Preparation and Properties of New Polyimides and Polyamides Based on 1,4-Bis(4-amino-2-trifluoromethylphenoxy)naphthalene

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ABSTRACT: A novel, trifluoromethyl-substituted, bis(ether amine) monomer, 1,4-bis(4-amino-2-trifluoromethylphenoxy)naphthalene, was synthesized through the nucleophilic displacement of 2-chloro-5-nitrobenzotrifluoride with 1,4-dihydroxynaphthalene in the presence of potassium carbonate in dimethyl sulfoxide, followed by catalytic reduction with hydrazine and Pd/C in ethanol. A series of new fluorine-containing polyimides with inherent viscosities of 0.57–0.91 dL/g were prepared by reacting the diamine with six commercially available aromatic dianhydrides via a conventional, two-step thermal or chemical imidization method. Most of the resulting polyimides were soluble in strong polar solvents such as N-methylpyrrolidone and N,N-dimethylacetamide (DMAc). All the polyimides afforded transparent, flexible, and strong films with good tensile properties. These polyimides exhibited glass-transition temperatures (T_g's) (by DSC) and softening temperatures (by thermomechanical analysis) in the ranges of 252–315 and 254–301 °C, respectively. Decomposition temperatures for 5% weight loss all occurred above 500 °C in both air and nitrogen atmospheres. The dielectric constants of these polyimides ranged from 3.03 to 3.71 at 1 MHz. In addition, a series of new, fluorinated polyamides with inherent viscosities of 0.32–0.62 dL/g were prepared by the direct polycondensation reaction the diamine with various aromatic dicarboxylic acids by means of triphenyl phosphite and pyridine. All the polyamides were soluble in polar solvents such as DMAc and could be solution-cast into tough and flexible films. These polyamides had T_g's between 228 and 256 °C and 10% weight-loss temperatures above 400 °C in nitrogen or air. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 2377–2394, 2004

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INTRODUCTION

Aromatic polyamides and polyimides constantly attract interest because of their high-temperature resistance and mechanical strength.[1–3] However, most of them have high melting or softening temperatures (T_s's) and are insoluble in most organic solvents because of the rigidity of the backbone and strong interchain interactions. These properties make them generally intractable or difficult to process, thus limiting their applications. Therefore, incessant efforts have been expended to try to improve the processing characteristics of these relatively intractable polymers.[4–18] One of the approaches to increasing solubility and low-

ering the glass-transition temperature (T_g) and T_s is the introduction of flexible groups in the polymer backbone.[14–18] Ether linkages are the most popular, flexible linkages introduced into the polymer backbones. It has been generally recognized that aryl-ether linkage imparts properties such as better solubility and melt-processing characteristics and improved toughness as compared with polymers without an aryl-ether linkage. However, the decrease in mechanical properties on heating is almost always a consequence of the reduced chain stiffness or T_g. However, the attachment of bulky lateral groups can impart an increase in T_g by restricting the segmental mobility, while providing an enhanced solubility because of decreased packing density and crystallinity.[19–21] Combining these two structural modifications may minimize the trade-off between poor processability and improved physical properties of highly aromatic polymers.[22–27]

As described in our previous publications,[28–30] 1,4-bis(4-aminophenoxy)naphthalene and 1,4-bis(4-carboxyphenoxy)naphthalene were synthesized via the aromatic substitution reaction of 1,4-dihydroxynaphthalene with p-fluoronitrobenzene and p-fluorobenzonitrile, respectively, and were used to prepare aromatic polyamides and polyimides containing 1,4-bis(phenoxy)naphthalene in the backbones. The 1,4-naphthalenediyl unit has a structure similar to the 1,4-phenylene but with another benzene ring fused in the 2,3-position. The fused benzene ring can be regarded as a bulky pendent group that reduces chain-packing efficiency and intermolecular interactions such as hydrogen bonding in polyamides. In the meantime, the bulky pendent group gives more restricted rotation around the ether linkage. Therefore, organosoluble polyamides with moderate T_g's and high thermal stability could be achieved by the incorporation of the 1,4-bis(phenoxy)naphthalene unit in the main chain.[28,30] However, the polyimides based on 1,4-bis(4-aminophenoxy)naphthalene exhibited a limited solubility,[29] possibly because of the rigid nature of polymer backbones caused by the phthalimide structure. Recent studies demonstrated that polyimides derived from ether-bridged diamines with trifluoromethyl (CF_3) groups are soluble, high-temperature polymeric materials with low moisture uptake, a low dielectric constant, and high optical transparency.[31–36] Very recent studies have also shown the importance of fluorinated and naphthyl groups in the design of polyimides.[37–39] As part of our continuing efforts in de-

veloping tractable, high-performance polymers containing naphthalene units, this work describes the synthesis of a new CF_3-substituted bis(ether amine), 1,4-bis(4-amino-2-trifluoromethylphenoxy)naphthalene, and its use in the preparation of soluble polyamides and polyimides by the reaction of the diamine with dicarboxylic acids and dianhydrides. The solubility, tensile properties, crystallinity, and thermal properties of all the obtained polymers, together with moisture absorption and dielectric constants of the polyimides, were investigated and compared with unsubstituted derivatives, and tried to qualify the effect of the CF_3 group and phenoxy linkages.

EXPERIMENTAL

Materials

1,4-Dihydroxynaphthalene (TCI), potassium carbonate (K_2CO_3) (Fluka), 2-chloro-5-nitrobenzotrifluoride (Acros), 10 wt % palladium on charcoal (Pd/C) (Fluka), and hydrazine monohydrate (Acros) were used as received. N,N-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. 1,4-Bis(4-aminophenoxy)naphthalene (mp: 113–115 °C) was prepared by the aromatic nucleophilic substitution of 1,4-dihydroxynaphthalene with p-chloronitrobenzene in the presence of K_2CO_3 in DMAc and the subsequent Pd/C-catalyzed hydrazine reduction of the intermediate dinitro compound. Pyromellitic dianhydride (**3a**; PMDA) (Aldrich) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**3c**; BTDA) (Aldrich) were purified by recrystallization from acetic anhydride. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (**3b**; BPDA) (Oxychem), 4,4′-oxydiphthalic dianhydride (**3d**; ODPA) (Oxychem), 3,3′4,4′-diphenylsulfonetetracarboxylic dianhydride (**3e**; DSDA) (New Japan Chemical Co.), and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (**3f**; 6FDA) (Hoechst Celanese) were heated in vacuo at 250 °C for 3 h before use. The aromatic dicarboxylic acids such as terephthalic acid (**6a**) (TCI), isophthalic acid (**6b**) (TCI), 4,4′-biphenyldicarboxylic acid (**6c**) (TCI), 4,4′-dicarboxydiphenyl ether (**6d**) (TCI), 1,4-napthalenedicarboxylic acid (**6e**) (Wako), 2,6-napthalenedicarboxylic acid (**6f**) (TCI), 4,4′-dicarboxydiphenyl sulfone (**6g**) (New Japan Chemical), and 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**6h**) (TCI) were used as received. Commercially

obtained, anhydrous calcium chloride ($CaCl_2$) was dried *in vacuo* at 180 °C for 8 h before use.

Synthesis of 1,4-Bis(4-nitro-2-trifluoromethylphenoxy)naphthalene (1)

In a 250-mL flask, a reaction solution of 1,4-dihydroxynaphthalene (8.0 g, 0.05 mol), 2-chloro-5-nitrobenzotrifluoride (22.5 g, 0.10 mol), and potassium carbonate (13.8 g, 0.10 mol) in 100 mL of dimethyl sulfoxide (DMSO) was heated at 90 °C for 24 h. After cooling, the mixture was poured into 500 mL of methanol/water (1:1 by volume), and the precipitated yellowish brown solid was collected by filtration and dried. The yield of the product was 22.8 g (85%). The crude product was purified by crystallization from dimethylformamide (DMF)/water to afford pale brown crystals; mp: 213–214 °C.

ELEM. ANAL. Calcd. for $C_{24}H_{12}N_2O_6F_6$ (538.36): C, 53.54%; H, 2.24%; N, 5.20%. Found: C, 53.40%; H, 2.24%; N, 5.05%. IR (KBr): 1531, 1349 (—NO_2), 1259 (C—O), 1139 cm^{-1} (C—F). ^{1}H NMR (DMSO-d_6, δ, ppm): 8.61 (d, *J* = 2.8 Hz, 2H, H_f), 8.40 (dd, *J* = 9.2, 2.8 Hz, 2H, H_e), 7.93 (dd, *J* = 6.5, 3.2 Hz, 2H, H_b), 7.73 (dd, *J* = 6.5, 3.2 Hz, 2H, H_c), 7.54 (s, 2H, H_a), 7.18 (d, *J* = 9.2 Hz, 2H, H_d). ^{13}C NMR (DMSO-d_6, δ, ppm): 160.3 (C^6), 146.8 (C^2), 141.8 (C^9), 130.1 (C^8), 128.5 (C^3), 127.2 (C^5), 123.6 (C^{10}), 122.4 (q, $^1J_{C-F}$ = 271 Hz, C^{12}), 121.3 (C^4), 118.4 (q, $^2J_{C-F}$ = 32 Hz, C^{11}), 117.5 (C^7), 117.4 (C^1) (see Structure 1).
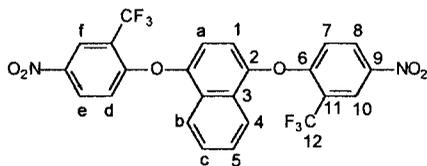

## Synthesis of 1,4-Bis(4-amino-2-trifluoromethylphenoxy)naphthalene (2)

A mixture of the purified dinitro compound **1** (12 g, 0.022 mol), 10% Pd/C (0.15 g), ethanol (100 mL), and hydrazine monohydrate (10 mL) was heated at reflux temperature for about 4 h. The reaction solution was filtered while hot to remove Pd/C, and the filtrate was poured into a saturated aqueous sodium chloride solution to give an light gray precipitate that was isolated by filtration and dried *in vacuo* (9.35 g, 88%; mp: 148–149 °C).

ELEM. ANAL. Calcd. for $C_{24}H_{16}N_2O_2F_6$ (478.39): C, 60.26%; H, 3.37%; N, 5.85%. Found: C, 60.01%;

H, 3.17%; N, 5.71%. IR (KBr): 3446, 3345, 3215 (—NH_2), 1259 (C—O), 1139 cm^{-1} (C—F). ^{1}H NMR (DMSO-d_6, δ, ppm): 8.20 (dd, *J* = 6.4, 3.3 Hz, 2H, H_b), 7.67 (dd, *J* = 6.4, 3.3 Hz, 2H, H_c), 7.01 (d, *J* = 2.6 Hz, 2H, H_f), 6.88 (d, *J* = 8.8 Hz, 2H, H_d), 6.84 (dd, *J* = 8.8, 2.6 Hz, 2H, H_e), 6.71 (s, 2H, H_a), 5.45 (4H, —NH_2). ^{13}C NMR (DMSO-d_6, δ, ppm): 148.8 (C^2), 145.5 (C^6), 143.2 (C^9), 126.9 (C^3), 126.3 (C^5), 123.7 (q, $^1J_{C-F}$ = 271 Hz, C^{12}), 122.0 (C^4), 121.5 (C^8), 121.3 (q, $^2J_{C-F}$ = 34 Hz, C^{11}), 118.6 (C^7), 110.9 (C^{10}), 110.6 (C^1) (see Structure 2).
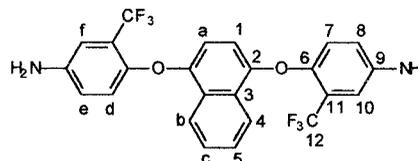
Crystal data: Monoclinic P2$_1$/C with *a* = 12.1013(3), *b* = 9.6823(3), and *c* = 19.1168(5) Å, α = 90.00, β = 106.0811, and γ = 90.00°, where D_c = 1.477 g/cm^3 for *Z* = 4 and *V* = 2152.16(10) Å^3. Bond length (Å) (the atom labeling used here is the same as in Fig. 4): F1—C1 1.321(3), F2—C1 1.336(3), F3-C1 1.326(3), F4-C24 1.320(4), F5-C24 1.335(4), F6-C24 1.314(4), O1-C7 1.390(3), O1-C8 1.404(4), O2-C15 1.387(3), O2-C18 1.396(3), N1-C4 1.393(4), N2-C21 1.409(4), C1-C2 1.492(4), C2-C3 1.392(4), C2-C7 1.385(3), C3-C4 1.386(4), C4-C5 1.386(4), C4-C5 1.379(4), C5-C6 1.385(4), C6-C7 1.367(4), C8-C9 1.415(4), C8-C17 1.342(4), C9-C10 1.414(4), C9-C14 1.425(4), C10-C11 1.350(5), C11-C12 1.397(5), C12-C13 1.361(4), C13-C14 1.407(4), C14-C15 1.423(3), C15-C16 1.356(4), C16-C17 1.408(5), C18-C19 1.383(4), C18-C23 1.380(3), C19-C20 1.363(5), C20-C21 1.376(5), C21-C22 1.376(4), C22-C23 1.382(4), C23-C24 1.491(4). Bond-angle (°): C7-O1-C8 119.4(2), C15-O2-C18 115.7(2), F1-C1-F2 105.2(2), F1-C1-F3 106.5(2), F1-C1-C2 113.7(2), F2-C1-F3 105.5(2), F2-C1-C2 112.5(2), F3-C1-C2 112.8(2), C1-C2-C3 120.2(2), C1-C2-C7 120.6(2), C3-C2-C7 119.3(2), C2-C3-C4 121.0(2), N1-C4-C3 119.5(3), N1-C4-C5 121.9(3), C3-C4-C5 118.5(3), C4-C5-C6 120.8(3), C5-C6-C7 120.4(3), O1-C7-C2 115.6(2), O1-C7-C6 124.4(2), C2-C7-C6 120.0(3), O1-C8-C9 119.3(2), O1-C8-C17 118.2(3), C9-C8-C17 122.2(3) C8-C9-C10 123.3(3), C8-C9-C14 118.2(2), C10-C9-C14 118.5(3), C9-C10-C11 120.1(3), C10-C11-C12 121.7(3), C11-C12-C13 120.0(3), C12-C13-C14 120.4(3), C9-C14-C13 119.3(2), C9-C14-C15 117.8(2), C13-C14-C15 122.8(2), O2-C15-C14
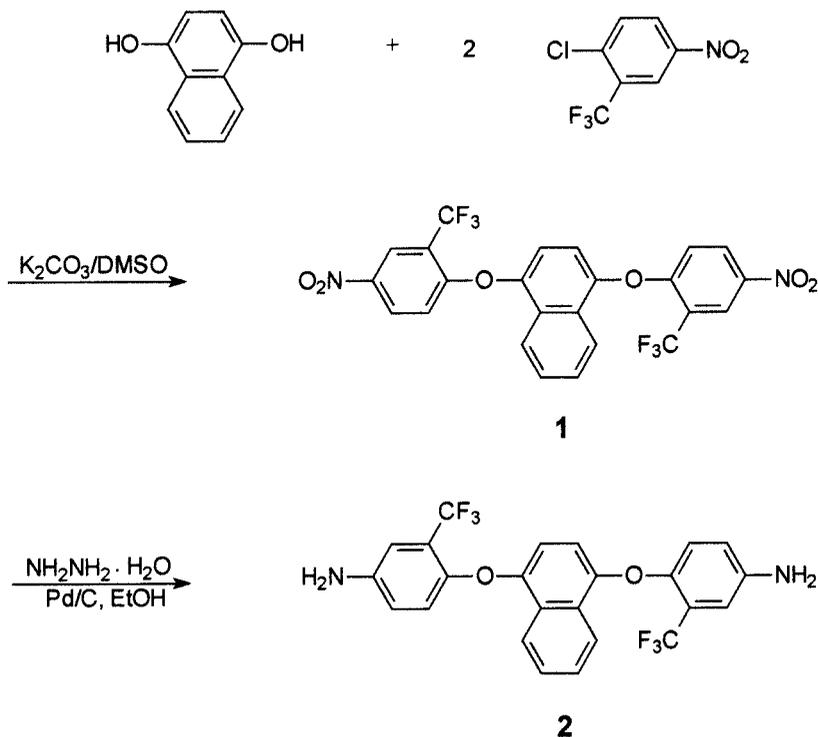
Scheme 1. Outline of the synthesis of diamine **2**.

114.4(2), O2-C15-C16 123.8(2), C14-C15-C16 123.8(2), C15-C16-C17 119.7(3), C8-C17-C16 120.3(3), O2-C18-C19 119.8(2), O2-C18-C23 120.7(2), C19-C18-C23 119.4(2), C18-C19-C20 120.2(3), C19-C20-C21 121.1(3), N2-C21-C20 120.4(3), N2-C21-C22 120.9(3), C20-C21-C22 118.6(3), C21-C22-C23 121.1(2), C18-C23-C22 119.4(2), C18-C23-C24 120.9(2), C22-C23-C24 119.6(2), F4-C24-F5 105.5(3), F4-C24-F6 106.4(3), F4-C24-C23 113.6(2), F5-C24-F6 105.5(2), F5-C24-C23 112.4(3), F6-C24-C23 112.8(3).

Polyimide Synthesis

The synthesis of polyimide **5a** was used as an example to illustrate the general synthetic route used to produce the polyimides. Into a solution of 0.687 g (1.44 mmol) of fluorinated diamine **2** in 9.5 mL of CaH$_2$-dried DMAc, 0.313 g (1.44 mmol) of PMDA was added in one portion. The mixture was stirred at ambient temperature for about 24 h to afford a viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) (**4a**) was 0.96 dL/g, measured in DMAc at a concentration of 0.5 g/dL. The poly(amic acid) **4a** was converted into polyimide **5a** with either a thermal or chemical imidization method. For the

thermal imidization method, the poly(amic acid) solution was spread on a glass plate and baked at 90 °C overnight for the removal of the casting solvent. The semidried 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, and 250 °C for 1 h. For the chemical imidization method, 5 mL of acetic anhydride and 2 mL of pyridine were added to the poly(amic acid) solution, and the mixture was heated at 100 °C for 1 h to effect a complete imidization. The resultant solution of the polymer was poured slowly into 250 mL of methanol giving rise to a fibrous precipitate, which was washed thoroughly with methanol and hot water, collected by filtration, and dried.

ELEM. ANAL. Calcd. for $(C_{34}H_{14}N_2O_6F_6)_n$ $(660.48)_n$: C, 61.83%; H, 2.14%; N, 4.24%. Found: C, 61.10%; H, 2.24%; N, 4.31%. IR (film): 1780, 1728 (C=O), 1379 (C—N), 1242 (C—O), 1140 cm^{-1} (C—F).

Polyamide Synthesis

A typical procedure for the preparation of polyamide **7a** is described as follows. A mixture of 0.718 g (1.5 mmol) of diamine **2**, 0.249 g (1.5

mmol) of terephthalic acid (**6a**), 0.2 g of calcium chloride, 0.6 mL of pyridine, 1.5 mL of triphenyl phosphite (TPP), and 2.5 mL of *N*-methylpyrrolidone (NMP) was stirred at 120 °C for 3 h. The obtained polymer solution was poured slowly into 250 mL of methanol giving rise to a fibrous precipitate, which was washed thoroughly with methanol and hot water, collected by filtration, and dried. The inherent viscosity of the polyamide (**7a**) was 0.50 dL/g, as measured at a concentration of 0.5 g/dL in DMAc containing 5 wt % LiCl at 30 °C.

IR (film): 3303 (N—H), 1250 (C—O), 1132 cm^{-1} (C—F). ^{1}H NMR (DMSO-d_6, δ, ppm) (for the assignment of peaks, see Fig. 7): 10.75 (amide protons), 8.44 (H$_f$), 8.18 (H$_g$), 8.14 (H$_b$), 8.07 (2H, H$_e$), 7.72 (H$_c$), 7.15 (H$_a$), 7.13 (H$_d$). ^{13}C NMR (DMSO-d_6, δ, ppm): 164.9 (C=O), 150.7, 147.9, 137.2, 134.6, 127.7, 127.5, 127.1, 125.5, 123.5 (q, $^1J_{C—F}$ = 271 Hz, CF$_3$), 121.6, 119.2, 119.1 (q, $^2J_{C—F}$ = 28 Hz) 118.9.

Preparation of the Polyamide Films

A solution of polymer was made by dissolving about 0.8 g of the polyamide sample in 8 mL of hot DMAc. The homogeneous solution was poured into a 9-cm diameter glass culture dish, which was placed in a 90 °C oven for 12 h for the slow release of the solvent. Then, the obtained semidried polyamide film was further dried *in vacuo* at 160 °C for 6 h. The obtained films had about 80 μm in thickness and were used for X-ray diffraction measurements, tensile tests, and thermal analyses.

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. ^{1}H and ^{13}C NMR spectra were measured on a JEOL EX 400 spectrometer at 399.65- and 99.00-MHz frequencies, respectively. The inherent viscosities of the polyamides were determined with a Cannon-Fenske viscometer, and those of the polyimides were determined with an Ubbelohde 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 (7.8 mm i.d. × 300 mm) connected in series were used with tetrahydrofuran (THF)
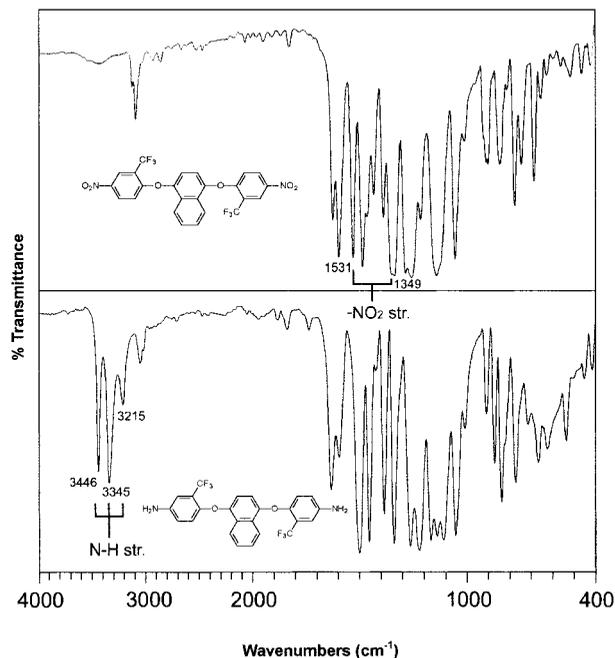

Figure 1. FTIR spectra of dinitro compound **1** and diamine **2**.

as the eluent and were calibrated with narrow polystyrene standards. The measurements were done at 35 °C with a flow rate of 1.0 mL/min. An Instron universal tester model 4400R with a load cell of 5 kg was used to study the stress–strain behavior of the 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 ca. 0.08 mm thick), and an average of at least three replicas was used. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer (operating at 40 kV and 30 mA) with graphite-monochromatized Cu Kα radiation (λ = 1.5418 Å). The scanning rate was 3°/min over a range of 2θ = 10–40°. 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 cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a heating rate of 20 °C/min under nitrogen. T_g's were read at the middle of the transition in the heat capacity. For polyimides, T_g's were taken from the second heating scan after quick cooling from 400 °C at a cooling rate of 200 °C/min. For polyamides, the samples were heated at
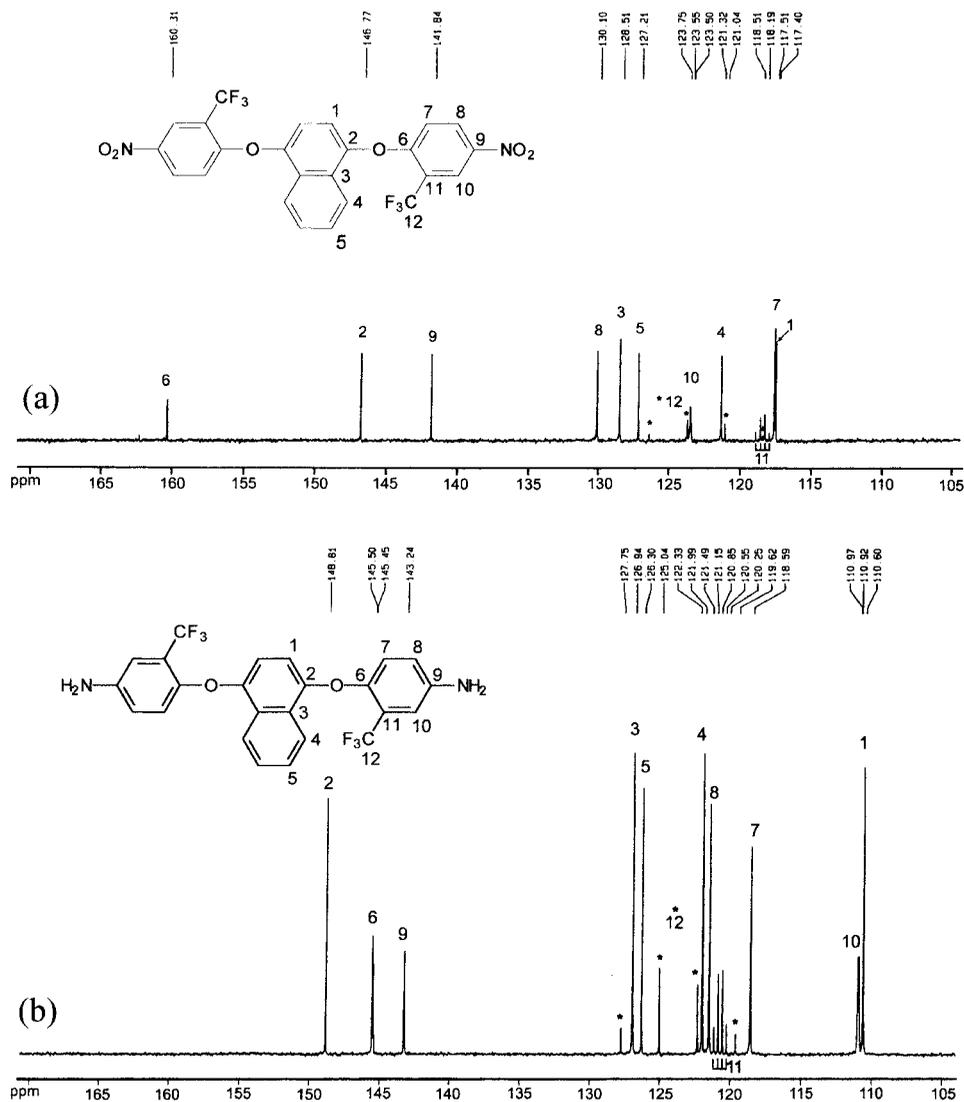
Figure 2. ^{1}H NMR spectra of (a) dinitro compound **1** and (b) diamine **2** in DMSO-d_6.

250 °C for 30 min before DSC experiments, and their T_g's were taken from the heating DSC traces. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted from 40 to 300 °C at a scanning rate of 10 °C/min with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. T_s's were taken as the onset temperature of probe displacement on the TMA traces. The dielectric property of the polyimide films was tested by the parallel-plate capacitor method with an HP-4194 Impedance/Gain Phase analyzer. The moisture absorption was determined by the change of the weight in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days.

RESULTS AND DISCUSSION

Monomer Synthesis

The fluorinated diamine **2** was prepared by the nucleophilic aromatic substitution reaction of 2-chloro-5-nitrobenzotrifluoride and 1,4-dihydroxynaphthalene in the presence of K_2CO_3 in DMSO, followed by Pd/C-catalyzed hydrazine reduction of the intermediate dinitro compound **1** (Scheme 1). The molecular structure of diamine **2** was confirmed by elemental, IR, NMR, and single-crystal X-ray diffraction analysis.

Figure 1 shows the FTIR spectra of dinitro compound **1** and diamine **2**. The characteristic bands representative of the nitro functionality were identified in the FTIR spectrum; these were the asymmetrical stretch at 1531 cm^{-1} and the

Figure 3. ^{13}C NMR spectra of (a) dinitro compound **1** and (b) diamine **2** in DMSO-d_6.

symmetrical stretch at 1349 cm^{-1}. After reduction, the characteristic bands of nitro groups disappeared, and the aromatic primary amine absorptions at 3446, 3345, and 3215 cm^{-1} were identified. The ^{1}H NMR spectra (Fig. 2) confirm that the nitro groups were completely converted into amino groups by the high field shift of the aromatic protons and by the signal at 5.45 ppm peculiar to the amino protons. In the ^{13}C NMR spectra (Fig. 3), upfield shifts of the aromatic carbon resonances, especially for the carbons para (C^6) and ortho (C^8, C^{10}) to the amino group, were observed in diamine **2** because of the resonance effect caused by the electron-donating amino group. All the spectroscopic data obtained agreed with the expected structures. The structure of

diamine **2** was further detailed by single-crystal X-ray diffraction analysis. The molecular structure of **2** (Fig. 4) shows that the benzene and naphthalene rings were not in the same plane because of CF$_3$ steric hindrance. This conformation was expected to decrease the packing efficiency of polymer chains and to enhance the solubility of its derived polymers.

Polymer Synthesis

The novel, fluorinated polyimides **5a–f** were prepared by the reaction of diamine **2** with various, commercially available dianhydrides (**3a–f**) to form the poly(amic acid)s **4a–f** followed by thermal or chemical imidization (Scheme 2). As shown
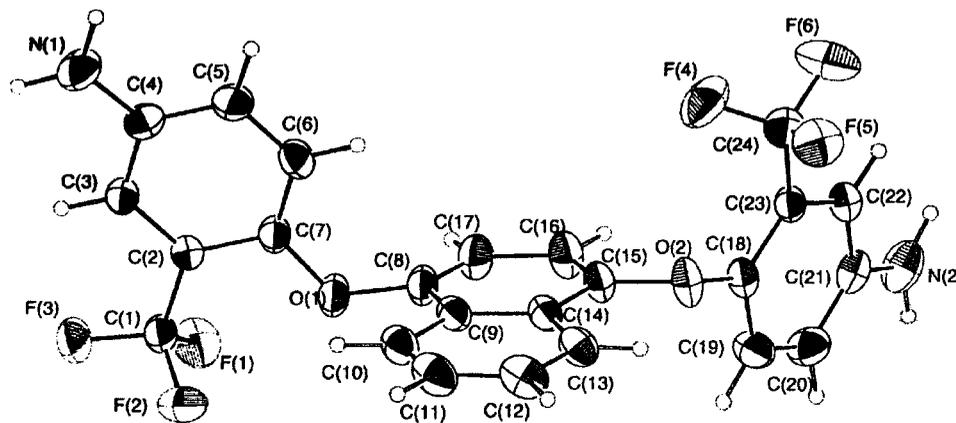
Figure 4. Model structure of diamine **2** by single-crystal, X-ray analysis.

in Table 1, the inherent viscosities of the poly-(amic acid) precursors were in the range of 0.65–1.12 dL/g, and those of the thermally imidized polyimides stayed in the range of 0.57–0.91 dL/g. The weight-average molecular weights (M_w's) of four THF-soluble polyimides were in the range of 46,000–58,000 on the basis of polystyrene standards. The elemental analysis values generally agreed with the calculated values for the proposed structures of polyimides. Structural features of these polyimides were also confirmed by FTIR spectroscopy. Figure 5 shows the IR spectra of thin-film sample of typical set of poly(amic acid) **4a** and polyimide **5a**. The complete conversion of amic acid to an imide ring was supported by the disappearance of the amic acid band at 1650–1700 and 2800–3500 cm^{-1}, together with the appearance of imide absorption bands 1780 cm^{-1} (asymmetrical C=O s), 1728 cm^{-1} (symmetrical C=O s), and 1379 cm^{-1} (C—N s).

According to the Yamazak–Higashi phosphorylation polyamidation technique,[40] a series of novel, fluorinated polyamides (**7a–h**) were prepared by the direct polycondensation of diamine **2** with various aromatic dicarboxylic acids **6a–h** in NMP solution containing dissolved CaCl$_2$, with TPP and pyridine as condensing agents (Scheme 3). The reaction conditions and results are summarized in Table 2. All polyamidations proceeded in homogeneous, transparent and viscous solutions throughout the reaction, and the polyamides were isolated as tough fibers in quantitative yields. These polyamides had inherent viscosities between 0.32 and 0.62 dL/g. GPC analysis revealed that the M_w of these polyamides ranged from 37,000 to 49,000. All the polyamides could be cast into flexible and tough films from DMAc so-

lutions. Structural features of these polyamides were verified by FTIR and NMR spectroscopies. They exhibited characteristic IR absorption bands of the amide group around 3300 cm^{-1} (N—H s) and 1660 cm^{-1} (C=O s), with the characteristic absorption bands of aryl ether stretching near 1250 cm^{-1} and C—F stretching near 1130 cm^{-1}. A typical IR spectrum for the thin film of polyamide **7a** is depicted in Figure 6. The ^{1}H NMR spectrum of the representative polyamide **7a** is illustrated in Figure 7, where all the peaks could be readily assigned to the protons in the repeat unit.

Properties of the Polyimides

The solubility behavior of the polyimides was tested qualitatively in various organic solvents, and the results are summarized in Table 3. Except for **5b** and **5c**, the polyimides can be dissolved not only in highly polar solvents such as NMP, DMAc, DMF, and DMSO but also in moderate polar solvents such as *m*-cresol and THF at room temperature or upon heating. As shown in Table 3, the polyimides prepared by chemical imidization with acetic acid anhydride and pyridine exhibited better solubility than thermally cured ones. The poor solubility of thermally cured polyimide might be attributed to partial crosslinking within polymer chains during thermal imidization. For comparison, the solubility behavior of the corresponding non-fluorinated **5′** series polyimides reported previously[29] is also presented in Table 3. All these referenced polyimides, except for **5e′**, which was soluble in NMP, were insoluble in NMP, DMAc, and DMF. Therefore, the large differences in solubility between the **5** and **5′** se-
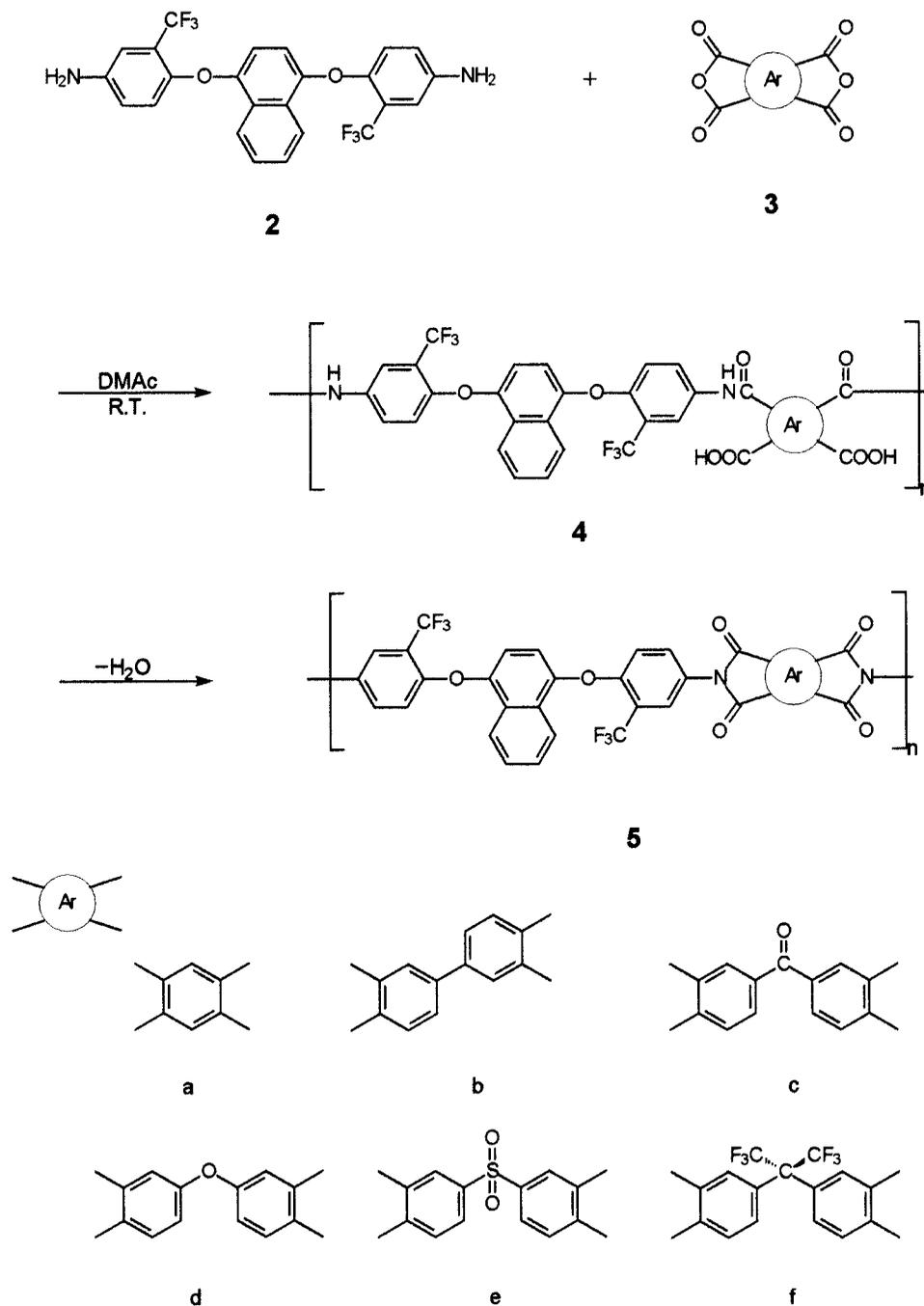
Scheme 2. Outline of polyimide synthesis.

ries could be attributable to the bulky CF_3 substituents, which increased the disorder in the chains and hindered dense packing, thereby decreasing the intermolecular interactions to enhance solubility. The WAXD patterns for film specimens of all the **5** series polyimides revealed their amorphous character. Such a behavior was expected because these polymers possessed 1,4-naphthalenedioxy units in the main chain as well as bulky CF_3 side groups that hindered the chain packing. The tensile properties of the polyimide films prepared by thermal curing are summarized in Table 4. These films had tensile strengths of 72–126 MPa, elongations to break of 4–13%, and tensile moduli of 1.6–2.0 GPa, indicating strong and tough materials.

Table 1. Inherent Viscosity of Poly(amic acid)s and Polyimides and Elemental Analyses of the Polyimides

Poly(amic acid)		Polyimide		GPC Data of Polyimides[b]			Elemental Analysis (%) of Polyimides				
Code	η_{inh}[a] (dL/g)	Code	η_{inh}[a] (dL/g)	M_n	M_w	M_w/M_n	Formula (Formula Weight)		C	H	N
4a	0.96	**5a**	0.88	29,000	48,000	1.67	$(C_{34}H_{14}N_2O_6F_6)_n$	Calcd.	61.83	2.14	4.24
							$(660.48)_n$	Found	61.10	2.24	4.31
4b	1.12	**5b**	0.62[c]	—[d]	—	—	$(C_{40}H_{18}N_2O_6F_6)_n$	Calcd.	65.23	2.46	3.80
							$(736.58)_n$	Found	64.26	2.65	4.03
4c	0.75	**5c**	0.73	—	—	—	$(C_{41}H_{18}N_2O_7F_6)_n$	Calcd.	64.41	2.37	3.66
							$(764.59)_n$	Found	63.80	2.44	3.65
4d	0.70	**5d**	0.69	35,000	58,000	1.63	$(C_{40}H_{18}N_2O_7F_6)_n$	Calcd.	63.84	2.41	3.72
							$(752.58)_n$	Found	63.16	2.55	3.87
4e	0.65	**5e**	0.57	29,000	47,000	1.62	$(C_{40}H_{18}N_2O_8S_1F_6)_n$	Calcd.	60.01	2.27	3.50
							$(800.64)_n$	Found	59.30	2.41	3.46
4f	1.08	**5f**	0.91	39,000	68,000	1.74	$(C_{43}H_{18}N_2O_6F_{12})_n$	Calcd.	58.25	2.05	3.16
							$(886.60)_n$	Found	57.86	2.16	3.05

[a] Measured in DMAc at a concentration of 0.5 g/dL at 30 °C unless otherwise indicated.
[b] Relative to polystyrene standards with THF as the eluent.
[c] Measured in concentrated sulfuric acid.
[d] Insoluble in THF.

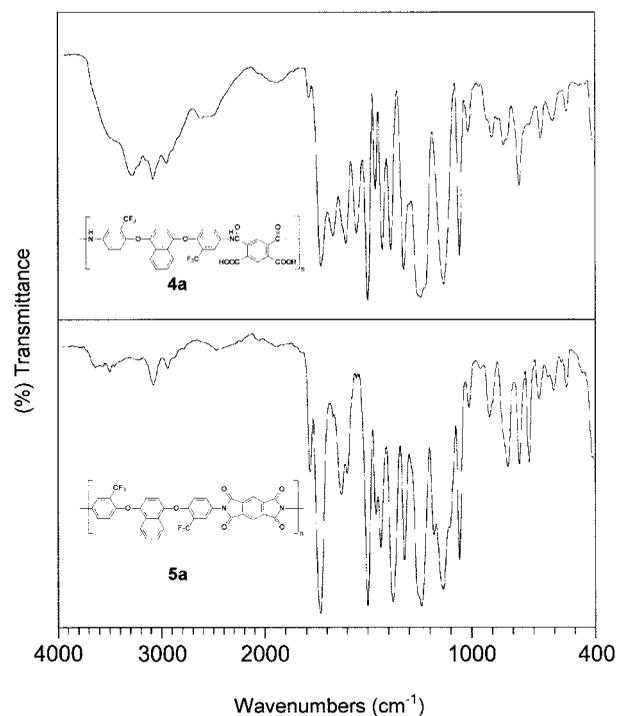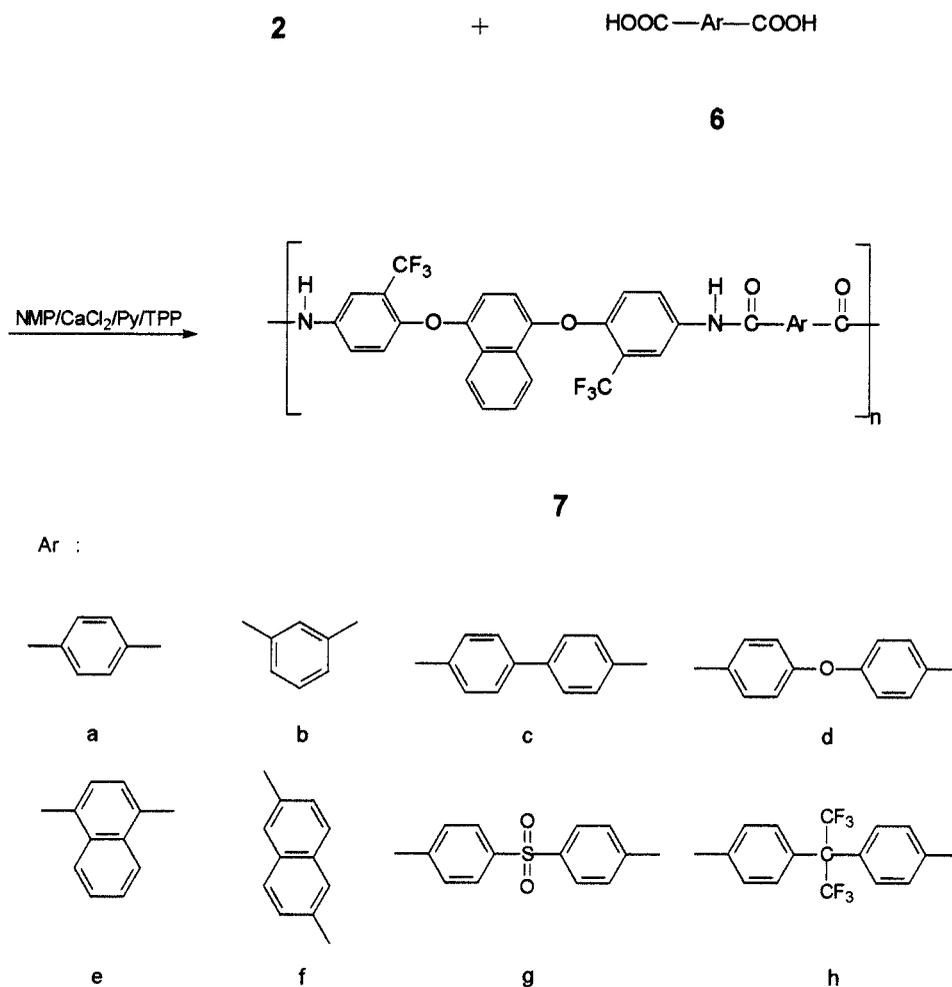The thermal behavior data of the fluorinated polyimides together with their referenced polyimides (**5′**) are summarized in Table 5. The T_g values of the **5a–5f** series polyimides measured by DSC were recorded in the 252–315 °C range. The increasing order of T_g generally correlated with that of chain rigidity. For example, polyimide **5d**, obtained from ODPA, showed the lowest T_g (252 °C) because of the presence of flexible ether linkages between the phthalimide units, and the highest T_g of 315 °C was observed for polyimides **5a** derived from PMDA. No melting endothermal peak was observed from DSC curves before decomposition of polyimides **5a–5f**. Thus, DSC measurements also revealed the amorphous nature of these fluorinated polyimides. For comparison, a series of analogous polyimides **5a′–5f′** based on 1,4-bis(4-aminophenoxy)naphthalene were also prepared and characterized by DSC. The T_g values of the **5′** series polyimides measured by DSC are also included in Table 5. These values are slightly higher than those reported previously.[29] This difference may be caused by the different heating history and instrumental sensitivity. As can been seen from Table 5, polyimides **5b–5e** showed slightly lower T_g values as compared with their counterparts **5b′–5e′** without the CF_3 substituents. This might be a result of reduced chain-to-chain interactions and packing because of the bulky pendent CF_3 groups. The T_s's (or apparent T_g' s) of the polyimide films were determined by the TMA method with a loaded penetration probe.

Figure 5. IR spectra of poly(amic acid) **4a** and polyimide **5a**.

2   +   HOOC—Ar—COOH

6

$\xrightarrow{\text{NMP/CaCl}_2\text{/Py/TPP}}$

7

Ar :

a   b   c   d

e   f   g   h

Scheme 3.   Outline of polyamide synthesis.

Table 2.   Synthesis Conditions, Inherent Viscosities, and Average Molecular Weights of Polyamides

Polymer	Amounts of Reagents Used[a]				η_{inh} (dL/g)[b]	$M_w{}^c$	$M_n{}^c$	Peak Max[c]
	NMP (mL)	Py (mL)	TPP (mL)	CaCl$_2$ (g)				
7a	2.5	0.6	1.5	0.2	0.50	39,000	21,000	34,000
7b	2	0.5	1.5	0.2	0.32	37,000	19,000	25,000
7c	3	0.8	1.5	0.3	0.62	43,000	24,000	39,000
7d	3	0.8	1.5	0.3	0.55	49,000	23,000	40,000
7e	3	0.8	1.5	0.3	0.57	48,000	23,000	41,000
7f	3	0.8	1.5	0.3	0.54	39,000	20,000	31,000
7g	2.5	0.6	1.5	0.2	0.45	39,000	21,000	35,000
7h	3	0.8	1.5	0.3	0.41	46,000	25,000	34,000

[a] 1.5 mmol each of the diacid and diamine monomer were used. Reaction temperature 120 °C, time: 3 h, NMP: *N*-methyl-pyrrolidone, Py: pyridine, and TPP: triphenyl phosphite.
[b] Measured in DMAc containing 5 wt % LiCl at 30 °C on 0.5 g/dL.
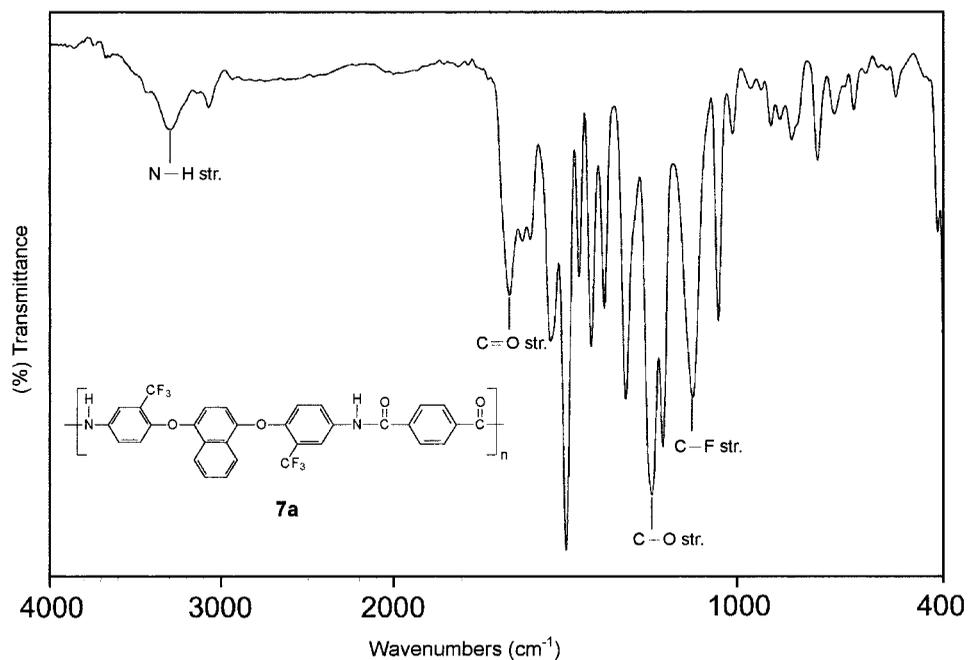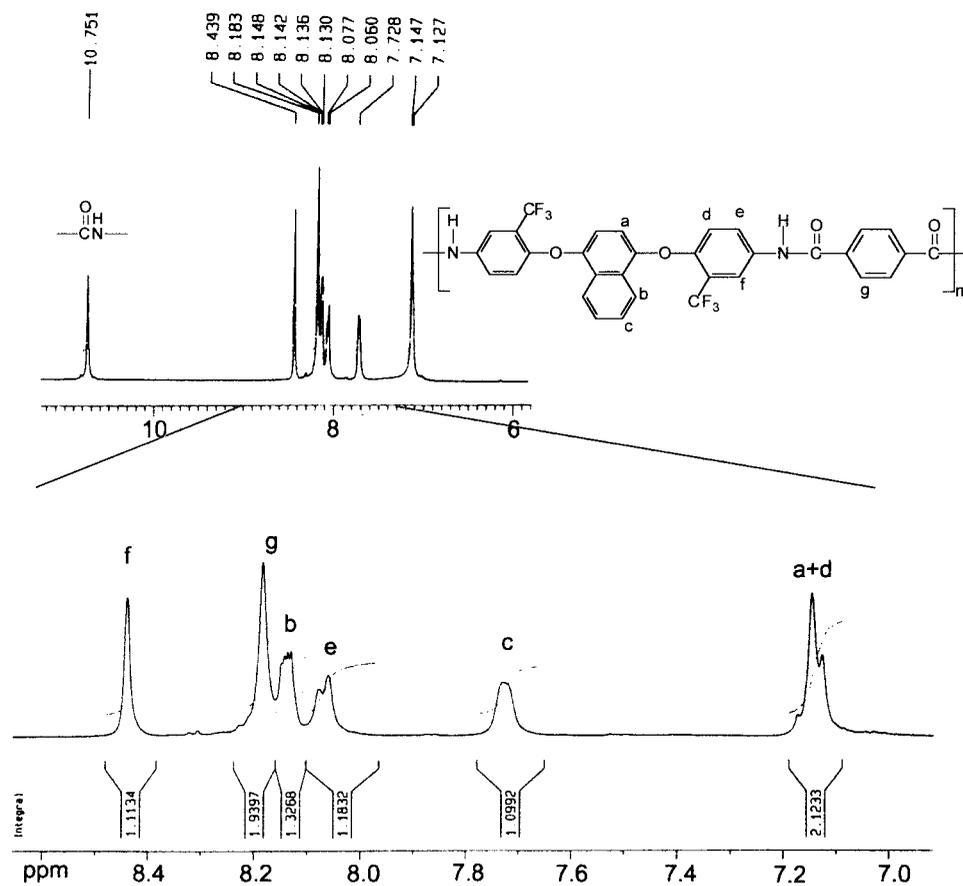[c] Molecular weights relative to polystyrene standards in THF.

Figure 6.   IR spectrum of polyamide **7a**.

**Figure 7.**   ¹H NMR spectrum of polyamide **7a** in DMSO-d_6.

Table 3. Solubility Behavior of the Polyimides Prepared via Thermal or Chemical Imidization[a]

| | Solvent | | | | | |
Polyimide	NMP	DMAc	DMF	DMSO	m-Cresol	THF
5a	+/+(−)[b]	+h/+ (−)	+/+ (−)	+h/+	+h/+h	+/+
5b	−/− (−)	−/− (−)	−/− (−)	−/−	−/−	−/−
5c	−/+ (−)	−/+ (−)	−/+ (−)	−/+	−/+h	−/+
5d	+h/+ (−)	+/+ (−)	+/+ (−)	+h/+h	+/+	+/+
5e	+/+ (+)	+/+ (−)	+/+ (−)	+h/+	+/+	+/+
5f	+/+	+/+	+/+	+h/+	+/+	+/+

[a] Qualitative solubility was tested with a 10-mg sample in 1 mL of solvent with stirring.

+: Soluble at room temperature; +h: soluble on heating at 100 °C (for THF, at boiling temperature); −: insoluble even on heating.

[b] Data in parentheses are those for analogous polyimides (**5′**) having the corresponding Ar unit as in the **5** series polyimides (see ref. 29).
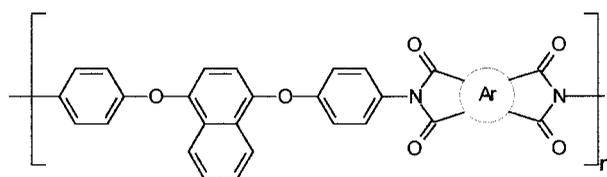
5′

As a representative example, the TMA trace of polyimide **5f** is reproduced in Figure 8. In most cases, the T_s values of these polyimides were comparable to the T_g values measured by the DSC technique. The trend of T_s variation with chain stiffness was similar to that of T_g. The thermal stability of the polyimides was evaluated by TGA measurements under both air and nitrogen atmospheres. Typical TGA curves for polyimide **5f** are illustrated in Figure 9. The decomposition temperatures (T_d's) at 5 and 10% weight losses in nitrogen and air atmospheres were read from the original TGA thermograms and are reported in Table 5. The T_d's at a 10% weight loss of the

Table 4. Tensile Properties of the Polyimide Films

Polyimide	Tensile Strength (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
5a	118	10	2.0
5b	119	13	1.9
5c	119	12	1.9
5d	126	13	2.0
5e	72	4	2.0
5f	108	10	1.6

fluorinated polyimides (**5a–5f**) in nitrogen and air remained in the ranges of 539–587 and 535–575 °C, respectively. They left more than a 54% char yield at 800 °C in nitrogen. Slightly higher T_d's for polyimides **5a–5e** as compared with **5a′–5e′** might be a result of strong C–F bonding. The TGA data indicated that these fluorinated polyimides had fairly thermal stability comparable to that of conventional aromatic polyimides.

The dielectric constants and the moisture absorption (weight percentage) of the polyimide films are reported in Table 6. Polyimides **5a–f** had lower dielectric constants (3.09–3.79 at 10 kHz) as compared with standard polyimides such as PMDA/ODPA (3.85). The low dielectric constants could be attributed to the presence of the bulky CF_3 groups, which resulted in less efficient chain packing and increased free volume. In addition, the strong electronegativity of fluorine and associated low polarizability of the C–F bonds results in a decreasing dielectric constant. The moisture absorption of the polyimides were in the 0.4–2.1% range. The polyimide **5f** exhibited the lowest moisture absorption because of the higher fluorine content in the repeat unit. Hence, the 6FDA-derived polyimide **5f** exhibited the lowest dielectric constant of 3.09 at 10 kHz because of higher free volume and hydrophobicity.

Table 5. Thermal Properties of the Polyimides

| Polyimide	$T_g{}^a$ (°C)	$T_s{}^b$ (°C)	T_d at 5% Weight Loss (°C)[c]		T_d at 10% Weight Loss (°C)[c]		Char Yield[d](%)
			In N_2	In Air	In N_2	In Air	
5a	315 (—)	301	555	521	583 (575)	556 (567)	57 (58)
5b	281 (288)[e]	286	558	542	586 (581)	575 (575)	59 (63)
5c	268 (281)	264	556	535	587 (530)	572 (527)	59 (64)
5d	252 (261)	254	558	526	584 (559)	557 (558)	58 (56)
5e	277 (292)	278	511	505	539 (521)	535 (517)	56 (54)
5f	274 (284)	275	545	529	568	552	54

[a] The samples were heated from 40 to 400 °C at a scanning rate of 20 °C/min; this was followed by rapid cooling to 40 °C at −200 °C/min in N_2. The midpoint temperature of the heat-capacity jump on the subsequent DSC trace (from 40 to 400 °C at 20 °C/min) was defined as T_g.

[b] Softening temperature, taken as the onset temperature of the probe displacement on the TMA trace. The film samples were heated at 300 °C for 30 min before the TMA experiment.

[c] Decomposition temperatures, recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 40 cm³/min.

[d] Residual weight percentage at 800 °C under nitrogen flow.

[e] Values in parentheses are those of analogous polyimides (**5′**) having the corresponding dianhydride residue as in the **5** series polyimides.
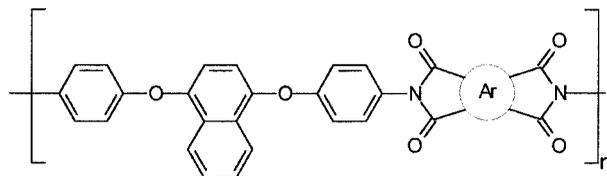
5'

Properties of the Polyamides

The solubility behavior of the fluorine-containing polyamides **7a–7h** was studied qualitatively, and the results are summarized in Table 7. Regardless of the nature of dicarboxylic acid components, the synthesized polyamides demonstrated good solubility in all the tested solvents. The high sol-
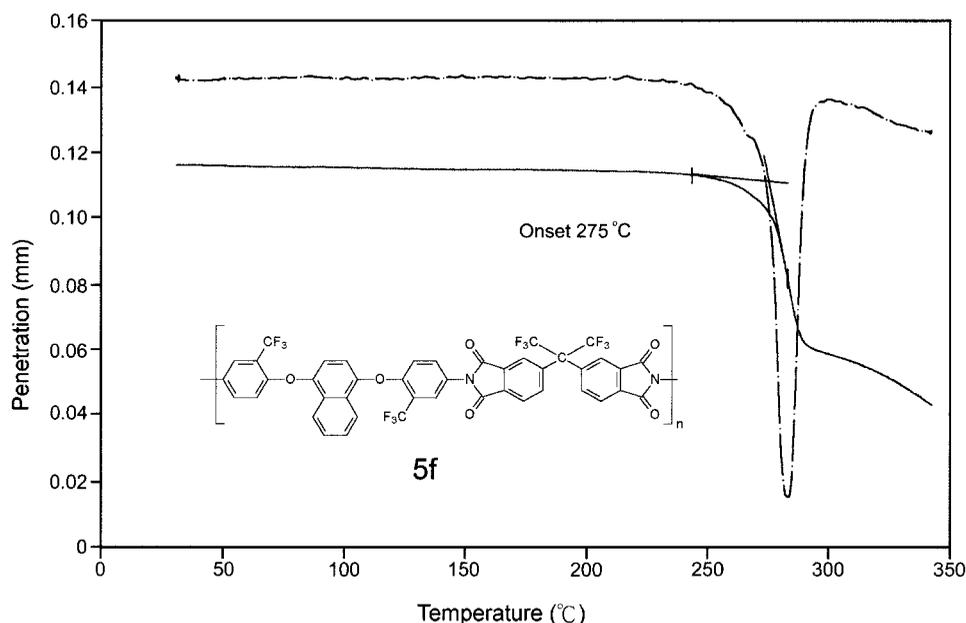
Figure 8. TMA curve of polyimide **5f** at a heating rate of 10 °C/min.
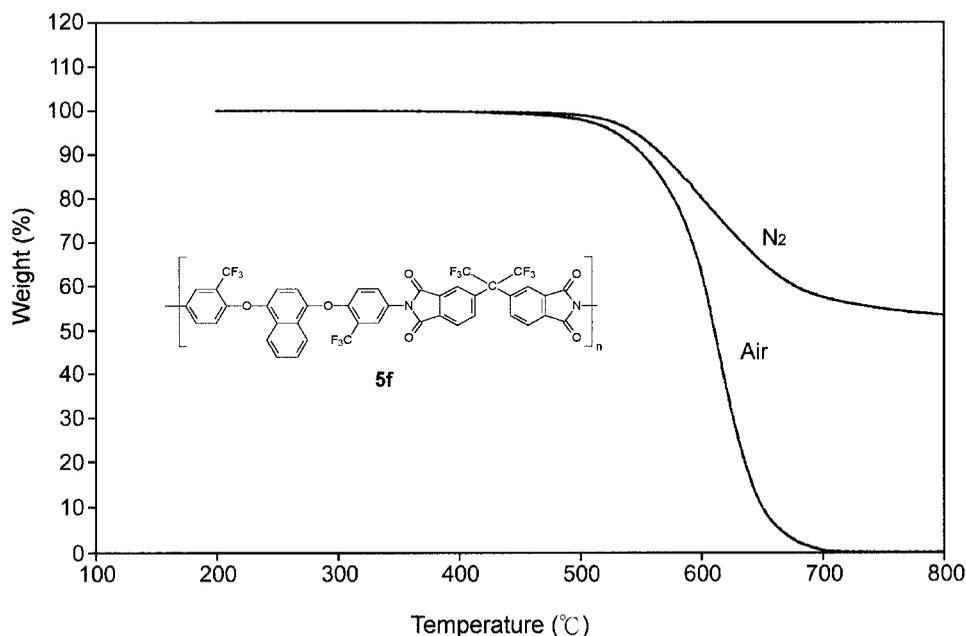
Figure 9. TGA curves of polyimide **5f** at a heating rate of 20 °C/min.

ubility of these polyamides was apparently due in part to the presence of the packing-disruptive CF_3 group in the polymer backbone, which resulted in increased chain-packing distances and decreased intermolecular interactions. One of the factors contributing to the enhanced solubility was the characteristic amorphous nature caused by the introduction of bulky CF_3 group and flexible ether linkage. As reported in a previous publication,[30] the polyamides **7a′**, **7c′**, and **7f′** as shown in the footnote of Table 7 showed a relatively lower solubility become of their semicrystalline characteristics as evidenced by the WAXD patterns. In contrast, all the fluorinated polyamides (**7a–7h**)

displayed amorphous patterns. Thus, the amorphous nature of these polyamides was reflected in their excellent solubility. Tough and flexible films of all polyamides could be obtained by casting from their solutions in DMAc. The tensile properties of the polyamide films are summarized in Table 8. Their tensile strengths, elongations to break, and initial moduli were in the ranges of 63–88 MPa, 6–11%, 1.5–2.2 GPa, respectively, indicating strong and tough films.

The thermal behavior data of these polyamides **7a–7h** are summarized in Table 9. These polyamides showed T_g values between 228 and 256 °C. The lower T_g values of **7b** and **7d** can be

Table 6. Moisture Absorption and Dielectric Constants of the Polyimides

Polyimide	Film Thickness (μm)	Moisture Absorption (wt %)	Dielectric Constant (Dry)		
			1 kHz	10 kHz	1 MHz
5a	126	2.1	3.74	3.71	3.60
5b	98	2.1	3.85	3.79	3.71
5c	147	1.3	3.56	3.53	3.46
5d	116	1.1	3.86	3.72	3.65
5e	114	1.8	3.53	3.51	3.42
5f	153	0.4	3.19	3.09	3.03
PMDA/ODA[a]	100	2.1	3.89	3.85	3.67

[a] A reference polyimide prepared from PMDA and 4,4′-oxydianiline [η_{inh} of the poly(amic acid) precursor: 2.90 dL/g].

Table 7. Solubility Behavior of Polyamides[a]

Polymer	Solvent[b]					
	NMP	DMAc	DMF	DMSO	m-Cresol	THF
7a	+ (±)[c]	+ (±)	+ (−)	+ (−)	+h (−)	+
7b	+ (+)	+ (+)	+ (+)	+ (+)	+h (±)	+
7c	+ (±)	+ (−)	+ (−)	+ (−)	+h (−)	+
7d	+ (+)	+ (+)	+(+)	+(+)	+h (+)	+
7e	+	+	+	+	+h	+
7f	+ (+)	+ (+)	+ (±)	+ (−)	+h (−)	+
7g	+ (+)	+ (+)	+ (+)	+ (+)	+h (+)	+
7h	+ (+)	+ (+)	+ (+)	+ (+)	+h (+)	+

[a] Qualitative solubility was tested with a 10-mg sample in 1 mL of solvent with stirring.
+: Soluble at room temperature; +h: soluble on heating at 100 °C (for THF, at reflux temperature); ±: partially soluble; −: insoluble even on heating.
[b] NMP: N-methyl-pyrrolidone, DMAc: N,N-dimethylacetamide, DMF: N,N-dimethylformamide, DMSO: dimethyl sulfoxide, and THF: tetrahydrofuran.
[c] Data in parentheses are those reported for the analogous polyamides (**7′**) having the corresponding diacid residue (Ar) as in the **7** series polyamides (see ref. 30).
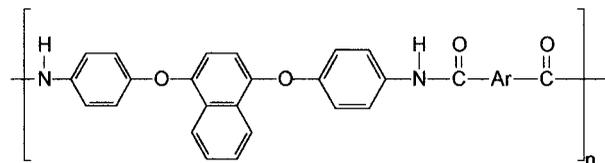
7'

explained in terms of the flexibility and low rotation barrier of their diacid moieties. Previously reported[30] T_g values of the corresponding polyamides (**7′**) without the CF$_3$ substituents are also listed in Table 9. When the two sets of polyamides were compared, the **7** series polyamides showed

Table 8. Tensile Properties of Polyamide Films

Polymer	Tensile Strength (MPa)	Elongation to Break (%)	Tensile Modulus (GPa)
7a	79	10	2.2
7b	63	6	1.8
7c	88	11	2.0
7d	75	8	1.6
7e	77	6	1.8
7f	80	9	1.6
7g	70	7	1.5
7h	70	8	1.5

Films were cast from slow evaporation of polymer solutions in DMAc. The cast films were further dried in vacuo at 160 °C for 6 h before the tensile test.

relatively lower T_g values. This might be a consequence of a significant reduction in the density of hydrogen bonding between chains because of the CF$_3$ groups. The T_s values of these polyamide films were also measured with TMA and the T_s values of these polyamides observed in the range of 216–241 °C. In most cases, the T_s values obtained by the TMA measurements are comparable to the T_g values measured by the DSC experiments. Thermal stability of the polyamides was evaluated by TGA measurements in air and nitrogen. T_d's at a 10% weight loss ranged from 421 to 469 °C in nitrogen and from 409 to 448 °C in air, which were relatively lower than those of the corresponding **7′** analogs. Lower T_d's for the **7** series as compared with the **7′** series might be a result of poor packing and weaker chain–chain interactions because of the presence of the CF$_3$ group.

CONCLUSIONS

A novel, fluorinated diamine monomer of 1,4-bis(4-amino-2-trifluoromethylphenoxy)naph-

Table 9. Thermal Properties of the Polyamides

| Polymer Code	$T_g{}^a$ (°C)	$T_s{}^b$ (°C)	T_d at 5% Weight Loss (°C)^c		T_d at 10% Weight Loss (°C)^c		Char Yield^d (%)
			In N_2	In Air	In N_2	In Air	
7a	234 (288)^c	223	389	360	445 (512)	418 (496)	59 (69)
7b	228 (260)	218	361	351	421 (494)	409 (483)	56 (64)
7c	256 (—)	238	407	364	463 (523)	427 (498)	62 (66)
7d	229 (250)	216	388	372	432 (504)	420 (495)	58 (65)
7e	246	241	402	379	445	427	58
7f	232 (263)	223	390	380	452 (512)	435 (500)	59 (63)
7g	243 (282)	240	393	378	451 (500)	439 (487)	57 (65)
7h	241 (255)	230	408	389	469 (505)	448 (497)	53 (62)

^{a} The samples were heated from 50 to 400 °C at a scanning rate of 20 °C/min; the midpoint temperature of the first DSC trace (from 50 to 400 °C at 20 °C/min) was defined as T_g.
^{b} Softening temperature, taken as the onset temperature of the probe displacement on the TMA trace. The film samples were heated at 300 °C for 30 min before the TMA experiment.
^{c} Decomposition temperatures, recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 40 cm^3/min.
^{d} Residual weight percentage at 800 °C under a nitrogen flow.
^{e} Data in parentheses are the reported values for the structurally similar polyamides (**7′**) with the corresponding —Ar— unit as in the **7** series polyamides (see ref. 30).
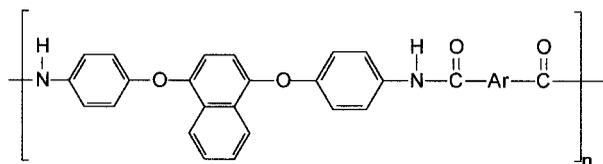
7'

thalene (**2**) was synthesized via a straightforward, high-yielding, two-step route including the Williamson etherification reaction. Two series of new fluorine-containing polyimides and polyamides were synthesized from such diamine with various aromatic dianhydrides and dicarboxylic acids, respectively. Most of the polyimides and all the polyamides were readily soluble in common organic solvents. All the newly obtained polyimides and polyamides were amorphous in nature and could be processed into transparent, flexible, and tough films. The results of the TGA, DSC, and TMA analyses showed excellent thermal stability of the polyimides even though the polyimides exhibited high solubility. However, the polyamides revealed a relatively lower thermal stability because of the incorporation of the CF$_3$ groups.

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