Semicrystalline and amorphous fluorine-containing polyimides*

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Semicrystalline and amorphous fluorine-containing polyimides were developed with high transition temperatures and good thermal stability. Polyimides derived from 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF) and pyromellitic dianhydride (PMDA) were semicrystalline and exhibited a melting point of 472°C as determined by differential scanning calorimetry (d.s.c.). Confirmation of the semicrystalline morphology was provided by wide-angle X-ray scattering (WAXS). Incorporation of 6F dianhydride (2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, 6FDA) as a comonomer in the PMDA/4-BDAF polyimide depressed the melting point to 440°C. The polyimides based on 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3F diamine, 3FDAM) were soluble and amorphous, probably as a result of the non-coplanar structure. D.s.c. and dynamic mechanical analysis showed a glass transition temperature exceeding 420°C for the PMDA/3FDAM-based polyimide. These fluorinated polyimide systems are currently under investigation as candidates for high-temperature applications.

(Keywords: polyimides; fluorine-containing polymers; high-T_g materials; 3F diamine; 4-BDAF; semicrystalline; amorphous)

INTRODUCTION

Polyimides are well known for their outstanding mechanical properties and thermal stability. Several polyimides have been developed that are suitable as adhesives, coatings and matrix resins, and have found a wide range of applications as high-performance materials in the aerospace and electronics industries[1-3]. However, further development of polyimides is required to meet the increasing demands on high-performance materials. For example, in advanced polymer composites, there is a well established need to produce polyimide resins that are processable and cost-effective, and can withstand temperatures of 600–700°F (316–371°C) for extended periods of time[4]. Our efforts have focused on developing processable, fully cyclized polyimides with very high glass transition temperatures to meet many of these demands.

In the past, we have shown that incorporation of the 6F dianhydride (2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, 6FDA) along with the utilization of molecular-weight control and solution cyclization methods result in processable, thermally stable polymers[5]. Using these techniques, we have recently incorporated '3F' monomers based on trifluoroacetophenone in polyimides[6-8]. The 3F diamine (first used by Alston and Gratz[9]) and other monomers are depicted in *Figures 1* and *2*. Fully cyclized polyimides containing the 3F diamine (3FDAM) have been prepared that are soluble in polar aprotic solvents and have glass transition temperatures (T_g) exceeding 420°C. The '3F' polyimides demonstrate exceptional thermal and mechanical properties.

More recently, we have focused on the incorporation of 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF). The pyromellitic dianhydride (PMDA)/4-BDAF polyimides were initially developed in the mid-1970s and proved to be tough, high-T_g materials with relatively good thermo-oxidative resistance and low water absorption[10]. However, the semicrystalline nature of the PMDA/4-BDAF polyimide has not been thoroughly investigated.

Our current studies show that the PMDA/4-BDAF polyimide has a very high melting point (T_m) near 470°C. The semicrystalline phase could certainly be exploited to improve solvent resistance and possibly to enhance the thermo-oxidative stability. However, the PMDA/4-BDAF polyimide cannot be melt processed owing to the very high T_m and subsequent degradation upon melting. Successful attempts to improve the tractability of polyimides have involved the incorporation of flexible bridging units[11-13], bulky side-groups[14], or the asymmetric *meta* catenation[15,16] into the rigid backbone. The 6F dianhydride with a hexafluoroisopropylidene unit and the 3F diamine with a phenyl trifluoroethylidene linkage are flexible comonomers; therefore, incorporation of these comonomers should depress the T_m as anticipated for random or statistical copolymers where the second

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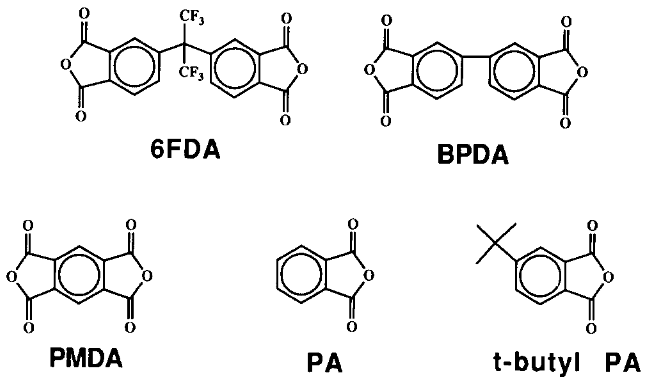

Figure 1 Dianhydrides and monofunctional anhydride end-capping reagents used for polyimide synthesis: 6FDA = 6F dianhydride; BPDA = biphenyl dianhydride; PMDA = pyromellitic dianhydride; PA = phthalic anhydride

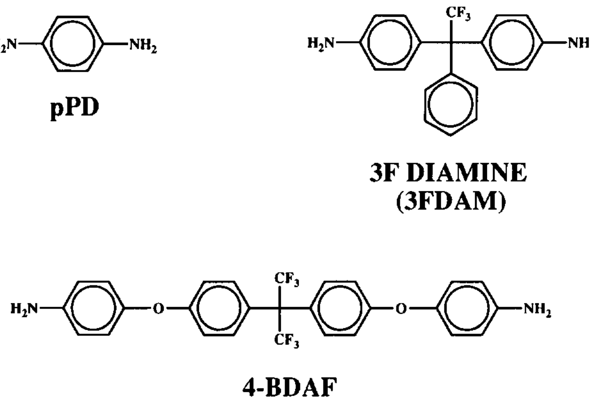

Figure 2 Diamines used for polyimide synthesis: *p*PD = *p*-phenylenediamine; 3FDAM = 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane; 4-BDAF = 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane

component (e.g. 6F dianhydride) does not crystallize. Thus, melt fabrication of the 4-BDAF-containing copolymers may be possible.

EXPERIMENTAL

Materials

Figures 1 and *2* illustrate the monomers that were utilized in the synthesis of the homopolyimides and copolyimides. The PMDA was donated by Allco, 6FDA was kindly provided by Hoechst-Celanese and biphenyl dianhydride (BPDA) was obtained from Chriskev Corporation. All of the dianhydrides were dried in a vacuum oven at temperatures exceeding 120°C for 24 h. Phthalic anhydride (PA) was obtained from Aldrich, t-butyl phthalic anhydride (t-butyl PA) was purchased from TCI and *p*-phenylene diamine (*p*PD) was purchased from Aldrich. PA, t-butyl PA and *p*PD were sublimed prior to use. The 4-BDAF was provided by Ethyl Corporation and dried in a vacuum oven at 125°C for 24 h before use. The 3F diamine was synthesized according to a previously published procedure[7]. *N*-Methylpyrrolidinone (NMP) and *o*-dichlorobenzene (DCB) were vacuum distilled from P_2O_5 and stored under N_2 atmosphere in sealed flasks. The NMP was distilled twice to ensure efficient removal of water as determined by automatic Karl Fischer titrations, which revealed that the water content of the NMP was below 150 ppm.

Polyimide synthesis

The poly(amic acid) was prepared in a four-necked flask equipped with a mechanical stirrer, nitrogen inlet, thermocouple and a drying tube. NMP was used as the solvent at a 15–20% (w/w) solid concentration. For the homopolymers, a calculated amount of phthalic anhydride was added to the prepared diamine solution to afford non-reactive end-groups and controlled molecular weights. Dianhydrides were added in small increments while the flask was under nitrogen purge. For the PMDA/6FDA/4-BDAF copolyimides, the same order of addition was followed. However, upon addition of the dianhydrides, the 6FDA was added first followed by PMDA. In the case of the PMDA/3F diamine/4-BDAF copolyimides, the 3F diamine was added to a solution of PMDA followed by the addition of PA. 4-BDAF was added last. In all cases, the temperature was held at room temperature for at least 24 h to obtain high molecular weight and to allow for equilibration to the most probable molecular weight distribution.

For soluble polyimides, cyclodehydration of the poly(amic acid) was carried out by solution imidization techniques[17]. These poly(amic acid)s were imidized in an 80/20 (v/v) solution of NMP/DCB. The imidization was carried out at 165°C for 24 h to ensure complete cyclization of the polyimide. The solution was then cooled to room temperature, precipitated in methanol, filtered and dried in a vacuum oven for 18 h at 200°C and for 2 h at 300°C. Films were cast from an NMP solution and were subsequently dried under vacuum at a final temperature of 300°C. The films were tough, transparent and yellow in appearance.

For the insoluble polyimides, thermal imidization of the poly(amic acid)s was required. The poly(amic acid) solutions were cast onto glass plates and placed in a vacuum oven. The films were heated incrementally at 100, 200 and 300°C for 1 h at each temperature.

Characterization

Intrinsic viscosity measurement. Intrinsic viscosity measurements were performed in NMP to determine the relative molecular weights. Cannon-Ubbelohde viscometers were used at a bath temperature of 25°C.

^{1}H n.m.r. spectroscopy. ^{1}H n.m.r. analysis was used to estimate the number-average molecular weights and spectra were obtained on a Varian 400 MHz n.m.r. on samples that had been dissolved in deuterated dimethylsulphoxide (DMSO).

*FTi.r. spectroscopy. FT*i.r. studies, using a Nicolet MX-1 *FT*i.r. spectrometer, gave qualitative information about the conversion of the poly(amic acid) to the polyimide.

Thermal analysis. A Perkin–Elmer DSC7 differential scanning calorimeter was used to determine the glass transition temperatures (T_g) and melting points (T_m). Scans were run at a heating rate of 10°C min^{-1}. Dynamic mechanical analysis (d.m.a.) was carried out on the 3F polyimide films using a Seiko model 200 DMS at 1 Hz. Thermo-oxidative stabilities were examined using a Perkin–Elmer TGA7 thermogravimetric analyser at a heating rate of 10°C min^{-1} in an air atmosphere. Isothermal t.g.a. was performed at 371°C in air. Thermomechanical analysis (t.m.a.) was performed on a

Seiko TMA 100. The scans were run with a 10 g load at 10°C min^{-1} in the penetration mode.

Wide-angle X-ray scattering. WAXS measurements were made in transmission with a Siemens X-ray diffractometer using Cu K_α radiation ($\lambda = 1.54$ Å). Samples were scanned through 2θ values of 3° to 60° at 0.05° increments with a dwell time of 10 s.

Solubility tests. The solubility of the fluorinated polyimides was tested by preparing 2 wt% solutions in small, capped glass vials. The solutions were stirred vigorously with a magnetic stir bar at room temperature. The level of solubility was evaluated after 18 h.

RESULTS AND DISCUSSION

The polyimides were prepared as shown in *Figure 3*. The monomers used in the polyimide synthesis are shown in *Figures 1* and *2*. Solution imidization was used to convert the poly(amic acid) intermediates quantitatively to the corresponding polyimides. Solution imidization of the poly(amic acid) was based on a cosolvent system of NMP and an azeotroping solvent, DCB. An 8:2 mixture of NMP:DCB efficiently removed the water formed upon the conversion of the amic acid to the imide. Solution imidization was performed at 165°C for 24 h whereas thermal imidization requires temperatures near 300°C.

To demonstrate the effectiveness of end-group and molecular-weight control, the number-average molecular weight of a series of PMDA/3F diamine polyimides end-capped with t-butyl phthalic anhydride was measured by ^1H n.m.r. A characteristic ^1H n.m.r. spectrum of the 20 000 g mol^{-1} polyimide is provided in *Figure 4*. The resonance observed at about 1.4 ppm is due to the t-butyl group, which can be ratioed to the aromatic

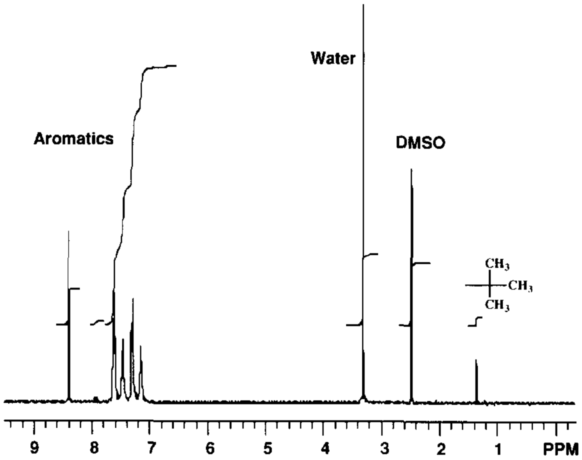

Figure 4 Proton n.m.r. spectrum of the 20 000 g mol^{-1} PMDA/3F diamine polyimide end-capped with t-butyl phthalic anhydride

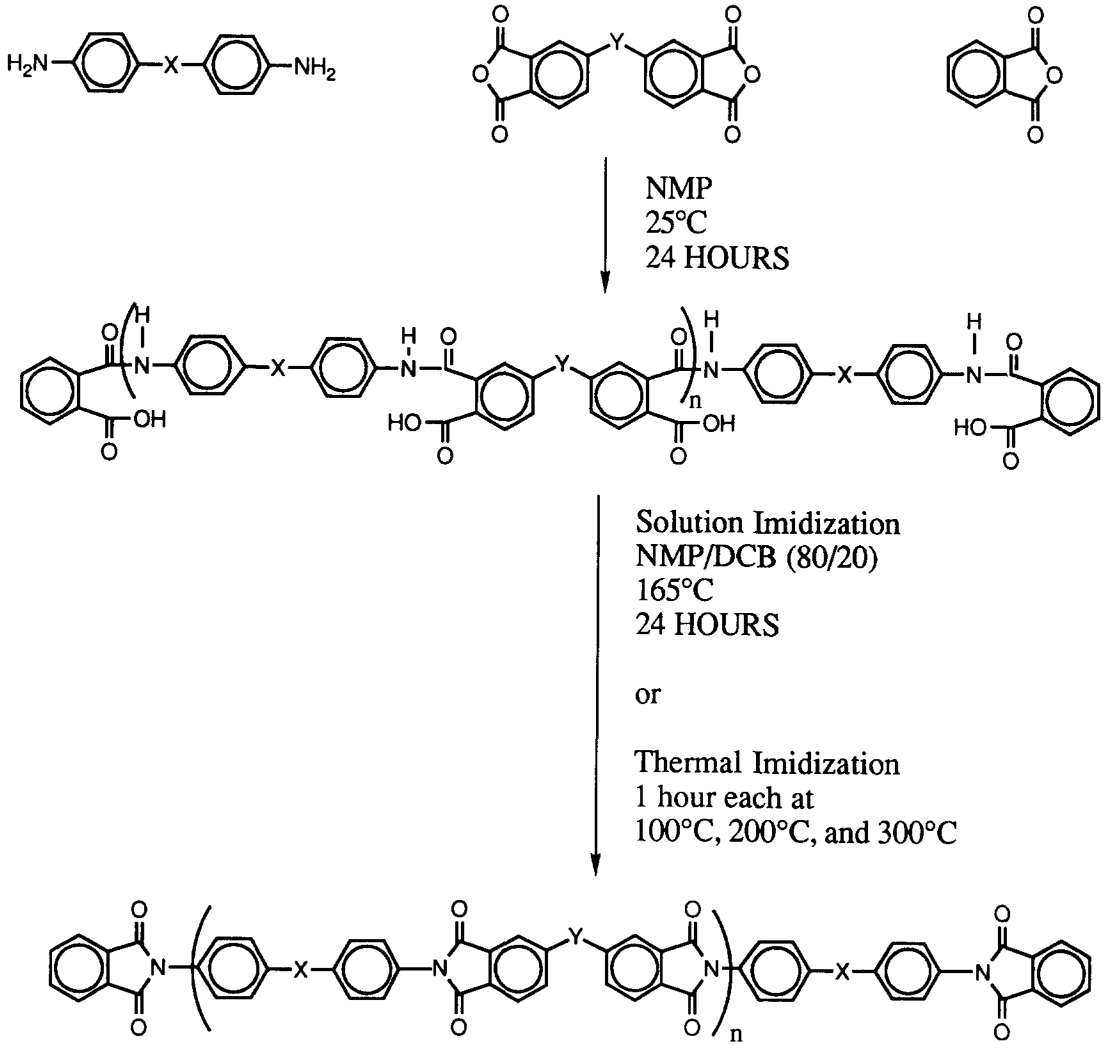

Figure 3 Synthetic scheme for fully cyclized polyimides

Table 1 '3F' polyimides

	$\langle M_n \rangle_{theor}$ (g mol^{-1})	$\langle M_n \rangle_{n.m.r.}$ (g mol^{-1})	$[\eta]$ (dl g^{-1})	T_g (°C)	5% wt loss (°C)
PMDA/3FDAM/t-butyl PA	10000	10200	0.32	–	–
	20000	18500	0.47	422	543
	30000	33600	0.65	432	541
BPDA/3FDAM/PA	30000	–	0.44	347	536
6FDA/3FDAM/PA	30000	–	0.36	314	527
PMDA(0.8)/6FDA(0.2)/3FDAM/PA	30000	–	0.50	392	554
PMDA(0.7)/6FDA(0.3)/3FDAM/PA	30000	–	0.46	379	547
BPDA/3FDAM(0.9)/*p*PD(0.1)/PA	30000	–	0.51	357	562

Table 2 Thermal summary of 4-BDAF-containing polyimides[a]

Polymer composition (mol%)			T_g (°C)	5% weight loss (°C)
BDAF	3FDAM	PMDA		
100	0	100	306 (T_m=472°C)	538
80	20	100	310	538
70	30	100	323	533
50	50	100	348	540
30	70	100	374	530
0	100	100	432	540
BDAF	6FDA	PMDA		
100	20	80	276 (T_m=440°C)	547
100	40	60	268	530
100	60	40	260	545
100	80	20	254	541
100	100	0	251	534

[a] $\langle M_n \rangle$ controlled to 30000 g mol^{-1} with phthalic anhydride

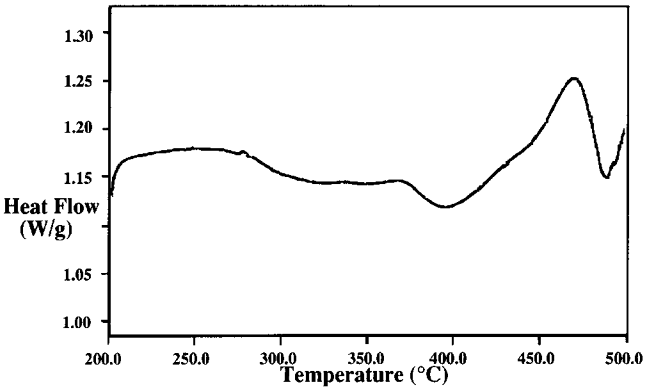

Figure 5 Differential scanning calorimetry thermogram of PMDA/4-BDAF/PA ($\langle M_n \rangle$ = 30000 g mol^{-1})

protons to estimate the number-average molecular weight. As seen in *Table 1*, the number-average molecular weights determined by ^{1}H n.m.r. agree well with the theoretical calculations. The intrinsic viscosities in *Table 1* seem reasonable given the calculated molecular weights.

The insoluble polyimides, such as the PMDA/4-BDAF polyimides, were imidized via the conventional thermal route. A final cure temperature of 300°C was necessary for removal of residual solvent and to ensure complete cyclization. The conversion of the amic acid to the fully imidized polymer was monitored by *FT*i.r.[17,18]. Complete cyclodehydration by both the solution and thermal imidization methods was confirmed by the appearance of the characteristic imide-related infrared absorption bands in the ranges 1770–1780 and 1710–1735 cm^{-1} as well as the disappearance of the amic acid band at 1535 cm^{-1}.

When synthesizing the potentially semicrystalline 4-BDAF-containing copolymers, the order of monomer addition is important to the final polyimide microstructure and morphology. To obtain random or statistical copolymers, the least reactive comonomers were added first to the reaction mixture. For the PMDA/6FDA/4-BDAF/PA copolyimides, the 6FDA was added first to the solution of the 4-BDAF and PA in NMP. The more reactive dianhydride, PMDA, was added last to optimize random incorporation of the comonomers. The same reasoning holds for the PMDA/4-BDAF/3F diamine/PA copolyimides. The less reactive 3F diamine was added to a prepared solution of PMDA in NMP. PA was then added followed by 4-BDAF.

The T_g values of the 4-BDAF-containing polyimide homopolymers and copolymers were measured by d.s.c. The results are summarized in *Table 2*. The PMDA/4-BDAF polyimide exhibited a melting endotherm on the first heat at ~470°C. Controlled-molecular-weight PMDA/4-BDAF/PA polyimide had a larger endothermic peak, suggesting a greater degree of crystallization, than that of the uncontrolled-, presumably higher-molecular-weight PMDA/4-BDAF polyimide. The glass transition temperature of the PMDA/4-BDAF/PA polyimide was 306°C, determined from the second heat (10°C min^{-1}) after a rapid cool starting from above the T_m. T.m.a. showed a T_g of 305°C for the PMDA/4-BDAF/PA polyimide.

The T_m of the PMDA/4-BDAF polyimide homopolymer (*Figure 5*) is too high to allow melt fabrication since the polymer degrades at temperatures just above the T_m. However, through the incorporation of flexible comonomers, the T_m can be depressed to a temperature where melt fabrication may be feasible. The 6FDA and 3F diamine were copolymerized into the PMDA/4-BDAF polyimides since neither system is crystallizable. The d.s.c. and t.g.a. scans for the 4-BDAF copolymers are shown in *Table 2*. Incorporating 20% of the 6FDA lowered the T_m by 30°C to 440°C and lowered the T_g to 276°C. The T_m was measured on the second heat after slow cooling from 420°C at 10°C min^{-1}. Any significant crystallinity disappeared upon incorporation of 40% or greater 6FDA. Incorporation of the 3F diamine increased the glass transition temperature of the 4-BDAF-containing polyimides. A T_g of 374°C was obtained for a 4-BDAF-containing polyimide with 70 mol% of the 3F diamine. So far, there has been no conclusive evidence of a crystalline phase in any of the 4-BDAF/3F diamine copolyimides studied. However, the copolyimides with a high mole percentage of 4-BDAF remain insoluble, which may indicate that they are partially ordered.

Wide-angle X-ray diffraction was conducted on a series of controlled-molecular-weight PMDA/4-BDAF homopolymers and a copolymer containing 20 mol% of 6FDA. The homopolyimides with target molecular weights of 20 000, 30 000 and 40 000 g mol^{-1} display reflections at $2\theta = 18.8°$ ($d = 4.71$ Å) and a broad amorphous halo centred at $2\theta \sim 16°$ (*Figure 6*). The low-intensity diffraction peaks indicate some level of ordering in these materials. The uncontrolled-molecular-weight PMDA/4-BDAF polymer exhibited broad reflections superimposed on the amorphous halo, which suggests that, at a very high molecular weight, a modest level of crystallinity is present. The 4-BDAF/(20%)6FDA/(80%)PMDA/PA copolyimide displayed an endothermic transition at 440°C when analysed by d.s.c. WAXS showed a diffraction peak near $2\theta = 19°$, which provides evidence that the endothermic transition is due to melting.

The semicrystalline fluorinated polyimides were insoluble in all common organic solvents, NMP and *m*-cresol. This insolubility is attributed to the crystalline phase. The copolymer solubility was a function of the comonomer concentration as shown in *Table 3*. Approximately 50 mol% of the comonomer, 6FDA or 3F diamine, was required to induce solubility. These polyimides were soluble in chloroform ($CHCl_3$), tetrahydrofuran (THF) and NMP.

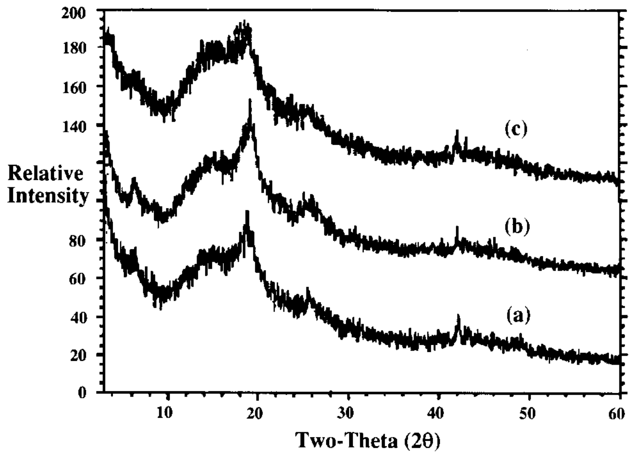

Figure 6 Wide-angle X-ray diffraction of different molecular weight PMDA/4-BDAF/PA polyimides: (a) 20 000 g mol^{-1} ($\eta_{inh} = 0.67$ dl g^{-1}); (b) 30 000 g mol^{-1} ($\eta_{inh} = 0.75$ dl g^{-1}); (c) 40 000 g mol^{-1} ($\eta_{inh} = 0.86$ dl g^{-1}). Inherent viscosities were measured at 25°C at a concentration of 0.52 dl g^{-1}

Table 3 Solubility study of 4-BDAF polyimides[a]

Polymer composition (mol%)			Imidization method	Solvents[b]		
				THF	$CHCl_3$	NMP
BDAF	3FDAM	PMDA				
100	0	100	Thermal	I	I	I
70	30	100	Thermal	I	I	I
50	50	100	Thermal	M	M	I
30	70	100	Soln	S	S	S
0	100	100	Soln	M	M	S
BDAF	6FDA	PMDA				
100	20	80	Thermal	I	I	I
100	40	60	Thermal	I	I	I
100	60	40	Soln	S	S	M
100	80	20	Soln	S	S	S

[a] $\langle M_n \rangle$ controlled to 30 000 g mol^{-1} with phthalic anhydride
[b] S = soluble, M = marginally soluble, I = insoluble

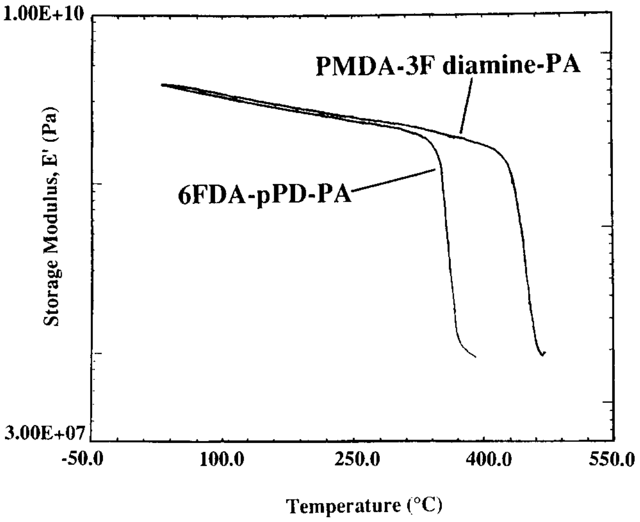

Figure 7 Dynamic mechanical analysis of PMDA/3F diamine/PA and 6FDA/*p*PD/PA polyimides

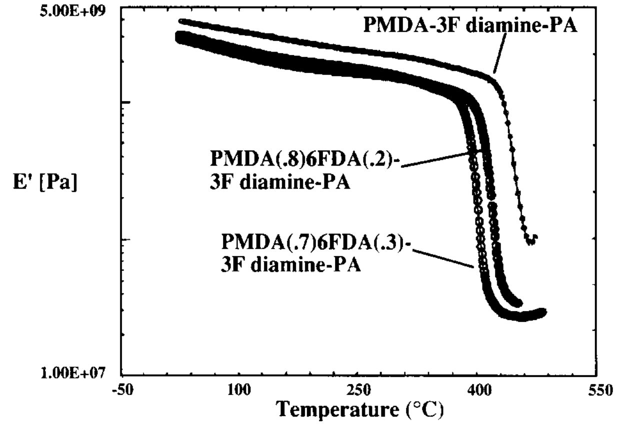

Figure 8 Dynamic mechanical analysis of PMDA/6FDA/3F diamine polyimides

The PMDA/3F diamine polyimides exhibit glass transition temperatures exceeding 420°C. Dynamic mechanical analysis, shown in *Figure 7*, compared the dynamic storage modulus of a PMDA/3F diamine/PA polyimide with the state-of-the-art high-temperature polyimide based on 6FDA/*p*PD/PA. The storage modulus for the 6FDA/*p*PD/PA polyimide declined sharply around 350°C corresponding to the glass transition temperature. The PMDA/3F diamine maintains mechanical integrity over a temperature range of 350 to 400°C and the storage modulus did not drop off until 430°C.

The '3F' polyimides containing either the BPDA or the 6FDA were more soluble and had lower glass transition temperatures than the PMDA/3F diamine polyimide. The BPDA/3F diamine polyimide had a T_g of 350°C, and the 6FDA/3F diamine polyimide had a T_g of 313°C (*Table 1*). Utilizing BPDA and 6FDA as comonomers in the '3F' polyimides allowed effective control of the polyimide properties. For example, at a 8:2 ratio of PMDA to 6FDA the copolyimide had a T_g of 392°C, and at a 7:3 ratio the T_g of the copolyimide was 379°C. *Figure 8* compares the dynamic storage

Table 4 Solubility of '3F' polyimides[a]

Polyimide	NMP	$CHCl_3$	THF	Toluene
PMDA/3FDAM/PA	S	M	M	I
PMDA(0.8)/6FDA(0.2)/3FDAM/PA	S	S	S	I
BPDA/3FDAM/PA	S	S	S	I
BPDA/3FDAM(0.9)/*p*PD(0.1)/PA	S	S	M	I
BPDA/3FDAM(0.8)/*p*PD(0.2)/PA	I	–	–	–
3FDA/*p*PD/PA	S	S	S	I

[a] S = soluble, M = marginally soluble, I = insoluble

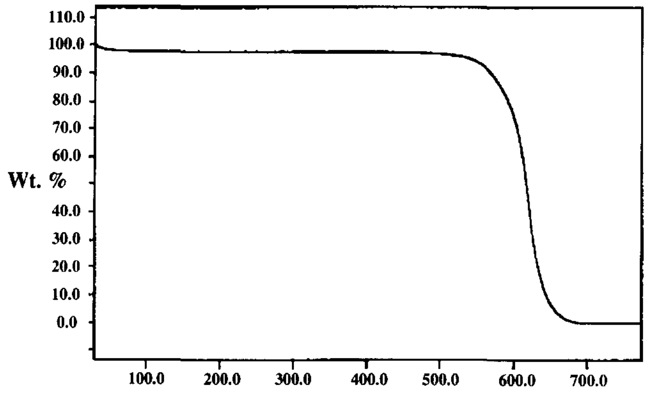

Figure 9 Dynamic t.g.a. of a PMDA/3F diamine/PA polyimide

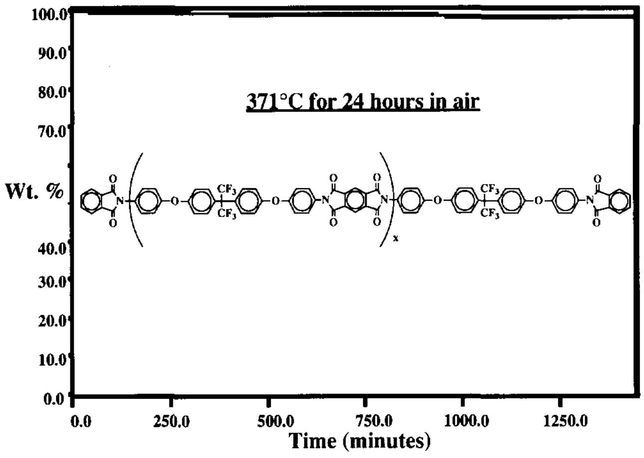

Figure 10 Isothermal t.g.a. of PMDA/4-BDAF/PA ($\langle M_n \rangle = 25\,000$ g mol^{-1}): 371°C for 24 h

modulus of the PMDA/6FDA/3F diamine copolyimides with that of the PMDA/3F diamine. The T_g of the BPDA/3F diamine polyimide was raised to 357°C by incorporating 10 mol% *p*PD. Incorporating larger amounts of *p*PD ($\geq$20 mol%) to the BPDA/3F diamine polyimide rendered it insoluble in NMP.

All of the 3F diamine-containing polyimides were soluble in polar aprotic solvents such as NMP and DMSO. As seen in *Table 4*, the BPDA/3F diamine and the 6FDA/3F diamine are also soluble in THF and $CHCl_3$. Incorporating 6FDA as a comonomer into the PMDA/3F diamine polyimides increased the solubility in THF and $CHCl_3$. The solubility of the BPDA/3F diamine was decreased by incorporating *p*PD. None of the 3F diamine-containing polyimides are soluble in toluene.

The dynamic thermogravimetric analysis of the fluorine-containing polyimides demonstrated short-term thermal stability above 450°C in air. As shown in *Tables 1* and *2*, a 5% weight loss occurred by 530–560°C. A typical dynamic t.g.a. thermogram of a PMDA/3F diamine polyimide is presented in *Figure 9*. Since dynamic t.g.a. is not a realistic measure of a material's long-term stability, isothermal t.g.a. studies were initiated. An isothermal t.g.a. of the 25 000 g mol^{-1} PMDA/3F diamine polyimide shows that relatively little weight loss occurred after 48 h at 371°C (700°F) in air. The isothermal t.g.a. of the 30 000 g mol^{-1} PMDA/4-BDAF/PA polyimide exhibited very little weight loss after 24 h at 371°C in air (*Figure 10*). Although these are short-term results, additional studies are in progress.

CONCLUSIONS

The synthesis of amorphous and semicrystalline high-temperature polyimides based upon the 3F and BDAF monomers has been demonstrated. T_g values as high as 430°C were seen for soluble, fully cyclized PMDA/3F diamine polyimides. The glass transition temperature and solubility of the 3F diamine-containing polyimides were successfully modified through the incorporation of various comonomers. The PMDA/4-BDAF polyimide exhibited a well defined high melting point by d.s.c. near 470°C. Exothermic degradation is observed shortly above this very high T_m. The melting point of the 4-BDAF-containing polyimides was depressed by the incorporation of the flexible comonomer 6FDA. Further evidence of the semicrystalline nature of the 4-BDAF-containing polyimides was provided by WAXS. The 3F diamine- and the 4-BDAF-containing polyimides demonstrated good thermo-oxidative stability under both dynamic and isothermal conditions.

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