Structure–property relationships in PMR-type polyimide resins: 4. Investigation of materials derived from diamino(diaryl)methanes*

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(Received 24 September 1993)

Polyimide oligomers (prepolymers) and resins of the PMR-15 type have been prepared from 5-norbornene-2,3-dicarboxylic half acid ester (NE), 3,3′,4,4′-benzophenonetetracarboxylic diester (BTDE) and a series of diamines including, and related to, 3,3′-diaminobenzophenone, viz. 3,3′-diaminobenzhydrol, 3-[(*m*,*m*′-diamino)benzhydryloxy]propyne (MDA–OMA) and 3,3′-diaminodiphenyl-α,α'-difluoromethane (FMDA). The PMR synthetic pathway (monomers→prepolymer→resin) has been assessed by dynamic mechanical thermal analysis. The T_g values for resins incorporating BTDE are significantly lowered compared to that for PMR-15 itself. The fluorine-containing PMR-15 type of resin (from FMDA) is of higher thermal stability than PMR-15 itself.

(Keywords: PMR-type polyimide resins; structure–property relations; diamino(diaryl)methanes)

INTRODUCTION

A leading resin amongst high-temperature advanced composite matrix materials is the NASA-developed[2] PMR-15 (*Figure 1*). However, one of the monomers, methylenedianiline (MDA), is a suspected carcinogen, and recent reports indicate that US authorities may restrict its use in many applications[3]. Such action would undoubtedly cause serious problems for manufacturers and users of PMR-15.

The search[4] for a less-toxic MDA replacement monomer has been made more difficult because of the requirement to match the combination of properties offered by MDA both during production, and in the ultimate properties, of PMR-15 resin. In this paper we describe the synthesis of compounds related to MDA, and their incorporation into resins akin to PMR-15. An objective of the programme was the preparation of new materials possessing the desirable properties of PMR-15 using diamines of lower toxicity. The synthesis of a novel diamine monomer containing an acetylenic function is also described.

EXPERIMENTAL

Materials

4,4′-Diaminodiphenylmethane (methylene dianiline, MDA), 5-norbornene-2,3-dicarboxylic half acid ester (NE) and 3,3′,4,4′-benzophenonetetracarboxylic diester (BTDE) were supplied by BP International plc. All other diamine monomers used in this work (see *Figure 2*) were synthesized from readily available 3,3′-dinitrobenzophenone (**1a**)[5]. The reported procedures[6] for the reductions (**1a**→**1b**→**1c**) proved to be efficient—(i) $SnCl_2$, conc. HCl (80%), (ii) Zn/Hg, conc. HCl, 6 h (80%). It was subsequently found that partial reduction (**1b**→**1d**) could be achieved in 70% yield by shortening the reaction time in the Clemmenson process from 6 h to 3 h. Use of the benzhydrol derivative (**1d**) in polymer synthesis has been reported[7], but physical and spectral characteristics have not been described. I.r., n.m.r. and mass spectral data are in accord with structure **1d** and are described in a later subsection. The benzhydrol derivative (**1d**) was transformed (NaH, propargyl bromide) into the propargyl ether (**1e**) as a colourless oil in 80% yield. It was purified chromatographically, but decomposed slowly at room temperature over a few weeks. Polymer studies using this monomer were conducted on freshly synthesized material. It proved impossible to obtain an analytically

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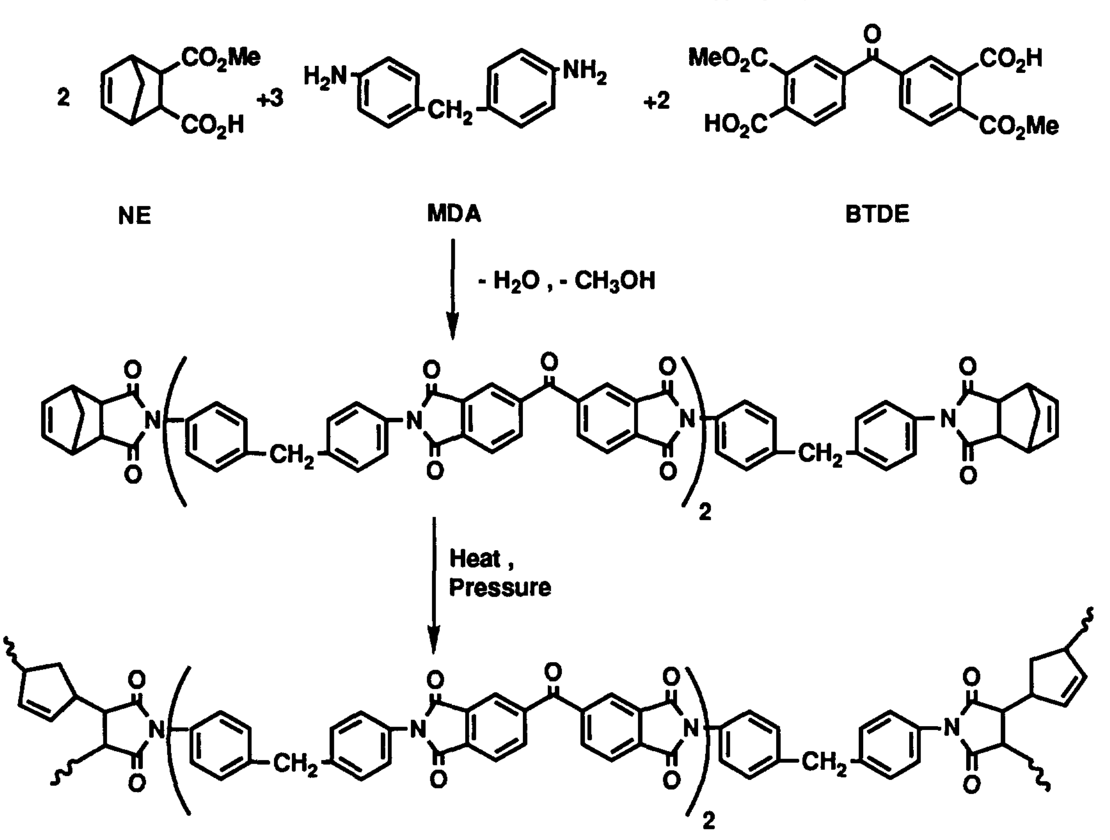
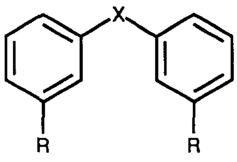


Figure 1 Synthesis of PMR-15: polymerization of monomeric reactants (PMR systems)



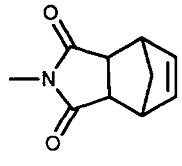
	X	R	Acronym
1a	CO	NO_2	-
1b	CO	NH_2	-
1c	CH_2	NH_2	m-MDA
1d	CHOH	NH_2	MDA-OH
1e	$CHOCH_2C\equiv CH$	NH_2	MDA-OMA
1f	CCl_2	NO_2	-
1g	CF_2	NO_2	-
1h	CF_2	NH_2	FMDA
1i	CH_2		

Figure 2 Structure of synthesized diamines

pure sample, but spectroscopic data (i.r., n.m.r., m.s.) were in accord with structure **1e** (see later subsection).

3,3′-Dinitrobenzophenone (**1a**) was also used to prepare 3,3′-dinitrodiphenyl-α,α′-dichloromethane (**1f**) (PCl_5, $POCl_3$, cf. ref. 8) and thence the α,α′-difluoro analogue (**1g**) (SbF_3, Br_2). The yield in the last reaction (75%) is considerably greater than that achieved (12%) in a synthesis of **1g** by the nitration of diphenyl-α,α′-difluoromethane[8]. Quantitative reduction of the dinitro compound **1g** was achieved by catalytic hydrogenation over palladium on charcoal.

Synthesis of 3,3′-diaminodiphenylmethane (*1c*). A mixture of 3,3′-diaminobenzophenone (4.0 g, 0.019 mol) and amalgamated zinc (20.0 g) in ethanol (5 ml) and water (20 ml) was stirred and heated under reflux. A stream of dry hydrogen chloride gas was bubbled through the mixture for 6 h. The product was cooled, made slightly alkaline with 20% aqueous sodium hydroxide, and extracted with ethyl acetate. The organic extract was dried (Na_2SO_4) and evaporated to leave a solid that was recrystallized from a mixture of ethyl acetate and petroleum ether (b.p. 40–60°C). The product 3,3′-diaminodiphenylmethane (**1c**) (3.0 g, 80%) had m.p. 85–87°C (lit.[9] 82–83°C).

Synthesis of 3,3′-diaminobenzhydrol (*1d*). The procedure of the previous subsection was repeated with the length of time for passing hydrogen chloride gas reduced to 3 h. The crude product from ethyl acetate extraction was purified by column chromatography (silica gel) with ethyl acetate as eluant to give 3,3′-diaminobenzhydrol (**1d**) (2.85 g, 70%), m.p. 132–134°C. I.r. (KBr): 3550, 3425, 3340, 1625, 1600, 1590, 1485, 1460, 1380, 1340,1320, 1300, 1280, 1260, 1210, 1170, 1160, 1145, 1020, 990, 880, 865 and 800 cm^{-1}. ^1H n.m.r. (d_6-DMSO) (see *Figure 3* for assignments): $\delta = 4.95$ (br s, 4H, NH_2), 5.36 (d, 1H, H_E, $J = 3.8$ Hz), 5.53 (d, 1H, OH, $J = 3.8$ Hz), 6.39 (dm, 2H, H_B, $J_{BD} = 7.6$, J_{AB}, $J_{BC} = 1.0, 2.0$ Hz) (unassigned), 6.52 (br d, 2H, H_C, $J_{CD} = 7.6$ Hz), 6.58 (br t, 2H, H_A) and 6.95 ppm (t, 2H, H_D, $J_{BD} = J_{CD} = 7.6$ Hz). Assignments and coupling

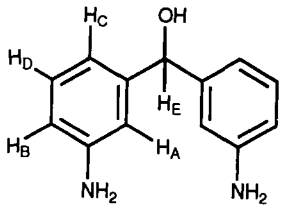


Figure 3 ^1H n.m.r. assignments for benzhydrol (**1d**)

constants were made (in part) by decoupling from H_E and H_D in separate irradiation experiments. ^{13}C n.m.r. (d_6-DMSO): $\delta = 74.9$, 112.0, 112.3, 114.2, 128.3, 146.5 and 148.2 ppm. m/z 214 ($M^{\cdot+}$), $C_{13}H_{14}N_2O$ requires 214. Found: C, 72.9; H, 6.6; N, 13.1%. $C_{13}H_{14}N_2O$ requires: C, 72.9; H, 6.5; N, 13.1%.

Preparation of 3-[(m,m′-diamino)benzhydryloxy]propyne (1e). 3,3′-Diaminobenzhydrol (428 mg, 2 mmol) and sodium hydride (48 mg, 2 mmol) were stirred in dry dimethylformamide (8 ml) at −20°C under an atmosphere of dry nitrogen for 30 min. Propargyl bromide (270 mg, 2 mmol) was added slowly and the mixture was stirred at −20°C for 4 h. Methanol (0.5 ml) was added to decompose unreacted sodium hydride, the mixture was stirred for 15 min at room temperature and then it was extracted with ethyl acetate (25 ml). The extract was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to leave a yellow oil. The product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether (2:3) eluant) to give 3-[(*m*,*m*′-diamino)benzhydryloxy]propyne (**1e**) (403 mg, 80%) as a colourless oil. I.r.: 3450 (br), 3360, 3260 (br), 3040, 2930, 2860, 2110, 1680, 1660, 1610, 1490, 1470, 1440, 1415, 1390, 1315, 1295, 1255, 1170, 1160, 1090, 1060, 1020, 995 and 870 cm^{-1}. ^1H n.m.r. ($CDCl_3$): $\delta = 2.52$ (t, 1H, $C{\equiv}C\underline{H}$, $J = 3$ Hz), 3.62 (s, 4H, NH_2), 4.2 (d, 2H, $C{\equiv}C\underline{CH_2}$, $J = 3$ Hz), 5.5 (s, 1H, $\underline{CH}O$) and 6.5–7.3 ppm (m, 8H, Ar–H). m/z 252.1267 ($M^{\cdot+}$, 96%), $C_{16}H_{16}N_2O$ requires 252.1262; m/z 198 ($M^{\cdot+}$–C_3H_2O). An analytically pure sample could not be obtained. Found: C, 73.7; H, 6.3; N, 10.2%. $C_{16}H_{16}N_2O$ requires: C, 76.2; H, 6.35; N, 11.1%.

Preparation of 3,3′-dinitrodiphenyl-α,α′-dichloromethane (1f). 3,3′-Dinitrobenzophenone (10.0 g, 0.036 mol), phosphorus pentachloride (9.8 g, 0.047 mol) and phosphorus oxychloride (1 ml) were heated at 150°C for 30 min and then 120–130°C for 4 h. Phosphorous oxychloride was evaporated under reduced pressure and the residue was recrystallized from benzene to give cream coloured 3,3′-dinitrodiphenyl-α,α′-dichloromethane (**1f**) (6.01 g, 50%), m.p. 94–96°C. I.r.: 3090, 1620, 1610, 1540, 1530, 1480, 1435, 1380, 1360, 1350, 1310, 1285, 1200, 1100, 960, 900, 835 and 800 cm^{-1}. m/z, no $M^{\cdot+}$; m/z 291 and 293 ($M^{\cdot+}$–Cl). ^1H n.m.r. ($CDCl_3$): $\delta = 7.63$ (m, 1H), 7.92 (m, 1H), 8.26 (m, 1H) and 8.51 ppm (m, 1H). Found: C, 48.0; H, 2.80; N, 8.70%. $C_{13}H_8Cl_2N_2O_4$ requires: C, 47.70; H, 2.45; N, 8.56%.

Preparation of 3,3′-dinitrodiphenyl-α,α′-difluoromethane (**1g**). 3,3′-Dinitrodiphenyl-α,α′-dichloromethane (2.67 g, 0.008 mol), antimony trifluoride (1.2 g, 0.007 mol) and bromine (three drops) were heated at 140°C for 2–3 min until the mixture became liquid. The product was cooled, washed with 20% hydrochloric acid, and recrystallized from methanol to give cream coloured 3,3′-dinitrodiphenyl-α,α′-difluoromethane (**1g**) (1.80 g, 75%), m.p. 118–120°C (lit.[9] 117–118°C). m/z 294 ($M^{\cdot+}$), $C_{13}H_8F_2N_2O_4$ requires 294. ^1H n.m.r. ($CDCl_3$): $\delta = 7.68$ (m, 1H), 7.86 (m, 1H) and 8.35 ppm (m, 2H). ^{19}F n.m.r. ($CDCl_3$): $\delta = -90.1$ ppm.

Preparation of 3,3′-diaminodiphenyl-α,α′-difluoromethane (**1h**). 3.3′-Dinitrodiphenyl-α,α′-difluoromethane (0.30 g, ~0.001 mol) in ethyl acetate (20 ml) was treated with hydrogen in the presence of 5% palladium–charcoal catalyst (10 mg) at room temperature in a conventional glass hydrogenation apparatus. After the theoretical amount of hydrogen had been consumed, the product was filtered and the solvent evaporated. The residue was recrystallized from ethyl acetate/petroleum ether to give colourless 3,3′-diaminodiphenyl-α,α′-difluoromethane (**1h**) (0.238 g, quant.), m.p. 50–52°C, m/z 234 ($M^{\cdot+}$). I.r.: 3420, 3340, 3225, 3030, 1620, 1490, 1460, 1320, 1300, 1280 (sh), 1220, 1200, 1170, 1100, 1050, 990, 890, 875 and 830 cm^{-1}. ^1H n.m.r. ($CDCl_3$): $\delta = 6.65$–7.25 (m, 8H, Ar–H) and 3.7 ppm (br s, 4H, NH_2). ^{19}F n.m.r. ($CDCl_3$): $\delta = -89.2$ ppm (m). Found: C, 67.0; H, 5.3; N, 11.9%. $C_{13}H_{12}F_2N_2$ requires: C, 66.6; H, 5.1; N, 11.9%.

Polymer synthesis and evaluation

The PMR synthetic route is a two-stage process: production of oligomeric or prepolymeric intermediates at 190°C, followed by a high-temperature/high-pressure cure schedule to produce the crosslinked resin. Full operational details are given elsewhere[10], together with those of the techniques employed in characterization of oligomers and polymers.

RESULTS AND DISCUSSION

MDA, and the analogues listed in *Figure 2* (**1c–e**, **1h**), were converted[10], with NE and BTDE, into PMR-15 oligomer (prepolymer) and related materials. These routine procedures gave highly coloured, amorphous products (*Table 1*). The average molecular weights obtained for the oligomers are recorded as polystyrene equivalents in the absence of Mark–Houwink parameters for oligomeric polyimides or a more appropriate calibration standard. The results illustrate the polydisperse nature of such oligomers, which have been demonstrated[10,11] to contain a variety of species of different hydrodynamic volume, probably related to the chain-length distribution of the oligomeric products. Fully imidized NE–diamine–NE 'model' compounds (e.g. **1i**) were synthesized for each diamine, and were identified as being present in each relevant chromatogram; these low-molar-mass materials comprise a major component of each oligomeric product.

Table 1 Molecular-weight parameters from g.p.c. for oligomeric PMR intermediates

Diamine	M_n[a]	M_w[a]	*PD*[a]	Oligomer colour
MDA	1222	3870	3.2	Orange-yellow
m-MDA	1312	7566	5.7	Yellow
FMDA	952	2325	2.4	Pale yellow
MDA–OH	1194	3345	2.8	Orange
MDA–OMA	1251	3555	2.8	Orange-yellow

[a] Determined as 'polystyrene equivalents'

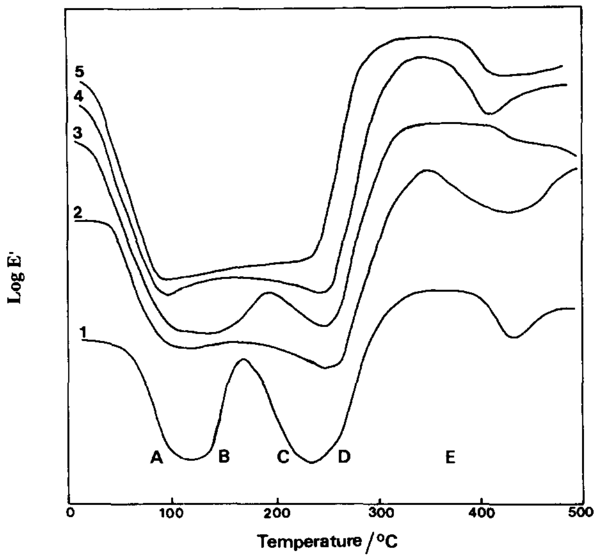


Figure 4 D.m.t.a. thermograms (E') of NE + diamine comonomers for varying diamines: (1) MDA, (2) *m*-MDA, (3) FMDA, (4) MDA-OH, (5) MDA-OMA

The *m*-MDA-containing material possesses a high-MW tail to the chromatogram, accounting for the unusually high M_w and polydispersity (PD) values. FMDA-containing prepolymer yielded the lowest molecular-weight parameters of the MDA family, which reflects the lowered basicity, and hence lowered reactivity, of fluoroalkylene-containing diamines in polyimide synthesis[12,13].

It was shown by infra-red spectroscopic analyses that the prepolymer formulations described in *Table 1* were largely imide-linked, although non-imide units were also detected; e.g. absorption due to anhydride units at 1850 cm^{-1} is generally apparent in i.r. spectra of the oligomers in addition to that of imide at 1780 cm^{-1}.

The PMR synthetic route can be modelled via dynamic mechanical thermal analysis (d.m.t.a.) through the *in situ* staging (to oligomeric intermediates) and curing of monomers supported on glass braid. This is of particular advantage in PMR systems: d.m.t.a. traces yield valuable information regarding the processes involved in the cure cycle and their effects upon the resultant matrix. In contrast, other techniques, such as d.s.c. are conspicuously ineffective in the study of either curing, or cured, PMR systems. The need to support the initial mixture of monomers for d.m.t.a. analysis means that absolute values of the real, E', and imaginary, E'', components of the tensile modulus of the resin are not accessible. It is the mechanical behaviour of the resin/glass braid composite that is examined. Consequently, in presentations of d.m.t.a. data, as exemplified by *Figures 4* and *5*, the units of E' have been omitted. (Since even changes in E' do not reflect, directly, mechanical performance of a particular resin, compared to analogous mixtures containing other diamines: the plots serve to identify temperatures marking the onset of certain processes in curing matrices or transitions in cured systems.)

D.m.t.a. traces obtained for NE + diamine comonomer mixtures are illustrated in *Figure 4* for each diamine through the complete thermal cycle (0–500°C at 5°C min^{-1}). Assignments[10] regarding the processes occurring in each region of the thermogram are discussed below (taking NE + MDA comonomer mixture as an example), and have been tested through a series of interruptive cycles and recycling experiments.

Region A (< 100°C). The tensile modulus falls as the material softens. MDA melts (90°C) and poly(amido-ester) will form and subsequently soften as T increases. Relatively large quantities of NE–MDA–NE and NE–MDA will be present at this stage, even in 'full PMR formulations'.

Region B (110–170°C). Staging, resulting in chain extension (involving BTDE in PMR formulations), will occur, resulting in production of higher-molar-mass poly(amido-esters). Imidization of NE species will increase chain stiffness. The combination of these effects results in an increase in tensile modulus, peaking at ca. 160°C.

Region C (170–250°C). As temperature increases in this region, the oligomeric mixture of polyimides and poly(amido-esters) softens, producing a rapid drop in modulus.

Region D (250–350°C). Above 250°C the onset of curing is evident (pure NE–MDA–NE would melt at 250°C). Increased rigidity in the matrix will result from both intramolecular chemistry (e.g. imidization), forming more rigid polymer backbones, and intermolecular reactions (including those involving NE decomposition), leading to formation of a crosslinked 3d network. At the higher T end of this region, the tensile modulus attains its highest value.

Region E (> 350°C). The form of the temperature dependence of the d.m.t.a. trace in this region varies according to PMR formulation but will show features of the following effects to varying degrees: (a) glass transitions of the polyimide matrix (onset ca. 400°C for NE + MDA); (b) further matrix stiffening, presumably resultant upon further crosslinking, chemical reactivity being enhanced not only by 'normal' thermal activation but also consequent upon the increased macromolecular mobility above the glass transition; and (c) degradation may be apparent at temperatures in excess of 450°C resulting in deterioration of mechanical performance (cf. NE + FMDA formulation in *Figure 4*).

The form of the d.m.t.a. trace depends upon several factors, including the stoichiometry of the PMR formulation; and it is clear from *Figure 4* that the structure of the diamine monomer also plays a major role. The *meta*-linked diamines all exhibit less matrix stiffening during the chain extension/imidization occurring in region B than does the *para*-linked MDA. This behaviour

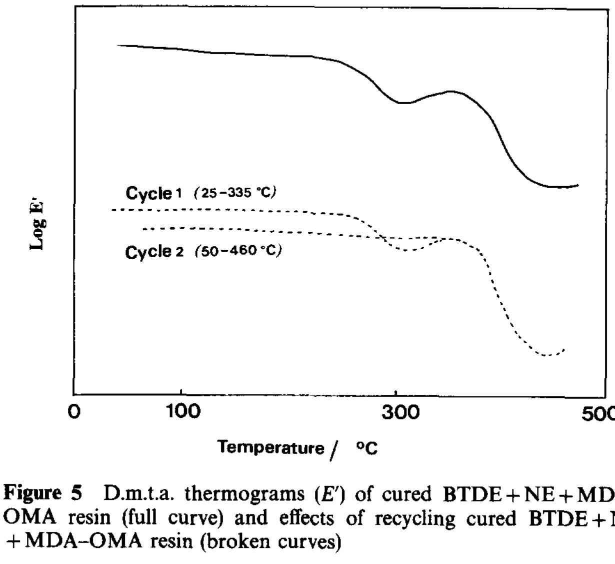


Figure 5 D.m.t.a. thermograms (E') of cured BTDE + NE + MDA-OMA resin (full curve) and effects of recycling cured BTDE + NE + MDA-OMA resin (broken curves)

Table 2 Effect of diamine structure on the physical properties of cured NE + diamine formulations

Diamine	T_g(°C)	
	E'_{onset}	$E'_{1/2}$
MDA	366	412
m-MDA	T_g not apparent	
FMDA	T_g not apparent	
MDA-OH	229	290
MDA-OMA	See *Figure 5*	

Table 3 Effect of diamine structure on the physical properties of cured PMR formulations

Diamine	T_g(°C)		
	E'_{onset}	$E'_{1/2}$	E''_{max}
MDA	293	358	361
m-MDA	161	215	207
FMDA	198	235	231
MDA-OH	189	243	245
MDA-OMA	263	284	304[a]

[a] Loss peak ill-defined

also carries through to d.m.t.a. studies of PMR formulations incorporating BTDE where NE–diamine–NE species are a major component and act as an efficient plasticizing agent[10]. The inherent stiffness introduced into PMR polyimide intermediates as the BTDE and imide content is increased is offset somewhat by this mechanism, and points to these materials retaining a degree of tractability prior to the onset of crosslinking for even relatively high chain lengths. This may enhance the processability of such systems during the fabrication of large structural components.

It should be noted that the features evident in the d.m.t.a. trace at temperatures in excess of 350°C (region E) are not necessarily the same as those obtained in braids cured using the standard cure cycle. In the present work, the absence of applied pressure would cause loss of cyclopentadiene (from decomposition of the NE 'end-caps' of the oligomers), whereas the conventional PMR cure cycle would ensure incorporation of cyclopentadiene in the crosslinked resin.

The glass transitions of braid-supported, fully cured NE + diamine resins are given in *Table 2*. (These resins were prepared from oligomeric species staged at 190°C (as described in the 'Experimental' section) by a standard high-temperature/high-pressure cure cycle, as previously described[10]). No glass transitions are apparent for the FMDA- or *m*-MDA-containing resins. NE + MDA-OMA resin shows unusual features when examined by d.m.t.a. (*Figure 5*). The temperature dependence of the tensile modulus shows two transitions (at 277 and 392°C) during the thermal cycle from room temperature to 500°C, together with a degree of matrix stiffening after the initial transition and prior to the second transition. In a separate d.m.t.a. experiment on freshly cured material, the heating cycle was terminated at 335°C (i.e. at the onset of the second transition); cf. cycle 1, *Figure 5*. Upon cooling to room temperature, a reduced value of E' was recorded for the resin. Subsequent analysis (cycle 2, *Figure 5*) revealed that the 'first transition' is eliminated following the thermal treatment of cycle 1: a single glass transition with T_g ($E'_{1/2}$) of 395°C is observed in cycle 2.

Inclusion of MDA-OMA monomer introduces the possibility of ethynyl crosslinking mechanisms in addition to the standard PMR norbornenyl crosslinking mechanism. The onset of crosslinking for ethyne units generally occurs at slightly higher temperatures than that from the norbornene retro Diels–Alder reaction, and it is possible that this PMR formulation can undergo crosslinking by both mechanisms. If the 'conventional' cure cycle adopted in preparation of the resins studied in this work (218°C for 50 min followed by 330°C for 4 h under 20 atm pressure of N_2)[10] leaves a proportion of unreacted propargyl units within the matrix, further reaction may become apparent in subsequent examination by d.m.t.a. In other words, macromolecular mobility above the first glass transition (at 227°C) in freshly cured resin would allow further crosslinking to occur, which would result in the observed matrix stiffening and raised (or second) glass transition. Interestingly, the linear polyimide derived from BTDE + MDA-OMA possessed a T_g of 277°C ($E'_{1/2}$; E''_{max} 282°C) and showed considerable matrix stiffening above the glass transition, presumably due to ethynyl crosslinking.

Glass transition temperature data for PMR resins incorporating BTDE are given in *Table 3*. All the *meta*-linked diamines produced resins of significantly lowered T_g compared to that obtained for PMR-15 (containing *para*-linked MDA). The effect of PMR stoichiometry on resin T_g is presented in *Tables 4–6* for MDA, MDA-OH and MDA-OMA. Cured PMR formulations of MDA + BTDE + NE exhibit a lowering of the glass transition temperature as the stoichiometry of the polyimide (backbone vs. end-cap) increases; this is a reflection of the increasing contribution of BTDE species to the matrix backbone resulting in behaviour closer to linear BTDE–MDE polyimide systems (lit.[14] T_g 290°C).

Replacement of MDA by MDA-OH produced resins that showed no systematic variation of T_g with stoichi-

Table 4 Glass transition data (d.m.t.a., 10 Hz) for cured PMR (BTDE/MDA/NE) formulations of varying stoichiometry

Stoichiometry[a]	T_g(°C)		
	E'_{onset}	$E'_{1/2}$	E''_{max}
$n=0$	366	412	–
$n=1$	312	370	369
$n=2$	293	358	361
$n=3$	229	286	(265)[b]
$n=4$	230	274	290

[a] n = repeat unit in oligomer (see *Figure 1*)
[b] Loss peak ill-defined

Table 5 Glass transition data for cured PMR (BTDE/MDA-OH/NE) formulations of varying stoichiometry

Stoichiometry[a]	T_g(°C)		
	E'_{onset}	$E'_{1/2}$	E''_{max}
$n=0$	229	290	–
$n=1$	157	241	249
$n=2$	189	243	245
$n=3$	239	279	287
$n=4$	205	261	267

[a] n = repeat unit in oligomer (see *Figure 1*)

Table 6 Glass transition data for cured PMR (BTDE/MDA-OMA/NE) formulations of varying stoichiometry

	T_g(°C)		
Stoichiometry[a]	E'_{onset}	$E'_{1/2}$	E''_{max}
$n=0$		See *Figure 5*	
$n=2$	263	284	304[b]
$n=4$	218	274	276

[a] n = repeat unit in oligomer (see *Figure 1*)
[b] Loss peak ill-defined

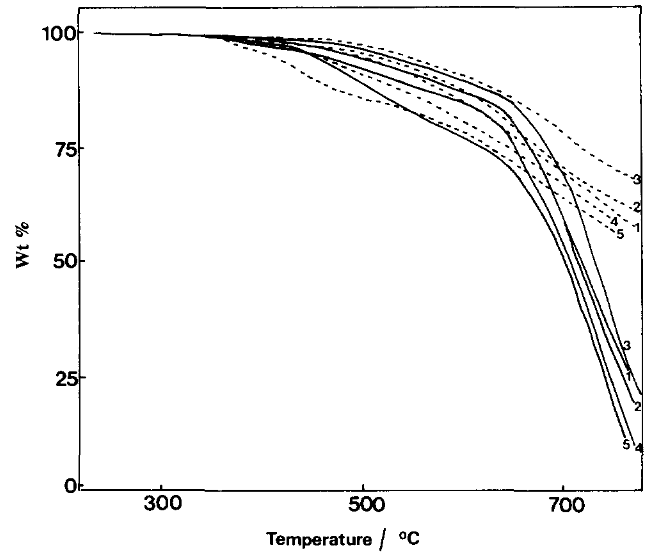


Figure 6 Thermogravimetric analysis of cured resins in N_2 (broken curves) and air (full curves) for varying diamines: (1) MDA, (2) *m*-MDA, (3) FMDA, (4) MDA-OH, (5) MDA-OMA

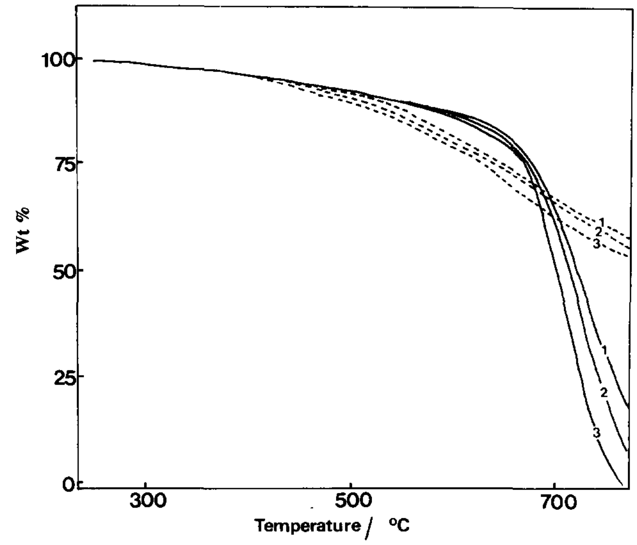


Figure 7 Thermogravimetric analysis of cured BTDE + NE + MDA-OH resins in N_2 (broken curves) and air (full curves) for varying stoichiometry: $n=1$, $n=2$ and $n=3$

ometry. Benzhydrol-type tetracarboxylic acid dimethyl esters when incorporated into linear polyimides undergo a disproportionation reaction at 270°C[15] producing linking units of $-CH_2-$ and $-CO-$ with H_2O evolved as a volatile residue. The presence of a small molecule within the matrix in variable quantities, and a multiplicity of polyimide types as random copolymer segments, may be expected to generate non-predictable physical properties as encountered with MDA-OH-containing resins.

The inclusion of MDA-OH into PMR resins also lowers the thermal stability of these resins relative to comparable formulations containing most of the other diamines (*Figure 6*). Increasing stoichiometry, and hence increasing MDA-OH content, also results in decreasing thermal stability of the resin (*Figure 7*). Resins incorporating MDA-OMA exhibit lower thermal stability than the equivalent MDA-OH-containing resin. One explanation might be that residual, unreacted propargylic ether units might influence the thermal behaviour of the resin. Being aliphatic in character, they would be expected to be more labile than closely related aromatic polyimide counterparts.

The fluorine-containing FMDA produced a resin of higher thermal stability than PMR-15 (see *Figure 6*). This feature is in general accord with work[16] on linear polyimide systems containing much longer fluoroalkylene chains.

The difference in stability of the *m*-MDA- and MDA-containing PMR resins is minimal. This is in contrast to data reported[9,17] for linear polyimides, although the literature contains contradictory reports. For example, Bell *et al.*[9] found that *meta* linkages provided polyimides of higher stability, whilst Dine-Hart and Wright[17] found *para* linkages to be more resilient. No explanation was offered to account for the differences in stability, although both papers highlight the difficulties inherent in producing polyimides of reproducible thermal stabilities whilst employing the same monomers and imidization conditions.

CONCLUSIONS

New diamine monomers, related to MDA, have been synthesized, including a novel compound containing an acetylenic group. The polymerization of monomers to oligomeric intermediates and cured resins proceeded smoothly and all diamines used showed characteristics indicative of good processability. Sufficient data have been produced to indicate the chemical and physical complexities inherent in cured PMR formulations incorporating MDA-OH or MDA-OMA. Enhanced thermal stability is achieved through incorporation of the difluoromethylene-linked FMDA.

ACKNOWLEDGEMENT

The authors would like to thank BP International plc for permission to publish this paper.

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