

Tris(3-aminophenyl)phosphine Oxide-Based Nadimide Resins. II*

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SYNOPSIS

A series of phosphorus-containing nadimide end-capped resins having different backbones was prepared by reacting *endo*-5-norbornene-2,3-dicarboxylic acid anhydride (nadid anhydride), pyromellitic dianhydride (PMDA)/3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA)/2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F) and tris(3-aminophenyl)phosphine oxide (TAP) in glacial acetic acid/acetone. Structural characterization of the resins was done by elemental analysis, FTIR, and ¹H-NMR. Thermogravimetric studies revealed a multistep decomposition reaction for uncured resins. Residual weight at 800°C in nitrogen was found to be 50–60%. Resins cured at 300°C for 1 h in air atmosphere were stable up to 440 ± 20°C and decomposed in a single step above this temperature. The char yields of cured resins were in the range 63–71.5%. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Endo-5-norbornene-2,3-dicarboximide (nadimide) end-capped polyimides are important polymer precursors for the preparation of processable and void-free heat-resistant polymers having potential applications as matrix resins in advanced fiber-reinforced composites. Recent research efforts in this area have been primarily directed toward the development of new and improved resin systems capable of better elevated temperature performance than that of the state-of-the-art resins.^{1–4}

Incorporation of phosphorus and nitrogen in the polymer backbone generally leads to an improvement in flame resistance and high-temperature performance of polymers.⁵ In our earlier papers, we reported the synthesis of maleimide and nadimide end-capped resins having excellent thermal stability and flame resistance.^{6–10} Thermal polymerization of nadimido¹¹ derivatives of 1-[dialkoxy phosphinyl

methyl]-2,4-diaminobenzene and its 2,6-isomer has also been reported to give cross-linked resins with a high limiting oxygen index. Phosphorus-containing cross-linkable polyimides having pendant maleimido or nadimido groups have been reported in the literature.^{12–14}

The anaerobic char yields of nadimide resins at 800°C with or without phosphorus are, however, lower than the corresponding maleimide resins and range from 40 to 60% in most cases. In our recent communication, we reported novel nadimide resins based on amide-amine/cardoamine having char yields greater than 70%. The purpose of the present investigations was to develop nadimide resins based on tris(3-aminophenyl)phosphine oxide having high char yield, good thermal stability, and fire-resistance properties.

Eight nadimide oligomers were prepared by reacting nadid anhydride (NA), tris(3-aminophenyl)phosphine oxide (TAP), and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA)/pyromellitic dianhydride (PMDA)/2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F). NA was first reacted with TAP in 2 : 1 molar ratio to give bisnadimide P-1. This oligomer was then chain-extended with PMDA/BTDA/6F.

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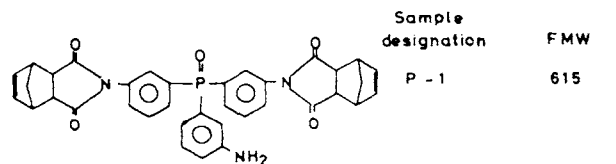
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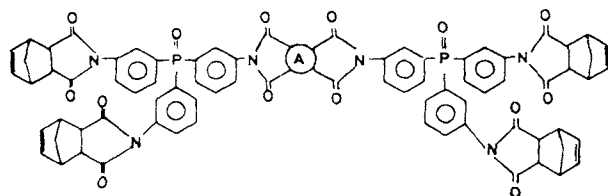
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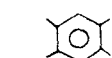
The structure of the oligomers along with sample designation and formulated molecular weight (FMW) is given in Scheme I.



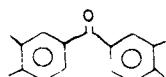
Structure of chain extended nadimides



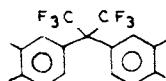
Where A



Sample designation	FMW
P-1P	1412

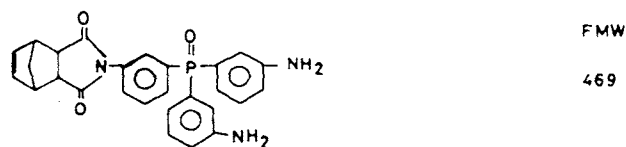


P-1B	1516
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P-1F	1638
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In the second series, NA was reacted with TAP in 1 : 1 molar ratio to give a monoadimide P-2:



Enhanced oxidative stability has been reported in nadimides having higher FMW.⁴ Therefore, the effect of FMW on thermal behavior of nadimides was investigated by treating P-2 (1 mol) with PMDA/BTDA/6F (0.75 mol) to obtain oligomer P-2P, P-2B, and P-2F with FMW 2422, 2734, and 3100, respectively.

EXPERIMENTAL

Materials

Glacial acetic acid (BDH) and acetic anhydride (BDH) were distilled at atmospheric pressure before use. Acetone (BDH) was dried overnight over sodium sulfate, refluxed for 1 h, and distilled at at-

mospheric pressure. NA (E. Merck), BTDA (Koch Light), PMDA (Fluka), and 6F (Hoechst) were purified by recrystallization from acetic anhydride. Anhydrous sodium acetate (Sarabhai Chemicals) was obtained by fusion. TAP was prepared from triphenylphosphine oxide (Koch Light) by nitration and subsequent reduction according to the procedure reported earlier.¹⁵

Synthesis of Nadimides

Appropriate quantities of NA and TAP in glacial acetic acid (20 mL) were refluxed for 8 h at 120°C and the imides were recovered by precipitation in water. The precipitated imides were washed several times with water and aqueous sodium bicarbonate and after drying were recrystallized from chloroform.

Chain Extension with Dianhydrides

The amino end-capped mono- and bisnadimides were refluxed in acetone with PMDA/BTDA/6F for 4 h at 60°C. The resulting amic acid was chemically cyclized by the addition of sodium acetate and acetic anhydride as cyclodehydrating agent. This reaction was carried on for 4 h. The imides were precipitated in water, washed several times with water and aqueous sodium bicarbonate, and dried under vacuum.

CHARACTERIZATION

A Nicolet MX-I FTIR spectrophotometer was used for recording spectra of various nadimides in KBr pellets. ¹H-NMR spectra were recorded on a Jeol-JNM-FX-100 FT-NMR spectrophotometer using DMSO-*d*₆ or CDCl₃ as solvents and tetramethylsilane as an internal standard.

A DuPont 9900 thermal analyzer having a 910 DSC module was used for studying the curing behavior. A sample of about 10 ± 2 mg was heated from room temperature to 450°C in static air at 10°C/min.

A DuPont 1090 thermal analyzer having a 951 TG module was used for assessing the relative thermal stability of the nadimide resins. Thermogravimetric traces were recorded in nitrogen atmosphere (flow rate 60 mL/min) at a heating rate of 10°C/min. A sample of 10 ± 2 mg was used. Isothermal curing was also done at 250 and 300°C for 1 h each. DSC and TG traces of the uncured and cured samples were recorded. The relative thermal stability of various resin samples was evaluated by determining

Table I Physical Characteristics of Nadimide Resins

Sample Designation	% Yield	Solubility			
		Acetone	CHCl ₃	DMF	DMSO
P-1	96	++	++	++	++
P-1P	53	++	++	++	++
P-1B	61	--	--	++	++
P-1F	50	++	++	++	++
P-2	94	++	++	++	++
P-2P	40	--	--	++	++
P-2B	61	--	--	++	++
P-2F	43	--	--	++	++

-- insoluble; ++ highly soluble.

(a) the initial decomposition temperature (T_1), (b) the temperature of maximum rate of weight loss (T_{max}), and (c) char yield at 800°C. In those cases where decomposition proceeded in more than one step, weight loss at each step was also noted.

RESULTS AND DISCUSSION

The nadimide oligomers were obtained in powder form with a light brown color and yield ranging from 40 to 96%. Some of the physical characteristics of the oligomers are shown in Table I. Only resin sam-

ples P-1, P-1P, P-1F, and P-2 were soluble in low boiling solvents. Elemental analysis (C, H, N) of some of the nadimide resins was done (Table II). In some of the samples, the carbon content observed was much lower than the calculated value. Results of nitrogen and hydrogen content, however, agreed fairly well.

In the FTIR spectra of nadimide resins, characteristic bands due to imide groups appeared at 1784 and 1722 cm^{-1} ($\nu_{C=O}$), and 1370 \pm 10, 1130 \pm 10, and 725 \pm 10 cm^{-1} . The presence of NH_2 groups in the bisnadimide P-1, mononadimide P-2, and the chain-extended P-2 nadimides was indicated by N—H

Table II Results of Elemental Analysis of Nadimide Resins

Sample Designation	Formula	Elemental Analysis ^a		
		C	H	N
P-1	C ₃₆ H ₃₀ N ₃ O ₅ P	59.9 (70.24)	4.1 (4.88)	6.4 (6.38)
P-1P	C ₈₂ H ₅₈ N ₆ O ₁₄ P ₂	65.1 (69.69)	4.7 (4.11)	6.4 (5.95)
P-1B	C ₈₉ H ₆₂ N ₆ O ₁₅ P ₂	65.0 (70.45)	4.6 (4.09)	5.7 (5.54)
P-1F	C ₉₁ H ₆₂ N ₆ O ₁₄ P ₂ F ₆	61.7 (66.67)	4.3 (3.79)	4.9 (5.13)
P-2P	C ₁₃₈ H ₉₀ N ₁₂ O ₂₄ P ₄	60.5 (68.37)	4.3 (3.71)	7.9 (6.93)
P-2B	C ₁₅₉ H ₁₀₂ N ₁₂ O ₂₇ P ₄	60.3 (69.78)	4.1 (3.74)	5.3 (6.14)
P-2F	C ₁₆₅ H ₁₀₂ N ₁₂ O ₂₄ P ₄ F ₁₈	62.1 (63.87)	4.6 (3.29)	7.6 (5.42)

^a Figures in parentheses indicate calculated values.

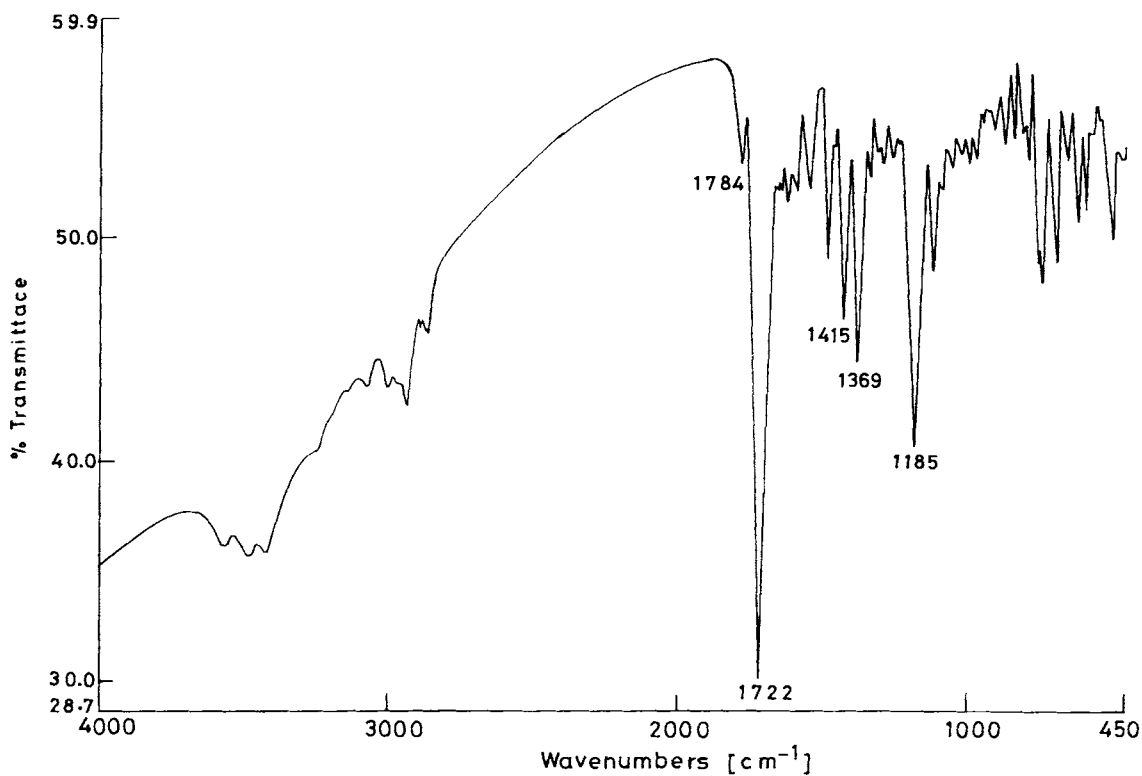


Figure 1 IR spectrum of P-1 nadimide resin.

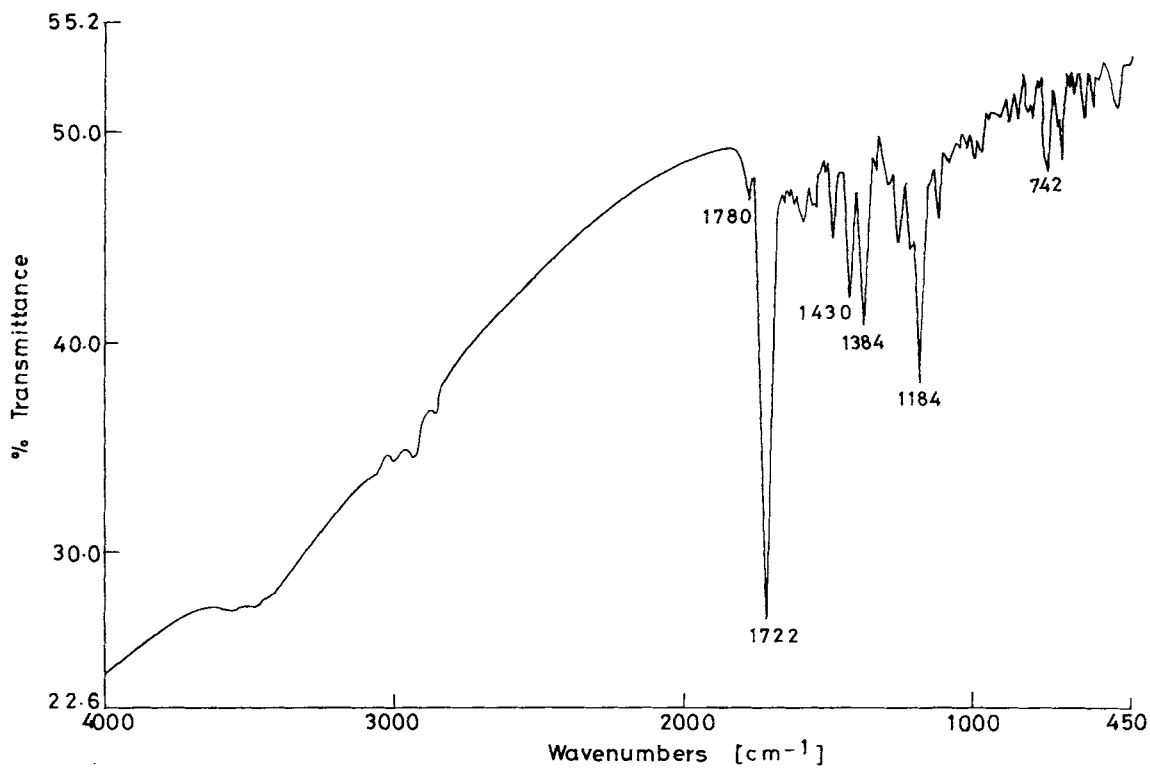
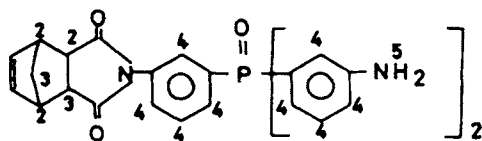


Figure 2 IR spectrum of P-1F nadimide resin.

stretching at 3230 cm^{-1} . The absorption bands due to $\text{P}-\text{C}_6\text{H}_5$ and $-\text{P}=\text{O}-$ were observed at 1430 and 1185 cm^{-1} . In samples containing BTDA, a shoulder at 1630 cm^{-1} due to $\nu_{\text{C}=\text{O}}$ of ketone was present. IR spectra of P-1 and P-1F are shown in Figures 1 and 2.

The $^1\text{H-NMR}$ spectra of P-1, P-2, P-1P, and P-1F were recorded in CDCl_3 . For P-1B and chain-extended P-2 resins, $^1\text{H-NMR}$ spectra were recorded in $\text{DMSO}-d_6$. The chemically equivalent protons resonating at different positions in mononadimide P-2 can be grouped as follows:



The aromatic protons H-4 appeared at $\delta = 7.2$ – 8.3 ppm (12H, m) and olefinic protons H-1 at $\delta = 6.14$ ppm (2H, s). The NH_2 group appeared at $\delta = 2.0$ ppm. The presence of residual uncyclized amic acid was also indicated by the appearance of a resonance signal at $\delta = 9.60$ ppm. In the chain-extended

P-2 resins, similar resonance peaks were observed. Since the spectrum was recorded in $\text{DMSO}-d_6$, therefore integration in the aliphatic region was slightly complicated because of the residual protons of solvent and moisture. The ratio of total aromatic to olefinic protons was used for structural characterization of these resins. $^1\text{H-NMR}$ spectra of P-1P and P-1F are shown in Figures 3 and 4.

Thermal Behavior of Nadimide Resins

Uncured Nadimide Resins

TG traces of the uncured nadimide resins in nitrogen revealed a multistep decomposition. Weight loss (< 5%) was observed in the temperature range of 150 – 200°C . In the DSC traces, an endothermic transition was seen in this temperature range. The transition may therefore be attributed to the desorption of solvent/moisture. Introduction of phosphorus in the backbone increases hydrophilicity. Residual amide acid may also undergo cyclodehydration and lose water. Approximately 6–12% weight loss was observed in the temperature range of 220 –

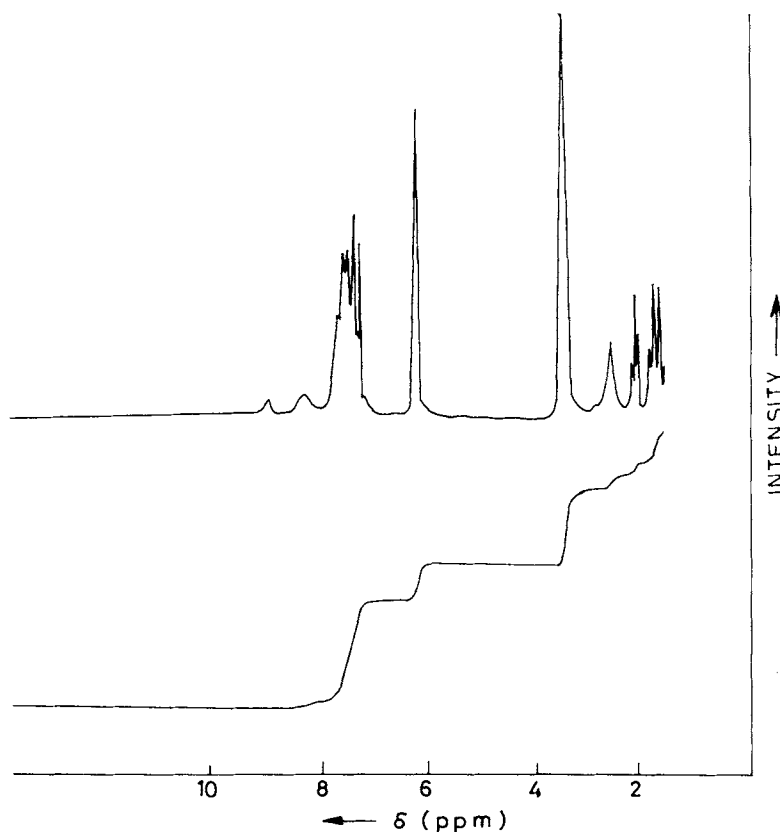


Figure 3 $^1\text{H-NMR}$ spectrum of P-1P nadimide resin.

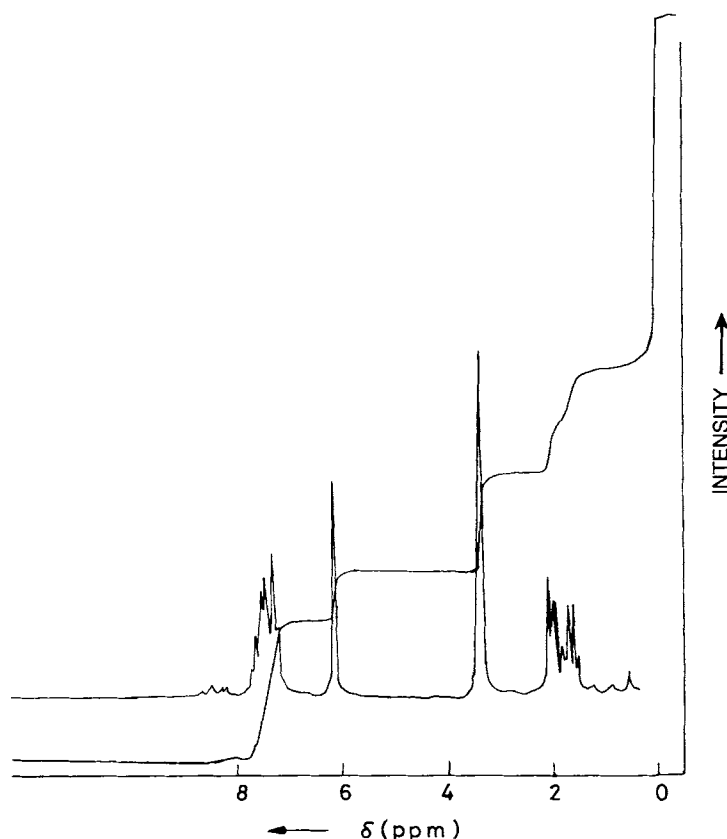


Figure 4 $^1\text{H-NMR}$ spectrum of P-1F nadimide resin.

400°C. This corresponds to an exothermic transition in the DSC traces. The transition may be attributed to the curing of the nadimides via a retero Diels-Alder reaction in which *in situ* formation of cyclopentadiene and maleimide units takes place initially, followed by polymerization. The third step of decomposition was in the temperature range of 410–

600°C, which is due to the breakdown of polymer backbone. Maximum weight loss was observed in this region (25–37%). Table III gives the curing behavior of the nadimide resins. Detailed results of TG studies are given in Table IV. Char yield depended on the backbone and was in the range 50–60%. In general, the uncured nadimide resins containing one or two free amino groups were thermally less stable. Char yield for P-1 and P-2 was 49.2 and 51.75%, respectively. Introduction of PMDA or BTDA in the backbone gave polymers with high char yields. Chain extension with 6F anhydride did not increase char yield. Increase in FMW resulted in a decrease in high-temperature performance. DSC traces of P-2F and P-1F are given in Figure 5(a) and (b). TG traces of uncured P-1P and P-1B are given in Figure 6(a) and (b).

Table III Curing Behavior of Nadimide Resins

Sample Designation	Curing Temperature (°C) ^a		
	T_1	T_{exo}	T_f
P-1	237	276	307
P-1P	232	277	357
P-1B	250	280	350
P-1F	216	287	339
P-2	245	286	313
P-2P	241	263	338
P-2B	168	196	223
P-2F	247	290	331

^a T_1 = temperature of onset of exotherm; T_{exo} = temperature of peak position; T_f = temperature of completion of exotherm.

Curing of Nadimide Resins

Since in the DSC scan curing exotherm was around 200–310°C, initially isothermal curing of the nadimides was therefore done at 250°C for 1 h in

Table IV TG of Uncured Nadimide Resins

Sample Designation	T_1 (°C)	T_{max} (°C)	T_2 (°C)	Y_c (%)
P-1	135	170	220 (2.90)	49.2
		318	350 (10.78)	
		542	640 (37.04)	
P-1P	255	160	190 (4.32)	60.00
		334	420 (6.54)	
		521	600 (31.74)	
P-1B	150	175	220 (2.15)	57.25
		316	400 (8.33)	
		527	650 (34.08)	
P-1F	155	177	220 (2.97)	51.70
		289	400 (12.27)	
		533	650 (34.45)	
P-2	145	157	175 (3.44)	51.75
		321	350 (6.82)	
		488	590 (37.90)	
P-2P	150	175	240 (4.42)	56.00
		315	375 (11.29)	
		528	600 (24.53)	
P-2B	115	162	225 (4.48)	59.00
		329	395 (12.03)	
		566	620 (27.00)	
P-2F	150	178	205 (3.36)	55.00
		285	370 (10.50)	
		553	615 (32.76)	

Figures in parentheses indicate percent weight loss at each step.

air atmosphere. The resins thermally cured at 250°C dissolved readily in DMF, indicating low molecular weight products. The TG traces of these resins were similar to those of corresponding uncured resins. Therefore, the same samples were further cured at 300°C for 1 h. Resins insoluble in DMF were obtained by such a treatment. Curing at this temperature resulted in weight loss (4–11%). This may be due to the loss of cyclopentadiene generated during retero Diels–Alder reaction of the nadimide group.

Cured Nadimide Resins

In DSC traces of cured samples, no exotherm was noticeable. In the TG traces, a one-step decomposition was observed. Detailed TG results of cured resins are given in Table V. Char yields at 800°C (Y_c) increased significantly (10–14%). The resins

were stable up to $440 \pm 20^\circ\text{C}$. P-2B exhibited the highest char yield. Introduction of PMDA or BTDA resulted in higher char yields. TG traces of cured P-1P and P-1B are given in Figure 6(c) and (d).

CONCLUSION

In this paper, performance of the nadimide resins was studied based on two parameters: FMW and backbone structure of the resin. Increase in FMW only marginally affected thermal stability of cured resins. Introduction of 6F resulted in lower char yields of cured resins when compared to PMDA- or BTDA-based resins. On curing at 300°C, phosphorus-containing nadimides synthesized in the present work exhibited char yields ranging from 63 to 71.5%. However, these char yields are lower than those obtained with amide–amine/cardoamine. It may be because curing was done at a higher temperature

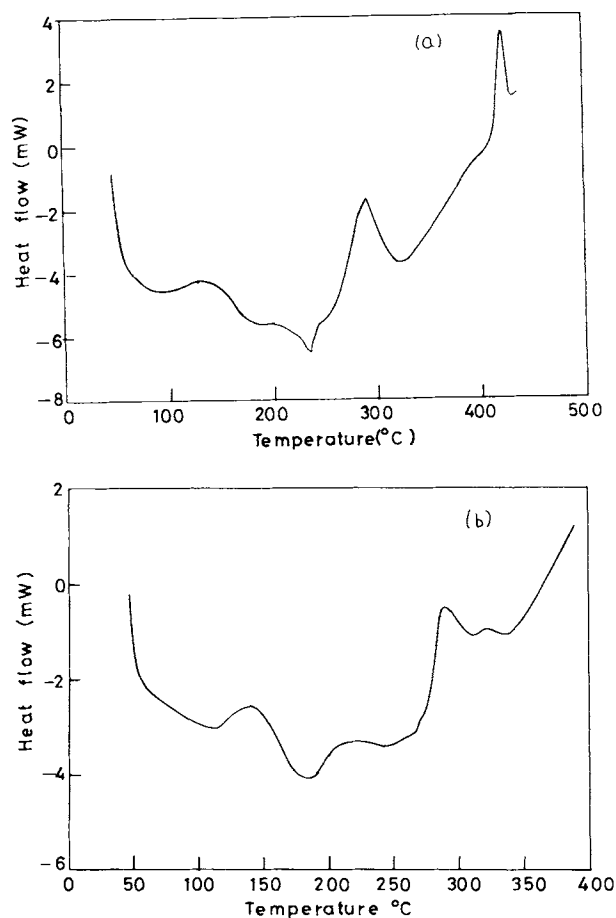


Figure 5 DSC traces of nadimide resins: (a) P-2F; (b) P-1F.

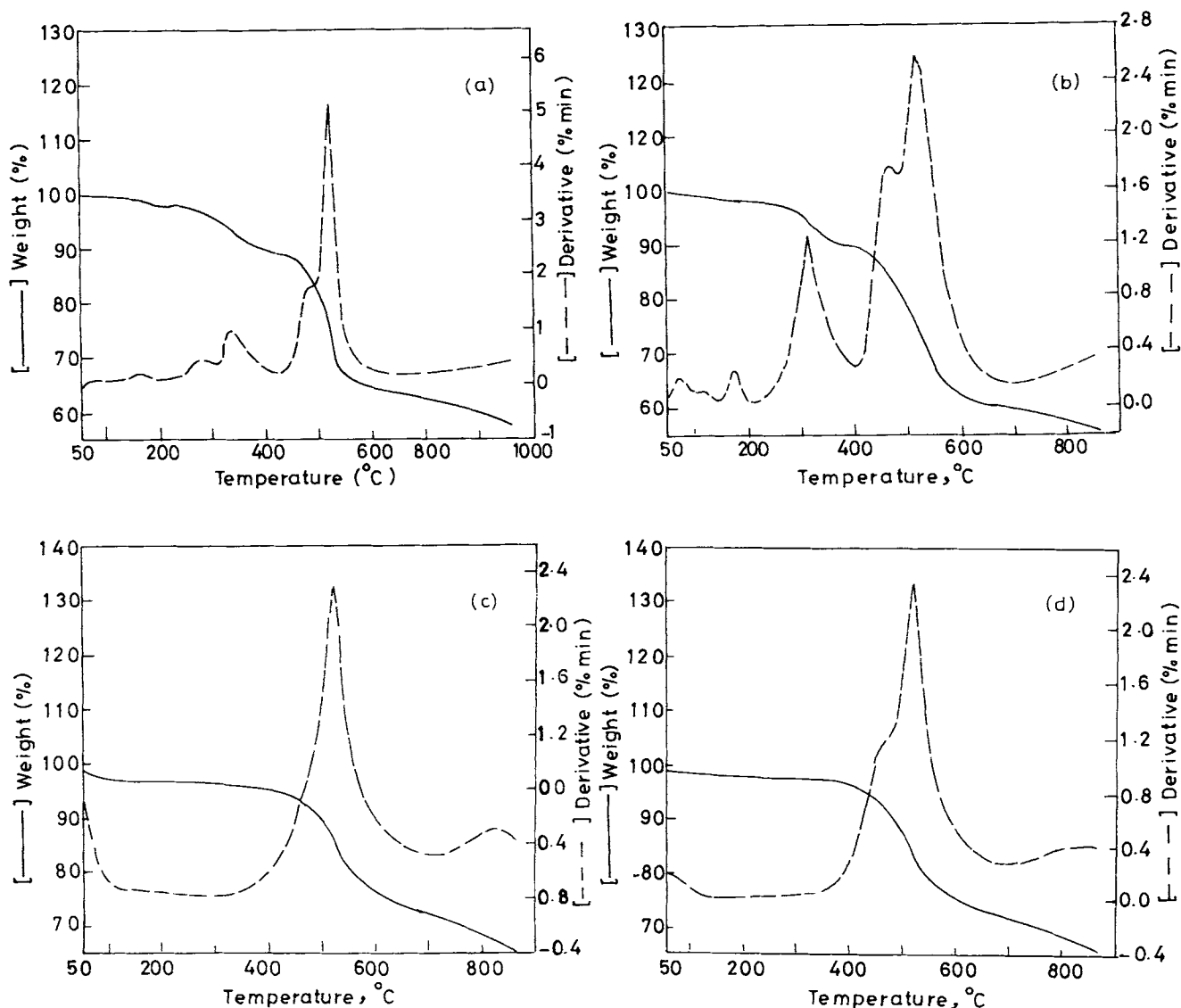


Figure 6 TG traces of nadimide resins: (a) uncured P-1P; (b) uncured P-1B; (c) cured P-1P; (d) cured P-1B.

(i.e., 325°C) in those resin samples. Further studies on the effect of curing temperature on char yields will throw light on this subject.

Table V TG of Cured Nadimide Resins

Sample	T_1 (°C)	T_{max} (°C)	Y_c (%)
P-1P	470	545	70.0
P-1B	425	550	69.5
P-1F	445	540	65.5
P-2P	432	522	68.5
P-2B	458	552	71.5
P-2F	445	556	63.0

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