Structure–Property Relationships in Polymerization of Monomeric Reactant Type Polyimide Resins. 2. New Polyimides Incorporating Alkylenedianilines[1]

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ABSTRACT: New polyimide thermoset resins have been synthesized incorporating alkylenedianilines as the diamine components. The variations in intrinsic chain mobility resultant upon differences in the alkylene chain lengths produced cured resins which exhibited a wide range of T_g values (290–386 °C). The structural variants of diamine within the resin formulations also effected lowering of the apparent onset temperatures for cross-linking, during cure, as the alkylene "spacer" units were extended. All resins exhibited good thermal and thermooxidative stabilities, with temperatures for 10% weight loss in the region of 450–500 °C.

1. Introduction

Advanced composites have become an established high-performance structural material over the last 20 years, and their use in the aerospace industry is expanding. The primary driving force for the use of composites lies in the weight and cost savings achieved.[2] The stiffness/weight and strength/weight ratios for advanced composites are superior to those for traditional metal/metal alloy construction materials.

In applications where continuous use temperatures do not exceed 130 °C, epoxy-based composites have dominated the technology. However, use of state-of-the-art epoxies is limited to temperatures of around 150 °C while there is a requirement within the aerospace industry for advanced composites capable of surviving higher temperatures. Aeroengines are a prime example.

Materials initially developed to meet these more demanding performance criteria concentrated on the synthesis of polymers that contained mainly aromatic and heterocyclic units such as polyimides. Early polyimides, while possessing outstanding thermal stability, presented severe processing problems. These problems were partially overcome through the development of the reverse Diels–Alder (RDA) curing mechanism.[3] However, polyimide resins have become viable engineering materials largely as a result of the introduction of the PMR (polymerization of monomeric reactants) approach to polyimide synthesis.[4,5] The leading high-temperature resin systems available today are the NASA developed PMR-15 (see Figure 1) and the modified or second generation PMR polyimides.[6–8]

PMR polyimide properties are dependent on polymer structure.[9,10] Improved resin characteristics will be achieved through a better appreciation of the basic structure–property relationships which apply to PMR polyimides. In this work, we seek to establish the role played by diamine flexibility in the determination of resin properties. Inclusion of an alkylenedianiline series of varying chain length allows subtle flexibility variation in the macromolecular backbone without significant alteration of the chemical identity of the polyimide.

2. Experimental Section

2.1. Materials (cf. Table I). Benzophenonetetracarboxylic diacid diester (BTDE), nadic acid ester (NE), and bis(4-aminophenyl)methane (methylenedianiline, MDA) were used as supplied by BP International plc. Bis(4-aminophenyl)ethane (ethylenedianiline, EDA) was obtained from Aldrich and 4,4′-diaminobiphenyl (benzidine, BENZ) from Fluka. Bis(4-aminophenyl)propane (propylenedianiline, PDA) and bis(4-aminophenyl)butane (butylenedianiline, BDA) were synthesized via the route illustrated (Figure 2), involving nitration of the appropriate diphenylalkane followed by catalytic reduction of the 4,4′-dinitro compound. The preparation of PDA via known intermediates[11] was carried out following literature methods,[12] but BDA monomer and intermediate compounds were previously undocumented.

2.1.1. Preparation of 1,4-Diphenylbutane. 1,4-Diphenylbutane was prepared from bromobenzene, sodium, and 1,4-dibromobutane in diethyl ether by the method of van Alphen[11] in 94% yield [bp 108–109 °C (0.1 Torr), mp 52 °C]. The material was used in the nitration step without purification to analytical standard.

2.1.2. Preparation of 1,4-Bis(4′-nitrophenyl)butane. This compound was prepared in 42% yield by the general method of ref 12 but was purified by column chromatography (silica gel, ethyl acetate/petroleum ether (5:95) eluant) to give a product with mp 131–135 °C, IR ν_{max} (KBr) 1520 and 1340 (NO_2), ^1H NMR ($CDCl_3$) δ 1.6–1.8 (m, CH_2, 4p), 2.6–2.8 (m, CH_2, 4p), 7.2 and 8.1 (A_2B_2, Ar–H, 8p), MS m/z 300 (M^+). $C_{16}H_{16}N_2O_4$ requires 300. The compound was used in the reduction step without purification to analytical standard.

2.1.3. Preparation of BDA. This was prepared from bis-(4-nitrophenyl)butane as follows. Bis(4-nitrophenyl)butane (9.0 g, 0.03 mol) was catalytically hydrogenated (H_2, 5% Pd–C) in ethyl acetate (50 mL), in a conventional glass apparatus. The product was filtered through Celite, and the solution was evaporated under reduced pressure to dryness. The residual off-white solid was purified by column chromatography (silica gel, methanol/chloroform (3:97) eluant) to give BDA (6.1 g, 85%): mp 86.5–88 °C, IR ν_{max} (KBr) 3380, 3320, and 3200 cm^{-1} (NH_2), ^1H NMR ($CDCl_3$) δ 1.4–1.8 (m, CH_2, 4p), 2.4–2.7 (m, CH_2, 4p), 3.3–3.7 (s, br, NH_2, 4p), 6.5–7.2 (m, Ar-H, 8p), MS m/z 240 (M^+). $C_{16}H_{20}N_2$ requires 240. Found: C, 79.7; H, 8.6; N, 11.8. Calcd for $C_{16}H_{20}N_2$: C, 80.0; H, 8.3; N, 11.7.

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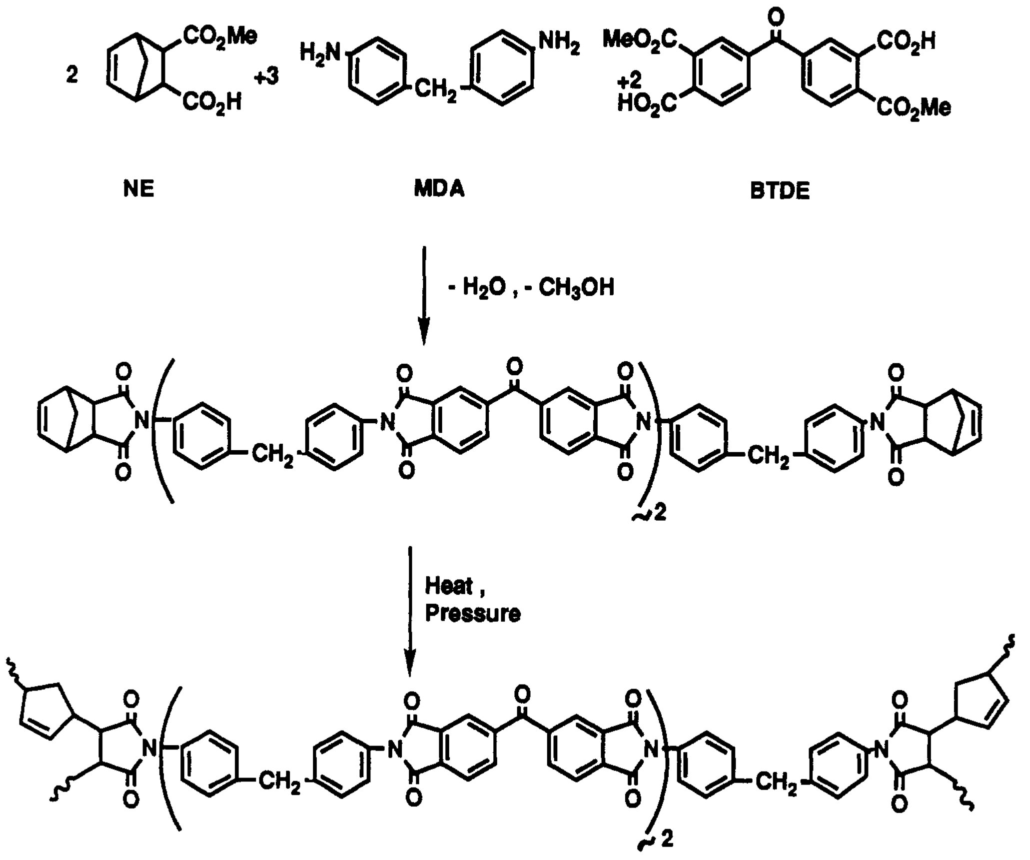
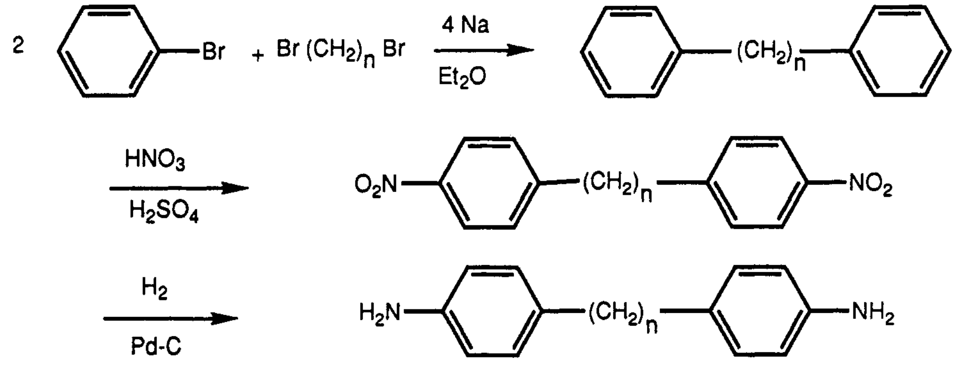


Figure 1. Synthesis of PMR-15.

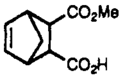
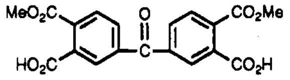
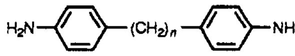


PDA (n =3)
BDA (n =4)

Figure 2. Synthesis of PDA and BDA.

2.2. Polymer Synthesis and Evaluation. Details of the synthetic route to the oligomeric and polymeric products and of the physicochemical characterization techniques employed are given elsewhere.[2,10] The PMR synthetic route is a two-stage process involving the production of oligomeric polyimides from homogeneous monomer mixtures (the stoichiometry of which is given in Table I) at 190 °C followed by a cure schedule including a final cure at 335 °C under 20 bar N_2 pressure. Dynamic mechanical thermal analysis (DMTA) of glass braid-supported monomer and resin formulations [using a Polymer Laboratories DMTA unit (at 20 Hz and 5 °C/min)], providing information on cure profile and ultimate resin physical properties, and thermogravimetry (in air and N_2 atmospheres) [using a Perkin-Elmer Series 7 TGA] were the principal analytical techniques employed.

Table I. Monomers Used in Polymerizations

monomer structure	acronym	rel molar quantities used used in polymns
	NE	2
	BTDE	2
	BENZ(n=0) MDA(n=1) EDA(n=2) PDA(n=3) BDA(n=4)	3

3. Results

DMTA can be used in modeling studies of PMR curing processes through the examination of glass braid-supported monomer mixtures.[1,9,10] The response of the PMR monomer formulations to DMTA characterization varies, dependent on the alkylene chain length present in the dianiline employed (Figure 3). The temperature profile for all the dianilines shows the five temperature regions evident in the thermograms obtained for PMR-15 (in-

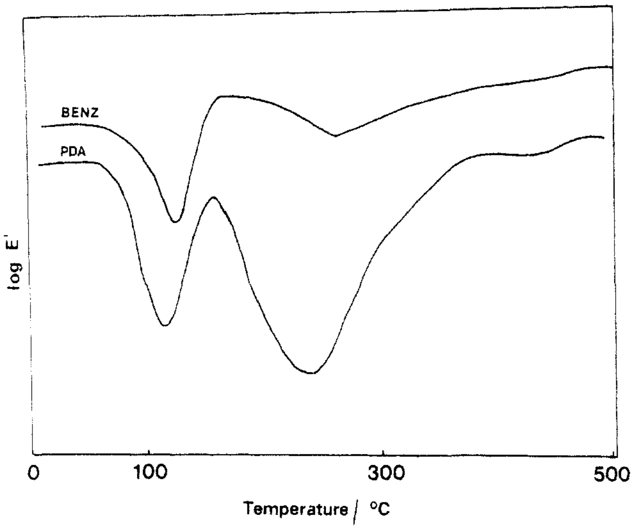


Figure 3. DMTA traces (E' vs T) for PMR monomer formulations supported on glass braid.

Table II. Cross-Linking Parameters for the PMR Monomer Formulations by DMTA

diamine	cross-linking onset T/°C	high T cross-linking
BENZ	264	√
MDA	259	√
EDA	250	×
PDA	239	√
BDA	232	√

corporating MDA).[9,10] Initial behavior (below ~170 °C) is essentially similar for all dianilines. The trough in tensile modulus (E'), observed at *ca.* 110 °C, occurs as a result of the onset of chain extension of the softening monomer/low chain length amido–ester oligomeric mixture extant at lower temperatures. The temperature-induced increase in modulus, produced by such chain extension and imidization of NE amido–ester substituents, continues until about 160 or 170 °C. Thereafter the modulus is observed, once more, to decrease as the reacting mixture softens. Higher temperature behavior shows a modulus "trough" at *ca.* 250 °C which becomes more prominent with increasing alkylene chain length. The trough marks the onset of curing of the materials. The increase in modulus, evident at higher temperatures, will result from two effects:

(i) Intramolecular reactions (imidization) will produce oligomers of more rigid character, in turn, rendering the matrix less pliant.

(ii) The resin begins to cure as a result of intermolecular interaction, *notably* that of decomposition of the NE reactive end groups (*cf.* the second step in the idealized PMR reaction scheme, shown in Figure 1).

In addition to exaggeration of the tensile modulus trough marking the onset of cure, increasing the alkylene chain length also results in lowered onset temperatures for the NE cross-linking reaction evident in the DMTA traces (Table II). Once curing is complete, the modulus of the resin attains its ultimate value. In some instances, a further drop in modulus is observed at temperatures greater than 400 °C. This trend reflects the effects of the "tail end" of the glass transition region of the cured resin.

The limited molecular mobility conferred upon the cross-linked resin by the "subdued" glass transition may allow further cross-linking to occur, evident through a further increase in E'. Most of the PMR formulations containing the alkylenedianilines show a degree of additional cross-linking in this higher temperature region.

Table III. Physical Properties of PMR Resins Incorporating the Various Alkylenedianilines

	T_g/°C		
diamine	E'(onset)	E'($^1/_2$)	T(deg)[a] onset/°C
BENZ	304	386	>500
MDA	293	358	481
EDA	272	334	477
PDA	197	286	>500
BDA	211	295	>500

[a] Onset of degradation of mechanical integrity.

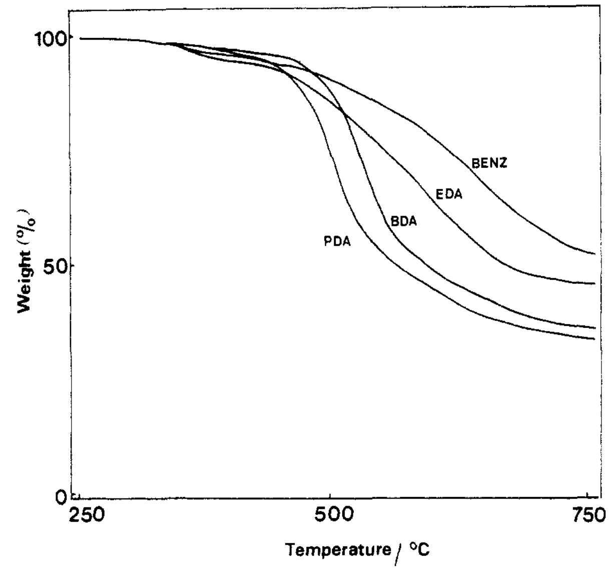


Figure 4. Thermogravimetric analysis of cured resins in nitrogen.

The glass transition of the cured resins may be conveniently studied by DMTA. (The effect of the transition in such highly cross-linked systems is too small to be detected by DSC.) The transition temperature is a function of the diamine employed in the PMR formulations. Data on the glass transition temperatures of the cured resins (Table III) reveal a steady decrease in the temperature of the transition as the alkylene chain length increases from BENZ through to PDA: The PMR resin containing BDA exhibits a T_g similar to that containing PDA. The onset of degradation of mechanical integrity for the resin during DMTA operation is well above the glass transition in every case.

Thermogravimetric analyses of the cured resins in both nitrogen and air (illustrated in Figures 4 and 5) indicate the high thermal resilience of all alkylenedianiline-based PMR polyimides.

4. Discussion

It is clear from the DMTA data obtained on the PMR formulations incorporating alkylenedianiline monomers that the inherent flexibility within the dianiline (resultant upon varying the alkylene chain length) plays a major role in the determination of both the PMR reaction profile and the resultant physical properties of the cross-linked resin networks.

The increasing flexibility available within the alkylenedianiline series as the alkylene chain increases from BENZ(n=0) to BDA(n=4) provides for thermosets with inherently greater macromolecular mobility within the polyimide backbone, without significant alteration of the physicochemical nature of the repeat unit. This increase in the freedom of motion available within the resin results in a regular decrease in the temperature of the glass transition from 386 °C (BENZ) to ~290 °C (PDA and

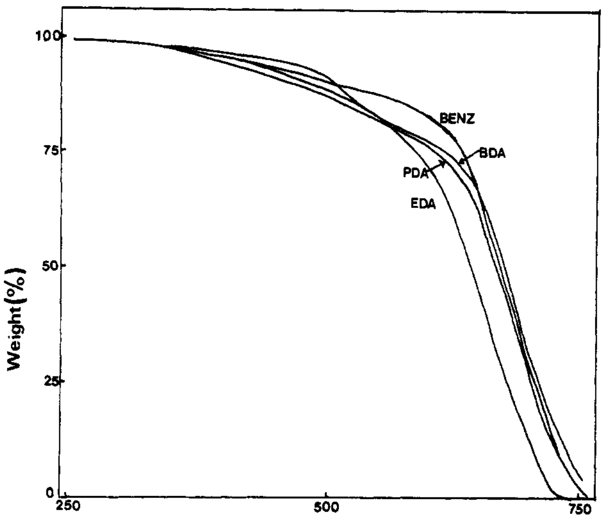


Figure 5. Thermogravimetric analysis of cured resins in air.

BDA). At these latter chain lengths, the T_g are of similar value. This perhaps reflects the similarity of the relatively less inhibited segmental motion available to the polyimide backbone, when incorporating either PDA or BDA into the structure, through the weakening influence on chain rigidity which the linking $(CH_2)_3$ or $(CH_2)_4$ units introduce. In contrast, the rigidity imparted to resins incorporating BENZ diamine derives from the restricted motion of the central biphenyl unit present in the imide repeat structure and results in the high transition temperature observed for this formulation.

The cross-linked PMR polyimides evince glass transitions (*cf.* Table III) at temperatures in excess of those obtained from comparable linear polyimide systems. The linear polyimide derived from BTDA + MDA possesses a transition at 290 °C,[13] considerably below that of the corresponding PMR resin (*ca.* 358 °C). In the BTDA + BENZ linear system, glass transition temperatures have been quoted as either 346[14] or 382 °C,[15] compared to that of 386 °C for the PMR system. No literature data exist for linear polyimides comprising BTDA + EDA, PDA, or BDA. The cross-links present in PMR polyimides also somewhat offset the effects of the increased flexibility within the differing dianiline structures (e.g., BENZ versus MDA). The difference in temperature of the glass transitions of the PMR resins containing BENZ or MDA is significantly less than that observed for the corresponding linear polyimides. The effect is such that an increase in the alkylene chain from $n = 0$ to $n = 4$ in the $(CH_2)_n$ units within the PMR polyimides produces a shift in T_g which is roughly equivalent to that resultant upon an increase from $n = 0$ to $n = 1$ in *linear* systems.

The onset of prepolymer cross-linking through nadic end-cap reactions (observed during DMTA modeled curing studies, as the polyimide matrix stiffens and the modulus increases) shows an inverse relationship with alkylene chain length (*cf.* Table II). The reason behind this reduction in cross-linking onset temperature with increasing chain length is not obvious. The increasing mobility of the diamines BENZ ≪ MDA < EDA < PDA ∼ BDA may facilitate more efficient cross-linking (and possibly a slightly higher cross-link density in the resultant resin), but simple increased physical motion should not, of itself, cause lowered onset temperatures. Clearly, rationalization of the dependence of cure temperature upon diamine characteristics must be sought through considerations of structural influences other than mobility alone. Indications of a plausible explanation of the influence of alkylene chain length upon cross-linking reactivity may be apparent in reports of attempts to lower cure temperatures through variations in end-cap structure, as discussed below.

It has been the aim of several studies to effect a reduction in the temperature requirement of the cure schedule for PMR resins. This has been achieved through introduction of *m*-aminostyrene end-cap[16] or mixed end-cap systems including *p*-aminostyrene[17] or *N*-phenylnadimide.[18] Substituted nadimides have also been successfully employed in this context.[19,20] The rationale behind the success of these compounds is that they generate stable radicals, able to promote reaction at lower temperatures. No reduction in cure temperature has yet been identified from the inclusion of different non-end-cap species. However, the work of Alston[21,22] is particularly relevant to the present study. He prepared PMR polyimide resin composites in which MDA was replaced, separately, by bis(4-aminophenyl) ether (ODA) and 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane. It was found that MDA played a key role in obtaining high-temperature mechanical properties and in obtaining low weight losses from the composite during isothermal aging at 316 °C. It is probable that the highly reactive benzylic methylene of MDA is of importance in synergistic cross-linking with the nadimide end cap.[21,22] In the alkylenediamine series, the presence of greater quantities of abstractable aliphatic protons (and hence possible radical sites) as the chain length increases may lead to increased probability of stable radicals (i.e., substituted benzylic radicals, after rearrangement) being formed. These radicals would then facilitate the cross-linking reaction as in the case of the end-cap systems. Alternatively, the softening of the oligomeric mixture might simply be enhanced by the presence of longer chain dianilines. (The onset of cure in PMR-15, in which the alkylenedianiline is MDA, occurs at 250 °C.[10] This happens to coincide with the melt temperature of the NE–MDA–NE[10] model compound, which is a relatively highly concentrated component within the oligomeric constituents of the matrix at this stage.[10] Unfortunately, melting point data for other NE–alkylenedianiline–NE model compounds are not available). In view of the complexity of the staged oligomeric mixtures involved, the melting point of a single (albeit dominant) component might not be the parameter principally effective in determining the onset of cure. [It should be noted that, in our experience, the diamine constituent generally exercises limited control upon the cure onset temperature (e.g., see ref 23 and publications to follow from this continuing research program)].

A further possibility could be that the lengthening alkylene chain of the diamine series provides a greater aliphatic proportion of the polyimide backbone with which the aliphatic (alicyclic) norbornene end caps can associate. Thus the presence of purely aliphatic regions (or domains) may arise within the bulk polyimide. The miscibility of any aliphatic region within the prepolymeric and formative resin matrix toward reverse Diels–Alder (RDA) reaction products will be greater than that for the otherwise aromatic polyimide structure. Any synergistic interaction arising from such compatibility may stabilize the transition state and lead to a reduction in the activation energy of the RDA reaction, and hence lead to the lowered onset temperatures apparent for cross-linking.

Whatever the cause of the observed behavior, a lowering of the cure temperature will be beneficial to the ultimate resin, resulting in lower thermal stresses in the matrix[24] in addition to less severe processing conditions being required during resin production.

The thermogravimetric analysis of the cured resins under nitrogen may indicate a more efficient or "cleaner" cross-linking taking place with the introduction of longer alkylene chains. The loss of weight of resins containing BENZ and EDA at 350–450 °C is thought to arise from the decomposition of double Diels–Alder adducts and related species which have been shown[25,26] to be produced during the cure of phenylnadimides. This initial weight loss is essentially absent in PDA- and BDA-containing resins. It seems unlikely that double Diels–Alder adducts arising in PDA and BDA resins are more stable than those for the other resins, and their enhanced stabilities would seem to point to a significantly lower double Diels–Alder adduct content within the PDA/BDA resins. This may be indicative of a more "classical" cross-linking taking place (as illustrated in the "idealized" PMR scheme of Figure 1) and also results in dynamic thermogravimetric data more akin to those observed in linear polyimides[27] than has previously been observed in PMR systems. It may be advantageous to conduct model compound studies with a view to clarifying this area further and to examine whether incorporation of a small PDA or BDA content in "conventional" PMR polyimides would lead to more efficient cross-linking in these polymers without significant deterioration of resin properties.

However, it cannot be ruled out that PDA/BDA resins have a different mode of decomposition from the other resins, especially since, in thermooxidative decomposition, PDA/BDA resins evince weight loss above 450 °C through multiple or competing pathways in contrast to that evident for the other resins.

5. Conclusions

The work reported in this paper has focused on producing chemically equivalent PMR polyimide resins of controlled flexibility and examining the effect structural variation plays in the determination of resin properties. The main observations are listed below:

1. New monomer synthesis has extended the range of alkylenedianiline monomers available for polyimide production.
2. PMR resin production including these monomers proceeds smoothly to good quality thermosets.
3. A wide range of resin T_g values is accessible through dianiline structural variation.
4. Lowered apparent onset temperatures for resin cure are observed with longer chain alkylene dianilines.
5. Good thermal and thermooxidative resilience is shown by all PMR resins examined.

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