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The Ring-opening Polymerization of Ethylene-methylphosphite

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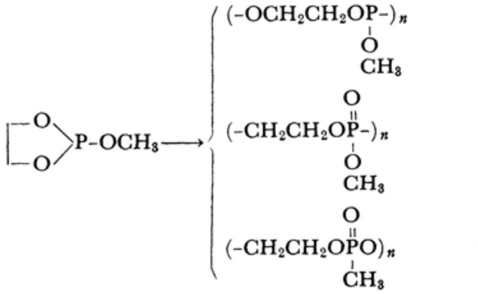
Several Lewis acids have been found to be effective catalysts for the polymerization of ethylene-methylphosphite, giving a solid polymer with a poly(ethylene-methylphosphonate) structure. The use of $Al(C_2H_5)_3$ gave a wax-like polymer with the structure of poly(ethylene-methoxyphosphinate), while Na and Li in liquid NH_3 at $-78°C$ produced a jelly-like polymer partly composed of poly(ethylene-methylphosphite).

Recently, there have been several studies of the ring-opening polymerization of species of phosphorus containing cyclic molecules, e. g., cyclic phosphonites,[1] cyclic phosphites,[2,3] cyclic phosphonates,[4] and cyclic phosphates.[5]

It can be seen in the patent descriptions that the ring-opening polymerization of cyclic phosphites has been investigated with several kinds of catalyst systems,[2] but no information on the structure of polymers has been given. The present authors have reported that the ring-opening polymerization of ethylene-alkylphosphites at higher temperatures gave a polymer with the structure of poly(ethylene-alkylphosphonate).[3] It is known that a tautomeric pair of trivalent and pentavalent structures exists in phosphorus compounds like enol- and keto-forms of carbonyl compounds, and that the former is less stable than the latter. In addition, Mukaiyama et al. reported that the polymerization products of cyclic phosphonites have the structure of poly(ethylene-alkylphosphinate), and suggested an intermediate of an open-chain carbonium-cation type with a phosphoryl group.[4]

The present paper concerns a study of the catalyst and the polymerization products. It was found that the polymerization products were composed of the three types of polymers represented by the following formulae:



$(\text{-OCH}_2\text{CH}_2\text{O}\underset{\substack{|\\ \text{O}\\ \text{CH}_3}}{\text{P}}\text{-})_n$ (I)

$(\text{-CH}_2\text{CH}_2\text{O}\overset{\text{O}}{\underset{\substack{|\\ \text{O}\\ \text{CH}_3}}{\text{P}}}\text{-})_n$ (II)

$(\text{-CH}_2\text{CH}_2\text{O}\overset{\text{O}}{\text{P}}\underset{\substack{|\\ \text{CH}_3}}{\text{O}})_n$ (III)

These structures were confirmed by means of infrared absorption spectra and their hydrolyzed products.

Experimental

Ethylene Methylphosphite.—This compound was prepared from ethylene phosphochloridite, methanol and dimethylaniline according to the method of Arbuzov and Zoroastrova[6]; b. p. 40—41°C/12 mmHg, n_D^{20} 1.4484. The infrared spectrum of this compound is shown in Fig. 1. The ethylene phosphochloridite employed was prepared by the following method: Into 1 mol. of ethylene glycol there was stirred drop by drop, 1.5 mol. of phosphorus trichloride at room temperature. Then the reaction mixture was refluxed

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[1] T. Mukaiyama, T. Fujisawa, Y. Tamura and Y. Yokota, *J. Org. Chem.*, **29**, 2572 (1964).

[2] U. S. Pat. 2893961 (1959).

[3] T. Shimidzu, T. Hakozaki, T. Kagiya and K. Fukui, *J. Polymer Sci.*, **B3**, 871 (1965).

[4] V. V. Korshak, I. A. Gribova and M. A. Andreeva, *Izv. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, **1957**, 631.

[5] K. A. Petrov, E. E. Nifant'ev and L. V. Fedorchuk, *Vysokomolekulyarnye Soedineniya*, **2**, 417 (1960).

[6] A. Y. Arbuzov and V. M. Zoroastrova, *Izv. Akad. Nauk U. S. S. R., Otdel. Khim. Nauk*, **1950**, 770.

TABLE I. SUMMARY OF THE RING-OPENING POLYMERIZATION OF ETHYLENE-METHYLPHOSPHITE

Run	Catalyst	Temp. °C	Time hr.	Yield g.	Appearance	[η]	Infrared (cm^{-1}) 1300	1255	1225	1175
1	—	180	9	0.92	White jelly	0.38	+	+	+	−
2-1	$AlCl_3$	100	6	0.88	Colorless jelly	0.40	±	+	+	+
2-2	$AlCl_3$	180	6	0.95	Colorless hard solid	1.24	+	+	+	−
3-1	$TiCl_3$	30	240	—	Not changed					
3-2	$TiCl_3$	100	7	0.80	Violet vis. liquid	0.12	+	+	+	−
4	BF_3 etherate	180	6	0.91	Brown tacky solid	1.01	+	+	+	−
5-1	P_2O_5	30	240	—	Not changed					
5-2	P_2O_5	180	7	0.81	Colorless liquid	0.08	+	+	+	−
6	96% H_2SO_4	160	5	0.56	Yellow vis. liquid	0.29	+	+	+	−
7	36% HCl	160	5	0.44	White vis. liquid	0.31	+	+	+	−
8	CH_3COOH	160	5	0.01	Colorless liquid	0.08	+	+	+	−
9	H_3PO_4	160	5	0.01	Colorless liquid	0.08	+	+	+	−
10	Na	0	—		Exothermal decomp.					
11	$NaOCH_3$	50	120	0.59	Colorless jelly	0.51	+	+	+	−
12	Na in NH_3	−78	480	0.05	Colorless jelly	0.55	−	+	+	+
13	Li in NH_3	−78	480	0.08	Colorless jelly	0.44	−	+	+	+
			Chloroform extract 0.03				(−	−	−	+)
14	$NaNH_2$ in THF	−78	480	0.05	Colorless jelly	0.39	−	+	+	+
15-1	$Al(C_2H_5)_3$	30	240	0.70	White vis. liquid	0.12	−	+	+	+
15-2	$Al(C_2H_5)_3$	180	7	0.95	White wax	1.34	+	+	+	+
16	$Al(C_2H_5)_3$ etherate	180	6	0.90	White wax	1.44	+	+	+	+
17	AIBN	180	7		Not changed					

(Monomer, 1.0 g. Catalyst, 0.04 g. The ratio of cat. and solvent = 1/20, when solv. is used.)

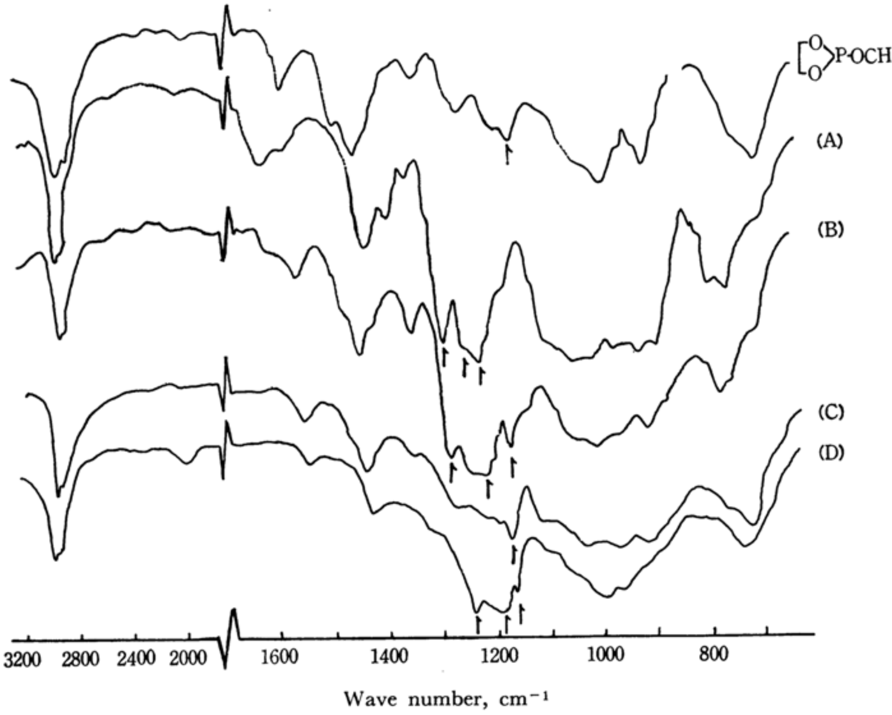


Fig. 1. Infrared spectra of the monomer and typical polymerized products.

TABLE II. THE RESULTS OF THE HYDROLYSIS OF THE POLYMERS

Polymer	Curve in Fig. 1	Product		
		Yield of hydrolysis	Calcd.	Found
Run 1	A	49%	$CH_3O_3PNa_2$: C, 8.58; H, 2.16	C, 8.41; H, 2.01
Run 15-2	B	41%	$C_2H_5O_4PNa_2$: C, 14.13; H, 2.97	C, 13.81; H, 3.08
Chloroform extract of run 13	C	ca. 54%	O_4PNa_3: C, 0; H, 0	C, 0.02; H, 0.04

for 5 hr. Ethylene phosphochloridite was distilled under reduced pressure: b. p. 64—69°C/45—50 mmHg, n_D^{20} 1.4953.

Catalyst.—Materials of a commercial grade were employed.

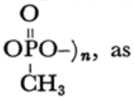
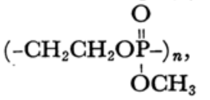
Polymerization was carried out in a sealed glass tube under a nitrogen atmosphere. The resultant polymer was washed by dry methanol, and the remaining monomer, as well as a volatile material, were removed under reduced pressure at a temperature below 50°C. The intrinsic viscosity was measured in a solution of dimethylformamide at 9°C.

The infrared absorption spectra were obtained from a KBr disk of the polymer.

The hydrolytic degradation of the polymer was carried out by refluxing it for three hours in 5 ml. of an aqueous 0.10 N sodium hydroxide solution with 30 ml. of dioxane under a nitrogen stream. After the contents had been kept standing overnight at room temperature, the precipitate was crystallized from ethanol. The identification of the polymer structure was aided by a study of its infrared spectrum and by its elementary analysis.

Results and Discussion

The results of the polymerization of ethylene-methylphosphite with various catalysts are summarized in Table I.

Ethylene-methylphosphite can be polymerized without a catalyst at high temperatures. Still, aluminum chloride and boron fluoride etherates are effective catalysts for the polymerization. They give solid polymer with the structure of poly(ethylene-methylphosphonate), (-CH₂CH₂-  $(-CH_2CH_2-O\underset{CH_3}{\overset{O}{P}}O-)_n$, as was reported in a preceding paper.[3) Sodium methylate also gives a jelly-like polymer at relatively low temperatures. Triethylaluminum is an effective catalyst, giving a brittle wax-like polymer the infrared spectrum of which differs a little from that of the above-mentioned polymers. This polymer has the structure of poly(ethylene-methoxyphosphinate),  $(-CH_2CH_2O\underset{OCH_3}{\overset{O}{P}}-)_n$, as is confirmed by the infrared spectrum indicated in Fig. 1 (curve B) and also by the hydrolyzed product, sodium β-hydroxyethylphosphonate.

Lithium and sodium in liquid ammonia can hardly be effective catalysts for the polymerization, but they give polymers with infrared spectra different from those of the polymers which are obtained by means of the other catalysts. Radical initiators such as 2, 2′-azobisisobutyronitrile do not polymerize ethylene-methylphosphite.

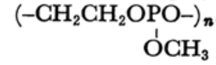
Figure 1 shows typical infrared spectra of the polymers. Curve A is that of run 1, while curve B is that of run 2-1. On the basis of these data, the absorptions at 1300 cm^{-1} (P-CH_3), 1255 and 1225 cm^{-1} (P=O) and 1175 cm^{-1} (P–OCH_3) were adopted as the key bands. These absorptions in each polymer are tabulated in Table I. Table II shows the results of the hydrolysis of the polymers.

The polymers which were obtained at the higher temperatures have absorptions at about 1300, 1255, and 1255 cm^{-1}, and their hydrolyzed products are mainly sodium salts of methyl-phosphonic acid. Conversely, the polymers which are obtained by triethylaluminum and at relatively lower temperatures (run 15 and run 2-1) have an absorption at 1175 cm^{-1} and their hydrolyzed products are mainly sodium β-hydroxyethylphosphonate. Besides, the polymers obtained by lithium and sodium in liquid ammonia at lower temperatures have a broad absorption spectrum in the range from 1170 to 1240 cm^{-1}. This suggests that the polymers have P=O and P–OCH_3 groups. To obtain those absorptions more evidently the polymer (run 13) was extracted in chloroform under nitrogen at room temperature. The results are shown in Tables II and III.

TABLE III. THE SEPARATION OF THE POLYMERS OF RUN 13 AND THEIR INFRARED ABSORPTIONS

	Absorptions at			
	1175	1225	1255	1300 cm^{-1}
Chloroform extr.	+	−	−	−
Residue	+	+	±	±

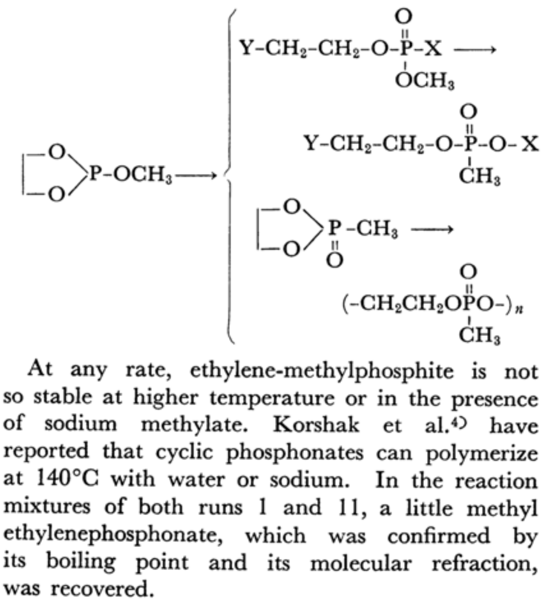
Extracted for 5 hr. under a nitrogen stream at 60°C.

The chloroform-extract of the polymer was readily oxidized when it was kept standing in the air; its infrared spectrum is shown in Fig. 1 (curve D). It has absorptions at about 1175, 1225, and 1255 cm^{-1}, but it has no characteristic absorption of the P–N bond and –NH_2 groups. On the basis of those data, we confirmed the structure of the chloroform-extract to be poly(ethylene-methylphosphite),  $(-CH_2CH_2\underset{\displaystyle OCH_3}{\underset{|}{O}PO}-)_n$.

No other chloroform extract with an infrared absorption spectrum of the type of curve D was found.

Thus the type of polymers produced by the ring-opening polymerization of ethylene-methylphosphite can be written as in the scheme presented at the beginning of the page. In Fig. 1, curves A, B, and C are obviously those of the polymers III, II, and I respectively.

It is interesting that the polymer of the type III is given, although it is not yet clear as to whether the polymer results from the methyl migration of an open-chain intermediate or from the ethylene-methylphosphonate which was primarily produced by a rearrangement of ethylene-methylphosphite. The latter scheme seems to be more plausible in view of the stability of the phosphoryl-type structure in phosphites.



At any rate, ethylene-methylphosphite is not so stable at higher temperature or in the presence of sodium methylate. Korshak et al.[4] have reported that cyclic phosphonates can polymerize at 140°C with water or sodium. In the reaction mixtures of both runs 1 and 11, a little methyl ethylenephosphonate, which was confirmed by its boiling point and its molecular refraction, was recovered.

Recently Denny and Giacin have reported that trialkyl phosphite and *p*-toluene sulfonic acid methyl ester yield dialkyl methyl-phosphonate.[7] It should be noted that the preparation of ethylene-methylphosphite from ethylenephosphochloridite and sodium methoxide is not easy since they are much more liable to methylphosphonate. The polymer of the type II may be produced through the so-called Arbuzov rearrangement. The polymer of the type I is a very particular one. The catalyst system, sodium in ammonia, gave the polymer of the type I while sodium amide did not yield this type of polymer. It goes without saying that sodium amide must exist in liquid ammonia. If it were not for an interaction of ammonia with trivalent *P* atom in ethylene-methylphosphite in the course of polymerization, it is hard to understand how such an enol-form could be stable.

Summary

The ring-opening polymerization of ethylene-methylphosphite has been carried out using several catalyst systems. By using an acidic catalyst, such as aluminum chloride, titanium(III) chloride, boron fluoride, etc., and by working at higher temperatures, we have produced a solid polymer with the structure of poly(ethylene-methylphosphonate), the intrinsic viscosity of which in DMF is ca. 1. When triethylaluminum was used, and when we worked at relatively lower temperatures, we obtained a wax-like polymer with the structure of poly(ethylene-methoxyphosphinate), the intrinsic viscosity of which in DMF is over 1. Sodium and lithium in liquid ammonia at −78°C, although they were not very effective catalysts for the polymerization, gave a jelly-like polymer with part of the structure of poly(ethylene-methylphosphite).

These structures have been confirmed by a study of their infrared spectra and their hydrolyzed products.

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[7] D. B. Denny and J. Giacin, *Tetrahedron Letters*, **1964**, 1747.