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THERMAL BEHAVIOUR OF ETHYNYL AND ETHENYL TERMINATED IMIDE RESINS

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Abstract

A series of ethynyl and ethenyl end-capped imide resins were synthesised by the reaction of 9,9-bis(4-aminophenyl) fluorene (BAF) with pyromellitic dianhydride (PMDA)3/3′, 4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA)/2,2-bis(3,4-dicarboxy phenyl) hexafluoropropane dianhydride (6F) and 3-ethynyl aniline/maleic anhydride. Structural characterisation was done by infra red and elemental analysis. Thermal characterisation was done by differential scanning calorimetry and thermogravimetric analysis. The decomposition temperatures of cured resins were above 200°C in nitrogen atmosphere. Char yield at 800°C ranged from 59–65.5%.

Keywords: bis maleimide, char yield, curing, ethynyl terminated imide

Introduction

The ethynyl terminated imide resins (ETI's) are very attractive for use at elevated temperatures and find applications as adhesive and as high performance matrices for advanced fiber reinforced composites [1]. These oligomers have excellent shelf lives and can be cured by heating (above 300°C) without the evolution of volatile products. The properties of the crosslinked polymer network thus formed depend primarily on the backbone structure, crosslink density, and cure temperature.

Studies on the effect of structure on properties of ethynyl terminated imide resins are well documented in the literature and have been the subject of several reviews [2–4]. Phosphorus containing oligoimides based on 3-ethynyl aniline as

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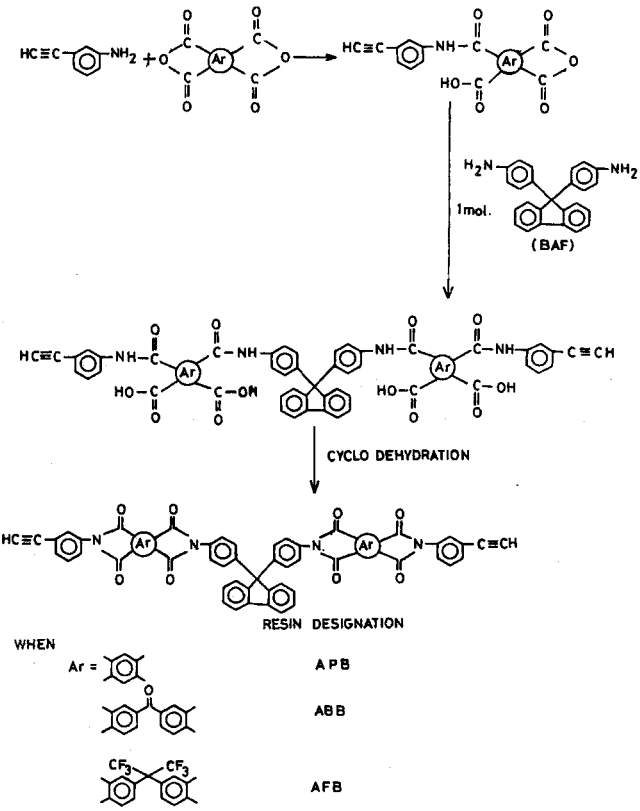
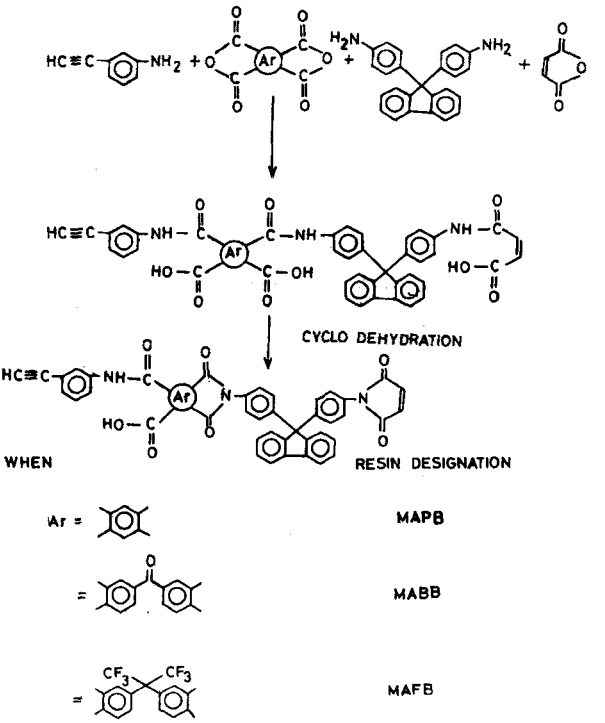
an end-capper and different combination of tris (3-aminophenyl) phosphine oxide/bis(3-aminophenyl)methyl phosphine oxide and 2,2-bis(3,4-dicarboxy phenyl) hexafluoropropane dianhydride/ 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride/pyromellitic dianhydride have been reported by Varma *et al.* [5].

Maleimide/nadicimide end capped resins based on 9,9-bis(4-aminophenyl) fluorene (BAF) have been reported to have good thermal and flame resistance properties [6–9]. Incorporation of such fused ring structure in the backbone of ethynyl terminated imide resins may affect thermal characteristics of these resins. Such studies have not been reported in the literature. Therefore, in order to investigate the effect of structure on thermal behaviour of ETI's, the following resins were synthesised (Scheme 1).



Scheme 1 Synthesis of ETI's

In order to study the curing of ethynyl and maleimide terminated imide resins, following resins were also synthesised (Scheme 2).



Scheme 2 Synthesis of imide oligomers with mixed end-caps

Experimental

Materials

3-Ethynyl aniline (Alpha product) was distilled under reduced pressure (69°C, 0.35 mm of mercury). 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA), pyromellitic dianhydride (PMDA), 2,2-bis(3,4-dicarboxyphenyl) hexafluoro propane dianhydride (6F) (Hoechst) were recrystallised from acetic anhydride and were vacuum dried before use. 9,9-bis(4-aminophenyl) fluorene (BAF) was purified by crystallisation. Acetone (BDH) was dried over anhydrous K_2CO_3 and distilled before use. Anhydrous sodium acetate (BDH) was obtained by fusion. Acetic anhydride was distilled under atmospheric pressure.

Synthesis of ethynyl terminated imides

3-ethynyl aniline (0.006 mol) was dissolved in dry acetone in a 250 mL flask equipped with condenser, a solid transfer tube and a magnetic stirrer. Stoichiomet-

ric amounts of dianhydride (BTDA/PMDA/6F) (0.006 mol) was added with constant stirring in several portions. The solution was refluxed for 8 h. Then (0.003 mol) of BAF was added and the solution was refluxed for 8 h with constant stirring. Cyclodehydration was accomplished by adding acetic anhydride (6 mL) and fused sodium acetate (2 g). Stirring was cotinued for another 4 h. The imide so formed was precipitated by adding it to ice cold water. The precipitates were filtered and washed with dil sodium bicarbonate solution and then water to remove all the traces of acids. The precipitates were then dried at 60°C in vacuum oven.

Synthesis of imide resins having mixed end-caps

The 3-ethynyl aniline (0.003 mol) was dissolved in dry acetone in a 250 mL flask equipped with a condenser, a solid transfer tube and a magnetic stirrer. Dianhydride (0.003 mol) was added and the solution was refluxed for 8 h. Then (0.003 mol) of BAF was added and solution was refluxed for 8 h. Then maleic anhydride (0.0033 mol) was added with constant stirring in several portions and refluxing done for 8 h. Cyclodehydration was accomplished by adding acetic anhydride (6 mL) and fused sodium acetate (2 g) and reaction continued for 4 h. The imide was precipitated by adding to ice cold water.

Characterisation

A Perkin-Elmer 240 C elemental analyser was used for the determination of C, H and N content. Structural characterisation was done by recording IR spectra in KBr pellets using a Nicolet 5 DX FTIR spectrometer. Curing studies were done using a DuPont 1090 thermal analyser having 910 DSC module. The exothermic transition due to curing reaction was characterised by determining onset temperature of curing (T_o), exothermic peak position (T_e) and temperature of completion of exotherm (T_2). The heat of polymerisation (ΔH) was determined from the area under the curve. A 951 TG module was used to evaluate the thermal behaviour of uncured as well as isothermally cured resins. A heating rate of 10°C min^{-1} and 11±2 mg of sample was used. The relative thermal stability of resins was evaluated by determining initial decomposition temperature (T_i), temperature of maximum rate of mass loss (T_{max}) and final decomposition temperature (T_f). The temperature T_o, T_i, T_f and T_2 were obtained by extrapolation. Char yield at 800°C was also determined from TG trace. Isothermal ageing studies were carried out for 100 h in air atmosphere at 325°C in a muffle furnace. Percent mass loss was recorded at regular intervals of time.

Results and discussion

The ethynyl terminated imide oligomers were obtained in powder form having a white to brown colour and yield ranging from 64 to 92% (Table 1). The ETI's and mixed end-capped imides were soluble in DMF, DMSO and DMAc.

In the FTIR spectra, characteristic bands due to imide groups appeared at 1784±10 cm^{-1} and 1722 cm^{-1} (νC=O), 1370±10, 1130±10, 725±10 cm^{-1}. In samples containing BTDA, a broad absorption band was observed at 1700 with a shoulder at 1630±10 cm^{-1}, due to carbonyl stretching of the benzophenone group. In all the samples absorption at 3295±10 cm^{-1} was observed and assigned to ethynylic (≡C–H stretch) group. The absorption due to maleimido double band was observed at 1640 cm^{-1} in mixed end-capped imides. IR spectrum of MABB is shown in Fig. 1a.

Table 1 Results of elemental analysis and physical characteristics of ETI's

Sample	Formula (FMW)	Elemental analysis[a] N/%	C/%	H/%	Yield	Colour
MAPB	$C_{47}H_{25}O_6N_3$	4.68	71.02	3.77	78.4	pale
	(727)	[5.77]	[77.57]	[3.43]		yellow
MABB	$C_{54}H_{29}N_3O_7$	4.49	74.87	3.80	67.7	greenish
	(831)	[5.01]	[77.97]	[3.48]		yellow
MAFB	$C_{56}H_{29}O_6F_6N_3$	2.97	65.6	3.31	75.4	white
	(893)	[4.70]	[75.2]	[3.24]		
APB	$C_{61}H_{30}O_8N_4$	5.96	72.0	4.13	64.6	brown
	(946)	[5.91]	[77.3]	[3.17]		
ABB	$C_{75}H_{38}O_{10}N_4$	4.75	74.30	4.07	76.1	light
	(1154)	[4.85]	[77.98]	[3.29]		yellow
AFB	$C_{79}H_{38}O_8F_6N_4$	3.46	66.4	3.92	92.5	brownish
	(1224)	[4.57]	[77.4]	[3.10]		yellow

FMW: Formula molecular weight.
[a] Figures in parentheses indicate calculated values.

The results of elemental analysis (C,H,N) of various ethynyl terminated imide resins are given in Table 1.

In the DSC scan of these resins (Fig. 1b) an exotherm due to curing reaction was observed in the temperature range of 190±20–330±30°C. The exothermic peak position was at 258±6°C. Variation in the structure of the resins only marginally affected the curing behaviour. In the TG traces of uncured resins a two step decomposition was observed in most of the samples (Fig. 2a).

An initial mass loss of 4–7% was observed in the temperature range of 150–300°C. Major mass loss was observed above 400°C. The char yield at 800°C depended on the structure of the resins and was lowest in AFB (54%). Resins with mixed end-caps had higher char yields, indicating thereby that solid state condensation reaction leading to carbonaceous char are facilitated by the presence of maleimido end caps.

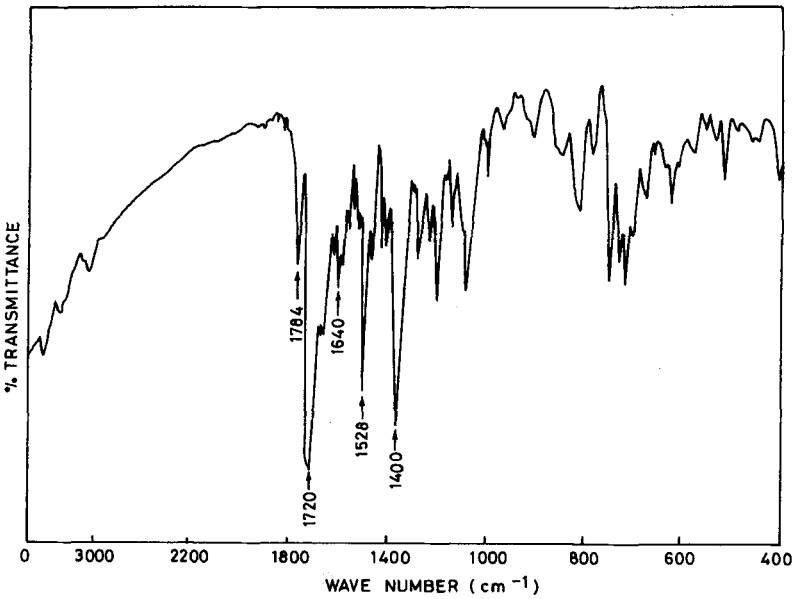


Fig. 1a IR spectrum of MABB

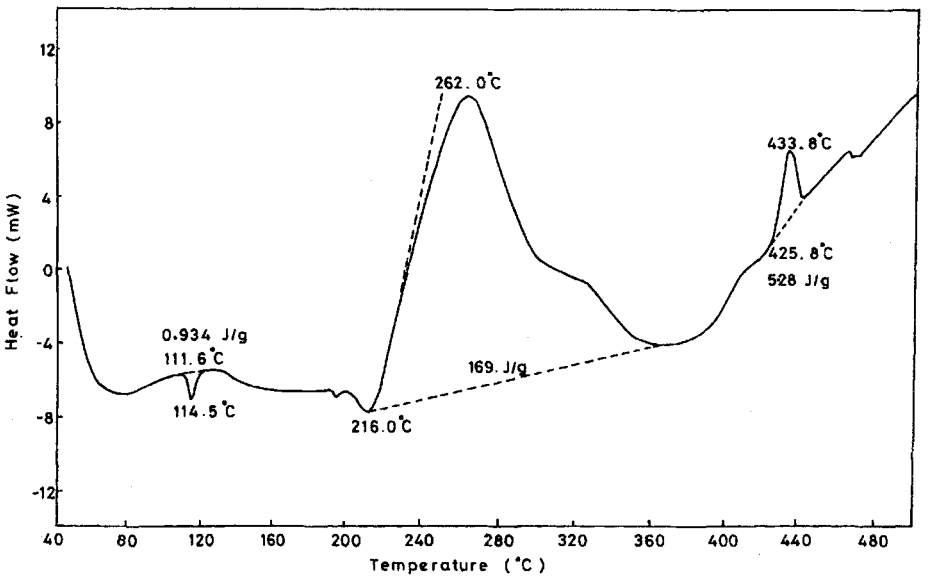


Fig. 1b DSC scan of ABB

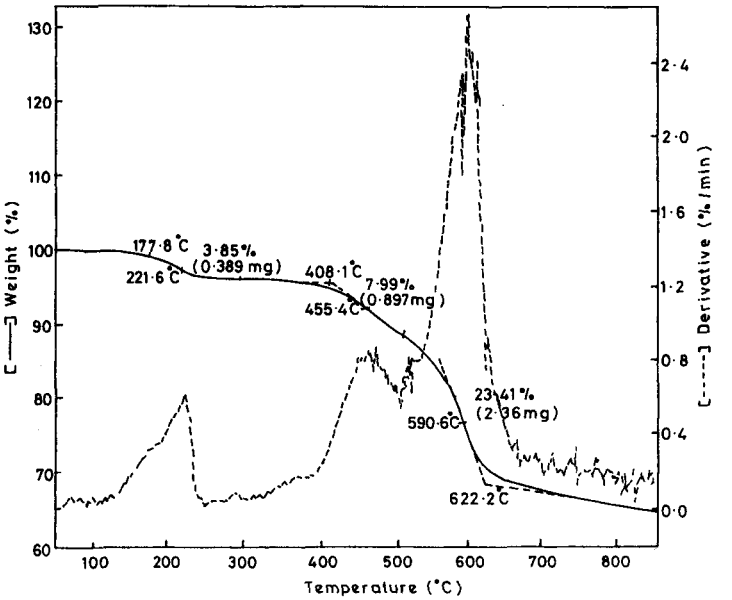


Fig. 2a TG trace of uncured ABB

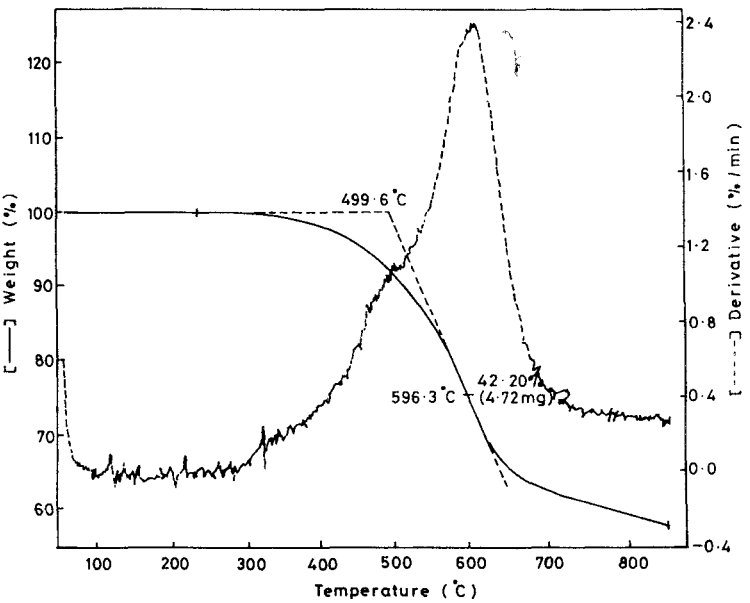


Fig. 2b TG trace of CMAPB

Table 2 Characterisation of DSC curing exotherm of ETI's (rate of heating 10°C min^{-1} in static air)

Sample	T_o/	T_e/	T_f/	ΔH/J g^{-1}
		°C		
MAPB	232	252	300	65.1
MABB	222	261	340	58.9
MAFB	219	263	340	95.1
APB	237	258	320	81.9
ABB	216	262	362	169.0
AFB	215	264	325	87.7

Table 3 Thermogravimetric studies of uncured ETI's

Sample	T_i/	T_{max}/	T_f/	Y_c/%
		°C		
APB	400	588	700	62.5
ABB	408	591	700	65.2
AFB	450	581	750	54.0

Table 4 Thermogravimetric studies of cured ETI's

Sample	T_i/	T_{max}/	T_i/	Y_c/%
		°C		
CMAPB	500	596	650	59.5
CMABB	390	481	510	64.5
	(510)	(610)	(665)	
CMAFB	377	448	510	62.5
	(510)	(572)	(700)	
CAPB	453	577	630	61.5
CABB	346	424	470	65.2
	(470)	(583)	(628)	
CAFB	294	350	420	59.0
	(420)	(572)	(634)	

Figures in parenthesis indicate temperature of mass loss in second step.

Isothermal curing of ETI's was done at 225°C for 5 h. A mass loss of 1.6–4% was observed during isothermal curing in most cases except MABB where ~9% mass loss was observed.

Relative thermal stability of the cured ETI's were also evaluated in nitrogen atmosphere. The results are summarised in Table 4 (Fig. 2b).

A two step decomposition above ~380°C was observed in some cases. The T_{max} value was highest in resins having benzophenone unit in the backbone (CMABB and CABB) while lowest value was observed in resins having hexafluoroisopropylidene unit in the backbone (CAFB, CMAFB).

Thermo-oxidative stability of ETI's

The isothermal ageing studies of ETI's were carried out at 325°C for 100 h and mass loss was measured (Fig. 3) as a function of time. The ETI's containing hexafluoro isopropylidene units in the backbone, exhibited highest thermo-oxidative stability.

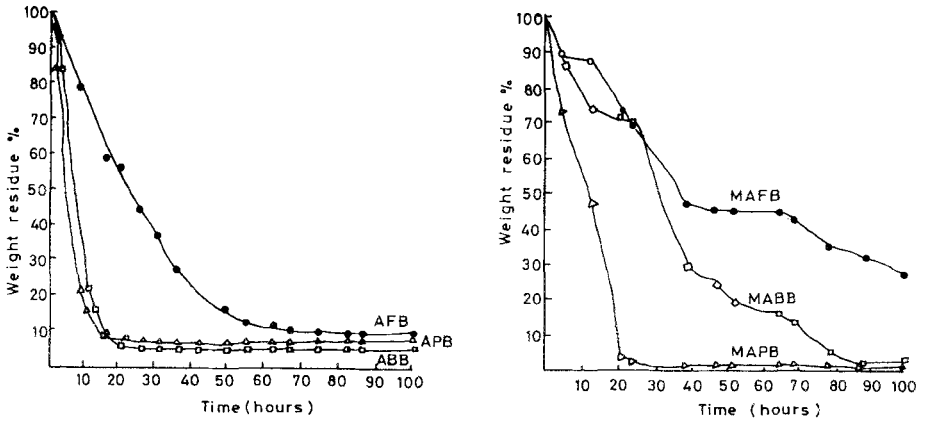


Fig. 3 Isothermal ageing curves at 325°C

Conclusion

Ethynyl terminated imide resins (ETI's) based on 9,9-bis (4-aminophenyl)fluorene exhibited very good thermal stability on isothermal curing at 225°C for 5 h. The initial decomposition temperature was lowest in ETI based on 6F and highest in PMDA based resins. The temperature of maximum rate of mass loss was, also lowest in 6F based resins and highest in PMDA based resins. Resins having both ethynyl and ethenyl end caps, started decomposing at a lower temperature (~50°C lower) than the corresponding ethynyl end capped resins. However, the char yield was higher in the mixed end-capped resins.

References

1 N. Bilow in 'Resins for Aerospace' (ACS symposium series, 132) (C. A. May Ed.) American Chemical Society, Washington D. C., 1980, Ch. 13.
2 I. K. Varma, Sarfaraz Alam and L. D. Kandpal, J. Macromol. Sci. Rev. C, 33 (1993) 291.
3 P. M. Hergenrother, J. Macromol. Sci. Rev., Macromol Chem. C 19 (1980) 1.
4 Encyclopedia of Polymer Science and Engg., Vol. I (H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges, Ed., Wiley Int. (Pub.) NY, 1986, p. 61.
5 (a) I. K. Varma, Phosphorus Containing Addition Polyimides, Paper Presented at Ist Intern. Conf. on Frontier of Polymer Research, New Delhi, Jan. 1991.
5 (b) Sarfaraz Alam, M. Tech. Thesis, Ethynyl Terminated Imides, IIT, Delhi 1990.
6 I. K. Varma, G. M. Fohlen and J. A. Parker, J. Polym. Sci., Polym. Chem., Ed., 28 (1983) 191.
7 I. K. Varma, Ashok Gupta and Sangita, J. Polym. Sci., Polym. Lett., Ed., 20 (1982) 621.
8 I. K. Varma and S. Sharma, Polymer, 26 (1985) 1561.
9 I. K. Varma, G. M. Fohlen and J. A. Parker, ACS Sym. Ser. 195 (1982) 253.