Phosphorylation of the Waste Products from the Dimethyl Terephthalate Production with the Dimethyl Ester of the 1,2-Di(methoxycarbonyl)Ethane Phosphonic Acid

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SYNOPSIS

It is demonstrated that the dimethyl ester of 1,2-di(methoxycarbonyl)ethane phosphonic acid can be used as a phosphorylating agent of the production wastes of dimethyl terephthalate. The products obtained have different characteristics depending on the mode of phosphorylation.

INTRODUCTION

It is well known[1-3] that the combustion resistance of rigid polyurethane foams can be enhanced by the introduction of phosphorus-containing compounds. The application of the reactive modifiers[4] show that the effect of the fire retardant in this case is more stable, which is an important advantage of this type of anthyprenes.

The aim of this study is the synthesis and characterization of the oligoester alcohols on the basis of waste products from the dimethyl terephthalate production and dimethyl ester of 1,2-di(methoxycarbonyl)ethane phosphonic acid by means of their transesterification with diethylene glycol.

EXPERIMENTAL

Starting Compounds

Waste products from the production of dimethyl terephthalate (Technological Chemical Combine "D. Dimov") with the characteristics given in Table I are used. Dimethyl ester of 1,2-di(methoxycarbonyl)etane phosphonic acid (Bayer, Germany) and diethylene glycol (Nephtochim, Bulgaria) were used.

General Method for the Synthesis Conduction

Single-Step Phosphorylation

Residue 1, diethylene glycol and dimethyl ester of 1,2-di(methoxycarbonyl)ethane phosphonic acid, was mixed together in a four-necked flask provided with a stirrer, thermometer, Vigruex column, condensor, and a capillary inlet for nitrogen bubbling. The reaction is conducted in the temperature range 180–230°C to a completion degree of 80%. After distillation is over the temperature is lowered to 130°C and the volatiles and moisture are eliminated by vacuum distillation at 11 mmHg.

The synthesis of the products from residue 1, diethylene glycol and dimethyl ester of 1,2-di(methoxycarbonyl)ethane phosphonic acid, was performed at the following molar ratios: 1 : 3, 6 : 0.11; 1 : 3, 8 : 0.22; 1 : 4, 1 : 0.33; 1 : 4, 6 : 0.48.

Two-Step Phosphorylation

A 291-g (1-mol) solution of residue 1, containing 40% methyl ester groups with acid number 9.9 mg KOH/g and 382 g (3.6 mol) diethylene glycol are mixed in a four-necked flask provided with a stirrer, thermometer, a Vigreux column, condensor, and a capillary inlet for nitrogen bubbling. The reaction is carried out in the temperature range 170–230°C to a completion degree of 80–85%. After the distillation is over the temperature is lowered to 100°C and the volatiles and moisture are eliminated by

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Journal of Applied Polymer Science, Vol. 46, 41–48 (1992)

CCC 0021-8995/92/010041-08$04.00

Table I Composition of Residue 1 from the production of dimethyl terephthalate

Composition	Residue 1 (%)
Di- and trimethyl esters of diphenyltricarboxylic acids	Up to 10
Dimethyl esters of diphenyldicarboxylic acids	20–25
Dimethyl esters of 3,4-benzocoumaric acid	10–15
Monomethyl terephthalate	2–3
Dimethyl terephthalate	8–10
Dimethyl ortophthalate	3–4
Methyl ester of *p*-toluylic acid	1–2
p-Toluylic acid	1–2
Resinous substances	Up to 20
Unidentified products	2

vacuum distillation at 15 mmHg. The obtained oligoester alcohol is subjected to transesterification with 27 g (0.11 mol) dimethyl ester of 1,2-di(methoxycarbonyl)ethane phosphonic acid. The reaction is first conducted at 180°C, and after the distillation ceases the temperature is raised to 200°C.

The synthesis of the oligoester alcohols from residue 1 and diethylene glycol was performed at the following molar ratios: 1 : 3.6, 1 : 3.8, 1 : 4.1, 1 : 4.6. To such obtained reaction products was added dimethyl ester of 1,2-di(methoxycarbonyl)ethane phosphonic acid in moles: 0.17, 0.22, 0.33, 0.48.

Characterization

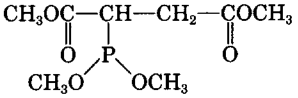
The products were characterized as follows: acid number is determined by titration of sample with potassium hydroxide in the presence of phenolphthalene; hydroxyl number is determined by the acetylation method; -methyl ester groups are determined by gas chromatography; water content is determined by Carl Fischer method; viscosity is determined by Hoppler; diethylene glycol content is determined by gas chromatography; hydrolysis resistance is determined by the titration of sample with HCl after treating of the sample with NaOH; and phosphorus content is determined by standard procedure.

RESULT AND DISCUSSION

The synthesis of the phosphorus-containing oligoester alcohols on the basis of waste products from the dimethyl terephthalate production was conducted in two ways: single-step joint transesterification and two-step transesterification of the waste products with diethylene glycol followed by transesterification of the dimethyl ester of 1,2-di(methoxycarbonyl)ethane phosphonic acid with the oligoester alcohol.

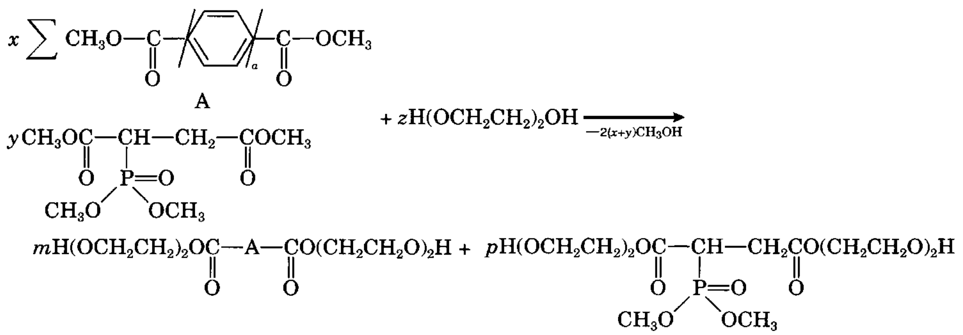
Single-Step Phosphorylation

The dimethyl ester of 1,2-di(methoxycarbonyl)-ethane phosphonic acid.



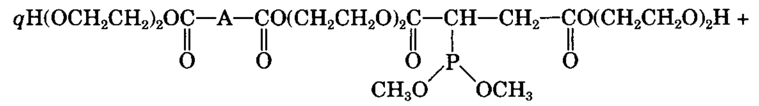
$$CH_3O\underset{\|}{\overset{}{C}}(O)-CH(P(OCH_3)(OCH_3))-CH_2-\underset{\|}{C}(O)OCH_3$$

is used as a phosphorus-containing comonomer in the synthesis of oligoester alcohols from the dimethyl terephthalate production wastes and diethylene glycol by means of a transesterification reaction:



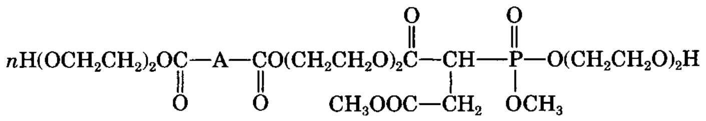
I

II



$$q\mathrm{H(OCH_2CH_2)_2O}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{{-}A{-}}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{O(CH_2CH_2O)_2}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{-}\underset{\substack{|\\ \mathrm{P(OCH_3)_2}}}{\mathrm{CH}}\mathrm{-CH_2-}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{O(CH_2CH_2O)_2H} +$$

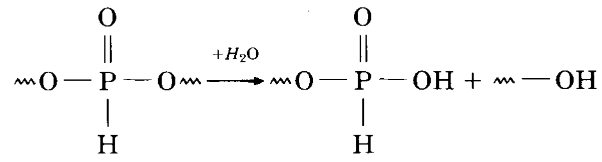
III



$$n\mathrm{H(OCH_2CH_2)_2O}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{{-}A{-}}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{O(CH_2CH_2O)_2}\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{C}}\mathrm{-}\underset{\substack{|\\ \mathrm{CH_3OOC-CH_2}}}{\mathrm{CH}}\mathrm{-}\overset{\substack{\mathrm{O}\\ \|}}{\underset{\substack{|\\ \mathrm{OCH_3}}}{\mathrm{P}}}\mathrm{-O(CH_2CH_2O)_2H}$$

IV

The experimentally observed time dependence of the conversion degree (Fig. 1) reveals that the phosphorus-containing monomer suppresses the transesterification reaction between the waste products and diethylene glycol (curves 1). Up to a conversion degree of 17 and 25% (curves 3 and 4) it may be assumed that the transesterification reaction of the waste products with diethylene glycol proceeds faster in the presence of the phosphonate. This is most likely related to the higher phosphonate concentration, which under these conditions is transesterified at a rate higher than that for the waste products. As a consequence the amount of methanol evolved is larger than in the cases when the concentration of the modifier is low and the major amount of methanol is produced in the waste products transesterification reaction. The reduction in the rate of transesterification of residue 1 in the presence of phosphonate could be explained by the increased acidity of the reaction system (Fig. 2). The increase in the acid number is associated with the hydrolysis of the P — O — C bond, leading to the accumulation of the acid P — OH groups:



$$\sim\mathrm{O}-\overset{\substack{\mathrm{O}\\ \|}}{\underset{\substack{|\\ \mathrm{H}}}{\mathrm{P}}}-\mathrm{O}\sim \xrightarrow{+H_2O} \sim\mathrm{O}-\overset{\substack{\mathrm{O}\\ \|}}{\underset{\substack{|\\ \mathrm{H}}}{\mathrm{P}}}-\mathrm{OH} + \sim-\mathrm{OH}$$

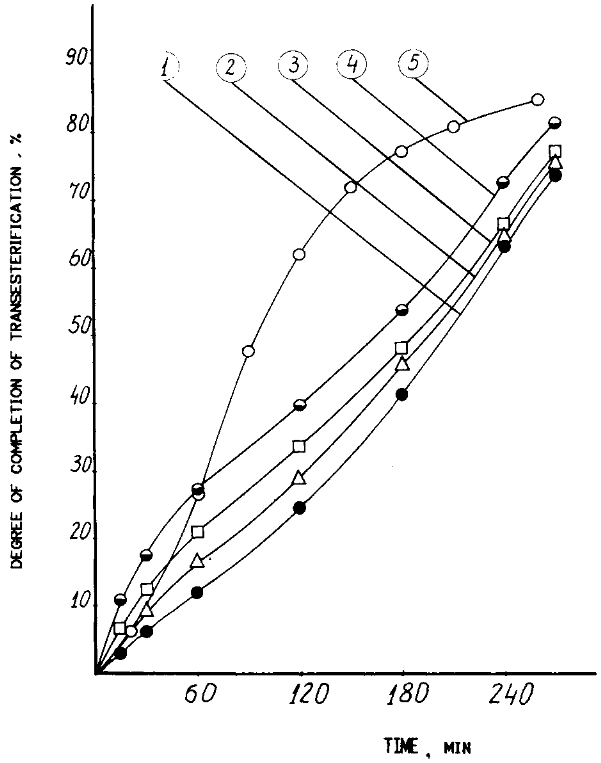


Figure 1 Time dependence of the degree of completeness of the transesterification reaction of residue 1 and dimethyl ester of 1,2-di(methoxycarbonyl)ethane phosphonic acid with diethylene glycol at the phosphorus content: curve 1, 0.5%; curve 2, 1.0%; curve 3, 2.0%; curve 4, 2.0%; and curve 5, 0.0%.

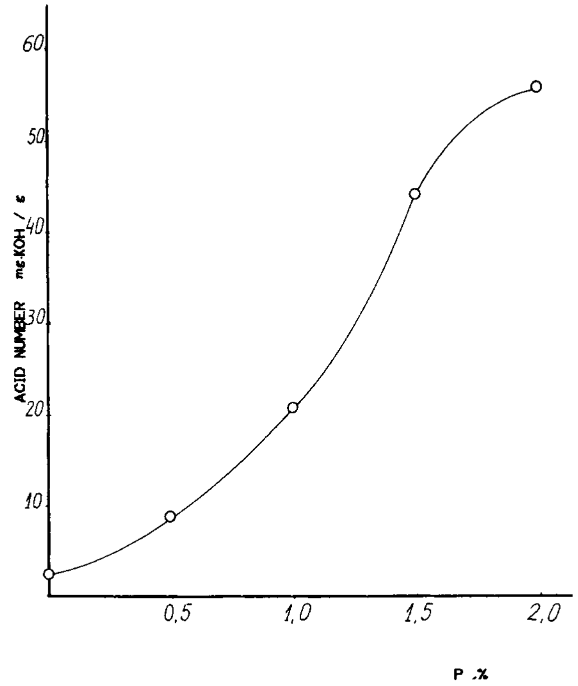


Figure 2 Dependence of the acid number of the end product on the phosphorus content.

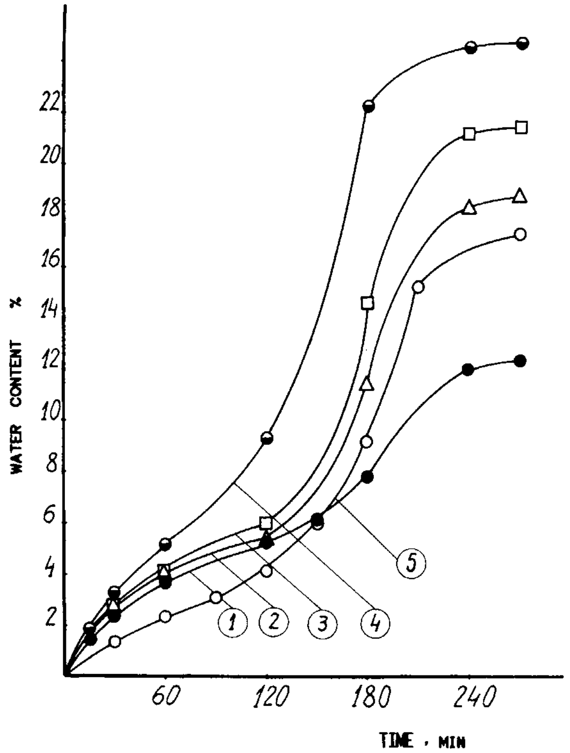
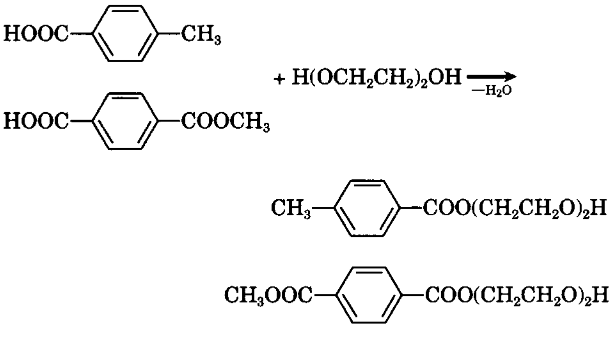


Figure 3 Time dependence of the water content in the distillate at phosphorus content: curve 1, 0.5%; curve 2, 1.0%; curve 3, 1.5%; curve 4, 2.0%; and curve 5, 0.0%.

Water is evolved as a result of esterification of pure monocarbonic acids, which exist in the waste product with diethylene glycol:



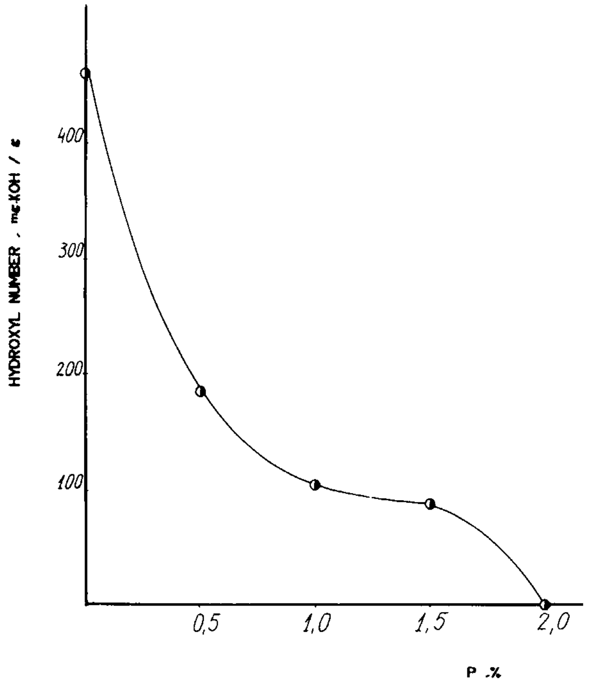


Figure 4 Dependence of the hydroxyl number of the end product on the phosphorus content.

The higher acidity of the reaction system is the cause for the acceleration of the dehydration of the hydroxyl-containing compounds. This is confirmed by the water content in the alcohol distillate (Fig. 3). The experimentally found values of the hydroxyl number confirm the procedure of the dehydration reaction (Fig. 4). It was established that the increase of the concentration of the modifier leads to significant decreasing of the hydroxyl number. At a phosphonate concentration of 0.48 mol/L (2.0% P) the end product contains extremely low hydroxyl groups,

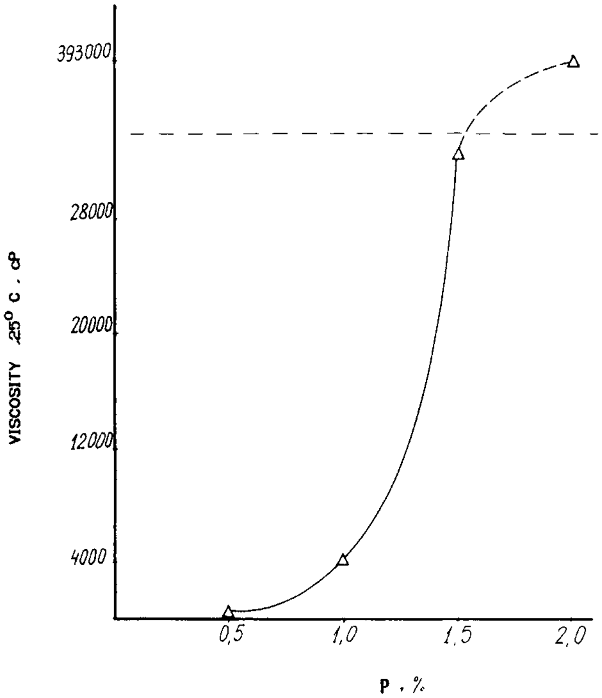


Figure 5 Dependence of the viscosity of the oligoester alcohol on the phosphorus content.

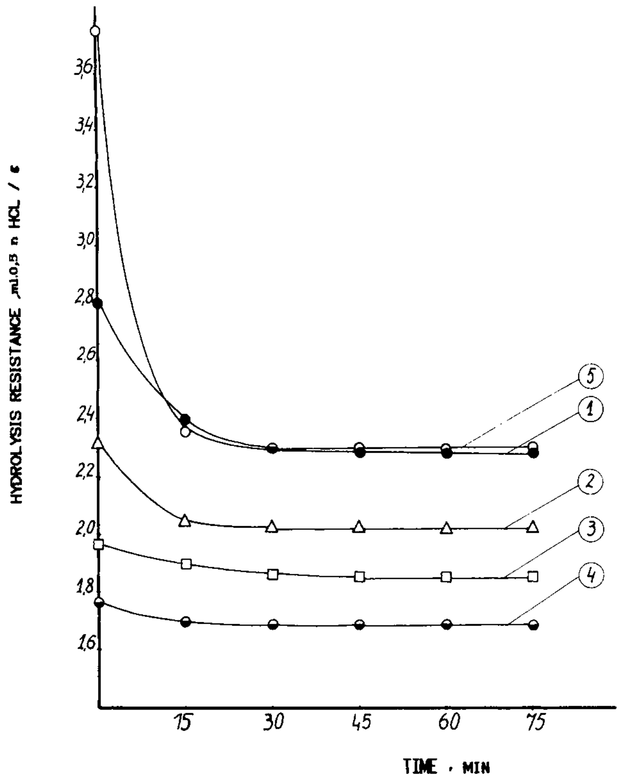


Figure 6 Time dependence of the hydrolysis resistance of oligoester alcohol modified with dimethyl ester of 1,2-di(methoxycarbonyl)ethane phosphonic acid at phosphorus content: curve 1, 0.5%; curve 2, 1.0%; curve 3, 1.5%; curve 4, 2.0%; and curve 5, 0.0%.

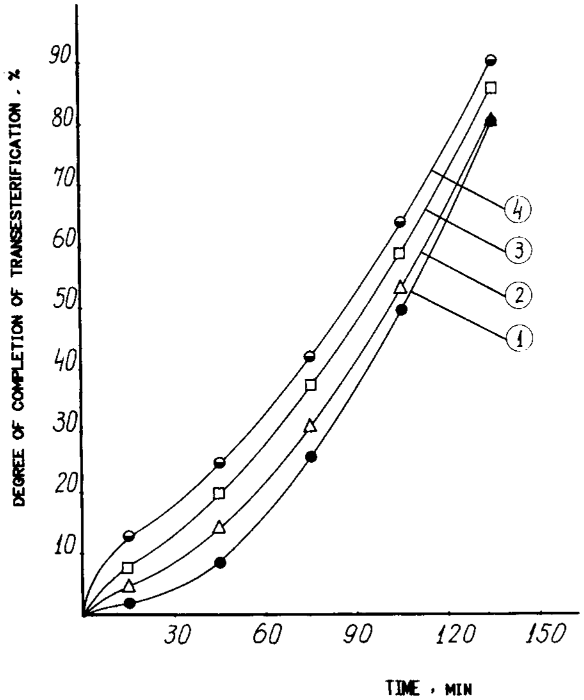
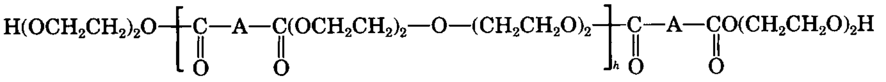


Figure 7 Time dependence of the degree of completion of the transesterification reaction of dimethyl ester of 1,2-di(methoxycarbonyl)ethane phosphonic acid with oligoester alcohols on the basis of residue at the phosphorus content: curve 1, 0.5%; curve 2, 1.0%; curve 3, 1.5%; curve 4, 2.0%.

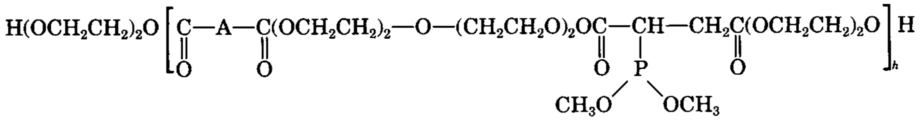
i.e., a complete linking of the oligomer molecules has taken place by means of the dehydration reaction. The viscosity of the oligoester alcohol determined at 50°C, −392,900 cP is evidence for the high molecular mass of the end product (Fig. 5).

The dehydration reaction leads to the formation of the fragments with the following structure:



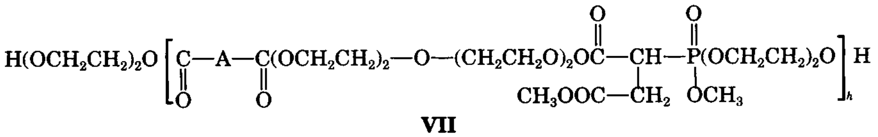
$$\mathrm{H(OCH_2CH_2)_2O}\!\left[\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}-\mathrm{A}-\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{(OCH_2CH_2)_2}-\mathrm{O}-\mathrm{(CH_2CH_2O)_2}\right]_h\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}-\mathrm{A}-\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{O(CH_2CH_2O)_2H}$$

V



$$\mathrm{H(OCH_2CH_2)_2O}\left[\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}-\mathrm{A}-\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{(OCH_2CH_2)_2}-\mathrm{O}-\mathrm{(CH_2CH_2O)_2O}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}-\underset{\substack{| \\ \mathrm{P} \\ \mathrm{CH_3O}\diagup\;\diagdown\mathrm{OCH_3}}}{\mathrm{CH}}-\mathrm{CH_2}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{(OCH_2CH_2)_2O}\right]_h\mathrm{H}$$

VI



$$\mathrm{H(OCH_2CH_2)_2O}\left[\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}-\mathrm{A}-\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{(OCH_2CH_2)_2}-\mathrm{O}-\mathrm{(CH_2CH_2O)_2O}\overset{\substack{\mathrm{O} \\ \|}}{\mathrm{C}}-\underset{\substack{| \\ \mathrm{CH_3OOC-CH_2}}}{\mathrm{CH}}-\underset{\substack{| \\ \mathrm{OCH_3}}}{\overset{\substack{\mathrm{O} \\ \|}}{\mathrm{P}}}\mathrm{(OCH_2CH_2)_2O}\right]_h\mathrm{H}$$

VII

The concentration of these products will depend on the molar ratio between the starting compounds. The increase of the concentration of the phosphonate will determine the increase of the concentration of structures **VI** and **VII**.

The values of the hydrolysis resistance (Fig. 6) demonstrate that the introduction of phosphorus leads to the decrease in the hydrolysis resistance, but in the case of structure **VI** the proceeding of the

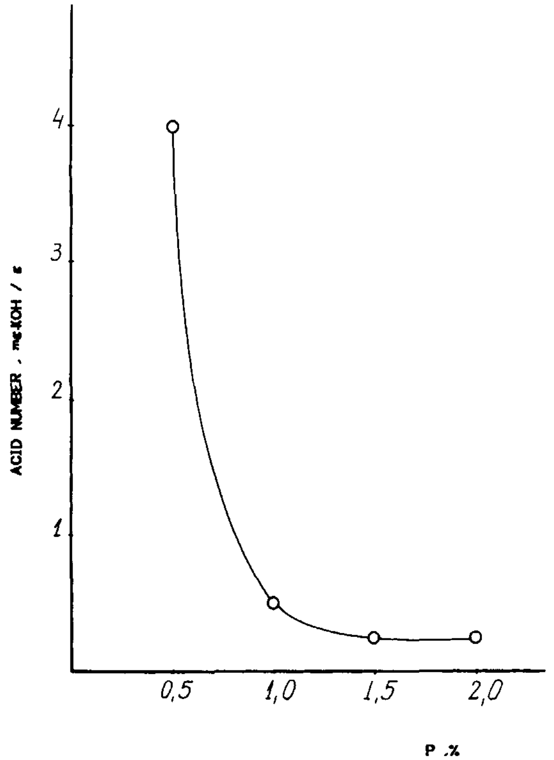


Figure 8 Dependence of the acid number of the end product on the phosphorus content.

hydrolysis is not connected with the decreasing of the molecular mass because in the reaction takes place the methoxy group, which is bonded with phosphorus atom.

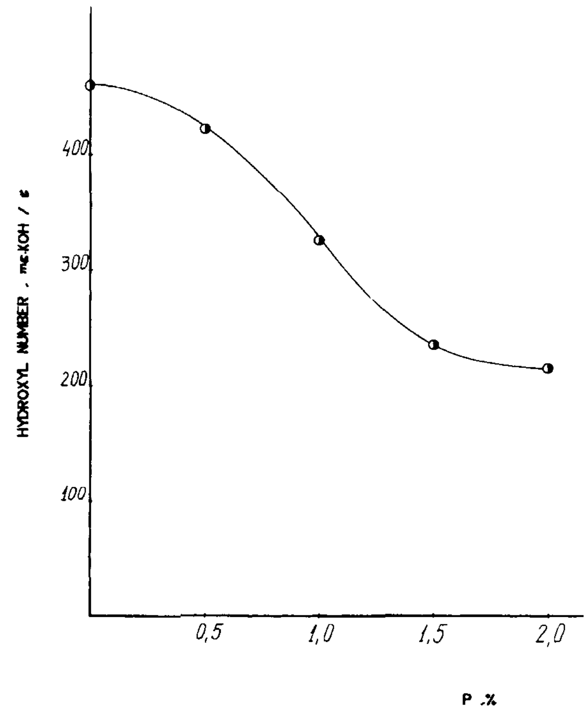
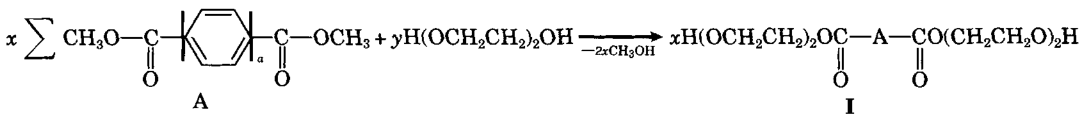


Figure 9 Dependence of the hydrohyl number of the oligoester alcohols on the phosphorus content.

The products thus synthesized are of interest as phosphorus-containing plastisizers having in mind their high viscosity and low hydroxyl number.

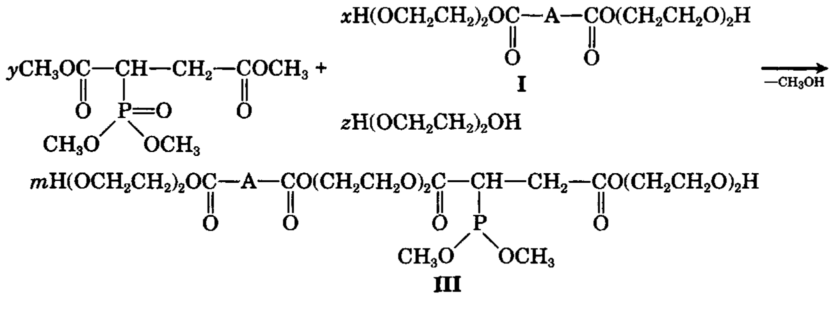
Two-Step Phosphorylation

In this case the transesterification of residue 1 with diethylene glycol is carried out in the first step:



$$x\sum \underset{A}{CH_3O-\underset{\underset{O}{\|}}{C}-\left[C_6H_4\right]_a-\underset{\underset{O}{\|}}{C}-OCH_3} + yH(OCH_2CH_2)_2OH \xrightarrow[-2xCH_3OH]{} \underset{I}{xH(OCH_2CH_2)_2O\underset{\underset{O}{\|}}{C}-A-\underset{\underset{O}{\|}}{C}O(CH_2CH_2O)_2H}$$

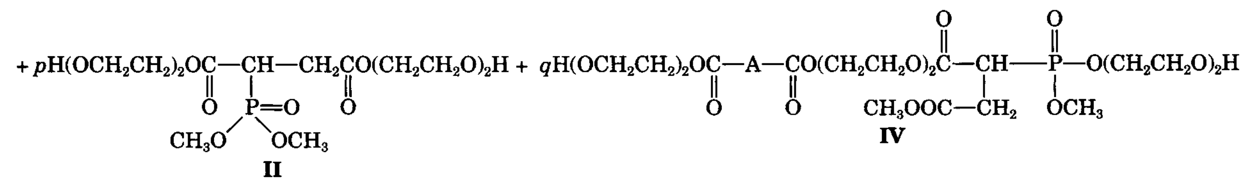
In the second step the transesterification of the dimethyl ester of 1,2-di(methoxycarbonyl)ethane phosphonic acid with the hydroxyl-containing product (I) and diethylene glycol proceeds:



$$y\,CH_3O\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3O\quad OCH_3}{\underset{|}{P=O}}}{CH}-CH_2-\underset{\underset{O}{\|}}{C}OCH_3 + \underset{I}{xH(OCH_2CH_2)_2O\underset{\underset{O}{\|}}{C}-A-\underset{\underset{O}{\|}}{C}O(CH_2CH_2O)_2H} \quad zH(OCH_2CH_2)_2OH \xrightarrow[-CH_3OH]{}$$

$$mH(OCH_2CH_2)_2O\underset{\underset{O}{\|}}{C}-A-\underset{\underset{O}{\|}}{C}O(CH_2CH_2O)_2\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3O\quad OCH_3}{\underset{|}{P}}}{CH}-CH_2-\underset{\underset{O}{\|}}{C}O(CH_2CH_2O)_2H$$

III



$$+p\mathrm{H(OCH_2CH_2)_2O}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\underset{\underset{\mathrm{CH_3O\quad OCH_3}}{\mathrm{P{=}O}}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{O(CH_2CH_2O)_2H}+q\mathrm{H(OCH_2CH_2)_2O}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{A}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{O(CH_2CH_2O)_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{CH_3OOC-CH_2}}{\underset{|}{\mathrm{CH}}}-\overset{\mathrm{O}}{\overset{\|}{\underset{\underset{\mathrm{OCH_3}}{|}}{\mathrm{P}}}}-\mathrm{O(CH_2CH_2O)_2H}$$

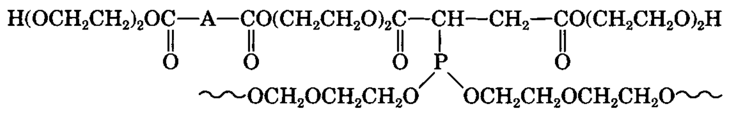
II **IV**

The shape of the curves expressing the time dependence of the degree of completeness of the transesterification of the phosphonate with hydroxyl-containing product (**I**) and diethylene glycol amount of methanol is evolved within ca. 2 h (Fig. 7).

In this kind of synthesis the acid number of the end product decreases with the increase of the phosphonate concentration (Fig. 8). This result shows that the phosphonate accelerates the rate of esterification reaction. The hydroxyl number also decreases (Fig. 9), which implies that both the reaction of esterification and dehydration take place as a result of which water is evolved (Fig. 10). These results confirm the assumption that in the conditions of single-step phosphorylation at 230°C the phosphonate is subjected to thermal degradation resulting in the increase of the acid number of the end product.

In dehydration of the hydroxyl-containing oligomers in reaction mixture results in products with the same structure as **VI, VII,** and **VIII.**

The experimental values of the viscosity (Fig. 11) reveal that in this method of synthesis the four methoxy groups of the phosphonate are involved in the transesterification reaction. It can be supposed that at this condition proceeds the formation of a starlike polymer:



$$\mathrm{H(OCH_2CH_2)_2O}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{A}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{O(CH_2CH_2O)_2}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\underset{\underset{\sim\sim\mathrm{OCH_2OCH_2CH_2O}\quad\mathrm{OCH_2CH_2OCH_2CH_2O}\sim\sim}{\mathrm{P}}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{O(CH_2CH_2O)_2H}$$

The total solubility of the end product reveals that there has not been a crosslinking. Such an assumption explains the significantly lower viscosities found.

The oligoester alcohols synthesized by the two-step method show the same hydrolysis resistance as that synthesized by the single-step method (Fig. 12).

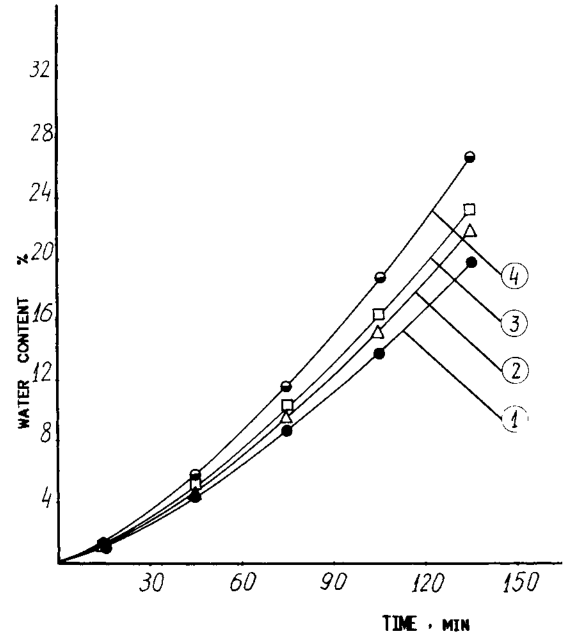


Figure 10 Time dependence of the water content in the distillate at phosphorus content: curve 1, 0.5%; curve 2, 1.0%; curve 3, 1.5%; and curve 4, 2.0%.

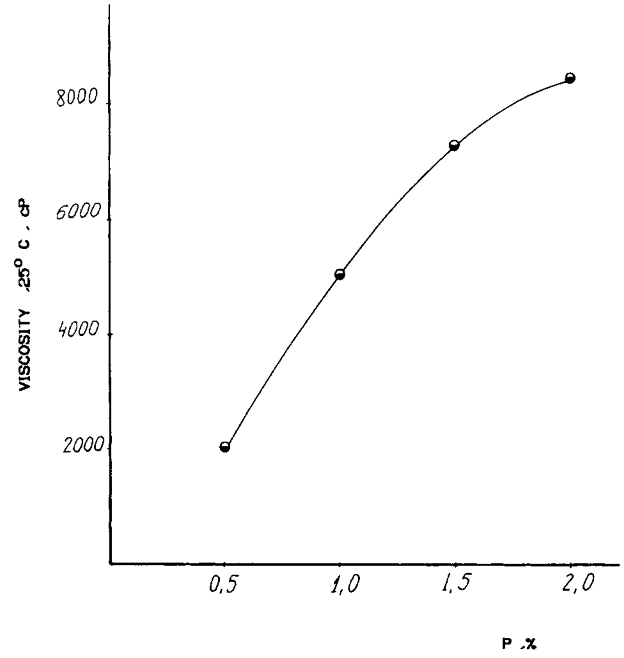


Figure 11 Dependence of the viscosity of the oligoester alcohols on the phosphorus content.

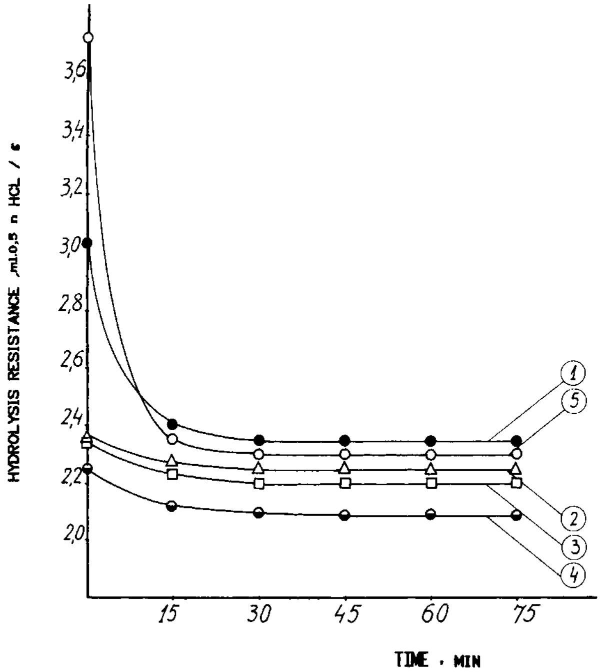


Figure 12 Time dependence of the hydrolysis resistance of oligoester alcohols synthesized by two-step phosphorylation at phosphorus content: curve 1, 0.5%; curve 2, 1.0%; curve 3, 1.5%; curve 4, 2.0%; and curve 5, 0.0%.

The results of the present investigation demonstrate that the diemethyl ester of 1,2-di(methoxycarbonyl)ethane phosphonic acid can be successfully used as a phosphorylating agent for the waste products in the production of dimethyl terephthalate by means of their transesterification with diethylene glycol.

Depending on the method of phosphorylation, single-step or two-step, the end products have different properties. Some of them are of interest as hydroxyl-containing compounds for the synthesis of rigid polyurethane foams or isocyanurates, while the others with a low content of hydroxyl groups or without any such groups are suitable as plasticizers or adhesives for polymer materials.

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Received June 12, 1991
Accepted October 30, 1991