



Syntheses and Properties of Aromatic Polyimides Based on 1,1-Bis[4-(4-aminophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane and 1,1-Bis[4-(4-aminophenoxy)phenyl]-1-phenylethane

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Abstract

A series of fluorinated polyimides were prepared from 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane with various aromatic tetracarboxylic dianhydrides via a conventional two-step procedure. These polyimides were amorphous in nature and afforded flexible and tough films. Some polyimides derived from less stiff dianhydrides were soluble in polar organic solvents. The glass-transition temperatures (T_g) of these polyimides ranged from 252 to 324 °C, and softening temperatures (T_s) stayed in the 254~322 °C range. Decomposition temperatures (T_d) at 10% weight loss all occurred above 569 °C in both air and nitrogen atmospheres. For a comparative study, another series of analogous polyimides based on 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane were also prepared and characterized.

Introduction

Aromatic polyimides have earned a reputation as high-performance materials based on their excellent thermal stability, chemical resistance, and mechanical properties [1, 2]. These properties have led to the use of polyimides in a wide variety of applications, such as polymer matrices for high temperature advanced composites, membranes for the low energy separation of industrial gases, inter-metal dielectrics, high temperature adhesives and coatings, and photoresists. However, their applicability has been limited in some fields because aromatic polyimides are normally insoluble in common organic solvents and have extremely high glass-transition or melting temperatures, which preclude melting processing. Consequently, the search of new polyimides with better processability while maintaining their thermal stability should result in new materials for many applications. A number of successful approaches to increase solubility and processability of polyimides without sacrificing their high thermal stability employ the introduction of flexible or asymmetric linkages in the polymer main chain or the incorporation or lateral attachment of bulky groups in/on the polymer backbone [3–10].

Fluorinated polyimides are well known to possess a number of unique properties and there are several excellent reference sources available [11, 12]. In particular, fluorinated polyimides containing the hexafluoroisopropylidene (6F) group, either in the dianhydride or in the diamine component, display several attractive characteristics [13–17]. Polyimides containing the 6F group in the main chain have much lower dielectric constants and water uptake than observed

for conventional polyimides. Solubility is another advantage that the bulky 6F group provides when incorporated into the backbone, due to inhibited close chain packing. In previous publications, we have demonstrated that incorporation of both hexafluoroisopropylidene (6F) and ether links in the backbone of various aromatic polymers, such as polyamides [18], polyimides [19], polybenzoxazoles [20], and polyoxadiazoles [21], resulted in an enhanced tractability without forfeiture of thermal stability. In continuation of our research in the preparation of processable high temperature polymers, we have synthesized a fluorinated diamine, 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (**3b**, Scheme 1) that led to a series of polyimides containing 1-phenyl-2,2,2-trifluoroethylidene (Ph3FEt) and ether links in the backbone when reacted with various commercially available aromatic dianhydrides. The bulky Ph3FEt connecting groups would reduce the packing efficiency and decrease polymer interchain interactions. Thus, it was expected that the processability of the obtained polyimides would be improved. A balance between flexibility and structural rigidity is achieved by incorporating flexible ether linkages and hindered Ph3FEt units in the polymer main chain. Although some polyimides derived from diamine **3b** have been described previously [22], the properties of the polyimides prepared from this diamine were not well known. Therefore, the present work deals with the synthesis and characterization of polyimides derived from diamine **3b** and six common dianhydrides. Moreover, the structurally similar polyimides on the basis of a non-fluorinated bis(ether amine), 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**3a**) were also prepared and characterized for comparison, and the effect of

fluorine substituents on the properties of the polyimides was elucidated.

Experimental

Materials

1,1-Bis(4-hydroxyphenyl)-1-phenylethane (**1a**, from Mitsui Petrochemical Ind., Tokyo, Japan) was used without previous purification. *p*-Chloronitrobenzene (from TCI), potassium carbonate (K_2CO_3) (from Fluka), 10% palladium on charcoal (Pd/C) (from Fluka), and hydrazine monohydrate (from Acros) were also used as received. 1,1-Bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**3a**) was prepared in two steps starting from the aromatic substitution reactions of bisphenol **1a** with *p*-chloronitrobenzene (Scheme 1). The synthetic details of diamine **3a** have been reported previously [23]. Commercially available aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA; **4a**) (from Aldrich), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA; **4c**) (from Aldrich), 4,4'-oxydiphthalic dianhydride (ODPA; **4d**) (from Oxychem), 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA; **4e**) (from New Japan Chemical Co.) were purified by recrystallization from acetic anhydride. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA; **4b**) (from Oxychem) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; **4f**) (from Hoechst Celanese) were purified by vacuum sublimation. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride (CaH_2) and stored over 4 Å molecular sieves.

Synthesis of 1,1-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane (**1b**)

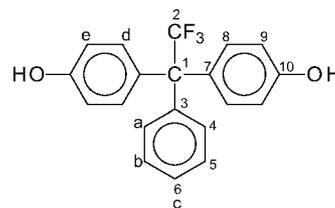
In a three-neck, 300-mL round-bottom flask equipped with a stirring-bar, gas inlet and drying tube, 25 g (0.145 mol) of α, α, α -trifluoroacetophenone, 54 g (0.574 mol) of phenol, and 1 g of zinc chloride ($ZnCl_2$) were added. The flask was immersed in a temperature controlled silicone oil bath at 100 °C. Via the gas inlet, dry hydrogen chloride (HCl) gas was bubbled into the reaction mixture. Within 1 h of the introduction of HCl gas, the reaction mixture gradually became viscous and formed a pale orange-yellow solid. The crude product was washed repeatedly by boiling water and recrystallized from methanol/water (100 mL/50 mL) to afford 41.4 g (84%) of off-white pure 3F-bisphenol **1b** with a melting point of 234~235 °C (by DSC at a heating rate of 2 °C/min) (lit. [24] 231~232 °C).

IR (KBr): 3300~3600 (O–H stretching), 1200~1260 (C–O stretching), 1147 cm^{-1} (C–F stretching).

1H NMR (DMSO- d_6 , δ , ppm): 9.30 (s, 2H, –OH), 7.27 (d, $H_b + H_c$, 3H), 7.13 (d, H_a , 2H), 6.90 (d, H_d , 4H), 6.75 (d, H_e , 4H).

^{13}C NMR (DMSO- d_6 , δ , ppm): 158.6 (C^{10}), 142.6 (C^3), 132.4 (C^8), 132.2 (C^7), 131.2 (C^4), 129.8 (q, $^1J_{C-F} =$

280 Hz, C^2), 129.5 (C^5), 129.0 (C^6), 116.3 (C^9), 64.4 (q, $^2J_{C-F} = 23$ Hz, C^1).



ELEM. ANAL. Calcd. for $C_{20}H_{15}F_3O_2$ (344.33): C, 69.76%; H, 4.39%. Found: C, 69.54%; H, 4.21%.

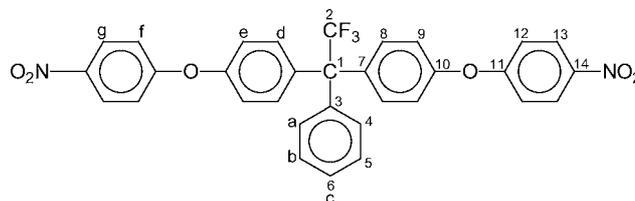
Synthesis of 1,1-bis[4-(4-nitrophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (**2b**)

In a 250-mL round-bottom flask, 10 g (0.03 mol) of 3F-bisphenol **1b** and 9.15 g (0.06 mol) of *p*-chloronitrobenzene were dissolved in 80 mL of dry DMF. Then, 8 g (0.06 mol) of potassium carbonate was added, and the suspension solution was refluxed at 150 °C for 7 h. After cooling, the mixture was poured into 300 mL of methanol/water (1 : 2 by volume), and the precipitated yellow solid was collected by filtration, and washed thoroughly with methanol and water. The crude product was recrystallized from DMF/methanol to afford 15 g (yield 88%) of light yellow crystals (mp = 196~197 °C, by DSC; lit. [22] 196~197 °C).

IR (KBr): 1550 (N=O asymmetric stretching), 1350 (N=O symmetric stretching), 1250 (C–O stretching), 1182 cm^{-1} (C–F stretching).

1H NMR (DMSO- d_6 , δ , ppm): 8.28 (d, H_g , 4H), 7.45 (m, $H_b + H_c$, 3H), 7.25 (two overlapped AB doublets, $H_a + H_d$, 6H), 7.20 (two overlapped AB doublets, $H_e + H_f$, 8H).

^{13}C NMR (DMSO- d_6 , δ , ppm): 162.0 (C^{11}), 154.2 (C^{10}), 142.7 (C^{14}), 139.1 (C^3), 135.8 (C^7), 131.5 (C^8), 129.2 (C^4), 128.6 (C^5), 128.2 (C^6), 127.1 (q, $^1J_{C-F} = 287$ Hz, C^2), 126.2 (C^{13}), 119.9 (C^9), 118.0 (C^{12}), 63.9 (q, $^2J_{C-F} = 24$ Hz, C^1).



ELEM. ANAL. Calcd. for $C_{32}H_{21}N_2F_3O_6$ (586.52): C, 65.53%; H, 3.61%; N, 4.78%. Found: C, 65.11%; H, 3.58%; N, 4.77%.

Synthesis of 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (**3b**)

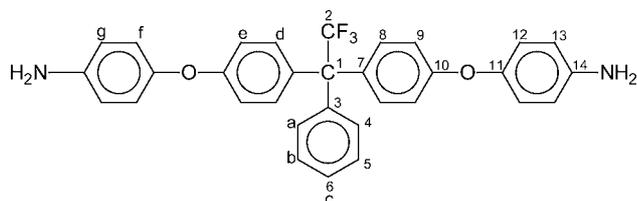
The dinitro compound **2b** (15 g, 0.026 mol) and 10% Pd/C (0.1 g) were suspended in 150 mL ethanol in a 250-mL flask. The suspension solution was heated to reflux, and hydrazine monohydrate (20 mL) was added dropwise to the mixture. After a further 10-h reflux, the catalyst was removed by hot

filtration. The filtrate was poured into 50 mL of water to give an off-white powder that was isolated by filtration and dried *in vacuo* at 100 °C overnight. Yield = 10.3 g (78%); mp = 171~173 °C (by DSC) (lit. [22] 169~170 °C).

IR (KBr): 3450, 3383 (N–H stretching), 1240 (C–O stretching), 1175 cm⁻¹ (C–F stretching).

¹H NMR (DMSO-*d*₆, δ, ppm): 7.35 (m, H_b + H_c, 3H), 7.08 (d, H_a, 4H), 6.96 (d, H_d, 4H), 6.88 (overlapped AB doublets, H_e + H_f, 8H), 6.63 (d, H_g, 4H), 5.02 (s, –NH₂, 4H).

¹³C NMR (DMSO-*d*₆, δ, ppm): 160.0 (C¹⁰), 147.1 (C¹¹), 146.2 (C¹⁴), 141.1 (C³), 133.6 (C⁷), 131.9 (C⁸), 130.4 (C⁴), 129.5 (C⁵), 129.0 (C⁶), 127.6 (q, ¹J_{C–F} = 284 Hz, C²), 122.5 (C¹²), 116.7 (C⁹), 115.9 (C¹³), 63.7 (q, ²J_{C–F} = 23 Hz, C¹).



ELEM. ANAL. Calcd. for C₃₂H₂₅F₃N₂O₂ (526.56): C, 72.99%; H, 4.79%; N, 5.32%. Found: C, 72.91%; H, 4.78%; N, 5.24%.

Polyimide Synthesis

The synthesis of polyimide **8a** is used as an example to illustrate the general synthetic route used to produce the polyimides. To a solution of 0.7071 g (1.343 mmol) of diamine **3b** in 9.5 mL of CaH₂-dried DMAc in a 50-mL round-bottom flask, 0.2929 g (1.343 mmol) of dianhydride PMDA was added in one portion. Thus, the solid content of the solution is approximately 10 wt%. The mixture was stirred at room temperature for about 3 h to afford a highly viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) **6a** was 1.70 dL/g, measured in DMAc at a concentration of 0.5 g/dL at 30 °C. The polymer solution was poured into a 11-cm glass culture dish that was placed in a 90 °C oven for removal of the casting solvent. The semi-dried poly(amic acid) film was further dried and converted to the polyimide by sequential heating at 150 °C for 30 min, 200 °C for 30 min, 250 °C for 30 min, and 300 °C for 1 h. The polyimide film was soaked in hot water to facilitate removal from the glass substrate. The inherent viscosity of the polyimide **8a** was 0.86 dL/g, measured in concentrated sulfuric acid at a concentration of 0.5 g/dL at 30 °C.

Measurements

Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analysis was made on a PerkinElmer 2400 CHN analyzer. ¹H and ¹³C NMR spectra were recorded on a JEOL EX 400 spectrometer at 399.65 and 99.00 MHz frequencies, respectively.

The inherent viscosities of the polymers were determined with an Ubbelohde viscometer at 30 °C. An Instron universal tester model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the polyimide samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.08 mm thick), and an average of at least five individual determinations was used. Wide-angle X-ray diffraction measurements were performed at room temperature (ca. 25 °C) on a Siemens Kristalloflex D5000 X-ray diffractometer (operating at 40 kV and 20 mA) with nickel-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) or a Shimadzu XRD 6000 X-ray diffractometer using graphite-monochromatized Cu K α radiation. The scanning rate was 3°/min over a range of $2\theta = 5\sim 45^\circ$. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 4~6 mg of samples in flowing nitrogen (flow rate 20 cm³/min) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Pyris 1 DSC at a heating rate of 20 °C/min under nitrogen. Glass-transition temperatures (T_g) were read at the middle of the transition in the heat capacity and were taken from the second heating scan after quick cooling from 400 °C at a cooling rate of 200 °C/min. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted from 40 °C to 300 °C at a scanning rate of 10 °C/min using a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (T_s) were taken as the onset temperature of probe displacement on the TMA traces.

Results and Discussion

Polymer Synthesis

The flexible, multi-ring bis(ether amine)s **3a** and **3b** were synthesized in two steps starting from the aromatic substitution reactions of bisphenols **1a** and **1b**, respectively, with *p*-chloronitrobenzene, followed by subsequent hydrazine Pd/C-catalyzed reduction of the intermediate dinitro compounds (Scheme 1). The polyimides were prepared by the reaction of diamine **3a** or **3b** with various dianhydrides to form the poly(amic acid)s, followed by thermal imidization, as illustrated in Scheme 2. As shown in Table 1, the inherent viscosities of the poly(amic acid) precursors were in the range of 0.84~1.70 dL/g. Some of the polyimides such as **7d–f** and **8d–f** derived from the flexible dianhydrides of ODPA, DSDA and 6FDA were soluble in polar solvents like DMAc. Therefore, the characterization of inherent viscosity was carried out without any difficulty, and the inherent viscosities of these polyimides were in the range of 0.68~1.09 dL/g, as measured in DMAc. The characterization of inherent viscosity for the organic insoluble polyimides was carried out with concentrated sulfuric acid as the solvent. For comparison, the inherent viscosities of the organosoluble

Table 1. Inherent viscosities of poly(amic acid)s and polyimides.

Poly(amic acid)		Polyimide	
Code	$\eta_{inh}^{(a)}$ (dL/g)	Code	η_{inh} (dL/g) ^(b)
			In DMAc
			In conc. H ₂ SO ₄
5a	0.94	7a	– ^(c)
5b	1.25	7b	–
5c	0.99	7c	–
5d	1.09	7d	0.97
5e	0.97	7e	0.83
5f	0.84	7f	0.68
6a	1.70	8a	–
6b	1.61	8b	–
6c	1.02	8c	–
6d	1.16	8d	1.09
6e	1.04	8e	0.91
6f	0.94	8f	0.80

(a) Measured in DMAc at a concentration of 0.5 g/dL at 30 °C.

(b) Measured at a concentration of 0.5 g/dL at 30 °C.

(c) Insoluble in DMAc.

polyimides were also characterized in concentrated sulfuric acid. As shown in Table 1, the fluorinated polyimides **8a–f** exhibited inherent viscosities of 0.34~0.89 dL/g, as measured in concentrated sulfuric acid. However, it is worth mentioning that sulfuric acid dissolved but simultaneously degraded polyimides **7a–f**. For example, polyimides **7d–f** with inherent viscosities of 0.68~0.97 dL/g in DMAc when dissolved in concentrated sulfuric acid had inherent viscosities ranging from 0.02 to 0.15 dL/g. The degradation of these polymers is likely to be related to the presence of acid-sensitive phenylethylidene ($-\text{C}(\text{C}_6\text{H}_5)(\text{CH}_3)-$) linkages between phenylene units along the macromolecular backbone. The fluorinated polyimides **8a–f** seemed to be less sensitive to sulfuric acid, probably because of the more hindered trifluoromethyl group in the Ph3FET ($-\text{C}(\text{C}_6\text{H}_5)(\text{CF}_3)-$) unit. These results also indicate that the polyimides derived from **3b** exhibited better acid-resistance than their counterparts from **3a**.

Figure 1 shows the IR spectra of thin-film samples typical poly(amic acid)/polyimide sets of **5a/7a** and **6a/8a**. The complete conversion of *o*-carboxyl amide to the imide ring was evidenced by the disappearance of the amic acid bands at 1650~1700 cm^{-1} and 2800~3500 cm^{-1} , together with the appearance of characteristic imide absorption bands at 1780 cm^{-1} (asymmetrical C=O stretching), 1720 cm^{-1} (symmetrical C=O stretching), 1380 cm^{-1} (C–N stretching). The fluorinated polymers **6a** and **8a** revealed a stronger absorption band around 1100 cm^{-1} , due to the presence of $-\text{CF}_3$ groups.

Polymer Properties

The crystallinity of the prepared polyimides were determined by wide-angle X-ray diffraction measurements using nickel-filtered Cu K α radiation. The diffraction patterns of all the **7** and **8** series are presented in Figure 2. All the two series polymers showed almost completely amorphous dif-

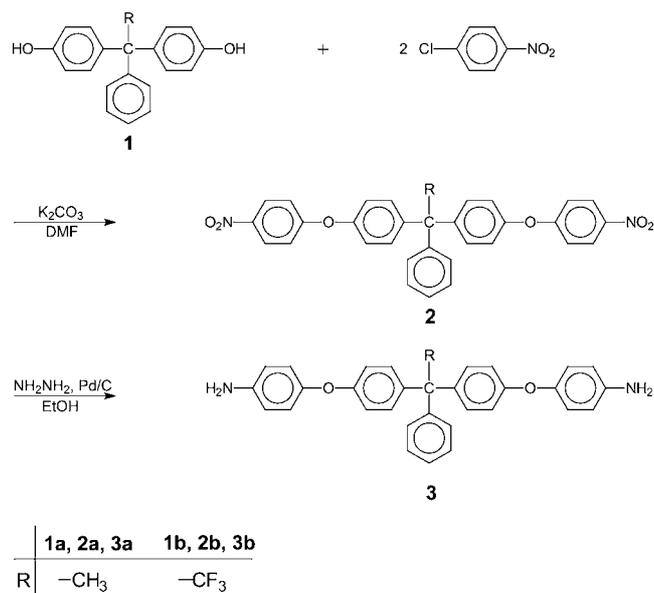
Table 2. Tensile properties of the polyimide films.

Polymer code	Tensile strength (MPa)	Elongation to break (%)	Tensile modulus (GPa)
7a	94	12	2.02
7b	109	14	2.00
7c	120	10	2.18
7d	110	15	2.01
7e	107	9	2.09
7f	96	7	2.06
8a	87	11	1.96
8b	108	15	1.89
8c	115	10	2.00
8d	103	14	1.85
8e	107	11	1.92
8f	105	11	1.98

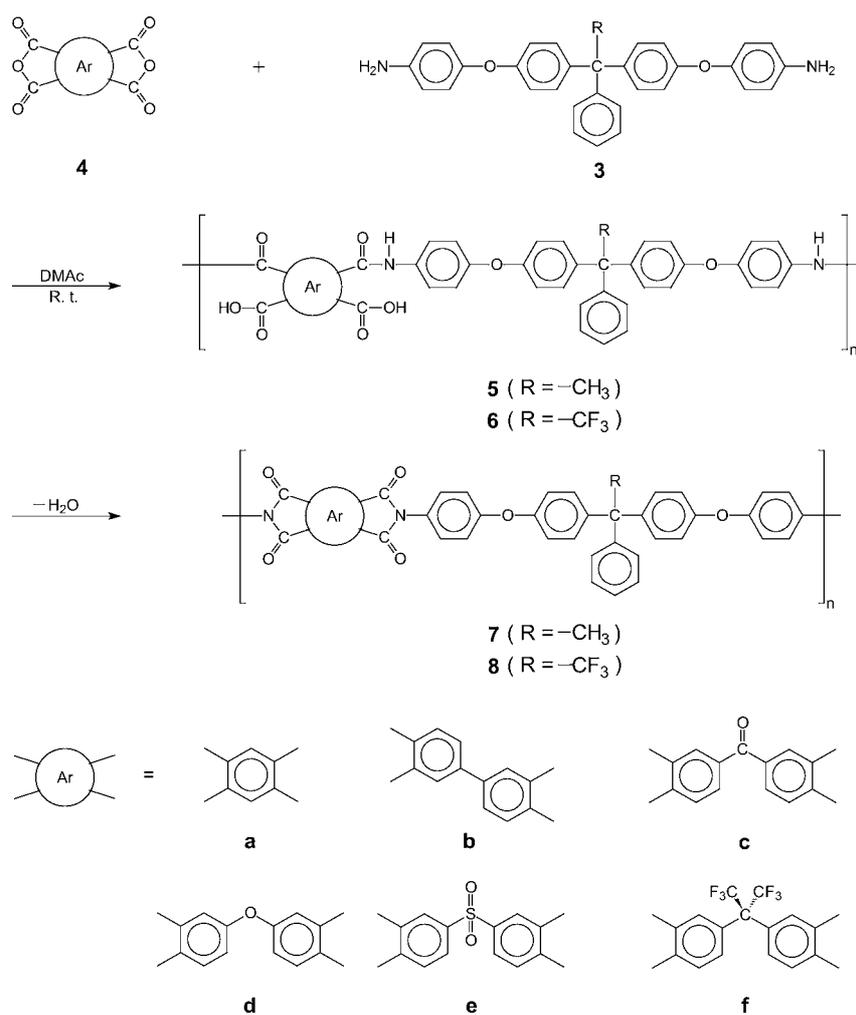
fraction patterns. This is reasonable because of the presence of bulky, non-coplanar 1,1,1-triphenylethylidene and 1,1,1-triphenyl-2,2,2-trifluoroethylidene cores that will disrupt the chain packing and inhibit chain-chain interactions.

All the polyimides could afford flexible and tough films. The tensile properties of these flexible films are summarized in Table 2. The polymer films had tensile strengths of 94–120 MPa, elongations to break of 7–15%, and tensile moduli of 1.85–2.18 GPa. All the polymers behaved as ductile materials with good tensile strengths and moderate elongations to break. Generally, the casting films of the **8a–f** series exhibited slightly lower strengths and moduli than those of the **7a–f** series, possibly due to increased free volume and decreased cohesive force caused by the trifluoromethyl group.

The solubility of the polyimides was determined qualitatively, and the results are listed in Table 3. The organosolubility behavior of polymers generally depended on their chain packing ability and intermolecular interactions that was affected by the rigidity, symmetry, and regularity of the molecular backbone. Thus, the polyimides derived from more flexible dianhydrides such as ODP, DSDA, and 6FDA displayed a higher solubility than those obtained from more rigid components like PMDA, BPDA, and BTDA. When the two sets of polyimides are compared, the solubility behavior of the **8a–f** series polyimides is similar to the **7a–f** series polyimides. This result may indicate that the bulkiness of 1,1,1-triphenylethylidene or 1,1,1-triphenyl-2,2,2-trifluoroethylidene core plays a more dominant role in enhancing the solubility of these polymers than the replacement of the methyl group by the trifluoromethyl group. Furthermore, the imidization method can also affect the solubility of polyimides. As shown in Table 3, polyimide **8d** prepared by chemical imidization method using acetic anhydride and pyridine exhibited better solubility than thermally cured one. The poor solubility of the thermally cured polyimide might be attributed to partial crosslinking within polymer chains or the tight chain packing and aggregation during imidization at elevated temperatures.



Scheme 1. Synthetic route to diamine monomers.



Scheme 2. Synthesis of polyimides.

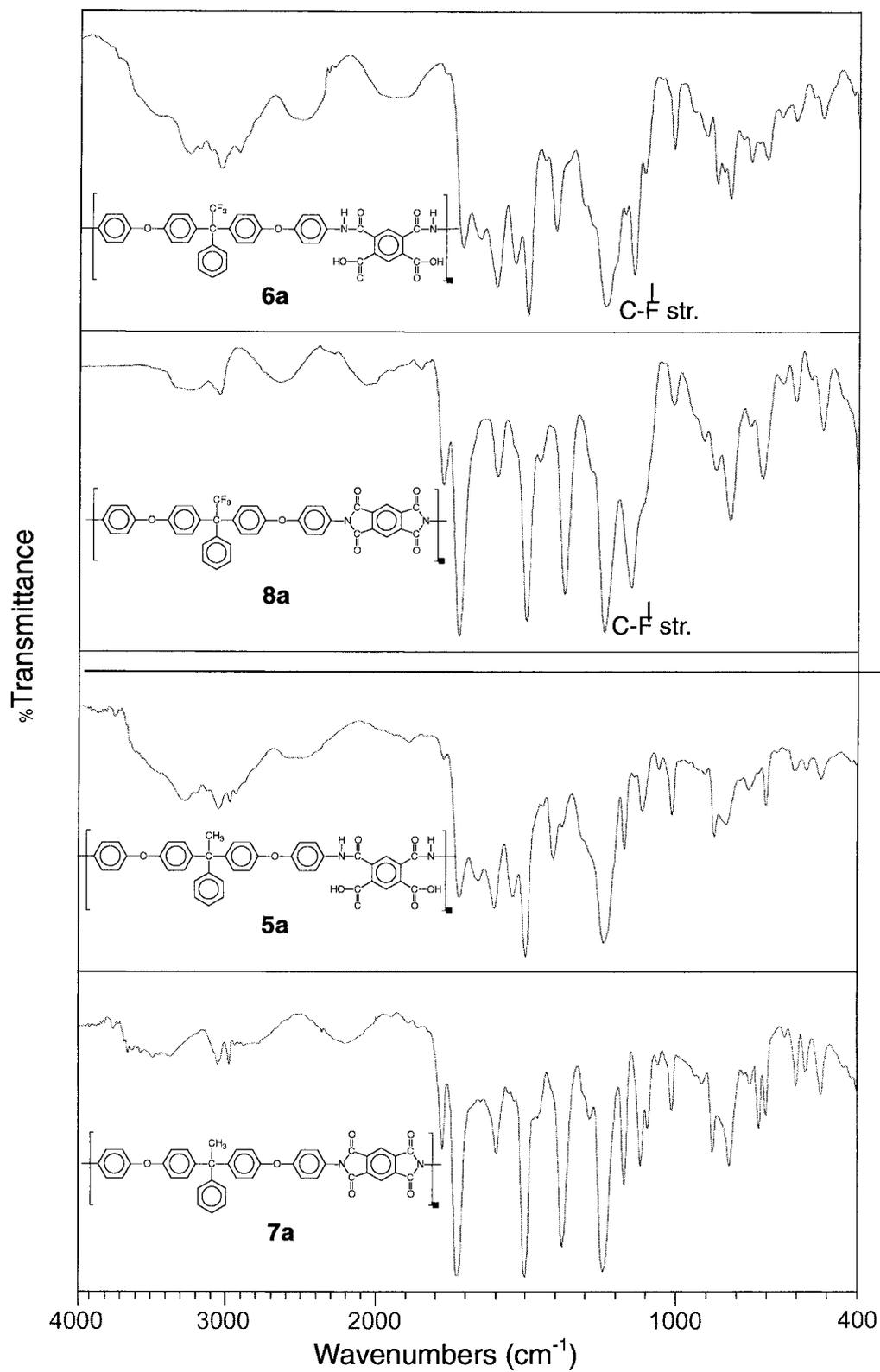


Figure 1. IR spectra of typical poly(amic acid)/polyimide sets **5a/7a** and **6a/8a**.

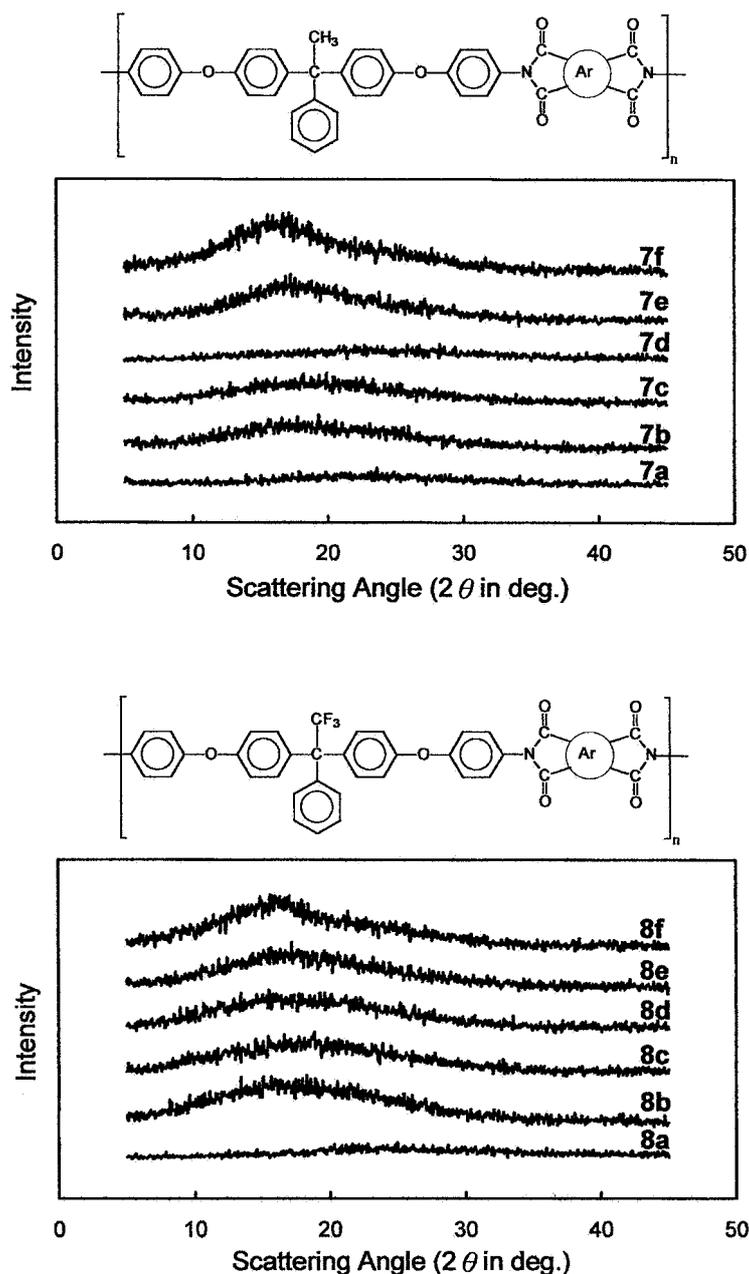


Figure 2. Wide-angle X-ray diffraction patterns of the polyimides.

DSC, TMA, and TGA were used to investigate the thermal properties of the polyimides. The results are summarized in Table 4. In the DSC experiments, all the polymers were rapidly cooled from 400 °C to 50 °C to form predominantly amorphous samples, and, thus, distinct glass-transitions could be observed on the subsequent heating DSC traces. The T_g values of these polyimides were in the 248~324 °C range, in general, following the decreasing order of chain flexibility and steric hindrance of the dianhydride components. Although polyimides **7a** and **8a** showed amorphous X-ray diffraction patterns, they revealed a broad, medium-intensity melting endotherms around 456 and 472 °C, respectively. The results indicate that these polymers may have a higher crystallization tendency upon heating. As can be seen from Figure 3, a slight increase in crystallinity was observed if the film samples of **7a** and

8a were annealed at elevated temperatures such as 400 °C for 30 min. These results are consistent with that reported in literature [22]. The softening temperatures (T_s) (may be referred as apparent T_g) of the polyimide films were determined by the TMA method using a loaded penetration probe. A typical TMA thermogram for polyimides **7d** and **8d** are illustrated in Figure 4. All the T_s values detected by TMA are comparable to the T_g values with DSC. The polymers derived from ODPa had the lowest T_g and T_s values in both **7** and **8** series polyimides due to the flexible ether linkage between phthalimide units. When the two series of polyimides are compared, the **8** series polyimides generally revealed slightly higher T_g and T_s values. This might be a consequence of higher steric hindrance of segmental mobility caused by the trifluoromethyl groups.

Table 3. Solubility behavior of the polyimides.

Polymer code	Solubility ^(a)					
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
7a	-	-	-	-	-	-
7b	+h	-	-	-	+h	-
7c	+h	-	-	-	-	-
7d	+h	+h	+h	-	+h	-
7e	+	+	+	+h	+h	-
7f	+	+	+	+h	+h	+
8a	-	-	-	-	-	-
8b	+h	-	-	-	+h	-
8c	-	-	-	-	-	-
8d	+h(+) ^(b)	+h(+)	+h(+)	-(+h)	+h(+)	-(+)
8e	+(+)	+(+)	+(+)	+h(+h)	-(+)	+(+)
8f	+	+	+	+h	+h	+

^(a) Qualitative solubility tested with 10 mg of sample in 1 mL of the solvent. +: soluble at room temperature; +h: soluble on heating at 100°C; -: insoluble even on heating. NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

^(b) The results given in parentheses are those of the samples of cyclodehydrated by the chemical imidization method.

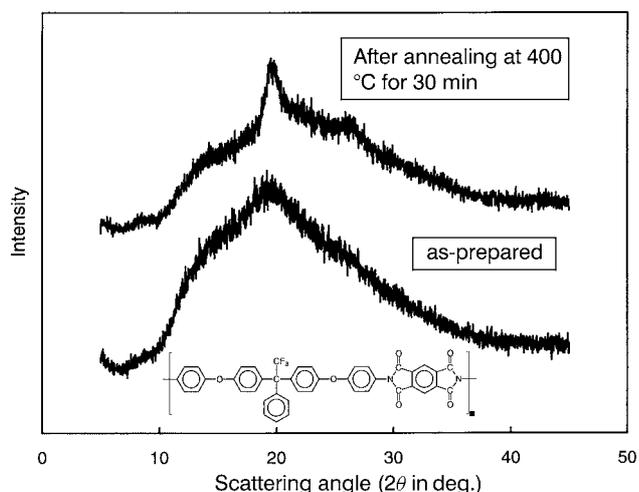
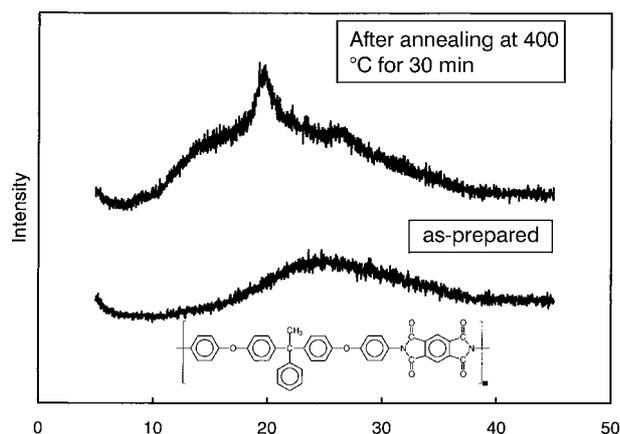


Figure 3. X-ray diffraction patterns of the as-prepared film of polyimides 7a and 8a and that after isothermal annealing at 400°C for 30 min.

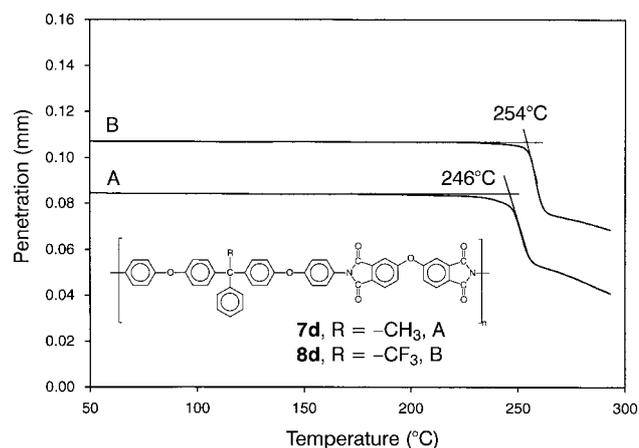


Figure 4. TMA thermograms of polyimides 7d and 8d at a heating rate of 10°C/min.

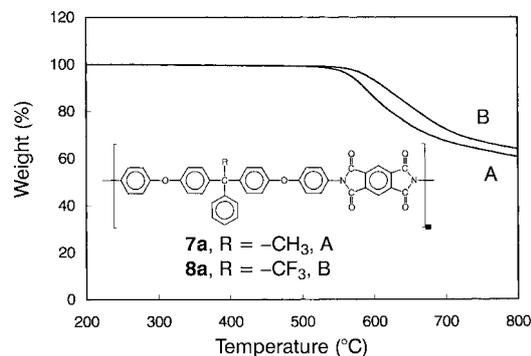


Figure 5. TGA curves of polyimides 7a and 8a at a heating rate of 20°C/min.

Representative TGA thermograms of polyimides 7a and 8a are reproduced in Figure 5. All the other polyimides showed similar patterns of degradation with no significant weight loss before 500°C in nitrogen or air, but with more than 50 wt% residue remaining when heated to 800°C in

Table 4. Thermal properties of polyimides.

Polymer code	$T_g^{(a)}$ (°C)	$T_s^{(b)}$ (°C)	$T_d^{(c)}$ (°C)		Char yield ^(d) (%)
			N ₂	Air	
7a	312	313	587	574	60
7b	273	271	600	592	67
7c	258	251	580	584	58
7d	248	246	583	580	57
7e	273	273	550	544	52
7f	267	266	588	573	63
8a	324	322	616	587	64
8b	270	272	628	602	68
8c	257	257	616	597	60
8d	252	254	616	593	65
8e	279	282	584	569	60
8f	271	272	599	576	61

(a) Midpoint temperature of baseline shift on the second DSC heating trace (rate 20 °C/min) of the sample after quenching from 400 °C.

(b) Softening temperature measured by TMA (penetration method) with a constant applied load of 10 mN at a heating rate of 10 °C/min.

(c) Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.

(d) Residual weight % at 800 °C in nitrogen.

nitrogen. Some thermal behavior data are also summarized in Table 4. The decomposition temperature (T_d) at 10% weight loss of polyimides **7a–f** were recorded in the range of 550~600 °C in nitrogen and 544~592 °C in air, and those of polyimides **8a–f** were recorded in the range of 584~628 °C in nitrogen and 569~602 °C in air. In all cases, the fluorinated polyimides **8a–f** exhibited higher T_d values in comparison to their analogous **7a–f** counterparts might be a result of stronger C–F bonding of the trifluoromethyl groups.

Conclusions

Two series of polyimides have been synthesized from the bis(ether diamine)s **3a** and **3b** with aromatic dianhydrides via a conventional two-step polymerization. All of the polyimides afforded flexible and tough films. The polyimides derived from dianhydrides with ether, sulfone, or hexafluoroisopropylidene bridging groups were soluble in polar organic solvents. All the polyimides had T_g values higher than 248 °C and were thermally stable, with 10% weight loss temperatures being recorded above 540 °C. The fluorinated polyimides synthesized from **3b** showed higher T_g values, thermal stability, and acid-resistance compared to the corresponding polyimides from non-fluorinated **3a**.

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References

1. D. Wilson, P. M. Hergenrother and H. D. Stenzenberger, Eds., *Polyimides*, Chapman and Hall, New York, 1990.

2. M. K. Ghosh and K. L. Mittal, Eds., *Polyimides: Fundamentals and Applications*, Marcel Dekker, New York, 1996.
3. S. Tamai, A. Yamaguchi and M. Ohta, *Polymer*, **37**, 3683 (1996).
4. Y. Imai, *High Perform. Polym.*, **7**, 337 (1995).
5. G.-S. Liou, M. Maruyama, M. Kakimoto and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **36**, 2021 (1998).
6. Y.-T. Chern and H.-C. Shiue, *Macromolecules*, **30**, 4646 (1997).
7. S.-H. Hsiao and C.-T. Li, *Macromolecules*, **31**, 7213 (1998).
8. D.-J. Liaw, B.-Y. Liaw and C.-M. Yang, *Acta Polym.*, **50**, 332 (1999).
9. S.-H. Hsiao, C.-P. Yang and K.-Y. Chu, *Macromolecules*, **30**, 165 (1997).
10. C.-H. Chou, D. S. Reddy and C.-F. Shu, *J. Polym. Sci. Part A: Polym. Chem.*, **40**, 3615 (2002).
11. S. Sasaki and S. Nishi, in *Polyimides: Fundamentals and Applications*, M. K. Ghosh and K. L. Mittal, Eds., Marcel Dekker, New York, 1996, p. 71.
12. G. Houghman, P. E. Cassidy and K. Johns, Eds., *Fluoropolymers 2: Properties*, Plenum, New York, 1999, p. 233.
13. R. A. Hayes (assigned to E. I. DuPont Co.), U.S. Pat. 4,912,197 (1990).
14. T. Matsuura, Y. Hasuda, S. Nishi and N. Yamada, *Macromolecules*, **24**, 5001 (1991).
15. Y. S. Negi, Y. Suzuki, I. Kawamura, T. Hagiwara, Y. Takahashi, M. Iijima, M. Kakimoto and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **30**, 2281 (1992).
16. D. A. Stoakley, A. K. St. Clair and C. I. Croall, *J. Appl. Polym. Sci.*, **51**, 1479 (1994).
17. D.-H. Lee, S.-Y. Koo, D.-Y. Kim and H.-J. Choi, *J. Appl. Polym. Sci.*, **76**, 249 (2000).
18. S.-H. Hsiao and C.-H. Yu, *J. Polym. Res.*, **3**, 239 (1996).
19. S.-H. Hsiao and C.-H. Yu, *Polym. J.*, **29**, 994 (1997).
20. S.-H. Hsiao and C.-H. Yu, *Macromol. Chem. Phys.*, **199**, 1247 (1998).
21. S.-H. Hsiao and C.-H. Yu, *J. Polym. Sci. Part A: Polym. Chem.*, **36**, 1847 (1998).
22. M. H. Brink, D. K. Brandom, G. L. Wilkes and J. E. McGrath, *Polymer*, **35**, 5018 (1994).
23. S.-H. Hsiao, C.-P. Yang, M.-H. Chung and H.-C. Hsiao, *J. Polym. Sci. Part A: Polym. Chem.*, **38**, 247 (2000).
24. M. H. Woodard, M. E. Rogers, D. K. Brandom, G. L. Wilkes and J. E. McGrath, *ACS Polym. Prepr.*, **33**(2), 333 (1992).