

Methyl Nadimide Resins: Synthesis and Characterization*

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SYNOPSIS

This article describes the synthesis and characterization of several methyl nadimides end-capped resins based on tris(3-aminophenyl)phosphine oxide. These resins were prepared by reacting methyl-5-norbornene 2,3-dicarboxylic anhydride (methyl nadic anhydride) (MNA), 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, IR, and ¹H-NMR. Thermal characterization of uncured resins using DSC and TGA techniques revealed an exothermic transition accompanied by a weight loss in the temperature range of 200–350°C. Residual weight at 800°C in nitrogen was found to be 47–55%. Isothermal curing of the resins was done at 340°C for 1 h in an air atmosphere. The cured resins were stable up to 400 ± 20°C.

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INTRODUCTION

Thermoset addition polyimides,^{1–3} such as maleimide and nadimide end-capped resins, have been commercially exploited in the past as high-temperature-resistant matrices for advanced composites. PMR-15, which is an alcoholic solution of the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid, the dimethyl ester of benzophenone tetracarboxylic acid, and 4,4'-diaminodiphenyl methane has been extensively investigated in the past. The effect of structural variation on properties of these resins has been reported.

One of the problems associated with nadimide end-capped resin is the high temperature required for curing. Earlier studies with substituted maleimides indicated that the presence of a methyl sub-

stituent (e.g., citraconimide) reduces the curing temperature.^{4,5} However, the presence of alkyl groups reduces the thermal decomposition temperature, whereas incorporation of phosphorus in the polymer backbone leads to improved flame resistance in thermosetting polyimides.^{6–13} It was, therefore, considered of interest to study the effect of such substituents in nadimides on thermal behavior. The purpose of the present investigation was to study the effect of the structure of methyl nadimides based on tris(3-aminophenyl)phosphine oxide on thermal characteristics.

EXPERIMENTAL

Twelve methyl nadimide oligomers were prepared by reacting methyl nadic anhydride (MNA), tris(3-aminophenyl)phosphine oxide (TAP), and 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA)/pyromellitic dianhydride (PMDA)/2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F). The structure of these resins can be depicted as

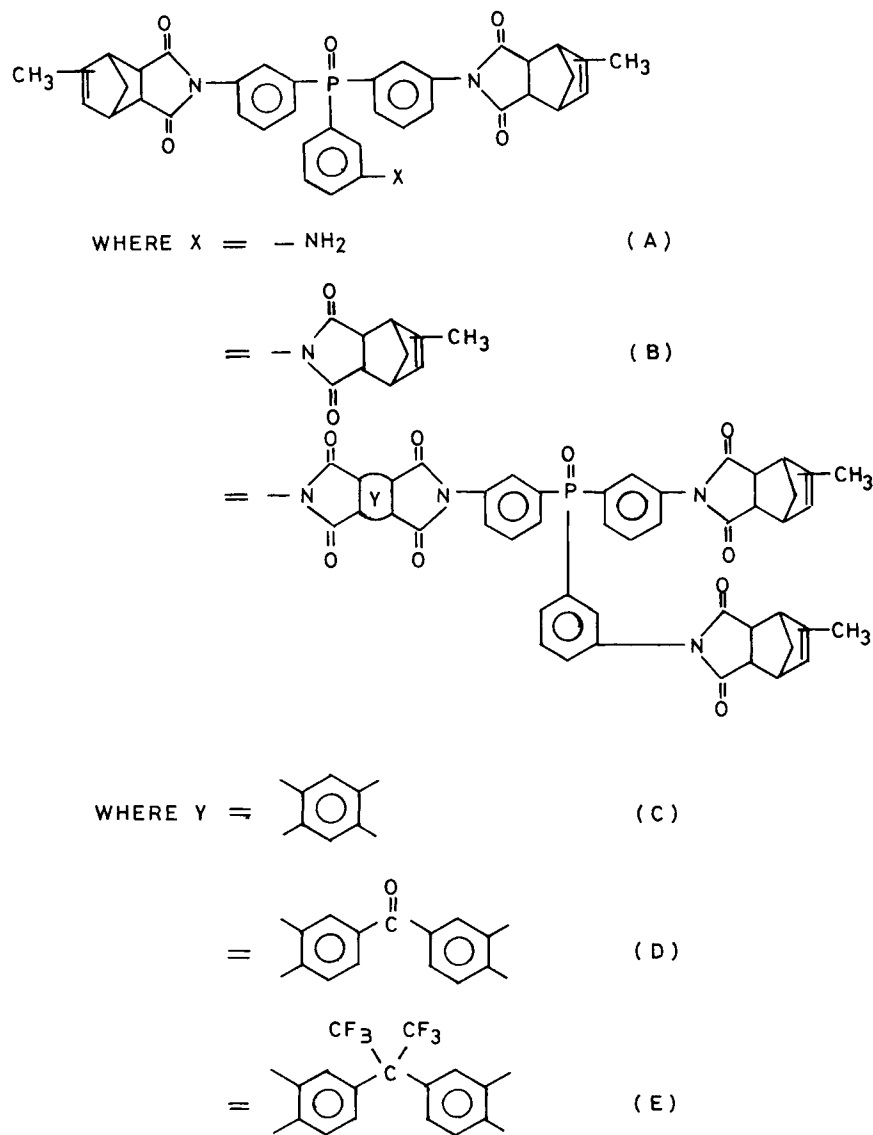
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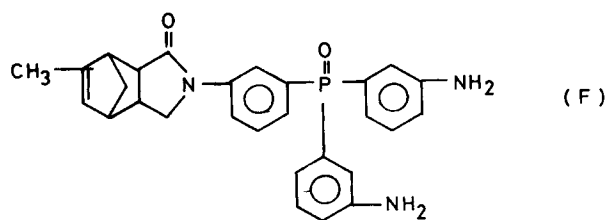
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Scheme 1

Resins with higher FMW (formula molecular weight) were prepared by reacting the methyl nadimide F with stoichiometric amounts of BTDA/PMDA/6F. The molar ratio of various reactants and resin designations are given in Table I:



Scheme 2

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 atmospheric pressure. MNA (Aldrich) was distilled under reduced pressure. BTDA (Kochlight), 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 (Aldrich) by nitration and subsequent reduction according to the procedure reported earlier.¹⁴

Table I Synthesis of Methyl Nadimides and Details of Reaction Conditions

Sample No.	Quantity of Reagents (Moles)					Resin Designation	FMW
	MNA	TAP	BTDA	PMDA	6F		
1	0.02	0.01	—	—	—	A	643
2	0.03	0.01	—	—	—	B	803
3	0.04	0.02	—	0.01	—	C	1454
4	0.04	0.02	0.01	—	—	D	1558
5	0.04	0.02	—	—	0.01	E	1680
6	0.01	0.01	—	—	—	F	458
7	0.01	0.01	—	0.0075	—	G	2478
8	0.01	0.01	0.0075	—	—	H	2790
9	0.01	0.01	—	—	0.0075	I	3156
10	0.01	0.01	0.005	—	—	J	1252
11	0.01	0.01	—	—	0.005	K	1390
12	0.01	0.01	—	0.005	—	L	1132

Preparation of A–F Resins

Appropriate quantities of MNA (0.01/0.02/0.03 mol) and TAP (0.01 mol) in glacial acetic acid (20 mL) were refluxed for 12 h at 120°C and the imides were recovered by precipitation in ice water. The precipitated imides were washed several times with water and aqueous sodium bicarbonate and, after drying, were purified using chloroform as the solvent.

Reaction A–F with Dianhydrides

The amino end-capped mono- and bismethyl nadimides (0.01/0.02 mol) were refluxed in acetone with PMDA/BTDA/6F (0.0075/0.005 mol) for 4 h at 55–60°C. The resulting amic acid was chemically cyclized by the addition of sodium acetate and acetic anhydride as the 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. The purification was done by using CHCl_3 or DMSO as the solvent and reprecipitation in petroleum ether or water, respectively.

CHARACTERIZATION

A Nicolet MX-I FTIR spectrophotometer was used for recording IR spectra in KBr pellets. $^1\text{H-NMR}$ spectra were recorded on a Jeol-JNM-FX-100FT NMR spectrophotometer using $\text{DMSO-}d_6$ as the solvent and tetramethylsilane as an internal standard. A Perkin-Elmer 240-C elemental analyzer was

used for determining the C, H, and N content of the resins.

A DuPont 9900 thermal analyzer having a 910 DSC module was used for studying the curing behavior in static air atmosphere. A sample size of 10 ± 2 mg and a heating rate of 10°C/min was used in scanning.

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 a nitrogen atmosphere (flow rate 60 mL/min) at a heating rate of 10°C/min. A sample size of 10 ± 2 mg was used.

RESULTS AND DISCUSSION

The methyl nadimide oligomers were obtained in powder form having a white to brown color and yield ranging from 39 to 96%. Some of the physical characteristics of the oligomers are shown in Table II.

Only samples **A**, **B**, and **C** were soluble in low boiling solvents. The results of elemental analysis (C, H, N) of various methyl nadimide resins are given in Table III. A good correlation between observed and calculated values was observed (Table III).

In the FTIR spectra of nadimide resins, characteristic bands due to imide groups appeared at 1784 ± 10 and 1720 cm^{-1} ($\nu \text{ C=O}$), 1375 ± 10 , 1128 ± 10 , and $720 \pm 15 \text{ cm}^{-1}$. The presence of NH_2 groups in **A** and **F** was indicated by N—H stretching vibration at 3230 cm^{-1} (Fig. 1). In samples containing BTDA, a broad absorption band was ob-

Table II Physical Characteristics of Methyl Nadimides Resins

Sample Designation	Color	% Yield	Acetone	Solubility		
				CHCl ₃	DMF	DMSO
A	Light brown	95	++	++	++	++
B	White	96	++	++	++	++
C	Light brown	43	+	+	++	++
D	Yellow	59	--	--	++	++
E	Light yellow	41	+	+	++	++
F	Brown	93	++	++	++	++
G	Light brown	39	--	--	++	++
H	Yellow	59	--	--	++	++
I	Light yellow	41	--	--	++	++
J	Yellow	56	--	--	++	++
K	Light yellow	40	--	--	++	++
L	Brown	49	--	--	++	++

--, Insoluble; ++, highly soluble; +, partially soluble.

served at 1700 cm^{-1} with a shoulder at 1668 cm^{-1} , which is due to carbonyl stretching of the benzophenone group. The absorption bands due to P—C₆H₅ and —P— groups were observed at 1432 and

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1180 cm^{-1} , respectively.

The ¹H-NMR spectra of methyl nadimide resins were recorded in DMSO-*d*₆/CDCl₃ solvent. The aromatic protons appeared as a multiplet at δ 7.2–8.3 ppm and the olefinic protons appeared at δ 5.9 ppm (Fig. 2). The methyl and methylene protons of nadimide bridge was observed at δ 1.2–2.0 ppm (broad multiplet); the remaining aliphatic protons were

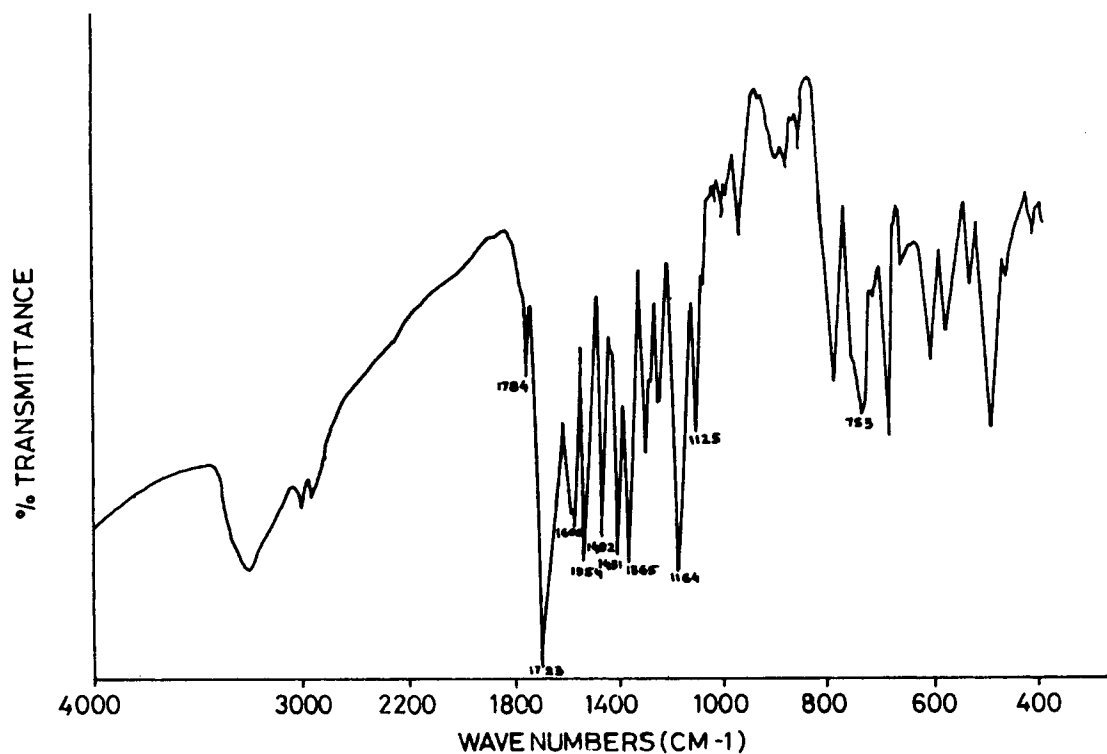
**Figure 1** IR spectrum of methyl nadimide resin A.

Table III Results of Elemental Analysis of Methyl Nadimide Resins

Sample Designation	Formula	Elemental Analysis ^a		
		C (%)	H (%)	N (%)
A	C ₃₈ H ₃₄ N ₃ O ₅ P	(70.91)	(5.28)	(6.53)
		70.24	5.46	6.84
B	C ₄₈ H ₄₂ N ₃ O ₇ P	(71.73)	(5.23)	(5.23)
		70.17	5.48	5.22
C	C ₈₅ H ₆₄ N ₆ O ₄ P ₂	(70.15)	(4.40)	(5.77)
		69.92	4.32	5.98
D	C ₉₂ H ₆₈ N ₆ O ₁₅ P ₂	(70.86)	(4.36)	(5.39)
		70.15	4.62	5.68
E	C ₉₄ H ₆₈ N ₆ O ₁₄ P ₂ F ₆	(67.14)	(4.04)	(5.00)
		66.82	3.92	4.87
F	C ₂₆ H ₂₆ N ₃ O ₃ P	(67.97)	(5.66)	(9.15)
		67.14	5.35	8.83
G	C ₁₄₂ H ₉₈ N ₁₂ O ₂₄ P ₄	(68.74)	(3.95)	(6.77)
		65.92	3.82	7.21
H	C ₁₆₃ H ₁₁₀ N ₁₂ O ₂₇ P ₄	(70.10)	(3.94)	(6.02)
		69.74	4.16	6.39
I	C ₁₆₉ H ₁₁₀ N ₁₂ O ₂₄ P ₄ F ₁₈	(64.25)	(3.48)	(5.32)
		63.88	3.87	5.76
J	C ₇₃ H ₅₄ N ₆ O ₁₁ P ₂	(69.96)	(4.31)	(6.70)
		69.08	4.13	6.26
K	C ₇₅ H ₅₄ N ₆ O ₁₁ P ₂ F ₆	(64.74)	(3.88)	(6.04)
		62.89	4.14	6.44

^a Figures in parentheses indicate calculated values.

seen at δ 3.4–2.8 ppm (multiplet). In cases where free amino groups were present, NH protons were seen at δ 2.08 ppm. Since the spectrum was recorded

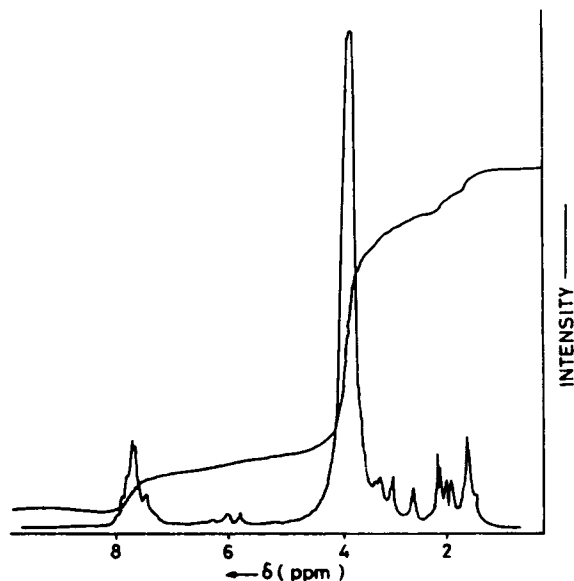


Figure 2 ¹H-NMR spectrum of methyl nadimide resin E in DMSO-*d*₆.

in DMSO-*d*₆, integration in the aliphatic region was slightly complicated because of the residual protons of solvent DMSO-*d*₆ and moisture in the solvent. Therefore, the ratio of total aromatic to olefinic protons was used for the structural characterization.

Thermal Behavior of Uncured Resins

The complimentary techniques DSC and TGA were used to study the thermal behavior of uncured resins. Such studies are useful in understanding the type of reactions that may take place on heating.

In the DSC scans of most resins, an endotherm was observed in the temperature range of 100–150°C (Fig. 3). A weight loss of approximately 4% was indicated in TG traces during this transition. This can be attributed to the desorption of moisture. The hydrophilicity of resins is increased by the presence of phosphorus in the backbone. In resin F, which contained two free amino groups, weight loss in this temperature range was higher (~ 10%). A second endotherm due to melting was observed in resin samples B, E, I, and K. However, in other resin samples, an exothermic transition was observed in the temperature range of 220–400°C. From the exo-

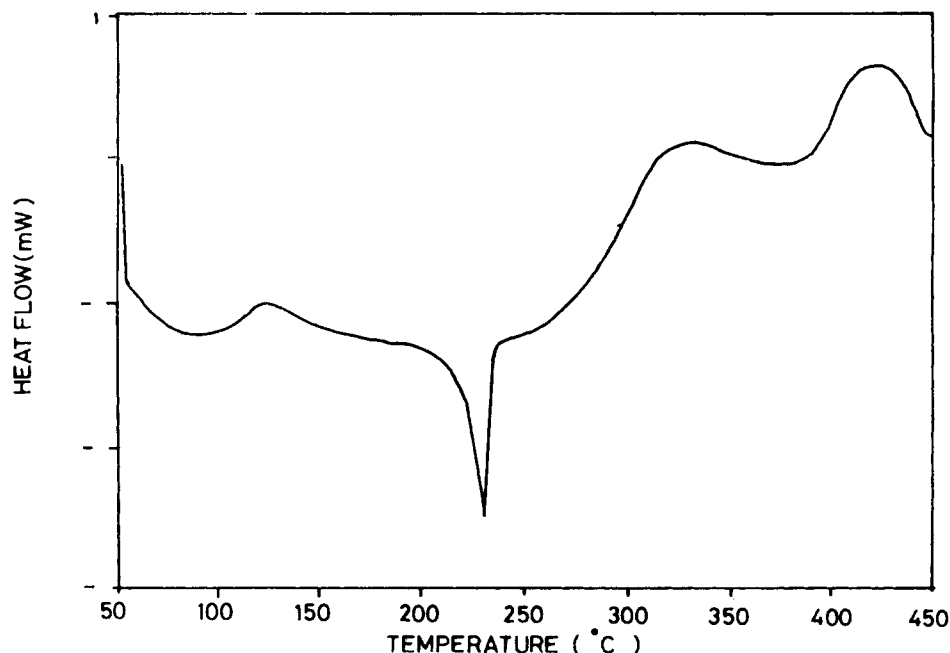


Figure 3 DSC trace of methyl nadimide resin I.

thermic transition, the onset temperature of curing (T_i), the temperature of exothermic peak position (T_{exo}), and temperature of the completion of curing (T_f) were noted and the results are summarized in Table IV. An approximate 5–12% weight loss was observed in the temperature range of 220–400°C. The thermal transition of methyl nadimides can be summarized as (1) endo–exo isomerization; (2) a

retro Diels–Alder reaction leading to formation of maleimide and methyl cyclopentadiene; (3) polymerization of methyl nadimides; and (4) polymerization of *in-situ*-generated maleimide and methyl cyclopentadiene.¹⁵

The transition in the temperature range of 220–400°C may be attributed to the curing of the methyl nadimides via a retro Diels–Alder reaction in which

Table IV Thermal Characterization of Uncured Resins

Sample Designation	Temperature of Exothermic Transition (°C)			Wt. Loss in Temperature Range of 250–400°C ^a (%)	Y_c^b (%)
	T_i	T_{exo}	T_f		
A	279	362	421	11	—
B	223	253	300	5	47
C	283	289	320	8	—
D	282	309	370	11	51.5
E	285	325	380	10	49
F	279	347	410	12	46.5
G	—	337	370	5	55.5
H	260	324	370	12	52.5
I	265	319	375	—	54.5
J	—	—	—	7	44
K	272	280	310	—	48.5
L	—	—	—	—	52.5

^a From TG analysis.

^b Char yield at 800°C.

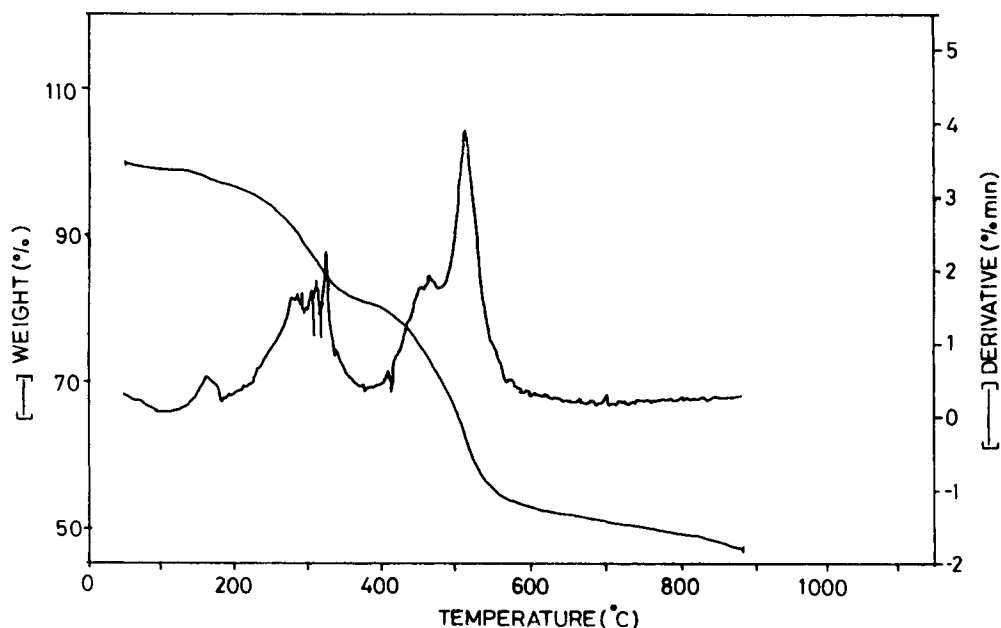


Figure 4 TG trace of uncured methyl nadimide resin E.

in situ formation of methyl cyclopentadiene and maleimide units takes place initially, followed by polymerization. Some of the methyl cyclopentadiene might have escaped as volatile, leading to weight loss during the exothermic transitions. A decrease of almost 50°C in the onset temperature of curing and exothermic peak position is observed in methyl nadimides compared with those of nadimide resins.⁹

In the TG traces, further weight loss (20–38%) was observed in the temperature range of 410–650°C, which is due to the breakdown of the polymer backbone (Fig. 4). Char yield depended on the backbone structure and was in the range 44–56%.

Curing of Methyl Nadimide Resins

Isothermal curing of the methyl nadimides was done at 300°C for 1 h in an air atmosphere. However, these thermally treated resins were partially soluble in DMSO, indicating, thereby, the presence of uncross-linked material. Therefore, the samples were further heated at 340°C for 1 h. Resins insoluble in DMSO were obtained by such a treatment. Isothermal curing at 300/340°C was accompanied by weight loss (< 10%), which may be due to the evolution of methyl cyclopentadiene generated during the retro Diels–Alder reaction.

In DSC traces of these samples, no exotherm was noticeable. In the TG traces, a single-step decomposition was observed in C, D, E, and A (Fig. 5) above 400°C, whereas in other samples, a weight

loss of 3–14% was observed in the temperature range of 250–400°C. From the TG trace, the extrapolated onset temperature of weight loss (T_1), the temperature of maximum rate of weight loss (T_{max}), and char yield at 800 and 900°C were noted. The results of these studies are given in Table V.

The char yield of cured resins at 800°C (Y_c) was higher (7–18%) than that of the uncured resins. Thus, the char yield of uncured resins was 44–55%, whereas that of cured resins was 53–69.5%.

Char yield depended on the backbone structure. Resins G, H, and I, which were based on PMDA, BTDA, and 6F, respectively, showed the following order of char yield: $G < H < I$; a similar trend was observed in resins J, K, and L and resins D and E (Table V). Therefore, it can be concluded that resins based on PMDA are the most stable, followed by resins based on BTDA and 6F. Resins containing free amino groups (F, J, K, and L) had lower char yields.

An increase in FMW of the resin with a similar backbone structure resulted in a decrease in char yield. Thus, resin D (FMW 1558) had a char yield of 69.5%, whereas resin H (FMW 2790) had a char yield of 59%. Similarly, in resin E (FMW 1680) and I (FMW 3156), char yields were 57 and 53.5%, respectively.

Isothermal aging of cured methyl nadimide resins was carried out at 340°C in a muffle furnace. The % weight loss after 150 and 300 h of aging is recorded in Table V. The methyl nadimide resins containing

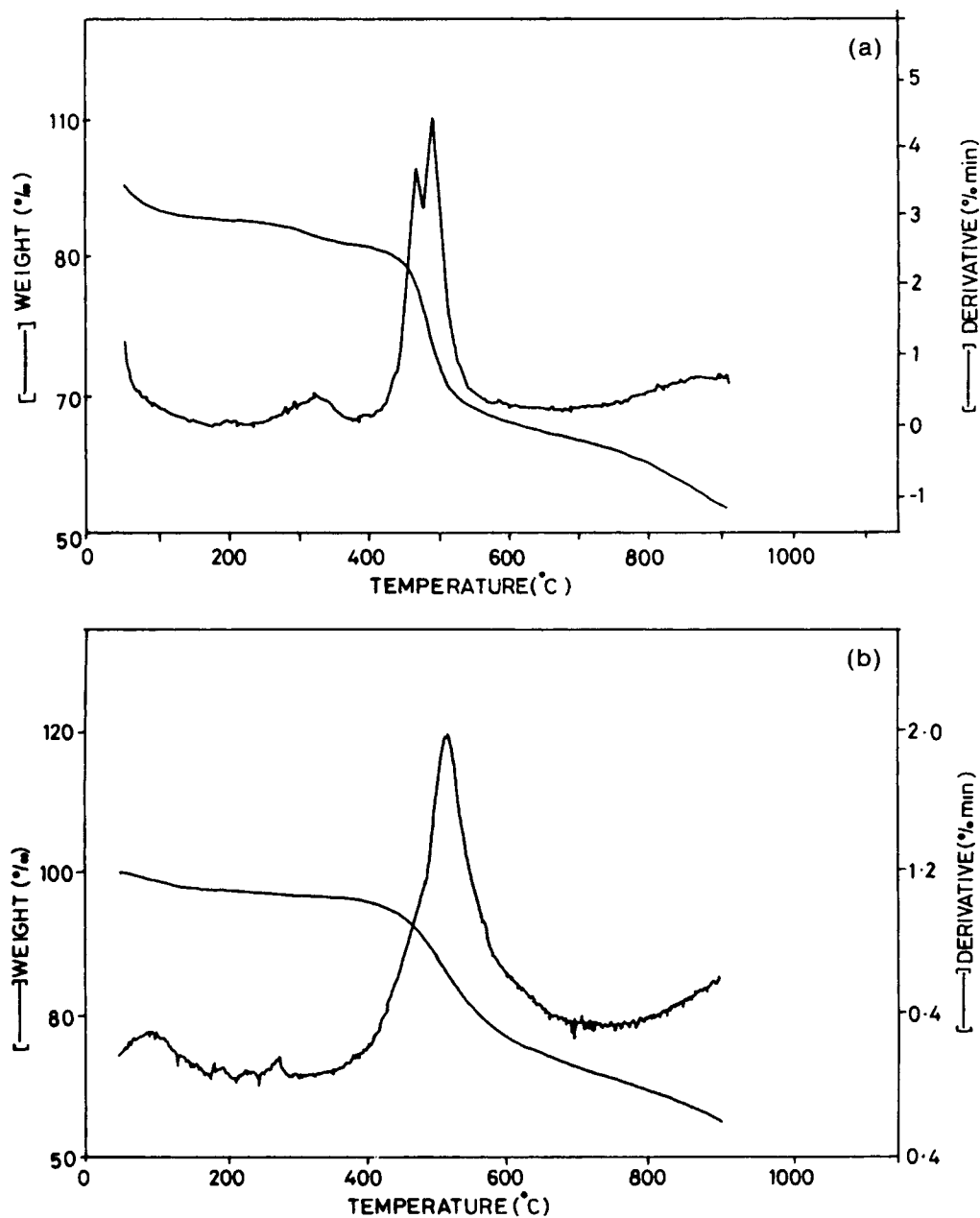


Figure 5 TG traces of cured methyl nadimide resin: (a) B; (b) D.

6F in the backbone showed a minimum weight loss as compared to BTDA/PMDA-containing resins, thereby showing high thermooxidative stability.

CONCLUSIONS

On the basis of the resins studied, the following conclusions can be drawn:

1. Methyl substitution on an olefinic bond of nadimide reduced the onset temperature of curing and the exothermic peak position.
2. Increase in the FMW of the resins resulted in decrease in the char yield.
3. Introduction of 6F in the backbone resulted in lower char yield of the cured resins when compared to BTDA or PMDA.
4. Methyl nadimide resins having 6F in the

Table V Thermal Behavior of Nadimide Resins Cured at 300°C for 1 h and 340°C for 1 h

Sample Designation	T_i (°C)	T_{max} (°C)	Y_c (%)		% Wt. Loss at 340°C for 150/300 h
			800°C	900°C	
B	455	490	60.0	54.0	32.8/39.0
D	460	509	69.5	65.0	39.8/52.0
E	473	523	57.0	49.0	41.4/50.0
F	420	484	54.5	44.0	52.4/65.0
G	420	516	64.5	60.0	52.6/63.0
H	485	550	59.0	50.0	46.7/59.0
I	507	548	53.5	49.0	33.3/43.0
J	460	542	60.0	56.0	63.3/70.0
K	500	548	55.0	46.0	37.4/48.8
L	400	501	61.0	57.0	45.1/52.2

backbone exhibited higher thermooxidative stability at 340°C than that of BTDA/PMDA-containing methyl nadimide resins.

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