Polyimides derived from 2-methyl-2-propyl-1,3-bis(4-aminophenoxy)propane and 2,2-dimethyl-1,3-bis(4-aminophenoxy)propane

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(Received 10 October 1993; revised 25 October 1993)

A new series of thermoplastic polyimides derived from 2,2-dimethyl-1,3-bis(4-aminophenoxy)propane (MD) and a new diamine 2-methyl-2-propyl-1,3-bis(4-aminophenoxy)propane (MPPD) have been prepared and characterized. These materials were selected on the basis of their potential to serve as low-cost matrix resins able to perform at 170°C. They were synthesized from reasily available aromatic dianhydrides such as 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and the above diamines. The glass transition temperature (T_g) and crystalline melt temperature (T_m) of these polymers containing flexible alkylene-dioxy units varied from 200 to 230°C and from 300 to 375°C, respectively. Polymers decomposed in air between 435 and 455°C as witnessed by thermogravimetric analysis. Work was focused on the polymer prepared from 4,4′-oxyphthalic anhydride (ODPA) and MPPD, which had a T_g of 200°C and could be readily melt processed below 305°C.

(Keywords: thermoplastic polyimides; synthesis; thermal properties)

INTRODUCTION

In the last few years, as a result of continuing efforts on high-performance structural resins, adhesives and composite matrices for advanced aerospace applications, several new aromatic polyimides containing ether linkages between aromatic rings have been prepared[1–6]. The work reported here was undertaken as part of a continuing programme on high-performance thermoplastic composites where the major objective was to develop novel processing and fabrication techniques, as well as relationships between neat resin properties and composite performance. The work was driven by the material requirements for commercial aircraft applications, which include the following: high resin modulus of at least 3 GPa; toughness, preferably of the ductile failure mode; the ability to perform at 100°C as witnessed by a glass transition temperature (T_g) of at least 175°C; and low manufacturing cost as well as good processability. To this end, the syntheses and evaluation of several new thermoplastic polyimides with potential use as matrix materials for carbon-fibre-reinforced composites have been carried out.

Several of the polyimides already under development in this laboratory have considerable promise in this area[6,7], especially PI-2, which is prepared from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 2,2-dimethyl-1,3-bis(4-aminophenoxy)propane (MD). Both the neat resin and its fibre-reinforced composites exhibit excellent properties[7]. However, its melt processability still presents some difficulties owing to crosslinking with apparent decomposition at temperatures slightly above its melting point (T_m). One way to lower the processing temperature is to reduce crystallinity or to lower the T_m significantly below the crosslinking temperature (~320–330°C). To achieve this objective, a new asymmetric diamine of structure similar to MD, 2-methyl-2-propyl-1,3-bis(4-aminophenoxy)propane (MPPD), has been synthesized. The synthesis and the properties of a new series of polyimides based on both MD and MPPD are described herein.

EXPERIMENTAL

N-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc) and *N*,*N*-dimethylsulfoxide (DMSO) were distilled under reduced pressure over calcium hydride prior to use; *m*-cresol was distilled under reduced pressure over phosphorus pentoxide (P_2O_5).

Monomers

Anhydrides. 3,3′4,4′-Benzophenonetetracarboxylic dianhydride (BTDA), 4,4′-oxyphthalic anhydride (ODPA), 3,3′,4,4′-biphenyltetracarboxylic anhydride (BPDA) and 3,3′,4,4′-diphenylsulfone dianhydride (DSDA) were obtained from commercial sources and were sublimed under reduced pressure yielding off-white solids.

2,2-Dimethyl-1,3-bis(4-aminophenoxy)propane (MD). This was prepared according to the procedure described in ref. 7 as follows. The dinitro-substituted precursor was synthesized by reaction of 1-chloro-4-nitrobenzene with 2,2-dimethyl-1,3-propanediol, followed by recrystalliza-

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0032-3861/94/20/4456–06

Table 1 Properties of MPPD and MD polyimides

Code	Polymer	η_{inh}[a] (dl g^{-1})	Film quality	Solubility[b] NMP	DMAc	*m*-Cresol
4a	BTDA/MPPD	0.75	Tough, flexible	sp(h)	i	s(h)
	BTDA/MPPD-1[c]	1.23	Opaque, brittle	sp(h)	i	s(h)
4b	BTDA//MPPD/MD	0.71	Tough, flexible	sp(h)	i	s(h)
	BTDA//MPPD/MD-1[c]	0.90	Opaque, tough	sp(h)	i	s(h)
4c	ODPA/MD	0.83	Tough, flexible	s(h)	i	s
4d	ODPA/MPPD	0.77	Tough, flexible	s	s(h)	s
4e	BPDA/MD	0.99	Opaque, brittle	i	i	s(h)
4f	BPDA/MPPD	0.92	Opaque, brittle	i	i	s(h)
4g	DSDA/MD	0.24	– (poor)	s	s	s
4h	DSDA/MPPD	0.30	– (poor)	s	s	s

[a] Inherent viscosity in *m*-cresol at 30°C with a concentration of 0.5 g dl^{-1}
[b] Solubility tested at 15% (w/w) for 24 h at room temperature. If insoluble, samples were gently heated. Solubility: s = soluble; sp = sparingly soluble; i = insoluble; (h) = heated
[c] Polymer obtained by the one-step method in *m*-cresol

tion from ethyl acetate (m.p. 165–166°C). The hydrogenation of this compound over a Pd/C catalyst and recrystallization from ethanol gave the desired diamine in 85% yield, m.p. 115–116°C (lit.[11] m.p. 115–116°C).

2-Methyl-2-propyl-1,3-bis(4-nitrophenoxy)propane. This was prepared following a similar route to MD. A solution of 1-chloro-4-nitrobenzene (78.8 g, 0.50 mol), 2-methyl-2-propyl-1,3-propanediol (26.4 g, 0.20 mol) and K_2CO_3 (41.4 g, 0.30 mol) in 100 ml of DMSO was stirred and heated at reflux under nitrogen (N_2) for 24 h. The mixture was then allowed to cool to room temperature, and poured into 1.5 litres of ice/water. The precipitate was collected by filtration, washed several times with water, ethanol and ether, and then dried at 70°C under reduced pressure. The product was recrystallized twice from ethanol to give 66.0 g (84%) of pale yellow crystals: m.p. 125–126°C. Analysis calculated for $C_{19}H_{22}N_2O_6$: C, 60.96%; H, 5.88%; N, 7.48%. Found: C, 60.78%; H, 6.01%; N, 7.40%.

2-Methyl-2-propyl-1,3-bis(4-aminophenoxy)propane (MPPD). The dinitro-substituted intermediate (20.00 g, 0.053 mol), 0.48 g of 5% Pd/C and 100 ml of methylene chloride (CH_2Cl_2) were placed in a 250 ml Parr pressure bottle. The bottle was charged with 4 atm of hydrogen and agitated for 20 h at room temperature. The reaction mixture was filtered, and the filtrate was concentrated under reduced pressure to afford an oil. The oil crystallized from a 1/1 mixture of ethanol/water upon storage at −10°C for 2 days. The crystals were collected by filtration, washed with water and dried under reduced pressure. A few crystals were separated and the rest were recrystallized. The filtrate was seeded with the previously separated crystals and allowed to stand for 24 h at −10°C. During this time, white needles were formed to afford, once dried, 12.0 g (72%) (m.p. 42–43°C). ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 6.66 (q, 8H, aromatic), 3.74 (d, 4H, $-CH_2O$), 3.35 (s, 4H, NH_2), 1.41 (m, 4H, $-C-CH_2-CH_2$), 1.04 (s, 3H, $-C-CH_3$), 0.89 (t, 3H, CH_3-CH_2-). Analysis calculated for $C_{19}H_{26}N_2O_2$: C, 72.61%; H, 8.28%; N, 8.92%. Found: C, 72.01%; H, 8.42%; N, 8.62%.

Polymer synthesis

Two-step method. The dianhydride (6.36 mmol) was slowly added to a stirred solution of the diamine (6.36 mmol) in NMP (solids content 15% w/w) under N_2 at room temperature. After the solution was stirred for 24 h, 9.54 mmol of triethylamine and 9.54 mmol of acetic anhydride were added. Some of the polymerization solutions gelled almost immediately after addition of the anhydride. The gel usually dissipated after stirring overnight at room temperature to form a viscous yellow solution. This solution was then poured into 400 ml of rapidly stirred ethanol. The precipitate that formed was collected by filtration, washed with ethanol and then dried under reduced pressure, at 150°C for 4 h, and again at 250°C for 2 h. Typical yield was 95%.

Once isolated, the solubility of the polymers in NMP was greatly reduced. Most of them could not be redissolved at room temperature, as shown in *Table 1*.

One-step method. The dianhydride (6.36 mmol) was added to a stirred solution of the diamine (6.36 mmol) in *m*-cresol (15% solids w/w) containing three drops of isoquinoline under a rapid N_2 flow. The reaction mixture was slowly heated to 200°C. The solution was then heated at reflux for 3 h. During this time, the water of imidization was removed by distillation and any *m*-cresol lost was replaced so as to keep the total volume of the solution constant. After cooling, the polymer was isolated by pouring the yellow, viscous reaction mixture into a blender containing 700 ml of 95% ethanol. The fibrous precipitate that formed was collected by filtration, washed with ethanol and ether, and dried under reduced pressure at 125°C for 4 h and again at 250°C for 2 h. Yields were higher than 90%.

Characterization

Infra-red and nuclear magnetic resonance spectra. These were recorded on Beckman FT2100 and Varian Gemini 200 spectrometers, respectively.

Inherent viscosities. These were measured in a Canon Ubbelohde No. 200 viscometer using *m*-cresol solutions containing 0.5 g dl^{-1} of polymer at 30°C.

Elemental analyses. These were carried out by Galbraith Laboratories Inc., Knoxville, Tennessee.

Solubility. Solubility of the polyimides was tested qualitatively at room temperature with 15 wt% solutions of NMP, DMAc and *m*-cresol; if insoluble after 24 h they were gently heated.

Differential scanning calorimetry. D.s.c. was performed on a DuPont 1090 Thermal Analyzer at a heating rate of 10°C min^{-1} under nitrogen atmosphere. Samples were heated to 400°C in the first run, quenched and rerun. For semicrystalline polyimides, crystalline melt temperatures (T_m) were taken as the minima of the melting endotherm. The glass transition temperatures (T_g) were obtained from the second heating run at the inflection point in the change in heat capacity.

Thermogravimetric analysis. T.g.a. was done on a DuPont 951 Thermogravimetric Analyzer at a heating rate of 10°C min^{-1} in flowing air and nitrogen.

Films. Films of the different polyimides were cast in a Teflon mould from 15 wt% solutions of *m*-cresol or NMP, and then dried under vacuum at 150°C.

Compression-moulded specimens. In a rectangular stainless-steel mould equipped with vacuum ports, polymer powder was compression moulded at its melting temperature under 276 atm for 15–20 min (or 90°C above T_g for amorphous polymer), using a heated hydraulic press. The resulting samples were $30 \times 50 \times 1.5\,mm^3$.

Dynamic mechanical thermal analysis. This was performed on a Polymer Laboratories DMTA at 4°C min^{-1} and 1 Hz using the single cantilever mode.

Fracture energies. G_{Ic} values were obtained using the double torsion fracture test[8]. Three compact tension specimens ($30 \times 50 \times 3.2\,mm^3$) of the ODPA/MPPD polymer were machined, a precrack was made via a cold razor blade, and they were tested at room temperature. Then the remnants of these samples were used in three-point bending to determine the modulus. The mechanical testing was done on an Instron Universal Testing machine (model 1130).

RESULTS AND DISCUSSION

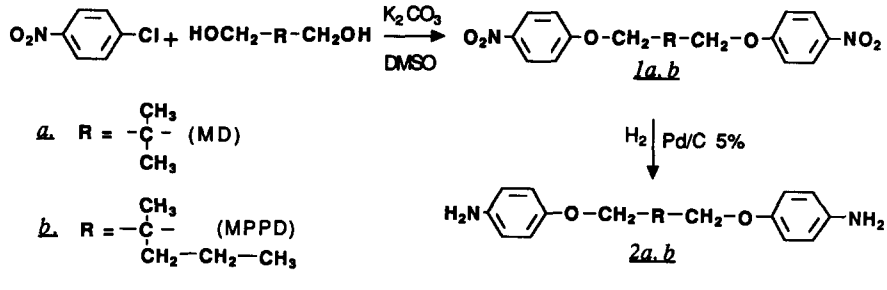
Synthesis

Both diamines MD and MPPD were synthesized in overall good yields according to *Scheme 1*. The dinitro-substituted compounds (**1**) were prepared in 78–84% yields by treatment of 4-chloronitrobenzene with 2,2-dimethyl-1,3-propanediol and 2-methyl-2-propyl-1,3-propanediol in DMSO containing K_2CO_3. The diamines (**2**) were obtained in 72–85% yields by hydrogenation of the corresponding dinitro-substituted compound. Crystallization of the crude MPPD was difficult owing to its low melting point (42–43°C).

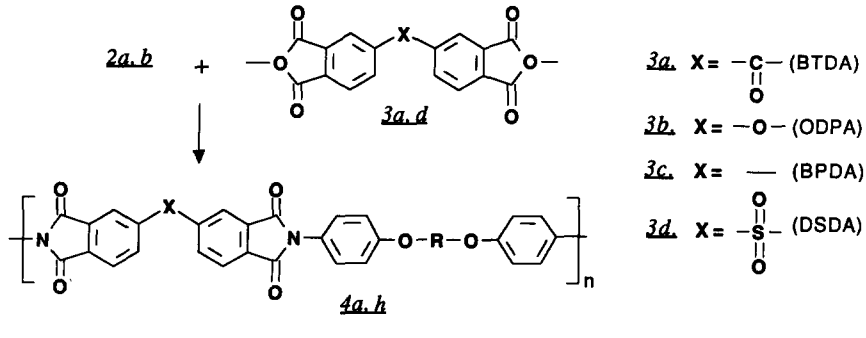
The polyimides (**4a–h**; see *Table 1*) were prepared as shown in *Scheme 2*. All polyimides were synthesized at room temperature by the two-step polymerization method in NMP solutions. Chemical imidization was achieved by treatment with acetic anhydride and triethylamine[9]. In an attempt to disrupt the polymer symmetry, a copolyimide of MPPD and MD (1/1 molar ratio) with BTDA was also prepared by slowly adding solid BTDA to a solution of the diamines. To evaluate the influence of the polymerization method on the crystallinity of the resulting polymer, polyimide BTDA/MPPD and copolyimide BTDA//MPPD/MD were also prepared by the one-step polymerization method in *m*-cresol at 200°C.

Polyimide characterization

The inherent viscosities of 0.5 g dl^{-1} *m*-cresol solutions of the polymers at 30°C are summarized in *Table 1*. The



Scheme 1



Scheme 2

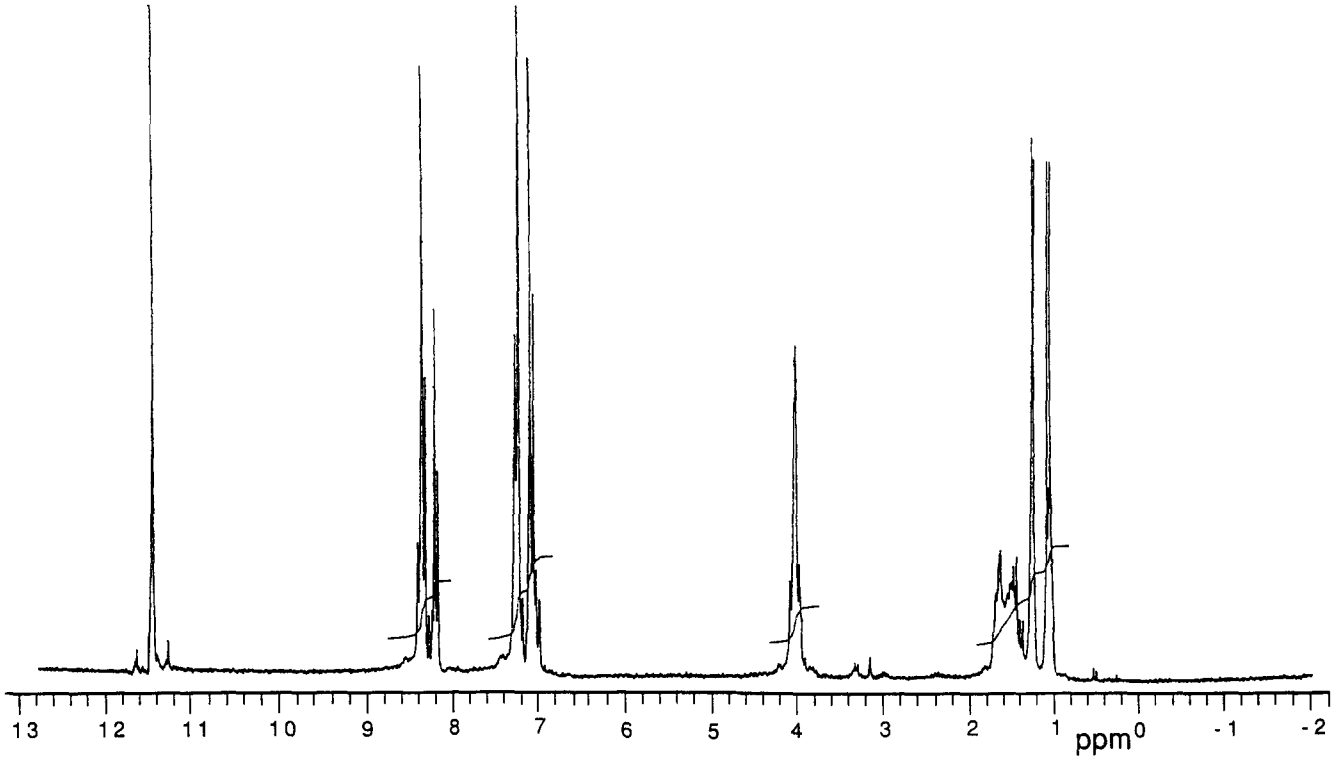


Figure 1 The 200 MHz ^{1}H n.m.r. spectrum of BTDA/MPPD-2 obtained in a 60/40 (v/v) mixture of $(CF_3CO)_2O/CDCl_3$

reactions of BTDA, ODPA and BPDA with both diamines for the most part yielded high-molecular-weight, film-forming polymers with inherent viscosities higher than 0.7 dl g^{-1}. Although the polymerizations were allowed to proceed for several hours, the reaction mixtures became viscous in approximately 10–15 min, especially in the polymerizations with BPDA. On the other hand, the DSDA anhydride produced polyimides with unexpected low viscosities. The polyimides obtained by the two-step method had lower viscosities than the corresponding polymers obtained by the one-step procedure.

Films cast from *m*-cresol solutions of the BTDA polymers obtained by the two-step method were tough, flexible and transparent. On the other hand, the films of the same polymers obtained by the one-step method were opaque and slightly brittle. Tough and transparent films of the ODPA polyimides could also be cast from NMP solutions. The films of the BPDA polyimides that were cast from *m*-cresol solutions were opaque and brittle. I.r. spectra of the films showed characteristic imide bands[9] at 1780, 1380 and 725 cm^{-1}. No amidic absorptions (at 3240–3220 or at 1550 cm^{-1}) were detected, indicating that high degrees of imidization were attained.

The ^{1}H n.m.r. (200 MHz) spectrum of BTDA/MPPD (*Figure 1*) confirmed the proposed chemical structure. The absorptions due to the protons of the dianhydride moiety appear between 8.20 and 8.40 ppm. The doublet of doublets at 7.00–7.30 ppm corresponds to the aromatic protons of the diamine. The signals of the methylene protons next to the ether linkage are centred at 3.97 ppm. The signals in the area of 0.90–1.50 ppm can be attributed to the remainder of the aliphatic protons. This aliphatic pattern is explained in ref. 10. The ratio of the integrated areas under the absorption peaks was in agreement with the calculated distribution of protons. Furthermore, no signals due to amidic protons could be detected.

Polyimide properties

The solubilities of these polymers were tested in NMP, DMAc and *m*-cresol (*Table 1*). The ODPA and DSDA produced polyimides with greater solubility than similar polyimides obtained from BTDA, which in turn were slightly more soluble than the corresponding BPDA derivatives. The enhanced solubility of the DSDA polymers was most likely due to their low molecular weight. In this series the structure of the diamine did not appreciably affect the polymer's solubility, except in the case of the polymers based on ODPA. In the ODPA-based polyimides, the presence of the propyl substituent in the diamine MPPD resulted in polyimides that were slightly more soluble than the corresponding MD derivatives.

The polymers' glass transition temperatures (T_g) and melting temperatures (T_m) were determined with d.s.c. (*Table 2*). The d.s.c. thermograms of the polyimides and copolyimides based on BTDA were characteristic of semicrystalline polymers and were similar to that of the BTDA/MD homopolymer[11]. As an example, thermograms of BTDA/MPPD are shown in *Figure 2*. The thermogram obtained on the first run showed a baseline shift near 200°C followed by a crystallization exotherm with a maximum around 260°C, and a melting endotherm with a minimum near 296°C. Thus, the replacement of MD with MPPD in the BTDA polymer resulted in a 20–30°C decrease in both T_g and T_m. After quenching in liquid N_2 and reheating, the same pattern was obtained but with a large decrease in the melting endotherm. No increase in the T_g was observed in the second or third run, indicating that no crosslinking had taken place.

Table 2 Results of the thermal characterization of MPPD and MD polyimides

Code	Sample	T_g[a] (°C)	T_m[b] (°C)	ΔH_m[b] (J g^{-1})	$T_{5\%}$[c] (°C)	T_{onset}[c] (°C)
4a	BTDA/MPPD	200	296	16	434	445
	BTDA/MPPD-1[d]	196	312	47	448	445
4b	BTDA//MPPD/MD	211	308	18	440	435
	BTDA//MPPD/MD-1[d]	212	324	30	464	453
4c	ODPA/MD	217	304	2	447	430
4d	ODPA/MPPD	202	–	–	453	441
4e	BPDA/MD	228	250	2	462	446
			377	15		
4f	BPDA/MPPD	215	260	7	451	452
			350	12		
4g	DSDA/MD	222	347	9	436	419
4h	DSDA/MPPD	207	–	–	454	439

[a] Mid-point in slope change of d.s.c. thermograms for quenched samples, heating rate 10°C min^{-1}
[b] Minimum of melting endotherm and its area for fresh samples (first run) (10°C min^{-1})
[c] Temperature at which powdered samples showed 5% weight loss in air (t.g.a., 10°C min^{-1})
[d] Polymer obtained by the one-step method in *m*-cresol

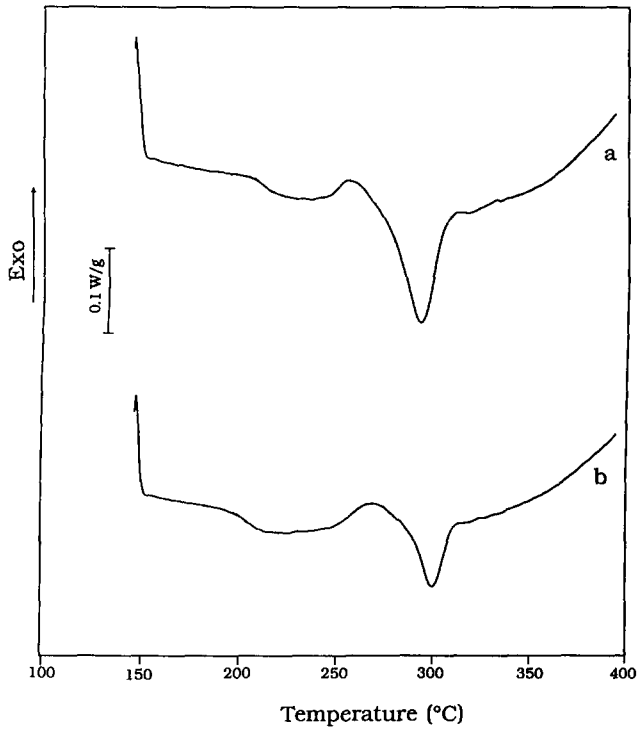


Figure 2 D.s.c. thermograms for BTDA/MPPD: (a) first run; (b) second run after quenching in liquid nitrogen. (Heating rate 10°C min^{-1})

The BTDA polymers prepared by the one-step method had considerably higher degree of crystallinity than the same polymers prepared by the two-step method. This was reflected in the properties of their films and substantiated by the large differences in their melting enthalpies (ΔH_m). The $\Delta H_m = 47$ J g^{-1} of the BTDA/MPPD polymer prepared in one step was surprising, since the ΔH_m of the BTDA/MD has been reported[11] to be ≈ 30 J g^{-1}. It is speculated that the much higher polymerization temperature used in the one-step method allowed the polymer to assume a more favourable conformation for packing[9].

The ODPA/MD polymer was also semicrystalline. However, its degree of crystallinity was very low as witnessed by its ΔH_m of only 2 J g^{-1}. The tendency of this polymer to crystallize was low, as it did not recrystallize after it was heated above its T_m. The T_g and T_m of the polymer were slightly lower than those of BTDA/MD[11]. The T_g of the ODPA/MPPD polymer, which was totally amorphous, was 20–30°C lower than that of BTDA/MD[11].

Both of the BPDA polymers were semicrystalline but their ΔH_m values indicated that their degrees of crystallinity were low. The T_g of the BPDA/MD polymer was comparable to that of BTDA/MD, while the T_g of BTDA/MPPD was slightly lower[11]. The d.s.c. thermograms obtained on the first run on both of the polymers contained two melting endotherms, indicating the presence of two different crystalline states. However, when the d.s.c. samples were quenched from 400°C with liquid N_2 and reheated, no melting endotherms were observed. This indicates that the polymers do not readily undergo crystallization.

The DSDA/MPPD polymer was amorphous whereas the DSDA/MD was semicrystalline. Owing to their low molecular weight, the data obtained from these polymers were not compared with data from the other polyimides.

The BTDA copolymer prepared from MPPD and MD by the one-step method was semicrystalline with a ΔH_m lower than that of BTDA/MPPD. In fact the ΔH_m was similar to that of BTDA/MD. The copolymer's T_g and T_m were 10–15°C lower than those of BTDA/MD. Thus, the copolymerization resulted in a polymer with a lower degree of crystallinity than that of the BTDA/MPPD homopolymer.

Test samples for d.m.t.a. analysis were prepared by compression moulding the polymers at their melting temperatures for 15 min under 276 atm. Good consolidation was obtained. The d.m.t.a. thermograms for BTDA/MPPD and ODPA/MPPD are shown in *Figure 3*. The BTDA/MPPD thermogram is characteristic of semicrystalline polymers. It has a small drop in modulus near 200°C (T_g), followed by an abrupt discontinuity corresponding to melting. The curve for ODPA/MPPD shows a large drop in the modulus and a pronounced maximum in the loss factor at its T_g, typical of an amorphous or slightly crystalline polymer. The second drop in modulus above 250°C indicates that the polymer may have crystallized during moulding.

The thermal stability of the polyimides was evaluated with t.g.a. The temperatures at which the polymers underwent 5% weight loss when heated at 10°C min^{-1} in air are given in *Table 2*. Both series of polyimides exhibited good resistance to thermo-oxidative degradation up to 400°C. This stability did not seem to be affected by the change in the diamine structure, since the thermal stabilities of both series were similar. The polyimides containing sulfone linkages were the least thermally stable. However, this was probably due to their lower molecular weights. The BPDA polymers displayed the best thermo-oxidative stability.

Mechanical properties of ODPA/MPPD

The compression moulding studies indicated that the polyimide with the most potential as a matrix resin in advanced composites was OPDA/MPPD. It had high molecular weight and could be readily processed below

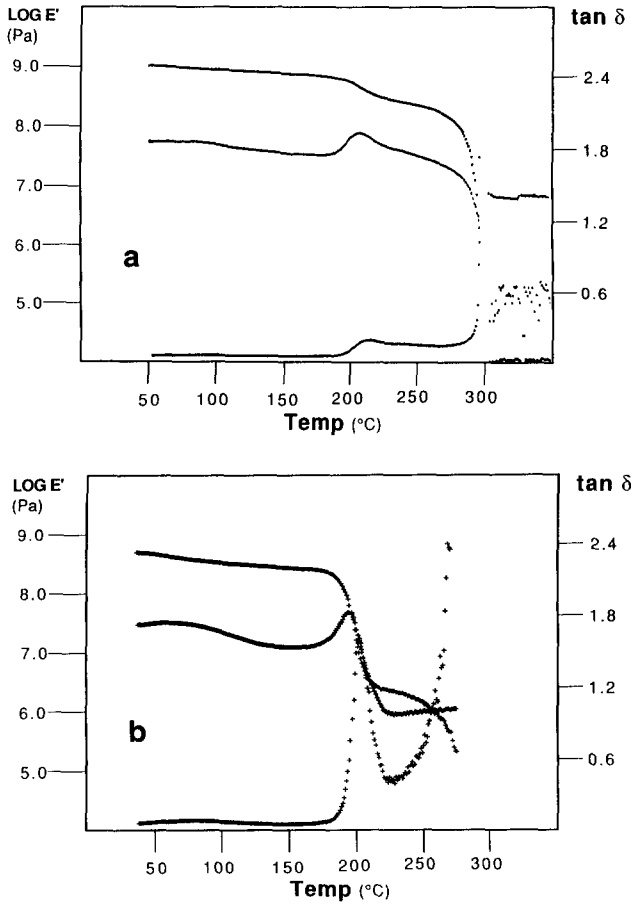


Figure 3 Log E', log E'' and tan δ *versus* temperature for (a) BTDA/MPPD and (b) ODPA/MPPD. (Frequency 1 Hz)

305°C. Thus, it was prepared in larger amounts for mechanical testing.

A three-point bending mode was used to determine the modulus, which was found to be 2.13 GPa. The critical strain-energy release rate or fracture energy (G_{Ic}), which was determined from precracked specimens using the double torsion method, was 1.1 kJ m^{-2}. Although these values are lower than those reported for semicrystalline polyimides, such as PI-2[7], they are typical of many other thermoplastics. The polymer will be evaluated in carbon-fibre-reinforced composites in the near future. Another possible application for this polymer may be as a high-temperature adhesive, since preliminary assays of the adhesive properties were promising.

CONCLUSIONS

A new asymmetric diamine containing a flexible alkylenedioxy unit, MPPD, has been synthesized. Using this diamine and MD, a new series of polyimides with structures similar to PI-2 have been synthesized and characterized. Both the one- and two-step polymerization methods were used to synthesize the initial polymers in this study. Since the two-step method afforded polymers with lower degrees of crystallinity, it was used to prepare the remainder of the polymers. The polyimides prepared from MPPD had T_g and T_m values 10–20°C lower than those of the corresponding MD polymers. However, attempts to compression-mould the resins revealed that only the amorphous polymer could be readily melt processed. This polymer had $T_g = 202$°C, $E = 2.13$ GPa and $G_{Ic} = 1.1$ kJ m^{-2}.

ACKNOWLEDGEMENTS

The Spanish Ministry of Education and Science is gratefully acknowledged for the postdoctoral grant and Dr A. Fradet for his invaluable discussions and suggestions.

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