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SYNTHESIS OF PHOSPHORUS-CONTAINING POLYURETHANES FROM OLIGOETHERS PREPARED FROM BIS(CHLOROMETHYL) METHYLPHOSPHINE OXIDE AND GLYCOLS

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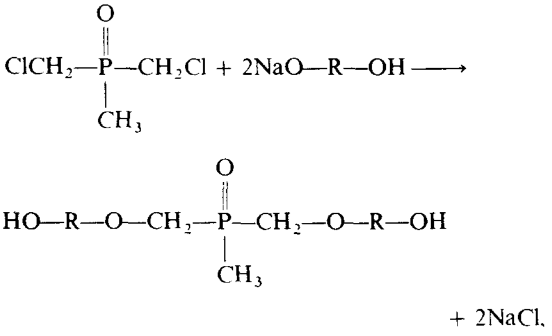
Abstract—Oligoethers with hydroxyl end-groups were prepared in boiling toluene from bis(chloromethyl)methylphosphine oxide and glycols used as monosodium glycolates. From these oligoethers and diisocyanates (hexamethylenediisocyanate and 2,4-toluene-diisocyanate), phosphorus-containing polyurethanes were synthesized.

INTRODUCTION

In previous papers we showed that oligoethers with hydroxyl end-groups could be synthesized from bis(chloromethyl)methylphosphine oxide (DCMMPO) and bisphenols. These oligoethers were successfully used for the synthesis of phosphorus-containing polyether-esters, possessing increased resistance to combustion [1,2].

We now report the results of the synthesis of similar oligomers from DCMMPO and glycols and their use for the preparation of phosphorus-containing polyurethanes. Synthesis of the oligoethers can be represented thus:



$$ClCH_2-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{P}}-CH_2Cl + 2NaO-R-OH \longrightarrow$$

$$HO-R-O-CH_2-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{P}}-CH_2-O-R-OH + 2NaCl,$$

where $R = CH_2CH_2-O-CH_2CH_2$ or $(CH_2)_n$ $n = 2$–8.

EXPERIMENTAL

Starting materials

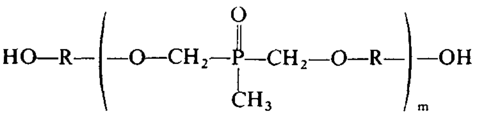
Toluene was dried over sodium and distilled. Dimethylsulphoxide (Fluka commercial product) was dried over CaH_2 at 100° and distilled at 56–61°/5–6 mm Hg. DCMMPO is a white crystal substance, very hygroscopic and soluble in methanol, chloroform and aromatic hydrocarbons. It was prepared by the method of Kabachnik and Tsvetkov [3], m.p. 49–50°, b.p. 138–139°/4–5 mm Hg. Glycols: ethane diol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, heptane-1,7-diol, octane-1,8-diol and bis(2-hydroxyethyl) ether were commercial products; they were purified by dissolving 1–2 g of sodium in 40–50 g of the corresponding glycol and then distilling under reduced pressure. Hexane-1,6-diol and octane-1,8-diol were only distilled under reduced pressure. Hexamethylene diisocyanate (Fluka commercial product) and toluene-2,4-diisocyanate (Schuchardt commercial product) were used after distillation.

Preparation of oligoethers

(a) *Monosodium glycolates.* Ethane diol 7·81 g (0·126 mol) and 40 ml dry methanol were placed in a three-necked round-bottomed flask, provided with reflux condenser and a tube for bubbling nitrogen. To this solution, 2·90 g (0·126 g atom) sodium were added in small portions under a constant stream of nitrogen. After complete dissolution, the methanol was distilled off; the residue, monosodium glycolate of ethane diol, was dried at 100°/1–2 mm Hg to constant weight. Quantitative yield—10·52 g.

(b) *Oligoethers.* After powdering of the monosodium glycolate of ethane diol in the reaction flask under a slow but steady stream of nitrogen, 10 ml of toluene were added. At room temperature and with stirring, 7·06 g (0·0438 mol) DCMMPO dissolved in 30 ml of toluene were added dropwise. An exothermic reaction was apparent at this stage. The mixture thus prepared was refluxed with constant stirring in nitrogen for 7 hr. After cooling, the upper layer was removed. The residue was extracted three times with 26 ml of benzene and dissolved in 25 ml water. This solution was acidified with 3 M hydrochloric acid to pH 5·5–6 and the water was removed under vacuum. The syrupy product, containing particles of sodium chloride, was dried azeotropically with a mixture of benzene and ethyl alcohol (1:4) and then dissolved in 50 ml of the same mixture. The sodium chloride was removed by filtration and the solvent was evaporated. The residue was extracted again with ether or benzene. From the yellowish or light-brown syrupy prod-

Table 1. Preparations of phosphorus-containing oligoethers



$$HO-R-\left(-O-CH_2-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}}-CH_2-O-R-\right)_m-OH$$

No.	R	Yield (%)	Content of OH groups (%) Calcd. for m = 1	Content of OH groups (%) Found	Elemental analysis-phosphorus (%) Calcd. for m = 1	Elemental analysis-phosphorus (%) Found	Molecular weight Calcd. for m = 1	Molecular weight Found*
1	$-(CH_2)_2-$	54·3	16·02	11·15	14·62	14·24	212	304·9
2	$-(CH_2)_3-$	82·2	14·16	11·00	12·91	11·85	240	309·9
3	$-(CH_2)_4-$	74·2	12·68	7·71	11·56	12·54	268	440·9
4	$-(CH_2)_5-$	73·8	11·48	11·02	10·84	10·26	296	308·5
5	$-(CH_2)_6-$	75·4	10·49	11·09	9·56	9·57	324	306·4
6	$-(CH_2)_7-$	77·6	9·65	9·98	8·80	7·94	352	340·6
7	$-(CH_2)_8-$	43·6	8·95	10·43	8·18	6·65	380	326·3
8	$-CH_2CH_2-O-CH_2CH_2-$	94·5	11·83	13·44	10·33	8·65	300	252·9

* Calculated from terminal hydroxyl groups.

uct, the excess of ethane diol was distilled under vacuum. Yield 5·03 g (59·3 per cent).

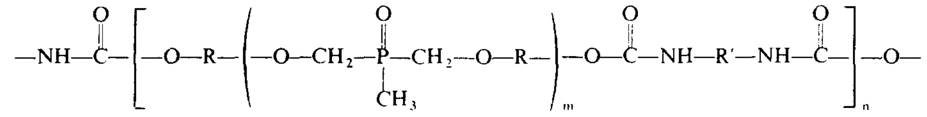
The monosodium glycolates of the remaining glycols and the oligoethers from them and DCMMPO were prepared similarly (Table 1). The oligoethers synthesized from heptane-1,7-diol and octane-1,8-diol (Nos. 6 and 7, Table 1) were isolated by dissolving in dry hot benzene, filtration of the solution and distillation of the benzene.

Preparation of polyurethanes

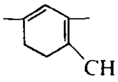
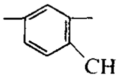
Hexamethylenediisocyanate 1·27 g (0·0075 mol) and 2 ml dimethylsulphoxide were placed in a three-necked round-bottomed flask of 100 ml, provided with a stirrer, a tube for a bubbling nitrogen and a reflux condenser. A solution of 7 ml dimethylsulphoxide and 2·17 g (0·0071 mol) oligoether obtained from ethane diol and DCMMPO was then added in one portion. The reaction mixture was stirred slowly and heated at 135–140° for 3 hr under a slow stream of nitrogen. The resulting polyurethane was isolated from the reaction mixture by pouring the solution into benzene. The precipitated polyurethane was washed with ether and ethyl alcohol and then dried in a vacuum oven at 50–60°. Yield 2·80 g (81·5 per cent).

The polyurethanes from the remaining oligoethers were prepared similarly (Table 2).

Table 2. Preparation of phosphorus-containing polyurethanes



$$-NH-\overset{\overset{\displaystyle O}{\|}}{C}-\left[-O-R-\left(-O-CH_2-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}}-CH_2-O-R-\right)_m-O-\overset{\overset{\displaystyle O}{\|}}{C}-NH-R'-NH-\overset{\overset{\displaystyle O}{\|}}{C}-\right]_n-O-$$

No.	R	R′	Yield (%)	Melting point	$\eta_{sp/c}$ in DMF* (dl/g)	Phosphorus content (%) Calcd.	Phosphorus content (%) Found
1	$-(CH_2)_2-$	$-(CH_2)_6-$	81·5	91–95	0·08	9·20	8·93
2	$-(CH_2)_3-$	$-(CH_2)_6-$	55·2	94–96	0·21	7·62	6·87
3	$-(CH_2)_4-$	$-(CH_2)_6-$	73·0	104–107	0·09	9·11	8·83
4	$-(CH_2)_5-$	$-(CH_2)_6-$	55·0	94–100	0·14	6·62	6·47
5	$-(CH_2)_6-$	$-(CH_2)_6-$	71·8	122–130	0·20	6·17	4·06
6	$-(CH_2)_6-$		76·8	94–100	0·15	6·09	6·01
7	$-(CH_2)_7-$	$-(CH_2)_6-$	60·0	108–111	0·15	5·40	4·95
8	$-(CH_2)_7-$		94·7	84–86	0·12	5·32	5·08
9	$-(CH_2)_8-$	$-(CH_2)_6-$	84·5	115–120	0·23	4·38	3·76
10	$-CH_2CH_2-O-CH_2CH_2-$	$-(CH_2)_6-$	58·5	88–90	0·22	5·20	4·82

* Dimethylformamide.

Characterization of the oligoethers and the polyurethanes obtained from them

The molecular weights of the oligoethers were calculated from the contents of hydroxyl groups, determined by acetylation with acetic anhydride in pyridine.

The i.r. spectra of films of the oligoethers and those of the polyurethanes, in KBr pellets, were taken using a Zeiss-Jena UR-10 instrument.

Viscosity measurements were carried out using 0·5 per cent solutions of the polymers in dimethylformamide at 25° with an Ostwald viscometer.

The resistance to thermal degradation was evaluated under dynamic conditions in air by measuring weight losses with a torsional balance. The rate of temperature increase for all cases was 10°/min.

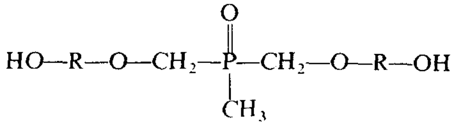
The resistance to combustion of the polymer was evaluated by attaching 0·01 g of the polymer to a metal rod and allowing it to ignite in the flame of a gas-burner; the interval between the removal of the sample from the burner and cessation of burning was recorded.

RESULTS AND DISCUSSION

Although it is well-known that glycols react with alkaline metals to give mono-substituted glycolates, only the preparation and properties of monosodium glycolates obtained from ethane diol and propane-1,3-diol have hitherto been described [4–7]. Forcrand has shown that glycols are able to replace alcohols from their alcoholates giving monosubstituted glycolates [4]. On this basis, we prepared in dry methanol the monosodium glycolates of ethane diol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, heptane-1,7-diol octane-1,8-diol and bis(2-hydroxyethyl) ether. After distillation of the solvent and drying, all glycolates were obtained as white hard, porous masses which could be powdered.

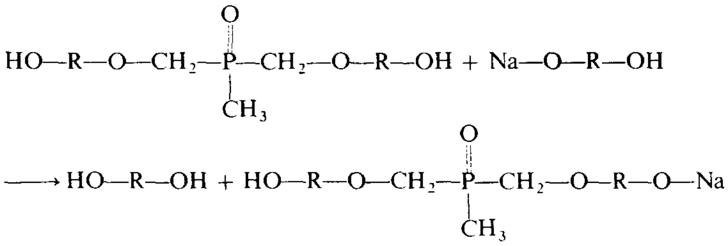
From the monosodium glycolates of the glycols and DCMMPO, phosphorus-containing oligoethers with hydroxyl end-groups were synthesized in boiling toluene (Table 1). Although the glycolates are insoluble in the reaction medium, the yields in all cases were comparatively high.

The molecular weights of the oligoethers in most cases were higher than those corresponding to the formula:



$$\mathrm{HO{-}R{-}O{-}CH_2{-}\underset{\displaystyle CH_3}{\overset{\displaystyle O}{\overset{\|}{P}}}{-}CH_2{-}O{-}R{-}OH} \qquad \mathrm{(I)}$$

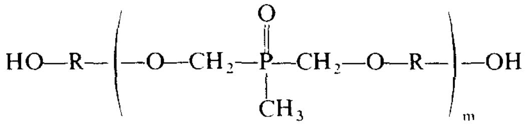
This discrepancy is probably due to exchange reactions between the monosubstituted or disubstituted product and the corresponding glycolate according to the scheme:



$$\mathrm{HO{-}R{-}O{-}CH_2{-}\underset{\displaystyle CH_3}{\overset{\displaystyle O}{\overset{\|}{P}}}{-}CH_2{-}O{-}R{-}OH + Na{-}O{-}R{-}OH}$$

$$\longrightarrow \mathrm{HO{-}R{-}OH + HO{-}R{-}O{-}CH_2{-}\underset{\displaystyle CH_3}{\overset{\displaystyle O}{\overset{\|}{P}}}{-}CH_2{-}O{-}R{-}O{-}Na}$$

As a result of this reaction, higher molecular products are synthesized:

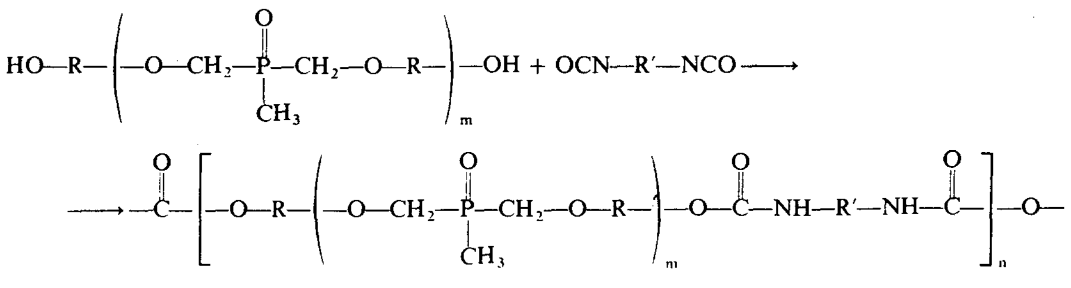


$$\mathrm{HO{-}R{-}\left({-}O{-}CH_2{-}\underset{\displaystyle CH_3}{\overset{\displaystyle O}{\overset{\|}{P}}}{-}CH_2{-}O{-}R{-}\right)_{m}{-}OH}$$

The molecular weights of the oligoethers synthesized from higher boiling glycols (containing six or more carbon atoms per molecule) are lower than those calculated according to formula (I). This means that the isolated products are mixtures of phosphorus-containing oligoethers of the above structure and considerable quantities of the glycols. All these conclusions are in good agreement with results of elemental analysis of phosphorus. The proposed structure of the oligoethers is further confirmed by the i.r. spectra. They show characteristic absorption bands typical for the ether bond at 1100–1140 cm^{-1}, for phosphoryl groups ($P{=}O$) at 1175 cm^{-1}, for methylene units at 2800–2900 cm^{-1}, for the $P{-}CH_3$ bond at 1300 cm^{-1}, for hydroxyl groups at 3100–3400 cm^{-1}. Absorption bands at 2550–2700 cm^{-1}, characteristic of hydroxyl groups directly bound to the phosphorus atom, were absent.

All oligoethers are syrupy, light yellow or light brown products. Their solubility in organic solvents changes as the number of the methylene units increases, as is the case with the corresponding glycols. All of them are freely soluble in methyl and ethyl alcohols, pyridine, dimethylformamide and water, except that the product from octane-1,8-diol is only partly soluble in water. The oligoethers are not soluble in chloroform, acetone, ether or aromatic hydrocarbons, but those synthesized from heptane-1,7-diol and octane-1,8-diol (nos. 6 and 7, Table 1) are soluble in hot benzene.

From diisocyanate and these phosphorus-containing oligoethers with terminal hydroxyl groups, polyurethanes were synthesized:



$$HO{-}R{-}\left({-}O{-}CH_2{-}\underset{CH_3}{\underset{|}{\overset{O}{\overset{\|}{P}}}}{-}CH_2{-}O{-}R{-}\right)_m{-}OH + OCN{-}R'{-}NCO \longrightarrow$$

$$\longrightarrow {-}\overset{O}{\overset{\|}{C}}{-}\left[{-}O{-}R{-}\left({-}O{-}CH_2{-}\underset{CH_3}{\underset{|}{\overset{O}{\overset{\|}{P}}}}{-}CH_2{-}O{-}R{-}\right)_m{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R'{-}NH{-}\overset{O}{\overset{\|}{C}}{-}\right]_n{-}O{-}$$

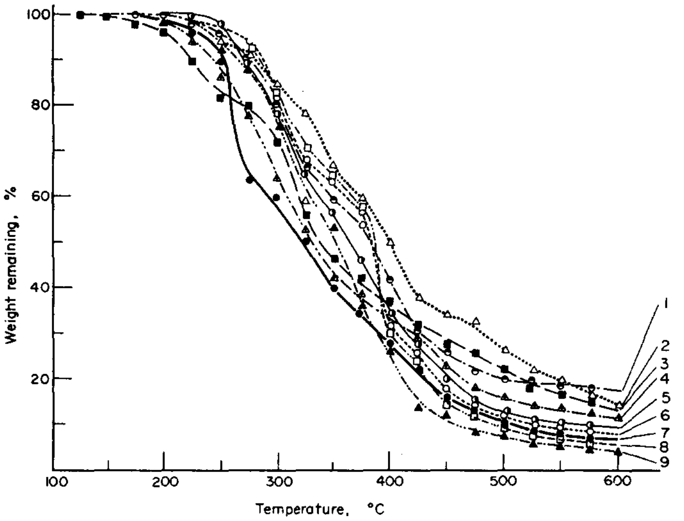


Fig. 1. Thermogravimetric analysis of polyurethanes at a heating rate of 10°/min. Polyurethane prepared from hexamethylenediisocyanate and: (1)–oligoether from pentane-1,5-diol; (2)–oligoether from butane-1,4-diol; (3)–oligoether from ethane diol; (4)–oligoether from bis(2-hydroxyethyl) ether; (5)–oligoether from hexane-1,6-diol; (6)–oligoether from propane-1,3-diol; (7)–ethane diol; (8)–oligoether from heptane-1,7-diol; (9)–oligoether from octane-1,8-diol.

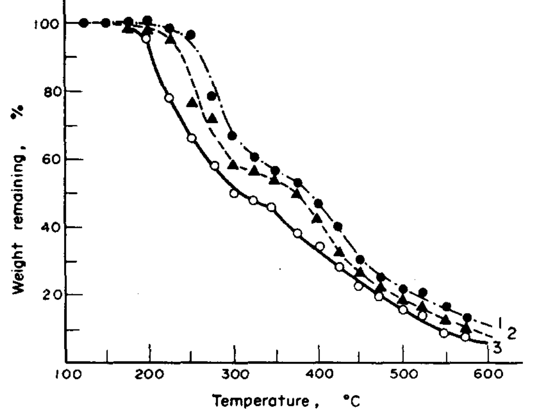


Fig. 2. Thermogravimetric analysis of polyurethanes at a heating rate of 10°/min. Polyurethane prepared from toluene-2,4-diisocyanate and: (1)–oligoether from hexane-1,6-diol; (2)–oligoether from heptane-1,7-diol; (3)–ethane diol.

All polyurethanes are readily synthesized in dimethylsulphoxide according to known methods in high yields (Table 2). They are solid white products with not very high melting points. As shown by Figs. 1 and 2, their thermal stability in air is not lower, but in most cases higher, than the thermal stability of similar ordinary polyurethanes not containing phosphorus. Decomposition begins at about 220–240° with a weight loss of about 50 per cent over an interval of 100°.

The polymers are easily soluble in dimethylformamide, *m*-cresol and formic acid. They are insoluble in methyl and ethyl alcohols, aromatic and aliphatic hydrocarbons, ether, acetone, etc. Their structure is confirmed by elemental analysis for phosphorus. The i.r. spectra possess absorption bands at 1690–1720 cm^{-1}, 1250–1270 cm^{-1} characteristic of C=O and C—O of the urethane groups at 1100–1120 cm^{-1} for ether bonds, at 1160–1180 cm^{-1} for phosphoryl groups

(P=O), at 2800–2900 cm^{-1} for methylene units. Absorption bands at 2550–2700 cm^{-1}, characteristic of the hydroxyl groups directly bonded to the phosphorus atoms, were absent.

All polyurethanes possess self-extinguishing properties. In a flame, they ignite with difficulty and burn; after removal from the flame, they extinguish. Under the same conditions, similar phosphorus-free polyurethanes ignite much more easily and, after removal from the flame, they burn completely.

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Résumé—On a préparé des oligoéthers comportant des groupes hydroxyles terminaux dans le toluène bouillant à partir de l'oxyde de bis(chlorométhyl)méthylphosphine et de glycols sous forme de glycolates monosodiques. A partir de ces oligoéthers et de diisocyanates (hexaméthylène diisocyanate et toluène 2,4-diisocyanate), on a synthétisé des polyuréthanes contenant du phosphore.

Sommario—Si sono preparati degli oligoeteri con gruppi terminali idrossilici in toluene bollente, partendo da ossido di bis(clorometil)metilfosfina e glicoli impiegati come glicolati monosodici. Partendo da tali oligoeteri e diisocianati (esametilenediisocianato e 2,4-toluene-diisocianato), si sono sintetizzati dei poliuretani contenenti fosforo.

Zusammenfassung—Oligoäther mit Hydroxyl-Endgruppen wurden hergestellt durch Umsetzung von Chlormethyl-methylphosphinoxid mit Mononatriumglykolaten in siedendem Toluol. Durch Umsetzung dieser Oligoäther mit Diisocyanaten (Hexamethylendiisocyanat und 2,4-Toluoldiisocyanat) wurden phosphorhaltige Polyurethane synthetisiert.