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PHOSPHORUS-CONTAINING NADIMIDE RESINS: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

A series of phosphorus-containing nadimide-endcapped resins was prepared by reacting *endo*-5-norbornene-2,3-dicarboxylic acid anhydride (nadic anhydride), 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride, and tris(3-aminophenyl)phosphine oxide in glacial acetic acid/dimethylformamide. Structural characterization of resins was done by elemental analysis, FTIR, and ^{1}H NMR. In DSC traces of these resins, an exothermic transition associated with crosslinking was observed above 280°C. Thermogravimetric studies revealed a multistep decomposition reaction. Residual weight at 800°C in nitrogen was found to depend on the backbone structure and ranged from 42 to 60%.

INTRODUCTION

Imide resins endcapped with *endo*-5-norbornene-2,3-dicarboximide (nadimide) have been investigated since the early 1970s as matrix resins for advanced fiber-reinforced composites [1], resulting in the commercial development of PMR-15 resin [2], which is being used in aerospace components [3]. Attempts have been made to improve the thermooxidative stability of PMR-15 by replac-

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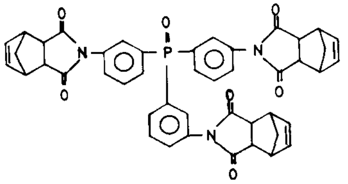
ing the aromatic diamine (i.e., 4,4′-diaminodiphenylmethane) with 4,4′-oxydianiline and 1,1-bis(4-aminophenyl)-2,2,2-trifluoroethane [4].

Incorporation of phosphorus and nitrogen into the backbone of synthetic polymers generally leads to an improvement in flame resistance [5]. We have described several phosphorus-containing bisimide resins with excellent thermal stability and outstanding flame resistance [6-9]. Thermal polymerization of nadimido [10] derivatives of 1-[(dialkoxyphosphinyl)methyl]-2,4-diaminobenzene and its 2,6 isomer has also been reported to give a cross-linked resin with a high limiting oxygen index.

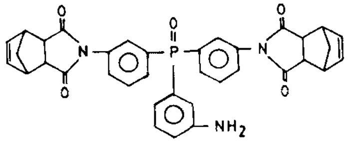
In this paper we report the synthesis and characterization of norbornenyl-endcapped polyimide resins containing phosphorus in the backbone. These preformed imide monomers were prepared by reacting nadic anhydride (NA), 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (BTDA), and tris(3-aminophenyl)phosphine oxide (TAP) in glacial acid. Five resin samples with the following structures were prepared:

I



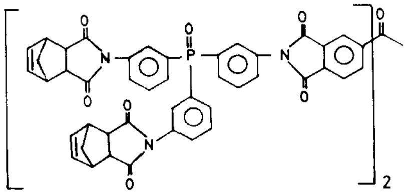
$((NA)_3 \cdot TAP)$

II



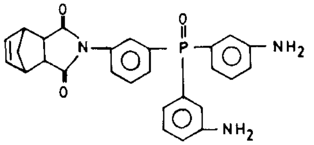
$((NA)_2 \cdot TAPNH_2)$

III



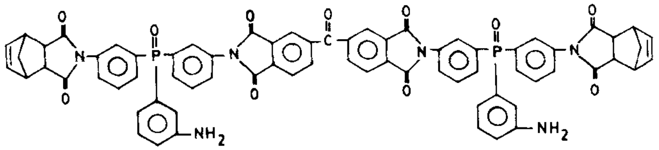
$([(NA)_2\ TAP]_2 \cdot BTDA)$

IV



$((NA)\ TAP\ (NH_2)_2)$

V



([(NA)TAPNH$_2$]$_2$ BTDA)

EXPERIMENTAL

Materials

Dimethylformamide (E. Merck) (DMF) was dried over P_2O_5 and then distilled under reduced pressure. Glacial acetic acid (BDH) and acetic anhydride (BDH) were distilled at normal pressure before use. BTDA (Koch Light) was purified by recrystallization from acetic anhydride and dried under vacuum for 24 h at 80°C. Nadic anhydride (E. Merck) was recrystallized from acetic anhydride and then from chloroform. Tris(3-aminophenyl)phosphine oxide (TAP) was prepared from triphenylphosphine oxide (Koch Light) by nitration and subsequent reduction, according to the procedure reported earlier [10].

SYNTHESIS OF NADIMIDES

Five nadimide resins were prepared by changing the molar ratio of the amine (TAP) to the anhydride. Preliminary experiments showed that nadimides prepared with DMF as solvent were of inferior purity compared to those made in glacial acetic acid, which was, therefore, used as the synthesis solvent.

Appropriate quantities of NA and TAP in glacial acetic acid (20 mL) were refluxed for 8 h, and then the imide was recovered by precipitation. The precipitated imides were washed several times with water, aqueous $NaHCO_3$, distilled water, and, after drying, were recrystallized from chloroform. Details are given in Table 1. Refluxing the mono- and bisnadimides with appropriate quantities of BTDA yielded the resins. The yield was 80-90%.

CHARACTERIZATION

A Perkin-Elmer 240C elemental analyzer was used. A Nicolet MX-I FTIR spectrophotometer was used to record spectra of KBr pellets. ^{1}H-NMR spec-

TABLE 1. Synthesis of Nadimides: Details of Reaction Conditions [solvent: DMF (15 mL), glacial acetic acid (20 mL)]

	Quantities of reagents (g)		
Designated structure[a]	NA	TAP	BTDA
$(NA)_3TAP$	4.92	3.23	–
$(NA)_2TAP{\cdot}NH_2$	3.28	3.23	–
$(NA)TAP(NH_2)_2$	1.64	3.23	–
$[(NA)_2TAP]_2BTDA$	3.28	3.23	1.61
$[(NA)TAP{\cdot}NH_2]_2BTDA$	1.64	3.23	1.61

[a] NA = Nadic anhydride. TAP = Tris(3-aminophenyl)phosphine oxide. BTDA = 3,3′4,4′-Benzophenonetetracarboxylic acid dianhydride.

tra were recorded on a Jeol JNM-FT-NMR spectrophotometer with $CDCl_3$ as solvent and tetramethylsilane as internal standard. A Du Pont HPLC with a UV detector and ODS column was used for determining the purity with $CHCl_3$ as solvent, and a flow rate of 2 mL/min at 35°C.

A Du Pont 1090 thermal analyzer with a 910 DSC module was used for studying the curing behavior. A sample of about 11 ± 2 mg was heated from room temperature to 450°C in static air at 10°C/min.

A Du Pont 1090 thermal analyzer with a 951 TG module was used for assessing the relative thermal stability of the nadimide resins. Thermogravimetric traces were recorded in nitrogen (flow rate 100 mL/min) at 10°C/min on 11 ± 1 mg samples.

RESULTS AND DISCUSSION

A good correlation between observed and calculated elemental analyses was found for $(NA)_3TAP$ and $(NA)_2TAP{\cdot}NH_2$ (Table 2).

In the FTIR spectra of nadimides, characteristic bands due to imide groups appeared at 1784 ± 10 and 1720 ($\nu_{C=O}$), 1384, 1128, and 725 ± 15 cm^{-1}. The presence of the H_2N group in bis- and mononadimides was indicated by HN stretching at 3230 cm^{-1}. In samples containing BTDA, a broad absorption band was observed at 1700 with a shoulder at 1668 cm^{-1}, which

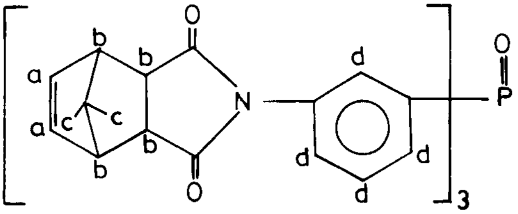
TABLE 2. Results of Elemental Analysis of Nadimides

Designated structure	Formula	Elemental analysis[a] C	H	N
$(NA)_3TAP$	$C_{45}H_{36}O_7N_3P$	70.56 (70.96)	4.84 (4.73)	5.90 (5.52)
$(NA)_2TAP \cdot NH_2$	$C_{36}H_{30}O_5N_3P$	69.60 (70.24)	4.34 (4.88)	6.33 (6.83)
$(NA)TAP(NH_2)_2$	$C_{27}H_{24}O_3N_3P$	68.23 (69.08)	5.01 (5.11)	7.83 (8.95)
$[(NA)_2TAP]_2BTDA$	$C_{89}H_{78}O_{15}N_6P_2$	67.85 (69.71)	4.05 (5.09)	5.90 (5.48)
$[(NA)TAP \cdot NH_2]_2BTDA$	$C_{71}H_{50}O_{11}N_6P_2$	65.84 (69.49)	4.42 (4.08)	7.58 (6.84)

[a] Figures in parenthesis indicate calculated values.

is due to carbonyl stretching of the benzophenone group. The absorption bands due to $P{-}C_6H_5$ and $-\overset{\|}{\underset{O}{P}}-$ were observed at 1432 and 1176 cm^{-1}, respectively.

Four sets of equivalent protons were observed in the ^1H-NMR spectrum of trisnadimide which resonate at different positions:



The aromatic protons *d* were observed at 7.78-7.27 (12H, m), olefinic protons *a* at 6.20 (6H, s), aliphatic protons *b* at 3.42-3.48 (12H, s), and methylene protons at 1.82-1.54 ppm (6H, quartet) (Fig. 1). In bisnadimide, in addition to the protons *d* (7.82-7.13, 12H), *a* (6.20-6.18, 4H), *b* (3.42, 8H), and *c* (1.82-1.52, 4H), $-NH_2$ protons were observed at 2.08 ppm (2H) (Fig. 2).

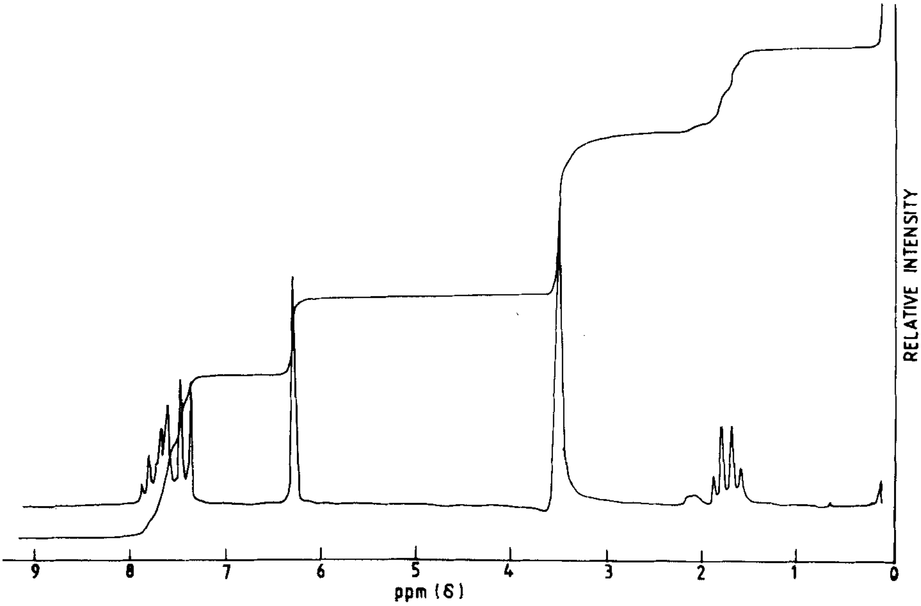


FIG. 1. ^{1}H-NMR spectrum of $(NA)_3TAP$.

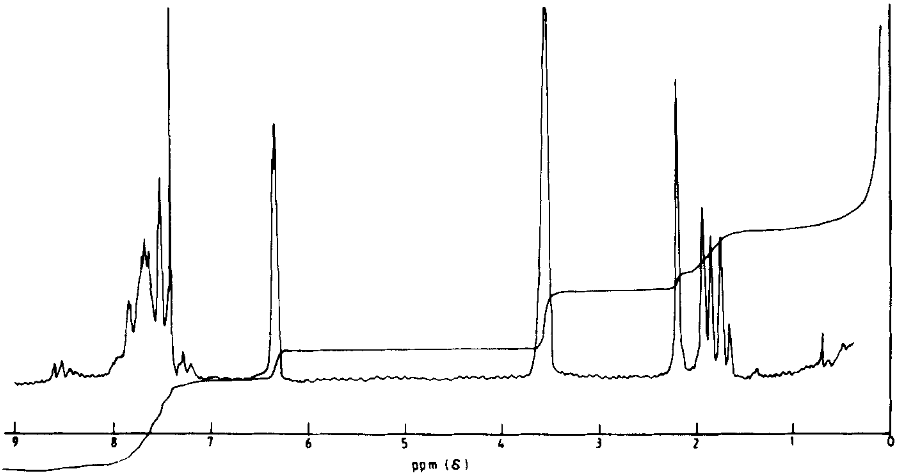


FIG. 2. ^{1}H-NMR spectrum of $(NA)_2TAP{\cdot}NH_2$.

The position of various proton resonance signals in $(NA)TAP(NH_2)_2$ was similar to that of bisnadimide. The presence of unreacted TAP was indicated in the spectrum. Similarly, in $[(NA)_2TAP]_2BTDA$, the presence of BTDA and TAP was indicated.

No endothermic transition due to melting was observed in the DSC traces of the nadimide resins. Two or more exothermic transitions were observed in most resin samples above 200°C (Fig. 3). In $(NA)_3TAP$ and $(NA)_2TAP \cdot NH_2$, an exotherm was also observed in the temperature range of 70-150°C with a peak position around 102 ± 1°C.

A strong exothermic reaction was indicated in the temperature range of 250-400°C in most of the nadimide resins (Table 3). T_{exo} for this transition was around 336 ± 2°C in most of the samples, except in $NA \cdot TAP(NH_2)_2$, where it appeared at 362°C. The heat of the curing reaction was higher for nadimides containing amino groups.

The important thermal reaction of nadimides can be summarized as [11]: 1) *endo-exo* isomerization, 2) Diels-Alder reversion reaction leading to formation of maleimide and cyclopentadiene, 3) polymerization of nadimides, and 4) polymerization of *in-situ* generated maleimides and cyclopentadiene.

The isomerization appears to occur rapidly, and apparent equilibrium in *endo/exo* mixtures can be attained in a few hours [12, 13] in the monomeric and oligomeric systems. The first exotherm observed in DSC traces in $(NA)_3TAP$ and $(NA)_2TAP \cdot NH_2$ can, therefore, be attributed to the isomerization reaction.

TABLE 3. Curing Behavior of Various Nadimides

	Curing temperature (°C)[a]			
Designated structure	T_i	T_{exo}	T_f	ΔH (J/g)
$(NA)_3TAP$	285	334	355	25.5
$(NA)_2TAP \cdot NH_2$	285	338	390	52.7
$(NA)TAP(NH_2)_2$	305	362	400	47.6
$[(NA)TAP \cdot NH_2]_2BTDA$	269	297	314	9.6
	314	335	400	89.3

[a] T_i = Temperature of onset of exotherm. T_{exo} = Temperature of peak position. T_f = Temperature of completion of exotherm.

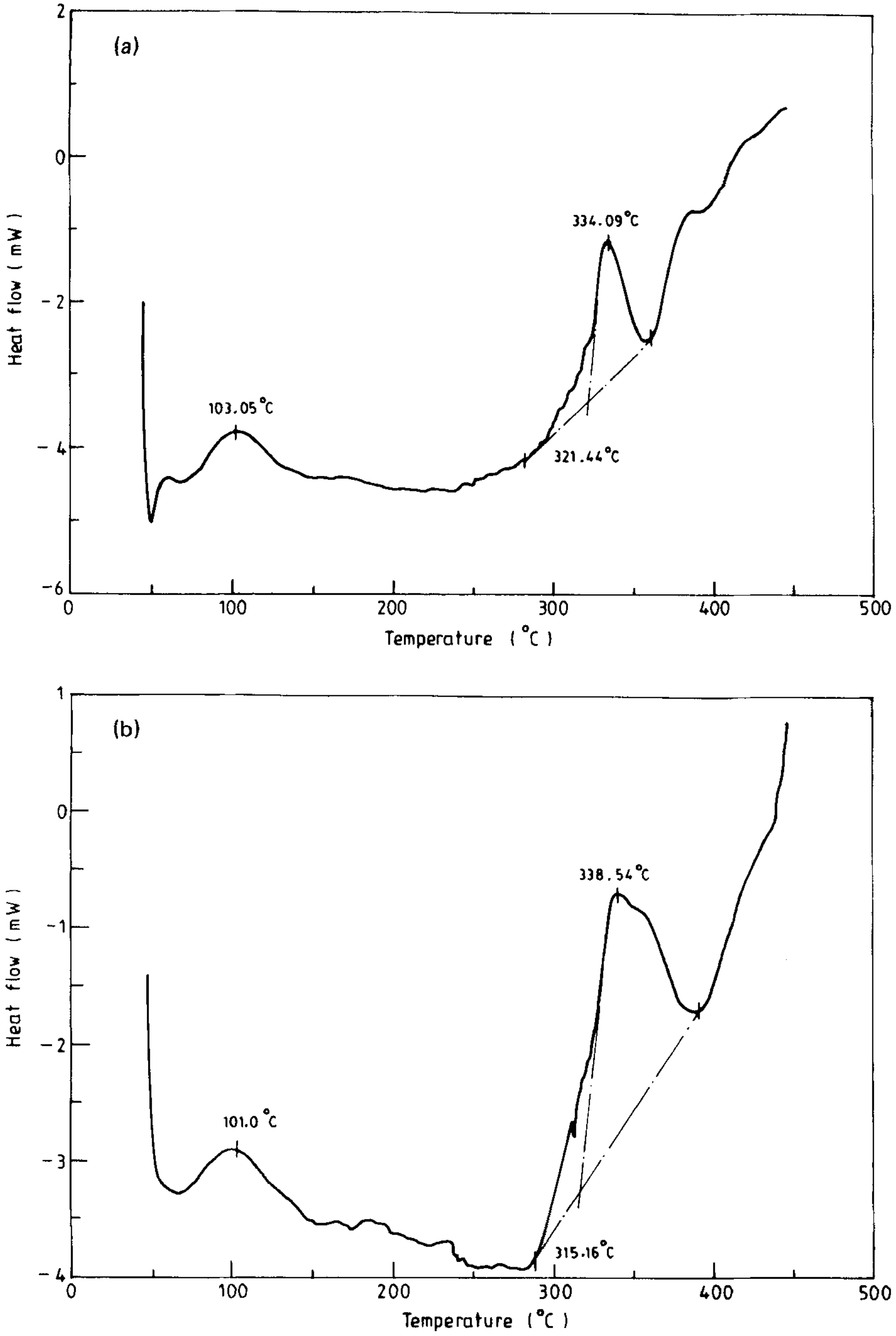
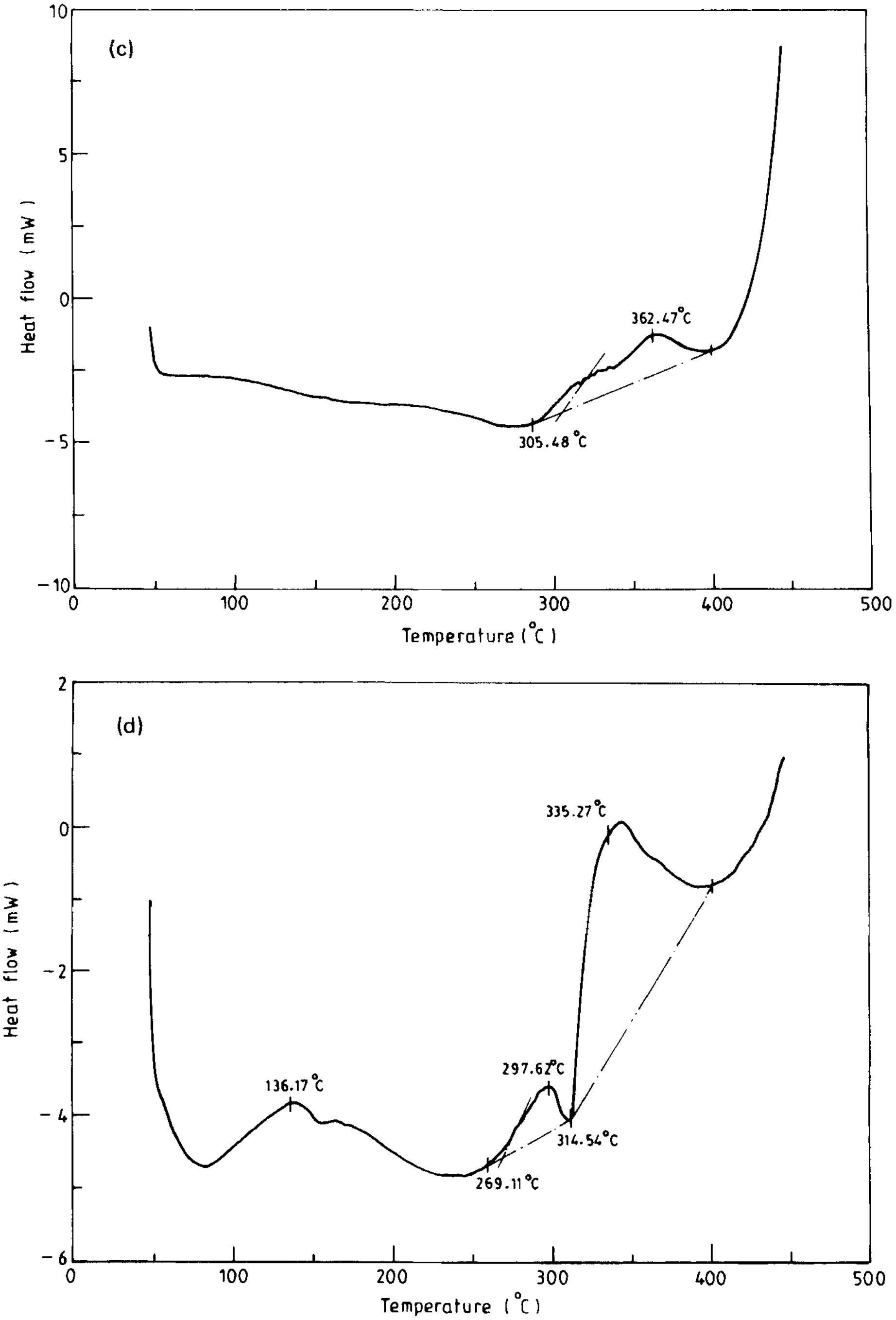
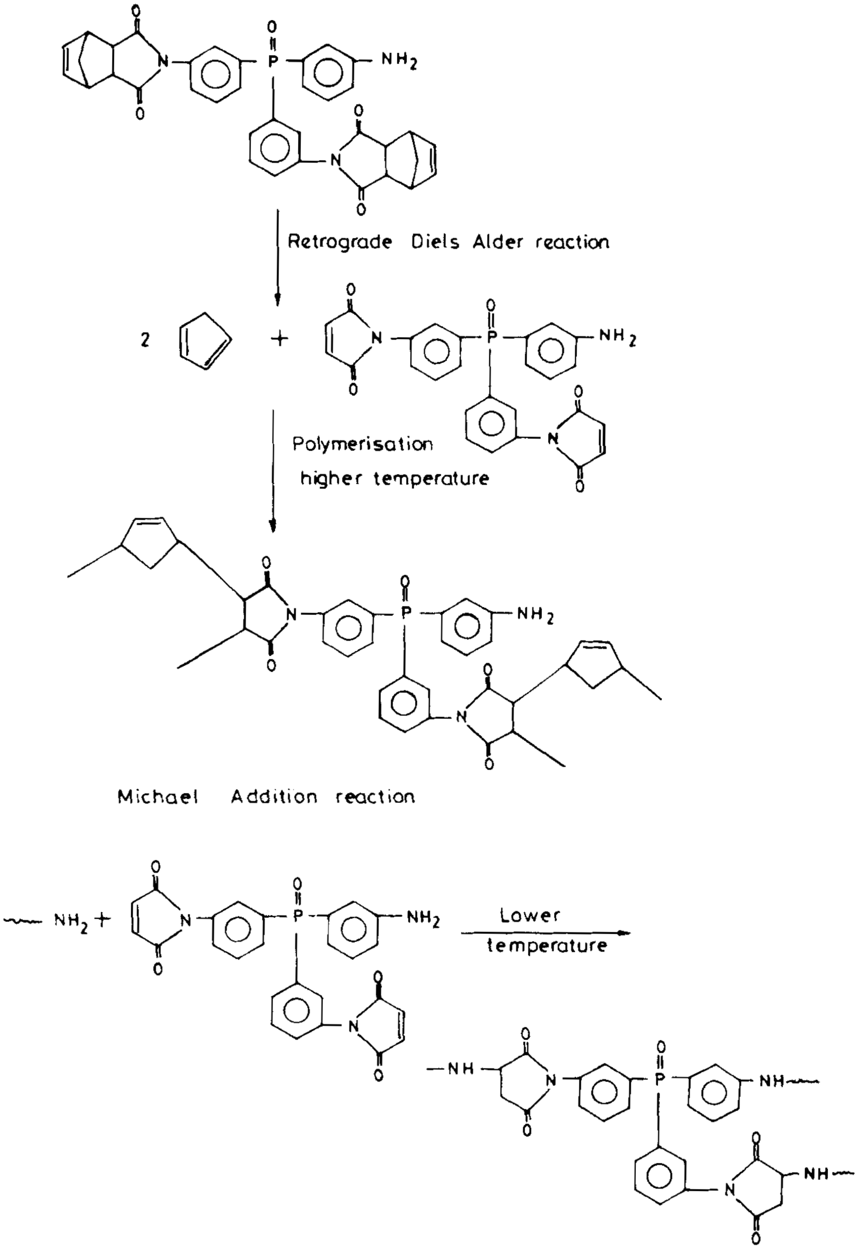


FIG. 3. DSC traces of various nadimides: (a) $(NA)_3TAP$, (b) $(NA)_2TAP{\cdot}NH_2$, (c) $(NA)TAP(NH_2)_2$, (d) $[(NA)TAP{\cdot}NH_2]_2BTDA$.


(c)
Heat flow (mW)
10
5
0
-5
-10
362.47°C
305.48°C
0
100
200
300
400
500
Temperature (°C)
(d)
Heat flow (mW)
2
0
-2
-4
-6
335.27°C
136.17°C
297.62°C
314.54°C
269.11°C
0
100
200
300
400
500
Temperature (°C)


Retrograde Diels Alder reaction
2
+
Polymerisation
higher temperature
Michael Addition reaction
Lower
temperature
NH2
N
P
O

SCHEME 1.

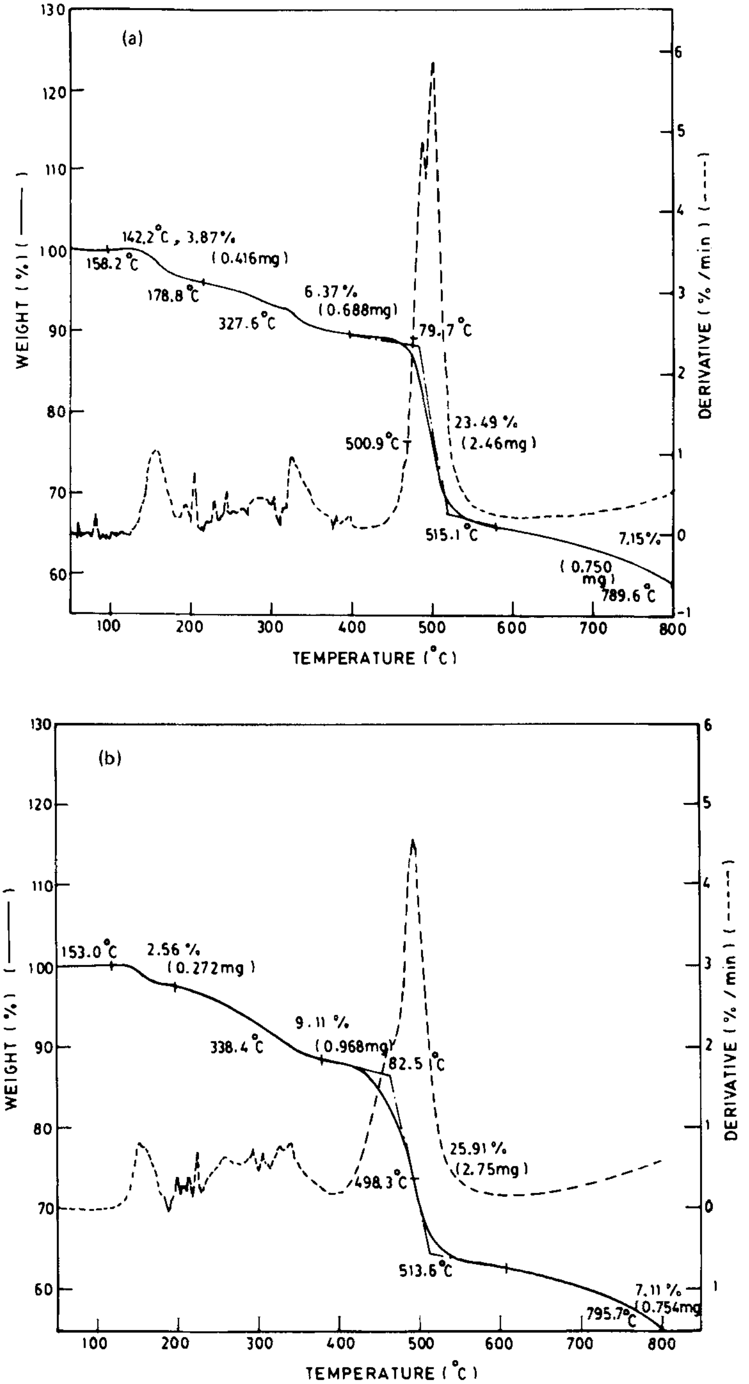


FIG. 4. TG traces of (a) $(NA)_3TAP$ and (b) $(NA)_2TAP{\cdot}NH_2$.

The second exothermic DSC transition may be attributed to curing of the nadimides. The results indicate that this is not influenced by the presence of NH_2 groups in the backbone. For maleimide resins, on the other hand, Michael-type addition reactions between the electron-deficient maleimido group and the electron-rich amino group lead to a significant reduction in T_{exo} [8]. If a maleimido group was generated during a retrograde Diels-Alder reaction, then a decrease in T_{exo} of nadimides containing $-NH_2$ groups would be expected, but this was not observed in the present work. From the DSC results it is not possible to distinguish between the onset of the curing reaction (T_i) and the retro-Diels-Alder reaction. However, even if both reactions were occurring simultaneously, a decrease in T_{exo} would be expected according to Scheme 1.

Thermogravimetric traces under nitrogen (Fig. 4) indicated a multistep decomposition in most of the nadimides. Detailed results are given in Table 4. The highest char yield at 800°C (Y_c) was observed in trisnadimide; the lowest in $[(NA)TAP \cdot NH_2]_2BTDA$. These char yields are much higher than the values reported for nadimides not containing the phosphine oxide group (28-38%).

TABLE 4. TG Studies of Various Nadimides under Nitrogen[a]

Designated structure	T_1 (°C)	T_{max} (°C)	T_2 (°C)	Y_c (%)
$(NA)_3TAP$	142	158	179	
	310	327	375	
	480	501	515	60
$(NA)_2TAP \cdot NH_2$	130	153	185	
	315	338	375	
	485	514	499	50
$(NA)TAP(NH_2)_2$	149	158	210	
	320	347	370	
	347	486	525	50

TABLE 4 (continued)

Designated structure	T_1 (°C)	T_{max} (°C)	T_2 (°C)	Y_c (%)
$[(NA)_2TAP]_2BTDA$	148	186	191	
	192	297	322	
	370	503	575	53
$[(NA)TAP \cdot NH_2]_2BTDA$	134	150	–	
	293	303	525	
	303	483	527	42

[a] T_1 = Initial decomposition temperature. T_{max} = Temperature of maximum rate of weight loss. T_2 = Final decomposition temperature. Y_c = Char yield at 800°C.

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