

Polyimides. IV. Synthesis and Characterization of Fluorinated Copolyimides

Mukesh Kumar Madhra,¹ Mamta Sharma,² Susanta Banerjee¹

¹Synthetic Chemistry Division, Defence Research and Development Establishment, Jhansi Road, Gwailor 474002, India

²Analytical Services Wing, Defence Research and Development Establishment, Jhansi Road, Gwailor 474002, India

Received 1 May 2003; accepted 19 December 2003

DOI 10.1002/app.20387

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of new copolyimides were synthesized by the reaction of pyrometallic dianhydride, benzophenone tetracarboxylic acid dianhydride, and 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane (6FDA) with two diamines, 4,4'-bis(aminophenoxy)-3,3'-trifluoromethyl terphenyl and 4,4'-diaminodiphenyl ether, at a 50:50 ratio by a thermal imidization route. The complete spectral assignment of the copolymer derived from 6FDA was done with the help of distortionless enhancement of polarization transfer 90° and two-dimensional heteronuclear (C, H) shift correlation spectroscopy. The various types of couplings in the copolymers were assigned with the help of two-dimensional correlated spectroscopy (COSY) homonuclear correlation spectroscopy. A long-range connectivity was also observed by a heteronuclear correlation spectroscopy via long-range coupling experiment. The copolyimides derived from 6FDA were soluble in common organic solvents such as *N,N*-dimethyl formamide, *N,N*-dimethyl

acetamide, dimethyl sulfoxide, *N*-methyl pyrrolidone, and chloroform. Water absorption values, after the samples were boiled in water for 72 h, were in the range 0.3–0.7%. These polyimides had low dielectric constants of 2.79–3.01 at 1 MHz, low refractive indices of 1.655–1.705 at 589.3 nm, and high optical transparencies (>90%). The onset temperature for 5% weight loss for these polyimides, as assessed by thermogravimetric analysis, was up to 551°C in air, indicating a very high thermal stability, and the polyimides showed glass-transition temperatures as high as 316°C. Transparent thin films of these polyimides exhibited tensile strengths up to 93 MPa, moduli of elasticity up to 3.1 GPa, and elongations at break up to 24% depending on the exact repeat unit structure. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 235–246, 2004

Key words: NMR; thermal properties; mechanical properties; dielectric properties

INTRODUCTION

Aromatic polyimides have received considerable interest for high-technology applications because of their thermal stability and mechanical strength.^{1,2} Since the introduction of the still-prevalent chemistry based on pyrometallic dianhydride (PMDA), benzophenone tetracarboxylic acid dianhydride (BTDA), and 4,4'-diaminophenyl ether (ODA), a number of commercial products with improved properties derived from other monomers are now available.³ Despite the numerous polymeric structures that have been studied over the past several decades, the search for new ones continues unabated because emerging applications demand even better performances not met by current commercial products. Desired improvements include a higher mechanical stiffness and strength, a lower moisture absorption, a low dielectric constant (ϵ), a low coefficient of thermal expansion,

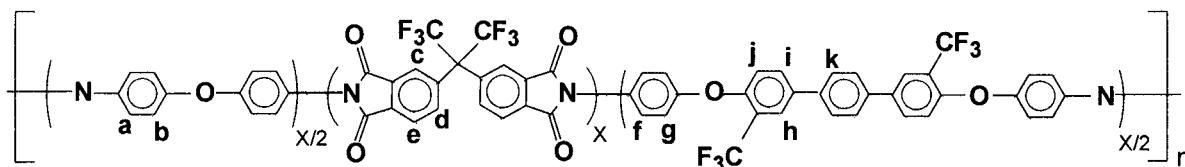
and ease of processing.⁴ The difficulties in processing arise from the insolubility and high melting temperature of most aromatic polyimides.

The use of monomers containing pendent trifluoromethyl groups and hexafluoroisopropylidene bridging moieties appears to be particularly effective.⁵ Thus, the polyimides based on trifluoromethyl groups have been reported to be soluble in amide, ketones, and chlorinated hydrocarbons.^{6,7} Other means of solubilization of polyimides includes the introduction of flexible linkages,^{8,9} bulky substituents,^{10,11} or bulky units in the polymer backbone^{12–14} or noncoplanar^{15,16} or alicyclic¹⁷ monomers.

ODA is widely used in the synthesis of polyimides, but the polyimides synthesized from this diamine are insoluble or have poor solubility, depending on the dianhydride used. To increase solubility, Chung and Kim¹⁸ designed a new diamine monomer, 2-trifluoromethyl-4,4'-diaminophenyl ether, with the same structure as ODA except for one trifluoromethyl group at the two position of one of the benzene rings. With the introduction of one trifluoromethyl group in the polymer structure, they achieved the solubilization of the polymers with glass-transition temperatures (T_g 's) from 246 to 295°C.

Correspondence to: S. Banerjee (susanta_b20012001@yahoo.com).

Contract grant sponsor: Defense Research & Development Organization (DRDO) (to M.K.M.).



Scheme 1

So to achieve a combination of desired properties such as solubility, thermal stability, and mechanical properties, it is necessary to merge the properties of each polyimide into one system. Such modification of properties is generally achieved through copolymerization or polymer blending. Copolymerization is particularly attractive because tailoring the properties of the resulting polymers is possible even on molecular levels, which cannot be achieved through the blending approach.

Copolymerization, with either a diamine and two dianhydrides or a dianhydride and two different diamines, leads to random copolymerization with distorted chemical sequences.^{19–24} The chemical disorder could affect the chain dynamics controlling the degree of interchain associations and entanglements. Therefore, the physical properties of the copolymers could be affected by chemical disorder.

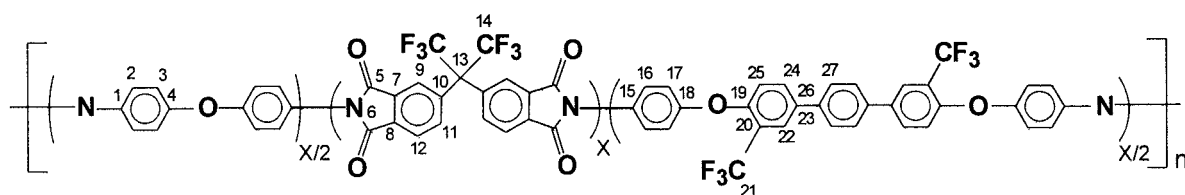
In this context, we synthesized copolyimides containing two diamines and different dianhydride units. We describe herein the successful synthesis and chemical characterization of the alternating copolyimides consisting of ODA and 4,4'-bis(aminophenoxy)-3,3'-trifluoromethyl terphenyl (ATFT) as diamine units and the reaction of these in a 50:50 ratio with different dianhydrides, including PMDA, BDTA, and 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane (6FDA).

EXPERIMENTAL

General considerations

The elements carbon and hydrogen were analyzed by the Prejel method, and nitrogen was analyzed by the Kjeldhal method. ¹H-NMR (400 MHz), ¹³C-NMR (100 MHz), and ¹⁹F-NMR (376 MHz) spectra were recorded on a Bruker DPX 400 MHz instrument [reference = 0 ppm with tetramethyl silane (¹H-NMR and ¹³C-NMR

of CFCl₃ (¹⁹F-NMR)]. CDCl₃ was used as a solvent unless specified otherwise. To elucidate the proton-proton connectivity; a two-dimensional (2D) ¹H–¹H correlated spectroscopy (COSY) spectrum was recorded with a 90° mixing pulse. For the assignment of the complicated ¹³C-NMR spectrum, a 2D ¹H–¹³C heteronuclear correlation experiment (XHCORR) with a distortionless enhancement of polarization transfer (DEPT) 45° pulse for ¹³C was performed. The directly attached proton carbon signals (CH) were assigned with a ¹³C DEPT 90° pulse. For a more precise interpretation and a correlation between quaternary carbons and protons, a 2D heteronuclear correlation spectroscopy via long-range coupling (COLOC) experiment was also performed. IR spectra of the polymer films were recorded with a Nicolet Impact 410 spectrophotometer. Gel permeation chromatography was performed with a Waters instrument. Tetrahydrofuran (THF) was used as an eluent, and Styragel HR-4 columns were used. The molecular weights and polydispersity values are reported versus a monodisperse polystyrene standard. Differential scanning calorimetry (DSC) measurements were made on a TA Instruments DSC-2920 instrument at a heating/cooling rate of 20°C/min under nitrogen. *T_g* values were measured on a TA Instruments thermogravimetric analyzer (model TGA-2950). A heating rate of 10°C/min was used for the determination of the decomposition temperature (*T_d*) at 5% weight loss under synthetic air. Dynamic mechanical analysis (DMA) was performed on a Netzch DMA-242 instrument in the tension mode on thin film (80–100 μ) samples at a heating rate of 5°C/min (1 and 10 Hz). The mechanical properties of the thin polymer films were evaluated at room temperature on a Rheometric minimat instrument under a strain rate of 5%/min. The refractive indices were measured by Abbe's method with an Atago 4T-type



Scheme 2

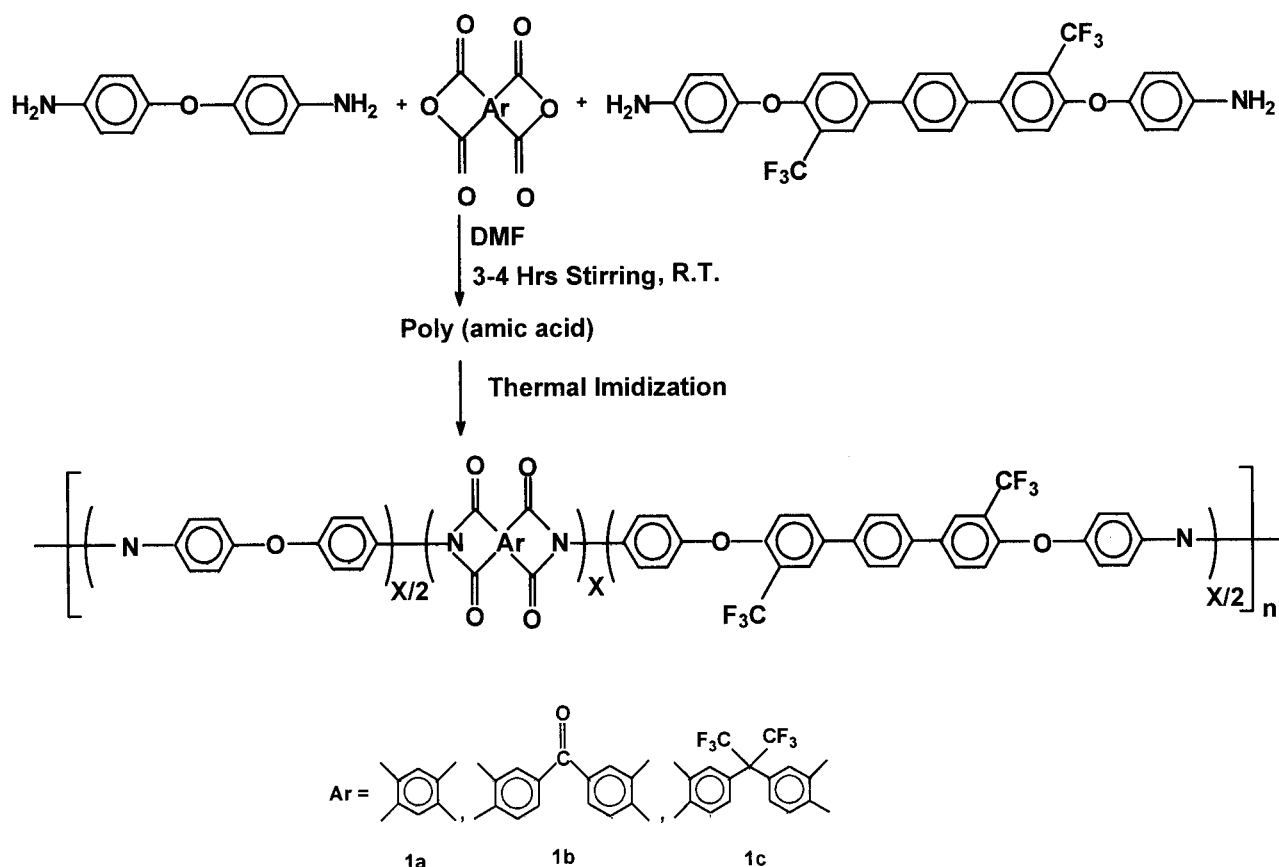


Figure 1 Reaction scheme and structures of the copolymers.

refractometer. The measurements were performed at 35°C and a light wavelength of 589.3 nm from the sodium D line. The dielectric constants of the copolyimide films (20 μm) were measured with a parallel plate capacitor method with a YHP 4278 capacitance meter at 1 MHz at 30°C and a relative humidity of 45%. The water absorption rates of the vacuum-dried films were measured with a Mettler microbalance with a sensitivity of 10^{-6} g after the films were immersed in double-distilled water for 72 h at 30°C. Ultraviolet-visible (UV-vis) spectra of the polymer films were recorded with a Speccord Version 2.1 E Analytik Jena AE instrument.

Starting materials

All reagents were purchased from Aldrich, Fluka (Switzerland), Chempure, or Fluorchem Chemical Co.

TABLE I
Solubility of the Copoly(ether imides)

Polymer	NMP	DMF	DMAc	DMSO	THF	CHCl ₃	Acetone
1a	=	=	-	-	-	-	-
1b	=	=	-	-	=	-	-
1c	+	+	+	0	+	+	-

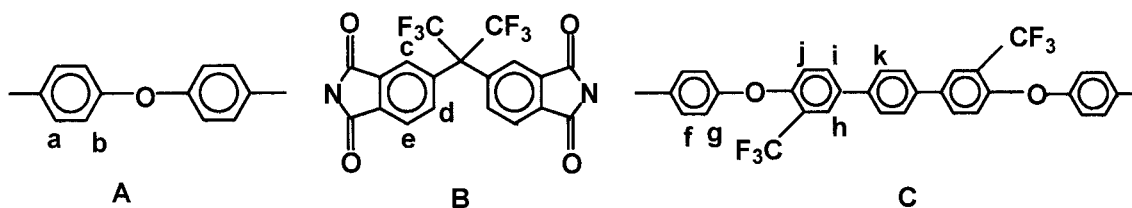
+ = soluble at room temperature; 0 = soluble on heating; = = swelled; - = insoluble at reflux.

and were used as received unless noted otherwise. PMDA and BDTA (Fluka) were purified by sublimation under reduced pressure. 6FDA (99.99%) was purchased from Lancaster Chemical Co. and was heated at 180°C before use. Dimethylformamide (DMF; E. Merck, India) was purified by stirring with NaOH and distilling twice from P₂O₅ under reduced pressure. ODA was recrystallized from ethanol. A detailed synthesis of the terphenyl diamino compound ATFT was reported earlier.⁶

Polymerization

All polymerization reactions were carried out in a nitrogen flow with a 50:50 ratio of the diamine monomers ATFT, ODA, and the dianhydrides (PMDA, BDTA, or 6FDA). A representative polymerization procedure follows.

A 50-mL, round-bottom flask equipped with a nitrogen inlet and a stirring bar was charged with 0.399 g (6.876 mmol) of ATFT and 0.137 g (6.876 mmol) of ODA in 10 mL of dry DMF. The solution was stirred until the diamine dissolved completely; 0.3 g (1.375 mmol) of PDA was slowly added to this solution. The resulting highly viscous solution was stirred slowly and continuously for 3 h at room temperature (RT). The poly(amic acid) solution was cast onto clean dry



Scheme 3

glass plates by a doctor blade. The films were dried in an oven at 80°C for 6 h; at 150, 200, 250, and 300°C for 1 h at each temperature; and at 350°C for 15 min. The polyimide films were removed by immersion of the glass plates in boiling water.

ANAL. Calcd for polyimide 1a ($C_{54}H_{28}F_6N_4O_7$)_n (958.82 g/mol)_n: C, 67.64%; H, 2.94%; N, 5.84%. Found: C, 67.13%, H, 2.82%, N, 5.59%.

IR (KBr, cm^{-1}) for polyimide 1a: 3051 (aromatic C—H), 1777 (C=O asymmetric stretching), 1716 (C=O symmetric stretching), 1378 (C—N stretching), 1335, 1235, 1207 (C—O—C), 1328, 1167 (C—F multiple stretch bending), 726 (C=O bending).

ANAL. Calcd for polyimide 1b ($C_{61}H_{32}F_6N_4O_8$)_n (1062.93 g/mol)_n: C, 68.92%; H, 3.03%; N, 5.27%. Found: C, 68.71%, H, 2.92%, N, 4.89%.

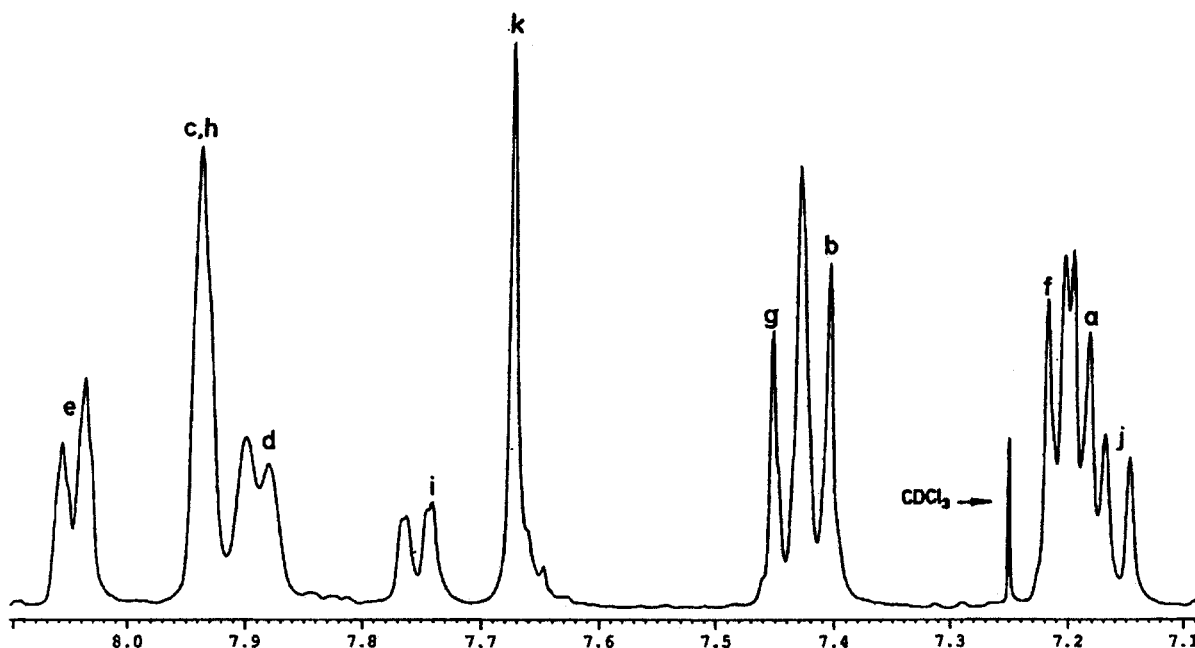
IR (KBr, cm^{-1}) for polyimide 1b: 3067 (aromatic C—H), 1781 (C=O asymmetric stretching), 1728 (C=O symmetric stretching), 1675–1500, 1436 (aromatic C=C), 1382 (C—N stretching), 1332, 1279, 1204 (C—O—C), 1329, 1177 (C—F multiple stretch bending), 724 (C=O bending).

ANAL. Calcd for polyimide 1c ($C_{63}H_{32}F_{12}N_4O_7$)_n (1184.94 g/mol)_n: C, 63.85%; H, 2.72%; N, 4.72%. Found: C, 63.04%, H, 2.6%, N, 4.69%.

IR (KBr, cm^{-1}) for polyimide 1c: 3073 (aromatic C—H), 1788 (C=O asymmetric stretching), 1727 (C=O symmetric stretching), 1619–1514, 1437 (aromatic C=C), 1378 (C—N stretching), 1337, 1263 (C—O—C), 1303, 1141 (C—F multiple stretch bending), 723 (C=O bending).

1H -NMR ($CDCl_3$, δ , ppm): 7.99–7.97 (d, $J = 7.9$ Hz, 4H, H_e), 7.95 (bs, 2H, H_h), 7.88 (s, 4H, H_c , obtained from 2D 1H - 1H COSY NMR), 7.86–7.84 (d, $J = 7.9$ Hz, 4H, H_d), 7.70–7.67 (d, $J = 8.74$ Hz, 2H, H_i), 7.61 (s, 4H, H_k), 7.39–7.37 (d, $J = 8.3$ Hz, 4H, H_g), 7.37–7.34 (d, $J = 8.29$ Hz, 4H, H_b), 7.16–7.14 (d, $J = 8.36$ Hz, 4H, H_f), 7.14–7.12 (d, $J = 8.29$ Hz, 4H, H_a), 7.11–7.09 (d, $J = 8.74$ Hz, 2H, H_j).

^{13}C -NMR ($CDCl_3$, δ , ppm): 166.14 (ODA), 166.11 (terphenyl, C5), 165.98 (ODA), 165.95 (terphenyl, C6, ODA), 156.62 (C18), 156.53 (C4), 154.08 (C19), 139.21 (q, $J = 3.62$ Hz, C10), 138.60 (C26), 136.06 (C23), 135.96 (C11), 132.64 (C8), 132.35 (C7), 131.71 (C24), 128.16

Figure 2 1H -NMR spectrum of polymer 1c.

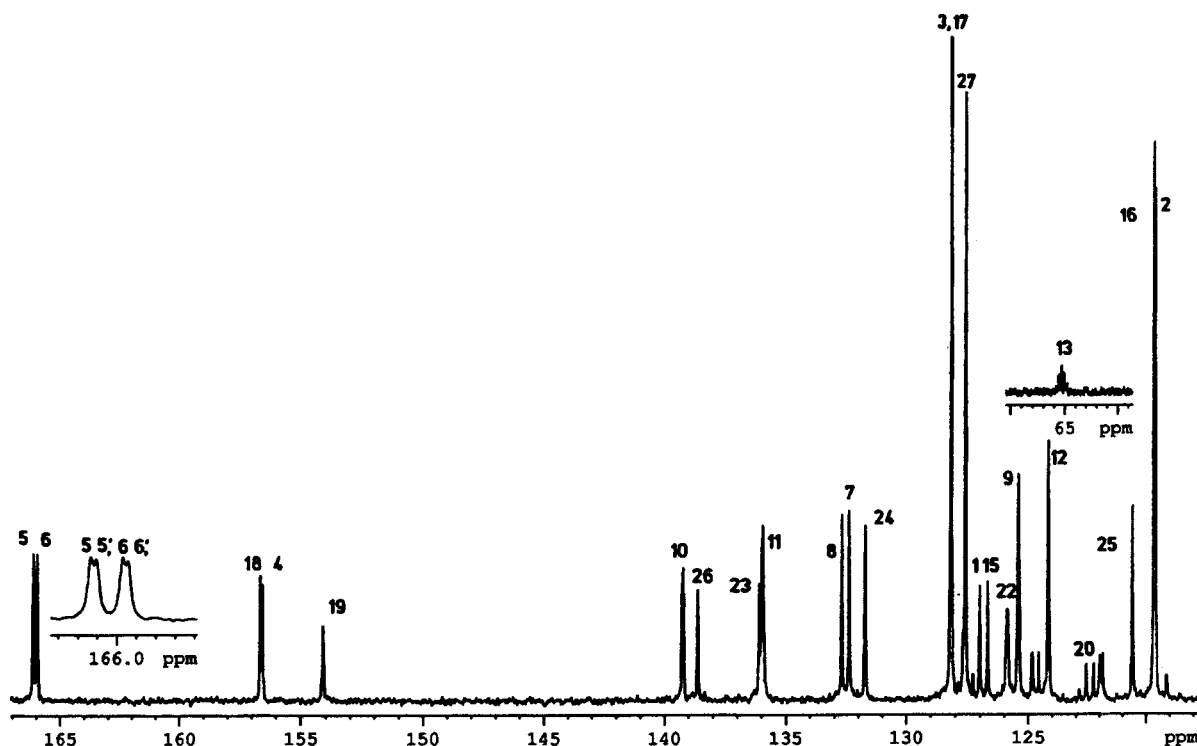


Figure 3 ^{13}C -NMR spectrum of polymer 1c.

(C3, C17), 123.37 (d, $J = 287$ Hz, C14), 127.57 (C27), 123.13 (q, $J = 272$ Hz, C21), 126.94 (C1), 126.62 (C15), 122.40 (q, $J = 4.8$ Hz, C22), 125.40 (C9), 124.18 (C12), 122.40 (q, $J = 29$ Hz, C20), 120.57 (C25), 119.67 (C16), 199.60 (C2), 65.44 (q, $J = 26$ Hz, C13).

^{19}F -NMR (CDCl_3 , δ , ppm): -63.62 (F1), -62.22 (21), 166.14, 166.11 (C5), 165.98, 165.95 (C6).

RESULTS AND DISCUSSION

Synthesis of polymers

The diamino monomers, ATFT and ODA, were reacted with PMDA, BTDA, and 6FDA to give the corresponding poly(ether imides), as shown in Figure 1.

The syntheses of polyimides were carried out via a poly(amic acid) intermediate; the diamines (ATFT and ODA) were reacted with equimolar amounts of PMDA, BTDA, or 6FDA in DMF at RT. Initially, both of the diamines were dissolved in a measured amount of dry DMF, and the dianhydride monomers were added to this slowly. In all of the cases, the reaction mixture became highly viscous within 10–15 min; the reactions were continued for 3–4 h. The poly(amic acid) solutions were cast on clean glass plates and heated through various stages up to 350°C to remove the solvent and the water formed by the imidization. Transparent, pale yellowish films were obtained in all of the cases. All of the polyimide films were tough. Gel permeation chromatography of poly(ether imide) 1c

was run in THF solvent. The number-average molecular weight of this polymer was 23,850 with a polydispersity index of 1.32, indicating a high molar mass.

Polymer solubilities

The solubilities of the resulting polyimides were investigated in different organic solvents. We attempted to obtain a 10% (w/v) solution of all of the polymers in different solvents, as presented in Table I. The solubility behavior of these copolyimides did not show significant improvements in comparison to their homopolymer analogs.⁶ This was possibly due to the formation of random copolyimide structures. Park et al.²⁴ observed drastic differences in solubility between alternating copolyimides and their corresponding random isomers. Polymer 1c was soluble in a number of common organic solvents, including *N*-methyl pyrrolidone (NMP), *N,N*-dimethyl acetamide (DMAc), DMF, THF, dimethyl sulfoxide (DMSO), and CHCl_3 . This was due to the presence of a bulky CF_3 group in both the diamine and the dianhydride monomer, which led to an increased fractional free volume and, hence, increased the solubility.

Spectroscopy

The formation of poly(ether imides) was confirmed by Fourier transform infrared (FTIR) spectroscopy. FTIR

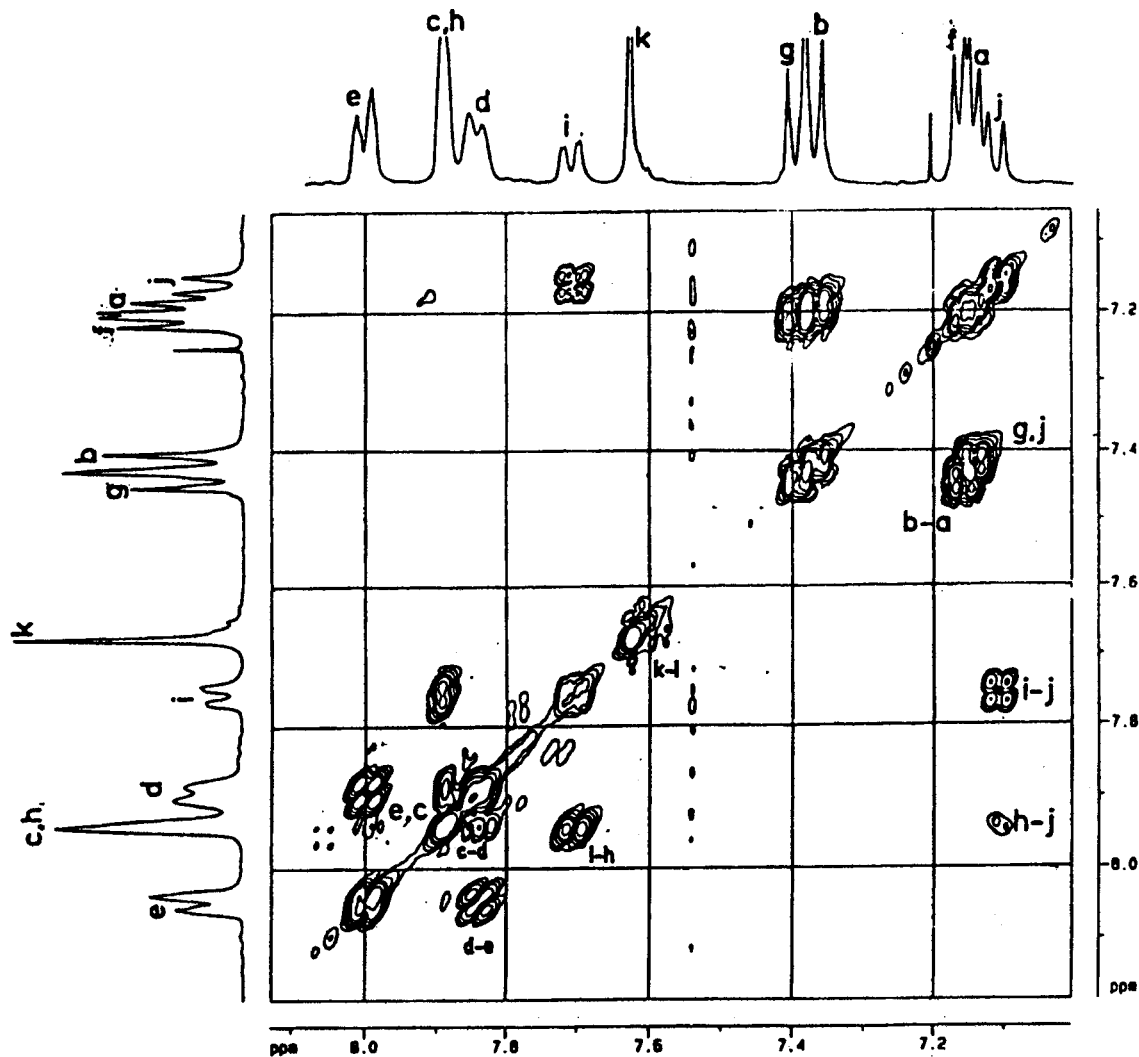


Figure 4 2D ^1H - ^1H COSY spectrum of polymer 1c.

spectra of the polyimide films prepared by the thermal imidization method showed absorption bands at about 1780 cm^{-1} ($\text{C}=\text{O}$ asymmetric stretching), 1730 cm^{-1} ($\text{C}=\text{O}$ symmetric stretching), 1378 cm^{-1} ($\text{C}-\text{N}$ stretching), and 721 cm^{-1} ($\text{C}=\text{O}$ bending), which are characteristic for imide rings.^{5,6} The absence of absorption bands at $3400\text{--}2900\text{ cm}^{-1}$ corresponding to amide ($-\text{NH}-$) and acid ($-\text{OH}$) stretching, at 1720 cm^{-1} corresponding to $\text{C}=\text{O}$ stretching of carboxylic acid, and at 1660 cm^{-1} corresponding to $\text{C}=\text{O}$ stretching (amid groups) in the spectra of the polyimides indicated complete imidization. UV-vis spectroscopic studies of the polymers revealed that polymer 1c had a greater transparency than polymers 1a and 1b, which was directly related to the color intensity of the film. The decreased color of polymer 1c was due to the disturbed conjugation by 6F groups placed between aromatic rings. All of the polymer films (thickness = $30\text{--}40\text{ }\mu\text{m}$) showed high optical transparencies of more than 90% and cutoff wavelengths at about 480,

476, and 376 nm for polymers 1a, 1b, and 1c, respectively. No distinct peak maxima were observed.

NMR study

Copolymer 1c was soluble in CDCl_3 ; therefore, the detailed interpretation of this copolymer by NMR was possible. The ^1H -NMR experiment on copolymer 1c showed a distinct splitting pattern; however, the mode of addition was random.²⁴ The molar ratio of units A, B, and C were calculated. The molar fractions were obtained from the normalized area of the resonance signal with a nonlinear least squares deconvoluting program by the ^1H -NMR spectrum of polymer 1c, as shown in Figure 2. From this, we found that n moles of unit B reacted with $n/2$ moles of each unit A and C, which was, in fact, the actual feed ratio in the experiment. The ^{13}C -NMR spectrum of polymer 1c (Fig. 3) showed two different values each for carbons 5 and 6 (166.14 and 166.11 for C5 and 165.98 and 165.95 for

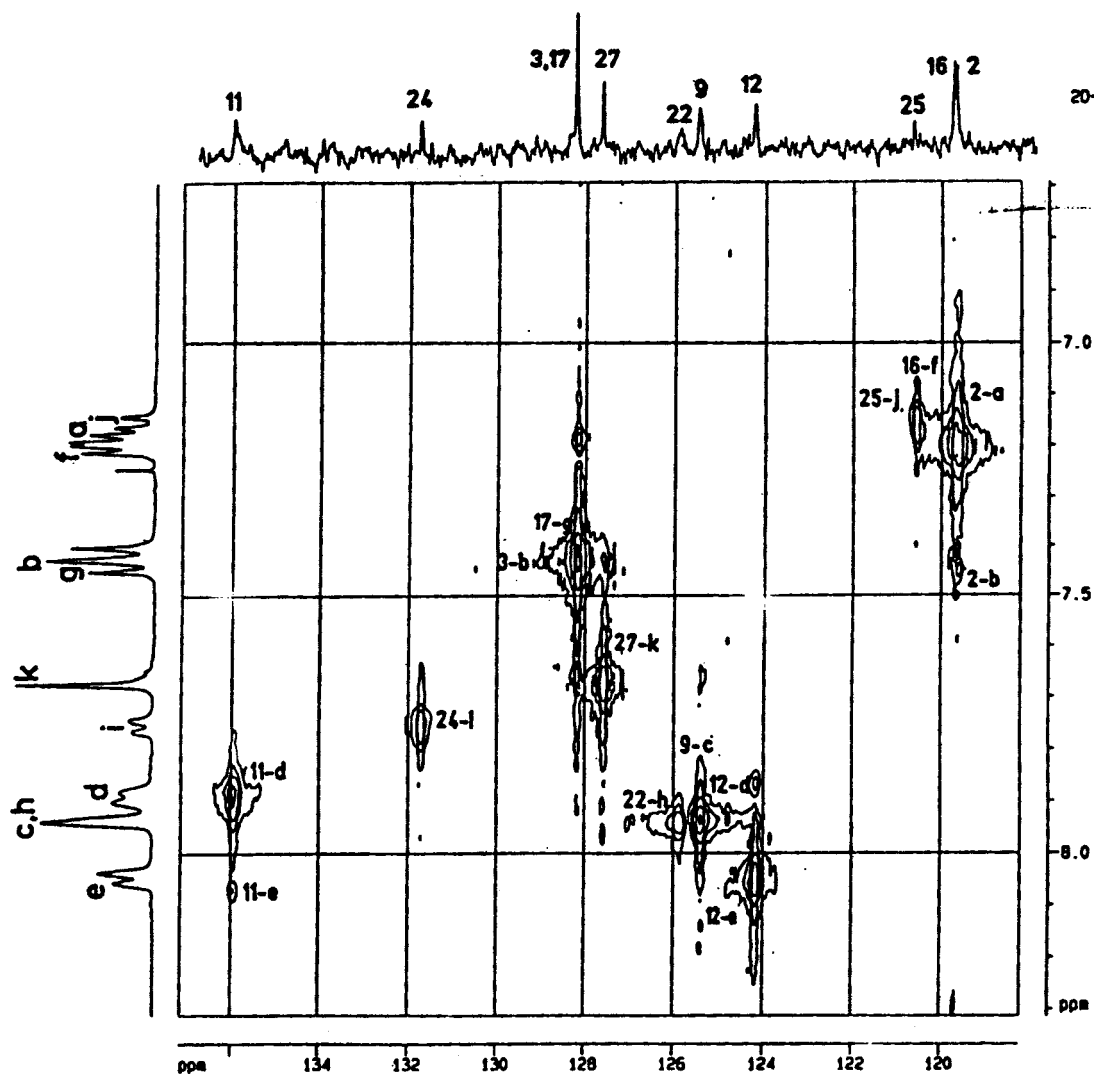


Figure 5 2D XCORR spectrum of polymer 1c.

C6), which suggested that the 166.14 and 165.98 values corresponded to the C=O of the 6FDA moiety attached to ODA and the 166.11 and 165.95 values corresponded to the C=O of the 6FDA moiety attached to the terphenyl. Another interesting observation was that in the $^1\text{H-NMR}$ spectrum of polymer 1c, the intensity ratio of proton signals due to unit B (c, d, and e) was double that of the intensity ratio of the proton

signals from units A (a, b, f, and d) and C (f, d, j, i, h, and k).

To elucidate the NMR splitting patterns and chemical shift assignment, a homospin decoupling experiment was performed. We further confirmed these by a 2D $^1\text{H-}^1\text{H}$ COSY experiment, as shown in Figure 4. Long-range $^1\text{H-}^1\text{H}$ connectivities were also observed, which were not otherwise very clear in the $^1\text{H-NMR}$ spectrum. On the basis of the splitting patterns and the position of the chemical shifts, the proton resonance corresponding to protons a–k could easily be assigned. Protons a–k, in the range 7–8 ppm, apparently arose from the proposed structure, where A, B, and C were represented by ODA, 6FDA, and the terphenyl moieties, respectively. The a and b protons of unit A were expected to show different chemical shifts than the f and g protons of unit C. Proton a appeared at a lower field than proton g, which was due to the more inductive

TABLE II
Thermal Properties of the Copoly(ether imides)

Polymer	T_g (°C)		T_d (°C) for 5% weight loss in air	T_d (°C) for 10% weight loss in air
	DSC	DMA ^a		
1a	316	304	531	570
1b	259	255	551	592
1c	272	265	524	552

^a Tan δ peak at 10 Hz:

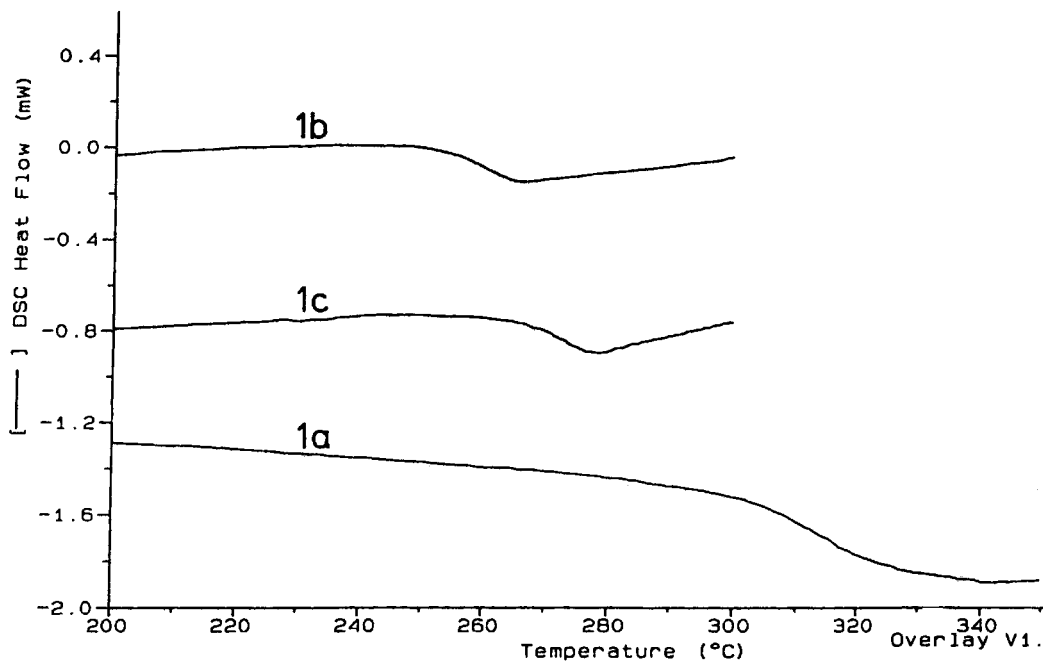


Figure 6 DSC curves of the copolymer.

deshielding effect by the carbonyl group of unit B than the CF_3 group of unit C.

In the homonuclear COSY experiment, the contours for three-bond (j-l, f-g, a-b, and d-e), four bond (e-d and l-h), and five-bond (c-e, j-h, and k-l) connectiv-

ity were observed, depending on the mixing time. The contours for the different connectivities are shown in Figure 4.

By a DEPT 90°C experiment, only C-H carbon signals were assigned. This connectivity was further

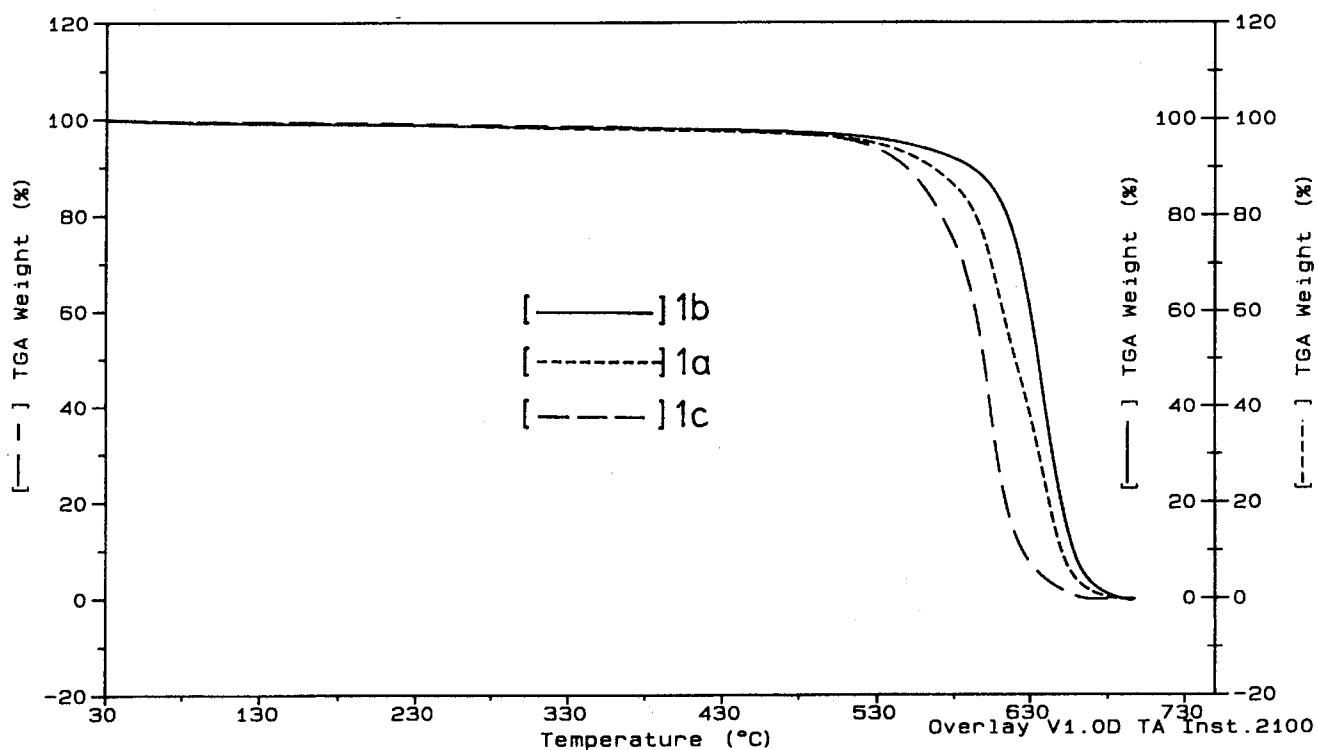


Figure 7 TGA thermograms of the copolymer.

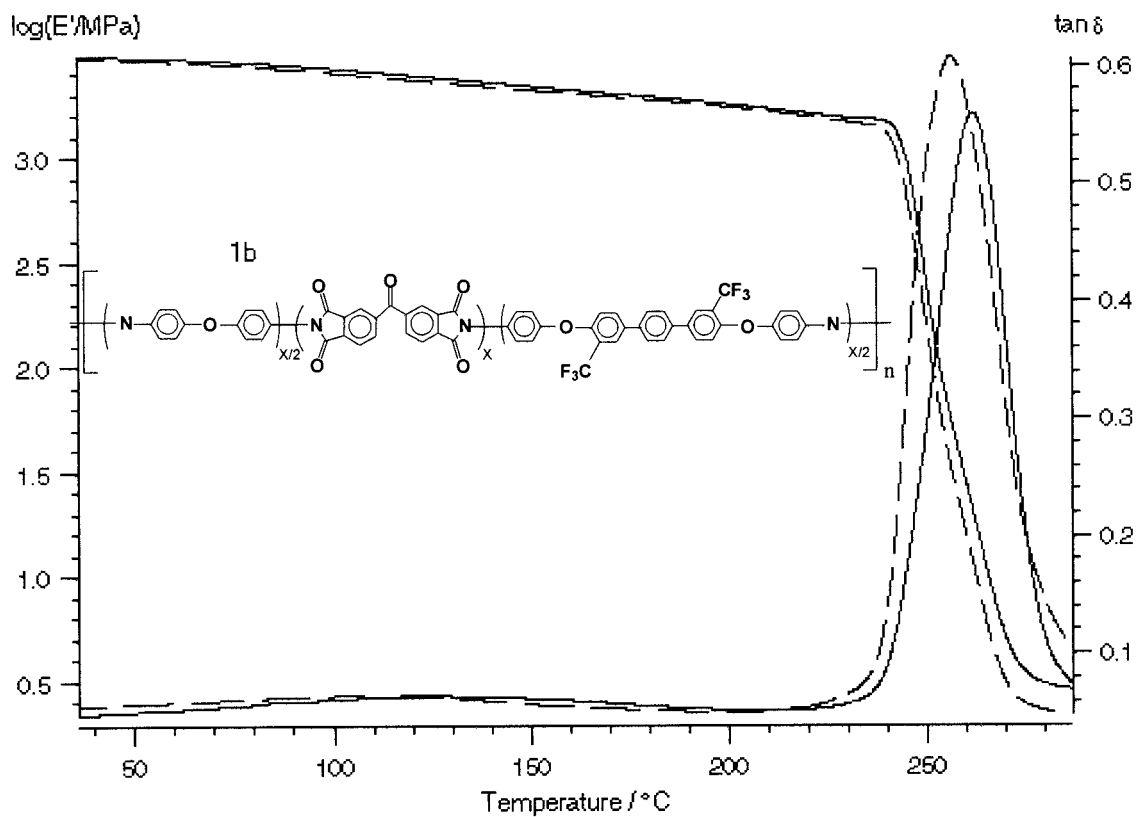
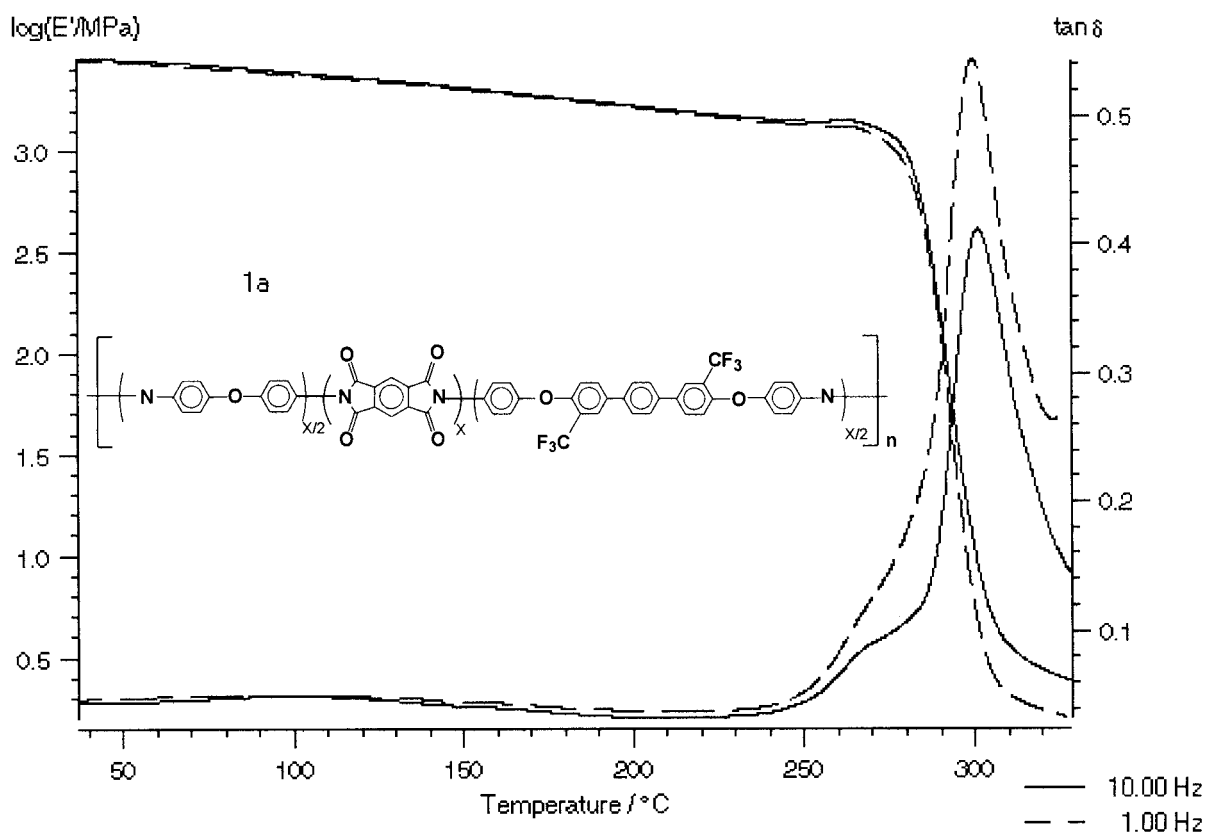


Figure 8 DMA plots of the poly(ether imides).

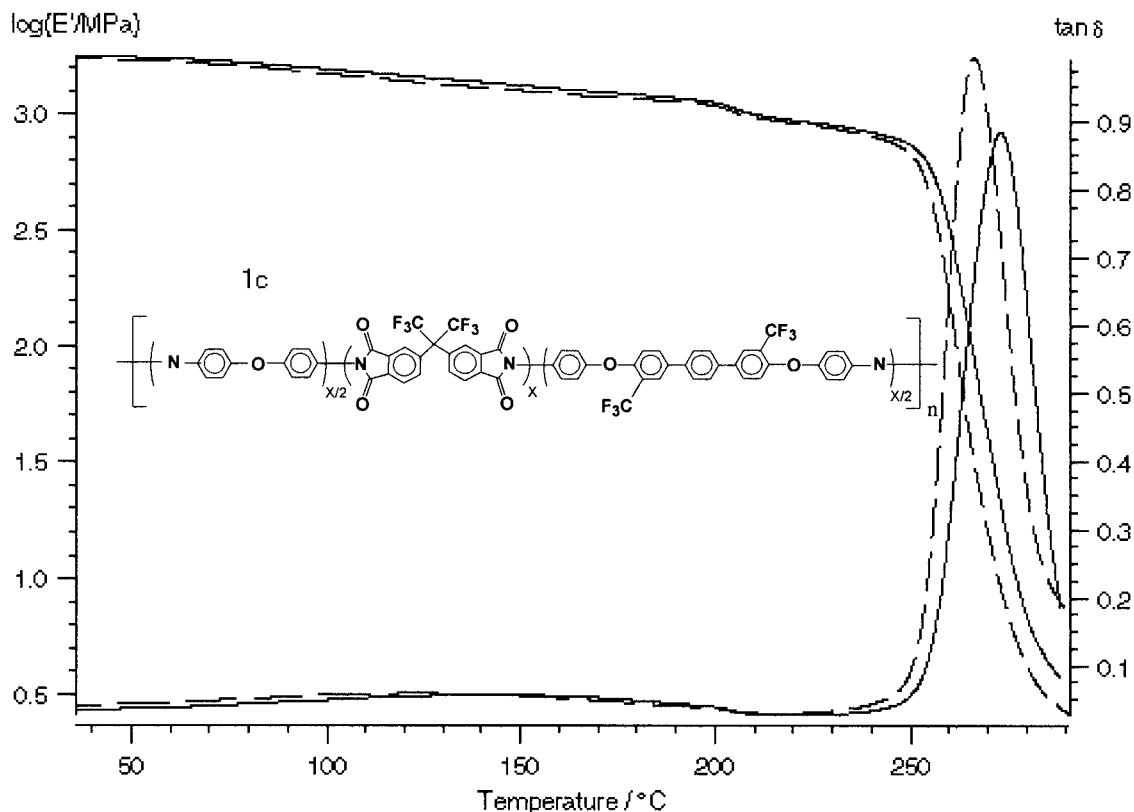


Figure 8 (Continued from the previous page)

confirmed by a 2D XCORR experiment with a DEPT 45°C pulse for ^{13}C . With the aid of the proton spectrum assignments, the protonated carbons were readily assigned. The correlation contour is shown in Figure 5. The result obtained for this experiment further supported our ^{13}C and ^1H interpretations.

Long-range connectivity was also observed by a COLOC experiment for the unambiguous assignment of the ^{13}C -NMR chemical shifts. This assigned the two-bond correlation of the quaternary carbon with the proton correctly.

^{19}F -NMR spectroscopy further supported the findings obtained from ^1H -NMR and ^{13}C -NMR spectroscopy. The ^{19}F signal for the CF_3 of unit B and the CF_3 of unit C were observed at -63.62 and -62.22 ppm, respectively. The integration ratio of 2:1 for these peaks indicated that the molar ratio of units B and C was 2:1.

Thermal properties

The T_g values of the copolyimides were evaluated by DSC and dynamic mechanical thermal analysis. None of the polymers exhibited crystallization or melt transition in the DSC measurements. The T_g values are summarized in Table II. Figure 6 shows the T_g values of the copolymers. The highest T_g was shown for polymer 1a because it had the most rigid polymer

backbone.²⁴ However, there was a decrease in the T_g values of these polymers compared to those of the homopolymers synthesized from ODA/PMDA, ODA/BTDA, and ODA/6FDA. This was due to the increase in flexibility in the structures of the homopolymers, which was due to the increase in ether linkages. These copolymers exhibited outstanding thermal stabilities. The 5% weight loss temperature in air of these polymers was in the range 524–551°C. The T_d values for 5 and 10% for the copolymers are summarized in Table II. Figure 7 shows the thermogravimetric analysis (TGA) thermograms of the copolyimides.

DMA measurements

The T_g values taken from the $\tan \delta$ peaks at 10 Hz are given in Table II. These values were comparable to the

TABLE III
Mechanical Properties of the Copoly(ether imides)

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
1a	87	2.9	24
1b	93	3.1	21
1c	72	1.9	13

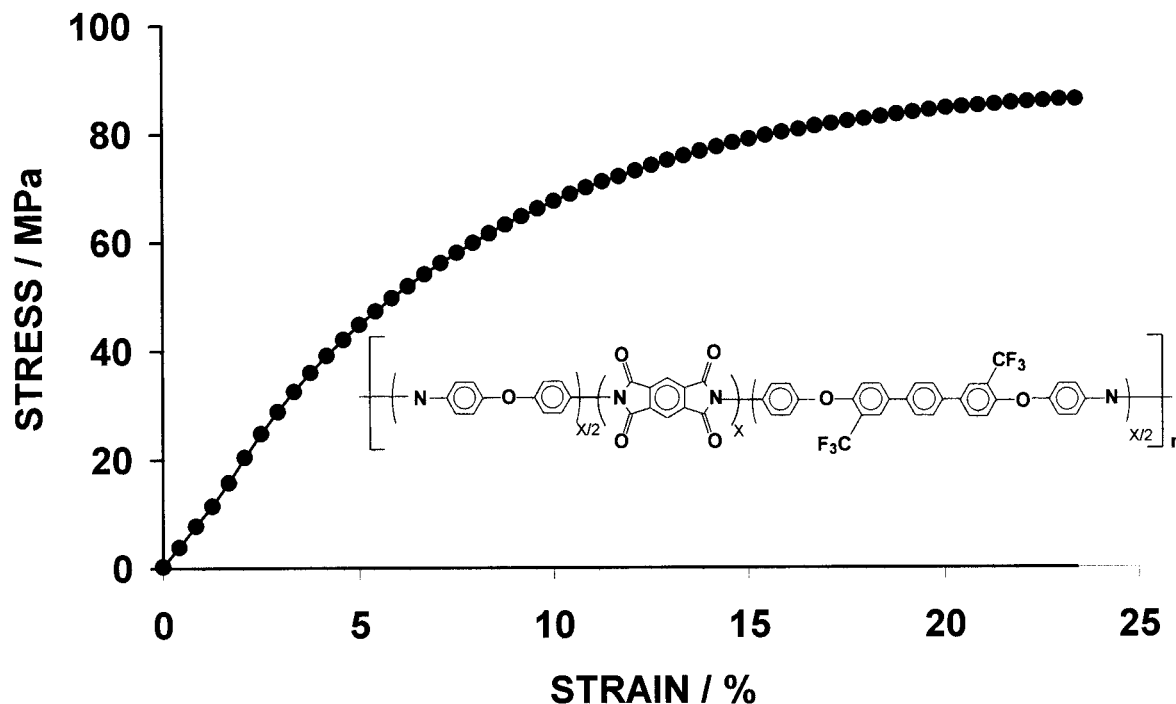


Figure 9 Mechanical plot for copolymer 1a.

calorimetric T_g values. The polymers retained their mechanical properties up to their T_g 's, as shown by the storage modulus plots of the polymers. Figure 8 shows the DMA plots of the polymers.

Mechanical properties

The mechanical properties of the prepared poly(ether imide) films are shown in Table III. The polymers exhibited ductile behavior with an elongation up to 24%. The high percentage of elongation was due to the presence of a flexible ether linkage.^{25,26} The polymers exhibited tensile strengths up to 93 MPa and Young's moduli up to 2.24 GPa. Figure 9 shows the mechanical plot for copolymer 1a.

Water absorption

Water absorption is important with regard to the practical application of polymers in microelectronics. The absorbed water in the polymer structure affects the performance and long-term stability of a polymer.²⁵ The water absorption rates of the films were measured after the vacuum-dried films were dipped in double-distilled water for 72 h at 30°C. The values were in the range 0.3–0.7%, as shown in Table III. The 6FDA-containing copolyimides showed the lowest water absorption (0.3%), which was due to the presence of the hydrophobic $-\text{C}(\text{CF}_3)_2$ unit.

Dielectric properties and refractive index (RI)

The dielectric constant values were determined from the RI values (with sodium D light, wavelength = 589.3 nm) of the polymer films and with a capacitance meter at 1 MHz, 30°C, and a relative humidity of 45%. The values are presented in Table IV. The refractive indices of the polymers were in the range 1.555–1.705.

The dielectric constant values of the films were very close to the values calculated from increments by the methods given in Van Krevelen's book on the *Properties of Polymers*.²⁷ With the mass increments method, the values were 2.9, 2.93, and 2.76 for polymers 1a, 1b, and 1c, respectively. The small difference in values obtained from the mass increment method and the experimental method from capacitance values were due to the fact that the experimentally reported values

TABLE IV
Dielectric and Other Physical Properties of the Poly(ether imides)

Polymer	Fluorine content (%)	Water absorbance (%)	RI (n)	ϵ_O	ϵ_{wet} (1 MHz)
1a	12.06	0.6	1.697	2.88	3.01
1b	10.86	0.7	1.705	2.91	2.99
1c	19.47	0.3	1.655	2.74	2.79

ϵ_O = dielectric constant ($\epsilon_O = n^2$)²⁷ ϵ_{wet} = dielectric constant at a relative humidity of 45%.

were those of the wet dielectric properties. When the dielectric constants of copolyimides 1a, 1b, and 1c were compared to the polymers based on PMDA/ODA ($\epsilon = 3.4$), BTDA/ODA ($\epsilon = 3.15$), and 6FDA/ODA ($\epsilon = 2.79$), we found a remarkable decrease in the dielectric constant. The dielectric constant values were strongly influenced by the fluorine content; the values decreased as the fluorine content increased (Table IV). This could be attributed to three effects: changes in free volume, changes in hydrophobicity, and changes in total polarizability.²⁸ The lowest dielectric constant value, for polymer 1c, was due to the combination of all three factors. The water uptake of this polymer was the lowest among the series (only 0.3%).

CONCLUSIONS

New copolyimides were prepared by the reaction of the diamine monomers ATFT and ODA with different aromatic dianhydrides. The overlapped and complex ¹H-NMR and ¹³C-NMR spectra were well resolved with the help of DEPT 90°C, 2D XHCORR, 2D heteronuclear single quantum coherence (HSQC), and 2D ¹H-¹H correlation spectra. These polymers had high thermal stabilities (T_d 5% = 551°C) and mechanical strengths (tensile strength = 93 MPa, Young's modulus = 2.4 GPa, and elongation at break = 24%). They showed valuable properties for electronic applications, including low moisture absorption, a low dielectric constant, and high optical transparency. In addition to applications in electronics, these materials may find use in plastics, fibers, and membranes.

The authors thank K. Sekhar, Director, Defense Research & Development Establishment (DRDE), Gwailor, India, and D. K. Jaiswal (Head, Synthetic Chemistry) for the provision of the necessary facilities and for useful discussion.

References

1. Polyimides: Synthesis, Characterization and Applications; Mittal, K., Ed.; Plenum: New York, 1984; Vols. 1 and 2.
2. Sroog, C. E. *J Polym Sci Part D: Macromol Rev* 1976, 11, 161.
3. St. Clair, A. K.; St. Clair, T. L.; Slem, W. S. In *Proceedings of the 2nd International Conference on Polyimides: Recent Advances in Polyimide Science and Technology*; Weber, W. D.; Gupta, M. R., Eds.; Society of Plastics Engineers: 1987; p 16.
4. Maier, G. *Prog Polym Sci* 2001, 26, 3.
5. Bruma, M.; Fitch, J. W.; Casidy, P. E. *J Macromol Sci Rev C* 1996, 36(1), 119.
6. Banerjee, S.; Madhra, M. K.; Salunke, A. K.; Maier, G. *J Polym Sci Part A: Polym Chem* 2002, 40, 1016.
7. Mahdra, M. K.; Salunke, A. K.; Banerjee, S.; Prabha, S. *Macromol Chem Phys* 2002, 203, 1238.
8. Mercer, F. W.; Goodman, T. D. *High Perform Polym* 1993, 5, 97.
9. Hergenrother, P. M.; Havens, S. J. *Macromolecules* 1994, 27, 4659.
10. Imai, Y.; Malder, N. N.; Kakimoto, M. *J Polym Sci Polym Chem Ed* 1984, 22, 2189.
11. Liaw, D. J.; Liaw, B. Y.; Yang, C. M. *Macromolecules* 1999, 32, 7248.
12. Eastmond, G. C.; Paprotny, J.; Irwin, R. S. *Macromolecules* 1996, 29, 1382.
13. Chern, Y. T.; Wang, W. L. *J Polym Sci Part A: Polym Chem* 1996, 34, 1501.
14. Hasio, S. H.; Yang, C. P.; Yang, C. Y. *J Polym Sci Part A: Polym Chem* 1997, 35, 1487.
15. Zeng, H. B.; Wang, Z. Y. *Macromolecules* 2000, 33, 4310.
16. Al-Masari, M.; Fritsch, D.; Kricheldorf, H. R. *Macromolecules* 2000, 33, 7127.
17. Hasio, S. H.; Li, C. T. *Macromolecules* 1998, 31, 7213.
18. Chung, I. S.; Kim, S. Y. *Macromolecules* 1999, 32, 3171.
19. Oishi, Y.; Itoyo, K.; Kakimoto, M.; Imai, Y. *Polym J* 1989, 21, 771.
20. Lee, G.; Quin, G. *Polym J* 1989, 21, 751.
21. Leung, L.; Williams, D. J.; Karasz, F. E.; MacKnight, W. J. *Polym Bull* 1980, 16, 457.
22. Hedrik, J. L.; Labadie, J. W.; Palmer, T. D.; Russell, T. P. In *Polyimides: Materials, Chemistry and Characterization*; Feger, C.; Khojasteh, M.; McGrath, J. E., Eds.; Elsevier: Amsterdam, 1989; p 61.
23. Chung, T. S.; Vora, R. H.; Jaffe, M. *J Polym Sci Part A: Polym Chem* 1991, 29, 1207.
24. Park, J. W.; Lee, M.; Lee, M. H.; Liu, J. W.; Kim, S. D.; Chang, J. Y.; Rhee, S. B. *Macromolecules* 1994, 27, 3459.
25. Salunke, A. K.; Madhra, M. K.; Sharma, M.; Banerjee, S. *J Polym Sci Part A: Polym Chem* 2002, 40, 55.
26. Okamoto, K. I. In *Polyimides: Fundamentals and Applications*; Ghosh, M. K.; Mittal, K. L., Eds.; Marcel Dekker: New York, 1996; p 265.
27. Van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1990; p 321.
28. Hougham, G.; Tesoro, G.; Viehbeck, A.; Chapple-Sokol, J. D. *Macromolecules* 1994, 27, 5964.