(4) Polymers with a mixed arrangement of substituents form thermal dehydrochlorination and carbonization products with a higher electrical conductivity than those obtained from polyvinylchloride.

Translated by E. O. PHILLIPS

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ORGANOPHOSPHORUS POLYAMIDES BASED ON METHYLDI-(*m*-AMINOPHENYL)PHOSPHINE OXIDE*

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IT HAS been shown previously that phosphine oxide derivatives containing two carboxyl groups can serve as starting materials for the production of polyamides [1–3]. The present work was concerned with the synthesis of a phosphine oxide containing two amino groups and the polycondensation of this with dicarboxylic acids. The starting material was methyldiphenylphosphine oxide, prepared by the method of Arbuzov [4], and which has now become available as a result of a new method of preparation of diphenylchlorophosphine [5]. The complete scheme of the synthesis is as follows. 1) Disproportionation of phenyldichlorophosphine in the presence of aluminium chloride, 2) conversion of dichlorophenylphosphine to the methyl ester of diphenylphosphinic acid, 3) isomerization (in contrast to the

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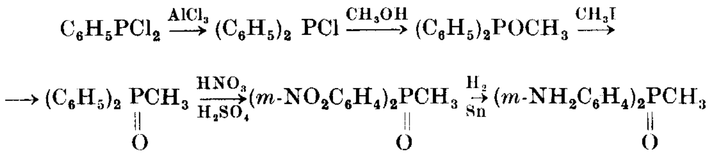
* Vysokomol. soyed. **5**: No. 9, 1309–1314, 1963.

method of reference [4] isomerization of the methyl ester was carried out in ether, which improves the smoothness of the reaction, the yield and purity of the product), 4) nitration of the methyldiphenylphosphine oxide and 5) reduction of the product to methyldi-(*m*-aminophenyl)phosphine oxide.



$$C_6H_5PCl_2 \xrightarrow{AlCl_3} (C_6H_5)_2\,PCl \xrightarrow{CH_3OH} (C_6H_5)_2POCH_3 \xrightarrow{CH_3I}$$

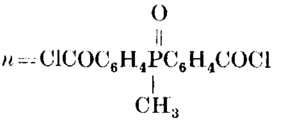
$$\longrightarrow (C_6H_5)_2\,\underset{\displaystyle O}{\underset{\|}{P}}CH_3 \xrightarrow[H_2SO_4]{HNO_3} (m\text{-}NO_2C_6H_4)_2\underset{\displaystyle O}{\underset{\|}{P}}CH_3 \xrightarrow[Sn]{H_2} (m\text{-}NH_2C_6H_4)_2\underset{\displaystyle O}{\underset{\|}{P}}CH_3$$

With regard to the position of the NO_2 groups, it has been proved that triphenylphosphine oxide nitrates in the *meta*-position [6] and it must be assumed that in the present case the nitro-group is in the *meta*-position.

Methyldi-(*m*-aminophenyl)phosphine oxide is a crystalline substance melting at 145–147°. It is readily soluble in water and alcohol and exhibits the properties of an aromatic amine. According to Bride, Cummings and Pickles [7] this compound boils at 250–260° at 0·02–0·03 mm. These authors do not quote a melting point. It forms a dipicrate, is acetylated by acetic anhydride giving methyldi-(*m*-acetylaminophenyl)phosphine oxide, is easily diazotized and the *bis*-diazo compound couples with *β*-naphthol to form a red–orange dye.

Methyldi-(*m*-aminophenyl)phosphine oxide (MDPO) was condensed with some dicarboxylic acid chlorides by the interfacial method. This gave phosphorus-containing polyamides, some of the properties of which are presented in Table 1. These polyamides are white or light-yellow powders, readily soluble in hydro-

TABLE 1. PROPERTIES OF PHOSPHORUS-CONTAINING POLYAMIDES OBTAINED FROM METHYLDI-(*m*-AMINOPHENYL)PHOSPHINE OXIDE AND THE ACID CHLORIDES OF SOME DICARBOXYLIC ACIDS

Experiment No.*	Dicarboxylic acid chloride	Yield of polyamide, % of theory	Temperature, °C		Reduced viscosity $[\eta_{sp}/c]_{c=0\cdot5}$
			of onset of softening †	of fibre formation	
1	 $n\text{-}ClCOC_6H_4\underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle O}{\overset{\|}{P}}}}C_6H_4COCl$	85	320	342–345	0·40
2	$n-ClCOC_6H_4COCl$	88	290	325–330	0·44
3	$ClCO(CH_2)_4COCl$	32	141	199–203	0·28
4	$ClCO(CH_2)_8COCl$	35	133	170–175	0·46

* Determined by heating under a layer of paraffin [8].

† The softening points of polyamides prepared by the equilibrium polycondensation method [7], under conditions giving polymers of low molecular weight, were for 2 — 230° and for 3 — 184°.

chloric, sulphuric and formic acids, and in cresol and benzyl alcohol. They are less soluble in dimethylformamide and insoluble in chloroform, acetone, dioxan, benzene and cyclohexane.

The X-ray diffraction patterns show that all these polyamides are amorphous. They can all be formed into fibres.

For the polymer obtained with methyldi-(*p*-carboxyphenyl)phosphine oxide, in order to find the optimal conditions of preparation a study was made of the variation of the reduced viscosity and yield of the polymer with change in concentration of the reagents. The results are presented in Fig. 1.

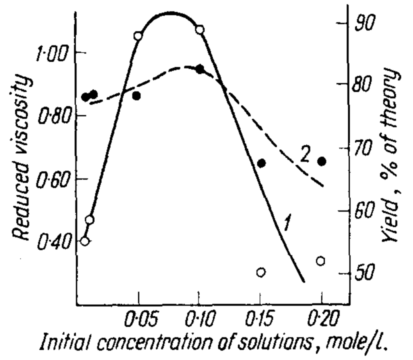


FIG. 1. Variation in the reduced viscosity (*1*) and yield (*2*) of the polyamide with initial concentration of methyldi-(*m*-aminophenyl)phosphine oxide and the acid chloride of methyl-di-(*p*-carboxyphenyl)phosphine oxide.

It is seen from Fig. 1 that the polymer of highest viscosity (and therefore of highest molecular weight) is obtained in highest yield when the concentration of the reagent solutions is 0·05–0·10 mole/l.

From Table 1 it is seen that in the preparation of polyamides from the phosphorus-containing diamine and aliphatic or aromatic dicarboxylic acid chlorides the yield of the polyamides depends to a considerable extent on the nature of the acid chloride used. When the acid chloride is aromatic, i.e. the acid chloride of methyldi-(*p*-carboxyphenyl)phosphine oxide or of terephthalic acid, the yield of polyamide is higher than when the acid chloride is aliphatic (adipic or sebacic). This is evidently associated with the higher rate of hydrolysis of aliphatic diacid chlorides in comparison with aromatic acid chlorides under the conditions of interfacial polycondensation, which has been demonstrated previously [9].

It is noteworthy that the polyamides from MDPO are of higher molecular weight than those obtained under the same conditions from ordinary aromatic diamines. This is possibly associated with the basic properties of the P=O group of the oxide.

The variation in softening point of the polyamides with composition (Fig. 2) follows the same relationships as for polyamides obtained from methyldi-(*p*-carboxyphenyl)phosphine oxide with various diamines [2]. Thus from Table 1 and Fig. 2 it is seen that the softening point and flow temperature fall with increasing length of the carbon chain of the dicarboxylic acid. On the other hand polyamides containing aromatic dicarboxylic acid units soften at a considerably higher temperature than those containing aliphatic dicarboxylic acid units.

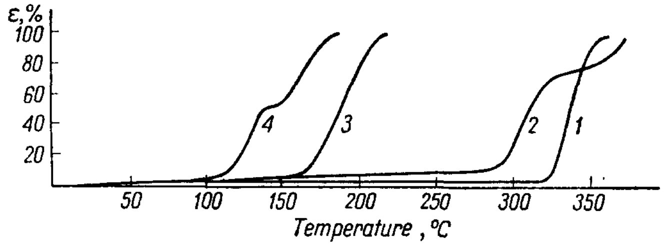
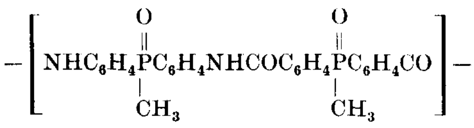


FIG. 2. Thermomechanical curves of polyamides obtained from methyldi-(*m* aminophenyl)-phosphine oxide and various acid chlorides: *1*—acid chloride of methyldi-(*p*-carboxyphenyl)-phosphine oxide; *2*—terephthalyl chloride; *3*—adipyl chloride; *4*—sebacyl chloride.

An interesting and valuable property of these polyamides is their nonflammability. When placed in the flame of a burner they smoulder and char, but when removed from the flame they extinguish immediately. This nonflammability is associated with the presence of phosphoryl groups in the polymers. In this connection the polyamide in which both components contain phosphorus, i.e. the polymer with the repeating unit is of great interest.

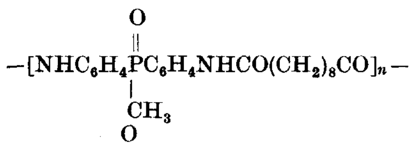
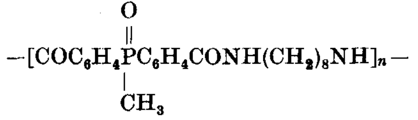


$$-\left[\mathrm{NHC_6H_4\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{P}}C_6H_4NHCOC_6H_4\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{P}}C_6H_4CO}\right]-$$

The phosphorus content of this polymer is about 12% whereas in the polyamides with only one phosphorus-containing components the phosphorus content is ~8%. This polymer is also interesting because it has a high melting point (it softens at about 320° and does not decompose up to 370°).

Two of us have reported previously [10] that the melting point of polyamides is dependent on their content of amide groups, which form hydrogen bonds, and is independent of the manner in which these are distributed in the macromolecule. This can be illustrated by our results on polymers containing phosphorus heteroatoms. Thus the polyamide from MDPO and sebacic acid described above is similar in this respect to the polyamide described previously from methyldi-(*m*-carboxyphenyl)phosphine oxide and octamethylenediamine. It would therefore be expected that their flow temperatures would be the same.

TABLE 2. COMPARISON OF SOME PROPERTIES OF PHOSPHORUS-CONTAINING POLYAMIDES OF COMPARABLE STRUCTURE*

Structural unit of polyamide	Temperature, °C		Reduced viscosity
	of onset of softening	of fibre formation	
 $-[NHC_6H_4\overset{O}{\overset{\|}{\underset{CH_3}{\underset{\|}{P}}}}C_6H_4NHCO(CH_2)_8CO]_n-$	133	169–175	0·46
 $-[COC_6H_4\overset{O}{\overset{\|}{\underset{CH_3}{\underset{\|}{P}}}}C_6H_4CONH(CH_2)_8NH]_n-$	133	156–158	0·30

* In both phosphorus-containing components the functional groups are in the *meta*-position.

It is seen from Table 2 that the softening points of these polyamides coincide. The difference in the temperature of fibre formation is possibly associated with the difference in molecular weight of the two polyamides. The presence of aromatic nuclei directly attached to the amide groups can also have an effect here.

EXPERIMENTAL

Methyl ester of diphenylphosphinic acid. Triethylamine (22 g, 0·22 mole) in 40 ml of ether was added with stirring and cooling to 0–5°, to 44 g (0·2 mole) of diphenylchlorophosphine [5] in 20 ml of ether under a stream of nitrogen. A solution of 6·4 g (0·2 mole) of methanol in 40 ml of ether was then added over a period of 1 hour. The mixture was stirred for a further hour at room temperature and allowed to stand overnight. Triethylamine hydrochloride was then filtered off, the ether evaporated and the residue distilled *in vacuo*. This yielded 35·5 g (82% of theory) of a substance of b.p. 117–119/3 mm, n_D^{20} 1·6040, d_4^{20} 1·1002. According to reference [4], b.p. 151–152°/10 mm, n_D^{20} 1·6030, d_4^{20} 1·1040, yield 52%.

Methyldiphenylphosphine oxide. Methyl iodide (2 g, 0·014 mole) was added dropwise, with stirring, to 5 g (0·023 mole) of the methyl ester of diphenylphosphinic acid in 20 ml of dry ether at 35–40°. The mixture was stirred for a further hour at this temperature and then allowed to stand overnight. The colourless, crystalline product was filtered off and washed with ether. Yield, 4·8 g (96% of theory) of m.p. 110–112°. According to reference [4], m.p. 108–109°.

Methyldi-(m-nitrophenyl)phosphine oxide. Methyl-diphenylphosphine oxide (30 g, 0·14 mole) was added gradually with stirring, to a mixture of 30 ml of nitric acid (s.g. 1·52) and 60 ml of sulphuric acid (s.g. 1·83) at a rate adjusted to keep the temperature of the mixture below 15–20°. The reaction mixture was then added carefully to a large quantity of ice-water. An oil then separated and this gradually formed a yellowish solid deposit. The solid product was filtered off, washed with water until the water became free from acid, dried and recrystallized from alcohol. Yield 30 g (74% of theory) of a substance of m.p. 199–200°. According to reference [7], m.p. 205–205·5°.

		C		H		P		N	
	Found, %:	C 51·4;	51·5;	H 4·0;	3·8;	P 10·1;	10·3;	N 9·4;	9·3.
$C_{13}H_{11}O_5PN_2$.	Calculated, %:	C 51·0;		H 3·6;		P 10·1;		N 9·2.	

Methyldi-(m-aminophenyl)phosphine oxide. Methyldi-(*m*-nitrophenyl)phosphine oxide (5 g) was added gradually to a mixture of 14 g of granular tin and 50 ml of concentrated hydrochloric acid, keeping the temperature of the mixture below 30–35° (with cooling). The mixture was then allowed to stand overnight. On the following day the reaction mixture was heated at 60° for 5 hours. The tin was then filtered off, the filtrate was diluted with water to 400 ml and hydrogen sulphide was passed through the solution until all the tin had been precipitated. The stannic sulphide was filtered off and washed with water, and the combined filtrate and washings were evaporated *in vacuo* to dryness. The residue was dissolved in 20 ml of absolute alcohol, and sodium ethoxide (0·8 g of sodium in 25 ml of absolute alcohol) was added to the solution. Sodium chloride was filtered off and washed with a small quantity of alcohol. The alcohol was evaporated from the solution and the residue was recrystallized from dichloro-ethane. Yield, 2·6 g (60% of theory) of a faintly yellow substance of m.p. 145–147°.

Found, %: C 63·5; 63·2; H 6·3; 6·2; P 12·4; 12·4; N 11·7; 11·7.
$C_{13}H_{15}OPN_2$. Calculated, %: C 63·4; H 6·1; P 12·6; N 11·4.

The picrate of methyldi-(m-aminophenyl)phosphine oxide melted at 153–155° (from alcohol)

Found, %: C 42·1; 42·3; H 3·2; 3·4; P 3·9; 4·3; N 15·4; 15·4.
$C_{25}H_{21}O_{15}PN_8$. Calculated, %: C 42·6; H 3·0; P 4·4; N 15·9.

Methyldi-(m-acetylaminophenyl)phosphine oxide. Two grams of acetic anhydride was added to 0·45 g (0·0018 mole) of methyldi-(*m*-aminophenyl)phosphine oxide and the mixture was heated on the boiling water bath for 30 minutes. The solid product was filtered off and washed with ether. Yield 0·52 g (86% of theory) of a substance of m.p. 275–277° (from aqueous alcohol).

Found, %: C 62·0; 62·0; H 6·1; 6·5; P 9·3; 9·6.
$C_{17}H_{18}O_3PN_2$. Calculated, %: C 62·6; H 5·9; P 9·5.

Bis-azo dye from methyldi-(m-aminophenyl)phosphine oxide and β-naphthol. β-Naphthol (0·72 g) in 10 ml of 10% alkali solution was added to the solution obtained by diazotization of 0·62 g of methyldi-(*m*-aminophenyl)phosphine oxide. The mixture was acidified with concentrated hydrochloric acid and the precipitate was filtered off and washed with water to neutral reaction. The product was dried to constant weight at 75°. Yield 0·94 g (67% of theory) of a red–orange material.

Found, %: C 71·6; 72·0; H 4·9; 4·8; P 5·3; 5·3.
$C_{33}H_{25}O_3PN_4$. Calculated, %: C 71·2; H 4·5; P 5·6.

Methyldi-(p-chloroformylphenyl)phosphine oxide Methyldi-(*p*-carboxylphenyl)phosphine oxide (9·50 g) was heated with 30 ml of thionyl chloride until a clear solution was obtained (temperature not above 50°). The excess thionyl chloride was then distilled off *in vacuo*. The residue was dissolved in 80–100 ml of dry benzene and reprecipitated by dry petroleum ether. Yield 9·34 g (86% of theory), m.p. 110–112°.

Found, %: C 52·9; 52·7; H 3·5; 3·2; P 8·6; 8·8; Cl 20·5; 20·0.
$C_{15}H_{11}PO_3Cl_2$. Calculated, %: C 52·8; H 3·2; P 9·0; Cl 20·8.

Saponification number. Found: 650; 642; Calculated 658.

The polycondensation reaction was carried out by the method described in reference [8] by stirring a solution of the acid chloride in benzene with a solution of the diamine in aqueous alkali. The polyamide formed was washed with benzene to remove excess acid chloride, and then with water, and dried in a vacuum oven. The initial concentration of the two reagent solutions was 0·01 mole/l. This had been found previously to be the optimal concentration for the preparation of polyamides from organophosphorus dicarboxylic acids (phenyl and methyl-di-(*p*-carboxyphenyl)phosphine oxides [8].

CONCLUSIONS

(1) Methyldi-(*m*-aminophenyl)phosphine oxide has been synthesized by a new route and some derivatives of this compound have been prepared.

(2) Polyamides containing phosphoryl groups have been prepared by interfacial polycondensation of methyldi-(*m*-aminophenyl)phosphine oxide with the acid chlorides of certain dicarboxylic acids, including that of methyldi-(*p*-carboxyphenyl)phosphine oxide.

Translated by E. O. PHILLIPS

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