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POLYESTERS BASED ON BROMINE-CONTAINING BIS(*p*-METHOXYCARBONYLPHENOXYMETHYL)-METHYLPHOSPHINE OXIDE

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Abstract—A phosphorus- and bromine-containing bifunctional monomer has been prepared from bis(chloromethyl)methylphosphine oxide and the sodium salt of methyl 3-bromo-4-hydroxybenzoate. From this monomer, bis(2-bromo-4-methoxycarbonylphenoxymethyl)methylphosphine oxide and glycols, polyesters have been obtained by transesterification in the melt. Similarly, using dimethyl terephthalate and ethylene glycol, copolymers containing different amounts of Br and P have been prepared. They are actually polyethyleneterephthalates containing different amounts of phosphorus and bromine. The critical oxygen index is used in the evaluation of the resistance of copolyesters to combustion. It is shown that the P- and Br-containing copolyesters possess a significantly higher resistance to combustion than similar P- and P- and Cl-containing polymers with the same P content.

Phosphorus-containing compounds find considerable application as agents that improve the resistance to combustion of various polymers.

Our studies [1–3] have shown that phosphorus-containing dicarboxylic acids, bis(*p*-carboxyphenoxymethyl)methylphosphine oxide and its chlorine-containing analogue as well as their derivatives, are convenient starting monomers for the preparation of phosphorus-containing polymers and copolymers with increased resistance to combustion. It was considered interesting to prepare bromine-containing bis(*p*-methoxycarbonylphenoxymethyl)methylphosphine oxide and use it to obtain polyesters with increased resistance to combustion. The use of various phosphorus-and bromine-containing flame retardants for polyethyleneterephthalate has been well described [4–8].

The aim of the present work was the synthesis of bis(2-bromo-4-methoxycarbonylphenoxymethyl)methylphosphine oxide and polyesters and copolyesters based on it. A comparison of the resistance to combustion for the prepared phosphorus- and bromine-containing copolyesters and similar phosphorus- and phosphorus- and chlorine-containing polymers was also carried out.

EXPERIMENTAL

Starting compounds

Literature methods were used to prepare bis(chloromethyl)methylphosphine oxide [9] (m.p. 49–50°) and the methyl ester of 3-bromo-4-hydroxybenzoic acid [10] (m.p. 107°). Dimethyl terephthalate was purified by recrystallization from ethanol, m.p. 141–142°. The aliphatic glycols were purified by fractional distillation: ethylene glycol, b.p. 197°, $n_D^{20} = 1.4315$; diethylene glycol, b.p. 245°, $n_D^{20} = 1.4470$; 1,2-propylene glycol, b.p. 189°, $n_D^{20} = 1.4324$.

Synthesis of bis(2-bromo-4-methoxycarbonylphenoxymethyl)-methylphosphine oxide

A solution of methyl 3-bromo-4-hydroxybenzoate (127.0 g, 0.545 mol) in dry methanol (200 ml) was added dropwise to a stirred solution of sodium methoxide obtained from 13.8 g of sodium and 150 ml dry methanol. The solvent was then removed under reduced pressure, the residue washed with benzene and dried under vacuum over P_2O_5 to give 136.3 g (98.5% yield) of the sodium derivative of methyl 3-bromo-4-hydroxymethyl benzoate.

A solution of bis(chloromethyl)methylphosphine oxide (23.5 g, 0.140 mol) in dry anisole (100 ml) was added dropwise to a stirred suspension of the sodium derivative of 3-bromo-4-hydroxymethyl benzoate (73.8 g, 0.292 mol) in the same solvent (300 ml) heated to 120–140°. The reaction mixture was maintained under these conditions for about 4.5 hr; it was then brought to room temperature, washed with a 5% aqueous NaOH solution (100 ml), water and dried over Na_2SO_4. After filtering, the solvent was distilled off under vacuum and the residue recrystallized from methanol to give 68.2 g (85%) of a white crystalline substance, m.p. 142–143°.

For $C_{19}H_{19}Br_2O_7P$, calc. %: C 41.5; H 3.5; Br 29.0; P 5.6; found %: C 41.6; H 3.3; Br 28.8; P 5.5.

Synthesis of bis(2-bromo-4-carboxyphenoxymethyl)methylphosphine oxide

Bis(2-bromo-4-methoxycarbonylphenoxymethyl)methylphosphine oxide (3.4 g, 0.006 mol) was added to a solution of KOH (1.4 g, 0.025 mol) in 10:1 by volume methanol–water (16 ml). The mixture was refluxed for 2 hr, the solvent distilled off under vacuum, the residue acidified with conc. HCl and the precipitate filtered off and washed with water. Recrystallization from aqueous dimethylformamide afforded 2.6 g (82%) of a colourless crystalline substance, m.p. 282–283°.

For $C_{17}H_{15}Br_2O_7P$, calc. %: C 39.2; H 2.9; Br 30.6; P 5.9; found %: C 39.2; H 3.0; Br 30.4; P 6.1.

Preparation of the polyesters

The phosphorus- and bromine-containing polyesters were obtained by transesterification in the melt. The mix-

ture of bis(2-bromo-4-methoxycarbonylphenoxymethyl)-methylphosphine oxide (1.37 g, 0.0025 mol) and ethylene glycol (0.46 g, 0.0075 mol) with zinc acetate (0.0056 g) and Sb_2O_3 (0.0014 g) as catalysts was heated under N_2 for 5 hr at 160–170° during which time the methanol was completely removed. Heating was maintained for 3 hr at 230°, the temperature gradually brought to 260°, a vacuum of 15 mm Hg then applied, and the reaction mixture was kept under these conditions for 1.5 hr. The pressure was decreased to 2–3 mm Hg and at this temperature the polycondensation process was allowed to continue for 4 hr. The melt was then cooled under a stream of N_2 and the polyester (1.3 g) purified by precipitating its chloroform solution with petroleum ether.

The phosphorus- and bromine-containing copolyesters were prepared similarly by adding to the dimethyl terephthalate and ethylene glycol starting mixture bis(2-bromo-4-methoxycarbonylphenoxymethyl)methylphosphine oxide in an amount corresponding to the desired phosphorus content in the final polymer.

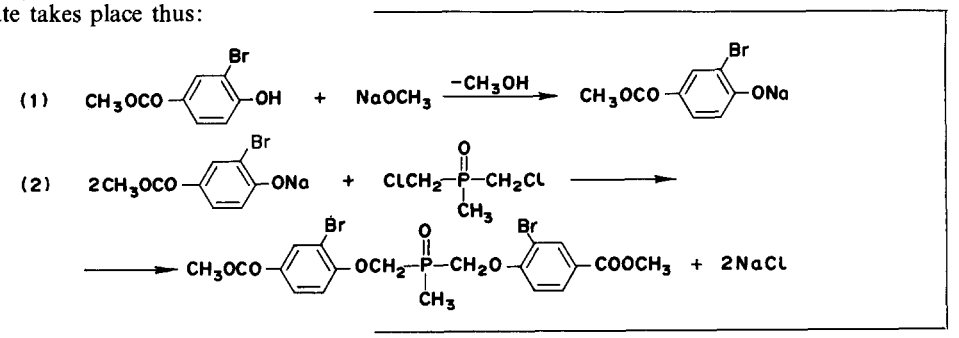
The phosphorus-, and phosphorus- and chlorine-containing copolymers as well as their starting monomers have been described [1].

Characterization of the polymers

The viscosity evaluations were carried out using 0.5% solutions in an Ostwald viscometer. The infrared spectra were recorded on a UR 20 spectrometer using KBr pellets. Thermogravimetric analysis was conducted in air at a rate of heating of 5°/min using an MOM instrument. The resistance to combustion, expressed as a critical oxygen index, was determined on a Stanton Redcroft instrument, the samples being prepared by impregnation by repeated immersion in a hot solution of 100/10 mm glass pieces and then drying them to constant weight.

RESULTS AND DISCUSSION

The synthesis of bis(2-bromo-4-methoxycarbonylphenoxymethyl)methylphosphine oxide (BMPO) was carried out by the procedure developed for the preparation of similar phosphorus-containing monomers [11]. The interaction between bis(chloromethyl)methylphosphine oxide and methyl 3-bromo-4-hydroxybenzoate takes place thus:



Hydrolysis of BMPO with an alcoholic solution of KOH led to the corresponding phosphorus- and bromine-containing dicarboxylic acid–bis(2-bromo-4-carboxyphenoxymethyl)methylphosphine oxide.

Phosphorus- and bromine-containing polyesters were synthesized from BMPO and aliphatic glycols via transesterification in the melt. As melts or in the cooled state, they are glass-like, semitransparent substances which on re-precipitation become colourless or slightly gray powders. Long fibres can be drawn from the melts of the newly obtained products; solutions form transparent, thin, films adhering well to glass or metal surface.

Some general properties of the new polyesters are listed in Table 1. The temperature of softening of the polyesters clearly decreases with increase of the number of methylene groups in the glycol moiety, a common property of all similar polymers. The products are soluble mainly in chloroform, dimethylsulphoxide, nitrobenzene etc. The presence of phosphorus and bromine in the polyesters accounts for increased resistance to combustion. Ignited samples of the polymers cease burning immediately on removal from the flame.

The properties of the synthesized polymers (especially their resistance to combustion) render the starting monomer (BMPO) a suitable flame-retardant for reducing the combustibility of polyethyleneterephthalate. It can be assumed that the desired effect will be brought about by the introduction of small amounts of BMPO.

By conducting transesterification in the melt, dimethylterephthalate, BMPO and ethylene glycol lead to copolymers which actually are phosphorus- and bromine-containing polyethyleneterephthalate. The amounts of BMPO used in the starting monomer mixture are chosen so as to ensure the presence of 0.5, 1.0 and 1.5% of phosphorus in the synthesized copolymers. The mol ratios of the starting monomers, as well as some characterization data, are given in Table 2.

The phosphorus- and bromine-containing component of polyethyleneterephthalate decreases the softening temperature of the latter while improving its solubility.

The thermal stability of polyethyleneterephthalate is not impaired by the introduction of BMPO. The thermogravimetric data from studies of phosphorus- and bromine-containing copolymers are given in Fig. 1. The character of the curves remains almost the same for all three copolymers as well as for the polyethyleneterephthalate homopolymer. Significant losses in weight occur within the 300–350° range and at 450° about 90% of the polymers are destroyed.

The structure of the homo- and copolymers is substantiated by infrared spectra exhibiting absorption bands at 1190 cm^{-1} ($\nu_{P=O}$), 1300–1250 cm^{-1} (ν_{P-CH_3}), 1720 cm^{-1} ($\nu_{C=O}$), 1600, 1580 cm^{-1} ($\nu_{C=C\ aromatic\ rings}$), 1110 cm^{-1} ($\nu_{1,2,4\text{-trisubstituted aromatic ring}}$), 2960–2920 cm^{-1} (ν_{CH_2}).

The effect of the phosphorus- and bromine-containing component on the resistance to combustion of polyethyleneterephthalate is depicted in Table 2 and Fig. 2 (curve III). The oxygen index of the copolymers increases with rise of the phosphorus and bromine

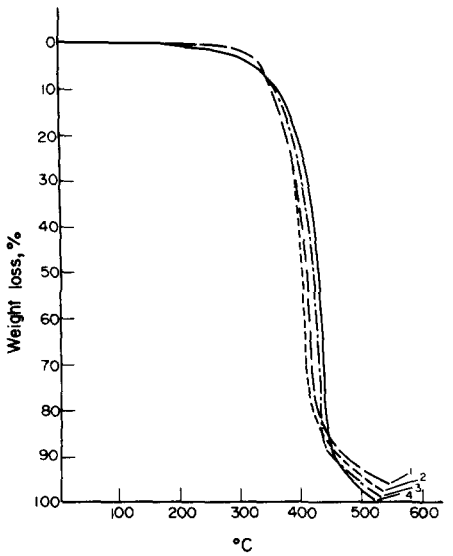


Fig. 1. Thermogravimetric analysis of phosphorus- and bromine-containing copolyesters. Phosphorus content, %: 1—1.5; 2—1.0; 3—0.5; 4—0.

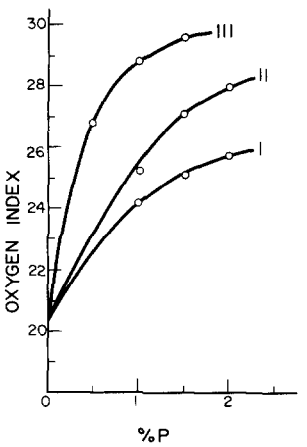
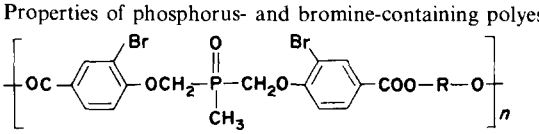


Fig. 2. Oxygen index of copolyesters: I—phosphorus-containing polymers; II—phosphorus- and chlorine-containing polymers; III—phosphorus- and bromine-containing polymers.

contents. Small quantities of BMPO have significant effect.

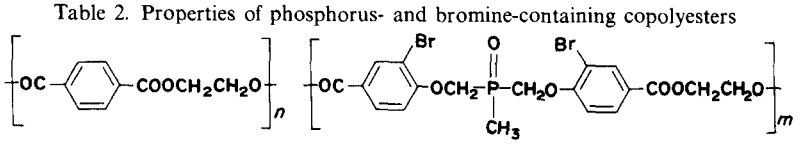
A comparison of the resistance to combustion of the synthesized phosphorus- and bromine-containing copolyesters with similar phosphorus- and phosphorus- and chlorine-containing polymers would be of interest. Bis(*p*-methoxycarbonylphenoxymethyl)methylphosphine oxide (MCPO) was used as a reference type of flame-retardant [11]. The phosphorus- and chlorine- and phosphorus- and bromine-containing monomers can be considered as MCPO with aromatic groups carrying chlorine and bromine atoms.

Table 1. Properties of phosphorus- and bromine-containing polyesters



R	Yield (%)	Temperature of softening (°C)	η_{sp}/c (dl/g in $CHCl_3$)
$-CH_2CH_2-$	98	132–142	0.21
$-CH_2CH-$ $\quad\quad\vert$ $\quad\quad CH_3$	95	125–140	0.16
$-(CH_2)_2-O-(CH_2)-_2$	99	96–110	0.20

Table 2. Properties of phosphorus- and bromine-containing copolyesters



Composition of starting monomer mixture (mol %) Dimethylterephthalate	BMPO	Phosphorus content (%)	Bromine content (%)	Yield (%)	Temperature of softening (°C)	η_{sp}/c* (dl/g)	Oxygen index (OI) (% O_2)
100†	—	—	—	—	258–260	0.54	20–21‡
96.7	3.3	0.5	2.6	98	241–245	0.41	26.8
93.0	7.0	1.0	5.1	98	220–227	0.38	28.8
88.8	11.2	1.5	7.7	96	196–204	0.36	29.6

* In a phenol/tetrachloroethane 3:2 mixture.
† Polyethyleneterephthalate produced at the "D. Dimov" Works, Yambol.
‡ From ref. [12].

Table 3. Properties of phosphorus- and phosphorus- and chlorine-containing copolyesters

Type of polymer	Composition of the starting mixture of monomers (mol %) Dimethylterephthalate	P or P and Cl monomer	Content of P (%)	Content of Cl (%)	Yield (%)	Temperature of softening (°C)	η_{sp}/c* (dl/g)	Oxygen index (OI) % O_2
I	93.4	6.6	1.0	—	99	238–246	0.30	24.2
I	89.8	10.2	1.5	—	97	232–240	0.44	25.1
I	85.8	14.2	2.0	—	96	208–214	0.42	25.7
II	93.0	7.0	1.0	4.6	98	213–218	0.30	25.2
II	88.9	11.1	1.5	6.9	97	187–193	0.32	27.1
II	84.1	15.9	2.0	9.2	95	155–164	0.36	28.0

* In a 3:2 phenol/tetrachloroethane mixture.

By transesterification in the melt, dimethylterephthalate and ethylene glycol phosphorus-containing copolyesters (I) with various amounts of phosphorus are prepared from MCPO. In the same way using bis(2,6-dichloro-4-methoxycarbonylphenoxymethyl)-methylphosphine oxide, phosphorus- and chlorine-containing copolymers (II) were synthesized. The prepared products were modified with various amounts of phosphorus and chlorine polyethyleneterephthalate:

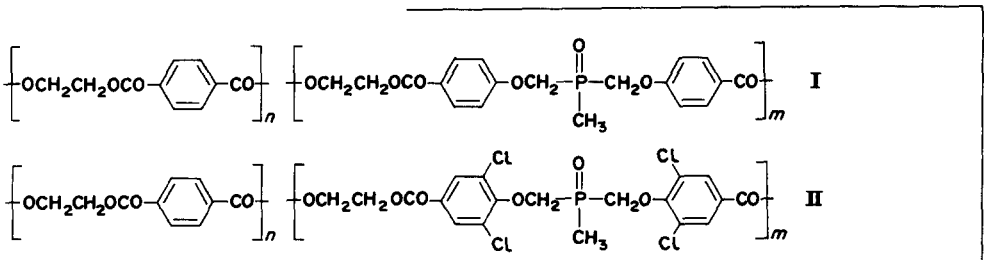


Table 3 shows some characteristic properties of the copolymers, the mol ratios of the starting monomers and the phosphorus and chlorine content. Table 2 can be used for comparing with the corresponding phosphorus- and bromine-containing copolyesters.

Partial replacement of the aromatic hydrogen atoms in MCPO with chlorine and bromine atoms was found significantly to affect the resistance to combustion of the studied polymers. Figure 2 shows the relationship between the oxygen index and the phosphorus content of the copolymers. A marked effect of resistance to combustion is evident for the phosphorus- and halogen-containing polymers. Especially notable was this effect for phosphorus- and bromine-containing products.

It is known [12] that, in order to satisfy the requirements for resistance to combustion, polyethyleneterephthalate should possess an oxygen index of 27. The following conclusions can be drawn regarding the type of flame-retardant used in this investigation from the curves given in Fig. 2. The preparation of modified polyethyleneterephthalate possessing an oxygen index of about 27 requires comonomer (flame retardant) proportions ensuring the presence of the following quantities of phosphorus in the final polymer—4–5% for phosphorus-containing polyethyleneterephthalate; 1.5%—for phosphorus and chlorine-containing polymer and 0.6% for phosphorus- and bromine-containing polymer.

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