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Anionic Graft Polymerization of Propylene Sulfide on Cellulose. I

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Synopsis

The anionic graft polymerization of propylene sulfide on cellulose membrane was studied. Alkali cellulosates were used to initiate graft polymerization, and graft polymers of high polypropylene sulfide content were obtained in good yields. The graft polymerization was accompanied by a certain extent of homopolymerization. The effects of reaction solvent, monomer concentration, cellulosate degree of substitution, and type of the alkali metal cellulosate on the graft polymer composition, yield, and on the molecular weight of the grafted side chains were investigated.

INTRODUCTION

The anionic polymerization of episulfides was only recently subjected to intensive studies.[1,2] Marvel and Weil[3] have shown that propylene sulfide can be polymerized by sodium ethoxide. Sigwalt and co-workers[1] have shown that the polymerization propagates by mercaptide anion, derived from the opened episulfide ring. By using sodium naphthalene in tetrahydrofuran (THF) as initiator, living polymers were obtained.[1]

Preliminary studies of the possibility of anionic graft polymerization of episulfides were reported in the literature. Most graft polymerization reactions, were carried on cellulose. Champetier[4] reported the grafting of ethylene and propylene sulfide on alkali cellulose. Lazier and Signaigo[5] reacted dithioglycidol with alkali cellulose, rayon, polystyrene, and other polymers. Cremonesi[6,7] investigated the grafting of ethylene sulfide on cellulose in the gas phase and in solution.

In the present work a detailed study of the anionic graft polymerization of propylene sulfide on cellulose membrane (cellophane film) is reported. Alkali metal cellulosate was used for initiating the graft polymerization.[8–10] Such method of initiation may prove to be a useful tool for the chemical modification of cellulose, since it was shown[11] that the conversion of cellulose to its cellulosate derivative did not lead to chemical degradation or to a change in its mechanical properties.

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* Deceased July 16, 1970.

EXPERIMENTAL

Materials

Dimethyl sulfoxide (DMSO) was dried and fractionally distilled *in vacuo* over calcium hydride. Tetrahydrofuran (THF) (Fluka) was dried over sodium benzophenone ketyl.[12] Propylene sulfide (Fluka) was freshly fractionally distilled over calcium hydride under argon.

Cellulose membrane (Arthur H. Thomas dialyzer tubing, No. 4465-A2) was used.

Preparation of Alkali Metal Cellulosate

The reaction was carried in a closed glass cylinder equipped with a self-sealing rubber cap through which reagents can be added with a syringe. The cellulose membrane (0.535 g) was swelled in DMSO (40 ml) for 2 hr The DMSO was replaced by dry methanol (40 ml), and the methanol was exchanged four times within 4 hr. Alkali methoxide solution (50 ml) of a desired concentration was added. The reaction mixture was shaken mechanically for 10 min, and the methoxide solution was decanted. Excess of alkali methoxide was removed from the membrane by extraction with dry DMSO and the degree of substitution (DS) of the cellulosate was determined by a known procedure.[11]

Graft Polymerization

The graft polymerization was carried out at room temperature under argon under anhydrous conditions. To the alkali metal cellulosate dry DMSO (50 ml) was added, followed by the required amount of propylene sulfide. The reaction cylinder was kept under constant shaking and at the end of the reaction, the DMSO solution was decanted and the cellulose membrane was neutralized by 2% acetic acid. The membrane was washed with water followed by ethanol and dried *in vacuo* over phosphorus pentoxide at 50°C. Homopolymer was removed by extraction with benzene for 48 hr. The amount of homopolymer formed was determined from weight loss after extraction. Gas chromatography was carried out by using a Packard gas chromatograph Model 7300/7400. Nitrogen was used as carried gas (15 ml/min), and 1.80 mμ of 0.3 cm I.D. column containing the SE 30 (15%) packing on Chromosorb P 60/80 was used. The injection temperature was held at 200°C, the column temperature at 100°C, and the detector temperature at 200°C. Toluene was used as internal reference.

Isolation of the Grafted Poly(propylene Sulfide) Side Chains

Graft polymer (1.0 g) was ground by a Wiley mill and treated with 72% sulfuric acid (10 ml) for 16 hr at 5°C. The reaction mixture was diluted with water (29 ml) and the hydrolysis was allowed to proceed at 100°C for 4 hr. The poly(propylene sulfide) was isolated by centrifugation, washed with water, and dried *in vacuo* over phosphorus pentoxide. The polymer was dissolved in benzene, filtered, and isolated by removal of the benzene *in vacuo*.

Intrinsic Viscosity of the Grafted Poly(propylene Sulfide)

The intrinsic viscosities were calculated from one-point viscosity measurement[13] at a concentration of 0.1 g polymer/100 ml benzene at 20°C by using the equation:

$$\eta = \eta_0 e^{[\eta]c}$$

RESULTS

The alkali metal cellulosates were prepared by exchange reaction of cellulose with alkali methoxide solution in methanol. The cellulosate degree of substitution (DS) was controlled by the alkali methoxide concentration.[11] The per cent conversion of monomer in the graft polymerization reaction was determined either from the weight increase of the membrane or by gas chromatography technique. The effect of time on the graft polymerization was studied by using lithium cellulosate (DS = 0.87) (Table I, series A) and potassium cellulosate (DS = 0.73) (Table I, series B). The yields as well as the poly(propylene sulfide) content of the graft polymers increased with increasing the reaction time. The graft polymerization was accompanied to a certain extent by homopolymerization. No significant homopolymerization was observed at low conversions.

The influence of monomer concentration was studied (Table II). Increasing the monomer concentration led to an increase in the poly(propylene sulfide) content of the graft polymers (ca. 30% to 70%), to a decrease in the graft polymerization yield, and to an increase in homopolymerization yield. Thus in the graft polymerization initiated by potassium cellulosate (Table II, series B) increase from 2% to 44% in homopolymerization yield was observed, while in that initiated by lithium cellulosate (Table II, series A), the increase was from about 1% to 20% in the monomer range investigated.

In the cellulosate DS range studied, there was no significant change in the yield of the pure graft polymers and in their poly(propylene sulfide) content with change in the cellulosate DS (Table III).

The alkali metal counterion of the cellulosate did not influence the graft polymerization yield or the poly(propylene sulfide) content of the graft polymers with the same cellulosate (DS = 0.65) (Table IV). The graft polymerization yield was found to depend on the reaction solvent. Best results were obtained in DMSO (Table V).

To find out the molecular weight of the grafted side chains, the graft polymers were subjected to total hydrolysis of the cellulosic backbone. The insoluble poly(propylene sulfides), thus severed from the graft polymers, containing a glucose endgroup, were isolated, and their molecular

TABLE I
Effect of Time on Graft Polymerization[a]

Expt. no.	Reaction time, hr	Monomer conversion, %[b]	Graft polymerization yield, %[c]	Homopolymerization yield, %[d]	Poly(propylene sulfide) in crude graft polymer, %	Poly(propylene sulfide) in graft polymer, %[e]
Series A						
323	5 (min)	16.0	16.0	0.0	22.0	22.0
319	0.5	33.3	33.3	0.0	36.9	36.9
322	2.0	41.5	39.7	1.8	42.2	41.0
321	4.0	52.0	49.8	2.2	47.7	46.6
309	24.0	79.2	65.0	14.2	58.1	53.4
Series B						
310	2 (min)	11.3	11.3	0.0	16.7	16.7
311	5 (min)	16.5	16.5	0.0	22.5	22.5
312	0.5	19.1	17.9	1.2	26.0	23.9
313	4.0	64.4[f]	47.2	14.2	51.8	45.3
314	24.0	98.3[g]	72.0	26.3	63.2	55.8

[a] Experimental conditions: cellulose membrane (0.535 g) was swelled in DMSO and reacted with 2.20N lithium methoxide solution (50 ml) to give lithium cellulosate, DS = 0.97 (series A), and with 1.95N potassium methoxide (50 ml) to give potassium cellulosate, DS = 0.73 (series B). Reaction with propylene sulfide (0.941 g, 0.254 mole/l.) was carried in DMSO (50 ml) at room temperature.

[b] Determined from the weight increase of the cellulose membrane.

[c] Calculated from weight increase after extraction of homopolypropylene sulfide.

[d] The difference between monomer conversion and graft polymerization yield.

[e] Determined after extraction of the homopolymer from the crude product.

[f] 64.7% by gas chromatography.

[g] 95.7% by gas chromatography.

TABLE II

Effect of Monomer Concentration on Graft Polymerization[a]

Expt. no.	Propylene sulfide, mole/l	Monomer conversion, %[b]	Graft polymerization yield, %[c]	Homopolymerization yield, %[d]	Poly(propylene sulfide) in crude graft polymer, %	Poly(propylene sulfide) in graft polymer, %[e]
Series A						
214	0.127	74.8	74.2	0.6	39.6	39.5
218	0.254	43.7	43.0	0.7	43.5	43.1
215	0.508	46.1	36.7	9.4	61.8	56.3
216	0.762	51.2	31.6	19.6	72.6	62.4
217	1.016	48.6	31.0	17.6	77.2	68.5
Series B						
188	0.127	56.6	54.6	2.0	33.2	32.5
190	0.254	52.9	43.4	9.5	48.2	43.3
187	0.508	54.9	38.9	15.6	65.7	57.7
189	1.016	73.9	29.2	44.7	83.7	67.3

[a] Experimental conditions: cellulose membrane (0.535 g) was swelled in DMSO and reacted with 2.20N lithium methoxide solution (50 ml) to give lithium cellulosate, DS = 0.97 (Series A), and with 1.90N potassium methoxide (50 ml) to give potassium cellulosate, DS = 0.73 (Series B). Graft polymerization was carried in DMSO (50 ml), reaction time 8 hr.

[b] Determined from the weight of the cellulose membrane.

[c] Calculated from weight increase after extraction of homopoly(propylene sulfide).

[d] The difference between monomer conversion and graft polymerization yield.

[e] Determined after extraction of the homopolymer from the crude product.

TABLE III

Effect of Potassium Cellulosate DS[a]

Expt. no.	Potassium methoxide solution, N	Cellulosate DS	Monomer conversion, %[b]	Graft polymerization yield, %[c]	Homopolymerization yield, %[d]	Poly(propylene sulfide) in crude graft polymer, %	Poly(propylene sulfide) in graft polymer, %[e]
318	0.20	0.21	—	64.0	—	—	52.9
317	0.50	0.36	58.4	55.6	2.8	50.9	50.4
316	1.00	0.54	57.4	50.2	7.2	50.2	46.8
313	2.00	0.73	61.3	47.2	14.1	51.8	45.3
315	3.00	0.80	79.3	55.0	24.3	58.3	49.2

[a] Experimental conditions: cellulose membrane (0.535g) was swelled in DMSO and reacted with potassium methoxide solution. Graft polymerization of propylene sulfide (0.941 g, 0.254 mole/l.) was carried in DMSO (50 ml), reaction time 4 hours.

[b] Calculated from the weight increase of the cellulose membrane.

[c] Calculated from the weight increase of the cellulose membrane after extraction of the homopolypropylene sulfide.

[d] The difference between monomer conversion and graft polymerization yield.

[e] Determined after extraction of the homopolymer from the crude product.

TABLE IV

Effect of Alkali Metal Cellulosate on the Graft Polymerization[a]

Expt. no.	Alkali metal	Graft polymerization yield, %[b]	Poly(propylene sulfide) in graft polymer, %[c]
222	K	58.2	50.6
223	K	61.1	51.8
224	Na	57.5	50.3
225	Na	60.0	51.3
228	Li	62.2	52.2
229	Li	60.3	51.4

[a] Experimental conditions: cellulose membrane (0.535 g) was swelled in DMSO (50 ml) and reacted with 1.50*N* alkali methoxide (50 ml) to give alkali cellulosate, DS = 0.65. Graft polymerization of propylene sulfide (0.941 g, 0.254 mole/l.) was carried in DMSO (50 ml) at room temperature, reaction time 4 hr.

[b] Determined from the weight increase of the cellulose membrane after extraction of homopolymer.

[c] Determined after extraction of the homopolymer from the crude product.

TABLE V

Effect of Reaction Solvent on Graft Polymerization[a]

Expt. no.	Solvent	Graft polymerization yield, %[b]	Poly(propylene sulfide) in graft polymer, %[c]
253	DMSO	45.6	44.5
256	DMSO	40.3	41.5
257	THF	9.6	14.5
258	THF	10.9	16.1
259	Benzene	33.0	36.7
260	Benzene	26.0	31.4

[a] Experimental conditions: cellulose membrane (0.535 g) was swelled in DMSO (50 ml) and reacted with 2.09*N* lithium methoxide (50 ml) to give lithium cellulosate, DS = 0.97. Graft polymerization of propylene sulfide (0.941 g, 0.254 mole/l.) was carried in 50 ml solvent at room temperature.

[b] Determined from the weight increase of the cellulose membrane after extraction of homopolypropylene sulfide.

[c] Determined after extraction of the homopolymer from the crude product.

weights were determined from viscosity measurements by using the relationship:[14]

$$[\eta] = 0.33 \times 10^{-4} M_w^{0.86}$$

If it is assumed that an alcoholate group on the cellulose backbone can initiate graft polymerization of a single side chain, then the efficiency of the alcoholate groups in initiating graft polymerization can be calculated from the molecular weight of the grafted polypropylene sulfide and its content in the graft polymers. The efficiency of the alkoxides in initiating the graft polymerization thus determined, and the molecular weights of the grafted side chains were found to depend on the reaction conditions. Thus

TABLE VI

Dependence of Molecular Weight on Reaction Conditions[a]

Expt. no.	Reaction time, hr	[Monomer], mole/l.	Cellulosate DS	Alkali cellulosate	Poly(propylene sulfide) in graft polymer, %	[η] dl/g	M_w[b]	Initiator efficiency, %[c]	Anhydroglucose units per grafted side chain
Series A									
311	5 (min)	0.254	0.73	K	22.5	0.086	8,890	0.74	185
312	0.5	0.254	0.73	K	23.9	0.106	11,960	0.59	231
313	4.0	0.254	0.73	K	45.3	0.139	16,390	1.14	120
314	24.0	0.254	0.73	K	55.8	0.204	25,610	1.11	133
Series B									
313	4.0	0.254	0.73	K	45.3	0.139	16,390	1.14	120
316	4.0	0.254	0.54	K	46.8	0.199	24,880	1.07	173
317	4.0	0.254	0.36	K	50.4	0.216	27,360	1.61	172
318	4.0	0.254	0.21	K	52.9	0.224	28,490	3.05	155
Series C									
188	8.0	0.127	0.73	K	32.5	0.095	10,530	1.04	133
190	8.0	0.254	0.73	K	43.3	0.123	14,180	1.22	114
187	8.0	0.508	0.73	K	57.7	0.172	20,990	1.48	93
Series D									
222	4.0	0.254	0.65	K	50.6	0.123	14,180	1.79	84
224	4.0	0.254	0.65	Na	50.3	0.125	14,490	1.74	87
229	4.0	0.254	0.65	Li	51.4	0.152	18,190	1.45	104

[a] Experimental conditions: The experiment numbers refer to runs cited in previous Tables: Series A, see Table I; Series B, see Table III; Series C, see Table II; Series D, see Table IV.

[b] Calculated according to $[\eta] = 0.33 \times 10^{-4} M_w^{0.86}$.

[c] Based on the cellulosate DS.

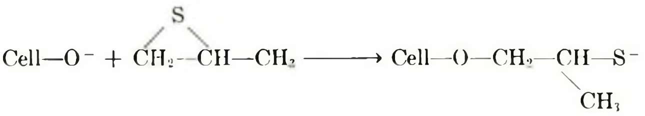
the efficiency was very low (about 1–3%), it did not change with the polymerization time (Table VI) but it decreased with increasing potassium cellulosate DS (Table VI) and increased with increasing monomer contentration (Table VI). The molecular weights increased with time, decreased with increasing cellulosate DS and increased with increasing monomer concentration (Table VI). The number of anhydroglucose units per grafted side chain varied between 80 to 230, depending on the reaction conditions (Table VI). The results obtained with different alkali metal counterions (Table VI) showed that with potassium and sodium both the efficiency of the cellulosate and the molecular weights of the grafted chains were the same. With lithium cellulosate the efficiency was lower and the molecular weights were higher.

DISCUSSION

In the present anionic graft polymerization it was shown that although the grafting on the cellulose membrane was a heterogeneous reaction, graft polymers having a high content of poly(propylene sulfide) can be obtained in high yield.

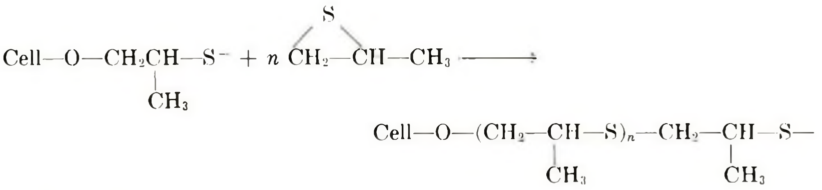
The course of the graft polymerization of propylene sulfide on the alkali metal cellulosate may be described by the following scheme [eqs. (1)–(3)]:

Initiation:



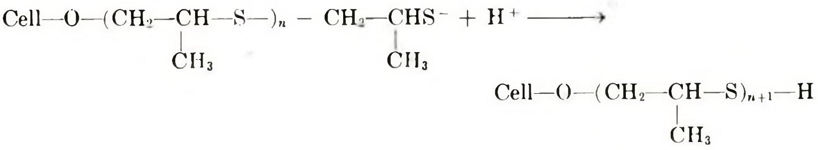
(1)

Propagation:



(2)

Termination:



$$\text{Cell—O—(CH}_2\text{—}\underset{\displaystyle \text{CH}_3}{\text{CH}}\text{—S—)}_n - \text{CH}_2\text{—}\underset{\displaystyle \text{CH}_3}{\text{CH}}\text{S}^- + \text{H}^+ \longrightarrow \text{Cell—O—(CH}_2\text{—}\underset{\displaystyle \text{CH}_3}{\text{CH}}\text{—S)}_{n+1}\text{—H} \quad (3)$$

The mercaptide ion formed in the initiation reaction propagates graft polymerization. The mercaptan endgroup formed in the termination reaction may remain intact, or may be oxidized to the corresponding disulfide. However using the *N*-ethyl maleimide procedure[15] for the detection of mercaptan groups and 1,4-dithiothreitol (Cleland's reagent[16]) recommended for the determination of disulfide bonds in wool[17] for the detection of disulfide linkages, no such groups were detected. This may be due to their very small concentration in the graft polymers. Actually the molecular weights of the grafted side chains were relatively high so that the concentration of such groups is expected to be too low to be determined. The negative results also indicate that practically no single propylene sulfide units attached to the cellulosic backbone are present as would have been the case if part of the mercaptopropyl units formed on initiation remained as such and did not propagate polymerization.

The low efficiency of the alkoxide groups in initiating polymerization may be due to the greater nucleophilicity of the growing mercaptide anions which lead to a higher propagation rate as compared with initiation. Furthermore, steric effects in initiation may be higher than those encountered in the case of the propagation.

The suggested scheme for the graft polymerization does not account for homopolymer formation, which as shown was negligible at low conversion but increased with increasing per cent conversion of monomer or cellulosate concentration. Chain transfer to monomer during the propagation of the graft polymerization, which was found to be serious in the case of the corresponding anionic graft polymerization of propylene oxide[18] (where abstraction of a proton from the methyl group of the monomer occurred) does not seem to be dominant in this case, since it was reported[1] that this reaction does not occur readily with mercaptide ion.

A more plausible route for homopolymer formation may be abstraction of a proton from the methyl group of the propylene sulfide by cellulosate groups, and this is expected to increase with increasing cellulosate DS, as found. There is also the possibility that traces of alkali methoxide, used in the metallation reaction, remained rather strongly adsorbed on the cellulose membrane and were not removed in the solvent exchange treatment. The fact that homopolymer formation was negligible at low conversions points out that initiation of such a reaction is slow and is in agreement with these possibilities for homopolymerization. On increasing the monomer concentration there is a large increase in the extent of the homopolymerization, and this can be explained by the fact that homopolymerization, although it may be initiated by a relatively small number of initiation sites, it can, being a homogeneous reaction, compete effectively with the heterogenous graft polymerization.

The molecular weights of the grafted side chains were found to increase with the reaction time and with monomer concentration. This can be explained if chain transfer to monomer is not dominant, and there is absence of termination. Actually the anionic polymerization of propylene sulfide in aprotic solvents was shown to be a "living" one.[1]

With the three alkali metals investigated it was found that the yields of the graft polymer were the same but the molecular weights of the grafted side chains initiated by the lithium cellulosate were higher. This means that the amount of the lithium alkoxide centers that participated in the grafting were smaller. This smaller efficiency may be due to the more covalent nature of the lithium alkoxide bond, which even in dimethyl sulfoxide is not completely dissociated.

References

1. P. Sigwalt, in *Ring-Opening Polymerization,* K. C. Frisch and S. L. Reegen, Eds., Dekker, New York, 1969, p. 191.
2. J. P. Kennedy and E. Tornqvist, *Polymer Chemistry of Synthetic Elastomers,* Interscience, New York, 1969, Part II, p. 833.
3. C. S. Marvel and E. D. Weil, *J. Amer. Chem. Soc.,* **76,** 61 (1954).
4. G. Champetier and F. Hennequin-Lucas, *C. R. Acad. Sci.* (Paris), **252,** 2785 (1961).
5. W. A. Lazier and F. K. Signaigo, U. S. Pat. 2,396,957 (1946).
6. P. Cremonesi, *Ric. Doc. Tessile,* **3,** 162 (1966); *Chem. Abstr.,* **66,** 105785a (1967).
7. P. Cremonesi, *Ric. Doc. Tessile,* **3,** 25 (1966); *Chem. Abstr.,* **66,** 11997u (1967).
8. B. A. Feit, A. Bar-Nun, M. Lahav, and A. Zilkha, *J. Appl. Polym. Sci.,* **8,** 1869 (1964).
9. Y. Avny and L. Rebenfeld, *Text. Res. J.,* **38,** 684 (1968).
10. M. Tahan and A. Zilkha, *J. Polym. Sci. A-1,* **7,** 1839 (1969).
11. Y. Avny and L. Rebenfeld, *Text. Res. J.,* **38,** 599 (1968).
12. A. Zilkha and Y. Avny, *J. Polym. Sci. A,* **1,** 549 (1963).
13. D. K. Thomas and T. A. J. Thomas, *J. Appl. Polym. Sci.,* **3,** 129 (1960).
14. V. E. Eskin and A. E. Nesterov, *Vysokomol. Soedin.,* **8,** 141 (1966).
15. N. M. Alexander, *Anal. Chem.,* **30,** 1292 (1958).
16. W. W. Cleland, *Biochemistry,* **3,** 480 (1964).
17. H. D. Weigmann and L. Rebenfeld, *Text. Res. J.,* **36,** 202 (1966).
18. G. Ezra and A. Zilkha, *Europ. Polym. J.,* **6,** 1305 (1970).

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Anionic Graft Polymerization of Propylene Sulfide on Cellulose. II. Absorption of Iodine, Silver, and Mercury on the Graft Polymers

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Synopsis

The adsorption of iodine, silver nitrate, and mercuric chloride by cellulosic membranes grafted with polypropylene sulfide was investigated. It was found that the grafted polypropylene sulfide adsorbed iodine by complexation from aqueous solution or from gaseous phase. Adsorption from water led to the formation of a complex with molar ratio of I_2 to propylene sulfide units of 1, and that while the complex formed from gaseous iodine had a molar ratio I_2 to propylene sulfide approaching 2. Most of the sulfide groups participated in complexation. It was found that the complexation of the polysulfide was accompanied by degradation which was attributed to halogenation of the polysulfide at the tertiary carbon atoms. The iodine complex was more stable in water than in organic solvents, where most of the iodine was desorbed. The graft polymers adsorbed also by complexation silver nitrate and mercuric chloride. Adsorption could be described by a Freundlich type isotherm. At low concentrations most of the silver nitrate present in solution was adsorbed.

INTRODUCTION

Complexes of halogens and heavy metal salts with n donors such as sulfides are well known.[1] The products formed with halogens can be also regarded as sulfonium compounds.[2a] The primary reaction of the halogens with alkyl sulfides is the formation of the n complex.[1]

$$R_2S + X_2 \rightleftharpoons R_2S:X_2$$

The complexes of alkyl sulfides with iodine are more stable than those with other halogens and have a characteristic absorption at 308 mμ.[3] With simple alkyl halides this addition is quantitative and may be used for their estimation.[3] Since these reactions are reversible, these compounds are excellent halogenating agents. This halogenation frequently involves the alkyl or aryl groups of the sulfide itself.[1,2a]

Complexes of alkyl sulfides with silver nitrate and mercuric chloride were reported in the literature.[1] With silver nitrate the molar ratio of the silver

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* Deceased July 16, 1970.

to sulfur in the complex was generally 1:1. With mercuric chloride, molar ratios of 2:1, 1:1, 1:2 and others were obtained.[1]

Little has been reported on the donor properties of sulfide bonds in polymers. Champetier[4] reported the graft polymerization of ethylene and propylene sulfides on alkali cellulose and noticed that the graft polymers gave complexes with silver nitrate in aqueous solution. We have shown in the previous work[5] that graft polymers of poly(propylene sulfide) are obtained by reaction between cellulose alcoholate and propylene sulfide. The present work deals with the adsorption of iodine, silver nitrate, and mercuric chloride on cellulose membranes grafted with polypropylene sulfide. The cellulose membranes used were of high poly(propylene sulfide) content and did not contain mercaptan groups. These graft polymers may be of interest as membranes, ion-exchange resins, and in their complexed form as chemical reagents.

EXPERIMENTAL

Poly(propylene sulfide)-grafted cellulose membranes were prepared as previously described.[5] The cellulose membrane used was dialyzer tubing, No. 4465-A2 from Arthur H. Thomas Company.

Adsorption of Iodine from Aqueous Solution

Grafted cellulose membrane (0.120 g) was kept in standard iodine solution (BDH) (50 ml) at constant temperature for the required length of time. The total amount of iodine taken up by the membrane was determined by titrating an aliquot of the iodine solution with standard thiosulfate solution. The amount of iodine that was adsorbed by complexation was determined by titrating the membrane with thiosulfate. The difference between these two titrations gives the amount of iodine which reacted with the membrane.

Adsorption of Iodine from Saturated Iodine Atmosphere

Grafted cellulose membrane (0.120 g) was kept in saturated iodine atmosphere, at constant temperature. The total amount of iodine taken up by the grafted membrane was determined from its weight increase, that of complexed iodine was determined by titration, while the amount of reacted iodine was calculated from the difference.

Adsorption of Silver Nitrate and Mercuric Chloride

Grafted cellulose membrane (0.090 g) was kept in standard silver nitrate and mercuric chloride solution at constant temperature, for the required amount of time. The amount of complexed silver nitrate was determined by titration of the solution with standard ammonium thiocyanate and from weight increase of the grafted membrane. Adsorption of mercuric chloride was determined from weight increase of the grafted membrane.

RESULTS

Adsorption of Iodine by the Graft Polymer

The adsorption of iodine by poly(propylene sulfide) grafted on cellulose membranes was investigated both in solution and in the gas phase. The amount of iodine which interacted with the polymer in aqueous solution was determined from the decrease of the iodine solution concentration. It was found that most of the iodine that was taken up from solution was adsorbed as a result of complex formation with the graft polymer and could be titrated by thiosulfate, while the other part reacted with the graft polymer and could not be recovered.

The amount of iodine which was taken up from the iodine solution by the graft polymer increased with time (Fig. 1). With a graft polymer containing 48% poly(propylene sulfide) and an 0.1*N* aqueous iodine solution, a maximum value of 7.3×10^{-3} mmole I_2/g graft polymer was taken up after 5 hr. In a control experiment with ungrafted cellulose membrane it was found that the iodine that was taken up from solution by the cellulose was much lower, 2.0×10^{-6} mmole I_2/g. Therefore the adsorption of iodine by the cellulose in the graft polymers was neglected. Out of the iodine that was taken up from solution by the graft polymer, that part which was adsorbed by complexation reached a maximum value in a short reaction time and later decreased, being accompanied by an increase in the amount of iodine which reacted with the graft polymer (Fig. 1).

Graft polymers having different poly(propylene sulfide) contents were compared as regards their iodine adsorption from 0.1*N* iodine solution (Table I). A molar excess of iodine to the propylene sulfide units was used. The amount of complexed iodine increased with increasing the polypropylene sulfide content, but the increase was not linear. Thus a graft containing 23% polypropylene sulfide adsorbed 2.36 mmole I_2/g graft, while that

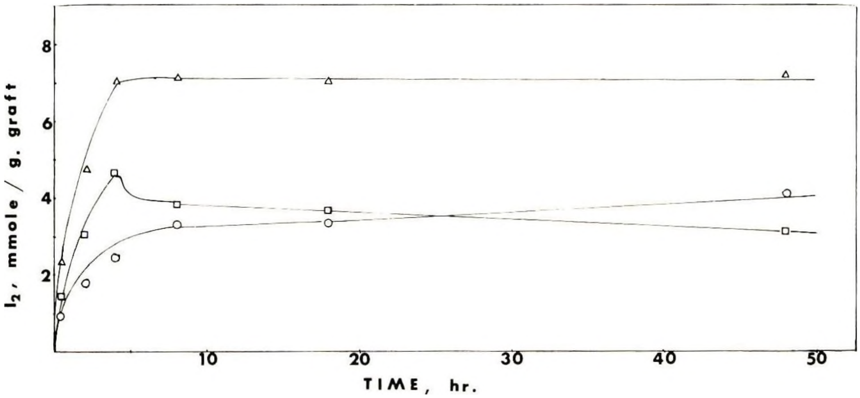


Fig. 1. Time dependence of iodine adsorption from aqueous solution: (△) total iodine taken up; (□) adsorbed iodine (○) reacted iodine. Graft polymer of 48% poly(propylene sulfide) content was used.

TABLE I
Dependence of Iodine Adsorption on Poly(propylene Sulfide) Content of the Graft Polymer[a]

Expt. no.	Poly-(propylene sulfide) content, %	Iodine (I_2), mmole/g			[Iodine]/[Propylene sulfide segment]		
		Reacted	Complexed[b]	Total	Reacted	Complexed	Total
210	23	1.83	2.36 (56.3)	4.19	0.59	0.76	1.35
205	37	2.64	3.41 (56.4)	6.05	0.53	0.68	1.21
206	43	2.83	3.82 (57.4)	6.65	0.48	0.66	1.14
208	48	4.16	3.14 (63.0)	7.30	0.64	0.48	1.12
215	54	3.53	4.30 (55.0)	7.83	0.48	0.59	1.07
216	62	2.86	4.42 (60.7)	7.28	0.34	0.53	0.87
217	68	3.53	4.81 (57.5)	8.34	0.39	0.52	0.91

[a] Experimental conditions: graft polymer (0.120 g) was allowed to stay in aqueous 0.1*N* iodine solution (50 ml) for 18 hr at room temperature. Complexed iodine was determined by titration with thiosulfate.

[b] The values given in the parentheses are the percentages of complexed iodine calculated from the total iodine taken up.

containing 68% adsorbed only 4.81 mmole. Nearly 60% of the iodine taken up from the iodine solution was complexed by the graft polymer and the polypropylene sulfide content of the graft polymer did not change significantly this value (Table I). It can be seen from the molar ratio of complexed I_2 to propylene sulfide units in the graft polymer that most sulfide bonds participated in complex formation. This molar ratio was found to decrease with increase in poly(propylene sulfide) content of the graft polymers.

The amount of iodine that reacted with the graft polymer increased with increasing the poly(propylene sulfide) content of the graft. About 40%

TABLE II
Degradation of the Graft Polymers in Aqueous Iodine Solution[a]

Expt. no.	Poly (propylene sulfide) content, %	Reacted iodine, mmole/g	Weight loss, %	
			Grafted membrane	Poly (propylene sulfide)
210	23	0.59	19	83
177	28	0.54	23	81
205	37	0.53	31	83
190	42	0.49	36	87
206	43	0.48	37	87
182	49	0.42	36	74
208	48	0.64	39	81
215	54	0.48	46	86
216	62	0.34	48	78

[a] Experimental conditions as in Table I.

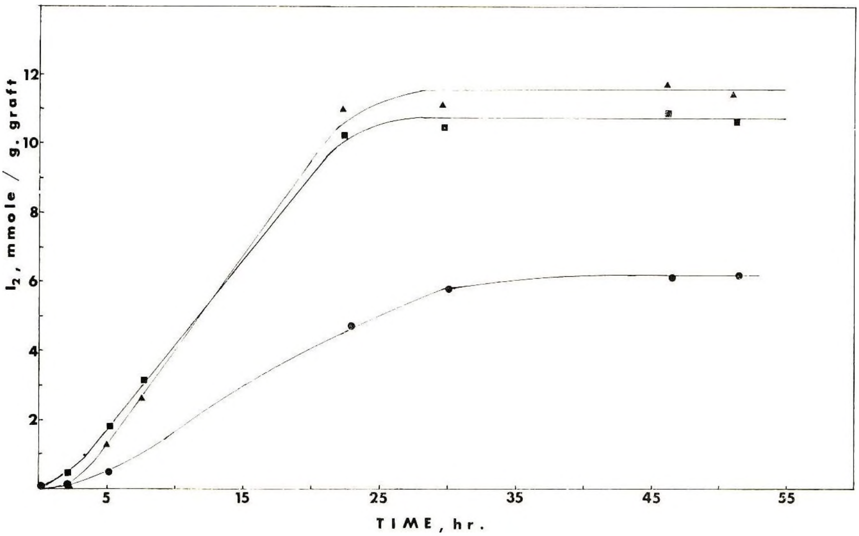


Fig. 2. Adsorption of gaseous iodine by graft polymers of various poly(propylene sulfide) contents: (▲) 51%; (■) 46%; (●) 26%.

of the iodine taken up from the iodine solution reacted with the graft polymer.

It was found that partial degradation of the polymers occurred during their interaction with the aqueous iodine solution (Table II). This degradation was accompanied by weight loss of the graft polymers, which increased with increase in the polypropylene sulfide content of the graft polymers. It should be attributed to the chemical degradation of the poly(propylene sulfide) alone, since in a control experiment with ungrafted cellulose membrane no weight loss was found.

The adsorption of iodine vapor from a saturated iodine atmosphere was investigated with graft polymers of different polysulfide contents (Fig. 2); the maximum amount of iodine taken up was reached within 30 hr. Increase in the poly(propylene sulfide) content led to an increase in the amount of iodine taken up, but the ratio of iodine to propylene sulfide units remained constant. Thus a graft polymer of 51% polysulfide content took up 11.5 mmole I_2/g graft, corresponding to a molar ratio of iodine to propylene sulfide of 1.67. A similar graft polymer of 46% poly(propylene sulfide) content took up 10.4 mmole I_2/g, corresponding to a molar ratio of 1.67, while a graft polymer of 26% polysulfide content took up 6.0 mmole I_2/g, corresponding to a molar ratio of 1.70. In a control experiment with an ungrafted cellulose membrane, it was found that under the same conditions less than 0.5×10^{-6} mmole I_2/g cellulose was adsorbed.

The desorption of the graft polymers in air at room temperature is described in Figure 3. After 400 hr, the graft polymers still contained iodine. The amount of complexed iodine and reacted iodine at the end of the desorption experiment was determined for the graft polymers containing 26%

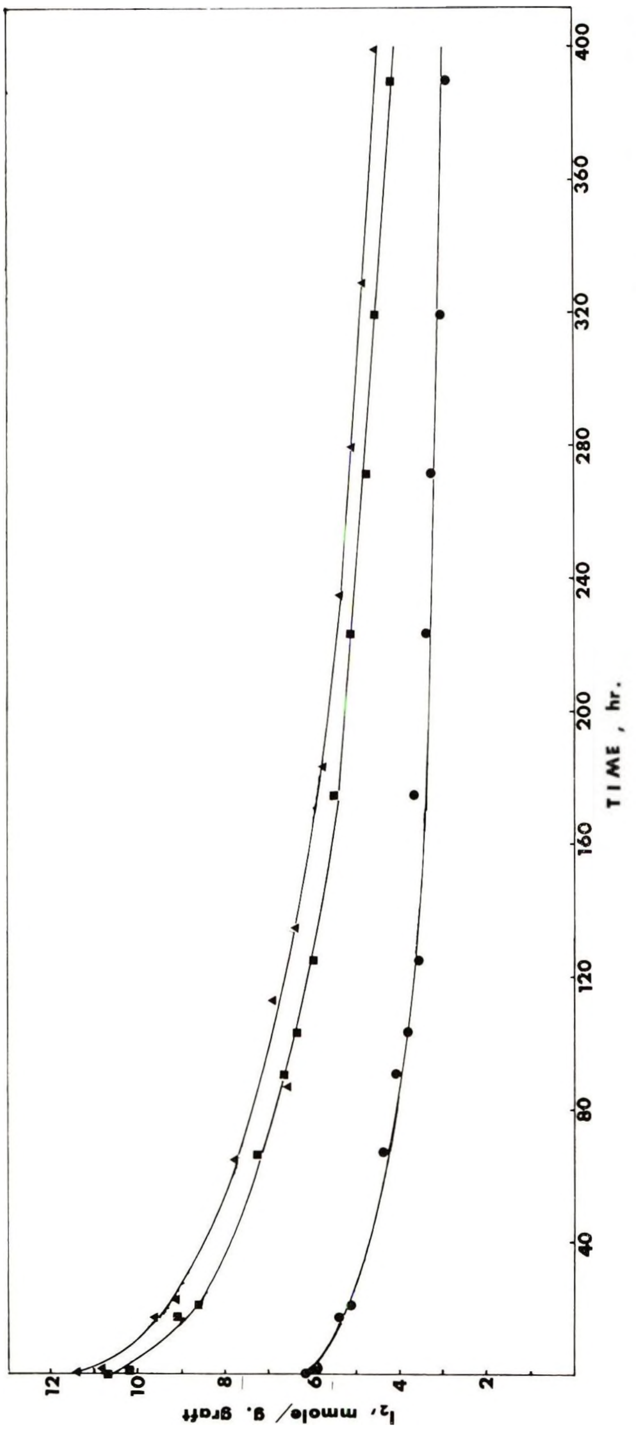


Fig. 3. Desorption of iodine in air from the graft polymers of various poly(propylene sulfide) contents: (▲) 51%; (■) 46%; (●) 26%.

and 46% poly(propylene sulfide). The total amount of iodine that remained attached to the polymers was 2.90 and 4.20 mmole/g, respectively, and out of this, the amount of reacted iodine was 0.84 and 0.37 mmole I_2/g graft, respectively. From these results it can be calculated that at least 86–96% of the iodine taken up by the graft polymer from the iodine atmosphere was adsorbed by complexation.

The stability of the iodine–graft polymer complex in different solvents was determined. A graft polymer of 51% polysulfide content was allowed to take up iodine from a saturated iodine atmosphere until the molar ratio of iodine to propylene sulfide was 0.85. The complexed graft polymer was allowed to stay in 50 ml solvent for 70 hr at 30°C, and the released iodine was determined by titration. It was found that 7.5% of the complexed iodine was released in water, 50% in benzene and 75% in alcohol.

Adsorption of Silver Nitrate by the Graft Polymers

The adsorption of silver nitrate from aqueous solution, by the graft polymers was investigated. Experiments were performed with a molar excess of silver nitrate to the propylene sulfide units. It can be seen (Table III) that within 7 min 50% of the maximum value of adsorption was obtained, and within 2 hr adsorption was almost complete. A maximum value of adsorbed silver nitrate of 3.02 mmole/g graft, corresponding to a molar ratio of silver nitrate to propylene sulfide of 0.53 was obtained. A control experiment with ungrafted cellulose membrane showed that all the silver nitrate adsorption should be attributed to the polypropylene sulfide. The adsorption of silver nitrate from solution was affected by temperature. Increase in temperature led to decrease in adsorption (Table IV).

The adsorption of silver nitrate from aqueous solutions of different concentrations by the graft polymer is given in Tables V and VI. Experiments were performed with either a molar excess of silver nitrate (Table V)

TABLE III
Silver Nitrate Adsorption (Time Dependence)[a]

Graft polymer, g	Adsorption time, hr	Adsorbed silver nitrate, g			[Adsorbed silver nitrate] / [Propylene sulfide segmer]
		From weight increase	From titration[b]	Mmole/g	
0.079	7 (min)	0.024	0.023	1.34	0.24
0.087	0.5	0.044	0.042	2.81	0.50
0.084	2.0	0.044	0.043	2.98	0.53
0.083	4.0	0.043	0.042	2.94	0.52
0.086	16.0	0.046	0.044	3.02	0.53

[a] Experimental conditions: graft copolymer containing 42% poly(propylene sulfide) was used. Adsorption was carried at 20°C, using $0.1N$ silver nitrate solution (15 ml).

[b] Determined from the decrease of the titer of the silver nitrate solution.

TABLE IV
Silver Nitrate Adsorption (Temperature Dependence)[a]

Graft polymer, g	Temperature, °C	Adsorbed silver nitrate, mmole/g[b]	[Adsorbed silver nitrate] / [Propylene sulfide segmer]
0.078	5	3.19	0.55
0.075	30	2.85	0.49
0.079	50	2.77	0.48
0.090	80	2.51	0.43

[a] Experimental conditions: graft polymers of 43% poly(propylene sulfide) content were kept in 0.1*N* silver nitrate solution (25 ml) for 22 hr.

[b] Determined from the decrease of the titer of silver nitrate solution.

TABLE V
Silver Nitrate Adsorption (Excess Silver Nitrate)[a]

Graft polymer, g	Silver nitrate, *N*	Silver nitrate equilibrium concentration, mmole/g[b]	Adsorbed silver nitrate, mmole/g[b]	[Adsorbed silver nitrate] / [Propylene sulfide segmer]
0.095	0.760	733.5	6.97	1.01
0.083	0.415	392.0	6.91	1.00
0.094	0.200	183.1	4.50	0.65
0.082	0.100	88.0	3.66	0.52
0.078	0.050	40.8	2.89	0.42

[a] Experimental conditions: graft polymer of 51.3% poly(propylene sulfide) content was used. Adsorption was carried out at 20°C for 24 hr with the use of 0.1*N* silver nitrate solution (25 ml).

[b] Determined from the decrease of the titer of the silver nitrate solution.

or a molar excess of propylene sulfide units (Table VI). In the former case a molar ratio of one between silver nitrate and propylene sulfide units was obtained on using concentrated silver nitrate solutions. In the second case the per cent of silver nitrate adsorption increased with decrease of

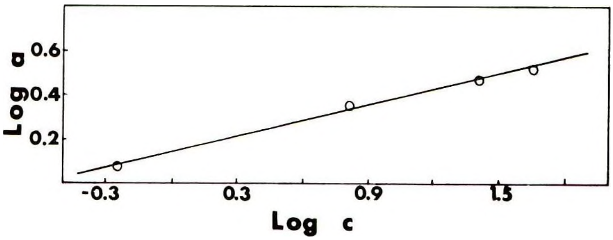


Fig. 4. Adsorption of silver nitrate. a = silver nitrate adsorbed, mmole/g graft polymer; c = equilibrium silver nitrate concentration, mmole/l.

TABLE VI
Silver Nitrate Adsorption
(Excess of Propylene Sulfide Segmers)[a]

Graft g	Silver nitrate, N	Silver nitrate equilibrium concentration mmole/g[b]	Adsorbed silver nitrate		[Adsorbed silver nitrate] / [Propylene sulfide segmer]
			mmole/g	%[c]	
0.165	0.100	45.4	3.31	54.6	0.47
0.083	0.050	25.5	2.96	48.8	0.42
0.081	0.025	6.5	2.28	74.0	0.32
0.080	0.010	0.6	1.18	94.0	0.17

[a] Experimental conditions: graft polymer of 52% poly(propylene sulfide) content was used. Adsorption was carried out at 20°C for 48 hr with the use of silver nitrate solution (20 ml).

[b] Determined from the decrease of the titer of the silver nitrate solution.

[c] Percentage of silver nitrate introduced.

silver nitrate concentration. From an 0.01N solution 94% of the silver nitrate was complexed by the graft polymer.

The adsorption at different silver nitrate concentrations (Table VI) can be described by a Freundlich-type isotherm (Fig. 4), $a = Kc^{1/n}$; a being the amount of silver nitrate adsorbed per gram adsorbent, namely grafted polypropylene sulfide; c is the equilibrium concentration, and K and n are constants. In the presence of excess propylene sulfide units, K was 1.38 and $n = 4.2$, and with excess $AgNO_3$, K was 1.19 and $n = 3.71$.

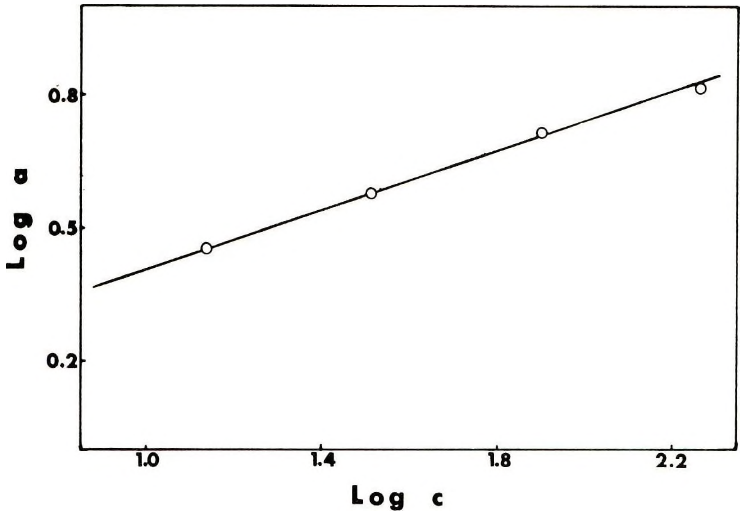


Fig. 5. Adsorption of mercuric chloride. a = mercuric chloride adsorbed, mmole/g graft polymer; c = equilibrium mercuric chloride concentration, mmole/l.

Adsorption of Mercuric Chloride by the Graft Polymers

The extent of adsorption of mercuric chloride from aqueous solution by the graft polymers was time-dependent (Table VII). After 24 hr almost all sulfide bonds participated in complex formation leading to a molar ratio of mercuric chloride to propylene sulfide units close to 1. Adsorption was also investigated at several concentrations in the presence of molar excess of mercuric chloride (Table VIII). The adsorption can be described by a Freundlich-type isotherm (Fig. 5).

TABLE VII
Mercuric Chloride Adsorption
(Time Dependence)[a]

Reaction time, hr	Adsorbed mercuric chloride, mmole/g[b]	[Adsorbed mercuric chloride] / [Propylene sulfide segmer]
5 (min)	0.74	0.11
0.25	1.16	0.17
0.50	1.73	0.25
1.00	2.79	0.40
6.00	5.25	0.76
24.00	6.58	0.96

[a] Experimental conditions: graft polymer (0.086 g) of 51% poly(propylene sulfide) content was left in 0.206M mercuric chloride solution at 20°C.

[b] Calculated from weight increase.

TABLE VIII
Mercuric Chloride Adsorption[a]

Graft polymer, g	Mercuric chloride, M	Mercuric chloride equilibrium concentration, mmole/l.[b]	Adsorbed mercuric chloride, mmole/g[c]	[Adsorbed mercuric chloride] / [propylene sulfide segmer]
0.087	0.024	13.71	2.84	0.41
0.085	0.046	32.56	3.79	0.55
0.089[d]	0.086	70.63	4.82	0.70
0.091	0.086	69.00	4.69	0.68
0.084	0.097	79.72	5.13	0.75
0.086	0.206	183.00	6.58	0.96

[a] Experimental conditions: graft polymer of 51% poly(propylene sulfide) content was kept for 24 hr at 20°C in mercuric chloride solution (25 ml).

[b] Determined from weight increase of the graft polymer.

[c] Determined from weight increase.

[d] Experiment was performed at pH 6.

DISCUSSION

Cellulose membranes grafted with poly(propylene sulfide) showed high adsorption capacity for iodine from aqueous solution and from the gas phase. Adsorption is by complexation of the iodine with the sulfide bond of the graft polymer, and it is expected that increase in poly(propylene sulfide) content will lead to an increase in complexed iodine, as found. It was found that from aqueous solution (contrary to adsorption from the gas phase) the amount of the sulfide bonds participating in complexation decreased with increase in poly(propylene sulfide) content. This may be attributed to a decrease in the accessibility of the grafted cellulose membrane with increase in its poly(propylene sulfide) content. With gaseous iodine, accessibility of the reagent is expected to be less hindered.

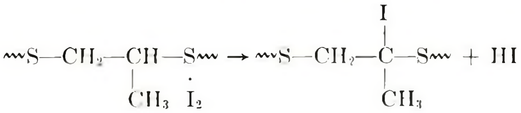
The highest molar ratio of complexed iodine to propylene sulfide units, in the graft obtained in aqueous solution was 0.76. This ratio indicates that in the complex approximately one iodine molecule (I_2) is complexed by the sulfur of the sulfide bond. The results obtained in the adsorption of gaseous iodine, indicate that under these conditions complexation of another iodine molecule takes place. From the high molar ratio obtained (1.70) it can be seen that most sulfide bonds were complexed with two iodine molecules. Such complexes of iodine are known.[6]

The extent of complexation varies with the solvent in which the adsorption is carried out. Best results were obtained in the absence of solvent. The iodine–poly(propylene sulfide) graft polymer complex is rather stable in water but is less stable in organic solvents such as methanol and benzene, i.e., solvents which have high solvation or complexation for iodine.

The complexation reaction with iodine was accompanied by degradation of poly(propylene sulfide). This degradation led to scission of the grafted side chains, and thus to a weight decrease of the graft polymer. A possible route for the degradation reaction is described below. It is known that halogen complexed by sulfur can migrate to a neighboring carbon atom and lead to substitution accompanied by hydrogen halide evolution.[2c] Thus the complex of chlorine with dimethyl sulfide was converted to its α-chloro derivative and that of bromine diphenyl sulfide was converted to its *p*-bromo derivative.[2a]

$$CH_3SCH_3 + Cl_2 \rightarrow (CH_3)_2SCl_2 \rightarrow CH_3—S—CH_2Cl + HCl$$

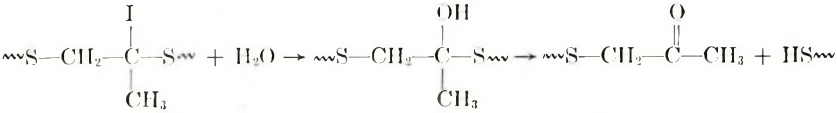
In the case of the iodine interaction with the graft polymer there was, besides the iodine which was adsorbed by complex formation, iodine which reacted with the graft polymer. The iodine may have reacted either by direct substitution, quite possibly at the tertiary carbon atom, which is the most active site in poly(propylene sulfide), or by migration of the iodine in the sulfur complex to this site leading to a segmer of halosulfide.



$$\sim S—CH_2—\underset{CH_3}{\underset{|}{CH}}—\underset{I_2}{\underset{\cdot}{S}}\sim \;\rightarrow\; \sim S—CH_2—\overset{I}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}—S\sim + HI$$

The fact that the amount of iodine complexed by the graft in water passed through a maximum, while the amount of reacted iodine increased with time, may suggest that the complexed iodine may have disappeared, in such a reaction.

Now the substituted iodine in the poly(propylene sulfide) chain is both in an α- and β- position relative to a sulfur atom. β-Halosulfides are known to undergo rapid hydrolysis,[2b] the phenomenon being attributed to the formation of episulfonium ion in a rate determining step. The iododerivative of the poly(propylene sulfide) is therefore expected to be hydrolyzed in water to the α-hydroxysulfide derivative, which in turn is unstable in water and can hydrolyze with rupture of the sulfide bond, forming a mercaptan and an aldehyde or ketone:



$$\sim\text{S}-\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{I}}{\text{C}}}-\text{S}\sim + \text{H}_2\text{O} \rightarrow \sim\text{S}-\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\text{S}\sim \rightarrow \sim\text{S}-\text{CH}_2-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{CH}_3 + \text{HS}\sim$$

Such a reaction will lead to scission of the poly(propylene sulfide) grafted side chains from the cellulosic backbone. The fact that the degradation was especially manifested only in the experiments performed in water supports the suggested scheme for the degradation.

The graft polymers based on the cellulosic membranes adsorbed silver nitrate and mercuric chloride. The complexation yields were high, and in concentrated solutions all sulfide bonds in the graft polymer participated in complexation irrespective of the heterogenous nature of the reaction, leading to molar ratios of metal salt to sulfur in the graft polymer of 1:1. This complexation is an equilibrium reaction, and it could be described by a Freundlich-type isotherm. With a molar excess of metal salt, the K value of silver nitrate adsorption was 1.19 and of mercuric chloride absorption was 1.20. The n values determined were 3.71 and 3.03, respectively.

The fact that the complexation reaction is an equilibrium one, then indicates that an increase in the molar ratio of propylene sulfide units in the graft polymer to silver nitrate could lead to increase in complexation. This in fact was found, and experiments conducted in the presence of such a molar excess showed that the per cent of complexed silver nitrate increased with decrease in its concentration. Thus from $0.01N$ solution, 94% of the silver nitrate was complexed.

In conclusion, the graft polymers of poly(propylene sulfide) on cellophane have been shown to have good adsorption for iodine and for metal salts such as silver nitrate and mercuric chloride. These properties of the grafted cellulose membranes may be of practical interest. Further studies in this area are in progress.

References

1. E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Vol. II, Chemical Publishing Co., New York, 1960, p. 47.
2. S. Patai, Ed., *The Chemistry of the Ether Linkage*, Interscience, New York-London, 1967, (a) p. 598; (b) p. 591.
3. S. H. Hastings, *Anal. Chem.*, **25**, 420 (1953).
4. G. Champetier and F. Hennequin-Lucas, *C. R. Acad. Sci.* (Paris), **252**, 2785 (1961).
5. E. Cohen, Y. Avny, and A. Zilkha, *J. Polym. Sci. A-1*, **9**, 1471 (1971).
6. F. Feigel and A. Bondi, *Monatsh. Chem.*, **53**, 508 (1929).

Received December 1, 1970

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Polymerization of 4-Vinylpyridinium Salts. III. A Clarification of the Mechanism of Spontaneous Polymerization

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Synopsis

The mechanism of the spontaneous polymerization of 4-vinylpyiridine on quaternization or protonation has been investigated. Results indicate that initiation is caused by the nucleophilic attack of 4-vinylpyridine on the double bond of 4-vinylpyridinium ion. It was shown that halide ions do not contribute significantly to the initiation. In the case of acid salts of 4-vinylpyridine a hydrogen-transfer polymerization occurred to give an ionene polymer with pyridinium units in the main chain. The "matrix" polymerization of 4-vinylpyridine on poly(phosphoric acid) or poly(acrylic acid) also resulted in ionene formation. Conditions under which stable 4-vinylpyridinium salts can be obtained are discussed.

INTRODUCTION

The spontaneous polymerization of 4-vinylpyridine upon quaternization or protonation to form the corresponding poly-4-vinylpyridinium salt has been of considerable interest.[1-9] Previous investigations of these reactions indicated that stable 4-vinylpyridinium salts are not normally obtained. Kabanov et al. reported[1] that the spontaneous polymerization resulting from the reaction of 4-vinylpyridine with alkyl halides was unaffected by free-radical inhibitors, that neither acrylonitrile nor styrene were incorporated into the polycation, and that the resulting polymer contained no unquaternized pyridine groups. It was proposed that spontaneous polymerization resulted from the addition of the counterion to the β-position of the double bond of the 4-vinylpyridinium walt to yield a highly resonance stabilized zwitterion (Ia, R = alkyl or H). Propagation to form the poly-4-vinylpyridinium salt was considered to occur by the specific addition of

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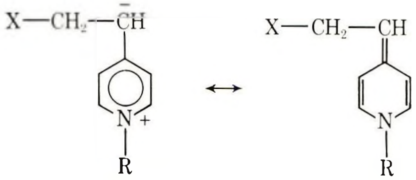
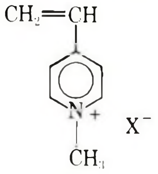


I a, X = counterion
b, X = 4-vinylpyridinium

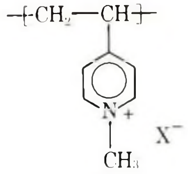
I to a 4-vinylpyridinium ion, thereby maintaining a resonance stabilized zwitterionic endgroup.[1]

It has also been suggested that the spontaneous polymerization of 4-vinylpyridine upon quaternization could result from a charge-transfer polymerization between neutral vinylpyridine and quaternized vinylpyridine.[10] The neutral pendent pyridine functions were then believed to be quaternized after their incorporation into the polymer.

Recently, however, an alternative method of initiation was suggested for the spontaneous polymerization of 4-vinylpyridine upon quaternization. In a study of the quaternization of 4-vinylpyridine by methyl *p*-toluenesulfonate we were able to isolate the stable monomeric salt 4-vinyl-*N*-methylpyridinium *p*-toluenesulfonate (VMPTS, IIa) from the initial stage of the reaction. As the reaction progressed, spontaneous polymerization to give IIIa occurred. An NMR study showed that although VMPTS was stable



II

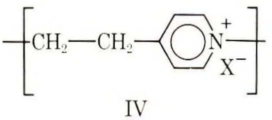


III

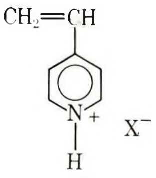
a, $X = p\text{-}CH_3C_6H_4SO_3^-$
b, $X = CH_3SO_4^-$
c, $X = I^-$

in DMSO-d_6, polymerization could be initiated by the addition of pyridine. From these results it was suggested that the spontaneous polymerization was caused by the attack of unquaternized 4-vinylpyridine on the β-position of the double bond of a 4-vinylpyridinium ion to give a zwitterionic propagating species (Ib). The proposed initiation step was supported by the synthesis of a dimeric model compound from the addition of pyridine to VMPTS.[11]

Since acid salts of 4-vinylpyridine were expected to polymerize by a similar mechanism, the spontaneous polymerization of 4-vinylpyridine by strong acids in aqueous solution was also studied. In contrast to previously reported results[1] it was found that poly-4-vinylpyridinium salts did not form.[12] Instead, either ionene polymers with the pyridinium units in the main chain (IV) or monomeric vinyl salts (V) were obtained. The assignment of structure IV, a poly(1,4-pyridiniumdiyl ethylene salt), was confirmed by the independent synthesis of IVd from the intermolecular con-



IV



V

a, $X = CF_3COO^-$
b, $X = I^-$
c, $X = NO_3^-$
d, $X = Cl^-$

densation of 4-(2-chloroethyl)pyridine and by the preparation of a model dimeric compound.[12]

This investigation is concerned with the further elucidation of the mechanism of spontaneous polymerization of 4-vinylpyridinium salts and of the structure of the resulting polymers. The syntheses and stabilities of several monomeric 4-vinylpyridinium salts are also described.

EXPERIMENTAL

4-Vinyl-*N*-Methylpyridinium Methyl Sulfate (IIb)

To a solution of 3 ml (32 mmole) of dimethyl sulfate in 70 ml of anhydrous tetrahydrofuran (THF) at −10°C was added 1 ml (10 mmole) of 4-vinylpyridine. After 24 hr at −10°C the crystals were filtered, washed with THF and with ether, and then dried for 12 hr *in vacuo* at 25°C yielding 1.1 g (50%) of colorless needles, mp 73–75°C. NMR (D_2O) showed δ 8.8 and 8.0 (4H, 2*d*, $J = 6$ Hz, pyridinium CH), 7.0, 6.4, and 6.0 (3H, 3*d* of *d*, $J_{\text{gem}} = 1$ Hz, $J_{cis} = 10$ Hz, $J_{trans} = 18$ Hz, $-CH{=}CH_2$), 4.3 (3H, *s*, $N{-}CH_3$) and 3.8 (3H, *s*, $CH_3SO_4^-$).

ANAL. Calcd for $C_9H_{14}NSO_4$: C, 46.74%; H, 5.66%; N, 6.06%; S, 13.86% Found: C, 46.54%; H, 5.86%; N, 6.03%; S, 13.69%.

4-Vinyl-*N*-methylpyridinium Iodide (IIc)

To 5 ml (81 mmole) of iodomethane in 75 ml of dry 1,2-dimethoxyethane at −10°C was added 1 ml (10 mmole) of 4-vinylpyridine. After 16 hr at −10° the yellow methiodide crystals were filtered, washed with dimethoxyethane and with ether and then dried, yielding 656 mg (25%) of large yellow needles, mp 137°C with polymerization. NMR (D_2O) showed δ 8.8 and 8.0 (4H, 2*d*, $J = 6$ Hz, pyridinium CH), 7.0, 6.4, and 6.0 (3H, 3*d* of *d*, $J_{\text{gem}} = 1$ Hz $J_{cis} = 10$ Hz, $J_{trans} = 18$ Hz, $-CH{=}CH_2$) and 4.3 (3H, *s*, $N{-}CH_3$).

ANAL. Calcd for $C_8H_{10}NI$: C, 38.87%; H, 4.08%; N, 5.67%; I, 51.36%. Found: C, 38.84%; H, 4.12%; N, 5.62%; I, 51.38%.

4-Vinylpyridinium Nitrate (Vc)

To 1 ml (15 mmole) of 70% HNO_3 in 50 ml. of THF at 0°C was added dropwise with stirring a solution of 0.5 ml (5 mmole) of 4-vinylpyridine in

THF. The crystals were filtered, washed with THF and with ether, and then dried *in vacuo*, giving a quantitative yield of 4-vinylpyridinium nitrate, mp 155°C. NMR (D_2O) gave δ 8.8 and 8.0 (4H, 2*d*, $J = 6$ Hz, pyridinium CH), and 7.0, 6.4, and 6.0 (3H, 3*d* of *d*, $J_{gem} = 1$ Hz, $J_{cis} = 10$ Hz, $J_{trans} = 18$ Hz, —CH═CH₂).

ANAL. Calcd for $C_7H_8N_2O_3$: C, 50.00%; H, 4.79%; N, 16.66%. Found C, 49.89%; H, 4.85%; N, 16.80%.

4-Vinylpyridinium Iodide (Vb)

This monomeric salt was prepared by a procedure similar to the above with 1 ml (7.5 mmole) of 57% hydriodic acid. A quantitative yield of 4-vinylpyridinium iodide was obtained, mp 175°C with polymerization. NMR (D_2O) gave δ 8.8 and 8.0 (4H, 2*d*, $J = 6$ Hz, pyridinium CH), and 7.0, 6.4, and 6.0 (3H, 3*d* of *d*, $J_{gem} = 1$ Hz, $J_{cis} = 10$ Hz, $J_{trans} = 18$ Hz, —$CH{=}CH_2$).

ANAL. Calcd for C_7H_8NI: C, 36.23%; H, 3.04%; N, 6.04%; I, 54.69%. Found: C, 36.14%; H, 3.26%; N, 6.10%; I, 54.83%.

NMR Studies of 4-Vinyl-*N*-methylpyridinium Salts

The effects of salts on the stability of 4-vinyl-*N*-methylpyridinium methyl sulfate (IIb) were investigated. NMR spectra revealed that no polymerization occurred after 2 weeks when 2.15 mmole of either NaBr, NaI, $NaClO_4$, or Na_2SO_4 was added to a solution of 50 mg. (2.15 mmole) of IIb in DMSO-d_6. The monomer was stable for this time in the absence of added salts. When one equivalent of NaCN was added to a DMSO-d_6 solution of IIb, no monomer could be detected after 30 min. A similar study with 5 mole-% NaCN showed that 70% polymerization had occurred after 16 hr.

The stability of 4-vinyl-*N*-methylpyridinium iodide in DMSO-d_6 and in D_2O was also investigated. It was found that no polymer formation could be observed after 2 weeks.

1-Methyl-4-benzhydrylidine-1,4-dihydropyridine (VIa).

This pyridone methide was prepared by a modification of the procedure of Chichibabin and Benevolenskaya.[13] Diphenyl-4-pyridylmethane was quaternized quantitatively with dimethyl sulfate in benzene. The precipitate was dissolved in water and added to 2N NaOH. The precipitated methide was extracted into ether, the solution was dried over Na_2SO_4 and Na_2CO_3, and the ether was removed *in vacuo*. The resulting oil was dissolved in 300 ml ethanol containing 1 g NaOH and cooled to −10°C, giving orange needles, mp 109–110°C (lit.[13] mp 112–113°C). NMR (DMSO-d_6) gave δ 7.05 (10H, *s*, phenyl CH), 6.2 and 5.75 (4H, 2*d*, $J = 8$ Hz, dihydropyridine CH) and 2.95 (3H, *s*, N—CH_3).

Matrix Polymerization of 4-Vinylpyridine on Poly(phosphoric Acid)

To 0.5 ml (5 mmole) of 4-vinylpyridine in 5 ml H_2O was added 275 mg (4.9 meq) of poly(phosphoric acid) (approx. $H_6P_4O_{13}$) in 5 ml of H_2O. After 3 days the solution was lyophilized, giving a white powder which was shown to be ionene polyphosphate. NMR (D_2O) gave δ 7.0–9.1 (4H, br, pyridinium CH), and 5.0 (2H, br, N—CH_2). The α-methylene hydrogens undergo complete deuterium exchange in less than 30 min.

Poly(acrylic Acid)

Poly(acrylic acid) was obtained by heating a degassed 50% dioxane solution of freshly distilled acrylic acid containing 1 mole-% benzoyl peroxide at 60°C for 24 hr. The polymer was purified by exhaustive dialysis against deionized water followed by lyophilization. The molecular weight of the poly(acrylic acid), determined viscometrically in 2*N* NaOH at 24°C by using the formula, $[\eta] = 1.5 \times 10^{-3} M^{0.54}$, was 150,000.[14]

Matrix Polymerization of 4-Vinylpyridine on Poly(acrylic Acid)

To a solution of 100 mg (1.4 mmole) of poly(acrylic acid) in 10 ml of H_2O was added 0.105 g (1 mmole) of 4-vinylpyridine. After 3 hr the solution was opaque, and a white precipitate had formed. Upon addition of 150 mg of $NaHCO_3$ the solution cleared, and the precipitate redissolved giving a viscous, colorless solution. The solution was placed on a column of the strongly basic anion exchange resin Dowex 1-X8, 100–200 mesh in the chloride form. The sample was eluted with 200 ml of water, the eluate was lyophilized, and the resulting solid was dried *in vacuo*. In this procedure the polyacrylate was not removed because it was excluded from the anion-exchange resin.[15] NMR showed this material to contain 1 equivalent of ionene polymer to 1.4 equivalents of polyacrylate.

Polymerization of 4-Vinylpyridine by Monomeric Acids

Ionene formation in a solution of 4-vinylpyridine in acetic acid (ca. 10%) was followed by NMR spectroscopy. Initially, only 4-vinylpyridinium ion was observed. However, after 80 min, 80% conversion to ionene polymer was observed. The NMR spectrum of a solution of 4-vinylpyridine in trifluoroacetic acid indicated only 4-vinylpyridinium ion was present after 3 days.

Poly-4-vinylpyridine

To 1 ml (36 meq) of 96% H_2SO_4 was added 0.5 ml (5 mmole) of 4-vinylpyridine. After 15 min the reaction mixture was added to 100 ml H_2O and stirred for 2 days until the polymer dissolved. The pH of the solution was adjusted to 9 by addition of Na_2CO_3. The precipitated poly-4-vinylpyridine was separated by filtration and purified by two reprecipitations from methanol to ether. NMR (DMSO-d_6) showed δ 8.2 (2H, br, pyridinium

CH), 6.7 (2H, br, pyridinium CH), and 2.6–1.0 (3H, br, backbone CH). Poly-4-vinylpyridine could also be obtained by addition of 4-vinylpyridine to a heterogeneous mixture of benzene or nitromethane and excess sulfuric acid, followed by purification as described above.

Deuterium Exchange

The deuterium exchange of the α-methylene protons of the ionene prepared from 4-vinylpyridine and trifluoroacetic acid in nitromethane was studied as a 10% solution in D_2O under various conditions. A study of the effect of temperature revealed that complete exchange of the α-methylene protons occurred after 24 hr at 80°C. The characteristic absorptions of the vinyl endgroup also disappeared, and two broad absorptions at 6.0δ and 6.4δ of the shape expected for an α-*d*-vinyl group were observed.[16] In 1*N* DCl, the NMR spectrum remained unchanged after 3 days. In 0.5*M* Na_2CO_3 in D_2O, the ionene was degraded within 48 hr to a gum which contained 4-vinylpyridine. When 20 mole-% of 4-vinylpyridine was added to the ionene solution, 50% deuterium exchange occurred after 39 hr. The formation of 4-vinylpyridinium-α-*d* groups was also believed to occur in this case.

RESULTS AND DISCUSSION

Nucleophilic Addition: Initiation

The initiation of the spontaneous polymerization of 4-vinylpyridinium salts has been considered to arise from a nucleophilic attack on the activated double bond. Initiation by this process is supported by the reported additions of nucleophiles such as cyanide,[17] sulfide,[18] sulfite,[17] thiourea,[19] and primary, secondary, and tertiary amines[20,21] to 2- and 4-vinylpyridine under acidic catalysis. Kabanov et al. have suggested that the spontaneous polymerization of 4-vinyl-*N*-methylpyridinium halides was initiated by the nucleophilic attack of the halide ion on the activated double bond.[1]

In order to investigate the proposed initiation mechanism of Kabanov et al., the additions of various anions to 4-vinyl-*N*-methylpyridinium methyl sulfate (VMPMS, IIb) were investigated by NMR spectroscopy. We have previously shown that 4-vinyl-*N*-methylpyridinium *p*-toluenesulfonate can be obtained in low yield from the reaction of 4-vinylpyridine and methyl *p*-toluenesulfonate in benzene at room temperature.[11] This yield can be improved greatly by doing the reaction in anhydrous tetrahydrofuran (THF) for 1 week at −10°C. It was also found that a 50% yield of VMPMS could be obtained from the reaction of 4-vinylpyridine and dimethyl sulfate in THF for 1 day at −10°. The latter salt was utilized for the nucleophilic addition studies because it was more readily available and because the NMR absorption of the counterion did not obscure the spectrum of either the 4-vinyl-*N*-methylpyridinium ion (II) or the resulting polycation (III).

The NMR spectrum of a 10% solution of VMPMS showed no observable polymerization after 2 weeks at room temperature. This is consistent with the previously reported stability of VMPTS.[11] When 1 equivalent of NaBr, NaI, Na_2SO_4, or $NaClO_4$ was added to a 10% solution of VMPMS in DMSO-d_6 or D_2O no polymerization could be detected after 2 weeks. However, when 1 equivalent of NaCN was added to the DMSO-d_6 solution, all monomer was consumed within $^1/_2$ hr. When only 0.05 equivalent of NaCN was added, 70% conversion to poly-4-vinyl-*N*-methylpyridinium methyl sulfate (IIb) had occurred after 16 hr.

The fact that no addition could be observed with either bromide or iodide ion militates against the initiation mechanism suggested by Kabanov et al. Although it may appear unusual that halide ions do not add to the double bond, it should be noted that the reactivities of nucleophiles in S_N2 substitution and in addition to sp^2-carbon have been shown to be unrelated.[22–24] In particular, it has been noted that nucleophilic reactivity in addition reactions corresponds closely with basicity, with weak bases such as iodide and bromide being unreactive.[22–24] Furthermore, it was recently shown for the polymerization of several vinyl monomers that the initiation ability of anions increased with their basicity.[25] From the results of this investigation and previous studies it appears that the reactivity of nucleophiles toward 4-vinylpyridinium salts is also related to their basicity.

Since bromide and iodide are much weaker bases than 4-vinylpyridine, the spontaneous polymerization of 4-vinyl-*N*-alkylpyridinium halides can also be considered to be caused by attack of unquaternized 4-vinylpyridine.[11] Consequently, it could be expected that an alkyl halide salt, once formed and removed from excess 4-vinylpyridine, would be stable in solution. In order to investigate this possibility we have prepared 4-vinyl-*N*-methylpyridinium iodide (VMPI, IIc) and have studied its stability in solution. The methodide salt was prepared in moderate yield from the reaction of 4-vinylpyridine with excess iodomethane in dry 1,2-dimethoxyethane at −10°C. NMR studies indicate that this salt is stable in DMSO-d_6 or D_2O solution for 2 weeks.

Since the attack of iodide on the 4-vinylpyridinium ion is a reaction between two oppositely charged species to give a neutral (or zwitterionic species), the rate of reaction might be expected to increase greatly in nonpolar solvents. On the other hand, the rate of addition of pyridine to the 4-vinylpyridinium ion should be relatively unaffected by the polarity of the solvent. Although the rate of addition of iodide ion has been shown to be negligible in a polar solvent, iodide addition could become significant in nonpolar solvents. The relative rates of these additions were easily determined in dichloromethane since the methiodide monomer is slightly soluble in this solvent,* while the polymer is insoluble. When 1 mmole of pyridine was added to a solution of 1 mmole of VMPI in 35 ml of dichloromethane, 70 mg of IIIc was obtained after 1 day. However, when no pyridine was

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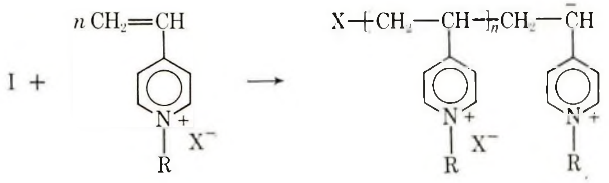
* The solubility of this monomer is probably due to the formation of a charge-transfer complex with partial neutralization of charge.

added, only 6 mg of precipitate, which may be due to the presence of trace impurities, had formed after 2 days. This difference in reactivity indicates that pyridine attack is much faster than iodide attack in both polar and nonpolar solvents.

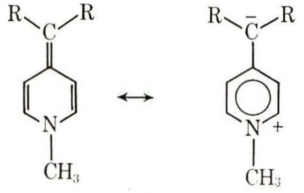
The initiation of spontaneous polymerization of 4-vinyl-*N*-alkylpyridinium salts by 4-vinylpyridine was probably not considered likely by Kabanov et al. because iodometric titration did not indicate the presence of unreacted double bonds. However, it has been established that the addition of electrophiles, such as I^+ in the iodometric titration, does not occur with electron-deficient double bonds.[26] Consequently, it is not surprising that no unreacted double bonds were detected by this method.

Propagation

The mechanism of propagation has been considered to occur from the nucleophilic addition of I to a 4-vinylpyridinium ion to continuously regenerate a zwitterionic endgroup [reaction (1)]. Since the active group is a 4-pyridine methide, the proposed propagation mechanism was investigated by utilizing 1-methyl-4-benzhydrylidine-1,4-dihydropyridine (VIa), a pyridone methide which can be obtained in a stable crystalline state. The more closely related analog of the growing chain end, VIb, has been reported to be an unstable oil which could not be purified.[27]



(1)



VIa, $R = C_6H_5$
b, $R = H$

NMR studies showed that when 2 mole-% VIa was added to a 10% solution of VMPI or VMPTS in DMSO-d_6, complete conversion to the corresponding polymers occurred within 10 min. These results support the proposed propagation step of Kabanov et al. The rapid addition of the methide is in accord with its high basicity (pK_a of 12.1 for its conjugate acid).[27] Since the zwitterion of the chain-end is a stronger base than VIa, it would be expected to add to a vinylpyridinium ion even faster. The initiation step in the spontaneous polymerization is significantly slower than the propagation step, most likely because the zwitterionic endgroup is much more basic than 4-vinylpyridine (pK_a 5.6).[5]

Charge-Transfer Polymerization

In a study of the spontaneous polymerization of 2-vinylpyridine with iodomethane, Iwatsuki et al. found that at low conversion (0.05–0.5%) the product was only 80% quaternized.[10] It was also found for a variety of partially quaternized polymers that there was a charge-transfer absorption at 360 mμ which had a maximum absorbance at 70% quaternization. From these data it was suggested that the spontaneous polymerization resulted from a charge-transfer copolymerization of 2-vinyl-*N*-methylpyridinium iodide (electron acceptor) and 2-vinylpyridine (electron donor), followed by complete quaternization of the neutral, pendent pyridine groups. This method of polymerization was also suggested for the spontaneous polymerization of 4-vinylpyridinium derivatives.

The presence of a charge-transfer band between 1,4-dimethylpyridinium ion and iodide ion has been well established.[28] It seems likely that the charge-transfer absorption noted by Iwatsuki et al. occurred from the interaction of pyridinium and iodide and not from the interaction of pyridinium and pyridine. Indeed, in poly-4-vinyl-*N*-methylpyridinium iodide, prepared by polymerization of 4-vinylpyridine with iodomethane, we have found a charge-transfer absorption at 360 mμ of 0.35 for a $5 \times 10^{-3}M$ solution, a value which is similar to that reported by Iwatsuki et al. However, in poly-4-vinyl-*N*-methylpyridinium *p*-toluenesulfonate, prepared by polymerization of 4-vinylpyridine with methyl *p*-toluenesulfonate, an absorption of only 0.02 was observed for a $5 \times 10^{-3}M$ solution.

If a charge-transfer copolymerization were operative, it could be expected that the 4-vinyl-*N*-methylpyridinium ion would undergo charge-transfer polymerization with other electron-donating vinyl monomers. Since butyl vinyl ether has been shown to participate readily in charge-transfer polymerizations as an electron donor,[29] it could be expected that this monomer would charge-transfer copolymerize with VMPI. NMR and infrared spectra indicate that no incorporation of the vinyl ether occurred when 4-vinylpyridine was quaternized with methyl iodide in butyl vinyl ether as solvent.

The lack of complete quaternization at very low conversion in the spontaneous polymerization of 2-vinylpyridine by methyl iodide would be expected if initiation occurred by attack of 2-vinylpyridine. This spontaneous polymerization is probably similar to that previously described for 4-vinylpyridine.

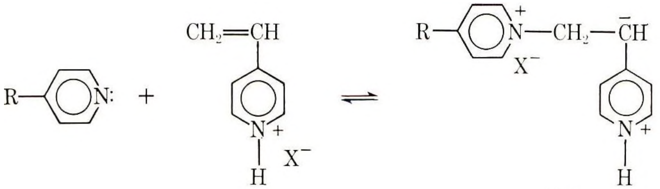
Ionene Polymers

The protonation of 4-vinylpyridine[3–8] has been reported to yield the corresponding poly-4-vinylpyridinium salt. When polymeric acids were employed, several unusual features were noted. The rate of polymerization was markedly higher than with monomeric analogs and only protonated vinylpyridinium ions reacted to form an insoluble, stoichiometric, polyacid–polybase complex. For these reasons, this reaction was termed a "matrix" polymerization.[4,5]

Since it has been shown that the reactions of 4-vinylpyridine with monomeric acids can yield ionene polymers (IV),[12] an investigation of the product obtained from the reaction of 4-vinylpyridine with poly(acrylic acid) and poly(phosphoric acid) in aqueous solution was undertaken. In both systems, NMR spectra revealed that ionene formation had occurred from these matrix polymerizations. Under the conditions employed there were no indications of the formation of poly-4-vinylpyridinium salts. It is interesting to note that Gvozdetzskii and Kabanov determined at $\overline{DP}_n$ of 20 by gel permeation chromatography for the product from the matrix polymerization of 4-vinylpyridine on poly(phosphoric acid).[7] This value is similar to the $\overline{DP}$ of 15–20 determined by NMR endgroup analysis for the ionene polymer prepared from trifluoroacetic acid and 4-vinylpyridine in nitromethane.[12]

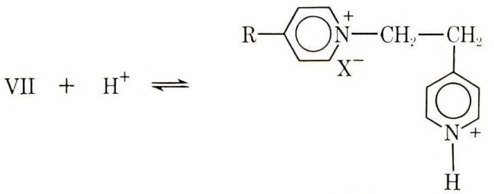
Since ionene formation occurred with poly(acrylic acid), a weak polymeric acid, the reaction of 4-vinylpyridine with a weak monomeric acid was also studied. An NMR time study of a solution of 4-vinylpyridine in glacial acetic acid revealed that 80% conversion to ionene polymer occurred after 80 min. A similar study with strongly acidic trifluoroacetic acid revealed only the presence of the 4-vinylpyridinium ion. Ionene formation can apparently occur in the presence of excess weak acid because protonation is not complete and neutral pyridine groups are present to allow polymerization to occur.

The kinetics of the polymerization of 4-vinylpyridine in various aqueous buffer systems have also been studied by Kabanov et al.[6,8] The initial rate of polymerization was found to be dependent upon the monomer concentration and the pH of the solution. The pH dependence exhibited a



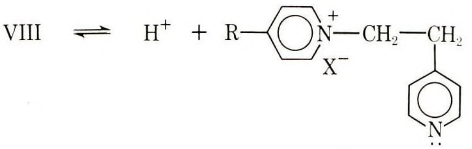
VII

(2)



VIII

(3)

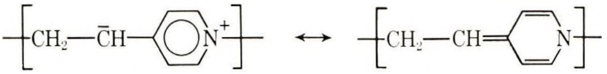


IX

(4)

sharp maximum near the pK_a of 4-vinylpyridinium ion. This result is in accord with a propagation step which involves the addition of a neutral pyridine to a vinylpyridinium ion as must occur in ionene formation [reactions (2)–(4)]. Reaction (2) is identical to the proposed initiation mechanism for the spontaneous polymerization of 4-vinyl-*N*-alkylpyridinium salts to give poly-4-vinylpyridinium salts. However, in this case reaction (3) is much faster than reaction (1), so that only VIII is formed. This compound can then lose a proton to regenerate a nucleophilic species (IX) capable of further addition.

It has been shown that the 4-methyl protons of 1,4-dimethylpyridinium iodide undergo rapid deuterium exchange.[30] Since the ionene polymers also have methylene protons adjacent to the 4-position, it was expected that these α-methylene protons would also exchange, and this exchange could indeed be observed under a variety of conditions. The facile exchange of these protons can presumably occur by the abstraction of a proton by base to give a resonance stabilized zwitterion (X). This can then undergo deuteration or elimination. The latter process leads to polymer degradation.



X

(5)

It has previously been suggested that stable 4-vinylpyridinium salts can be prepared when quaternization is rapid, when the counterion is a poor nucleophile, and when no excess 4-vinylpyridine is present.[11,12] Several 4-vinylpyridinium salts have been prepared by fulfilling these conditions. In addition to the previously reported preparation of the trifluoroacetic acid salt (Va),[12] the hydriodic (Vb) and nitric acid (Vc) salts of 4-vinylpyridine have also been prepared by addition of 4-vinylpyridine to excess acid in THF at 0°C. Ionene formation results when the acid salts are dissolved in solvents in which dissociation occurs.

The formation of poly-4-vinylpyridine was noted when 4-vinylpyridine was added to a heterogeneous mixture of excess sulfuric acid and benzene or nitromethane, followed by neutralization. The same product could also be obtained in neat sulfuric acid. It is highly unlikely that the propagating zwitterion can exist in concentrated sulfuric acid, since related compounds undergo rapid protonation.[27] In this case polymerization could be of a cationic nature.

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References

1. V. A. Kabanov, K. V. Aliev, T. I. Patrikeeva, O. V. Kargina, and V. A. Kargin, in *Macromolecular Chemistry, Prague 1965* (*J. Polym. Sci. C*, **16**), O. Wichterle and B. Sedlaček, Eds., Interscience, New York, 1967, p. 1079.

2. V. A. Kabanov, K. V. Aliev, and V. A. Kargin, *Polym. Sci. USSR*, **10**, 1873 (1968).

3. V. A. Kabanov, T. I. Patrikeeva, O. V. Kargina, and V. A. Kargin, in *Macromolec-*

ular Chemistry, Tokyo–Kyoto 1966 (*J. Polym. Sci. C*, **23**), I. Sakurada and S. Okamura, Eds., Interscience, New York, 1968, p. 357.

4. O. V. Kargina, M. V. Ul'yanova, V. A. Kabanov, and V. A. Kargin, *Polym. Sci. USSR*, **9**, 380 (1968).

5. V. A. Kabanov, V. A. Petrovskaya, and V. A. Kargin, *Polym. Sci. USSR*, **10**, 1077 (1968).

6. V. A. Kabanov, V. A. Petrovskaya, and A. N. Gvozdetzkii, paper presented at IUPAC International Symposium on Macromolecular Chemistry, Budapest, 1969; *Preprints*, II, 381.

7. A. V. Gvozdetzskii and V. A. Kobanov, *Vysokomol. Soedin.*, *B*, **11**, 377 (1969).

8. V. A. Kabanov and V. A. Petrovskaya, *Vysokomol. Soedin.*, **10**, 797 (1968).

9. T. Otsu, M. Ko, and T. Sato, *J. Polym. Sci. A-1*, **8**, 789 (1970).

10. S. Iwatsuki, T. Kokubo, K. Motomatsu, M. Tsuji, and Y. Yamashita, *Makromol. Chem.*, **120**, 154 (1968).

11. J. C. Salamone, B. Snider and W. L. Fitch, *J. Polym. Sci. B*, 9, 13 (1970); paper presented at the 160th National ACS Meeting, American Chemical Society, Chicago, Sept. 13–18, 1970; *Polym. Preprints*, **11**, No. 2, 652 (1970).

12. J. C. Salamone, B. Snider, and W. L. Fitch, *Macromolecules*, **3**, 707 (1970).

13. A. E. Chichibabin and S. V. Benevolenskaya, *Ber.*, **61B**, 547 (1928).

14. R. Sakamoto, *Nippon Kagaku Zasshi*, **83**, 386 (1962).

15. J. A. Kitchener in *Ion Exchangers in Organic and Biochemistry*, C. Calmon and T. R. E. Kressman, Eds., Interscience, New York, 1957, p. 55.

16. T. Yoshino, Y. Manabe, and Y. Kikuchi, *J. Amer. Chem. Soc.*, **86**, 4670 (1964).

17. W. E. Doering and R. A. N. Weil, *J. Amer. Chem. Soc.*, **69**, 2461 (1947).

18. C. Mansch and W. Carpenter, *J. Org. Chem.*, **22**, 936 (1957).

19. L. Bauer and L. A. Giardella, Jr., *J. Org. Chem.*, **26**, 82 (1961).

20. A. P. Phillips, *J. Amer. Chem. Soc.*, **78**, 4441 (1956), and references cited therein.

21. F. E. Cislak and L. M. Sutherland, U.S. Pat. 2,512,789 (1950).

22. T. R. Kim and Y. S. Choe, *Daehan Hwahak Hwoejce*, **10**, 158 (1966).

23. W. R. Jencks and J. Carriuolo, *J. Amer. Chem. Soc.*, **82**, 1778 (1960).

24. Z. Rappaport in *Advances in Physical Organic Chemistry*, Vol. 7, V. Grold, Ed., Academic Press, New York, 1969, pp. 72–74.

25. K. Yamaguchi and Y. Minoura, *J Polym. Sci. A-1*, **8**, 1571 (1970).

26. N. D. Cheronis and T. S. Ma, *Organic Functional Group Analysis by Micro and Semimicro Methods*, Wiley, New York, 1964, p. 379.

27. J. A. Berson, E. M. Evleth, Jr., and Z. Hamlet, *J. Amer. Chem. Soc.*, **87**, 2887 (1965), and references cited therein.

28. E. M. Kosower and J. A. Skorcz, *J. Amer. Chem. Soc.*, **82**, 2195 (1960).

29. M. Gilbert, F. F. Miller, S. J. Averill, E. J. Carlson, V. L. Folt, M. J. Heller, F. D. Stewart, R. F. Schmidt, and M. L. Trumbull, *J. Amer. Chem. Soc.*, **78**, 1669 (1956).

30. T. I. Abramovich, I. P. Gragerov, and V. V. Perekalin, *J. Gen. Chem. USSR*, **31**, 1836 (1961).

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Effect of Amines on the Ceric Ion-Initiated Polymerization of Vinyl Monomers. I. Polymerization of Acrylonitrile by Ceric Ion–Triethylamine Catalyst System

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Synopsis

The polymerization of acrylonitrile was studied in aqueous solution with ceric ammonium sulfate in the presence of triethylamine as initiator at 30, 40, and 50°C. The rate of polymerization was found to be linear with the concentration of the amine and independent of ceric ion concentration. A reaction scheme involving initial complex formation between ceric ion and the amine and subsequent disproportionation of the conplex to produce free radicals is proposed for the initiation reaction. The termination step is postulated as involving oxidation of the polymer chains by ceric ions. The results have been explained in the light of the proposed reaction scheme.

INTRODUCTION

Ceric salts in presence of various organic reducing agents have been used as effective initiators in the polymerization of vinyl monomers. Most of the investigations however, have been made with alcohols, glycols, amides etc.,[1–6] as reducing agents. No detailed study has been made with amines as reducing agents. In a previous communication[7] we reported a few preliminary observations with ceric ion-amine redox systems as initiators in vinyl polymerization. In the present paper, we report a detailed study on the aqueous polymerization of acrylonitrile initiated by ceric ammonium sulfate in presence of triethylamine.

EXPERIMENTAL

Materials

Acrylonitrile from Koch-Light Laboratories Ltd. was purified following the method of Bamford et al.[8]

Triethylamine was freed from primary and secondary amines by refluxing with acetic anhydride. It was then dried over activated alumina and distilled twice under reduced pressure.

All other reagents used were of either E. Merck G. R. grade or B. D. H. Analar grade quality and were used as received without further purification.

Ceric ammonium sulfate was dissolved in $1M$ sulfuric acid to make a stock solution of $0.05M$ in ceric sulfate. This stock solution was used to prepare the polymerization recipes.

Nitrogen used for deaeration of the experimental system was purified by passing through several columns of Fieser's solution, then through lead acetate solution, and finally dried by passing through a tower of concentrated sulfuric acid. However, while flushing aqueous solutions the nitrogen is further passed through a tower containing distilled water in order to compensate for any loss of water vapor which might occur during long flushing of the aqueous solutions.

Doubly distilled water, which was further boiled for some time to remove any dissolved gas, was used for preparing polymerization recipes and all the standard solutions.

Polymerization Procedure

The reaction vessel was a 100-ml Pyrex tube sealed at the bottom and fitted at the top with B-24 standard joints carrying inlet and outlet tubes for nitrogen. The inlet and outlet tubes were fitted with Pyrex vacuum stopcocks and were provided with a B-14 cone and a B-14 socket at their ends, respectively, so that all the vessels for a particular set of experiments could be deaerated side by side in order to maintain identical conditions.

In a typical experiment, the reaction vessels containing appropriate quantities of water, acid, and ceric solution were flushed with nitrogen for 30 min. The vessels were then disconnected from each other after closing the stopcocks of the outlet and inlet tubes and placed inside a water bath set at the required temperature (accuracy within ±0.05°C). After the vessels had attained the temperature of the bath, required amounts of the amine and monomer (which were deaerated separately) were introduced quickly, and the components were mixed by shaking. There was some induction period before the polymerization started which was indicated by the appearance of a haze in the initially clear solution. The turbidity increased as the polymerization progressed, and ultimately the polymers precipitated out. Stirring the reaction mixture hastened the precipitation of polymer which is known to affect the rate of polymerization in heterogeneous systems and has been reported by Yuguchi and Watanabe to depress the rate.[9] The reaction solution was therefore left undisturbed in our study. For calculation of the rate of polymerization, the point of appearance of the turbidity was taken as the zero point. After definite intervals, the vessels were removed from the bath, opened, and 50 cc of hydroquinone solution (1.0%) was introduced. The contents of the vessel were then poured into a large volume of water and the precipitated polymer was filtered through a weighed, sintered, gooch crucible, washed thoroughly with warm water, and dried in *vacuo* at 40–45°C to a constant weight.

RESULTS

Acrylonitrile was polymerized in aqueous solution at 30, 40, and 50°C with ceric ammonium sulfate in sulfuric acid in presence of triethylamine. A typical set of time–conversion curves for 30°C at various triethylamine concentrations (1.65×10^{-2} to 4.90×10^{-2} mole/l.) at constant ceric ion (8.3×10^{-4} mole/l.) and monomer concentrations (1.0125 mole/l.) are shown in Figure 1. The acid strength of the medium was also kept constant.

The relationship between the rates of polymerization and the corresponding amine concentrations for the three temperatures are shown in Figure 2. The rate of polymerization was found to vary linearly with the amine concentration for all the temperatures.

It can be seen from Figures 1 and 2 that while ceric ion alone can initiate polymerization, the addition of triethylamine to the reaction system increased the rate of polymerization. Further, the induction period was found to decrease with increasing amine concentration.

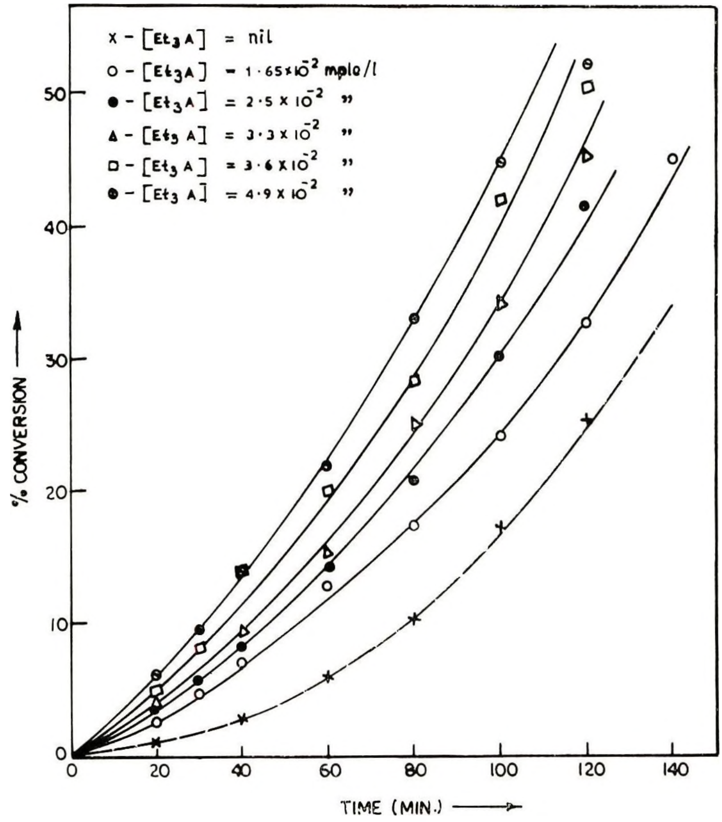

Fig. 1. Effect of triethylamine on the ceric ion-initiated polymerization of acrylonitrile at 30°C; $[\mathrm{Ce^{IV}}] = 8.3 \times 10^{-4}$ mole/l.; $[\mathrm{H_2SO_4}] = 1.66 \times 10^{-1}$ mole/l.; [M]-1.0125 mole/l.

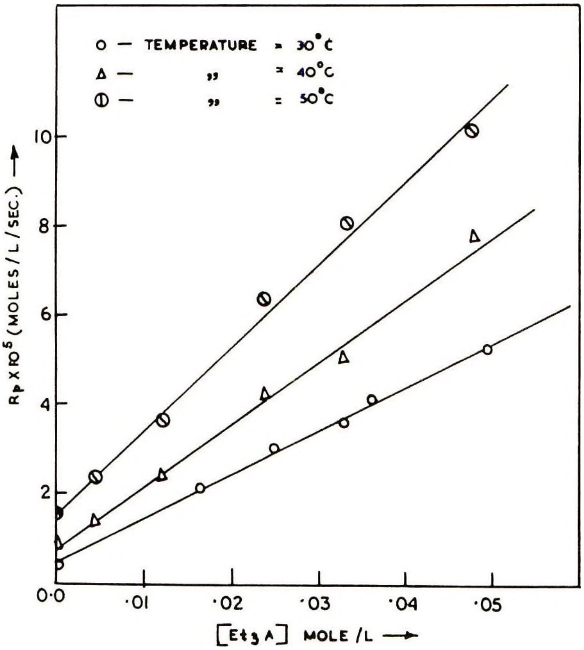

Fig. 2. Dependence of R_p on triethylamine concentration at [M] = 1.0125 mole/l.; [Ce^{IV}] = 8.3 × 10^{-4} mole/l.; [H_2SO_4] = 1.66 × 10^{-1} mole/l.

Table I shows the effect of ceric ion concentration on the rate of polymerization. It can be seen that the rate is independent of the initial ceric ion concentration under otherwise identical conditions.

The influence of monomer concentration on the rate was next studied to determine the overall polymerization rate equation. The concentration of the monomer was kept within its solubility range at the particular temperature under investigation. The results for 30, 40, and 50°C are summarized in Table II.

The effects of variations of sulfate ion and H$^+$ ion concentrations were also studied, and the results are reported in Table III and Table IV, respec-

TABLE I

Effect of [Ce^{IV}] on the Rate of Polymerization[a]

[M], mole/l.	[Ce^{IV}] × 10^4, mole/l.	Initial rate R_p × 10^6, mole/l.-sec
1.0125	0.6	35.02
	8.3	35.42
	15.0	35.86
	30.0	34.99
0.3800	0.6	9.64
	8.3	9.88
	30.0	9.90

[a] [Et$_3$A] = 3.3 × 10^{-2} mole/l.; [H_2SO_4] = 1.66 × 10^{-1} mole/l.; 30°C.

tively. The concentration of sulfate ion was varied by adding sodium sulfate. R_p was found to decrease with increasing sulfate ion concentration, whereas the reverse was true for H$^+$ ion concentration.

TABLE II
Effect of Monomer Concentration on the Rate of Polymerization[a]

Temperature, °C	[M], mole/l.	Initial rate $R_p \times 10^6$, mole/l.-sec
30	0.225	5.06
	0.380	9.90
	0.6384	18.60
	1.0125	35.42
40	0.225	8.81
	0.5062	20.76
	0.7593	35.43
	1.0125	50.23
50	0.225	11.99
	0.38	24.70
	0.5062	33.49
	0.7593	58.84
	1.0125	79.66

[a] $[\mathrm{Ce^{IV}}] = 8.3 \times 10^{-4}$ mole/l.; $[\mathrm{H_2SO_4}] = 1.66 \times 10^{-1}$ mole/l.; $[\mathrm{Et_3A}] = 3.3 \times 10^{-2}$ mole/l.

TABLE III
Effect of Sulfate Ion on the Rate of Polymerization at 30°C[a]

$[\mathrm{Na_2SO_4}] \times 10^2$, mole/l.	Initial rate $R_p \times 10^5$, mole/l.-sec
0	3.64
1.22	2.28
2.03	1.62
3.00	1.35

[a] $[\mathrm{M}] = 1.0125$ mole/l; $[\mathrm{Et_3A}] = 1.65 \times 10^{-2}$ mole/l; $[\mathrm{Ce^{IV}}] = 8.3 \times 10^{-4}$ mole/l; $[\mathrm{H^+}] = 35.0 \times 10^{-2}$ mole/l.

TABLE IV
Effect of Hydrogen Ion Concentration on the Rate of Polymerization at 30°C[a]

$[\mathrm{H^+}]$, mole/l.	Initial rate $R_p \times 10^5$, mole/l.-sec
0.35	3.64
0.25	2.86
0.15	2.09

[a] $[\mathrm{M}] = 1.0125$ mole/l.; $[\mathrm{Et_3A}] = 1.65 \times 10^{-2}$ mole/l.; $[\mathrm{Ce^{IV}}] = 8.3 \times 10^{-4}$ mole/l.

The activation parameter for overall rate of polymerization was determined by plotting log R_p against $1/T$ in Figure 3. A straight line was obtained, from the slope of which the activation energy was calculated to be about 10 kcal/mole.

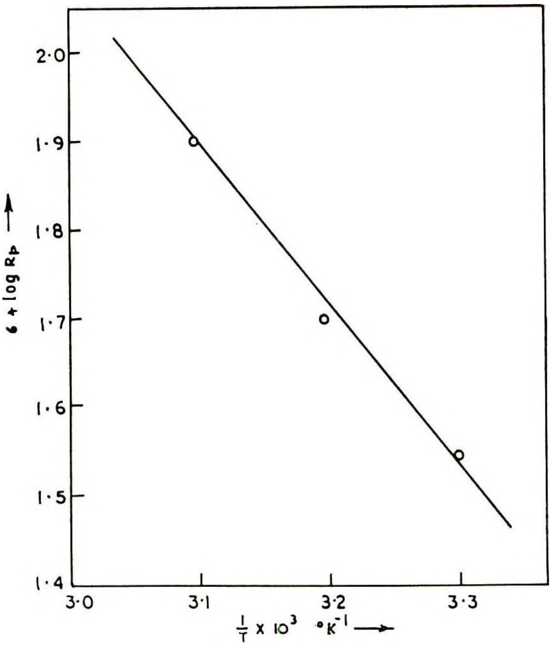

Fig. 3. Dependence of initial rate on absolute temperature at [M] = 1.0125 mole/l.; $[Ce^{IV}] = 8.3 \times 10^{-4}$ mole/l.; $[Et_3A] = 3.3 \times 10^{-2}$ mole/l.

DISCUSSION

The polymerization of acrylonitrile in aqueous media initiated by ceric ion in presence of triethylamine shows characteristic features of heterogeneous polymerization. The reaction system, though homogeneous before initiation of polymerization, becomes heterogeneous as soon as polymerization starts due to the insolubility of the polymer in aqueous phase. With the progress of polymerization, autocatalysis of the reaction ascribable to radical occlusion due to precipitation of the polymer, is also observed (Fig. 1).

From Figures 1 and 2, it can be seen that the presence of triethylamine along with ceric salt considerably increases the rate of aqueous polymerization of acrylonitrile over that initiated by ceric salt alone. Induction period was also found to be reduced in presence of the amine. Evidently, some oxidation–reduction process takes place between the ceric salt and triethylamine, producing cerous ion and a transient free-radical species which initiates the polymerization.

The primary function of an activator in a redox system is to act as an electron donor, and it facilitates the production of primary radicals by interaction with the catalyst. In case of the ceric ion–alcohol redox system it has been shown by Duke and co-workers[10,11] and later by Ardon[12] that ceric ions form reversible complexes with alcohols and glycols and that the disproportionation of these complexes is the rate-determining step of the oxidation-reduction processes. In the case of alcohols, the mechanism of the initiation reaction can be written quite generally as shown in eq. (1),

$$\mathrm{Ce^{IV}} + \mathrm{RCH_2OH} \overset{K'}{\rightleftharpoons} \mathrm{B'} \xrightarrow{k_d'} \mathrm{Ce^{III}} + \mathrm{H^+} + \mathrm{R\dot{C}HOH} \tag{1}$$

where $\mathrm{Ce^{IV}}$ represents the ceric complexes present in aqueous solution, B′ the ceric–alcohol complex and $\mathrm{R\dot{C}HOH}$ a free radical which can initiate polymerization.

The above scheme was adopted by Mino et al.[2] and Katai et al.[4] in their studies of the polymerization of acrylamide and acrylonitrile involving ceric ions in presence of alcohols, poly(vinyl alcohol), and glycol as reducing agents.

A similar complex formation between ceric salt and triethylamine can be visualized in our system also:

$$\mathrm{Ce^{IV}} + \mathrm{A} \overset{K}{\rightleftharpoons} \mathrm{B} \xrightarrow{k_d} \mathrm{Ce^{III}} + \mathrm{H^+} + \dot{\mathrm{R}} \tag{2}$$

where $\mathrm{Ce^{IV}}$ is ceric ion or any inorganic complex thereof present in the solution, A is the amine, B is the ceric–triethylamine complex, and $\dot{\mathrm{R}}$ is the free radical formed on the amine. K is the equilibrium constant for the complex formation, and k_d represents the rate constant for the decomposition of the complex.

In presence of a monomer, the free radical $\dot{\mathrm{R}}$ starts the chain reaction as shown in eqs. (3)–(8).

$$\dot{\mathrm{R}} + \mathrm{M} \xrightarrow{k_i} \dot{\mathrm{M}} \tag{3}$$

$$\mathrm{Ce^{IV}} + \mathrm{M} \xrightarrow{k_i'} \dot{\mathrm{M}} + \mathrm{Ce^{III}} + \mathrm{H^+} \tag{4}$$

$$\dot{\mathrm{M}}_n + \mathrm{M} \xrightarrow{k_p} \dot{\mathrm{M}}_{n+1} \tag{5}$$

$$\dot{\mathrm{M}}_n + \mathrm{M} \xrightarrow{k_{tr,\mathrm{M}}} \mathrm{M}_n + \dot{\mathrm{M}} \tag{6}$$

$$\dot{\mathrm{M}}_n + \mathrm{A} \xrightarrow{k_{tr,\mathrm{A}}} \mathrm{M}_n + \dot{\mathrm{A}} \tag{7}$$

$$\dot{\mathrm{M}}_n + \mathrm{Ce^{IV}} \xrightarrow{k_t} \mathrm{M}_n + \mathrm{Ce^{III}} + \mathrm{H^+} \tag{8}$$

Here M represents the monomer, $\dot{\mathrm{M}}$ the radical formed by the reaction of primary radicals or ceric ion with monomer, $\dot{\mathrm{M}}_n$ and M_n the growing polymer chain and dead polymer, respectively, and the k are the rate constants for the respective reactions. Reaction (4) takes account of the fact that ceric ion, by itself, can initiate polymerization in absence of the amine.

The reactions (2), (3), and (4) thus represent the initiation steps, reaction (5) the propagation step, and reactions (6) and (7) the chain transfer reactions involving monomer and amine, respectively.

It has been seen from Table I that at constant pH and sulfate ion concentration the rate of polymerization is independent of the total ceric ion concentration. This indicates that ceric ion is responsible for both the initiation and termination of the polymer chain. Reaction (8) represents the oxidative termination of the polymer chain by ceric ion. Oxidative termination by ceric salt has also been reported by various other workers.[2,4,13,14]

Assuming that the equilibrium between the forward and backward reactions to form the ceric ion–triethylamine complex is established rapidly compared to the decomposition rate of the complex and if all the primary radicals $\dot{\mathrm{R}}$ are captured by the monomer, we get the expression (9) for the rate of polymerization R_p, by applying steady-state assumption to both $[\dot{\mathrm{R}}]$ and $[\dot{\mathrm{M}}]$ separately,

$$\begin{aligned} R_p &= k_p[\mathrm{M}][\dot{\mathrm{M}}] \\ &= (k_p/k_t)(k_dK[\mathrm{A}][\mathrm{M}] + k_i'[\mathrm{M}]^2) \end{aligned} \tag{9}$$

The average degree of polymerization $\bar{P}_n$ is given by,

$$\bar{P}_n = \frac{k_p[\mathrm{M}][\dot{\mathrm{M}}]}{k_t[\mathrm{Ce^{IV}}][\dot{\mathrm{M}}] + k_{tr,\mathrm{M}}[\mathrm{M}][\dot{\mathrm{M}}] + k_{tr,\mathrm{A}}[\mathrm{A}][\dot{\mathrm{M}}]} \tag{10}$$

or

$$\begin{aligned} \frac{1}{\bar{P}_n} &= \frac{k_{tr,\mathrm{M}}}{k_p} + \frac{k_{tr,\mathrm{A}}[\mathrm{A}]}{k_p[\mathrm{M}]} + \frac{k_t[\mathrm{Ce^{IV}}]}{k_p[\mathrm{M}]} \\ &= C_\mathrm{M} + C_\mathrm{A}\frac{[\mathrm{A}]}{[\mathrm{M}]} + \frac{k_t[\mathrm{Ce^{IV}}]}{k_p[\mathrm{M}]} \end{aligned} \tag{11}$$

Here, $C_\mathrm{M} = k_{tr,\mathrm{M}}/k_p$ and $C_\mathrm{A} = k_{tr,\mathrm{A}}/k_p$ represent the chain transfer coefficients with respect to the monomer and the amine, respectively.

Inspection of eq. (9) shows that the expression for R_p contains no term involving ceric ions, i.e., R_p is independent of the ceric ion concentration, which is in agreement with our experimental observation.

Equation (9) further shows that the plot of R_p against amine concentration should be linear, which has also been observed (Fig. 2). Extrapolation of the data to zero amine concentration gives R_p values which are in reasonable agreement with the experimental data for R_p obtained in absence of the amine. A similar linear dependence of R_p on glycol concentration has been found by Katai et al.[4] in their study with acrylonitrile polymerization initiated by the ceric ion–ethylene glycol redox system.

Table V
Values of Different Rate Constants

Temperature, °C	$(k_p/k_t)k_i' \times 10^6$, l./mole-sec (From Fig. 2)	$(k_p/k_t)k_dK \times 10^4$, l./mole-sec (From Fig. 2)	k_p/k_t[a]	$k_i' \times 10^8$, l./mole-sec	$k_dK \times 10^5$, l./mole-sec
30	4.87	9.88	58.8	8.28	1.68
40	7.32	13.83			
50	14.64	18.45			

[a] Data of Saha and Chaudhuri.[15]

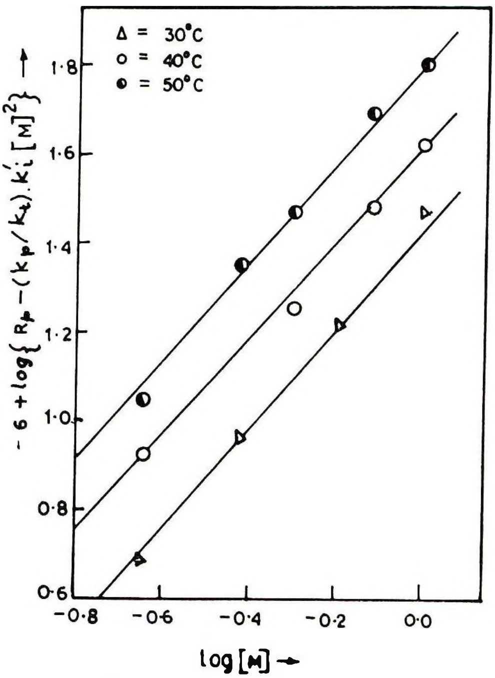

Fig. 4. Plot of log $\{R_p - (k_p/k_t)k'_i[M]^2\}$ vs. log [M] at three different temperatures. $[Ce^{IV}] = 8.3 \times 10^{-4}$ mole/l.; $[Et_3A] = 3.3 \times 10^{-2}$ mole/l.; $[H_2SO_4] = 1.66 \times 10^{-1}$ mole/l.

It can be seen from eq. (9) that the intercept on the R_p axis in Figure 2 represents $(k_p/k_t)k_i'[M]^2$. Since monomer concentration is known, $(k_p/k_t)k_i'$ can be calculated. Moreover, the slope of Figure 2 gives $(k_p/k_t)k_dK$. The values are reported in Table V.

As regards the dependence of R_p on monomer concentration, it can be seen that the rate equation (9) contains two terms involving monomer concentration, one depending on the first power and the second on the square of the monomer concentration. It is evident that the first term refers to the polymerization by the redox system, whereas the second to the polymerization by ceric ion alone. Depending on the system concerned and conditions involved, one or the other term may play a major part in the polymerization reaction resulting in a first order or second order dependence of the rate on monomer concentration. This may be the reason for different order between 1 and 2 observed by different authors in polymerization initiated by different ceric ion systems. Equation (9) shows that a plot of log $\{R_p - (k_p/k_t)k_i'[M]^2\}$ vs. log [M] should give a straight line having a slope equal to unity. The plots which are shown in Figure 4 are found to be linear as expected, with slopes nearly equal to 1. From the intercepts we get the values of $(k_p/k_t)k_dK$ (8.34×10^{-4}, 12.93×10^{-4} and 19.56×10^{-4} l./mole-sec at 30, 40, and 50°C, respectively), which are found to be in reasonable agreement with the values obtained from the plot of R_p against amine concentration (Table V).

The reaction scheme suggested above, therefore, adequately describes the polymerization process occurring in the present system. This indicates that the assumptions made are reasonably valid at least in the range of concentrations of reactants employed in the present study.

From a knowledge of the $(k_p/k_t)k_i'$ and $(k_p/k_t)k_dK$ values as determined above (Table V), k_i and k_dK can be evaluated, provided k_p/k_t is known. k_p/k_t can be determined with the help of eq. (11) if the degree of polymerization of the polymer is known. The molecular weights of the polymers in the present system could not be determined as the polymers were insoluble in usual solvents. However, when triethanolamine was used in place of triethylamine, the polymers obtained were soluble and $\bar{P}_n$ could be determined. The foregoing scheme for ceric–triethylamine system was found to be valid with ceric–triethanolamine system also, and k_p/k_t from the latter case was found[15] to be 58.8 at 30°C. This value for k_p/k_t was utilized for calculating k_i' and k_dK values (Table V). This is not unreasonable, considering the similarity of the effects of triethylamine and triethanolamine in ceric ion-initiated polymerization of acrylonitrile.[15]

Now, from the kinetic scheme developed for the system, it can be shown that,

$$R_i/R_i' = (k_dK/k_i')\ [\mathrm{A}]/[\mathrm{M}] \tag{12}$$

where R_i refers to the rate of initiation by the ceric ion–amine system and R_i' that by ceric ion alone.

Since the value obtained for k_i,' i.e., the rate constant for initiation by ceric ion alone, is very small compared to that for k_dK, it is evident from eq. (12), that the rate of initiation by the ceric ion–triethylamine system will be higher than that by ceric ion alone as long as the ratio $[\mathrm{A}]/[\mathrm{M}]$ is not less than about 10^{-3}. Actually, it has been found by us that the rate of ceric ion disappearance by reduction with monomer is so slow in absence of the amine that accurate determination of ceric ion disappearance by titration was difficult. From eq. (9) it can be seen that, at low monomer concentration, the term $k_i'[\mathrm{M}]^2$ may be negligible compared to $k_dK[\mathrm{A}][\mathrm{M}]$, and the rate may show first-order dependence on monomer under such conditions. Our experimental results also show similar trends. From the above discussions it is evident that the contribution to the overall rate of polymerization due to ceric ion alone is quite small compared to that due to the redox initiator. (We have found that with the highest monomer concentration employed by us, the contribution due to ceric ion alone is not more than 15% of the total rate at 30°C.)

Activation Parameters

The knowledge of R_p and the kinetic constants, $(k_p/k_t)k_dK$ and $(k_p/k_t)k_i'$ at 30, 40, and 50°C have been utilized in the computation of activation parameters by plotting them against $1/T$ (Figs. 3 and 5). From the plot of $\log R_p$ against $1/T$, the overall activation energy for the rate of polymerization for the present system is found to be about 10 kcal/mole. This is similar to the order of values usually observed in redox polymerization.[16,17]

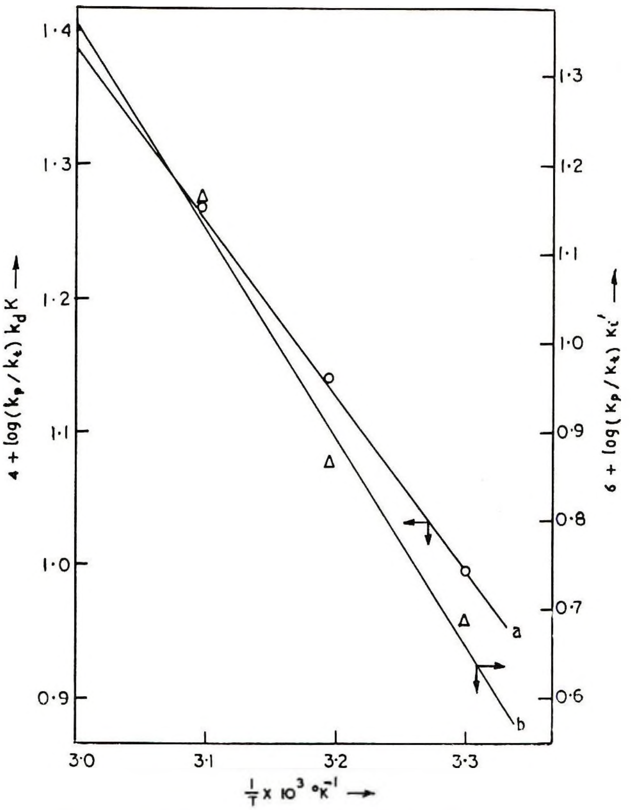

Fig. 5. Variation of (*a*) $(k_p/k_t)\,k_dK$ and of (*b*) $(k_p/k_t)\,k'_i$ with temperature.

From Figure 5, the values for $(E_p - E_t + E_{k_dK})$ and $(E_p - E_t + E_i')$ are obtained as 6.2 and 10.7 kcal/mole, respectively. From these values, we get a value of 4.5 kcal/mole for $(E_i' - E_{k_dK})$, i.e., the activation energy needed for initiation by ceric ion alone is about 5 kcal/mole higher than E_{k_dK}. As can be seen from eq. (12), this indicates that initiation by ceric ion–amine system will be more facilitated than by ceric ion alone. Further, the value of E_p for acrylonitrile in water has been reported by Dainton et al.[18] to be 4.1 kcal/mole. Using this value for E_p, we get the following values:

$$E_{k_dK} - E_t = 2.1 \text{ kcal/mole}$$

and

$$E_i' - E_t = 6.6 \text{ kcal/mole}$$

In other words, the termination of the polymer chain by ceric ion is energetically favored over initiation by ceric ion either alone or in presence of the amine.

Tables III and IV show that the rate of polymerization increases with increase of H^+ ion concentration, while the effects of sulfate ion concentration is the reverse, i.e., the rate decreases with increase in sulfate ion concentration at constant hydrogen ion concentration. It is known that cerium forms complex ions with various anions, and several complexes involving sulfate ions are possible in ceric sulfate solution.[19] The relative concentrations of these different complexes which are in equilibrium with each other are functions of the pH and sulfate ion concentrations. The various complexes will have different reactivities, each one with its own characteristic rate constant, and as such the values of the kinetic constants which have been determined earlier are only overall values. It is thus evident that any change in the conditions which affects the relative concentrations of the complexes will change the overall values of the constants such as k_dK, k_i, k_i' and k_t, and hence the overall rate of polymerization. For these reasons the kinetic constants in the present study were determined at particular concentrations of ceric, hydrogen, and sulfate ions and are valid under these conditions only. Katai et al.[20] found that highly sulfated complexes, which predominate at higher SO_4^{2-} or HSO_4^- and lower H^+ ion concentrations, are the less reactive species as regards the complex formation with ethylene glycol. It is possible that the same holds for complex formation with amine also. However, from the variation of the overall rate of polymerization with H^+ and SO_4^{2-} concentrations observed in our study, it is not possible to draw any conclusion regarding the individual reactivities of the various ceric complexes towards each reaction step.

References

1. G. Mino and S. Kaizerman, *J. Polym. Sci.*, **31**, 242 (1958).
2. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Polym. Sci.*, **38**, 393 (1959).
3. J. Lalitha and M. Santappa, *Vijnana Parishad Anusandhan Patrika*, **4**, 139 (1961).
4. A. A. Katai, V. K. Kulshrestha, and R. H. Marchessault, in *Fourth Cellulose Conference* (*J. Polym. Sci. C*, **2**), R. H. Marchessault, Ed., Interscience, New York, 1963 p. 403.
5. G. M. Guzman, *Anales Real Soc. Espan. Fis Quim. Madrid*, **B60**, 307 (1964).
6. G. M. Guzman, *Anales Real Soc. Espan. Fis Quim. Madrid*, **B60**, 523 (1964).
7. S. K. Saha and A. K. Chaudhuri, *J. Indian Chem. Soc.*, **42**, 735 (1965).
8. C. H. Bamford and A. D. Jenkins, *Proc. Roy. Soc.* (*London*), **A216**, 515 (1953).
9. S. Yuguchi and M. Watanabe, *Kobunshi Kagaku*, **17**, 108 (1960).
10. F. R. Duke and A. A. Forist, *J. Amer. Chem. Soc.*, **71**, 2790 (1949).
11. F. R. Duke and R. F. Bremer, *J. Amer. Chem. Soc.*, **73**, 5179 (1951).
12. M. Ardon, *J. Chem. Soc.*, **1957**, 1811.
13. V. S. Ananthanarayanan and M. Santappa, *J. Appl. Polym. Sci.*, **9**, 2437 (1965).
14. S. Kimura and M. Imoto, *Makromol. Chem.*, **42**, 140 (1960).
15. S. K. Saha and A. K. Chaudhuri, unpublished results.
16. W. M. Thomas, E. A. Gleason, and G. Mino, *J. Polym. Sci.*, **24**, 43 (1957).
17. A. Katchalsky and G. Blauer, *Trans. Faraday Soc.*, **47**, 1560 (1951).
18. F. S. Dainton and R. S. Eaton, *J. Polym. Sci.*, **39**, 313 (1959).
19. E. Hardwick and T. J. Robertson, *Can. J. Chem.*, **29**, 828 (1951).
20. A. A. Katai, V. K. Kulshrestha, and R. H. Marchessault, *J. Phys. Chem.*, **68**, 522 (1964).

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Spectroscopy of Irradiated Vinyl Chloride–Propylene Copolymers

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Synopsis

Spectra of vinyl chloride–propylene copolymers irradiated at low temperature in vacuum have been obtained at selected temperatures in the range 130–335°K. Copolymers and PVC homopolymer pass through identical intermediate states of dehydrochlorination in which alkyl, allyl, and polyenyl radicals are observed. Substantial spectral differences between copolymers and PVC appearing in the final states of dehydrochlorination after warming above room temperature are consistent with shorter average polyene lengths in the copolymers. This probably results from termination of polyene growth by propylene comonomer. Spectral differences at long wavelength between copolymers with varying amounts of propylene are minor compared to the basic changes between copolymer and homopolymer.

INTRODUCTION

Radiation-induced degradation of poly(vinyl chloride) is characterized in part by loss of hydrogen chloride, color formation, and a steady-state population of free radicals.[1–6] While several mechanisms have been proposed to account for dehydrochlorination,[4] there is general agreement as to the final state in which conjugated double bonds (polyenes) as well as stable polyenyl radicals[3,4] appear along the PVC chains. Numerous estimates have placed the maximum polyene length at from seven[7] to 16–17[1] conjugated double bonds, but spectra of degraded PVC films indicate the presence of an assortment of polyene lengths.

In a recent study of PVC homopolymer irradiated at low temperature, Salovey et al.[8] obtained ultraviolet visible spectra in vacuum at 159, 243, and 286°K and after warmup to 363–373°K. Distinct spectral changes appearing at each temperature were associated with alkyl, allyl (2520 Å), dienyl (2910 Å), trienyl (3300 Å), and polyene-polyenyl radical growth (4000–6000 Å). Spectra representing PVC in advanced states of dehydrochlorination, where long-chain polyene-polyenyl radical bands predominate, included clear contributions from allyl and short-chain polyenyl radicals in the region 2000–4000 Å as well. From this observed dependence of spectral band position on polyene length and from the appearance of ultraviolet-visible spectra of PVC at high levels of dehydrochlorination it is apparent that ultraviolet-visible spectroscopy provides a means of evaluating the polyene population of dehydrochlorinated PVC.

In recent years, vinyl chloride copolymers have become commercially available. These incorporate small percentages of such comonomers as propylene randomly dispersed along the polymer chains. If the effect of the comonomers is to block dehydrochlorination, such copolymers raise the interesting possibility that shorter polyene sequences may, on the average, result in the degraded state. To test this possibility and to determine the mechanism of dehydrochlorination of irradiated vinyl chloride–propylene copolymers, three such copolymers were subjected to electron irradiation and spectral studies at selected temperatures. Vinyl chloride homopolymer, reported earlier, has been included in the experiments as a point of reference. Conclusions have been drawn as to the effect of propylene comonomer on average polyene sequence length and rate of dehydrochlorination. A gross mechanism for free-radical dehydrochlorination in irradiated copolymers is proposed.

EXPERIMENTAL

Three PVC copolymers, designated P-1, P-2, and P-3, and a high molecular weight PVC homopolymer were employed for the experiments. Trace metal analysis by emission spectroscopy detected Ca, Mg, Fe, Al, Cu, and Si for the copolymers and Ti, Cu, Al, Mg, and Ca for the homopolymer at estimated levels of 0.00001–0.00009%, with Ca in P-3 and Ti in the homopolymer at levels of 0.0001–0.0009%. Total ash content for all samples was less than 0.01%. Infrared analysis of the four samples by potassium bromide disk indicated some C=O at 1730 cm^{-1} in PVC homopolymer and none in the copolymers. Density measurements on the copolymers established 3.3% propylene for P-1, 4.7% for P-2, and 5.5% for P-3.[9,10] Average lengths of uninterrupted vinyl chloride, in terms of molecules vinyl chloride/molecule propylene, were calculated as 19.7 for P-1, 13.6 for P-2, and 11.6 for P-3, assuming random distribution of propylene.

Films of the four materials were molded between 0.010 in. sheet Mylar-backed 6 × 6 × $^1/_2$-in. aluminum plates at 15 tons total pressure on the film areas, with a preheating time of 1–2 min at 3 tons pressure. Molding conditions for the four materials were: for PVC homopolymer, 8 min at 130–132°C; for P-1, P-2, and P-3, 7 min at 123–127°C. Eight to ten thickness measurements over the spectral portion of the film by means of an electronic micrometer (J. W. Dice Co.) yielded average thicknesses of 2.9 mils for P-2, 3.3 mils for P-3, and 3.2 mils for the homopolymer, with errors estimated at ±0.1 mil. Micrometer measurements on P-1 gave 4.5 ± 0.5 mils. Film dimensions were 7 × 25 mm.

All experiments were performed in a cryostat designed to expose film samples to electron irradiation at low temperatures in vacuum and to permit subsequent spectral measurements over a wide temperature range.[11] Films inside the cryostat were mounted across three slit openings each of 0.125 × 0.782 in. on a support normal to electron and spectral beams. Rotation between the horizontal, for irradiation, to the vertical was accomplished by means of a manually operated probe. Standard 0.005 in.

copper–constantan thermocouples monitored film-center and film-support temperatures throughout each experiment. Thermal gradients were observed across the $^1/_8$-in. film widths and were attributed to heating of the films in vacuum by thermal radiation. These gradients varied with temperature of the film support, being 50–69°K with film support at 85°K, 28–36°K with support at 201°K, zero at room temperature, and 16–19°K with support at 351°K. Film temperatures reported are maximum, deriving from thermocouples mounted in the lower center of each film, with the upper portion reserved for the spectral beam. Low-temperature spectra were observed to be highly insensitive to temperature changes within broad temperature intervals, implying that one species alone predominates in each temperature interval across the gradient. Notwithstanding thermal gradients, the clear advantage to analysis in vacuum lies in the rapid removal of hydrogen chloride gas at each temperature minimizing recombination reactions and hydrogen chloride autocatalytic effects. Cryostat pressures were normally near 10^{-5} torr.

A Van de Graaff accelerator (High Voltage Engineering) operating with a beam current of 50 μA at 1 MeV delivered a dose of 5 Mrad to the polymer at a rate of 0.081 Mrad/sec. Spectra were recorded on a Cary Model 14 spectrophotometer. In each figure the lower curve is of arbitrary spectral intensity. Scattering from the quartz cell windows displaced this and all subsequent curves by a constant amount, yielding absolute spectral intensity differences in all figures.

Results and Discussion

Repeated studies of the three copolymers following irradiation and warmup indicated identical behavior up to advanced stages of dehydrochlorination where minor differences were noted. To evaluate the effect of propylene comonomer on polyene sequence length, a direct comparison with PVC homopolymer was necessary. Accordingly, P-3 and P-2 together with the homopolymer were included in the same experiment, being thus subject to the same dose and thermal history. P-3 has been selected to represent copolymer results in comparison with PVC homopolymer. Differences between P-1, P-2, and P-3 are briefly discussed.

Figures 1 and 2 summarize irradiation-induced changes in the P-3 copolymer film. Figure 1*A*, a control spectrum of the copolymer at 147°K, is identical to that for the homopolymer, at 133°K (Fig. 3*A*). Absorption around 2200 Å is evidently the long-wavelength edge of a PVC electronic band with $\lambda_{\max}$ below 2000 Å.[12]

Figure 1*B* was recorded at 152°K, 100 min after irradiation to a total dose of 5 Mrad at 140°K. Spectral changes indicate band growth to the blue of 2200 Å; only the long wavelength edge appears. A discontinuity at 2500 Å implies secondary band growth in this region. The curve was unchanged after $18^3/_4$ hr storage at 154°K and is assigned to alkyl radicals generated by electron irradiation and stabilized at this temperature. Previous workers[3] have irradiated PVC at 77°K and obtained ESR data interpreted as cor-

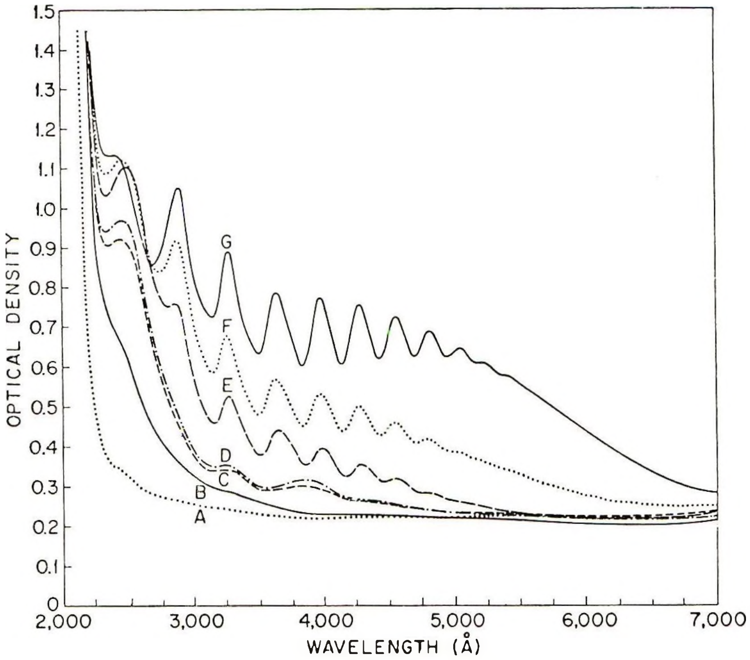
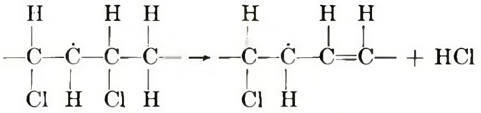


Fig. 1. Irradiated copolymer P-3 *in vacuo*: (*A*) control, unirradiated, 147°K; (*B*) 100 min after irradiation at 140°K, recorded at 152°K; (*C*) warmed from 154 to 238° K over 2.0 hr, stored at 238°K for 4.2 hr; (*D*) stored at 237–238°K, 21.2 hr; (*E*) warmed from 237 to 298°K over 1.75 hr, stored at 298°K, 2.7 hr (intensity adjusted); (*F*) stored at 298–299°K for 72.7 hr; (*G*) warmed from 298 to 325°K over 4.9 hr, then warmed at 298–332°K over 2.3 hr.

responding to the alkyl radical mixture $—CH_2—\dot{C}H—CH_2—$, $—CHCl—\dot{C}H—CHCl—$, $—CH_2—\dot{C}Cl—CH_2—$. Alkyl radicals in irradiated polyethylene have been assigned to 2150 Å.[13]

The spectrum (Fig. 1*C*) obtained after a 2-hr warmup from 154 to 238°K and storage at 238°K for 4.2 hr, reveals major band growth at 2460 Å, the position of which suggests that it is related to the secondary band noted previously. Slow growth of this species at 237°K is evident in Figure 1*D*, the spectrum representing 17 hr further storage at 237°K. Two additional bands, considerably less intense, appeared at this temperature at 3250 Å and 3850 Å. Their origin is not clear at this time and no assignment is made. Band growth at 2460 Å is assigned to allyl radicals resulting from dehydrochlorination next to an alkyl radical [eq. (1)].



$$—\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}—\underset{\mathrm{H}}{\dot{\mathrm{C}}}—\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}—\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}— \rightarrow —\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}—\underset{\mathrm{H}}{\dot{\mathrm{C}}}—\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}— + \mathrm{HCl} \qquad (1)$$

Of the three possible alkyl radical species, that with chlorine adjacent to the radical is considered likely to stabilize itself in this manner. Allyl radicals

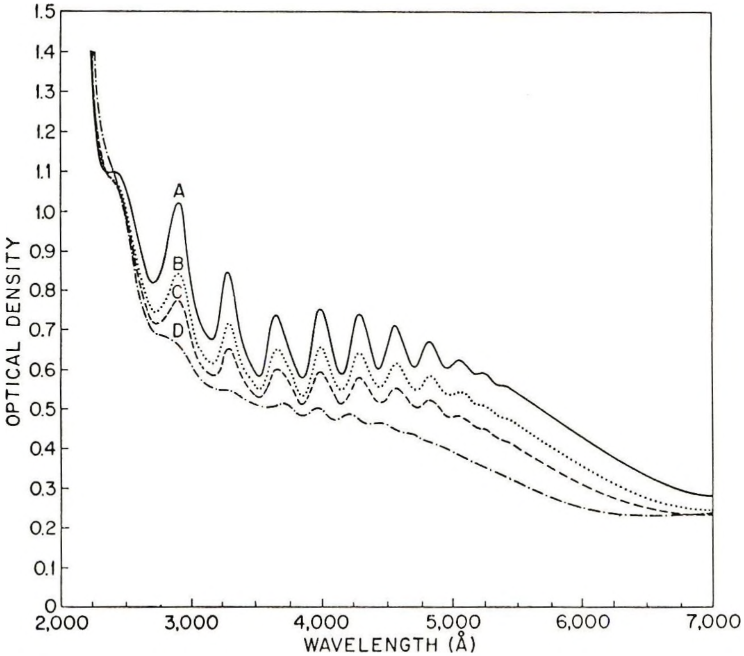
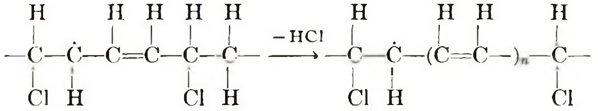


Fig. 2. Irradiated copolymer P-3 in oxygen, 298°K: (*A*) similar to Fig 1*G*; (*B*) Exposed to 1 atm O_2, 55 min; (*C*) exposed 129 min; (*D*) exposed 18.8 hr at room temperature.

have been observed in irradiated polyethylene with assigned ultraviolet absorption at 2580 Å.[13,14]

In the third stage of the warmup, films were warmed to 298°K over 105 min. Curves *E* and *F* of Figure 1 are spectra resulting after storage for 2.7 and 70.0 hr additional at 299°K. A banded structure from 2700 to 5100 Å superimposed on a broad continuum appears and evolves slowly at room temperature. It is noteworthy that the band at 2460 Å has increased and shifted as well. Such banded spectra are characteristic of long-chain polyenes. Loss of successive molecules of hydrogen chloride adjacent to allyl radicals initially yields polyenyl radicals [eq. (2)].



$$-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\dot{\mathrm{C}}}-\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\xrightarrow{-\mathrm{HCl}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\dot{\mathrm{C}}}-(\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}-)_n-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}- \qquad (2)$$

As polyenyl radicalc oncentrations increase, crosslinking, chain transfer, and other radical termination reactions occur, transforming some polyenyl radicals into polyenes. The mixture of polyenes and polyenyl radicals therefore accounts for spectra observed at room temperature. Reported spectra for polyenes and polyenyl radicals in irradiated polyethylene indicate a separation of about 500 Å between polyenes and their corresponding radicals, with the radical band at longer wavelength. λ_{max}

for polyenes and polyenyl radicals shifts to the red on increasing conjugation length from one to five double bonds.[13]

A final stage in the thermal treatment of the copolymer involved heating for 4.93 hr to a maximum of 325°K and subsequent heating for 2.33 hr to a maximum of 332°K. Curve *G* of Figure 1, recorded at room temperature, is the spectral response to heating. Considerable intensification of the banded structure has occurred, with extension of the banding past 5100 Å. The broad continuum is likewise intensified and developed well into the visible. No corresponding growth of the band at 2460 Å is evident; on the contrary, the nearly constant intensity of this band together with growth of spectral intensity immediately adjacent strongly suggests that the band at 2460 Å has declined. Consistent with this is the appearance of a well resolved singlet at 2900 Å (Fig. 1*G*), formerly a shoulder on the larger 2460 Å band (Fig. 1*E*). Curve *G* of Figure 1 indicates growth of long-chain polyene and polyenyl radical concentration due to thermally accelerated dehydrochlorination, transforming allyl and polyenyl radicals present at room temperature (Fig. 1*E*, 1*F*) into longer sequences.

On termination of the warmup spectra, all of which were recorded in vacuum, the cell was opened to pure oxygen at room temperature. Figure 2 illustrates the spectral response with time of exposure to oxygen, this

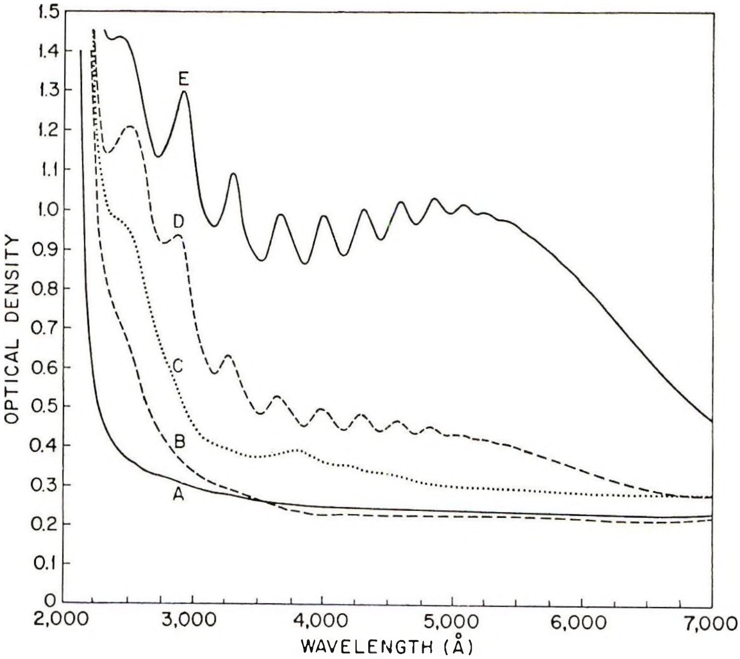


Fig. 3. Irradiated vinyl chloride homopolymer in vacuo: (*A*) control, unirradiated 133°K; (*B*) 95 min after irradiation at 122°K; (*C*) warmed from 135 to 231°K over 2.0 hr, stored at 229°K for 21.1 hr; (*D*) warmed from 229 to 298°K over 1.75 hr, stored at 298–299°K for 72.6 hr; (*E*) warmed from 298 to 328°K over 4.9 hr then warmed at 298–335°K over 2.3 hr.

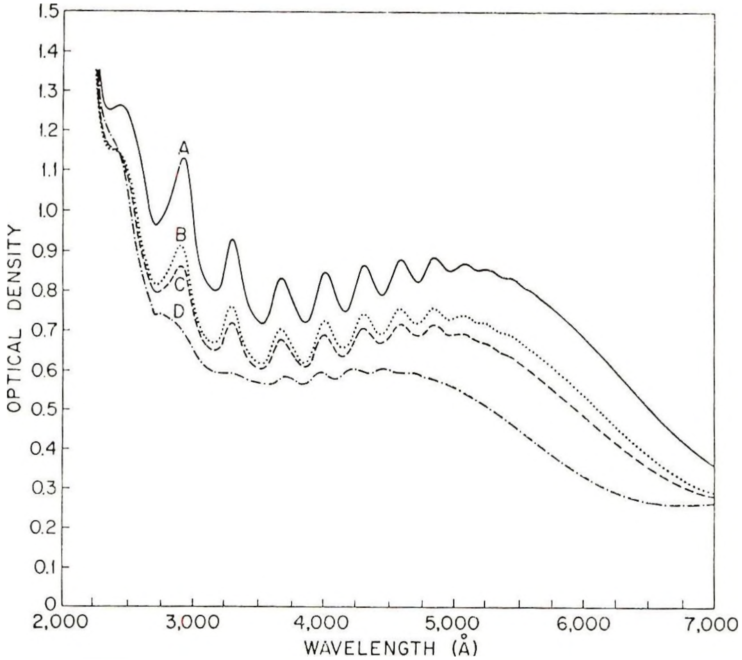


Fig. 4. Irradiated vinyl chloride homopolymer in oxygen, 298°K: (*A*) similar to Fig. 3*E*; (*B*) exposed to 1 atm O_2, 50 min; (*C*) exposed 124 min; (*D*) exposed 18.6 hr at room temperature.

being a measure of the extent to which the species present are subject to free radical scavenging. Figure 2*A* is similar to Figure 1*G;* Figures 2*B*, 2*C*, and 2*D* represent exposures to oxygen for 0.92, 2.2, and 18.8 hr, respectively. All bands as well as the broad continuum decrease with time of oxygen exposure, with traces of the banded structure remaining from 3200 Å to 4700 Å. It is noted that oxidation products absorb in the region 2000–3000 Å, which undoubtedly accounts for a portion of the intensity remaining in this region. The rapid initial response to oxygen followed by an apparent leveling off lends support to the view that polyenyl radicals as well as polyenes exist at this stage of the dehydrochlorination with the former accounting for much of the initial reaction with oxygen. While polyenes as well as polyenyl radicals would be expected to react rapidly with oxygen, it is not unreasonable to assume that the latter react more rapidly. Kinetic data on the relative rates of reaction of these two species are lacking, however, as data on bleaching of degraded PVC in oxygen[15] refer to the polyene-polyenyl radical mixture. With the assumption that polyenyl radicals react faster, Figure 2*D* may represent the spectrum of a residual population of less-reactive polyenes together with oxidation products. Upon prolonged storage in air it is observed that residual polyenes are significantly reduced as well.

Corresponding states in the radiolysis of the homopolymer (Figs. 3 and 4) have been previously discussed[8] and are included here for comparison.

Films for copolymer P-3 and homopolymer received the same dose, thermal treatment, and oxygen exposure. It is clear that the two systems exhibit similar response to radiation and warmup to room temperature. Significant differences in behavior appeared only after heating above room temperature.

Figure 5 presents copolymer and homopolymer spectra on common coordinates with appropriate adjustment for film thickness. Corresponding states in the thermal history of copolymer and homopolymer are represented by A–B and C–E. Curves A and B of Figure 5 were obtained following storage for 72.7 and 72.6 hr at 298–299°K after warmup from 230–240°K. Figure 5C was recorded at room temperature after heating the copolymer for 4.93 hr to a maximum of 325°K followed by 2.33 hr heating to a maximum of 332°K. Figure 5E represents the corresponding response for heating of PVC homopolymer for 4.93 hr to a maximum of 328°K and 2.33 hr to a maximum of 335°K. Figure 5D represents the spectrum of the homopolymer after 4.93 hr heating to 328°K.

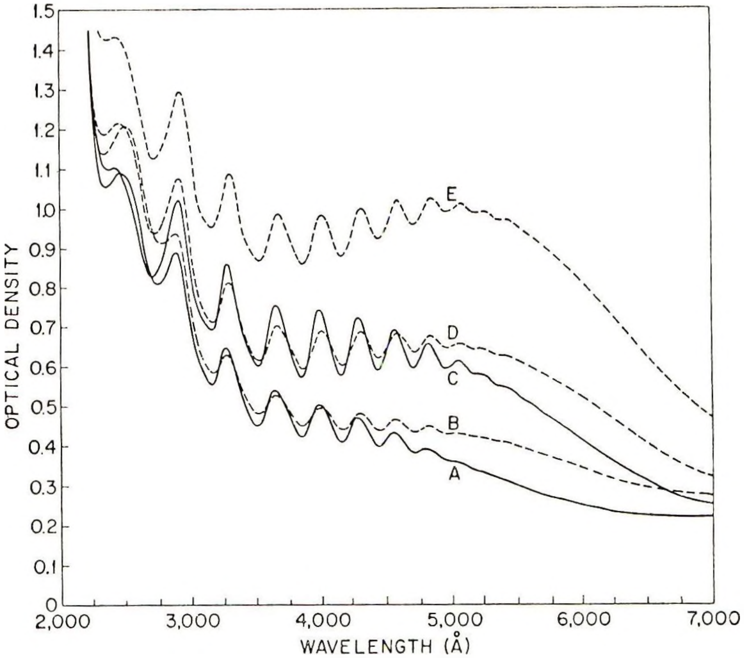


Fig. 5. Spectra of (- -) vinyl chloride homopolymer and (——) propylene copolymer P-3: (A) P-3 copolymer irradiated *in vacuo*, stored at 298–299°K for 72.7 hr (Fig. 1F); (B) PVC homopolymer irradiated *in vacuo*, warmed from 229 to 298°K over 1.75 hr, stored at 298–299°K for 72.6 hr (Fig. 3D); (C) P-3 copolymer irradiated *in vacuo*, warmed from 298 to 325°K over 4.9 hr, then warmed at 298–332°K for 2.3 hr; (D) PVC homopolymer heated from 298 to 328°K over 4.9 hr; (E) PVC homopolymer irradiated *in vacuo*, warmed from 298 to 328°K over 4.9 hr, then warmed at 298–325°K for 2.3 hr (Fig. 3E).

An observation of prime importance in Figure 5 is the difference in contour between homopolymer and copolymer curves. Note the appearance of a distinct maximum (Fig. 5*E*) at 5100 Å and relatively intense absorption from 5100 to 7000 Å. This development, already evident in Figure 5*B*, is best compared to copolymer spectra in the pair of curves 5*C*–5*D*. Absorption for PVC homopolymer (Fig. 5*D*), rises abruptly to 4900 Å where it levels off, intensifying again at 3400 Å. The copolymer spectrum (Fig. 5*C*) shows no such leveling off; it increases throughout the spectral range. Equally important is the area between curves *C* and *D*, from 4800 to 7000 Å, the difference due to increased absorption in this region by PVC homopolymer.

Polyene spectra are often characterized by a banded structure superimposed on a continuum, the peak of which shifts to longer wavelengths with increasing polyene length.[13,16] Assuming negligible perturbation of the polyenes and polyenyl radicals by the surrounding environment, it may be concluded that spectra of the mixture of polyenes and polyene radicals along PVC chains likewise relate to their length. An interpretation of Figure 5 is therefore possible: greater spectral absorbance in the long wavelength region for the homopolymer indicates the presence of longer polyene lengths than for PVC–propylene copolymer irradiated to the same dose and subjected to a similar thermal history. Propylene units along copolymer chains apparently block dehydrochlorination, yielding shorter polyene sequences on the average.

A tentative conclusion regarding rate of dehydrochlorination may also be drawn from Figure 5. While the experiments described were not designed specifically for quantitative measurements of polyene growth by spectroscopy, large differences in rate of polyene growth would be noted. Curves 5*A* and 5*B* for copolymer and homopolymer suggest comparable rates of growth at room temperature. Curves 5*C* and 5*E* suggest a faster rate of polyene growth for the homopolymer above room temperature. As total spectral absorption in the 7000–2000 Å region has been taken as proportional to total hydrogen chloride loss,[17] the implication is a greater dehydrochlorination of homopolymer above room temperature following irradiation, compared to the copolymer.

Copolymers P-1 and P-2 with 3.3% and 4.7% propylene were analyzed by the same methods. As expected, these systems passed through the same postulated states as P-3 following irradiation and warmup. Spectra of the highly dehydrochlorinated states revealed only slightly increased absorption compared to P-3 in the long wavelength region, consistent with longer polyene sequences on the average. Apparently, small changes in propylene content lead to small differences in visible absorption at long wavelengths.

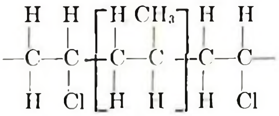
Conclusions

PVC–propylene copolymers irradiated at low temperatures and subjected to controlled thermal history pass through the same states of dehydrochlorination as vinyl chloride homopolymers, reported earlier. Differences in polyene chain length appear after exposure to room temperature and above. Ultraviolet-visible spectra indicate longer polyene lengths in PVC homopolymer than in the copolymers, based on spectral absorbance in the 5100–7000 Å regions of the spectra. Total spectral growth from 7000 to 2000 Å supports a faster rate of dehydrochlorination for PVC homopolymer following irradiation and heating above room temperature.

It is concluded that propylene units randomly dispersed along the copolymer chains effectively block dehydrochlorination or "unzipping" yielding, on the average, shorter polyene lengths.

A lower rate of dehydrochlorination in the copolymers could be explained if the chain transfer rate constant is less than the propagation rate constant. This is likely to be true, especially since the experiments were all carried out below the T_g of the polymers.

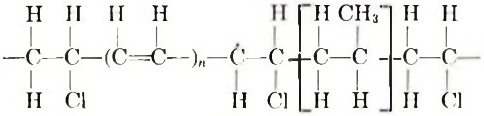
It remains to illustrate the mechanism whereby propylene comonomer blocks dehydrochlorination. A typical structure for PVC-propylene copolymer is I.



$$-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-\left[\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\right]-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-$$

I

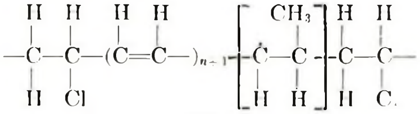
If a polyenyl radical with n double bonds exists in the vicinity of the propylene group (structure II)



$$-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-(\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}-)_n-\underset{\mathrm{H}}{\dot{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-\left[\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\right]-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-$$

II

additional loss of HCl yields III,



$$-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-(\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}-)_{n-1}-\left[\underset{\mathrm{H}}{\dot{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\right]-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-$$

III

which cannot dehydrochlorinate further in the right-hand direction. Propylene units to the left would block dehydrochlorination in that direction by a similar mechanism.

The slight spectral differences between three PVC–propylene copolymers with 3.3%, 4.7%, and 5.5% propylene may be due to an insensitivity of polyene spectra to small changes in polyene sequence length, in which case the obvious spectral differences appearing in vinyl chloride homopolymer spectra imply considerably longer polyene and polyenyl-radical sequences in the latter.

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References

1. G. J. Atchison, *J. Appl. Polym. Sci.*, **7**, 1471 (1963).
2. G. J. Atchison, *J. Polym. Sci.*, **49**, 385 (1961).
3. S. Ohnishi, Y. Nakajima, and I. Nitta, *J. Appl. Polym. Sci.*, **6**, 629 (1962).
4. A. A. Miller, *J. Phys. Chem.*, **63**, 1755 (1959).
5. E. J. Lawton and J. S. Balwit, *J. Phys. Chem.*, **65**, 815 (1961).
6. B. R. Loy, *J. Polym. Sci.*, **50**, 245 (1961).
7. D. E. Winkler, *J. Polym. Sci.*, **35**, 3 (1959).
8. R. Salovey, R. V. Albarino, and J. P. Luongo, *Macromolecules*, **3**, 314 (1970).
9. L. Weintraub, J. Zufall, and C. A. Heiberger, *Polym. Eng. Sci.*, **8**, 64 (1968).
10. T. W. Huseby, private communication.
11. R. V. Albarino and R. Salovey, *Appl. Specty.*, **24**, 418 (1970).
12. S. Onari, *J. Phys. Soc. Japan*, **26**, 500 (1969).
13. D. C. Waterman and M. Dole, *J. Phys. Chem.*, **74**, 1906 (1970).
14. D. M. Bodily and M. Dole, *J. Chem. Phys.*, **44**, 2821 (1966).
15. W. C. Geddes, *Rubber Chem. Technol.*, **40**, 177 (1967).
16. A. E. Gilliam and E. S. Stern, *Electronic Absorption Spectroscopy*, Edward Arnold, London, 1958, pp. 80–88.
17. C. Forgacs, *Israel J. Chem.*, **7**, 463 (1969).

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Mechanism of Stabilization of Polypropylene by Ultraviolet Absorbers

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Synopsis

The ultraviolet screening properties of 2-hydroxyphenylbenzotriazoles and 2-hydroxybenzophenones in polypropylene film were investigated by using photochemical and spectroscopic techniques. The effect of light screening on polymer photostability was examined by using filter solutions, and the fraction of ultraviolet light absorbed by stabilized film was calculated and compared to flexural failure times. It was found that the 2-hydroxyphenylbenzotriazoles behave primarily as screeners of ultraviolet light whereas the 2-hydroxybenzophenones are both screeners and excited-state quenchers. The quenching characteristics of the latter have not been isolated and mechanistically examined, but it is probably similar in nature to that of the nickel chelate stabilizers.

Introduction

Several different types of organic stabilizers have been used in the protection of polyolefins from ultraviolet degradation. These stabilizers are usually divided into two classes because of the different mechanisms by which they prevent photodegradation. The ultraviolet absorbers (e.g., 2-hydroxybenzophenones and 2-hydroxyphenylbenzotriazoles) reportedly function as light screeners, harmlessly disposing of the absorbed energy.[1,2] The reactive stabilizers (usually nickel chelates) are believed to operate by an energy-quenching mechanism, i.e., quenching the excited-states of polymer molecules by an energy transfer process.[3–5] In this work we have examined the mechanism of stabilization of the so-called ultraviolet absorbers and have shown that they do not all behave as light screeners only. The 2-hydroxybenzophenones function as screeners but also act by a second mechanism which extends the polymer film lifetime by several orders of magnitude over that resulting from a screening effect alone. Our results indicate that they are excited-state quenchers and their quenching effectiveness is less than that of the nickel chelate stabilizers.

Two different approaches were used to arrive at the above conclusion. In one, the light-screening properties of the stabilizers were actually measured by comparing the flexural strength of stabilized polypropylene film to that of unstabilized film screened by filter solutions. The second technique involved calculations of the per cent light absorbed by the polymer (LAP) for various concentrations of different stabilizers. A comparison of

LAP to the flexural failure time of the corresponding polypropylene film was used to separate the light-absorption and energy-quenching properties of stabilizers.

Experimental

All irradiation experiments were conducted on 5-mil polypropylene film. The film was prepared from a dry-blended mixture of the desired ultraviolet stabilizer in nominal 3 MF polypropylene and was compression-molded at 20,000 lb pressure and 190°C for 2 min. Thermal degradation of the film during processing was prevented by the 2,6-di-*tert*-butyl-*p*-cresol present in the polypropylene fluff (~0.03%). Both the ultraviolet-stabilized and unstabilized films were prepared by the above process.

Two different ultraviolet irradiation apparata were used. A cylindrical reactor with a 450-W Hanovia high-pressure mercury lamp was used to generate the light-screening data. In this system, each film was mounted behind a 1-cm Pyrex filter cell. Only ethanol was used in the filter cell in front of the ultraviolet-stabilized film. A filter solution of the appropriate stabilizer was used in the cells for the unstabilized film so that the polypropylene absorbed the same amounts and same wavelengths of light in both the stabilized and unstabilized cases. The ultraviolet absorption spectra of the stabilized films were used to determine the concentrations of ultraviolet stabilizers needed in the filter solutions. In the experiments involving 0.1% ultraviolet stabilizer, the film was rotated 180° after every 50 hr of exposure to insure uniform light absorption. The temperature in this reactor was maintained at 30–35°C. The data used in the LAP analysis were generated from 5-mil film exposed to ultraviolet light in an Atlas Twin Enclosed Carbon Arc Weather-Ometer modified by the addition of eight fluorescent sunlamps.[6] The temperature of the Weather-Ometer was approximately 65°C and the relative humidity 45%.

Samples in both experiments were tested for failure by 180° flex-bend. Each film was tested roughly every 40 hr until the first specimen of a formulation failed, after which the other specimens of that formulation were tested every 20 hours. Failure times were obtained by averaging the individual failure times of three to four samples of each formulation, and were found to be reproducible to ±20%. Although the flex-bend test is somewhat subjective, it is as objective a measure of physical property changes caused by light aging as the stress-crack test,[7] the stiffness test,[8] and other techniques for measuring brittle strength.[9]

To test the screening properties of ultraviolet stabilizers, 5-mil polypropylene film containing either 2-hydroxy-4-*n*-octoxybenzophenone (UV-1) or 2-(3′,5′-di-*tert*-butyl-2′-hydroxyphenyl)-5-chlorobenzotriazole (UV-2) were irradiated in the cylindrical reactor. These films were compared to unstabilized film screened by the appropriate filter solutions. Filter solution concentrations were adjusted so that the polypropylene in the unstabilized films absorbed the same amounts and wavelengths of light as that of

TABLE I
Screening Solutions

No.	Stabilizer and concentration	Filter solution concentrations
I-A	0.25% UV-1	Ethanol only
I-B	Unstabilized	2.38×10^{-5} M UV-1 in ethanol
II-A	0.1% UV-1	Ethanol only
II-B	Unstabilized	$1.42 \times 10^{-5}M$ UV-1 in ethanol
III-A	0.1% UV-2	Ethanol only
III-B	Unstabilized	$1.35 \times 10^{-5}M$ UV-2 in ethanol

the stabilized film containing the corresponding ultraviolet stabilizer. The filter solution concentrations are given in Table I.

Filter solutions were replaced every 50 hr before photodecomposition could cause any changes in their ultraviolet-absorption properties.

Light-Screening Effects

The failure times for the three sets of stabilized and unstabilized polypropylene film are listed in Table II.

Each of the three film sets were irradiated separately in the cylindrical reactor and no attempts were made to correct for lamp intensity fluctuations. Consequently, the failure time data can only be reliably compared for the stabilized and unstabilized film within each set. In addition, set I films were not rotated during the irradiation period. As a result, the light absorbed and degradation in the 0.25% UV-1 stabilized film occurred more on the surface than with the unstabilized film. In order to insure uniform absorption throughout the film, this run was repeated with 0.1% stabilized film and the films were rotated 180° after each 50-hr irradiation period (set II). The same conclusions can be drawn from these results as from the set I data.

The results in Table II show that UV-2 functions primarily as a screener of ultraviolet light. The failure times for the stabilized and unstabilized films are essentially equal within experimental error. Only 5–10% of the UV-2 in the stabilized film was lost during the irradiation period.

TABLE II
Polypropylene Film Ultraviolet-Screening Results

No.	Polypropylene film	Failure time, hr
I-A	0.25% UV-1	1230 ± 170[a]
I-B	Unstabilized[b]	450 ± 80
II-A	0.1% UV-1	1100 ± 200
II-B	Unstabilized[b]	225 ± 60
III-A	0.1% UV-2	800 ± 160
III-B	Unstabilized[b]	670 ± 150

[a] Standard deviation.

[b] Screened by the appropriate stabilizer filter solution listed in Table I.

The UV-1 data indicate that this stabilizer does not function simply as a light screener. The stabilized film lasted at least three times as long as the unstabilized film even though the latter was screened by a UV-1 filter solution such that the polypropylene itself absorbed the same amount and same wavelengths of light in both the stabilized and unstabilized films. Approximately 75–85% of UV-1 was lost in the stabilized film during the irradiation period (determined from ultraviolet spectra), so the difference between the stabilized and unstabilized films is even greater than a factor of three. This difference cannot be due to any antioxidant properties of UV-1 because: (1) the film temperature never exceeded 35°C and (2) UV-2 should be a better thermal stabilizer than UV-1, since the former has a hindered phenol segment in its structure, yet the failure times for stabilized and unstabilized films in the UV-2 case are essentially equal. The results of the UV-1 screening study can be rationalized if it is assumed that it acts as an energy quencher of excited polymer molecules in addition to being a light screener. Pivovarov[10] and Nurmukhametov[11] have proposed a similar mechanism to explain the stabilization effectiveness of 2-hydroxybenzophenones.

LAP Curves

Our second method for examining the light absorption properties of ultraviolet stabilizers involves correlating the per cent light absorbed by the polymer (LAP) for various stabilizer concentrations with the corresponding film failure times. Based on the results of our light-screening experiments, such correlations with UV-1 and UV-2 should demonstrate that the latter acts primarily as a light screener whereas the former behaves as both a screener and an excited-state quencher. Data on the behavior of [2,2′-thiobis(4-*tert*-octylphenolato)]-*n*-butylamine nickel (II) (UV-3) is also included in this analysis, since nickel chelate stabilizers are believed to behave primarily as excited-state quenchers.[3,5] The film failure data for these stabilizers are listed in Table III. The modified Weather-Ometer was used to obtain these results.

The ultraviolet absorption spectra of stabilized and unstabilized 5-mil films (unirradiated) were measured and are shown in Figures 1 and 2 for rep-

TABLE III
Film Failure Data for LAP Calculations

Stabilizer concentration, (%)	Time to failure, hr		
	UV-1	UV-2	UV-3
0	70 ± 15[a]	70 ± 15	70 ± 15
0.1	190 ± 40	100 ± 15	100 ± 15
0.25	390 ± 60	150 ± 30	340 ± 40
0.5	580 ± 100	210 ± 30	690 ± 80

[a] Average deviation from the mean.

resentative samples. LAP was calculated by using these spectra and eq. (1):

$$\% \text{ LAP} = 100 \times \sum_{\lambda_1}^{\lambda_2} [1 - T(\lambda)] \left[\frac{A_p(\lambda)}{A_p(\lambda) + A_s(\lambda)} \right] \tag{1}$$

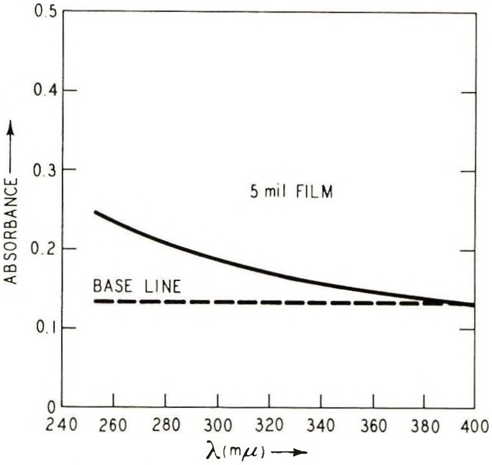

Fig. 1. Ultraviolet absorption spectrum of unstabilized polypropylene film.

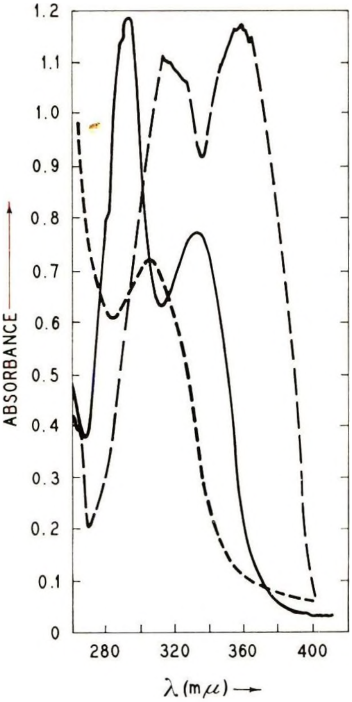

Fig. 2. Ultraviolet absorption spectra of ultraviolet stabilizers in 5-mil polypropylene film: (——) 0.25% UV-1; (– –) 0.25% UV-2; (- -) 0.5% UV-3.

where $T(\lambda)$ is the total light transmitted by the polymer–stabilizer system at wavelength λ, $A_p(\lambda)$ is the absorbance of unstabilized polypropylene at λ, and $A_s(\lambda)$ is the absorbance of ultraviolet stabilizer in polypropylene at λ. Calculations of LAP by using eq. (1) assume that the quantum yield of polymer degradation is independent of wavelength, the degradation products do not absorb, and the absorption spectra of polymer and stabilizer do not change during degradation. These conditions do not hold completely in the real system, but, as will be seen, the LAP–failure time comparison is useful in analyzing the screening and excited-state quenching properties of stabilizers.

Probably most of the absorption shown in Figure 1 for unstabilized polypropylene film is due to light scattering. Some of the light scattering was subtracted as shown by the artificial base line; any remaining uncertainty will only affect the absolute magnitude and not the relative values of LAP. Since light scattering is essentially the same for all films, conclusions based on the relative differences in LAP for different stabilization systems will be valid.

Calculated values of LAP for the 3000–3800 Å system are shown in Table IV. A constant spectral energy distribution was assumed for the modified Weather-Ometer.

TABLE IV
Light Absorbed by the Polymer (LAP)

Stabilizer concentration, %	LAP, %		
	UV-1	UV-2	UV-3
0	4.4	4.4	4.4
0.1	3.3	2.8	3.9
0.25	2.4	1.7	3.4
0.50	1.6	0.9	2.9

The LAP values were also calculated by using the spectral energy distributions of carbon arcs and fluorescent sunlamps as determined by Hirt.[12] This changed the magnitude of LAP but again did not change the relative values for the different stabilizer systems. Since we are primarily interested in the relative behavior of LAP, the data in Table IV will be used in this discussion.

Plots of LAP versus film failure times for UV-1, UV-2, and UV-3 are shown in Figure 3. The UV-2 curve follows exactly that which would be predicted for a light screener, i.e., according to the kinetics of photooxidation of polymers, the effectiveness of an absorber varies as the square root of the change in concentration.[13] Consequently, the failure point for 0.5% UV-2 stabilized film should be the square root of five times that for 0.1% stabilized film (or 2.24 × 100 = 224 hr). A value of 210 hours was actually measured. This again shows that UV-2 acts only as a screener of ultraviolet light.

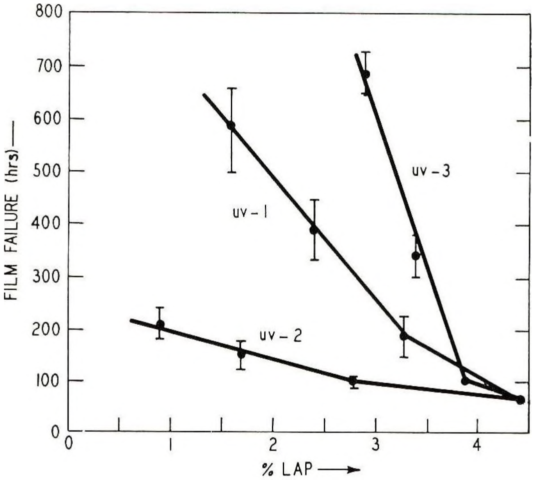

Fig. 3. LAP plot.

The UV-1 and UV-3 curves in Figure 3 do not follow the square root dependency on concentration. The stabilization effectiveness of UV-1 is greater than can be predicted by simple light screening. At the same level of polymer light absorption, UV-1 and UV-3 are much better stabilizers than UV-2. We propose that UV-1, like UV-3 and the other nickel chelates, is an excited-state quencher.

Schmitt[14] and Claudet[2] have calculated the "protective effectiveness" of ultraviolet absorbers which they define to be the ratio of radiant energy absorbed by an unprotected polymer to the energy absorbed by the polymer in a system protected with an ultraviolet absorber. This factor is similar to LAP and was used to compare the protective ability of the various stabilizers. However, the LAP plots give more insight regarding the mechanism of stabilization when it is realized that the light absorbers may stabilize polymers by both screening and energy quenching processes.

Summary and Conclusions

There has been a tendency in the literature to assume that those ultraviolet stabilizers which have high absorptivities function primarily as light screeners in protecting polymers. Our results prove that this is true for the 2-hydroxyphenylbenzotriazoles; however, the 2-hydroxybenzophenones operate by an additional mechanism which is even more important than their screening properties. This mode is probably one of excited-state quenching. It is not unreasonable that organic molecules of this type can be energy quenchers. Many studies of the energy transfer and energy quenching properties of aromatic and unsaturated organic compounds have been reported in the literature.[4,15,16] However, it is interesting that the 2-hydroxybenzophenones are apparently good excited-state quenchers, whereas the 2-hydroxyphenylbenzotriazoles show no such quenching capabilities. This must be related to the nature and positions of the energy levels of these molecules or to the mechanism of energy transfer.[16,17] We are presently engaged in a detailed study of the quenching properties of these stabilizers using photochemical energy transfer techniques. The results will be reported elsewhere.

In our study of the screening properties of ultraviolet absorbers, we have developed two different methods for evaluating stabilization effectiveness. These techniques can be used for testing any stabilizers in all types of polymers. The experimental ultraviolet screening test is useful in isolating the screening behaviors of stabilizers in order to evaluate other properties like energy quenching or antioxidant effects. The LAP analysis can be used with existing polymer failure data to examine in detail the effects of stabilizer concentration, ultraviolet screening, energy quenching, light-intensity distributions, or even synergism in various stabilization formulations. Both of these techniques are aimed at developing a better fundamental understanding of the stabilization mechanism.

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References

1. W. L. Hawkins and F. H. Winslow, in *Crystalline Olefin Polymers*, R. A. V. Raff and K. W. Doak, Eds., Interscience, New York, 1964, Chap 8.
2. J. H. Claudet, G. C. Newland, H. W. Patton, and J. W. Tamblyn, *SPE Trans.*, **1**, 26 (1961).
3. P. J. Briggs and J. F. McKellar, *J. Appl. Polym. Sci.*, **12**, 1825 (1968).
4. M. Heskins and J. E. Guillet, *Macromolecules*, **1**, 97 (1968).
5. J. C. W. Chien and W. P. Conner, *J. Amer. Chem. Soc.*, **90**, 1001 (1968).
6. J. W. Tamblyn and G. M. Armstrong, *Anal. Chem.*, **25**, 460 (1953).
7. G. C. Newland and J. W. Tamblyn, *J. Appl. Polym. Sci.*, **8**, 1949 (1964).
8. W. C. Warner and E. E. Gruber, *Ind. Eng. Chem. Prod. Res. Develop.*, **5**, 219 (1966)
9. A. Rudin, in *Crystalline Olefin Polymers*, R. A. V. Raff and K. W. Doak, Eds., Interscience, New York, 1964, Chap. 1.
10. A. P. Pivovarov, Y. A. Ershov, and A. F. Lukovnikov, *Plast. Massy*, **No. 10, 7** (1966).
11. R. N. Nurmukhametov, D. N. Shigorin, and L. A. Mileshina, *Vysokomol. Soedin.*, **9**, 26 (1967).
12. R. V. Hirt, R. G. Schmitt, N. D. Searle, and A. P. Sullivan, *J. Opt. Soc. Am.*, **50**, 706 (1960).
13. F. H. McTigue and M. Blumberg, in *Weatherability of Plastic Materials Appl. Polymer Symp.*, **4**, M. R. Kamal, Ed., Interscience, New York, 1967, p. 175.
14. R. G. Schmitt and R. C. Hirt, *J. Appl. Polym. Sci.*, **7**, 1565 (1963).
15. S. K. Lower and M. A. El-Sayed, *Chem. Revs.*, **66**, 199 (1966).
16. N. J. Turro, *Molecular Photochemistry*, Benjamin, New York, 1965, Chap. 5.
17. G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

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Effect of Formaldehyde on the Cationic Polymerization of Styrene

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Synopsis

Polymerization of styrene has been carried out in the presence of formaldehyde at 30°C in benzene solution by using boron trifluoride etherate as a catalyst. The rate of polymerization in the initial stage was accelerated with addition of formaldehyde, while the steady-state rate of polymerization was retarded in the presence of formaldehyde. The acceleration for the rate of polymerization was found only in a short time from the beginning. The steady-state rate of polymerization followed the equation:

$$R_x = \frac{-d[\mathrm{M}]}{dt} = \frac{k_1[\mathrm{C}]_0^2[\mathrm{M}]^2}{k_2 + k_3[\mathrm{F}]_0}$$

where $[\mathrm{C}]_0$ and $[\mathrm{F}]_0$ are initial concentrations of catalyst and formaldehyde, $[\mathrm{M}]$ is the monomer concentration, and k_1, k_2, and k_3 are constants. It has been assumed that the chain-transfer reaction does not involve formaldehyde itself but rather the reaction products of formaldehyde, such as polystyrene having ethoxy or hydroxymethyl ends. The apparent chain-transfer constant for the added formaldehyde has been determined to be 1.63.

INTRODUCTION

Numerous studies have been conducted on the thermal stability of polyoxymethylene. In one of these,[1] the copolymerization of formaldehyde with styrene and cyclic acetal with the use of cationic catalysts was attempted, and the copolymers obtained were found to have good thermal stability. The reactivity of formaldehyde with styrene in cationic polymerization has not been reported because of the significant difference in their reactivities and of the poor reproducibility in the polymerization.

It is known that water,[2,3] alcohols, organic acids,[4,5] and ethers[6-8] can act as chain transfer agent, terminator, or co-catalyst in the cationic polymerization. It was reported by Okamura et al.[9] that the cationic polymerization of styrene was inhibited by the presence of a small amount of vinyl esters or acrylates. These unsaturated esters have been considered to react with the growing polymeric cation, leading to formation of stable or inactive ends.

Formaldehyde monomer is polymerized in the presence of cationic catalysts to polyoxymethylenes of moderate molecular weight.[10-13] On the other hand, styrene monomer was well known to polymerize with an observable rate in the presence of cationic catalysts. It is interested to know how the cross propagation reaction in the copolymerization of these monomers may proceed. The aim of the present study was to get information about the effect of a catalytic amount of formaldehyde in the cationic polymerization. To this end, the boron trifluoride etherate-catalyzed polymerization of styrene has been investigated at 30°C in benzene as a solvent under nitrogen atmosphere.

RESULTS AND DISCUSSION

Rate of Polymerization of Styrene in the Presence of Formaldehyde

As can be seen in Figure 1, time-conversion curves were influenced by addition of formaldehyde. It was shown that the initial rate of polymerization increased with increasing formaldehyde concentration, while in a few minutes after the beginning the rate of polymerization decreased with increasing formaldehyde concentration. The rate of polymerization was found to be dependent on the square of the monomer concentration, as shown in Figure 2. However, the unusual observation was made that the values of $[M]_0/[M]$ extrapolated to zero time in Figure 2 were not unity but larger and different. Since the initial monomer concentration should be $[M]_0$, it was suggested that styrene monomer has been consumed at unusual rate during an early period in the polymerization. Shortly after the beginning of reaction, steady-state polymerization of styrene has commenced, where the rate of polymerization is dependent on the square of monomer concentration. In the steady state, formaldehyde or its reaction

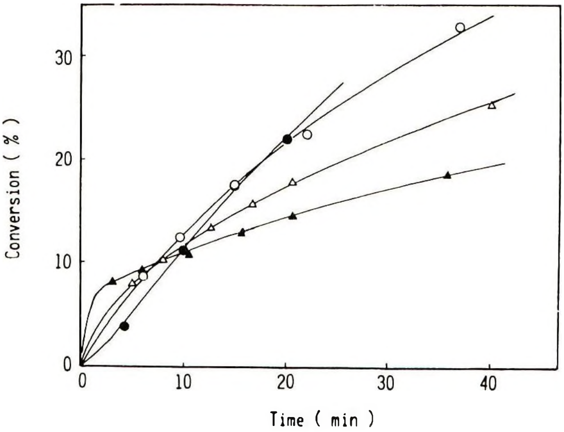

Fig. 1. Effect of formaldehyde on the time-conversion curve for cationic polymerization of styrene in benzene at 30°C: (●) [F] 0; (○) [F] = 1.72×10^{-3} mole/l.; (△) [F] = 4.88×10^{-3} mole/l.; (▲) [F] = 1.38×10^{-2} mole/l. $[M]_0$ = 2.27 mole/l.; $[BF_3 \cdot O(C_2H_5)_2]$ = 6.35×10^{-3} mole/l.

products have been considered to act as chain-transfer agent or retarder, so that the rate of polymerization decreases with increasing formaldehyde concentration.

In the absence of formaldehyde, it was observed that the polymerization of styrene was initiated at some time after the beginning, i.e., an induction period was observed. It has been reported that the polymerization of styrene catalyzed by $BF_3 \cdot O(C_2H_5)_2$ showed no induction period in the presence of water[14,15] but showed some induction period under the extremely anhydrous conditions.[6]

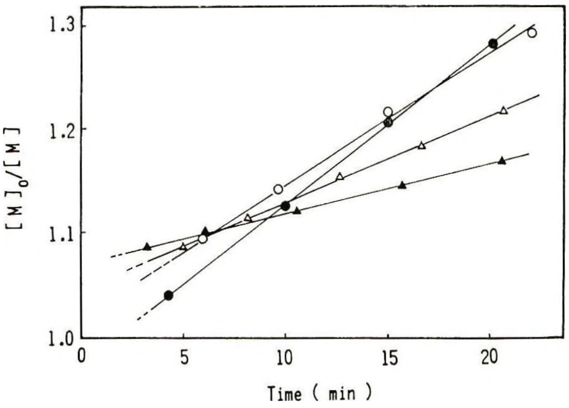

Fig. 2. Second-order plots for the polymerization of styrene. Symbols as shown in Fig. 1.

Effect of Formaldehyde at Steady State. It was shown by Higashimura and Okamura[4] that the rate of cationic polymerization was affected by an additive as summarized in reactions (1)–(6).

Complex Formation:

$$C + AB \rightleftharpoons CAB \text{ or } C' \tag{1}$$

Initiation:

$$C + M \xrightarrow{k_i} M_1^* \tag{2}$$

$$C' + M \xrightarrow{k_{ir}} M_1^* \tag{3}$$

Propagation:

$$M_n^* + M \xrightarrow{k_p} M_{n+1}^* \tag{4}$$

Termination:

$$M_n^* \xrightarrow{k_t} P_n \tag{5}$$

$$M_n^* + AB \xrightarrow{k_{tr}} P_n + (?) \tag{6}$$

Here AB, C, C′, M, M*, and P_n are additive, catalyst, complex, monomer, growing active polymer, and dead polymer, respectively. The rate equation has been introduced under an assumption of steady concentration of the growing active polymer M_n^*, thus:

$$\begin{aligned} R_x &= -d[\mathrm{M}]/dt \\ &= k_p[\mathrm{M}]^2(k_i[\mathrm{C}] + k_{ix}[\mathrm{C}']/k_t + k_{tx}[\mathrm{AB}]) \end{aligned} \tag{7}$$

In the present study, it might be considered that $BF_3 \cdot O(C_2H_5)_2$ catalyst would exchange its ligand with formaldehyde as shown in eq. (8).

$$BF_3 \cdot O(C_2H_5)_2 + CH_2O \rightleftharpoons BF_3 \cdot OCH_2 + (C_2H_5)_2O \tag{8}$$

A difference in stability of each complex could be evaluated by comparison of the electron-donating ability of the ligands, i.e., formaldehyde and diethyl ether. It appeared that the lower the ionization potential of donor, the more stable the BF_3–donor complex was.[16] Since diethyl ether has a lower ionization potential than formaldehyde (Table I), $BF_3 \cdot O(C_2H_5)_2$ will be more stable than $BF_3 \cdot OCH_2$.

In addition, the greater stability of $BF_3 \cdot O(C_2H_5)_2$ was supported by the results that $BF_3 \cdot CH_3OH$ complex liberated methanol which acted as a chain-transfer agent or a terminator in the $BF_3 \cdot O(C_2H_5)_2$-catalyzed polymerization of styrene,[18] and that methanol and acetic acid were only chain-transfer agent or terminator in the cationic polymerization of styrene.[5] Consequently, the ligand exchange reaction might not be taken into account, and diethyl ether was not considered to present in the polymerization system of this study.

Therefore the elementary reactions (1) and (3) as shown above were neglected, and the eq. (7) has been modified as follows:

$$R_a/R_x = 1 + (k_{tx}/k_t)[\mathrm{AB}] \tag{9}$$

where R_a was the rate of polymerization without formaldehyde. The experimental result (Fig. 2) yields eq. (10):

$$R_x = k_x'[\mathrm{M}]^2 \tag{10}$$

Then R_a/R_x was replaced by k_a'/k_x', where k_a' and k_x' were constants for the overall rate of polymerization without and with formaldehyde, respectively. The value of k_a'/k_x' was related to the concentration of formaldehyde $[\mathrm{F}]_0$, as shown in Figure 3. The linear relation in Figure 3 supports eq. (9), and indicates a value for k_{tx}/k_t of 1.6×10^2.

TABLE I
Ionization Potential of Some Organic Compounds as Electron Donors

Electron donor	First ionization potential, eV[a]
H_2O	12.61, 12.6, 12.59
CH_2O	10.90, 10.87
CH_3OH	10.95, 10.85
CH_3COOH	10.7, 10.66, 10.38
$(C_2H_5)_2O$	9.65, 9.53

[a] Data of Vedeneyeu et al.[17]

Investigation of the effect of catalyst concentration on the rate of polymerization leads to the interesting result (Fig. 4) that the rate of polymerization is dependent on the square of catalyst concentration. The results reported in the literature[14–16] have shown a linear relation between rate of polymerization and catalyst concentration.

The rate equation was assumed to be expressed as follows:

$$R_a = k_a[\mathrm{C}]^n[\mathrm{M}]^2 \tag{11}$$

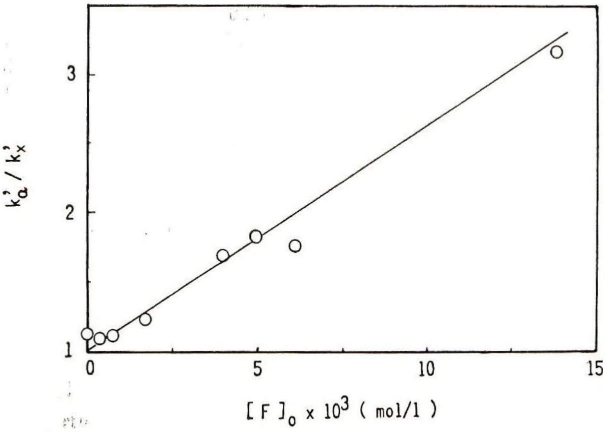

Fig. 3. Effect of formaldehyde on the steady-state rate of polymerization of styrene $[\mathrm{M}]_0 = 2.27$ mole/l.; $[\mathrm{BF_3 \cdot O(C_2H_5)_2}]_0 = 6.35 \times 10^{-3}$ mole/l.; in benzene, 30°C.

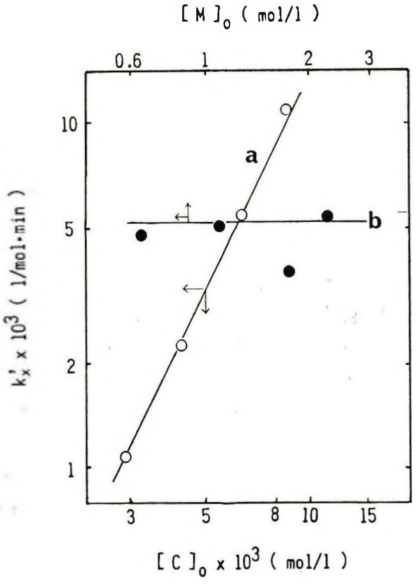

Fig. 4. Effects of initial concentration of monomer and $\mathrm{BF_3 \cdot O(C_2H_5)_2}$ on the steady-state rate of polymerization: (*a*) $[\mathrm{M}]_0 = 2.27$ mole/l., $[\mathrm{F}]_0 = 1.72 \times 10^{-3}$ mole/l.; (*b*) $[\mathrm{BF_3 \cdot O(C_2H_5)_2}]_0 = 6.35 \times 10^{-3}$ mole/l., $[\mathrm{F}]_0 = 1.72 \times 10^{-3}$ mole/l.

TABLE II

Effect of Catalyst Concentration on the Rate of Polymerization[a]

Run no.	$[C]_0 \times 10^3$, mole/l.	$[F]_0/[C]_0$, mole/mole	$k_r' \times 10^3$ l./mole-min	k_a'/k_r'	
				$n = 1$	$n = 2$
C–1	2.87	0.599	1.08	2.82	1.28
C–2	4.24	0.408	2.28	2.07	1.31
F–4	6.37	0.270	5.44	1.24	1.24
C–3	8.60	0.201	11.1	0.82	1.11
F–3	6.35	0.120	5.96	1.13[b]	
F–5	6.35	0.625	3.97	1.70[b]	
F–8	6.35	2.17	2.12	3.18[b]	
F–0	6.35	0	6.74 $(=k_a')$	1.00	

[a] $[M]_0 = 2.27$ mole/l., 30°C, in benzene solution.

[b] Calculated by using the value of No. F–0 only.

where $k_a[C]^n = k_a'$, and n was one or two. Some values of k_a'/k_r' were calculated by using eq. (11) in both cases, $n = 1$ and $n = 2$. The results of calculation are shown in Table II.

The rate of polymerization was shown to be well dependent on the square of catalyst concentration regardless of presence or absence of formaldehyde in the present study. It was explained that the unusual dependence of catalyst concentration on the rate was caused by the heterogeneity of polymerization solution in the presence of catalytic amounts of water (0.6–3.1×10^{-3} mole/l.). One of the reasons for such an unusual observation, would be an initiation mechanism following eq. (2′) instead of the usual initiation step, eq. (2).

$$2C + M \xrightarrow{k_i} M^* \qquad (2')$$

Effect of Formaldehyde at Early Stage. The acceleration of polymerization at the beginning may be explained by high reactivity of formaldehyde; thus the added formaldehyde has preferably reacted with catalyst to form the growing cation, leading to the formation of polystyrene having formaldehyde units in the end groups. The polymers containing formaldehyde ends were considered to act as chain-transfer agent or retarder.

Addition of formaldehyde to the polymerization solution at steady state causes the rate of polymerization to accelerate once more, as shown in Figure 5. Thereafter, the polymerization assumes a steady state again, but the rate of polymerization is now somewhat lower than that before the addition of formaldehyde.

Since the accelerating effect of formaldehyde on the initial rate of polymerization could not be evaluated by comparing the rate of polymerization at steady state, the extrapolated values of $[[M]_0/[M]]$ to zero time have been related to the concentration of formaldehyde as shown in Figure 6. A linear relation between $([M]_0/[M])_{t\to 0}$ and $[F]_0$ was observed. In other words, the styrene monomer consumed at the beginning was proportional to the initial concentration of formaldehyde up to an order of catalyst con-

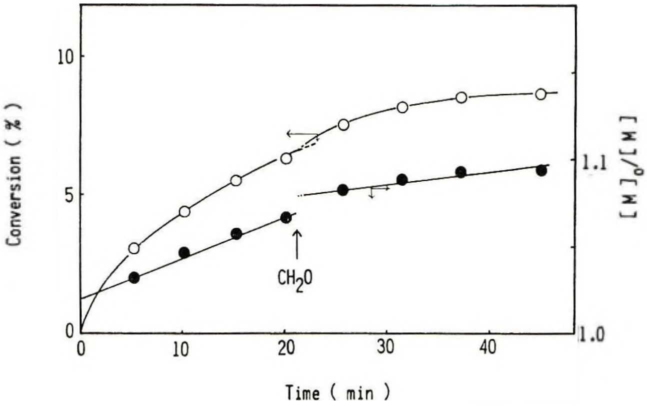

Fig. 5. Effect of addition of formaldehyde at steady-state on (○) conversion and (●) $[M]_0/[M]$. $[M]_0 = 2.27$ mole/l.; $[BF_3 \cdot O(C_2H_5)_2]_0 = 2.87 \times 10^{-3}$ mole/l.; $[F]_0 = 1.72 \times 10^{-3}$ mole/l.; added formaldehyde $= 0.5 \times 10^{-2}$ mole (ca. $[F] = 2 \times 10^{-3}$ mole/l.).

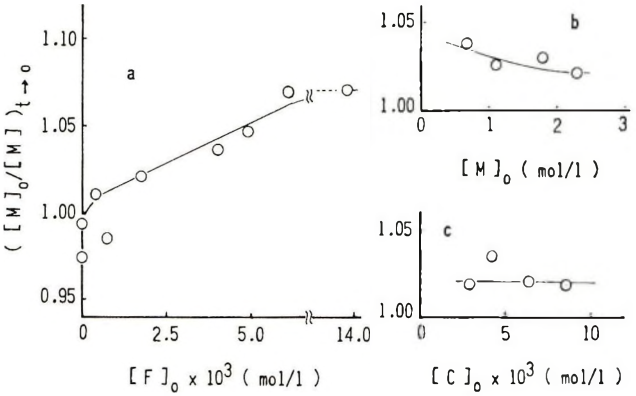

Fig. 6. Effects of initial concentrations of monomer, catalyst and formaldehyde on the extrapolated values of $([M]_0/[M])_{t\to 0}$: (*a*) $[M]_0 = 2.27$ mole/l., $[C]_0 = 6.35 \times 10^{-3}$ mole/l.; (*b*) $[C]_0 = 6.35 \times 10^{-3}$ mole/l., $[F]_0 = 1.72 \times 10^{-3}$ mole/l.; (*c*) $[M]_0 = 2.27$ mole/l., $[F]_0 = 1.72 \times 10^{-3}$ mole/l.

centration. While the values of $([M]_0/[M])_{t\to 0}$ were not affected by catalyst concentration, those values decreased slightly with increasing monomer concentration.

Degree of Polymerization

If cationic polymerization of styrene were influenced by addition of formaldehyde as a chain-transfer agent, the degree of polymerization might be represented by the equation of Overberger et al.[19] as follows:

$$1/P_x = (1/P_0) + (k_{tr}[AB]/k_p[M]) \qquad (12)$$

where P_x and P_0 are degrees of polymerization in the presence and absence of additive, respectively, and k_{tx}/k_p is the chain-transfer constant to the additive.

As it was confirmed that the degree of polymerization was independent to the conversion, reciprocal degree of polymerization for the polymers obtained at conversions of 11–15% has been plotted against the concentration of formaldehyde as shown in Figure 7, and a linear relation between them is given. The apparent chain-transfer constant for formaldehyde (k_{tx}/k_p) was calculated to be 1.63, which is comparable to the chain-transfer constant of acetic acid, (1.44)[5] and that of hydroxymethyl-ended polyether, (6).[8]

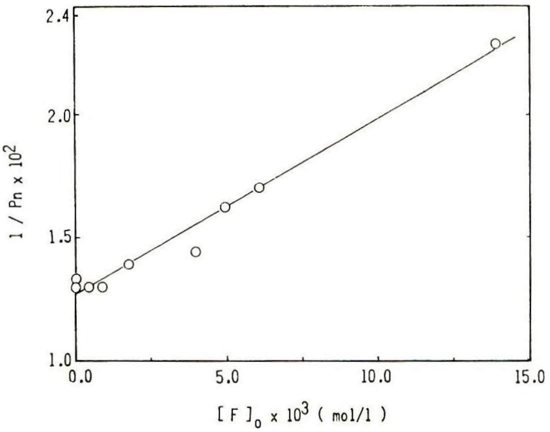

Fig. 7. Relationship between $1/P_n$ of polystyrene and $[F]_0$. $[M]_0$ = 2.27 mol /l.; $[C]_0$ = 6.35 × 10^{-3} mole/l.

If the value obtained here were the true chain-transfer constant for formaldehyde itself, it might be the relative reactivity of formaldehyde to styrene ($1/r_2$) for the copolymerization of formaldehyde (M_1) and styrene (M_2). From this assumption r_2 has been calculated to be 0.61; however, this was not consistent with the apparent reactivity ratio of $r_2 \approx 0$ for the cationic copolymerization at −78°C in toluene solution.[22a] Thus it was concluded that any chain transfer reaction occurring was not to formaldehyde itself but to the reaction product of formaldehyde with other compounds.

Relation of the reciprocal monomer concentration with the reciprocal degree of polymerization at constant molar ratio of catalyst to formaldehyde is shown in Figure 8. It was reported that the self-termination constant for styrene was smaller than 0.1 × 10^{-2} for BF_3-initiated polymerization in benzene[20] and could be neglected as compared to the other chain transfer constants. Then eq. (13) was introduced

$$\frac{1}{P_x} = \left(\frac{k_{tm}}{k_p} - b\frac{k_{ts}}{k_p}\right) + \left(a\frac{k_{ts}}{k_p} + \frac{k_{tx}}{k_p}[\mathrm{AB}]\right)\frac{1}{[\mathrm{M}]} \qquad (13)$$

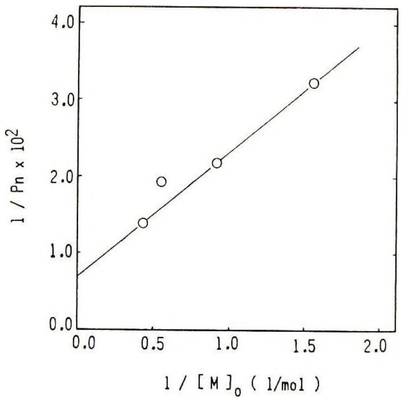

Fig. 8. Relationship between $1/P_n$ of polystyrene and $1/[M]_0$. $[C]_0 = 6.35 \times 10^{-3}$ mole/l.; $[F]_0 = 1.72 \times 10^{-3}$ mole/l.

where $a = 11.10$ mole/l. and $b = 1.294$ are constants for the polymerization. Therefore, the values of the chain transfer constants k_{ts}/k_p and k_{tm}/k_p for benzene and styrene monomer, respectively, were calculated to be 0.13×10^{-2} and 0.81×10^{-2}, respectively. In this calculation it was assumed that [AB] was the same as $[F]_0$ and k_{tx}/k_p was 1.63 as obtained above. These chain transfer constants for benzene and styrene agree well with those reported in the literature,[20] i.e., 0.11×10^{-2} and 0.82×10^{-2} respectively. It was concluded, therefore, that the cationic polymerization of styrene at steady state goes through an identical propagation mechanism whether formaldehyde was present in the polymerization system or not.

Mechanism of Polymerization

It was recognized that a small amount of formaldehyde is dissolved in hydrocarbon solvent as a monomeric form.[21,22b] In this study, styrene monomer has never been polymerized with addition of a catalytic amount of formaldehyde only. On the other hand, formaldehyde monomer could be polymerized by BF_3; the initiation mechanism proposed is as shown in eqs. (14) and (15).[26,27]

$$BF_3 + CH_2O \rightarrow {}^-BF_3{-}OCH_2{}^+ \tag{14}$$

$$\left.\begin{aligned} &BF_3 + CH_2O \rightarrow BF_3 \leftarrow OCH_2 \\ &BF_3 \leftarrow OCH_2 + BF_3 \rightarrow [BF_2OCH_2]^+BF_4^- \end{aligned}\right\} \tag{15}$$

While the mechanism of initiation for the $BF_3 \cdot O(C_2H_5)_2$-initiated polymerization of formaldehyde has not been shown yet clearly, it could be estimated to be similar to those for styrene and vinyl ethers [eqs. (16)].[23]

$$\left.\begin{aligned} &BF_3 \cdot O(C_2H_5)_2 \rightleftharpoons BF_3 \cdot OC_2H_5^- + C_2H_5^+ \\ &BF_3 \cdot OC_2H_5^- + C_2H_5^+ + CH_2O \rightarrow [BF_3 \cdot OC_2H_5]^{-\,+}CH_2OC_2H_5 \end{aligned}\right\} \tag{16}$$

In the case of the catalyst system BF_3–H_2O, a similar mechanism for initiation has been proposed.[22c]

The acceleration of polymerization rate observed at the initial stage in the present study may be explained by the difference between formaldehyde and styrene in the reactivity to the catalyst. Thus, the initiation including catalyst and formaldehyde as shown in eqs. (16) would take place mainly at an early stage as compared to the initiation including catalyst and styrene. When all of the formaldehyde added had been consumed, the cationic polymerization of styrene was carried out through the usual initiation mechanism.

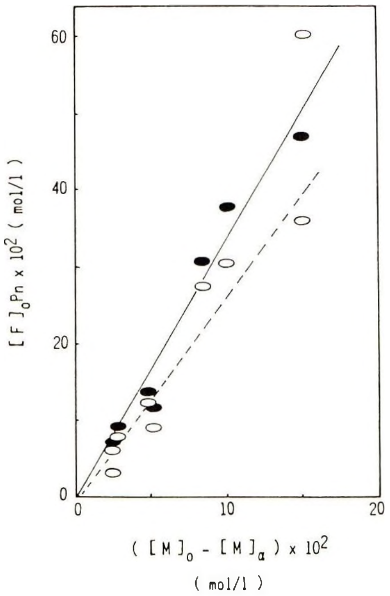

Fig. 9. Relationship between [F]$_0$ P_n and ([M]$_0$ − [M]): (○) observed value of P_n; (●) P_n calculated by using k_{tm}/k_p and k_{ts}/k_p assuming k_{tx}/k_p to be zero at the beginning of polymerization.

It was interesting to see that the quantity of monomer consumed instantaneously at the beginning, i.e., $[M]_0 - [M]_\alpha$, is related to the molar quantity of styrene monomer contained in polystyrene believed to contain formaldehyde ends, i.e. $[F]_0P_n$, as shown in Figure 9, where $[M]_\alpha$ is given from $([M]_0/[M]_\alpha)_{t=0}$. Since the value of P_n used was determined for the polymer obtained at steady state and $[M]_0 - [M]_\alpha$ would not be true moles of monomer consumed at zero time, $[F]_0P_n$ was not equal to but proportional to $[M]_0 - [M]_\alpha$. As a result, it may be suggested that formaldehyde added has reacted at an early stage in the polymerization of styrene, leading to the rapid initiation and the formation of compounds believed to act as chain-transfer agents or retarders, i.e., ethoxy- or hydroxy-methyl-ended polystyrene.

EXPERIMENTAL

Purification of Reagents

Styrene. Commercial monomer was washed with 20% of sodium hydroxide and then 20% of sodium bisulfite. It was then washed with water repeatedly, dried over calcium chloride, and finally was distilled under nitrogen at reduced pressure over barium oxide; bp 51–53°C/26–28 mm.

Formaldehyde. This was obtained by pyrolysis of α-polyoxymethylene and purified by prepolymerization through two traps held at -15°C. It was then dissolved in benzene and used as benzene solution.

$BF_3 \cdot O(C_2H_5)_2$. Commercial reagent was fractionally distilled under reduced pressure in nitrogen atmosphere, only the middle cut being retained; bp 55°C/43 mm.

Catalyst was used as benzene solution.

Benzene. This was purified by the usual methods, and dried over sodium metal.

Polymerization

All the polymerizations were conducted in a 500-ml, five-necked flask equipped with reflux condenser, stirrer, inlet tubes for reagents and nitrogen, silicone rubber-mounted tube, and exit tube for polymerized solution and nitrogen. Reactions were conducted at 30°C under a stream of nitrogen. The connections were glass joints with the exception of the exit tube, which was connected with a silicone rubber stopper. The exit tube has a buret for measuring the polymerization solution taken out.

Styrene monomer and benzene were distilled into the polymerization flask, and formaldehyde as benzene solution was added to the flask through the rubber mounting by using a hypodermic syringe. The concentration of formaldehyde in benzene was determined by the iodine method[22] prior to or at the same time of polymerization. The concentration of water in the

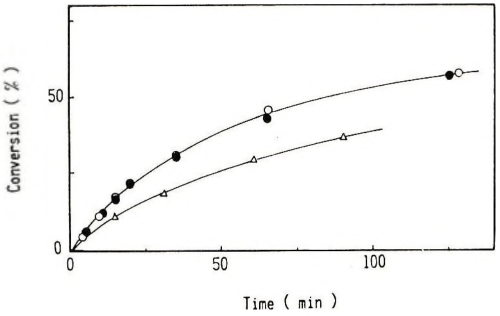

Fig. 10. Reproducibility in the cationic polymerization of styrene at 30°C in benzene: (○) [water] = 1.98×10^{-3} mole/l.; (●) [water] = 2.08×10^{-3} mole/l.; (△) [water] = 5.82×10^{-3} mole/l. $[M]_0 = 2.27$ mole/l.; $[C]_0 = 6.31\text{–}6.46 \times 10^{-3}$ mole/l.

solution of polymerization was determined by the Karl-Fischer method on an aliquot taken with use of hypodermic syringe; this was found to be 0.6–3.1 mmole/l. and comparable to that reported in the literature.[24]

The polymerization was started with an addition of catalyst solution to the flask through the rubber mounting by using a hypodermic syringe. Aliquots of the polymerization solution were transferred to the buret, measured, and poured into a large amount of methanol at suitable time intervals. The polymer was reprecipitated into methanol from benzene solution and dried under reduced pressure at 60°C to constant weight.

The reproducibility of experiments is shown in Figure 10. The rate of polymerization in the present study was found to be higher than that reported in the literature.[14,15,18] This suggested that a small amount of water acted as a cocatalyst; however, larger amounts of water (>5 mmole/l.) retard the rate of polymerization.

The degree of polymerization was determined by measurement of reduced viscosity at 25°C in benzene solution (c = 0.35–0.60 g/dl) in which the equation of Pepper was used:[25]

$$[\eta] = 2.27 \times 10^{-4}\bar{M}_n^{0.72} \tag{17}$$

The degree of polymerization of some polymers was also determined by ebulliometry and found to be in agreement with that determined by viscometry as shown in Table III.

TABLE III
Degree of Polymerization Determined by Different Methods

Sample	η_{sp}/c, dl/g	Degree of polymerization	
		By viscometry[a]	By ebulliometry[b]
1	0.076	30.9	31.5
2	0.094	41.4	42.4
3	0.110	51.6	53.2

[a] Calculated with use of the eq. (17).

[b] Determined by using a Takara E-4 ebulliometer in benzene solution.

Infrared spectra of polymers did not show distinct hydroxyl group absorption at 3400–3500 cm.$^{-1}$

References

1. W. Fukuda and H. Kakiuchi, *Kogyo Kagaku Zasshi*, **67**, 1665 (1964).
2. C. G. Overberger, R. J. Ehrig and A. R. Marcus, *J. Amer. Chem. Soc.*, **80**, 2456 (1958).
3. R. O. Colclough and F. S. Dainton, *Trans. Faraday Soc.*, **54**, 386 (1958).
4. T. Higashimura and S. Okamura, *Kobunshi Kagaku*, **13**, 342 (1956).
5. T. Higashimura and S. Okamura, *Kobunshi Kagaku*, **17**, 57 (1960).
6. M. Imoto and S. Aoki, *Makromol. Chem.*, **63**, 141 (1963).
7. T. Higashimura and S. Okamura, *Kobunshi Kagaku*, **15**, 702 (1958).
8. Y. Minoura and M. Mitoh, *Makromol. Chem.*, **128**, 41 (1969).

9. T. Higashimura and S. Okamura, *Kobunshi Kagaku*, **17**, 635 (1960).

10. H. Staudinger, *Die Hochmolekularen Organischen Verbindungen Kautschuk und Zellulose*, Springer, Berlin (1932).

11. J. E. Carothers and R. G. W. Norrish, *Trans. Faraday Soc.*, **32**, 195 (1936).

12. J. C. Bevington and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A205**, 517 (1951).

13. W. Fukuda and H. Kakiuchi, *Kogyo Kagaku Zasshi*, **65**, 2054 (1962).

14. K. Saotome and M. Imoto, *Kobunshi Kagaku*, **15**, 373 (1958).

15. S. Okamura, T. Higashimura, and Y. Sakurada, *Kobunshi Kagaku*, **16**, 49 (1959).

16. H. A. Skinner, in *Cationic Polymerization and Related Complexes*, P. H. Plesch, Ed. Heffer, Cambridge, 1953, p. 28.

17. V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medevedev, and Ye. L Frankevich, *Bond Energies, Ionization Potentials and Electron Affinities* (Engl. Transl.) Arnold, London, 1966.

18. S. Okamura, T. Higshimura, and Y. Ogawa, *Kobunshi Kagaku*, **16**, 239 (1959).

19. C. G. Overberger and G. F. Endres, *J. Amer. Chem. Soc.*, **75**, 6349 (1953).

20. Y. Sakurada, T. Higashimura, and S. Okamura, *J. Polym. Sci.*, **33**, 496 (1958).

21. S. A. Schou, J. chim. phys., **26**, 72 (1929); *Chem. Abstr.*, **23**, 3438 (1929).

22. M. Imoto, H. Kakiuchi, and K. Ko, Eds., *Formaldehyde*, Asakura, Tokyo, 1965, (a) p. 88; (b) p. 6; (c) p. 67; (d) p. 414.

23. J. D. Coombes and D. D. Eley, *J. Chem. Soc.*, **1957**, 3700; J. P. Kennedy, *J. Polym. Sci.*, **38**, 263 (1959).

24. T. Higashimura and S. Okamura, *Kobunshi Kagaku*, **15**, 708 (1958).

25. D. C. Pepper, *J. Polym. Sci.*, **7**, 347 (1951).

26. W. Kern, H. Cherdron, and V. Jaacks, *Angew. Chem.*, **73**, 177 (1961).

27. O. Vogl and W. M. D. Bryant, *J. Polym. Sci. A*, **2**, 4633 (1964).

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Fundamental Studies on Cationic Polymerizations: Molecular Weights and Molecular Weight Distributions of Polyisobutylenes Produced by γ-Irradiation (Free Ions) and Chemical Catalysis (Ion Pairs)

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Synopsis

The molecular weights ($\bar{M}_n$, $\bar{M}_v$, and $\bar{M}_w$)and molecular weight distributions of polyisobutylenes synthesized by γ-irradiation in the range 29 to −78°C have been determined. The plots of log $\bar{M}_n$, log $\bar{M}_v$, and log $\bar{M}_w$ versus $1/T$ are linear and parallel ($E_{\bar{M}} = -6.3_6 \pm 0.5$), and $\bar{M}_w/\bar{M}_n \approx 3.0 \pm 0.5$ over this temperature range. The viscosity-average molecular weights of polyisobutylenes obtained by γ-irradiation were compared with those of polymers prepared by BF_3, $EtAlCl_2$, and $AlCl_3$. It is found that, at the same polymerization temperature, the $\bar{M}_v$ of radiation-induced polyisobutylenes, which propagate by free carbonium ions, is significantly higher than those synthesized by the Lewis acids, which probably propagate via ion pairs. The implications of these findings are discussed, and it is concluded that the counterion in the proximity of the growing cation impedes propagation to a greater extent than it does the competing process of chain transfer to monomer.

INTRODUCTION

It has been established that the radiation-induced cationic polymerization of isobutylene under anhydrous conditions occurs through propagation by free ions,[1] whereas the propagating species in catalyzed polymerizations are probably carbonium-ion/counterion pairs. The problem of the nature of the propagating entities in carbonium-ion initiated polymerizations has been discussed in detail recently in various review articles.[2-4] Essentially, the argument that ion pairs associated to a greater or lesser degree are the propagating entities in catalyzed cationic polymerizations rests on the fact that various initiators such as $AlCl_3$, BF_3, $TiCl_4$, $AlEtCl_2$, under substantially identical conditions give very different rates of polymerizations and produce a wide spectrum of molecular weights. If the propagating carbonium ions were kinetically free, such differences would not be expected to arise.

It occurred to us that a readily available basis for comparison between cationic propagation by free ions and ion pairs resides in the investigation of the effect of temperature on the molecular weight distributions of polyisobutylenes obtained with radiation initiation and with chemical initiation, i.e., BF_3, $AlCl_3$, etc. Similarities and differences emerge, and the mechanistic implications are considered.

EXPERIMENTAL

The materials used and polymerization technique have been described.[1] The only change was to use graduated tubes so that the total amount of sample was known before irradiation. γ-Irradiations were carried out either in a modified Gammacell-200 source[1] or in another ^{60}Co source located in the Reactor Chemistry Division of the Oak Ridge National Laboratory. Dose rates were calibrated by means of the standard ferrous-ion dosimeter. The temperature rise of the sample during the period of irradiation did not exceed 2 or 3°C in most of the experiments reported. After irradiation, the polymers were carefully isolated and dried to determine percent conversion.

Number-average molecular weights $\bar{M}_n$ were obtained by membrane osmometry in toluene solution at 30°. Viscosity-average molecular weights $\bar{M}_v$ were calculated from measurements at a single concentration (0.1%) in diisobutylene solution at 20.0°C by using the equation of Flory.[5] In addition, the number-, viscosity-, and weight-average molecular weights ($\bar{M}_n$, $\bar{M}_v$, $\bar{M}_w$) and the molecular weight distributions (MWD) were obtained with a commercial gel-permeation chromatograph (GPC) (Waters Associates) using four polystyrene gel columns (10^6, 10^5, 10^4 and 10^3 Å pore size ratings) and THF solvent at 23°C. The molecular weights were obtained from GPC elution volumes with the aid of a calibration curve prepared from narrow polyisobutylene fractions covering the $\sim 10^3$ to $\sim 10^6$ range. From GPC results $\bar{M}_n$, $\bar{M}_v$, and $\bar{M}_w$ were obtained by standard procedures by using data taken at 1/2 count (2.5 ml elution volume).

Unsaturations were determined by the method of Gallo et al.[6]

RESULTS

Rates and $G(-m)$ Values

According to the results in Table I, the rates of polymerization (percent conversion per unit time) and the $G(-m)$ values (molecules of monomer converted to polymer per 100 eV) at the same dose rate are about a factor of ten greater at the higher temperatures, i.e., above -22°C, than below this approximate value. Previous work[1] has also shown that the maximum attainable rates can be obtained more reproducibly at higher temperatures.

The dose rates listed in Table I differ only by a factor of 2.5, so from the dose rate dependence of the polymerization rate one would expect[1] the maximum ratio of $G(-m)$ values at these two dose rates to be $\sqrt{2.5}$ or 1.6. According to two data points obtained at 0°C (not included in Table I), this ratio was found to be 2.0, in fair agreement with expectation.

TABLE I

Effect of Molecular Weights of Polyisobutylenes Obtained in Radiation-Induced Polymerization

Temp, °C	Irradiation time, sec	Dose rate, eV/g sec	Conversion wt-%	$G(-m)$, molecules/100 eV	Unsaturation, mole-%	Molecular weights × 10^{-3}					
						Osmometry	Viscometry	GPC			
						$\bar{M}_n$	$\bar{M}_v$	$\bar{M}_n$	$\bar{M}_v$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
29	480	5.1×10^{13}	13.4	5.9×10^{6}	—	28.0	32.7	21.5	58.2	72.8	3.38
0	180	5.1×10^{13}	19.1	2.2×10^{7}	1.50	—	101.7	42.9	127.5	164.0	3.82
−22	360	5.1×10^{13}	10.4	5.8×10^{6}	—	—	290	215	472	539	2.51
−24	1200	5.1×10^{13}	6.9	1.2×10^{6}	—	221	369	242	468	528	2.19
−31	540	5.1×10^{13}	4.6	1.8×10^{6}	—	—	632	219	639	745	3.40
−41	1200	5.1×10^{13}	7.9	1.3×10^{6}	0.04	—	575	331	691	785	2.37
−47	600	1.3×10^{14}	8.5	1.2×10^{6}	—	~600	2,400?	564	3,367?	4,100?	
−70	600	1.3×10^{14}	18.7	2.6×10^{6}	—	>1 × 10^{3}	4,820	1,980	5,740	6,800	3.44
−78	1200	5.1×10^{13}	7.9	1.3×10^{6}	0.04	—	5,520				

Molecular weights are determined by chain transfer to the monomer over the range of temperature examined. This conclusion follows since the kinetic chain length $G(-m)/G_i$ (where $G_i < 1$ is the yield of initiating species[1] in molecules/100 eV) is always much greater than the degree of polymerization. Evidently termination of the kinetic chain by either ion recombination or impurities has negligible influence on molecular weights in this work.

Irradiation Dose and Molecular Weight Distribution

Since the possibility exists that the polymer will suffer radiation damage soon after its birth during the experiment, the effect of the total dose on the molecular weights and/or molecular weight distributions must be evaluated independently.

To this end, a polymer was prepared at −70°C ($\bar{M}_n$ by GPC = 1,980,000, Table I) and reirradiated *in vacuo* at −78°C to a dose of 1.5×10^{17} eV/g, i.e., a dose twice that used originally to produce the sample. A comparison of GPC molecular weights before and after reirradiation is given in Table II.

Both distributions were almost symmetrical, and the maxima of both curves were almost at the same count, corresponding to a molecular weight of 5,200,000. Thus reirradiation lowers $\bar{M}_n$ but enhances $\bar{M}_v$ and $\bar{M}_w$. This is peculiar, because after reirradiation one would expect to find lowered $\bar{M}_w$ and $\bar{M}_v$ with somewhat reduced $\bar{M}_n$. (These MWD determinations were repeated with a new set of columns but the results were essentially the same.) These results are most likely due to experimental variation caused by the difficulties associated with determining very high molecular weights. A calculation also indicates that the danger of chain degradation under the conditions used is small. Thus assuming that the G value for random main-chain scission in polyisobutylene is 5, the probability for scission of a 2×10^6 $\bar{M}_n$ molecule with a dose of 1.5×10^{17} eV/g is 0.025. Thus the irradiation doses used do not significantly alter the original molecular weights.

A further comment is necessary in view of some previous results by Stannett et al.[7] which showed that the molecular weights of the polyisobutylene prepared at −78°C under their conditions were controlled by the concurrent radiation-induced degradation of the polymer. The essential difference between the two studies is that the doses used by us (Table I) were only of the order of 0.001 Mrad, whereas Stannett et al.[7] used ca. 1 Mrad. We were able to obtain polymer at these much lower doses because our G values are at least a thousandfold higher than those attained in earlier

TABLE II

	$\bar{M}_n \times 10^{-3}$	$\bar{M}_v \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$
Before reirradiation	1980	5740	6800
After reirradiation	1350	6840	8900

work.[7,8] The data of Stannett et al.[7] at -78°C extrapolated to zero dose give close to 10^8 for $\bar{M}_v$, which is not in very good agreement with 6×10^6 for $\bar{M}_v$ as directly determined by us. While it is difficult to determine precise molecular weights above 10^6 by GPC, we believe that the overall consistency of our data (*vide infra*) and the absence of complications from radiation-induced degradation supports our results.

Molecular Weights and Molecular Weight Distributions

The effect of polymerization temperature on the various molecular weight averages are shown in Figure 1. The scatter of the data around the lines is

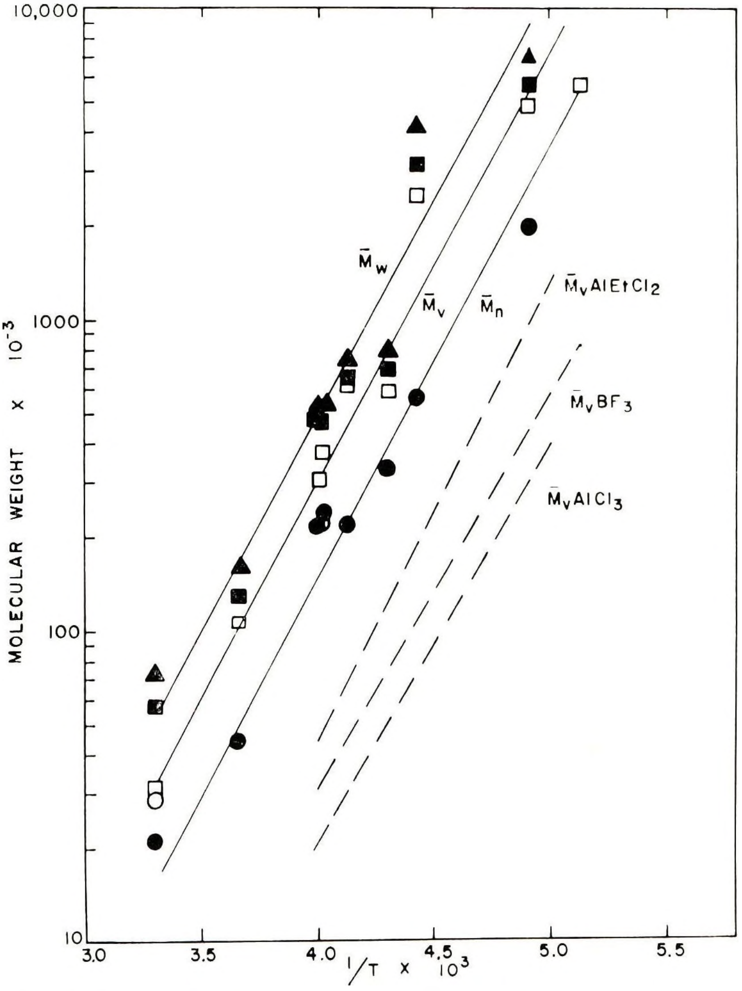


Fig. 1. Effect of polymerization temperature on the weight-, viscosity-, and number-average molecular weights of polyisobutylenes obtained by various initiators: (——) molecular weight averages of radiation-initiated polymerizations; (- -) viscosity-average molecular weights of catalytically produced polymer;[9] (▲) $\bar{M}_w$ by GPC; (■) $\bar{M}_v$ by GPC; (□) $\bar{M}_v$ by viscometry; (●) $\bar{M}_n$ by GPC; (○) $\bar{M}_n$ by osmometry.

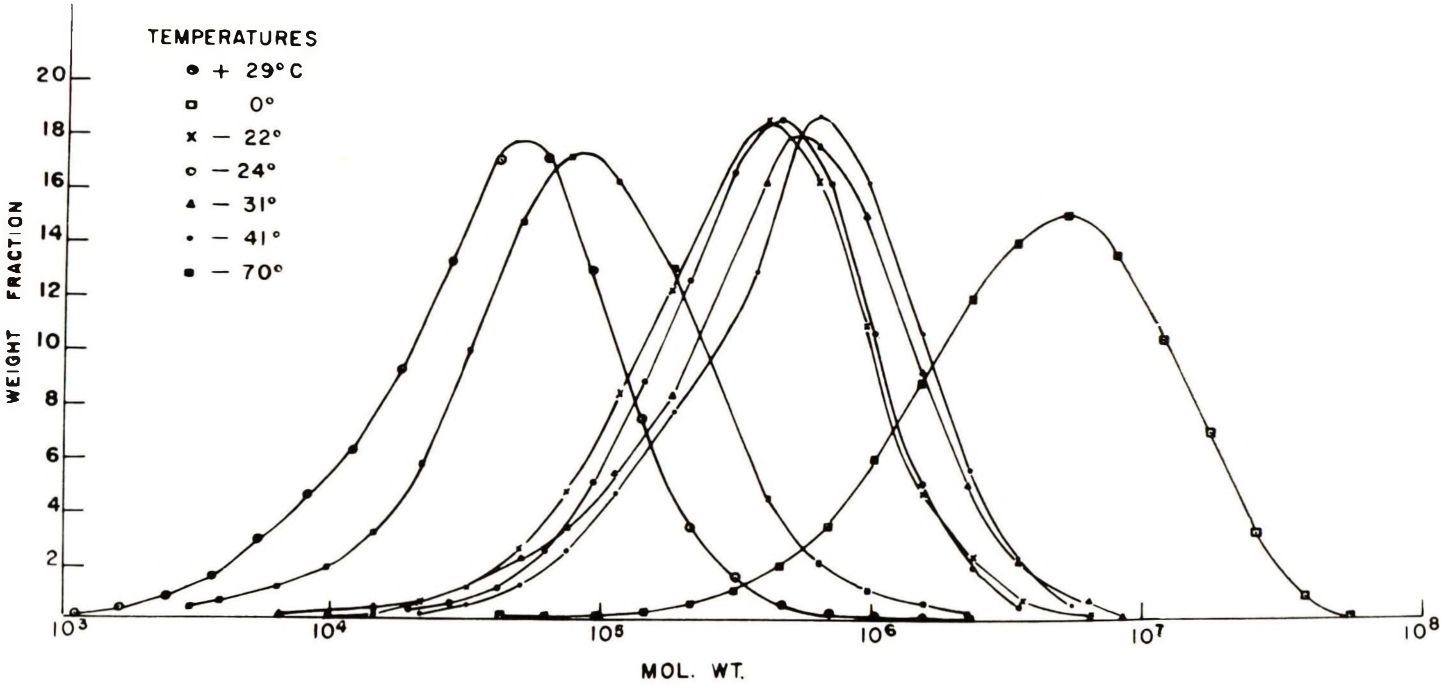


Fig. 2. Effect of polymerization temperature on the molecular weight distribution of polyisobutylenes prepared by radiation-induced polymerization.

considerable. There is a noticeable discrepancy between $\overline{M}_n$ obtained by osmometry and the GPC technique. Also, the $\overline{M}_v$ values obtained by viscometry are consistently lower than those found by GPC. The reason for this discrepancy is unknown. The $\overline{M}_v$ (viscometric and GPC) and $\overline{M}_w$ values of the polymer obtained at -47°C are clearly too high (the data which are considered questionable are indicated by a question mark in Table I). In spite of this scatter the information conveyed by Figure 1 is valuable: it indicates a linear relationship between the logarithm of various molecular weight averages and $1/T$. Significantly, the slopes of the lines are similar within experimental variation. This reciprocal effect of the temperature on the molecular weights is well known.[9,10] For comparison we have also included corresponding plots of $\overline{M}_v$ values (by viscometry) obtained in a previous study of isobutylene polymerization initiated by $AlCl_3$, BF_3, and $AlEtCl_2$ catalysts in methyl chloride solution.[9] All $\overline{M}_v$ plots are parallel within experimental error, and, significantly, the vertical displacement between the lines is such that the molecular weights obtained in catalytic polymerization are much lower than those produced by radiation-induced polymerization at the same temperature.

That the various log $\overline{M}$ versus $1/T$ lines for the radiation-induced polymerization are parallel over about three decades of $\overline{M}$ from $+29$ to -70°C implies that the molecular weight distributions characterized by $\overline{M}_w/\overline{M}_n$ are independent of the polymerization temperature in this range. This is borne out by the calculated polydispersity ratios $\overline{M}_w/\overline{M}_n = 3.0 \pm 0.5$ shown in Table I and by inspecting the original GPC distribution curves in Figure 2. This figure shows normalized MWD as weight fractions versus log $\overline{M}$ for seven polyisobutylenes prepared between $+29$ and -70°C. All the distributions appear to be unimodal and slightly skewed toward low molecular weights.

DISCUSSION

The results show a considerable dependence on the polymerization temperature T. The logarithm of $\overline{M}_n$, $\overline{M}_v$, and $\overline{M}_w$ for radiation-induced polyisobutylenes increases linearly with $1/T$. The molecular weight dispersity ratio $\overline{M}_w/\overline{M}_n$ is 3.0 ± 0.5 in the range from $+29$ to -70°C. All the slopes of the log $\overline{M}$ versus $1/T$ lines are parallel; thus the $E_{tr,\mathrm{m}} - E_p$ calculated from the linear Arrhenius plots for radiation-induced and catalytically initiated polymerizations are essentially the same. The molecular weights of radiation-induced polyisobutylenes are much higher than those of materials obtained by catalytic polymerization at the same temperature.

The fact that the molecular weights of radiation-induced polyisobutylenes increase with decreasing polymerization temperatures whereas the polymerization rates are not particularly sensitive to the irradiation temperature[1] indicates that the molecular weights are governed by the ratio of rates of propagation and transfer to the monomer ($k_p/k_{tr,\mathrm{m}}$). We cannot explain the deviation of the dispersity ratio (3.0 ± 0.5) from the theoretical value of 2.0.

From the slope of the lines in Figure 1, $E_p - E_{tr,m} = -6.3_6 \pm 0.5$ kcal/mole. With this information, the activation entropies for the radiation-induced polymerization can be calculated as follows. For this system, the absolute rate constant for propagation at 0°C is $k_p = 1.5 \times 10^8$ l./mole-sec.[1] While there is some uncertainty about the precise value of E_p, a previous discussion[1] suggested that this is in the region of 2 kcal/mole. Adopting this estimate yields $A_p = 6.0 \times 10^9$ l./mole-sec.
Since

$$\overline{DP}_n = (A_p/A_{tr,m}) \exp\{-(E_p - E_{tr,m})/RT\}$$

we obtain $A_{tr,m}/A_p = 1.40 \times 10^2$ (calculated from $E_p - E_{tr,m} = -6.3_6$ kcal/mole. Proceeding by $A_{tr,m}/A_p = \exp\{(\Delta S_{tr,m}\ddagger - \Delta S_p\ddagger)/R\}$, we obtain $\Delta S_{tr,m}\ddagger - \Delta S_p\ddagger = 9.8$ cal/deg. The absolute value of the activation entropy change for propagation $\Delta S_p\ddagger$ is calculated from the equation

$$A_p = (ekT/h) \exp\{\Delta S_p\ddagger/R\}$$

to give $\Delta S_p\ddagger = -15.6$ cal/deg for the $1M$ standard state of bimolecular reaction, and hence $\Delta S_{tr,m}\ddagger = -5.8$ cal/deg.

Comparison of the data for all the systems shows that the radiation-induced polymerization which proceeds through free carbonium ions produces the highest molecular weight products. Since $AlEtCl_2$ produces the highest molecular weights of the three catalytic systems, it is conceivable that this initiator gives rise to the least encumbered growing carbonium-ion/counterion pair. Conversely, the $AlCl_3$ system which gives the lowest molecular weights possesses the tightest ion pair. From Figure 1, $E_{tr,m} - E_p = 5.8$, 5.9, and 5.9 kcal/mole for the polymerizations with $AlEtCl_2$, BF_3, and $AlCl_3$, respectively. By assuming that $\bar{M}_v/\bar{M}_n = 2$, the $A_{tr,m}/A_p$ values for these three catalyst systems are 220, 500, and 610, and from these values we obtain the corresponding entropy differences $\Delta S_{tr,m}\ddagger - \Delta S_p\ddagger = 10.7$, 12.4, and 12.8 cal/deg.

It is interesting to compare these results with those obtained by Hayes and Pepper[11] for the polymerization of styrene by sulfuric acid in ethylene dichloride. These authors found $\Delta S_{tr,m}\ddagger - \Delta S_p\ddagger = 17$ cal/deg and $E_{tr,m} - E_p = 7.5$ kcal/mole. We might add that these and similar results obtained in other studies of cationic polymerization are derived from fairly reliable molecular weight determinations and do not depend on rate measurements or questionable assumptions about the mechanism of polymerization.

Table III is a compilation of available activation parameters for the radiation-induced (free ion) and catalytically-initiated (ion pair) polymerization of isobutylene.

Caution should be exercised when comparing the results obtained for the radiation-induced polymerization with those for the catalytically initiated polymerizations, because the former polyisobutylenes were obtained in bulk ($12.5M$) polymerization whereas the latter were prepared in $3.17M$ methyl chloride solution. This choice of techniques was dictated by ex-

TABLE III
Activation Parameters for Radiation-Induced and Catalytically-Initiated Polymerization of Isobutylene[a]

	Catalytically initiated polymerization[b]			γ-Radiation-induced polymerization[c]
	$AlCl_3$	BF_3	$AlEtCl_2$	
A_p, l./mole-sec				6.0×10^9
$A_{tr,m}$, l./mole-sec				8.4×10^{11}
$A_{tr,m}/A_p$	610	500	220	140
E_p, kcal/mole				2
$E_{tr,m}$, kcal/mole				8.3_6
$E_{tr,m} - E_p$, kcal/mole	5.9	5.9	5.8	6.3_6
$\Delta S_p\ddagger$, cal/deg				−15.6
$\Delta S_{tr,m}\ddagger$, cal/deg				−5.8
$\Delta S_{tr,m}\ddagger - \Delta S_p\ddagger$, cal/deg	12.8	12.4	10.7	9.8

[a] The values are calculated from the results given in this paper and from previous data.[1]

[b] Growing species: ion pairs.

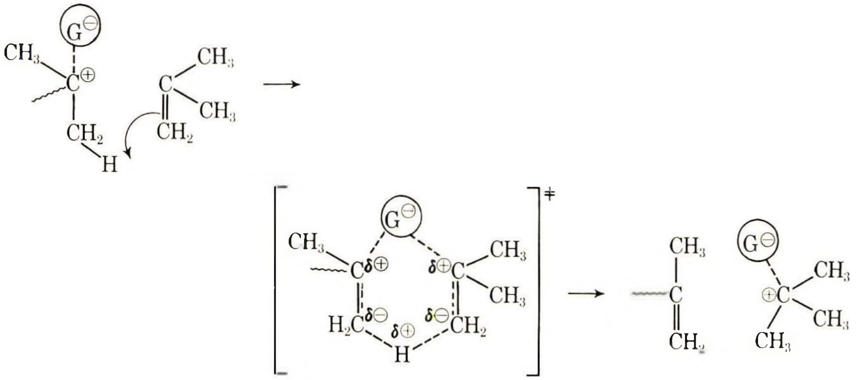
[c] Growing species: free ions.

perimental necessity since, on the one hand, isobutylene cannot be polymerized with high rates by γ-rays in the presence of methyl chloride diluent,[12] while, on the other hand, the catalytic polymerization of this monomer in bulk might lead to erroneous results due to local heat effects. Also, the monomer concentration (dilution) might affect the slope of the log $\bar{M}$ versus $1/T$ lines, as has been shown in the isobutylene–methyl chloride-$AlCl_3$ system.[13] However, the parallel between the slopes of the lines of the Arrhenius type in Figure 1 is striking and invites some careful speculation.

If it is assumed that the molecular weights are in the main determined by the ratio $k_p/k_{tr,m}$, the parallel lines in Figure 1 indicate that $E_p - E_{tr,m} \approx -6.0$ kcal/mole. It is remarkable that the results for free-ion and ion-pair polymerization should be so similar. Evidently the presence of the counterion affects (increases or decreases) E_p and $E_{tr,m}$ by essentially the same amount. This in turn indicates that the counterion affects both propagation and transfer to monomer by an equal extent in the approach to the transition state. Again, it should be emphasized that these considerations are true only if the mechanism of propagation and transfer remain the same in the absence and presence of a solvent. This is probably the case with an inert solvent since random collisions with it do not change the energetics of the reaction.

As $E_p - E_{tr,m}$ in the radiation-induced and catalytically initiated polymerizations are essentially the same, the factor responsible for the large difference in molecular weights is the difference in $A_{tr,m}/A_p$ for free-ion and ion-pair processes. The ratio of frequency factors was calculated (cf. Table III) for the catalyzed polymerizations by assuming that the ratio $\bar{M}_v/\bar{M}_n \approx 2$ applies for catalytically initiated processes. This latter equivalence might not hold exactly but the introduction of a small correction factor would not affect the essential conclusion that the lower molecular weights associated with the catalytic polymerization result from a higher ratio of frequency factors $A_{tr,m}/A_p$ for catalytic over radiation polymerization. This conclusion expresses concisely the information contained in Figure 1.

The fact that $\Delta S_{tr,m} - \Delta S_p$ is larger for ion-pair polymerization than for free-ion systems indicates that the counterion strongly influences the overall structure of the ion-pair transition states. Hayes and Pepper[11] have already referred to the generally smaller "steric requirements" for monomer transfer relative to propagation which means that the transition state of monomer transfer is much less compressed than that of propagation. The transition state for propagation can be regarded as a compact and sterically demanding one, since the π-orbital system of the incoming monomer must approach closely (~1.5 Å) to overlap with the unfilled p-orbital of the carbonium ion. The large negative entropy of activation which must apply for ion-pair propagation evidently reflects a large displacement of the counterion from its initial position in the ground state. In contrast, the transition state for chain transfer to the monomer does not have to be such a compact one. One representation of the latter may be a "loose" six-membered ring structure:[14]



where $G^{\ominus}$ is the counteranion. In this transition state the counterion assists chain transfer to the monomer.

In summary, the present results may be interpreted by assuming that the counterion in the proximity of the growing carbonium ion impedes the propagation to a greater extent than it does the competing process of transfer to the monomer. Some generalizations about the propagation and transfer steps from both thermodynamic and kinetic considerations may be offered. We know that propagation involves an unfavorable entropy change but the reaction is strongly exothermic. Hence we may regard propagation as an energy-driven process. In comparison, the entropy demand of transfer to monomer is much less stringent than that associated with propagation. The exothermicity of transfer to monomer is very low and might be due to the slightly more favorable solvation of the small *tert*-butyl cation as compared to that of the polymer cation. Consequently, transfer to monomer may be depicted as entropy-driven, and the process is favored relative to propagation by increasing temperature.

According to these results and conclusions then, highest molecular weight polyisobutylenes can be synthesized at the highest rate by free carbonium ions. Thus to achieve highest molecular weights with catalytic initiation, one should use a poorly nucleophilic, easily dissociable counteranion which can be specifically solvated. In this vein, it is not surprising that in the +29 to −78°C range, $AlEtCl_2$ (i.e., the initiator which gives rise to the largest counteranion among the three examined) produces the highest molecular weight polymer. Below about −78°C, BF_3 produces highest molecular weights,[9] but the reason for this crossover is unknown.

For highest molecular weights, carbonium-ion solvation is undesirable, and specific counteranion solvation would be desirable. Unfortunately, all the common solvents are nucleophilic and are unable to solvate anions. Indeed the success of anionic systems for "living" polymerizations is partly due to the ease of specific solvation of countercations. Preferential counteranion solvation in carbonium-ion polymerizations might perhaps be achieved with electron-deficient systems such as $AlEt_3$, $ZnEt_2$, etc. However, cationic polymerizations in liquids such as these have not yet been described.

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References

1. R. B. Taylor and F. Williams, *J. Amer. Chem. Soc.*, **91**, 3728 (1969).
2. D. C. Pepper, in *Friedel-Crafts and Related Reactions*, G. A. Olah, Ed., Interscience, New York, 1964, Vol. II, Chap. 30, p. 1293.
3. T. Higashimura, in *Structure and Mechanism in Vinyl Polymerization*, T. Tsuruta and K. F. O'Driscoll, Eds., Dekker, New York, 1969, Chap. 10, p. 313.
4. Z. Zlamal, in *Kinetics and Mechanisms of Polymerization*, G. E. Ham, Ed., Dekker New York, 1969, Chap. 6, p. 231.
5. P. J. Flory, *J. Amer. Chem. Soc.*, **65**, 372 (1943).
6. S. G. Gallo, H. K. Wiese, and J. Nelson, *Ind. Eng. Chem.*, **40**, 1277 (1948).
7. V. Stannett, F. C. Bahstetter, J. A. Meyer, and M. Szwarc, *Int. J. Appl. Radiation Isotopes*, **15**, 747 (1964).
8. F. Williams in *Fundamental Processes in Radiation Chemistry*, P. Ausloos, Ed., Interscience, New York, 1968, p. 515.
9. J. P. Kennedy and R. G. Squires, *Polymer*, **6**, 579 (1965).
10. J. P. Kennedy and R. M. Thomas, *Advan. Chem. Ser.* **34**, 111 (1962).
11. M. J. Hayes and D. C. Pepper, *Proc. Roy. Soc.* (London), **A263**, 63 (1961).
12. A. Shinkawa and F. Williams, unpublished results.
13. J. P. Kennedy and R. M. Thomas, *J. Polym. Sci.*, **55**, 311 (1961).
14. J. P. Kennedy and R. M. Thomas, *J. Polym. Sci.*, **49**, 189 (1961).

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Cationic Polymerization of Vinyl Compounds in the Presence of Tetra-*n*-butylammonium Salts

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Synopsis

The effects of salts were examined in cationic polymerization of vinyl compounds. Cationic polymerization of styrene was carried out at 0°C, with acetyl perchlorate, stannic chloride, stannic chloride–trichloroacetic acid and boron trifluoride etherate as catalysts. Tetra-*n*-butylammonium perchlorate, fluoroborate and iodide were used as salts. The presence of small amounts of the salts changed both the polymerization rate and the molecular weight of polymer considerably. The consideration of various effects led to the conclusion that the results are explicable principally on the basis of counterion exchange. To confirm this, the copolymerization of 2-chloroethyl vinyl ether with α-methylstyrene was investigated at $-78°C$. The copolymer composition curve when stannic chloride was used as catalyst was changed and coincided with that of polymer obtained with acetyl perchlorate catalysis when the perchlorate salt was added. This supports the concept of counterion exchange.

INTRODUCTION

It is well known that neutral salts can affect the rates of ionic reactions in solution. The results have been interpreted principally on the basis of the change in ionic strength and the mass-law effect. Ingold and his collaborators[1] have carried out an extensive investigation of the effect of salts on substitution reactions, especially on solvolysis. Winstein et al.[2] found both normal and special salt effects in solvolysis on the basis of their detailed experimental results. On the other hand, there have been few papers on the salt effect in electrophilic addition to unsaturated compounds, which is intimately related to cationic polymerization. Recently, several studies have been reported on the salt effect in electrophilic addition.[3-5] For example, in a series of studies on the halogenation of olefins, it was found that a neutral salt acted not only as an electrolyte but also as a nucleophile.[3,4]

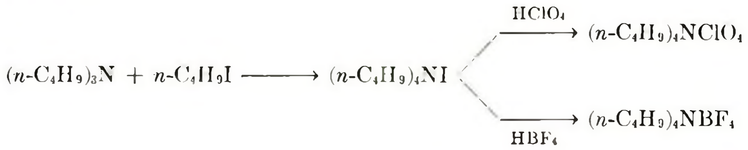
In view of the nature of ionic polymerizations, salt effects are to be anticipated. In practice, it has been confirmed that a common ion depresses the dissociation of an ion pair and decreases the rate of propagation in anionic polymerization.[6,7] In cationic polymerization there have been only two papers[8,9] on salt effects, in which it was concluded that the added salt depresses the dissociation of an ion pair similar to that in anionic polymerization, since the common salt lowers both the reaction rate and the molecular weight of the polymer formed.

However, the function of an added salt as a nucleophile has not been considered in cationic polymerization, although it has been observed in electrophilic addition reactions. Therefore, in order to elucidate the functions of added salts in cationic polymerization, we have investigated (1) the influence of tetra-*n*-butylammonium salts on the cationic polymerization of styrene catalyzed by acetyl perchlorate and metal halides and (2) the effect of tetra-*n*-butylammonium perchlorate on the composition of a copolymer obtained by cationic copolymerization of 2-chloroethyl vinyl ether with α-methylstyrene. The results were mainly interpreted in terms of counterion exchange and a terminating function of the added (tetra-*n*-butyl ammonium) salts.

EXPERIMENTAL

Materials

Three salts, tetra-*n*-butylammonium perchlorate ($n\text{-Bu}_4\text{NClO}_4$), tetra-*n*-butylammonium fluoroborate ($n\text{-Bu}_4\text{NBF}_4$) and tetra-*n*-butylammonium iodide ($n\text{-Bu}_4\text{NI}$) were synthesized by a procedure [eq. (1)] similar to Fujinaga's method.[10]



$$(n\text{-C}_4\text{H}_9)_3\text{N} + n\text{-C}_4\text{H}_9\text{I} \longrightarrow (n\text{-C}_4\text{H}_9)_4\text{NI} \begin{cases} \xrightarrow{\text{HClO}_4} (n\text{-C}_4\text{H}_9)_4\text{NClO}_4 \\ \xrightarrow[\text{HBF}_4]{} (n\text{-C}_4\text{H}_9)_4\text{NBF}_4 \end{cases} \qquad (1)$$

Table I shows the composition and melting point of the salts obtained. As seen from Table I, the purity of the salts was more than 99.8%.

TABLE I
Composition and Melting Point of Tetra-*n*-butylammonium Salts

	Composition found (calcd)[a]				Mp, °C	
Salt	H, %	C, %	Cl or I, %	O, %	Obs.	Lit.[11]
$n\text{-Bu}_4\text{NClO}_4$	10.58 (10.62)	56.28 (56.25)	10.48 (10.38)	18.55 (18.74)	217	213
$n\text{-Bu}_4\text{NBF}_4$	11.33 (11.03)	58.18 (58.42)	—	—	163	161.8
$n\text{-Bu}_4\text{NI}$	9.84 (9.83)	51.87 (52.07)	34.63 (34.39)	—	147	148

[a] Value in parenthesis is calculated value.

Styrene and α-methylstyrene were washed by aqueous alkaline solution, dried by standing over sodium sulfate, and then distilled twice from calcium hydride immediately prior to use, and 2-chloroethyl vinyl ether was purified by a similar method.

Acetyl perchlorate ($AcClO_4$) was synthesized as described previously.[12,13] The concentration was determined spectroscopically on the basis of the reaction (2) [$(C_6H_5)_3C^+$: $\epsilon_{435} = 3.69 \times 10^4$ l./mole).[14]

$$(C_6H_5)_3COH + AcClO_4 \longrightarrow (C_6H_5)_3C^+ + ClO_4^- + AcOH \qquad (2)$$

Stannic chloride ($SnCl_4$) and boron trifluoride etherate ($BF_3 \cdot OEt_2$) were purified by distillation. Methylene chloride, benzene, toluene, and nitrobenzene were purified by the usual methods.

Procedures

Polymerization was carried out in a flask fitted with a double cap and under a nitrogen atmosphere. Salt solutions were added to the monomer solutions through the double cap by a syringe, and polymerization was then initiated by addition of the catalyst solution.

Rates of polymerization were determined by measuring concentrations of unreacted monomer by gas chromatography. A first-order plot of monomer consumption was linear in all cases. Polymer was precipitated in a large quantity of methanol, washed, filtered, and dried. In the case of polymers which are soluble in methanol, after the evaporation of volatile materials the polymers were purified by freeze-drying.

Copolymer compositions were determined by measuring the residual monomer concentrations by gas chromatography.

Limiting viscosity numbers $[\eta]$ were determined in benzene solution at 30°C.

RESULTS AND DISCUSSION

Effect of Tetra-*n*-butylammonium Salts on the Cationic Polymerization of Styrene

Styrene was polymerized at 0°C by various catalysts with or without the tetra-*n*-butylammonium salt. In all cases a constant initial concentration of styrene (1.00 mole/l.) was used. In the procedure described above, the reaction system contained a small amount of water (ca. 1 mmole/l.). No polymerization occurred in the presence of the tetra-*n*-butylammonium salt without the addition of an acidic catalyst.

Effect of n-Bu_4NClO_4 *on the Cationic Polymerization of Styrene with Various Catalysts*

To clarify the effect of a neutral salt on the rate of cationic polymerization of styrene, styrene was polymerized in methylene chloride solution with various concentrations of added salt. *n*-Bu_4NClO_4 was used as the salt, and $AcClO_4$, $SnCl_4$, $SnCl_4$–CCl_3CO_2H (1:1 mole ratio) and $BF_3 \cdot OEt_2$ as catalysts. $AcClO_4$ was the only catalyst having the same anion as the added salt.

As Figure 1 shows, the rates of polymerization at low concentration of *n*-Bu_4NClO_4 increased to a maximum value in polymerization catalyzed by metal halides. At higher concentrations of *n*-Bu_4NClO_4 the rates of polymerization decreased. On the other hand, when $AcClO_4$ was used as catalyst, a small amount of n-Bu_4NClO_4 caused a rapid reduction in rate and then the rate decreased gradually with increasing the concentration of the salt. The behavior of $AcClO_4$–n-Bu_4NClO_4 system is very similar to that of the $HClO_4$–n-Bu_4NClO_4 system, as reported by Pepper.[8,9]

Figure 2 shows the limiting viscosity numbers $[\eta]$ of the resultant polymers. $[\eta]$ was decreased significantly by the addition of small amounts of

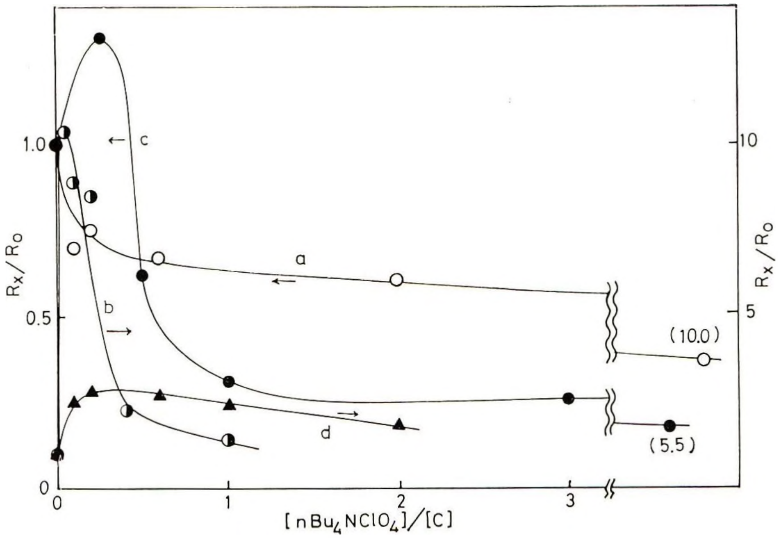


Fig. 1. Effect of n-Bu_4NClO_4 on the rate of polymerization initiated by various catalysts in CH_2Cl_2 at 0°C and $[M]_0 = 1.00$ mole/l.: (○) (a) $AcClO_4 = 0.50$ mmole/l., $R_0 = 1.57\%$/min; (◑) (b) $SnCl_4 = 5.0$ mmole/l., $R_0 = 0.95\%$/min; (●) (c) $SnCl_4$/CCl_3CO_2H (1/1 mole ratio) = 1.0 mmole/l., $R_0 = 4.61\%$/min; (▲) (d) $BF_3 \cdot OEt_2$ = 5.0 mmole/l., $R_0 = 0.35\%$/min.

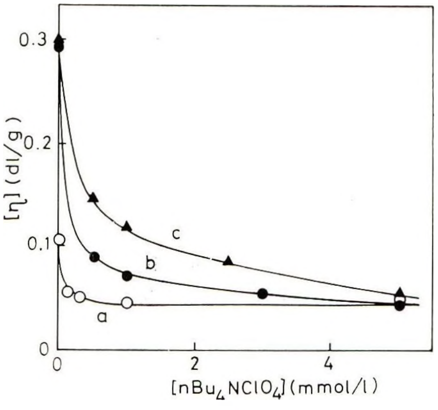


Fig. 2. Effect of n-Bu_4NClO_4 on the limiting viscosity numbers of the polymer obtained by various catalysts: (○) (a) $AcClO_4$; (●) (b) $SnCl_4$; (▲) (c) $BF_3 \cdot OEt_2$. Polymerization conditions are the same as in Fig. 1.

salt and gradually decreased further with increasing of the concentration of the salt, approaching a constant value irrespective of the catalyst used.

Effect of n-Bu_4NClO_4 *on the Cationic Polymerization of Styrene in Various Solvents*

The acceleration effect of *n*-Bu_4NClO_4 on the polymerization of styrene initiated by $SnCl_4$ is shown in Figure 3. A small amount of *n*-Bu_4NClO_4 increased the rate of polymerization irrespective of the nature of the sol-

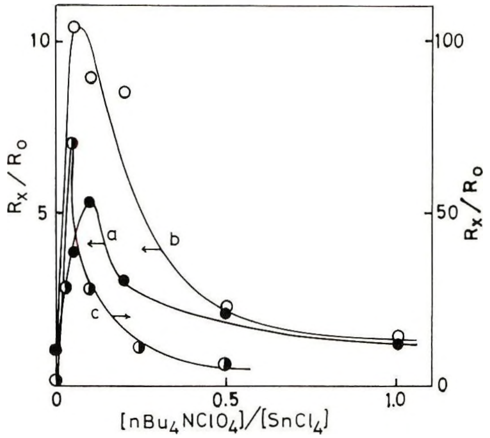


Fig. 3. Effect of *n*-Bu_4NClO_4 on the rate of polymerization catalyzed by $SnCl_4$ in various solvents at 0°C and $[M]_0 = 1.00$ mole/l.: (●) (*a*) $C_6H_5NO_2$, [C] = 5.0 mmole/l., $R_0 = 9.52\%$/min; (○) (*b*) CH_2Cl_2, [C] = 5.0 mmole/l., $R_0 = 0.95\%$/min; (◑) (*a*) CH_2Cl_2/benzene (3/1 volume ratio), [C] = 10.0 mmole/l., $R_0 = 0.14\%$/min.

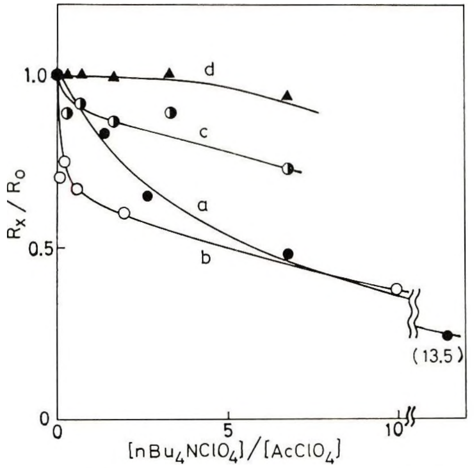


Fig. 4. Effect of *n*-Bu_4NClO_4 on the rate of polymerization catalyzed by $AcClO_4$ in various solvents at 0°C at $[M]_0 = 1.00$ mole/l.: (●) (*a*) $C_6H_5NO_2$, [C] = 0.37 mmole/l., $R_0 = 9.58\%$/min; (○) (*b*) CH_2Cl_2, [C] = 0.50 mmole/l., $R_0 = 1.57\%$/min; (◑) (*c*) CH_2Cl_2/benzene (3/1 volume ratio), [C] = 1.48 mmole/l., $R_0 = 2.22\%$/min; (▲) (*d*) CH_2Cl_2/benzene (1/3 volume ratio), [C] = 1.48 mmole/l., $R_0 = 0.23\%$/min.

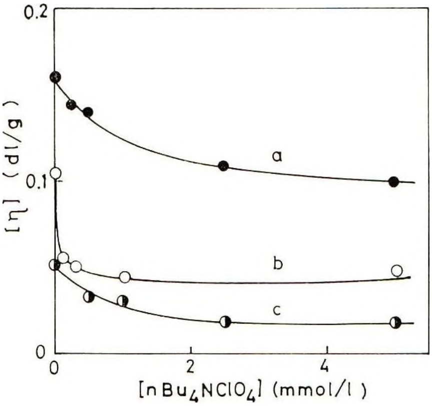


Fig. 5. Effect of n-Bu_4NClO_4 on the limiting viscosity numbers of the polymer obtained by $AcClO_4$: (●) (a) $C_6H_5NO_2$; (○) (b) CH_2Cl_2; (◑) (c) CH_2Cl_2/benzene (3/1 volume ratio). Polymerization conditions are the same as in Fig. 4.

vent, and further addition of the salt decreased the rate. A discussion of the relationship between the nature of the solvent and variation in rate is difficult since the amount of water, as cocatalyst, was not controlled.

On the other hand, the effect of n-Bu_4NClO_4 on the polymerization of styrene initiated by $AcClO_4$ could be compared in various solvents. As shown in Figure 4, the depression of the rate of polymerization due to the addition of the salt decreased with decreasing polarity of the solvent, except for the remarkable decrease of the rate by an addition of a small amount of the salt in methylene chloride.

[η] of the polymer decreased to a constant value in each solvent as shown in Figure 5, and [η] of polymer produced in a polar solvent was higher than that produced in a nonpolar solvent.

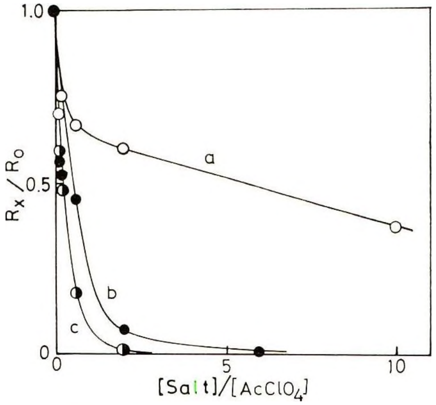


Fig. 6. Effect of various tetra-n-butylammonium salts on the rate of polymerization catalyzed by $AcClO_4$ in CH_2Cl_2 at 0°C at $[M]_0 = 1.00$ mole/l., $[C] = 0.50$ mmole/l.: (○) (a) n-Bu_4NClO_4, $R_0 = 1.57\%$/min; (●) (b) n-Bu_4NBF_4, $R_0 = 1.99\%$/min; (◑) (c) n-Bu_4NI, $R_0 = 1.69\%$/min.

Effect of Varying the Negative Ion of the Salt

The influence of negative ions was examined by using tetra-*n*-butylammonium salts having various negative ions. Styrene was polymerized by $AcClO_4$ or $SnCl_4$ in methylene chloride in the presence of *n*-Bu_4NClO_4, *n*-Bu_4NBF_4, or *n*-Bu_4NI. *n*-Bu_4NBF_4 and *n*-Bu_4NI strikingly decreased the rate of polymerization catalyzed by $AcClO_4$ and by $SnCl_4$ (Figs. 6 and 7). *n*-Bu_4NI retarded polymerization more strongly than *n*-Bu_4NBF_4 did.

The presence of *n*-Bu_4NBF_4 or *n*-Bu_4NI also decreased the rate of polymerization also in a mixture of methylene chloride and benzene, and the retarding effect of the salt was smaller in a nonpolar solvent than in a polar solvent.

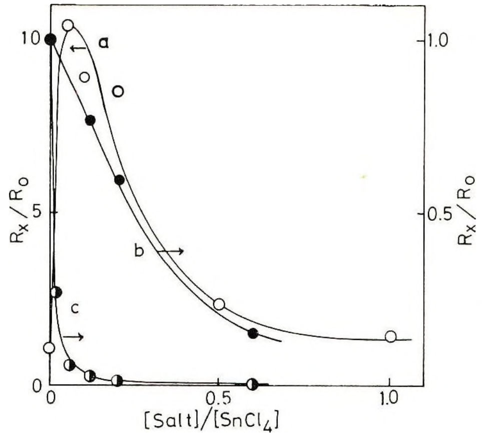


Fig. 7. Effect of various tetra-*n*-butylammonium salts on the rate of polymerization catalyzed by $SnCl_4$ in CH_2Cl_2 at 0°C at $[M]_0$ = 1.00 mole/l., [C] = 5.0 mmole/l.: (○) (*a*) *n*-Bu_4NClO_4, R_0 = 0.95%/min; (●) (*b*) *n*-Bu_4NBF_4, R_0 = 0.99%/min; (◑) (*c*) *n*-Bu_4NI, R_C = 0.90%/min.

Discussion

It is well known that a compound forming a proton or carbonium ion acts as a cocatalyst in the polymerization of styrene catalyzed by a metal halide. However, the accelerating effect by neutral salt, such as *n*-Bu_4NClO_4, has not been observed in the cationic polymerization of styrene.

The neutral salt effect on the rates of ionic reactions in solution is mainly a result of the change in ionic strength and mass-law effect, as described in the introduction. Furthermore, it has often been observed that neutral salts add directly to olefins in an electrophilic addition reaction.[3–5] Therefore, we considered three possible effects of the salt on the polymerization of styrene.

(i) Change in Ionic Strength. The termination reaction is a reaction between ionic species, while initiation and propagation are ion–dipolar molecule reactions. Therefore, if the change in ionic strength influences the reaction rate, the overall rate should increase with increasing ionic strength, accordingly by addition of salt. However, in the system with $AcClO_4$ as catalyst, n-Bu_4NClO_4 did not increase the rate of polymerization and the effect of the salt depended on the nature of catalysts employed. Therefore, the change in rate due to change in ionic strength may be neglected in comparison with that of some other salt effect. This agreed with the conclusion of George et al.[15]

(ii) Change in Dissociation by a Common Ion. It was observed by Pepper that n-Bu_4NClO_4 decreased not only the rate of polymerization but also the molecular weight of the polymer in the polymerization of styrene with perchloric acid.[8,9] From this it was suggested that the addition of n-Bu_4-$NClO_4$ prevented the dissociation of the propagating ion and consequently the propagation through free ions. In the present work the addition of n-Bu_4NClO_4 to a polymerization system catalyzed by $AcClO_4$ also decreased the rate of polymerization and the molecular weight of a resultant polymer. This result also seems to be interpretable by the explanation proposed by Pepper.

However, addition of the salt in concentrations of more than a half mole of a catalyst lowered the rate of polymerization irrespective of the nature of a catalyst. Therefore, the decrease in a rate of polymerization due to the addition of n-Bu_4NClO_4 must be explained by a termination or transfer reaction of a propagating chain by n-Bu_4NClO_4, the mechanism of which is not clear yet.

(iii) Exchange of a Counterion at the Growing Chain End with the Salt. n-Bu_4NClO_4 having no common ion increased the rate of polymerization catalyzed by $SnCl_4$, $SnCl_4$–CCl_3CO_2H or $BF_3 \cdot OEt_2$. It was observed that the cationic polymerization of styrene was accelerated by tetracyanoethylene from which a proton or carbonium ion was not produced.[16] This was explained by the stabilization of a counterion in a growing chain end due to complexing with tetracyanoethylene, a strong electrophile. However, such electrophilic behavior is improbable about n-Bu_4NClO_4.

In electrophilic addition to olefins, an anion produced from a neutral salt adds to an olefin.[3–5] In the same way, it is easily anticipated that the anion of a salt interacts with a propagating carbonium ion in cationic polymerization. In the latter case, as the anion may be more stable than that in the addition reaction to an olefin, the anion will not add to the propagating carbonium ion, but rather will form an ion pair; in consequence, the polymerization proceeds with an exchanged counterion [eq. (3)].

$$\sim\!\overset{\oplus}{C}\cdots\overset{\ominus}{B} + n\text{-}Bu_4NClO_4 \rightleftharpoons \sim\!\overset{\oplus}{C}\cdots ClO_4^{\ominus} + n\text{-}Bu_4NB \qquad (3)$$

Here, if the rate of a growing carbonium ion having $ClO_4^{\ominus}$ as counterion is greater than that having $B^{\ominus}$ as the counterion, the addition of n-Bu_4NClO_4 will increase the rate of polymerization. The polymerization with $SnCl_4$. $SnCl_4$–CCl_3CO_2H. or BF_3OEt_2 in the presence of a small amount of n-Bu_4-$NClO_4$ can be explained by this mechanism.

On the other hand, the presence of n-Bu_4NBF_4 or n-Bu_4NI decreased the rate of polymerization. This may be due to the slow polymerization with $BF_4^{\ominus}$ or $I^{\ominus}$ as a counterion.

The occurrence of counterion exchange was also supported on the basis of the molecular weights of the polymers. The molecular weights of the polymers approached a constant value in the presence of large concentrations of n-Bu_4NClO_4, irrespective of the catalyst. This is attributed to the fact that the counterion in a growing chain end is completely exchanged by $ClO_4^{\ominus}$ in the presence of a large amount of n-Bu_4NClO_4.

It has been reported that in the living anionic polymerization of styrene an added salt and a propagating chain end interacted metathetically and the counterion was exchanged,[17] that is, the exchange of a counterion occurred when $NaBPh_4$ was added to living polystyrene having $K^{\oplus}$ counterion, as $KBPh_4$ was less soluble than $NaBPh_4$.

We believe that the present work provided the first example of an exchange reaction of counterion in cationic polymerization.

Effect of *n*-Bu_4NClO_4 on the Cationic Copolymerization of 2-Chloroethyl Vinyl Ether with α-Methylstyrene

To confirm the occurrence of counterion exchange in cationic polymerization, the effect of an addition of the salt on the monomer reactivity ratios in copolymerization was examined. Copolymerization of 2-chloroethyl vinyl ether (CEVE) with α-methylstyrene (αMS) produces copolymers the composition of which is very sensitive to the catalyst employed, i.e., to the nature of the counterion.[13,18] It is expected, therefore, that the copolymer composition will be changed by the addition of the salt, if the counterion is changed by the addition of a salt.

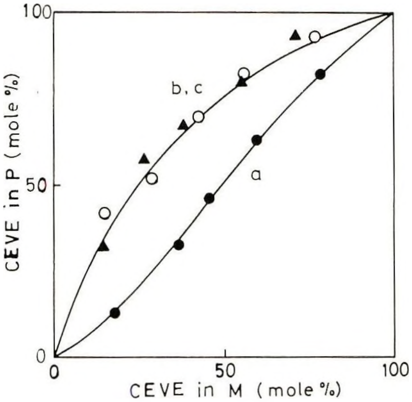


Fig. 8. Salt effect of copolymer compositions in copolymerization of CEVE with αMS in CH_2Cl_2 at −78°C at $[M]_0$ = 0.50 mole/l.: (●) (*a*) $SnCl_4$ = 3.0 mmole/l.; (○) (*b*) $AcClO_4$ = 0.22 mmole/l.; (▲) (*c*) $SnCl_4$ = 1.0 mmole/l., n-Bu_4NClO_4 = 3.0 mmole/l.

Effect of n-*Bu_4NClO_4 on Copolymer Composition*

The compositions of copolymers of CEVE with αMS obtained with $SnCl_4$ and $AcClO_4$ as catalysts were very different, as Figure 8 shows. When three times as much *n*-Bu_4NClO_4 was added to a polymerizing system catalyzed by $SnCl_4$ ([*n*-Bu_4NClO_4] = 3[$SnCl_4$]), the copolymer composition curve became identical with that obtained with $AcClO_4$ catalyst as shown in Figure 8. On the other hand, no change in copolymer composition was observed when trichloroacetic acid was added to the same system.

The same effect of *n*-Bu_4NClO_4 on copolymer composition was also found in polymerizations in a mixed solvent of methylene chloride and toluene. As Figure 9 shows, the addition of one and half times as much *n*-Bu_4NClO_4

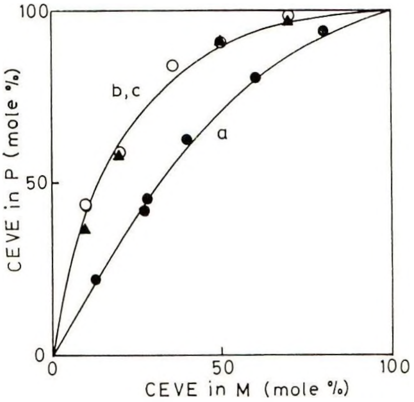


Fig. 9. Salt effect on copolymer compositions in copolymerization of CEVE with αMS in CH_2Cl_2–toluene solution (1:3 volume ratio) at −78°C at $[M]_0$ = 0.50 mole/l.: (●) (*a*) $SnCl_4$ = 5.0 mmole/l.; (○) (*b*) $AcClO_4$ = 0.37 mmole/l.; (▲) (*c*) $SnCl_4$ = 2.0 mmole/l., *n*-Bu_4NClO_4 = 3.0 mmole/l.

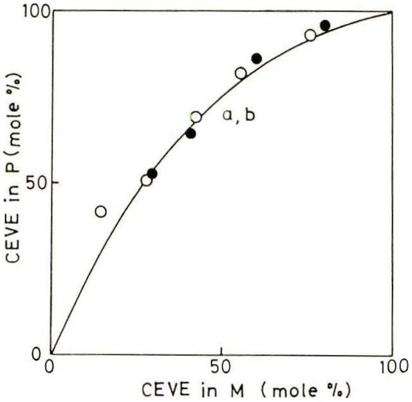


Fig. 10. Salt effect on copolymer compositions in copolymerization of CEVE with αMS in CH_2Cl_2 at −78°C at $[M]_0$ = 0.50 mole/l.: (○) (*a*) $AcClO_4$ = 0.22 mmole/l.; (●) (*b*) $AcClO_4$ = 0.22 mmole/l., *n*-Bu_4NClO_4 = 3.0 mmole/l.

as $SnCl_4$ changed the copolymer composition obtained by $SnCl_4$ catalyst to that obtained with $AcClO_4$.

On the other hand, in the copolymerization catalyzed by $AcClO_4$, addition of ten times as much n-Bu_4ClO_4 as catalyst produced no effect in the copolymer composition (Fig. 10).

Discussion

The presence of large concentration of common ion does not affect the copolymer composition as shown in Figure 10. Meanwhile, the coincidence of the composition curves *b* and *c* in Figures 8 and 9 establishes that the counterions are identical, that is, $ClO_4^{\ominus}$ in both systems. The amount of n-Bu_4ClO_4 added to the copolymerization system appears to be sufficient to cause complete exchange of counterion, since the molecular weight of a polymer obtained under these conditions was almost identical with that obtained by $AcClO_4$ (Fig. 2).

At the present time, it is not clear whether a counterion is exchanged during the propagation step or before propagation directly by the reaction of catalyst and the salt. However, this paper establishes that the exchange of a counterion takes place in the polymerization of styrene and in the copolymerization of CEVE with αMS.

References

1. L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, **1940**, 960 and subsequent papers.
2. A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763 (1956); and subsequent papers.
3. R. P. Bell and M. Pring, *J. Chem. Soc. B*, **1966**, 1119.
4. J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1477 (1969) and related papers.
5. R. C. Fahey, M. W. Monaham, and C. A. McPherson, *J. Amer. Chem. Soc.*, **92**, 2810 (1970).
6. H. Hostalka, R. V. Figini, and G. V. Schulz, *Makromol. Chem.*, **71**, 198 (1964).
7. D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 609, 612 (1965).
8. L. E. Darcy, W. P. Millrine, and D. C. Pepper, *Chem. Commun.*, **1968**, 1441.
9. B. MacCarthy, W. P. Millrine, and D. C. Pepper, *Chem. Commun.*, **1968**, 1442.
10. T. Fujinaga, K. Izutsu, K. Umemoto, T. Arai, and K. Takaoka, *Nippon Kagaku Zasshi*, **89**, 105 (1968).
11. Beilstein, *Handbuch der Organischen Chemie*, Springer-Verlag, Berlin, 1962, E-III, Vol. 4, p. 293.
12. V. Jaacks and W. Kern, *Makromol. Chem.*, **62**, 1 (1963).
13. T. Masuda and T. Higashimura, *J. Macromol. Sci. Chem.*, **A5**, 547 (1971).
14. W. R. Longworth and C. P. Mason, *J. Chem. Soc. A*, **1966**, 1164.
15. J. George, H. Mark, and H. Wechsler, *J. Amer. Chem. Soc.*, **72**, 3896 (1950).
16. I. M. Panayatov, I. K. Dimtrov, and I. E. Bakerdjiev, *J. Polym. Sci. A-1*, **7**, 2421 (1969).
17. M. Szwarc, *Carbanions, Living Polymers, and Electron-Transfer Processes*, Interscience, New York, 1968, p. 158.
18. T. Masuda, T. Higashimura, and S. Okamura, *Polymer J.*, **1**, 19 (1970).

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Polymerization, Copolymerization, and Terpolymerization of 1-Isopropylidene-dicyclopentadiene by Anionic Coordination Catalysts

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Synopsis

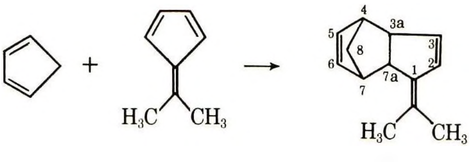
A detailed investigation of the terpolymerization reaction of ethylene and propylene with 1-isopropylidene-dicyclopentadiene (II) was carried out by employing vanadium-based anionic coordinate catalysts [preferentially $V(Acac)_3$–$AlEt_2Cl$]. The influence of some polymerization parameters, i.e., concentration of II, of the catalyst; polymerization time, etc., were particularly examined. The catalysts were found to be active in C_2H_4–II copolymerization also, but neither C_3H_6–II copolymer nor II homopolymer were obtained. By using the 5,6-dihydro derivative of II as comonomer, it was found through ultraviolet, infrared, and NMR analyses that the incorporation of II in polyethylene or ethylene–propylene chains took place randomly and by selective opening of the norbornene double bond. The quantitative determination of the unsaturation present in C_2H_4–C_3H_6–II terpolymer was studied by means of absorption of iodine halides and through a spectroscopic ultraviolet method. Reference was made to terpolymer samples containing ^{14}C-labeled II. The content of II was generally less than 35 wt-% both in copolymer and in terpolymer prepared. The relatively high reactivity of II is discussed in terms of norbornene ring strain and compared with the reactivity of 1-isopropylidene-3a,4,7,7a-tetrahydroindene (I) previously reported.

INTRODUCTION

The synthesis of terpolymers based on ethylene and propylene and containing conjugated double bonds has been recently reported.[1–3] By means of typical Ziegler-Natta catalyst systems, soluble random terpolymers could be obtained when polycyclic trienes[4] having a conjugated diene system were used as termonomers.

In the case of 1-isopropylidene-3a,4,7,7a-tetrahydroindene (I), several variables related to the terpolymer synthesis[1] and some spectroscopic molecular properties of the polymer were studied.[3] Furthermore, copolymers of ethylene with I have been described, whereas homopolymers of I could not be obtained by anionic coordinate catalysts.[3]

In the present paper a new terpolymer containing conjugated double bonds and a new copolymer obtained from ethylene and 1-isopropylidene-dicyclopentadiene (II) are reported. The triolefin II was synthetized by a Diels-Alder reaction in which 6,6-dimethylfulvene acts as dienophile.[5]



II

The interest in this class of terpolymers rests on the widely accepted premise that compounds such as I or II, containing conjugated double bonds, do not behave well in α-olefins terpolymerization.[6-8] Indeed, linear trienes of this type react quickly with the catalyst centers and give an inhibiting effect. Furthermore, they enter in the polymer chains in a nonrandom way and only in low amounts.

On the contrary, the use of II has confirmed the previous result[3] obtained with I, i.e. anionic coordinate catalysts promote the selective opening of the isolated double bond of I or II, whereas the conjugated diene system remains substantially unchanged. Moreover, the use of II involves a low interference of comonomer with the catalyst centers, and a high reactivity of II in the polymerization reaction is observed; hence α-olefins terpolymers with high contents of conjugated double bonds can easily be prepared.

EXPERIMENTAL

Materials

The triolefin (II) was prepared and purified as previously reported;[4] it had $n_D^{20} = 1.5439$, $d_4^{25} = 0.9748$, gas-chromatographic purity $> 99\%$. Ultraviolet, infrared, and NMR spectroscopic data are reported in Tables I–III. The molecular weight was found (mass spectrometry) to coincide with the calculated one.

Ethylene, propylene (polymerization grade), and n-heptane (pure grade) were Phillips products and were purified as described previously.[3] Other products ($TiCl_4$, VCl_4, $TiCl_3$, organo-aluminum derivatives, etc.) were pure

TABLE I

Ultraviolet Spectroscopic Data for a Copolymer and a Terpolymer Based on II Compared with Monomer II and 5,6-Dihydro-II

	λ_{max}, mμ
Monomeric II	254[a]
5,6-Dihydro-II	252[b]
C_2H_4–II copolymer[c]	254
C_2H_4–C_3H_6-II terpolymer[d]	253

[a] ϵ = 16,340 l./mole-cm.

[b] ϵ = 15,550 l./mole-cm.

[c] Containing 25.2 wt-% of II.

[d] Containing 6 wt-% of II, 53% C_2H_4.

TABLE II
Infrared Spectroscopic Data for Copolymer and Terpolymer Based on II Compared with Monomeric II and 5,6-Dihydro-II

Infrared bands, cm^{-1}			
Monomer II	5,6-dihydro-II	C_2H_4–II copolymer[a]	C_2H_4–C_3H_6–II terpolymer[b]
3050 (s)	3050 (s)	3055 (m)	3055 (m)
3030 (m)	3035 (s)	3035 (m)	3035 (m)
1650 (w)	1654 (w)	1658 (w)	1656 (w)
1622 (w)	—	—	—
1565 (m)	1567 (w)	1570 (w)	1570 (w)
1440 (s)	1442 (s)	1462 (vs)	1452 (vs)
1364 (s)	1365 (s)	1378 (s)	1374 (vs)
1286 (s)	1290 (s)	1369 (s)	1260 (m)
902 (s)	—	1358 (s)	934 (m)
828 (s)	832 (s)	1262 (m)	848 (m)
752 (vs)	755 (vs)	934 (w)	—
713 (vs)	—	850 (m)	720 (s)
	632 (s)	722 (s)	655 (m)
		654 (m)	

[a] Containing 25.2 wt-% of (II).
[b] Containing 6 wt-% of (II), 53% of C_2H_4.

grade commercial reagents and used without preliminary treatment or purified as in the previous study[3] by fractional distillation.

Radioactively tagged II was prepared, analogously to labeled I,[9] from acetone-1,3-^{14}C (supplied by the Radiochemical Center, Amersham, England) which was employed in the synthesis of 6,6-dimethylfulvenemethyl-

TABLE III
NMR Spectroscopic Data for II, Terpolymer Based on II, and 5,6-Dihydro-II

	δ referred to TMS		
Protons	Monomer II	5,6-dihydro-II	C_2H_4–C_3H_6–II[a] terpolymer
H_3	6.02 (quartet)	6.28	—
$H_5 + H_6$	5.63 (triplet)	—	—
H_2	5.52 (doublet)	5.67	—
$H_4 + H_7 + H_{3a}$	3.02 (singlet)	—	—
$H_4 + H_7$	— "	2.98	—
H_{7a}	2.70 (complex multiplet)	—	—
$H_{3a} + H_{7a}$	— "	2.34	—
$=C(CH_3)_2$	1.61 (doublet)	1.72	1.72
H_8	1.32 (quartet)	1.46	—
$H_5 + H_6$	— (singlet)	1.19	—
$CH_2 + CH$	—	—	(wide) 1.23
$C—CH_3$	—	—	(wide) 0.83

[a] Containing 6 wt-% of II and 53% of C_2H_4; measurements were carried out in CCl_4 solutions.

^{14}C. The labeled fulvene derivative was then condensed with cyclopentadiene and recovered according to the conditions previously reported.[4] The radioactive II had a gas-chromatographic purity greater than 99.5%, and the radiochemical yield was 60% with respect to acetone.

The 5,6-dihydro-II was prepared through reduction of II with $H_3AlN(CH_3)_3$, according to the procedure adopted in the case of dicyclopentadiene.[10] The yield, calculated on the basis of the number of H—Al$<$ bonds, was 65% in 8 hr at 75°C; bp 53–54°C/0.05 mm Hg; $n_D^{20} = 1.5376$, MW = 174 (mass spectrometry).

Anal. Calcd for $C_{13}H_{18}$: C, 89.65%; H, 10.34%. Found: C, 89.30%; H, 10.72%.

The structure of the product was confirmed by ultraviolet, infrared, and NMR analyses (Table I–III).

Polymerization

The terpolymerization of II with α-olefins was carried out under mild conditions at normal pressure in a glass apparatus with a semi-flow technique[1] previously employed also in ethylene–propylene copolymerization.[11,12] The same assembly, equipped with a Teflon stopcock at the bottom of the jacketed reaction vessel, gave reproducible gravimetric results in the kinetic curves (cf. Fig. 4*A*). The temperature of the polymerization solution (inside) was kept constant to within ±1°C.

In order to obtain a constant level of unsaturation in the terpolymer, continuous addition of II to the feed during the polymerization time was accomplished by dilution of the triene in the polymerization solvent (5%) and by regular addition from a buret connected to the reactor. The quantities of II which had to be added at regular intervals of time (generally every minute) were calculated from preliminary runs and by analyzing the resulting content of II in the polymer.

Copolymerization and homopolymerization runs were done in three-necked flasks equipped with a mechanical stirrer under an atmosphere of pure nitrogen and placed in a thermostatted bath. The catalysts were generally prepared *in situ* by adding the organoaluminum compound to a mixture of solvent and monomers at the polymerization temperature. Immediately afterwards the transition metal compound was added to the stirred mixture. In some homopolymerization experiments the initial temperature was raised after several hours in order to increase the polymer yield.

The polymers obtained were purified by washing with distilled water containing 1 wt-% of surfactant (Dresinate, Hercules Powder Co.) and by dissolution and precipitation from methanol. The polymers were dried at room temperature under vacuum and analyzed as soon as possible.

Analyses

Infrared spectroscopic investigations (Perkin-Elmer Model 125) were carried out on films obtained by evaporation of terpolymer solution in hydrocarbon or on KBr disks in the case of copolymer.

Ultraviolet measurements (EPS-3T Hitachi Spectrophotometer) were made on *n*-hexane solutions, whereas the NMR spectra (Varian A-60) were obtained from CCl_4 solutions of the polymers.

Molecular weight measurements were made by mass spectrometry technique with an LKB-9000 instrument.

The degree of unsaturation of the terpolymers was determined in CCl_4–$CHCl_3$ solution by halogenation with ICl or IBr according to a procedure widely described elsewhere.[9] The iodometric titer was tested by employing ^{14}C-labeled II in terpolymerization runs and counting the polymer radioactivity. The radioactivity measurement was made by using a liquid scintillation technique and an internal standard (toluene-methyl-^{14}C). The final results were obtained by comparing the specific count rate of the terpolymer samples with the specific count rate of radioactive II.

Before analyses the samples were thoroughly washed, purified by double dissolution and precipitation, and subjected both to radioactive counting and IBr absorption.

Another evaluation of the concentration of II in terpolymers was carried out by ultraviolet measurement of the absorbance at 253 mμ of *n*-hexane terpolymer solutions of known concentration and taking into account the molar extinction coefficient of 5,6-dihydro-II (cf. Table I).

The ethylene content of terpolymer was obtained by infrared analysis according Natta et al.;[11] in the case of C_2H_4–II copolymer the elemental analysis was utilized to obtain the composition, as was done previously for C_2H_4–I copolymer.[3]

The intrinsic viscosities were measured as reported previously.[3] The terpolymer fractionation was carried out by a fractional precipitation technique;[13] the solvent was toluene, and the nonsolvent was ethanol. More simple fractionations were obtained, in the case of C_2H_4–II copolymer, with Kumagawa extractions.[11]

CuKα radiation was used for x-ray analysis with a standard generator. The thermal behavior of the polymer samples was examined with the Du Pont, Model 900, differential thermal analyzer (heating rate of 10°C/min using glass beads as a reference).

RESULTS

Ethylene–Propylene–II Terpolymers

Several vanadium-based catalyst systems, in union with organometallic aluminum compounds or alane derivatives,[14] were found effective in producing α-olefin–II terpolymers. However, the investigations reported in this paper have been performed, for the most part, with the system $V(Acac)_3$–Et_2AlCl which gave a good thermal control of the polymerization reaction. The same aged catalyst was used previously in ethylene–propylene copolymerization[15] and, without aging, in the synthesis of terpolymers[9] and copolymers[3] of I with α-olefins.

Polymerization Results

The catalyst system V(Acac)$_3$–AlEt$_2$Cl loses a great deal of its catalytic activity during aging, but when it is prepared *in situ*, a constant overall polymerization rate can be observed in the C_2H_4–C_3H_6 copolymerization (Fig. 1). This constancy extends, under the present experimental conditions to the polymerization time studied, though some time is required to form catalyst centers.

However, even though the overall copolymerization rate remains constant, the type of the active centers changes during the first step of the polymerization as was previously observed.[16] In fact, the composition of the copolymer produced under experimental conditions which avoid mass transfer problems[17,18] changes during the polymerization time (Fig. 2).

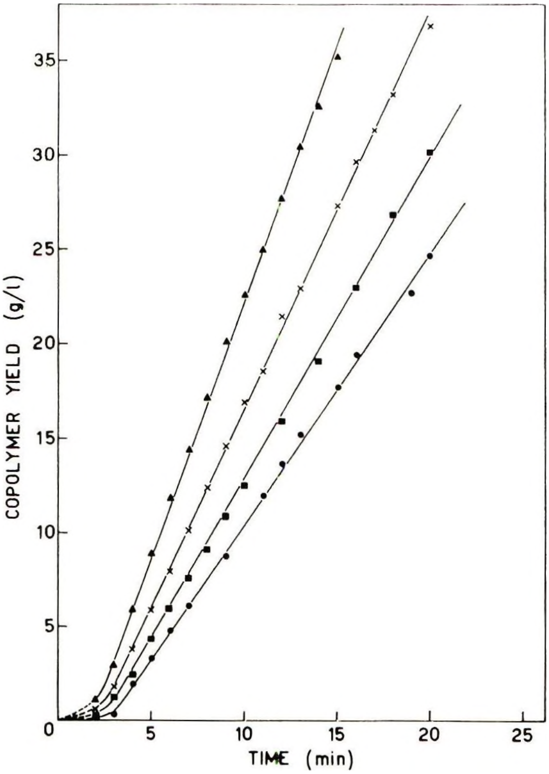


Fig. 1. Yield–time curves for C_2H_4–C_3H_6 copolymerization at various [V(Acac)$_3$]: (▲) = 0.0522 g/l.; (×) = 0.0348 g/l.; (■) = 0.0261 g/l.; (●) = 0.0174 g/l. Experimental conditions: T = 0°C; n-heptane = 1000 ml.; molar ratio in the gaseous phase C_3H_6/C_2H_4 = 2.0; flow of the monomer stream = 900 l./hr; molar ratio AlEt$_2$Cl/V(Acac)$_3$ = 6.0.

The observed regular behavior of the adopted catalyst (Fig. 1) allows one to show the influence of II on the overall kinetics of the terpolymerization reaction.

According to Figure 3, an initiation stage is observed, which is similar but shorter than the corresponding step of the copolymerization reaction. Once the maximum rate is attained, a continuous decrease of the polymerization rate appears, and this decrease is related to the initial termonomer concentration. This is proved by the necessity of increasing the catalyst concentration, proportionally to the initial concentration of II, in order to obtain the nearly equal yields in Figure 3. At the same time, the $\overline{M}_v$ increases continually with time (Fig. 3*c*) for the first 20 min, although more slowly than it occurs in C_2H_4–C_3H_6 copolymerization (Fig. 2), whereas the contents of ethylene and II contents are continually decreasing over the range of time explored.

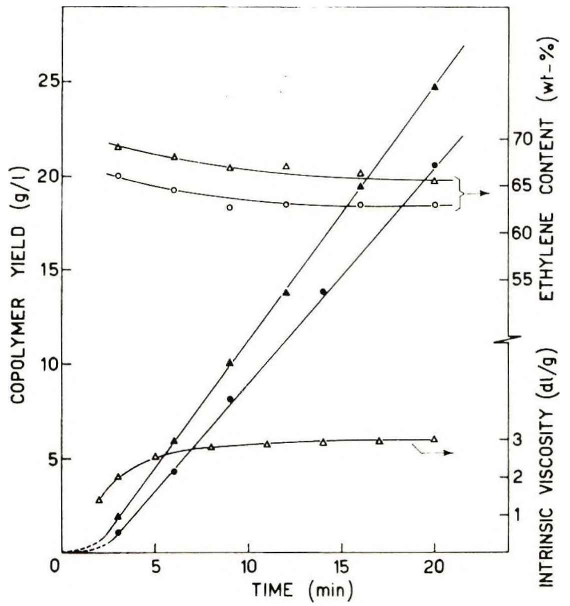


Fig. 2. C_2H_4–C_3H_6 overall copolymerization kinetics at lower polymer yields: (▲) [V(Acac)$_3$] = 0.0070 g/l.; (●) [V(Acac)$_3$] = 0.0063 g/l.

Therefore, the influence of II on the terpolymerization process is different from the influence of I. In fact, under the conditions of Figure 3, the terpolymers based on I showed constant levels of unsaturation and of C_2H_4, whereas the overall polymerization rate was more drastically reduced.[9] On the other hand, when the concentration of II is maintained constant during the polymerization time by continuous addition of the third monomer to the feed, terpolymers having nearly constant levels of C_2H_4 and II can be obtained (Fig. 4). Under these conditions the yield–time curves are slightly changed with respect to the previous ones (Fig. 3). The [η]–time diagrams

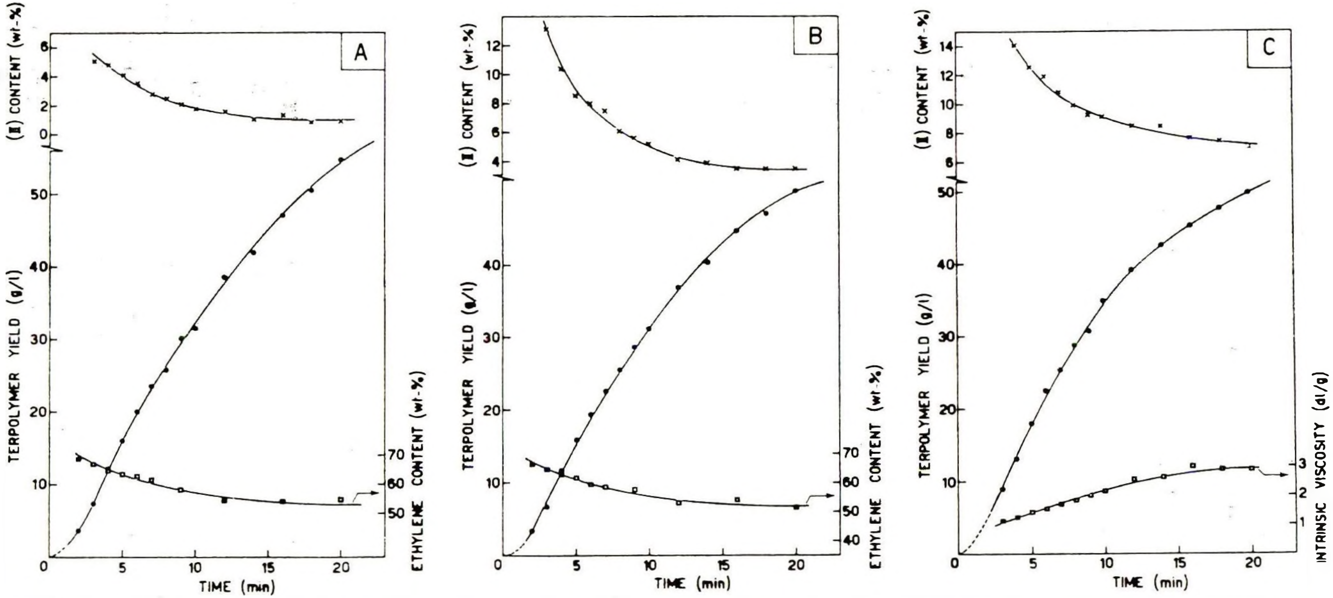


Fig. 3. Influence of reaction time on the C_2H_4–C_3H_6–II terpolymerization process. (*A*) [II] = 0.975 g/l., [V(Acac)$_3$] = 0.104 g/l.; (*B*) [II] = 1.950 g/l., [V(Acac)$_3$] = 0.139 g/l.; (*C*) [II] = 2.925 g/l., [V(Acac)$_3$] = 0.157 g/l. II is added to the feed before start of polymerization. Conditions as in Fig. 1.

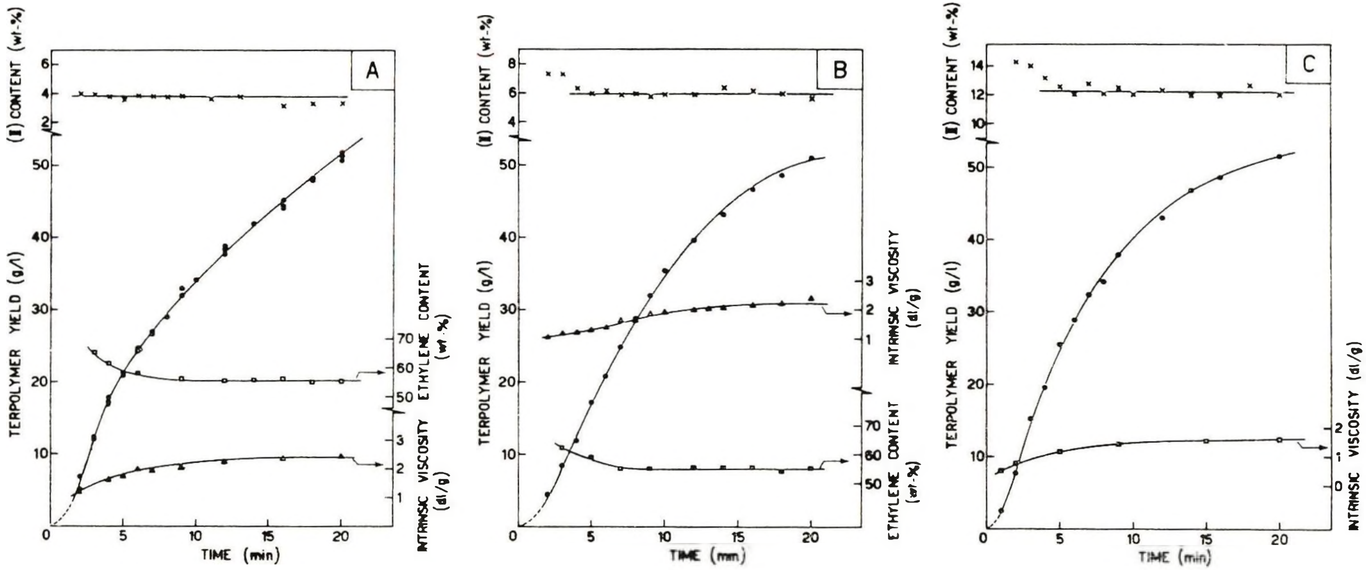


Fig. 4. Yield–time curves for C_2H_4–C_3H_6–II terpolymerization: (*A*) [V(Acac)$_3$] = 0.139 g/l, [II] = 0.487 + 0.858 g/l.; (*B*) [V(Acac)$_3$] = 0.174 g/l., [II] = 0.975 + 1.716 g/l.; (*C*) [V(Acac)$_3$] = 0.244 g/l., [II] = 1.950 + 3.431 g/l. Part of compound II was added to the feed before start of polymerization and then supplied continuously during the reaction time. General conditions as in Fig. 1.

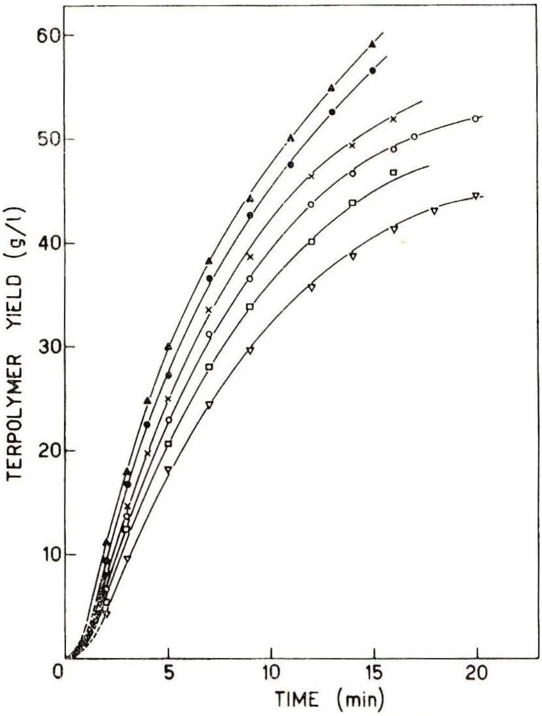


Fig. 5. Influence of the concentration of II on C_2H_4–C_3H_6–II overall terpolymerization kinetics: (▲) [II] = 0.335 g/l.; (●) [II] = 0.671 g/l.; (×) [II] = 1.342 g/l.; (○) [II] = 2.681 g/l.; (□) [II] = 4.020 g/l.; (▽) [II] = 5.360 g/l. General conditions as in Fig. 4; $[V(Acac)_3]$ = 0.174 g/l.

show asymptotic values after the first 10 min which are dependent on the concentration of II.

The influence of the termonomer concentration on the terpolymerization reaction is seen more clearly in Figure 5. As is generally observed in these

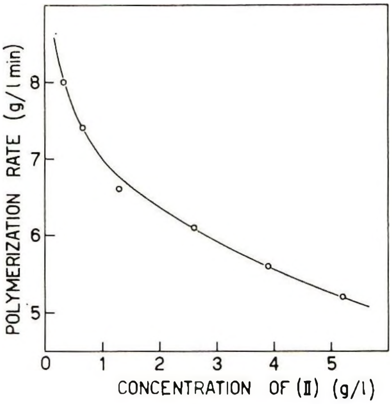


Fig. 6. Dependence of the maximum overall terpolymerization rate on the concentration of II. Conditions as in Fig. 5.

processes,[19] the increase of the termonomer concentration reduces the overall maximum polymerization rate (Fig. 6).

The content of II in the terpolymer is regularly dependent on the total concentration of the termonomer employed (Fig. 7), while the ethylene content remains practically unaffected (Fig. 4). At the same time the in-

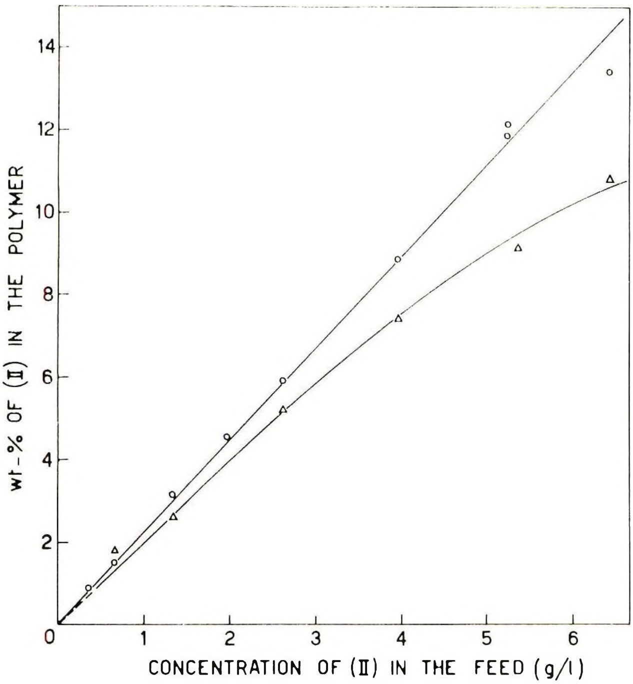


Fig. 7. Dependence of the content of II in the terpolymer on the total concentration of (II) in the feed: (○) chemical method; (△) spectroscopic method. Conditions of Fig. 5.

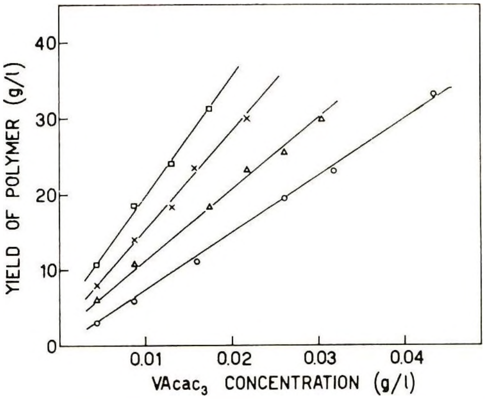


Fig. 8. Influence of the catalyst concentration on the terpolymer yield: (□) [II] = 0.0; (×) [II] = 0.098 + 0.172 g/l.; (△) [II] = 0.292 + 0.515 g/l.; (○) [II] = 0.487 + 0.858 g/l. Conditions as in Fig. 4, polymerization time = 20 min.

trinsic viscosity falls appreciably (Fig. 4 and 9); obviously II is responsible for chain-breaking processes.

Finally, Figures 8 and 9 show the influence of the catalyst concentration. The diagrams indicate the existence of linear correlations between polymer yield and V(Acac)$_3$ concentration in the range of concentration explored. No dependence was found for $[\eta]$ or C_2H_4 content on V(Acac)$_3$ concentration. On the contrary the content of II in the polymer decreases when the catalyst concentration increases. In these correlations the behavior of II is opposite to that seen with I.[9]

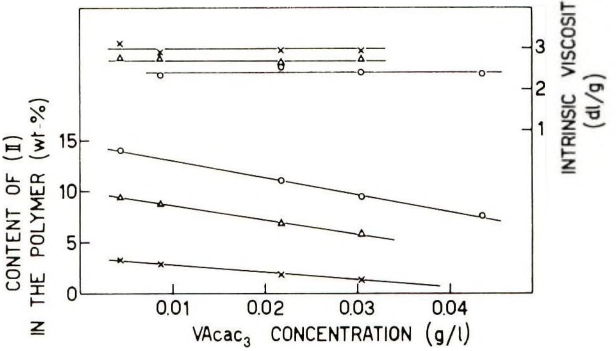


Fig. 9. Influence of the catalyst concentration on $[\eta]$ and on the content of II in the polymer. Conditions as in Fig. 8.

Terpolymer Properties

Ethylene–propylene–II terpolymers are completely amorphous under x-ray examination. They are soluble in hydrocarbons or halogenated

TABLE IV
Fractionation of C_2H_4–C_3H_6–II Terpolymer[a]

Fraction	Weight of the fraction, g	$[\eta]$, dl/g[b]	C_2H_4, wt-%	II, wt-%
1	1.05	3.62	63	4.67
2	1.06	3.46	63	5.30
3	2.00	3.20	62	5.00
4	1.98	2.90	64	5.30
5	1.57	2.91	63	5.20
6	1.70	2.80	62	4.93
7	0.97	2.82	58	4.65
8	1.52	1.84	58	4.42
9	n.d.[c]	0.61	n.d.[c]	n.d.[c]
Initial terpolymer	14.0	2.92	62	4.90

[a] Prepared according to Fig. 4.
[b] In toluene, at 30°C.
[c] Not determined.

hydrocarbons and contain the monomers distributed randomly in the macromolecules, as is demonstrated by the fractionation data of Table IV.

Spectroscopic Investigation

Tables I–III summarize the results of ultraviolet, infrared, and NMR spectroscopic investigations of the terpolymers and compare them with the corresponding results obtained for the monomer II and its 5,6-dihydro derivative.

The ultraviolet spectra of the terpolymer solution show an absorbance at 253 mμ which can be attributed to a polysubstituted conjugated double bond system.[20] The same band is also present in monomer II and 5,6-dihydro-II.

The infrared spectra of the polymers are characterized by bands shown by 5,6-dihydro-II. In fact this compound, which does not contain unsaturation of norbornene type as it is demonstrated by MNR spectra (Table III), shows two bands at 3035 and 3055 cm^{-1} which should be assigned to olefinic =C—H stretching of the cyclopentene ring. The same bands are present in the polymer spectra.

Indeed, this band was assigned to a *cis*-double bond in a five-membered cycloolefin, but the latter was generally associated with the norbornene ring.[21–23] A further disagreement arises for the band at 1567 cm^{-1}, which is present both in 5,6-dihydro-II and in polymers based on II, because a number of norbornene derivatives have absorption in the region of 1575 cm^{-1} (double-bond stretching).[22–24]

The data of Table II refer to samples obtained with the catalyst system V(Acac)$_3$–AlEt$_2$Cl. Quite similar results are observed in the infrared spectroscopic investigations of terpolymers prepared with different vanadium-based catalyst and under different experimental conditions.

In order to resolve the above discrepancy, a number of attempts to terpolymerize C_2H_4, C_3H_6, and 5,6-dihydro-II were carried out. By employing the same procedure adopted to synthetize true terpolymers based on II, we always obtained typical ethylene–propylene copolymer which showed no bands in the regions of 3000–3100 and 1620–1680 cm^{-1} where, generally, absorptions due to cyclopentene unsaturations[22] are observed. This conclusion agrees with IBr halogenation measurements (cf. next section) and with vulcanization experiments carried out with a typical recipe for this class of elastomer;[25] both the tests were negative.

Finally, in the NMR spectra (Table III) three signals are present at 0.83, 1.23, and 1.72 ppm. The first is due to methyl protons, the second to methylenic and methyne protons, and the third can be attributed to the isopropylidene group.

The spectroscopic data are thus consistent with an opening of the norbornene double bond of II when the triolefin is inserted into an ethylene–propylene copolymer chain.

Determination of Unsaturation

The unsaturation in the terpolymer presented in this paper was determined quantitatively by IBr absorption: the correction for the side reactions was carried out by using a radiochemical calibration as standard. This was achieved after previous experiments with the terpolymer based on I[9] and after unsuccessful attempts in determining the unsaturation of monomeric II.

Preliminary runs were carried out with ICl which distinguishes between double bond absorption and secondary (splitting out and substitution) reactions.[26] The method has been used previously with rubbers of low unsaturation[27] and also recently with terpolymers based on ethylene and propylene.[28,29]

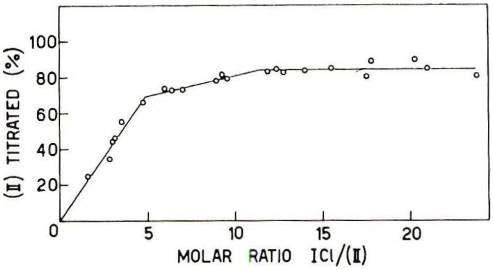


Fig. 10. Absorption of ICl on monomeric II at different ICl/(II) molar ratios. Reaction time = 30 min; room temperature; solvent, CCl_4–$CHCl_3$ (60:40).

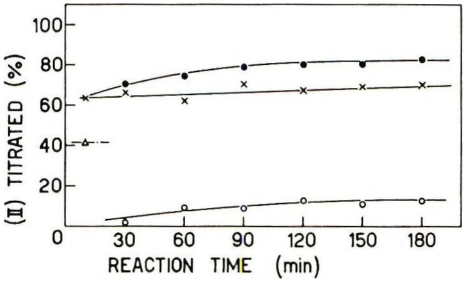


Fig. 11. Influence of the reaction time on the titration of monomeric II by ICl absorption at molar ratio ICl/II = 11.8: (●) total iodometric titration; (×) corrected iodometric titration; (△) splitting out reaction; (○) substitution reaction.

Nevertheless, we obtained incomplete titration with monomeric II, as can be seen in Figure 10, even when molar ratios ICl/(II) > 12 were employed.

No significant increase of the unsaturation level was gained with higher reaction times (Fig. 11). The most unusual fact emerging from these attempts is the predominant role of the splitting our reaction. These results were quite similar to the corresponding ones observed in the ICl absorption on monomeric I.[9]

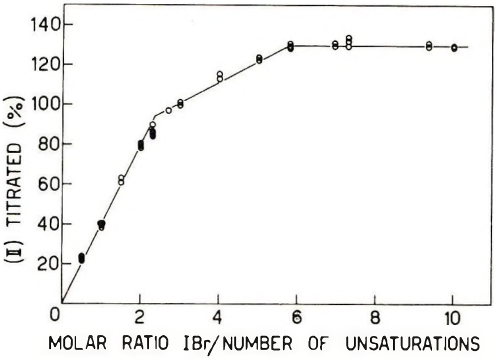


Fig. 12. Influence of the concentration of IBr on the iodometric titration of monomeric II. Conditions as in Fig. 10.

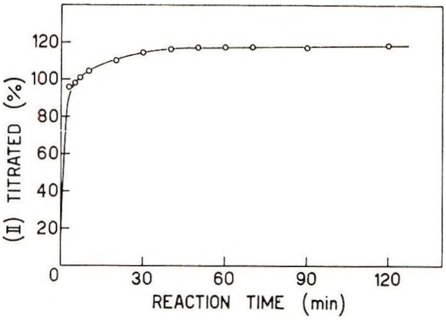


Fig. 13. Dependence of the titration of monomeric II with IBr on the reaction time. Ratio IBr/number of unsaturations = 3.6.

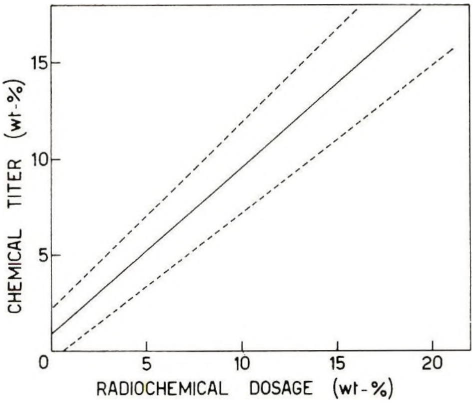


Fig. 14. Correlation between radiochemical and chemical (IBr absorption) assay of II in terpolymer with 95% confidence limits.

When IBr was employed, the content of unsaturation was higher than the theoretical level. An asymptotic value exceeding the theoretical one by 30% was obtained for a ratio IBr/unsaturation $\simeq 6$ (Fig. 12), whereas no influence was exerted by the reaction time after 40 min (Fig. 13).

Because of the difficulty of applying the correction described for ICl[26] to the IBr method,[9] we decided, in order to determine correctly the content of II, to follow the previous procedure.[9] Several samples of terpolymer containing different amounts of ^{14}C-labeled II were titrated with IBr and, at the same time, were counted for their radioactivity. The results of radiochemical and chemical measurements, presented in Figure 14, fall on a straight line which does not pass through the origin, as it could be expected because of the side reactions. Reproducibility was low in the evaluation of the higher levels of II.

Attempts to employ ultraviolet measurements in determining the content of II in our terpolymer resulted in the data given in Figure 7. The spectroscopic method agrees with the chemical method within experimental error for low levels of unsaturation.

Copolymers of Ethylene and II

Valuable insight into the reactivity of I with anionic coordinate catalyst has been obtained by studying the ethylene–I copolymerization.[3] The same aim was present in this investigation, where the ethylene–II copolymerization was explored with vanadium-based Ziegler-Natta catalysts.

Owing to the high reactivity of ethylene, very low olefin concentrations were used, and consequently the catalyst concentration was relatively high. The catalyst systems employed were: $V(Acac)_3$–$AlEt_2Cl$, VCl_4–$AlEt_2Cl$–

TABLE V

Ethylene–II Copolymerization with $V(Acac)_3$–$Al(C_2H_5)_2Cl$ System[a]

$VAcac_3$, g	C_2H_4, l./hr[b]	Time, min	Yield, g	Conversion of II, %	C, %[c]	Content of II in polymer wt-%
0.0174	200	10	2.1	40	86.35	13
0.0348	100	15	2.4	67.2	86.63	19.1
0.0696	50	10	2	73.9	86.92	25.2
0.1044	30	10	1.9	76.1	87.05	27.3
0.1044	16	15	2	96.8	87.35	33.0
0.0696	50	5	2.8[d]	0	85.73	0
0.0174	200	4	2.5[e]	0	85.77	0

[a] Experimental conditions: n-heptane = 200 cm^3; II = 0.682 g; T = 0°C; Al/V molar ratio = 6.0; total pressure = 1 atm.

[b] Ethylene stream was diluted with pure nitrogen; overall flow rate = 300 l./hr at S.T.P.

[c] Mean values from different samples.

[d] 5,6-dihydro-II was employed as comonomer; $[\eta]$ = 6.60 dl/g in decalin at 135°C.

[e] Polyethylene reference: $[\eta]$ = 14.55 dl/g.

TABLE VI

Ethylene–II Copolymerization with VCl_4–$Al(C_2H_5)_2Cl$–Anisole System[a]

VCl_4, g	C_2H_4, l./hr	Time, min	Yield, g	Conversion of II, %	C, %[b]	Content of II in polymer, wt-%	Infrared A_{1658}/A_{717}
0.0097	200	6	0.9	4.8	85.90	3.6	0
0.0097	100	15	0.5	13.4	86.63	18.2	[c]
0.0193	50	6	1.0	32.8	86.82	22.4	0.034
0.0386	30	10	1.2	63.4	87.50	36.0	0.048
0.0579	16	11	1.0	51.5	87.45	35.1	[c]
0.0193	50	8	1.4[d]	0	85.68	0	[e]
0.0097	200	4	3.5[f]	0	85.70	0	[e]

[a] Experimental conditions as in Table V, except $T = -20°C$; anisole/Al = 0.5.

[b] Average content from different samples.

[c] Not determined.

[d] 5,6-Dihydro-II was employed as comonomer; $[\eta] = 3.35$ dl/g in decalin at 135°C.

[e] Spectra typical of polyethylene, particularly near 700 cm^{-1}.

[f] Polyethylene reference: $[\eta] = 9.32$ dl/g.

anisole, and VO(O-*n*-But)$_3$–$AlEt_2Cl$–anisole; the results are reported in Tables V–VII.

Under the same experimental conditions propylene does not copolymerize with II in the presence of these catalysts.

C_2H_4–II copolymer separates from the reaction solvent due to crystallization of the polyethylene segments. The elemental analysis data of the polymer obtained were, as in the case of C_2H_4–I copolymer,[3] indicative of insertions of II into the polyethylene chain. It is worth noting that in the attempts to copolymerize C_2H_4 and 5,6-dihydro-II, the elemental analysis always gives values corresponding to ethylene homopolymer (Tables V–VII).

TABLE VII

Ethylene–II Copolymerization with VO(O-*n*-C_4H_9)$_3$–$Al(C_2H_5)_2Cl$–Anisole System[a]

VO(O-n-C_4H_9)$_3$, g	C_2H_4, l./hr	Time, min	Yield, g	Conversion of II, %	C, %[b]	Content of II in polymer, wt-%
0.0572	200	10	1.7	29.7	86.31	11.9
0.0572	100	15	1.3	46.5	86.94	24.4
0.1144	50	15	1.0	41.5	87.12	28.3
0.1430	30	15	0.9	40.9	87.25	31.0
0.0858	100	12	2.0[c]	0	85.64	0
0.0286	200	9	4.8[d]	0	85.65	0

[a] Experimental conditions as in Table V, except Al/V = 10, anisole/Al = 1.0.

[b] Mean values from different samples.

[c] 5,6-Dihydro-II was employed as comonomer; $[\eta] = 8.25$ in decalin at 135°C.

[d] Polyethylene reference: $[\eta] = 10.50$ dl/g.

TABLE VIII
X-Ray and DTA Measurements on C_2H_4–II Copolymers

Sample	Catalyst system	Content of II, wt-%[a]	[η], dl/g	Crystal-linity, %[b]	Melting point, °C[c]	ΔH_f, cal/g
Polyethylene	VAcac$_3$–AlEt$_2$Cl	0	14.5	78	137.0	30
Copolymer	"	5.8	[d]	63	136.5	29
Pseudo-copolymer[e]	"	0	6.6	85	134.5	33
Polyethylene	VO(OC$_4$H$_9$)$_3$–AlEt$_2$Cl[f]	0	10.5	78	135.5	28
Copolymer	"	28.3	[d]	18	(125)	(2)
Pseudo-copolymer[e]	"	0	8.3	80	134.5	33
Polyethylene	VCl$_4$–AlEt$_2$Cl[f]	0	9.3	83	137.0	36
Copolymer	"	34.8	[d]	23	(120)	[d]
Pseudo-copolymer[e]	"	0	3.4	89	133.5	34

[a] By elemental analysis.

[b] By x-ray evaluation.

[c] DTA evaluation at the endpoint.

[d] Not determined.

[e] Polyethylene resulting from attempts to copolymerize C_2H_4 with 5,6-dihydro-II.

[f] Complexed with anisole.

According to Table I, the ultraviolet spectra of the *n*-hexane soluble fraction of the copolymer show absorption at 254 mμ, typical of the conjugated diene system of monomeric II and of 5,6-dihydro-II.

The infrared spectra (Table II) present the same features observed for C_2H_4–C_3H_6–II terpolymer, which have been discussed above.

The increasing concentration of II in the feed produces increasing levels of II in the copolymer (Fig. 15), as the ratio of the absorbance at 1650 (stretching of the cyclopentene double bond) and 717 cm^{-1} (CH_2 sequences) gives a semiquantitative evaluation of the relative content of II. Also the polyethylene crystallinity band (727 cm^{-1}) decreases as the content of II increases. These results agree with the elemental analysis data (Table VI). Furthermore, x-ray and DTA measurements support the copolymer structure of the polymer under investigation (Table VIII).

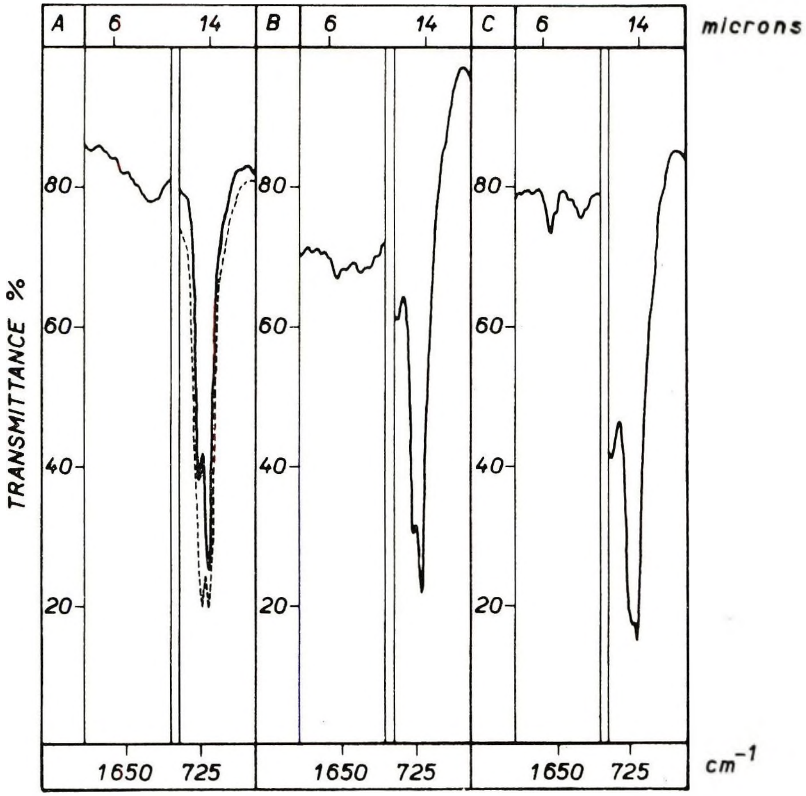


Fig. 15. Infrared spectra near 700 and 1650 cm^{-1} of various C_2H_4–II copolymers: (*A*) 3.6 wt-% II, $A_{1650}/A_{717} = 0$; $A_{1650}/A_{727} = 0$; (*B*) 22.4 wt-% II, $A_{1650}/A_{717} = 0.0344$, $A_{1650}/A_{727} = 0.0394$; (*C*) 36.0 wt-% II, $A_{1650}/A_{717} = 0.0482$, $A_{1650}/A_{727} = 0.0584$. The broken line refers to a polyethylene sample prepared under the same conditions.

The content of II in the copolymer obtained was, generally, less than 35 wt-%, whereas the conversion could reach high levels under the conditions reported in Tables V–VII. In similar experiments[3] I showed about fivefold lower reactivity.

The participation of II in the copolymerization reaction takes place through opening of the norbornene double bond, as in the terpolymerization reaction examined above. In fact, attempts to copolymerize C_2H_4 and 5,6-dihydro-II always yield ethylene homopolymer. Ultraviolet or infrared evidence did not support the presence of 5,6-dihydro-II in the polyethylene chain. In particular, the band at 727 cm^{-1} was quite similar to the corresponding one observed in polyethylene prepared with the same catalyst.

The fact that the behavior of II is the same in copolymerization and terpolymerization reaction confirms that the same polymerization mechanism applies in both processes, involving the selective opening of the norbornene double bond.

Attempts to Homopolymerize II

Previous investigations carried out with the aim of homopolymerizing I, indicated the double bonds of the conjugated system to be nonreactive in the presence of typical anionic coordinate catalysts.[3] On the other hand, very recently, the norbornene unsaturation of dicyclopentadiene was found to open by means of Ziegler-Natta catalysts[23] and to give a homopolymer possessing different types of structural units.

Since some cyclic diolefins can be homopolymerized with the anionic coordinate catalysts in a manner different from that involved in terpolymerization,[30] we attempted to homopolymerize II with some catalysts based on Ti, V, Mo, and W together with different organometallic Al derivatives (Table IX). No solid polymer was obtained with typical anionic coordinate systems, i.e., $TiCl_3$–AlR_3 or $V(Acac)_3$–AlR_2Cl. Under the experimental conditions used, the polymer obtained had the same enchainment derived from the 1,4-opening of the conjugated diene system.

The spectroscopic evidence for this conclusion is reported in detail in another paper[31] and will only be briefly summarized here. In the ultraviolet region the absorption at 254 mμ (conjugated diene system) is completely absent. The infrared spectra show bands typical of norbornene structure (3050, 1568, 723 cm^{-1}) and of cyclopentene unsaturation (3030, 1623 cm^{-1}). In the NMR spectra the main signals are at 0.93 [—$C(CH_3)_2$-group], 5.13 ($H_5 + H_6$ protons) and 6.0 ppm (H_2 protons).

The assigned structure was always observed in the cationic polymerization of II[31] and was in agreement with the fact that the polymers obtained (Table IX) were of very low MW and that the yield became higher as the acidity of the catalyst increased.

DISCUSSION

The behavior of the triene II, both in terpolymerization and in copolymerization reaction with α-olefins, was in part different from the corresponding compound I previously described. From the evaluation of the parameters

TABLE IX
Anionic Coordinate Homopolymerization of II

Transition metal compd		Al compound		Solvent							
Type	Wt, g	Type	Wt, g	Type	Vol, ml	II, g	T, °C	Time, hr	Conversion, %	[η], dl/g	Notes
$TiCl_3$–HA	0.371	$Al(C_2H_5)_3$	0.821	n-Heptane	50	4.88	50	24	Trace	—	Catalyst aged 10 min at 60°C
"	0.170	$Al(i\text{-}C_4H_9)_3$	0.653	"	30	3.90	80	24	0	—	
"	0.283	"	1.089	"	30	3.90	20	24	0	—	
"	0.289	"	1.119	"	5	4.88	15	24	—	—	Oily product
$TiCl_4$	0.190	"	0.594	"	30	3.90	20	18	7.7	—	Insoluble product
"	0.190	$Zn(C_2H_5)_2$	0.309	"	15	4.88	15	24	0	—	
VAcac$_3$	0.348	$Al(C_2H_5)_2Cl$	0.482	Toluene	30	3.90	0 to 20	3–15	Trace	—	
"	0.115	"	1.446	"	20	3.90	15	24	"	—	
VCl_4	0.193	"	0.723	n-Heptane	60	3.90	−20 to 20	1–18	20.5	0.48	
"	0.193	$Al(i\text{-}C_4H_9)_3$	0.594	"	30	3.90	−20 to 20	3–15	—	—	Oily product
"	0.193	$Al(C_2H_5)_3$	0.228	"	20	3.90	15	24	8.9	0.21	
$MoCl_5$	0.547	"	0.684	Toluene	30	3.90	0 to 20	3–15	6.4	0.25	
WCl_6	0.397	$Al(C_2H_5)_2Cl$	0.301	"	20	3.90	16	24	10.5	0.02	

regulating the terpolymer and copolymer synthesis, II appears to be about fivefold more reactive than I. This property of II can be attributed to the strain present in the norbornene ring, and several results reported in the foregoing sections can be interpreted on this basis. Indeed, the well known reactivity of the norbornene ring towards different reagents rests on the same assumption.[32]

The high reactivity of II in the terpolymerization and copolymerization reaction is responsible for the high utilization of the triene, as it is generally observed for comonomers having the norbornene ring[19] and requires a continuous supply of II during the first minutes of the reaction in order to obtain a polymer of constant composition.

Furthermore, the low interference of II with the catalyst centers, whose activity is, however, lowered by the presence of II, is due to the high reactivity of II in the polymerization reaction, because terpolymers having a relatively high content of unsaturation (> 15 wt-%) can be obtained with relatively low concentration of triene in the feed.

Also, under cationic catalysis, which gives the selective 1,4-opening of the conjugated double bond system of the triene, II was found more reactive than I by means of copolymerization experiments.[31] Therefore, the particular reactivity of II appears to be an inherent characteristic of the molecule, present both in the isolated double bond and in the conjugated diene system.

Chain-breaking processes depending on the concentration of (II) are operating during the terpolymer synthesis. Certainly they take place through termination reactions (cf. the influence of the concentration of II on the kinetic curves and on $[\eta]$) and, probably, through a transfer reaction to II, as it was observed[33] in the case of I.

The increase of molecular weight and the change of terpolymer composition with time are limited to the first polymerization period. The same phenomena extend over a longer time in the corresponding ethylene–propylene copolymerization. These results together with the absence of chain-transfer reactions to the catalyst components,[15] reveal a stabilizing effect exerted by II on the catalyst centers.

By employing the 5,6-dihydro derivative of II, both in terpolymerization and in copolymerization experiments, it has been demonstrated that such a compound is not reactive under anionic coordinate catalysis. In this respect II is quite similar to I, i.e., the isolated double bond of these triolefins is selectively opened by Ziegler-Natta catalysts, whereas the conjugated double bond system remains unchanged.

In spite of the strain present in the norbornene ring, attempts to homopolymerize II were unsuccessful. In order to explain this negative result, it is interesting to observe that the polymerization of dicyclopentadiene by means of anionic coordinate catalyst was successful only under somewhat drastic conditions.[23] Furthermore, low yield and low molecular weight were obtained, together with different types of structural units in the chains. These data indicate the existence of difficulties in the propagation reaction via norbornene double-bond addition. On the contrary, the behavior of dicyclopentadiene in the terpolymerization with C_2H_4 and C_3H_6 discloses a high reactivity of the diene.[19]

On the whole, both II and dicyclopentadiene show some analogy with the behavior of cyclopentene in homopolymerization and copolymerization reactions.[34] According to cycloolefin polymerization studies,[35] the failure of II to homopolymerize seems to be due to steric interference between the monomeric units of the chain. This interference is strongly reduced in copolymerization or terpolymerization of II with α-olefins, and a random insertion of II in the polymer chains takes place at a relatively high rate.

References

1. S. Cesca, S. Arrighetti, and W. Marconi, *Chim. Ind.* (Milan), **50,** 171 (1968).
2. R. J. Sonnenfeld, G. R. Kahle, and O. G. Buck, *J. Appl. Polym. Sci.*, **13,** 365 (1969).
3. S. Cesca, A. Roggero, T. Salvatori, A. De Chirico, and G. Santi, *Makromol. Chem.*, **133,** 161 (1970).
4. S. Cesca, W. Marconi, and A. Roggero, *Chim. Ind.* (Milan), **49,** 1160 (1967).
5. Ital. Pat. 792,906, assigned to SNAM Progetti (March 13, 1967).
6. N. M. Seidov, M. A. Dalin, Yu. G. Gambarov, I. A. Azutyunov, and R. D. A. Abdublaev, *Kauchuk i Rezina*, **25,** 3 (1966).
7. M. E. Samuels and K. H. Wirth, *Rubber J.*, **149,** 46 (1967).
8. J. E. Capito, P. Innes, and R. D. Allen, *J. Inst. Rubber Ind.*, **8,** 228 (1968).
9. S. Cesca, A. Roggero, G. Bertolini, and W. Marconi, *Chim. Ind.* (Milan), **50,** 183 (1968).
10. S. Cesca, M. L. Santostasi, W. Marconi, and M. Greco, *Ann. Chim.* (Rome), **55,** 682 (1965).
11. G. Natta, G. Mazzanti, A. Valvassori, and G. Pajaro, *Chim. Ind.* (Milan), **39,** 733 (1957).
12. W. Marconi, S. Cesca, and G. Della Fortuna, *Chim. Ind.* (Milan), **46,** 1131 (1964).
13. R. W. Hall, in *Techniques of Polymer Characterization* P. W. Allen, Ed., Butterworths, London, 1959, p. 27.
14. Ital. Pat. 778,353, assigned to SNAM Progetti (February 3, 1965); Ital. Pat. 813,867, assigned to SNAM Progetti (August 8, 1967).
15. G. Natta, G. Mazzanti, A. Valvassori, G. Sartori, and D. Fiumani, *J. Polym. Sci.*, **51,** 411 (1961).
16. S. Cesca, A. Roggero, G. Bertolini, and W. Marconi, *Chim. Ind.* (Milan), **50,** 1299 (1968).
17. G. Bier, W. Hoffmann, G. Lehmann, and G. Seydel, *Makromol. Chem.*, **58,** 1 (1963).
18. G. Lehmann and A. Gumboldt, *Makromol. Chem.*, **70,** 23 (1964).
19. R. German, R. Hank, and G. Vaughan, *Kautschuk Gummi*, **19,** 67 (1966).
20. R. B. Woodward, *J. Amer. Chem. Soc.*, **64,** 72 (1942).
21. G. Sartori, F. Ciampelli, and N. Cameli, *Chim. Ind.* (Milan), **45,** 1478 (1963).
22. R. J. De Kock and A. Veermans, *Makromol. Chem.*, **95,** 179 (1966).
23. G. Dall'Asta, G. Motroni, R. Manetti, and C. Tosi, *Makromol. Chem.* **130,** 153 (1969).
24. L. Kaplan, H. Kwarth, and P. V. Schleyer, *J. Amer. Chem. Soc.*, **82,** 2341 (1960).
25. G. Ghetti, G. Corradini, V. Bulla, and M. Bruzzone, *Chim. Ind.* (Milan), **51,** 1361 (1969).
26. T. S. Lee, I. M. Kolthoff, and M. A. Mairs, *J. Polym. Sci.*, **3,** 66 (1948).
27. T. S. Lee, I. M. Kolthoff, and E. Johnson, *Anal. Chem.*, **22,** 995 (1950).

28. M. E. Tunnicliffe, D. A. Mackillop, and R. Hank, *Europ. Polym. J.*, **1**, 259 (1965).

29. R. Hank, *Kautschuk Gummi*, **18**, 295 (1965).

30. I. Pasquon, A. Valvassori, and G. Sartori, in *The Stereochemistry of Macromolecules*, A. D. Ketley, Ed., Dekker, New York, 1967, Vol. I, p. 177.

31. S. Cesca, A. Priola, A. De Chirico, and G. Santi, *Makromol. Chem.*, **143**, 211 (1971).

32. E. H. Rodd, *Chemistry of Carbon Compounds*, Elsevier, Amsterdam, 1953, Vol. 2A, p. 338.

33. S. Cesca, S. Arrighetti, A. Roggero, and W. Marconi, *Chim. Ind.* (Milan), **50**, 1203 (1968).

34. G. Natta, G. Dall'Asta, G. Mazzanti, I. Pasquon, A. Valvassori, and A. Zambelli, *Makromol. Chem.*, **54**, 95 (1962).

35. J. Boor, E. A. Youngman, and M. Dimbat, *Makromol. Chem.*, **90**, 26 (1966).

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Free-Radical Polymerizations Initiated by Triethylaluminum–Cuprous Chloride Mixtures

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Synopsis

Methyl methacrylate was polymerized by triethylaluminum-cuprous chloride catalyst. A study of the polymerization kinetics indicated that the overall rate was represented by the equation, $R_p = K[\mathrm{AlEt_3}][\mathrm{CuCl}]^{1/2}[\mathrm{M}]^2$. The overall activation energy was 16.5 kcal/mole. From ESR measurement and the results of copolymerization of methyl methacrylate with styrene, it was suggested that the catalytic system has the character of a radical initiator. A polymerization scheme was also proposed.

Introduction

It was found that methyl methacrylate was polymerized by triethylaluminum and cuprous chloride. Polymerization kinetics in this catalytic system was studied at room temperature (20 ± 1°C). The rate of polymerization showed a first-order dependence on triethylaluminum concentration, a one-half order dependence on cuprous chloride and a second-order dependence on monomer concentration, the overall activation energy of polymerization being 16.5 kcal/mole.

In order to characterize this catalytic species, copolymerization of methylmethacrylate with styrene was carried out, the composition curve being similar to that of the usual radical copolymer. Moreover, an ESR signal was observed in $\mathrm{AlEt_3}$–CuCl (1:1 mole ratio)–methyl methacrylate mixture, although in an $\mathrm{AlEt_3}$–CuCl mixture with the absence of monomer, no signal was observed. On the basis of these data, it was suggested that polymerization by this catalytic system followed a radical mechanism.

Experimental

Triethylaluminum (Ethyl Corporation) and cuprous chloride were used without further purification. Monomer and solvent were purified by the usual method. Polymerization was carried out as follows. To a given quantity of *n*-hexane in a glass tube, cuprous chloride and triethylaluminum were added and mixed with shaking. Immediately, a black brown precipitate formed. After several minutes, monomer or monomer mixture was added. The tube was sealed under a nitrogen stream and immersed in a thermostat for the given time. The polymerization product was poured into methanol containing a small quantity of hydrochloric acid; the precipitate was washed repeatedly with methanol and dried in a vacuum oven.

In the case of copolymerizations of styrene with acrylonitrile, the three procedures for catalyst preparation were chosen as follows: (a) CuCl → $AlEt_3$ → monomer mixture, (b) CuCl → monomer mixture → $AlEt_3$, (c) $CuCl_2$ → monomer mixture → $AlEt_3$.

The copolymer analysis were carried out by pyrolytic gas chromatography for styrene–methyl methacrylate copolymer, by fluorine analysis for 1,1,5-trihydroperfluoropentyl methacrylate–methyl methacrylate copolymer and by nitrogen analysis (Kjeldahl) for styrene–acrylonitrile copolymer.

Results and Discussion

The effects of triethylaluminum, cuprous chloride, and monomer concentration on the polymerization rate in a early stage were studied; the results are shown in Figures 1–3. From these results at 20°C, the overall rate of polymerization of methyl methacrylate was obtained by eq. (1).

$$R_p = k[\mathrm{AlEt_3}][\mathrm{CuCl}]^{1/2}[\mathrm{M}]^2 \qquad (1)$$

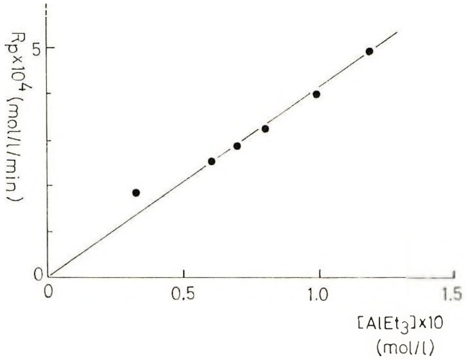

Fig. 1. Polymerization rate vs. triethylaluminum concentration. [CuCl] = 0.0653 mole/l.; (M) = 6.3 mole/l.

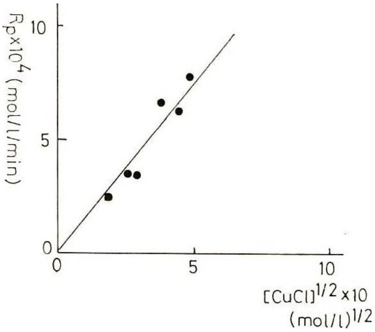

Fig. 2. Polymerization rate vs. cuprous chloride concentration. [AlEt$_3$] = 0.0805 mole/l.; [M] = 6.3 mole/l.

An attempted polymerization of methyl methacrylate by only triethylaluminum or cuprous chloride yielded no polymer at room temperature in 24 hr.

In order to ascertain whether the polymerization proceeds by a radical or ionic mechanism, ESR measurements in the polymerization medium were carried out. The ESR signal obtained on adding methyl methacrylate to the triethylaluminum–cuprous chloride (1:1 mole ratio) reaction product in *n*-hexane is shown in Figure 4, and it was noticed that the signal remained even in the later stage of polymerization. In the triethylaluminum–cuprous chloride reaction product in *n*-hexane, no distinct signal was observed, however.

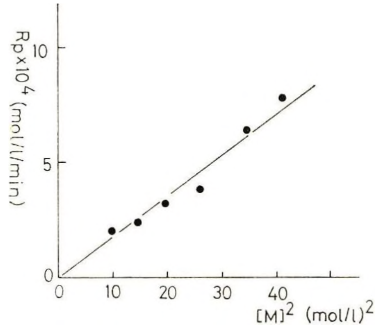

Fig. 3. Polymerization rate vs. monomer concentration. $[AlEt_3]$ = 0.0805 mole/l.; $[CuCl]$ = 0.0653 mole/l.

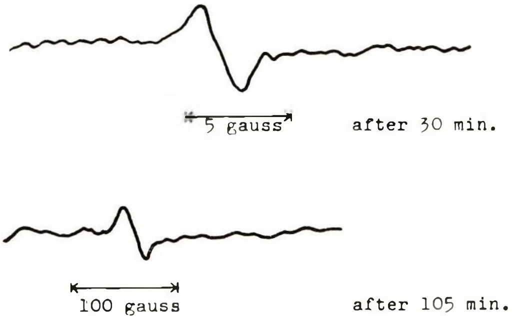

Fig. 4. ESR in triethylaluminum–cuprous chloride–methyl methacrylate mixture at 20°C.

The other evidence supporting the radical mechanism was obtained from the results of copolymerization of methyl methacrylate with styrene. The composition curve of the copolymerization, as shown in Figure 5. Triethylaluminum–cuprous chloride was also an effective catalyst for halogen-containing monomer, such as 1,1,5-trihydroperfluoropentyl methacrylate, and so copolymerization of the monomer with methyl methacrylate was possible.

The composition curves in the copolymerizations by triethylaluminum–cuprous chloride and benzoyl peroxide catalysts[1] are shown in Figure 6.

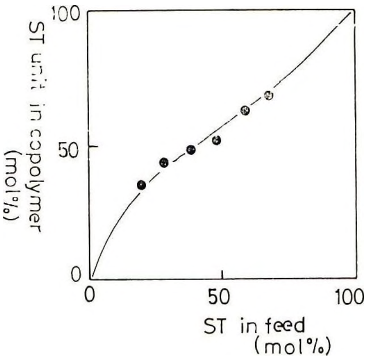

Fig. 5. Composition curve in styrene-methyl methacrylate copolymerization by $AlEt_3$–CuCl catalyst. $[AlEt_3] = 0.0805$ mole/l.; $[CuCl] = 0.0653$ mole/l.; $([ST] + [MMA]) = 9.2$ mole/l.

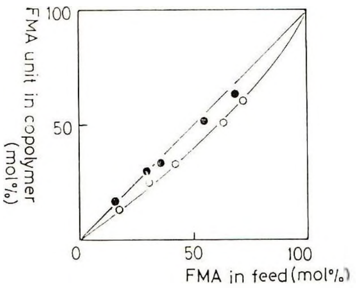

Fig. 6. Composition curve in copolymerization of 1,1,5-trihydroperfluoropentyl methacrylate with methyl methacrylate by (●) $AlEt_3$–CuCl or (○) benzoyl peroxide at 30°C. $AlEt_3$/CuCl (mole ratio) = 2.41; total monomer concentration = 2.0 mole/l.

These copolymerization results support the radical initiator character of the triethylaluminum–cuprous chloride catalyst.

In polymerization of methyl methacrylate, the overall, activation energy was 16.5 kcal/mole (Fig. 7).

To explain the results of methylmethacrylate polymerization kinetics, the polymerization scheme shown in eqs. (2)–(7) was postulated.

$$AlEt_3 + CuCl \rightarrow C^* \tag{2}$$

$$AlEt_3 + M \xrightleftharpoons{K_1} AlEt_3 \cdot M \tag{3}$$

$$C^* + AlEt_3 \cdot M \xrightleftharpoons{K_2} (\text{Complex}) \tag{4}$$

$$(\text{Complex}) + M \xrightarrow{k_i} M \cdot \tag{5}$$

$$M \cdot + M \xrightarrow{k_p} M_i \cdot \tag{6}$$

$$2M_i \cdot \xrightarrow{k_t} \text{Polymer} \tag{7}$$

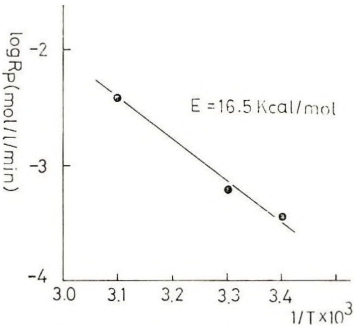

Fig. 7. Arrhenius plot of methyl methacrylate polymerization by $AlEt_3$–CuCl catalyst. $[AlEt_3] = 0.0805$ mole/l.; $[CuCl] = 0.0653$ mole/l.; $[M] = 6.3$ mole/l.

Here C* is the reaction product of triethylaluminum with cuprous chloride, and $AlEt_3 \cdot M$ and (Complex) are complexes of triethylaluminum with monomer and of C* with $AlEt_3 \cdot M$, respectively. K_1 and K_2 are equilibrium constants in reactions (3 and (4); k_i, k_p and k_t are rate constants of initiation, propagation, and termination, respectively.

If bimolecular termination and steady state are assumed, eqs. (8) and (9) are derived.

$$[\mathrm{Complex}] = \frac{K_2[\mathrm{C}]^*}{1 + K_2[\mathrm{C}]^* + K_2\left\{K_1[\mathrm{M}][\mathrm{AlEt_2}]/(1 + K_1[\mathrm{M}])\right\}} \frac{K_1[\mathrm{M}][\mathrm{AlEt_3}]}{1 + K_1[\mathrm{M}]} \tag{8}$$

$$[\mathrm{M}_i\cdot] = (k_i/k_t)^{1/2}[\mathrm{Complex}]^{1/2}[\mathrm{M}]^{1/2} \tag{9}$$

When $1 \gg K_1[M]$, and $[C^*]$ is low, $K_2[C]^*$ is small compared to unity, and then

$$[\mathrm{Complex}] = \frac{K_2[\mathrm{C}]K_1[\mathrm{M}][\mathrm{AlEt_3}]}{1 + K_1[\mathrm{M}] + K_1K_2[\mathrm{M}][\mathrm{AlEt_3}]}$$

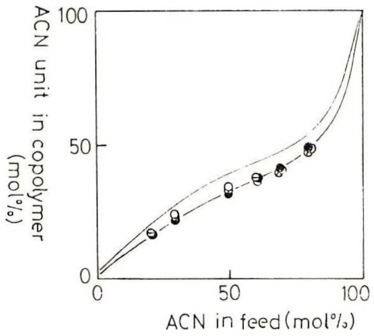

Fig. 8. Composition curve in acrylonitrile-styrene copolymerization in $AlEt_3$–CuCl (mole ratio = 2.4) at 20°C with different orders of addition of reactant and catalyst components: (⊖) CuCl ← M ← $AlEt_3$; (●) $CuCl_2$ ← M ← $AlEt_3$; (○) CuCl ← $AlEt_3$ ← M; (——) curve for conventional radical catalysis.[1]

The overall rate equation is given in eq. (10).

$$R_p = k_p\left(\frac{k_i}{k_t}\right)^{1/2}\left[\frac{K_1K_2[\mathrm{C}]^*[\mathrm{M}][\mathrm{AlEt_3}]}{1 + K_1[\mathrm{M}] + K_1K_2[\mathrm{M}][\mathrm{AlEt_3}]}\right]^{1/2}[\mathrm{M}]^{3/2} \qquad (10)$$

If $K_1[\mathrm{M}] + K_1K_2[\mathrm{M}][\mathrm{AlEt_3}] \ll 1$ and $[\mathrm{C^*}] \propto [\mathrm{AlEt_3}][\mathrm{CuCl}]$ are assumed, eq. (10) may be simplified to eqs. (11) and (12).

$$R_p = k_p(k_iK_1K_2/k_t)^{1/2}[\mathrm{C^*}]^{1/2}[\mathrm{AlEt_3}]^{1/2}[\mathrm{M}]^2 \qquad (11)$$

$$R_p \propto [\mathrm{AlEt_3}][\mathrm{CuCl}]^{1/2}[\mathrm{M}]^2 \qquad (12)$$

Thus, the agreement of eq. (11) with the experimental eq. (1) may supported kinetic scheme (2)–(7).

Further information on the applicability of eqs. (2) and (3) was obtained by results of copolymerization of acrylonitrile with styrene. The copolymerizations were carried out with two different orders of addition of catalyst and monomer. In the first series of experiments, monomer and then triethylaluminum were added to cuprous chloride ($\mathrm{CuCl} \leftarrow \mathrm{M} \leftarrow \mathrm{AlEt_3}$). In the second, triethylaluminum and then monomer was added to cuprous chloride ($\mathrm{CuCl} \leftarrow \mathrm{AlEt_3} \leftarrow \mathrm{M}$). The copolymerization composition curves obtained by the two catalytic systems were similar, as shown in Figure 8. This fact shows that triethylaluminum does not only interact with cuprous chloride but also with polar monomer; that is, the reactions $\mathrm{AlEt_3} \rightarrow \mathrm{CuCl} \rightarrow \mathrm{C^*}$, $\mathrm{AlEt_3} + \mathrm{M} \rightarrow \mathrm{AlEt_3{\cdot}M}$ proceed competitively.

These results seem to show different behavior from that in the case of $\mathrm{AlEt_2Cl}$ or $\mathrm{AlEtCl_2}$ catalysts for alternating copolymerizations of acrylonitrile with propylene, ethylene, and styrene,[2] because alkylaluminum chlorides (e.g., $\mathrm{AlEt_2Cl}$, $\mathrm{AlEtCl_2}$)are known to form tight complexes with such polar monomers as acrylonitrile.[2–4]

References

1. T. Alfrey, Jr., J. J. Bohrer, and H. Mark, *Copolymerization*, Interscience, New York, 1952, p. 35.

2. M. Hirooka, H. Yabuuchi, S. Morita, S. Kawasumi, and J. Nakaguchi, *J. Polym. Sci. B.*, **5**, 47 (1967).

3. J. Furukawa, Y. Iseda, K. Haga, and N. Kataoka, *J. Polym. Sci. A-1*, **8**, 1147 (1970).

4. J. Furukawa, E. Kobayashi, and Y. Iseda, *Polym. J.* (Japan), **1**, 155 (1970).

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Synthesis of Poly(arylene Ethylene) Oligomeric Hydroperoxides and Their Use as Initiating Agents of Radical Polymerization*

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Synopsis

The oxidation to hydroperoxide of poly(arylene ethylenes) (PAE) by oxygen carried out in solutions at 80–110°C. The effect of initiating additions and the nature of solvent relative to the content of hydroperoxide groups in oxidized PAE were investigated. The oxidation to hydroperoxides in PAE occurs at the methylene groups, and the synthesized hydroperoxides are secondary peroxides. The decomposition of PAE hydroperoxides in toluene and chlorobenzene at concentrations of 0.006–0.03 mole/l. for hydroperoxide in the presence and absence of *N*-phenyl-α-naphthylamine (PNA) was studied. The decomposition of one hydroperoxide has been studied in the presence of cobaltous and manganese resinates and of PNA in chlorobenzene at 30–50°C. The addition of PNA to a chlorobenzene solution of PAE hydroperoxide containing cobaltous or manganese resinate accelerates the hydroperoxide decomposition, reduces the activation energy, and changes the reaction order from the second-order to first-order. The synthesized hydroperoxides initiate the radical polymerization of styrene and methyl methacrylate. The initiating activity of one of the synthesized hydroperoxides of PAE for polymerization of styrene (60°C) in the presence and absence of activating addition of manganese resinate was also evaluated.

INTRODUCTION

From a practical aspect, the purpose of the present work, i.e., oxidation of polymers to hydroperoxides, is opposite to the aims of investigators whose goal is stabilization of polymers. Nevertheless, in both cases a general theoretical problem of polymer resistability to radical oxidation attack is being solved; the nature of the peroxides formed is clarified and routes of their transformation under various conditions are evaluated.

A number of works on the synthesis of polymeric hydroperoxides by oxidation of respective polymers[2–9] are known. Such hydroperoxides may be used as initiators of vinyl monomer radical polymerization to initiate graft copolymerization. Polystyrene,[3] isopropylated polystyrene,[2] polyolefins,[5,6,8,9] poly-4-vinylcyclohexane-1,[4] and cellulose[7] are among the materials subjected to oxidation.

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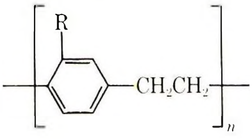
* Paper presented at the International Symposium on Macromolecular Chemistry, Budapest, 1969.[1]

This work contains data on oxidation by oxygen of low molecular weight poly(arylene ethylenes) (PAE) to hydroperoxides and introduction of hydroperoxide groups into the polymer. PAE were obtained by Friedel-Crafts reaction from benzene and its aklyl derivatives with 1,2-dichlorethane in the presence of $AlCl_3$.[10]

RESULTS AND DISCUSSION

Oxidation of Poly(arylene Ethylenes)

Oxidation of poly(phenylene ethylene), poly(cumylene ethylene), and poly(tolylene ethylene), having the general formula I



I

where R = H, CH_3, $CH(CH_3)_2$; n = 10–60.,* was performed by molecular oxygen or air in solution at 80–110°C in the presence or absence of benzoyl peroxide as a source of free radicals. Depending on oxidation conditions and on the nature of the oxidized oligomer, the content of hydroperoxide groups varies over a wide range and may reach 10 per 100 elementary links of chain.

In all cases attack is on the hydrogen atom of the main chain methylene group, which is the most mobile due to the proximity of the aromatic nucleus. The presence of secondary hydroperoxide groups in oxidized PAE is proved by the results of iodometric titration and infrared spectra. The infrared spectra of decomposition products from the hydroperoxides obtained[11,12] proved, that under the present conditions all PAE are being oxidized at the methylene group. Thermal decomposition was performed under nitrogen by heating $^1/_2$ hr at a temperature ranging from 20 to 300°C. The infrared spectra of the oxidized poly(phenylene ethylene) (R = H), poly(tolylene ethylene) ($R{=}CH_3$) and poly(cumylene ethylene) [$R{=}CH(CH_3)_2$], as well as the spectra of thermal decomposition products of PAE hydroperoxides, are of identical character in the regions characteristic for absorption of OOH groups[12,13] (3480 cm^{-1}) and $-$ C=O groups (1690 cm^{-1}) respectively. No other absorption peaks typical for other oxygen-containing groups have been found. The absorption at 1690 cm^{-1} is characteristic for aryl ketones, which are decomposition products of secondary hydroperoxides.

The characteristic reaction of poly(phenylene ethylene hydroperoxide) decomposition products with 2,4-dinitrophenylhydrazine and formation of oligomeric hydrazone also proves that the secondary hydroperoxide

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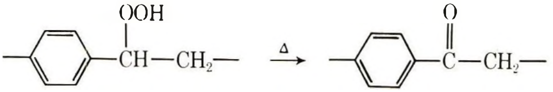
* Oligomers of higher molecular weight are obtained if dibenzyl is used instead of benzene.

groups introduced into the oligomer on oxidation, turn into ketones during thermal decomposition [eq. (1)].


(1)

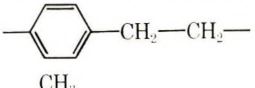
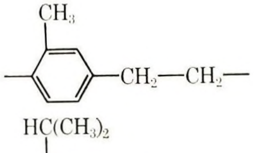
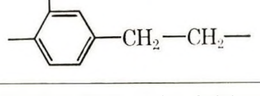
The content of carbonyl groups in the thermal decomposition product of the hydroperoxide was determined from the nitrogen content of the oligomeric hydrazone obtained by the reaction with 2,4-dinitrophenylhydrazine: 2.23 ± 0.13% nitrogen was found in the oligomeric hydrazone (the calculated content of nitrogen for 100% transformation of hydroperoxide groups ketone was 2.24%). Iodometric titration of the thermal decomposition products showed that they contain no hydroperoxice groups. A sufficiently strong absorption peak at 1690 cm^{-1}, which is characteristic for aryl ketones, is present in the infrared spectra of the thermal decomposition products, but it disappears in the infrared spectrum of oligomeric hydrazone; absorption appearing at 1330 cm^{-1} was attributed to C—NO_2. Comparison of molecular weights of oligomeric hydroperoxides and their thermal decomposition products indicates that no visible destruction of macromolecules takes place in this case.

The oxidation of poly(cumylene ethylene), occurring not at the isopropyl group, as might be expected, but at the methylene group, is probably related to the same factors as the noneffective oxidation of tertiary carbon in polystyrene,[1] namely, steric hindrance, violation of coplanarity conditions being required for resonance stabilization of the free radical which is being formed. Comparative oxidation (to hydroperoxides) of poly(phenylene ethylene), poly(tolylene ethylene), and poly(cumylene ethylene) (Table I), show oxidation of the latter two to be considerably less extensive.

The fact that the C—H links are less subject to free-radical attack in poly(cumylene ethylene) (III) than in poly(phenylene ethylene) (I) has

TABLE I

Comparative Oxidation of PAE by Molecular Oxygen in Cumene[a]

Structure	Elementary unit	Content of active oxygen, %
I		0.626
II		0.251
III		0.272

[a] Temperature, 80°C; oxidation time, 8 hr, initiator, benzoyl peroxide.

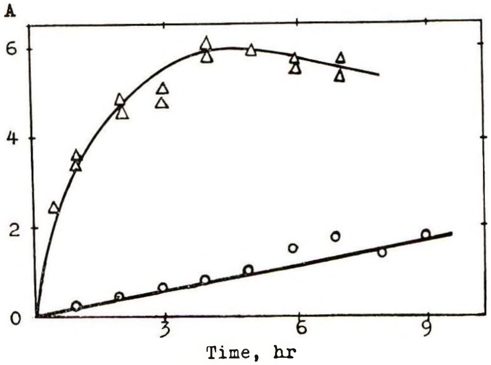
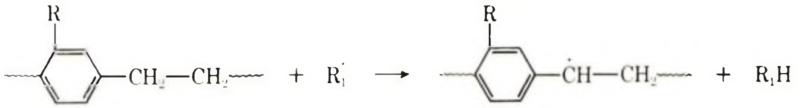


Fig. 1. Relation between average content of hydroperoxide groups per 100 links of polymeric chain *A* and time for oxidation of I by air oxygen at 110°C: (△) in cumene, (○) in tetralin.

been proved by experiments[14] on block graft copolymerization of methacrylic acid onto PAE in the presence of benzoyl peroxide at 80°C by the chain transfer method. The first stage of oxidation of poly(arylene ethylenes) up to peroxides consists in the abstraction of a hydrogen atom from the oxidized chain. This is similar to the first stage of graft copolymerization by chain transfer to the polymer [eq. (2)].



(2)

Therefore, under comparable conditions, the portion of PAE involved in block graft copolymerization and the mobility of the attacked C—H bonds of the oligomer chain should be related. Actually, the amount of I participating in the block graft copolymerization with methacrylic acid is approximately three times the amount of III involved in the same reaction (compare with data of Table I).

The most effective medium for formation of hydroperoxide groups in polymer on oxidation is cumene or tetralin, which have high chain-transfer

TABLE II

Comparative Oxidation of Poly(phenylene Ethylene) (I) in Air[a]

Solvent	Initiating system	Content of active oxygen in oxidized I, %
Toluene	—	0.0024
Xylene	Manganese resinate (0.01 g-atom Mn/l.)	0.0031
Xylene	Benzoyl peroxide (0.07 mole/l.)	0.046
Cumene	Benzoyl peroxide (0.07 mole/l.)	0.246

[a] Temperature, 95°C; reaction time, 6 hr.

constants. The lower effectiveness of tetralin in comparison with cumene on oxidation of structure I, for example, is probably explained by the high termination constant of the tetralyl peroxy radical (Fig. 1). The effectiveness of cumene during oxidation is also shown by the data of Table II.

The nature of the solvent also plays an important role in determining the rate of oxidation of PAE to hydroperoxides, as noted by Manson and Cragg[3] during oxidation of a copolymer of styrene and 4-vinylcyclohexene-1 to the hydroperoxide. The solvent functions as the hydrogen donor in the third stage of oxidation:

$$RH \xrightarrow{K_i} R^\cdot \qquad (3)$$

$$R^\cdot + O_2 \xrightarrow{K_o} RO_2^\cdot \qquad (4)$$

$$RO_2 + SH \xrightarrow{K_p} RO_2H + S^\cdot \qquad (5)$$

where RH is the polymer and SH is the solvent. The high values of chain-transfer rate constants (K_p) for cumene provide for a sufficiently high output of hydroperoxide groups in oxidized I.

The hydroperoxides of PAE are rather stable at a room temperature. Thus, no change was found in IH* when it was allowed to stand in air for one and a half months.

Decomposition of Oligomeric Hydroperoxides

Decomposition of IIIH in toluene (Fig. 2) and of IH in chlorobenzene (Fig. 3) at hydroperoxide concentrations of 0.006–0.03 mole/l. takes place through a reaction which is nearly first-order. The molecular weight of a sector of the oligomeric chain containing one hydroperoxide group has

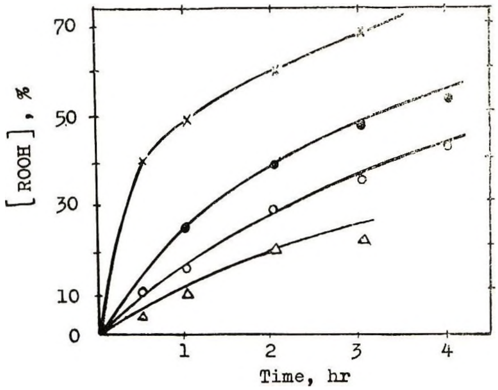


Fig. 2. Relation between the number of decomposed hydroperoxide groups and time for decomposition of IIIH in toluene (0.006 mole/l. of hydroperoxide): (△) 130°C; (○) 140°C; (●) 142°C; (X) 150°C.

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* Hydroperoxides obtained by oxidation of the oligomeric structures I, II, and III are designated IH, IIH, and IIIH, respectively.

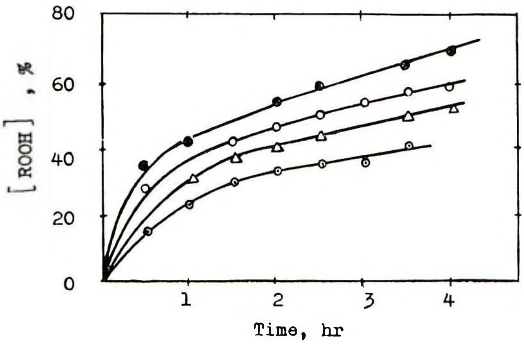


Fig. 3. Decomposition of IH in chlorobenzene (0.03 mole/l.): (⊙) 135°C; (△) 140°C; (○) 145°C; (⊗) 150°.

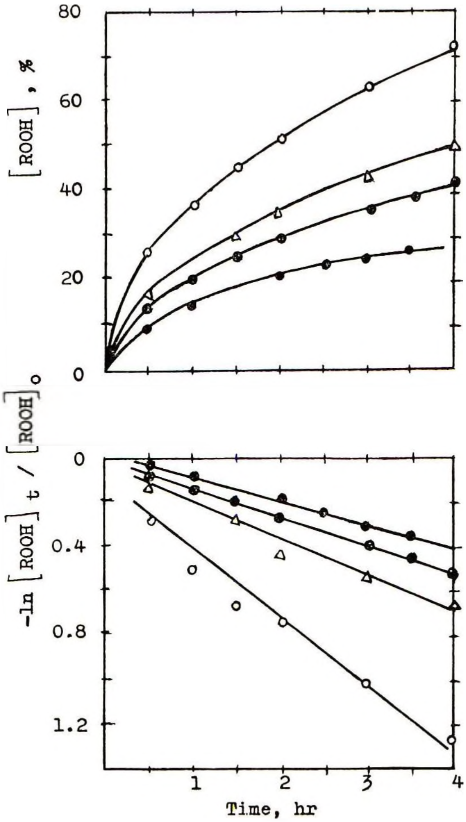
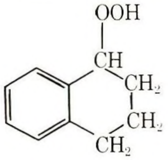
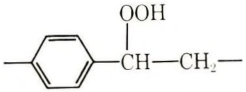
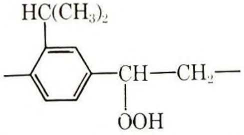


Fig. 4. Dependence of [ROOH] and ln ([ROOH]t/[ROOH]$_0$) on time for decomposition of IH in chlorobenzene (0.03 mole/l.) in the presence of PNA (0.06 mole/l.) at various temperatures: (●) 140°C, (⊗) 145°C, (△) 150°C, (○) 155°C.

TABLE III
Data on Decomposition of Some Secondary Hydroperoxides

Structure	Formula	Decomposition temperature, °C	Decomposition conditions			Decomposition rate constant, $K_d \times 10^4$, sec^{-1}	Activation energy E_d, kcal/mole	Reference
			[Inhibitor] (PNA), mole/l.	[Peroxide], mole/l.	Solvent			
IVH		150.6	0.041	0.054	White medicinal oil	1.0	31.4	15
			—	0.054	White medicinal oil	1.6	—	15
IH		150	0.06	0.03	Chloro-benzene	0.46	31.6	11
IIIH		150	—	0.006	Toluene	1.33	—	11

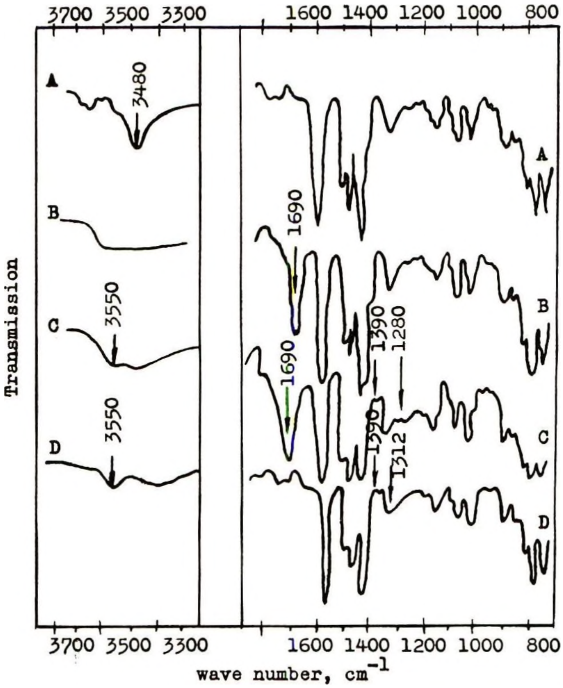


Fig. 5. Infrared spectra of (*A*) IH; (*B*) the product of the thermal decomposition of IH in chlorobenzene (0.03 mole/l.); (*C*) the product of activated decomposition of IH in chlorobenzene (0.03 mole/l.) in the presence of cobaltous resinate (0.018 g-atom Co/l.; (*D*) the product of decomposition of IH in the presence of cobaltous resinate (0.018 g-atom Co/l.) and PNA (0.075 mole/l.).

been taken as a mole of hydroperoxide. Addition of *N*-phenyl-α-naphthylamine (PNA) inhibitor allows the decomposition induced by free radicals to be repressed.[15] In this case, the rate of decomposition slows down (Fig. 4), the reaction goes on monomolecularly, and the decomposition activation energy for IH, for example, approximates the decomposition activation energy of the low molecular hydroperoxide of tetralyl (IVH) (Table III). The calculated rate constants for decomposition of IH in the presence of PNA are 7.26×10^{-5}, 4.09×10^{-5}, 3.11×10^{-5}, and 1.80×10^{-5} sec^{-1} at 155, 150, 145, and 140°C, respectively. In general $K = 1 \times 10^{12}\, e^{-31600}/RT$.

The difference between the behavior of the oligomeric hydroperoxide of IH and a low molecular analog (hydroperoxide of ethylbenzene, for example, which may be taken, as well as IVH, as its model) is revealed through the nature of the decomposition in the presence of oil-soluble activators i.e., salts of variable valence metals. While the hydroperoxide of ethylbenzene in the presence of cuprous stearate or cobaltous acetate[16,17] and the hydroperoxide of *n*-decyl in the presence of cobaltous stearate[18] decompose in chlorobenzene in accordance with a first-order reaction, the oligomeric IH under approximately similar conditions (0.03 mole/l., 30–60°C) in the presence of cobaltous resinate decomposes by a second-order reaction relative to hydroperoxide.[19] Addition of PNA to the system IH-cobaltous resinate in chlorobenzene leads not only to an increase in rate of decomposition of IH, but also to a change of reaction order. In the latter case, the reaction becomes first-order with respect to hydroperoxide and the activation energy of the gross process decreases from 13.5 to 11.0 kcal/mole.

At the presence of oil-soluble salts of variable valence metals (cobaltous and manganese resinates) the synthesized oligomeric hydroperoxides decompose with a considerable speed at 30-50°C while in the absence of activators in the solution, perceptible decomposition occurs only at temperatures in excess of 100°C.

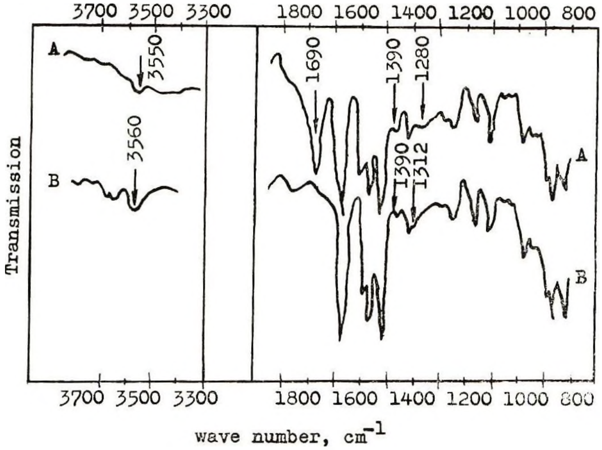


Fig. 6. Infrared spectra of products of activated decomposition of IH in chlorobenzene (0.03 mole/l.): (*A*) product obtained in the presence of manganese resinate (0.025 g-atom Mn/l.); (*B*) product obtained in the presence of manganese resinate (0.025 g-atom Mn/l.) and PNA (0.075 mole/l.).

The infrared spectra of products of IH decomposition in chlorobenzene in the presence of cobaltous and manganese resinates (films from benzene solutions) indicate that the decomposition of IH at 30-60°C and hydroperoxide concentration of 0.03 mole/l. leads primarily to aryl ketones, as seen from the appearance of intense absorption at 1690 cm^{-1} which is characteristic for aryl ketone groups (Fig. 5 and 6). In this case, formation of secondary alcohols (increase of absorption intensity at 1390 and 1280 cm^{-1}, as well as absorption at 3550 cm^{-1}) and carboxyl or carbonyl groups (1390 cm^{-1}) is also possible. The formation of secondary alcohol groups in decomposition products of IH is proved by the occurrence of the typical reaction for secondary alcohols on heating them with sulfur.[20] Hydrogen sulfide formed in this case is qualitatively detected by the appearance of a brown spot (lead sulfide) on filter paper soaked with lead acetate.

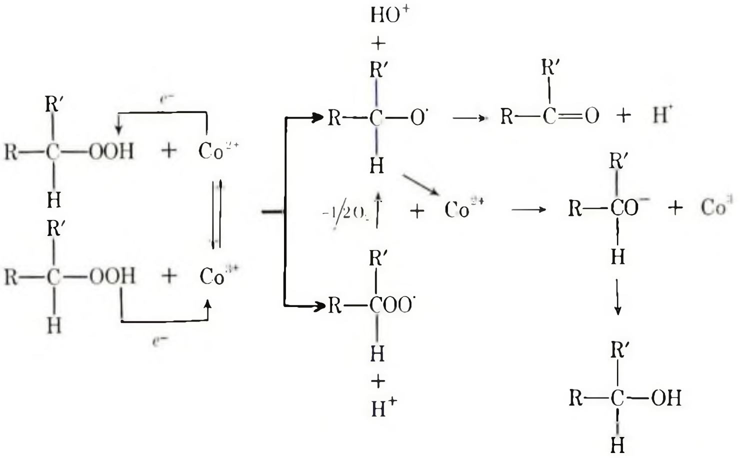
It is known from the literature[21] that some secondary hydroperoxides, such as IH, decompose completely in 15 min at 80°C in the presence of cobalt and manganese salts, a formation of mixture of the respective ketones and alcohols.

The data obtained on consideration of free-radical formation at intermediate stages of decomposition (initiation of methyl methacrylate polymerization at 23°C) allows one to propose the scheme of reaction shown in eqs. (6) and (7):[19]

$$Mn^{2+} + 2ROOH \rightarrow RO^{\cdot} + ROO^{\cdot} + H_2O + Mn^{2+} \quad (6)$$

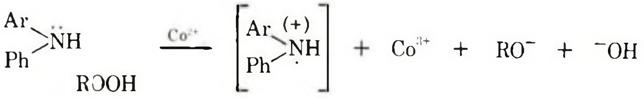
$$Co^{2+} + 2ROOH \rightarrow RO^{\cdot} + ROO^{\cdot} + H_2O + Co^{2+} \quad (7)$$

For example:



The degradation of the oligomeric chain may occur simultaneously with the formation of carboxyl or carbonyl groups.

The infrared spectra of products of IH decomposition in chlorobenzene (0.03 mole/l.) in the presence of cobaltous (manganese) resinate and PNA indicate the absence of aryl ketone groups (absence of absorption at 1690 cm^{-1}). Most probably, the decomposition in this case, proceeds to formation of secondary aryl alcohols (absorption at 3550 cm^{-1}). The polymerization of methyl methacrylate at 23°C in this system does not take place for longer than 11 hr. In the presence of cobaltous resinate and PNA, the IH may decompose according to the scheme (9):



Other reactions[19] are also possible.

Shown in Figures 5 and 6 are infrared spectra of IH and its products of decomposition under various conditions.

Initiating Activity

Besides salts and amines of metals of variable valence other compounds, including olefins,[22,23] may accelerate the decomposition of hydroperoxides.

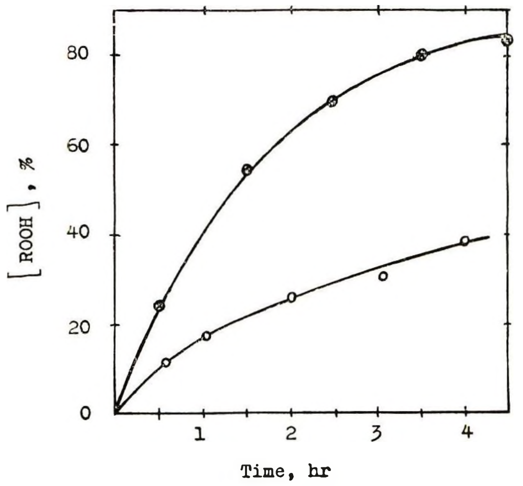


Fig. 7. Decomposition of IIIH in toluene (0.0103 mole/l.): (○) in the absence of styrene at 140°C and (⊗) in the presence of styrene (0.29 mole/l.) at 120°C.

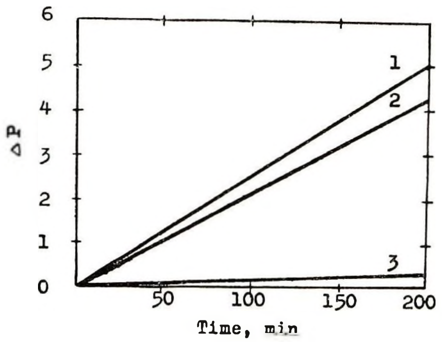
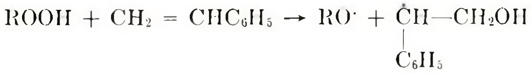


Fig. 8. Polymerization of methyl methacrylate in a dilatometer at 60°C at the presence of initiators: (*1*) III (0.03 mole/l. of hydroperoxide groups); (*2*) benzoyl peroxide (0.015 mole/l.); (*3*) in the absence of initiating additions. ΔP denotes the relative units proportional to the depth of polymerization.

Stannett and Mesrobian[22] have indicated, that the rate of decomposition of cumyl hydroperoxide increase considerably with the addition of vinyl monomers with the polymerization of the latters in this case. It is proposed, that the induced decomposition of hydroperoxide in the presence of styrene proceeds in accordance with eq. (10):

$$\mathrm{ROOH + CH_2 = CHC_6H_5 \rightarrow ROO^{\cdot} + CH_3\dot{C}HC_6H_5} \qquad (10)$$

thus initiating radical polymerization of the monomer. Denisov[24] suggested another mechanism [eq. 11]:



$$\mathrm{ROOH + CH_2 = CHC_6H_5 \rightarrow RO^{\cdot} + \underset{\displaystyle C_6H_5}{\underset{|}{\dot{C}H}}{-}CH_2OH} \qquad (11)$$

which allows him to explain thermodynamics and kinetics of the process.

Acceleration of the decomposition of the oligomeric hydroperoxide (IIIH) of poly(cumylene ethylene) in the presence of styrene also takes place (Fig. 7), in which case a noticeable amount of polystyrene is formed. IH and the system of IH–variable valency metal salt are also initiating agents for styrene and methyl methacrylate, comes (Table IV, Fig. 8).

TABLE IV
Polymerization of Methyl Methacrylate in the Presence of Various Initiating Systems at 60°C

Polymerization method	Initiating system	Polymerization time, hr	Output of polymer, %	$[\eta]^b$
Emulsion[a]	IH–$FeSO_4$	8	20	0.435
Block	IH–manganese resinate	3	70	0.735
Block	IH	22	30	0.920
Block	Benzoyl peroxide	3	25	1.45

[a] At 22°C.
[b] At 25°C in benzene.

The linear dependence of W versus $[I]^{1/2}$ for polymerization of styrene (Fig. 8), where W is the rate of polymerization, $[I]$ is the concentration of initiator, along with the retardation and inhibition of polymerization by common inhibitors and retarding agents of radical polymerization (PNA, hydroquinone) indicates the free-radical nature of the initiation.

The initiating activity of the system may be quantitatively evaluated by the slope of the tangent to the curve in coordinates W, $[I]^{1/2}$. For polymerization of styrene (60°C) the initiating activity of IH is twice as high as that of hydroperoxide of isopropylated polystyrene at the same temperature.[2] Addition of manganese resinate (0.051 g-atom Mn/l.) to the system IH–styrene increases the initiating activity approximately fivefold.

The PAE hydroperoxides initiate the polymerization of other vinyl monomers also. A previous publication[14] contains data on initiation of polymerization of methacrylic acid by IH.

EXPERIMENTAL

Oxidation of PAE

The PAE were oxidized by molecular oxygen or by air oxygen in solution in compliance with the described methods.[11,25] The oxidized PAE were separated by precipitating them from the solutions into methyl alcohol, washed with several portions of methyl alcohol until the smell of solvent in which the oxidation was carried out disappeared, and then dried in vacuo at room temperature to constant weight. Special experiments on combined reprecipitation showed that undecomposed benzoyl peroxide, used as a source of free radicals, is not present in hydroperoxide of PAE separated as described above. All solvents used in oxidation were purified by standard methods. The benzoyl peroxide was purified by precipitation from acetone solution into distilled water followed by vacuum drying to constant weight.

The manganese resinate was prepared as follows. A 47-g portion of rosin (colophony) was heated to 170°C in a Wolff bottle equipped with a mixer and a pipe for blowing with nitrogen. The mixer was started and 2.7 g of finely crushed manganese peroxide was gradually added in small portions. After all the manganese peroxide had been added, the temperature was raised to 230–240°C and maintained for 4 hr, during time a light flow of nitrogen was maintained. The reaction mixture was cooled, the manganese resinate formed was dissolved in 100 ml of benzene, the solution was filtered to remove unreacted manganese peroxide and then solvent removed by evaporation. The content of manganese amounted to 0.63%. The manganese resinate obtained was also used for investigation of decomposition of IH.

Preparation of Oligomeric Hydrazone

IH was decomposed in a test tube heated for $^1/_2$ hr to 300°C. Before heating, the contents of the tube were subjected to vacuum (40 mm) and then blown with purified nitrogen. Preparation of oligomeric hydrozone was carried out by two modified methods described by Shriner and Fuson.[26]

Method 1. A 1.2-g portion of thermal decomposition product of IH was dissolved in 20 ml of dioxane and then 0.05 g of 2,4-dinitrophenylhydrazine was added. The contents of the flask were heated to the boil with reflux condenser; 2–3 drops of concentrated HCl were added, after which the contents of the flask were boiled for 2–3 min. The solution was cooled and poured into 30 ml of ethanol. Approximately after 30 min sediment formation was observed. The sediment was separated and washed with several 15-ml portions of ethanol. Finally the oligomeric hydrazone obtained was dried in vacuo at 60°C to constant weight.

Method 2. Concentrated H_2SO_4 (0.1 ml) and 1.5 ml of water was added to 0.1 g of 2,4-dinitrophenylhydrazine. The solution was diluted with 5 ml of dioxane, then the thermal decomposition product of IH was added to 20 ml of dioxane, and the mixture allowed to stand for 2 hr at room temperature. The solution was poured into 45 ml of ethanol. After approximately 30 min., a precipitate formed which was processed in the way as for method 1.

On analysis both methods show nitrogen contents, which is indicative of complete substitution of carbonyl groups. The determination accuracy was limited by the accuracy of the elementary analysis. Relative error did not esceed 6%.

The control for complete separation of 2,4-dinitrophenylhydrazine not entering the reaction from oligomeric hydrazone was difficult. The reaction of ketone with 2,4-dinitrophenylhydrazine with formation of crystalline hydrazones was used to determine free 2,4-dinitrophenylhydrazine in the extract. Acetone, *n*-hexyl methyl ketone, and β-naphthyl methyl ketone were tested for this purpose. Acetone and *n*-hexyl methyl ketone provide no possibility for qualitative determination of the presence of 2,4-dinitrophenylhydrazine at its concentration of approximately 0.01 wt-%. β-Naphthylemethylketone gives a red deposit of hydrazone with 2,4-dinitrophenylhydrazine if the concentration of the latter is near 0.01 wt-%. Extraction of polymeric hydrazone by ethanol was carried out, until the extract stops to give a typical reaction with β-naphthyl methyl ketone. The reaction of 2,4-dinitrophenylhydrazine with β-naphthyl methyl ketone was carried out in compliance with method I. A pure grade of 2,4-dinitrophenylhydrazine with a melting point of 197°C was used.

Determination of Hydroperoxides

Oxidized PAE (0.1–0.3 g) or such a quantity of its solution in toluene or chlorobenzene (for investigation of thermal decomposition kinetics) which contains this weight of PAE was taken. A 10-ml portion of benzene not containing peroxides was added, 10 ml of glacial acetic acid was added to this solution, and oxygen in the solution removed by bubbling in nitrogen for 2 min. A 2-ml portion of 33% aqueous KI was then added to the solution with continuing bubbling in of nitrogen. After 1 min, the nitrogen flow was stopped, the flask evacuated and kept for 4 hr in the dark at room temperature. The solution was then diluted by an equal volume of water and titrated with 0.01 *N* sodium thiosulfate with at continuous shaking. The endpoint was determined by the discoloration of the lower layer of water. If pure reagents are used, no check experiment is necessary.

The mean relative error of iodometric measurements does not exceed 1%.

Infrared Spectra

The infrared spectra were taken by means of a UR-10 spectrometer on films from the respective benzene solutions. Distilled benzene (chemically pure grade) was used for spectroscopic measurements.

Kinetic Measurements

The thermal decomposition kinetics of PAE hydroperoxides in solution was investigated in sealed ampoules, first flushed with nitrogen gas purified by pyrogallol alkali solution. The ampoules were placed into a thermostat, where the temperature was maintained accurate within ±0.2°C. After a given time, the ampoules were rapidly cooled down by cold water and opened. The content of residual hydroperoxide groups was determined as described above. The activated decomposition of IH in chlorobenzene in the presence of cobaltous resinate was studied in the same way, except that the solutions of IH in chlorobenzene and of resinate in chlorobenzene were prepared separately and blended in ampoules directly before the kinetic measurements. For determination of hydroperoxide content at the presence of resinates, the water layer was separated after 4 hr in the dark in a separatory funnel first flushed with nitrogen. The water layer was transferred into an Erlenmeyer flask, flushed with nitrogen, and then the separated iodine was titrated with sodium thiosulfate. (The titration in the presence of resinates dissolved in chlorobenzene leads to higher results due to reduction of thiosulfate by cobalt and manganese salts.)

Cobaltous resinate was prepared as follows. A 25-g portion of rosin (colophony) was melted in a Wolff bottle equipped with a mixer and a pipe for nitrogen blowing. The mixer was started, and 2.3 g of crushed cobaltous acetate was added at a temperature of 190°C. The temperature was raised to 220–330° and maintained for 4 hr under a light flow of nitrogen. The reaction mixture was cooled, the formed cobaltous resinate was dissolved in 70 ml of benzene, the solution was filtered and concentrated by evaporation of solvent. The cobalt content comprised 2.16%.

Initiating Activity

IIIH was decomposed in toluene (Fig. 7) inside sealed glass ampoules previously degassed by repeated freeze-thaw cycles. To investigate the $W - [I]^{1/2}$ dependence (Fig. 9), a solution of different concentration of IH in freshly distilled styrene was prepared; 10 ml of each solution was transferred into glass ampoules. The filled ampoules were degassed by freeze-thaw cycles in liquid nitrogen in vacuo and then sealed off. The polymerization was performed at 60±0.1°C. The ampoules were heated for a time exceeding that time required for transformation by no more than 14%. This interval was determined for each value of [I] by a series of preliminary experiments.

The degree of conversion was calculated from the total amount of polymer separated by pouring the contents of each ampoule into methanol followed by decantation, washing, and drying, after which a correction for the amount of oligomeric hydroperoxide previously added to the system was introduced. The concentration of oligomeric initiator was expressed, as in

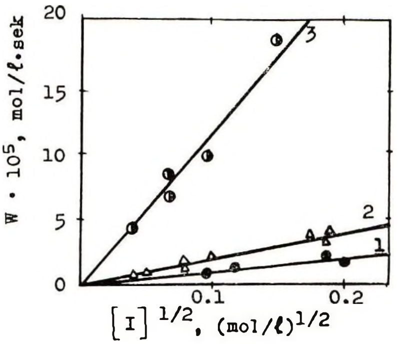


Fig. 9. Polymerization of styrene at 60°C in the presence of initiators: (*1*) hydroperoxide of isopropylated polystyrene;[2] (*2*) III; (*3*) III and manganese resinate (0.051 g-atom Mn/l.).

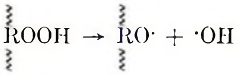
all previous cases, by the number of hydroperoxide moles per litre of solution.

The dilatometric measurements (Fig. 8) were performed in a dilatometer provided with a mercury seal at a temperature of 60 ± 0.05°C. The dilatometric cell containing monomer and dissolved initiator was degassed by multiple freeze-thaw cycles. The conversion monomer to polymer was evaluated in relative units ΔP proportional to the drop in mercury level in the capillary.

APPENDIX

Use of polymeric and oligomeric hydroperoxides as initiators makes possible the synthesis (on their base) of block graft copolymers slightly contaminated by homopolymer.[27]

On thermal decomposition of polymeric hydroperoxides in the presence of monomer, homopolymerization of monomer generally takes place in addition to block graft copolymerization. It is initiated either by hydroxyl radicals appearing on homolytic decomposition of hydroperoxide groups



$$\text{ROOH} \rightarrow \text{RO}\cdot + \cdot\text{OH}$$

or by the radicals of vinyl monomers appearing on induced decomposition of hydroperoxide groups. The use of redox systems not only permits an increase in the rate of hydroperoxide group decomposition and the polymerization at rather low temperatures (Table IV), but also suppresses, in considerable degree, the homopolymerization. In this case, the hydroperoxide decomposition mainly leads to formation of polymeric radicals, as a single-electron reduction of organic hydroperoxide almost always gives an alkoxyl radical.[28] Metz and Mesrobian were the first to utilize the redox system polymeric hydroperoxide–water-soluble variable valence metal salt for the synthesis of graft copolymers not contaminated by homopolymer.[2]

In a previous study we have used oligomeric hydroperoxide IH with a molecular weight of 4000 and an average content of hydroperoxide groups of 2.2 per oligomeric chain as an initiator of methyl methacrylate polymerization.[29] The redox system IH–$FeSO_4$ led to formation of a block graft copolymer containing only 7.5 wt-% of poly(methyl methacrylae). The grafting efficiency in this case was 0.91. In the usual suspension polymerization, 27.6% homopolymer is formed and the grafting efficiency is 0.66.

In conclusion, we would like to remark on the usage of such terms as block graft copolymerization and block graft copolymers in relation to the systems containing oligomeric hydroperoxides. In the usual sense, the term graft copolymers which is obviously derived from the similarity with vegetable hybrids,[30] implies commensurability as to the size of backbone and side branches.

The oligomeric initiators occupy an intermediate position between the low molecular and high molecular ones (for example, the hydroperoxide of isopropylated polystyrene) being, however nearer to the high molecular ones. Availability of chemical links between oligomeric (main) and polymeric (raised) chains leads to a considerable modification of properties of both in their hybrid as it occurs in graft copolymers. This fact sharply separates the oligomeric hydroperoxides from low molecular ones, as the nature of the latter does not affect the properties of the polymers obtained. An example may be illustrated by copolymerization products of methacrylic acid and IH possessing a number of specific properties including high emulsifying ability relative to oil-water systems.[31]

References

1. A. E. Chuchin, *Preprints Intern. Symp. Macromol. Chem. Budapest*, **5**, 31 (1969).
2. D. J. Metz and R. B. Mesrobian, *J. Polym. Sci.*, **16**, 345 (1955).
3. W. Hahn and H. Lechtenböhmer, *Makromol. Chem.*, **16**, 350, 1955.
4. J. A. Manson, L. H. Cragg, *Can. J. Chem.*, **36**, 858 (1958).
5. G. Natta, E. Beati, and F. Severini, *J. Polym. Sci.*, **34**, 685 (1959).
6. E. Beati, F. Severini, and G. Clerici, *Makromol. Chem.*, **61**, 104 (1963).
7. B. P. Morin, Yu. S. Kriazhev, and Z. A. Rogovin, *Vysokomol. Soedin.*, **7**, 1463 (1965).
8. C. E. H. Bawn and A. S. Chandhri, *Polymer*, **9**, 123 (1968).
9. J. C. W. Chien, E. J. Vandenberg, and H. Jabloner, *J. Polym. Sci. A-1*, **6**, 381 (1968).
10. G. S. Kolesnikov, A. E. Chuchin, and B. I. Boev, *Vysokomol. Soedin.*, **8**, 153 (1966).
11. A. E. Chuchin, Thesis, Moscow, 1966.
12. A. E. Chuchin and G. S. Kolesnikov, *Vysokomol. Soedin.*, **8**, 431 (1966).
13. A. B. Kariakin, V. A. Nikitin, and K. I. Ivanov, *Zh. Fiz. Khim.*, **27**, 1856 (1953).
14. A. E. Chuchin, G. S. Kolesnikov, A. S. Tevlina, and A. P. Kulikov, *Plastmassy*, **1967**, No. 6, 19.
15. J. R. Thomas and O. L. Harle, *J. Phys. Chem.*, **63**, 1027 (1959).
16. A. G. Korsun, V. Ya. Shliapintokh, and N. M. Emanuel, *Izv., Akad. Nauk SSSR, Otdel, Khim. Nauk*, **1961**, 788.
17. I. V. Zacharov, and V. Ya. Shliapintokh, *Dokl. Akad. Nauk SSSR*, **150**, 1969 (1963).
18. G. M. Bulgakova and Z. K. Maizus, and I. P. Skibida, *Kinetika Katalys*, **7**, 332 (1966).
19. A. E. Chuchin, V. A. Lazarev, and M. B. Fromberg, *Vysokomol. Soedin. A*, **10**, 2555 (1968).
20. F. Feigl, *Spot Tests In Organic Analysis*, American Elsevier, New York, Russ. ed. State Chemical Publishing House, Moscow, 1962, p. 239.
21. E. G. E. Hawkins, *Organic Peroxides, Their Formation and Reactions*, London, E.a. F.F. Spon Ltd, 1961, Khimya Publishing House, Moscow, 1964.
22. V. Stannett and R. B. Mesrobian, *J. Amer. Chem. Soc.*, **72**, 4125 (1950).
23. C. Walling and J. W. Chang, *J. Amer. Chem. Soc.*, **76**, 4878 (1954).
24. E. T. Denisov and L. N. Denisova, *Dokl. Akad. Nauk SSSR*, **157**, 907 (1964).
25. G. S. Koleshikov, A. E. Chuchin, and B. I. Boev, *Vysokomol. Soedin.*, **8**, 1085 (1966).
26. R. Shriner and R. Fuson, *The Systematic Identification of Organic Compounds*, Wiley, New York, 1935; Russ. ed. Foreign Languages Publishing House, Moscow. 1950.

27. R. Y. Ceresa, *Block and Graft Copolymers*, Butterworths, London, 1966; Russ. ed. Mir Publishing House, Moscow, 1964.

28. W. A. Waters, *Mechanism of Oxidation of Organic Compounds*, Wiley, New York, 1964; Russ. ed. Mir Publishing House, Moscow, 1966, p. 52.

29. A. E. Chuchin, G. S. Kolesnikov, and A. Ia. Vainer, *Vysokomol. Soedin.*, **10,** 182 (1968).

30. A. E. Chuchin, *Pryroda*, **1968,** No. 7, 62.

31. A. E. Chuchin, G. S. Kolesnikov, A. S. Tevlina, and A. P. Kulikov, Copyright Certificate, USSR, No. 193060 (1967).

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Assessment of the State of Order of Hydroxyl Groups and of Molecular Segments in Hydrocellulose

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Synopsis

Through a study of the selective distribution of substituents introduced into hydrocellulose from reaction with *N,N*-diethylaziridinium chloride, the change in selective availability of hydroxy groups at C-2, C-3, and C-6 has been followed as a function of duration of hydrolysis to form the hydrocellulose. The hydrocellulose formed at a particular duration of hydrolysis showed maximum selective availability of hydroxyl groups; this was found to coincide with minimum moisture regain and minimum breadth at half height for 101, $10\bar{1}$, and 002 peaks in x-ray diffractograms. These points are discussed in terms of the structures of the hydrocelluloses at various stages of hydrolysis and in terms of the sequence of changes which is now associated with the conversion of fibrous cotton to "exemplar hydrocellulose," i.e., the hydrocellulose having the highest degree of crystalline order, and subsequently, to less highly ordered hydrocelluloses.

INTRODUCTION

It is emphasized by Warwicker et al.[1] that the fringe-micellar theory is inadequate as a description of the supramolecular structure of cotton and that a crystalline-fibril theory best accounts for swelling and related phenomena. Chemical reactions of cotton then must be regarded as occurring on surfaces of fibrils. The special nature of those accessible regions on surfaces, whose attack by acid results in hydrocellulose and whose attack during chemical finishing reactions may be the cause for loss in strength, is not clear. Peterlin and Ingram,[2] in discussing the elementary fibrils, refer to some interruptions in the crystalline core in the longitudinal direction; Jeffries et al.[3] mention sites of lattice disorder along the length of the fibrils and note that these are short (less than 50 Å) and not of the nature of noncrystalline regions.

It was the object of this study to explore for new evidence regarding the state of order of hydrocellulose relative to that of the original fibrous cotton cellulose, with the ultimate objective of obtaining evidence concerning the nature of the acid-sensitive accessible regions. Specifically, the approach was to examine the change in the state of order of hydroxyl groups in acces-

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sible regions in progressing from cotton to hydrocelluloses formed in various periods of hydrolysis. The state of order of hydroxyl groups was estimated from the deviation of accessibility of hydroxyl groups at C-2, C-3, and C-6 from equality. It has been shown previously that in cotton the hydroxyl groups at C-6 and C-3 are less available (i.e., selectively accessible) than the hydroxyl groups at C-2[4] and that this selective accessibility is related to the ordered presentation of hydroxyl groups on crystalline surfaces in a manner which is consistent with the ordered arrangements of segments of the cellulose chain in the unit cell of cellulose lattice I.[5]

EXPERIMENTAL

Materials

The cotton cellulose was desized, scoured, bleached 80 × 80 printcloth, the same as used in preceding studies.[4,5]

N,N-Diethylaziridinium chloride was obtained from 2-chloroethyldiethylamine hydrochloride as described earlier.[5]

The hydrocelluloses were prepared by subjecting Wiley-milled fabric (to pass a 20-mesh screen) to 2.5*N* hydrochloric acid at reflux for various periods of time.[4,5] This is essentially the procedure of Nelson and Tripp.[6]

Reactions

N,N-Diethylaziridinium chloride was reacted with samples of hydrocellulose in the manner described previously;[4,5] essentially, the hydrocellulose was impregnated with a 0.5*M* solution of *N,N*-diethylaziridinium chloride, and this was suspended in aqueous sodium hydroxide of the selected normality for 45 min, prior to filtering, washing, etc.

The chemically-modified celluloses were hydrolyzed to mixtures of glucose and *O*-[2-(diethylamino)ethyl]-D-glucoses with sulfuric acid by the procedure of Rowland et al.[7] Glucose was removed from the hydrolyzate by fermentation,[5] and this was followed by dissolution and equilibration of anomers in pyridine[5] and by silylation by the method of Sweeley et al.[8]

Analyses

The relative proportions of 2-*O*-, 3-*O*-, and 6-*O*-[2-(diethylamino)ethyl]-D-glucopyranoses were measured by gas-liquid chromatography of the silylated mixtures from above.[9]

The extent of crystalline order in the samples of cellulose was determined by a computer-based correlation analysis of x-ray diffraction data similar to that of Wakelin et al.[10] but modified according to the technique of Patil et al.[11] The half-maximum line breadths were measured essentially as described by Patil et al.;[11] however, the curve resolution was conducted with the duPont curve resolver. The 101 and $10\bar{1}$ peaks were constrained to $2\theta = 14.7°$ and $16.3°$, respectively. The 002 peak was resolved from a small peak at approximately $2\theta = 21°$, whose precise position and size varied with the requirements to match the diffractogram of each sample of cellulose. These resolutions were conducted with a generally similar, but slightly varying, background for "amorphous" scatter as shown by Patil et al.[11] The "amorphous" background and the peak at approximately $2\theta = 21°$ were subtracted prior to the final tracing of the 101, $10\bar{1}$, and 002 peaks.

Ambient moisture content is the percentage of moisture in the cellulose at equilibrium with ambient temperature and humidity (approximately 24°C and 40% RH). Moisture regain was determined by a modification[12] of the ASTM Method D 629-59T.

RESULTS AND DISCUSSION

Distributions of 2-(Diethylamino)ethyl Substituents in Hydrocelluloses

The selectivity with which *N,N*-diethylaziridinium chloride reacts with the hydroxyl groups at C-2, C-3, and C-6 in fibrous cotton (in nonmercerizing media) as compared to the selectivity of reaction with the hydroxyl groups of decrystallized cotton provides the basis for the conclusions reached in a preceding study.[4] These conclusions are that reactions in fibrous cotton occur, at least in part, on surfaces of crystalline regions and that the

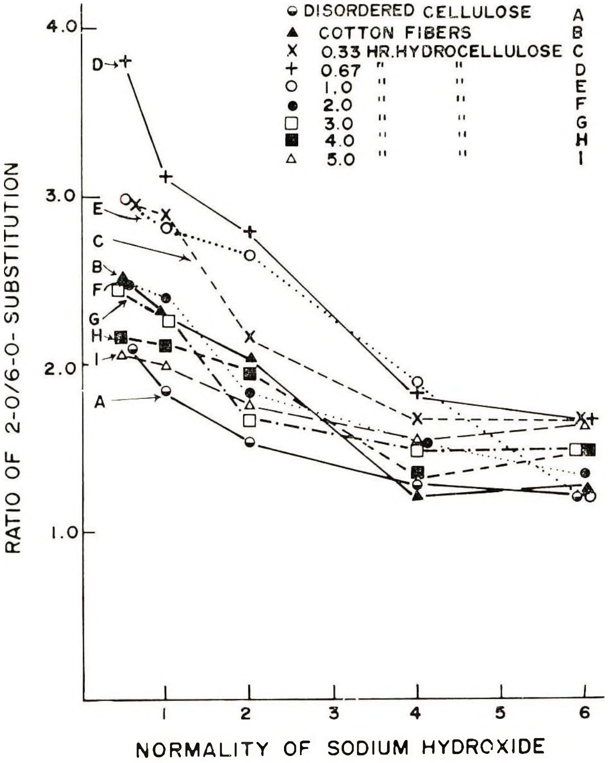

Fig. 1. Ratio of 2-*O*-/6-*O* substitution for a variety of celluloses as a function of the normality of the sodium hydroxide involved in the reaction medium.

hydroxyl groups at C-6 and C-3 are less available than the hydroxyl groups at C-2 on the surfaces of the crystalline structural units of cotton cellulose. For this purpose, the comparison of the distribution of substituents in crystalline cellulose versus in decrystallized cellulose must be made under a specific set of reaction conditions; the normality of the base which is employed to promote the reaction is particularly important, since it has been found that this, in itself, has an effect upon the relative reactivities of the hydroxyl groups at C-2, C-3, C-6. The effect of the base concentration is a chemical effect which operates independently of any swelling action of the base and which is described in a separate paper.[13]

The selective availability of the hydroxyl groups at the C-2, C-3, and C-6 positions of the *D*-glucopyranosyl units of cellulose is most simply followed by an examination of the 2-*O*-/6-*O*-ratio of substituents in the sample under consideration versus the corresponding ratio in a decrystallized cellulose. Thus, in Figure 1 compare curve *B* for the 2-*O*-/6-*O*-ratio of substituents in fibrous cotron to curve *A* for the ratio in decrystallized cellulose. It is significant that the selective availability of the hydroxyl group at C-2 disappears when the reaction is conducted in sodium hydroxide of 4*N* or higher concentrations. This is due to the fact that 4*N* sodium hydroxide is a borderline mercerizing agent for the fibrous cellulose and thereby swells the structure to make hydroxyl groups of formerly crystalline regions equally available at C-2, C-3, and C-6. The distribution of substituents which results under these conditions is that which reflects the inherent differences in reactivities of the hydroxyl groups at C-2, C-3, and C-6 in this specific reaction medium.

The selectivity of distribution of substituents from reactions of hydrocelluloses is summarized in Table I and is shown in the ratios of 2-*O*-/6-*O*-substitution in curves *C* through *I* of Figure 1. These hydrocelluloses differ from one another in the duration of hydrolysis involved in their formation; the duration increases from 0.33 hr for samples of curve *C* to 5 hr for samples of curve *I*. It may be noted from the specific data points on these curves that the order of progression of 2-*O*/6-*O*-substitution varies slightly from one basic medium to another; however, for reactions in a specific normality of base below 4*N*, there is a general consistency in increases of the 2-*O*/6-*O*-ratio from the original cotton to the 0.33 hr hydrocellulose and to the 0.67 hr hydrocellulose followed by progressive decreases as duration of the hydrolysis in the preparation of the hydrocellulose increases thereafter.

As a matter of convenience and as a means of emphasizing the special characteristics of the hydrocellulose exhibiting the highest selective availability of hydroxyl groups (i.e., the 0.67 hr hydrocellulose), it is designated "exemplar" hydrocellulose (EHC).

The uniquely high selectivity of distribution of substituents at the 2-*O*-positions relative to those at the 6-*O*-positions which results from the reactions of EHC is very apparent in Figure 2. Since each set of points that is connected together by a line in this figure represents the results of reactions conducted under identical conditions, differences in the ratios of 2-*O*/6-*O*-

TABLE I
Results of Reactions of *N*,*N*′-Diethylaziridinium Chloride with Hydrocelluloses

Concn of base for retion, *N*	Hydrocellulose for reaction		2-Diethylaminoethyl hydrocellulose		
	Duration of hydrolysis, hr	Yield of hydrocellulose, %	Nitrogen content, %[a]	Distribution of substituents[b]	
				2-*O*-	3-*O*-
0.5	0.33	92.0	0.12	2.97	0.32
	0.67	90.4	0.10	3.80	0.41
	1.0	91.6	0.08	2.98	0.38
	2.0	88.3	0.16	2.47	0.19
	3.0	85.6	0.23	2.44	0.24
	4.0	81.9	0.19	2.15	0.21
	5.0	79.4	0.19	2.07	0.20
1.0	0.33		0.10	2.89	0.34
	0.67		0.10	3.11	0.32
	1.0		0.07	2.83	0.32
	2.0		0.18	2.41	0.22
	3.0		0.19	2.29	0.22
	4.0		0.13	2.13	0.22
	5.0		0.18	2.00	0.23
2.0	0.33		0.10	2.16	0.27
	0.67		0.09	2.79	0.36
	1.0		0.08	2.65	0.28
	2.0		0.17	1.82	0.21
	3.0		0.24	1.69	0.18
	4.0		0.21	1.96	0.18
	5.0		0.21	1.77	0.22
4.0	0.33		0.21	1.69	0.34
	0.67		0.22	1.82	0.31
	1.0		0.14	1.90	0.33
	2.0		0.22	1.55	0.23
	3.0		0.18	1.52	0.25
	4.0		0.21	1.32	0.23
	5.0		0.21	1.57	0.22
6.0	0.33		0.10	1.66	0.30
	0.67		0.16	1.68	0.32
	1.0		0.16	1.21	0.22
	2.0		0.17	1.36	0.21
	3.0		0.17	1.49	0.27
	4.0		0.25	1.49	0.20
	5.0		0.21	1.65	0.24

[a] These values are very sensitive to the precise procedure (e.g., amount of agitation) of reaction. Variations here are attributed to procedure rather than nature of the hydrocelluloses. The distribution of the substituents is not sensitive to the extent of reaction at this level of reaction.[7]

[b] Based on unity for the 6-*O*-position.

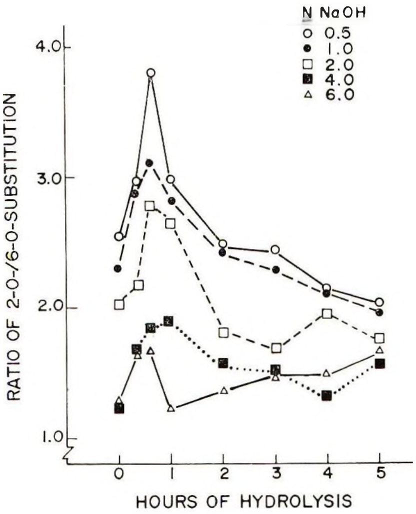

Fig. 2. Variation is ratio of 2-*O*-/6-*O* substitution with duration of hydrolysis involved in preparation of the hydrocellulose.

substitution reflect differences in the relative availabilities of the hydroxyl groups at C-2 and C-6. The selective accessibilities of the hydroxyl groups will be discussed in a following section; it is sufficient to point out here that selective accessibilities (i.e., deviations from equal accessibilities) increase as the ratios of 2-*O*-/6-*O*-substitution increase.

Selective Accessibilities of Hydroxyl Groups at C-2, C-3, and C-6 on the Surfaces of Hydrocelluloses

In preceding studies[4,5] it was estimated that the selective accessibilities of the hydroxyl groups of fibrous cotton (lattice I) and of EHC were $[O_6H]_a/[O_2H]_a = 0.77$ and 0.54, respectively, and $[O_3H]_a/[O_2H]_a = 0.32$ and 0.29, respectively. These values are based on (a) the relative distributions of substituents resulting from reactions of crystalline, fibrous cotton (e.g., dP_{6x}/dP_{2x}) in a specific normality of base, (b) the corresponding value from reaction of decrystallized cellulose (e.g., dP_{6d}/dP_{2d}), and (c) eq. (1) which

$$[O_6H]_a/[O_2H]_a = dP_{6x}dP_{2d}/dP_{2x}\,dP_{6d} \qquad (1)$$

was derived from kinetic expressions such as shown in eq. (2), where k and a refer to rate constants and

$$dP_6/dt = k_6a_{O_6}a_R \qquad (2)$$

activities, respectively, of the specific hydroxyl groups, hydroxyl ions ($O^{\ominus}$), and reagent (R).

Values of selective accessibilities of hydroxyl groups in all of the hydrocelluloses were estimated in this manner, by using the values of relative reactivities of the hydroxyl groups in decrystallized cellulose (i.e., dP_{6d}/dP_{2d}

TABLE II
Accessibilities of Hydroxyl Groups at C-6 and C-3 Relative to Those at C-2 in Cotton Cellulose and Hydrocelluloses

Hydrolysis time, hr	$[O_6H]_a/[O_2H]_a$ at various base concentrations[a]					$[O_3H]_a/[O_2H]_a$ at various base concentrations[b]				
	0.5*N*	1.0*N*	2.0*N*	4.0*N*	6.0*N*	0.5*N*	1.0*N*	2.0*N*	4.0*N*	6.0*N*
0.0	0.82	0.76	0.72	1.04	0.98	0.28	0.36	0.33	0.45	1.13
0.33	0.71	0.61	0.69	0.76	0.75	0.28	0.32	0.40	0.76	0.70
0.67 (EHC)	0.55	0.56	0.53	0.71	0.73	0.28	0.28	0.42	0.65	0.74
1.0	0.70	0.62	0.56	0.68	1.02	0.33	0.31	0.34	0.66	0.70
2.0	0.85	0.73	0.81	0.83	0.91	0.20	0.25	0.37	0.56	0.60
3.0	0.86	0.76	0.88	0.85	0.83	0.26	0.26	0.34	0.62	0.70
4.0	0.98	0.82	0.76	0.98	0.83	0.25	0.28	0.30	0.66	0.52
5.0	1.01	0.88	0.84	0.82	0.75	0.25	0.31	0.40	0.53	0.56

[a] Calculated by use of eq. (1) with the 6-*O*/2-*O* distribution of substituents in crystalline cottons, i.e., dP_{6x}/dP_{2x}, as listed in Table I, and the ratio of 2-*O*-/6-*O*- relative reactivities of the hydroxyl groups in disordered celluloses, i.e., dP_{2d}/dP_{6d}, as summarized in Table II of the previous work.[5]

[b] Calculated from an equation analogous to eq. (1) from the appropriate data of Table I of this work and of Table II of the previous report.[5]

and dP_{3d}/dP_{2d}) which are summarized in a preceding report.[5] The calculated selective accessibilities are summarized in Table II. It may be noted from values in this table that the selective accessibilities of the hydroxyl groups at C-6 relative to those at C-2 are similar (within experimental error) for reactions in 0.5*N*, 1.0*N*, and 2.0*N* sodium hydroxide. As a result of reactions in each of these normalities of base, EHC exhibits the maximum selective accessibility (i.e., the greatest deviation from equal accessibilities). The values of selective accessibilities of the hydroxyl groups at C-3 relative to those at C-2 show considerable scatter. It is not possible to distinguish among the various hydrocelluloses on the basis of the selective accessibilities of the hydroxyl groups at C-3; in most cases, these values fall in the range of 0.30 ± 0.10.

Estimation of Relative Surface Areas for the Hydrocelluloses

Moisture regain values have been employed for[14] and interpreted as[15] relative measurements of the accessible surfaces in cellulose fibers or particles. Values of moisture regain for the series of hydrocelluloses under consideration are plotted as a function of duration of hydrolysis in Figure 3; these data are supplemented with values for moisture content for the same series of samples and for related samples resulting from the same type of hydrolysis. In each case, a minimum value of moisture regain or moisture content characterizes the EHC. Thus, the sample of hydrocellulose resulting from 0.67 hr hydrolysis is indicated to have the least surface (external plus internal) of all of the hydrocelluloses. This initial decrease followed by increase in moisture regain of hydrocelluloses has been observed earlier[16–18] without significant conclusions being reached. Nelson and Tripp[6] reported

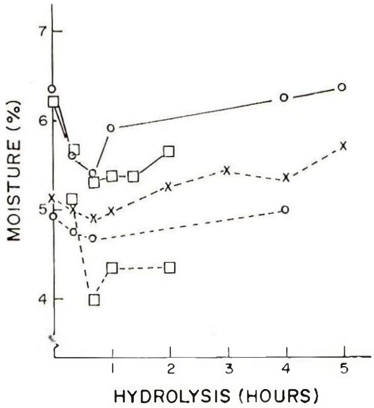

Fig. 3. Plots of moisture (——) regain and (- -) moisture contents (different conditions from moisture regain, see Experimental Section) for hydrocelluloses (○) from the main series of experiments, (□) from a second lot or print cloth hydrolyzed with $2.4N$ hydrochloric acid, and (×) from a griege yarn.

that, for hydrocelluloses collected from hydrolyses with concentrations of hydrochloric acid ranging from 0.1 to $2.5N$, moisture regain passed through a minimum when plotted as a function of percentage residue. This not only provides some confirmation for the present observations and indicates that the formation of an EHC is not peculiar to the present experiments but also suggests that an EHC may be produced under all conditions for formation of hydrocellulose.

Size and Shape of Hydrocellulose Particles

Numerous attempts were made to obtain quantitative measurements to determine the nature of changes in size and shape of the hydrocellulose particles during the course of the 5-hr hydrolysis. Difficulty was encountered in obtaining sufficiently discrete particles under mild conditions for meaningful measurements. It appeared that the aggregates in 0.33-hr hydrocellulose were larger than those in the 5-hr hydrocellulose and that the former were more like shattered, but unseparated, sections of the fibers. The impression was that the hydrocellulose particles in 5-hr hydrocellulose were shorter than those in 0.33-hr hydrocellulose but similar in lateral dimension. Krässig and Kappner[19] have reported measurements showing the decrease in length, Morehead[20] has followed decreases in degree of polymerization as a measure of length of particles, Rånby[21] has indicated that the particles retain their original width throughout much of the hydrolysis, and Sharples[22] has provided strong evidence for hydrolytic end-attack on the particles. Thus, changes in dimensions of the hydrocellulose particles throughout the course of the hydrolysis are indicated to be progressively toward shorter lengths. On this basis, the minimum in moisture regain for EHC may be attributed to a minimum in internal surface for this sample. Increases in moisture regain for subsequent samples of hydrocellulose are due to increases in external surfaces on the particles as well as increases in internal surfaces, as indicated in the next section.

Comparative Values on Crystallinity of Hydrocelluloses

By the correlation analysis method of Wakelin et al.,[10] it was estimated from x-ray diffraction that the original cotton (ground to pass a 20-mesh screen) was 80% lattice I and that the hydrocelluloses were 87–90% lattice I. The remainder was attributed to "amorphous" scatter. There was no trend among these results and no explanation for the single value (2-hr hydrocellulose) which fell as low as 84% lattice I. The increase in lattice I from original cotton to hydrocellulose was confirmed in a second set of samples hydrolyzed with $2.4N$ hydrochloric acid for durations up to 2 hr. Again, no trend was observed among the samples of hydrocellulose.

TABLE III
Relative Breadths of Peaks at Half Heights from X-Ray Diffractograms

Hydrolysis time, hr	Peak breadth on hydrolysis in $2.5N$ HCl solution			Peak breadth on hydrolysis in $2.4N$ HCl solution		
	101 peak	$10\bar{1}$ peak	002 peak	101 peak	$10\bar{1}$ peak	002 peak
0.0	—	—	—	1.05	1.24	1.10
0.33	1.00	1.05	1.01	1.02	1.17	1.10
0.67 (EHC)	1.00	1.00	1.00	1.00	1.00	1.00
1.0	1.00	1.09	1.01	1.04	1.07	1.05
1.33	—	—	—	1.05	1.04	1.05
2.0	1.00	1.09	1.01	1.09	1.08	1.07
3.0	1.06	1.07	1.02	—	—	—
4.0	1.06	1.08	1.04	—	—	—
5.0	1.06	1.09	1.04	—	—	—

Trends were observed in the breadths at half height of the 101, $10\bar{1}$, and 002 peaks in x-ray diffractograms. These trends, which are summarized in Table III, show that the minimum breadths are associated with the EHC. Since minimum peak breadth at half maximum of the peak is associated with maximum breadth of lattice in the direction perpendicular to the plane from which the x-rays are diffracted, the minimum breadth of peak may be taken as measure of extent of perfection in this comparison. EHC is indicated to have the broadest crystalline lattice structure. This structure in EHC represents an improvement over that in the original cotton cellulose, in the preceding sample of hydrocellulose, and in the following samples of hydrocellulose. It appears from these limited experiments that the changes in breadth of crystal structure which take place during the hydrolysis decrease in the following order: (a) most change perpendicular to the $10\bar{1}$ plane, (b) substantially less change perpendicular to the 002 plane, and (c) least change, but only slightly less than (b) perpendicular to the 101 plane.

SUMMARY AND CONCLUSIONS

Through a study of selective distribution of 2-(diethylamino)ethyl substituents from reaction of *N*,*N*-diethylaziridinium chloride with samples of hydrocellulose, it has been possible to assess the selective availability or selective accessibility of the hydroxyl groups at C-2, C-3, and C-6 on the surfaces of crystalline regions. The highest selective accessibility (i.e., the greatest deviation from equal accessibility) was found to characterize EHC, the hydrocellulose formed from 0.67-hr hydrolysis under these particular conditions (2.5*N* hydrochloric acid at reflux). The unique nature of EHC has been confirmed by the observations that this material exhibits minimum moisture regain and minimum breadths at half heights for the 101, 10$\bar{1}$, and 002 peaks in x-ray diffractograms.

The gradual transformation of fibrous cotton to a highly ordered hydrocellulose, i.e., EHC, followed by gradual disordering of the EHC is subject to interpretation as follows. The molecular chains of cellulose in the highly crystalline elementary fibrils are attacked by acid at regions along the lengths of these fibrils. The attack occurs most pronouncedly at molecular segments which lie in regions of disorder or around points of discontinuity. A region of disorder is defined as a region of substantial dimension, perhaps 10–50 Å in the longitudinal direction of the elementary fibril and extending to a major depth in the fibril if not completely through it; in such a region, the lateral order of packing is disrupted without major loss in orientation of the molecular segments. The D-glucopyranosyl units in such a region may be especially susceptible to hydrolytic attack because they are more readily accessible or because they are under strain (or both).

A point of discontinuity is defined as a region of quite limited extent, perhaps traversing 5–10 Å longitudinally and the same in depth in the elementary fibril (i.e., to a minor fraction of the total depth of the elementary fibril); such a region of discontinuity of crystalline order may be the result of the termination of a molecular chain of cellulose, or the result of a dislocation developed during growth, or a fault developed during subsequent treatments (i.e., drying, swelling, etc.).

On progression from fibrous cotton to EHC, the substantial increases in order of presentation of hydroxyl groups on the crystalline surfaces, in percentage of lattice I, in breadth of crystal perfection, and in compactness of the residues of elementary fibrils (i.e., decrease in internal surface) suggest that the elementary fibrils in fibrous cotton have undergone a release of strain upon hydrolysis to hydrocellulose and that the new freedom allowed to the elementary fibrils (in the strained regions) facilitates an extension of the development of crystal structure. The concept which is proposed is stated in three parts. First, the hydrolytic attack occurs predominantly at regions of disorder which are especially susceptible due to strain.[2,3,20] and due to an increase in accessibility which is the result of disruption of perfect crystalline order which, in turn, is caused by a bending strain. Secondly, it is conceived that as strain is released, segments of the cellulose chain which were previously restrained from crystalline order are allowed to relax into states of high linear and lateral order which culminate in EHC. Finally, penetration of the aqueous reagent into the hydrocellulose particles continues and develops increased internal surfaces; simultaneously, hydrolysis of molecular segments continues, perhaps predominantly from the ends of the particles[22] but also on the sides of the elementary fibrils which are accessible as $10\bar{1}$ planes. The result is decrease in particle size of the hydrocellulose and in degree of polymerization of the cellulose. It appears reasonable that there is a simultaneity of all of these processes but that the magnitude of the effects accentuate molecular hydrolysis first, recrystallization second, and crystal and molecular degradation third.

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References

1. J. O. Warwicker, R. Jeffries, R. L. Colbran, and R. N. Robinson, Shirley Institute Pamphlet No. 93, Manchester, England, 1966.
2. A. Peterlin and P. Ingram, *Text. Res. J.*, **40**, 345 (1970).
3. R. Jeffries, D. M. Jones, J. G. Roberts, K. Selby, S. C. Simmons, and J. O. Warwicker, *Cellulose Chem. Technol.*, **3**, 255 (1969).
4. S. P. Rowland, E. J. Roberts, and C. P. Wade, *Text. Res. J.*, **39**, 530 (1969).
5. S. P. Rowland, E. J. Roberts, and J. L. Bose, *J. Polym. Sci.*, *A-1*, **9**, 1429 (1971).
6. M. L. Nelson and V. W. Tripp, *J. Polym. Sci.*, **10**, 577 (1963).
7. S. P. Rowland, V. O. Cirino, and A. L. Bullock, *Can. J. Chem.*, **44**, 1051 (1966).
8. C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Am. Chem. Soc.*, **85**, 2497 (1963).
9. E. J. Roberts and S. P. Rowland, *Can. J. Chem.*, **45**, 261 (1967).
10. J. H. Wakelin, H. S. Virgin, and E. G. Crystal, *J. Appl. Phys.*, **30**, 1654 (1959).
11. N. B. Patil, N. E. Dweltz, and T. Radhakrishnan, *Text. Res. J.*, **32**, 460 (1962).
12. S. P. Rowland, V. O. Cirino, and A. L. Bullock, *Text. Chem. Colorist*, **21**, 450 (1969).
13. E. J. Roberts, C. P. Wade, and S. P. Rowland, *Carbohydrate Res.*, **17**, 393 (1971).
14. R. Jeffries, *J. Appl. Polym. Sci.*, **8**, 1213 (1964).
15. W. A. Reeves, R. M. Perkins, and L. H. Chance, *Text. Res. J.*, **30**, 179 (1960).
16. R. F. Nickerson, *Ind. Eng. Chem.*, **34**, 1480 (1942).
17. G. F. Davidson, *J. Text. Inst.*, **34**, T87 (1943).
18. R. F. Nickerson and J. A. Habrle, *Ind. Eng. Chem.*, **39**, 1507 (1947).
19. H. Krässig and W. Kappner, *Makromol. Chem.*, **44/46**, 1 (1961).
20. F. F. Morehead, *Text. Res. J.*, **20**, 549 (1960).
21. B. G. Ranby, *Tappi*, **35**, 53 (1952).
22. A. Sharples, *Trans. Faraday Soc.*, **54**, 913 (1958).
23. E. W. Fischer, *Ann. N.Y. Acad. Sci.*, **89**, 620 (1961).

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Criticisms of Claims in the Field of Isomerization Polymerization. I. Polymerization of *p*-Methylstyrene

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Synopsis

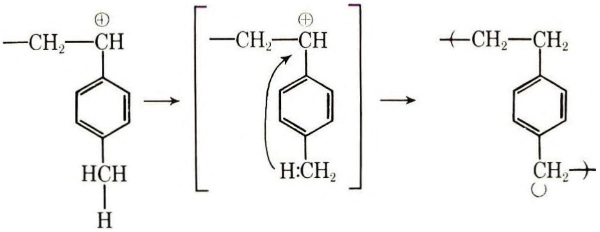
The polymerization of *p*-methylstyrene with cationic initiators at low temperatures has been reinvestigated. It was found that, contrary to claims by Krentsel et al., this polymerization produces a conventional 1,2 structure and consequently proceeds by a conventional mechanism.

Introduction

The interesting young field of isomerization polymerization[1] (defining equation: $n\mathrm{A} \rightarrow \left(\!-\mathrm{B}-\!\right)_n$) is experiencing some growing-pains. During the past few years a number of claims concerning isomerization polymerizations have appeared in the scientific literature which need to be examined and scrutinized closely. In this series of papers some of these claims will be examined in the light of old and new experimental evidence and theoretical argument.

Polymerization of *p*-Methylstyrene

Recently Prishchepa et al.[2,3] claimed that poly-*p*-methylstyrene obtained by low-temperature cationic polymerization contains "anomalous structures" which were alleged[3] to arise from "an intermediate complex."



This unusual claim interested us and therefore it was decided to reinvestigate this reaction. Experiments were carried out independently in the U.S. (J. P. K.) and in England (P. L. M. and P. H. P.) under conditions as far as possible identical to those employed by the Russian investigators and under other, similar conditions (cf. Experimental).

Prishchepa et al.[2,3] polymerized *p*-methylstyrene by the use of $BF_3 \cdot Et_2O$ in toluene and ethyl chloride solvents in the temperature range from −130°C to 0°C. The conclusion that rearrangement occurred during polymerization was based mainly on infrared and NMR evidence. The infrared evidence was presented in the form of intensity ratios calculated from peaks at 2860 (for $-CH_2-$ groups) and 3020 (for aromatic protons) cm^{-1}. Figure 1 of ref. 3 shows the 2800–3100 cm^{-1} region of two infrared spectra obtained with unspecified samples.

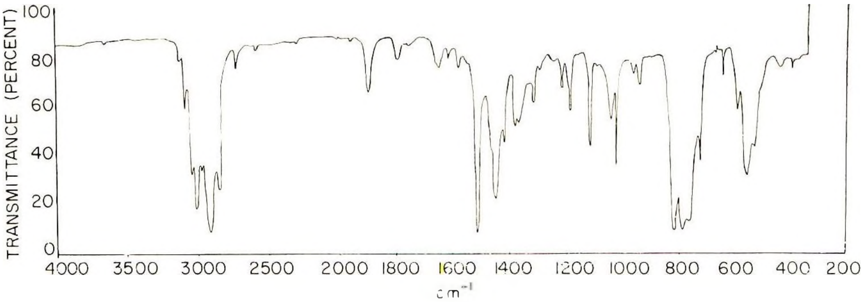


Fig. 1. Infrared spectrum of a poly-*p*-methylstyrene prepared with $BF_3 \cdot OEt_2$ (sample II in Table II).

The quality of these spectra is too low for quantitative analysis. Also it is hard to understand why the $-CH_3$ region has not been analyzed concurrently. The rearranged structure should contain fewer methyl groups than the conventional polymer, and if this had been found, it would have been further good evidence for rearrangement.

The (non-integrated 60 MHz) NMR scan in Figure 2*b* of ref. 3 is alleged to be another piece of evidence for the rearranged polymer structure. Figure 2*a* is a NMR scan of a conventional poly-*p*-methylstyrene obtained under unspecified conditions, whereas Figure 2*b* was obtained with a rearranged polymer, again of undefined origin. From these NMR spectra the Russian authors estimated that ~35% of the polymer was of rearranged structure. While the NMR scans in Figure 2*a* and 2*b* of ref. 3 are different, this difference alone is insufficient to demonstrate conclusively the rearranged structure. Indeed, of the four well-resolved peaks in the aliphatic region, two (at ~1.6 ppm and 2.00 ppm) remain unassigned. In spite of numerous trials we were unable to synthesize a polymer with a NMR spectrum resembling that shown in Fig. 2*b* of ref. 3. Rather, all our products exhibited NMR (and infrared) spectra indicative of unrearranged, conventional $-CH_2CH(C_6H_4CH_3)-$ repeat units.

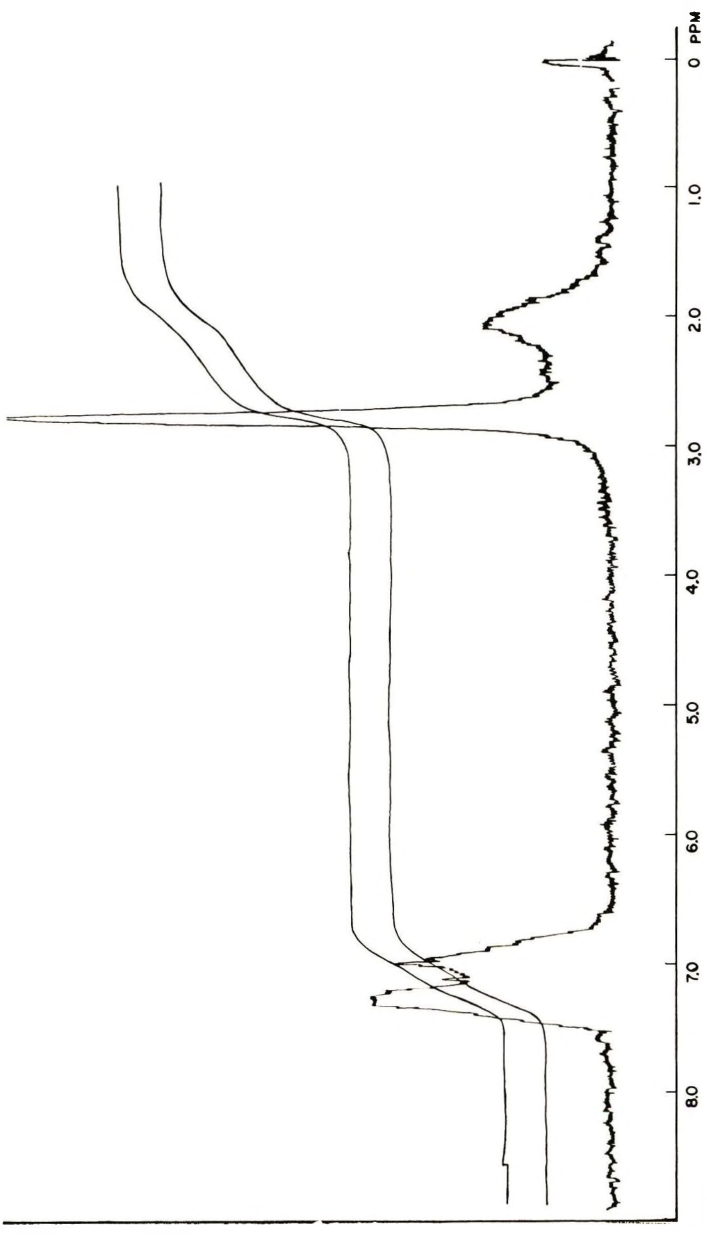


Fig. 2. Nuclear magnetic resonance spectrum of a poly-*p*-methylstyrene prepared with $BF_3 \cdot OEt_2$ (sample II in Table II).

Some other facts presented by Prishchepa et al.[2,3] are either meaningless because of their incompleteness, or obscure because of lack of details or interpretation. For example, in the absence of supporting evidence the statement was made that "some of the samples showed partially crystalline structure by x-ray diffraction analysis." This was attributed to long $-CH_2-CH_2-CH_2-C_6H_4-$ sequences in the chain. Finally, according to the authors, thermal degradation *in vacuo* (2°C/min. to 450°C) indicates that with increasing fraction of rearranged units in the polymer (by infrared evidence), the maximum rate of thermal decomposition shifts towards higher temperature. The degradation curves (Fig. 3 in ref. 3) show that the polymer starts to degrade at ~330°C and the degradation rate reaches a maximum between 380 and 410°C; this maximum is followed by a region of decreasing rates between 390 and 420°C, then a reversal, and another maximum between 400 and 430°C. It is hard to accept these facts as further evidence for the postulated rearranged structure.

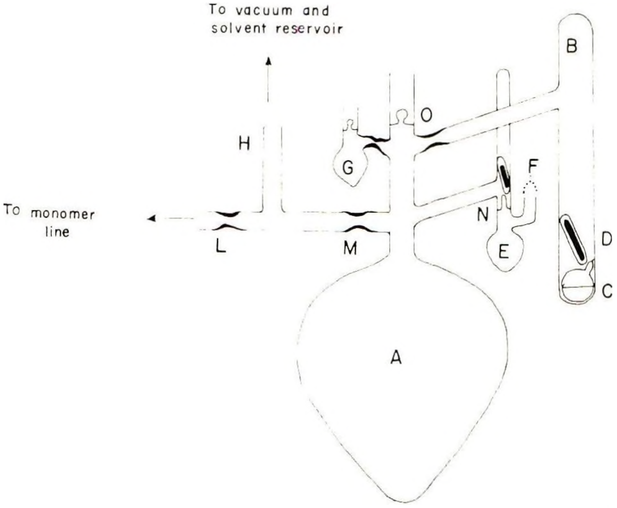
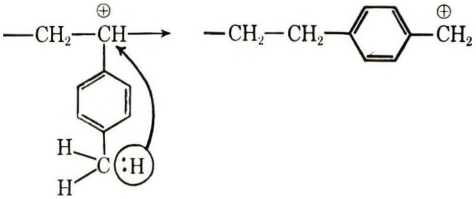


Fig. 3. Apparatus used in vacuum experiment for "step one."

We have carried out polymerizations of *p*-methylstyrene with various catalysts, e.g., benzoyl peroxide, perchloric acid, ethylaluminum dichloride, and aluminum bromide, in addition to $BF_3 \cdot OEt_2$, the initiator used by the Russian workers. Methylene dichloride, ethyl chloride, and toluene were used as solvents in the temperature range from 0 to −130°C, and monomer conversions ranged from ~1 to 96%. Experiments were carried out under nitrogen atmosphere and under high vacuum conditions. Polymer samples were analyzed by infrared and NMR spectroscopy (cf. Experimental). In spite of considerable effort and careful experimentation we could not obtain any evidence for isomerization polymerization.

In the course of this work we have had the opportunity to converse with Professor Krentsel, who recommended low catalyst concentrations and low monomer conversions at low temperatures as optimum conditions for rearrangement. However, even after following these guidelines we were unable to confirm the existence of the postulated rearranged polymer structure (cf. Vacuum Experiments).

From the theoretical point of view our findings are not surprising and, indeed, a polymerization mechanism involving hydride migration:



would be unreasonable on many counts. First of all, the rearrangement of a secondary benzylic carbonium ion to a primary cation is energetically unfavorable. Furthermore, as there is no direct overlap between the empty *p* orbital of the secondary benzylic carbonium ion and a hydrogen of the *para* methyl group, a direct hydride transfer is spacially impossible. Finally it is very difficult to envisage a reasonable mechanism for a hydride shift along an aromatic ring system. Indeed a diligent search of pertinent organic chemical literature failed to reveal such, or a similar, hydride shift mechanism.

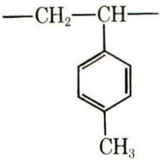
At this point it is worth mentioning that Disselhof and Braun[4] had sought evidence for an isomerization polymerization of *p*-isopropylstyrene involving a hydride shift from the isopropyl group. This would at least be energetically favorable, since a tertiary carbonium ion would be formed at the expense of a secondary ion. They compared the infrared and NMR spectra of polymers made with radical initiators and with $AlCl_3$, $TiCl_4$, $SnCl_4$, BF_3, and H_2SO_4 in the temperature range 30° to −78°C, but found all the spectra to be virtually identical.

Subsequently, and independently, one of us (J. P. K.)[1] attacked the same problem by studying the structure of poly-*p*-isopropylstyrenes prepared with $AlCl_3$ in EtCl in the temperature range −78° to −168°C. Here too, no sign of any isomerization could be found.

Again independently, Magagnini and Plesch[5] compared the spectra of polymers made from *p*-isopropylstyrene with benzoyl peroxide in bulk at 60°C and with $AlBr_3$ in EtCl at −130°C, and they were also unable to detect any differences.

Thus it is clear that a transannular hydride shift does not occur even in this case.

Thus on the basis of experimental evidence and theoretical considerations we conclude that in contradiction to Krentsel and co-workers[2,3] the repeat structure of poly-*p*-methylstyrene obtained with common Lewis acids e.g., $BF_3 \cdot OEt_2$, $AlBr_3$ or Brønsted acids, e.g., $HClO_4$, is a conventional one:



Experimental

p-Methylstyrene was prepared from *p*-bromotoluene by the Grignard reaction. The resulting crude carbinol was dehydrated directly under reduced pressure by slowly contacting it with fused $KHSO_4$ at ~200°C. The *p*-methylstyrene, bp 68°C/13 mm Hg, 99.6% pure by GLC, was stored over a trace of picric acid. Before use it was freshly distilled.

Methylene dichloride was purified by washing a commercial product (Koch-Light) with H_2SO_4 and distilled water, drying it first with $CaCl_2$ and then with P_2O_5 and fractionating it carefully. The purified solvent was then degassed and refluxed on the vacuum line over sublimed P_2O_5. It was then taken off the vacuum line before use and kept in a flask closed with a stopcock through which it was syringed for each experiment. Ethyl chloride (BDH) was bubbled through H_2SO_4, passed over soda lime, and condensed directly into the reaction vessel. Toluene was purified by successive washings with H_2SO_4, $NaHCO_3$, distilled water, dried with sodium wire, and fractionated. Benzoyl peroxide was purified by precipitation from chloroform and dried under vacuum. Perchloric acid was used in CH_2Cl_2 solution, contained in vials prepared as described.[6] Boron fluoride etherate (BDH) was purified by repeated fractionations under reduced pressure in dry nitrogen atmosphere. The product was further purified on the vacuum line by bulb-to-bulb distillation and filled into vials. Aluminum bromide was prepared by reaction of aluminum with bromine and was purified by repeated distillations and filled into vials on the vacuum line. (These vials were prepared by V. Shmarlin at Keele.) Ethylaluminum dichloride (Texas Alkyls Inc.) was distilled before use.

Polymerizations were carried out by the syringe technique (transferring reagents under nitrogen with syringes), dry-box technique (manipulation of chemicals in a nitrogen-filled stainless-steel enclosure[7]) and under high vacuum conditions (cf. below).

The results of polymerizations conducted by the first two techniques are shown in Table I. The headings are self-explanatory. Experiments PM1 to PM3 have been carried out in test tubes maintained at the desired temperature. Polymerization was initiated by crushing catalyst vials prepared under high vacuum. In experiments PM5 and PM6 the monomer was added to catalyst–solvent mixtures under similar conditions. Experiments PM7 and PM11 were carried out in cylindrical flasks filled with the solvent. The monomer and the catalyst were introduced with a syringe through a rubber cap. In the experiments with $AlBr_3$ (PM10 and PM11), the catalyst solution was prepared by crushing a catalyst vial under 2–3 ml of an-

TABLE I
Polymerization of *p*-Methylstyrene

Expt. no.	Solvent	$[M]_0$, M	Catalyst	$[C]_0 \times 10^3$, M	T, °C	Time, min	Yield, %	R^a
—	—	—	Bz_2O_2	—	60	—	—	0.74
PM1	CH_2Cl_2	0.703	$HClO_4$	1.76	0	90	>70	0.76–0.79
PM2	CH_2Cl_2	0.372	$HClO_4$	0.49	0	3	91	0.73–0.75
PM3	CH_2Cl_2	0.703	$HClO_4$	1.76	−91	15	85	0.72–0.77
PM5	CH_2Cl_2	0.703	$BF_3 \cdot Et_2O$	15.84	−90	15	13.7	0.75–0.78
PM6	CH_2Cl_2	0.703	$BF_3 \cdot Et_2O$	15.84	0	15	93	0.74–0.75
PM7	C_2H_5Cl	0.234	$BF_3 \cdot Et_2O$	~7	−130	30	~1	0.82–0.91
PM8	C_2H_5Cl	0.176	$BF_3 \cdot Et_2O$	~58	−100	20	~8	0.74–0.77
PM9	$C_6H_5CH_3$	0.281	$BF_3 \cdot Et_2O$	~100	−98 ÷ −78	72	<1	0.77
PM10	CH_2Cl_2	0.703	$AlBr_3$	12.05	−90	10	96.4	0.8
PM11	C_2H_5Cl	0.281	$AlBr_3$	4.90	−130	10	55.7	0.72
JK32	C_2H_5Cl	0.200	$AlEtCl_2$	15.3	−130	75	87.0	

[a] R = ratio of the heights of the absorption bands at 2860 and 3030 cm^{-1}.

hydrous methylene dichloride and syringing the solution into the reactor. In experiments PM1, PM10, and PM11 a pink color developed after catalyst addition. In run PM9 the temperature rose from −98 to −78°C during reaction.

Experiment JK32 was carried out in a dry box filled with nitrogen (moisture content ~30 ppm) by introducing gradually a solution of $AlEtCl_2$ in ethyl chloride into a monomer–ethyl chloride charge at −130°C. Polymerizations were terminated by the addition of a few milliliters of cooled methanol or propanol. Subsequently the precipitated products were washed twice with ethanol and dried *in vacuo* at 45°C for about 10 hr.

In the polymerization with benzoyl peroxide the monomer was introduced into a Pyrex ampoule containing 0.02 mole-% initiator. The ampoule was connected through a liquid nitrogen trap to an oil pump. The monomer was thoroughly degassed by repeated freeze-thawing cycles. The ampoule was sealed and placed in a water bath at 60°C. After partial polymerization (about 10 hr) the semisolid product was diluted with benzene and the polymer was recovered by precipitation into methanol, reprecipitated twice from benzene, and dried.

Polymers were analyzed by infrared and NMR spectroscopy. Infrared analysis was carried out with PE 521, 257, and 221 instruments with polymer films cast from a CCl_4 solution on NaCl or KBr plates. NMR analysis was carried out with a Varian T60 (60 MHz) instrument in the temperature range from ambient to 103°C and with a JEOL 60 MHz instrument at 100 and 150°C; ~10% hexachlorobutadiene solutions and TMS external standards were used.

The infrared spectra of the products were obtained and the ratio of the intensities of the absorption bands at 2860 and 3030 cm^{-1} were calculated. Qualitatively and quantitatively all the spectra were very similar. A representative infrared spectrum is shown in Figure 1. All the spectra were substantially identical and indistinguishable from that obtained with the polymer produced with benzoyl peroxide initiator. Polymers PM7 and PM9 exhibited a weak unidentified peak at 1265 cm^{-1}; this peak could be due to some unidentified impurity, since very low conversions were obtained when these samples were prepared.

The NMR spectrum of a polymer sample prepared with $\mathrm{BF_3{\cdot}OEt_2}$ catalyst in toluene solvent at −87 to −94°C (sample II in Table II) is shown in Figure 2. Chemical shifts with peak assignments (and their relative intensities from integration) are: ~2.05 ppm, $\mathrm{—CH_2—}$, (*2*); ~2.45 ppm, $—\overset{|}{\mathrm{C}}\mathrm{H}—$, (*1*); ~2.8 ppm, $\mathrm{—CH_3}$, (*3*); and 6.7–7.5 ppm, aromatic protons, (*4*). This corresponds with the conventional unrearranged structure, $\mathrm{—CH_2—}\overset{|}{\mathrm{C}}\mathrm{H—C_6H_4—CH_3}$. Spectra obtained at 150° did not show improved resolution. In no case were we able to reproduce the spectrum shown in Figure 2*b* of ref. 3. The reason for this discrepancy remains obscure.

TABLE II
Polymerization of *p*-Methylstyrene under Vacuum in Toluene[a]

Sample		$[\mathrm{M}]_0$, *M*	Catalyst	$[\mathrm{C}]_0 \times 10^3$, *M*	*T*, °C	Time, hr	Yield, %	R^b
Step one	I	0.285	$\mathrm{BF_3{\cdot}Et_2O}$	20.4	−87 to −94	1.5	11.5	0.72
	II	0.285	$\mathrm{BF_3{\cdot}Et_2O}$	20.4	−87 to −94	2	11.0	0.74
Step two	III	0.264	$\mathrm{AlBr_3}$	0.4	−89 to −95	1	0.6	0.72

[a] The amount of solvent used was 850 ml.

[b] See Table I.

Vacuum Experiments

In the course of these studies Professor Krentsel advised us (P. L. M. and P. H. P.) that in order to maximize rearrangement, experiments should be carried out at low monomer concentration ($[\mathrm{M}] = 0.2M$), low catalyst concentration ($[\mathrm{C}] = 0.01\text{–}0.04M$), and at low temperatures (~−90°C).

It should be noted that under the recommended conditions the yields of polymer obtained by Krentsel et al. were usually below 1% (cf. Table I in ref. 3). Considering the extremely low yields, we thought that the peculiarities in the infrared and NMR spectra of the samples obtained by the Russian investigators could have been due to the presence of unidentified impurities.

Thus, in line with the above suggestion, a two-step polymerization experiment with carefully purified materials under high vacuum conditions was carried out. The plan was to polymerize *p*-methylstyrene first to very low conversions ("step one"), and subsequently to distill over the unreacted monomer and solvent to a second reactor for further polymerization ("step two"). It was reasoned that if impurities in the monomer were re-

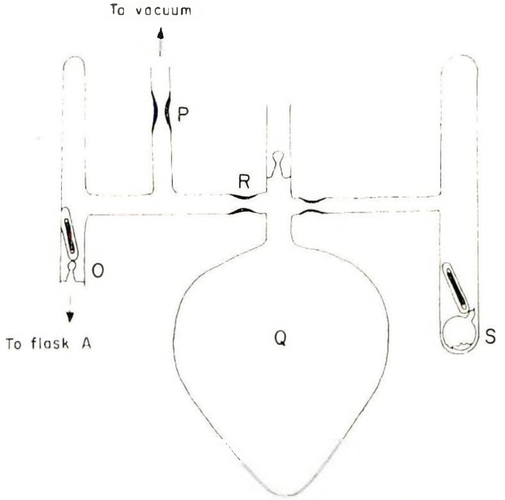


Fig. 4. Apparatus used in vacuum experiment for "step two."

sponsible for the peculiar spectra, the polymer from "step one" should contain the corresponding structures, whereas the second polymer crop should be obtained with the purest possible monomer.

The apparatus used in the first and second steps of these experiments is shown in Figures 3 and 4. The "step one" polymerization was carried out in an assembly which consisted of a one liter flask (A) with a side-tube (B) containing the $BF_3.OEt_2$ in a vial (C) and a magnetic breaker (D). The small flask (E) contained an excess (with respect to catalyst) of *N,N'*-di-(2-naphthyl)-*p*-phenylenediamine to kill the reaction. This high molecular weight amine was selected as a terminator so as to prevent its passage into the second reactor during the subsequent distillation. Flask E with the killing agent was connected through F to the vacuum line and through break-seal N to the polymerization vessel. The small flask (G) was used

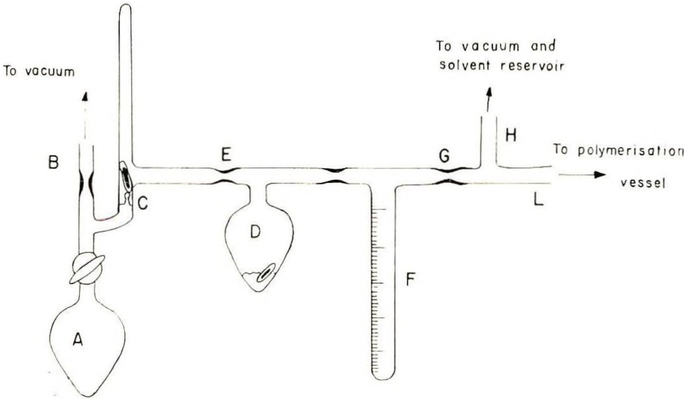


Fig. 5. Apparatus used in vacuum experiment for purification of the monomer.

for sampling during the run. Flask A was attached through H to the vacuum line and to the solvent reservoir, and through L to the monomer line.

The monomer was degassed under high vacuum in the presence of BaO, distilled under high vacuum into flask A (Fig. 5) and stored at about −10°C for 8 months. During this period partial polymerization occurred. Final purification was carried out in the apparatus shown in Figure 5. Flask A was connected to the vacuum line through B, the partly polymerized monomer was thoroughly degassed and the line was sealed off at

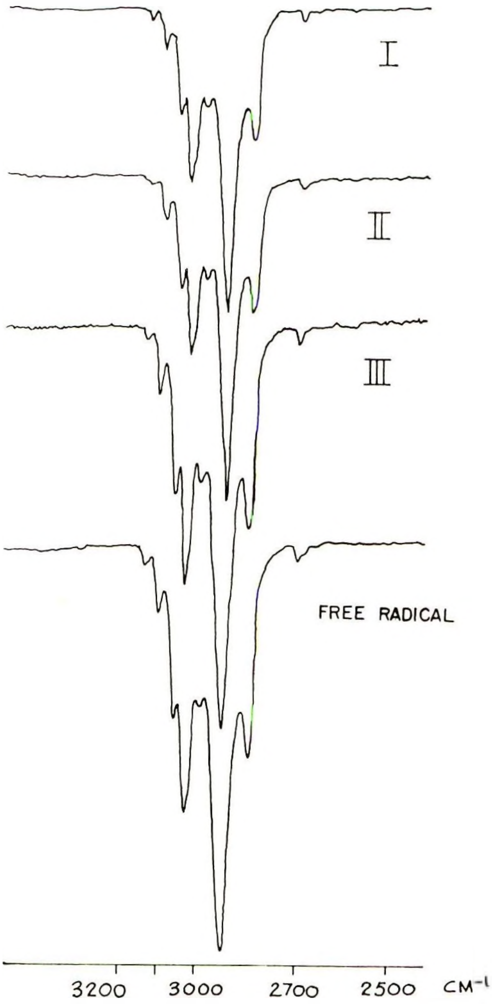


Fig. 6. Comparison of infrared spectra of poly-*p*-methylstyrenes obtained under high vacuum with cationic and radical initiators: I = sample I in Table II; II = sample II in Table II; III = sample III in Table II; free radical = polymer obtained with benzoyl peroxide.

constriction B. At the same time flask D with some BaO in it was baked at 300° under high vacuum for five hours. Subsequently the break-seal C was broken and the monomer distilled into D. Flask A with the polymer (~15%) was sealed off at constriction E. The monomer was stored over BaO for three days with occasional stirring. Again a slight (~3%) polymerization occurred. Finally the residual monomer was distilled into measuring buret F and thence to the polymerization vessel through tube L. The buret was sealed off at G.

Toluene, purified as described above and stored under vacuum over BaO was distilled into the polymerization vessel through tube H (Fig. 3). At the same time the amine in the small flask E was thoroughly degassed through F which was then sealed off. The whole polymerization system was then sealed off at M and flask A was immersed in a CH_2Cl_2 mush at ~-95°C. After about 1 hr of thermal equilibration, catalyst vial C was broken and the $BF_3 \cdot OEt_2$ was distilled into flask A (gently shaken) over a period of 8 min. Flask A was then stored in the cooling bath at -95° and shaken occasionally. This was reaction "step one."

After 90 min a small amount of the solution was tipped into the precooled flask G and sealed off. A mixture of ethanol and ammonia was quickly run into G through the break-seal and the polymer sample was precipitated in methanol. (Sample I).

The polymerization in flask A was stopped after 120 min by breaking seal N and quickly mixing the amine with the solution. Flask A was then placed back in the cooling bath, the temperature of which was allowed to rise slowly to ambient over a period of 2 days.

Subsequently flask A was connected to the "step two" polymerization assembly (Fig. 4) through line O with a break-seal. The latter assembly was then pumped out and sealed at P. Break-seal O was crushed and the unreacted monomer and solvent were distilled from flask A to flask Q by immersing the latter into liquid nitrogen. Flask Q was then sealed off at R and thermally equilibrated at -90°C. The catalyst vial S containing $AlBr_3$ was crushed and the system rapidly mixed. After 1 hr the reaction was stopped by adding an excess of NH_3–ethanol mixture through the break-seal, and the polymer was recovered by precipitation in an excess of methanol. (Sample III).

The residue in flask A of Figure 3 was extracted twice with benzene, and the solution was filtered into an excess of methanol. The precipitation was repeated four times. (Sample II).

The results of the first and second polymerization steps are shown in Table II. Sample I is the small amount of polymer removed into flask G during the polymerization with $BF_3 \cdot OEt_2$. Sample III was obtained subsequently with $AlBr_3$. Aluminum bromide was used to initiate the second polymerization step because infrared analysis had shown that the "step one" had yielded conventional polymers. Therefore, it would have been senseless to continue the second phase of the experiment with the same $BF_3 \cdot OEt_2$ catalyst.

Infrared analysis of all the samples (Fig. 6) gave an intensity ratio of about 0.73. Indeed, the spectra of the three samples are superimposable, and they are also identical to the spectrum of a poly-*p*-methylstyrene produced with benzoyl peroxide initiator; consequently the polymers possess a conventional structure. Therefore, we conclude that isomerization polymerization did not occur in either the first step with $BF_3 \cdot OEt_2$, or in the second step with $AlBr_3$.

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References

1. J. P. Kennedy, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark, N. G. Gaylord, and N. Bikales, Eds., Interscience, New York, 1967, Vol. 7, p. 754.
2. N. D. Prishchepa, Y. Y. Goldfarb, and B. A. Krentsel, *Vysokomolek. Soedin.*, **8**, 1658 (1966).
3. N. D. Prishchepa, Y. Y. Goldfarb, B. A. Krentsel, and M. V. Shishkina, *Vysokomolek. Soedin.*, **9**, 2426 (1967) and *Polymer Science U.S.S.R.*, **9**, 2743 (1967).
4. R. Disselhof and D. Braun, Diploma work by R. Disselhof, Darmstadt, 1964.
5. P. L. Magagnini and P. H. Plesch, unpublished results (1968).
6. A. Gandini and P. H. Plesch, *J. Chem. Soc.*, **1965**, 6019.
7. J. P. Kennedy and R. M. Thomas, *Advan. Chem. Ser.*, **34**, 111 (1962).

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Criticisms of Claims in the Field of Isomerization Polymerization. II. Polymerization of *o*-Isopropylstryene

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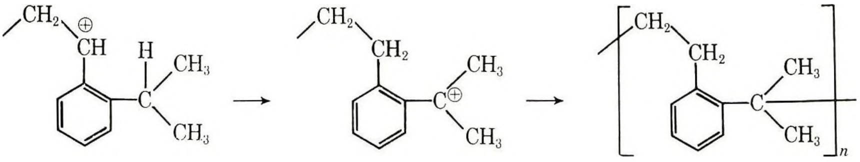
Synopsis

The polymerization of *o*-isopropylstyrene with free radical (benzoylperoxide, heat) and cationic ($AlCl_3$, $AlBr_3$) initiators has been investigated. It is concluded that, contrary to an earlier prediction and to a claim by Aso et al., both the radical and carbonium ion polymerizations of *o*-isopropylstyrene proceed by conventional mechanisms which give the same 1,2 repeat unit.

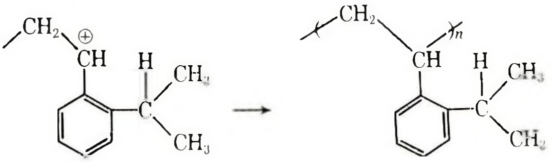
INTRODUCTION

Some time ago one of us[1] suggested that *o*-isopropylstyrene (*o*-iPrS) under cationic conditions might undergo the energetically favored, trans-spatial hydride-jump polymerization [eq. (1)].



(1)

Unfortunately there was a serious flaw in this theory, a flaw which was found only much later, indeed, only after a considerable amount of experimentation led us to the conclusion that the postulated isomerization-polymerization does not occur and that the cationic polymerization of *o*-iPrS, in fact, proceeds exclusively by the conventional route [eq. (2)].



(2)

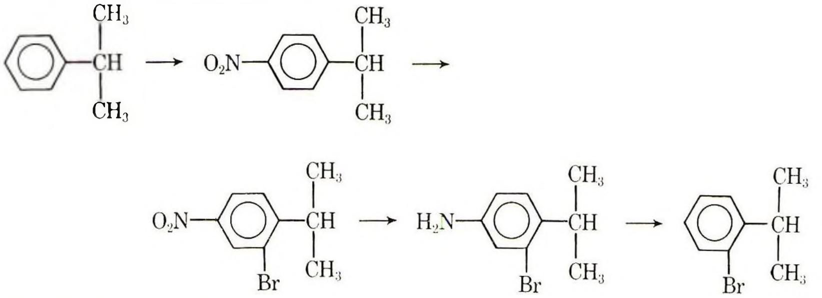
At the time we were carrying out our experiments, unknown to us, Aso, Kunitake, and Shinkai were also experimenting along these lines and also postulated the trans-spatial hydride-jump polymerization for *o*-iPrS. According to their infrared results,[2] *o*-iPrS in the presence of $AlCl_3$ undergoes isomerization-polymerization and they estimated that under favorable conditions about 20% of hydride-jump polymerization occurs.

We disagree with the conclusions of the Japanese investigators and in this paper present data and arguments which in our opinion show that trans-spatial hydride-jumps do not and cannot occur in systems such as *o*-isopropylstyrene.

EXPERIMENTAL

Monomer Synthesis

o-iPrS was synthesized from *o*-bromocumene by the Grignard route. The *o*-bromocumene was obtained in four steps [eq. (3)] from cumene by following the procedure of Crawford and Stewart:[3]



(3)

To obtain a high-purity endproduct (at the expense of yield), the isolation of the *para* isomer from the nitration mixture was carried out with extra precautions.

Cumene (Schuchardt) was fractionated under reduced pressure and a product of 99.3% purity (by GLC) was used for nitration. Cumene (1000 g) was nitrated by Sterling and Bogert's[4] procedure. The oily product, thoroughly washed and dried, was fractionated under reduced pressure through a 1-m column packed with glass helices (reflux ratio: 10:1). A series of 25 ml portions was collected and analyzed by GLC. The fractions with higher than 97% purity were combined and refractionated with generous foreruns and tails.

The product was of 98.3% purity (by GLC); bp 84°C/0.5 mm Hg; n_D^{12} 1.5395.

The bromination of *p*-nitrocumene, the reduction to 3-bromo-4-isopropylaniline, and the deamination to *o*-bromocumene were carried out according to Crawford and Stewart.[3]

The *o*-bromocumene was fractionated twice under reduced pressure, and 95 g of product with bp 84°C/13 mm Hg, n_D^{20} 1.5405 was obtained; the purity was 98.6% by GLC.

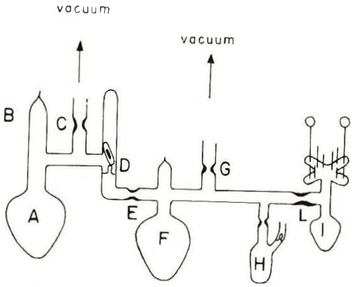


Fig. 1. Glass apparatus used in the purification of *o*-isopropylstyrene.

o-Bromocumene was reacted with Mg turnings in anhydrous diethyl ether in the usual way. The Grignard reagent was then reacted with purified anhydrous acetaldehyde and the resulting carbinol was dehydrated with fused $KHSO_4$ at 200°C. The *o*-iPrS–water mixture was separated, and the product was twice fractionated under reduced pressure in the presence of a trace of picric acid, yielding 40 g *o*-iPrS; bp 73.5°C/8.5 mm Hg; purity 98.7% by GLC.

The product was introduced into flask A (Fig. 1) through tube B which was then sealed. The monomer was thoroughly degassed through C and the constriction C was sealed off. Breakseal D was crushed and the monomer was transferred to flask F by cooling the latter with liquid N_2. Flask F contained about 10 g BaO previously baked at 300°C for 10 hr under vacuum. Flask A was sealed off at constriction E. The monomer was stored over BaO (with occasional magnetic stirring) at room temperature for 48 hr. It was then degassed again through G and the assembly sealed off at G. Part of the monomer was distilled into ampoule H (fitted with a breakseal), sealed off, and stored for further use. The rest was distilled into tipping assembly I and sealed off at L. The monomer vials were prepared by the usual method and their contents determined by the midpoint method.[5] The infrared spectrum of the fractionated monomer is shown in Figure 2.

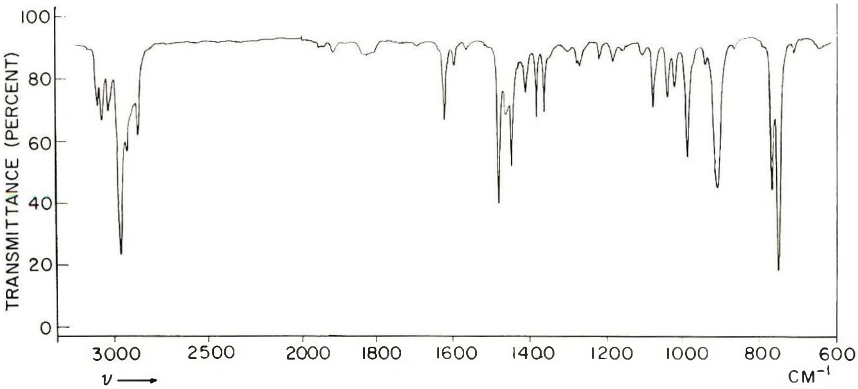


Fig. 2. Infrared spectrum of *o*-isopropylstyrene.

Methylene dichloride (Carlo Erba) was purified and dried. It was stored over sublimed P_2O_5 in a flask connected to the vacuum line through a dispensing buret and a metal valve.

Ethyl chloride (BDH) (ampoule A in Fig. 3) was distilled through H_2SO_4 (washing tower B) and collected over sublimed P_2O_5 in flask D attached to the vacuum line, frozen and sealed off at C. The solvent was then degassed through E which was then sealed off. Breakseal F was crushed and the solvent distilled into flask G, which contained BaO baked at 300°C under vacuum. The apparatus was sealed off at H. The solvent was dispensed to the polymerization assemblies through buret I and metal valve L.

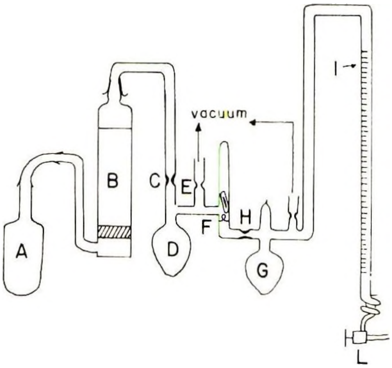


Fig. 3. Glass apparatus used in the purification of ethyl chloride.

Aluminum chloride (Schuchardt) was melted in an ampoule under vacuum, in the presence of aluminum powder. It was sublimed twice under vacuum and collected into vials.

Anhydrous aluminum bromide (Schuchardt) was transferred to a Pyrex ampoule containing some aluminum powder. The ampoule was evacuated and the aluminum bromide melted (some reflux) for 3 hr. The catalyst was then sublimed four times under vacuum and collected into vials.

Benzoyl peroxide (Carlo Erba) was crystallized from chloroform and dried under vacuum.

The origin and purity of materials used in the polymerizations carried out in the dry-box filled with nitrogen have been described previously.[6–8]

Procedure

The radical polymerization of *o*-iPrS was carried out by introducing a vial of monomer, together with 2.5 mg benzoyl peroxide (0.1 mole-%) into a Pyrex ampoule. This was then evacuated on the vacuum line and sealed off. The monomer vial was crushed with a magnet and the ampoule immersed in a bath at 75°C. After 48 hr the semisolid product was dissolved in benzene and the solution poured into methanol under agitation. The polymer was precipitated twice and dried under vacuum at 70°C for 24 hr.

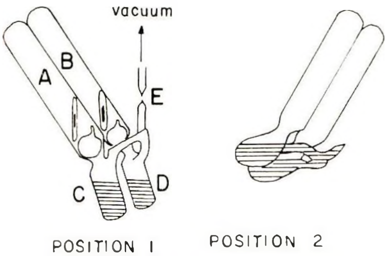


Fig. 4. Glass apparatus used in the polymerization of *o*-isopropylstyrene.

The cationic polymerizations of *o*-iPrS were carried out in the apparatus shown in Figure 4. The monomer vial was placed in arm A and the catalyst vial in arm B of the assembly. It was evacuated and the solvent was run into bulbs C and D. The assembly was sealed off at E and the vials were broken at room temperature. The mixing of the separate solutions was prevented by keeping the assembly in position I. The polymerization assembly was then immersed in a cooling mixture. For the polymerization at −90°C and −126°C, a CH_2Cl_2 and a methylcyclohexane cooling mush were employed, respectively.

After thermal equilibration, the apparatus was turned to position II and the monomer and catalyst solutions were mixed rapidly. Polymerization was terminated by melting with the torch a small hole at the top of one of the arms through which a small amount of precooled ammonia-methanol mixture was introduced. The polymer was separated by pecipitation into methanol as described above.

The monomer in ampoule H was stored in the dark at room temperature for about 60 days. During this time some of the monomer polymerized as shown by a slight increase in the viscosity of the liquid. This liquid was purified and used in further experiments as follows.

In a stainless steel dry box[5] filled with nitrogen (moisture content ~30 ppm), the ampoule was opened and methanol was added slowly in increments until no more polymer precipitated. The methanol, which contained the unreacted monomer, was carefully decanted. The polymer was washed with additional methanol, and the methanol fractions were combined. The polymer (0.713 g) was recovered and dried.

The combined methanol solution was washed with water four times. The monomer layer separated cleanly; it was stored over BaO at −20°C for one week. The purity was 99.8+% by GC.

This monomer was polymerized with $AlCl_3$ in ethyl chloride solution at −130 and −138°C. The catalyst solution was $AlCl_3$ dissolved in methyl chloride (0.063*M* $AlCl_3$ in CH_3Cl). All these experiments were carried out by first preparing a monomer–ethyl chloride mixture in a test tube, cooling the system to the selected temperature, and adding the catalyst solution (precooled to −78°C) slowly in increments. Polymerizations started immediately on the introduction of the first drop of catalyst as shown by the appearance of a yellow color, a slight temperature rise and the formation of a precipitate. Polymerizations were terminated by the introduction of precooled n-propanol, followed by precipitation into an excess of methanol and drying *in vacuo* at 50°C.

The softening ranges of the products were obtained by visual observation on a hot-stage microscope. The molecular weights were determined by a vapor pressure osmometer (Mechrolab 301 A) or a high-speed membrane osmometer (Hewlett-Packard 501). The infrared spectra were obtained with a Perkin-Elmer 521 instrument with polymer films prepared by evaporation of CS_2 or benzene solutions on KBr disks. For some polymers the spectra of CS_2 solutions or KBr pellets were also recorded. The NMR spectra were determined with 20% hexachlorobutadiene solutions and HMDS internal standards at 90 and 175°C with a Varian HA-100 instrument at 100 MHz and a JEOL 1000 (4HA) at 60 MHz.

RESULTS AND DISCUSSION

Results and polymerization conditions are shown in Table I.

Experiments 1–4 were carried out under high vacuum conditions, whereas runs 6–8 were done in a dry-box under nitrogen atmosphere. Sample 5 was obtained at room temperature during storage in the dark. Thus samples 1 and 5 are free-radical polymers whereas the others are cationically polymerized products. The NMR spectra of samples 2, 3, 4, 5, and 8 were recorded and analyzed.

Figure 5 shows the NMR spectrum of a polymer obtained with $AlCl_3$ at $-138°$ (sample 8 in Table I). The spectrum was recorded at 90°C in hexachlorobutadiene solution with HMDS as internal lock signal. The scan consists of four broad peaks at 3.18 (6.82), 7.38 (2.62), 8.54 (1.66) and 9.23τ (0.77 ppm) which are assigned, respectively, to the aromatic, methine, methylene and methyl protons. The prominent feature of the spectrum is the doublet ($J \sim 6.2$ cps) superimposed on the methyl peak at 9.23τ. The

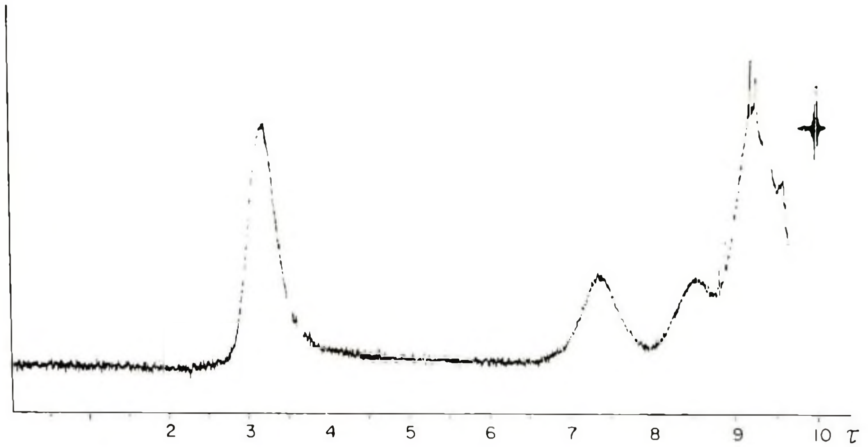


Fig. 5. NMR spectrum of poly-o-isopropylstyrene (sample 8 in Table I).

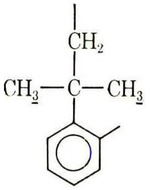
TABLE I

Polymerization of *o*-Isopropylstyrene with Free-Radical and Cationic Initiators

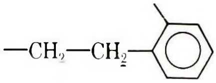
Sample	Initiator	Solvent	Initiator concn, mole/l.	Monomer concn, mole/l.	Temp, °C	Time	Conversion, %	$\bar{M}_n \times 10^{-3}$	Softening range, °C
High Vacuum Experiments									
1	Bz_2O_2	—	0.1 mole-%	Neat (5.75)	75	2 days	54	27	
2	$AlCl_3$	CH_2Cl_2	3.85×10^{-3}	0.4	−85 to −90	17 hr	36	10	154–174
3	$AlBr_3$	C_2H_5Cl	5.93×10^{-3}	0.4	−126	10 min	68	47.2	123–150
4	$AlBr_3$	CH_2Cl_2	5.84×10^{-3}	0.4	0	10 min	28	31.4	112–129
Dry-box Experiments									
5	—	—	—	Neat (5.75)	Room	60 days		25.5	117–170
6	$AlCl_3$	C_2H_5Cl	1.9×10^{-5}	2.94	−125 to −130	10 min	11.2		
7	$AlCl_3$	C_2H_5Cl	3.7×10^{-5}	1.96	−127 to −130	90 min	28.1	21.0	159–197
8	$AlCl_3$	C_2H_5Cl	8.8×10^{-4}	1.96	−137 to −138	41 min	34.1	30.87	174–202

doublet indicates the presence of isopropyl groups. Higher temperatures (e.g., 175°C) did not result in improved resolution; the methyl doublet at 9.23τ tends to collapse to a broad peak in spectra recorded at elevated temperatures. This effect was also noted by Aso et al.[2]

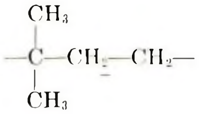
While the NMR spectrum of the poly-*o*-iPrS agrees well with that expected of a conventional polymer, NMR evidence alone is insufficient to refute conclusively the presence of hydride-rearranged structures. In other words, on the basis of the available NMR data it is impossible to exclude the possibility that signals due to geminal dimethyl groups



might be hidden under the ill-resolved methyl band and to exclude with finality the possibility that the 7.38τ band might be due to



while the 8.54τ band is only due to



$$-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-CH_2-$$

We confirm the Japanese workers' claim that the NMR spectra of polymers obtained with cationic initiators under various conditions are essentially the same. The only difference worth noting between our NMR data and those of the Japanese investigators is in the position of the peaks: For example, the methyl peak reported by Aso et al.[2] is at 1.1 p.m or 8.9τ, whereas in our spectrum it falls at 9.23τ. This difference is quite large and cannot be attributed to a difference in lock-signals. Indeed the 9.23τ band with HMDS is expected to be at about 9.18τ with TMS. This discrepancy might be due to the different solvents used in these studies (*o*-dichlorobenzene by Aso et al. and hexachlorobutadiene by us).

The strongest argument against rearrangement from our NMR studies is the fact that polymers produced by radicals and by Lewis acids gave essentially identical spectra. However, as stated above, in spite of efforts in this direction the resolution of these spectra was insufficient for a detailed, meaningful structure analysis.

Infrared spectroscopy proved to be more fruitful in our structure studies. Infrared spectra of all samples were recorded and analyzed. Figure 6 compares two representative infrared spectra: one obtained with a polymer sample prepared by $AlBr_3$ at −125° (sample 3 in Table I) and another

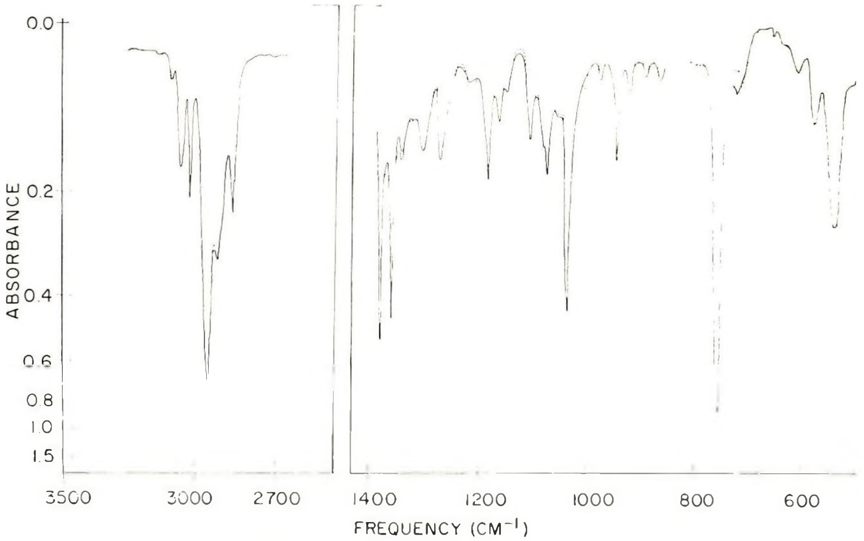


Fig. 6. Comparison of infrared spectra of poly-*o*-isopropylsytenes: (——) cationic polymer ($AlBr_3$ at −125°C); (. . .) free-radical polymer (Benzoyl peroxide at 75°C).

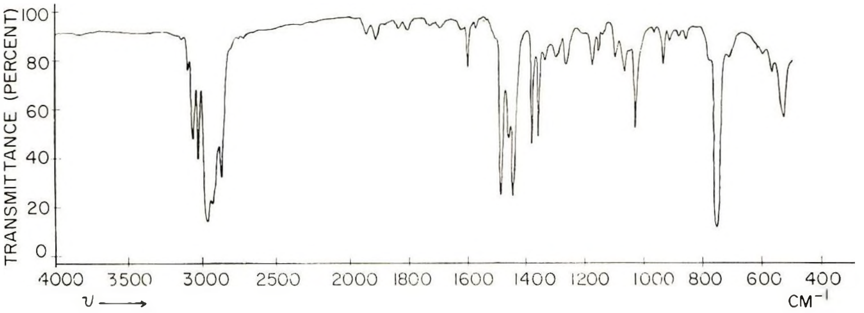


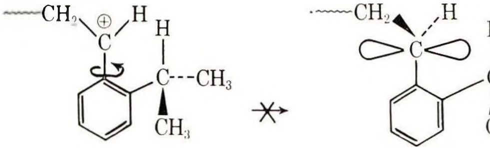
Fig. 7. Infrared spectrum of a cationic poly(*o*-isopropylstyrene (sample 2 in Table I).

produced by benzoyl peroxide at 75°C (sample 1 in Table I). Conclusively, these spectra are essentially superimposable. This is strong evidence that in spite of the fundamentally different polymerization conditions the two polymers are essentially of the same structure. Since the polymer synthesized by benzoyl peroxide initiation is most likely of a conventional structure and does not contain rearranged structures, we conclude that the cationically polymerized product is also of a conventional structure. Indeed, all the polymer samples obtained in our studies showed essentially identical and superimposable infrared spectra. A detailed examination of the individual spectra confirms the conclusion that both the radical and Lewis acid polymerized samples are identical and of conventional enchainment. Figure 7 is the spectrum of a polymer prepared with $AlCl_3$ at about −90°C (sample 2 in Table I). It indicates clearly *ortho* disubstitution (peaks at 754 cm^{-1} for out-of-plane wagging of four adjacent aromatic hydrogens, plus stretching frequencies at 1444, 1485, 1572, and 1598 cm^{-1} and above 3000 cm^{-1}, plus the characteristic six band overtone range between 1650 and 1950 cm^{-1}) and the presence of isopropyl groups (peaks at 1160, 1180, 1360, 1380, 1443, and the doublet in the range 2920–2960 cm^{-1}). The fact that of the two methyl peaks at 1360 and 1380 cm^{-1} the latter is the stronger one, indicates the predominance of isopropyl groups in preference to geminal dimethyls. Also, all the samples analyzed exhibit, within what is considered to be experimental variation, about the same absorption ratio D_{1180}/D_{1380} (i.e., the ratio of intensities of the peaks at 1180 and 1380 cm^{-1}) associated probably with an isopropyl vibration and symmetric CH_3 deformation, respectively. This indicates that the relative amount of isopropyl groups in the polymers obtained by radical and cationic techniques under various conditions remains essentially the same.

Aso and co-workers,[2] on the basis of infrared results, concluded that the cationically polymerized polymer contained about 20% of rearranged repeat units. These workers used the absorption ratio D_{1180}/D_{3060}, i.e., the ratio of intensities associated with isopropyl groups and aromatic protons, respectively, for the characterization of their polymers. The conclusions of the Japanese investigators based on infrared results are in error because of the following facts. (*1*) The use of the 3060 cm^{-1} band, associated with aromatic C–H vibration, as an internal standard is objectionable because of the possibility of ring alkylation during carbonium ion polymerization. Such ring alkylation during polymerization would decrease the intensity of this reference band. Very rapid ring alkylation might occur during carbonium ion polymerization even at very low temperatures.[9,10] (*2*) The differences between the infrared intensity ratios obtained by Aso et al.[2] with polymers prepared by various catalysts are too small and may be due to subjective errors in drawing the base-lines. The low intensity of the 1180 cm^{-1} band (as compared to the high intensity of the 3060 cm^{-1} band), coupled with the modest resolution of Aso's infrared spectra, is a dangerous combination for quantitative infrared work. Even with our better resolved spectra, by drawing acceptable but slightly different baselines for the peaks in question, we have obtained ~20% variation in the calculated intensity ratios.

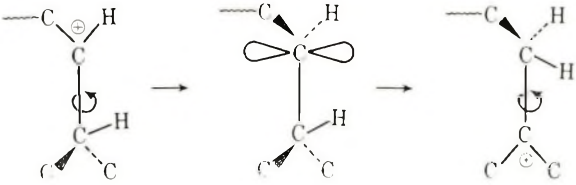
THEORETICAL CONSIDERATIONS

From the theoretical point of view the trans-spatial hydride-jump as postulated earlier[1] is rather unlikely. The gist of the argument is that the initially formed benzyl cation would lose conjugation energy during $H^{\ominus}$ migration, which is energetically unfavorable [eq. (4)].



(4)

In other words, in order to reach a favorable orbital overlap between the empty p orbital and the H of the isopropyl group, the p orbital would be required to rotate a full 90° and thus would lose its conjugation with the aromatic ring system. Most likely the carbonium ion is reluctant to give up this conjugation energy which in effect amounts to an unsurmountable energy barrier to rearrangement. These considerations, of course, do not hold for open-chain aliphatic rearrangements where resonance stabilization with aromatic rings does not exist. Indeed aliphatic 1,2 hydride shifts involving isopropyl structures occur quite readily[1] [eq. (5)].



(5)

The hydride-jump mechanism would also be forbidden by the Woodward-Hoffman orbital symmetry rules. According to the conservation of orbital symmetry, 1,4 sigmatropic shifts constrained to proceed suprafacially (of which an example would be the hydride jump proposition) must take place with inversion at the migrating group. Since in the o-isopropylstyryl carbonium ion the hypothetical migrating group would be a hydride ion, i.e., a group which cannot invert, such a migration would not be allowed.*

The authors gratefully acknowledge Mr. G. Turchi's help in the synthesis of o-isopropylstyrene.

References

1. J. P. Kennedy, in *Encyclopedia of Polymer Science and Technology*, Interscience, New York, 1967, Vol. 7, p. 754.
2. C. Aso, T. Kunitake, and S. Shinkai, *Kobunshi Kagaku*, **26**, 280 (1969).
3. M. Crawford and F. H. C. Stewart, *J. Chem. Soc.*, **1952**, 4443.
4. E. C. Sterling and M. T. Bogert, *J. Org. Chem.*, **4**, 20 (1939).
5. P. P. Rutherford, *Chem. Ind.* (London), **1962**, 1614.
6. J. P. Kennedy and R. M. Thomas, *Advan. Chem. Ser.*, **34**, 111 (1962).
7. J. P. Kennedy and R. G. Squires, *Polymer*, **6**, 579 (1965).
8. J. P. Kennedy and R. M. Thomas, *J. Polym. Sci.*, **49**, 189 (1961).
9. J. P. Kennedy and R. B. Isaacson, *J. Macromol. Sci.*, **1**, 541 (1969).
10. J. P. Kennedy, C. A. Cohen, and W. Naegele, *J. Polym. Sci. B*, **2**, 1159 (1964).

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Complex of Copper(II) with Phenoxo and Hexamethylphosphoramide Ligands and Its Decomposition

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Synopsis

The 2,4,6-trichlorophenoxo-hexamethylphosphoramide(HMPA)-copper(II) complex was isolated by the reaction of copper(II) chloride with 2,4,6-trichlorophenol, sodium methoxide, and HMPA in methanol solvent under an atmosphere of nitrogen. This complex has the composition of $Cu \cdot HMPA \cdot 2(C_6H_2Cl_3O)$. The molecular weight determination was consistent with the copper(II) complex of binuclear structure. The infrared, electronic, and ESR spectra and magnetic susceptibility of the copper(II) complex are discussed in relation to its structure. Decomposition of the copper(II) complex in refluxing benzene yielded poly(dichlorophenylene oxide), coupling product of the 2,4,6-trichlorophenoxo ligand of the copper(II) complex. Electron spin resonance (ESR) measurements on the copper(II) complex in the solid state in a degassed sealed tube at 120 ± 5°C indicated that the phenoxy radical was generated during the period of decomposition and the intensity of the ESR spectra based on copper(II) ion decreased with the measurement time. From these ESR spectra, a possible initial step involving one electron transfer of the decomposition of the 2,4,6-trichlorophenoxo-HNPA-copper(II) complex is discussed.

INTRODUCTION

It has been reported[1] that the complex of copper(I) salt with an amine such as pyridine under oxygen has a catalytic activity for the oxidative coupling reaction of the phenolic derivatives. Blanchard et al.[2] reported that in the oxidative coupling reaction, the active oxidizing agent is the cupric ion-pyridine complex and the role of the oxygen is to keep the copper(I) ions in the divalent state. They also prepared a number of copper(II)-phenoxo-pyridine complexes and made clear their characteristics; they furthermore decomposed the copper(II) complexes to obtain poly(dihalogenophenylene oxide).

In order to synthesize aromatic ether polymer, the oxidative displacement reactions of halogenated phenol derivatives with a variety of oxidizing agents have been reported by a number of workers.[3-6] More recently, a series of phenoxo complexes of copper(II) containing a variety of halophenoxo ligands and a variety of amine ligands has been prepared by Harrod.[7]

In the preceding papers[8,9] the oxidative coupling polymerization of 2,6-dimethylphenol with the copper(I) chloride–hexamethylphosphoramide (HMPA) system was described.

In this paper we will report on the preparation and properties of complex of copper(II) with phenoxo- and HMPA ligands which may be considered as a model of the reaction intermediate of the oxidative coupling reaction of phenol derivatives. The phenol derivative dealt with in this report is 2,4,6-trichlorophenol. Elementary analysis as well as molecular weight determination showed the 2,4,6-trichlorophenoxo–pyridine–copper(II) complex isolated by Blanchard et al.[2] to have the composition $(C_6H_2Cl_3O)_2 \cdot Cu \cdot (Pyridine)_2$ which was a mononuclear structure. Harrod[7] prepared a series of the similar monomeric copper(II)–phenoxo–amine complex. However, with the present HMPA ligand instead of amine, the copper(II) complex obtained had the composition $(C_6H_2Cl_3O)_2 \cdot Cu \cdot (HMPA)$, hence the formulation and the properties of the present complex of copper(II) obtained had the composition $(C_6H_2Cl_3O)_2 \cdot Cu \cdot (HMPA)$, hence the formulation and the properties of the present complex of copper(II) obtained with 2,4,6-trichlorophenoxo- and HMPA ligands are worthy of investigation. Also, to study the initial step of the decomposition of the present copper(II) complex, ESR measurements were carried out.

EXPERIMENTAL

Reagents

Methanol was refluxed with magnesium metal and distilled two times. Reagent grade anhydride copper(II) chloride was used after drying at 110°C under vacuum for 5 hr. Reagent-grade sodium methoxide was used without further purification. 2,4,6-trichlorophenol was purified by recrystallization from n-hexane.

Preparation of 2,4,6-Trichlorophenoxo–HMPA-Copper(II) Complex

A 1.35-g (0.01 mole) portion of copper(II) chloride was dissolved in 40 ml of methanol. To the clear, green, homogeneous solution was added 3.95 g (0.02 mole) of 2,4,6-trichlorophenol, followed by the addition of 10 ml methanolic solution of 1.08 g (0.02 mole) of sodium methoxide. To the resulting heterogeneous brown mixture was added 4.5 ml (0.025 mole) of HMPA. The whole was stirred magnetically for 2 hr, the resulting solid were collected by filtration, and the weight of this solid was 5.0 g. This solid was recrystallized from hot benzene solution containing a small amount of HMPA. The reaction described above was performed at 0°C under a nitrogen atmosphere.

ANAL. Calcd for $(C_6H_2Cl_3O)_2 \cdot Cu \cdot (HMPA)$: C, 33.97%; H, 3.46%; N, 6.61%. Found: C, 34.24%; H, 3.98%; N, 6.58%.

Microanalyses were performed by the Microanalysis Center, Kyoto University.

Infrared Spectrum

The infrared spectrum of the copper(II) complex was obtained on a Shimadzu spectrophotometer Model IR-27. A potassium bromide disk of the solid was used.

Electronic Spectrum

The far-infrared spectrum of the complex was obtained with a Hitachi recording spectrophotometer, Model ESP-3T. Visible and Ultraviolet spectra were measured by Shimadzu spectrophotometer Model UV-50M instrument. All spectra of the complex were obtained in benzene solution which was purified by a standard procedure; 1-cm. cells were used.

Electronic Spin Resonance (ESR) Spectra

At Room Temperature. The ESR Spectra of the complex obtained with a Model JES-3BS-X instrument of JEOL Co. equipped with 100 KHz modulation. The complex was measured in the solid-state at room temperature with the use of Mn^{++} as *g*-maker.

At 120 ± 5°C. The copper(II) complex was placed in a sample tube, and the sample tube was attached to a vacuum line. After removal of the air in the sample tube, the sample tube was sealed off under reduced pressure, and the temperature of the ESR cavity was raised to 120 ± 5°C. The time-dependent ESR spectra at 120 ± 5°C were measured through a period of about 2 hr.

At Low Temperature. ESR measurements on the copper(II) complex in sealed tubes at −67 and −120°C were performed with variable-temperature equipment. The ESR spectrum of the complex at −196°C was obtained by using a quartz Dewar.

Magnetic Susceptibility Measurements

The measurement of magnetic susceptibility was carried out by a Shimazu Model MB-1A magnetic balance. Diamagnetic corrections were estimated from Pascal's constants and the magnetic moments were corrected for N_α by using the equation:

$$\mu_{\text{eff}} = \sqrt{8T(\chi_M - N_\alpha)}$$

where T is the absolute temperature, χ_M the magnetic susceptibility per gram ion; N_α, the temperature-independent contribution arising from the second-order Zeeman splitting, is given its usual value of 6×10^{-5} cgsu.

Molecular Weight Measurement

Molecular weight determination of the complex was made by a cryoscopic method with the use of reagent-grade benzene solution.

Decomposition of the Copper(II)–HMPA–2,4,6-Trichlorophenoxo Complex

A 1-g portion of the copper(II)–HMPA–2,4,6-trichlorophenoxo complex was thermally decomposed by refluxing a solution of the copper(II) complex in 30 ml of benzene. Following reflux for 5.5 hr, a brown precipitate was formed and removed by filtration. The filtrate was poured into 100 ml of methanol to yield a white precipitate (0.42 g). This white precipitate was identified as poly(dichlorophenylene oxide) by its infrared spectrum and elementary analysis.

ANAL. Calcd for $C_6H_2Cl_2O$: C, 44.76%; H, 1.25%; Cl, 44.05%. Found: C, 44.56%; H, 1.36%; Cl, 42.84%.

The polymer obtained was a white, amorphous material with a softening range of 210–230°C. This polymer had intrinsic viscosity in chloroform at 25°C of 0.08 dl/g.

The precipitate isolated changed gradually in color from brown to yellow green on standing in an air atmosphere. Although further identification of the precipitate was not performed, the precipitate is thought to be a copper(II) complex with HMPA as ligand on the basis of its infrared spectrum.

Nuclear Magnetic Resonance Spectra of the Polymer

The proton NMR spectrum of the polymer was obtained at 220 MHz by using a Varian HR 220-MHz spectrometer with TMS as an internal standard. The spectrum of polymer was taken in $CDCl_3$ at room temperature. The NMR spectrum of poly(2,6-dimethyl-1,4-phenylene oxide), which was synthesized by the copper-amine method,[1] was taken on a JEOL-3H-60 spectrometer at 60 MHz by using $CDCl_3$ solvent containing TMS as an internal standard.

RESULTS

The analytical data for the copper(II) complex with HMPA and 2,4,6-trichlorophenoxo group shows that this complex has the composition, $(C_6H_2Cl_3O)_2 \cdot Cu \cdot (HMPA)$. The molecular weight of the copper(II) complex determined by a cryoscopic method was about 1200, which corresponds to twice that (636) of the formula of $(C_6H_2Cl_3O) \cdot Cu \cdot (HMPA)$. The complex has a brown color and the decomposition point of this complex was ca. 146°C. The complex is soluble in benzene but decomposes slowly over a long period of time. The decomposition of the copper(II) complex is avoided in benzene containing a small amount of HMPA. In methanol, the brown copper(II) complex is not soluble and decomposes to produce a yellow-green precipitate.

The infrared spectrum of the complex obtained is shown in Figure 1. As shown in Figure 1, the infrared spectrum definitely indicates the absence of the O—H stretching of 2,4,6-trichlorophenol and/or water in the copper(II)

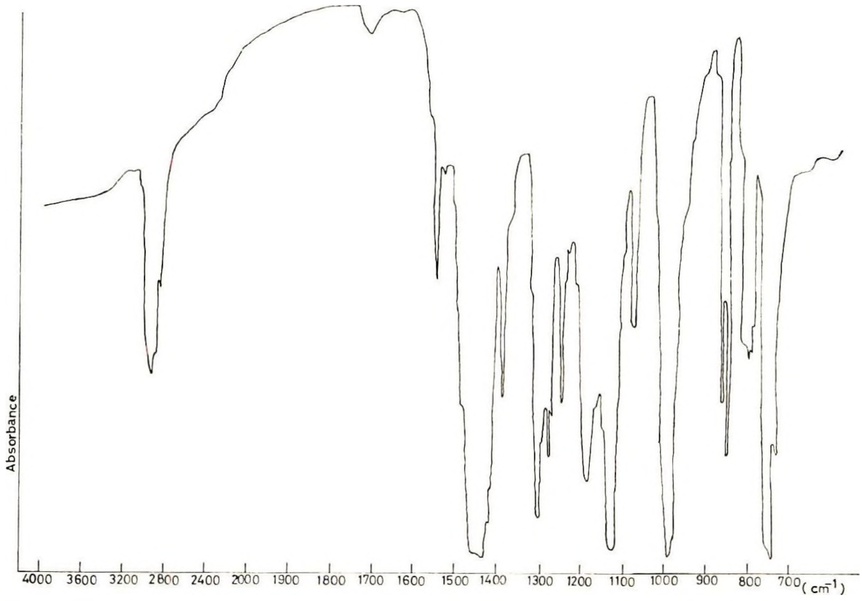


Fig. 1. Infrared spectrum of the copper(II) complex with 2,4,6-trichlorophenoxo and HMPA as ligands (KBr disk).

complex. Donoghue and Drago[10] synthesized a complex of copper(II) salt with HMPA which had the formula, $Cu\cdot(NO_3)_2\cdot 2HMPA$, and assigned 1188 cm^{-1} to the P=O stretching of HMPA. On the basis of this result, the absorption near 1185 cm^{-1} in Figure 1 is assigned to the P=O stretch-

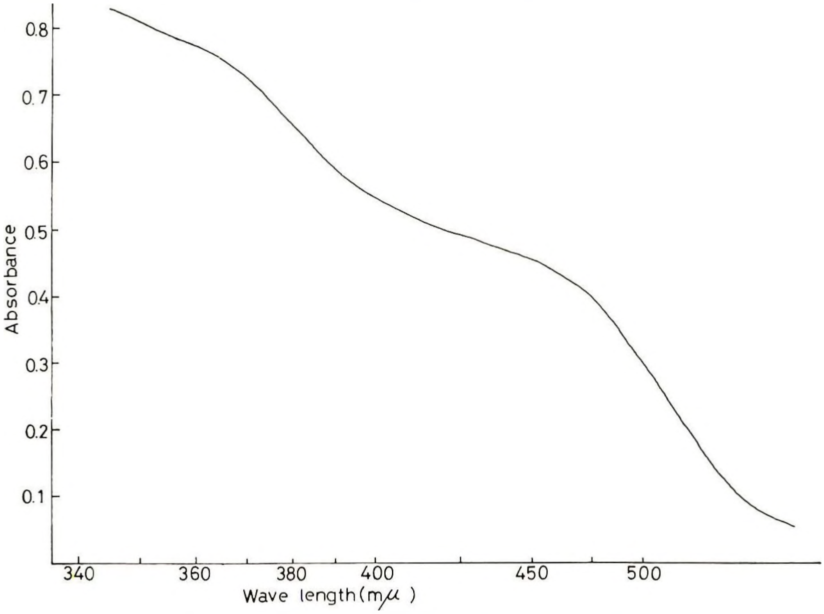


Fig. 2. Absorption spectrum of the copper(II) complex (visible ray region).

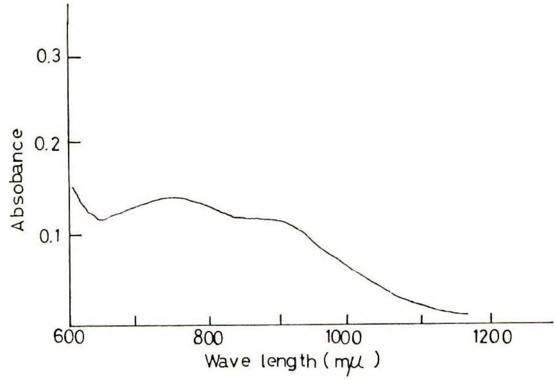


Fig. 3. Absorption spectrum of the copper(II) complex (far-infrared region).

ing of HMPA of the present copper(II) complex. Also, the band near 2900 cm^{-1} is assigned to the C—H stretching of $N(CH_3)_2$ moieties of HMPA. On the other hand, the absorptions at 1475, 1280, 860, and 740 cm^{-1} in Figure 1 may be due to 2,4,6-trichlorophenoxo moieties, since the infrared spectrum of 2,4,6-trichlorophenol showed the absorptions in the same region noted above. The electronic spectra of the copper(II) in benzene solution are summarized in Figures 2 and 3. The λ_{max} of the complex appears in Table I.

This copper(II) complex is paramagnetic at room temperature. Figure 4 shows the ESR spectrum of the copper(II) complex at solid state at room temperature; both an anisotropic spectrum at near 3000 G and a broad spectrum at near 5500 G are observed. The intensity of the latter spectrum depends upon the measurement temperature, and decreases with the decrease of the measurement temperature as shown in Figure 5. Its behavior resembles that of an ion of spin 1 and parallels the decreasing magnetic susceptibility obtained by susceptibility measurement. The former spectrum, which consists of four lines in $g_{\parallel}$ and one line in $g_{\perp}$, is a typical one caused by Cu(II) ion and indicates that the copper(II) complex is a distorted octahedral or square-planar structure.

TABLE I
Absorption Spectra Data for 2,4,6-Trichlorophenoxo-HMPA-Copper (II) Complex and $Cu(NO_3)_2 \cdot 2HMPA$ Complex

Copper(II) complex (in benzene)		$Cu(NO_3)_2 \cdot 2HMPA$ (in CH_3NO_2)[a]	
λ_{max}, mμ	ϵ per copper ion	λ_{max}, mμ	ϵ'
336	(shoulder)		
465	(shoulder)	378	55
740	108	750	110
910	(shoulder)		

[a] Data of Donoghue and Drago.[10]

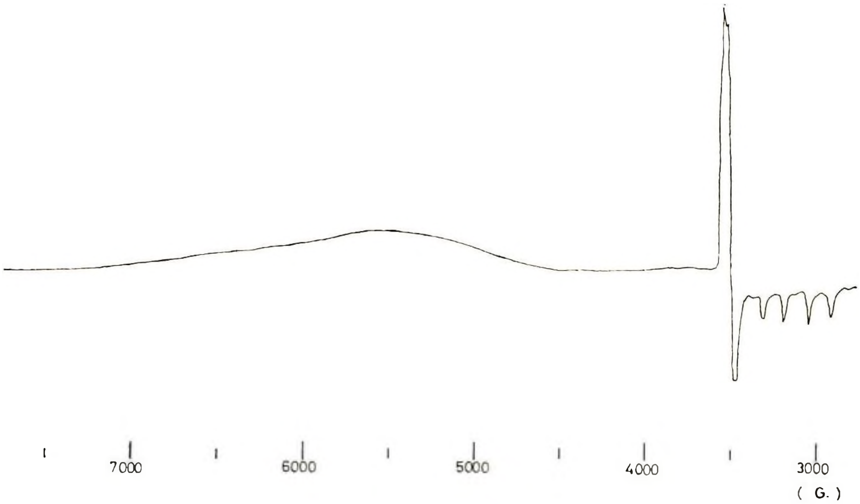


Fig. 4. ESR spectrum of the copper(II) complex (room temperature).

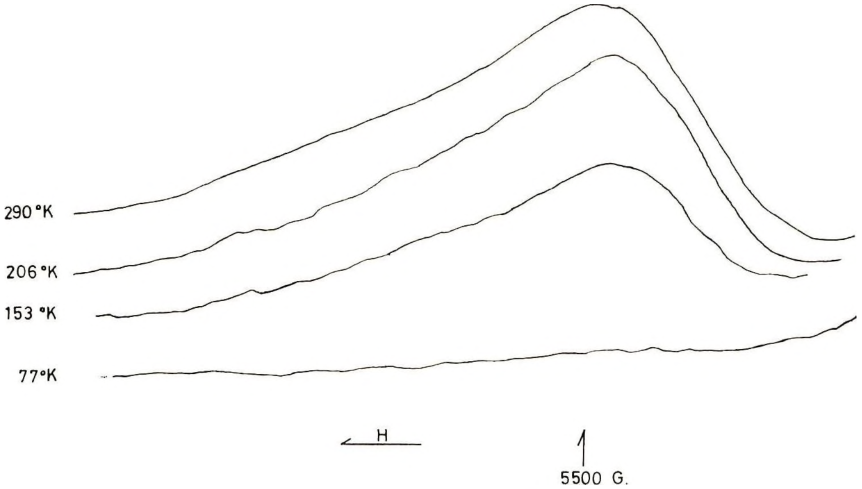


Fig. 5. Variation of the intensity of the ESR spectra of the copper(II) complex at near 5500 G with measurement temperature.

The magnetic moment of the copper(II) complex at 25°C was 1.25BM. This value is smaller than 1.73 BM, which is the magnetic moment of the general mononuclear copper(II) complex.

Figure 6 shows the variation of magnetic susceptibility of the complex with measurement temperature. The magnetic susceptibility exhibits a maximum at about 280°K and then decreases as the temperature falls. Hence, the susceptibility seems to be explained by assuming that isolated pairs of copper ions were coupled together by an exchange force, each pair forming a lower singlet state and an upper triplet state, the latter only being paramagnetic. Decomposition of the present copper(II) complex in benzene at its boiling point yielded the polymer. The polymer

$$\text{2,4,6-trichlorophenoxo–HMPA–copper(II) complex} \xrightarrow{\Delta} \text{poly(dichlorophenylene oxide)}$$

obtained was identified as poly(dichlorophenylene oxide) by elementary analysis, and its infrared spectrum is shown in Figure 7. Blanchard et al.[2] suggested that poly(dihalophenylene oxide) obtained by the decomposition of phenoxo–pyridine–copper(II) complex is branched, since its infrared spectrum indicates there is little or no residual hydroxyl, and also the relation between intrinsic viscosity and molecular weight of the polymer is unreasonable for a linear chain structure. As shown in Figure 7, the infrared spectrum hardly possesses a residual hydroxyl absorption, which is consis-

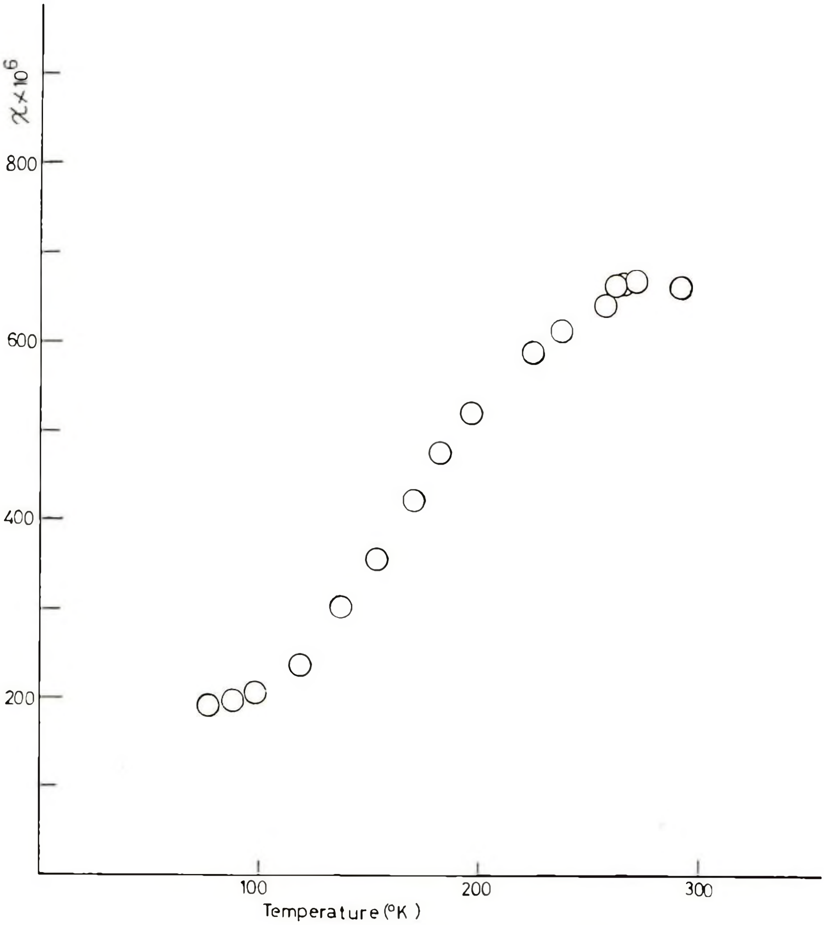


Fig. 6. Variation of magnetic susceptibility with temperature for the copper(II) complex.

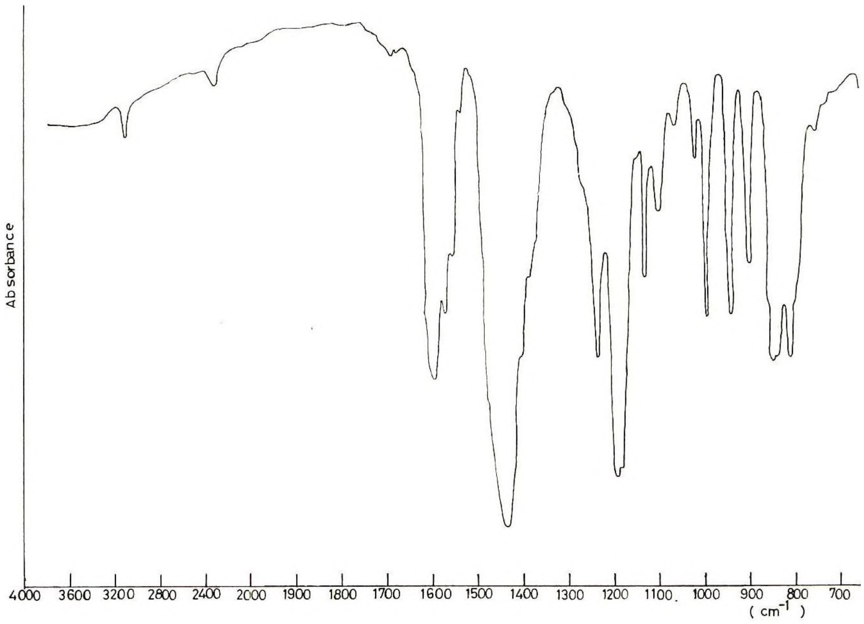
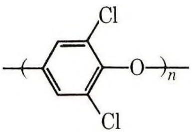


Fig. 7. Infrared spectrum of the polymer obtained (KBr disk).

tent with the structure of the polymer obtained by Blanchard et al. This observation is not, however, conclusive evidence for structural assignment of polymer. We tried to obtain the 220 MHz NMR spectrum of the polymer to gain more conclusive data which would indicate whether the polymer is a linear chain or a branched structure. The NMR spectrum of polymer is shown in Figure 8. If the structure of polymer is linear,



the signal of the phenyl ring protons would be observed as a singlet.* The spectrum actually obtained, however, gave a different figure which showed overlapped broad peaks around τ2.3–4.7. The observation of these peaks would indicate the presence of some phenyl rings which have different substituents. To judge from this result, it is reasonable to consider that the polymer obtained has a branched structure, for example, resulting from addition of *ortho* halogen on elimination of *para* halogen in the phenyl ring.

* The NMR spectrum of poly(2,6-dimethyl-1,4-phenylene oxide), which is considered a linear chain structure, showed a singlet based on phenyl ring proton at τ = 3.76 and a singlet based on methyl proton at τ = 7.99 ($CDCl_3$, 60 MHz). The NMR spectrum of this polymer is shown in Figure 9.

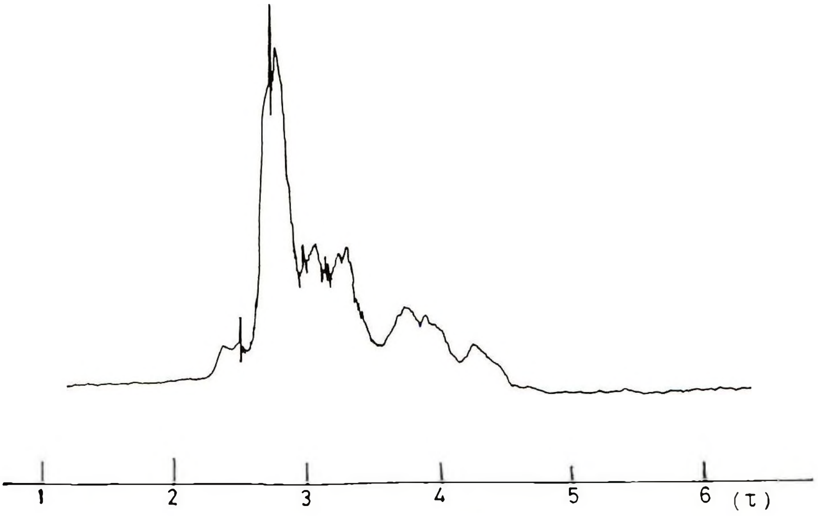


Fig. 8. NMR spectrum of the polymer obtained (in $CDCl_3$, 220 MHz).

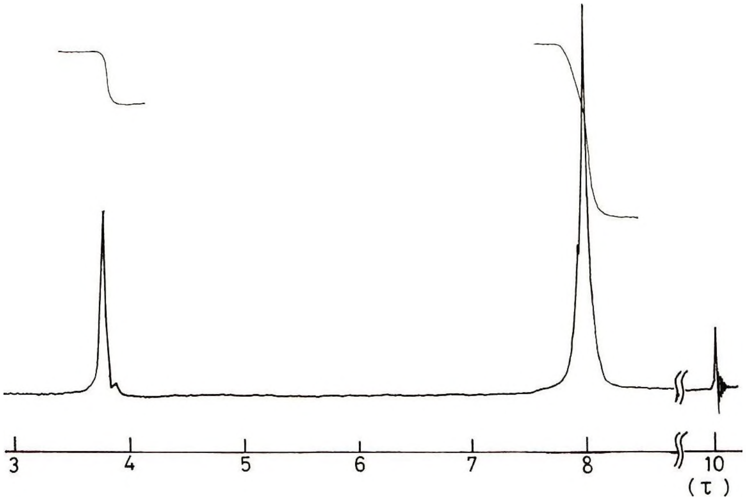


Fig. 9. NMR spectrum of poly(2,6-dimethyl-1,4-phenylene oxide) (in $CDCl_3$, 60 MHz).

To study the process of thermal decomposition of the copper(II) complex, ESR measurements of the copper(II) complex in an out-gassed, sealed tube were performed at 120 ± 5°C. The ESR spectra of the copper (II) complex are shown in Figure 10. At the initial stage of elevated temperature, the ESR spectrum was similar to that shown in Figure 4. But as shown in Figure 10, one peak appears at near $g = 2$ in the process of thermal decomposition. Though the hyperfine structure was not observed under the present condition (see Discussion), this peak may be due to a free radical which is presumably a intermediate in the process of thermal decomposition as Ochiai[11] suggested for the ESR spectra of $CuCl_2$–pyridine–

OH$^-$ or oxidized CuCl–pyridine with 2,6-di-*tert*-butylphenol. On the other hand, the intensity of the spectrum based on copper(II) ion decreased with the measurement time. Until about 30 min from the initial time the intensity of free radical increased. Thereafter, however, the intensity of the free radical began to decrease. The intensity based on copper(II) ion almost disappeared after 100 min.

DISCUSSION

The infrared spectrum of the copper(II) complex obtained shows that this complex has a phenoxo group and HMPA as a ligand. Donoghue and Drago[10] has reported that in the Co(II), Ni(II), and Cu(II) complexes with HMPA, the reduction of the P = O stretching frequency as compared with the value in the free ligand indicates that complex formation occurs through the oxygen on the ligand molecule, HMPA. In the present complex, the P = O stretching frequency was near 1185 cm^{-1}. This result indicates that

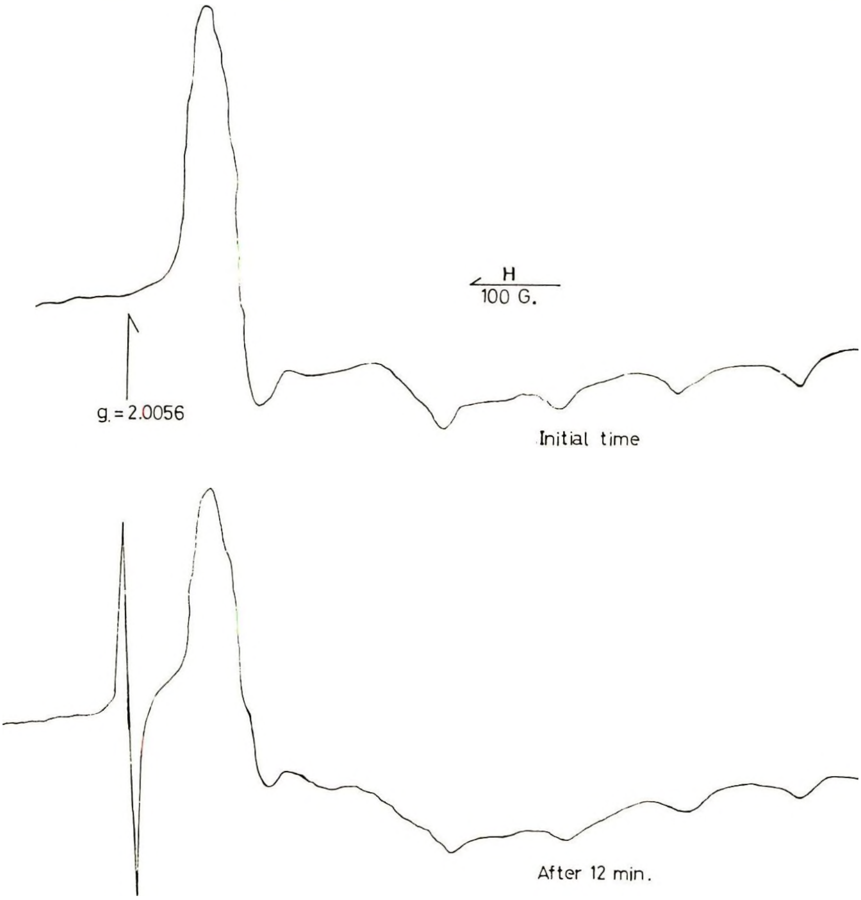


Fig. 10 (*continued*)

the present phenoxo–HMPA–copper(II) complex formation occurs also through the oxygen on the HMPA molecules. It is also evident from the infrared spectrum that this copper(II) complex does not contain water.

The elementary analysis of the copper(II) complex showed that this complex has the composition, $Cu\cdot(C_6H_2Cl_3O)_2\cdot HMPA$, and also that the molecular weight is compatible with the view that the complex has a binuclear structure.

The copper(II) ion has one unpaired electron in the $3d$ shell, and its ion was considered to have a magnetic moment close to the spin-only value, 1.73 BM. However, copper(II) compounds having a subnormal mag-

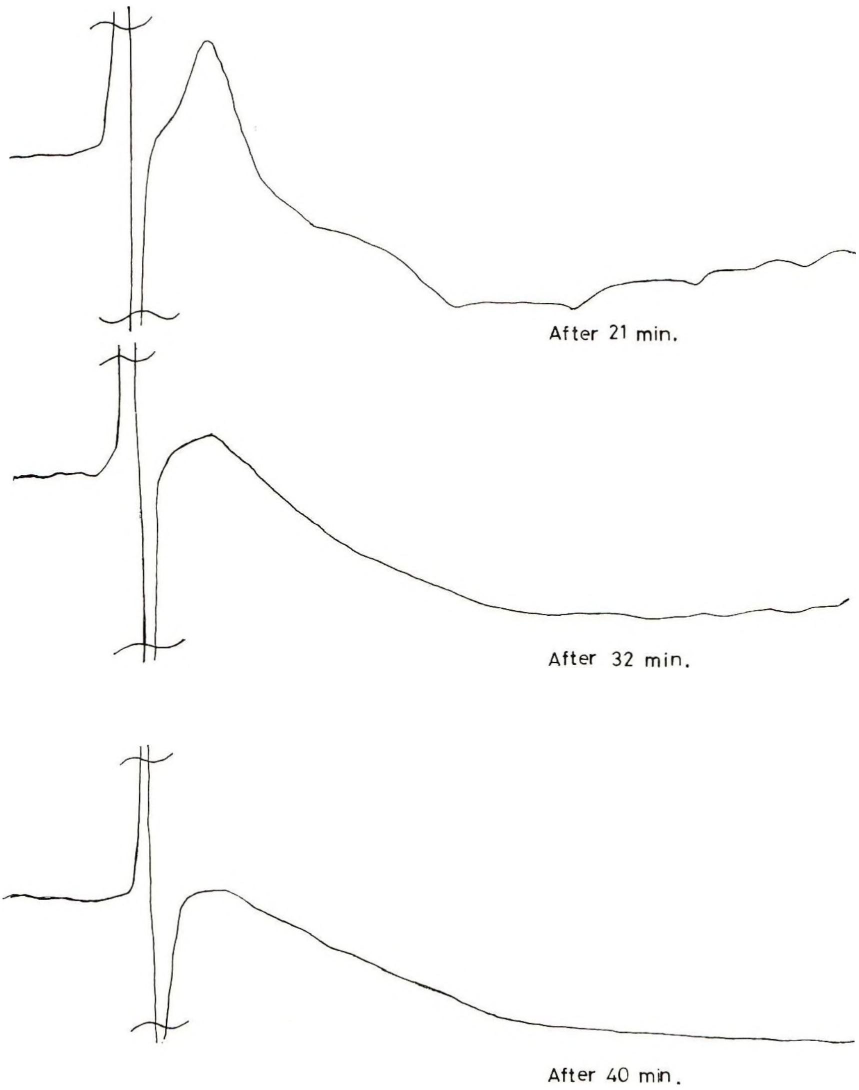


Fig. 10 (*continued*)

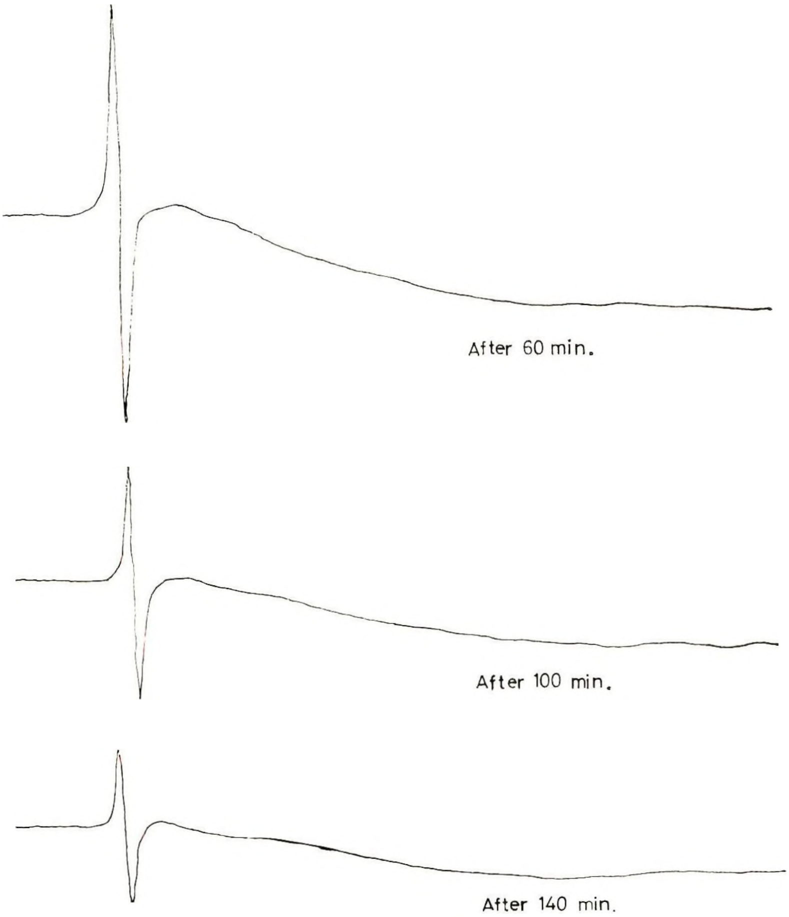


Fig. 10. Variation of ESR spectra of the copper(II) complex in out-gassed sealed tube at 120 ± 5°C.

netic moment, less than 1.73 BM, are dimeric, containing two copper(II) ions in a molecule.[12] The magnetic moment at room temperature of the solid complex as given in the preceding section is a subnormal value, apart from 1.73 BM. This finding is in accord with the conclusion that this complex is a binuclear structure.

The variation curve of magnetic susceptibility of the copper(II) complex with temperature shows the pairwise antiferromagnetic interaction. In general,[13] the magnetic properties of spin = 1 are well explained by the phenomenon mentioned above, the therefore this fact is strong evidence that the present copper(II) complex obtained has a binculear structure.

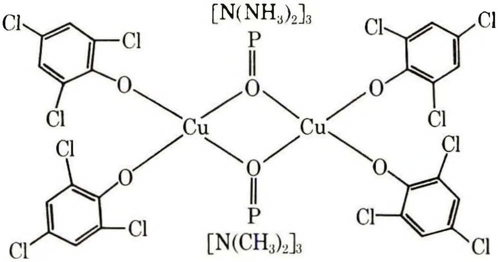
Kokoszaka et al.[14] have observed the ESR spectra of polycrystalline form of copper propionate monohydrate, and found a high-field (near 5800 G), parallel component of the spin = 1 spectrum at the X band. From the above observation, the ESR peak at near 5500 G in Figure 4 will be considered to be one based on spin = 1, although no copper nuclear hyperfine structure was observed. Also, as shown in Figure 5, the tendency of the intensity of the ESR peak to decrease with decreasing the measurement temperature, finally to disappear at liquid nitrogen temperature, may be strong evidence[13] that the ESR absorption at near 5500 G is based on spin = 1, resulting from isolated pairs of copper(II) ions. This tendency is consistent with the temperature dependence of the magnetic susceptibility noted above.

These magnetic properties indicate that the present copper(II) complex is a binuclear structure in which the copper–copper ion interaction in a molecule is different from that of a monoculear structure such as copper(II)–phenolate–amine complex. However, in the anisotropic spectrum in the region of about 3000 G of normal mononuclear copper(II) compounds which have axial symmetry it is rather difficult to make assignments. It appears reasonable that the signal is caused by a small amount of spin = $^1/_2$ species which are monomeric copper(II) species.[14]

Harrod[7] studied the absorption spectrum of the phenoxo–amine complexes of copper(II) and discussed in terms of four regions: a ligand band system in the 40–50 kK (1 kK = 1000 cm^{-1}) region; the 35 kK system, arising, at least partly, from a phenolate ligand transition; the 27 kK band appearing as a shoulder; and the 20 kK band which is suggested as a metal-to-ligand charge transfer. As shown in Table I, the bands at 366 mμ (27 kK) and 465 mμ (22 kK) may be attributed to charge transfer bands caused by the ligand–copper ion interaction, particularly the 465 mμ band may be due to a metal-to-ligand charge transfer as pointed out by Harrod.[7] On the other hand, the absorption bands at 740 and 910 mμ are thought to be ligand field bands. Once again, from Table I, the absorption bands of the present copper(II) complex resembles to that of $Cu(NO_3)_2 \cdot 2HMPA$ for which is thought[11] to be a planar complex. This similarity of absorption spectrum may indicate that the present complex has a planar structure rather than a tetrahedral one.

Based on these consideration described above, the structure of the present copper(II) complex with 2,4,6-trichlorophenoxo and HMPA as ligand is concluded to be a binuclear complex formed through the oxygen atoms on HMPA and the 2,4,6-trichlorophenoxo group, respectively, as shown in I.

However, it is not certain whether the phenyl group and/or $(CH_3)_2N$ groups in HMPA are located in the same plane described above. These



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groups may be distorted from the plane including copper ion, since these groups are both sterically bulky. Although further investigation might be required to establish the stereochemistry of the ligands coordinated to copper ion with certainty, we believe the structure I to be a likely one.

The attempt to study a thermal decomposition of the copper(II) complex is interesting in relation to the oxidative coupling reaction of phenol derivatives with a copper complex.

The polymerization of *p*-halogen-substituted phenol derivatives have been reported by many investigators, and potassium ferricyanide, lead dioxide, iodine, 2,4,6-tri-*tert*-butylphenol radical, peroxides, and persulfates etc. have been used as initiators.[1] Staffin and Price[3] suggested that the initiation step was a one-electron oxidation to a phenoxy radical by their observation that the polymerization of 4-bromo-2,6-dimethylphenolate ion at −70°C with iodine catalysis developed green colors which persisted at low temperature but faded at room temperature and also proposed the most

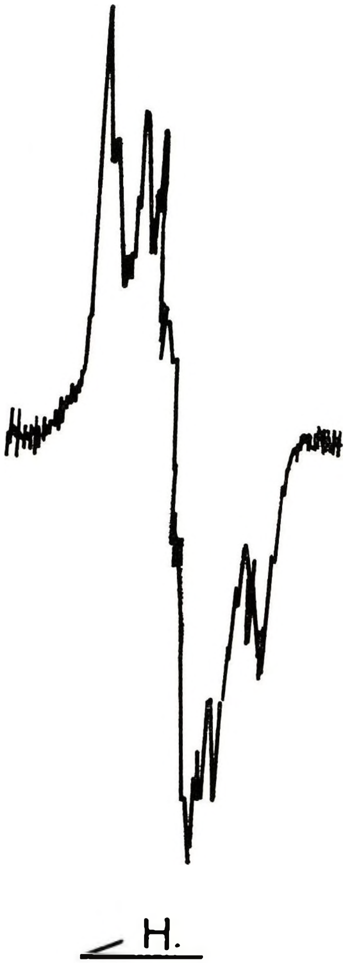
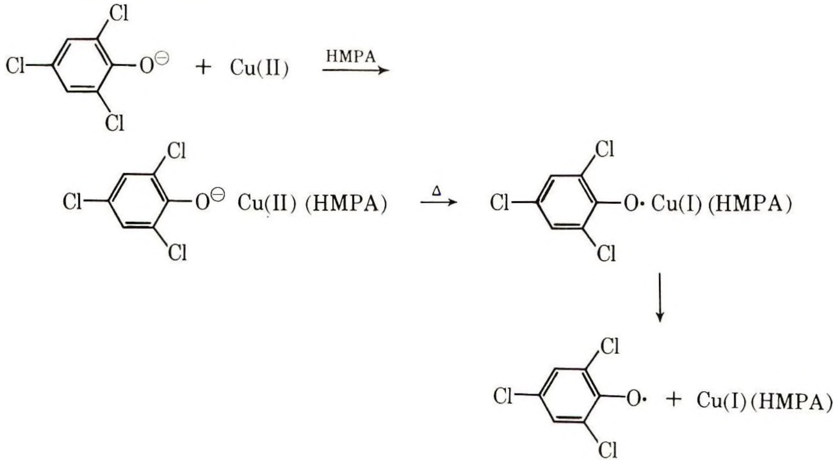


Fig. 11. ESR spectrum of the radical in the region of about $g = 2$.

likely course for the propagation step in the polymerization was aryloxy displacement of bromine ion from the phenolate ion. Also Hunter and Joyce[15] noted the formation of transient blue to blue-green colors in the decomposition of phenoxo–silver complex to yield the corresponding poly(phenylene oxide). Similar phenomena have been observed by some workers.[16]

Although Blanchard and his co-workers[2] investigated the decomposition of 2,4,6-tribromophenolate–silver complex and examined the resulting blue-green solution by ESR, no ESR signal was observed. However, on the oxidative coupling reaction of a hindered phenol such as 2,6-di-*tert*-butyl-4-methylphenol with the copper(I)–pyridine complex with oxygen, Korbunova et al.[17] reported that the corresponding phenoxy radical as a reaction intermediate was detected by ESR measurement. It is of interest to investigate the present copper(II) complex to detect phenoxy radical during the decomposition of the copper(II) complex. For this purpose, ESR spectra of the copper(II) complex in an outgassed sealed tube were measured at elevated temperature (120 ± 5°C). The ESR spectrum of the copper(II) complex is found to depend on the measurement time, as shown in Figure 7. These results indicate with some certainty that the phenoxy radical occurs as an intermediate in the decomposition of the copper(II) complex as observed by Korbunova et al.[17] The decay of the ESR spectrum based on the copper(II) ion may be interpreted as follows.

When the phenoxy radical originates from the copper(II) ion coordinated with the 2,4,6-trichlorophenoxo group one electron will transfer from 2,4,6-trichlorophenolate as a ligand to the copper(II) ion; copper(II) ion is reduced to copper(I) ion which is not an ESR-detectable species. Thus during the decomposition of the copper(II) complex in an out-gassed sealed tube, the intensity of the ESR spectrum based on copper(II) ion decreases inversely when the intensity of the ESR spectrum of the phenoxy radical increases. From these observations of ESR spectra, an initial step involving one-electron transfer in the course of the decomposition of the copper(II) complex appears reasonable.



As shown in Figure 10, a decrease in the phenoxy radical occurs after a certain time. This observation may be due to consumption of the phenoxy radical for the formation of polymer. Thus in the process of decomposition of the present copper(II) complex in an out-gassed sealed tube, the concentration of phenoxy radical, which is considered to be a reaction intermediate, showed a maximum value.

The characterization of the phenoxy radical generated by the decomposition of the present copper(II) complex is of interest in connection with the propagation step of the polymerization. Figure 11 shows the enlarged ESR spectrum of the radical in the region of about $g = 2$ (after 140 min). As shown in Figure 11, it was impossible to identify the ESR spectrum because of the complexity of the hyperfine structure and its low resolution. In spite of this, Figure 11 suggests that the ESR spectrum of the secondary radical derived from the polymer radical may be differentiated from that of the primary phenoxy radical in its stability.*

References

1. A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Amer. Chem. Soc.*, **81**, 6335 (1959).
2. H. S. Blanchard, H. L. Finkbeiner, and G. A. Russell, *J. Polym. Sci.*, **58**, 469 (1962).
3. G. D. Staffin, and C. C. Price, *J. Amer. Chem Soc.*, **82**, 3632 (1960).
4. C. J. Kurian and C. C. Price, *J. Polym. Sci.*, **49**, 267 (1961).
5. J. R. Hall, *J. Polym. Sci. B*, **4**, 463 (1966).
6. A. S. Hay, *Fortschr. Hochpolym. Forsch.*, **4**, 496 (1967).
7. J. F. Harrod, *Can. J. Chem.*, **47**, 637 (1969).
8. T. Yonezawa, S. Tsuruya, and T. Kawamura, *J. Polym. Sci. B*, **6**, 447,(1968).
9. T. Yonezawa, S. Tsuruya, S. Tsuchiya, and T. Kawamura, *Kogyo Kagaku Zasshi*, **71**, 1007 (1968).
10. J. T. Donoghue, and R. S. Drago, *Inorg. Chem.*, **2**, 572 (1963).
11. E. Ochiai, *Tetrahedron*, **20**, 1831 (1964).
12. M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Revs.*, **64**, 99 (1964).
13. B. Bleaney, and K. D. Bowers, *Proc. Roy. Soc.* (London), **A214**, 451 (1952).
14. G. F. Kokosz'ka, M. Linzer, and G. Cordon, *Inorg. Chem.*, **7**, 1730 (1968).
15. W. H. Hunter and F. E. Joyce, *J. Amer. Chem. Soc.*, **39**, 2640 (1917).
16. C. D. Cook, N. D. Gilmour, *J. Org. Chem.*, **25**, 1429 (1960).
17. L. V. Korbunova, M. L. Khidekel, and G. A. Razuvaev, Doklady Akademii Nauk SSSR, 147, 368 (1962).

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* This ESR peak did not disappear over a period of a few days in an out-gassed, sealed tube.

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Structures of Reagent Residues Resulting from Reactions of Divinyl Sulfone with Cotton Cellulose

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Synopsis

Cotton cellulose in fabric form was crosslinked with divinyl sulfone by catalysis with solutions of sodium hydroxide of normalities ranging from 0.1 to 4.0. The molecular chains of cellulose were hydrolyzed with sulfuric acid to yield hydrolyzates from which simple substituted glucoses (i.e., those bonded to a single unit of DVS), the simple crosslinked glucoses (i.e., those joined together by a single unit of DVS), and complex structures (i.e., those substituted or crosslinked with more than one unit of DVS in the chain) were isolated and measured. The fractions of the reagent residues in the forms of the structures noted above were found to change substantially with the concentration of base employed to catalyze the reaction. The constitution of the reagent residues resulting from reaction in 0.1*N* base was remarkably simple: 82% of the DVS residues in the form of simple crosslinks and 18% in the form of simple substituents. Complex structures accounted for as much as 70% of the DVS residues under other conditions of reaction.

Introduction

When fibrous cellulose is treated with a difunctional reagent, various types of structures may be introduced, e.g., simple substituents involving a single reagent unit, simple crosslinks involving a single reagent unit, and complex structures involving multiple units of reagent in each substituent of crosslink. Each of these structures, which in total constitute the "reagent residues," may be joined to the cellulose through ether linkages at the 2-*O*-, 3-*O*-, and 6-*O*-positions of the D-glucopyranosyl units.

Relatively few studies have been conducted to delineate the structures of reagent residues in cottons chemically modified with di- and polyfunctional reagents. When definitive results have been obtained, it has been found that (a) the number of effective crosslinks from formaldehyde is substantially fewer than the number of moles of bound reagent,[1] (b) the average linkage from formaldehyde involves 1.5 to 3.0 units of reagent,[2] (c) the numbers of crosslinkages and covalent bonds between reagent and cellulose per mole of tris(1-aziridinyl)phosphine oxide or tris(2-chloroethyl)phosphoramide are remarkably low,[3,4] and (d) the fractions of reagent residues in the form of simple crosslinkages (i.e., a single unit of reagent joining two D-glucopyranosyl units) developed with sodium methylbis(2-sulfatoethyl)amine and methylbis(2-chloroethyl)amine are no higher than approximately 0.26.[5]

It is immediately and impressively evident that, at least in these cases, the simple "classical" crosslink which is most often written in structural illustrations is a minor product of the reaction. It is also evident that there is considerably more chemistry to the crosslinking than has been generally recognized: thus, reagent may be converted to simple substituent groups (i.e., involving a single unit of reagent), simple crosslinks, long substituent groups, and long crosslinks. These reactions, which consume reagent, are competitive and sometimes reversible. If a simple crosslink is the desired structure for optimum balance of performance characteristics, then considerable study must be conducted to determine how this may be formed most efficiently and most effectively. There is, in fact, no evidence that the simple crosslink is the desired structure. It is known that performance qualities of a chemically modified cotton fabric are dependent upon the reagent and upon the conditions of reaction. It is desirable to know how the structures developed by the reagent residues are dependent upon the reagent and upon the conditions of reaction.

This report is concerned with the structures of reagent residues resulting from reactions of cotton fabric with divinyl sulfone (DVS). The reactions were conducted in solutions of sodium hydroxide ranging in normality from 0.1 to 4.0. The reactions of methyl vinyl sulfone, the monofunctional analog of DVS, were studied earlier in these media;[6] the ratio of 2-*O*- to 6-*O*-substitution at equilibrium distribution in the cotton was found to be sensitive to the concentration of base and ranged from 0.27 in 0.5*N* base (no reaction in 0.1*N* base) to 0.10 in 4*N* base. Perhaps more pertinent, the tendencies for methyl vinyl sulfone and DVS to form bis- and polyethers, respectively, were observed to increase with increasing concentration of base.[6,7] Thus, slightly different distribution of linkages and substantially different lengths of substituents and crosslinks were anticipated from the reactions of DVS in the various basic media.

Experimental

The details of the preparation of DVS-modified cottons have already been described;[7] print cloth (desized, scoured, bleached) was padded through a solution of DVS (11% DVS in water) followed by immersion in a solution of sodium hydroxide of the selected normality. Samples for these analyses were selected from 15, 60, and 180-min periods of reaction in the basic media, and, except in one case, the amounts of reagent residues "bound" in the cotton were very similar, i.e., 1.8–2.3%, except in the cotton-treated in 4*N* base; in that case 3.6% of residues were "bound" in the cotton.

Samples of fabrics were hydrolyzed to mixtures of glucose, substituted glucoses, and crosslinked glucoses by dissolving the chopped fibers in 72% sulfuric acid and, subsequently, refluxing during two stages of dilution.[8] Free glucose was removed by fermentation,[8] and the mixture of substituted and crosslinked glucoses was obtained as a freeze-dried concentrate. The validity of this method for isolation of hydrolyzates without cleavage of the ether linkages between glucose and DVS units has been reported earlier.[8]

Identification and analyses of the components involved paper chromatography and gas-liquid chromatography.[9] Authentic samples of glucoses substituted at the 2-*O*-, 3-*O*-, and 6-*O*-positions with the $HOCH_2CH_2SO_2CH_2CH_2$— group and glucoses crosslinked at the 2,2′-*O*-3,3′-*O*-, and 6,6′-*O*-positions with the —$CH_2CH_2SO_2CH_2CH_2$— residue served as the basis for locating and identifying the unknown on chromatograms. Quantitative determinations were based on densitometric measurements on paper chromatograms. Gas–liquid chromatograms were of qualitative value, only, since crosslinked glucoses (and other less volatile components) dissociated partially at the high temperatures required in the column.

Results and Discussion

The samples of print cloth crosslinked with DVS that were analyzed in this study are identified in Table I. All of the hydrolyzates of these samples showed chromatographic evidence of the presence of 6-*O*-substituted glucose and 6,6′-*O*-crosslinked glucose. There was no evidence for the presence of 2-*O*- or 3-*O*-substituted glucoses nor for 2,2′-*O*- or 3,3′-*O*-crosslinked glucoses. Since reversible reactions are involved and since there was no evidence of substitution in the 2-*O*- and 3-*O*-positions in the simple substituted structures, it is reasonable to expect no crosslinked compositions involving

TABLE I
Analytical Data on Cotton Celluloses Modified with Divinyl Sulfone

			Quantitative chromatographic analyses[b]			
Sodium hydroxide solution, *N*	Reaction period min[a]	Sulfur content of fabric, %	Simple substituted glucose mmole × 10^5	Simple crosslinked glucoses, mmole × 10^5	Complex structures, mmole × 10^5	Total, mmole × 10^5
0.1	180	0.51	1.3	4.6	0.5	6.4
0.5	60	0.48	1.3	2.3	5.5	9.1
1.0	60	0.62	1.3	1.9	7.3	10.6
2.0	15	0.55	1.0	4.8	2.2	8.0
4.0	60	0.96	1.4	6.2	(−0.3)[c]	7.3

[a] The time of immersion of the DVS-soaked fabric in base of the indicated normality (details in ref. 7).

[b] Data are expressed in millimoles of sulfur × 10^5; this corresponds to mmoles of DVS residues and, therefore to mmoles of simple substituted glucoses and mmoles of simple crosslinks. Under "Total" is indicated the mmoles of sulfur-containing material applied to the paper for chromatographic analysis. The value indicated for mmoles of complex structures is the difference between the total and the sum of simple substituents plus simple crosslinks.

[c] This is an indication of the error in these analyses which is estimated at ± 4%.

these positions in unsymmetrical structures such as 2,6′-*O*- or 3,6′-*O*-crosslinks. The absence of evidence for linkages in the 2-*O*- and 3-*O*-positions is surprising, in view of the fact that the equilibrium distributions in cotton cellulose treated with methyl vinyl sulfone was found to range in ratio of 2-*O*- to 6-*O*-distribution from 0.1 to 0.27 for reactions in 4.0*N* and 0.5*N* base, respectively, and in 3-*O*- to 6-*O*-distribution from approximately 0.08 to 0.17 for reactions in the same media.[6]

Some of the hydrolyzates from DVS cottons showed a broad, rather featureless streak in the paper chromatogram on which the spot for the 6,6′-*O*-crosslinked glucose was superimposed. The streak is attributed to complex structures: i.e., substituted and crosslinked glucoses involving more than one unit of reagent. These complex structures appear in paper chromatograms between the origin and approximately R_G 0.5; the spot for the 6,6′-*O*-crosslinked glucose appears at R_G 0.56, that for the hydroxy-terminated 6-*O*-substituted glucose appears at R_G 1.25, and that for the vinyl-terminated 6-*O*-substituted glucose appears at R_G 1.65[9] (R_G is the quotient of the distance traveled by the compound and the distance traveled by D-glucose).

The results of these analyses of the structures of reagent residues resulting from reactions of DVS with cotton fabric are summarized in Table I in terms of (*a*) millimoles of sulfur (from DVS residues) in the sample applied to the paper for chromatography, (*b*) millimoles of sulfur in the simple 6-*O*-substituted glucose fraction, (*c*) millimoles of sulfur in the simple 6,6′-*O*-cross-

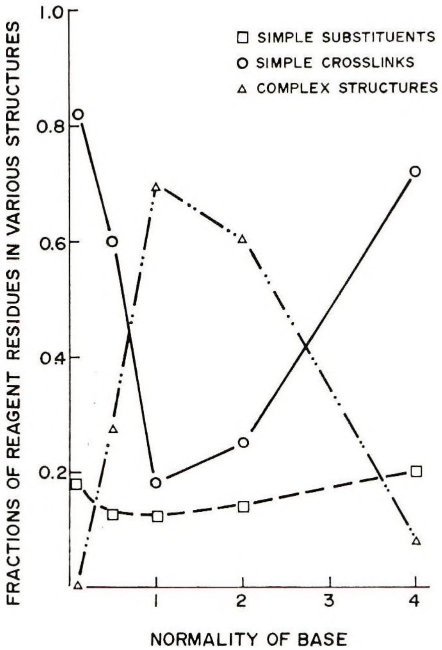

Fig. 1. Fractions of reagent residues from DVS in various structural forms in the chemically modified cottons. Chemical reactions were conducted in solutions of different normalities of sodium hydroxide.

linked glucose fraction, and (*d*) millimoles of sulfur attributed to the complex structures (i.e., the difference between *a* and the sum of $b + c$). It is apparent that the differences from one to another of the crosslinked compositions lie mainly in the amounts of simple crosslinked structures and of complex structures.

The proportions of the various structural units in these crosslinked cottons are shown graphically in Figure 1. The fraction of simple substituents is quite similar from one to another of the crosslinked cotton compositions; however, the fractions of simple crosslinks and of complex structures change markedly and in opposite directions. The structures of reagent residues in the cottons crosslinked in 0.1*N* and 4.0*N* base involve a single unit of DVS in crosslinks (predominantly) and substituents, which in total account for 92 to 100% of the reagent. On the other hand, the structures of reagent residues resulting from reactions in 1.0*N* and 2.0*N* base involve approximately 70% and 61%, respectively, of the reagent in the form of complex structures: i.e., those having two or more units of DVS in the structure. In these cases, the average number of DVS units per structural unit must be 1.53 and 1.44, at minimum, for the compositions resulting from reactions in 1.0*N* and 2.0*N* base, respectively; these values are calculated assuming that the complex structures have only two units of DVS per structural units. Thus, the average length of the linkages (substituents plus crosslinks) in these crosslinked compositions increases from 1.0 DVS unit per linkage for the product of reaction in 0.1*N* base to 1.53 minimum for the product of reaction in 1.0*N* base and then decreases to approximately 1.05 for the product of reaction in 4.0*N* base.

An indication of the state of swelling of the cotton fiber during the crosslinking in each of the basic media is shown by the values of water of imbibition obtained on samples of the unmodified cotton after immersion in each of the basic media (without DVS). The values were 31.9%, 31.9%, 34.5%, 35.6%, and 41.2% for cotton previously immersed in 0.1*N*, 0.5*N*, 1.0*N*, 2.0*N*, and 4.0*N* sodium hydroxide, respectively. The small increases in swelling from 0.1*N* to 2.0*N* base are interpreted as increases in lateral separations of the surfaces of the microstructural units. The larger increase in swelling (i.e., in water of imbibition) between 2.0*N* and 4.0*N* base is attributed to a partial penetration of the medium into the formerly crystalline regions, i.e., beneath the surfaces of the microstructural units. This is evident from the decrease in crystalline lattice I content of the cellulose to the level of 72% for the cotton crosslinked in the 4.0*N* base. The value for the initial cotton was 87% and the values for the cottons crosslinked in 0.1*N* to 2.0*N* base were 81–83%. The penetration beneath the surfaces of the formerly crystalline microstructural units in the 4.0*N* medium is visualized to occur as described by Warwicker and Wright;[10] thus, sheets of cellulose molecules near the former surface of the microstructural unit are displaced relatively small distances from one another and perhaps into the former void space between microstructural units; thus, the size of the latter voids is decreased. The overall result of increasing concentration of base upon the distance between hydroxyl groups on vicinal surfaces of microstructural units or on vicinal sheets of cellulose molecules is: (a) a progressive increase in extent of separation between surfaces in proceeding from $0.1N$ to $2.0N$ base, and (b) substantially decreased degree of separation between sheets of cellulose in the $4.0N$ base.

The foregoing concept of the state of the microstructure of the cotton in the various basic media is interpreted to be coupled with the chemistry of DVS in the following manner. DVS reacts reversibly with hydroxyl groups on the surfaces of the microstructural units or on the surfaces of sheets of cellulose chains to develop vinylsulfonylethyl substituent groups. A slower reaction occurs between DVS and water. The vinyl function of a substituent group reacts reversibly with hydroxyl groups of cellulose which lie within reach of the substituent chain. If this reaction of the vinyl group does not occur due to absence of a suitable hydroxyl group, competition occurs between the slow reaction of the vinyl function of the substituent with water to form a 2-hydroxyethylsulfonylethyl substituent and the rapid reverse reaction at the substituent linkage to release DVS. Equilibrium strongly favors development of DVS linkages to cellulose through the oxygen at C-6. DVS reacts with the 2-hydroxyethylsulfonylethyl substituents to extend the substituent chains to two units of DVS. The vinyl function on an extended substituent chain then reacts with a cellulosic hydroxyl group which lies in suitable proximity or it undergoes alternate reactions leading to formation of 2-hydroxy-ethylsulfonylethyl as described above; however, the reverse of the reaction with DVS is slow (if it occurs at all under these conditions) compared to other reactions. The chain extension reaction occurs on 2-hydroxyethylsulfonylethyl units of chains involving more than one unit of DVS and this continues, as above, resulting in long substituent chains and long crosslinks; polyether of DVS may result from a similar sequence of reactions involving the hydroxyl group rather than the cellulosic group on the terminal position. The structures in which the reagent residues are isolated depend on the proximities of the cellulosic hydroxyl groups for potential reaction with the vinyl functions of the substituent chains; close proximity favors conversion of the substituent group to a crosslink.

It is concluded that reactions of di- or polyfunctional reagents with cellulosic hydroxyl groups in reversible, "wet-cure" reactions such as these reactions of DVS are exceedingly complex. The structures of the reagent residues which result are dependent upon the chemistry of the reagent and the physical availabilities of hydroxyl groups for completion of crosslinkages in the cellulose.

References

1. S. P. Rowland and A. W. Post, *J. Appl. Polym. Sci.*, **10**, 1751 (1966).
2. J. D. Guthrie, *Text. Res. J.*, **37**, 40 (1967).
3. S. P. Rowland, E. J. Roberts, and S. M. Stark, Jr., *Text. Res. J.*, **40**, 405 (1970).
4. E. J. Roberts, M. A. F. Brannan, and S. P. Rowland, *Text. Res. J.*, **40**, 699 (1970).
5. E. J. Roberts, M. A. F. Brannan, and S. P. Rowland, *Text. Res. J.*, **40**, 237 (1970).

6. V. O. Cirino, A. L. Bullock, and S. P. Rowland, *J. Polym. Sci., A-1*, **7**, 1225 (1969).

7. S. P. Rowland, V. O. Cirino, and A. L. Bullock, *Text. Chemist Colorist*, **1**, 450 (1969).

8. S. P. Rowland, V. O. Cirino, and A. L. Bullock, *Can. J. Chem.*, **44**, 1051 (1966).

9. V. O. Cirino, A. L. Bullock, and S. P. Rowland, *Carbohydrate Res.*, in press.

10. J. O. Warwicker and A. C. Wright, *J. Appl. Polym. Sci.*, **11**, 659 (1967).

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Vinyl Polymerization Initiated by Chromic Acid–Reducing Agent Systems

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Synopsis

A kinetic study of the thermal polymerization of acrylonitrile initiated by chromic acid–reducing agent (*n*-butanol, ethylene glycol, cyclohexanone, and acetaldehyde) systems was made. Chromic acid alone did not initiate polymerization under deaerated or undeaerated conditions. On the basis of the experimental determination of the dependencies of various variables on the rate of polymerization R_p, the rate of chromium (VI) disappearance $-R_M$, the degree of polymerization DP, etc., a reasonable kinetic scheme was arrived at. The mechanism with the reducing agents, *n*-butanol, cyclohexanone, and ethylene glycol, was found to be similar but different from that with acetaldehyde. Evidence has been presented to prove the formation of radical intermediates formed by the oxidation of the reducing agent by Cr(IV). Rate parameters for oxidation of the reducing agent and polymerization of the monomer were evaluated.

INTRODUCTION

Studies on aqueous vinyl polymerization initiated by metal ions[1-5] in their higher valence states, Co(III), Ce(IV) etc. have provided valuable information regarding the mechanistic details of individual steps. On theoretical grounds (E_0 for Cr(VI)–Cr(III) couple[6] = 1.33 V), it was expected that Cr(VI) might also initiate vinyl polymerization. The use of redox systems for initiation of polymerization has been frequently reported in the literature[1-3] but those involving chromic acid–reducing agent or chromic acid alone have not been employed so far for kinetic studies except for the emulsion copolymerization study of styrene and butadiene by Kolthoff and Meehan.[7] We report in this paper our results in the redox systems involving Cr(VI)–reductant as initiators of polymerization of acrylonitrile. These studies while furnishing interesting information on polymerization kinetics have thrown light on the general mechanism of chromic acid oxidations in which the unstable species Cr(IV) and Cr(V), but no radical intermediates were suggested.[8,9] Rate parameters for oxidation of the reducing agent by Cr(VI) and for polymerization of the monomer by Cr(VI)–reducing agent have been evaluated.

EXPERIMENTAL

Reagents

Acrylonitrile (American Cyanamid, U.S.A., or BDH, U.K.), methyl methacrylate, and methyl acrylate (Rohm and Haas, U.S.A.) monomers were purified by standard methods. Chromic acid solutions were prepared by dissolving chromium trioxide (BDH, AR) in distilled water. Perchloric acid (E. Merck, G.R. 60%), nitric, and sulfuric acids (AR, Basynth, India) were used for maintaining the acidity of reaction mixtures and for preparing other reagents. Sodium perchlorate ($1.0N$) was used for maintaining ionic strength. Other reagents like ferrous ammonium sulfate, *o*-phenanthroline, potassium hydrogen phthalate, potassium iodide, sodium thiosulfate, sodium chloride, potassium dichromate, etc., were either BDH (AR) or Merck (GR) products. Solvents (dimethylformamide, acetone, etc.) were fractionally distilled after purification and the middle fractions were collected. In the preparation of ferroin indicator and purification of *n*-butanol and acetaldehyde, standard procedures were employed. Cerous perchlorate was prepared by dissolving cerous carbonate (Bhabha Atomic Research Centre, Bombay, India) in perchloric acid, gently warming, and filtering if necessary. Deaeration of the system, Cr(VI)–reducing agent–monomer, was done by passing nitrogen freed from oxygen (Fieser's solution) through the system.

Estimations

Changes in [Cr(VI)] were determined either by titrimetry for [Cr(VI)] $\geq 5 \times 10^{-4}M$ or by spectrophotometry for [Cr(VI)] $< 5 \times 10^{-4}M$ (see below), the usual iodometric procedure of Wiberg and Mill[10] being unsuitable in polymerization experiments. The cerous perchlorate was estimated by oxidizing a known volume of the solution with ammonium persulfate in presence of silver nitrate to ceric perchlorate and estimating the latter titrimetrically by standard ferrous. The free acid content of the cerous solution was determined by an ion-exchange method.[11]

Experimental Procedure

For experiments on oxidation of substrates used as reducing agents, a three-necked glass vessel fitted with ground glass joints was used, one neck serving as an inlet for passing nitrogen through the system and the second for removal of aliquots at different time intervals. The reaction in the system, Cr(VI)–reducing agent–acid, was arrested by addition of excess ferrous sulfate solution; the unreacted ferrous was estimated by cerimetry.

For polymerization experiments, two types of vessels were used, depending on the total volume of the reaction mixture. The first type was a glass tube (80 ml) fitted with B-24 ground joint head through which two glass tubes were fused. The second type was a Pyrex conical flask (250 ml) fitted with a quickfit B-24 socket and a B-24 cone carrying an inlet and an outlet tubes for passage of nitrogen. To the reaction mixture containing reducing agent, monomer, and acid and deaerated for 20–30 min, a chromic acid solution which was deaerated separately was added. The temperature of the reaction mixture (30–45°C) was kept constant in a thermostat (controlled to ±0.1°C by a toluene regulator and a Sunvic hot wire vacuum switch relay). The reaction was usually carried out for 20–30 min. The reaction was stopped by addition of excess ferrous solution; the precipitated polymer was filtered, washed with water, and dried to constant weight at 60°C in a vacuum oven. The rate of polymerization was calculated from the weight of polymer obtained. From the filtrate the change in [Cr(VI)] was followed by estimating the unreacted [Fe(II)] either by titration against standard ceric ammonium nitrate or by spectrophotometry after addition of *o*-phenanthroline and measuring the optical density of ferrous–*O*-phenanthroline complex at $\lambda = 510$ nm and reference to a previously calibrated plot of optical density vs [Fe(II)]. From the changes in [Cr(VI)] the rate of Cr (VI) disappearance, $-R_M$ was computed. The conversion of Cr(VI) at the steady state was ~40%. The molecular weights, $\bar{M}_w$ of the purified polymers were obtained by viscometry by using the appropriate Mark–Houwink relationship. The viscosities of polymer solutions (0.1%) were determined in an Ubbelohde-type suspended-level dilution viscometer in a Kerb viscometric bath maintained to ± 0.1°C for polyacrylonitrile in dimethylformamide at 30°C.

The equation:[12]

$$[\eta] = 3.35 \times 10^{-4} \bar{M}_w^{0.72}$$

was employed.

EXPERIMENTAL RESULTS AND DISCUSSION

Preliminary Experiments

Chromic acid alone was found to be not effective as initiator of vinyl polymerization. Preliminary experiments carried out with chromic acid and methyl acrylate (MA) or methyl methacrylate (MMA) in acid media ($HClO_4$, HNO_3, and H_2SO_4) under deaerated conditions at 45°C showed that no polymerization took place even though there was a decrease in [Cr(VI)]. The rate of Cr(VI) disappearance $-R_M$ did not have a simple order with respect to [Cr(VI)], and the rate, sluggish initially, increased with time till the disappearance was complete. The same results were obtained under different ratios [MA]/[Cr(VI)] = 30–120. It might, therefore, be concluded that chromic acid in acid medium oxidized MA (or MMA), not leading to polymerization of the latter, probably the functional group and not the π bond of the monomer being involved in oxidation. Such monomer oxidations were observed[1,2] as side reactions with Co(III) and Ce(IV) also as initiators. With acrylonitrile monomer (AN), on the other hand, there was no such decrease in [Cr(VI)] and no polymerization of the monomer either. However, the redox system, Cr(VI)–reducing agent, was found to initiate polymerization of AN. Reducing agents, such as isopropyl alcohol, formaldehyde, *tert*-butyl alcohol, sodium arsenite, gave only small amounts of polymer (~2%) whereas *n*-butanol, isoamyl alcohol, ethylene glycol, cyclohexanone, propionaldehyde, and benzaldehyde gave large amounts of polymer (~5%) without any induction periods. Systematic studies were therefore carried out with the latter reducing agents.

As a preliminary to our polymerization studies, oxidation of substrates (reductants in polymerization studies) in the absence of monomer under deaerated conditions was studied. In the case of reducing agents (R), *n*-butanol, cyclohexanone, ethylene glycol, and acetaldehyde, the rate of chromium (VI) disappearance, $-R_M$, in $HClO_4$ medium depended on the first

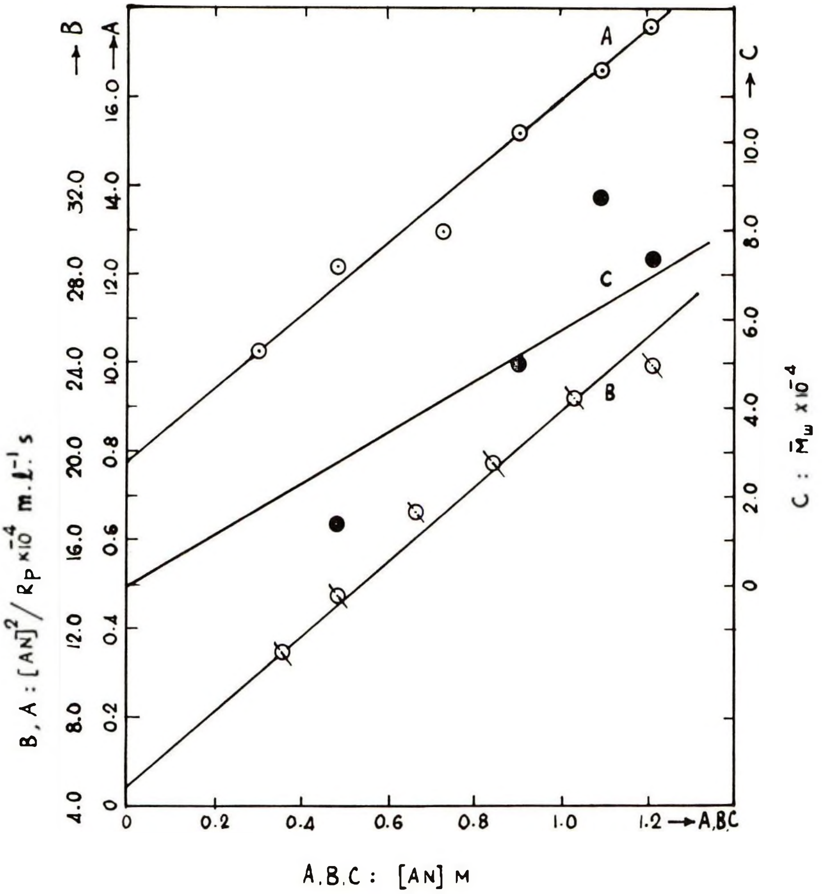

Fig. 1. Variation of R_p and $\bar{M}_w$ with [AN]: (*A*) $[AN]^2/R_p$ vs. [AN] at 45.0°C in $HClO_4$, [Cr (VI)] = $5.445 \times 10^{-3}M$, [ethylene glycol] = $0.215M$, $[H^+]$ = $0.7328M$, μ = $0.996\ M$; (B) $[AN]^2/R_p$ vs. [AN] at 45.0°C in $HClO_4$, [Cr (VI)] = $5.35 \times 10^{-3}M$, [cyclohexanone] = $0.1698M$, $[H^+]$ = $1.393M$, μ = $1.40M$; (*C*) $\bar{M}_w$ vs. [AN] at 45.0°C in $HClO_4$, [Cr(VI)] = $5.445 \times 10^{-3}M$; [ethylene glycol] = $0.215M$, $[H^+]$ = $0.7328M$; μ = 0.996 M.

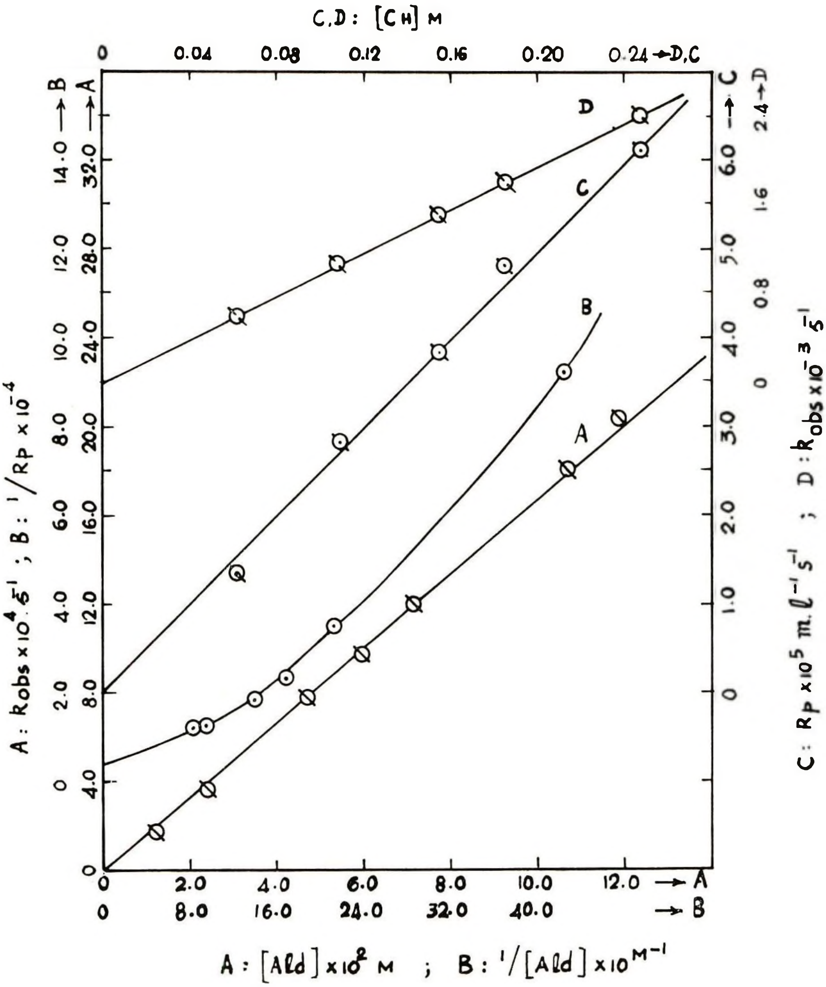

Fig. 2. Variation of R_p and k_{obs} with [reducing agent]: (A) k_{obs} vs. [acetaldehyde] at 45.0°C in $HClO_4$, [Cr(VI)] = 5.463 × $10^{-3}M$, [AN] = 0.603M, [H^+] = 0.296M, μ = 0.3M; (B) 1/R_p vs. 1/[acetaldehyde] at 45.0°C in $HClO_4$, [Cr(VI)] = 5.463 × $10^{-3}M$, [AN] = 0.603M, [H^+] = 0.296M, μ = 0.3M; (C) R_p vs. [cyclohexanone] at 45.0°C in $HClO_4$, [Cr(VI)] = 5.351 × $10^{-3}M$, [AN] = 0.9042M, [H^+] = 1.393M, μ = 1.40M; (D) k_{obs} vs [cyclohexanone] at 45.0°C in $HClO_4$, [Cr(VI)] = 5.351 × 10^{-3} M, [AN] = 0.9042M, [H^+] = 1.393M, μ = 1.40M.

power of [Cr(VI)], the first power of [R], and second power of [H^+] in all cases except for cyclohexanone, where an order of unity for [H^+] was observed (cf. oxidation of secondary alcohols,[9] of butanol,[14] and of cyclohexanone reported by Waters et al.[15]). Formation of chromate ester followed by its decomposition in a rate-determining step were assumed,[9,10,16–18] in the oxidations of alcohols, aldehydes, ketones, and glycols. For the substrates studied by us, there is ample evidence[9] for assuming that the rate-determining step in these cases is a two-electron transfer reaction and the intermediate species formed in the rate-determining step is Cr(IV) and not Cr(V). The facts that when Ce(III) or Mn(II) is added to Cr(VI)–substrate system, oxidation rate was retarded and the induction factor was ~0.5 were in favor of Cr(IV) being the active intermediate.

Rate of Polymerization, R_p

Variation of R_p with [AN]. The fact that plots of log R_p versus log [AN] gave slopes varying from 1.4 to 1.7 and that the rate decreased with [Cr(VI)] indicated the termination to be of linear type. The terminating species might be either Cr(VI) or Cr(IV) but the latter, on the basis of interaction of two unstable species of low concentration Cr(IV) + M. seemed unlikely. Morever, steady state would not have been reached if the termination involved Cr(IV). The plots of $[AN]/R_p$ versus [AN] were linear with all the reducing agents studied (Fig. 1).

Variation of R_p with [R]. With *n*-butanol, ethylene glycol, and cyclohexanone, dependence of R_p on the first power of [R] (Fig. 2*C*) may be understood in terms of linear termination by Cr(VI) (cf. Katai et al.[19] for Ce(IV)-initiated polymerization). With acetaldehyde as reducing agent, the order observed was ~2 at low [R] and tended to unity at high [R]. A plot of $1/R_p$ versus 1/[R] was also a curve with an intercept (Fig. 2*B*).

Variation of R_p with [Cr(VI)]. The additional evidence for linear termination was that R_p varied inversely with [Cr(VI)], the plots of $1/R_p$ versus [Cr(VI)] were linear (Fig. 3).

Variation of R_p with [H⁺]. For *n*-butanol, the order with respect to $[H^+]$ was exactly 2, (Fig. 4); this must be understood in terms of protonation of chromic ester formed. In the case of ethylene glycol, the plot of R_p versus $[H^+]^2$ was linear only up to $[H^+] = 0.9M$; for $[H^+] > 0.9M$, the rate leveled off. In our studies on oxidation no such leveling off was noted, and it was therefore unlikely that the latter phenomenon had anything to do with protonation of chromic ester. Plots of $1/R_p$ versus $1/[H^+]^2$ were linear with intercepts for ethylene glycol and acetaldehyde systems (Fig. 5*A*). For the cyclohexanone system, R_p versus $[H^+]$ was linear up to $[H^+] = 0.7M$ and leveled off at $[H^+] > 0.7M$ (Fig. 4*B*).

R_p in Various Acids. R_p values were highest in $HClO_4$ medium and decreased in the order, $HClO_4 > HNO_3 > H_2SO_4$. The acid anions probably complex with monochromate ion, reducing the latter's oxidizing power (cf. Stewart and Lee[20] for variation of oxidation rates of isopropyl alcohol). Addition of Cl^- decreased R_p, the decrease being marked at first, and then R_p tended to remain constant (Table I). Formation of chlorochromate ion, probably a weak oxidant might be the cause for the decrease.

Effect of Initially Added Cr(III) or Ce(III) on R_p. R_p remained unaffected by initially added Cr(III) at constant ionic strength, μ (Table I), which excluded equilibrium of the type:

$$\mathrm{Cr(III)} + \mathrm{Cr(V)} \rightleftharpoons 2\,\mathrm{Cr(IV)}$$

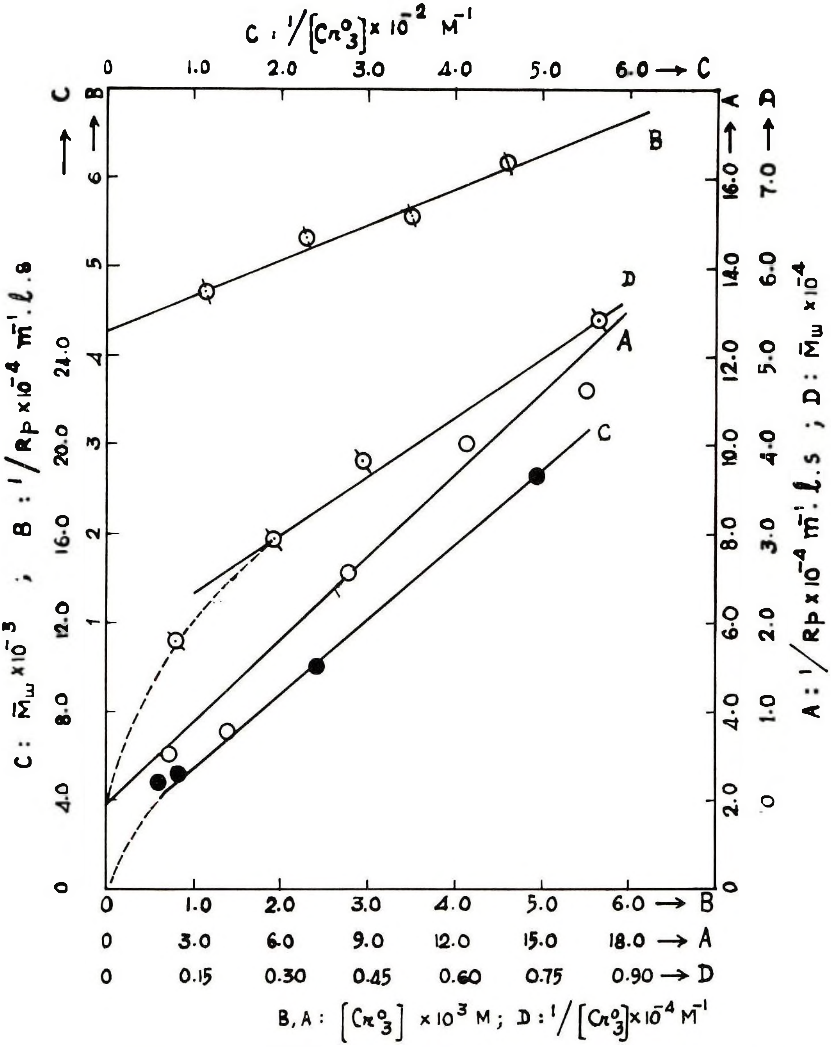

Fig. 3. Variation of R_p and $\bar{M}_w$ with [Cr (VI)]: (*A*) $1/R_p$ vs. [Cr(VI)] at 35.5°C in $HClO_4$, [AN] = $0.603M$, [acetaldehyde] = $4.92 \times 10^{-2}M$, [H^+] = $0.5704M$, $\mu = 0.6M$; (*B*): $1/R_p$ vs. [Cr(VI)] at 45.0°C in $HClO_4$, [AN] = $0.6038M$, [*n*-butanol] = $4.2 \times 10^{-2}M$, [H^+] = $0.6952M$, $\mu = 0.8M$; (*C*): $\bar{M}_w$ vs. 1/[Cr(VI)] at 35.5°C in $HClO_4$, [AN] = 0.603 M, [acetaldehyde] = $4.92 \times 10^{-2}M$, [H^+] = 0.5704 M, $\mu = 0.6M$; (*D*) $\bar{M}_w$ vs. 1/[Cr(VI)] at 45.0°C in $HClO_4$, [AN] = $0.6038M$, [*n*-butanol] = $4.2 \times 10^{-2}M$, [H^+] = $0.6952M$, $\mu = 0.8M$.

postulated in the study of the exchange of Cr(III) and Cr(IV) in acid solutions.[21] The addition of even small amounts of cerous perchlorate, [Cr(VI)]/[Ce(III)] = 10 decreased R_p by nearly 50%. Retardation of oxidation of substrates by Cr(VI) in the presence of cerous salts noticed by many workers[8] was attributed to the removal of reactive intermediate chromium species. This fact is of course not helpful in deciding whether

TABLE I

Effects of Initially Added Cr^{3+}, Chloride Ions, and Monomer on Rates[a]

Monomer added; $[Cr(VI)] = 5.351 \times 10^{-3}M$, $[H]^{+} = 1.393M$			Cl⁻ added; $[Cr(VI)] = 5.147 \times 10^{-3}M$, $[AN] = 0.9042M$			Cr^{+3} added; $[H^{+}] = 0.5703$ M,, $[AN] = 0.85M$		
$[AN]$, M	$R_p \times 10^5$, mole/l.-sec	$k_{obs} \times 10^3$, sec^{-1}	$[Cl^{-}] \times 10^3M$	$R_p \times 10^5$, mole/l.-sec	$k_{obs} \times 10^4$, sec^{-1}	$[Cr^3 \times 10^{3+}$, M	$R_p \times 10^5$, mole/l.-sec	$k_{obs} \times 10^4$, sec^{-1}
0.3620	1.190	1.439	0.824	2.470	6.570	0.487	4.079	6.801
0.4824	1.718	1.452	1.648	2.214	—	0.975	2.727	6.613
0.6630	2.537	1.441	2.472	2.128	6.463	1.950	3.072	6.609
0.8442	3.634	1.432	4.120	1.647	6.377	3.900	3.266	6.783
1.0250	4.686	1.452	12.360	1.054	6.083	5.850	3.394	6.822
1.2060	6.082	1.451	20.590	0.799	5.780	—	—	—

[a] [Cyclohexanone] = $0.1698M$; 45.0 ± 0.1°C.

the initiating species is Cr(IV) or R. We found, contrary to the observation of Mosher and Driscoll[22] that polymerization of monomer was not completely eliminated by Cr(III).

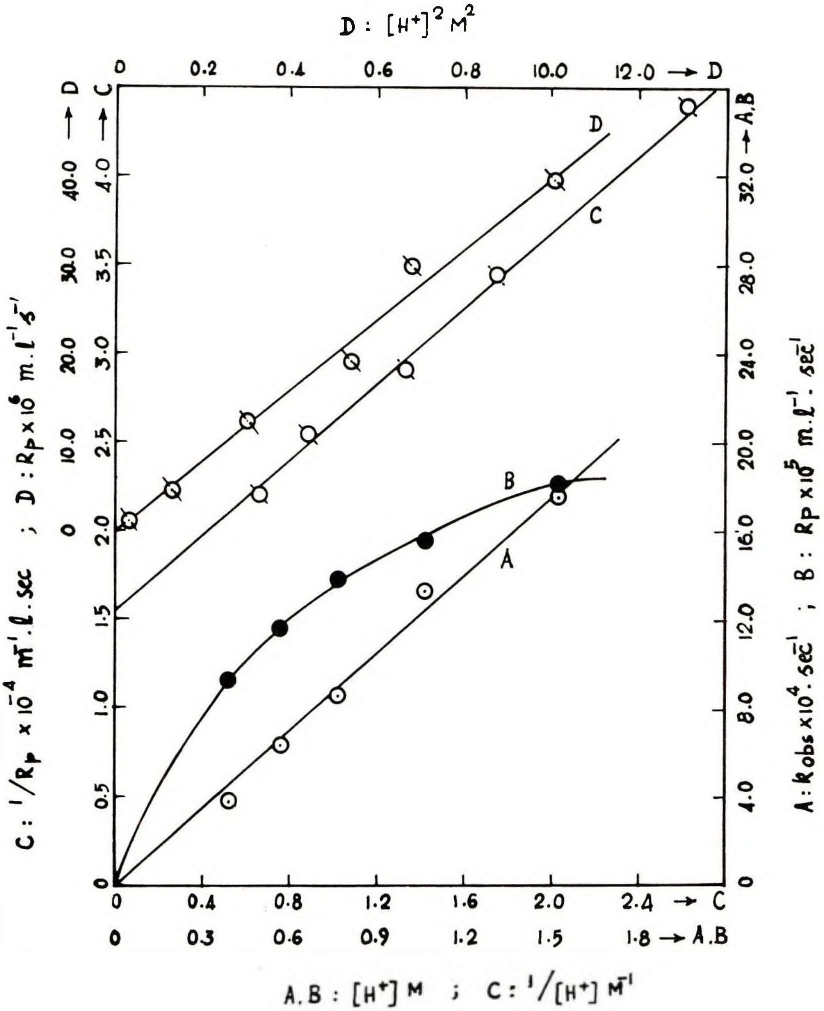

Fig. 4. Variation of R_p and k_{obs} with $[H^+]$: (*A*) k_{obs} vs. $[H^+]$ at 45.0°C in $HClO_4$, $[Cr(VI)] = 5.15 \times 10^{-3}M$, $[AN] = 0.9042M$, $[\text{cyclohexanone}] = 0.1698M$, $\mu = 1.52M$; (*B*) R_p vs. $[H^+]$ at 45.0°C in $HClO_4$, $[Cr(VI)] = 5.15 \times 10^{-3}M$, $[AN] = 0.9042M$, $[\text{cyclohexanone}] = 0.1698M$, $\mu = 1.52M$; (*C*) $1/R_p$ vs. $1/[H^+]$ at 45.0°C in $HClO_4$, $[Cr(VI)] = 5.15 \times 10^{-3}M$, $[AN] = 0.9042M$, $[\text{cyclohexanone}] = 0.1698M$, $\mu = 1.52M$; (*D*) R_p vs. $[H^+]^2$ at 45.0°C in $HClO_4$, $[Cr(VI)] = 4.617 \times 10^{-3}M$, $[AN] = 0.6038M$, $[n\text{-butanol}] = 4.20 \times 10^{-2}M$, $\mu = 0.8M$.

Effect of Ionic Strength on R_p. An increase in the ionic strength of the medium at constant $[H^+]$ increased R_p, in keeping with the observations with other metal ions.[1,23] The increase in R_p may be due either to a salt

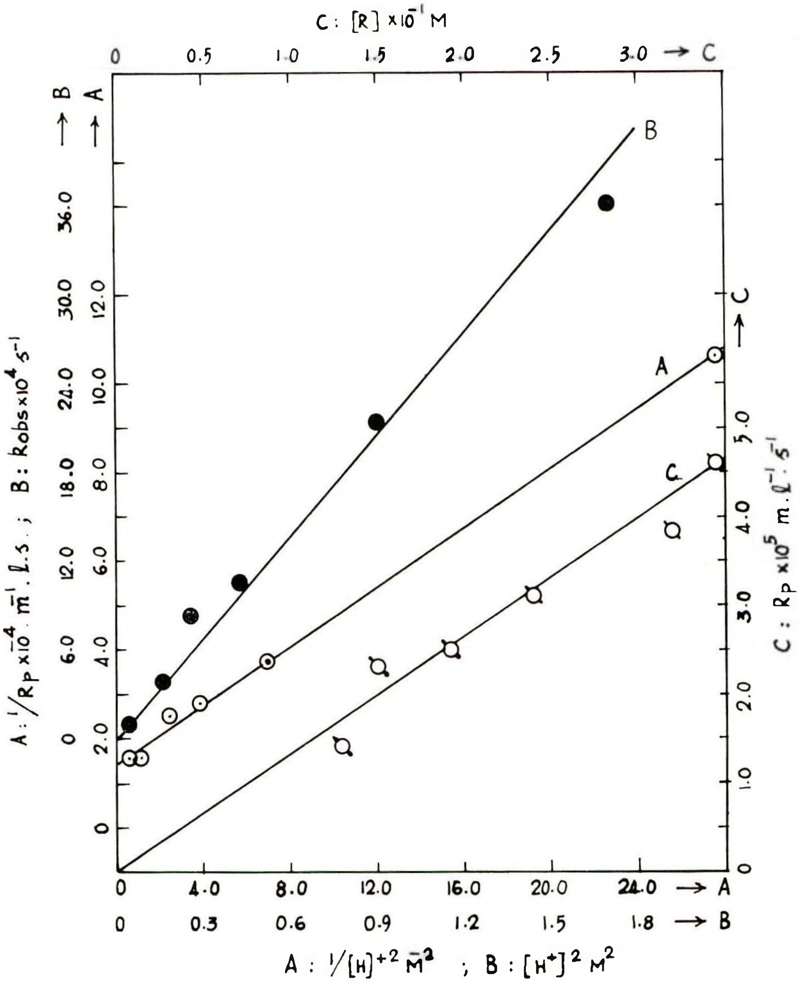

Fig. 5. Variation of R_p and k_{obs} with $[H^+]$ and [reducing agent]: (*A*) $1/R_p$ vs. $1/[H^+]^2$ at 35.5°C in $HClO_4$, $[Cr(VI)] = 5.15 \times 10^{-3}M$, $[AN] = 0.6029M$, [acetaldehyde] $= 4.922 \times 10^{-2}M$, $\mu = 1.5M$; (*B*) k_{obs} vs. $[H^+]^2$ at 35.5°C in $HClO_4$, $[Cr(VI)] = 5.15 \times 10^{-3}M$, $[AN] = 0.6029M$, [acetaldehyde] $= 4.922 \times 10^{-2}M$, $\mu = 1.5M$; (*C*) R_p vs. [ethylene glycol] at 45.0°C in $HClO_4$, $[Cr(VI)] = 5.302 \times 10^{-3}M$, $[AN] = 0.603M$, $[H^+] = 0.733M$, $\mu = 1.0M$.

effect in the propagation step[24] or an increase in the rate of oxidation with μ.

Rate of Chromium(VI) Disappearance, $-R_M$:

Variation of $-R_M$ with [Cr(VI)]. The rate of chromium (VI) disappearance was dependent on the first power of [Cr(VI)]; the conversion Cr(VI) reached nearly 40% at the steady state. The pseudo first-order rate constant, k_{obs}, remained almost constant for a wide range of [Cr(VI)] for all reducing agents except for acetaldehyde for which it decreased at high [Cr(VI)]. Probably in the latter case, operation of the equilibrium suggested by Westheimer and Leo:[25]

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

(where $HCrO_4^-$ is the active oxidant) exerted its influence on $HCrO_4^-$. For the acetaldehyde system, k_{obs} remained constant after correcting for this equilibrium. For all the reducing agents, $-R_M$ depended on the first power of [Cr(VI)] in the absence of monomer also. The rate constant for oxidation k_1 compared very well with that obtained in presence of monomer (Table II).

Variation of $-R_M$ with [AN]. $-R_M$ was found to be independent of [AN] (Table 1), showing that Cr(VI) was not directly involved in initiation. This finding was similar to the observation of Roček and Radowsky[26] that when cyclobutanol was added in the oxidation of V(IV) by Cr(VI), $-R_M$ was unaffected despite extensive oxidation of cyclobutanol.

Variation of $-R_M$ with [R]. Plots of k_{obs} versus [R] were linear (Fig. 2*A* and 2*D*) and passed through the origin. This showed that if radicals from the reducing agent were the initiating species, only a small fraction of them initiated polymerization.

Variation of $-R_M$ with [H$^+$]. For *n*-butanol, ethylene glycol, and acetaldehyde, $-R_M$ depended on $[H^+]^2$ (Fig. 5*B*), whereas for cyclohexanone a first-order dependence was observed (Fig. 4*A*).

Effect of Initially added Cl$^-$, Cr(III), or Ce(III). k_{obs} decreased with added Cl$^-$. Such an inhibition in rate observed in the oxidations of al-

TABLE II
Rate Parameters for Oxidation and Polymerization at 45.0 ± 0.1°C

	n-Butanol	Ethylene glycol	Cyclo-hexanone	Acet-aldehyde
Rate constant for oxidation without monomer $k_1 \times 10^2$				
From k_{obs} vs. $[H^+]$ or $[H^+]^2$	6.86	2.12	0.76	—
From k_{obs} vs. [R]	6.66	2.20	—	—
Rate constant for oxidation with monomer $k_1 \times 10^2$				
From k_{obs} vs. H^+ or $[H^+]^2$	7.83	2.85	0.68	15.97
From k_{obs} vs. [R]	7.15	1.17	0.71	19.28
$k_{t2}/k_p \times 10^{-1}$				
From $[AN]^2/R_p$ vs. [AN]	2.62	—	3.49	—
From $1/R_p$ vs. [Cr(VI)]	3.64	4.58	2.39	—
From $1/R_p$ vs. $1/[H^+]$ or $1/[H^+]^2$	—	4.32	—	—
$k_3/k_i \times 10^1$				
From $[AN]/R_p$ vs. [AN]	10.4	—	2.72	—
From $1/R_p$ vs. [Cr(VI)]	6.9	3.207	6.72	—
From $1/R_p$ vs. $1/[H^+]$ or $1/[H^+]^2$	—	2.87	—	—

cohols[27] and phosphoric acid[28] was attributed to the participation of the weaker oxidant, CrO_2Cl^- in oxidations. $-R_M$ was unaffected by added Cr(III) but it decreased by about 40% by the addition of cerous perchlorate (Table I).

Molecular Weights

The molecular weights of the polymers were dependent on the first power of [AN], inversely on $[CrO_3]$, and independent of other variables (Figs. 1*C* and 3*D*).

KINETIC SCHEME

Of the possible reaction schemes examined, that involving initiation by Cr(IV) or R· and termination by Cr(VI) satisfied the experimental results. The active oxidizing agent is the acid chromate ion, $HCrO_4^-$.

Reaction of acid chromate ion with reducing agent R:

$$HCrO_4^- + R + 2H^+ \xrightarrow{k_1} Cr(IV) + Product \tag{1}$$

Reaction of tetravalent chromium with R:

$$R + Cr(IV) \xrightarrow{k} R^{\cdot} + Cr(III) + H^+ \tag{2}$$

Reaction of primary radical R· with Cr(VI):

$$R^{\cdot} + Cr(VI) \xrightarrow{k_3} Cr(V) + Product. \tag{3}$$

The pentavalent chromium is reduced to Cr(III) by reaction with reducing agent:

$$R + Cr(V) \rightarrow Product + Cr(III) \tag{4}$$

Initiation of polymerization by reaction of a primary radical with monomer:

$$R^{\cdot} + M \xrightarrow{k_i} M^{\cdot} \tag{5a}$$

Initiation of polymerization by reaction of Cr(IV) with monomer:

$$Cr(IV) + M \xrightarrow{k_i^1} M^{\cdot} + Cr(III) + H^+ \tag{5b}$$

Propagation of polymerization:

$$\begin{gathered} M^{\cdot} + M \xrightarrow{k_p} M^{\cdot}_2 \\ \vdots \\ M^{\cdot}_{n-1} + M \xrightarrow{k_p} M^{\cdot}_n \end{gathered} \tag{6}$$

Termination of polymerization:

$$M^{\cdot}_n + Cr(VI) \xrightarrow{k_{t_2}} M_n + Cr(V) + H^+ \tag{7}$$

Under conditions of eq. (5a) for initiation and by making the usual steady-state assumptions for free radicals and unstable intermediates, we have

$$R_p = \frac{k_p k_1 k_i [\mathrm{AN}]^2 [\mathrm{R}][\mathrm{H}^+]^2}{k_{t2}\{k_3[\mathrm{Cr(VI)}] + k_i[\mathrm{AN}]\}} \tag{8}$$

Equation (8) may be transformed to eq. (9):

$$\frac{[\mathrm{AN}]^2}{R_p} = \frac{k_{t2}k_3[\mathrm{Cr(VI)}]}{k_p k_1 k_i [\mathrm{R}][\mathrm{H}^+]^2} + \frac{k_{t2}[\mathrm{AN}]}{k_p k_1 [\mathrm{R}][\mathrm{H}^+]^2} \tag{9}$$

Then

$$-R_{\mathrm{M}} = 2k_1[\mathrm{Cr(VI)}][\mathrm{R}][\mathrm{H}^+]^2 \tag{10}$$

and chain length n is given by

$$n = k_p[\mathrm{AN}]/k_{t2}[\mathrm{Cr(VI)}] \tag{11}$$

The proportionalities between experimental rates and n on the one hand and various variables on the other [eqs. (8)–(11)] were satisfactorily observed.

Radical Production and Initiation of Polymerization

The facts that Cr(VI) alone neither oxidized nor polymerized AN discounted the reaction between Cr(VI) and monomer as the radical-production step. Initiation of polymerization of AN by the system Cr(VI)–reductant in acid media and reduction of Cr(VI) suggested that the possible radical production steps might be Cr(VI) + R or Cr(V) + R or Cr(IV) + R. On the basis of the reasonable assumption that Cr(VI) is a two-electron oxidant, that step (1) of the kinetic scheme is predominant, the reaction Cr(IV) + R [eq. (2) in the kinetic scheme] rather than Cr(V) + R. [eq. (4) in the kinetic scheme] appears as a plausible radical production step. Another possible reaction for radical production might be between Cr(IV) and the product in eq. (1) of the kinetic scheme. In the chromic acid oxidation of phenyl *tert*-butyl alcohol to which AN was added, polymerization of the latter reported by Mosher and Driscoll[22] was attributed to production of radicals from the reaction between Cr(IV) and product. But under our experimental conditions of large[15] [R], it is likely that the reaction Cr(IV) + R takes precedence, and the reaction Cr(IV) + product might be discounted. Yet another possible radical production reaction is Cr(IV) + M [eq. (5b) in the kinetic scheme]. If reaction (5b) in preference to (5a) were to take place, expressions (8)–(11) would be identical except for replacement of k_1 by k_i^1 in eqs. (8) and (9). In the presence of an organic substrate, the reaction between Cr(IV) and R would take place in preference to that between Cr(IV) and monomer, and hence eq. (5b) could be neglected. The species responsible for radical production might be Cr(IV) and not Cr(V). The work of Roček and Radkowsky[26] also showed that Cr(IV) and not Cr(V), oxidized cyclobutanol.

The suggested kinetic scheme explains satisfactorily the results involving Cr(VI) and *n*-butanol, cyclohexanone and ethylene glycol as reducing agents at all concentrations and those of Cr(VI)–acetaldehyde system at high concentrations of the latter. At low [R], the primary radical from acetaldehyde R$^{\cdot}$ ($CH_3{-}\dot{C}{=}O$) may not be easily oxidized by Cr(VI), and the former may add on to another aldehyde molecule producing a secondary radical [eq. (12)]

$$CH_3CHO + R^{\cdot} \rightarrow R^{\cdot}_2 \tag{12}$$

Alternatively, the primary radical R$^{\cdot}$ might also abstract a hydrogen atom from another aldehyde molecule [eq. (13)]

$$R^{\cdot} + CH_3CHO \rightarrow RH + CH_3\dot{C}O \tag{13}$$

No distinction is made between these two alternative reactions in deriving an expression [eq. (14)] for R_p for acetaldehyde at low [R].

$$R_p = \frac{k_p k_i k_1 k_2([AN][R][H^+])^2}{k_{t2}\{k_2[R] + k_3[Cr(VI)]\}(k_4[R] + k_i[AN])} \tag{14}$$

Reduction of order of [R] from 2 to unity and curvature of $1/R_p$ versus 1/[R] plots (Fig. 2*B*) at high [R] may be understood in terms of eq. (14). Also the leveling off in the plots of R_p versus $[H^+]^2$ for ethylene glycol and acetaldehyde (and of R_p versus $[H^+]$ for cyclohexanone) (Fig. 5*A*) may not have anything to do with complete protonation of chromate ester, since no such leveling off was noticed in our oxidation studies. We suggest the leveling off effects in polymerization experiments might be due to an acid dependence in reaction (3) of the kinetic scheme for the two cases:

$$R^{\cdot} + Cr(VI) + 2H^+ \rightarrow Cr(V) + \text{product} \tag{15}$$

for ethylene glycol, acetaldehyde and

$$R^{\cdot} + Cr(VI) + H^+ \rightarrow Cr(V) + \text{product} \tag{16}$$

for cyclohexanone. The experimental results may be understood in term of a modified equation of eq. (8) in which $k_3[Cr(VI)]$ in the denominator is replaced respectively for the two represented by eqs. (15) and (16) cases by $k_3[Cr(VI)][H^+]^2$ or k_3 $[Cr(VI)][H^+]$. For cyclohexanone, the chromate ester seemed to involve only one proton whereas for other reducing agents it involved two protons.

Our conclusions that the species responsible for radical production was Cr(IV) and not Cr(V) and that the initiating species R$^{\cdot}$ are supported by the work of Mosher and Driscoll.[22] In the chromic acid oxidation of phenyl *tert*-butyl alcohol to which AN was added, polymerization of the latter was noticed. If Cr(V) were the radical-producing species, autocatalysis would be expected, and this was found to be absent.

Rate Constants

k_1 in presence of monomer and in its absence were obtained from the plots of k_{obs} versus [R] or $[H^+]$ or $[H^+]^2$, and they were found to be in good agreement (Table II) within the limits of experimental error. The composite rate constants, k_{t2}/k_p and k_3/k_1 (Table II) for the systems were obtained from (a) slopes and intercepts, respectively, of plots of $[AN]^2/R_p$ versus [AN]; (b) intercepts and slopes, respectively, of plots of $1/R_p$ versus [Cr(VI)]; and (c) intercept and slope, respectively, of the plot of $1/R_p$ versus $1/[H^+]$ or $1/[H^+]^2$. Since k_3/k_i (Table II) is the ratio of the rate constant for the consumption of R by Cr(VI) and monomer, respectively, the magnitude of the value indicated that only a small percentage of the radicals was used for initiation. It seemed probable that Cr(VI) completed more effectively with monomer for radicals formed within a solvent cage. The values of k_{t2}/k_p obtained in the present study were far greater than those reported with other metal ion systems,[1,23] i.e., Ce(IV), V(V), showing that Cr(VI) was an effective terminator of polymer chains. The composite parameters for the acetaldehyde system could not be separated because of the complex nature of eq. (14).

References

1. V. S. Ananthanarayanan and M. Santappa, *J. Appl. Polym. Sci.*, **9**, 2437 (1965).
2. K. Jijee, M. Santappa, and V. Mahadevan, *J. Polym. Sci. A-1*, **4**, 377 (1966).
3. R. S. Konar and S. R. Palit, *J. Indian Chem. Soc.*, **38**, 481 (1961).
4. E. A. S. Cavell and A. C. Meeks, *Polymer*, **8**, 79 (1967).
5. R. S. Konar and S. R. Palit, *J. Polym. Sci. A*, **2**, 1731, (1964).
6. W. M. Latimer, *Oxidation Potentials*, 2nd ed., Prentice-Hall, New York, 1959.
7. I. M. Kolthoff and E. J. Meehan, *J. Polym. Sci.*, **9**, 327 (1952).
8. W. A. Waters, *Quart. Revs.*, **12**, 277 (1958).
9. F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949).
10. K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3022 (1958).
11. D. W. Bhatnagar, *J. Sci. Ind. Res. (India)*, **B16**, 23 (1957).
12. T. Shibukawa, M. Sume, A. Vehida, and K. Swahori, *J. Polym. Sci., A-1*, **6**, 147 (1968).
13. J. D. Roberts and M. Cessario, *Basic Principles of Organic Chemistry*, Benjamin, New York, 1964.
14. A. C. Chatterji and S. K. Mukherjee, *Z. Anorg. Allgem. Chem.*, **280**, 110 (1955).
15. P. A. Best, J. S. Littler, and W. A. Waters, *J. Chem. Soc.*, **1962**, 822.
16. R. M. Lanes and D. G. Lee, *J. Chem. Educ.*, **45**, 269 (1968).
17. R. Stewart and D. G. Lee *Can. J. Chem.*, **42**, 439 (1964).
18. N. Venkatasubramanian and G. Srinivasan *Proc. Indian Acad. Sci.*, **71**, 1 (1970).
19. A. A. Katai, V. K. Kulshrestha, and R. H. Marchessault, in *Fourth Cellulose Conference* (*J. Polym. Sci. C*, **2**), R. H. Marchessault, Ed., Interscience, New York, 1963, p. 403.
20. R. Stewart, *Oxidation Mechanisms: Application to Organic Chemistry*, Benjamin, New York, 1964.
21. C. Altmann and E. L. King, *J. Amer. Chem. Soc.*, **83**, 2825 (1961).
22. W. A. Mosher and E. L. Driscoll, *J. Amer. Chem. Soc.*, **90**, 4189 (1968).
23. S. Saccubai and M. Santappa, *J. Polym. Sci. A-1*, **7**, 643 (1969).
24. C. H. Bamford, A. D. Jenkins, and R. Johnston, *J. Polym. Sci.*, **29**, 355 (1958).
25. A. Leo and F. H. Westheimer, *J. Amer. Chem. Soc.*, **74**, 4383 (1952).
26. J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **90**, 2987 (1968).
27. M. Cohen and F. H. Westheimer, *J. Amer. Chem. Soc.*, **74**, 4387 (1952).
28. G. P. Haight, M. Rose, and J. Preer, *J. Amer. Chem. Soc.*, **90**, 4809 (1968).

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Triad Tacticity of Polyacrylonitrile

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Synopsis

The high-resolution NMR spectra of polyacrylonitrile-β,β-d_2 prepared by radical polymerization were determined, and the stereoregularity of the polymer was studied. The NMR spectra of methine protons of polyacrylonitrile-β,β-d_2 in dimethyl sulfoxide-d_6 and a mixture of nitromethane-d_3 and ethylene carbonate showed three partially resolved multiplets. The deuterium-decoupled spectra of the polymer were measured, and three well resolved peaks were observed in the two solvents and dimethylformamide-d_7. These three peaks were analyzed by comparison with the NMR spectra of model compounds and polyacrylonitrile-α-d, and they were assigned to isotactic, heterotactic, and syndiotactic triads with decreasing magnetic field. This order seems to be unchanged in other solvents. Triad stereoregularity of the polymer was determined according to the assignment. Polymerizations of acrylonitrile-β,β-d_2 by radical initiators between −78°C and 60°C were explained by the Bernoulli trial propagation step. The polymers had an atactic structure, independent of polymerization temperature. This shows that in free-radical polymerization of acrylonitrile, the chain end is not represented as having any particular stereochemistry. Other stereochemical control is necessary to produce tactic polymers. The triad tacticity of isotactic polyacrylonitrile was also determined.

INTRODUCTION

The importance of investigations on the structure of polymers by NMR spectroscopy is increasing very rapidly. We have been studying polymer stereochemistry by NMR in order to elucidate the polymerization mechanism and therefore, to devise methods for controlling the propagation step.

The stereoregularity of polyacrylonitrile has been studied by means of physical properties,[1-3] x-ray diffraction,[4-9] and infrared spectroscopy.[10-14] but many data are ambiguous. High-resolution NMR spectroscopy has been used as a quantitative method, but there were different conclusions on the stereoregularity of polyacrylonitrile among the various investigators.[15-17] We have determined the stereoregularity of polyacrylonitrile (PAN) in isotactic and syndiotactic diads from the methylene proton spectrum of polyacrylonitrile-α-d (PAN-α-d)[16] and suggested a reason for the different conclusions.[18] The triad tacticity of PAN was first found by Bargon et al.,[17] who obtained three partially resolved methine proton multiplets by decoupling from methylene protons and assigned the signals to isotactic, heterotactic, and syndiotactic triads with decreasing magnetic field. Since the decoupled methine proton spectrum was not sufficiently sharp, the triad tacticity was not quantitatively estimated. We wish to report in this paper the NMR spectra of polyacrylonitrile-β,β-d_2 (PAN-β,β-d_2) of much higher resolution than that of the above authors. We will also report the relations between the change of polymerization conditions and triad stereoregularity and then discuss the mechanism of radical polymerization.

EXPERIMENTAL

Monomer

Acrylonitrile-β,β-d_2 (AN-β,β-d_2) was prepared from acrylonitrile-d_3 (AN-d_3) by D-H exchange in H_2O with CaO as catalyst, according to the literature method of preparing acrylonitrile-α-d (AN-α-d) by H-D exchange.[19] AN-d_3 was synthesized by deuteration of cyanoacetylene-d (CA-d) as reported by Yoshino et al.[20] CA-d was prepared by two methods; one was that of the above authors and the other was as follows. Cyanoacetylene (CA, 16 ml) was kept with 10 ml. of D_2O ($D = 95\%$) in a glass vessel with occasional shaking for several days. Then, the upper layer of CA was decanted, dried over $CaCl_2$, and distilled *in vacuo*. The CA-d obtained and 21 ml of D_2O ($D = 99.8\%$) were subjected to the same operation. The yield was about 75%, and the deuterium content of CA-d twice exchanged in D_2O was 95% or more.

The overall yield of synthesis of AN-β,β-d_2, calculated on CA-d ($D = 98\%$), was about 31%. For a single D-H exchange of AN-d_3, the hydrogen content at the α-position of AN-β,β-d_2 was about 80% ($D = 20\%$).[21] This seems, however, to improve the resolution by reducing the possible effect of the long-range coupling between different neighboring pentads[22] and the effect of residual β-proton. The spectrum is shown in Figure 1. We at-

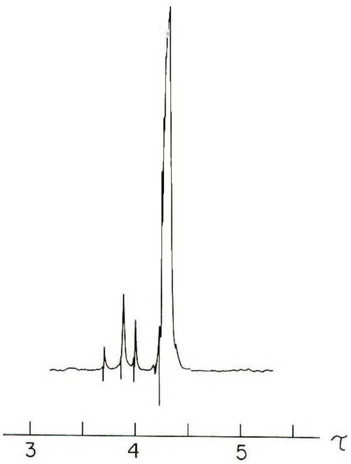


Fig. 1. NMR spectrum of acrylonitrile-β,β-d_2 measured at room temperature (neat) (CH, 4.30τ; nondeuterated CH_2, 3.71, 3.89, and 4.00τ).

tribute the singlet at 4.3τ to the α-proton and the three peaks at 3.7–4.0τ to the β-proton. The β-hydrogen content was found to be 8%. All the isotopic contents were obtained by NMR or mass spectroscopy.

Polymerization

AN-β,β-d_2 containing about 5% of propionitrile-d_5 (by gas chromatography) was polymerized with azobisisobutyronitrile (AIBN) at 60°C, with γ-rays at 0°C and −78°C, and with ultraviolet light at −40°C, all in toluene. PAN-β,β-d_2 formed was poured into methanol, filtered, and dried in vacuo. Polymerization of AN-β,β-d_2 in urea canal complex was performed according to the method of White,[23] except that γ-irradiation was used instead of x-irradiation.

NMR Analysis

The dried polymer was dissolved in NMR solvents, filtered and sealed. NMR solvents were dimethyl sulfoxide-d_6 (DMSO-d_6, D = 99%), a mixture (1:1) of nitromethane-d_3 (D = 99%) and ethylene carbonate [CD_3NO_2–$(CH_2O)_2CO$], and dimethylformamide-d_7 (DMF-d_7, D = 99%). For DMSO-d_6 used as solvent was dehydrated, degassed, and sealed to avoid the overlapping of the side band of absorbed water on the methine proton signal. The spectrum was run on a Japan Electron Optics Laboratory JNM 4H-100 (100MHz) spectrometer. Deuterium decoupling was carried out when necessary. Triad tacticity was determined by measurement of the relative area of the peaks in NMR spectra assuming a Lorentzian line shape. The measurement of area was carried out four times, and the average value was adopted. The maximal standard deviation was 1.1%.

RESULTS AND DISCUSSION

Results of Polymerization

The results of radical polymerization of AN-β,β-d_2 are shown in Table I. There were considerable differences in conversion of monomer to polymer but the stereoregularity seems to be unaffected by the polymer yield.

TABLE I
Radical Polymerization of Acrylonitrile-β,β-d_2

No.	Initiator	Temp, °C	Solvent	Time, hr	Conversion, %
1	AIBN	60	Toluene	2	24
2	γ-rays (1.3 × 10^5r)	0	Toluene	21	79
3	Ultraviolet light	−40	Toluene	12	1
4	γ-rays (1.3 × 10^6r)	−78	Toluene	95	5
5	γ-rays (9.5 × 10^4r)	−78	none[a]	20	97

[a] As urea canal complex.

Infrared Spectra of PAN-β,β-d_2

Figure 2 shows the infrared spectra of PAN-β,β-d_2. Figures 2*A*, 2*B* are spectra of polymers with random configuration, prepared with AIBN at 60°C and by γ-ray irradiation at 0°C, respectively; Figure 2*C* is the spectrum of isotactic polymer prepared by γ-irradiation of the urea canal complex. Absorptions at 3600–3400 and 1630 cm^{-1} are background from the KBr pellet. The formation of carbonyl group in the polymer structure ap-

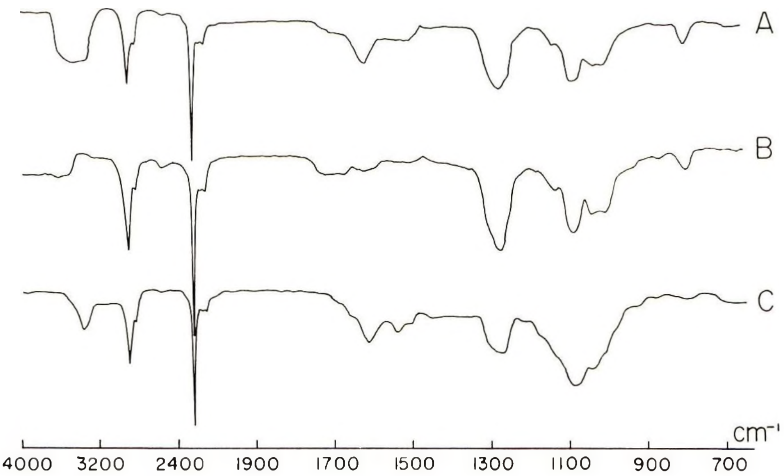


Fig. 2. Infrared spectra of polyacrylonitrile-β,β-d_2: (*A*), (*B*) polymers with random configuration, prepared with AIBN at 60°C and by γ-ray irradiation at 0°C, respectively, both in toluene; (*C*) isotactic polymer prepared by γ-ray irradiation of urea canal complex.

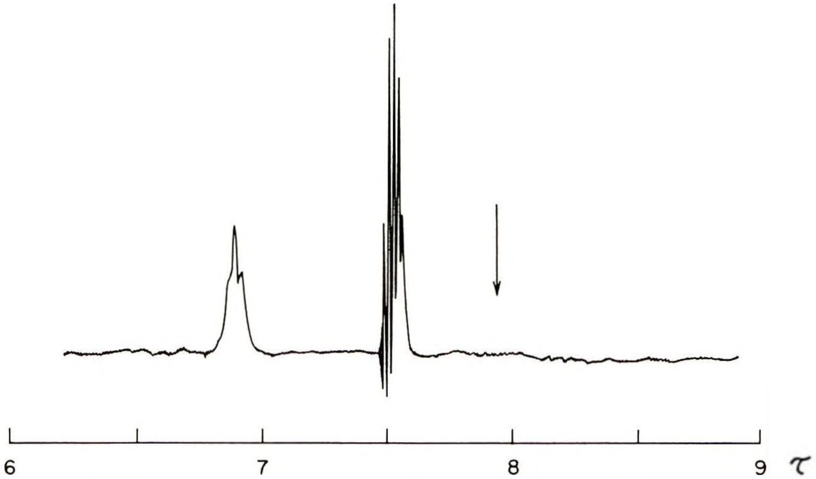


Fig. 3. NMR spectrum of polyacrylonitrile-β,β-d_2 measured at 120°C in DMSO-d_6. [Signals at 7.5τ due to hydrogen atoms remaining in DMSO-d_6; the position of the β-proton signal of polyacrylonitrile (7.9τ) is indicated by an arrow.]

pears to be very slight. This is also shown in the NMR spectrum of Figure 3, in which no absorptions other than α-hydrogen were observed. There are no substantial differences detected between the spectra *A* and *B*, but there are some differences between *A* or *B* and *C*. In the spectrum of isotactic PAN-β,β-d_2 (Fig. 3*C*), absorptions at 1090 and 1050 cm^{-1} are stronger than those of atactic polymers (Fig. 3*A*, 3*B*).

Though many investigators have reported on the structure of PAN by means of infrared spectroscopy,[10–14] it seems that it is difficult to elucidate the differences of polymer stereoregularity only by infrared spectroscopy.

Analysis of NMR Spectra of PAN-β,β-d_2 in DMSO-d_6

NMR spectra of PAN-β,β-d_2 are shown in Figure 4. When DMSO-d_6 was used as solvent for measurement, there are obvious differences between the methine proton spectrum of PAN-β,β-d_2 polymerized with AIBN as catalyst at 60°C and that of the polymer obtained from the urea canal complex. The methine proton spectrum of the former (Fig. 4*A*) indicates three peaks at 6.90, 6.88, and 6.86τ, of which the peak at 6.88τ is highest, but the spectrum of the latter (Fig. 4*B*) shows the highest peak at 6.90τ.

From the diad tacticity of PAN-α-*d*, it is known that PAN prepared with a radical initiator has a random configuration consisting of equal amounts of isotactic and syndiotactic diads and that an isotactic polymer is obtained from γ-ray irradiation of the acrylonitrile urea canal complex.[18,25]

Furthermore, the analysis of NMR spectra in this solvent of *meso*- and *dl*-2,4-dicyanopentanes, which are model compounds of isotactic and syndiotactic PAN, respectively, has shown that the chemical shift of the methine proton (7.108τ) of the meso form is in a higher magnetic field than that (7.087τ) of the *dl* form.[18] Yamadera and Murano reported the NMR spectra of stereoisomers of 2,4,6-tricyanoheptane as three-unit model compounds of PAN in chloroform and NaCNS–D_2O and indicated that the sig-

TABLE II
Tacticity of Polyacrylonitrile-β,β-d_2

			Tacticity				
	Polymerization temperature,		Triad, %			Diad, %[b]	
No.[a]	°C	NMR Solvent	*S*	*H*	*I*	*s*	*i*
1	60	CD_3NO_2–$(CH_2O)_2CO$	25	47	28	48	52
"	"	DMSO-d_6	23	49	28	48	52
"	"	DMF-d_7	26	46	28	49	51
2	0	CD_3NO_2–$(CH_2O)_2CO$	24	50	26	49	51
"	"	DMSO-d_6	24	48	28	48	52
3	−78	CD_3NO_2–$(CH_2O)_2CO$	25	46	29	48	52
5	−78	"	9	29	62	24	76
"	"	DMSO-d_6	15	31	54	30	70
"	"	DMF-d_7	11	28	61	25	75

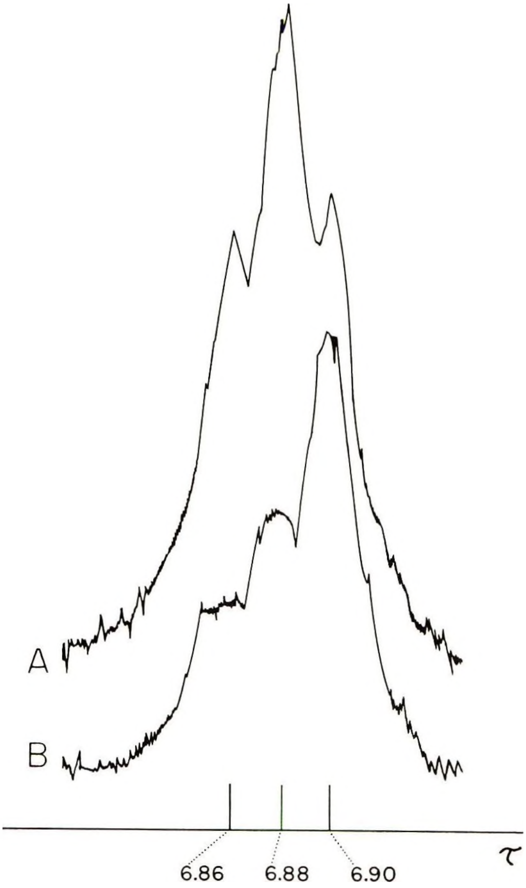
[a] Same as those of Table I.

[b] Derived from triad tacticities $i = I + H/2$ and $s = S + H/2$.

nals of methine protons in triads appear in the order, isotactic, heterotactic, and syndiotactic methines from the higher magnetic field.[24]

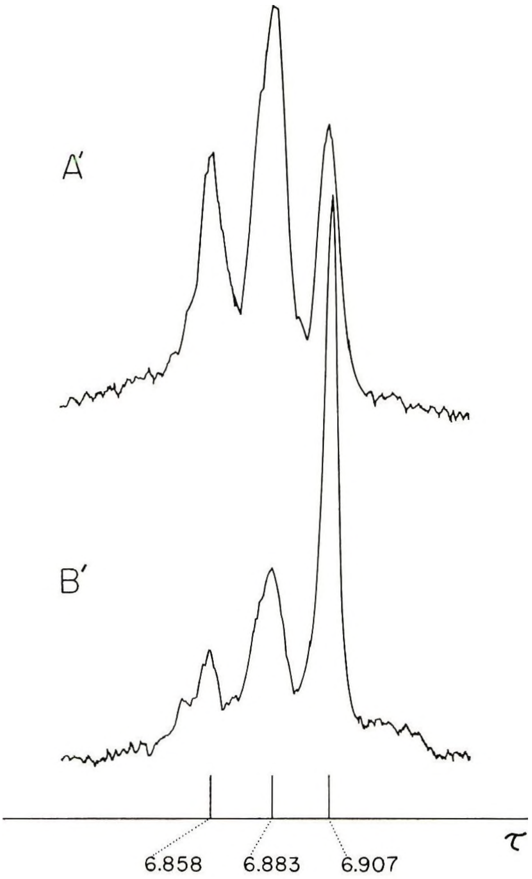
We also found that in DMSO-d_6 signals of the methine proton in triads of the three-unit model compounds isolated as in the method of the above authors, show the same tendency as in chloroform and NaCNS–D_2O; that is, the order is isotactic (7.05τ), heterotactic (7.04τ), and syndiotactic (7.02τ).

Therefore, it is concluded that the three peaks due to methine protons of PAN-β,β-d_2 are assignable to isotactic, heterotactic, and syndiotactic triads with decreasing magnetic field. This assignment agrees with that of Bargon et al.[17] The tacticity in isotactic (*I*), heterotactic (*H*), and syndiotactic (*S*) triads was estimated, and the results are shown in Table II. The deuterium-decoupled spectra corresponding to Figures 4*A* and 4*B* are shown in Figure 4*A*′ and 4*B*′, respectively. The spectra are sharper, and three splittings are clearly observed.



(*a*)

Fig. 4 (*continued*)



(b)

Fig. 4. Methine proton spectra of polyacrylonitrile-β,β-d_2 measured at 120°C in DMSO-d_6; (*A*), (*A′*) polymer obtained with AIBN as catalyst; (*B*), (*B′*) polymer prepared by γ-ray irradiation of urea canal complex; (*A′*) and (*B′*) are the deuterium-decoupled spectra.

Analysis of NMR Spectra of PAN-β,β-d_2 in CD_3NO_2–$(CH_2O)_2CO$

Similar but well-resolved spectra, as shown in Figure 5, were obtained in CD_3NO_2–$(CH_2O)_2CO$ as solvent. In this case, the chemical shifts of the three peaks are 6.901, 6.865, and 6.831τ. The relative intensity of three peaks of atactic polymers does not depend on the polymerization temperature, but in the case of isotactic polymer signal at 6.901τ is the highest one. Therefore, we can also assign the three peaks to isotactic, heterotactic, and syndiotactic triads with decreasing magnetic field as in the case of DMSO-d_6 solvent. This assignment agrees with Bargon's result on the decoupled spectrum in this solvent. Although the poor resolution of their spectrum precluded quantitative discussion, our sharp spectra provide unquestion-

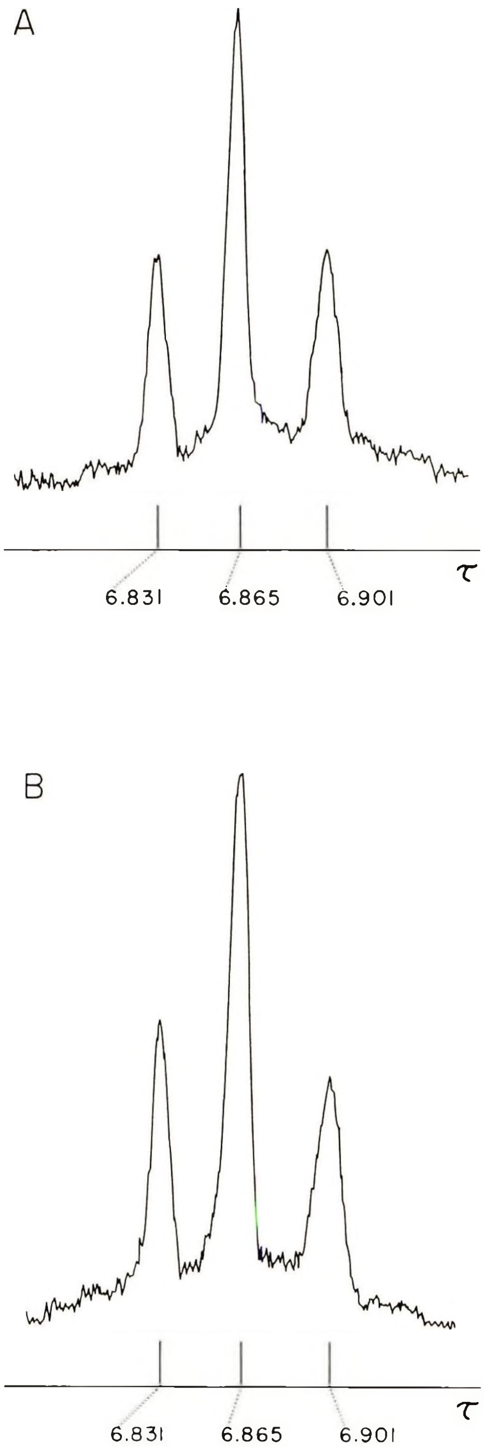


Fig. 5 (*continued*)

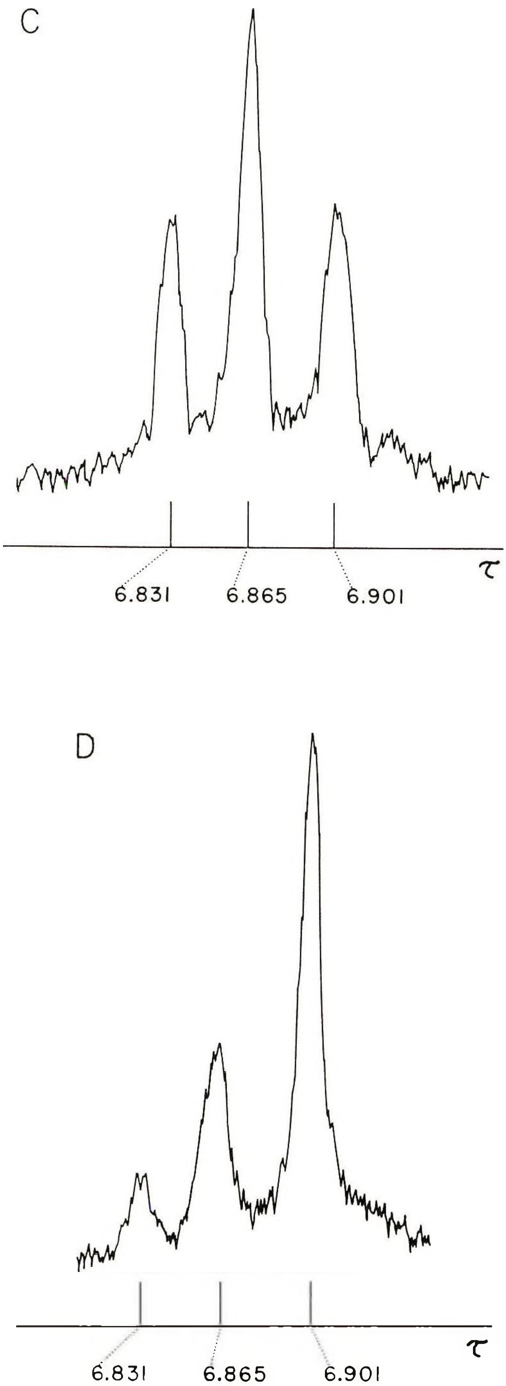


Fig. 5. Deuterium-decoupled methine proton spectra of polyacrylonitrile-β,β-d_2 polymerized by a radical initiator at (*A*) 60°C, (*B*) 0°C, and (*C*) −78°C, and (*D*) by γ-ray irradiation of urea canal complex [measured at 140°C in CD_3NO_2–$(CH_2O)_2CO$].

able evidence to the assignment of triad signals and also allow quantitative measurement.

Analysis of NMR Spectra of PAN-β,β-d_2 in DMF-d_7

In Figure 6, NMR spectra of PAN in DMF-d_7 are shown. The central peak of the quintet signal (6.75τ) due to methine protons of isotactic polymer is in higher magnetic field by about 1 Hz than that (6.74τ) of polymer having a random configuration. However, information about triad tacticity could not be obtained from the spectra.

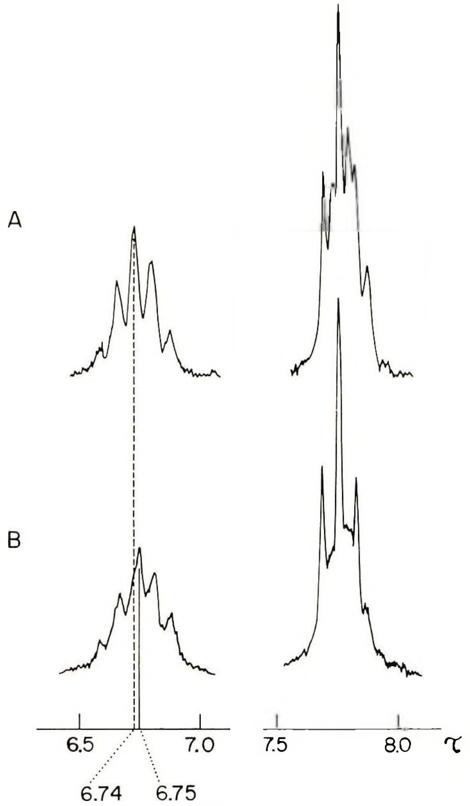


Fig. 6. NMR spectra of polyacrylonitriles of (*A*) random configuration and (*B*) isotactic configuration measured in DMF-d_7.

NMR spectra of PAN-β,β-d_2 with deuterium decoupling techniques are shown in Figure 7. In the case of DMF-d_7 as solvent for NMR measurement, the chemical shifts of methine protons showed almost the same trend as in other solvents. Therefore, as mentioned in the former two solvents, three peaks can be assigned to isotactic, heterotactic, and syndiotactic triads from the higher magnetic field.

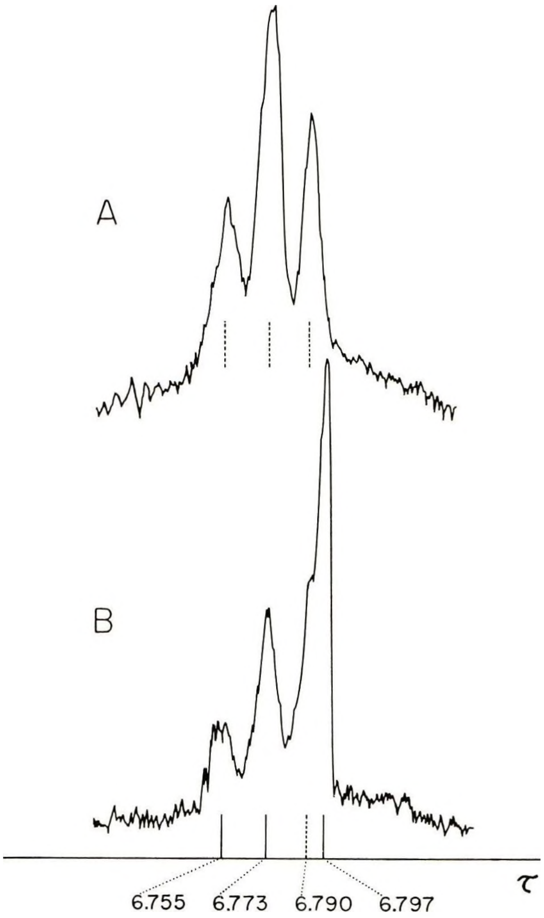


Fig. 7. Deuterium-decoupled methine proton spectra of polyacrylonitrile-β,β-d_2 measured at 140°C in DMF-d_7: (*A*) polymer prepared with AIBN as catalyst at 60°C; (*B*) polymer prepared by γ-ray irradiation of urea canal complex.

Effect of Solvent on the Chemical Shifts of Methine Protons

The order of triad chemical shifts of methine protons does not change, regardless of whether DMSO-d_6, CD_3NO_2–$(CH_2O)_2CO$, or DMF-d_7 is used as solvent. There were different conclusions on the stereoregularity of PAN based on diads, possibly because individual investigator used different solvents for NMR measurement. Besides the three solvents described above, $NaCNS$–D_2O[15] and $HClO_4$–H_2O[25] have been used as solvents for NMR measurement of PAN. Well resolved spectra, however, are not obtained in the both solvents. In the case of $NaCNS$–D_2O, H-D exchange of α-hydrogen probably accounts for poorly resolved spectra as reported by Hunter.[26] The effect of solvent on methylene proton absorptions of PAN has been discussed from the viewpoint of equivalence or nonequivalence of *meso* methylene protons.[18,25,27]

It seems, however, that the effect of solvent on the chemical shifts has not been made clear, and has been discussed only qualitatively, except for a few simple molecules. The fact that the order of chemical shifts of triad methine protons in isotactic, heterotactic, and syndiotactic configurations does not change in the three solvents which have a wide range of dielectric constants (DMSO, 45.0; DMF, 36.1; CH_3NO_2, 35.9; $(CH_2O)_2CO$, 89.1), suggests that the order of the chemical shift will not change in other solvents. The chemical shifts of methine protons in various solvents are shown in Table III. The additional partly resolved peaks caused by a pentad effect are observed as the splittings of syndiotactic triad in Figures 4*B'*, 5*D*, and 7*B*, and as those of isotactic triad in Figure 7. In DMSO-d_6 solvent, pentad signals are also observed at elevated temperatures, discussion of which will be reported elsewhere.

TABLE III
Chemical Shifts of Triad Methine Proton in Different Solvents

NMR Solvent	Chemical shifts of methine proton, τ		
	Syndiotactic	Heterotactic	Isotactic
DMSO-d_6	6.858	6.883	6.907
CD_3NO_2–$(CH_2O)_2CO$	6.831	6.865	6.901
DMF-d_7	6.755	6.773	6.790, 6.797

Triad Tacticity of PAN-β,β-d_2 and Mechanism of Polymerization

Triad tacticity of PAN-β,β-d_2 is shown in Table II. Small differences in triad tacticity observed in different solvents for NMR measurements might be due to difficulty in resolving triad signals, because there are only small differences in chemical shifts of the peaks. It seems that CD_3NO_2–$(CH_2O)_2CO$, in which methine protons are well resolved, is most suited for determination of triad tacticity. In Table II, Nos. 1–3 refer to polymerization in toluene and No. 5 to polymerization of urea canal complex. From this table, we can consider the mechanism of free-radical polymerization of PAN as follows; in the case of polymerization in toluene, the mechanism follows Bernoulli statistics, and the tacticity does not change in the range of polymerization temperature from −78°C to 60°C.

Bovey has reported that the difference in the activation enthalpies $\Delta(\Delta H_p\ddagger)$ and entropies $\Delta(\Delta S_p\ddagger)$ of the syndiotactic and isotactic diad addition process for polymerization is given as[28]

$$\Delta(\Delta S_p\ddagger) = \Delta S_i\ddagger - \Delta S_s\ddagger = R\ln[P_m/(1 - P_m)] + \Delta(\Delta H_p\ddagger)/T \quad (1)$$

where

$$\Delta(\Delta H_p\ddagger) = \Delta H_i\ddagger - \Delta H_s\ddagger$$

$\Delta H_i\ddagger$ and $\Delta H_s\ddagger$ are the enthalpies of activation for isotactic and syndiotactic addition, respectively; P_m is the probability of isotactic addition, R is the gas constant, and T is absolute temperature. When our results are treated with eq. (1), it is found that $\Delta(\Delta H_p\ddagger)$ is equal to zero (0.02 ± 0.02 kcal/mol), and the probability of isotactic diad addition is governed by only the magnitude of the difference in activation entropy, $\Delta(\Delta S_p\ddagger)$ (0.0 ± 0.2 e.u.) in the polymerization. This temperature independence does not agree with a previous report.[29]

Therefore, it appears that in the propagation of PAN by a radical mechanism no stereochemical control is operative, and only atactic polymers are obtained. Although the polymerization of acrylonitrile in toluene is heterogeneous, in a homogeneous polymerization too, this will be the same, and only atactic polymer will be obtained, irrespective of the polymerization temperature. It appears that certain stereochemical control is necessary to obtain highly tactic PAN in radical process.

For example, PAN-β,β-d_2 obtained from the urea canal complex, that is, a kind of organized polymerization, is an isotactic-rich polymer (Table II, No. 5). This polymer does not obey Bernoulli trials, that is, heterotactic content is less but syndiotactic configuration is larger than calculated.

Though it was reported that syndiotactic PAN was obtained by γ-ray irradiation of acrylonitrile arranged in montmorillonite,[30,31] it was found that the polymer obtained under the same experimental conditions contained a ring structure.

Polymerization of the complex of acrylonitrile and Lewis acid has been reported[32,33] but it seems as that although the formation of complex increases Q and e values and reactivity, it will not give any control on the stereochemical process in the propagation.

The stereoregularity in triad is in good agreement with that in diads, determined first by us[16] and later by two other investigators.[25,34]

References

1. W. R. Krigbaum and N. Tokita, *J. Polym. Sci.*, **43**, 467 (1960).
2. R. Chiang, *J. Polym. Sci. A*, **3**, 2019 (1965).
3. H. Inagaki, K. Hayashi, and T. Matsuo, *Makromol. Chem.*, **84**, 80 (1965).
4. C. L. Arcus and A. Bose, *Chem. Ind.* (London), **78**, 456 (1959).
5. Z. Menčik, *Vysokomol. Soedin.*, **2**, 1635 (1960).
6. C. R. Bohn, J. R. Schaefgen, and W. O. Statton, *J. Polym. Sci.*, **55**, 531 (1960).
7. R. Stéfani, M. Chevreton, M. Garnier, and C. Eyraud, *C.R. Acad. Sci.* (Paris), **251**, 2174 (1960).
8. V. F. Holland, S. B. Mitchell, W. L. Hunter, and P. H. Lindenmeyer, *J. Polym. Sci.*, **62**, 145 (1962).
9. P. H. Lindenmeyer and R. Hosemann, *J. Appl. Phys.*, **34**, 42 (1963).
10. C. Y. Liang and S. Krimm, *J. Polym. Sci.*, **31**, 513 (1958).
11. C. Y. Liang, F. G. Pearson, and R. H. Marchessault, *Spectrochim. Acta*, **17**, 568 (1961).
12. H. Tadokoro, S. Murahashi, R. Yamadera, and T. Kamei, *J. Polym. Sci. A*, **1**, 3029 (1963).
13. R. Yamadera, H. Tadokoro, and S. Murahashi, *J. Chem. Phys.*, **41**, 1233 (1964).
14. D. E. Witenhafer and J. L. Koenig, *J. Macromol. Sci. B*, **2**, 147 (1968).
15. R. Yamadera and M. Murano, *J. Polym. Sci. B*, **3**, 821 (1965); *J. Polym. Sci. A-1*, **5**, 1059 (1967).

16. K. Matsuzaki, T. Uryu, M. Okada, K. Ishigure, T. Ohki, and M. Takeuchi, *J. Polym. Sci. B*, **4**, 487 (1966).

17. J. Bargon, K.-H. Hellwege, and U. Johnsen, *Kolloid-Z.*, **213**, 51 (1966).

18. K. Matsuzaki, T. Uryu, M. Okada, and H. Shiroki, *J. Polym. Sci. A-1*, **6**, 1475 (1968).

19. L. C. Leitch, *Can. J. Chem.*, **35**, 345 (1957).

20. T. Yoshino, H. Iwanaga, and K. Kuno, *J. Amer. Chem. Soc.*, **89**, 6773 (1967).

21. W. F. Cockburn and C. E. Hubley, *Appl. Spectry*, **11**, 188 (1957).

22. A. L. Segre, P. Ferruti, E. Toja, and F. Danusso, *Macromolecules*, **2**, 35 (1969).

23. D. M. White, *J. Amer. Chem. Soc.*, **82**, 5678 (1960).

24. M. Murano and R. Yamadera, *J. Polym. Sci. B*, **5**, 483 (1967); *J. Polym. Sci. A-1*, **6**, 843 (1968).

25. T. Yoshino, H. Kenjo, and K. Kuno, *J. Polym. Sci. B*, **5**, 703 (1967).

26. W. L. Hunter, *J. Polym. Sci. B*, **5**, 23 (1967).

27. M. Murano, *Makromol. Chem.*, **112**, 281 (1968).

28. F. A. Bovey, *J. Polym. Sci.*, **46**, 59 (1960).

29. M. Murano and R. Yamadera, *J. Polym. Sci. B*, **5**, 333 (1967).

30. O. L. Glavati, L. S. Polak, and V. V. Shchekin, *Neftekhim.*, **3**, 905 (1963).

31. O. L. Glavati and L. S. Polak, *Neftekhim.*, **4**, 77 (1964).

32. M. Imoto, T. Ohtsu, and M. Nakabayashi, *Makromol. Chem.*, **65**, 194 (1963).

33. S. Yabumoto, K. Ishii, and K. Arita, *J. Polym. Sci. A-1*, **7**, 1577 (1969).

34. G. Svegliado, G. Talamini, and G. Vidotto, *J. Polym. Sci. A-1*, **5**, 2875 (1967).

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Interfacial Synthesis of Polyphosphonate and Polyphosphate Esters. V. Poly(phosphonate esters) Containing Thymidine, 2-Deoxy-D-ribose, or Xanthine

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Synopsis

Poly(phosphonate esters) were synthesized by base-promoted interfacial polycondensation of phenylphosphonic dichloride with thymidine and with 2-deoxy-D-ribose. The products give evidence of P-Cl endgroups. The thymidine product is a high polymer with a weight-average number of repeating units, $\overline{DP}_w$, greater than 250. The 2-deoxy-D-ribose product is separable into soluble and insoluble (crosslinked) fractions having identical infrared spectra. Xanthine is also reactive in the process employed.

The chemical syntheses of natural and especially unnatural analogs of nucleic acids is extremely valuable. Besides making available such materials in copious amounts, of high purity, and of special molecular design, synthesis also provides unique substrates for the examination of nuclease specificities, for studies of helix crystallization and small molecule association phenomena, for studies of energy transfer photometry, for potential drug applications, and other studies.

Trials at nonenzymatic syntheses of polynucleotides have interested a limited number of chemists. Various chemical approaches and results leading to oligonucleotides have been reviewed.[1,2] Among the rare claims of a true polymerization, i.e., a single reaction that yields a high polymer. Schramm and co-workers have reported forming polynucleotides of molecular weights of 15–50 × 10^3 from 2′-deoxynucleotides in a medium generated from phosphorus pentoxide and diethyl ether.[3] In this paper we report the use of phosphorylchloride anhydrides with nucleosides in a base-controlled system of interfacial polymerization.[4–8]

In the interfacial technique, two fast-reacting comers are dissolved in separate, usually immiscible liquids, one of which is generally water. The water phase contains the diol or triol and an alkaline reaction promoter. The other phase consists of the diacid halide in an inert organic liquid of low viscosity. Polymerization occurs at or near the liquid interface—a physi-

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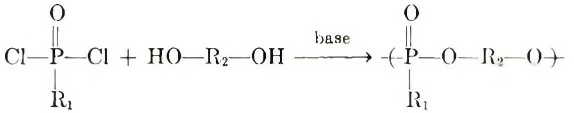
cal environment which itself may bear significantly on biochemical processes. Reaction is instantaneous, and reactant conversion is also when rapid stirring is employed.

The first reported use of interfacial polymerization in the synthesis of poly(phosphonate esters) was by Kuznetsov et al.[9] and by Aufderhaar[10] in 1961. The first reported synthesis of poly(phosphate esters) by interfacial polymerization was made by Rabek and Prot in 1963.[11] Previous abiotic syntheses employing phosphoryl halides and esters were all accomplished either by the relatively slow methods of solution polymerization or by high temperature fusion of the reactants. The results of these methods have been comprehensively reviewed by Gefter.[12]

As part of an investigative program of studies of chemical evolution, it has been the desire of the authors to develop synthetic control of rapid, low-temperature poly(phosphate ester) reactions. Such studies have included non-enzymatically catalyzed rapid hydrolyses[13–15] and transesterifications of phosphate esters, as well as an extended study of the potential of interfacial syntheses of other phosphorus-containing polymers.[15–19]

The authors studied in detail the influential factors in a productive, rapid interfacial polycondensation of hydroquinone with phenylphosphonic dichloride,[4–6] illustrated by eq. (1), in which R_2 = C_6H_5 and R_2 = *p*-phenylene:



$$\mathrm{Cl{-}\underset{R_1}{\overset{O}{\overset{\|}{P}}}{-}Cl + HO{-}R_2{-}OH \xrightarrow{\text{base}} {-}\!\!(\underset{R_1}{\overset{O}{\overset{\|}{P}}}{-}O{-}R_2{-}O)\!\!{-}} \qquad (1)$$

One function of the base is to ionize the diol to an effective nucleophilic agent which is capable of very high reaction rates. A second important function is to consume acids generated by the condensation reaction. These include the phosphoryl acids generated by solvolysis and saponification of the phosphoryl chloride reactant and the intermediate oligomer end-groups and acids generated by chain degradation through attack on ester groups in the polymeric product. Hydroquinone, which possesses acid dissociation constants somewhat greater than those of saccharide hydroxyl groups, was chosen for test case study because the competing hydrolytic side reactions are particularly serious with this diol.

Experiences with hydroquinone in such studies revealed that the polycondensation reactions could be made to succeed over the competing reactions, but that product yield and molecular weight are very sensitive to many reaction parameters, as has been found in interfacial polymerizations of nylon 66.[20] Parenthetically, experiences in the latter reactions differ from the present system, for which evidence has been found that the site of reaction is in the aqueous phase,[6] whereas that for interfacial polymerization of nylons is probably situated in the organic phase.

Previous extant technique in strongly basic interfacial polymerizations employed sodium or potassium hydroxides. In order to provide sufficient number of acid-neutralizing equivalents, these hydroxides had to be used at such concentration or at such dilution of the aqueous phase that good yields and high molecular weights (which are especially characteristic of DNA-polynucleotides) could not be achieved. Saponification of polymer product, promulgated by the intrinsic dissociability of an acidic diol, is especially pronounced at practical concentrations of sodium hydroxide. The requirements of moderate basicity and high alkaline capacity were satisfied by means of the use of conventional buffers, or alternatively, a base such as barium hydroxide, wherein the highest pH of the aqueous phase may be controlled by the solubility of the base in water at selected temperatures and the alkaline capacity may be provided by the reservoir of undissolved excess of that base.[4] High-speed stirring and rapid reaction rate minimizes contact time between alkali and the polymer, which separates from the liquid phase. The use of barium hydroxide in the condensation of hydroquinone proved much superior to sodium hydroxide, especially with regard to product molecular weight, where $\bar{M}_w > 10^5$ were obtained.

The system developed for hydroquinone was then applied to thymidine and to 2-deoxyribose, without commitment to the extensive labors of optimizing the properties of yield and molecular weight.

Phenylphosphonic dichloride (Eastman Organic Chemicals) was vacuum-distilled, and the fraction boiling in the range 104.0–104.5°C/4 mm was used (lit. bp 104.0°C/4 mm). Thymidine and 2-deoxy-D-ribose were purchased from California Corporation for Biochemical Research (Los Angeles, Calif.). General polymerization procedure and apparatus are described elsewhere.[4–7] The reaction apparatus is essentially a specially designed reaction jar fitted on a Waring Blendor (stirring rate 17,500 rpm). Infrared spectra were obtained by using potassium bromide pellets and employing a Perkin Elmer-621 infrared spectrophotometer.

Phenylphosphonic dichloride (0.20 ml, 1.4 mmole) in 15 ml carbon tetrachloride is quickly added, with stirring, to the reaction jar containing thymidine (340 mg, 1.4 mmole) and barium hydroxide (882 mg, 2.8 mmole) in 15 ml water. After a few seconds a light gray solid begins to precipitate from the reaction mixture. After 3 min of blender stirring time at 25°C, yields of 15, 18, and 19% were recovered from triplicate runs.

The products have softening ranges between 60 and 90°C and are soluble to the extent of about 0.5% (w/v) in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). They are insoluble in distilled water, 0.1*N* aqueous hydrochloric acid, 0.1*N* aqueous sodium acetate, acetone, carbon tetrachloride, benzene, ethanol, and toluene.

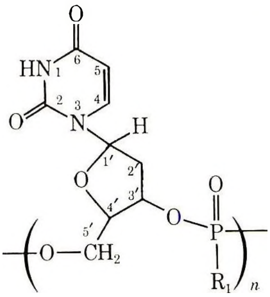
Figure 1 shows the infrared spectrum of the solid. From the spectrum it is tentatively concluded: (1) that there are P—O—C (alkyl) bonds present, shown by a peak at 1040 cm^{-1}, which is observed in other compounds containing this linkage;[21,22] (2) that the $C_6H_5P{=}O$ group is present, as seen in the bands at 1440, 1005, 715, and 687 cm^{-1}, characteristic of the P-phenyl group;[21b,22] and (3) that the broad bands of thymidine in the range 3500–2900 cm^{-1} and the thymidine endocyclic amide bands at 1710–1650 cm^{-1} are present in the spectrum.

The P—N stretching frequency has been assigned to the region between 820 and 680 cm^{-1} in some compounds, but this correlation is not always found to be valid.[21a] Thus no conclusion is presently made as to the presence or absence of P—N bonds.

That P—N bonds may be formed during polycondensations in the presence of NaOH is indicated by our condensation of the purine xanthine with $POCl_3$ and with phenyl phosphorodichloridate in 5 min at room temperature. The former gave an 86% yield of an insoluble (network) polymer, and the latter gave a water soluble, acetone insoluble product in 8% yield. The formation of P—N bonds in the present synthesis seems less likely since Carraher and Winthers[16] report yields of only 3–6% after 15 min in the condensation of urea with phenylphosphonic dichloride in the presence of NaOH. Urea should have a reactivity comparable to the amide nitrogen at position 1 in thymidine, especially in the presence of base.

The thymidine polymer was dissolved in DMSO and precipitated by addition to a tenfold volume of carbon tetrachloride (97% recovery). The weight-average molecular weight $\bar{M}_w$ was determined in DMSO at 25°C employing a Brice-Phoenix light-scattering photometer, Model 2000-D at 546 nm. The refractive index increment, dn/dc, had the value 0.20 ml/g. The Debye dissymmetry coefficient z showed no dissymmetry correction for molecular weight was necessary. Thus, it was found that $\bar{M}_w = 8.93 \times 10^4$ corresponding to $\overline{DP}_w \sim 250$. Viscometry was conducted in the same solvent at 25°C employing a Cannon-Ubbelohde semimicro dilution viscometer. A limiting viscosity number, LVN, of 23 ml/g was found using serial dilutions and graphical extrapolation.

Natural DNA and RNA polynucleotides possess a recurring head-to-tail chain backbone linkage of the ribosyl 3′- and 5′-hydroxyl groups. The product of thymidine and phenylphosphonic dichloride may possess a random distribution of linkages including 3′–3′ and 5′–5′ phosphate diester groups. Alternatively, it may contain a predominance of the "natural" 3′–5′ linkage as a result of an expected difference in reactivities between the primary 5′- and secondary 3′-hydroxyl groups. Thus, a 5′-*O*-phenylphosphonylchloride nucleoside derivative could be formed at a stage prior to polymerization; such an intermediate would be a polymerizable difunctional monomer of the A-B type. Enzymatic hydrolysis experiments can elucidate the distribution of diester attachments.



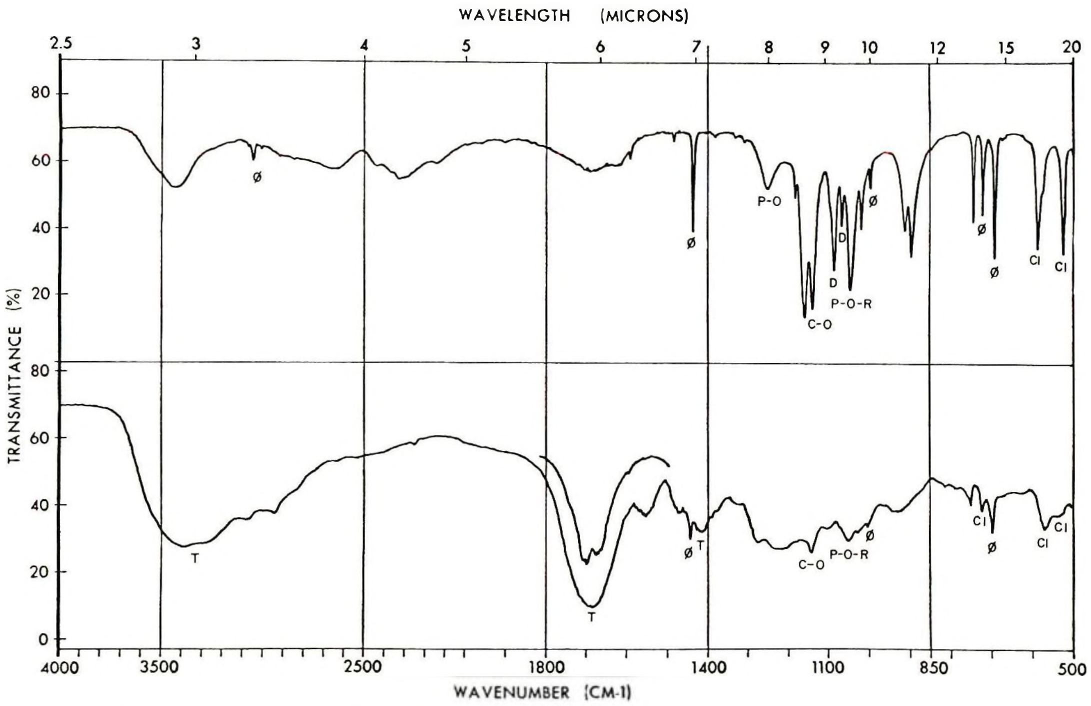


Fig. 1. Infrared spectra of polymers from the base-promoted interfacial polycondensation of phenylphosphonic dichloride with thymidine (lower curve), and with 2-deoxy-D-ribose (upper curve). Tentative assignments of peak are given, where T = thymidine, ϕ = phenyl, and D = deoxyribose. The inset segment (ca 1700 cm^{-1}) shows a variation occasionally found in the thymidine polymer spectrum.

Phenylphosphonic dichloride (3.5 mmole) in 15 ml carbon tetrachloride was added, with stirring, to the reaction jar of the blender, containing 2-deoxy-D-ribose (3.08 mmole) and barium hydroxide (5.0 mmole) in 30 ml water. A white material precipitated from the reaction mixture after 80 sec. After 5 min total stirring time at 25°C, a 15% yield (assuming the acid chloride and triol reacted in a 1:1 molar ratio) was recovered (fraction 1). The reaction mixture was filtered and set aside for 24 hr. Another 7% yield of product (fraction 2) was formed. Storage for another 24 hr yielded nothing else.

Fraction 1 is insoluble in all solvents tried and did not soften below a temperature of 300°C. Fraction 2 is soluble in acetone, dimethyl sulfoxide, and dimethylformamide, and is insoluble in water, carbon tetrachloride, aqueous 1*N* hydrochloric acid solution, ether, benzene, or ethanol. Fraction 2 has a LVN of 6 ml/g in acetone, and a softening range of 173–185°C.

There is no noticeable difference in the relative intensities, positions or number of absorption bands between the spectra of fractions 1 and 2, shown in Figure 1. Of particular importance are the presence of the following bands with the given assignments: (1) a band at 1250 cm^{-1}, characteristic of the P=O band;[21a,22] (2) bands at 1439, 995, 718, and 692 cm^{-1}. characteristic of the presence of the P-phenyl or phenyl group;[21b,21c,22] (3) similarity among several bands with bands of deoxyribose; (4) a band at 913 cm^{-1} which may arise from the C—O stretching found in cyclic ethers;[21] (5) a band at 1137 cm^{-1} which may be attributed to C—O stretching found in saturated secondary alcohols; and (6) a band at 1040 cm^{-1} attributed to the P—O—C (alkyl) group.[21a,22] It is tentatively concluded on the basis of infrared spectra that both fractions are poly(phosphonate esters). The melting behavior and solubility differences show that fraction 1 has some crosslinking. This implies that the 1′-, 3′-, and 5′-hydroxyl groups of 2-deoxy-D-ribose are all susceptible to phosphonylation under the present reaction conditions.

There are at least three possible endgroups: i.e. P—Cl, P—OH, and alkyl-OH. None of the products from thymidine or deoxyribose show bands between 3615–3600 cm^{-1}, which is the absorption region characteristic for stretching of free O—H bonds in substituted or unsubstituted alcohols.[21] Intramolecular association of such bonds would cause a lowering of the absorption frequency to 3450 cm^{-1}, confusing the bands with those of amide N—H stretching. The exact location of the O—H stretch in P—OH groups has not been positively defined but is considered by many to be in the region of 2700–2550 cm^{-1}.[21] The products have some weak absorption in this region.

Significantly, however, products from both thymidine and deoxyribose give positive Beilstein tests for halides. Both show prominant absorption bands around 570 cm^{-1}, as do the products of hydroquinone polymerizations by this method.[5–7]

This spectral region is assigned to absorption by the P—Cl group.[2] Samples of the product with thymidine were treated with an aqueous solution of sodium hydroxide. As the treatment time increased there was a decrease in the 570 cm^{-1} band until it disappeared. At this time the product gave a negative Beilstein test. These results allow the conclusion that at least some of the products from the condensation with thymidine and deoxyribose contain P—Cl endgroups, which may be exploited to lengthen the polymer chains, or to prepare block polymers.

The immediate extension of the method should be toward the preparation of triester polyphosphates which could be characterized by conventional solution methods for non-electrolytes and which subsequently would be readily and selectively hydrolyzed to yield nucleic acid analogs.[23] *p*-Nitrophenylphosphorodichloridate was selected for polycondensation by our method to a polyphosphate ester [eq. (1), $R' = p\text{-}O_2N{-}C_6H_4O{-}$]. Thymidine failed in this first effort to yield polymer in sufficient amount for purification and characterization, whereas the use of hydroquinone gave a 65% product yield.

This paper is taken in part from the Ph.D. thesis of C. E. Carraher, 1968, University of Missouri-Kansas City, Kansas City, Missouri.

References

1. A. M. Michelson, *The Chemistry of Nucleosides and Nucleotides*, Academic Press, New York, 1963, Chap. 7.
2. H. G. Khorana, *Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest*, Wiley, New York, 1961, Chap. 5; also *Chem. Eng. News*, **33**, 148 (1967).
3. G. Schramm, H. Grotsch, and W. Pollmann, *Angew. Chem.*, **73**, 619 (1961); *ibid.*, **74**, 53 (1962).
4. F. Millich and C. Carraher, Jr., U.S. Pat. 3,491,061 (Jan. 20, 1970).
5. F. Millich and C. Carraher, Jr., *J. Polym. Sci. A-1*, **7**, 2669 (1969).
6. F. Millich and C. Carraher, Jr., *J. Polym. Sci. A-1*, **7**, 2773 (1969).
7. F. Millich and C. Carraher, Jr., *J. Polym. Sci. A-1*, **8**, 163 (1970).
8. F. Millich and C. Carraher, Jr., *Macromolecules*, **3**, 253 (1970).
9. E. V. Kuznetsov, I. M. Shermergorn, and V. A. Belyaeva, U.S.S.R. Pat. 137,673 (1961).
10. E. Aufderhaar, Dissertation, Bonn, 1961.
11. T. Rabek and T. Prot, *Roczniki Chem.*, **37**, 747 (1963).
12. Y. L. Gefter, *Organophosphorus Monomers and Polymers* (Pergamon Press, New York, 1962.
13. F. Millich and E. L. Hayes, *J. Amer. Chem. Soc.*, **86**, 2914 (1964).
14. F. Millich and G. K. Baker, in preparation.
15. G. K. Baker, Ph.D. thesis, University of Missouri-Kansas City, 1968.
16. C. Carraher and D. Winthers, *J. Polym. Sci. A-1*, **7**, 2417 (1969).
17. C. Carraher and D. Posey, *J. Polym. Sci. A-1*, **7**, 2436 (1969).
18. C. Carraher and P. Billion, *Makromol. Chem.*, **128**, 143 (1969).
19. C. Carraher and T. Brandt, *Makromol. Chem.*, **126**, 66 (1969).
20. P. W. Morgan, *Condensation Polymers: By Interfacial and Solution Methods*, Interscience, New York, 1965, Chap. V.
21. C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York, 1963, (a) p. 294; (b) p. 293; (c) p. 161.
22. Y. Shuto, *Kogyo Kagaku Zasshi*, **67**, 367 (1964).
23. F. Millich and K. V. Seshadri, unpublished results.

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Copolymerization Characteristics of S-Vinyl-*O-tert*-Butylthiocarbonate*

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Synopsis

Poly-*S*-vinyl-*O*-*tert*-butylthiocarbonate is an excellent precursor to poly(vinyl mercaptan) because the *tert*-butyloxycarbonyl blocking group can be removed by either acid hydrolysis or thermolysis under conditions which minimize the oxidation of the liberated mercaptan to disulfide. Dilatometric studies of the homopolymerization of *S*-vinyl-*O*-*tert*-butylthiocarbonate demonstrated that the polymerization rate was directly proportional to the concentration of free-radical initiator; no thermal initiation was observed. The molecular weight of the homopolymers and copolymers ranged from 30,000 to 50,000 (GPC). Copolymerization of *S*-vinyl-*O*-*tert*-butylthiocarbonate (M_2) with styrene, ($r_1 = 3.0$, $r_2 = 0.2$), methyl methacrylate ($r_1 = 1.40$, $r_2 = 0.17$) and vinyl acetate ($r_1 = 0.04$, $r_2 = 11.0$) indicated that a sulfur atom adjacent to the vinyl group increases the resonance stability ($Q_2 = 0.5$) and the electron density ($e_2 = -1.4$) of the double bond and the corresponding radical. Water-soluble copolymers could be prepared by incorporating either *N*-vinylpyrrolidone ($r_1 = 0.12$, $r_2 = 3.94$) or *N*-isopropylacrylamide ($r_1 = 1.17$, $r_2 = 0.3$) with M_2. The water solubility of the copolymers decreased markedly when the *tert*-butyloxycarbonyl group was removed. Copolymers of M_2 with *N*-vinyl-*O*-*tert*-butylcarbamate ($r_1 = 0.13$, $r_2 = 5.10$) were utilized to prepare crosslinked poly(vinyl amine–vinyl mercaptan); the crosslinking resulted from urea linkages formed during thermolysis of the copolymer.

INTRODUCTION

Polymers containing mercaptan groups have been utilized as crosslinking agents, redox resins, and sequestering agents.[1] The facile oxidation of mercaptans to disulfides plays an important role in biological processes, both in maintaining the secondary and tertiary structure of enzymes as well as participating as an intermediate in the reactive site. Our interest in enzyme models prompted the preparation of a series of copolymers containing mercaptan moieties in an effort to duplicate the phenomenal catalytic properties of natural enzymes. Further impetus to this work was generated by the discovery that sulfhydryl-containing substrates were effective radiation prophylactics.[2] This behavior is attributed to the

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* This paper is dedicated to Prof. Werner Kern in honor of his 65th birthday.

† To whom inquiries should be addressed.

ability of mercaptans to inhibit free radical reactions by the formation of stable thiol radicals; a recent ESR investigation on an irradiated sample of one of our vinyl mercaptan–vinyl pyrrolidone copolymers has confirmed the presence of stable radicals.[3]

The ultimate physiological applications of our copolymers placed several restrictions on the method for introducing the mercaptan group. A meaningful evaluation of the catalytic reactivity of the copolymers requires a precise knowledge of the sequence distribution to establish the environment of the reactive site. This requirement eliminates one common method of preparing polymercaptans, i.e., introduction of the thiol group into polymer substrates by replacement of a displaceable functional group. Okawara has employed this technique to incorporate a significant number of thiol groups for production of sequestering agents and crosslinked polymers.[4] However, displacement reactions are accompanied by side reactions which prevent a quantitative conversion to polymercaptan and complicate the structure of the copolymers formed. Therefore, we directed our attention to the copolymerization of vinyl mercaptan derivatives.

Direct synthesis of polymers containing free sulfhydryl substituents is impossible, due to their reactivity as inhibitors. The monomer must contain the mercaptan moiety protected by a blocking group, which can subsequently be removed quantitatively under mild conditions. A number of vinyl mercaptan derivatives have been evaluated, including vinyl thioacetate,[5,6] vinyl thiobenzoate,[7] vinyl mercaptals,[8,9] methacryloyloxyalkyl isothiuronium salts,[10] *S*-vinyl-*O*-alkylthiocarbonates, thiocarbamates[11], and *S*-vinyl-*N*,*N*-dialkyldithiocarbamates.[12] Most of these protective groups must be removed by alkaline hydrolysis. Since autoxidation of mercaptans is extremely rapid in basic media,[13] this technique usually yields crosslinked insoluble polymers. Our applications required soluble substrates, so monomers containing acid or thermally labile blocking groups were surveyed. *S*-Vinyl-*O*-*tert*-butylthiocarbonate(I) fulfilled both of these criteria and polymerized readily under free radical conditions.[14,15] The thermal lability of the *tert*-butyloxycarbonyl group is particularly advantageous, because it can be utilized in copolymers containing pH-sensitive substituents. Therefore, a detailed study of its copolymerization characteristics was initiated.

EXPERIMENTAL

Reagents and Comonomers

Styrene was extracted with 10% aqueous NaOH, washed with water and dried over CaH_2. Methyl methacrylate, vinyl acetate, and *tert*-butyl methacrylate were extracted with 5% NaOH, washed with water and dried over anhydrous $MgSO_4$ or $CaCl_2$. All of the monomers distilled *in vacuo* immediately prior to the copolymerization experiment only center cuts were used. *N*-Isopropylacrylamide was recrystallized twice from hexane to a constant melting point, mp 64.5–65°C (lit.[16] mp 62°C). *N*-Vinyl-*O-tert*-butylcarbamate was prepared from vinyl isocyanate and *tert*-butanol in 81.5% yield according to the procedure of Shulz and Hartmann.[17] Two recrystallizations from hexane produced analytically pure material, mp 66.5–67°C (lit[17] mp 66°C). Azobisisobutyronitrile was recrystallized from methanol (mp 102–103°C decomp.). *tert*-Butyl alcohol was distilled from CaH_2 and stored over Linde 4-A molecular sieves. Tetrahydrofuran (THF) was passed through a column of basic alumina, distilled and stored over molecular sieves.

S-Vinyl-*O-tert*-Butylthiocarbonate (I)

The procedure of Overberger and Daly[14,15] was modified to improve the yield. *S*-(β-Chloroethyl)chlorothioformate was prepared from ethylene sulfide and phosgene.[18] A potassium *tert*-butoxide solution in THF was prepared by dissolving 39.1 g (1.0 g-atom) of potassium metal in 550 ml of *tert*-butanol at 70°C (reflux) evaporating the alcoholate solution to dryness *in vacuo*, and adding 550 ml of anhydrous THF. The potassium *tert*-butoxide solution was cooled to −30°C and a solution of 53 g (0.333 mole) *S*-(β-chloroethyl)chlorothioformate in 200 ml of THF was added dropwise over a 2-hr interval. The mixture was stirred for 2 hr at −30°C after the addition was completed. The mixture was allowed to warm to room temperature, neutralized with glacial acetic acid and worked up immediately. After removing the potassium chloride by centrifugation, the solvent was evaporated under reduced pressure from the clear supernatant solution. Fractional distillation of the oily residue from the evaporation afforded 32 g (60%) of *S*-vinyl-*O-tert*-butylthiocarbonate, bp 60–61°C/15 mm. The purity was ascertained from an NMR spectrum by comparing the relative intensity of the vinyl proton region (5.4–6.73 δ) to the *tert*-butyl group (1.51).

The monomer assayed routinely between 93 and 95% pure. The impurity, di-*tert*-butyl carbonate, was considered to be an inert diluent, and corrections for its presence were made when calculating the copolymer feed ratios.

Polymerization

Pure monomer (I) and AIBN catalyst were weighed into a dilatometer, and polymerization was initiated by immersing the dilatometer in an oil bath at 70°C. After following the polymerization for the desired interval, the polymer was isolated by pouring the mixture into methanol, dissolving the polymer in THF, and reprecipatating in methanol. The conversion was calculated from the weight of polymer remaining after drying for 48 hr at 40°C *in vacuo*. The rate of polymerization was calculated from the initial volume contraction by using equation 1:

$$R_p = \frac{\Delta V}{\Delta T}\left(\frac{1}{VK}\right) \qquad (1)$$

TABLE I

Copolymerization of *S*-Vinyl-*O*-*tert*-butylthiocarbonate (M_2) with Styrene (M_1)

Feed									
M_1		M_2		Mole fraction in feed, M_1	Poly-merization time, min[a]	Conversion, %[b]	S, %	Mole fraction in copolymer	
g	(mmole)	g	(mmole)					m_1[c]	m_1[d]
0.572	(5.5)	7.21	(45)	0.109	90	6.46	15.54	0.224	0.315
1.022	(9.82)	6.406	(40.0)	0.197	60	2.59	11.33	0.434	0.513
1.606	(15.42)	5.601	(35.0)	0.306	120	9.03			0.587
2.118	(20.35)	4.802	(30.01)	0.404	60	3.38	7.07	0.646	0.726
2.542	(24.43)	4.00	(25.0)	0.494	55	6.84	5.09	0.746	0.746
3.572	(34.3)	2.403	(15.0)	0.696	65	9.85			0.797
4.168	(40.04)	1.601	(10.01)	0.800	30	4.33	2.54	0.873	0.898
4.716	(45.3)	0.8	(5.0)	0.901	75	14.7			0.929
4.683	(45.0)	0.8	(5.0)	0.900	30	5.1			0.866
5.006	(88.09)	0.401	(2.54)	0.951	30	6.93	0.54	0.973	0.894

[a] Polymerization temperature, 70°C; initiator, 41.0 mg (0.5 mole-%) azobisisobutyronitrile.

[b] Precipitant, methanol; reprecipitated from THF into methanol.

[c] Calculated from elemental analysis.

[d] Spectrophotometric determination of styrene content at 260 mμ.

TABLE II

Copolymerization of *S*-Vinyl-*O-tert*-butylthiocarbonate (M_2) with Methyl Methacrylate (M_1)

Feed									
M_1		M_2		Mole fraction in feed, M_1	Poly-merization time, min[a]	Conversion, %[b]	S, %	Mole fraction in copolymer	
g	(mmole)	g	(mmole)					m_1[c]	m_1[d]
0.388	(3.88)	4.006	(25.00)	0.135	19	2.98	13.98	0.302	0.311
1.087	(10.87)	4.003	(24.98)	0.303	19	5.40	10.20	0.491	0.469
2.430	(24.30)	4.004	(24.99)	0.493	19	5.30	7.43	0.628	0.607
4.661	(46.61)	3.384	(21.12)	0.688	19	4.28	4.40	0.780	0.744
4.669	(46.69)	1.974	(12.36)	0.791	18	4.78	3.03	0.848	0.823
4.696	(46.96)	0.880	(5.49)	0.895	18	5.69	1.48	0.926	0.928

[a] Polymerization temperature, 70°C; initiator, 5.0 mg (0.05 mole-%) azobisisobutyronitrile.

[b] Precipitant, methanol; reprecipitated from THF into methanol.

[c] Calculated from elemental analysis.

[d] Estimated by quantitative NMR measurement at $\delta = 3.65$ ($—OCH_3$).

TABLE III

Copolymerization of *S*-Vinyl-*O*-*tert*-butylthiocarbonate (M_2) with Vinyl Acetate (M_1)

Feed								
M_1		M_2						
g	(mmole)	g	(mmole)	Mole fraction in feed M_1	Polymerization time, min[a]	Conversion, %[b]	S, %	Mole fraction in polymer m_1[c]
0.441	(5.12)	7.208	(44.98)	0.102	30	13.96	20.10	0.0
0.888	(10.3)	6.407	(39.98)	0.205	12	4.95	19.74	0.013
1.292	(15.0)	5.601	(34.95)	0.300	22	8.55	20.56	0.0
2.150	(24.97)	4.005	(24.99)	0.50	21	6.31	20.61	0.0
3.049	(35.42)	2.405	(15.01)	0.702	31	12.66	18.95	0.052
3.853	(44.76)	0.801	(5.00)	0.900	32	14.03	12.98	0.35
4.62	(53.67)	2.165	(13.51)	0.799	125[d]	15.90	15.13	0.244
5.013	(58.23)	2.282	(14.24)	0.804	50	1.37	14.79	0.261
4.62	(53.67)	1.53	(9.548)	0.849	148	15.5	14.69	0.266
4.62	(53.67)	1.53	(9.548)	0.849	123	13.10	14.00	0.300
5.003	(58.13)	1.612	(10.06)	0.853	50	3.40	13.82	0.309
4.62	(53.67)	0.455	(2.84)	0.95	148	19.20	6.90	0.654
4.62	(53.67)	0.455	(2.84)	0.95	105	6.35	8.50	0.575

[a] Polymerization temperature, 70°C; initiator, 41 mg (0.5 mole-%) AIBN.

[b] Precipitant, petroleum ether at −20°C, reprecipitated from THF and lyophilized from benzene.

[c] Calculated from elemental analysis.

[d] Initiator concentration decreased to 5.0 mg (0.05 mole-%) on the remaining runs.

where the total contraction K was estimated from gravimetric conversion data to be 14.41. The intrinsic viscosities of the polymers were measured in THF at 30°C. Number-average molecular weights were determined in toluene at 30°C by using SS-08 membranes in a Mecrolab 501 membrane osmometer. The molecular weight distributions were obtained on a Waters Model 200 gel-permeation chromatograph.

Copolymerization

The comonomers were weighed into 10 ml drying ampoules containing 41 mg (0.5 mole-%) AIBN. The total molar composition of the monomer mixture was maintained at 0.05 mole while the feed ratio was varied. The ampoules were degassed in vacuum by three alternate freeze-thaw cycles and then sealed *in vacuo*. The tubes were immersed in either a 65 or 70°C oil bath until a noticeable increase in viscosity indicated the formation of copolymer. The copolymers were precipitated in either methanol, petroleum ether, or ether and reprecipitated twice from an appropriate solvent–nonsolvent combination.

TABLE IV
Copolymerization of *S*-Vinyl-*O-tert*-butylthiocarbonate(M_2) with *N*-Vinylpyrrolidone(M_1)

Mole fraction in feed, M_1	Polymerization time, min[a]	Conversion %	N in polymer, %	Mole fraction in polymer m_1
0.3	20	10.6[b]	1.38	0.10
0.5	20	13.0[c]	2.52	0.18
0.7	20	14.0[c]	4.44	0.32
0.9	20	16.0[d]	7.80	0.57

[a] Polymerization temperature, 65°C; initiator 0.5 wt-% AIBN.

[b] Precipitant, methanol.

[c] Precipitant, pentane.

[d] Precipitant, ether.

TABLE V
Copolymerization of *S*-Vinyl-*O-tert*-butylthiocarbonate(M_2) with *N*-Isopropylacrylamide(M_1)

Mole fraction in feed M_1	Polymerization Time[a], min	Conversion, %[b]	N in polymer, %	Mole fraction in polymer m_1
0.1	180	1.8	3.05	0.246
0.5	65	17.5	7.71	0.625
0.7	40	13.5	9.53	0.770
0.9	60	12.5	10.83	0.877

[a] Polymerization temperature, 70°C; initiator, 0.5 wt-% AIBN; solvent, benzene; [M], 5 mole/l.

[b] Precipitant, pentane; lyophilized from benzene.

The precipitates were either dried in a vacuum oven at 40°C for 48 hr or lyophilized from benzene. The copolymers from vinyl acetate were very gummy and difficult to purify until they were freeze-dried. The dried copolymer samples were weighed to determine the extent of conversion. The composition of the copolymers was estimated by elemental analysis. (Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.) The composition of the methyl methacrylate copolymers was confirmed by NMR analysis of 5 wt-% copolymer solutions in $CDCl_3$. The styrene content was determined spectrophotometrically at 260 mμ in $CHCl_3$. The results are summarized in Tables I–VII.

TABLE VI
Copolymerization of *S*-Vinyl-*O*-*tert*-butylthiocarbonate(M_2) with *N*-Vinyl-*O*-*tert*-butylcarbamate(M_1)

Mole fraction in feed M_1	Polymerization time, min[a]	Conversion, %	N in polymer, %	Mole fraction in polymer m_1
0.2	240	8.95[b]	0.54	0.055
0.4	240	1.3[b]	0.97	0.099
0.5	240	3.5[b]	1.54	0.185
0.7	360	1.6[c]	2.84	0.288
0.9	420	1.9[c]	5.65	0.575

[a] Polymerization temperature, 70°C; initiator, 0.5 wt-% AIBN; solvent, benzene; [M], 2 mole/l.

[b] Precipitant, methanol.

[c] Precipitant, pentane.

TABLE VII
Copolymerization of *S*-Vinyl-*O*-*tert*-butylthiocarbonate (M_2) with *tert*-Butyl Methacrylate (M_1)

Mole fraction in feed M_1	Feed ratio, M_1/M_2	Mole fraction in polymer m_1	Copolymer composition ratio m_1/m_2
0.117	0.132	0.365	0.575
0.329	0.490	0.571	1.332
0.535	1.15	0.735	2.78
0.726	2.65	0.832	4.96
0.908	9.87	0.962	25.37

The reactivity ratios were estimated by either the method of intercepts or the Fineman-Ross method and refined by the curve fitting technique.[19] The computer program written by Montgomery and Fry[20] was used to generate the integral copolymer composition for the curve-fitting approach.

RESULTS AND DISCUSSION

Homopolymerization

S-Vinyl-*O*-*tert*-butylthiocarbonate (I) polymerizes readily in bulk or solution in the presence of free radical initiators. The effect of initiator con-

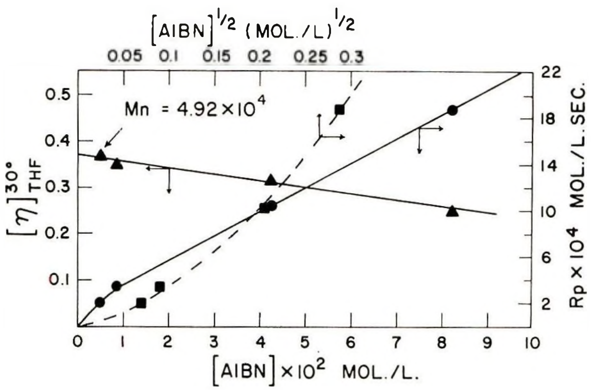


Fig. 1. Effect of initiator concentration upon the rate of polymerization R_p of *S*-vinyl-*O*-*tert*-butylthiocarbonate. The intrinsic viscosity of the polymers demonstrates the molecular weight dependence. Polymerization conditions: [M] = 5.6 mole/l., 70°C.

centration upon the rate of polymerization *Rp* was evaluated dialtometrically and the results are summarized in Table VIII. The unique aspect of this data is illustrated in Figure 1; the rate of polymerization appears to be directly proportional to the initiator concentration rather than the expected one-half order dependence. The intrinsic viscosities of the samples were inversely proportional to initiator concentration, which is consistent with the kinetic data. Interpretation of this phenomenon will require further investigation, but it is clear that the normal kinetic assumptions used to derive the rate expressions are not valid in this case.

The molecular weight of 49,000 observed for one of the polymer samples is equivalent to a degree of polymerization (DP) of 300. This appears to be the highest molecular weight attainable under these conditions, but it is an order of magnitude greater than the DP achieved for poly(vinyl thioacetate) under similar conditions.[5] Although these results indicate that I is less reactive than vinyl thioacetate as a chain transfer agent, the molecular weights of the copolymers described below are rather low (40,000–

TABLE VIII
Dilatometric Evaluation of *S*-Vinyl-*O*-*tert*-butylthiocarbonate Polymerization[a]

[I], mole/l. × 10^2	Conversion, %/sec × 10^4	R_p, mole/l.-sec × 10^4	[η] (30°C, THF)	$\bar{M}_n \times 10^{-4}$ [b]
0.498	0.342	1.934	0.365	4.48 (4.9)[c]
0.825	0.597	3.371	0.349	4.05
4.265	1.840	10.403	0.316	3.95
8.295	3.30	18.66	0.248	2.85

[a] Polymerization temperature, 70°C; initiator, azobisisobutyronitrile, [M], 5.67 mole/l. corrected for the presence of di-*tert*-butyl carbonate.

[b] Estimated from GPC chromatogram of 0.125% solution in THF.

[c] Measured in toluene at 30° with Mecrolab Model 501 membrane osmometer.

50,000). The chain-transfer characteristics of *S*-vinyl monomers represent a major disadvantage when high molecular weight copolymers with good mechanical properties are desired.

Copolymerization

The copolymerization characteristics of *S*-vinyl-*O*-*tert*-butylthiocarbonate were determined by measuring the relative reactivity of I toward styrene, methyl methacrylate and vinyl acetate. These comonomers

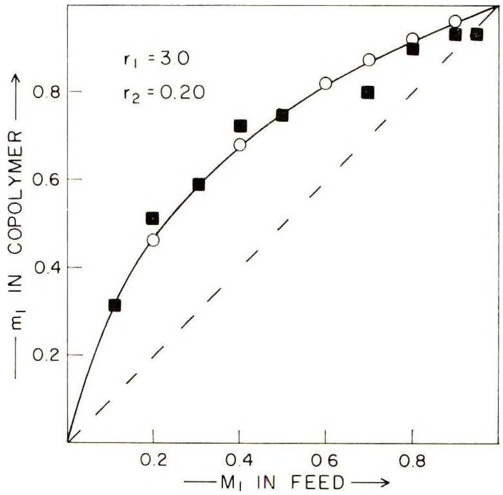


Fig. 2. Copolymer composition curve for the copolymerization of *S*-vinyl-*O*-*tert*-butylthiocarbonate (M_2) with styrene (M_1): (■) Experimental; (○) instantaneous copolymer compositions at 5% conversion calculated from reactivity ratios cited.

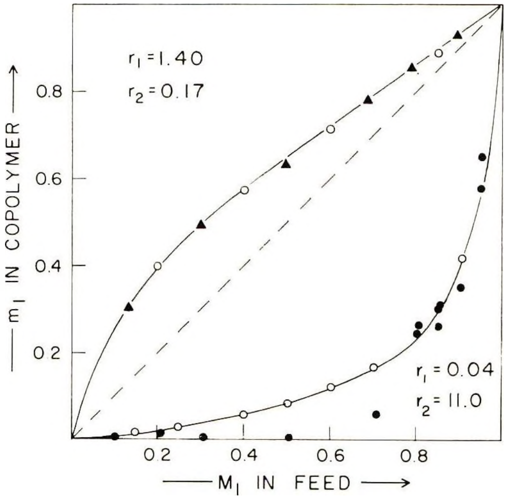


Fig. 3. Copolymer composition curve for the copolymerization of I with (▲) methyl methacrylate (M_1) and (●) vinyl acetate (M_1); (○) calculated compositions.

TABLE IX
Reactivity Ratios of *S*-Vinyl-*O*-*tert*-butylthiocarbonate (M_2) with Comonomers (M_1)

M_1	Method of calculation	r_1	r_2
Styrene	1	1.95 ± 0.1	0.21 ± 0.05
	1	2.15 ± 0.2[a]	0.15 ± 0.05[a]
	2	2.5 ± 0.2	0.35 ± 0.05
	2	3.0 ± 0.1[a]	0.20 ± 0.05[a]
Methyl methacrylate	1	1.25 ± 0.05	0.25 ± 0.05
	1	1.20 ± 0.1[b]	0.22 ± 0.05[b]
	2	1.40 ± 0.05	0.17 ± 0.05
	2	1.28 ± 0.05[b]	0.20 ± 0.05[b]
Vinyl acetate	1	0.06 ± 0.01	11.0 ± 1.0
	2	0.04 ± 0.01	11.0 ± 1.0
N-Vinylpyrrolidone	1	0.12 ± 0.02	3.9 ± 0.1
	2	0.12 ± 0.01	3.94 ± 0.05
N-Isopropylacrylamide	1	1.11 ± 0.05	0.30 ± 0.05
	2	1.17 ± 0.05	0.30 ± 0.05
N-Vinyl-*O*-*tert*-butylcarbamate	1	0.13 ± 0.05	5.30 ± 0.1
	2	0.12 ± 0.05	5.10 ± 0.1
tert-Butyl methacrylate	1	1.85 ± 0.1	0.19 ± 0.05
	2	1.70 ± 0.05	0.15 ± 0.05

[a] Spectrophotometric determination of styrene content at 260 mμ.
[b] Estimated by quantitative NMR analysis of copolymers.

represent a wide range of copolymerizabilities, extending from the resonance stabilized styrene with negative polarity (Q, 1.0; e, -0.8) through the negatively polarized nonstabilized vinyl acetate (Q, 0.028; e, -0.3) to the positively polarized methyl methacrylate (Q, 0.74; e, 0.4).[21] Thus the reactivity ratios observed when I was copolymerized with each of these comonomers should define the Q, e parameters for I and indicate the types of comonomers which would yield random copolymers.

The copolymerizations were run with neat monomer mixtures, 0.5 mole-% azobisisobutyronitrile being used as an initiator. In spite of all precautions, the copolymerizations frequently proceeded so rapidly that conversions greater than 10% were obtained. In these cases the initial monomer concentration in the feed was used to obtain a first approximation of the reactivity ratios and then the computer program for generating an integrated copolymer composition at all conversions was used to refine the values. The copolymer composition was determined by elemental analysis and either ultraviolet or NMR spectrometry when these techniques proved applicable. The data obtained was analyzed by the method of Fineman and Ross (method 1). The calculation was checked and refined by the curve fitting technique (method 2) with a computer program by use of the Mayo and Lewis equation[22] to calculate the average composition of the copolymers at the precise per cent conversion obtained experimentally.

TABLE X

Copolymerization Parameters of *S*-Vinyl-*O*-*tert*-butylthiocarbonate and Related Monomers

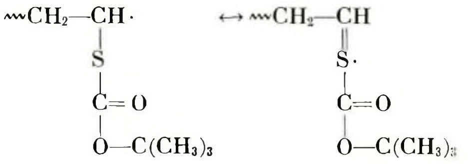
M_1	Q_1[a]	e_1[a]	M_2	r_1	r_2	Q_2	e_2	Ref.
Styrene	1.0	−0.80	$CH_2{=}CH{-}S{-}\overset{\overset{O}{\|}}{C}{-}O{-}C(CH_3)_3$	3.0	0.2	0.59	−1.51	This work
Methyl methacrylate	0.74	0.40	$CH_2{=}CH{-}S{-}\overset{\overset{O}{\|}}{C}{-}O{-}C(CH_3)_3$	1.4	0.17	0.33	−0.80	"
Vinyl acetate	0.026	−0.22	$CH_2{=}CH{-}S{-}\overset{\overset{O}{\|}}{C}{-}O{-}C(CH_3)_3$	0.04	11.0	0.65	−1.13	"
Styrene	1.0	−0.80	$CH_2{=}CH{-}S{-}\overset{\overset{O}{\|}}{C}{-}N(C_2H_5)_2$	4.4	0.14	0.40	−1.49	13
Styrene	1.0	−0.80	$CH_2{=}CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}N(C_2H_5)_2$	32	0.03	0.019	−1.10	13
Styrene	1.0	−0.80	$CH_2{=}CH{-}S{-}\overset{\overset{S}{\|}}{C}{-}N(C_2H_5)_2$	4.05	0.143	0.45	−1.54	12
Styrene	1.0	−0.80	$CH_2{=}CH{-}S{-}\overset{\overset{O}{\|}}{C}{-}CH_3$	4.0	0.25	0.25	−0.8	9
N-Vinylpyrrolidone	0.14	−1.14	$CH_2{=}CH{-}S{-}\underset{\underset{O}{\|}}{C}{-}O{-}C(CH_3)_3$	0.12	3.94	0.53	0.027	This work
tert-Butyl methacrylate	0.91	−0.44	$CH_2{=}CH{-}S{-}\underset{\underset{O}{\|}}{C}{-}O{-}C(CH_3)_3$	1.70	0.15	0.52	−1.61	"

---

[a] Data from Mayo and Lewis.[22]

After a satisfactory pair of reactivity ratios was obtained, the program was used to generate the instantaneous copolymer composition curve for copolymerization carried to five percent conversion. The copolymer composition curve for styrene (M_1) and *S*-vinyl-*O*-*tert*-butylthiocarbonate (M_2) is shown in Figure 2; similar curves for methyl methacrylate and vinyl acetate copolymerizations with I are depicted in Figure 3. The reactivity ratios calculated by both method 1 and method 2 are summarized in Table IX. The values obtained from NMR measurements on methyl methacrylate copolymers correlate well with those derived from the elemental analysis and provide additional information in the sequence distribution in the copolymers. We are currently examining the sequence distribution of the styrene and the methylacrylate copolymers in detail.

The data obtained from the copolymerization of I were used to calculate the Q and e copolymerization parameters.[21] As Table X indicates, a rather broad range of values is obtained, but this is not unusual because the errors inherent to the reactivity ratios are compounded in the calculation. The relative high values obtained for Q_2 confirm the stabilizing influence of a sulfur atom both to the adjacent double bond and the growing radical. This phenomenon has been attributed to the ability of sulfur to expand its octet and participate in d–π orbital overlap with the double bond and has been confirmed spectrophotometrically.[6,8] A similar rational can be applied to the stabilization of the growing radical; this stabilization also



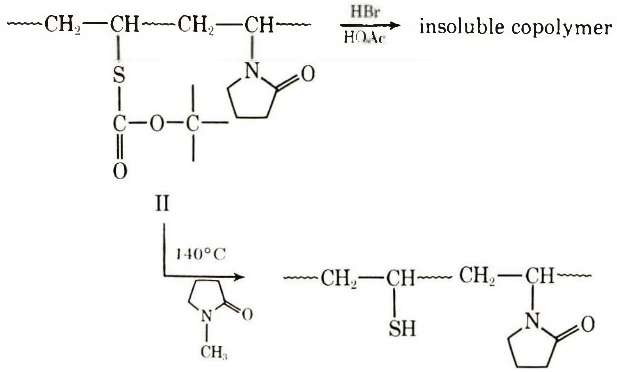
applies to radicals generated by abstraction of an α-hydrogen from the polymer backbone. Chain transfer of this type would either lead to branched chains or chain scission. These side reactions are probably responsible for the low molecular weights observed in both homo- and copolymerizations involving I. Either the monomer or the growing polymer exhibits a high chain-transfer constant which leads to chain termination by radical transfer processes.

The e parameter was originally conceived to account for electrostatic interactions by assuming that the product e_1e_2 represents the attraction or repulsion of static charges. Subsequent efforts to establish this correlation quantitatively have failed but the qualitative concept of the e value has been retained. Thus, the negative values of e_2 observed for I indicate that the adjacent sulfur atom enhances the electron density of the double bond. However, large fluxuations in the e values do not significantly influence the copolymerization ratios observed because the Q factor essentially determines the relative polymerizability of the monomer. The last two entries in Table X illustrate this point; both values are negative yet there is a marked difference in the copolymerizability of the corresponding monomers.

The predominant stabilizing influence is the adjacent sulfur atom. Although there is a very significant difference between the Q_2 values of *S*-vinyl and *O*-vinyl-*N*,*N*-diethylcarbamates, very little change is noted upon either replacing the carbonyl function with a thiocarbonyl (*S*-vinyl-*N*,*N*-diethyldithiocarbonate) or varying the carbonyl substituent from alkyl to *O*-alkyl. This indicates that the polymerizability of all *S*-vinyl derivatives will be similar, regardless of the nature of the other substituents attached to the sulfur atom. Thus the selection of an *S*-vinyl monomer as a precursor to a poly(vinyl mercaptan) should be based upon the relative ease of removing the blocking group from polymer. In this respect, *S*-vinyl-*O*-*tert*-butylthiocarbonate has a distinct advantage, because the *tert*-butyloxycarbonyl blocking group can be removed by either acid hydrolysis or mild thermolysis.

Water-Soluble Copolymers

Since most physiological application of polymercaptans required a water soluble polymeric substrate, the copolymerization of *S*-vinyl-*O*-*tert*-butylthiocarbonate with water-soluble comonomers was surveyed. Incorporation of *N*-vinylpyrrolidone into the copolymers seemed particularly attractive because poly-*N*-vinylpyrrolidone can be used as a plasma extender and thus is nontoxic and physiologically compatible. The pyrrolidone ring was attacked by the strongly acidic conditions required to remove the *tert*-butyloxocarbonyl blocking group, but this difficulty was easily surmounted by themolytic removal.



II

III

Copolymers of *S*-vinyl-*O*-*tert*-butylthiocarbonate (M_2) and *N*-vinylpyrrolidone (M_1) were prepared from a wide range of feed ratios (Fig. 4). Normal copolymerization behavior was observed and the reactivity ratios obtained, $r_1 = 0.12$; $r_2 = 3.94$, demonstrate enhanced reactivity of the *S*-vinyl monomers over *N*-vinyl monomers. This reactivity is advantageous because only small concentrations of the *S*-vinyl monomer in the monomer

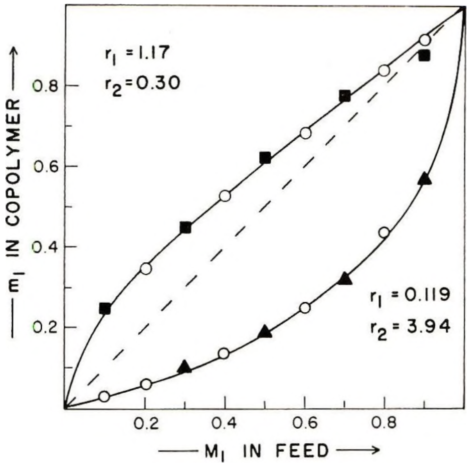


Fig. 4. Copolymer composition curve for the copolymerization of I with (■) N-isopropylacrylamide (M_1) and (▲) *N*-vinylpyrrolidone (M_1); (○) calculated compositions.

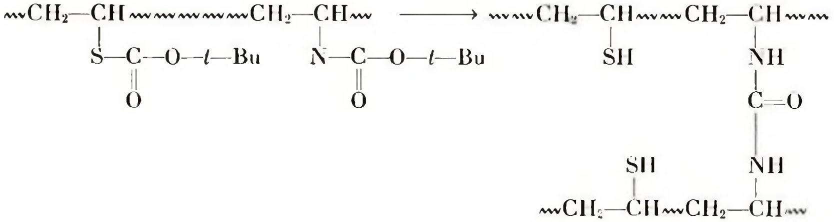
feed are required to produce copolymers containing a significant vinyl mercaptan content. The copolymers with structure II containing > 60% of *N*-vinylpyrrolidone were water-soluble but the corresponding polymercaptan analogs, III were insoluble in aqueous media. Dissolution of III in methanol, chloroform, dimethylformamide, dimethyl sulfoxide, and 5% aqueous sodium hydroxide occurred rapidly at room temperature, indicating that disulfide crosslinks were not responsible for the poor aqueous solubility properties. The sulfhydryl groups appear to be more hydrophobic than their *tert*-butyloxycarbonyl precursor and force the copolymer out of solution; indeed, a 95 mole-% *N*-vinylpyrrolidone content was required to achieve solubility in neutral aqueous media.

N-Isopropylacrylamide has also been utilized to enhance the water solubility of copolymers. Conceivably, the secondary structure of the isopropylamide substituent is more hydrophilic than the tertiary amide structure found in *N*-vinylpyrrolidone, and water-soluble copolymers with ≥ 5% vinyl mercaptan compositions could be prepared. The acrylamide structure is resistant to the hydrolytic action of both strong acids and bases so the properties of the vinyl mercaptan copolymers could be studied over the entire pH range. Copolymerization of *N*-isopropylacrylamide (M_1) with *S*-vinyl-*O*-*tert*-butylthiocarbonate (M_2) proceeded smoothly (Fig. 3) and the *N*-isopropylacrylamide proved to be more reactive than I (r_1 = 1.17; r_2 = 0.3). Water-soluble copolymers were obtained, but removal of the *tert*-butyloxycarbonyl blocking group by either acid hydrolysis or thermolysis yields insoluble vinyl mercaptan copolymers. In addition, the isopropylamide moiety seemed to increase the reactivity of the mercaptan group because the polymers darkened very rapidly and became insoluble in dimethylsulfoxide. Thus, *N*-vinylpyrrolidone remains the best comonomer for producing a water-soluble polymercaptan substrate.

Polyfunctional Vinyl Mercaptan Copolymers

The possibility of preparing amino mercaptan copolymers for model enzyme substrate evaluation was also explored. *N*-Vinyl-*O*-*tert*-butylcarbamate (M_1) was prepared from vinyl isocyanate and *tert*-butanol and copolymerized with the analogous *S*-vinyl compound (M_2). The copolymerization results were erratic, but copolymers could be obtained for all feed ratios (Fig. 5). It was difficult to obtain copolymers containing high percentages of the *N*-vinyl monomer due to the large difference in the reactivity ratios, i.e., $r_1 = 0.13$; $r_2 = 5.10$. The copolymers probably contain long blocks of poly-*S*-vinyl-*O*-*tert*-butylthiocarbonate coupled by isolated *N*-vinyl-*O*-*tert*-butyl carbamate linkages rather than a random distribution of comonomers.

The removal of the *t*-butoxycarbonyl blocking group is complicated by the reactivity of the amino substituent. Thermolytic cleavage lead to a crosslinked resin due to the formation of urea linkages.[23] The isolation of the *N*-vinyl moieties mitigrates against cyclic urea formation and leads to insoluble resins at a relatively low extent of blocking group removal. Acid hydrolysis yield the amine hydrobromide salt which could be con-



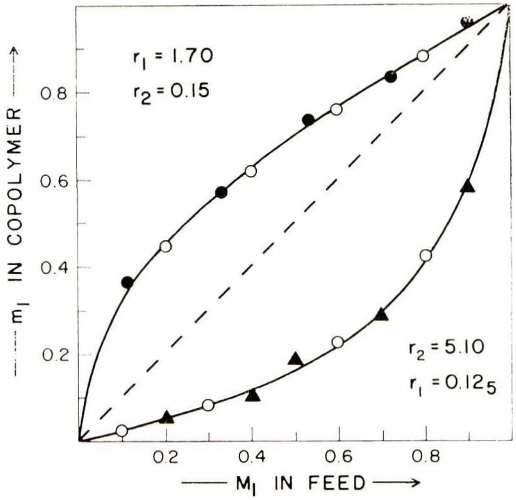


Fig. 5. Copolymer composition curve for the copolymerization of I with (●) *tert*-butyl methacrylate (M_1) and (▲) *N*-vinyl-*O*-*tert*-butylcarbamate (M_1); (O) calculated compositions.

verted to the free poly(vinylamine–vinyl mercaptan) copolymer by treatment with an ion-exchange resin but the recovery of copolymer from the resin was extremely difficult.

Poly(*tert*-butyl methacrylate–*S*-vinyl-*O*-*tert*-butylthiocarbonate) copolymers were prepared as potential precursors to a poly(methacrylic acid–vinyl mercaptan) substrate. The copolymerization results confirm the superior reactivity of acrylic or methacrylic monomers over the *S*-vinyl-*O*-*tert*-butylthiocarbonate (M_2) (r_1 = 1.70, r_2 = 0.15), but copolymers could be obtained over the entire range of feed ratios (Fig. 4).

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References

1. E. J. Goethals, *J. Macromol. Sci. Revs.*, **1**, 74 (1968).

2. Z. M. Bacq, *Chemical Protection against Ionizing Radiation*, Thomas, Springfield, Ill., 1965.

3. H. Moenig and H. Ringsdorf, *Makromol. Chem.*, **127**, 204 (1969).

4. T. Nakagawa, Y. Taniguchi, and M. Okawara, *Kogyo Kagaku Zasshi* **70**, 2382 (1967).

5. G. Hardy, J. Varga, K. Nytrai, I. Tsajlik, and L. Zubonyai, *Vysokomol. Soedin.*, **6**, 758 (1964), and references cited therein.

6. M. Imoto, M. Kinoshita, and T. Irie, *Kogyo Kagaku Zasshi*, **72**, 1210 (1969).

7. S. Nakazawa, M. Kinoshita, and M. Imoto, *Kogyo Kagaku Zasshi*, **70**, 1452 (1967).

8. R. Kroker and H. Ringsdorf, *Makromol. Chem.*, **121**, 240 (1969).

9. K. Gollmer and H. Ringsdorf, *Kolloid-Z. Polym.*, **216/217**, 325 (1967).

10. T. K. Dykstra and D. A. Smith, *Makromol. Chem.*, **134**, 209 (1970).

11. C. G. Overberger, H. Ringsdorf, and N. Weinshenker, *Makromol. Chem.*, **64**, 126 (1963); *J. Org. Chem.*, **27**, 4331 (1962).

12. T. Nakai, K. Shioya, and M. Okawara, *Makromol. Chem.*, **108**, 95 (1967).

13. A. A. Oswald and T. J. Wallace, in *The Chemistry of Organic Sulfur Compounds*, Vol. 2, N. Kharash and C. Y. Meyers, Eds., Pergamon Press, New York, 1966, Chap. 8.

14. C. G. Overberger and W. H. Daly, *J. Amer. Chem. Soc.*, **86**, 3402 (1964).

15. C. G. Overberger, K. H. Burg, and W. H. Daly, *J. Amer. Chem. Soc.* **87**, 4125 (1965).

16. H. Plant and J. J. Ritter, *J. Am. Chem. Soc.*, **73**, 4076 (1951).

17. R. C. Schulz and H. Hartmann, *Monatsh.*, **92**, 303 (1961).

18. H. Ringsdorf and C. G. Overberger, *Makromol. Chem.*, **44**, 418 (1961).

19. G. E. Ham, *Copolymerization*, Interscience, New York, 1964.

20. D. R. Montgomery and C. E. Fry, in *The Computer in Polymer Science* (*J. Polym. Sci. C*, **25**), J. B. Kinsinger, Ed., Interscience, New York, 1968, p. 59. We are indebted to Drs. Charles U. Pittman for sending us a copy of this program translated into Fortran IV.

21. T. Alfrey, Jr. and C. C. Price, *J. Polym. Sci.*, **2**, 10 (1947).

22. F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).

23. G. O. Schulz and H. J. Harwood, paper presented at 150th American Chemical Society Meeting, January 1966, Phoenix; *Polymer Preprints*, **7**, 356 (1966).

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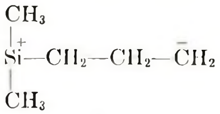
NOTES

Ring-Opening Polymerization of 1,1-Dimethyl-2,3-Benzo-1-Silacyclobutene

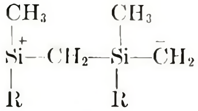
INTRODUCTION

The preparation of polysilmethylenes by thermal or catalytic ring-opening polymerization of silacyclobutanes have been of interest because of the structural analogy of these polymers to the polysiloxanes.[1-8] Recently, in a study of the effects of temperature and certain additives on the polymerization of 1,1-dimethylsilacyclobutane, Nametkin and Vdovin[4] proposed an unusual ionic mechanism for polymerization which involved the heterolytic cleavage of the Si—CH$_2$ bond to give a zwitterionic initiating species (I). A similar ionic mechanism has also been suggested by Kriner[6] in a study of the catalyzed polymerizations of various 1,3-disilacyclobutane derivatives by metal salts. Ring-opening was considered to occur by a heterolytic fission of the disilacyclobutane to give a zwitterionic intermediate (II) which could then dimerize or initiate chain propagation by either electrophilic or nucleophilic attack on the uncleaved four membered ring. Further support for the existence of a zwitterionic intermediate (II, R = CH$_3$) in the ring opening polymerization of silacyclobutanes was obtained from a study of the H$_2$PtCl$_6$·6H$_2$O catalyzed polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane.



$$\overset{CH_3}{\underset{CH_3}{\overset{+}{Si}}}-CH_2-CH_2-\overset{-}{C}H_2$$

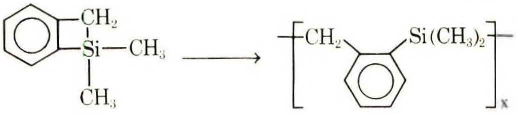
I



$$\overset{CH_3}{\underset{R}{\overset{+}{Si}}}-CH_2-\overset{CH_3}{\underset{R}{Si}}-\overset{-}{C}H_2$$

II

In order to study further the mechanism of ring-opening polymerization of silicon-containing four-membered rings, the polymerization of 1,1-dimethyl-2,3-benzo-1-silacyclobutene (III) to poly[methylene(dimethylsilylene)-1,2-phenylene] (IV) was studied by thermal, radical and ionic initiation. This silacyclobutene was expected to polymerize readily because of the release of the high strain energy upon ring-opening.[9] Studies of the effects of acid and base on II have shown that ring-opening occurs very readily with the aryl-silicon bond cleaved by acid and the methylene-silicon bond cleaved by base.[9] The polymerization of the related diphenyl analog of III has also been reported to occur from a catalytic ring-opening by (cyclohexene)$_2$Pt$_2$Cl$_6$.[5]



III IV

EXPERIMENTAL

Monomer Preparation

1,1-Dimethyl-2,3-benzo-1-silacyclobutene was prepared by the method of Eaborn, Walton and Chan,[9] yield 33%, b.p. 58–60°/10mm; NMR in CCl_4, τ 2.9 (4H, m, benzo CH), 7.9 (2H, s, —CH_2—), 9.55 (6H, s, Si—CH_3); mass spectrum (MS-9), 70 eV, M^+ 148, base peak 133 (M—CH_3).

Polymerization

In a dry polymerization tube was placed 0.5 g (0.0034 mole) of 1,1-dimethyl-2,3-benzo-1-silacyclobutene and 5 ml of solvent (where applicable). The mixture was placed in a dry ice-acetone bath and three times flushed with nitrogen and degassed. When boron trifluoride etherate or butyl lithium were employed, these catalysts were added under nitrogen through a side arm in the polymerization tube. After degassing, the tubes were sealed *in vacuo* and heated for the times designated in Table I. The tubes were then opened and the contents poured into a large excess of methanol. The white polymer was filtered, dissolved in xylene and reprecipitated into methanol.

TABLE I
Effect of Temperature and Solvent

Solvent	Temp. (°C)	Time (hr)	Conv. (%)	$[\eta]$ [a]
—	150	1	80	0.19
—	150	20	83	0.65
Benzene	80	20	61	0.21
Benzene	100	48	93	0.49
Benzene	150	20	95	0.81
Benzene	300[b]	0.1	78	2.0
Hexane	300[b]	0.1	60	1.4

[a] Determined in benzene at 25°C.

[b] Reaction done in an argon atmosphere.

An NMR spectrum of a saturated solution of IV in CCl_4 (1–2%) had absorptions at τ 2.8 (4H, m, benzo CH), 7.6 (2H, br s, —CH_2—) and 9.85 (6H, br s, Si—CH_3).

ANAL. Calcd for $C_9H_{12}Si$: C, 72.90; H, 8.15; Si, 18.94. Found: C, 72.94; H, 8.15; Si, 18.88.

RESULTS AND DISCUSSION

Studies of the polymerization of silacyclo-alkanes and -alkenes have been concerned with catalyzed initiation by ionic or coordination catalysts or by thermal initiation with or without certain additives. In this investigation the effects of thermal initiation, free radical initiation and inhibition, and ionic initiation on the ring-opening polymerization of III were studied in order to provide a further insight into the mechanism of polymerization.

In Table I are listed the results of the thermal polymerizations of III in the presence and absence of solvent. If the polymerization were a radical process, it could be expected that as the temperature is increased, a greater concentration of radicals would form which, of course, would lead to a lowering of the molecular weight of the polymer. It is noted from Table I that this did not occur because both the %-conversion and the intrinsic viscosity increased with increasing temperature in the temperature range of 80–300°C.

TABLE II
Effects of Radical Scavengers and Catalysts

Additive	Mole-%	Solvent	Temp. (°C)	Time (hr)	Conv. (%)	$[\eta]$ [a]
Oxygen	satd.	—	150	1	80	0.11
Hydroquinone	2	—	150	20	80	0.54
Hydroquinone	2	Benzene[b]	300	0.1	70	1.6
AIBN	1	Benzene	80	20	0	—
BPO	1	Benzene	100	48	92	0.10
DPPH	1	Benzene	150	20	5	0.07

[a] Determined in benzene at 25°C.
[b] Reaction done in an argon atmosphere.

These results are similar to those reported for the thermal polymerization of 1,1-dimethylsilacyclobutane in which a zwitterionic intermediate was suggested.[4]

From Table I it can also be observed that there is an effect of solvent on the polymerization. The conversion and the intrinsic viscosity both increased slightly in the solution polymerization in benzene at 150°C relative to the bulk polymerization at this temperature. It is also noted that in a comparison of the reactions in benzene and in hexane, the former solvent was somewhat more effective, possibly because of the greater solubility of the polymer in this solvent.

The results of the thermal polymerizations suggest that a radical species is not involved in the reaction. From a study of the effects of radical scavengers and radical initiators (Table II) it was found that none of the systems investigated had a higher conversion or a higher intrinsic viscosity than that obtained by thermal initiation. When the radical inhibitors oxygen and hydroquinone were employed, the conversions were essentially unaffected, but there was a slight decrease in viscosity. When the free radical inhibitor 2,2-diphenyl-1-picrylhydrazyl (DPPH) was added, marked depression of the polymerization was noted. Although this fact could indicate a quenching of a radical intermediate, it is inconsistent with the retarding effects observed for the free radical initiators, azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO). The inhibitory effect of DPPH

TABLE III
Effects of Ionic Catalysts

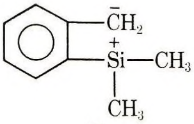
Additive	Mole-%	Solvent	Temp. (°C)	Time (hr)	Conv. (%)	$[\eta]$ [a]
Butyl lithium	1	Tetrahydrofuran	−50	48	1	—
Butyl lithium	1	—	25	40	68	0.17
Butyl lithium	1	Benzene	150	20	36	0.07
Boron trifluoride etherate	1	—	150	20	52	0.07
Aluminum chloride	1	Benzene	150	20	67	0.25
Chloroplatinic acid	0.5	—	150	20	45	0.08
Sodium	1	—	150	20	46	0.06

[a] Determined in benzene at 25°C.

could perhaps be related to the strong inhibition noted for amines in the ring-opening polymerization of 1,1-dimethylsilacyclobutane[4] and not to a radical quenching. In support of the fact that the ring-opening is not a radical process, we were unable to observe an electron spin resonance signal for a thermal polymerization in benzene at 90°C.

Although the lack of the electron spin resonance signal could have been caused by a low concentration of radicals at the temperature studied or by the existence of short-lived radicals, the results given in Tables I and II indicate that the polymerization of III is ionic in character. It is therefore somewhat surprising to note that neither the anionic, cationic or electron donating catalysts were which studied (Table III) facilitated the polymerization in relation to the thermal polymerizations. The reaction of butyl lithium with III at 25°C for 40 hr did give a higher molecular weight polymer than could have been obtained by thermal means under the same temperature. However, the reaction of butyl lithium with III in benzene at 150°C gave a drastically lower molecular polymer than that obtained by thermal initiation at this temperature.

These studies suggest that the ring-opening of III involves a heterolytic fission of the Si—CH$_2$ bond to form a zwitterion (V).[10] The assignment of charge in V is in accord



V

with Pauling electronegativities which predict a 12% ionic character to the Si—C bond,[11] with silicon being electropositive relative to carbon.

The increase in intrinsic viscosity with increasing temperature in the thermal polymerizations indicates that chain propagation occurs from a combination of zwitterionic intermediates. An individual attack of the siliconium ion or the carbanion of V and III is less likely, since if either of the latter propagation mechanisms were operative, it could be expected that the cationic or the anionic catalysts would have significantly enhanced the conversion and the intrinsic viscosity. Indeed, this did not occur as each ionic catalyst strongly retarded the polymerization. Instead, it is conceivable that the ionic catalysts, as well as the other additives which were studied, reacted with a growing chain to terminate polymerization.

References

1. V. M. Vdovin, L. S. Pushchevaya, and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, **141**, 843 (1961).
2. N. S. Nametkin, V. M. Vdovin, and U. I. Zav'yalov, *Dokl. Akad. Nauk SSSR*, **162**, 824 (1965).
3. D. R. Weyenberg and L. E. Nelson, *J. Org. Chem.*, **30**, 2618 (1965).
4. N. S. Nametkin and V. M. Vdovin, *J. Polym. Sci. C*, **4**, 1043 (1965).
5. W. R. Bamford, L. C. Lovie, and J. A. C. Watt, *J. Chem. Soc.*, 1137 (1966).
6. W. A. Kriner, *J. Polymer Sci. A-1*, **4**, 444 (1966).
7. N. S. Nametkin, V. M. Vdovin, V. A. Poletaev, and V. I. Zav'yalov, *Dokl. Akad. Nauk SSSR*, **175**, 1068 (1967).
8. G. Levin and J. B. Carmichael, *J. Polym. Sci. A-1*, **6**, 1 (1968).
9. C. Earborn, D. R. M. Walton, and M. J. Chan, *J. Organometal. Chem.*, **9**, 251 (1965).
10. Other resonance structures for V, such as an *o*-dimethylsilaxylylene, might be written.

11. C. Earborn and R. W. Bott, in *Organometallic Compounes of the Group IV Elements, Vol. 1: The Bond to Carbon, Part I* (A. G. MacDiarmid, Ed.), Marcel Dekker, Inc., New York, N. Y., 1968, p. 359.

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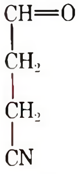
Polymerization of β-Cyanopropionaldehyde. IX. Anionic Copolymerization with Phenyl Isocyanate

INTRODUCTION

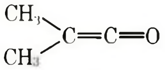
In the preceding study,[1,2] anionic copolymerization of β-cyanopropionaldehyde ($NC—CH_2—CH_2—CHO$, CPA) with dimethylketene [$(CH_3)_2C=C=O$, DMK] was carried out, and the mode of bond-opening of DMK was discussed from the NMR structural analytical data of resulting copolymers.

Since Shashoua[3,4] conducted the polymerization of isocyanates having heterocumulative double bonds as well as DMK, many investigators have studied the polymerization of isocyanates[5-18] and also their copolymerization with some aldehydes.[19-22] The present investigation is concerned with the anionic copolymerization of CPA with phenyl isocyanate ($C_6H_5N=C=O$, PhI) initiated by benzophenone–dilithium complex (Li_2-BzPh) and discussion of the structure of the resulting copolymer.

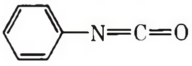


$CH=O—CH_2—CH_2—CN$

I
CPA



II
DMK



III
PhI

EXPERIMENTAL

The technique employed here was essentially the same as that described in the preceding papers.[2,23]

Materials

CPA, tetrahydrofuran (THF), and benzophenone (BzPh) were purified as already described.[23] PhI was distilled *in vacuo* after a careful removal of moisture. Li_2-BzPh and the cyclic trimer of CPA, 2,4,6-tris(β-cyanoethyl)-*s*-trioxane, were prepared in the same way as described in the preceding papers.[2,23] 3-Phenyloxazolidone-2 and 2-*N*-phenylimino-1,3-dioxolane were prepared according to methods described elsewhere.[24,25]

Polymerization

A cold solution of CPA and PhI in THF was added to a THF solution of Li_2-BzPh with vigorous stirring. Termination was carried out by adding a small amount of methanol directly into the polymerization system. The resulting copolymer was washed with a large amount of methanol and dried under reduced pressure. The average molecular weight of the polymer $\overline{M}_n$ was measured by vapor-pressure osmometry (Hewlett-Packard Model 302) in dimethylformamide (DMF) at 37°C.

Structural Analyses of the Copolymers

Infrared spectra of the copolymers were measured by the KBr method by using a Hitachi grating infrared spectrophotometer, Model 215. NMR analysis was made in deuterated chloroform with a JNM-4H-100 spectrometer.

RESULTS AND DISCUSSION

The results of copolymerization of CPA with PhI with use of Li_2-BzPh are given in Tables I and II.

TABLE I

Anionic Copolymerization of β-Cyanopropionaldehyde with Phenyl Isocyanate[a]

Expt. no.	Monomer CPA, g	Monomer PhI, g	Monomer Mole fraction of CPA	Li_2–BzPh, mole-% (based on monomer)	Time, min	Polymer yield, %[b]	Mole fraction of CPA in copolymer[c]
43	3.12	0	1.00	0.10[d]	1440	63.6	1.00
73	4.36	5.58	0.53_4	0.10	10	80.5	0.41_8
103	7.85	1.23	0.90_1	0.05	1.5	5.6	0.73_0
79	7.58	1.29	0.89_4	"	12	44.4	0.78_9
89	6.61	2.36	0.80_1	"	2	50.2	0.63_5
88	4.62	5.31	0.55_5	"	1.5	39.6	0.45_2
86	2.06	8.93	0.24_8	"	1	37.6	0.24_3
87	0.89	10.81	0.10_5	"	0.7	40.0	—
74	0	11.74	0	0.02	3	15.1	0

[a] At $<10^{-4}$ mm Hg, −78°C; solvent, THF; volume ratio of solvent to monomer, 5.

[b] Calculated for the total weight of the monomers.

[c] Estimated from the elementary analytical data.

[d] Na_2–BzPh.

Copolymerization proceeded in a homogeneous phase except for the case of extremely low or high mole fractions of CPA in monomer feed (experiments 79, 86, 87, 103, and 124), in contrast with homopolymerization of CPA and PhI.[3,4,23,26] The rate of copolymerization was much higher than that of homopolymerization of CPA. The resulting polymer obtained as a white powder was found on the basis of the elementary analysis to be composed of CPA and PhI structural units. The composition in the monomer feed had remarked effects on both the polymer composition and the copolymerization rate.

Table III shows a comparison of some properties of CPA–PhI copolymers and the homopolymers. The copolymers (as seen in samples 88 and 89) were soluble in DMF, chloroform, and THF, and insoluble in benzene. The average molecular weight $\bar{M}_n$ and softening point of the copolymer were not so high.

TABLE II

Anionic Copolymerization of β-Cyanopropionaldehyde with Phenyl Isocyanate[a]

Expt. no.	Monomer CPA, g	Monomer PhI, g	Monomer Mole fraction of CPA	Time, min	Polymer yield, %[b]	Mole fraction of CPA in copolymer[c]
124	7.60	1.18	0.91_2	2	5.3	0.75_1
91	6.62	1.20	0.88_8	0.5	0.5	0.69_5
123	7.14	1.80	0.85_1	0.7	4.2	0.66_5
85	6.79	2.87	0.77_2	5	7.3	0.57_2
125	6.24	3.62	0.71_2	1	3.8	0.50_1
77	5.86	3.60	0.70_0	2	6.4	0.52_4
82	4.23	6.06	0.50_0	1	4.5	0.38_3
84	3.14	7.44	0.37_7	2	16.9	0.32_0

[a] At $<10^{-4}$ mm Hg, −78°C; initiator, Li_2-BzPh, ca. 0.02 mole-% based on monomer; solvent, THF; volume ratio of solvent to monomer, 5.

[b] Calculated for the total weight of the monomers.

[c] Estimated from the elementary analytical data.

TABLE III
Properties of CPA–PhI Copolymers

Sample no.[a]	Mole fraction of CPA in copolymer	M_n[b]	Softening point, °C	Solubility[c]			
				DMF	Chloroform	THF	Benzene
43	1.00	3000	—	±	0	0	0
79	0.78_9	7190	~75	+	±	±	0
89	0.63_5	2880	91–94	+	+	+	0
88	0.45_2	—	109–113	+	+	+	0
86	0.24_3	—	113–118	+	+	±	0
74	0	—	190–199	0	0	0	0

[a] Sample numbers refer to products of experiments listed in Table I.

[b] By vapor-pressure osmometry in DMF at 37°C.

[c] Solubility at room temperature: (+) soluble; (±) partially soluble; (0) insoluble.

From the copolymerization data in the system of CPA (M_1) and PhI (M_2) the values of monomer reactivity ratios, $r_1 = 0.18 \pm 0.05$ and $r_2 = 0.8 \pm 0.1$, were determined by using the Mayo-Lewis integral scheme (see Fig.1). The values are different from those in the previous CPA–DMK system under the same conditions, as shown in Table IV. Although ionic polymerization is generally known to be dependent in a complex way on many factors, these apparent values under the present condition are thought to be of use for the comparison of reactivity of the monomers. The rate of addition of PhI monomer to the CPA alcoholate anion is found in terms of the values of $1/r_1$ to be more than three times that of DMK monomer. The values of r_1r_2 show that the alternating tendency of DMK is larger than that of PhI. Such a difference of the reactivity may be attributable to the polarity of heterocumulative double bonds and the conjugation effect of phenyl group.

In Figure 2 are given infrared spectra of CPA-PhI copolymers, where x represents a mole fraction of CPA unit in the copolymer. These spectra have characteristic absorption bands at 2250 cm^{-1} based on the nitrile group, at 1600, 1500, 760, and 690 cm^{-1} on the phenyl group, and also at 1730 cm^{-1} where no absorption appears in the spectra of their own homopolymers.[3,4,27] Owing to the possibility of polymerization of PhI monomer through the opening of the C=O group in addition to that of the C=N

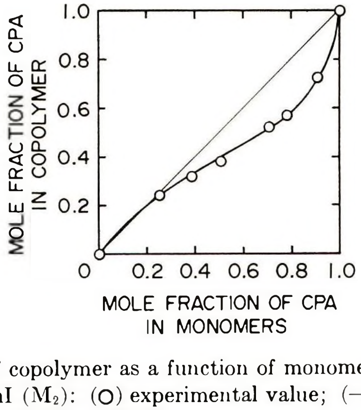


Fig. 1. Composition of copolymer as a function of monomer composition in the system of CPA (M_1) and PhI (M_2): (O) experimental value; (——) calculated from $r_1 = 0.18$, $r_2 = 0.8$. Li$_2$-BzPh; THF; −78°C.

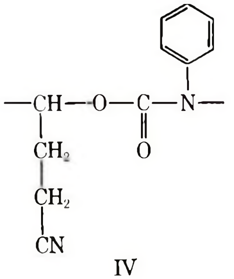
TABLE IV
Monomer Reactivity Ratios in Copolymerizations of CPA (M_1)[a]

M_2	r_1	r_2	r_1r_2	$1/r_1$
DMK[b]	0.6 ± 0.1	0.04 ± 0.03	0.024	1.67
PhI	0.18 ± 0.05	0.8 ± 0.1	0.144	5.56

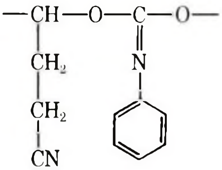
[a] With Li_2-BzPh; THF; −78°C.

[b] Data of Sumitomo and Hashimoto.[1,2]

group,[5,6,10–13,28–31] the bond formations IV and V may be considered as resulting from the cross propagation between CPA and PhI.



IV



V

Iwakura et al.[6,14] determined the opening mode of the N═C═O group from the results of the aminolysis of polyisocyanates and concluded that diisocyanates polymerized through the opening of both C═N and C═O groups and monoisocyanates through the opening of only C═N group. It was so difficult to chemically analyze the structure of the random copolymer in the present system that a NMR method was adopted here for the qualitative analysis of its microstructures.

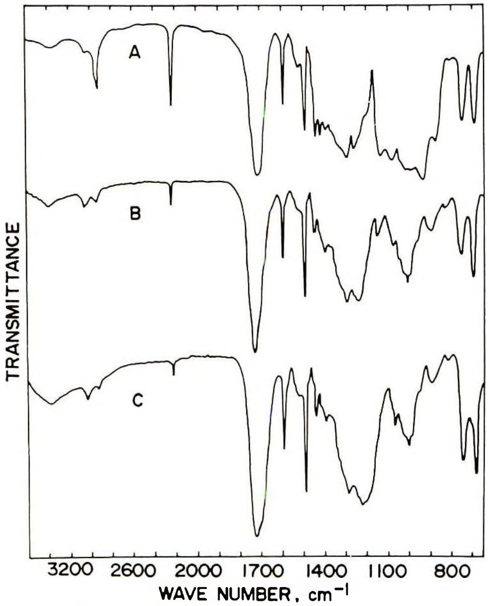


Fig. 2. Infrared spectra of CPA-PhI copolymers (KBr): (*A*) chloroform-soluble fraction of sample 79, $x = 0.78_4$; (*B*) sample 88, $x = 0.45_2$; (*C*) sample 86, $x = 0.24_3$.

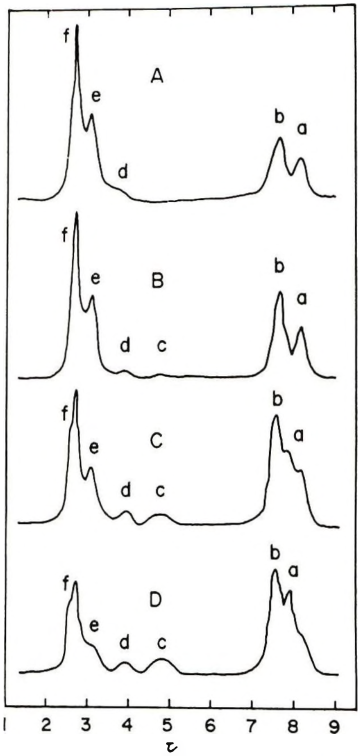
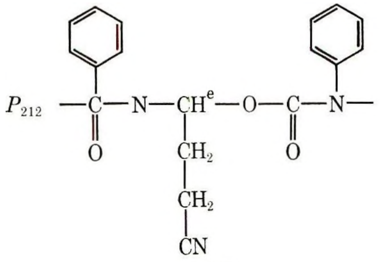
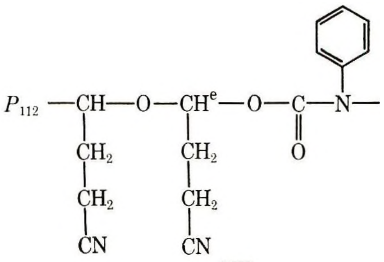


Fig. 3. NMR spectra of CPA–PhI copolymers: (*A*) sample 88, $x = 0.45_2$; (*B*) sample 125, $x = 0.50_1$; (*C*) sample 123, $x = 0.66_5$; (*D*) sample 124, $x = 0.75_1$. All in 15% deuterated chloroform solution, 70°C.

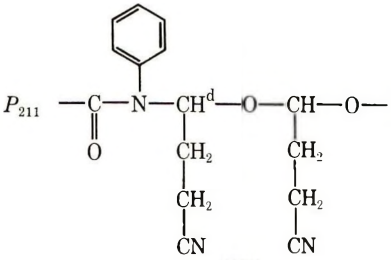
NMR spectra of CPA–PhI copolymers are given in Figure 3. Peaks *a* (τ, 8.0–8.3) and *b* (τ, 7.5–7.7) may be attributed respectively to α- and β-methylene protons of CPA unit by analogy with α- and β-methylene peaks of the CPA cyclic trimer, 2,4,6-tris(β-cyanoethyl)-*s*-trioxane. The big peak *f* and the shoulder peak *e* at 2.8–3.2τ may come from the phenyl protons of PhI unit. The methine proton of CPA unit is elucidated to give peaks *c* (τ, 4.8) and *d* (τ, 4.0) and also partially peak *e* from the viewpoint of intensity ratios of the methine peaks to the methylene peaks. In order to discuss the mode of bond opening of PhI monomer by means of the analysis of the microstructure of the copolymer, it is important to assign the methine proton of CPA unit. If PhI monomer polymerizes through the opening of its C=N bond, the triads of CPA units, P_{212}, P_{112}, P_{211}, and P_{111}, respectively, are shown as VI–IX.



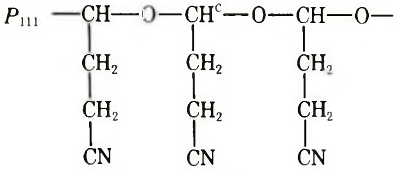
VI



VII



VIII



IX

Methine protons of the central CPA unit are assignable as indicated here from the following consideration. The peak c (τ, 4.8) must be due to the methine proton of the triad P_{111} from the observation that the methine proton of CPA cyclic trimer gives a peak at 4.9τ.[2] As the methine peak due to the triad P_{211} should be observed at a lower magnetic field than that of the triad P_{111} owing to the influence of neighboring phenyl group, peak *d* may come from the methine proton of the triad P_{211}. In view of the fact that an ester group generally shields protons more strongly than an urethane group does, the peaks based on the methine protons of the triads P_{212} and P_{112} are considered to appear at a lower magnetic field. Taking account of the intensity ratio of the methine peaks, these methine peaks may be contained within the peak of phenyl protons. When PhI monomer, on the other hand, opens its C═O bond, the triads are expressed as in IX–XII.

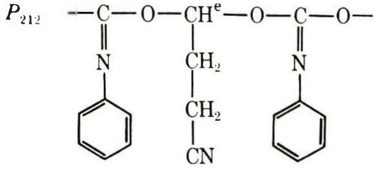
TABLE V
Intensity Ratio of Methine Peak

Sample no.[a]	Run number	Ratio of triad[b]		Intensity Ratio of peak
		$P_{111}:P_{211}$	$P_{111}:P_{211}+P_{112}$	$c:d$[c]
125	72.2	0.08:0.20	0.08:0.40	0.10:0.15
123	62.3	0.28:0.25	0.28:0.50	0.35:0.26
103	52.3	0.41:0.23	0.41:0.46	0.47:0.26
124	49.6	0.45:0.22	0.45:0.44	0.48:0.26

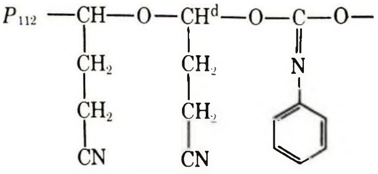
[a] Sample numbers refer to products of experiments listed in Tables I and II.

[b] Calculated from the run number.

[c] Based on the peak intensity of four methylene protons.



X



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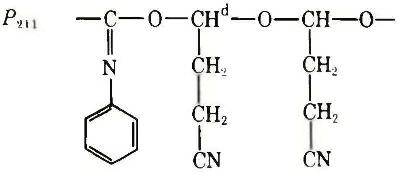

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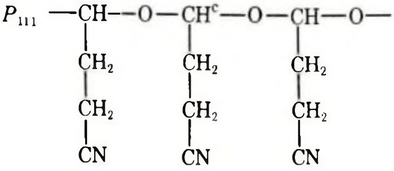

IX

In the NMR spectra of the model compounds, 3-phenyloxazolidone-2 has two triplet peaks on the methylene protons at τ values of 5.6 and 6.05 and 2-*N*-phenylimino-1,3-dioxolane a singlet peak at 5.65τ. From these observations the methine protons of the triads P_{112} (VII) and P_{211} (VIII) should not be equivalent, but the methine protons (XI and XII) are equivalent. Assuming that the present copolymerization system is explained by simple terminal model, the triads should be calculated from the run number, R[32] (see Table V).

As shown in Table V the intensity ratio of peak *c* to peak *d* based on the peak intensity of four methylene protons satisfactorily agrees with the ratio of P_{111} to P_{211} than the ratio of P_{111} to $P_{211} + P_{112}$. This fact may suggest that PhI monomer enters the chain preferentially through the opening of the C=N bond. This is analogous to the situation described in another copolymerization system of CPA–methyl isocyanate.[33] More quantitative discussion may require data from NMR obtained at a higher magnetic field strength.

References

1. H. Sumitomo and K. Hashimoto, paper presented at IUPAC International Symposium on Macromolecular Chemistry, Budapest, 1969; *Preprints*, II-157 (1969).
2. K. Hashimoto and H. Sumitomo, *Polym. J.*, **1**, 190 (1970).
3. V. E. Shashoua, *J. Amer. Chem. Soc.*, **81**, 3156 (1959).
4. V. E. Shashoua, W. Sweeny, and R. F. Tiez, *J. Amer. Chem. Soc.*, **82**, 866 (1960).
5. G. Natta, J. DiPietro, and M. Gambini, *Makromol. Chem.*, **56**, 200 (1962).
6. Y. Iwakura, K. Uno, and K. Ichigawa, *J. Polym. Sci., A*, **2**, 3387 (1964).
7. C. G. Overberger, S. Ozaki, and H. Mukamal, *J. Polym. Sci. B*, **2**, 627 (1964).
8. R. C. Schulz and R. Stenner, *Makromol. Chem.*, **72**, 202 (1964).
9. W. Burchard, *Makromol. Chem.*, **67**, 182 (1963).
10. N. S. Schneider, S. Furusaki, and R. W. Lenz, *J. Polym. Sci. A*, **3**, 933 (1965).
11. H. Yu, A. J. Bur, and L. J. Fetters, *J. Chem. Phys.*, **44**, 2568 (1966).
12. G. C. Corfield and A. Cranshaw, *Chem. Commun.*, **1966**, 85.
13. C. G. Overberger and J. A. Moore, in *Encyclopedia of Polymer Science and Technology*, Vol. 7, Interscience, New York, 1967, p. 743.
14. Y. Iwakura, K. Uno, and N. Kobayashi, *J. Polym. Sci. A-1*, **6**, 1087 (1968).
15. T. W. Campbell, J. J. Monagle, and V. S. Foldi, *J. Amer. Chem. Soc.*, **84**, 3673 (1962).
16. J. J. Monagle, T. W. Campbell, and H. F. McShanen Jr., *J. Amer. Chem. Soc.*, **84**, 4288 (1962).
17. J. J. Monagle and J. V. Mengenhauser, *J. Org. Chem.*, **31**, 2321 (1966).
18. H. Hamada, T. Iwai, K. Hayashi, and S. Okamura, *Kobunshi Kagaku*, **22**, 639 (1965).
19. H. Takida and K. Noro, *Kobunshi Kagaku*, **22**, 463 (1965).
20. Yu. P. Getmanchuk, Yu. L. Spirin, and R. I. Dryabileva, *Vysokomol. Soedin.*, **10**, 139 (1968).
21. M. C. Raes, J. V. Karavinos, and H. J. Dietrich, *J. Polym. Sci. A-1*, **6**, 1067 (1968).
22. Y. Kitahama, H. Ohama, and H. Kobayashi, *J. Polym. Sci. A-1*, **7**, 935 (1969).
23. H. Sumitomo and K. Hashimoto, *J. Polym. Sci. A-1*, **7**, 1331 (1969).
24. R. Tsuzuki, K. Ichikawa, and M. Kase, *J. Org. Chem.*, **25**, 1009 (1960).
25. T. Mukaiyama, T. Fujisawa, and T. Hyugaji, *Bull. Chem. Soc. Japan*, **35**, 687 (1962).
26. K. Hashimoto and H. Sumitomo, *J. Polym. Sci., A-1*, **7**, 1549 (1969).
27. H. Sumitomo and K. Kobayashi, *J. Polym. Sci. A-1*, **4**, 907 (1966).
28. J. Furukawa, S. Yamashita, M. Maruhashi, and K. Harada, *Makromol. Chem.*, **85**, 80 (1965).
29. J. Furukawa, S. Yamashita, K. Harada, and H. Satani, *Kogyo Kagaku Zasshi*, **70**, 1013 (1967).

30. K. Harada, J. Furukawa, and S. Yamashita, *Makromol. Chem.*, **131,** 185 (1970).
31. K. Harada, A. Deguchi, J. Furukawa, and S. Yamashita, *Makromol. Chem.*, **132,** 281 (1970).
32. H. J. Harwood and W. M. Ritchey, *J. Polym. Sci. B*, **2,** 601 (1964).
33. K. Hashimoto and H. Sumitomo, *J. Polym. Sci. A-1*, **9,** 107 (1971).

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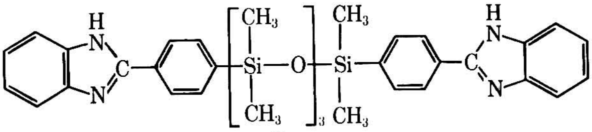
Preparation and Properties of Some Disiloxane and Tetrasiloxane Compounds

Attempts have been made to prepare polymers that exhibit a balance between thermal stability and elastic properties. A possible approach to the preparation of such materials is to prepare copolymers containing stable siloxane units (soft segments) joined together by heat stable aromatic heterocyclic units (stiff segments). It has been reported that in the absence of oxygen and at temperatures above 350°C, linear methylpolysiloxane $(Me_2SiO)_n$ degrades readily to yield volatile cyclic materials $(Me_2SiO)_{3-9}$.[1] Formation of stable cyclic siloxanes is presumed to be the driving force and so it is reasoned that in order to acquire maximum stability, the polysiloxane segments must contain fewer siloxane units than are required for the cleavage to stable cyclic siloxanes. To test this hypothesis, the synthesis of a monomer containing a tetrasiloxane moiety has been undertaken.



I

The TGA curves on this product (I) in air and nitrogen are shown in Figure 1. The breakdown temperature under nitrogen at 400–450°C indicates that the stability of this tetrasiloxane is of the same order as polymers with a long chain siloxane sequence. The unusual breakdown curve in air with an appreciable weight residue of 30% from 600–900°C, and the leveling off of the curve between 450°C and 650°C suggests the following:

(1) Initial breakdown, occurring at about 400°C, involves the splitting out and cyclization of siloxane.

(2) The leveling off of the curve between 450°C and 600°C signifies oxidation of siloxanes and probable SiO_2 formation (which may account for the white residue) to the extent of 30%.

This information appears to indicate that substitution of a short chain siloxane sequence between high T_g units will not add significantly to the thermal stability or to the improvement of elastomeric properties at elevated temperatures. Therefore, further investigations on these polymers were abandoned.

Some model compounds containing disiloxane units were synthesized to see whether imidazole, thiazole or oxazole units would serve best as stiff segments in such a structure. The thiazole was the lowest melting and the imidazole the highest melting of the three.

EXPERIMENTAL

Preparation of the Bisbenzimidazole, Bisbenzothiazole and Bisbenzoxazole: Disiloxane Compounds. A mixture of 1,3-bis(*p*-carbophenoxyphenyl)-1,1,3,3-tetramethyldisiloxane[2] (0.005 mole) and *o*-phenylenediamine, *o*-aminothiophenol, and *o*-aminophenol (0.01 mole), respectively, were heated under nitrogen at 250°C for 15 min. Heating was then continued at 0.1 mm pressure for another hr between 250° and 300°C. The contents of the flask were removed, ground to a fine powder and reheated for 1 hr at 300°C. The products were obtained in essentially quantitative yield.

The benzimidazole derivative was recrystallized from a mixture of DMF and water and melted above 330°C.

ANAL. Calcd. for $C_{30}H_{30}Si_2O$: C, 69.46%; H, 5.83%; N, 10.80%; Si, 10.82%. Found: C, 69.16%; H, 5.74%; N, 10.67%; Si, 10.86%.

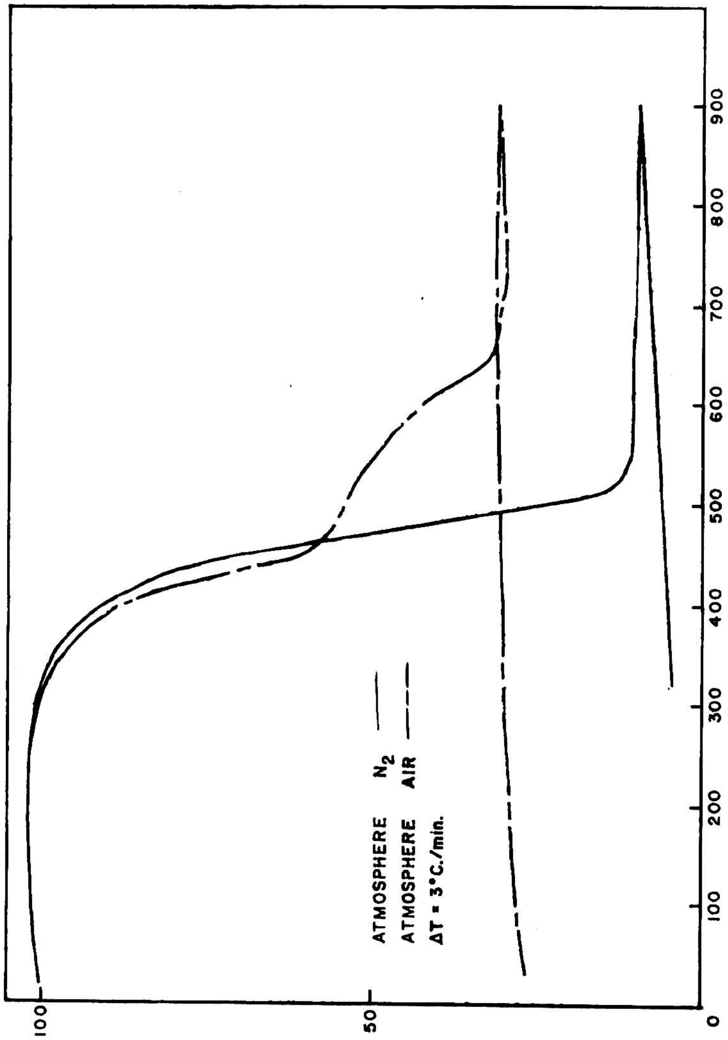


Fig. 1. TGA Curve of Product I.

The thiazole derivative was recrystallized from ethanol; mp 119–122°C.

Anal. Calcd. for $C_{30}H_{28}Si_2S_2O$: C, 65.17%; H, 5.11%; N, 5.07%; S, 10.60%; Si, 10.16%. Found: C, 65.34%; H, 5.18%; H, 4.80%; S, 10.80%; Si, 10.71%.

The oxazole derivative was also recrystallized from ethanol; mp 139–142°C.

Anal. Calcd. for $C_{30}H_{28}Si_2O_3$: C, 69.20%; H, 5.42%; N, 5.38%; Si, 10.79%. Found: C, 69.16%; H, 5.37%; N, 5.48%; Si, 10.10%.

Preparation of *p*-Bromobenzaldehyde Diethylacetal.[3] Into a one-liter round bottom flask equipped with a nitrogen inlet tube and a condenser protected with a drying tube was placed 16 g (0.66 mole) of magnesium turnings. Small portions of 250 ml of dry ether and 120 g (0.508 mole) of *p*-dibromobenzene were introduced to initiate the reaction. The reagent and the solvent were then added portionwise at such a rate as to maintain the mixture refluxing slowly. After the Grignard reagent had formed, an excess of triethyl orthoformate (100 g) and 200 ml of dry benzene were added. The mixture was refluxed under nitrogen overnight. Upon termination of the reaction, it was decanted. About 200 ml of dry ether was used to wash the product off the solid residue. The product (54 g, 42%) was then isolated by vacuum distillation at 96°C/0.35 mm.

Preparation of 1,7-bis(*p*-Benzaldehyde)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane. The Grignard reagent of *p*-bromobenzaldehyde diethylacetal (31.2 g, 0.126 mole) was prepared in 200 ml of THF under nitrogen with 3.06 g (0.126 mole) of magnesium turnings. Into a three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, a condenser protected with a drying tube and an addition funnel, were placed 22.18 g (0.063 mole) of dichlorooctamethyltetrasiloxane[4] and 100 ml of THF. To this was added dropwise the Grignard solution over a period of 30 min. It was stirred at room temperature overnight. This was followed by heating at reflux for 4 hr. The organic layer was taken into ether (800 ml), washed thoroughly with water which hydrolyzes the acetal and dried over magnesium sulfate. The solvent was removed. It was impossible to distill the residue in vacuo because it decomposed.

Preparation of the bis-Bisulfite Adduct of the Aldehyde. The bisaldehyde, (0.009 mole) and sodium bisulfite (2.20 g, 0.021 mole) were added to a stirred solution of 125 ml of methanol containing 19 ml of water. The reaction mixture was stirred overnight at room temperature. The product was filtered. After washing with 60 ml of warm methanol, the white product was dried in vacuo for 8 hr at 100°C.

Reaction of the bis-Bisulfite Adduct with *o*-Phenylenediamine to Give Compound I. The same procedure as described by Higgins and Marvel[5] was used). 1,7-bis(*p*-benzaldehyde)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane bis-bisulfite adduct (1.745 g, 0.025 mole) and *o*-phenylenediamine (0.54 g, 0.005 mole) were added to 50 ml of DMF and the reaction mixture was heated at reflux for 1 hr in a nitrogen atmosphere. The reaction mixture was then poured out into water and it was filtered and washed with water. The product was recrystallized from DMF/H_2O, mp: 210–215°C.

Anal. Calcd: C, 61.22%; H, 6.35%; N, 8.40%; Si, 16.84%; Found: C, 60.43%; H, 6.51%; N, 7.99%; Si, 16.95%.

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References

1. M. J. Hunter, J. F. Hyde, E. L. Warrick, and H. J. Fetcher, *J. Am. Chem. Soc.*, **68** 667 (1946); C. W. Lewis, *J. Polymer Sci.*, **33,** 153 (1958) and references cited therein.
2. J. E. Mulvaney and C. S. Marvel, *J. Polymer Sci.*, **50,** 541 (1961).
3. A. E. Tschitschibabin, *Ber.*, **37,** 188 (1903).
4. W. Patnode and D. F. Wilcock, *J. Am. Chem. Soc.*, **68,** 358 (1946).
5. Jerry Higgins and C. S. Marvel, *J. Polymer Sci. A-1,* **8,** 171 (1970).

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Photopolymerization of Hydroquinone Diacrylate

An α,β-unsaturated carbonyl compound such as acrylate is known to add rapidly an active hydrogen compound such as amine or alcohol to yield an addition compound in the presence of a basic catalyst in a manner as the Michael reaction. Phenyl acrylate and hydroquinone diacrylate are much more reactive[1-3] to nucleophiles than other acrylates of aliphatic alcohols because of the inductive effect of the phenoxy group. While the addition reaction of hydroquinone diacrylate (HDA) with diols was investigated, it was found that the polymerization reaction took place with a poor reproducibility of polymer yield and it was sensitive to light in laboratory room. This discovery led to a study of the photopolymerization of HDA in various solvents.

Experimental

HDA was synthesized by the reaction of 1 mole of hydroquinone and 2 moles of acryloyl chloride in tetrahydrofuran (THF) in the presence of 2 moles of triethylamine as an acid acceptor. HDA was recrystallized three or four times from ethanol–*n*-hexane so that impurities including triethylamine or inhibitors were removed completely. The yield of HDA was 60%, mp 88–89°C.

Solvents were carefully purified by conventional methods before use. A given amount of HDA was dissolved in various solvents and the solution was sealed in a glass tube *in vacuo;* the tube in a water bath kept at 30°C was then exposed to sunshine. In an alternate method, an HDA solution was placed in a cylindrical tube (2.5 × 10 cm) in air or *in vacuo* and the solution was irradiated at a distance of 1.5 cm from a high-pressure mercury lamp (3660A, 450 W) for a given period. Then, the solution was poured in dry ether and polymer was collected by filtration.

Copolymerization of HDA with styrene was carried out at a total monomer concentration of 1 mole/l *in* THF in *vacuo* and in air, by irradiation with the same mercury lamp. The copolymer formed was precipitated by ether and subsequently fractionated from acetone.

Results

When an HDA solution in sealed tubes was exposed *in vacuo* in direct sunshine, polymer started to precipitate after 30 min, and the whole solution became a highly swollen solid within 2 hr. Results of the photopolymerization of HDA in various solvents in vacuum by direct sunshine are shown in Table I, which indicates that solvent has a marked influence on the polymer yield. THF accelerates the polymerization of HDA to give a quantitative yield of polymer; more electron-donating solvents, triethylamine or dimethylaniline, did not cause the polymerization of HDA within 2 hr.

TABLE I
Photopolymerization of HDA by Direct Sunshine[a]

Solvent	Volume solvent, ml	Polymer yield, %	η_{sp}/c in H_2SO_4
Dimethylaniline	10	0	—
Triethylamine	20	Trace	—
Ethanol	20	35	0.14
Benzene	10	38	0.36
DMAc	10	70	0.22
DMF	10	77	0.30
THF	10	100	0.10

[a] HDA 0.5 g; 30°C; *in vacuo*, 2 hr.

TABLE II
Photopolymerization of HDA by a Mercury Lamp[a]

Solvent	Volume solvent, ml	In air		*In vacuo*	
		Polymer yield, %	η_{sp}/c[b]	Polymer yield, %	η_{sp}/c[b]
Acetone	10	7	—	34	0.28
Ethanol	20	8	—	40	0.10
Benzene	10	12	0.20	48	0.22
Triethylamine	20	18	0.10	42	0.04
Ethyl ether	20	41	0.14	40	0.10
Dioxane	10	63	0.24	65	0.20
DMF	10	62	0.26	80	0.22
THF	10	85	0.12	85	0.08
THF[c]	10	56	0.06	70	0.06

[a] HDA, 0.5 g; 30°C, 1 hr; in a quartz tube.
[b] In H_2SO_4 at 30°C.
[c] In the presence of 2.7 mg of hydroquinone as inhibitor.

The photo-induced polymerization of HDA by a high-pressure mercury lamp was carried out in various solvents in air or *in vacuo;* results are summarized in Table II, where the same trend of solvent effect on the polymer yield was observed. THF was the best solvent to yield polymer rapidly.

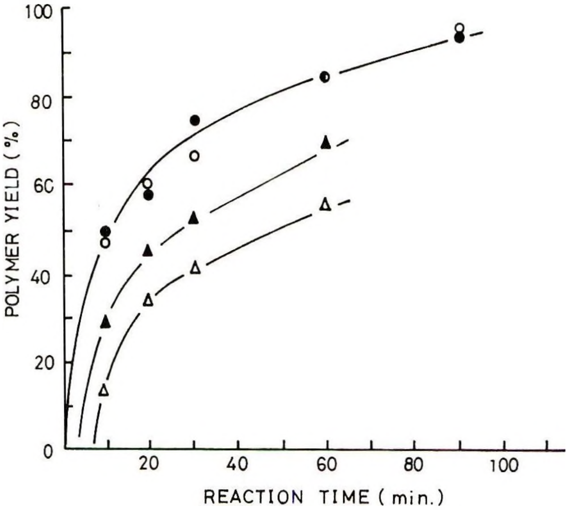

Fig. 1. Effect of hydroquinone on the photopolymerization of HDA: (△) in air; (▲) *in vacuo;* (○) without hydroquinone in air; (●) without hydroquinone *in vacuo.* HDA, 0.5 g; hydroquinone, 2.7 mg/10 ml in THF; 30°C; high-pressure mercury lamp (450 W).

Since polymer yields in air were not significantly different from those obtained *in vacuo,* oxygen is presumed to have no significant effect on the polymerization. However, when hydroquinone was added to the solution, the polymerization was retarded, as can be seen in Figure 1.

The rates of photo-induced polymerization of HDA in various solvents were determined in air under the irradiation of a high-pressure mercury lamp (Fig. 2); it is seen that HDA polymerizes very rapidly to a quantitative yield of polymer in THF. Irradiation of THF in air by a high-pressure mercury lamp may have caused autoxidation of THF, hence resulting in the acceleration of the polymerization. However, when carefully purified THF was irradiated for 2 hr under vacuum under the same reaction conditions THF did not cause the polymerization of HDA at all after the THF solution of HDA was heated at 60°C in a dark place for 48 hr. Therefore, the accelerating effect of THF on the photo-induced polymerization can not be attributed to the autoxidation of THF. Since other ether solvents, such as ethyl ether or dioxane, resulted in a good yield of polymer as indicated in Table II, the ether group may play a specific role in the photo-induced polymerization of HDA.

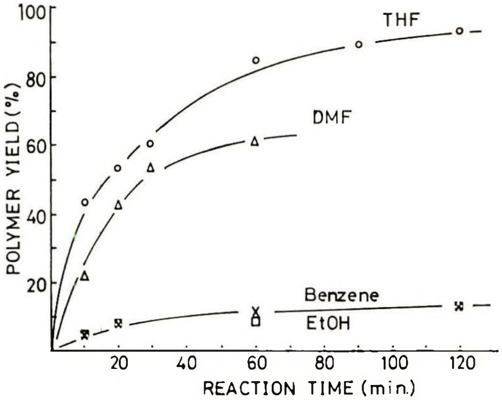

Fig. 2. Photopolymerization of HDA in various solvents in air. HDA, 0.5 g/10 ml; 30°C; mercury lamp.

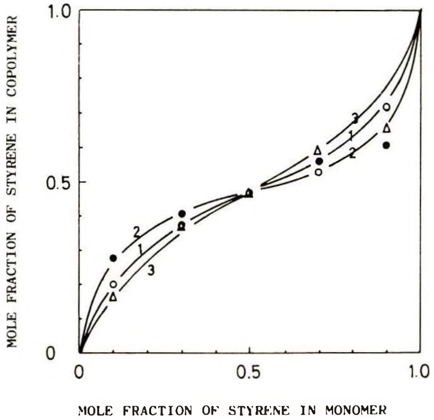

Fig. 3. Copolymer composition curve of acetone-soluble polymer in styrene and HDA system: (*1*) photopolymerization *in vacuo*; (*2*) photopolymerization in air; (*3*) thermal polymerization at 60°C (AIBN). St + HDA = 1 mole/l. in THF; 30°C; mercury lamp.

It was also found that phenyl acrylate, which has a structure similar to that of HDA, has a much lower activity for the photo-induced polymerization. Although the reason for the high sensitivity of HDA in causing the photo-induced polymerization is not yet clear, the polymerization may proceed through a radical mechanism, since the polymerization was retarded in the presence of hydroquinone.

TABLE III
Monomer Reactivity Ratios

	r_{HDA}	r_{St}
Photocopolymerization in air	0.20	0.12
Photocopolymerization *in vacuo*	0.34	0.17
Thermal copolymerization	0.42	0.27

The HDA polymer obtained by the photo-induced polymerization swelled in dimethylformamide or dimethylacetamide, and no solvents were available to prepare a real solution. Although concentrated sulfuric acid did dissolve the polymer, the polymer might undergo degradation, since no polymer was reprecipitated when the sulfuric acid solution of the polymer was poured in excess of water, and free hydroquinone and poly(acrylic acid) were recovered from the aqueous solution.

The photo-induced copolymerization of HDA with styrene was carried out in THF by irradiation with the mercury lamp. The copolymerization took place immediately after irradiation and the whole solution became a highly swollen gel within 1/2 hr. The copolymers obtained could be fractionated by acetone. The compositions of acetone-soluble and acetone-insoluble copolymers, as determined by elementary analysis, are shown in Figure 3 and compared with the compositions of copolymer obtained by the thermal copolymerization with azobisisobutyronitrile. It is evident in Figure 3 that the compositions of acetone-soluble copolymer are slightly dependent on the copolymerization conditions. The monomer reactivity ratios were calculated and are given in Table III.

TABLE IV
Overall Rates of Copolymerization of HDA with Styrene

	Overall rate, %/hr		
HDA/St ratio	Photo (vacuum)	Photo (air)	Thermal (AIBN)
1/9	0.5	0.8 (40)[a]	1.5
3/7	5.0	4.8 (11)[a]	5.0
5/5	6.5	6.5 (10)[a]	10.0
7/3	12.5	14.5 (9)[a]	13.5
9/1	18.0	20.0 (6)[a]	17.0

[a] Polymerization started after an induction period (min).

The overall rate of the copolymerization increased with increasing amount of HDA, and the apparent overall rates are summarized in Table IV. The acetone-insoluble copolymer only partly dissolved in common organic solvents and its composition is rich in HDA, compared with the composition of acetone-soluble copolymer.

References

1. K. Sanui and N. Ogata, *Bull. Chem. Soc. Japan*, **41**, 1968 (1968).
2. J. G. Erickson, *J. Polym. Sci. A-1*, **4**, 519 (1966).
3. N. Ogata, K. Tanaka and M. Tabuchi, *Kobunshi Kagaku, Japan*, **26**, 271 (1969).

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*Influence of Sample Size on Radiation Damage of Polyethylene**

A sample of highly crystalline polyethylene of density 0.96 g/cm^3 and of particle size 60–80μ (Super Dylan, Sinclair Koppers Company) was melted under vacuum to provide films of thickness about $10^3\mu$. The powder and cuttings from the crystalline films, of area ca 0.1 cm^2, were degassed and, together, sealed in vacuum in ampules. The ampules were exposed to Co-60 γ-rays at ambient temperature at a dose rate of 3.2 Mrad/hr. Several days after irradiation the ampules were heated at 80°C for 24 hours to remove trapped radicals and the samples then exposed to air. Samples were examined in an atmosphere of nitrogen at a heating rate of 20°C/min by differential thermal analysis (duPont 900 Thermal Analyzer). The minimum of a singlet endothermal peak was taken as a measure of a melting temperature. A second run gave lower values by one or two degrees and these are the values reported here, where the quantity of importance is the depression of the melting point.

TABLE I
Influence of Experimental Conditions on Depression of Melting Point on Irradiation of Polyethylenes

Density of polyethylene	low	high	low	high	
Form of polyethylene	bulk granules	bulk	bulk	bulk	powder (60–80μ)
Environment during γ-irradiation	vacuum	vacuum	air	vacuum	vacuum
Post-irradiation treatment	none	melted in air	none	annealed in vacuum at 80°C	
Depression of m.p. at low doses °C/Mrad	0.03	0.01	0.04	0.04	0.04
Depression of m.p. at high doses	not studied	levels off (2 points)	continues to fall	levels off	continues to fall
Reference	2	3	4	present work	

γ-Irradiation of the polyethylene film, designated as the bulk sample in Figure 1, results in a depression of the melting point for doses up to about 100 Mrad but it will be seen that further irradiation has relatively little effect. The powder sample initially has a similar slope but differs in that the melting point continues to drop up to the highest dose studied of 320 Mrad. Other work shows that depression of the melting point in a number of polymers, including polyethylene, provides a measure of overall radiation-induced chemical change of the polymer molecules.[1] Therefore, the results in Figure 1 are interpreted to mean that after a low dose, <10 Mrad, the overal chemical change in the two types of sample is similar but that after higher doses the change is smaller in bulk. Further evidence for this interpretation was obtained from measurements of gel content, following extraction of samples in boiling xylene under nitrogen. After a dose of 70 Mrad the gel content of bulk samples was 72%, while that of powder samples was >85%; the latter result is reported as a lower limit because some powder may have been lost during the extraction of soluble polymer.

For comparison with the present results previous data on the radiation-induced depression of the melting point of polyethylene have been collated in Table I. One notabe

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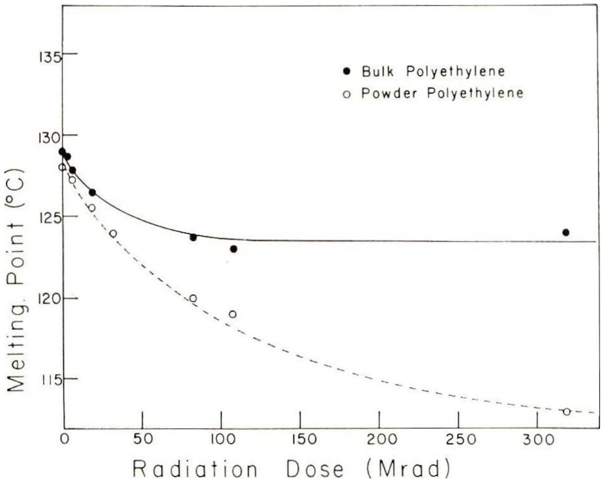

Fig. 1. Dependence of the melting point depression of polyethylene upon irradiation dose: (●) bulk sample, (○) powder sample.

feature is that despite the variety of experimental conditions there is some measure of agreement that for low doses (<ca10 Mrad) the depression of the melting point is about 0.04°C/Mrad. On the other hand, there is difference concerning behavior with increasing dose inasmuch as in some cases the melting point continues to fall whereas in others it levels off. Again this trend is taken to be indicative of chemical change in the polymer molecules and the explanation suggested for the decrease in rate with increasing dose is that trapped radicals accumulate in the samples and undergo back reactions with gaseous products such as hydrogen atoms and hydrogen molecules. It is to be expected that these reactions would be more effective the greater the distance which has to be traversed before the mobile species escape from the surface of the sample. Therefore, it is to be expected that they would be more pronounced in massive samples with a low surface to volume ratio. Previously, back reactions of trapped radicals with hydrogen atoms have been postulated to account for a decrease in rate of accumulation of alkyl radicals in polyethylene with increase in dose.[5] Reaction of alkyl radicals in polyethylene with hydrogen molecules has been demonstrated[6,7] and invoked to account for decreased yields of hydrogen under experimental conditions where escape of the gas from the polymer was impeded during irradiation.[8] The present explanation is consistent with observations that the depression of the melting point continues with increasing dose under other conditions where radical accumulation is not favoured. Cases include irradiation of the solid polymer in the presence of air[4] and irradiation in vacuum at a temperature above the melting point.[3] In view of the large amount of careful work done on the radiation chemistry of polyethylene it may appear improbable that a basic effect such as the influence of sample geometry should have been overlooked. Possibly this is because attention has been centered on quantitative study of crosslink formation which has proved very difficult to relate to dose because of large concurrent changes in the pattern of unsaturation.

Evidence of an influence of film thickness on the radiolysis of a polymer has been presented previously in the case of poly(ethylene terephthalate). First, an unidentified reaction product with an absorption maximum at 3250Å was reported to decrease in concentration with an increase in film thickness in the range studied of from 55 to 1000μ.[9] Closer examination of the data indicates that at low doses the concentration is independent of thickness and so the results are similar to those reported above for polyethylene and may be explained similarly. Independently, it has also been reported that the yield of gas and the limiting viscosity number is smaller in thicker films of PET.[10] These latter findings also seem consistent with the present explanation.

In conclusion, evidence has been presented that at low doses of γ-rays the damage of polyethylene is not noticeably dependent on sample geometry. By contrast, at higher doses the damage is smaller in samples of low surface to volume ratio. Previously, related data have been reported for PET. It is suggested that these effects are due to the back reactions of trapped polymer radicals with mobile species such as hydrogen atoms and gaseous molecules. In view of the potential importance of this effect in helping to unravel the radiation chemistry of polymers and because of the simplicity of the melting point technique it is to be hoped that similar studies will be made of other crystalline polymers.

References

1. R. M. Kusy and D. T. Turner, unpublished work.
2. M. Dole and W. H. Howard, *J. Phys. Chem.*, **61,** 137 (1957).
3. L. Mandelkern, D. E. Roberts, J. C. Halpin, and F. P. Price, *J. Am. Chem. Soc.*, **82,** 46 (1960).
4. E. Keneally, J. Gard, and G. Adler, *J. Polym. Sci. A*, **2,** 1463 (1964).
5. A. T. Koritskii, Iu. N. Molin, V. N. Shanshev, N. Ia. Buben, and V. V. Voevodskii, *Vysokomol. soed.*, **1,** 1182 (1959).
6. Ya. M. Varshavskii, G. Ya. Vasil'ev, V. L. Karpov, Yu. S. Lazurkin, and I. Ya. Petrov, *Doklady Akad. Nauk SSSR,* **118,** 315 (1958).
7. M. Dole and F. Cracco, *J. Phys. Chem.*, **66,** 193 (1963).
8. M. Dole, T. F. Williams, and A. J. Arvia, *Proc. Int. Conference Peaceful Uses of Atomic Energy*, Paper 818, Geneva (1958).
9. J. W. Boag, G. W. Dolphin, and J. Rotblat, *Radiation Research*, **9,** 589 (1958).
10. H. Sobue and A. Kajiura, *Kogyo Kagaku Zasshi*, **62,** 1908 (1959).

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Effect of the Surfactant on the Hydrolysis Rate of Polyvinyl Acetate

Polyvinyl acetate (PVAc) dissolves into high concentrated anionic surfactant aqueous solution such as sodium dodecyl sulfate (SDS). The mechanism of the dissolution has been explained by the formation of water soluble polymer-surfactant complex by means of the adsorption of surfactant on the polymer.[1] By the study of the saponification of PVAc in surfactant solution, it is desirable to obtain some new information about the mechanism of the saponification of PVAc and the state of the complex. In this paper, saponification rate of PVAc dissolved into SDS by NaOH was studied.

PVAc was prepared from polyvinyl alcohol (PVA). Commercial PVA (Gosenol NH-20, degree of polymerization about 2000, Nihon Gosei Co.) was completely acetylated by acetic anhydride in pyridine. This PVAc was purified by reprecipitation with acetone and water. SDS was purified by recrystallization from ethyl alcohol and ex-

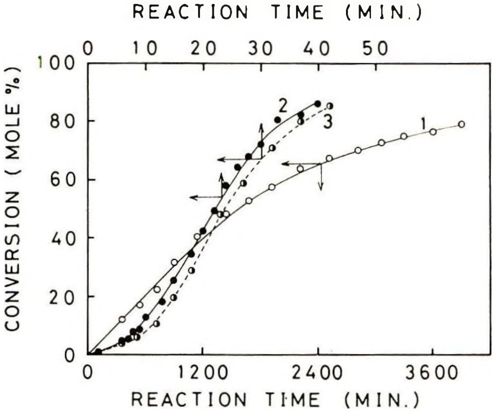

Fig. 1. The relationship between the reaction time and the conversion: (1) PVAc–SDS in water, concentration of PVAc = 0.0230 base mole, NaOH/PVAc = 1.15 by mole; (2) PVAc in water–acetone, concentration of PVAc = 0.0195 base mole, NaOH/PVAc = 1.23 by mole; (3) PVAc–SDS in water–acetone, concentration of PVAc = 0.0200 base mole, NaOH/PVAc = 1.18 by mole.

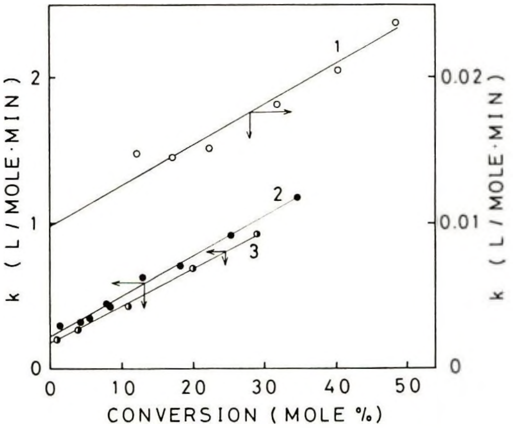

Fig. 2. The relationship between the conversion and the rate constant of the reaction: (1) PVAc–SDS in water; (2) PVAc in water–acetone; (3) PVAc–SDS in water–acetone.

traction with petroleum ether. Acetone, NaOH and HCl were the reagent grade materials (Wako Chem. Ind. Co.). PVAc–SDS solution was prepared from solubilized PVAc in a 15 wt-% SDS solution by heating and mixing, with a weight ratio of PVAc/SDS equal to $^1/_3$.

Into PVAc–SDS aqueous solution, PVAc in water/acetone mixed solvent ($^3/_7$ by volume) and PVAc–SDS in water/acetone mixed solvent ($^3/_7$ by volume), NaOH was added and PVAc was saponified at 25°C, where the concentration of the monomer unit of PVAc in reacting solution was about 0.02 mole/l and the ratio of NaOH and PVAc was equal to about 1.2 by mole, respectively. After the fixed time, 10 ml of reacting solution was pipetted out and was poured into the solution containing water, acetone, and the excess amount of HCl over the alkali in pipetted reacting solution to stop the reaction. This acidic solution was titrated immediately with $^1/_{10}$-N NaOH aqueous solution and the amount of saponified ester was calculated. The ratio of water and acetone before the titration was always adjusted to $^3/_7$ by volume.

The relationship between the reaction time and the conversion is shown in Figure 1. Both reaction rate for PVAc and PVAc–SDS in water–acetone are almost the same and that for PVAc–SDS in water is very small compared with them. From the results in Figure 1, apparent rate constants were calculated with the following integral equation of bimolecular reaction:[2]

$$k = 2.303/t(b - a) \times \log a(b - x)/b(a - x)$$

where a and b are the initial concentration of acetyl group and base (mole/l) and x is the amount of saponified group (mole/l) at the reaction time, t. In Figure 2, k's were plotted as a function of conversion. In Figure 2, k_0, which is the extrapolated value of k to the conversion equal to zero, is 0.2 l·mole^{-1}·min^{-1} for the reaction in water–acetone independent of the existence of SDS and agrees with the result by Sakaguchi et al.[2] For the reaction of PVAc–SDS in water, k_0 becomes 0.01 l·mole^{-1}·min^{-1} and is far smaller than that in water–acetone. When the concentration of PVAc is over 0.1 g/100ml, SDS adsorbs on PVAc totally and the concentration where there is total adsorption decrease with added salt.[3,4] Therefore, at the concentration of this experiment, it can be expected that SDS adsorbs onto PVAc totally. From the above results, it is considered that the ester groups of PVAc in SDS aqueous solution are masked by the adsorbed SDS and the approach of the catalyst ion, OH$^-$, to the group may consequently be prevented by means of steric hindrance or electric repulsion force against adsorbed SDS. In the mixed solvent of water–acetone, PVAc–SDS complex may not be formed or, at least, no interaction between SDS and PVAc to prevent the saponification of the ester group of PVAc may exist. Accordingly, the rate for PVAc–SDS in water–acetone becomes almost the same as that for PVAc in water–acetone.

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References

1. T. Isemura and A. Imanishi, *J. Polym. Sci.*, **33**, 337 (1958).
2. Y. Sakaguchi, Z. Sawada, M. Koizumi, and K. Tamaki, *Chem. High Polymers (Japan)*, **23**, 890 (1966).
3. H. Arai and S. Horin, *J. Colloid Interface Sci.*, **30**, 372 (1969).
4. S. Horin and H. Arai, *J. Colloid Interface Sci.*, **32**, 547 (1970).

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An Infrared Study of Same Polybenzyls

Heretofore, the absence of infrared absorption in the 12.6 μ region of polybenzyls has been taken as evidence that the polymer is highly branched.[1-3]

We herein report evidence that polybenzyls containing essentially completely linear *para* structures may not exhibit this characteristic *para* substitution pattern.

Our evidence is based primarily on (a) the diminution of these bands upon melting and recooling, (b) pyrolysis of the polymers to yield primarily the *para* isomer of xylene, and (c) bromination and oxidation of the polybenzyls to yield linear polymers which do exhibit the 12.6 μ band. NMR and infrared spectra of the brominated and oxidized polymers are consistent with Jacobson's proof of these structures.[4]

We suggest that the absence of the characteristic infrared bands may be due to conformational factors in the solid polymer.

EXPERIMENTAL

Analysis

The infrared spectra of the polymers were obtained with a Perkin-Elmer PE-337 infrared spectrophotometer as dispersions in KBr, 5 wt-% (Fig. 1). NMR spectra were determined in CCl_4 solutions, 20 wt-%, with 1% TMS internal standard, at room temperature with a Varian A 60 magnetic resonance spectrometer.

Polymerizations

The polymers were prepared by either the action of $AlCl_3$ (anhydrous, J. T. Baker, Reagent) on benzyl chloride (99.8%, J. T. Baker, Reagent) in ethyl chloride (USP, J. T. Baker) solution in the method described by Kennedy[3] or by the action of $FeCl_3$ (anhydrous, resublimed, Fisher) on benzyl chloride in a variety of solvents. This second method will be described briefly.

Polymer I. Benzyl chloride, 0.2 mole, was dissolved in 100 ml ethyl chloride under dry N_2 at -10°C. A cooled solution of $FeCl_3$, 0.002 mole, in 50 ml ethyl chloride, was added to the rapidly stirred benzyl chloride solution. After all the catalyst had been added, the vessel was allowed to warm to ca. 5°C, where the reaction started slowly as evidenced by the development of a dark red color and HCl evolution. After ca. $1^1/_2$ hours, the reaction was terminated by the addition of 50 ml methanol which annihilated the red color and precipitated the polymer. The ethyl chloride was allowed to boil off slowly and the remaining products were washed with an excess of methanol. The polymer was dissolved in dioxane and reprecipitated as a white powder with ice water. Drying in vacuum at 50°C resulted in 7 g (39% yield) of dried polymer, mp 89–90°C (polymer I), in agreement with the literature.[2,3] The infrared spectrum is reproduced in part in Figure 1.

Polymer II. Benzyl chloride, 0.2 mole, and $FeCl_3$, 0.004 mole, were allowed to react under conditions identical to those described above for polymer I. The yield was 7.5 g (42% yield) of dried polymer, mp 90–95°C (polymer II). The infrared peaks at 8, 9.1, and 12.6 μ (Fig. 1) diminished in intensity upon heating the polymer to the molten state and subsequent recooling.

Polymer III. Benzyl chloride, 0.1 mole, was added dropwise to 0.025 mole of $FeCl_3$ suspended in 50 ml CH_2Cl_2 at 0°C over a period of 4 hr. The resulting black solid was washed with methanol which gradually changed the color to bright orange. Extraction of this solid with benzene in a soxhlet extractor for several days resulted in a black solution still containing catalyst. Repeated washing of the precipitated polymer with methanol failed to remove completely the catalyst. The infrared spectrum, as a thin film on a KBr plate, is reported in Figure 1.

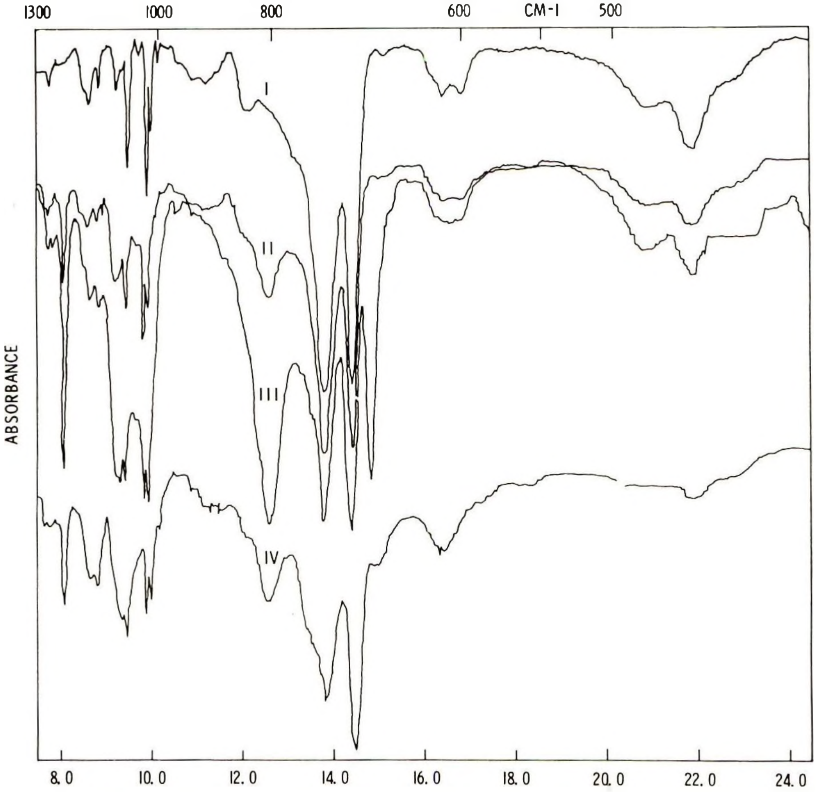

Fig. 1. Partial infrared spectra of polybenzyls: Polymers prepared at monomer:-$FeCl_3$ ratios of (*I*) 100:1, (*II*) 50:1, and (*III*) 4:1; (*IV*) spectrum of the brominated polybenzyl I.

Bromination of Polybenzyl

A 1-g portion of polybenzyl (I) was dissolved in 50 ml CCl_4 and heated gently to reflux. A short-wave ultraviolet light source was focused on the flask and 1 g (10% excess) of Br_2, dissolved in 20 ml CCl_4, was slowly added to the stirred polymer solution. HBr was gradually evolved and the solution was refluxed under ultraviolet light overnight. After 24 hr, the reaction mixture was cooled and the polymer was precipitated with ethanol and dried *in vacuo* at 50°C. A quantitative yield of brown polymer was obtained which softened around 135°C and flowed at ca. 150°C. The infrared spectrum was determined as a KBr dispersion, 3 wt-%. The NMR spectrum was determined in 30% (w/v) CCl_4 solution, with the use of 1% TMS as internal standard at room temperature.

Oxidation of Polybenzyl

Polybenzyl (I) (0.5 g) was added to a solution of 50 ml glacial acetic acid and 5 g chromium trioxide. The mixture was refluxed for 2 hr, cooled, and the resulting green solution extracted with benzene. Most of the benzene was removed under reduced pressure, and the remaining product was washed with an excess of methanol and dried in vacuum at 50°C to yield a white solid melting above 200°C.

Pyrolysis of Polybenzyl

Pyrolysis of polybenzyl (I) was carried out in an evacuated glass vessel equipped with a dry ice trap. The sample was heated very gently until the first products began to collect (ca. 400°C). Examination of these products by gas chromatography showed, by peak area, 73% toluene, 18% benzene, and 2% *p*-xylene. No *o*-xylene was detected. However, if the polymer was heated strongly past this initial point, orthoxylene was found to comprise 0.2% of the products, again by relative peak area.

References

1. H. C. Haas, D. I. Livingston, and M. Saunders, *J. Polym. Sci.*, **15,** 503 (1955).
2. L. Valentine and R. W. Winter, *J. Chem. Soc.*, **1956,** 4768.
3. J. P. Kennedy and R. B. Isaacson, *J. Macromol. Chem.*, **1,** 54152 (1966).
4. R. A. Jacobson, *J. Am. Chem. Soc.*, **54,** 1513 (1930).

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Study of the Kinetics of the Polymerization of N-Vinyl Pyrrolidone by Viscometry

During an investigation into the use of cupric sulphate-hydrazine as an initiator of vinyl polymerization, it became desirable to study the aqueous solution polymerization of *N*-vinyl pyrrolidone.

Since the polymer is very soluble in water, the technique of following the polymerization by isolating the polymer was considered to be impracticable because of the difficulty of finding suitable precipitants. It was therefore decided to establish whether the kinetics of the polymerization could be followed by observing the change in specific viscosity during the course of the polymerization.

The viscosity of a polymer solution is affected by both the molecular weight of the polymer and its concentration in solution. To determine the effect of the molecular weight of poly(*N*-vinyl pyrrolidone) on the specific viscosity of its solution in water, different samples of the polymer were prepared from benzene solutions of the monomer. Experimental conditions such as temperature, reaction time, and the concentration of the initiator (azobisisobutyronitrile) were altered so as to give as wide a variation in molecular weight as possible. The polymers were precipitated from the benzene solution with petroleum ether. The specific viscosities of solutions of each polymer in water were determined at different concentrations and a graph was plotted of "specific viscosity" against "concentration." The graphs for all the polymers were found to be co-linear and to pass through the origin. This result agrees with the observation of Breitenbach and Schmidt[1] that the degree of polymerization of poly(*N*-vinyl pyrrolidone) is unaffected by the concentration of initiator and the reaction temperature. A sample of poly(*N*-vinyl pyrrolidone) was also prepared in aqueous solution using cupric sulphate-hydrazine. The polymer was isolated by distilling off sufficient water (under reduced pressure) so as to enable the polymer to be precipitated as a sticky mass with acetone. This was then washed with diethyl ether and dried at 30°C in a vacuum oven. The viscosity average molecular weight of this polymer was found to be 5.3×10^4 compared with 1×10^4 for the polymer prepared in benzene at 85°C using 0.05% azobisisobutyronitrile, and 2.7×10^4 for the polymer prepared in benzene at 60°C using 0.1% azobisisobutyronitrile.

The poly(*N*-vinyl pyrrolidone) used in the preparation of the calibration curve was prepared under different conditions to those prevailing during the actual kinetic study. Since the viscosity average molecular weights of the polymers vary only slightly, the percentage conversion of monomer to polymer obtained from the calibration curve will differ only slightly from the actual values and comparisons made between the rate of polymerization under various reaction conditions are justified.

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Reference

1. J. W. Breitenbach and Schmidt, *A. Monatsch*, **83**, 833.

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Effects of Precipitating Polymer on the Rates of Vinyl Polymerization Initiated by the Cupric Sulphate-Hydrazine System

The aqueous solution polymerizations of methyl methacrylate initiated by the cupric sulphate-hydrazine system, both in the presence and absence of oxygen, have been described previously.[1,2] In the presence of oxygen,[1] a decrease in the rate of polymerization was observed at high conversions and was attributed to the adsorption of primary radicals on the surface of the precipitating polymer (which was in the form of a sol) since the addition of a suspension of poly(methyl methacrylate) to the reaction mixture decreased the overall rate of polymerization.

The effect of precipitating polymer is further seen from a study of the solution polymerizations of acrylonitrile and *N*-vinyl pyrrolidone when poly(acrylonitrile) forms as a flocculant precipitate while poly(*N*-vinyl pyrrolidone) remains in solution. The kinetics of the acrylonitrile polymerization were studied as described previously[1] and those of the *N*-vinyl pyrrolidone polymerization were followed by viscometry.

The curve of percentage conversion against time for the acrylonitrile polymerization shows the same decrease in rate in the presence of precipitating polymer as does the polymerization of methyl methacrylate; whereas in the *N*-vinyl pyrrolidone polymerization, the polymerization follows first order kinetics throughout the reaction. This confirms that the decreased rate observed in the methyl methacrylate and acrylonitrile polymerizations is, in fact, due to the precipitating polymer as was suggested previously[1] since the reaction conditions in all the three polymerizations were the same. Only low yields of poly(acrylonitrile) were obtained, however, since the acrylonitrile rapidly reacts with hydrazine, a reaction which does not initiate polymerization.

The graph showing the dependence of the rate of polymerization on the concentration of cupric sulphate is of the same form for all the three monomers studied; i.e., with increasing cupric sulphate concentration the rate increases to a maximum and then decreases. In the polymerization of *N*-vinyl pyrrolidone, the rate increases to a maximum at a cupric sulphate concentration of 4×10^{-5} mole liter.$^{-1}$ In this polymerization, in which there is no precipitating polymer, this maximum occurs at a cupric sulphate concentration greater than those at which the corresponding maxima occur in the polymerizations of methyl methacrylate and acrylonitrile. These are 9×10^{-6} mole liter^{-1}[1] and 2×10^{-5} mole liter^{-1} cupric sulphate, respectively. It thus seems that a given surface area is required before sufficient primary radicals are adsorbed and annihilated on the surfaces present to cause a significant decrease in the polymerization rate. This surface is provided by both the polymer and the insoluble cupric hydroxide formed.[1] As the surface area of one component is increased, the contribution to the total area required from the other component is decreased; e.g., the surface area of the precipitated polymer increases as follows:

poly(*N*-vinyl pyrrolidone) < poly(acrylonitrile) < poly(methyl methacrylate)
[no precipitated polymer] [precipitated polymer] [polymer forms colloidal particles];

while the cupric sulphate concentrations (at which the rates of polymerization decrease) increase in the following order:

methyl methacrylate polymerization < acrylonitrile polymerization < *N*-vinyl pyrrolidone polymerization.

The conclusion to be drawn from this work is that for this initiating system, the rate of polymerization is decreased by the precipitating polymer. This result is unexpected since the gel effect is usually the dominant feature in heterogeneous polymerizations[3] and results in a rapid increase in the rate of polymerization once precipitation has occurred.

However, the present work agrees with that of Palit and Guha[4] who observed an initial decrease in polymerization rate as polymer precipitated.

The authors would like to thank Geigy (U.K.). Ltd., Manchester, England, for a grant to P. I. Lee which enabled the work to be carried out.

References

1. J. Bond and P. I. Lee, *J. Polym. Sci. A-1*, **7**, 379 (1969).
2. J. Bond and P. I. Lee, *J. Polym. Sci. A-1*, **6**, 2621 (1968).
3. C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, *Kinetics of Vinyl Polymerisations by Radical Mechanisms*, Butterworth, London, 1958.
4. S. R. Palit and T. Guha, *J. Polym. Sci.*, **34**, 243 (1959).

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On the Physico-Chemical Properties of Polyvinyl Fluoride Obtained by γ-Irradiation

Polyvinyl fluoride (PVF) is one of the least studied among fluorine containing polymers. This is explained by the fact that the very first samples obtained were characterized by low thermal and light stability;[1] due to this it has been classified as nonpromising polymer. Besides, until recently, it was thought that vinyl fluoride is a monomer which polymerizes with difficulty.

However, recent research showed that this monomer polymerizes as easily as many other vinyl monomers. A marked peculiarity of this monomer is that because of its high reactivity the vinyl fluoride radical is very sensible to various impurities. For this reason, a vital requirement when dealing with vinyl fluoride is the maintenance of a high degree of purity of the monomer; it guarantees easy polymerization and a high-quality polymer, both in the sense of thermal, chemical, and light stability.

There is a wide range of information in the literature, relating to the chemically initiated polymerization of vinyl fluoride and the properties of the polymers obtained.[2,3]

Because of the fact that radiational polymerization is one of the promising methods of the synthesis of polymers with good operating (service) qualities, study of the radiation polymerization of vinyl fluoride and the properties of the polymers obtained has been of great interest.

It was stated earlier that much the same as in chemical polymerization, the carefully purified monomer easily polymerizes by the radiation method as well.[4] Already at a dosage of 12 R/sec and a dose of 0.5 MR, the degree of conversion reaches a value of 95% and above.

It was shown that such impurities as acetylene greatly inhibit polymerization. Oxygen is also known to influence the kinetic of polymerization, a factor which confirms a free radical mechanism of the polymerization process. It was discovered that such liquids as difluoroethane, benzene, and carbon tetrachloride influence the process of polymerization, mainly by reducing its rate and causing the formation of polymers with much lower weights and polymers that are wholly soluble.

The aim of this work was to study the physico-chemical properties of polyvinyl fluoride obtained by the radiation-chemical method and to compare them with the properties of the chemically obtained polymer.

Polymerization was carried out by irradiating the monomer, in both liquid and gaseous phases, with the use of γ-rays of Co^{60} at a temperature of 38°C. Highly purified vinyl fluoride was used in all experiments. Polymerization in balk was undertaken at a dose rate of 10R/sec and a dose of 0.5 MR.

A careful study of the influence of the conditions of synthesis on the structure of the molecular chain of polyvinyl fluoride, its crystallinity and thermal stability, was carried out.

We interpreted the chain structure and crystallinity of polyvinyl fluoride from the infrared spectra of the polymer obtained under different conditions as is shown in Figure 1. Depending on the conditions of synthesis, splitting of peaks into dublets in the region of 820–830 cm^{-1} is observed. PVF, obtained by radiational polymerization in the gaseous phase, show the smallest amount of splitting, while the largest amount was observed in the polymer obtained when the process was conducted in bulk. Such peak splitting, which is related to the pendulum oscillation of CH_2-groups, is closely connected with the degree of crystallinity of the polymer. On the basis of this phenomenon, it is easy to observe changes in the degree of crystallinity of PVF in relation to the conditions of its synthesis. Judging from this, crystallinity increases by the following order: PVF obtained in gaseous phase, PVF synthesized in the presence of a chemical initiator in bulk, PVF produced by polymerization in emulsion and finally, PVF where polymerization was induced by γ-irradiation in bulk. Decrease in the degree of irregularity is also observed in this order. This is connected with the probability of the formation of such monomer fragments with "head to head" and "tail to tail" structure, which is shown by a change in the intensity of the absorption bands in the region of 1425 and 1450 cm^{-1}.[5]

Study of the thermochemical properties of PVF, carried out on V. A. Kargin's balance in an interval of −120°C to 300°C showed that this polymer has a very low glass transition point. By our data (Fig. 2) this value is −70°C, independent of the conditions of synthesis of the polymer, and the melting point is about 195°C. From the thermodynamical curves it is also seen that in PVF, which is a crystalline polymer, in regions between the glass transition temperature and the softening point temperature of fluidity, which corresponds to the highly-elastic state of amorphous polymers, a certain amount of reversible deformation is developed. This, in fact, made it possible to discover the region of transformation from glass to highly-elastic state at definite load values. This can be explained from the point of view of molecular movement. It has been established that at decreased temperatures, the revolving movements of the units of the polymer chain of fluorine containing polymers decrease more slowly than, for example, those of polyethylene, and do not stop at low temperatures. It is connected with the small radius of the fluorine atom and the conditional absence of space factors which hinder the rotation of units around their axis. For this reason the low temperature of glass transition of PVF (−70°C) is caused by the peculiarity of the structure of PVF and makes it possible to use this polymer as a freeze-proof material at relatively low temperatures.

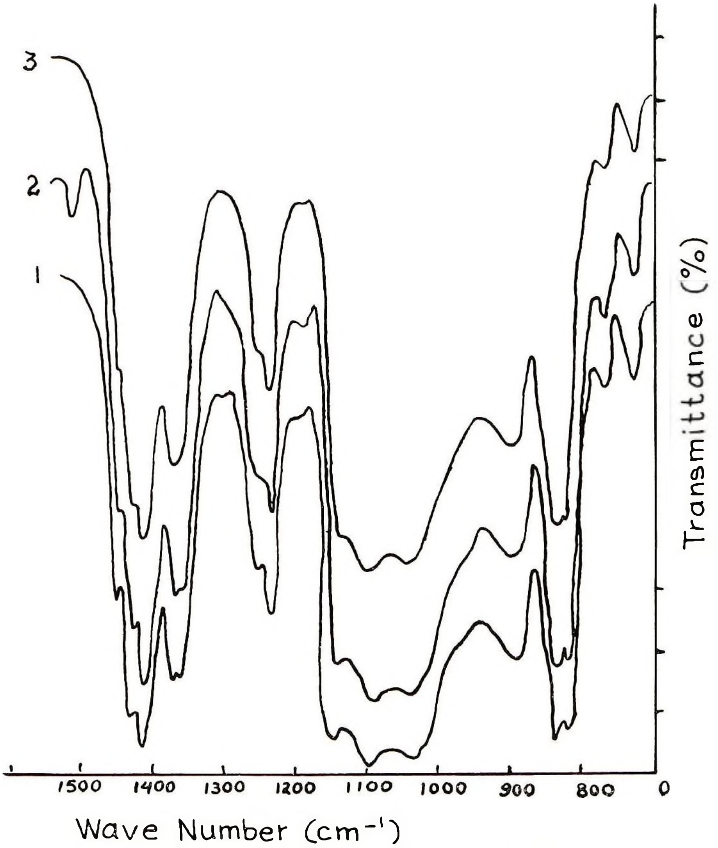

Fig. 1. Infrared spectra of PVF. (*1*) Radiation PVF obtained in gaseous phase. (*2*) PVF obtained by chemical polymerization. (*3*) Radiational PVF obtained in bulk.

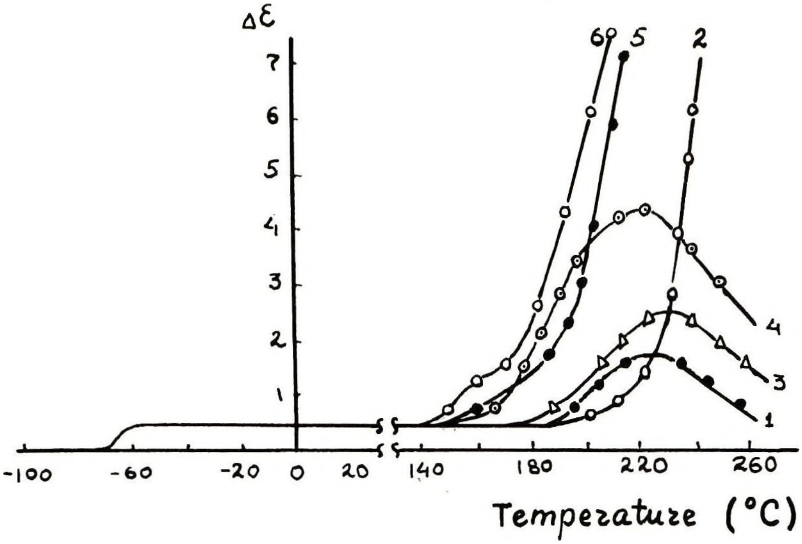

Fig. 2. Thermomechanical curves of different samples of PVF. (*1*) Radiational PVF obtained in bulk. (*2*) PVF obtained by chemical polymerization. (*3–6*) PVF plastified with dibutyl phthalate. Content of plasticizer: 3–10.0%; 4–18.7%; 5–28.3%; 6–35.4%.

On the basis of thermomechanical data conclusions can be made as to differences in the character of flow of samples of PVF, obtained by different methods. Deformation of flow of PVF obtained by radiation passes through a maximum, proving that high temperature processes of structnre formation occur which are connected with the branching of the polymer chain. At the same time, deformation of flow of PVF showed no indication of the processes of structure formation at high temperatures and was followed by the evolution of hydrogen fluoride, when thermomechanical readings are taken in the presence of air.

PVF belongs to the class of thermoplastic polymers with a high melting temperature. Melting is accompanied by partial decomposition of the polymer in air. As a result of this the plastification of this polymer is of great interest, from the point of view of reducing its melting point, thereby avoiding thermal decomposition. There are no data about the plastification of this polymer in literature. We directed our study on the plastification of PVF with the use of dibutyl phthalate and tricresolphosphate. The PVF samples were produced under various conditions. Results show that these compounds into the polymers in different quantities (Fig. 2) reduce both their temperature of glass transition and their melting temperature, and as should be expected, are in accordance with the law of molar portions. The introduction of 25–30% of the plasticizer decreases the amount of structure formation in the process of flow, a phenomenon which is observed in radiation-initiated PVF and which confirms the earlier conclusion that a decrease in the deformation of flow in radiation-initiated PVF is caused by the process of structure formation.

A study of the solubility of PVF in different solvents—dimethyl formamide (DMFA), hexamethyl phosphoramide (HMPA), cyclogexane and dioxane—showed that the solubility of the polymer is dependent both on the nature of the solvent and on the conditions under which synthesis of the polymer was conducted. At room temperature all samples only swell to various degrees in the above mentioned solvents. Besides, in DMPA, HMPA, and in cyclohexane, swelling is followed by the formation of a glassy gelatinous mass. At boiling temperatures of these solvents, the solubility of the polymer varies.

Thus the solubilities of PVF produced by radiation in bulk are as follows: in DMFA, 30–35%; in HMPA, 22–27%; in cyclohexanone, 10–15%; and in dioxane, 1–5%. At the same time, it was noted that with increase in the dosage of irradiation, the solubility of the polymer increases. For example, in DMFA the polymer obtained at a dose rate of 100 R/sec is 80–90% soluble, while that obtained at 13 R/sec is only 25–35% soluble.

The solubility of PVF, obtained under various conditions in any solvent decreases in the same order, as stated above, when judging the degree of polymer crystallinity.

Data characterizing the thermal stability of samples obtained were also taken. This study was conducted at a temperature interval of 170–350°C, both in the presence of air and in vacuum.

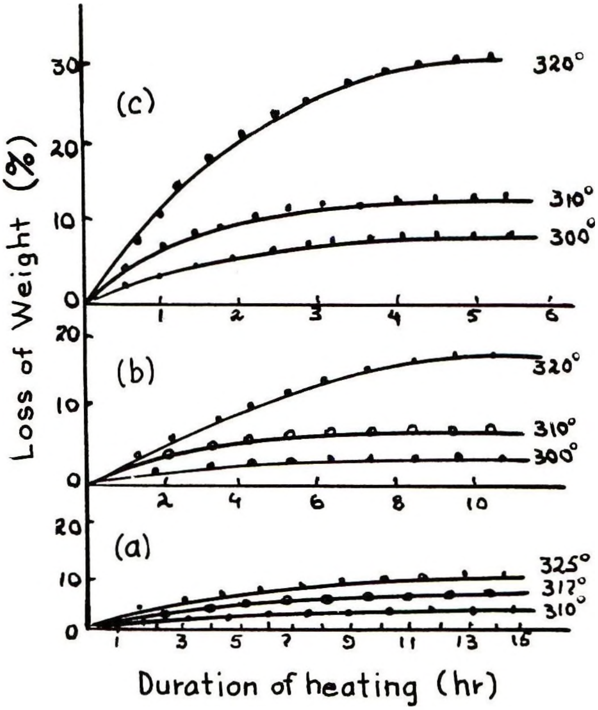

Fig. 3. Kinetics of weight loss of different samples of PVF in vacuum. (*a*) Radiation PVF obtained in bulk. (*b*) Radiation PVF obtained in gaseous phase. (*c*) PVF obtained by chemical polymerization.

Kinetic curves of polymer weight loss show that thermal degradation of all samples proceeds at a reducing rate, and the kinetic equation of loss of weight indicates a first-order reaction. The highest rate of the evolution of volatile products is observed at the beginning of the process. This is then followed by a marked drop. The value of loss in weight is a function of temperature (Fig. 3).

Radiation-initiated PVF, obtained by bulk polymerization, is thermally stable in vacuum up to 300°C. At this temperature no more than 3% weight loss in observed during the first two hours; while PVF, obtained by polymerization in the presence of chemical initiators, shows a 6% weight loss for the same period. This is evidence of the fact that radiation polymerized PVF is thermally more stable than the same polymer produced by both the chemical method and by radiation polymerization in gaseous phase.

Conclusions

1. The infrared spectra, thermomechanical properties, solubility, and thermal stability of polyvinyl fluoride, produced by radiation and chemical polymerization under various conditions, were studied.

2. It was discovered that differences in the solubility, thermomechanical properties, and thermal stability of radiation-polymerized polyvinyl fluoride is caused by the branching of the macromolecules.

References

1. A. Newkirk, *J. Am. Chem. Soc.*, **68**, 2467 (1946).
2. V. L. Simril and B. A. Curry, *Modern Plastics*, **36**, 11, 121, 122, 124–125 (1959).
3. C. H. Kalb, D. D. Coffman, T. A. Ford, and F. L. Johnston, *J. Appl. Polym. Sci.*, **4**, 10, 53 (1960).
4. Kh. U. Usmanov, A. A. Yulchibaev, G. S. Dordjin, and Kh. Yuldasheva, *Proceedings of the Second Tihany Symposium on Radiation Chemistry, Budapest*, 1967, p. 511.
5. J. L. Koenig and S. S. Mannion, *J. Pol. Sci. A-2*, **4**, 3, 401 (1966).
6. W. P. Slichter, *J. Pol. Sci.*, **24**, 173 (1957).

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ERRATA

Four-Center Type Photopolymerization in the Solid State. IV. Polymerization of α,α'-Dicyano-*p*-benzenediacrylic Acid and Its Derivatives

Fusae Nakanishi and Masaki Hasegawa

[article in *J. Polym. Sci. A-1*, **8,** 2151 (1970)]

In Table I, on p. 2154, the polymer yield of *n*-propyl ester ($R{=}COO\text{-}n\text{-}C_3H_7$) was described as "qualitative," but it should be "quantitative."

Synthesis and Polymerization of 5-Vinyl-2,2′-Bithiophene

Edward Gipstein, William A. Hewett, and Omar U. Need

[article in *J. Polym. Sci. A-1*, **9,** 813 ((1971)]

The last sentence in the first paragraph on p. 813 should be amended to read: ". . . three major absorption bands at 340 mμ, 242 mμ, and 198 mμ. . . ."

Optical Rotatory Properties and Conformations of Esters and Polyesters of *trans*-1,2-Cyclohexanedicarboxylic Acid

C. G. Overberger, G. Montaudo, Toshiyuki Furyama,
and Murray Goodman

[article in *J. Polymer Sci.*, C, **31,** 33 (1970)]

In the by-line, Dr. Furuyama's first name was misspelled; it should read "Toshiyuki."

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