

# Synthesis, Physical and Thermal Characterization of Phosphorus-Containing Homopolymers and Copolymers Based on 2,4-Bis(4-Aminophenoxy)-6-Diethoxyphosphinyl-s-Triazine

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## Synopsis

Novel phosphorus-containing homopolyimides, homopolyamides, and homopolyureas were prepared by reacting 2,4-bis(4-aminophenoxy)-6-diethoxyphosphinyl-s-triazine (BADT) with pyromellitic or benzophenone tetracarboxylic dianhydride, terephthaloyl chloride, and tolylene diisocyanate, respectively. In addition, the corresponding copolymers that contained approximately 3% phosphorus were prepared by reacting BADT and 4,4'-diaminodiphenyl sulfone with the aforementioned reagents. These polymers were characterized by inherent viscosity measurements, infrared (IR) and proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectroscopy as well as by differential thermal analysis (DTA) and dynamic thermogravimetric analysis (TGA). Their thermal properties were compared with those of the corresponding nonphosphorylated polymers. The copolymers were stable up to 233–272°C in nitrogen or air atmosphere. The homopolymers showed a relatively lower thermal stability. Furthermore, a model diimide, diamide, and diurea were synthesized from the reactions of BADT with phthalic anhydride, benzoyl chloride, and phenyl isocyanate, respectively. The physical and thermal characteristics of these model compounds were correlated with those of the corresponding homopolymers.

## INTRODUCTION

Flame retardation of polymers may be accomplished either utilizing fire-retardant additives or by modification of their structure.<sup>1,2</sup> According to the latter approach phosphorus- and/or halogen-containing monomers are synthesized which subsequently homopolymerized or copolymerized at the desirable concentrations with common monomers.

In connection with our interest in development of new fire-resistant polymers,<sup>3-5</sup> we carried out the synthesis and characterization of several phosphorus-bearing homopolyimides, homopolyamides, and homopolyureas as well as the corresponding copolymers derived from 2,4-bis(4-aminophenoxy)-6-diethoxyphosphinyl-s-triazine (BADT). The presence of the phenoxy groups in this diamine is expected to improve the flexibility of polymers and especially of the more rigid polyimides. However, the pendant diethoxyphosphinyl groups attached to the s-triazine ring will disrupt chain packing of polymers,

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thus increasing their solubility. The polymers synthesized are expected to possess moderate thermal stability because of the thermally sensitive diethoxyphosphinyl groups<sup>3-5</sup> and the medium thermal stability of the *s*-triazine ring.<sup>6</sup>

## EXPERIMENTAL

### Instrumentation

Infrared (IR) spectra were recorded on a Perkin-Elmer 710B spectrometer utilizing KBr pellets. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were obtained using a Varian T-60A spectrometer at 60 MHz in DMSO-d<sub>6</sub> solution. Chemical shifts ( $\delta$ ) are given in ppm with tetramethylsilane as an internal standard.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a DuPont 990 thermal analyzer system. DTA measurements were made using a high temperature (1200°C) cell in N<sub>2</sub> atmosphere at a flow rate of 60 cm<sup>3</sup>/min. Dynamic TGA measurements were made at a heating rate of 20°C/min in atmospheres of N<sub>2</sub> or air at a flow rate of 60 cm<sup>3</sup>/min.

Melting points were determined on an Electrothermal melting point apparatus IA6304 (Electrothermal Engineering Ltd., U.K.) and are uncorrected. The inherent viscosities of polymers were determined for solutions of 0.5 g/100 mL in DMF at 30°C using an Ubbelohde suspended level viscometer.

### Reagents and Solvents

The synthesis and characterization of BADT has been described elsewhere.<sup>7</sup> In brief, the reaction of cyanuric chloride with an equimolar amount of triethyl phosphite afforded 2,4-dichloro-6-diethoxyphosphinyl-*s*-triazine. The latter reacted subsequently with sodium 4-nitrophenoxide to yield 2,4-bis(4-nitrophenoxy)-6-diethoxyphosphinyl-*s*-triazine. Next, it was hydrogenated utilizing palladium on activated carbon as catalyst.

Pyromellitic dianhydride (PMDA) and benzophenone tetracarboxylic dianhydride (BTDA) (Aldrich) were recrystallized from acetic anhydride. 4,4'-Diaminodiphenylsulfone (DDS) and terephthaloyl chloride (Aldrich) were recrystallized from methanol and *n*-heptane, respectively. Phthalic anhydride (Merck) was sublimed under reduced pressure. Phenyl isocyanate (Merck) was distilled under reduced pressure (bp 55°C/13 mm). Toluene diisocyanate (Merck) utilized a mixture of the 2,4- and 2,6-isomer of 65% and 35%, respectively, was also distilled under reduced pressure (bp 126°C/11 mm). *N,N*-dimethylformamide (DMF) (Aldrich) was dried by refluxing and fractionally distilled from calcium hydride. Benzoyl chloride (BDH) was used as supplied.

### Preparation of Phosphorus-Containing Homopolymers and Copolymers

The quantities of reagents which were mixed, the reaction yields, the inherent viscosity values, and the phosphorus content of copolymers are listed in Table I.

TABLE I  
Quantities of Reagents, Reaction Yields, Inherent Viscosities, and Phosphorus Content of Copolymers

Compound	BADT <sup>a</sup> (g)	DDS <sup>b</sup> (g)	PMDA <sup>c</sup> (g)	BTDA <sup>d</sup> (g)	TPC <sup>e</sup> (g)	TDI <sup>f</sup> (g)	Yield (%)	$\eta_{inh}^g$ (dL/g)	P <sup>h</sup> (%)
1a	2.1569		1.0906				85	0.21	
1b	1.7828	0.7004	1.5168				90	0.23	3.08
1c		1.9865	1.7450				86	0.31	
2a	2.1569			1.6111			92	0.20	
2b	1.7828	0.3856		1.8316			84	0.22	3.06
2c		1.7382		2.2556			86	0.32	
3a	2.5883				1.2181		82	0.14	
3b	2.0058	0.8532			1.6410		83	0.15	3.13
3c		1.4899			1.2181		80	0.16	
4a	3.0197					1.2191	93	0.14	
4b	1.7828	0.8800				1.3368	87	0.15	3.10
4c		2.4831				1.7416	95	0.15	

<sup>a</sup>2,4-Bis(4-aminophenoxy)-6-diethoxyphosphinyl-s-triazine.

<sup>b</sup>4,4'-Diaminodiphenylsulfone.

<sup>c</sup>Pyromellitic dianhydride.

<sup>d</sup>Benzophenone tetracarboxylic dianhydride.

<sup>e</sup>Terephthaloyl chloride.

<sup>f</sup>Toluene diisocyanate.

<sup>g</sup>Inherent viscosity values determined for 0.5 g/dL DMF at 30°C.

<sup>h</sup>Phosphorus content of copolymers (theoretical value 3.20%).

The phosphorus content of copolymers was colorimetrically determined.<sup>8</sup> For this purpose, about 0.26 g of the phosphorylated compound was dissolved in a mixture of concentrated nitric acid (25 mL) and perchloric acid (10 mL), and the solution was refluxed for 15 h. A yellow color was obtained by adding ammonium molybdate and ammonium vanadate, the intensity of which was measured utilizing an ultraviolet-visible spectrometer at 420 nm. Calibration was performed by means of analytical grade  $\text{KH}_2\text{PO}_4$ .

### General Synthesis of Polyimides

Homopolyimides 1a and 2a were prepared as follows. BADT was placed in a three-necked flask that contained DMF as solvent and fitted with a nitrogen inlet and a calcium chloride drying tube. Nitrogen was bubbled through the solution which was stirred by a magnetic bar. An equimolar amount of PMDA or BTDA was added portionwise to this stirred solution. Stirring of the reaction mixture at ambient temperature was continued for 4 h in a stream of nitrogen. The polyamic acid required for characterization was isolated by pouring an aliquot of the reaction solution over crushed ice. To the remaining solution, acetic anhydride and fused sodium acetate (300 mL and 27 g, respectively, per mol of water condensed) were added and the mixture was heated at 100°C for 3 h. Alternatively, cyclodehydration was accomplished by refluxing the solution for 2.5 h without adding a dehydrating agent. The mixture was subsequently poured over crushed ice. The solid thus obtained was filtered, washed with water, and dried.

In a likewise manner copolyimides 1b and 2b were prepared by reacting a mixture of BADT and DDS with an equimolar amount of PMDA or BTDA, respectively.

#### *General Synthesis of Polyamides*

Homopolyamide 3a was prepared by the following procedure. A three-necked flask equipped with a dropping funnel and a nitrogen inlet was charged with a solution of BADT in DMF. A double-molar amount of pyridine was added. Terephthaloyl chloride dissolved in DMF was added dropwise under nitrogen atmosphere to the stirred solution which was cooled by an ice bath. After addition of terephthaloyl chloride, the reaction took place for 15 min in an ice bath, followed by 1 h at room temperature. The mixture was poured into water and the solid precipitated was filtered, washed with a dilute solution of hydrochloric acid, next with a solution of  $\text{Na}_2\text{CO}_3$ , finally with water, and dried.

The same procedure was used to prepare copolyamide 3b by reacting a mixture of BADT and DDS with an equimolar amount of terephthaloyl chloride.

#### *General Synthesis of Polyureas*

Homopolyurea 4a was prepared as follows. A three-necked flask equipped with a dropping funnel and a nitrogen inlet was charged with a solution of BADT in DMF. Toluene diisocyanate diluted with DMF was added portionwise to the stirred solution under nitrogen atmosphere. The mixture was heated at  $80^\circ\text{C}$  for 2 h in a stream of nitrogen. Homopolyurea was isolated by pouring the mixture into water. The solid resulting was filtered, washed with a dilute solution of hydrochloric acid, next with a solution of  $\text{Na}_2\text{CO}_3$ , finally with water, and dried.

Copolyurea 4b was similarly prepared by reacting a mixture of BADT and DDS with an equimolar amount of toluene diisocyanate.

### **Preparation of Model Compounds**

#### *Synthesis of Diamic Acid and Diimide 5*

Granular phthalic anhydride (10.0 mmol) was added to a solution of BADT (5.0 mmol) in DMF (12 mL). The mixture was stirred at ambient temperature under nitrogen atmosphere for 4 h. Diamic acid was isolated by pouring an aliquot of the reaction solution over crushed ice. The solid thus obtained was filtered, washed with water, and dried. It was recrystallized from DMF–MeOH (1 : 1 vol/vol) (mp  $176\text{--}178^\circ\text{C}$ ).

IR (KBr)  $\text{cm}^{-1}$ : 3420–3250 (NH stretching); 1555 (NH deformation); 1670 (C=O); 3060, 1620 (aromatic); 1655 (C=N); 1212 (ether bond); 1228 (P=O); 1065–1030 (P–O–C).

$^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ )  $\delta$ : 10.90 (s, 2H,  $-\text{COOH}$ ); 8.80 (s, 2H,  $-\text{NHCO}-$ ); 7.70 (m, 4H, aromatic ortho to  $-\text{NH}-$ ); 7.30 (m, 12H, other aromatic); 4.25 (m, 4H,  $-\text{OCH}_2\text{CH}_3$ ); 1.30 (t, 6H,  $\text{OCH}_2\text{CH}_3$ ).

Cyclodehydration of diamic acid to diimide 5 was carried out by adding acetic anhydride (4 mL) and fused sodium acetate (0.27 g) to the reaction solution and heating at  $100^\circ\text{C}$  for 3 h. The mixture was subsequently poured over crushed ice. The solid resulting was filtered, washed with water, and dried (3.01 g, 87%). It was recrystallized from  $\text{DMF-MeOH}$  (3 : 1 vol/vol) (mp  $202-205^\circ\text{C}$ ).

IR (KBr)  $\text{cm}^{-1}$ : 1790, 1732, 1395, 734 (imide structure); 3060, 1605, 1512 (aromatic); 1670 ( $\text{C}=\text{N}$ ); 1217 (ether bond); 1238 ( $\text{P}=\text{O}$ ); 1065–1030 ( $\text{P}-\text{O}-\text{C}$ ).

$^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ )  $\delta$ : 7.85–7.30 (m, 16H, aromatic); 4.20 (m, 4H,  $-\text{OCH}_2\text{CH}_3$ ); 1.25 (t, 6H,  $-\text{OCH}_2\text{CH}_3$ ).

#### Synthesis of Diamide 6

Benzoyl chloride (10 mmol) diluted with DMF (3 mL) was added dropwise to a stirred solution of BADT (5.0 mmol) in DMF (10 mL) which contained pyridine (10.0 mmol). The reaction took place at about  $0^\circ\text{C}$  for 20 min and then at room temperature for 3 h under nitrogen atmosphere. The mixture was subsequently poured into water. The solid thus obtained was filtered, washed with a dilute solution of hydrochloric acid, next with a solution of  $\text{Na}_2\text{CO}_3$ , finally with water, and dried (2.85 g, 89%). It was recrystallized from *p*-dioxane (mp  $147-149^\circ\text{C}$ ).

IR (KBr)  $\text{cm}^{-1}$ : 3380–3240 (NH stretching); 1552 (NH deformation); 1670 ( $\text{C}=\text{O}$ ); 3050, 1615, 1503 (aromatic); 1655 ( $\text{C}=\text{N}$ ); 1217 (ether bond); 1235 ( $\text{P}=\text{O}$ ); 1068–1032 ( $\text{P}-\text{O}-\text{C}$ ).

$^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ )  $\delta$ : 9.20 (s, 2H,  $-\text{NHCO}-$ ); 8.05 (s, 4H, aromatic ortho to  $-\text{CO}-$ ); 7.65 (m, 4H, aromatic ortho to  $-\text{NH}-$ ); 7.20 (m, 4H, aromatic ortho to  $-\text{O}-$ ); 4.10 (m, 4H,  $-\text{OCH}_2\text{CH}_3$ ); 1.20 (t, 6H,  $-\text{OCH}_2\text{CH}_3$ ).

#### Synthesis of Diurea 7

A mixture of BADT (6.0 mmol), phenyl isocyanate (12.0 mmol), and DMF (14 mL) was stirred under nitrogen atmosphere for 1 h and then heated at  $80^\circ\text{C}$  for 2 h. It was subsequently poured into water. The solid resulting was filtered, washed with a dilute solution of hydrochloric acid, next with a solution of  $\text{Na}_2\text{CO}_3$ , finally with water, and dried (3.70 g, 92%). It was recrystallized from *p*-dioxane (mp  $172-174^\circ\text{C}$ ).

IR (KBr)  $\text{cm}^{-1}$ : 3410–3250 (NH stretching); 1565 (NH deformation); 1680 ( $\text{C}=\text{O}$ ); 3045, 1615, 1500 (aromatic); 1663 ( $\text{C}=\text{N}$ ), 1213 (ether bond); 1230 ( $\text{P}=\text{O}$ ); 1065–1037 ( $\text{P}-\text{O}-\text{C}$ ).

$^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ )  $\delta$ : 8.50 (s, 4H,  $-\text{NHCONH}-$ ); 7.50 (m, 8H, aromatic ortho to  $-\text{NH}-$ ); 7.05 (m, 8H, other aromatic); 4.20 (m, 4H,  $-\text{OCH}_2\text{CH}_3$ ); 1.15 (t, 6H,  $-\text{OCH}_2\text{CH}_3$ ).

## RESULTS AND DISCUSSION

### Synthesis, Characterization, and Thermal Properties of Polymers

Scheme 1 shows the chemical structures of the phosphorus-containing homopolymers and copolymers based on BADT as well as of the corresponding common polymers that were synthesized for comparative purposes. DDS, which showed a reactivity comparable to that of BADT, was used as comonomer for the preparation of copolymers. The latter contained approximately 3% phosphorus. DDS was also used for the synthesis of common polymers.

Polymers 1 and 2 containing imide groups were prepared by the two-stage polycondensation method<sup>9-12</sup> utilizing DMF as solvent. However, other polar aprotic solvents such as *N,N*-dimethylacetamide (DMAc), *N*-methyl-pyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) could also be used. PMDA or BTDA was added to the diamine solution. The polyamic acid forming reaction was fast and exothermic. The inherent viscosity ( $\eta_{inh}$ ) values of the polyamic acid solutions were determined (Table I). Cyclodehydration was accomplished by adding acetic anhydride and fused sodium acetate to the polyamic acid solution and moderate heating.

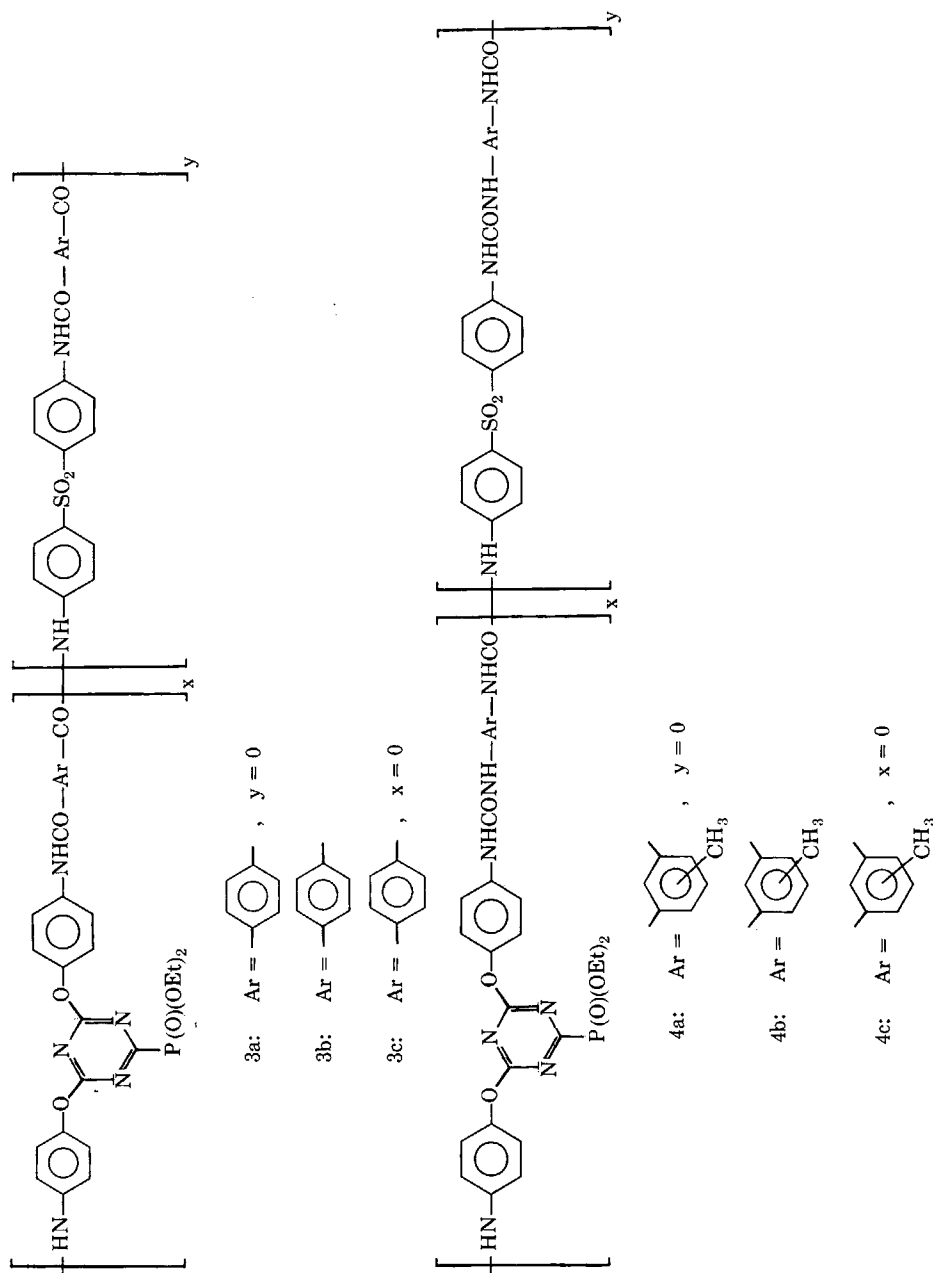
Polymers 3 containing amide groups were prepared by reacting terephthaloyl chloride with diamines in the presence of an acid acceptor such as pyridine. The reaction was completed at room temperature, although DDS shows a relatively low nucleophilicity due to the electron-withdrawing sulfonyl group.

Polymers 4 bearing ureylene groups were synthesized from the reaction of tolylene diisocyanate with diamines. This reaction was monitored by IR measurements of the mixture on the basis of the isocyanate group absorption. The reaction was completed by moderate heating. DMF, which behaves as a weak base, catalyzed the urea forming reaction.

The inherent viscosity values of all polymers are summarized in Table I. It can be seen that the molecular weight of polymers was reduced with increasing concentration of phosphorus. An analogous behaviour has been observed in many other phosphorylated polymers.<sup>3-5</sup> Polyimides showed a higher degree of polymerization than polyamides and polyureas.

The structure of polymers was confirmed by IR and <sup>1</sup>H-NMR spectroscopy. IR and <sup>1</sup>H-NMR spectral data of homopolymers are listed in Table II. The IR spectra of intermediate polyamic acids showed characteristic absorptions around 3420–3240, 1675, 1310, and 871 cm<sup>-1</sup>. These bands disappeared after cyclodehydration and new absorptions near 1780, 1725, and 1380, and 725 cm<sup>-1</sup> associated with the imide structure were observed. Polyamides exhibited absorption bands at about 3430–3240 cm<sup>-1</sup> (NH stretching), 1547 cm<sup>-1</sup> (NH deformation), and 1660 cm<sup>-1</sup> (amide carbonyl). Polyureas absorbed also at these spectrum regions due to the ureylene groups. All phosphorylated polymers showed absorption bands around 1240 and 1060–1020 cm<sup>-1</sup> assigned to P=O and P—O—C linkages, respectively. These bands were weaker in copolymers. From Table II it can be seen that in polyamides and polyureas





Scheme 1 (Continued)



TABLE II  
 Physical Characteristics of Homopolymers

Sample	IR spectral data	<sup>1</sup> H-NMR spectral data <sup>a</sup>
	KBr (cm <sup>-1</sup> )	δ <sup>b</sup> (ppm)
1a	1792, 1725, 1382, 728 (imide structure); 3065, 1618, 1517 (aromatic); 1662 (C=N); 1222 (ether bond); 1247 (P=O); 1060-1035 (P-O-C)	11.10 (s, <sup>c</sup> 2H, —COOH); 8.70 (s, 2H, —NHCO—); 8.00-7.70 (m, <sup>d</sup> 2H, aromatic of PMDA ring and 4H, aromatic ortho to —NH—); 7.20 (m, 4H, aromatic ortho to —O—); 4.30 (m, 4H, —OCH <sub>2</sub> CH <sub>3</sub> ); 1.35 (t, <sup>e</sup> 6H, —OCH <sub>2</sub> CH <sub>3</sub> )
2a	1785, 1722, 1373, 722 (imide structure); 3045, 1612, 1515 (aromatic); 1658 (C=N); 1217 (ether bond); 1248 (P=O); 1057-1028 (P-O-C)	11.00 (s, 2H, —COOH); 8.50 (s, 2H, —NHCO—); 7.90 (m, 6H, aromatic of BTDA rings); 7.50 (m, 4H, aromatic ortho to —NH—); 7.10 (m, 4H, aromatic ortho to —O—); 4.15 (m, 4H, —OCH <sub>2</sub> CH <sub>3</sub> ); 1.20 (t, 6H, —OCH <sub>2</sub> CH <sub>3</sub> )
3a	3420-3250 (NH stretching); 1547 (NH deformation); 1662 (C=O); 3055, 1612, 1503 (aromatic); 1648 (C=N); 1218 (ether bond); 1230 (P=O); 1058-1023 (P-O-C)	8.90 (s, 2H, —NHCO—); 8.10 (m, 4H, aromatic of terephthalic ring); 7.70 (m, 4H, aromatic ortho to —NH—); 7.05 (m, 4H, aromatic ortho to —O—); 4.20 (m, 4H, —OCH <sub>2</sub> CH <sub>3</sub> ); 1.30 (t, 6H, —OCH <sub>2</sub> CH <sub>3</sub> )
4a	3405-3240 (NH stretching); 1546 (NH deformation); 1678 (C=O); 3045, 1604, 1503 (aromatic); 1655 (C=N); 1220 (ether bond); 1238 (P=O); 1060-1037 (P-O-C)	8.30 (s, 4H, —NHCONH—); 7.50 (m, 7H, aromatic ortho to —NH—); 6.90 (m, 4H, aromatic ortho to —O—); 4.25 (m, 4H, —OCH <sub>2</sub> CH <sub>3</sub> ); 2.20 (s, 3H, C <sub>6</sub> H <sub>3</sub> CH <sub>3</sub> ); 1.25 (t, 6H, —OCH <sub>2</sub> CH <sub>3</sub> )

<sup>a</sup> Instead of homopolyimides 1a and 2a, the <sup>1</sup>H-NMR spectra of the corresponding homopolyamic acids were obtained.

<sup>b</sup> In DMSO-d<sub>6</sub> solution.

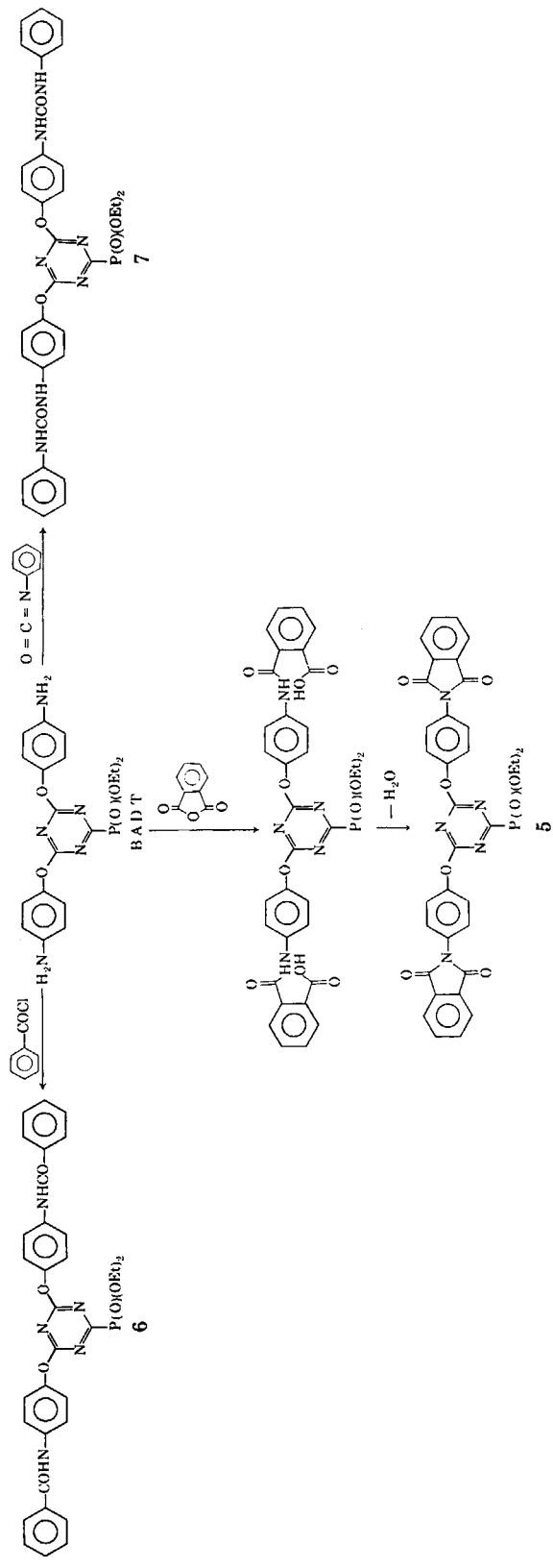
<sup>c</sup> Singlet.

<sup>d</sup> Multiplet.

<sup>e</sup> Triplet.

the P=O absorption was at a lower wavenumber than that of polyimides because of the intramolecular hydrogen bonding. All polymers showed an absorption band around 1650 cm<sup>-1</sup> due to the C=N stretching vibrations. In addition, a sharp absorption that characterizes the substituted melamine structure appeared near 820 cm<sup>-1</sup>. The <sup>1</sup>H-NMR spectra of phosphorylated homopolymers showed a multiplet at about 4.30 δ and a triplet at 1.25 δ associated with the diethoxyphosphinyl groups. Instead of homopolyimides 1a and 2a, the corresponding polyamic acids were characterized by <sup>1</sup>H-NMR spectroscopy because of their higher solubility in polar aprotic solvents.

The phosphorus content of copolymers was colorimetrically determined.<sup>8</sup> They contained 3.06-3.13% phosphorus whereas the calculated value on the



Scheme 2

basis of the amounts of the reagents which were mixed was 3.20% (Table I). This supports that incorporation of BADT in the polymer backbone was almost quantitative when DDS was used as comonomer. However, a copolyamide prepared, under identical experimental conditions, by reacting a mixture of BADT and *p*-phenylenediamine with an equimolar amount of terephthaloyl chloride, contained 0.40% phosphorus whereas its calculated value was 3.20%. The higher nucleophilicity of *p*-phenylenediamine than that of DDS should be responsible for this behavior.

The polymers were thermally characterized by DTA and TGA. Figure 1 presents typical DTA scans of homopolyamide 3a, copolyamide 3b, and the corresponding common polyamide 3c in N<sub>2</sub> atmosphere. The exotherms appeared in these traces were attributed to thermal degradation of polymers because the TGA thermograms showed a large rate of weight loss at the same temperature regions. It can be seen that copolyamide was more thermally stable than homopolyamide and less stable than the nonphosphorylated polyamide. This behavior was also confirmed by TGA. In addition, it is seen that thermal decomposition occurred in more than one step indicating overlapping degradation reactions.

Several TGA data of the phosphorylated as well as of the corresponding nonphosphorylated polymers are listed in Table III. More particularly, the relative thermal and thermooxidative stability of polymers can be assessed by comparing the initial decomposition temperature IDT, the maximum polymer decomposition temperature PDT<sub>max</sub>, and the char yield Y<sub>c</sub> both in N<sub>2</sub> and air. Figure 2 shows typical TGA thermograms of polyimides 1a, 1b, and 1c in N<sub>2</sub>.

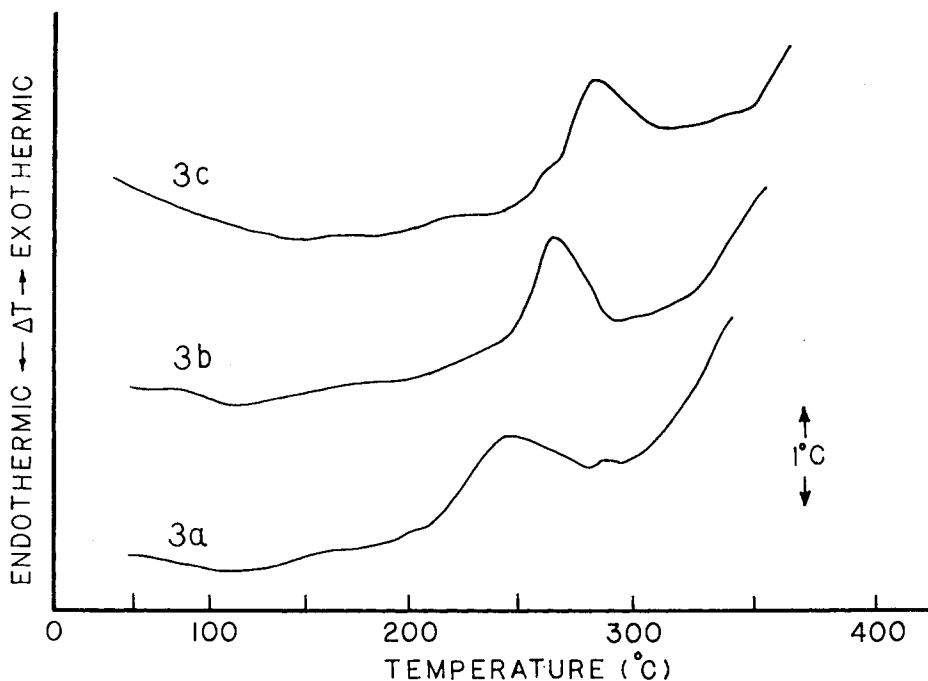


Fig. 1. DTA scans of polyamides 3a, 3b, and 3c in N<sub>2</sub> atmosphere.

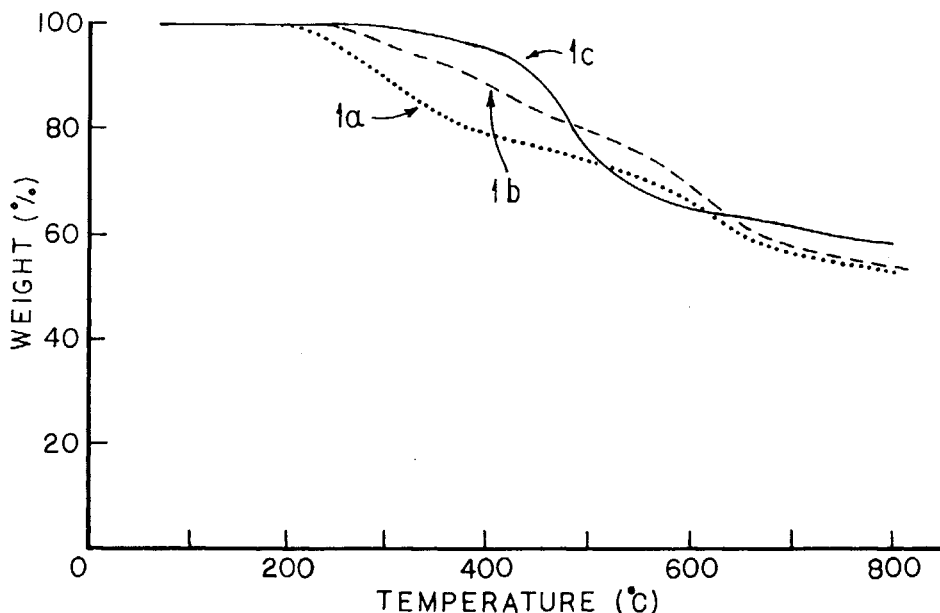


Fig. 2. Typical TGA traces of poly(pyromellitimides) 1a, 1b, and 1c in  $N_2$  atmosphere.

It can be seen that thermal and thermooxidative stability of polymers was reduced with increasing concentration of phosphorus. Polyimides 1, containing pyromellitimide units, were more thermally stable than the corresponding polyimides 2 derived from BTDA. Polyureas were the least thermally stable polymers obtained. In most cases, the anaerobic char yield of phosphorylated polymers was almost same with that of the corresponding non-phosphorylated polymers. In contrast, phosphorylated polymers afforded higher char yield in air atmosphere. Since the ratio  $IDT_{air}/IDT_{N_2}$  varied from 0.97 to 1.02, thermal degradation of polymers was not seriously affected by the presence of oxygen.

### Model Compounds

To obtain fundamental information about the structure of polymers and to investigate their thermal characteristics, several model compounds were synthesized according to the chemical reactions outlined in Scheme 2. These compounds were prepared under the same experimental conditions utilized for preparing the corresponding phosphorylated homopolymers. More particularly, diimide 5 was synthesized by reacting BADT with phthalic anhydride. The intermediate diamic acid was cyclodehydrated by chemical means. In addition, diamide 6 and diurea 7 were synthesized from the reactions of BADT with benzoyl chloride and phenyl isocyanate, respectively.

The IR spectra of model compounds were in agreement with those of the corresponding homopolymers. As an example, the IR spectra of model diamide 6 and homopolyamide 3a are given in Figure 3 for comparison. On the other hand, the  $^1H$ -NMR spectra of model compounds confirmed their structures (see Experimental).

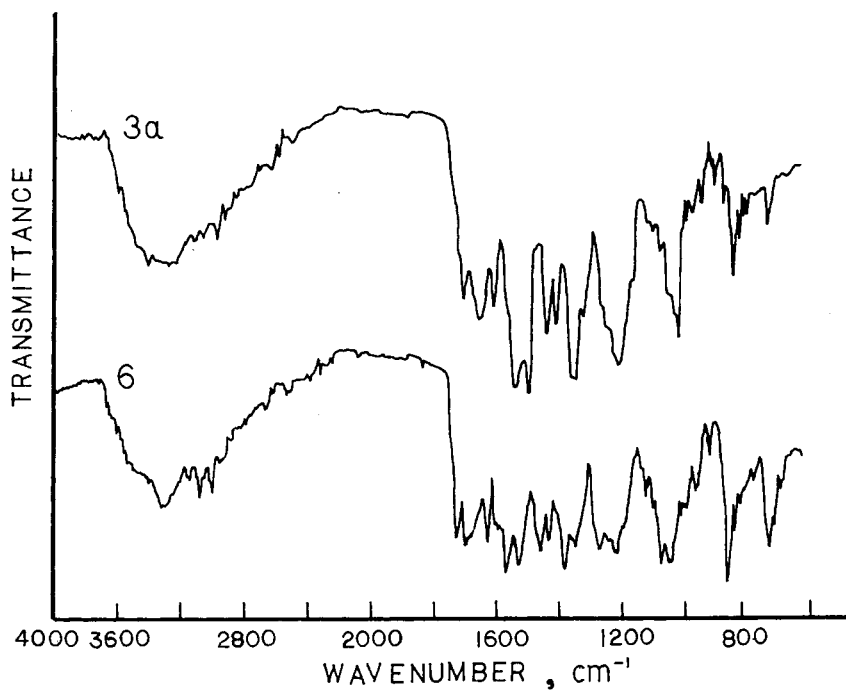


Fig. 3. IR spectra of model diamide 6 and homopolyamide 3a.

TABLE III  
Thermal and Thermooxidative Stability of Polymers and Model Compounds

Sample	N <sub>2</sub>			Air			$\frac{IDT_{air}}{IDT_{N_2}}$
	IDT <sup>a</sup> (°C)	PDT <sub>max</sub> <sup>b</sup> (°C)	Y <sub>c</sub> (800°C) <sup>c</sup> (%)	IDT (°C)	PDT <sub>max</sub> (°C)	Y <sub>c</sub> (650°C) (%)	
1a	238	322	53	235	312	43	0.99
1b	272	441	54	272	401	40	1.00
1c	333	501	58	322	506	11	0.97
2a	234	336	56	233	325	38	0.99
2b	265	359	56	257	348	33	0.97
2c	392	553	59	389	545	4	0.99
3a	230	363	46	227	330	36	0.99
3b	242	370	46	238	337	31	0.98
3c	285	476	45	277	348	4	0.97
4a	204	276	38	204	277	41	1.00
4b	233	305	32	237	303	29	1.02
4c	241	340	30	236	345	11	0.98
5	244	356	30	244	354	31	0.99
6	238	350	36	239	332	32	1.00
7	210	275	37	211	273	40	1.00

<sup>a</sup>Initial decomposition temperature.

<sup>b</sup>Maximum polymer decomposition temperature.

<sup>c</sup>Char yield at 800°C.

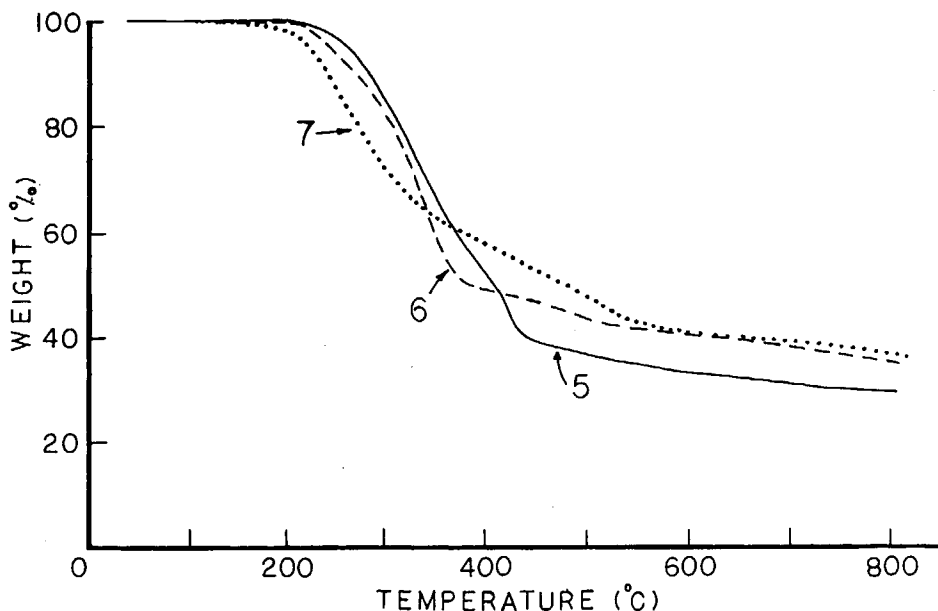


Fig. 4. TGA thermograms of model compounds 5, 6, and 7 in  $N_2$  atmosphere.

Several TGA data of model compounds are listed in Table III. These data are in good agreement with those of the corresponding homopolymers. However, the model compounds afforded a lower char yield because of their lower molecular weight. Figure 4 presents the TGA traces of model compounds in  $N_2$ . It can be seen that diamide was less thermally stable than diimide and more stable than diurea.

### CONCLUSIONS

The reactions of BADT with pyromellitic or benzophenone tetracarboxylic dianhydride, terephthaloyl chloride, and tolylene diisocyanate yielded phosphorus-bearing homopolyimides, homopolyamides, and homopolyureas, respectively. In addition, BADT in combination with DDS reacted with the aforementioned reagents to afford random copolymers. Inherent viscosity measurements revealed that the molecular weight of polymers was reduced with increasing concentration of phosphorus. Polyimides showed a higher degree of polymerization than polyamides and polyureas. The IR spectra of the phosphorylated polymers showed absorption bands associated with the  $P=O$  and  $P-O-C$  linkages. Determination of phosphorus in copolymers showed that incorporation of BADT in their backbone was almost quantitative when DDS was used as comonomer. The copolymers were stable up to 233–272°C in  $N_2$  or air. The homopolymers showed a relatively lower thermal stability. Certain TGA data of model compounds were in good agreement with those of the respective homopolymers.

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