

Properties of Polypyromellitimides Containing Phosphorus

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SYNOPSIS

The paper deals with the synthesis and characterization of seven polypyromellitimide samples having varying contents of phosphine oxide and ether linkages in the backbone with pendant maleimido groups. Curing characteristics and thermal stability of polymers were evaluated by differential scanning calorimetry and dynamic thermogravimetry. It was observed that an increase in pendant maleimido groups resulted in an increase in the heat of polymerization. Char yield also increased with increase in phosphorus content. Conductivity and dielectric parameters were also evaluated. The mechanism of conduction was found to be a combination of electronic and ionic type.

INTRODUCTION

We have recently reported synthesis of several polypyromellitimides containing phosphine oxide in the backbone and maleimido groups as pendant side chains.^{1,2} These polymers were obtained by solution polycondensation reaction in DMF in three steps. The first step involved the reaction of equimolar amounts of maleic anhydride (MA) and tris(*m*-aminophenyl) phosphine oxide (TAP) in DMF at 60°C for 2 h to give an intermediate TAP-MA which was not isolated from solution. It is expected that, by such a reaction, one amino group of TAP, on average, will react with maleic anhydride. Low temperature polycondensation was then carried out at 0–5°C by the addition of 4,4'-diaminodiphenyl ether (DADPE) and pyromellitic dianhydride (PMDA) followed by cyclodehydration of the poly(amide-acid) by chemical means. In the present work, intermediate TAP-MA was prepared in acetone solution and characterized before using it for synthesis of polypyromellitimides. Thermal and electrical properties of the polymers thus obtained were then evaluated.

EXPERIMENTAL

Materials

Tris(*m*-aminophenyl) phosphine oxide was prepared by a method described elsewhere.³ Pyromellitic dianhydride (Fluka) was crystallized from acetic anhydride and dried in vacuum at 60°C before use. Maleic anhydride and 4,4'-diaminodiphenyl ether (Fluka) were used as received.

Synthesis of TAP-MA

TAP (3.23 g) was dissolved in distilled dry acetone (50 mL) in a three-necked flask fitted with a nitrogen inlet, a condenser having a CaCl₂ guard tube and a solid transfer tube. Maleic anhydride (0.98 g) was added with constant stirring in two to three portions. The solution was refluxed for 4 h under nitrogen atmosphere with constant stirring. TAP-MA was recovered from this solution by using a rotary evaporator.

Synthesis of Polypyromellitimides

TAP-MA (0.001–0.0075) and DADPE (0.01 mol) were placed in a three-necked flask and the requisite amount of DMF was added so as to give a 10% so-

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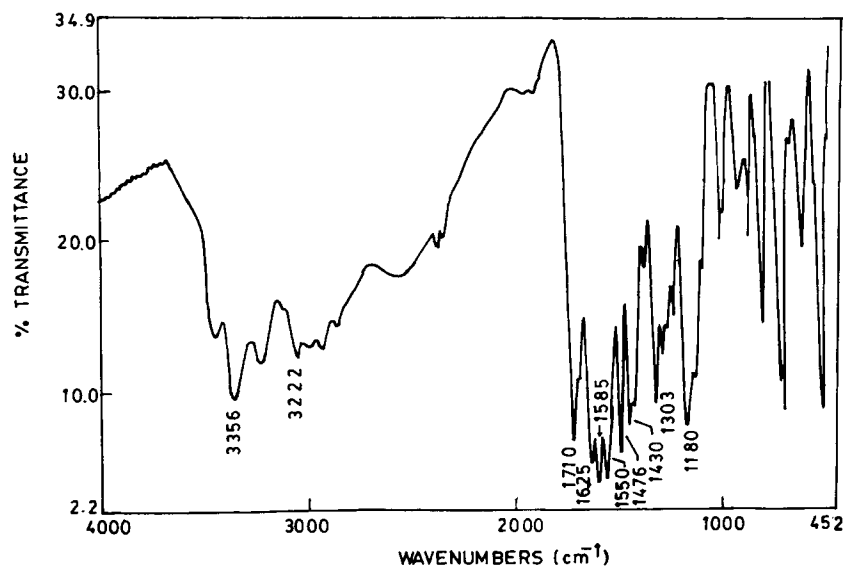


Figure 1 Infrared spectrum of TAP-MA.

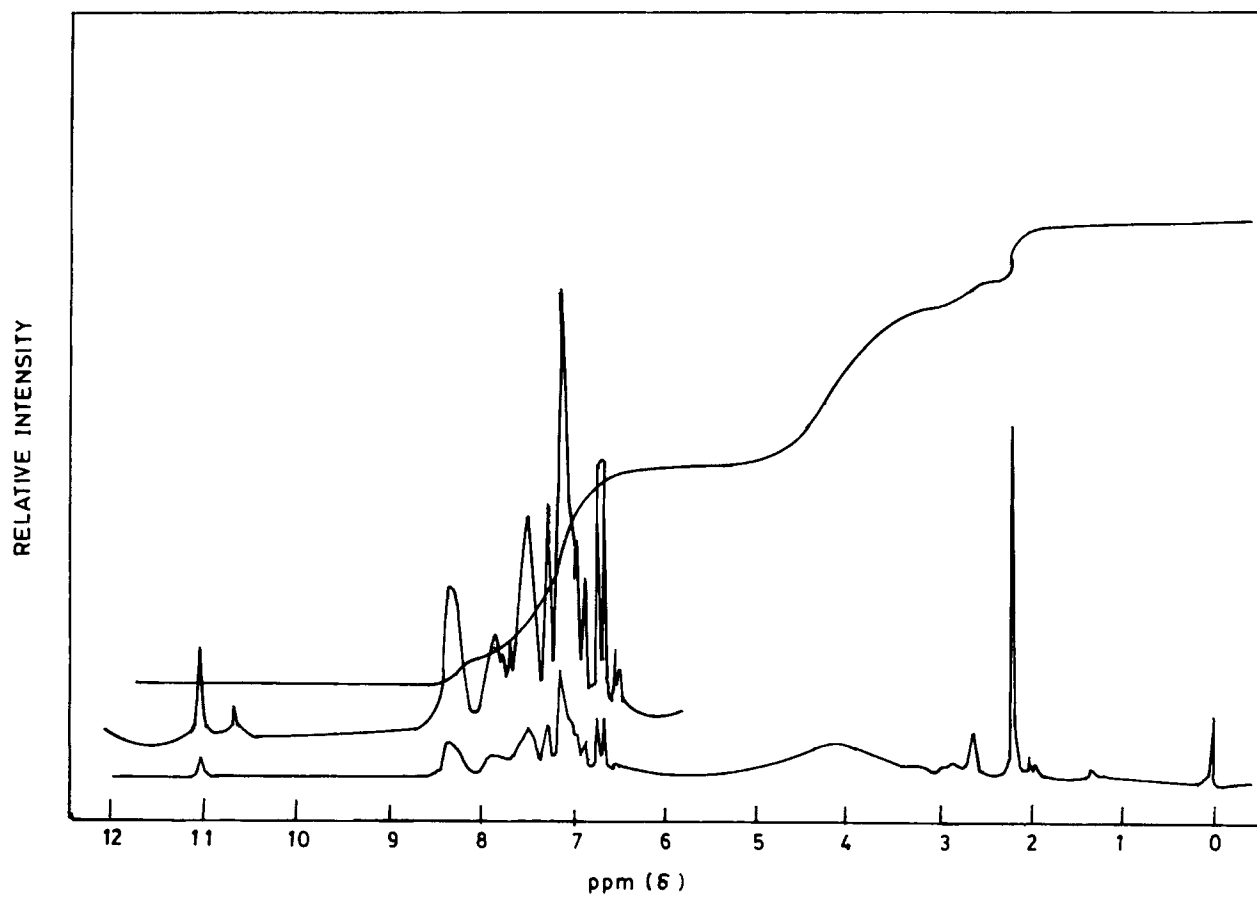


Figure 2 ¹H-NMR spectrum of TAP-MA.

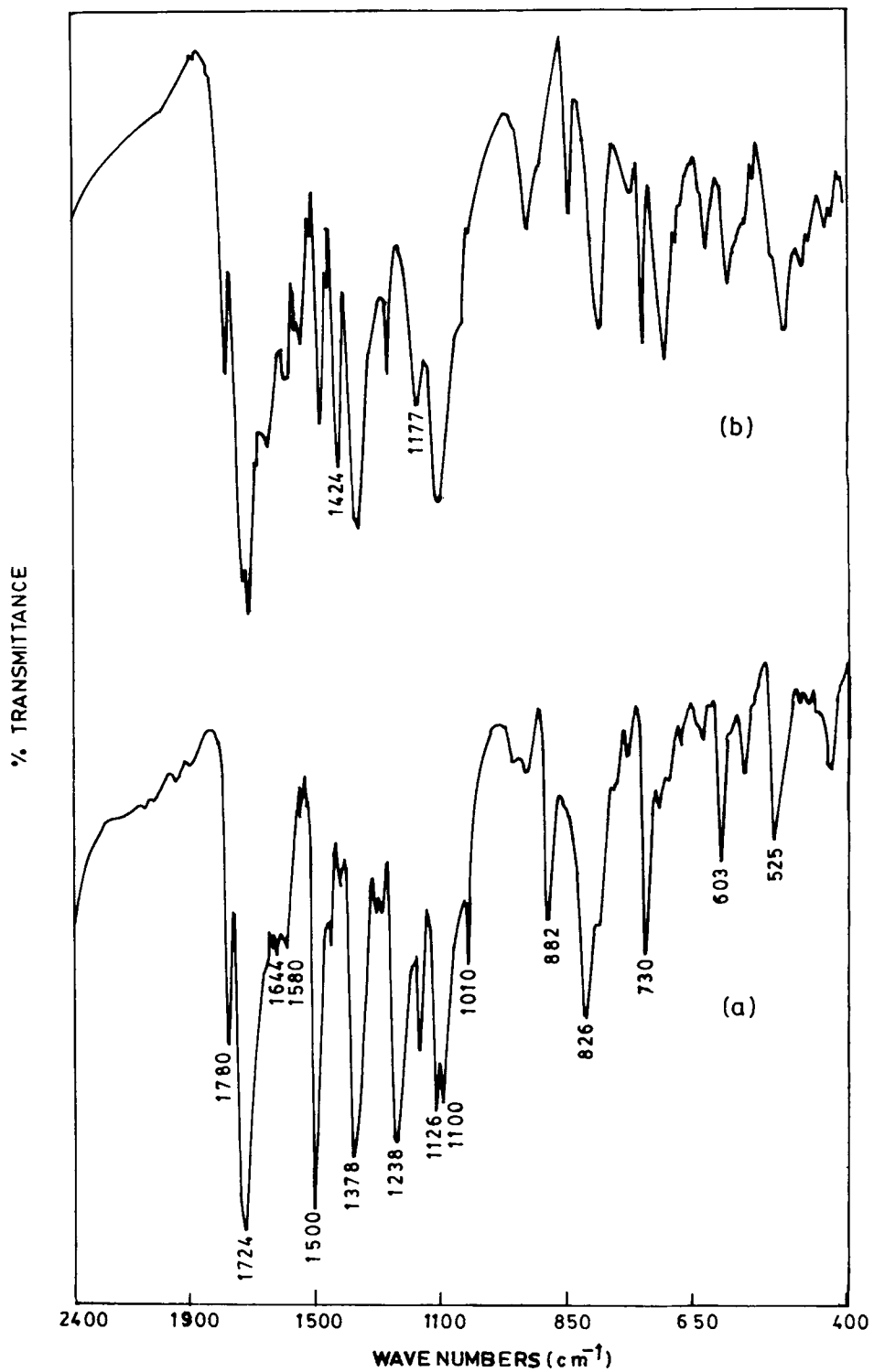


Figure 3 Infrared spectrum of polyimides: (a) PE₁₀; (b) P.

Table I Synthesis and Characterization of Poly(amide-Acids)^a

Sample Designation	Molar Concentration of			[η] (dL/g)
	TAP	MA	PMDA	
E	0.000	0.000	0.01	1.76
PE ₁₀	0.001	0.001	0.011	1.29
PE ₅	0.002	0.002	0.012	0.69
PE _{3.3}	0.003	0.003	0.013	0.44
PE ₂	0.005	0.005	0.015	0.43
PE _{1.3}	0.0075	0.0075	0.0175	0.31
P	0.01	0.01	0.01	0.20

^a Molar concentration of DADPE = 0.01 (all samples except P).

lution. After cooling the contents to 0–5°C, a stoichiometric amount of PMDA was added and stirring was continued for 4 h in nitrogen atmosphere. Films of these copoly(amide-acid)s were prepared by casting on a glass plate with subsequent drying at 60–70°C. Cyclodehydration of these poly(amide-acid) films was done thermally by heating for 1 h each at 100 and 200°C and 0.5 h at 250°C in nitrogen atmosphere. Chemical cyclodehydration of poly(amide-acid)s was done by adding pyridine/acetic anhydride/toluene (1 : 1 : 1 by volume) to the DMF solution. The precipitates of polyimides thus obtained were left for 24 h in the cyclodehydrating mixture for completion of reaction. The precipitates were then collected, washed several times with dioxane, and dried overnight at 50°C. The details of reaction conditions and sample designation are given in Table I.

CHARACTERISATION

Equivalent weight of TAP-MA was determined by the acetylation method. IR spectra of TAP-MA and

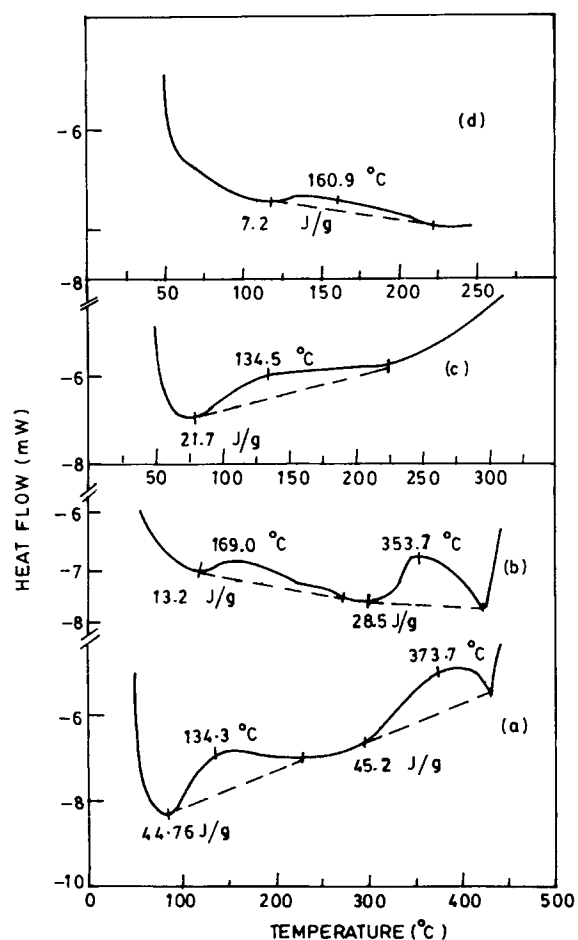
Table II DSC Scans of Copolyimides Prepared by Chemical Cyclodehydration of Poly(amide-Acids)

Sample	T_1 (°C)	T_{exo} (°C)	T_2 (°C)	ΔH (J/g)
PE ₁₀	68.4	100.0	197.6	33.5
PE _{3.3}	79.6	123.8	188.1	26.9
PE ₂	81.0	114.3	200.0	35.8
PE _{1.3}	75.9	109.5	226.2	47.7
P	81.5	117.3	221.2	76.0

Table III Results of DSC Scans of Polyimide Films

Polymer Sample	T_1 (°C)	T_{exo} (°C)	T_2 (°C)	ΔH (J/g)
PE ₁₀	104.8	150.2	216.6	16.6
	357.7	374.3	419.0	7.8
PE _{3.3}	118.0	160.9	221.4	7.2
PE ₂	128.4	169.0	266.6	13.2
	307.1	353.7	423.8	28.5
PE _{1.3}	85.7	134.5	220.0	21.7
P	90.4	134.3	228.6	44.8
	311.1	373.7	430.9	45.2

polypyromellitimides were recorded in KBr pellets using a Nicolet 5 DX FTIR spectrophotometer. ¹H-NMR spectrum of TAP-MA was recorded in DMSO-d₆ using tetramethylsilane as an internal

**Figure 4** DSC scans of polyimide films: (a) P; (b) PE₂; (c) PE_{1.3}; (d) P.

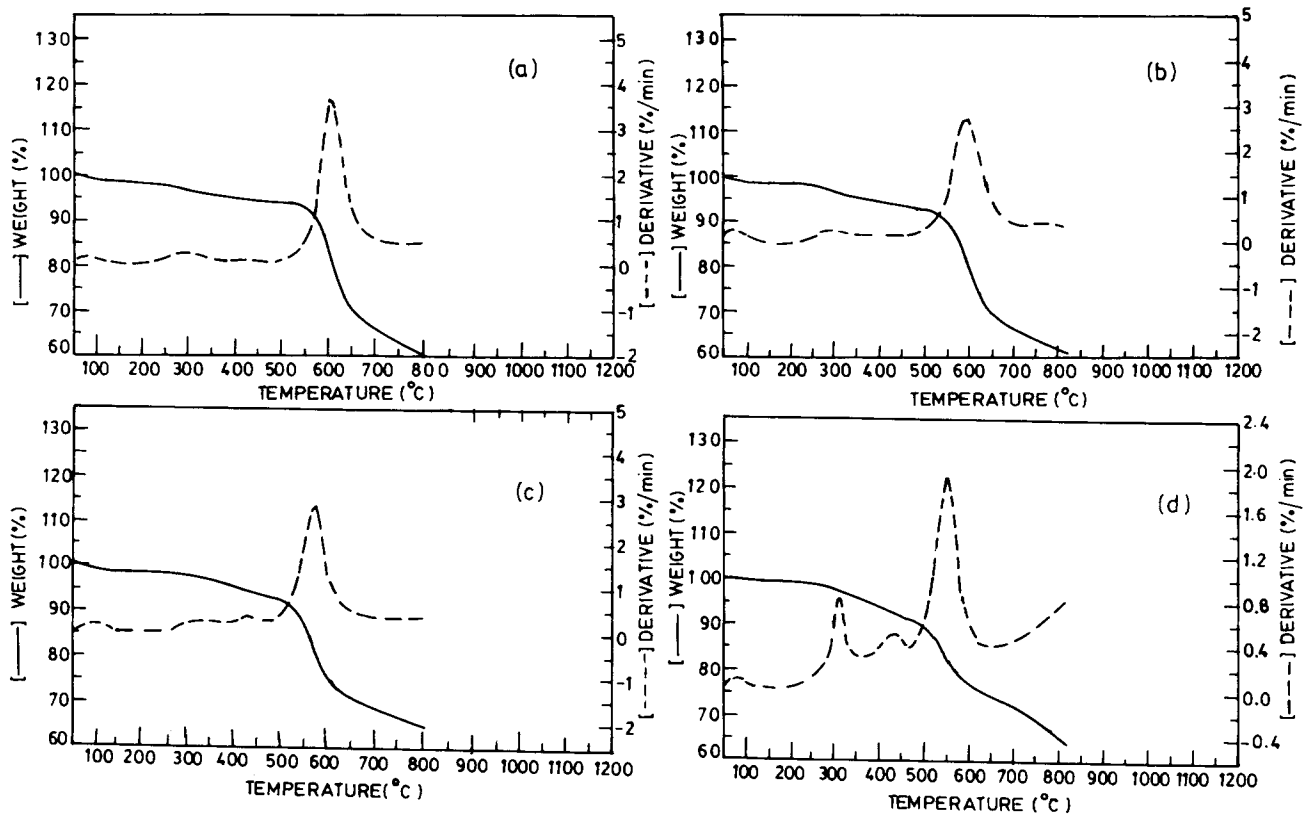


Figure 5 Thermogravimetric traces of polyimide films: (a) PE₁₀; (b) PE_{3.3}; (c) PE₂; (d) P.

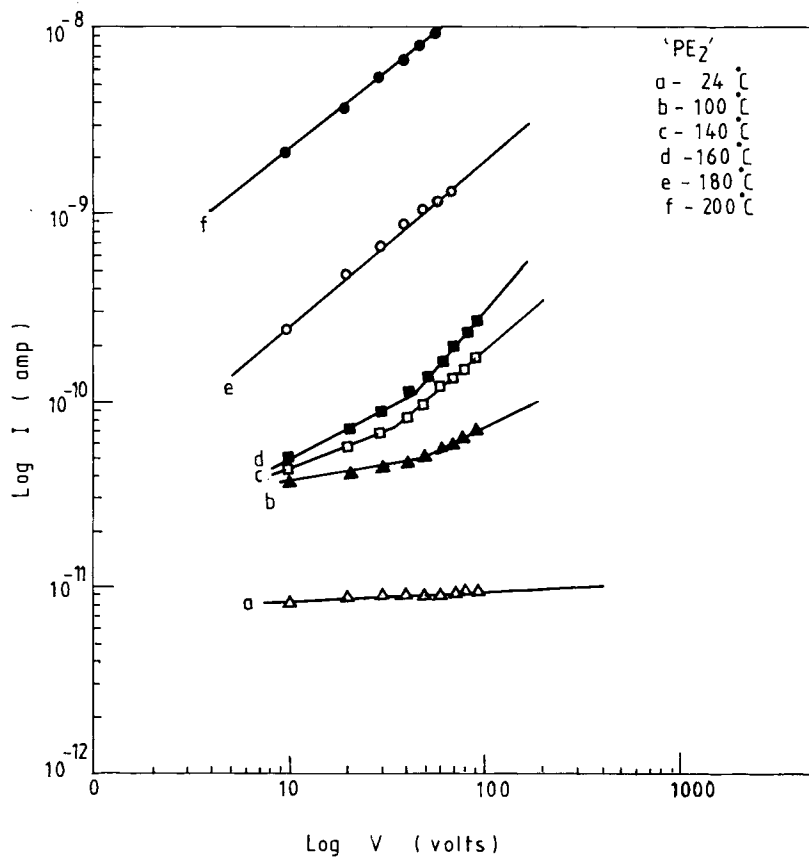


Figure 6 Logarithmic plot of current vs. voltage of polyimide film (PE₂) at different temperatures.

Table IV Results of Thermogravimetric Analysis of Various Copolyimide Films

Polymer Sample	Temperature (°C)	Weight		
		Loss (%)	T_{max} (°C)	Y_c (%)
PE ₁₀	245–350	3.8	301.7	60.5
	576–640	34.4	610.7	
PE _{3.3}	246–325	3.8	283.0	62.0
	555–640	33.0	595.3	
PE ₂	324–450	4.8	427.3	65.0
	535–605	29.0	572.3	
PE _{1.3}	337–440	4.0	376.0	61.7
	550–625	34.3	589.2	
P	275–415	6.0	307.4	65.5
	505–585	28.0	545.3	

standard. Intrinsic viscosity of various poly (amide-acid)s was determined in DMF at 30°C using an Ubbelohde suspension viscometer.

A DuPont 1090 thermal analyzer having a 910 DSC module and 951 TG module was used to evaluate thermal behavior of polyimide films. A sample weight of 10 ± 3 mg and a heating rate of 10°C/min were used.

For conductivity measurements, the films were sandwiched between two aluminium electrodes and the whole system was kept in a furnace for one hour to attain constant temperature. For better contact, films were coated with aluminium. An Aplab high voltage regulated power supply (Model 7111) was used for field variation. Current measurements were done on a 610C Keithley electrometer. Temperature was varied from ambient to 200°C. For capacitance and loss measurements a 4192 ALF impedance an-

Table V Slope Values from log I vs. log V Plot of Polyimide Films^a

Polymer Sample	Temperature (°C)				
	100	140	160	180	200
PE ₁₀	0.76	0.86	0.83	0.92	0.84
	(1.48)	(1.12)	(1.23)	(1.25)	
PE _{3.3}	0.81	0.96	1.1	0.91	0.77
	(1.30)				
PE ₂	0.09	0.40	0.51	0.81	0.78
	(0.67)	(0.81)	(1.17)	—	—
P	0.07	0.54	0.61	0.94	0.89
	(0.89)	(1.18)	(1.23)		

^a Numbers in parentheses are the values at higher field.

Table VI β -Values Calculated from ln I vs. $V^{1/2}$ Plots of Polyimide Films

Polymer Sample	Temperature (°C)				
	100	140	160	180	200
PE ₁₀	0.35	0.41	0.41	0.44	0.40
	(0.28)	(0.27)	(0.23)	(0.31)	(0.20)
PE _{3.3}	0.36	0.32	0.49	0.44	0.59
	(0.27)	(0.25)	(0.31)	(0.27)	(0.18)
PE ₂	0.06	0.18	0.28	0.44	0.38
	(0.10)			0.22	0.17
P	0.20	0.24	0.17	0.47	0.46
				(0.20)	(0.22)

^a Numbers in parentheses are the values at higher field.

alyzer (Hewlett Packard), range 5 Hz–13 MHz, bridge was used and frequency was varied from 100 Hz to 1 MHz at 25 and 200°C.

RESULTS AND DISCUSSION

Amine equivalent weight of TAP–MA was found to be 243 (theoretical value 210.5). In the IR spectrum of TAP–MA, bands due to carbonyl stretch of maleimido group at 1710 cm^{-1} , P=O (1180 cm^{-1}), P–C₆H₅ (1430 cm^{-1}), –C₆H₅ (1585 and 1476 cm^{-1}), –NH– at 1550 cm^{-1} , and amino groups (3222–3356 cm^{-1}) were observed (Fig. 1). In the NMR spectrum of TAP–MA resonance, signals due to amino and amido protons were observed at $\delta = 2.2$ (4H, s) and 8.1–8.6 ppm (1H, broad) respectively. Aromatic ring protons appeared at 6.8–8.05 ppm (12H, m). Olefinic protons at ($\delta = 6.65$ –6.75, 2H, d) and hydroxy protons ($\delta = 11.05$, 1H, s) were also observed (Fig. 2).

The intrinsic viscosity of poly (amide-acid)s ranged from 1.76–0.20 dL/g. A decrease in $[\eta]$ was

Table VII Dielectric Constant (ϵ) and tan δ Values of Polyimide Films at 100 kHz^a

Polymer Sample	ϵ		tan δ	
	25°C	200°C	25°C	200°C
PE ₁₀	5.04	3.91	0.018	0.016
PE _{3.3}	5.55	—	0.021	—
PE ₂	5.93	4.10	0.016	0.019
P	7.65	4.73	—	—

^a [ϵ (PMDA–DADPE) \sim 3.2–3.4].

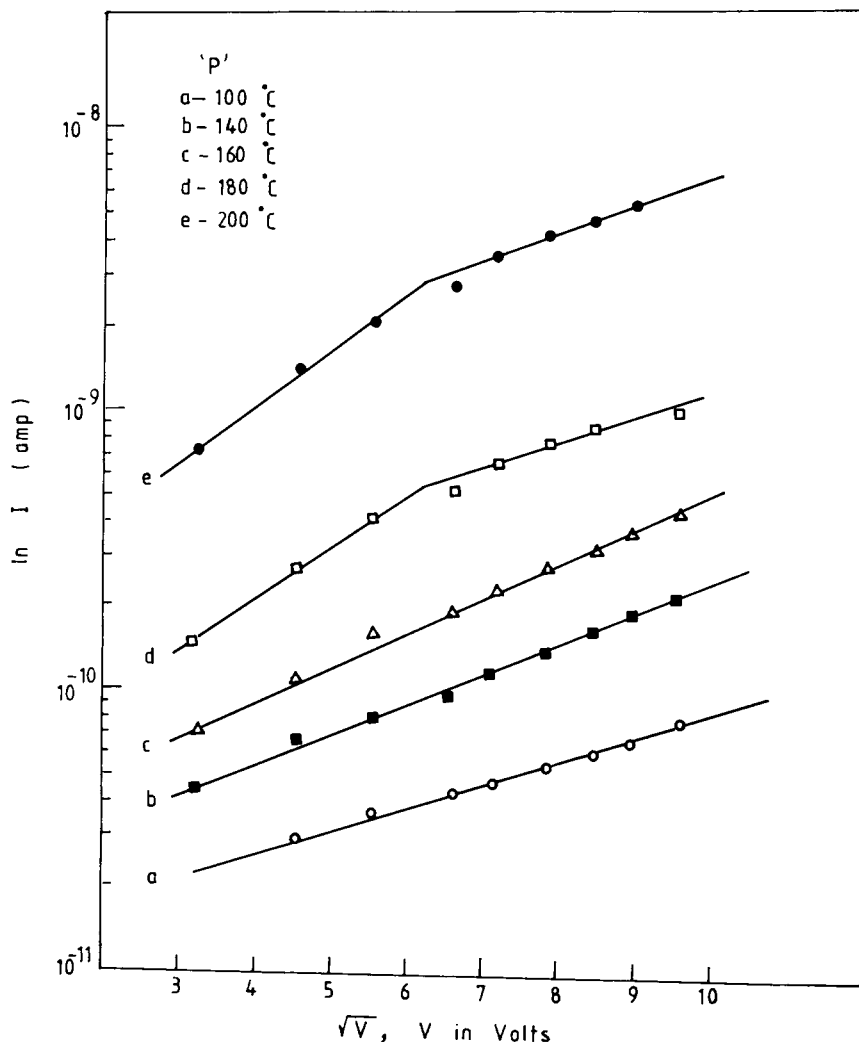


Figure 7 Dependence of current on square root of voltage of polyimide (P) at different temperatures.

observed by increasing TAP-MA content in the backbone. In the IR spectra of copolyimides, characteristic absorption bands due to imide groups (1780 , 1724 , 1126 , and 730 cm^{-1}), $\text{P}=\text{O}$ (1180 cm^{-1}), $\text{P}-\text{C}_6\text{H}_5$ (1430 cm^{-1}), $\text{C}-\text{N}$ (1378 cm^{-1}), $\text{C}-\text{O}-\text{C}$ (1238 cm^{-1}), and residual amido group (1644 cm^{-1}) were observed (Fig. 3).

In the DSC traces of copolyimides a broad exotherm in the temperature range of 68 – 226°C was observed for samples prepared by the chemical cyclodehydration method. This exotherm arises due to curing of maleimido double bonds. From these DSC scans, the temperature of onset of exotherm (T_1), temperature of end of exotherm (T_2), the exothermic peak temperature (T_{exo}), and the heat of reaction (ΔH) were noted (Table II). As expected, an increase in maleimido content in polyimides re-

sulted in an increase in the ΔH values. In copolyimide films obtained by thermal cyclodehydration two exothermic transitions were observed (Fig. 4). The exotherm in the temperature range of 86 – 267°C may be due to polymerization of residual maleimido groups. In these samples the ΔH also increased with an increase in the maleimido content in copolyimides (Table III). However, these ΔH values were lower than those obtained in chemically cyclodehydrated samples. The second exotherm was observed in the temperature range of 311 – 430°C and may be due to cyclization and a decomposition reaction.

In the thermogravimetric traces of copolyimide films, approximately 1% weight loss due to absorbed moisture was observed around 125°C . Besides this, two distinct regions of weight loss were observed

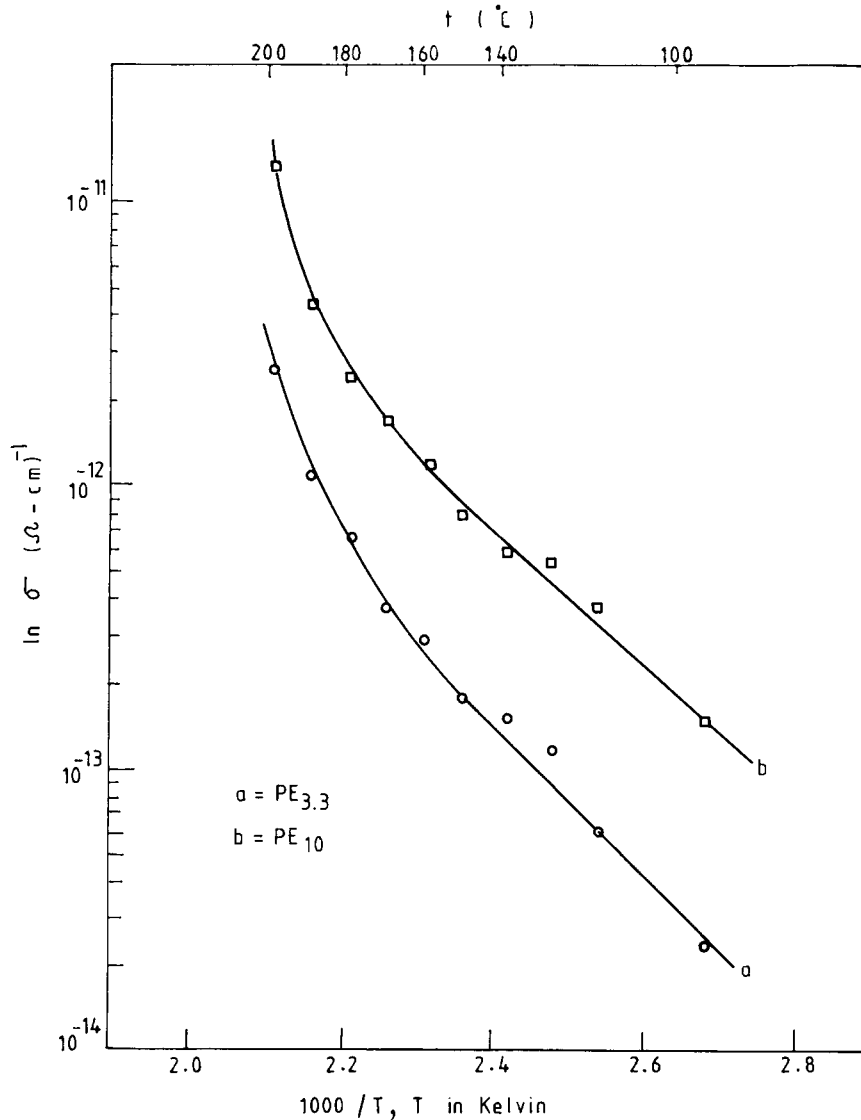


Figure 8 Plot of conductivity vs. reciprocal temperature of copolyimides.

due to cyclization of the residual amide acid and the decomposition reaction (Fig. 5). From these TG traces, percentage weight loss in the two regions, temperature of maximum rate of weight loss (T_{max}), and char yields (Y_c) at 800°C were recorded (Table IV). An increase in char yield was observed with an increase in phosphorus content in the backbone.

Variation of current as a function of voltage was determined for various copolyimide films from 25 to 200°C (Fig. 6). A linear relationship was observed in all the samples indicating an ohmic behavior (Table V). However, at lower temperature and field, a sublinear behavior was observed in polyimides having a higher percentage of phosphorus in the backbone.

The plots of $\log I$ vs. $V^{1/2}$ indicated a voltage-dependent variation in the slopes in most of the polymer samples (Fig. 7). The Schottky coefficient (β) was also calculated at 200°C and the values were

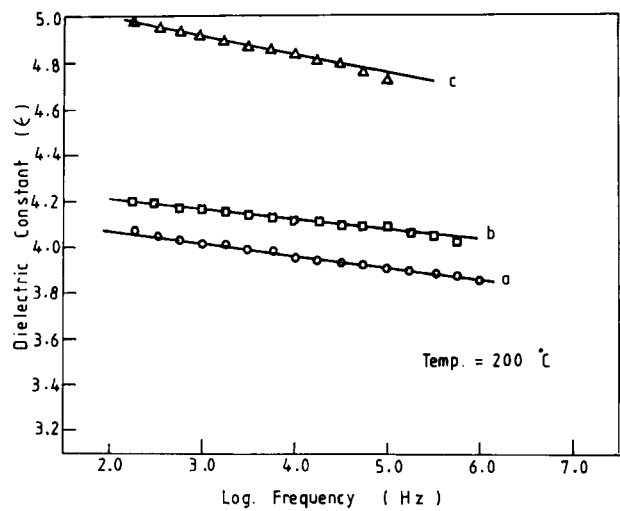


Figure 9 Dependence of dielectric constant on frequency of copolyimides at 200°C: (a) PE₁₀; (b) PE₂; (c) P films.

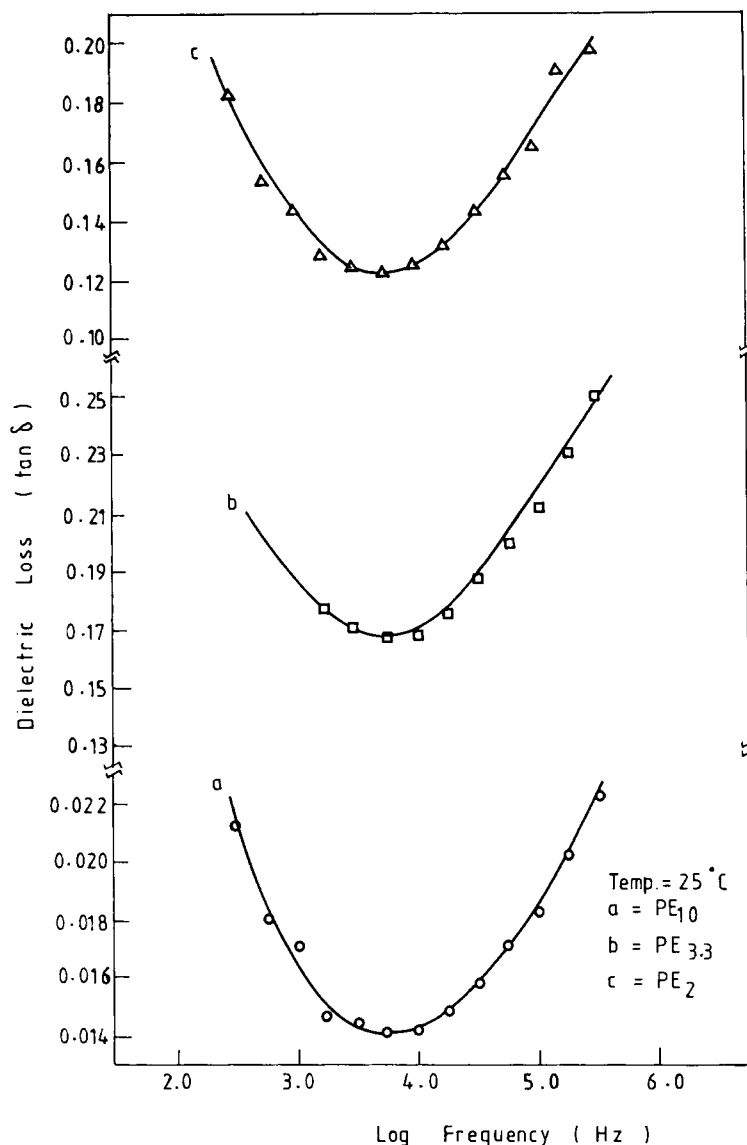


Figure 10 Plot of $\tan \delta$ vs. frequency of copolyimides at 200°C.

found to be 0.054, 0.054, and 0.069 for sample PE₁₀, PE₂, and P, respectively. The slope values were four or five times the theoretical values except in one or two cases (Table VI). Therefore, the mechanism of conduction might be a combination of electronic or ionic type. The activation energy for conduction in PE_{3.3} and PE₁₀ films was also calculated (Fig. 8). For PE_{3.3} the values at lower and higher regions observed were 0.203 and 0.53 eV and for PE₁₀ the values were 0.26 and 0.62 eV.

The frequency dependence of dielectric constant and $\tan \delta$ were determined at 25 and 200°C (Table VII). Increase in phosphorus content resulted in an increase in dielectric constant (Fig. 9). The dielectric loss with varying frequency up to 1 MHz was also determined (Fig. 10).

CONCLUSIONS

The following conclusions can be drawn on the basis of the above work:

1. A decrease in intrinsic viscosity is observed in copoly(amide-acid)s by increasing the content of tris(*m*-aminophenyl) phosphine oxide in the initial feed.
2. An increase in heat of polymerization was observed with increase in maleimido content.
3. Char yield increased in polymers containing a higher content of phosphorus.
4. An ohmic behavior was observed in copolyimide films and the mechanism of conduction

might be a combination of electronic and ionic type.

5. Increase in phosphorus content resulted in an increase in dielectric constant.

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