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POLYURETHANE FOAMS BASED ON DIMETHYLAMINOMETHYLPHOSPHINE OXIDE ADDUCTS WITH ETHYLENE AND PROPYLENE OXIDES

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Abstract—Dimethylaminomethylphosphine oxide (DMAO) is prepared by the Gabriel method from dimethylchloromethylphosphine oxide. Adding to DMAO, ethylene or propylene oxides affords dimethyl-*N*,*N*-bis(2-hydroxyethyl)aminomethylphosphine oxide (DMEO) and dimethyl-*N*,*N*-bis(2-hydroxypropyl)aminomethylphosphine oxide (DMPO). It is found that DMEO and DMPO can be employed as reactive flame retardants for reducing the combustibility of rigid polyurethane foams without impairing their physical and mechanical properties.

INTRODUCTION

The tertiary phosphine oxides containing primary amino groups can be used for preparing derivatives as well as for modifying or synthesizing phosphorous-containing polymers.

A few similar compounds are listed in the literature e.g. phenyl-bis(aminomethyl)phosphine oxide [1], methyl-bis(aminomethyl)phosphine oxide [2] and tris-(aminomethyl)phosphine oxide [3, 4].

We now report the preparation of dimethylaminomethylphosphine oxide, its adducts with ethylene and propylene oxides and the use of the latter products in modifying rigid polyurethane foams. This work is a continuation of our studies on the synthesis of phosphorus-containing monomers and polymers from tertiary phosphine oxide containing chloromethyl groups [2, 5, 6].

EXPERIMENTAL

Starting compounds

Dimethylchloromethylphosphine oxide, potassium phthalate, hydrazine hydrate (98%), ethylene and propylene oxides were commercial products.

The preparation of the rigid polyurethane foams involved: silicon oil "DC-193" (Dow Corning), dimethylcyclohexylamine (BASF), "Freon 11" (Du Pont), oligomeric diphenylmethanediisocyanate "Suprasec DNR" (ICI) and two types of polyols viz. polyetherpolyol No. 1 prepared from sugar and propylene oxide with hydroxyl value of 630 mgKOH/g, and polyetherpolyol No. 2 prepared from glycerol and propylene oxide with a hydroxyl value of 530 mgKOH/g.

Dimethyl phthalimidomethylphosphine oxide (DPO)

The mixture of dimethylchloromethylphosphine oxide (DMCO) (32.3 g, 0.26 mol) and potassium phthalimide (58.3 g, 0.32 mol) in 120 ml xylene or anisol was refluxed with stirring for 18 hr. After cooling to room temperature, the mixture was filtered and DPO extracted from the solid product by dissolving in chloroform or methylene chloride and removing subsequently the solvent. The crude DPO (56.8 g) was recrystallized from toluene or a chloroform–diethyl ether mixture.

Dimethylaminomethylphosphine oxide (DMAO)

A solution of hydrazine hydrate (21.2 g, 0.42 mol) in ethanol (150 ml) was added to a mixture of DPO (98.5 g, 0.42 mol) in ethanol (400 ml) with stirring and refluxing under argon. The refluxing was continued for 10 hr and the mixture was filtered. After the removal of the solvent, the residue (41.5 g) was fractionally distilled under reduced pressure.

Dimethyl-N,N-bis(2-hydroxyethyl)aminomethylphosphine oxide (DMEO)

Ethylene oxide (30.6 g, 0.694 mol) was added portionwise to the stirred under N_2 DMAO (37.2 g, 0.347 mol) at 130–150°C and a pressure of 0.2–0.3 MPa. The reaction mixture was stirred additionally for 30 min under the same conditions and then subjected to a residual pressure of 19.4 hPa at 80°C. Yield 67.8 g. Dimethyl-*N*,*N*-bis(2-hydroxypropyl)aminomethylphosphine oxide (DMPO) was prepared similarly. The properties of the synthesized DPO, DMAO, DMEO and DMPO are listed in Table 1.

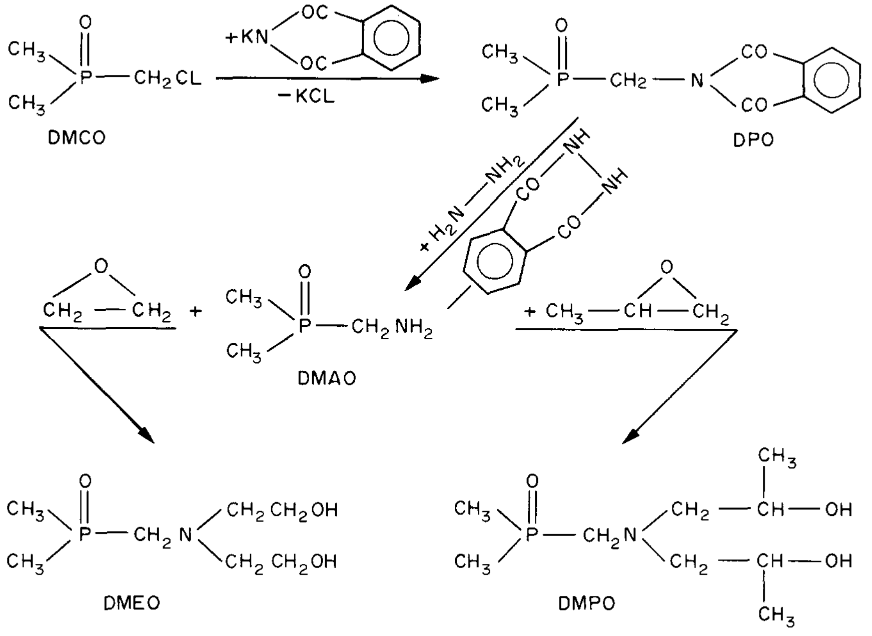
Preparation of rigid polyurethane foams

The oligomeric diphenylmethane diisocyanate (component B) (142 parts by weight), was added to the well homogenized mixture of polyetherpolyol No. 1 (70 parts by weight), polyetherpolyol No. 2 (30 parts by weight), silicon oil (1.5 parts by weight) freon 11 (40 parts by weight) and dimethylcyclohexylamine (0.2 parts by weight). The mixture was vigorously stirred for 10 sec. and then poured into an open box with dimensions of 30 × 20 × 30 cm.

Rigid polyurethane foams with DMEO and DMPO were prepared similarly. In all cases, the ratio between the hydroxyl groups and the isocyanate ones was 1:1.05. The conditions of preparation and the properties of the polyurethane foams are given in Table 3.

Characterization of the synthesized products

The melting points were determined with a Kofler microscope. The i.r. spectra were recorded in KBr pellets or neat on UR-20 apparatus. The ^{1}H-NMR spectra were taken on Bruker 250 MHz instrument at room temperature in $CDCl_3$ with TMS as internal standard. The ^{31}P-NMR spectra were obtained using the same instrument at 101.26 MHz in chloroform against 85% phosphoric acid. The hydroxyl numbers were obtained via acetylation in pyridine [7]. The viscosities of DMEO and DMPO were determined with an



Scheme I

Ubbelohde viscometer. The properties of the polyurethane foams were determined as follows: the density according to Bulgarian State Standard 9846-72; the coefficient of thermal conductivity on an Anacon 88 apparatus according to ASTM-C-518; compressive strength and flex strength according to Bulgarian State Standard 9851-72 and Bulgarian State Standard 10838-73 respectively on an Instron 1122 dynamometer, the oxygen indexes according to ASTM-D-2863 on an FTA instrument of Stanton Redcroft Co., England.

RESULTS AND DISCUSSION

Dimethylaminoethylphosphine oxide is easily accessible making use of the Gabriel method and dimethylchloromethylphosphine oxide, the yields in both stages exceeding 90% (see Scheme 1, Table 1). The isolation of the intermediate DPO is carried out by extracting the reaction mixture with chloroform or methylene chloride and recrystallization with toluene or a chloroform–diethyl ether mixture. In this way DPO is obtained sufficiently pure to permit the synthesis of DMAO without complications. It is also easily isolated since it can be distilled under comparatively mild conditions. Like other primary amines [8, 9], DMAO reacts smoothly with ethylene or propylene oxides in 1:2 mol ratio. This interaction proceeds without catalysts i.e. with ethylene oxide at 130–150°C and 0.2–0.3 MPa and with propylene oxide under somewhat more strenuous conditions at 140–150°C and 0.5–0.6 MPa. DMEO and DMPO are obtained respectively.

The structures of DPO, DMAO, DMEO and DMPO are assigned on the basis of data from elemental analysis for nitrogen and phosphorus, hydroxyl group content (Table 1), i.r., ^{1}H- and ^{31}P-NMR spectroscopy (Table 2). The integral intensities in ^{1}H-NMR spectra correspond to the assumed structures.

The i.r. spectra of the four products contain absorption bands due to the phosphoryl (P=O) and the CH$_3$–P groups at 1160–1180 cm^{-1} and 1300–1310 cm^{-1}, respectively. The i.r. spectrum of DPO contains bands characteristic of the imide ring i.e. 720–735 cm^{-1}, 1375–1380 cm^{-1}, 1720–1730 cm^{-1} and 1780 cm^{-1}; the spectrum of DMAO has bands due to the NH$_2$ function at 2800–3000 cm^{-1} and 3100–3600 cm^{-1}; the spectra of DMEO and DMPO have bands for hydroxyl groups at 3100–3600 cm^{-1}.

Table 1. Some characteristics of dimethylaminomethylphosphine oxide (DPO), dimethylaminomethylphosphine oxide (DMAO), dimethyl-*N*,*N*-bis(2-hydroxyethyl)aminomethylphosphine oxide (DMEO) and dimethyl-*N*,*N*-bis(2-hydroxypropyl)aminomethylphosphine oxide (DMPO)

Compound	Yield (%)	Boiling-point $\left(\frac{^\circ C}{hPa}\right)$	Melting point (°C)	Analysis Nitrogen (%) Calc.	Found	Phosphorus (%) Calc.	Found	Hydroxyl groups content (%) Calc.	Found	n_d^{20}	d_4^{20}	Viscosity 20°C (cP)
DPO	94	—	167–168	5.90	5.90	13.03	13.06	—	—	—	—	—
DMAO	94.5	$\frac{120\text{–}121}{0.3\text{–}0.4}$	35–37	12.73	13.07	28.60	28.92	—	—	—	—	—
DMEO	Quant.	—	—	6.80	7.17	15.53	15.88	17.60	17.44	1.4982	1.2411	14200
DMPO	Quant.	—	—	5.90	6.27	13.42	13.85	15.33	15.24	1.4828	1.1183	17800

Table 2. NMR data of DPO, DMAO, DMEO and DMPO (δ in ppm; J_{H-H} and J_{H-P} in Hz)

	^{1}H-NMR data, protons*											
	CH_3–P=O		CH_2–P=O		Ar–H	C–NH_2	N–CH_2–C		C–CH_2–O	C–CH_3		^{31}P-NMR data
Compound	δ	$^2J_{H-P}$	δ	$^2J_{H-P}$	δ	δ	δ	$^3J_{H-H}$	δ	δ	$^3J_{H-H}$	δ
DPO	1.6 (d)	12	4.1 (d)	8	7.6–7.9	—	—	—	—	—	—	+41.9
DMAO	1.4 (d)	13	2.9 (d)	7	—	1.5 (s)	—	—	—	—	—	+42.4
DMEO	1.5 (d)	12	2.9 (d)	5	—	—	2.8 (t)	5	3.6 (m)	—	—	+42.9
DMPO	1.5 (d)	12	3.0 (d)	4	—	—	2.6 (m)	—	3.8† (m)	1.1 (d)	7	+41.5

*Signal assignment of the hydroxyl protons is difficult, because of overlapping with signals of the protons C–CH_2–O and C–CH–O.
†C–CH–O protons signal.

DPO and DMAO are crystalline substances. DPO is soluble in chloroform, methylene chloride, DMF and water. DMAO is highly hydroscopic and soluble in organic solvents such as chloroform methylene chloride, alcohols, acetone, tetrahydrofuran, benzene toluene, xylene, dioxane (on heating), DMF and dimethylacetamide.

The phosphorus-containing diols DMEO and DMPO are viscous colourless liquids soluble in chloroform, methylene chloride alcohols and acetone. They are insoluble in aromatic and aliphatic hydrocarbons. Left in the open, they absorb atmospheric moisture; as shown by Fig. 1, they are considerably more hydroscopic than ethylene glycol and triethanolamine.

DMEO and DMPO are studied as reactive flame retardants for rigid polyurethane foams. Similarly structured organo-phosphorus compounds are widely studied and used for this purpose [10–12]. The results are given in Table 3. It can be seen that the inclusion of DMEO and DMPO in amounts of 15 and 30% with respect to the polyol component (component A) improves significantly the critical oxygen indexes i.e. ΔOI is within the limits of 2.7–6.0% O_2. Those high ΔOI values are due to the inclusion of 0.9–1.8% of phosphorus in the polyurethanes.

Since DMEO and DMPO are also tertiary amines, they react clearly as catalysts in the process of urethane formation. An indication for this effect is the high reaction rates observed (short reaction times T_1, T_2 and T_3) in comparison with control samples. It is even necessary in the preparation of rigid polyurethanes with DMEO to cool the components A and B prior to mixing. This allows a decrease in the concentration of the dimethylcyclohexylamine used as a catalyst.

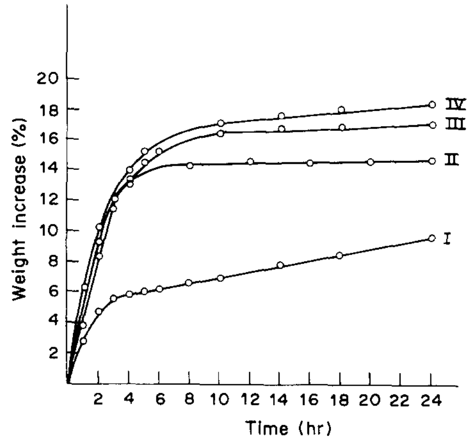


Fig. 1. Water absorption of: (I) triethanolamine; (II) ethylene glycol; (III) DMEO; (IV) DMPO.

DMEO and DMPO do not affect adversely the physical and mechanical properties of the rigid polyurethane foams (Table 3). Thus, DMEO and DMPO

Table 3. Preparation and properties of the rigid polyurethane foams, modified with DMEO and DMPO

Characteristics	Without PCD	Phosphorus containing diols (PCD) DMEO		DMPO	
PCD quantity toward to polyol component A (%)	0	15	30	15	30
Phosphorus content in the polyurethane foams (%)	0	1.03	1.80	0.90	1.65
Components temperature before mixing (°C)	22	18	18	22	22
T_1—cream time (sec)	17	13	5	22	17
T_2—gel time (sec)	80	54	23	55	40
T_3—tack free time	143	114	58	90	75
Free rise density (kg/m^3)	30.6	32.4	35.3	34.0	34.9
Thermal conductivity (W/m.K)	0.0193	0.0194	0.0212	0.0193	0.0190
Compressive strength at 10% deflection:					
—parallel to foam rise (MPa)	0.150	0.184	0.347	0.204	0.225
—perpendicular to foam rise (MPa)	0.082	0.113	0.299	0.131	0.102
Hysteresis at 10% deflection:					
—parallel to foam rise (%)	76.1	65.9	74.8	76.7	75.6
—perpendicular to foam rise (%)	69.2	65.5	75.9	70.6	61.2
Flexure strength (MPa)	0.233	0.431	0.448	0.456	0.547
Flexural modulus (MPa)	2.79	7.63	7.74	8.84	10.54
Maximal strain (%)	11.6	11.3	10.9	13.5	11.6
Critical oxygen index (% O_2)	19.7	23.3	25.7	22.4	24.7
Increasing of the critical oxygen index (% O_2)	—	3.6	6.0	2.7	5.0

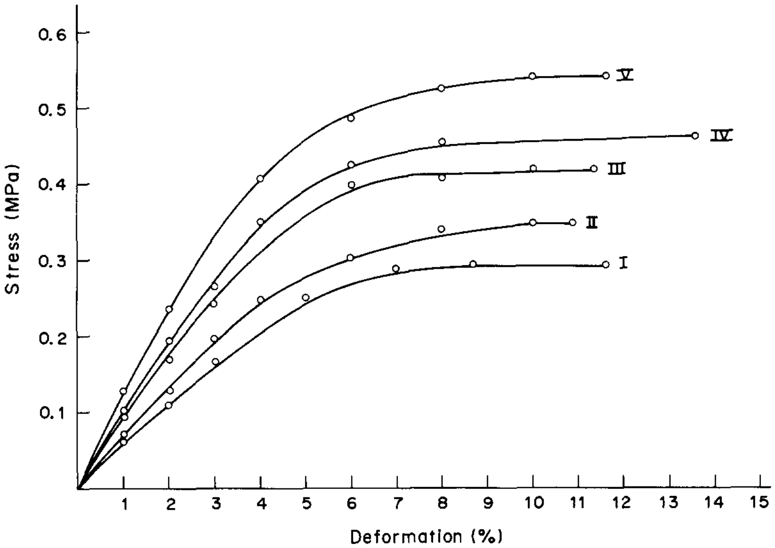


Fig. 2. Relationship between stress and deformation in flex test of rigid polyurethane foams containing in the polyol component: (I) control sample; (II) 30% DMEO; (III) 15% DMEO; (IV) 15% DMPO; (V) 30% DMPO.

do not affect the type and size of the cells of the rigid foams, as indicated by the observation that the thermal conductivity remains practically constant, with the exception of the case of polyurethane foam prepared with 30% DMEO where the high rate of formulation of the foam results in opening of the cells. DMEO and DMPO increase the compressive strength of the polyurethane foams both parallel and perpendicular to the foam rise; the same effect is also observed for the flexural strength (Table 3, Fig. 2). This latter effect is also an indication that DMEO and DMPO are included in the structure of the polymer.

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