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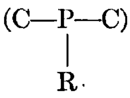
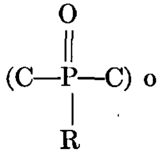
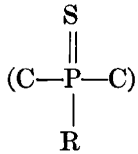
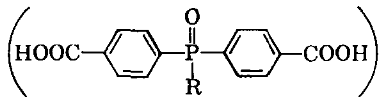
Polyamides Containing Phosphorus. I. Preparation and Properties*

JOSEPH PELLON and W. G. CARPENTER, *Chemical Research Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut*

INTRODUCTION

Phosphorus chemistry related to trivalent phosphorus (phosphines) has been greatly expanded in recent years. It was of interest to extend this into the polymer field by introducing trivalent phosphorus into a polymer backbone structure and studying the resultant structural effects. While polymers containing other phosphorus groups are known,[1,2] phosphine units had not previously been incorporated into well-defined polymer systems. The present study deals with the preparation and characterization of polyamides containing phosphine  $(\mathrm{C{-}\underset{\underset{\displaystyle R}{|}}{P}{-}C})$ and related oxide  $(\mathrm{C{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R}{|}}{P}}{-}C})$ or sulfide  $(\mathrm{C{-}\overset{\overset{\displaystyle S}{\|}}{\underset{\underset{\displaystyle R}{|}}{P}}{-}C})$ groups in their backbone structure.

Polyesters and polyamides derived from bis(*p*-carboxyphenyl)-phosphine oxides



have previously been prepared by Korshak, Frunze and co-workers[3-7] and others.[8-9] Efforts to prepare polymers of the class considered here by less conventional routes have also been described.[10-14]

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EXPERIMENTAL

Materials

Phosphorus-Containing Monomers. The monomers bis(3-aminopropyl)-phenylphosphine, b.p. 140–150°C./1 mm., $n_D^{25} = 1.5722$; bis(3-aminopropyl)-*n*-octylphosphine, b.p. 155–163°C./0.5 mm., $n_D^{25} = 1.4948$, anal. theory, C 64.62, H 12.69, P 11.92, N 10.77: found C 64.23, H 12.85, P 11.85, N 10.88, and bis(3-aminopropyl)-isobutylphosphine, b.p. 94°C./0.2 mm., $n_D^{25} = 1.5014$, anal. theory, C 58.52, H 12.25, P 15.19, N 13.73; found, C 58.52, H 12.46, P 14.89, N 13.63 were prepared by the free radical-initiated (azobisisobutyronitrile) addition of allylamine to the appropriate phosphine. Bis(2-cyanoethyl)phenylphosphine[15] was similarly prepared from phenylphosphine and acrylonitrile. Bis(3-aminopropyl)phenylphosphine oxide, b.p. 290–302°C./0.45, $n_D^{25} = 1.5690$ was prepared by hydrogen peroxide oxidation of bis(3-aminopropyl)phenylphosphine. Bis(2-cyanoethyl)phenylphosphine sulfide, m.p. 74–75°C., anal. theory, C 58.07, H 5.34, P 12.50, N 11.29, S 12.90: found C 57.77, H 5.41, P 12.47, N 11.28, S 12.63 was obtained by treatment of bis(2-cyanoethyl)phenylphosphine with sulfur. Bis(3-aminopropyl)methylphosphine oxide, 165–166°C./0.2 mm., $n_D^{25} = 1.5098$, anal. theory, C 47.19, H 10.67, P 17.41, N 15.73; found, C 46.57, H 11.93, P 16.94, N 15.86 was prepared from bis(2-cyanoethyl)-methylphosphine[16] by first oxidizing the phosphine with hydrogen peroxide in acetic acid followed by catalytic reduction of the nitrile groups with Raney cobalt in ethanol. 3-Aminopropyl-4-aminobutylmethylphosphine oxide, b.p. 186–188°C./0.5 mm., $n_D^{25} = 1.5060$, anal. theory, C 49.98, H 11.01, N 14.58, P 16.11; found C 49.93, H 11.01, N 14.11, P 15.46, was similarly prepared. Bis(2-carboxyethyl)phenylphosphine oxide, m.p. 203.5–205°C. anal. theory, C 53.33, H 5.55, P 11.48; found C 53.17, H 5.85, P 11.35 was prepared directly from bis(2-cyanoethyl)phenylphosphine by hydrolysis with sodium hydroxide in aqueous solution. Bis-(2-carboxyethyl)methylphosphine oxide, m.p. 161–163°C., anal. theory, C 40.39, H 6.25, P 14.90; found C 33.50, H 5.70, P 15.87 was similarly prepared from bis(2-cyanoethyl)methylphosphine. Bis(*p*-carboxyphenyl)-phenylphosphine oxide, m.p. 334–336°C. was prepared by the method of Morgan and Herr.[17]

Coreactants. The following chemicals were used as received: hexamethylenediamine, piperazine, sebacic acid, dimethyl oxalate, and terephthalic acid (Distillation Products Ind.); decamethylenediamine and 3-methyladipic acid (Aldrich Chemical Co.); bis(carboxyethyl)sulfide (Evans Chemetics Ind.); 3,3′-(methylimino)-bispropylamine (American Cyanamid Co.); *m*-cresol and formic acid (J. T. Baker Chem. Co.). Heptamethylenediamine (m.p. 28°C., b.p. 74–76°C./2 mm.) was kindly supplied by Dr. P. Paré of this laboratory.

Polymer Synthesis

Preparation of Polyamides from the amine salt or equivalent amounts of diamine and diacid components[18] was carried out in 30 × 1.8 cm. tubes formed by closing one end of a length of Fischer-Porter glass piping. These tubes were sealed during the first stage of the polymerization either by using a special stainless steel screw-type closure[19] or preferably by a high pressure, three-way valve (Fischer-Porter Co.). Polymerizations were carried out under deaerated conditions. In a typical preparation 2 g. of the salt of adipic acid and bis(3-aminopropyl)phenylphosphine were placed in a tube which was then deaerated and sealed. The initial polymerization stage involved heating for 2 hr. at 200°C. in a Wood's metal bath having a Thermocap temperature controller. Polymerization was completed by an additional heating period of 2 hr. at 250°C., during which time the pressure was reduced to a few millimeters.

The polyamide obtained, poly-bis(3-aminopropyl)phenylphosphine adipamide, is a hard, clear, colorless to faint yellow polymer having an $[\eta]_{\mathrm{HCOOH}}^{30°}$ in the range of 2 to 3.

Anal. Calc.: C; 64.6%; H, 8.08%; N, 8.38%; P, 9.28%. Found: C, 63.25%; H, 8.29%; N, 8.86%; P, 9.10%.

It is soluble in formic acid, cresol, dimethylformamide, dimethyl sulfoxide, and aqueous alcohol and has a softening temperature at 70–80°C. It readily forms fibers and films, shows good metal bonding characteristics and is considerably less flammable than nylon 66.

In a typical polyamide preparation starting with a diamine and a phosphorus-containing dinitrile,[20] 2 g. (9.3 mmole) of bis(2-cyanoethyl)phenylphosphine, 1.08 g. (9.3 mmole) of hexamethylenediamine and 2.68 g. (32.2 mmole) of water were placed in a glass tube which was then inserted in an autoclave. After deaeration the autoclave was heated for 20 hr. at 200°C. At the end of this heating period, the autoclave was allowed to cool and liberated ammonia slowly vented. Polymerization was completed by further heating for 2 hr. at 255°C. at autogeneous pressures and finally 2 hr. at 255°C. at reduced pressure.

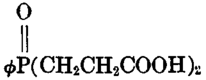
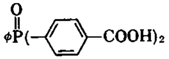
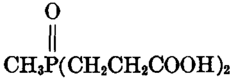
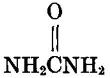
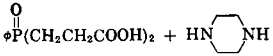
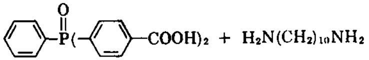
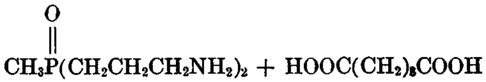
Polymer Characterization

Reduced and intrinsic viscosities were determined in Cannon-Ubbelodhe dilution viscometers. Adhesive tests were performed on test blocks of $^1/_2$ in.^{2} circular contact area. Metal blocks were cleaned with carborundum paper (#400/w), washed with acetone, and immersed in cleaning solutions: aluminum blocks were immersed for 10 min. in dichromate solution, steel for 2 min. in a mixture of nitric acid, hydrochloric acid, and formaldehyde, and copper dipped into nitric acid. After rinsing and air-drying, the blocks were heated on a hot plate to temperature sufficient to melt the polymer. Polymer was melted onto the blocks which were then pressed together under minimum pressure to insure proper spreading and joint formation. After conditioning (>24 hr. at 23°C., 50% R.H.) the force required to rupture the joint (in tension) was measured on the Baldwin tester. In a few designated cases the samples were conditioned 24 hr. at 23°C. over Drierite. In most cases, a minimum of three deter-

TABLE I

Summary of Physical Data on Phosphorus Polyamides and Related Materials

No.	Coreactant	Appearance	Reduced viscosity, dl./g.[a]	Softening temp., °C.[b]	Flow temp., °C.	Density, g./cc.[c]
	A. Adipic acid polyamides					
1	$H_2N(CH_2)_6NH_2$	Hard, tough, white, opaque	1.53	220	268	1.13
2	$H_2N(CH_2)_7NH_2$	Hard, tough, off-white, opaque	0.94	—	245	1.104
3	$\phi P(CH_2CH_2CH_2NH_2)_2$	Hard, tough, transparent, colorless	2.64	72	200	1.16
4	$n\text{-}C_8H_{17}P(CH_2CH_2CH_2NH_2)_2$	Soft, tough, white, opaque	0.87	135	160–170	1.08
5	$i\text{-}C_4H_9P(CH_2CH_2CH_2NH_2)_2$	Hard, tough, transparent, colorless	1.5	100–110	120	—
6	$\phi\overset{\overset{O}{\|}}{P}(CH_2CH_2CH_2NH_2)_2$	Soft, tough, transparent, straw yellow	1.35	100	125–160	—
7	$CH_3\overset{\overset{O}{\|}}{\underset{\underset{(CH_2)_4NH_2}{\vert}}{P}}\text{—}(CH_2)_3NH_2$	Hard, tough, transparent, colorless, tends to become tacky in air	0.91	70–80	145–147	1.15
8	$CH_3\overset{\overset{O}{\|}}{P}(CH_2CH_2CH_2NH_2)_2$	Hard, tough, transparent, slightly yellow	1.20	90–100	165	1.2
9	$CH_3N(CH_2CH_2CH_2NH_2)_2$	Hard, brittle, transparent, slightly brown	0.36	70–75	105–110	1.11–1.12
	B. Hexamethylenediamine polyamides					
10	$HOOCCH_2\underset{\underset{CH_3}{\vert}}{CH}CH_2CH_2COOH$	Hard, tough, white opaque	1.12	170	230–235	1.094
11	$\phi P(CH_2CH_2CN)_2$	Transparent, greenish solid	0.30	42–48	52–95	—
12	$\phi\overset{\overset{S}{\|}}{P}(CH_2CH_2CN)_2$	Hard, transparent, dark colored	0.17	65–70	87–130	—

13	 $\phi\overset{O}{\overset{\parallel}{P}}(CH_2CH_2COOH)_2$	Hard, tough, translucent, colorless	0.4	50–60	120–155	—
14		Hard, tough, transparent, colorless	$[\eta]^{0.42}_{cresol}$	228	Never free flowing	—
15	 $CH_3\overset{O}{\overset{\parallel}{P}}(CH_2CH_2COOH)_2$	Hard, brittle, transparent, yellow	0.50	68–72	100–140	—
16	$S(CH_2CH_2COOH)_2$		0.46	203–205	215–216	—
	C. Bis(3-aminopropyl)phenylphosphine polyamides					
17	$HOOC(CH_2)_8COOH$	Hard, tough, transparent, colorless	0.83	37	50–60	1.102
18	$CH_3OOCCOOCH_3$	Hard, brittle, transparent, straw yellow	0.42	74–75	80–100	1.208
19	 $NH_2\overset{O}{\overset{\parallel}{C}}NH_2$	Hard, brittle, transparent, colorless	0.70	84	105	1.174
20		Hard, tough, translucent, straw yellow	1.47	135	165–240	—
	D. Miscellaneous					
21	$n\text{-}C_8H_{17}P(CH_2CH_2CH_2NH_2)_2 + CH_3OOCCOOCH_3$	Soft, tough, transparent, yellow	0.33	40–42	65–70	1.086
22		Hard, brittle, translucent, colorless	0.33	95–105	155–190	—
		Hard, tough, transparent colorless	$[\eta]^{0.43}_{cresol}$	175 195	210 270	—
24	 $CH_3\overset{O}{\overset{\parallel}{P}}(CH_2CH_2CH_2NH_2)_2 + HOOC(CH_2)_8COOH$	Hard, tough, transparent, pale yellow	0.63	35–40	60–100	

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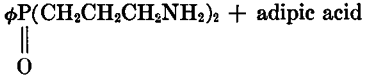
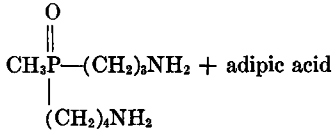
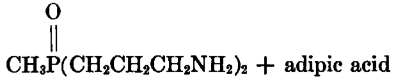
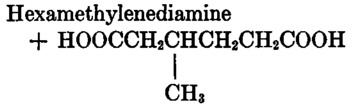
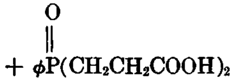
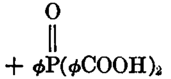
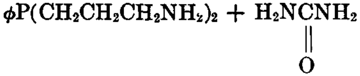
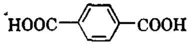
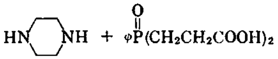
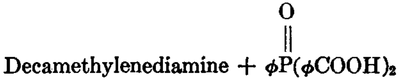
[a] Reduced viscosity in formic acid at 30°C. and 0.1% concentration.

[b] Initial softening of polymer under mild probing on a Fisher John's melting point apparatus.

[c] Gradient density technique.

TABLE II
Polymer Solubilities

		Stability[a]											
No.[b]	Monomers	Chloro-benzene	Hexane	Acetone	Aceto-nitrile	Water	Chloroform	Ethanol (2B)	5% HCl	Dimethyl-formamide	C-7 Fluoro-alcohol	Cresol	Formic acid
1	Hexamethylenediamine + adipic acid	—	—	—	—	—	—	—	—	—	—	+2	+3
2	$H_2N(CH_2)_7NH_2$ + adipic acid	—	—	—	—	—	—	—	—	—	—	+3	+3
3	$\phi P(CH_2CH_2CH_2NH_2)_2$ + adipic acid	—	sw	—	—	—	—	+	+3	+2	—	+	+3
4	$n\text{-}C_8H_{17}P(CH_2CH_2CH_2NH_2)_2$ + adipic acid	sw	—	—	—	—	+3	—	sw	+1	+1	+1	+3
5	$i\text{-}C_4H_9P(CH_2CH_2CH_2NH_2)_2$ + adipic acid	—	—	+2	—	sw	—	—	+2	sw	—	+2	+2
6	 $\phi\underset{\overset{\Vert}{\mathrm{O}}}{\mathrm{P}}(\mathrm{CH_2CH_2CH_2NH_2})_2$ + adipic acid	—	—	—	—	sw	sw	+3	+2	+1	+2	+2	+3
7	 $\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\Vert}{\underset{\underset{(\mathrm{CH_2})_4\mathrm{NH_2}}{\vert}}{\mathrm{P}}}}\text{—}(\mathrm{CH_2})_3\mathrm{NH_2}$ + adipic acid	—	—	—	—	+2	—	+2	+2	—	+2	+2	+3
8	 $\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{P}}}(\mathrm{CH_2CH_2CH_2NH_2})_2$ + adipic acid	—	—	—	—	+3	—	+1	+3	—	+2	+2	+3
9	$CH_3N(CH_2CH_2CH_2NH_2)_2$ + adipic acid	—	—	—	—	+3	+3	+3	+3	+1	+2	+2	+3
10	 Hexamethylenediamine + $\mathrm{HOOCCH_2}\underset{\underset{\mathrm{CH_3}}{\vert}}{\mathrm{CH}}\mathrm{CH_2CH_2COOH}$	—	—	—	—	—	—	—	—	—	+3	+3	+3

13	Hexamethylenediamine  $+ \phi\overset{\overset{O}{\|}}{P}(CH_2CH_2COOH)_2$	—	—	—	sw	sw	sw	+2	sw	+2	+2	+2	+2
14	Hexamethylenediamine  $+ \phi\overset{\overset{O}{\|}}{P}(\phi COOH)_2$	—	—	—	—	—	—	sw	—	+2	+1	+1	sw
16	Hexamethylenediamine $+ S(CH_2CH_2COOH)_2$	—	—	—	—	—	—	—	—	+1	sw	+2	+3
17	$\phi P(CH_2CH_2CH_2NH_2)_2$ + sebacic acid	—	—	—	—	—	sw	—	sw	—	+3	+3	+3
18	$\phi P(CH_2CH_2CH_2NH_2)_2$ $+ CH_3OOCCOOCH_3$	—	—	—	sw	—	+2	—	+3	+3	+2	+2	+3
19	 $\phi P(CH_2CH_2CH_2NH_2)_2 + H_2N\underset{\underset{O}{\|}}{C}NH_2$	—	—	—	—	—	sw	sw	+3	+3	+3	+3	+3
20	$\phi P(CH_2CH_2CH_2NH_2)_2$ 	—	—	—	—	—	—	sw	sw	+2	—	+2	+2
21	$n\text{-}C_8H_{17}P(CH_2CH_2CH_2NH_2)_2$ $+ CH_3OOCCOOCH_3$	—	—	—	+2	—	+3	—	+3	+1	+3	+3	+3
22		—	—	—	sw	sw	+3	+1	+3	+3	+2	+2	+3
23	 $\text{Decamethylenediamine} + \phi\overset{\overset{O}{\|}}{P}(\phi COOH)_2$	—	—	—	—	—	sw	sw	—	+3	+2	+2	sw

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[a] Code: (+3) immediately soluble (2–3 hr.); (+2) soluble on standing 24 hr.; (+1) soluble on heating; (sw), swollen; (—) insoluble even after heating.

[b] Numbering system is not consecutive but corresponds to that of Table I.

minations was made on each polymer, and the scatter of the results was about 20%. Tensile and flexural strength data were determined with an Instron tester by slightly modified ASTM test procedures. Thermogravimetric analysis was determined by heating samples in air at a rate of 10°C./min.

RESULTS AND DISCUSSION

Experimental Results

Successful polyamide preparations are listed in Table I. Several previously known polyamides not containing phosphorus were prepared for comparative purposes and are included in the table. Solubility data are summarized in Table II. A thermogram comparison of nylon 66 with polyamides containing a phosphine and a phosphine oxide group is given in Figure 1.

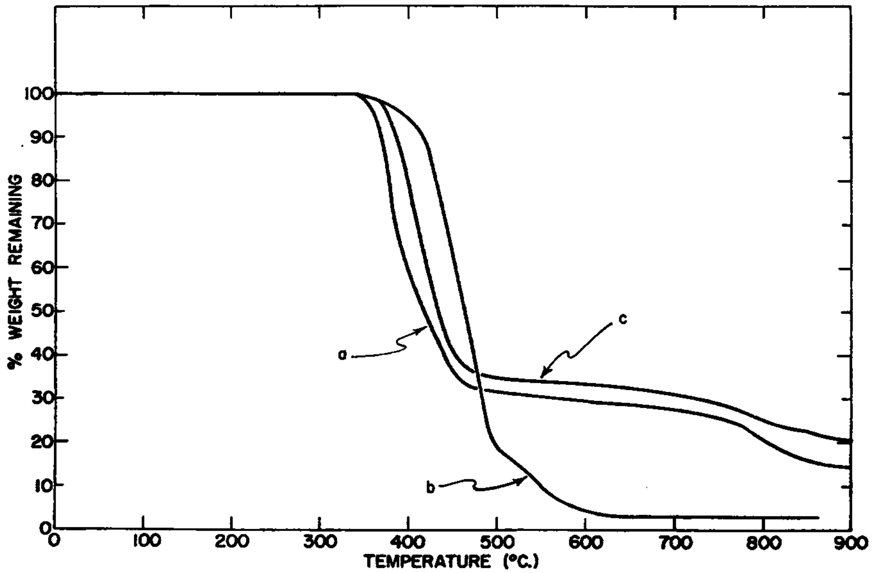
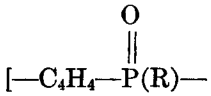
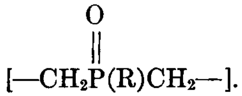


Fig. 1. Comparison of thermogravimetric behavior of polyamides: (*a*) polyamide from $\phi P(CH_2CH_2CH_2NH_2)_2$ + $HOOC(CH_2)_4COOH$; (*b*) polyamide from $NH_2(CH_2)_6NH_2$ + $HOOC(CH_2)_4COOH$; (*c*) polyamide from $\phi \underset{\underset{O}{\|}}{P}(CH_2CH_2CH_2NH_2)_2$ + $HOOC(CH_2)_4COOH$.

Polymer Preparation

Several alternate synthetic routes are available for the preparation of polyamides.[21] A number of these were tried during the course of this work. Bulk polymerization with diacid and diamine components was found to be the preferred method. Solution polymerization in cresol, either in the regular manner or by the technique described by Batzer et al.,[22] gave materials which tended to be yellow in color and had lower intrinsic viscosities. Several attempts at interfacial polymerizations[23] with bis(3-aminopropyl)phenylphosphine and various diacyl halides gave only poor yields of polymer with low solution viscosity.

In contrast to the corresponding dinitriles, phosphine diacids, $RP(R'COOH)_2$, are not easily prepared. For this reason direct polyamide synthesis from phosphorus-containing dinitriles was attempted. This technique gave polymers with reasonably high solution viscosities. However, in a direct comparison of the polymerization of bis(2-cyanoethyl)phenylphosphine oxide or bis(2-carboxyethyl)phenylphosphine oxide with hexamethylenediamine, the diacid route gave better results.

As summarized in Table I, this study has resulted in the preparation of a new series of well-defined polymers containing phosphine units in their backbone structure. Furthermore the previously known series of polyamides containing aromatic phosphine oxide units[3–6]  $[-C_4H_4-\overset{\overset{O}{\|}}{P}(R)-C_4H_4-]$ has been extended by us to include methylene phosphine oxide units  $[-CH_2\overset{\overset{O}{\|}}{P}(R)CH_2-]$.

Polymer Properties

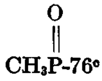
Softening Temperature and Density. The data presented in Table I indicate that the phosphorus-containing polyamides generally are transparent, light-colored materials. In contrast to regular nylons, they are amorphous and soften at relatively low temperatures. Further analysis of structural effects on softening behavior is presented in the second publication of this series.[24].

The phosphorus polyamides have higher densities than regular nylons (compare polymers 3, 7, and 8 with polymer 2 in Table I). This is somewhat unexpected in view of their amorphous state. The increased density apparently reflects a greater density for the individual polymer chains.

Solubility. Polymer solubility data have been summarized in Table II. The phosphine and phosphine oxide polyamides were found to exhibit a range of solubilities much greater than that of regular nylons. This range of solubility extends from formic acid and cresol, in which virtually all polyamides are soluble to various other less acidic polar solvents. Individual polymers, for example, were found to be soluble in dimethylformamide, ethanol, water, chloroform, and 5% HCl. The greater range of solubility for the phosphorus polyamides over nylons 66 and 76 is due in part to the amorphous character of the phosphorus polyamides. It is known for example that *N*-substituted hydrocarbon polyamides also have greater solubility as a result of reduction of the polar interactions of the amide linkages. The solubility of the phosphine polyamides in dilute hydrochloric acid is due to the basicity of the phosphorus atom. Similarly, the water solubility of the methylphosphine oxide polyamides results from the tendency of phosphine oxides to form hydrates.[25] Extended solubility range is also exhibited by the amine-containing polyamide.

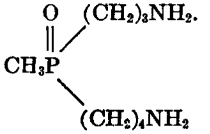
It was discovered by Dr. B. L. Williams of this laboratory that solutions of poly(bis-3-aminopropylphenylphosphine adipamide) [designated φP-66] in formic acid showed a loss in reduced viscosity on standing. A 1% solution of φP-66 in formic acid having an initial reduced viscosity of 1.2 (0.1% solution, 30°C.) gave a reduced viscosity of 0.60 after standing at room temperature for 200 hr. The other phosphine polyamides listed in Table I showed a similar loss of viscosity to varying (lesser) degrees except for the bis(3-aminopropyl)phenylphosphine polyamides of urea (polymer 19) and dimethyl oxalate (polymer 18). (Numbers in parentheses here and in the following discussion refer to the number given the polymer in the tables.) On the other hand, nylon 66 (polymer 1) and the polyamides containing phosphine oxide, amine (polymer 9) and sulfide linkages (polymer 15) were stable in formic acid. The reason for the apparent instability of the phosphine polyamides in acid has not yet been determined. However, the change in viscosity has been studied sufficiently so that the possibility of a simple deaggregation process was eliminated.

TABLE III
Adhesive Bond Strengths

Polymer designation	Tensile, psi			Lap shear tension on aluminum, psi	Impact (Izod) on aluminum, ft. lb./in.
	Aluminum	Steel	Copper		
Nylon 66[a]	9700	9900	10,900	3800	0.33
Nylon 610[a]	8300	7700	9,000	3100	0.15
φP-66[b]	6500	6200	6,400	4100	0.21
 $CH_3\overset{O}{\overset{\|}{P}}$-76[c]	5500 (9000)[d]	(5300)[d]	(7000)[d]	(3500)[d]	0.48

[a] Special samples obtained from duPont.

[b] Polyadipamide from $\phi P(CH_2CH_2CH_2NH_2)_2$.

[c] Polyadipamide from  $CH_3P(=O)((CH_2)_3NH_2)((CH_2)_4NH_2)$

[d] Dry storage conditions.

Adhesion. Among the advantages generally claimed in the patent literature for introducing phosphorus into a polymer is improved metal bonding characteristics. It was, therefore, of interest to compare the adhesive behavior of the phosphorus polyamides with that of regular nylons. Results are given in Table III. It was found that the polyamides generally have high metal adhesive bond strengths. Furthermore the bond strengths are not greatly altered by the introduction of the phosphorus groups. This could result from a masking of the interfacial characteristics of the phosphorus groups by the amide groups. It could also indicate that the bond strengths are not sensitive to the interfacial forces.

TABLE IV
Comparison of Polyamide Mechanical Properties[a]

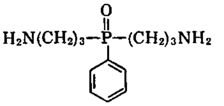
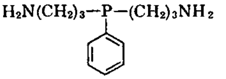
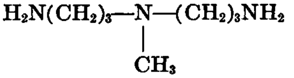
Polymer	Tensile strength, psi	Elongation, %	Flexural strength, psi	Flexural modulus $\times 10^{-5}$, psi
Nylon 66	10,500[b]	90[b]	—	4
Nylon 610	7,000[b]	90[b]	—	2.6
ϕP-66	5,900	3	13,800	3.7

[a] Except where otherwise indicated these data were obtained by standard methods used in this laboratory.

[b] Data of Floyd.[26]

Mechanical Properties. Comparison of mechanical properties of nylon 66 and nylon 610 with ϕP-66 (see Table IV) shows no major differences except in terms of percentage elongation at the break point.

TABLE V
Thermal Gravimetric Analysis of Adipic Acid Polyamides (Heating in Air)

No.	Comonomer	T_{10}, temp. at 10% weight loss	Total weight loss, %
1	$H_2N-(CH_2)_6NH_2$	415	97
2		385	80
3		370	85
4	 $H_2N(CH_2)_3-N(CH_3)-(CH_2)_3NH_2$	335	79

Adhesive and mechanical test data would seem to indicate minor direct effect by P or P=O. In generalizing on the fiber properties of silicon-containing polyamides, Speck[27] also states that "in general the polyamides had properties which appeared to be little different from those of their carbon analogs" (although the data on the carbon analog were not disclosed). Low elongation (5%) was also observed for the silicon-containing polymers.

Thermal Stability. The results of thermal stability tests are summarized in Table V in terms of the temperature at which 10% weight loss occurred. The differences between nylon 66 (polymer 1), $\phi\overset{O}{\overset{\|}{P}}$-66 (polymer 2), and ϕP-66 (polymer 3) were found to be small. On the other hand CH_3N-66 (polymer 4) was significantly less stable. Lack of thermal stability can account in part for the difficulty of preparing CH_3N-66 polymers of high intrinsic viscosity. A similar lower thermal stability (relative to nylon 66) was noted by Frunze and Korshak[28] for the sulfur-containing polyamides, particularly in the case where an —SO_2— linkage was involved. The authors considered the lower C—S bond strength (61.5 kcal./mole while C—C bond is 80 kcal./mole) to be responsible.

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Synopsis

This study has for the first time provided a series of high molecular weight polymers having trivalent phosphorus in the backbone structure (as phosphine-containing polyamides) and has extended the series of phosphine oxide polyamides beyond the previously disclosed bis(carboxyphenyl)phosphine oxide types. It was found that bulk polymerization rather than solution or interfacial procedures was the preferred method of preparing these materials. The phosphorus polyamides generally were found to be amorphous, relatively low softening materials having an extended solubility range. Most polyamides containing trivalent phosphorus slowly degrade in formic acid solution. A comparison of the thermal stability, adhesive bond strengths, and mechanical behavior of typical polyamides containing phosphine or phosphine oxide groups in their backbone structure to those of analogous regular nylons disclosed no major differences.

Résumé

Cette étude a pour la première fois fourni une série de polymères de haut poids moléculaire renfermant du phosphore trivalent dans la chaîne (comme des polyamides renfermant du phosphore) et la série des polyamides oxyde de phosphore a été étendue au dela des types de bis(carboxyphényl)oxyde de phosphore découvert antérieurement. On a trouvé que la polymérisation en masse était la méthode la plus adéquate de préparation de ces matériaux plutôt que le procédé en solution ou d'interface. On a trouvé que les polyamides de phosphore étaient généralement amorphes, les matériaux à point de ramollissement relativement bas ayant un domaine étendu de solubilité. La plupart des polyamides contenant du phosphore trivalent se dégradent lentement dans une solution d'acide formique. Une comparaison de la stabilité thermique, des forces d'adhésion et du comportement mécanique entre des polyamides typiques renfermant des groupes phosphorés ou des groupes oxydes de phosphore dans leur chaîne et les nylons analogues réguliers ne montrent pas de différences majeures.

Zusammenfassung

In der vorliegenden Arbeit werden zum ersten Mal eine Reihe hochmolekularer Polymerer mit dreiwertigem Phosphor in der Hauptkette (als phosphinhältige Polyamide) beschrieben und die Reihe Mer Phosphinoxydopolyamide über die früher endeckten Bis-(Carboxyphenyl)-phosphinoxydtypen hinaus erweitert. Es wurde gefunden, dass die Polymerisation in Substanz für die Herstellung dieser Materialien besser geeignet ist als Lösungs- oder Grenzflächenverfahren. Die Phosphorpolyamide

waren allgemein amorphe Stoffe mit relativ niedrigem Erweichungspunkt und einem weiten Löslichkeitsbereich. Die meisten Polyamide mit dreiwertigem Phosphor wurden in ameisensaurer Lösung langsam abgebaut. Ein Vergleich der thermischen Beständigkeit, der Klebefestigkeit und des mechanischen Verhaltens von typischen Polyamiden mit Phosphinoder Phosphinoxydgruppen in der Hauptkette mit denen des analogen regulären Nylons ergab keine growen Unterschiede.

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