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Polyaddition Reaction of Biscarbodiimides. II. Synthesis of Polyguanidines by Polyaddition Reaction of Biscarbodiimides with Diamines

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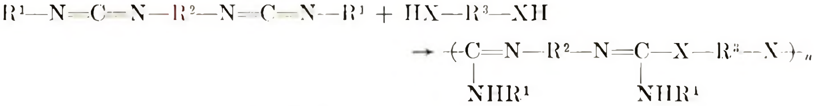
Synopsis

A series of polyguanidines was prepared by the polyaddition reaction of biscarbodiimides with diamines. The polyaddition reaction was carried out in solution. The polymers thus obtained had intrinsic viscosities up to 0.84 and molecular weights up to 15 000. The structure of the polymers was identified by comparison of their infrared spectra with those of model compounds, elementary analysis, and a study of the reaction conditions. Thermogravimetric study indicated that the polyguanidines decomposed over 170°C under nitrogen. The polyguanidines were highly resistant to hydrolytic degradation by strong acid or alkali. The polyguanidines had basic groups and formed stable hydrochloric salts when they were treated with hydrochloric acid.

INTRODUCTION

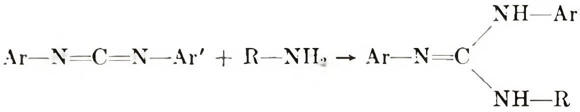
The polyaddition reaction of biscarbodiimides gave new polymers.[1] Thus, aliphatic biscarbodiimides reacted with diols in the presence of cuprous chloride[2] to form poly(pseudourea ether) (I) and with dithiols to form poly(pseudothiourea ether) (II).[1] The reactions are summarized in eq. (1):



$$R^1{-}N{=}C{=}N{-}R^2{-}N{=}C{=}N{-}R^1 + HX{-}R^3{-}XH \rightarrow \left(\underset{NHR^1}{\underset{|}{C}}{=}N{-}R^2{-}N{=}\underset{NHR^1}{\underset{|}{C}}{-}X{-}R^3{-}X \right)_n \qquad (1)$$

I; X=O: Poly(pseudourea ether)
II; X=S: Poly(pseudothiourea ether)

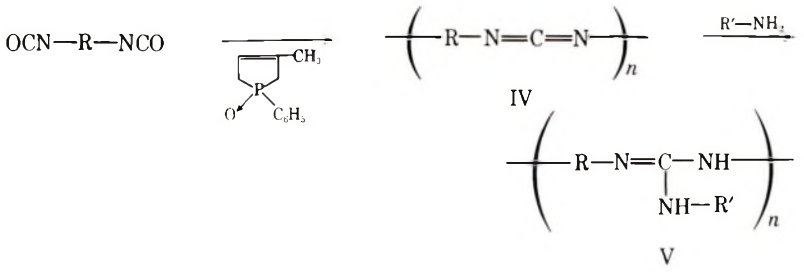
It is well known that reaction of aromatic carbodiimides with amines results in high yields of the corresponding guanidines (III),[3] as shown in eq. (2):



(2)

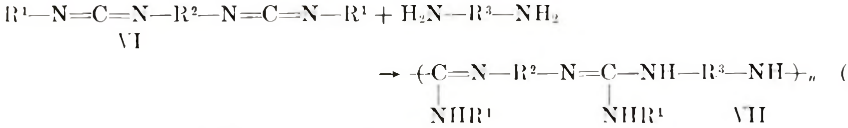
III

Lyman and Sadri have prepared polyguanidines (V) from polycarbodiimides (IV) and monoamines through the above reaction.[4] IV was prepared from diisocyanates by the method of Campbell et al.[5,6] These reactions may be summarized as in eq. (3):



(3)

The biscarbodiimides with aromatic groups (VI) were found to have enough reactivity to aliphatic amines to give bisguanidines quantitatively in a short period.[7] This reaction was extended to the synthesis of new polyguanidines (VII). The reaction may be given as in the eq. (4). Preliminary results have been presented briefly elsewhere.[8]



$$\underset{\text{VI}}{R^1{-}N{=}C{=}N{-}R^2{-}N{=}C{=}N{-}R^1} + H_2N{-}R^3{-}NH_2 \rightarrow \underset{\text{VII}}{\left(\underset{\substack{|\\ NHR^1}}{C}{=}N{-}R^2{-}N{=}\underset{\substack{|\\ NHR^1}}{C}{-}NH{-}R^3{-}NH\right)_n} \quad (4)$$

	R^1	R^2
VI-1:	= *t*-butyl,	= *p*-phenylene
VI-2:	*t*-butyl,	*m*-phenylene
VI-3:	2,6-xylyl,	*p*-phenylene

As far as we know, this was the first synthesis of polyguanidines by polymer formation from low molecular weight materials.

This paper will describe and discuss the details of the polyaddition reaction of biscarbodiimides with diamines.

RESULTS AND DISCUSSION

Polyaddition Reaction

The polyaddition reaction of VI with diamines was carried out in solution to form polyguanidines (VII). In most cases, a toluene solution of the two components was stirred and heated to reflux under nitrogen for 7 hr. The results are summarized in Table I. The polymers thus obtained in high yields had intrinsic viscosities up to 0.84 and molecular weights up to 15 000, which corresponds to 36 repeating units.

The structure of VII was identified by elementary analysis and infrared spectra. The infrared spectra of polymers of structure VII were quite similar to those of model compounds. An example is given in Figure 1 together with that of a model compound. A strong absorption band at 1625 cm^{-1} (C=N) is characteristic.

The effect of the mole ratio of both components on the viscosity of the polymer was studied. Inherent viscosities are plotted against the VI-1-nonamethylenediamine mole ratio as shown in Figure 2. The highest

TABLE I

Polyguanidines from Biscarbodiimides and Diamines[a]

Polyguanidine	Biscarbodiimide	Diamines	Yield, %	mp, °C	$[\eta]$, dl/g[b]	MW × 10^{-3}[c]	Number of repeating units
VII-1	VI-1	Nonamethylene	74	107	0.84	15	36
2	"	Heptamethylene	87	104	0.59	8.4	21
3	"	Hexamethylene	86	101	0.53[d]	10	26
4	"	Tetramethylene	92	104	0.22	6.0	17
5	"	Trimethylene	95	114	0.15	3.9	11
6	"	Ethylene	85	149	0.32[e]	—	—
7	VI-2	Nonamethylene	83	—	—	—	—
8	"	Hexamethylene	77	96	0.25[d]	4.2	11
9	VI-3	Nonamethylene	97	112	0.30	ca. 10	ca. 20
10	"	Hexamethylene	99	122	0.20[d]	10	20

[a] A toluene solution was stirred and heated to reflux for 7 hr under nitrogen.

[b] Measured in dimethylformamide at 30°C.

[c] Measured in benzene by vapor pressure osmometer (Mechrolab Model 301A).

[d] η_{inh}; measured at a concentration of 0.5 g/100 ml in dimethylformamide and at 30°C.

[e] η_{inh}; measured at a concentration of 0.5 g/100 ml in chloroform and at 30°C.

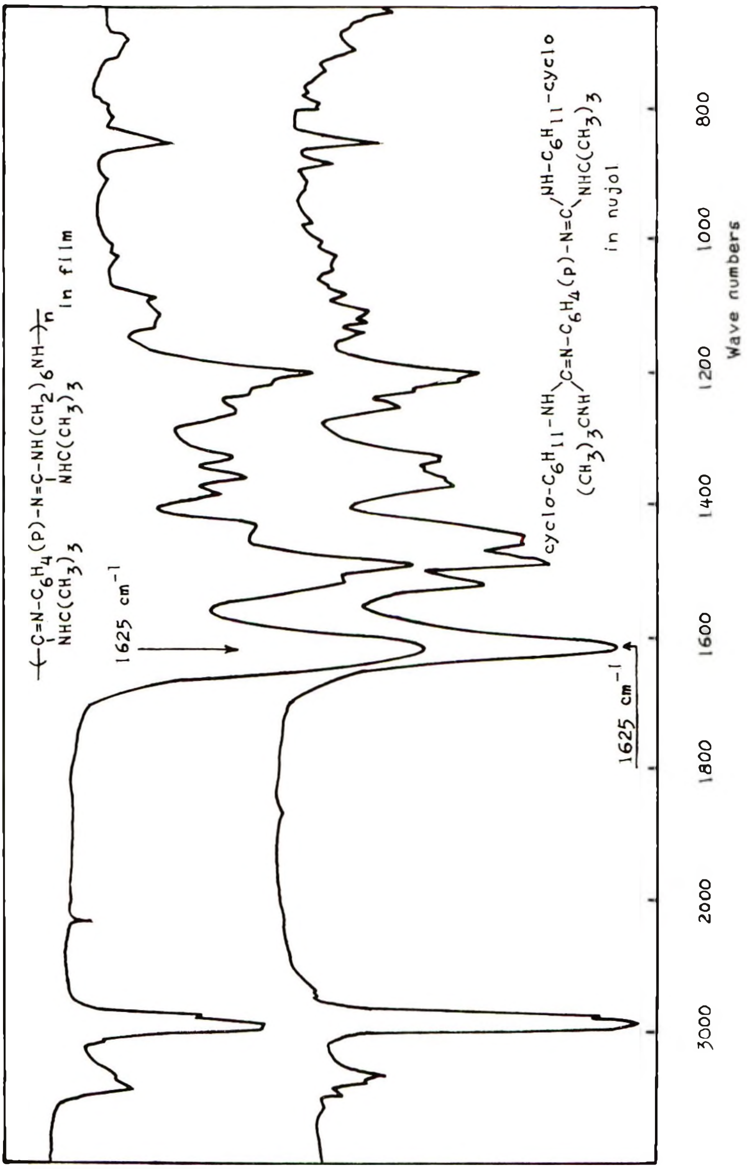


Fig. 1. Infrared spectra of polyguanidine VII-3 and the bisguanidine.

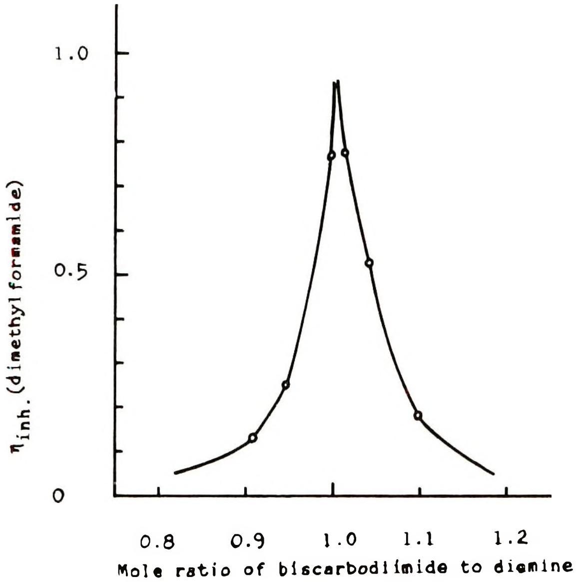


Fig. 2. Effect of reactant ratio on the viscosity of the polyguanidine prepared from *p*-phenylenebis(*tert*-butylcarbodiimide) and nonamethylenediamine in toluene. η_{inh} obtained at 30°C, 0.5g/100 ml dimethylformamide.

viscosity was obtained at the mole ratio of unity. The inherent viscosity rises increasingly rapidly as this ideal ratio is approached. These results indicate that this polymer formation reaction is truly a polycondensation reaction and that there is no side reaction which leads to branched polymer. Therefore, the polymer obtained is to have a linear structure composed of arylene and alkylene groups joined alternatively to each other. Such a polymer could be obtained by no other known method, and could be considered to be a kind of copolymer.

In this polyaddition reaction, the reaction temperature had a marked effect on the structure of the polymer formed. The temperature of reflux-

TABLE II

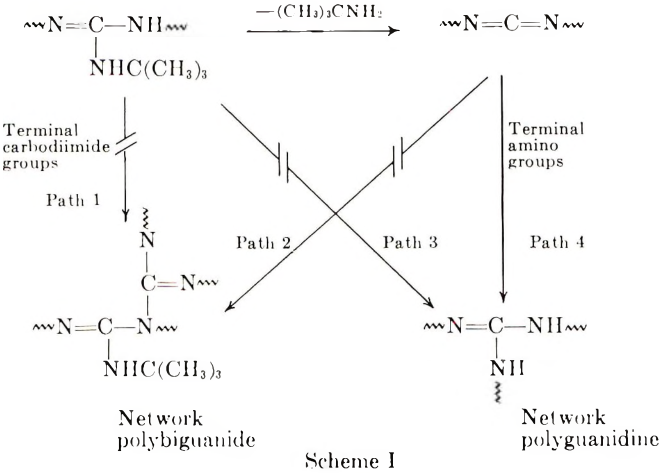
Effect of Reaction Temperature on the Polyaddition Reaction of *p*-Phenylenebis(*tert*-butylcarbodiimide) (VI-1) and Hexamethylenediamine

Polyaddition conditions				
Solvent	Temperature, °C	Time, hr	Yield, %	Products
Toluene	50	7	19	$\eta_{inh} = 0.10$[a]
Toluene	110 (reflux)	7	86	$\eta_{inh} = 0.53$
Xylene	140 (reflux)	7	(46)	Large insoluble fraction
Xylene	140 (reflux)	3	79	Large insoluble fraction
Anisole	153 (reflux)	6	92	Large insoluble fraction
Anisole	153 (reflux)	2.75	82	Large insoluble fraction

[a] Measured at a concentration of 0.5 g/100 ml of dimethylformamide and at 30°C.

ing toluene was most suitable for producing high molecular weight soluble polymer, as shown in Table II. The reaction did not seem to proceed sufficiently at 50°C. The inherent viscosity of the polymer formed was low, and its infrared spectrum showed the presence of considerable amounts of unreacted carbodiimide linkages. The use of temperatures higher than the boiling point of toluene, such as the temperature of refluxing xylene and anisole, gave insoluble polymers which could result from crosslinking.

It seemed reasonable to conclude that the most probable route for the crosslinking mentioned above was the addition reaction of terminal amino groups to carbodiimide groups in polymer chains formed by the elimination of *tert*-butylamine from guanidine linkages (path 4) as shown in Scheme I.



Scheme I

Much stronger carbodiimide bands were found in the infrared spectra of the polymers obtained in refluxing xylene or anisole than in the spectra of those obtained in refluxing toluene. The thermogravimetric analysis of VII exhibited an initial weight loss at about 170°C as shown in Figure 3. *tert*-Butylamine was recovered in 40% yield on the thermal decomposition of the adduct of VI-1 and benzylamine. Therefore, carbodiimide linkages appeared to be formed in the polymer chain by the elimination of *tert*-butylamine from polyguanidine in refluxing xylene or anisole, even if the weight loss was first detected at 170°C by thermogravimetric analysis. From the results described above, the formation of carbodiimide seemed to have some relation to crosslinking.

Carbodiimides reacted with aliphatic amines much faster than with guanidines. Infrared spectra showed that the intensity of absorption band at 2170 cm^{-1} (—N=C=N—) decreased rapidly after mixing phenyl-*tert*-butylcarbodiimide and aliphatic amines at room temperature. An intense absorption band remained at 2170 cm^{-1} after refluxing for 7 hr a toluene solution of phenyl-*tert*-butylcarbodiimide and the bisguanidine derived from VI-1 and benzylamine. Thus, reaction paths 1 and 2 in the Scheme I would be eliminated. Thus, the reaction of carbodiimide on the chain end

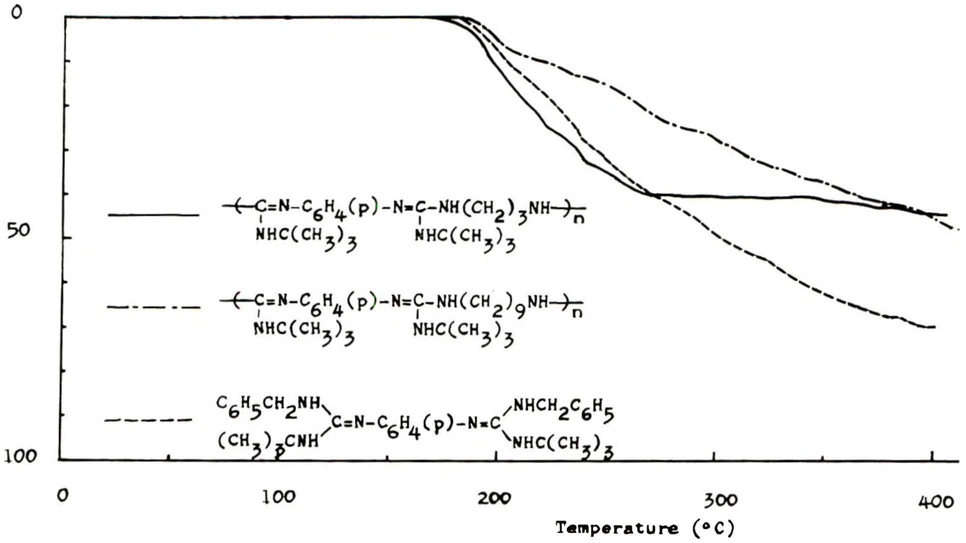
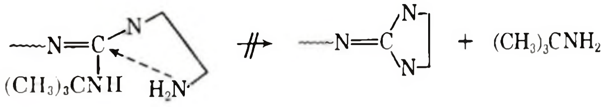


Fig. 3. Weight loss (%) of the polyguanidines (VII-1 and VII-5) and the bisguanidines by thermogravimetric analysis in nitrogen atmosphere, 2.5°C/min.

with a terminal amino group gives the linear polyguanidine. The reaction of carbodiimide formed in the polymer chain with terminal amino group would lead to the formation of network polymers.

There is another possibility for forming crosslinks. That is the reaction of guanidine with a terminal amino group. If guanidine should undergo a substitution reaction with amine, the reaction of carbodiimide with ethylenediamine would give a ring compound easily as shown in eq. (5).

 (5)

The formation of high molecular weight polymer from VI-1 and ethylenediamine suggested that such a substitution reaction did not occur. This fact would eliminate this possibility.

TABLE III
Effect of Reaction Time on the Extent of Polyaddition Reaction of *p*-Phenylenebis-(*tert*-butylcarbodiimide) (VI-1) and Hexamethylenediamine in Refluxing Toluene

Reaction time, hr	Yield, %	η_{inh}, dl/g[a] In dimethylformamide	η_{inh}, dl/g[a] In toluene
3	87	0.40	—
7	86	0.53	0.28
15	95	0.64	0.33

[a] Measured at a concentration of 0.5 g/100 ml of solvent and at 30°C.

The effect of reaction period on the extent of polymerization was studied, and the results are summarized in Table III. The data illustrate that as the period for the polyaddition reaction in refluxing toluene was prolonged, the inherent viscosity increased, but the yield remained virtually constant. The results show that the reaction was sure to proceed stepwise.

Properties of Polyguanidines (VII)

Clear films were cast from solutions of VII with intrinsic viscosities higher than 0.20. The solvents used were benzene, toluene, dimethylformamide, etc.

The melting points of VII ranged from 95°C to 150°C. Polymers VII-1–VII-5 and VII-7–VII-10 were soluble in many organic solvents such as benzene, toluene, anisole, *N*-methylpyrrolidone, dimethylformamide, and *m*-cresol. VII-6 was soluble only in chloroform among the solvents tested. VII had pendant bulky groups such as *tert*-butyl or 2,6-xylyl which made the isolation of VI possible.[7] Those groups might weaken the intermolecular force and make VII easily soluble in various solvents.

TABLE IV
Alkaline Treatment of Polyguanidines (VII)[a]

Polyguanidine	Recovery of polymer, %	mp, °C	η_{inh}, dl/g[b] Recovered polymer	η_{inh}, dl/g[b] Original polymer
VII-3	(98)[c]	—	—	0.53
VII-6	83	139	0.21	0.32[d]
VII-8	(97)[c]	—	—	0.25
VII-9	57	89	0.53	0.30
VII-10	76	129	0.30	0.20

[a] VII was refluxed with 20% aqueous NaOH for 7 hr.

[b] Measured at a concentration of 0.5 g/100 ml in dimethylformamide and at 30°C unless otherwise noted.

[c] Yield of the crude insoluble product.

[d] Measured at a concentration of 0.5 g/100 ml of chloroform and at 30°C.

TABLE V
Polyguanidine Hydrochlorides

Polyguanidine	Yield, %	mp, °C	[η], dl/g[a]
VII-1	(91)[b]	—	—
VII-2	75	—	114
VII-4	69	220[c]	20
VII-6	69	295[d]	26
VII-9	79	180	25

[a] Measured in water at 30°C.

[b] Crude insoluble product.

[c] Decomposed and colored without melting.

[d] Melted with decomposition.

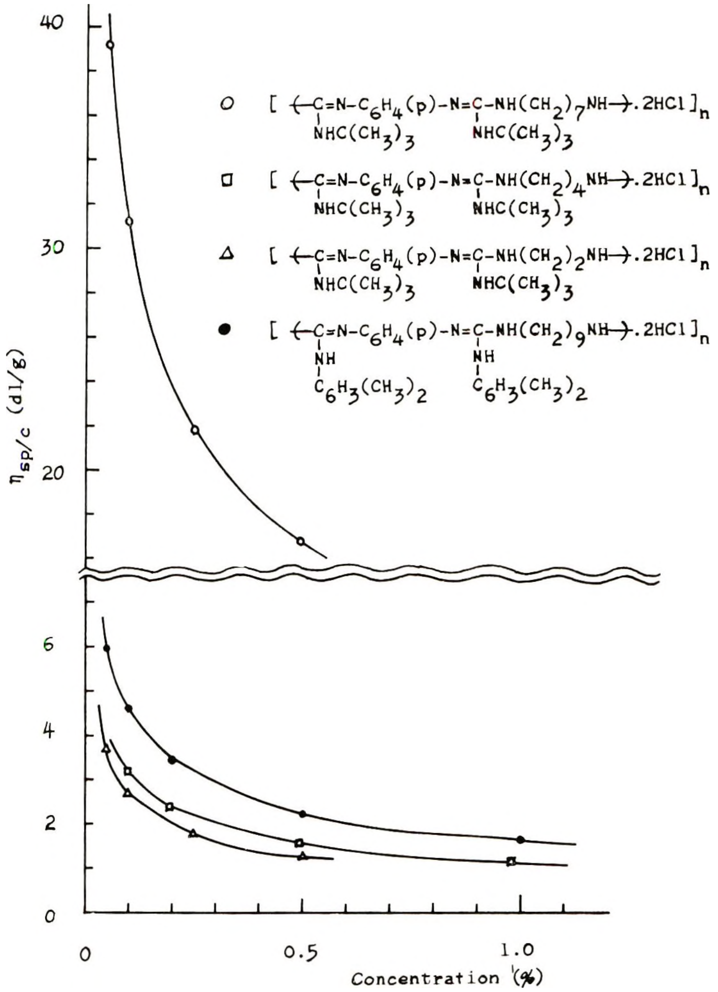


Fig. 4. Reduced viscosity plots of polyguanidine hydrochlorides (30°C, in distilled water).

Thermogravimetric analysis (Fig. 3) shows an initial weight loss in nitrogen around 170°C. *tert*-Butylamine was recovered in about 40% yield by the thermal decomposition of the adduct of VI-1 and benzylamine. The bath temperature ranged from 190°C to 250°C. In view of these results, one might conclude that VII was unstable above 170°C. This decomposition seems to result in the development of crosslinks of the polymer formed in refluxing xylene or anisole as mentioned before.

VII was highly resistant to hydrolytic degradation by strong acid or alkali. On refluxing with 20% aqueous sodium hydroxide for 7 hr VII did not show any cleavage of the main chains. In some cases, VII was recovered unchanged and in others, VII yielded in insoluble polymers on such treatment. The results are summarized in Table IV. The infrared spectra

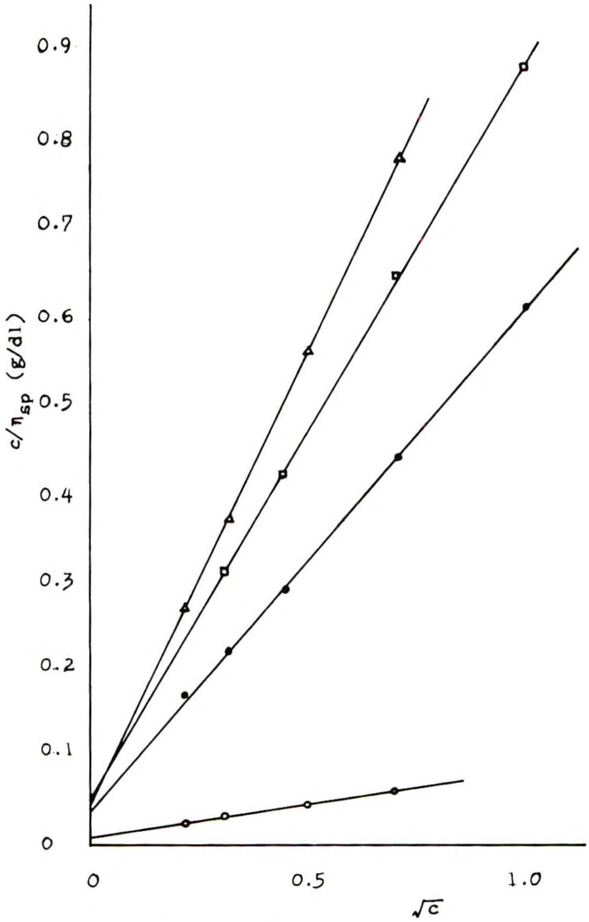


Fig. 5. Reciprocal reduced viscosity plots of polyguanidine hydrochlorides by the Fuoss equation. Code as in Fig. 4.

of compounds of type VII recovered were identical with those before the alkaline treatment. The viscosity was increased by the alkaline treatment in the case of VII-9 and VII-10. The reason for this increase is not clear at present.

VII was not hydrolyzed with refluxing concentrated hydrochloric acid, but formed the hydrochlorides of VII (VII·2HCl). The results are shown in Table V. Transparent films were cast from the solution of VII·2HCl in water or dimethylformamide. The solution viscosity plots form typical curves of polyelectrolytes as shown in Figures 4 and 5.

EXPERIMENTAL

Monomers

Biscarbodiimides (VI). *p*-Phenylenebis(*tert*-butylcarbodiimide) (VI-1), *m*-phenylenebis(*tert*-butylcarbodiimide) (VI-2), and *p*-phenylenebis(2,6-

xylylcarbodiimide) (VI-3) were prepared by the treatment of the corresponding thiourea with sodium hypochlorite, as previously reported.[7] VI-1 and VI-2 were distilled twice in a nitrogen stream, and VI-3 was recrystallized three times from ether.

Diamines. These were distilled twice in a nitrogen stream.

Solvents

Toluene, xylene, and anisole were distilled over sodium and stored also over sodium wire.

Polymers

Polyaddition Reaction of VI with Diamines. All the polyaddition reactions were carried out by the same procedure and the results are given in Tables I–III. A typical preparation was as follows.

A solution containing 1.35 g (5 mmole) of VI-1, 0.79 g (5 mmole) of nonamethylenediamine, and 10 ml of dry toluene was stirred and heated to reflux under nitrogen. The reaction mixture became viscous gradually. After 7 hr, the reaction mixture was poured into a large amount of petroleum ether (bp 40–80°C) to precipitate the polymer formed. The fibrous polymer was collected by filtration and dried at 70°C under high vacuum. The yield was 1.57 g (74%), and the intrinsic viscosity measured in dimethylformamide at 30°C was 0.84. The polymer was soluble in various solvents such as benzene, toluene, anisole, chloroform, dimethylformamide, *N*-methylpyrrolidone, and *m*-cresol.

ANAL. Calcd for $(C_{25}H_{44}N_6)_n$: C, 70.05%; H, 10.35%; N, 19.61%. Found: C, 69.93%; H, 10.03%; N, 19.05%.

Alkaline Treatment of VII. VII was refluxed with 20% aqueous sodium hydroxide, and the results are given in Table IV. A typical procedure was as follows.

VII-6 (0.50 g) was steeped in 20% aqueous sodium hydroxide. The mixture was refluxed for 7 hr and cooled. The insoluble product was taken out, washed thoroughly with water, and dried under vacuum. It was dissolved in chloroform and poured into petroleum ether (bp 40–80°C) to precipitate the polymer. The yield was 83%, and the inherent viscosity of the polymer recovered was 0.21. The infrared spectra of the recovered polymers were identical with those of the original polymers.

Acid Treatment of VII. VII was refluxed with concentrated hydrochloric acid, and the results are given in Table V. A typical procedure was as follows.

VII-4 (0.52 g) was steeped in concentrated hydrochloric acid (20 ml). The mixture was refluxed for 7 hr, then poured into acetone to precipitate the product, collected by filtration, and dried under vacuum. It was then dissolved in distilled water, and the solution was poured into acetone to precipitate the polymer again. The polymer was collected by filtration and dried under vacuum at 70°C to give the hydrochloride of VII-4 in

69% yield. It decomposed at about 220°C and discolored without melting. The intrinsic viscosity in water at 30°C was 20.

ANAL. Calcd for $(C_{20}H_{36}N_6Cl_2)_n$: Cl, 16.44%. Found: Cl, 15.92%.

Model Reaction

Thermal Decomposition of the Adduct of VI-1 and Benzylamine. When 14.5 g (0.03 mole) of the adduct was heated in a distilling apparatus, 1.7 g of a liquid was obtained as a distillate. The bath temperature ranged from 190°C to 250°C. The liquid reacted with phenyl isothiocyanate to form phenyl *tert*-butylthiourea. The formation of phenyl *tert*-butylthiourea confirmed that the liquid was *tert*-butylamine. The thiourea melted at 117°C (lit.[9] 118–119°C). The infrared spectrum was identical with that of an authentic sample. The yield of *tert*-butylamine was 40%.

References

1. Y. Iwakura, R. Tsuzuki, and K. Noguchi, *Makromol. Chem.*, **98**, 21 (1966).
2. E. Schmidt and F. Moosmüller, *Liebigs Ann. Chem.*, **597**, 235 (1955).
3. H. G. Khorana, *Chem. Revs.*, **53**, 145 (1953).
4. D. J. Lyman and N. Sadri, *Makromol. Chem.*, **67**, 1 (1963).
5. T. W. Campbell and J. J. Monagle, *J. Amer. Chem. Soc.*, **84**, 1493 (1962);
6. T. W. Campbell and K. C. Smeltz, *J. Org. Chem.*, **28**, 2069 (1963).
7. Y. Iwakura and K. Noguchi, *Bull. Chem. Soc. Japan*, **40**, 2383 (1967).
8. Y. Iwakura and K. Noguchi, *J. Polym. Sci.*, **B5**, 821 (1967).
9. B. W. Howk, E. L. Little, S. L. Scott, and G. M. Whitman, *J. Amer. Chem. Soc.*, **76**, 1899 (1954).

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Thermal Decomposition Products of Polyisobutylene

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Synopsis

Polyisobutylene was decomposed at 325, 345, and 365°C under vacuum, and the volatile products were trapped by using liquid nitrogen. The products, C_1–C_{24} hydrocarbons, were analyzed by gas chromatography. The formation of the main products is discussed on the basis of a free-radical mechanism. Intramolecular radical transfer can account for the production of most fragments including dimers, trimers, tetramers, and so on, of isobutylene.

A knowledge of decomposition products is necessary in understanding the mechanism of thermal decomposition of polymers. Published information on the decomposition products of polyisobutylene is very scarce. Straus and Madorsky[1] used mass spectrometry for the analysis of decomposition products of this polymer: the major products having up to six carbons were analyzed, but isomers were not separated. van Schooten and Evenhuis[2] used gas chromatography. They simplified the analysis by hydrogenating all the olefins to paraffins, and then presented data on the combined amounts.

The purpose of this investigation was to obtain more complete information on the volatile thermal decomposition products of polyisobutylene in order to elucidate the mechanism of decomposition of this polymer.

EXPERIMENTAL

Material

A commercial grade of polyisobutylene having a viscosity-average molecular weight of 90000 was purified by dissolving it in benzene, precipitating it with acetone, and then washing it with methanol. The residual methanol was removed by drying under vacuum. These operations were carried out in the dark in a nitrogen atmosphere in order to prevent oxidation.

Thermal Decomposition

The apparatus for the thermal decomposition of polyisobutylene was similar to that used by Madorsky and Straus.[3] A sample weighing 0.5 g

TABLE I
Gas Chromatographic Conditions

Condition	Type of column	Stationary phase	Carrier gas	Detector	Temperature
1	Packed, 6 ft, $^1/_8$ in. od	60–80 mesh silica gel deactivated with 4% silicone oil DC 200	Helium, 20 psi	Flame ionization	Programmed: 10°C/min from 60 to 200°C
2	Support coated open tubular 100 ft, 0.02 in. id	Squalane	Helium, 5 psi	"	Isothermal: −17, 0, 50, 100, and 150°C Programmed: 6°C/min from 60 to 150°C
3	Open tubular 150 ft, 0.02 in. id	Apiezon L	Helium, 20 psi	"	Isothermal: 100 and 180°C Programmed: 10°C/min from 60 to 250°C

was placed in a small Pyrex tube connected to a liquid nitrogen trap and a vacuum pump. After the system was flushed with helium and evacuated to 1×10^{-3} mm Hg, the vacuum line to the pump was closed, and an electric furnace provided with wheels was moved quickly along steel tracks to position the sample in the hot zone. The sample was decomposed for 20 min at 325, 345, or 365°C.

Most of the volatile decomposition products were collected in a liquid nitrogen trap; some condensed inside the cooler parts of the pyrolysis tube and the tube leading to the trap. By removing the liquid nitrogen, the fraction volatile at room temperature was transferred from the trap into a gas-sampling bottle of known volume. The condensates in the tubes and trap were washed with a predetermined amount of benzene, which was known from preliminary experiments to be a minor component of the decomposition products. The benzene extract and the fraction volatile at room temperature were analyzed separately; then combined amounts of each product were obtained.

Analysis

The chromatographic conditions used to analyze the decomposition products are presented in Table I. The identification of peaks was carried out as described below.

Lower Hydrocarbons from C_1 to C_5. Gas–solid chromatography (condition 1) and gas–liquid chromatography (condition 2) were used; retentions of the peaks were compared with those of known compounds.

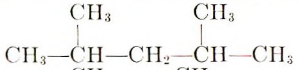
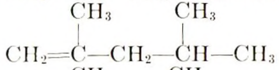
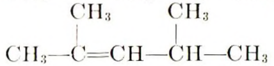
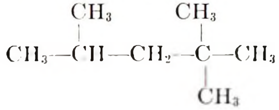
Hydrocarbons from C_4 to C_{24}. Gas–liquid chromatography (conditions 2 and 3) was used along with the following: (*a*) subtraction technique to remove unsaturated hydrocarbons from a mixture of products to facilitate identification of some of the peaks[4]; (*b*) comparison of retention indices with those of known compounds with the use of *n*-alkanes as standards; (*c*) hydrogenation of alkenes followed by identification of resulting alkanes; and (*d*) the linear relationship between boiling point and retention index.

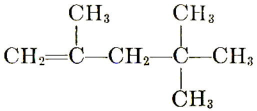
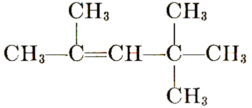
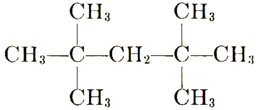
RESULTS AND DISCUSSION

Analysis of Products

Data obtained from chromatograms of decomposition products of polyisobutylene pyrolyzed at 365°C are presented in Figure 1. The relative areas of peaks found at different retention indices for both pyrolysis products and hydrogenated pyrolysis products, are shown along with the names of compounds that were identified. Six peaks that had retention indices between 100 and 600 were identified without difficulty. Seven of the eleven peaks with indices between 600 and 800 were also identified, but with more effort. For example, the identification of peaks P_{11} and P_{12}, of Figure 1 was carried out as follows. The subtraction technique showed

TABLE II
Identification of Peaks having Retention Indices between 600 and 800 with Squalane

Peak	Retention index obtained[a]	Saturated (S) or unsaturated (U)	Assigned formula	Retention index of assigned compound[b]	Boiling point of assigned compound, °C[c]	Location of peak after hydrogenation same as
a	630.3	S	 $\mathrm{CH_3{-}\overset{CH_3}{\overset{\vert}{C}}H{-}CH_2{-}\overset{CH_3}{\overset{\vert}{C}}H{-}CH_3}$	630	80.5	a
b	638.5	U	 $\mathrm{CH_2{=}\overset{CH_3}{\overset{\vert}{C}}{-}CH_2{-}\overset{CH_3}{\overset{\vert}{C}}H{-}CH_3}$	637.5	81.6	a
c	640.7	U	 $\mathrm{CH_3{-}\overset{CH_3}{\overset{\vert}{C}}{=}CH{-}\overset{CH_3}{\overset{\vert}{C}}H{-}CH_3}$	641	83.3	a
d	687.6	U	—	—	—	?
e	690.9	S	 $\mathrm{CH_3{-}\overset{CH_3}{\overset{\vert}{C}}H{-}CH_2{-}\overset{CH_3}{\overset{\vert}{\underset{\underset{CH_3}{\vert}}{C}}}{-}CH_3}$	690	99.2	e

	705.5	U	 $CH_2{=}C(CH_3){-}CH_2{-}C(CH_3)_2{-}CH_3$	704	101.4	e
g	716.3	U	 $CH_3{-}C(CH_3){=}CH{-}C(CH_3)_2{-}CH_3$	715	104.9	e
h	755.1	U	—	—	—	—[d]
i	762.8	U	—	—	—	—[d]
j	773.6	S	 $CH_3{-}C(CH_3)_2{-}CH_2{-}C(CH_3)_2{-}CH_3$	—	122.3	j
k	794.2	U	—	—	—	—[d]

---

[a] Liquid phase; squalane, 50°C; *b* = 0.415.

[b] Literature values.[6]

[c] Data of Ferris.[5]

[d] Two peaks were obtained by hydrogenation; retention indices were 729 and 749. The former is due to 2,5-dimethylhexane.

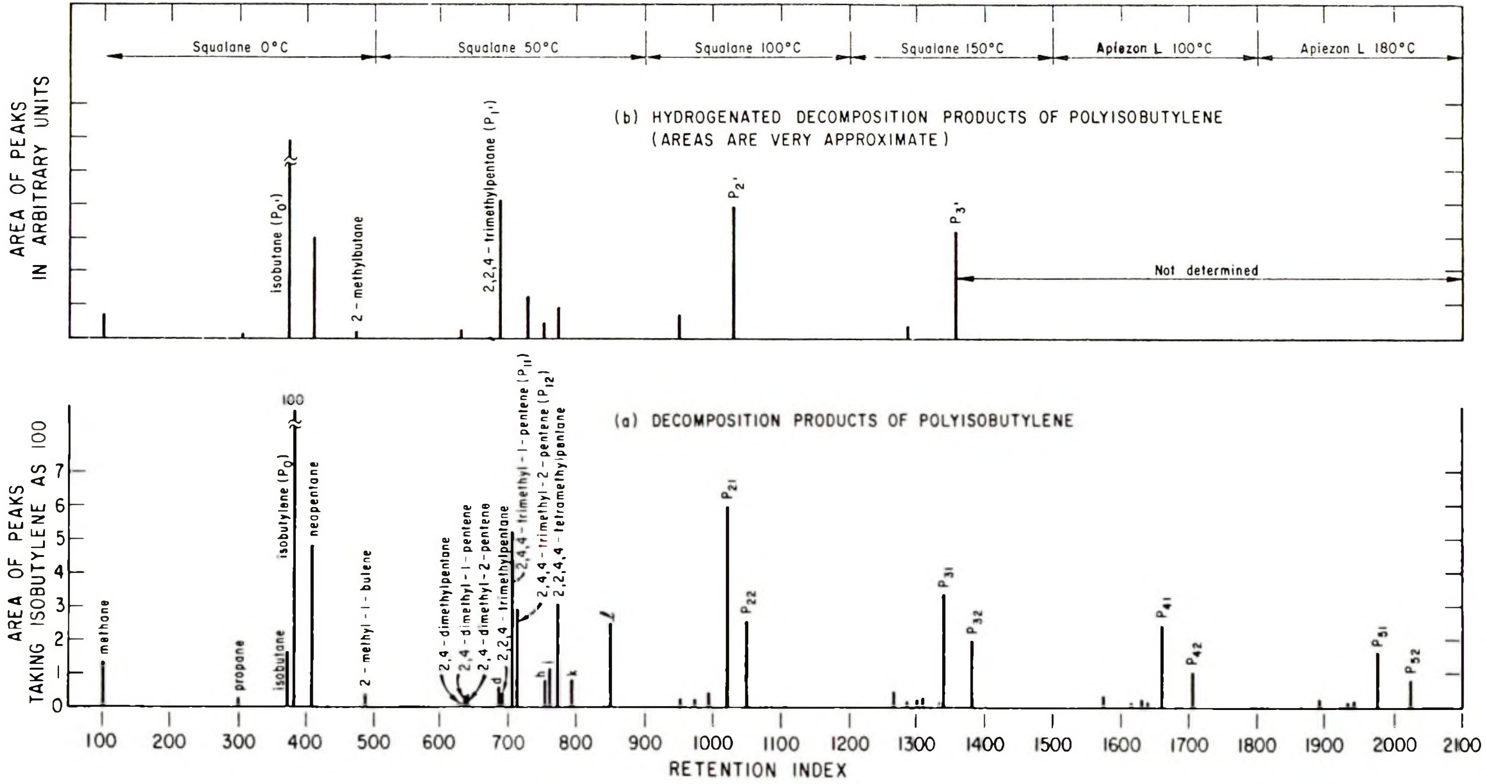


Fig. 1. Area of peaks vs. retention index.

that these two peaks were caused by unsaturated hydrocarbons. Hydrogenation of these products followed by analysis showed that they combined to form a single peak P_1', indicating that they have the same carbon skeleton. Boiling point data of alkanes, cyclanes, and aromatics[5] were examined to find compounds that have an estimated retention index close to that of P_1'. Two such compounds were 1,1-dimethylcyclopentane and 2,2,4-trimethylpentane. The former could have been formed by hydrogenation of three different cycloalkenes, none of which had an estimated retention index similar to those of P_{11} or P_{12}. The latter has two unsaturated forms, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. Their estimated retention indices agreed with those of P_{11} and P_{12}. In addition, the retention index of a pure sample of 2,2,4-trimethylpentane agreed with that of P_1'. Similar methods were used to identify other peaks with retention indices between 600 and 800. These results are presented in Table II.

In Figure 1 a pattern consisting of groups of peaks is noted. Peaks P_0, P_{11}, P_{21}, P_{31}, P_{41}, and P_{51} are uniformly spaced; peaks P_0, P_{12}, P_{22}, P_{32}, P_{42}, and P_{52} are also uniformly spaced, suggesting that they form two homologous series. The hydrogenated peaks P_0', P_1', P_2', and P_3' form another series. Peaks P_{n1} and P_{n2} (where $n = 1, 2, \ldots$) resulted from unsaturated compounds and had the same carbon skeleton as P_n'. Peak P_0 was identified as isobutylene and P_{11} and P_{12} as 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene (dimers of isobutylene), respectively. The above knowledge and consideration of the mechanism of decomposition suggest that P_{21} and P_{22} are the trimers 2,4,4,6,6-pentamethyl-1-heptene and -2-heptene, P_{31} and P_{32} are the tetramers, and so on. Unfortunately, data on retention indices and boiling points of these compounds were not available for positive identification of trimers, tetramers and pentamers. The retention indices and estimated boiling points of prominent peaks are given in Table III, along with boiling points of branched alkenes having the same number of carbon atoms as the trimers, tetramers, and pentamers. The similarity of boiling points is considered to be supporting evidence for the identification of these peaks. The boiling point of peak P_2' (which was considered to be due to 2,2,4,4,6-pentamethylheptane) obtained from boiling point-retention index relation was 184°C. As the boiling point of this compound could not be found in the literature, it was computed by using an empirical method to determine the physical properties of hydrocarbons.[7] These properties are determined from the next lower paraffins from which they can be derived by substitution of a methyl group for a hydrogen atom. The boiling point of this compound, derived from that of 2,2,4,4-tetramethyl heptane, was 184.3°C.

The three largest hydrogenated pyrolysis products were isobutane, 2,2,4-trimethylpentane, and 2,2,4,4,6-pentamethylheptane. This finding agrees with experimental results that have been reported earlier.[2]

The main volatile decomposition products of polyisobutylene obtained at the three different pyrolysis temperatures are presented in Table IV.

TABLE III
Retention Indices and Boiling Points of Oligomers of Isobutylene

	Retention index	Chromatographic data	Estimated boiling point, °C	Similar compound	Boiling point, °C
Monomer; isobutylene (2-methylpropene)	387	Squalane, 0°C	−6.90[a]		
Dimer; 2,4,4-trimethyl-1-pentene	703.7	Squalane, 50°C	101.44[a]		
Dimer; 2,4,4-trimethyl-2-pentene	715.2	" "	104.91[a]		
Trimer; 2,4,4,6,6-pentamethyl-1-heptene	1023	Squalane, 100°C	182	Triisobutylene (mixed trimers)	179–181[b]
Trimer; 2,4,4,6,6-pentamethyl-2-heptene	1051	" "	188	2,2,3,5,5-Pentamethyl-3-heptene	178
Tetramer; 2,4,4,6,6,8,8-heptamethyl-1-nonene	1340	Squalane, 150°C	245	2,7-Dimethyl-3,6-diisopropyl-4-octene	247
Tetramer; 2,4,4,6,6,8,8-heptamethyl-2-nonene	1378	" "	252		
Pentamer; 2,4,4,6,6,8,8,10,10-nonamethyl-1-undecene	1660	Apiezon L, 100°C	299	2,2,4,7,10,12,12-Heptamethyl-6-tridecene	290
Pentamer; 2,4,4,6,6,8,8,10,10-nonamethyl-2-undecene	1707	" "	306		
Hexamer; 2,4,4,6,6,8,8,10,10,12,12-undecamethyl-1-tridecene	1975	Apiezon L, 180°C	342		
Hexamer; 2,4,4,6,6,8,8,10,10,12,12-undecamethyl-2-tridecene	2022	" "	348		

[a] Literature value.[4]

[b] Literature value.[8]

TABLE IV

Thermal Decomposition Products of Polyisobutylene on Pyrolysis at Various Temperatures T

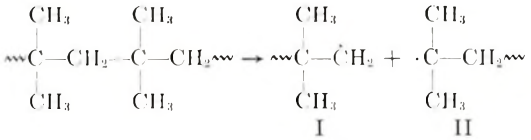
	$T = 325°C$		$T = 345°C$		$T = 365°C$	
	Polymer, wt-%	Volatiles, mole-%[a]	Polymer, wt-%	Volatiles, mole-%[a]	Polymer, wt-%	Volatiles, mole-%[a]
Methane	0.104	13.6	0.22	5.9	0.47	3.9
Propane	0.006	0.29	0.0019	0.19	0.078	0.24
Isobutane	0.044	1.59	0.18	1.37	0.58	1.35
Isobutylene	1.72	64.3	10.2	78.9	33.9	81.6
Neopentane	0.36	10.3	0.79	4.7	1.64	3.1
2-Methyl-1-butene	0.006	0.19	0.043	0.27	0.136	0.26
2,4-Dimethylpentane	0.0003	0.006	0.004	0.017	0.030	0.040
2,4-Dimethyl-1-pentene	0.0010	0.021	0.018	0.077	0.113	0.16
2,4-Dimethyl-2-pentene	0.0010	0.021	0.018	0.077	0.128	0.18
Peak d	0.0011	0.023	0.025	0.11	0.195	0.27
2,2,4-Trimethylpentane	0.0011	0.021	0.018	0.069	0.117	0.14
2,4,4-Trimethyl-1-pentene	0.086	1.61	0.49	1.91	1.77	2.13
2,4,4-Trimethyl-2-pentene	0.063	1.12	0.31	1.18	1.01	1.21
Peak h	0.006	0.12	0.062	0.24	0.27	0.33
Peak i	0.008	0.15	0.078	0.30	0.41	0.49
2,2,4,4-Tetramethylpentane	0.071	1.17	0.39	1.31	1.07	1.12
Peak k	0.011	0.18	0.082	0.28	0.29	0.31
Peak l	0.012	0.20	0.13	0.45	0.84	0.89
2,4,4,6,6-Pentamethyl-1-heptene	0.26	3.20	0.75	1.94	2.06	1.65
2,4,4,6,6-Pentamethyl-2-heptene	0.10	1.23	0.27	0.69	0.77	0.61
Total volatiles analyzed	2.8		14.1		45.9	
(100 − Residue), wt-%	4.9		15.7		46.8	

[a] Molecular weights of unidentified compounds were estimated from their retention indices.

Mechanism of Thermal Decomposition

In a previous paper, the formation of volatile thermal decomposition products of polyethylene was discussed on the basis of a free-radical mechanism.[4] The formation of the decomposition products of polyisobutylene will be examined on the same basis. A possible reaction scheme is given below.

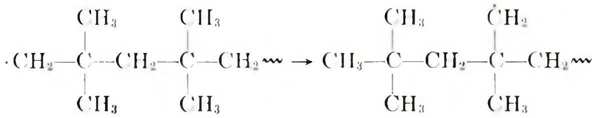
Initiation. Random scission of polymer chain should produce two different types of macroradicals, one of which is primary (I), and the other, tertiary (II).



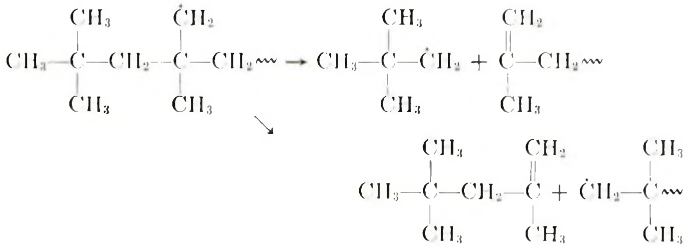
$$\sim\mathrm{\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2}\sim \;\rightarrow\; \underset{\mathrm{I}}{\sim\mathrm{\underset{CH_3}{\overset{CH_3}{C}}-\dot{C}H_2}} + \underset{\mathrm{II}}{\mathrm{\cdot\underset{CH_3}{\overset{CH_3}{C}}-CH_2}\sim} \qquad (1)$$

Propagation. Both types of radicals produced by initiation could produce the monomer, isobutylene.

Intramolecular Radical Transfer, Followed by Decomposition. The propagation reactions must compete with intra- and intermolecular radical transfer reactions. A radical produced by initiation or decomposition can be transferred to another carbon in the same chain, which then decomposes to form an alkane radical and an alkene, e.g.,



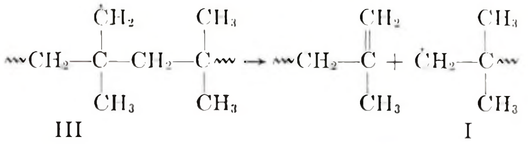
$$\mathrm{\cdot CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2}\sim \;\rightarrow\; \mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{\dot{C}H_2}{C}}-CH_2}\sim \qquad (2)$$



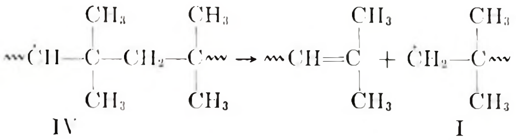
$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{\dot{C}H_2}{C}}-CH_2}\sim \;\rightarrow\; \mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\dot{C}H_2 + \underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}}-CH_2}\sim \qquad (3)$$

$$\searrow\; \mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}} + \dot{C}H_2-\underset{CH_3}{\overset{CH_3}{C}}}\sim \qquad (4)$$

Intermolecular Radical Transfer, Followed by Decomposition. When intermolecular radical transfer takes place, two types of macroradicals,



$$\underset{\mathrm{III}}{\sim\mathrm{CH_2-\underset{CH_3}{\overset{\dot{C}H_2}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}}\sim} \;\rightarrow\; \sim\mathrm{CH_2-\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}}} + \underset{\mathrm{I}}{\mathrm{\dot{C}H_2-\underset{CH_3}{\overset{CH_3}{C}}}\sim} \qquad (5)$$



$$\underset{\mathrm{IV}}{\sim\mathrm{\dot{C}H-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}}\sim} \;\rightarrow\; \sim\mathrm{CH{=}\underset{CH_3}{\overset{CH_3}{C}}} + \underset{\mathrm{I}}{\mathrm{\dot{C}H_2-\underset{CH_3}{\overset{CH_3}{C}}}\sim} \qquad (6)$$

TABLE V

Volatile Decomposition Products of Polyisobutylene Resulting from Intramolecular Radical Transfer at 365°C

Transfer to:	Primary or secondary	Alkene	Alkane
		Starting from primary radical (I)	
3rd carbon	Secondary	2,4,4-Trimethyl-2-pentene (P_{12}), 1.21	Methane, (3.9)[a]
Methyl group attached to 4th carbon	Primary	2,4,4-Trimethyl-1-pentene (P_{11}), 2.13	2,2-Dimethylpropane (neopentane), (3.1)
5th carbon	Secondary	2,4,4,6,6-Pentamethyl-2-heptene, (P_{22}) 0.61	2,2-Dimethylpropane
Methyl group attached to 6th carbon	Primary	2,4,4,6,6-Pentamethyl-1-heptene, (P_{21}) 1.65	2,2,4,4-Tetramethylpentane, (1.12)
7th carbon	Secondary	2,4,4,6,6,8,8-Heptamethyl-2-nonene, (P_{32}) 0.43	2,2,4,4-Tetramethylpentane
		Starting from tertiary radical (II)	
2nd carbon	Secondary	2,4-Dimethyl-2-pentene, 0.18	Methane
Methyl group attached to 3rd carbon	Primary	2,4-Dimethyl-1-pentene, 0.16	2-Methylpropane (isobutane), (1.35)
4th carbon	Secondary	2,4,4,6-Tetramethyl-2-heptene, not determined	2-Methylpropane
Methyl group attached to 5th carbon	Primary	2,4,4,6-Tetramethyl-1-heptene, not determined	2,2,4-Trimethylpentane, (0.14)
6th carbon	Secondary	2,4,4,6,6,8-Hexamethyl-2-nonene, not determined	2,2,4-Trimethylpentane

[a] Methane could be produced following radical transfer to any primary or secondary carbon of polyisobutylene.

III and IV, are produced. Decomposition of these radicals results in the formation of primary macroradicals (I).

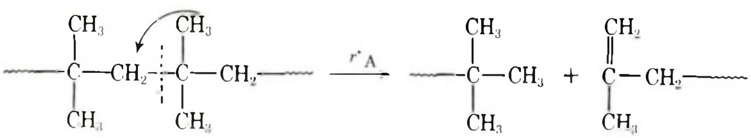
Termination. The termination reactions could proceed by the combination of two radicals or by disproportionation, which results in the formation of an alkane and an alkene. As both reactions involve two radicals, the amount of products formed by termination in the present experiments is considered small.

The formation of the main volatile decomposition products of polyisobutylene can be explained by two competing reactions; propagation, and intramolecular radical transfer and subsequent decomposition. The proportion of monomer in the volatile products depends on the relative rates of these two reactions. A proportionately larger amount of monomer was produced in the decomposition of polyisobutylene as compared with that of polyethylene,[4] indicating that intramolecular radical transfer is relatively more difficult in the decomposition of polyisobutylene. Three out of four hydrogen atoms of this polymer are primary, which require higher activation energy for transfer than secondary hydrogen; and also secondary hydrogen is sterically obstructed by the two methyl groups attached to every other carbon atom of the polymer chain. Thus, propagation reaction predominates over transfer reactions resulting in the production of large amounts of monomer.

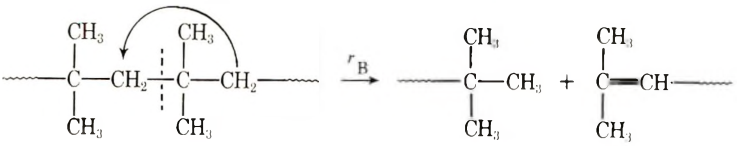
The formation of different volatile decomposition products of polyisobutylene as a result of intramolecular radical transfer is presented in Table V. This mechanism can account for the formation of all the main volatile products except for the monomer isobutylene. The amounts of each substance produced at a pyrolysis temperature of 365°C are shown in terms of mole per cent of volatiles. The amounts of products that could be accounted for by more than one reaction are given in parentheses. The volatile products formed as a result of intramolecular transfer from primary radicals (I) were much greater than from tertiary radicals (II). This difference is probably due to the greater availability of primary radicals (I) as a result of intermolecular transfer by reactions (5) and (6), and the relative instability of primary radicals (I) which causes them to favor transfer.

The presence of a pattern consisting of pairs of peaks, P_{n1} and P_n (where $n = 1, 2, \ldots$), in Figure 1 can also be explained by intramolecular radical transfer followed by decomposition. P_{n1} is 1-alkene produced by transfer to primary carbon and P_{n2} is 2-alkene produced by transfer to secondary carbon. The mole ratio of P_{n1} to $P_{(n+1)2}$ depends on the relative ease of radical transfer to primary carbon and to secondary carbon. The experimental findings for this ratio were in the range of 2.9–3.8. The theoretical value of this ratio was found to be 1.24, by: (*a*) assuming the difference in activation energy between transfer to primary carbon and secondary carbon to be 2000 cal., (*b*) considering the number of transferable hydrogen atoms to be 6 for primary carbon and 2 for secondary carbon, and (*c*) taking into account the number of possible β-scissions following transfer, i.e., 3 for primary and 6 for secondary carbon. The discrepancy between the theoretical value and the experimental values indicates that less radical transfer to secondary carbon took place than suggested by this theory. This was probably due to the steric hindrance caused by the presence of methyl groups.

The experimental data were also examined on the basis of another mechanism that has been considered by a number of investigators. Repeated random splitting of a polymer chain resulting in simultaneous saturation and unsaturation is shown in eqs. (7) and (8).



$$\sim\!-\overset{CH_3}{\underset{CH_3}{C}}-CH_2\,\vdots\,\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\!\sim\ \xrightarrow{r_A}\ \sim\!-\overset{CH_3}{\underset{CH_3}{C}}-CH_3+\overset{CH_2}{\underset{CH_3}{\overset{\|}{C}}}-CH_2-\!\sim \qquad (7)$$



$$\sim\!-\overset{CH_3}{\underset{CH_3}{C}}-CH_2\,\vdots\,\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\!\sim\ \xrightarrow{r_B}\ \sim\!-\overset{CH_3}{\underset{CH_3}{C}}-CH_3+\overset{CH_3}{\underset{CH_3}{C}}{=}CH-\!\sim \qquad (8)$$

Reaction (7) should produce a saturated end and a 1-alkene end, and reaction (8) should produce a saturated end and a 2-alkene end. Combination of these four ends with four other ends produced in the same way should result in six different types of compounds: one alkane, two alkenes (1-alkene and 2-alkene), and three alkadienes. If the reaction rate $r_A = r_B$, equal amounts of 1-alkene, 2-alkene, and alkane should be produced. If $r_A > r_B$, the three largest products in decreasing order should be 1-alkene, alkane, 2-alkene; if $r_A < r_B$, the order should be 2-alkene, alkane, 1-alkene. The experimental findings were in conflict with the above mechanism; large amounts of 1-alkene and 2-alkene were produced, but only small amounts of alkane.

CONCLUSIONS

The formation of thermal decomposition products of polyisobutylene has been explained on the basis of a free radical mechanism in which intramolecular radical transfer is assumed to play an important role. The amount of products formed following radical transfer to primary carbon atoms was much greater than that from transfer to secondary carbon atoms. This difference suggests that transfer to secondary carbon is obstructed by the methyl groups attached to every other carbon atom of the polymer chain. For the same reason, propagation reaction predominates over intramolecular radical transfer reactions, yielding a large amount of monomer. The formation of dimers, trimers, tetramers, and so on found in the decomposition products can be explained by intramolecular radical transfer reactions.

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References

1. S. Straus and S. L. Madorsky, *J. Res. Nat. Bur. Stand.*, **66**, 401 (1962).
2. J. van Schooten and J. K. Evenhuis, *Polymer*, **6**, 343 (1965).
3. S. L. Madorsky and S. Straus, *J. Res. Nat. Bur. Stand.*, **63A**, 261 (1959).
4. Y. Tsuchiya and K. Sumi, *J. Polym. Sci.*, in press.
5. S. W. Ferris, *Handbook of Hydrocarbons*, Academic Press, New York (1959).
6. D. A. Tourres, *J. Gas Chromatog.*, **5**, 35 (1967).
7. A. W. Francis, *Ind. Eng. Chem.*, **35**, 442 (1943).
8. *Handbook of Chemistry and Physics*, Chem. Rubber Publishing Co., Cleveland, 48th ed., 1967, p. C-508.

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Diffusion-Controlled Rate Constant of Termination Reaction in Radical Polymerization

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Synopsis

Smoluchowski's theory has been modified and the improved theory was applied to diffusion-controlled polymerization. This application proved that the rate-controlling process is not transrational diffusion but the segmental diffusion. The segmental diffusion-controlled rate constant was derived by the collision theory. This rate constant explains the experimental fact that the diffusion-controlled rate constant of bimolecular termination in radical polymerization of alkyl methacrylate is inversely proportional to solution viscosity and independent of the molecular weight of the polymeric free radical.

INTRODUCTION

The diffusion-controlled rate constant of bimolecular termination in the radical polymerization of alkyl methacrylate[1–3] is inversely proportional to solution viscosity and independent of the molecular weight of the polymeric free radical. Such phenomena have been experimentally analyzed on the basis of transrational diffusion between radicals controlling termination and on the basis that segmental diffusion of the radical chain end in the coiled polymeric free radical is the rate-controlling process in termination. It was inferred that the latter is more important than the former in the case of the higher alkyl methacrylates.[3] On the other hand, most theoretical treatments have discussed the diffusion-controlled termination in view of transrational diffusion.[4–7] Recently, according to Smoluchowski's theory treating the kinetics of colloidal reaction,[8] Schultz and Fischer[9] derived a diffusion-controlled rate constant of termination which can explain the experimental facts. But the polymeric free radical increases in degree of polymerization (according to radius $\bar{r}$ when it is spherical) with elapsed time after propagation has begun, even if two polymeric free radicals do not react with each other. On the other hand, a colloidal particle does not increase its radius, unless two colloidal particles react with each other.[8] Accordingly, the behavior of a polymeric free radical and a colloidal particle can not be treated in the same way; thus it is impossible that the original Smoluchowski theory should apply to diffusion-controlled polymerization. It thus appears that the diffusion-controlled rate constant derived by Schultz and Fischer[9] is meaningless.

In this paper, Smoluchowski's theory was modified so that it can completely treat diffusion-controlled polymerization. On assuming that the rate-controlling process of termination is transrational diffusion, the transrational diffusion-controlled rate constant was derived by this modified theory and its value found equal to about 10^9 l/mole-sec. This result proves that the rate-controlling process of termination is not transrational diffusion, but segmental diffusion, because the observed rate constant of termination is equal to about 10^7 l/mole-sec. This fact and my discussion[6] make clear that the discussions from the standpoint of transrational diffusion are meaningless. The segmental diffusion-controlled rate constant was derived by the collision theory and the proper parts of the treatment of Schultz and Fischer.[9]

Transrational Diffusion-Controlled Rate Constant

Two spherical polymeric free radicals with the radius R are taken into consideration. One of them exists in the center of a spherical coordinate and the other is diffusing.[8] Suppose that a transrational diffusion process is occurring at a stationary spherical coordinate. Let r be the distance from the center of sphere and t the elapsed time after the increase of radius R has begun from radius R_0; then in such a spherical coordinate Fick's laws give eq. (1).

$$\frac{1}{D}\frac{\partial C}{\partial t} = \text{div grad } C = \frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r} \tag{1}$$

where D is the diffusion constant of polymeric free radical of degree of polymerization n and C the concentration of such a polymer. Generally, D is given by eq. (2) in the most simple case.[5]

$$D = D_1 n^{-1/2} = D_1(n_0 + k_p M t)^{-1/2} \tag{2}$$

where D_1 is the diffusion constant of polymeric free radical of $n = 1$, n_0 the degree of polymerization of polymeric free radical at $t = 0$ ($R = R_0$), k_p the rate constant of propagation, and M monomer concentration. When the degree of polymerization of the polymeric free radical increases from 1 to n_0 for t_0, n_0 is given by $n_0 = k_p M t_0$. Then eq. (2) becomes eq. (3):

$$D = D_1[k_p M(t_0 + t)]^{-1/2} \tag{3}$$

On putting $x = \int_0^t D\,dt$ and solving eq. (1) under the following initial and boundary conditions:[8]

$$\begin{array}{ll} C = {}^*C & t = 0\ (x = 0),\ r \geq R \\ C = 0 & t = 0\ (x = 0),\ r < R \\ C = 0 & t > 0\ (x > 0),\ r \leq R \\ C = {}^*C & r \rightarrow \infty \end{array}$$

yields eq. (4), where $*C$ is initial concentration:

$$(\partial C/\partial r)_{r=R} = *C[(1/R + (\pi x)^{-1/2}] \tag{4}$$

According to the Gaussian segment distribution function,[10] R is given by

$$R = ln^{1/2} = l[k_p M(t_0 + t)]^{1/2} \tag{5}$$

where l is segmental length. When $R \ll (\pi x)^{1/2}$, eqs (3), (4), and (5) give eq. (6).

$$4\pi DR^2(\partial C/\partial r)_{r=R} = 4\pi DR*C = 4\pi lD_1*C \tag{6}$$

According to Smoluchowski's treatment, eq. (6) gives the transrational diffusion-controlled rate constant k_t:

$$k_t = 4\pi lD_1N_L \times 10^{-3} \text{ l/mole-sec} \tag{7}$$

where N_L is Avogadro's number.

When $l = 5 \times 10^{-8}$ cm and $D_1 = 10^{-5}$ cm^2/sec are introduced into eq. (7), k_t is equal to 3.8×10^9 l/mole-sec. This value is comparable to the rate constant of combination reaction between small radicals.[5] This fact gives the previous conclusion that the rate-determining step of termination is not transrational diffusion but segmental diffusion.

Segmental Diffusion-Controlled Rate Constant

According to Lewis' collision theory, the reaction velocity v_t of combination reaction between the spherical polymeric free radicals[9] with radius $\bar{r}$ is given by

$$v_t = Z_t p_t \text{ numbers/l-sec} \tag{8}$$

where Z_t is the collision frequency and p_t the probability of a combination reaction occurring per one collision. When u_t is the diffusive velocity of spherical polymeric free radical, Z_t is given by

$$Z_t = 8^{1/2}u_t(\bar{r}N_LN_n)^2 \tag{9}$$

where N_n is the concentration of a polymeric free radical of polymerization degree n. According to the treatment of Schultz and Fischer,[9] the time for one polymeric free radical being in collision with another is given by $2\bar{k}\bar{r}/u_t$ where $\bar{k}$ is the ratio of the maximum overlap length to $2\bar{r}$. Then p_t is given by

$$p_t = \frac{3 \times 10^3\bar{k}^3(3 - \bar{k})k_R}{\pi u_t\bar{r}^2N_L} \tag{10}$$

where k_R is the rate constant of combination reaction between radical chain ends in overlap volume. Equations (8)–(10) give eq. (11).

$$v_t/N_L = -dN_n/dt = 72^{1/2}\bar{k}^3(3 - \bar{k})\,N_Lk_RN_n^2 \tag{11}$$

Accordingly, k_S is given by

$$k_S = 72^{1/2}\bar{k}^3(3 - \bar{k})k_R \text{ l/mole-sec} \tag{12}$$

Again, let's derive k_R from collision theory. When u_S is the diffusive velocity of the radical chain end, the above treatment gives eq. (13):

$$-\frac{dS}{dt} = 2^{-1/2}\,\pi l^2 u_S N_L p_S \times 10^{-3} S^2 \tag{13}$$

where S is the concentration of radical chain end in spherical polymeric free radical and p_S is the probability of a combination reaction between radical chain ends occurring per collision in the overlap volume. Apparently, $p_S = 1$ when this combination reaction is diffusion-controlled, and $p_S = \exp\{-E/RT\}$ where E is the activation energy, R is the gas constant, and T, the absolute temperature, when it is not. Then k_R is given by

$$k_R = 2^{-1/2}\,\pi l^2 u_S N_L p_S \times 10^{-3}\ \text{l/mole-sec} \tag{14}$$

At last, the segmental diffusion-controlled rate constant of termination ($p_S = 1$) is given by

$$k_S = 6\pi l^2 u_S N_L \bar{k}^3\,(3 - k) \times 10^{-3}\ \text{l/mole-sec} \tag{15}$$

DISCUSSION

When Einstein's equation

$$D_S = h u_S/6$$

where D_S is the segmental diffusion constant and h the diffusive distance per collision, is introduced into eq. (15), we obtain

$$k_S = 36\pi N_L l^2\,\bar{k}^3\,(3 - \bar{k})(D_S/h) \times 10^{-3}\ \text{l/mole-sec} \tag{16}$$

When h, $\bar{k}$, and ηD_S (where η is solution viscosity) are constant, respectively, k_S is apparently in inverse proportion to solution viscosity and independent of the molecular weight of polymeric free radical.

Identifying h as the average distance between centers of mass of solvent molecules,[7] we consider the equation

$$h = 10^{-20} V_m/6 \tag{17}$$

where V_m is the molar volume of solvent. According to eq. (17), h is equal to 5.5×10^{-8} cm at $V_m = 10$ mole/l. On introducing $h = 5.5 \times 10^{-8}$ cm and $l = 5 \times 10^{-8}$ cm into eq. (16), k_S is given by

$$k_S = 3.0 \times 10^{15}\,\bar{k}^3\,(3 - \bar{k})\,D_S\ \text{l/mole-sec} \tag{18}$$

When $k_S = 10^7$ l/mole-sec and $D_S = 10^{-5}$ cm²/sec, eq. (18) gives $\bar{k} = 0.07$.

A relationship of segmental length, the ratio of the maximum overlap length to the diameter of polymeric free radical, and the segmental diffusion constant will be examined to obtain a relationship between segmental length and the diffusion-controlled rate constant of termination.[3]

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References

1. S. W. Benson and A. M. North, *J. Amer. Chem. Soc.*, **8,** 1339 (1959).
2. A. M. North and G. A. Reed, *Trans. Faraday Soc.*, **57,** 859 (1961).
3. A. M. North and G. A. Reed, *J. Polym. Sci. A*, **1,** 1311 (1963).
4. G. V. Schultz, *Z. Physik. Chem.* (Frankfurt), **8,** 284 (1956).
5. P. E. M. Allen and C. R. Patrick, *Makromol. Chem.*, **47,** 154 (1961).
6. K. Ito, *J. Polym. Sci.*, in press.
7. P. E. M. Allen and C. R. Patrick, *Makromol. Chem.*, **72,** 106 (1964).
8. M. V. Smoluchowski, *Z. Physik. Chem.*, **92,** 129 (1917).
9. G. V. Schultz and J. P. Fischer, *Makromol. Chem.*, **107,** 253 (1967).
10. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N.Y., 1953.
11. W. C. M. Lewis, *J. Chem. Soc.*, **1918,** 471.

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Preparation of Polyhydrouracils and Polyiminoimidazolidinones

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Synopsis

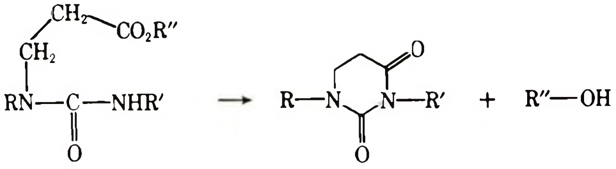
Polyhydrouracils and polyiminoimidazolidinones were prepared by ring formation along the chain of appropriately substituted polyureas. Cyclization of 2-carbomethoxyethyl-substituted polyureas in a polyphosphoric acid medium gave the polyhydrouracils. The polyurea precursors were prepared from *N*,*N*′-bis(2-carbomethoxyethyl)-1,6-hexanediamine and *N*,*N*′-di(2-carbomethoxyethyl)-1,4-cyclohexanebis(methylamine) with methylenebis(4-phenyl isocyanate), 2,4-toluene diisocyanate, and 3,3′-dimethoxy-4,4′-biphenylene diisocyanate. These polyureas were soluble in *m*-cresol, dimethylformamide, and chloroform, had inherent viscosities of up to 0.8, and could be cast into tough films. The polyhydrouracils had similar physical properties and could also be cast into films. The polyhydrouracils melted at temperatures 100–150°C higher than their polyurea precursors. Polyiminoimidazolidinones were prepared by cyclization of α-cyanoalkyl-substituted polyureas in the presence of *n*-butylamine. The intermediate polyureas, which were not isolated, were prepared from methylenebis(4-phenyl isocyanate) with *N*,*N*′-bis(1-cyanocyclohexyl)-1,6-hexanediamine, *N*,*N*′-bis(1-cyanocyclohexyl)-*m*-xylylenediamine and *N*,*N*′-bis(1-cyanocyclopentyl-1,6-hexanediamme. The polyiminoimidazolidinones were soluble in *m*-cresol, dimethylformamide, and chloroform and had low inherent viscosities of 0.14–0.28. Thermogravimetric analyses showed that the polyhydrouracils underwent rapid decomposition at 400°C, whereas an analogous unsubstituted polyurea decomposed at 300°C. On the other hand, the polyiminoimidazolidinones showed no greater thermal stability than the unsubstituted polyurea.

INTRODUCTION

The purpose of the present investigation was to examine the feasibility of preparing five- and six-membered heterocyclic rings, specifically polyiminoimidazolidinones and polyhydrouracils, by cyclization reactions along the backbone of appropriately substituted polyureas.

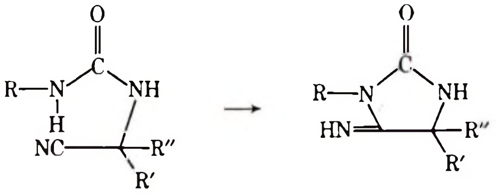
Although no reports of polyhydrouracil preparation are known to the authors, the preparation of polyhydantoins was recently described by Imai,[1] who used methods similar to those employed in the current work. Polyhydantoins and their analogs, which are closely related to the polyiminoimidazolidinones, have also been prepared by the polycycloaddition reaction of diisocyanates with bis(carbamoyl cyanides),[2] by polycondensation of bishydantoins with formaldehyde,[3] and by thermally induced cyclization of substituted polyureas.[4]

The formation of hydrouracils was shown by Schlögl[5] and Morsch[6] to proceed in good yield by the acid catalyzed cyclization of ureidopropionates [eq. (1)].



(1)

Iminoimidazolidinone formation was found by McKay, et al.[7] to occur when α-cyanoalkylureas with bulky substituents at the α-carbon were warmed in alcohol [eq. (2)].



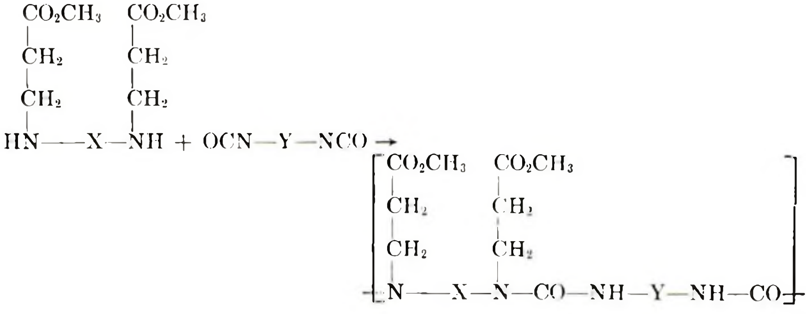
(2)

The present paper deals with the application of these reactions to similarly substituted polyureas to give the corresponding heterocyclic polymers.

RESULTS AND DISCUSSION

2-Carbomethoxyethyl-Substituted Polyureas

Polycondensation of *N*,*N*′-bis(2-carbomethoxyethyl) diamines with methylenebis(4-phenyl isocyanate), 2,4-toluene diisocyanate, and 3,3′-dimethoxy-4,4′-biphenylene diisocyanate gave new polyureas with pendant carbomethoxyethyl groups [eq. (3)].



$$\mathrm{HN(CH_2CH_2CO_2CH_3)\!-\!X\!-\!NH(CH_2CH_2CO_2CH_3) + OCN\!-\!Y\!-\!NCO \rightarrow \left[\!-N(CH_2CH_2CO_2CH_3)\!-\!X\!-\!N(CH_2CH_2CO_2CH_3)\!-\!CO\!-\!NH\!-\!Y\!-\!NH\!-\!CO\!-\right]_n} \quad (3)$$

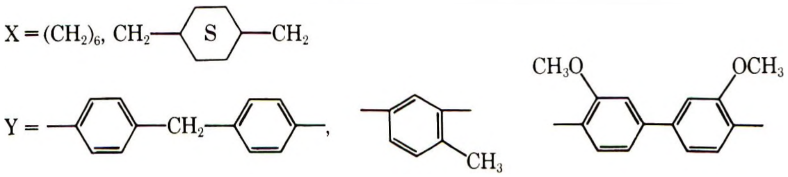
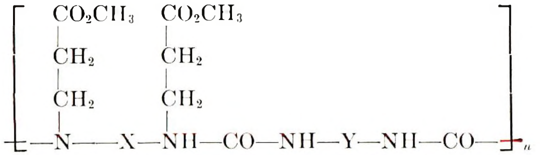
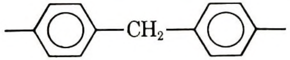
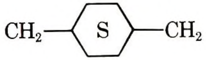
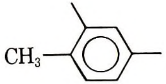
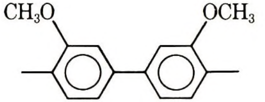


TABLE I

Polyureas from Diisocyanates and *N*,*N*′-Bis(2-carbomethoxyethyl) Diamines[a]



$$\left[-\overset{\substack{CO_2CH_3\\|\\CH_2\\|\\CH_2\\|}}{N}-X-\overset{\substack{CO_2CH_3\\|\\CH_2\\|\\CH_2\\|}}{NH}-CO-NH-Y-NH-CO-\right]_n$$

Polymer number	X	Y	Reactants, mmole[b]	Solvent[c]	Time, hr.	Yield, %	η_{inh}[d]	PMT, °C[e]
1	$(CH_2)_6$		12.6	20/20; 20/20	9	89	0.50	135
1	"	"	8.8	" "	23	85	0.47	125
1	"	"	3.2	6/6; 6/6	19	82	0.81	135
1	"	"	"	" "	5	82	0.64	135
2		"	"	" "	8.5	72	0.48	175
2	"	"	10.0	5/20; 5/20	18	92	0.6	175
2	"	"	2.1	5/5; 5/5	8	70	0.31	160
3[f]	$(CH_2)_6$		5.2	6/0; 6/12	6	75	0.16	85
4	"		3.0	10; 12	1.5	86	0.51	130

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[a] Reactions carried out at room temperature.

[b] Equimolar concentrations of each reactant.

[c] Ratio of chloroform/tetramethylene sulfone, (ml) for diamine and diisocyanate solutions. Polymer 4 prepared in dimethylformamide.

[d] In *m*-cresol at 25°C; polymer concentration of 0.5 g/100 ml.

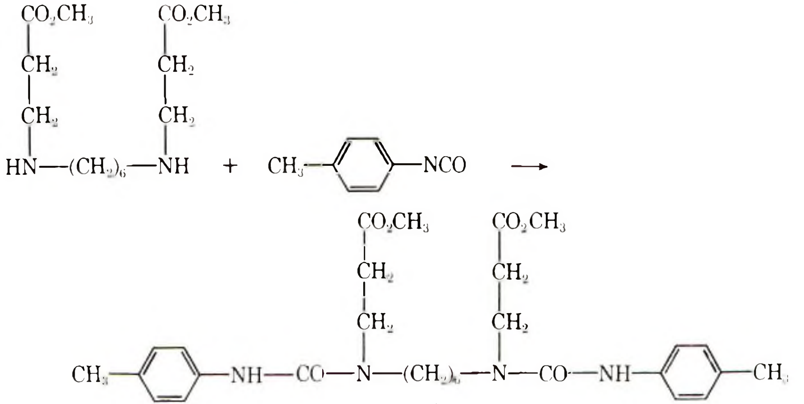
[e] Polymer melt temperature.

[f] Reaction run at 56°C.

The polymerizations were carried out in a mixed solvent system of chloroform and tetramethylene sulfone which had been shown by Kwolek to be an effective medium for the preparation of other polyureas.[8] Polyurea formation involving 3,3′-dimethoxy-4,4′-biphenylene diisocyanate was conducted in dimethylformamide due to the poor solubility of this diisocyanate in the chloroform–tetramethylene sulfone solution. Table I summarizes the most satisfactory polymerization conditions, and the yields, inherent viscosities, and melting points of the polyureas. The polymers were soluble in *m*-cresol, dimethylformamide and chloroform. Tough transparent films were obtained by solution casting of polymers 1, 2, and 4.

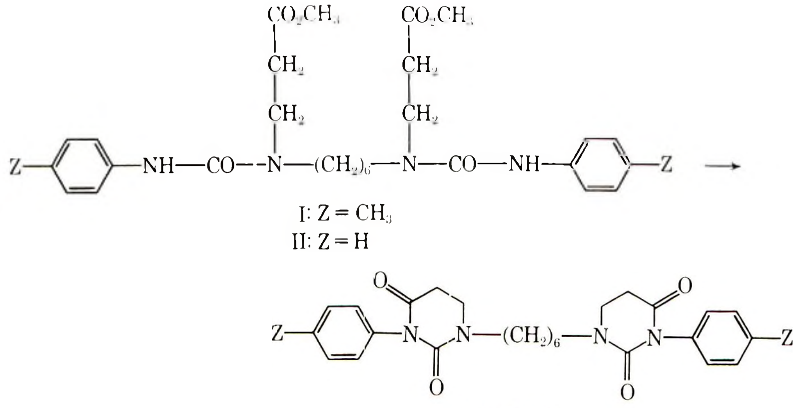
Cyclization of Model Bisureas

Model compounds were synthesized to facilitate identification of the polymers and to investigate hydrouracil formation. *N*,*N*′-Bis(2-carbomethoxyethyl)-1,6-hexanediamine reacted with p-tolyl isocyanate to give the model bisurea I [eq. (4)].



(4)

I



I: Z = CH_3
II: Z = H

(5)

III: Z = CH_3
IV: Z = H

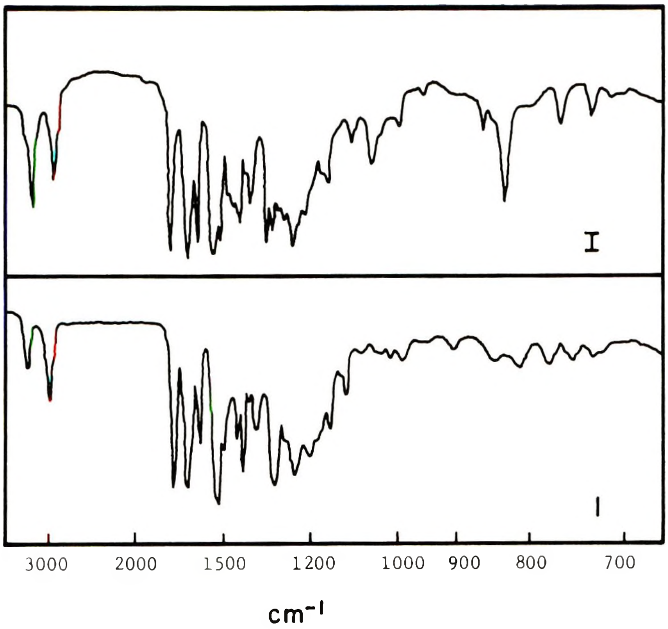


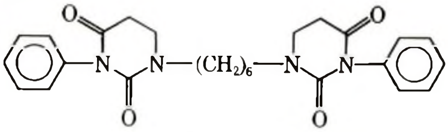
Fig. 1. Infrared spectra of compound I and polymer 1.

Infrared spectra of the bisurea I and of the polyurea 1 are shown in Figure 1. They are essentially identical with characteristic bands at 3400 cm^{-1} (NH), 1740 cm^{-1} (ester C=O), 1650 cm^{-1} (urea C=O), and 1510 cm^{-1} (amide II).

Cyclization of the bisurea I to form the bishydrouracil III, as shown in eq. (5), was accomplished by heating in polyphosphoric acid.

TABLE II

Preparation of Bishydrouracil IV from Bisurea II



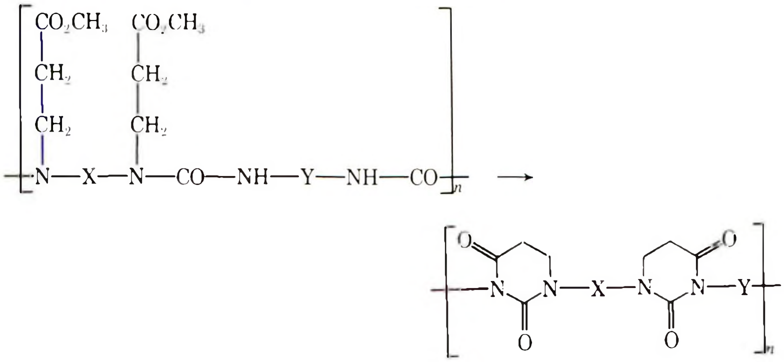
Solvent	Vol. solvent, ml/g bisurea	Time, hr	Temp, °C	Yield, %
DMF[a]	10	7.5	153	0
HCl (conc.)	10	2	98	68
PPA	12.5	1.3	115	88
TFP	27	1.5	112	46
TMS/CHCl$_3$	10/10	2.5	96	0

[a] DMF, dimethylformamide; PPA, polyphosphoric acid; TFP, tetrafluoropropanol plus 3 ml concentrated H$_2$SO$_4$; TMS/CHCl$_3$, tetramethylene sulfone/chloroform saturated with hydrogen chloride.

A study of various conditions for cyclization, carried out on the analogous urea II, showed that polyphosphoric acid was the most effective agent (Table II). Formation of the hydrouracil IV did occur in other acidic media, but the yield was poorer. An attempt to achieve cyclization thermally by heating in refluxing dimethylformamide gave no hydrouracil.

Polyhydrouracils

Treatment of the polyureas described previously with polyphosphoric acid gave the corresponding polyhydrouracils [eq. (6)].



(6)

Table III summarizes the conditions employed for several of the cyclization reactions in addition to physical and analytical data for the products. Numerous experiments indicated that cyclization in polyphosphoric acid was most readily accomplished by heating for 1.5 hr at 115–120°C.

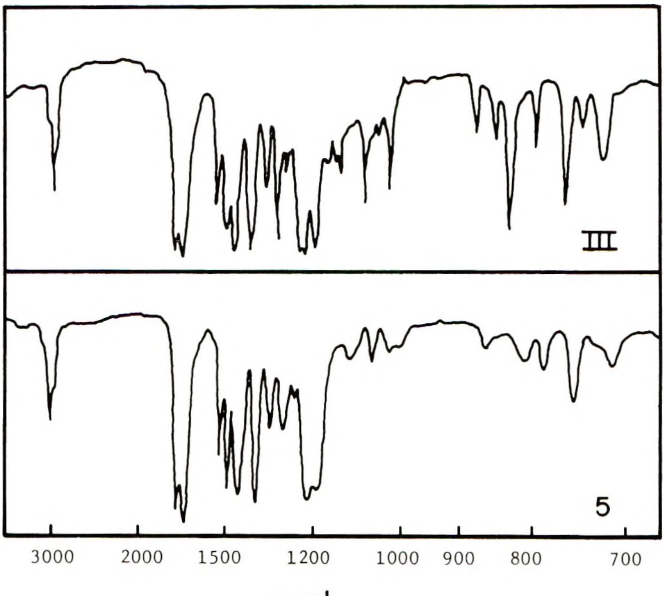
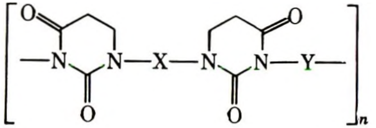
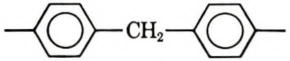
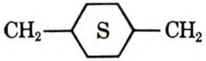
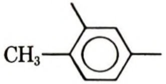
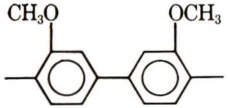


Fig. 2. Infrared spectra of compound III and polymer 5.

TABLE III

Polyhydrouracils



Polymer number	X	Y	Time, hr	Temp, °C	Yield, %	PMT, °C	η_{inh}[a]	Analyses (calcd) and found		
								C, %	H, %	N, %
5	$(CH_2)_6$		1.0	115	65	230	0.80	(68.34) 68.52	(6.37) 6.64	(11.81) 11.72
5	"	"	1.5	115	28[b]	230	0.64	68.09	6.58	11.97
5[c]	"	"	1.0	100	75	210	0.41	67.68	6.76	11.75
6		"	1.7	111	89	300	0.37	(69.58) 69.38	(6.44) 6.59	(11.19) 11.38
6	"	"	2.0	118	94	300	0.52	68.47	6.62	11.30
7	$(CH_2)_6$		1.5	117	70	208	0.18	(63.30) 61.43[d]	(6.58) 7.07	(14.06) 13.62
8	$(CH_2)_6$		1.7	120	70	280	0.52	(64.60) 64.43	(6.20) 6.42	(10.76) 10.77

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[a] In *m*-cresol at 25°C., polymer concentration of 0.5 g/100 ml.
[b] The low yield was due to loss of product during two reprecipitations from a 5% dimethylformamide solution of the polymer.
[c] Methanesulfonic acid as cyclization medium, polyphosphoric acid in all other cases.
[d] A residue of 1.4% was reported.

Data from the third preparation of polymer 5 show that methanesulfonic acid can also be used to effect cyclization.

The values for inherent viscosity of the polyhydrouracils were dependent upon the values of the starting polyureas; in no case was a significant increase or decrease observed. For example, cyclization of polyureas 2 ($\eta_{\text{inh}} = 0.31$), 3 ($\eta_{\text{inh}} = 0.16$), and 4 ($\eta_{\text{inh}} = 0.51$) gave polyhydrouracils 6 ($\eta_{\text{inh}} = 0.37$), 7 ($\eta_{\text{inh}} = 0.18$), and 8 ($\eta_{\text{inh}} = 0.52$), respectively.

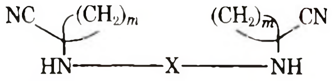
The infrared spectra and analytical data confirmed the formation of the hydrouracil units. Figure 2 shows the spectra of the bishydrouracil III and of the polyhydrouracil 5. The characteristic urea absorptions at 3 400 and 1 510–1 535 cm^{-1} had disappeared, the carbonyl absorption at 1 740 and 1 660 cm^{-1} had shifted to 1 724 and 1 680 cm^{-1}, and the fingerprint region of the spectrum of the polymer was similar to that of the model compound, showing that polyhydrouracil formation was complete.

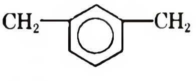
The NMR spectrum of polyhydrouracil 5 in $CDCl_3$ consisted of an aromatic multiplet centered at 2.82τ, methylene protons adjacent to the aromatic ring centered at 5.97τ, methylene protons adjacent to a nitrogen atom centered at 6.58τ, methylene protons adjacent to a carbonyl group centered at 7.22τ, and a complex grouping of normal aliphatic protons centered at 8.50τ in a ratio of 8:2:8:4:8. There was no trace of the methoxyl protons at 6.3τ which were present in the uncyclized precursor.

The polyhydrouracils, like their precursors, were soluble in chloroform, dimethylformamide, and *m*-cresol. The melting points of the cyclized polymers were 100–150°C higher than of their precursors in spite of the fact that the last remaining hydrogen bonding site had been removed. This suggests a much more rigid structure in the cyclized polymers. Flexible transparent films of polyhydrouracils 5, 6, and 8 could be cast from solution.

TABLE IV

N,N'-Bis(1-cyanocycloalkyl)diamines

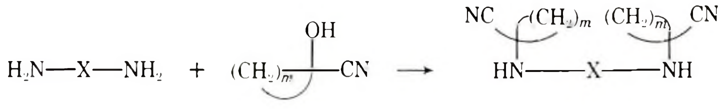


X	*m*	Yield, %	mp, °C	Analyses (calcd) and found		
				C, %	H, %	N, %
	5	66	119–121	(75.39) 75.77	(8.63) 8.49	(15.98) 15.98
$(CH_2)_6$	5	69	101–102[a]	(72.68) 72.55	(10.37) 10.47	(16.95) 17.28
"	4	67	76–78	(71.48) 71.44	(10.00) 10.02	(18.52) 18.43

[a] Lit.[9] mp 104–105°C.

Monomers for Polyiminoimidazolidinones

The *N*,*N′*-bis(1-cyanocycloalkyl)diamines used in the preparation of polyiminoimidazolidinones were prepared by the reaction of a diamine with the cyanohydrin of cyclopentanone or cyclohexanone [eq. (7)].



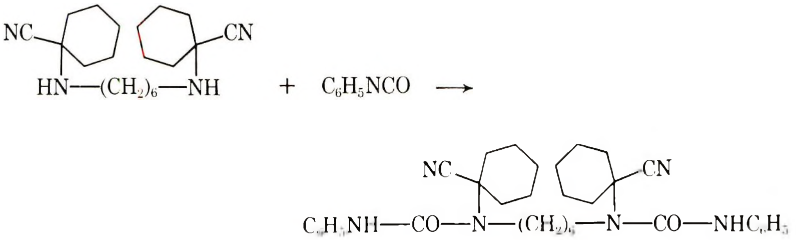
$m = 4, 5$

(7)

The yields, melting points, and analyses of the monomers are shown in Table IV.

Model Iminoimidazolidinones

N,*N′*-Bis(1-cyanocyclohexyl)-1,6-hexanediamine was added to phenyl isocyanate to give model compound V [eq. (8)].

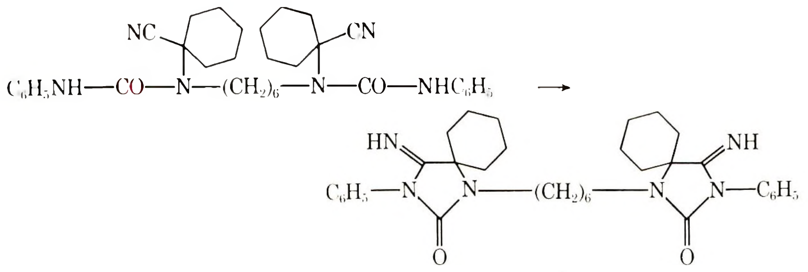


(8)

V

The infrared spectrum of compound V showed the expected bands at 2260 cm^{-1} (C≡N) and 1650 cm^{-1} (C=O).

When a suspension of V in methanol was allowed to stand for two days, the following transformation occurred to yield compound VI [eq. (9)].



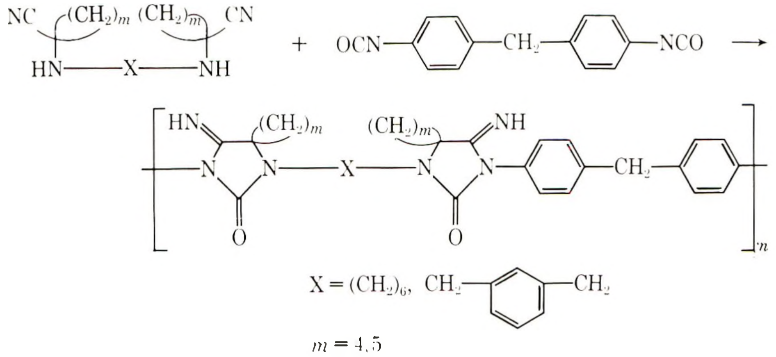
(9)

VI

Compound VI melted at 255–257°C whereas V melted at 116–118°C. The infrared spectrum of VI showed no nitrile band at 2260 cm^{-1}, but did have two strong carbonyl bands at 1665 and 1745 cm^{-1}, typical of the iminoimidazolidinone ring. A similar transformation occurred on addition of 0.05 ml of *n*-butylamine to a dimethylformamide-chloroform solution of 0.2 g. of V. Further proof of structure was obtained by acid hydrolysis of compound VI to the corresponding bishydantoin VII, of satisfactory analysis, whose infrared spectrum showed two carbonyl bands at 1 715 and 1 770 cm^{-1}.

Polyiminoimidazolidinones

Polyiminoimidazolidinones were prepared from the diamines listed in Table IV by polycondensation with methylenebis(4-phenyl isocyanate) as shown in eq. (10).


(10)

The reaction conditions and the polymer properties are listed in Table V. Cyclization of the intermediate α-cyanoalkyl substituted polyurea occurred on addition of n-butylamine to the polymer solution. This behavior was parallel to that observed in the case of the model compound V.

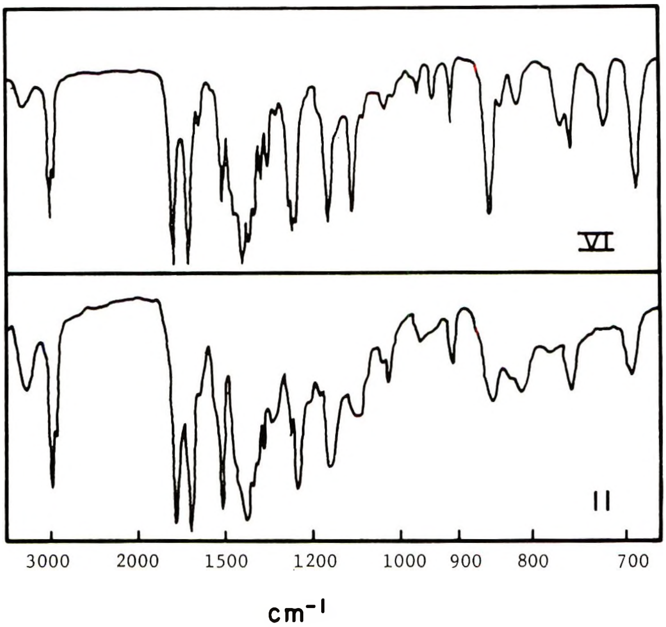
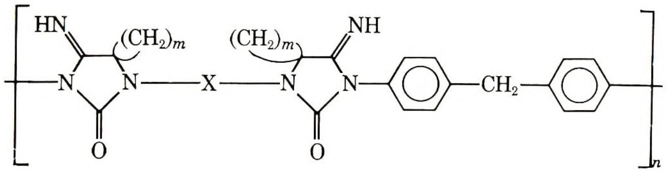


Fig. 3. Infrared spectra of compound VI and polymer II.

TABLE V

Polyiminoimidazolidinones



Polymer number	X	m	Monomer mmole	Solvent, ml[a,b]	Temp, °C	Time, hr	Yield, %	PMT, °C	η_{inh}[c]	$\bar{M}_n$[d]
9		5	5.0	0/20	25	20	85	215	0.18	2990
10	(CH$_2$)$_6$	4	6.0	15/30	50	6	68	184	0.28	3120
11	"	5	4.0	8/15	50	3	76	167	0.20	3200
11	"	"	"	15/30	50	4	78	165	0.15	—
11	"	"	"	18/15	0	22	52	163	0.19	—
11	"	"	"	18/15	25	3	79	175	0.25	—

[a] Volume ratio of dimethylformamide/chloroform.
[b] Reactions quenched with 1.5 ml of n-butylamine.
[c] In m-cresol at 25°C., polymer concentration of 0.5 g/100 ml.
[d] Determined by vapor pressure osmometry in CHCl$_3$.

The polymers were small, with molecular weights, determined by vapor pressure osmometry, in chloroform solution, of less than 3300. This was not surprising, however, in view of the highly hindered nature of the diamine monomer.

The polymers were white powders soluble in chloroform, *m*-cresol, and dimethylformamide. Polymer films could not be prepared due to the low molecular weights.

The infrared spectra of polymer 11 and model compound VI are shown in Figure 3. The characteristic bands are the absorptions in the carbonyl region at 1665 and 1745 cm^{-1}, the similarity of the fingerprint region between 1100–1450 cm^{-1} and the absence of a nitrile band at 2260 cm^{-1}.

Thermogravimetric Analyses

Thermal degradation studies of the polymers were made by measuring the weight loss in a nitrogen atmosphere at a programmed heating rate of

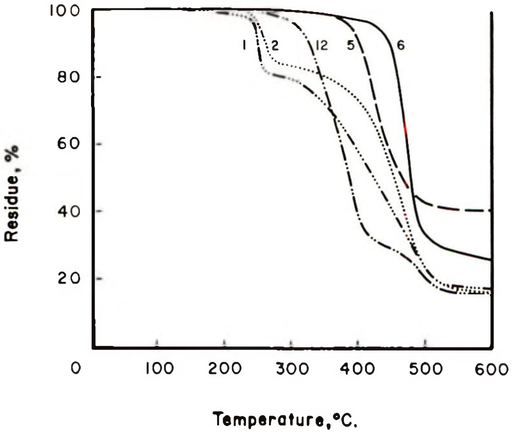
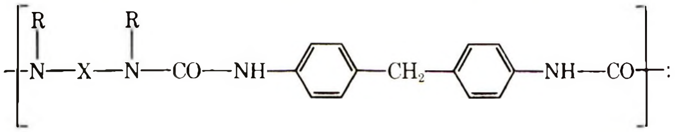
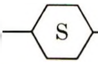
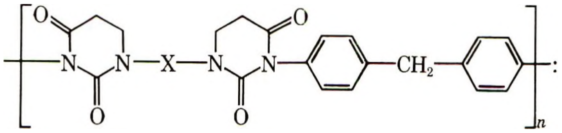
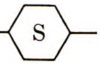


Fig. 4. Thermogravimetric analyses of polyureas and polyhydrouracils:



(–····)polymer 1, R = $CH_2CH_2CO_2CH_3$, X = $(CH_2)_6$; (···)polymer 2, R = $CH_2CH_2CO_2CH_3$, X = CH_2CH_2; (··–··)polymer 12, R = H, X = $(CH_2)_6$;



(– –)polymer 5, X = $(CH_2)_6$; (———)polymer 6, X = CH_2CH_2.

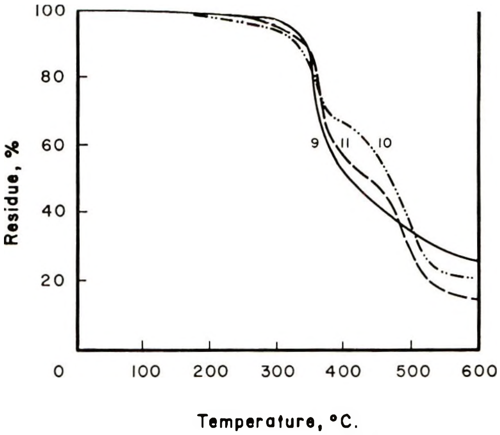
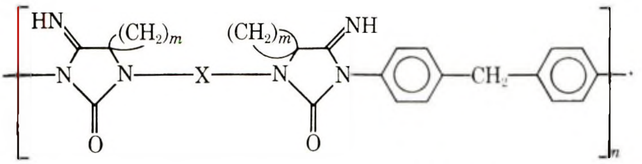
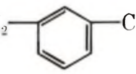


Fig. 5. Thermogravimetric analyses of polyiminoimidazolidinones,



(——)polymer 9, X = CH$_2$––CH$_2$,

$m = 5$; (– –)polymer 10, X = $(CH_2)_6$, $m = 4$; (-···)polymer 11, X = $(CH_2)_6$, $m = 5$.

20°C/min. Figure 4 shows the curves for polyureas 1 and 2, the corresponding polyhydrouracils 5 and 6, and an unsubstituted polyurea made from 1,6-hexanediamine and methylenebis(4-phenyl isocyanate) 12. The substituted polyureas 1 and 2 showed an initial weight loss of 15–18% at about 250°C which was due to loss of methanol and also methyl acrylate. The nature of the degradation products was shown by trapping the pyrolysis distillate and analyzing by gas chromatography. Removal of the pendant carbomethoxyethyl groups by cyclization to the corresponding polyhydrouracil eliminated this low temperature weight loss as shown by curves 5 and 6. The increased stability of the polyhydrouracils as compared to the analogous unsubstituted polyurea can be seen in curves 5 and 12. The tendency of ureas to decompose at higher temperatures into amines and isocyanates was apparently retarded by hydrouracil ring formation.

Thermal degradation curves of the polyiminoimidazolidinones are shown in Figure 5. Severe degradation began at about 300°C similar to the behavior of polyurea 12. The iminoimidazolidinone ring imparted no additional thermal stability to the polymers. Attempts to hydrolyze the imine groups to give a polyhydantoin, which would be expected to improve the thermal properties of the polymer in view of Imai's work, were not successful.

EXPERIMENTAL

Monomers and Model Compounds

***N*,*N'*-Bis(2-carbomethoxyethyl)-1,6-hexanediamine.** Acrylonitrile (37.7 g) was added to 41.4 g of 1,6-hexanediamine and the solution was stirred for 24 hr. The crude product was poured into 372 ml of 7 *N* hydrochloric acid and the mixture was heated at reflux for 12 hr. On cooling, 90 g of the β-amino acid hydrochloride precipitated out. Addition of acetone to the mother liquors yielded an additional 52 g of the amino acid hydrochloride and ammonium chloride. The salts were suspended in 330 ml of methanol and 37 ml of concentrated sulfuric acid. After heating at reflux for 33 hr, the solution was cooled and the solids filtered. An aqueous solution of the amino ester salts was neutralized with sodium hydroxide and extracted with ether. The ether layer was dried and concentrated. The residual solid was recrystallized from ether–petroleum ether to give 40 g (40%) of product, mp 31.5–33°C.

ANAL. Calcd for $C_{14}H_{28}N_2O_4$: C, 58.30%; H, 9.79%; N, 9.72%. Found: C, 58.21%; H, 9.71%; N, 9.84%.

***N*,*N'* - Bis(2 - carbomethoxyethyl) - 1,4 - cyclohexanebis(methylamine).** Acrylonitrile (31.8 g) was added to 42.7 g of 1,4-cyclohexanebis(methylamine). The resulting diadduct (44 g) was hydrolyzed with 200 ml of a 10% sodium hydroxide solution. After acidification with hydrochloric acid, 46 g of the β-amino acid hydrochloride precipitated. The amino acid salt (10 g) was esterified in a hydrogen chloride saturated solution of methanol (100 ml) containing 5% concentrated sulfuric acid. The amino ester hydrochloride was suspended in chloroform and made alkaline with ammonia. Precipitated ammonium chloride was removed by filtration and the chloroform was evaporated. The residual liquid was taken up in ether, dried over magnesium sulfate and the solvent removed. The product, which solidified on cooling, consisted of 4.5 g (51%), mp 28–30°C.

ANAL. Calcd for $C_{16}H_{30}N_2O_4$: C, 61.12%; H, 9.62%; N, 8.91%. Found: C, 61.29%; H, 9.80%; N, 8.88%.

***N*,*N'*-Bis(2-carbomethoxyethyl)-*N*,*N'*-bis(*p*-tolylcarbamoyl)-1,6-hexanediamine (I).** A solution of 0.75 g of *N*,*N'*-bis(2-carbomethoxyethyl)-1,6-hexanediamine in 5 ml of benzene was added to a solution of 0.69 g of *p*-tolyl isocyanate in 5 ml of benzene. After stirring for 5 hr at room temperature, the solid was filtered and dried. Recrystallization from ethanol–water gave 1.3 g (90%) of product, mp 117.5–119°C.

ANAL. Calcd for $C_{30}H_{42}N_4O_6$: C, 64.96%; H, 7.63%; N, 10.10%. Found: C, 64.63%; H, 7.89%; N, 9.89%.

***N*,*N'*-Bis(2-carbomethoxyethyl) - *N*,*N'* - bis(phenylcarbamoyl) - 1,6 - hexanediamine (II).** Compound II was prepared from 2.5 g of phenyl isocyanate and 2.0 g of *N*,*N'*-bis(2-carbomethoxyethyl)-1,6-hexanediamine in dimethylsulfoxide. The solid which precipitated on pouring the solution into ether was recrystallized from aqueous acetone. Compound II, obtained in 70% yield, melted at 117.5–118.5°C.

ANAL. Calcd for $C_{28}H_{38}N_4O_6$: C, 63.86%; H, 7.27%; N, 10.64%. Found: C, 63.96%; H, 7.10%; N, 10.53%.

1,1′-Hexamethylenebis(3-*p*-tolylhydrouracil) (III). A solution of 0.5 g of I in 15 g of polyphosphoric acid was heated for 75 min at 100–115°C. The solution was poured into 25 ml of water and the solid filtered. Recrystallization from ethanol gave 0.32 g (73%) of product, mp 199–200°C.

ANAL. Calcd for $C_{28}H_{34}N_4O_4$: C, 68.55%; H, 6.99%; N, 11.42%. Found: C, 68.36%; H, 7.01%; N, 11.42%.

1,1′-Hexamethylenebis(3-phenylhydrouracil) (IV). A solution of 1.0 g of II in 15 g of polyphosphoric acid was heated for 75 min at 110–115°C. The solution was poured into 25 ml of water and the precipitated solid collected. The filtrate was extracted three times with methylene chloride. The solid and the methylene chloride extracts were combined, dried over magnesium sulfate, and evaporated. The product was 0.76 g (88%) of IV, mp 162–164°C.

ANAL. Calcd for $C_{26}H_{30}N_4O_4$: C, 67.51%; H, 6.54%; N, 12.11%. Found: C, 67.81%; H, 6.54%; N, 12.27%.

***N,N′*-Bis(1-cyanocyclohexyl)-1,6-hexanediamine.** Cyclohexanone cyanohydrin[10] (12.5 g) was added to 5.8 g of 1,6-hexanediamine and allowed to stand for 18 hr. The solid mass was recrystallized from benzene to give 11.4 g (69%) of product, mp 101–102°C (lit,[9] mp 104–105°C).

The other cyanocycloalkyl diamine monomers were prepared in a similar manner. The elemental analyses, melting points and yields of these compounds are shown in Table IV. Cyclopentanone cyanohydrin was prepared according to the method of Emmons and Freeman.[11]

***N,N′*-Bis(1-cyanocyclohexyl)-*N,N′*-bis(phenylcarbamoyl)-1,6-hexanediamine (V).** A solution of 0.71 g of phenyl isocyanate in 5 ml of benzene was added to 1.0 g of *N,N′*-bis(1-cyanocyclohexyl)1,6-hexanediamine in 10 ml of benzene. The solution was stirred for 18 hr and then poured into petroleum ether. The precipitated product weighed 1.58 g (92%), mp 116–118°C. When attempts were made to recrystallize the compound from ethanol for analysis, it was converted to compound VI.

1,1′-Hexamethylenebis(3-phenyl-4-imino-5,5-pentamethylene-2-imidazolidinone) (VI). A suspension of 0.6 g of V in 30 ml of methanol was stirred for 45 hr at room temperature. The solid, collected on a filter and dried, weighed 0.52 g (88%), mp 255–257°C.

ANAL. Calcd for $C_{34}H_{44}N_6O_2$: C, 71.80%; H, 7.80%; N, 14.78%. Found: C, 72.17%; H, 7.58%; N, 14.82%.

1,1′-Hexamethylenebis(3-phenyl-5,5-pentamethylenehydantoin) (VII). Compound VI (0.35 g) was heated for 90 min in 7 ml of 3*N* trifluoroacetic acid. The solid which separated on cooling was chromatographed on silicic acid. The hydantoin, which melted at 258–260°C was obtained in 78% yield.

Anal. Calcd for $C_{34}H_{42}N_4O_4$: C, 71.55%; H, 7.42%; N, 9.82%. Found: C, 71.44%; H, 7.60%; N, 9.66%.

Polymers

Polyureas. The polymers were prepared under the conditions outlined in Table I. A typical example is the following preparation of polyurea 1.

A solution of 0.910 g of *N*,*N*′-bis(2-carbomethoxyethyl)-1,6-hexanediamine dissolved in 6 ml of chloroform and 6 ml of tetramethylene sulfone was added over a period of 15 min to a solution of 0.800 g of methylenebis-(4-phenyl isocyanate) dissolved in 6 ml of chloroform and 6 ml of tetramethylene sulfone. After stirring for 5 hr at room temperature, a solution of 1 ml of *n*-butylamine dissolved in 3 ml of chloroform was added to quench any unreacted isocyanate groups. The solution was poured into benzene to precipitate the polymer. The polymer was dissolved in dimethylformamide and the solution poured into water to give 1.4 g (82%) of white fibrous material. The inherent viscosity in *m*-cresol was 0.64 (concentration of 0.5 g/100 ml at 25°C).

Anal. Calcd for polymer 1, $(C_{29}H_{38}N_4O_6)_n$: C, 64.67%; H, 7.11%; N, 10.40%. Found: C, 64.48%; H, 7.09%; N, 10.32%.

Calcd for polymer 2, $(C_{31}H_{40}N_4O_6)_n$: C, 65.94%; H, 714%; N, 9.92%. Found: C, 65.82%; H, 7.06; N, 9.68%.

Calcd for polymer 3, $(C_{23}H_{34}N_4O_6)_n$: C, 59.72%; H, 7.41%; N, 12.11%; Found: C, 59.72%; H, 7.67%; N, 12.22%.

Calcd for polymer 4 $(C_{30}H_{40}N_4O_8)_n$: C, 61.63%; H, 6.90%; N, 9.58%. Found: C, 61.46%; H, 7.01%; N, 9.49%.

Polyhydrouracils. The polymers were prepared under the conditions outlined in Table III. A typical example is the following preparation of polyhydrouracil 8.

A mixture of 0.8 g of polyurea 4 in 22 ml of polyphosphoric acid, prepared from 22.5 g of phosphorus pentoxide and 15 ml of 85% orthophosphoric acid, was heated at 120°C for 1.7 hr and then poured into 150 ml of water. The solid was washed repeatedly with water, dissolved in 10 ml of dimethylformamide, and the solution poured into 50 ml of water. The precipitate was again washed repeatedly with water and dried *in vacuo* at 90°C for 6 hr. The polymer, which weighed 0.5 g (70%), had an inherent viscosity of 0.51 in *m*-cresol (0.5 g/100 ml at 25°C).

A similar procedure was followed with methanesulfonic acid as the cyclization medium.

Polyiminoimidazolidinones. The polymers were prepared under the conditions outlined in Table V. A typical example is the following preparation of polyiminoimidazolidinone 11.

A solution of 1.30 g *N*,*N*′-bis(1-cyanocyclohexyl)-1,6-hexanediamine and 1.00 g methylenebis(4-phenyl isocyanate) in 15 ml of chloroform and 8 ml of dimethylformamide was heated for 3 hr at 50°C. *n*-Butylamine

(1.5 ml) was added, and the solution was stirred for 30 min. The chloroform was removed *in vacuo*, and the remaining solution was poured into water to precipitate the polymer. The polymer, which weighed 1.75 g (76%), had an inherent viscosity of 0.20 in *m*-cresol (0.5 g/100 ml at 25°C).

ANAL. Calcd for polymer 9, $(C_{37}H_{40}N_6O_2)_n$: C, 73.97%; H, 6.71%; N, 13.99%. Found: C, 73.84%; H, 7.08%; N, 13.52%.

Calcd for polymer 10, $(C_{33}H_{40}N_6O_2)_n$: C, 71.71%; H, 7.29%; N, 15.21%. Found: C, 71.58%; H, 7.41%; N, 15.09%.

Calcd for polymer 11, $(C_{35}H_{44}N_6O_2)_n$: C. 72.38%; H, 7.64%; N, 14.47%. Found: C, 72.25%; H, 7.78%; N, 14.33%.

Abstracted from the Ph.D. dissertation (1968) of Jon D. Hartzler, Armstrong Cork Company Research Fellow, 1964–1967.

References

1. Y. Imai, *J. Polym. Sci. A-1*, **5**, 2289 (1967).
2. A. Oku, M. Okano, and R. Oda, *Makromol. Chem.*, **78**, 186 (1964).
3. A. O. Rogers, Fr. Pat. 1,386,691 (1965).
4. R. H. Sallé, B. J. Sillion, and G. P. de Gaudemaris, *J. Polym. Sci. A-1*, **4**, 2903 (1966).
5. K. Schlögl, *Monatsh. Chem.*, **89**, 61 (1958).
6. K. Morsch, *Monatsh. Chem.*, **64**, 333 (1934).
7. A. F. McKay, G. Y. Paris, and D. L. Garmaise, *J. Amer. Chem. Soc.*, **80**, 6276 (1958).
8. S. L. Kwolek, *J. Polym. Sci. A*, **2**, 5149 (1964).
9. B. V. Lokshin, O. A. Gluskova, *Zh. Obshch. Khim.*, **32**, 1391 (1962).
10. B. Tchoubar, *Bull. Soc. Chim. France*, **1949**, 160.
11. W. D. Emmons and J. P. Freeman, *J. Amer. Chem. Soc.*, **77**, 4387 (1955).

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Effects of Metal Salts on Polymerization. VI. Photo and Thermally Catalyzed Polymerization of *N*-Vinylimidazole in the Presence of Metal Salts

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Synopsis

Polymerization of 2-methyl-1-vinylimidazole (MVI) and 2-ethyl-1-vinylimidazole (EVI) was found to be markedly photosensitized in the presence of oxidizing metal salts such as $UO_2(NO_3)_2$, $Ce(NH_4)_2(NO_3)_6$, $Hg(CH_3COO)_2$, $AgNO_3$; non-oxidizing metal salts such as Zn^{II} did not act as photosensitizers. The interaction of monomer with a metal salt is discussed on the basis of infrared and electronic spectroscopy. This photopolymerization is very specific with respect to the kind of monomer. The polymerization of noncomplexing monomer (styrene) is not photosensitized by these metal salts. Consequently, photosensitized electron transfer between monomer and metal salt via complex formation is considered to be the most probable initiation mechanism. Cupric acetate and sodium chlorolaurate, which have been reported as efficient initiators for the polymerization of vinylpyridine and *N*-vinylcarbazole, respectively, act as linear terminators of growing radicals. The radical polymerizability of the zinc complex of MVI was studied by means of copolymerization with styrene. The reduction of the reactivity of MVI on complexing was explained by correlating with the spectroscopic observations. Because the polymerization system is heterogeneous, a detailed discussion was not possible.

INTRODUCTION

The use of oxidizing metal salts to initiate vinyl polymerization has been attempted for acrylonitrile,[1] styrene,[2] methyl methacrylate,[2] vinylpyridine,[3] vinylcarbazole,[4] and others. These polymerization systems may be initiated by the direct oxidation of monomer,[2] by the redox reaction between central metal ion and anion or ligand,[1] or by some unclassified processes involving complex formation.[2] Our interests are mostly directed to the first case, in particular, the oxidation of monomer by an electron-transfer process, since the direct oxidation of monomer could initiate both cationic and radical polymerization, depending upon the natures of monomer and metal salt. An example of the amphoteric catalytic activity of oxidizing metal salts has been presented for the polymerization of vinylpyridines and *N*-vinylcarbazole by cupric, ferric and ceric salts.[4-6] When oxidizing metal salts are used as catalysts, the former monomer polymerizes only by a radical mechanism, whereas the polymerization of later monomer is always cationic. This finding has been claimed as evidence in support of charge-transfer initiation via ion-radical formation. The factors which decide the nature of propagating species are, however, unknown. Radical polymerization of vinylpyridine is understandable, since this monomer cannot be polymerized by a cationic mechanism due to its strong basicity. *N*-Vinylcarbazole is capable of polymerizing both by cationic and radical mechanisms. Nevertheless, cationic polymerization alone has been observed.

Knowledge concerning polymerization of *N*-vinylimidazole, which is considered to have properties intermediate between vinylpyridine and *N*-vinylcarbazole, would provide additional information on the relation of monomer structure with the mechanism of oxidative polymerization. *N*-Vinylimidazole has a large and negative *e* value, as does *N*-vinylcarbazole, and also has a strong basic nitrogen capable of complex formation with metal salt as does vinylpyridine. This monomer has been studied by Murahashi and co-workers[7] who concluded that polymerization by a radical mechanism alone was possible. In the present study, it was found that *N*-vinylimidazole was sensitive to light in the presence of various oxidizing metal salts whereas thermal polymerization was hardly induced by oxidizing metal salts.

The effects of complex formation of monomer on the propagation reaction are of both experimental and theoretical interest. Polymerization of complexed *N*-vinylimidazole was attempted by using the same technique reported in an earlier part of this series.[8] Owing to the insolubility of polymer complexes, homogeneous polymerization system, which is essential for detailed discussion, could not be established.

EXPERIMENTAL

Materials

2-Methyl-1-vinylimidazole(MVI) and 2-ethyl-1-vinylimidazole (EVI), provided by Toho Rayon Co. Ltd. were purified by repeated distillation under reduced pressure over potassium hydroxide and finally distilled immediately before use. Styrene and methyl methacrylate were purified by accepted procedures.

All metal salts (guaranteed reagent grade) were used without further purification. Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol.

Polymerization

Polymerization was carried out *in vacuo* after degassing the reaction mixture by three freeze–thaw cycles at a pressure below 10^{-4} mm Hg. When the system was to be irradiated by light, the procedure was the same as described before. A hard glass tube, which cuts off the ultraviolet region below 310–320 mμ, (diameter 12 mm) was used as polymerization vessel. Since the polymerization vessel was cylindrical, the absolute photoenergy absorbed in the polymerization system could not be measured. The rate of reduction of potassium ferrioxalate actinometer in the same reaction vessel was 7.15–7.60 × 10^{-5} mole/l.-sec, $[\mathrm{Fe^{III}}]_0 = 6 \times 10^{-3}M$ under the same irradiation conditions.

The reaction mixture after being polymerized was poured into an acetone–*n*-hexane ($^1/_4$) mixture to precipitate polymer. Trace amounts of metal salt complexed with monomer could not be eliminated by reprecipitation. For the copolymerization mixture of MVI with styrene prepared in the presence of large excess of zinc acetate, methanol was used as precipitant.

The viscosity of polymer was measured in 0.1 *N* hydrochloric acid.

Copolymer Composition

The copolymer composition of *N*-vinylimidazole with styrene or methyl methacrylate was determined by nitrogen content as measured by the Kjeldahl method. For copolymer prepared in the presence of a large excess of zinc acetate, the content of zinc salt incorporated in the polymer was determined by chelate titration after decomposing the polymer by heating in a crucible. The weight of sample for nitrogen analysis was corrected for the metal salt content in copolymer.

Preparation of Solid Complexes

Aqueous solutions of metal salt were added with EVI. The crystals formed immediately or after standing overnight in a refrigerator were collected, dried, and recrystallized from alcohol. The analytical data for the complexes are summarized in Table I.

TABLE I
Metal Complexes of 2-Ethyl-1-Vinylimidazole

Complex	Mp, °C	Metal content, %	
		Found	Calcd
$(\mathrm{EVI})_2\mathrm{ZnCl_2}$	119[a]	17.2	17.19
$(\mathrm{EVI})_2\mathrm{HgCl_2}$	72–75	40.8	38.92
$(\mathrm{EVI})_2\mathrm{CoCl_2}$	109[a]	15.3	15.76
$(\mathrm{EVI})_2\mathrm{AgNO_3}$	102–105	25.9	26.07

[a] Start of melting.

Spectroscopy

Infrared spectra of free monomers and their complexes as liquid films and KBr disks, respectively, were measured by a DS-402G spectrometer (Japan Spectroscopic Co.). Electronic spectra were measured by a Shimadzu MPS-50 recording spectrometer.

RESULTS AND DISCUSSION

Comparison of Polymerization of MVI and EVI

Polymerizability of MVI and EVI is shown in Figure 1. Both of the imidazole monomers are polymerizable either thermally by a radical

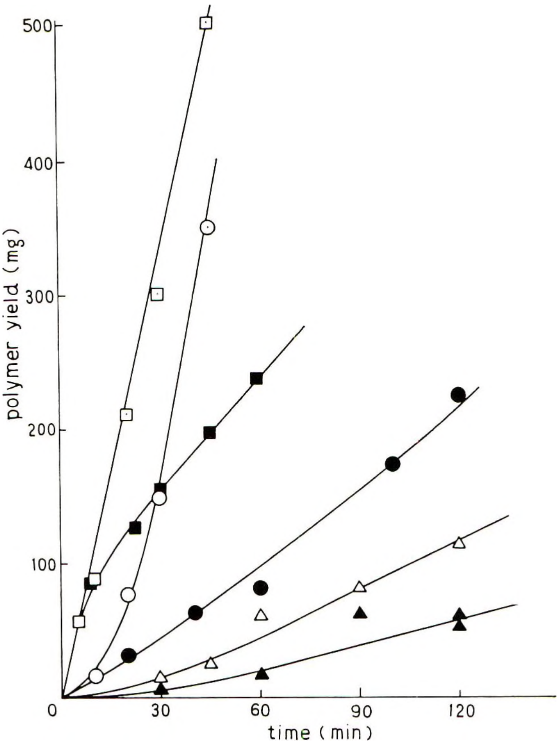

Fig. 1. Polymerization of 2-alkyl-1-vinylimidazole: (□) MVI 1.5 ml, $[Ce(NH_4)_2(NO_3)_6] = 10^{-3}$ *M*, irradiated at 30°C *in vacuo;* (■) EVI 1.5 ml, $[Ce(NH_4)_2(NO_3)_6] = 10^{-3}$ *M;* irradiated at 30°C *in vacuo;* (○) MVI 1.5 ml, [AIBN] = 10^{-2} *M*, 50°C *in vacuo*, dark polymerization; (●) EVI 1.5 ml, [AIBN] = 10^{-2} *M*, 50°C *in vacuo*, dark polymerization; (△) MVI 1.5 ml, irradiated at 30°C *in vacuo;* (▲) EVI 1.5 ml irradiated at 30°C *in vacuo.*

initiator or by photoirradiation. The MVI shows prominent autoacceleration and forms an insoluble polymer as described previously by Murahashi.[7] Since there seems to be no fundamental difference between MVI and EVI, EVI which provides soluble polymer was used in the following photosensitized experiments.

Photosensitization by ceric salt was marked. Although the ceric salt has been used for thermal sensitizer in combination with alcohols, amines, or other reducing agents,[9] this is the first case reported of strong photoinitiating activity by the ceric salt without activators.

Photopolymerization of EVI Sensitized by Various Metal Salts

Results of photopolymerization by various metal salts are shown in Figure 2 and Table II. All metal salts are soluble in monomer at least up to a concentration of $10^{-3}M$. Although metal salts could influence the rates of propagation and termination as well as of initiation, effects other than photoinitiation could be neglected. As shown in Figure 3, the effect

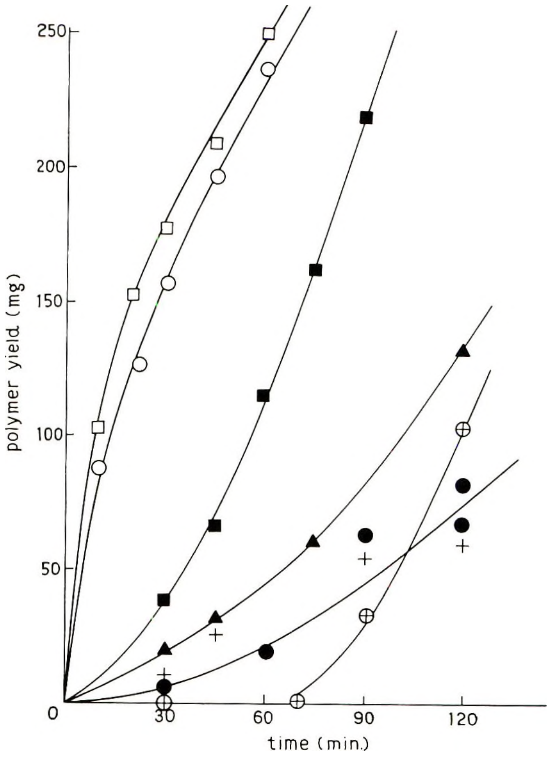

Fig. 2. Photopolymerization of EVI at 30°C (EVI 1.5 ml; [metal salt] = $10^{-3}M$): (●) no metal salt; (▲) $AgNO_3$; (■) $Hg(CH_3COO)_2 \cdot 2H_2O$; (○) $Ce(NH_4)_2(NO_3)_6$; (□) $UO_2(NO_3)_2 . 6H_2O$; (+) $Zn(CH_3COO)_2 . 2H_2O$; (⊕) $NaAuCl_4 \cdot 2H_2O$.

of the salts on catalyzed thermal polymerization is negligible with the exceptions of $Cu(OOCCH_3)_2$ and $NaAuCl_4$, indicating that linear termination by most of the metal salts and also the change of monomer reactivity by complex formation are not of major importance. As will be discussed in the next section, the reactivity of complexed monomer is indeed different from free monomer. However, under the present conditions of photopolymerization, the fraction of complexed monomer is extremely small. None of these metal salts shown in Figure 2 acts as a thermal initiator in the dark, even at 50°C. Consequently, the differences in time–conversion curves in Figure 2 are attributable entirely to the differences in activity of the metal salts as photosensitizer.

The inhibitory effect of $NaAuCl_4$ and $Cu(CH_3COO)_2$ requires explanation. The gold salt is a very strong oxidizing agent and capable of oxidizing a growing polymer radical. The radical polymerization of styrene is also inhibited in the presence of the gold salt as shown in Figure 6. On the other hand, cupric acetate is a good electron-transfer initiator for the radical polymerization of 4-vinylpyridine, whereas the linear termination is not detected by the kinetic study.[3] The linear termination reaction in-

TABLE II
Polymerization of EVI in the Presence of Various Metal Salts[a]

Metal salt	Polymerization time, min	Yield, mg	[η], dl/g[b]
None	90	64.0	1.78
$Ce(NH_4)_2(NO_3)_6$	10	87.9	1.72
"	22	128.1	1.83
"	30	156.6	1.76
"	45	196.9	1.89
"	60	238.2	1.78
$UO_2(NO_3)_2$	10	102.5	~1.5
$Hg(CH_3COO)_2$	60	115.9	2.10
$AgNO_3$	120	132.2	1.46
$Zn(CH_3COO)_2$	120	57.1	1.70
None[c]	53	102.4	1.60
$Ce(NH_4)_2(NO_3)_6$[c]	60	102.1	1.69

[a] EVI, 1.5 ml; metal salts, $10^{-3}M$; irradiated at 30°C *in vacuo* unless otherwise noted.
[b] In 0.1N HCl at 25°C.
[c] In the dark at 50°C, [AIBN] = $10^{-2}M$, *in vacuo*.

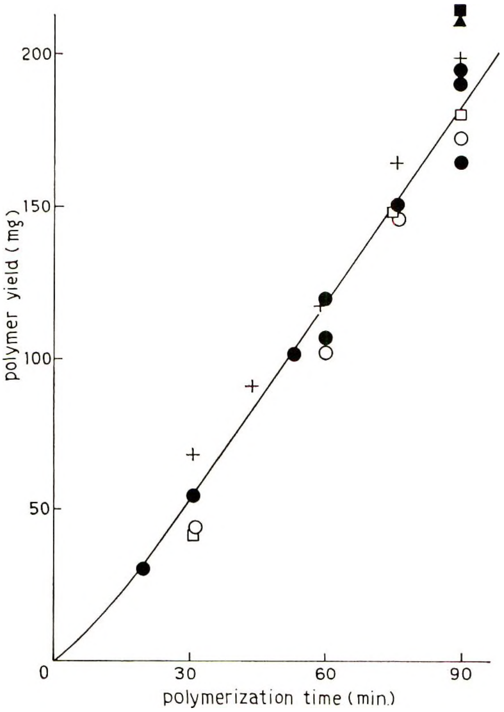

Fig. 3. Polymerization of EVI at 50°C in the dark. EVI 1.5 ml, [AIBN] = $10^{-2}M$, [metal salt] = $10^{-3}M$. The polymerization is inhibited in the presence of $Cu(CH_3COO)_2 \cdot 2H_2O$ or $NaAuCl_4 \cdot 2H_2O$: (●) without metal salt; (○) $Ce(NH_4)_2(NO_3)_6$; (□) $UO_2(NO_3)_2 \cdot 6H_2O$; (+) $Zn(CH_3COO)_2 \cdot 2H_2O$; (▲) $AgNO_3$; (■) $Hg(CH_3COO)_2$.

volving a redox process would be strongly controlled by the polarity parameter as studied by Bamford[10] for the reaction of growing radicals with ferric chloride. The large and negative *e* value of *N*-vinylimidazole indicates the ease of the oxidation of growing radical in comparison with 4-vinylpyridine, which has a more positive *e* value than *N*-vinylimidazole. When an organic radical is oxidized by cupric salts via an electron-transfer process, the high electron density at the radical site is an especially favorable condition.[11]

The intrinsic viscosity of polymer lies in the range 1.5–2.1.

The nature of the propagating species in photopolymerization of MVI sensitized by ceric ammonium nitrate is identical with that of ordinary radical polymerization initiated by azobisisobutyronitrile, as judged by the identity of copolymer compositions when the mixtures of MVI and methyl methacrylate are polymerized by these two processes.

Radical Copolymerization of MVI in Concentrated Zinc Acetate Solution

As mentioned in the previous section, a small amount of metal salt ($10^{-3}M$) does not affect the rate of catalyzed polymerization in the dark. When the concentration of complexed monomer increases, the effect of the salt on the propagation reaction would become important. Polymerization of metal-complexed monomer has been extensively studied for vinylpyridines,[8] methyl methacrylate,[12,13] and acrylonitrile,[14] and the reactivity has been discussed on the basis of electronic and infrared spectroscopy[8] and quantum chemical calculations.[16]

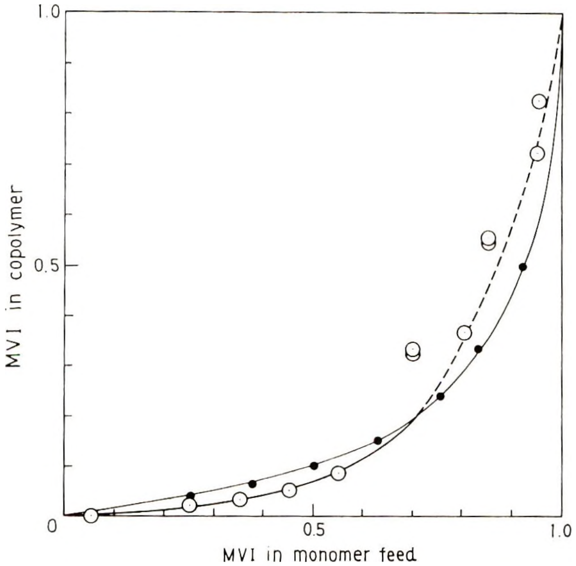

Fig. 4. Copolymerization of MVI (M_1) with styrene: (○) saturated solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ in DMSO, $[Zn^{II}] \approx 2M$; (●) bulk polymerization at 60°, data of Murahashi et al.[7]

TABLE III

Copolymerization of MVI–Styrene(M_2) in the Presence of $Zn(CH_3COO)_2$[a]

Expt no.	MVI, ml	St, ml	Time, hr:min	Yield, mg	Zn content, %	N, %	MVI in copolymer, mole fraction
1	0.1	1.9	26:17	543	1.4	0.157	0.005
2	0.5	1.5	14:00	343	1.7	0.69	0.021
3	0.7	1.3	13:40	537	6.7	0.91	0.034
4[b]	0.9	1.1	9:03	426	6.6	1.34	0.048
5	1.1	0.9	9:10	206	5.3	2.27	0.085
6	1.4	0.6	9:00	75	27.1	8.82	0.332
7	1.4	0.6	41:06	684	23.6	8.60	0.324
8[b]	1.6	0.4	15:43	433	23.3	9.83	0.370
9	1.7	0.3	8:50	129	27.5	14.50	0.550
						14.70	0.558
10[b]	1.9	0.1	9:03	1405	24.6	19.1	0.727
						21.8	0.837

[a] $(M_1 + M_2) = 2$ ml; saturated solution of zinc salt in 10 ml DMSO; 2 mg AIBN; 50°C.

[b] AIBN 10 mg.

N-Vinylimidazole is an exceptional monomer since the extent of conjugation between vinyl group and imidazole ring decreases when the monomer is complexed, whereas other monomers such as vinylpyridines enhance conjugation by complex formation. The result of copolymerization of MVI with styrene is shown in Figure 4 and Table III. The amount of zinc salt incorporated in the copolymer increases with increasing imidazole content in the copolymer. Although zinc content determined by chelate titration was subtracted from the weight of the sample, large corrections for samples prepared at higher concentration of MVI would cause large errors in composition analysis. Definitive values of r_1 and r_2 could not be determined, owing in part to the analytical uncertainty at high MVI content and in part to the possible dependence of the structure of MVI complexes on the $[\mathrm{MVI}]/[\mathrm{Zn^{II}}]$ ratio. Analytical data of samples prepared at low MVI fractions in feed monomer would be more accurate. From experiments 1–5 in Table III, r_2 is calculated to be 20 ± 4, where M_1 is MVI. Comparison of this reactivity ratio with published data[7] ($r_1 = 0.069$, $r_2 = 8.97$, where M_1 is MVI) suggests decreased reactivity of MVI when the monomer is complexed. The change of monomer reactivity can be interpreted as a result of reduced conjugation brought about by complex formation.[15]

The polymerization system is in part heterogeneous, since the formation of stable higher-order complexes of polyvinylimidazole causes the polymer to precipitate as a polymer complex crosslinked by zinc salt. The solution behavior of polyvinylimidazole is different from that of polyvinylpyridine. The stability data of zinc complexes of imidazole indicate that $\mathrm{ZnL_2}$ is the predominant species even with $[\mathrm{Zn}] > [\mathrm{L}]$, where L is imidazole. (Here $\log K_1 = 3.15$, $\log K_2 = 2.95$ in 0.058*N* KCl at 25°C,[17] where K_1 and K_2 are the first and the second formation constants of $\mathrm{Zn^{II}}$–imidazole complex, respectively.) On the contrary, the second formation constant of the pyridine–zinc complex is much smaller than the first formation constant ($\log K_1 = 1.41$, $\log K_2 = -0.30$ in 0.1*N* KCl at 25°C),[17b] which reflects on the solubilization of vinylpyridine polymer under condition of $[\mathrm{Zn}] > [\mathrm{L}]$ via formation of one-to-one complex.

The present polymerization system seems to be controlled by two factors, namely the heterogeneity and the reactivity of complexed monomer and radical. However, it is not possible to discuss these two factors independently.

Spectroscopy of Metal Salt–Vinylimidazole Complexes

The shift of π–π^* transition spectra of vinylimidazole by complex formation has been discussed for the resonance structures Ia, Ib.[15]

Ia Ib

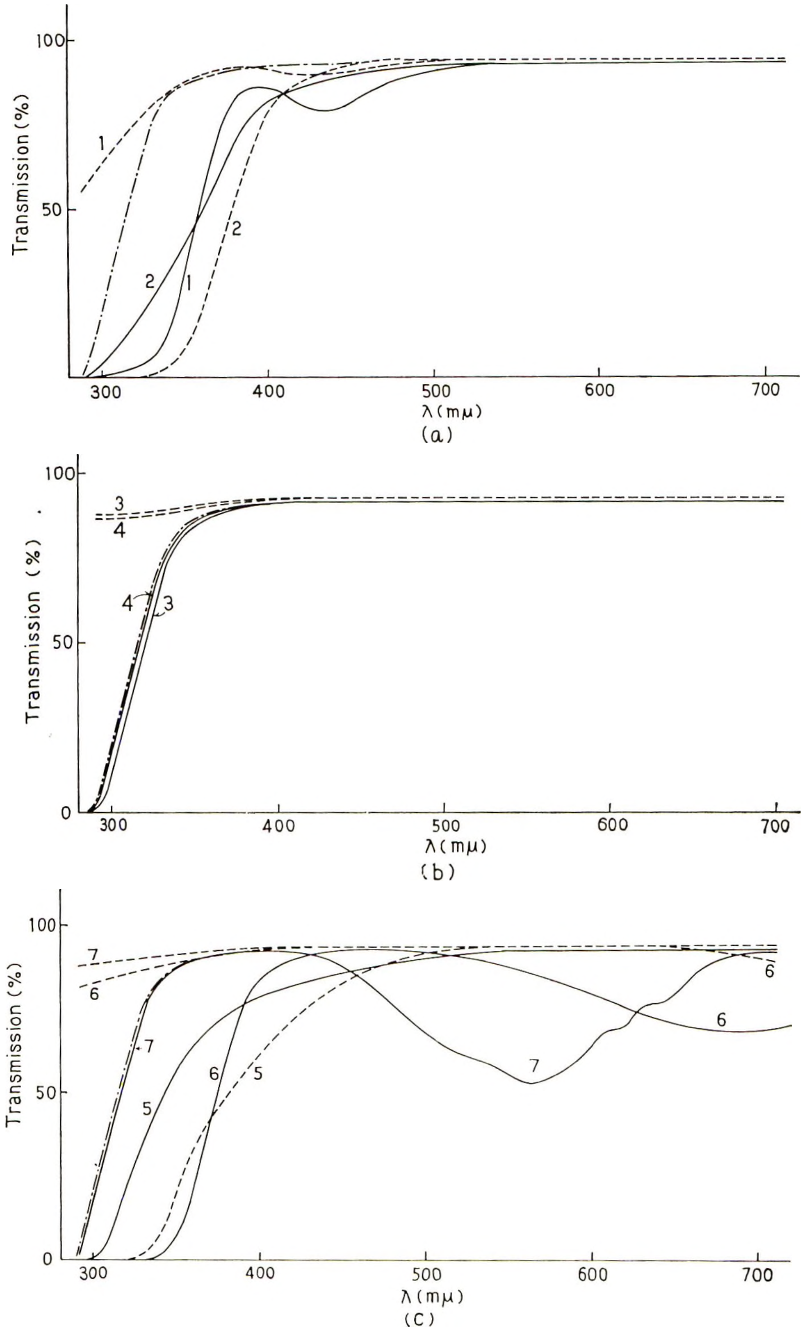

Fig. 5. Absorption spectra of various metal salts in water and in EVI-water (1/1) mixture. (*a*) 1. $UO_2(NO_3)_2 \cdot 6H_2O$ $10^{-3}M$; 2. $Ce(NH_4)_2(NO_3)_6$ $10^{-3}M$: ——, in EVI/H_2O; — —, in H_2O; —·EVI/H_2O. (*b*) 3. $Hg(CH_3COO)_2$ $10^{-3}M$; 4. $AgNO_3$ $10^{-3}M$: ——, in EVI/H_2O; — —, in H_2O; —·, EVI/H_2O. (*c*) 5. $NaAuCl_4 \cdot 2H_2O$ $10^{-3}M$; 6. $Cu(CH_3COO)_2 \cdot 2H_2O$ $10^{-3}M$; $CoCl_2 \cdot 6H_2O$ $10^{-3}M$: ——, in EVI/H_2O; — —, in H_2O; —·, EVI/H_2O.

The contribution of resonance would reduce the conjugation between vinyl and imidazole groups, namely, the vinyl group is thought to be more isolated when the monomer is complexed. The present results of infrared spectroscopy determining the stretching vibration of vinyl group clearly support the contribution of the resonance Ia ↔ Ib. The isolated double bond should require a higher energy for stretching vibration, as indicated by the blue shift shown in Table IV. The magnitude of the blue shift of the C=C stretching vibration is roughly proportional to the electronegativity of the central metal ion.

TABLE IV
Shift of the Stretching Vibration of
Vinyl Group by Complex Formation

	$\nu_{-CH=CH_2}$, cm^{-1}	$\Delta\nu$, cm^{-1}[a]	Electronic structure	Electronegativity
EVI	1642			
EVI–HCl	1652	+10	$1S^0$	2.1
$(EVI)_2ZnCl_2$	1650	+8	$3d^{10}$	1.66
$(EVI)_2CoCl_2$	1649	+7	$3d^7$	1.70
$(EVI)_2HgCl_2$	1647	+5	$5d^{10}$	1.44
$(EVI)_2AgNO_3$	1645	+3	$4d^{10}$	1.42

[a] $\Delta\nu = (\nu)$ complex $- (\nu)$ free.

The electronic spectra of metal salts dissolved in a EVI–water mixture and also in water are shown in Figure 5. The glass reaction vessel for photopolymerization is transparent to the wavelength region longer than ~300 mμ, and very effective photosensitizers such as Ce^{IV} and UO_2^{++} exhibit strong absorption in the near-ultraviolet to visible region. Absorption of light is certainly a necessary but not sufficient condition for photosensitization. The cobaltous salt, for example, exhibits absorption in the visible region but does not act as photosensitizer. Although assignment of absorption bands of Ce^{IV} and UO_2^{++} is not clear, the absorption bands are most likely to be charge-transfer bonds. Since Ce^{IV} and UO_2^{++} ions are of d^{10} structure, the assignment of ligand field bands is out of question. Comparison of absorption spectra of metal salts in water with those in EVI–water mixture indicates the interaction of metal salts with EVI.

Mechanism of Photoinitiation

Since the effective photosensitizers for polymerization of *N*-vinylimidazole are all oxidizing metal salts, there seems to be little doubt that a photoredox process is involved in the initiation process. A possible mechanism of initiation may be oxidation of anions or direct oxidation of monomer. The former mechanism has been proposed for the photosensitized initiation by ion-pair complexes such as $FeCl^{2+}$.[18] When monomer does not take part in the initiation process, the initiator system should be nonselective with respect to the kind of monomer. This disagrees with the present finding, since polymerization of styrene is not photosensitized when a styrene–acetonitrile mixture (1/1 by volume) containing $10^{-2}M$ of ceric ammonium nitrate or uranyl nitrate is irradiated *in vacuo* at 30°C as shown in Figure 6. In the presence of metal salt, the photopolymerization

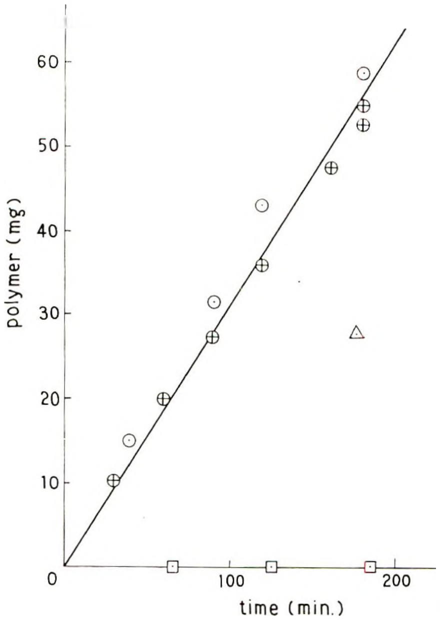

Fig. 6. Polymerization of styrene in the presence of metal salts in the dark: (⊕) without metal salt; (○) $Ce(NH_4)_2(NO_3)_6$; (△) $UO_2(NO_3)_2 \cdot 6H_2O$; (□) $NaAuCl_4 \cdot 2H_2O$. Styrene, 1 ml; CH_3CN, 1 ml; [AIBN] = $10^{-2}M$; [metal salt] = $10^{-2}M$; 50°C, *in vacuo*.

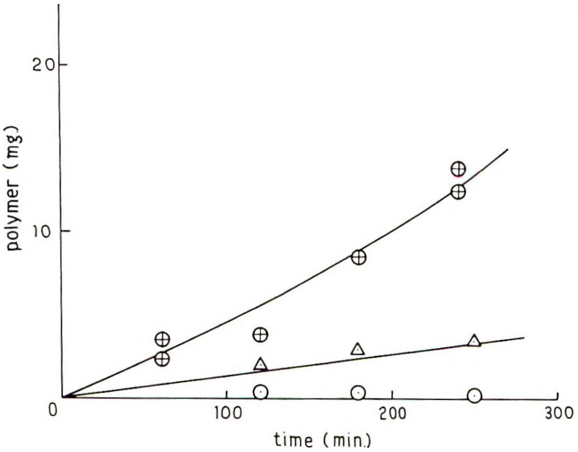

Fig. 7. Photopolymerization of styrene in the presence of metal salts: (⊕) without metal salt; (○) $Ce(NH_4)_2(NO_3)_6$; (△) $UO_2(NO_3)_2 \cdot 6H_2O$. Styrene, 1 ml.; CH_3CN, 1 ml; [metal salt] = $10^{-2}M$, 30°C, *in vacuo*.

of styrene is even slower than the spontaneous photopolymerization. The simultaneous occurrence of initiation and termination reactions is very unlikely, since the catalyzed radical polymerization of styrene is not affected by the ceric salt and only slightly retarded in the presence of uranyl nitrate, as shown in Figure 7. It is therefore concluded that these metal salts alone are not effective photoinitiators and they exhibit initiating activities in combination with specific monomers or activators.

Both infrared and π–π^* transition spectra of monomer–metal salt systems indicate the polarization of monomer in the complexed state. When the metal salt is oxidizing, the metal salt–monomer interaction would lead to total electron transfer via photo or thermal excitation. The concept of electron transfer initiation is very tempting by analogy to oxidative polymerization of vinylpyridine[3] and *N*-vinylcarbazole[4] initiated by oxidizing metal salts.

Although the photosensitization is difficult to envisage under the present experimental conditions with the use of a multichromatic light source, two possibilities of electron-transfer initiation may be considered. The first is the direct photosensitization of the absorption band of the monomer–metal salt systems, possibly caused by charge-transfer interactions, which leads to the total electron transfer from the monomer to the metal salts, resulting in the production of active species. The second is the reaction of metal salt with the photo-excited monomer. This possibility could not be precluded, since the monomer alone is also efficiently excited, as indicated by the fair rate of spontaneous photopolymerization in the absence of metal salt. However, the effective oxidizing metal salts as photosensitizer exhibit strong absorptions in the near ultraviolet region. The sequence of the intensity of absorption is $\mathrm{Ag^{I}} < \mathrm{Hg^{II}} < \mathrm{Au^{III}}, \mathrm{Ce^{IV}}, \mathrm{UO_2^{++}} < \mathrm{Cu^{II}}$ which agrees well with the sequence of photosensitizer activity, with exceptions of $\mathrm{Au^{III}}$ and $\mathrm{Cu^{II}}$. These two metal salts are strong linear terminators, as has been mentioned before.

From these discussions, the first mechanism which claims the utilization of photo energy absorbed by the metal salt–monomer interactions would be more favored.

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References

1. H. W. Schnecko, *Makromol. Chem.*, **66**, 19 (1963).
2. J. P. Herman and G. Smets, *J. Polym. Sci. A*, **3**, 3175 (1965).
3. S. Tazuke and S. Okamura, *J. Polym. Sci. A-1*, **4**, 141 (1966).
4. S. Tazuke, T. B. Tjoa, and S. Okamura, *J. Polym. Sci. A-1*, **5**, 1911 (1967).
5. S. Tazuke, K. Nakagawa, and S. Okamura, *J. Polym. Sci. B*, **3**, 923 (1965).
6. C.-H. Wang, *Chem. Ind.* (London), **1964**, 751.
7. S. Murahashi, S. Nozakura, A. Umehara, and K. Obata, *Kobunshi Kagaku*, **21**, 625 (1964).
8. S. Tazuke and S. Okamura, *J. Polym. Sci. A-1*, **5**, 1083 (1967).
9. G. M. Guzman, *Anales Real. Soc. Espan. Fis. Quim. Madrid*, **B58**, 189 (1962).

10. C. H. Bamford, A. D. Jenkins, and R. Johnston, *Trans. Faraday Soc.*, **55**, 418 (1959).
11. J. K. Kochi and F. F. Rust, *J. Amer. Chem. Soc.*, **84**, 3946 (1962).
12. C. H. Bamford, S. Brumby, and R. P. Wayne, *Nature*, **209**, 292 (1966).
13. M. Imoto, T. Otsu, and Y. Harada, *Makromol. Chem.*, **65**, 180 (1963).
14. M. Imoto, T. Otsu, and M. Nakabayashi, *Makromol. Chem.*, **65**, 194 (1963).
15. S. Tazuke and S. Okamura, *J. Polym. Sci. B*, **5**, 95 (1967).
16. S. Tazuke, K. Tsuji, T. Yonezawa, and S. Okamura, *J. Phys. Chem.*, **71**, 2957 (1967).
17. *Stability Constants*, complied by L. G. Sillen and A. E. Martell, Special Publication No. 17, Chemical Society, London, 1964, (a), p. 388; (b) p. 441.
18. G. Oster and N.-L. Yang, *Chem. Revs.*, in press.

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Polybis(phosphinato)fluoroalanes*

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Synopsis

A new class of coordination polymers, polybis(phosphinato)fluoroalanes, $[Al(F)(OPRR'O)_2]_n$, where R,R′ are alkyl, phenyl, or benzyl, was prepared and studied. The properties of these polymers are influenced by the phosphinate (R) substituents; polymers having *n*-alkyl groups with more than five carbons are flexible and exhibit unusual hydrolytic stability. A polymer was obtained with a degree of polymerization of 104 by incorporating a 2:1 ratio of benzyl(*n*-heptyl) and di-*n*-octyl phosphinate groups. The properties of the flexible materials are consistent with linear rather than highly crosslinked or network systems. Feasible structures are proposed for the polymers.

INTRODUCTION

Polymeric bisphosphinates of zinc,[1,2] chromium,[3,4] cobalt,[5,6] and titanium[7] are known and are prepared generally by replacing acetate or chloride groups with phosphinate groups. Bis(phosphinates) of aluminum have been heretofore unknown, and very few monofluoroalanes[8,9] (monofluorides of aluminum) have been reported. Polybis(phosphinate)fluoroalanes,† represented by the general empirical formula $[Al(F)(OPRR'O)_2]_n$, were prepared in our laboratory by reacting diethylfluoroalane,[8,9] $(C_2H_5)_2AlF$, with phosphinic acids in tetrahydrofuran (THF) at Dry Ice temperature.

$$2nR_2P(O)OH + n(C_2H_5)_2AlF \rightarrow [Al(F)\,(OPR_2O)_2]_n + 2nC_2H_6$$

These polymers were also prepared by reacting etherated alane,[10] $AlH_3\cdot 0.3[(C_2H_5)_2O]$, and phosphinic acids at Dry Ice temperature in a 1:1 mole ratio, followed by hydrogen fluoride addition.

$$2nR_2P(O)OH + nAlH_3 \rightarrow \underset{\substack{\text{Proposed}\\ \text{intermediate}}}{[Al(H)\,(OPR_2O)_2]_n} \xrightarrow{nHF} [Al(F)\,(OPR_2O)_2]_n$$

This study concerns the preparation and characterization of this new series of inorganic coordination polymers.

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†The nomenclature is simplified by using the substituted alane (AlH_3) convention, i.e., $\{Al(F)[OP(n\text{-}C_6H_{13})_2O]_2\}$ is polybis(di-*n*-hexylphosphinato)fluoroalane.

TABLE I
Properties and Analyses of Polybis(phosphinato)fluoroalanes

$$\left[(OR_2PO)_m\overset{\displaystyle F}{\overset{|}{Al}}(OPR'R''O)_{2-m}\right]_n$$

Polymer number	m	R	R′	R″	Analysis Calcd C, %	 H, %	 Al, %	 P, %	 Found C, %	 H, %	 Al, %	 P, %	Mp, °C	Mol wt (THF)	Properties
I	0	CH_3	—	—	20.70	5.21	11.63	26.69	20.53	5.22	11.22	25.30	385–430[a]	Insol	Sublimes brittle
II	0	C_5H_{11}	—	—	52.62	9.72	—	—	52.14	9.72	—	—	250–260	Insol	Brittle
III	0	C_6H_5	—	—	60.01	4.20	5.62	12.90	60.00	4.67	5.50	12.35	420–450	Insol	Brittle
IV	0	C_6H_{13}	—	—	56.24	10.23	—	—	56.40	10.20	—	—	185–230	Semisol	Soft, flexible
V	0	C_8H_{17}	—	—	61.49	10.98	4.32	—	60.00	11.08	4.17	—	200–220	Semisol	Soft, flexible
VI	1	C_6H_{13}	C_8H_{17}	C_8H_{17}	59.13	10.63	4.74	10.89	59.15	10.86	5.57	10.55	110–130	Semisol	Soft, flexible
VII	1	C_7H_{15}	$C_{12}H_{25}$	$C_{12}H_{25}$	64.37	11.37	3.81	—	64.30	11.45	3.64	—	70–85	Semisol	Soft, flexible
VIII	⅔	C_8H_{17}	$C_6H_5CH_2$	C_7H_{15}	61.10	9.09	4.68	10.74	60.90	9.00	4.58	11.05	240–270[b]	78,000[b] ($n = 104$)	Flexible, coherent film

[a] Melts with sublimation.

[b] Molecular weight and melting point of fractionated polymer.

EXPERIMENTAL

All reactions were carried out in a dry box or under a dry nitrogen atmosphere. The tetrahydrofuran (THF) was distilled from sodium–biphenyl complex. Diethylfluoroalane was purchased from Texas Alkyls, Inc. Etherated alane,[10] bis(tetrahydrofuran)chloroalane,[11] and phosphonic and phosphinic acids[12] were prepared and purified by previously described procedures.[12] Infrared spectra, x-ray powder diffraction patterns, differential thermal analyses, gel-permeation chromatographs, and ebulliometric molecular weight measurements were obtained as previously reported.[12] Membrane osmometry measurements, $\bar{M}_n > 10\,000$, were carried out in THF using a Mechrolab Model 501 membrane osmometer, and values reported were obtained by extrapolation to infinite dilution. Thermogravimetric analyses were performed under nitrogen at a heating rate of 10°C/min. The mass spectra were obtained on Varian CH4B and Consolidated Engineering Corporation CEC 110B mass spectrometers by direct introduction techniques. The Nier peak matching technique was used to obtain accurate masses.

Elemental analyses were performed in our laboratories and are reported in Table I. Fluoride ion concentrations were obtained in water–polymer mixtures by titrating with thorium nitrate.[13] The determinations were confirmed by acidification of the samples, steam distillation of the hydrofluoric acid, and titration of the fluoride by the procedure of Belcher and West.[14]

Preparation of $\{Al(Cl)[OP(C_6H_{13})_2O]_2\}_n$

Polybis(di-*n*-hexylphosphinatochloroalane was prepared by reacting $AlH_2Cl \cdot 2(THF)$[11] with di-*n*-hexylphosphinic acid in a 1:2 mole ratio. A 4.173 g sample (0.020 mole) of $AlH_2Cl \cdot 2(THF)$ in 300 ml THF was slowly added to a stirred solution of 9.373 g (0.040 mole) $(n\text{-}C_6H_{13})_2P(O)OH$ in 1000 ml of THF at Dry Ice temperature. After addition, the solution was allowed to warm to room temperature; the solvent was removed under reduced pressure, and the product dried under high vacuum for 24 hr. A quantitative yield of a colorless, flexible, waxy material was obtained. The molecular weight in THF was 3100.

ANAL. Calcd for $C_{24}H_{32}AlClO_4P_2$: C, 54.59%; H, 9.91%; Al, 5.10%; P, 11.71%. Found: C, 54.80%; H. 9.96%; Al, 5.08%; P, 11.50%.

Preparation of $[Al(F)(OPR_2O)_2]_n$

Method A. Preparation of polybis(phosphinato)fluoroalanes requires the reaction of $(C_2H_5)_2AlF$ and $R_2P(O)OH$ in a 1:2 mole ratio. For a typical example, $\{Al(F)[OP(n\text{-}C_6H_{13})_2O]_2\}_n$ was prepared by slowly adding 0.020 mole of $(C_2H_5)_2AlF$ (heptane solution) in 500 ml THF to a stirred solution of 9.373 g (0.040 mole) of $(C_6H_{13})_2P(O)OH$ in 1500 ml of THF at Dry Ice temperature. After addition, the solution was allowed to warm to room temperature and the reaction mixture refluxed for 2 hr. The solvent was removed under reduced pressure and the colorless product dried under high vacuum for 12 hr. A quantitative yield of polymer was obtained.

Method B. This method requires the reaction of a 2:1 mole ratio of phosphinic acid and etherated alane, $AlH_3 \cdot 0.3[(C_2H_5)_2O]$, followed by the addition of hydrogen fluoride. For a typical example, 0.060 mole of diphenylphosphinic acid in 500 ml THF was slowly added to a stirred solution of 0.030 mole of etherated alane in 2000 ml of THF at Dry Ice temperature. After the addition was completed, 0.030 mole of hydrogen fluoride was added. The product was isolated in a manner similar to procedure A.

Fractionation of Polymer VIII

The solid polymer, VIII, was dissolved by warming in THF to form a 1 wt-% solution. Sufficient absolute methanol was added to precipitate the solid polymer which was collected on a filter. After this procedure was repeated twice, the solid polymer was dried under vacuum for 24 hr.

ANAL. Calcd for $C_{88}H_{156}Al_3F_3O_{12}P_6$:[*] C, 61.10%; H, 9.09%; Al, 4.68%. Found: C, 63.0%; H, 9.9%.

The low molecular weight fraction was isolated from the solution obtained by the first fractionation. After the THF–methanol solution was removed under reduced pressure, the resulting viscous liquid was dried under high vacuum for 24 hr.

ANAL. Found: C, 59.8%; H, 8.50%; Al, 5.49%.

RESULTS AND DISCUSSION

The reaction of phosphinic acids with diethylfluoroalane is the most convenient method for preparing polybis(phosphinato)fluoroalanes, although identical polymers were obtained by using etherated alane and hydrogen fluoride (method B). The best results were achieved when the reaction temperatures were kept below −30°C.

The organic substituents on the phosphinate moieties have a very pronounced effect upon polymer properties. Polymers with CH_3, n-C_5H_{11}, and C_6H_5 groups (polymers I, II, and III) are insoluble, high-melting, and brittle; polymers with n-alkyl groups with six or more carbons are lower-melting, flexible, and partially soluble. Mixtures of phosphinates (VI and VII) lower the melting points and an unsymmetric acid results in a polymer (VIII), with increased solubility. The comparative thermal stabilities, as measured by thermogravimetric and differential thermal analyses, are also dependent upon the substituent (R) groups. The methyl and phenyl phosphinates are the most stable polymers, with incipient decomposition at approximately 500°C. As the size of the alkyl groups increases, the

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[*] The empirical formula for the polymer repeating unit is $C_{29.33}H_{52}AlFO_4P_2$.

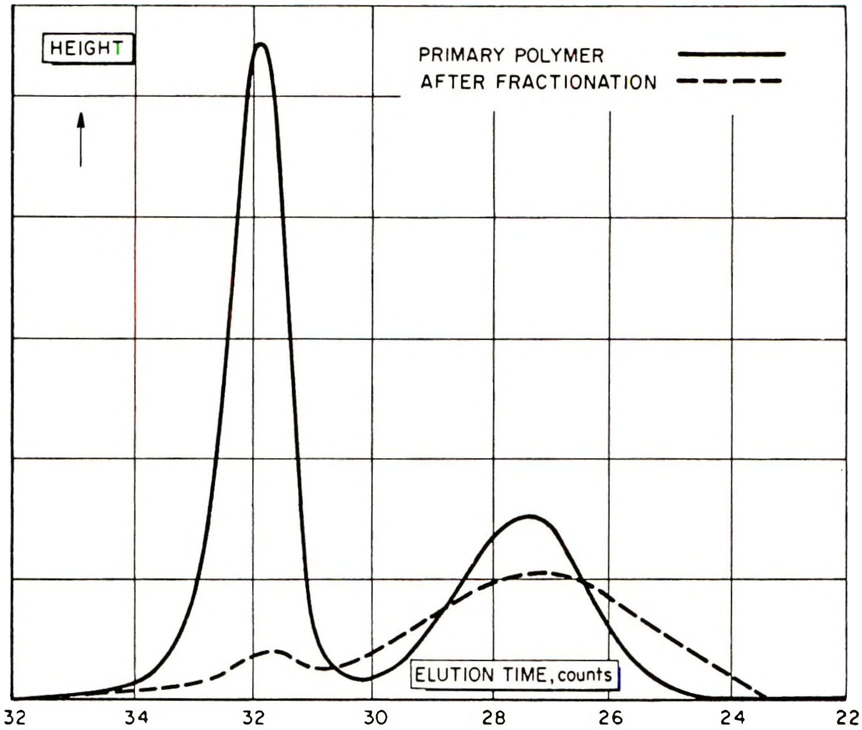

Fig. 1. Gel permeation chromatographs of polymer VIII.

thermal stability decreases. Decomposition usually begins between 350 and 400°C for polymers with large alkyl groups (IV through VIII).

The polybis(phosphinato)fluoroalanes are crystalline by x-ray diffraction, but, as the size of the R group increases, the diffraction pattern generally has fewer and broader bands. Polymers I–IV have between 20 and 50 sharp lines; polymer VIII has only five bands. It is interesting that polymer IV, $\{Al(F)[OP(C_6H_{13})_2O]_2\}_n$, and polybis(di-*n*-hexylphosphinato)chloroalane, $\{Al(Cl)[OP(C_6H_{13})_2O]_2\}_n$, have identical x-ray diffraction patterns. Trifluoroalane (AlF_3) was not detected in any of the samples, thus eliminating the possibility of disproportionation reactions involving the formation of AlF_3. Bis(dimethylphosphinato)fluoroalane (I), is markedly different from the other polymers and does not have typical polymeric characteristics. This material can be sublimed at 350–500°C under vacuum, and the sublimate has an identical elemental analysis and infrared spectrum as the original sample. The mass spectrum, obtained by heating the sample in a mass spectrometer, was complicated and became even more complex as the temperature was increased. The spectrum contained common *m/e* peaks at 297, 296, 217, and 139 for temperatures above approximately 300°C. Possible empirical formulas for these peaks are $C_4H_{12}Al_2F_3O_4P_2$, $C_4H_{13}AlFO_6P_3$, $C_3H_9AlFO_4P_2$, and $C_2H_6AlFO_2P$. This suggests that material I may sublime by a mechanism involving more than one gas-phase species. The x-ray diffraction of a fused sample of I differs from the original sample. In contrast, the other polymers in Table I have identical x-ray diffraction patterns before and after fusion. Some higher melting polymers give sharper patterns after fusion.

Polymers II–VII precipitate from THF solution as partially soluble gels soon after the reaction solution is warmed to ambient temperature; therefore, molecular weight measurements could not be obtained. Because polymer VIII was soluble, it could be studied in greater detail. The molecular weight of the polymer directly after preparation was 7700, but gel-permeation chromatography (Fig. 1, primary polymer) indicated that this measurement represented an average of two molecular weight fractions. The fractions were separated by gel-permeation chromatography, and elemental analysis of the low molecular weight fraction was essentially identical to the original (VIII). Insufficient material was obtained for accurate analysis of the high polymer fraction.

Separation of polymer VIII was also attained by a fractionation involving the precipitation of polymer from a THF-methanol solution. The gel-permeation chromatograph (Fig. 1, after fractionation) of the least soluble, high molecular weight fraction indicated good separation. The molecular weight was 78000, and a clear, flexible, coherent film was obtained by solvent evaporation. The low molecular weight fraction (VIII) was isolated as a viscous oil having an elemental analysis consistent with the unfractionated polymer. The gel permeation studies indicated that this fraction does not increase in molecular weight and probably represents low molecular weight cyclics or terminated (end-capped) chains. Polymers III–VII may also contain low molecular weight fractions, since some material can be extracted from the partially soluble solids with THF.

Successive gel-permeation chromatographs of the unfractionated polymer VIII solution indicated that the high polymer fraction increased in molecular weight with time. This effect is also illustrated by comparison of the gel-permeation chromatographs (Fig. 1) of the fractionated high polymer with the initial polymer (chromatographed soon after preparation). The capability of the inorganic coordination polymers to grow in solution has also been observed with polyphosphinato(phosphonato)alanes,[12] and tris-(phosphinato)alanes.[15] Similar observations have been reported for other metal phosphinates.[16]

The polymerization of polybis(phosphinato)fluoroalanes in solution probably involves the displacement of THF solvent ligands by the stronger coordinating phosphinato (P═O) moieties at the coordinate sites of the aluminum. Since two (P═O) coordinate ligands are available for each aluminum, network type structures are possible.* Linear chains, however, will result if repeating units contain bridged eight-membered ring structures similar to those previously proposed for metal phosphinates.[1–7,18,19]

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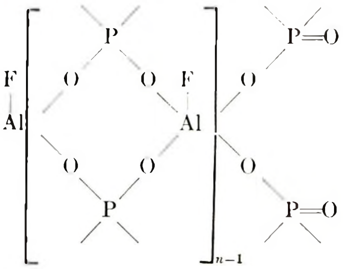
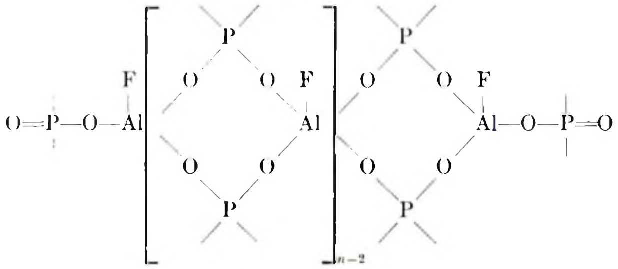
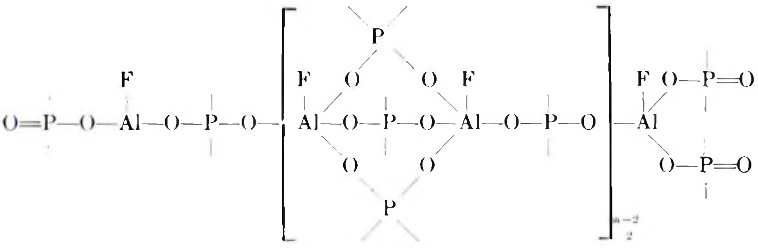
*The monomer unit, $[Al(F)(OPR_2O)_2]$, could be considered[17] "tetrafunctional" because it has two coordinating (P═O) moieties and at least two coordination sites available per aluminum.

The growth of polymer VIII in solution can be explained by assuming the existence of uncoordinated (P=O) moieties at the chain ends; if in solution there is no bond cleavage of the main polymer chains, four processes may be proposed by which linear growth could occur: (*1*) an end group with two free phosphinato moieties could attack an adjacent monomer with no free phosphinato moieties, thus forming a double-bridged structure (Ia);[1–7] (*2*) reaction between endgroups having one free phosphinato moiety should result in the same double-bridged repeating unit (Ib); (*3*) if a reaction takes place between endgroups having one and two free phosphinato moieties, respectively, a tris(phosphinato) bridge should be formed; an alternate single and triple-bridged structure[18,19] (II) is not inconsistent with this growth process; (*4*) a reaction between an endgroup with one free phosphinato moiety and a group with tris(phosphinato) bridging to the adjacent monomer unit should result in the same repeating unit as Structure II. The latter type of chain growth, however, seems unlikely.

Some chain branching as well as linear chain growth could be expected with any of these processes.


Structure Ia*


Structure Ib*


Structure II*

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*Coordinated THF solvent associated with the aluminum atoms are not shown in these structures but it is understood that the aluminum has a possible inner sphere coordination number of five or six. The organic groups have been deleted.

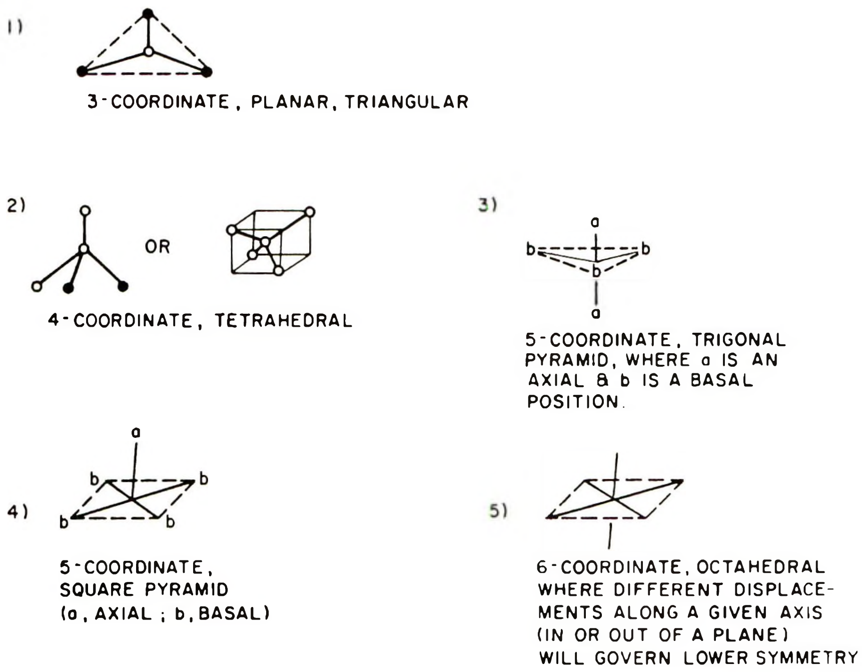

Fig. 2. Illustrations of different symmetries.

The structures Ia, Ib, and II illustrate only the molecular linkage and not the stereochemistry of the repeating units.* In either case, the aluminum atoms could have inner sphere coordination numbers of either five (non-solvated) or six. Many possible stereoisomers are possible for either the double or alternate single and triple-bridged structure. In the solid state, the bonding could become even more complex because of the possibility of fluorine bridging and three-coordinate oxygen.

Chain termination could result from deviation from exact stoichiometry, cyclization, or the presence of any strong competing ligand. Prior exposure of the alanes, $AlH_3 \cdot 0.3[(C_2H_5)_2O]$ or $(C_2H_5)_2AlF$, to trace amounts of water or air should also lead to chain termination. Coordination of a phosphinato moiety to the same aluminum ion (i.e., chelation) could in theory lead to termination but, since the polymers grow in solution, this type of bonding is very doubtful.

There is no evidence that bis(phosphinato)fluoroalanes disproportionate to tris(phosphinato)alanes and trifluoroalane, although a small amount of disproportionation involving tris(phosphinato)alane and difluoro-(phosphinato)alane may be possible.

$$2[Al(F)(OPR_2O)_2] \rightleftarrows [AlF_2(OPR_2O)] + [Al(OPR_2O)_3]$$

From the gel-permeation chromatography and fractionation studies of VIII, it is apparent that extensive disproportionation of this type does not

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*See Appendix for a brief discussion of the stereochemistry.

take place. The elemental analyses, however, are not inconsistent with the high polymer fraction containing a small amount of tris(phosphinato)-alane as a copolymer and the low fraction containing a trace of difluoro-(phosphinato)alane, since in the first case the carbon analyses is slightly high and, in the latter case, slightly low.

Several attempts to prepare high molecular weight polybis(di-*n*-hexylphosphinato)chloroalane were unsuccessful, with degrees of polymerization of only between five and six. The low molecular weights may possibly be related, in this case, to disproportionation reactions producing end termination groups such as $—AlCl_2$. We have previously demonstrated that polychloro(phosphonato)alanes, $[—Al(Cl)O—P(O)(R)O—]_n$, form lower molecular weight polymers than polyfluoro(phosphonato)alanes, $[—Al(F)O—P(O)(R)O—]_n$, apparently because of the difference in bridging strength[20] of —Cl and —F in solution. The same rationale could apply to polybis(phosphinato)chloroalanes. More work relating to Al—F—Al bridging has been completed and will be published.[20]

Infrared spectra of the solid nonsolvated polymers were obtained. The PO_2 asymmetric and symmetric bands appear in the regions of 1140–1160 cm^{-1} and 1080–1090 cm^{-1}; no characteristic phosphoryl bonds were observed above 1200 cm^{-1}. Comparison of the infrared data with those for $(CH_3)_2P(O)_2Na$[21] suggests that the P—O bonds are equivalent and that both phosphinato moieties are bridging. These data are consistent with other related Al—O—P and Sn—O—P systems.[21,22]

With the exception of polymer I, (Table I), the polybis(phosphinato)-fluoroalanes are resistant to hydrolysis. For example, on the basis of soluble fluoride concentration, only 0.17% and 0.22% hydrolysis was detected after heating polymer VIII at 100°C in distilled water and in 1*M* sodium hydroxide solution for 7 days. No change was observed in physical appearance. In contrast, polymer I, after treatment with distilled water at 100°C for 2 hr indicated 88% hydrolysis of the fluoride. The difference in hydrolytic stability of the Al—F bond in polymers VIII and I apparently is not entirely due to the steric effects of hydrophobic character of the organic, R, groups, since polyfluoro(methylphosphonato)alane, $[—Al(F)O—P(O)(CH_3)O—]_n$, under the same conditions (100°C, 2 hr) indicated only 0.02% hydrolysis of the fluorine. In direct contrast to polybis(di-*n*-hexylphosphinato)fluoroalane, polybis(di-*n*-hexylphosphinato)chloroalane became hard upon extended exposure to the atmosphere, presumably by crosslinking through the hydrolytically reactive Al—Cl bonds.

SUMMARY AND CONCLUSIONS

Polybis(phosphinato)fluoroalanes, $[Al(F)(OPR_2O_2)]_n$, were prepared by reacting $(C_2H_5)_2AlF$ with phosphinic acids or by sequentially reacting etherated alane with phosphinic acids and hydrogen fluoride. These reactions were complete and fast, without detectable side reactions or disproportionation. When R is CH_3, C_6H_{11}, and C_6H_5, the materials

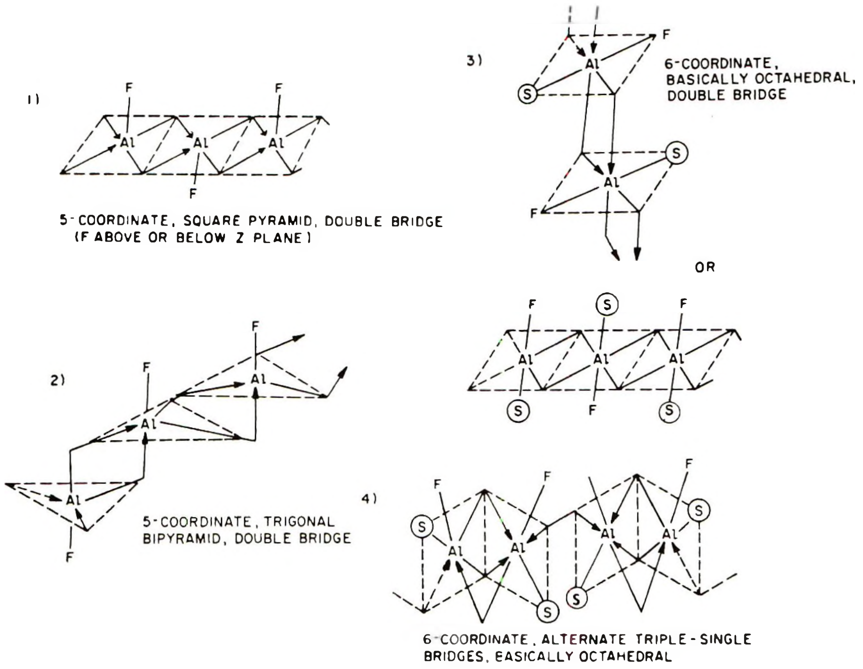


Fig. 3. Possible structures for polybis (phosphinatoalanes) with five- and six-coordinate aluminum. The solid lines represent bonds. The arrows designate phosphinate bridges, but the direction is primarily for "bookkeeping" purpose. Ⓢ represents coordinated solvent molecules. (4) may be visualized as bridging along the three-fold faces of the octahedron.

are high melting and brittle. The methyl derivative can be sublimed *in vacuo.* Polymers having n-alkyl groups with six or more carbon atoms are flexible and melt at a lower temperature. The incorporation of an unsymmetrical phosphinic acid gave a flexible, soluble polymer which was separated into high and low molecular weight fractions. The high molecular weight fraction ($n = 104$) "grows" in THF solution probably by a process involving displacement of solvent by coordinating phosphinato (P=O) moieties at the coordinate sites of the aluminum. The low molecular weight fraction does not exhibit solution growth and probably represents cyclics or terminated chains.

The effect of the organic substituents upon polymer properties is probably related to the steric nature of the R groups. The larger organic groups shield the inorganic backbone more effectively, and thus decrease chain interaction while increasing polymer flexibility and solubility. The R group may also cause changes in polymer crystallinity, structure, and molecular weight.

The relatively high crystallinity of the polymers is consistent with regular repeating structures. The flexible polymers are probably linear rather than highly branched or crosslinked. Structures are proposed for the repeating units with double-bridged and alternate single and triple-bridged structures.

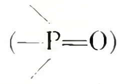
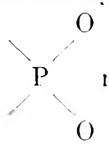
Either five or six coordinate aluminum is possible. Six-coordinate aluminum probably involves solvent coordination in solution and fluorine bridging in the solid state. The infrared spectra are consistent with the proposed structures.

The materials exhibited the expected thermal stabilities for coordination polymers of this type. The Al—F bond in most of the materials has unusually high hydrolytic stability. Differences in water sensitivity between polymers with methyl and larger organic groups cannot be completely explained by hydrophobic effects.

APPENDIX

The exact coordination number of aluminum in poly[bis(phosphinato)-fluoroalanes] has not been determined in either the solid state or solution; therefore, the question of exact structure and mechanism of growth must remain unanswered. In the absence of quantitative data, it is helpful to invoke simple stereochemical and symmetry arguments to determine which structures are possible on the basis of available data.

Aluminum(III) compounds are known with three, four, five, and six-coordinate states. Examples are: (*1*) halide vapors, AlX_3, at elevated temperatures (three-coordinate, planar triangular);[23,24] (*2*) halide vapors, $(AlX_3)_2$, (X=Cl, Br, I) below 400°C (four-coordinate dimers, tetrahedral);[24] (*3*) bis(trimethylamino)alane, $AlH_3 \cdot 2N(CH_3)_3$, (five-coordinate, trigonal bipyramid),[25] (*4*) complex aluminosiloxanes, $C_8H_{24}Al_3X_5O_6Si_4$, (X=Cl, Br) [one five-coordinate, square pyramid aluminum(III)];[26] (*5*) trifluoroalane, $(AlF_3)_n$, (six-coordinate, basically octahedral).[27] Illustrations of the different symmetries are given in Figure 2.[28]

The relative energies of the different molecular configurations will be determined by such factors as the availability of unfilled bonding or non-bonding orbitals, the number and nature of coordinating ligands, steric interaction between ligands (including cation to anion ratios), and crystal lattice stabilization. By using the factors above, three-coordinate, four-coordinate, and coordinate states greater than six can be eliminated for all practical purposes. Three-coordinate aluminum (sp^2 orbitals) leaves a low energy p orbital not utilized in bonding and clearly leaves only monomers in solution. Four-coordinate aluminum (sp^3) would utilize only one of the two available phosphinato groups for bridging, and this difference should be observed in the infrared spectra. Free phosphoryl  $(-\overset{\diagdown}{\underset{\diagup}{P}}{=}O)$ bands are not observed and the spectra can be most readily interpreted in terms of symmetrical and asymmetrical modes of  $>P<^{O}_{O}$ moieties. Seven or higher coordinate groups can be ruled out because of steric hindrance between ligands, an insufficient number of "bridging" moieties, and the use of higher energy configurations.

A brief examination of the trigonal bipyramid, square pyramid, and modified octahedral symmetries indicates a large number of potential structures for the polybis(phosphinato)fluoroalanes, (see Fig. 3). Clearly, the fluorine moiety can occupy either an axial or basal position in the five-coordinate states with a variable number of bridging groups. The site symmetry will be the highest for an axial fluorine and double bridging in the square pyramid configuration. The same basic arguments apply for the six-coordinate state, but two bridging phosphinato moieties and non-bridging fluorine moieties can only occupy five sites. In a six-coordinate configuration, the last site will probably be occupied by a solvent molecule in solution and a fluorine-bridging moiety in the solid state.

Simple but inconclusive arguments can be advanced why the six-coordinate state should be favored. (*1*) Tetrahydrofuran has been shown to be a strong coordinating ligand in solution,[11] and there are theoretical reasons for assuming the energy barrier between the five-coordinate state (especially square pyramid, dsp^3) and six-coordinate state (d^2sp^3) is small.[29] (*2*) The fluorine moiety is also capable of bridging, and there is no reason to assume the total absence of such bonding in the solid state. (*3*) The x-ray diffraction powder patterns of $AlF(OPR_2O)_2$ and $Al(OPR_2O)_3$ compounds are often very similar[30] when the same phosphinato moieties are used. Data are reasonably conclusive that tris(phosphinato) bridging does take place in polytris(phosphinato)alanes; this suggests structural similarity between the two types of poly(phosphinato)alanes. (*4*) Finally, the hydrolytic stability of certain polybis(phosphinato)alanes suggests that inner sphere coordinate sites are filled, and the molecule is less susceptible to attack by disruptive bases. This condition is best satisfied by six-coordination.

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References

1. B. P. Block, S. H. Rose, C. W. Schaumann, E. S. Roth, and J. Simkin, *J. Amer. Chem. Soc.*, **84,** 3200 (1962).
2. S. H. Rose and B. P. Block, *J. Polym. Sci. A-1*, **4,** 573 (1966).
3. B. P. Block, J. Simkin, and L. R. Ocone, *J. Amer. Chem. Soc.*, **84,** 1749 (1962).
4. A. J. Saraceno and B. P. Block, *J. Amer. Chem. Soc.*, **85,** 2018 (1963).
5. G. E. Coates and D. S. Golighly, *J. Chem. Soc.*, **1962,** 2523.
6. H. Rose and B. P. Block, *J. Polym. Sci. A-1*, **4,** 583 (1966).
7. G. H. Dahl and B. P. Block, *Inorg. Chem.*, **6,** 1439 (1967).
8. K. Ziegler and R. Köster, *Ann. Chem.*, **608,** 1 (1957).
9. A. W. Laubengayer and G. F. Lengnick, *Inorg. Chem.*, **4,** 503 (1966).
10. A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69,** 1199 (1947).

11. D. L. Schmidt and E. E. Flagg, *Inorg. Chem.*, **6,** 1262 (1967).
12. D. L. Schmidt and E. E. Flagg, *J. Polym. Sci.*, *A-1*, **6,** 3235 (1968).
13. C. Eger and A. Yarden, *Anal. Chem.*, **28,** 512 (1956).
14. R. Belcher and T. S. West, *Talanta*, **8,** 863 (1963).
15. E. E. Flagg and D. L. Schmidt, *J. Amer. Chem. Soc.*, **80,** 4173 (1968).
16. A. J. Saraceno, J. P. King, and B. P. Block, *J. Polym. Sci. B*, **6,** 15 (1968).
17. W. H. Carothers, *Chem. Rev.*, **8,** 353 (1931).
18. F. Giordano. L. Randaccio, and A. Ripamonti, *Chem. Commun.*, **1,** 19, 1239 (1967).
19. V. Giancotti, F. Giordano, L. Randaccio, and A. Ripamonti, *J. Chem. Soc.*, **1968,** 757, 763.
20. E. E. Flagg and D. L. Schmidt, *J. Inorg. Nucl. Chem.*, in press.
21. R. A. Nyquist, *J. Mol. Structure*, **2,** 111 (1968).
22. R. A. Nyquist, D. L. Schmidt, E. E. Flagg, and R. E. Ridenour, in preparation.
23. A. Snelson, *J. Phys. Chem.*, **71,** 3203 (1967).
24. K. J. Palmer and N. Elliott, *J. Amer. Chem. Soc.*, **60,** 1852 (1938).
25. C. W. Heitsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, **2,** 508 (1963).
26. C. Ercolani, A. Camilii, and G. Satori, *J. Chem. Soc. A*, **1966,** 606.
27. J. A. A. Ketelaar, *Z. Krist.*, **85,** 119 (1933).
28. F. A. Cotton, *Chemical Applications of Group Theory*, Wiley, New York, 1963.
29. G. E. Kimball, *J. Chem. Phys.*, **16,** 727 (1940).
30. E. E. Flagg and D. L. Schmidt, to be published.

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Effects of Metal Salts on Polymerization. Part VII. Radical Polymerization and Spectra of Vinylpyridine in the Presence of Cobaltous Chloride

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Synopsis

The radical polymerizability of vinylpyridines in the presence of cobaltous chloride was studied in DMF solution, and the results were correlated with the spectroscopic data obtained for methanol solution. In general, the behavior of vinylpyridine complexed with cobaltous chloride is qualitatively the same as that of zinc complexes reported previously. The rates of polymerization were enhanced by the addition of cobaltous chloride when 4-vinylpyridine(4-VP) or 2-methyl-5-vinylpyridine(MVP) was the monomer, whereas the polymerization of 2-vinylpyridine(2-VP) was retarded by cobaltous chloride. The monomer reactivity of all the vinylpyridines was also enhanced by complex formation as studied by copolymerization with styrene. The enhancement of reactivity of 4-VP complexed with cobaltous chloride is somewhat smaller than that of the corresponding zinc complex.

INTRODUCTION

In earlier papers of this series,[1,2] the effects of the salts of the IIb group elements on the polymerization of vinylpyridines and on the infrared spectra of the monomers were discussed. Explanation for these salt effects implies the consideration of the nature of π-bonding in the coordination bond formed between vinylpyridine and metal salt. The electronic spectroscopic data of vinylpyridine also indicate the importance of π-bonding in coordination compounds.[3] On the basis of the π-type interaction between metal salt and ligand, a simple model of molecular orbital calculation was attempted.[4] The calculated reactivities and the experimental results are in qualitative but fair agreement. The application of the quantum chemical approach and the electronic spectroscopic data on the π–π^* transition band can successfully elucidate the reactivities of several other metal-complexed vinyl compounds such as acrylonitrile and methyl methacrylate complexed with zinc chloride. Consequently, the π-type interaction between metal salt and ligand seems to be a general feature even if the d-orbitals of metal salt are filled.

There arises a question how a metal ion with filled d-orbitals could bring about π-type interaction with ligands. From the viewpoint of valency state ionization energy, the p_π–p_π interaction is more likely than the d_π–p_π

overlap which is generally considered as the origin of back donation in the coordination compounds of essentially σ-type.[4]

In the expectation that the change of central metal ion from a post-transition metal to a transition metal might cause some change in polymerizability of complexed monomer, the effects of cobaltous chloride on the polymerization of vinylpyridine were studied. The polymerization behaviors is, however, qualitatively the same as that of the zinc complexes reported previously. The different nature of coordination bonding in cobaltous and zinc complexes could not be discussed from the view point of chemical reactivity.

EXPERIMENTAL

Materials

4-Vinylpyridine(4-VP), 2-methyl-5-vinylpyridine (MVP), 2-vinylpyridine (2-VP), and styrene (St) were purified as mentioned previously.[2] *N*,*N*-Dimethylformamide(DMF) was a guaranteed reagent grade and purified by distillation after being dried.

Cobaltous chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) was reagent grade material and used without further purification. When the anhydrous salt was required, the crystallization water was removed by refluxing with thionyl chloride, the excess of thionyl chloride then being removed under reduced pressure (10^{-5} mm Hg). The anhydrous cobaltous salt was divided into small portions and stored in sealed tubes.

Azobisisobutyronitrile(AIBN) as polymerization initiator was recrystallized twice from methanol.

Polymerization and Copolymerization

The polymerization mixture containing the required amounts of monomer, metal salt, initiator, and solvent was bubbled with dry nitrogen gas from A shown in Figure 1 for at least 15 min. Then, the deoxygenated solution in F was introduced into the dilatometer (C) by a positive nitrogen pressure applied at E. The dilatometer was separated at D and placed in a thermostated water bath. Polymerization started immediately without an induction period. Precipitation and elimination of metal salt from polymer were the same as mentioned before.

The composition analysis of copolymer of vinylpyridine with styrene was made by nitrogen analysis and infrared spectroscopy. It was not possible to remove the cobalt salt from the copolymer completely, particularly when the vinylpyridine content in copolymer was high, although the purification of polymer by reprecipitation was repeated. The analysis of copolymer seemed to be influenced by the presence of cobalt salt and consequently the analytical data fluctuated considerably at high vinylpyridine content. When the vinylpyridine content was low, analysis by infrared spectroscopy and nitrogen analysis agreed well. The key bands for analysis by infrared spectroscopy were 1 230 cm^{-1} (4-VP) and 1 010 cm^{-1}

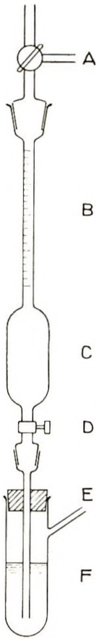

Fig. 1. Apparatus for Polymerization.

(St) for the 4-VP–St system, 990 cm^{-1} (2-VP) and 1 070 cm^{-1} (St) for the 2-VP–St system, and 1 140 cm^{-1} (MVP) and 1 180 cm^{-1} (St) for the MVP–St system, respectively.

Spectroscopy

The complexes between vinylpyridines and $CoCl_2$ were prepared by the dropwise addition of 0.02 mole of the amine to a hot ethanol solution of $CoCl_2$ (0.01 mole). The crystalline complexes were separated after cooling and dried in a desiccator over potassium hydroxide. The analytical data are shown in Table I. The infrared spectra of complexes were measured as KBr disks.

TABLE I

Vinylpyridine Complexes of Cobaltous Chloride

L	Co (calcd), %		Co (found), %
	CoL_4Cl_2	CoL_2Cl_2	
4-VP	10.71	17.32	10.8
2-VP	10.71	17.32	16.2
MVP	9.72	16.00	13.8

Electronic spectroscopy was carried out in methanol solution by use of a Shimadzu SV-50A recording spectrometer.

RESULTS AND DISCUSSION

Homopolymerization of Vinylpyridine

The effects of cobaltous chloride on homopolymerization of vinylpyridines are shown in Figures 2, 3 and 4. The general trend of the salt effect is very much the same as that of the IIb group metal salts,[2] namely, acceleration of the polymerization of 4-VP and MVP, and retardation of the polymerization of 2-VP are observed. The rapid jump of R_p in Figure 2 on the addition of a small amount of cobaltous chloride is in part due to the heterogeneous polymerization system. This heterogeneity of polymerization continues to a much higher ratio of metal salt/4-VP in comparison with the previous zinc salt systems. The first and second formation constants (K_1 and K_2) of pyridine–cobalt complexes are given as log K_1 = 1.14 and log K_2 = 0.4, whereas those of relevant zinc complexes are 1.41 and −0.30.[5] The higher second formation constant of cobaltous ion with pyridine base would favor the crosslinked structure of poly(4-VP)–cobaltous complexes, which is reflected in the formation of the insoluble polymer complexes up to high Co^{II}/4-VP ratio. Heterogeneity is not observed, at least in the polymerization of MVP and 2-VP in DMF. The polymers of MVP and 2-VP are sterically hindered for the intermolecular complex formation bridged by cobaltous ion.

The viscosity of poly(4-VP) and poly(MVP) is also affected in the same way as the R_p when cobaltous chloride is added to the polymerization system. Since the polymerization of styrene is not influenced by cobaltous chloride as shown in Figure 2, the interaction of the metal salt with the

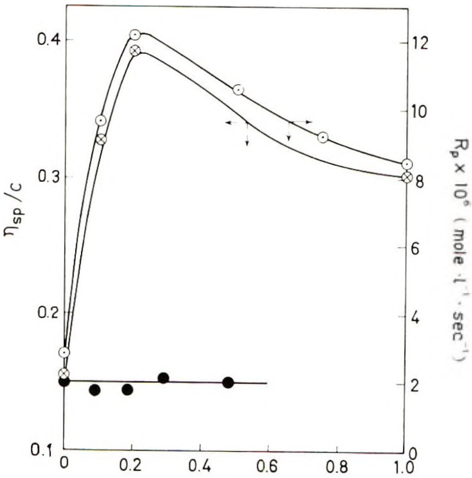

Fig. 2. Polymerization of 4-VP and styrene in the presence of $CoCl_2 \cdot 6H_2O$ at 50°C in DMF: [4-VP] = 0.43M, [AIBN] = $3.66 \times 10^{-2}M$. (○) R_p for 4-VP, (⊗) viscosity of polymer measured in ethanol at 25°C., polymer 0.5 g/100 ml; (●) R_p for styrene, [St] = 0.43M, [AIBN] = $3.66 \times 10^{-2}M$.

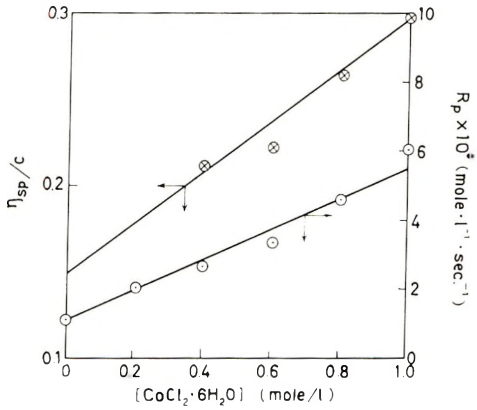

Fig. 3. Polymerization of MVP in the presence of $CoCl_2 \cdot 6H_2O$ at 50°C in DMF: (○) R_p, [MVP] = 0.43 M, [AIBN] = $3.66 \times 10^{-2} M$; (⊗) viscosity of polymer measured in ethanol at 25°C., polymer 0.5 g/100 ml.

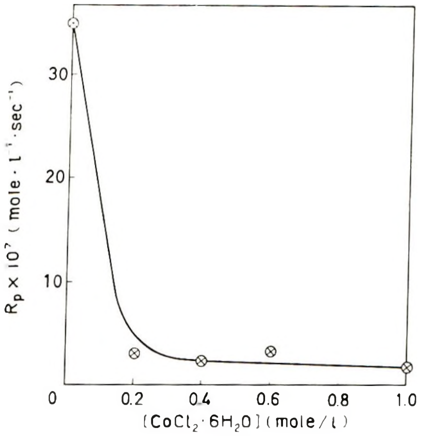

Fig. 4. Polymerization of 2-VP in the presence of $CoCl_2 \cdot 6H_2O$ at 50°C in DMF, [2-VP] = 0.43M, [AIBN] = $1.00 \times 10^{-4} M$.

growing polymer radical is unlikely. Consequently, the salt effect on polymerization of vinylpyridine could be interpreted as a result of complex formation of monomer and probably radical as well, with cobaltous chloride at the basic nitrogen. Such complex formation would influence the rate of propagation. If the cobaltous salt were capable of complexing with the carbon radical at a radical site or influencing the rate of initiation, a salt effect should have been observed in the polymerization of styrene.

Since vinylpyridine would not occupy all of the coordination sites of cobaltous salt, the coordination atmosphere other than the position occupied by the monomer might be influential. However, no difference between anhydrous and hydrous cobaltous salts could be detected from the polymerization experiments shown in Table II. Also the presence of a

TABLE II
Rate of Polymerization of 4-VP in the Presence of Cobaltous Chloride

Metal salt	Salt concn, mole/l.	$R_p \times 10^6$, mole/sec.
$CoCl_2$	1.0	8.34
$CoCl_2 \cdot 6H_2O$	1.0	8.36
None	—	2.86

TABLE III
Absorption Spectra of $CoCl_2$ in DMF

Content of water $[H_2O]/[CoCl_2]$	λmax, mμ	
	Peak I	Peak II
0	532	613
1.2	533	616
3.6	534	615
6.0	533	615
12.1	532	615
In water	515	—

small amount of water affects scarcely the absorption spectra of cobaltous chloride in DMF (Table III).

Other metal salts also had marked effects on polymerization. For example, nickelous chloride accelerates the polymerization of 4-VP very much. This polymerization is, however, heterogeneous even in the saturated solution of nickelous chloride in DMF (0.2*M*). This solubility is certainly too small to bring about a soluble 1:1 complex between poly-(4-VP) and metal salt. The solubility and the redox interaction of metal salt with radicals are the main factors in the suitability of metal salts as complexing agents.

Copolymerization of Vinylpyridine with Styrene

The copolymer composition curves are shown in Figure 5. The observed monomer reactivity ratios are summarized in Table IV, together with the known values for vinylpyridine–St systems. Relatively large errors in r_1

TABLE IV
Monomer Reactivity Ratios of Vinylpyridine–Styrene Systems[a]

M_1	r_2	r_1
4-VP	0.54–0.62	0.52–0.7
4-VP–$CoCl_2 \cdot 6H_2O$	0.21 ± 0.1	1.9 ± 0.25
2-VP	0.55	0.9–1.81
2-VP–$CoCl_2 \cdot 6H_2O$	0.18 ± 0.05	1.33 ± 0.7
MVP	0.6–0.88	0.68–1.19
MVP–$CoCl_2 \cdot 6H_2O$	0.3 ± 0.2	1.80 ± 0.2

[a] The data for free VP–St pair are taken from Ham[7] and those of the complexed VP–St pair are calculated from Figure 6.

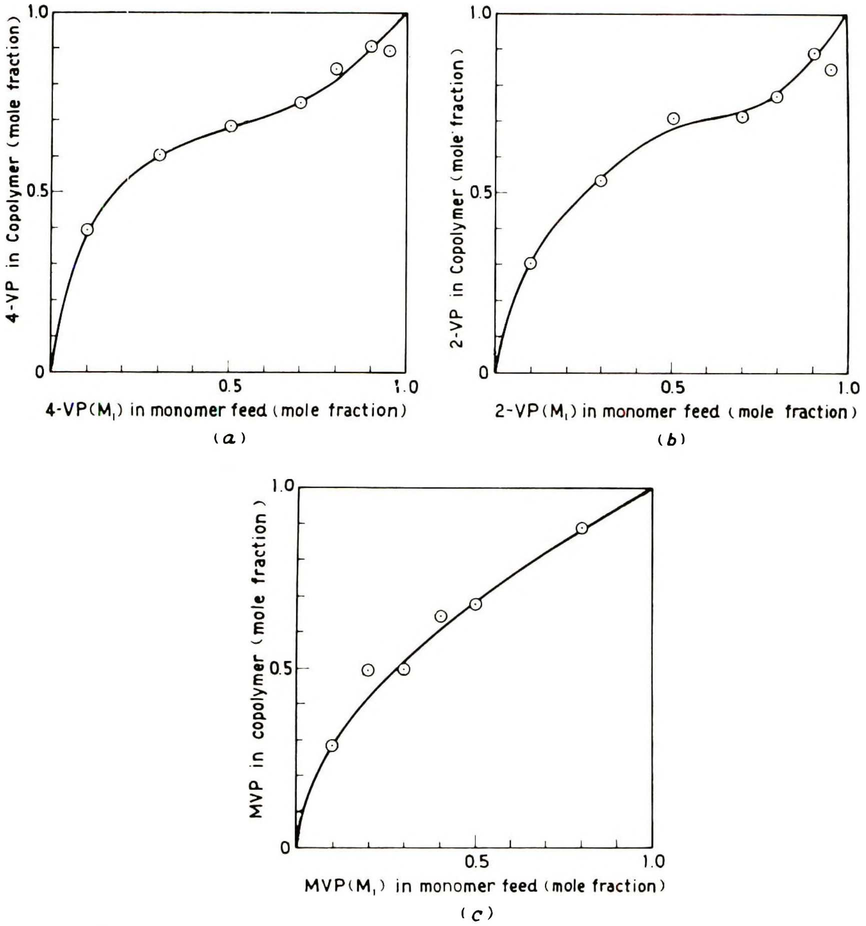

Fig. 5. Copolymerization of 4-VP, 2-VP, and MVP in the presence of $CoCl_2 \cdot 6H_2O$ at 50°C in DMF at [VP] + [St] = 0.86*M*, $[Co^{II}]$ = 1.0 *M*: (*a*) 4VP–St, [AIBN] = $3.66 \times 10^{-2} M$, (*b*) 2-VP–St, [AIBN] = $1.0 \times 10^{-1} M$; (*c*) MVP–St, [AIBN] = $3.66 \times 10^{-2} M$.

seem to be due in part to the technical difficulty of composition analysis but also come from more fundamental matter. Under the present experimental conditions, where the ratio of cobaltous salt to total monomer concentration is fixed, the extent of complex formation would depend on the monomer feed ratio. A basic solvent such as DMF might reduce the stability constants of VP–Co^{II} system due to competitive complex formation of the solvent molecule with cobaltous ion. As judged by the time–conversion curve for the 4-VP–$CoCl_2$ system (Fig. 4), complete complex formation is unlikely even at $[Co^{II}]/[4\text{-VP}]$ greater than 2.

The copolymerization systems shown in Figure 5 would be, in fact, multicomponent systems depending upon the VP content in the feed monomer. Particularly, the contribution of uncomplexed VP seems to increase when the VP content in the monomer feed increases. Consequently, the value of r_2 which is mainly decided by the data obtained at low VP concentration would better correspond to the reactivity of complexed VP.

Reactivities of vinylpyridine indicated by the reciprocal of r_2 are increased, apparently as a result of complex formation, similar to the case of the previously studied zinc complex systems.

Spectroscopy and Reactivity of Complexed Monomers

The stoichiometry of solid complexes of vinylpyridine with cobaltous chloride seems to depend on the structure of monomer. Sterically hindered 2-VP forms only 2:1 complex, whereas four molecules of 4-VP could coordinate to a cobaltous ion. Complexes of 2-VP and 4-VP with cobaltous chloride have been prepared, and it has been reported that the stretching vibration of vinyl group is scarcely influenced by complex formation.[6] Our results on the infrared spectroscopy of the C=C stretching vibration of vinyl group also indicate that the range of fluctuation of the band caused by complex formation is within 1 cm.$^{-1}$.

The electronic spectra of 4-VP in methanol are, however, considerably affected by the addition of cobaltous chloride, as shown in Figure 6. The amount of red shift reaches a saturation value at relatively low concentration of cobaltous chloride, indicating the high stability of 4-VP–Co^{II} complexes in methanol. In comparison with the 4-VP–$ZnCl_2$ system, the value of $\Delta\nu$ is 400 cm^{-1} for the 4-VP–$CoCl_2$ system whereas it is 1450 cm^{-1} for the 4-VP–$Zn(OAc)_2$ system.[3] The smaller interaction of cobaltous ion with the conjugated system of vinylpyridine is shown by both infrared and electronic spectroscopic data.

The discussion above could also be applied to the comparison of reactivities of zinc and cobaltous complexes of 4-VP. The reactivity towards

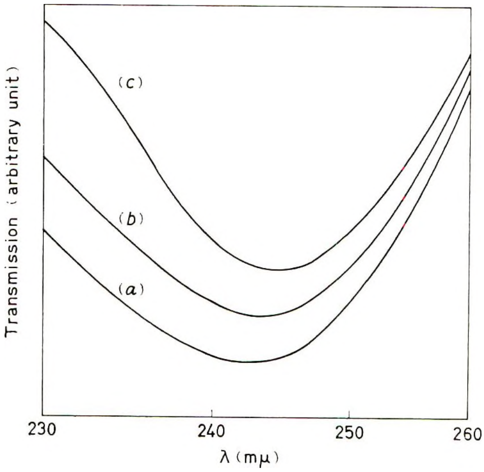

Fig. 6. π-π^* transition spectra of 4-VP in methanol: (*a*) [4-VP] = $2.7 \times 10^{-5}M$, (*b*) [4-VP] = $2.7 \times 10^{-5}M$, [$CoCl_2 \cdot 6H_2O$] = $2.0 \times 10^{-3}M$; (*c*) [4-VP] = $2.7 \times 10^{-5}M$, [$CoCl_2 \cdot 6H_2O$] = $9.1 \times 10^{-3}M$.

TABLE V
Comparison of Reactivities of Cobaltous and Zinc Complexes

Change caused by complex formation	Cobaltous complex	Zinc complex
Shift in the π–π^* transition band of 4-VP	−400 cm^{-1}[a]	−1450 cm^{-1}[b]
Rate of homopolymerization of 4-VP, $R_p^{\text{complex}}/R_p^{\text{free}}$	2.9[c]	5.0[d]
Monomer reactivity of 4-VP, $(1/r_2)^{\text{complex}}/(1/r_2)^{\text{free}}$	2.6[e]	6.8[f]

[a] From Fig. 6.
[b] Data of Tazuke and Okamura.[3]
[c] From Table II.
[d] Data of Tazuke et al.[4]
[e] From Table IV; M_2 is styrene.
[f] Data of Tazuke and Okamura; M_2 is styrene.

styryl radical of 4-VP complexed with $CoCl_2$, as determined by the value of $1/r_2$, is smaller than that of 4-VP complexed with zinc acetate. The smaller conjugation of cobaltous salt with 4-VP corresponds to the smaller activation of monomer. The relevant information is tabulated in Table V.

It is rather striking that only small change is brought about by changing the metal ion from zinc to cobalt. The properties of cobaltous ion other than the presence of empty *d*-orbitals are very much the same as those of zinc ion. The ion radii of Co^{++} and Zn^{++} are almost identical, i.e., 0.72 and 0.74 Å, respectively. From the standpoint of electron affinity, zinc ion would form more stable complexes than cobalt ion. The ligand field stabilization of cobalt complexes, however, adds extra stabilization to the complexes and as a whole, the first stability constants are nearly the same for cobalt and zinc complexes in most cases. The magnitude of the stability constants does not seem to be the major determining factor for the salt effect on polymerization.

The electron affinity of the first transition metal ions which is relevant for the formation of high spin complexes of metal ions should correspond to filling 4*s* and 4*p* orbitals, which seem to be better acceptors than any vacant *d* orbitals. These relevant electron affinities rise steadily from titanium (II) to zinc (II).[8] Consequently, because of its higher electron affinity, zinc (II) would have a stronger influence on the electronic structure of vinylpyridine molecule than cobalt (II). We seek for further examples to confirm the correlation of change in reactivity of vinylpyridine with the electron affinity of complexing metal ions and investigated the salt effects using manganese and nickelous salts. Because of poor solubility of these salts, the polymerization study could not be done under conditions comparable to zinc or cobalt salts.

When labile high spin complexes are formed with the first transition metal ions, the electronic structure of the *d*-shell of metal ions seems to be of minor importance, since the electronic effects of complexing on the ligand reactivities would be largely decided by the electron-accepting character of the 4*s* and 4*p* orbitals. No systematic change of chemical reactivity of ligand was observed when various metal complexes of pyridine were phenylated by a radical mechanism.[9]

References

1. S. Tazuke, N. Sato, and S. Okamura, *J. Polym. Sci. A-1*, **4**, 2461 (1966).
2. S. Tazuke and S. Okamura, *J. Polym. Sci. A-1*, **5**, 1083 (1967).
3. S. Tazuke and S. Okamura, *J. Polym. Sci. B*, **5**, 95 (1967).
4. S. Tazuke, K. Tsuji, T. Yonezawa, and S. Okamura, *J. Phys. Chem.*, **71**, 2957 (1967).
5. *Stability Constants*, compiled by L. G. Sillén and A. E. Martell, Special Publication No. 17, Chemical Society, London, 1964, p. 440.
6. N. H. Agnew and L. F. Larkworthy, *J. Chem. Soc.*, **1965**, 4669.
7. G. E. Ham, *Copolymerization*, Interscience, New York, 1964, pp. 845–863.
8. F. J. G. Rossotti, in *Modern Coordination Chemistry*, J. Lewis and R. G. Wilkins, Ed., Interscience, New York, 1960, p. 42.
9. R. J. Gritter and A. W. Godfrey, *J. Amer. Chem. Soc.*, **86**, 4725 (1964).

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Room-Temperature Polycondensation of β-Amino Acid Derivatives. V.* Synthesis of Hydrophilic Polyamide by the Polycondensation of β-Amino Acid Derivatives

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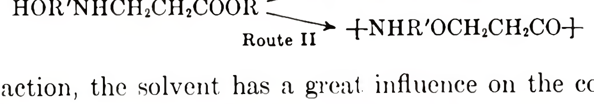
Synopsis

N-(Hydroxyalkyl) β-alanine ester which was obtained from amino alcohol and acrylate yielded polyamide at room temperature in the presence of a basic catalyst. Alkali and alkali earth metal alkoxides had a strong catalytic effect on the room-temperature polycondensation of *N*-(hydroxyethyl)-β-alanine esters. The catalytic activity of metal alkoxides decreased in the order: Li > Na > K > Cs and Ca > Zn > Mg. Aluminum and titanium alkoxide had a weak catalytic effect, while boron (III), tin (IV), antimony (V), and tellurium (VI) alkoxides did not show any catalytic activity for the polycondensation. It was also found that solvent had an effect on the course of the polycondensation of *N*-(hydroxyethyl)-β-alanine esters, and the highest molecular weight polymer was formed only in methanol solution. The solid-phase polycondensation of the low molecular weight prepolymer resulted in a high molecular weight polymer with an inherent viscosity of 1.0 in the presence of a catalytic amount of phosphoric acid. The polymer obtained is hydrophilic and its moisture absorption is more than twice that of nylon 6.

INTRODUCTION

It was previously shown[2-4] that acrylate adds to amino alcohols and polycondensation follows at room temperature in the presence of an alkoxide to form polyamides or polyamide ethers as shown in eq. (1).

$CH_2{=}CHCOOR + NH_2R'OH \rightarrow$



$$\mathrm{HOR'NHCH_2CH_2COOR}\begin{array}{l}\xrightarrow{\text{Route I}}\ +\!\overset{\mathrm{R'OH}}{\overset{|}{\mathrm{N}}}\mathrm{CH_2CH_2CO}\!+\\ \xrightarrow[\text{Route II}]{}\ +\!\mathrm{NHR'OCH_2CH_2CO}\!+\end{array} + \mathrm{ROH} \qquad (1)$$

In this reaction, the solvent has a great influence on the course of the polycondensation. Mainly polyamide is formed in alcohol solution via route I, while polyamide ether is obtained in tetrahydrofuran via route II through rearrangement.[5] The formation of polyamide through the poly-

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* For part IV, see Ogata and Sanui.[1]

condensation between amino and ester groups in alcohol solution was explained on the basis of the increase in the nucleophilicity of the amino group in alcohol, while the formation of polyamide ether in tetrahydrofuran was attributed to the increase in the nucleophilicity of the hydroxyl group in this solution.[1]

In this study, effects of temperature, catalyst, and solvent on the polycondensation of *N*-(hydroxyethyl)-β-alanine esters have been investigated. Also, the thermal polycondensation of a prepolymer having a molecular weight of around 2 000 was carried out in solution or in the solid phase in the presence of various catalysts, in order to obtain a high molecular weight polyamide.

EXPERIMENTAL

Room-Temperature Polycondensation of *N*-(Hydroxyethyl)-β-alanine Methyl Ester

N-(Hydroxyethyl) β-alanine methyl ester, which was obtained from ethanolamine and methyl acrylate,[5] was purified by fractional distillation *in vacuo* and dissolved in methanol at a concentration of 1 mole/l. and 5 mole-% of various metal alkoxides were added to the solution. The polycondensation reaction took place immediately, and a white polymer precipitated gradually on standing at 30°C. The rate of polycondensation in the presence of various catalysts was measured by weighing the polymer precipitated in a given period. The molecular weight of the obtained polymer was determined by an amino end group titration in water or in a 50/50 mixture of methanol and phenol.

N-(Hydroxyethyl)-β-alanine methyl ester was polymerized in the presence of 5 mole-% of lithium methoxide in such solvents as methanol, dioxane, and cyclohexanone or in mixed solvents of these solvents with methanol.

Solution Polycondensation of Poly-*N*-(hydroxyethyl)-β-alanine

Poly-*N*-(hydroxyethyl)-β-alanine with a molecular weight of 1 500–2 000 was heated at 150°C under a nitrogen atmosphere in various solvents in the presence of 1 mole-% of catalysts. The reaction proceeded in a homogeneous phase. The polymer solution was poured into methanol after a given period of heating and the precipitated polymer was collected. The solution viscosity of the polymers in sulfuric acid was measured.

Solid-Phase Polycondensation or Poly-*N*-(hydroxyethyl)-β-alanine

Several acidic catalysts such as H_3PO_4 or $SnCl_4$ were absorbed by the prepolymer with a molecular weight of around 2000 by dipping the prepolymer in a methanol solution of the catalysts and then evaporating the methanol. The solid-phase polycondensation was carried out by heating the prepolymer at 164°C in 2 mm Hg vacuum in the presence of 1 mole-%

of various catalysts. The solution viscosity of the polymers was measured in sulfuric acid. The melting point of the polymers was measured by differential thermal analysis. The moisture absorption of the polymer was measured at 25°C by weighing the vacuum-dried polymer in various relative humidities.

RESULTS AND DISCUSSION

Variables in Room-Temperature Polycondensation

The rate of formation of alcohol-insoluble polymer in the presence of various metal alkoxides is summarized in Figure 1. These results indicate that the catalytic activity of alkali and alkali earth metal alkoxides decreases in the order: Li > Na > K > Cs and Ca > Zn > Mg, respectively. On the other hand, aluminum and titanium alkoxides had a small catalytic activity, while boron (III), tin (IV), antimony (V), and tellurium (VI) alkoxides had no catalytic effect on the polycondensation. It was found for the room-temperature polycondensation that the catalytic effect of alkali metal alkoxides increased with decreasing basicity of the metal, and lithium alkoxide was the most effective catalyst.

In order to elucidate the solvent effect on the polycondensation reaction, *N*-(hydroxyethyl)-β-alanine methyl ester was polymerized at 30°C for 5 days in such solvents as methanol, dioxane, and cyclohexanone. These solvents were effective in increasing the nucleophilicity of amine, hence the reaction of acrylate took place almost exclusively with amine in these solvents.[1]

As can be seen in Table I, the yield of the alcohol-insoluble polyamide was remarkably high only in methanol, and other solvents had almost no effect on the polycondensation. When lithium chloride was dissolved in methanol in the amount of 10 wt-%, the polycondensation reaction pro-

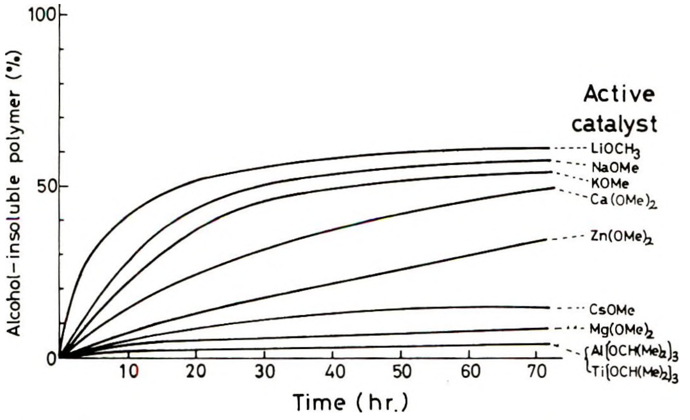


Fig. 1. Rate of formation of alcohol-insoluble polymer from *N*-(hydroxyethyl)-β-alanine methyl ester (1 mole/l.) in the presence of various metal alkoxides in CH_3OH at 30°C, catalyst concentration 5 mole-%.

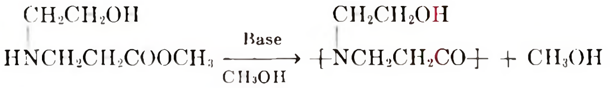
TABLE I
Effect of Solvent on the Polycondensation of N-(Hydroxyethyl)-β-alanine Methyl Ester[a]

Solvent	Temp, °C	Time, hr	Yield, %	MW
Methanol	30	120	68.5	1300
Dioxane	30	120	Trace	—
Cyclohexanone	30	120	Trace	—
Methanol	64	10	93.6	1900
Methanol + LiCl 10 wt-%	66	10	40.0	2400
Dioxane	101	10	2.9	2600
Cyclohexanone	155	10	1.5	—
Cyclohexanone–methanol (20/80)	68	10	6.3	2000
" " (30/70)	69	10	5.3	4700
" " (40/60)	71	10	0.9	—
" " (50/50)	73	10	8.2	3300
Dioxane–methanol (50/50)	69	10	8.5	1700
Water–methanol (50/50)	80	10	5.3	6000

[a] Monomer concn, 1 mole/l.: catalyst, CH_3OLi, 5 mole-%.

ceeded in a homogeneous phase, and a white polymer was precipitated on pouring the solution into an excess of methanol. However, the yield of the alcohol-insoluble polymer was much less than that in the polymerization in methanol alone, although the molecular weight of the polymer was higher.

It was confirmed that all of the alcohol-insoluble polymers had the poly-N-(hydroxyethyl)-β-alanine structure and the polycondensation reaction took place as shown in eq (2).



$$\mathrm{H\overset{\overset{\displaystyle CH_2CH_2OH}{|}}{N}CH_2CH_2COOCH_3} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{Base}} \mathrm{+\!\overset{\overset{\displaystyle CH_2CH_2OH}{|}}{N}CH_2CH_2CO\!+} + \mathrm{CH_3OH} \tag{2}$$

Table I shows also the results of the polycondensation in the mixed solvents of methanol and cyclohexanone, dioxane, or water. It is seen that the polymer yield decreased remarkably when other solvents were added to the methanol solution. In a mixed solvent of water and methanol, polyamide having a molecular weight of about 6000 was obtained in poor yield, and this result may be attributable to solubility of the low molecular weight polymer in water.

From these results, it was found that the room-temperature polycondensation of N-(hydroxyethyl)-β-alanine methyl ester yielded polyamide with a low molecular weight and there was a barrier to the growth of the polymer in the polycondensation reaction. This result can not be explained on the basis of a requirement of a heterogeneous phase for the polycondensation reaction, since the polymer yield decreases in a homogeneous phase, as can be seen by the effect of LiCl or water. The decrease of the polymer yield in a homogeneous phase might be attributed to the equilibrium reaction between amide and ester groups which will be published later,[6] and a high yield of the polymer is obtained only when the polymer is precipitated out of the reaction medium. Therefore, it is essentially difficult to obtain a high molecular weight polymer by the room-temperature polycondensation.

Thermal Polycondensation of Poly-*N*-(hydroxyethyl)-β-alanine

Poly-*N*-(hydroxyethyl)-β-alanine with a molecular weight of 1500 to 2000 was heated at 150°C under a nitrogen atmosphere in various solvents in the presence of various catalysts. The reaction proceeded in a homogeneous solution.

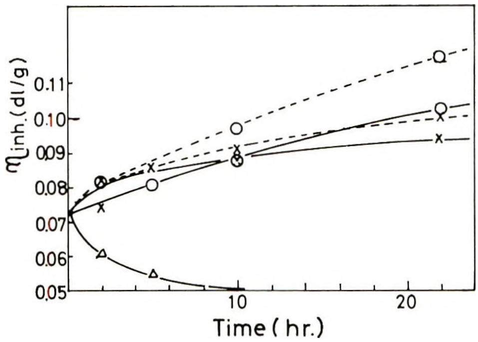


Fig. 2. Solution polycondensation of poly-*N*-(hydroxyethyl)-β-alanine in a homogeneous phase with (——) H_3PO_4 and (- -) $SnCl_4$ catalyst (1 mole-%): (○) HMPA solvent; (×) DMAc solvent with 10 wt-% LiCl; (△) *m*-cresol solvent. Monomer concentration 10g/dl; 150°C.

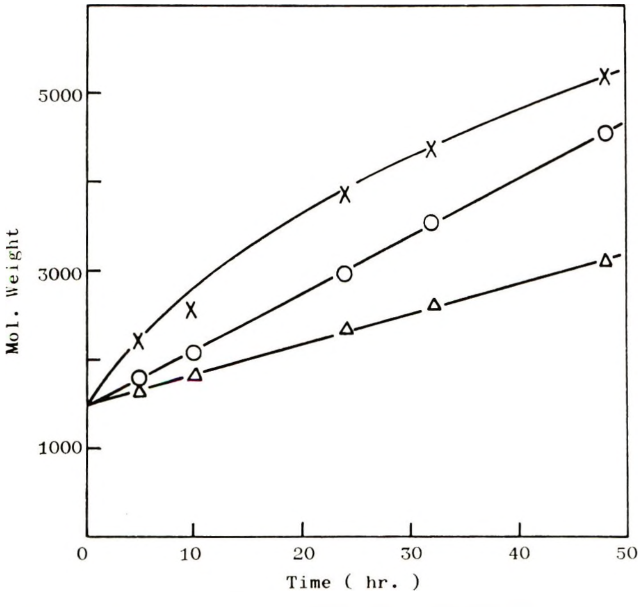


Fig. 3. Solution polycondensation of poly-*N*-(hydroxyethyl)-β-alanine in various monomer concentrations in HMPA at 150°C: (△) 10 g/dl; (○) 20 g/dl; (×) 40 g/dl.

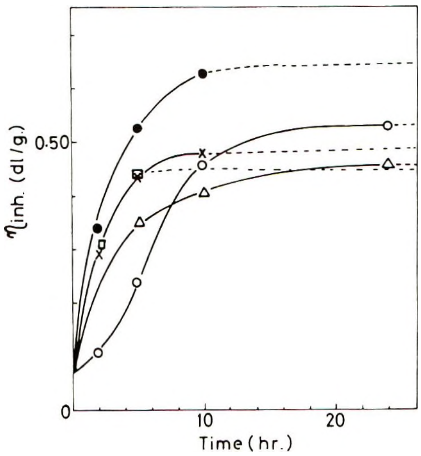


Fig. 4. Rate of solid-phase polycondensation of poly-*N*-(hydroxyethyl)-β-alanine with various catalysts: (○) none; (△) CH_3OLi; (×) $SnCl_4$; (□) $TiCl_4$; (●) H_3PO_4. Reaction conditions: 164°C, 2 mm Hg, catalyst concentration 1 mole/l.

It is seen in Figure 2 that the inherent viscosity of the polymer increased gradually on heating in dimethylacetamide containing 10 wt-% of LiCl or in hexamethylphosphoramide (HMPA) in the presence of catalytic amount of H_3PO_4 or $SnCl_4$, while the polymer was decomposed gradually by a long heating in *m*-cresol.

The solution polycondensation of the prepolymer in HMPA was carried out at various concentrations of the prepolymer. The results are shown in Figure 3, where it is seen that the molecular weight of the polymer increases with increasing prepolymer concentration in the solution. However, the molecular weight of the polymer did not exceed 5300, even after heating the solution for 48 hr at 150°C.

Solid-phase polycondensation of the prepolymer was carried out at various temperatures. The highest molecular weight of the polymer was obtained by heating the prepolymer at 164°C *in vacuo*.

The increase with time in the inherent viscosity of the polymer in the presence of various catalysts is shown in Figure 4. It was found that phosphoric acid is an effective catalyst for the solid-phase polycondensation of poly-*N*-(hydroxyethyl)-β-alanine, and a polymer of relatively high molecular weight having an inherent viscosity of 0.63 was obtained by using the prepolymer with a molecular weight of 2000. However, prolonged heating in the presence of acidic catalysts caused crosslinking of the polymer, and the polymer hardly dissolved in sulfuric acid. $SnCl_4$ caused especially rapid crosslinking of the polymer.

Table II summarizes the results of the solid-phase polycondensation just before the crosslinking reaction occurs. The inherent viscosity of the resulting polyamide increased to 1.0 in the presence of H_3PO_4 catalyst when the prepolymer with a molecular weight of 4000 was used as starting material.

TABLE II

Solid-Phase Polycondensation of Poly-N-(Hydroxyethyl)-β-alanine[a]

						Solubility[c]		
Prepolymer MW	Catalyst (1 mole-%)	Final time, hr	Final η_{inh}, dl/g[b]	Mp, °C	Hot m-cresol	Hot HMPA	Hot DMAc with LiCl 10 wt-%	Concentrated H_2SO_4
2000	None	24	0.53	200–208	Sw	I	I	S
2000	CH_3OLi	24	0.46	185–195	Sw	I	I	S
2000	$SnCl_4$	10	0.48	188–197	Sw	I	I	S
2000	$TiCl_4$	5	0.44	190–200	Sw	I	I	S
2000	H_3PO_4	10	0.63	190–215	Sw	I	I	S
2000	BF_3OEt_2	10	0.49	190–205	Sw	I	I	S
4000	H_3PO_4	10	1.00	196–205	Sw	I	I	S

[a] Reaction conditions: 164°C, 2 mm Hg.

[b] In H_2SO_4 at 30°C.

[c] S = soluble, I = insoluble; Sw = swelling.

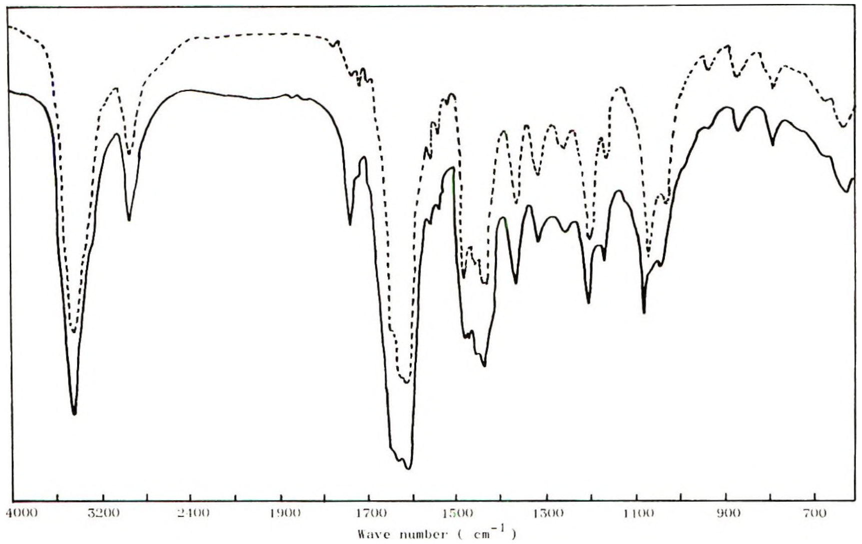
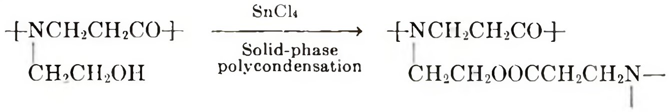


Fig. 5. Infrared spectra: (- -) prepolymer; (——) polymer obtained by solid-phase polycondensation in the presence of $SnCl_4$ for 24 hr.

Figure 5 shows the infrared spectra of the prepolymer and the highly crosslinked polymer which was obtained by solid-phase polycondensation in the presence of $SnCl_4$. The infrared spectrum of the crosslinked polymer showed a absorption peak in the range of 1 720–1 730 cm^{-1} assigned to the ester carbonyl group (Fig. 5). Therefore, it is presumed that the crosslinking reaction takes place between pendant hydroxyl and ester groups [eq (3)].

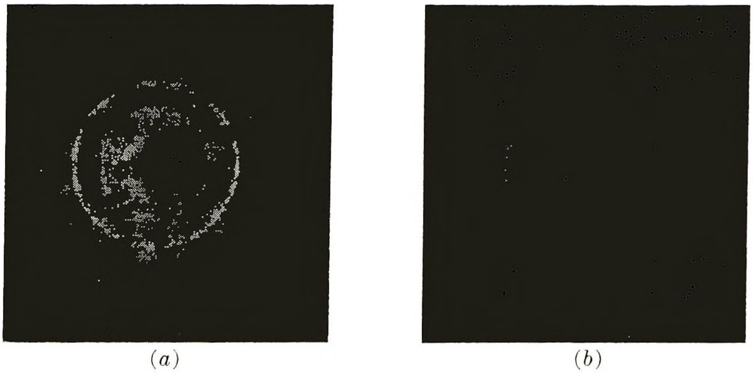


$$\underset{\displaystyle CH_2CH_2OH}{\underset{|}{\text{+}NCH_2CH_2CO\text{+}}} \xrightarrow[\text{Solid-phase polycondensation}]{SnCl_4} \underset{\displaystyle CH_2CH_2OOCCH_2CH_2N\text{—}}{\underset{|}{\text{+}NCH_2CH_2CO\text{+}}} \qquad (3)$$

Properties of Poly-*N*-(hydroxyethyl)-β-alanine

As is seen in Table II, the melting point of the polymer is in the range 190–200°C. Polymer having a molecular weight of below 2 000 is soluble in water, DMF, DMAc, HMPA, or formic acid, while polymer with an inherent viscosity above 0.2 does not dissolve in any of the common organic solvents, including DMF, DMAc, DMSO, HMPA, and CF_3COOH. The high polymer dissolves only in concentrated sulfuric acid. Differential thermal analysis of the polymer showed that the polymer decomposed at temperature of above 230°C. Therefore, it was very difficult to spin the polymer to fiber by the melt-spinning method.

The x-ray diffraction pattern of poly-*N*-(hydroxyethyl)-β-alanine showed that the polymer had a highly crystalline structure, as can be seen in Figure 6. Therefore, the poor solubility of the polymer in organic solvents might be attributed to the highly crystalline structure. This highly crystalline structure of the polymer is unexpected, since *N*-hydroxyalkylated nylon 6



(a) (b)

Fig. 6. X-ray diffraction pattern of the polymer: (a) MW = 4000; (b) η_{inh} = 1.0.

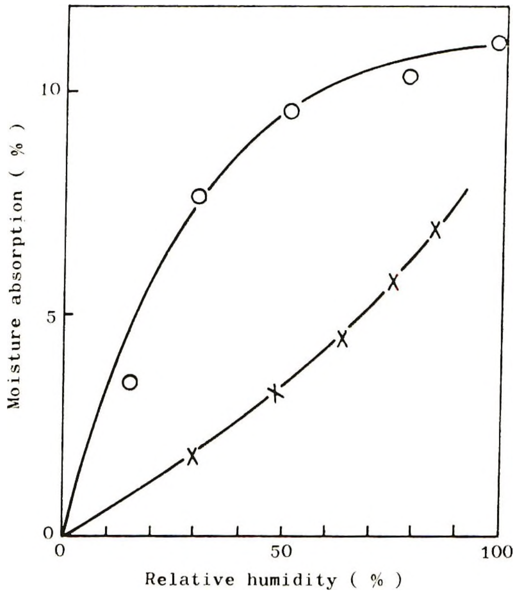


Fig. 7. Moisture absorption of the polymer at 25°C: (○) poly-*N*-(hydroxyethyl)-β-alanine; (×) nylon 6.

or 66 has an amorphous structure. We wish to study this crystalline structure further.

The moisture absorption of the polymer is very high, presumably owing to the pendant hydroxyethyl group, as shown in Figure 7 and the moisture absorption of the polymer is around 10% at 60% RH at 25°C, which is twice that of nylon 6.

Further investigations on the physical properties of these highly crystalline polymers are in progress and the results will be reported in the near future.

The authors wish to thank Dr. Y. Kinoshita of Toyo Rayon Co. for measuring the X-ray diffraction of the polymer.

References

1. K. Sanui and N. Ogata, *Bull. Chem. Soc. Japan*, **41**, 1968 (1968).
2. N. Ogata and T. Asahara, *J. Polym. Sci. B*, **4**, 273 (1966).
3. N. Ogata and Y. Asahara, *Bull. Chem. Soc. Japan*, **39**, 1486 (1966).
4. N. Ogata, T. Asahara, and K. Sanui, *J. Polym. Sci. A-1*, **6**, 1195 (1968).
5. K. Sanui and N. Ogata, *Kogyo Kagaku Zasshi*, **70**, 2051 (1967).
6. N. Ogata and K. Sanui, *J. Polym. Sci.*, in press.

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New Method for Preparing Saturated and Unsaturated Aliphatic Polyurethanes

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Synopsis

Saturated and unsaturated aliphatic polyurethane were obtained from three different routes. In route 1, 1,4-dichloro-2-butene, sodium cyanate, and methanol were reacted to give dimethyl 2-butene-1,4-dicarbamate. This is hydrogenated easily to give dimethyl butane-1,4-dicarbamate. Ester exchange reaction of this compound with glycol gave saturated aliphatic polyurethane. In another procedure, route 2, 1,4-dichloro-2-butene, sodium cyanate and excess glycol were reacted to give bis(ω-hydroxyalkyl)-2-butene-1,4-dicarbamate. This was hydrogenated to give bis(ω-hydroxyalkyl)-butane-1,4-dicarbamate. A glycol elimination reaction gave poly(polymethylene tetramethylenedicarbamate). By route 3, 1,4-dichloro-2-butene, sodium cyanate, and glycol were reacted to give poly(polymethylene 2-butene-1,4-dicarbamate), a new unsaturated aliphatic polyurethane.

INTRODUCTION

Polyurethanes can be usually obtained by two methods.[1] One method is the polyaddition reaction of diisocyanate with diol. The other is the polycondensation reaction of glycol bis(chloroformate) with diamine. Because diisocyanate is obtained from diamine and phosgene, diamine is a necessary raw material for both the above methods.

A new method for preparing saturated and unsaturated polyurethanes without using diamine has been described in a preliminary report.[2] The present paper is a detailed report of the method. The starting materials are 1,4-dichloro-2-butene, diols, and alkali cyanate.

The reaction of alkali halide and alkali cyanate is well known.

Himel and Richards[3] and Graham[4] reported the preparation of tetramethylene diisocyanate from 1,4-dichlorobutane and sodium cyanate, but these patents are ambiguous because of the reason mentioned in the previous report.[2] Kitano and Fukui[5] reported the preparation of *n*-alkyl isocyanate from alkyl bromide and potassium cyanate and *sec*-alkyl isocyanate from *sec*-alkyl chloride and potassium cyanate. Zenner et al.[6] reported the preparation of methoxymethyl isocyanate from chloromethyl methyl ether and sodium cyanate. The synthesis of carbamate from alkyl

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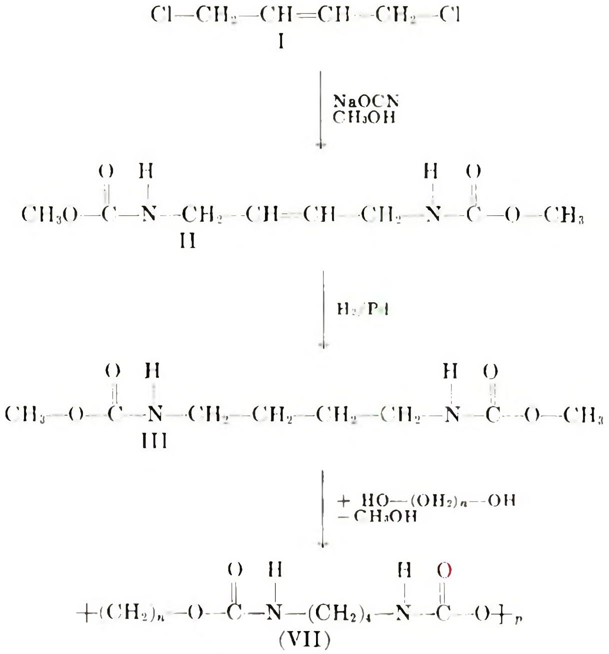
* Toyo Koatsu Industries Inc., is now named Mitsui-Toatsu Chemicals Inc.

halide, alkali cyanate and alcohol was first demonstrated by Kaiser[7] and investigated in more detail by Nagasawa et al.[8] Recently Argabright et al.[9] reported several new carbamates, including the diethyl 2-butene-1,4-dicarbamate, and studied this reaction kinetically. Fukui and Kitano[10] reported the preparation of isocyanurate from alkyl bromide and alkali cyanate.

1,4-Dichloro-2-butene is obtained easily from butadiene and chlorine. It is used as an intermediate for the preparation of chloroprene or hexamethylenediamine. Therefore it is cheap enough to be used as a starting material for the preparation of carbamates or polyurethanes.

When 1,4-dichloro-2-butene is heated with sodium cyanate, 1,4-diisocyanato-2-butene should be easily formed; unfortunately, 1,4-diisocyanato-2-butene is not stable enough to permit its isolation under the reaction conditions giving isocyanurate. Therefore the reaction was carried out in alcohol or glycol. With a case of alcohol, unsaturated carbamate was obtained; in the case of glycol, unsaturated polyurethane was obtained.

As shown in the previous report,[2] the polyurethanes can be obtained by three different routes. Route 1 is shown in Scheme 1.



$$\mathrm{Cl{-}CH_2{-}CH{=}CH{-}CH_2{-}Cl}\quad \text{I}$$

$$\Big\downarrow\ \mathrm{NaOCN},\ \mathrm{CH_3OH}$$

$$\mathrm{CH_3O{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{N}{-}CH_2{-}CH{=}CH{-}CH_2{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_3}\quad \text{II}$$

$$\Big\downarrow\ \mathrm{H_2/Pd}$$

$$\mathrm{CH_3{-}O{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{N}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_3}\quad \text{III}$$

$$\Big\downarrow\ \begin{matrix}+\ \mathrm{HO{-}(CH_2)_n{-}OH}\\ -\ \mathrm{CH_3OH}\end{matrix}$$

$$\mathrm{+\!\!\!\!-(CH_2)_n{-}O{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{N}{-}(CH_2)_4{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}O\!-\!\!\!\!+_p}$$

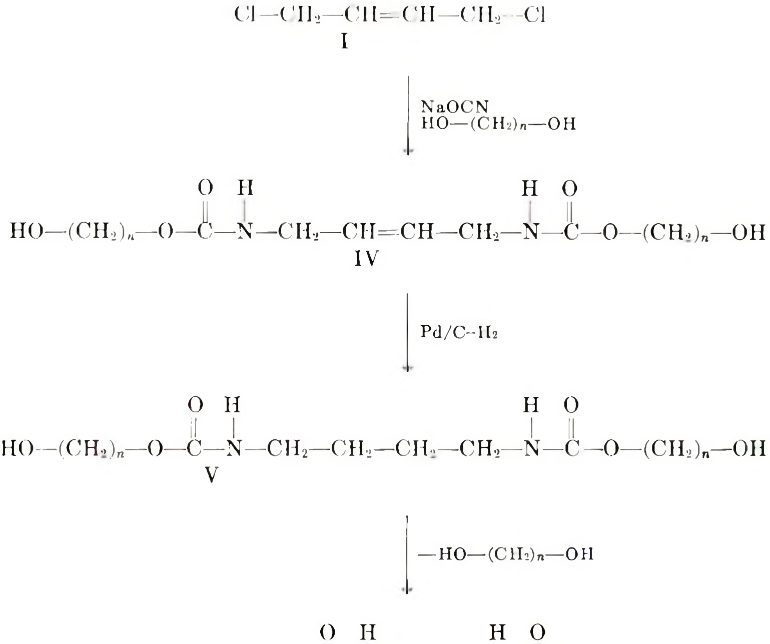
(VII)

Scheme 1. Route 1.

In a typical reaction, *trans*-1,4-dichloro-2-butene (I), sodium cyanate, and methanol are reacted in dimethylformamide (DMF) at reflux temperature, usually 93–97°C, for about 15 hr. Dimethyl *trans*-2-butene-1,4-dicarbamate (II), mp 134°C, is obtained. Siefken[11] reported the preparation of this compound from an unidentified 1,4-diisocyanato-2-butene, but no details were given. Dimethyl *trans*-2-butene-1,4-dicarbamate is easily hydrogenated with Pd/C-H_2 (700 psi) in methanol at room temperature, giving dimethyl butane-1,4-dicarbamate (III), mp 127°C. The infrared spectrum of III is substantially the same as that of the authentic sample obtained from tetramethylene diisocyanate and methanol.

The ester exchange reaction of III with glycol is a known reaction, reported by Murahashi and Nakanishi[12] and German chemists[13] about 25 years ago. The reaction of dimethyl butane-1,4-dicarbamate with glycol is not an easy reaction, however. Some of the glycols, such as 1,2-ethylene glycol and 1,4-butanediol, gave only low molecular weight polymers. 1,6-Hexamethylenediol gave a high molecular weight polymer.

Route 2 is a synthetic route to obtain polyurethane through the reactions shown in Scheme 2.



$$Cl{-}CH_2{-}CH{=}CH{-}CH_2{-}Cl \quad \text{I}$$

$$\xrightarrow[\text{HO—(CH}_2)_n\text{—OH}]{\text{NaOCN}}$$

$$HO{-}(CH_2)_n{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}CH_2{-}CH{=}CH{-}CH_2{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}(CH_2)_n{-}OH \quad \text{IV}$$

$$\xrightarrow{\text{Pd/C–H}_2}$$

$$HO{-}(CH_2)_n{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}(CH_2)_n{-}OH \quad \text{V}$$

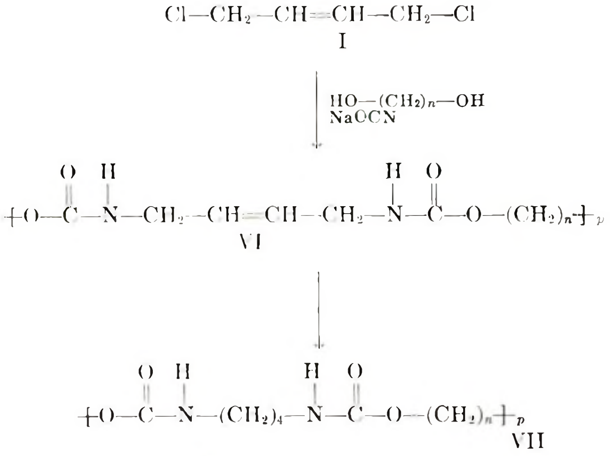
$$\xrightarrow{-\text{HO—(CH}_2)_n\text{—OH}}$$

$$\left[(CH_2)_n{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}(CH_2)_4{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O\right]_p \quad \text{VII}$$

Scheme 2. Route 2.

The *trans*-1,4-dichloro-2-butene, sodium cyanate, and excess glycol are reacted in DMF at 120°C for 4 hr. The bis (ω-hydroxyalkyl)-2-butene-1,4-dicarbamates (IV) obtained are hydrogenated with Pd/C-H_2 (700 psi) in methanol at room temperature. Bis(ω-hydroxyalkyl)-butane-1,4-dicarbamates V were obtained quantitatively. These dicarbamates (V) were heated at 180–190°C under reduced pressure to yield poly(polymethylene tetramethylenedicarbamate) (VII).

Route 3 is a synthetic route to obtain polyurethane through the path shown in Scheme 3.



Scheme 3. Route 3.

The *trans*-1,4-dichloro-2-butene, sodium cyanate, and glycol were heated in DMF at 120°C for 3 hr. After separating the inorganic material and solvent, the residue was heated from 25 to 150°C in 2 hr under vacuum and at 150–155°C/0.01 mm Hg for 3 hr. Unsaturated aliphatic polyurethane (VI) was obtained; this can be hydrogenated easily with Pd/C-H_2 at room temperature to give poly(polymethylene tetramethylenedicarbamate) (VII).

The saturated and unsaturated aliphatic polyurethanes and intermediate products mentioned above were all characterized by NMR and infrared spectra and elemental analyses.

EXPERIMENTAL

Reagents

DMF. Commercial reagent was refluxed with phosphorus pentoxide for 2 hr and distilled; the heart cut was employed, bp 153°C.

***trans*-1,4-Dichloro-2-butene.** This was obtained from Tokyo Kasei, E.P. grade, and distilled, bp 51°C/18 mm Hg.

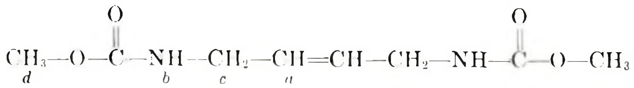
Sodium Cyanate. This was obtained from Kishida Chemical, CP grade, and was used without further purification.

Route 1.

Dimethyl *trans*-2-butene-1,4-dicarbamate (II). Sodium cyanate (49 g 0.768 mole) and 100 ml of DMF were heated at 70°C with stirring for 30 min. To this mixture, 30.4 g (0.96 mole) of methanol was added all at one time. Then 40.0 g (0.32 mole) of *trans*-1,4-dichloro-2-butene was added from a dropping funnel in 30 min. The reaction was continued for 5 hr at 105°C (bath temp), 96°C (inner temp); 6.35 g (0.1 mole) of sodium cyanate was added and the heating was continued for an additional 10 hr. At this time no 1,4-dichloro-2-butene was detected by gas chromatography. After cooling, the inorganic salts were filtered and washed with DMF. The combined filtrate was vacuum-distilled to remove unreacted starting material and solvent. The residue was triturated with chloroform and filtered. Evaporation of chloroform gave 42.1 g (65.0 %) of dimethyl *trans*-2-butene-1,4-dicarbamate. Small amount of it was recrystallized from methanol–petroleum ether (1:5) and then subjected to vacuum sublimation at 150°C/0.1 mm Hg, mp 134°C.

ANAL. Calcd. for $C_8H_{14}N_2O_4$: C, 47.56%; H, 6.98%; N, 13.87%. Found: C, 47.17%; H, 7.07%; N, 13.98%.

The NMR spectrum ($CDCl_3$) of II gives signals at τ 4.36 (1H), 5.10 (1H), 6.24 (2H), and 6.35 (3H), corresponding to hydrogens *a*, *b*, *c*, and *d*, respectively.



$$\underset{d}{CH_3}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{b}{NH}{-}\underset{c}{CH_2}{-}\underset{a}{CH}{=}CH{-}CH_2{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_3$$

Dimethyl Butane-1,4-dicarbamate (III). Dimethyl *trans*-2-butene-1,4-dicarbamate (5.6 g, 0.0278 mole) was dissolved in 35 ml of methanol. A mixture of 0.2 g of 5% palladium on carbon was stirred with hydrogen gas (700 psi) in an autoclave at room temperature. The depression of hydrogen pressure stopped in 10 min. After filtering off of the catalyst, the solvent was distilled off. The residue, 5.0 g (88.5%), was dimethyl butane-1,4-dicarbamate (IV), mp 127°C (recrystallized from methanol). The infrared spectrum of III is substantially the same as that of the authentic sample obtained from tetramethylene diisocyanate and methanol. The mixed melting point is 127°C.

Poly(hexamethylene tetramethylenedicarbamate) (VII, *n* = 6) from Dimethyl Butane-1,4-dicarbamate (II). 2.0 g (0.0098 mole) of dimethyl butane-1,4-dicarbamate, and 4.63 g (0.0392 mole) of 1,6-hexandiol were placed in a small reaction tube having a capillary tube and one outlet. A stream of purified nitrogen was bubbled through the capillary tube throughout the reaction. The outlet was connected to the receiver, which was cooled at −78°C. The receiver was connected to a calcium chloride tube, which was either open to the air or connected to a vacuum pump. The reaction mixture was heated at 170°C/760 mm Hg for 2 hr, 198–200°C/760 mm Hg for 9 hr, 180–183°C/760–2 mm Hg for 0.5 hr, 180°C/2–0.14 mm Hg for 0.5 hr, 190°C/0.1 mm Hg for 5 hr, 195–200°C/0.1 mm Hg for 1 hr. At this point, a small amount of sample was taken out and found to be unspinnable. The main reaction mixture was further heated at 200°C/0.1 mm Hg for 4 hr. An aliquot taken at this time was somewhat spinnable and had an inherent viscosity of 0.25 dl/g.* The reaction mixture was heated further at 205–210°C/0.1 mm Hg for 2 hr. An aliquot taken at this time was spinnable and had an inherent viscosity of 0.32 dl/g. The mixture was finally heated at 205–210°C/0.1 mm Hg for 4 hr more. Dur-

* All inherent viscosities in this report were measured with 0.05 g polymer in 10 ml *m*-cresol at 30°C.

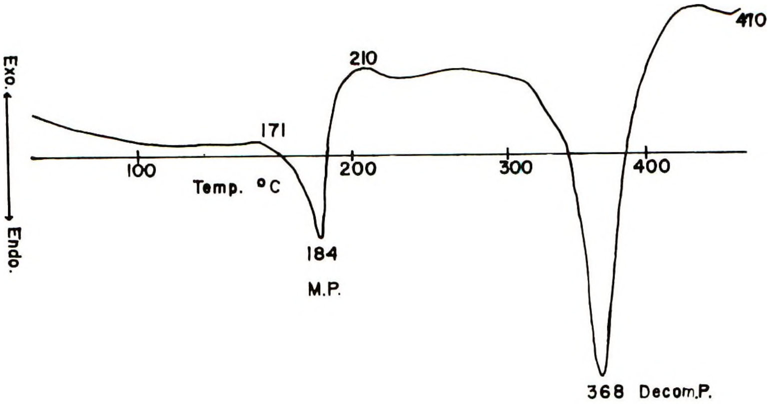


Fig. 1. DTA of poly(hexamethylene tetramethylenedicarbamate).

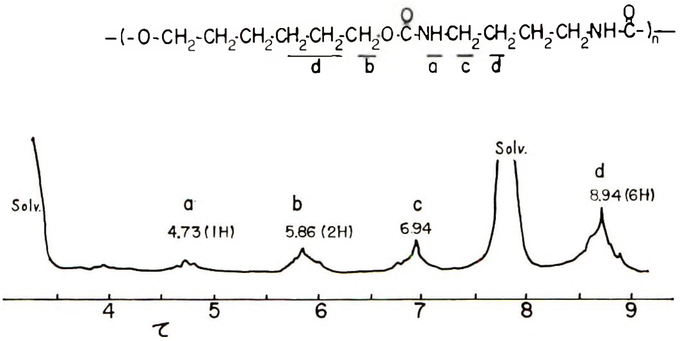
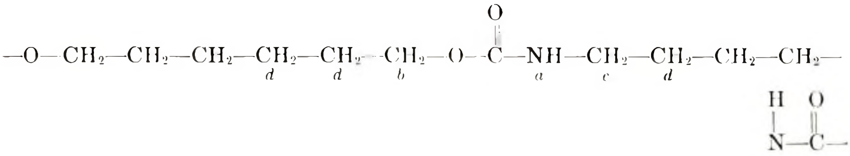


Fig. 2. NMR spectrum of poly(hexamethylene tetramethylene dicarbamate) in *m*-cresol at 45°C.

ing this time the viscosity of the heated solution increased further. The viscous substance obtained was an easily spinnable polymer. The yield of poly(hexamethylene tetramethylenedicarbamate) (VII, $n = 6$) was 2.42 g (95.6%). The differential thermal analysis (DTA) curve of the polymer is shown in Figure 1, mp 184°C,† decomposition point 368°C (DTA).

ANAL. Calcd. for $C_6H_{11}NO_2$; C, 55.82%; H, 8.53%; N, 10.85%. Found: C, 55.57%, H, 8.50; N, 10.59%.

The inherent viscosity is 0.56 dl/g. The NMR spectrum (*m*-cresol) (Fig. 2) shows signals at τ 4.73 (1 H), 5.86 (2 H), 6.96 (2 H), and 8.74 (6 H) corresponding to hydrogens *a*, *b*, *c*, and *d*, respectively.



$$-O-CH_2-CH_2-\underset{d}{CH_2}-\underset{d}{CH_2}-\underset{b}{CH_2}-O-\overset{O}{\overset{\|}{C}}-\underset{a}{NH}-\underset{c}{CH_2}-\underset{d}{CH_2}-CH_2-CH_2-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-$$

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† Hoshino and Iwakura[14] have synthesized this substance from tetramethylene diisocyanate and 1,6-hexanediol, mp 189–190°C. The difference of melting points may come from a difference in molecular weight and also may be due to the different melting point measuring methods.

Poly(ethylene Tetramethylenedicarbamate) (VI, *n* = 2). Dimethyl butane-1,4-dicarbamate (3.06 g, 0.015 mole), ethylene glycol (0.93 g, 0.015 mole), and 40 mg of antimony trioxide were heated at 170°C for 6 hr and at 200°C for 2 hr, at 150°C/0.6 mm Hg for 1 hr. An aliquot removed at this point showed inspinable polymer, mp 195–199°C inherent viscosity 0.2 dl/g. The reaction mixture was heated further with 0.1 g of tetramethylene diisocyanate at 180°C for 1 hr and at 210°C for 2 hr. The 2 g of polymer obtained was mostly insoluble in *m*-cresol.

ANAL. Calcd for $C_4H_7NO_2$: C, 47.50%; H, 6.97%; N, 13.90%. Found: C, 48.09%; H, 9.32%; N, 14.62%.

Dimethyl butane-1,4-dicarbamate (3.06 g, 0.015 mole), ethylene glycol (0.93 g, 0.015 mole), 4 mg zinc acetate, and 4 mg calcium acetate were heated at 170°C for 18 hr, at 170°C/17 mm Hg for 3 hr, and then at 180–185°C/0.4–0.1 mm Hg for 1 hr. Polymer was obtained in 2 g (66%) yield; softening point 300–310°C; insoluble in *m*-cresol.

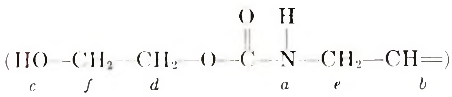
ANAL. Calcd for $C_4H_7NO_2$: C, 47.50%; H, 6.97%; N, 13.90%. Found: C, 51.89%; H, 7.94%; N, 21.06%.

Route 2

Bis (β-hydroxyethyl)-2-butene-1,4-dicarbamate (IV, *n* = 2). Sodium cyanate (60 g, 1.0 mole) and 100 ml DMF were heated at 70°C with stirring, then 62 g (1.0 mole) ethylene glycol was added. Then *trans*-1,4-dichloro-2-butene (50 g, 0.4 mole) was added in 1 hr, the reaction mixture being heated at 103°C. Heating gas continued at 115°C for another 30 min. When the bath temperature reached 125°C, the temperature of the reaction mixture suddenly rose to 140°C; the oil bath was taken off, but the temperature of the reaction mixture attained a maximum of 153°C in 8 min. The temperature dropped gradually, and the reaction mixture was allowed to stand overnight. No *trans*-1,4-dichloro-2-butene was detected in the reaction mixture by gas chromatography. The inorganic salts were filtered off and washed with DMF. The combined filtrate was vacuum-distilled to remove unreacted ethylene glycol and solvent. The final distillation was at 80°C/0.01 mm Hg. Bis(β-hydroxyethyl)-2-butene-1,4-dicarbamate (101 g, 98.6%) was obtained as a viscous residue.

ANAL. Calcd for $C_{10}H_{18}N_2O_6$: C, 45.80%; H, 6.91%; N, 10.68%. Found: C, 46.20%; H, 7.22%; N, 11.68%.

The infrared spectrum of this compound is shown in Figure 3. Characteristic peaks are 3300 (—OH), 1700 (C=O), 1270 (ester C—O—C), and 975 cm^{-1} (*trans* double bond). NMR spectrum of this compound is shown in Figure 4. Signals at τ 4.25 (1H), 4.5 (1H), 5.45 (1H), 5.9 (2H), and 6.3–6.5 (4H) correspond to hydrogens *a*, *b*, *c*, *d*, *e*, and *f*, respectively.



$$(\underset{c}{HO}—\underset{f}{CH_2}—\underset{d}{CH_2}—O—\overset{\overset{\displaystyle O}{\|}}{C}—\underset{a}{\overset{\overset{\displaystyle H}{|}}{N}}—\underset{e}{CH_2}—\underset{b}{CH}=)_2$$

IV, *n* = 2

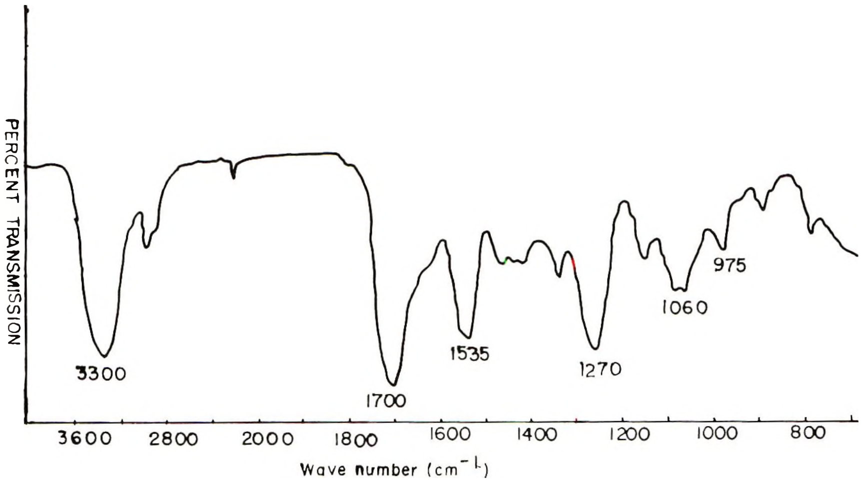


Fig. 3. Infrared spectrum of bis(β-hydroxyethyl)-2-butene-1,4-dicarbamate.

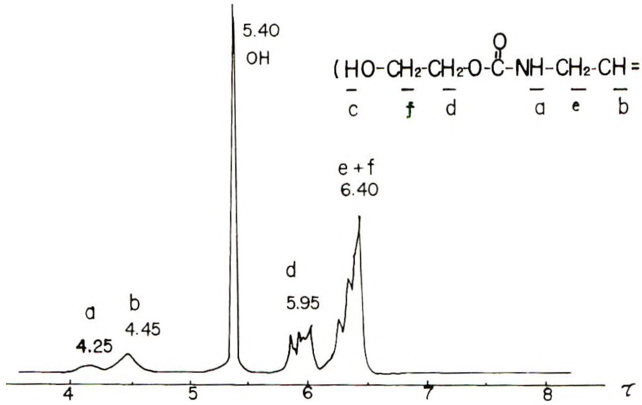
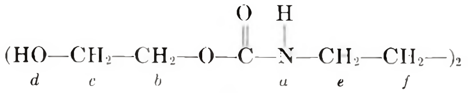


Fig. 4. NMR spectrum of bis(β-hydroxyethyl)-2-butene-1,4-dicarbamate in D_2O at 25°C.

Bis(β-hydroxyethyl)-butene-1,4-dicarbamate (**V**, n = **2**). Bis(β-hydroxyethyl)-2-butene-1,4-dicarbamate (101.0 g) was hydrogenated with Pd/C–H_2 (700 psi) in methanol at room temperature. The reaction was completed in 1.5 hr, yielding 101.5 g (99.8%) of bis(β-hydroxyethyl)butane-1,4-dicarbamate. The 978 cm^{-1} absorption due to *trans* double bond of the starting material disappeared completely, indicating that the hydrogenation was complete. Characteristic infrared peaks were at 3310 (—OH), 1698 (C═O), and 1260 cm^{-1} (ester C—O—C). The NMR spectrum, shown in Figure 5, shows signals at τ 4.05 (1H), 5.95 (2H), 6.38 (2H), 6.45 (1H), 6.95 (2H), and 8.56 (2H) corresponding hydrogens *a*, *b*, *c*, *d*, *e*, and *f*, respectively.



$$(\underset{d}{\mathrm{HO}}{-}\underset{c}{\mathrm{CH_2}}{-}\underset{b}{\mathrm{CH_2}}{-}\mathrm{O}{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\underset{a}{\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}}{-}\underset{e}{\mathrm{CH_2}}{-}\underset{f}{\mathrm{CH_2}}{-})_2$$

V, n = 2

Bis(δ-hydroxybutyl)-2-butene-1,4-dicarbamate (IV, *n* = 4). Sodium cyanate (60 g, 1.0 mole), 1,4-butanediol (90 g, 1.0 mole), and *trans*-1,4-dichloro-2-butene (50 g, 0.4 mole) were reacted in a similar manner as ethylene glycol; 123 g (96.5%) bis(δ-hydroxybutyl)-2-butene-1,4-dicarbamate was obtained as a viscous liquid. Characteristic infrared peaks were found at 3330 (—OH), 2950, 2880 (—CH_2—), 1700 (C=O), 1265 (ester C—O—C), and 978 cm^{-1} (*trans* double bond).

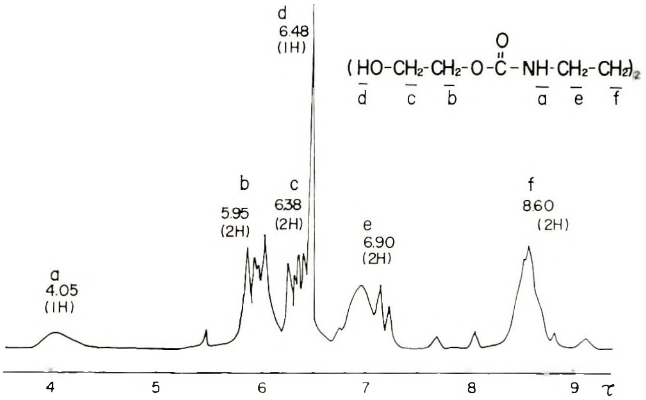
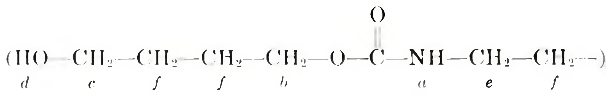


Fig. 5. NMR spectrum of bis(β-hydroxyethyl) butane-1,4-dicarbamate, neat, at 25°C.

Bis(δ-hydroxybutyl)-butane-1,4-dicarbamate (V, *n* = 4). A 123-g portion of IV (*n* = 4) was easily hydrogenated with Pd/C–H_2 (700 psi) in methanol at room temperature; 116 g. (96%) (I→V) total yield of bis(δ-hydroxybutyl)-butane-1,4-dicarbamate was obtained. The 978 cm^{-1} absorption due to the *trans* double bond of the starting material disappeared completely, indicating that the hydrogenation was complete. Characteristic infrared peaks were found at 3310 (—OH), 1700 (C=O), and 1262 cm^{-1} (ester C—O—C).

ANAL. Calcd for $C_{14}H_{26}N_2O_6$: C, 52.50%; H, 8.82%; N, 8.75%; MW, 320. Found: C, 52.24%; H, 9.38%; N, 8.15%; MW, 323, 310.7 (VPO in benzene).

The NMR spectrum shows signals at τ 4.05 (s, 1H), 5.96 (*t*, *J* = 6.0 cps, 2H), 6.44 (*t*, *J* = 6.0 cps, 2H), 6.44 (*s*, 1H), 6.88 (*m* 2H), and 8.43 (*m* 6H) corresponding to hydrogens *a*, *b*, *c*, *d*, *e*, and *f*, respectively.



$$(\underset{d}{HO}—\underset{c}{CH_2}—\underset{f}{CH_2}—\underset{f}{CH_2}—\underset{b}{CH_2}—O—\overset{\overset{O}{\|}}{C}—\underset{a}{NH}—\underset{e}{CH_2}—\underset{f}{CH_2}—)_2$$

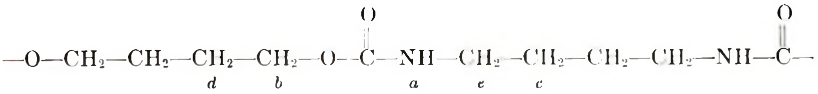
V, *n* = 4

Poly(tetramethylene tetramethylenedicarbamate) (VII, *n* = 4). Bis-(δ-hydroxybutyl)-butane-1,4-dicarbamate (15 g, 0.05 mole) was heated at 175°C/13 mm Hg for 3 hr and then at 180–182°C/0.35 mm Hg for 14 hr. An aliquot (328-B) was taken, and the rest of the reaction mixture was heated at 180–182°C/0.25 mm Hg for 1 hr more (Sample 328-C).

Sample 328-B was a pale greenish, spinnable polymer, having an intrinsic viscosity in *m*-cresol of 0.27 dl/g, mp 192°C, decomposition at 340°C (DTA). Sample 328-C was a rubberlike elastomer which was not spinnable. It was insoluble in *m*-cresol.

Anal. Calcd for $C_5H_9NO_2$: C, 52.20%; H, 7.89%; N, 12.12 %. Found (328-B): C, 51.74%; H, 8.20%; N, 12.13%. Found (328-C): C, 52.03%; H, 8.15%; N, 12.62%.

The NMR spectrum of 328-B in DMSO-d_6 shows signals at τ 3.25 (1H), 6.06 (2H), 7.00 (2H), and 8.45 (4H), corresponding to hydrogens *a*, *b*, *c*, and *d* + *e*, respectively.



$$-O-CH_2-CH_2-\underset{d}{CH_2}-\underset{b}{CH_2}-O-\overset{O}{\overset{\|}{C}}-\underset{a}{NH}-\underset{e}{CH_2}-\underset{c}{CH_2}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-$$

VII, $n = 4$

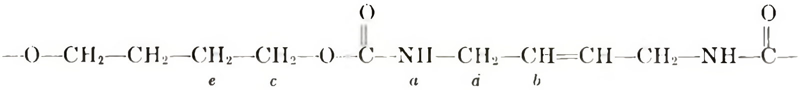
The infrared spectrum of 328-B and that of the authentic sample obtained from tetramethylene diisocyanate and 1,4-butanediol are substantially the same.

Route 3

Poly(tetramethylene-2-butene-1,4-dicarbamate) (VII, *n* = 4). In 250 ml of DMF, 105 g (0.64 × 2.53 mole) of sodium cyanate was added and heated at 70–80°C with stirring. To this mixture, 80 g (0.64 mole) of *trans*-1,4-dichloro-2-butene was dropped over 15 min at 100–110°C; the temperature of the reaction mixture rose suddenly to 168°C then dropped gradually. The reaction was finished in 2.5 hr. After the reaction, no *trans*-1,4-dichloro-2-butene was detected by gas chromatography. The inorganic salts were filtered off and washed with DMF. The combined filtrate was vacuum-distilled to remove unreacted 1,4-butanediol and solvent. At the final stage, a new distillation receiver is attached and the reaction mixture is heated at 150–155°C/0.01 mm Hg for 3 hr. The reaction mixture became viscous. Unsaturated aliphatic polyurethane, poly(tetramethylene 2-butene-1,4-dicarbamate) (VI, *n* = 4) 125.6 g (98.3%) was obtained, mp 85–95°C.

Anal. Calcd for $C_5H_8NO_2$: C, 52.12%; H, 7.02%; N, 12.27% Found: C, 52.83%; H, 7.12%; N, 12.14%; Cl, 0.40%.

The inherent viscosity was 0.10 dl/g. The NMR spectrum (DMSO-d_6) (Fig. 6) shows signals at τ 2.92 (1H), 4.35 (1H), 6.0 (2H), 6.40 (2H), and 8.37 (2H) corresponding to hydrogens *a*, *b*, *c*, *d*, and *e*, respectively.



$$-O-CH_2-CH_2-\underset{e}{CH_2}-\underset{c}{CH_2}-O-\overset{O}{\overset{\|}{C}}-\underset{a}{NH}-\underset{d}{CH_2}-\underset{b}{CH}=CH-CH_2-NH-\overset{O}{\overset{\|}{C}}-$$

VII, $n = 4$

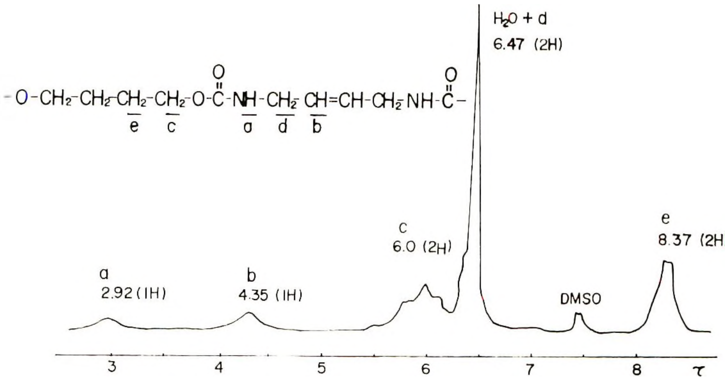


Fig. 6. NMR spectrum of poly(tetramethylene 2-butene-1,4-dicarbamate) in DMSO-d_6 at 25°C.

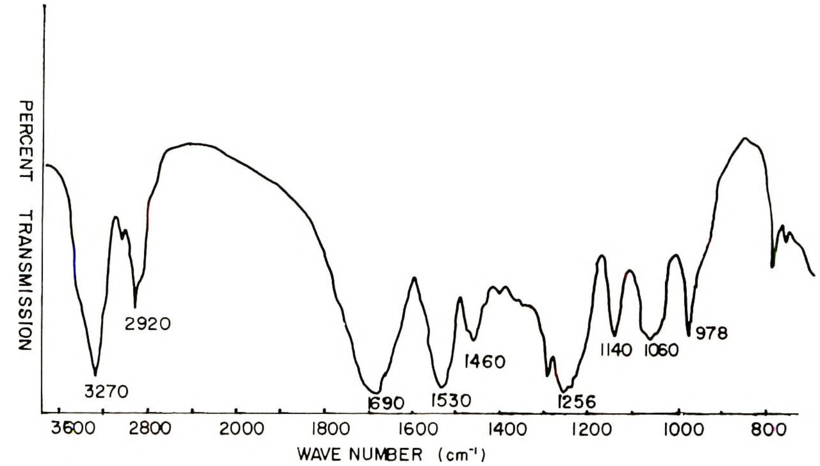


Fig. 7. Infrared spectrum of poly(tetramethylene 2-butene-1,4-dicarbamate) (KBr disk).

Characteristic infrared peaks are found at 3 260 (NH), 1 687 (C=O), and 978 cm^{-1} (*trans* double bond), as shown in Figure 7.

Poly(tetramethylene tetramethylenedicarbamate) (VII, *n* = 4) from Poly(tetramethylene 2-butene-1,4-dicarbamate) (VI, *n* = 4). A 8.4 g portion of VI, ($n = 4$), 0.2 g of 1% palladium on carbon, 35 ml of methanol and hydrogen gas (700 psi) were stirred at room temperature for 2 hr, theoretical amount of hydrogen was absorbed. Filtration of catalyst and evaporation of methanol gave 7.9 g (98.0%) of poly(tetramethylene tetramethylenedicarbamate).

ANAL. Calcd for $C_{10}H_{18}N_2O_4$: C, 52.20%; H, 7.89%; N, 12.18%. Found: C, 52.68%; H, 8.28%; N, 11.81%.

The inherent viscosity was 0.10 dl/g. The infrared and NMR spectra of this sample and those of the authentic sample were substantially the same.

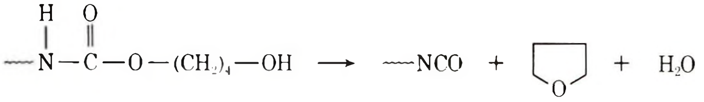
RESULTS AND DISCUSSION

As shown in the experimental section, polyurethanes can be synthesized by three different routes.

Route 1

The ester exchange reaction of dimethyl butane-1,4-dicarbamate with glycol is a most important reaction in route 1. This reaction proceeded well in the case of 1,6-hexanediol, but in the 1,4-butanediol and ethylene glycol, the reaction proceeded with difficulty. The reaction of dimethyl butane-1,4-dicarbamate with butanediol is shown in Table I.

As shown in Table I, the highest inherent viscosity in this system is only 0.20 dl/g. Longer heating gave insoluble, elastic, unspinnable polymer. Two reasons can be considered. One is ring formation which occurs easily at the δ-hydroxybutyl carbamate end. As mentioned in experimental part, the reaction tube is connected with receiver cooled at −78°C. In this receiver, 1,4-butanediol and about 2% of tetrahydrofuran were obtained. The formation of tetrahydrofuran was confirmed as follows. The unknown component was separated by preparative gas chromatography. Mass fragmentation pattern of the unknown sample was very similar to that of tetrahydrofuran. The retention time of the sample in gas chromatography was identical with that of tetrahydrofuran; therefore the side reaction (1) can be considered.


(1)

The isocyanate group formed by eq (1) can react with the urethane linkage to form an allophanate linkage. The isocyanate group can react with water to form a urea linkage. The urea and isocyanate give a biuret compound. The allophanate and biuret together account for the three-dimensional, insoluble, and elastic polymer.

1,4-Butandiol or δ-hydroxybutyl carbamate can easily give a five-membered cyclic compound, tetrahydrofuran. The hydroxyl endgroup is eliminated to give an isocyanate endgroup; 1,6-hexanediol or ω-hydroxyhexyl carbamate gives cyclic ether only with difficulty. Therefore, 1,6-hexanediol gives better, higher molecular weight, linear polymer than does 1,4-butanediol.

Another factor in the reaction is the melting point difference. The melting point of poly(hexamethylene tetramethylenedicarbamate) is 184°C, and that of poly(tetramethylene tetramethylenedicarbamate) is 194°C. The reaction was carried out at about 190–195°C. The rate of reaction of the isocyanate group with hydroxyl group is much faster than that of the isocyanate group with urethane linkage, but in the final stage of polymerization, the reaction rate is controlled by diffusion, because of the low concentration of hydroxy groups and the high viscosity. The isocya-

TABLE I
Reaction of Dimethyl Butane-1,4-dicarbamate with 1,4-Butanediol

	Carbamate		1,4-Butanediol		Catalyst		Heating		Heating (vacuum)		Polymer yield		Analysis[a]			[η]
Expt	g	mole	g	mole	Type	mg	Temp, °C	Time, hr	Temp, °C/mm Hg	Time, hr	g	%	C, %	H, %	N, %	dl/g
339	2.04	0.01	3.96	0.044		0	195	30	190/0.3	30	1.657	72	48.60	8.77	14.85	Insol.
340	2.04	0.01	3.96	0.044		0	100–220	4	210/760 → 0.23	8	1.65	72	52.69	7.98	13.58	Insol.
341	1.02	0.005	1.98	0.022		0	100	1	150/760 → 0.75	2					13.85	0.15
							200	5	186/0.25	0.75	1.06	92.6			15.33	insol.
342	1.02	0.005	1.98	0.022	Sb_2O_3	2	100	1	200/760 → 0.5	1.5					14.75	0.20
							220	3	200/0.2	0.2	0.91	79.2			15.67	insol.
344	2.00	0.01	3.53	0.039	Sb_2O_3	2	186–210	4	170/760 → 0.45	0.7			51.73	8.09	11.81	0.11
					$C_a(OA_c)_2$	3			170/0.08	0.5	2.09	87.7	51.68	8.12	11.79	0.17

[a] Calcd for $C_{10}H_{18}N_2O_4$: C, 52.20%; H, 7.89%; N, 12.12%.

nate group reacts with urethanes as well as hydroxyl groups. This allophanate linkage gives a three-dimensional, rubber-like polymer. In the experiments mentioned in this paper, the reaction mixture was stirred with a slow stream of nitrogen gas, methanol or diol gas being evolved. Stirring is almost zero in the reaction of poly(tetramethylene tetramethylenedicarbamate) formation, where the melting point of the polymer is very close to the reaction temperature. However, stirring was possible in the poly(hexamethylene tetramethylenedicarbamate) formation reaction, where the melting point of the polymer is about 6–11°C lower than the reaction temperature. The fact that gel formation proceeded very quickly when the polymer viscosity increased and gel formation started can be explained by the stirring efficiency and the reaction of isocyanate with urethane.

The reactions of dimethyl butane-1,4-dicarbamate with ethylene glycol provided polymer which gave poor analysis. The reason is as follows. Equimolar amounts of dimethyl butane-1,4-dicarbamate and ethylene glycol were used in these experiments, but excess glycol should be used, because of the low boiling point of ethylene glycol (197°C) which is close to the reaction temperature.

Route 2

The reaction of glycol, 1,4-dichloro-2-butene and sodium cyanate, proceeded well to give bis (ω-hydroxyalkyl)-2-butene-1,4-dicarbamate (IV). The reduction of IV with hydrogen met with no difficulty and gave bis(ω-hydroxyalkyl)butane-1,4-dicarbamate (V). In the glycol elimination reaction of V, bis(δ-hydroxybutyl) butane 1,4-dicarbamate gave poly(tetramethylene tetramethylenedicarbamate) (VII, $n = 4$) quantitatively;

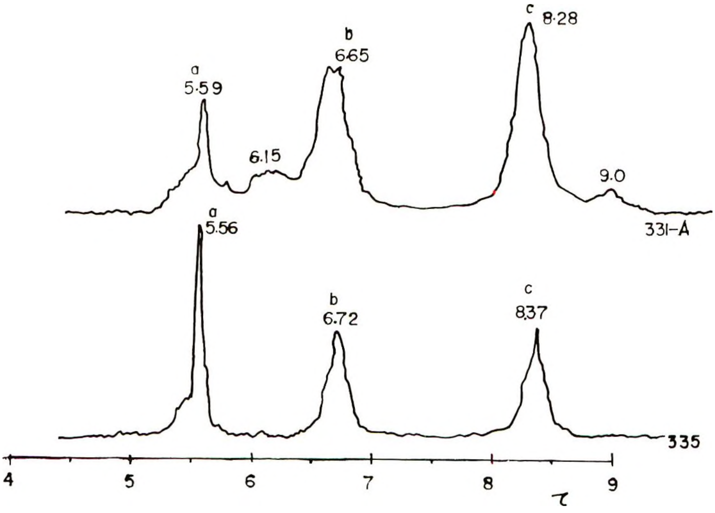


Fig. 8. NMR spectra of poly(ethylene tetramethylenedicarbamate) samples in CF_3COOH at 25°C: (331-A) obtained from dimethyl butane-1,4-dicarbamate and ethylene glycol; (335) obtained from tetramethylene diisocyanate and ethylene glycol.

TABLE II

Glycol Elimination Reaction of Bis(β-Hydroxyethyl)butane-1,4-dicarbamate (V, $n = 2$)

		Catalyst	Heating			Polymer							Distillate		
								Analysis[a]						Analysis		
Expt	V (n = 2) g	$(Sb_2O)_3$, mg	Temp, °C	Pressure, mm Hg	Time, hr	Wt, g	%	C, %	H, %	N, %	[η], dl/g	Wt, g	C, %	H, %	N, %
331A	15.0	0	125	14	2										
			170	14	2										
			170–180	0.14	7	0.4 (331-A-1)	39.3	48.54	7.61	13.60	0.07	Total			
			180	0.14	2	4.1 (331-A-2)		50.76	7.84	17.09	0.07	7.3	—	—	—
331-B	15.0	15	125	14	2										
			170	14	2										
			170–180	0.14	7	0.4 (331-B-1)	41.8	48.81	7.66	16.39	0.17	Total			
			180	0.14	2	4.4 (331-B-2)		51.24	7.93	17.78	0.12	7.1	41.65	9.52	3.42

[a] Calcd for $C_8H_{14}N_2O_4$: C, 47.50%; H, 6.93%; N, 13.86%.

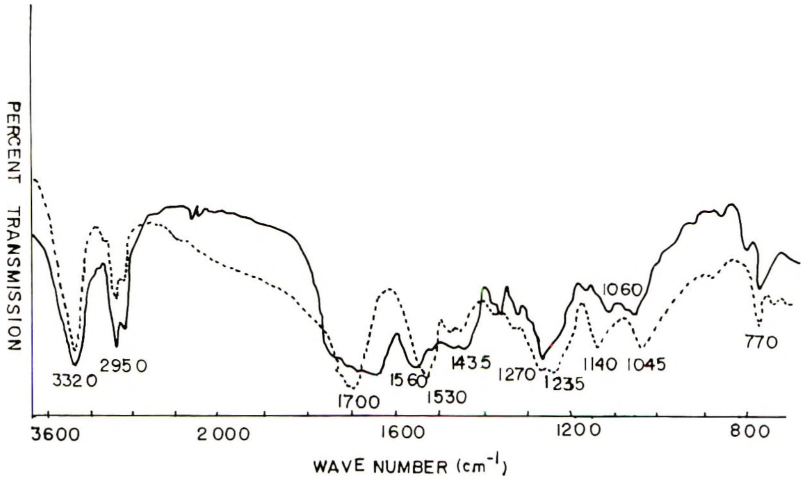


Fig. 9. Infrared spectra of poly(ethylene tetramethylenedicarbamate) samples: (——) 331-A; (- -) 335.

the structure was well established as shown in experimental section. Bis-(β-hydroxyethyl) butane-1,4-dicarbamate, however, gave low molecular weight polymer. The ethylene glycol elimination reaction is shown in Table II.

As shown in Table II, the inherent viscosity of the polymer was very low. More heating gave polymer which is partly insoluble in *m*-cresol. The inherent viscosity of the soluble part was low. In this heating process, the nitrogen content of the polymer increased and the polymer weight decreased. The distillate caught at the trap, contained a material containing nitrogen. These three facts show that degradation of polymer occurred. The NMR of the polymer (331-A1) obtained in this experiment and that of an authentic sample obtained from tetramethylene diisocyanate and ethylene glycol were compared as shown in Figure 8. In polymer 331-A1, unknown signals were found at τ 6.0–6.3 and 9.0 (probably methyl). The signal areas at τ 5.59 were smaller than theoretical. The signals at τ 5.59, 6.65 (2H), and 8.28 (2H) were assigned to *a*, *b*, and *c* hydrogens, respectively.

The infrared spectra of two samples were also different, as shown in Figure 9.

Route 3

As shown in experimental section, poly(tetramethylene 2-butene-1,4-dicarbamate) was obtained by the reaction of 1,4-dichloro-2-butene, sodium cyanate, and 1,4-butanediol. The structure of this substance was confirmed. The inherent viscosity of this substance was not very high. This may be due to insufficient heating in this experiment. The hydrogenation of poly(tetramethylene 2-butene-1,4-dicarbamate) proceeded easily. The inherent viscosity of the hydrogenated product was the same as that of the starting material.

When we compare the three routes, the following facts were found.

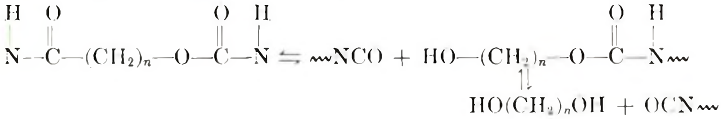
Route 1 is a better route to obtain pure and colorless polymer, because we can purify dimethyl 1,4-butanedicarbamate, but the yield is not high.

Route 2 is an easy route to get polymer in fairly high yield, but the purification of the intermediate is not possible, and therefore the product has a pale green color.

Route 3 is very similar to route 2. In general, the inherent viscosity of the polymer is too low for a polymer of good spinnability to be obtained. This may be overcome by having vigorous stirring, especially at the final stage of polymer formation reaction.

Another important factor is the choice of a suitable glycol. 1,6-Hexanediol appears to be the best diol because the melting point of the polyurethane formed therefrom is low, and ring ether formation is difficult. The reaction taking the course, I → IV → VI was not tried in this experiment, but it should give high molecular weight polymer. Because the double bond in the polymer chain lowers the melting point, and network formation is prevented.

A third important thing for obtaining good polymer is that the bulk polymer viscosity be measured in the final stage of the polymerization. In this experiment, the viscosity measurement was impossible because the amount of sample was too small, and therefore the endpoint of the polymerization could not be measured. Therefore, in some cases the reaction was stopped too early, in some cases too late. In the polyurethane-forming reaction, are equilibrium between dissociation[15,16] and readdition exists [eq (2)].



$$\overset{H}{\underset{}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_n-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}} \rightleftharpoons \sim NCO + HO-(CH_2)_n-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}\sim$$

$$\Big\updownarrow \quad HO(CH_2)_nOH + OCN\sim \qquad (2)$$

When low molecular weight component is formed, this component is evaporated off easily. The dissociation is predominant at higher temperature and becomes pronounced at over 200°C. Therefore, if the polymerization is carried out at over 200°C, the isocyanate group is easily formed and glycol is evaporated. The isocyanate group then reacts with the urethane linkage, giving side chains or crosslinkages.

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References

1. J. H. Saunders and K. C. Frisch, *Polyurethanes, Chemistry and Technology, Vol. I, Chemistry*, Interscience, New York, 1962, p. 3.
2. S. Ozaki, *J. Polym. Sci. B*, **5**, 1053 (1967).
3. C. M. Himel and L. M. Richards (to Ethyl Corp.), U.S. Pat. 2,866,801 (1958).
4. B. Graham (to Ethyl Corp.), U.S. Pat. 2,866,802 (1958).

5. K. Fukui and H. Kitano, Japanese Pat. 36-4372 (1962).
6. K. F. Zenner, G. Oertel, and H. Holtschmidt (to Bayer), German Pat. 1,205,087 (1965).
7. D. W. Kaiser (to American Cyanamid), U.S. Pat. 2,697,720 (1954).
8. A. Nagasawa, H. Kitano, and K. Fukui, *Bull. Japan. Petrol. Inst.*, **6,** 72 (1964).
9. P. A. Argabright, H. D. Rider, and R. Sieck, *J. Org. Chem.*, **30,** 3317 (1965).
10. K. Fukui and H. Kitano, U.S. Pat. 3,037,979 (1962).
11. W. Siefken, *Ann. Chem.*, **562,** 122 (1949).
12. S. Murahashi and N. Nakanishi, *Gosei Sen-i Kenkyu*, **1,** 333 (1944).
13. I. G. Farb, Fr. Pat. 85,5814 (1940).
14. T. Hoshino and Y. Iwakura, *Gosei Sen-i Kenkyu*, **1,** 394 (1944).
15. T. Mukaiyama and Y. Hoshino, *J. Amer. Chem. Soc.*, **78,** 1946 (1956).
16. T. Mukaiyama and M. Iwanami, *J. Amer. Chem. Soc.*, **79,** 73 (1957).

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Relationship between Structures and Activities of Silver Salt–Organic Halide Catalyst Systems for Styrene Polymerization

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Synopsis

The rate of bulk polymerization of styrene initiated by silver salt–organic halide systems was measured at 0°C. Neither of the catalyst components initiated the polymerization when used alone, while combined catalysts containing both components initiated the polymerization in the case that the components reacted with each other with precipitation of silver halide. The rate in the early stage of the polymerization increased with an increase in reaction time. Plots of yield against the second power of time gave a linear relation in the early stage of the polymerization. The slope of the line was taken as a measure of catalytic activity. The catalytic activity was markedly influenced by the kinds of the components. The activities of silver perchlorate–organic halide systems increased in the following order of halides: chloride < bromide < iodide in most cases. The activities of silver perchlorate–organic chloride systems increased with a decrease in ionization potentials of the organic groups of the chlorides. The activities of silver salt–benzyl bromide systems increased with a decrease in the pK_a values of conjugate acids of silver salts. From these results, it was concluded that the facility of ionic dissociation of the catalyst components determined the activities.

INTRODUCTION

It has been known that silver perchlorate reacts with organic halides to form organic perchlorates capable of acting as a Friedel-Crafts catalyst.[1,2] Catalytic activities of these systems for polymerization have, however, been little known, except that silver perchlorate–1-phenylethyl bromide system initiated the polymerization of styrene, which was briefly reported by Gandini and Plesch.[3]

The aim of this paper is to determine the variations in catalytic activities of silver salt–organic halide systems for styrene polymerization with changes in the catalyst components and to determine the relation between the catalytic activity and electronic nature of the substituents of the components.

EXPERIMENTAL

Materials

Styrene, conventionally purified, was dried over calcium chloride, and distilled at reduced pressure. Commercial silver salts were dried *in vacuo* for a few hours before use. Commercial organic halides were dried over calcium chloride and distilled before use; allyl chloride (bp 45.5°C), isopropyl chloride (bp 36°C), isopropyl bromide (bp 60°C), isopropyl iodide (bp 90–90.5°C), *tert*-butyl chloride (bp 51°C), *tert*-butyl bromide (bp 74°C), benzyl chloride (bp 62°C/11 mm), benzyl bromide (bp 73–74°C/8 mm). 1-Phenylethyl chloride was prepared[4] by the reaction of styrene with hydrogen chloride, dried over calcium chloride, and distilled (bp 71°C/11 mm). *tert*-Butyl iodide was prepared[5] by the reaction of *tert*-butyl alcohol with potassium iodide, and purified by the method of Tones and Ogg, Jr.[6] (bp 42°C/95 mm). Diphenylmethyl chloride was prepared as reported by Rule and Bain[7] (bp 114°C/1 mm). Commercial triphenylmethyl chloride was used without purification (mp 99–106°C).

Technique

An Erlenmeyer flask (50 ml) which had an outlet protected by a guard tube containing desiccant (calcium chloride) was used as a reaction vessel. Silver salt (0.5 mmole) was dissolved in 45 ml of styrene cooled at 0°C and 5 ml of cooled styrene solution containing 0.5 mmole of organic halide was added to this solution. The reaction mixture was kept at 0°C in an ice bath. A 1-ml portion of the reaction mixture was taken out by using an injector at regular time intervals and quenched by methanol. The yield was determined by precipitating the polymer in methanol, drying *in vacuo*, and weighing.

RESULTS AND DISCUSSION

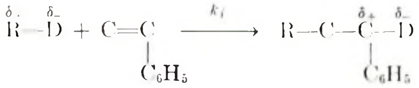
When either the silver salt or organic halide was used alone as a catalyst, the polymer yield was less than 0.5% at 100 hr, while rapid polymerization occurred when catalyst systems whose components reacted with each other with precipitation of silver halides were used.

This result is consistent with the following reaction mechanism shown in eqs. (1)–(3).

Activation reaction:

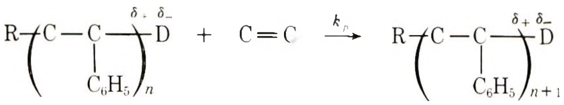
$$\mathrm{R{-}X} + \mathrm{Ag{-}D} \xrightarrow{k_a} \overset{\delta_+}{\mathrm{R}}{-}\overset{\delta_-}{\mathrm{D}} + \mathrm{Ag{-}X} \qquad (1)$$

Initiation reaction:

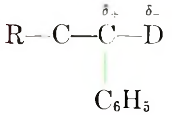


$$\overset{\delta_+}{\mathrm{R}}{-}\overset{\delta_-}{\mathrm{D}} + \underset{\substack{|\\ \mathrm{C_6H_5}}}{\mathrm{C{=}C}} \xrightarrow{k_i} \mathrm{R{-}C{-}}\underset{\substack{|\\ \mathrm{C_6H_5}}}{\overset{\delta_+}{\mathrm{C}}}{-}\overset{\delta_-}{\mathrm{D}} \qquad (2)$$

Propagation reaction:



$$\mathrm{R}\left(\mathrm{C{-}}\underset{\substack{|\\ \mathrm{C_6H_5}}}{\mathrm{C}}\right)_n\overset{\delta_+\ \delta_-}{\mathrm{D}} + \mathrm{C{=}C} \xrightarrow{k_p} \mathrm{R}\left(\mathrm{C{-}}\underset{\substack{|\\ \mathrm{C_6H_5}}}{\mathrm{C}}\right)_{n+1}\overset{\delta_+\ \delta_-}{\mathrm{D}} \qquad (3)$$



$R—C—\overset{\delta+}{C}(C_6H_5)—\overset{\delta-}{D}$

$\overset{\delta+}{R}—\overset{\delta-}{D}$ and $R—C—\underset{C_6H_5}{\overset{\delta+}{C}}—\overset{\delta-}{D}$ were termed active species and initiating species, respectively; k_a, k_i, and k_p are the rate constants of the activation, initiation and propagation reaction, respectively.

Time Course of the Reaction and Definition of the Measure of Catalytic Activity

The time course is shown in Figures 1 and 2. In the early stage of the polymerization, rate acceleration was observed in most catalyst systems.

As was discussed previously,[8] this rate-acceleration phenomenon is characteristic of a nonstationary polymerization with slow initiation: that is, it is considered that the number of moles of propagating species increases with time to cause the rate-acceleration phenomenon if initiation occurs continuously without appreciable termination. The plots of yield against the second power of time are shown in Figure 3. Linear relations in the early stage of the polymerization are seen to hold well. As is shown by the

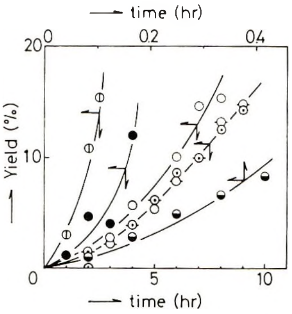


Fig. 1. Time–conversion curves of bulk polymerization of styrene by silver perchlorate–organic halide systems at 0°C: (⦶) benzyl bromide; (●) 1-phenylethyl chloride; (⊙) isopropyl iodide; (○) *tert*-butyl chloride; (-○-) triphenylmethyl chloride; (◒) diphenylmethyl chloride. Catalyst concentration, $AgClO_4$ and RX, 0.1 mole-%.

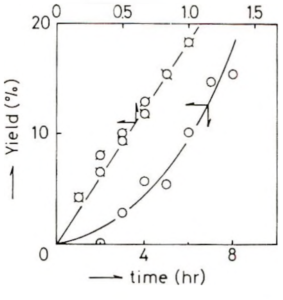


Fig. 2. Time–conversion curves of bulk polymerization of styrene by silver perchlorate–organic halide systems at 0°C: (Ọ) *tert*-butyl iodide; (Ø) *tert*-butyl bromide; (○) *tert*-butyl chloride. Catalyst concentration, $AgClO_4$ and RX, 0.1 mole-%.

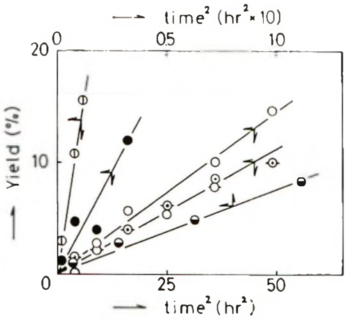


Fig. 3. Plots of yield *vs.* the second power of time: (⦶) benzyl bromide; (●) 1 phenylethyl chloride; (⊙) isopropyl iodide; (○) *tert*-butyl chloride; (-○-) triphenylmethyl chloride; (◒) diphenylmethyl chloride. Reaction temperature 0°C; catalyst concentration, $AgClO_4$ and RX, 0.1 mole-%.

following derivation, the time course of this type is realized when termination does not occur and the initiation rate is constant. The assumption of no termination is supported by the fact that there is no termination in the styrene polymerization initiated by perchloric acid[3] (the propagating species of this system is the same as that of the present case).

$$d[\mathrm{P}^*]/dt = R_i = \text{constant} = C_i$$

Therefore, $[\mathrm{P}^*] = C_i t$.

Accordingly,

$$M_p = \int R_p\, dt = \int k_p[\mathrm{P}^*][\mathrm{M}]_0\, dt = k_p[\mathrm{M}]_0 C_i t^2/2 \tag{4}$$

Here P^* is the propagating species, R_i the initiation rate, M_p the polymer yield, k_p the propagation rate constant, $[\mathrm{M}]_0$ the initial monomer concentration. Therefore, we defined the slope of the line (in Fig. 3) as the measure of the catalytic activity.

On the other hand, as shown in Figure 2, in the case of silver perchlorate–*tert*-butyl bromide or silver perchlorate–*tert*-butyl iodide systems, early stage acceleration was not observed, but a linear relation between yield and the reaction time held, and the polymerizations proceeded most rapidly. As was discussed previously,[8] this linear relationship is characteristic of a stationary polymerization with a rapid initiation. It is considered that initiation in these polymerization systems occurs rapidly and is complete immediately after the polymerization starts; propagation then occurs without termination. It follows that the initiation rates of the silver perchlorate–*tert*-butyl bromide or silver perchlorate–*tert*-butyl iodide systems were larger than any other catalyst system. The catalytic activities of these systems can not be numerically defined in the same way as the case in which the acceleration phenomenon was observed. It is apparent, however, that the catalytic activities of these systems are the largest in these catalyst systems.

Variation in Catalytic Activities with Kinds of Components

Effect of Halogens in the Organic Halides. When the kind of halogen was changed in silver perchlorate–benzyl halide or silver perchlorate–isopropyl halide systems, catalytic activities increased in the order of chloride < bromide < iodide for the halides, and the early-stage rate acceleration was observed in the time–conversion curve. In the silver perchlorate–*tert*-butyl halide systems, the activities increased in the following order of halides, chloride ≪ bromide = iodide; and the yield for the systems with *tert*-butyl bromide and iodide increased linearly with time.

TABLE I

Variation in Catalytic Activity with the Kind of Halogen in Organic Halides[a]

R	X	$D(\overset{+}{R}—\overset{-}{X})$, kcal/mole[b]	Catalytic activity, %/hr²
$(CH_3)_3C$—	Cl	156	2.94×10^{-1}
	Br	149	[c]
	I	137	[c]
$C_6H_5CH_2$—	Cl	148	3.14×10^{-2}
	Br	141	2.70
$(CH_3)_2CH$—	Cl	165	0.00
	Br	158	0.00
	I	146	2.40×10^{-1}

[a] Reaction temperature, 0°C; catalyst concentration, $AgClO_4$ and RX, 0.1 mole-%.

[b] Calculated from the relation: $D(\overset{+}{R}—\overset{-}{X}) = D(R—X) + I(R\cdot)—E(X\cdot)$, where $D(R—X)$ is the bond dissociation energy, $I(R\cdot)$ is the ionization potential of the organic radical, and $E(X\cdot)$ is the electron affinity of the halogen radical. $D(R—X)$ data for benzyl and isopropyl halides from Vedeneyev et al.;[9] $D(R—X)$ data for *tert*-butyl halide from Roberts and Skinner;[10] $I(R\cdot)$ data from Cohen et al.;[11] $E(X\cdot)$ data from the Chemical Society of Japan.[12]

[c] Although the catalytic activity could not be determined numerically, it was the largest.

As is clearly seen from eqs. (1)–(3), the active species from the different catalyst systems are the same, in spite of the change in halogens in organic halides. Therefore, the rate constants of the initiation and propagation are independent of the organic halide used. Accordingly, it was concluded that a marked variation in the activities with the kind of halogen resulted from the variation in the rate of activation. It was also confirmed that the faster the precipitation of silver halide, i.e., the faster the activation reaction, the larger the activity.

Since the activation reaction proceeds through an ionic intermediate, it is considered that the greater the ease of ionic dissociation of organic halide in solution, the faster the rate of activation. The results in Table I which show that the catalytic activities increase with a decrease in ionic dissociation energy of organic halide are in accordance with this consideration.

On the other hand, when the rates of activation and initiation exceed a certain limit, the initiation reaction is completed immediately after the polymerization starts and the polymerization exhibits the characteristics of polymerization with a rapid initiation. In this case, even if the rates of the activation and initiation increase further, the overall rate of polymerization does not vary. This is the case with *tert*-butyl bromide and *tert*-butyl iodide.

Effect of Organic Groups in the Halides. It was considered that the change in organic groups might cause a change in the rates of the activation and the initiation without affecting the propagation. It was observed that the rate of the precipitation of silver halide (the activation reaction) as well as the overall rate varied markedly with the change in the organic groups; the larger the rate of the precipitation of silver halide, the larger the activity (except for the case of triphenylmethyl chloride). The data in Table II are arranged in the order of the magnitude of the ionic dissociation energy of organic halides.

TABLE II
Variation of Catalytic Activity with Kind of Organic Groups in Halides[a]

R	$I(R\cdot)$, eV[b]	$D(R^+—X^-)$, kcal/mole[c]	Catalytic activity, %/hr²
$(CH_3)_2CH—$	7.90	165	0.00
$CH_2=CHCH_2—$	8.15	158	0.00
$C_6H_5CH_2—$	7.76	148	3.14×10^{-2}
$(CH_3)_3C—$	7.42	156	2.94×10^{-1}
$C_6H_5CH(CH_3)—$	(7.50)[d]	(141)[d]	7.70×10^{-1}
$(C_6H_5)_2CH—$	7.32	(134)[d]	9.65×10
$(C_6H_5)_3C—$	7.26[e]	(125)[d]	2.40×10^{-1}

[a] Reaction temperature, 0°C; catalyst concentration, $AgClO_4$ and RX, 0.1 mole-%.

[b] Data from Cohen et al.[11]

[c] $D(R—X)$ data for isopropyl, allyl, and benzyl chlorides from Vedeneyev et al.;[9] $D(R—X)$ data for *tert*-butyl chloride from Roberts and Skinner.[10]

[d] Estimated value.

[e] $I(R\cdot)$ data from Chemical Society of Japan.[12]

The activities are seen to increase with a decrease in the ionic dissociation energy except in the case of triphenylmethyl chloride. These results may be explained by considering that mainly the rate of the activation reaction determines the overall rate and that a change in the organic groups causes a change in the rate of the activation reaction. On the other hand, in the case of triphenylmethyl chloride, the activity was not so large, though the precipitate was formed rapidly. The characteristic feature of the catalytic activity with the use of triphenylmethyl chloride as a component was also observed in the polymerization of isobutene initiated by aluminum alkyl-organic halides systems.[13] These results may be interpreted by considering that the active species formed from triphenylmethyl chloride is too stable to react with monomer in the initiation.

TABLE III
Variation of Catalytic Activity with Kind of Anionic Groups of Silver Salts[a]

Ag-D	pK_a(HD)	Catalytic activity, %/hr²
CH_3COOAg	4.8[b]	0.00
CF_3COOAg	0.2[b]	1.76×10^{-1}
$AgNO_3$	−1.6[c]	1.36×10^{-4}
$AgClO_4$	−8[c]	2.70
$AgBF_4$	—	4.96

[a] Reaction temperature, 0°C; catalyst concentration, AgD and RX, 0.1 mole-%.
[b] Data of Kortüm et al.[14]
[c] Data of Albert and Serjeant.[15]

Effects of Anionic Groups in Silver Salts. The results obtained with the use of benzyl bromide with various silver salts are summarized in Table III. Activities vary markedly with the kinds of anionic groups in the silver salts.

It is considered that anionic group in silver salts influences all three reactions (1)–(3), and that the rate constant of every reaction increases with a decrease in ionic dissociation energies of the reacting species such as silver salt, active species, and initiating species. The results in Table III are consistent with the parallel between ionic dissociation energy and pKa value of the conjugate acid.

References

1. H. Burton and P. F. G. Praill, *J. Chem. Soc.*, **1953,** 827.
2. H. Burton and P. F. G. Praill, *J. Chem. Soc.*, **1957,** 832.
3. A. Gandini and P. H. Plesch, *J. Chem. Soc.*, **1965,** 4826.
4. M. S. Kharasch and M. Kleiman, *J. Amer. Chem. Soc.*, **65,** 11 (1943).
5. H. Stone and H. Shechter, in *Organic Synthesis, Coll. Vol.* **4**, Wiley, New York, 1963, p. 323.
6. J. L. Tone and R. A. Ogg, Jr., *J. Amer. Chem. Soc.*, **59,** 1943 (1947).
7. H. G. Rule and J. Bain, *J. Chem. Soc.*, **1930,** 1894.
8. T. Kagiya, M. Izu, and K. Fukui, *Bull. Chem. Soc. Japan*, **40,** 1045 (1967).
9. V. I. Vedeneyev, L. V. Gurvich, V. N. Kondratyev, V. A. Medvedev, and Ye. L. Frankevich, *Bond Energies, Ionization Potentials and Electron Affinities*, Arnold, London, 1966.
10. J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45,** 339 (1949).
11. S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, in *Progress in Physical Organic Chemistry*, Vol. I, Interscience, New York, 1963.
12. *Kagaku Binran*, Chemical Society of Japan, 1966.
13. J. P. Kennedy, paper presented at the International Symposium on Macromolecular Chemistry, Tokyo-Kyoto, 1966; *Preprints*, 1.2, 47.
14. G. Kortüm, W. Vogel, and K. Andrussow, *Dissociation Constant of Organic Acids in Aqueous Solution*, IUPAC, Butterworths, London, 1961.
15. A. Albert and E. P. Serjeant, *Ionization Constant of Acids and Bases*, Methuen, London, 1962.

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Polymerization of β-Cyanopropionaldehyde. III. Polymerization by Organoaluminum and by Organoaluminum–Titanium Chloride Complexes

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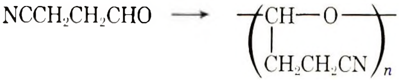
Synopsis

The mechanism of formation and stereoregularity of poly(cyanoethyl)oxymethylene have been studied. The polymerization was carried out at −78°C with use of aluminum compounds [$Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$, $Al(C_2H_5)Cl_2$, and $AlCl_3$] and complex catalysts [$Al(C_2H_5)_3$–$TiCl_4$, $Al(C_2H_5)_3$–$TiCl_3$, and $Al(C_2H_5)_2Cl$–$TiCl_3$] as initiators. The stereoregularity of poly(cyanoethyl)oxymethylene was estimated from the optical density ratio, D_{1258}/D_{1270}, in the infrared absorption spectrum. Polymer yields were observed to depend upon the aluminum compound used as initiators, while the stereoregularity of the polymer was nearly independent of the particular aluminum compound used. As the catalyst ratio of titanium chloride to aluminum compound increased, the polymer yield was found to increase to a maximum and then to decrease with further increase of the ratio. It is supposed that titanium chlorides themselves increase the acid strength of aluminum compounds through chlorination, resulting in the change of the polymer yield. The highest stereoregularity of poly(cyanoethyl)oxymethylene was attained by increasing the molar ratio of titanium trichloride to aluminum and by treating β-cyanopropionaldehyde (CPA) with titanium trichloride prior to the polymerization. Complex formation of the nitrile group of CPA with titanium is considered responsible for the increase in stereoregularity. A propagation mechanism is also proposed.

It was established in the previous papers[1–3] that high molecular weight poly(cyanoethyl)oxymethylene can be prepared from β-cyanopropionaldehyde (CPA) at −78°C with use of ionic catalyst [eq. (1)].



$$NCCH_2CH_2CHO \longrightarrow \left(\begin{array}{l} CH-O \\ | \\ CH_2CH_2CN \end{array}\right)_n \qquad (1)$$

The resulting polymer was divided into crystalline and amorphous polymers by elution fractionation with acetone and dimethylformamide (DMF) as solvents. Crystalline and amorphous bands were assigned in the infrared absorption spectra, and an intense infrared dichroism was also observed for polymer films. X-ray analysis of an oriented polymer film demonstrated that crystalline poly(cyanoethyl)oxymethylene belongs to a triclinic system with a fiber repeat distance of 4.95 Å.[2]

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This note presents the results of further study into the mechanism of formation and stereoregularity of poly(cyanoethyl)oxymethylene with emphasis on the role of a series of organoaluminum compounds and of titanium chlorides used as catalysts.

EXPERIMENTAL

Reagent

The preparation of CPA was carried out by the same method as that previously described.[1,2]

Triethylaluminum, diethylaluminum chloride, and ethylaluminum dichloride (all from Ethyl Corp.) were purified by distillation under reduced pressure. Aluminum trichloride was sublimed three times *in vacuo*. Titanium tetrachloride was distilled after refluxing with about 1% of copper powder. Titanium trichloride (α-type) was commercially obtained (Stauffer Co.).

Methylene chloride was washed with an aqueous solution of sodium carbonate, distilled over phosphorus pentoxide, and stored over calcium hydride. Toluene was refluxed on sodium after washing with concentrated sulfuric acid and then with water before distillation. These solvents were fractionally distilled again prior to use.

Polymerization

Preparations of polymerization systems were carried out in a dry box filled with dry nitrogen gas. When organoaluminum compound alone was used as initiator, monomer and initiator, both diluted with solvent, were mixed slowly in a glass ampoule on cooling at −78°C.

Polymerization systems employing complex catalysts were prepared according to either of the following procedures.

Condition I. Aluminum compound was reacted with titanium chloride in solution in a glass ampoule at a fixed temperature. After a given aging period, cold monomer solution was added on cooling at −78°C.

Condition II. The monomer was aged with titanium compound in solution for a definite time with occasional shaking. After cooling to −78°C cold organoaluminum solution was added to initiate the polymerization.

An ampoule was sealed under vacuum after evacuation under cooling with liquid nitrogen and was placed in a Dewar bottle filled with solid carbon dioxide. Methods of termination and elution fractionation and the measurement of solution viscosity of polymer were as described in the previous papers.[1,2]

Although the reproducibility of the polymerizations is not always so good, the discussion below is believed to find sufficient justification.

Molecular Weight of Polymer

Molecular weight of poly(cyanoethyl)oxymethylene was measured by means of vapor-pressure osmometry (Hewlett Packard Model 302) using DMF as solvent at 65°C. The molecular weight, for example, of an acetyl-endcapped amorphous poly(cyanoethyl)oxymethylene having a solution viscosity number, η_{sp}/c, of 0.452 was found to be 11000.

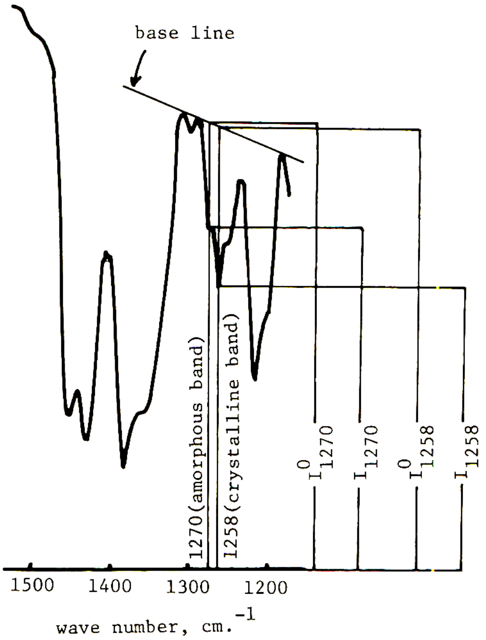


Fig. 1. Measurement of optical density ratio, D_{1258}/D_{1270}, of poly(cyanoethyl)oxymethylene. $D_{1258}/D_{1270} = [\log(I°_{1258}/I_{1258})]/[\log(I°_{1270}/I_{1270})]$.

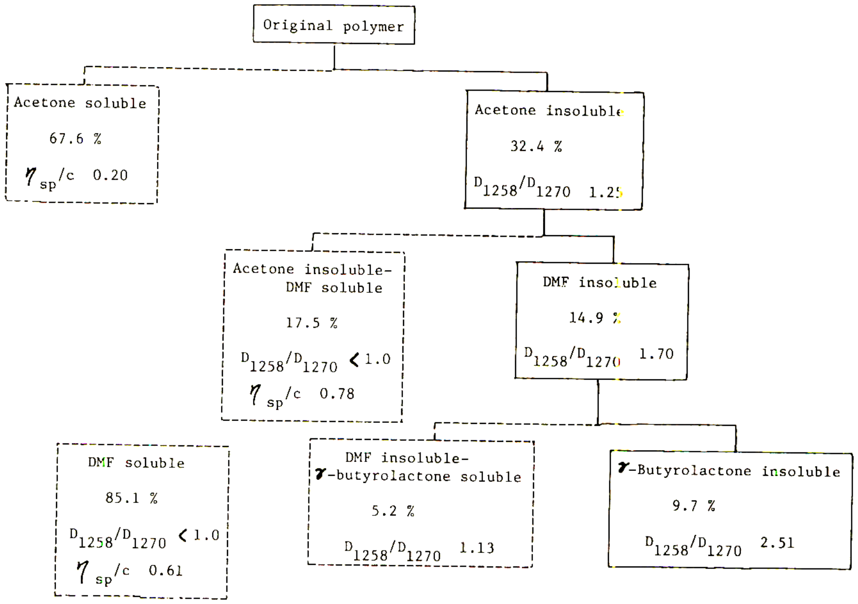


Fig. 2. Results of Elution Fractionation with acetone, DME, and γ-butyrolactone as solvents: (- -) soluble fraction; (——) insoluble fraction.

Measurement of Stereoregularity

Optical density ratio, D_{1258}/D_{1270}, was calculated by means of the baseline method from the infrared absorption spectrum for hot-pressed polymer film as shown in Figure 1. The band at 1258 cm^{-1} was assigned to the crystalline band and that at 1270 cm^{-1} to the amorphous one.[2] Amorphous polymers, which show stronger absorption at 1270 cm^{-1} than at 1258 cm^{-1}, have the values of $D_{1258/1270}$ lower than unity. On the other hand, the values of D_{1258}/D_{1270} of crystalline isotactic poly(cyanoethyl)oxymethylene are larger than unity. Hence the values of D_{1258}/D_{1270} may be adopted as a measure of stereoregularity. As a matter of fact, the results of elution fractionation with acetone, DMF, and γ-butyrolactone as solvents (Fig. 2) indicate that the polymer with the larger D_{1258}/D_{1270} shows the less solubility. The stereoregularity of acetaldehyde polymer is estimated conveniently from the per cent content of the chloroform-insoluble fraction. The content of DMF-insoluble fraction of poly(cyanoethyl)oxymethylene described here is found to depend upon the molecular weight as well as the stereoregularity.

RESULTS AND DISCUSSION

Polymerization Initiated by Aluminum Compounds

The results of polymerization of CPA at −78°C with the use of only organoaluminum and aluminum trichloride as initiators are given in Table I. Polymer yields are observed to vary with different initiators, while optical density ratios, D_{1258}/D_{1270}, of DMF-insoluble fractions remain nearly unchanged. These aluminum compounds are generally regarded as Lewis acids, and their acid strength is supposed to increase with the substitution of alkyl groups by electron-negative chlorine atoms. This was demonstrated by an infrared absorption study on the adducts of these aluminum compounds with xanthone.[4,5]

It is shown in Table II that CPA treated with chlorinated aluminum compounds (diethylaluminum chloride, ethylaluminum dichloride, and

TABLE I

Polymerization of CPA Initiated by $Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$, $Al(C_2H_5)Cl_2$, and $AlCl_3$[a]

Run no.	Catalyst	Time, days	Polymer yield, %	DMF-insoluble fraction		η_{sp}/c of DMF-soluble fraction[b]
				%	D_{1258}/D_{1270}	
312	$Al(C_2H_5)_3$	1	33.9	33.6	1.53	—
298	$Al(C_2H_5)_2Cl$	1	82.0	7.3	1.50	0.17
259	$Al(C_2H_5)Cl_2$	6	19.7	25.6	1.56	0.32
273	$AlCl_3$	7	6.0	—	—	—

[a] CPA, 10 g; catalyst, 1 mole-% to monomer; solvent, methylene chloride, 20 g; −78°C.

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

TABLE II

Cyclic Trimer from CPA with Organoaluminum Compounds[a]

Run no.	Catalyst	Time, days	Yield of cyclic trimer, %
258	$Al(C_2H_5)_3$	2	0
262	$Al(C_2H_5)_2Cl$	1	2.0
261	$Al(C_2H_5)Cl_2$	1	23.3
274	$AlCl_3$	1	49.7

[a] CPA, 10 g; catalyst, 1 mole-% to monomer; 20°C.

aluminum trichloride) at room temperature forms a cyclic trimer, 2,4,6-tris(β-cyanoethyl)-s-trioxane. The yield is found to increase with increasing number of chlorines attached to aluminum. It is well known that the cyclic oligomers of aldehydes such as trioxane, paraldehyde, and metaldehyde can be prepared from their parent aldehydes with an acid catalyst.[6-8] It is most reasonable to consider that the chlorinated aluminum compounds act as Lewis acids for CPA, leading to initiation of cationic polymerization at low temperature.

Triethylaluminum, on the other hand, did not give cyclic trimer but a yellow-greenish viscous liquid which was thought to be some condensation product through the aldehyde group. When triethylaluminum was treated with an equimolar amount of CPA at −78°C, an ethyl group was transferred from aluminum to carbon of the aldehyde group to give $NCCH_2CH_2$-$CH(C_2H_5)$—O—$Al(C_2H_5)_2$ (I).[9] The product I may be supposed to act as an initiator for the coordinated anionic polymerization of CPA as will be discussed elsewhere.[9,10]

In this manner there seems to be a fundamental difference between the polymerization mechanisms initiated with triethylaluminum and with the other chlorinated aluminum compounds. However, it appears that the following observations in Table I are available for the discussions on the polymerization by complex catalysts: (1) catalytic species with moderated acid strength are necessary to give high polymer yield; (2) polymerization by strong Lewis acid such as aluminum trichloride is very slow; (3) stereoregularity of poly(cyanoethyl)oxymethylene is almost independent on the acid strength of initiators.

Polymerization with the Use of Complex Catalysts

In Table III are given the data of polymerization of CPA with triethylaluminum–titanium tetrachloride as catalyst. In the preparation condition I, triethylaluminum was allowed to react with titanium tetrachloride in solution at room temperature for 30 min. A brown-black precipitate considered as a typical Ziegler type complex catalyst was formed. When the cold monomer solution was added on cooling at −78°C, little change was observed in the appearance of the complex catalyst. Preparation condition II, in which CPA was mixed with titanium tetrachloride in solution at −78°C, afforded a reddish orange solution. The addition of triethylaluminum solution kept the clear color nearly unchanged and produced no precipitate.

Tables IV and V summarize the results of polymerization of CPA with use of triethylaluminum–titanium trichloride and diethylaluminum chlo-

TABLE III

Polymerization of CPA with use of $Al(C_2H_5)_3$–$TiCl_4$[a]

Run no.	CPA, g	Preparation catalyst[b]	Molar ratio Ti/Al	Polymer yield, %	DMF-insoluble fraction %	DMF-insoluble fraction D_{1258}/D_{1270}	η_{sp}/c of DMF-soluble fraction
155	20	I	0.2	74.7	1.8	1.36	—
160	10	“	0.6	30.2	18.5	1.50	—
156	20	“	1.0	17.2	11.6	1.54	0.28
141	10	“	1.8	0.5	—	—	—
142	20	“	3.0	0	—	—	—
255	10	II	0.6	40.2	21.1	1.48	0.97
257	“	“	2.0	18.9	6.0	1.66	0.46

[a] $Al(C_2H_5)_3$, 1 mole-% to monomer; weight ratio of solvent (methylene chloride) to monomer, 2; −78°C; time, 1 day.

[b] I, triethylaluminum was treated with titanium tetrachloride at room temperature for 30 min; II, CPA was aged with titanium tetrachloride at −78°C.

TABLE IV

Polymerization of CPA with $Al(C_2H_5)_3$–$TiCl_3$[a]

Run no.	Preparation of catalyst[b]	Molar ratio Ti/Al	Solvent	Polymer yield, %	DMF-insoluble fraction, %	DMF-insoluble fraction, D_{1258}/D_{1270}	η_{sp}/c of DMF-soluble fraction
163	I	0.2	Methylene chloride	70.7	15.7	1.34	0.94
164	“	0.9	“	56.6	20.7	1.22	0.82
166	“	4.6	“	63.0	8.2	1.67	0.34
169	“	9.5	“	33.5	16.6	2.36	0.47
170	“	20.5	“	0	—	—	—
172	“	0.3	Toluene	30.7	23.4	2.11	0.078
173	“	0.8	“	31.4	34.9	1.95	0.19
174	“	1.0	“	35.0	30.6	2.54	0.17
175	“	5.9	“	38.7	26.5	2.23	0.19
176	“	8.9	“	26.2	54.4	3.56	0.27
242	II	0.2	Methylene chloride	59.2	27.7	2.00	1.13
243	“	1.1	“	73.2	26.1	1.99	—
244	“	4.4	“	70.6	24.1	2.70	0.22
245	“	10.2	“	61.1	11.7	3.65	0.14

[a] CPA, 10 g; triethylaluminum, 1 mole-% to monomer; solvent, 20 g; −78°C; time, 1 day.

[b] I, triethylaluminum was treated with titanium trichloride at room temperature for 2 hr; II, aging of CPA with titanium trichloride was carried out at room temperature for 1 hr.

TABLE V

Polymerization of CPA with $Al(C_2H_5)_2Cl$–$TiCl_3$[a]

Run no.	Preparation of catalyst[b]	Molar ratio Ti/Al	Polymer yield, %	DMF-insoluble fraction,		η_{sp}/c of DMF-soluble fraction
				%	D_{1258}/D_{1270}	
231	I	0.2	86.6	1.9	1.90	—
228[c]	"	1.2	33.1	14.9	1.70	0.61
233	"	4.9	0.7	—	—	—
232	II	0.2	55.7	15.5	1.93	—
230	"	1.2	20.8	59.8	2.56	—
234	"	5.2	30.6	21.3	2.73	—

[a] CPA, 10 g; $Al(C_2H_5)_2Cl$, 1 mole-% to monomer; solvent, methylene chloride, 20 g; −78°C; time, 1 day.

[b] I, complex catalyst were prepared at −78°C. II, aging of CPA with titanium trichloride was carried out at room temperature for 1 hr.

[c] The product was fractionated (cf. Fig. 2).

ride–titanium trichloride complex catalysts, respectively. Under both reaction conditions I and II, a purple-colored titanium trichloride precipitate remained at the bottom of the ampoule.

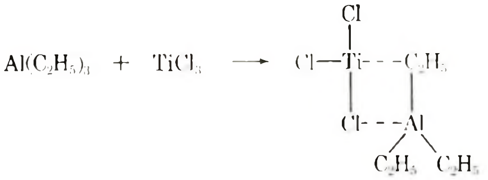
There are some differences in the results of polymerization in methylene chloride and in toluene, as shown in Table IV. Polymer yields are higher in methylene chloride than in the toluene. Toluene gives polymers with higher DMF-insoluble content, with higher optical density ratio D_{1258}/D_{1270} and with lower solution viscosity than does methylene chloride. These tendencies are essentially the same as those observed in the previous paper.[2] Hence it seems that a nonpolar solvent decreases the activity of the catalysts and promotes their steric control in the polymerization of CPA compared with a polar solvent.[11]

Polymerization of α-olefins by Ziegler-Natta type catalysts is generally considered to take place on the titanium site as an active center. CPA was polymerized by neither titanium tetrachloride nor titanium trichloride itself, probably because their acid strength is too strong, but by aluminum compounds alone, suggesting that active species of complex catalyst for the polymerization of CPA may come from the aluminum compounds.

It is observed in Tables III–V that addition of an appropriate amount of titanium tetrachloride or titanium trichloride to the aluminum compound increases the polymer yield. The polymer yield reaches a maximum value and then decreases with increasing the ratio of the amount of titanium chloride to aluminum compound. With more than a certain amount of titanium chloride, practically no polymerization of CPA occurs.

It was already known that organoaluminum compounds react with titanium chlorides in a solvent to form the intermediates shown in eqs. (2) and (3).[12] Titanium is alkylated and then reduced.

$$Al(C_2H_5)_3 + TiCl_4 \longrightarrow [Al(C_2H_5)_3 \cdot TiCl_4] \quad (2)$$


(3)

and at the same time the aluminum compound is chlorinated, leading to diethylaluminum chloride, ethylaluminum dichloride, and aluminum trichloride.

It has been assumed that triethylaluminum is converted to coordinated anionic catalyst, but it may be reasonable in the present system that if it is partially chlorinated, it acts as a cationic initiator for CPA. The degree of chlorination of aluminum is considered to depend upon the titanium chlorides and their amounts. The apparent variations in catalytic activity shown in Tables III–V may be explained by assuming that titanium chlorides themselves increase the acid strength of aluminum compounds through chlorination, resulting in the change of the polymer yield.

Stereoregularity of Poly(cyanoethyl)oxymethylene

When CPA was mixed with an excess of titanium tetrachloride in solution at a low temperature, a yellow brownish precipitate was formed. The complex, isolated as a hygroscopic powder, is soluble in methanol, ethanol, acetone, dimethylformamide, and CPA and insoluble in pyridine and THF. Treatment of the complex with 2,4-dinitrophenylhydrazine in acidic ethanol gave the 2,4-dinitrophenylhydrazone of CPA. The titanium content of the complex was determined colorimetrically[13] to be 17.7%. It may be suggested that CPA and titanium tetrachloride form a 1:1 complex, the titanium content of which is calculated to be 17.6%.

Titanium tetrachloride was dissolved in a large amount of CPA to give an orange solution. It had a new visible absorption maximum at 360 mμ. The peak disappeared by adding a small amount of water. CPA shows a carbonyl stretching absorption peak at 1 720 cm^{-1} and a nitrile stretching absorption peak at 2 250 cm^{-1} in the infrared spectrum. It should be noticed in the infrared spectrum of 1:1 complex of CPA with titanium tetrachloride as Nujol mull that the carbonyl peak is shifted to 1678 cm^{-1}, and on the other hand, the nitrile peak to 2 300 cm^{-1}. On mixing CPA with titanium trichloride, shifts of the carbonyl group to 1 600 cm^{-1} and of the nitrile group to 2 270 cm^{-1} are also observed, although a stoichiometric adduct was not isolated.

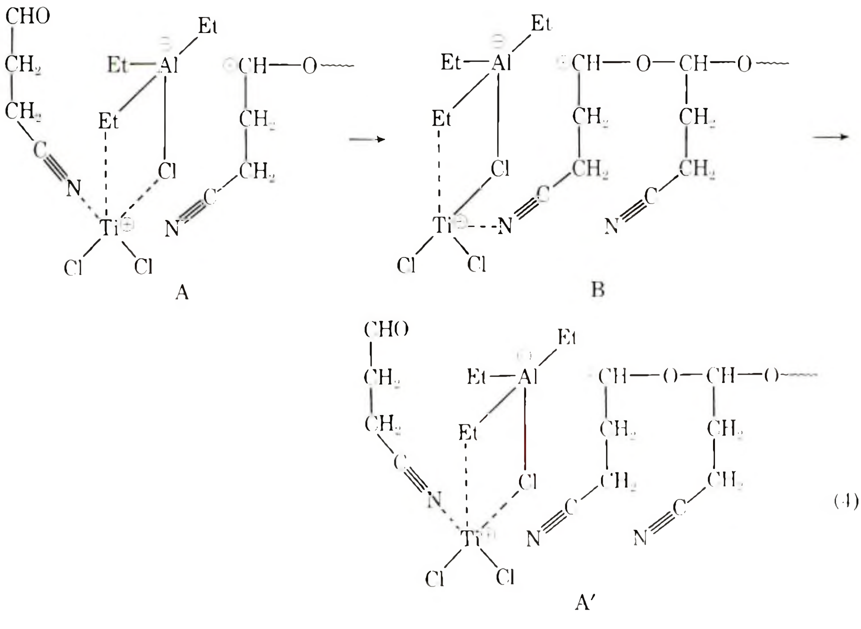
Complex formation by the interaction of a compound containing carbonyl group with Lewis acid is summarized and discussed in the publication by Olah.[14] A number of complexes of aliphatic or aromatic nitrile compounds with Lewis acids were also studied by infrared spectroscopy.[15] It was reported in the literature[14,15] that complex formation brings a shift of the nitrile frequency to higher region, in contrast with the shift of the carbonyl frequency to lower region. These shifts are, respectively, generally regarded as an evidence of the complex formation. While the literature cites few references to compounds containing both C=O and C≡N groups such as CPA, it is likely that CPA is reversibly coordinated with titanium compounds at both groups of aldehyde and nitrile.

The coordination is supposed to reflect upon the following remarkable results (Table III, IV and V) of the stereoregularity of polymer.

(1) Increasing the molar ratio of titanium compound to aluminum compound increases the optical density ratio, D_{1258}/D_{1270}. (2) The optical density ratio is apparently larger in condition II in which CPA was previously aged with a titanium compound than in condition I.

It seems reasonable from these results to assume that the stereoregularity of poly(cyanoethyl)oxymethylene increases as CPA undergoes coordination with titanium chlorides. It seems possible that the carbonyl group of CPA is allowed to undergo cationic polymerization induced by partially chlorinated aluminum compounds, and that the nitrile group coordinated with titanium chloride makes a contribution to the steric control in the polymerization.

A detailed mechanism must be the subject of future research, but a probable scheme may be proposed for the propagation reaction in the triethylaluminum–titanium trichloride system. Despite the fact that several initiation mechanisms have been proposed for the polymerization of acetaldehyde with Lewis acid,[8,16,17] no experimental proof has been obtained. The authors confine the present consideration to the propagation reaction, and hence the propagating chain end alone appears in the scheme. Although the mechanism is considered to be highly speculative and suitably applicable only to the catalytic systems containing titanium trichloride, it is believed that the presentation of the scheme [eq. (4)] may be indispensable.



(4)

State A shows that the aluminum compound and the nitrile group of CPA are competitively coordinated with chlorine vacancy, which was defined as an electron defect due to a chlorine deficiency, on the crystal surface of titanium trichloride.[12b] The chlorinated aluminum compound intermediately formed is assumed to act as a counteranion for the propagating carbonium cation. Addition of the aldehyde group to the propagating chain end is followed by desorption of the nitrile group from titanium. This process may take place repeatedly, accompanied by an insertion of the approaching monomer molecule into the new chlorine vacancy.

As the coordination occurs only at chlorine vacancies on the surface, rather large amounts of titanium compound may be needed to increase effectively the stereoregularity of polymer. Titanium tetrachloride is a much stronger chlorination agent than titanium trichloride. Titanium tetrachloride, consequently, exhibits less steric control for polymerization of CPA than titanium trichloride.

References

1. H. Sumitomo and K. Kobayashi, *J. Polym. Sci. A-1*, **4**, 907 (1966).
2. H. Sumitomo and K. Kobayashi, *J. Polym. Sci. A-1*, **5**, 2247 (1967).
3. H. Sumitomo and K. Kobayashi, paper presented at the International Symposium on Macromolecular Chemistry, Tokyo and Kyoto, Japan, 1966; *Preprints*, I 197.
4. D. Cook, *Can. J. Chem.*, **41**, 522 (1963).
5. T. Saegusa, *Kogyo Kagaku Zasshi*, **70**, 1903 (1967).
6. F. Fieser and M. Fieser, *Textbook of Organic Chemistry*, Heath, Boston, 1950, p. 195.
7. R. Hollmann, *Z. Physik. Chem.*, **43**, 129 (1903).
8. O. Vogl, *J. Polym. Sci. A*, **2**, 4591 (1964).
9. K. Kobayashi and H. Sumitomo, paper presented at the 21st Annual Meeting of the Chemical Society of Japan, April 1968.
10. H. Fujii, I. Tsukuma, T. Saegusa, and J. Furukawa, *Makromol. Chem.*, **82**, 32 (1965).
11. O. Vogl and W. M. D. Bryant, *J. Polym. Sci. A*, **2**, 4633 (1964).
12. L. Reich and A. Schindler, *Polymerization by Organometallic Compounds*, Interscience, New York, 1966, (a) pp. 137 and 247; (b) p. 132.
13. *Bunsekikagaku-Binran* (*Handbook of Analytical Chemistry*), Japan Society for Analytical Chemistry, Maruzen, Tokyo, 1961, p. 304.
14. G. A. Olah and M. X. Meyer, *Friedel-Crafts and Related Reactions*, Vol. I, G. E. Olah, Ed., Interscience, New York, 1964, p. 623.
15. H. J. Coerver and C. Curran, *J. Amer. Chem. Soc.*, **80**, 3522 (1958).
16. O. Vogl, *J. Macromol. Sci.* (*Chem.*), **A1**, 243 (1967).
17. S. Ohta, T. Saegusa, and J. Furukawa, *Kogyo Kagaku Zasshi*, **67**, 608 (1964).

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Polymerization of 3,4-Dihydro-2H-Carboxyaldehyde (Acrolein Dimer). Part II. Copolymerization with Isocyanates

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Synopsis

Copolymers of 3,4-dihydro-2H-pyran-2-carboxyaldehyde (acrolein dimer) with phenyl isocyanate were obtained under several conditions. Infrared and NMR analyses showed that the isocyanate always reacted with acrolein dimer forming urethane linkages, not block units of isocyanate. An alternating copolymer was obtained from the copolymerization in the presence of anionic catalysts such as butyllithium at room temperature, irrespective of the monomer ratios employed. The isocyanate content in the copolymer prepared with an $Al(C_2H_5)_2Cl$ catalyst was increased by elevating polymerization temperature. The copolymerizability of aldehydes with the isocyanate depends upon the polarity of aldehyde group.

INTRODUCTION

In the preceding paper[1] it was reported that polymerization of acrolein dimer through the aldehyde group could not take place beyond two units at room temperature because formation of two successive linkages of this type was prohibited. Clearly, there was a ceiling temperature in the polymerization with the use of anionic catalysts. Furthermore, Shashoua et al.[2] and Natta et al.[3] have reported that anionic polymerization of an isocyanate gave a polymer below −20°C, but no polymer formed at room temperature.

While the present work was in progress, Furukawa et al.[4] reported the copolymerization of ethylene oxide with phenyl isocyanate and observed fractions consisting of alternating copolymers. It was expected from the reactivity of acrolein dimer and isocyanates that perfectly alternating copolymers could be obtained by copolymerization of acrolein dimer with isocyanates, irrespective of monomer ratios employed, by the use of anionic catalysts at room temperature.

The purpose of the present work is to report the synthesis of these alternating copolymers and analyses of their structures by infrared and NMR methods. The reactivity of acrolein dimer and the characteristics of the copolymerization between the two monomers is also discussed.

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EXPERIMENTAL

Materials

Acrolein dimer was prepared by the same procedure as in the previous report.[1] Phenyl isocyanate was distilled under nitrogen atmosphere, bp 48°C/10 mm Hg. Toluene was purified by refluxing and distilling commercial reagent over sodium metal under nitrogen, bp 110.8°C. Commercial organometallic compounds were used as initiators.

Polymerization Procedures

The copolymerizations were usually carried out by the following procedure. Acrolein dimer, isocyanate, and toluene were charged into an ampoule under nitrogen, and then a catalyst was injected into the system at polymerization temperature. To terminate the polymerization the mixture was diluted with toluene and poured into petroleum ether or hexane. The white powdery polymer which was precipitated was washed with fresh methanol and hexane, dried by suction, and finally dried in a vacuum oven at 35°C for 24 hr.

Analyses of Polymer Compositions and Structures

Infrared and NMR analyses of the polymer composition and structure were carried out with Hitachi-EPI-2 and Varian A-60A instruments, respectively. The polymer composition was also determined by nitrogen analyses.

RESULTS

Synthesis of Copolymers between Acrolein Dimer and Isocyanates and their Properties

The results of copolymerization of acrolein dimer with isocyanates at 15°C are shown in Tables I and II.

TABLE I
Copolymerization of Acrolein Dimer with Isocyanates at 15°C[a]

Expt. no.	Isocyanate	Initiator	Conversion, %	N in polymer, %	Calculated N content of 1:1 copolymer, %	Melting point, °C
1	C_6H_5NCO	$AlEt_2Cl$	88.0	4.72	6.06	
2	C_6H_5NCO	$ZnEt_2$	95.0	5.85	6.06	150
3	CH_3NCO	$AlEt_2Cl$	76.8	ND[b]		Discolored
4	CH_3NCO	$ZnEt_2$	70.0	6.67	8.26	125
5	C_2H_5NCO	$AlEt_2Cl$	20.0	ND		
6	C_2H_5NCO	$ZnEt_2$	100.0	6.66	7.75	115

[a] Isocyanate, 0.1 mole; monomer, 0.1 mole; catalyst concentration, 1 mole-% of monomer; monomer concentration, 10 vol-% of toluene; polymerization time, 24 hr.

[b] ND = not determined.

TABLE II
Copolymerization of Acrolein Dimer (AD) with Phenyl Isocyanate (PI) with the Use of $Al(C_2H_5)_2Cl$ at 15°C[a]

Expt. no.	Monomer			Copolymer yield, g	N in copolymer, %	D_{1740}[b] / D_{1498}	$\eta_{sp/c}$[c]	CS_2-soluble fraction, %
	AD, g	PI, g	PI, mole-%					
7	3.0	1.0	24.4	1.97	1.75	3.10		17
8	3.0	2.0	39.0	3.18	2.89	2.95		
9	3.0	3.0	48.9	3.96	4.30	2.95	0.13	67
10	3.0	5.0	61.3	5.29	4.39	3.05	0.32	
11	3.0	6.8	69.4	5.19	5.00	2.95	0.29	
12	0.0	2.0	100.0	0	—			

[a] Polymerization time, 15 min; initiator, 1 mol-% of AD; solvent: toluene 15 cc.
[b] The ratio of the optical density at 1740 cm^{-1} to that at 1498 cm^{-1}.
[c] $\eta_{sp/c}$: 0.5 g/100 cc $CHCl_3$ at 35°C.

Under conditions such that homopolymerization of phenyl isocyanate did not occur with $Al(C_2H_5)_2Cl$ and that acrolein dimer did not give a polymer in the presence of $Al(C_2H_5)_3$ at room temperature, polymers were obtained in the copolymerization of acrolein dimer and isocyanates and found to contain nitrogen.

Some of the polymers obtained were partly soluble in carbon disulfide; particularly, the polymer (expt. 2) having a 1:1 monomer unit composition was completely soluble, whereas neither the polymer of acrolein dimer nor poly(phenyl isocyanate) was soluble in the same solvent.

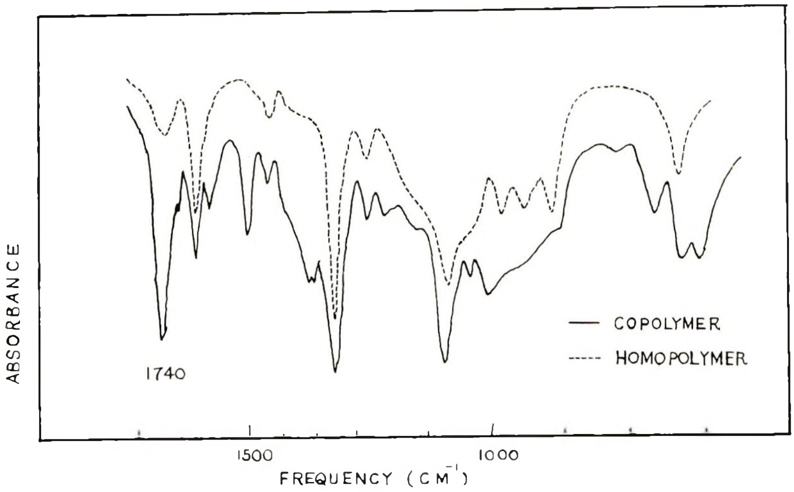


Fig. 1. Infrared spectra: (——) copolymer (expt. 9) obtained from acrolein dimer and phenyl isocyanate by use of $Al(C_2H_5)_2Cl$ at room temperature; (- -) homopolymer produced from acrolein dimer under the same conditions. KBr disk method.

These facts show that the polymers obtained contain copolymers of acrolein dimer with isocyanates, and are not simple mixtures of the polymer of acrolein dimer and polyisocyanate.

The infrared spectrum of the polymer obtained with $Al(C_2H_5)_2Cl$ showed a strong single characteristic absorption band at 1740 cm^{-1} bands at 1600, 1498, 760, and 690 cm^{-1} due to monosubstituted benzene, and also absorption bands at 1242 and 1078 cm^{-1} due to cyclic unsaturated ether group which are the same as that of the polymer of acrolein dimer, as shown in Figure 1.

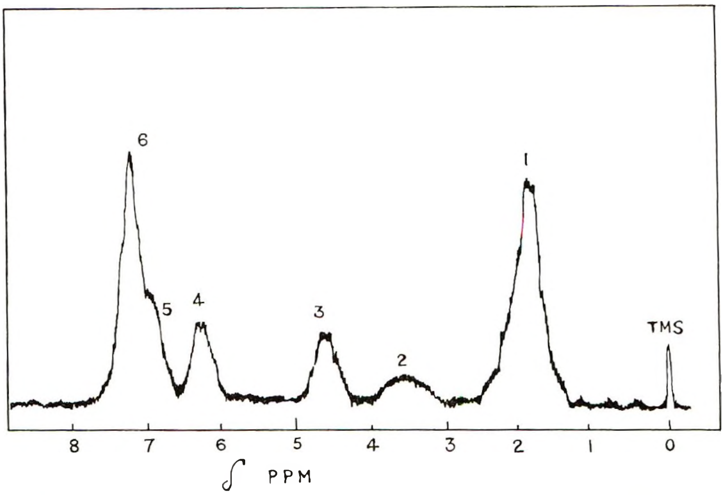


Fig. 2. NMR spectrum of 1:1 copolymer (expt. 28) obtained from acrolein dimer and phenyl isocyanate with $Al(C_2H_5)_3$ at room temperature. The NMR spectra were measured on 0.1 g copolymer in 1 ml of $CDCl_3$ at 60°C.

Figure 2 shows the NMR spectrum of the copolymer (expt. 28) obtained with $Al(C_2H_5)_3$ catalyst at room temperature: this polymer was proved to have nearly a 1:1 composition by nitrogen analysis, as seen in Table III. The spectrum had a characteristic chemical shift at 6.80 ppm, in addition to one at 7.12 ppm due to protons in the phenyl group and those at 4.60 and 6.22 ppm due to protons of the unsaturated ether group in acrolein dimer unit.

On the other hand, NMR spectrum of a copolymer having a larger amount of acrolein dimer unit than phenyl isocyanate (such as the copolymer obtained in expt. 27) had, besides those mentioned above, two broad chemical shifts at 5.3 and 5.6 ppm between those which appear in the spectrum of the polymer of acrolein dimer.

The copolymers obtained at room temperature from acrolein dimer and isocyanates were soluble in aromatic hydrocarbons and alkyl and aryl halides, such as toluene, xylene, chloroform, and monochlorobenzene; the nearly 1:1 copolymers were also soluble in carbon disulfide.

TABLE III
NMR and N Analyses of Copolymers Obtained from Acrolein Dimer and Phenyl Isocyanate at Room Temperature[a]

	Peak no.	Chemical shift, ppm	Intensity of shift C-26[b]	C-27[c]	C-28[d]
	1	1.81	4.4	7.5	4.0
	2	3.55	1.0	1.0	1.1
	3	4.60	1.0	1.0	1.0
	4	6.22	1.0	1.0	1.0
	5	6.80	0.8	0.5	1.1
	6	7.12	4.0	2.5	5.3
	7	Others	0	1.0	0
AD/PI in copolymer					
N, %[e]			1.4	3.5	1.2
NMR[f]			1.3	3.4	1.0

[a] Catalyst concentration, 1 mole-% of AD; monomer concentration, 20 vol-% in toluene; polymerization time, 24 hr.

[b] CS_2-soluble fraction of the copolymer obtained from the 1:2 monomer composition; $Al(C_2H_5)_2Cl$ catalyst.

[c] CS_2-insoluble fraction of the copolymer obtained from 2:1 monomer composition, $Al(C_2H_5)_2Cl$ catalyst.

[d] Copolymer soluble in CS_2 obtained from 1:1 monomer composition; $Al(C_2H_5)_3$ catalyst.

[e] Calculated from nitrogen analysis.

[f] AD/PI mole ratio is determined by calculation of (intensity of all the proton except peak 6)/8/(intensity of peak 6)/5.

The 1:1 copolymer obtained from phenyl isocyanate had a melting point at 150°C, while those from methyl isocyanate and from ethyl isocyanate had melting points at 125°C and 115°C, respectively.

Various Factors Affecting Copolymerization of Acrolein Dimer with Phenyl Isocyanate

Table IV shows the effects of catalysts on copolymerization at 15°C.

As shown in Table V, decreasing the temperature decreased the copolymerization rate and the ratio D_{1740}/D_{1240} and increased the content of toluene-insoluble material in the copolymer; this material was found to be a polymer of acrolein dimer obtained by aldehyde group polymerization.

The effects of monomer composition on the copolymerization are shown in Table VI.

With the use of butyllithium, the increase of the content of isocyanate in the monomer compositions generally increased the rate of polymerization, and the polymer obtained was found to have 1:1 polymer composition irrespective of monomer feed and conversion; with $Al(C_2H_5)_2Cl$, addition of a small amount of isocyanate diminished the rate of polymerization and at low conversions (total conversions 13–17%, acrolein dimer conversions

TABLE IV
Copolymerization of Acrolein Dimer with Phenyl Isocyanate with Various Catalysts at 15°C[a]

Expt. no.	Initiator	Conversion, %	N in copolymer, %
13	$AlEtCl_2$	5.3	0.92
14	$AlEt_2Cl$	66.0	2.80
15[b]	$AlEt_3$	87.0	5.12
16	$MgEt_2$	69.6	4.79
17	EtMgBr	Large amount	ND
18[c]	C_4H_9Li	69.8	6.08
19	$ZnEt_2$	95.0	5.85
20	Et_3N	0.0	—

[a] Initiator concentration, 1 mole-% of AD; monomer composition, AD/PI = 1; monomer concentration, 20 vol-% of toluene; polymerization time, 20 hr.

[b] 3 hr.

[c] 1 hr.

TABLE V
Effects of Temperature on Copolymerization of Acrolein Dimer with Phenyl Isocyanate with the Use of $Al(C_2H_5)_2Cl$[a]

Expt. no.	Polymerization temperature, °C	Conversion, %	D_{1740}/D_{1240}	D_{1740}/D_{1498}	Insoluble fraction, %[b]	N in soluble part, %[c]
21	20	77	1.08	3.0	0	4.80
22	0	75	1.06	3.0	8.4	3.94
23	−20	38	0.68	2.9	47.7	2.92
24	−40	44	0.13	3.0	93.3	0.95
25	−78	32	0.16	2.8	88.4	—

[a] Initiator concentration, 1 mole-% of AD, polymerization time, 18 hr.

[b] Toluene-insoluble fraction in the copolymer.

[c] N content of toluene-soluble part of the copolymer.

18–30%) the copolymer obtained had a higher content of acrolein dimer unit than that in the monomer feed.

Table VII shows the results of aldehydes with phenyl isocyanate.

Acrolein dimer, methacrolein dimer, and cyclohexene-3-carboxyaldehyde gave copolymers having nearly 1:1 monomer unit compositions with the use of $Al(C_2H_5)_3$ at room temperature.

DISCUSSION

Copolymer Structures

It was shown above that copolymers were obtained in the polymerization of acrolein dimer with phenyl isocyanate.

TABLE VI
Effects of Monomer Composition on Copolymerization of Acrolein Dimer with Phenyl Isocyanate at 15°C

$Al(C_2H_5)_2Cl$[a]			C_4H_9Li[b]		
Monomer Composition, PI mole-%	Conversion, %	Polymer Composition, PI mole-%	Monomer Composition, PI mole-%	Conversion, %	Monomer Composition, PI mole-%
0 [c]	74.6	0	0	0	—
2.3[c]	58.2	1.2			
4.6[c]	52.2	1.7			
25.0	13.4	3.0	9	0	—
33.3	16.8	6.4	34	41	47
42.9	14.1	7.8	44	77	46
50.0	13.5	10.3	50	80	49
60.0	12.6	22.4	61	65	50

[a] Initiator, $Al(C_2H_5)_2Cl$, 0.5 mole-% of AD; AD, 2.1 cc; toluene, 18 cc; polymerization time, 30 min.

[b] Initiator, butyl Li, 0.66 mole-% of AD; AD, 1.05; toluene, 9 cc; polymerization time, 60 min.

[c] AD, 2 cc, toluene, 18 cc, polymerization time, 50 min.

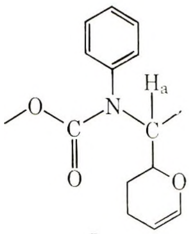
TABLE VII
Copolymerization of Aldehydes and Phenyl Isocyanate with Al-Containing Compound at 15°C[a]

			N, %	
Aldehydes	Catalyst	Yield, g	Observed in polymer	Calculated for 1:1 copolymer
Butyraldehyde	$AlEt_2Cl$	0		
	$AlEt_3$	0		
Methacrolein dimer	$AlEt_2Cl$	0		
	$AlEt_3$	0.28	5.06	5.40
Cyclohexene 3-carboxyaldehyde	$AlEt_2Cl$	0		
	$AlEt_3$	1.71	5.75	6.10
Acrolein dimer	$AlEt_2Cl$	1.30	4.72	6.06
	$AlEt_3$	1.74	5.12	
Acrolein	$AlEt_2Cl$	0.75	4.78	7.95

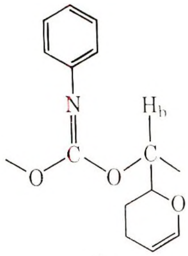
[a] Aldehydes, 1.0 cc; phenyl isocyanate, 1.0 cc; toluene, 8 cc; catalyst concentration, 1 mole-% of isocyanate; polymerization time, 24 hr.

It is furthermore expected that the isocyanate units in the copolymer are found to be urethane linkages (I) or imino ether ones (II), not block units derived from isocyanate.

Infrared spectra of the copolymers had no absorption band at 1749 cm^{-1}, which is characteristic of poly(phenyl isocyanate) according to Furukawa et al.,[4] who also expected that the absorption band at 1700 and 1730 cm^{-1} were assigned to $\nu_{C=N}$ or $\nu_{C=O}$ in alternate copolymers between ethylene oxide and phenyl isocyanate.



I



II

In addition to these facts, the ratios of the optical density at 1 740 cm^{-1} to that at 1 498 cm^{-1} due to phenyl group in the copolymer were constant irrespective of monomer composition, polymerization temperature, and polymer compositions, as shown in Table II and V. This means that isocyanate enters into a constant specific reaction.

These facts indicate that isocyanates always react with acrolein dimer, forming structure I or II. It was not possible by chemical analysis to determine which was the structure of the copolymer.

However, the copolymers are supposed to have structure I, because the chemical shift at 6.8 ppm is probably due to a proton, H_a in the structural unit I; the protons, H_a, attached to *N*-substituted urethane groups are closer to the benzene ring than that in the structural unit II and seem to be shielded by the aromatic ring current, showing the extremely low field signal at 6.8 ppm, whereas the proton in structure II is not affected by benzene ring current and therefore is expected to have the same or near chemical shifts (4.5–5.5 ppm) as the acetal group protons of polyacetaldehyde.

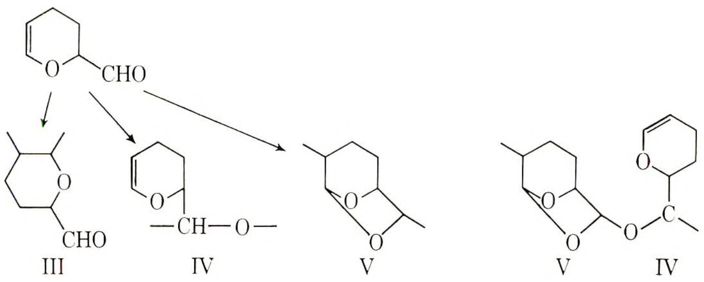
Particularly, as seen from Table III and Figure 2, the ratio of the peak areas due to each proton in the NMR of the copolymer (expt. 28) was 4:1:1:1:5, which agreed with the ratio of protons in the structural unit I. Therefore typical copolymer (such as in expt. 28) obtained by copolymerization initiated by anionic organometallic compound at room temperature are expected to have the complete repeating units of the type I and to be an alternating copolymer.

Copolymerizability and Reactivity of Acrolein Dimer

The main factors affecting the copolymerizability with isocyanates are the nature of the initiator and polymerization temperature.

Initiator for the copolymerization are divided into three groups: cationic catalyst, such as $AlC_2H_5Cl_2$; weak cationic catalyst, such as $Al(C_2H_5)_2Cl$; and anionic organometallic compounds such as butyllithium, $(C_2H_5)_2Mg$, C_2H_5MgB, and $Al(C_2H_5)_3$.

The first group, $Al(C_2H_5)Cl_2$, initiates III or V type polymerization as shown in eq. (1), but little copolymerization of acrolein dimer with isocyanate. Therefore homopolymerization of acrolein dimer occurs almost exclusively.



(1)

The second group initiator, $Al(C_2H_5)_2Cl$, belongs to the group of weak cationic catalysts considered in the previous paper.[1] This initiator initiates not only the copolymerization with isocyanate but also III and V type polymerizations therefore producing the copolymer having more acrolein dimer units than that in monomer employed, as shown in Table VI. There are chemical shifts at 5.3 and 5.6 ppm in the NMR spectrum of the copolymer having more acrolein dimer units (expt. 27), and both peaks are probably due to the V–IV units.

On the other hand, the third group, anionic metallic compound, initiated neither the homopolymerization of acrolein dimer nor isocyanate at room temperature, but gave alternate copolymerization at the same temperature (although polymerization conversions were high). Table VI shows that the 1:1 copolymer was obtained with butyllithium irrespective of conversion and monomer compositions.

It was, therefore, proved that the aldehyde group of the acrolein dimer is reactive, but two successive linkages of aldehyde group polymerization of acrolein dimer do not occur at room temperature with anionic organometallic compound; there was a ceiling temperature in the polymerization with anionic catalyst.

In conclusion, polymerization conditions giving the alternating copolymer of acrolein dimer with isocyanate are use of an anionic organometallic compound as initiator and polymerization at room temperature.

The effect of polymerization temperature on the copolymerizability with the use of $Al(C_2H_5)_2Cl$ is shown in Table V; and D_{1740} corresponds to the urethane linkage related to the isocyanate reaction with IV, while D_{1240} is assigned to the cyclic vinyl ether group related to the IV type polymerization; then decreasing D_{1740}/D_{1240} means increasing IV, type polymerization of acrolein dimer. Therefore decreasing the temperature increased IV-type polymerization.

The copolymerizations of aldehydes depend upon the polarity of aldehyde group and the structure of the substituent; the copolymerization seems to occur easily if the substituents of aldehyde group are electronegative and have secondary or tertiary carbon groups attached to the aldehyde group.

References

1. Y. Kitahama, H. Ohama, and H. Kobayashi, *J. Polym. Sci. C*, in press.
2. V. E. Shashoua, W. Sweeny, and R. F. Tietz, *J. Amer. Chem. Soc.*, **82**, 866 (1960).
3. G. Natta, J. Di Pietro, and M. Cambini, *Markromol. Chem.*, **56**, 200 (1962).
4. J. Furukawa, S. Yamashita, M. Marubashi, and K. Harada, *Markomol. Chem.*, **85**, 80 (1965).

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Poly-*as*-triazines

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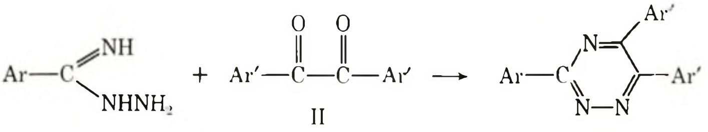
Synopsis

Two high molecular weight ($\eta_{inh} > 1.0$) soluble poly-*as*-triazines have been prepared by the solution polycondensation in *m*-cresol of 2,6-pyridinediyl dihydrazidine with *p,p'*-oxybis(phenyleneglyoxal hydrate) and with *p,p'*-oxydibenzil. Thermal characterization of the poly-*as*-triazines by TGA showed polymer decomposition temperatures of ~400°C after a 300°C cure in argon. Poly-*as*-triazines exhibited weight losses <8% after aging in static air at 316°C for 200 hr. Clear yellow films cast for *m*-cresol solutions exhibited good flexibility and toughness even after aging at 316°C for 200 hr in air and after refluxing in 10% aqueous potassium hydroxide solution for 24 hr.

INTRODUCTION

Although *s*-triazine polymers[1–4] have received synthetic attention in recent years, the successful preparation of an all-aromatic soluble high molecular weight polytriazine has not been disclosed. In addition, essentially no attempts to synthesize *as*-triazine polymers have been reported. Case[5,6] recently described the preparation of *as*-triazine model compounds in high yields by the cyclocondensation of hydrazidines (I) with diketones (II) as shown in eq. (1), where Ar = Ar' = aromatic.



I II *as*-triazine (1)

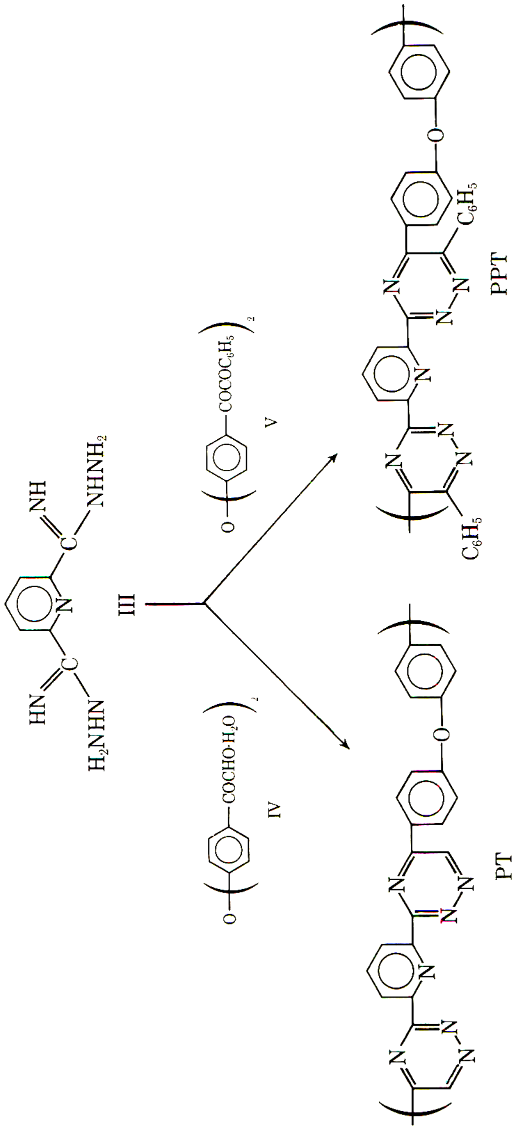
This reaction appeared suitable for polymer formation and therefore was utilized in the preparation of high molecular weight soluble poly-*as*-triazines from the reaction of 2,6-pyridinediyl dihydrazidine (III) with *p,p'*-oxybis(phenyleneglyoxal hydrate) (IV) and with *p,p'*-oxydibenzil (V) to provide poly[3,3'-(2'',6''-pyridinediyl)-5,5'-(*p,p'*-oxydiphenylene) di(*as*-triazine)] (PT) and poly[3,3'-(2'',6''-pyridinediyl)-5,5'-(*p,p'*-oxydiphenylene)-di(6-phenyl-*as*-triazine)] (PPT), respectively, as shown in eq. (2).

EXPERIMENTAL

Reactants

2-Pyridyl Hydrazidine. This reactant was synthesized for model compound work following the procedure of Case[5] and obtained as white needles, mp 95-96°C (lit.[5] mp 95–96°C).

(2)


HN
H$_2$NHN
NH
NHNH$_2$
III
O
COCHO·H$_2$O
2
IV
O
COCOC$_6$H$_5$
2
V
PT
PPT
C$_6$H$_5$
C$_6$H$_5$

2,6-Pyridinediyl Dihydrazidine (III). Hydrazine hydrate (95%, 20 ml) was added to a solution of 2,6-dicyanopyridine (2.8 g) in ethanol (250 ml) at 40°C. The resulting clear yellow reaction solution was stirred at 50–55°C for 2 hr to form a white suspension which was cooled and filtered. The resulting white solid was recrystallized from water (250 ml) to afford pale yellow needles (3.0 g, 75% yield) of 2,6-pyridinediyl dihydrazidine, mp 230–231°C with decomposition.

ANAL. Calcd for $C_7H_{11}N_7$: C, 43.51%; H, 5.74%; N, 50.76%. Found: C, 43.72%; H, 5.76%; N, 50.77%.

***p,p'*-Oxybis(phenyleneglyoxal Hydrate) (IV).** Following a known procedure,[7] *p,p'*-diacetyldiphenyl ether prepared by the Friedel-Crafts acetylation of diphenyl ether in methylene chloride was oxidized with selenium dioxide in aqueous dioxane. The crude product was recrystallized from a mixture of dioxane and water (2:1) to afford white crystals (60% overall yield) of *p,p'*-oxybis(phenyleneglyoxal hydrate), mp 140.5–142°C (lit.[7] mp 122°C).

ANAL. Calcd for $C_{16}H_{14}O_7$: C, 60.38%; H, 4.43%. Found: C, 60.18%; H, 4.41%.

***p,p'*-Oxydibenzil (V).** A solution of diphenyl ether (17.0 g, 0.10 mole) and phenylacetyl chloride (30.9 g, 0.20 mole) in methylene chloride (50 ml) was added during 1 hr to a suspension of anhydrous aluminum chloride (26.6 g, 0.20 mole) in methylene chloride (150 ml) at 15–20°C under nitrogen. The resulting brown reaction mixture was stirred at ambient temperature for 18 hr followed by pouring onto crushed ice and hydrochloric acid. The organic phase was separated and washed successively with water, aqueous sodium bicarbonate, and water followed by drying over anhydrous magnesium sulfate. Concentration to about 75 ml followed by cooling provided a cream-colored solid (33.0 g, 82% yield), mp 166–168.5°C. Recrystallization from benzene afforded near-white crystals of *p,p'*-di(phenylacetylphenyl) ether, mp 169–170°C (lit.[8] mp 169–170°C). To a mixture of selenium dioxide (11.1 g, 0.10 mole) in glacial acetic acid (150 ml) at 60°C, *p,p'*-di(phenylacetylphenyl) ether (20.0 g, 0.050 mole) was added. The reaction mixture was refluxed for 24 hr, followed by a hot filtration. The clear yellow filtrate was concentrated to about 75 ml and cooled to provide a yellow solid (18.5 g, 86% yield), mp 103–106°C, after thorough washing with methanol. Recrystallization from a mixture of ethyl acetate and *n*-hexane afforded yellow crystals of *p,p'*-oxydibenzil, mp 108–109°C (lit.[8] mp 106.4–107.4°C).

ANAL. Calcd for $C_{28}H_{18}O_5$: C, 77.41%; H, 4.18%. Found: C, 77.38%; H, 4.10%.

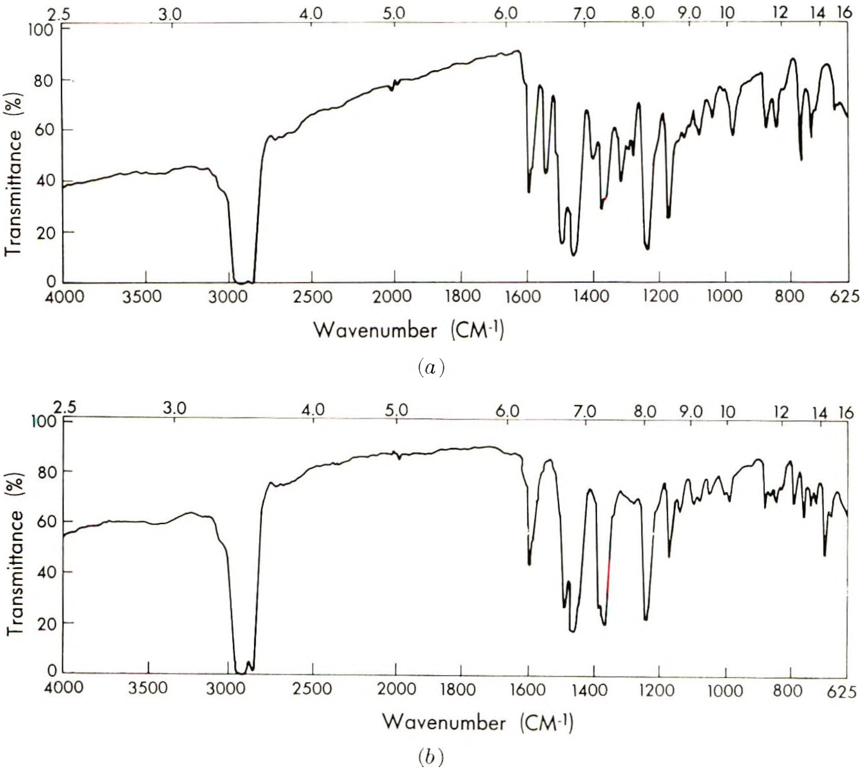
In addition, initial attempts to prepare other dihydrazidines such as the 3,5-pyridinediyl and *p*-phenylene from the reaction of hydrazine with the corresponding dinitrile or the imino ether failed to provide polymer grade reactants. Apparently the 2,6-pyridinediyl dihydrazidine is stabilized through hydrogen bonding which inhibits the known[9] decomposition of hydrazidines to a mixture of components such as dihydro-1,2,4,5-tetrazines and 1,2,4-triazoles.

Solvents

With the exception of ethanol, all solvents employed in the synthesis of model compounds and polymers were redistilled prior to use.

Model Compounds

Prior to polymer synthesis, a series of model compounds (VI–XI) as shown in eqs. (3) and (4) were prepared as a guide to polymer synthesis. Model compounds VI, VII, X, and XI were synthesized by refluxing stoichiometric quantities (0.010 mole) of the two reactants in ethanol (30 ml) under argon for 18 hr. The reaction mixture was concentrated by simple distillation to about 15 ml followed by cooling. Filtration provided pure model compounds in high yields ($>70\%$). Model compounds VIII and IX were similarly prepared by refluxing stoichiometric amounts (0.010 mole) of the two reactants in *m*-cresol under argon for 18 hr, followed by partial concentration and dilution with ethanol. Filtration after



(*a*)

(*b*)

Fig. 1. Infrared spectra (Nujol mulls) of model compounds: (*a*) *p,p'*-bis {5-[3(2-pyridyl)-*as*-triazinyl]}diphenyl ether (VIII); (*b*) *p,p'*-bis{5-[3(2-pyridyl)-6-phenyl-*as*-triazinyl]} diphenyl ether (IX).

TABLE I
Characterization of Model Compounds

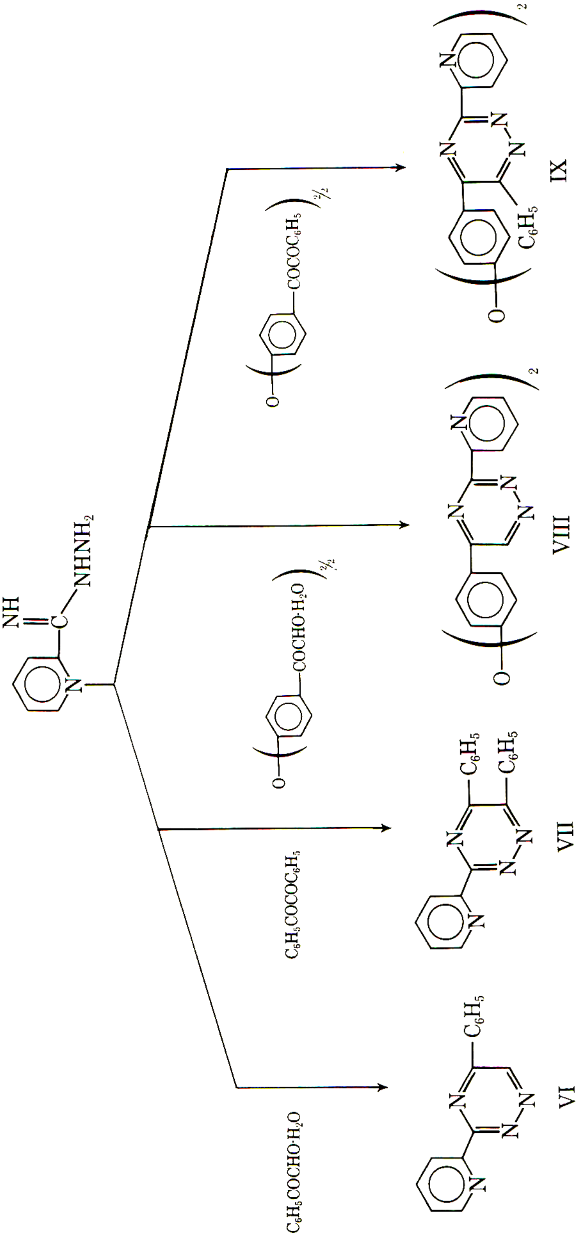
	Model compound	Reaction solvent	Mp, °C	Formula	Elemental analysis[a]		
					C, %	H, %	N, %
VI	3-(2-Pyridyl)-5-phenyl-*as*-triazine	Ethanol	140–141[b]	$C_{14}H_{10}N_4$	—	—	—
VII	3-(2-Pyridyl)-5,6-diphenyl-*as*-triazine	Ethanol	193.5–194.5[c]	$C_{20}H_{14}N_4$	—	—	—
VIII	*p,p′*-Bis {5-[3(2-pyridyl)-*as*-triazinyl]} diphenyl ether	*m*-Cresol	275–276	$C_{28}H_{18}N_8O$	69.47 (69.70)	3.83 (3.76)	23.04 (23.23)
IX	*p,p′*-Bis {5-[3(2-pyridyl)-6-phenyl-*as*-triazinyl]} diphenyl ether	*m*-Cresol	142–143.5	$C_{40}H_{26}N_8O$	75.44 (75.69)	4.10 (4.13)	17.03 (17.66)
X	2,6-Bis[3-(5-phenyl)-*as*-triazinyl]pyridine	Ethanol	239–241	$C_{23}H_{15}N_7$	70.73 (70.91)	3.90 (3.89)	24.81 (25.19)
XI	2,6-Bis[3-(5,6-diphenyl)-*as*-triazinyl]pyridine	Ethanol	310–311	$C_{35}N_{23}H_7$	77.53 (77.61)	4.09 (4.28)	18.01 (18.11)

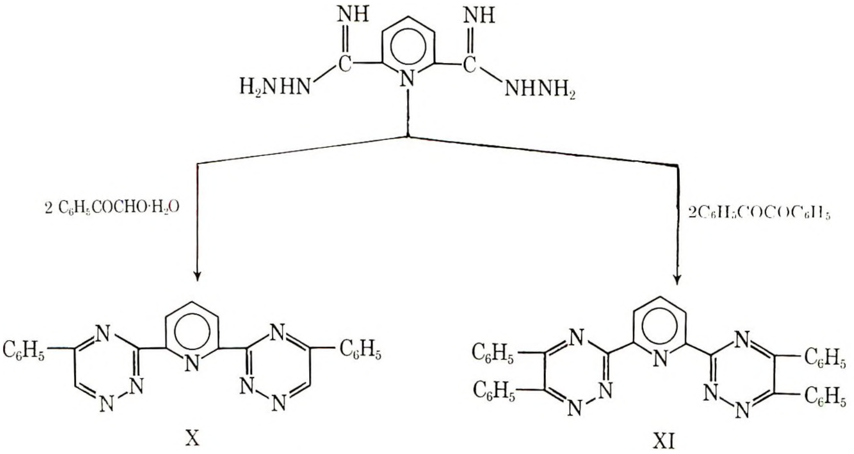
[a] Theoretical values reported in parentheses.

[b] Lit.[10] mp 140.5–141°C.

[c] Lit.[5] mp 189–190°C.

(3)


NH
C
NHNH$_2$
N
C$_6$H$_5$COCHO·H$_2$O
C$_6$H$_5$COCOC$_6$H$_5$
COCHO·H$_2$O
2/2
COCOC$_6$H$_5$
2/2
O
VI
VII
VIII
IX
C$_6$H$_5$
2



(4)

cooling provided pure model compounds in high yield (75%). It should be noted that model compounds VIII and IX were also prepared in refluxing ethanol but required recrystallization to obtain pure material.

In addition, model compounds VII and XI were also prepared as crude products by melt condensation under argon at 150–250°C. Two recrystallizations were required to obtain analytically pure material.

Characterization of the model compounds is shown in Table I. The infrared spectra of model compounds VIII and IX are presented in Figure 1.

Polymers

Generally, polymers were prepared by solution polymerization in *m*-cresol although other solvents such as pyridine, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and dimethyl sulfoxide were given a cursory examination. Melt polycondensation failed to provide high molecular weight polymer apparently due to the decomposition of the dihydrazidine.

The following is a representative example of polymer preparation: *p,p'*-Oxydibenzil (4.342 g, 0.010 mole) as a fine powder was added quickly to a solution of 2,6-pyridinediyl dihydrazidine (1.932 g, 0.010 mole) in *m*-cresol (25.1 ml) at room temperature under argon. The reaction mixture was vigorously stirred for 10 min to form a clear, viscous orange solution which was heated to 200°C during 2 hr and maintained at 200°C for 2 hr. The resulting polymer was isolated as a fibrous yellow solid by pouring the viscous *m*-cresol solution into methanol in a Waring Blendor. Thorough washing with methanol followed by drying for 5 hr at 200°C, *in vacuo*, provided a quantitative yield of yellow polymer having an inherent viscosity (η_{inh}, 0.5% H_2SO_4 at 25°C) of 0.66 and a polymer melt temperature of ~340°C.

ANAL. Calcd for $(C_{35}H_{21}N_7O)_n$: C, 75.66%; H, 3.81%; N, 17.65%. Found: C, 75.52%; H, 3.75%; N, 17.53%.

The yellow polymer was pulverized and placed in a polymerization tube under argon. The polymerization tube was introduced into a preheated oil bath at 300°C and maintained at 300°C for 1 hr. During this heating phase the polymer sintered slightly and changed from yellow to a light brown color. No detectable weight loss was observed. The resulting light brown polymer exhibited an η_{inh} of 1.10.

ANAL. Calcd for $(C_{35}H_{21}N_7O)_n$: C, 75.66%; H, 3.81%; N, 17.65%. Found: C, 75.71%; H, 3.76%; N, 17.36%.

DISCUSSION

The model compound work was performed prior to polymer synthesis to obtain information regarding the reaction conditions necessary for polymer formation and to obtain model compounds for comparison with the polymers. As previously indicated in the experimental section, a number of model compounds were prepared in high yields by the solution cyclocondensation of hydrazidines with glyoxal and benzil type reactants.

The location of the substituent on the 5-position of the triazine ring in model compounds VI, VII, IX, and X can be predicted based upon a consideration of the electronic effects of the reactants. As a representative example, the reaction of 2-pyridyl hydrazidine with phenylglyoxal presumably proceeds initially by nucleophilic attack of the terminal hydrazino nitrogen of the hydrazidine on the terminal or aldehyde carbonyl of the glyoxal since it is the more electron deficient. This is supported by the work of Culbertson and Parr,[10] who characterized 3,5-disubstituted *as*-triazines prepared in this manner by means of nuclear magnetic resonance spectroscopy.

In polymer work, the relative increase in molecular weight of the PT and PPT was followed by characterizing samples isolated periodically by quenching the *m*-cresol solution with methanol in a Waring blender. The resulting fibrous yellow polymers were dried at 200°C under pump vacuum for 5 hr prior to characterization. As indicated in Table II, relatively high molecular weight polymers can be formed directly in *m*-cresol. This polymer solution can be used conveniently in application work for film casting and adhesive tape and prepreg preparation.

The polymer attained an η_{inh} of ~0.7 after 2 hr in refluxing *m*-cresol, whereas an additional 24 hr failed to increase the molecular weight substantially.* The polymer isolated by quenching the *m*-cresol solution with methanol was placed in a polymerization tube under argon and advanced by introducing it into a preheated oil bath at 300°C and maintaining at 300°C for 1 hr. The infrared spectra of the polymers as Nujol mulls at

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*This type of behavior was also observed in polyquinoxaline synthesis.[11] The polyquinoxalines attained a relatively high molecular weight in *m*-cresol but failed to advance significantly even after a long reflux period. Further advancement was obtained by isolating the polyquinoxaline and subjecting the fibrous yellow solid to melt condensation.

TABLE II

Characterization of Poly-*as*-triazines

	PT					PPT				
			Elemental analysis[d]					Elemental Analysis[e]		
Conditions[a]	η_{inh}, dl/g[b]	PMT, °C[c]	C, %	H, %	N, %	η_{inh}, dl/g[b]	PMT, °C[c]	C, %	H, %	N, %
10 min at RT *m*-cresol	0.51	~340	—	—	—	0.45	~300	—	—	—
1 hr at RT, *m*-cresol	0.54	>350	—	—	—	0.50	~310	—	—	—
2 hr at 95°C, *m*-cresol	0.72	—	—	—	—	0.60	~320	—	—	—
2 hr at 200°C, *m*-cresol	0.77	—	68.23	3.33	24.14	0.66	~340	75.52	3.75	17.53
24 hr at 200°C, *m*-cresol	0.81	—	—	—	—	0.68	~340	—	—	—
1 hr at 300°C, solid phase	1.25	—	68.74	3.37	24.31	1.10	—	75.71	3.76	17.41
1 hr at 400°C, solid phase	Insoluble	—	70.43	3.28	15.14	Insoluble	—	74.41	3.76	17.36

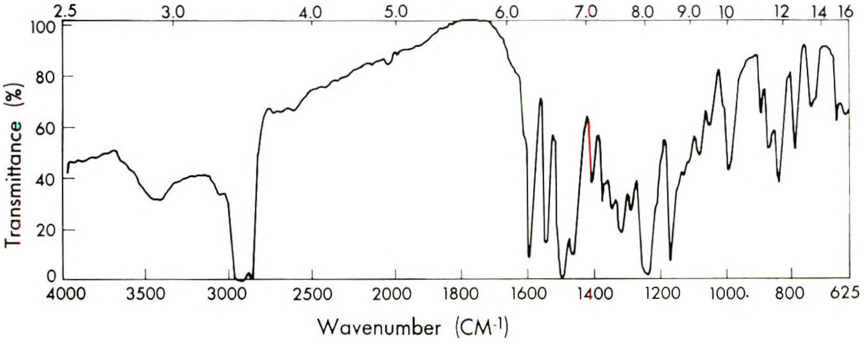
[a] Accumulative.

[b] In 0.5% H_2SO_4, 25°C.

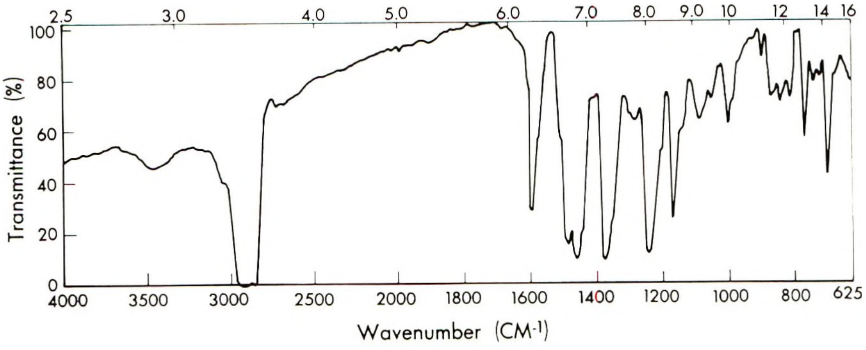
[c] Polymer melt temperature (actually a softening rather than a true melt).

[d] Calculated for $(C_{23}H_{13}N_7O)_n$: C, 68.48%; H, 3.25%; N, 24.31%.

[e] Calculated for $(C_{35}H_{21}N_7O)_n$: C, 75.66%, H, 3.81%; N, 17.65%.



(a)

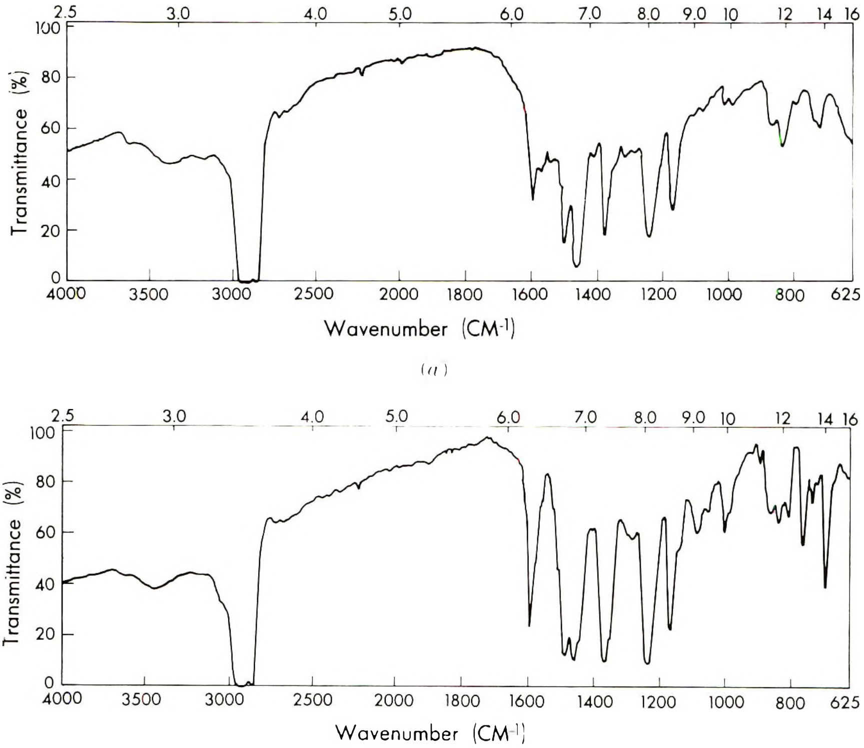


(b)

Fig. 2. Infrared spectra (Nujol mulls) of poly-*as*-triazines cured at 300°C: (*a*) poly-[3,3′-(2″,6″-pyridinediyl)-5,5′-(*p,p*′-oxydiphenylene)di(*as*-triazine)] (PT); (*b*) poly-[3,3′-(2″,6″-pyridinediyl)-5,5′-(*p,p*′-oxydiphenylene)di(6-phenyl-*as*-triazine) (PPT).

this stage compared favorably with those of the corresponding model compound, as shown in Figures 1 and 2. Further advancement was attempted at 400°C under argon, but the polymers underwent partial degradation losing ~3% and ~8% by weight for the PPT and PT, respectively. As shown in Table II, the elemental analyses of the polymers after exposure at 400°C under an argon atmosphere has changed, appreciably for the PT and only slightly for the PPT. The nitrogen value for the PT has decreased by ~6%, while the total of the elemental analysis has decreased to 91.85% (theoretical total 96.04%). No valid explanation is offered to explain this difference except to indicate that perhaps the polymer has degraded to a material which is difficult to thoroughly analyze. Duplicate determination on two different samples provided similar results.

The infrared spectra as shown in Figure 3 for the PT after the 400°C treatment is significantly different from the material cured at 300°C, whereas the infrared spectrum of the PPT is essentially identical to that before the 400°C exposure. The weak absorption at 4.45μ present in the spectra of the 400°C cured polymers may be attributed to $C \equiv N$ and/or $C \equiv C$ formation resulting from polymer degradation. The infrared



(*a*)

(*b*)

Fig. 3. Infrared spectra (Nujol mulls) of poly-*as*-triazines cured at 400°C: (*a*) PT; (*b*) PPT.

spectrum of PT cured at 400°C has changed significantly and bears little resemblance to the spectrum of the polymer cured at 300°C. The infrared spectrum and elemental analysis indicates a drastic thermal breakdown of the polymer after 1 hour at 400°C in argon. The broad ill-defined absorptions at 2.9 μ in the infrared spectra are apparently due to water from the air which is absorbed by the polymer during the mulling procedure. This is further indicated by TGA, which showed an initial weight loss commencing at about 75°C. The polymers were dried at 200°C under high vacuum prior to elemental analysis, which was sufficient for water removal.

EVALUATION

Thermogravimetric analysis (TGA) was performed by using a Dupont 950 thermogravimetric analyzer on samples of PT and PPT which had been exposed to each of the following accumulative reaction conditions; 2 hr at 200°C in *m*-cresol under argon, followed by solid-phase advancement at 300°C for 1 hr under argon, and this followed by solid phase exposure at 400°C for 1 hr under argon. The thermograms of the polymers after exposure under the first two conditions were essentially identical and are represented in Figure 4 for the 300°C cured polymers. It is interesting to note that duplicate TGA on two different samples each of the PT and PPT provided thermograms which showed a two stage breakdown with the initial weight loss break higher in air (~425°C) than in helium (~400°C). This unexpected phenomenon may be attributed to oxygen pickup which masks the initial weight loss in air. As shown in Figure 5, the thermograms of the materials cured at 400°C exhibited single breaks in air and in helium starting at ~400°C and ~450°C, respectively, although the major weight loss in air occurred at ~500°C. By TGA, no distinct difference in the thermal and oxidative stability of the PT and PPT was observed.

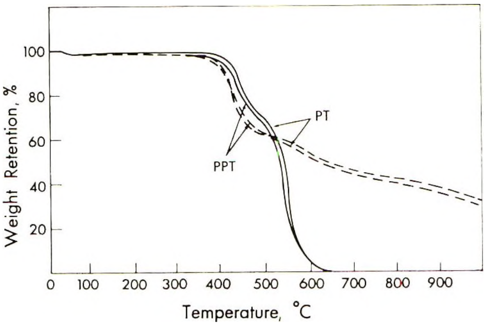


Fig. 4. Thermograms of poly-*as*-triazines cured at 300°C: (——) in air; (- -) in helium. $\Delta T = 7$°C/min; particle size = 140–240 mesh.

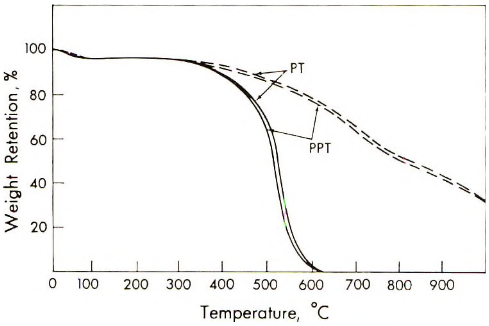
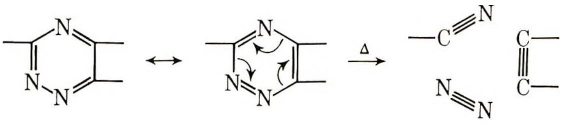


Fig. 5. Thermograms of poly-*as*-triazines cured at 400°C: (—) in air; (- -) in helium. $\Delta T = 7$°C/min; particle size = 140–240 mesh.

The oxidative stability of the PT and PPT which had been cured through 1 hr at 300°C in argon was evaluated by isothermal gravimetric analysis. Samples (particle size <60 mesh) aged in a static air oven at 316 ± 6°C for 200 hr exhibited weight losses of 3.5% and 8.0% for the PPT and PT, respectively. As indicated, the PPT displayed slightly better weight retention under these conditions than the PT.

Since the poly-*as*-triazines possess an aromatic structure, the thermal stability was anticipated to be higher than observed. The relatively poor thermal stability has been tentatively attributed to the initial thermal elimination of nitrogen, as indicated in eq. (5).



(5)

This postulate is being investigated and will be the subject of a forthcoming paper on the thermal degradation of poly-*as*-triazines.

FILMS

Clear yellow films were prepared by casting polymer solutions in *m*-cresol onto a glass surface followed by forced air drying at 100°C and drying *in vacuo* at 200°C. The films exhibited good flexibility and toughness even after aging in a static air oven at 316°C for 200 hr. The PT film exhibited slight darkening, while the PPT film appeared to retain its original color. A preliminary hydrolytic evaluation of the films was conducted by refluxing in 10% aqueous potassium hydroxide solution for 24 hr. The films retained good flexibility and toughness and exhibited no change in their infrared spectra. However, the films exhibited decreased flexibility (resistance to fingernail crease) after refluxing in 40% aqueous potassium hydroxide for 10 hr. The relative degree of degradation appeared to be more prominent in the PT film.

References

1. G. F. Ehlers and J. D. Ray, *J. Polym. Sci. A*, **2,** 4989 (1964).
2. G. F. Ehlers and J. D. Ray, *J. Polym. Sci. A-1*, **4,** 1645 (1966).
3. D. R. Anderson and J. M. Holouka, *J. Polym. Sci. A-1*, **4,** 1689 (1966).
4. O. R. Pierce, W. X. Bajzer, and G. A. Grindahl, AFML-TR-65-78 (March, 1965) AD480448L.
5. F. H. Case, *J. Org. Chem.*, **30,** 931 (1965).
6. F. H. Case, *J. Org. Chem.*, **31,** 2398 (1966).
7. G. P. Gandermaris and B. J. Sillon, *J. Polym. Sci. B*, **2,** 203 (1964).
8. M. A. Ogliaruso, L. A. Shadoff, and E. I. Becker, *J. Org. Chem.*, **28,** 2725 (1963).
9. E. H. Rodd, *Chemistry of Carbon Compounds*, Elsevier, Amsterdam, 1954, Vol. IIIA, p. 565.
10. B. M. Culbertson and G. R. Parr, *J. Heterocyclic Chem.*, **4,** 422 (1967).
11. P. M. Hergenrother and H. H. Levine, *J. Polym. Sci. A-1*, **5,** 1453 (1967).

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Preparation and Properties of Condensation Polymers Containing a Phosphorus–Nitrogen Heterocycle and Derivatives of Hydroquinone

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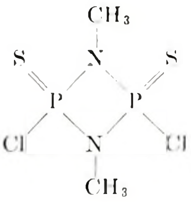
Synopsis

Condensation polymers were obtained by the reaction of several aromatic dihydroxy compounds (especially substituted hydroquinones) and 1,3-dimethyl-2,4-dithio-2,4-dichloro-1,3-diaza-2,4-diphosphetidine. The condensation polymers thus obtained were investigated on their thermal behavior. The thermal stability is lowered in the following series: hydroquinone ≈ resorcinol > tetramethylhydroquinone ≫ tetrachloro-hydroquinone ≈ tetrafluorohydroquinone ≫ pyrocatechol. The infrared spectra of these new polymers have been measured and are discussed in detail.

INTRODUCTION

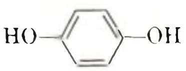
Some condensation reactions were carried out in 1960 by Coover et al.,[1] who investigated polymers formed by condensation reactions of aromatic dihydroxy compounds with phosphorochloridates. In particular, they prepared condensation products from phenylphosphonic dichloride and hydroquinone and determined softening points, flammability, crystallinity, and infrared spectra. Further, the kinetics of the condensation of phenylphosphonic dichloride and hydroquinone and the influence of a catalyst on the kinetics of this reaction are discussed.

The investigations carried out in this laboratory used several aromatic dihydroxy compounds (especially substituted hydroquinones) and 1,3-dimethyl-2,4-dithio-2,4-dichloro-1,3-diaza-2,4-diphosphetidine(I)[2]



I

as starting materials. The thermal stability of the condensation polymers thus yielded should depend on the following points: (*1*) the electronegativity and the bond dissociation energy of the substituents bonded to the aromatic dihydroxy compounds (II, III, IV);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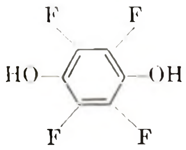
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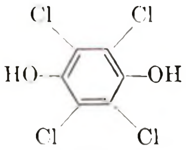
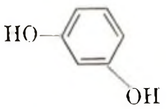

IV

(*2*) the relative position (*o*-, *m*-, *p*-) of the dihydroxy groups to each other in the benzene ring (II, V, VI);


II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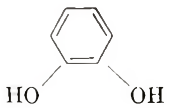
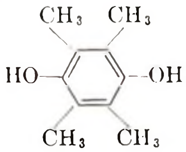

VI

(*3*) the possible sterical influence of four methyl and trifluoromethyl groups which may be substituted for the four hydrogen atoms on the benzene ring of hydroquinone (VII, VIII).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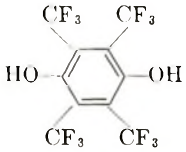
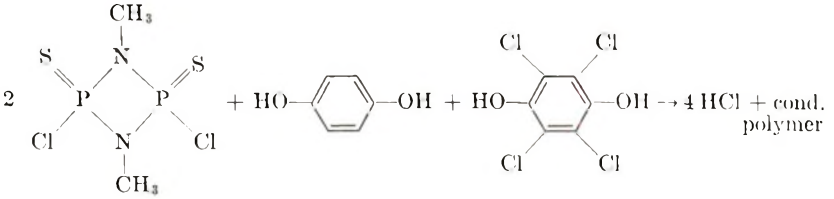

VIII

On the other hand, one can try to change the mechanical and in some way the thermal properties of the condensation polymers yielded by mixing two different dihydroxy benzenes (molecular ratio, e.g. of I: II: IV-2:1:1) by following the scheme of eq. (1):


(1)

Thus we can expect that the polymers obtained by the condensation reaction of I and III or VIII should be the most thermally stable polymers, while the condensation products of I and VII or VI should be less stable. Perfluorinated polymers (e.g., Teflon) have very good thermal qualities. (Estimation of the bond dissociation energy of the C—F bond in CF_4 gives 124 kcal/mole; the same energy for the C—H bond in CH_4 is 101 kcal/mole.) Therefore a condensation polymer yielded by condensation of a perfluorinated organic monomer and a diazadiphosphetidine should be thermally more stable than the unfluorinated counterpart.

EXPERIMENTAL

Materials

The diazadiphosphetidine (I) was prepared by the method of Becke-Goehring et al.[2] and has been further purified by sublimation. Its purity was shown by analysis.

ANAL. Calcd: Cl, 27.79%; P, 24.24% S, 25.18%. Found: Cl, 27.45%; P, 24.67%; 24.39%; S, 23.71%. (The S analysis may be low because of some hydrolysis while weighing the sample.)

Its ^{31}P NMR spectrum and its infrared spectrum agreed very well with the literature.[2]

The hydroquinone was obtained from commercial sources (reinst, E. Merck AG./Darmstadt).

Tetrafluorohydroquinone (III) was obtained from Imperial Smelting Corp. Several recrystallizations from petrol ether (100–140°C) yielded a product of mp 159–162°C. Its composition is confirmed by its infrared spectrum. The ^{19}F NMR spectrum of III consists only of a single peak with a chemical shift of 164.4 ppm towards an internal standard of $CFCl_3$.

Tetrachlorohydroquinone (IV) was obtained from Farbenfabriken Bayer; it was used without further purification.

Tetramethylhydroquinone (VIII) was prepared after the procedure of Rügheimer and Hankel.[3] It has been found that it is necessary to purify the tetramethylquinone by sublimation. Reduction of this quinone takes place most readily with $SnCl_2$ and hydrochloric acid in a water-alcohol mixture. The melting point after drying was 230–231°C.

ANAL. Calcd: C, 72.30%; H, 8.48%. Found C, 72.08% H, 8.12%.

The *m*- and *o*-dihydroxybenzenes (V and VI, respectively) were commercial products (reinst, E. Merck AG/Darmstadt).

Tetrakis(trifluoromethyl)hydroquinone (VIII) was not prepared (see results and discussion).

Procedures

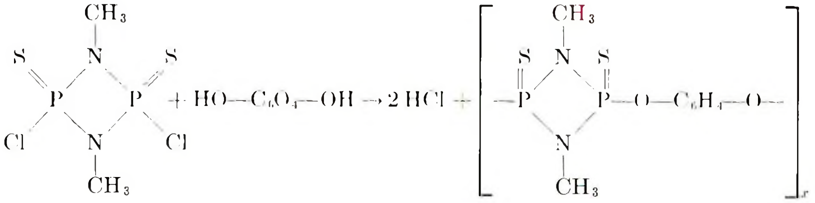
Condensation reactions were carried out in an oil bath at 200, 180, and in one case at 100°C. The oil was stirred and temperature controlled automatically. The reaction vessel was a round-bottomed flask fitted with two necks. One of these necks was used for a stirrer, while the other was used as exit for a gas inlet tube (two coaxial glass tubes). Throughout the reaction dry nitrogen, containing less than 15 ppm O_2, passed through the apparatus. The reaction vessel was put into the oil bath at reaction temperature. Some time later the reaction started, as could be seen by hydrogen chloride evolved. HCl evolved throughout the reaction passed the reaction flask through a glass tube into a cooling trap cooled with liquid nitrogen. Weighing of the condensed HCl followed after removal of N_2 from the cooling trap.

Infrared spectra were reported with a Perkin-Elmer Model 221 and a Perkin-Elmer Model 457 spectrophotometer. It was very difficult to powder the polymers for preparation of the KBr disks, especially those obtained by the reaction of hydroquinone and resorcinol. The substances were powdered under dry nitrogen.

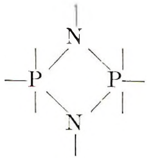
RESULTS AND DISCUSSION

Preparation and Properties of the Condensation Polymers

The condensation reactions yield polymers that are hard, brittle (with exception of the condensation product of I with pyrocatechol, which is waxy or a viscous liquid) and to a certain extent flame-resistant. The polymer containing perchlorohydroquinone begins to swell on heating with an open flame, and gas is evolved. Equation (2) describes the condensation reactions carried out (molecular ratio 1:1):


(2)

Properties of the condensation polymers obtained are listed in Table I. Thermal degradation curves (of some of the polymers) are shown in Figure 1. From Table I and Figure 1 we see that the thermally most stable polymers are obtained if the hydrogen atoms are not substituted by halogen atoms and the OH groups are not too close to each other (*o*-dihydroxybenzenes). The unexpected thermal instability of the polymers containing halogen atoms on the benzene ring may be explained by the fact that the monomeric halogen substituted hydroquinones (especially the quinones) have halogenating qualities. On the other hand, Kozlov and Drach[4] found on chlorinating $(CH_3NPCl_3)_2$ that splitting



of the N—P—N—P ring occurred. The main product was $CCl_3N=PCl_3$. A similar reaction may take place on thermal degradation of the above polymers containing halogenated benzene rings. From the data obtained one can get the following series of thermal stability for polymers of the composition mentioned above: hydroquinone ≈ resorcinol > tetramethylhydroquinone ≫ tetrachlorohydroquinone ≈ tetrafluorohydroquinone ≫ pyrocatechol.

TABLE I
Reaction Conditions and Properties of the Synthesized Condensation Polymers

	Reaction conditions		HCl, g			
Polymer	Time, min	Temp, °C	Calcd	Found	Polymer properties	Decomp. temp, °C
I + hydroquinone	60	180	1.1	1.2	Not soluble	540
	45	200	0.8	0.7	Very hard, tenacious, pale yellow	590
I + tetrafluoro-hydroquinone	60	162	0.8	1.0	Dark brown	
	60	160	0.4	0.4	Hard, brittle	
	130	133	Not determined		Not soluble	180
	150	133			Dark brown, brittle	190
	50	162				
I + tetrachloro-hydroquinone	120	180	0.7	1.0	Dark brown	
	35	180	0.6	0.6	Hard, brittle	180
	45	180	0.8	0.6	Not soluble	160
	150	160	0.4	0.5		160
I + tetramethyl-hydroquinone	20	210	0.5	0.5	Brown, hard, brittle, not soluble	510
	60	160				
I + resorcinol	150	180	0.5	0.3	Hard tenacious	570
	105	165	0.6	0.6		
	120	180			Pale yellow, not soluble	560
I + pyrocatechol	240	160	0.4	0.4	Waxy, pale yellow	170
	60	100	0.5	0.7	Mixture of pale yellow viscous liquid and white solid	
	10	180				
I + hydroquinone + tetrachloro-hydroquinone (2:1:1)	120	180	0.7	0.3	Very hard, brown	165 550
	20	180	0.7	1.0	brittle, not soluble	180
	90	180				

The degradation curves of the thermally more stable polymers first show a slight decrease, which may be caused by some unreacted material. A strong decrease indicates decomposition. As can be seen from the degradation curve, the same polymer (I + II) shows a somewhat higher decomposition point (50°C) after being extracted with ether for several hours. In contrast to the above polymers, the condensation products of

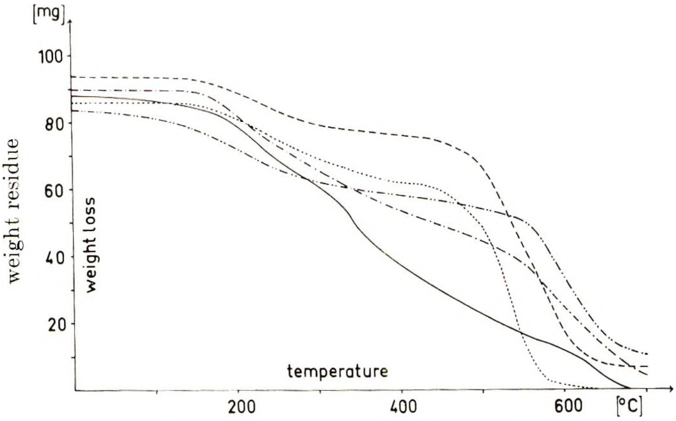
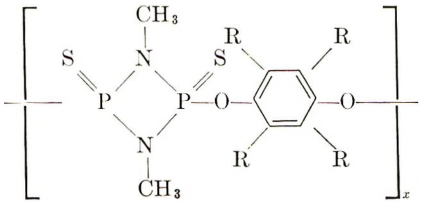


Fig. 1. Thermal degradation curves: (– –) polymer of I and II; (–. .–) polymer of I and II (after extraction with ether); (——) polymer of I and III; (–.–) polymer of I and IV; (- - -) polymer of I and VII.

I and III or IV decompose continuously. The mixed condensation polymer (I + II + IV) shows similar behavior on heating.

The formulae of the polymers (with exception of products obtained from condensation of I and V or VI) are given by IX



IX

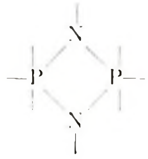
where R may be H or F, Cl, $CH_3(CF_3)$. In all cases the same diazadiphosphetidine (I) was used for the condensation reaction. Only the substituents R and the relative position of the hydroxy groups to each other were changed.

In case of the polymer prepared from I and V compared with the corresponding product obtained from I and II, no steric hindrance is found for two diazadiphosphetidine rings connected with the aromatic dihydroxy compound. The decomposition point of these polymers is nearly the same. In contrast to these polymers, the polymer prepared from I and VI is a waxy solid or a viscous liquid. Strong mutual hindrance of the diazadiphosphetidine rings bonded to the pyrocatechol leads to low molecular weight products. Therefore volatilization of the low molecular weight fractions overlaps thermal degradation. A weight loss is recorded at a much lower temperature than in the case of the polymers from I + II and I + V. The possible influence of the substituents, e.g., F and H, could not be determined by thermal degradation studies, because the polymers obtained by condensation of I and tetrafluoro-(III) or tetrachlorohydroquinone (IV) show halogenating qualities, which cause decomposition of the P—N heterocycle. This is the reason for not preparing a condensation polymer of I and VIII.

Infrared Spectra

The increasing reaction between I and the aromatic dihydroxy benzenes was followed by infrared spectroscopy. The infrared spectra from the polymers are very complex. Therefore it is difficult, if not impossible, to assign all bands to characteristic group frequencies. In Table II infrared data of the condensation polymers are listed. The assignments naturally depend on assigned spectra of the diazadiphosphetidine and the dihydroxybenzenes. Unfortunately we have found little material about the infrared spectra of four-membered P—N heterocycles. Downs[5] has published a complete assignment of $(CH_3NPF_3)_2$. But this is of limited value for our investigations, because his assignment depends on a vapor-phase infrared spectrum. Yagupsky[6] has published a complete assignment of the bands found both in the infrared spectra of $(CH_3NPF_3)_2$ and $(CH_3NPCl_3)_2$. He compares calculated and measured spectra. Chapman et al.[7] assign only a strong band in the 847 cm^{-1} region to the P—N stretching vibration. This is confirmed by Haszeldine,[8] who investigated several four-membered P—N heterocycles with various substituents and found a band of strong to very strong intensity in the range of 845–910 cm^{-1}.

According to the above assignments, we assign a strong band at 861 cm^{-1} found in the solid state of $[CH_3NP(S)Cl]_2$ (I) not only to the P—N stretching frequency but as characteristic for four-membered rings,



as proposed by Yagupsky[6] for $(CH_3NPCl_3)_2$ and $(CH_3NPF_3)_2$. In all spectra of the polymers this band could be found (see Table II). Fortunately the dihydroxybenzenes do not in general give rise to bands in this region; those bands which do occur can be easily separated from the P-N band. Thus we can conclude, that the four-membered P-N heterocycle is not decomposed during the time of condensation.

Two bands[9] for the P=S stretching vibration should be found in the range 550–872 cm^{-1}, but only one band in the region of 668 cm^{-1} of medium intensity found for both the polymers and I should be assigned tentatively to this vibration.

A band of strong to very strong intensity in the range of 905–996 cm^{-1} is correlated with the P—O—C vibration,[10] while a weak band[11] is found in the 1030 cm^{-1} region. Such absorption bands are found (Table II), indicating reaction between I and II–VII. In the case of the condensation polymer I + III, this assignment is of tentative character because of the

TABLE II
Infrared Data for Condensation Polymers

Polymer	Wavenumber, cm^{-1} [a]						
	—C—H (aliphatic)	—C—H (aromatic)	—C—F (aromatic)	—C—Cl (aromatic)	P—O—(C) (aromatic)	P—N (ring)	P=S
I + hydroquinone	2940 (vw)	3062 (m)	—	—	1018 (w)? 922 (vs)?	860 (w)?	—
I + tetrafluoro-hydroquinone	2940 (vw)	—	1030 (vs)? 1015 (vs)?	—	—	870 (vs)	672 (m)
I + tetrachloro-hydroquinone	2945 (w)	—	—	718 (s)	1030 (m) 950 (vs)	868 (vs)	668 (m)
I + tetramethyl-hydroquinone	—	—	—	—	—	860 (vs)	675 (m) 690 (m)?
I + resorcinol	2940 (vw)	3060 (m)	—	—	979 (vs) 1010 (vw)? 965 (vs)?	863 (vs)	671 (m)
I + pyrocatechol	2938 (w)	3062 (w)	—	—	1030 (w)? 950 (vs)?	866 (vs)	680 (m)? 620 (m)?
I + hydroquinone + tetrachlorohydro-quinone (2:1:1)	2938 (vw)	3060 (w)?	—	720 (w)?	1032 (w) 930 (vs)?	865 (vs)	—

[a] Intensity: v = very; s = strong; w = weak; m = medium.

appearance of a "triplet" of bands near 1 000 cm^{-1} which may be due to aromatic C—F stretching frequencies.[12,13] On the other hand, strong bands in the range 420–587 cm^{-1} due to P—Cl bonds [$CH_3NP(S)Cl]_2$: 500 cm^{-1} and a very strong and often broad band* indicating OH groups disappear during the reaction.

A weak band in the range of 2940–2948 cm^{-1} was found to be the C—H stretching frequency of the CH_3 group bonded to nitrogen. I absorbs in this case at 2944–2946 cm^{-1}. Aromatic C—H stretching vibration[7] occurs in the 3030 cm^{-1} region. Very few infrared data have been reported for organic compounds containing C—Cl bonds. Therefore we assign tentatively a medium to strong band at 718 cm^{-1} of the polymers to the C—Cl stretching vibration. We are confirmed in this way, for some substances† contain bands in this region which can be correlated to C—Cl bonds. No attempts have been made to assign observed bands between 1650 and 1450 cm^{-1} to C—C stretching vibrations.

Therefore the infrared measurements confirm our assumption that the polymers are linear and agree very well with the formulae given.

* p-HO-C_6H_4-OH, 3250; m-HO-C_6H_4-OH, 3240; o-HO-C_6H_4-OH, 3360, 3490; p-HO-C_6F_4-OH, 3335; p-HO-C_6Cl_4-OH, 3390; p-HO-$C_6(CH_3)_4$-OH, 3395 cm^{-1}.

† p-H_2N-C_6Cl_4-NH_2, 677 (s); p-H_2N-CH_2-C_6Cl_4-CH_2-NH_2, 657 (s); p-HO-C_6Cl_4-OH, 715 (vs) cm^{-1}.

References

1. H. W. Coover, R. L. McConnell, M. A. McCall, *Ind. Eng. Chem.*, **52,** 409 (1960).
2. M. Becke-Goehring, L. Leichner, B. Scharf, *Z. Anorg. Allgem. Chem.*, **343,** 154 (1966).
3. L. Rügheimer and M. Hankel, *Ber.*, **29,** 2171 (1896).
4. E. S. Kozlov and B. S. Drach, *Zh. Obshch. Khim.*, **36,** 760 (1966).
5. A. J. Downs, *Chem. Commun.*, **1967,** 628.
6. M. P. Yagupsky, *Inorg. Chem.*, **6,** 1770 (1967).
7. A. C. Chapman, W. S. Holmes, N. L. Paddock, and H. T. Searle, *J. Chem. Soc.*, **1961,** 1825.
8. M. Green, R. N. Haszeldine, and G. S. A. Hopkins, *J. Chem. Soc. A*, **1966,** 1766.
9. R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta*, **20,** 1679 (1964).
10. R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta*, **20,** 489 (1964).
11. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen, London, 1964.
12. D. G. Weiblein, in *Fluorine Chemistry*, Vol. II, J. H. Simons, Ed., Academic Press, New York, 1954.
13. N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction* to Infrared and Raman Spectroscopy, Academie Press, New York, 1964.
14. R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta*, **21,** 861 (1965).

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NOTES

Homopolymerization of Gaseous Hexafluorobutyne-2 at Ambient Conditions

Hexafluorobutyne, $CF_3C{\equiv}CCF_3$, can be polymerized with good yield in the gas phase at room temperature and subatmospheric to atmospheric pressures to a white hydrophobic substance. This is achieved by employing nitrosyl hexafluoroarsenate formed and activated *in situ* together with boron trifluoride and weak ultraviolet radiation ($\lambda \geq 3100$ Å) as catalyst.

Perfluorobutyne-2 was first used for polymerization in 1956, as a copolymer for several halogenated olefins with peroxydic catalysts.[1] Its first homopolymerization occurred in 1957 under the influence of high energy radiation[2,3] and later in solution with complexes as catalysts.[4,5] Until recently, the homopolymerization of straight-chain internal olefins by other than extreme conditions was unknown;[6] mild conditions brought about only copolymerization. The first homopolymerization in the gas phase was performed with butene-2 in 1964 on neutral clay surfaces or with a Ziegler catalyst;[7] however, best yields were obtained in the presence of acidified montmorillonite and triethylaluminum at 90°C. The exact parallel could be found in the case of perfluorobutyne-2: Here likewise, a contact polymerization appears to take place in the two-dimensional mobile layer on the solid catalyst's ($NOAsF_6$) surface, but only with the additional help of an activated (UV radiation) promotor (BF_3). Neither AsF_5 alone nor BF_3 is effective, nor $AsF_5 + BF_3$ without UV radiation, nor the $NOAsF_6$ sold by different suppliers. $NOAsF_6$ has to be synthesized in an especially active form by condensing NOF and AsF_5 on top of the solid substances C_4F_6 and BF_3 at -196°C. The slow warming of the container to room temperature results in the formation of $NOAsF_6$ while BF_3 and C_4F_6 are evaporating. The molecules of BF_3 and C_4F_6 pass through the $NOAsF_6$ lattice in statu nascendi, dissipate the heat of formation and prevent an agglomeration of the finely dispersed crystals. Thus, the $NOAsF_6$ powder obtained possesses a large surface with good catalytic activity. Adsorbed on this $NOAsF_6$, the C_4F_6 acts as donor towards the excited BF_3—as in other complexes, e.g., with chlorotris (triphenylphosphine)-rhodium(I)[8]—and this BF_3 adduct may represent the transition state that initiates the polymerization.

There may be a number of active solids which display catalytic activity for this type of homopolymerization in the gas phase; one advantage of $NOAsF_6$ and related compounds, as compared to clay, e.g., consists in their water solubility, so that the pure polymer is immediately available as a fluffy white powder. The polymer is slightly soluble in polar organic solvents like acetone or isopropyl alcohol; it is stable at temperatures up to at least 450°C and shows no evidence of melting or burning at much higher temperatures, when it decomposes and evaporates. Refluxing for 3 days in concentrated nitric acid causes a 0.3% weight loss, heating in air at 465°C for 3 hr a 17.8% weight loss. When subjected to pressures of 20,000 lb/in.^{2} at room temperature, hard disks are formed with too low a transparency to give a UV spectrum. Isopropyl alcohol solutions of this polymer show an absorption band at 254 mμ, which indicates a structure with one double bond per unit.[3] This unsaturation provides the possibility of forming ladder molecules which may result in high tensile strength, thermal stability, and chemical inertness. It is therefore suggested that materials from perfluorobutyne-2 may be useful for work with corrosive substances, as special column packing in chromatography, or as coatings for exposed surfaces. The infrared spectrum of the polymer impregnated in KBr pellets has strong absorptions at 8.05, 8.36, 8.50, and 8.80 μ and appears to be identical with the material produced by γ-radiation.

Experimental

A 1-liter Pyrex glass flask with stopcock is evacuated and part of its bottom immersed in liquid nitrogen. 14 mmols of C_4F_6 (Peninsular Chem Res., Inc., Gainesville, Florida), 4 mmols of BF_3 (The Matheson Co., East Rutherford, N.J.), 8 mmols of AsF_5 (Ozark-Mahoning Co., Tulsa, Oklahoma) and 5 mmols of NOF (prepared from NO and F_2), in this order, are condensed into the flask. The nitrogen in the dewar underneath is poured out, a GE sun lamp and a cool air blower directed at the flask for ca. 16 hr. For removal of the remaining gases one evacuates the flask, and to remove the solid catalyst one adds water and washes the polymer on the filter with additional water. After drying at 110°C, 0.9 g of material are obtained which corresponds to a yield of 41%.

ANAL. Calc. for $(C_4F_6)_n$: C, 29.63%; F, 70.37%; Found: C, 29.33%; F, 69.66%.

Gratitude is expressed to Miss Rita Juurik for analyses.

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References

1. A. N. Bolstad and F. J. Honn, U.S. Pat. 2,966,482 (1960, filed 1956).
2. H. L. Gewanter and H. C. Brown, *Dissertation Abstr.*, **23**, 831 (1962); *J. Org. Chem.*, **25**, 2071 (1962).
3. J. F. Harris, U.S. Pat. 3,037,010 (1962, filed 1957).
4. J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, **1962**, 3488.
5. M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, **1965**, 6629.
6. *Chem. Eng. News*, February 10, 1964, p. 42.
7. *Chem. Eng. News*, February 3, 1964, p. 39.
8. M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, **1965**, 6629.

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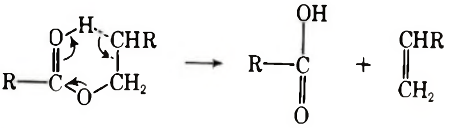
Thermally Stable Polyesters

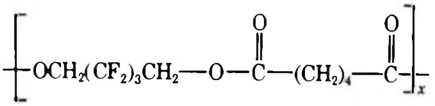
The principal mode of thermal breakdown of polyesters prepared from aliphatic diols and aliphatic dibasic acids is by alkyl-oxygen scission via a cyclic transition state[1] [eq. (1)].



(1)

Hine[2] formally classified this reaction under four-center types. This mode of breakdown requires a β-hydrogen on the alcohol segment, with the resultant breakdown occurring at moderate temperatures.

Therefore, poly(hexafluoropentamethylene adipate) (I) was prepared, since the β-hydrogens are replaced by fluorine.



$$\left[OCH_2(CF_2)_3CH_2—O—\overset{O}{\overset{\|}{C}}—(CH_2)_4—\overset{O}{\overset{\|}{C}} \right]_x$$

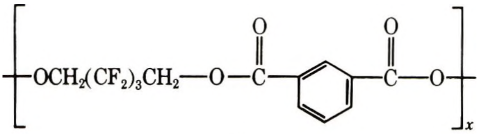
I

Although the decomposition temperature of 380°C was not considered to be outstanding, it was higher than that of a related ester, 2-ethylhexyl adipate, which reportedly[3] decomposed at 280°C.

When the β-elimination path is blocked, the next thermal degradation route available is via a radical mechanism resembling that for hydrocarbons.[4] Apparently, hydrogen abstraction from an α-carbon initiates the process, as illustrated by eq. (2), for a phenyl ester.

$$R'CH_2CH_2—CO_2C_6H_5 \rightarrow R'CH_2\dot{C}HCO_2C_6H_5 \rightarrow R'\cdot + CH_2{=}CHCO_2—C_6H_5 \qquad (2)$$

Poly(hexafluoropentamethylene isophthalate) (II) was prepared in order to reduce this free-radical type of degradation route.



II

This polyester has a substantially improved decomposition temperature over the analogous adipate (480°C in helium based on TGA). Tough, flexible films could be melt-pressed, and strong fibers could be drawn from the colorless molten polymer. The drawn fibers displayed a tendency to crystallize when held under tension. In addition, the thermal stability of poly(hexafluoropentamethylene *o*-phthalate) was found to be essentially the same as the isophthalate.

To verify the effect of blocking the β-elimination route with fluorine by using hexafluoropentanediol, poly(pentamethylene isophthalate) was prepared. The thermal stability was reduced drastically over the polyester of hexafluoropentanediol, being 150°C lower in helium than the fluorinated analogue.

It might be expected that the free-radical type degradation route could be blocked by using fluorine as a replacement for the aromatic group. Poly(hexafluoropentamethylene perfluoroglutarate) (III) was prepared but had no better thermal stability than the adipate.

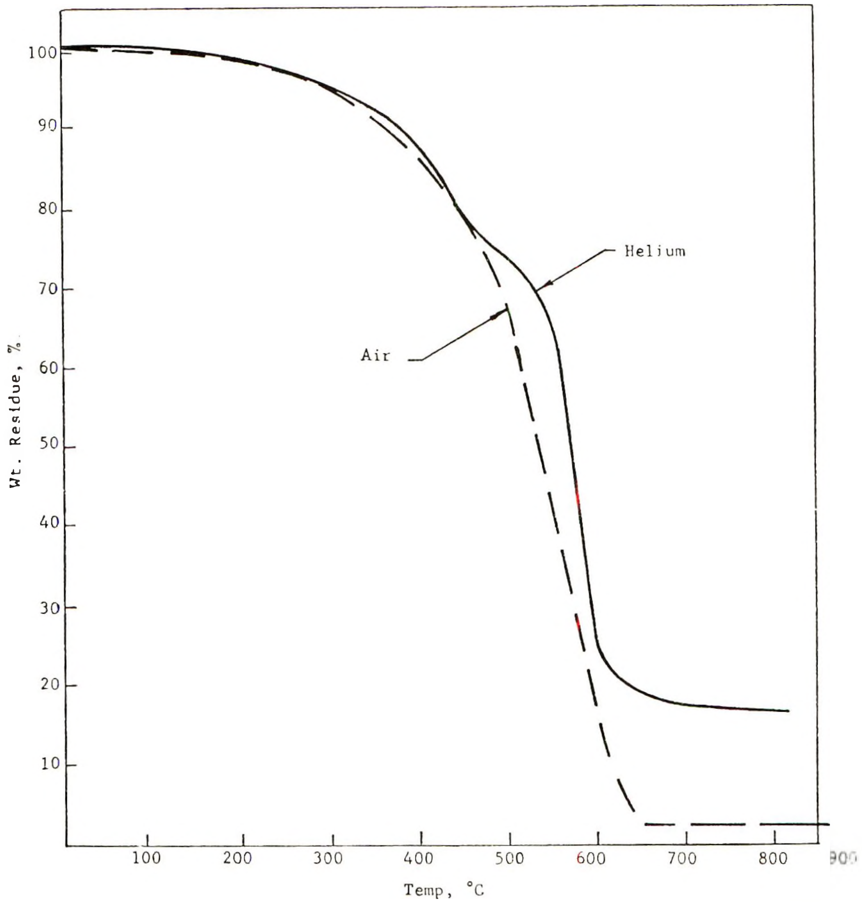
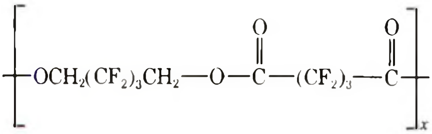


Fig. 1. Thermogram of poly(hexafluoropentamethylene oxybisbenzoate) in air and helium.

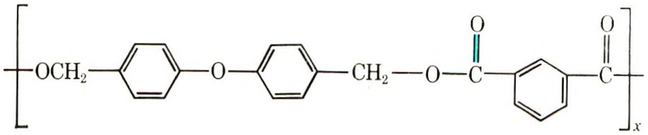


$$\left[-OCH_2(CF_2)_3CH_2-O-\overset{\overset{O}{\|}}{C}-(CF_2)_3-\overset{\overset{O}{\|}}{C}- \right]_x$$

III

Since esters from perfluorinated acids are extremely sensitive to hydrolysis, this type of polyester would be of little use.

A polyester (IV) was prepared from isophthaloyl chloride and oxybis(benzyl alcohol) in order to determine the effect of the benzyl group on thermal stability.



IV

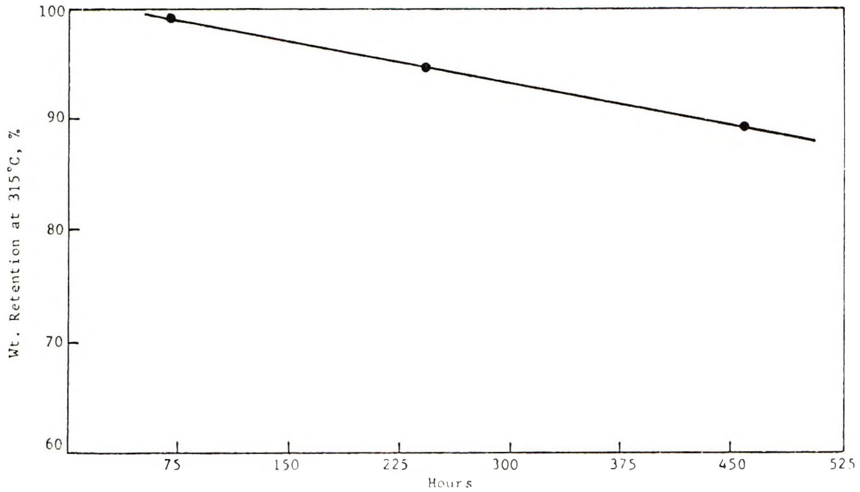
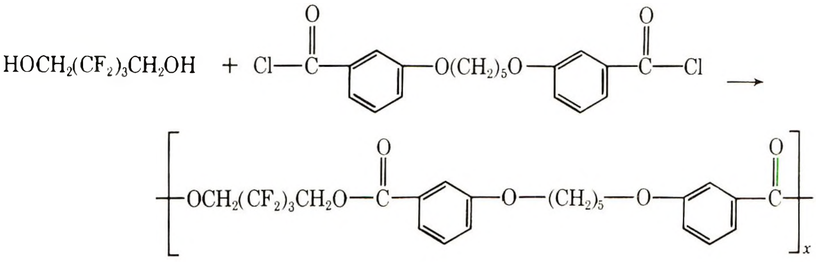


Fig. 2. Isothermal weight loss of poly(hexafluoropentamethylene oxybisbenzoate)

Based on TGA, this polyester had the same order of thermal instability as poly-(pentamethylene isophthalate). The mode of decomposition, however, is almost certainly a free radical type.

A polyester (V) containing mixed aromatic-aliphatic ether groups was prepared from hexafluoropentanediol and 1,5-bis(*p*-carbonylphenoxy)pentane. This polymer exhibited excellent thermal stability, 480°C in helium (based on TGA).

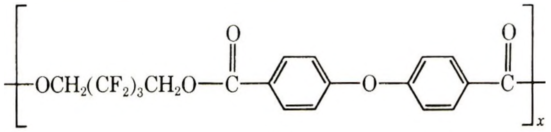


(3)

V

In view of the relative instability of the simple mixed ethers, the good thermal stability of this polyester was unexpected.

An extremely thermally stable and promising polyester (VI) containing aromatic ether linkages was prepared based on hexafluoropentanediol. This polymer, poly-(hexafluoropentamethylene oxybisbenzoate), had a decomposition temperature of about 500–525°C in helium (based on TGA) as seen in Figure 1.

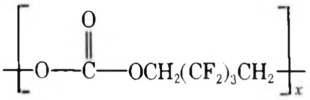


VI

The colorless polymer was quite tough, and flexible films could be prepared by melt pressing.

Since the apparent thermal stability of poly(hexafluoropentamethylene oxybisbenzoate) was so outstanding, efforts were made to determine the isothermal weight loss at 315°C. After 455 hr, this polymer had lost only 10.6% of its weight (Fig. 2), and its color was relatively unchanged.

The polycarbonate of hexafluoropentanediol (VII) was prepared; it also had excellent thermal stability, decomposing at 450°C.



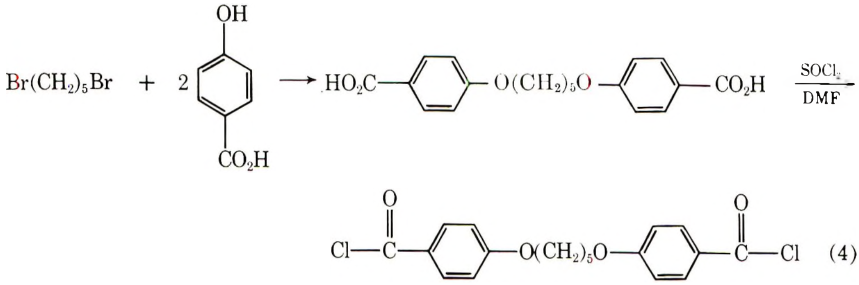
$$\left[O - \overset{O}{\overset{\|}{C}} - OCH_2(CF_2)_3CH_2 \right]_x$$

VII

This polymer is apparently unaffected by oxidation, since the decomposition temperature in air and helium is identical. The polymer obtained was a white crystalline wax. Hydroxyl-terminated prepolymers have been prepared and used to make polyurethanes.[5]

Experimental

Monomers. 1,5-Bis(*p*-carboxyphenoxy)pentane was prepared by a procedure similar to that reported in the book by Sorenson and Campbell.[6]



(4)

A 212.6 g sample of 1,5-bis(*p*-carboxyphenoxy)pentane was refluxed in 750 ml of thionyl chloride containing 20 ml of dimethylformamide for 24 hr. After vacuum distillation, the residue was recrystallized from hexane, yielding 52.6 g (22.5%) of 1,5-bis(*p*-chlorocarbonylphenoxy)pentane which melted at 97–98°C.

Oxybis-*p*(benzoyl chloride) was prepared from the corresponding diacid by this same method.

All other monomers were purchased and purified to obtain polymer grade starting materials.

Polymers. The polyesters were prepared by the following representative procedure. The diacid chloride and diol were mixed at room temperature for $^1/_2$ hr under nitrogen, then slowly heated to 180°C over a $2^1/_2$ hr period. The mixture was then heated to 260°C and held at that temperature for $2^1/_2$ hr under nitrogen, followed by a $^1/_2$ hr period under vacuum. Caution was required, since the glass reaction vessel generally shattered on cooling.

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References

1. C. D. Hurd and C. H. Blunck, *J. Amer. Chem. Soc.*, **60**, 2419 (1938).
2. J. Hine, *Physical Organic Chemistry*, McGraw-Hill, New York, 1956, p. 453.
3. D. W. McCready et al., WADC Contract No. W-33-038-AC-21457.

4. C. D. Hurd and C. W. Bennett, *J. Amer. Chem. Soc.*, **51**, 1200 (1929).

5. J. Hollander, F. Trischler, and E. Harrison, Paper 44W, presented at 154th National American Chemical Society Meeting, Chicago, Illinois, September 1967.

6. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961, p. 141.

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Utilization of Orientation Effect for Determination of Glass Transition Temperature of Polystyrene Thermoplastics

It is known that during processing of polystyrene thermoplastics by means of injection molding, molecular states of order are formed through shear and tensile forces which considerably influence the strength and deformation behavior of the moldings.[1-5] Deformation of material caused by processing forces macromolecules into a high degree of order (orientation) and thereby a state of low entropy. This orientation represents the source of a force tending to bring system to a statistically more probable state i.e., higher entropy. This entropic-elastic power P_e for one macromolecule is given[5] by

$$P_e = KTh/Za^2 \qquad (1)$$

where K is the Boltzman constant, T is the absolute temperature, h is the distance between the ends of the chain, Z is the number of moving elements in the chain, and a is the length of the macromolecule. P_e is thereby proportional to the degree of orientation (stretching) of the macromolecule and the absolute temperature. The relation (1) is valid only when plastic deformation of the macromolecules does not occur.

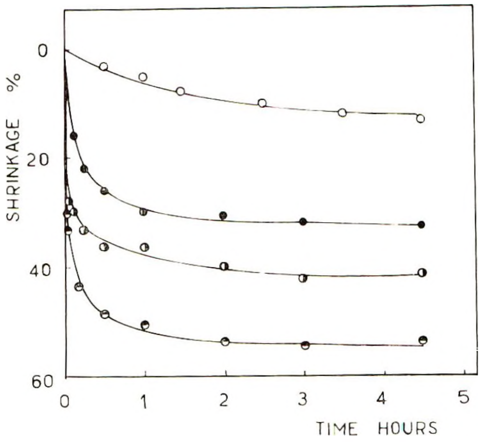

Fig. 1. Time dependence of shrinkage of test specimens (mechanically blended tough polystyrene) tempered at various temperatures: (○) 90°C; (●) 100°C; (◑) 110°C; (◓) 130°C.

At relatively low temperatures when the mobility of chains is at a minimum (there exist only vibration motions of atoms around equilibrium positions or motions of atom groups) this relatively weak force cannot lead to a decrease in the degree of order of the material. A decrease in degree of ordering is possible only after heating of the material above the glass transition temperature, when micro-brownian motion of segments of the polymer chains occurs. This makes possible application of the entropic-elastic power, and shrinkage of molecules and thereby deformation of the sample ensue.

The method is based on following the course of deformation of the samples in dependence on temperature. In the case of uniaxially oriented samples it is a measure of their deformation length shrinkage s after tempering at certain temperatures.

$$S\% = (l_0 - l)/l_0 \times 100$$

where l_0 is the distance between marks on sample before tempering and l is the distance between the same marks on sample after tempering.

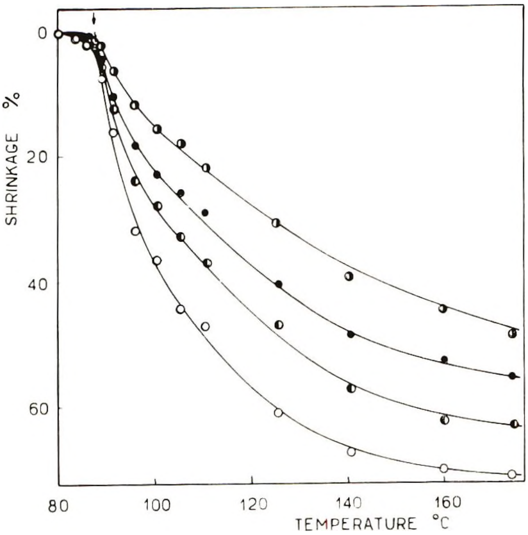

Fig. 2. Temperature dependence of shrinkage of test specimens (mechanically blended tough polystyrene) made at various molding temperatures: (○) 170°C; (◐) 190°C; (●) 210°C; (◑) 250°C.

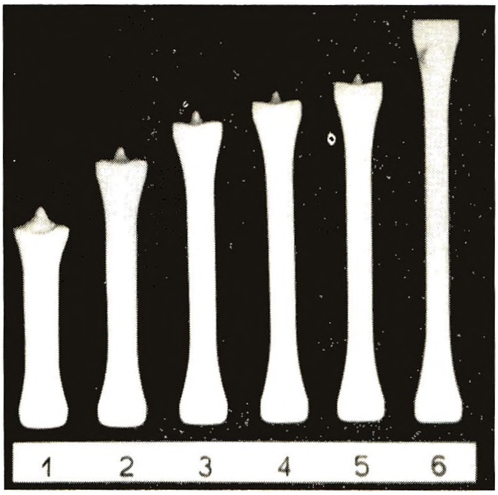

Fig. 3. Changes of shrinkage of test specimens (mechanically blended tough polystyrene) made at various molding temperatures and tempered 1 hr at 110°C: (*1*) 170°C; (*2*) 190°C; (*3*) 210°C; (*4*) 230°C; (*5*) 250°C, (*6*) untempered specimen.

We took measurements of shrinkage in a Höppler ultrathermostat with a 5 liter tempering vessel. We used ethylene glycol as working liquid which made possible measurements in the required temperature range (20–180°C) and ensured free contraction of samples during tempering (the samples floated on the surface of the liquid). In order to prevent deformation of soft samples (an important factor during measurement at higher temperatures when plastic flow of material occurs), we took them from the bath by means of a special instrument. The test specimens used were of the type usually used for testing of mechanical properties of polymers. The samples were prepared by an injection-

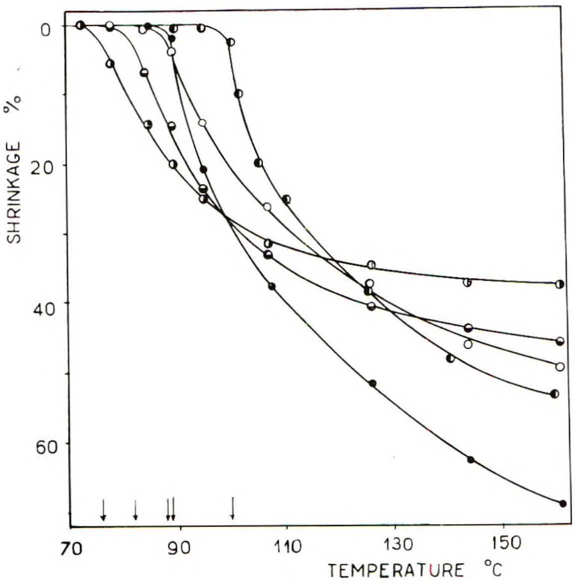

Fig. 4. Temperature dependence of shrinkage of test specimens from various types of polystyrene thermoplastics: (◑, ◒) grafted types of tough polystyrenes; (○) mechanically blended tough polystyrene, (●) polystyrene (atactic); (◐) ABS copolymer.

molding technique on a CSB 12-4-5 injection plunger machine at a fusion chamber temperature of 190°C, theoretical molding pressure of 600 kp/cm^2, and a form temperature of 30–40°C. i.e., at conditions usual for preparation of test specimens from polystyrene thermoplastics.

Measuring involves only putting marks on the test specimens and measuring the distance between them. After 1 hr tempering we take the specimens out of the bath and after cooling we determine the shrinkage. Figure 1 shows the time dependence of shrinkage of specimens tempered at various temperatures. It is evident that shrinkage of test specimens takes place mainly in the beginning phase of tempering. After about only 1 hr almost equilibrium values of shrinkage are attained, which do not depend on the time of tempering. When we plot on these equilibrium values in dependence on temperature (values reached after 1 hr tempering are sufficient for practical purposes) we obtain Figure 2. Initial shrinkage of samples here is related with the micro-brownian motion in the main transition region; the extrapolated point of intersection of the curve with the level of zero shrinkage we consider the glass transition temperature of the polymer. Here can be seen a certain similarity with the penetrometric[6] or thermomechanical[7] method, but with the difference that deformation of material is not here caused by external force but by an internal force in the material. (The present method differs from these methods in that the internal force is not constant but is a function of temperature.) Use of test specimens molded at low temperatures is the most convenient for this measurement. Figures 2 and 3 show that with decreasing molding temperature the shrinkage of the test specimens increases i.e., the degree of orientation increases and the sensibility of the method is also increased thereby. We see also from the figure that the extrapolated points of all curves intersect the level of zero shrinkage practically at one point, corresponding to the glass transition temperature T_g of the polymer, although measurements were taken on samples with various degrees of orientation. This is in accordance with results of penetrometric measurements,[6] in which it was found that the glass transition temperature of a material is virtually independent of load and thereby also of magnitude of internal force. Figure 4 gives temperature dependences for various types of polystyrene thermoplastics. The figure indicates great differences in glass transition temperatures (also in degrees of orientation) among individual types of materials and also relatively good exactness of determination of T_g of polymer by means of this method.

One major advantage of the method lies in the fact that no special apparatus is needed, in contrast with the penetrometric method which requires a measuring cell and device for temperature control. A second advantage is that it is possible to take measurements on a great number of specimens (15–20 samples in our case). In contrast to penetrometric and thermomechanical methods, the described method can be used only when samples are prepared by means of an injection molding technique (or by some other technique leading to formation of an oriented structure) which is however the most widespread method of preparation of test specimens for estimation of mechanical properties of polystyrene thermoplastics. Only one test specimen, continuously tempered at the various individual temperatures, is required to obtain the whole curve. The advantage of this operation lies also in the fact that during this process the internal stress (i.e., forces resulting from deformation of valence angles or equilibrating positions of atoms) in specimens is already released at temperatures below the glass transition temperature so that T_g value cannot be affected thereby. When we take discontinuous measurements there exist no shifts of T_g caused by differences of temperature between heating medium and sample. The method is convenient for determination of T_g of polystyrene phase in polystyrene, tough polystyrenes, and ABS copolymers.

References

1. H. J. Orthmann, *Kunststoffe*, **55**, 167 (1965).
2. H. J. Orthmann, *Kunststoff Rundschau*, **14**, 221 (1967).
3. F. H. Müller, *Kunststoffe*, **57**, 369 (1967).
4. H. Wiegland and H. Vetter, *Kunststoffe*, **57**, 276 (1967).
5. H. Wiegland and H. Vetter, *Kunststoffe*, **56**, 761 (1966).
6. F. Rybnikář, *Chem. Listy*, **52**, 896 (1958).
7. V. A. Kargin and T. S. Sogolova, *Zh. Fiz. Khim.*, **23**, 530 (1949).

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Copolymers of Starch and Polyacrylonitrile: The Soluble Fraction

As part of an investigation of the influence of reaction variables on the composition of starch graft copolymers, we have made a detailed study of starch–polyacrylonitrile (PAN) copolymers prepared by ceric ammonium nitrate initiation. Although extraction of polymers with dimethylformamide (DMF) removed ungrafted PAN from the relatively insoluble graft copolymers, the DMF-soluble fractions at times contained more than 15% carbohydrate, and in some reactions the soluble fraction represented more than half of the isolated solid. Although we expected that in most instances the DMF-soluble material contained largely ungrafted PAN, these fractions had never been examined in detail and the possibility existed that a significant amount of graft copolymer was also dissolved by DMF. Determination of the percentages of ungrafted PAN and soluble graft copolymer in the DMF-soluble portions was therefore important to understanding graft copolymerization of PAN onto starch. Ultracentrifugation in a density gradient solution of DMF and bromoform[1] was a convenient method of analysis for the two components and showed that their relative amounts depended on the method used to pretreat starch before the grafting reaction.

Experimental

The unmodified wheat starch was Supergel from Industrial Grain Products, Ltd. The acid-modified corn starch was Flojel 75 from National Starch and Chemical Corp., and the hypochlorite-oxidized corn starch was Claro 5591 from Corn Products Co. In both products, starch granules were intact. The preparation of enzyme-modified wheat starch has been described.[2] This product had no intact starch granules and was 76% soluble in water at room temperature (4.4% slurry).

Graft polymerizations were carried out as previously described.[3] Granules of unmodified wheat starch were disrupted by dissolving the starch in dimethyl sulfoxide, precipitating with methanol, and heating the precipitated starch in water at 85°C.[3] Granules of acid-modified corn starch were disrupted by heating in water at 85°C. For reactions with granular starches, aqueous slurries were allowed to react with monomer and initiator without heating. Reaction products were exhaustively extracted with DMF and the percentage PAN in the soluble fraction determined from nitrogen analysis.

The density gradient solution was prepared by diluting 10.12 g of bromoform to 50 ml with DMF. Solubility of the DMF-soluble polymer in the density gradient solution was determined by stirring a suspension of the polymer in the solution at room temperature, filtering, and determining the weight of solid in a portion of the filtrate. For ultracentrifugation, an accurately weighed sample of soluble polymer was dissolved in a known volume of density gradient solution to give a polymer concentration of 0.5%.

A Spinco Model E analytical ultracentrifuge with schlieren optics and a titanium rotor was used at a speed of 59780 rpm. Single-sector aluminum cells of 3 mm thickness were used. Thicker cells caused parts of the pattern to blacken, presumably due to refraction of the light beam out of the optical system.[4] Aluminum cells were not corroded by the bromoform in the solvent system if care was taken while filling the cell not to scratch the aluminum with the point of the hypodermic needle. Fresh aluminum surfaces were rapidly attacked. Equilibrium was reached after a running time of 48 hr, as evidenced by no further change in the schlieren pattern after an additional 45 hr.

Results and Discussion

The starch samples used as starting materials and the soluble fractions from reaction products are shown in Table I, along with conversions of acrylonitrile (AN) to ungrafted PAN and of AN plus starch to DMF-soluble graft copolymer. Soluble graft copolymer and PAN were well separated on the schlieren patterns, and the lower density PAN component was identified by comparison with the pattern of PAN synthesized in the absence of starch. The pattern for each component was integrated and the area under each integrated curve determined. Relative amounts of the two components were then calculated from relative areas.[4] In two instances, the percentage of ungrafted PAN in a two-component unknown was also calculated by comparing the area value for PAN (from double integration) with that from a run with a single-component PAN solution of known concentration. Graft copolymer was then determined by subtraction of the percentage of ungrafted PAN from 100%. Since percentages obtained by this method (84 and 67% PAN) were close to those calculated from relative areas (88 and 65% PAN), the two components apparently have similar *dn/dc* values.

TABLE I
Composition of Soluble Fractions and Calculated Conversions

	DMF soluble fraction		$CHBr_3$–DMF-soluble fraction			Conversions, %	
Starch	% of total isolated solids	Total PAN content, %[a]	% of DMF-soluble fraction	Ungrafted PAN, %[b]	Graft copolymer, %[b]	AN to ungrafted PAN	AN + starch to soluble copolymer[c]
Unmodified wheat (disrupted)	25	85.5	95	86	14	35	6
Unmodified wheat (granular)[d]	3	—	—	—	—	<4	<3
Acid-modified corn (disrupted)	56	80.5	48	66	34	27	35
Acid-modified corn (granular)	17	98	98	100	0	24	<1
Hypochlorite-oxidized corn (granular)	32	96	88	100	0	42	3
Enzyme-modified wheat (76% water soluble)	51	87.7	80	95	5	61	11

[a] Calculated from nitrogen analysis.

[b] Calculated from schlieren patterns.

[c] Percentage of combined weight of starting materials (starch and AN) converted to soluble graft copolymer.

[d] Not examined in the ultracentrifuge. Upper limits for conversions were calculated assuming that the DMF-soluble fraction was either all PAN or all graft copolymer.

For calculation of conversions, it was assumed that all polymer insoluble in the density gradient solution was starch–PAN copolymer. This assumption was reasonable, since ungrafted PAN(molecular weight 306,000), synthesized in the absence of carbohydrate, was readily dissolved by this solvent system.

Table I shows that DMF extraction of most reaction products removes largely ungrafted PAN; as suspected, however, there are instances where conversion to DMF-soluble graft copolymer is relatively high. It is evident that higher yields of DMF-soluble copolymer result when starch granules are disrupted before the grafting reaction. There have been indications that granule disruption gives rise to a larger amount of soluble copolymer in both the starch–PAN[3] and starch–poly(methyl methacrylate)[5] systems; however, our work represents the first quantitative analysis of the soluble fraction.

Polymerization onto small carbohydrate fragments (either present in the modified starches or produced by hydrolysis in the acidic reaction mixture) could be one factor leading to the relatively high conversions in some reactions to the polymers referred to as ungrafted PAN. If the percentage of carbohydrate in such polymers were low enough, the carbohydrate portions would amount to little more than endgroups and would not be detectable by the density gradient method.

We thank N. W. Taylor, C. R. Russell, and C. E. Rist for their helpful discussions. We also thank Mrs. B. R. Heaton for nitrogen analyses.

References

1. H. A. Ende and V. Stannett, *J. Polym. Sci. A*, **2**, 4047 (1964).
2. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Polym. Sci. A-1* in press.
3. R. C. Burr, G. F. Fanta, C. R. Russell, and C. E. Rist, *J. Macromol. Sci. A*, **A-1** 1381 (1967).
4. R. Buchdahl, H. A. Ende, and L. H. Peebles, in *First Biannual American Chemical Society Polymer Symposium* (*J. Polym. Sci. C*, **1**), H. W. Starkweather, Jr., Ed., Interscience, New York, 1963, p. 153.
5. C. E. Brockway and K. B. Moser, *J. Polym. Sci. A*, **1**, 1025 (1963).

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Étude du Mécanisme et de la Cinétique de la Réaction d'Amorçage de la Polymérisation du Cyclopentadiène par l'Hexachloroantimoniate de Triphénylméthyle

Nous avons signalé récemment la possibilité d'obtention de hauts polymères du cyclopentadiène amorcés par un sel à carbocation stable, l'hexachloroantimoniate de triphénylméthyle $(C_6H_5)_3C^+SbCl_6^-$.[1] Il résultait de nos premières observations que l'hypothèse la plus vraisemblable concernant le mécanisme d'amorçage de la polymérisation était celle d'une fixation directe du carbocation $(C_6H_5)_3C^+$ sur la double liaison du monomère. Nour apportons ici la preuve de l'intervention d'un tel mécanisme et nous précisons l'aspect cinétique de la réaction d'amorçage.

PARTIE EXPERIMENTALE

La purification des réactifs et la préparation de l'amorceur ont déja été indiquées.[1]

Preparation des Oligomères

Nour avons opéré dans le chlorure de méthylène a la température ambiante avec une forte concentration en amorceur $[C]_0 = 3{,}2.10^{-2}$ mole/litre et une faible concentration en monomère $[M]_0 = 0{,}16$ mole/litre. Le milieu réactionnel prend une coloration rouge intense dès l'introduction du monomère dans le mélange CH_2Cl_2-$(C_6H_5)_3C^+SbCl_6^-$. Après 1$^1/_2$ h de réaction, la solution est versée dans un large excès d'hexane où l'amorceur non consommé précipite. Après filtration, l'hexane est évaporé et le résidu solide est redissous dans un minimum de CCl_4. La solution est alors versée dans quelques millilitres de méthanol (bon solvant des dérivés du triphénylméthane) où le polymère précipite. Celui-ci est filtré, séché, puis purifié par dissolutions et précipitations ultérieures jusqu'à obtention d'un spectre infra-rouge constant.

La masse moléculaire moyenne en nombre des oligomères a été mesurée dans le benzène à 37°C à l'aide d'un osmomètre à tension de vapeur Mechrolab 302.

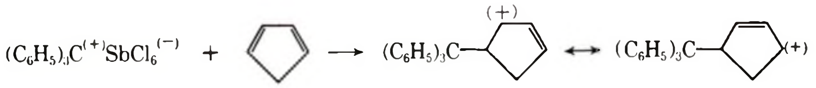
Mesures spectrophotomètriques

Les spectres de RMN ont été enregistrés sur des appareils Perkin-Elmer 60 MHz et Varian HA 100, les spectres UV sur Cary 15 et les spectres infra-rouges sur appareil Perkin-Elmer 225.

RÉSULTATS ET DISCUSSION

Mécanisme de l'Amorcage

Nous avions précédemment écarté-aprés vérification expérimentale—l'éventualité d'un amorçage par $SbCl_5$ ou par l'acide hexachloroantimonique, et des observations d'ordre cinétique permettaient d'envisager l'addition directe de $(C_6H_5)_3C(^+)$ sur le cyclopentadiène:



(1)

$$(C_6H_5)_3C—M_1^{(+)} + {}_nM \longrightarrow (C_6H_5)_3C—M_{n+1}^{(+)} \qquad (2)$$

Ce mécanisme entraîne l'incorporation d'un groupement triphénylméthyle dans chaque chaîne de polymère. Nous avons donc cherché à mettre en évidence de tels groupements dans des polycyclopentadiènes de très bas poids moléculaires.

Des oligomères ont été préparés a la température ambiante, avec une forte concentration en amorceur. Le $\overline{DP}_n$ théorique déterminé à partir des consommations expérimentales de monomère et d'amorceur est de 5 environ. La masse moléculaire du produit purifié, mesurée à l'aide d'un osmomètre à tension de vapeur est voisine de 1700. Cette valeur est très supérieure à la valeur théorique, mais il faut remarquer que les précipitations successives éliminent certainement les plus bas oligomères. Cette purification avait pour but d'éliminer avec certitude l'amorceur n'ayant pas réagi et ses produits d'hydrolyse.

Le spectre de RMN de ces oligomères présente une raie intense dont le déplacement chimique $\delta = 7{,}16$ ppm correspond exactement à la résonance des protons aromatiques du triphénylméthane. Le rapport du nombre de protons éthyléniques ($\delta = 5{,}55$ ppm) au nombre de protons saturés (δ de 1 à 3 ppm) est inférieur à $^1/_2$, ce qui indique une saturation partielle du motif cyclopentènique. Nous avons néanmoins évalué le DP_n de ces oligomères en utilisant le rapport du nombre de protons aromatiques à la somme des protons éthyléniques et saturés. La valeur obtenue est voisine de 25, ce qui conduit à une masse moléculaire moyenne de 1900 en supposant l'incorporation d'un groupement triphénylméthyle par chaîne. L'accord avec la masse moléculaire expérimentale est satisfaisant.

Le spectre infra-rouge présente également des absorptions caractéristiques. Les bandes de vibration de valence =C—H des cycles benzéniques monosubstitués apparaissent en épaulement de la bande $\nu_{=C-H}$ du polymère à 3020 et 3083 cm^{-1}. La bande de vibration de déformation à 700 cm^{-1} est également très intense et nous avons pu l'utiliser pour évaluer le DP_n des oligomères. On trouve dans ces conditions un groupement triphénylméthyle pour 35 motifs cyclopentèniques environ.

L'accord de cette mesure avec celle que nous avions déduite du spectre de RMN n'est pas parfait, mais il est possible de conclure que l'amorçage de la polymérisation se produit essentiellement par fixation directe du carbocation $(C_6H_5)_3C(^+)$ sur le monomère, sans que l'on puisse exclure totalement l'intervention de réactions de transfert.

Etude cinétique de la Réaction d'Amorçage

Nous avons suivi par spectrophotométrie l'évolution de la réaction du cyclopentadiène avec l'hexachloroantimoniate de triphénylméthyle. Ce sel présente à 410 et 435 mμ une absorption caractéristique du carbocation $(C_6H_5)_3C(^+)$. Les coefficients d'extinction molaires apparents ϵ que nous avons obtenus[1] sont très proches des valeurs indiquées dans la littérature pour le cation $(C_6H_5)_3C(^+)$ totalement dissocié.[2,3]

Nous avons constaté que les valeurs de ϵ à 410 et 435 mμ augmentaient faiblement quand la température s'abaisse. Compte tenu de l'augmentation de concentration due à la contraction du solvant, ϵ_{410} est compris entre 35900 à +20°C et 37000 à −70°C. Cette variation de l'absorption est linéaire, identique pour les deux maximums et ne s'accompagne d'aucun changement de longueur d'onde des pics. Comme d'autre part la loi de Beer-Lambert est vérifiée pour les deux maximums, à toute température, pour la gamme de nos concentrations en amorceur [C], nous avons considéré que chaque molécule de sel complexe est ionisée sous forme de paires d'ions et peut donner naissance à un centre actif. La vitesse de la réaction d'amorçage s'exprime alors par l'équation:

$$V_a = -d(C)/dt = k_a\,[M]^{\alpha}[C]^{\beta}$$

Les ordres partiels α et β et la constante k_a ont été déterminés en suivant la disparition des carbocations $(C_6H_5)_3C(^+)$ consommés dans la réaction (1).

Ordres relatifs à l'Amorceur et au Monomère

Lorsque le monomère est ajouté à la solution d'amorceur, la concentration de ce dernier décroît suivant une loi exponentielle en fonction du temps, ainsi que le montre la Figure 1 sur laquelle sont représentées les variations du logarithme de la concentration [C] en amorceur en fonction du temps de réaction pour différentes concentrations initiales en monomère $[M]_0$. L'ordre partiel en amorceur est donc égal à 1. La pente des droites obtenues est égale à $K = k_a[M]^{\alpha}$ et comme la conversion est faible pendant la durée de ces

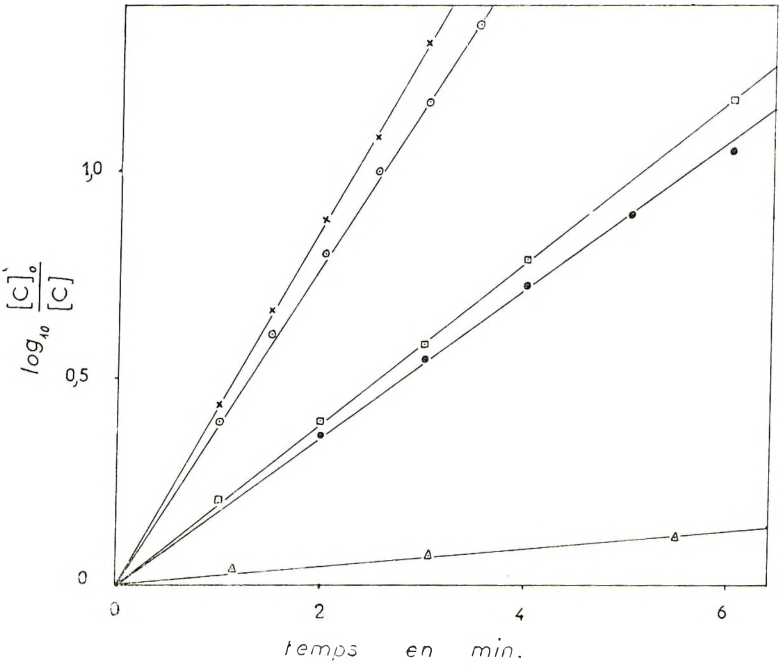


Fig. 1. Loi du premier ordre pour la consommation de l'amorceur en présence de cyclopentadiene à +25°C, $[C]_0 = 0.8 \times 10^{-3}$ mole/litre: (×) $[M]_0 = 0{,}90$ mole/litre; (⊙) $[M]_0 = 0{,}70$ mole/litre; (⊡) $[M_0] = 0{,}50$ mole/litre; ● $[M]_0 = 0{,}35$ mole/litre; (◬) $[M]_0 = 0{,}012$ mole/litre.

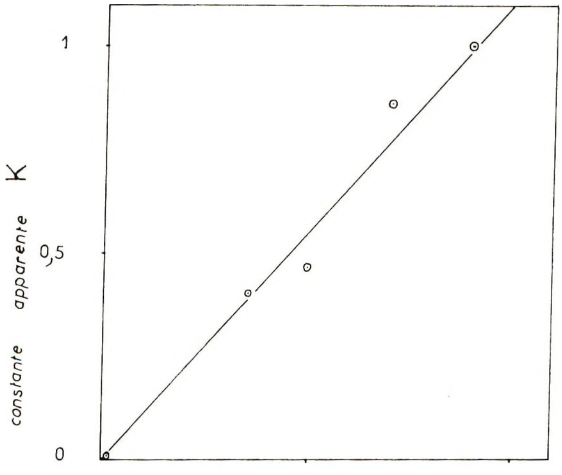


Fig. 2. Variation de la constante apparente de vitesse d'amorçage K en fonction de la concentration initiale en monomère à +25°C.

expériences, on peut admettre que [M] est peu différent de $[M]_0$ jusqu'à consommation totale de l'amorceur. Si l'on porte la valeur de K en fonction de $[M]_0$, on obtient une droite de pente k_a, ce qui montre que l'ordre relatif au monomère est également unitaire (Fig. 2).

Variation de k_a avec la Température

Nous avons suivi la vitesse de décroissance du maximum d'absorption à 410 $m\mu$ à quatre températures comprises entre +25 et −70°C à l'aide d'une cellule spéciale conçue au laboratoire pour les études à basse température. Les courbes obtenues en portant log $[C_0]$ en fonction du temps sont des droites dont les pentes permettent de calculer les constantes k_a pour chaque température (Fig. 3 et Tableau I).

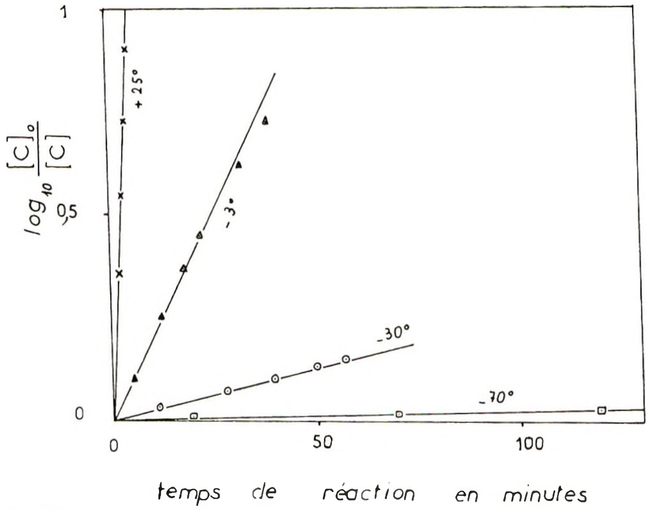


Fig. 3. Influence de la température sur la vitesse de la réaction d'amorçage.

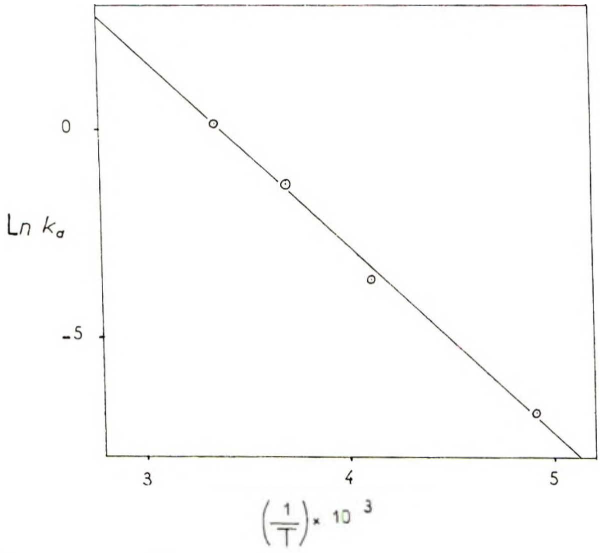


Fig. 4. Verification de la relation d'Arrhénius pour la constante de vitesse d'amorçage k_a.

TABLEAU I
Valeurs de la Constante de Vitesse d'Amorçage à Différentes Températures

T, °C	$[(C_6H_5)_3C^+SbCl_6^-]$, mmole/litre	$[M]_0$, mole/litre	$k_a \times 10^3$ l./mole-min
+25	0, 8	0, 35	1100
− 3	0, 87	0, 242	195
−30	0, 90	0, 242	24, 6
−70	1	0, 242	1, 02

Energie d'Activation de la Réaction d'Amorçage

Nous avons fait une évaluation graphique de cette énergie d'activation en utilisant la relation classique d'Arrhenius. La Figure 4 montre que ln k_a varie linéairement en fonction de $1/T$ et l'évaluation de la pente conduit à une énergie d'activation $E_a = 9{,}2 \pm 1{,}0$ kcal/mole. Le facteur de fréquence est de $5{,}0 \times 10^6$ environ.

CONCLUSION

La présence d'environ un groupement triphénylméthyle par chaîne d'oligomère montre que la réaction d'amorçage de la polymérisation du cyclopentadiène par l'hexachloroantimoniate de triphénylméthyle à la température ambiante, se produit essentiellement par fixation directe du carbocation stable sur une double liaison du monomère. L'étude cinétique de l'amorçage, menée à différentes températures, indique que ce mécanisme est vraisemblablement indépendant de la température de polymérisation. L'aspect cinétique très simple de cette réaction permet d'affirmer que, les réactions de transfert mises à part, chaque molécule d'amorceur peut, sans l'intervention d'un cocatalyseur quelconque, donner naissance à une chaîne de polymère, phénomène assez inhabituel en polymérisation cationique des monomères éthyléniques.

Il faut noter d'autre part que ces résultats sont parfaitement en accord avec ceux de l'étude cinétique, réalisée récemment par Higashimura, Fukushima et Okamura,[4] de la réaction d'amorçage de la polymérisation du styrolène et de l'α-méthylstyrolène par un amorceur de la même famille, le pentachlorostannate de triphénylméthyle.

References

1. G. Sauvet, J. P. Vairon, et P. Sigwalt, *Compt. Rend.* **265C**, 1090 (1967).
2. L. C. Anderson, *J. Amer. Chem. Soc.*, **52**, 4567 (1930).
3. V. Gold et B. W. V. Hawes, *J. Chem. Soc.*, **1951**, 2102.
4. T. Higashimura, T. Fukushima, et S. Okamura, *J. Macromol. Sci.* (*Chem.*), **A1**, 683 (1967).

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BOOK REVIEWS

Macromolecular Reviews, Volume 3, A. Peterlin, M. Goodman, S. Okamura, B. H. Zimm, and H. Mark, Eds., Interscience, New York, 1968, 437 pp. $15.00.

Volume 3 of this series preserves the format of its predecessors in a series of five contributions. The quality of the reviews is good, and they will be a tremendous aid to anyone requiring background in one of the areas covered. The topics vary widely, and although such scope may not be a serious consideration for library acquisition, fewer individual purchasers may be interested in so wide a spread of subject matter.

The book opens with "Copolymerization in the Crystalline Solid State" by Herz and Stannett. Their chapter starts with a general discussion of phase diagrams and methods, then summarizes and interprets data now available on individual systems. At the moment the field is in an early stage of development and the general picture is not wholly clear. For this reason the chapter is an excellent source of research ideas. Several other reviews of solid state polymerization have appeared recently, but the present one is alone in its concentration on copolymerization.

Reich's chapter on "Polymer Degradation by Differential Thermal Analysis Techniques" is complementary to the Reich and Levi review of thermogravimetric analysis in Volume 1 of this series. The present review covers some related data on TGA and IR, but the large body of work on thermal transitions is not within its scope. After a brief discussion of kinetic parameters and their derivation from DTA, individual polymers are discussed in detail. These materials include the major vinyl polymers as well as a number of condensation and ring opening types. The DTA curves are often difficult to interpret, but taken with other evidence they provide a rapid means of gaining insight into degradation processes.

Beevers has contributed a comprehensive report on "The Physical Properties of Polyacrylonitrile and Its Copolymers." This review is considerably longer than the others, comprising 130 pages plus 361 references. It discusses solution properties, crystallinity, spectroscopy, x-ray examination, thermal transitions, and structural changes at high temperatures. All of these topics are considered from a fundamental point of view and primarily for the homopolymer or for compositions close to it. The review will be extremely useful to those concerned with acrylic fibers and does not overlap earlier reviews on polymerization mechanism.

A chapter on "Hydrodynamic Properties of DNA" stands alone in these three volumes in dealing with a biopolymer. Bloomfield's paper covers special aspects of sedimentation and viscosity measurement, correlation of these properties with molecular weight, the various DNA structures in solution, and structural transformations. Special problems are considered arising from the extremely high molecular weight of DNA and from the sensitivity of double stranded DNA to thermal, chemical, and shear forces. The chapter has been written to appeal not only to the specialist but also to the more general polymer chemist whose interest has been aroused by the enormous importance of DNA.

The final chapter is by Henderson and Szwarc and is entitled "The Use of Living Polymers in the Preparation of Polymer Structures of Controlled Architecture." It outlines the development over the last 12 years of methods for conducting polymerization of vinyl monomers while virtually eliminating the termination step. The authors discuss the importance of this technique in preparing polymers with a sharp molecular weight distribution and elaborate on the criteria that must be met. Use of nearly monodisperse polymers in establishing property-size relationships is considered. Preparation and properties of block copolymers by this technique are discussed in some detail. The review closes with examples of controlled architecture in star-shaped, graft, comb-shaped, and functionally ended polymers.

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Polyesters—Volume 2, Unsaturated Polyesters and Polyester Plasticizers Brian Parkyn, F. Lamb, and B. V. Clifton, American Elsevier Co., New York, 1967. 168 pp. $8.50.

This small book discusses two poly compounds. The first 100 pages cover the condensation products of dihydric or polyhydric alcohols and dibasic or polybasic acids. Such products are commonly designated unsaturated polyester resins. The next 60 pages treat the preparation properties and behavior of polyester plasticizers.

Regarding unsaturated polyesters, no one aspect is discussed in detail. The objective is to present a brief overview with key references. The authors appear to talk at one sitting to the mixed audience of chemist and technologist.

Actually, there is enough theory on stabilization, inhibition, catalysis, and polymerization mechanism to remove the mystique for the fabricator who must understand sufficient modicum to practice his craft and does not need total background.

From the standpoint of direction to a specific reader audience, the book suggests its greatest value is to serve the large group of engineers and technologists who are regularly pushing the horizon for composite structures, frequently reinforced with fibers. This commercial field which started with innocent housings for radar and moved systematically into fishing rods, boats, buttons, skis, and Hollywood stage settings has needed a work which tells enough about resins to enable the creative engineer to perfect the next and succeeding applications.

Regarding polyester plasticizers, the same objective attains in a subject less complicated and more unidirectional. The work touches base with a bit of theory, suggested compositions, properties, structural effects, and molecular weight concluding with hints at formulations utilizing poly(vinyl chloride) and poly(vinyl acetate).

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Organic Synthesis via Metal Carbonyls. Volume 1. Irving Wender and Piero Pino, Eds., Wiley, New York, 1968. xiv + 517. $18.95.

This first book of a two volume series adds to the rapidly expanding secondary literature of the interdisciplinary field of homogeneous catalysis. Five chapters authored by prominent workers in the subject field focus on carbonyl containing transition metal complexes and their role in organic synthesis.

Chapter 1. Metal Carbonyls: Preparation, Structure, and Properties. By F. Calderazo, R. Ercoli, and G. Natta. 272 pp. with 1410 references.

Chapter 2. Organometallic Derivatives from Metal Carbonyls and Acetylene Compounds. By W. Hübel. 70 pp. with 146 references.

Chapter 3. Cyclic Polymerization of Acetylenes by Metal Carbonyl Compounds. By C. Hoogzand and W. Hübel. 29 pp. with 86 references.

Chapter 4. Organic Syntheses via Alkyl and Acylcobalt Tetracarbonyls. By R. F. Heck. 39 pp. with 32 references.

Chapter 5. Reactions of Nitrogen Compounds. By A. Rosenthal and I. Wender. 62 pp. with 124 references.

This work *is not*, as the chapter titles suggest, a compendium of selected and checked laboratory procedures—the prominent display of the phrase "organic syntheses" in the series title is unfortunate. The editors are well justified, however, in their zeal to attract the organic chemist to these well-written treatises.

The some 1800 references of Volume 1 assure this series a place on the reference shelf as a supplement to up-to-date inorganic texts and recent monographs on homogeneous catalysis. Reference value is enhanced by a combined 50 page index which supplements detailed tables of content for each chapter.

Selection of material from a vast and rapidly expanding literature always creates problems. In this case, the primary criterion for selection—the presence of carbonyl ligands in the metal complex—creates a danger of an unbalanced and incomplete view. The prospective reader should bear in mind that the ability of a transition metal complex to accomplish a synthetically useful result for the organic chemist is not uniquely endowed by the carbonyl ligand; a discussion of topics such as olefin cyclizations, dimerizations and additions which excludes carbonyl-free complexes excludes chemistry already of industrial importance.

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High Polymers, Vol. XXIII, Polymer Chemistry of Synthetic Elastomers, Part I, Joseph P. Kennedy and Erik G. M. Törnqvist, Eds., Interscience, New York, N. Y., 1968. XIV + 490 pp. $25.00.

Synthetic Rubber, edited by G. S. Whitby, appeared in 1954 and has stood alone as the comprehensive reference on this subject. *Polymer Chemistry of Synthetic Elastomers* aims to update *Synthetic Rubber*. We have here for consideration only the first of two volumes, Part I, containing five chapters. There are 12 articles by 16 authors, of whom at least a majority are in the first rank of the active workers who could have been chosen.

The first chapter is a compact review of elastomer physics, included in acknowledgment of the fact that elastomer chemistry is not enough. The second chapter is an interesting historical review, with unusual emphasis on the patent literature. The third, *The Status and Future of Elastomer Technology, 1966* has a somewhat anomalous position in this book. On one hand its emphasis on the immediate present (1966) makes it seem immediately out of date, a hard fate for a reference work. On the other hand it becomes in this book the major or only repository for the sorts of technological lore which helped make *Synthetic Rubber* so valuable. As just one example, the subject of rubber reinforcement, which is neglected in the rest of the text, is at least surveyed here.

The two remaining chapters, on free radical and cationic elastomers, occupy much the greater portion of Part I. The major subtopics, each of which is separately authored, are SBR, nitriles, neoprene, acrylics, and fluoro rubbers; butyl, polyvinyl ethers, polyethers, and polyacetals. In mode of presentation, and choice and order of topics, each author has been a free agent. There is virtue in the resulting nonuniformity, since the quality of the articles is high.

This is the major strength of the book: the articles are good because of the competence and diligence of the authors. As a book, however, it is not a match for *Synthetic Rubber*. In a rubber chemistry library, "Whitby" is a book with frayed binding, and lettering which is becoming illegible with wear. Kennedy and Törnqvist are much less likely to win that accolade.

The reasons are fairly easy to pinpoint and would have been fairly easy to avoid. Principally, it does not have a useful subject index. The result will be that searchers after facts will not rely on this book, because the facts here are nearly inaccessible, however abundant they may be. For example, "polybutadiene" receives four citations out of the at least two dozen which can be found in a moderately careful scan of the text. The alert searcher for polybutadiene facts would have checked out "butadiene" as well (even without a cross-reference, which is lacking here) but he would still have found only about half the nuggets that lie buried. I have checked out a few other categories and am obliged to report that coverage of this index approached adequacy in none of them. The author index does appear to be the product of a consistently applied system, and consequently appears to be complete and inclusive.

There are other shortcomings which testify to too loose an editorial rein. Terminology is inconsistent from chapter to chapter, so that we find one author abbreviating butadiene as Bd, another as BD, and still another as Budi. Typographical errors, grammatical lapses, and ambiguities are rather numerous in some chapters, and absent in others, a circumstance which suggests again an abdication of editorial responsibility.

The value of the book should not be overlooked. Every rubber chemist will want to read at least the topics impinging on his own areas of specialization. If there is tighter editing and a much improved index in the forthcoming Part II (which is to contain anionic, condensation, modified, and other rubbers), the work should also become a durable reference.

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Conformation of Macromolecules. (Vol. XXII of High Polymer Series.) T. M. Birshtein and O. B. Ptitsyn, Interscience, New York, 1966. 350 pp. $14.50.

The authors of this book have been prominently associated with the important advances in the theoretical interpretation of the shape of long chain polymers based on the assumption that it may be represented by a small number of discrete rotational states for every bond in the chain backbone. This concept, developed in all its consequences by M. V. Volkenstein and his collaborators at the Institute of High Molecular Weight Compounds of the Soviet Academy of Sciences in Leningrad, has had a profound effect on the interpretation of the crystal structure of synthetic polymers, the interpretation of chain flexibility in solution and, more recently, on various attempts to interpret or predict the conformations of globular protein molecules. A summary of the work carried out by the Leningrad group was first presented to the English reading public by Volkenstein (Vol. XVII of this series) and it is fortunate that his monograph is now being supplemented by the detailed and more broadly based exposition of Birshtein and Ptitsyn.

The book contains the following chapter headings: (*1*) Flexibility of Macromolecules and their Physical Properties. (*2*) Internal Rotation and Rotational Isomerism. (*3*) Conformations of Macromolecules and Mechanism of Their Flexibility. (*4*) Statistics of One-Dimensional Cooperative Systems. (*5–6*) Theory of Dimensions and Dipole

Moments of Macromolecules, (*a*) General Methods, (*b*) Real Chains. (*7*) Comparison of the Theory with Experiment and Conformations of Typical Macromolecules in Solution. (*8*) Conformations of Macromolecules and Mechanical Properties of Polymers. (*9*) Theory of Conformational Transitions in Polypeptide Chains. (*10*) Effect of External Factors on Conformational Transitions in Polypeptide Chains. (*11*) Theory of Conformational Transitions in Polynucleotide Chains.

The treatment throughout the book is authoritative. However, since this field of investigation is extremely active, it is inevitable that a great deal of work should have been accomplished since the book was written. This is particularly true of the extensive studies of the flexibility of macromolecules published recently by Flory and his school and the work on the conformation of polypeptides by Ramachandran, Scheraga, Liquori and others. One subject which this reviewer would have liked to see included in the book is a discussion of rates of conformational transitions. There is, however, no question that this volume should be obtained by anyone interested in theoretical aspects of the physical chemistry of macromolecules.

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ERRATUM

Morphology of Nascent Polyolefins Prepared by Ziegler-Natta Catalysis

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Captions to the Figures are as follows:

Fig. 1. Catalyst-laden reaction mixture from PS73. Optical micrograph, 160×.

Fig. 2. Toluene suspension of globules from PS19. Note the fibrous texture. Optical micrograph, crossed nicols, 66×.

Fig. 3. "Spiked" globules from PS11 under toluene. Optical micrograph, crossed nicols, 160×.

Fig. 4. Cluster of elongated globules from PBu 62. Optical micrograph, crossed nicols, 66×.

Fig. 5. "Catenoid" globules from PP68 suspended in toluene. Optical micrograph, side illumination, 18×.

Fig. 6. Pair of interconnected globules from PBu 61. Optical micrograph, crossed nicols, 40×.

Fig. 7. Globules with large spikes from PS74. Optical micrographs, crossed nicols, 160×. In B a spike showing an apparent spiral structure is visible near the upper right corner.

Fig. 8. Surface of dried globules from PS77 showing spikes with apparent spiral structures. Optical micrograph, steep oblique illumination, 520×.

Fig. 9. Globules from preparation PS11 (some catalyst is still present in this sample). Note the birefringent skin. Optical micrograph, crossed nicols, 160×.

Fig. 10. Large globule from PS11 dried on a glass slide. Note the fibrous texture. Optical micrograph, steep oblique illumination, 520×.

Fig. 11. Globule from PS73, freeze-dried from benzene and "fixed" in a partly collapsed state. Scanning electron microscope, 1000×.

Fig. 12. Convoluted strands of polymer from an unstirred styrene polymerization (PS83). Optical micrographs, 40×. (*a*) crossed nicols, (*b*) Same specimen area with transmitted light.

Figure 13. Samples of PS96 withdrawn at various times during the course of the reaction. Optical micrographs, all 160×. *Upper left:* 10 min. after t_0; a cluster of catalyst particles and fibrous matter can be seen. (What appears to be the outline of a globule near the center of the frame is an air pocket under the cover glass.) *Upper right:* 35 min. after t_0; the faint outline of globules is visible. *Lower left:* 75 min. after t_0; *Lower right:* 150 min. after t_0; globules near maturity. When the reactions are allowed to proceed beyond this stage spikes sometimes develop.

Fig. 14. Portion of the wall dissected from a very large globule from PE66 suspended in toluene; optical micrograph, crossed nicols, 66×.

Fig. 15. Detail of globule wall from PE66 showing several layers or lamellae of fibrils. Scanning electron microscope, 900×.

Fig. 16. Replica of the surface of a globule from PS77. Electron micrograph, 38500×.

Fig. 17. Replica of the surface of a globule (PS11). Electron micrograph, 73000×.

Fig. 18. Fibrils obtained by manual agitation of a suspension of globules from PP68. Platinum shadowed at 45°. Electron micrograph, 52000×.

Fig. 19. Schematic illustrations showing possible ways of interpreting the "notched" structure of the fibrils: (*a*) the helicoidal model; (*b*) the stacked or inclined platelet model. (It may be noted that if P is reduced until the adjacent turns of the helix are in contact, both models appear superficially identical. This feature would make differentiation between the two models difficult solely on the basis of electron microscopy.)

Fig. 20. "Shish-kebab" fibrils of PE49, a preparation not stirred during synthesis. The fibrils were separated manually from a large cluster. Note the presence of multiple central filaments in some of the larger structures. Platinum shadowed at 45°. Electron micrograph, 52000X.

Fig. 21. Replicas of various areas of polymer film recuperated from the "dry" polymerization PE81. Platinum shadowed at 45°. Electron micrographs: (*a*) appearance typical of about 50% of total area, 10,500×; (*b*) appearance of remainder, 17,500X; (*c*) higher magnification of area similar to a; note fibrils, 37000×.

Fig. 22. Tabular crystals of PE82 recuperated from a preparation using a homogeneous catalyst. Platinum shadowed at 45°. Electron micrograph 37000×.

Fig. 23. Short lath-like crystals recuperated from a low temperature polymerization of propylene (PP54). Platinum shadowed at 45°. Electron micrograph, 55000×.

Fig. 24. Wide-angle x-ray diffraction diagram of fibril bundles of PS77 with corresponding line diagram showing some of the principal reflections.

Fig. 25. Electron diffraction diagrams of P4MP69 fibrils: (A—top) incident beam normal to the plane of the sample, isotropic rings are obtained; (B—center) sample plane inclined 45° with respect to the incident electron beam; the reflections shown in A have split into arcs, (note; the instrumental constant is close but not identical to that in A); (C—bottom) line drawing showing the principal reflections in B.

Fig. 26. Fibril models showing possible location of fold planes. Arrow indicates the direction of the fibril axis: (*a*) fold planes radial to the fibril axis; (*b*) fold planes along the lateral faces of the fibril.