Polyimides. I. Preparation and Properties of Phosphorus-Containing Polyimides

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Synopsis

Phosphorus-containing polyimide resins were prepared by reacting benzophenone tetracarboxylic acid dianhydride with (3-aminophenyl) methyl phosphine oxide (DAP). Copolyimides were also prepared using DAP and 4,2′,4′-triaminobenzanilide (TAB) and tris(3-aminophenyl) phosphine oxide (TAP) and pyromellitic dianhydride (PMDA). The homopolymer showed good thermal properties and little degradation below 400°C. The lapshear strengths of these polyimides depended on the backbone structure. Copolymerization improved thermal and mechanical properties. The glass-fabric-reinforced laminate prepared from one of the copolymer resins had a tensile strength of 43,430 psi.

INTRODUCTION

In industry there is a need of organic matrix resins with high temperature capabilities and flame resistance. Since polymers containing phosphorus as an integral part of the backbone are known to be thermally stable and flame-retardant, efforts have been made to synthesize phosphorus-containing polyimides. For example, polyanhydride–imides,[1] and poly(amide–imides)[2-4] have been reported in the literature.

These polymers had good thermal stability, and were soluble in organic solvents. The outstanding flame resistance of phosphorus containing bisimide resins has earlier been reported.[5-7] In this paper we report the synthesis of condensation polyimides from benzophenone tetracarboxylic acid dianhydride (BTDA) and bis(3-aminophenyl) methyl phosphine oxide. The structure of various copolymers prepared in the present work are given in Scheme 1 (throughout the text these polymers are referred by the letter designation shown in parenthesis):

(B–DAP)

(B–DAP$_m$–TAP$_n$)

CCC 0021-8995/83/092805-08$01.80
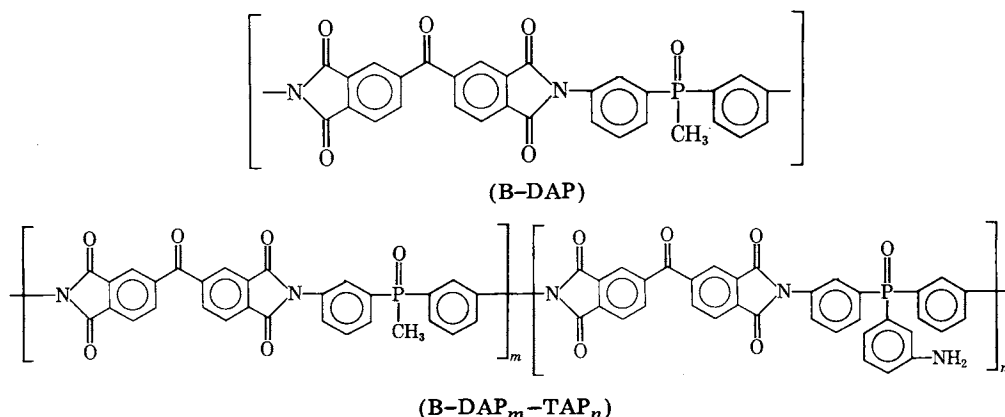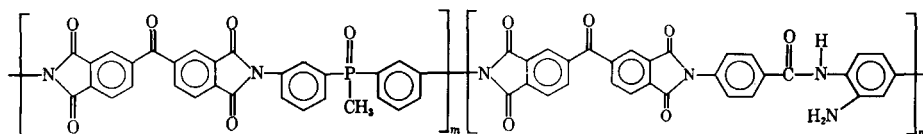
(B–DAP$_m$–TAB$_n$)
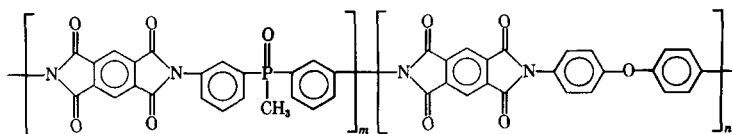
(P–DAP$_m$–E$_n$)

In copolymers the value of m and n will depend on the ratios of diamine taken in the initial monomer feed. The thermal stability and adhesive properties were also evaluated.

EXPERIMENTAL

Starting Materials

Dimethyl formamide (E. Merck) (DMF) was dried over P_2O_5 and then vacuum-distilled. It was stored over molecular sieves (3 Å) for 24 h before use. Acetic anhydride (BDH), pyridine (BDH), benzene (BDH), toluene (BDH), and carbon tetrachloride (BDH) were distilled at normal pressure before use.

BTDA (ICN) was purified by recrystallization from acetic anhydride. It was vacuum dried for 24 h at 80°C before use (mp 226°C).

Bis(3-aminophenyl) methyl phosphine oxide (DAP) was prepared according to the method reported in the literature.[8] Tris(3-aminophenyl) phosphine oxide (TAP) was prepared[9] from triphenyl phosphine oxide by nitration followed by reduction with $SnCl_2/HCl$ (mp 260°C).

4,2',4'-Triaminobenzanilide (TAB) was prepared by the reduction of the condensation product of p-nitrobenzoylchloride with 2,4-dinitroaniline (mp 197–200°C). The IR spectra of this compound showed characteristic absorption bands due to the amide group (1630–1600 cm^{-1}) and the amine group (3420–3300 cm^{-1}).

Preparation of Polyimide: The polymerization was carried out in DMF solution. A typical reaction leading to the formation of B–DAP polyamic acid and polyimide is described.

Bis(3-aminophenyl) methyl phosphine oxide (0.005 mol) was dissolved in 20 mL DMF in a three-necked flask equipped with a nitrogen inlet tube and a solid transfer tube. The solution was stirred and cooled to 0°C. Nitrogen was bubbled through the solution to provide an inert atmosphere. After the diamine dissolved, 0.005 mol of BTDA was added. More DMF was added so as to have a solid content of 10% (w/v). The temperature was maintained at 0°–5°C for 5–6 h. The solution was then allowed to warm to room temperature (24–30°C), the stirring was continued for further 2 h. The polyamic acid thus prepared was stored, as such, at low temperatures.

Polyamic acid films were prepared by casting a DMF solution on glass plate. These were vacuum-dried and were converted to imide form by cyclization at $225 \pm 5°C$.

Characterization of Polyimides: The intrinsic viscosity of a DMF solution of polyamic acid was determined at 30°C with a Ubbelohde suspension-level viscometer. Density of small pieces of polyimide films was determined by the suspension method using xylene and carbon tetrachloride. The IR spectra of polyimides were recorded in films as well as in KBr pellets with a Perkin-Elmer 580-B Grating Infrared Spectrophotometer.

Thermal analysis was carried out using a Stanton Red Croft TG-750 Thermogravimetric Analyzer in nitrogen atmosphere. A heating rate of 10°C/min and sample weight of ~5 mg was used. DTA was done by using Stanton Red Croft DTA 673-4 and DSC was carried out using a DuPont 990 Thermal Analyzer along with a DSC module (DuPont 900).

Adhesive Testing Using Aluminum Adherends

Aluminum adherends were fabricated according to ASTM-D-1002-72. The following dimensions were used: (i) thickness of the sheet, 1.62 ± 0.125 mm; (ii) width of the sheet, 25.4 ± 0.25 mm; (iii) length of the sheet, 101.6 ± 0.25 mm; (iv) length of the overlap, 12.7 ± 0.25 mm.

The aluminum adherends were first abrased with 100-grit emery cloth. After washing the surface was etched for 30 min at 60°C in chromic acid solution (5 parts Cr_2O_3, 5 parts concd H_2SO_4, and 80 parts water). They were then rinsed in distilled water and air-dried at 70°C in an oven.

DMF solutions of polyamic acids (10%) were coated on aluminium joints, and then strips were dried in an oven at a temperature of 120°C. Samples with a 12.7 mm overlap were bonded at a pressure of 250 psi and a temperature of 250°C, for a period of 30 min. The specimens were then cooled to 100°C under pressure. Room-temperature lap shear strength was determined using an Instron Model 1121. A chart speed of 10 cm/min and a crosshead speed of 2 mm/min were used.

Fabrication of Glass Fabric–Imide Resin Laminates

The $B-DAP_9-TAB_1$ copolymer resin in DMF solution was coated on RP-8 epoxy compatible glass fabric (5 in. × 5 in.). The prepegs were dried in an air oven for 30 min. Test laminates were obtained by stacking six plies of dried prepegs in a platen press preheated to 275°C. A contact time of 2.5 min with a pressure of 10 psi was used to remove the trapped solvent. Later the pressure was increased to 500 psi, and curing was done for 30 min. At the end, the press was cooled to room temperature. The tensile strength was evaluated according to the ASTM D-638. A gauge length of 2.0 in. a crosshead speed of 0.05 in./min, and a sample width of 0.25 in. were used.

RESULTS AND DISCUSSION

The conditions and results of polymerization reaction are given in Table I. The copolyamic acids have been named according to the molar ratios of the di-

TABLE I
Polyamic Acids: Conditions of Polymerization and Characterization of Polymers

| No. | Sample | Quantities of Starting materials (g) | | | | | DMF (cm^3) | $[\eta]^a$ (dL/g) | Density^b (g/cm^3) |
		BTDA	DAP	TAP	TAB	E			
1	B–DAP	1.61	1.23	—	—	—	28.4	0.19	1.401
2	B–DAP$_9$–TAP$_1$	1.073	0.738	0.1076	—	—	19.2	0.46	1.351
3	B–DAP$_4$–TAP$_1$	1.073	0.656	0.2014	—	—	19.3	0.78	1.344
4	B–DAP$_9$–TAB$_1$	2.146	1.476	—	0.1613	—	37.8	0.51	1.281
5	P–DAP$_1$–E$_9$	2.18	0.292	—	—	1.6	40.7	1.33	—

^{a} In DMF at 30°C.
^{b} Imide state.

amines taken in the initial monomer feed. For example, the polyamic acid prepared from copolymerization of BTDA with DAP and TAP in molar ratios of (0.0026 and 0.0006) has been named as B–DAP$_4$–TAP$_1$.

The lowest intrinsic viscosity was obtained with B–DAP polyamic acid and highest with P–DAP$_1$–E$_9$ under the same reaction conditions. Since $[\eta]$ is an indication of molecular weight, it is quite likely that B–DAP$_1$–E$_9$ had a higher molecular weight. The reaction of diamine with dianhydride is a nucleophilic substitution reaction where the amine acts as a nucleophile. Therefore, the higher the nucleophilicity of the amine the faster would be the reaction. The inductive and resonance effects influence the basic character as well as the nucleophilic nature of the amines. Greater reactivity of diaminodiphenylether in comparison to other amines used in the present work may be the reason for increased chain growth in these polymers. Phosphine oxide substituent is a (−I) group, and, since it is present at m-position, hence it will also reduce the reactivity of amino groups in DAP and TAP. The flexible link in the form of carbonyl group present in the BTDA moiety could be another reason for the low value of $[\eta]$.
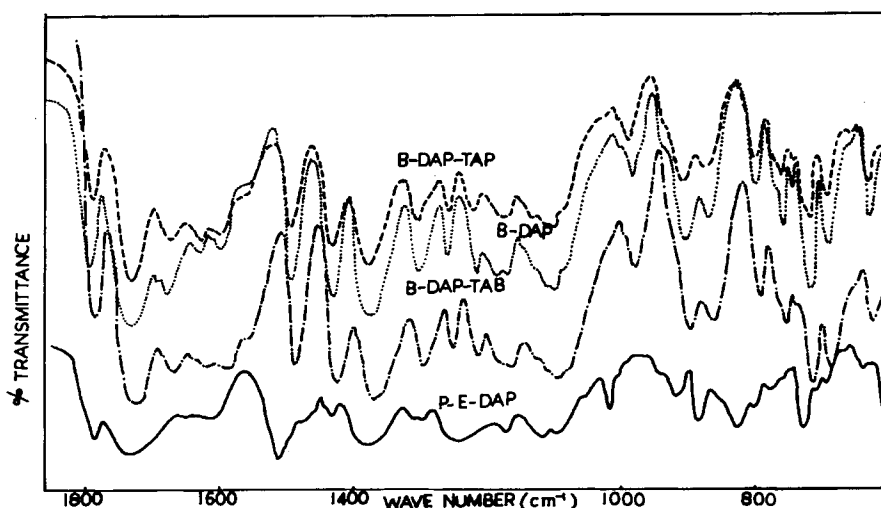

Fig. 1. IR spectra of polyimides.

B–DAP polyimide was found to be soluble in DMF, DMAC, NMP, and DMSO. Hence its intrinsic viscosity was also determined in DMF at 30°C. A slightly high $[\eta]$ value was observed for B–DAP polyimide when compared to B–DAP polyamic acid. Polyimides are more rigid than polyamic acids, and this may be the reason for higher $[\eta]$ values of this polymer.

The addition of triamines TAP and TAB resulted in increase in $[\eta]$. However, a high molar ratio of triamine resulted in rapid gelation.

The density of the B–DAP polyimide was found to be 1.401 g/cm^3. The value was decreased when it was copolymerized with triamines.

Characteristic imide bands were observed in the IR spectra of these polyimides (Fig. 1). Strong absorptions in the range 1770–1780 cm^{-1} and 1720–1730 cm^{-1} arising due to the imide group were present. Strong bands in the range 1325–1390 cm^{-1} (imide II), 1105–1120 cm^{-1} (imide III) and 710–720 cm^{-1} (imide IV) were also observed in the spectra of all the polyimides. Along with these absorptions, other absorptions arising because of P=O (at 1175 $\pm$ 15 cm^{-1}), P–C$_6$H$_5$ at 1425 cm^{-1}, C$_6$H$_5$ (at 1585 $\pm$ 10 cm^{-1} and 1480 cm^{-1}), and C–N at 1375 $\pm$ 5 cm^{-1} were also observed.

The thermogravimetric traces of these polyimide samples in nitrogen atmosphere are given in Figure 2. The major decomposition of all these polyimides commenced in the range 450–505°C. Polyimides B–DAP and B–DAP$_9$–TAP$_1$ lost 10% weight at 225°C and 260°C, respectively. This may be due to the release
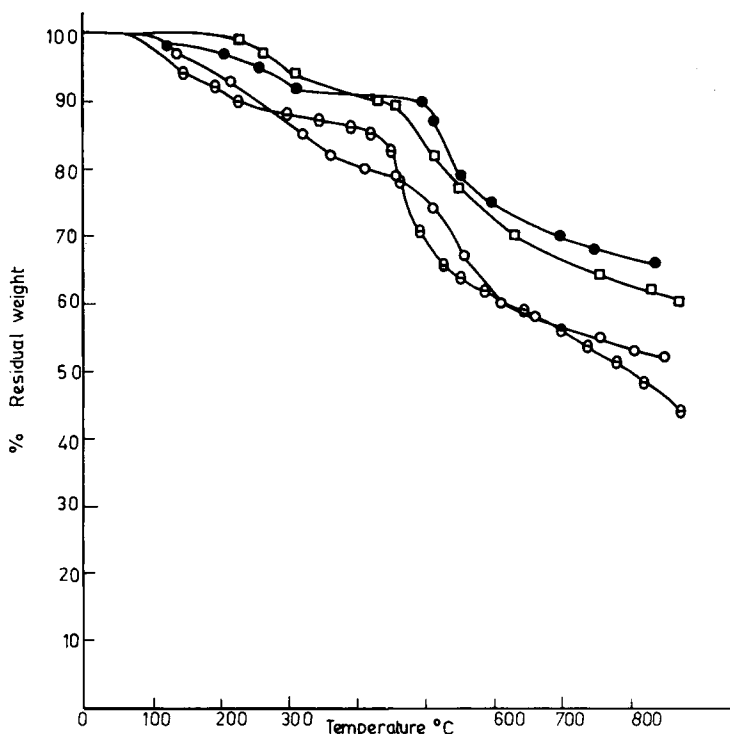

Fig. 2. TG traces of polyimides in nitrogen atmosphere: (O) B–DAP$_9$–TAP$_1$; (●) B–DAP$_4$–TAP$_1$; (▫) B–DAP$_9$–TAB$_1$; (⊖) B–DAP.

TABLE II
Thermal Behavior of Polyimides in Nitrogen Atmosphere

Property tested	B–DAP	B–DAP$_9$–TAP$_1$	B–DAP$_4$–TAP$_1$	B–DAP$_9$–TAB$_1$
IDT[a] (°C)	450	485	505	460
Temp of 20% weight loss	465	—	545	525
Temp of 30% weight loss	495	540	690	630
Temp of 40% weight loss	610	615	—	—
Char yield at 800°C (%)	49.5	52	66	62.5
IPDT[b] (°C)	643	648	729	707
T_{max}[c] (°C)	475	537	525	512
Activation energy (kJ/mol)	122	63	105	85

[a] IDT = initial decomposition temperature.
[b] IPDT = integral procedural decomposition temperature.
[c] T_{max} = temperature of maximum rate of decomposition.

of trapped solvents in the polymers. B–DAP$_4$–TAP$_1$ polyimide started decomposing at a higher temperature. The incorporation of triamine TAP or TAB resulted in an increase in temperatures of decompositions (Table II).

Integral procedural decomposition temperature (IPDT) was calculated in the temperature range of 25–850°C.[10] An increase in IPDT was observed with copolymerization. Another criterion used to evaluate thermal stability was the anaerobic char yields of polymers at 800°C. Here also an improvement in char yield was observed with copolymerization. The char yield of polyimide B–DAP was 49.5%, whereas the copolyimide B–DAP$_4$–TAP$_1$ had a char yield of 66%.

The activation energy E^* for the decomposition of polyimides in nitrogen atmosphere were calculated by the method of Dharwadkhar and Karkhanawala.[11] Polyimide B–DAP had an activation energy of 122 kJ/mol whereas the copolyimides had a lower value (Table II).

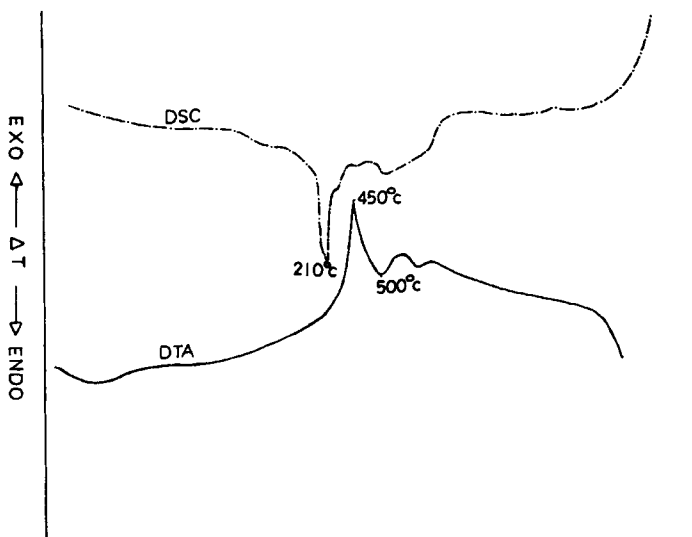Typical DTA and DSC traces of B–DAP polyimide in air atmosphere are

Fig. 3. DTA and DSC traces of B–DAP polyimide in air atmosphere.

TABLE III
Lap Shear Strength of Polyimides

No.	Sample	Lap shear strength (psi)
1	B–DAP	695
2	B–DAP$_9$–TAP$_1$	845
3	B–DAP$_4$–TAP$_1$	—
4	B–DAP$_9$–TAB$_1$	1327

presented in Figure 3. This polyimide showed an exotherm at 450°C in DTA, which was assigned to the decomposition of the polyimide. Two small and broad peaks were also observed above 500°C and are attributed to thermooxidation of the polyimide. DSC study of this polyimide indicated a transition temperature at 210°C.

The data on the lap shear strength of these polyimides is given in Table III. The lap shear strength of B–DAP polyimide was 695 psi with aluminum adherends. In B–DAP$_9$–TAB$_1$ the lap shear strength was found to be 1327 psi. In sample B–DAP$_4$–TAP$_1$ the metal failed rather than the joint. The effect of structure on adhesive properties of polyimides has been reported earlier.[12,13] The higher lap shear strength and thermal stability of triamine containing polyimides may be due to crosslink formation between the carbonyl group of BTDA and free amino group in the triamine moiety leading to an azomethine, $>$C = N-linkage. The phosphorus-containing copolyimides show promise as adhesives, even though no attempt has been made to maximize the strength by varying temperature and pressure of bonding.

The tensile strength of the glass fabric reinforced B–DAP$_9$–TAB$_1$ polyimide having 20% resin content was found to be 43,430 psi, which is comparable to the state-of-the-art polyimide laminates.

CONCLUSION

These studies show that modification of the structure of phosphorus containing polyimides by copolymerization with di- and triamines results in an improvement in thermal properties and adhesion. Some of the polyimides studied appear to have excellent potential for use as structural adhesives and resin matrices for advanced composites.

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