

Synthesis of *N,N'*-Bis [(Dialkoxyphosphinyl) Methyl]-1,4-Benzenediamines and the Corresponding Polymers

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Synopsis

The title diamines were synthesized by condensation of 1,4-phenylenediamine with para-formaldehyde and a suitable phosphorus acid triester. The *N,N'*-dibenzoyl derivatives of the above compounds were also prepared. New flame-retardant polyamides were synthesized under various experimental conditions by condensation of these diamines with terephthaloyl dichloride. The polyamides produced have low viscosities. Blends with polystyrene (PS) have been made and their flammabilities determined.

INTRODUCTION

The general acceptance of wholly aromatic polyamides as useful engineering plastics led to the search for flame resistant polyamides for specific end uses.¹ These are usually prepared either by the addition of flame-retardant additives in certain polyamides or by synthesizing copolyamides containing flame-retardant groups.²⁻⁷ The polycondensation of phosphorus-containing monomers usually produces polymers with low molecular weights.^{3,8} This disadvantage can be overcome by copolymerizing these monomers with a suitable pair of an aromatic amine and acid dichloride.

In the present work the synthesis of new *N,N'*-bis[(dialkoxyphosphinyl)methyl]-1,4-benzenediamines (1) is reported. These amines can react with various acid dichlorides yielding polyamides. Thus in this report the polyterephthalamides of these phosphorus containing amines were synthesized under varying polymerization conditions.

EXPERIMENTAL

Reagents and Instrumentation

1,4-Phenylenediamine was purified by vacuum sublimation. Terephthaloyl dichloride was purified by recrystallization from *n*-hexane. Triesters of phosphorus acid were purified by standard procedures. Solvents such as ethyl acetate, xylene, and chloroform were purified by methods described elsewhere.⁹

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Melting points were measured on a Büchi apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 137 Infracord Spectrometer. $^1\text{H-NMR}$ spectra were obtained at 60.0 MHz on a Varian T-60A Spectrometer with tetramethylsilane as an internal standard. Chemical shifts are given in ppm (δ). Elemental analysis (C,H,N) was performed by the Microanalytical Laboratory of the National Hellenic Foundation in Athens, Greece and by Galbraith Laboratories Inc., Knoxville, TN. Elemental analysis of phosphorus was performed by combustion in an oxygen flask¹⁰ and colorimetric determination at 400 nm.

TGA was performed on a DuPont 990 Thermal Analyzer coupled with a DuPont 951 TGA accessory. A heating rate of 20°C/min was used, and a flow rate of 50 cm³/min for both nitrogen and air atmospheres. DSC measurements were performed using a DuPont 910 calorimeter cell coupled with a 990 programmer-recorder. Program heating rate was 20°C/min and flow rate 30 cm³/min. Calibration was made using Indium standard. The limiting oxygen index (LOI) of the polymers was determined according to the ASTM D 2863-70 method.

Synthesis of Compounds

N,N'-Bis[(Dialkoxyphosphinyl)methyl]-1,4-Benzenediamines (1a–1d)

The diamines *N,N'*-bis [(dimethoxyphosphinyl)methyl]-1,4-benzenediamine (1a), *N,N'*-bis[(diethoxyphosphinyl)methyl]-1,4-benzenediamine (1b), *N,N'*-bis[(di- β -chloroethoxyphosphinyl)methyl]-1,4-benzenediamine (1c), and *N,N'*-bis[(diphenoxyphosphinyl)methyl]-1,4-benzenediamine (1d) were synthesized by the reaction of 1,4-phenylenediamine, paraformaldehyde, and the corresponding trialkyl or triphenyl phosphite in mol ratios 1:2:2 under conditions shown in Table I. The diamines 1a, 1c, and 1d were precipitated by cooling, while 1b was precipitated by addition of ether and cooling. Compounds were purified by recrystallization from ethyl acetate (1a), benzene-ether (1:1) (1b), ethanol (1c), and dimethylformamide-ethanol (3:4) (1d).

Poly[N,N'-Bis(dialkoxyphosphinyl)methyl-1,4-phenyleneterephthalamides]³

Method A. Recrystallized diamine 1a or 1b (10 mmol) was dissolved in 10 mL CHCl_3 . Triethylamine (3.1 mL) was added to the solution and stirred in an ice bath. Terephthaloyl dichloride (10 mmol) in 5 mL CHCl_3 was added dropwise under argon.¹¹ After the completion of addition, the ice bath was removed and the solution was stirred for 2 h at room temperature. In the case of polymer 3a the solution became viscous and could not be stirred. To complete the reaction, it was kept at room temperature for 16 h, treated with 100 mL of *n*-hexane, and filtered. The solid was purified by extraction with methanol in a soxhlet and dried under vacuum. In the case of polymer 3d the solvent was removed, and the resulting solid was treated with benzene. The $\text{Et}_3\text{N}\cdot\text{HCl}$ was removed by filtration and the polymer precipitated with *n*-hexane, filtered, and dried under vacuum.

Method B. Recrystallized 1a or 1b (4 mmol) was dissolved in 8 mL of chlorobenzene under an Argon atmosphere. Terephthaloyl dichloride (4 mmol) was added and stirred for 1 h at room temperature and then at reflux for 20 h.¹² The resulting suspension was treated with *n*-hexane and filtered. The solid was dried at 70°C in high vacuum.

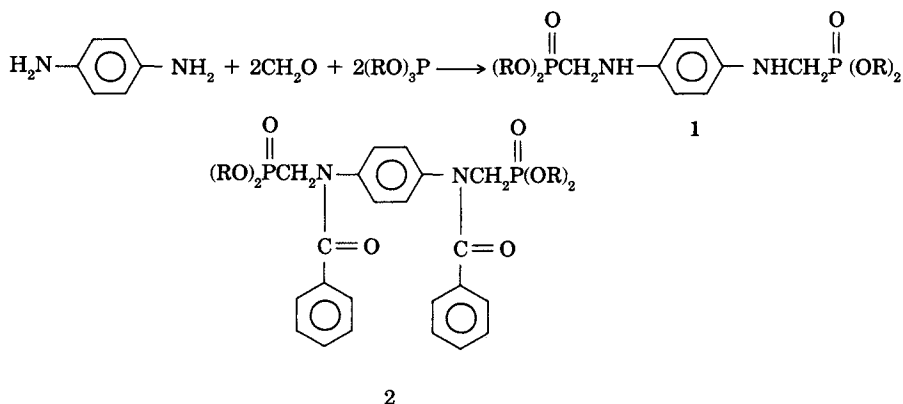
Method C. The above procedure was employed. *o*-Dichlorobenzene was employed instead of chlorobenzene.

Blends of Polystyrene with Polymer 3d

Both polymers in the proper ratio were dissolved in tetrahydrofuran (THF). The solvent was removed and the solid product dried at 50°C and high vacuum.

RESULTS AND DISCUSSION

The phosphinyl methyl diamines were synthesized by condensation of 1,4-phenylenediamine with paraformaldehyde and phosphorus acid triesters. The reactions took place in an aprotic solvent, in the temperature range 77–110°C, for a few hours in the absence of catalysts (see Table I). In addition, the *N,N'*-dibenzoyl derivatives (2a, 2b) were prepared, by reaction of 1a and 1b with benzoylchloride in the presence of pyridine. The later reaction was completed in a few minutes. The reactions are given below:



1a, 2a: R = CH₃; 1b, 2b: R = C₂H₅; 1c: R = CH₂CH₂Cl; 1d: R = Ph

The compounds synthesized were characterized by elemental analysis (see Table II) and by ¹H-NMR and IR spectroscopy (see Table III).

TABLE I
Reaction Conditions for the Synthesis of *N,N'*-Bis [(Dialkoxyphosphinyl)methyl]-1,4-Benzenediamines

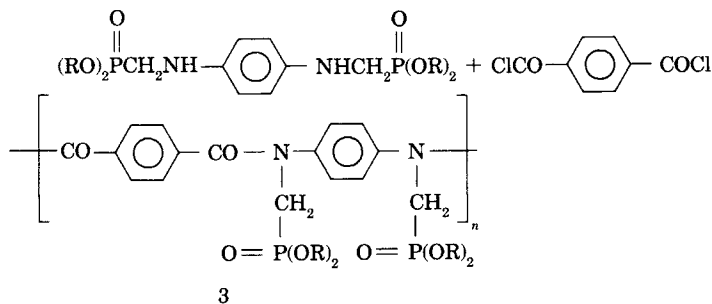
R	Solvent	Temp (°C)	Time (h)	Yield (%)	MP (°C)
CH ₃	Ethyl acetate	77	1.0	74	116–7
C ₂ H ₅	Xylene	110	3.5	50	96–7
CH ₂ CH ₂ Cl	Ethyl acetate	77	1.5	80	115–6
Ph	Ethyl acetate	77	1.0	47	158–163

TABLE II
 Elemental Analysis of *N,N'*-Bis[(Dialkoxyposphinyl)methyl]-1,4-Benzenediamines

Compound	Formula	Elemental analysis (%) ^a			
		C	H	N	P
1a	C ₁₂ H ₂₂ N ₂ O ₆ P ₂	40.96 (40.94)	6.27 (6.31)	7.72 (7.96)	17.5 (17.59)
1b	C ₁₆ H ₃₀ N ₂ O ₆ P ₂	47.28 (47.06)	7.47 (7.41)	6.80 (6.86)	15.1 (15.18)
1c	C ₁₆ H ₂₆ Cl ₄ N ₂ O ₆ P ₂	35.34 (35.20)	5.02 (4.76)	5.14 (5.13)	13.3 (13.35)
2b	C ₃₀ H ₃₈ N ₂ O ₈ P ₂	58.74 (58.44)	6.02 (6.21)	4.68 (4.54)	9.9 (10.05)

^a () = calculated.

Polymers were prepared by condensation of these phosphinylmethyl diamines with terephthaloyl dichloride as shown below:



3a, 3b, 3c: R = CH₃; 3d, 3e: R = C₂H₅

The resulting polymers have low viscosities. Attempts to increase the molecular weight by changing the polymerization procedure had limited success only. The conditions of polymerization and the flammabilities of the polymers produced are summarized in Table IV.

The flammabilities of the above polymers show an increase with increasing polymerization temperature. All these polymers show intumescence during burning. This phenomenon has also been observed in other phosphorus-modified polymers.¹³

The thermal properties (TGA, DSC) of the polyamides were examined in different environments (nitrogen and air). The thermogravimetric analysis (see curve 3a in Fig. 1) shows a narrow decomposition range at 260°C with the same weight loss in nitrogen and in air. This supports the view that it is a pyrolytic stage of decomposition. The TGA thermogram of polymer 3d, at the same pyrolytic stage, shows a greater weight loss. Polymer 3c does not show any weight loss around 260°C. This observation in combination with the absence of a melting endotherm in the DSC thermogram of polymer 3c (see Fig. 2) could support the proposition that polymer 3c has a crosslinked structure.

TABLE III
Spectroscopic Data of *N,N'*-Bis[(Dialkoxyporphinyl)methyl]-1,4-Benzenediamines

Compound	Solvent	¹ HNMR		IR KBr (cm ⁻¹)
		PPM		
1a	CDCl ₃	6.6 (s, 4H, aromatic protons); 3.8 (d, <i>J</i> _{POCH} = 11 Hz, P—OCH ₃); 3.5 (d, <i>J</i> _{POCH} = 13 Hz, P—CH ₂)	3330 (NH); 3020–2910 (=CH); 1525 (aromatics); 1290 (C—N); 1250 (P=O); 1060–1020 (P—O—C)	
2a	CDCl ₃	7.2 (m, 10H, aromatic protons); 7.1 (s, 4H, aromatic protons); 4.3 (d, 4H, <i>J</i> _{POCH} = 12 Hz, P—CH ₂); 3.7 (d, 12H, <i>J</i> _{POCH} = 10 Hz, P—O—CH ₃)	2900 (=CH); 1630 (C=O); 1500 (aromatics); 1310 (C—N); 1245 (P=O); 1020–1010 (P—O—C)	
1b	CDCl ₃	6.4 (s, 4H, aromatic protons); 4.0 (m, 8H, P—OCH ₂ CH ₃); 3.4 (b, 2H, NH); 3.3 (d, 4H, <i>J</i> _{POCH} = 13 Hz, P—CH ₂); 1.2 (t, 12H, POCH ₂ CH ₃)	3250 (NH); 2900–2800 (=CH); 1525–1500 (aromatics); 1310–1280 (C—N); 1240 (P=O); 1040–1010 (P—O—C)	
2b	CDCl ₃	7.3 (m, 10H, aromatic protons); 7.1 (s, 4H, aromatic protons); 4.3 (d, <i>J</i> _{POCH} = 12 Hz, P—CH ₂); 4.2 (m, P—O—CH ₂ CH ₃); 1.2 (t, 12H, P—OCH ₂ CH ₃)	3000–2900 (=CH); 1650 (C=O); 1520 (aromatics); 1320 (C—N); 1240 (P=O); 1060–1015 (P—O—C)	
1c	CDCl ₃	6.7 (s, 4H, aromatic protons); 4.3 (m, 8H, P—OCH ₂ CH ₂ Cl); 3.6 (t, P—O—CH ₂ CH ₂ Cl)	3300 (NH); 2900–2800 (=CH); 1520 (aromatics); 1290 (C—N); 1245 (P=O); 1035–1010 (P—O—C)	
1d	DMSO-d ₆	7.3 (m, 20H, aromatic protons); 6.7 (s, 4H, aromatic protons); 5.4 (b, 2H, NH); 3.9 (d, 4H, <i>J</i> _{POCH} = 10 Hz, P—CH ₂)	3280 (NH); 1480 (aromatics); 1210–1185 (P=O); 945–925 (P—O—C)	

TABLE IV
Conditions of Synthesis and Properties of Poly[*N,N'*-Bis(Dialkoxyphosphinyl)methyl-1,4-Phenyleneterephthalamides]

Polymer	Diamine	Polymerization procedure	Yield (%)	η_{inh} (dL/g)	LOI
3a	1a	A	50	0.11 ^a	40.5
3b	1a	B	67	0.07 ^a	57.5
3c	1a	C	95	0.05 ^a	74.5
3d	1b	A	94	0.04 ^b	32.0
3e	1b	B	88	0.07 ^c	38.0

^a 0.5 g/100 mL H₂SO₄ 98%.

^b 0.5 g/100 mL CHCl₃.

^c 0.5 g/100 mL DMAC.

The DSC thermograms (see Fig. 2) of polymers 3a and 3d show endotherms at 193 and 188–198°C, respectively. These are attributed to melting transitions. Polymer 3c shows a broad endotherm at 180°C which in combination with the TGA weight loss can be attributed to the vaporization of traces of *o*-dichlorobenzene.

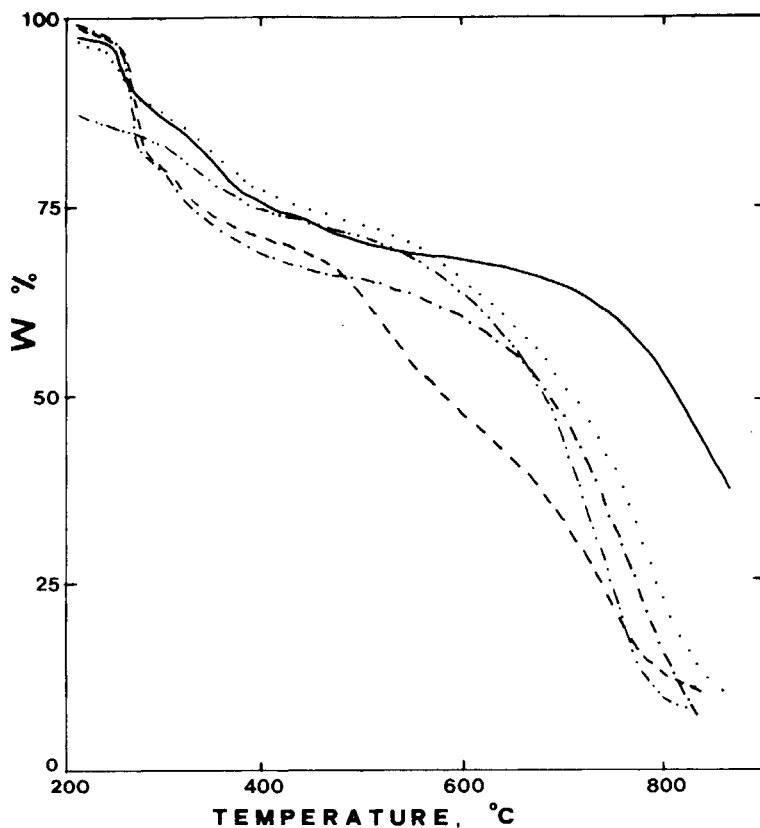


Fig. 1. TGA thermograms of the synthesized polyamides. Polyamide 3a in nitrogen (—) and in air (···); 3c in nitrogen (- · - ·); 3d in nitrogen (- · - ·) and air (- - -).



Fig. 2. DSC thermograms of polyamides 3a, 3c, and 3d.

It is reported that intumescent polymers impart inflammability.¹³ Therefore, preliminary tests were made on the fire retardance of polystyrene (PS) blended with various proportions of fire-retardant polymer 3d. The particular polymeric additive was chosen because of its self extinguishing character (LOI 32) and its mutual solubility with PS in tetrahydrofuran. Table V gives the results of these tests. The almost linear increase of LOI (see Fig. 3) does not indicate any extraordinary effect. As DSC measurements

TABLE V
Blends of Polystyrene (PS) with Polymer 3d

% PS	% 3d	P,W (%)	LOI
100	0	0	18.5
85	15	1.73	20.2
75	25	2.88	21.2
65	35	4.02	21.7
50	50	5.75	22.8

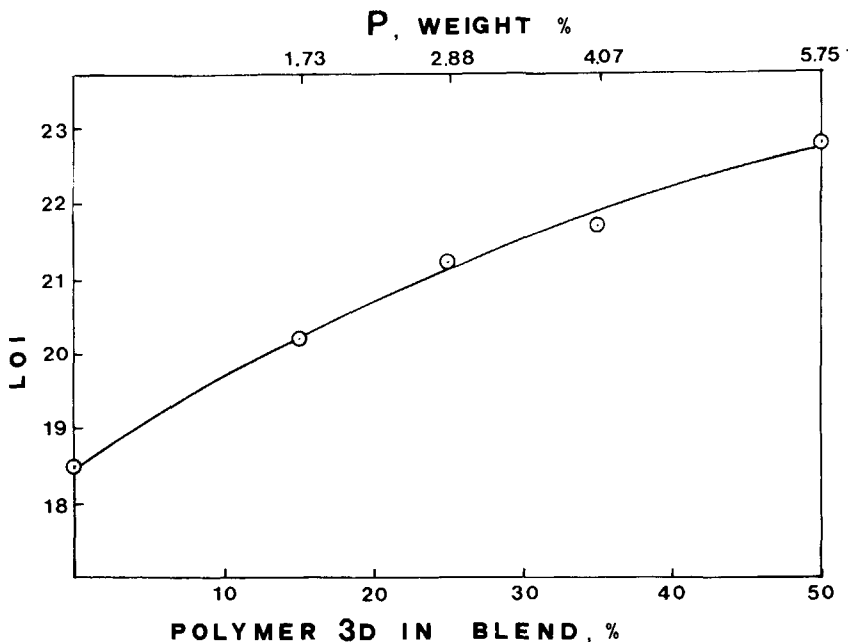


Fig. 3. LOI of blends of polyamide 3d with polystyrene as a function of 3d content in blend and also of the phosphorus content in the blend.

showed, blends in the solid state were not compatible. Therefore, no further evaluation of their solid state properties was carried out.

CONCLUSIONS

The synthesized polyamides 3 have low viscosities. Change to more drastic conditions of the polymerization procedure does not affect molecular weights. This in combination with the results on the synthesis of the model compounds shows that the low molecular weights obtained cannot be attributed to a lower reactivity of the phosphinylmethyl diamines. For the polymers prepared under drastic conditions, thermal analysis data in combination with substantially higher values of inflammability supports the existence of a crosslinked structure.

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References

1. Du Pont Technical Bulletin on Kevlar, 1980.
2. V. V. Korshak, *J. Polym. Sci.*, **31**, 319 (1958).
3. T. M. Frunze et al., *Izv. Akad. Nauk SSSR, Otdel Khim. Nauk*, 783 (1958).
4. A. Rio, Ger. Pat 1,947,339 (1970).
5. P. W. Morgan, U.S. Pat. 2,646,420 (1953); *Chem. Abstr.*, **47**, 10276 (1953).
6. A. A. Koutinas, A. K. Tsolis, P. Demertzis, "Symposium on Recent Aspects of Polymer Flammability" at the ACS 180th National Meeting, *Org. Coating Plast. Chem. Prepr.*, **43**, 97.

7. J. Mikroyannidis, *J. Appl. Polym. Sci.*, **29**, 691 (1984).
8. J. Mikroyannidis and D. Kourtides, *J. Appl. Polym. Sci.*, **29**, 941 (1984).
9. J. Riddick and W. Bunger, *Organic Solvents*, 3rd ed., Wiley-Interscience, New York, 1970.
10. ASTM E-205-64 (1970).
11. S. Kwolek and P. Morgan, U.S. Pat. 3,063,966 (1962).
12. C. W. Stephens, U.S. Pat. 3,296,201 (1967).
13. R. Hindersinn and G. Witschard, in *Flame Retardancy of Polymeric Materials*, W. Kuryla and A. Papa, Eds., Marcel Dekker, New York, 1978, Vol. 4.

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