

Synthesis and Characterization of Phosphorus-Containing Polyamides and Copolyamides Based on 1-[(Dialkoxyphosphinyl)methyl]-2,4- and -2,6-Diaminobenzenes

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Synopsis

Phosphorus-containing polyamides and copolyamides were prepared from 1-[(dialkoxyphosphinyl)methyl]-2,4- and -2,6-diaminobenzenes. The polymers were characterized by infrared and proton nuclear magnetic resonance spectroscopy, differential scanning calorimetry, and thermogravimetric analysis. Their thermal properties were compared with those of the corresponding common polyamides. In addition, the fire resistance of some polyamides was evaluated by determining their limiting oxygen index value.

INTRODUCTION

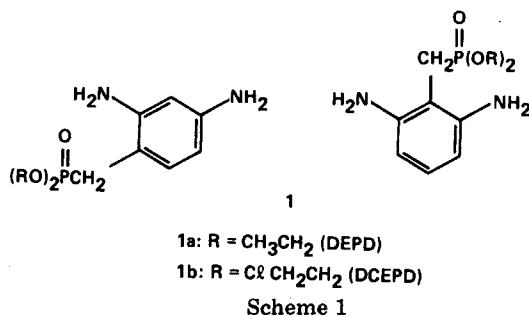
Structurally modified polyamides have been synthesized to improve their thermal and thermal-oxidative stability.¹ This approach involves the synthesis of polyamides and copolyamides from monomers bearing certain elements or groups that were effective as part of fire-retardant or thermal-stabilizing additives. The efficiency of such groups or elements is likely to be higher when they are present as an inherent part of the polymer chain, rather than as a component of a physical mixture.

The most interesting monomers for the synthesis of structurally modified polyamides are those containing phosphorus. A large number of phosphorus-bearing diacids and diamines were successfully used to prepare fire-retardant or thermally stable polyamides.²⁻¹⁵

The present work is concerned with the synthesis and characterization of fire-resistant polyamides and copolyamides prepared from 1-[(dialkoxyphosphinyl)methyl]-2,4- and -2,6-diaminobenzenes (1). These compounds were synthesized by nitration and subsequent catalytic hydrogenation of the corresponding (dialkoxyphosphinyl)methyl benzenes. Infrared (IR) and proton nuclear magnetic resonance (¹H-NMR) spectroscopy indicated that the product consisted of about 90% 2,4-diamino and 10% 2,6-diamino isomers (J. A. Mikroyannidis, to appear).

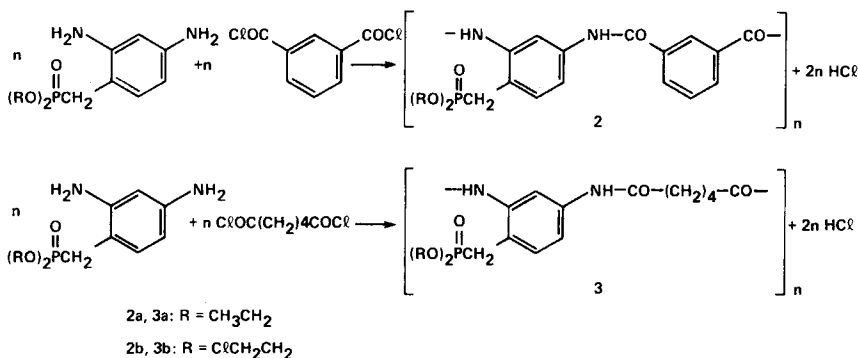
A separation of the above isomers is not necessary for many purposes. A mixture of these isomers was therefore used as starting material for preparing the phosphorus-containing polyamides.

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RESULTS AND DISCUSSION

The synthesis of the phosphorus-containing polyamides was carried out by reacting 1 with an acid chloride, such as isophthaloyl dichloride or adipoyl dichloride. The reaction of 1-[(dialkoxyphosphinyl)methyl]-2,4-diaminobenzene, which is the predominant isomer in the synthesized compound 1, with an acid chloride is shown as follows:



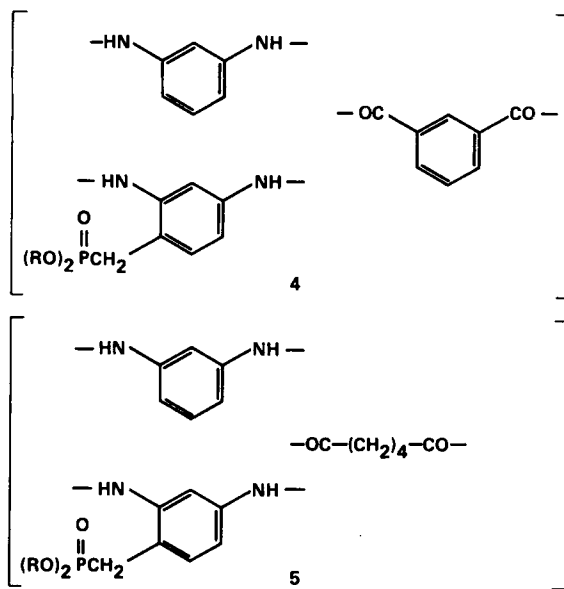
Furthermore, random copolyamides were prepared by reacting 1 and *m*-phenylenediamine with an acid chloride. The copolyamides synthesized may be presented by the chemical structures shown in Scheme 3.

In addition, the common polyamides shown in Scheme 4 were prepared for comparative purposes by reacting *m*-phenylenediamine with an acid chloride under identical experimental conditions.

The aforementioned reactions occur rapidly under mild conditions in the presence of an acid acceptor such as pyridine. The most preferred solvent is *N,N*-dimethylacetamide (DMAC).

The structure of the polyamides was verified by elemental analysis (Table I) and IR and ¹H-NMR spectroscopy (Table II). The IR spectra of the phosphorus-containing polyamides indicate that the intensity of the P=O stretching frequency at 1247–1215 cm⁻¹ and the P—O—C absorption band at 1079–961 cm⁻¹ increase progressively with increasing concentration of phosphorus moieties in polymers.

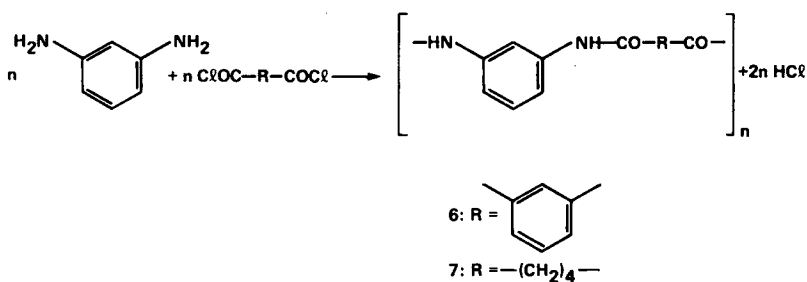
It is impossible to assign the signals caused by the secondary amide protons in the ¹H-NMR spectra of polyamides. This could, perhaps, be a result of the



4a, 5a: R = CH₂CH₂

4b, 5b: R = Cl-CH₂CH₂

Scheme 3



Scheme 4

fast exchange of these protons with the solvent or with the traces of moisture associated with the solvent.

The polyamides 2a, 2b and 3a, 3b have a low molecular weight, as indicated from their value of inherent viscosity (η_{inh}) (Table III). The copolyamides 4a, 4b and 5a, 5b have a comparatively higher molecular weight. The common polyamides 6 and 7, prepared under identical experimental conditions, show the highest molecular weight obtained. These viscosity data suggest that the molecular weight of the polyamides is reduced when their concentration is increased in the phosphorus moieties. The low molecular weight and softening point of the polyamides 2a, 2b and 3a, 3b impede any potential use as a fiber-forming material. However, the copolyamides 4a, 4b, and 5a, 5b are more attractive systems for modifying conventional synthetic fibers to improve their hydro-

TABLE I
 Elemental Analysis of Polyamides

Polymer	Formula	Elemental analysis (%)				
		C	H	Cl	N	P
2a	C ₁₉ H ₂₁ N ₂ O ₅ P	58.46 (58.78) ^a	5.46 (5.41)		6.93 (7.22)	7.66 (7.98)
2b	C ₁₉ H ₁₉ Cl ₂ N ₂ O ₅ P	49.69 (49.92)	4.26 (4.16)	15.39 (15.51)	5.92 (6.13)	6.60 (6.78)
4a						1.44 (1.92)
4b				5.14 (5.48)		2.09 (2.39)
3a	C ₁₇ H ₂₅ N ₂ O ₅ P	55.14 (55.46)	6.99 (6.79)		7.23 (7.61)	7.93 (8.41)
3b	C ₁₇ H ₂₃ Cl ₂ N ₂ O ₅ P	46.98 (46.71)	5.12 (5.26)	16.10 (16.23)	6.87 (6.41)	7.10 (7.09)
5a						1.52 (2.00)
5b				4.84 (5.81)		2.04 (2.54)

^a Numbers in parentheses indicate the calculated values.

philicity and/or fire resistance. It is suggested that the strong polar character of the —P=O group,¹⁶ along with the amide structure, is responsible for the noticeable hydrophilicity.

The polyamides prepared were thermally characterized through DSC and TGA. Typical DSC thermograms are presented in Figure 1.

A broad endothermic peak was exhibited in most of the DSC thermograms of polyamides between 80°C and 180°C, along with a weight loss of ~3% attributed to adsorbed water, despite the fact that the samples were dried in a vacuum oven.

Some of the thermal characteristics of polyamides obtained from their DSC thermograms are listed in Table IV. It was impossible to distinguish a glass transition (T_g) or melting (T_m) temperature in the DSC thermograms of some polyamides. Sharp, reproducible endothermic baseline shifts were obtained for several polyamides that probably correspond to the T_g . In the case of poly(*m*-phenylene isophthalamide) (6), a T_g value of 250°C was found. Gan et al.¹⁷ reported a T_g value of 275°C for a polymer of the same structure with an intrinsic viscosity of 1.97 dL/g. The discrepancy is probably due to the adsorbed water and/or the different molecular weights of the polymers. A T_g value of 158°C was found for poly(*m*-phenylene adipamide) (7), which is in good agreement with the value of 160°C reported in the literature.¹⁸ The T_g values of the copolyamides 4a and 5a are close to those of the corresponding parent polyamides 6 and 7, respectively. However, the T_g values of the polyamides 2b, 3a, and 3b having a comparatively higher phosphorus content are significantly lower as compared with those of the parent polyamides.

The large endothermic peaks that appeared in the DSC thermograms of several polyamides are attributed to melting. The T_m values obtained from the intersection of the tangent to the front side of the peak with the base line are given in Table IV. Since almost every wholly aromatic polyamide that contains neither

TABLE II
 Physical Characteristics of Polyamides

Polymer	IR	Solvent	¹ H-NMR
	KBr (cm ⁻¹)		PPM
2a	3370-3160 (NH stretching); 1675 (C=O); 1604 (aromatic); 1523 (NH deformation); 1245-1215 (P=O); 1048-963 (P-O-C)	DMSO-d6	8.67-7.37 (m, 7H, aromatic); 3.97 (m, 4H, CH ₃ CH ₂ O); 3.45 (d, J _{PCH} = 22 Hz, 2H, PCH ₂); 1.15 (t, 6H, CH ₃ (CH ₂ O))
2b	3375-2963 (NH stretching); 1671 (C=O); 1604 (aromatic); 1524 (NH deformation); 1247 (P=O); 1078-1022 (P-O-C); 722, 668 (C-Cl)	DMSO-d6	8.75-7.56 (m, 7H, aromatic); 4.33 (m, 4H, ClCH ₂ CH ₂ O); 3.90 (m, 4H, ClCH ₂ CH ₂ O); 3.67 (d, J _{PCH} = 22 Hz, 2H, PCH ₂)
4a	3475-3175 (NH stretching); 1655 (C=O); 1606 (aromatic); 1534 (NH deformation); 1243 (P=O); 1046-1023 (P-O-C)		
4b	3400-3175 (NH stretching); 1659 (C=O); 1606 (aromatic); 1535 (NH deformation); 1242 (P=O); 1079-1021 (P-O-C); 719, 686 (C-Cl)		
3a	3375-3175 (NH stretching); 2930, 2865 (CH ₂ stretching); 1669 (C=O); 1604 (aromatic); 1528 (NH deformation); 1220 (P=O); 1051-961 (P-O-C)	DMSO-d6	7.80-7.20 (m, 3H, aromatic); 3.93 (m, 4H, CH ₃ CH ₂ O); 3.23 (d, J _{PCH} = 22 Hz, 2H, PCH ₂); 2.33 (broad, 4H, COCH ₂); 1.67 (broad, 4H, CH ₂); 1.13 (t, 6H, CH ₃ (CH ₂ O))
3b	3375-3175 (NH stretching); 2930, 2865 (CH ₂ stretching); 1684-1669 (C=O); 1602 (aromatic); 1528 (NH deformation); 1225 (P=O); 1077-1020 (P-O-C); 732, 667 (C-Cl)	DMSO-d6	7.87-7.17 (m, 3H, aromatic); 4.10 (m, 4H, ClCH ₂ CH ₂ O); 3.73 (m, 4H, ClCH ₂ CH ₂ O); 3.37 (d, J _{PCH} = 22 Hz, 2H, PCH ₂); 2.37 (broad, 4H, COCH ₂); 1.53 (broad, 4H, CH ₂)
5a	3375-3175 (NH stretching); 2947, 2868 (CH ₂ stretching); 1662 (C=O); 1606 (aromatic); 1535 (NH deformation); 1220 (P=O); 1051-961 (P-O-C)		
5b	3375-3175 (NH stretching); 2947, 2868 (CH ₂ stretching); 1665 (C=O); 1606 (aromatic); 1536 (NH deformation); 1220 (P=O); 1077-1023 (P-O-C); 729, 668 (C-Cl)		

N-substitution nor ortho-phenylene units begins to decompose near its melting point, determination of the melting temperature is usually very difficult. The use of differential thermal analysis to determine the melting point of such high-melting polymers has become generally accepted as the best technique. From Table IV it can be seen that the copolyamides 4a, 4b and 5a, 5b show a lower melting temperature as compared with the corresponding parent polyamides. Apparently, the reduction of melting temperatures should be attributed to the disruption in chain packing caused by the introduction of the bulky (dialkoxy-

TABLE III
Values of Inherent Viscosity, Phosphorus Content, and Thermal Stability of Polyamides in N₂ Atmospheres

Polyamide	η_{inh}^a	P (%)	Temperature (°C)			Char yield (%) residue at 650°C
			PDT	PDT _{max}	TCP	
2a	0.14	7.66	329	373	550	76
2b	0.16	6.60	258	289	450	60
4a	0.22 ^b	1.44	430	480	630	73
4b	0.33	2.09	340	450	640	66
6	0.47 ^b	0	455	527	645	60
3a	0.10	7.93	311	364	500	51
3b	0.11	7.10	215	253	377	51
5a	0.31	1.52	391	431	499	54
5b	0.34	2.04	332	398	461	51
7	0.36 ^b	0	411	463	509	34

^a 0.5 g/dL in *N,N*-dimethylformamide at 25°C.

^b 0.5 g/dL in concentrated H₂SO₄ at 25°C.

TABLE IV
Some Thermal Characteristics of Polyamides

Polyamide	T_g (°C)	T_m (°C)
2a	204	287
2b	174	— ^a
4a	256	286
4b	— ^a	260
6	250	387
3a	64	— ^a
3b	50	— ^a
5a	166	206
5b	— ^a	158
7	158	216

^a A [∞] transition temperature cannot be distinguished.

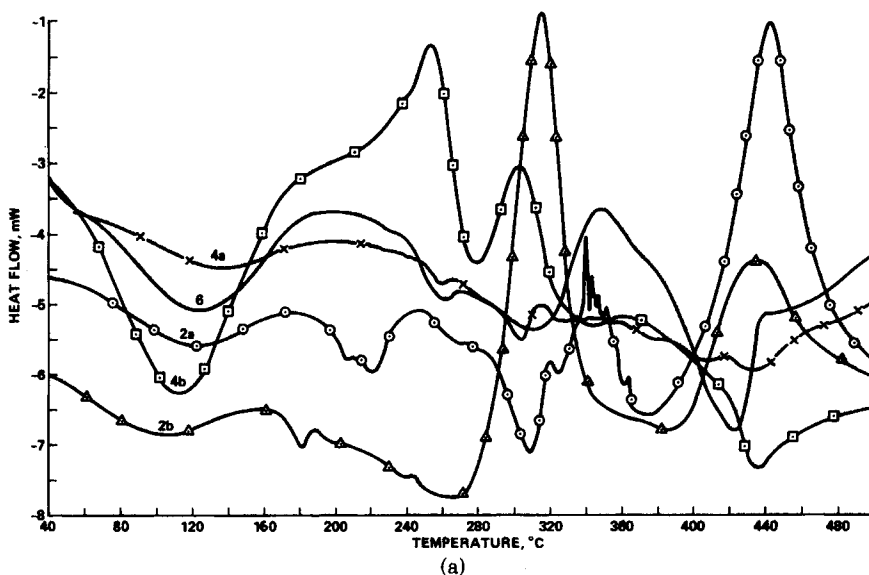
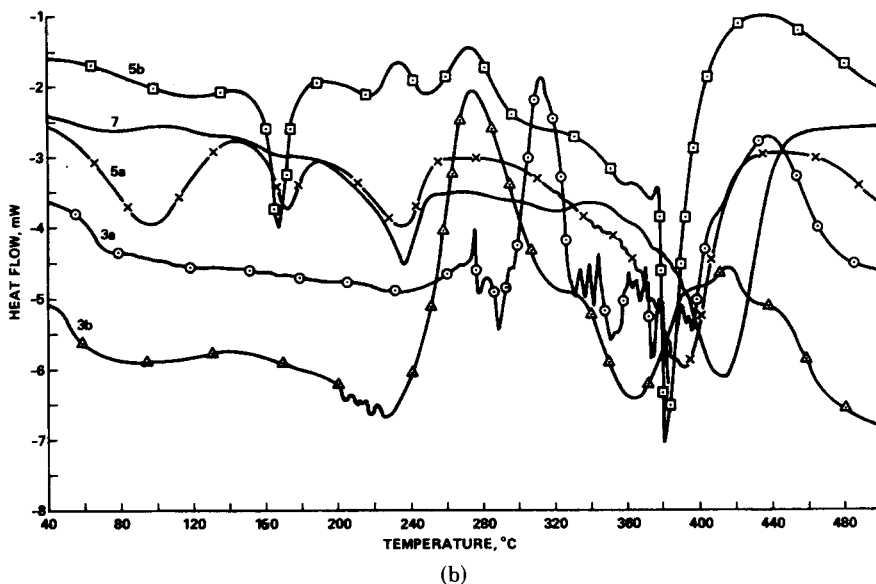


Fig. 1. DSC thermograms of polyamides in N₂: (a) polyamides 2, 4, and 6; (b) polyamides 3, 5, and 7.



(b)
Fig. 1 (Continued from the previous page.)

phosphinyl)methyl group. It should be noted that the introduction of the bulkier [di(2-chloroethoxy)phosphinyl)methyl group resulted in a greater reduction of the melting temperature of the polymers.

The large exothermic peaks observed in the DSC thermograms of the polyamides 2a, 2b and 3a, 3b correspond to their pyrolysis, as confirmed by TGA data. The polyamides 2a and 3a are pyrolyzed at a significantly higher temperature than the corresponding polyamides 2b and 3b. Apparently, the more bulky [di(2-chloroethoxy)phosphinyl)methyl group is thermally degraded more readily than the (diethoxyphosphinyl)methyl group.

Thermogravimetric analytical data of the polyamides in nitrogen are shown in Figure 2. The polymer decomposition temperature (PDT), the maximum polymer decomposition temperature (PDT_{max}), the temperature of complete pyrolysis (TCP), and the char yield at 650°C are shown in Table III. The PDT and TCP were determined by the intersection of the tangent to the steepest portion of the TGA curve, with the strain-line part of the curve before and after the polymer degradation, respectively. The PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred. From this table it can be seen that all phosphorus-containing polyamides have a lower PDT and a higher char yield than the corresponding common polyamides.

The thermal stability of the polymers decreased steadily with increasing concentration of the phosphorus-containing sequences in the chains. This may be attributed to the easy thermal dissociation of the phosphorus moieties and the low degree of polymerization of these polymers. As previously mentioned, the polyamides containing [di(2-chloroethoxy)phosphinyl)methyl groups show a significantly lower PDT than those with (diethoxyphosphinyl)methyl groups.

Some TGA data of the polyamides obtained in nitrogen and air atmospheres

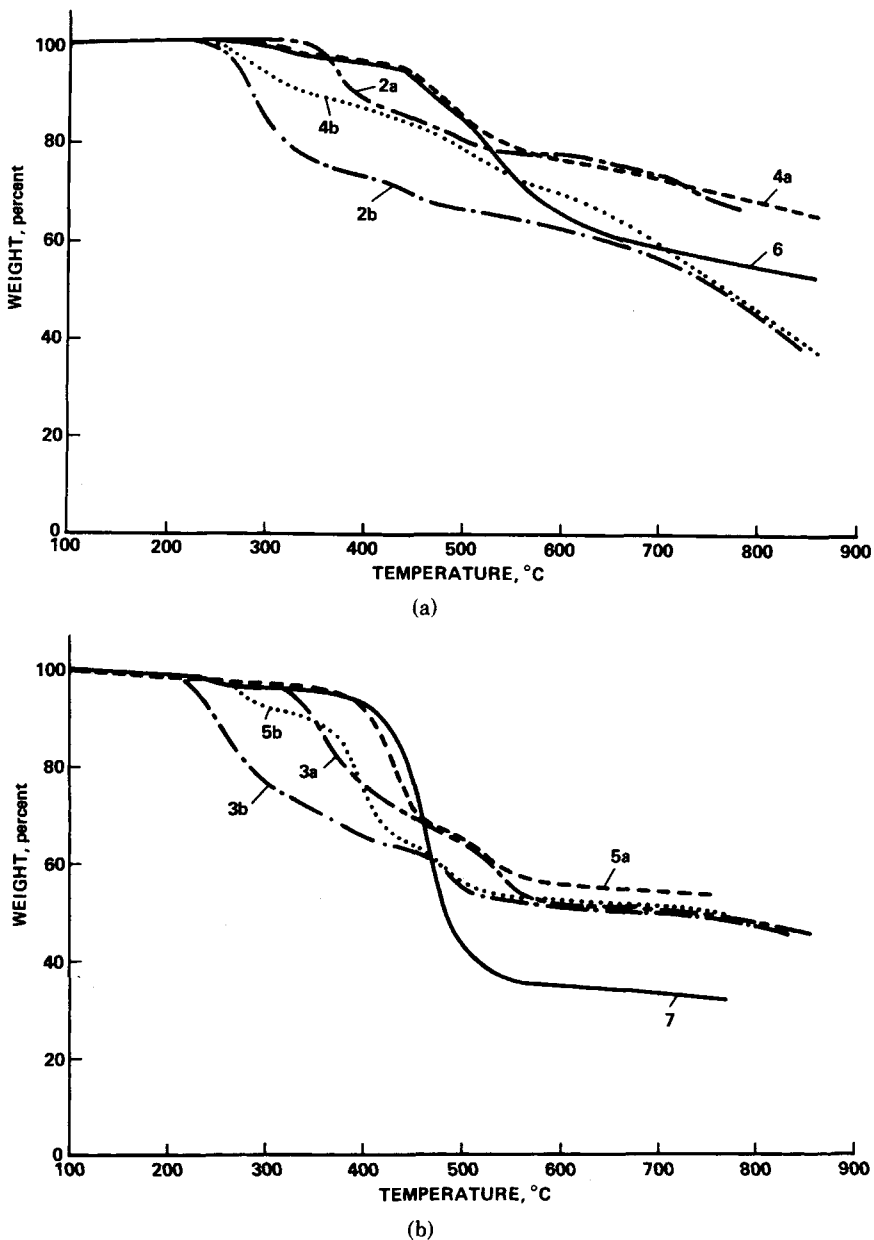


Fig. 2. TGA thermograms of polyamides in N₂: (a) polyamides 2, 4, and 6; (b) polyamides 3, 5, and 7.

are shown in Table V. As expected, the synthesized polyamides exhibit a lower thermal stability in air, as compared with that in N₂.

Note that the introduction of the (dialkoxyphosphinyl)methyl group causes the solubility of the polyamides to increase greatly. For example, the poly(*m*-phenylene isophthalamide) (6) is soluble only in such solvents as concentrated sulfuric acid and formic acid, whereas the polyamides 2a and 2b are soluble in

TABLE V
 TGA Data of Polyamides

Polyamide	Weight loss in nitrogen (%)			Weight loss in air (%)		
	400°C	550°C	700°C	400°C	550°C	700°C
2a	11	21	27	17	26	60
2b	26	35	43	26	42	60
4a	5	22	29	4	22	79
4b	14	27	41	12	71	97
6	10	30	43	4	20	94
3a	25	46	50	20	33	59
3b	35	48	50	34	45	70
5a	9	43	46	6	32	70
5b	27	47	50	20	45	84
7	8	64	67	5	53	96

solvents such as chloroform and acetone. The greater solubility range of the phosphorus-containing polyamides over the common polyamides is probably due to the lower molecular weight and their amorphous character. The lack of crystallinity in polyamides 2a, 2b and 3a, 3b may be attributed to the bulkiness of the (dialkoxylphosphinyl)methyl groups and to the subsequent disruption in the chain packing. The increased solubility of the polyamides effected by the incorporation of the (dialkoxylphosphinyl)methyl group is important from a technological point of view, since fabrication of certain high-molecular-weight wholly aromatic polyamides is difficult or even impossible because of their poor solubility.¹⁹

The fire resistance of some polyamides was evaluated by determining their LOI value. The LOI values determined and the content of the polymers in phosphorus and chlorine are shown in Table VI. It can be seen that the phosphorus-containing polyamides show a significantly higher degree of fire-resistance than the corresponding common polyamides. However, the significance of these LOI data should not be overemphasized, since the low molecular weight of the phosphorus-containing polyamides may have contributed to the high LOI values by permitting low-viscosity melts to drip during burning. The role of dripping in obtaining high LOI values was demonstrated earlier for polyamides.²⁰

Furthermore, it was shown that the polyamides 2a, 2b and 3a, 3b may be used as an additive or for melt-blending with common polyamides to increase their fire-resistance. Specifically, the polyamide 2a was used as a fire-retardant ad-

 TABLE VI
 Fire-Resistance of Polyamides

Polyamide	P (%)	Cl (%)	LOI
4a	1.44	0	52.0
4b	2.09	5.14	52.6
6	0	0	46.4
5a	1.52	0	45.0
5b	2.04	4.84	45.7
7	0	0	29.4

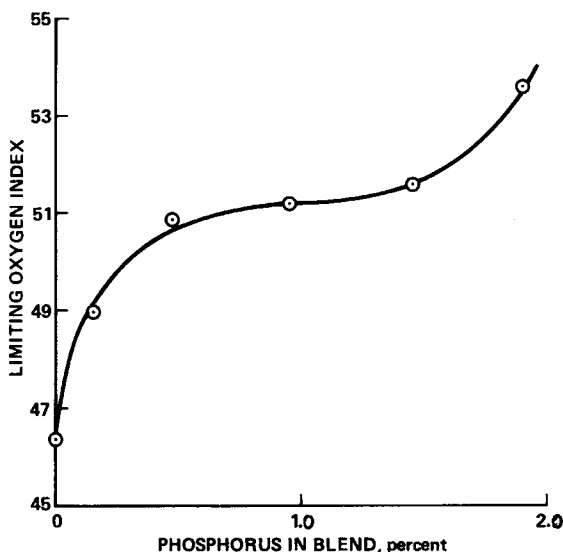


Fig. 3. LOI of blends of polyamides 2a and 6 as a function of the blend content in phosphorus.

ditive to 6. For this purpose, powder of 2a was mixed with powder of 6 in various proportions. The LOI values of the specimens formed by hot-pressing the mixtures in a mold were determined, and the results are shown in Table VII and plotted in Figure 3.

The copolyamide 4a contained 1.44% P and had an LOI value of 52.0. It can be seen from Table VII that a blend of polyamides 2a and 6, containing 1.46% P, exhibited an LOI value of 51.6. Thus, the efficiency of the (dialkoxyphosphinyl)methyl groups is higher when they are an inherent part of the polymer chain, rather than as a component of a physical mixture.

EXPERIMENTAL

General

A Varian EM-390 NMR spectrometer at 90 MHz was used to record the ^1H -NMR spectra. Chemical shifts (δ) are given in parts per million with tetramethylsilane as an internal standard. A Nicolett FT-IR Spectrometer with KBr pellets was used to record IR spectra. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a DuPont 1090 Thermal Analyzer. Measurements were made at a heating rate of $20^\circ\text{C}/\text{min}$ in atmospheres of N_2 or air at a flow rate of $80\text{ cm}^3/\text{min}$.

TABLE VII
Limiting Oxygen Index of Blends of Polyamides 2a and 6

Phosphorus in blend (%)	0	0.24	0.48	0.95	1.46	1.90
Additive in blend (%)	0	3.75	7.50	15.00	23.00	30.00
LOI	46.4	49.0	50.9	51.2	51.6	53.6

The limiting oxygen index (LOI) of the polyamides was determined with a Stanton Redcroft flammability unit (ASTM D 2863-74). The LOI specimens measuring 70×6.5 mm were formed by hot-pressing polyamide powder in a mold. The mixture of nitrogen and oxygen passed upward through the chimney at a flow rate of 18 L/min.

Elemental analyses were performed by Huffman Laboratories, Inc., Wheat Ridge, Colorado.

Reagents and Solvents

The dihydrochloride salt of DEPD was purified by washing with acetone. It decomposed at temperatures higher than 128°C . DCEPD was purified by recrystallization from benzene (mp $116\text{--}119^{\circ}\text{C}$). Commercial-grade dihydrochloride salt of *m*-phenylenediamine was used. Isophthaloyl dichloride was recrystallized from *n*-hexane. Adipoyl dichloride and pyridine were distilled under reduced pressure. *N,N*-dimethylacetamide (DMAC) was dried by refluxing and fractionally distilled from calcium hydride.

Preparation of Phosphorus-Containing Polyamides and Copolyamides

Preparation of the Polyamides 2a and 2b. Dihydrochloride salt of DEPD (6.29 g, 19.0 mmol), 60 mL of DMAC, and pyridine (6.01 g, 76.0 mmol) were placed in a three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a nitrogen inlet. The mixture was stirred to dissolve the dihydrochloride salt of DEPD and cooled to $0\text{--}1^{\circ}\text{C}$. A solution of isophthaloyl dichloride (3.86 g, 19.0 mmol) in 30 mL of DMAC was added by drops in a nitrogen atmosphere. The reaction took place for 10 min in an ice bath, followed by 60 min at room temperature. The mixture was poured into about 600 mL of methanol, and the resulting precipitate was filtered, washed repeatedly with methanol, and dried at 80°C in a vacuum oven. Polyamide 2a was obtained in an 82% yield (6.05 g).

In a likewise manner, polyamide 2b was prepared by reacting DCEPD (3.28 g, 10.0 mmol) with isophthaloyl dichloride (2.04 g, 10.0 mmol) in the presence of pyridine (1.59 g, 20.0 mmol). The yield was 85% (3.90 g).

Preparation of the Copolyamides 4a and 4b. Dihydrochloride salt of DEPD (2.21 g, 6.7 mmol), dihydrochloride salt of *m*-phenylenediamine (6.21 g, 34.3 mmol), and pyridine (12.96 g, 163.8 mmol) were dissolved in 80 mL of DMAC. Isophthaloyl dichloride (8.32 g, 41.0 mmol), dissolved in 60 mL of DMAC, was added to the above solution and the mixture reacted as did the 2a polyamide. Copolyamide 4a was obtained in a 90% yield (9.70 g).

The same procedure used to obtain 4a was used to obtain 4b; DCEPD (2.99 g, 9.1 mmol) and dihydrochloride salt of *m*-phenylenediamine (5.81 g, 32.0 mmol) reacted with isophthaloyl dichloride (8.37 g, 41.2 mmol) in the presence of pyridine (11.59 g, 146.5 mmol). The yield was 94% (11.10 g).

Preparation of the Polyamides 3a and 3b. DEPD was formed in situ by adding pyridine (7.24 g, 91.6 mmol) to the dihydrochloride salt of DEPD (7.58 g, 22.9 mmol) in 60 mL of DMAC. Adipoyl dichloride (4.19 g, 22.9 mmol), diluted with 30 mL of DMAC, was added to this solution while it was stirred in a nitrogen

atmosphere at 0–1°C. The mixture was subsequently stirred for 60 min at room temperature and poured into water. The resulting precipitate was dried overnight at 90°C in a vacuum oven. Polyamide 3a was obtained in an 81% yield (6.83 g).

In a likewise manner, polyamide 3b was prepared by reacting DCEPD (3.36 g, 10.3 mmol) with adipoyl dichloride (1.88 g, 10.3 mmol) in the presence of pyridine (1.62 g, 20.5 mmol). The yield was 76% (3.41 g).

Preparation of the Copolyamides 5a and 5b. Dihydrochloride salt of DEPD (2.94 g, 8.9 mmol), dihydrochloride salt of *m*-phenylenediamine (8.78 g, 48.0 mmol), and pyridine (18.00 g, 227.6 mmol) were dissolved in 100 mL of DMAC. Adipoyl dichloride (10.41 g, 56.9 mmol) diluted with 40 mL of DMAC was added to the above solution and the mixture reacted as did the 3a polyamide. The copolyamide 5a was obtained in an 84% yield (11.55 g).

Similarly, copolyamide 5b was prepared by reacting DCEPD (2.91 g, 8.9 mmol) and dihydrochloride salt of *m*-phenylenediamine (6.16 g, 34.0 mmol) with adipoyl dichloride (7.85 g, 42.9 mmol) in the presence of pyridine (12.16 g, 153.8 mmol). The reaction yield was 81% (9.16 g).

CONCLUSIONS

Polyamides obtained by the reaction of the compounds (1) with an acid chloride, such as isophthaloyl dichloride or adipoyl dichloride, had relatively low molecular weights. Copolyamides obtained by the reaction of 1 and *m*-phenylenediamine with the previously mentioned acid chlorides yielded somewhat higher molecular weights. The IR spectra of the phosphorus-containing polyamides illustrate the characteristic absorption bands of P=O and P—O—C groups. In addition, the structure of the polymers was verified by elemental analysis and ¹H-NMR spectroscopy. The phosphorus-containing polyamides were thermally characterized by DSC and TGA, and their properties were compared with those of the corresponding common polyamides. The *T_g* and *T_m* values of the polymers are decreased with increasing concentration of the phosphorus moieties. The phosphorus-containing polyamides indicated a lower PDT and a higher char yield than the corresponding common polyamides. In addition, the phosphorus-containing polyamides exhibited a considerably higher degree of fire resistance than did the corresponding common polyamides.

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