Studies on Polypyromellitimides Containing Phosphorus*

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Synopsis

The paper describes the synthesis of several polypyromellitimide samples containing phosphine oxide in the backbone and maleimido groups as pendant side chains. These polymers were obtained by solution polycondensation reaction in DMF in three steps. First step involved the reaction of equimolar amounts of maleic anhydride (MA) and tris(3-aminophenyl) phosphine oxide (TAP) in DMF at 60°C for 2 h. Low temperature polycondensation was carried out at 0–5°C by the addition of 4,4'-diaminodiphenyl ether (DADPE) and pyromellitic dianhydride. Cyclodehydration of poly(amide acid) thus obtained was done by chemical means. Various copolymers thus obtained were characterized by intrinsic viscosity measurements, elemental analysis, and IR spectroscopy. Thermal behavior and curing characteristics of copolyimides were evaluated by thermogravimetry and differential scanning calorimetric studies. An increase in the char yield at 800°C was observed on increasing phosphine oxide content of polyimides.

INTRODUCTION

High temperature photosensitive insulating materials are required to achieve a high degree of integration in solid state technology. Glass/ sputtered quartz is commonly used as passivation material in the manufacture of integrated circuits. The advantages of Si_3N_4 or SiO_2 are their high purity, chemical inertness, and low permeability to water vapors. However, when applied as a thicker coat, the problem of mechanical defects such as pinholes, microcracks etc. arises.

Recently polyimides have been considered as a replacement of glass/sputtered quartz.[1-11] The precursor of polyimides, i.e., poly(amide acid) dissolve in organic solvents (e.g., N-methyl pyrrolidone/N,N-dimethyl formamide) to give a viscous solution which can be spun onto wafers to create a relatively planar surface that is ideal for the next level metallization.
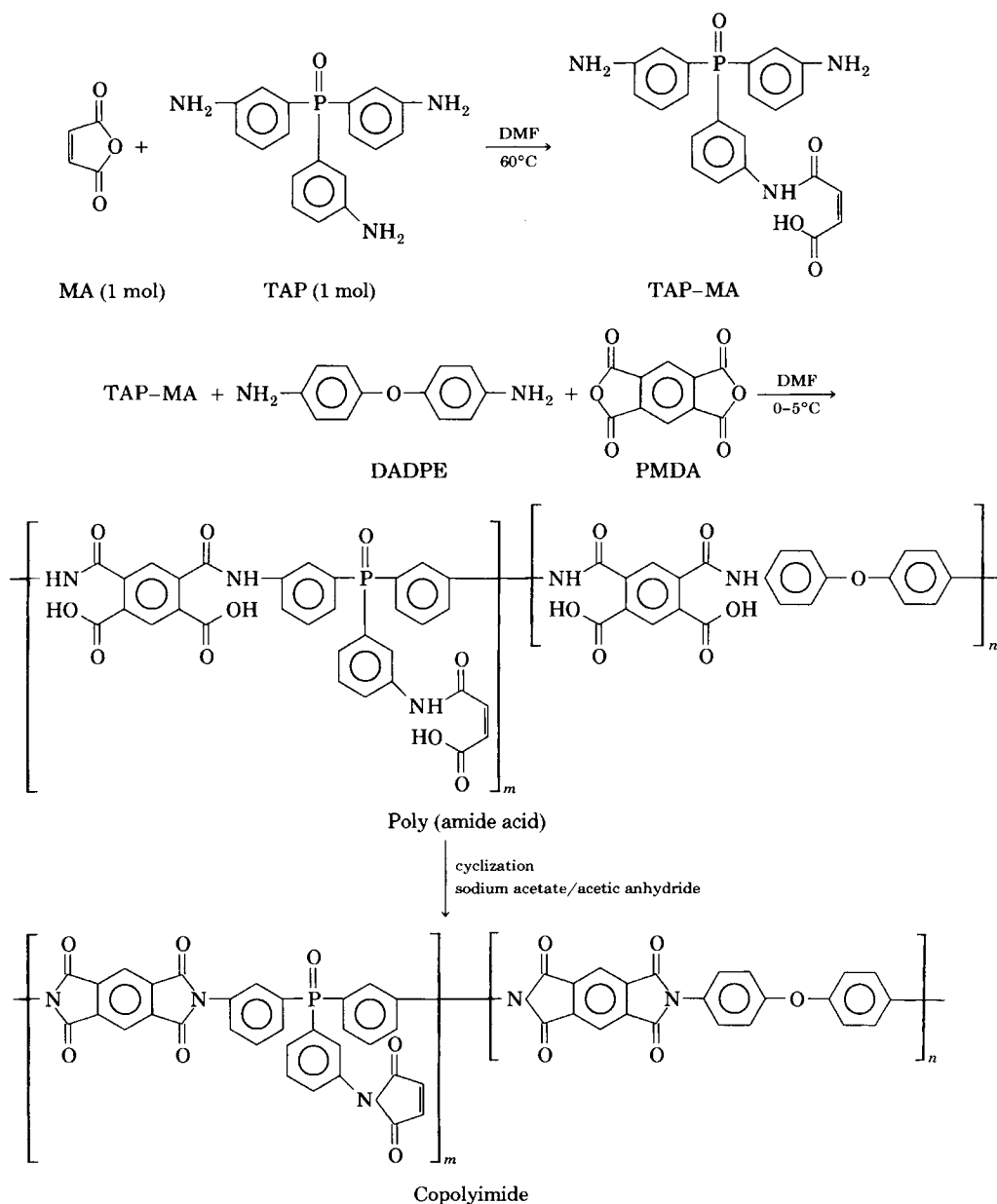
Scratch protection is a must for a good electrical chip as it proceeds from wafer fabrication to multiprobe and to final assembly area. It is, therefore, desirable that overcoat should have good thermal stability, mechanical strength, low value of Young's modulus (to minimize the cracking of the overcoat), and good adhesion to the metal and primary passivation layer (to maintain integrity). It is possible to realize these properties in polyimides by structural modifications.

There is an increasing demand to develop polyimide resins having high thermal stability, photosensitivity, and better adhesion than the state-of-the-

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art polyimide resins. The present studies were undertaken to develop polyimide containing olefinic double bonds (which can impart photosensitivity to the material) and to improve adhesive properties.

Our earlier studies have revealed that incorporation of phosphorus in the polyimide backbone improves the thermal stability and adhesion.[12] Therefore, in the present work copolyimides were prepared by reacting pyromellitic dianhydride (PMDA) with 4,4'-diaminodiphenyl ether (DADPE) and tris(3-aminophenyl) phosphine oxide (TAP). Since TAP is a trifunctional amine, pendant maleimido groups were incorporated in this amine prior to its reaction with PMDA, according to the following reaction scheme:

MA (1 mol)   TAP (1 mol)   TAP–MA

DMF
60°C

TAP–MA + DADPE + PMDA   DMF
0–5°C

Poly (amide acid)

cyclization
sodium acetate/acetic anhydride

Copolyimide

Value of m and n will depend on the ratio of amines taken in the initial monomer feed. Preliminary studies, describing the synthesis, characterization (IR, elemental analysis, intrinsic viscosity, etc.) and thermal behavior of the copolyimide resins, forms the basis of the present article.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA) (Fluka) was crystallized from acetic anhydride and dried in vacuum at 60°C before use. N,N-dimethylformamide (DMF) (E. Merck) was used as such. Anhydrous sodium acetate (BDH) was obtained by fusion. Acetic anhydride was distilled under normal pressure. Maleic anhydride (MA) and 4,4'-diaminodiphenyl ether (DADPE) (Fluka) were used as such. Tris(3-aminophenyl) phosphine oxide (TAP) was prepared from triphenyl phosphine oxide (Fluka) by nitration followed by reduction with Pd/C and hydrazine hydrate as described elsewhere.[13]

Polymerization

Polyimides were prepared by a two-step polycondensation reaction. The poly(amide acid) precursor was first prepared in DMF by reacting aromatic amines (TAP/DADPE) with MA and PMDA. Cyclodehydration of these intermediates (amide acid) was done by using sodium acetate and acetic anhydride. A typical procedure is described.

Tris(3-aminophenyl) phosphine oxide (TAP) (0.001–0.0075 mol) was dissolved in DMF (so as to give 10% solution) in a three-necked flask equipped with a nitrogen inlet tube, a solid transfer tube, and a reflux condensor. Maleic anhydride (0.001–0.0075 mol) was added in small portions. The solution was stirred at 60°C for 2 h. The mixture was then cooled to 0–5°C. Then 4,4'-diaminodiphenyl ether (DADPE) (0.01 mol) and requisite amount of DMF was added so as to make the solid content 10% (w/w). After a homogeneous solution was obtained, PMDA was gradually added, and stirring was continued for 4 h in nitrogen atmosphere. A viscous solution indicating polymerization was obtained at the end of this period. The solution was then

TABLE I
Synthesis of Copolyimides: Details of Reaction Conditions[a]

| Sample no. | Molar concentration of | | | Designation of polyimides |
	TAP	MA	PMDA	
1	0.000	0.000	0.01	E
2	0.001	0.001	0.011	PE_{10}
3	0.002	0.002	0.012	PE_5
4	0.003	0.003	0.013	$PE_{3.3}$
5	0.005	0.005	0.015	PE_2
6	0.0075	0.0075	0.0175	$PE_{1.3}$
7	0.01	0.01	0.01	P

[a] Molar concentration of DADPE = 0.01 mol (sample nos. 1–6); solvent = DMF (10% solution); reaction temperature = 60°C, 2 h, for initial reaction of TAP and MA, and = 0–5°C, 4 h, for reaction of TAP–MA, DADPE, and PMDA.

warmed to room temperature (32 ± 2°C). Cyclization was done by adding stoichiometric amounts of fused sodium acetate and excess of acetic anhydride to this solution. The solution was stirred for further 1 h at room temperature. The product was then precipitated in water, filtered, and washed several times with water (till free from acetic acid). Finally the washing was done with acetone, and the product was dried.

The details of synthesis and the designation of copolyimides thus prepared and given in Table I. Homopolymer (sample no. 1) is based on PMDA and DADPE and has been used as reference. Six copolyimides were prepared by changing the TAP/MA ratios with respect to DADPE (or PMDA) in the feed (samples nos. 2–6 of Table I). The copolymides have been designated according to this molar ratio in the initial feed. For example a copolyimide prepared by reacting 0.005 TAP–MA and 0.01 mol of DADPE in the initial feed has been designated as PE_2 (Table I).

CHARACTERIZATION

The incorporation of phosphine oxide moieties in copolyimides may influence their solubility behavior. Hence the solubility of polyimides in DMF was determined. For this purpose accurately weighed copolyimide sample (approximately 0.2 g) was added to 10 mL of DMF, and the mixture was maintained at 100 ± 5°C for 2 h. Residual polymer was isolated by filteration, washed with acetone, and then dried at 60°C till a constant weight was obtained. The percentage solubility was then determined using the formula

$$\% \text{ solubility} = \frac{W_0 - W_1}{W_0} \times 100$$

where W_0 = initial weight of the copolyimide sample and W_1 = weight of residue after DMF extraction. The intrinsic viscosity of the poly(amide acid) in DMF was determined at 30°C using a Ubbelhode suspension level viscometer.

A Perkin-Elmer 240C elemental analyzer was used for the determination of C, H, and N content of various copolyimides. Structural characterization was done by recording IR spectra of polymers in KBr pellets using a Nicolet 5 DX FTIR spectrophotometer.

Since the copolyimides contain a vinylic double bond (maleimide group), therefore, curing reaction in nitrogen atmosphere was studied using a DuPont 1090 thermal analyzer having a 910 DSC module. A heating rate of 10°C/min and sample size of 10 ± 3 mg was used.

Isothermal curing of all copolyimide samples was done at 220 ± 5°C for 4 h. For this purpose the polyimides were heated in shallow aluminum dishes in an air oven. Thermal behavior of uncured and cured polyimides was evaluated by using a 950 TG module.

RESULTS AND DISCUSSION

The copolyimides were yellow to brown powders. Polyimide E was found to be almost insoluble in DMF while the percentage solubility increased with

TABLE II
Results of Solubility of Copolyimides in DMF and Intrinsic Viscosity Evaluation
of Poly(amido Acid)s in DMF

Sample	Solubility (%)	Intrinsic viscosity (dL/g)
E	3.33	1.76
PE_{10}	8.90	1.10
PE_5	10.30	0.50
$PE_{3.3}$	13.81	0.48
PE_2	10.24	0.38
$PE_{1.3}$	14.03	0.33
P	37.49	0.11

increase in the TAP concentration in the backbone. Maximum solubility of 38% was observed in sample P (Table II).

The intrinsic viscosity $[\eta]$ of the poly(amide acid)s at 30°C in DMF ranged from 1.76 dL/g (sample E) to 0.11 dL/g (sample P) (Table II). Thus an increase in TAP residue in the imide backbone leads to a reduction in $[\eta]$. Intrinsic viscosity is an indication of hydrodynamic volume of a polymer. For similar backbone structure, an increase in $[\eta]$ indicates a higher molecular weight of the polymer. In the present polymer samples the backbone structure was modified by incorporation of maleimido and phosphine oxide moieties. Relative concentration of polar groups is thus increased in the backbone. Therefore, it is expected that in a polar solvent like DMF such poly(amido acid)s would have more expansion in size, thereby increasing the hydrodynamic volume. However, our results indicate lower $[\eta]$ values on incorporation of phosphine oxide and maleimido groups. Therefore, it can be concluded that the molecular weight of copolyimides is lower than that of sample E.

The formation of poly(amide acid)s proceeds by a step growth mechanism where the degree of polymerization is dependent on the initial monomer concentration, duration of polymerization, and specific rate constant (k) of the polycondensation reactions. Since in our studies the first two parameters were kept constant, therefore, the variation in degree of polymerization (and hence the molecular weight) is due to decrease in k values for TAP/MA system. 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/nucleophilic nature of the amines. Phosphine oxide is a $(-I)$ group, and, since it is present at m position, hence it will reduce the reactivity of amino groups in TAP. Thus one can account for the observed decrease in $[\eta]$ of copolyimides on the basic of difference in reactivity of amines.

Results of elemental analysis of various polymer samples are given in Table III. A higher hydrogen content and a lower carbon content are observed in all polymer samples. This may be due to incomplete cyclization. The presence of residual (amide acids) in the backbone may be responsible for this variation in observed value. For example, theoretical C and H content for poly(amide acid) PE_5 and PE_2 is 62.44% 3.37% and 61.83%, 3.39%, respectively.

TABLE III
Results of Elemental Analysis of Copolyimides

Sample no.	Sample	Percentage of [a]		
		Nitrogen	Carbon	Hydrogen
1	E	6.44	63.77	3.27
		(7.32)	(69.11)	(2.62)
2	PE_{10}	7.34	63.25	3.62
		(7.31)	(68.65)	(2.63)
3	PE_5	7.11	63.58	3.00
		(7.29)	(68.30)	(2.64)
4	$PE_{3.3}$	7.13	63.50	3.48
		(7.28)	(68.02)	(2.65)
5	PE_2	7.18	64.13	3.85
		(7.26)	(67.61)	(2.67)
6	$PE_{1.3}$	6.83	62.28	3.71
		(7.25)	(67.26)	(2.68)
7	P	6.56	63.82	3.70
		(7.18)	(65.64)	(2.74)

[a] Figures in parentheses indicate the calculated values for various polymer samples.
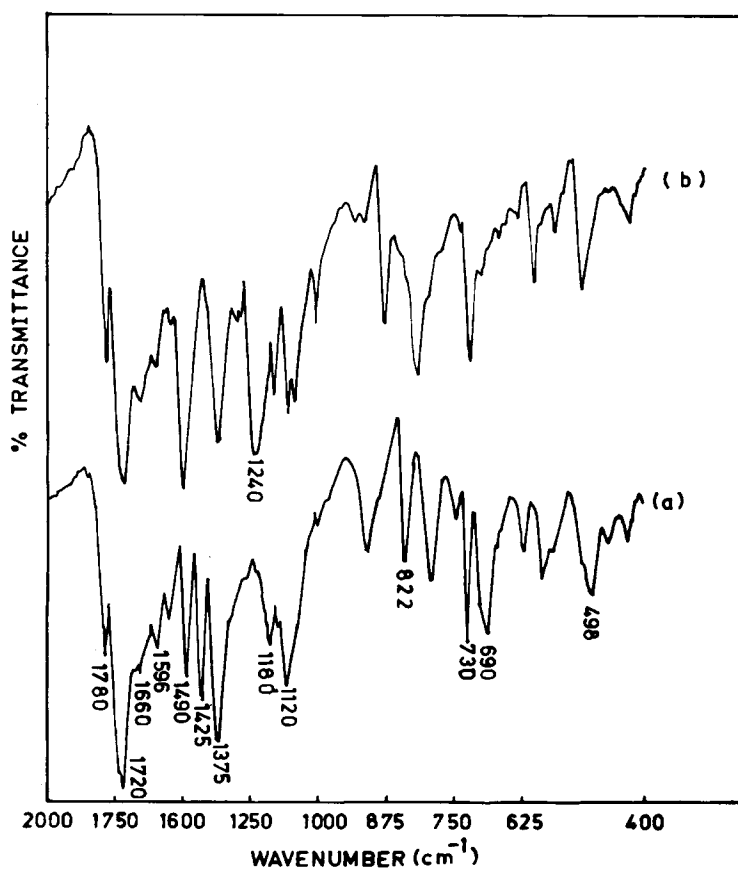
Fig. 1.   Infrared spectra of polyimides: (a) sample P; (b) sample E.
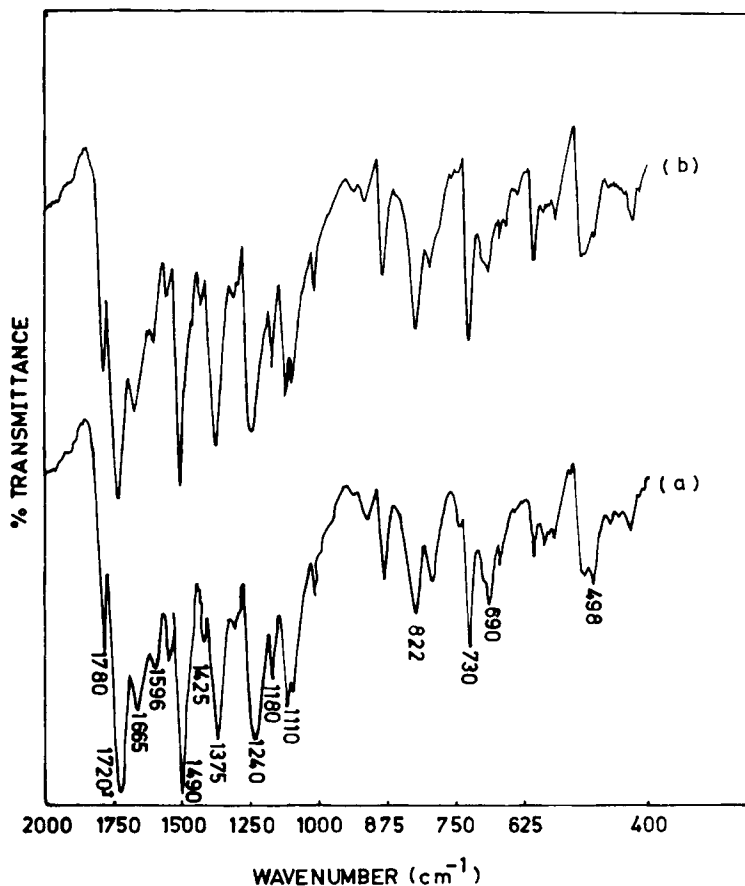
Fig. 2. Infrared spectra of copolymides: (a) sample PE_2; (b) sample $PE_{3.3}$.

In the IR spectra of sample P, strong bands due to imido group were observed at 1720, 1780, and 730 cm^{-1} (Fig. 1). The absorption band at 1720 cm^{-1} is attributed to $\nu_{C=O}$ of maleimido group. Characteristic absorption bands due to P=O at 1180 cm^{-1}, P—C_6H_5 at 1425 cm^{-1}, —C_6H_5 at 1490 and 1596 cm^{-1}, and C—N at 1375 cm^{-1} were also observed. In polyimide E, the characteristic absorption bands due to ether linkage at 1240 cm^{-1} was also observed (Fig. 1). In the copolyimides containing different molar ratios of TAP and DADPE, the characteristic peaks indicative of TAP and DADPE residues in the backbone were observed. The relative intensities of these absorption bands depended on the molar concentration of amines taken in the initial feed (Fig. 2). In all the polyimide samples, absorption bands of varying intensities were observed at 1660 ± 5 cm^{-1}. This may be attributed to secondary amido groups of poly(amide acid). On the basis of elemental analysis and IR results it is clear that the treatment of poly(amide acid)s with sodium acetate and acetic anhydride leaves residual amido groups in the backbone.

DSC traces for all these polyimide samples were recorded in the temperature range of 50–400°C. A prominent exothermic transition in the tempera-
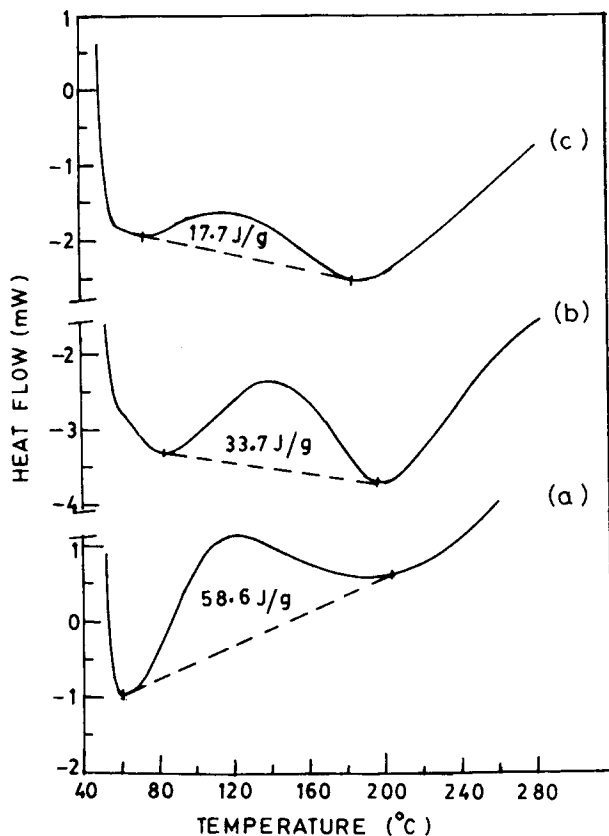
Fig. 3. DSC traces of copolyimides in nitrogen atmosphere (heating rate 10°C/min): (a) sample P; (b) sample PE$_2$; (c) sample PE$_{3.3}$.

ture range of 72–202°C was observed in sample P. The existence of this transition is indicative of (a) polymerization of maleimido double bonds present as pendent substituent on polypyromellitimide backbone or (b) cyclodehydration of residual poly(amide acid) groups. Similar exothermic transitions were observed in all the copolyimide samples (Fig. 3). From these traces, the temperature of onset of exothermic transition (T_1), temperature of end of exotherm (T_2), exothermic peak temperature (T_{exo}), and heat of reaction (ΔH) were noted down (Table IV). An increase in ΔH is observed as the maleimido content is increased.

Since exothermic transition is also expected on cyclodehydration reaction of residual amide acid to imide, and would be accompanied with a weight loss in this region; therefore, thermogravimetric analysis of uncured copolyimide samples was carried out in nitrogen atmosphere. A slight weight loss was observed in the temperature range 100–150°C. This may be attributed to the loss of absorbed water from these polymer samples. A second weight loss (5–8%) in the temperature range of 160–275°C was also observed. Major weight loss was observed above 500 ± 5°C, and a residual char yield (Y_c) at 800°C was found to be lowest in sample E (50.2%) and maximum in sample P (57%). From these thermogravimetric traces, the temperature for maximum

TABLE IV
Results of DSC Scans of Copolyimide Samples

Polymer sample	T_1 (°C)	T_{exo} (°C)	T_2 (°C)	ΔH (J/g)
PE_{10}	102.7	136.1	175	9.00
$PE_{3.3}$	79.3	119.8	184	17.7
PE_2	92.0	140.9	195	33.7
$PE_{1.3}$	80.7	134.1	199	49.7
P	72.3	112.6	202	58.6

rate of weight loss (T_{max}) was determined for all copolyimide samples. Since the decomposition occurred in two distinct steps, therefore, two T_{max} values were observed in all the copolyimides. The results of TG analysis are summarized in Table V. Comparison of TG and DSC results of polymer samples indicate a significant difference in T_{max-1}(TG) and T_{exo}(DSC) values, the T_{max-1} being 80°C higher than T_{exo} in all the copolyimides. It can, therefore, be concluded that the T_{exo} observed in DSC in the temperature range of 72–202°C is due to polymerization of the double bond of the maleimide group. However, if one compares the curing reaction of bismaleimide resins where the T_{exo} values are in the temperature range of 220–260°C,[14] then observed values in present copolyimide samples are on the lower side. A decrease in T_{exo} values has been reported earlier in chain extended bismaleimide resins.[15] It, therefore, appears that the maleimido double bond might have undergone a chain extension reaction with free amino groups.

Isothermal curing of the resins was done at 220 ± 5°C for 4 h. The DSC and TG traces of the cured resins were also recorded for comparison with uncured resins. In the TG traces, a slight weight loss in the temperature range of 100–150°C was observed in all samples and is due to absorbed moisture. The major weight loss was in temperature range of 450–650°C (Fig. 4). The

TABLE V
Results of Thermogravimetric Analysis (in Nitrogen Atmosphere) of (Uncured) Copolyimides

Polymer sample	Temperature range (°C)	Weight loss (%)	T_{max} (°C)	Y_c (%)
E	160–275	6.0	237.5	50.0
	275–800	42.0	559.3	
PE_{10}	160–275	8.0	205.0	54.0
	275–800	36.0	550.5	
PE_5	160–275	6.5	229.0	51.5
	275–800	38.0	554.7	
$PE_{3.3}$	160–275	7.0	205.3	53.5
	275–800	37.0	560.7	
PE_2	160–275	6.5	228.0	54.0
	275–800	36.0	551.0	
$PE_{1.3}$	160–275	6.5	226.4	55.0
	275–800	36.0	550.3	
P	160–275	5.0	222.6	57.0
	275–800	36.0	585.3	
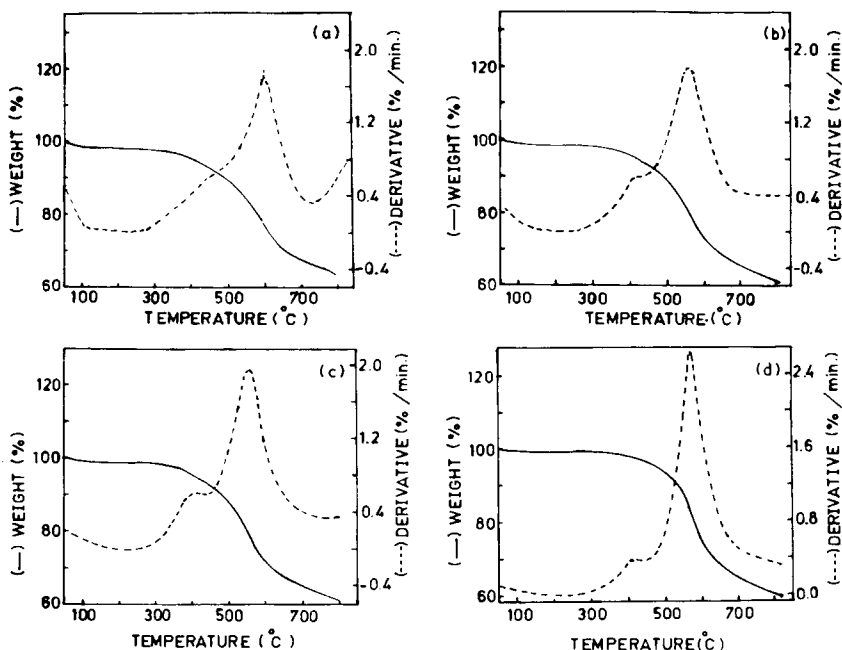
Fig. 4. Thermogravimetric traces of copolyimides cured at 220 ± 5°C for 4 h (heating rate 10°C/min): (a) sample P; (b) sample $PE_{1.3}$; (c) sample PE_2; (d) sample PE_5.

maximum char yield at 800°C was observed in sample P (65%) and lowest in sample E (57.6%). These results clearly indicate that incorporation of TAP/maleimido group increase the char yields in these copolyimides (Table VI).

A clear-cut exothermic transition as observed in the DSC traces of uncured copolyimide samples was not observed after curing was done at 220 ± 5°C. However, a slight deviation in the base line was observed in the temperature range 100–250°C. This may be indicative of residual curing in some of these copolyimides (Fig. 5).

On the basis of the above results it can be concluded that addition of amines to maleimido double bond takes place during the polymerization of TAP with maleic anhydride. This reaction was carried out at 60°C, and only 1

TABLE VI
Results of Thermogravimetric Analysis of Various Copolyimides Cured at 220 ± 5°C for 4 h

Polymer sample	Temperature range (°C)	Weight loss (%)	T_{max} (°C)	Y_c (%)
E	80.1–126.5	2.58		
	493.4–590.0	39.79	560.8	57.63
PE_{10}	475.5–600.0	39.48	556.9	60.52
PE_5	504.0–625.0	39.35	571.0	60.65
$PE_{3.3}$	480.2–635.0	39.30	564.7	60.70
PE_2	457.0–605.0	37.64	553.1	62.36
$PE_{1.3}$	456.3–610.0	37.32	556.0	62.68
P	479.3–645.0	35.06	592.9	64.98
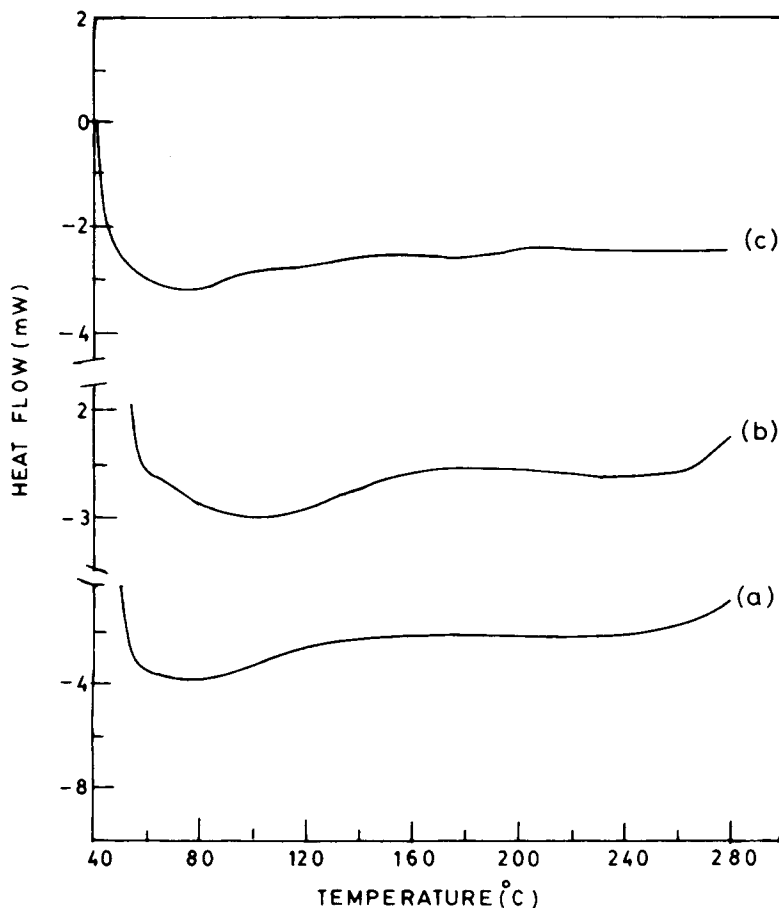
Fig. 5. DSC traces of copolyimides cured at 220 ± 5°C for 4 h (heating rate 10°C/min): (a) sample P; (b) sample PE$_2$; (c) sample PE$_5$.

mol of MA was added to 1 mol of the trifunctional TAP. Thus an excess of amino groups were available during this reaction. Nucleophilic addition of some of these amino groups to the maleimido double bond might have taken place under these reaction conditions according to the following scheme:

TAP–MA
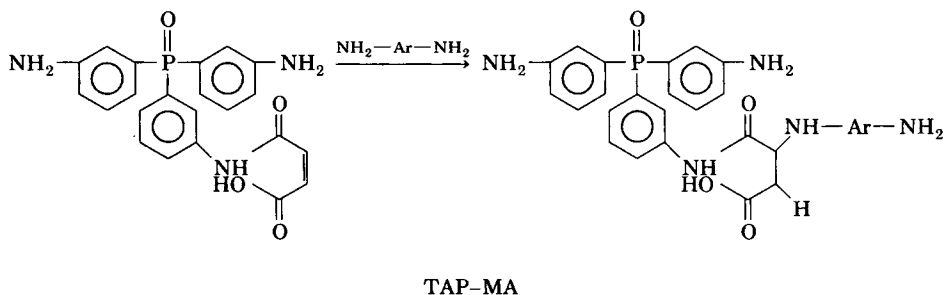
Such a reaction would lead to a reduction in curing temperature of maleimido double bonds as indicated in DSC traces. Also a stoichiometric

imbalance of —NH$_2$ and —COOH (functional groups) groups will take place, which would also lead to a reduction in molecular weight and intrinsic viscosity of the copolymers. Further studies to evaluate these copolyimides are in progress.

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