

# Polyimides 6: Synthesis, Characterization, and Comparison of Properties of Novel Fluorinated Poly(Ether Imides)

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**ABSTRACT:** Five new poly(ether imides) have been prepared on reaction with oxydiphthalic anhydride (ODA) with five different diamines: 1,4-bis(*p*-aminophenoxy-2'-trifluoromethyl benzyl) benzene, 4,4'-bis(*p*-aminophenoxy-2'-trifluoromethyl benzyl) benzene, 1,3-bis(*p*-aminophenoxy-2'-trifluoromethyl benzyl) benzene, 2,6-bis(*p*-aminophenoxy-2'-trifluoromethyl benzyl) pyridine, and 2,5-bis(*p*-aminophenoxy-2'-trifluoromethyl benzyl) thiophene. Synthesized polymers showed good solubility in different organic solvents. The polyimide films have low water absorption of 0.3–0.7%, low dielectric constants of 2.82–3.19 at 1 MHz, and high optical transparency at 500 nm (>73%). These polyimides showed very high

thermal stability with decomposition temperatures (5% weight loss) up to 531°C in air and good isothermal stability; only 0.4% weight loss occurred at 315°C after 5 h. Transparent thin films of these polyimides exhibited tensile strength up to 147 MPa, a modulus of elasticity up to 2.51 GPa and elongation at break up to 30% depending upon the repeating unit structure. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 821–832, 2004

**Key words:** fluoropolyimides; glass transition temperature; thermal properties; mechanical properties; dielectric constant; optical transparency

## INTRODUCTION

Polyimides are an interesting class of polymers because of their number of outstanding properties, such as excellent thermal and thermooxidative stability, solvent resistance, and mechanical and electrical properties.<sup>1–8</sup> These materials were considered for use in numerous applications, which require robust organic materials including composites and precursors for high-performance aerospace materials as well as membranes for gas separation. Polyimides with low dielectric constant, low refractive index, low water absorption, and low coefficient of thermal expansion are receiving attention for interlayer dielectrics in electronic devices such as integrated circuits.<sup>6,9,10</sup>

The main drawbacks of these classes of polymers are their insolubility and intractability, which cause difficulties in both synthesis and processing. Therefore, the processing of the polyimides is generally carried out via soluble poly(amic acid) precursors, which are cast onto glass plates and converted to thin polyimide films by a rigorous thermal treatment. However, this process has severe inherent limitations, including emission of volatile byproducts during curing and storage instability of the poly(amic acid) intermediate.<sup>11</sup>

To utilize the thermal stability of polyimides for further applications, and also to take advantage of other properties of these classes of polymers, it is desirable to synthesize soluble and/or melt-processible variations. Solubilizations of the polyimides were targeted by several means, such as introduction of flexible linkages, bulky substituents, and bulky units within the polymer backbone, non-coplanar, or alicyclic monomers.<sup>12</sup> The main concept behind all these approaches is the reduction of several types of polymer chain–chain interactions, reduction of chain packing, and charge transfer electronic polarization interactions. Polyimides containing hexafluoroisopropylidene (6F), pendent trifluoromethyl, or trifluoromethoxy groups are of special interest.<sup>13–29</sup> Incorporation of these groups serves to increase the free volume<sup>26</sup> of the polyimides, thereby improving various properties including solubilities, electrical insulating properties, without forfeiture of thermal stability. These groups also reduce water absorption, crystallinity, and color, while they increase flame resistance, gas permeability, and optical transparency.

In continuation of our research on semifluorinated poly(ether imides),<sup>12,30,31</sup> we report in this article on the successful synthesis of five novel poly(ether imides) and their detailed characterization including thermal, mechanical, and dielectric properties.

## Experimental

### General considerations

Carbon and hydrogen of the compounds were analyzed by Prejel method and nitrogen was analyzed by Kjeldhal method. <sup>1</sup>H-NMR (400 MHz) and <sup>19</sup>F-NMR

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(100 MHz) spectra were recorded on a Bruker ARX 400 instrument (Switzerland) [reference, 0 ppm with TMS ( $^1\text{H}$ - and) or  $\text{CFCl}_3$  ( $^{19}\text{F}$ -NMR)]. IR spectra of the polymer films were recorded with a Bruker IFS 55 spectrophotometer instrument. DSC measurements were made on a TA Instruments DSC-2920 instrument, at a heating/cooling rate of  $20^\circ\text{C}/\text{min}$  under nitrogen. Glass transition temperature ( $T_g$ ) was taken at the middle of the step transition in the second heating run. Thermogravimetry was measured on a TA Instruments thermogravimetric analyzer (model TGA-2950). A heating rate of  $10^\circ\text{C}/\text{min}$  was used for determination of the decomposition temperature ( $T_d$ ) at 5% weight loss under synthetic air. Isothermal gravimetric was performed at  $315^\circ\text{C}$  for 5 h in air on a TA-2950 instrument. Dynamic mechanical thermal analysis was performed on a Netzsch DMA-242 instrument (Germany) in the tension mode on thin film samples with a heating rate of  $5^\circ\text{C}/\text{min}$  (1 and 10 Hz). Mechanical properties of the thin polymer films were performed at room temperature on a Miniature Materials Tester (Rheometric Science) under strain rate of 5%/min. Dielectric constant of the poly(ether imide) films (20  $\mu\text{m}$ ) was measured by the parallel plate capacitor method with a YHP 4278 capacitance meter at 1 kHz at a temperature  $30^\circ\text{C}$ . Dry specimens were made by keeping the samples at  $140^\circ\text{C}$  for 4 h under high vacuum. Water absorption of the films was measured by a Mettler microbalance of sensitivity of  $10^{-6}$  g after immersing the films into double-distilled water for 72 h at  $30^\circ\text{C}$ . UV-Vis spectra of the polymer films were recorded with a Speccord Version 2.1 E, Analytik Jena AE instrument (Germany).

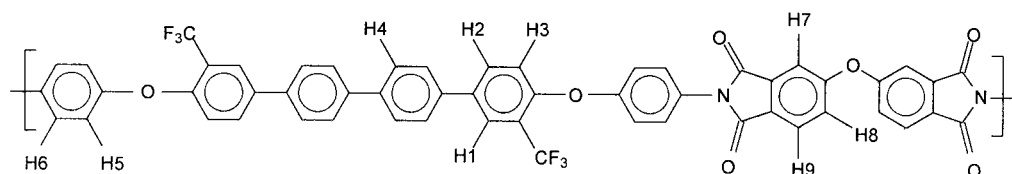
### Starting materials

All reagents were purchased from Aldrich, Fluka, Chempure, or Fluorochem Chemical Co. and used as received unless otherwise noted. Oxydiphthalic anhydride (ODA; 99.99%, Fluka, Switzerland) was heated at  $180^\circ\text{C}$  prior to use. *N,N*-dimethylformamide (DMF; E. Merck, India) was purified by stirring with NaOH and distilled twice from  $\text{P}_2\text{O}_5$  under reduced pressure. Detailed syntheses of the diamine monomers are reported in previous articles.<sup>12,30,31</sup>

### Polymerization

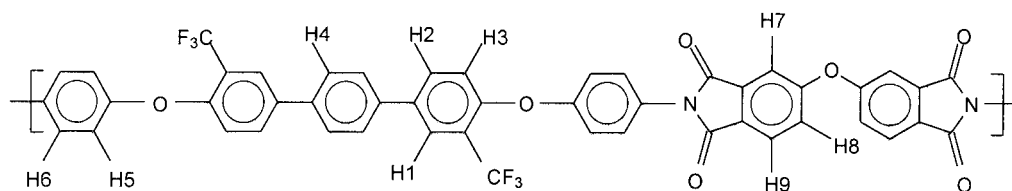
An equimolar amount of diamine and dianhydride monomer was reacted under constant flow of nitrogen. A representative polymerization procedure is as follows.

In a 50-mL round-bottomed flask equipped with a nitrogen inlet, a stir bar and Dean-Stark trap fitted with a condenser was charged with 0.6 g (1.0335 mmol) of 1,3-bis [3'-trifluoromethyl-4'(4'-amino benzyloxy) benzyl] benzene and 10 mL of DMF. The solution was stirred until the diamine dissolved completely; 0.32 g (1.0335 mmol) (ODA) was slowly added to this solution. The resulting highly viscous solution was stirred slowly and continuously for 3 h at room temperature under nitrogen. The poly(amic acid) solution was cast onto clean and dry glass plates by a doctor blade; the films were dried in an oven at  $80^\circ\text{C}$  for 6 h, at 150, 200, 250, and  $300^\circ\text{C}$  for 1 h at each temperature, and  $350^\circ\text{C}$  for 15 min. Polyimide films were removed by immersing the glass plates in boiling water.

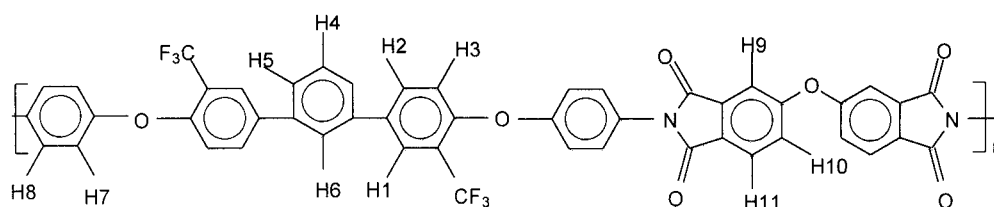


*Polyimide 1a*. ANAL. calc. for  $(\text{C}_{54}\text{H}_{28}\text{F}_6\text{O}_7\text{N}_2)_n$  (930.81 g  $\text{mol}^{-1}$ )<sub>n</sub>: C, 69.73%; H, 3.03%; N, 3.01%. Found: C, 68.53%; H, 2.83%; N, 2.98%; IR (KBr) ( $\text{cm}^{-1}$ ): 3492 ( $-\text{N} < \text{stretch}$ ); 3074, 3050 (aromatic C—H stretching); 1786 and 1737 (asymmetric and symmetric  $-\text{CO}-$  stretch); 1619 (C=C ring stretching band); 1508, (band due to C—F absorption); 1375 (asymmetric C—O—C stretch);

1143, 1050 (symmetric C—O—C stretch); 722 (aromatic C—H band out-of-plane).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.96 (d,  $J = 8$  Hz, 2H, H9); 7.89 (s, 2H, H1); 7.64(m, 10H, H2, and H4); 7.50 (s, 2H, H7); 7.40 (m, 6H, H6, and H8); 7.15(m, 6H, H3, and H5).  $^{19}\text{F}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm)  $-62.14$  ( $\text{CF}_3$ ).

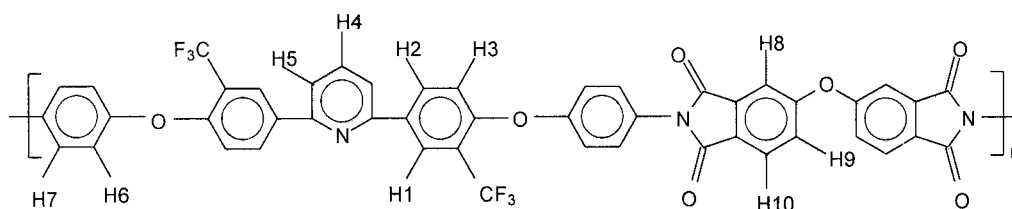


*Polyimide 1b.* ANAL. calc. for  $(C_{48}H_{24}F_6O_7N_2)_n$  (854.72 g mol<sup>-1</sup>)<sub>n</sub>: C, 67.45%; H, 2.83%; N, 3.27%. Found: C, 66.83%; H, 2.63%; N, 3.11%; IR (KBr) (cm<sup>-1</sup>): 3493 (—N < stretch); 3072, 3048 (aromatic C—H stretching); 1782 and 1732 (asymmetric and symmetric —CO— stretch); 1612 (C=C ring stretching band); 1506 (band due to C—F absorption); 1372 (asymmetric C—O—C stretch);



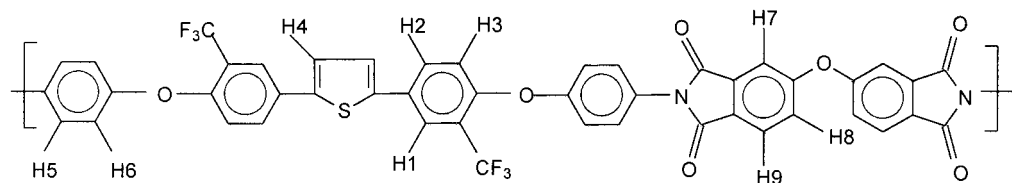
1140, 1048 (symmetric C—O—C stretch); 720 (aromatic C—H band out-of-plane). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm) 7.92 (d, J = 8 Hz, 2H, H<sub>9</sub>); 7.84 (s, 2H, H<sub>1</sub>); 7.64 (d, J = 8 Hz, 2H, H<sub>2</sub>); 7.58 (s, 4H, H<sub>4</sub>); 7.47 (s, 2H, H<sub>7</sub>); 7.36 (m, 6H, H<sub>7</sub> and H<sub>6</sub>); 7.09 (m, 6H, H<sub>3</sub>, and H<sub>5</sub>). <sup>19</sup>F-NMR (CDCl<sub>3</sub>): δ (ppm) -62.11 (CF<sub>3</sub>).

*Polyimide 1c.* ANAL. calc. for  $(C_{48}H_{24}F_6O_7N_2)_n$  (854.71 g mol<sup>-1</sup>)<sub>n</sub>: C, 67.45%; H, 2.83%; N, 3.27%. Found: C, 66.76%; H, 2.73%; N, 3.19%; IR (KBr) (cm<sup>-1</sup>): 3492 (—N < stretch); 3068, 3047 (aromatic C—H stretching); 1780 and 1729 (asymmetric and symmetric —CO— stretch); 1614 (C=C ring stretching band); 1511 (band due to C—F absorption); 1371 (asymmetric C—O—C stretch);



1141, 1051 (symmetric C—O—C stretch); 719 (aromatic C—H band out-of-plane). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm) 7.92 (d, J = 8 Hz, 2H, H<sub>11</sub>); 7.85 (s, 2H, H<sub>1</sub>); 7.66 (m, 3H, H<sub>2</sub>, H<sub>6</sub>); 7.47 (m, 5H, H<sub>4</sub>, H<sub>5</sub> and H<sub>9</sub>); 7.37 (m, 6H, H<sub>8</sub> and H<sub>10</sub>); 7.09 (m, 6H, H<sub>3</sub> and H<sub>7</sub>). <sup>19</sup>F-NMR (CDCl<sub>3</sub>): δ (ppm) -62.07 (CF<sub>3</sub>).

*Polyimide 1d.* ANAL. calc. for  $(C_{47}H_{23}F_6O_7N_3)_n$  (855.70 g mol<sup>-1</sup>)<sub>n</sub>: C, 65.97%; H, 2.70%; N, 4.91%. Found: C, 65.13%; H, 2.52%; N, 4.78%; IR (KBr) (cm<sup>-1</sup>): 3491 (—N < stretch); 3071, 3047 (aromatic C—H stretching); 1779 and 1729 (asymmetric and symmetric —CO— stretch); 1618 (C=C ring stretching band); 1506 (band due to C—F absorption); 1372 (asymmetric C—O—C stretch);



1139, 1046 (symmetric C—O—C stretch); 718 (aromatic C—H band out-of-plane). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm) 8.39 (s, 2H, H<sub>1</sub>); 8.2 (d, J = 8 Hz, 2H, H<sub>2</sub>); 7.94 (d, J = 8 Hz, 2H, H<sub>10</sub>); 7.82 (m, 1H, H<sub>4</sub>); 7.66 (d, J = 8 Hz, 2H, H<sub>5</sub>); 7.50 (s, 2H, H<sub>8</sub>); 7.40 (m, 6H, H<sub>7</sub>, and H<sub>9</sub>); 7.13 (m, 6H, H<sub>3</sub>, and H<sub>6</sub>). <sup>19</sup>F-NMR (CDCl<sub>3</sub>): δ (ppm) -62.20 (CF<sub>3</sub>).

*Polyimide 1e.* ANAL. calc. for  $(C_{46}H_{22}F_6O_7N_2)_n$  (860.74 g mol<sup>-1</sup>)<sub>n</sub>: C, 64.18%; H, 2.57%; N, 3.25%. Found: C, 63.84%; H, 2.48%; N, 3.09%; IR (KBr) (cm<sup>-1</sup>): 3495 (—N < stretch); 3070, 3044 (aromatic C—H stretching); 1779 and 1727 (asymmetric and symmetric —CO— stretch); 1619 (C=C ring stretching band); 1508 (band due to C—F absorption); 1375 (asymmetric C—O—C stretch);

1143, 1050 (symmetric C—O—C stretch); 722 (aromatic C—H band out-of-plane). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm) 7.93 (d, J = 8 Hz, 2H, H<sub>9</sub>); 7.82 (s, 2H, H<sub>1</sub>); 7.63 (d, J = 8 Hz, 2H, H<sub>2</sub>); 7.47 (s, 2H, H<sub>7</sub>); 7.38 (m, 6H, H<sub>5</sub>, and H<sub>8</sub>); 7.21 (s, 2H, H<sub>4</sub>); 7.10 (d, J = 8 Hz, 4H, H<sub>6</sub>); 6.99 (d, J = 8 Hz, 2H, H<sub>3</sub>). <sup>19</sup>F-NMR (CDCl<sub>3</sub>): δ (ppm) -62.04 (CF<sub>3</sub>).

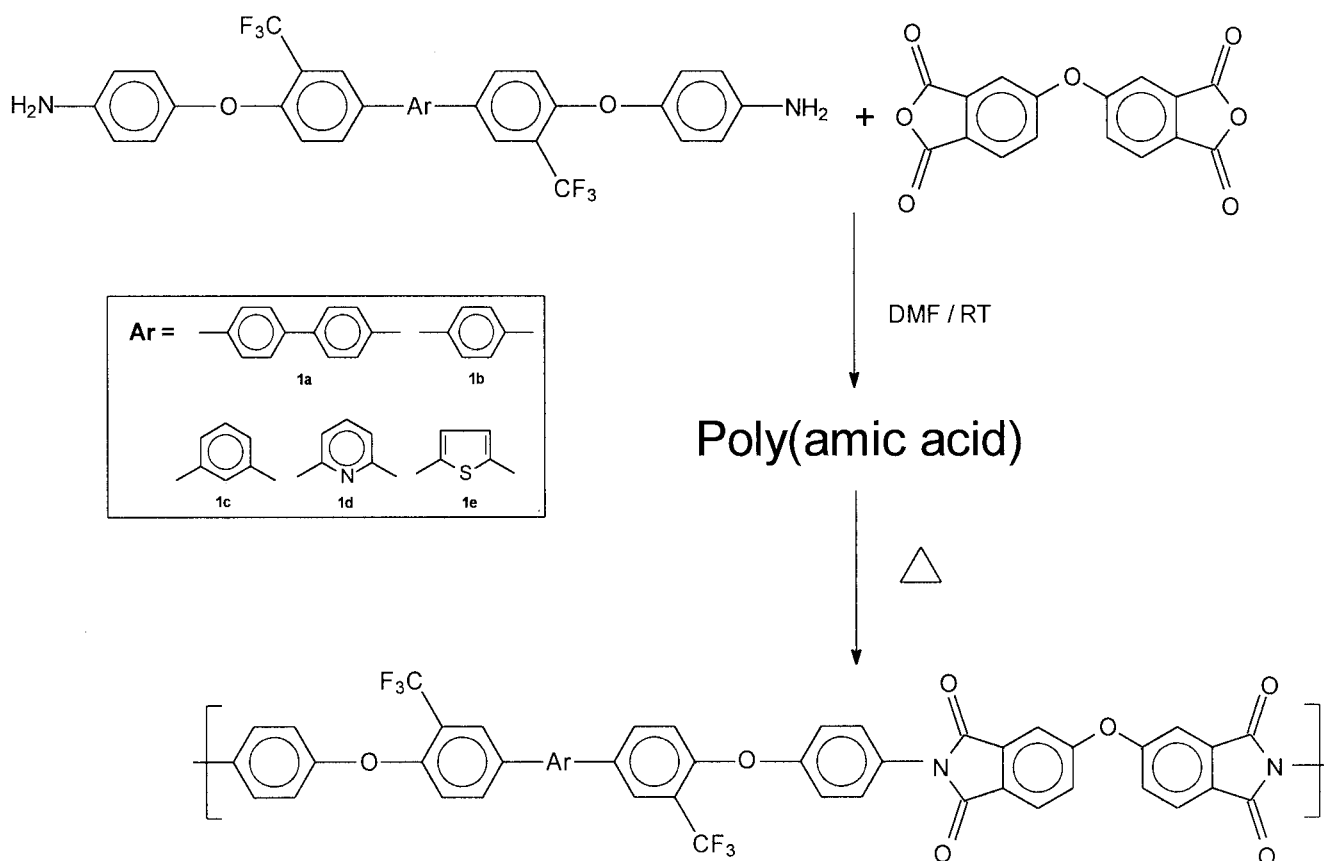


Figure 1 Reaction scheme and structures of the poly(ether imides).

## RESULTS AND DISCUSSION

The diamino monomers were reacted with ODPA to give the corresponding poly(ether imides), as shown in Figure 1.

The syntheses of polyimides were carried out via poly(amic acid) intermediate. Initially, diamines were dissolved in a measured amount of dry DMF and the dianhydride monomer was added to it slowly. In all cases, the reaction mixture became highly viscous within 10–15 min; the reactions were continued for 3 h. The inherent viscosities and molar masses of the poly(ether imides) shown in Table I indicated formation of high molar masses. The poly(amic acid) solu-

TABLE I  
Physical Properties of the Poly(Ether Imides)

Polymer	$\lambda_{inh}$	$M_n$	PDI	Light trasmission at 500 nm (%)
1a	1.12	65,700	2.91	73
1b	1.03	42,320	2.65	71
1c	0.85	36,280	1.85	69
1d	1.22	55,850	3.12	65
1e	0.82	-	-	70

$\lambda_{inh}$ , 0.5 weight % solution of pol(ether imide) films in DMF at 30°C.

tions were cast on clean glass plates and the film was heated through various stages up to 350°C to remove solvent and water formed by the imidization. Transparent, pale-yellowish films were obtained in all cases. All polyimides films were tough.

### Polymer solubility

The solubilities of the resulting poly(ether imides) by thermal imidization were investigated in different organic solvents. The solubility behavior of these polymers in different solvents is presented in Table II. These polymers exhibited very good solubility behavior in common organic solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMF, *N,N*-dimethyl acetamide (DMAc), and *N*-methyl-2-pyrrolidinone. Insolubility of these polymers in DMSO, while their solubility in amide solvents, such as NMP, DMF, DMAc, at room temperature (although these types of dipolar aprotic solvents have similar properties) indicates that polarity alone is not the only parameter sufficient for selecting a polymer solvent. In comparison to the previously reported semifluorinated poly(ether imides),<sup>26,27</sup> these polymers exhibited dramatic improvement in solubility. This is possibly due to additional ether linkage in dianhydride moiety.

TABLE II  
Solubility of the Polyimides

Polymer	NMP	DMF	DMAc	DMSO	THF	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	Acetone
1a	+	+	+	-	-	+	+	-
1b	+	+	+	-	+	+	+	-
1c	+	+	+	-	+	+	+	-
1d	+	+	+	-	+	+	+	-
1e	+	+	+	-	-	+	+	-

+, Soluble; -, insoluble at reflux.

### Spectroscopy

The formation of poly(ether imides) was confirmed by FTIR spectroscopy. FTIR spectra of the polyimide films prepared by thermal imidization method show the absorption bands at about 1780 cm<sup>-1</sup> (C=O asymmetric stretching), 1730 cm<sup>-1</sup> (C=O symmetric stretching), 1378 cm<sup>-1</sup> (C-N stretching), 721 cm<sup>-1</sup> (C=O bending) corresponding to the characteristic of imide bands.<sup>25-26</sup> No absorption band existed at 3400-2900 cm<sup>-1</sup> corresponding to amide (-NH-) and acid (-OH) stretching 1720 cm<sup>-1</sup> corresponding to C=O cm<sup>-1</sup> stretching of carboxylic acid, 1660 corresponding to C=O cm<sup>-1</sup> amide stretching of the polyimides.<sup>30,31</sup> <sup>1</sup>H-NMR spectra of the polymers did not show any amide or acid protons, indicating full imidization. The representative <sup>1</sup>H-NMR spectrum of

poly(ether imide) **1e** is shown in Figure 2. There is very good matching of integrated peak areas for different chemically different protons in all polymers. The analytical details of the polymers are provided in Experimental. UV-Vis spectroscopic studies of the polymers revealed that polymers have very good optical transparency at 500 nm.

### Glass transition temperature versus polymer structure

The poly(ether imides) exhibited no crystallization or melting transition in DSC measurements. These polymers show glass transition temperature, which indicates amorphous or glassy morphology. DSC curves of the polymers are shown in Figure 3. The glass

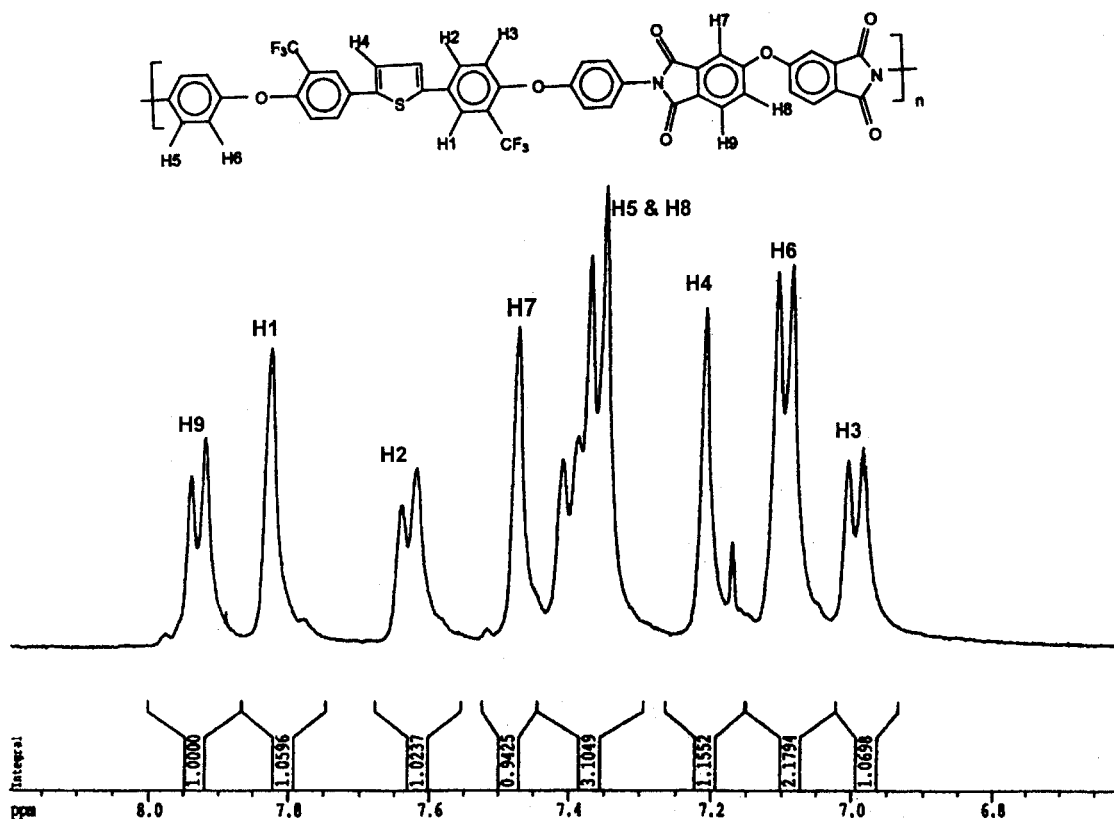


Figure 2 <sup>1</sup>H-NMR spectrum of poly(ether imide), **1e**.

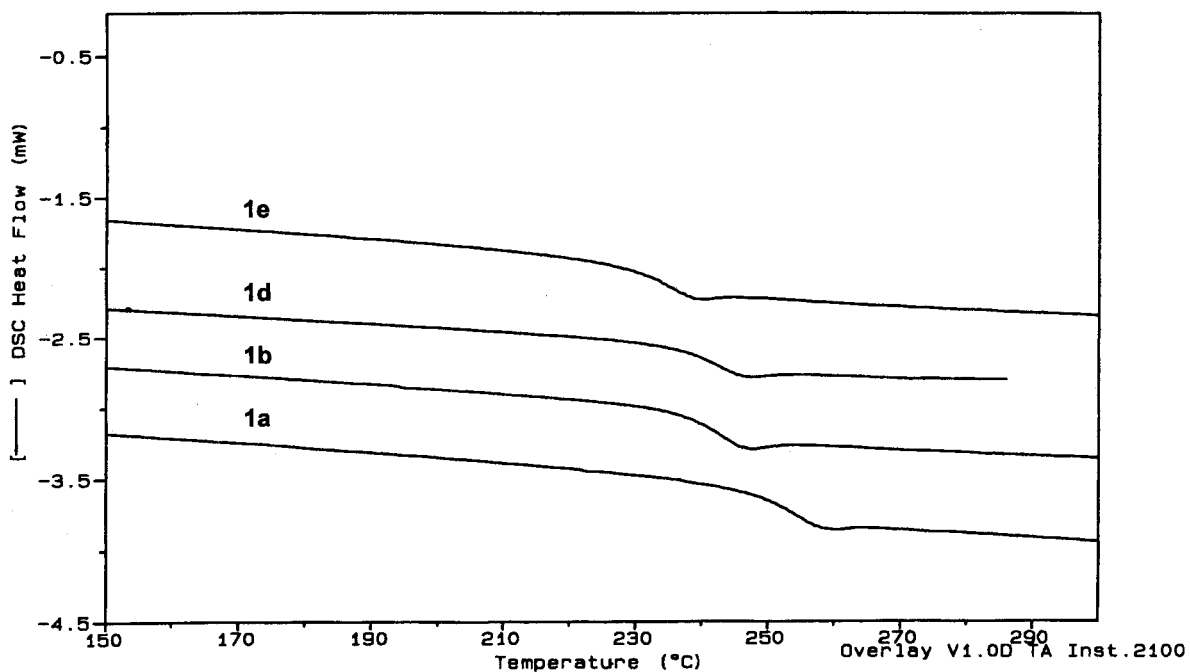
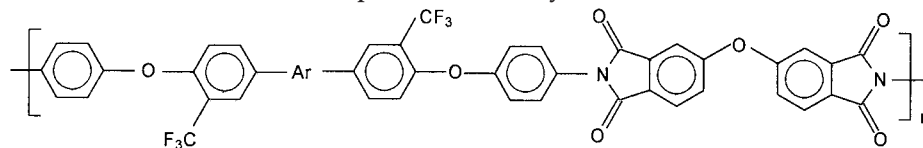


Figure 3 DSC plots of the poly(ether imides).

TABLE III  
Thermal Properties of the Poly(Ether Imides)

Polymer	Ar	$T_g$ (°C)		$T_d$ (°C)		Weight loss in air (315°C/5 h)
		DSC	DMA (tan $\delta$ )	5% Weight loss	10% Weight loss	
1a		254	258	531	563	0.4
1b		242	246	519	553	0.5
1c		211	222	517	548	0.6
1d		241	250	514	559	0.7
1e		234	239	486	526	1.4

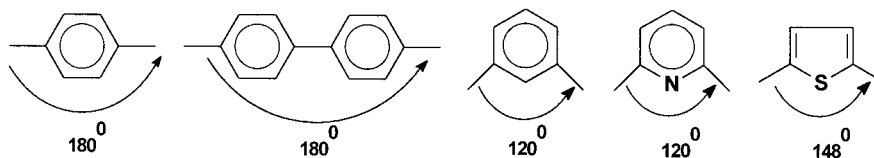


Figure 4 Catenation angles of the different substituted arylene groups.

transition values are summarized in Table III. The polymers 1a and 1b exhibited higher  $T_g$  values than other polymers, which is due to the presence of rigid quadriphenyl and terphenyl unit in the backbone.<sup>31</sup>

It is interesting at this stage to compare the glass transition temperatures of the polymers shown in Table III. The polyimides containing 4,4'-diphenyl biphenyl (quadriphenyl) unit in the polymer backbone exhibited highest glass transition temperatures in comparison to the analogous polyimides containing 1,4-diphenyl benzene, 1,3-diphenyl benzene, 2,6-diphenyl pyridine, and 2,5-diphenyl thiophene moieties. The following order on glass transition temperature is obtained: quadriphenyl > 1,4-diphenyl benzene > 2,6-diphenyl pyridine > 2,5-diphenyl thiophene  $\geq$  1,3-diphenyl benzene. This order could be explained on considering three factors: rigidity, catenation angle of the different groups (Fig. 4), and polarity. A macromolecule exhibits more extended geometry (i.e., higher catenation angle providing by the different building blocks is expected to have higher glass transition temperature). Similarly, if the polymer molecule is built up of rigid units, it is expected to have higher

glass transition temperature. The highest glass transition temperature of the polymer 1a is due to its most rigid backbone structure compared to others. The catenation angle between 4,4'-diphenyl biphenyl and 1,4-diphenyl benzene is the same; however, the polymers containing 4,4'-diphenyl biphenyl units exhibiting higher  $T_g$  is due to the rigidity of this unit. The polyimides containing 1,5-diphenyl benzene is expected to have lower glass transition temperature compared to the above two, as it has less extended geometry (catenation angle  $120^\circ$ ) and the same result is obtained. It will be more interesting to take a close look at the glass transition temperatures of the polyimides containing 1,6-phenyl pyridine and 1,5-phenyl thiophene units and their comparison to the polyimides containing 1,5-diphenyl benzene. Although the catenation angle of 1,6-diphenyl pyridine unit is  $28^\circ$  lower than 1,5-diphenyl thiophene unit (catenation angle for 1,6-diphenyl pyridine unit is  $120^\circ$  and for thiophene is  $148^\circ$ ),<sup>32</sup> the  $T_g$ 's of the pyridine-containing polymer is higher. The high  $T_g$  of polymer-containing pyridine moiety may be due to the polarity of the pyridine ring. Thiophene has a more extended geometry than pyri-

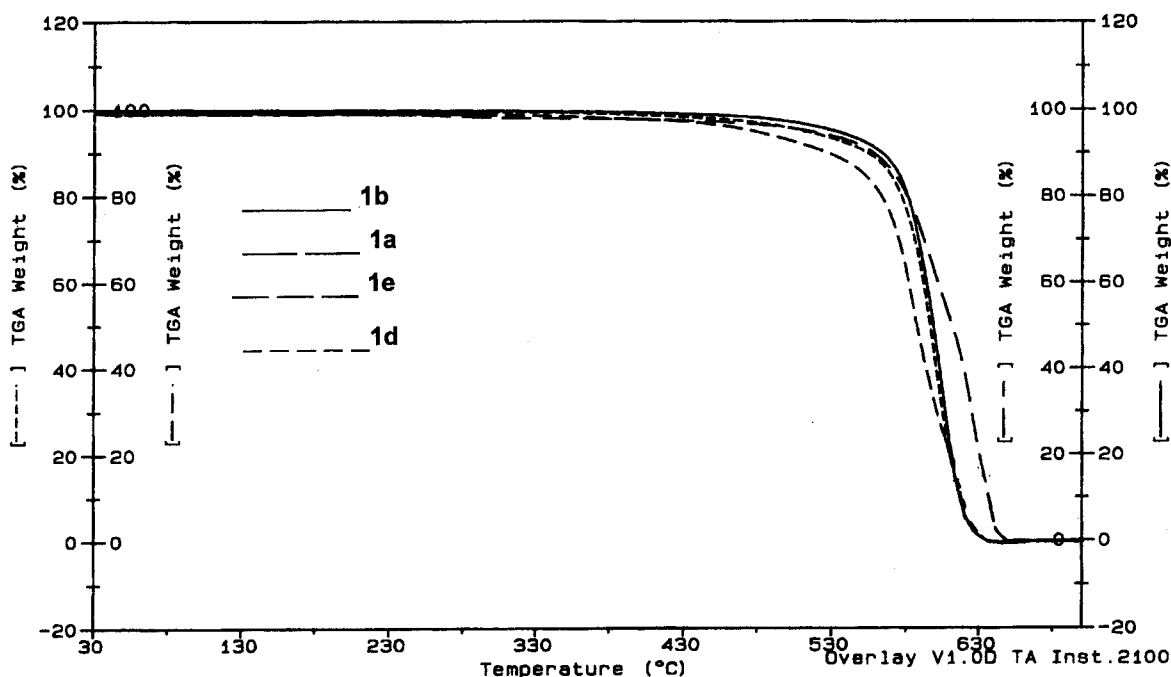
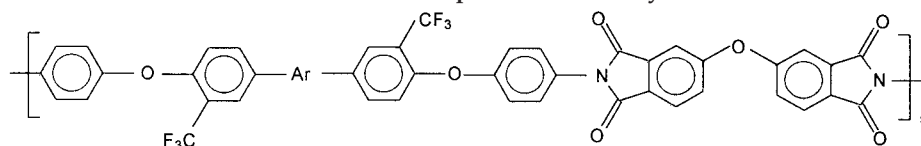


Figure 5 TGA plots of the poly(ether imides).

TABLE IV  
Mechanical and Dielectric Properties of the Poly(Ether Imides)



Polymer	Ar	Tensile break (MPa)	Modulus (GPa)	Elongation at break (%)	Dielectric constant (1 MHz)	Water absorption (%)
1a		147	2.18	30	2.82	0.4
1b		129	2.51	22	2.88	0.4
1c		118	1.74	5	2.92	0.6
1d		131	1.58	6	3.24	0.9
1e		116	2.23	15	3.19	0.8

dine; at the same time pyridine has four times more polarity than thiophene ( $\mu_{\text{pyridine}} = 7.4 \times 10^{-30}$  Cm;  $\mu_{\text{thiophene}} = 1.83 \times 10^{-30}$  Cm),<sup>33</sup> which is the probable reason for higher  $T_g$  for pyridine ring containing polymer.

The  $T_g$  values of these polymers are higher than commercial poly(ether imide), Ultem 1000 ( $T_g$ , 217°C), based on bisphenol-A(diphthalic anhydride) (BPADA) and (*m*-phenylene diamine) (MPD)<sup>34</sup> and comparable to BTDA-ODA ( $T_g$ , 279°C)<sup>35</sup> based polyimide. However, the  $T_g$  values of these polymers are lower than Kapton films derived from PMDA-ODA ( $T_g$ , 390°C).<sup>7</sup>

### Thermal stability

The thermal properties of the poly(ether imides) were evaluated by TGA. The TGA curve for the polymer is shown in Figure 5. The thermal properties of the polymers are summarized in Table III. The 5% weight loss temperature in the air of these polymers is in the range of 486–531°C. In general, all these polymers showed very good high thermal stability in air as expected for polyimides except **1e**. Low thermooxidative stability of polymer **1e** in comparison to others is due to the presence of oxidizable thiophene ring in the polymer

backbone. This is in agreement of our previous findings with polymers containing thiophene moiety. It could be possible that at high temperature thiophene moiety gets oxidized to thiophene oxide and loses its aromaticity with a consequence of low thermal stability. This hypothesis was proved when the thermal stability of these polymers was investigated under nitrogen atmosphere; a comparable result was obtained in all cases. As 5% weight loss temperature does not provide much information about the suitability of a material for long-term applications at high temperatures, the isothermal stabilities of the poly(ether imides) were investigated at 315°C for 5 h. The polymers exhibited very good isothermal stability with a loss of as minimum as 0.4 wt % in the case of **1a**.

### DMA measurements

The dynamic mechanical behaviors of the polymer films are shown in Figure 6. The  $T_g$ 's taken from the  $\tan \delta$  peaks at 10 Hz are given in Table III. These values are comparable with the calorimetric  $T_g$  values. The polymers retained very good mechanical properties up to  $T_g$ 's as can be observed from the storage modulus plots of the polymers.



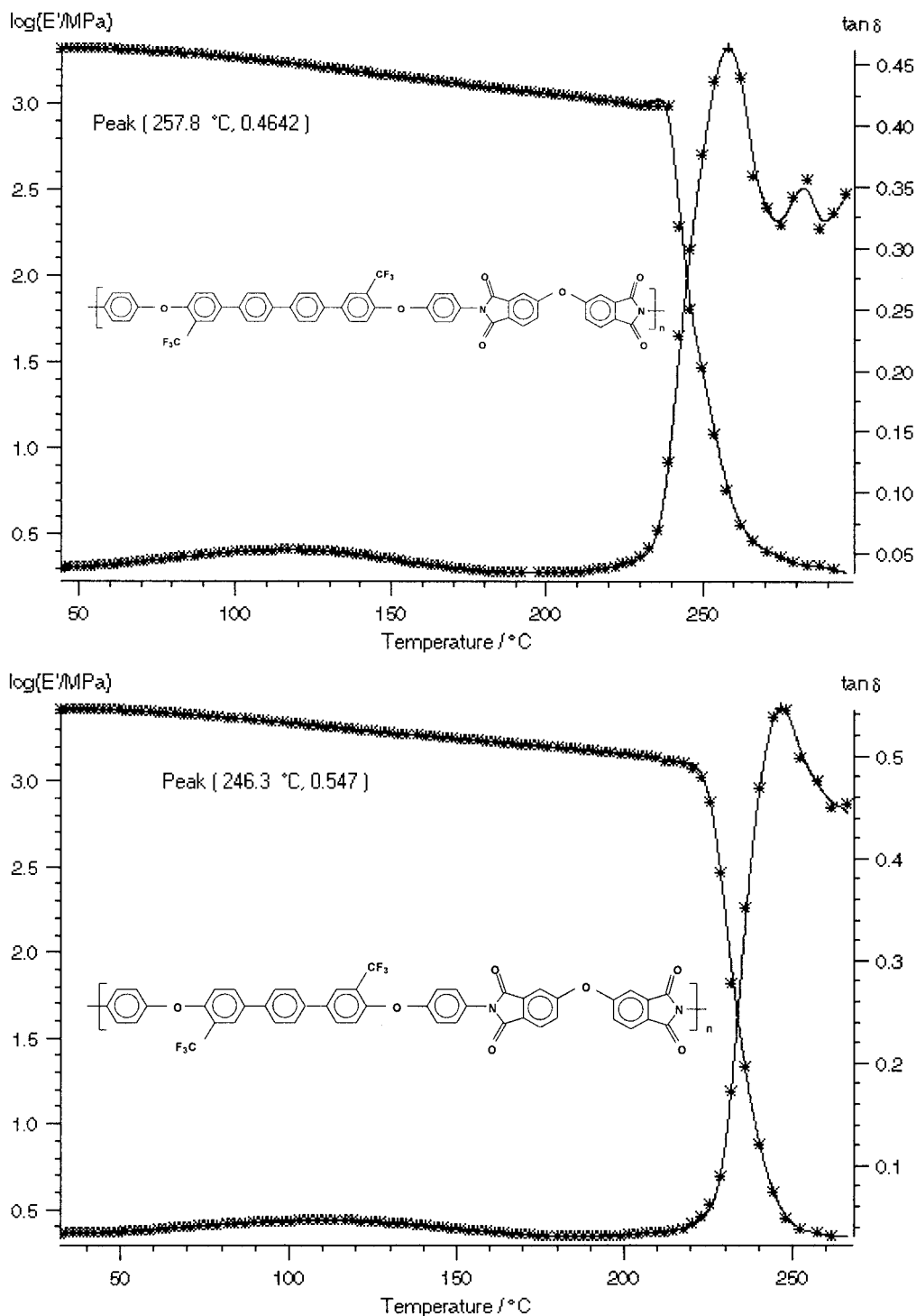


Figure 6 DMA plots of the poly(ether imides).

### Mechanical properties

The mechanical properties of thin polyimide films cast from DMF are shown in Table IV. In general, the mechanical properties of the polyimide films are excellent and exhibited very high tensile strength and modulus. The polyimides containing most rigid quad-

riphenyl unit exhibited highest tensile strength up to 147 MPa and Young modulus up to 2.18 GPa. These polymers also exhibited very high elongation at break up to 30% (Fig. 7). Our previous experience with the poly(aryl ethers) containing quadriphenyl moieties exhibited higher tensile strength and higher elongation at break in comparison to the similar poly(aryl ethers)

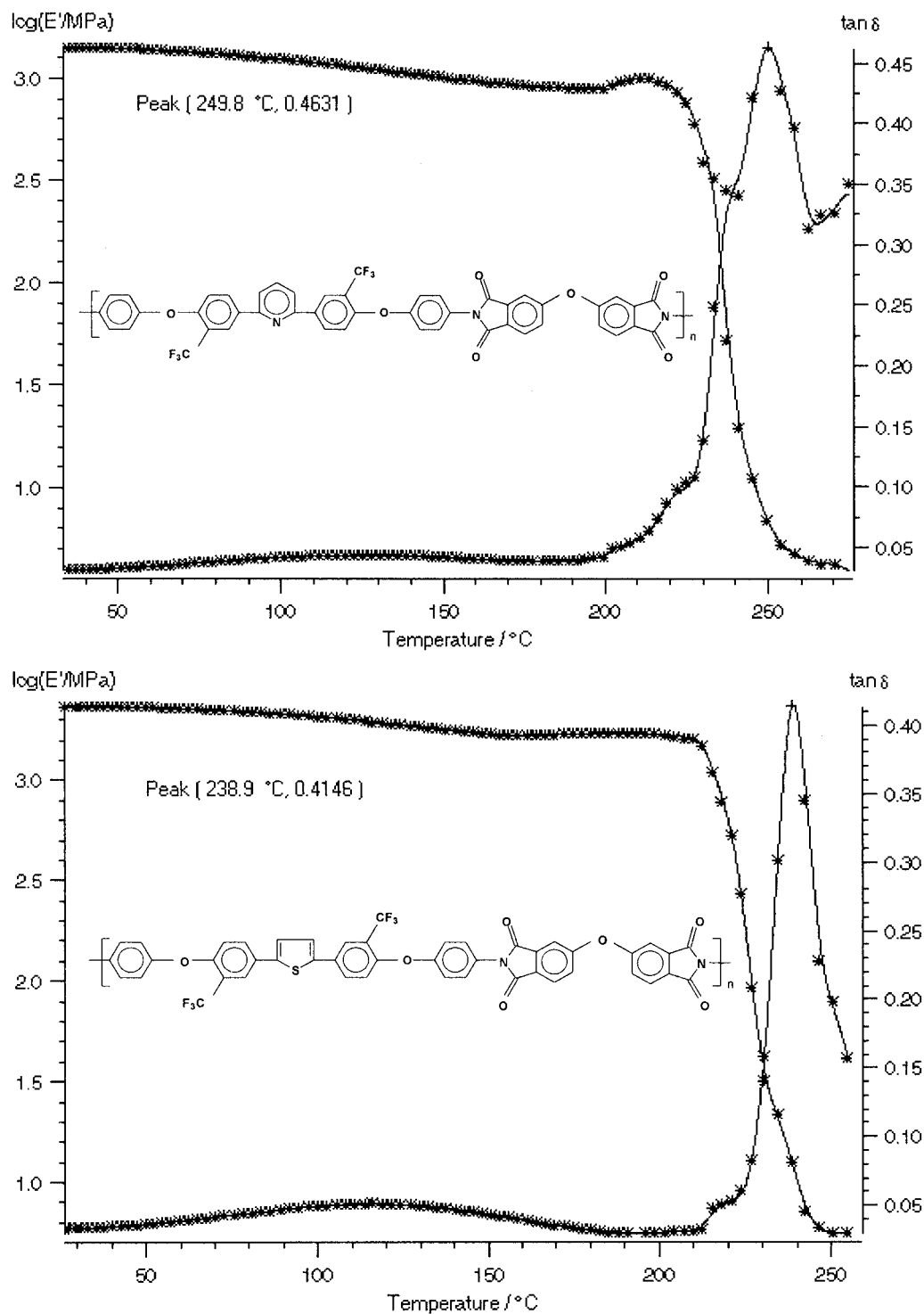


Figure 6. (Continued from the previous page)

containing terphenyl moieties.<sup>28,29</sup> It is also observed from the Table IV that the polymers having more extended geometry results in more elongation at break than the polymers having less extended geometry. Polyimides containing 1,3-phenyl (**1c**) and 2,6-pyridine moieties (**1d**) exhibited very low elongation at break in comparison to the polymers containing 1,4-

phenyl, 1,4-biphenyl moieties. Surprisingly, the polymer with 2,5-thiophene moiety (**1e**) showed somewhat more elongation at break than **1c** and **1d**.

These values are comparable to those of many other commercially available polyimides (Ultem 1000: tensile strength, 105 MPa; tensile modulus, 3.0 GPa; elongation at break, 60%; Ultem 6000: tensile strength, 103

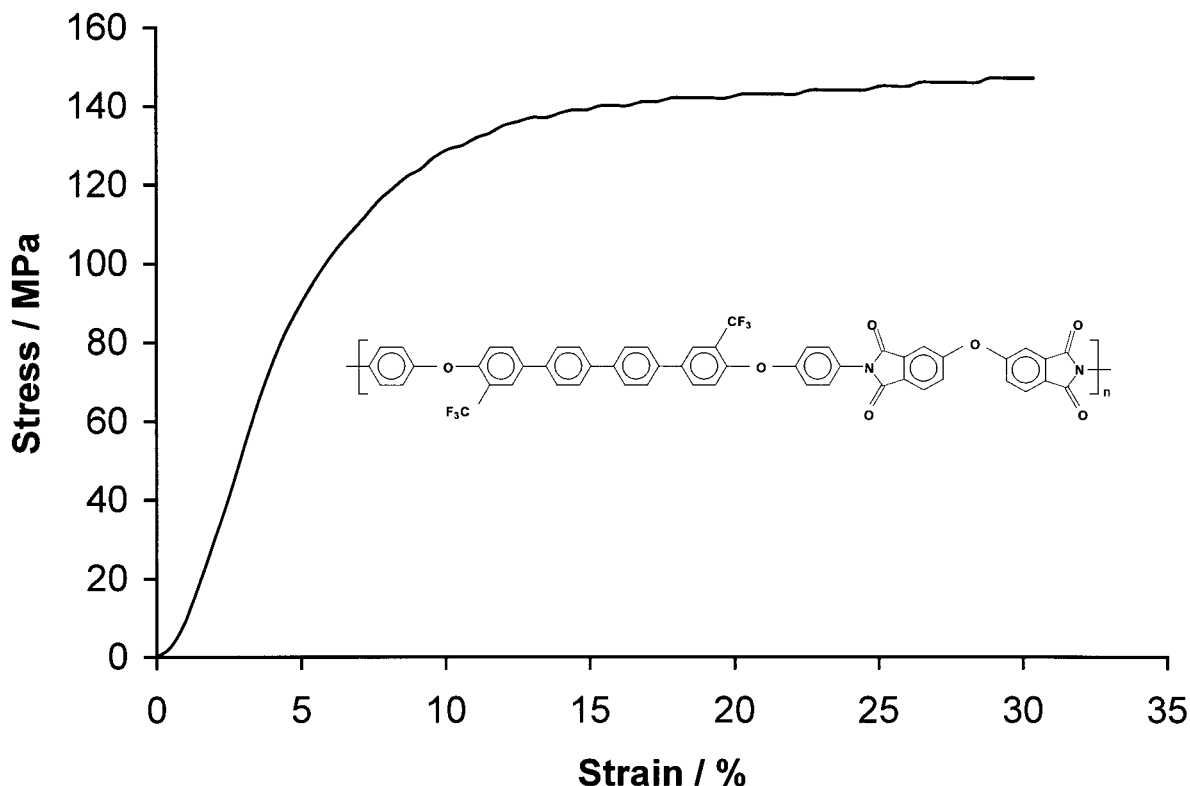


Figure 7 Representative stress-strain plot of poly(ether imide), **1a**.

MPa; elongation at break, 30%; Avimid N: tensile strength, 110 MPa; tensile modulus, 4.13 GPa; elongation at break, 6%).<sup>7</sup>

#### Dielectric properties

The dielectric constant of the polymer films was determined from capacitance values by using a capacitance meter 1 MHz at 30°C under wet conditions (relative humidity, 45%). The dielectric constant values are presented in Table IV. The dielectric constant values for **1a**, **1b**, and **1c** are compared with the theoretical dielectric constants values, calculated from the group increments given in Van Kravlen's book on properties of polymers.<sup>36</sup> Water-adsorption values of these polymers are as low as 0.4 wt % in the case of **1a** characteristics of semifluorinated poly(ether imides). The dielectric constant values of these films are lower than Kapton H ( $\epsilon = 3.5$  at 1 kHz), Upilex R ( $\epsilon = 3.5$  at 1 kHz), Upilex S ( $\epsilon = 3.5$  at 1 kHz), and Ultem 1000 ( $\epsilon = 3.15$  at 1 kHz) type of polyimide materials and comparable to those of many semifluorinated poly(ether imides) (6FDA-MPD:  $\epsilon = 3.0$ ; 6FDA-7FMDA:  $\epsilon = 2.9$ ; 6FDA-13 FMDA:  $\epsilon = 2.7$ ).<sup>8,35</sup>

#### CONCLUSION

Five new poly(ether imides) were prepared on reaction of oxydiphthalic anhydride with different triflu-

oromethyl-substituted diamines. The polymers were well characterized for their thermal, mechanical, and dielectric properties. The synthesized polymers exhibited very good solubility in different organic solvents. The resulting poly(ether imides) are amorphous, exhibiting outstanding thermal stability in air such as many other thermally stable polyimides without substituents. These polymers have high mechanical strength and high modulus. Poly(ether imides) based on these materials were shown to have valuable properties for electronic applications, such as low moisture absorption, low dielectric constant, and high optical transparency. These polymers may find use in plastics, fiber, and membrane for separation applications.

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#### References

- Lai, J. H., Ed. *Polymers for Electronic Applications*; CRC Press: Boca Raton, FL, 1989.
- Bessonov, M. I.; Koton, M. M.; Kudryavtsev, V. V.; Laius, L. A., Eds., *Polyimides*; Consultants Bureau: New York, 1987.
- Verbicky, J. W., Jr. *Encyclopedia of Polymer Science and Engineering*; Mark, H. F.; Bikales, N.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1988; Vol. 12, p. 364.

4. Feger, C.; Khojastah, M. M.; McGrath, J. E., Eds. *Polyimides: Materials, Chemistry, and Characterization*; Elsevier: Amsterdam, 1989.
5. Abadie, M. J. M.; Sillion, B., Eds. *Polyimides and Other High Temperature Polymers*; Elsevier: Amsterdam, 1991.
6. Ghosh, M. K.; Mittal, K. L., Eds. *Polyimides*; Marcel Dekker: New York, 1996.
7. Takekoshi, T. *Encyclopedia of Chemical Technology*; Kirk; Othmer, Eds.; Wiley: New York, 1996; Vol. 19, pp. 813–837.
8. Hougham, G. *Fluorine Containing Polymers in Fluoropolymers: Properties*; Hougham, G. G.; Casidy, P. E.; Johns, K.; Davidson, T., Eds.; Plenum Press: New York, 1999; Chapter 13, pp. 233–276.
9. Feger, C.; Khojastah, M. M.; McGrath, J. E., Eds. *Polyimides: Materials, Chemistry and Characterization*; Elsevier: Amsterdam, 1989.
10. Goff, D. L.; Yuan, E. L.; Long, H.; Neuhaus, H. J. in *Organic Dielectric Materials with Reduced Moisture Absorption and Improved Electrical Properties*; Lupinski, J. H.; Moore, R. S., Eds.; Polymeric Materials for Electronics Packaging and Interconnection; American Chemical Society: Washington, DC, 1989; pp. 93–100.
11. Sroog, C. E. *J Polym Sci Rev Macromol* 1976, 11, 161.
12. Banerjee, S.; Madhra, M. K.; Salunke, A. K.; Maier, G. *J Polym Sci, Part A: Polym Chem* 1992, 40, 1016 [and references therein].
13. Rogers, H. G.; Gaudina, R. A.; Hollised, W. C.; Kalyanaraman, P. S.; Manello, J. S.; McGowan, C.; Minns, R. A.; Sahatjian, R. S. *Macromolecules* 1985, 18, 1058.
14. Husk, G. R.; Cassidy, P. E.; Geherit, K. L. *Macromolecules* 1988, 21, 1234.
15. Cassidy, P. E.; Aminabhavi, T. M.; Farley, J. M. *JMS Rev Macromol Chem Phys* 1989, C29 (2 & 3), 365.
16. Haris, F. W.; Hsu, S. L. C. *High Perform Polym* 1989, 1, 3.
17. Ichino, T.; Sasaki, S.; Matsuura, T.; Nishi, S. *J Polym Sci, Polym Chem Ed* 1990, 28, 331.
18. Mercer, F. W.; Goodman, T. D. *High Perform Polym* 1991, 3, 297.
19. Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* 1991, 24, 5001.
20. Cheng, S. Z. D.; Arnold, F. E., Jr.; Ziang, A.; Hsu, S. L. C.; Harris, F. W., *Macromolecules* 1991, 24, 5856.
21. Feiring, A. E.; Auman, B. C.; Wonchoba, E. R. *Macromolecules* 1993, 26, 27779.
22. Houghama, G.; Tesoro, G.; Shaw, J. *Macromolecules* 1994, 27, 3642.
23. Hougham, G.; Tesoro, G.; Viehbeck, A.; Chapple-Sokol, J. D. *Macromolecules* 1994, 27, 5964.
24. Park, J. W.; Lee, M.; Liu, J. W.; Kim, S. D.; Chang, J. Y.; Rhee, S. B. *Macromolecules* 1994, 27, 3459.
25. Burma, M.; Fitch, J. W.; Cassidy, P. E. *JMS Rev Macromol Chem Phys* 1996, C36 (1), 119.
26. Hougham, G.; Tesoro, G.; Viehbeck, A. *Macromolecules* 1996, 29, 3453.
27. Al-Masari, M.; Kricheldorf, H. R.; Fritisch, D. *Macromolecules* 1999, 32, 7853.
28. Chung, I. S.; Kim, S. Y. *Macromolecules* 2000, 33, 3190.
29. Dang, T. D.; Mather, P. T.; Alexander, M. D.; Grayson, C. J.; Houtz, M. D.; Spry, R. J.; Arnold, F. E. *J Polym Sci, Part A: Polym Chem* 2000, 38, 1991.
30. Madhra, M. K.; Banerjee, S.; Salunke, A. K.; Prabha, S. *Macromol Chem Phys* 2002, 203, 1238.
31. Banerjee, S.; Madhra, M. K.; Salunke, A. K.; Jaiswal, D. K. *Polymer* to appear.
32. Banerjee, S.; Maier, G.; Burger, M. *Macromolecules* 1999, 32, 4279.
33. Katritzky, A. R.; Rees, C. E.; Eds. *Comprehensive Hetrocyclic Chemistry*; Vols. 2 and 4; Elsevier: Amsterdam, 1984; Chapters 2.04 and 3.13.
34. Chung, T. S.; Vora, R. H.; Jaffe, M. *J Polym Sci, Polym Chem Ed* 1991, 29, 1207.
35. Maier, G. *Prog Polym Sci* 2001, 26, 3.
36. Van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1990, p. 321.