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Abstract

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ADDITION OF ACID ESTERS OF PHOSPHORUS ACIDS TO UNSATURATED POLYESTERS

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As we have shown in earlier studies, dialkyl phosphites, dialkyl thiophosphites, and acid esters of phosphonous acids add to unsaturated electrophilic reagents in the presence of alkaline catalysts ([1]). These reactions proceed very readily and quantitatively with esters of unsubstituted α,β-unsaturated carboxylic acids and with esters of unsaturated dibasic acids ([2]).

In the present investigation we have extended the addition reaction of acid esters of phosphorus acids to unsaturated polyesters. The addition of nucleophilic reagents to unsaturated polyesters has been almost entirely unstudied ([3]). Apart from theoretical interest, the reactions under study are also of practical significance, since phosphorus-containing polyesters have recently begun to find use as plasticizers for various polymers, varnishes and coatings, as components for the preparation of fire-resistant materials, etc. ([4]). We used polyesters obtained from maleic anhydride and various glycols. Maleic anhydride with a slight excess of glycol was heated in a nitrogen atmosphere, in the presence of hydroquinone, at 170–180° for three hours. Further heating was continued in vacuum, for varying times, at a residual pressure of 10–30 mm. The polyesters obtained, which were viscous resins with molecular weights from 700 to 4000, were purified by reprecipitation from dioxane solutions with ether and dried in vacuum at 100° to constant weight.

For the initial study, polyethylene glycol maleate with molecular weight 750 was used. The molecular weight of the polyesters was calculated on the basis of determination of the number of terminal groups—hydroxyl and carboxyl ([5]). Diethyl phosphorous acid, taken in excess, was added to it, calculated for addition to all double bonds. In the absence of a catalyst the reaction does not proceed; in the presence of a small amount of sodium methylate it proceeds very vigorously, accompanied by heating of the reaction mixture to 70°. The addition product was purified by reprecipitation from a dioxane solution with ether, followed by drying in vacuum at elevated temperature. The addition product —poly(diethylphosphono)ethylene succinate—is a solid hygroscopic resin, which rapidly goes out when removed from a flame. The results of analysis for phosphorus (calculated: % P 11.07; found 11.11) show that the addition of diethyl phosphorous acid occurred at all double bonds of the unsaturated polyester:

$$\mathrm{HO[-CO-CH{=}CH-COOCH_2CH_2O-]_{nH}} + n\,(\mathrm{C_2H_5O})_2\mathrm{POH} \rightarrow$$

$$\rightarrow \mathrm{HO[-COCH-CH_2COOCH_2CH_2O-]_{nH}}$$

$$\mathrm{O{=}P(OC_2H_5)_2}$$

In order to determine the possibility of partial and complete addition of acid esters of phosphorus acids to the double bonds of an unsaturated polyester with higher molecular weight, the addition of diethyl-

phosphorous acid in various molar ratios to polyethylene glycol maleate with molecular weight 3600. As in the preceding experiment, the reactions were carried out in the presence of sodium methylate and were accompanied by a considerable thermal effect. The resins were purified by reprecipitation. The results obtained are presented in Table 1.

Table 1

Molar ratio of polyester to diethylphosphorous acid	P content in addition products, % calculated	P content in addition products, % found	Characteristics of the addition products
1 : 1.3	9.57	9.69	Soft resin, extinguishes when removed from the flame
1 : 0.6	6.91	6.67	Thick, viscous liquid
1 : 0.3	4.09	3.89	Thick, viscous liquid

As follows from the analytical data, the diethylphosphorous acid introduced into the reaction is practically quantitatively added at the double bonds of the polyester. Thus, our experiments have shown the possibility of obtaining phosphorus-containing polyesters containing any specified amount of phosphonic groups and double bonds. Addition of diethylthiophosphorous acid and of certain cyclic phosphorous acids—ethylene glycol phosphorous acid and 1,3-butylene glycol phosphorous acid—was then carried out with polyethylene glycol maleate of molecular weight 3600. In all cases the acids were taken in slight excess, to ensure their addition at all double bonds of the unsaturated polyester. The results are summarized in Table 2.

Table 2

Acid	P content in addition products, % calculated	P content in addition products, % found	Characteristics of the addition products
$(C_2H_5O)_2PSH$	9.12	8.84	Soft resin, has an unpleasant odor, extinguishes when removed from the flame
$\begin{matrix} OCH_2CH_2 \\ HOP \quad O \\ OCH_2CH_2 \end{matrix}$	9.17	9.02	Thick, soft liquid of dark color
$\begin{matrix} OCH_2 \\ HOP \quad CH_2 \\ OCH \\ CH_3 \end{matrix}$	9.63	9.28	Thick, viscous liquid of dark color

Finally, addition reactions to unsaturated polyesters of different molecular weights, obtained from maleic anhydride and various glycols, with diethyldithiophosphoric acid were studied. The results of the experiments are summarized in Table 3.

The addition products at all double bonds of the polyesters are rubber-like or solid substances

$$HO[-CO-CH=CHCOOCH_2CH_2O-]_{nH} + n\,(C_2H_5O)_2PSSH \rightarrow$$

$$\rightarrow HO\left[\begin{matrix} -CO-CH-CH_2-COOCH_2CH_2O- \\ | \\ S \\ | \\ -S=P(OC_2H_5)_2 \end{matrix}\right]_n H.$$

Table 3

No.	Glycol	Mol. wt. of polyester	Molar ratio of glycol polyester and dithiophosphoric acid	P content, % calculated	P content, % found	S content, % calculated	S content, % found	Characteristics of phosphorus-containing polyesters
1	Ethylene glycol	1053	1 : 1.3	9.43	8.64	19.50	19.12	Rubber-like product of yellow color
2	β-Thiodiglycol	1058	1 : 1.3	7.97	7.82	24.72	24.21	Solid product of brown color
3	1,4-Butylene glycol	1753	1 : 1.3	8.69	8.02	17.96	17.57	Solid substance of gray color
4	Diethylene glycol	1103	1 : 1.3	8.30	8.01	17.18	16.80	Viscous brown resin
5	Same	2335	1 : 0.7	6.85	6.45	14.15	13.55	Viscous fluid resin
6	Same	2335	1 : 1.3	8.31	7.72	17.18	16.60	Rubber-like, light-yellow resin

No.	Glycol	Mol. wt. of polyester	Molar ratio of glycol polyester and dithiophosphoric acid	P content, % calculated	P content, % found	S content, % calculated	S content, % found	Characteristics of phosphorus-containing polyesters
7	Same	3183	1 : 0.5	5.53	5.19	11.44	10.95	Very viscous orange resin
8	Same	3183	1 : 1.3	8.33	7.94	17.22	16.74	Hard orange resin

Table 4

Glycol	Mol. wt. of polyester	P content, % found	P content, % calculated	S content, % found	S content, % calculated	Characteristics of the addition products
Ethylene glycol	1053	9.71	10.08	10.32	10.40	Viscous yellow resin
Diethylene glycol	1103	8.46	8.60	8.79	9.05	Viscous brown resin
1,4-Butylene glycol	1753	8.89	9.19	9.34	9.48	Solid product of gray color

The products of incomplete addition are viscous resins. Some polyesters (1-4)

dissolve in water with the formation of opalescent solutions. All the polyesters are insoluble in alcohol and dioxane.

Owing to the presence in the polyesters of a large amount of sulfur, they all continue to burn when removed from the flame. We have shown the possibility of mixed addition of various phosphorus acids to unsaturated polyesters. Table 4 gives the characteristics of phosphorus-containing polyesters obtained by successive addition to unsaturated polyesters of diethyl phosphorous and diethyl dithiophosphoric acids. Both acids were taken on the basis of addition to half of all the double bonds present in the unsaturated polyester. All the polyesters obtained in this way are viscous resins or solid products, soluble in water; they continue to burn when removed from the burner flame.

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REFERENCES

1. A. N. Pudovik, *Usp. Khim.*, **23**, 5, 549 (1954).
2. A. N. Pudovik, *ZhOKh*, **22**, 11, 2047 (1952); *Izv. AN SSSR, OKhN*, 1952, No. 5, 926.
3. V. V. Korshak, S. V. Vinogradova, *Heterochain Polyesters*, Moscow, 1958.
4. E. L. Gefter, *Phosphorus-Organic Monomers and Polymers*, Moscow, 1960.
5. I. P. Losev, O. Ya. Fedotova, *Practicum in the Chemistry of High-Molecular Compounds*, Moscow, 1959.

Note: Figure translations are in progress. See original paper for figures.