 7.815, 7.746, and 7.679 τ are very strong compared with those in Figure 1*A*. We assigned the peaks to a triplet due to isotactic methylene protons in our previous report.

To simplify the methylene proton spectrum the NMR spectra of polyacrylonitrile-α-*d* were measured. Figures 2*A* and 2*B* are the NMR spectra of polyacrylonitrile-α-*d*'s polymerized under the same conditions as the polyacrylonitriles exhibited in Figures 1*A* and 1*B*, respectively. Figure 2*A* indicates two peaks at 7.788 and 7.746 τ due to methylene protons, while Figure 2*B*, which is the spectrum of polyacrylonitrile-α-*d* obtained from the urea complex, shows a strong peak at 7.746 τ with a shoulder at 7.788 τ.

In the case of polyacrylonitrile-α-*d* the NMR signal of methylene protons in isotactic configuration must be a singlet if they are equivalent and a quartet if nonequivalent. In the previous report[8] we used polyacrylonitrile-α-*d* with a deuterium content of 80–90% at the α position, and so there was a small peak or a shoulder at 7.72 τ, which was attributed to the methylene protons in nondeuterated units. Since the deuterium content at the α position of polyacrylonitrile-α-*d* used in this paper is 98%, such a small peak near 7.72 τ cannot be observed.

From the analysis of the NMR spectra of *meso*- and *dl*-2,4-dicyanopentanes, the isotactic and syndiotactic dimer models of polyacrylonitrile, respectively, we have known that the chemical shift of the methylene protons in syndiotactic configuration is in a higher magnetic field than that of the methylene protons in isotactic configuration in the dimethylformamide-d_7 solution.[8]

Accordingly, two peaks at 7.788 and 7.746 τ in polyacrylonitrile-α-*d* are attributable to the methylene protons in syndiotactic and isotactic configu-

TABLE I

Chemical Shifts and Coupling Constants of Polyacrylonitrile (cps)

Configuration	Solvent	$J_{gem(H_{\beta_2}-H_{\beta_1})}$	$J_{vic(H_\alpha-H_{\beta_1})}$	$J_{vic(H_\alpha-H_{\beta_2})}$	$\nu_{gem(H_{\beta_1}-H_{\beta_2})}$
Isotactic	Dimethylformamide-d_7	—	6.8	6.8	0
	Dimethylsulfoxide-d_6	−14.7	5.0	8.2	6.6
Syndiotactic	Dimethylformamide d_7	—	7.3	7.3	0
	Dimethylsulfoxide-d_6	—	6.5	6.5	0

rations, respectively. The singlet absorption due to methylene protons in isotactic configuration shows that they are equivalent in the dimethylformamide-d_7 solution.

In the NMR spectrum of polyacrylonitrile three peaks at 7.862, 7.788, and 7.716 τ are attributable to a triplet ($J_{\mathrm{CH_2-CH}} = 7.3$ cps) due to syndiotactic methylene protons, whereas those at 7.815, 7.746, and 7.679 τ are attributable to a triplet ($J_{\mathrm{CH_2-CH}} = 6.8$ cps) due to isotactic methylene protons. The chemical shifts and coupling constants calculated from the NMR spectra measured on the dimethylformamide-d_7 solutions are given in Table I.

Analysis of NMR Spectrum of Polyacrylonitrile in Dimethylsulfoxide-d_6 Solution

Previously we reported[15] that only three peaks due to methylene protons were observed in the 60 Mc./sec. NMR spectrum measured from polyacrylonitrile solution in dimethylsulfoxide-d_6, and probably isotactic methylene proton signals overlap a triplet due to syndiotactic methylene protons.

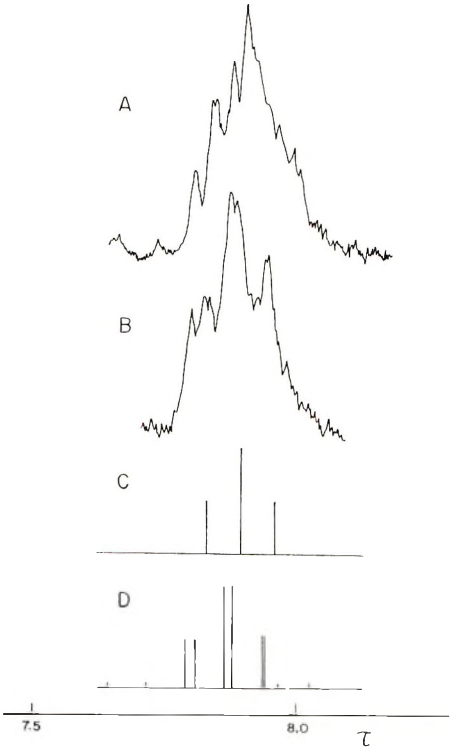

Fig. 3. Methylene proton spectra of polyacrylonitriles of (*A*) random and (*B*) isotactic configurations; (*C*) calculated spectrum ("stick spectrum") of syndiotactic methylene protons; (*D*) calculated spectrum ("stick spectrum") of isotactic methylene protons; in dimethylsulfoxide-d_6 solutions.

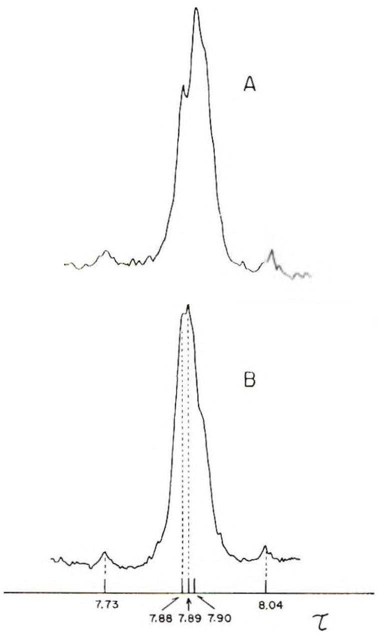

Fig. 4. Methylene proton spectra of polyacrylonitrile-α-d's of (A) random and (B) isotactic configurations, in dimethylsulfoxide-d_6 solutions.

The 100 Mc./sec. NMR spectrum shown in Figure 3, however, indicates the splitting of the methylene signals into isotactic and syndiotactic ones. In order to carry out the analysis of the spectrum of polyacrylonitrile easily the NMR spectra of polyacrylonitrile-α-d's of both isotactic and random configurations were measured on the dimethylsulfoxide-d_6 solution. The spectrum of isotactic polyacrylonitrile-α-d, shown in Figure 4B, indicates a quartet at 8.04, 7.89, 7.88, and 7.73 τ due to methylene protons in isotactic configuration, whereas in the spectrum of polyacrylonitrile-α-d of a random configuration, shown in Figure 4A, there is a large singlet at 7.90 τ due to those in syndiotactic configuration together with the quartet, in which a peak at 7.89 τ is hidden in the singlet at 7.90 τ.

Comparing Figure 3A, which is the spectrum of polyacrylonitrile of a random configuration, with Figure 3B, which is that of isotactic polymer, we see that the three peaks at 7.96, 7.90, and 7.83 τ observed in Figure 3A almost disappear in Figure 3B. Therefore, the triplet at 7.96, 7.90, and 7.83 τ is attributable to the signal of syndiotactic methylene protons; the other peaks, to a multiplet due to isotactic methylene protons.

Chemical shifts and coupling constants were calculated from the spectra of polyacrylonitrile and polyacrylonitrile-α-d and are shown in Table I. The difference in chemical shift between the methylene protons in isotactic configuration is 6.6 cps, indicating the nonequivalency of the protons in the dimethylsulfoxide-d_6 solution. With the use of these constants theoretical spectra of methylene protons in syndiotactic and isotactic configurations are shown in Figure 3 with the observed spectra.

Dependence of Stereoregularity on Temperature of Radical Polymerization

Figures 1 and 5 indicate that the line width of the syndiotactic triplet is broader than that of the isotactic triplet. Hence, it is difficult to determine the stereoregularity of polyacrylonitrile simply by comparing the peak height of the syndiotactic triplet with that of the isotactic triplet. Acrylonitrile-*α-d* was, therefore, polymerized under various conditions, to examine the dependence of stereoregularity on the temperature of radical polymerization.

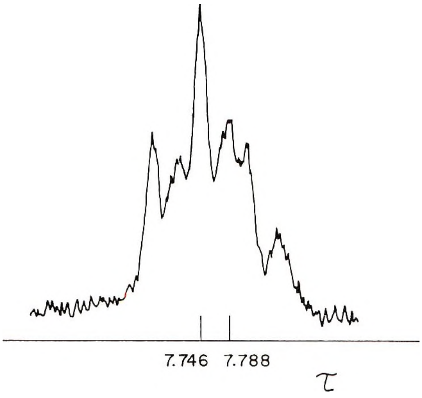

Fig. 5. Methylene proton spectrum of polyacrylonitrile of random configuration, measured in an extended sweep, in dimethylformamide-d_7 solution.

The NMR spectra of polyacrylonitrile-*α-d*'s polymerized by a radical mechanism at 80, 40, 0, and −78°C. are shown in Figures 6 and 2*A*. Half-height widths of the syndiotactic and isotactic singlets were estimated. Calculating from the spectra of polyacrylonitrile-*α-d*'s polymerized

TABLE II
Stereoregularity of Polyacrylonitrile-*α-d*'s

No.	Polymerization conditions: Initiator	Polymerization conditions: Temp., °C.	Stereoregularity, Isotactic diad, %
1	Benzoyl peroxide	80	51
2	Redox catalyst	40	50
3	Gamma-ray irradiation	0	50
4	Ultraviolet light	−40	48
5	Gamma-ray irradiation	−78	53
6	Acrylonitrile-*α-d*–urea canal complex, gamma-ray irradiation	−78	75

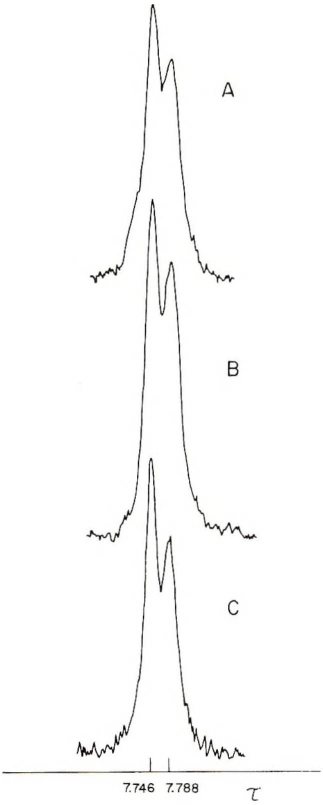

Fig. 6. Methylene proton spectra of polyacrylonitrile-α-d's polymerized by radical mechanism at (*A*) 80°C., (*B*) 0°C., and (*C*) −78°C., in dimethylformamide-d_7 solutions.

between 80 and −78°C., the half-height widths of the syndiotactic and isotactic singlets are 3.8 and 2.8 cps, respectively.

The determination of the stereoregularity of polyacrylonitrile-α-d's was carried out by estimating syndiotactic and isotactic signal areas. The results are shown in Table II.

Polyacrylonitrile-α-d, polymerized with benzoyl peroxide as catalyst at 80°C., has a configuration consisting of 51% isotactic diads, and the polymer prepared by gamma-ray irradiation at −78°C. consists of 53% isotactic diads. In addition, the stereoregularity of all the polymers polymerized at other temperatures between 80 and −78°C. is also estimated as about 50% of isotactic diads.

Therefore, in the radical polymerization polyacrylonitrile prepared in the temperature range from 80 to −78°C. has a random configuration consisting of about 50% isotactic and about 50% syndiotactic diads and, accordingly, the stereoregularity does not depend upon the polymerization temperature.

The stereoregularity of polyacrylonitrile-α-d obtained by gamma-ray irradiation of the urea complex consists of 75% isotactic diads, as shown

TABLE III

Chemical Shifts and Coupling Constants of *meso*- and *dl*-2,4-Dicyanopentanes

Isomer	Chemical shift τ				Coupling constant, cps				Solvent
	CH_3	H_{β_1}	H_{β_2}	H_α	$J_{H_{\beta_1}-H_\alpha}$	$J_{H_{\beta_2}-H_\alpha}$	$J_{H_{\beta_2}-H_{\beta_1}}$	$J_{CH_3-H_\alpha}$	
dl	8.67	8.138	8.138	7.087	7.27	7.27	−13.91	7.0	Dimethylsulfoxide-d_6
meso	8.69	8.194	8.028	7.108	8.14	6.24	−13.79	6.5	"
dl	8.63	8.078	8.078	7.037	7.02	7.02	−15.10	7.0	Dimethylformamide-d_7
meso	8.64	8.126	7.968	7.057	6.60	7.27	−14.41	7.0	"

in Table II. The reason that the polymer has less isotacticity than that obtained by Yoshino et al.[11] may be that the polymerization conditions are different; that is, we used gamma-ray irradiation instead of x-ray irradiation.

It may be concluded that the methylene protons in isotactic configuration are equivalent in such solvents as dimethylformamide-d_7 and CD_3NO_2–$(CH_2O)_2CO$[10] and are nonequivalent in such solvents as dimethylsulfoxide-d_6, NaSCN–D_2O,[11] and $HClO_4$–H_2O.[11]

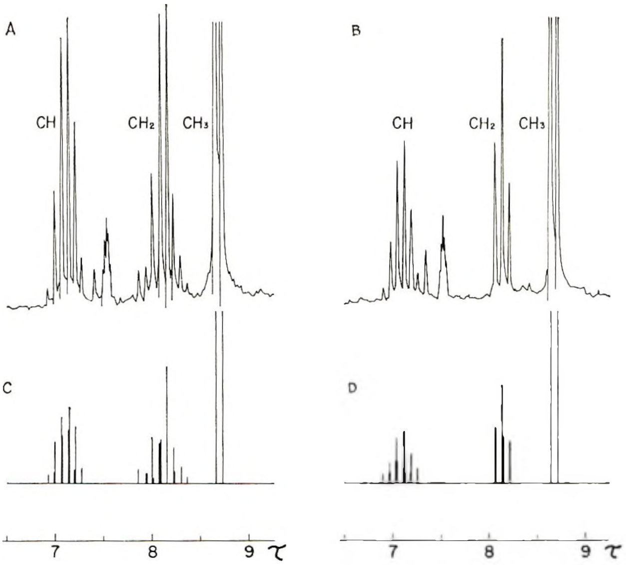

Fig. 7. NMR spectra of (*A*) *meso*- and (*B*) *dl*-2,4-dicyanopentanes; (*C*) calculated spectrum ("stick spectrum") corresponding to *A*; (*D*) calculated spectrum ("stick spectrum") corresponding to *B*. Absorptions near 7.5 and 7.4 τ are due to protons in dimethylsulfoxide-d_6 and in water, respectively. In dimethylsulfoxide-d_6 solutions.

Yamadera and Murano[9] carried out an analysis of NMR spectra measured from the polyacrylonitrile solution in NaSCN–D_2O on the basis of a premature conclusion that the isotactic methylene protons are equivalent besides the syndiotactic ones and, as a result, underestimated the ratio of isotactic to syndiotactic configurations. On the other hand, Bargon et al.[10] might have overestimated the ratio, since they probably calculated it by comparing the peak height of isotactic methylene proton signals with that of syndiotactic ones.

No information about the stereoregularity has yet been obtained from the methine proton spectrum measured from the dimethylformamide-d_7 or dimethylsulfoxide-d_6 solution, except for the observation that there is a difference in the spectrum of methine protons decoupled from methylene protons between polyacrylonitriles of isotactic and of random configurations.

Although Hunter[16] recently reported that the exchange of methine protons of polyacrylonitrile occurs in NaSCN–D_2O and in KSCN–D_2O solutions at elevated temperatures, we found that the methine protons were stable in the dimethylformamide-d_7 or dimethylsulfoxide-d_6 solution at 120°C. However, the discoloration of polyacrylonitrile in dimethylsulfoxide-d_6 solution was observed at about 150°C.

Analysis of NMR Spectrum of *meso*- and *dl*-2,4-Dicyanopentanes

In the previous report[8] the analysis of NMR spectra of *meso*- and *dl*-2,4-dicyanopentanes, dimer models of isotactic and syndiotactic polyacrylonitriles, respectively, was carried out by the Fujiwara method.[17] Only in the case of the dimethylsulfoxide-d_6 solution were full constants reported.

In this paper, in order to calculate chemical shifts and coupling constants from the spectra measured from the dimethylformamide-d_7 and dimethylsulfoxide-d_6 solutions, a computer program,[18] written by Castellano and Bothner-By, was used. This program can perform the least-squares adjustment of a calculated NMR spectrum to an observed one and give accurate values. The chemical shifts and coupling constants obtained are given in Table III. The theoretical NMR spectrum of 2,4-dicyanopentanes is shown in Figure 7 together with the observed spectrum.

The center of methylene protons of the *dl* dimer appears at a higher magnetic field than that of the *meso* dimer in both solvents. In the case of the dimer model the differences between the chemical shifts of the methylene protons of the *meso* dimer are 16.6 and 15.8 cps in dimethylsulfoxide-d_6 and dimethylformamide-d_7 solutions, respectively, while in the case of polyacrylonitrile those of methylene protons in isotactic configuration are 6.6 and 0 cps in dimethylsulfoxide-d_6 and dimethylformamide-d_7 solutions, respectively.

Therefore, the dimer model can suggest that in the NMR spectrum of polyacrylonitrile the chemical shift of methylene protons in syndiotactic configuration is in a higher magnetic field than is that of methylene protons in isotactic configuration, but it cannot suggest whether the methylene protons in isotactic configuration are equivalent in a certain solvent or not.

Note Added in Proof: Recently, Svegliado et al. (*J. Polymer Sci. A-1*, **5**, 2875, 1967) have analyzed the 100 Mc./sec. NMR spectrum of polyacrylonitrile in dimethylsulfoxide-d_6 solution, but the chemical shifts and coupling constants calculated by them are slightly different from ours.

We wish to thank Dr. A. A. Bothner-By, of the Mellon Institute, Pittsburgh, for the computer program of the NMR spectrum and K. Aizawa and H. Miyazaki, of the Faculty of Agriculture, University of Tokyo, for measurements of the NMR spectra.

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The Mechanism of Consumption of Ceric Salt with Cellulosic Materials

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Synopsis

Efforts were made in the present study to elucidate the mechanism of graft copolymerization of cellulose in the presence of a ceric salt as initiator. When cellulose is treated with an aqueous solution of the ceric salt, ceric ion is consumed in a roughly first-order reaction in the oxidation of cellulose and in the adsorption on cellulose, and the ratio of the rate constants of oxidation and adsorption is about 1:3 in the case of sulfite pulp. Ceric ion is adsorbed so strongly on cellulose as not to be readily desorbed by treatment with water, dilute acid, or dilute alkali. The number of moles of adsorbed ceric ion was approximately equal to the number of moles of the total carbonyl groups in the cases of cotton and sulfite pulp, which are low in hemicellulose content, and was several times as large in the cases of kraft pulp and semichemical pulp, which contain about 22% hemicellulose. In these samples, however, it was interesting to note that the amount of the adsorbed ceric ion was roughly equal to the amount consumed in oxidation. Cellulose on which ceric ion is adsorbed reacts with methyl methacrylate to yield graft copolymers; a higher molecular weight of grafts, smaller number of grafts, and lower graft efficiency than in a standard polymerization were observed. Since the stability of the adsorbed ceric ion is high, a contribution of the adsorbed ceric ion to the graft copolymerization appears small, and the oxidation reaction, which proceeds slightly more slowly than adsorption, seems more important to the graft copolymerization.

INTRODUCTION

A number of investigators have reported on the use of ceric salt as initiator in the graft copolymerizations of vinyl monomers and cellulose. It is well known that alcohols form complexes with transition-metal ions,[1] and the formation of a similar complex is assumed between cellulose and ceric ion.[2-4] Kulkami and Mehta[5] found that cellulose adsorbs a considerable amount of ceric ion when treated with an aqueous solution of a ceric salt, and the bond is so strong as not to be readily severed by treatment with hot water. They inferred that a stable complex is formed between cellulose and ceric ion and that the active hydroxyl group in cellulose participates in the formation of this complex. However, details of the structure of the complex are not known.

Cellulose that has been treated with an aqueous solution of a ceric salt retains an activity for graft copolymerization at a high level after being washed with water.[6-9]

In the present study the consumption of ceric ion due to adsorption or oxidation was followed by using various cellulosic materials, the effect of ceric ion adsorbed on cellulose on the graft copolymerization was examined, and efforts were made to clarify the mechanism of graft copolymerization of cellulose in the presence of a ceric salt as initiator.

EXPERIMENTAL

Materials

Commercial absorbent cotton (cotton), sulfite pulp from softwoods (SP), sulfate pulp from hardwoods (KP), semichemical pulp from hardwoods (SCP), and oxidized SP and SCP were used as cellulosic materials. Purified methyl methacrylate was used as the vinyl monomer; ceric ammonium nitrate of extra pure grade, as the ceric salt. Determination of the total carbonyl group in the cellulose sample was carried out by the hydroxylamine method.[10]

Determination of Ceric Ion

The amount of ceric ion in an aqueous solution was determined by adding a given amount of ferrous sulfate and back-titrating with ceric sulfate with *o*-phenanthroline as indicator. The amount of ceric ion adsorbed on the cellulose sample was determined by this procedure while the cellulose sample was suspended in water.

Reaction of Cellulose Sample with Ceric Salt

The cellulose sample (0.500 g.) was placed in a 200 cm.^{3} flask, 42.5 cm.^{3} of an aqueous solution of the ceric salt of a known concentration containing 15 cm.^{3} of 0.1N nitric acid was added, and the mixture was kept at 45°C. The reaction was allowed to proceed for a given period of time, the cellulose was filtered, and the concentration of ceric ion in the filtrate and the amount of ceric ion adsorbed on the cellulose were determined. The determination of the adsorbed ceric ion was carried out on the cellulose sample, which was washed three times with about 100 cm.^{3} of distilled water.

Graft Copolymerization of Cellulose on Which Ceric Ion is Adsorbed

The polymerization reaction was carried out at 45°C. for 60 min. in a system consisting of 0.500 g. of cellulose on which ceric ion was adsorbed, 2.5 cm.^{3} of methyl methacrylate, 0.127 g. of a nonionic emulsifier, 10 cm.^{3} of 0.1N nitric acid, and water, the total being made up to 42.5 cm.^{3} with water and kept under nitrogen. The per cent grafting, average molecular weight of grafts, and number of grafts were determined by methods given previously.[6,11]

RESULTS AND DISCUSSION

Adsorption of Ceric Ion on Cellulose

SP and SCP that had been treated with an aqueous solution of ceric salt were treated in various manners, and the remaining ceric ion was determined. The results are shown in Table I. It is seen that ceric ion is very strongly adsorbed on the cellulose sample and is not easily desorbed by being washed with water or treated with a dilute acid or alkali. SCP adsorbs a much larger amount of ceric ion than SP but slightly less strongly.

TABLE I
Stability of Ceric Ion Adsorbed on Cellulose

	Ceric ion before treatment, mmoles per 100 g. cell.	Treatment, cm.^{3}	Ceric ion after treatment, mmoles per 100 g. cell.
Sample SP:[a]			
	10.90	H_2O, 1000	10.50
	"	" 3000	10.43
	"	0.1*N* HCl 200	8.30
		" 500	8.25
	"	0.1*N* NaOH, 200	9.79
	"	0.1*N* HCl 0.1*N* NaOH	8.18
Sample SCP:[a]			
	57.60	H_2O, 1000	52.70
	"	" 3000	50.70
	"	0.1*N* HCl, 200	47.80
	"	" 500	38.20

[a] These samples were prepared under the following conditions; concentration of ceric salt, 10 mmoles/l.; liquor ratio, 85; temperature, 45°C.; time, 60 min. Adsorbed ceric ion was measured on the sample (0.500 g.), which was washed three times with about 100 cm.^{3} of distilled water.

SP that had been treated with an aqueous solution of the ceric salt and washed with water was dehydrated by being subjected to a centrifugal force of about 6700*g* and the amounts of adsorbed ceric ion before and after the centrifugation were determined. Since practically no difference was observed, it is assumed that the adsorption of ceric ion has no relation to free water.

The relationships between the time of treatment of the cellulose material with an aqueous solution of the ceric salt and the amount of the adsorbed ceric ion are shown for cotton, SP, and SCP in Figures 1 and 2. The amount of the adsorbed ceric ion became constant at each concentration of the ceric salt after 10–20 min. for each cellulose sample.

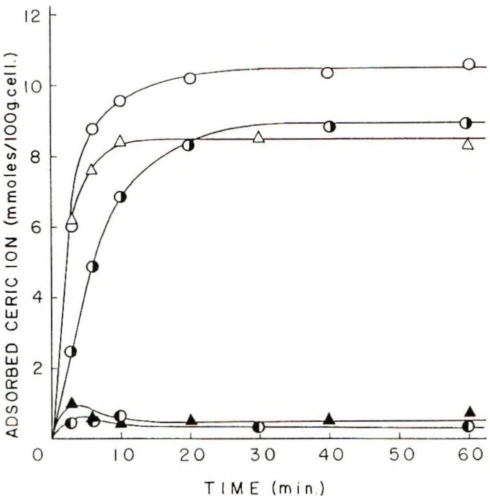

Fig. 1. Adsorption of ceric ion on SP and cotton. For SP, [Ce^{4+}], mmoles/l.: (○) 10; (◑) 5; (◐) 1. For cotton, [Ce^{4+}], mmoles/l.: (△) 10; (▲) 1.

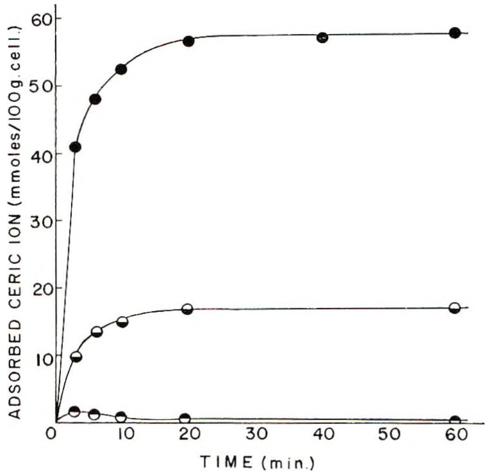

Fig. 2. Adsorption of ceric ion on SCP; [Ce^{4+}], mmoles/l.: (●) 10; (◒) 5; (◓) 2

The relationships between the concentration of the ceric salt used and the amount of the adsorbed ceric ion obtained upon treatments at 45°C. for 60 min. are shown in Figure 3. It appears that there exists an equilibrium adsorption of ceric ion characteristic of each cellulose sample.

It is not yet clear by what mechanism ceric ion is bonded to cellulose. However, considering the fact that the amount of the adsorbed ceric ion is 10–20 times as much as that of the carboxyl group in the cellulose sample, and the desorption of ceric ion is difficult with a dilute acid or alkali, the bond in question appears not simply ionic.

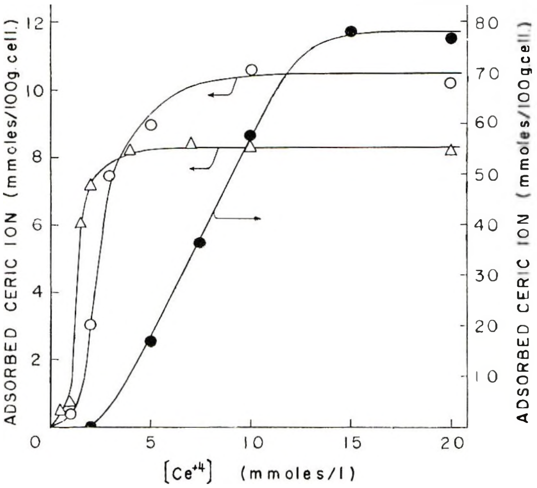

Fig. 3. Effect of the concentration of ceric salt on amount of adsorbed ceric ion: (○) SP; (△) cotton; (●) SCP.

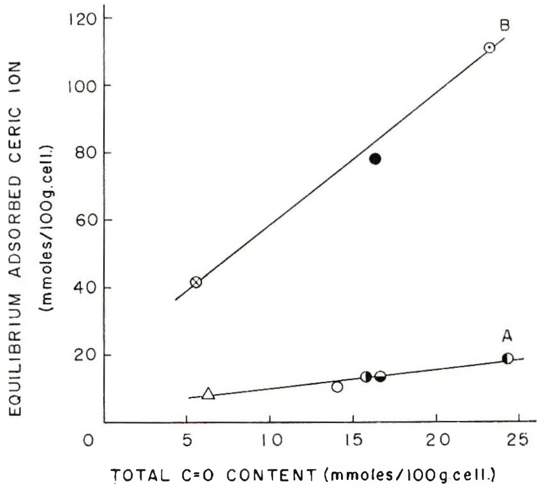

Fig. 4. Relationship between amount of equilibrium adsorbed ceric ion and total carbonyl in cellulose sample: (△) cotton; (○) SP; (◑) SP oxidized with NaClO (pH 7); (◓) SP oxidized with $K_2Cr_2O_7$; (◐) SP oxidized with NaClO (pH 10); (⊗) KP; (●) SCP (⊙) SCP oxidized with $NaClO_2$.

The relationships between the amount of equilibrium adsorption of ceric ion and the total carbonyl groups in the cellulose sample are given by two straight lines, as shown in Figure 4. The straight line A is related to cotton, SP, and oxidized SP, which have low hemicellulose contents, and a good linear relationship is seen between the amount of equilibrium adsorption and the total carbonyl for these cellulose samples. On the other hand, the straight line B is related to KP and SCP, and the adsorption of ceric ion amounts to four to five times as much as that of the total carbonyl in these samples. The cellulose samples represented by the straight line B are prepared from hardwoods and contain about 22% hemicellulose, which appears closely related to the adsorption of ceric ion.

Changes in the total carbonyl group in the cellulose sample caused by treatment with an aqueous solution of the ceric salt were studied. The sample, which had been treated with the ceric salt, was washed thoroughly with water, and the amount of the adsorbed ceric ion was determined with ferrous sulfate. After this the sample was treated successively with ferrous sulfate, 0.1*N* hydrochloric acid, water, and ethanol, dried in air, and the total carbonyl was determined by the hydroxylamine method. The results obtained on SP and SCP are shown in Table II. In SP the total carbonyl after 60 min. of treatment does not show any difference from the initial value and is approximately equal to the amount of the adsorbed ceric ion. In SCP the total carbonyl increases considerably after 60 min. of treatment, but the amount of the adsorbed ceric ion is much larger, being about three times as much as the total carbonyl.

TABLE II
Changes of Total Carbonyl Group in SP and SCP in Treatment with Aqueous Solution of Ceric Salt

	Concn. ceric salt, mmoles/l.	Time of treatment, min.	Tot. carbonyl content, mmoles per 100 g. cell.	Adsorbed ceric ion, mmoles per 100 g. cell.
Sample SP:				
	—	—	11.7	—
	10.0	30	12.9	10.64
	"	60	11.5	10.50
	"	180	12.6	10.40
	"	480	14.4	10.98
	5.0	60	12.0	10.40
	15.0	60	11.5	10.81
Sample SCP:				
	—	—	15.8	—
	20.0	60	25.5	76.20

Stability of the Adsorbed Ceric Ion

It is known that cellulose treated with an aqueous solution of the ceric salt retains an activity for graft copolymerization and does so for a prolonged period of time.[6–9] This activity, however, seems to be related to a change with time of the amount of the adsorbed ceric ion.

In Figure 5 are shown the changes with time of the amount of ceric ion adsorbed on the cellulose sample that has been treated with a given concentration of the ceric salt at 45°C. for 60 min., the changes were examined in a system identical with that of the above-mentioned graft copolymerization except for the absence of vinyl monomer and the nonionic emulsifier. The

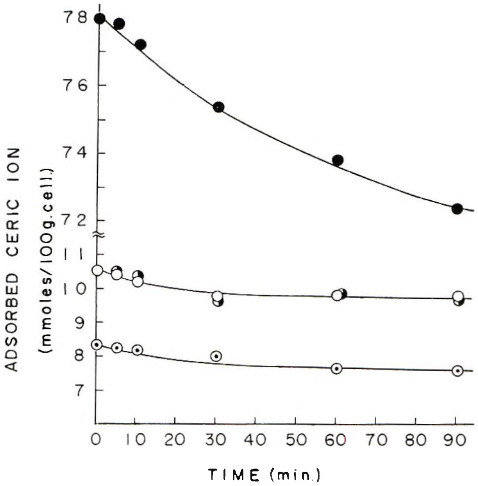

Fig. 5. Changes in amount of adsorbed ceric ion with time: (○) SP on which ceric ion was adsorbed (air atmosphere); (◑) SP on which ceric ion was adsorbed (nitrogen atmosphere); (⊙) SP washed with 0.1N HCl (air atmosphere); (●) SCP on which ceric ion was adsorbed (air atmosphere).

amount of the adsorbed ceric ion gradually decreased with time, and about a 6–8% decrease was indicated after 60 min., regardless of the cellulose sample and the atmosphere. It is inferred that approximately the same amount of ceric ion as this decrease is consumed in the graft copolymerization.

Number of Grafts in Graft Copolymers

The cellulose samples with various amounts of the adsorbed ceric ion were prepared by varying the cellulose sample, concentration of the ceric salt solution, and time of treatment. These cellulose samples were subjected to graft copolymerization in the manner described above, and the number of grafts in the graft copolymers were measured; the results are shown in Table III. The number of grafts are about 0.019 mmoles for cotton, about 0.039 mmoles for SP, and about 0.053 mmoles for SCP, per 100 g. of cellulose in each case. Distinct differences are thus seen among the different cellulose samples. The number of grafts is generally not affected by the amount of adsorbed ceric ion and is slightly lower when the amount of adsorbed ion is short of the total carbonyl in the cellulose sample.

As mentioned above, the consumptions of the adsorbed ceric ion during the graft copolymerization are estimated to be about 0.8 and 4 mmoles per 100 g. of cellulose for SP and SCP, respectively, and since the measured numbers of grafts are 0.039 and 0.053 mmoles per 100 g. of cellulose, respectively, the proportion of the graft formation to the consumption of the adsorbed ceric ion is 1 (SP) to 5% (SCP). The graft efficiencies are shown in Table III: 80% for cotton, 75% for SP, and 70% for SCP. These values are slightly lower than the 80–90% obtained in the same materials under

TABLE III

Graft Copolymerization of Methyl Methacrylate on Cellulose Sample on which Ceric Ion is Adsorbed

Sample	Concn. ceric salt, mmoles/l.	Time of treatment, min.	Adsorbed ceric ion, mmoles per 100 g. cell.	Grafting, %	Graft efficiency,[a] %	Avg. mol. wt. of grafts[b] ($\times 10^{-4}$)	Number of grafts ($\times 10^{2}$), mmoles per 100 g. cell.
Cotton	1.0	60	0.75	63.6	85.6	724	0.88
"	5.0	"	8.30	121.4	79.0	724	1.68
"	10.0	"	8.41	138.4	79.4	724	1.92
SP	2.0	60	2.30	145.4	76.9	540	2.70
"	5.0	"	9.30	195.8	75.9	500	3.92
"	10.0	"	10.30	192.2	76.0	531	3.62
SCP	5.0	60	17.00	183.0	60.8	346	5.29
"	10.0	"	57.50	204.0	71.6	380	5.27
"	15.0	"	78.00	211.8	73.8	398	5.32
SP	5.0	5	4.40	92.2	72.8	294	3.13
"	"	11	6.50	182.2	77.1	466	3.91
"	"	20	8.30	207.2	77.0	575	3.61
"	"	60	9.30	195.8	75.9	500	3.92

[a] Weight of grafted polymer per total weight of polymer, times 100.

[b] Determined viscometrically by the equation of Chinai and co-workers.[12]

standard polymerization conditions.[6] It thus seems difficult to expect a larger number of grafts and higher efficiency in the graft copolymerization from the adsorbed ceric ion.

In the present polymerization system the molecular weights of the grafts are independent of the amounts of the adsorbed ceric ion and appear to be dependent on the kind of cellulose. It is worth notice that the molecular weights of the grafts are very high, in the order of several millions in all cases.

Reaction of Cellulose with Ceric Salt

As mentioned above, it is apparent that cellulose adsorbs ceric ion very strongly when treated with an aqueous solution of the ceric salt. In addition, it is conceivable that ceric ion is simultaneously consumed in oxidation of the cellulose sample.

The total ceric ion remaining after treatment for a given period of time was measured and designated A. On the other hand, the cellulose sample was filtered from a separate, similarly treated system, and the amount of ceric ion remaining in the filtrate was determined and designated B. The sum of ceric ion adsorbed on the filtered cellulose sample and B is approximately equal to A, and the changes of A and B with time are shown for SP and SCP in Figures 6 and 7, respectively.

If the ordinate axis is expressed on a logarithmic scale, A is found to consist of two straight lines of different slopes in the case of SP, and each reaction may be regarded as approximately first-order. The reaction rate constants related to these two straight lines are expressed as k_a and k_b, as

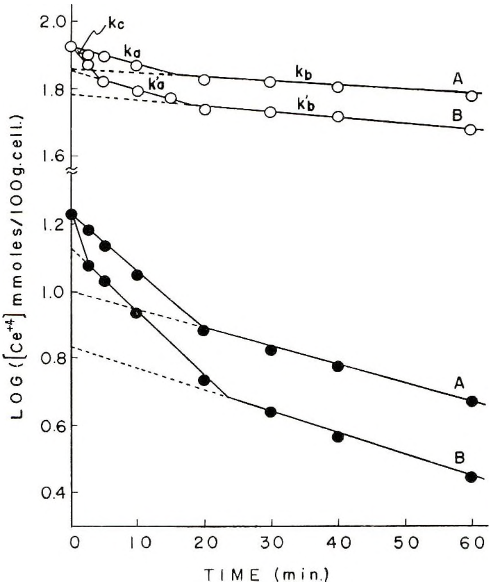

Fig. 6. Consumption of ceric ion with SP; [Ce^{4+}], mmoles/l.: (○) 10; (●) 2.

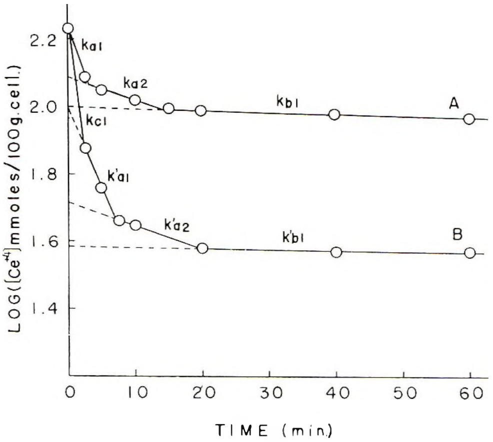

Fig. 7. Consumption of ceric ion with SCP; $[Ce^{4+}]$ 20 mmoles/l.

shown in the figure. *B* contains two straight lines representing the reaction rate constants k'_a and k'_b, which are approximately equal to k_a and k_b, respectively, and besides these *B* contains another straight line showing the reaction rate constant k_c, which is larger than k'_a and k'_b. Since *A* represents the amount of ceric ion consumed in the oxidation, k_a may be regarded as the reaction rate constant of oxidation of the easily reacting portion[6,11] of SP with ceric ion. *B* represents the amount of ceric ion consumed both in the adsorption of SP and in the oxidation of SP and, since k'_a corresponds to the reaction rate constant of oxidation, judging from the slope of the straight line, k_c is assumed to be the reaction rate constant of adsorption. That is, the consumption of ceric ion by SP may be broken down into oxidation and adsorption, and the reaction rate constant of the latter is about three times as large as that of the former. This relationship was also observed at different concentrations of the ceric salt.

In the case of SCP the consumption of ceric ion is slightly more complicated, and the reaction rate constant of oxidation cannot be expressed simply. However, the reaction rate constant of adsorption (k_{c_1}), which was obtained by the same analytical method as that used in the case of SP, is

TABLE IV
Consumption of Ceric Ion Due to Oxidation and Adsorption for Cellulose

Sample	Concn. ceric salt, mmoles/l.	Consumption ceric ion due to oxidation, mmoles per 100 g. cell.	Consumption ceric ion due to adsorption, mmoles per 100 g. cell.
SP	2.0	7.00	3.50
	10.0	10.50	12.40
SCP	20.0	70.00	72.40

estimated to be considerably larger than the reaction rate constant of oxidation. The amounts of ceric ion consumed in adsorption and oxidation were obtained by extending the straight lines in Figures 6 and 7 until they crossed the ordinate axis and reading off the intercepts. These are shown in Table IV.

When the concentrations of the ceric salt used are 10 mmoles/l. for SP and 20 mmoles/l. for SCP, the amounts of the adsorbed ceric ion are in agreement with the equilibrium values shown in Figure 3, and it is apparent that approximately the same amounts of ceric ion as those adsorbed are consumed in the oxidation reaction. In the case of SP the amount of ceric ion consumed in adsorption and oxidation agrees with the total carbonyl. In the case of SCP, however, the amount of ceric ion corresponding to the intercept of the ordinate axis formed by extensions of the straight lines k_{a_2} and k_{b_2} (or k'_{a_2} and k'_{b1}) is roughly equal to the total carbonyl, and the existence of another oxidation reaction, different from oxidation related to carbonyl, and having a larger reaction rate constant k_{a_1}, is inferred. This oxidation may be caused by hemicellulose. When SP is treated with an aqueous solution of the ceric salt having a concentration of 2 mmoles/l., the amount of the adsorbed ceric ion was lower than the equilibrium value (10.6 mmoles per 100 g. of cellulose) and also lower than the amount consumed in the oxidation reaction. The rate of adsorption of ceric ion should be higher than the rate of oxidation, and it is inferred that most of the ceric ion in aqueous solution was first adsorbed on cellulose, the adsorbed ion was gradually consumed in the oxidation reaction, and the amount of adsorbed ion before long became smaller than the amount consumed in oxidation. As is apparent in Figures 1 and 2, the amount of the adsorbed ceric ion shows a maximum after a certain reaction time when low concentrations of the ceric salt are used, and this phenomenon may be explained by a mechanism such as that described above.

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Rate of Sulfonation of Bead Polymers of Styrene Crosslinked with 1,2,4- and 1,3,5-Trivinylbenzene

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Synopsis

Bead copolymers of styrene crosslinked with 1,2,4- and 1,3,5-trivinylbenzene (TVB) are sulfonated at different rates. The copolymer beads with 4% 1,3,5-TVB sulfonate more slowly than do those with 8% 1,2,4-TVB. The 8% 1,2,4-TVB crosslinked polystyrene beads sulfonate at about the same rate as do the beads prepared with 8% *p*-DVB crosslinkage.

As part of a study of the chemical behavior of differently crosslinked polystyrene beads we have studied the rates of sulfonation of a series of such beads crosslinked with 2–8% of 1,2,4-trivinylbenzene and 4% of 1,3,5-trivinylbenzene. The techniques used in the preparation and characterization of the trivinylbenzene isomers have been described previously.[1] The bead copolymerization, sulfonation, and rate measurement techniques used were the same as those for similar studies of polystyrene beads crosslinked with divinylbenzene (DVB).[2–4]

The rate data, summarized in Figure 1, show that the 1,2,4-TVB crosslinked beads sulfonate more rapidly than do the 1,3,5-TVB types. The 4%, 1,3,5-TVB beads sulfonate less rapidly than do the 8% 1,2,4-TVB beads. The rate of sulfonation of the 8% 1,2,4-TVB beads is about the same as that of the 8% *p*-divinylbenzene crosslinked beads as previously observed.[2] Although these rate data are probably dependent on the specific conditions used in these studies and thus do not afford absolute rate values, they are believed to provide reliable comparisons.

We have reported[5] the results of studies of the copolymerization kinetics of the styrene–1,2,4-trivinylbenzene systems ($r_1 = 1.80$, $r_2 = 1.12$ neglecting the high TVB compositions) which, although they do not give an entirely satisfactory solution of the copolymer equation, do establish kinetic differences when compared to other systems.

The rate results are, therefore, in accord with our previous hypothesis that the structural network differences determined by, or related to, kinetic differences are distinguishable chemically. It now appears, furthermore, that an understanding of these facts will ultimately lead to the definition of structures which have enhanced utility.

Experimental

The monomers were vacuum-distilled just prior to use: styrene n_{D}^{20} 1.5468; 1,2,4-trivinylbenzene b.p. 57°C./2 mm., n_{D}^{25}, 1.6052; 1,3,5-trivinylbenzene, b.p. 60°C./2 mm., n_{D}^{25}, 1.5930. The trivinylbenzenes were 99+% isomerically pure by gas–liquid chromatography.[1]

The bead copolymers were prepared by techniques described previously[3] with carboxymethyl cellulose (1 g. in 250 ml. of water) as dispersing agent, with 0.5% benzoyl peroxide initiator, and at 80°C. The beads were sieve-sized to separate the 30 mesh beads used in the sulfonations.

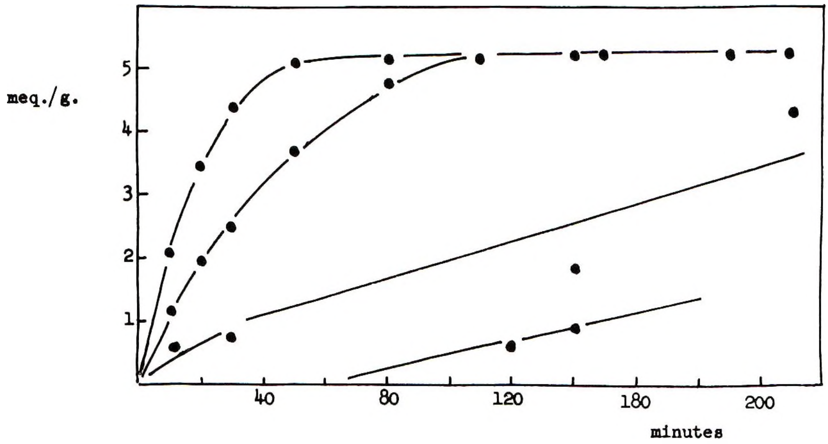

Fig. 1. Rate of sulfonation of crosslinked bead copolymers of styrene at 80°C. with 96.2% sulfuric acid in meq./g. of dry resin: from top to bottom: 2%, 4%, and 8% 1,2,4-TVB and 4% 1,3,5-TVB.

The sulfonations were run on 30 mesh beads, swollen in ethylene dichloride, with 96.2% sulfuric acid at 80°C. Capacities on aliquots taken at time intervals were determined as previously described.[2] The data are summarized in Figure 1.

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2. R. H. Wiley and T. K. Venkatachalam, *J. Polymer Sci. A*, **3**, 1063 (1965); *J. Polymer Sci. A-1*, **4**, 1892 (1966).
3. R. H. Wiley, J. K. Allen, S. P. Chang, K. Musselman, and T. K. Venkatachalam, *J. Phys. Chem.*, **68**, 1776 (1964).
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Polymers with Quinoxaline Units. IV. Polymers with Quinoxaline and Oxazine Units*

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Synopsis

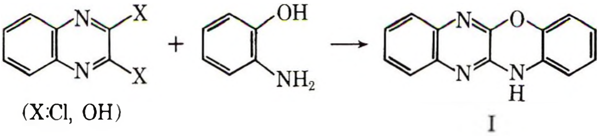
Six ladder or partly ladder polymers have been prepared by the condensation of diaminodiphenols with tetrachloro- or terahydroxyquinoxaline derivatives with the use of poly(phosphoric acid), pyridine, and naphthalene as reaction media. The polymers thus obtained are highly colored powdery materials which are slightly soluble in concentrated sulfuric acid and methanesulfonic acid. These polymers show good thermal stability.

INTRODUCTION

In the previous publication,[1] it has been reported that the condensation of diaminodithiophenols with tetrachloroquinoxaline derivatives produced high molecular weight materials which contained quinoxaline and thiazine recurring units and that these polymers exhibit good thermal stability. In a continuation of this work, some new polymers and model compounds with quinoxaline and oxazine units have been synthesized. This paper describes the preparation of thermally stable ladder or partly ladder polymers with quinoxaline and oxazine recurring units by the condensation of diaminodiphenols with tetrasubstituted quinoxaline derivatives.

DISCUSSION

The melt condensation of 2,3-dichloroquinoxaline with *o*-aminophenol and the solution condensation of 2,3-dihydroxyquinoxaline with *o*-aminophenol in benzoic acid to give quinoxalinobenzoxazine (I) have been reported.[2]



This reaction seemed to offer a promising synthetic route for ladderlike polymers with quinoxaline and oxazine units, hence it was reexamined

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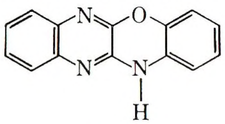
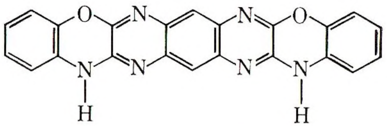
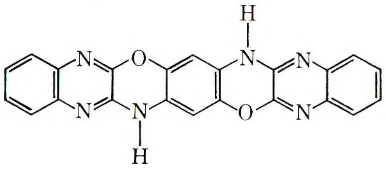
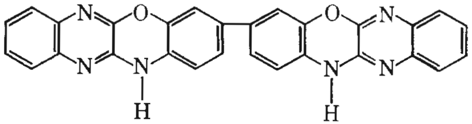
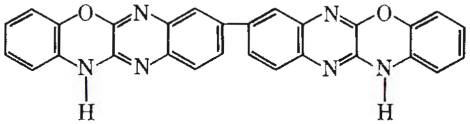
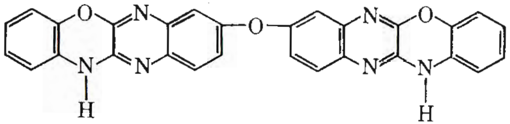
* This work was presented in part at the Miami Beach meeting of the American Chemical Society, April 1967.

TABLE I
Model Compounds with Quinoxaline and Oxazine Units

No.	Starting materials	Reaction medium	Reaction temp., °C.	Probable structure	M.p., °C.	$\lambda_{\max}$, mμ[a]
I	2,3-Dichloroquinoxaline + *o*-aminophenol	Naphthalene	210		316–318	273, 227
II	2,3,7,8-Tetrachloro-1,4,6,9-tetraazaanthracene + *o*-aminophenol	Pyridine	115		>350	318, 265(sh) 245
III	2,3-Dichloroquinoxaline + 2,5-diamino-1,4-dihydroxy benzene	Naphthalene	210		>350	278, 262 246

IV	2,3-Dihydroxyquinoxaline + 3,3′-dihydroxybenzidine	Poly(phosphoric acid)	250		>350	323, 276(sh) 245
V	2,2′,3,3′-Tetrachloro-6,6′-bisquinoxaline + *o*-aminophenol	Pyridine	115		>350	320, 282, 256
VI	2,2′,3,3′-Tetrachloro-6,6′-diquinoxalyl ether + *o*-aminophenol	Pyridine	115		>350	318, 283(sh), 262, 234

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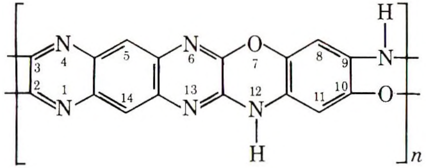
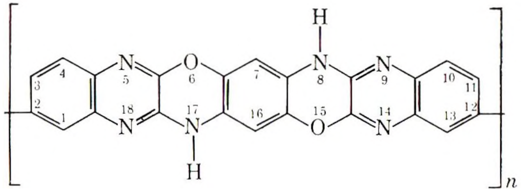
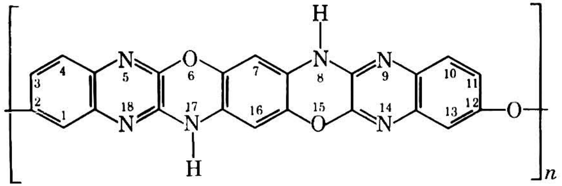
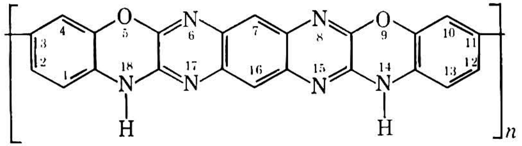
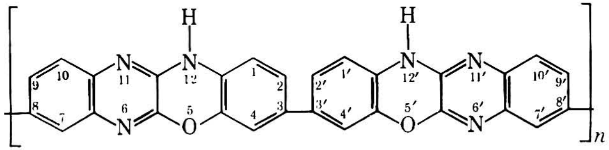
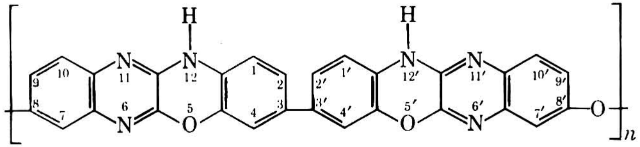
[a] Ultraviolet spectra were taken in concentrated sulfuric acid.

TABLE II
Polymers with Quinoxaline and Oxazine Recurring Units

No.	Structure	Reaction medium	Appearance	η_{inh}[a]	$\lambda_{\max}$, mμ[b]
I		Pyridine	Black powder	0.54	321, 263, 248
		PPA	Black powder	0.85	266, 245
II		PPA	Black powder	0.48	320, 270

III		Pyridine	Black powder	0.35	226, 238
IV		Pyridine PPA	Black powder Black powder	0.38 0.68	316, 282(sh), 318, 243
V		PPA	Black powder	0.47	264
VI		Naphthalene Pyridine	Dark brown powder Dark brown powder	0.36 0.40	321, 262, 243 319, 258, 239

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[a] Viscosities were taken in concentrated sulfuric acid at 30°C.

[b] Ultraviolet spectra were taken in concentrated sulfuric acid.

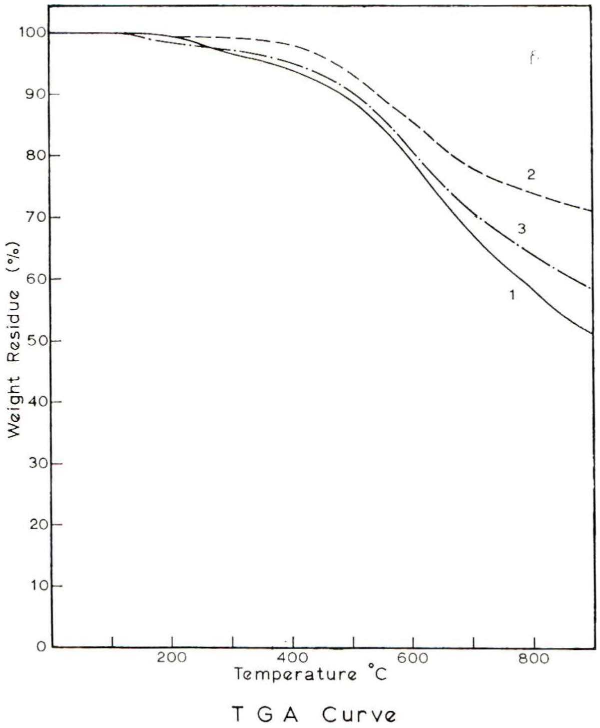

Fig. 1. Thermogravimetric analysis curves: (*1*) polymer I, in helium, ΔT = 180°C./hr.; (*2*) polymer II, in nitrogen, ΔT = 150°C./hr.; (*3*) polymer IV, in helium, ΔT = 180°C./hr.

under various conditions to seek an optimum reaction condition for the preparation of polymers. Condensation of 2,3-dichloroquinoxaline with *o*-aminophenol yielded quinoxalinobenzoxazine in pyridine and naphthalene, while it was unsuccessful in dimethylacetamide, which was conveniently used as a reaction medium for the condensation of aminothiophenols with chloroquinoxaline derivatives.[1] Quinoxalinobenzoxazine was prepared also by the condensation of 2,3-dihydroxyquinoxaline with *o*-aminophenol in poly(phosphoric acid) (PPA). Five other model compounds have been synthesized by the condensation of aminophenols with chloro or hydroxyquinoxaline derivatives. These are listed in Table I, together with ultraviolet data on them.

Polymerizations were carried out by heating the tetrachloroquinoxaline derivatives and the diaminophenols in pyridine or naphthalene under nitrogen. The tetrahydroxy derivatives were condensed with the diaminophenols in poly(phosphoric acid).

The results on the preparation of polymers with quinoxaline and oxazine recurring units are summarized in Table II.

These polymers are highly colored powdery materials and insoluble in common organic solvents. They are also very difficulty soluble in such solvents as hexamethylphosphoramide, dimethyl sulfoxide, and dimethylformamide, but slightly soluble in concentrated sulfuric acid and methanesulfonic acid. The carbon analysis was generally poor, presumably due to difficulties encountered in burning of the polymers with fused aromatic rings. Thermogravimetric analysis on some of these polymers was run in nitrogen or helium at the heating rate of 150°C. or 180°C./hr. Figure 1 shows the thermogravimetric curves. In every case, initial weight loss occurs about 450°C. The unexpectedly poor stability of polymer I which is supposed to have the highest stability is believed to be due to incomplete ring closure.

EXPERIMENTAL

Materials

2,3,7,8 - Tetrahydroxy (or Tetrachloro) - 1,4,6,9 - tetraazaanthracene. These compounds were prepared as described in the literature.[3]

2,2′,3,3′ - Tetrahydroxy (or Tetrachloro) - 6,6′ - bisquinoxaline. These compounds were prepared as described in the literature.[3]

2′,2′,3,3′ - Tetrachloro - 6,6′ - diquinoxalyl Ether. This compound was prepared as described in the previous paper.[1]

2,5-Diamino-1,4-dihydroxybenzene. This compound was synthesized from 2,5-dihydroxy-*p*-benzoquinone by the following route. 2,5-Dihydroxy-*p*-benzoquinone was converted to 2,5-dimethoxy-*p*-benzoquinone by bubbling hydrogen chloride in hot methanol solution.[4] 2,5-Dimethoxy-*p*-benzoquinone thus obtained was aminated with ammonia in hot ethanol followed by reduction with stannous chloride in concentrated hydrochloric acid. 2,5-Diamino-1,4-dihydroxybenzene dihydrochloride was obtained as a white powder.

ANAL. Calcd. for $C_6H_{10}N_2Cl_2$: C, 33.83%; H, 4.68%; N, 13.15%; Cl, 33.32%. Found: C, 33.64%; H, 4.43%; N, 13.14%; Cl, 33.28%.

3,3′-Dihydroxybenzidine. This compound was prepared by heating *o*-dianisidine dihydrochloride and anhydrous aluminum chloride in toluene.[5]

ANAL. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.66%; H, 5.60%; N, 12.94. Found: C, 66.44%; H, 5.58%; N, 13.00%.

Model Compounds

Condensation of 2,3-Dichloroquinoxaline with *o*-Aminophenol (Model Compound I). A mixture of 2,3-dichloroquinoxaline (0.9960 g., 0.005 mole), *o*-aminophenol (0.5459 g., 0.005 mole) and naphthalene (5.0 g.), was heated at 210°C. for 7 hr. After cooling to room temperature, ethyl alcohol (200 ml.) was added to the flask to dissolve naphthalene, and the resulting yellow crystalline material was filtered. This was stirred in dilute ammonium hydroxide at room temperature, washed with water and cold methanol, and dried under reduced pressure. The yield of yellow needles melting at 316–318°C. was 0.67 g. (57%).

ANAL Calcd for $C_{14}H_9N_3O$: C, 71.43%; H, 3.85%; N, 17.85%. Found: C, 71.16%; H, 3.98%; N, 17.82%.

Condensation of 2,3,7,8-Tetrachloro-1,4,6,9-tetraazaanthracene with *o*-Aminophenol (Model Compound II). A solution of 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene (0.6400 g., 0.002 mole) and *o*-aminophenol (0.4802 g., 0.0044 mole) in pyridine (20 ml.) was heated to reflux for 20 hr. After cooling, ethanol (200 ml.) was added to the reaction mixture. The resulting brown precipitate was heated at 340°C. for 6 hr. under vacuum (0.25 mm. Hg). The product was extracted with ethanol for 3 days and with benzene for 1 day in a Soxhlet extractor. The yield of the brown powdery residue was 0.70 g. (93%) after drying under reduced pressure at 60°C.; m.p. > 350°C.

ANAL. Calcd. for $C_{22}H_{12}N_6O_2$: C, 67.34%; H, 3.08%; N, 21.42%. Found: C, 66.54%; H, 3.12%; N, 23.89%.

Condensation of 2,3-Dichloroquinoxaline with 2,5-Diamino-1,4-dihydroxybenzene (Model Compound III). A mixture of 2,3-dichloroquinoxaline (0.9964 g., 0.005 mole), 2,5-diamino-1,4-dihydroxybenzene dihydrochloride (0.5332 g., 0.0025 mole), and naphthalene (5.0 g.) was heated at 210°C. for 24 hr. The reaction mixture was treated as described in the preparation of model compound II. The black powdery material weighed 0.58 g. (59%) after drying under reduced pressure at 60°C.; m.p. > 350°C.

ANAL. Calcd. for $C_{22}H_{12}N_6O_2$: C, 67.34%; H, 3.08%; N, 21.42%. Found: C, 67.26%; H, 3.81%; N, 19.31%.

Condensation of 2,3-Dihydroxyquinoxaline with 3,3′-Dihydroxybenzidine (Model Compound IV). A mixture of 3,3′-dihydroxybenzidine (1.0820 g., 0.005 mole) and 2,3-dihydroxyquinoxaline (1.6210 g., 0.010 mole) in poly(phosphoric acid) prepared from 45 g. of phosphorus pentoxide and 10 ml. of water was heated at 250°C. for 20 hr. The dark brown solution was poured into 1 liter of dilute ammonium hydroxide in a blender to afford a tan precipitate, which was washed with dilute alkali and water, and subsequently extracted with boiling water for several days. The residue weighed 1.98 g. (85%); m.p. > 350°C.

ANAL. Calcd. for $C_{28}H_{16}N_6O_2$: C, 71.79%; H, 3.46%; N, 17.42%. Found: C, 70.76%; H, 3.45%; N, 17.29%.

Condensation of 2,2′,3,3′-Tetrachloro-6,6′-bisquinoxaline with *o*-Aminophenol (Model Compound V). A solution of 2,2′,3,3′-tetrachloro-6,6′-bisquinoxaline (0.396 g., 0.001 mole) and *o*-aminophenol (0.240 g., 0.0022 mole) in pyridine (20 ml.) was heated to reflux for 20 hr. under a nitrogen atmosphere. The reaction mixture was treated as described in the preparation of model compound II. The brown powdery material was obtained in a yield of 88%; m.p. > 350°C.

ANAL. Calcd. for $C_{28}H_{16}N_6O_2$: C, 71.79%; H, 3.46%; N, 17.92%. Found: C, 71.38%; H, 3.61%; N, 19.59%

Condensation of 2,2′,3,3′-Tetrachloro-6,6′-diquinoxalyl Ether with *o*-Aminophenol (Model Compound VI). A solution of 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl ether (0.412 g., 0.001 mole) and *o*-aminophenol (0.240 g., 0.0022 mole) in pyridine (25 ml.) was heated at refluxing temperature for 20 hr. under a nitrogen atmosphere. The black reaction mixture was poured into 200 ml. of water with vigorous stirring to yield a brown solid. This was washed with water and ethanol, subsequently heated at 330°C. for 6 hr. under vacuum. The brown powdery product, after extracting with ethanol and benzene successively, weighed 0.38 g. (80%); m.p. > 350°C.

ANAL. Calcd. for $C_{28}H_{16}N_6O_3$: C, 69.41%; H, 3.31%; N, 17.35%. Found: C, 68.75%; H, 3.70%; N, 18.45%.

Polymers

General Conditions of Polymerization. Polymerization was generally carried out as follows. Equimolar amounts of a tetrachloroquinoxaline derivative and a diaminodiphenol were heated in pyridine at 110°C. or in naphthalene at 210°C. under a nitrogen atmosphere. During the heating a polymeric material precipitated out of the solution. When pyridine was used as a reaction medium, the polymeric material was isolated from the reaction mixture by treating a large volume of water and subsequently extracting with ethanol and benzene in a Soxhlet extractor. When naphthalene was used, the product was separated from the reaction mixture by treating with a large volume of ethanol and washing with dilute ammonium hydroxide followed by extracting with ethanol and benzene. Since the polymers thus obtained seemed to retain uncyclized units to some extent, they were heated in a rotating flask at 330°C. for several hours under vacuum.

Condensations of tetrahydroxyquinoxaline derivatives with diaminodiphenols were performed in poly(phosphoric acid) above 200°C. to yield polymers identical to those obtained in an organic solvent. The polymers produced in polyphosphoric acid, however, retained some residues which were very difficult to remove.

Polymer I by Condensation of 2,3,7,8-Tetrachloro-1,4,6,9-tetraazaanthracene with 2,5-Diamino-1,4-dihydroxybenzene in Pyridine.* A mixture of 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene (1.1194 g., 0.0035 mole) and 2,5-diamino-1,4-dihydroxybenzene dihydrochloride (0.7457 g., 0.0035 mole) was heated in pyridine (30 ml.) at 110°C. for 24 hr. under a nitrogen stream. The black reaction mixture was poured into 1 liter of water with vigorous stirring to give a black precipitate. It was collected, washed with water and ethanol, and dried. The product was heated in a rotating flask at 320°C. for 5 hr. under vacuum, washed with dilute ammonium hydroxide and water, and subsequently extracted with ethanol and

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* Polymer I = poly(12*H*-pyrazino[2′,3′:6,7]quinoxalino[2,3-*b*][1,4]benzoxazine-2,3:9,10-tetrayl-9-imino-10-oxy).

benzene successively. The black powdery material weighed 0.89 g. (81%) after drying under reduced pressure at 45°C. for 24 hr.; m.p. > 350°C. This compound was about 20% soluble in concentrated sulfuric acid and the soluble portion showed an inherent viscosity of 0.54 (c = 0.04% at 30°C.).

ANAL. Calcd. for $(C_{16}H_6N_4O_2)_n$: C, 61.15%; H, 1.93%; N, 26.74%. Found: C, 61.02%; H, 3.03%; N, 22.68%.

Polymer I by Condensation of 2,3,7,8-Tetrahydroxy-1,4,6,9-tetraazaanthracene with 2,5-Diamino-1,4-dihydroxybenzene in Poly(phosphoric Acid). In a three-necked 250-ml. flask was charged 45 g. of phosphorus pentoxide and, with ice cooling, 9 ml. of distilled water was added dropwise to it over 10 min. After the addition was completed, the heterogeneous mixture was heated at 200°C. for 1 hr. with stirring under nitrogen to yield homogeneous poly(phosphoric acid). It was cooled to approximately 100°C., and 2,3,7,8-tetrahydroxy-1,4,6,9-tetraazaanthracene (1.2310 g., 0.005 mole) and 2,5-diamino-1,4-dihydroxybenzene dihydrochloride (1.0654 g., 0.005 mole) were added in this order. The reaction mixture was gradually raised to 240°C. and kept for 24 hr. The very viscous solution was poured into 1 liter of dilute ammonium hydroxide in a blender to yield a black precipitate. It was separated, washed with water, and extracted with boiling water for several days and with methanol for 1 day. The black residue was dried under reduced pressure at 60°C. The yield was 1.55 g. (98%). This compound was about 60% soluble in methanesulfonic acid and concentrated sulfuric acid. The inherent viscosity of the soluble part was 0.85 (c = 0.13% at 30°C.)

ANAL. Found: C, 58.05%; H, 2.87%; N, 24.84%; residue 2.04%.

Polymer II by Condensation of 2,2′,3,3′-Tetrahydroxy-6,6′-bisquinoxaline with 2,5-Diamino-1,4-dihydroxybenzene Dihydrochloride.* A mixture of 2,2′,3,3′-tetrahydroxy-6,6′-bisquinoxaline (1.6133 g., 0.005 mole) and 2,5-diamino-1,4-dihydroxybenzene dihydrochloride (1.0654 g., 0.005 mole) was heated in poly(phosphoric acid) at 230°C. for 24 hr. The resulting viscous solution was treated as described in the preparation of polymer I. The black powdery material weighed 1.75 g. (90% yield). It was soluble in concentrated sulfuric acid, and methanesulfonic acid, and very slightly soluble in dimethyl sulfoxide. The inherent viscosity was 0.48 (c = 0.2% at 30°C.)

ANAL. Calcd. for $(C_{22}H_{10}N_6O_2)_n$: C, 67.69%; H, 2.58%; N, 21.53%. Found: C, 65.38%; H, 3.23%; N, 19.95%.

Polymer III by Condensation of 2,2′,3,3′-Tetrachloro-6,6′-diquinoxalyl Ether with 2,5-Diamino-1,4-dihydroxybenzene in Pyridine.† A mixture

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* Polymer II = poly(8,17-dihydroquinoxalino[2,3-*b*]-quinoxalino[2′3′:5,6][1,4]oxazino[2,3-*g*][1,4]benzoxazine-2,12-diyl).

† Polymer III = poly(8,17-dihydroquinoxalino[2,3-*b*]quinoxalino[2′3′:5,6][1,4]oxazino[2,3-*g*][1,4]benzoxazine-2,12-diyl-12-oxy).

of 2,2′,3,3′-tetrachloro-6,6′-diquinoxalylether (2.0605 g., 0.005 mole) and 2,5-diamino-1,4-dihydroxybenzene dihydrochloride (1.0656 g., 0.005 mole) was heated in pyridine (40 ml.) at 115°C. for 24 hr. The work-up was carried out as described in the preparation of polymer I. The dark-brown powdery material was obtained in a yield of 74%. It was about 30% soluble in concentrated sulfuric acid, and the soluble part had an inherent viscosity of 0.35 (c = 0.07% at 30°C.).

ANAL. Calcd. for $(C_{22}H_{10}N_6O_3)_n$: C, 65.03%; H, 2.48%; N, 20.68%. Found: C, 65.53%; H, 3.66%; N, 19.82%.

Polymer IV by Condensation of 2,3,7,8-Tetrachloro-1,4,6,9-tetraaza-anthracene with 3,3′-Dihydroxybenzidine in Pyridine.* A mixture of 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene (1.1197 g., 0.0035 mole) and 3,3′-dihydroxybenzidine (0.8622 g., 0.0035 mole) was heated in pyridine (25 ml.) at refluxing temperature under nitrogen. The black reaction mixture was treated as described in the preparation of polymer I. The black powdery material weighed 1.34 g. (94%) after drying under reduced pressure at 50°C. This compound was about 15% soluble in concentrated sulfuric acid, and the soluble part showed an inherent viscosity of 0.38 (c = 0.03% at 30°C.).

ANAL. Calcd. for $(C_{22}H_{10}N_6O_2)_n$: C, 67.69%; H, 2.58%; N, 21.53%. Found: C, 66.77%; H, 3.39%; N, 18.95%.

Polymer V by Condensation of 2,2′,3,3′-Tetrahydroxy-6,6′-bisquinoxaline with 3,3′-Dihydroxybenzidine in Poly(phosphoric Acid).† 2,2′,3,3′-Tetrahydroxy-6,6′-bisquinoxaline (1.6113 g., 0.005 mole) and 3,3′-dihydroxybenzidine (1.0812 g., 0.005 mole) were condensed in poly(phosphoric acid) (70 g.) at 230°C. for 24 hr. under a nitrogen atmosphere. The polymerization and work-up were carried out as described in the preparation of polymer I in poly(phosphoric acid). The black powdery material weighed 1.84 g. (79%). It was soluble in concentrated sulfuric acid and methanesulfonic acid and slightly soluble in formic acid. The inherent viscosity was 0.49 (c = 0.2% at 30°C.).

ANAL. Calcd. for $(C_{23}H_{14}N_6O_2)_n$: C, 72.10%; H, 3.02%; N, 18.02%. Found: C, 66.13%; H, 3.80%; N, 17.98%; residue 4.71%.

Polymer VI by Condensation of 2,2′,3,3′-Tetrachloro-6,6′-diquinoxalyl Ether with 3,3′-Dihydroxybenzidine in Naphthalene.‡ A mixture of 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl ether (1.0307 g., 0.0025 mole), 3,3′-dihydroxybenzidine (0.5408 g., 0.0025 mole) and naphthalene (8.0 g.) was heated at 210°C. for 18 hr. under a nitrogen atmosphere. After cooling, ethanol (300 ml.) was added to the reaction mixture to dissolve

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* Polymer IV = poly(14*H*, 18*H*-benzo[1″,2″:5,6; 5″,4″:5′,6′]dipyrazino[2,3-*b*:2′,3′-*b*′]bis[1,4]benzoxazine-3,11-diyl).

† Polymer V = poly(3,3′-bi-12*H*-quinoxalino[2,3-*b*][1,4]benzoxazine-8,8′-diyl).

‡ Polymer VI = poly(3,3′-bi-12*H*-quinoxalino[2,3-*b*][1,4]benzoxazine-8,8′-diyl-8′-oxy).

naphthalene. A tan solid which remained undissolved in ethanol was treated in dilute ammonium hydroxide, washed with water and ethanol several times and dried. The tan powder was again heated in a rotating flask at 330°C. for 6 hr. under vacuum and subsequently extracted with ethanol and benzene successively in a Soxhlet extractor. The yield of the tan powder was 1.02 g. (85%). This compound was about 30% soluble in concentrated sulfuric acid, and the soluble part showed an inherent viscosity of 0.36 (c = 0.06% at 30°C.).

ANAL. Calcd. for $(C_{28}H_{14}N_6O_3)_n$: C, 69.71%; H, 2.93%; N, 17.42%. Found: C, 64.53%; H, 2.52%; N, 16.40%.

Polymer VI by Condensation of 2,2′,3,3′-Tetrachloro-6,6′-diquinoxalyl Ether with 3,3′-Dihydroxybenzidine in Pyridine. A mixture of 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl ether (2.0604 g., 0.005 mole) and 3,3′-dihydroxybenzidine (1.0815 g., 0.005 mole) was heated in pyridine (40 ml.) at 115°C. for 24 hr. The black reaction mixture was treated as described in the preparation of polymer I. The yield of dark brown powdery material was 1.92 g. (79%). This compound was soluble in concentrated sulfuric acid and showed an inherent viscosity of 0.40 (c = 0.2% at 30°C.).

ANAL. Found: C, 68.52%; H, 3.97%; N, 16.63%.

We are indebted to Dr. G. Ehlers, Air Force Materials Laboratory, Wright-Patterson Air Force Base, for thermogravimetric curves.

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Copolymerization of Allyl Esters of Some Fatty Acids

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Synopsis

Attempts have been made unsuccessfully to homopolymerize a number of allyl esters of substituted fatty acids by radical initiation in emulsion systems. Copolymerizations of these allyl esters with styrene, methyl methacrylate, and vinyl chloride have been investigated. Of these comonomers, styrene and methyl methacrylate do not copolymerize well with the allyl esters, whereas vinyl chloride does. Reactivity ratios for the radical copolymerization of allyl 11-iodoundecanoate, M_1, and vinyl chloride, M_2, determined at 60°C. in benzene, are $r_1 = 0.42$ and $r_2 = 1.64$. A copolymer of allyl 10,11-dibromoundecanoate and vinyl chloride was fractionated and found to be fairly homogeneous.

Through the Western Utilization Research and Development Division of the Agricultural Research Service, the following allylic compounds were made available to us by Dr. J. S. Aggarwal of Hyderabad-Deccan, India: allyl undecanoate (AUA), allyl 10-/11-phenylundecanoate (APU), allyl 10,11-dibromoundecanoate (ADBU), allyl 11-iodoundecanoate (AIU), allyl 12-hydroxystearate (AHS), and allyl 12-ketostearate (AKS). Since it is well recognized that homopolymerization of allylic compounds with radical initiators generally gives low molecular weight materials,[1] we emphasized their copolymerization and report herein results of this study.

Emulsion homopolymerization of AUA, APU, ADBU, and AIU has been conducted, but without much success. Thus, with 1% diethyl azobisisobutyrate or 1% potassium persulfate as the initiator, polymerizations were carried out at 60°C. for a period of 4-8 days. At the end of the reaction, the product was taken up into ether and purified. Infrared spectra and refractive indices of the materials indicated that polymerization did not proceed to any appreciable extent.

Copolymerization experiments with the allyl esters are shown in Table I. Attempts to prepare copolymers of styrene and methyl methacrylate with the allyl esters only resulted in products which contained very little of the allylic comonomers. These results are in line with the monomer reactivity ratios found in literature.[2] They are $r_1 = 0$ and $r_2 = 90 \pm 10$ for a bulk copolymerization of allyl acetate (M_1) and styrene (M_2) at 60°C., and $r_1 = 0$ and $r_2 = 23$ for that of allyl acetate (M_1) and methyl methacrylate (M_2) under the same condition.

TABLE I
Copolymerization of Allyl Esters and Vinyl Monomers[a]

Run no. and allyl ester	Comonomers, %[b]			Initiator[c]	Temp., °C.	Time, hr.	Conversion, %	η_{inh}[d]	Ester in polymer, %
	VCl	St	MMA						
COADBU-1	50			R	27	15	53	0.49	40.8
COADBU-6	50			P	60	72	81	e	—
COADBU-8[f]	50			A	60	44	57	0.24	47.3
COAIU-1	50			P	60	75.5	38	0.28	44.9
COAIU-2	50			R	27	15	35	0.32	37.0
COAPU-1	50			P	60	75.5	14	0.63	22.1
COAPU-2	50			R	60	15	23	0.26	25.8
COAUA-1	50			P	60	75.5	88	0.36	44.8
COAHS-1	50			P	60	75.5	71	0.78	28.9
COAKS-1	50			P	60	75.5	61	0.73	40.6
COADBU-3		50		P	60	24	48	e	3.7
COADBU-5		50		P	60	42	52	e	4.5
COAPU-3		50		P	60	24	45	0.33	0
COAIU-3		50		P	60	24	51	1.22	2.5
COAPU-5			50	P	60	76	43	1.30	5.4
COADBU-9			50	P	60	76	40	2.20	12.8

[a] The polymerization was conducted in 5 parts of deaerated water, using 1% initiator and 1% Siponate DS-10 in the standard radical system; in the redox system, 1% ORR (Office Rubber Research) soap was used instead.

[b] Comonomers: St = styrene, MMA = methyl methacrylate, VCl = vinyl chloride.

[c] Initiators: R = redox system which consists of 1% ferrous sulfate heptahydrate, 10% sodium pyrophosphate decahydrate, and 2% benzoyl peroxide; P = potassium persulfate; A = α,α'-azobisisobutyronitrile.

[d] Inherent viscosities were measured on 0.2% THF solutions at 30°C.

[e] These samples had become insoluble.

[f] Solution polymerization in 5 ml. benzene/10 g. of monomers.

TABLE II
Fractionation of a Copolymer of Allyl Dibromoundecanoate and Vinyl Chloride[a]

				Analyses					
				Found			Calculated		
Fraction	% by wt.	η_{inh} (30°C.)	Allyl ester, %	C, %	H, %	X, %[b]	C, %	H, %	X, %[b]
A	11.4	0.26	54.4	41.55	5.55	48.68	41.35	5.59	48.53
B	60.1	0.21	53.8	41.40	5.69	48.84	41.32	5.58	48.62
C	16.8	0.13	45.3	40.87	5.46	49.94	40.87	5.46	49.90
D	5.0	0.07	44.9	40.94	5.45	50.21	40.84	5.45	49.96

[a] The sample (COADBU-8) contained 47.3% ADBU and 52.7% VCl, weighed 4.465 g. and had an inherent viscosity of 0.24. There was 93.3% recovery from the fractionation.

[b] Total halogen.

However, when vinyl chloride was the comonomer, allyl compounds were found to enter into the copolymers in rather significant amounts. The polymerization is characterized by a slow rate, and usually a low conversion, which is what one might expect from an allyl polymerization. Evidence for the incorporation of the allylic compounds comes from the compositions calculated from their elemental analyses. The copolymers exhibit a characteristic ester absorption at 1740 cm.$^{-1}$ in the infrared spectra. The possibility of allyl esters being present as impurities in the copolymers can be eliminated on the basis that the C=C stretching frequency at 1655 cm.$^{-1}$ is not seen in the spectra. Furthermore, extensive purification of the copolymer by many reprecipitations from tetrahydrofuran (THF) and methanol did not change the composition. That it might be a mixture of two homopolymers rather than a true copolymer seems unlikely inasmuch as that allyl esters do not homopolymerize readily with radical catalysts. The homogeneity of the copolymer was demonstrated by a fractionation experiment. Thus a sample of allyl 10,11-dibromoundecanoate–vinyl chloride copolymer was dissolved in THF and fractionally precipitated in methanol. Results shown in Table II suggest that more than 70% by weight of the sample consists of copolymers of comparable sizes and compositions. Films of the vinyl chloride copolymers which can be cast from THF solutions are rather brittle.

It was considered that a study of the reactivity ratios of an allyl ester and vinyl chloride might be desirable. Allyl 11-iodoundecanoate was chosen for this purpose because of its availability. The copolymerization was carried out in benzene at 60°C. with α, α'-azobisisobutyronitrile as the initiator. Compositions of the copolymers calculated from carbon and hydrogen analyses along with the charged compositions, conversion, and viscosities are listed in Table III. The reactivity ratios of allyl 11-iodoundecanoate (M_1) and vinyl chloride (M_2) are found to be $r_1 = 0.42$ and $r_2 = 1.64$. The reported value for a bulk copolymerization of allyl acetate (M_1) and vinyl chloride (M_2) at 40°C. is $r_2 = 1.16$; r_1 is not available.[1]

TABLE III

Determination of Reactivity Ratios of Allyl 11-Iodoundecanoate (M_1) and Vinyl Chloride (M_2) in a Solution Copolymerization at 60°C.[a]

Composition		Conversion,		Analyses			
				Found		Calculated	
Charged, m_1/m_2	Found, M_1/M_2	%	η_{inh}[b]	C, %	H, %	C, %	H, %
0.110	0.065	14	0.25	40.78	5.49	41.01	5.44
0.294	0.171	7	0.20	42.89	5.96	43.02	5.93
0.582	0.327	3	0.17	44.27	6.34	44.48	6.29

[a] The polymerization was run in benzene, with α,α'-azobisisobutyronitrile as the initiator, for 3 hr.

[b] Inherent viscosities were determined in 0.2% THF solutions at 30°C.

Bartlett and Nozaki[3] studied the copolymerization of allyl acetate and maleic anhydride and found that the monomers enter the copolymerization in an 1:1 ratio. It is suggested that the tendency of the two monomers to act as electron donor and electron acceptor, respectively, possibly is responsible for the unusual behavior of the copolymerization. We do not know if vinyl chloride behaves like maleic anhydride which has the ability to accept electrons but not enough resonance stabilization to make it a chain inhibitor. On the other hand, vinyl chloride, being a gas at room temperature, no doubt increases the pressure in a polymerization system considerably. For instance, a charge of 2 g. (0.032 mole) of vinyl chloride in a 110-ml. pressure bottle (1.5 × 7 in.) would increase the pressure by about 8 atm. at 60°C. It has been shown by Walling and Pellon[4,5] that the rate of polymerization of allyl acetate increases exponentially with pressure. Under high pressure, allylic radicals are still formed, but they now add to monomer, and therefore the degradative nature of chain transfer becomes insignificant. It would seem plausible that the extra pressure due to the vinyl chloride vapor may be in some way responsible for the copolymerization of allyl esters and vinyl chloride to occur.

EXPERIMENTAL

Monomers

Of the six monomers prepared in Dr. Aggarwal's laboratory, AUA, APU, ADBU, and AIU exhibited satisfactory purity by thin-layer chromatography and were used without further purification. The two derivatives

TABLE IV
Analyses and Compositions of Copolymers of Allyl Esters

Sample no.	Found			Allyl ester in polymer, %	Calculated		
	C, %	H, %	X, %		C, %	H, %	X, %[a]
COADBU-1	40.56	5.33	50.42	40.8	40.60	5.39	50.63
COADBU-8	41.02	5.73	49.75	47.3	40.97	5.49	49.60
COAIU-1	42.69	5.93	47.60	44.9	42.62	5.83	47.46
COAIU-2	41.92	5.64	46.44	37.0	41.65	5.65	49.23
COAPU-1	47.56	5.86	44.22	22.1	47.51	5.93	44.21
COAPU-2	49.10	6.11	42.01	25.8	49.03	6.12	42.11
COAUA-1	54.52	7.93	31.82	44.8	54.20	7.72	31.32
COAHS-1	48.36	6.86	40.21	28.9	48.74	6.81	40.38
COAKS-1	53.42	7.53	34.21	40.6	53.09	7.53	33.71
COADBU-3	90.06	7.60	1.54	3.7	89.97	7.62	2.02
COADBU-5	90.37	7.45	2.07	4.5	90.13	7.71	1.87
COAPU-3	91.62	7.67	0	0	92.31	7.69	0
COAIU-3	91.21	7.85	1.02	2.5	91.18	7.68	0.91
COAPU-5	60.83	8.13	0	5.4	61.10	8.11	0
COADBU-9	57.80	7.91	4.89	12.8	57.97	7.78	5.33

[a] Total halogen.

of stearic acid, AHS and AKS were much contaminated and colored as received. Thus AHS and AKS were each chromatogramed on a silica gel column, using petroleum ether (b.p. 30–60°C.) as an eluent, followed by a recrystallization from ether and petroleum ether. AHS has a melting point of 52.0–52.5°C., and AKS, 43.0–44.5°C. These allyl esters were characterized by their infrared absorptions at 1740 cm.$^{-1}$, due to the ester function, and 1655 cm.$^{-1}$, attributable to the C=C stretching frequency. Refractive indices and boiling points are: AUA, $n_D^{32.5}$ = 1.4334, b.p. 150°C./1 mm.; APU, n_D^{25} = 1.4875, b.p. 175°C./2 mm.; AIU, n_D^{34} = 1.4630, b.p. 175°C./2 mm.; ADBU, n_D^{34} = 1.4912, b.p. 192°C./2 mm.

Polymerization

All the emulsion polymerizations were run in pressure bottles (1.5 × 7 in.), following the general procedure described in a previous communication.[6] Analytical data of the copolymers are given in Table IV.

Determination of Reactivity Ratios

The copolymerization of AIU and vinyl chloride (VCI) was carried out in freshly distilled benzene. In a typical run, 3.06 g. (8.7×10^{-3} mole) of AIU and 4.95 g. (8.05×10^{-2} mole) of vinyl chloride were charged into a pressure bottle which contained 0.08 g. of α,α'-azobisisobutyronitrile and 4 ml. of benzene. The solution was degassed three times to ca. 1 mm. and then filled with nitrogen. Excess vinyl chloride was then distilled into the polymerization tube, and the excess was allowed to boil off. It was capped and the polymerization vessel was tumbled in a water bath thermostatted at 60°C. After 3 hr. the polymerization was terminated. The polymer which precipitated in methanol was repeatedly reprecipitated from THF and methanol and dried in vacuum oven. Results are shown in Table III. The reactivity ratios were determined graphically by the method of Mayo and Lewis.[7]

Fractionation of a Copolymer of ADBU and VCl

A sample of the polymer (4.465 g.) was dissolved in 70 ml. of THF, to which 70 ml. of methanol and 2 drops of concentrated sulfuric acid were added. This was allowed to settle at room temperature for a day and thus was the first fraction obtained. The second fraction was precipitated by the addition of another 30 ml. of the nonsolvent and again allowing a day for complete precipitation. To the filtrate was again added 70 ml. of methanol to yield the third fraction. Finally, the last fraction was isolated by adding to the third filtrate an additional 100 ml. of methanol. Results are to be found in Table II.

This is a partial report of work done under contract with the Western and Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is supervised by Dr. Glenn Fuller of the Western Division.

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Homopolymers and Copolymers of Vinyl Ethers of Rosin-Derived Alcohols

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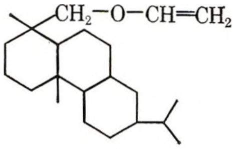
Synopsis

Two vinyl ethers of rosin-derived alcohols were homopolymerized with free-radical and cationic initiators. A polymer was obtained from the vinyl ether of the alcohol from Foral in good conversion by free-radical initiators but it was not a high molecular weight product. Cationic initiators were more effective; boron trifluoride etherate proved to be best. All of the homopolymers were obtained as white powders with high crystallinity. Copolymerizations of the vinyl ethers and vinyl chloride have been studied with the use of free-radical initiators. Cationic-initiated copolymers of the vinyl ethers and isobutyl vinyl ether were studied. Those containing less than 20% of the rosin vinyl ethers were rubbery, of high molecular weight, and could be crosslinked with peroxide.

INTRODUCTION

In continuation of the studies on the preparation of polymers containing terpenes and various terpene derivatives,[1-9] two vinyl ethers from rosin-derived alcohols have been studied. One of the monomers consisted primarily of the vinyl ether of tetrahydroabietol (I) and the other had some unsaturation in the ring system.



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The work described in this paper was undertaken to determine the optimum conditions for polymerizing these vinyl ethers and to investigate the properties of the resultant polymers. In addition, studies on the copolymerization of the vinyl ethers and isobutyl vinyl ether in cationic systems and of the vinyl ethers and vinyl chloride in radical-initiated systems were conducted to prepare polymers which might have useful properties.

RESULTS AND DISCUSSIONS

Monomer

Samples of monomers were provided as water-clear, viscous oils by Dr. Glen W. Hedrick of the Naval Stores Research Laboratory, Southern Utilization Research and Development Division, Agricultural Research Service. One of the monomers was the vinyl ether of the alcohol made by the reduction of the acid group in Foral (VEAF) (a commercial completely hydrogenated rosin made by Hercules, Inc.) with lithium aluminum hydride. The other was the vinyl ether of Abitol (VEA) which is another Hercules commercial rosin-derived alcohol which contains some methyl hydroabietate and residual unsaturation in the ring system. The commercial Abitol was further reduced with lithium aluminum hydride to remove ester. The vinyl ethers were made from the alcohols by the procedure of Teeter et al.[10–14] The monomers were distilled without inhibitor under reduced pressure. VEAF gave some polymer in the residue of the distillation. The center cuts having the following physical constants for polymerizations: VEAF, b.p. 127–129°C./0.07 mm., n_D^{30}, 1.5077, 95% vinyl ether by hydrogenation; VEA, b.p. 120–121°C./0.05 mm., n_D^{30}, 1.5127, 85–86% vinyl ether by hydrogenation.

Thin-layer chromatography of the vinyl ethers on silica gel indicated two spots for VEAF and three spots for VEA, as might be expected from such mixtures. A main spot was shown at $R_f = 0.97$ with the use of petroleum ether as an eluent. VEA contained one impurity which could not be seen in VEAF. Infrared spectra of the monomers showed the characteristic absorption bands of vinyl ethers. In the spectrum of VEA, there was also an absorption band at 823 cm.$^{-1}$, indicating some residual unsaturation in the ring system. No hydroxyl bands were observed.

Homopolymerization

Free Radical-Initiated Homopolymerization. As VEAF could be polymerized by heating *in vacuo*, homopolymerization with free-radical initiators was conducted in emulsion and in bulk. The experimental data are given in Table I. The polymers were obtained as white powders, soluble in tetrahydrofuran and could be molded into clear but very brittle films. Conversion and viscosity were affected by conditions used in the polymerization of VEAF. VEA polymers varied only slightly with system and catalyst used. No high molecular weight polymer was obtained.

It has been known that only low molecular weight, syrupy polymers were obtained by free-radical polymerization of alkyl vinyl ethers.[15] Aryl vinyl ethers can be polymerized thermally, but not by sulfuric acid.[16] Phenyl vinyl ether has been polymerized by cationic initiators such as boron trifluoride etherate and stannic chloride.[17] VEAF seemed to be more similar to an aryl vinyl ether rather than an alkyl vinyl ether.

Analytical data on both polymers indicated slightly lower percentage of carbon and hydrogen as compared to the monomers, which may be due to

TABLE I
Free-Radical Polymerization of VEAF and VEA[a]

Run no.	Monomer	System	Catalyst	Amt. catalyst, %	Conversion, %	η_{inh}[b]	Analysis C, %	Analysis H, %
I-1	VEAF	Bulk	AIBN	5	26.6	0.047	82.61	11.89
I-2	"	"	DEABIB	5	34.0	0.048	—	—
I-3	"	Emulsion[d]	$K_2S_2O_8$	2.5	Trace	—	—	—
I-4	"	"	AIBN	5	16.5	0.057	82.27	11.96
I-5	"	"	DEABIB	5	47.0	0.057	82.76	11.74
I-6	VEA	Bulk	AIBN	5	7.7	0.037	82.40	11.36
I-7	"	"	DEABIB	5	9.2	0.044	—	—
I-8	"	Emulsion[d]	$K_2S_2O_8$	5	7.8	0.041	—	—
I-9	"	"	AIBN	5	6.9	0.043	83.30	11.30
I-10	"	"	DEABIB	5	7.5	0.037	80.86	11.10

[a] All of the polymerizations were conducted at 60 ± 2°C. by tumbling end-over-end for 48 hr. (in emulsion) or 72 hr. (in bulk).

[b] Determined on the solutions of 0.192–0.425 g./100 ml. of THF at 30°C.

[c] VEAF monomer: C, 83.23%; H, 12.40%. VEA monomer: C, 83.83%; H, 11.77%; Calcd. for $C_{22}H_{38}O$: C, 82.95%; H, 12.03%.

[d] Siponate DS-10 was used as emulsifier.

TABLE II
Cationic Polymerization of VEAF and VEA[a]

Run no.	Monomer	Catalyst	Temperature, °C.	Conversion, %	η_{inh}[b]	Analysis C, %	Analysis H, %
II-1[c]	VEAF	$BF_3O(C_2H_5)_2$	−78	100	0.346	—	—
II-2	"	"	0	96	0.186	82.81	11.84
II-3	"	$SnCl_4$	−78	14	0.052	—	—
II-4	"	"	0	98	0.118	82.83	12.11
II-5	VEA	$BF_3O(C_2H_5)_2$	−78	88	0.476	—	—
II-6	"	"	0	89	0.154	83.40	11.63
II-7	"	$SnCl_4$	−78	54	0.037	—	—
II-8	"	"	0	92	0.109	83.49	11.49

[a] All of the polymerizations were conducted for 2 hr. with the use of a monomer (5.0 g.) and *n*-heptane (20 ml.).

[b] Determined on solutions of 0.375–0.430 g./100 ml. of THF at 30°C.

[c] Monomer solution was dried over sodium.

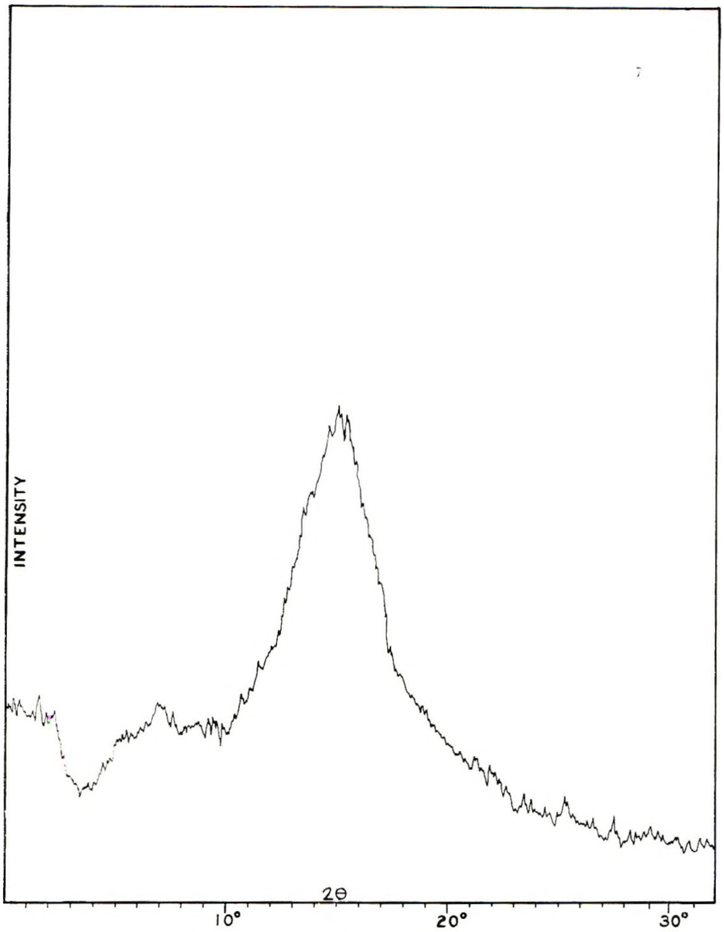

Fig. 1. X-ray diffraction pattern of PVEAF.

removal of hydrocarbon impurities in the monomers. Infrared spectra of polymers indicated the presence of some remaining unsaturation.

Cationic Homopolymerization. Polymerization with boron trifluoride etherate and solution polymerization with stannic chloride were conducted. The data are given in Table II.

Polymerizations of VEAF and VEA with boron trifluoride etherate at −78°C. led to the formation of polymers having higher inherent viscosity than those obtained at 0°C. This is consistent with the literature[18] work on other vinyl ethers.

Polymerizations of VEAF and VEA with stannic chloride yielded polymers of lower inherent viscosity and lower conversion at −78°C. than at 0°C. These results were consistent with the available information on the polymerization of other vinyl ethers.[5,19]

The polymers obtained at low temperature indicated high crystallinity as revealed by their high melting point, (the highest one was over 150°C.) and good peaks in the x-ray diffraction pattern (Figs. 1 and 2).

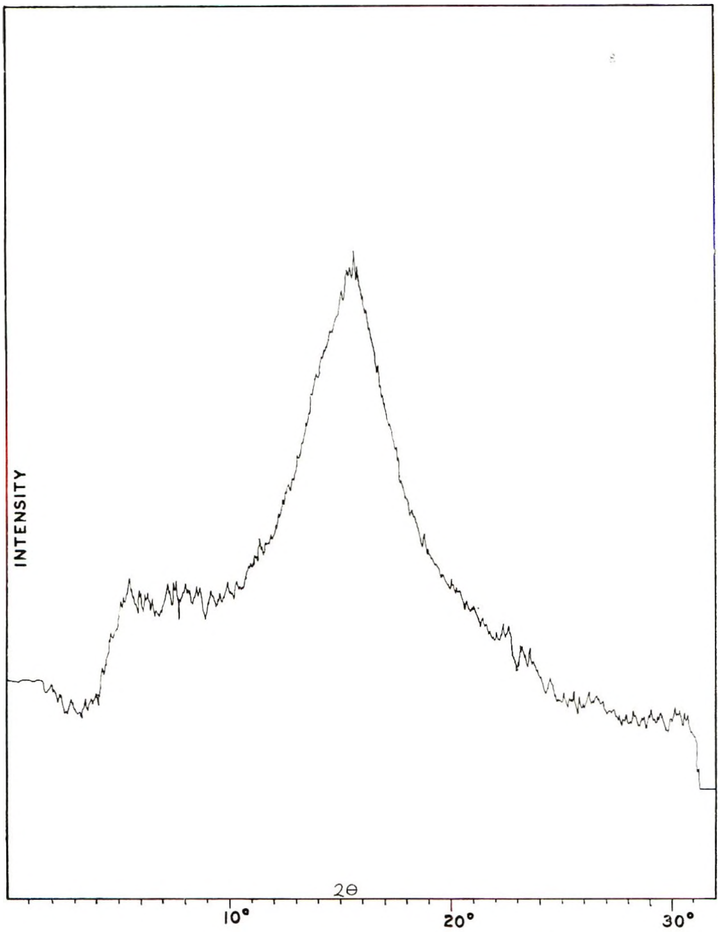

Fig. 2. X-ray diffraction pattern of PVEA.

All of the polymers were obtained as white powders soluble in tetrahydrofuran and could be molded at about 160°C. into transparent but brittle films. Analytical data on the polymers agreed closely to those for a polyvinyl ether of abietol in the case of PVEAF, but with higher carbon and lower hydrogen content for PVEA. The infrared spectra of the polymers showed no absorption bands characteristic for monomers. It is believed that the VEAF polymer consists of poly(vinyl tetrahydroabietol). The infrared spectrum of VEA polymer showed the characteristic band at 823 cm.$^{-1}$ which could be seen in VEA monomer but not in VEAF monomer.

Curing of the bulk homopolymer with peroxides was investigated. The curing composition was prepared in a tetrahydrofuran solution with 10% dicumyl peroxide (Di-Cup, Hercules Powder Co., 96–99% pure) and the cure itself was done on a cast, dried film at 160°C. for 2 hr. An insolubilized material was obtained, but the crosslinking appeared to be not so effective as shown in the curing of poly(vinyl tetrahydroabietate).[2]

TABLE III
Free-Radical Copolymerization of VEAF and VCl[a]

Run no.	Charged composition		Catalyst	Amt. catalyst, %	Conversion, %	η_{inh}[b]	Analysis			Calculated polymer composition[c]	
	VCl, wt.-%	VEAF, wt.-%					C, %	H, %	Cl, %	VCl, wt.-%	VEAF, wt.-%
III-1	95	5	$K_2S_2O_8$	2	71.4	0.61	39.23	5.98	55.80	98.0	2.0
III-2	90	10	"	2	61.3	0.45	39.78	5.22	53.11	96.9	3.1
III-3	85	15	"	2	65.3	0.51	42.25	6.02	51.47	91.3	8.7
III-4	80	20	"	2	72.4	0.63	43.36	5.72	49.44	86.7	13.3
III-5	70	30	"	2	67.8	0.38	46.23	5.91	46.91	82.4	17.6
III-6	90	10	DEABIB	4	64.5	0.32	42.33	5.46	51.93	91.0	9.0
III-7	80	20	"	4	50.3	0.21	45.41	5.82	47.43	84.5	15.5
III-8	70	30	"	4	58.0	0.21	46.66	6.04	46.48	81.5	18.5

[a] All of the polymerizations were conducted at 60 ± 2°C. by tumbling end-over-end for 48 hr. Siponate DS-10 used as emulsifier.

[b] Determined on the solutions of ca. 0.42/100 ml. of THF at 30°C.

[c] Based on the analysis, assuming VEAF to be the vinyl ether of tetrahydroabietol.

TABLE IV

Free-Radical Copolymerization of VEA and VCl[a]

Run no.	Charged composition VCl, wt.-%	Charged composition VEA, wt.-%	Catalyst	Amt. catalyst, %	Conversion, %	η_{inh}[b]	Analysis C, %	Analysis H, %	Analysis Cl, %	Calculated polymer composition[c] VCl, wt.-%	Calculated polymer composition[c] VEA, wt.-%
III-1	95	5	K_2S_2Ol	2	71.4	0.61	39.23	5.98	55.80	98.0	2.0
III-2	90	10	"	2	61.3	0.45	39.78	5.22	53.11	96.9	3.1
III-3	85	15	"	2	65.3	0.51	42.25	6.02	51.47	91.3	8.7
III-4	80	20	"	2	72.4	0.63	43.36	5.72	49.44	86.7	13.3
III-5	70	30	"	2	67.8	0.38	46.23	5.91	46.91	824.	17.6
III-6	90	10	DEABIB	4	64.5	0.32	42.33	5.46	51.93	91.0	9.0
III-7	80	20	"	4	36.8	0.19	46.43	6.27	47.44	82.0	18.0
IV-6	70	30	"	4	32.6	0.15	47.56	6.05	45.45	79.5	20.5

[a] All of the polymerizations were conducted at 60 ± 2°C. by tumbling end-over-end for 48 hr. Siponate DS-10 used as emulsifier.

[b] Determined on the solutions of ca. 0.4 g./100 ml. of THF at 30°C.

[c] Based on the analysis, assuming VEA to be the vinyl ether of tetrahydroabietol.

TABLE V
Cationic Copolymerization of VEAF and IBVE[a]

Run no.	Charged composition		Conversion, %	η_{inh}[b]	Analysis		Calculated polymer composition[c]		Properties of film
	IBVE, wt.-%	VEAF, wt.-%			C, %	H, %	IBVE, wt.-%	VEAF, wt.-%	
V-1	100	0	98	2.93	—	—	—	—	—
V-2	90	10	95	2.99	72.20	11.85	98	2	Clear, rubbery, soft, sticky
V-3	76	24	61	3.26	72.96	11.96	91	9	"
V-4	75	25	89	3.49	73.92	13.06	82	18	"
V-5	50	50	67	1.69	75.90	11.88	64	36	Clear, tough, tacky
V-6	25	75	19	1.04	77.24	12.07	52	48	Hazy, tough

[a] All of the polymerizations were conducted for 2 hr. at −78°C. with use of $BF_3 \cdot O(C_2H_5)_2$ as catalyst and *n*-heptane as solvent.

[b] Determined on solutions of 0.413–0.156 g./100 ml. of tetrahydrofuran at 30°C.

[c] Based on the analysis assuming VEAF to be the vinyl ether of tetrahydroabietol.

TABLE VI
Cationic Copolymerization of VEA and IBVE[a]

Run no.	Charged composition IBVE, wt.-%	Charged composition VEA, wt.-%	Conversion, %	η_{inh}[b]	Analysis C, %	Analysis H, %	Polymer composition[c] IBVE, wt.-%	Polymer composition[c] VEA, wt.-%	Properties of film
VI-1	90	10	91	3.24	72.58	11.90	94	6	Clear, rubbery, sticky
VI-2	75	25	60	3.61	73.09	12.08	90	10	"
VI-3	50	50	95	1.94	76.03	11.68	63	37	Hazy, tough
VI-4	25	75	95	0.60	80.06	11.64	26	74	Clear, brittle

[a] All of the copolymerizations were conducted for 2 hr. at −78°C. with use of $BF_3 \cdot O(C_2H_5)_2$ as catalyst and *n*-heptane as solvent.

[b] Determined on solutions of 0.120–0.275 g./100 ml. of tetrahydrofuran at 30°C.

[c] Based on the analysis assuming VEA to be the vinyl ether of tetrahydroabietol.

Copolymerization

Copolymers of Vinyl Ethers and Vinyl Chloride

VEAF–Vinyl Chloride Copolymers. Copolymers of VEAF and VCl have been prepared with the use of free-radical catalysts and data are given in Table III. The polymers were obtained as white or pale brown materials. All of these polymers were soluble in tetrahydrofuran. The infrared spectrum of the polymers have no absorption bands for unsaturation. All polymers gave brittle films.

VEA–Vinyl Chloride Copolymer. Six different VEA–VCl copolymers have been prepared. The experimental data are given in Table IV.

Copolymers of Vinyl Ethers and Isobutyl Vinyl Ether

VEAF–Isobutyl Vinyl Ether Copolymers. Copolymers of VEAF and isobutyl vinyl ether have been prepared with different compositions in order to see if some useful copolymers could be prepared. The experimental data are given in Table V.

The copolymers were obtained as white rubbery materials and white powders depending on the charged composition. All of the polymers were soluble in tetrahydrofuran and *n*-heptane. At about 140°C. the copolymers could be molded into films which had the properties given in Tables V and VI.

It is surprising that the copolymerization of isobutyl vinyl ether with VEAF (25% or less) led to the formation of copolymers having higher viscosity than with either homopolymer. The conversion appeared to be the lowest in the copolymerization of VEAF–IBVE at the 1:1 molar ratio.

The copolymer containing 9% of VEAF could be cured by peroxide, to give an insoluble polymer in the same manner as the homopolymer.

The copolymers containing up to 20% of vinyl ether of the rosin alcohols may find applications in the elastomer, adhesives and coatings field. The copolymers containing 30–50 of VEAF may be useful in the plastic field.

VEA–Isobutyl Vinyl Ether Copolymers. Four different VEA copolymers have been prepared. The experimental data are given in Table VI.

The copolymers were obtained as white rubbery materials and white powders depending on the charged composition. The copolymers were soluble in tetrahydrofuran and could be molded into films at about 140°C. which showed the properties given in Table VI.

VEA–IBVE (10/90) copolymer could be cured at the same curing composition as used on the VEAF–IBVE (9/91) copolymer.

EXPERIMENTAL

Homopolymerization of VEAF and VEA

Free-Radical Polymerization in Emulsion. VEAF (4.0 g.), AIBN (0.2 g.), Siponate DS-10 (0.04 g.), and air-free distilled water (12 ml.) were charged in a pressure tube, cooled to Dry Ice–acetone temperature, and then evacuated under 0.1 mm. pressure and filled with nitrogen three times. The mixture was emulsified at room temperature and polymerized at 60 ± 2°C. for 48 hr. A good emulsion was formed. This was poured into 200 ml. of methanol and 100 ml. of acetone. The isolated material was dissolved in 20 ml. of THF and poured into 200 ml. of methanol. The mixture was allowed to stand for 3 days before filtering. The yield was 0.66 g. (16.5%) of vacuum oven-dried (50°C./24 hr.) white powder. The procedure for the other free radical polymerizations in emulsion was similar to the one described.

Free-Radical Polymerization in Bulk. VEAF (2.0 g.) and DEABIB (0.1 g.) were charged in a glass ampule (1 × 5 in.), cooled to Dry Ice–acetone temperature, evacuated under 0.1 mm. and flushed with nitrogen three times before sealing. Then the mixture was polymerized at 60 ± 2°C. for 72 hr. The transparent sticky gel which formed was dissolved in 20 ml. of THF and poured into 200 ml. of methanol. The yield was 0.68 g. (34.0%) of vacuum oven-dried (50°C./24 hr.) white powder. The procedure for the other free-radical polymerization in bulk was similar to the one described.

Cationic Polymerization Initiated by Boron Trifluoride Etherate. A 50-ml., three-necked flask was fitted with nitrogen inlet and outlet tubes and a rubber serum-bottle cap and dried under 0.04 mm. for about 2 hr. VEA (5.0 g.) was charged into the flask and dried under 0.04 mm. for $^1/_2$ hr. *n*-Heptane (20 ml.) was charged through the serum cap with the use of syringe under a nitrogen stream. The flask was cooled to Dry Ice–acetone temperature and boron trifluoride etherate (0.02 ml.) was added through the serum cap by use of a micro syringe under vigorous stirring with a magnetic stirrer. After 30 min., more boron trifluoride etherate (0.02 ml.) was added. After 2 hr., 5 ml. of methanol was added. The mixture was warmed to room temperature and after most of the solvent had evaporated, the residue was dissolved in 10 ml. of THF and this solution was poured into 300 ml. of methanol. The isolated material was dissolved into 30 ml. of THF and poured into 300 ml. of methanol. The mixture was allowed to stand for 2 days before filtration. The yield was 4.4 g. 88% of vacuum oven-dried (50°C./24 hr.) white powder. The procedure for the other cationic polymerization initiated by boron trifluoride etherate was similar to the one described.

Cationic Polymerization Initiated by Stannic Chloride. A 50-ml., three-necked flask was fitted with nitrogen inlet and outlet tubes, and a rubber serum-bottle cap, and dried under 0.04 mm. for about 2 hr. VEAF (5.0 g.) was charged into the flask and dried under 0.04 mm. for 0.5 hr. *n*-Heptane (20 ml.) was charged under a nitrogen stream with the use of syringe. The flask was cooled with ice water and 1 ml. of *n*-heptane solution of stannic chloride (0.052 g. of $SnCl_4$/1 ml. of *n*-heptane) was added through the serum cap by the use of a micro syringe under vigorous stirring with a magnetic stirrer. After 2 hr., 5 ml. of methanol was added to the reaction mixture. After most of the solvent was evaporated under vacuum, the residual jelly-like material was dissolved in 20 ml. of THF and poured into 200 ml. of methanol. The isolated material was dissolved in 30 ml. of THF and poured into 300 ml. of methanol. The yield was 4.88 g. (98%) of vacuum oven-dried (50°C./24 hr.) white powder. The procedure for the other stannic chloride initiated polymerization was similar to the one described above.

X-Ray Analysis of VEAF and VEA. X-ray diffraction patterns were obtained for PVEAF (II-1) and PVEA (II-5) powders. A Phillips x-ray diffractometer with a Cu target (operated by Mr. R. Eastwood) was used. The major machine settings were: 40 kv., 20 ma., with a Ni filter.

The scan of the diffracted x-rays of both polymers indicate one maximum. ($2\theta = 15.0$ for PVEAF and 15.3 for PVEA.) For $\lambda = 1.54$ A. the spacing distances are 5.91 A. for poly VEAF and 5.68 A. for poly VEA, respectively.

Copolymerization

VEAF–Vinyl Chloride and VEA–Vinyl Chloride Copolymers. Copolymerizations of VEAF–VCl and VEA–VCl were conducted in the usual emulsion system. VEAF (0.25 g.), $K_2S_2O_8$ (0.1 g.), Siponate DS-10 (0.1 g.), and air-free, distilled water (12 ml.) were charged under nitrogen in a pressure tube (1 × 7 in.), that was evacuated under 0.1 mm. Hg and flushed with nitrogen three times at Dry Ice–acetone temperature. Then VCl was charged in excess and was allowed to boil down to 4.75 g. After capping the tube, the contents were emulsified at room temperature and then polymerized at 60 ± 2°C. by tumbling end-over-end for 48 hr. The reaction mixture was poured into the methanol and allowed to settle overnight. A small amount of aqueous sodium chloride solution was also added to settle the emulsion. The isolated polymer was dissolved in 50 ml. of THF and reprecipitated in 250 ml. of methanol. The mixture was allowed to stand for two days before filtering. The polymer was isolated, washed with methanol sufficiently, then dried in a vacuum oven at 50°C. for 2 days. The yield was 3.57 g. (71.4%) of white material. The infrared spectrum showed no characteristic absorption bands for the monomer. The polymerization procedure for the other polymers given in Tables III and IV was similar to the one described.

VEAF–Isobutyl Vinyl Ether and VEA–Isobutyl Vinyl Ether Copolymers. VEAF (20.0 g.) was diluted with *n*-heptane to 100 ml. in a volumetric flask and dried over sodium. The VEAF solution thus prepared (2.0 ml., 0.4 g. of VEAF) isobutyl vinyl ether freshly distilled over sodium (3.6 g.) and *n*-heptane dried over sodium were charged into a 100 ml., three-necked flask equipped with nitrogen inlet and outlet tubes and a rubber serum cap in dry box. The flask was sealed off and removed from the dry box. After the flask was cooled to Dry Ice–acetone temperature under a nitrogen stream, boron trifluoride etherate (3 drops) was added through the rubber serum cap with the use of a microsyringe under vigorous stirring. After 30 min., boron trifluoride etherate (three drops) was added again. The polymerization was conducted for a total of 2 hr. and then 10 ml. of methanol was added to stop the reaction. The mixture was warmed to room temperature and most of the solvent was evaporated under reduced pressure. Then, the mixture was dissolved in 50 ml. of tetrahydrofuran and poured into 300 ml. of methanol. The isolated material was dissolved in 50 ml. of tetrahydrofuran and poured into 100 ml./200 ml. of acetone/methanol solution. The yield was 3.8 g. (95%) of vacuum oven-dried (50°C./24 hr.) white rubbery material. The procedure for the other composition was similar to the one described above.

The procedure for the copolymerizations of VEA and isobutyl vinyl ether was similar to the one described for VEAF and isobutyl vinyl ether.

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Determination of Elementary Rate Constants of Styrene Polymerization Catalyzed by Rhenium Pentachloride

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Synopsis

Rate constants of the propagation and transfer processes for the cationic polymerization of styrene catalyzed by rhenium pentachloride were obtained by kinetic analysis. Also, dependence of the propagation constant on the dielectric constant of the system was examined. Comparison of these data with those of the other systems with different catalysts suggests that the present catalyst is a strong Lewis acid and the size of the counterion is very large.

Introduction

In the previous report on the cationic polymerization of styrene catalyzed by $ReCl_5$, the ratio of transfer to propagation rate constant was determined by kinetic measurements.[1] In the present study, from the more detailed analysis of kinetic measurements, determination of the elementary rate constants was performed.

For the determination of rate constants of the cationic polymerization of styrene, reports by Pepper et al.[2,3] using H_2SO_4 and $HClO_4$, by Higashimura et al.[4-6] using I_2 and $SnCl_4$, and by Plesch et al.[7,8] using $TiCl_4$ have been published. However, no data are available for the polymerization by $ReCl_5$. Therefore, it is of interest to determine the rate constants in the latter case and to clarify the polymerization mechanism.

Experimental

Although most of the data used for the determination of the rate constants were taken from the previous study,[1] a few measurements of $[\eta]$ of the polymer obtained under various conditions as shown in Tables I and II were added. The experimental procedure was the same as in the previous report.

Results

From Table II, it is obvious that $[\eta]$ becomes constant in the stationary state. Therefore, degrees of polymerization referred to in the discussion are those calculated from constant values of $[\eta]$ in the stationary state.

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TABLE I[a]

Catalyst concn. $[C_0]$, mmole/l.	Temp., °C.	Monomer concn. $[M]_0$, mole/l.	$[\eta]$
1.15	10	3.24	0.216
0.145	20	1.57	0.182
0.145	20	2.16	0.188
0.145	20	2.67	0.187

[a] Reaction conditions: initial ethylene dichloride $[E]_0$ = 4.23 mole/l.; initial ethyl monochloroacetate $[ECA]_0$ = 0.79 mole/l.; initial benzene $[S]_0$ = 3.76 mole/l.

TABLE II[a]

Polymerization time, min.	$[\eta]$
30	—
60	0.192
90	0.206
120	0.214
150	0.216
180	0.214
240	0.216

[a] Reaction conditions: polymerization temperature, 10°C.; $[M]_0$ = 2.16 mole/l.; $[C]_0$ = 1.15 mmole/l.; $[E]_0$ = 4.23 mole/l.; $[S]_0$ = 3.76 mole/l.; $[ECA]_0$ = 0.795 mole/l.

The polymerization mechanism proposed in the previous report,[1] though modified to some extent, is adopted here.

Complex formation:

$$M + C \overset{K}{\rightleftharpoons} X \tag{1}$$

Initiation:

$$M + X \xrightarrow{k_i} M^+ + Y^- \tag{2}$$

Propagation:

$$\begin{aligned} M^+ + M &\xrightarrow{k_p} M_2^+ \\ M_{n-1}^+ + M &\xrightarrow{k_p} M_n^+ \end{aligned} \tag{3}$$

Transfer:

$$M_n^+ + M \xrightarrow{k_{trm}} P + M^+ \tag{4}$$

Termination:

$$M_n^+ \xrightarrow{k_t} P + \ldots \tag{5}$$

$$M_n^+ + S \xrightarrow{k_{ts}} P + \ldots \tag{6}$$

$$M_n^+ + S' \xrightarrow{k_{ts}'} P + \ldots \tag{7}$$

Here, M is monomer, C catalyst, X complex between C and M, M_n^+ growing cation, P polymer, S benzene, Y^- counterion, and S′ ethyl monochloroacetate which was used to dissolve the catalyst.

As described in the previous report,[1] the processes (1) and (2) had to be assumed in order to explain the dependence of stationary rate R_s and induction time τ on the concentrations of catalyst and monomer. Instead of eqs. (1) and (2), one-step initiation, $2M + C \rightarrow M^+ + Y^-$, can also explain kinetic results, but it may be more reasonable to consider formation of a π complex between $ReCl_5$ and styrene initially as in the case of $SnCl_4$ and styrene.[1,9] Further details of processes (1) and (2) will not be discussed here, because enough data to clarify the mechanism are not available. For the growing cation, a cation not containing $ReCl_5$ was assumed in the present report instead of that containing $ReCl_5$ of the previous report,[1] because the ultraviolet absorption of the growing cation agreed well with that of $\phi C^+H(Me)$ observed and predicted theoretically by Hanazaki and Nagakura;[10] the counterion Y^- is considered to be a large anion, perhaps containing Re, as will be discussed below. For the same reason, the possibility that the cation aries by dissociation to $[ReCl_4]^+[ReCl_6]^-$ may be rejected. Also, the possibility of formation of the cation from a small amount of a cocatalyst such as water is low because monomer and solvent were carefully purified and dried over sodium.

In the previous report, reactions (6) and (7) described above were considered as the transfer reactions. However, in the stationary-state treatment, it was implicitly assumed that species produced by these reactions do not participate in the propagation process, and a good agreement between calculated and experimental rate expressions was obtained. Therefore, it is more reasonable to define them as termination reactions.

Irrespective of the above described modification, the kinetic treatment of the previous report[1] was applicable with minor changes of definition of rate constants.

In the nonstationary state, where $e^{-k_T t} \ll 1$, the following relation was obtained:[1]

$$\ln [M]_0/[M] = (k_i k_p/k_T)[M]_0[X]_0[t - (1/k_T)] \tag{8}$$

Here

$$k_T = k_t + k_{ts}[S] + k_{ts'}[S'] \tag{9}$$

Also, by using the relation,

$$([X]_0/[M]_0[C]_0) = K \tag{10}$$

eq. (11) is obtained:

$$\ln [M]_0/[M] = (Kk_i k_p/k_T)[M]_0^2[C]_0(t - 1/k_T) \tag{11}$$

Therefore, a linear relationship between ln $[M]_0/[M]$ and t is expected. The experimental result shown in Figure 1 satisfies this relationship, where deviation at $t = 30$ min. may be due to the inapplicability of the assumption $e^{-k_T t} \ll 1$. From the intercept and the slope of the straight line in this figure, k_T can be determined.

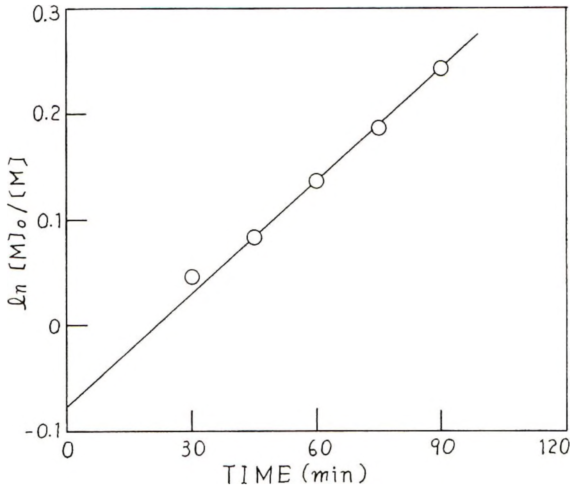

Fig. 1. Change in ln $[M]_0/[M]$ with time; $[M]_0 = 5.23$ mole/l.; $[C]_0 = 0.550$ mmole/l. $[S]_0 = 3.38$ mole/l.; $[S']_0 = 0.946$ mole/l.

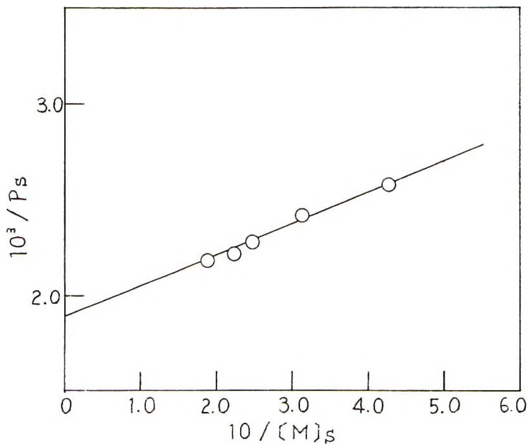

Fig. 2. Change in $1/P_S$ with $1/[M]_S$ at 10°C.; $[ECA]_0 = 0.946$ mole/l.; $[C]_0 = 0.550$ mmole/l.

As discussed in the previous report,[1] the relation expected between the degree of polymerization P_S and the stationary-state concentration of monomer $[M]_S$ is

$$1/P_S = k_T/(k_p[M]_S) + (k_{trm}/k_p) \tag{12}$$

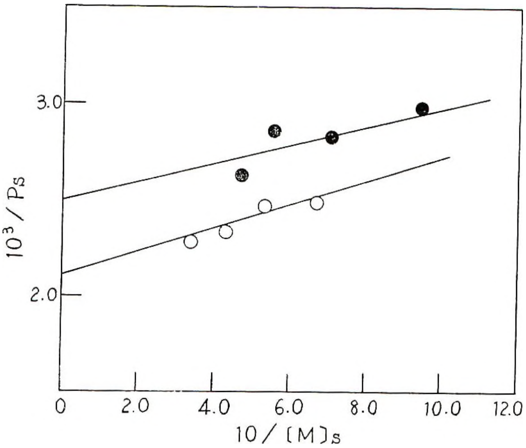

Fig. 3. Change in $1/P_S$ with $1/[M]_S$ in the ethylene dichloride–benzene system $[E]_0 = 4.23$ mole/l.; $[ECA]_0 = 0.793$ mole/l.: (○) at 10°C., $[C]_0 = 1.11$ mmole/l.; (●) at 20°C., $[C]_0 = 0.145$ mmole/l.

The experimental result shown in Figure 2 satisfies this relationship. Since P_S, $[M]_S$, and k_T are known, k_p and k_{trm} can be determined from Figure 2. Also, the stationary-state polymerization rate R_S is given by eq. (13):

$$R_S = (Kk_ik_p/k_T)[C]_S[M]_S^3 \tag{13}$$

Therefore, by substituting k_p and k_T obtained above into Kk_ik_p/k_T which is obtained from eq. (13), Kk_i, can be determined.

Rate constants obtained in this way and frequency factor A, activation energy E, and activation entropy $\Delta S\ddagger$ obtained from the temperature dependence are shown in Tables III and IV, respectively. Here, k_t is considered to be substantially zero, since the calculated value is very small or negative. Also, $\Delta S\ddagger$ was calculated by using the equation:

$$A = e(kT/h)\, e^{\Delta S\ddagger/R} \tag{14}$$

TABLE III

Temp., °C.	$Kk_i \times 10^1$, l.^{2}/mole^2-min.	k_p, l./mole-min.	$k_{trm} \times 10^2$, l./mole-min.
0	1.04	14.6	3.11
10	3.81	34.8	6.96
20	6.93	95.4	23.6

TABLE IV[a]

	Kk_i	k_p	k_{trm}
E, kcal./mole	16.9	11.8	16.9
A	3.29×10^{10}	4.53×10^{10}	870×10^{11}
$\Delta S\ddagger$, e.u.	—	−11.62	−4.97

[a] Reaction conditions: temperature, 10°C.; $[M]_0 = 2.61$ mole/l.; $[S]_0 = 6.75$ mole/l.

TABLE V[a]

$[C]_0$, mmole/l.	k_p, l./mole-min.
0.275	30.1
0.555	34.8
1.100	33.6

[a] Reaction conditions: temperature, 10°C.; $[M]_0$ = 2.61 mole/l.; $[S]_0$ = 6.75 mole/l.

TABLE VI[a]

$[M]_0$, mole/l.	$[S]_0$, mole/l.	k_p, l./mole-min.
6.10	2.25	34.7
5.23	3.38	34.8
4.36	4.50	27.7
3.49	5.63	30.6
2.61	6.75	32.6

[a] Reaction conditions: temperature 10°C.; $[C]_0$ = 0.550 mmole/l.

TABLE VII[a]

Volume ratio benzene: ethylene dichloride	Dielectric constant ϵ	k_p, l./mole-min.
1:0	2.69	34.8
3:1	4.39	37.7
1:1	5.78	77.7
3:1	7.13	145.7

[a] Reaction conditions: temperature, 10°C.; $[C]_0$ = 1.15 mmole/l.; $[M]_0$ = 2.16 mole/l.

Values of k_p at various catalyst and monomer concentrations are shown in Tables V and VI.

Then, from the experimental results with ethylene dichloride–benzene mixtures in various ratios as solvent, values of k_p were calculated. First, k_{trm}/k_p was calculated from the intercept of Figure 3 by using the eq. (12) and k_p was obtained by substituting k_{trm} of Table I into k_{trm}/k_p. Results are shown in Table VII.

In Table VII, the dielectric constant of the system ϵ was calculated from the dielectric constants[11,12] of styrene, benzene, ethylene dichloride, and ethyl monochloroacetate by assuming additivity.

Discussion

In Table VIII, rate constants of propagation and monomer transfer for the cationic polymerization are compared with values for other systems.

Each elementary process in the polymerization will be examined. Kinetic parameters of the processes shown in eqs. (1) and (2) cannot be sepa-

TABLE VIII

Researcher	Catalyst	Solvent	Monomer concentration, mole/l.	Temp., °C.	k_p, l./mole-min.	E_p, kcal./mole	A_p	$k_{trm} \times 10^2$, l./mole-min.	A_{trm}	E_{trm}, kcal./mole
Kanoh et al.[12]	I_2	$(CH_2Cl)_2$	0.87	30	0.22	626.5	$10^{1.3}$–10^{22}	0.46	—	9.8–11.
Kanoh et al.[5,13]	$SnCl_4$	"	1.75	30	25.2	—	—	—	—	—
Longworth and Plesch[14]	$TiCl_4$	"	—	30	360	—	—	—	—	—
Hayes and Pepper[15]	$HClO_4$	"	1.75	25	222	9.6	$10^{7.6}$	2.6	$10^{4.5}$	8.3
Hayes and Pepper[2]	H_2SO_4	"	0.35	25	456	8.5	10^8	12	10^{11}	16
Pepper and Reiley[16]	$HClO_4$	$(CH_2Cl)_2$–CCl_4, (64:16)	1.74	20	81	—	—	--	—	—
"	$HClO_4$	$(CH_2Cl)_2$–CCl_4 (55:40)	0.435	20	24	13.0	—	—	—	—
This work	$ReCl_5$	C_6H_6–	2.16	20	95.4	11.4	$10^{10.6}$	23.6	$10^{11.9}$	16.9
"	$ReCl_5$	$(CH_2Cl)_2$ C_6H_6 (1:1)	2.16	20	223.6	—	—	58.6	—	—

rated at present. Therefore, the reason why the combined activation energy for these reactions is higher than that in the case of $SnCl_4$[17] is not obvious.

For the process (3), k_p is comparable to those in other cases with polar solvents in spite of the fact that a nonpolar solvent was used in our case. Since k_p increased as a polar solvent (ethylene dichloride) was added, k_p is supposed to be very high in the polar solvent. Therefore, it is considered that $ReCl_5$ is a stronger Lewis acid than $SnCl_4$. This is supported by the fact that $ReCl_5$ is an effective catalyst for the polymerization of trioxane,[18] isobutylene,[11] isobutyl vinyl ether,[19] and α-methylstyrene.[19] However, $ReCl_5$ did not initiate the polymerization of methyl methacrylate and acrylonitrile,[19] monomers which are believed not to polymerize via a cationic mechanism. The fact that the activation entropy in the present case is higher than those in other cases, as shown in Table VIII, indicates that solvation in the transition state is smaller in the present case. This small solvation may be due to the use of nonpolar solvent, and also to the large size of the counterion. The change of k_p with ϵ shown in Table VII is similar to that in the case of $HClO_4$,[15] but the extent of this change is smaller than that in the latter case. This may be due to the large size of the counterion Y^- in the present case. The fact that k_p does not depend on the monomer concentration as shown in Table VI is different from the observations of Pepper et al.,[15] but it may be explained as follows. Since a polar solvent, ethylene dichloride, is used in the latter case, the dielectric constant of the system changes markedly as the concentration of monomer, along with that of ethylene dichloride, changes, whereas, since the nonpolar solvent benzene is used in our case, this change is small and also k_p does not change appreciably. The fact that k_p does not depend on the catalyst concentration, as shown in Table V, is characteristic of the ion-pair polymerization.[20] In the previous report,[1] Cl^- was assumed to be the counterion, but the above discussion suggests that the counterion may be a large anion, perhaps one containing Re.

For the monomer transfer process [eq. (4)], k_{trm} and its frequency factor and activation energy are higher than those in other cases (Table VIII). This may be due to the fact that the nonpolar solvent benzene was used.

For the termination process, k_t was negligibly small. This agrees with the conclusion of Plesch[20] that the self-termination reaction does not occur in a nonpolar solvent. The reason why a stationary state of polymerization was achieved in our case may be that the active centers are destroyed by the termination by ethyl monochloroacetate. This effect will be described in detail in a forthcoming report.

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On the Heat of Solution of Polymer with Solvent: Polydimethylsiloxane–Solvent Systems

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Synopsis

Heats of mixing and excess volumes at infinite dilution have been obtained at 25°C. for polydimethylsiloxane or its lower oligomers in various solvents by using a twin conduction microcalorimeter and from the pycnometric specific volumes. From those values, excess energies ΔE_v^{M} at constant volume have been determined. The prediction on intramolecular conformation contributions to the heat of solution as proposed by Bianchi has been evaluated by the values of ΔE_v^{M}. The heat of solution in the polymer–solvent systems was interpreted by the expression for ΔE_v^{M} derived from the Van Laar-Hildebrand work on simple liquid mixtures with the solubility parameters of polymers obtained from indirect measurements. The values of conformational intramolecular energy change calculated from dilute solution properties were difficult to rationalize with our results. Our present results suggest that systems in a nonideal state can not be distinguished for certain from those in the ideal state. This conclusion based on apparent values does not deny the possible effect of the conformational energy change.

INTRODUCTION

Direct measurements of the heat of mixing in polymer–solvent systems have been performed by several workers.

The great majority of recent studies has dealt with the application of the Prigogine theory for polymer solutions.[1,2] Recently, other studies have been reported. An effect of the conformational energy change of a polymer on the heat of solution in polymer–solvent systems has been pointed out by Bianchi.[3] He has predicted that the heat of mixing of a polymer with a solvent is described by at least three main terms: the Hildebrand term given for simple liquid mixtures, the conformational change on mixing, and the volume change on mixing. Experiments have been made by him and his co-workers on the excess volumes in polyisobutylene(PIB)–solvent systems[4] and on the heat of solution in certain polymer–Θ-solvent systems.[5] They have actually proved that the heat of solution at constant volume, in the absence of strong interaction, is positive, and that the heat of solution of amorphous polymers with Θ-solvents roughly conforms to the Scatchard-Hildebrand expectation for simple liquid mixtures. However, the presence of the exothermic conformational energy change has not been confirmed yet in practice.

The present work was undertaken to examine the above prediction. The heats of solution of polydimethylsiloxane (PDS) with various solvents were determined and examined.

EXPERIMENTAL

Materials

PDS was a commercial silicone (KF 96, 500 cs., Shinetsu Chemicals Co., Japan), fractionally precipitated with a benzene–methanol system. After repeated washings with water, the polymer was dried under vacuum at 110°C. The number-average molecular weights $\bar{M}_n$ was determined by using a Mechrolab vapor-pressure osmometer Model 301A to be 1.30×10^4.

The lower oligomers of PDS, hexamethyldisiloxane (HMDS), octamethyltrisiloxane (OMTS), and decamethyltetrasiloxane (DMTS), were obtained by fractional distillation. Commercial Silicone KF 96 fluids with viscosities of 0.65, 1.0, and 1.5 cs. were distilled, and the fractions boiling at 99.5, 152, and 192°C., respectively, were used as samples.

The solvents were commercial products of the highest quality, fractionally distilled before use.

Heat of Mixing Measurements

Direct determination of the heat of mixing ΔH_p^{M} at infinite dilution was performed by using a twin conduction microcalorimeter of Tian-Calvet type equipped with thermomodules instead of thermocouples for the detection of the temperature difference between two mixing cells. Here the thermomodules were also given the role of a thermal conductor. ΔH_p^{M} values at infinite dilution were obtained at 25°C. in final concentration of 0.1–0.2%, 0.2–0.4 g. of polymer or the lower oligomer samples being used.

Apparatus and Procedure

The mixing vessel used in this experiment is shown in Figure 1. A is a standard bed of constant temperature made of forged aluminum; B is a thermoelement composed of 16 coupled thermomodules which detects the temperature difference between the mixing cell and the standard bed although allowing thermal conduction. The thermal electromotive force is 5.7 mv./°C. C is a mixing cell made of nickel-plated copper. A Teflon stirring shaft (D) supplies electricity to generate standard heats through carbon brushes at terminals (F). Manganin wire of 1 kΩ is dipped in liquid-Teflon held in a nickel-plated copper cap attached at the end of the stirring shaft. The Teflon bar (E) has a breaking up part made of nickel-plated copper. Mixing is carried out by breaking an ampule of the liquid sample if it is of low viscosity, or by pulling up the sample dipped in mercury if the sample is of high viscosity or is a cast material. The ampule is put on a small glass dish arranged on a rack (J) made of Teflon, and nickel-plated copper or cast matter is dipped in mercury in a glass tube also

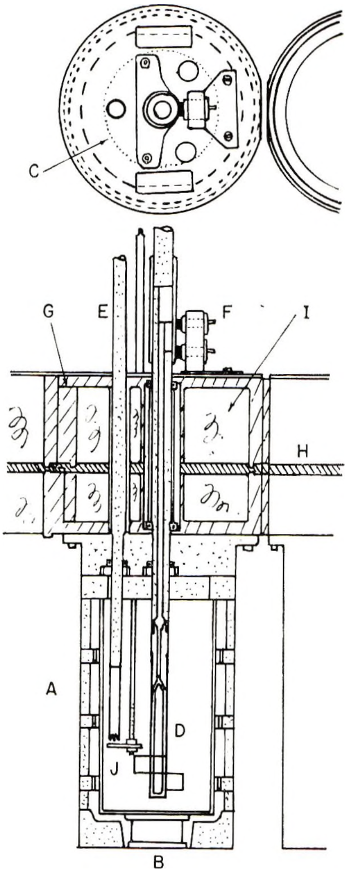

Fig. 1. The mixing cell for calorimetric measurements.

arranged on it. In this experiment, the former mixing procedure was used for all samples. In the other mixing cell the same operation is performed at the same time, but an ampule of solvent is used instead of solutes. Two more bars of this sort are inserted in the cell for other purposes. All these bars and shaft are sealed with Teflon O-rings. The Bakelite cover (G) of the mixing vessel is filled with rock wool (I). The standard bed is wrapped with rock wool and the around six sides of the circumference are arranged temperature control plates (H) of copper, which are fitted with heaters in series and parallel; and the temperature is controlled within 0.01°C. by using a desk-type thermistor detector. Control plates are also packed with rock wool outside for adiabatic purpose. The temperature difference is amplified and recorded continuously. With the aid of the amplifier a change of $\pm 5 \times 10^{-6}$°C. can be detected.

The principle of the twin conduction calorimeter[7] is summarized in eq. (1):

$$Q = \sigma \int_{t_1}^{t_2} \Delta T dt + H[\Delta T]_{t_1}^{t_2} \tag{1}$$

where Q is generated heat, σ is thermal conductivity of thermal conductor, t is time, and ΔT is difference in temperature between mixing cell and the standard bed. Before and at the end of heat change $\Delta T = 0$, and eq. (1) becomes:

$$Q = \sigma \int_0^\infty \Delta T dt \tag{2}$$

To carry out the experiment, it is necessary to eliminate the differential term [the second term of eq. (1)] completely, and eq. (2) was accepted as fairly accurate. The calibrations were performed by electrical standard heats and also by heats of dilution of aqueous KCl solutions. Apparent values of σ and the effective total heat capacity H of sample, solvent, mixing cell, and a part of thermal conductor were about 0.4 cal./deg.-sec., and 30–40 cal./deg., respectively.

The ΔH_p^{M} values were calculated from the ratio of the integrated area in the actual mixing and those of the electrical standard heats measured five times.

For the actual procedure 180 ml. of solvent was used in every mixing cell and 0.2–0.4 g. solute was used for each measurement. The stirring bars were twin-rotated at 16 rpm for every measurement. Thin-walled glass ampules with a capillary tip were used in order to diminish the resistance to breaking and to avoid the mixture of air. Solutes were transferred into ampules by an injector. The measurements were performed from two to four within ± 2% being the standard deviation.

Excess Volume Measurements

The excess volume on mixing ΔV^{M} at infinite dilution were calculated from the pycnometric specific volumes of polymer solutions at concentrations of 0.5–5%. The measurements on solutes, solvents, and solutions were performed by using a 30 ml. pycnometer at 25°C. The specific volumes of the oligomers and the polymer obtained were as follows and were essentially identical with values in the literature:[8,9] HMDS, 1.3196_1 ml./g.; OMTS, 1.2279_0 ml./g.; DMTS, 1.1766_1 ml./g.; PDS ($\bar{M}_n = 1.30 \times 10^4$), 1.0319 ml./g.

Excess Energies at Constant Volume

The excess energies ΔE_v^{M} at constant volume were calculated according to conventional thermodynamic relations[10] from ΔH_p^{M}, ΔV^{M} at constant pressure and internal pressure P of pure solvents found in the literature,[11] because the difference in P for pure solvents and for dilute polymer solutions is negligibly small.

$$\Delta H_p^{\mathrm{M}} = \Delta E_v^{\mathrm{M}} + T(\partial P/\partial T)_v \Delta V^{\mathrm{M}} + \ldots \simeq \Delta E_v^{\mathrm{M}} + P\Delta V^{\mathrm{M}} \tag{3}$$

The treatment of data is the same as in the literature,[4] except that P values corrected against temperature change were used in our calculation.

RESULTS AND DISCUSSION

Tables I and II show the measured ΔH_p^{M} and ΔV^{M} of PDS and the lower oligomers with various solvents. The calculated ΔE_v^{M} are given in the last column of each table. The solubility parameter of solvents and the P of pure solvents are also given in Table I. In Table II, ΔE_v^{M} per base mole of PDS for the lower oligomers are shown in parentheses for comparison. We have no reported values for ΔE_v^{M} to compare with the values in this experiment and only ΔH_p^{M} for the PDS–n-heptane system can be referred to. The ΔH_p^{M} in Table I almost agrees with the value[1] (36 ± 2 cal./base mole) for the PDS ($\bar{M}_v = 1 \times 10^5$–$2 \times 10^5$)–$n$-heptane system at 24.5°C.

Interaction forces between segments of this polymer and nonpolar solvents should be mainly of the London type, because the polar character, which is observed in the oligomers,[13] of the polymer decreases due to an internal compensation effect of the main chain. At infinite dilution, eq. (4) proposed from the Scatchard-Hildebrand solubility parameter theory[10] predicts the simple relation between the molar excess energy ΔE_v^{M} at constant volume and the solubility parameters, given in eq. (5) for one mole solute at infinite dilution, assuming $\varphi \simeq 1$ and $V_m\varphi_2 \simeq V_2$,

$$\Delta E_v^{\mathrm{M}} = V_m (\delta_1 - \delta_2)^2 \varphi_1\varphi_2 \tag{4}$$

$$(\Delta E_v^{\mathrm{M}}/V_2)^{1/2} \simeq |\delta_1 - \delta_2| \tag{5}$$

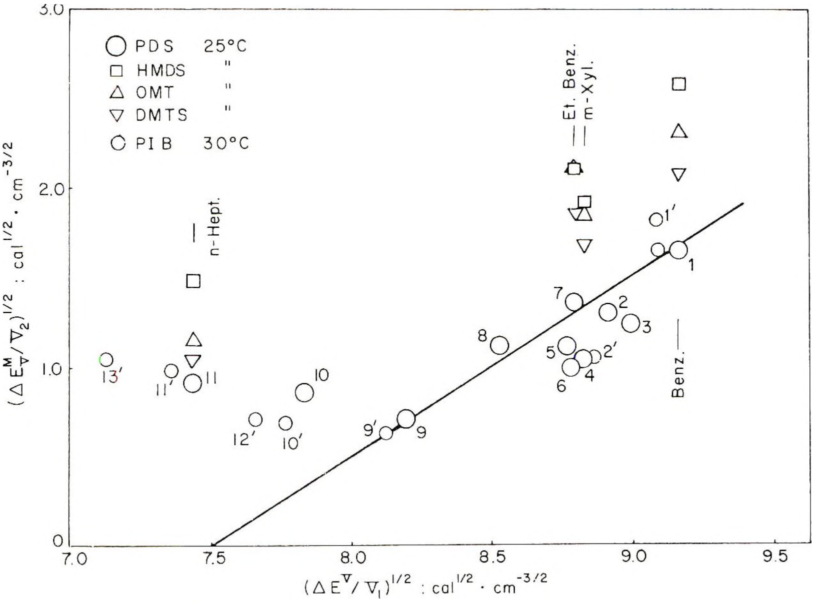

Fig. 2. Plots of $(\Delta E_v^{\mathrm{M}}/V_2)^{1/2}$ against the solubility parameter of solvents for polydimethylsiloxane, the lower oligomers, and polyisobutylene: (*1*) benzene; (*2*) toluene; (*3*) *o*-xylene; (*4*) *m*-xylene; (*5*) *p*-xylene; (*6*) mesitylene; (*7*) ethylbenzene; (*8*) isopropylbenzene; (*9*) cyclohexane; (*10*) methylcyclohexane; (*11*) *n*-heptane; (*12*) *n*-decane; (*13*) *n*-hexane.

TABLE I. Heats of Mixing and Excess Volumes at Infinite Dilution and Excess Energies Calculated from Values in Polydimethylsiloxane ($\bar{M}_n$ = 1.30 × 10^4)–Solvent Systems at 25°C.

No.	Solvent	δ_1 cal.$^{1/2}$ cm.$^{-3/2}$ [a]	P, cal. cm.$^{-3}$ [b]	ΔH_p^M cal./g.	ΔH_p^M cal./base mole	ΔV^M, cm.^{3}/base mole	ΔE_v^M, cal./base mole
1	Benzene	9.16	88.9	2.68	199	−0.07	206
2	Toluene	8.91	83.6	1.31	96.8	−0.39	129
3	*o*-Xylene	8.99	84.2	1.03	76.3	−0.48	117
4	*m*-Xylene	8.82	81.5	0.716	53.1	−0.36	82
5	*p*-Xylene	8.77	81.5	0.771	57.2	−0.46	95
6	Mesitylene	8.78	81.9	0.887	65.8	−0.10	74
7	Ethylbenzene	8.79	83.3	1.52	113	−0.34	141
8	Isopropylbenzene	8.53	82.0	0.989	73.3	−0.36	95
9	*n*-Heptane	7.43	60.1	0.423	31.4	−0.55	64.5
10	Cyclohexane	8.19	76.5	0.709	52.6	+0.18	39
11	Methylcyclohexane	7.83	69.9	0.697	51.7	−0.11	59

[a] Calculated from the literature values of latent heats of vaporization.[12]

[b] Calculated from the ratio of P to C.E.D. at 20°C.,[11] for values of C.E.D. at 25°C.

TABLE II. Heats of Mixing and Excess Volumes at Infinite Dilution and Excess Energies Calculated from Those Values in PDS Oligomers–Solvent Systems at 25°C.

		ΔH_p^M, cal./mole (cal./g.)			ΔV^M, cm.^{3}/mole			ΔE_v^M, cal./mole[a]		
No.	Solvent	HMDS	OMTS	DMTS	HMDS	OMTS	DMTS	HMDS	OMTS	DMTS
1	Benzene	1276(7.86)	1483(6.27)	1505(4.91)	−1.5	−0.7	−0.6	1406(643)	1545(485)	1559(377)
4	*m*-Xylene	534(3.29)	777(2.72)	768(2.50)	−3.1	−3.1	−3.1	785(359)	1027(322)	1018(246)
7	Ethylbenzene	631(3.99)	943(3.11)	931(3.04)	−3.7	−4.0	−4.0	941(430)	1278(401)	1263(305)
9	*n*-Heptane	220(1.35)	264(1.02)	261(0.85)	−4.2	−2.1	−2.5	474(217)	392(123)	408(99)

[a] Values in parentheses show the ΔE_v^M of PDS.

where V_m is the volume of mixture, φ is volume fraction, δ is solubility parameter, and V is molar volume, subscripts 1 and 2 referring to solvent and solute, respectively.

In Figure 2, $(\Delta E_v^{\mathrm{M}}/V_2)^{1/2}$ is plotted against δ_1. Values of ΔH_p^{M} and ΔV^{M} of PIB–solvent systems at 30°C. were obtained from the literature and ΔE_v^{M} values are calculated. They are shown in Table III and are also included in Figure 2. Both ΔH_p^{M} and ΔE_v^{M} were endothermic for our experiments. Equation (5) indicates that the ΔE_v^{M} are positive endothermic and can be represented by a straight line with extrapolated intercept δ_2 at $\Delta E_v^{\mathrm{M}} = 0$ and unit slope. In Figure 2, a straight line for $\delta_2 = 7.50$ is shown. The reported value of δ_2 for PDS is found between 7.4 and 7.5 at 25°C. from the ratio of P to C.E.D. on the basis of the value of P for PDS ($\bar{M} = 15{,}000$).[14]

The value δ_2 for PIB at 30°C. is 7.5 from the literature.[15] The behavior in Figure 2 shows a similar tendency for PDS PIB, and it is supposed that the intermolecular attractive field resides mainly in the peripheral methyl groups of the polymers. The predicted relations agree with the experimental results except for certain methylbenzene and paraffinic hydrocarbon systems. Similar deviations from the predicted relation are observed for the systems with lower oligomer and the same solvents.

TABLE III

Excess Energies Calculated from Reported Values of Heat of Mixing and of Excess Volume at Infinite Dilution in Polyisobutylene–Solvent Systems at 30°C.

Solvent	ΔH_p^{M}, cal./base mole	ΔV^{M}, cm.^{3}/base mole (30°C.)[a]	P, cal./cm.^{3} (30°C.)[b]	ΔE_v^{M}, cal./base mole
Benzene	220[c]	−0.54	87.5	173
	260[d]			213
Toluene	99.3[c]	−0.32	82.5	73
Methyl cyclohexane	−15.7[d]	−0.68	68.8	31
Cyclohexane	−9.6[d]	−0.46	75.2	25
n-Decane	−7.3[d]	−0.60	65.2	32
n-Heptane	−24[d]	−1.43	59.1	61
n-Hexane	−34[d]	−1.80	54.9	65

[a] Data of Cuniberti and Bianchi.[4]

[b] Calculated from the ratio of P to C.E.D. at 20°C. by using the values of C.E.D. at 30°C.[11]

[c] Data of Cuniberti and Bianchi ($\bar{M}_n = 4.5 \times 10^3$, at 30°C.)[4]

[d] Data of Delmas et al. ($\bar{M}_v = 3 \times 10^4$, at 24.5°C.)[1]

In order to determine the difference of interaction in (a) polymer–solvent systems and (b) oligomer–solvent systems, the ratio of the contact energy of (a) to that of (b), w_{12}/w_{12}', was calculated on the basis of lattice theory. Equation (8) is obtained from eq. (6) for PDS and eq. (7) for the oligomers by a simple additivity assumption.[10, 16]

$$\Delta E_v{}^{M}/V_2 = \frac{Nzw_{11}}{2V_1} + \frac{Nzw_{22}}{2V_2} - \frac{Nzw_{12}}{V_1} \tag{6}$$

$$\Delta E_v{}^{M\prime}/V_2{}' = \frac{Nzw_{11}}{2V_1} + \frac{Nzw_2{}'{}_2{}'}{2V_2{}'} - \frac{Nzw_{12}{}'}{V_1} \tag{7}$$

$$\Delta E_v{}^{M\prime}/V_2{}' - \frac{Nzw_{11}}{2V_1} = \frac{Nzw_2{}'{}_2{}'}{2V_2{}'} - \frac{W_{12}{}'}{w_{12}} \cdot \frac{Nzw_{12}}{V_1} \tag{8}$$

Here N denotes Avogadro's number, z denotes co-ordination number, and the prime shows corresponding values for oligomer.

The relations of $(\Delta E_v{}^{M}/V_2)_{\text{oligomer}}$–C.E.D. (solvent) versus $Nzw_{12}/2V_1$ for PSD–solvent systems are shown in Figure 3. We can deduce C.E.D. of oligomers from the linearly extrapolated intercept at $Nzw_{12}/2V_1 = 0$. Using the value of δ_2(PDS) = 7.50, we have 6.4 for HMDS, 6.4 for OMTS, and 6.6 for DMTS as the δ_2 of the oligomers. This value of HMDS agrees with the value 6.4 presumed from reported values of the latent heat of vaporization in the temperature range 59–101 °C.[17] In spite of polar interactions, the observed δ_2 values of oligomer are lower than that of PDS. This may be attributed to the methyl endgroups of the oligomer which prevent close packing of the molecules, thus reducing molecular cohesion. From the slopes of the straight lines in Figure 3, $w_{12}{}'/w_{12}$ were obtained directly. The ratios of the contact energies, $w_{12}/w_{12}{}'$, for each solvent

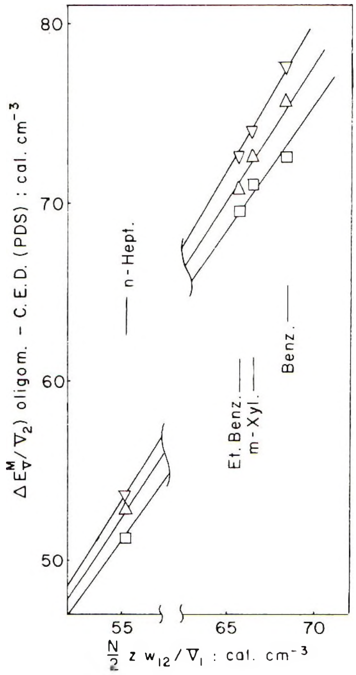

Fig. 3. Plots of $(\Delta E_V^M/V_2)$ oligomer – C.E.D. (PDS) against $Nzw_{12}/2V_1$ for the oligomers of polydimethylsiloxane.

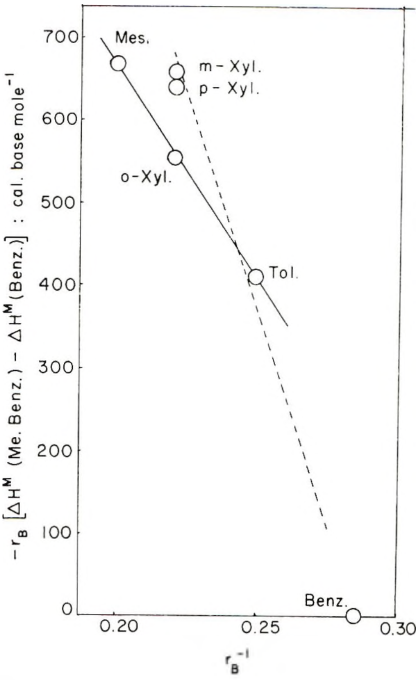

Fig. 4. Relations of the differences in heat of mixing for the polydimethylsiloxane–methylbenzenes and the polydimethylsiloxane–benzene with the number of segments r_B.

systems were calculated from eqs. (6) and (7) adopting the C.E.D. of oligomers. Nearly invariable values were obtained for an oligomer, irrespective of the solvents, as shown in Table IV. From this result, it seems reasonable to assume that deviations in certain solvent systems are not peculiar to polymer systems. Usually, these values have been reported as $\lesssim 1$.[18] In this experiment, values above unity would indicate that the intermolecular interactions for PDS with solvents are different than those for the polar oligomers.

The deviations observed in Figure 1 suggest other interpretations. For the PDS–methylbenzene systems, for example, the heat of solution de-

TABLE IV
Comparison of Contact Energies between Polydimethylsiloxane and the Oligomers with Same Solvents

		w_{12}/w_{12}'		
Solvent		HMDS	OMTS	DMTS
Benzene		1.21	1.17	1.13
m-Xylene		1.18	1.17	1.13
Ethylbenzene		1.19	1.17	1.14
n-Heptane		1.20	1.17	1.14
	Avg.	1.20	1.17	1.14

creases with increasing basic donor strength of the solvent molecule. Further, ΔH_p^{M} in these systems have a characteristic feature as shown in Figure 4. Between the difference in ΔH_p^{M} and the number of segments of solvent r_B, we find regularity similar to that found in PIB–ether or ester systems which have been studied.[2] This relation, found from the application of the Prigogine theory to ΔH_p^{M} [eq. (12) in ref. 2], may warrant the following suggestion. The interaction energies between PDS segment and a methyl group in *o*-xylene or mesitylene (1,3,5-trimethylbenzene) solvent are smaller than the energies with *m*- or *p*-xylene solvent. Comparable divergences from regular solution treatment have been noted[19] in system which contain only paraffinic hydrocarbons with nothing but bonding electrons. The deviations in this experiment, however, must be further investigated.

According to Bianchi's method, we have calculated the conformational intramolecular energy changes ΔE_{conf} from dilute solution properties for PDS,[20] which are shown in Table V.

$$\Delta E_{\mathrm{conf}} = -\epsilon\frac{2\exp\{-\epsilon/RT\}(2+\exp\{-\epsilon/RT\})}{[1+2\exp\{-\epsilon/RT\}]^2}(\alpha-1) \qquad (9)$$

where ϵ is the energy difference, given by $\epsilon_{gauche}-\epsilon_{trans}$; and α is the expansion factor.

TABLE V
Conformational Energy Changes on Mixing for Polydimethylsiloxane–Solvent Systems at 25°C.

Solvent	Θ, °K.[a]	α[a]	ΔE_{conf}, cal./base mole
Benzene	267	1.16	−69
Toluene	240	1.18	−78
Xylene	225	1.19	−82
Cyclohexane	205	1.28	−121
Methyl cyclohexane	160	1.30	−129
n-Heptane	100	1.35	−151

[a] Values reported by Kuwahara and Kaneko.[20]

The ϵ value for PDS is found to be about 1000 cal./mole from the value of $\epsilon\delta-\epsilon\sigma$.[21] For PIB, it is calculated from the data[22] of $[\eta]_\Theta$ as 960 cal./mole. The values of $\Delta E_{\mathrm{conf}}/(\alpha-1)$ at 25°C. calculated on the basis of the ϵ values are −430 cal./base mole for PDS and −480 cal./base mole for PIB. Such large values raise new difficulties in interpreting the experimental results. In addition, the exothermic effect due to cooperated orientation of certain solvent molecules, the endothermic effect due to disentanglement of polymers, and the like may contribute to the heat of solution on polymer systems. An experiment[5] has been carried out on the heat of mixing of amorphous polymers in Θ solvents in which the conformational energy change is expected to be absent owing to the compensation of volume exclusion. Our present results suggest that systems in a nonideal state can not be distinguished for certain from those in the ideal state.

In view of the above facts, the Scatchard-Hildebrand theory satisfactorily explains the relations. The most reasonable conclusion to be drawn from the available data is that the heat of solution in polymer–solvent systems may be interpreted by the theory of simple liquid mixtures of low molecular weights, apparently, with the δ_2 of polymers obtained from indirect measurements. For polymers, direct determination of C.E.D. is impossible, and the relationship between C.E.D. and δ has yet not been established. Therefore, our conclusion based on apparent values does not deny the possible effect of the intramolecular conformational energy change. It is thought that reasonable evaluation of contributions of intramolecular conformation change to the heat of solution will be difficult without a better grasp of the intermolecular energy of polymer–solvent pair contacts. Possibly an improved expression for this latter energy proposed in a recent study[23] might be used.

The large difference between mixing parameter κ_0 and infinite dilution parameter κ_1 has been pointed out.[24,25] In the present experiments on PDS–solvent systems, the differences between the heat of solution at infinite dilution and the heat of dilution obtained from dilute solution properties were as follows: benzene, 80 cal./mole; toluene, 55 cal./mole; *m*-xylene, 22 cal./mole; and *n*-heptane, 31 cal./base mole. These values are similar to those for PIB–solvent systems.

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Determination of Concentration of Propagating Species in Cationic Polymerization of Tetrahydrofuran

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Synopsis

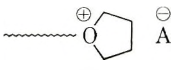
A spectroscopic method is described for the determination of the concentration of propagating species, [P*], in the polymerization of tetrahydrofuran catalyzed by a mixture of $AlEt_3$–H_2O (1:0.5) and epichlorohydrin. A phenyl ether group was introduced at the polymer chain end by the quantitative reaction of the propagating species with excess sodium phenoxide. From the amount of phenyl ether groups in the polymer and of the remaining sodium phenoxide, [P*] was determined by means of ultraviolet spectroscopy. The [P*] value so determined was found to be in good agreement with that calculated from the amount and molecular weight of polymer based on a stepwise addition mechanism without chain transfer or termination. The present method of [P*] determination was employed to examine the course of polymerization. It has now been found that [P*] increases progressively during an induction period and remains unchanged in the subsequent period of polymerization.

INTRODUCTION

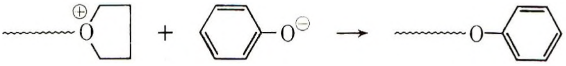
In our recent studies it was shown that the cationic polymerization of tetrahydrofuran (THF) by the ternary catalyst system $AlEt_3$–H_2O (1:0.5) and epichlorohydrin (ECH) proceeds through a mechanism of stepwise addition, in which propagating species are formed in an induction period and continue to grow without being interrupted by chain transfer or termination.[1] The concentration of propagating species, [P*], was determined from the amount and molecular weight of the product polymer according to

$$[P^*] = [(\text{polymer, g.})/(\text{mol. wt.})] \times [1/(\text{Vol. react. syst.})] \qquad (1)$$

The present studies deal with the direct determination of the concentration of propagating species in the THF polymerization by the above-mentioned ternary catalyst. In anionic living polymerization of vinyl monomer the measurement of the concentration of propagating species was once accomplished successfully by an ultraviolet (UV) technique.[2] In the field of cationic polymerization, however, no such attempt has been made. In the cationic polymerization of THF the cyclic trialkyloxonium ion, which is assigned to the propagating species, shows no absorption of suffi-



cient intensity in the near-UV region. Hence, phenyl ether group was introduced into the polymer chain by quantitative reaction of the propagating species with sodium phenoxide, i.e.:


(2)

The amount of the phenyl ether group introduced was determined by its UV absorption (secondary band).

The results obtained here were confirmatory of the results of the previous kinetic studies.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF), Epichlorohydrin (ECH), Triethylaluminum ($AlEt_3$), and Methylene Dichloride. Commercial reagents were purified as described in previous papers.[1,3]

Sodium Phenoxide Solution. To a solution of purified phenol in dry THF (concentration of ca. 10^{-2} mole/l.) an excess of metallic sodium was added, and the mixture was stirred for several hours at room temperature under nitrogen atmosphere. Then sodium metal was removed by filtration through a sintered-glass funnel under nitrogen atmosphere. The UV spectrum of this solution showed no absorption due to free phenol.

$AlEt_3$–H_2O (1:0.5) System. This system was prepared as described in a previous paper.[1]

Triethyloxonium Tetrafluoroborate. This system, $(C_2H_5)_3\overset{\oplus}{O}\overset{\ominus}{BF_4}$, was prepared according to the method of Meerwein et al.[4] and was further purified by reprecipitation from its methylene dichloride solution with ether and dried *in vacuo* at room temperature. The salt was used immediately after its preparation.

Polymerization Procedure

Polymerization was carried out under nitrogen atmosphere. At 0°C. ECH was added to a catalyst solution in THF monomer, to start the polymerization. At a desired time of reaction excess sodium phenoxide in THF was added, to stop the polymerization. The short-stopping mixture was stirred for 1 hr. at room temperature and then treated with a large excess of 1*N* aqueous sodium hydroxide solution. The decomposition mixture was extracted with methylene dichloride. A separate reference run showed that the THF polymer was transferred almost quantitatively into methylene dichloride phase. The extract was dried over anhydrous potassium carbonate, centrifuged, and subjected to UV measurement.

UV Measurements

The clear methylene dichloride solution, after it had been diluted to a specified volume, was subjected to UV measurement, and the phenyl ether group in polymer was analyzed. Absence of sodium phenoxide in the methylene dichloride extract was shown by the UV spectrum.

The aqueous phase of the extraction process was freed from monomer and solvent by evaporation under reduced pressure (20–30 mm. Hg), diluted with 1*N* aqueous sodium hydroxide solution to a specified volume, and then subjected to UV spectroscopic analysis for the remaining sodium phenoxide.

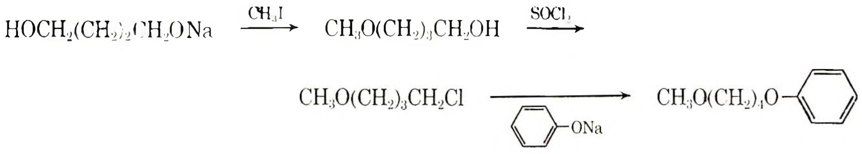
UV spectra were taken at room temperature with a Shimazu SV-50 spectrophotometer (Shimazu Seisakusho, Japan).

Molecular Weight Determination

Osmotic molecular weights were determined by means of a Mechrolab Model 502 membrane osmometer. Benzene was the solvent.

Preparation of Model Compound

4-Methoxybutyl phenyl ether (I) was synthesized by the following series of reactions:



(I)

4-Methoxybutanol prepared from methyl iodide and monosodium alcoholate of tetramethylene glycol[3] was converted into 4-methoxybutyl chloride by treatment with thionyl chloride in pyridine–chloroform at 0°C. Methoxybutyl chloride was then converted into 4-methoxybutyl phenyl ether (I) by being treated with sodium phenoxide in absolute ethanol at 90°C. The product (I) was isolated and purified by distillation under reduced pressure; b.p. 111°C. at 5 mm. Hg.

ANAL. Calcd. for $C_{11}H_{16}O_2$: C, 73.30%; H, 8.95%. Found: C, 73.57%; H, 9.01%.

The structure of the product was confirmed by its infrared and NMR spectra.

RESULTS AND DISCUSSION

Extinction Coefficients

Sodium Phenoxide. The molar extinction coefficient, $\epsilon_{\max}$, of sodium phenoxide was determined from the slope of the linear relationship between the optical density at 288 mμ and the concentration of phenol in 1*N* aqueous sodium hydroxide solution; at 288 mμ it was 2.85×10^3 l./mole-cm.

Phenyl Ether Group. The extinction coefficient of phenyl ether group at the polymer end was estimated from the coefficients of two phenyl alkyl ethers, model compound (I) and phenetole. In methylene dichloride and diethyl ether the two phenyl ethers showed the same absorption spectra (secondary band) of $\lambda_{\max}$ at 272 mμ with the same extinction coefficients.

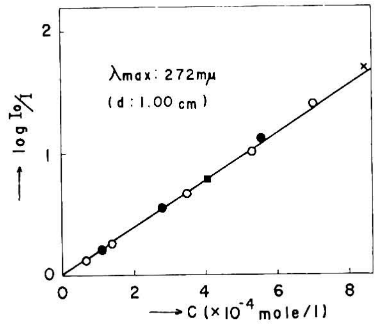
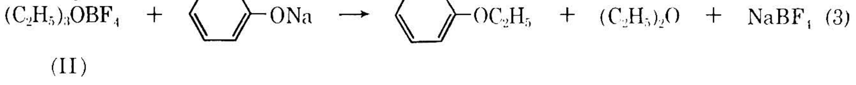


Fig. 1. Extinction coefficient of phenyl alkyl ethers: ⌬$O(CH_2)_4OCH_3$, (○) in CH_2Cl_2, (●) in Et_2O; ⌬OC_2H_5, (×) in CH_2Cl_2, (□) in Et_2O.

Figure 1 shows that ϵ_{max} of phenyl alkyl ether is not affected by the change of alkyl group. The presence of ether linkage in the alkyl group does not exert any noticeable effect on ϵ_{max} at 272 mμ. The UV spectrum of the THF polymer having phenyl ether group strongly resembled the spectra of the two phenyl alkyl ethers, (I) and phenetole. From these findings the ϵ_{max} value of (I), 1.93 × 10^3 l./mole-cm., was reasonably assigned also to the phenyl ether group of polymer.

Reaction of Sodium Phenoxide with Oxonium Salt

For the determination of [P*] by the present method the propagating species of cyclic trialkyloxonium ion should be quantitatively converted into phenyl ether by the treatment with sodium phenoxide. An almost quantitative extent of reaction between trialkyloxonium salt and sodium phenoxide was established in a model reaction with triethyloxonium tetrafluoroborate (II):



$$(C_2H_5)_3\overset{\oplus}{O}\overset{\ominus}{BF_4} + C_6H_5ONa \longrightarrow C_6H_5OC_2H_5 + (C_2H_5)_2O + NaBF_4 \quad (3)$$

(II)

TABLE I
Reaction of Sodium Phenoxide with Triethyloxonium Tetrafluoroborate at Room Temperature for 1 hr.

[⌬–ONa] × 10^{-5},[a] mole	[$(C_2H_5)_3OBF_4$] × 10^{-5},[b] mole	[⌬–OC_2H_5] × 10^{-5}, mole	Yield,[c] %	Δ[⌬–ONa][d] × 10^{-5}, mole
5.64	1.85	1.83	99	1.63
5.64	2.18	2.14	98	1.96

[a] Solution in 5 ml. of THF.
[b] Solution in 5 ml. of $(CH_2Cl)_2$.
[c] Based upon $(C_2H_5)_3OBF_4$.
[d] Amount of sodium phenoxide consumed.

The oxonium salt (II) in ethylene dichloride was allowed to react with sodium phenoxide in THF at room temperature, and the reaction mixture was treated in the same way as that for the polymerization system. The amount of phenetole produced was determined by means of UV spectroscopy. The results are shown in Table I.

As may be seen from Table I, reaction (3) is almost quantitative. Therefore we assume that the propagating species (cyclic trialkyloxonium ion) also is quantitatively converted into the corresponding phenyl ether according to eq. (2).

It was established by a separate experiment that sodium phenoxide did not react with ethylene dichloride under these conditions.

Determination of [P*] in Polymerization System

In the determination by UV spectroscopy of the propagating-species concentration in polymerization it should be valid that sodium phenoxide reacts exclusively with propagating species to form phenyl alkyl ether. In the THF polymerization with $AlEt_3$–H_2O (1:0.5) and ECH it might be possible that phenyl alkyl ether is formed by the reaction of sodium phenoxide with free ECH in the polymerization system or with the chloromethyl group of ECH unit in the polymer chain. However, the following experiments showed that ECH and other catalyst components and also the dead THF polymer did not react with sodium phenoxide under the present experimental conditions.

(*a*) When ECH was mixed with sodium phenoxide, no phenyl alkyl ether was formed, and sodium phenoxide was not consumed.

(*b*) Sodium phenoxide was not consumed in the treatment of sodium phenoxide with $AlEt_3$–H_2O (1:0.5).

(*c*) The polymerization system was first terminated by a small amount of aqueous sodium hydroxide solution and then was treated with sodium phenoxide. In this case phenyl alkyl ether was not formed, and sodium phenoxide was not consumed.

Based on the foregoing observations, the determination of [P*] in the THF polymerization by $AlEt_3$–H_2O (1:0.5) and ECH was performed. Since

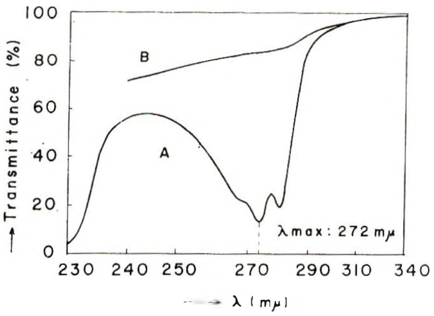


Fig. 2. Ultraviolet spectra of polytetrahydrofuran: (A) polymer having end group of phenyl ether; (B) polymer without phenyl ether group.

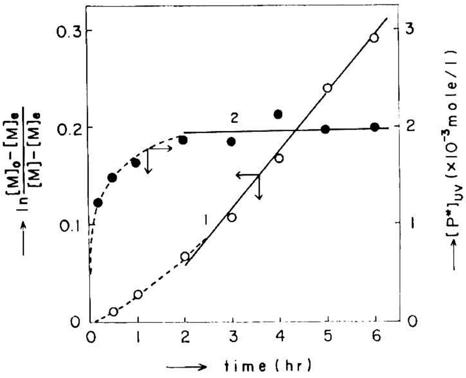


Fig. 3. Polymerization of tetrahydrofuran by $AlEt_3$–H_2O (2:1) and ECH: (1) first-order plot; (2) $[P^*]_{UV}$ time relationship.

poly-THF itself has a weak absorption, as shown in Figure 2, a correction was made in each run for the absorption due to the polymer that was prepared separately in a parallel polymerization run without treatment with sodium phenoxide.

The results in Table II and Figure 3 show the concentration of propagating species at various reaction times.

TABLE II
Polymerization of THF by $AlEt_3$–H_2O (1:0.5) and ECH: Concentration of Propagating Species[a]

Polymn. time, hr.	Polymer yield, %	$[P^*] \times 10^{-3}$, mole/l. From [PhOR][b]	$[P^*] \times 10^{-3}$, mole/l. From Δ[PhONa][c]	$[P^*]_{0s} \times 10^{-3}$ mole/l. from $\bar{M}_n$	Mol. wt.[d] $\bar{M}_n \times 10^4$
First stage					
10 min.	—	1.23	—	—	—
0.5	1.0	1.48	1.40	—	—
1	2.5	1.63	1.52	—	—
Second stage					
2	5.6	1.87	1.80	—	—
3	8.7	1.84	1.60	—	—
4	13.2	2.15	2.02	2.39	4.69
5	18.3	1.96	2.03	2.15	7.85
6	21.7	1.98	2.03	2.04	10.4

[a] Polymerization conditions: THF, 0.125 mole ($[M]_0$ = 12.6 mole/l.); $AlEt_3$, 1.78 × 10^{-3} mole ($[AlEt_3]_0$ = 0.178 mole/l.); ECH, 2.02 × 10^{-4} mole ($[ECH]_0$ = 0.020 mole/l.); bulk polymerization at 0°C.

[b] Amount of phenyl ether group of polymer, i.e. concentration of propagating species.

[c] Amount of sodium phenoxide consumed.

[d] Number-average molecular weight determined by osmometry.

There is a remarkable agreement between the [P*] values from phenyl ether group and from the consumption of sodium phenoxide. Furthermore, the concentration of propagating species from phenyl ether group, $[P^*]_{UV}$, is in good agreement with $[P^*]_{0s}$, which is the concentration of propagating species calculated according to eq. (1) with the number-average molecular weight determined by osmometry.

Figure 3 demonstrates that $[P^*]_{UV}$ increases gradually in the first stage of reaction (per cent conversion is within 5%) and then remains unchanged during the subsequent stage of polymerization. The first stage corresponds to the induction period, during which propagating species are formed according to the reactions disclosed in our previous paper.[3] These findings are taken as confirming the results of our previous kinetic studies, i.e., a stepwise addition polymerization mechanism without chain transfer or termination.

We have presented a new method of determining propagating species in THF polymerization with $AlEt_3$–H_2O–ECH catalyst. This method has been conveniently employed in kinetic studies of THF polymerization with other catalyst systems, and the results will be published in the near future. In addition, the application of this method to various polymerization systems will be the subject of future investigations.

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Polycarboxyhydrazides with Ferrocenylene Groups in the Main Chain*

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Synopsis

Polycarboxyhydrazides essentially of the type $\lbrack C_{10}H_8Fe—CONHNHCO\rbrack_n$ are synthesized by low-temperature solution condensation of 1,1′-di(chlorocarbonyl)ferrocene with hydrazine or 1,1′-ferrocenedicarboxyhydrazide and hexamethylphosphoramide as solvent. In an analogous manner the polycondensation of 1,1′-di(chlorocarbonyl)ferrocene with oxalyldihydrazide leads to polyhydrazides essentially possessing the structure $\lbrack C_{10}H_8Fe—CONHNHCO—CONHNHCO\rbrack_n$. Both polymer types exhibit inherent viscosities (0.08–0.19 dl./g.) considerably lower than reported for analogous aliphatic or benzene-aromatic polyhydrazides. This behavior points to premature chain termination via heterobridging imide groups as a result of the well-documented tendency of appropriately substituted ferrocene compounds to undergo intramolecular cyclization. In addition, elemental analytical and spectroscopic evidence, coupled with the failure of both polymer types to undergo cyclodehydration to the corresponding 1,3,4-oxadiazole polymers upon heat treatment, suggests some structural irregularities in the aliphatic connecting segments arising from ferrocenoylation of secondary amino groups with resultant branching. With the polyhydrazide prepared from 1,1′-di(chlorocarbonyl)ferrocene and 1,1′-ferrocenedicarboxyhydrazide it is shown spectroscopically that treatment with alkali results in conversion of the nonconjugated hydrazide structure of the connecting segments into the polyconjugated tautomeric enol form comprising azine groups.

INTRODUCTION

As part of a comprehensive examination of the interannular resonance effects in metallocene polymers, conducted in connection with a study of the use potential of such polymers as semiconductor materials, we have synthesized a number of polymeric compounds containing 1,1′-ferrocenylene units in the backbone. The present paper is concerned with the polymeric carboxyhydrazides (I) and (II) (see following page).

RESULTS AND DISCUSSION

The synthesis of the polycarboxyhydrazide (I) was effectuated by following the approach first utilized by Frazer and Wallenberger[1–4] in the

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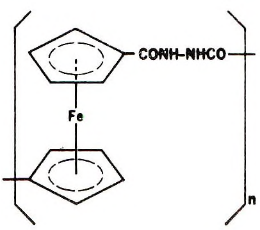
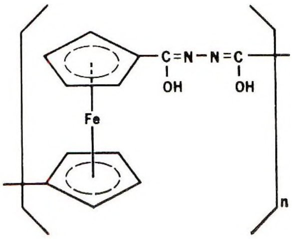
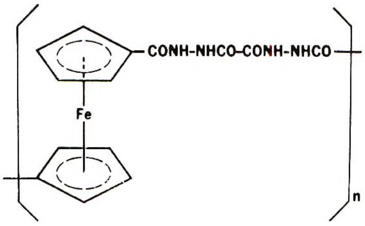
* Part XX in the series Metallocene Polymers; for Part XIX see reference 33.



I

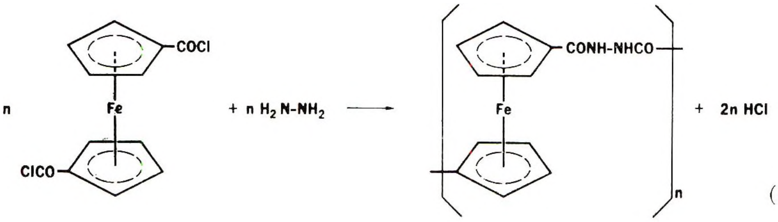


Ia

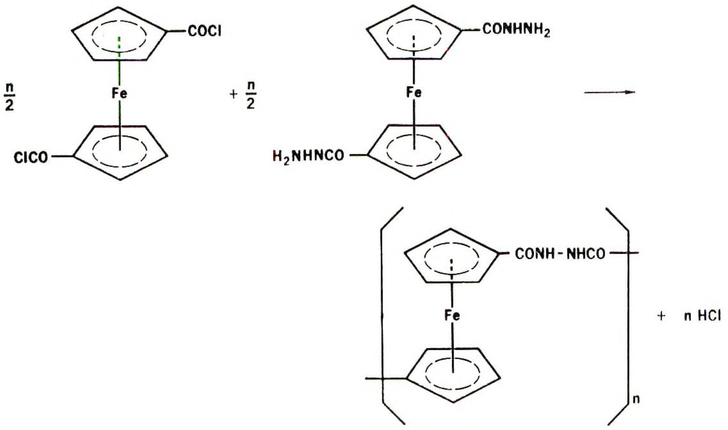


II

preparation of aliphatic or benzene-aromatic and heteroaromatic polyhydrazides through low-temperature solution condensation. In the present case 1,1′-di(chlorocarbonyl)ferrocene was reacted either with hydrazine or with 1,1′-ferrocenedicarboxyhydrazide according to eqs. (1a) and (1b), respectively.



(1a)



(1b)

NOTE: Preceding attempts to obtain (I) by condensation of 1,1′-ferrocenedicarboxylic acid with hydrazine sulfate in fuming sulfuric acid or polyphosphoric acid at 25–50°C. failed, rapid protolytic cleavage of the metallocene predominating over the regular polycondensation reaction under these conditions. High-temperature solution techniques were not employed in this work, after earlier reports[1,2,5–8] had shown that aromatic polyhydrazides, when prepared by such techniques at 100–210°C., exhibited low degrees of polymerization and, frequently, poor solubility characteristics.

The reaction partners, employed in stoichiometric or near-stoichiometric quantities, were stirred in hexamethylphosphoramide solution for 14–24 hr. at 3–5°C.; this was followed in several cases by additional reaction periods at temperatures up to 60°C. The quantities of solvent used varied from 16 to 40 moles for every mole of diacid chloride. The product, in all cases remaining in solution throughout the polycondensation, was precipitated by excess water in yields of 75–85%, and the crude polymer was purified by reprecipitation. No organic solvents of the types successfully employed by Frazer and Wallenberger in their polyhydrazide study, such as dimethylsulfoxide or tetramethylenesulfone, were suitable for this reprecipitation because of the poor solubility of the crude product in such solvents. The polymer did, however, dissolve in concentrated sulfuric acid; when quickly dissolved in this acid and reprecipitated by water, it was recoverable without having undergone noticeable hydrolytic degradation, as indicated by viscometric data. (Such degradation, however, which was similarly observed with other polycarboxyhydrazides,[3] became evident as samples of the polymers were allowed to stand in sulfuric acid solution for more than 12 hr. at room temperature.) After this exposure to the strong mineral acid the polymer showed enhanced solubility in hexamethylphosphoramide containing 3% lithium chloride, permitting viscometric measurements in this solvent system.

The experimental variables for six representative runs are summarized in Table I, as are the analytical results for the reprecipitated polymeric products. The table contains two experiments (Nos. 5 and 6) that were conducted under rigorously anhydrous conditions (solvent dried over disodioanthracene) and examined for the detrimental effects of moisture on the molecular weight. Conventional drying procedures were employed in the remainder of the experiments.

The tabulated data show improved stoichiometric control and, as a consequence, improved solubility and enhanced consistency in the calculated and the found elemental composition in those condensations (Nos. 2–4), in which 1,1′-ferrocenedicarboxyhydrazide, rather than free hydrazine (No. 1), was employed; similar results had earlier been obtained by Frazer and Wallenberger.[2,3] The findings also demonstrate that the molecular weight was not significantly affected by extended reaction periods and increased temperatures (e.g., Nos. 3 and 4) or by the use of the most rigorously anhydrous experimental conditions (Nos. 5 and 6) instead of more conventional conditions.

A comparatively low molecular weight range is indicated for all samples

TABLE I

Preparation and Composition of Polycarboxyhydrazides

	Molar concentrations												
Expt. no.	1,1′-Di-(chloro-carbonyl) ferro-cene	Hydra-zine deriva-tive[a]	Hexa-methyl-phos-phor-amide	Addition period, hr.	Reaction period,[b] hr.	Temp., °C.	Crude polymer yield, %	η_{inh}, dl./g. H_2SO_4	η_{inh}, dl./g. HMP-LiCl	Anal., found[c] C	H	Fe	N
1	1.0	1.0	19	1.5[d]	14.0	3–5	73.0	0.13	0.17[e]	51.89	4.66	19.62	8.72
2	1.0	1.0	16	2.0	15.0[f]	3–5	81.9	—	0.12	51.97	4.26	19.59	9.59
3	1.0[g]	1.0	16	2.0	16.0/3.0[h]	3–5, 55[h]	81.5	0.11	0.13	52.75	3.99	20.07	9.57
4	1.0	1.0	40	8.0	21.0/1.2	3–5, 60	83.3	0.09	0.14	52.92	4.01	19.71	—
5[i]	1.05	1.0	40	8.0	20.1/1.2	3–5, 60	85.9	0.11[j]	—	—	—	20.11	9.89
6[i]	1.0	1.05[k]	20	7.0	16.0/11.0	3–5, 60	79.7	0.08	0.11	52.31	3.98	19.92	9.92
7	1.0	1.05[k]	27	9.0	13.0	3–5	87.8	0.12	0.17[l]	46.87	3.69	14.92	15.28
8	1.0	1.0	27	9.0	13.0/5.5	3–5, 60	92.3	0.13	0.19[l]	46.79	3.78	15.13	15.41

[a] Hydrazine in No. 1; 1,1′-ferrocenedicarboxyhydrazide in Nos. 2–6; oxalyldihydrazide in Nos. 7 and 8.

[b] After completion of acylhalide addition.

[c] Anal. Calcd. for I: C 53.33%; H 3.70%, Fe 20.74%, N 10.37%. Calcd. for II: C 47.22%, H 3.40%, Fe 15.68%, N 15.73%.

[d] Higher yield (78.5%) at 5.0 hr.

[e] No. 1 partially soluble; Nos. 2–8 almost completely soluble. Viscosity values corrected for insolubles wherever required.

[f] Essentially the same results at 24 hr.

[g] Essentially the same results with 1.05 or 0.95 mole.

[h] Denotes 16.0 hr. at 3–5°C., followed by 3.0 hr. at 55°C.

[i] Experiments conducted under more rigorously anhydrous conditions; see text.

[j] 0.09 dl./g. after 24 hr. of standing at 25°C.; 0.05 dl./g. after 36 hr. at 25°C.

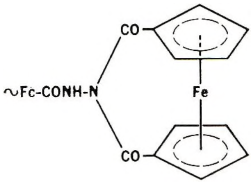
[k] Same results with 1.0 mole.

[l] Similar values in DMSO-LiCl.

listed, the inherent viscosity values invariably being below 0.2 dl./g. This unexpectedly low viscosity ceiling, as compared to a range of 0.3–1.0 and higher attained in the aforementioned benzene-aromatic cases[3,4] and later investigations,[9] is probably the result of competing intramolecular side reactions entailing chain termination via heterobridged endgroups, represented, for example, by the segment (IIIa).

NOTE: The tendency of reactive 1,1′-substituted ferrocene derivatives of suitable geometry to undergo intramolecular cyclization to heterobridged products is well documented, and exemplifying cases have been given.[10–14] This propensity, encountered in the present two cases of polyhydrazide formation, may as well be a critical factor in other types of polycondensation or polyaddition reaction, preventing optimal linear chain growth. For example, polyesters and polyamides of unexpectedly low molecular weight were obtained[10,15,16] from 1,1′-di(carbomethoxy)ferrocene or 1,1′-di(chlorocarbonyl)ferrocene, and similarly low degrees of polymerization were reported for polybenzimidazoles prepared from 1,1′-di(carbophenoxy)ferrocene[17] and also for polyurethanes and polyureas obtained with the use of 1,1′-di(hydroxyalkyl)ferrocenes or 1,1′-ferrocenedicarboxyazide.[10]

The found N contents of the polymer, somewhat lower than calculated for (I), are consistent with such heterobridged endgroups [and also with segments (IIIb); see below].



IIIa

In further accord with the existence of endgroups (IIIa) is the IR spectrum of the polymer, reproduced in the upper curve of Figure 1. The strong carbonyl absorption (amide I band), while showing its highest-intensity peak at the proper position near 6.1 μ expected for open-chain —CONH— segments, is considerably broadened toward the short-wavelength side.

NOTE: A strong shoulder at 5.9 μ, moreover, suggests the presence of free carboxyl groups generated by hydrolysis of chlorocarbonyl endgroups. In samples exposed for several hours to concentrated sulfuric acid this absorption invariably increased in intensity, indicating additional creation of COOH groups through hydrolytic chain degradation.

The broadening may be anticipated for a strained imide link whose carbonyl group is no longer in plane with the adjacent cyclopentadienyl ring. A similar shift of the carbonyl stretching band toward shorter wavelengths in going from such open-chain acylferrocene derivatives as 1-acetyl-1′-ethylferrocene to the corresponding heteroannularly bridged ketones, such as α-keto-1,1′-trimethyleneferrocene, was observed by other workers.[18–20]

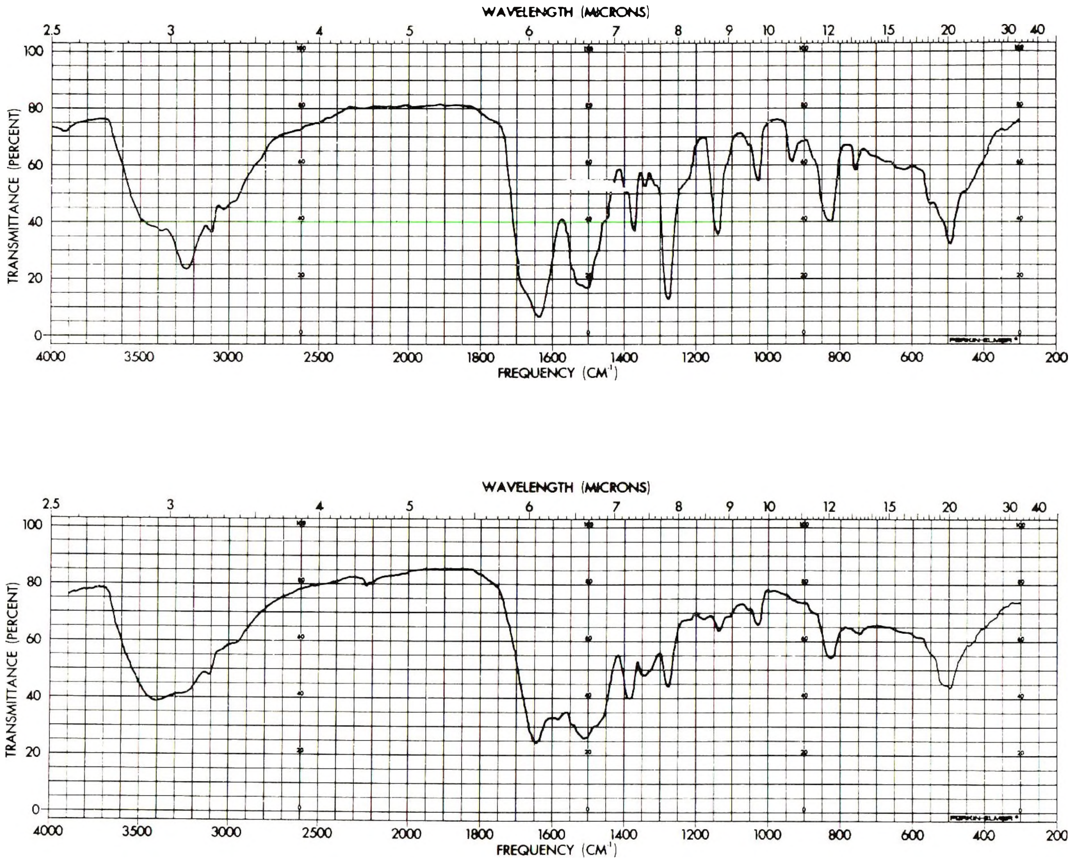
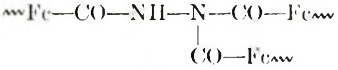


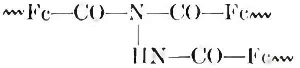
Fig. 1. Infrared spectra (KBr disks): (upper curve) polymer I (No. 3, Table I); (lower curve) polymer I, heat-treated (No. 4, Table II).

The comparatively poor solubility characteristics of polymer (I), contrasting with the excellent solubility of most benzene-aromatic polyhydrazides,[3,4,9] may reasonably be accounted for by assuming a minor degree of branching via segment structures, as shown, for example, by (IIIb) and (IIIc), the latter having resulted from further ferrocenoylation at the primary amino group of such segments as (IIId). The generation of segments (IIId), whose occurrence in the polymer is indicated by broad infrared absorption (primary amino group) appearing at the low-wavelength side (near 2.9 μ) of the secondary N—H stretching band, would be expected to be favored by the powerful electron-releasing ability of the ferrocene system.



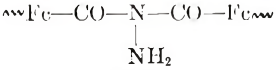
$$\sim\text{Fc—CO—NH—}\underset{\underset{\text{CO—Fc}\sim}{|}}{\text{N}}\text{—CO—Fc}\sim$$

(IIIb)



$$\sim\text{Fc—CO—}\underset{\underset{\text{HN—CO—Fc}\sim}{|}}{\text{N}}\text{—CO—Fc}\sim$$

(IIIc)

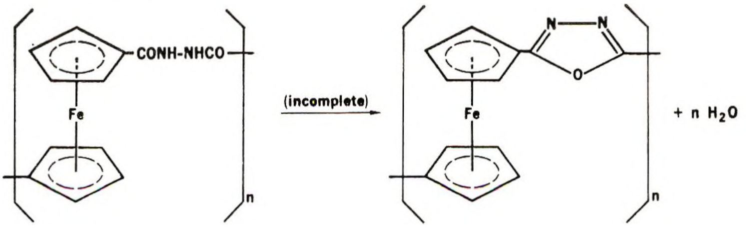


$$\sim\text{Fc—CO—}\underset{\underset{\text{NH}_2}{|}}{\text{N}}\text{—CO—Fc}\sim$$

(IIId)

The presence of the various segments (III) in the polymer is supported by its failure to undergo complete cyclodehydration to the corresponding 1,3,4-oxadiazole derivative [eq. (2)] under the conditions of thermal treatment reported[1,7,21–23] to be suitable for smooth cyclodehydration of analogous aliphatic or benzene-aromatic and heteroaromatic polyhydrazides.

Note Added in Proof. In a recent publication, Lorkowski and collaborators[37] obtained polyhydrazides I and II by a similar procedure as described in this paper. The products were only partially soluble or completely insoluble, and no viscosity data were reported. These workers were able, however, to synthesize two soluble polyhydrazides (η_{inh} 0.21 and 0.17 dl./g.) by copolymerizing 1,1′-di(chlorocarbonyl)ferrocene with isophthaloyl dihydrazide and adipic dihydrazide. Attempts to cyclodehydrate any of the low polyhydrazides by thermal treatment (220–270°C.) failed, decomposition proceeding concomitantly with the heteroaromatic ring closure. Other dehydration efforts, using $POCl_3$ (at 130°C.) as a medium, also proved unsuccessful except with the polyhydrazide containing the *m*-phenylene unit, the latter polymer giving the expected poly-1,3,4-oxadiazole (no η_{inh} reported).



(2)

The incompleteness of the cyclodehydration reaction of eq. (2) follows from infrared (Fig. 1, lower curve) and elemental analytical (Table II) data of the heat-treated samples. While the presence of oxadiazole units is suggested by the increased iron contents and the emergence or intensity enhancement of bands at 6.33, 6.75, 7.22 μ (ring-stretching vibrations)[24] and 9.75 μ (C—O stretching of =C—O—C=),[25] the found oxygen contents,

TABLE II
Thermal Treatment of Polycarboxyhydrazides

Expt. no.	Poly-hydrazide used,[a] no.	Heating cycle[b]		Anal. Found for products[c]			η_{inh}, dl./g. in H_2SO_4
		Time, hr.	Temp., °C.	Fe	N	O	
1	1	15.0/3.5/1.5	180/225/250	14.71	4.60	20.09	0.12
2	3	5.0/1.0/14.0	180/200/220	22.00	8.49	11.71	0.08
3	3	5.0/1.0/2.7	180/220/240	20.97	9.04	—	0.09
4	3	5.0/1.0/3.0	180/230/260[d]	23.02	8.35	13.30	—
5	8	13.5/1.5/4.0	170/220/240	15.80	12.31	—	0.12
6	8	13.5/15.0/12.5	170/230/255	16.33	11.91	18.14	0.10

[a] Numbers taken from Table I.

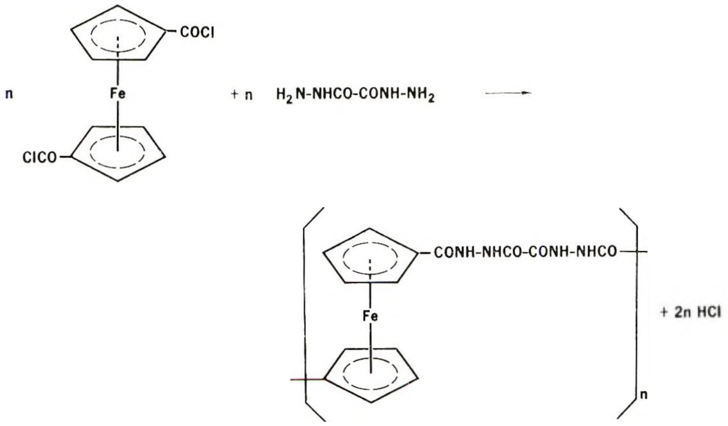
[b] Reactions conducted at $\approx 10^{-2}$ torr.

[c] Anal. Calcd. for polyoxadiazole, $C_{12}H_8FeN_2O$: Fe 22.16%, N 11.11%, O 6.35%. Calcd. for polyoxadiazole, $C_{14}H_8FeN_4O_2$: Fe 17.45%, N 17.50%, O 10.00%.

[d] Further heating for 8 hr. at 260°C. or for 2 hr. at 290°C. resulted in decomposition, product largely insoluble. Anal. Found: Fe 19.60%, N 71.7%, O 15.63%.

coupled with the retention, although in somewhat diminished intensities, of the amide I, II, and III bands at 6.10, 6.65, and 7.80 μ, clearly indicate an appreciable population of residual —CONH— and —CON< groupings in these heat-treated samples. In addition, the emergence of weak C≡N stretching absorption at 4.50 μ, its intensity undergoing further enhancement upon prolonged heating, points to the pyrolytic creation of nitrile groups, a reaction not observed in the case of unrestricted cyclodehydration of the benzene-aromatic polyhydrazides.[1,22,26] It is also apparent from the analytical data of Table II that the parent polyhydrazide on heat treatment lost 1% (and more) of its nitrogen, a fact that may be rationalized in terms of homolytic fission of the N—N bond in groupings of the type (IIId). In further accord with the existence of residual noncyclized moieties in the heat-treated products, the thermogravimetric analysis curves of such samples revealed considerably less thermal stability in the critical range 300–500°C. than had been anticipated for an all-aromatic poly(ferrocenylene–oxadiazolylene) system. For example, the thermogram of product No. 4, Table II, recorded in argon atmosphere, showed incipient weight loss near 300°C.; relative residual weights at 350, 400, and 500°C. were 87, 85, and 80%, respectively. (The same thermogram, however, indicated comparatively enhanced stability in the subsequent temperature region; residual weights were about 75% at 600°C. and 68% at 700°C., which compares favorably with, for example, the 63 and 58% shown at these temperatures by an all-aromatic oxadiazole polymer.[26])

By the same basic procedure as employed in the case of eq. (1b) 1,1′-di(chlorocarbonyl)ferrocene was reacted with oxalyldihydrazide accordto eq. (3).



(3)

The experimental conditions, comparable to those employed before, are summarized for two typical condensations in Table I (Nos. 7 and 8). Commensurate with the increased length of the bridging segments, the polymeric product (II) exhibited improved solubility; to a large extent, and without prior sulfuric acid treatment, the crude polymer dissolved in hexamethylphosphoramide or dimethylsulfoxide containing 3% lithium chloride.

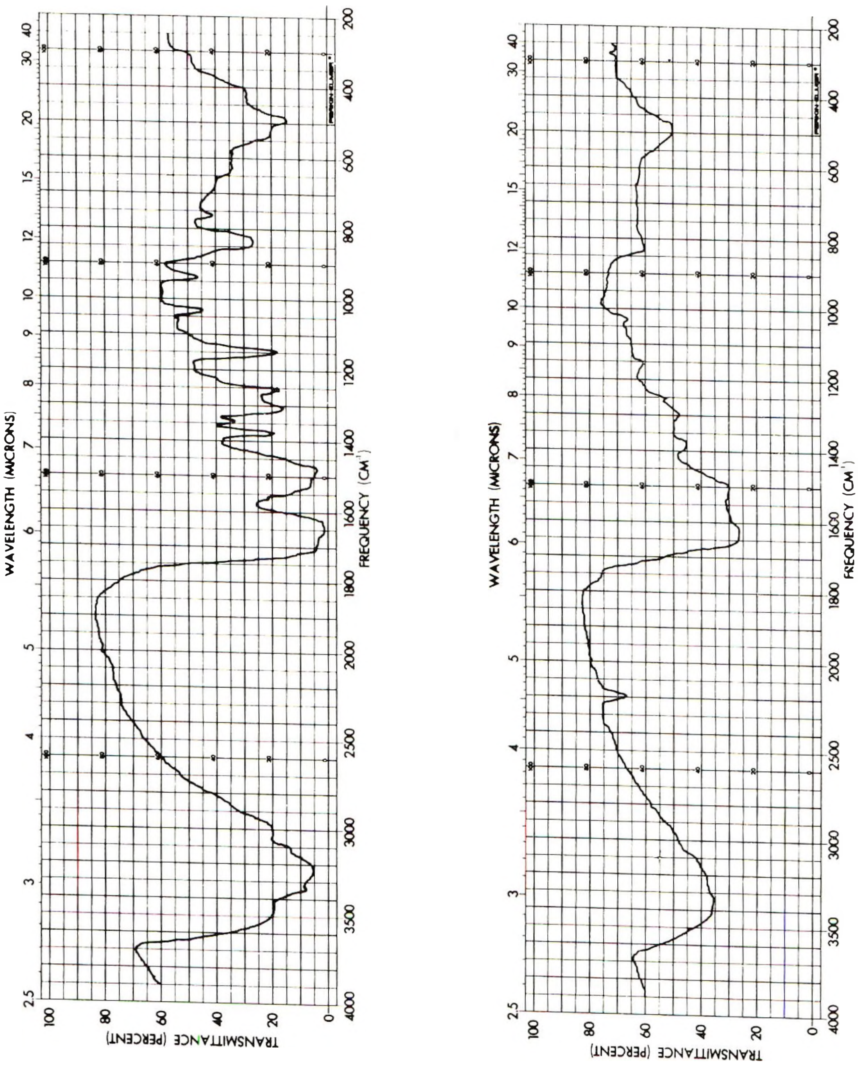


Fig. 2. Infrared spectra (KBr disks): (upper curve) polymer II (No. 8, Table I); (lower curve) polymer II, heat-treated (No. 6, Table II).

The table shows, however, that the inherent viscosities, determined either in dimethylsulfoxide–lithium chloride or sulfuric acid solution, were not substantially higher than those measured for (I).

Note: It can be seen from the tabulation that the viscosity values determined in organic solvents invariably are greater than those determined in sulfuric acid. This phenomenon, common to most polymer systems that are capable of forming polyelectrolytes in the strong mineral acid, cannot be traced to hydrolytic chain degradation, as is evidenced by the observation that η_{inh} values as high as 0.17 dl./g. again were measured in HMP–LiCl or DMSO–LiCl on samples previously reprecipitated from sulfuric acid.

Moreover, heat treatment as before gave products that were only incompletely cyclodehydrated, as is manifested in the IR spectra (Fig. 2) and the elemental compositions listed in Table II (Nos. 5 and 6). Obviously, in this reaction the competitive termination mechanism operative is the same as that in the preceding case and leads to heterobridged imide endgroups, and the existence of branching segments analogous to (IIIb), (IIIc), and (IIId), the last most conspicuously indicated by the drastically reduced nitrogen contents of the heat-treated samples, may also safely be assumed.

In accord with the absence of conjugation in the hydrazido bridging segments of (I) and (II), both polymers gave electronic spectra not substantially differing from 1,1′-ferrocenedicarboxyhydrazide or 1,1′-ferrocenedicarboxyamide. This spectral similarity becomes evident from Table III, in which λ_{max} values of the two characteristic ligand field bands[27] in the 300–500 mμ region are listed both for these mononuclear compounds and for representative fractions of the two polyhydrazides. Table III also contains the spectral data for ferrocenylcarboxyhydrazide. The wavelengths listed for this monofunctional hydrazide show negligible blue shifts relative to both the heteroannularly disubstituted compound and the polymeric hydrazides, well reflecting the resistance of the ferrocene system to the transmission of electronic effects from one cyclopentadienyl ring to the other (for examples of this behavior of ferrocene compounds, see Lundquist and Cais,[28] Nesmeyanov and Perevalova,[29] and, notably, Rosenblum et al.[30]). A similar lack of conjugation across the central iron atom in oligomers and

TABLE III
Ligand-Field Bands of Polyhydrazides and Monomeric Model Compounds[a]

Compound	η_{inh}, dl./g.[b]	Wavelength, mμ (molar extinction coefficient in parentheses)	
Ferrocenecarboxyhydrazide	—	342 sh (480)	443 (250)
1,1′-Ferrocenedicarboxyhydrazide	—	—[c]	445 (270)
1,1′-Ferrocenedicarboxyamide	—	343 sh (580)	445 (220)
Polycarboxyhydrazide I	0.11	345 sh (600)	443 (400)
Polycarboxyhydrazide II	0.17	—[c]	444(—)[d]
Polyazine Ia	0.11[e]	365 sh (—)[d]	480 (—)[d]

[a] In HMP; sh = shoulder.
[b] In HMP–LiCl.
[c] Maximum not distinguishable.
[d] Extinction coefficient not determined because of incomplete solubility.
[e] Determined on parent polyhydrazide prior to alkali treatment.

polymers comprising heteroannularly bonded intrachain-type ferrocenylene units was previously reported.[31–33]

Polymer (I) was converted to the polyconjugated structure (Ia) by digestion with aqueous alkali in much the same way as reported[3] for polyhydrazides of the nonferrocene type. Consistent with this enolization, the polymer so treated, when separated by filtration, briefly washed, and speedily vacuum-dried, turned dark orange in color and gave an IR spectrum that failed to exhibit the well-defined peak due to N—H stretching at 3.08 μ and showed the peak at 3.23 μ (possibly due to a Fermi resonance involving N—H stretching and other overtone and combination bands[34] partially superimposed upon the ferrocene C—H stretching band) in greatly diminished intensity. Instead, strong and very broad absorption emerged with highest intensity at 2.9 to 3.0 μ, where bonded and nonbonded enolic hydroxyl stretching would be expected. In addition, the strong amide I band at 6.10 μ was replaced by C—N stretching absorption at 6.16 μ, and the amide III band near 7.8 μ, which essentially represents a mixed vibration involving C—N stretching and secondary N—H bending,[35,36] was reduced to near-zero intensity. In further corroboration of the assignment (Ia), the electronic spectrum was characterized by a considerable red shift of the two aforementioned ligand-field bands relative to the unconjugated polyhydrazide (I) (Table III). However, for reliable results it was necessary to dissolve the polymer quickly (although incompletely) and immediately record the spectrum, before the tautomeric keto structure (I) was generated.

The electrophysical behavior of polymers (I) and (II) will be the subject of a forthcoming publication.

EXPERIMENTAL

Analyses, Materials

Melting points, uncorrected, were determined up to 300°C. Infrared spectra were taken on potassium bromide disks with a Perkin-Elmer spectrometer, Model 521. A Cary UV spectrometer, Model 14, was used for recording the electronic spectra; the solvent was hexamethylphosphoramide containing 3% by weight lithium chloride and 0.1% by weight ascorbic acid, the latter to prevent oxidation during the relatively long dissolution periods. Thermogravimetric analyses were performed in argon with a DuPont Thermoanalyzer, Model 950, recording from 25 to 800°C. at a heating rate of 15°C./min. Inherent viscosities, η_{inh} (in deciliters per gram), were measured at 25.00 ± 0.05°C. with a Manning-Fenske type of viscometer. The solvents were concentrated sulfuric acid, hexamethylphosphoramide (HMP), and dimethylsulfoxide (DMSO), the latter two containing 3% by weight lithium chloride for solubility enhancement; solute concentrations were 0.3% w/v. Owing to initial and rather erratic viscosity increases in sulfuric acid, all η_{inh} values measured in this solvent were obtained after a 12-hr. conditioning period, during which the solutions, contained in stoppered flasks, were allowed to stand at room temperature. Polymer viscosities measured in the organic solvents were corrected for minor portions of insolubles recovered and reweighed.

The carbon, hydrogen, and nitrogen analyses were performed by G. I. Robertson, Jr., Florham Park, N. J. The oxygen and iron contents were determined by neutron activation analysis on a Texas Nuclear Corporation Neutron Generator, Model 9501, coupled with a RCL 512 Multichannel Analyzer; 14 M.e.v. energy at a neutron flux of 10^8 cm.$^{-2}$ sec.$^{-1}$ was used for inducing radioactivity in the sample.

Oxalyldihydrazide was obtained commercially. Hydrazine, anhydrous (98%), was used as the commercial product; for use in experiments Nos. 5 and 6 (Table I) the compound was further dried with CaO and was redistilled at room temperature under reduced pressure (7–9 mm.), the necessary precautions being taken against explosion hazard. Ferrocenecarboxyhydrazide was prepared as described,[12] except that the total reflux time was prolonged to 26 hr.; m.p., 158–160°C. (lit.:[12] 159–160°C.). 1,1′-Ferrocenedicarboxyhydrazide was obtained in 80–90% yield from 1,1′-di(carbomethoxy)ferrocene by heating this ester for 24 hr. with the 24-fold molar amount of anhydrous hydrazine in methanolic solution at reflux temperature. The dihydrazide, poorly soluble in this solvent, partially crystallized from the solution; additional portions were separated by concentrating the mother liquor. Recrystallization from ethanol furnished the compound as orange-brown prisms; m.p., 221–225°C. decompd. (sealed cap).

ANAL. Calcd. for $C_{12}H_{14}FeN_4O_2$: C 47.72%, H 4.68%, Fe 18.49%. Found: C 47.82%, H 4.83%, Fe 18.51%.

The diester used in this preparation, m.p. 114°C., was obtained from a commercial source (Research Inorganic Chemical Co., Sun Valley, Calif.), which also provided 1,1′-di(chlorocarbonyl)ferrocene, m.p. 97–99°C.

Polycondensation Reactions

Polycondensation of 1,1′-Di(chlorocarbonyl)ferrocene with Hydrazine. The reaction variables for the representative condensation described below are summarized in Table I (Expt. No. 1). All glassware was oven-dried, and the reaction was conducted under a blanket of prepurified nitrogen.

The solution of 2.78 g. (0.087 mole) of anhydrous hydrazine in 200 g. of HMP (dried over Linde Molecular Sieves, type 3A) was placed in a 500 ml. round-bottom flask, equipped with a mechanical stirrer and an equalizing dropping funnel, and inserted in an ice bath. When the temperature of the solution had reached 3°C., the precooled solution of 27.0 g. (0.087 mole) of 1,1′-di(chlorocarbonyl)ferrocene in 96 g. of dry HMP was added dropwise and with vigorous stirring over a period of 1.5 hr., a temperature of 3–5°C. in the mixture being maintained. Stirring at this temperature was continued for 14 hr., and the crude polyhydrazide (I) was precipitated from the filtered solution by 1500 ml. of water. The dark-brown precipitate, separated by filtration or centrifugation, was thoroughly washed with water and hot methanol and was dried over P_2O_5 *in vacuo.* The yield was 19.5 g. (73.0%). The crude product was infusible and predominantly insoluble in all common solvents except concentrated sulfuric acid. Reprecipitation from the latter (200 ml.; 10.0 g. of stannous chloride added for reduction of ferricenium centers) by excess water and drying for 4 days at 140°C. over P_2O_5 *in vacuo* produced 15.1 g. of polymer as a tan-colored solid, which now dissolved not only in the strong mineral acid but also partially in warm HMP containing 3% lithium chloride. All analytical data for this product are collected in Table I.

Samples (0.4 g.) of the polymer were subjected to a heat treatment under reduced pressure ($\approx 10^{-2}$ torr) in an attempt to cyclize the hydrazide bridging segments to 1,3,4-oxadiazole rings. In a typical experiment, summarized in Table II (No. 1), the heating cycle was 15 hr. at 180°C., 3.5 hr. at 225°C, and 1.5 hr. at 250°C. The resulting black, infusible solid, for which all analytical data are given in the same table, was soluble in concentrated sulfuric acid but insoluble in all common organic solvents.

Polycondensation of 1,1′-Di(chlorocarbonyl)ferrocene with 1,1′-Ferrocenedicarboxyhydrazide. Typical experiments involving the condensation of 1,1′-di(chlorocarbonyl) ferrocene with 1,1′-ferrocenedicarboxyhydrazide are summarized in Table I (Nos. 2–6). The general technique employed was analogous to that described in the immediately foregoing paragraphs, except that in Nos. 5 and 6 special precautions were observed to ensure absolutely anhydrous conditions. For illustration, experiment No. 5 is described below.

The reaction flask, equipped as described before, was charged with 12.0 g. (0.397 mole) of 1,1′-ferrocenedicarboxyhydrazide in a dry box under prepurified nitrogen. The flask with contents was baked for 1.5 hr. at 100°C. under nitrogen purge and was allowed to cool to room temperature. HMP (200 g.), distilled over disodioanthracene,[38] was added through a column packed with Linde Molecular Sieves, type 3A, and the resulting slurry was cooled to 3°C. Under a blanket of prepurified nitrogen the precooled solution of 13.0 g. (0.0416 mole) of 1,1′-di(chlorocarbonyl)ferrocene in 104 g. of HMP (dried as before) was added over a period of 8.0 hr., and stirring was continued for 20 hr. at 3–5°C., followed by 1.2 hr. at 60°C. Workup as described above gave 18.41 g. (85.9%) of crude polymer (I). The product, when reprecipitated from concentrated sulfuric acid, showed almost complete solubility in the HMP–LiCl system (the same improved solubility behavior was exhibited by all other polyhydrazides prepared from 1,1′-di(chlorocarbonyl)ferrocene and 1,1′-ferrocenedicarboxyhydrazide). Viscometric data and elemental analyses are listed in Table I. The analytical results for representative polymer samples subjected to cyclodehydration at various temperature levels are compiled in Table II.

Polycondensation of 1,1′-Di(chlorocarbonyl)ferrocene with Oxalyldihydrazide. The procedure for the condensation of 1,1′-di(chlorocarbonyl)-ferrocene with oxalyldihydrazide was analogous to that described above for the first polycondensation. The experimental variables for two typical runs are summarized in Table I (Nos. 7 and 8). The crude polymers (II) were lighter in color than (I) and showed enhanced solubility in HMP–LiCl or DMSO–LiCl. Viscometric and elemental analytical results for the reprecipitated products are found in the same table. A sample of the crude polymer No. 7, when reprecipitated from DMSO–LiCl instead of concentrated sulfuric acid, gave inherent viscosities of 0.10 and 0.14 dl./g. in concentrated sulfuric acid and in HMP–LiCl, respectively.

Samples of polymer No. 8 (Table I) were heated under the conditions summarized in lines 5 and 6, Table II, in which the analytical results for the treated polymers also are given. The products, which were blackish, infusible solids, were essentially soluble in concentrated sulfuric acid but largely insoluble in other common solvents.

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The Interaction of Ions with Nylon. Part I. Absorption of Simple Acids

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Synopsis

The paper describes the titration relations for nylon 66 samples of different endgroup contents both for aqueous and alcohol solutions. The effect of temperature change is also considered. The results are consistent with a zwitterion structure of the nylon, carboxyl groups being protonated on acid titration. The acid groups are shown to be weaker than the corresponding monomeric acids in aqueous solution, owing to their environment inside the polymer. Individual ionic affinities are calculated from the experimental absorption isotherms and are in agreement with values obtained from a simple electrostatic theory. The low sulfate ion affinity can be explained by assuming interaction for this ion with single, fixed, isolated sites.

INTRODUCTION

When a polymer such as nylon or wool, containing ionizable groups, is placed in an aqueous solution of an electrolyte ion, absorption occurs, and pH titration curves can be obtained. Although a great deal of work has been done on the acid–base properties of wool, less information has been obtained with nylon. Wall et al.[1–3] studied the absorption of sodium hydroxide and hydrochloric acid by nylon 66 and interpreted their results on the Gilbert-Rideal[4] theory. Myagkov and Pakshver[5] studied the absorption of various acids by nylon and explained their results by using an ion-exchange theory. More recently Mathieson et al.[6] published data illustrating the effects of salt, temperature, and chemical modification of the nylon on the acid–base titration curves; their results were explained by a polyelectrolyte theory.[7] This paper describes the titration relations for nylon 66 samples of different endgroup contents both for aqueous and alcohol solutions. The effect of temperature change is also considered. A model of the substrate is proposed, and the interpretation of the results is consistent with a zwitterion structure of the nylon. The value of the pK for the carboxyl groups present in the nylon is higher than the value obtained by Mathieson and Whewell,[7] but it is shown that, if their calculations are modified to allow for the unequal numbers of carboxyl and amino endgroups, their results and the present results are in good agreement (Appendix I).

EXPERIMENTAL

The four types of nylon 66 used were kindly supplied by I.C.I. Nylon 1 was commercial nylon staple fiber. Nylons 2, 3, and 4 were in the form of chippings specially prepared by I.C.I. Since the chippings were unsuitable for equilibrium work, nylons 2, 3, 4 were dissolved in formic acid and precipitated by pouring the solution into distilled water. Traces of the acid were removed by prolonged washing with distilled water, until the conductivity of the washings, after standing for 24 hr., was less than 2×10^{-6} mho. Nylon 1 was extracted with ether and alcohol and subjected to prolonged washing with distilled water. All the nylons were dried and then stored at 20°C. and 65% R.H. for conditioning.

The carboxyl endgroup content was determined by dissolving the polymer in benzyl alcohol[8] at 170–180°C. The amino endgroup content was obtained by dissolving the nylon in a solution of 70% phenol and 30% methanol. The carboxyl and amino contents are listed in Table I.

A 20 g. portion of nylon 1 was acetylated by refluxing with 20 ml. of acetic anhydride and 120 ml. of benzene for 48 hr. The nylon was soaked first in methanol and then in water and conditioned at 20°C. and 65% R.H. An amino endgroup analysis indicated that less than 0.002 meq./g. of terminal amine remained after acetylation.

TABLE I

Nylon no.	Carboxyl content, meq./g.	Amine content, meq./g.
1	0.085	0.038
2	0.110	0.038
3	0.083	0.018
4	0.93	0.90

Acid–Base Titration Curves

The acid titration curves were obtained by equilibrating nylon samples of 0.5–1.0 g. with 100 cm.^{3} of acid solution covering the pH range 2.7–4.4. Smaller samples, of 0.3 g., were used with nylon 4. With these simple acids 24 hr. is sufficient time for equilibrium to be attained, but in all cases a minimum time of 48 hr. was allowed. The acid sorbed by the nylon was obtained from the difference between the initial and final conductivities of the equilibrating solution. The initial and final pH values were measured using a Pye pH meter with a standard glass electrode. In all the experiments carried out the theoretical pH calculated from the concentration of the final equilibrating solution agreed with the measured pH value.

The acid sorbed from solutions of 50% ethanol and 50% water hydrobromic acid was also obtained from conductivity measurements. The pH of the alcohol solutions agreed closely with the −log activities of the acid solutions on the assumption that these were close to those for HCl. Bacarella et al.[9] have shown that glass electrodes are suitable for pH measurements in methanol–water mixtures, and the results obtained in ethanol–water mixtures indicate that this also applies in these solutions.

Basic titration curves are more difficult to obtain than the corresponding acid titration curves because of the effect of atmospheric carbon dioxide. All sodium hydroxide solutions were made up with boiled, distilled water in an atmosphere of nitrogen. The alkali sorbed was calculated from the differences in initial and final pH of the solutions. Nitrogen was bubbled through the solution while the pH was being measured. This was checked by the conductivity measurement, and good correspondence between the two methods was obtained. A period of 4 days was allowed for equilibrium to be attained. All the equilibrium work was carried out at 25°C., except for one series with nylon 1 and hydrobromic acid, which was carried out at 60°C. for the purpose of investigating the effect of temperature on the isotherm.

RESULTS

The results are illustrated in Figures 1–7. Figures 1, 2, and 3 show the titration curves of nylons 2, 3, and 4 with hydrobromic and sulfuric acids, and these indicate a shift of the sulfuric acid isotherm, with respect to the HBr one, toward higher pH's as the number of terminal amine groups increases. Figures 1 and 2 approach maxima at about 0.018 and 0.038 meq./g., respectively, in agreement with the number of amino groups present. Previous results[6] with commercial-type nylons (drawn and highly oriented) indicate that some of the amino groups are inaccessible. For example, the results for nylon 1 (Fig. 4) show that only 0.034 meq./g. is titratable from a total of 0.038 meq./g. This presumably means that some of the amino groups are embedded in crystallites in the fiber but, when the nylons

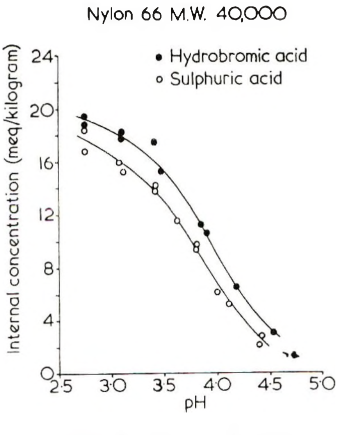

Fig. 1. Absorption isotherms for sulfuric acid and hydrobromic acid in nylon 66 (nylon 3) at 25°C.

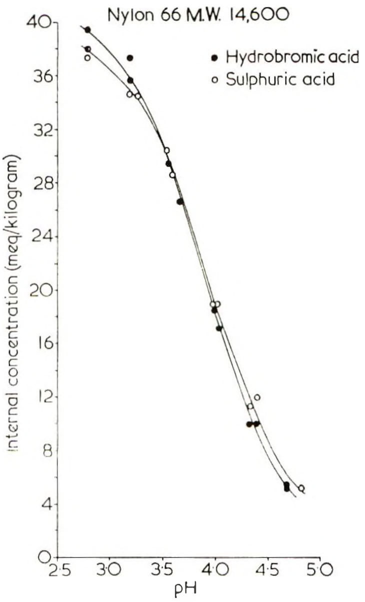

Fig. 2. Absorption isotherms for sulfuric acid and hydrobromic acid in nylon 66 (nylon 2) at 25°C.

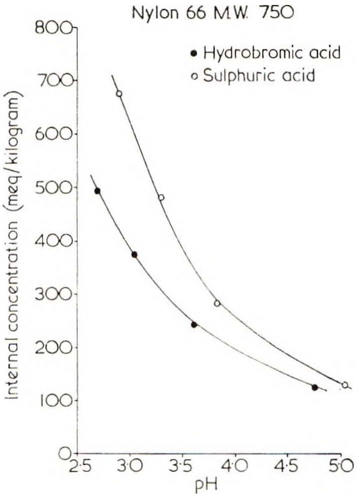

Fig. 3. Absorption isotherms for sulfuric acid and hydrobromic acid in nylon 66 (nylon 4) at 25°C.

are dissolved in formic acid, the crystallites are destroyed and the amino groups freed.

Figure 4 shows the titration curves of HBr in nylon 1 at 25 and 60°C. Less acid is sorbed at 60 than at 25°C. Figure 5 gives the titration curve of HBr in nylon 1 in aqueous solutions and in solutions of 50% ethanol and 50% water at 25°C. The effect of the alcohol is to increase the acid

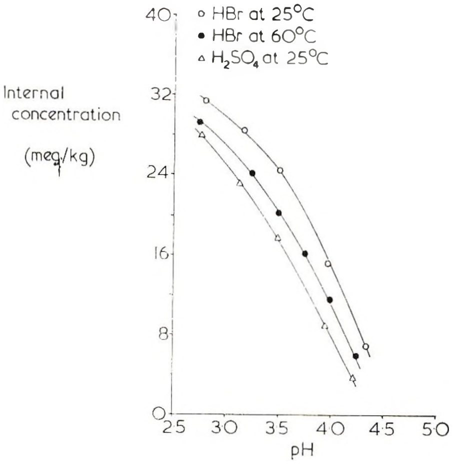

Fig. 4. Titration curves of nylon 1 with HBr, and H_2SO_4 at 25°C.

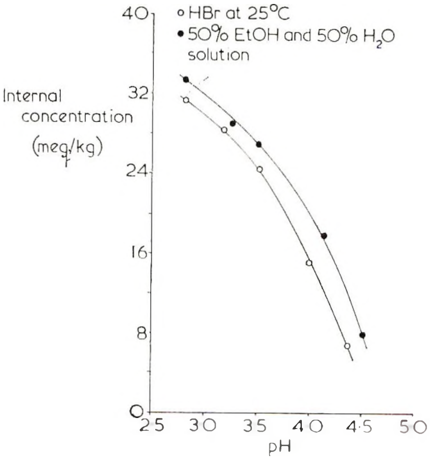

Fig. 5. Titration curves of nylon 1 with aqueous hydrobromic acid and solution of 50% EtOH and 50% H_2O.

sorbed at a given pH. Figure 6 gives the corresponding curves in keratin and includes the results of Steinhardt et al.[10] for comparison. The alkali titration curves for acetylated and unacetylated nylon 1 are shown in Figure 7. These agree reasonably well with the results of Mathieson et al.[6] Figure 8 shows the results of Barve.[11]

DISCUSSION

General

The absorption of acids by polymers such as nylon and keratin, which exist in the zwitterion form, is equivalent to the back-titration of the carboxyl groups in the polymer. The p*K* value of the carboxyl group will

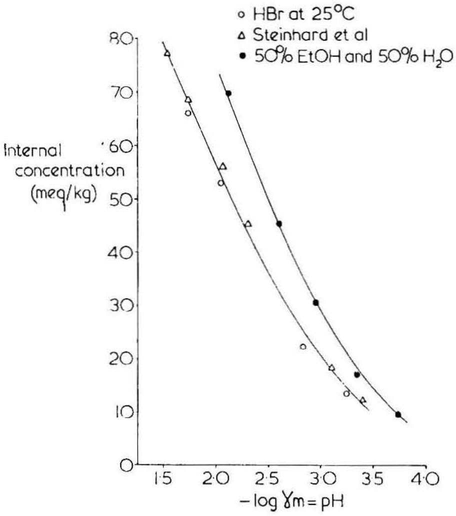

Fig. 6. Titration curves of keratin with HBr at 25°C., including the results of Steinhardt et al., and of solutions of 50% EtOH and 50% H_2O.

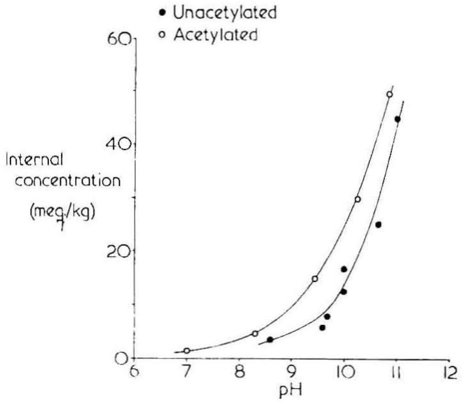

Fig. 7. Titration curves of acetylated and unacetylated nylon 1 with NaOH at 25°C.

be determined by the dielectric constant of the surrounding medium. If the anion, sorbed along with the hydrogen ion, has no appreciable affinity for the substrate, then the pK of the acid groups can be obtained directly from pH value corresponding to the midpoint of the acid titration curve. It has long been known that with keratin[12] twice the pH of the midpoint of the titration curve is approximately equal to the pK value of glutamic acid, the main acid group present in the polymer. This means that the carboxyl groups are situated in an aqueous environment with a dielectric constant not very different from 80. The effect of temperature on the titration curves and the data obtained with alcoholic solutions can be explained qualitatively, at least, in terms of the known pK values of carboxylic acids under similar conditions, but this is not the case with nylon.

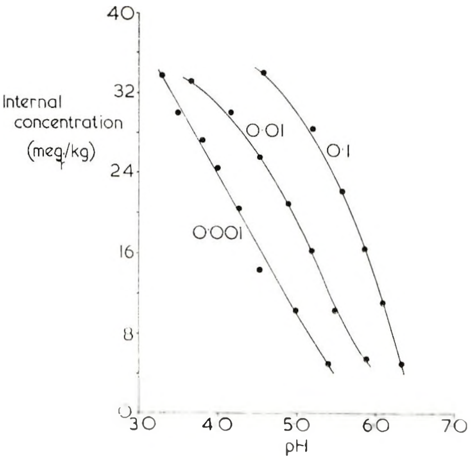

Fig. 8. Titration curves of nylon 66 with HCl at 22.5°C. in the presence of NaCl at various concentrations. (Reproduced by permission of Barve.[11])

Adipamic acid, which represents a reasonably close approximation to the monomeric unit concerned in the nylon 66 chain, has a pK value of 4.63,[13] but the value obtained from twice the pH value of the midpoint of the HBr–nylon 66 titration curve (nylon 1; see Fig. 4) is 7.8. This indicates that the acid groups present in the polymer are weaker than the corresponding monomeric acids in aqueous solution. There are at least two possible reasons for this: the electronic contribution of the molecular backbone to the pK and the effect of the low dielectric constant hydrocarbon matrix on the pK. The first possibility appears unlikely because of the slight effect of hydrocarbon chain length on the pK values of higher carboxylic acids. The second reason seems the more probable since, if the region surrounding the charged groups is of low dielectric constant, the energy needed to ionize the groups will be increased. This effect should give rise to greater hydrogen ion and inorganic ion affinities for the absorption of monobasic mineral acids in nylon (e.g., HCl, HBr) than in a polymer such as keratin. Since nylon contains relatively few terminal endgroups (e.g., 0.038 meq./g. terminal NH_2), an additional complication arises in the absorption of a simple dibasic acid such as H_2SO_4. Owing to the large distances between neighboring sites, an SO_4^{2-} ion will be unable to neutralize two positive sites simultaneously, and this is probably related to the apparent negative affinity[14] of the SO_4^{2-} ion, as will be discussed.

Affinity of Acids for Nylon

The affinity of an acid for nylon can be calculated directly from the midpoint of the experimental acid titration curve by means of the Gilbert-Rideal[4] titration theory, but if the individual ion affinities are required, the pK value of the carboxyl groups must be known. An estimate of the pK value may be obtained from acid titration determined in the presence of salt, and Barve's data are available for this purpose; these have been used, in conjunction with the titration results now obtained, for determining anion affinities for simple acids.

The internal equilibrium may be written

$$([\mathrm{COO}^-]/[\mathrm{COOH}])h = K \tag{1}$$

where K is the dissociation constant defined relative to the internal solution, $[\mathrm{COO}^-]$ is the concentration of ionized carboxyl groups, and $[\mathrm{COOH}]$ is the concentration of unionized carboxyl groups; internal activity coefficients have been neglected. In a polymer such as nylon, which exists in the zwitterion state but contains unequal numbers of acidic and basic groups, eq. (1) can be used for calculate K at the isoionic point. If the total number of acid groups is A and the number of basic groups, $[\mathrm{NH_3}^+;]$, is B, and if $A > B$, then at the isoionic point there will be B charged COO^- and $A - B$ uncharged COOH groups. The values of A and B were approximately 90×10^{-3} meq./g. and 38×10^{-3} meq./g., respectively, as determined by Barve.

The equilibrium between ions inside the polymer and those in the external solution may be written

$$h/H = C/c = n/N = \lambda \tag{2}$$

where H, C, and N refer respectively to the external H^+, Cl^-, and Na^+, and h, c, and n refer, respectively, to the internal H^+, Cl^-, and Na^+; $\lambda = \exp\{\psi F/\mathrm{RT}\}$, where ψ is the potential on the fiber. At the isoionic point ψ equals zero, so eq. (1) may be written

$$B/(A - B)10^{-\mathrm{pH}} = K$$

and the value of K determined by inserting in this equation the isoionic pH.

Values of the isoionic pH were determined by extrapolating Barve's titration curves[11] to zero acid sorbed. If the Cl^- has no affinity for the polymer, these curves should go through the same isoionic point. The three curves do not go through the same point, but since there are insufficient data for predicting the isoionic point with any accuracy, three values of K were obtained, and the mean value was taken: $K = 4.56 \times 10^{-7}$, or $\mathrm{p}K = 6.34$. This high $\mathrm{p}K$ value refers to the dissociation occurring inside the polymer and must obviously reflect the effect of the low dielectric constant of the substrate on this reaction. With this value of the $\mathrm{p}K$ the individual ion affinities can be obtained from the total acid affinity.

Allowing for the unequal numbers of acidic and basic endgroups, the total affinity of the monobasic acid (HX) for the nylon may be written[15]

$$-\Delta\mu_{\mathrm{HX}} = RT \ln (A - B + C_f)(/(B - C_f) + RT \ln \theta_x/(1 - \theta_x) - RT \ln [\mathrm{H}][\mathrm{X}] \tag{3}$$

where C_f is the acid sorbed and θ_x is the degree of saturation of the basic sites. At the midpoint of the titration curve $B = 2C_f$ and $\theta_x = 0.5$, and

$$-\Delta\mu_{\mathrm{HX}} = 2.3RT \log_{10} (A - C_f)/C_f + 4.6RT(\mathrm{pH}_{\mathrm{midpoint}}) \qquad (4)$$

and, for a dibasic acid,

$$-\Delta\mu_{\mathrm{H_2X}} = 4.6RT \log_{10} (A - C_f)/C_f + 2.3RT \log_{10} 2 + 6.9RT(\mathrm{pH}_{\mathrm{midpoint}}) \qquad (5)$$

The hydrogen ion affinity is equal to $-\Delta\mu_{\mathrm{H}} = 2.3RT(\mathrm{p}K)$, and the bromide ion affinity is equal to

$$-\Delta\mu_{\mathrm{Br}} = -\Delta\mu_{\mathrm{HBr}} - \{2.3RT[\mathrm{p}K + \log_{10} (A - C_f)/C_f]\}$$

The values of the total acid affinity and the individual ion affinities are tabulated in Table II for the various types of nylon used.

TABLE II

Acid	Nylon no.	$-\Delta\mu_{\mathrm{HX}}$ or $-\Delta\mu_{\mathrm{H_2X}}$, kcal./mole	$-\Delta\mu_{\mathrm{H}}$, kcal./mole	$-\Delta\mu_{\mathrm{X}}$, kcal./mole
HBr	1	11.50	8.7	2.0
	2	11.96	8.7	2.26
	3	12.3	8.7	2.40
H_2SO_4	1	16.50	17.4	−2.50
	2	18.90	17.4	−0.50
	3	18.75	17.4	−1.05

The results in Table II indicate that the bromide ion has a mean positive affinity of 2.22 kcal./mole whereas the sulfate ion has a mean negative affinity of −1.4 kcal./mole. Calculated this way, the apparent negative affinity of the SO_4^{2-} is smaller than that previously reported.[14]

In calculating the values in Table II it was assumed that the pK value obtained from Barve's results was the same as that for the three types of nylon (nylons 1, 2, and 3). Since the number of groups present are not so dissimilar, this seems a reasonable approximation.

Individual Ion Affinities

The greater ion affinities in nylon than in keratin may be explained by assuming that the differences between the two substrates arise from purely electrostatic considerations. This obviously greatly oversimplifies the problem, but reasonable values for the ion affinities can be obtained.

When small inorganic ions are sorbed into keratin, they do not decrease the free energy of the system, and no preferential absorption occurs; that is, the environment in the polymer is essentially the same as in the external solution. In nylon, however, the situation is quite different; the sites, although surrounded by water, are embedded in a matrix of low dielectric constant, so that the energy involved in neutralizing a site will be greater than in keratin. Following Gurney,[16] the free-energy change accompanying proton transfer may be written $\Delta\mu_{\mathrm{H}} = -RT \ln K = A + B/\epsilon$, where

A and B are constants. The first term represents the free-energy contribution due to the electronic effect, and the second term is the electrostatic contribution. If the first term remains constant from keratin to nylon, the increased affinity of the ion for the nylon will be given by the difference between the two electrostatic contributions. The decrease in the electrostatic free energy of the system, $-\Delta G$, will be approximately $-{}^1/_2(e^2/\epsilon r)$, where ϵ is the effective dielectric constant in the surrounding medium at distances greater than r, the closest distance of approach, so that the difference between the two electrostatic contributions will be equal to $-(-{}^1/_2(e^2/80r) - {}^1/_2(e^2/\epsilon r)$, where the effective dielectric constant in the keratin is put equal to 80. The bromide ion affinity will be given by a similar expression. The value of r will vary from ion to ion, but if for simplicity the value of r is assumed to be constant, the ion affinities in Table II may be obtained with $\epsilon_{\text{nylon}} = 15$ and $r = 5$ A., which seem reasonable values. If the hydrogen ion affinity in keratin is taken to be 5.3 kcal./mole, the values obtained for the individual ion affinities in nylon are $-\Delta\mu_{\text{H}} = 7.5$ kcal./mole and $-\Delta\mu_{\text{Br}} = 2.2$ kcal./mole. The calculated hydrogen ion affinity is lower than the value given in Table II, which probably indicates that a smaller value of r should have been used for this ion.

On this model the affinity of a divalent ion that neutralizes two sites simultaneously would be approximately 4.8 kcal./mole, which compares with the actual SO_4^{2-} ion affinity of -1.4 kcal./mole. This apparent anomaly can be removed by assuming that the SO_4^{2-} ion interacts with single, isolated, positive sites. This appears a reasonable assumption, since in nylon with 0.038 meq./g. of amino endgroup there will be relatively large distances between adjacent sites and the SO_4^{2-} will be unable to bridge two sites. A rough estimate[17] of this distance (R) may be obtained by assuming the sites to be arranged on a regular cubic array; hence, $0.038\ NR^3 = 1000$, where N is Avogadro's number, and hence $R = 35$ A. The position of minimum energy will occur when the SO_4^{2-} ion is near one of the fixed sites, and the difference in energy between the bridged and the unbridged state will be equal to the work done in moving a single charge from one site to an adjacent one, i.e., $\int_5^{35} (e^2/\epsilon r^2)/dr$, and this should be equal to $-(2\Delta\mu_{\text{Br}} - \Delta\mu_{\text{SO}_4})$, where $-\Delta\mu_{\text{SO}_4}$ is the experimental sulfate affinity. The divalent ion affinities in Table II were obtained by assuming interaction with two sites when $\theta_{\text{SO}_4} = {}^1/_2$ at half saturation of the available carboxyl groups; now, if single-site interaction occurs, θ SO_4 is equal to a ${}^1/_4$, not ${}^1/_2$ and this gives rise to an additional term of 0.4 kcal./mole, which must be added on to the $\Delta\mu_{\text{SO}_4}$ values given in Table II. If the mean values of $-\Delta\mu_{\text{Br}}$ and $-\Delta\mu_{\text{SO}_4}$ are taken, then $-(2\Delta\mu_{\text{Br}} - \Delta\mu_{\text{SO}_4})$ is 3.5 kcal./mole and $\int_5^{35} (Ne^2/\epsilon r^2)\ dr$ is 3.6 kcal./mole.

If the number of sites is greatly increased, the distance between sites decreases, and the effect of the hydrocarbon substrate on the pK and the ion affinities is decreased. This is observed with nylon 4 (Fig. 3, which has 0.9 mmole/g. of NH_3^+ sites (R = 12 A.). The pK value and the bromide ion affinity will be decreased, and the SO_4^{2-} will be able to neutralize two groups, so that the curve of H_2SO_4 versus nylon moves to pH values lower than those of the curve of HBr versus nylon. Barve's results also indicate specific interaction between the inorganic ion and the fixed sites, as indicated in Appendix II.

The results with alcoholic solutions are in agreement with the idea that it is the low dielectric constant in the nylon substrate which determines the internal pK value. Figure 6 shows that the HBr–keratin titration pH is shifted from 2.3 to 2.625 in the presence of 50% alcohol. Thus, the pK is increased from 4.6 to 5.25 in the alcohol solution and is characteristic of carboxylic acids. It is a measure of the increase in electrostatic work which has to be done in ionizing the carboxyl groups. The percentage change in the pK value (14.2%) compares favorably with the values given by Edsall and Blanchard[18] for carboxylic acids in 50% solutions, where a 19% change was obtained. The good agreement between the two examples implies that the charged groups in the keratin are in an aqueous environment, so that the effective dielectric constant is in the region of 80.

Figure 5 shows that the HBr–nylon titration pH is shifted from 3.87 to 4.12 in the presence of 50% alcohol, so that if the midpoint of the titration curve is taken as a measure of the pK, the percentage change in the pK value obtained is 8%. Thus in the nylon the alcohol does increase the pK but not as much as would be expected (aminocaproic[18] acid changes in pK from 4.6 to 6.0 in 50% alcohol). This difference may be explained by assuming that the controlling factor in determining the pK inside the polymer is the low dielectric constant of the hydrocarbon matrix, the sites being surrounded by water molecules, so that when alcohol is introduced, the local dielectric constant is reduced, but not as much as if the substrate of low dielectric constant were not present. There must be some water molecule around the sites; otherwise, on the addition of alcohol this would increase the local dielectric constant and so decrease the pK value and shift the titration curve to pH values lower than those of the aqueous solution titration curves.

The results of Iijima and Sekido[19] for the heat of titration for HCl with nylon 6 appear to conflict with these ideas. Using the expression given by Gurney,[16] $\Delta\mu = A + B/\epsilon$, they found A = 7.31 kcal./mole and B = 2.60 kcal./mole.

They compared these values with the values obtained by King[20] in keratin (A = 2.9 kcal./mole, B = 2.9 kcal./mole), and they attributed the difference to the difference in nonelectrostatic term between the two substrates.

This is not necessarily the case since, if the hydrocarbon matrix affects the free-energy change, this will give rise to an additional electrostatic contribution, but since the dielectric constant of hydrocarbon material is not very temperature-dependent, this will not appear in B/ϵ. If this effect is taken into account, $\Delta\mu$ may be written $\Delta\mu = (A' + C/\epsilon_1) + D/\epsilon_2$, where

ϵ_2 is like that of water and is temperature-dependent and ϵ_1 is like that of hydrocarbon material and is not temperature-dependent.

The heat of titration obtained from the shift in the midpoint of the NBr–nylon titration curve (Fig. 4), $-\Delta H = 6.6$ kcal./mole, agrees with the value obtained by Iijima and Sekido[19] in nylon 6 and by Wall and Beresniewicz[3] in nylon 66.

Alkaline Titration Curves

The titration curves of NaOH in acetylated and unacetylated nylon 1 are shown in Figure 7. Since this nylon contains an excess of carboxyl groups over amino groups, the titration curve given for the unacetylated nylon will correspond to the dissociation of the excess carboxyl groups. An estimate of the pK of the carboxyl group may be obtained from the acetylated nylon titration curve. The value obtained, pK = 7.7 ,is higher than the value obtained in acid solution. No significance is attached to this difference, since the only accurate way of determining the pK is in the presence of salt.

Appendix I

Mathieson and Whewell in their theory for nylon obtained a pK value of 5.3 for the carboxyl groups, which is lower than the value obtained in this paper. The difference probably arises from the fact that they neglected to take into account the unequal numbers of acidic and basic groups present in the nylon. If this is done, their eq. (7)[4] becomes

$$\mathrm{pH} = Kp_0 - \log_{10}\,[(A - B + C_f)/(B - C_f)] - (0.4343/RT)\,(\chi F + \pi \bar{V}_{\mathrm{H}} - \Delta\mu_{\mathrm{H}}{}^{\circ})$$

where A is the number of carboxyl endgroups, B the number of amine endgroups, and C_f the acid sorbed. Values of the pK calculated from this equation are given in the table. Similar values of pK are obtained with the 0.04M and 0.1M KCl.

Titration of Nylon 66 by HCl in Presence of 0.02M NaCl

Mathieson	pH	Mathieson pK	Recalculated pK	Mean pK
0.1	5.94	(5.02)	6.23	
0.2	5.72	5.20	6.13	
0.3	5.49	5.25	6.03	
0.4	5.27	5.26		6.1
0.5	5.04	5.25	5.84	6.1
0.6	4.82	5.26		
0.7	4.58	5.24		
0.8	4.30	5.27	6.38	

Appendix II

Preferential absorption in the nylon may be taken into account by introducing ionic partition coefficients into eq. (2); that is, $h/_{\mathrm{H}} = Cp_{\mathrm{Cl}}/c$ where P_{Cl} is the partition coefficient for the Cl$^-$ ion and $1/p_{\mathrm{Cl}}$ reflects the internal activity coefficient. If the internal value of inbibed water is taken to be 10 cm.^{3} per 100 g. of nylon, the values of p_{Cl} may be calculated from eq. (6) for the three different salt concentrations obtained by

Barve with $A = 90$, $B = 38$, p$K = 6.3$, $c = C_f$, where C_f is the acid sorbed. The values of P_{Cl} are given in the table.

	p_{Cl} (at molar NaCl)		
meq. C_f, per 1,000 g.	0.1	0.01	0.001
5	1	3.16	11.5
10	1	4.0	12.3
15	2	4.0	10.0
20	2	4.0	8.5
25	2	3.16	7.3
30	2	2.5	6.7

It can be seen from this table that the P_{Cl} values remain approximately constant for a given salt concentration but increase with decreasing salt concentration. This means that as the external salt concentration decreases, the internal activity coefficient $1/P_{Cl}$ decreases; that is, the internal concentration does not fall as quickly as would be expected. This type of effect is characteristic of specific ionic interaction. This implies that the Cl^- ions interact with the NH_3^+ sites in the polymer, in dilute NaCl solutions. The energy involved for $p_{Cl} = 10$ (0.001M NaCl) is 2.3 $RT/\log p = 1.38$ kcal./mole.

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Relaxations of Selenium in Crystalline and Amorphous States

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Synopsis

Complex shear modulus at 33 kc./sec. is measured at temperatures of −150–150°C. for amorphous selenium and crystalline selenium with different crystallinities. The dielectric relaxation at 10 kc./sec. to 3 Mc./sec. is observed at temperatures of −32–25°C. for iodine-doped crystalline selenium. It is concluded from the results of this study and of others' that selenium exhibits four relaxations, α, β, γ, and δ, in order of descending temperature. The β relaxation is observed only in the amorphous sample above the glass temperature and is assigned to the primary relaxation. The α, γ, and δ relaxations are found in the crystalline selenium. The α relaxation, which is prominent in a highly crystalline sample, is assigned to the crystalline relaxation. The γ and δ relaxations increase in peak height with decreasing crystallinity and are attributed to the disordered region in the crystalline selenium. The dispersion map (logarithm of frequency versus reciprocal absolute temperature of loss maximum) of selenium is presented.

Introduction

The knowledge of relaxational phenomena in organic polymers is nowadays extended to a wide variety of polymer species and a wide range of temperature and frequency. Polyethylene, which has the simplest chemical structure in organic polymers, exhibits at least four relaxations: crystalline, grain-boundary, primary, and local-mode relaxations, in order of descending temperature.[1,2]

Selenium, one of the most familiar of inorganic polymers, is a single-atom species and has the simplest chemical structure of all the polymers. Moreover, it can be obtained in high chemical purity. For these reasons it is believed that studies of its properties will lead to a deeper and more general understanding of phenomena in other polymers. Nevertheless, the data on relaxations in Se are rather limited at present.

The crystal of Se is a hexagonal lattice in which chain molecules are arranged parallel to the c axis[3] with 3_1 spiral conformation. The strong anisotropy in thermal expansion,[4] which reflects the anisotropy of the crystalline binding force, is essentially analogous to other polymer crystals. The specific heat of the crystals, starting at low temperatures[5] increases

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with increasing temperature first in proportion to T^3, where T is the absolute temperature, which is typical of a three-dimensional lattice, and then to T, typical of a one-dimensional lattice. This fact is also indicative of the strong anisotropy of the crystalline field. Consequently, the crystalline relaxation, which comes from a large-amplitude vibration of crystalline chains,[2] is expected to appear in Se at temperatures below the melting point (217°C.).

Amorphous Se can be obtained by quenching molten Se to room temperature. In the amorphous phase the molecules take the form of either a linear chain or a Se_8 ring.[6,7] The average molecular weight of linear chains depends on the temperature from which the sample has been quenched. The glass temperature T_g of amorphous Se is observed around 30°C. in thermal-expansion measurement.[8] As a consequence, the primary relaxation which results from segmental motion of amorphous chains is expected above T_g.

The relaxation of amorphous Se above T_g has been investigated by Eisenberg and Teter[8] by the stress relaxation method. The dielectric relaxation at low temperatures was studied by Ludwig and Eckart.[9] The overall behavior of relaxations in Se, however, has not yet been revealed. The purpose of the present work was to investigate the dynamic mechanical properties of crystalline Se and amorphous Se over a wide range of temperatures and to clarify multiple relaxations in this material. The dielectric properties of an iodine-doped sample will be presented.

Experimental

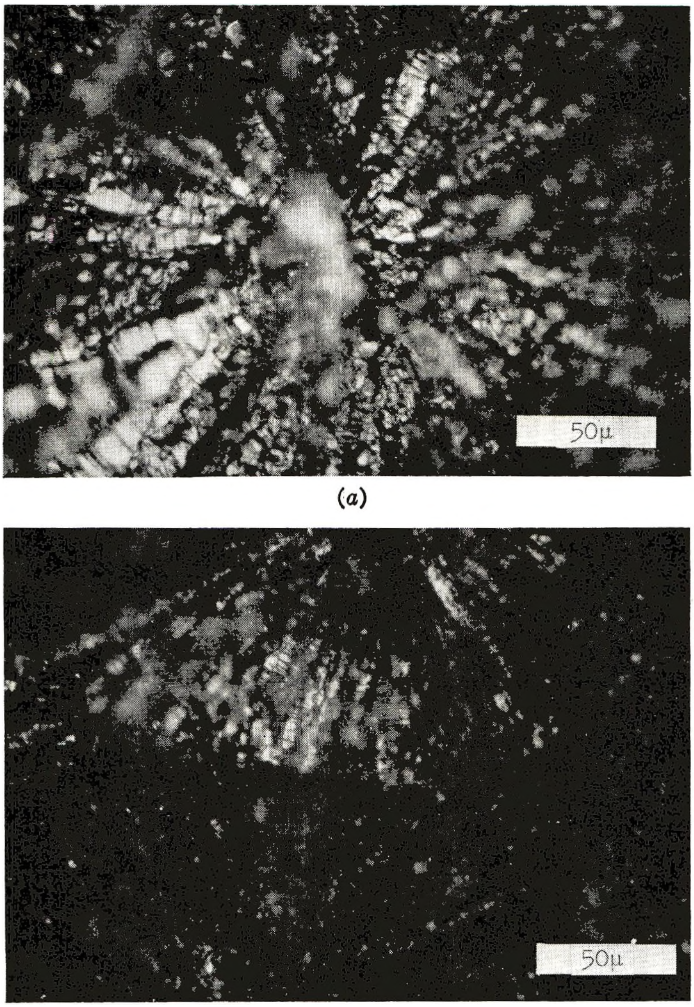
The selenium used in this experiment had a purity of 99.999% and was degassed at 300°C. for 1 hr. in vacuum prior to heat treatment.

Samples were given different heat treatments, as listed in Table I. The heat-treatment was given in an evacuated glass ampule. Three samples, S_{120} to S_{170}, were crystalline, among which S_{145} had the largest spherulite size. Figure 1 shows microscope photographs of the polished surface of S_{145} after it had been etched with 60% nitric acid.[10] Sample S_{170} showed no distinct spherulite structure. Sample S_g was prepared by quenching from 150 to 0°C. and was amorphous. The fracture surface of this sample was peculiar to the glassy or vitreous material. The densities

TABLE I

Samples of Selenium

Sample no.	Preparation
S_{120}	Crystallized at 120°C. for 4.5 hr.
S_{145}	Crystallized at 145°C. for 3.5 hr.
S_{170}	Crystallized at 170°C. for 2.5 hr.
S_g	Water-quenched from 250 to 0°C.
S_I	Iodine-doped 1% wt. in vacuum, quenched, and pressed into sheet at 140°C. for 1 hr.



(b)

Fig. 1. Photographs of etched surface of highly crystalline selenium (Se_{145}): (a) spherulite center; (b) spherulite boundary.

of the samples at 20°C. ranged from 4.28 g./cm.^{3} for S_g to 4.74 g./cm.^{3} for S_{145}.

The composite oscillator technique[11] in torsional vibration at 33 kc./sec. was employed for dynamic mechanical measurement. The specimen, of a circular rod shape 6 mm. in diameter, was cemented to a quartz torsional oscillator which had the resonant frequency of 33.157 kc./sec. and the same diameter as the specimen. The length of the specimen was adjusted so that the resonant frequency of the composite oscillator would be close to that of the quartz oscillator.

The frequency characteristic of the motional admittance of the composite oscillator was measured, and the complex shear modulus of the specimen

(G' and G'', real and imaginary parts, respectively) were calculated from the resonant-frequency shift and the half-width by well-known equations.[11] The electronic circuit was as previously described.[12]

The composite oscillator was set in a thermostat, in which air was replaced with dry nitrogen. The temperature was controlled with a silicone oil bath at high temperature and a liquid-nitrogen or methanol–Dry Ice bath at low temperature. The temperature was measured with a copper–constantan thermocouple fixed just near the specimen. The temperatures ranged from −150 to 150°C.

A conventional transformer bridge was used for measuring the dielectric constant ϵ' and loss ϵ'' at frequencies of 30 cps to 3 Mc./sec. The apparatus was exactly the same as one previously reported.[12] The specimen S_I was in the form of a thin sheet obtained by pressing the quenched Se, which had been doped in vacuum with 1% iodine in weight. The press temperature was 140°C. and, hence, the sample was crystalline. Two metal plates were used as electrodes. Vacuum-deposited metallic films were found unsuitable for the electrodes, because the specimen had numerous pinholes.

The loss value below 10 kc./sec. was governed by the d.c. conductivity, and hence the conductivity σ was obtained from low-frequency loss by the equation $\epsilon'' = \sigma/\omega$, where ω is the angular frequency, as a function of temperature.

Results

Figure 2 illustrates the real and imaginary parts of the shear modulus at 33 kc./sec. for three crystalline samples. Three loss peaks are found in Figure 2 around 135, 0, and −80°C., respectively, which will be called α, γ, and δ peaks herein. The primary relaxation (β peak), which might

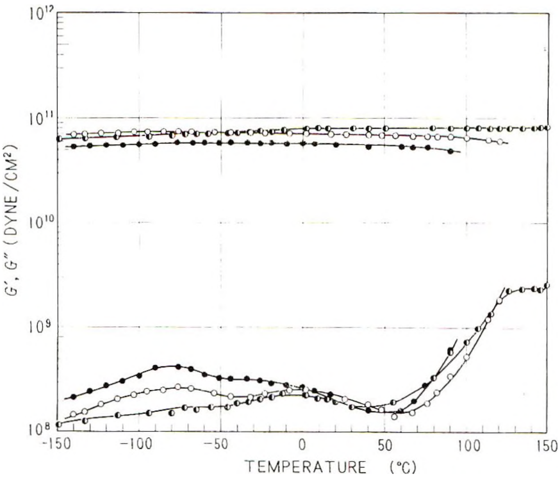


Fig. 2. Complex shear modulus at 33 kc./sec. for three crystalline samples of selenium: (○) S_{120}; (◐) S_{145}; and (●) S_{175}.

appear above T_g (30°C.), could not be distinguished in the crystalline samples.

Figure 3 shows the result for amorphous sample S_g. The value of G' agrees well with the data by Sieg and Miller.[13] The upswing in loss at

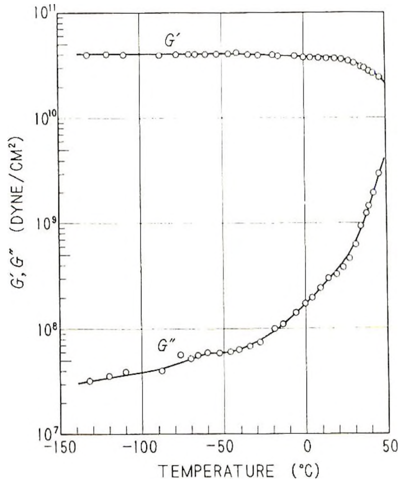


Fig. 3. Complex shear modulus at 33 kc./sec. for amorphous sample of selenium (S_g).

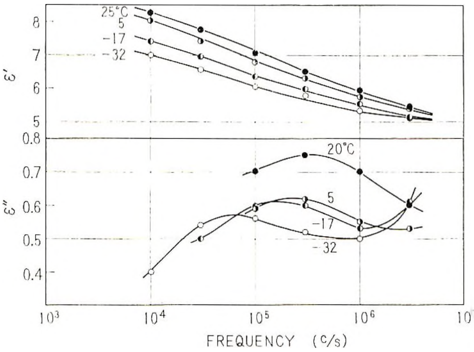


Fig. 4. Dielectric constant and loss for iodine-doped crystalline sample of selenium (S_I) at various temperatures.

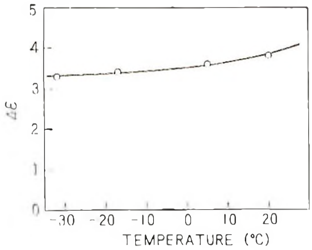


Fig. 5. Dielectric relaxation strength of γ peak for iodine-doped crystalline sample of selenium (S_I).

high temperatures indicates the β peak. We could not observe the loss maximum because of too high damping of the composite oscillator. The δ peak is only slightly observed in Figure 3.

The dielectric relaxation for sample S_I is given in Figure 4, where the loss peak corresponds to the γ peak, as will be described, and the upswing in dielectric loss at high frequency suggests the δ peak.

The dielectric relaxation strength $\Delta\epsilon$ of the γ peak is calculated by the Cole-Cole circular arc plot and represented in Figure 5, in which $\Delta\epsilon$ gradually increases with increasing temperature, as is the case of low-temperature relaxations of polar polymers.[14]

Discussion

Loss peak temperatures are plotted against frequency in Figure 6, which includes the present data together with those by Ludwig and Eckart[9] and Eisenberg and Teter.[8] The relaxation modulus as a function of time[8] was converted into the loss modulus as a function of frequency by means of an approximate relation between viscoelastic functions.[15]

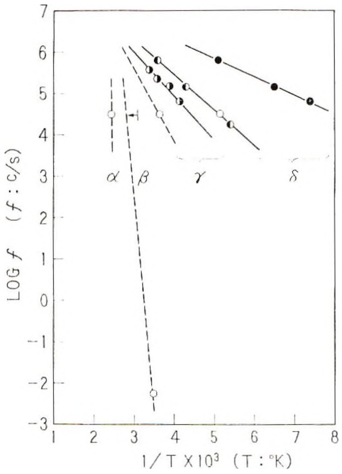


Fig. 6. Logarithm of frequency versus reciprocal absolute temperature of loss maximum for selenium: (○) mechanical (undoped), (◑) dielectric (1% iodine-doped); (◐) dielectric (undoped); (●) dielectric (0.1% bromine-doped).

The dielectric loss peak observed by Ludwig and Eckardt[9] is shifted to low temperature with increasing halogen content. Since the peak temperature of dielectric loss for the undoped sample agrees with the present mechanical δ peak, the peaks observed by Ludwig and Eckart may be labeled δ in the present nomenclature.

The dielectric loss peak in Figure 4 is somewhat lower in temperature position than the mechanical γ peak in Figure 2 but may be assigned to γ, if the temperature lowering by doping is assumed to occur also in this case.

It must be noted here that the glass transition of amorphous Se is also lowered by doping.[8]

Figure 6 indicates that Se exhibits four relaxations, among which the α peak is most distinctive of the crystalline sample and the β peak of the amorphous one. With reference to the behavior of many other polymers, it may be safely concluded that the α and β relaxations may be assigned to the crystalline and the primary relaxations, respectively.

The slope of the γ peak line in Figure 6 (1% iodine-doped) gives an activation energy of 4 kcal./mole, which appreciably differs from the activation energy of the d.c. conductivity of the same sample, 7 kcal./mole. This affords evidence that the peak does not come from the interface relaxation[16] among crystalline and disordered phases.

The peak height of both γ and δ peaks increases with decreasing crystallinity but almost disappears in the amorphous sample. This indicates that γ and δ relaxations should be assigned to the disordered region in the crystalline sample, and this region is essentially different in nature from the amorphous phase in the amorphous sample. Halogen atoms are included as doping in the disordered region and increase the mobility of chain segment. It is not clear at present why two relaxations, γ and δ, result from the disordered region. One possible explanation is that there are two kinds of region, and an alternative is that there occur two kinds of motion in the region.

As is well known, crystallizable polymers have the local-mode relaxation, which is attributed to torsional vibration of chains in the amorphous or disordered phase.[2,14] The strength of this relaxation increases with increasing amount of disordered phase and, at the same time, with the local regularity in this phase.[2,14] In the case of Se the local regularity means a 3_1 spiral conformation in the disordered phase. The increase of the sequence length results in a large amplitude of torsional vibration and, hence, an increase in relaxation strength.

On the basis of this discussion it may be inferred that the δ peak may be assigned to the local-mode relaxation of Se because the peak height increases with decreasing crystallinity and the peak is slightly observed in the amorphous sample, too, in which the local regularity may be very poor. The γ peak, which appears at a higher temperature than the δ peak and disappears completely from the amorphous sample, may come from the surface disorder of crystallites or a constrained disordered phase among crystallites. These interpretations are tentative, however, and may be proved only by further work.

It must be emphasized here that the level of loss modulus at low temperature is the lowest for the amorphous sample S_g and next lowest for the highly crystalline sample, S_{145}. Samples with intermediate crystallinity have a higher level of loss at low temperatures. This implies that inhomogeneity is the highest in an intermediate crystallinity.

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The Polymerization of 1,4-Pentadiene to [3.3.1]Bicyclo-Linked Chains*

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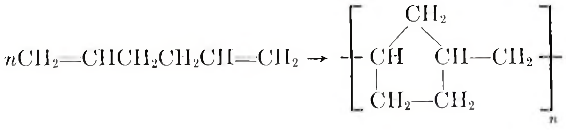
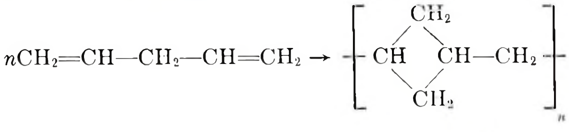
Synopsis

1,4-Pentadiene has been polymerized by Ziegler-Natta catalysts to give amorphous polymers which are up to 64 wt.-% soluble. The polymers all have residual unsaturation which is substantially less than one double bond per mer, some as low as 0.1 double bond per mer. The polymerizations proceed by an unusual double inter-, double intramolecular cyclopolymerization mechanism leading to the formation of [3.3.1]bicyclic repeat units. Some main-chain (internal) unsaturation as well as pendant-group (external) unsaturation is observed. The latter results from incompletely cyclized 1,4-pentadiene units. The former is due to some concurrent isomerization of 1,4- to 1,3 pentadiene, which then copolymerizes with the 1,4 diene. The extent of isomerization varied with the catalyst system used. The soluble polymer fractions were brittle for internal unsaturations of less than about 0.05 double bond per mer and were viscous for higher values. The insoluble fractions were brittle and are believed to be lightly crosslinked.

It is now well known that the polymerization of 1,5 and 1,6 dienes can proceed by an alternating inter-intramolecular cyclopolymerization mechanism, giving, respectively, polymers with methylene-linked 5- and 6-membered rings. In this way for 1,5-hexadiene the reaction proceeds:[1,2]



If 1,4-pentadiene polymerized in a manner analogous to that of 1,5-hexadiene and 1,6-heptadiene, as has been recently proposed for Ziegler-Natta-catalyzed 1,4-perfluoropentadiene,[3] a polymer with methylene-linked 4-membered rings would then result:



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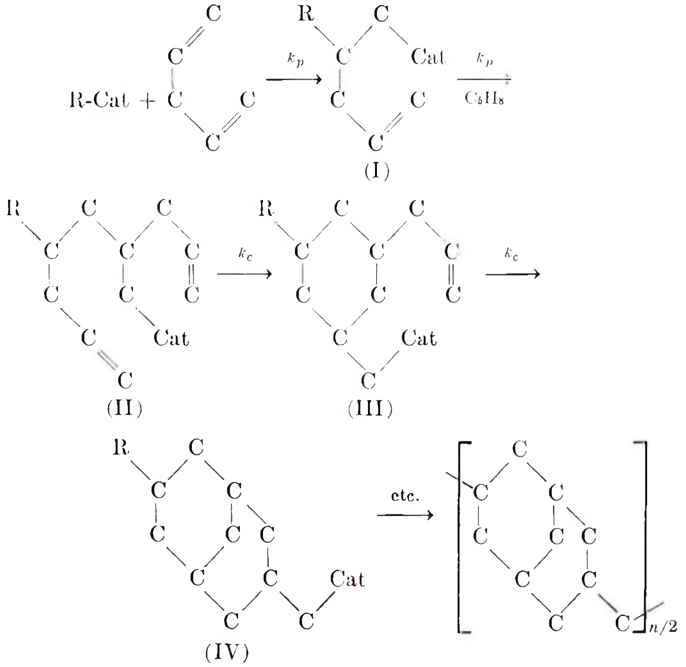
However, the CH_2 stretching frequencies of the 1,4-pentadiene polymers that we have prepared were found to be characteristic of unstrained 6-membered rings rather than of highly strained 4-membered rings.[4] We explain this observation on the basis that the rate of 4-membered ring closure is sufficiently low, owing to associated ring strain, for the following mechanism leading to bicyclo [3.3.1] structures to apply.[5,6] Here R-Cat represents a Ziegler-Natta catalyst, and k_p and k_c are the polymerization and cyclization rate constants, respectively.



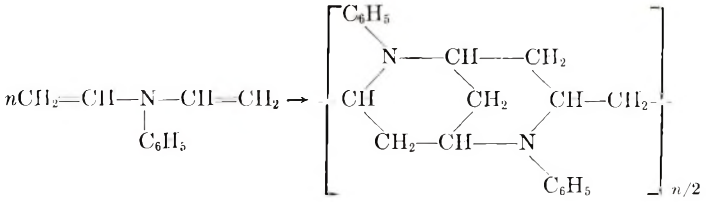
(I)

(II)

(III)

(IV)

This sequence of reaction steps was also independently proposed by Chang and Price for the free-radical polymerization of divinylaniline:[7]



A considerable variety of other cyclopolymerizations which result in bicyclic structures have been previously reported. These include the polymerization of terminal trienes,[8] the polymerization of cyclic dienes,[9-13] and the copolymerization of cyclic vinyl monomers with 1,4 dienes.[14] However, the work by Chang and Price under homogeneous free-radical conditions appears to be the only other published report that bicyclic units may be formed via a homopolymerization mechanism of a simple linear 1,4 diene.

EXPERIMENTAL

Starting Materials

1,4-Pentadiene was obtained from Columbia Chemical Company. It was sold as 98% pure grade but, in fact, on thorough examination by gas-phase chromatography (thermal conductivity detector) no impurities were detected. It was used without further purification.

The solvent, *n*-heptane, was obtained from Matheson, Coleman & Bell, 98–99° grade. It was purified by treatment with sulfuric acid and potassium permanganate–sulfuric acid solution and then dried by refluxing over sodium, filtering, and distilling from a small amount of added aluminum triethyl.

Aluminum triethyl and aluminum diethyl chloride were obtained from Texas Alkyls Inc. and used without further purification. Titanium tetrachloride, purified grade, was obtained from Fisher Scientific Company. The titanium trichloride catalysts, hydrogen-reduced activated (HA) and aluminum-reduced activated (AA), were obtained from the Stauffer Chemical Company and used as received.

Polymerization

By appropriate purge-stream techniques the starting materials were placed in a glass tube under an argon atmosphere in the following order: titanium trichloride catalyst, a previously prepared solution of aluminum alkyl in heptane, a previously prepared solution of monomer in heptane, and any additional heptane desired. With $TiCl_4$ the aluminum alkyl solution was added first. The contents were thoroughly degassed, and the tube was sealed. It was placed in a constant-temperature bath, and the contents were agitated during the reaction period by rocking. The tubes were opened and the contents poured into a large excess of methanol acidified by the addition of 1 vol.-% hydrochloric acid to precipitate the polymer. The mixture was left overnight in a refrigerator. The solids were then separated, washed repeatedly with methanol, and dried under vacuum.

These solids were extracted with heptane at room temperature and gave two fractions. The yield of polymer was taken as the sum of these products. The heptane-insoluble fraction was invariably a brittle powder, substantially insoluble in a variety of common solvents. The heptane-soluble fractions were, depending on reaction conditions, either viscous liquids of very high viscosity or glasses.

The reaction conditions, yields, and polymer solubilities are given in Table I together with the residual unsaturation found by infrared spectroscopy.

Polymer Characterization

Unsaturation in the soluble polymer fractions was measured by quantitative infrared spectroscopy with a Perkin-Elmer Model 21 spectrophotom-

TABLE I

Reaction Conditions, Yield, and Polymer Characteristics

Run no.	Monomer concn.,[a] mole/l.	Catalyst type[b]	Concn. Ti catalyst,[c] mole/l.	Yield polymer, %	Heptane soly., %	Internal[d] double bond per mer	External[e] double bond per mer
1	4.4	A	0.04	56	42	0.08	0.32
2[f]	3.9	A	0.04	44	—	0.05	0.28
3	2.9	A	0.05	54	43	0.12	0.32
4	1.9	A	0.05	47	44	0.20	0.27
5	0.6	A	0.05	42	46	0.20	0.16
6	2.0	A	0.015	16	27	0.25	0.33
7	1.8	B	0.05	37	51	0.18	0.32
8	1.9	C	0.05	36	45	0.06	0.20
9[g]	1.9	C	0.05	46	38	0.09	0.21
10	1.8	D	0.05	19	50	0.04	0.18
11	0.9	D	0.05	8	44	0.04	0.17
12	0.9	D	0.05	14	64	0.04	0.08

[a] The solvent was *n*-heptane.

[b] Catalysts: (A) $Al(Et)_3$–$TiCl_3$ (AA), (B) $Al(Et)_3$–$TiCl_3$ (HA), (C) $Al(Et)_3$–$TiCl_4$, (D) $Al(Et)_2Cl$–$TiCl_4$.

[c] Al/Ti mole ratio was about 1.5 in each run except run 12, in which it was 0.77.

[d] From absorption maximum in range 10.95–10.98 μ, *trans*, and 13.50–13.65 μ, *cis*.[15]

[e] From absorption at 10.34 μ.[15]

[f] From Hoglen.[5]

[g] Temperature 70°C. in all runs except run 9 in which it was 40°C. Reaction time, about 96 hr. in all runs except run 9, in which it was 720 hr.

eter. The method of Morero et al.[15] was employed. The values obtained are given in Table I.

The soluble fractions were examined in carbon disulfide solution. The insoluble fractions were examined in Nujol mulls and potassium bromide pellets. The infrared spectra of the soluble and insoluble portions were found to be qualitatively very similar, and it was concluded that the two fractions differ primarily in that the insoluble fraction is lightly crosslinked.

A number of the polymer fractions, those of runs 10, 11, and 12, were examined in detail in the 2900 cm.$^{-1}$ region with a Perkin-Elmer Model 421 diffraction-grating infrared spectrophotometer. Examination of the CH_2 stretching frequencies in this region permits a determination of the nature of the ring structure.[4–7] The absorptions in this region were found to have a mean of symmetric and asymmetric CH_2 stretching frequencies in the range 2875–2885 cm.$^{-1}$, with a difference between the symmetric and asymmetric values in the range 68–69 cm.$^{-1}$.

The mean of the symmetric and asymmetric frequencies for 4-membered rings is expected to be in the range 2969–2936, with a difference in the range 75–81 cm.$^{-1}$.[4] The corresponding mean absorption previously reported for bicyclo [3.3.1]nonan-3-one is 2893 cm.$^{-1}$ with a difference of 72 cm.$^{-1}$, and, for cyclohexanone, 2905 cm.$^{-1}$ with a difference of 75 cm.$^{-1}$. In the reported work on the polymerization of divinyl aniline the absorptions fell in the range 2892–2916 cm.$^{-1}$.[7] On that basis it was concluded in that work that the polymer did not have a methylene-linked 4-membered ring structure. We have reached the same conclusion with regard to the 1,4-pentadiene polymers.

Crystallinity

None of the polymer fractions obtained exhibited crystallinity on examination by x-ray diffraction spectroscopy (Norelco Model 12021). By comparison, the cyclopolymers of 1,6-hexadiene[2,16] obtained with Ziegler-Natta catalysts are crystalline, but the bicyclopolymers of 1-methylene-4-vinylcyclohexane,[10] 4-vinylcyclohexene,[11] and 2-allyl-1-methylenecyclohexane,[12] prepared with Ziegler-Natta catalysts, are not.

Molecular Weights

The molecular weights of the soluble polymer fractions were determined by Schwarzkopf Microanalytical Laboratories by means of a Mechrolab Model 301 vapor-pressure osmometer. The molecular weights of these fractions were low, with a range corresponding to 17–30 monomer units.

DISCUSSION

As seen in Table I, the heptane-soluble pentadiene polymers which we obtained all had a degree of unsaturation substantially less than the one double bond per mer to be expected if the polymerization took place without cyclization. The best polymer, in the sense of having the lowest residual unsaturation (run 12), had only one double bond per 8 mers.

Additionally, the relatively high solubility of the polymers, 64 wt.-% in run 12, strongly indicates a cyclopolymerization mechanism.

This conclusion is supported by the relatively high densities and softening points of the soluble fractions. These had softening points as high as 75°C. By comparison, a glass transition temperature of −50°C. has been reported for the saturated acyclic analogue, poly-1-pentene.[17] The densities of the soluble fractions ranged from about 0.97 to 0.99 g./cm.^{3}, the higher densities being found for the polymers of lowest unsaturation. By comparison, a density of 0.87 g./cm.^{3} for (isotactic) poly-1-pentene has been reported.[17]

Internal Unsaturation

The polymers all had internal (main-chain) unsaturation in addition to the residual external (pendant-group) unsaturation resulting from uncyclized monomer units. This internal unsaturation was almost entirely *trans* and appears to be due to catalyzed partial isomerization of the monomer to 1,3-pentadiene, which then copolymerizes with the 1,4-pentadiene. The presence of 1,3-pentadiene was verified by vapor-phase chromatographic examination of the vapor phase above the polymerizing solution. The fact that 1,3-pentadiene reportedly homopolymerizes by 1,4 addition, giving *trans* unsaturation with the type of catalyst used,[18] further supports this view. Partial isomerization of 1,4-perfluoropentadiene to the 1,3 isomer with subsequent copolymerization was also reported by Brown et al.[3] Rearrangements of terminal diolefins by Ziegler-Natta catalysts, giving internal double bonds, have been previously reported.

The extent of isomerization depended on the catalyst system used. As measured by the degree of internal unsaturation, isomerization was most severe with aluminum triethyl–$TiCl_3$, less severe with aluminum triethyl–$TiCl_4$, and almost negligible with aluminum diethylchloride–$TiCl_4$.

The softening points of the soluble polymer fractions would be expected to depend on the frequency of interruption of the recurring, stiff, cyclic chain units, as reflected by the degree of internal unsaturation and the related external unsaturation (see later discussion) and therefore, in turn, on the catalyst system. This is summarized in Table II.

TABLE II
Polymer Character[a]

Catalyst system	Internal unsaturation (double bonds per mer)	External unsaturation (double bonds per mer)	Soluble-fraction polymer character
$Al(Et)_3$–$TiCl_3$	0.18–0.25	0.32–0.33	Viscous
$Al(Et)_3$–$TiCl_4$	0.06–0.09	0.20–0.21	Viscous-brittle[b]
$Al(Et)_2Cl$–$TiCl_4$	0.04	0.18	Brittle

[a] Initial monomer concentration approximately 2.0*M*.

[b] Transition near room temperature.

Since the extent of isomerization appears to be somewhat higher for lower initial monomer concentrations (see Table I), the polymerizations compared in Table II all had the same initial monomer concentration.

A similar dependence of the polymer softening point on internal unsaturation was also reported by Brown et al. for poly-1,4-perfluoropentadiene.[3]

External Unsaturation

External unsaturation results in the polymer whenever an intermolecular propagation step takes place before the cyclizations steps are complete. This unsaturation is expected to be less for lower monomer concentrations, since the rate of intermolecular propagation is assumed to be dependent on monomer concentration, while the rate of the cyclization reaction is independent.

The kinetic treatment of this system is much simplified if it is assumed that the rate of closure of the first ring in the bicyclic unit, (II) → (III), is about the same as that of the second ring, (III) → (IV), and that the propagation steps of (II) and (III) to 1,4 diene can be represented by a single k_p. It can be seen that a single residual external double bond will result in the polymer chain when (and only when) a monomer unit adds to either of the chain-end types (II) and (III); similarly, a cyclized unit results in the polymer when (and only when) one of these chain-end types undergoes cyclization. Assuming an intermolecular polymerization rate which is first-order with respect to monomer concentration M and an intramolecular cyclization rate independent of monomer, the fraction f of externally unsaturated polymer units will then be the ratio of the relative rates of the intermolecular step to the combined rates of both inter- and intramolecular steps during the growth of each polymer chain:

$$f = k_pM/(k_pM + k_c) \tag{1}$$

A more general derivation, in which the rate constants for the two ring-closure steps are considered separately, leads to:[6]

$$f = [k_pM/(2k_{c_1} + k_pM)]\,[(k_pM + k_{c_1} + k_{c_2})/(k_pM + k_{c_2})] \tag{2}$$

where k_{c_1} and k_{c_2} are the cyclization rate constants, respectively, for the first and second ring closures in the bicyclic unit. Equation (2) reduces to eq. (1) when $k_{c_1} = k_{c_2} = k_c$. Barton has also recently published some compatible kinetic expressions applicable to 1,4 diene monomers.[19]

To test these relationships with the data on 1,4-pentadiene polymerization, it is necessary first to consider the effect of 1,3-pentadiene copolymerization on the course of reaction. Copolymerization of 1,3-pentadiene would be expected to contribute to external unsaturation whenever it adds to a chain end with pendant double bonds, interrupting the bicyclization sequence. If the cyclization steps are rapid compared with intermolecular propagation, as suggested by the low residual external unsaturation, and if the amount of copolymerization is small, as suggested by the low internal unsaturation, then about one half of the growing chain ends will be found at any time with saturated bicyclic units (IV) and half with only a single pendant double bond (I). Thus, to a first approximation the 1,3-pentadiene mer units, as measured by internal unsaturation, should contribute by an amount equal to one half their number to additional external unsaturation.

In Table III values are given for k_c/k_p obtained from eq. (1) by using the experimental values of external unsaturation corrected for 1,3-pentadiene copolymerization by subtracting one half the internal unsaturation. The values for k_c/k_p obtained in this way are substantially constant, as is to be expected if eq. (1) is correct for this system.

TABLE III

Ratio of Cyclization and Polymerization Rate Constants k_c/k_p

Run. no.	Catalyst	Corrected[a] external double bonds per mer	Mean monomer[b] concn., moles/l.	Calculated[c] k_c/k_p
1	$Al(Et)_3$–$TiCl_3$ (AA)	0.28	3.3	8.4
2	"	0.26	3.0	8.8
3	"	0.26	2.1	6.0
4	"	0.17	1.4	7.0
5	"	0.060	0.49	7.7
6	"	0.21	1.80	7.0
7	$Al(Et)_3$–$TiCl_3$ (HA)	0.23	1.50	5.0
8	$Al(Et)_3$–$TiCl_4$	0.17	1.55	7.6
9	"	0.17	1.45	7.3
10	$Al(Et)_2Cl$–$TiCl_4$	0.16	1.66	8.7
11	"	0.15	0.88	5.0
12	"	0.064	0.87	12.8

[a] Corrected by subtracting one half the internal unsaturation.

[b] Arithmetic mean of initial and final monomer concentrations.

[c] Calculated by eq. (1).

It is interesting that eq. (1) is the same (with other notation) as that derived by Roovers and Smets for the (mono) cyclopolymerization of a 1,6 diene, acrylic anhydride.[20] It is therefore not possible to distinguish between the proposed bicyclic mechanism and a (mono) cyclopolymerization mechanism (for example, the 4-membered ring-closure alternative in the present system) simply by demonstration of the applicability of eq. (1). It is significant, however, that the value of k_c/k_p (in our notation) that was obtained for 6-membered ring closure in the polymerization of acrylic anhydride at 70°C. was about 4.7. This is in excellent agreement with the range of values of k_c/k_p of 5.0–12.8 found in the present work for the assumed closure of 6-membered rings in bicyclic units. This also tends to support the view that 6-membered bicyclic closure, rather than 4-membered monocyclic closure, is taking place in the polymerization of 1,4-pentadiene.

There have been other reports of polymerizations in which substituted 1,4 dienes functionally capable of giving 4-membered ring cyclopolymers did not do so. These are summarized in Table IV. Matsoyan et al.[22] in particular have emphasized that the cyclopolymerization of certain substituted 1,4 dienones does not lead to the formation of the 4-membered rings that would be expected from the inter-intramolecular mechanism typical of 1,6 dienes.

TABLE IV
Reported Structures in the Polymerization of 1,4 Dienes and Related Monomers

Monomer	Reported structure of polymer repeat unit	Monomer units per polymer repeat unit	Ref. no.
1,4-Pentadiene, $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$	[3.3.1]Bicyclic 6-membered rings	2	5,6
Divinyl aniline, $CH_2{=}CH{-}(C_6H_5N){-}CH{=}CH_2$	[3.3.1]Bicyclic 6-membered rings	2	7
1,4-Perfluoropentadiene, $CF_2{=}CF{-}CF_2{-}CF{=}CF_2$	Monocyclic 4-membered rings	1	3
Dialkyl divinyl ketones, $RCH{=}CH{-}CO{-}CH{=}CH{-}R'$	Monocyclic 5- or 6-membered rings, depending on R, R′, plus one residual double bond per ring	2	22
Dibenzalacetone $C_6H_5{-}CH{=}CH{-}CO{-}CH{=}CH{-}C_6H_5$	Monocyclic 5-membered rings	1	21

In sum, it appears that the polymerizations of 1,4 dienes and related monomers apparently do not, in general, follow the same course as those of the higher 1,5 and 1,6 dienes. Because of the relatively low rate of 4-membered ring closure other cyclopolymerization mechanisms become operative, involving in certain cases two monomer units per polymer repeat unit with the formation of bicyclic units, as in the present 1,4-pentadiene polymerization.

The variety of structures indicated in Table IV suggests that this will prove a fruitful area of investigation for the synthesis of new polymer structures. The related variation represented by the copolymerization of 1,4 dienes with single double-bond monomers leading to monocyclic ring-containing polymers has been investigated recently by Butler and his co-workers.[23]

This paper is taken in part from the Ph.D. dissertation of R. A. Shelden, Princeton University, 1963, and in part from the Ph.D. dissertation of J. J. Hoglen, Princeton University, 1961.

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Electrical Conductivity of *N*-Substituted Polyamides

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Synopsis

The electrical volume and surface resistivity of some poly(*N*-chloroalkoxylmethyl caproamides) were measured as a function of voltage at 39% R.H. and under vacuum. The results were compared with non-*N*-substituted polycaproamide. Polarization and depolarization phenomena were observed. The mechanism of conduction is discussed, and important deviations from Ohm's law, observed in dry samples, suggest that charge carriers are injected from the electrodes and that the current–voltage characteristics may be interpreted on the assumption of space-charge-limited current theory.

Electrical properties of polyamides have been the subject of many publications, but they mostly treated their behavior in an a.c. electric field and the relation between relaxation phenomena in this field and the mobility of chain segments, atoms, or groups.[1–6] The influence of thermal treatments,[1] gamma irradiation,[6] and ultraviolet irradiation[7] on the electrical properties of polyamides was also reported. Only in recent years was more attention given to the d.c. conductivity of these polymers. Studies of the electrical conductivity of polyamides have suggested that two mechanisms of conductivity should be considered: ionic[1–6] and electronic.[8–10] The ionic conductivity mechanism was considered mainly on the basis of dielectric loss studies, on the assumption that protons are involved as charge carriers. In only a few cases was a direct evidence of ionic charge transfer obtained.[7,11] In some recent works it was suggested that electronic conductivity[8,10] should be taken into account because of the rather high activation energy of conductivity and observed photoconductivity.[12] Seanor[13–15] has shown that, depending on the temperature range, the electrical conductivity of polyamides may be electronic or ionic. In the publication on the anisotropy of conduction, he[14] has shown that below 90°C. the conductivity is primarily electronic and above 120°C. it is ionic.

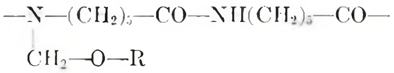
All these investigations show that the electrical conductivity of polyamides is influenced by the temperature, thermal history, and physical structure (crystallinity) of the sample and by the amide group concentration.[16]

Poly(*N*-chloroalkoxy methylcaproamide) shows several interesting properties,[17] especially an increased solubility in common solvents. It seems that *N*-substituted polyamides should have different electrical properties from those of nonsubstituted polyamides. It is the purpose of this paper to give some preliminary results on the influence of different substituents on the nitrogen atom of the polyamide on the d.c. conductivity, with emphasis on the dependence of the electric field strength on conductivity.

EXPERIMENTAL

Materials

Purification of the starting polycaproamide of $\overline{\mathrm{DP}} = 210$, general methods of chloroalkoxymethylation in formic acid, purification, and some properties of the products have been previously reported.[18] These polymers after removal of the chloroalkoxy substituents show a small increase of molecular weight, which may be due to some small degree of branching during the chloroalkoxymethylation. The general formula of the polycaproamides obtained is



$$\underset{\displaystyle CH_2-O-R}{-N}-(CH_2)_5-CO-NH(CH_2)_5-CO-$$

where the substituents R and the corresponding sample designations are $-(CH)_3$ (MM), $-(CH_2)_2Cl$ (M3), $-CH-(CH_2Cl)_2$ (M2), and $-CH_2$-CCl_3 (M6), respectively. The chlorine content in the samples, as a measure of degree of substitution, is given with some electrical data in Table I.

All measurements were carried out with thin films cast from 5 to 10 wt.-% solutions in 60:40 (by volume) chloroform–methanol mixtures. After solvent evaporation at normal pressure the samples were dried at 60°C. at reduced pressure (4–5 mm. Hg). The films were cast directly on quartz or mica plates with previously vacuum-deposited metal electrodes or on glass plates and then transferred (after drying) onto support plates with electrodes. No changes in the measured properties were observed with these two different methods of sample treatment. The films of the unsubstituted polycaproamide were obtained from a 5% wt. solution in 2-chloroethanol. After evaporation of the solvent at 80–100°C. the films were dried at 100°C. under reduced pressure (5 mm. Hg).

Electrical Conductivity Measurements

The measurements of volume and surface resistivities were carried out in the same electrical system and the same general methods of sample preparation as in the previous works.[19] In all our experiments vacuum-deposited electrodes and guard rings of aluminum, gold, and silver were applied. With suitable treatment in vacuum the electrodes were rather stable, and they did not peel off from the sample's surface.

TABLE I

Volume and Surface Resistivities of *N*-Chloroalkoxymethyl-Substituted Polyamides at 25°C., R.H. = ~37%

Substituent R	Sample	Chlorine content, %	Volume resistivity, ohm.-cm.	Surface resistivity, ohm/cm.^{2}	Electrodes
$—CH_3$	MM	—	1.3×10^9	6×10^9	Au–Au
$—CH_2CH_2Cl$	M3-5	6.65	1.8×10^{10}	2×10^{10}	Au–Al
	M3-6	5.40	6×10^8	2×10^9	Au–Al
$—CH_2CCl_3$	M6-6	<6	2×10^9	3×10^{10}	Al–Al
	M6-2	18	1.5×10^{10}	4×10^{11}	Al–Al
			1.4×10^{10}	1.5×10^{11}	Ag–Al
			1.0×10^{10}	3.6×10^{11}	Au–Al
	M6-1	21	1×10^{10}	1×10^{11}	Al–Al, Au–Al
	M6-4	31.9	1×10^{11} 2.5×10^{11}	2×10^9	Ag–Al, Au–Al
$—CH—(CH_2Cl)_2$	M2-5	<6	1×10^9	3.5×10^9	Ag–Al, Au–Al
	M2-6	12	1.5×10^8	1×10^8	Ag–Al, Au–Al
	M2-10	16	2×10^8	2×10^8	Ag–Al, Au–Al
	M-2-9	>20	8×10^8	2×10^8	Ag–Al, Au–Al
—	Poly(caproamide)		8×10^7	3×10^7	Au–Al, Ag–Al

Before vacuum deposition of the electrodes the samples were in a vacuum container for 24 hr. This treatment in high vacuum allows us to obtain a constant amount of solvent in the sample, and further treatment in vacuum did not introduce weight changes in the specimens investigated. All electrical measurements were made in an atmosphere of known relative humidity and under vacuum better than 10^{-3} torr.

The conductivity cell was immersed in a thermostat bath controlled at 25 ± 0.1°C. The current dependence on voltage was determined after at least 20 min., when potential was applied. The current I dependence on voltage V was measured in the same system as that used for the determination of volume resistivity.

RESULTS

The current intensity I of the prepared films was measured at constant temperature and under constant low-humidity conditions. Some experiments were repeated in vacuum. Sometimes in the first run the current intensity was higher than in the second run if not enough time was taken between measurements. However, after a number of experiments at different voltages reproducible current values were obtained. Typical current–voltage characteristics for sample M6-4 with 31.9% chlorine content, supplied with Au–Au electrodes, is shown in Figure 1. On increasing of the voltage the plots of log I versus log V were linear, but in a few cases, especially at low degrees of substitution, some hysteresis during an increase or decrease of voltage was found.

On the basis of measured current, voltage, sample thickness, and dimensions the values of volume and surface resistivities were calculated for the

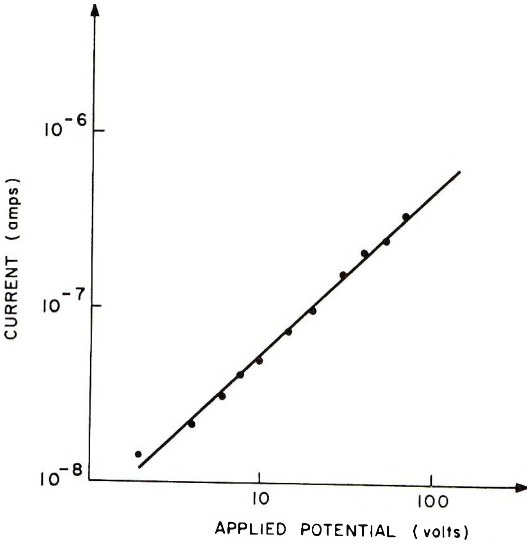


Fig. 1. Current–voltage characteristics for sample M6-4 poly(N-chloroalkoxymethyl caproamide); 25°C., relative humidity 37%, sample thickness 20 μ.

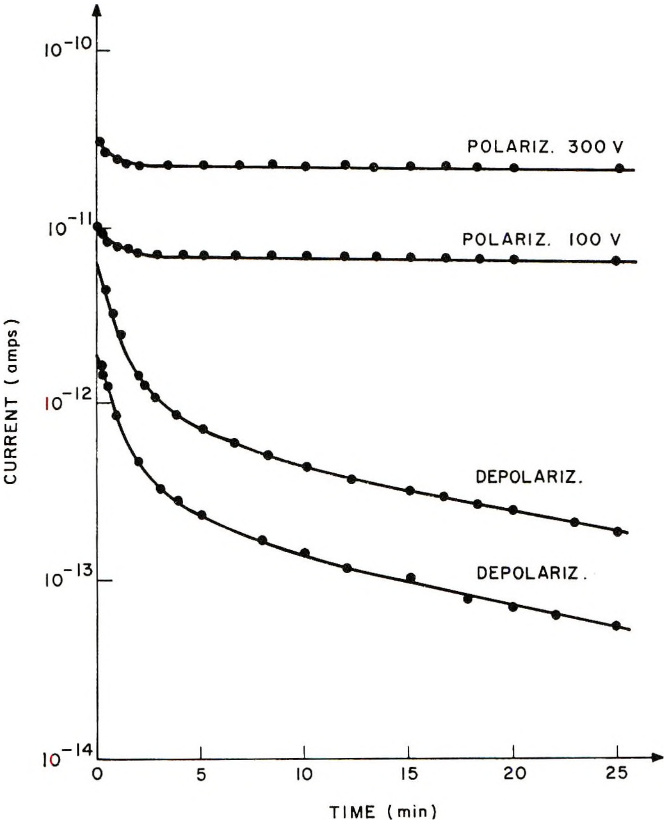


Fig. 2. Polarization and corresponding depolarization curves for sample M6-1 poly-(*N*-chloroalkoxymethyl caproamide); 25°C., relative humidity 37%, sample thickness 5 μ. Applied voltage values indicated on polarization curves.

above-mentioned *N*-substituted polyamide films. These data are given in Table I. A similar set of experiments carried out in vacuum at 25°C. showed that the specific resistivity of all investigated samples is 3–4 orders of magnitude higher.

An independent set of measurements was performed to investigate the decrease of current at constant voltage (polarization) at 25°C. At this temperature it was also possible to measure the decay of the back emf when the potential was switched off (depolarization). One of the typical polarization and depolarization curves, obtained for the sample M6-1, is presented in Figure 2. No simple relation between current intensity *I* and time *t* for the polarization and depolarization curves was found.

DISCUSSION

The results presented above show that at R.H. = 39% the resistivity of poly(*N*-chloroalkoxymethylated caproamides) is larger than that of the starting polycaproamide, for which the resistivity value is in agreement with the data given in the literature;[20] however, the differences in volume resistivity are not very large. The surface resistivities measured in the same conditions for all *N*-substituted polycaproamides are much higher than these obtained for pure polycaproamide film. It shows that the substitution of amide hydrogen with an aliphatic group decreased markedly the hydrogen bonding formation, not only between neighboring chains, but also with atmospheric water, which influences mostly the surface conductivity. The application of metal electrodes with different work functions does not influence in a distinct manner the volume resistivities measured at R.H. = 39%.

The source of charge carriers in the investigated substance and under the given experimental conditions are most probably the carbonyl groups of the amide linkages (π electrons of the amide group), as was suggested in the case of proteins[21,22] and nylon 66.[14,15] The creation of charge carriers probably occurs between two polymer chains linked by a hydrogen bond through the assistance of chain rotation and oscillation of the amide proton in the two positions of minimum energy in the hydrogen-bonded amide linkage. The transfer of charge carrier occurs in an activated hopping process, in which the activation energy is controlled by the distance between two amide groups of different polymer chains and leads to the anisotropy of conductivity which was found by Seanor[14] in oriented nylons. All these facts indicate the importance of hydrogen bonding for charge transfer in polyamides.

When the number of hydrogen bonds in the system is reduced due to a substitution of hydrogen atoms at nitrogen by the aliphatic groups, an increase of the resistivity should be expected according to our experimental results and the results given by Boyd.[3] This influences both the creation and transfer of charge carriers.

Since the conductivity is rather low, even in the range of medium relative humidity in which these investigations were carried out, it is not possible to determine exactly whether it is ionic or electronic; however, the electronic part seems to be more important. The role of water in the conductivity of polyamides is not simple, because water can act as an impurity of high electric constant as well as a plasticizer. Water adsorbed or absorbed in polyamides can extend the network of hydrogen bonds, act as an electron donor [in this case the mechanism of conductivity could be changed completely],[23,24] or facilitates self-ionization of amide groups; moreover, water itself could be taken as a possible source of protons. However, at room temperature below the α glass transition the self-ionization process, which occurs with a rather low activation energy, seems to be not very important. In this case, even though the self-ionization process of the nonsubstituted amide group in the polymer chain creates protons, their mobility is low and they can hardly contribute to the charge transfer. This follows also from Seanor's discussion[15] of protonic conductivity in nylon 66 above 120°C. At higher temperatures the proton mobility is determined by the local mobility of polymer chains, and the activation

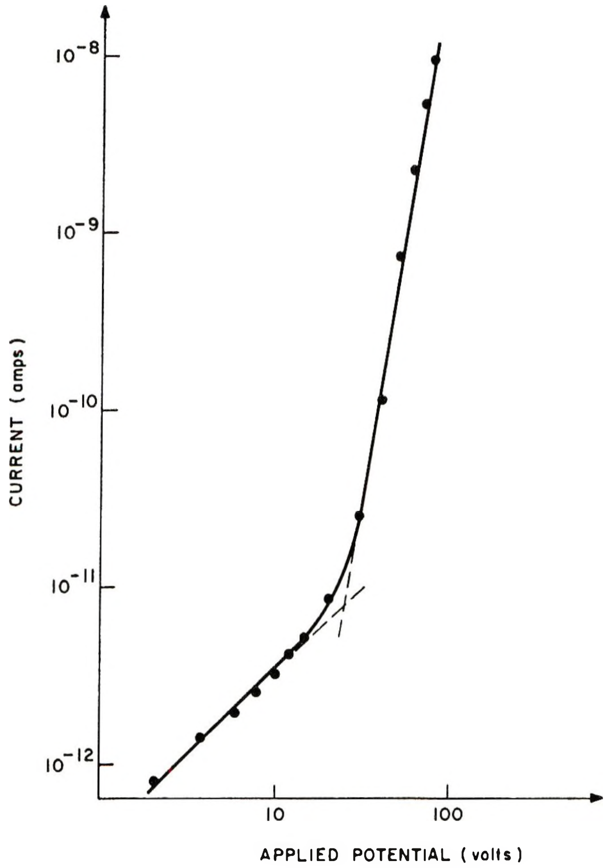


Fig. 3. Current–voltage characteristics for sample M2-5 poly(*N*-chloroalkoxymethyl caproamide); 25°C., under vacuum, sample thickness 15 μ.

energy of charge carrier transport is low. This leads to charge transfer by protons moving, probably, from chain to chain in a tunnelling process between the rotating chains, rather than to an activated hopping process.

In the absence of a relation between the mass of water absorbed (in the above-given conditions of relative humidity) and the electrical conductivity of our samples we shall not discuss further the possibility of application of equations derived by Hearle,[25] Rosenberg,[26] and other workers[27,28] that relate the conductivity value σ with the mass m of adsorbed water. Since the diffusion of water vapor into polyamides is non-Fickian in nature, and the distribution of amide groups in *N*-substituted polyamides is random, one would expect to find water clusters between the polymer chains; this further complicates the question under discussion.

With all the poly(*N*-chloroalkoxymethyl caproamides) investigated and at the given voltage range and relative humidity we did not observe deviations from Ohm's law (Fig. 1). However, under vacuum with well-outgassed samples a different dependence on the electric field was found. The current–voltage characteristics (log I versus log V curves) consisted of two distinct straight lines with different slope coefficients n. The typical current–voltage characteristics obtained for the sample M2-5 with 1.47% chlorine content is shown in Figure 3. This figure shows an ohmic part ($n = 1$) and a nonohmic part ($n = 6.4$) of the current–voltage characteristics. Such a current–voltage characteristic cannot be interpreted by assuming ionic conductivity. It differs from the log I versus log V obtained in the case of ionic conductivity, which would lead to deviations from Ohm's law, described by an equation of the form $I = A \sinh bV$, where A and b are constants.

The relation between current I and voltage V, as presented in Figure 3, may be described by the general equation $I = AV^n$, where A and n are constants that depend on the dielectric material, the electrode material, and the range of applied voltage. Similar current–voltage characteristics were obtained by us in the case of other polymers.[29,30] The assumption of charge carrier injection from the electrodes and their trapping in the material leads to appearance of space-charge-limited currents (SCLC), which allow us to expect a current–voltage relation of the type given in Figure 3. A more detailed analysis of current–voltage characteristics, obtained under vacuum, of different poly(*N*-chloroalkoxymethyl caproamides) and nylon 6 will be presented in a forthcoming publication.

Assuming only intrinsic conductivity, if mobile carriers are to be obtained (the electrons and holes or the positive and negative ions), they must be first separated by sufficiently large distances to overcome the coulombic attraction. The electronic conduction depends on the correct spatial configuration of two polymer chains. Thus, both electronic and ionic conductivities show dependence on the molecular motion and recombination rate. At low temperature (below T_g) the ionic conductivity seems to be unimportant because of a sufficiently high rate of recombination. The concentration of intrinsic electronic charge carries at constant temperature does not change, and the steep sectors in the current–voltage characteristics are probably due to the injection of charge carriers from the electrode and their trapping. The nature of traps and the mechanism of charge carrier injection (Schottky emission or thermoionic emission) is still uncertain, and some suggestions concerning this problem may be reached by actual investigation of the thermally stimulated currents and thermal activation energy E_a dependence on voltage and sample thickness, such as we made with other polymers.[31,32]

The typical polarization curves of two different voltages applied at 39% R.H. and at 25°C., given in Figure 2, show that after 25 min. the current reached a steady value (only a very small decrease of this current intensity was found over very long time periods). The depolarization curves exhibit a continuous decrease with time. No simple relation between current intensity I and time t for all polarization and depolarization curves could be obtained. In some cases, especially at the beginning of the polarization curves, the product $I \times t$, was constant, but it was not a general relation.

Supplemental experiments that are being carried out on well degassed samples under vacuum and in different gases will supply more data on polarization and depolarization phenomena in the *N*-substituted and nonsubstituted polycaproamides.

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Preparation of Polymers Containing Sugar Residues

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Synopsis

The synthesis of five different polymers containing sugar residues on side chain is described. 1-*O*-Methacryloyltetra-*O*-acetyl-D-glucose, 1-*O*-methacryloyltetra-*O*-acetyl-D-galactose, and 6-*O*-methacryloyltetra-*O*-acetyl-D-glucose were prepared and polymerized. The polymethacrylates obtained were converted into water-soluble polymers by removing the acetyl protective group with sodium methoxide. 6-*O*-Methacryloyldiisopropylidene-D-galactose was also prepared and polymerized. The isopropylidene protective group was removed by acid hydrolysis. Poly(*N*-methacryloylglucosamine) was prepared directly by the polymerization of *N*-methacryloyl-D-glucosamine without the use of any protective group.

INTRODUCTION

Some polymers containing sugar residues on the side chain have already been synthesized and show an expected hydrophilicity and high reactivity of the hemiacetal group: examples are poly(6-*O*-methacryloyl-D-galactose), poly(6-*O*-acryloyl-D-galactose),[1] poly(1-*O*-methacryloyl-L-sorbose),[2] and poly(3-*O*-methacryloyl-D-glucose).[3,4]

To obtain linear polymers containing sugar residues it is necessary to prepare monovinyl derivatives of sugar. Therefore, all the hydroxy groups but one must be selectively protected before the introduction of an unsaturated group. The isopropylidene group has so far been used in this way in the synthesis of such polymers, as described in the literature. In this paper the acetyl group was used as the protective group, and three kinds of new polymer were obtained.

The present work was undertaken to prepare backbone polymers susceptible to grafting by the ceric ion method. Our previous studies of graft copolymerization onto cellulose[5] and poly(vinyl alcohol)[6] by the ceric ion method have shown that grafting is likely to occur at the hemiacetal or 1,2 glycol unit. Therefore, the polymers obtained in this work are thought to be susceptible to grafting by the ceric ion method. The results of the grafting will be published later.

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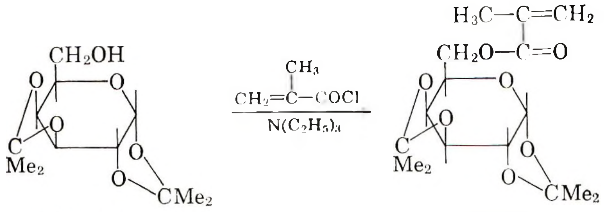
RESULTS AND DISCUSSION

Monomer Synthesis

Each monomer was prepared as follows.

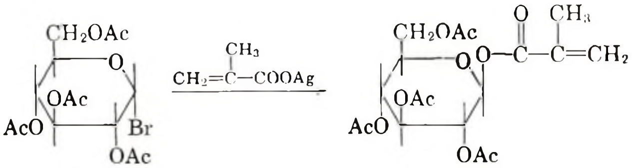
(*a*) 1,2:3,4-Di-*O*-isopropylidene-6-*O*-methacryloyl-D-galactose, or 6-MDIGa (II), was recently prepared by Bird et al.[1] in the reaction of 1,2:3,4-di-*O*-isopropylidene-D-galactose, or DIGa (I),[7a] and methacrylic anhydride, but in this study 6-MDIGa (II) was prepared in relatively good yield by the reaction of DIGa (I) and methacryloyl chloride in the presence of triethylamine as hydrogen chloride acceptor:



DIGa (I) 6-MDIGA (II)

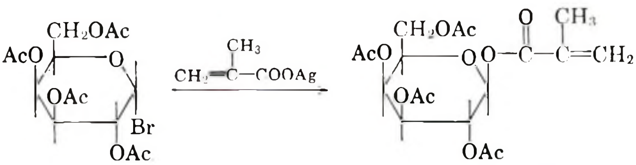
DIGa (I) was prepared by the reaction of galactose and acetone in the presence of zinc chloride.

(*b*) 1-*O*-Methacryloyl-2,3,4,6-tetra-*O*-acetyl-D-glucose, or 1-MTAGlu (IV), was prepared in the reaction



(III) 1-MTAGlu (IV)

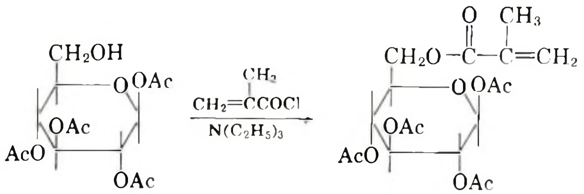
(*c*) 1-*O*-Methacryloyl-2,3,4,6-tetra-*O*-acetyl-D-galactose, or 1- MTAGa (VI), was prepared in the reaction



(V) 1-MTAGA (VI)

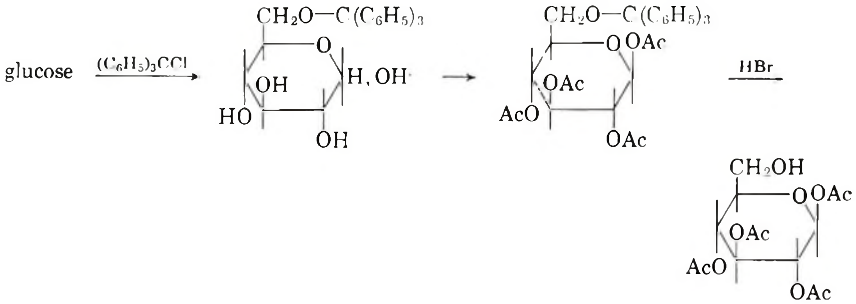
1-MTAGlu (IV) and 1-MTAGa (VI) were prepared in the reaction of the corresponding bromides (III) and (V) with silver methacrylate, respectively. An attempt to esterify the bromides (III) and (V) with sodium methacrylate was unsuccessful.

(*d*) 1,2,3,4-Tetra-*O*-acetyl-6-*O*-methacryloyl-D-glucose, or 6-MTAGlu (VIII), was obtained in the reaction of TAGlu (VII) and methacryloyl chloride in the presence of triethylamine:

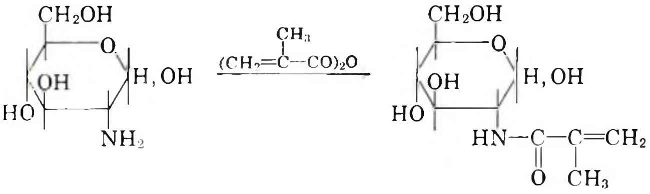


TAGlu (VII) 6-MTAGlu (VIII)

TAGlu (VII) was prepared by the usual method:[8]



(*e*) *N*-Methacryloyl-D-glucosamine, or *N*-MGA (IX), was prepared in the reaction



N-MGA (IX)

The methacrylamide (IX) was prepared by a method similar to the synthesis of *N*-acetyl-glucosamine, described in the literature.[9]

The monomers obtained in (*a*) to (*e*) were characterized by elemental analysis and infrared spectra. The melting points and specific rotations are given in Table I.

TABLE I

Yields, Melting Points, and Specific Rotations of Monomers

Monomer	Yield, %	M.p., °C.	$[\alpha]_D^{20}$ in chloroform
6-MDIGa	65	62.5–63	−43.8
6-MTAGlu	83	118–119	+24.1
1-MTAGa	62	98–100	+19.4
1-MTAGlu	52	102–104.5	+9.8
N-MGA	37	193–194 (decmpd.)	+54.5[a]

[a] In water.

Polymerization

Each monomer was polymerized in benzene, except *N*-MGA, which was polymerized in DMF, at 60°C. with AIBN as initiator. The intrinsic viscosities $[\eta]$ and specific rotations $[\alpha]_D^{20}$ of the polymers are given in Table II. The high intrinsic viscosity of p(6-MDIGa) in comparison with those of other polymers may be explained by the fact that chain transfer to the acetyl or hydroxy group is more likely than chain transfer to the isopropylidene group.

TABLE II
Intrinsic Viscosities and Specific Rotations of Polymers

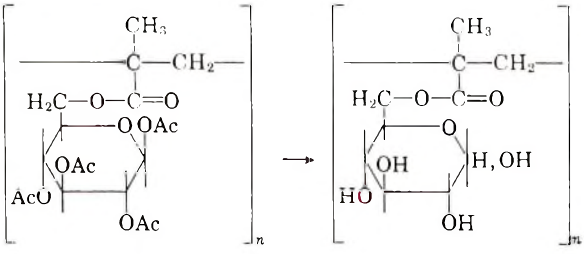
Polymer	$[\eta]^a$	$[\alpha]_D^{20\,b}$
p(6-MDIGa)	0.48–1.15	−51.8
p(6-MTAGlu)	0.28	+27.2
p(1-MTAGlu)	0.30	+1.2
p(1-MTAGa)	0.20	+2.2
p(*N*-MGA)	0.20^c	$+83.5^c$

[a] In benzene at 30°C.
[b] In chloroform.
[c] In water.

Copolymers of MMA and 6-MDIGa or 6-MTAGlu were also prepared. The copolymer composition was determined on the basis of the NMR spectrum or the specific rotation. The two independent methods gave consistent values within the range of experimental error. The compositions of the copolymers were 12 mole-% 6-MDIGa and 88% MMA, and 30% 6-MTAGlu and 70% MMA, respectively.

Removal of Protective Group

Removal of the acetyl group from p(6-MTAGlu), p(1-MTAGlu), and p(1-MTAGa) was carried out at room temperature in chloroform–methanol solution with sodium methoxide catalyst, giving poly(6-methacryloyl-D-glucose), poly(1-methacryloyl-D-glucose), and poly(1-methacryloyl-D-galactose), respectively.



The solution became heterogeneous as the reaction proceeded, owing to the insolubility of the deacetylated polymers in the solvent. After 30 min. no further appreciable change was observed. Deacetylated polymer

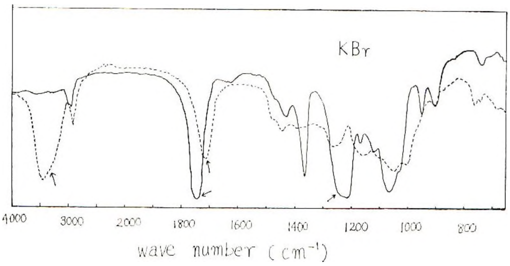


Fig. 1. Infrared spectra: (——) p(6-MTAGlu); (- - -) p(6-MGlu).

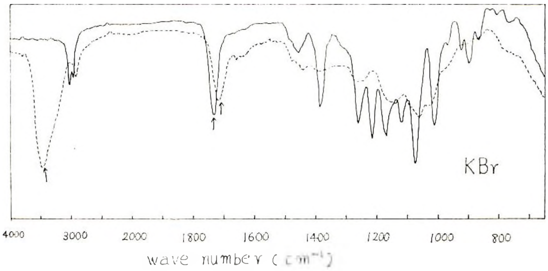


Fig. 2. Infrared spectra: (——) p(6-MDIGa); (- - -) p(6-MGa).

was isolated by precipitation with methanol. Typical infrared spectra of the polymer before and after the reaction are shown in Figure 1. The appearance of the strong absorption of —OH at 3500 cm.$^{-1}$ and the disappearance of the absorption of the acetyl group at 1220 cm.$^{-1}$ are evidence of the elimination of the acetyl group. The shift of the absorption of carbonyl to a lower frequency is interpreted as partly the effect of hydrogen bonding and partly the change of ester from acetate to methacrylate.

The removal of the isopropylidene group was carried out by the method of Bird et al.[1] Infrared spectra before and after the reaction are shown in Figure 2. A quantitative determination of the reducing power with sodium hypoiodite[10] gave a value of 90–92%. Deacetonation or deacetylation of the corresponding copolymers was carried out by the same method as

TABLE III

Intrinsic Viscosities and Specific Rotations of Polymers

Polymer	$[\eta]$[a]	$[\alpha]_D^{20}$[b]
Poly(6-methacryloyl-D-galactose)	0.54–1.30	+65
Poly(1-methacryloyl-D-glucose)	0.30	+1.4
Poly(1-methacryloyl-D-galactose)	—[c]	+32.7
Poly(6-methacryloyl-D-glucose)	0.24	+77.8
Poly(*N*-methacryloyl-D-glucosamine)	0.20	+83.5

[a] In water at 30°C.

[b] In water.

[c] The curve of η_{sp}/c versus c shows a behavior similar to that of polyelectrolytes.

described above and was confirmed by the infrared spectrum. The intrinsic viscosities and specific rotations of the deacetylated or deacetonated polymers are given in Table III. All these polymers are soluble in water and have strong hydrophilicity.

EXPERIMENTAL

Monomer Synthesis

1-*O*-Methacryloyl-2,3,4,6-tetra-*O*-acetyl-D-glucose. 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide (21.3 g.), which was prepared according to the literature,[7b] was dissolved in anhydrous benzene. The silver methacrylate (10 g.) was added, and the mixture was refluxed for 1 hr. After removal of the solid substance by filtration benzene was evaporated under reduced pressure, to give a viscous liquid. Recrystallization from cyclohexane gave the pure product (11.2 g.): yield 52%, m.p. 102–104.5°C., $[\alpha]_D^{20}$ +9.8 (in chloroform).

ANAL. Calcd. for $C_{18}H_{24}O_{11}$: C, 51.92%; H, 5.81%. Found: C, 51.92%; H, 5.94%.

1-*O*-Methacryloyl-2,3,4,6-tetra-*O*-acetyl-D-galactose. 2,3,4,6-Tetra-*O*-acetyl-D-galactopyranosyl bromide (8.0 g.), which was prepared in the same way as 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl bromide, was dissolved in anhydrous benzene, and silver methacrylate (3.8 g.) was added. The mixture was stirred with a magnetic stirrer for 1 hr. at room temperature. After removal of the solid substance by filtration benzene was evaporated under reduced pressure, to give a viscous liquid. Recrystallization from a cyclohexane–ether mixture gave the desired product (5.0 g.); yield 62%, m.p. 98–100°C., $[\alpha]_D^{20}$ −43.8 (in chloroform).

ANAL. Calcd. for $C_{18}H_{24}O_{11}$: C, 51.92%; H, 5.81%. Found: C, 52.27%; H, 5.92%.

1,2,3,4-Tetra-*O*-acetyl-6-*O*-methacryloyl-D-glucose. 1,2,3,4-Tetra-*O*-acetyl-D-glucose (4.7 g.)[8] was dissolved in benzene (25 ml.), and methacryloyl chloride (1.6 g.) was added. The solution was cooled to 0–5°C. with an ice bath, and the triethylamine (1.5 g.) was added dropwise to the stirred solution. The solution was stirred for a further 2 hr. at room temperature. Triethylamine hydrochloride was removed by filtration, and the filtrate was concentrated under reduced pressure, giving a viscous substance. Recrystallization from a chloroform–*n*-hexane mixture gave the desired product; yield 83%, m.p. 118–119°C., $[\alpha]_D^{20}$ +24.1 (in chloroform).

1,2,3,4-Di-*O*-isopropylidene-6-*O*-methacryloyl-D-galactose. 1,2:3,4-Di-*O*-isopropyline-D-galactose (10.2 g.)[7a] was dissolved in anhydrous ether (40 ml.), and triethylamine(4.0 g.) was added as hydrogen chloride acceptor. The solution was cooled to 0–5°C. with an ice bath, and then methacryloyl chloride (4.1 g.), which was diluted with an equal volume of anhydrous ether, was added dropwise to the stirred solution for 40 min. The solution was stirred for a further 1 hr. to allow the reaction to proceed.

The precipitate was removed by filtration and was washed with ether. After the ether evaporated under reduced pressure, *n*-hexane was added, and a small quantity of polymer that seemed to be produced during the reaction was precipitated and filtered off. *n*-Hexane was then evaporated, to give a viscous liquid. Recrystallization from a methanol–water mixture gave the pure product (8.4 g.); yield 65%, m.p. 62.5–63.5°C., $[\alpha]_D^{20}$ -43.8 (in chloroform).

N-Methacryloyl-D-glucosamine

Glucosamine hydrochloride (4.3 g.) was dissolved in a mixture of water (100 ml.) and methanol (10 ml.), and then Amberlite IRA-400 (CO_3^{2-} form) anion-exchange resin (120 ml.) was added. After cooling of the mixture to 0–5°C. methacrylic anhydride (4.0 g.) was added. The mixture was stirred for 3 hr. The Ion-exchange resin was removed by filtration, and the filtrate was concentrated with a rotary evaporator at a temperature below room temperature. Above room temperature gelation seemed to occur. The remaining solid substance was dissolved in a small quantity of water, and then ethanol was added. Ether was then added, until the solution became slightly turbid. Repetition of this treatment gave the pure product; yield 37%, m.p. 193–194°C. (decomposition).

ANAL. Calcd. for $C_{10}H_{17}O_6N$: C, 48.58%; H, 6.93%; N, 5.67%; Found: C, 48.38%; H, 7.12%; N, 5.60%.

Polymerization

Homopolymers of five monomers obtained were prepared by solution polymerization in benzene or dimethylformamide in nitrogen atmosphere with azobisisobutyronitrile as initiator at 60–70°C. Copolymers of 1,2:3,4-di-*O*-isopropylidene-6-*O*-methacryloyl-D-galactose or 1,2,3,4-tetra-*O*-acetyl-6-*O*-methacryloyl-D-glucose with methyl methacrylate were also prepared under the same conditions.

Deacetylation Reaction of Polymers

Poly(1-*O*-methacryloyl-2,3,4,6-tetra-*O*-acetyl-D-glucose) was dissolved in chloroform, and an equal volume of methanol solution containing sodium methoxide as catalyst was added. The mixture was allowed to react with stirring at room temperature for 30 min., during which time a white precipitate separated out.

The mixture was then poured into methanol. The deacetylated polymer was filtered, washed thoroughly with methanol, dried, and obtained in almost quantitative yield.

The deacetylation reaction of poly(1-*O*-methacryloyl-2,3,4,6-tetra-*O*-acetyl-D-galactose) and poly(1,2,3,4-tetra-*O*-acetyl-6-*O*-methacryloyl-D-glucose) were carried out by the method described above. $(C_{10}H_{16}O_7)_n$ requires C, 48.38% and H, 6.50%. Found: for poly(1-methacryloyl-D-glucose):

C, 47.7%; H, 6.38%; for poly(1-methacryloyl-D-galactose): C, 47.0%; H, 6.56%; and for poly(6-*O*-methacryloyl-D-glucose): C, 47.0%; H, 6.81% (all three dried over phosphorus pentoxide for 3–4 days at 0.2 mm. Hg).

Deacetylation Reaction of Polymer

P(6-MDIGa) was dissolved in formic acid, and water was gradually added as the reaction proceeded. The solution was stirred for 4 hr. with a magnetic stirrer at 60°C. After dialysis, to remove formic acid, the solution was freeze-dried (insoluble materials, if present, were filtered off before drying).

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Copolymerization of Vinylsilanes with Styrene

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Synopsis

New vinylsilanes (M_2), i.e. phenylvinylsilane (I), allylmethylsilane (II), allylphenylsilane (III), and *p*-vinylphenylmethylsilane (IV), were prepared and copolymerized with styrene (M_1). The monomer reactivity ratios were $r_1 = 5.7$ and $r_2 = 0$, $r_1 = 36$ and $r_2 = 0$, $r_1 = 29$ and $r_2 = 0_1$, and $r_1 = 0.91$ and $r_2 = 1.1$, respectively. From the results of infrared and NMR spectra it was indicated that the vinylsilanes participated in copolymerization in the form of a vinyl type of polymerization and not in the form of a hydrogen-transfer type of polymerization. The reaction of copolymer with alcohols and methyl methacrylate and appropriate catalysts was investigated.

INTRODUCTION

A number of studies of the synthesis and polymerization of vinylsilanes and copolymerization of them have been presented.[1-4] According to Scott and Price,[3] the reactivity ratios of triethoxyvinylsilane and trimethylvinylsilane (M_2) with styrene (M_1) were an r_1 of 22 and 26 and an r_2 of 0, respectively. *p*-Vinylphenyldimethylsilane (M_2) was copolymerized with styrene (M_1), and the copolymerization parameters were obtained[4] as $r_1 = 0.56$, $r_2 = 1.00$, $Q_2 = 0.97$, and $e_2 = -0.04$. Further, the ionic polymerization of trimethylvinylsilane with alkyllithium catalyst was reported by Nametkin et al.,[5] and high molecular weight polymers were obtained.

Vinyldimethylsilane and allyldimethylsilane were polymerized, through polyaddition of a silicon-hydrogen bond to an unsaturated bond, with a platinum catalyst.[6] *n*-Octyltrichlorosilane was obtained by heating a mixture of trichlorosilane and 1-octene in the presence of diacetylperoxide.[7] An azo compound also was used as initiator.[8]

In the present investigation new monomers of four vinylsilanes were prepared through Grignard reaction followed by reduction with lithiumaluminum hydride, and the homopolymerization and copolymerization with styrene were carried out with azobisisobutyronitrile (AIBN) as radical initiator at 60°C.; r_1 and r_2 values were estimated.

The structural analysis of the copolymers by means of infrared and NMR spectra showed there was no addition of SiH to the double bond. Moreover, the reactions between the copolymer and various alcohols and the reaction of addition of methyl methacrylate to copolymer were carried out, and the reaction condition and effect of catalyst were examined qualitatively by infrared analysis.

EXPERIMENTAL

Syntheses of Monomers

Phenylvinyldichlorosilane was synthesized in the Grignard reaction from vinyltrichlorosilane rather than from phenyltrichlorosilane, because the latter produced an unfavorable by-product. Phenylvinylsilane (I) was prepared from phenylvinyldichlorosilane by reduction with lithiumaluminum hydride. Allylmethylsilane (II), allylphenylsilane (III), and *p*-vinylphenylmethylsilane (IV) were prepared by similar methods. The results are summarized in Table I.

Phenylvinyldichlorosilane. Phenylvinyldichlorosilane was prepared from vinyltrichlorosilane and phenylmagnesium bromide by Momonoi's procedure; b.p. 95–98°C. at 9 mm. [lit. (9): b.p. 103°C. at 17 mm.], yield 46%.

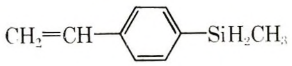
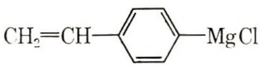
Phenylvinylsilane (I). To a stirred slurry of 4.8 g. (0.126 mole) of lithiumaluminum hydride in 25 ml. of dry ether was added dropwise a solution of 50.8 g. (0.25 mole) of phenylvinyldichlorosilane in 50 ml. of dry ether over a period of 1 hr. The reaction mixture was then heated slightly, and stirring was continued for several hours; then the mixture allowed to stand overnight. The reaction mixture was poured onto crushed ice, to hydrolyze the inorganic halide. The aqueous phase was separated, and the ether layer was dried over anhydrous sodium sulfate. After removal of ether by distillation the liquid residue was fractionated at reduced pressure; the fraction boiling at 44–47°C. at 9 mm. was collected and redistilled. The yield of phenylvinylsilane boiling at 48.1–49.2°C. at 10 mm. was 15.0 g. (47%).

Allylmethyldichlorosilane. This compound was prepared from methyltrichlorosilane and allylmagnesium bromide by Momonoi's procedure. The yield of allylmethyldichlorosilane boiling at 117–118°C. was 34% [lit.[10] 117–118°C.].

Allylmethylsilane (II). To a stirred slurry of 17 g. (0.45 mole) of lithiumaluminum hydride in 80 ml. of anhydrous dibutyl ether was added dropwise a solution of 82 g. (0.53 mole) of allylmethyldichlorosilane in 180 ml. of the purified dibutyl ether over a period of 1 hr. The reaction mixture was then refluxed and stirred for 1 hr., after which the product was distilled directly from the reaction mixture. The crude product distillate was washed, to be free of acid, with cold water, dried over anhydrous sodium sulfate, and then fractionated at atmospheric pressure. Allylmethylsilane was obtained; b.p. 47.6–47.8°C., yield 17 g. (30%).

Allylphenyldichlorosilane. The synthesis of this material was similar to the preparation of allylphenyldichlorosilane. The crude product boiling at 80–90°C. at 4 mm. was redistilled under reduced pressure, yielding allyl-

TABLE I
Syntheses of Monomers

Monomer	Starting chlorosilane	Grignard reagent	Yield of Grignard reaction, %	Yield of reduction reaction, %	B.p., °C., and pressure, mm. Hg	Elemental analysis, % C, calcd., found	Elemental analysis, % H, calcd., found	Identification of SiH_2 IR, cm.$^{-1}$	NMR, τ
$CH_2{=}CHSiH_2Ph$ (I)	$CH_2{=}CHSiCl_3$	PhMgBr	46	47	48.1–49.2, 10	71.57, 71.41	7.51, 7.22	2250, 937, 845	5.44, doubl.
$CH_2{=}CHCH_2SiH_2CH_3$ (II)	CH_3SiCl_3	$CH_2{=}CHCH_2MgBr$	34	30	47.6–47.8, 760	—	—	2140	5.7, broad
$CH_2{=}CHCH_2SiH_2Ph$ (III)	$PhSiCl_3$	$CH_2{=}CHCH_2MgBr$	30	54	66.8–68.6, 6	72.90, 73.18	8.16, 7.97	2200	5.60, tripl.
 (IV)	CH_3SiCl_3		41	56	55.4–56.0, 3	72.90, 72.81	8.16, 8.04	2175	5.7, broad

phenyldichlorosilane; b.p. 103–107.5°C. at 18 mm. [lit.[10] 114–116°C. at 19 mm.], yield 30%.

Allylphenylsilane (III). This material was synthesized by a slightly modified procedure for vinylphenylsilane. Fractionation of the crude product under reduced pressure gave allylphenylsilane; b.p. 66.8–68.6°C. at 61 mm., yield 54%.

***p*-Vinylphenylmethyldichlorosilane.** The method of synthesis of *p*-vinylphenyldimethylchlorosilane reported by Grever and Reese[4] was employed. Fractionation of the products afforded *p*-vinylphenylmethyldichlorosilane; b.p. 71–75°C. at 2 mm. [lit.[11] 85°C. at 1.7 mm.], yield 41%.

***p*-Vinylphenylmethylsilane (IV).** To a solution of 1.5 g. (0.039 mole) of lithiumaluminum hydride in 30 ml. of THF was added dropwise a solution of 15.5 g. (0.0715 mole) of *p*-vinylphenylmethyldichlorosilane in 30 ml. of the anhydrous THF over a period of 0.5 hr. The reaction mixture was then heated slightly to 30–40°C. and stirring was continued for 0.5 hr.; it was then allowed to stand overnight. Onto the mixture of 20 ml. of an aqueous solution of 1*N* HCl about 300 g. of crushed ice and 100 ml. of ether the reaction product was poured. The aqueous phase was separated, and the ether layer was dried over anhydrous sodium sulfate. After removal of the ether by distillation the liquid residue was fractionated at reduced pressure. *p*-Vinylphenylmethylsilane was obtained; b.p. 55.4–56.0°C. at 3 mm., yield 5.9 g. (56%).

Homopolymerization

Homopolymerization of phenylvinylsilane (I) was carried out by using gamma irradiation from a ^{60}Co source or various ionic initiators such as sodium-napththalene, BuLi, $NaOCH_3$, KOH, BF_3OEt_2, and Et_3Al–$TiCl_3$ in sealed ampules of 10 ml. capacity containing 3 ml. of the monomer. None of them could initiate the polymerization of the monomer. However, an oily polymer could be obtained with 10 wt.-% of AIBN as initiator at 60°C., reacting for several days. When H_2PtCl_6 was used as catalyst at 70°C., a vigorous reaction occurred, and a soluble polymer was obtained. The polymer became insoluble when exposed to the air. Allylmethylsilane (II) gave a polymer with Et_3Al–$TiCl_3$ catalyst.

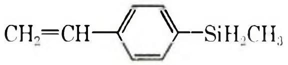
Copolymerization

Vinylsilanes, (I)–(IV), copolymerized with styrene. The mole fractions of monomer in the monomer mixture and in the copolymer are summarized in Table II. The monomer reactivity ratios are summarized in Table III.

Copolymerization Procedure. Copolymerization was carried out in a sealed ampule of 20 ml. capacity. About 5 g. of a mixture of styrene (M_1) and a vinylsilane (M_2) was kept in an atmosphere of nitrogen at 60°C. for 2–8 hr. using 1.0 mole-% of AIBN. Polymerization was stopped by cooling the ampule to room temperature when about 10% conversion was reached. The resulting viscous solution was poured into a large amount of methanol.

TABLE II

Vinylsilanes (M_2)-Styrene (M_1) Copolymers[a]

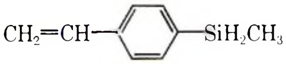
F	f	F	f
$CH_2{=}CHSiH_2Ph$ (I):		$CH_2{=}CHCH_2SiH_2CH_3$ (II):	
0.365	2.50	0.542	37.8
0.470	5.15 (0.06, 3,800)[b]	1.08	22.9
0.622	5.25	1.23	40.5 (0.12, 3,000)[b]
0.825	7.98 (0.09, 6,200)[b]	1.36	38.7
0.960	8.75	1.70	63.8 (0.15, 5,400)[b]
2.28	11.87		
3.99	12.22		
9.03	38.66		
$CH_2{=}CHCH_2SiH_2Ph$ (III):			
0.481	16.1	0.942	0.706
0.780	23.0 (0.14, 6,600)[b]	1.48	1.29
1.26	33.6	2.15	2.04
1.62	37.4	3.28	3.14
2.26	82.5 (0.17, 15,000)[b]	5.35	4.99
		12.1	10.1

[a] $F = M_1/M_2$, ratio of monomers in monomer mixture; $f = m_1/m_2$, ratio of monomers in copolymer.

[b] C = 0.25 g./dl. in benzene; first figure in parentheses, η_{sp}/C; second figure in parentheses, molecular weight.

TABLE III

Monomer Reactivity Ratios

Monomer	Styrene r_1	Monomer r_2	Q	e
$CH_2{=}CHSiH_2Ph$	5·7	0	—	—
$CH_2{=}CHCH_2SiH_2CH_3$	36	0	—	—
$CH_2{=}CHCH_2SiH_2Ph$	29	0	—	—
	0.91	1.1	1.1	−0.80

After drying the polymer was submitted to elemental analyses for determination of r_1 and r_2 values.

Determination of Monomer Reactivity Ratios. From the elemental analyses for C and H of the copolymers the monomer reactivity ratios of vinylsilanes (I)–(IV), M_2, with styrene, M_1, were determined by the method of Fineman and Ross.[12] The Alfrey-Price Q and e values[13] were obtained from their monomer reactivity ratios in the copolymerization with styrene.

Viscosity and Molecular Weight Measurement. The reduced specific viscosity was determined at 30°C., in benzene solution, at $C = 0.25$ g./dl., with an Ostwald viscometer. The molecular weight was determined with a vapor-pressure osmometer, Mechrolab Model 302, at 37°C.

Spectra Analyses. Infrared absorption spectra were obtained with a Hitachi Model EPI-2 double-beam spectrometer and thin copolymer film cast from carbon tetrachloride solution on salt plates. The NMR spectra of the copolymers were measured at 60°C., in 10% carbon tetrachloride solution with a Japan Electron Optics Laboratory C-60 spectrometer. The chemical shifts were measured in parts per million from tetramethylsilane internal reference (10.0 ppm) at 60°C. for polymer and at room temperature for monomer.

Reaction of Copolymer. A sample of copolymer (0.1 g.) was dissolved in tetrahydrofuran (THF), and after the addition of an appropriate amount of alcohols the polymer solution was refluxed. The mixture was poured into methanol, and the precipitated polymer was collected by filtration and subjected to infrared analyses. The addition reaction of methyl methacrylate was carried out by using 0.1 g. of copolymer, 5.0 g. of methyl methacrylate, 11 mg. of $H_2PtCl_6 \cdot 10H_2O$, and 4.3 mg. of *p-tert*-butylcatechol as inhibitor. The resulting copolymer was purified by reprecipitation from benzene solution into methanol three times. After drying the polymer was submitted to infrared analyses.

RESULTS AND DISCUSSION

Structure of Copolymer

Since the silicon–hydrogen bond might add to a double bond in the process of copolymerization, there was the possibility that a corresponding polymerization of the hydrogen-transfer type might occur. Therefore, the structures of the copolymers were examined by infrared and NMR spectral analyses. The copolymer of vinylphenylsilane (I) and styrene has a typical infrared absorption in the vicinity of 940 and 840 cm.$^{-1}$, arising from bending and wagging, respectively, of SiH_2 deformation.[14] The intensity of the two infrared absorption bands increased with increasing fraction of vinylsilane (I) in the copolymer. This is shown in Figure 1.

In the NMR spectrum of the copolymer of (I) and styrene a doublet signal at a τ value of 5.47, due to the coupling of a hydrogen at neighboring carbon atom, was obtained. The doublet signal suggested that vinylsilane polymerized only through the double bond. The NMR spectra of the copolymer of allylphenylsilane (III) had a triplet signal at $\tau = 5.68$, attributed to SiH hydrogen (Fig. 2). This signal indicated that (III) also underwent vinyl polymerization.

Reaction of Copolymer

Reactions between the copolymer and various alcohols were carried out. The reaction conditions and the effect of catalyst were examined by infrared

TABLE IV

Reaction of Copolymer with Alcohols[a]

Alcohol and ratio to SiH function		Catalyst and ratio to SiH function		THF, ml.	Reflux time, hr.	Infrared absorption of reaction product, cm.$^{-1}$			
						SiH, 2180	SiOC, 1000–1100	Alcoholic substituents and characteristic absorption	
CH_3OH,	204	NaOH,	4.3	5.4	$^1/_3$	none	s	—$SiOCH_3$,	1075
C_2H_5OH,	47	KOH,	0.99	5	1[b]	m	m	—$SiOC_2H_5$,	1148
$NCCH_2CH_2OH$,	280	$ZnCl_2$,	16.3	10	3	m	m	—CN,	2270
$NCCH_2CH_2OH$,	290	$NaOCH_3$,	6.3	10	3	w	m	—CN,	2270
$NCCH_2CH_2OH$,	97	KOH,	5.5	10	4	vw	s	—CN,	2270
$CH_2{=}CHCH_2OH$,	91	KOH,	0.46	10	1	w	s	—$CH{=}CH_2$,	1650 910

[a] Amount of copolymer used, 0.100 g.; composition of copolymer styrene/phenylvinylsilane (I), 7.0; molecular weight 1100; m middle, s strong, w weak, vw very weak.

[b] Room temperature.

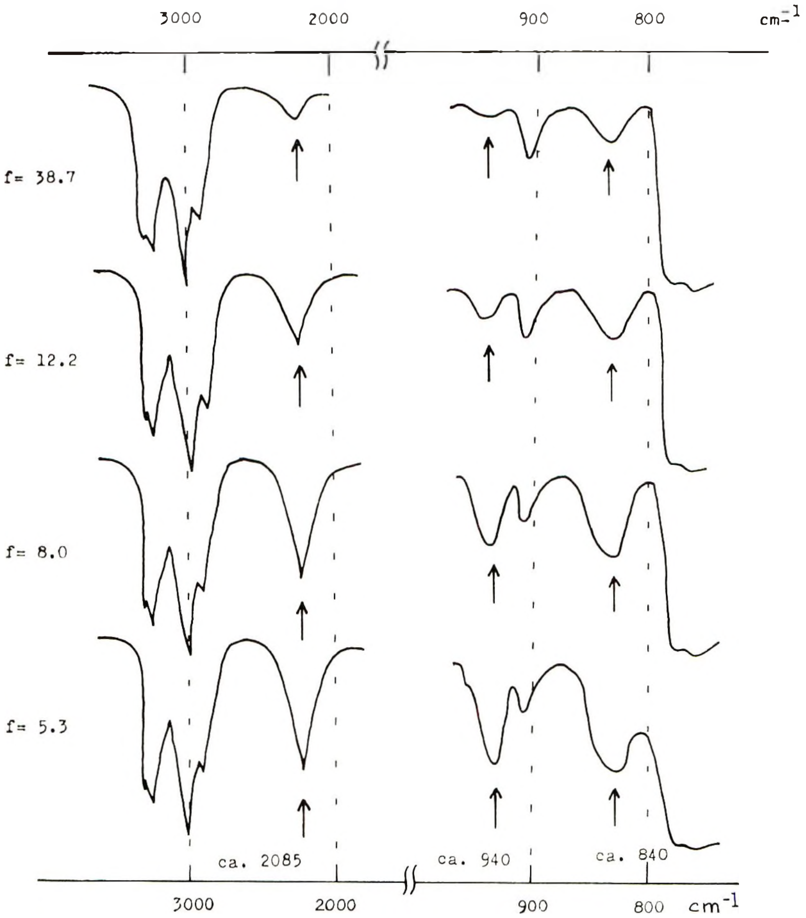
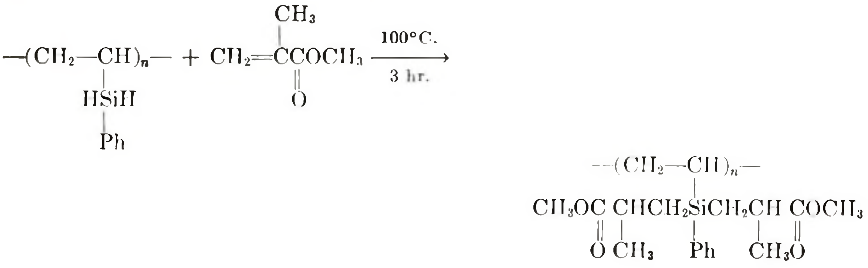


Fig. 1. Infrared spectra of copolymers; f = ratio of styrene to phenylvinylsilane (I), monomers in copolymer.

analyses qualitatively. The results of the polymer reaction with alcohols are shown in Table IV. They demonstrate that potassium hydroxide was the most effective catalyst and that under appropriate conditions alcoholysis proceeded quantitatively. However, in the absence of THF solvent no reaction occurred. The addition reaction of methyl methacrylate and copolymer was carried out with H_2PtCl_6 as catalyst and *p-tert*-butylcatecohol as radical inhibitor:



$$-(CH_2-\underset{\underset{\underset{Ph}{|}}{HSiH}}{\overset{}{CH}})_n- + CH_2{=}\overset{\overset{CH_3}{|}}{\underset{\underset{O}{\|}}{C}}COCH_3 \xrightarrow[3\ hr.]{100^\circ C.}$$

$$\begin{array}{c} -(CH_2-CH)_n- \\ | \\ CH_3O\underset{\underset{O}{\|}}{C}\,\underset{\underset{CH_3}{|}}{CH}CH_2\underset{\underset{Ph}{|}}{Si}CH_2\underset{\underset{CH_3}{|}}{CH}\,\underset{\underset{O}{\|}}{C}OCH_3 \end{array}$$

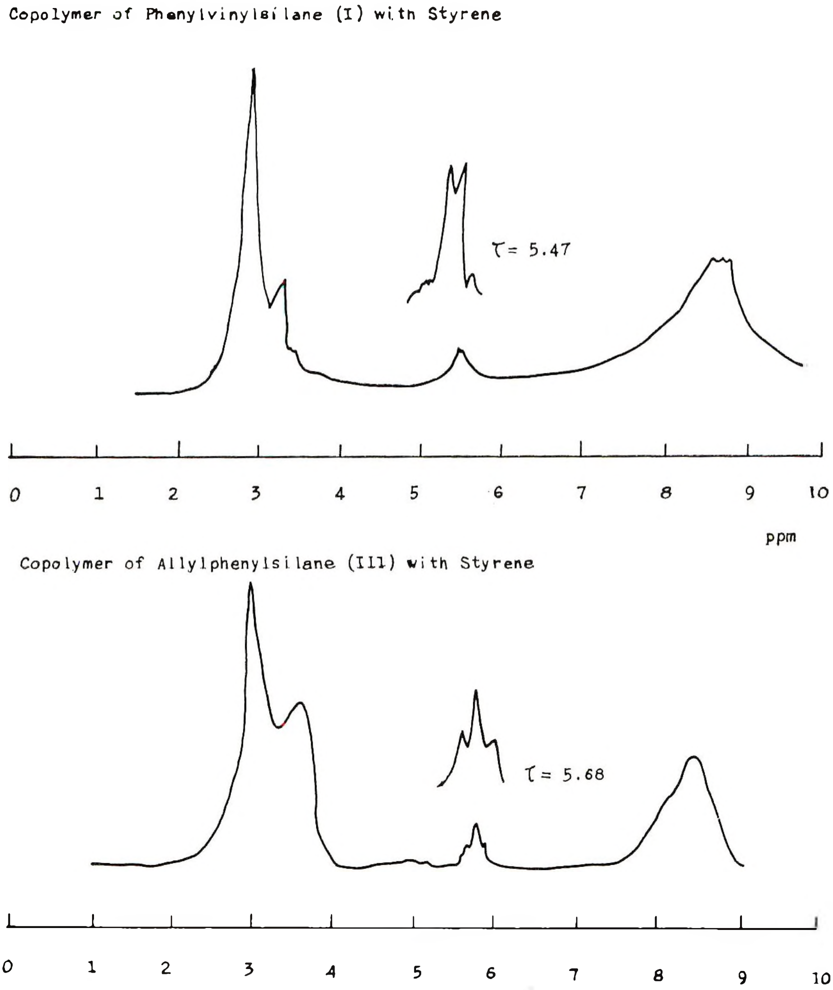


Fig. 2. NMR spectra of copolymers: (top) copolymer of phenylvinylsilane (I) and styrene; (bottom) copolymer of allylphenylsilane (III) and styrene.

The infrared spectra of the product showed no absorption band at 2180 cm.$^{-1}$ that could be attributed to SiH_2 stretching vibration, but a band appeared at 1725 cm.$^{-1}$, which was characteristic of ester. The polymer was soluble in benzene and ether but was tarry in carbon tetrachloride.

CONCLUSIONS

(*1*) New vinylsilanes (M_2), phenylvinylsilane (I), allylmethylsilane (II), allylphenylsilane (III), *p*-vinylphenylmethylsilane (IV), were prepared and copolymerized with styrene (M_1). The monomer reactivity ratios were $r_1 = 5.7$ and $r_2 = 0$, $r_1 = 36$ and $r_2 = 0$, $r_1 = 29$ and $r_2 = 0$, and $r_1 = 0.91$ and $r_2 = 1.1$, respectively.

(*2*) According to the structure of the copolymer obtained, the copolymerization of these vinylsilanes proceeded through a vinyl type of polymerization, and there was no evidence that silicon–hydrogen added to an unsaturated bond.

(*3*) The copolymer reacted with various alcohols and methyl methacrylate in solvent with appropriate catalyst.

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Reaction between Ethanol and Silicon–Hydrogen of Poly(*p*-vinylphenyldimethylsilane)

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Synopsis

A kinetic approach to the polymer reaction, with KOH as catalyst, between ethanol and poly(*p*-vinylphenyldimethylsilane) containing silicon–hydrogen as a functional group on the side chain was carried out. The rate equation was obtained by measuring the initial rate of the model reaction as $v = k[\mathrm{KOH}][\mathrm{SiH}][\mathrm{EtOH}]$ in benzene and $v = k[\mathrm{KOH}][\mathrm{SiH}]$ in methyl ethyl ketone. It was observed that the rate of reaction was affected by the polarity of the solvents. In the polymer reaction the rate constant decreased markedly with increasing ethanol concentration. A change of viscosity of the polymer in various solvents was observed to have a good correlation with the decrease in reaction rate in corresponding solvents. In mixed solvents, consisting of both good and poor solvents for the polymer, the reaction rate depended upon two factors, the entanglement of the polymer chain and the polarity of the solvents. The equivalent globular model of the polymer chain is suggested for study of the polymer reaction. A schematic local-distribution curve of the reaction species is proposed.

INTRODUCTION

Some kinetic studies of the reaction of triorganosilanes with ethanol in the presence of KOH have been made.[1-4] The rate of reaction is confirmed to be proportional to the first order of the concentrations of silane and hydroxy anion, respectively, and the reaction is considered to proceed through an S_N2 type of mechanism.[1] However, the kinetic order with respect to ethanol has not been decided clearly.

In the present study a kinetic approach to the polymer reaction between ethanol and polymer containing a silicon–hydrogen bond has been made and to the reaction of a model compound in aprotic solvents. In this study it was made clear that the kinetic order of ethanol was either zero or first and that the expansion or contraction of a polymer chain in a solvent has a significant correlation with the rate of polymer reaction.

EXPERIMENTAL

Silanes

p-Vinylphenyldimethylsilane was synthesized according to the method of Grever and Reese.[5] The yield was 40%, based on *p*-chlorostyrene; b.p. 48°C. at 0.8 mm. [lit.[5] 61°C. at 0.3 mm.].

ANAL. Calcd. for $C_{10}H_{14}Si$: C 74.00%, H. 8.69%. Found: C 73.11%, H 8.5%.

The polymerization was carried out in sealed tubes under nitrogen with α,α'-azobisisobutyronitrile as initiator at 60°C. The polymer produced was precipitated from a large amount of methanol. Further purification of the polymer was carried out by reprecipitation from a large amount of methanol. The purified polymer was dried for 24 hr. at 60°C. *in vacuo.* A polymer having $[\eta] = 0.45$ dl./g. in toluene at 30°C. A melting point of 153–156°C.

ANAL. Calcd. for $C_{10}H_{16}Si$: C 74.00%, H 8.69%. Found: C 73.92%, H 8.35%.

The quantity of silicon–hydrogen in the polymer chain was estimated by the volume of the hydrogen gas evolved on ethanolysis in dimethyl sulfoxide–methyl ethyl ketone. Found and calcd.: 102%.

p-Methylphenyldimethylsilane was prepared by reducing *p*-methylphenyldimethylchlorosilane with lithiumaluminum hydride. The yield was 43%, based on *p*-chlorotoluene. The pure material had a boiling point of 69–71°C. at 20 mm. [lit. [6] 181–182°C.].

ANAL. Calcd. for $C_9H_{14}Si$: C 71.93%, H 9.39%. Found: C 71.93%, H 9.21%.

Other Materials

The catalyst solution was prepared by dissolving potassium hydroxide in absolute ethanol; b.p. 78.4°C., $n_D^{20} = 1.3607$. The concentration of catalyst solution was determined by titration with 0.1 or 0.01*N* HCl. All solvents were purified by the usual method. Benzene, toluene, and *n*-heptane were refluxed over sodium wire for 24 hr. and distilled. Dimethylsulfoxide and methyl ethyl ketone were refluxed over calcium hydride and distilled.

Kinetic Measurement

The experiment was carried out with a modified Warburg manometer apparatus; see Figure 1. A typical run was made as follows. Into a conical flask equipped with an inside bulb was charged a silane solution with enough alcohol to give the desired final concentration, and into the inside bulb was put alcoholic potassium hydroxide. The flask was placed in a bath and was connected to a manometer. After the flask had been

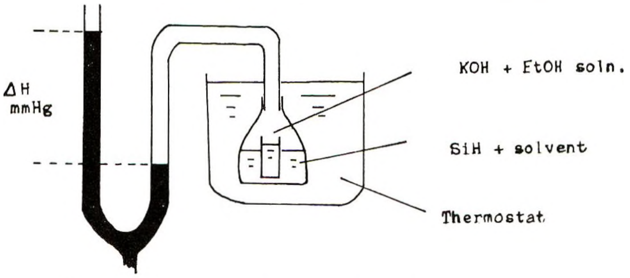


Fig. 1. Apparatus for measuring initial reaction rate.

allowed to stand about 20 min. at a fixed temperature, the pressure was brought to that of atmosphere in the flask–manometer system, and the excess gas was removed from the system. The run was started by shaking the flask twice every second. The pressure of the gas evolved was read at intervals. The error of the manometer was about 0.2 cm. Hg. The vapor pressure of the solvents was known from the blank run without potassium hydroxide. The dissolution of the gas into the solvents, the volume change on mixing of ethanol and solvent, the change of atmospheric pressure, and the temperature were ignored.

RESULTS AND DISCUSSION

Kinetics of Reaction of the Model Compound

The reaction of silicon–hydrogen with ethanol has been studied by a number of workers.[1–4] Price examined the kinetics of alcoholysis in 95% ethanol and concluded that the reaction was first order with respect to

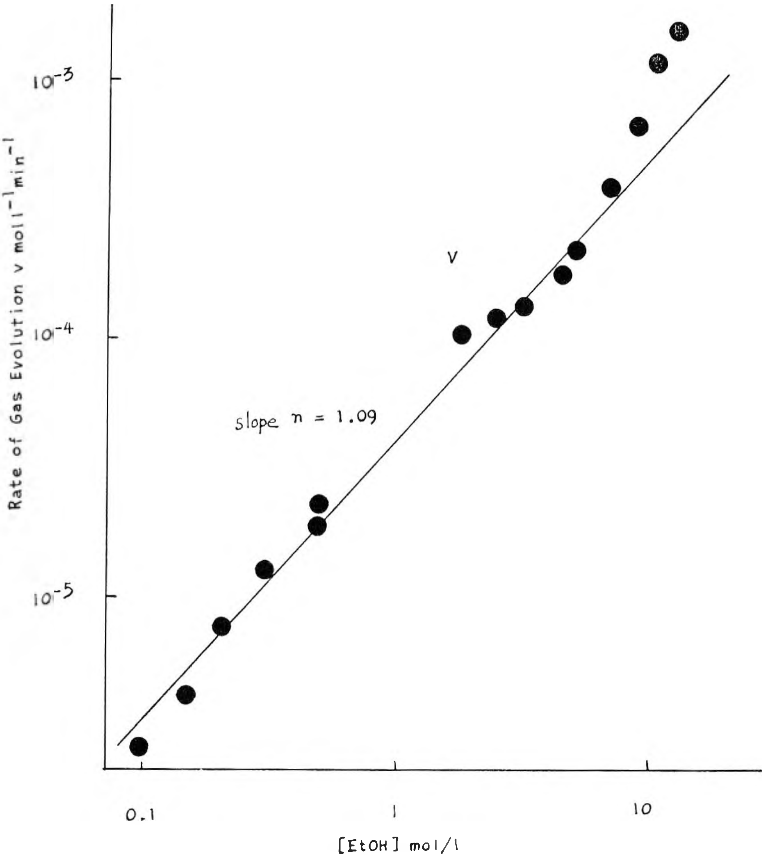


Fig. 2. Dependence of the model reaction in benzene on ethanol concentration. Reaction conditions: [SiH] 0.199 mole/l., [KOH] 1.53×10^{-2} mole/l., at 29.3°C.

silane and potassium hydroxide.[1] However, he showed no clear evidence that the reaction was first order with respect to ethanol. The present work contained kinetic studies of the reaction of *p*-methylphenyldimethylsilane with ethanol in the presence of potassium hydroxide in organic solvents such as benzene and methyl ethyl ketone. The kinetic order with respect to ethanol was determined from the relationship between the logarithms of the initial reaction rates and the logarithms of the ethanol concentrations; see Figures 2 and 3.

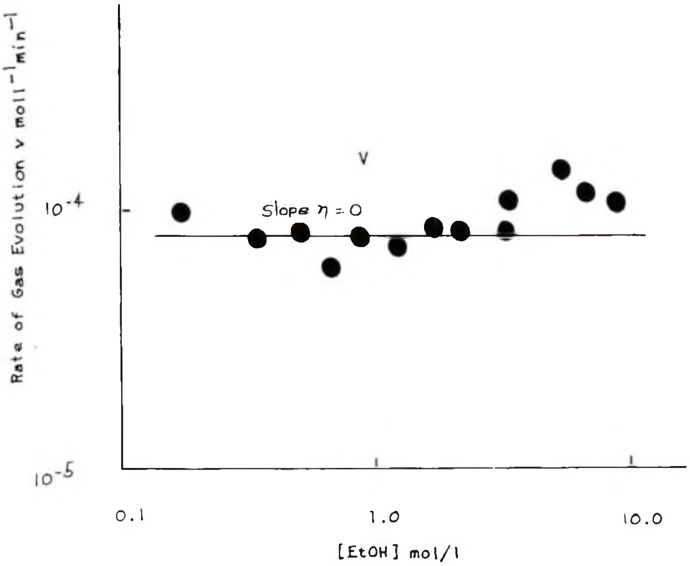


Fig. 3. Dependence of model reaction in methyl ethyl ketone on the ethanol concentration. Reaction conditions: [SiH] 0.0995 mole/l., [KOH] 9.75×10^{-4} mole/l., at 30°C.

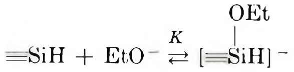
First-order and zero-order reactions with respect to ethanol were obtained in benzene and methyl ethyl ketone, respectively, as solvent. In the same way kinetic orders with respect to silane and potassium hydroxide were determined to be first order either in benzene or in methyl ethyl ketone. Thus, the reaction rates may be expressed by the following equations:

$$\text{In benzene,} \quad v = k[\text{KOH}][\text{SiH}][\text{EtOH}]$$

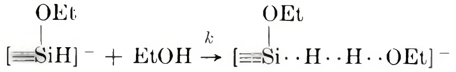
$$\text{In methyl ethyl ketone,} \quad v = k[\text{KOH}][\text{SiH}]$$

To account for the experimental results the following reaction scheme is proposed. In this scheme the third reaction step in the reaction in benzene and the second reaction step in the reaction in methyl ethyl ketone are assumed to be the rate-determining steps:

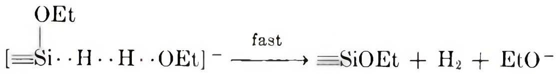
$$\text{KOH} + \text{EtOH} \rightleftarrows \text{K}^+ + \text{EtO}^- + \text{H}_2\text{O} \qquad (1)$$

 (2)

$$\equiv\text{SiH} + \text{EtO}^- \overset{K}{\rightleftarrows} [\equiv\overset{\overset{\text{OEt}}{|}}{\text{Si}}\text{H}]^- \qquad (2)$$

 (3)

$$[\equiv\overset{\overset{\text{OEt}}{|}}{\text{Si}}\text{H}]^- + \text{EtOH} \xrightarrow{k} [\equiv\overset{\overset{\text{OEt}}{|}}{\text{Si}}\cdot\cdot\text{H}\cdot\cdot\text{H}\cdot\cdot\text{OEt}]^- \qquad (3)$$

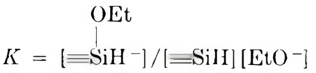
 (4)

$$[\equiv\overset{\overset{\text{OEt}}{|}}{\text{Si}}\cdot\cdot\text{H}\cdot\cdot\text{H}\cdot\cdot\text{OEt}]^- \xrightarrow{\text{fast}} \equiv\text{SiOEt} + \text{H}_2 + \text{EtO}^- \qquad (4)$$

It will be natural to assume that the equilibrium in reaction (1) is shifted toward the right-hand side of the equation, so that the concentration of alkoxy anion should be practically equal to the concentration of potassium hydroxide initially added:

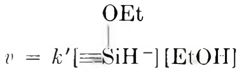
$$[\text{EtO}^-] \approx [\text{KOH}] \qquad (5)$$

K, the equilibrium constant in reaction (2), is given by the equation

 (6)

$$K = [\equiv\overset{\overset{\text{OEt}}{|}}{\text{Si}}\text{H}^-]/[\equiv\text{SiH}][\text{EtO}^-] \qquad (6)$$

If k' represents the rate constant of reaction (3), the reaction rate can be expressed as follows:

 (7)

$$v = k'[\equiv\overset{\overset{\text{OEt}}{|}}{\text{Si}}\text{H}^-][\text{EtOH}] \qquad (7)$$

From eqs. (5), (6), and (7) the following relationship is obtained:

$$v = k[\text{KOH}][\equiv\text{SiH}][\text{EtOH}] \qquad (8)$$

where k is the rate constant for the overall reaction.

For the reaction in methyl ethyl ketone the rate equation may be expressed as follows:

$$v = k''[\equiv\text{SiH}][\text{EtO}^-] \qquad (9)$$

From eq. (5):

$$v = k[\text{KOH}][\equiv\text{SiH}] \qquad (10)$$

The relationships thus derived are in complete agreement with the experimental data.

As shown in Figure 2, at a low concentration of ethanol the reaction was first order with respect to ethanol, but above 10 vol.-% ethanol there was a steady increase in the kinetic order of the reaction with respect to ethanol, finally reaching about second order at 50 vol.-% ethanol. This change probably is due to the increase in the dielectric constant with increasing concentration of ethanol (ϵ = 25.1) in the reaction mixture.

Kinetics of Reaction of Polymer

The dependence of the rate constant of the polymer reaction with ethanol upon the ethanol concentration was estimated for methyl ethyl ketone (Fig. 4) and for toluene (Fig. 5), both at 29.3°C., at a polymer concentration of 1.8 g./dl. There was a marked decrease of reaction rate constant with increasing ethanol concentration both in either methyl ethyl ketone and in toluene. The experimental results indicated that, in contrast to the zero-order reaction (in methyl ethyl ketone) or the first-order reaction

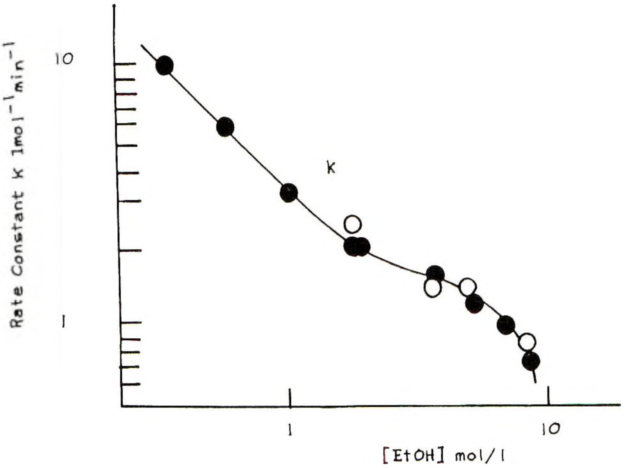


Fig. 4. Dependence of rate constant of polymer reaction in methyl ethyl ketone on ethanol concentration at 29.3°C. Intrinsic viscosity [η] of polymer in toluene at 30°C.: (●) 0.45; (○) 0.17.

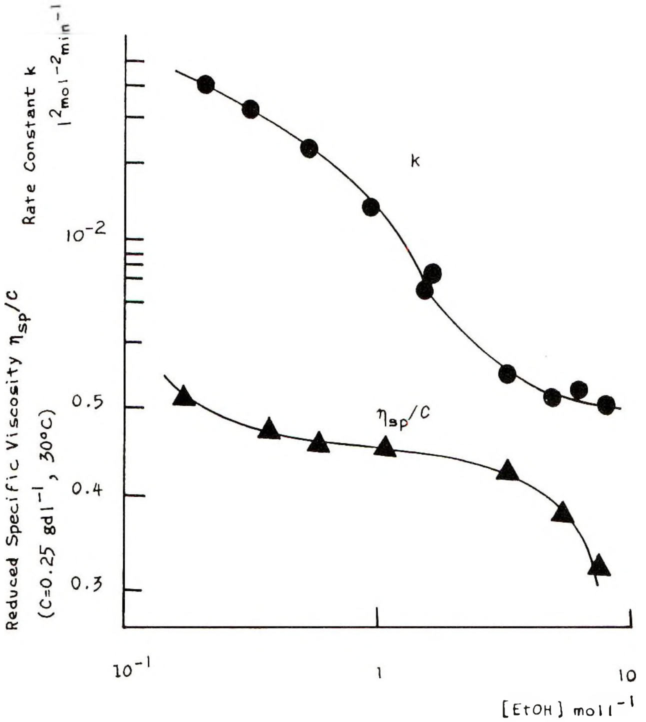


Fig. 5. Dependence of rate constant of polymer reaction in toluene on ethanol concentration at 29.3°C.

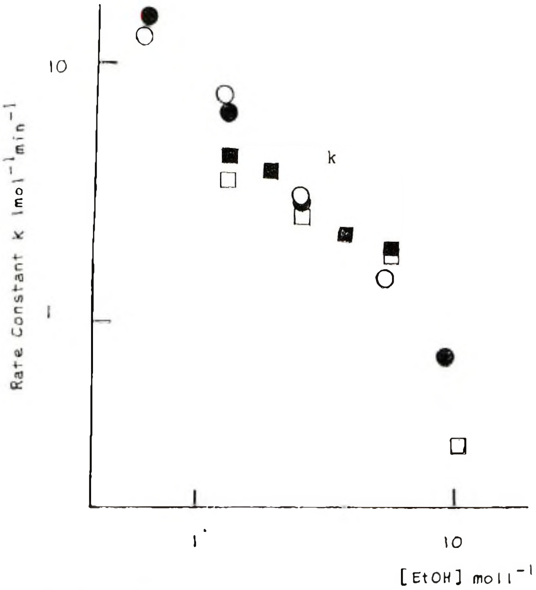


Fig. 6. Dependence of rate constant on polymer concentration in methyl ethyl ketone at 30°C. Polymer concentration C (g./dl.): (○) 0.23; (●) 0.45; (■) 0.9; (□) 1.8.

(in benzene) of the model compound, the reaction of the polymer was found to be of a lower-order dependence on the ethanol concentration. In methyl ethyl ketone and toluene as solvents the apparent kinetic orders of the polymer reaction with respect to ethanol concentration were -1.06 to -0.67 and -0.14 to 0.72, respectively.

The dependence of the rate constant on the polymer concentration was examined for methyl ethyl ketone at polymer concentrations from 0.23 to 1.8 g./dl.; see Figure 6.

The decrease in rate constant with increase of ethanol concentration tended to become rather distinct when the polymer concentration was decreased from 1.8 to 0.23 g./dl. At this concentration of ethanol the reaction mixture was clearly homogeneous, but with an increase of the concentration of ethanol the polymer solution became opaque, and finally precipitation of the polymer took place. On complete precipitation of the polymer there was no reaction. Therefore, it would be reasonable to assume that the "lower" values of the kinetic order with respect to ethanol in the reaction of poly(p-vinylphenyldimethylsilane) with ethanol in methyl ethyl ketone and in toluene are caused by the smaller expansion of the polymer coil.

As the reaction of silicon–hydrogen with ethanol does not occur without KOH, the reduced specific viscosity of the polymer next was measured in mixed solvents toluene–ethanol, at which time the above-described study of the reaction rate was made. A parallelism was observed between the changing viscosities and the reaction rate constants (Fig. 5). The rate constant of the polymer reaction decreased with the decrease in viscosity.

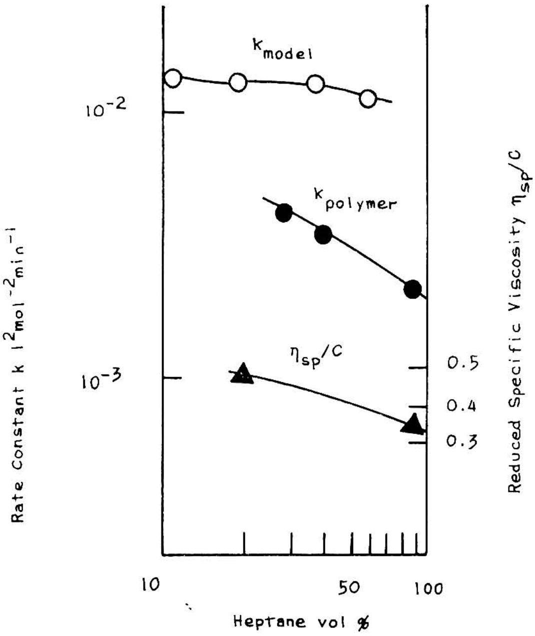


Fig. 7. Reaction in toluene-heptane mixtures at 29.3°C.: (○) rate constant in model reaction, k_{model}; (●) rate constant in polymer reaction, $k_{polymer}$; (▲) reduced specific viscosity, η_{sp}/C, $C = 0.25$ g./dl. at 30°C.

In a polymer reaction the distribution of reactive centers of the polymer should coincide with the distribution of the segments of the polymer. Consequently, the reactivity of the polymer will depend on the shape of the polymer chain in the medium. As is well known, the addition of a nonsolvent of a polymer to a solution of the polymer causes a lowering of the viscosity of the polymer solution. This change has been attributed to the degree of expansion of the random coil of the polymer chain. It may be said that the lowering in rate constant of the polymer reaction is due to the aggregation of the polymer in the reaction mixture.

NOTE: The intrinsic viscosity $[\eta]$ of a polymer in a medium may be expressed[7] by the equation $[\eta] = [\eta]_\Theta \alpha^3$, where $[\eta]_\Theta$ is the viscosity of the polymer in a Θ solvent, and α is the expansion factor, which corresponds to the equilibrium extension of a sphere over an unperturbed equivalent sphere.

To confirm the above-stated theory the following experiments were carried out. A reaction of the polymer with ethanol in the presence of KOH was carried out in a mixture of toluene and heptane. The concentrations of the polymer, ethanol, and catalyst were fixed, and the ratio of toluene and heptane was varied. The variation in rate constants of the reaction in mixtures of varied ratios of heptane and toluene and the variation in viscosity of the polymer in the same mixture are shown in Figure 7.

The rate constants of the reactions of the model compound and the polymer were compared. Heptane acted as a poor solvent in this system,

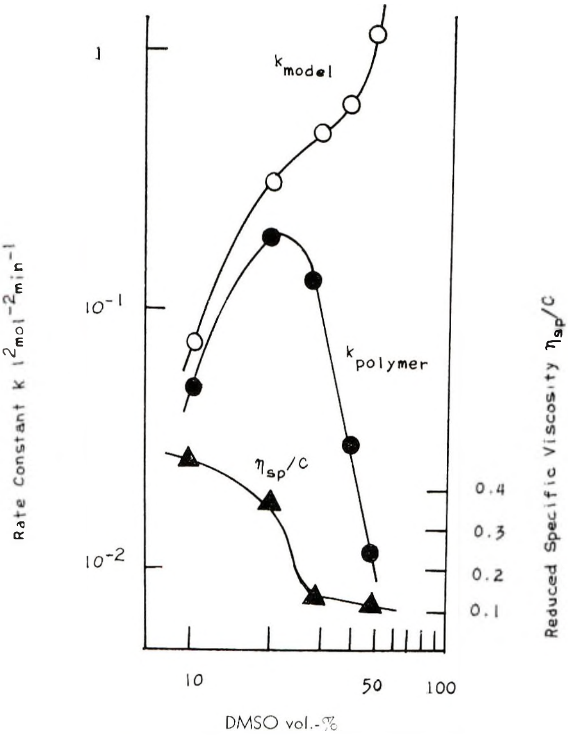


Fig. 8. Reaction in DMSO–toluene mixtures at 29.3°C.: (○) rate constant in model reaction, k_{model}; (●) rate constant in polymer reaction, $k_{polymer}$; (▲) reduced specific viscosity η_{sp}/C, with $C = 0.25$ g./dl. at 30°C.

and the viscosity of the polymer, η_{sp}/C, decreased with the decrease in ratio of toluene to heptane. The rate constants of the polymer reaction decreased markedly when the viscosity decreased. However, the rate constants of the model reaction were little affected by the change in component of the mixed medium.

Similar reactions were followed in a mixture of toluene and dimethylsulfoxide (DMSO). The results are summarized in Figure 8. In this case DMSO acts as a nonsolvent. In a mixture containing low concentrations of DMSO the rate constant $k_{polymer}$ increased with the amounts of DMSO. However, there was an optimum ratio of toluene to DMSO for the polymer reaction. In the reaction of the model compound there was a steady increase in reaction rate constants. The observed increase in reaction rate constants in both the polymer and the model reactions with increasing amounts of DMSO may be caused by the increase in polarity of the reaction system. In the reaction of polymer the effect of DMSO in coagulating the polymer might, above a certain concentration of DMSO, have caused a decrease in the rate constant of the reaction.

In an ordinary organic solvent the densities of the segments of the polymer have a Gaussian distribution.[8] Thus, the distribution of

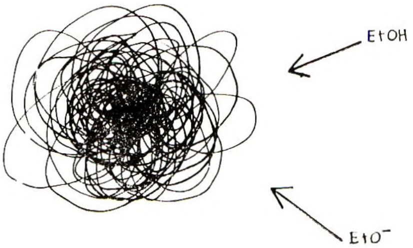


Fig. 9. Equivalent globular model.

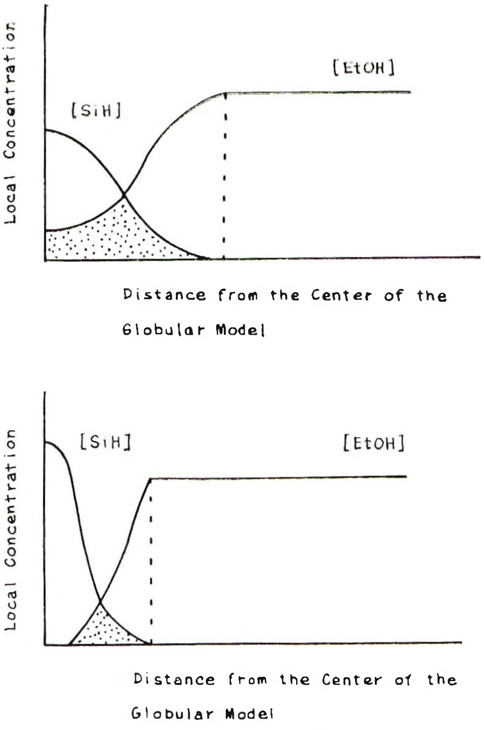


Fig. 10. Distribution of concentration of reaction species: (top) in good solvent; (bottom) in poor solvent.

concentration of silanes in the polymer molecules is supposed to be a function of the distance from the center of a molecule (Figs. 9 and 10). Now, on the addition of ethanol and KOH to the polymer solution these substances penetrate into the polymer coil and react with silicon–hydrogen on the polymer chain. The concentration of ethanol inside the polymer coil may be lower than that outside, owing to the fact that ethanol is a poor solvent for this polymer. At the initial stage the reaction will be shown by an overlapping of the curves for silane and for ethanol. On the addition of a nonsolvent or a poor solvent the radius of the sphere contracts, and the area becomes smaller. Therefore, the rate constants of the reaction decrease. On the addition of a large amount of a poor solvent the polymer precipitates, no reactants such as solvent, KOH, or ethanol, can come into the sphere of the polymer, and no reaction whatever will take place.

A comparison of the reactions of two kinds of polymer having different average molecular weights corresponding to intrinsic viscosities $[\eta]$ of 0.45 and 0.17 dl./g. showed that there existed little difference in reaction rates under the given experimental conditions. The results are plotted in Figure 3.

According to the reaction model described above, a difference in reactivity between these two species must appear. Therefore, the result seems to be rather inconsistent with the explanation. Perhaps an imperceptible effect of molecular weight on the expansion of the polymer chain may account for the discrepancy.

NOTE: The expansion factor α has a relation with the molecular weight[9] as follows: $\alpha^5 - \alpha^3 \propto M^{1/2}$; thus the equivalent sphere increases very slowly as the chain length increases.

CONCLUSIONS

(*1*) The rate equation for the reaction between silane and ethanol has been obtained as $v = [\text{KOH}][\text{SiH}][\text{EtOH}]$, in benzene, and $v = k[\text{KOH}][\text{SiH}]$, in methyl ethyl ketone.

(*2*) In the reaction between ethanol and poly(p-vinylphenyldimethylsilane) the rate constant shows good correlation with the viscosity of the polymer in corresponding mixed solvents.

(*3*) According to the equivalent-sphere model of polymer chain the rate constant of the polymer reaction seems to depend on the extent of the expansion of the polymer coil in solution.

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Solvent Effect on NMR Spectra of Poly(methyl Methacrylate)

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Synopsis

The NMR spectra of stereoblock poly(methyl methacrylate) in several solvents were measured. It is concluded from the following experimental results that the solute–solvent complexes are formed in benzene solution: the chemical shifts measured in C_6H_6 go to a lower field than do those in $CDCl_3$, except those of the ester methyl group, which splits into three resonances, and the shifts in the aromatic solvents are so different from those in the aliphatic solvents that Buckingham's theory cannot be applied to the results. The analysis of the temperature dependence of the chemical shifts of PMMA in benzene solution gave the heat of formation of the complex: $\Delta H = 2.8 \pm 0.5$ kcal./mole.

Introduction

The effects of solvent on the NMR spectra of low molecular weight compounds have been much examined[1] for the purpose of choosing a suitable solvent for NMR measurement and of studying the nature of the interaction between solvent and solute molecules. The effects on the spectra of high polymers, however, have scarcely been studied, because the main purpose of an NMR study of a polymer has been the investigation of its molecular structure, such as composition, configuration, and conformation. That is, it is necessary to obtain a good NMR spectrum of the polymer in order to investigate the polymer structure in detail. For this reason the solvent effect has been investigated mainly for the purpose of selecting a good solvent. However, it was thought worthwhile to investigate the nature of the interaction between polymer and solvent, because it may be related to the physical and thermodynamic properties of the polymer solution[2] (viscosity, flow birefringence, polymer–solvent interaction parameter, and so on) and may also disclose the nature of the interaction between the polymer and the additives (stabilizing agents, etc.).

Recently Ramey and Messick[3] systematically investigated the effects of solvents on poly(methyl methacrylate) and other polymers but did not report in detail on the nature of the interaction between polymer and solvent. In this publication we wish to report that we are led to the conclusion that each monomer unit of poly(methyl methacrylate) (PMMA) forms a π complex in benzene solution.

Experimental

The stereoblock PMMA was prepared at 20°C. with phenylmagnesium bromide as catalyst according to the usual procedures.[4] The stereoregularity of the polymer, estimated from NMR signals of the α-methyl group, and the molecular weight are as follows: isotactic 44.2%, heterotactic 22.2%, syndiotactic 33.6%, $M_v = 7.7 \times 10^4$. The NMR spectra were measured in 5% benzene, bromobenzene, furan, pyridine, methylene chloride, trichloroethylene, $CDCl_3$, and nitromethane solutions with the use of JNM 3H-60 (60 Mc./sec.) and 4H-100 (100 Mc./sec.) spectrometers (Japan Electron Optics Laboratory Co., Ltd.) in the temperature range from 27 to 124°C.

Results and Discussion

Figure 1 shows the NMR spectra of PMMA measured at 100 Mc./sec. in $CDCl_3$ and benzene solutions. As Ramey and Messick[3] reported, three ester methyl resonances are observed according to their stereoregularities in the benzene solution, though in the $CDCl_3$ solution only one peak can be observed. The chemical shifts of PMMA measured in $CDCl_3$ and C_6H_6 solutions at 84°C. are listed in Table I. The table clearly shows that all the signals except those of the ester methyl group shift to low field on going from a $CDCl_3$ to a benzene solution. (CCl_4 is thought to be a better reference solvent,[5] but we cannot help choosing $CDCl_3$ as reference, because

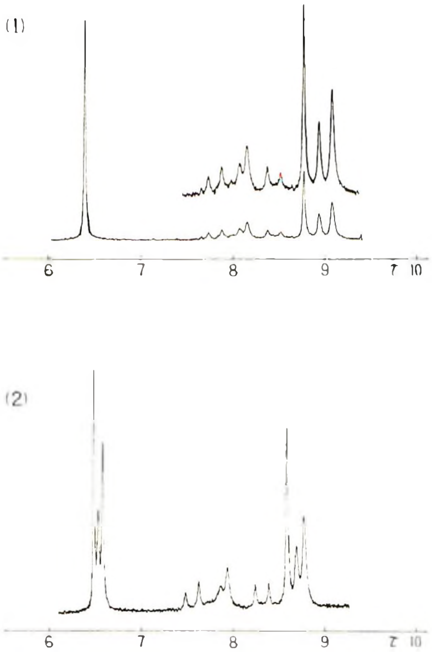

Fig. 1. NMR spectra of poly(methyl methacrylate) measured at 84°C. (100 Mc./sec.): (*1*) in $CDCl_3$ solution (upper figure is amplified); (*2*) in benzene solution.

PMMA is not very soluble in CCl_4. The effects of solvents including $CDCl_3$ will be published in the near future.) This fact may suggest that a specific interaction exists between the polymer and the solvent in a benzene solution.

Two effects may be considered to affect the chemical shifts of the polymer in different solvents[1] (the effect of the Van der Waals forces between the solute and solvent molecules may be negligible, because the heat of vaporization at the boiling point of benzene as a measure of the Van der Waals forces[6] does not differ so much from that of $CDCl_3$). One is the effect of an electric field; the other, of the specific solvent–solute interaction.

The effect of the electric field is considered first. From Buckingham's theory[7] it is shown that a linear relation holds between the chemical shifts of the solute and the factor $(\epsilon - 1)/(2\epsilon + 2.5)$, where ϵ is the dielectric constant

TABLE I

Chemical Shifts of Poly(methyl Methacrylate) Measured in $CDCl_3$ and C_6H_6

δ, ppm from TMS		(At 84°C.)
$CDCl_3$	C_6H_6	$\delta CDCl_3 - \delta C_6H_6$
α-Methyl:		
s 0.918	1.233	−0.315
h 1.061	1.315	−0.254
i 1.224	1.414	−0.190
Methylene:		
1.560	1.696	−0.136
2.188	2.442	−0.254
Ester methyl:		
	s 3.421	0.183
3.604	*h* 3.472	0.132
	i 3.517	0.087

TABLE II

Relation between Separations of Three Methyl Resonances and Factor of Electric Field Effect (60 Mc./sec. at 70°C.)

	α-Methyl group separation, cps			
Solvent	$i - s$	$i - h$	Ester, methyl group	$\frac{(\epsilon - 1)}{(2\epsilon + 2.5)}$
Trichloroethylene	18.7	10.2	single	0.258
$CDCl_3$	19.6	10.2	"	0.320
Nitromethane	19.6	10.8	"	0.472
Methylene chloride	19.6	10.4	"	0.391
1,2-Dichloroethane	20.6	11.0	"	0.403
Benzene	11.1	6.2	$i - s$ = 6.5 cps, $i - h$ = 3.4 cps	0.180
Pyridine	13.9	8.3	three	0.455
Furan	13.9	8.6	three	0.232
Bromobenzene	14.1	7.6	three	0.331

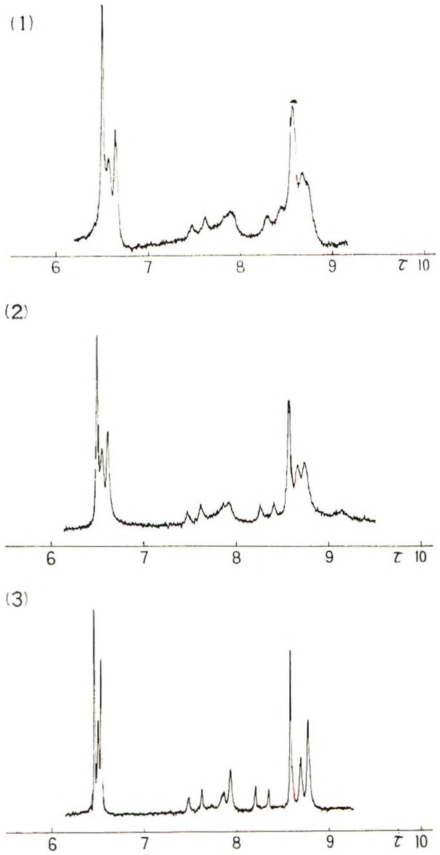

Fig. 2. NMR spectra of poly(methyl methacrylate) in benzene solution measured (100 Mc./sec.) at (°C.): (*1*) 27; (*2*) 50; (*3*) 128.

of the solvent. The separations between the three methyl resonances and this factor are listed in Table II, where $i - s$ or $i - h$ denote the separation between the isotactic and either the syndiotactic or the heterotactic peak. Table II shows that the separations of the three α-methyl resonances in aliphatic solvents are much larger than those in aromatic solvents, though the splittings for the ester methyl group are not observable in nonaromatic solvents, and that a regular relation exists between the separations of the three methyl resonances and the dielectric constants in aliphatic solvents (nitromethane is thought to have a magnetic anisotropy effect[6]), though in aromatic solvents no relation exists.

An analogous relation is observed in the methylene parts of the spectra. Because the PMMA used in the measurements is of the stereoblock type, the methylene part of the spectra shows an AB quartet due to the isotactic part together with the multiplet due to the syndiotactic part. In the aliphatic solvents the chemical-shift differences between the two methylene protons of the isotactic part $(\Delta\nu)$ are less than those measured in the aromatic solvents. Moreover, the $\Delta\nu$'s in the aliphatic solvents show a linear relation with $(\epsilon - 1)/(2\epsilon + 2.5)$ of the solvents, which is not found in the aromatic solvents.

These facts suggest that in the aromatic solvents a stereospecific solvent–solute interaction exists. The effect of temperature on PMMA in a benzene solution was measured. Figure 2 shows the NMR spectra, and the chemical-shift changes with temperature are shown in Figure 3. It is very interesting to note that the α-methyl signals shift to high field with increase in temperature, though the ester methyl signals go to low field. Furthermore, the separations of the α-methyl resonances, and also those of the ester methyl resonances change with temperature. The 100 Mc./sec. measurements show that the separation of the α-methyl resonances $(i - s)$ amount to 14.7 cps at 27°C. and 18.3 cps at 142°C. On the other hand, the separation of the ester methyl resonances $(i - s)$ shows 14.0 cps at 27°C. and 6.2 cps at 142°C. That is, the α-methyl resonances move to high field, and the separation becomes wider with temperature, though the ester methyl resonances move to low field and the separation becomes narrower. This result supports the view that PMMA forms π complexes in benzene solution.

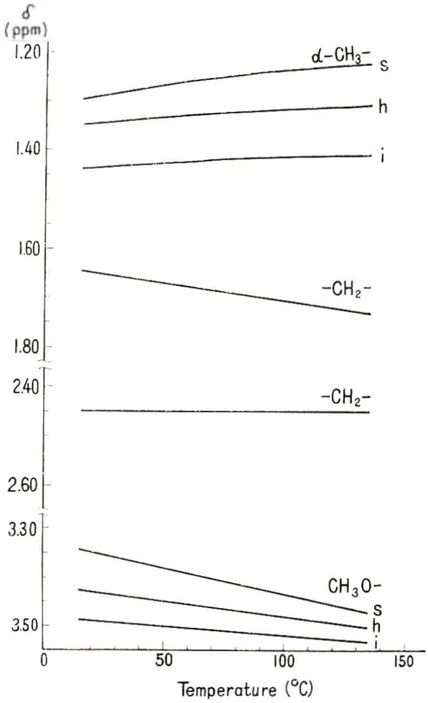

Fig. 3. Chemical-shift change of poly(methyl methacrylate) in benzene solution, vs. temperature.

Incidentally, those complexes encountered in NMR spectroscopy may be very short-lived compared with complexes of the usual sort. However, there undoubtedly exists a weak stereospecific solvent–solute interaction.

Assuming that each monomer unit of the polymer forms a π complex with one benzene molecule, we analyzed the result for the ester methyl group by the method proposed by Abraham.[8] Because in a CCl_4 solution the ester methyl group of the polymer shows a single peak, we assumed that the separation of the ester methyl resonances ($i - s$) of the uncomplexed polymer is 0 cps. We found that the separation ($i - s$) on complexing is 24 ± 4 cps, and ΔH, the heat of formation of the complex, is 2.8 ± 0.5 kcal./mole.

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Ordered Structures of Styrene–Butadiene Block Copolymers in the Solid State

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Synopsis

Several narrow molecular weight distribution block copolymers were prepared by a two-stage anionic polymerization technique. Films cast from these solutions were studied by electron microscopy. Replicas showed that the film surfaces were composed of layered structures with various orientations. Micrographs of ultrathin sections of stained films demonstrate that layered structures occur throughout the film. The widths of the copolymer layer spacings increase with increasing molecular weight and agree quite well with the calculated values.

INTRODUCTION

In a previous publication[1] several interesting properties of the A-B type of block copolymer were discussed. Although the major interest was centered on the solution properties and the iridescent colors of the higher molecular weight copolymers, the observation of surface structures in cast films was also reported. A question was raised concerning possible internal structures in the films and the effect of copolymer molecular weight and molecular weight distribution on these internal structures. In this paper we shall report the preliminary results of an investigation designed to answer these questions.

Block Copolymer Synthesis

Block copolymers, consisting of two homopolymer sequences, can be readily prepared by anionic polymerization.[2] In this investigation butyllithium was used as the anionic initiator, and the copolymerizations were carried out in toluene solutions. The polymerization reactions occurred in two separate steps;[3] the styrene monomer was polymerized first, to give narrow molecular weight distribution "living" chains, and the butadiene was then added to form the second block of the copolymer. The molecular weights were varied by successively reducing the amount of initiator in a series of copolymerizations.

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Electron Microscope Observations

Typical surface structures of films from three narrow molecular weight distribution copolymers are shown in Figure 1 (*A*, *C*, and *E*). These are electron micrographs of chromium-shadowed silicon monoxide surface replicas, which were prepared by a two-step technique that employs poly(vinyl alcohol) in the first step. The films were colorless, but the replicas show an aligned structure. The variations in the direction and orientation of the spacings are probably dependent upon the local conditions of drying. In general, the alignment becomes more discrete with increasing molecular weight, although variations exist in different localized regions of the film surfaces. To allow molecular mobility, the wet films were enclosed in a solvent-saturated atmosphere for 3 days before drying. The spacing measurements, shown in Table I, were obtained by averaging the values across several sets of lines in the micrographs. The spacing widths varied somewhat, depending upon the angle of observation, but the average values increased with increasing molecular weight.

TABLE I
Styrene–Butadiene Block Copolymer Series

Sample no.	Inherent viscosity, dl./g.	Molecular weight, light-scattering	E.M. spacing measurement, A.	
			Surface	Interior
I	0.86	157,000	590	500
II	0.89	185,000	710	650
III	1.10	237,000	1070	710
IV	1.78	612,000	irreg.	990

The interior structures of films from the same copolymer solutions are shown in Figure 1 (*B*, *D*, and *F*). The films used for these observations were prepared several months after those from which the replicas were obtained and were dried relatively quickly in a laboratory hood. A small portion of the film was embedded in epoxy resin, faced in the microtome, stained with osmium tetroxide, and then sectioned. The ultrathin sections were about 1000 A. in thickness. Since the osmium tetroxide adds to the double bonds in the butadiene units, it hardens the rubber and selectively stains the polybutadiene portions of the copolymer molecules.[4] The interior of the films also show regular alignment. These regions appear somewhat analogous to grains in metals; the observed size of these regions depends on the drying conditions and the orientation of these multidirectionally aligned, layered structures when sectioned. The spacing of the internal layers correlate with those of the surface.

The short-range alignment of the layered structures in the film interior is shown better at lower magnification in Figure 2 (*A*, *B*, and *C*). Many differently oriented regions are seen, the size of these regions varying in different portions of the sections. The large, indefinite, dark and light

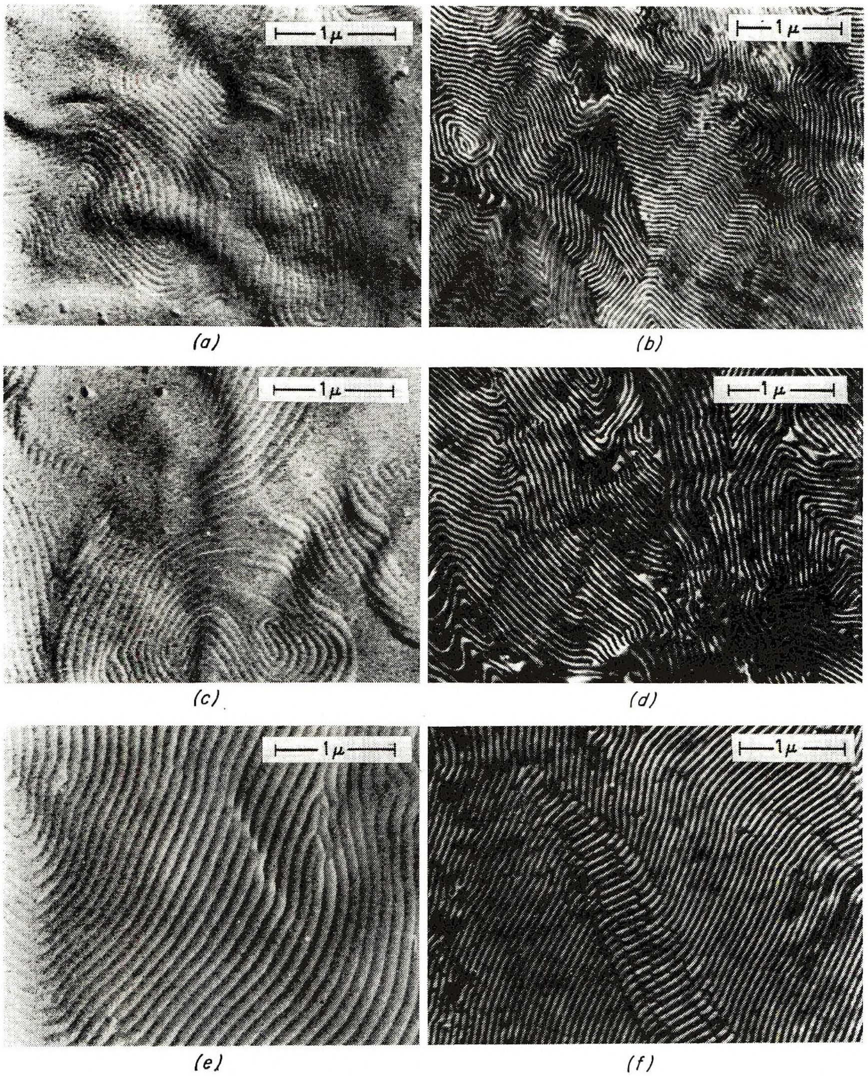

Fig. 1. Surface and interior structure of three narrow molecular weight block copolymer films: (A, B) sample I; (C, D) sample II; (E, F) sample III.

lines across the micrograph were caused by the microtome knife during sectioning. Figure 2*D* shows surface structure from the same film that was sectioned for Figure 2*C*. It is interesting to note the presence of many spiral structures in this particular area. Many different spacing widths can be observed in this micrograph.

The surface replicas (Fig. 2*E*) of a film from the highest molecular weight copolymer (sample IV, which possessed a two-peaked molecular weight distribution) shows a more gross structure with little alignment. Ultrathin sections of a film cast under room conditions from the same solution did not

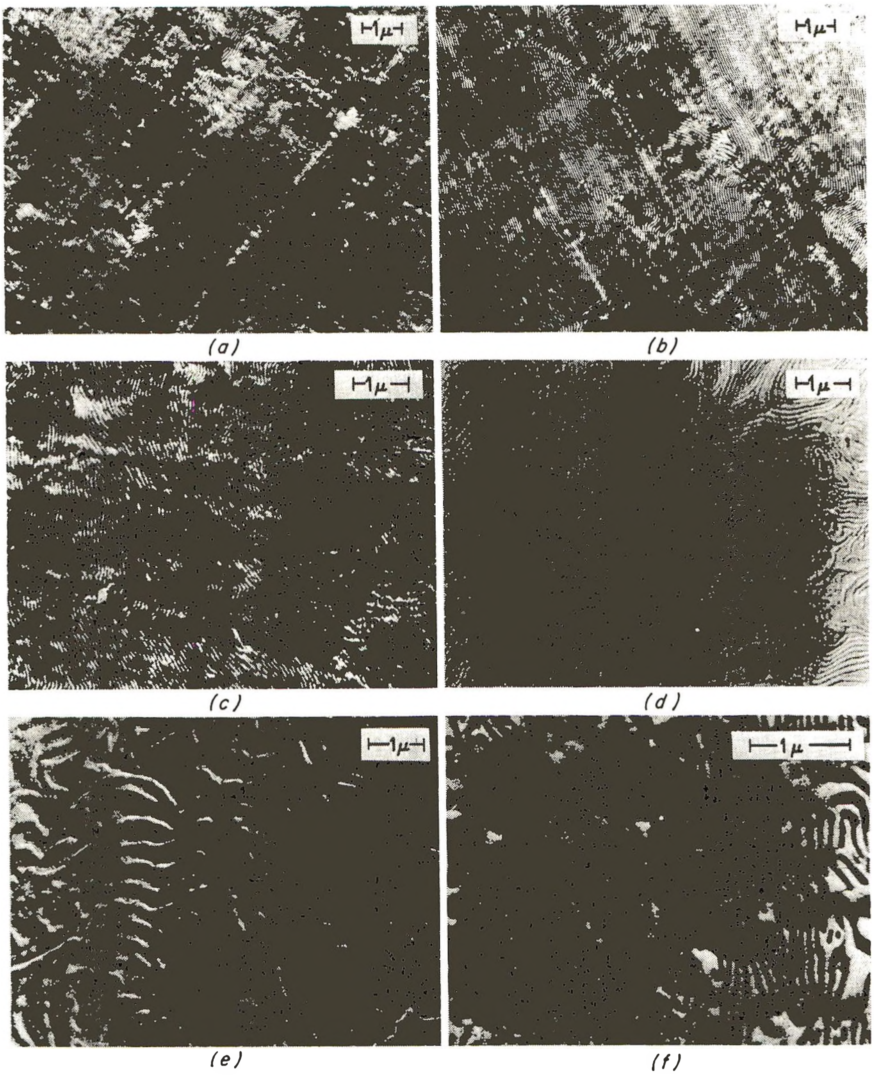

Fig. 2. Structure of films: (*A*, *B*, *C*) interior, from samples I, II, and III, at lower magnification; (*D*) surface, film shown in *C*; (*E*) surface, film from sample IV, a two-peaked molecular weight distribution copolymer; (*F*) interior, film from sample IV.

show regular alignment. However, when the copolymer solution was diluted before drying, the interior of a cast film possessed regions of layered structures (Fig. 2*F*). The extent of these layered structures was not as large as that observed of the single-peaked copolymers.

Block Copolymer Characterization

The copolymers were characterized by measuring the inherent viscosity in toluene (0.2 g./100 ml.) at 25°C., and the molecular weights were determined by light-scattering. The molecular weight distributions were

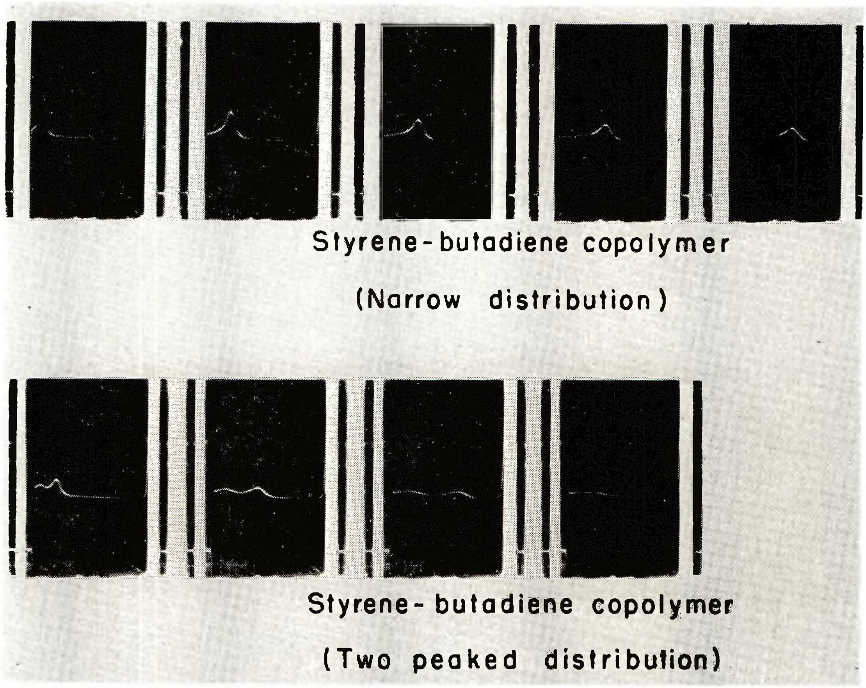

Fig. 3. Ultracentrifuge sedimentation Schlieren patterns.

characterized by examination of the sedimentation patterns from the ultracentrifuge. In these determinations 2-pentanone was used as the best approximation to a theta solvent. Figure 3 illustrates typical Schlieren patterns from a narrow single-peaked copolymer sample and a broad two-peaked copolymer sample. The properties of the four block copolymers (60:40 styrene/butadiene) of increasing molecular weight prepared by the two-step technique are listed in Table I.

Samples I, II, and III in Table I are narrow molecular weight distribution copolymers, as evidenced by a narrow sedimentation boundary in the ultracentrifuge, whereas sample IV possessed a two-peaked distribution. The inherent viscosity and light-scattering molecular weight determinations indicate that each successive sample possessed a higher molecular weight. Also shown are the average-spacing measurements from electron micrographs of both the surface and interior of the copolymer films. The average-spacing measurements were obtained from several regions where the alignment appeared most regular and compact because the orientation of the planes, when replicated, and the angle of cutting of the planes during sectioning affect the spacing distances. The smallest spacing value would probably represent spaces normal to the planes, which would correspond to the actual plane distances. Each measurement was usually across five spaces. The surface structure of sample IV was too irregular to give spacing measurements; however, measurements of the interior were obtained from a film that had been formed from a dilute copolymer solution.

The spacings of the four samples increase regularly with increasing molecular weight. The agreement between the surface and interior spacing measurements is reasonable considering all of the possible sources of discrepancy. For example, films for sectioning were prepared months later than, and under different drying conditions from, those used for replication. Different techniques and different electron microscopes were used, and the spacings varied somewhat from region to region.

From the copolymer composition and the light-scattering value for the molecular weight one can calculate a root-mean-square end-to-end distance for each portion of a linear block copolymer molecule on the basis of unperturbed chain dimensions, according to Flory[5] and Bueche[6] and with data from the *Polymer Handbook*.[7] These calculated values for the series of copolymers of increasing molecular weight are shown in Table II. We assumed complete entanglement of like portions of two calculated block copolymer molecules, to determine the value of the spacing for layers of the copolymer molecules. When like segments of two separate copolymer molecules are completely entangled, the volumes are additive; therefore, the diameter increases by a factor of the cubed root of 2 and, consequently, the calculated copolymer spacing was determined by multiplying $D_{\mathrm{PBD}} + D_{\mathrm{PS}}$ by 1.26. In Table II these values are compared with values obtained from measurements of the spacings in ultrathin sections of the films. The measured and calculated values are in good agreement, considering the assumptions involved in the calculated determinations and the possible errors involved in the average-spacing measurements.

TABLE II
Comparison of Calculated and Measured Copolymer Spacings

Copolymer mol. wt.	PBD mol. wt.	D_{PBD}, A.	PS mol. wt.	D_{PS}, A.	Calcd. copolymer spacing, A.	Measd. copolymer spacing, A.
157,000	63,000	203	94,000	236	553	500
185,000	74,000	220	111,000	256	599	650
237,000	95,000	250	142,000	290	680	710
612,000	245,000	401	367,000	467	1094	990

Morphology of Other Block Copolymers

Solutions and films of lower molecular weight copolymers were transparent and colorless; however, many of the higher molecular weight copolymers exhibited a blue color in solution, which usually persisted in films upon drying. Figure 4*A* illustrates the surface structure of a blue film that was dried under room conditions. Layered structures are not observed, and the surface contains many spheroidal and extended structures in the size range of the visible spectrum.

The interior of the same film displays many layered structures at different orientations (Fig. 4*B*) that are reminiscent of the grain structure in metals. These layered regions are short-ranged, usually extending only 1 to 3 μ before the orientation is altered. To determine whether the layers were preferentially oriented, sections were cut perpendicular to those of the previous sections. The structure of these sections (Fig. 4*C*) is not altered appreciably. When the film was sectioned parallel to its surface, the layered structure still persisted but appeared somewhat coarser (Fig. 4*D*). These sections indicate that under these conditions the evaporation of the

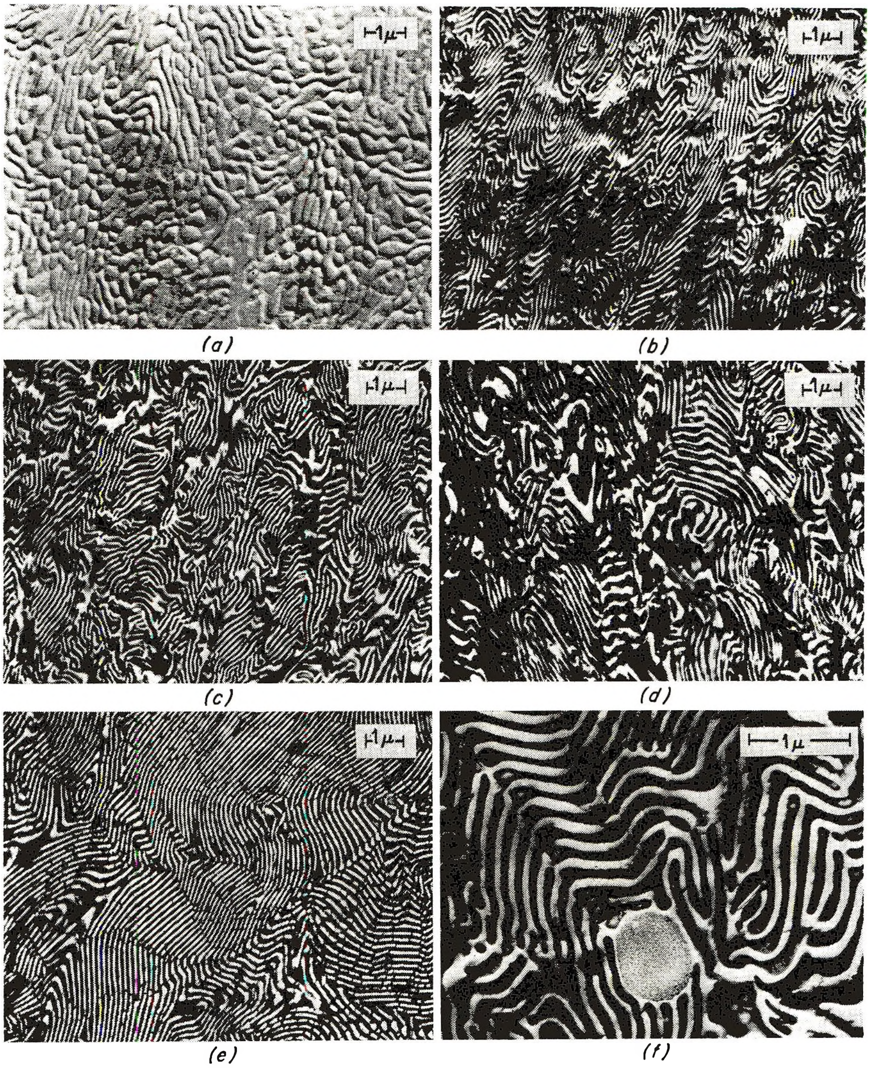

Fig. 4. Structure of a rectangular film exhibiting a blue color: (*A*) surface structure; (*B*) sectioned parallel to end; (*C*) sectioned parallel to side; (*D*) sectioned parallel to surface; (*E*) section of same copolymer dried slowly into a film exhibiting iridescence; (*F*) section of film from a 1% solution of same copolymer.

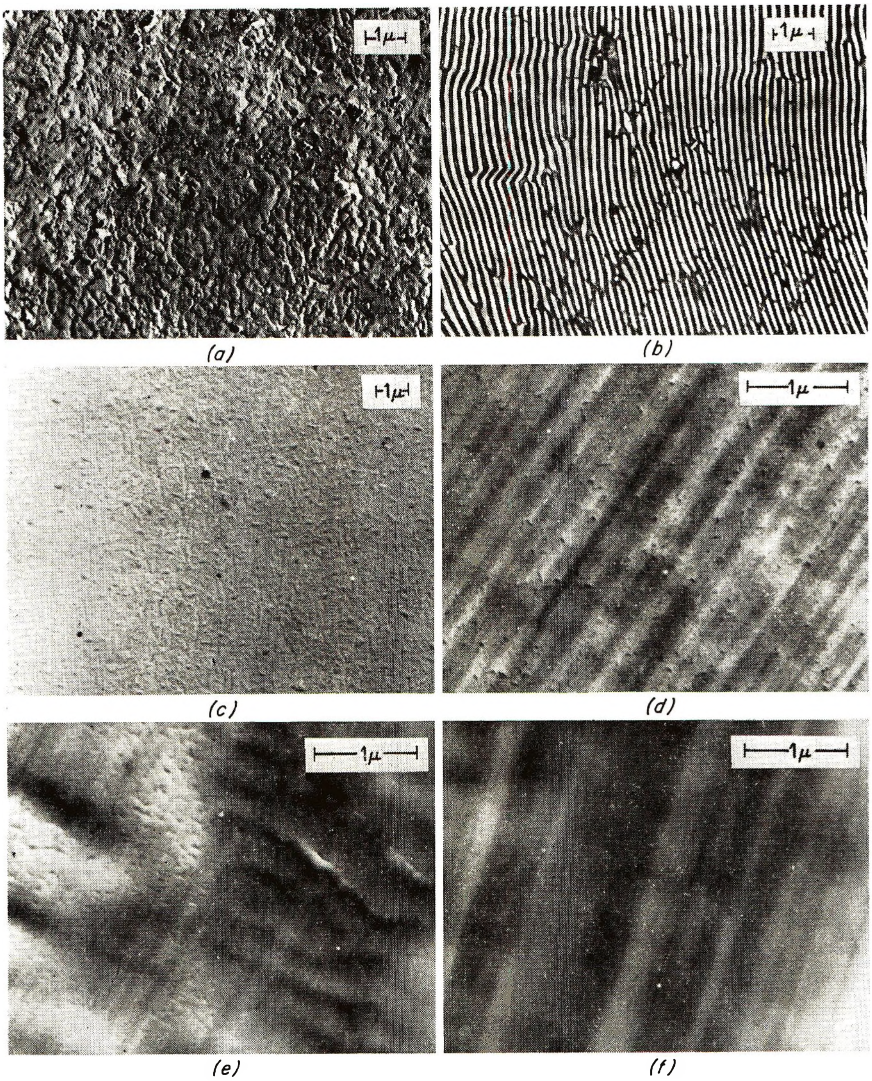

Fig. 5. Structure of films: (*A*) surface, slowly dried, iridescent film; (*B*) interior, same film; (*C*) surface of a styrene–butadiene–styrene sandwich copolymer film; (*D*) interior, film from same sandwich copolymer; (*E*) interior, film cast from same sandwich copolymer diluted to 5% solids; (*F*) interior, sandwich copolymer film containing 70% polybutadiene.

solvent from the surface did not produce large regions of preferentially layered structures.

A film from the same copolymer solution was slowly dried under a polyester film. After 28 days the edge of the copolymer film exhibited iridescence. Sections from this edge show that the aligned regions extend over a greater distance (Fig. 4*E*) than those in previous films; the spacing widths vary in some areas. When this copolymer was diluted to concentrations of 10, 5, and 1%, the solutions were colorless but dried into light-blue films. Layered structures were observed in cross-sections of these films. However, in the film cast from the 1% solution spherical configurations were observed in a few isolated regions (Fig. 4*F*). This indicates that the molecular structure in films might be affected by changes in concentration of the solutions.

A thin film of another high molecular weight copolymer was covered with a polyester film, so that months were required for the copolymer to dry. This film appeared multicolored. Replicas of its surface did not show alignment (Fig. 5*A*); either the polyester film prevented molecular alignment, or it was destroyed by the removal of the polyester film. Sections of the film interior contained regular alignment over extended regions (Fig. 5*B*). This, again, indicates that drying slowly enhances larger and more precisely layered structures.

Colored solutions were not obtained when a styrene–butadiene–styrene sandwich type of block copolymer (60% butadiene) was prepared by a three-step method. Alignment was not observed in the surface of films (Fig. 5*C*) or in sections of the film interior (Fig. 5*D*). Diluting the copolymer to a concentration of 5% before casting the film did not produce regular structures in the subsequent sections (Fig. 5*E*). Increasing the butadiene content of the sandwich copolymer to 70% did not produce aligned structures in sections of the film interior (Fig. 5*F*). The molecular arrangement of these sandwich copolymers may alter the effectiveness of the osmium tetroxide to fix and stain the butadiene units in these films. This work is preliminary, and additional experiments are planned for a study of the molecular arrangement of these copolymers.

Discussion

In the work of Sadron[8] and Skoulios et al.[9] the solution structures of block copolymers of polystyrene–polyethylene oxide are described as spherical, cylindrical, and layered, depending on the concentration. Their findings were made on relatively low molecular weight copolymers with a low-angle x-ray-scattering technique.

In this work a series of styrene–butadiene block copolymers of increasing molecular weight was studied in the solid state by electron microscopy. In general, a high degree of ordering was found in copolymer films cast from both concentrated and dilute solutions. The spacing of the layered structures increased with increasing molecular weight. Staining the copolymer permitted observation and measurement of the polystyrene and polybutadiene portions of the copolymer molecules in layered structures. The measured size of these portions increased with increasing molecular weight. The root-mean-square end-to-end distances of the polystyrene and polybutadiene portions of the molecules was calculated on the assumption of complete separation. The ratio of calculated line widths of the polystyrene portion to the polybutadiene portion is the same whether we assume no or complete entanglement of like portions of the block copolymer molecules and is equal to 1.16; the ratios determined from measured values for samples I, II, III, and IV ranged from 1.1 to 1.2, in good agreement with the calculated value. The measured values for the polystyrene and polybutadiene dimensions are in good agreement with the calculated values if one takes molecular entanglement into account. The amount of homopolymer produced in these copolymerizations was not determined, but homopolymer, if present, could alter the size of the existing phases and also cause disruption of the layered structures.

In general, we may conclude that the spacings observed agree well with the dimensions calculated for polymer molecules, considering the assumptions and inaccuracies involved. The structures observed in the electron microscope are, then, essentially alternate molecular layers of polystyrene and polybutadiene. If the molecular layers are sufficiently large, the films exhibit colors, as evidenced by the higher molecular weight samples.

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Synthesis and Thermogravimetric Analysis of Diol-Linked Tetrameric Hexaphenyldichlorophosphonitrile Polymers

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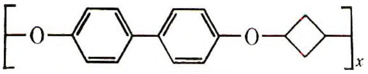
Synopsis

Several high molecular weight polymers have been prepared from the reactions of hexaphenyldichlorophosphonitrile tetramer with *p,p'*-biphenol, 4,4'-oxydiphenol, resorcinol, and benzidine. A simple fractionation procedure yielded samples of the biphenol-linked polymer with molecular weights of approximately 500,000. DTA and TGA studies of this polymer in a variety of environments indicate thermal degradation is initiated in the phosphonitrile ring.

INTRODUCTION

The preparation of polymeric materials from the reactions of cyclic phosphonitriles with aromatic dihydroxy linking agents has been described by several authors.[1-7] The reactions of hexaphenyldichlorophosphonitrile tetramer with several diols have been carried out in this laboratory and have been reported.[8] In this paper we wish to describe the preparation and fractionation of some of the more promising candidates from this series, plus the synthesis of a polymer employing benzidine as a linking agent. We also wish to present polymer stability data, based on thermogravimetric analyses, which indicate the sources of degradation of polymers in various enivronments.

The material of principal interest is the polymer I:



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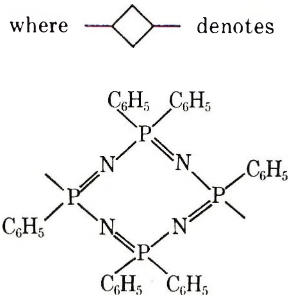
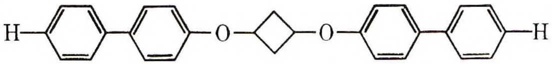


because it could be prepared from high-purity starting materials and the crude product was easily fractionated by the procedure described below. This polymer also has what was considered to be one of the simplest and most stable diol-linking agents; hence, it would be the best candidate for thermal stability studies. Polymers with the linking agents m—O—C_6H_4—O—, p—NH—C_6H_4—C_6H_4—NH—, and p,p'—O—C_6H_4—O—C_6H_4—O—, plus the model compound II



II

were also examined for a comparison of thermal stabilities.

EXPERIMENTAL

Apparatus

Molecular weights were determined on a Mechrolab Model 502 membrane osmometer at 37°C. with toluene as solvent. Solute concentrations ranged between 1.0 and 4.0 mg./ml. for a set of four determinations for each polymer sample. The instrument was calibrated regularly with standard polystyrene polymers supplied by ARRO Laboratories, Inc., Joliet, Illinois. Standards at 51,000, 97,200, 411,000, and 860,000 number-average molecular weight were used.

Thermogravimetric analyses were carried out on a DuPont Model 950 thermal balance with a scan rate of 5°C./min. and gas flow of 1 ft.^{3}/hr. In the one analysis done under vacuum, pressure was maintained at approximately 20 μ throughout the run. In the cases where wet atmospheres were desired, the gas was passed via sintered glass bubbler through a water column; otherwise, air, oxygen, and nitrogen were used directly from the tank. All gases were determined to be dry and free of contaminants by mass spectral analysis. Sample weights ranged from 3.5 to 65.0 mg.

Reagents

Hexaphenyldichlorophosphonitrile tetramer (m.p. 304–305°C.), III was prepared by the reaction of sodium azide with a 1:1 mixture of phenyldichlorophosphine and diphenylchlorophosphine[8] and purified by recrystallizing four times from dry toluene followed by vacuum drying at 180°C. for 24 hr. The p,p'-biphenol was purified by benzene extraction in a Soxhlet apparatus for 24 hr. to remove p-hydroxybiphenyl, dried in vacuum for 18 hr. at 150°C. and then zone-refined through 75 passes on a Sloan-McGowan zone melter. The 4,4′-oxydiphenol was recrystallized twice from benzene and dried in vacuum at 150°C. for 24 hr. Benzidine was recrystallized twice from anhydrous ethanol and vacuum-sublimed. Biphenyl from Eastman Organic Chemicals was distilled twice under vacuum. Resorcinol (Mallinckrodt A. R. Grade) was sublimed twice *in vacuo*. Xylene was distilled from lithium aluminum hydride.

Preparation of Hexaphenylbis(phenylphenoxy)phosphonitrile Tetramer (II). A mixture of III (5.00 g., 0.007 mole) and *p*-hydroxybiphenyl (3.93 g., 0.023 mole) was heated in a glass ampule attached to a vacuum line. At 205–210°C., the reaction was vigorous with the quantitative amount of hydrogen chloride (0.014 mole) evolved in 6.5 hr. Excess *p*-hydroxybiphenyl was separated by sublimation and the reaction product was crystallized from acetonitrile to give 6.2 g. of II, (m.p. 198–200°C.).

ANAL. Calcd. for $C_{60}H_{48}P_4N_4O_2$: C, 73.5%; H, 4.9%; P, 12.7%; N, 5.7%; O, 3.3%; mol. wt. 980. Found: C, 73.4%; H, 4.9%; P, 12.6%; N, 5.7%; O, 3.3%; mol. wt. 967 (determined on a Mechrolab Model 301 vapor-phase osmometer).

Polymerization Reactions

p,p′-*Biphenol*

Melt Reaction. In a typical experiment III (14.26 g., 0.02 mole) and *p,p*′-biphenol (3.72 g., 0.02 mole) were intimately mixed and loaded into a heavy-walled glass ampule which was attached to a vacuum line. The tube was heated by means of an oil bath at 220°C. Evolution of hydrogen chloride commenced after 1 hr. and the gas was continuously removed from the reaction zone by condensation in a −196°C. trap. After 4 hr., when HCl generation became slow, the temperature of the oil bath was raised to 275°C. and heated 6 hr. more until gas evolution ceased. Infrared analysis of the gas (435 ml. std. conditions 98%) indicated that it was hydrogen chloride containing a trace of toluene. A small amount (35 mg.) of white sublimate in the neck of the reaction ampule was identified as a mixture of unreacted biphenol and ammonium chloride. The polymer (IA), a pale yellow glass melting 185–220°C. was soluble in common organic solvents.

ANAL. Calcd. for $C_{48}H_{38}P_4N_4O_2$: C, 69.7%; H, 4.6%; P, 15.0%; N, 6.8%; O, 3.9%. Found: C, 70.0%; H, 4.3%; P, 14.7%; N, 6.8%; O, 4.0%; Cl, 0. $\bar{M}_n$ = 42,700 (crude product).

Solution Reaction–Biphenyl. A mixture of III (49.6532 g., 69.59 mmole), *p,p*′-biphenol (12.9594 g., 69.60 mmole) and biphenyl (50 g.) was placed in a 250-cc. round-bottomed flask with a 10-in. long neck fitted with a detachable condenser. The apparatus was attached to a vacuum line and provision was made for continuous purging by dry helium gas. The reaction mixture was heated to the reflux temperature of biphenyl, 256°C., for 4 hr., during which time about 75% of the calculated amount of hydrogen chloride was evolved. The gas was collected in two liquid nitrogen traps from which it could be passed to a measuring system on the vacuum line. The entraining helium was passed through a calcium sulfate drying tube, a mercury bubbler, and a sodium hydroxide solution before it was allowed to escape.

Heating at reflux was continued for 24 hr.; at the end of this time 90% of the total hydrogen chloride was evolved. Biphenyl was then distilled off under vacuum after the detachable condenser was replaced by a receiver.

Although the reaction mixture was heated at 285°C. under vacuum for 5 hr. after the solvent had been removed, less than 1 mole-% hydrogen chloride was evolved. During this final heating period, a small amount of material, which was identified as NH_4Cl (70 mg.), together with a trace of unreacted III, sublimed from the melt.

The reaction flask was broken and the solid polymer was recovered, ground in a mill and the resulting fine powder dissolved in benzene. The solution was filtered to remove glass particles and then freeze-dried. The molecular weight of the gross sample (IB) was 115,000.

4,4′-Oxydiphenol

Melt Reaction. III (7.13 g., 0.01 mole) was reacted with 4,4′-oxydiphenol (2.20 g., 0.01 mole) in a manner similar to that described for melt reactions of *p,p′*-biphenol, with the exception that the reaction mixture was also heated at 320°C. for 2 hr.; 92 mole-% of the theoretical amount of hydrogen chloride was evolved. The sublimate (35 mg.) was examined by infrared analysis and was shown to be largely $[(C_6H_5)_2PN]_3$, together with traces of NH_4Cl and unreacted diol. The product was a yellow, brittle resin which started to soften at 150°C.

ANAL. Calcd. for $C_{48}H_{38}P_4N_4O_3$: C, 68.5%; H, 4.5%; P, 14.7%; N, 6.7%; O, 5.7%. Found: C, 68.7%; H, 4.5%; P, 14.9%; N, 6.8%; O, 6.1%; Cl, 0; $\bar{M}_n$ 5000.

This polymerization was repeated and the reaction temperature was held at 180–185°C. for 42 hr. and at 225–230°C. for 8 hr. During the heating cycle, a total of 86.4% of the theoretical amount of hydrogen chloride was generated. No sublimation of reactants or by-products was noted. The properties of the resinous product were similar to those described above, although the molecular weight (8250) was slightly higher.

Solution Reaction. A slurry of III (14.26 g., 0.02 mole) and 4,4′-oxydiphenol (4.04 g, 0.02 mole) in 100 ml. anhydrous xylene was heated under nitrogen with vigorous stirring. After 1 hr. at reflux, hydrogen chloride evolution began. The solution became clear after two weeks, and the reaction was continued for an additional week until the effluent gas was no longer acidic. The solvent was then evaporated *in vacuo* and the solid product was heated at 275°C. for 2.5 hr. The light-tan, brittle resinous product had a molecular weight of 29,000. Fractional precipitation of this polymer from a benzene–heptane solution yielded a first fraction (15% of sample weight) with a molecular weight of 135,000.

Resorcinol–Melt Reaction

A mixture of III (12.5 g., 0.017 mole) and resorcinol (2.0 g., 0.017 mole) was loaded into a glass ampule and was heated *in vacuo* at 220°C. After 10 hr. the evolution of gas became negligible, and the reaction temperature was raised to 265°C. for 2 hr. The hydrogen chloride generated was

691 ml. std. conditions, 91% of the theoretical amount. The light-brown resinous product softened over the range 130–150°C.

Anal. Calcd. for $C_{42}H_{34}P_4N_4O_2$: C, 67.2%; H, 4.5%; P, 16.5%; N, 7.5%; O, 4.3%. Found: C, 67.3%; H, 4.7%; P, 16.2%; N, 7.5%; O, 4.1%; Cl, 0; $\bar{M}_n$ 25,000.

Fractional precipitation of this product yielded a polymer, 12% by weight, which had a molecular weight of 104,500.

Benzidine–Melt Reaction

An ampule containing 3.68 g. of benzidine (0.02 mole) and 14.26 g. of III (0.02 mole) was heated gradually over a 6-hr. period to 290°C. The reaction temperature was maintained for 16 hr. During this period 87.5% of the theoretical amount of hydrogen chloride was evolved. Benzidine dihydrochloride (55 mg.) was recovered as a sublimate. The product began to soften at 205°C. and was insoluble in benzene.

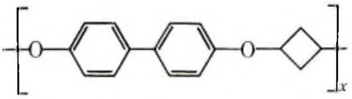
Anal. Calcd. for $C_{48}H_{40}P_4N_6$: C, 69.9%; H, 4.9%; P, 15.0%; N, 10.2%. Found: C, 69.5%; H, 5.2%; P, 15.2%; N, 10.4%; Cl, 0.24%.

Polymer Fractionation

A 3.1-g. sample of polymer IA was dissolved in 325 ml. benzene. The solution was heated at 55°C., and 75 ml. heptane was added slowly with stirring. The solution was then allowed to cool overnight. The polymer which had collected as an oil in the bottom of the container was recovered

TABLE I

Fractionation of



Polymers

Fraction no.	Weight, g.	Weight %	Cumulative wt. %	$\bar{M}_n$
		Fractionation of Polymer IA		
1	0.64	20.6	20.6	259,000
2	0.46	14.8	35.4	183,600
3	0.52	16.8	52.2	77,700
4	0.70	22.6	74.8	58,300
5	0.43	13.9	88.7	24,800
6	0.08	2.6	91.3	16,400
7	0.15	4.8	96.1	7,460
8	0.02	0.7	96.8	3,720
9	0.01	0.3	97.1	1,600
		Fractionation of Polymer IB		
1	0.495	9.5	9.5	541,000
2	1.22	23.5	33.0	233,000
3	1.22	23.5	56.5	65,900
4	0.665	12.8	69.3	23,300

by decanting the solution, dissolving the residue in 20 ml. of benzene, completely reprecipitating the polymer with 200 ml. heptane, and again decanting the solution. The fraction was dissolved in benzene, freeze-dried, and weighed. The original benzene–heptane mother liquor was warmed to 55°C. and additional heptane added to cause slight turbidity. The second, and subsequent fractions were isolated in the manner described above. The results of fractionations of two samples of *p,p'*biphenol-linked polymer are given in Table I.

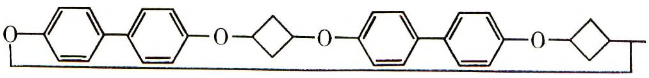
Vacuum Pyrolysis of III–Biphenol Polymer

Samples of polymer IA, fraction 3, were pyrolyzed under vacuum to recover and measure the amounts of volatile products. In a typical experiment, the sample was placed in a 300 × 15 mm. tube and evacuated on a vacuum system fitted with liquid nitrogen (−196°C.) traps and Sprengel pump for collecting noncondensable gases. The samples were heated under static vacuum at about 550°C. for 15 hr., evolved benzene being collected in the −196°C. traps. The hydrogen was pumped to a calibrated bulb and characterized by its mass spectrum. The sublimate was collected from the reaction vessel above the heated zone and was characterized as $[(C_6H_5)_2PN]_3$ by its infrared spectrum. The temperature of 550°C. was chosen for heating, because no further evolution of hydrogen or benzene was observed above this point. The results of three pyrolyses are shown in Table II.

RESULTS AND DISCUSSION

Table III shows the results of temperature-scan pyrolyses of several polymers in a variety of atmospheric environments. The arbitrary criterion for stability was the temperature at which the initial sample weight was decreased by 10%. This point was chosen rather than the initial departure from the starting sample weight baseline, because this point was not always easy to see and occasionally traces of solvent caused minor departures from the baseline.

The data in Table III are presented to show the effects of polymer molecular weight and gaseous environment on thermal stability. An examination of thermograms 5, 6, 7, 8, 9, and 13 shows that the 10% decomposition point of the same polymer varies only slightly with molecular weight. The average 10% temperature was 473 ± 5°C. The range of molecular weights covered by these thermograms is from 9,200 (~10 monomer units) to 50,000 (~600 monomer units). Thermogram 16 shows thermal stability of the dimer (V)



V

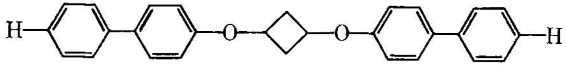
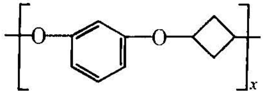
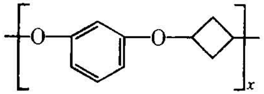
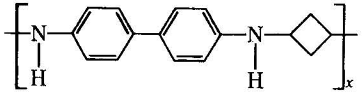
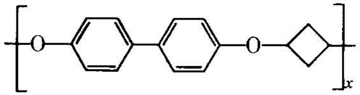
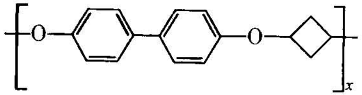
TABLE II

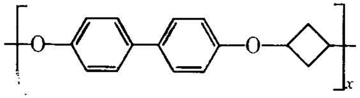
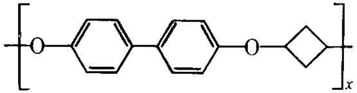
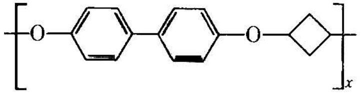
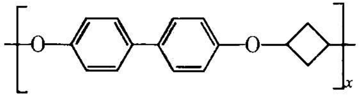
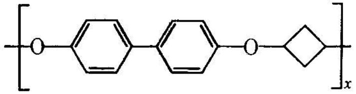
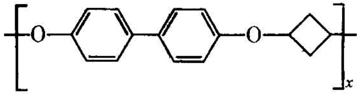
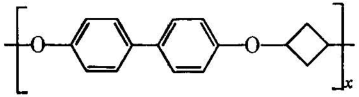
Vacuum Pyrolyses of III–Biphenol Polymer

					Mole ratios			
Sample no.	Sample wt., g. (mmole)[a]	Evolved benzene, g. (mmole)	Evolved trimer, g. (mmole)	Evolved hydrogen, ml. (mmole)	C_6H_6/sample	H_2/sample	H_2/C_6H_6	Trimer/sample
1	4.335	0.876	0.706	10.88				
	(5.24)	(11.24)	(1.19)	(0.48)	2.15	0.091	0.043	0.23
2	0.713	0.116	0.050					
	(0.863)	(1.49)	(0.084)		1.72			0.10
3	0.531	0.118	0.043					
	(0.643)	(1.51)	(0.072)		2.35			0.11

[a] Formula wt. of monomer = 826.

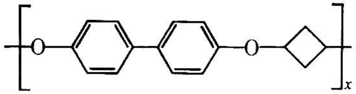
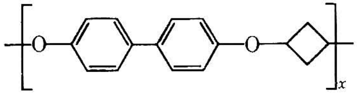
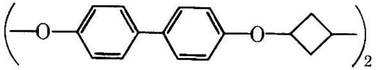
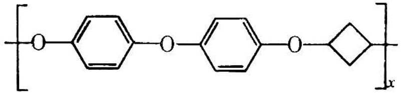
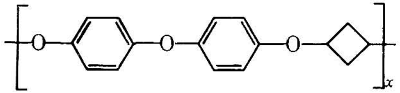
TABLE III
Temperature Scan Thermograms of Phosphonitrile Polymers

No.	Polymer structure	Polymer fraction	$\bar{M}_n$	Atmosphere	Sample wt., mg.	10% wt. loss, °C.	Total wt. loss, mg.	Remarks
1		—	980	N_2	15.0	400	15.0	Model compound (monomer)
2		1st	105,000	Wet air	17.3	390	17.3	
3		1st	105,000	N_2	20.4	460	10.4	
4		Crude	Not deter.	N_2	40.9	470	17.0	
5		Crude	9,200	N_2	28.6	477	Not meas.	a
6		Crude	30,300	N_2	21.4	478	Not meas.	a

7		Crude	52,000	N_2	39.0	475	Not meas.	a
8		Crude	115,000	N_2	11.4	465	5.5	
9		1st	259,000	Wet air	12.6	380	Not meas.	a
10		1st	541,000	N_2	12.7	465	5.5	
11		1st	541,000	Wet N_2	20.2	398	Not meas.	a
12		1st	541,000	O_2	15.2	457	Not meas.	a
13		1st	541,000	N_2	3.36	475	1.65	

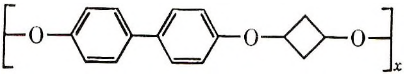
(continued)

TABLE III (*continued*)

No.	Polymer structure	Polymer fraction	$\bar{M}_n$	Atmosphere	Sample wt., mg.	10% wt. loss, °C.	Total wt. loss, mg.	Remarks
14		1st	259,000	Air	27.7	475	4.0	
15		1st	259,000	Vacuum	32.0	310	Not meas.	a
16		9th	1,600	N_2	14.5	450	7.6	
17		1st	135,000	N_2	9.65	362	7.2	
18		1st	135,000	Wet air	14.3	355	10.7	

[a] Weight loss did not reach a constant value before end of thermogram.

(M_n = 1600) whose 10% point was 450°C., considerably below the average of the higher molecular weight samples. Thermogram 1 is a monomeric model compound containing the P—O—C bonds of the diol-linked polymer,



The 10% point of this compound is lower (400°C.) than that of the dimer V.

These results show that, for polymers of about 10 monomer units and higher, decomposition is independent of chain length, suggesting random cleavage rather than chain unzipping from a labile end group. The presence of $[(C_6H_5)_2PN]_4$, $[(C_6H_5)_2PN]_3$, and benzene in the volatile residues of vacuum pyrolyses (Table II) suggests that rupture of the phosphonitrile tetramer ring may be the primary source of degradation.

Similar observations have been made by Korshak et al.,[9] who studied the pyrolysis of octaphenyltetraphosphonitrile (VI)

VI

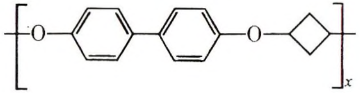
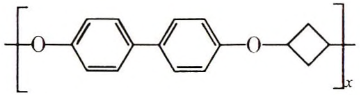
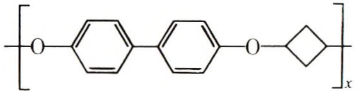
in sealed ampules up to 500°C. Mixtures of pentamers, hexamers, and higher polymers, plus benzene were obtained between 460 and 500°C. At temperatures below 420°C., trimers were also observed.

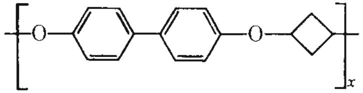
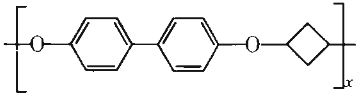
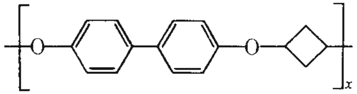
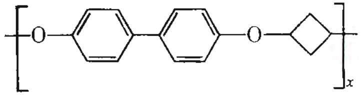
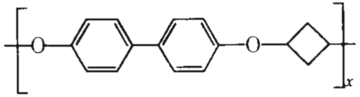
The effect of environment on the 10% point may be seen by examination of thermograms 9, 11, 12, 13 and 14. High molecular weight samples of polymers were examined in dry and wet nitrogen, dry oxygen, and dry and wet air. The 10% points in dry nitrogen and dry air were identical (475°C.) and in dry oxygen slightly lower (457°C.). In wet air the value decreased to 380°C. and in wet nitrogen a similar value was obtained (400°C.).

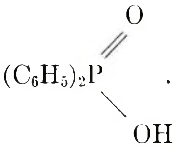
These results show a trend which suggests that moisture and perhaps oxygen lower the temperature at which decomposition begins. The low value of the 10% point (310°C.) in thermogram 15 suggests that at atmospheric pressure, volatile products form which are not swept away, but in vacuum these materials sublime or are condensed in traps. This result indicates that the onset of decomposition may be nearer 300°C. than 475°C., as indicated in atmospheric pressure thermograms.

Under the much harsher conditions described in Table IV, where samples are exposed for several hours at constant temperature, a more realistic picture of the thermal stability of the diol-linked polymers emerges. Even under the inert conditions of dry nitrogen, decomposition occurs between 300 and 350°C. and in ambient air, evidence of decomposition

TABLE IV
Constant-Temperature Thermograms of Phosphonitrile Polymers

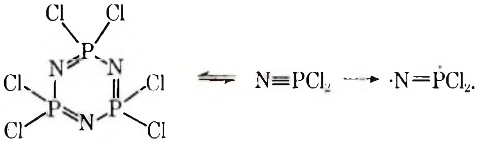
No.	Polymer structure	Fraction	$\bar{M}_n$	Atmosphere	Sample wt., mg.	Total time, hr.	Total wt. loss, mg.	Average wt. loss rate, mg./hr.	Temperature, °C.
1		1st	259,000	N_2	43.0	18.5	0.0	0.0	300
2		1st	259,000	N_2	25.5	5.0	5.6	1.12	350
3		1st	259,000	Wet air	11.4	3.3	8.0	2.42	300

4		Crude	Not deter.	Wet air	65.1	3.3	10.0	3.30	300
5		Crude	Not deter.	Wet air	38.0	18.0	11.0	0.61	245
6		1st	259,000	Wet air	12.2	19.2	5.2	0.28	225
7		1st	259,000	Air	55.0	2.0	3.0	1.50	350
8		1st	259,000	Air	55.0	24.0	2.2	0.093	300

is observed at 225°C. with the isolation of  $(C_6H_5)_2P(=O)OH$. It is apparent that long-term stability under ordinary atmospheric conditions is considerably lower (~250°C.) than short term stability under inert conditions (temperature scan TGA in dry N_2).

An examination of thermograms 3, 4, and 17 in Table III shows the stability of polymers with linking agents other than *p,p'*-biphenol. The compounds of 3 and 4 have essentially the same 10% points as the diol-linked polymer, but compound of thermogram 17 has a much lower value (362°C.). In this polymer it may be the $—C_6H_4—O—C_6H_4—$ group, which the other polymers do not have, that degrades at a lower temperature than the tetramer ring. This hypothesis is supported by thermogram 18 (Table III) which shows that the 10% point (355°C.) is only slightly affected by moisture and oxygen, suggesting that the linking agent degrades before the phosphonitrile ring, which is affected by moisture.

Although no work has been published on the kinetics and mechanism of decomposition of the type of polymer described above, Gimblett[10] has reviewed work on polydichlorophosphonitriles and has proposed a first-order mechanism for the formation of chain polymer from dichlorophosphonitrile timer.



The diradial undergoes a series of propagation, crosslinking, and termination reactions resulting in the formation of a rubbery polymer.

If the tetramer ring of the diol-linked polymers, described above, degraded in a similar manner by the elimination of $N{\equiv}P(C_6H_5)_2$ groups, a kinetic treatment from weight loss measurements could be carried out and our observation of $[N{=}P(C_6H_5)_2]_3$ formation and those of Korshak et al.[9] would be rationalized. However, our observation of the simultaneous formation of benzene and diphenylphosphonitrile trimer suggests that the degradation of I may be more complex, and weight loss measurements (TGA) may not yield data interpretable by the first-order kinetics, unless $N{\equiv}P(C_6H_5)_2$ is the initial degradation product.

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Ferrocene-Containing Polyesters and Polyamides

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Synopsis

A series of ferrocene-containing polyesters and polyamides were prepared by refluxing 1,1′-dichlorocarbonylferrocene with various diols and primary diamines in xylene–pyridine solvent. The polyamides were all solids, but some of the polyesters were liquids. Reported are the infrared spectra and solubility characteristics of all the polymers and, where possible, the molecular weight and molecular weight distributions. In general, these polyamides and polyesters were of relatively low molecular weight (below 4000), but the polyesters were readily chain extended and crosslinked by di- and triisocyanates. Elemental analyses are reported for all the polymers prepared.

INTRODUCTION

Only a few reports of polyamides and polyesters of ferrocene have appeared. Polyamides of ferrocene have been previously reported by Knobloch and Rauscher[1] and by Okawara et al.[2] In these studies 1,1′-dichlorocarbonylferrocene was reacted with various diamines for short periods (up to 5 min.) at ambient temperatures in the presence of organic or inorganic bases. High yields of the corresponding polyamides were obtained, but only low molecular weight polymers were formed. Reported here is the preparation of a series of solid polyamides by reacting 1,1′-dichlorocarbonylferrocene with several diamines in refluxing xylene–pyridine solutions for several hours.

Polyesters containing ferrocene in the backbone of the chain have been prepared previously by polyacylation of diols with 1,1′-dichlorocarbonylferrocene in the presence of pyridine[3] and NaOH,[1] by heating 1,1′-ferrocenedicarboxylic acid in the presence of ethylene glycol,[4] and by the transesterification of dimethyl-1,1′-ferrocenedicarboxylate with ethylene glycol.[1] A series of polyesters of ferrocene have now been prepared from 1,1′-dichlorocarbonylferrocene and a series of diols in refluxing xylene–pyridine. These polyesters, all of which were hydroxy-terminated, were cured with di- and triisocyanates. In addition, a melt-phase condensation between 1,1′-dichlorocarbonylferrocene and trimethylene glycol demonstrated that this technique can be used to increase polymer molecular weight.

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TABLE I

Ferrocene-Containing Polyesters and Polyamides Prepared from 1,1′-Dichlorocarbonylferrocene and Diols (or Diamines) in Refluxing Xylene–Pyridine Solution[a]

Polymer no.	Diol or diamine used	Yield, %			Appearance	Melting or softening point, °C.	Molecular weight[b]
		Xylene-soluble	Xylene-insoluble	Total			
1	1,10-Decanediol	82	8	90	Xylene-soluble, brown wax	Wax at 25, viscous liquid at 65	500–4000 range $\bar{M}_n = 1000$ GPC
					Xylene-insoluble, brown powder	Blackened at 350	—
2	Pentaerythritol	20	39	59	Soluble, brown powder	80–95	1300
					Insoluble, brown powder	130–137	—
3	1,1′-Dihydroxymethyl-ferrocene	27	30	57	Soluble, brown-black granular solid	85–110	1600
					Insoluble, brown powder	>470	—
4	Triethylene glycol	48	5	53	Soluble, dark brown liquid	Viscous liquid at 25	2300
					Insoluble, brown powder	80–95	—
4 (melt phase)	Triethylene glycol	34	2	36	Soluble, dark brown liquid	Viscous waxlike liquid at 35	6000[c]

5	Trimethylolpropane-monoallyl ether	83	5	88	Soluble, dark brown liquid	Viscous liquid at 25	600–3100 range $\bar{M}_n$ = 1600 GPC
5[d]	Trimethylolpropane-monoallyl ether	92	0	92	Dark brown liquid	Viscous liquid at 25	80% ~ 770 20% ~ 1010 GPC peaks
6	1,4-Diaminobutane	1–2	54	56	Insoluble, brown powder	160–180	—
7	1,6-Diaminohexane	5	51	56	Insoluble, dark brown powder	135–160	—
8	1,11-Diaminoundecane	4	49[e]	53	Insoluble, brown-black powder	85–110	—
9	Piperazine	26	28	54	Soluble, deep brown powder	150–160	1500
					Insoluble, yellow-brown powder	290–298	2400
10	*p*-Diaminobenzene	2	88	90	Soluble, brown powder	Darkens 220 m.p. >470	1000
					Insoluble, brown powder	Darkens 220 m.p. >470	—

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[a] Mole ratio of diol (or diamine) to 1,1′-dichlorocarbonylferrocene used in all cases was 1.

[b] All molecular weights are osmometric number-average values except where otherwise noted.

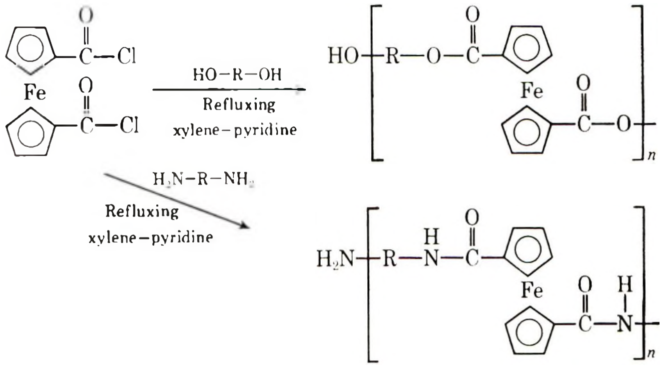
[c] Molecular weight is difficult to reproduce closely due to insolubility of polymer in solvents suitable for osmometer use.

[d] Dichloride was added dropwise to a solution of the diol already in the reaction flask.

[e] Dissolved in formic acid and reprecipitated with methanol.

RESULTS AND DISCUSSION

The polyesters and polyamides prepared according to eq. (1), and their physical properties and yields are summarized in Table I.



(1)

Here HO—R—OH is 1,10-decanediol (polymer 1), pentaerythritol (polymer 2), 1,1′-dihydroxymethylferrocene (polymer 3), trimethylene glycol (polymer 4), or trimethalolpropane monoallyl ether (polymer 5), and $H_2N—R—NH_2$ is 1,4-diaminobutane (polymer 6), 1,6-diaminohexane (polymer 7), 1,11-diaminoundecane (polymer 8), piperazine (polymer 9), or diaminobenzene (polymer 10). Table II presents the elemental analysis of all polymers obtained, and Tables III and IV contain the infrared spectra of these polymers obtained on a Perkin-Elmer 21 infrared spectrometer

TABLE II
Elemental Analysis of Ferrocene-Containing Polyesters and Polyamides

Polymer no.	Found				Calculated			
	C, %	H, %	N, %	Fe, %	C, %	H, %	N, %	Fe, %
1 soluble	63.5	6.2	—	13.7	64.2	6.8	—	13.6
2 soluble	55.2	5.0	—	14.3	54.5	4.8	—	15.0
2 insoluble	54.1	4.5	—	20.5	54.5	4.8	—	15.0
3 soluble	59.1	4.35	—	23.5	59.6	4.14	—	23.2
3 insoluble	59.4	4.26	—	23.3	59.6	4.14	—	23.2
4 soluble	55.5	5.24	—	14.5	55.7	5.15	—	14.4
5 soluble	60.4	5.48	—	14.2	60.3	5.53	—	14.1
5[a]	60.7	5.41	—	14.2	60.3	5.53	—	14.1
6 insoluble	59.3	5.33	8.42	17.0	59.0	5.51	8.60	17.15
7 insoluble	61.3	6.32	7.78	15.6	61.0	6.22	7.9	15.8
8 insoluble	65.7	7.65	6.51	13.6	65.2	7.56	6.63	13.2
9 soluble	58.9	5.26	8.75	16.5	59.4	4.95	8.64	17.3
9 insoluble	59.9	5.32	8.21	18.6	59.4	4.95	8.64	17.3
10 soluble	61.9	4.21	8.20	15.8	62.4	4.05	8.1	16.2
10 insoluble	62.2	4.20	8.19	16.0	62.4	4.05	8.1	16.2

[a] Dichloride was added dropwise to a solution of the diol already in the reaction flask.

TABLE III
Infrared Spectra of Ferrocene Containing Polyesters,
Band positions, cm.$^{-1}$

Polymer no.	Terminal OH group	C—H stretching		C—O stretching		CH_2 deformation	Ferrocene out-of-plane
		sp^2CH	sp^3CH	C=O	C—O		
1[a]	3320	3050	2810 2970	1701	1269 1139	1459	830
2 soluble	3402	3070	2935 2875	1717	1279 1346	1470	836
2 insoluble	3410	3068	2938 2879	1715	1278 1350	1470	837
3 soluble and insoluble[b]	3400	3060	2920	1718	1279 1136	1488	827
4 soluble	3480	3090	2940 2880	1722	1280 1145	1472	835
5 soluble[c]	3435	3050	2920 2960	1710	1276 1143	1471	828

[a] $(CH_2)_{10}$ rocking absorption 721 cm.$^{-1}$.

[b] Spectra of xylene-soluble and -insoluble polymers were superimposable.

[c] $>C=C<$ stretching band found at 1630 cm.$^{-1}$ and bands at 921 and 990 cm.$^{-1}$ are present. The 921 cm.$^{-1}$ band is due to out-of-plane deformation of $=CH_2$ group which is shifted toward higher frequency from its normal value of 910 cm.$^{-1}$ by 10–12 cm.$^{-1}$ by the presence of oxygen.[7] For instance, $R—O—CH_2—CH=CH_2$ usually shows a 12 cm.$^{-1}$ shift toward higher frequency from 910 cm.$^{-1}$. The 990 cm.$^{-1}$ band is assigned to the hydrogen deformation mode of $—C=CH_2$.[8]

equipped with NaCl optics. Molecular weights were obtained by using a Mechrolab Model 301A vapor-pressure osmometer, and in certain cases by gel permeation chromatography. Many of the polymers were insoluble in solvents which were suitable for osmometry, thus precluding the determination of their molecular weights. In general, polyesters and polyamides of ferrocene are solids. However, as the length of the organic chain between the ferrocene units increases, the softening point of the polymer decreases until waxlike polyesters such as polymer 1 and liquid polyesters (polymers 4 and 5) can be obtained.

The use of long reaction periods in refluxing xylene–pyridine media to produce high molecular weight polyamides and polyesters of ferrocene from 1,1′-dichlorocarbonylferrocene and diamines or diols does not appear practical. Only relatively low molecular weights were obtained which

TABLE IV

Infrared Spectra of Ferrocene-Containing Polyamides Band positions, cm.$^{-1}$

Polymer no.	*cis* and *trans* hydrogen-bonded NH	C—H stretching		Amide			CH_2 deformation	Ferrocene out-of-plane deformation C—H
		sp^2CH	sp^3CH	I	II	III		
6	3300 rounded	3050	2910 2830	1623[a]	1535	1292	1461	821
8	3320 rounded	3045	2910 2820	1624[a]	1532	1291	1460	820
8	3325 rounded	3045	2915 2825	1625[a]	1532	1294	1462	821
9	3340 rounded	3040	2940 2860	1633	—	—	1457	819
10[b]	3350 rounded	3045 3016	—	1632	1530	1301	1462	822

[a] The amide I band in polyamides 6–8 appears at lower frequencies than the usual 1630–1650 cm.$^{-1}$ range. This could be due to interaction with the strongly electron-donating ferrocene nucleus. However, it should be noted that in *N*-methylbenzamide the amide I band appears at 1649 cm.$^{-1}$ and does not show evidence of resonance interaction.[9]

[b] Phenyl C—H deformation at 1601 and 1499 cm.$^{-1}$.

could be due to the insolubility of the polymers or to impurities in the 1,1′-dichlorocarbonylferrocene. However, in the polyester series chain extension reactions were carried out by the use of toluene diisocyanate. In this way, mixed polyester–urethanes of ferrocene were prepared. The infrared spectra of polyesters 1–5 all exhibited alcohol OH stretching bands, but no trace of carboxylic acid carbonyl or hydroxyl stretching, and thus may be considered to be OH-terminated. These polyesters were cured with toluene triisocyanate at 200°C. for 30 hr. which resulted in totally insoluble and infusible crosslinked products.

Gel Permeation Chromatography

Polyesters 1 and 5 were examined by gel permeation chromatography (GPC) by use of a commercial Waters GPC Model 200 instrument and a gel column bank containing three columns of 10^3, 6×10^2, and 10^2 A. pore diameter. Benzene solvent was used in all cases. Calibration curves were constructed from commercial polystyrenes and polyglycols, and the molecular weight region below 2000 was additionally calibrated with ferrocene and a series of monomeric diesters prepared by reacting 1,1′-ferrocenedicarboxylic acid and several long-chain alcohols. The measured elution time of the ferrocene corresponded to a chain length of 5.8–6 A. according to the method developed by Moore.[5] This chain length corresponds to a Q value of 31.5. The number-average molecular weights of polymers 1 and 5 were calculated from the chromatograms by the method described by Cazes,[6] by use of Q values for these polymers calculated as described by Moore[5] and based on the theoretical repeating unit. Calculations were performed on an Olivetti-Underwood Program 101 electronic desk computer. We believe this is the first reported application of GPC to organometallic polymers.

Solubilities

The xylene-soluble fractions of polyesters 1–5 were generally soluble in benzene, but after reprecipitation from hot benzene or xylene their solubility was generally diminished. The xylene insoluble fractions of polymers 2, 3, 4, and 5 were insoluble in acetone, ethylene dichloride, and acetonitrile; all except polymer 3 were soluble in hot dimethylformamide.

Polyamides 6–10 were dissolved in warm *m*-cresol, a solvent used previously,[1] and were more readily dissolved in warm formic acid. Polyamides 6–10 were insoluble in acetone, methyl ethyl ketone, carbon tetrachloride, chloroform, diethyl ether, petroleum ether, tetrahydrofuran, 1,4-dioxane, benzene, toluene, and ethylene chloride. Polymer 9, derived from piperazine, was an exception since it was partially soluble in hot *m*-xylene and in 1,2,2-trichloroethane.

EXPERIMENTAL PROCEDURES

The 1,1′-dichlorocarbonylferrocene was obtained from Research Organic Chemical Co. (Sun Valley, California), and the diols and diamines were reagent chemicals obtained from Aldrich and Eastman Chemical Companies and used without further purification.

A 10 g. portion (0.032 mole) of 1,1′-dichlorocarbonylferrocene was dissolved into warm (70°C.) *m*-xylene which had been previously dried by stirring 24 hr. over CaH_2 followed by distillation from CaH_2. The diols or diamines to be used were dissolved in a second solution of xylene containing 2.5 mole of pyridine for each mole of diamine added. A third solution of *m*-xylene was brought to a gentle reflux in a round-bottomed three-necked flask equipped with a stirrer. The solutions of 1,1′-dichlorocarbonylferrocene and diol (or diamine) were then added dropwise from separate dropping funnels at equal rates over a 15 min. period. This was followed by a 24 hr. reflux period. The solution was then cooled, and the insoluble polymer and pyridine hydrochloride were filtered out. The xylene solution was extracted with aqueous NaCl solutions to remove residual pyridine hydrochloride, and the crude insoluble polymer was digested in H_2O twice to remove the pyridine hydrochloride in the solid. The crude insoluble polymer, as well as the xylene solution, were then extracted with aqueous Na_2CO_3 to remove any 1,1′-ferrocenedicarboxylic acid resulting from hydrolysis of the dichloride. The xylene solution was dried, partially aspirated, and poured into excess methanol to precipitate the xylene soluble polymer. The xylene soluble and insoluble polymers were first ground and then washed with both methanol and petroleum ether, and were vacuum-dried for 5 hr. at 60°C. 2 mm. Hg. Those polymers which were soluble in benzene–acetone were chromatographed over silica gel.

A melt-phase polymerization of 1,1′-dichlorocarbonylferrocene and trimethylene glycol (polymer 4) was conducted by mixing a 1:1 mole ratio of these reactants and adding excess tributylamine. This melt was first heated to 100°C. when it began to get stiff, and was then heated to 200°C. over a 2 hr. period with stirring, and maintained at 200°C. for 12 hr. The crude melt was kept mixable by small additions of tetramethylene sulfone during the reaction period. The crude polymer was cooled, washed, and digested by use of salt water, water, petroleum ether, and aqueous Na_2CO_3, to give a very viscous, waxlike liquid polymer soluble in benzene–acetone from which it was reprecipitated with methanol. This method produced a polyester with a $\overline{M}_n = 6000$, but the polymer yield was only 36%.

The author is indebted to Mr. B. J. Alley for programming the Olivetti-Underwood 101 electronic desk computer and to Mr. D. Strahm of the Rohm & Haas Co., Redstone Arsenal, Alabama, for performing several elemental analyses. The author also wishes to thank Mr. D. Van Landuyt for both calibrating and operating the gel permeation chromatograph.

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Molecular Weight Distribution of Cellulose Esters by Gel Permeation Chromatography and Fractional Precipitation*

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Synopsis

Fractional precipitation and gel permeation chromatography yield comparable information on the molecular weight distribution of various cellulose esters. The GPC technique applied to samples obtained by fractional precipitation gives a much more definitive analytical tool than either method used independently. One practical application of this work showed the same molecular weight distribution of two cellulose acetates prepared by different methods.

INTRODUCTION

The molecular weight distribution of natural and synthetic polymers has generated much interest because the physical properties of these polymers can be altered by changes in their molecular weight distributions.[1,2] In the field of cellulose some work has been reported on molecular weight distributions as determined by fractional precipitation and other solution methods. Detailed procedures for the preparation and fractionation of cellulose nitrates have been presented,[3,4] and Phillips and Linow have recently reviewed these procedures.[5] Cellulose acetates lend themselves to fractionation both by degree of polymerization,[6] and by degree of substitution when the acetate is not a triester and the proper solvent–nonsolvent system is used.[7,8] Husemann and Werner[9] have used the tricarbanilates to determine the molecular weight distribution of bacterially synthesized cellulose. Maley[10] and Cazes[11,12] have reported gel permeation fractionations of cellulose esters, but presented no data.

In this work we will discuss the application of fractional precipitation and gel permeation chromatography techniques to determine molecular weight distributions of cellulose esters. These methods were used to compare cellulose acetates prepared by two different acetylation schedules. One schedule was designed to give most of the viscosity (molecular chain length)

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reduction while the cellulose was in solution, and the other to give most of the viscosity reduction with the cellulose in suspension.

The cellulose acetates were converted to their tricarbanilates for fractionation to insure that fractional precipitation was by degree of polymerization and not by degree of substitution. The carbanilates are very high unit molecular weight esters and can be separated more precisely and easily by chain length than can the acetates.

Fractional precipitation and GPC gave comparable results, but the application of the two methods in sequence yielded more information than either method independently.

EXPERIMENTAL

Preparation of Cellulose Acetate with Most of the Viscosity Reduction in Suspension (Sample A)

Cotton linters (3 lb.) were acetylated in a 5-gal. acetylation mixer according to general procedures previously described,[13] except that the intrinsic viscosity of the cellulose as measured in cupriethylenediamine solution was reduced from 11.1 to 2.0 by an extended pretreatment with sulfuric acid catalyst in acetic acid prior to the acetylation reaction. The remaining viscosity reduction (2.0–1.16) occurred in the $1^1/_2$ hr. reaction period during which the cellulose was esterified and therefore partially or totally in solution. As soon as the solution was free from fiber and grain, reaction was stopped by the addition of aqueous acetic acid and the solution was poured into water to precipitate the product.

Preparation of Cellulose Acetate with Most of the Viscosity Reduction in Solution (Sample B)

Using the same methods and equipment as above, cotton linters were acetylated without any pretreatment; the acetic anhydride was added before any catalyst. The esterification solution was free of fiber and grain after 30 min. and the reaction was continued for an additional 45 min. to give as much viscosity reduction as possible, while the ester was partially or totally in solution (intrinsic viscosity 8.0–1.20). The excess anhydride was destroyed by the addition of aqueous acetic acid, and the product was precipitated into water.

Preparation of Tricarbanilates from the Cellulose Acetates

Cellulose acetate (50 g., 0.17 mole) was deacetylated by tumbling 24 hr. at room temperature in 2 liters of 5% $NaOCH_3$ in methanol. The regenerated cellulose (26.8 g. calculated) was filtered on a Buchner funnel and washed thoroughly with methanol until the wash liquors were neutral to pH paper. The cellulose was then solvent exchanged four times with dry pyridine to remove the methanol and placed in 400 ml. dry pyridine with 87 g. (0.72 mole, 50% excess theoretical) phenyl isocyanate. The mixture was tumbled slowly at room temperature, and after 2 hr. a clear, viscous solution resulted. After 4 hr., methanol was added to the reaction solution to destroy the excess phenyl isocyanate, and the tricarbanilate was isolated by pouring the solution into a methanol:water (1:1 by volume) mixture with vigorous stirring. The tricarbanilate was washed with methanol until the wash liquid was free from impurities as indicated by lack of ultraviolet absorbance at 280 mμ.

A small amount of stannous octanoate accelerates the reaction[14] and was used in some cases.

Precipitation Fractionation of Cellulose Tricarbanilates

A 10 g. sample of cellulose tricarbanilate was dissolved in 750 ml. acetone. The solution was filtered into a 3-liter, three-necked flask, an additional 250 ml. acetone being used for rinsing. The flask was equipped with a

TABLE I
Precipitation Fractionation Data of Carbanilate A

Fraction number	Fraction weight, mg.	Wt. %	Σ, wt. %	$I(x)$[a]	Intrinsic viscosity[b]	Ultraviolet absorbance[c]	$\bar{M}_w/\bar{M}_n$[d]
1	350	3.70	3.70	0.0185	—		
2	282	2.98	6.68	0.0519	0.33		
3	623	6.59	13.27	0.0997	0.47	1.263	1.6
4	571	6.04	19.31	0.1629	0.62	1.255	
5	609	6.44	25.75	0.2253	0.72		
6	500	5.29	31.04	0.2839	0.91		
7	659	6.97	38.01	0.3452	0.95		1.3
8	493	5.21	43.22	0.4061	1.10		
9	625	6.61	49.83	0.4652	1.22		
10	495	5.23	55.06	0.5244	1.29		
11	566	5.98	61.04	0.5805	1.49	1.260	1.3
12	345	3.64	64.69	0.6286	1.60		
13	459	4.85	69.54	0.6711	1.72		
14	445	4.70	74.24	0.7189	1.78		
15	342	3.62	77.86	0.7605	1.84		1.3
16	355	3.75	81.61	0.7973	2.02		
17	503	5.32	86.93	0.8427	2.14		
18	561	5.93	92.86	0.8989	2.30		
19	311	3.29	96.15	0.9450	2.67		1.4
20	169	1.79	97.94	0.9704	2.81	1.268	
21	77	0.81	98.75	0.9834	3.03		
22	119	1.26	100.01	0.9938	3.29	1.252	
Total	9459[e]						

[a] One-half the weight fraction plus the previous cummulative weight fraction.

[b] In *p*-dioxane.

[c] The intrinsic viscosity solutions (100 mg. cellulose tricarbanilate in 100 ml. solution) were diluted 10.0 ml. to 25.0 ml.

[d] By GPC fractionation of the precipitated fractions.

[e] Total taken, 10 g.

mechanical stirrer and dropping funnel and placed in a constant-temperature bath at 20°C.

A solution prepared by mixing equal volumes of acetone and 1% aqueous NaCl was slowly added to the tricarbanilate solution. An immediate turbidity resulted from the precipitation of NaCl in the predominantly acetone solution. This turbidity disappeared after 150–200 ml. had been added. After adding 220–240 ml. of precipitant a slight turbidity due to a precipitate of cellulose tricarbanilate appeared. After stirring for 5 min. the hazy solution was poured into four polyethylene bottles (Nalgene 16-500) and placed in an International Centrifuge, Model EXD, for 10 min. at 2500 rpm. The resulting supernatant solutions were poured back into the three-necked flask and placed in the constant temperature bath. The gelatinous precipitates in the bottles were recovered by adding 50 ml. portions of methanol and filtering on a Buchner funnel.

Subsequent fractions were isolated in the same manner by slowly adding 5 ml. portions of a milder precipitant, i.e., 75:25 (by volume) acetone–1% aqueous NaCl. After 13–15 fractions were isolated, the stronger nonsolvent (50:50 by volume acetone–1% aqueous NaCl) was added in increments of 10, 15, 25, and 50 ml. The last low molecular weight fraction was precipitated by addition of distilled water.

Collection of 21–22 fractions gave 93–95% recovery of starting material. A final residue was sometimes obtained by washing the three-necked flask and polyethylene bottles with acetone and evaporating the solution to dryness. Typical data are given in Table I.

Intrinsic Viscosity Measurements

All intrinsic viscosity measurements were mad ein a Wagner viscometer at 25.0 ± 0.1°C. with methylene chloride–methanol (90:10 by weight) for the acetates, and *p*-dioxane for the tricarbanilates.

Ultraviolet Absorbance Measurements

A 10 ml. portion of the solution of tricarbanilate from the intrinsic viscosity measurement was diluted to 25 ml. with *p*-dioxane. The ultraviolet absorbance at 280 mμ wavelength was read in a Beckman DU spectrophotometer using 1 cm. silica cells. An absorbance of 1.25–1.26, which corresponds to theoretical 8.1% nitrogen, provided a check on the completeness of carbanilation of the various fractions.

Fractionation of Cellulose Esters by Gel Permeation Chromatography

The molecular size distribution of the cellulose esters was obtained by using a Waters gel permeation instrument. The basic characteristics of the instrument and its operation have been described by Maley[10] and Cazes.[11,12] The instrument was operated at ambient temperatures with the use of 1 ml. of 0.5 wt.-% solutions in Eastman White Label tetrahydrofuran. Chromatographic columns with upper permeability ranges of 100,000, 8000, and 3000 A. were used.

RESULTS AND DISCUSSION

Analysis of Cellulose Esters

Table II gives the analyses of the cellulose acetates and the derived carbanilates. The intrinsic viscosity of both sets of esters was nearly the same.

TABLE II
Acetates and Carbanilates

	Sample A	Sample B
Viscosity reduction	Most in suspension	Most in solution
Cellulose acetates		
[η] in methylene chloride–methanol (90:10)	1.11	1.16
OH, %	1.08	0.25
Cellulose tricarbanilates		
[η] in *p*-dioxane	1.34	1.42
N, %[a]	7.95	7.96
Ultraviolet absorbance at 280 mμ (0.04% in *p*-dioxane)	1.255	1.260
$\bar{M}_w/\bar{M}_n$[b]	2.1	2.2

[a] Theoretical 8.12% for a tricarbanilate.
[b] Calculated from GPC fractionations.

The hydroxyl content in these esters corresponds to the amount of sulfate ester at the end of the esterification. The per cent hydroxyl in sample B was lower than that in sample A because the esterification was continued after the cellulose acetate sulfate triester was first formed; during this interval combined sulfate was replaced by acetyl.[15]

Stability of Viscosity

The data in Table III show that there was little or no viscosity reduction of the cellulose during the deesterification and carbanilation reactions. The deesterification reaction was followed over 36 hr. and samples of regenerated cellulose isolated at the two extremes (4 and 36 hr.) gave the same intrinsic viscosity in iron–sodium tartrate (FeTNa) solution. The acetyl content was less than 0.5% after 4 hr. reaction.

TABLE III
Stability of Viscosity

Reaction	Time, hr.	Intrinsic viscosity
Deesterification	4	1.75[a]
	36	1.67
Carbanilation	2	1.62[b]
	24	1.67

[a] In FeTNa.
[b] In *p*-dioxane.

The carbanilation reaction was followed for 24 hr., and the samples isolated at 2 and 24 hr. gave the same intrinsic viscosity in *p*-dioxane. Nitrogen and ultraviolet absorbance analyses indicated complete carbanilation after 2 hr. reaction.

Comparison of Molecular Weight Distributions

One would expect that the molecular weight distributions obtained by the two acetylation procedures (see Experimental Section) would differ. Cellulose exists as crystalline and amorphous regions which would be expected to have different penetrabilities to sulfuric acid during heterogeneous viscosity reduction. When the viscosity is reduced in solution, all the cellulose molecules, regardless of their origin from crystalline or amorphous areas, should have equal opportunity of chain cleavage; this should give a product of narrower DP distribution.

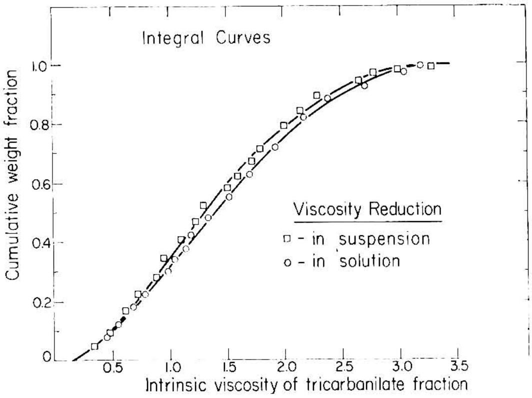

Fig. 1. Integral curves: (□) viscosity reduction in suspension; (O) viscosity reduction in solution.

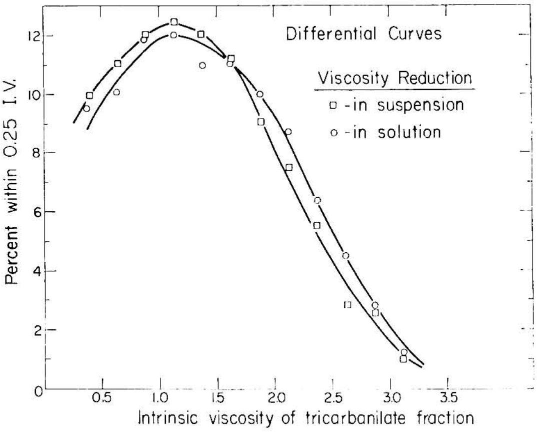

Fig. 2. Differential curves: (□) viscosity reduction in suspension; (O) viscosity reduction in solution.

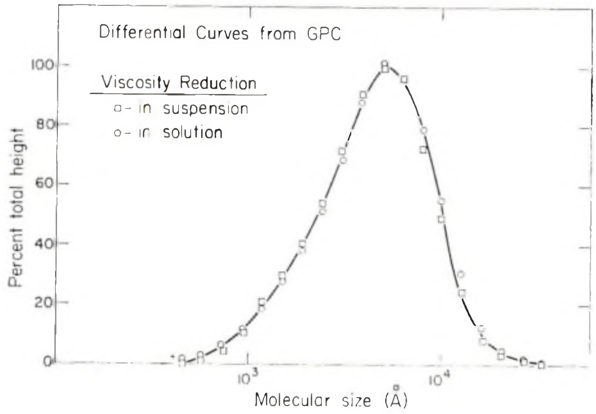

Fig. 3. Differential curves from GPC: (□) viscosity reduction in suspension; (O) viscosity reduction in solution.

However, the integral viscosity distribution curves for the two cellulose carbanilates (Fig. 1) indicate that the DP distributions as determined by fractional precipitation are almost identical. This similarity is also shown in differential distribution curves (Fig. 2), both of which show a maximum at intrinsic viscosity 1.1. This is verified by the differential distribution curves (Fig. 3) obtained from gel permeation fractionation of the same carbanilates. These curves both show a maximum at 6000 A. molecular size.

Fractional Precipitation and GPC Used in Sequence

Gel permeation chromatography used in sequence with fractional precipitation proved a very useful technique for obtaining a more detailed picture of the molecular weight distribution of cellulose esters. Figure 4 shows the results of combining the two methods to determine the distribu-

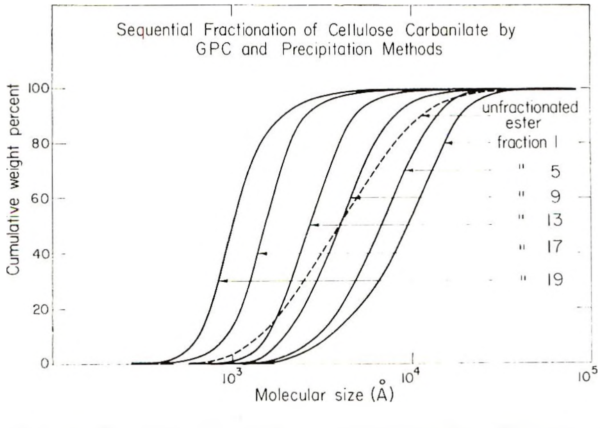

Fig. 4. Sequential fractionation of cellulose carbanilate by GPC and precipitation methods.

tion of cellulose tricarbanilate A discussed above. The steeper slopes of the distribution curves obtained by GPC of the individual fractions from a fractional precipitation indicate that the fractions are more homogeneous than the unfractionated material. $\bar{M}_w/\bar{M}_n$ is a measure of homogeneity and was calculated from GPC fractionation data to be 2.1 for sample A and 1.3–1.6 for representative fractions (Table I). For sample B, $\bar{M}_w/\bar{M}_n$ was 2.2 for the unfractionated material and 1.3–1.7 for various fractions. The curves also indicate high and low molecular weight material that is not easily seen in the distribution curve of the unfractionated carbanilate. For example, fractions 19 and 17 show 50 and 14%, respectively, of material lower than 1000 A. molecular size; the curve for unfractionated material shows less than 5% lower than 1000 A. Application of this technique to both sets of samples from fractional precipitation showed no difference in DP distribution.

We wish to acknowledge the work of Dr. Herbert Heynemann in the development of methods for preparing and fractionating the cellulose tricarbanilates.

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Study of the Substitution Pattern of Hydroxyethylcellulose and Its Relationship to Enzymic Degradation*

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Synopsis

The concentration of completely unsubstituted anhydroglucose (AHG) units in hydroxyethylcellulose (HEC) at varying average number of moles of substituent (MS) is in accord with a reaction rate ratio of 3:1:10:10 for the etherification of the C_2, C_3, C_6, and side chain hydroxyls. Assuming random substitution along the cellulose chain at these relative reaction rates, the degree of substitution (DS), average poly(ethylene oxide) side-chain length, and probably frequency of isolated and multiple adjacent unsubstituted AHG units have been projected as functions of MS. Such estimates of DS and side-chain length compare favorably with actual measurements made on a variety of samples by other investigators below a substitution level of 2.0 MS. Reducing end, intrinsic viscosity, and ultracentrifuge data on enzymically hydrolyzed HEC's varying from 1.9 to 3.7 in MS indicate resistance to chain scission is a function of substitution, best expressed in terms of a proposed substitution index, the percentage of substituted AHG units. The rate of chain scission under carefully controlled conditions is initially rapid, tapering to a very slow, essentially steady level. On relating the frequency of chain breaks to the predicted substitution pattern of these samples, this behavior is interpreted to mean that scission occurs relatively rapidly at multiple contiguous unsubstituted sequences, but much more slowly adjacent to isolated unsubstituted AHG units. A possible mechanism of enzyme attack, correlating molecular chain breaks with glucose released, has been developed.

INTRODUCTION

Cellulose and its derivatives are stable when dry, but are subject to enzymic hydrolysis by a variety of microorganisms in the presence of moisture. Resistance to degradation appears to be a function of the degree and uniformity of substitution of the hydroxyls on the anhydroglucose (AHG) repeating units of the cellulose chain. Siu[1] and Reese et al.,[2,3] as a result of extensive research in this field, concluded that as long as there is at least one firmly bound substituent on every AHG unit, the resulting derivative is not susceptible to microbiological attack.

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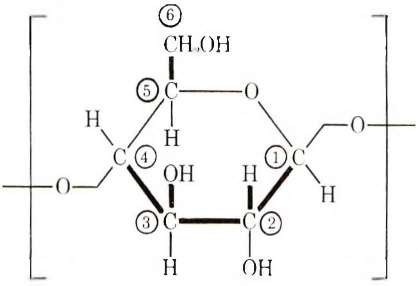
The obvious way to assure at least one substituent group on each chain unit is to provide for the complete substitution of all three hydroxyls on every unit; such a material would have a degree of substitution (DS) of



3.00. Complete substitution, in the case of most derivatives, however, is not feasible, partially because of steric hindrance encountered at high substitution levels, but primarily because of the effect of such substitution on physical properties (e.g., solubility).

In the case of hydroxyethylcellulose (HEC), the substituent group contains a hydroxyl which, in turn, may be substituted by additional reactant. As a result, poly(ethylene oxide) side chains are formed which contribute to an increase in the amount of reactant combined without a corresponding increase in DS. The substitution of HEC is usually expressed in terms of the average number of moles of substituent (MS) combined per mole of AHG units because there is no simple, reliable, direct analytical means of determining its DS. However, since completely unsubstituted AHG units appear to be the targets of enzyme attack, a much more meaningful substitution criterion—where biostability is concerned—is being proposed, the substitution index (SI), the percentage of substituted (at one or more of the three ring hydroxyls) AHG units. This index can be determined by complete acid hydrolysis of a sample followed by a measurement of the amount of glucose in the hydrolyzate. The resulting value, expressed as a percentage of the AHG units in the sample, subtracted from 100 gives the SI.

Although the exact mechanism of the enzymic hydrolysis of cellulose and cellulose derivatives is not known, most investigators believe that biological chain scission occurs between pairs of adjacent unsubstituted AHG units. Cayle[4] concluded this was the situation in the case of a series of sodium carboxymethylcellulose (CMC) samples which he degraded with a purified cellulolytic enzyme. Holden and Tracey[5] agreed that this is the *modus operandi* in the case of CMC, but postulated chain breaks adjacent to single unsubstituted units in the case of methylethylcellulose. Savage[6] also concluded that the point of attack seems to be chain linkages between substituted and unsubstituted AHG units, following his study of methylcellulose degradation. This paper describes a study of the substitution pattern of water-soluble HEC, and its effect on the rate and extent of the enzymic hydrolysis of this polymer.

EXPERIMENTAL

Samples

Seven HEC samples were used in this investigation: six representing high, medium, and low viscosity grades of two commercial substitution levels, and the seventh (studied less extensively) an experimental low-viscosity material of high MS. The properties of these samples are summarized in Table I.

DP Measurement

The average molecular weight or average chain length (degree of polymerization, DP, the average number of AHG units per molecule) of these samples, both original and degraded, was calculated from two types of information: (*1*) reducing ends value and (*2*) intrinsic viscosity. The former was determined by the method of Folin and Malmrös,[7] as modified by Fonty;[8] all reducing chain ends were assumed to have reducing power equivalent to that of glucose. This method gives a number-average value.

DP was also estimated from intrinsic viscosity via the relationship

$$[\eta]_{\mathrm{H_2O,25°C.}} = 1.1 \times 10^{-2}\overline{\mathrm{DP}}_w^{\,0.87}$$

reported by Brown et al.[9] In this case, the DP (derived from light-scattering measurements) is essentially a weight average. In the current work a ratio of $\overline{\mathrm{DP}}_w$ to $\overline{\mathrm{DP}}_n$ of 2 was assumed. This assumption is probably justified in the case of randomly degraded samples, but may be questionable when applied to the original materials. However, the estimates of average chain length based on reducing ends measurements (Table I, column 6) and intrinsic viscosity (column 7) are in reasonably good agreement, and have further been substantiated by independent weight-average equilibrium ultracentrifuge measurements by Stow.[10] From these data the averages listed in column 8 were obtained, and finally, the average number of molecules per 1000 AHG units given in column 9.

Intrinsic viscosities were determined from plots of η_{sp}/c versus c. Measurements were carried out in Ubbelohde viscometers at 25°C.; no shear rate corrections were made.

Acid Hydrolysis

To determine the incidence of completely unsubstituted AHG units in these samples, they were subjected to total acid hydrolysis (1 hr. in 72% H_2SO_4 at 30°C., followed by 5 hr. in 2.5% H_2SO_4 at 100°C.), essentially by the technique described in ASTM Method D1915-63.[11] Glucose in the hydrolyzates was determined as described below. The values given in columns 10 and 11 of Table I were derived from the data obtained by these procedures.

TABLE I

Properties of Hydroxyethylcellulose Samples Used in Enzymic Degradation Studies

Sample	Substitution level	Viscosity level	MS	M_0[a]	$\overline{DP}_n$ from reducing value	$\overline{DP}_n$ from $[\eta]$	Avg. indicated $\overline{DP}_n$	Avg. no. of molecules/ 1000 AHG units	Measured U/1000 AHG units[b]	Substitution index
1	Medium	High	2.53	275	1650	1400	1530	0.65	121	87.9
2	Medium	Medium	2.45	270	570	560	565	1.8	115	88.5
3	Medium	Low	2.48	271	240	160	200	5.0	109	89.1
4	Low	High	1.90	246	1480	1260	1370	0.73	172	82.8
5	Low	Medium	1.92	247	370	450	410	2.4	181	81.9
6	Low	Low	1.95	248	110	135	120	8.3	182	81.8
7	High	Low	3.7	325	—	175	175	5.7	42	95.8

[a] Average substituted AHG unit weight.

[b] U = unsubstituted AHG units.

Analysis for Free Glucose

Glucose was determined in acid-hydrolyzed and in enzymically degraded samples by the glucose oxidase method of Dahlqvist,[12] National Bureau of Standards dextrose being used as a standard.

Enzymic Hydrolysis

All degradation studies were carried out at 25°C. in an aqueous medium at pH 6 (phthalate buffer) containing 100 ppm. Ottasept extra (4-chloro-3,5-xylenol, Ottawa Chemical Company, Toledo, O.) as a preservative. It was demonstrated that this material does not inhibit the action of the cellulolytic enzyme.

The HEC concentration in all cases was 2 wt.-%. The degradation agent was Cellase 1000, a commercial enzyme complex described by the supplier (Wallerstein Laboratories, Staten Island, N. Y.) as a purified fungal cellulase preparation derived from a selected strain of *Aspergillus niger*. Other enzymes such as protease, amylase, pectinase, β-galactosidase, and cellobiase are known to be present in trace amounts. In this work it was also shown to possess appreciable β-glucosidase* activity.[13] Cellase 1000 was used at a concentration of 8 ppm. (400 ppm based on polymer weight).

RESULTS AND DISCUSSION

Substitution Pattern of HEC

Croon and Lindberg,[14] working with an HEC of MS 0.6, deduced from an analysis of the products of complete acid hydrolysis that the relative rate constants for etherification of the hydroxyls at the C_2, C_3, and C_6 positions, and the hydroxyethyl group formed at any one of these, are in the ratio 3:1:10:20. Based on this information it is possible to predict the concentration of unsubstituted AHG units for any substitution level, as indicated by the upper curve in Figure 1. If such estimates (Table II, column 3) for the seven samples used in this study are compared with the actual measured concentrations of completely unsubstituted AHG units (Table II, column 5), it is obvious that the former are much too high. However, if the relative rate constant for poly(ethylene oxide) side chain formation is reduced from 20 to 10, a new prediction of the progress of substitution is obtained (Fig. 1, lower curve) which yields reasonably accurate estimates of the concentration of unsubstituted AHG units (Table II, column 4).

Assuming the validity of the 3:1:10:10 reaction rate ratio, it is a simple matter to project the substitution pattern of HEC at any MS level, as illustrated in Figure 2. DS is the sum of the substitutions at the 2, 3, and 6 hydroxyls, and the ratio MS:DS is the number-average poly(ethylene

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* This enzyme strips unsubstituted AHG units from nonreducing chain ends, releasing glucose.

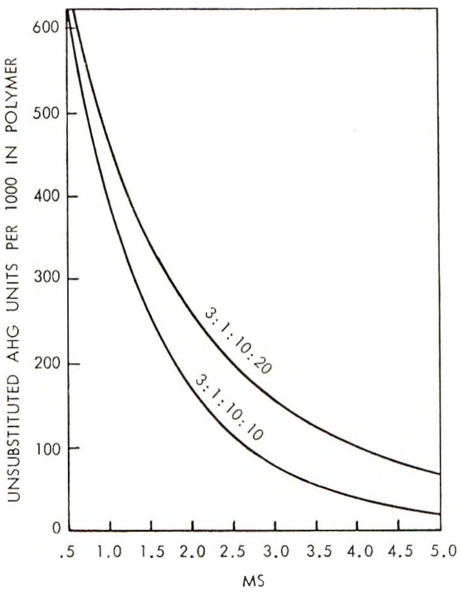

Fig. 1. Predicted concentration of unsubstituted AHG units in HEC of varying substitution based on two relative rate of substitution ratios for the available hydroxyls (indicated ratios = $k_2:k_3:k_6:k_{\text{chain}}$).

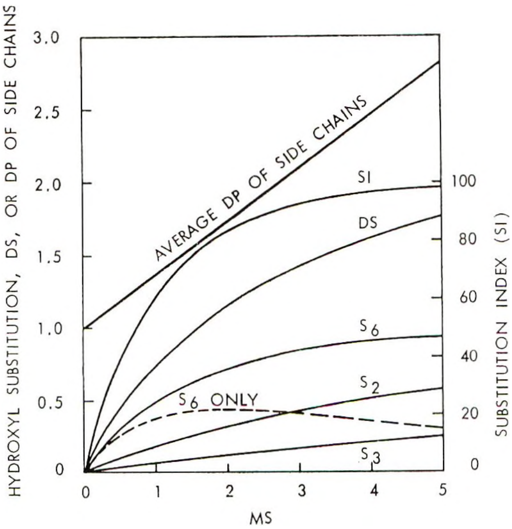

Fig. 2. Pattern of substitution predicted for HEC from relative reaction rates of hydroxyls ($k_2:k_3:k_6:k_{\text{chain}} = 3:1:10:10$).

oxide) side chain DP. The relationships between MS and DS, and MS and side chain length are in good agreement with those determined by Brownell and Purves[15] and Stratta[16] below MS 2.0. Above this substitution level Stratta's data indicate substantially no change in DS with increasing MS,

TABLE II
Concentration of Unsubstituted AHG Units in HEC Samples

		Unsubstituted AHG units/1000 units in polymer		
		Estimated from relative reaction rates ($k_2:k_3:k_6:k_{\text{chain}}$)		
Sample	MS	3:1:10:20	3:1:10:10	Measured
1	2.53	197	110	121
2	2.45	208	117	115
3	2.48	202	115	109
4	1.90	273	182	172
5	1.92	270	179	181
6	1.95	266	175	182
7	3.7	113	46	42

in contrast with the definite increase in SI (and, therefore, in DS) and improvement in biostability with MS reported herein.

Recently additional credence was given the proposed distribution pattern by the results of Clarke and Conner,[17] who used a pyrolysis–gas chromatographic method to liberate HEC substituent groups as the corresponding glycols, and to separate and identify the latter as their trimethyl silyl ether derivatives. Their findings indicated a DS of approximately 0.85 at MS 1.3, and 1.3 at MS 2.5—precise checks of values predicted from Figure 2.

Unsubstituted Sequences in HEC

If a random distribution is assumed for the unsubstituted AHG units in HEC, it is then possible to predict the probable frequency of such isolated units (1U) and sequences of two or more adjacent unsubstituted units (2U, 3U, etc.) at any SI level, as illustrated in Figure 3. A summary of

TABLE III
Estimated Frequency of Sequences of Unsubstituted AHG Units in HEC Samples

	Average frequency/1000 AHG units						
		Unsubstituted sequences of indicated length					
Sample	Total U	1U	2U	3U	4U	5U	Expected chain breaks at 2U+ sequences[a]
1	121	93	11.4	1.4	0.17	—	13.0
2	115	90	10.5	1.2	0.14	—	11.9
3	109	87	9.3	1.05	0.12	—	10.5
4	172	120	20.0	3.3	0.57	0.10	24.0
5	181	123	21.5	3.8	0.70	0.13	26.2
6	182	123.5	21.7	3.9	0.71	0.13	26.5
7	42	38.5	1.6	0.1	—	—	1.7

[a] Sums of columns 4 through 7.

TABLE IV

Predicted Final $\overline{DP}_n$ of Enzymically Degraded HEC Samples Based on Molecular Chain Breaks at Multiple Unsubstituted Sequences; and on Additional Scission at U–S_6 Combinations

	Average frequency/1000 AHG units							Predicted $\overline{DP}_n$ of enzymically degraded samples	
						Final molecules			
Sample	1U[a]	AHG units substituted at 6-hydroxyl only[b]	U–S_6[c]	Expected chain breaks at 2U$^+$ sequences[d]	Original molecules[e]	Scission at 2U$^+$ sequences only[f]	Scission at 2U$^+$ and at U–S_6[g]	Scission at 2U$^+$ sequences only[h]	Scission at 2U$^+$ and at U–S_6 combinations[i]
1	93	422	39	13.0	0.7	13.7	53	73	19
2	90	425	38	11.9	1.8	13.7	52	73	19
3	87	424	37	10.5	5.0	15.5	53	65	19
4	120	432	52	24.0	0.7	24.7	77	41	13
5	123	432	53	26.2	2.4	28.6	82	35	12
6	123.5	432	53	26.5	8.3	34.8	88	29	11
7	38.5	368	14.2	1.7	5.7	7.4	21.6	135	46

[a] Isolated unsubstituted AHG units; Table 3, column 3.

[b] See Figure 2, S_6 only.

[c] Product of columns 2 and 3 ÷ 1000.

[d] Table III, column 8.

[e] Table I, column 9.

[f] Sum of columns 5 and 6.

[g] Sum of columns 4, 5, and 6.

[h] 1000× reciprocal of column 7.

[i] 1000× reciprocal of column 8.

such predictions for the seven samples used in this study is given in Table III.

Furthermore, if the enzyme complex is able to effect chain scission only between adjacent unsubstituted AHG units (and neglecting, for the moment, possible glucose liberation in the case of multiple adjacent units), the frequency of chain breaks (2U + 3U + 4U + etc.) can also be predicted (Table III, column 8). Finally, if consideration is given to the average original chain length of these samples, an estimate of the ultimate average DP of the completely degraded products may be obtained (Table IV, column 9).

Rate and Extent of Enzymic Hydrolysis

Degradation of high, medium, and low viscosity grades of two substitution levels of HEC was followed for a total of 38 weeks by periodic measurements of reducing value, glucose content, and intrinsic viscosity. Typical reducing ends curves are shown in Figure 4. Curves for other samples of equivalent substitution were very similar. A quite different picture was obtained from intrinsic viscosity measurements (Fig. 5), however. These data indicate that at any degradation time, the average number of molecules per 1000 AHG units is not only a function of the substitution of a sample, but also reflects its original molecular size. Thus, fragments of the lower-viscosity HEC's remain smaller at every stage of degradation than those of the corresponding high viscosity grades from which they were derived. Apparently the chain scissions in the lower viscosity grades

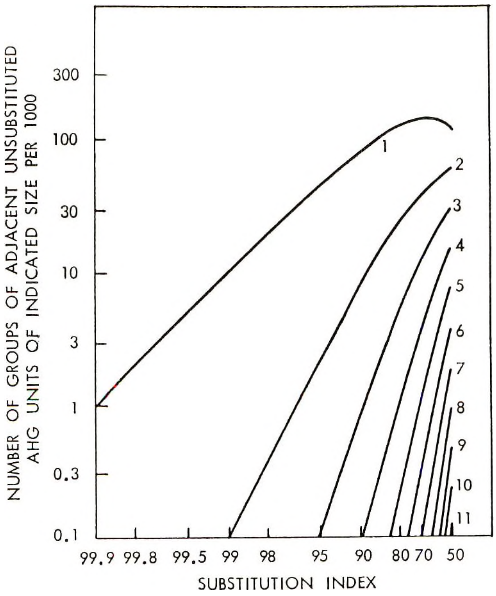

Fig. 3. Probable frequency of groups of adjacent unsubstituted AHG units of indicated size in cellulose derivatives with substitution indices in the range 50–100.

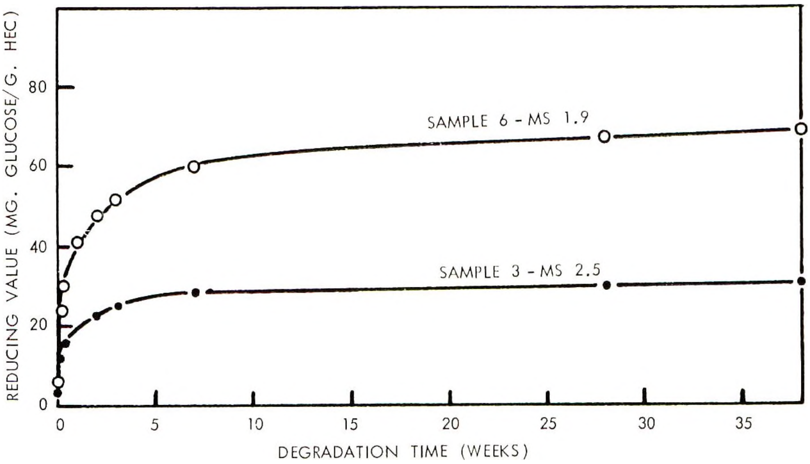

Fig. 4. Progress of enzymic degradation of hydroxyethylcellulose indicated by reducing ends measurements.

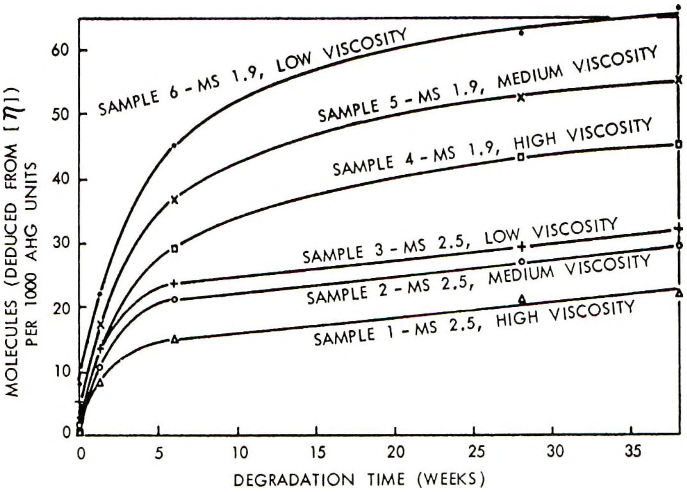

Fig. 5. Progress of enzymic degradation of HEC indicated by intrinsic viscosity measurements.

produced by peroxide degradation during their preparation occur primarily at sites which are not normally attacked by enzymes, thus resulting in a higher total of chain breaks in these samples.

The final extent of degradation of all seven HEC samples is summarized in Table V. The indicated chain lengths derived from reducing ends, intrinsic viscosity, and ultracentrifuge measurements are in good agreement with each other, but the average indicated DP's (Table V, column 6) are approximately half those predicted (Table IV, column 9), based on chain scission at multiple adjacent sequences only. Obviously, additional chain breaks must have occurred, probably at linkages between substituted and unsubstituted AHG units.

TABLE V
Actual $\overline{DP}_n$ of Enzymically Degraded HEC Samples

		Actual measured $\overline{DP}_n$			
Sample	MS	From reducing ends	From [η]	From ultracentrifuge studies	Avg.
1	2.53	28	45	—	37
2	2.45	30	34	42	35
3	2.48	30	31	—	31
4	1.90	16	22	—	19
5	1.92	17	18	20	18
6	1.95	16	15	—	16
7	3.7	—	59	—	59

Klop and Kooiman[18] recently reported the results of a study involving the identification of the lower molecular weight end-products resulting from the exhaustive enzymic hydrolysis of HEC of low substitution (DS 0.57) by *Myrothecium verrucaria* cellulase. They concluded that molecular chain scission may occur adjacent to an isolated unsubstituted glucosyl residue (U) provided the aglycone moiety is either unsubstituted, or substituted at the 6-hydroxyl only (S_6).

$$—S_X—S_X—U—U—S_X—S_X— \rightarrow —S_X—S_X—U_R + {}_{NR}U—S_X—S_X—$$

$$—S_X—S_X—U—S_6—S_X—S_X— \rightarrow —S_X—S_X—U_R + {}_{NR}S_6—S_X—S_X—$$

$$—S_X—S_X—S_6—U—S_X—S_X— \rightarrow \text{no scission}$$

Such cellulase action would always result in chain fragments with completely unsubstituted reducing chain ends.

The probable frequency of 6-substituted AHG units in the HEC samples used in this investigation (Table IV, column 3; data derived from broken curve in Fig. 2) is so high, U–S_6 combinations are very likely commonplace. The estimated frequency of such sequences is given in Table IV, column 4. If possible chain breaks at these combinations are added to those expected between adjacent unsubstituted units, the estimated average $\overline{DP}_n$ of the completely degraded products (Table IV, column 10) is appreciably lower than observed (Table V, column 6). Thus, it appears that if the scission of U–S_6 bonds is a factor in the enzymic hydrolysis of these samples, not all such sequences are attacked under the test conditions involved in this investigation.

It is obvious from this study that relatively rapid hydrolysis takes place (at a continually decreasing rate) during the early weeks of degradation, followed by a period (to the conclusion of the study) of nearly uniform rate at an appreciably reduced level.

Hypothesis Concerning Enzyme Action

During the original period of relatively rapid degradation, it is assumed that all of the multiple adjacent unsubstituted sequences are attacked,

TABLE VI

Glucose Liberated from HEC Samples by Molecular Chain Scission Resulting From Exhaustive Enzymic Hydrolysis

Sample	MS	Molecules of glucose/1000 AHG Units							
		1 × 2U[a]	2 × 3U[a]	3 × 4U[a]	4 × 5U[a]	Predicted glucose[b]	Actual glucose	Actual chain breaks[c]	Ratio, chain breaks/glucose
1	2.53	11.4	2.8	0.5	—	14.7	16.4	26	1.6
2	2.45	10.5	2.4	0.4	—	13.3	15.3	27	1.8
3	2.48	9.3	2.1	0.4	—	11.8	13.7	27	1.9
4	1.90	20.0	6.6	1.7	0.4	28.7	32.0	52	1.6
5	1.92	21.5	7.6	2.1	0.5	31.7	32.6	53	1.6
6	1.95	21.7	7.8	2.1	0.5	32.1	32.3	54	1.7
7	3.7	1.6	0.2	—	—	1.8	6.9	11.3	1.6

[a] See Table III, columns 4 through 7.

[b] Sum of columns 3 through 6.

[c] (1000 × reciprocal of column 6, Table V) minus column 9, Table I.

while in the latter stage scission occurs (at a very slow and approximately uniform rate) only next to single, isolated unsubstituted AHG units. Because the probable supply of the latter is comparatively large and the rate of hydrolysis is very slow, it is not surprising that this reaction can proceed for a very long time at a substantially undiminished rate.

As previously mentioned, one or more components of the mixture of enzymes comprising Cellase 1000 are capable of stripping unsubstituted AHG units from nonreducing cellulosic chain ends, freeing glucose. If it is assumed that enzyme-induced chain scission always occurs at unsubstituted sequences in such a way as to expose a single unsubstituted AHG unit at the newly formed reducing chain end, then one molecule of glucose should be released from 2U combinations, two from 3U sequences, etc. This mechanism would account for the liberation of the amount of glucose indicated in Table VI, column 7, for the samples considered in this study, assuming attack at all estimated groups of adjacent unsubstituted AHG units. A comparison of these values with the corresponding concentrations of glucose actually developed (Table VI, column 8) reveals excellent agreement except in the case of sample 7, the most highly substituted ether. If the proposed mode of enzyme attack is valid, this sample must contain more unsubstituted sequences than predicted.

It is of interest to note that in all samples a constant ratio of one molecule of glucose liberated for approximately every 1.7 chain breaks was observed during enzymic hydrolysis.

Homogeneous vs. Heterogeneous HEC

The assumptions made by Croon and Lindberg[14] in arriving at their 3:1:10:20 etherification rate ratio for the various hydroxyl groups available in the synthesis of HEC were: (*1*) all AHG units in cellulose are equally accessible for hydroxyethylation; (*2*) the ratios of the reaction rate constants remain constant throughout the reaction; (*3*) the rate constants are not changed by substitution on adjacent atoms; and (*4*) the effect of end groups is negligible. Since cellulose ethers are normally prepared in a heterogeneous system, it would be very surprising indeed if these assumptions were completely valid. Therefore, it is not unexpected that the substitution pattern in highly substituted (MS 1.9–3.7) HEC cannot be extrapolated precisely from that characteristic of a low (0.60) MS material. In this respect, the suggested 3:1:10:10 ratio cannot be valid over an unlimited range of substitution either, but it does give a reasonably accurate estimate of SI within the MS limits characteristic of most commercial water-soluble products. Even in the case of the sample studied by Croon and Lindberg, this ratio would predict the percentage of completely unsubstituted AHG units to be 56, as opposed to 63.8 determined experimentally.

A corollary to the above discussion is that if HEC could be produced by a homogeneous, or more nearly homogeneous process, more uniform substitution, accompanied by an appreciable change in properties, should result. Samples of improved solubility and increased biostability at a given MS level have actually been prepared in our laboratories by a partial solution technique, demonstrating the validity of this hypothesis.

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Solid-State Polymerization of Maleimide by 2,2′-Azobisisobutyronitrile

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Synopsis

The solid-state polymerization of maleimide by 2,2′-azobisisobutyronitrile was studied over the temperature range 65–85°C. The polymerization was carried out either by heating the solid mixture of maleimide and 2,2′-azobisisobutyronitrile or by heating the two compounds separately in twin ampules. The results of the kinetic study showed that the lifetime of the propagating radicals was short and that the rate of termination was proportional to the mole amount of propagating radicals. The ESR spectrum showed that stable radicals that were not main propagating radicals were in the polymerizing system.

INTRODUCTION

The polymerization of maleimide by free-radical initiators and anionic catalysts has been studied by several groups of workers.[1–8] We have found that maleimide polymerizes in the solid state under gamma-ray irradiation.[9,10] Stable radicals were found through ESR measurement of the irradiated solid monomer under conditions of polymerization. They were shown not to be main propagating species.[9,10] It was, however, suggested that this solid-state polymerization proceeds at least partially by a free-radical mechanism, since free-radical scavengers retarded it.

We studied solid-state polymerization with 2,2′-azobisisobutyronitrile to compare the characteristics of polymerization by gamma-ray irradiation with that by free-radical initiators.

EXPERIMENTAL

Materials

Commercial maleimide and 2,2′-azobisisobutyronitrile (AIBN) were purified by recrystallization from ethyl acetate and acetone, respectively. Maleimide (m.p. 93°C.) and AIBN were pulverized in a mortar before use. The average crystal sizes of the maleimide and the AIBN were about 50 and 200 mesh, respectively.

Procedure and Characterization of Polymer

A 500 mg. amount of maleimide and a measured amount of AIBN were mixed and placed in a glass ampule (1.2 cm. diam., 5 ml. capacity), which was sealed under vacuum. The ampule was heated in a constant-temperature bath. The temperature in the polymerizing system was measured with a thermocouple (alumel–chromel), the junction of which was placed in the middle of the solid mixture. The temperature was recorded with a Laboratory Recorder, Type LER-12A (Yokogawa Electric Works Ltd.).

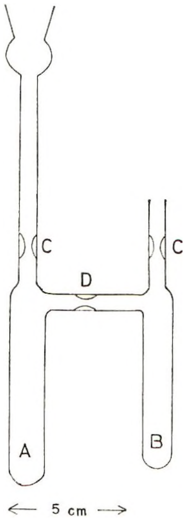

Fig. 1. Twin ampules.

Polymer was separated from residual monomer by washing with ether and was dried under vacuum. A twin ampule (Fig. 1) was also used as a reaction vessel, into which maleimide and AIBN were separately placed, maleimide in ampule A and AIBN in ampule B. The ampule was sealed under vacuum at C (Fig. 1).

The infrared spectra were determined with a Shimadzu Infracord Model IR-27 in KBr pellets. Differential thermal analyses were made with a Rigaku-Denki DTA apparatus. The specific viscosity of 0.2% polymer solution in *N*,*N*-dimethylformamide was measured in an Ubbelohde viscometer.

Rate of Decomposition of AIBN

The rate of decomposition of solid AIBN in the presence of maleimide under a nitrogen pressure of 1 atm. was estimated as the volume of the nitrogen evolved in unit time. The volume was measured by means of a gas buret attached to the reaction vessel.

ESR Spectrum

The ESR spectrum was measured with a Japan Electron Optics ESR Spectroscope (Model JES-3B). An estimation of the amount of radicals from the intensity of the ESR spectrum was made with a standard of a benzene solution of DPPH (10^{-3} mole-%).

RESULTS AND DISCUSSION

Effect of Reaction Temperature

When the bath temperature was below about 73°C., a slow, solid-state polymerization took place (Table I); the temperature of the polymerization system rose to the bath temperature after about 30 min. and was constant thereafter. Over the bath temperature range of about 75°C. to the melting point of the monomer (93°C.) a violent polymerization took place after a few minutes, and the temperature of the polymerization system rose to about 150°C. The rate of polymerization in solid state at 65°C. was lower than that in acetonitrile solution at the same temperature. The infrared spectrum, the melting point, measured by differential thermal analysis (about 400°C.), and the solubility of the polymer formed in the solid state were very similar to those of the polymer formed in solution.[1]

TABLE I
Effect of the Reaction Temperature on Polymer Yield

Maleimide, mg.	AIBN, mg.	React. temp., °C.	React. time, hr.	Polymer yield, wt.-%	η_{red}, dl./g.
481	20.3	72	47	43.4	0.32
480	20.1	65	47	11.5	0.29
484	821	"	47	94.3	0.21
499[a]	18.8	"	18	75.0	0.17

[a] In the solution of acetonitrile (5 ml.).

TABLE II
Influence of Crystal Size of Maleimide and AIBN on Polymer Yield[a]

Maleimide, mg.	AIBN, mg.	Crystal size Maleimide mesh	Crystal size AIBN mesh	Polymer yield, wt.-%
487	20.0	100–300	100–300	11.1
482	20.1	12–16	"	11.5
487	20.4	16–100	"	11.4
480	19.9	"	16–100	8.4
480	20.4	"	12–16	8.0

[a] Reaction temperature, 64°C.; reaction time, 49 hr.

Effect of Crystal Sizes of Maleimide and AIBN on Polymer Yield

As shown in Table II, the crystal size of maleimide had no effect on the polymer yield. On the other hand, the polymer yield of the solid-state polymerization of maleimide became slightly less with increasing crystal size of AIBN. This decrease of the rate may be attributed to the decrease in the initiation rate, since the primary free radicals from AIBN are more liable to recombine within the crystal when larger crystals of AIBN are used.

Solid-State Polymerization in Twin Ampules with AIBN

The results in Table III show that maleimide, which was separated from AIBN in a twin ampule, polymerized. As shown in the table, solid-state polymerization in the twin ampule took place even at 85°C. without the melting of the monomer, but at 90°C. solid monomer partially melted from the reaction heat.

TABLE III
Polymerization with Twin Ampules

Maleimide, mg.	AIBN, mg.	React. temp., °C.	React. time, hr.	Polymer yield, wt.-%
403	40.0	85	2.0	12.6
401	42.7	83	2.0	9.9
401	11.9	83	2.0	7.8
405	40.8	65	48	4.3

It is considered that the polymerization of maleimide in the twin ampule was initiated either by cyanisopropyl radicals, which traveled from B to A (Fig. 1) without recombination or by the vapor of AIBN or ketenimine, which is one of the recombination products of cyanisopropyl radicals.[11] If the former type of initiation took place, the polymer yield should have increased with increasing amounts of free radicals in ampule B, that is, with increasing rate of formation of free radicals. The results given in Table III show that the polymer yield only slightly increased when a fourfold amount of AIBN was used. Moreover, the observation of no signal from free radicals in the ESR measurement of the solid AIBN under decomposition at 65°C. indicated the extreme smallness of the concentration of free radicals in ampule B (less than 10^{-6} mole/l.). From these results it is considered that the solid-state polymerization in the twin ampules was initiated by the vapor of AIBN or ketenimine.

To determine the existence of the long-lived propagating radicals in this solid-state polymerization a two-stage polymerization was carried out; the results are summarized in Table IV.

After polymerization in the first stage was carried out under definite conditions with the twin ampules, ampule A was separated from ampule B

TABLE IV
Two-Stage Polymerization with Twin Ampules

Maleimide, mg.	AIBN, mg.	First stage		Second stage		Polymer yield, wt.-%
		Temp., °C.	Time, hr.	Temp., °C.	Time, hr.	
404.7	40.8	65	48	—	—	4.3
404.6	40.8	"	"	65	195	4.7
402.0	41.3	85	2	—	—	12.6
400.6	40.8	"	"	65	28	12.6
400.0	40.8	"	"	"	76	12.7
400.0	39.9	"	"	85	5	13.3

by sealing of the twin ampules at D (Fig. 1), which prevented further initiation. Then, the ampule A was further heated. As seen in Table IV, the polymer yield increased only slightly in the second stage. This result indicates the shortness of the lifetime of the propagating radicals in this polymerization.

Kinetic Features

Figure 2 shows the influence of reaction time on the polymer yield at 65 and 72°C. The reduced viscosity of the polymer obtained is plotted against irradiation time in Figure 3.

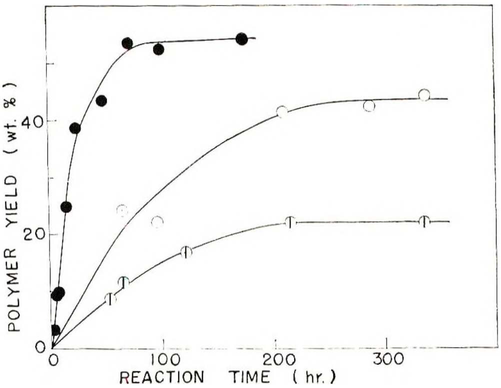

Fig. 2. Time–conversion curves of solid-state polymerization of maleimide with AIBN: (●) maleimide 500 mg., AIBN 4 wt.-%, reaction temperature 72°C.; (○) maleimide 500 mg., AIBN 4 wt.-%, reaction temperature 65°C.; (⦶) maleimide 500 mg., AIBN 2 wt.-%, reaction temperature 65°C.

As seen in Figure 2, polymerization continued for a long time, but conversion reached a limited value after about 200 hr. at 65°C. and after about 70 hr. at 72°C. The final conversion was nearly doubled when twice the amount of AIBN was used. The reduced viscosity scarcely varied with reaction time, with amount of AIBN used, and with reaction temperature.

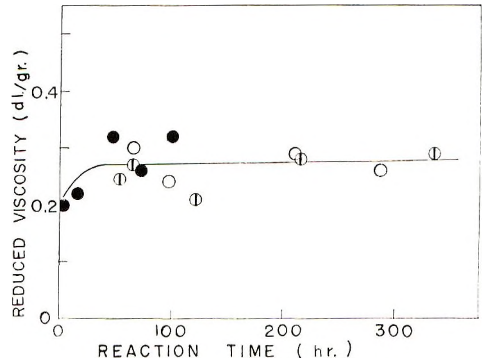

Fig. 3. Reduced viscosity of polymer formed under various conditions: (●) maleimide 500 mg., AIBN 4 wt.-%, reaction temperature 72°C.; (○) maleimide 500 mg., AIBN 4 wt.-%, reaction temperature 65°C.; (Φ) maleimide 500 mg., AIBN 2 wt.-%, reaction temperature 65°C.

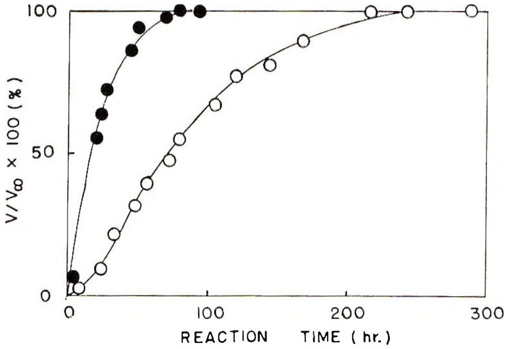

Fig. 4. Decomposition of AIBN in solid state: (●) maleimide 3.48 g., AIBN 152 mg., reaction temperature 72°C.; (○) maleimide 2.98 g., AIBN 132 mg., reaction temperature 65°C.; V, volume of nitrogen evolved; V_∞, volume readings obtained after 100 hr. at 72°C. and after 300 hr. at 65°C.

To determine the rate of initiation by AIBN the rate of decomposition of AIBN was measured in the presence of maleimide. In Figure 4 the amount of nitrogen evolved is plotted against time. The figure shows that the rate of decomposition in the solid state is much smaller than that in solution (the half-value period of AIBN in solution is about 8 hr. at 65°C.). Figure 5 shows that the rate of decomposition of AIBN in the solid state is expressed by a first-order rate equation after an induction period. The rate constant estimated from the slope was 5.76×10^{-2} hr.$^{-1}$ at 72°C. and 1.38×10^{-2} hr.$^{-1}$ at 65°C.

By comparing Figures 2 and 4 it is seen that the polymer yield reached a limited conversion when the decomposition of AIBN was over, both at 65 and at 72°C. This result is consistent with the conclusion noted above, that the lifetime of the propagating species of this solid-state polymerization is short.

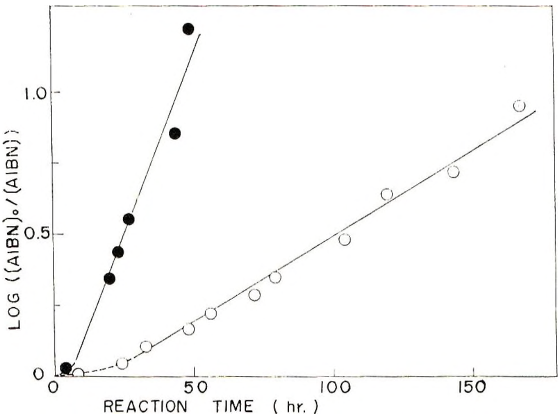

Fig. 5. First-order plot of decomposition of AIBN in solid state: (●) maleimide 3.48 g., AIBN 152 mg., reaction temperature 72°C.; (○) maleimide 2.98 g., AIBN 132 mg., reaction temperature 65°C.; [AIBN], in moles; [AIBN]$_0$, initial, in moles.

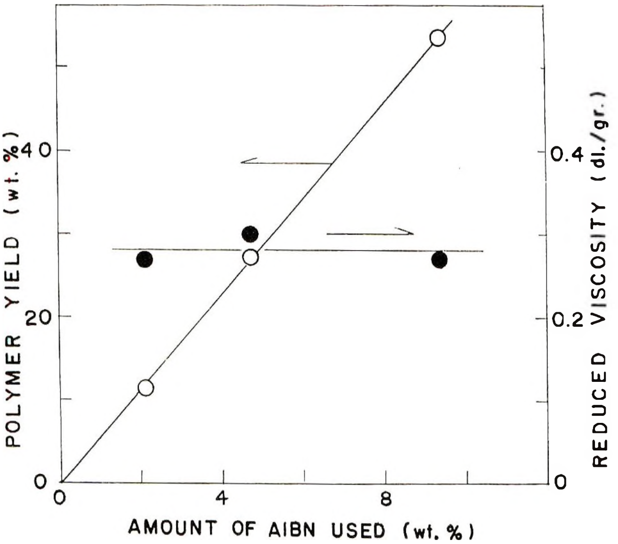

Fig. 6. Effect of amount of AIBN on polymer yield and reduced viscosity of polymer formed: maleimide 500 mg. reaction temperature 65°C., reaction time 65 hr.

It is suggested that the steady-state approximation with respect to the propagating radical is applicable to this polymerization because of the following two experimental results: the lifetime of the propagating radicals is short, and the reduced viscosity of the polymer formed was almost independent of the reaction time.

As seen in Figure 6, the reduced viscosity of the polymer scarcely changed with increasing amounts of AIBN at 65°C. This indicates that a termination whose rate is proportional to the number of moles of propagating radicals prevailed or that the transfer reaction controlled the molecular weight of the polymer. Figure 6 also shows the linear relationship between the polymer yield and the amount of AIBN used. In consideration of the kinetics of the polymerization, to which the steady-state approximation with respect to the propagating radical is applicable, it is suggested that the rate of termination was proportional to the number of moles of propagating radicals at 65°C. That the final conversion was almost doubled when twice the amount of AIBN was used is consistent with the kinetic feature of a dead-end polymerization[12] with a first-order termination with respect to the number of moles of propagating radicals.

From these considerations we concluded that a termination, whose rate was proportional to the number of moles of propagating radicals, prevailed in this polymerization. It is suggested that this termination is the degradative chain-transfer of propagating radicals effected through hydrogen abstraction from the imide group.

The radical formed by the chain transfer is considered to be unreactive because of its resonance stabilization. This degradative transfer has already been proposed by us in a study of the radiation-induced polymerization of this monomer[10] and by Nakayama and Smets in their study of the free-radical polymerization of this monomer in dimethylformamide.[8]

ESR Spectrum

Neither heating of solid AIBN nor heating of solid monomer at 65°C. gave an ESR spectrum; heating of the mixture of AIBN and maleimide at 65°C., however, gave the spectrum shown in Figure 7. The shape of this spectrum is similar to that of the stable radical formed by the gamma-ray irradiation of solid monomer at 65°C. We concluded that the same stable radical is formed during solid-state polymerization, whether initiated by AIBN or by gamma-ray.[10]

The change in concentration of this radical during polymerization is shown in Figure 8. Comparing Figures 8 and 2, it may be said that this radical scarcely decayed after the polymerization was over. This result

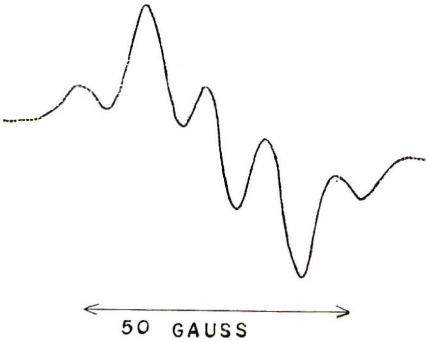

Fig. 7. ESR spectrum of stable radicals formed from heating of mixture of solid maleimide and AIBN: maleimide 301.1 mg., AIBN 20.2 mg., reaction time 150 hr. Wavelength of spectroscope, 3.16 cm.; frequency of main magnetic field, 100 kc./sec.

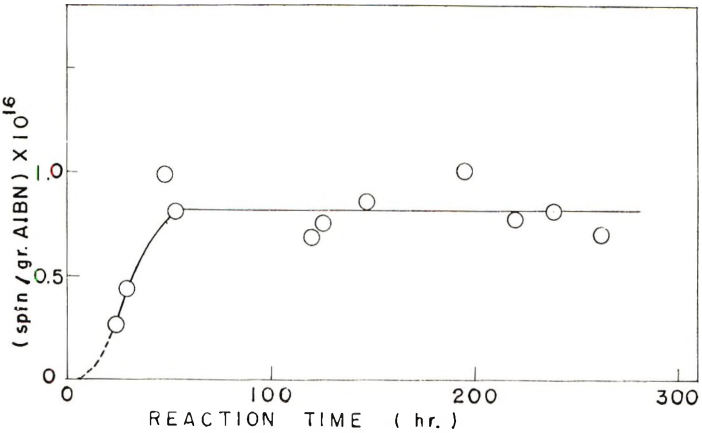

Fig. 8. Change of amount of free radicals with reaction time: maleimide 301.1 mg., AIBN 20.2 mg., reaction temperature 65°C.

leads to the same conclusion as in the case of gamma-ray-induced solid-state polymerization, namely, that this stable radical is not the main propagating species. It is inferred that the radical is formed by degradative chain transfer.

Comparison of AIBN and Gamma-Ray Initiation of Solid-State Polymerization

The properties of the polymers were very similar. In a kinetic study it was found that in both cases that the lifetime of the propagating species was short and that a termination whose rate was proportional to the number of moles of propagating species prevailed. Furthermore, the ESR spectra of the stable radicals exhibited the same shape in both cases. The radicals were found not to be the main propagating species in both cases. From these results it is suggested that the main propagating species of the gamma-ray-induced polymerization of this monomer is free radicals.

The authors are grateful to Sumitomo Atomic Energy Industries, Ltd., for supplying the equipment used in this study and wish to thank Dr. Nishiu and Mr. Fujiwara, who did the ESR work.

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Polymers Derived from Fluoroketones. II. Wettin Properties of Fluoroalkyl Acrylates and Methacrylates*

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Synopsis

The critical surface tension of wetting (γ_c) for certain branched-chain polymeric fluor alkyl acrylates and methacrylates was obtained. Polymeric materials utilized in t study can be represented by the repeating units $+CH_2—C(R)(COOCR'(CF_2X)_2)$- where R is H or CH_3, R′ is H or F, and X is F or Cl, by $+CH_2—CH(COO(CH_2)_nOC$ $(CF_3)_2)+$, where n is 2, 5, or 11, and by $+CH_2—C(R)(COOCH_2(CF_2)n'CF_3)+$, where is H or CH_3 and n' is 2 or 6. Monomer synthesis involved either the direct acylation a fluoroketone–metal fluoride adduct or a fluoroalcohol with acryloyl or methacrylo chloride or a displacement reaction between a fluoroketone–metal fluoride adduct and ω-bromoester. In general, modifications in the pendent fluoroalkyl group affected in a manner predictable from previous work by Zisman et al.; e.g., γ_c was increased wh either H or Cl was substituted for F in the side chain. In polymeric alkyl acrylates co taining a heptafluoroisopropyl side chain γ_c increased as the fluorocarbon group was moved from the proximity of the polymer backbone by intervening methylene grou A comparison of the wetting properties of polyacrylates containing either a perfluoroi propyl or n-perfluoropropyl group showed that the polymer containing the isopro group had a lower γ_c.

INTRODUCTION

Since the pioneering work of Zisman[1] there has been great interest in t use of fluorochemicals when low-energy surfaces are important. A maj part of the reported work dealing with surfaces rich in C—F has involv clean, polished surfaces coated with a monomolecular layer of a simp fluorinated compound containing a polar group, e.g., fluorocarbon aci The effect of chemical constitution on surface wettability has been clear demonstrated by studies utilizing an empirical quantity, the critical su face tension of wetting, γ_c. The critical surface tension of a solid surfa is normally obtained by measuring the contact angles θ, for a series pure, homologous liquids, on the horizontal solid surface. A plot of c sine θ versus the surface tension of the test liquids is then made, and t

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*Presented in part at the American Chemical Society meeting, New York, N. Sept. 1966.

graphical intercept of the straight line at $\cos \theta = 1$ is defined as the critical surface tension of wetting for the solid.[1]

Zisman and his co-workers[2] obtained a γ_c of 6 dyne/cm. for a monolayer of perfluorolauric acid, which represents the least wettable surface known. This low value presumably reflects the surface of close-packed perfluoroalkyl chains terminated by trifluoromethyl groups which are concentrated at the air–solid interface. The lowest γ_c reported for a polymeric substance, 10.6 dyne/cm., was obtained for the fluoroalkyl methacrylate, poly(1H,1H-pentadecafluorooctyl methacrylate).[3] It is not surprising to find a more wettable surface (higher γ_c) for the fluoroalkyl methacrylate than for an adsorbed monolayer of perfluorolauric acid. Closer packing of the fluoroalkyl groups would be expected to occur in a fluorocarbon acid monolayer than in a substance whose fluoroalkyl chains are covalently attached to alternate carbon atoms along the polymer backbone.

A good deal of research has concerned the effects of chemical constitution on the wetting properties of such fluorine-containing vinylic polymers as polytetrafluoroethylene,[4] poly(vinyl fluoride), and poly(vinylidine fluoride),[5] but very little has been reported on the surface properties of fluorinated polymers containing pendant fluoroalkyl groups, such as the fluoroalkyl acrylates. The reactivity and availability of fluorinated ketones led us to investigate the possibility of utilizing these compounds as intermediates in the preparation of model polymer systems for use in studies related to the effects of chemical constitution and structure on wetting.

This paper deals with an examination of the critical surface tension of polymeric fluoroalkyl acrylates and methacrylates with a variety of fluoroalkyl side chains. Three structural variations employed in this study are represented by the monomers (I), (II), and (III).

$$CH_2{=}\overset{R}{\overset{|}{C}}{-}COOCR'(CF_2X)_2$$

(I)

$R = H$ or CH_3, $X = F$ or Cl,
$R' = F$ or H

$$CH_2{=}CH{-}COO(CH_2)_nOCF(CF_3)_2$$

(II)

$n = 2, 5,$ or 11

$$CH_2{=}\overset{R}{\overset{|}{C}}{-}COOCH_2(CF_2)_{n'}CF_3$$

(III)

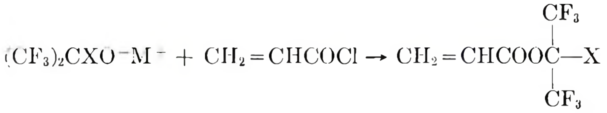
$n' = 2$ or 6

DISCUSSION

Fluorinated ketones react with a variety of nucleophilic agents such as alkoxide, cyanide, and fluoride,[6–8] and we have found that the intermediate addition products can often be converted to acrylates and methacrylates, as illustrated in eqs. (1) and (2):

$$(CF_3)_2C{=}O + MX \rightarrow (CF_3)_2CXO^-M^+ \qquad (1)$$

where M is alkali metal, X = CN^-, F^-, OCH_3^-, CH_3^-, or phenyl, and



$$(CF_3)_2CXO^-M^+ + CH_2{=}CHCOCl \rightarrow CH_2{=}CHCOOC(CF_3)_2{-}X \quad (2)$$

We have previously reported the preparation of a number of fluoroalkyl acrylates and methacrylates with structure (I) in which R′ is fluorine.[8] These monomers were prepared as illustrated in eqs. (1) and (2), with potassium fluoride and various perhaloketones. Acrylate monomers with structure (II) were prepared as illustrated in eqs. (3)–(6):[9]

$$(CF_3)_2C = O + KF \rightarrow (CF_3)_2CFO^-K^+ \quad (3)$$

$$(CF_3)_2CFO^-K^+ + Br(CH_2)_{n-1}COOR \rightarrow (CF_3)_2CFO(CH_2)_{n-1}COOR \quad (4)$$

$$(CF_3)_2CFO(CH_2)_{n-1}COOR \xrightarrow{LiAlH_4} (CF_3)_2CFO(CH_2)_nOH \quad (5)$$

$$(CF_3)_2CFO(CH_2)_nOH + CH_2 = CHCOCl \rightarrow (CF_3)_2CFO(CH_2)_nOOCCH = CH_2 \quad (6)$$

Acrylates and methacrylates with structure (III) and structure (I), where R′ is hydrogen, were prepared by the reaction of acryloyl or methacryloyl chloride with the appropriate fluorinated alcohol.[10]

Effect of the Substitution of Hydrogen and Chlorine on γ_c

Figure 1 gives a critical surface-tension plot for polyfluoroalkyl acrylates, in which hydrogen or chlorine has been substituted for fluorine on the fluoroalkyl side chain. In general, the magnitude of change of γ_c with fluorine substitution agrees with earlier work on adsorbed fluorocarbon acid monolayers and on fluorinated vinylic polymers.[1] That is, substitution of hydrogen for fluorine increases γ_c slightly, whereas chlorine promotes a larger increase in γ_c.

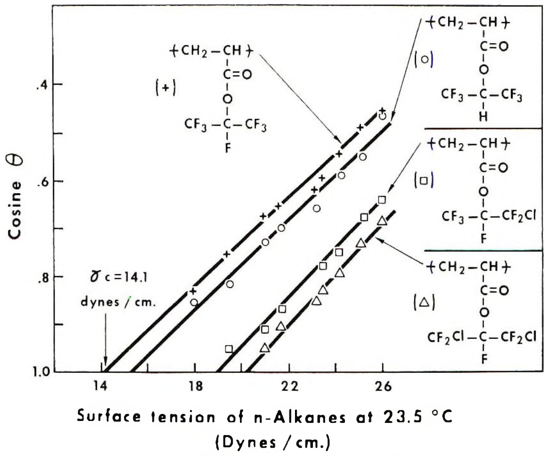
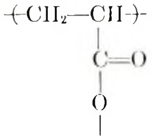


Fig. 1. Plots of γ_c versus n for several fluoroalkyl acrylates.

TABLE I

Effect of Hydrogen and Chlorine Substitution for Vinylic and Acrylate Polymers

Polymers[a] A		Polymers[a] B	$\Delta\gamma_c$ (incr. in γ_c), dyne/cm.	$\Delta\gamma_c$ per 1% decr. in F,[b] dyne/cm.
$-\!(\mathrm{CF_2CF_2})\!-_n$	→	$-\!(\mathrm{CF_2CFH})\!-_n$	3.5	0.55
$\mathrm{A{-}CF(CF_3)_2}$	→	$\mathrm{A{-}CH(CF_3)_2}$	1.3	0.33
$-\!(\mathrm{CF_2CF_2})\!-_n$	→	$-\!(\mathrm{CF_2CFCl})\!-_n$	12.5	0.44
$\mathrm{A{-}CF(CF_3)_2}$	→	$\mathrm{A{-}CF(CF_3)(CF_2Cl)}$	4.8	0.47

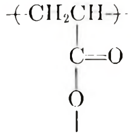
[a] A in formula refers to acrylate repeating unit 

$$\begin{array}{c} -\!(\mathrm{CH_2{-}CH})\!- \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{O} \\ | \end{array}$$

[b] $\Delta\gamma_c/[(\%\ \mathrm{F\ in\ A}) - (\%\ \mathrm{F\ in\ B})]$.

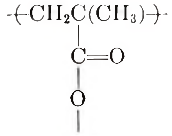
In Table I comparisons are made of the changes in γ_c for chlorine and hydrogen substitutions in vinylic and acrylate polymer systems. For the chlorine-substituted polymers it is of interest to compare the difference in γ_c between poly(tetrafluoroethylene) (TFE), in which γ_c is 18.5 dyne/cm.[4], and polychlorotrifluoroethylene (CTFE), in which γ_c is 31 dyne/cm.,[11] and between the polyacrylates $\mathrm{A{-}CF(CF_3)_2}$, 14.1 dyne/cm., and $\mathrm{A\text{-}CF(CF_3)(CF_2Cl)}$, 18.9 dyne/cm.; see Table I.

NOTE: In order to simplify the nomenclature and polymer identification, A refers to the repeating acrylate unit



$$\begin{array}{c} -\!(\mathrm{CH_2CH})\!- \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{O} \\ | \end{array}$$

and M refers to the repeating methacrylate unit



$$\begin{array}{c} -\!(\mathrm{CH_2C(CH_3)})\!- \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{O} \\ | \end{array}$$

For example, poly(heptafluoroisopropyl acrylate) is written $\mathrm{A{-}CF(CF_3)_2}$.

At first glance it appears that substitution of chlorine for fluorine has had a more profound effect on wettability in the TFE → CTFE system, where $\Delta\gamma_c = 12.5$ dyne/cm., than in the polyacrylate system $\mathrm{A{-}CF(CF_3)_2} \rightarrow \mathrm{A{-}CF(CF_3)(CF_2Cl)}$, where $\Delta\gamma_c = 4.8$ dyne/cm. However, if the change in γ_c is compared with the overall change in fluorine content per monomer unit in the two systems, it is found that in both systems the increase in γ_c per 1% decrease in fluorine content is between 0.44 and 0.47 dyne/cm. These figures were arrived at by subtracting the per cent fluorine content of a CTFE unit (49.13%) from the per cent fluorine content of a TFE unit (76.00%) and dividing this difference into the change in critical surface tension ($\Delta\gamma_c$ = 12.5 dyne/cm.). A somewhat similar comparison may be made in the substitution of hydrogen for fluorine. The increase in γ_c in the system TFE → $\leftarrow CF_2CFH \rightarrow_n$ is 3.5 dyne/cm., which corresponds to an increase of approximately 0.55 dyne/cm. for each 1% decrease in fluorine content. This is quite close to the change observed for the chlorine–fluorine substitution. It should be emphasized that γ_c in a particular fluorinated polymer is not necessarily dependent on the total fluorine content but, rather, on the arrangement of the fluorine atoms. For example, TFE with an overall 76% fluorine is more wettable (higher γ_c) than the polyacrylate A—$CF(CF_3)_2$, which has a 55% fluorine content. However, calculations of the sort indicated here could be important in estimating changes in γ_c in a given polymer system with changes in constitution.

In examinations of the changes in γ_c from the polyacrylate A—$CF(CF_3)_2$ to the hydrogen-substituted polyacrylate A—$CH(CF_3)_2$ an increase of 1.3 dyne/cm. was observed (Fig. 1). The increase in γ_c per 1% decrease in fluorine content in this system is approximately 0.32 dyne/cm., which indicates a smaller effect on γ_c than in the TFE → $\leftarrow CF_2CFH \rightarrow_n$ system (Table I). This may be due simply to a shielding effect, since the hydrogen in the polyacrylate A—$CH(CF_3)_2$ is in juxtaposition with two bulky trifluoromethyl groups.

Substitution of a second chlorine atom in the polyacrylate system A—$CF(CF_2Cl)(CF_3)$ → A—$CF(CF_2Cl)_2$ produced a minor increase in γ_c 18.9 dyne/cm. to 20.3 dyne/cm.; see Figure 1. This is in accord with the results of Zisman's study of the effect of progressive chlorination on wettability. A large difference in γ_c (8 dyne/cm.) was found between polyethylene and poly(vinyl chloride); however, the difference between polyvinyl chloride and poly(vinylidine chloride) was only 1 dyne/cm.[5]

Effect of Chain Length on γ_c

Zisman et al.[2] have shown with adsorbed monolayers of perfluorinated acids that the value of γ_c decreases with increasing chain length of the perfluoroalkyl segment. This effect was attributed to a more efficient packing of the perfluoroalkyl chain, so that the longer-chained fluorocarbon acids present a higher concentration of —CF_3 groups at the air–solid interface. Comparison of the γ_c values for the two fluoroalkyl acrylates poly(1H,1H-heptafluorobutyl acrylate), γ_c = 15.2 dyne/cm.) and poly(1H,1H-pentadecafluorooctyl acrylate), γ_c = 10.4 dyne/cm. (see Table II) indicates that this same phenomenon occurs in the polyacrylate systems. That is, as the fluorocarbon chain length is increased, γ_c decreases.

We have examined the effect of increasing the overall chain length in a fluoroalkyl acrylate system while keeping the size of the fluorocarbon group constant. Polymers were obtained from acrylates with the structure (II), where n is 2, 5, or 11. A plot of the critical surface tensions of these polymers versus alkylene chain length is given in Figure 2. A fairly regular

TABLE II
Critical Surface Tension for Fluoroalkyl Acrylates and Methacrylates

Polymer[a]	γ_c
$CF_3(CF_2)_6CH_2$—A	10.4
$CF_3(CF_2)_6CH_2$—M	10.6[b]
$CF_3(CF_2)_7SO_2N(CH_2CH_2CH_3)CH_2CH_2$—A	11.1[b]
$(CF_3)_2CF$—A	14.1
$(CF_3)_2CH$—M	14.8–15.4
$(CF_3)_2CF$—M	15.0
$CF_3(CF_2)_2CH_2$—A	15.2
$(CF_3)_2CH$—A	15.4
$(CF_3)_2CFO(CH_2)_2$—A	15.5
$(CF_3)_2CFO(CH_2)_5$—A	17.7
$(CF_3)(CF_2Cl)CF$—A	18.9
$(CF_3)(CF_2Cl)CF$—M	19.1
$(CF_2Cl)_2CF$—A	20.3
$(CF_3)_2CFO(CH_2)_{11}$—A	20.3

[a] A refers to acrylate repeat unit (see Table I). M refers to methacrylate repeat unit.

[b] Literature values (Bernett and Zisman[3]).

increase in γ_c was observed from the parent polymer, poly(heptafluoroisopropyl acrylate), 14.1 dyne/cm., to a polymer containing eleven methylene units interspersed between the perfluoroisopropoxy group and the main chain. It should be noted that γ_c increased by about 0.7 dyne/cm. per methylene group from the parent polymer up to five methylene units and then by about 0.4 dyne/cm. per methylene unit up to eleven methylene groups. Lengthening the nonfluorocarbon portion of the side chain obvi-

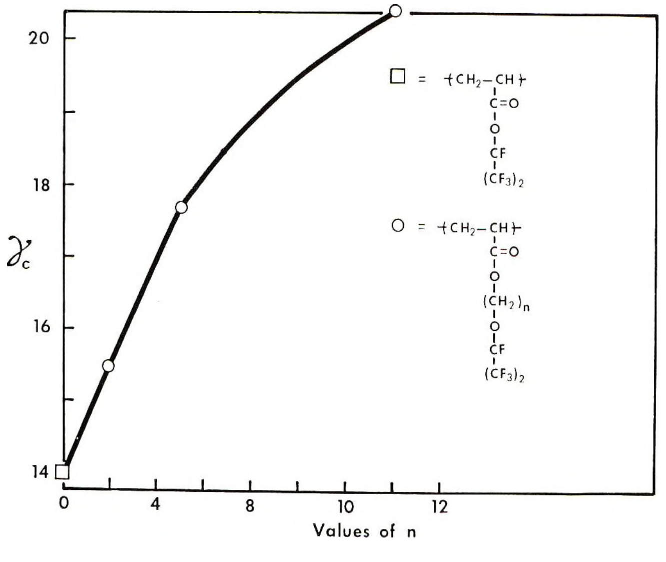


Fig. 2. Effect of chain length on γ_c for polyacrylates containing a heptafluoroisopropyl group.

ously did not result in improved alignment of the fluorocarbon segment, since there was a continual increase in γ_c as the alkylene chain length was increased. The increased wettability with increasing alkylene chain length in this case appears to be due to an overall increase in hydrocarbon content (or decrease in fluorine content) per monomer unit.

Perfluoroisopropyl versus *n*-Perfluoropropyl

Figure 3 illustrates γ_c plots for the two polyacrylates poly(hepta fluoroisopropyl acrylate) and poly(1H,1H-heptafluorobutyl acrylate). Both these polymers contain side chains with an equivalent number of fluorine atoms, and it can be seen that the polymer with the perfluoroisopropyl side chain gave a lower γ_c than the polymer containing the *n*-perfluoropropyl group. There are at least two plausible explanations of the observed differences in γ_c in these two polymer systems. Poly(heptafluoroisopropyl acrylate) may display a lower γ_c because the perfluoroisopropyl group has more of its fluorine atoms incorporated in the lower-energy —CF_3 groups. However, the lower γ_c may simply reflect the overall fluorine content of the monomer units. For if comparisons are made between the poly(1H,1H-heptafluorobutyl acrylate) and poly(heptafluoroisopropyl methacrylate), both having a fluorine content of 52.36%, one finds that they have γ_c values that are almost identical (15.2 dyne/cm. and 15.0 dyne/cm.); see Table II.

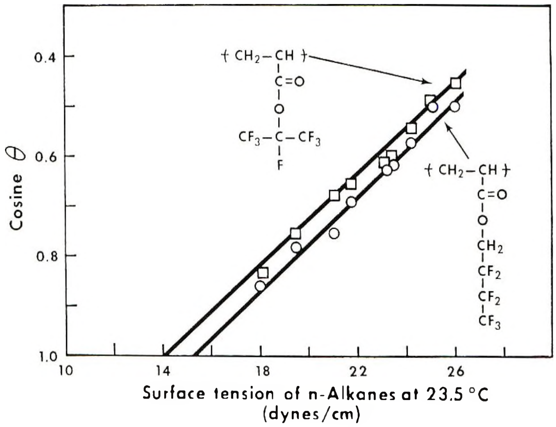


Fig. 3. Effect of branching on γ_c.

EXPERIMENTAL

Materials

Solvents used in this work were obtained from commercial sources and were dried and distilled before use. Anhydrous potassium fluoride was obtained from Allied Chemical Corp.; halogenated ketones, from Allied

Chemical Corp. and DuPont. The bromoesters were obtained from K & K Laboratories, Inc. Acryloyl and methacryloyl chloride were obtained from Borden Monomer-Polymer Laboratories. The following series of *n*-alkanes were obtained from Matheson, Coleman & Bell (catalogue number given after each compound): hexadecane (HX200), tetradecane (TX200), dodecane (DX2415), undecane (UX15), decane (DX30), nonane (NX808), octane (OX58), hexane (HX290); heptane was obtained from Eastman Chemical (2215). The alkanes were passed through a column of activated alumina before use. Surface tensions for the alkanes are given in Table III. The surface tension for another series of test liquids, comprising mixtures of methanol and water, is also given in Table III.

TABLE III
Surface Tensions of Test Liquids (dyne/cm.)

n-Alkanes	γ at 23.5°C.,[a] dyne/cm.	Methanol/water[b] ratio	γ at 23.5°C.,[a] dyne/cm.
Hexadecane	26.0	100:0	21.49
Tetradecane	25.1	95:5	22.64
Dodecane	24.2	90:10	24.79
Undecane	23.5	85:15	25.49
Decane	23.2	80:20	26.55
Nonane	21.7	75:25	28.09
Octane	21.0	70:30	29.48
Heptane	19.5	50:50	34.35
Hexane	18.0		

[a] Corrected surface tensions determined with a du Nouy Tensiometer.

[b] Per cent by volume.

Acrylates and Methacrylates with Structure (I), R′ Fluorine

The procedure for preparing acrylates and methacrylates with structure (I) has been reported previously and is illustrated by the following preparation of heptafluoroisopropyl acrylate. A 250-ml., three-necked round-bottomed flask, equipped with a stirring bar, gas inlet tube, and Dry Ice reflux condenser, was dried under vacuum by heating with a burner. Nitrogen was bled into the system, and 9.6 g. (0.16 mole) of anhydrous potassium fluoride was introduced, followed by 150 ml. of dry *N*,*N*-dimethylformamide. The mixture was stirred and cooled in an ice–water bath. After Dry Ice was placed in the reflux condenser and the DMF–KF slurry had cooled, 27 g. of hexafluoroacetone (0.16 mole) was added. Gas addition was complete after about 15 min. The cooling bath was removed and the mixture stirred until a clear solution was obtained. Adduct formation was assumed to be complete at this time, since no hexafluoroacetone was evolved when the solution was warmed to 50°C. Acryloyl chloride (12.9 ml., 0.16 mole) was then added dropwise with a syringe while the mixture was cooled to 5–10°C. with an ice bath. A precipitate of KCl formed during the acyl halide addition. The contents of the flask were stirred an additional 30 min. at room temperature and then poured into 300 ml. of cold (ca. 5°C.) water. The lower layer was collected and washed three times with water, dried, and distilled, giving a 70% yield of heptafluoroisopropyl acrylate; b.p. 86–88°C. at 760 mm.

Acrylates and Methacrylates with Structure (I), R′ Hydrogen

These monomers were purchased from Allied Chemical. The chemicals were washed with dilute NaOH, to remove inhibitor and then dried over $CaSO_4$ prior to use.

Acrylates with Structure (II)

The following procedure illustrates the synthesis of intermediates and the acrylates with structure (II). Physical properties and analytical data for the intermediates and the acrylates are given in Table IV.

TABLE IV
Properties and Analyses of Some Fluoroalkyl Acrylates and Some Intermediates

Compound	B.p. and press., °C. and mm. Hg	$n_D^{°C.}$	Anal., % C	Anal., % H	Anal., % F
$(CF_3)_2CFOCH_2COOCH_3$	125, 760	1.3167^{25}	—	—	50.15
$(CF_3)_2CFO(CH_2)_2OH$	120, 760	1.3114^{25}	25.95	2.37	56.38
$(CF_3)_2CFO(CH_2)_2OOCCH{=}CH_2$	78, 47	1.3424^{25}	33.93	2.44	—
$(CF_3)_2CFO(CH_2)_4COOCH_3$	167, 760	1.3477^{23}	35.96	3.74	43.4
$(CF_3)_2CFO(CH_2)_5OH$	75, 9	1.3472^{23}	34.89	4.13	48.05
$(CF_3)_2CFO(CH_2)_5OOCCH{=}CH_2$	64, 1.5	1.3684^{23}	40.54	3.90	41.94
$(CH_3)_2CFO(CH_2)_{10}COOCH_2CH_3$	245–250, 760	1.3949^{25}	48.44	6.45	30.4
$(CF_3)_2CFO(CH_2)_{11}OH$	120, 2	1.3848^{27}	46.43	6.47	37.54
$(CF_3)_2CFO(CH_2)_{11}OOCCH{=}CH_2$	130, 2	1.3932^{24}	48.07	6.03	32.50

Methyl 2-Heptafluoroisopropoxyacetate

The potassium fluoride–hexafluoroacetone 1:1 addition product (alcoholate) was prepared as described in the previous example, with 45.1 g. (0.78 mole) of KF, 129 g. (0.78 mole) of hexafluoroacetone, and 350 ml. of bis(2-methoxyethyl)ether (diglyme). After 119 g. (0.78 mole) of methyl bromoacetate was added to the alcoholate, the mixture was stirred and heated at 75–80°C. for 16 hr. Potassium bromide precipitated from solution during the reaction. The resulting slurry was cooled to 25°C. and poured into 600 ml. of cold (5°C.) water. The lower layer was washed three times with water and dried over $CaSO_4$ (205.4 g. of crude material). Distillation at atmospheric pressure with a Short vigreux column yielded 151 g. of product (75.5% yield); b.p. 124.5–129°C.

2-Heptafluoroisopropoxyethanol

A 1-liter three-necked flask equipped with mechanical stirrer was flame-dried and flushed with nitrogen. Lithium aluminum hydride (22 g., 0.58

mole) was added to the flask, followed by 500 ml. of anhydrous diethyl ether. The $LiAlH_4$–ether slurry was stirred at room temperature for about 0.5 hr. under a nitrogen blanket, then 152 g. (0.59 mole) of methyl heptafluoroisopropoxyacetate dissolved in 100 ml. of diethyl ether was added to the slurry over a 2 hr. period. The mixture was allowed to stand overnight at room temperature. Several lumps of unreacting $LiAlH_4$ were removed from the product after this time. The product was then poured slowly with stirring onto ice. The ice–water–ether mixture was then acidified with dilute H_2SO_4, and the ether was collected. The aqueous layer was extracted three times with ether, and the ether layers were combined. The ether was removed on a steam bath, leaving 127 g. of crude product. The crude product was distilled on an 18 in. spinning-band column, giving 60 g. (43% yield) of product; b.p. 120–121°C.

2-Heptafluoroisopropoxyethyl Acrylate

Into a dry, 250-ml. three-necked flask was placed 57 g. (0.25 mole) of 2-heptafluoroisopropoxyethyl alcohol. The alcohol was heated to 40–50°C. and 36 g. (0.4 mole) of acryloyl chloride was added over a 15 min. period from a dropping funnel. A slow nitrogen purge through the liquid was maintained during the reaction, to remove HCl. After the addition the mixture was heated at 45°C. with the N_2 purge overnight. Distillation yielded 50 g. (68% yield) of product; b.p. 79–82°C. at 52 mm.

Preparation of Acrylates with Structure (III)

The preparation of 1H,1H-pentadecafluorooctyl acrylate was carried out as previously described,[10] by the acylation of 1H,1H-pentadecafluoro-1-octanol with acryloyl chloride; b.p. 55°C. at 2 mm. The acrylate, 1H,1H-heptafluorobutyl acrylate, was purchased from Peninsular Chemresearch.

Preparation of Polymers

Polymers of the various acrylates and methacrylates were prepared by polymerization in a solution of 1,3-bis(trifluoromethyl)benzene with about 0.5–1 mole-% α,α'-azobisisobutyronitrile as the initiator. In general, the solvent/monomer volume ratio was 1:1. Polymerization was carried out in screw-cap vials by heating at 75–80°C. for 6 hr. At the end of this time polymer was precipitated from solution by the addition of methanol. The polymer was then redissolved in a minimum of 1,2,2,-trichlorotrifluoroethane and again reprecipitated with methanol. The polymers were dried in a vacuum oven at 80°C. at 1–2 mm. for 24 hr. Number-average molecular weights were determined with a Mechrolab Membrane Osmometer. With the exception of poly(11-heptafluoroisopropoxyundecyl acrylate) the $\overline{M}_n$ ranged from 70,000 to 110,000 (DP $\approx$ 400). Poly(11-heptafluoroisopropoxyundecyl acrylate) consistently yielded polymers of lower $\overline{M}_n$, DP $\approx$ 100.

Preparation of Polymer-Coated Glass Slides

Polymer solutions of 2–5 wt.-% were prepared with 1,1,2-trichlorotrifluoroethane. Glass micro slides (3 × 1 in.) were rinsed with trichlorotrifluoroethane and distilled water and dried. The slides were then immersed in the coating solution and slowly withdrawn in a vertical position from the solution. A motor-driven pulley system was used for withdrawing the slides from the polymer solution at a rate of about 3 in./min. The slides were then placed in a slide rack, heated at 100°C. for 30 min., and allowed to equilibrate at 23.5°C. at 45% R.H. for at least 2 hr. before use.

Contact-Angle Measurements and Determination of γ_c

The contact angles of the test liquids on polymer coated glass slides were measured by projecting profiles of the drops onto a screen, drawing tangent lines, and measuring the angle with a protractor. Drops were made with a hypodermic syringe equipped with a 26-gage needle. When two people were working together, we were able to obtain measurements of the more volatile alkanes, hexane and heptane, within about 30 sec. Each contact angle represents the average of measurements taken from at least six different drops. The measurements generally did not vary by more than 2°, although we occasionally had a larger variation, presumably due to surface irregularities. With the exception of poly(11-heptafluoroisopropoxyundecyl acrylate) the *n*-alkanes were used as test liquids. We were unable to get stable drops of *n*-alkanes on slides coated with the undecyl acrylate. Drops of an alkane such as hexadecane had initial contact angles of about 50°; however, the drop would gradualy spread over the surface. The gradual spreading of the alkanes on this surface presumably is due to the partial solubility of this particular polymer in the alkanes. The low $\bar{M}_n$ (DP $\approx$ 100) and hydrocarbon character of this polyacrylate would be expected to increase its solubility in alkanes.

The critical surface tension of wetting for a variety of fluoroalkyl acrylates and methacrylates was determined by extrapolation of the surface tension versus the cosine of the contact angle θ to $\cos\theta = 1$ (0 contact angle). The values of γ_c are given in Table II.

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

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Polymers Derived from Fluoroketones. III. Monomer Synthesis, Polymerization, and Wetting Properties of Poly (allyl Ether) and Poly(vinyl Ether)*

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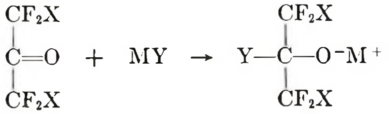
Synopsis

The synthesis and polymerization of a series of perhaloalkyl allyl and vinyl ethers derived from perhaloketones is described. Data on the critical surface tension of wetting (γ_c) for high molecular weight polymers of heptafluoroisopropyl vinyl ether and low molecular weight poly(heptafluoroisopropyl allyl ether) is also presented. Preparation of the allyl ethers is a one-step, high-yield displacement reaction between the potassium fluoride–perhaloacetone adduct and an allyl halide, such as allyl bromide. The vinyl ethers are prepared by a two-step process which involves displacement of halide from a 1,2-dihaloethane with a KF–perhaloacetone adduct and dehydrohalogenation of the 1-halo-2-perhaloalkoxyethane to a vinyl ether. Low molecular weight polymers were obtained with heptafluoroisopropyl allyl ether by using a high concentration of a free-radical initiator. The low molecular weight poly(heptafluoroisopropyl allyl ether) had a γ_c of 21 dyne/cm. No polymer was obtained with tributylborane–oxygen or with VCl_3–AlR_3, with gamma radiation, or by exposure to ultraviolet light. High molecular weight polymers were obtained from heptafluoroisopropyl vinyl ether by using either lauryl peroxide or ultraviolet light but not by exposure to BF_3–etherate. The γ_c for poly(heptafluoroisopropyl vinyl ether) ranged from 14.2 to 14.6 dyne/cm., and the significance of this value is discussed in relation to the γ_c for poly(heptafluoroisopropyl acrylate).

INTRODUCTION

In a continuation of a study of the effect of structure on polymer surface energy we prepared a series of allyl and vinyl ethers derived from perhaloketones and began a preliminary examination of the critical surface tension of wetting of polymers obtained from these allyl and vinyl ethers.

We have previously shown the feasibility of preparing polymers of acrylates[1,2] and glycidyl ethers[3] with a pendant side group that could be varied by the choice of appropriate intermediates:



$$\underset{\mathrm{CF_2X}}{\overset{\mathrm{CF_2X}}{\mathrm{C}}}\mathrm{=O} + \mathrm{MY} \rightarrow \mathrm{Y{-}}\underset{\mathrm{CF_2X}}{\overset{\mathrm{CF_2X}}{\mathrm{C}}}\mathrm{{-}O^-M^+}$$

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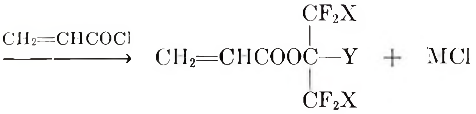


$$\xrightarrow{CH_2{=}CHCOCl} CH_2{=}CHCOO\overset{\displaystyle CF_2X}{\underset{\displaystyle CF_2X}{C}}{-}Y + MCl$$

where X is halogen, M is an alkali metal, and Y is F^-, CN^-, OCH_3^-, phenyl, etc. This paper deals with vinyl and allyl ethers with the following structures, where X is Cl or F

$$CH_2{=}CHOCF(CF_2X)_2 \quad \text{and} \quad CH_2{=}CHCH_2OCF(CF_2X)_2$$

DISCUSSION

Allyl ethers were prepared in excellent yields by displacement of halide from allyl bromide or chloride with the adduct obtained from a perhaloketone and potassium fluoride:

$$\begin{aligned}(CF_2X)_2C{=}O + KF \quad (CF_2X)_2CFO^-K^+ &\xrightarrow{CH_2{=}CHCH_2Br} \\ (CF_2X)_2CFOCH_2CH{=}CH_2 + \underline{KBr}\downarrow &\end{aligned} \qquad (1)$$

This is a high-yield (87%) displacement reaction that takes place readily in solvents such as *N*,*N*-dimethylformamide (DMF), acetonitrile, and the dimethyl ether of diethylene glycol (diglyme). The more polar solvent, DMF, is preferable, since normally all of the allyl bromide is consumed in this reaction, and the product allyl ether can be readily recovered in a pure state by distillation from the reaction mixture. In an alternate work-up procedure the crude-product mixture can be poured into cold water and the insoluble fluorocarbon layer recovered and washed with additional water to remove traces of solvent. This procedure, however, results in lower yields (ca. 60–70%), presumably owing to solubility losses during water-washing.

The vinyl ethers were prepared in a two-step process as shown:

$$\begin{aligned}(CF_2X)_2CFO^-K^+ + X'CH_2CH_2X' \rightarrow (CF_2X)_2CFOCH_2CH_2X' + KX'\downarrow \\ + \text{some } (CF_2X)_2CFOCH_2CH_2OCF(CF_2X)_2\end{aligned} \qquad (2)$$

$$(CF_2X)_2CFOCH_2CH_2X' \xrightarrow[\Delta]{\text{alc. KOH}} (CF_2X)_2CFOCH{=}CH_2 + KX' \qquad (3)$$

where X′ is Cl or Br and X is Cl or F. Both 1,2-dibromoethane and 1-bromo-2-chloroethane were employed in the initial step. When the former was utilized, the 1,2 diaddition product $(CF_2X)_2CFOCH_2CH_2OCF(CF_2X)_2$ was formed in amounts up to 26%, according to gas chromatographic analysis. The diaddition product was produced in minor amounts (2–3%) when 1-bromo-2-chloroethane was employed; however, the dehydrohalogenation was more difficult with 1-chloro-2-heptafluoroisopropoxyethane than with 1-bromo-2-heptafluoroisopropoxyethane.

The polymerization of heptafluoroisopropyl allyl ether was attempted with a number of free-radical initiators, ultraviolet light, gamma radiation, and a vanadium trichloride–triisobutyl aluminum catalyst.

Barney et al.[4] have reported the copolymerization of certain allyl compounds and thiocarbonyl fluoride with a tributylborane–oxygen initiation

TABLE I
Polymerization of Heptafluoroisopropyl Allyl Ether with Free-Radical Sources

Initiator	Initiator, mole-%	Temp., °C., and time, hr.	Conversion,[a] %
Benzoyl peroxide	2	100, 12	8
	10	100, 12	28
t-Butyl perbenzoate	2	100, 12	20
	10	100, 12	57
t-Butyl peroxide	2	135, 12	15
	10	135, 12	68
Lauryl peroxide	2	70, 12	12
	10	70, 12	54
Azodiisobutyronitrile	2	80, 12	10
	10	80, 12	42

[a] Per cent conversion corrected for weight of initiator as follows: % conversion = (wt. polymer)/(wt. monomer + wt. initiator) × 100.

system. We attempted the polymerization of heptafluoroisopropyl allyl ether with this system and also attempted copolymerization of the allyl ether with vinyl acetate. In both cases polymer formation did not occur. The presence of the allyl ether inhibited the formation of poly(vinyl acetate), since this polymer formed readily when heptafluoroisopropyl allyl ether was excluded from the charge.

Overberger and Davidson[5] reported the conversion of various olefins containing a trifluoromethyl group to crystalline high-melting solids by means of a vanadium trichloride–triisobutyl aluminum catalyst. We were unable to obtain solid polymer with this catalyst system and heptafluoroisopropyl allyl ether, but we did obtain a low molecular weight oil.

Low molecular weight (DP ≈ 5) oligomers were obtained with various peroxides (Table I), but exposure to ultraviolet light and a cobalt-60 source failed to produce a significant amount of polymer.

Degradative chain transfer[6] evidently accounts for the dependency of the conversion on initiator concentration and on the low molecular weight of the polymers when peroxides or other free-radical sources are used. The critical surface tension of wetting γ_c for the allyl ether oligomers was about 21 dyne/cm. On the basis of structural similarities to poly(heptafluoroisopropyl acrylate) and poly(heptafluoroisopropyl vinyl ether) and the γ_c for these polymers (14.1 dyne/cm.,[2,7] 14.2 dyne/cm., respectively) we predict that a high molecular weight polymer of heptafluoroisopropyl allyl ether would also have a γ_c of between 14 and 15 dyne/cm. The relatively high value of 21 dyne/cm. for the low molecular weight polyallyl ether must necessarily reflect a significant contribution of initiator end-groups in the polymer (*t*-butyl benzoyl in the case examined).[8]

We were able to obtain high molecular weight polymers (DP ≈ 370) from heptafluoroisopropyl vinyl ether by using either ultraviolet light or a

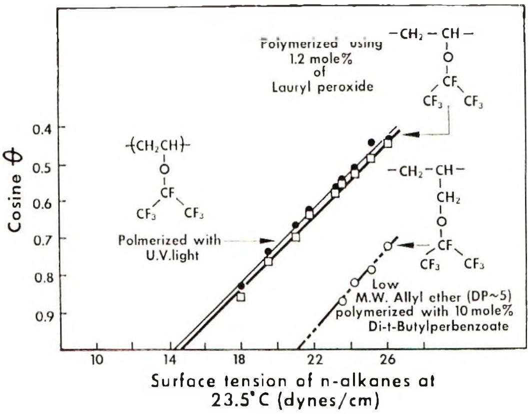


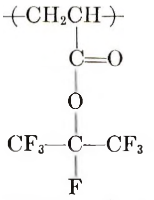
Fig. 1. Critical surface-tension plot for poly(vinyl ethers) and poly(allyl ethers).

peroxide such as lauryl peroxide; however, exposure to a Friedel-Crafts catalyst such as $BF_3 \cdot Et_2O$ failed to effect polymerization. The susceptibility of this vinyl ether to free-radical polymerization and its failure to undergo polymerization in the presence of $BF_3 \cdot Et_2O$ presumably is due to the strong inductive effects of the perfluoroalkyl group and oxygen on the vinyl group. Eley[9] has pointed out that the effect of an alkoxy group in general is to remove electrons from the double bond by the inductive effect +I but to inject electrons into the double bond by the mesomeric effect −E:

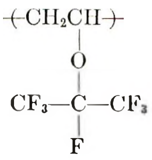
$$\underset{(+\mathrm{I})}{\mathrm{Alk} \leftarrow \mathrm{O} \leftarrow \mathrm{CH{=}CH_2}} \qquad \underset{(-\mathrm{E})}{\mathrm{Alk{-}\overset{+}{O}{=}CH{-}CH_2^-}}$$

When the alkyl group is not strongly electron-withdrawing, the mesomeric effect −E predominates, and the olefin favors reaction with protonic acids and electron acceptors; however, with a strongly electron-withdrawing group (such as heptafluoroisopropyl) the inductive effect (+I) seems to predominate, and the olefin becomes susceptible to attack by electron donors (such as a free radical).

We were surprised to find that the γ_c of poly(heptafluoroisopropyl vinyl ether), Figure 1, was almost identical with that of poly(heptafluoroisopropyl acrylate) found previously:



14.1 dyne/cm.



14.2 dyne/cm.

We had anticipated that the vinyl ether polymer would have a γ_c lower than that of the acrylate, since the overall fluorine content is somewhat higher in the vinyl ether repeat unit than in the acrylate repeat unit (62.7% fluorine in the vinyl ether, 55.3% fluorine in the acrylate).

One might also expect, because of closer proximity to the polymer main chain, a greater shielding of the hydrocarbon backbone by the perfluoroisopropyl group in the vinyl ether polymer and a resultant lower surface energy. One possible explanation of the results we observed could involve the difference in the glass transition temperature T_g between the vinyl ether polymer and the acrylate polymer. The CST (critical surface tension) in each case was obtained at 23.5°C., which is well below the T_g of the poly(vinyl ether) (ca. 55–65°C.) and above that of the polyacrylate (5–10°C.). Because of greater side-chain and main-chain mobility above the glass transition of a polymer, the concentration of $—CF_3$ groups at the air–solid interface may be higher above the T_g of certain polymers containing the perfluoroisopropyl side chain. This aspect of γ_c is at present being investigated with poly(heptafluoroisopropyl acrylate).

It is interesting to note the sensitivity of γ_c in reflecting slight changes in polymer composition. The γ_c for the polyvinyl ether initiated by ultraviolet light is 14.2 dyne/cm., whereas the polymer obtained with a 1.2 mole-% concentration of lauryl peroxide had a γ_c of 14.6 dyne/cm.; see Figure 1. This slight increase is presumed to be due to the contribution of $—CH_2—$ and $—CH_3$ arising from lauryl endgroups in the polymer.

EXPERIMENTAL

Heptafluoroisopropyl Allyl Ether

A dry 3-liter flask fitted with a stirring paddle, gas inlet tube, and a Dry Ice condenser was charged with 143.3 g. (2.5 mole) of anhydrous KF followed by 800 ml. of dry N,N-dimethylformamide. The mixture was stirred, and 410 g. (2.5 mole) of hexafluoroacetone was added at such a rate that the gas condensate dripped slowly from the Dry Ice condenser. A

TABLE II

Physical Properties of Allyl and Vinyl Ethers

Compound	B.p., °C., press., mm. Hg	n_D^{24}	d^{23}, g./ml.	Infrared,[a] cm.$^{-1}$, $=CH_2$
Allyl ethers:				
$(CF_3)_2CFOCH_2CH=CH_2$	63.5–4	1.2992	1.32	
$(CF_3)(CF_2Cl)CFOCH_2CH=CH_2$	93–4	1.3343	1.38	
$(CF_2Cl)_2CFOCH_2CH=CH_2$	128–9	1.3695	1.43	
Vinyl ethers				
$(CF_3)_2CFOCH=CH_2$	28–30	—		1652
$(CF_3)(CF_2Cl)CFOCH=CH_2$	58–60	1.3302		1648
$(CF_2Cl)_2CFOCH=CH_2$	101.5	1.3563		1648

[a] As a solution in CCl_4 on a Beckman Model IR 7 spectrophotometer.

clear solution of the hexafluoroacetone–KF adduct resulted after the addition. Allyl bromide (280 g., 2.3 moles) was then added in one shot. The Dry Ice condenser was replaced with a water-cooled condenser, and the solution was stirred and heated at 75°C. for 12 hr. The product was then removed from the DMF solution under vacuum and collected in a Dry Ice trap. Distillation on a short Vigreux column provided 453 g. (87% yield) of product; b.p. 63–64°C. at 760 mm.

ANAL. Calcd. for $C_6F_7H_5O$: C, 31.87%; F, 58.82%; H, 2.23%. Found: C, 31.35%; F, 58.4%; H, 2.43%.

The NMR and IR spectra were in accordance with the allyl ether structure.

The allyl ethers derived from monochloropentafluoroacetone and 1,1′-dichlorotetrafluoroacetone were similarly prepared, and their properties are given in Table II.

1-Bromo-2-heptafluoroisopropoxyethane and 1,2-Bis(heptafluoroisopropoxy)ethane

The hexafluoroacetone–potassium fluoride addition product was prepared in the manner described in the preparation of heptafluoroisopropyl allyl ether with 91 g. (0.55 mole) of hexafluoroacetone, 31.8 g. (0.55 mole) of anhydrous KF, and 300 ml. of dry diglyme [bis(2-methoxyethyl) ether]. A 103 g. amount (0.55 mole) of 1,2-dibromoethane was then added to the solution. The reaction mixture was stirred and heated at 70–80°C. Examination of the mixture at intervals by gas chromatographic analysis revealed the changes in composition with time shown in Table III.

TABLE III

React. time, hr.	Composition, %		
	$(CF_3)_2CFOCH_2$-CH_2Br	$(CF_3)_2CFOCH_2CH_2$-$OCF(CF_3)_2$	$BrCH_2CH_2Br$
18	20.8	4.6	74.6
66	38.6	21.5	39.9
90	40.7	25.5	33.8
110	40.2	26.2	33.6

After 110 hr. the reaction mixture was poured into 1 liter of water, and the lower layer was collected and washed several times with water and dried over $CaSO_4$. A crude product, 88 g., was obtained in this way. Most of the crude product was not purified further, but used directly in the dehydrohalogenation step. Analysis and physical properties were obtained from the individual compounds after purification of a small quantity by preparative gas chromatography.

$(CF_3)_2CFOCH_2CH_2Br$ anal; Calcd. for $C_5BrF_7H_4O$: C, 20.50%; F, 45.39%; H, 1.38%. Found: C, 21.07%; F, 45.2%; H, 1.50%. The boiling point of this compound was 105°C. at 760 mm., and the n_D^{24} was 1.3455.

$(CF_3)_2CFOCH_2CH_2OCF(CF_3)_2$ anal.; Calcd. for $C_8F_{14}H_4O_2$: C, 24.13%; F, 66.81%; H, 1.02%. Found: C, 24.17%; F, 68.9%; H, 1.00%. The boiling point of this compound was 122.5°C. at 760 mm.

Heptafluoroisopropyl Vinyl Ether

A three-necked, 500-ml. round-bottomed flask equipped with a reflux condenser, dropping funnel, thermometer, and stirring bar was flame-dried under a nitrogen blanket and then charged with 300 ml. of methanol and 160 g. of KOH. The methanol–KOH mixture was stirred and heated to 85°C. After the solution reached this temperature, 85 g. of the crude product obtained in the preceding example was added slowly over a 1 hr. period (composition by gas chromatographic analysis, 40.2% $(CF_3)_2CFOCH_2CH_2Br$, 26.2% $(CF_3)_2CFOCH_2CH_2OCF(CF_3)_2$, and 33.6% $BrCH_2CH_2Br$). During the addition the water temperature in the condenser was maintained at about 30–35°C. The product was collected in a Dry Ice trap attached to the exit of the reflux condenser. This material was distilled with a short Vigreux column, and four fractions were collected and analyzed by gas chromatography; see Table IV.

TABLE IV

Fraction	b.p. at 760 mm., °C.	Quantity, g.	Compsn.[a]
1	15–26	12	1:1 VE/VB
2	26–27	6	VE
3	27–28	7	VE
4	28–56	3	9:1 VE/methanol

[a] VE, heptafluoroisopropyl vinyl ether; VB, vinyl bromide.

Infrared and NMR spectra of the vinyl ether were in accordance with the assigned structure. Vinyl absorption occurred as a band of medium intensity at 1650 cm.$^{-1}$ (solution in CCl_4). Because of the volatility of the vinyl ether, combustion analysis was carried out on a sample that had been polymerized to a solid polymer with ultraviolet light.

ANAL. Calcd. for $C_5F_7H_3O$: C, 28.32%; F, 62.71%; H, 1.43%. Found: C, 28.10%; F, 61.8%; H, 1.43%.

In a similar fashion vinyl ethers were prepared from monochloropentafluoroacetone and 1,1′-dichlorotetrafluoroacetone (properties given in Table II).

1-Chloro-2-Heptafluoroisopropoxyethane

The reaction was carried out in the manner described for the preparation of 1-bromo-2-heptafluoroisopropoxyethane with 120 g. (0.72 mole) of hexafluoroacetone, 42 g. (0.72 mole) of anhydrous KF, 103.4 g. (0.72 mole) of 1-bromo-2-chloroethane, and 300 ml. of dry diglyme. The mixture was stirred and heated at 70–80°C. Examination of the mixture at intervals by gas chromatography revealed the product distributions shown in Table V.

TABLE V

	Composition, %		
React. time, hr.	$(CF_3)_2CFOCH_2$-$CH_2OCF(CF_3)_2$	$(CF_3)_2CFOCH_2$-CH_2Cl	$BrCH_2CH_2Cl$
18	1.7	31.9	66.4
66	2.7	46.3	51.0
90	2.9	48.5	48.6
110	2.8	52.9	44.3
180	2.8	73.0	24.2

After 180 hr. the reaction mixture was poured into 400 ml. of water, and the lower layer was collected and washed with additional water. A crude product, 140 g., was recovered. The pure product, 1-chloro-2-heptafluoroisopropoxyethane, was obtained by preparative gas chromatography for analytical purposes.

ANAL. Calcd. for $C_5ClF_7H_4O$: C, 24.16%; Cl, 14.26%; F, 53.51%; H, 1.63%. Found: C, 24.35%; Cl, 13.7%; F, 54.7%; H, 1.90%.

The boiling point of this compound was 93.5–94°C. at 760 mm.; n_D^{24} = 1.3142.

Heptafluoroisopropyl Allyl Ether

The effect of a number of free-radical sources was investigated at 2 and 10 mole-% of monomer concentration. The per cent conversion to polymer is given in Table I. All of the polymeric materials obtained in these reactions were low molecular weight. For example, the molecular weight of a sample obtained with 10 mole-% di-*t*-butyl peroxide was 1127 (obtained on a Mechrolab vapor-pressure osmometer). Exposure of the allyl monomer to ultraviolet light (principal wavelength, 2537 A.) for 140 hr. produced 1% conversion to a dark-brown resin.

Irradiation of Heptafluoroisopropyl Allyl Ether with Cobalt-60

In one case heptafluoroisopropyl allyl ether that had been redistilled before use was irradiated at a dose rate of 0.1 Mrad/hr. to a total dose of 4 Mrad. Samples were exposed to the source in the liquid state at 24°C. and in a solid, glassy state in liquid nitrogen.

In another series of attempts the allyl ether was distilled from fresh sodium before irradiation. In this case the dose rate was 0.05 Mrad/hr. to a total dose of 5 Mrad. Samples were exposed to the source in the liquid state at 24°C., in the liquid state in Dry Ice, and in a solid crystalline state in liquid nitrogen.

We were unable to detect polymer formation under any of these conditions, the samples being recovered unchanged after irradiation.

Attempted Polymerization of Heptafluoroisopropyl Allyl Ether with Tributylborane/Oxygen

Three flasks were dried and flushed with nitrogen. The following chemicals were introduced through a rubber septum in the order given:

Flask 1: 7 g. (0.03 mole) of heptafluoroisopropyl allyl ether, 0.0015 mole of tributylborane as a 50% solution in *n*-heptane, and 0.0007 mole of oxygen.

Flask 2: 0.015 mole of heptafluoroisopropyl allyl ether plus 0.15 mole of vinyl acetate, 0.0015 mole of tributylborane as a 50% solution in *n*-heptane, 0.0007 mole of oxygen.

Flask 3: 0.03 mole of vinyl acetate, 0.0015 mole of tributylborane as a 50% solution in *n*-heptane, 0.0007 of mole oxygen.

The contents of the flasks were stirred at room temperature (23°C.) for 24 hr. No polymer was formed in flasks 1 and 2. Exothermic polymerization occurred in flask 3 immediately after the introduction of oxygen.

Attempted Polymerization of Heptafluoroisopropyl Allyl Ether with $VCl_3/Al[C(CH_3)_3]_3$

A heavy-walled Pyrex tube was dried, flushed with nitrogen, and charged with 0.3 g. of VCl_3, 6 ml. of heptane, 1.5 ml. of heptafluoroisopropyl allyl ether and 0.45 ml. of triisobutyl aluminum. The tube was melt-sealed and rotated in an oil bath at 100°C. for 120 hr. After this time the contents of the tube were poured into methanol containing 5% hydrochloric acid. Approximately 0.8 g. of a brown, oily material separated. This low molecular weight oil was only slightly soluble in methanol but readily dissolved in acetone and other organic solvents.

Polymerization of Heptafluoroisopropyl Vinyl Ether

A 7 mm. o.d. Pyrex tube, sealed at one end, was charged with 0.84 g. of heptafluoroisopropyl vinyl ether (purified by preparative gas chromatography) and 20 mg. (1.2 mole %) of lauryl peroxide. The contents of the tube were cooled in a Dry Ice–acetone bath, placed on a manifold system, and evacuated. The glass tubing was then melt-sealed and placed in an oil bath for 12 hr. In this way 0.82 g. (98% conversion) of solid polymer was obtained which, after one precipitation from trichlorotrifluoroethane, had $\overline{M}_n$ of 72,300 (obtained on a Mechrolab membrane osmometer). The polymer, an optically clear, hard material, was insoluble in nonfluorinated solvents but readily soluble in such solvents as trichlorotrifluoroethane and 1,3-bis(trifluoromethyl) benzene.

In a similar fashion a 74% conversion to polymer was obtained with 0.25 mole-% lauryl peroxide.

A clear, hard polymer was obtained in 99% conversion by exposing the monomer in a quartz tube to ultraviolet light (principal wavelength 2537 A.).

Differential thermal analysis of the polymer revealed a change in heat capacity at about 55–65°C., which presumably is the glass transition temperature, and a thermal decomposition beginning around 250°C.

Measurement of γ_c of Polymer Surfaces

The critical surface tensions of polymer-coated glass slides were determined in a manner reported previously,[2,7] a homologous series of *n*-alkanes being used for contact-angle measurements.

The authors wish to thank Lowell Miller for conducting experiments on the irradiation of allyl ethers with cobalt-60.

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The Composition of Catalysts Prepared from Tri-*n*-propylaluminum, Anisole, and Titanium Tetrachloride*

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Synopsis

Catalysts were prepared from titanium tetrachloride and tri-*n*-propylaluminum or tri-*n*-propylaluminum anisole at [Al]/[Ti] molar ratios of 0.20–1.10. They were aged and filtered, and the solid and liquid portions were analyzed for aluminum, titanium, chlorine, and certain organic constituents. The analyses indicate that the solid of the nonetherate catalyst is predominantly $TiCl_3$, some $AlCl_3$ or aluminum alkyl chlorides being included. Only at [Al]/[Ti] = 1.10 was any alkyl group found in the solid. The same general results were found for the etherate catalyst, but the solid had a somewhat lower [Cl]/[Ti] ratio, indicating greater reduction or alkylation, or both, of the titanium species than in the nonetherate catalyst. The solid also contained some anisole at the higher [Al]/[Ti] ratios. The results lend general support to proposed reactions for the catalyst formation. The main differences in the etherate catalysts relative to the non-etherate system, particularly at the higher [Al]/[Ti] ratios, are the apparently greater reduction or alkylation of the titanium in the solids, the presence of anisole in the liquid and solid portions, and the presence of phenol in the liquid portion. The phenol presumably comes from cleavage of the anisole during the catalyst formation. Not all of the anisole has been accounted for in a materials balance, nor has all of the chlorine in the etherate catalysts. No propyl or isopropyl chloride was found in the catalysts; there is no signficant amount of polypropylene in any of the catalyst solids. Hence the fate of the alkyl groups remains undetermined at present.

It has been shown that a catalyst prepared from an aluminum alkyl etherate and titanium tetrachloride readily polymerizes isoprene to a high *cis*-1,4-polyisoprene.[1] Little is known of the composition of Ziegler-type catalysts prepared from aluminum alkyl etherates, particularly when titanium halides are used as cocatalysts. Moreover, literature data are scanty on the composition of such catalysts prepared from tri-*n*-propylaluminum and titanium tetrachloride,[2] especially at closely spaced increments of low [Al]/[Ti] molar ratios. It was therefore of interest to prepare several series of these catalysts and analyze them, to try to determine the nature of the catalytic species. Because of the protracted nature of these experiments the initial work completed thus far is being reported at this time, even though several unanswered questions on the fate of some of the catalyst components remain.

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* Contribution Number 392 from the Research Laboratories of the Goodyear Tire & Rubber Company.

EXPERIMENTAL

Materials

The tri-*n*-propylaluminum was obtained from Texas Alkyls, Inc. The manufacturer reported it was 96.4% (by weight) of TNPA and contained 1.9% hydride calculated as AlH_3. Analyses in this laboratory gave 1.3% hydride as AlH_3 and 18.2% aluminum (17.3%, theory, for pure TNPA). The "active" aluminum (sum of aluminum trialkyl plus dialkyl aluminum hydride[2a]) was 6.25 mmoles per gram of TNPA theory (6.40 for pure TNPA).

The $TiCl_4$ was from Pittsburgh Plate Glass Chemical Division. It was purified by the method of Clabaugh et al.[3] About 250 ml. of $TiCl_4$ was refluxed 2.5 hr. with a slow stream of chlorine (40–50 $cm.^3$/min.) passing through the flask. Then nitrogen was substituted for the chlorine and several feet of bright copper wire were added to the $TiCl_4$. It was then refluxed over the copper wire, and short lengths of copper wire were added periodically until some remained bright in the refluxing $TiCl_4$. It was then distilled under nitrogen through a 12 in. Vigreux column. About 150 ml. of a middle cut, boiling at 133–134°C. at 734.5 mm. (uncorrected), was collected. It analyzed as 24.6% Ti (25.3% theory) and 74.8% Cl (74.6% theory).

The anisole was Fisher reagent-grade, used as received. Gas chromatographic analysis showed it was 98.7% anisole with only a trace of phenol. Pentane and *n*-heptane were "pure" grade from the Phillips Petroleum Company. Pentane was used as received, but heptane was washed successively with concentrated H_2SO_4, potassium carbonate solution, and distilled water, and then distilled and stored over Drierite. All these materials were thoroughly sparged with nitrogen before use in catalyst preparations.

Catalyst Preparation and Separation

Fresh catalysts were prepared at ambient temperature ($\approx$25°C.) in a Blickman vacuum-type dry box. The main chamber was thoroughly evacuated and filled with lamp-grade nitrogen before the preparation and before the separation of each series of catalysts. The air lock could also be separately evacuated and filled with nitrogen. Every precaution was taken to keep the oxygen and moisture content of the main chamber as low as possible.

The catalysts were prepared with a constant amount of $TiCl_4$ in each, and the various [Al]/[Ti] molar ratios were achieved by varying the amount of tri-*n*-propylaluminum. All catalysts were prepared in the dry box in 4-oz., screw-capped glass bottles. Transfer of all reactants was done by hypodermic syringes. The total volume of each catalyst mixture was 50 ml. In all catalysts, except in one series, 0.01 mole of $TiCl_4$ was used. One series of non-etherate catalysts was prepared in which the quantities of reactants were doubled, but this did not alter the results of the catalyst analysis. The amounts of tri-*n*-propylaluminum required for the desired [Al]/[Ti] ratios were provided from either a 2.0*M* solution of tri-*n*-propylaluminum in *n*-heptane or one 2.0*M* in both tri-*n*-propylaluminum and anisole.

Catalyst mixtures were stored in the dry box at least 1 wk. (and usually 2–3 wk.) to insure complete reaction. They were periodically shaken, to mix thoroughly the solid and liquid phases of the catalysts. After the aging period the mixtures were pressure-filtered with nitrogen through a medium-porosity fritted-glass funnel. The filter cake was rinsed with five or six portions of pentane or heptane, which were combined with the filtrate. Checks of the filtrate with aqueous silver nitrate showed that this number of washings removed all soluble, hydrolyzable chlorides from the catalyst solid. The filtrates were stored in the dry box in tightly capped 4 oz. glass bottles, with a polyethylene gasket in the cap, until they were analyzed.

The solid was dried to constant weight under a slow stream of nitrogen in the dry box. Weights, accurate to the nearest milligram, were determined on a small Seederer-Kohlbusch balance, which could be taken into the dry box. The dried solids were kept in sealed weighing bottles, which were stored over Drierite in a small desiccator in the dry box. The final exact weights of the solids were determined on an analytical balance just prior to their hydrolysis.

It was interesting to note the color of the filtrates. In the non-etherate catalysts color changes from straw yellow at [Al]/[Ti] = 0.20 to colorless at [Al]/[Ti] = 0.50. Above this ratio a faint, yellow color appears and increases steadily until the ratio is 1.10, to a bright yellow. In the etherate catalysts the filtrate is reddish-orange at ratios 0.20 and 0.30, light yellow at 0.40, and colorless at 0.50 and 0.60. At a ratio of 0.70 a faint, blue color appears and increases in intensity as the ratio increases, until the filtrate at ratio 1.10 is very dark blue. The sources of these colors have not yet been determined. A difference could be noted in some of the solids also. All of the non-etherate catalyst solids and the etherate catalyst solids at ratio ≥ 0.50 were rather dense powders. The etherate catalyst solids from the low ratios, however, were very light, fluffy powders. These are the solids with the low aluminum contents (see under "Results").

Inorganic Analyses

Titanium, aluminum, and chlorine were determined in both the solid and filtrate portions of the catalysts by methods developed in these laboratories. The solids were hydrolyzed by carefully opening the weighing bottles beneath the surface of 5% sulfuric acid contained in a large beaker. This solution was rinsed into a volumetric flask with additional acid and diluted to the mark with the acid.

An aliquot was analyzed for titanium by masking aluminum with triethanolamine and sodium salicylate, adding an excess of hydrogen peroxide and disodium ethylene dinitrilotetraacetate (EDTA), cooling below 20°C., and titrating the excess EDTA with $0.0500M$ bismuth nitrate solution to the xylenol orange endpoint at pH = 1.5[4].

Another aliquot was analyzed for aluminum by oxidizing the titanium with hydrogen peroxide, removing the peroxide by boiling, and extracting the titanium, as its cupferron complex, with chloroform. Then 8-hydroxyquinoline was added to the extracted solution to form a yellow complex with aluminum, which was extracted into chloroform and measured spectrophotometrically at 390 mμ.[4]

A separate aliquot was analyzed for chloride by either potentiometric titration with silver nitrate or by Volhard titration.[5]

The filtrate was analyzed for aluminum, titanium, and soluble, hydrolyzable chlorides by carefully hydrolyzing the filtrate in a separatory funnel with 5% sulfuric acid. The aqueous layer was analyzed for titanium by converting all the titanium to the trivalent state with aluminum foil and titrating with standard ferric ammonium sulfate to a thiocyanate endpoint under a CO_2 atmosphere.[4] In a separate aliquot titanium was removed by extracting its cupferrate chelate with chloroform. The aqueous layer was treated with excess EDTA, which was back-titrated with a standard zinc chloride solution to the dithizone endpoint in 50% 2B-ethanol at pH = 4.5 to determine aluminum.[4] Chloride was determined as above.[5]

Organic Analyses

General. The several gas chromatographic (GC) approaches used to identify and estimate organic species in catalyst solids and liquids generally involved the prior addition of an internal standard to the sample, hydrolysis of the adjusted sample with aqueous HCl, and then follow-up chromatography under several separate conditions optimized for the various components of interest.

Relative retentions, usually from two columns, served to identify components detected from catalyzed samples. Identifications were confirmed in some instances by direct comparison of the retentions of suspect components with those of likely, known compounds.

An F&M Model 810 Gas Chromatograph (F&M Scientific Division, Hewlett Packard Corp.) equipped with a hydrogen flame-ionization detector was used for all GC analyses.

Alkyl Groups. This analysis was carried out specifically only for the etherate and non-etherate catalyst solids. It should, however, be applicable to catalyst liquids.

An exact aliquot (approx. 0.2 g.) of sample was added to a small vial equipped with a puncture-seal closure and the air volume of the vial was then partially evacuated. Approximately 3.5 ml. of 1:3 aqueous HCl were then syringed into the vial. After thorough contact of the sample with the aqueous acid an exact weight aliquot (≈0.2 ml.) of an *n*-butyllithium reagent (15.0 wt.-% in *n*-heptane, Foote Mineral Co., Exton, Pa.) was syringed into the vial. After hydrolysis of the *n*-butyllithium nitrogen was needled into the vial, to restore the gas volume of the vial to atmospheric pressure.

Vial and contents were warmed momentarily in a water bath (ca. 80°C.), after which approximately 200 μl. of the head gas were removed from the vial by means of a gas-tight syringe and were chromatographed. An aluminum column, 15 ft. × $^1/_{18}$ in., packed with 20% squalane on 60-80 mesh Gas Chrom P, and operated at 67°C., was used for the analysis. The *n*-butane, liberated from the *n*-butyllithium, served as the internal standard. Quantitative estimation of components was made from peak areas and the weights of sample and standard taken.

Propyl Chlorides. The samples were hydrolyzed with aqueous acid, and the hydrolysate was extracted with *n*-heptane. Aliquots of the *n*-heptane fraction were chromatographed with the squalane column and the conditions cited above (under "Alkyl Groups"). For quantitation an external standard containing known concentrations of *n*-propyl chloride and isopropyl chloride in *n*-heptane was proposed.

Anisole and Phenol. Normal undecane (C_{11} hydrocarbon) was added to the sample as an internal standard, after which the sample was hydrolyzed with aqueous acid. The hydrolysate was extracted in turn with *n*-heptane and ethyl ether. An aliquot of the combined extract was chromatographed with a column 20 ft. × $^1/_8$ in., packed with a mixed phase of 11% Apiezon L and 4% Carbowax 20M on 60-80 mesh Gas Chrom Z operated at 150°C. Chlorobenzene and propyl benzene could be detected, if present, under these conditions.

Diphenyl Ether. A separate aliquot of the organic extract (obtained as outlined above, under "Anisole and Phenol") was chromatographed on a column 8 ft. × $^3/_{16}$ in., packed with a mixed phase of 6% Apiezon L and 2% Carbowax 20M on 60-80 mesh Gas Chrom Z at 200°C.

It was proposed that the level of phenol (or anisole) determined earlier be used as a built-in internal standard for any diphenyl ether detected.

RESULTS

Solid Yields

The first quantity that was measured after separation of the solid and liquid phases of the catalyst was the yield of solid material. This was expressed in terms of grams of solid per mole of $TiCl_4$ in the original catalyst; the results are listed in Table I. At low [Al]/[Ti] ratios the non-etherate catalyst gave the higher yield of solid, but at ratios above 0.50 the etherate system gave more solid.

Inorganic Analyses of Solids

The separated solids from both the etherate and non-etherate catalysts were analyzed for Al, Ti, and Cl; the results are given in Table I. All of the solids have some aluminum content; this is in general agreement with the literature.[2,6–11] The non-etherate solids contain more aluminum in general than the etherate solids for the same Al/Ti molar ratio in the initial catalyst mixture. The amount of aluminum in the non-etherate solids varies irregularly as the [Al]/[Ti] ratio of the catalyst increases, but in the etherate solids the amount of aluminum steadily increases.

The titanium contents of the solids from both types of catalyst are of the same general magnitude.

TABLE I

Inorganic Analyses of Catalyst Solids[a]

$[AlR_3]$/ $[TiCl_4]$, moles	Solid yield, g./mole $TiCl_4$	Weight per cent			Total wt.-%, Al + Ti + Cl	[Cl/Ti][b]
		Al	Ti	Cl		
Non-etherate catalysts:						
0.20	124.6(2)	4.21	23.2	67.8	95.2	2.96
0.30	186.2	4.28	22.5	66.8	93.6	2.89
0.40	189.8(1)	—	—	—	—	—
0.50	178.3	2.63	25.1	65.2	92.9	3.11
0.60	179.8(1)	—	—	—	—	—
0.70	179.6	2.25	25.1	63.6	91.0	3.08
0.80	182.4(1)	—	—	—	—	—
0.90	183.6	3.32	23.1	59.8	86.2	3.03
1.00	189.8(1)	—	—	—	—	—
1.10	188.5	4.37(2)	24.7(2)	57.2(2)	86.3	2.83
Etherate catalysts:						
0.20	101.4(2)	0.60(2)	29.7(2)	62.3(2)	92.6	2.74
0.30	157.4	1.35	27.1	60.4	88.9	2.75
0.40	175.4(1)	—	—	—	—	—
0.50	181.6	1.62	26.5	60.1	88.2	2.85
0.60	186.0(1)	—	—	—	—	—
0.70	184.8	2.43	26.0	56.8	85.2	2.72
0.80	195.5(1)	—	—	—	—	—
0.90	190.7	2.71	25.4	50.9	79.0	2.51
1.00	210.5(1)	—	—	—	—	—
1.10	207	3.73(2)	23.1	47.0	73.8	2.56

[a] All results are averages of three determinations. Exceptions are designated by number of determinations in parentheses. All [Cl]/[Ti] ratios are the averages of two determinations.

[b] See under "Discussion" for method of calculation.

For all the non-etherate catalysts the titanium content of the solids remains fairly constant. In the etherate system, however, as the catalyst [Al]/[Ti] ratio increases, the titanium content of the corresponding solids slowly decreases.

In both types of catalysts the chlorine content of the solids decreases as the [Al]/[Ti] ratio of the catalyst increases. The solids from the non-etherate catalysts contain more chlorine than their counterparts from the etherate system.

The sum of the aluminum, titanium, and chlorine percentages for each solid is also given in Table I. Even at the lowest [Al]/[Ti] catalyst ratio these three elements do not quite account for all of the solid. As the ratio increases, the sum of these three elements declines steadily, and the decline is much sharper in the case of the etherate catalysts.

Inorganic Analyses of Filtrates

The filtrates of all catalysts were also analyzed for Al, Ti, and Cl. Only the readily hydrolyzable aluminum- or titanium-bound chlorine is determined in the analysis. These results are given in Table II, expressed in terms of per cent of the total element that was charged to the initial catalyst mixture.

TABLE II
Inorganic Analyses of Catalyst Filtrates[a]

Molar ratio $AlR_3/TiCl_4$	Element found, % of total		
	Al	Ti	Cl
Non-etherate catalyst:			
0.20	9.5	34.7*	26.6
0.30	5.1	6.7	5.0
0.50	67.5	0.31	13.5
0.70	78.6	0.81	18.0
0.90	77.8	0.77	19.9
1.10	74.8	1.17	22.0
Etherate catalyst			
0.20	93.7	34.7*	35.5
0.30	86.8*	12.3*	17.0
0.50	81.4	0.59*	12.8
0.70	84.4	2.3*	19.4
0.90	81.2	3.4	22.9
1.10	78.9	5.7	25.6

[a] Results are averages of two determinations, except where single determinations are noted by an asterisk.

In the non-etherate catalysts at [Al]/[Ti] ratios of 0.20 and 0.30 little aluminum is found in the filtrates, but in the etherate catalysts at the same ratios most of the aluminum was in the filtrate. At the higher ratios of both catalyst systems most of the aluminum appeared in the filtrate. For both catalyst systems at [Al]/[Ti] = 0.20 more than one third of the titanium was in the filtrate. At ratio 0.30 a small percentage of the titanium remained in solution in the filtrate, and at higher ratios very little titanium was found in the filtrates.

At [Al]/[Ti] = 0.20 a considerable amount of chloride was found in the filtrate, the etherate catalyst having a somewhat higher amount than the non-etherate. At ratio 0.30 little chloride (5%) was in the filtrate of the non-etherate catalyst, but the etherate sample still contained appreciable

TABLE III
Organic Analyses of Catalyst Solids[a]

Molar ratio $AlR_3/TiCl_4$	Weight per cent: CH_4 + ethane + ethylene	Propane + propylene	Isobutane	Isopentane + *n*-pentane	Anisole
Non-etherate catalyst:					
0.20	<0.01	0.3	0.02	0.01	—
0.30	<0.01	0.1	0.03	0.01	—
0.50	0.01	0.1	0.1	0.03	—
0.70	0.4	0.1	0.2	0.06	—
0.90	0.07	0.1	0.2	0.08	—
1.10	0.4	5.9	0.6	0.3	—
Etherate catalyst:					
0.30	—	0.02	0.01	0.04	0.2
0.50	—	0.03	—	0.04	0.1
0.70	0.03	0.5	—	0.04	1.2
0.90	0.02	0.5	0.03	0.04	2.2
1.10	0.2	3.5	0.02	0.02	8.3

[a] All results are single determinations.

chloride (17%). At the higher ratios for both catalysts moderate amounts of chloride remained in the filtrate, and its concentration increased slowly as the [Al]/[Ti] ratio of the catalyst increased.

Organic Analyses of Solids

Only one series of solids from both types of catalyst have been analyzed for their organic portions; see Table III. Only those components which appeared in any appreciable quantity are listed. A large number of alkanes, together with ethylene and propylene, were found in the gaseous hydrolysate fraction from the solids, but most were present in amounts ranging from a few hundredths of a per cent to less than 0.01%. The combined total of propane (the predominant hydrocarbon) plus propylene was the only alkyl residue that appeared in any appreciable quantity from the solids of either catalyst system. Only at [Al]/[Ti] = 1.10 for either type of catalyst was the total of these two hydrocarbons more than 1% of the solid. In the solids from etherate catalysts at [Al]/[Ti] = 0.70 anisole was present in amounts of more than 1% and totaled 8.3% of the solid at the ratio 1.10.

Organic Analyses of Filtrates

Two important results were noted: the absence of propyl or isopropyl chloride in all filtrates and the presence of phenol in the filtrates from the etherate catalysts. There is dispute in the literature over the occurrence in the liquid portion of the catalyst of alkyl chlorides (see under "Discussion"). In this work, too, no detectable amounts were found in either type

TABLE IV
Organic Analysis of Etherate Catalyst Filtrates[a]

Molar ratio $AlR_3/TiCl_4$	Phenol/(anisole + phenol) × 100
0.20	31
0.30	23
0.50	99
0.70	60
0.90	23
1.10	16

[a] Both phenol and anisole determinations were averages of duplicate runs.

of catalyst of chlorobenzene, *n*-propyl benzene, or diphenyl ether. The phenol in the etherate system presumably comes from the anisole, which must be cleaved to some degree during the catalyst-forming reaction. This has been observed in other studies in this laboratory.[12] The amounts of phenol in these filtrates are given in Table IV in terms of per cent of total of anisole plus phenol found in the filtrates. At the two lowest [Al]/[Ti] ratios the mixture in the filtrate is predominantly anisole. At ratio 0.50, however, a dramatic reversal occurred and almost solely phenol was present. As the ratio increased, the proportion of phenol fell rapidly, until at a ratio of 1.10 the mixture in the filtrate was again largely anisole.

Materials Balance

The amount of aluminum, titanium, chlorine, and anisole accounted for by the various analyses was calculated and compared with the amounts

TABLE V
Materials Balance of Catalyst Components[a]

Molar ratio $AlR_3/TiCl_4$	Per cent recovered			
	Al	Ti	Cl	anisole
Non-etherate catalyst:				
0.20	103	102	86	—
0.30	102	93	93	—
0.50	101	95	96	—
0.70	99	95	97	—
0.90	101	97*	98	—
1.10	99	99*	99*	—
Etherate catalyst:				
0.20	104	96*	79	73*
0.30	100	94*	84	55*
0.50	104	103	88	68*
0.70	110	103	92	82*
0.90	103	100	90	79*
1.10	105	99	91	80*

[a] All figures are results of duplicate determinations, except where single determinations are noted by an asterisk.

charged in the various catalysts. The results are given in Table V. Almost within experimental error all the titanium and aluminum was recovered in all catalyst samples. In the non-etherate catalyst at [Al]/[Ti] = 0.20 only about 85% of the chlorine was accounted for, however. As the ratio increased, the amount of chlorine recovered increased until, at a ratio of ≥ 0.50, 95% or more of the chlorine was recovered. For the etherate system, however, the figures were lower. At the ratio 0.20, only 79% of the chlorine was found and as the ratio increased, the amount of chlorine recovered increased. At ratios of ≥ 0.50 only about 90% of the chlorine was accounted for. The results for anisole were erratic but, with one exception at ratio 0.30, only about 70–80% of the anisole could be accounted for as either anisole or phenol.

The sum of aluminum, titanium, chlorine, and organic portions was calculated for the single sets of solids that were analyzed for organic groups (Table III). These results are in Table VI. It can be seen that inclusion of the alkyl group has, with the exception at [Al]/[Ti] = 0.90, accounted for nearly 95% of the non-etherate solids. It is always possible (in fact, probable) that traces of oxygen and water have reacted with the solids and filtrates during handling, since the dry box cannot be completely purged of them. This would account for some of the remaining 5% of the solids, as pointed out by previous authors.[2] Therefore, it is felt that nearly all of the composition of these solids has been determined.

TABLE VI
Component Totals for Catalyst Solids[a]

Molar ratio $AlR_3/TiCl_4$	Weight per cent Al	Ti	Cl	Alkyls[b]	Total
Non-etherate catalysts:					
0.20	4.3	23.5	69.8	0.1	97.7
0.30	4.5	23.1	67.6	0.2	95.4
0.50	2.8	24.8	65.7	0.3	93.6
0.70	2.6	25.8	63.9	0.4	92.7
0.90	3.9	23.8	58.8	0.5	87.0
1.10	4.4	24.9	57.5	7.2	94.0
Etherate catalysts:					
0.30	1.5	27.3	60.8	0.3	89.9
0.50	1.4	26.3	60.0	0.2	87.9
0.70	1.9	26.1	56.2	1.8	86.0
0.90	2.8	27.0	48.0	2.9	80.7
1.10	3.1	23.8	46.8	12.0	85.7

[a] All results are from single determinations.
[b] Plus anisole for the etherate catalysts.

For the solids from the etherate catalysts inclusion of the alkyl groups and anisole still leaves some appreciable amount of the solid unaccounted for (Table VI), particularly at the higher [Al]/[Ti] ratios.

Discussion

Equations representing possible reactions between aluminum alkyls and titanium tetrachloride have been proposed by many authors. A series of such equations, representing possible reactions at low [Al]/[Ti] molar ratios, is given in Table VII, following the suggestions of others.[7,13–15]

TABLE VII

Possible Reactions between AlR_3 and $TiCl_4$ at Various [Al]/[Ti] Ratios

	Grams solid/mole of $TiCl_4$
$0.20\ AlR_3 + TiCl_4 \rightarrow 0.20\ AlCl_3\downarrow + 0.60\ TiCl_3\downarrow + 0.40\ TiCl_4 + 0.60\ R\cdot$	119.3
$0.30\ AlR_3 + TiCl_4 \rightarrow 0.30\ AlCl_3\downarrow + 0.90\ TiCl_3\downarrow + 0.10\ TiCl_4 + 0.90\ R\cdot$	178.9
$0.333\ AlR_3 + TiCl_4 \rightarrow 0.333\ AlCl_3\downarrow + TiCl_3\downarrow + R\cdot$	198.7
$0.40\ AlR_3 + TiCl_4 \rightarrow 0.20\ AlCl_3\downarrow + TiCl_3\downarrow + 0.20\ AlRCl_2 + R\cdot$	181.0
$0.50\ AlR_3 + TiCl_4 \rightarrow TiCl_3\downarrow + 0.50\ AlRCl_2 + R\cdot$	154.3
$0.70\ AlR_3 + TiCl_4 \rightarrow TiCl_3\downarrow + 0.30\ AlRCl_2 + 0.40\ AlR_2Cl + R\cdot$	154.3
$0.90\ AlR_3 + TiCl_4 \rightarrow TiCl_3\downarrow + 0.10\ AlRCl_2 + 0.80\ AlR_2Cl + R\cdot$	154.3
$1.10\ AlR_3 + TiCl_4 \rightarrow TiCl_3\downarrow + AlR_2Cl + 0.10\ AlR_3 + R\cdot$	154.3
or	
$1.10\ AlR_3 + TiCl_4 \rightarrow TiCl_3\downarrow + 0.10\ TiRCl_2 + 1.1\ AlR_2Cl + R\cdot$	155.1[a]

[a] R = *n*-propyl.

Included in this table are theoretical yields of solids, assuming that all $AlCl_3$ and $TiCl_3$ are insoluble in aliphatic solvent while AlR_2Cl and $AlRCl_2$ would be soluble. At low [Al]/[Ti] ratios the solid yields are quite sensitive to the [Al]/[Ti] ratio of the initial catalyst. The results of the experimental solid yields, in Table I, bear this out and, in fact, the solid yields of the non-etherate catalysts at ratios of 0.20–0.40 agree fairly well with the theoretical yields listed in Table VII. The solid yields of the etherate catalysts at these low ratios fall below these theoretical solid yields. Elemental analyses showed, however, that these solids had low aluminum contents (Table I); most of the aluminum in these catalysts is in solution. It may be postulated the anisole complexes with the $AlCl_3$ in these solids

TABLE VIII

Comparison of Yields (g./mole $TiCl_4$) of $TiCl_3$ (Theory) and Experimental Solids

$[AlR_3]/[TiCl_4]$	$TiCl_3$, theory (from Table VII)	Etherate catalyst		Non-etherate catalyst
		Found	Corrd. for $AlCl_3$	
0.20	92.7	101.4	98.4	124.6
0.30	138.9	157.4	146.9	186.2

and solubilizes most of it. Therefore, at ratios of 0.20 and 0.30 the solids from the etherate catalysts might consist largely of $TiCl_3$. The yield of $TiCl_3$ at these ratios, according to the equations of Table VII, is given in Table VIII together with the actual solid yields from both types of catalyst.

Thus the solid yields of the etherate catalyst lie much closer to the theoretical yield of $TiCl_3$ than do those of the non-etherate catalysts, although they are still somewhat high. This discrepancy might be attributed to the small amount of aluminum species that is contained in the solids of the etherate catalyst. If all this aluminum is assumed to be $AlCl_3$, then the yield of solid can be corrected for $AlCl_3$ content by using the aluminum contents in Table I. These results are included in Table VIII and bring the solid yields of the etherate catalysts even closer to the theoretical $TiCl_3$ yield.

Saltman et al.[16] also reported solid yields based on the amount of $TiCl_4$ reacting. According to the equations of Table VII, all $TiCl_4$ that reacts, at $[Al]/[Ti] \leq 0.333$, should form $AlCl_3 \cdot 3TiCl_3$ (198.7 g. per mole of $TiCl_4$ reacting). Likewise, in the etherate catalysts, if all $AlCl_3$ were solubilized out of the solid, only $TiCl_3$ should be formed (154.3 g. per mole of $TiCl_4$ reacting). It was assumed that all titanium in the filtrates (Table II) was $TiCl_4$, and from these data the amount of $TiCl_4$ reacting was calculated. The yield of solid per mole of $TiCl_4$ reacted was then calculated; it is given in Table IX. The results for the non-etherate catalyst agree well with the predicted yield of $TiCl_3$. So does the result for the etherate catalyst at $[Al]/[Ti] = 0.20$; at a ratio of 0.30 the result is high. When the latter figure is corrected for the possible $AlCl_3$ in the solid, however, it agrees reasonably well with the predicted $TiCl_3$ yield. It may be noted here that the experimental yields for solids (Table I) reported in this paper are considerably higher than those reported by Saltman et al.[16] at comparable ratios. This is probably due to a considerable extent to the different aluminum alkyls; Saltman and his associates worked with triisobutylaluminum, which should have different reducing powers from those of tri-*n*-propylaluminum.

TABLE IX
Yields of Solids (g.) as a Function of $TiCl_4$ Reacting

$[AlR_3]/TiCl_4]$	Yield of solid, theory		
		Non-etherate catalyst:	
0.20	198.7		190.7
0.30	198.7		199.5
		Etherate catalyst:	
		Found:	Corrd. for $AlCl_3$
0.20	154.3	155.2	150.6
0.30	154.3	179.5	167.3

The yields of solids from these catalysts lends support to the reactions postulated in Table VII for the two lowest [Al]/[Ti] ratios. So too do the elemental analyses of these solids, which are given in Table I. Assuming that all of the aluminum in these solids is $AlCl_3$, the Cl/Ti ratio was calculated for these solids and is listed in Table I. For the non-etherate solids this ratio is very close to 3.0, corresponding to the postulated $TiCl_3$. For the etherate solids, however, it is slightly lower, possibly indicating additional alkylation or reduction of the titanium in this species or both (see below).

At $[Al]/[Ti] \geq 0.50$, however, in either catalyst system neither the solid yields nor the elemental analyses of the solids give agreement with the equations of Table VII. The solid yields are increasingly higher than those listed in Table VII. The solid is shown as being only titanium compounds; the elemental analyses in Table I show that all contain appreciable quantities of aluminum, however. Evidently the precipitated solid portion of these catalysts contains an absorbed or occluded aluminum species from the liquid portion of the catalyst. Assuming that this species is the same aluminum compound or compounds shown as products of the equations in Table VII, the Cl/Ti atomic ratio in these solids was calculated. The results in Table I show that for the non-etherate solids this ratio remains near 3.0 until the [Al]/[Ti] ratio of the catalyst exceeds 1.0. This assumption indicates, therefore, that titanium in the solid exists as $TiCl_3$, until excess aluminum trialkyl is present, if at all, in the solution ($[Al]/[Ti] > 1.0$; see Table VII). Then the $TiCl_3$ may be reduced or further alkylated or both.

In a like manner the [Cl]/[Ti] ratio of the etherate solids was calculated. They are uniformly lower than those of the corresponding non-etherate solids. They decline somewhat as the [Al]/[Ti] ratio of the catalyst increases above 0.50, reaching about 2.5 at the highest [Al]/[Ti] ratios. Thus, it would appear that the presence of the ether during the catalyst-forming reaction facilitates the alkylation or reduction, or both, of the titanium halide. Similar observations were made by Saltman et al., who used dioxane or dimethoxyethane.[16]

An alternative possibility is that the aluminum in the solids is $AlCl_3$. If this is so, then the calculated [Cl]/[Ti] ratios of the solids decline steadily as the [Al]/[Ti] ratio of the catalyst increases, reaching a value of about 2.0 (and even lower for the etherate catalyst) at the highest [Al]/[Ti] ratio. For $AlCl_3$ to be present the reduction would have to proceed through the intermediates AlR_2Cl and $AlRCl_2$ to $AlCl_3$. Since AlR_3 is by far the most powerful reducing agent, it should produce most, if not all, of the reduction of the $TiCl_4$, particularly as its amount in the mixture is increased. It therefore seems highly unlikely that the reduction reactions would proceed to the formation of $AlCl_3$ before all the $TiCl_4$ (or possibly some of the $TiCl_3$) had been reduced by the AlR_3. Rather, the opposite should be true, that is, as the amount of AlR_3 in the catalyst is increased, the amount of $AlCl_3$ in the solid should decrease (according to the equations of Table VII). Thus the assumption that the aluminum in the solid comes from the absorbed or chemically bound aluminum alkyl chlorides seems more likely. A similar argument has been advanced by Cooper and Rose.[2a]

The analysis of the filtrates for Al, Ti, and Cl (Table II) lends semiquantitative support also to the equations of Table VII, particularly for the non-etherate catalysts. According to these equations, at [Al]/[Ti] = 0.20 all of the aluminum should be in the solid and 40% of the titanium should remain in solution as $TiCl_4$. Experimentally it was found that only 9.5% of the aluminum was in solution but 34.7% of the titanium was soluble, in fair agreement with the predicted amounts. Likewise, at [Al]/[Ti] = 0.30 no aluminum should be in solution, but 10% of the titanium should be soluble. These figures compare with the 5.1 and 6.7 found, respectively, in solution. At [Al]/[Ti] = 0.50, no titanium but all the aluminum should be in the solution. Very little titanium was found in solution; the small amounts that were may have been fines from the solids that passed through the filter. The bulk of the aluminum, but not 100%, was found in solution. This reflects the aluminum that is carried down in the solid. In these solutions 25% of the chloride should be in solution, according to Table VII. The experimental results approached this value as the [Al]/[Ti] ratio increased.

With the etherate catalyst filtrates at [Al]/[Ti] = 0.20 and 0.30, the bulk of the aluminum is in solution in contrast to the predictions of Table VII and the results of the non-etherate catalysts. This apparently reflects the solubilizing action of the anisole on the $AlCl_3$. The amount of titanium in solution agreed fairly well with the predicted amount for the two catalysts (34.7 and 12.3%, compared to 40 and 10% from theory, respectively). At higher [Al]/[Ti] ratios slightly more aluminum and titanium were in solution than for the non-etherate catalysts. Again this may reflect some complexing and solubilizing power of the anisole.

In the analysis of the hydrolysis products of the solids (Table III) only at [Al]/[Ti] = 1.10 were significant amounts of hydrocarbons evolved, and these were C_3 compounds, as expected for propyl groups. There is some disagreement in the literature about whether alkyl groups are present in catalyst solids prepared at $[Al]/[Ti] < 1.0$, so no comparison with literature data is being made at present. The etherate solids also contained small amounts of anisole, with an appreciable amount at [Al]/[Ti] = 1.10. This anisole must be complexed to one of the metals in the solid in order to have survived several hydrocarbon washes.

The total composition of the solids after analysis for Al, Ti, Cl, and organic groups is given in Table VI. For the non-etherate catalysts these four materials largely account for all of the solids (with the exception in which [Al]/[Ti] = 0.90, which is out of line with all the other solids). Allowing for possible reaction with air or water or both[2] (see under "Results"), nearly all of the composition of these solids has been determined. This is not the case of the etherate solids; some 10–20% of their composition remains undetermined. A portion of this undetermined material could be polypropylene, obtained by polymerization of the propylene, which may come from decomposition of the propyl radicals during the catalyst-forming reaction. This has been reported by others.[2,11,17] Examination of the solutions of the hydrolysis products of the solids from either catalyst system shows little, if any, insoluble material. Polypropylene could be present in only trace quantities at the most, and this would not account for all the unexplained portion of the solids from the etherate catalyst. A careful analysis for these possible small quantities of polypropylene has not yet been made, however.

The gas chromatographic analysis of the filtrates disclosed two important facts: the absence of propyl and of isopropyl chlorides and the presence of considerable quantities of phenol in the etherate catalyst system. Organic chlorides may arise from the reaction of the alkyl radicals, postulated as forming during catalyst reaction (Table VII), with $TiCl_4$ forming $TiCl_3$ and RCl. This reaction has been proposed by some authors who have found alkyl chlorides in the liquid portion of the non-etherate type of Ziegler catalyst[6,13] but only at $[Al]/[Ti] < 1.0$. Friedlander and Oita found no alkyl halides in catalysts of triisobutylaluminum and $TiCl_4$, some of which were made at $[Al]/[Ti] < 1.0$.[7] Kern and Hurst reported no alkyl chloride in a catalyst of triethylaluminum and $TiCl_4$ at $[Al]/[Ti] = 3.0$.[17] In this work the absence of propyl and of isopropyl chlorides should thus rule out any reduction of the $TiCl_4$ by propyl radicals.

The presence of phenol in the filtrates must indicate that anisole is cleaved to some extent during the catalyst-forming reaction of the etherate system. This has been found in other studies in these laboratories.[12] The possibility exists that this cleavage reaction aids in some manner in the reduction of the $TiCl_4$ (e.g., by the formation of radicals that could reduce $TiCl_4$). This would help account for the apparent lower valence of titanium in the etherate catalyst solids.

A more complete study of the fate of the anisole is needed before any speculation can be made on a mechanism for this reaction, however. Table IV shows the proportion of phenol in the total amount of anisole plus phenol found in each catalyst filtrate. At $[Al]/[Ti] = 0.50$ nearly all the anisole has been converted to phenol. This is also the point at which the postulated concentration of $AlRCl_2$ in the reaction mixture is at its maximum (Table VII). Above this ratio the amount of phenol in the filtrate decreases in rough parallel to the postulated amount of $AlRCl_2$ present. At the two lowest ratios the aluminum species must form $AlRCl_2$ before passing on to $AlCl_3$.[14] This might account for the presence of phenol in these catalysts, if $AlRCl_2$ is the species that is cleaving the anisole. Again a thorough study of such a reaction needs to be done if this supposition is to be confirmed.

If anisole is being cleaved in the catalyst-forming reaction, various fragments might be present that could react in different ways with the catalyst components. Some possible reaction products were sought in the filtrates but not detected: chlorobenzene, *n*-propylbenzene, and diphenyl ether. No attempts have yet been made to determine the fate of the methyl group of the anisole.

A materials balance was determined for the various catalyst components and is given in Table V. Within what is probably experimental error all of the aluminum and titanium can be accounted for. In the non-etherate catalysts at the lower [Al]/[Ti] ratios not all of the chlorine is recovered by the inorganic analysis. This would indicate organic chlorides, and from literature data this would be the region of [Al]/[Ti] ratios in which propyl (or, possibly, isopropyl) chloride would be expected. As discussed above, however, we have not yet detected any in these samples. In none of the etherate catalysts was all of the chlorine recovered. Since phenol is found in these samples, which presumably comes from cleavage of the anisole, it is possible that various fragments from the anisole may in some manner consume some of the chlorine present. We have not yet detected any chlorinated organic species that would support such a reaction. A considerable portion of the anisole also is not recovered. There was chromatographic evidence of low levels of several alkylated phenols present in the filtrates. No experimental work was done in the studies being reported here to identify these small peaks, but separate work done in these laboratories on similar catalysts has given evidence of alkylated phenols.[12] These would help account for some of the anisole.

CONCLUSIONS

The yields of solid and the inorganic analyses of both the solid and liquid portions of the etherate and non-etherate catalysts indicate that the equations of Table VII give a fairly reasonable representation of the reaction between aluminum trialkyl and titanium tetrachloride at [Al]/[Ti] molar ratios of less than 0.333. The data of other authors also support these findings and x-ray examination of the solids has indicated they do contain β-$TiCl_3$.[2,9,10,18] At [Al]/[Ti] $\geq$ 0.50 these equations, it is believed, give a plausible picture of the reaction, except that the solid is not pure $TiCl_3$ but contains some aluminum species. The assumption that this was the aluminum alkyl chloride postulated as forming in the reaction leads to the conclusion that the titanium in the non-etherate solid is $TiCl_3$ until the [Al]/[Ti] ratio of the catalyst exceeds 1.0. However, few alkyl groups appear in the solid until a ratio of >1.0. Thus one cannot completely rule out the possibility that the aluminum species is $AlCl_3$, pending thorough examination of these solids by other techniques, such as x-ray analysis.

The solids from catalysts prepared in the presence of anisole have lower [Cl]/[Ti] ratios than the non-etherate solids, indicating a greater degree of reduction or alkylation, or both, of these solids. No propyl (or isopropyl) chloride was found in any of the catalyst filtrates, ruling out any reduction of the $TiCl_4$ by propyl radicals. However, phenol was found in the filtrates of the etherate catalysts. Assuming this came from cleavage of the anisole, then various organic fragments could be present during the catalyst-forming reaction, which could aid in the reduction or alkylation of the titanium species.

Thus the major differences between the etherate and non-etherate catalysts, particularly at [Al]/[Ti] ≥ 0.50, are the greater reduction or alkylation of titanium in the etherate solids, the presence of anisole in both the solid and liquid portions, and the presence of phenol in the liquid portion. Any or all of these factors could have considerable effect on the polymerization of isoprene with these catalysts. Before speculation about the mode of action of these catalysts can be made, however, several more questions must be answered about the catalyst-forming reaction, including the following:

(*1*) All of the chlorine must be accounted for, particularly in the etherate catalyst. The chlorine apparently is not disappearing as propyl or isopropyl chloride. Since it seems that part of the anisole is being decomposed during catalyst formation, there may be other organic fragments present in this catalyst system, which are capturing some of the chlorine.

(*2*) The fate of the alkyl groups from the aluminum alkyl must be determined. They do not seem to be forming alkyl chlorides. If they disproportionate into the respective alkane and alkene, as has been suggested by many workers, half of the alkyl groups could form polymer through polymerization of the alkene. Visual evidence indicated that little, if any, polypropylene was in the catalyst solid. Atactic polypropylene might be formed (and probably would be with this type of catalyst), which would be soluble and pass into the filtrate; we have not yet looked for this.

(*3*) The fate of all of the anisole must be resolved. The determination of the missing portions of the ether and clarification of the manner of formation of phenol in this system are needed. These should give a clearer picture of the behavior of these catalysts in isoprene polymerization relative to the usual Ziegler-type catalyst.[1]

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NOTES

Thermal Stability of Aromatic Polyamides from 4,4′-Oxydibenzoic Acid

Recent notes[1-3] describe the thermal stability of the wholly aromatic polyamides and copolyamides. These are unusually high-melting, slightly soluble compounds and have high thermal stability. In a previous work,[4] the preparation and thermal stability of aromatic polyamide, containing the 4,4′-oxydiphenylene group and derived from isophthaloyl or terephthaloyl chlorides and 4,4′-diaminodiphenyl ether, was reported. This present paper deals with the thermal stability of the wholly aromatic polyamides from 4,4′-oxydibenzoic acid derivatives.

Experimental

All aromatic diamines were purified by recrystallization or distillation. 4,4′-Oxydibenzoyl chloride was recrystallized from *n*-hexane to plates, m.p. 88°C. (lit.[5] m.p. 83°C.). The aromatic polyamides were prepared by interfacial polycondensation. Aromatic diamines (0.004 mole) and sodium hydroxide (0.008 mole) were dissolved in a mixture of water (100 ml.) and tetrahydrofuran (100 ml.). The solution was kept below 10°C., and 0.004 mole acid chloride dissolved in 200 ml. benzene was added all at once with vigorous stirring. The products were filtered off and washed with water and methanol. Melting points were determined by differential thermal analysis (DTA), and thermal stability was measured by thermogravimetric analysis (TGA) under nitrogen.

Results

The aromatic polyamides prepared are listed in Table I. All of aromatic polyamides were soluble in concentrated sulfuric acid, and insoluble in formic acid, acetic acid, and *m*-cresol. Also, polyamides from *m*-phenylenediamine, xylylenediamine, 4,4′-diaminodiphenyl ether and 4,4′-diaminodiphenyl sulfone were soluble in dimethylformamide and dimethylacetamide containing 5% dissolved LiCl, but the other four polyamides were merely partially soluble in this solvent system.

It was shown by x-ray diffraction that these polymers contain much crystalline material. DTA results indicate that these polymers, except III and VII, have melting points higher than 400°C. Polymer III from xylylene diamine and VII from 4,4′-diaminodiphenylsulfone melted at 352°C. and 400°C., respectively. The infrared spectra showed the characteristic absorption due to amide bonds (1650–1653, 1520–1531, and 1300–1315 cm.$^{-1}$).

The thermal stability of wholly aromatic polyamides was examined to determine how this varies with the chemical structure of aromatic diamines. The TGA results are shown in Figures 1 and 2. The data indicate that all polymers except III are stable up to about 350°C. and begin to decompose suddenly at temperatures above 400°C. However, the polymer containing the xylylene unit begins to decompose above 300°C. and loses 70% of its weight at 400°C. The weight loss data for these polymers are summarized in Table II.

As compared with the weight loss of these polymers at 400°C. they fall into three groups (polymer III; polymers I and VII; polymers II, IV, V, VI, VIII); all the others

TABLE I
Aromatic Polyamides Derived from 4,4′-Oxydibenzoyl Chloride

No.	Derivative of	Polymer yield, %	η_{sp}/c[a]	Melting point, °C.[b]	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
I	*m*-Phenylenediamine	81	0.35	>400(dec.)	72.72	72.65	4.27	4.22	8.48	8.44
II	*p*-Phenylene diamine	76	0.44[c]	>450(dec.)	72.72	72.68	4.27	4.00	8.48	8.22
III	Xylylenediamine[d]	84	1.00	352	73.73	73.98	5.06	5.16	7.82	7.88
IV	*o*-Toluidine	77	0.32[c]	>450(dec.)	77.40	77.12	5.10	5.38	6.45	6.20
V	Benzidine	73	0.37[c]	>450(dec.)	76.83	76.53	4.46	4.18	6.89	6.99
VI	4,4′-Diaminodiphenyl ether	80	0.49	>450(dec.)	73.92	73.68	4.30	4.02	6.63	6.78
VII	4,4′-Diaminodiphenyl sulfone	81	0.45	400	66.37	66.35	3.86	3.70	5.95	6.28
VIII	4,4′-Diaminodiphenylmethane	79	0.41	>400(dec.)	77.13	76.80	4.79	4.45	6.66	6.70

[a] Reduced specific viscosity was measured at 25°C. for a concentration of 0.5 g./100 ml. DMF containing 5% dissolved LiCl.

[b] Measured by DTA.

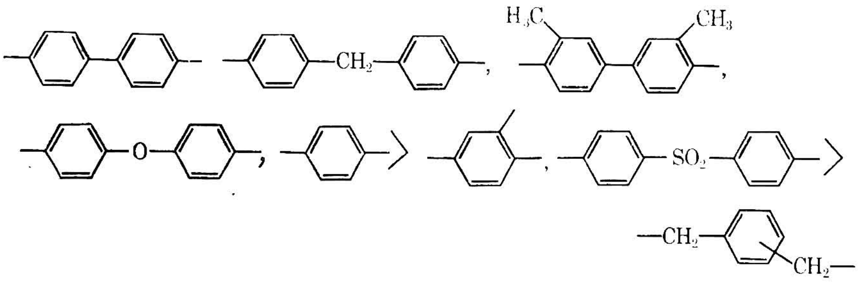
[c] Determined for a solution of concentrated sulfuric acid.

[d] Xylylenediamine consists of two components (*para*/*meta* = 30/70 by mole-%).

TABLE II
Relative Thermal Stabilities of Wholly Aromatic Polyamides

No.	Derivative of	Initial decomposition temp., °C.	350°C.	Wt. loss, % at various temperatures			
				400°C.	450°C.	500°C.	600°C.
I	*m*-Phenylenediamine	376	2	30	50	53	55
II	*p*-Phenylenediamine	355	9	19	39	46	50
III	Xylylenediamine	315	40	70	72	73	74
IV	*o*-Toluidine	382	6	12	34	49	51
V	Benzidine	378	1	8	28	43	46
VI	4,4′-Diaminodiphenyl ether	367	2	12	31	42	49
VII	4,4′-Diaminodiphenyl sulfone	356	4	32	42	47	51
VIII	4,4′-Diaminodiphenylmethane	380	3	9	31	45	53

except polymer III reach a weight loss between 46% and 55% at 600°C. The thermal stability of the polymers as a function of the diamine decreases in the following order:



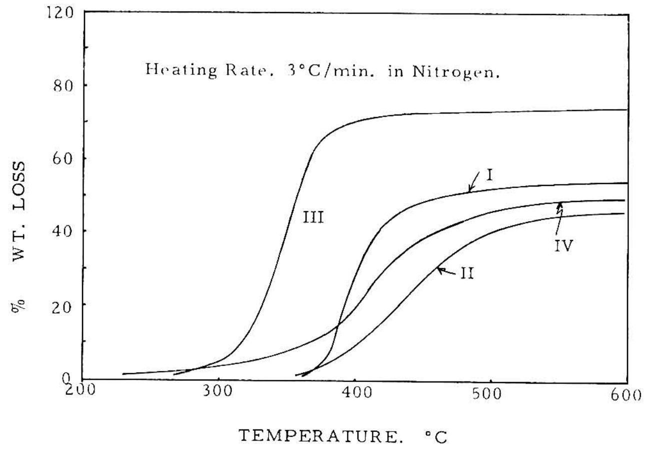


Fig. 1. Relative thermal stability of Aromatic Polyamides (Polymers 1-4 as in Table 1). Heating rate 3°C./min. in nitrogen.

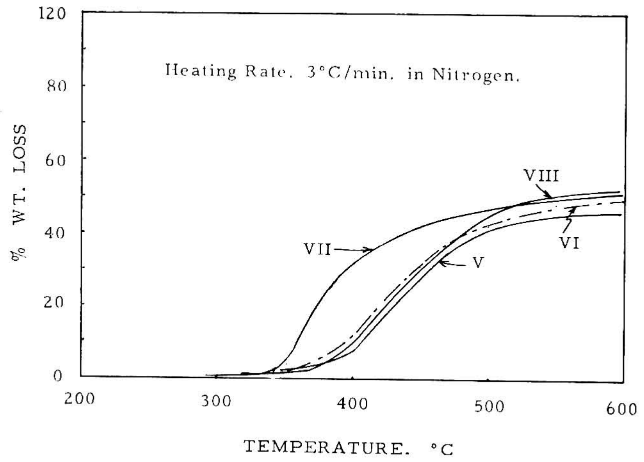


Fig. 2. Relative thermal stability of aromatic Polyamides (Polymers 5-8 as in Table 1). Heating rate 3°C./min in nitrogen.

On the basis of these results, it seems that polymers having *p*-phenylene links are generally more thermally stable than those having *m*-phenylene links. This is due to the symmetrical, rigid character of the *p*-phenylene links. In the flexible links between the *p*-phenylene groups, the sulfonyl link is less stable. The lower stability of polymer containing the sulfonyl link may be attributed to reduced interaction between adjacent polymer chains by increasing the rotation of the sulfonyl group at given temperature. The polymer with a xylylene link showed a poor stability, but this is probably the results of weakness arising from the aliphatic methylene group.

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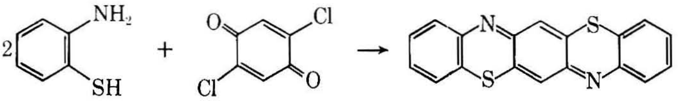
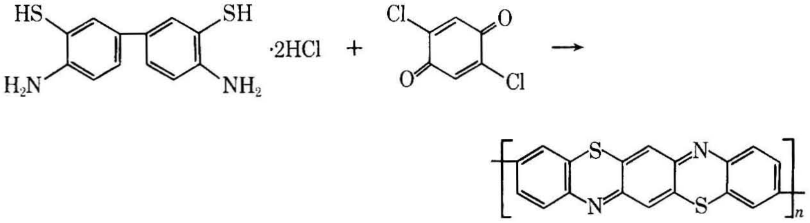
Polytriphenodithiazine

It is reported in the old literature[1] that *o*-aminothiophenol condenses with α-bromoacetophenone to give 2-phenylbenzothiazine in a fairly good yield. If 2,5-dichloro-*p*-benzoquinone could be substituted for α-bromoacetophenone, triphenodithiazine would result by the condensation of 2 moles of *o*-aminothiophenol and 1 mole of 2,5-dichloro-*p*-benzoquinone [eq. (1)].



(1)

Condensation of *o*-aminothiophenol with 2,5-dichloro-*p*-benzoquinone was carried out in dimethylacetamide to yield triphenodithiazine. This reaction, therefore, seemed to be applicable for the preparation of a polymer with triphenodithiazine recurring units [eq. (2)].



(2)

Equimolar amounts of 3,3′-dimercaptobenzidine dihydrochloride and 2,5-dichloro-*p*-benzoquinone were reacted in dimethylacetamide or in polyphosphoric acid to yield a black solid. This compound was slightly soluble in concentrated sulfuric acid but insoluble in such solvents as hexamethylphosphoramide, dimethyl sulfoxide, and dimethylacetamide. Although the analysis was fair, this polymer exhibited a good thermal stability; it lost only 3% of its weight at 500°C. and 93% at 900°C. in helium. Figure 1 shows the thermogravimetric analysis curve.

Condensation of 2,5-Dichloro-*p*-benzoquinone with *o*-Aminophenol

Freshly distilled o-aminothiophenol (2.5055 g., 0.02 mole) was added to an ice-cooled solution of 2,5-dichloro-*p*-benzoquinone (1.7700 g., 0.01 mole) in dimethylacetamide (50 ml.). The reaction mixture was allowed to come to room temperature. The dark brown turbid reaction mixture turned to a clear orange yellow solution. The reaction temperature was slowly raised to 140°C. over 2 hr. and held for 20 hr. After cooling, the dark brown reaction mixture was poured into dilute ammonium hydroxide to yield a violet solid. This was collected, washed with water, and subsequently heated in a rotating flask at 250–300°C. under vacuum for 5 hr. The yield of the dark violet powder was 2.32 g. (72%); m.p. > 350°C. The ultraviolet spectrum in concentrated sulfuric acid showed λ_{max} at 321, 283, and 263 mμ.

ANAL. Calcd. for $C_{18}H_{10}N_2S_2$: C, 67.90%; H, 3.16%; N, 8.80%; S, 20.14%. Found: C, 66.10%; H, 3.17%; N, 8.88%; S, 20.18%.

Condensation of 2,5-Dichloro-*p*-benzoquinone with 3,3′-Dimercaptobenzidine

To an ice-cooled solution of 2,5-dichloro-*p*-benzoquinone (0.8853 g., 0.005 mole) in dimethylacetamide (30 ml.) was added 3,3′-dimercaptobenzidine dihydrochloride (1.6064 g., 0.005 mole), and the resulting solution was allowed to come to room temperature. After it was stirred for 5 hr., the reaction temperature was slowly raised to 150°C. and maintained for 24 hr. The reaction mixture was treated as described in the preparation of triphenodithiazine. The black powdery material weighed 1.02 g. after drying under reduced pressure. This compound was soluble in concentrated sulfuric acid and had an inherent viscosity of 0.12 ($C = 0.2\%$ at 30°C). The ultraviolet spectrum in concentrated sulfuric acid showed λ_{max} at 303 and 250 mμ.

ANAL. Calcd. for $(C_{18}H_8N_2S_2)_n$: C, 68.33%; H, 2.55%; N, 8.85%; S, 20.27%. Found: C, 65.44%; H, 2.93%; N, 8.30%; S, 19.10%.

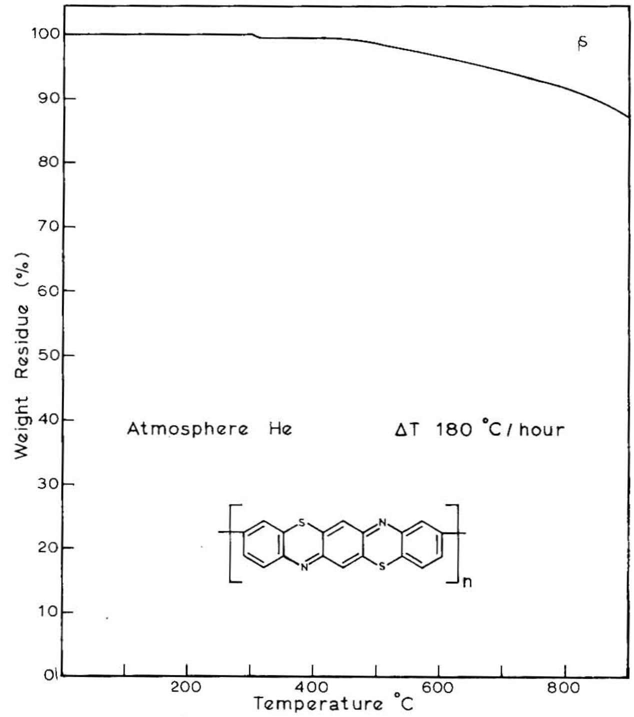


Fig. 1. TGA curve.

To a suspension of 3,3′-dimercaptobenzidine dihydrochloride (1.6060 g., 0.005 mole) in polyphosphoric acid (50 g.) was added 2,5-dichloro-*p*-benzoquinone (0.8850 g., 0.005 mole) at room temperature under a nitrogen stream. After the reaction mixture was stirred for 1 hr. at room temperature, the bath temperature was raised to 250°C. over 2 hr. When the reaction mixture had been heated at 250°C. for about 2 hr., it suddenly became jelly. However, it was heated as such for 24 hr. The black mass, while it was hot, was transferred into 1 liter of dilute ammonium hydroxide in a blender to give a black granular solid. This was pulverized, stirred in dilute ammonium hydroxide overnight, and subsequently extracted with water for 3 days and with ethanol for one day in a Soxhlet extractor. The black powder weighed 1.43 g. (90.5%) after drying under reduced pressure at 60°C. This compound was slightly soluble in concentrated sulfuric acid and the soluble part showed an inherent viscosity of 0.54 ($C = 0.07\%$ at 30°C.)

ANAL. Found: C, 63.77%; H, 2.70%; N, 8.21%; S, 18.78%; residue 1.73%.

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