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STRUCTURAL AND THERMAL CHARACTERISATION OF NADIMIDE RESINS

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Abstract

A series of hexachloronadimides containing phosphine oxide in the backbone were synthesized by the reaction of bis(3-amino phenyl) methyl phosphine oxide (BAP) with pyromellitic dianhydride (PMDA)/3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA)/2,2-bis(3,4-dicarboxy phenyl) hexafluoropropane dianhydride (6F) and hexachloronadic anhydride in glacial acetic acid/acetone.

Structural characterisation of the resins was carried out by infrared, nuclear magnetic resonance spectroscopy and elemental analysis. Thermal characterisation of uncured resin was done by differential scanning calorimetry and thermogravimetric analysis. The decomposition temperature of uncured resins were above 310±10°C with T_{max} 330±10°C in nitrogen atmosphere. Char yield at 800°C ranged from 37–42%.

Keywords: chair yield, curing, DSC, hexachloronadimides, IR, NMR, TG

Introduction

Endo-5-norbornene-2,3-dicarboxyimide (nadimides) end-capped polyimide have been investigated as matrix resins for advanced fibre reinforced composites. Recent research efforts in this area have been primarily directed towards the development of new and improved resins capable of better-elevated temperature performance than the state-of-the-art system [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, 6]. In our earlier papers, we reported the synthesis of maleimide, nadimide and acetylene end-capped imide resins based on tris(3-aminophenyl) phosphine oxide and bis(3-aminophenyl) methyl phosphine oxide. These resins had excellent thermal stability and flame resistance [7–13].

The present paper deals with the effect of the structure of hexachloronadimides based on bis(3-aminophenyl) methyl phosphine oxide on thermal characteristics.

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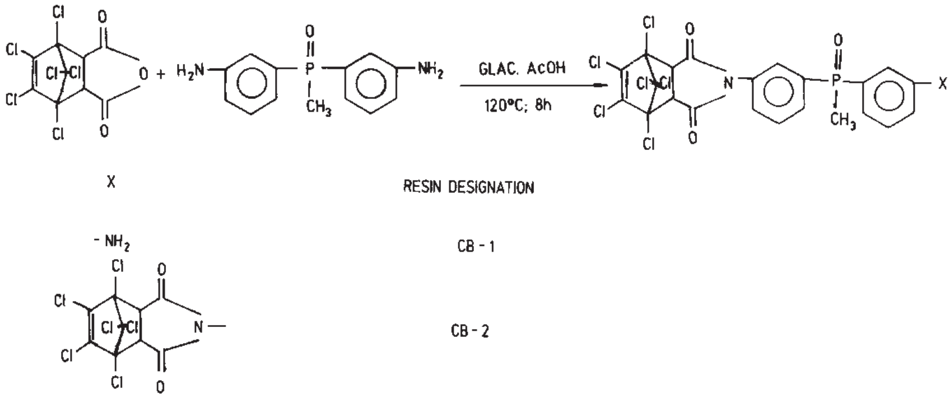
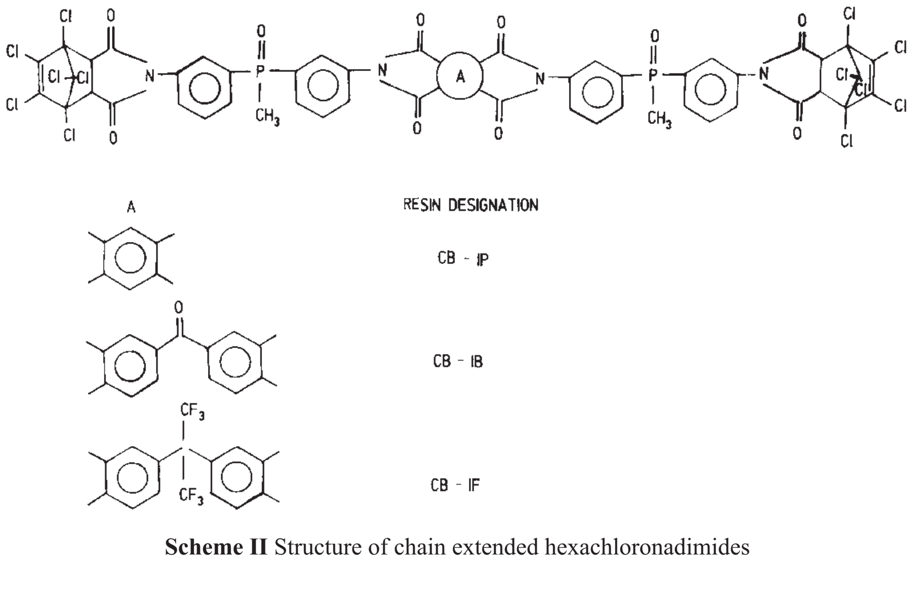
Experimental

Several hexachloronadimide oligomers were prepared by reacting hexachloronadic anhydride, and bis(3-amino phenyl) methyl phosphine oxide (BAP) (Scheme I).



Scheme I Reaction scheme for the synthesis of hexachloronadimides

Pyromellitic dianhydride (PMDA)/3,3'4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA)/2,2-bis(3,4-dicarboxy phenyl) hexafluoropropane dianhydride (6F) were used for chain extension. The structure of the oligomers along with sample designation and formula molecular mass (FMM) is given in (Scheme II).



Scheme II Structure of chain extended hexachloronadimides

Materials

Glacial acetic acid (BDH) and acetic anhydride (BDH) were distilled at atmospheric pressure before use. Acetone (BDH) was dried over anhydrous sodium sulphate overnight, refluxed for 1 h, and distilled at atmospheric pressure. Hexachloronadic anhydride (Aldrich), BTDA (Kochlight), PMDA (Fluka) and 6F (Hoechst) were purified by recrystallization from acetic anhydride. Anhydrous sodium acetate (Sarabhai Chemicals) was obtained by fusion. BAP was prepared according to the method reported elsewhere [16].

Synthesis of hexachloronadimides

Appropriate quantities of hexachloronadic anhydride and BAP in glacial acetic acid (20 ml) were refluxed for several h and the mono- and bis-nadimides were recovered by precipitation. The precipitated resins were washed several times with water and aqueous sodium bicarbonate and dried under vacuum. Purification of these resins was carried out by dissolving in chloroform and precipitating in methanol.

Chain extension with dianhydrides

Mono-nadimide (0.01 mol) was dissolved in acetone (20 ml) at 60°C and 0.005 mol of PMDA/BTDA/6F was added in portions. The solution was heated for 4 h followed by chemical cyclisation of the amic acid to imide, using sodium acetate and acetic anhydride as the cyclodehydrating agent.

Characterisation

A Nicolet MX-1 (FTIR) spectrophotometer was used for recording spectra of various hexachloronadimide in KBr pellets. ^{1}H-NMR spectra were recorded on a Jeol JNM-Fx-100 FT NMR spectrophotometer using DMSO-d_6 or $CDCl_3$ as the solvent and tetramethylsilane as an internal standard.

A DuPont 9900 thermal analyser having a 910 DSC module was used for studying the curing behaviour. A sample (10±2 mg) was heated from room temperature to 450°C in static air at 10°C min^{-1}.

A DuPont 1090 thermal analyser having a 951 TG module was used for assessing the relative thermal stability of the hexachloronadimide resins. Thermogravimetric traces were recorded in nitrogen atmosphere (flow rate 60 ml min^{-1}) at a heating rate of 10°C min^{-1}. A sample mass of 10±2 mg was used. The relative thermal stability of various resin samples was evaluated by determining (a) initial decomposition temperature (T_i), (b) temperature of maximum rate of mass loss (T_{max}) and (c) char yield at 800°C.

Results and discussion

The hexachloronadimide oligomers were obtained in powder from having white to brown colour. The physical characteristics of the hexachloronadimide oligomers are given in Table 1. The yields were in the range of 60–90%.

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

Table 1 Results of elemental analysis and physical characteristics of hexachloronadimide resins

Sample	Formula (FMM)	Elemental analysis*/%			Yield	Colour
		N	C	H		
CB-1	$C_{22}H_{15}N_2PO_3Cl_6$ (595)	4.70 (4.67)	44.36 (44.01)	2.52 (2.49)	80.1	pale yellow
CB-2	$C_{31}H_{15}N_2PO_5Cl_{12}$ (945)	4.08 (3.99)	47.23 (47.30)	2.04 (2.08)	90.2	white
CB-1P	$C_{54}H_{28}N_4P_2O_{10}Cl_{12}$ (1372)	2.96 (2.99)	39.36 (39.29)	1.58 (1.12)	70.4	light yellow
CB-1B	$C_{61}H_{32}N_4P_2O_{11}C_{12}$ (1476)	3.79 (3.80)	49.59 (49.60)	2.16 (2.09)	68.3	white
CB-1F	$C_{63}H_{32}N_4P_2O_{11}Cl_{12}F_6$ (1592)	3.51 (3.49)	47.00 (46.98)	2.01 (1.99)	59.2	white

* Figures in the brackets indicate calculated values

In the FTIR spectra of hexachloronadimide resins characteristic bands due to imide groups appeared at 1780±5 and 1720 cm^{-1} ($\nu_{C=0}$), 1380±10 and 725±10 cm^{-1}. The presence of NH_2 group in the mono-nadimide CB-1 was indicated by N–H stretching at 3230 cm^{-1}. The absorption bands due to P=O were observed at 1180±5 cm^{-1}. IR spectrum of CB-1 is shown in Fig. 1.

^{1}H-NMR spectra of hexachloronadimides were recorded in $CDCl_3$/DMSO-d_6. The aromatic protons appeared at 7.2–7.8 ppm and aliphatic protons 1–3 ppm. The ratio of total aromatic to aliphatic protons was used for structural characterisation of theses resins. ^{1}H-NMR spectrum of CB-2 is shown in Fig. 2.

No endothermic transition due to melting was observed in the DSC traces of the hexachloronadimide resins. The exothermic transition was observed in most resin samples above 200°C (Fig. 3). A strong exothermic reaction was indicated in the temperature range of 290–400°C in most of the hexachloronadimide resins (Table 2). The T_{exo} for this transition was around 335±5°C in most of the samples. A significant mass loss (23–37%) in the temperature range of 300–360°C was observed in TG traces which corresponds to T_{exo} region in DSC may be attributed to the loss of chlorine in the form of HCl.

The important thermal reaction of hexachloronadimides can be summarised as [15] i) endo–exo isomerization, ii) Diels–Alder reversion reaction leading to forma-

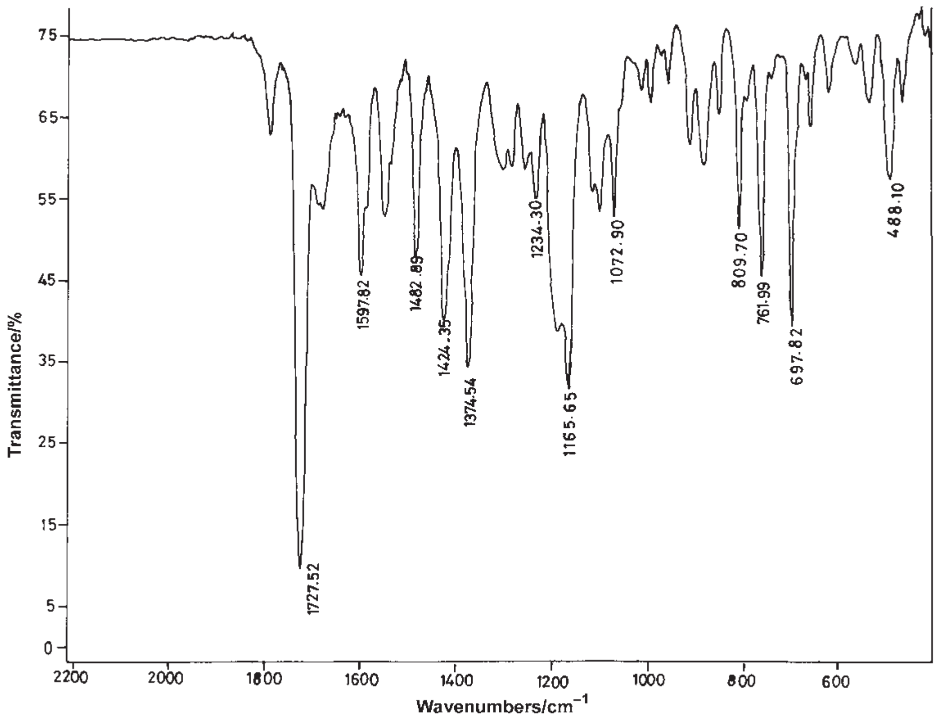


Fig. 1 IR spectrum of CB-1 resin

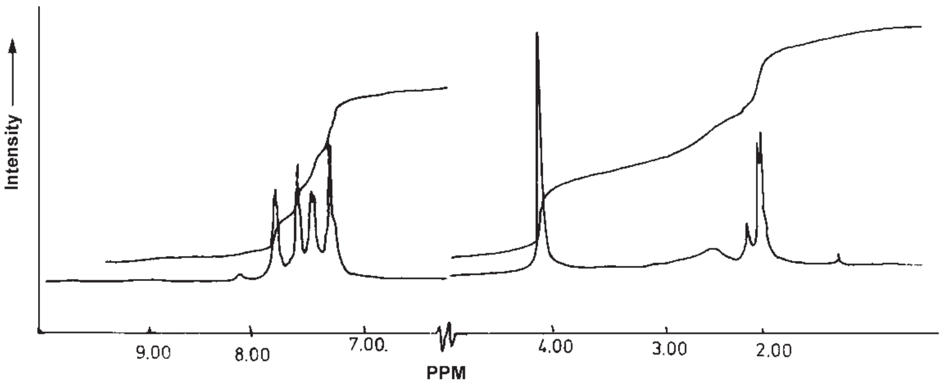


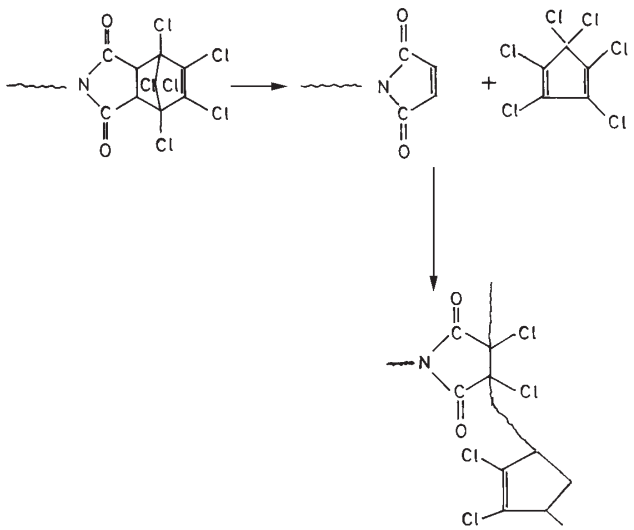
Fig. 2 ^{1}H-NMR spectrum of CB-2 resin

tion of maleimide and cyclopentadiene, iii) polymerisation of hexachloronadimides and iv) polymerisation of generated maleimides and cyclopentadiene.

Table 2 Characterisation of DSC curing exotherm of hexachloronadimide

Sample designation	T_i/°C	T_{exo}/°C	T_f/°C	ΔH/J g^{-1}
CB-1	299	330	392	–
CB-2	317	340	390	–
CB-1P	293	331	398	627
CB-1B	318	346	398	566
CB-1F	306	334	397	420

The exothermic DSC transition may be attributed to curing of the hexachloronadimides. 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} [16]. If maleimido group was generated during a retrograde Diels–Alder reaction, then a decrease in T_{exo} of hexachloronadimides containing $–NH_2$ groups would be expected, and this was 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 III.



Scheme III Curing of hexachloronadimide resins

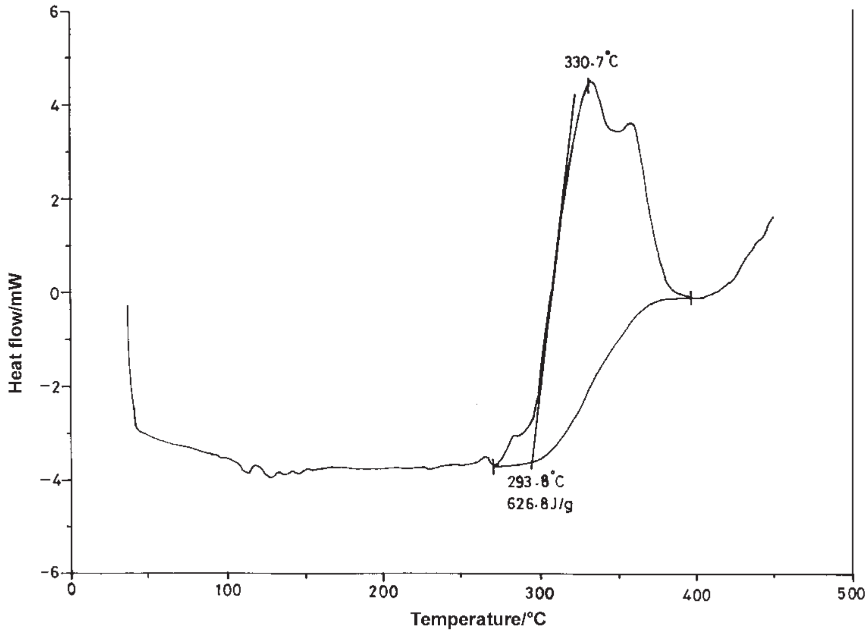


Fig. 3 DSC scan of CB-IP resin

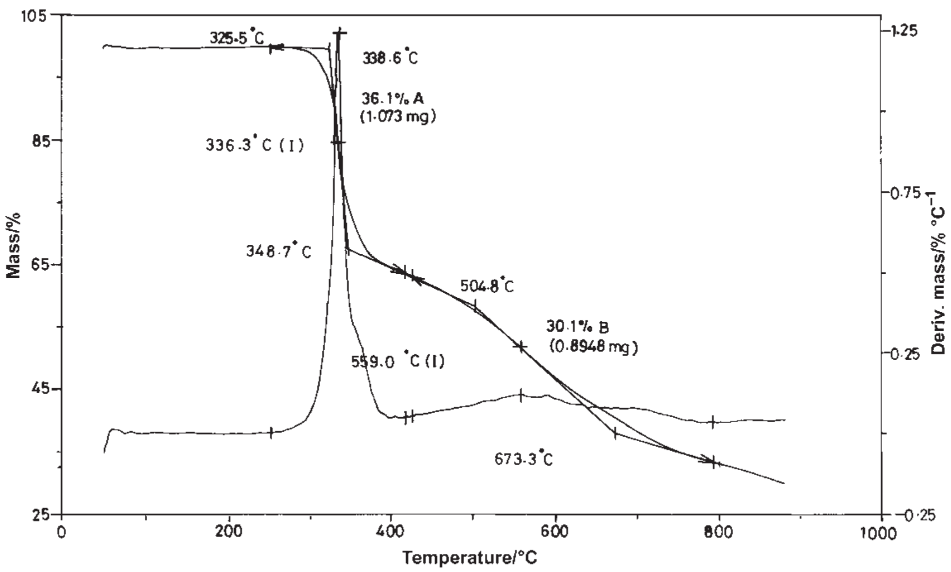


Fig. 4 TG trace of CB-2 resin

Table 3 Thermogravimetric studies of uncured hexachloronadimide

Sample designation	T_i/°C	T_{max}/°C	T_f/°C	Y_c/%
CB-1	275 330	313 334	328 (23) 325 (12)	43
CB-2	325 504	338 559	348 (36) 673 (30)	34
CB-1P	309	338	352 (31)	38
CB-1B	313	328	351 (37)	42
CB-1F	300 490	330 537	359 (31) 589 (24)	35

Thermogravimetric traces under nitrogen (Fig. 4) indicate a single step decomposition in most of the hexachloronadimides. Detailed results are given in Table 3. The highest char yield at 800°C (Y_c) was observed in CB-1 the lowest in CB-1F. These char yields are higher than the values reported for nadimides not containing the phosphine oxide group (28–30)%.

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