

Novel, Organosoluble, Light-Colored Fluorinated Polyimides Based on 2,2'-Bis(4-amino-2-trifluoromethylphenoxy)biphenyl or 2,2'-Bis(4-amino-2-trifluoromethylphenoxy)-1,1'-binaphthyl

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ABSTRACT: Two series of fluorinated polyimides were prepared from 2,2'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (**2**) and 2,2'-bis(4-amino-2-trifluoromethylphenoxy)-1,1'-binaphthyl (**4**) with various aromatic dianhydrides via a conventional, two-step procedure that included a ring-opening polyaddition to give poly(amic acid)s, followed by chemical or thermal cyclodehydration. The inherent viscosities of the polyimides ranged from 0.54 to 0.73 and 0.19 to 0.36 dL/g, respectively. All the fluorinated polyimides were soluble in many polar organic solvents, such as *N,N*-dimethylacetamide and *N*-methylpyrrolidone, and afforded transparent and light-colored films via solution-casting. These polyimides showed glass-transition temperatures in the ranges of 222–280 and 257–351 °C by DSC, softening temperatures in the range of 264–301 °C by thermomechanical analysis, and a decomposition temperature for 10% weight loss above 520 °C both in nitrogen and air atmospheres. The polyimides had low moisture absorptions of 0.23–0.58%, low dielectric constants of 2.84–3.61 at 10 kHz, and an ultraviolet–visible absorption cutoff wavelength at 351–434 nm. Copolyimides derived from the same dianhydrides with an equimolar mixture of 4,4'-oxydianiline and diamine **2** or **4** were also prepared and characterized. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 2416–2431, 2004

Keywords: trifluoromethyl group; fluorinated polyimides; light-colored; solubility; thermal properties; high performance polymers; structure–property relations; dielectric properties

INTRODUCTION

Aromatic polyimides are highly heat-resistant materials and have been widely used in many applications such as microelectronics, coatings, composite materials, and membranes.¹ However, their applicability has been limited because aro-

matic polyimides are normally insoluble and infusible in the fully imidized form because of their rigid-chain characteristics, leading to processing difficulties. Thus, polyimide processing is generally carried out with a poly(amic acid) intermediate and then is converted to a polyimide via rigorous thermal treatment. Problems often arise because the poly(amic acid)s are thermally and hydrolytically unstable. The water evolved during imidization also tends to cause voids in the final materials.² To overcome these problems, much

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research effort has been focused on designing and synthesizing new dianhydrides^{3–8} and diamines^{9–15} that resulted in soluble and processable polyimides in the fully imidized form without deterioration of their positive properties. One of the effective approaches in improving the solubility of aromatic polyimides is the incorporation of a crank and twisted non-coplanar structure such as biphenyl-2,2'-diyl and 1,1'-binaphthyl-2,2'-diyl units into the polymer main chain.^{16–21}

However, a low dielectric constant (k) is one of the most attractive properties of polyimide materials for microelectronics applications. To achieve a polymer structure with a low dielectric constant, repeating units with low polarity and low polarizability must be used.²² The incorporation of aliphatic adamantane or diamantane moiety results in low k polyimides because of high hydrophobicity, low polarity, and increased free volume.^{23–25} An alternative method in attaining processable low k aromatic polyimides is the introduction of fluorine atoms in the polymer structure, either as substituents of carbon atoms on the polymer backbone or as perfluoroalkyl side substituents. The most popular approach used was the introduction of hexafluoroisopropylidene groups in the main chain as bulky separator groups in the dianhydride or diamine monomers.^{26,27} The presence of the trifluoromethyl groups and the substitution of fluorine for hydrogen causes a dramatic change of properties. The combination of electronic and steric effects reduces the ability for interchain interactions and (particularly) hinders the formation of charge-transfer complexes, which is a major factor of molecular packing and intractability in aromatic polyimides. In the past two to three decades, a number of fluorine-containing dianhydrides and diamines have been designed to prepare fluorinated polyimides with increased solubility, low moisture absorption, low refractive indices, high optical transparency, and low dielectric constants while maintaining many of the advantages of polyimides.^{28,29}

Recent studies demonstrated that polyimides derived from ether bridged aromatic diamines with trifluoromethyl (CF_3) substituents were soluble, high-temperature polymer materials with high thermal stability, low moisture uptake, low dielectric constants, and high optical transparency.^{30–35} We have reported a series of polyimides¹⁸ from 2,2'-bis(4-aminophenoxy)biphenyl and 2,2'-bis(4-aminophenoxy)-1,1'-binaphthyl with various dianhydrides, which showed good solubility with high thermal stability. In continuation of our research interests in the preparation of pro-

cessable and low-dielectric-constant interlayer materials for microelectronic applications, we designed novel polyimides and copolyimides from the diamine monomers, 2,2'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl and 2,2'-bis(4-amino-2-trifluoromethylphenoxy)-1,1'-binaphthyl. These polymers were subjected to solubility tests and thermal, optical, and dielectric property measurements. The fluorine-containing polyimides are expected to exhibit enhanced solubility and diminished dielectric constants because of increased free volume caused by the introduction of bulky CF_3 groups.³⁶

EXPERIMENTAL

Materials

2,2'-Biphenol (Acros), 2,2'-dihydroxy-1,1'-binaphthyl (Acros), potassium carbonate (K_2CO_3) (Showa), sodium hydride (Aldrich), 2-chloro-5-nitrobenzotrifluoride (Aldrich), palladium 10% on activated charcoal (Pd/C) (Lancaster), and hydrazine monohydrate [Tokyo Chemical Industry (TCI)] were used as received. Commercially available, aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA; **5_a**) (Chriskev), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA; **5_c**) (Chriskev), 4,4'-oxydiphthalic dianhydride (ODPA; **5_d**) (TCI), and 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA; **5_e**) (TCI) were purified by recrystallization from acetic anhydride. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA; **5_b**) (Chriskev) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; **5_f**) (Chriskev) were purified by vacuum sublimation. 4,4'-Oxydianiline (4,4'-ODA) (TCI) was purified by recrystallization from ethanol. *N,N*-Dimethylacetamide (DMAc) (Tedia) was purified by distillation over calcium hydride and was stored over 4 Å molecular sieves.

Monomer Synthesis

2,2'-Bis(4-nitro-2-trifluoromethylphenoxy)biphenyl (1)

2,2'-Biphenol (12.0 g, 0.0644 mol) and 2-chloro-5-nitrobenzotrifluoride (29.2 g, 0.129 mol) were dissolved in 80 mL of DMAc in a 250-mL, round-bottom flask. Then, potassium carbonate (13.8 g, 0.1 mol) was added, and the suspension mixture was heated at 110 °C for 12 h. The mixture was allowed to cool and then was poured into 800 mL

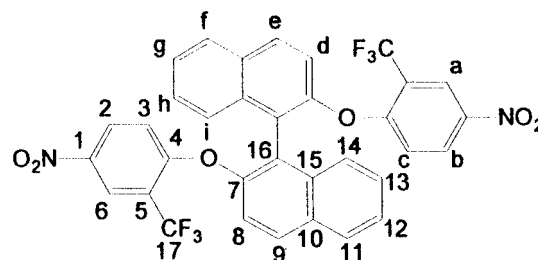
of water/methanol (1:1) to give a yellow solid, which was collected, washed repeatedly with methanol, and dried. The crude product was recrystallized from *N,N*-dimethylformamide (DMF)/methanol to give light yellow needles (30.9 g, 85%); mp: 142–144 °C (onset to the peak top temperature) according to differential scanning calorimetry (DSC) at a scanning rate of 10 °C/min.

IR (KBr): 1529, 1338 (—NO₂ stretch), 1292, 1278 (C—O stretch), 1135, 1149 cm⁻¹ (C—F stretch). ¹H NMR [deuterated dimethyl sulfoxide (DMSO-*d*₆), δ, ppm]: 8.35 (d, *J* = 2.6 Hz, 2H, Ha), 8.22 (dd, *J* = 2.6, 9.3 Hz, 2H, Hb), 7.47 (dd, *J* = 7.9, 8.9 Hz, 2H, He), 7.42 (d, *J* = 7.4 Hz, 2H, Hg), 7.33 (dd, *J* = 7.5, 7.5 Hz, 2H, Hf), 7.25 (dd, *J* = 8.1 Hz, 2H, Hd), 6.78 (d, *J* = 9.3 Hz, 2H, Hc). ¹³C NMR (DMSO-*d*₆, δ, ppm): 159.67 (C⁴), 150.19 (C⁷), 141.18 (C¹), 132.13 (C⁹), 130.53 (C¹¹), 129.59 (C²), 129.07 (C¹²), 126.25 (C³), 123.21 (q, ³*J*_{C—F} = 5 Hz, C⁶), 121.99 (q, ¹*J*_{C—F} = 271 Hz, C¹³), 121.07 (C¹⁰), 118.02 (q, ²*J*_{C—F} = 33 Hz, C⁵), 116.35 (C⁸). ELEM. ANAL. Calcd. for C₂₆H₁₄F₆N₂O₆ (564.40): C, 55.33%; H, 2.50%; N, 4.96%. Found: C, 55.36%; H, 2.65%; N, 5.00%.

2,2'-Bis(4-amino-2-trifluoromethylphenoxy)-biphenyl (2)

The dinitro compound **1** (16.25 g, 0.0288 mol) and 10% Pd/C (0.2 g) were suspended in 100 mL of ethanol in a 250-mL flask. The suspension solution was heated to reflux, and hydrazine monohydrate (8 mL) was added dropwise to the mixture over 30 min. After a further 4 h of reflux, the resultant clear, darkened solution was filtered hot to remove Pd/C, and the filtrate was then cooled to precipitate white-lump crystals (13.07 g, 90%); mp: 194–195 °C (onset to the peak top temperature) by DSC at a scanning rate of 10 °C/min.

IR (KBr): 3484, 3395 (N—H stretch), 1270, 1228 (C—O stretch), 1157, 1128 cm⁻¹ (C—F stretch). ¹H NMR (DMSO-*d*₆, δ, ppm): 7.38 (dd, *J* = 1.8, 7.5 Hz, 2H, Hg), 7.26 (dd, *J* = 7.7, 7.9 Hz, 2H, He), 7.09 (dd, *J* = 7.4, 7.5 Hz, 2H, Hf), 6.89 (d, *J* = 7.5 Hz, 2H, Hd), 6.64–6.72 (m, 6H, Ha,b,c), 5.34 (s, 4H, —NH₂). ¹³C NMR (DMSO-*d*₆, δ, ppm): 155.27 (C⁷), 145.19 (C⁴), 143.24 (C¹), 131.79 (C⁹), 128.99 (C¹¹), 128.04 (C¹²), 123.05 (q, ¹*J*_{C—F} = 271 Hz, C¹³), 122.45 (C²), 121.97 (C¹⁰), 120.82 (q, ²*J*_{C—F} = 33 Hz, C⁵), 118.53 (C³), 116.65 (C⁸), 110.65 (C⁶). ELEM. ANAL. Calcd. for C₂₆H₁₈F₆N₂O₂ (504.43): C, 61.91%; H, 3.60%; N, 5.55%. Found: C, 62.01%; H, 3.65%; N, 5.46%.



Structure 1

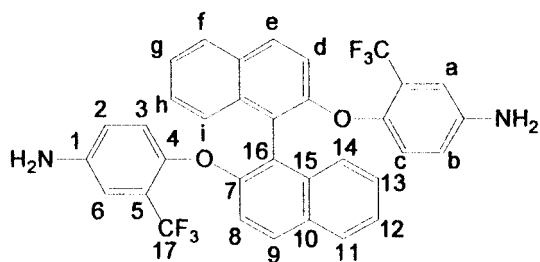
2,2'-Bis(4-nitro-2-trifluoromethylphenoxy)-1,1'-binaphthyl (3)

A mixture of sodium hydride (2.56 g, 0.101 mol) in 150 mL of DMF was stirred at room temperature. To the mixture, 2,2'-dihydroxy-1,1'-binaphthyl (14.32 g, 0.05 mol) and 2-chloro-5-nitrobenzotrifluoride (23.25 g, 0.10 mol) were added in sequence. The mixture was heated with stirring at 120 °C for 20 h. The mixture was allowed to cool and then was poured into 1.5 L of water/methanol (1:1) to give yellow solid, which was collected, washed repeatedly with methanol, and dried. The crude product was recrystallized from DMF/ethanol to give light yellow lump crystals (24.9 g, 75%); mp: 164–168 °C (by DSC) (lit.³⁷ 165–167 °C).

IR (KBr): 1524, 1356 (—NO₂ stretch), 1287 (C—O stretch), 1141 cm⁻¹ (C—F stretch). ¹H NMR (DMSO-*d*₆, δ, ppm): 8.24 (d, *J* = 2.7 Hz, 2H, Ha), 8.21 (d, *J* = 9.0 Hz, 2H, Hb), 8.06 (d, 2H, *J* = 8.7 Hz, He,f), 7.54 (d, 2H, *J* = 9.0 Hz, Hi), 7.52 (t, 2H, *J* = 7.2 Hz, Hh), 7.38 (t, *J* = 6.9 Hz, 2H, Hg), 7.24 (d, *J* = 8.4 Hz, 2H, Hd), 6.87 (d, *J* = 9.0 Hz, 2H, Hc). ¹³C NMR (DMSO-*d*₆, δ, ppm): 159.3 (C⁴), 148.3 (C⁷), 141.0 (C¹), 133.1 (C¹⁵), 131.3 (C¹⁰), 131.2 (C⁹), 129.3 (C¹¹), 128.4 (C¹³), 127.2 (C¹⁴), 126.1 (C²), 125.3 (C¹²), 123.5 (q, ¹*J*_{C—F} = 273 Hz, C¹⁷), 123.1 (C⁸), 122.4 (C³), 119.9 (C¹⁶), 117.9 (q, ²*J*_{C—F} = 32 Hz, C⁵), 116.2 (q, ³*J*_{C—F} = 5 Hz, C⁶). ELEM. ANAL. Calcd. for C₃₄H₁₈F₆N₂O₆ (664.54): C, 61.45%; H, 2.56%; N, 4.22%. Found: C, 61.78%; H, 3.00%; N, 4.56% (see Structure 1).

2,2'-Bis(4-amino-2-trifluoromethylphenoxy)-1,1'-binaphthyl (4)

The dinitro compound **3** (13.7 g, 0.021 mol) and 10% Pd/C (0.3 g) were suspended in 300 mL of ethanol in a 250-mL flask. The suspension solution was heated to reflux, and hydrazine monohydrate (10 mL) was added dropwise to the mixture over 30 min. After a further 5 h of reflux, about 100 mL of tetrahydrofuran (THF) were added to



Structure 2

dissolve the precipitate during the refluxing. The clear, darkened solution was filtered to remove Pd/C, and the filtrate was then distilled to remove the solvent. The crude product was purified by recrystallization from THF/ethanol to give white powdery crystals (10.5 g, 84%); mp: 271–273 °C (by DSC) (lit.³⁵ 264–266 °C).

IR (KBr): 3482, 3386 (N—H stretch), 1258 (C—O stretch), 1130 cm^{-1} (C—F stretch). ^1H NMR (DMSO- d_6 , δ , ppm): 8.00 (d, $J = 9.0$ Hz, 2H, He), 7.93 (d, $J = 8.0$ Hz, 2H, Hf), 7.44 (t, $J = 6.8$ Hz, 2H, Hg), 7.32 (t, $J = 6.8$ Hz, 2H, Hh), 7.20 (d, $J = 8.1$ Hz, 2H, Hi), 7.03 (d, $J = 9.0$ Hz, 2H, Hd), 6.83 (s, 2H, Ha), 6.72 (s, 4H, Hb,c), 5.37 (s, 4H, —NH₂). ^{13}C NMR (DMSO- d_6 , δ , ppm): 153.2 (C⁷), 145.4 (C⁴), 143.2 (C¹), 133.4 (C¹⁶), 129.8 (C⁹), 129.5 (C¹⁰), 128.0 (C¹¹), 126.6 (C¹³), 125.1 (q, $^1J_{\text{C—F}} = 276$ Hz, C¹⁷), 124.4 (C¹⁴), 122.0 (C¹²), 121.3 (C²), 120.9 (q, $^2J_{\text{C—F}} = 33$ Hz, C⁵), 120.5 (C¹⁵), 118.5 (C³), 117.2 (C⁸), 110.3 (C⁶). ELEM. ANAL. Calcd. for C₃₄H₂₂F₆N₂O₂ (604.54): C, 67.55%; H, 3.67%; N, 4.63%. Found: C, 67.34%; H, 4.17%; N, 5.07% (see Structure 2).

Polymer Synthesis

Homopolyimides

The polyimides were synthesized from diamines **2** and **4** and various dianhydrides via a two-step method. The synthesis of polyimide **9_e** was used as an example to illustrate the general synthetic route used to produce the polyimides. To a solution of 0.604 g (1 mmol) of diamine **4** in 3.5 mL of DMAc, 0.358 g (1 mmol) of dianhydride DSDA (**5_e**) was added in one portion. The mixture was stirred at room temperature overnight (ca. 12 h) to afford a viscous poly(amic acid) solution. The poly(amic acid) was subsequently converted to polyimide via a chemical-imidization process by treatment of 2 mL of pyridine and 5 mL of acetic anhydride at room temperature overnight. The

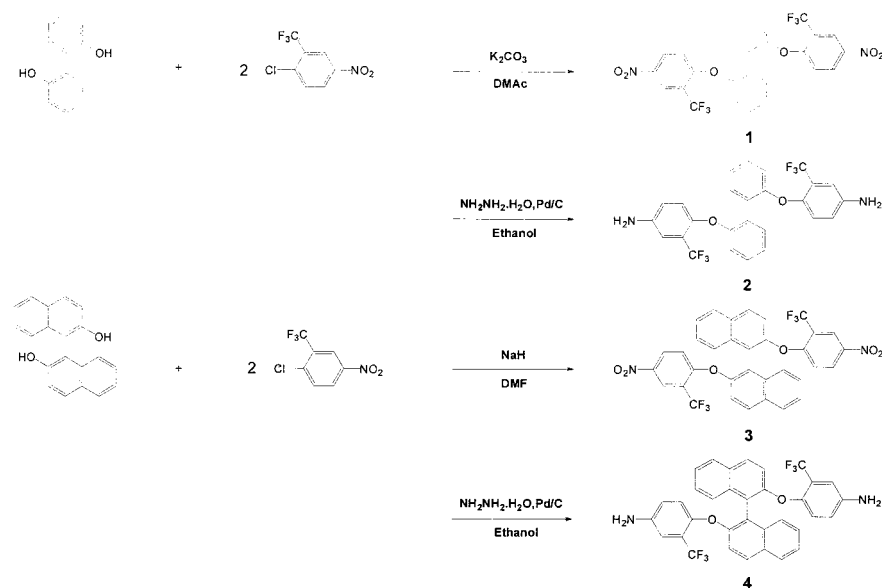
resulting homogeneous polyimide solution was trickled into 300 mL of methanol giving light yellow powder precipitate, which was washed thoroughly with methanol, collected by filtration, and dried. The precipitate was dissolved in 8 mL of DMAc, and the homogeneous solution was poured into a 9-cm glass culture dish, which was placed in a 90 °C oven for 12 h to remove the solvent. Then, the obtained film was further dried *in vacuo* at 160 °C for 6 h. The polyimide film was stripped from the glass substrate by being soaked in water. The inherent viscosity (η_{inh}) of polyimide **9_e** was 0.35 dL/g in DMAc at a concentration of 0.5 g/dL at 30 °C.

Copolyimides

Copolyimide **11_a** was synthesized as above from 0.302 g (0.5 mmol) of diamine **4**, 0.100 g (0.5 mmol) of 4,4'-ODA, and 0.310 g (0.1 mmol) of dianhydride ODPA (**5_a**) in 4 mL of DMAc. The mixture was stirred at room temperature for about 12 h to afford a highly viscous copoly(amic acid) solution. The solution was converted to copolyimide by a thermal-imidization process. The copoly(amic acid) solution was poured into a 9-cm glass culture dish, which was placed for about 4 h in a 90 °C oven to remove the casting solvent. The semidried copoly(amic acid) film was further dried and transformed into copolyimide **11_a** by sequential heating at 100, 150, 200, and 250 °C each for 1 h. The copolyimide film was stripped from the glass substrate by being soaked in water. The inherent viscosity of the copolyimide **11_a** was 0.52 dL/g in DMAc at a concentration of 0.5 g/dL at 30 °C.

Measurements

Infrared spectra were recorded on a PerkinElmer RXI Fourier transform infrared (FTIR) spectrometer. Elemental analyses were completed in a Heraeus CHN-OS rapid elemental analyzer. ^1H and ^{13}C NMR spectra were measured on a Bruker Avance 500-MHz FT-NMR spectrometer. The η_{inh} 's were determined at 0.5 g/dL concentration with a Tamson TV-2000 viscometer at 30 °C. Gel permeation chromatography (GPC) was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive-index detector. Two Waters 5- μm Styragel HR-2 and HR-4 columns connected in series were used with THF as the eluent. The molecular weight was calibrated with polystyrene standards. Wide-angle X-ray



Scheme 1. Synthesis of diamines **2** and **4**.

diffraction (WAXD) measurements were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-7000 X-ray diffractometer (40 kV, 20 mA), with graphite-monochromatized Cu K α radiation. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Varian Cary 50 Probe spectrometer. The dielectric properties of the polymer films were tested by the parallel-plate capacitor method with an HP-4194A impedance/gain-phase analyzer. Gold electrodes were vacuum-deposited on both surfaces of dried films. Experiments were performed at 25 °C in a dry chamber. An Instron universal tester model 4400R with a load cell of 5 kg was used to examine the stress–strain behavior of the polyimide film 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 an average of at least four individual determinations was used. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6–8-mg film samples heated in flowing nitrogen or air (flow rate: 20 cm³/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scanning rate of 20 °C/min in flowing nitrogen (20 cm³/min). The glass-transition temperatures (T_g 's) were read at the middle of the transition in the heat capacitor 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 50 to 300 °C at a scanning rate of 10 °C/min with a penetration probe of 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (T_s 's) were taken as the onset temperatures of probe displacement on the TMA traces. The equilibrium moisture absorption was determined by weighing the changes vacuum-dried film specimen before and after immersion in deionized water at 25 °C for 3 days.

RESULTS AND DISCUSSION

Monomer Synthesis

The two main monomers including CF₃-bis(ether amine)s **2** and **4** were prepared in two steps according to Scheme 1. The dinitro compounds **1** and **3** were synthesized by nucleophilic aromatic substitution of 2,2'-biphenol and 2,2'-dihydroxy-1,1'-binaphthyl, respectively, with 2-chloro-5-nitrobenzotrifluoride in the presence of potassium carbonate in DMAc and in the presence of sodium hydride in DMF, respectively. Diamines **2** and **4** were readily obtained in high purity and high yields by the catalytic reduction of intermediate dinitro compounds **1** and **3** with hydrazine monohydrate and Pd/C catalyst in refluxing ethanol.

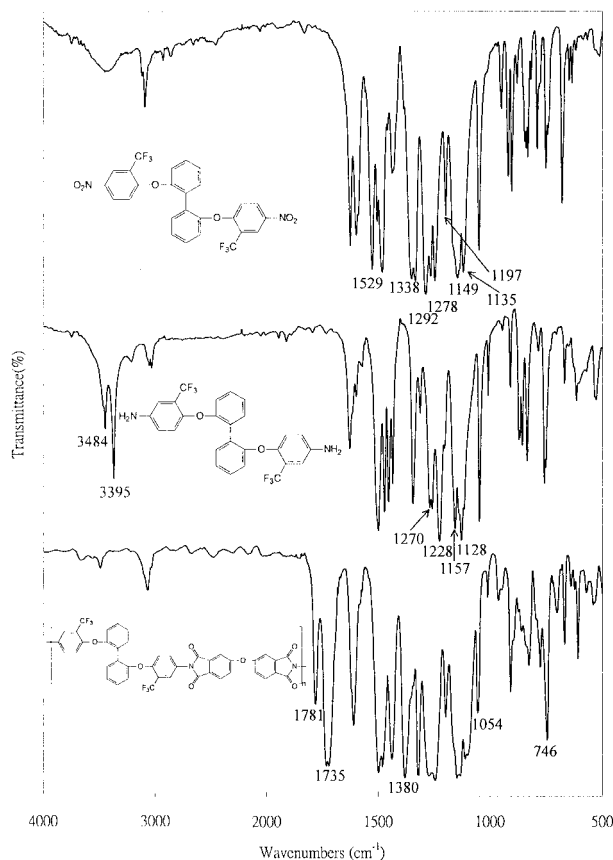


Figure 1. FTIR spectra of dinitro compound **1**, diamine **2**, and polyimide **8_a**.

The structures of **1–4** were confirmed by FTIR, NMR, and elemental analysis. The FTIR spectra of compounds **1** and **2** are shown in Figure 1. Dinitro compound **1** displayed characteristic absorption bands corresponding to asymmetric and symmetric NO_2 stretching at 1529 and 1338 cm^{-1} , respectively, which disappeared after reduction. Diamine compound **2** exhibited typical N—H stretching bands at 3484 and 3395 cm^{-1} . Both the dinitro and diamine compounds showed the —C—O—C— stretching band around 1250 cm^{-1} and the C—F stretching band around 1150 cm^{-1} , confirming the presence of the aromatic ether linkage and the CF_3 group. Figures 2 and 3 display the ^1H and ^{13}C NMR spectra of compounds **1** and **2**, respectively. The NMR spectra confirmed that the nitro groups had been converted into amino groups by the high field shift of the aromatic protons and carbons. The ^{13}C NMR spectra of compounds **1** and **2** showed two obvious quartets because of heteronuclear ^{13}C — ^{19}F coupling. The large quartet (C^{13}) centered at about 122.5 for **1** and 123.5 for **2** were due to the — CF_3

carbons. The one-bond C—F coupling constant in these cases was about 271 Hz. The CF_3 -attached carbon C^5 also showed a clear quartet centered at about 118.2 for **1** and 120.8 for **2** with a smaller coupling constant of about 33 Hz because of two-bond C—F coupling. The binaphthyl-containing compounds **3** and **4** exhibited similar characteristic absorption peaks, which were as reported.³⁷ Thus, all the spectroscopic data obtained agreed with the proposed chemical structures.

Polymer Synthesis

The new, fluorinated polyimides **8_{a–f}** and **9_{a–f}** were prepared by the reaction of diamines **2** and **4** with six commercially available dianhydrides **5_{a–f}** in DMAc at room temperature to form the precursor poly(amic acid)s **6_{a–f}** and **7_{a–f}**, followed by chemical or thermal imidization. Structures and codes of the polymers obtained are shown in Scheme 2. The amino groups in diamines **2** and **4** were less nucleophilic than a normal aromatic diamine because of the inductive deactivation of the CF_3 group, a result confirmed by the slow polymerization rate inferred from the data in Figure 4. As shown in Figure 4, the reaction of ODPA with untrifluoromethylated diamine 2,2'-bis(4-aminophenoxy)biphenyl^{18,38} proceeded relatively fast, and the η_{inh} of the resulting poly(amic acid) increased rapidly within 30 min; the η_{inh} reached about 0.96 dL/g after 1 h. In contrast, the reaction of ODPA with trifluoromethylated diamine **2** proceeded relatively slowly, and the η_{inh} 's reached only 0.52 dL/g after 7 h. However, the CF_3 diamine **2** was still sufficiently reactive to give high-molecular-weight poly(amic acid)s when they were allowed to polymerize for a sufficient length of time (ca. 12 h). Diamine **2** most likely retained its reactivity because the amino group was meta to the CF_3 group. As shown in Table 1, the η_{inh} 's of the intermediate poly(amic acid)s or the polyimides obtained from diamine **2** were in the range of 0.54–0.73 dL/g. The GPC data of the THF-soluble polyimides are also included in Table 1. With the exception of **8_a**, all the **8** series polyimides could afford flexible and tough films, indicating medium- to high-molecular-weight polymer formation. However, the molecular weights of the polyimides **9_{a–f}** ($\eta_{\text{inh}} = 0.19$ – 0.36 dL/g) derived from binaphthyl diamine **4** did not seem to be sufficiently high to permit the casting of flexible and tough films. One may think the formation of low-molecular-weight polymers is possibly attributed to the use of impure diamine monomer. We

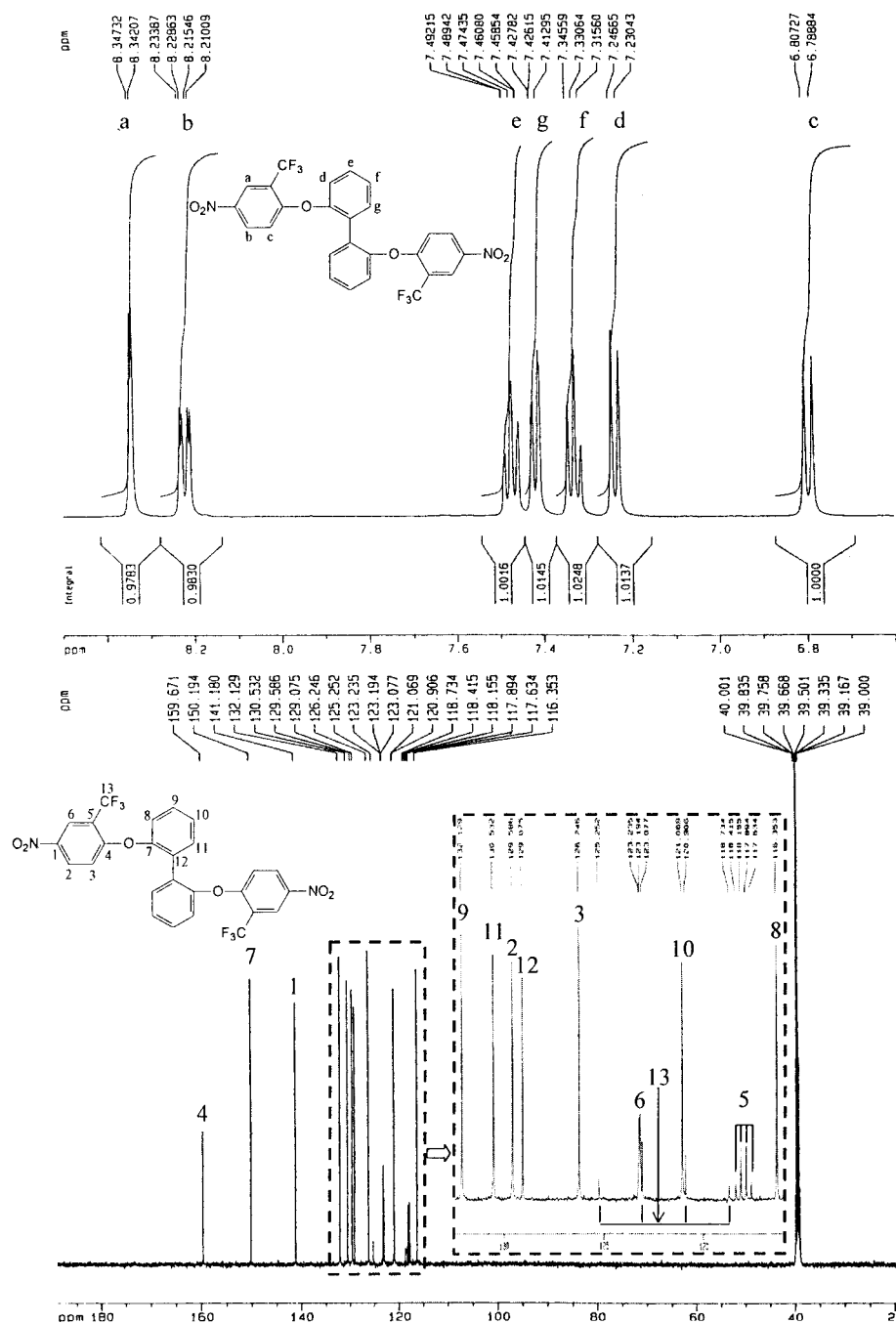


Figure 2. ^1H and ^{13}C NMR spectra of dinitro compound **1** in $\text{DMSO-}d_6$.

exclude the possibility of doubt because diamine **4** was pure white with a sharp melting temperature range of 271–273 °C. More importantly, a sample of the same diamine, when reacted with equimolar quantities of terephthalic acid or isophthalic acid in *N*-methylpyrrolidone (NMP) solution in the presence of calcium chloride, triphenyl phosphite, and pyridine rapidly (within 1 h) produced

highly viscous solutions. The product was isolated by precipitation into methanol to give a tough, fibrous precipitate, which could be solution-cast to form strong films with good mechanical properties. These results indicated that diamine **4** was both pure and sufficiently reactive. We propose, therefore, that the low molecular weight may be a consequence of the formation of cyclic oligomers

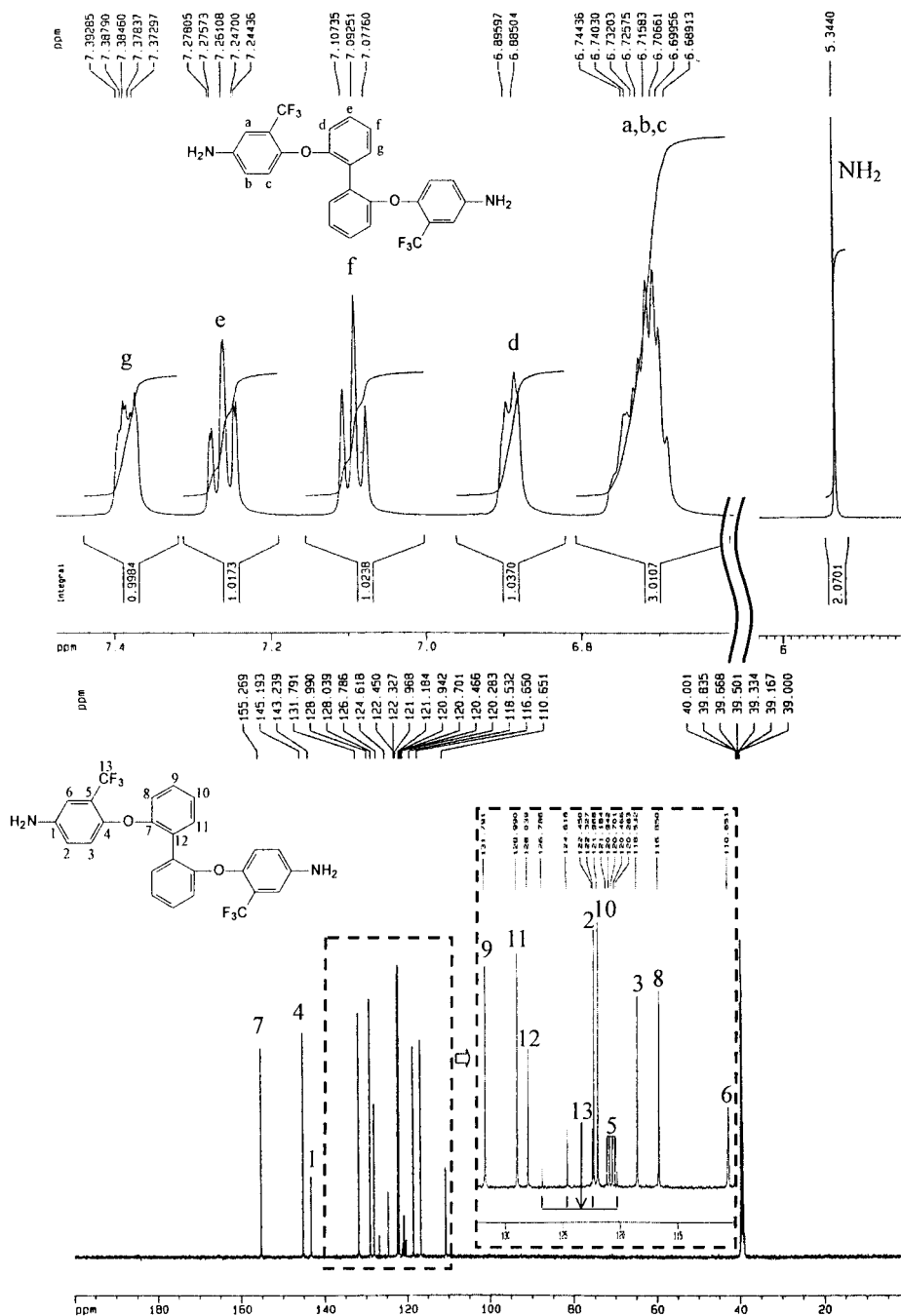
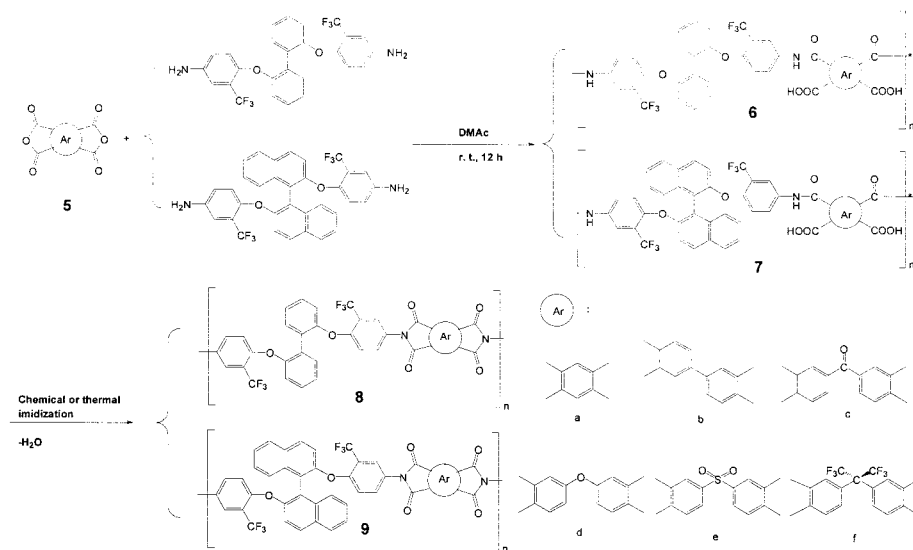


Figure 3. ^1H and ^{13}C NMR spectra of diamine **2** in $\text{DMSO-}d_6$.

during the reaction of diamine **4** with dianhydrides **5_{a-f}**. Presumably the 1,1'-binaphthyl-2,2'-diyl unit forced the growing chains to adopt such conformations to increase the rate coefficient for cyclization with regard to that for propagation. Nevertheless, this assumption is preliminary and should be studied more thoroughly. For enhancing the molecular weights and improving the

film-forming capability, we synthesized the **11** series copolyimides from the reaction of an equimolar mixture of 4,4'-ODA and diamine **4** with dianhydrides **5_{a-f}** (Scheme 3). For comparison, copolyimides **10_{a-e}** based on equimolar 4,4'-ODA/diamine **2** were also synthesized. The copolyimides were obtained with an increased η_{inh} ranging from 0.52 to 1.19 dL/g (measured in con-



Scheme 2. Synthesis of the polyimides.

centrated sulfuric acid at 30 °C), and most of them could form flexible, creasable films.

The formation of polyimides was confirmed with elemental analysis and IR and NMR spectroscopies. The elemental analysis values agreed with the calculated values of the proposed structures. A typical thin-film IR spectrum for the representative polyimide **8_d** is illustrated in Figure

1. All polyimides exhibited characteristic imide group absorptions around 1781 and 1735 (typical of imide carbonyl asymmetrical and symmetrical stretch), 1380 (C—N stretch), and 1054 and 746 cm^{-1} (imide ring deformation), with some strong absorption bands in the region of 1100–1300 cm^{-1} because of C—O and C—F stretching. Figure 5 shows a typical set of ^1H and ^{13}C NMR

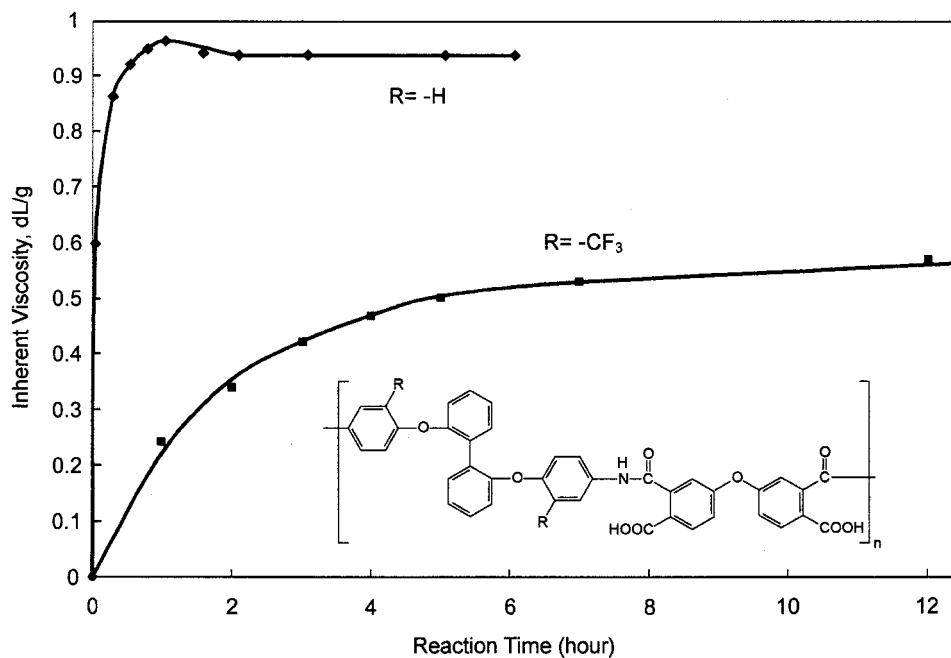


Figure 4. Viscosity change of poly(amic acid)s prepared in DMAc at 12% solid content at room temperature.

Table 1. Inherent Viscosity and GPC Data of the Polyimides

Code	η_{inh}^a (dL/g)	M_w^c	M_n^c	M_w/M_n
8_a	0.54	—	—	—
8_b	0.64 ^b	—	—	—
8_c	0.70 ^b	38,600	22,800	1.69
8_d	0.60	37,000	21,300	1.74
8_e	0.63	42,000	21,600	1.94
8_f	0.73	41,700	21,300	1.96
9_a	0.25	13,200	6,700	1.98
9_b	0.19	10,500	5,500	1.92
9_c	0.34	13,500	6,100	2.21
9_d	0.28	17,100	6,800	2.51
9_e	0.35	12,300	4,900	2.50
9_f	0.36	11,500	5,300	2.20

^a Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

^b Inherent viscosity of the poly(amic acid) precursor.

^c Relative to polystyrene standards, with THF as the eluent.

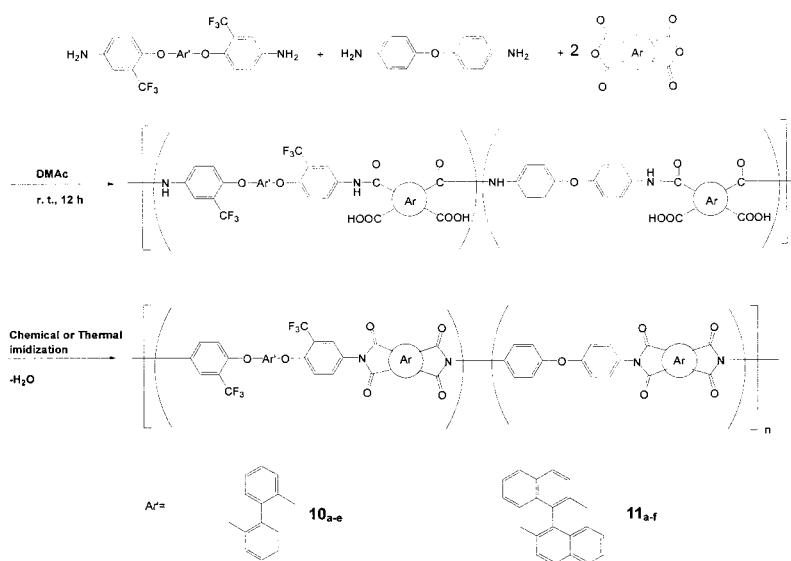
spectra of polyimide **8_e** in DMSO-*d*₆, where all the peaks have been readily assigned to the hydrogen and carbon atoms of the repeating unit.

Polymer Properties

Solubility and Film Properties

All the polyimides and copolyimides were characterized by WAXD studies. They failed to exhibit

any crystallinity apparently because of the non-coplanar structure and the presence of bulky CF₃ pendent groups. The amorphous nature of these polymers was also reflected in their excellent solubility. The solubility of the polyimides was tested qualitatively in various organic solvents. Tables 2 and 3 list the solubility behavior of all the fluorinated polyimides and copolyimides, with that of referenced nonfluorinated analogues reported previously.¹⁸ Most of the **8** and **9** series polyimides revealed excellent solubility in polar solvents such as NMP and DMAc and even in less polar THF and dichloromethane. Compared with the corresponding counterparts without the CF₃ substituents (the referenced **8'** and **9'** series polyimides), especially for those derived from more rigid dianhydride components such as PMDA, BPDA, and BTDA, the **8** and **9** series polyimides demonstrated enhanced solubility. This can be apparently attributed to the incorporation of CF₃ substituents, which increased the disorder in the polymer chains and further hindered close chain packing, thereby lowering cohesive energies to enhance solubility. When the **8** and **9** series of polyimides are compared, polyimides **9_{a-c}** showed higher solubility than the corresponding **8_{a-c}** counterparts. This might be due to a higher hindrance effect of the bulkier binaphthyl unit in the former. Another reason may be caused by the fact that the molecular weights of the **9** series were much lower than that of the **8** series. As expected, copolymerization with 4,4'-ODA as the comono-



Scheme 3. Synthesis of the copolyimides.

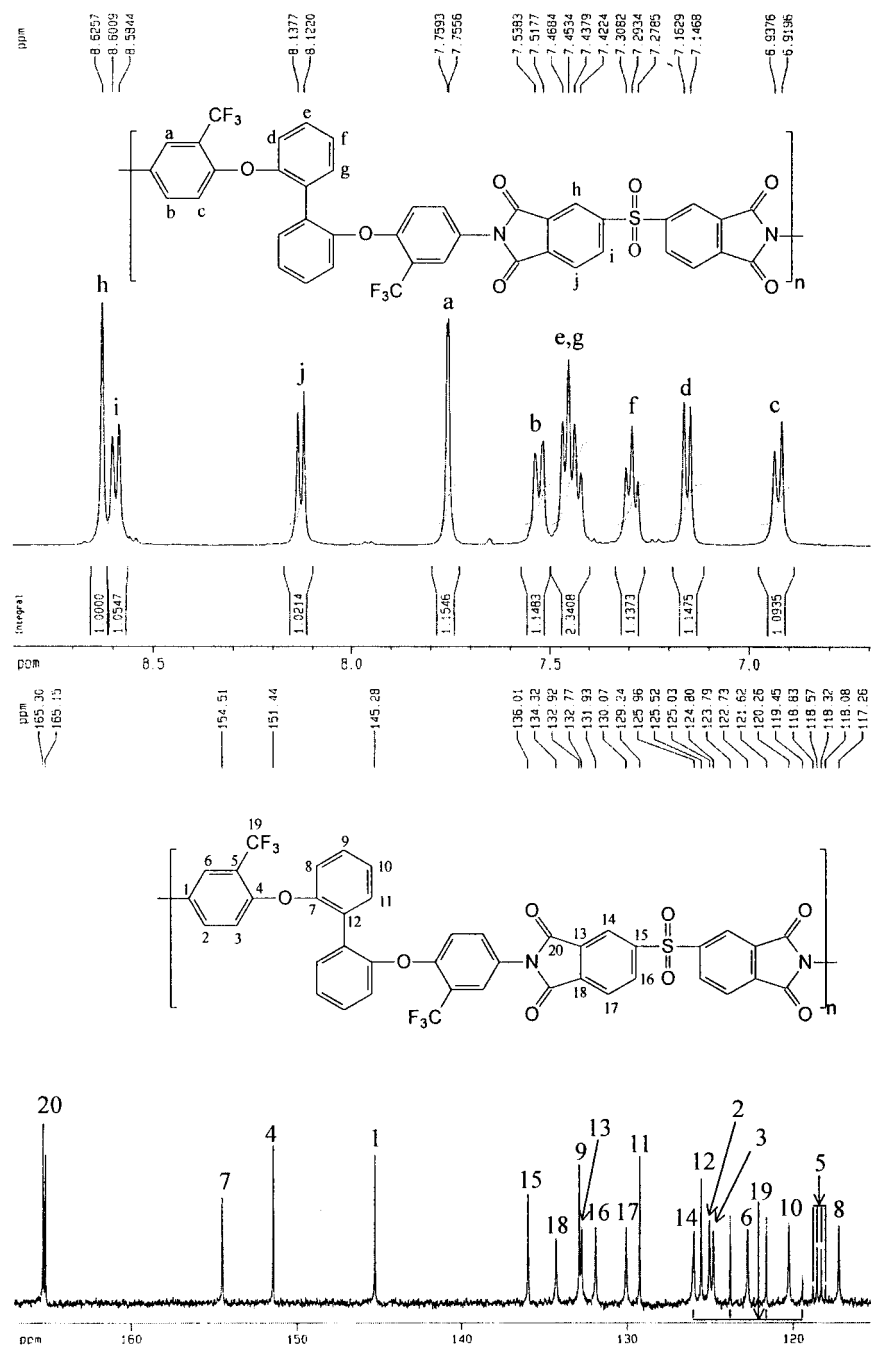


Figure 5. ¹H and ¹³C NMR spectra of polyimide **8_e** in DMSO-*d*₆.

mer resulted in a reduced solubility because of the increased chain rigidity. In some cases, such as **8_b**, the solubility of the polyimide sample prepared via chemical imidization revealed better solubility than that prepared via thermal imidization, a result similar to that reported in the literature.^{30,32}

As previously mentioned, all the **8** series except for **8_a** could afford flexible, good-quality films.

These films were subjected to a tensile test, and their tensile properties are listed in Table 4. The polymer films of **8_{b–f}** had tensile strengths of 55–74 MPa, elongations to break of 5–6%, and tensile moduli of 1.8–2.1 GPa. Their tensile strengths and moduli were slightly lower than the relevant **8'** series, possibly because of increased free volume and decreased cohesive force caused by the CF₃ group. As can be seen from Table 4, the

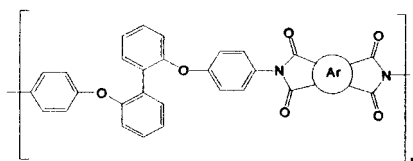
Table 2. Solubility Behavior^a of the Polyimides and Copolyimides Containing the 2,2'-Disubstituted Biphenylene Unit

Polymer Code ^b	Solvents ^c									
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF	CH ₂ Cl ₂	H ₂ SO ₄
8_a (H)	++	++	S	–	–	S	S	S	S	++
8_b (C)	++	++	++	++	+	++	++	++	++	++
8_b (H)	+–	+–	+–	+–	+–	+–	+–	+–	+–	+
8_c (H)	+	+–	+–	–	+–	+–	+–	+–	S	++
8_d (H)	++	++	++	+	+	++	++	++	++	++
8_e (H)	++	++	++	++	+	++	++	++	++	++
8_f (H)	++	++	++	++	+	++	++	++	++	++
8'_a (H)	–	–	–	–	–	–	–	–	S	+
8'_b (H)	S	S	–	–	+	–	–	–	S	++
8'_c (H)	–	–	–	–	+–	–	–	–	–	+
8'_d (H)	++	++	+	+	+	+	+	S	++	++
8'_e (H)	++	++	++	+	+	++	+	–	S	++
8'_f (H)	++	++	++	+	+	++	+	++	++	++
10_a (H)	+–	–	–	–	–	–	–	–	–	++
10_b (H)	+	+–	S	S	+	–	+	–	S	++
10_c (H)	–	–	–	+	+	–	–	–	–	+
10_d (H)	++	++	++	+	+	++	+	–	++	++
10_e (H)	+	+	++	+	+–	–	+	–	–	++

^a Solubility: (++) soluble at room temperature, (+) soluble on heating, (+–) partial soluble on heating, (S) swelling on heating, and (–) insoluble even on heating.

^b (H): Polyimides were prepared via the thermal-imidization method; (C): polyimides were prepared via the chemical-imidization method. Data of the referenced polyimides **8'** series have been reported (see ref. 18).

^c NMP: *N*-methylpyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; Py: pyridine; THF: tetrahydrofuran.

**8' series**

tensile strengths and moduli of the copolyimides **10_{a–e}** made with equimolar 4,4'-ODA and **2** were generally higher than films of the related homopolyimides. All of the **9** series polyimides could not afford good-quality and flexible films for tensile testing because of the lower molecular weights. However, copolyimides **11_{b–f}** obtained from equimolar 4,4'-ODA and **4** could form free-standing films. Their tensile properties are also included in Table 4. The cast films of copolyimides **11_b**, **11_c**, and **11_e** were slightly brittle, revealing a lower strength and modulus.

Thermal Properties

DSC, TMA, and TGA were used to investigate the thermal properties of the polyimides and copoly-

imides. The results are compiled in Table 5. In the DSC experiments, all the polymers were slowly heated to 400 °C and then rapidly cooled from 400 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 the **8** and **9** series polyimides ranged from 222 to 280 °C and from 257 to 351 °C, respectively. The increasing order of T_g generally correlated with that of chain rigidity. The higher T_g values for the **9** series as compared with the **8** series could be explained in terms of an increased steric hindrance effect because of the bulky binaphthyl unit. The T_g values of the **9** series polyimides were slightly lower than the **9'** series. This might be a result of increased free

Table 3. Solubility Behavior^a of the Polyimides and Copolyimides Containing the 2,2'-Disubstituted 1,1'-Binaphthylene Unit

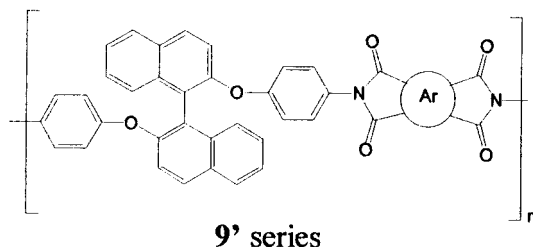
Polymer Code ^b	Solvents ^c								
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Pyridine	THF	CH ₂ Cl ₂	H ₂ SO ₄
9_a	++/(++) ^d	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)
9_b	++/(++)	++/(++)	++/(++)	+-(+-)	++/(++)	++/(++)	++/(++)	-(-)	++/(++)
9_c	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)
9_d	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)
9_e	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)
9_f	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)	++/(++)
9'_a	-	-	-	-	-	-	-	-	++
9'_b	-	-	-	-	+	-	-	-	++
9'_c	++	++	++	+	+	++	-	-	++
9'_d	++	++	++	++	+	++	-	-	++
9'_e	++	++	++	++	+	++	-	-	++
9'_f	++	++	++	++	+	++	-	-	++
11_a	+/(+)	-/(-)	-/(+-)	-/(+-)	+-(+-)	-/(+-)	-/(-)	-/(-)	+-(+-)
11_b	+/(+)	-/(-)	-/(-)	-/(-)	+-(++)	-/(-)	-/(-)	-/(-)	+-(+-)
11_c	+/(+)	-/(-)	-/(-)	-/(-)	+-(+-)	-/(-)	-/(-)	-/(-)	+-(+-)
11_d	++/(++)	++/(++)	++/(++)	+-(+-)	+-(+-)	++/(++)	++/(++)	++/(++)	++/(++)
11_e	++/(++)	++/(++)	++/(++)	++/(++)	+-(+-)	++/(++)	+-(+-)	-/(-)	++/(++)
11_f	++/(++)	++/(++)	++/(++)	++/(++)	+-(+-)	++/(++)	++/(++)	++/(++)	++/(++)

^a The solubility was determined with a 2-mg sample in 2 mL of solvent. ++ = soluble at room temperature; + = soluble on heating; +- = partial soluble on heating; and - = insoluble even on heating.

^b Data of the referenced polyimides **9'** series (prepared by thermal imidization) have been reported (see ref. 18).

^c NMP: *N*-methylpyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

^d The data shown in the parentheses are those of polymer samples prepared via chemical imidization.



volume caused by the introduction of the bulky CF₃ substituents. This result also may be affected by the molecular weight. The T_g 's (or apparent T_g 's) of the polyimide films were also determined by the TMA method with a loaded penetration probe. They were read from the onset temperature of the probe displacement on the TMA trace. As a representative example, the TMA trace of polyimide **9_f** is illustrated in Figure 6. In most cases, the T_g values obtained by TMA were comparable to the T_g values measured by the DSC technique. The thermal stability of the polyimides was evaluated by TGA measurements in both air and nitrogen atmospheres. Typical TGA curves for polyimide **9_f** are reproduced in Figure 7. The

decomposition temperatures of 10% weight loss in nitrogen and air atmospheres determined from the original TGA thermograms are given in Table 5. The TGA data indicated that these polyimides have fairly high thermal stability and are comparable to or higher than that of the structurally similar polyimides from nonfluorinated diamines.

Color and Optical Transparency

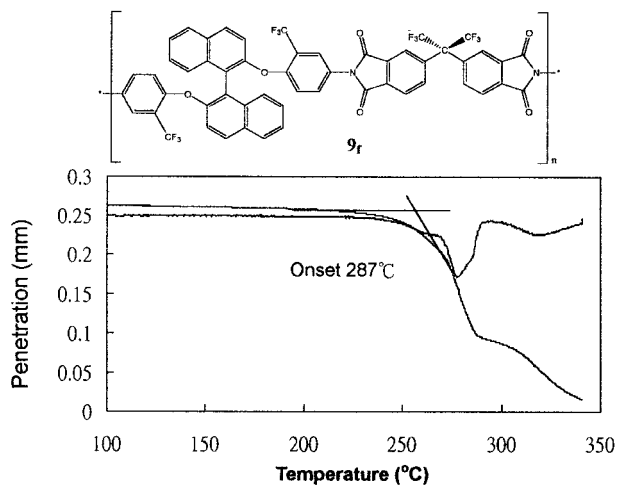
Diamines **2** and **4** contain the twisted 2,2'-disubstituted biphenyl and binaphthyl units, respectively, and two bulky CF₃ groups and thus provide a highly packing-disruptive structure to the polyimides. This was expected to interfere with

Table 4. Tensile Properties of Polyimide Films^a

Polymer	Strength at Break (MPa)	Elongation at Break (%)	Tensile Modulus (GPa)
8 _b	57	5	1.8
8 _c	71	6	2.1
8 _d	74	6	1.9
8 _e	66	5	2.0
8 _f	55	5	1.9
8' _b	87	6	2.4
8' _d	94	6	2.2
8' _e	88	5	2.5
8' _f	78	5	2.2
10 _a	64	5	2.0
10 _b	97	16	2.3
10 _c	117	8	2.4
10 _d	115	10	2.0
10 _e	64	5	2.1
11 _b	49	7	1.3
11 _c	31	5	1.9
11 _d	100	14	1.7
11 _e	18	3	1.4
11 _f	82	7	1.9

^a Polyimides were obtained by the thermal-imidization method.

the dense packing of molecular chains and lead to light-colored polyimide films. Thin films or polymer solutions were measured for optical transparency with UV-vis spectroscopy, with the cutoff wavelengths (absorption edge, λ_0) reported in Ta-


Figure 6. Typical TMA thermogram for polyimide **9_f** (heating rate: 10 °C/min; applied force: 10 mN).

ble 5. All the fluorinated polyimides revealed low λ_0 and high optical transparency, with a percentage of transmittance higher than 80% at 500 nm. The polyimides **8_f** and **9_f** produced from 6FDA were essentially colorless and showed relatively lower λ_0 values, and these can be explained by the reduction of the charge-transfer complex (CTC) between alternating electron-donor (diamine) and electron-accepter (dianhydride) moieties. The light color of the polyimides with the bulky and electron-withdrawing CF_3 groups in their dia-

Table 5. Thermal Behavior Data and Cutoff Wavelength (λ_0) from UV-Vis Spectra of Polyimides

Polymer	T_g (°C)	T_{10}^a (°C)		Char Yield ^b (%)	λ_0 (nm)
		In N ₂	In Air		
8 _a	280 (—) ^c	584 (581)	577 (555)	53 (53)	
8 _b	247 (236)	599 (581)	588 (558)	60 (59)	395 (413)
8 _c	237 (235)	586 (575)	574 (580)	58 (56)	385 (—)
8 _d	222 (221)	587 (572)	575 (577)	58 (55)	362 (372)
8 _e	244 (248)	527 (533)	543 (554)	54 (51)	391 (412)
8 _f	247 (244)	559 (562)	549 (550)	50 (56)	351 (376)
9 _a	351 (358)	577 (535)	576 (565)	60	— ^d /396 ^e
9 _b	306 (307)	603 (555)	603 (580)	64	412/392
9 _c	285 (290)	592 (535)	598 (570)	61	424/389
9 _d	272 (286)	585 (510)	592 (555)	60	409/373
9 _e	287 (294)	527 (480)	552 (525)	58	434/397
9 _f	287 (292)	558 (490)	540 (555)	58	356/352

^a Temperatures at which a 10% weight loss was recorded by TGA at a heating rate of 20°C/min.

^b Residual weight (percentage) when heated to 800 °C in nitrogen.

^c The values in the parentheses are those of the referenced polyimides **8'** and **9'** without the CF_3 group.

^d Measured in film.

^e Measured in solution (DMAc).

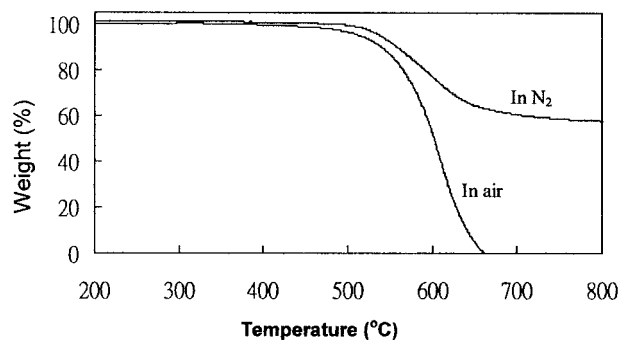


Figure 7. TGA curves of polyimide **9_f** at a heating rate of 20 °C/min.

mine moieties can be explained by the decrease of the intermolecular CTC through steric hindrance and an inductive effect (by decreasing the electron-donating property of diamine moieties). The decrease in chain–chain CTC formation also was understandable from the significant solubility of the polyimides prepared from CF₃-substituted diamines **2** and **4**.

Moisture Absorption and Dielectric Constants

The moisture absorption and dielectric constants of fluorinated polyimides **8** and **9** series are reported in Table 6. The measurements of the dielectric constants were performed between gold layers; the polyimide film was dried carefully, and a thin gold layer was vacuum-deposited on both surfaces of the polymer film. This procedure ex-

cluded any contact problems. Polyimides **8_{b–f}** revealed lower dielectric constants and moisture absorptions than analogous **8'_{b–f}** and PMDA/4,4'-ODA polyimide film. The decreased dielectric constants of the fluorinated polyimides could be attributed to the presence of bulky CF₃ groups, which resulted in less efficient chain packing and an increase in the fractional free volume and hydrophobicity.³⁴ For the **8** series polyimides, the dielectric constant and moisture absorption were minimized for polyimide **8_f** in which both the dianhydride and diamine portions of the polymer contained CF₃ groups. In comparison, polyimides **9_{c–f}** exhibited lower dielectric constants than the corresponding **8_{c–f}**. This might be attributable to the bulkier binaphthyl structure in the former.

CONCLUSIONS

Two series of organosoluble and light-colored fluorinated polyimides were prepared from the trifluoromethyl-substituted bis(ether amine)s **2** and **4** with various aromatic dianhydrides by a conventional, two-step thermal- or chemical-imidization method. Most of the polyimides derived from **2** could be cast to flexible and strong films with good thermal stability, moderate to high *T_g*'s (222–280 °C), and low dielectric constants. Although the polyimides of **4** could not afford flexible films, the copolyimides made with equimolar 4,4'-ODA and **4** might give good-quality films.

Table 6. Moisture-Absorption and Dielectric Constants of Polyimides

Polymer	Film Thickness (μm)	Moisture Absorption (%)	Dielectric Constant			
			1 kHz	10 kHz	1 MHz	40 MHz
8_b	32	0.46	3.61	3.63	3.58	3.65
8_c	82	0.57	3.39	3.28	3.22	3.24
8_d	30	0.58	3.56	3.55	3.50	3.57
8_e	46	0.26	3.59	3.61	3.55	3.59
8_f	30	0.23	3.03	3.03	2.99	3.04
8'_b	35	1.05	3.68	3.79	3.72	3.78
8'_d	51	0.77	3.54	3.58	3.52	3.58
8'_e	36	0.90	3.87	3.89	3.81	3.86
8'_f	34	0.81	3.44	3.47	3.41	3.47
9_c	126	0.46	3.13	3.07	3.02	3.06
9_d	126	0.51	3.10	3.01	2.90	3.01
9_e	97	0.43	3.39	3.49	3.53	3.48
9_f	92	0.25	2.84	2.84	2.80	2.85
PMDA/4,4'-ODA	29	1.84	3.89	3.85	3.67	3.60

These polyimides and copolyimides exhibited a good combination of properties required for high-performance materials and thus demonstrated a promising potential for future applications.

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