

Bis(3-aminophenyl)methyl Phosphine Oxide-Based (Methyl) Nadicimide Resins

SARFARAZ ALAM,¹ L. D. KANDPAL,¹ I. K. VARMA²

¹ Defence Materials & Stores Research & Development Establishment, P.O. DMSRDE, G.T. Road, Kanpur-208 013, India

² Centre for Polymer Science & Engineering, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi-110 016, India

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ABSTRACT: Ten nadicimide/methyl nadicimide end-capped oligomeric resins were prepared by reacting endo-5-norbornene-2,3-dicarboxylic acid anhydride (methyl nadic anhydride), pyromellitic dianhydride (PMDA)/3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA)/2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F), and bis(3-aminophenyl)methyl phosphine oxide (BAP) in glacial acetic acid/acetone. Structural characterization of the resins was done by elemental analysis, IR, and ¹H-NMR. Multistep decomposition was observed in the TG scan of uncured resins in a nitrogen atmosphere. Residual weight at 800°C depended on the structure and ranged between 25 and 51%. Isothermal curing of the resins was done at 300°C for 1 h in an air atmosphere. These cured resins were stable to 350 ± 30°C and decomposed in a single step above this temperature. The char yield of the resins increased on curing and was in the range 34–70%. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 861–869, 1997

INTRODUCTION

Endo-5-norbornene-2,3-dicarboximide (nadacimide) end-capped polyimides have been investigated as matrix resins for advanced fiber-reinforced composites. Recent research efforts in this area have been primarily directed toward the development of new and improved resins capable of better elevated temperature performance than the state-of-the-art systems.^{1–4} Incorporation of phosphorus and nitrogen into the polymer backbone generally leads to an improvement in flame resistance and high-temperature performance of polymers.^{5,6} In our earlier articles, we reported the synthesis of maleimide, nadacimide, and acet-

ylene end-capped resins based on tris(3-aminophenyl)phosphine oxide. These resins had excellent thermal stability and flame resistance.^{7–13} The present article deals with the effect of the structure of (methyl) nadacimide resins based on bis(3-aminophenyl)methyl phosphine oxide (BAP) on thermal characteristics.

EXPERIMENTAL

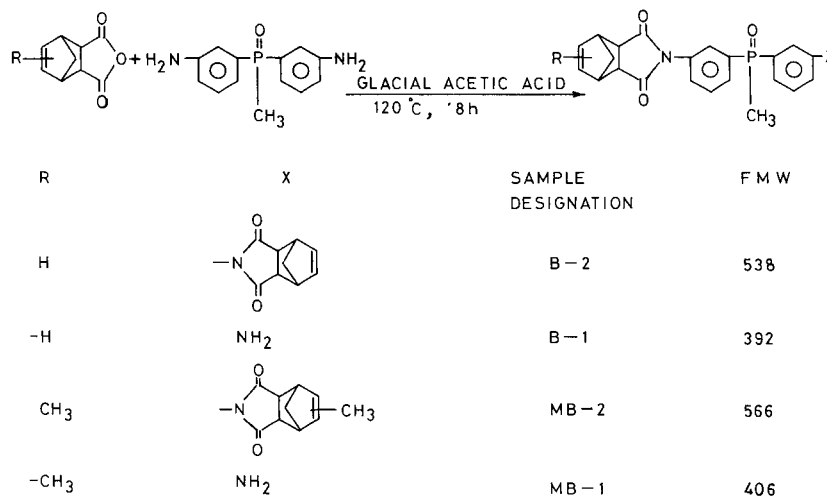
Several (methyl) nadacimide oligomers were prepared by reacting nadic anhydride (NA)/methyl nadic anhydride (MNA) with bis(3-aminophenyl)methyl phosphine oxide (BAP) (Scheme I).

Pyromellitic dianhydride (PMDA)/3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA)/2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F) was used for chain extension. The structure of the oligomers along with

Correspondence to: I. K. Varma.

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Scheme I Reaction scheme for synthesis of (methyl) nadicimides.

sample designation and formula molecular weight (FMW) is given in Scheme II.

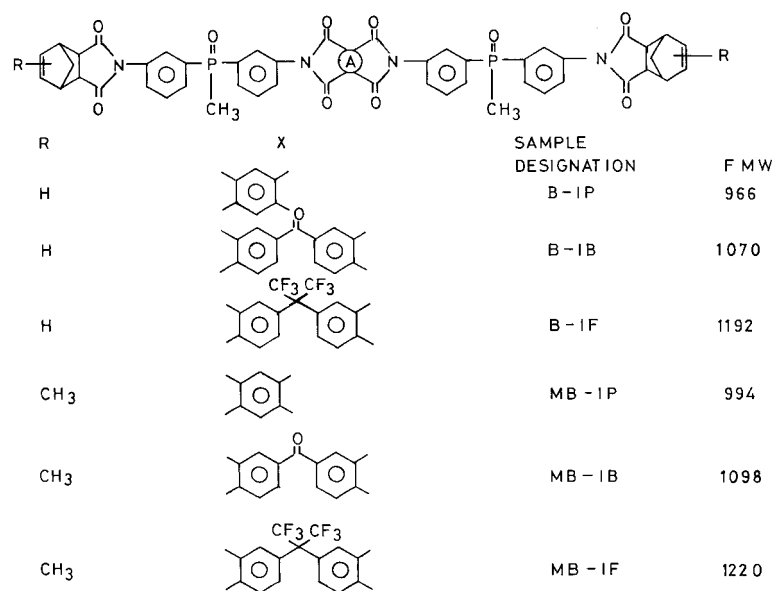
Materials

Glacial acetic acid (BDH) and acetic anhydride (BDH) were distilled at atmospheric pressure before use. Acetone (BDH) was dried over sodium sulfate overnight, refluxed for 1 h, and distilled at atmospheric pressure. NA (E. Merck), BTDA (Kochlight), PMDA (Fluka), and 6F (Hoechst)

were purified by recrystallization from acetic anhydride. MNA was distilled under reduced pressure. Anhydrous sodium acetate (Sarabhai Chemicals) was obtained by fusion. BAP was prepared according to the method reported elsewhere.¹⁰

Synthesis of (Methyl) Nadicimides

Appropriate quantities of NA/MNA and BAP in glacial acetic acid (20 mL) were refluxed for several hours, and the mono- and bisnadicimides were re-



Scheme II Structure of chain-extended (methyl) nadicimides.

Table I Physical Characteristics of (Methyl) Nadicimide Resins

Sample Designation	Yield (%)	Color	Solubility			
			Acetone	CHCl ₃	DMF	DMSO
B-1	97	Brown	++	++	++	++
B-2	96	Gray	++	++	++	++
MB-1	94	Yellow	++	++	++	++
MB-2	93	Dark yellow	++	++	++	++
B-1P	54	Light brown	++	+	++	++
B-1B	61	Brown	--	+	++	++
B-1F	51	Yellow	--	+	++	++
MB-1P	53	Light brown	+	+	++	++
MB-1B	59	Brown	+	+	++	++
MB-1F	49	Dark brown	+	+	++	++

(--) Insoluble; (+) partially soluble; (++) highly soluble.

covered by precipitation. The precipitated resins were washed several times with water and aqueous sodium bicarbonate and dried under a vacuum. Purification of these resins was done by dissolving in chloroform and precipitating in methanol.

Chain Extension with Dianhydrides

Mononadicimide/methyl nadicimide (0.01 mol) was dissolved in acetone (20 mL) at 60°C and 0.005 mol of PMDA/BTDA/6F was added in por-

Table II Results of Elemental Analysis of (Methyl) Nadicimide Resins

Sample Designation	Formula	Elemental Analysis ^a		
		C (%)	H (%)	N (%)
B-1	C ₂₂ H ₂₁ N ₂ O ₃ P	63.4 [67.3]	5.12 [5.35]	7.0 [7.14]
B-2	C ₃₁ H ₂₇ N ₂ O ₅ P	65.8 [69.1]	4.9 [5.01]	5.1 [5.2]
MB-1	C ₂₃ H ₂₃ N ₂ O ₃ P	66.0 [67.9]	5.41 [5.66]	5.9 [6.89]
MB-2	C ₃₃ H ₃₁ N ₂ O ₅ P	65.9 [69.9]	5.39 [5.47]	4.8 [4.94]
B-1P	C ₅₄ H ₄₀ N ₄ O ₁₀ P ₂	66.8 [67.0]	3.9 [4.14]	5.4 [5.70]
B-1B	C ₆₁ H ₄₄ N ₄ O ₁₁ P ₂	66.9 [68.4]	4.00 [4.11]	5.10 [5.2]
B-1F	C ₆₃ H ₄₄ N ₄ O ₁₀ P ₂ F ₆	62.8 [63.4]	3.4 [3.69]	4.3 [4.69]
MB-1P	C ₅₆ H ₄₄ N ₄ O ₁₀ P ₂	64.8 [67.6]	4.3 [4.4]	5.2 [5.63]
MB-1B	C ₆₃ H ₄₈ N ₄ O ₁₁ P ₂	65.2 [68.8]	4.2 [4.3]	5.0 [5.10]
MB-1F	C ₆₅ H ₄₈ N ₄ O ₁₀ P ₂ F ₆	61.2 [63.9]	3.2 [3.9]	4.3 [4.59]

^a Figures in brackets indicate calculated values.

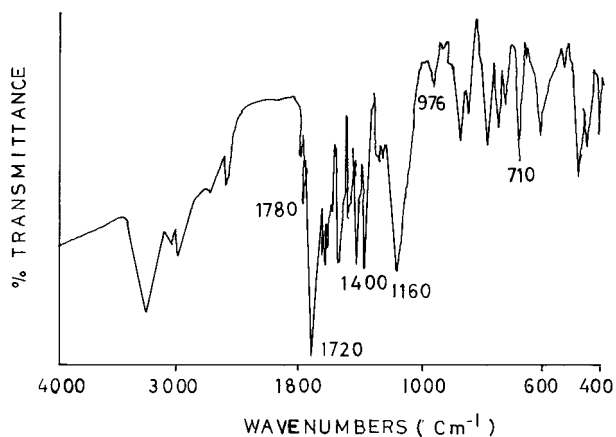
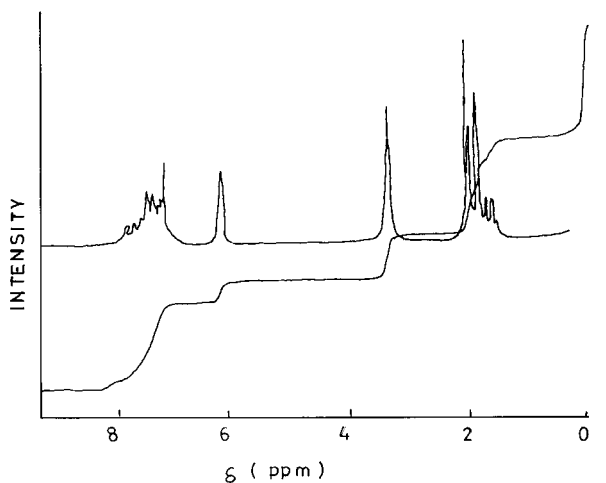
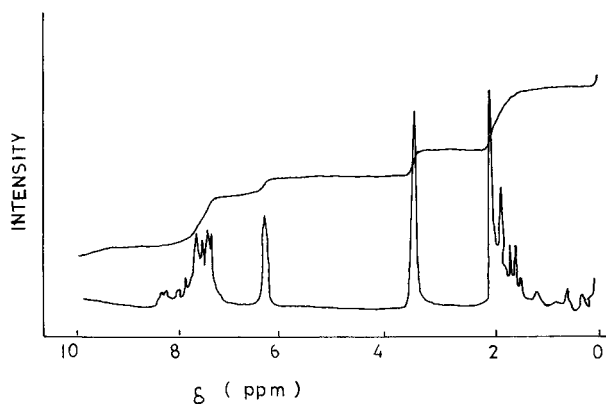


Figure 1 IR spectrum of methyl nadicimide resin MB-1.

tions. The solution was heated for 4 h followed by chemical cyclization of the amic acid to imide, using sodium acetate and acetic anhydride as the cyclodehydrating agent.



(a)



(b)

Figure 2 $^1\text{H-NMR}$ spectra of nadicimide resins: (a) B-1P; (b) B-1.

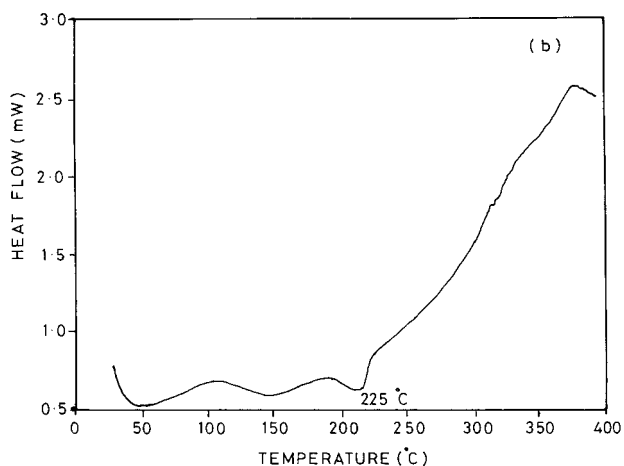
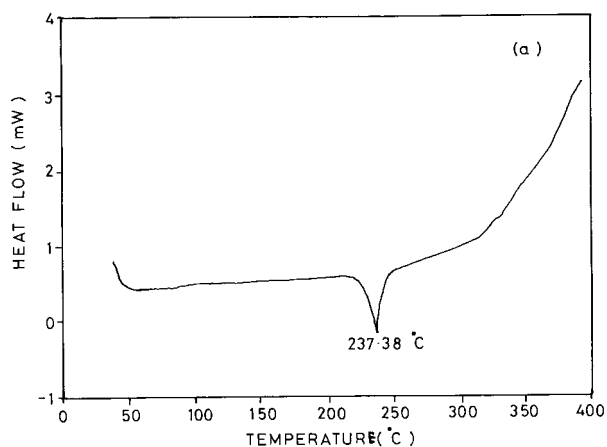


Figure 3 DSC traces of (methyl) nadicimide resins: (a) B-1F; (b) MB-1F.

Characterization

A Nicolet MX-I FTIR spectrophotometer was used for recording the spectra of various (methyl) nadicimides in KBr pellets. $^1\text{H-NMR}$ spectra were recorded on a JEOL-JNM-FX-100 FT NMR spectrophotometer using $\text{DMSO-}d_6$ or CDCl_3 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 10 ± 2 mg was heated from room temperature to 450°C in static air at $10^\circ\text{C}/\text{min}$.

A DuPont 1090 thermal analyzer having a 951 TG module was used for assessing the relative thermal stability of the (methyl) nadicimide resins. Thermogravimetric traces were recorded in a nitrogen atmosphere (flow rate $60\text{ mL}/\text{min}$) at a heating rate of $10^\circ\text{C}/\text{min}$. A sample of 10 ± 2 mg was used. The relative thermal stability of various

resin samples was evaluated by determining (a) the initial decomposition temperature (T_i), (b) the temperature of maximum rate of weight loss (T_{max}), and (c) the char yield at 800°C.

RESULTS AND DISCUSSION

The (methyl) nadicimide oligomers were obtained in powder form having a white to brown color. The physical characteristics of the (methyl) nadicimide oligoimides are given in Table I. The yields were in the range of 49–96%.

The samples B-1, B-2, MB-1, and MB-2 were highly soluble in low boiling solvents. The results of elemental analysis (C, H, N) of (methyl) nadicimide resins (Table II) showed a good correlation between observed and calculated values.

In the FTIR spectra of (methyl) nadicimide resins, characteristic bands due to imide groups appeared at 1782 ± 2 and 1720 cm^{-1} ($\nu_{C=O}$) and

1385 ± 10 and $725 \pm 10 \text{ cm}^{-1}$. The presence of NH_2 groups in the mononadicimide B-1 and MB-1 was indicated by N—H stretching at 3230 cm^{-1} . The absorption bands due to P— C_6H_5 and —P=O were observed at 1430 and 1185 cm^{-1} . In samples containing BTDA, a shoulder at 1630 cm^{-1} due to $\nu_{C=O}$ of ketone was present. The IR spectrum of MB-1 is shown in Figure 1.

The $^1\text{H-NMR}$ spectra of B-1, B-2, MB-1, and MB-2 were recorded in CDCl_3 , whereas $\text{DMSO-}d_6$ was used as a solvent for B-1P, B-1B, B-1F, MB-1P, MB-1B, and MB-1F resins. The aromatic protons appeared at $\delta = 7.2\text{--}8.3$ ppm and olefinic protons at $\delta = 6.14$ ppm [Fig. 2(a) and (b)]. The NH_2 group appeared at $\delta = 2.0$ ppm. Since the spectrum was recorded in $\text{DMSO-}d_6$, 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.

Thermal Behavior of Uncured (Methyl) nadicimide Resins

The TG traces of uncured (methyl) nadicimide resins in nitrogen revealed a multistep decomposition. An initial weight loss of $\sim 2\text{--}5\%$ was observed in the temperature range of $70\text{--}165^\circ\text{C}$ in most of the samples except B-2, where 10% loss was observed. In the DSC scan of the B-2 resin, a broad endothermic transition was observed in this region. The observed weight loss associated with the endothermic transition may be attributed to loss of absorbed moisture. Introduction of phosphorus into the backbone increases hydrophilicity. In B-1P and B-1B resin samples, a melting endotherm was observed at 173 and 176°C , respectively. No such endotherm was observed in the corresponding methyl nadicimides, i.e., MB-1P and MB-1B. A similar weight loss was observed in B-1, MB-1, B-2, and MB-2 resins in this temperature range. The FMW of B-1, MB-1, B-2, and MB-2 resins are comparable. The only difference is the presence of a methyl group in (methyl) nadicimide MB-1 and MB-2 resins. Therefore, it may be concluded that the presence of nonpolar methyl groups in methyl nadicimides did not affect the moisture absorption.

In DSC scans, a less prominent endotherm was observed in B-2 and B-1 resins in the temperature range of $200\text{--}300^\circ\text{C}$. A melting endotherm was observed in B-1F and MB-1F resins with a peak position at 237 and 225°C , respectively [Fig. 3(a)]

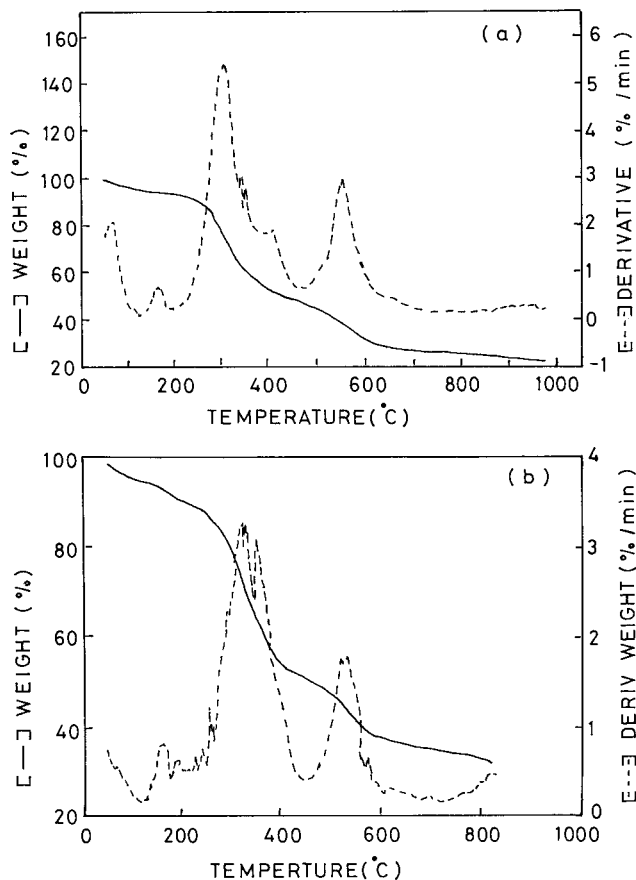


Figure 4 TG traces of uncured (methyl) nadicimide resins: (a) B-1F; (b) MB-1F.

Table III Results of Thermogravimetric Analysis of BAP-Based Uncured (Methyl) Nadicimide Resins

Sample No.	Sample Designation	FMW	T_1 (°C)	T_{\max} (°C)	T_f (°C)	Y_c (%)
1	B-1	392	103	115	139 (4.5)	39.0
			139	196	271 (5)	
			271	296	314 (11)	
			314	413	459 (30)	
2	MB-1	406	60	80	120 (3)	36.5
			170	196	216 (9)	
			274	287	306 (8.5)	
			348	395	495 (25)	
3	B-2	538	100	120	165 (10)	45.0
			220	340	380 (10)	
			420	470	580 (20)	
4	MB-2	566	200	325	339 (9)	51.0
			339	493	550 (27)	
5	B-1B	1070	75	125	150 (2.01)	49.0
			273	296	375 (15.8)	
			375	528	559 (28)	
6	MB-1B	1098	100	150	200 (2)	50.0
			269	309	334 (15.8)	
			503	530	600 (16.4)	
7	B-1P	966	80	98	120 (1.5)	33.0
			164	180	194 (2.5)	
			200	276	317 (14)	
			317	416	486 (43)	
8	MB-1P	994	100	125	160 (5)	29.0
			243	273	292 (14)	
			292	408	530 (42)	
9	B-1F	1192	61	75	100 (3)	25.0
			125	170	200 (4)	
			263	302	450 (48)	
			490	545	583 (16)	
10	MB-1F	1220	100	150	180 (5)	32.0
			263	326	322 (36)	
			504	527	527 (9)	

and (b)]. Only a shift of the base line was observed in this region for rest of the resins; softening of the resin accompanied by endo–exo isomerization may occur in this temperature range. A weight loss of 8.5–48% was observed in the temperature range of 200 ± 40 to $350 \pm 50^\circ\text{C}$. The maximum weight loss was seen in the resins containing 6F anhydride, i.e., B-1F and MB-1F [Fig. 4(a) and (b)]. This high weight loss may be due to a breakdown of the hexafluoroisopropylidene unit in the backbone. A weight loss of 16–43% was observed above 350°C .

In DSC scans, the onset of an exothermic transition was observed above 250°C . This may be due to the curing of (methyl) nadicimides via the retro Diels Alder (RDA) reaction.

Complete degradation of the nadicimide/methyl nadicimide occurs in the temperature range of 400 ± 50 to $600 \pm 50^\circ\text{C}$ (~ 15 –50% weight loss). A char yield of 25–51% was observed at 800°C in a nitrogen atmosphere. This is due to a solid-state condensation reaction leading to the formation of aromatic char residue. The results of the thermogravimetric analysis of BAP-

Table IV Weight Loss During Isothermal Curing of (Methyl) Nadicimides (Time = 1 h)

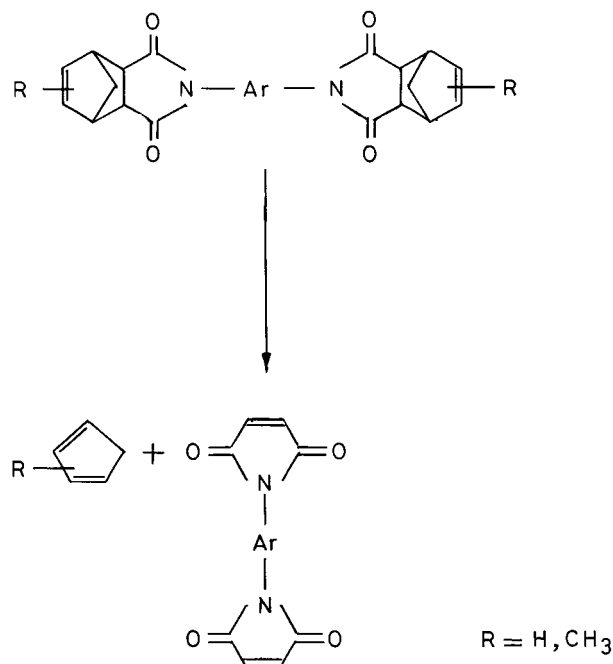
Sample No.	Resin Designation	Weight Loss (%)	
		250°C	300°C
1	B-1	3.7	10.0
2	MB-1	3.6	9.8
3	B-2	2.9	7.2
4	MB-2	2.8	6.4
5	B-1P	5.0	6.0
6	MB-1P	4.9	5.6
7	B-1B	4.0	5.6
8	MB-1B	4.9	6.2
9	B-1F	4.0	5.6
10	MB-1F	4.1	5.0

based (methyl) nadicimide resins are summarized in Table III. The resins containing the free amino groups B-1 and MB-1 were less stable than those which did not have such groups (resin B-2 and MB-2). Char yields of the (methyl) nadicimides containing BTDA were higher than the corresponding (methyl) nadicimides containing PMDA and 6F units. The presence of the methyl group in (methyl) nadicimide did not affect the char yield in a systematic manner.

Curing of Nadicimide Resins

Isothermal curing of the nadicimide resin was done at 250°C for 1 h in an air atmosphere. These resins readily dissolved in DMAc, indicating thereby only partial curing. The TG traces of these resins were also similar to those corresponding uncured resins. Therefore, the resins were further heated at 300°C for 1 h. Resins insoluble in DMAc were obtained by such a treatment. Heating at this temperature resulted in a 5–10% weight loss (Table IV). The cured resins have been designated by appending a prefix C to the letter designation of the resin.

nation of the resin (Table V). A close examination of the results at 300°C indicate that the weight loss is less in methyl nadicimides compared to the corresponding nadicimides. The weight loss during isothermal curing of nadicimides may be attributed to the loss of (methyl) cyclopentadiene formed as a result of the RDA reaction according to the following scheme:



Copolymerization of (methyl) cyclopentadiene with bismaleimide is believed to be the mechanism of the crosslinking reaction. The presence of an electron donor methyl group in methyl cyclopentadiene would facilitate such a copolymerization. Therefore, more of methyl cyclopentadiene would be trapped whereas cyclopentadiene evolution may be higher, thus accounting for higher weight loss in nadicimides:

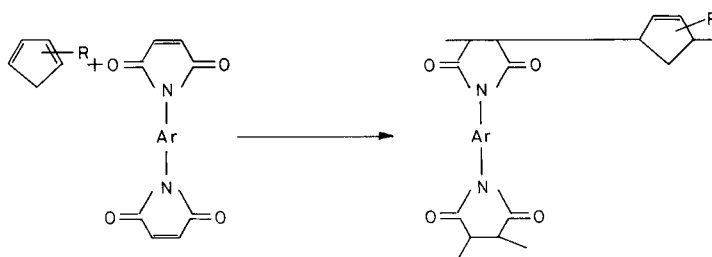


Table V TG Results of Cured (Methyl) Nadicimide Resins

Sample No.	Resin Designation	T_1 (°C)	T_{max} (°C)	T_f (°C)	Y_c (%)
1	CB-1	349	410	565	36.0
2	CMB-1	360	405, 506	570	45.0
3	CB-2	433	510	550	50.0
4	CMB-2	318	380, 502	540	57.0
5	CB-1P	337	410, 570	580	50.0
6	CMB-1P	270	410	595	34.0
7	CB-1B	395	410, 512	600	62.0
8	CMB-1B	390	590	600	70.0
9	CB-1F	240	365, 585	650	35.5
10	CMB-1F	290	390, 587	600	45.0

Thermal Behavior of Cured Resins

In DSC traces of cured samples, no exotherm was noticeable. In the TG traces, a one or two-step decomposition was observed. The resins were stable to $\sim 350 \pm 30^\circ\text{C}$ except resins CMB-1P and CB-1F, which started losing weight below 300°C

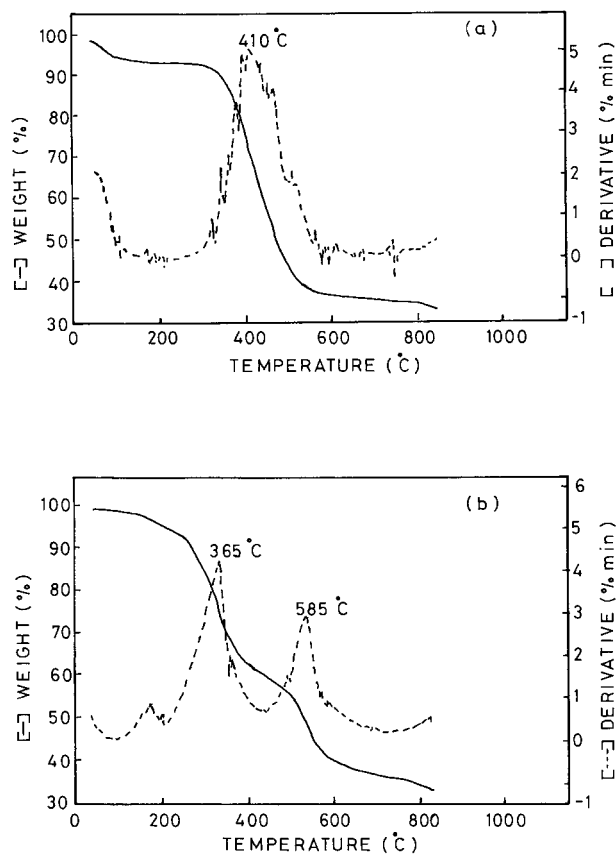


Figure 5 TG traces of cured (methyl) nadicimide resins: (a) CB-1F; (b) CMB-1P.

[Fig. 5(a) and (b)]. Char yield at 800°C (Y_c) increased significantly on curing. The TG results of cured resins are summarized in Table V. The char yields of methyl nadicimides were higher than those of the corresponding nadicimides.

One would have expected a lower char yield in methyl nadicimides due to the presence of a labile methyl group as a substituent. The observations are contrary to the expectations and may be due to participation of a methyl group in the condensation reaction with $\text{C}=\text{O}$ groups of nadicimides resin.

Isothermal Aging of Cured (Methyl) Nadicimides

The isothermal aging of cured (methyl) nadicimide resins was carried out at 340°C in a muffle furnace. The % weight loss after 150 and 300 h of

Table VI Weight Loss During Isothermal Aging at 340°C of Cured (Methyl) Nadicimides

Sample No.	Sample Designation	Weight Loss After	
		150 h	300 h
1	CB-1	47.0	48.5
2	CMB-1	29.2	31.2
3	CB-2	39.6	45.2
4	CMB-2	28.1	31.0
5	CB-1P	52.6	65.7
6	CMB-1P	50.0	55.1
7	CB-1B	22.8	31.5
8	CMB-1B	21.4	28.5
9	CB-1F	42.3	50.0
10	CMB-1F	46.6	49.3

aging is recorded in Table VI. Methyl nadicimides (MB-1, MB-2, MB-1P, MB-1B, and MB-1F) showed a lower weight loss on isothermal aging compared to the corresponding nadicimide resins (B-1, B-2, B-1P, B-1B, B-1F).

CONCLUSION

The volatile evolution during isothermal curing in the methyl nadicimide investigated in these studies was found to be lower than in the corresponding nadicimide resins. Earlier studies with maleimide endcapped resins have indicated that a methyl group at the olefinic bond affects the curing characteristics of the resins. It may be attributed to the electron-donor effect of a methyl group.^{14,15}

The char yield of the cured resins was also higher in the methyl nadicimides, indicating thereby the participation of a methyl group in the crosslinking reactions.

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