(2) It has been found that there is an increase in the size of both the crystalline and amorphous regions during the crystallization of polypropylene and capron annealed in the stretched state. The degree of crystallinity of polypropylene increases somewhat, and that of capron remains practically unchanged.

Translated by V. ALFORD

REFERENCES

1. **D. GUPTA**, Chem. Rev. **62**: 665, 1962
2. **R. CHÛGO**, J. Phys. Japan **18**: 124, 1963
3. **D. Ya. TSVANKIN**, Vysokomol. soyed. **6**: 2086, 1964
4. **D. Ya. TSVANKIN**, Vysokomol. soyed. **6**: 2091, 1964
5. **A. I. KITAIGORODSKII, D. Ya. TSVANKIN** and **Yu. M. PETROV**, Vysokomol. soyed. **5**: 1062, 1963
6. **K. Kh. RAZIKOV, Yu. A. ZUBOV, G. S. MARKOVA** and **V. A. KARGIN**, Vysokomol. soyed. **5**: 760, 1963
7. **Yu. A. ZUBOV, G. S. MARKOVA** and **V. A. KARGIN**, Vysokomol. soyed. **5**: 1171, 1963
8. **R. L. MILLER** and **L. E. NILSEN**, J. Polymer Sci. **44**: 391, 1960
9. **A. S. POSNER, L. MANDELKERN, C. R. WORTHINGTON** and **A. F. DIORIO**, J. Appl. Phys. 31: 114, 1960

SYNTHESIS OF POLYPHOSPHINITES BY TRANSESTERIFICATION*

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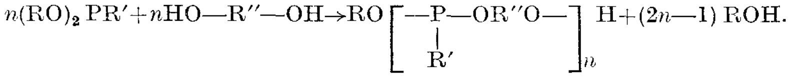
IN EARLIER communications we described the synthesis and properties of diphosphites [1–6]. It was shown that polymers could be produced by the Arbuzov regrouping method from diphosphites containing a common aromatic radical.

Continuing the research in the sphere of polyphosphites and polyphosphinites, we have studied the reaction of the transesterification of the di-methyl and diethyl esters of phenylphosphinous acid (MP and EP), and the ethyl ether of ethylphosphinous acid (EE) with certain glycols, leading to the formation of polyalkyleneglycolphosphinites



$$n(\mathrm{RO})_2\mathrm{PR}'+n\mathrm{HO{-}R''{-}OH}\rightarrow\mathrm{RO}\left[-\underset{\substack{|\\ \mathrm{R}'}}{\mathrm{P}}-\mathrm{OR''O}-\right]_n\mathrm{H}+(2n-1)\,\mathrm{ROH}.$$

We had already successfully used the method of transesterification to prepare polyalkyleneglycolphosphonates [7].

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* Vysokomol. soyed. **6**: No. 12, 2139–2144, 1964.

The phenyl and ethyl phosphinites were used in equimolar quantities; the polycondensation reaction rate could be estimated from the amount of alcohol liberated. For rapid and complete removal of the alcoholic vapours from the reaction mixture during the reaction, a current of dry nitrogen was passed through at constant rate.

The results of the kinetic studies of the reaction of MP with diethyleneglycol are given in Fig. 1. The reaction was carried out at 110, 120, 130, 140 and 150°. As the temperature rose there was an increase in the rate and the degree of the reaction (a). Up to 70% conversion the time dependence of the $(1-a)^{-1}$ values (Fig. 2) was shown by a straight line. This confirms that it is a second-order reaction. For reactions at the temperatures shown above the rate constants were as follows: $5{\cdot}56\times10^{-4}$, $8{\cdot}68\times10^{-4}$, $13{\cdot}89\times10^{-4}$, $20{\cdot}00\times10^{-4}$ and $33{\cdot}33\times10^{-4}$.

As we can see from Fig. 3, the temperature dependence of the log constant of the reaction rate is given by a straight line, and this is consistent with the Arrhenius equation. The activation energy of this reaction is 13,420±860 cal/mol.

When the influence of the nature of the glycol on the rate and degree of reaction was studied, it was found that the reactivity of the glycols fell in the following order: ethyleneglycol, diethyleneglycol, tetraethyleneglycol (Fig. 4).

We had already noted that the transesterification of dialkylphosphorous acids with glycols, which have a tendency to form cyclic phosphorous esters, takes place mainly via the phosphorous acid. In the case of glycols with which it is either difficult or impossible for cyclic esters to be formed, the reaction proceeds mainly or completely without formation of cyclic esters.

To study the intermediate products formed in the process of polycondensation of MP and diethyleneglycol, the reaction mixture was vacuum distilled after 2

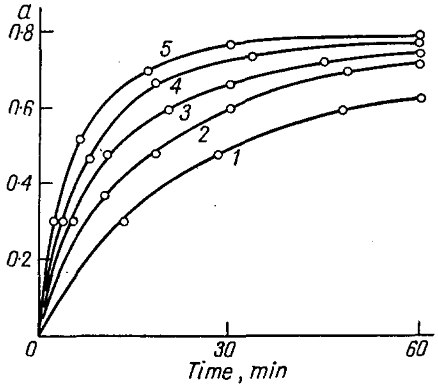


FIG. 1

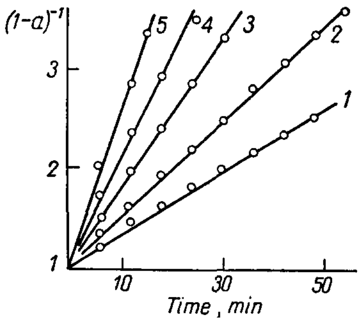


FIG. 2

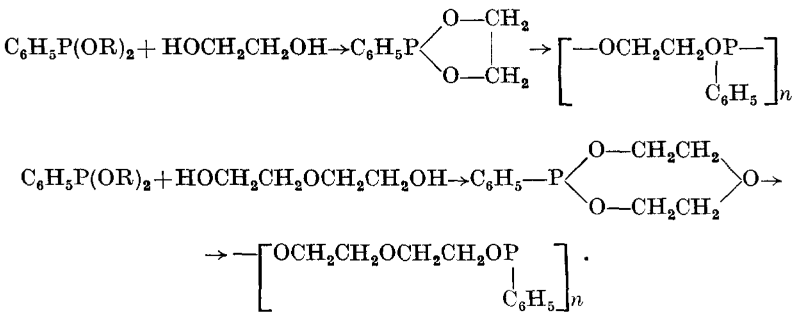
FIG. 1. Extent of reaction (a) of the dimethyl phenylphosphinite with diethyleneglycol: 1—110°; 2—120°; 3—130°; 4—140°; 5—150°.

FIG. 2. $(1-a)^{-1}$ vs. time in the reaction of the dimethyl phenylphosphinite acid with diethyleneglycol: 1—110°; 2—120°; 3—130°; 4—140°; 5—150°.

hr. heating at 140°. The original products were not separated. With a 70% yield a fraction was obtained which boiled at 125–132°/3 mm; it consisted mainly of diethyleneglycol phenylphosphinite, and the residue was a polyester. When the fraction obtained was again distilled with a yield of approximately 15%, a pure diethyleneglycol phenylphosphinite was produced; most of it was converted to the polyphosphinite which contained on average approximately three radicals of the original. Special experiments showed that there would be no degradation of the linear polyester under the conditions of the reaction, nor on distillation. When polycondensation was conducted under more vigorous conditions (at 170° and 10 hr. heating) no cyclic esters were found in the reaction mixture. The latter was a transparent highly viscous mass with $\eta_{sp}^{20}=0{\cdot}124$ (2% solution in dimethylformamide); held over a flame it extinguished it, and it was soluble in dioxane and dimethylformamide on heating. Ebullioscopic measurement of the molecular weight showed that the polyester consisted mainly of four radicals (molecular weight 850) of the original cyclic ester. Specimens of higher molecular weight $\eta_{sp}^{20}=0{\cdot}132$ were prepared by conducting the latter stage of polycondensation *in vacuo*.

Analogous results were also obtained from the reactions of EP and diethyleneglycol, MP and ethyleneglycol, and EE and diethyleneglycol. In all these cases cyclic phosphinites and polyesters were obtained where the degree of conversion was not very great.

The results show that the polycondensation of dialkyl phenyl- and ethylphosphinites with glycols of the aliphatic series proceeds mainly or entirely via cyclic phosphinites acid:



Unlike polymethylene cyclic compounds, cyclic compounds which contain phosphorus and some oxygen atoms in the ring are formed readily, and are stable even when the number of atoms making up the ring is more than six. Of course, in these cases stable and less stressed conformations will be formed, as shown by available findings [8]. An example is diethyleneglycolphosphite, the ring of which consists of ten atoms. This cyclic ester, which contains two phosphorus atoms in the ring, four oxygen and four carbon, is readily formed in the transesterification of diethylphosphoric acid with ethylene glycol, and it is a very stable compound [9].

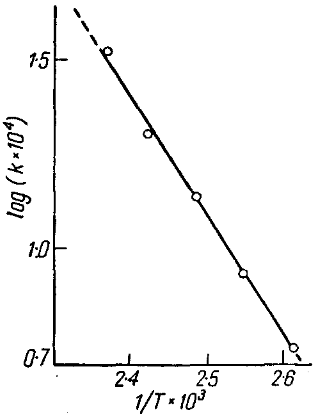


FIG. 3

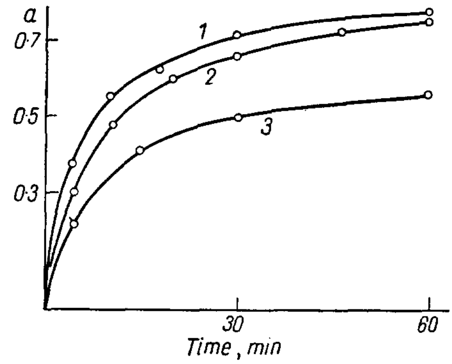


FIG. 4

FIG. 3. Log reaction rate constant of the dimethyl phenylphosphinite with diethyleneglycol vs. 1/T.

FIG. 4. Extent of reaction (*a*) of the dimethyl phenylphosphinite at 130° with ethyleneglycol (1), diethyleneglycol (*2*) and tetraethyleneglycol (*3*).

TABLE 1. PROPERTIES OF THE CYCLIC ESTERS OF ETHYL- AND PHENYLPHOSPHINOUS ACIDS

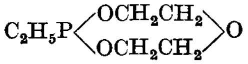
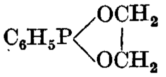
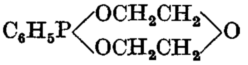
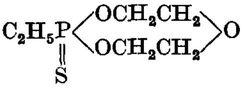
Compound	B.p., °C (mm)	M.p. °C	n_D^{20}	d_4^{20}	Yield, %	*MR*		Content P, %	
						experimental	theoretical	experimental	theoretical
 $C_2H_5P{<}\begin{matrix}OCH_2CH_2\\OCH_2CH_2\end{matrix}{>}O$	73–74 (12)	—	1·4745	1·1081	63	51·47	52·02	19·11	18·89
 $C_6H_5P{<}\begin{matrix}OCH_2\\ \mid \\OCH_2\end{matrix}$	88–89 (1)	—	1·5789	1·2453	52	44·75	45·65	18·31	18·45
 $C_6H_5P{<}\begin{matrix}OCH_2CH_2\\OCH_2CH_2\end{matrix}{>}O$	109(0·5)	—	1·5502	1·2027	15	56·51	56·89	14·31	14·61
 $C_2H_5\underset{\underset{S}{\parallel}}{P}{<}\begin{matrix}OCH_2CH_2\\OCH_2CH_2\end{matrix}{>}O$	102–103 (1·5)	65	—	—	60	—	—	15·88	15·81

TABLE 2. PROPERTIES OF POLYPHOSPHINITES

Original material		Reaction temperature, °C (time, hr.)	η_{sp}^{20} (2% solution in dimethylformamide)	Molecular weight, ebullioscopic method in benzene	Soluble in	Properties	P content, %	
phosphinite	glycol						experimental	theoretical
Dimethyl ester of ethylphosphinous acid	Diethyleneglycol	130 (4)	0·093	450	benzene, dioxane, dimethylformamide	A viscous, quite mobile fluid	17·01	17·30
Diethylester of phenylphosphinous acid	Ditto	140 (11)	0·125	860	dioxane, dimethylformamide	Very viscous transparent fluid, darkens when drawn out of flame	13·50	13·87
Dimethyl ester of ethyleneglycol phenylphosphinous acid	Ethyleneglycol	140 (4)	0·110	530	benzene, dioxane, dimethylformamide	Viscous transparent liquid	16·78	17·30
Ditto	Diethyleneglycol	140 (4)	0·103	640	Ditto	Ditto	14·25	14·30
,,	*Ditto*	170 (10)	0·124	—	dioxane, dimethylformamide	Very thick viscous liquid	14·32	14·61
,,	,,	170 (10 and 5 at 13 *mm*)	0·132	—	dimethylformamide	Almost solid transparent mass darkens when drawn out of flame	14·29	14·61
,,	Tetraethyleneglycol	140 (10)	0·120	800	benzene, dioxane, dimethylformamide	Viscous yellow liquid	—	—

Cyclic phospinites have the properties which are typical of esters containing trivalent phosphorus. For instance, when dialkyleneglycolethylphosphinite was heated with sulphur, alkyleneglycolethylthiophosphinite was obtained with a yield of 60%.

The characteristics of the cyclic esters prepared are shown in Table 1, and those of the polyesters in Table 2.

When stored at room temperature cyclic ethyl- and phenylphosphinites are rapidly polymerized. After 2–3 days viscous transparent liquids are obtained with a polymerization coefficient of 2–3. This incerases to 3–4 if they are heated for a few hours at 130–140°. If heating is performed at a higher temperature *in vacuo* higher molecular weight products are obtained with poor or no solubility in benzene and dioxane. The polyesters were purified by reprecipitation from the dioxane solutions by dietyl ether.

The IR spectra of the polyesters do not contain absorption frequencies typical of the phosphoryl group; this shows that the phosphorus is present in the trivalent state. This is also confirmed by the reaction with sulphur. When polyalkyleneglycolphenylphosphinite with molecular weight of 800 was heated with excess sulphur after reprecipitation, the product was polyalkyleneglycolphenylthiophosphinate. Analysis of the phosphorus and sulphur content showed that there had been combination at all of the phosphorus atoms.

After the present work had been completed a communication of Petrov and collaborators appeared [10], which described the synthesis of polyphosphites and polyphosphinites by the glycolysis of trivalent phosphorus amides. The authors consider that this method can be used to prepare phosphorus-containing polyesters of higher molecular weight.

EXPERIMENTAL

Procedure for polycondensation. Equimolar amounts of glycol and the phosphinite were placed in a flask with a bubble cap for passing through nitrogen and a column in which the temperature was kept at 77–78° by means of an external coil. The reaction flask was immersed in a flask containing Woods alloy, the temperature of which was kept constant by means of a contact thermometer and a relay.

The alcohol formed as a result of the reaction was condensed in a cooler after passing through the column, and collected in a graduated receiver. From the amount of alcohol separated the extent of the reaction was calculated and the time dependence determined.

To separate the cyclic products from the reaction mixtures the latter were vacuum distilled.

The polyesters were purified by reprecipitation from dioxane solutions in sulphate.

Addition of sulphur to polyalkyleneglycolphenylphosphinite. 10 g polyphosphinite purified by reprecipitation from solution in dioxane with sulphate, was mixed with 1·5 g sulphur and the reaction mixture heated until it had all dissolved. The product of combination was dissolved in dioxane, precipitated with ether and vacuum dried at 100°. The polyalkyleneglycolphenylthiophosphonate was a viscous brown mass; yield 90%.

Exp., %: P 12·38; S 12·5%. Theor., %: P 12·80; S 12·03.

Addition of sulphur to alkyleneglycol ethylphosphinite. 10 g alkyleneglycolethylphosphinite was placed in flask with a Vigré packing and then 2 g of ground sulphur was gradually added in a CO_2 flow. The considerable heating of the reaction mixture was accompanied by dissolution of the sulphur. The alkyleneglycolethylthiophosphinate was separated by vaccum distillation. 7·2 g (60% of the theoretical) was obtained with b.p. 102–103°/1·5 mm, m.p. 65°.

Exp., %: P 15·98. Theor., %: 15·81.

CONCLUSIONS

(1) Polyalkyleneglycolphenyl- and polyalkyleneglycolethylphosphinite have been obtained by transesterification of dialkylphenyl- and ethylphosphinites with ethyleneglycol.

(2) It has been found that the polycondensation of these esters with aliphatic glycols occurs mainly by formation of cyclic esters of phosphinous acids.

(3) Chemically the cyclic esters of phenyl- and ethylphosphinous acids, which are polyesters containing trivalent phosphorus atoms in their main ring, behave similarly to the esters of phosphinous acid. They readily combine with sulphur to form cyclic phenyl- or ethylthiophosphonates and polyalkyleneglycolphenyl- or polyalkyleneglycolethylthiophosphonates.

Translated by V. Alford

REFERENCES

1. **A. N. PUDOVIK** and **I. M. ALADZHEVA**, Zh. obsh. khim. **31**: 2052, 1961
2. **A. N. PUDOVIK** and **I. M. ALADZHEVA**, Zh. obsh. khim. **32**: 2005, 1962
3. **N. A. MUKMENEVA, P. A. KIRPICHNIKOV** and **A. N. PUDOVIK**, Zh. obsh. khim. **32**: 2193, 1962
4. **A. N. PUDOVIK, I. M. ALADZHEVA, I. A. SOKOLOVA** and **G. A. KOZLOVA**, Zh. obsh. khim. **33**: 102, 1963
5. **A. N. PUDOVIK** and **I. M. ALADZHEVA**: Zh. obsh. khim. **33**: 1816, 1963
6. **N. A. MUKMENEVA, P. A. KIRPICHNIKOV** and **A. N. PUDOVIK**, Zh. obsh. khim. **33**: 319, 1963
7. **A. N. PUDOVIK** and **G. I. YEVSTAFYEV**, Vysokomol. soyed. **5**: 886, 1963
8. Perspektivy razvitiya organ. khim. (Future Developments in Organic Chemistry). Fereign Literature Publishing House, 83, 1959
9. **A. OSTVALD**, Canadian Journal of Chemistry **37**: 1498, 1959
10. **K. A. PETROV, E. Ye. NIFANTYEV, R. G. GOL'TSEVA** and **L. M. SOLNTSEVA**, Vysokomol. soyed. **5**: 1691, 1963