

Addition Polyimides. IV. Effect of Structure on Thermal Characteristics

INDRA K. VARMA, SANGITA, and D. S. VARMA, *Centre for Materials Science and Technology and Department of Textile Technology, Indian Institute of Technology, Delhi Hauz Khas, New Delhi 110016, India*

Synopsis

Chain extension reaction of bis(*m*-maleimido phenyl) methyl phosphine oxide (BP) with 4,4'-diaminodiphenylmethane (BP-M), 4,4'-diaminodiphenyl ether (BP-E), 3,3'- and 4,4'-diaminodiphenyl sulfone (BP-DDS_m and BP-DDS_p respectively), tris(*m*-aminophenyl) phosphine oxide (BP-TAP), and 9,9-bis(*p*-aminophenyl) fluorene (BP-BAF) was carried out by refluxing 1:0.3 molar solution of BP:diamine. The melting temperature and exothermic peak associated with curing of BP decreased by such chain extension. The thermogravimetric analysis indicated more than 60% residual weight at 800°C in nitrogen atmosphere in BP-DDS_m, BP-DDS_p, and BP-TAP resins. These resins can be processed at low temperature and can be used for fabrication of composites with improved properties.

INTRODUCTION

In our earlier articles we have reported the synthesis of bismaleimide resins based on bis(*m*-aminophenyl) methyl phosphine oxide.¹⁻³ Graphite cloth laminates fabricated from these resins did not burn in pure oxygen even at elevated temperatures. These bisimides exhibited high char yields of 60–71% in nitrogen atmosphere at 800°C. However, curing of these resins was done at temperatures above 230°C. The major objective of the present investigations was to overcome the processing limitations of these bisimides while retaining the outstanding thermal stability and high char yields of the neat resins.

The facile addition reactions of nucleophiles with the electron deficient double bonds of maleimides are well documented in the literature.⁴⁻⁷ The reaction of aromatic diamines with maleimides (known as the Michael reaction) has been successfully employed to synthesize Keramid-601, a commercially available resin from Rhone-poulenc.⁸ Such a modification improves processability and solubility and reduces the melting point and inherent brittleness of the bisimide resin.^{9,10} In the present work an attempt has been made to modify the phosphorus-containing bismaleimide resin by chain extension with several aromatic diamines in acetone solution (Scheme I).

The melting points and curing characteristics of the modified resins were evaluated by DSC. The effect of structure of the modified resin on thermal stability was evaluated by thermogravimetric analysis in nitrogen atmosphere.

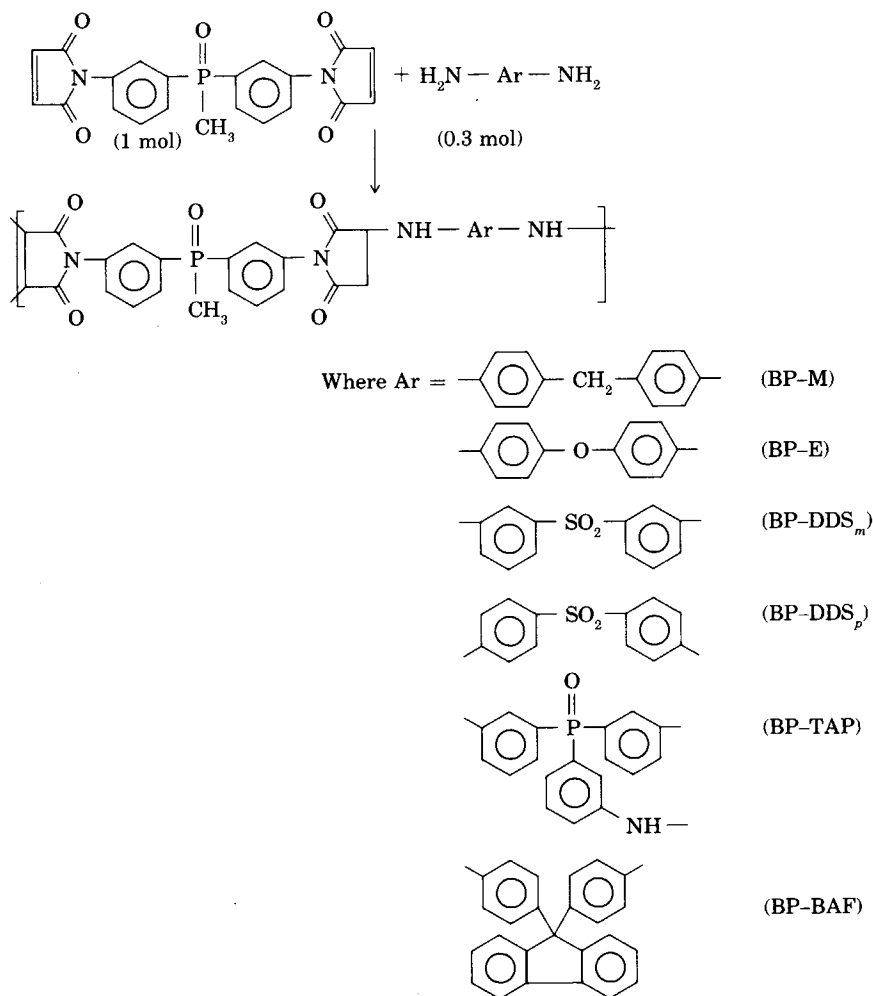
EXPERIMENTAL

Starting Materials. Bis(*m*-aminophenyl) methyl phosphine oxide¹¹ (mp 146–149°C) and bis(*m*-maleimidophenyl) methyl phosphine oxide^{1,2} (BP) were

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Scheme I. (Throughout the text these resins are referred to by the letter designations shown in parentheses).

prepared according to methods reported elsewhere. Tris(*m*-aminophenyl) phosphine oxide (mp 258–260°C) was prepared from triphenylphosphine oxide (Koch Light) by nitration and subsequent reduction with Pd-C/hydrazine hydrate.¹² Maleic anhydride (commercial grade), 4,4'-diaminodiphenyl methane (Fluka), 4,4'-diaminodiphenyl sulfone (Fluka), 3,3'-diaminodiphenyl sulfone (Hindustan Organic Chemicals, Ltd.) were used as such. 9,9-Bis(*p*-aminophenyl) fluorene was recrystallized from chlorobenzene. Acetone (BDH) was dried over anhydrous K₂CO₃.

Preparation of Bismaleimide-Amine Adducts. Linear polymers were prepared by refluxing bismaleimide (BP) with amines in molar ratios of 1:0.3 in acetone for 3–4 h till a homogeneous solution of the reactants was obtained. Acetone was removed under reduced pressure at a temperature of 50–55°C using a rotary evaporator. Shining powder of bismaleimide-amine adduct was obtained.

Partial curing of bismaleimide (BP) as well as the products of Michael reaction was done at $200 \pm 5^\circ\text{C}$ for 30 min in an air oven. All the resin samples were placed in separate shallow aluminium dishes and cured under same conditions. Orange to brownish-colored solids were obtained after curing.

The IR spectra of various resin samples were recorded in KBr pellets using a Perkin-Elmer 580B Infrared Spectrophotometer.

A DuPont 1090 Thermal Analyzer was used to evaluate the thermal behavior of the resins. The DSC measurements were done using a 910 DSC module in air atmosphere (static condition) at a heating rate of $10^\circ\text{C}/\text{min}$. Thermogravimetric analysis was carried out on a 951 TGA module in nitrogen atmosphere (flow rate 100 cc/min). Sample size of 10 ± 2 mg, and a heating rate of $10^\circ\text{C}/\text{min}$ was used.

RESULTS AND DISCUSSION

In the IR spectra of various bismaleimide-amine adducts typical absorption bands associated with imide groups at 1780 ± 5 cm^{-1} and 1720 cm^{-1} were observed. Other absorptions arising because of $\text{P}=\text{O}$ (at 1180 ± 5 cm^{-1}), $\text{P}-\text{C}_6\text{H}_5$ (at 1430 cm^{-1}), C_6H_5 (at 1595 and 1485 cm^{-1}), and $\text{C}-\text{N}$ (at 1375 ± 5 cm^{-1}) were also present. In addition to these absorption bands of bis(*m*-maleimidophenyl) methylphosphine oxide additional bands were observed at 1630 cm^{-1} (due to $\text{N}-\text{H}$ in plane bending vibration) and at 3380 – 3400 cm^{-1} ($\text{N}-\text{H}$ stretch) (Figs. 1 and 2). In BP-DDS_m and BP-DDS_p ab-

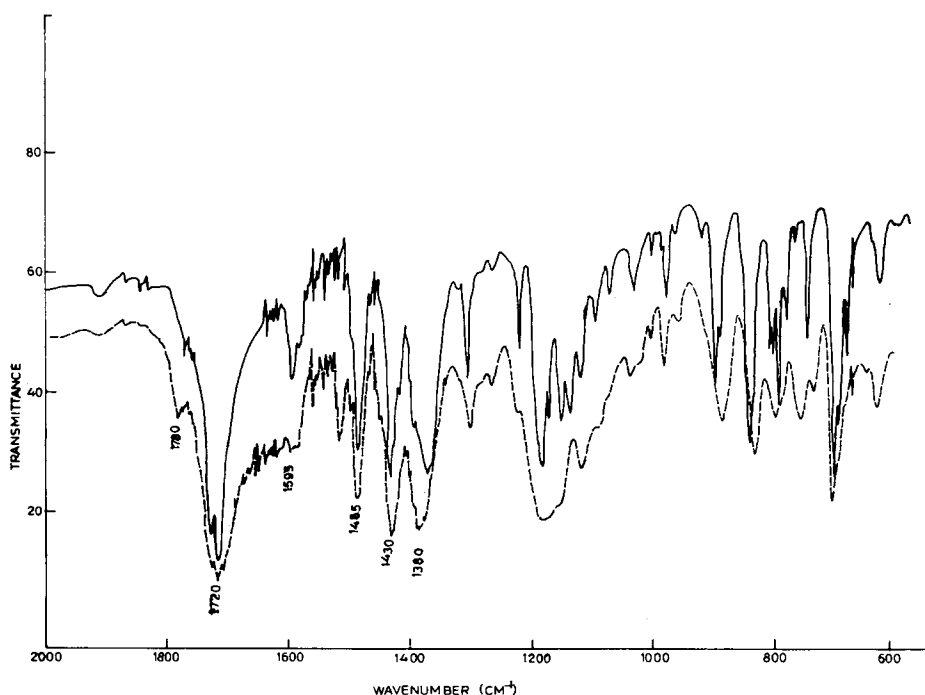


Fig. 1. IR spectra of bismaleimide resins: (—) bis(*m*-maleimidophenyl) methylphosphine oxide; (---) BP-BAF adduct.

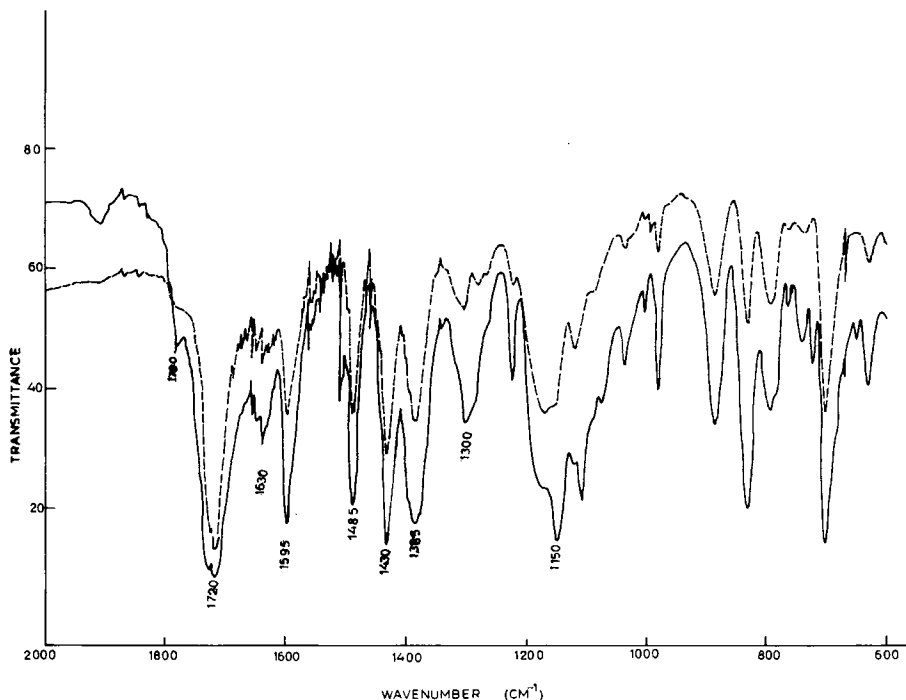


Fig. 2. IR spectra of bismaleimide-amine adducts: (—) BP-TAP adduct; (---) BP-DDS_p adduct.

sorption peaks due to SO₂ group at 1150 and 1300 cm⁻¹ (sym. and assym. stretch of SO₂ group, respectively) were observed. These results thus clearly indicate that the various bismaleimide-amine adducts contained both unreacted maleimide groups together with the products of Michael addition reaction.

DSC scans were made at 10°C/min in air atmosphere (static conditions). The various resin samples exhibited slightly different features (Figs. 3-5). In bis(*m*-maleimidophenyl) methylphosphine oxide, the endothermic peak associated with melting was observed at 184.2°C ($\Delta H_f = 78.8$ J/g). Following this was the exothermic transition due to curing which begins at 200°C. The exothermic peak (T_{exo}) was at 264°C and it terminated at 320°C (T_2). The onset temperature for curing (T_1) was obtained by extrapolating the front side of the exothermic peak to the base line. In BP-E resin sample an inflection corresponding to glass transition was observed around 50°C. An endothermic peak was found at 80°C. This was followed by a broad exotherm which had a slight bimodal character (Fig. 4). The exothermic peaks were at 176.6°C and 240°C. The peak terminated at 336°C. The exothermic transition occurred at higher temperatures in BP-DDS_m and BP-DDS_p resins. In these cases also a bimodal nature was noticeable. No distinct transition, associated with melting was observed in these samples. In BP-TAP resin a single exotherm with a peak at 197.6°C was present while in BP-M the twin exothermic peaks were quite distinct. Endothermic transitions due to melting were at 75°C and 93.5°C in BP-TAP and BP-M, respectively. The results of these studies are summarized in Table I.

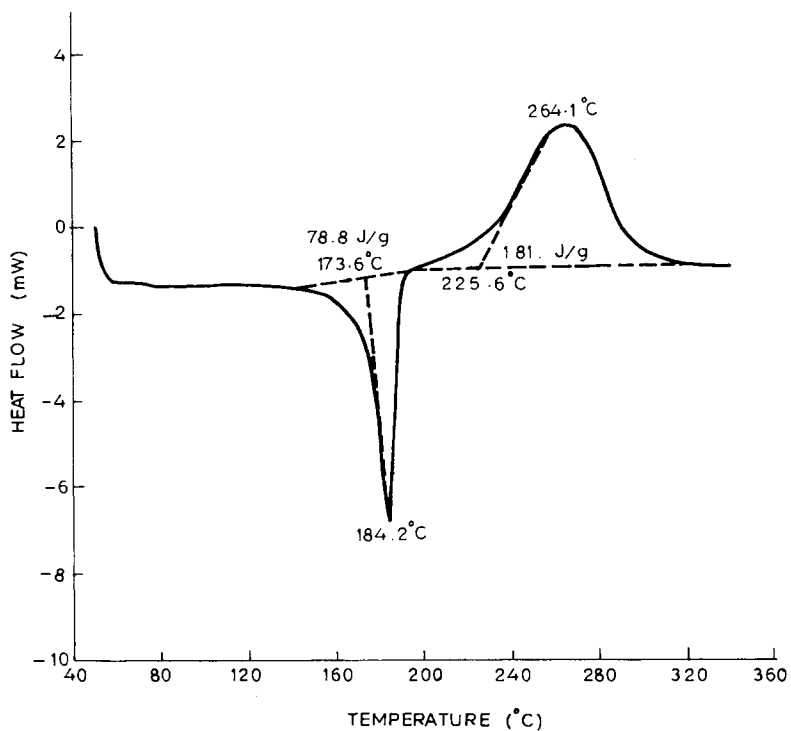


Fig. 3. DSC scan of bis(*m*-maleimidophenyl) methylphosphine oxide.

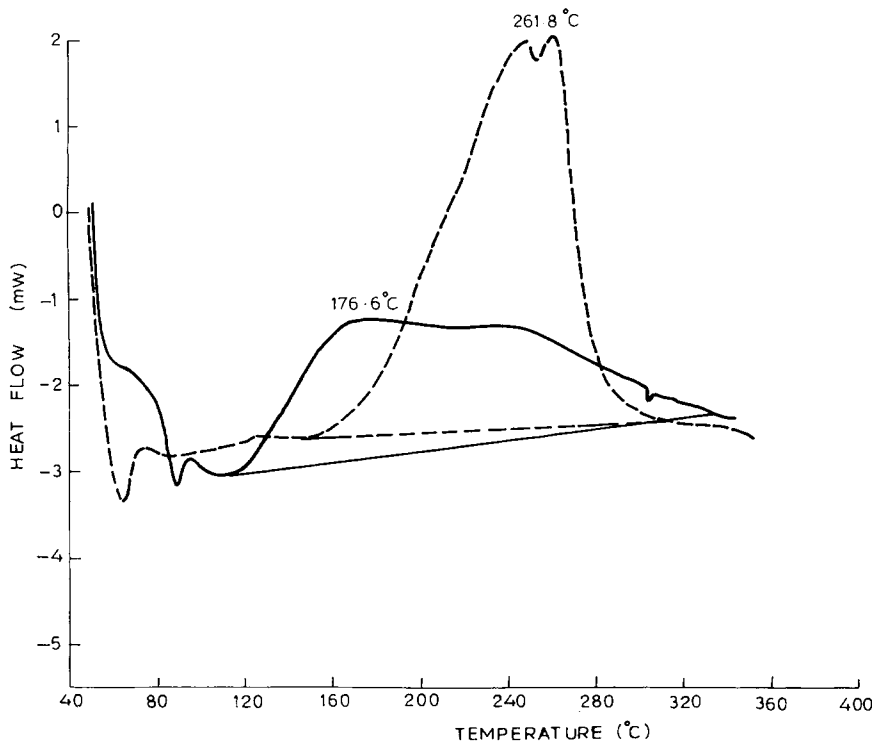


Fig. 4. DSC scans of bismaleimide-amine adducts: (—) BP-E resin; (---) BP-DDS₃ resin.

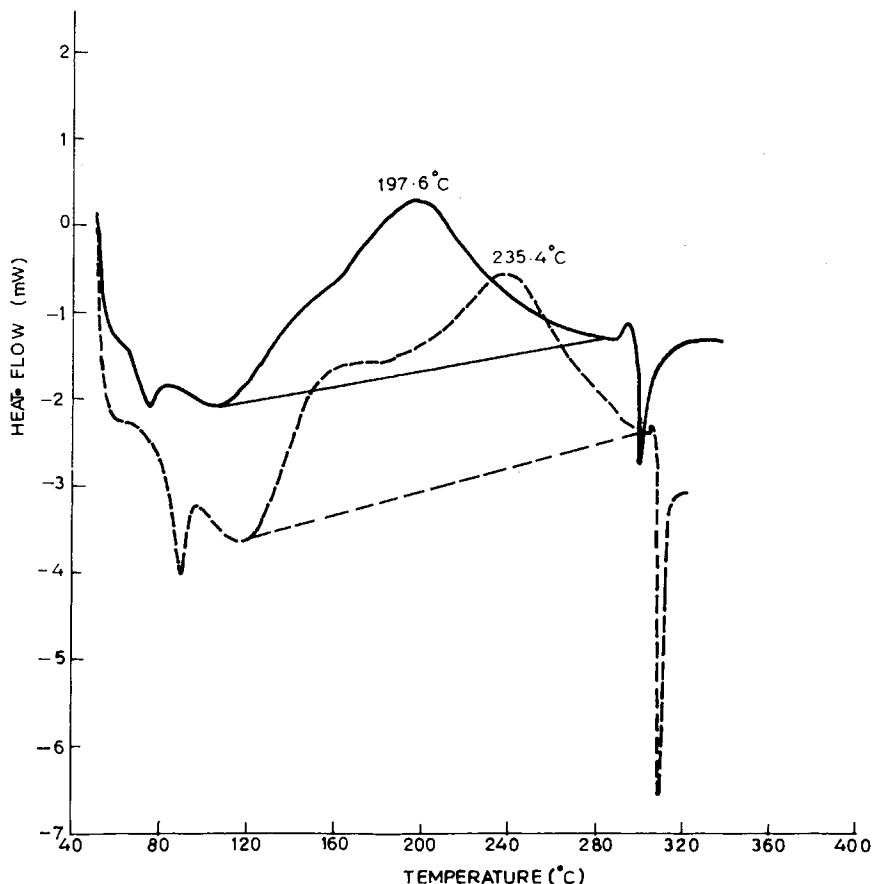


Fig. 5. DSC scans of bismaleimide-amine adducts: (—) BP-TAP resin; (---) BP-M resin.

This information suggests that the curing temperatures of various resins depend on the structure of the amine used for chain extension. In neat BP resin no significant curing takes place below 200°C while in all the Michael adducts of this bismaleimide and of aromatic amines curing begins at temperatures below 200°C. The temperature of exothermic peak is significantly lowered in the BP-amine adducts (Table I).

The heat of cure, ΔH was determined by measuring the area bounded by the exotherm. These results are also tabulated in Table I. The ΔH values for the various resin samples varied from 123 J/g to 196 J/g.

It is reasonable to assume that ΔH will decrease as the degree of cure of the resin is advanced. The partial curing of all the resin samples was, therefore, carried out at 200°C for 30 min, and the DSC scans of these resins were recorded. In partially cured BP resin a broad endothermic peak beginning at 77°C, with peak at 122.5°C and terminating at 180°C was observed. The exothermic peak was at 259.9°C, and T_1 and T_2 were at 228°C and 332°C, respectively (Fig. 6). A considerable reduction in the area of exothermic peak was observed in BP-amine adducts. The onset of exotherm increased to higher temperatures. For example in BP-E resin T_1 , T_{exo} , and T_2 were at 226.8°C, 257.8°C, and 322°C. A broad endotherm beginning from 78.6°C

TABLE I
DSC Results of bis(*m*-maleimidophenyl) Methylphosphine Oxide and Its Addition Products with Various Diamines

Sample	T_1 (°C)	T_{exo} (°C)	T_2 (°C)	ΔH (J/g)
BP	225.6	264	320	181
BP:DADPM	127	235.4	304	186
BP:DADPE	131.1	176.6	336	191
BP:DDS _{<i>m</i>}	220.7	244	304	127
BP:DDS _{<i>p</i>}	185	261.8	312	196
BP:TAP	148.7	197.6	284	170
BP:BAF	146.7	229.2	308	123

and ending at 180°C with a peak at 129.6°C was present. The effect of meta or para orientation of sulfone group in BP-DDS_{*m*} and BP-DDS_{*p*} had negligible effect on the exothermic transition in the advanced resins (Fig. 7). The T_{exo} values in the various resin samples varied from 254°C to 270°C. Much more distribution in T_{exo} was observed in uncured samples. The results of these investigations are tabulated in Table II.

A broadening of absorption bands was observed in the IR spectra of partially cured resins (Fig. 8). The general features of BP and BP: amine adducts were similar in the IR spectra.

Thermal stability of BP-amine adducts was evaluated by thermogravimetric analysis in nitrogen atmosphere. The relative thermal stability of uncured and partially cured resin samples was assessed by comparing the

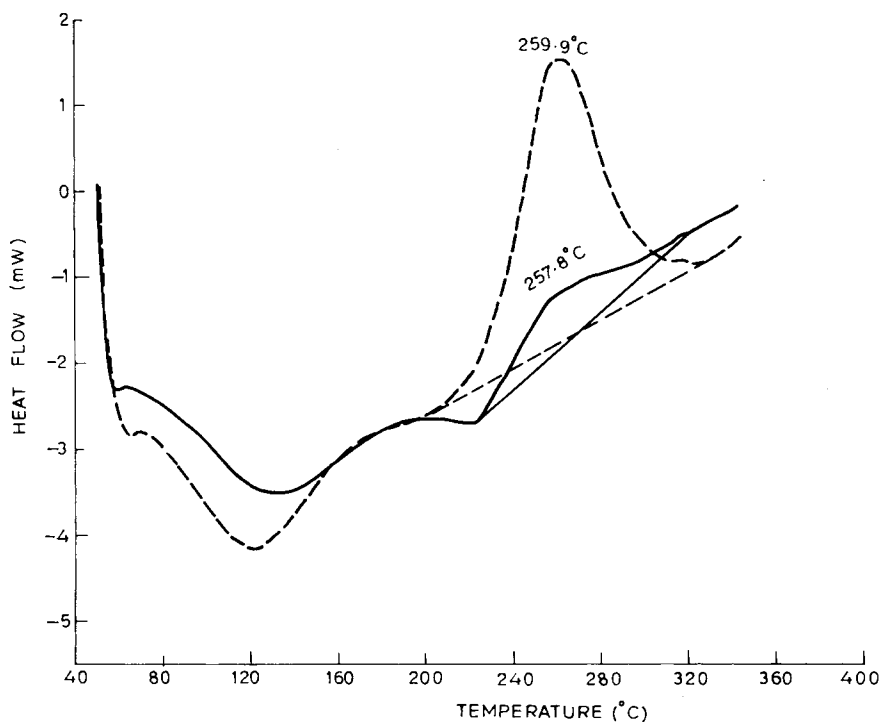


Fig. 6. DSC scans of BP resins cured at 200°C for 30 min: (---) BP resin; (—) BP-E resin.

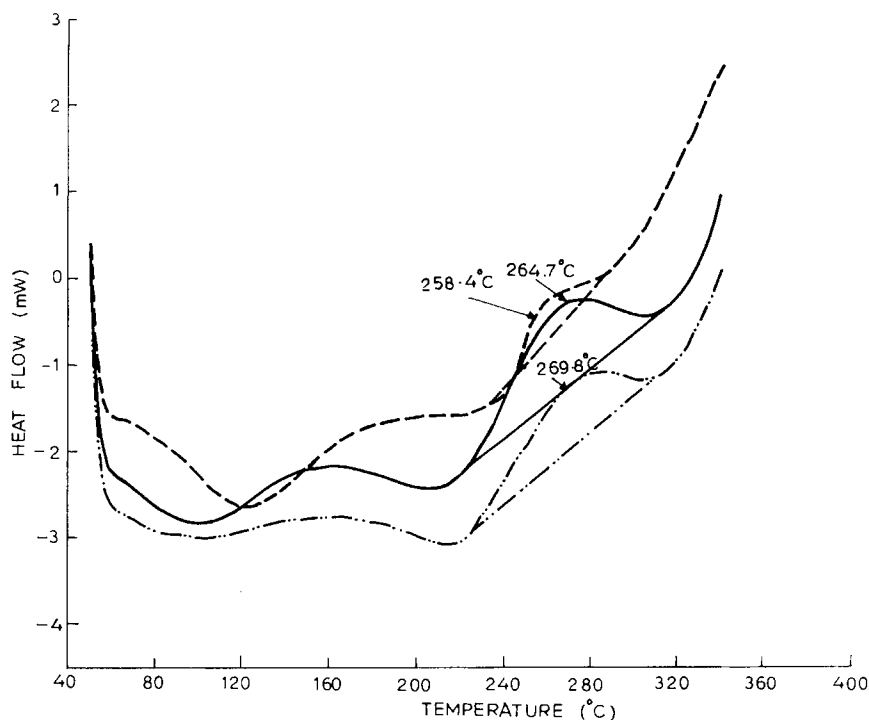


Fig. 7. DSC scans of bismaleimide-amine adducts cured at 200°C for 30 min: (.....) BP-DDS_m; (—) BP-DDS_p; (---) BP-TAP.

initial decomposition temperature (IDT—obtained by extrapolation), the temperature of maximum rate of weight loss (T_{\max}) integral procedural decomposition temperature (IPDT),¹³ and char yield (Y_c) at 800°C.

In BP uncured resin the decomposition occurred in two stages. The onset of degradation was around 424 (IDT) and T_{\max} at 432.9°C and 483°C were observed. About 29% weight loss occurred in the temperature range of 424–500°C. Slow decomposition occurred beyond this point and a char yield of 63.7% was obtained at 800°C. The IDT values were lowered in BP-amine adducts. A decrease in char yields was also observed. The two-step decomposition behavior was maintained in these resins.

TABLE II
DSC Results of BP-Amine Adducts Cured at 200°C
for 30 Min

Sample	T_1 (°C)	T_{exo} (°C)	T_2 (°C)	ΔH (J/g)
BP	228	260	332	103
BP:DADPM	224.4	254	312	28
BP:DADPE	226.8	257.6	322	21.7
BP:DDS _m	230.3	269.8	308	22.1
BP:DDS _p	229.6	264.7	312	33.1
BP:TAP	245.2	258.4	290	8.69
BP:BAF	248.8	270	302	3.95

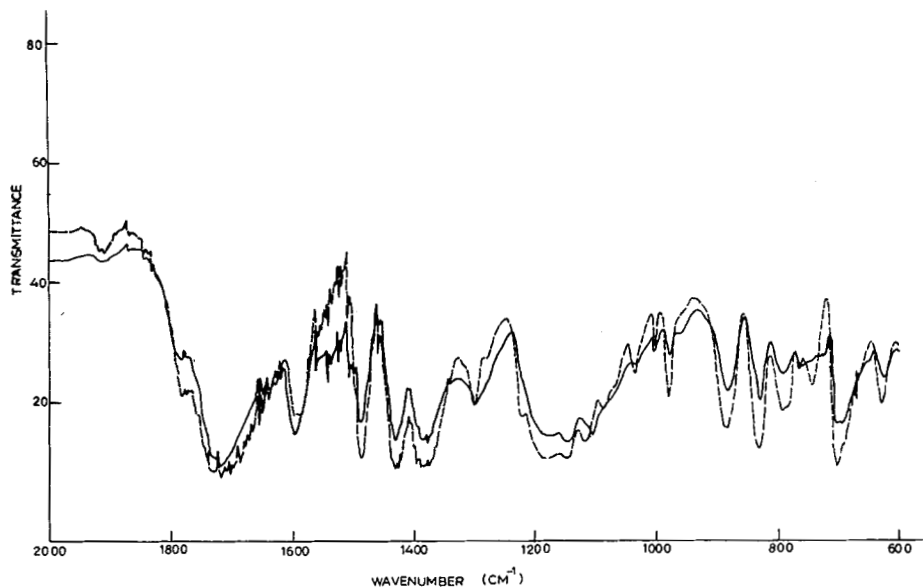


Fig. 8. IR spectra of partially cured resins (200°C for 30 min): (—) BP resin; (---) BP-DDS_p resin.

Partial curing of the resins resulted in an increase in char yields in almost all cases. The two-step decomposition behavior was retained in the resin samples. An increase of 12–15°C in the second T_{\max} was observed on curing (Fig. 9). The results of thermogravimetric analysis are summarized in Table III. The char yields of partially cured resins varied from 58% to 69%. On

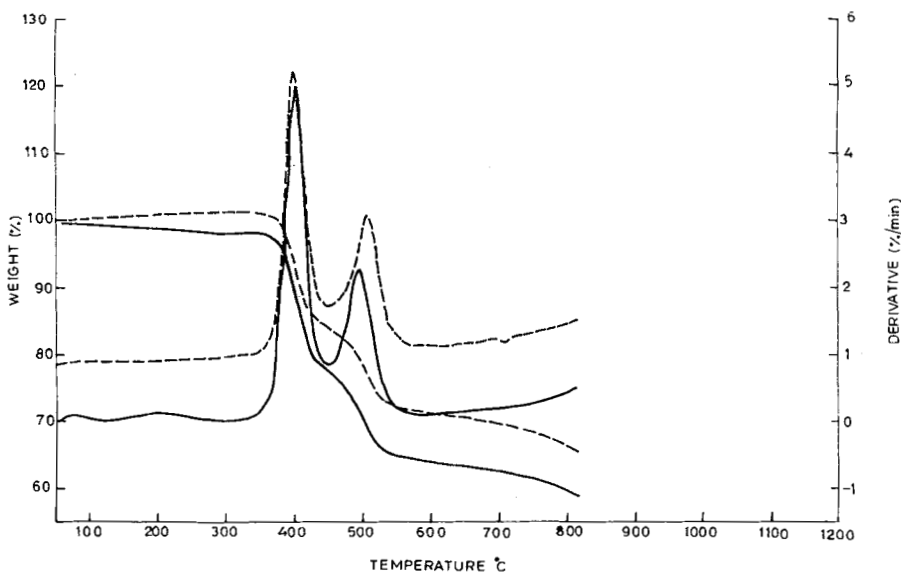
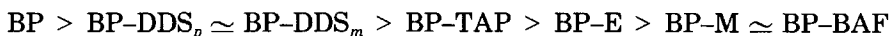


Fig. 9. Thermogravimetric traces of bismaleimide-amine adducts: (—) BP-DDS_p uncured resin; (---) BP-DDS_p cured at 200°C for 30 min.

TABLE III
Results of Thermogravimetric Analysis of Various BP-Amine Adducts (Rate of Heating
10°C/min, Atmosphere Nitrogen)

Sample	Time of curing (min)	IDT (°C)	IPDT (°C)	T_{max} (°C)	% Y_c at 800°C
BP	0	424.5	699	432.9, 483	63.7
	30	433	727	441, 497.4	69
BP:DADPM	30	378.4	660	409, 515	58
BP:DADPE	30	371.3	663	411.6, 514	58.4
BP:DDS _m	30	380	692	406.7, 510	66.4
BP:DDS _p	0	382	661	402, 495	60
	30	382.4	696	401, 507	65
BP:TAP	0	371.7	655	400, 499	60
	30	374	670	401.5, 513	61
BP:BAF	30	383	665	411.5, 521	58

the basis of char yields and IPDT values, the thermal stability of partially cured resins was in the following order:



A decrease in thermal stability of bisimides by Michael addition of aromatic diamines has been observed earlier.^{5,9} However, the better char yields of BP-DDS systems in comparison to BP-TAP are a bit surprising. Our earlier studies have indicated better char yields when TAP was used as chain extender. In BP-TAP resins about 2% loss in weight was observed below 150°C. This may be due to absorbed water. The hydrophilicity of the resins is increased by the incorporation of phosphorus in the backbone. No loss in weight below 150°C was observed in other samples. High char yields in bismaleimides having fluorene, anthrone, and phthalein groups as bridging units have been reported earlier.¹⁴ However, when fluorene-containing amine was used for chain extension of BP the char yields were similar to BP-M resin systems. This indicates that the presence of cardiac type group in amines does not influence the thermal stability of bismaleimide-amine adducts.

The significant conclusion of these studies is that bis(*m*-maleimidophenyl) methylphosphine oxide can be cured at a lower temperature by reaction with 3,3'- or 4,4'-diaminodiphenyl sulfone or tris(*m*-aminophenyl) phosphine oxide. The char yields of these resins are very good (61–66%). The processing of laminates can, therefore, be done at relatively milder conditions without significantly affecting the thermal stability of the product.

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References

1. I. K. Varma, G. M. Fohlen, Ming-ta Hsu, and J. A. Parker, "New Phosphorus containing Bisimide Resins," abstract, U.S.-Japan Polymer Symposium, Palm Springs, Calif., Nov. 1980.
2. I. K. Varma, G. M. Fohlen, and J. A. Parker, U.S. Pat. 4,276,344 (1981).

3. I. K. Varma, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2017 (1983).
4. J. V. Crivello, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **11**, 924, (1970); **14** (1), 294 (1973).
5. J. V. Crivello, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 1185 (1973).
6. I. K. Varma, A. Gupta, and Sangita, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 621 (1982).
7. R. Kreher and H. Hennige, *Tetrahedron Lett.*, **22**, 1911 (1973).
8. M. Bergain et al., Br. Pat. 1190718 (1978), to Rhone Poulenc.
9. I. K. Varma, A. K. Gupta, Sangita, and D. S. Varma, *J. Appl. Polym. Sci.*, **28**, 191 (1983).
10. I. K. Varma, Sangita, and D. S. Varma, *J. Polym. Sci., Polym. Chem. Ed.*, to appear.
11. D. A. Kourtides, J. A. Parker, T. W. Giants, N. Bilow, and Ming-ta Hsu, Proceedings of the Adhesives for Industry Conference, El Segundo, Calif., June 24-25, 1980.
12. I. K. Varma, G. M. Fohlen, and J. A. Parker, U.S. Pat. 4,395,557 (1983).
13. C. D. Doyle, *Anal. Chem.* **33**, 77 (1961).
14. I. K. Varma, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 283 (1982).

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