Synthesis and characterization of a novel '3F'-based fluorinated monomer for fluorine-containing polyimides*

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A novel '3F' fluorinated diamine monomer based on trifluoroacetophenone was synthesized via a straightforward, high yielding two-step procedure. Trifluoroacetophenone was reacted with 4-nitrophenyl phenyl ether to yield the 3F-dinitro compound, which was subsequently reduced to afford the fluorinated diamine, 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (3FEDAM). New amorphous and semicrystalline polyimides based on 3FEDAM were prepared and characterized by differential scanning calorimetry, thermogravimetric analysis and wide-angle X-ray scattering (WAXS). In particular, the 3FEDAM–pyromellitic anhydride–phthalic anhydride material exhibited a glass transition temperature of 308°C and a melting temperature of 476°C, which are quite similar to the values reported for '6F'-based systems. The semicrystalline nature was confirmed by WAXS analysis, and is consistent with the excellent solvent resistance observed for these polyimides.

(Keywords: fluorinated diamine; fluorinated polyimide, semicrystalline polyimide)

INTRODUCTION

Fluorine-containing polymers are well known to display a number of unique properties and there are several excellent reference sources available[1,2]. In particular, fluorinated polyimides containing the hexafluoroisopropylidene (6F) group, either in the dianhydride or in the diamine component, display several attractive characteristics[3-5] (refer to *Figure 1*). Polyimides containing the trifluoromethyl group in the polymer backbone have much lower dielectric constants and water absorption than observed for more conventional polyimides such as those based on 4,4′-oxydianiline (4,4′-ODA) and pyromellitic dianhydride (PMDA). It has been shown[6] that dielectric constants (ε') in the range of 2.4–2.8 at 10 GHz have been achieved for polyimides containing the trifluoromethyl groups, while the 4,4′-ODA/PMDA system has a ε' value of 3.2 at 10 GHz. A study[6] of the effect of moisture uptake on the dielectric values showed that the polyimides containing fluorinated alkyl groups had substantially lower water absorption and, therefore, the higher humidity had relatively little influence on the electrical properties. Solubility is another advantage that the bulky 6F group provides when bonded to the main chain, due to inhibited chain packing[3]. The solubility enables analysis by methods such as nuclear magnetic resonance (n.m.r.)[7] that have not been utilized with insoluble polyimides. In addition, the high bond dissociation energy[8] of the C–F bond provides enhanced thermal stability over those polyimides containing CH_3 groups. These characteristics have generated considerable interest in fluorinated polyimides in such areas as microelectronics.

Our research group is very interested in polyimides containing the trifluoroethylidene (3F) and the hexafluoroisopropylidene (6F) linkages. The 3F monomers were based on the precursor, trifluoroacetophenone. The 3F diamine, 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-

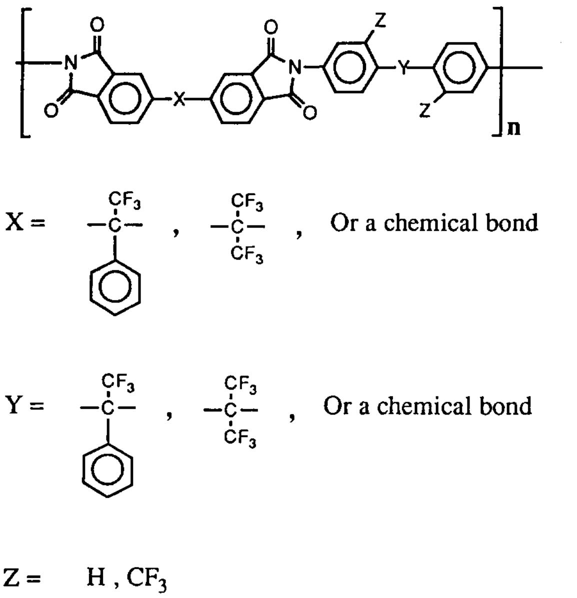

Figure 1 Fluorinated polyimides containing the '3F' or the '6F' group

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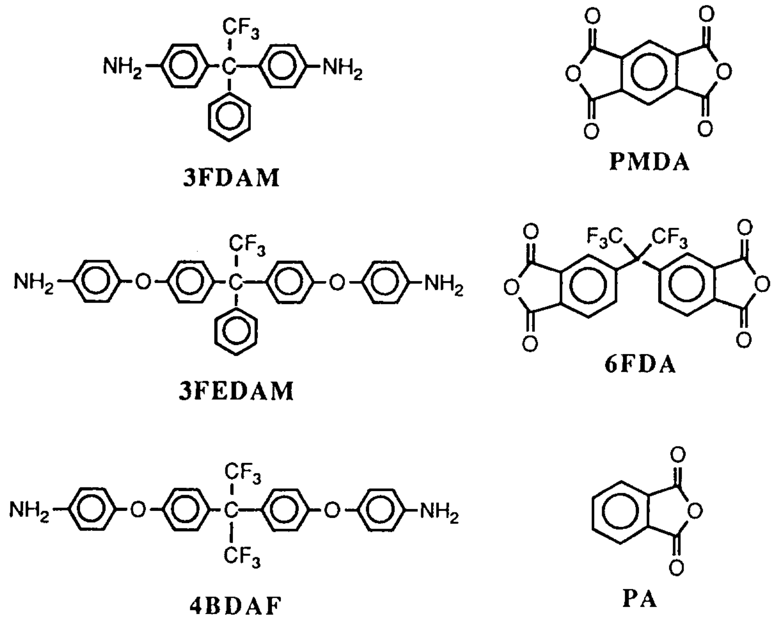

Figure 2 Diamines and dianhydrides used for polyimide synthesis

trifluoroethane (3FDAM) (see *Figure 2*) was first used by Alston and Gratz[9]. They demonstrated that the 3FDAM-based materials had exceptional thermal and mechanical properties. Fully cyclized 3FDAM containing polyimides prepared by the solution imidization technique with molecular weight and end group control were amorphous, soluble in polar aprotic solvents, demonstrated exceptional thermal and mechanical properties, and displayed high glass transition temperatures (T_g)[10,11]. The high T_g (some in the range of 430°C) may be ascribed to the bulky structure of the 3F group which retards segmental mobility and hence results in a more rigid system. The diamine, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4BDAF) (see *Figure 2*), provided polyimides with the 6F linkage. The 4BDAF–PMDA end-capped with phthalic anhydride (PA) to a number-average molecular weight of 30 000 g mol^{-1} was highly solvent resistant and developed a semicrystalline morphology which exhibited a melting temperature (T_m) of 472°C as determined by differential scanning calorimetry (d.s.c.). The ordering was confirmed by wide-angle X-ray scattering (WAXS) measurements[11].

It is of interest to investigate new organic materials that might set new standards for high temperature and high performance applications by attempting to combine the high T_g nature of the 3FDAM–PMDA system with the semicrystalline nature of the 4BDAF–PMDA system. We have now synthesized a novel diamine that has the '3F' link, which contributes to the high T_g, and ether links which provide sufficient chain mobility and proper symmetry to allow development of crystallinity. The novel diamine is 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (3FEDAM) (see *Figure 2*). This paper describes the synthesis of 3FEDAM and the characterization of homopolyimides and statistical copolymers prepared from this new monomer.

EXPERIMENTAL

Materials

The '3F'-based monomers are derived from trifluoroacetophenone, which was prepared by a previously reported method from our laboratory[10]. The 4-nitrophenyl phenyl ether and 1,2-dichloroethane (Aldrich) were used as received. Trifluoromethanesulfonic acid was purchased from Aldrich in sealed ampoules to ensure high purity, and was used as received. The reduction catalyst was 10% palladium on activated carbon (Aldrich) and was also used as received.

The monomers utilized in the synthesis of the homopolyimides and copolyimides are illustrated in *Figure 2*. The 4BDAF diamine was kindly provided by the Ethyl Corporation and was dried *in vacuo* at 125°C for 24 h before use. The PMDA (Allco) was highly pure and dried under low vacuum at 180°C for 4–6 h to remove moisture and to ensure cyclization of the anhydride moiety. Hoechst Celanese kindly donated 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) which was dried *in vacuo* at 160°C for 24 h prior to use. PA (Aldrich) was purified by sublimation prior to use. *N*-Methylpyrrolidinone (NMP) was dried over phosphorus pentoxide for 24 h, vacuum distilled, and stored in a sealed flask under nitrogen. The water content of the purified NMP was below 150 ppm as determined by automatic Karl Fischer titrations.

Monomer synthesis

1,1-Bis[4-(4-nitrophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (3F-dinitro). To a three-necked, 250 ml round-bottom flask equipped with a magnetic stirrer, nitrogen inlet, drying tube, condenser and addition funnel, trifluoroacetophenone (0.100 mol), 4-nitrophenyl phenyl ether (0.205 mol) and 1,2-dichloroethane (20% (w/v) solid concentration) were added, resulting in a homogeneous, yellow solution. Trifluoromethanesulfonic acid (0.105 mol) was added dropwise via an addition funnel over a period of 15 min producing a dark red solution. The mixture was allowed to stir at ambient temperature for 24 h after which the solvent was removed. The resulting orange solid was stirred in water for 1–2 h at 50°C, filtered, recrystallized twice from acetic acid and dried under vacuum at 110°C for 24 h, affording a tan-coloured powder (90%): m.p. 196–197°C. ^1H n.m.r. (400 MHz, DMSO-d_6): 8.26 (4H, d), 7.44 (3H, d), 7.24 (8H, m), 7.15 (6H, t). Analysis calculated for $C_{32}H_{21}N_2O_6F_3$: C, 65.50; H, 3.60; N, 4.82. Found: C, 65.44; H, 3.63; N, 4.73.

1,1-Bis[4-(4-aminophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (3FEDAM). A pressure reactor was charged with 0.100 mol of the 3F-dinitro compound, 0.001 mol of the palladium catalyst (10% Pd/C) with respect to the 3F-dinitro compound, and 200 ml each of tetrahydrofuran and ethyl acetate. The temperature and the hydrogen pressure were maintained at 50°C and 0.3 MPa, respectively, for 6–8 h. Filtration over Celite followed by evaporation of the solvent afforded an amber-coloured, highly viscous liquid which was recrystallized twice from absolute ethanol and dried *in vacuo* at 110°C for 24 h to yield an off-white powder (80%): m.p. 169–170°C. ^1H n.m.r. (400 MHz, DMSO-d_6): 7.38 (3H, d), 7.06 (3H, d), 6.94 (4H, d), 6.81 (8H, m), 6.58 (4H, d), 5.00 (4H, s). Analysis calculated for $C_{32}H_{25}N_2O_2F_3$: C, 73.4; H, 4.80; N, 5.32. Found: C, 72.75; H, 4.76; N, 5.27.

Polyimide synthesis

The first step in the preparation of the polyimides was the synthesis of the poly(amic acid). To a four-necked, round-bottom flask equipped with a mechanical stirrer, nitrogen inlet and a drying tube, the diamine was added. NMP was used as the solvent at a 15–20% (w/w) solid concentration. Carother's equation was used to calculate the amount of PA to introduce to the diamine solution to afford non-reactive end groups and control molecular weight. Lastly, the dianhydride was added as a solid while the flask was under a nitrogen purge. For the 3FEDAM–PMDA/6FDA–PA copolyimides, the less reactive dianhydride, 6FDA, was added before the PMDA to ensure randomization. The poly(amic acid) solution was allowed to stir at ambient temperature for 24 h.

The second step of the polyimide synthesis involved the cyclodehydration of the poly(amic acid). Solution imidization techniques were employed for those amorphous polyimides which were soluble in NMP[12,13]. Several of the fluorinated polyimides of interest were semicrystalline and were insoluble in NMP, therefore they were imidized by the more conventional thermal bulk cyclodehydration method. In this case, the poly(amic acid) solution was cast on a soft glass plate and placed in a vacuum oven for 1 h at each ambient temperature, 100, 200 and 300°C.

Characterization

H.p.l.c. analysis. Reversed phase high performance liquid chromatography (h.p.l.c.) analyses were performed on a Vista 5500. The mobile phase was 75% acetonitrile/25% methanol and a flow rate of 1 ml min^{-1} was utilized.

N.m.r. analysis. N.m.r. studies (in deuterated dimethyl sulfoxide) were performed on a Varian Unity NMR Spectrometer operating at 400 MHz with chemical shifts reported in ppm.

FTi.r. analysis. Fourier transform infra-red (*FT*i.r.) spectra were obtained with a Nicolet MX-1 FTIR Spectrometer which provided qualitative information describing the conversion of the poly(amic acid) to the polyimide. Also *FT*i.r. analysis was utilized to follow the reduction of the 3F-dinitro compound to the 3FEDAM diamine.

Thermal analysis. Thermal analysis was performed on a Perkin–Elmer Series 7 thermal analyser. D.s.c. was used to determine T_g and T_m. Scans were performed at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. Thermo-oxidative stabilities were determined on a Perkin–Elmer TGA7 thermogravimetric analyser at a heating rate of 10°C min^{-1} in an air atmosphere. Isothermal thermogravimetric analyses (t.g.a.) were performed at 371°C in an air atmosphere.

WAXS. WAXS measurements were made in transmission with a Siemens X-ray diffractometer using CuK$_\alpha$ radiation ($\lambda = 1.54$ Å). Samples were scanned through 2θ values of 3–60° at 0.05° increments, with a dwell time of 10 s.

Solubility tests. The solubility of the fluorinated polyimides was investigated by examining 1 wt% solutions in small capped glass vials. The solutions were stirred vigorously with a magnetic stir bar at room temperature. The solubility was qualitatively evaluated after 18 h.

Titration. An MCI Automatic Titrator model no. GT-05 was used in conjunction with a standard Glass-Body Combination Electrode with Ag/AgCl reference. The HBr titrant was dispensed by means of an automatic microburette with a volume resolution of 2 ml. The diamine was dissolved in chloroform and acetic acid was also added.

RESULTS AND DISCUSSION

A three-step synthesis of 3FEDAM has been reported in a preliminary communication[14]. Recently, 3FEDAM has

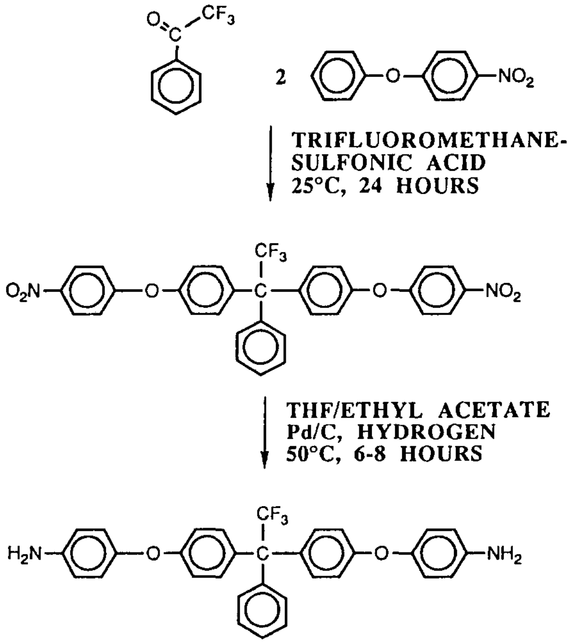

Figure 3 Synthetic scheme for the preparation of 3FEDAM via a two-step method

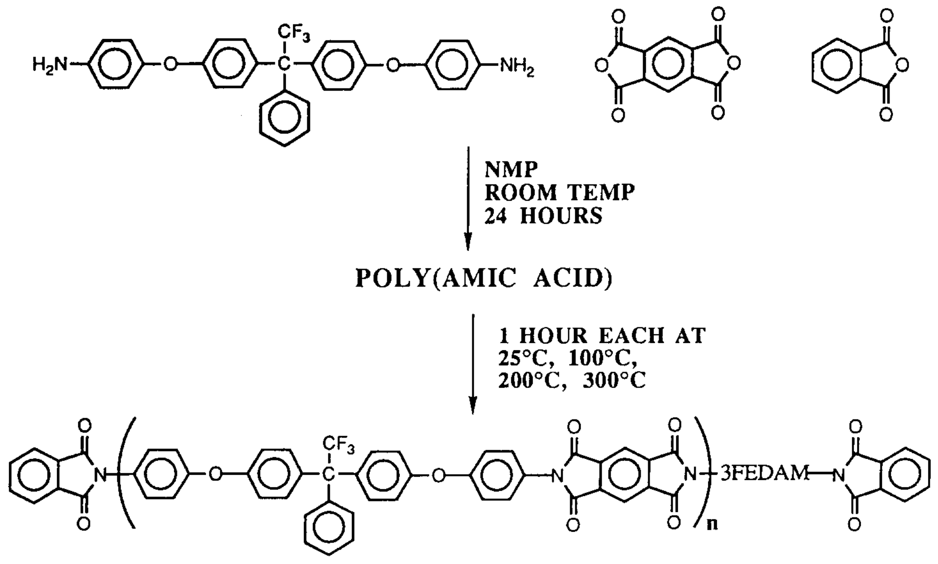

Figure 4 Synthetic scheme for the fully cyclized polyimides

Table 1 Thermal analysis of 3FEDAM–PMDA homopolyimides

Polymer	T_g (°C)[a]	T_m (°C)[a]	T.g.a. (°C)[b]
High *MW*	316	482 (A)	552
30K *MW*	308	476	528

Heating rate 10°C min^{-1}
[a] Nitrogen atmosphere; A, annealed sample
[b] Air atmosphere

been prepared via a new two-step method, as shown in *Figure 3*. The first step is a hydroxyalkylation reaction of trifluoroacetophenone with 4-nitrophenyl phenyl ether producing the 3F-dinitro compound, which is subsequently hydrogenated to afford the diamine, 3FEDAM. The 3F-dinitro compound was characterized by ^1H n.m.r. The chemical shift for the aromatic protons *ortho* to the electron-withdrawing nitro functionality appear downfield at 8.2 ppm, and the peak integration values matched the theoretical predictions. *FT*i.r. analysis showed that bands characteristic of the carbonyl stretch of trifluoroacetophenone disappear upon formation of the dinitro compound. Bands representative of the nitro functionality[15,16] were identified in the *FT*i.r. spectrum; these were the asymmetrical stretch at 1580 cm^{-1} and the symmetrical stretch at 1340 cm^{-1}. The band at 880 cm^{-1}, representative of the C–N stretch, was also apparent in the *FT*i.r. spectrum of the 3F-dinitro compound.

The 3FEDAM diamine was produced by the catalytic reduction of the 3F-dinitro compound. The course of the reaction was monitored by hydrogen consumption and by high resolution ^1H n.m.r. When the consumption of hydrogen ceased, the reaction was considered to be complete. There are two chemical shifts in the 3FEDAM ^1H n.m.r. spectrum, which assisted in determining the completion of the hydrogenation and the identification of the diamine. The primary aromatic amine protons appear at 5.0 ppm and a peak at 6.6 ppm denotes the aromatic protons *ortho* to the amine functionality. The chemical shift at 8.2 ppm was absent in the spectrum of 3FEDAM, indicating that the 3F-dinitro compound was quantitatively hydrogenated. I.r. spectroscopy was also employed to demonstrate conversion of the dinitro compound to the diamine compound. The aromatic primary amine absorptions at 3464 and 3377 cm^{-1} were identified and the bands for the nitro group were absent. H.p.l.c. analysis was utilized to ascertain the level of purity of 3FEDAM. This showed a single peak, indicating that the 3FEDAM was monomer grade purity.

Potentiometric titration was used to identify the diamine and the level of purity. Potentiometric titration has been used to determine the degree of imidization of polyimides[17] and to characterize the formation of poly(amide–imides)[18]. In this case, potentiometric titration provided the molecular weight of the diamine, which was 525.3 g mol^{-1}. The theoretical molecular weight for 3FEDAM is 526.5 g mol^{-1}, which is within instrumental error of the experimental result.

The polyimides were prepared by the reaction of diamines with dianhydrides to form the poly(amic acid) followed by thermal imidization, as illustrated in *Figure 4*. The resulting thermally imidized polyimide films were transparent and yellow to amber in colour. The conversion of the poly(amic acid) to the fully cyclized polyimide could be monitored by *FT*i.r.[14–16]. Complete cyclodehydration was confirmed by the appearance of characteristic imide-related i.r. absorption bands in the range of 1770–1780 cm^{-1} (symmetrical imide I), 1710–1735 cm^{-1} (asymmetrical imide I) and the disappearance of the amic acid band at 1535 cm^{-1} (refs 19–22).

These films were thermally analysed by d.s.c. and t.g.a. and the results are summarized in *Tables 1* and *2*. An uncontrolled molecular weight 3FEDAM–PMDA polyimide was synthesized by adding stoichiometric amounts of each monomer. A controlled molecular weight 3FEDAM–PMDA polyimide with a number average molecular weight of 30 000 g mol^{-1} was synthesized by introducing the monofunctional end-capping reagent, PA, and using Carother's equation for calculations. These polyimides were thermally analysed; the high molecular weight polyimide displayed a T_g of 316°C but did not exhibit an endothermic transition on the first heat in the d.s.c. thermogram. WAXS analysis showed a broad

Table 2 Thermal analysis of 3FEDAM–6FDA/PMDA–PA systems

Wt% 6FDA	T_g (°C)[a]	T_m (°C)[a]	T.g.a. (°C)[b]
0	308	476 (1)	528
10	286	461 (1)	560
20	277	440 (1)	559
30	284	None	550
100	257	None	557

[a] Nitrogen atmosphere at a heating rate of 10°C min^{-1}; 1, first heat
[b] Air atmosphere at a heating rate of 10°C min^{-1}

Table 3 The solubility[a] of 3FEDAM-based polyimides

Polymer	NMP	DMSO	$CHCl_3$	THF
3FEDAM–PMDA	I	I	I	I
3FEDAM–PMDA–PA	I	I	I	I
3FEDAM–BPDA–PA	S	I	S	I
3FEDAM–10%6FDA/PMDA–PA	I	I	I	I
3FEDAM–20%6FDA/PMDA–PA	I	I	I	I
3FEDAM–30%6FDA/PMDA–PA	I	I	I	I
3FEDAM–6FDA–PA	S	I	S	S

[a] 1% solids, room temperature, stirring, 24 h; I, insoluble; S, soluble

amorphous halo, indicating that the material was not crystalline. However, it was possible to induce crystallinity by annealing at 400°C for 30 min. The d.s.c. results of the annealed material showed a broad endotherm on the first heat. In the WAXS analysis of the annealed polyimide, the amorphous content decreased slightly while peaks indicative of crystallinity became apparent.

The controlled molecular weight 3FEDAM–PMDA–PA polyimide had a T_g of 308°C and a large endotherm on the first heat with a peak value of 476°C. The heat of fusion of this melting transition was not evaluated owing to the instability of the material. In the second heat of the thermogram, the endothermic transition was absent. The WAXS analysis of the original material showed a semicrystalline morphology. The crystallinity appeared to be enhanced by annealing at 400°C for 30 min. WAXS showed that the annealed 3FEDAM–PMDA–PA polyimide had less amorphous character and sharper peaks than the untreated polyimide. These results suggest that the crystallinity was enhanced by thermal treatment. It appears that these materials have the potential to crystallize; however, it is most likely that the rate of crystallization is very slow, as found in other stiff chain systems[23,24].

The 3FEDAM–PMDA–PA homopolymer degraded upon melting, therefore the material could not be melt processed. Consequently, several copolymers were prepared with the goal of depressing the T_m and producing a melt-stable material. The dianhydride, 6FDA, was selected based on previous studies[2,11,25]. As expected, the T_g and T_m (*Table 2*) decreased with increasing mole per cent of 6FDA incorporated in the 3FEDAM–PMDA system. The limit to the amount of 6FDA incorporated without destroying the crystallinity was determined to be approximately 20%. The 3FEDAM–20% 6FDA/PMDA–PA polyimide had a T_g of 277°C and a T_m of 440°C, and appeared to show satisfactory short-term thermal stability above T_m. The 20% 6FDA copolymer was semicrystalline, as shown by the WAXS analysis. However, the 30% 6FDA copolymer exhibited a broad amorphous halo, indicating the absence of crystallinity. This trend was also supported by the d.s.c. results.

Dynamic t.g.a. of the polyimides given in *Tables 1* and *2* showed that these fluorinated polymers were thermally stable to 475°C in air. The homopolymers and copolymers exhibited 5% weight loss temperatures greater than 500°C. An isothermal t.g.a. of the 30K 3FEDAM–PMDA–PA polyimide showed less than 2% weight loss after 24 h at 371°C in air.

These fluorinated, semicrystalline polyimides were highly solvent-resistant, as shown in *Table 3*. As expected, the semicrystalline polyimides are not soluble in polar aprotic solvents such as NMP, while the amorphous polyimides had enhanced solubility in the selected solvents. It required approximately 50 mol% incorporation of the comonomer, 6FDA, to impart solubility to the copolymers.

CONCLUSIONS

The 3FEDAM monomer was readily prepared in high yield via a two-step synthesis. The 3FEDAM–PMDA-based polyimides were semicrystalline with T_g values in the range of 277–316°C. These transition temperatures are essentially identical to the 4BDAF–PMDA systems studied previously[11]. The incorporation of the flexible comonomer, 6FDA, depressed the melting transition of the 3FEDAM–PMDA–PA homopolymer, providing a melt-stable material. However, incorporation of more than about 20% of the comonomer, 6FDA, destroyed the semicrystalline nature. The 3FEDAM-based polyimides studied were thermally stable and semicrystalline systems were highly solvent-resistant.

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