

Syntheses and Properties of Novel Fluorinated Polyamides Based on a Bis(ether-carboxylic acid) or a Bis(ether amine) Extended from Bis(4-hydroxyphenyl)phenyl-2,2,2-trifluoroethane

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ABSTRACT: Two series of novel fluorinated aromatic polyamides were prepared from 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane with various aromatic diamines or from 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane with various aromatic dicarboxylic acids with the phosphorylation polyamidation technique. These polyamides had inherent viscosities ranging from 0.51 to 1.54 dL/g that corresponded to weight-average and number-average molecular weights (by gel permeation chromatography) of 36,200–80,000 and 17,200–64,300, respectively. All polymers were highly soluble in aprotic polar solvents, such as *N*-methyl-2-pyrrolidone and *N,N*-dimethylacetamide, and some could even be dissolved in less-polar solvents like tetrahydrofuran. The flexible and tough films cast from the polymer solutions possessed tensile strengths of 76–94 MPa and initial moduli of 1.70–2.22 GPa. Glass-transition temperatures (T_g 's) and softening temperatures of these polyamides were observed in the range of 185–268 °C by differential scanning calorimetry or thermo-mechanical analysis. Decomposition temperatures (T_d 's) for 10% weight loss all occurred above 500 °C in both nitrogen and air atmospheres. Almost all the fluorinated polyamides displayed relatively higher T_g and T_d values than the corresponding non-fluorinated analogues. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 41: 420–431, 2003

Keywords: polyamides; fluorine-containing; new monomer; solubility; thermal properties; fluoropolymers; structure-property relations; high performance polymers

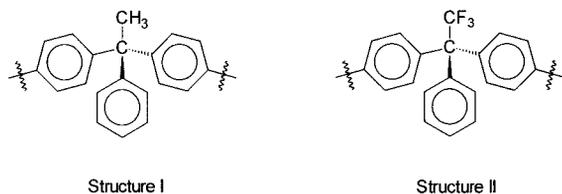
INTRODUCTION

Wholly aromatic polyamides (aramids) such as poly(1,4-phenyleneterethphalamide) have been well known for their high-temperature stability, excellent mechanical strength, and good chemical resistance that qualify them as high-performance polymeric materials.^{1,2} Fibers obtained from

anisotropic solutions of these materials have been used in applications where high thermal stability and mechanical strength are required. However, infusibility and limited solubility are characteristic properties of aramids that may restrict their synthesis, characterization, and applications. Therefore, considerable efforts have been made to increase the processability and solubility of aramids by structural modification. One of the most common approaches to increasing solubility and lowering the glass-transition temperature (T_g) and softening temperature (T_s) is the introduction

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Structure 1

of flexible bonds in the polymer backbone and/or bulky pendent groups along the main chain.^{3–16} Solubility can also be introduced by branching.¹⁷ Soluble or thermoplastic aramids may broaden applications in films, separation membranes, coatings, polymer blends, and composites.

In one of our recent publications,¹⁸ we report the synthesis and properties of aramids with aryl ether and bulky triphenylethane groups. The polyamides showed good solubility in polar organic solvents because of the three-dimensional, propeller-shaped triphenylethane cores (see structure I in Structure 1) that resulted in increased chain-packing distances and decreased intermolecular interactions. They also exhibited good film-forming capability and moderate T_g potential for moldability. However, the thermal stability of the polyamides was slightly decreased because of the less-stable aliphatic groups. Therefore, we decided to replace the triphenylethane unit by a corresponding fluorinated unit, triphenyl-2,2,2-trifluoroethane (structure II in Structure 1), in the polyamide backbone. The polyamides were expected to exhibit enhanced T_g because of the bulky structure of the trifluoroethylidene (3F) group that retards segmental mobility and results in a more rigid system. Moreover, the polyamides were also expected to possess increased thermal stability because of the higher C–F bond strength. Thus, two 3F-containing monomers, 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (**3a**) and 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (**3b**), were synthesized, starting from trifluoroacetophenone, and then polymerized with various aromatic diamines and dicarboxylic acids, respectively. The basic properties of these new fluorinated polyamides such as solubility, film-forming capability, mechanical properties, and thermal properties are discussed. Some properties of these polyamides are also compared with those of homologous counterparts without the fluorinated groups.

EXPERIMENTAL

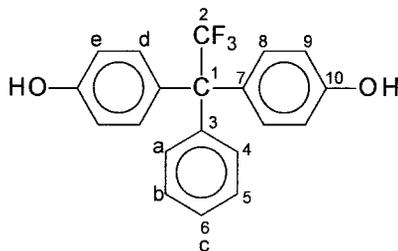
Materials

α,α,α -Trifluoroacetophenone (Acros), phenol (Wako), and triphenyl phosphite (TPP) (Fluka) were used as received. Pyridine, *N*-methyl-2-pyrrolidone (NMP), and *N,N*-dimethylformamide (DMF) were dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. Commercially obtained anhydrous calcium chloride (CaCl_2) and lithium chloride (LiCl) were dried under vacuum at 180 °C for 10 h before use. *p*-Phenylenediamine (**4a**, from TCI) was purified by vacuum sublimation. *m*-Phenylenediamine (**4b**, from Janssen) was purified by vacuum distillation. Benzidine (**4c**, from TCI), 4,4'-oxydianiline (**4d**, from TCI), 1,4-bis(4-aminophenoxy)benzene (**4e**, from TCI), and 1,3-bis(4-aminophenoxy)benzene (**4f**, from TCI) were used as received. As described in a previous publication,¹⁹ 4,4'-bis(4-aminophenoxy)biphenyl (**4g**) (mp: 198–199 °C) and bis[4-(4-aminophenoxy)phenyl] ether (**4h**) (mp: 128–129 °C) were prepared by the aromatic nucleophilic substitution reaction of *p*-chloronitrobenzene with 4,4'-biphenol and 4,4'-dihydroxydiphenyl ether, respectively, in the presence of potassium carbonate and subsequent reduction of the intermediate bis(*p*-nitrophenoxy) compounds with hydrazine monohydrate as the reducing reagent and palladium on carbon (Pd/C) as the catalyst. The commercially available aromatic dicarboxylic acids such as terephthalic acid (**6a**, from Fluka), isophthalic acid (**6b**, from Fluka), 4,4'-biphenyldicarboxylic acid (**6c**, from TCI), 4,4'-oxydibenzoic acid (**6d**, from TCI), 4,4'-sulfonyldibenzoic acid (**6e**, from New Japan Chemical Co.), 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**6f**, from Chriskev), 5-*tert*-butylisophthalic acid (**6g**, from Aldrich), 2,6-naphthalenedicarboxylic acid (**6h**, from TCI), and 1,4-naphthalenedicarboxylic acid (**6i**, from Wako) were used as received.

Monomer Synthesis

1,1-Bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane (1)

In a three-necked, 300-mL round-bottom flask equipped with a stirring bar, gas inlet, and drying tube, 25.0 g (0.145 mol) of α,α,α -trifluoroacetophenone, 54.0 g (0.574 mol) of phenol, and 1 g of zinc chloride (ZnCl_2) were added. The flask was



Structure 2

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 (100/50 mL) to afford 41.4 g (84%) of off-white pure 3F-bisphenol **1** with mp: 234–235 °C [by differential scanning calorimetry (DSC) at a heating rate of 2 °C/min; lit.²⁰ 231–232 °C].

IR (KBr): 3300–3600 (O—H stretching), 1200–1260 (C—O stretching), 1147 cm⁻¹ (C—F stretching). ¹H NMR [dimethyl sulfoxide (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). ¹³C NMR (DMSO-*d*₆, δ, ppm): 158.6 (C¹⁰), 142.6 (C³), 132.4 (C⁸), 132.2 (C²), 131.2 (C⁴), 129.8 (q, ¹J_{C—F} = 280 Hz, C²), 129.5 (C⁵), 129.0 (C⁶), 116.3 (C⁹), 64.4 (q, ²J_{C—F} = 23 Hz, C¹). ELEM. ANAL. Calcd. for C₂₀H₁₅F₃O₂ (344.33): C, 69.76%; H, 4.39%. Found: C, 69.54%; H, 4.21% (see Structure 2).

1,1-Bis[4-(4-cyanophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (2a)

In a 300-mL, round-bottom flask, 17.2 g (0.05 mol) of 3F-bisphenol **1** and 13.8 g (0.10 mol) of anhydrous potassium carbonate (K₂CO₃) were suspended in a mixture of 100 mL of dry DMF and 50 mL of toluene. Then the mixture was refluxed at 150 °C with a Dean–Stark trap for the azeotropic removal of water. After most of the toluene had been removed, *p*-fluorobenzonitrile (12.3 g, 0.10 mol) was added to the mixture, and heating was continued at reflux for 12 h. The resulting solution was allowed to cool to room temperature and then poured into 400 mL of water; a glutinous product aggregated in the bottom of the beaker. After being washed repeatedly with water, the solidified product was collected by filtration and

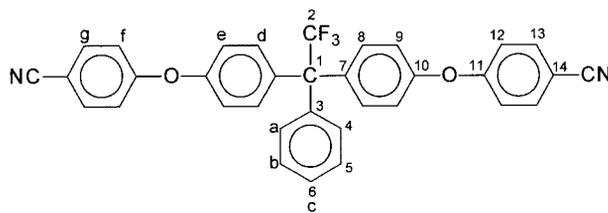
recrystallized from a mixture of acetonitrile/methanol (200 mL/100 mL) to afford 19.6 g (yield 72%) of pure white crystals (mp: 169–170 °C, by DSC).

IR (KBr): 2225 (C≡N stretching), 1240 (C—O stretching), 1157 cm⁻¹ (C—F stretching). ¹H NMR (CDCl₃, δ, ppm): 7.63 (d, H_g, 4H), 7.37 (m, H_b + H_c, 3H), 7.20 (two overlapped AB doublets, H_a + H_d, 6H), 7.08 (d, H_e, 4H), 7.03 (d, H_f, 4H). ¹³C NMR (CDCl₃, δ, ppm): 162.8 (C¹¹), 156.6 (C¹⁰), 141.4 (C³), 138.1 (C⁷), 135.9 (C¹³), 133.5 (C⁸), 131.4 (C⁴), 130.0 (C⁵), 129.7 (C⁶), 129.4 (q, ¹J_{C—F} = 286 Hz, C²), 121.0 (C¹²), 120.2 (—CN), 120.1 (C⁹), 107.9 (C¹⁴), 65.2 (q, ²J_{C—F} = 24 Hz, C¹). ELEM. ANAL. Calcd. for C₃₄H₂₁N₂F₃O₂ (546.55): C, 74.72%; H, 3.87%; N, 5.12%. Found: C, 74.50%; H, 3.62%; N, 4.99% (see Structure 3).

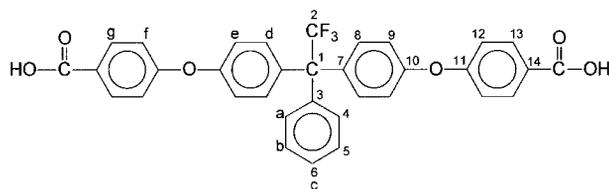
1,1-Bis[4-(4-carboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (3a)

Dicarboxylic acid **3a** was synthesized by the alkaline hydrolysis of dinitrile compound **2a**. A suspension of dinitrile **2a** (19 g, 0.035 mol) in a mixture of water (150 mL) and ethanol (150 mL) containing dissolved potassium hydroxide (20 g, 0.35 mol) was stirred at a reflux temperature for 20 h until no further ammonia were generated. The resulting hot solution was filtered to remove any insoluble impurities. The filtrate was cooled and acidified by concentrated HCl to pH = 2–3 when a white solid precipitated. The solid was collected by filtration, washed thoroughly with water, and dried to give 19.9 g (yield 98%) of diacid **3a** (mp: 292–294 °C, by DSC).

IR (KBr): 2500–3300 (carboxyl O—H stretching), 1689 (C=O stretching), 1246 (C—O stretching), 1155 cm⁻¹ (C—F stretching). ¹H NMR (DMSO-*d*₆, δ, ppm): 8.00 (d, H_g, 4H), 7.44 (m, H_b + H_c, 3H), 7.13 (overlapped AB doublets, H_a + H_d + H_e + H_f, 14H). ¹³C NMR (DMSO-*d*₆, δ, ppm): 168.9 (C=O), 162.0 (C¹¹), 157.1 (C¹⁰), 141.1 (C³), 136.7 (C⁷), 133.4 (C¹³), 132.9 (C⁸), 130.9 (C⁴), 130.2 (C⁵), 129.7 (C⁶), 129.3 (q, ¹J_{C—F} = 286 Hz,



Structure 3



Structure 4

(C²), 127.7 (C¹⁴), 120.6 (C¹²), 119.4 (C⁹), 64.6 (q, ²J_{C-F} = 24 Hz, C¹). ELEM. ANAL. Calcd. for C₃₄H₂₃F₃O₆ (584.55): C, 69.86%; H, 3.96%. Found: C, 69.42%; H, 3.62% (see Structure 4).

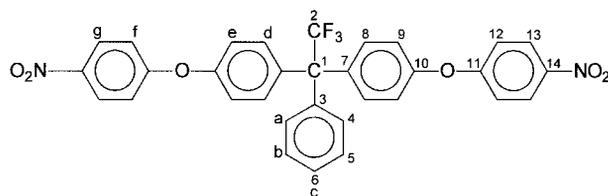
1,1-Bis[4-(4-nitrophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (2b)

In a 250-mL round-bottom flask, 10.0 g (0.03 mol) of 3F-bisphenol **1** and 9.2 g (0.06 mol) of *p*-chloronitrobenzene were dissolved in 80 mL of dry DMF. Then 8.0 g (0.06 mol) of potassium carbonate were 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.²¹ 196–197 °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). ¹³C NMR (DMSO-*d*₆, δ, ppm): 162.0 (C¹¹), 154.2 (C¹⁰), 142.7 (C¹⁴), 139.1 (C³), 135.8 (C⁷), 131.5 (C⁸), 129.2 (C⁴), 128.6 (C⁵), 128.2 (C⁶), 127.1 (q, ¹J_{C-F} = 287 Hz, C²), 126.2 (C¹³), 119.9 (C⁹), 118.0 (C¹²), 63.9 (q, ²J_{C-F} = 24 Hz, C¹). ELEM. ANAL. Calcd. for C₃₂H₂₁N₂F₃O₆ (586.52): C, 65.53%; H, 3.61%; N, 4.78%. Found: C, 65.11%; H, 3.58%; N, 4.77% (see Structure 5).

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 of 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 an additional 10 h of reflux, the catalyst was



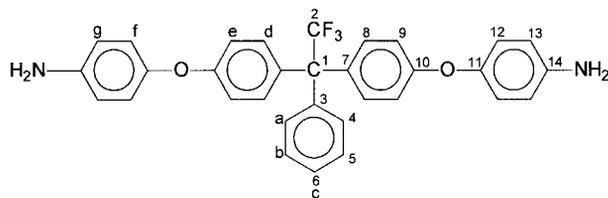
Structure 5

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.²⁰ 169–170 °C).

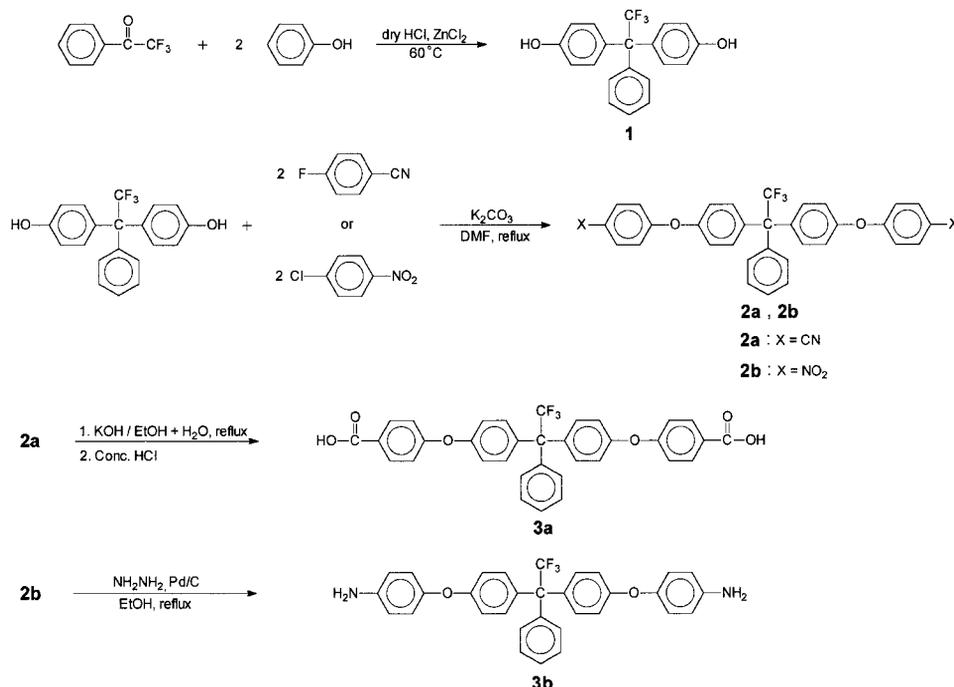
IR (KBr): 3450, 3383 (N—H stretching), 1240 (C—O stretching), 1175 cm⁻¹ (C—F stretching). ¹H NMR (DMSO-*d*₆, δ, ppm): 7.35 (m, H_b + H_c, 3H), 7.08 (d, H_a, 4H), 6.96 (d, H_a, 4H), 6.88 (overlapped AB doublets, H_e + H_f, 8H), 6.63 (d, H_g, 4H), 5.02 (d, —NH₂, 4H). ¹³C NMR (DMSO-*d*₆, δ, ppm): 160.0 (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% (see Structure 6).

Polymer Synthesis

The phosphorylation polycondensation method was used to prepare the polyamides. A typical example for the preparation of polymer **5a** is given. A flask was charged with 0.877 g (1.5 mmol) of diacid **3a**, 0.162 g (1.5 mmol) of *p*-phenylenediamine (**4a**), 0.3 g of CaCl₂, 0.8 mL of TPP, 0.8 mL of pyridine, and 3 mL of NMP. This mixture was heated with stirring at 120 °C for 3 h. As polycondensation proceeded, the solution gradually became viscous. The resulting highly viscous polymer solution was poured slowly into 300 mL of stirred methanol, giving a fibrous white precipitate that was filtered off, washed thoroughly



Structure 6



Scheme 1. Synthetic route for the 3F-bis(ether-carboxylic acid) **3a** and 3F-bis(ether amine) **3b**.

with methanol and hot water, and dried. The inherent viscosity of polymer **5a** was 1.27 dL/g, as measured at a concentration of 0.5 g/dL in dimethylacetamide (DMAc) containing 5 wt % LiCl at 30 °C.

IR (film): 3315 cm^{-1} (N—H stretching), 1656 ($\text{C}=\text{O}$ stretching), and 1242 cm^{-1} (C—O stretching). ELEM. ANAL. Calcd. for $(\text{C}_{40}\text{H}_{27}\text{F}_3\text{N}_2\text{O}_4)_n$ (655.66) $_n$: C, 73.10%; H, 4.14%; N, 4.27%; Found: C, 71.87%; H, 4.16%; N, 4.24%.

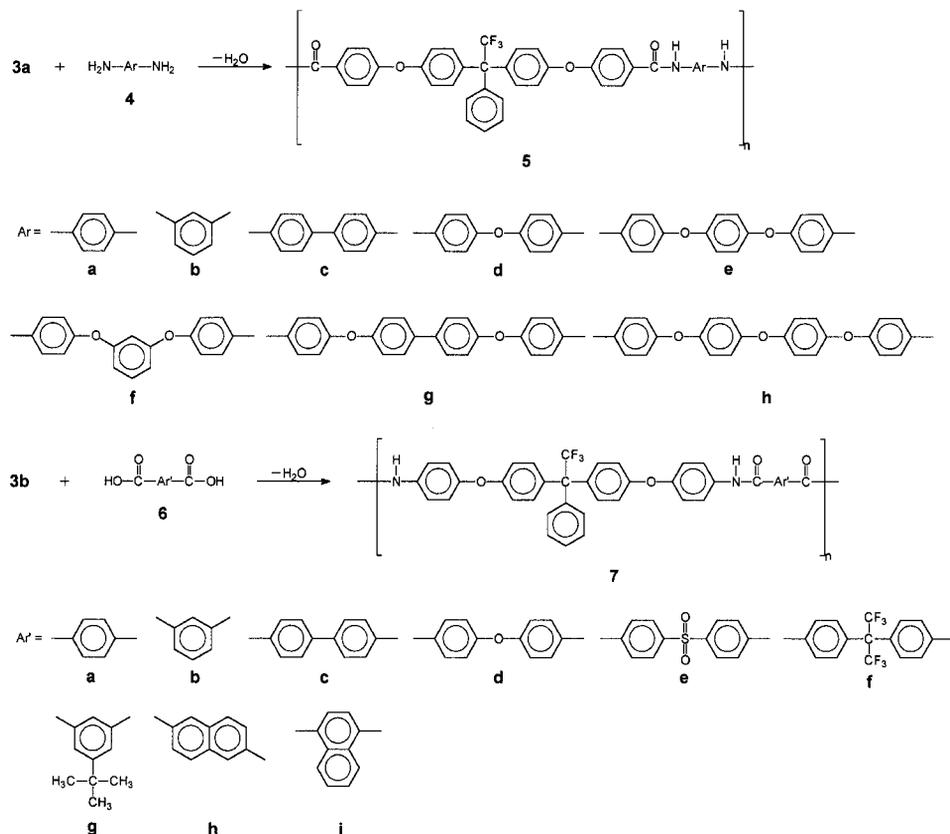
All other polyamides were synthesized by a similar procedure.

Preparation of the Polyamide Films

A polymer solution of approximately 10 wt % was made by the dissolution of about 1.0 g of polyamide in 10 mL of hot DMAc. The clear solution was poured into an 11-cm-diameter glass culture dish, which was placed in a 90 °C oven overnight for evaporation of the solvent. Then the obtained semidried polymer film was stripped from the glass substrate and further dried in vacuum at 160 °C for 6 h. The obtained films were about 0.08 mm thick and used for X-ray diffraction measurements, tensile tests, solubility 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. ^1H 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 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. \times 300 mm) connected in series were used with tetrahydrofuran (THF) as the eluent and 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 1130 with a load cell of 5 kg was used to measure 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 five individual determinations was used. Wide-angle X-ray diffraction



Scheme 2. Synthesis of polyamides.

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 ($\lambda = 1.5418 \text{ \AA}$). The scanning rate was 3°/min over a range of $2\theta = 5\text{--}45^\circ$. 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. 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 's) 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 100 °C/min. Thermo-mechanical 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_g 's were taken as the onset temperature of probe displacement on the TMA traces.

RESULTS AND DISCUSSION

Monomer Synthesis

The two main monomers containing both 3F and ether groups, 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (**3a**) and 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (**3b**), were synthesized with a three-stage procedure outlined in Scheme 1. The first step was an acid-catalyzed condensation reaction of α,α,α -trifluoroacetophenone with excess phenol producing 1,1-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane (3F-bisphenol **1**). In the second step, the intermediate compounds, 1,1-bis[4-(4-cyanophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (**2a**) and 1,1-bis[4-(4-nitrophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (**2b**), were synthesized by nucleophilic aromatic halogen displacement of *p*-fluorobenzonitrile and *p*-chloronitrobenzene, respectively, with bisphenol **1** in the presence of anhydrous potassium carbonate in DMF. In the third step, dinitrile **2a** was converted into **3a** by alkaline hydrolysis, and di-nitro compound **2b** was reduced to **3b** with hydr-

Table 1. 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 Maximum
	NMP (mL)	Py (mL)	TPP (mL)	CaCl ₂ (g)				
5a	3 + 2 ^d	0.8	0.8	0.3	1.27	— ^e	—	—
5b	2	0.5	0.8	0.2	1.22	61,000	36,800	60,400
5c	3	0.8	0.8	0.3	1.06	—	—	—
5d	2 + 2	0.5	0.8	0.2	1.54	65,600	47,000	64,500
5e	3 + 1	0.8	0.8	0.3	1.32	75,800	52,800	86,800
5f	3	0.8	0.8	0.3	0.95	60,300	34,900	51,100
5g	4 + 1	1.0	0.8	0.4	1.45	—	—	—
5h	3	0.8	0.8	0.3	0.85	36,200	17,200	20,400
7a	3 + 1	0.8	1.0	0.3	0.79	—	—	—
7b	2	0.5	1.0	0.2	0.78	80,000	54,600	116,000
7c	3 + 2	0.8	1.0	0.3	0.96	—	—	—
7d	2.5 + 1	0.6	1.0	0.25	0.83	78,000	59,000	110,000
7e	2.5 + 1	0.6	1.0	0.25	0.61	79,000	64,300	127,000
7f	2.5	0.6	1.0	0.25	0.68	73,600	52,000	135,000
7g	2	0.5	1.0	0.2	0.51	67,900	50,000	83,000
7h	3 + 1	0.8	1.0	0.3	1.14	—	—	—
7i	2.5	0.6	1.0	0.25	0.51	64,600	47,000	62,000

^a Monomer scale: 1.5 mmol for the **5** series and 1.25 mmol for the **7** series polymers; reaction temperature: 110 °C, time: 3 h, NMP: *N*-methyl-2-pyrrolidone, Py: pyridine, and TPP: triphenyl phosphite.

^b Measured in DMAc containing 5 wt % LiCl at 30 °C in 0.5 g/dL.

^c Molecular weights relative to polystyrene standards in THF by GPC.

^d “3 + 2” means that an initial amount of 3 mL of NMP was used, and an additional 1 mL of NMP was added when the reaction solution was too viscous to stir.

^e Insoluble in THF.

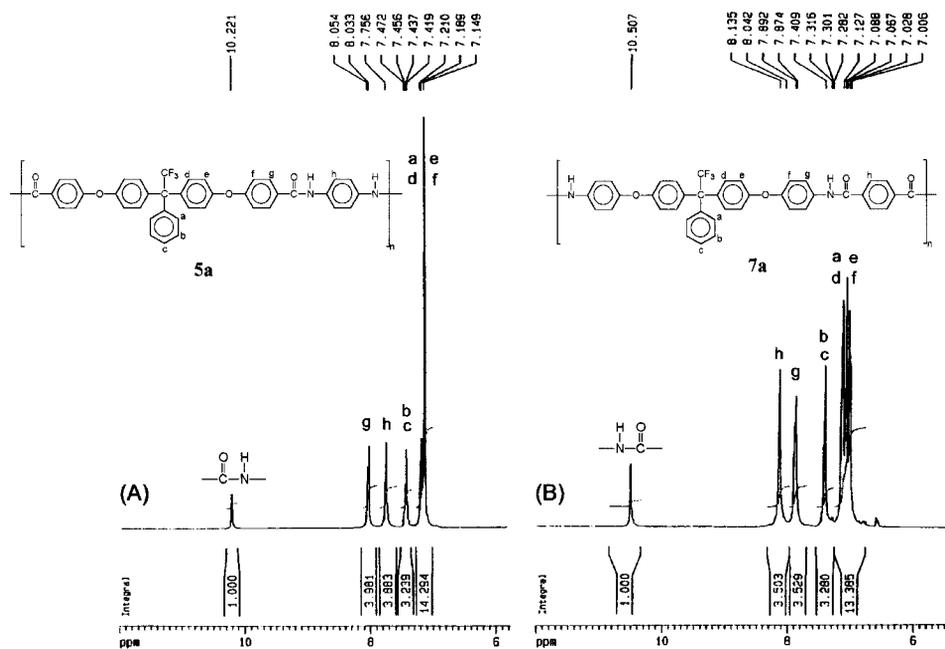


Figure 1. (A) ¹H NMR (DMSO-*d*₆) spectrum of polyamide **5a** and (B) ¹H NMR (DMSO-*d*₆) spectrum of polyamide **7a**.

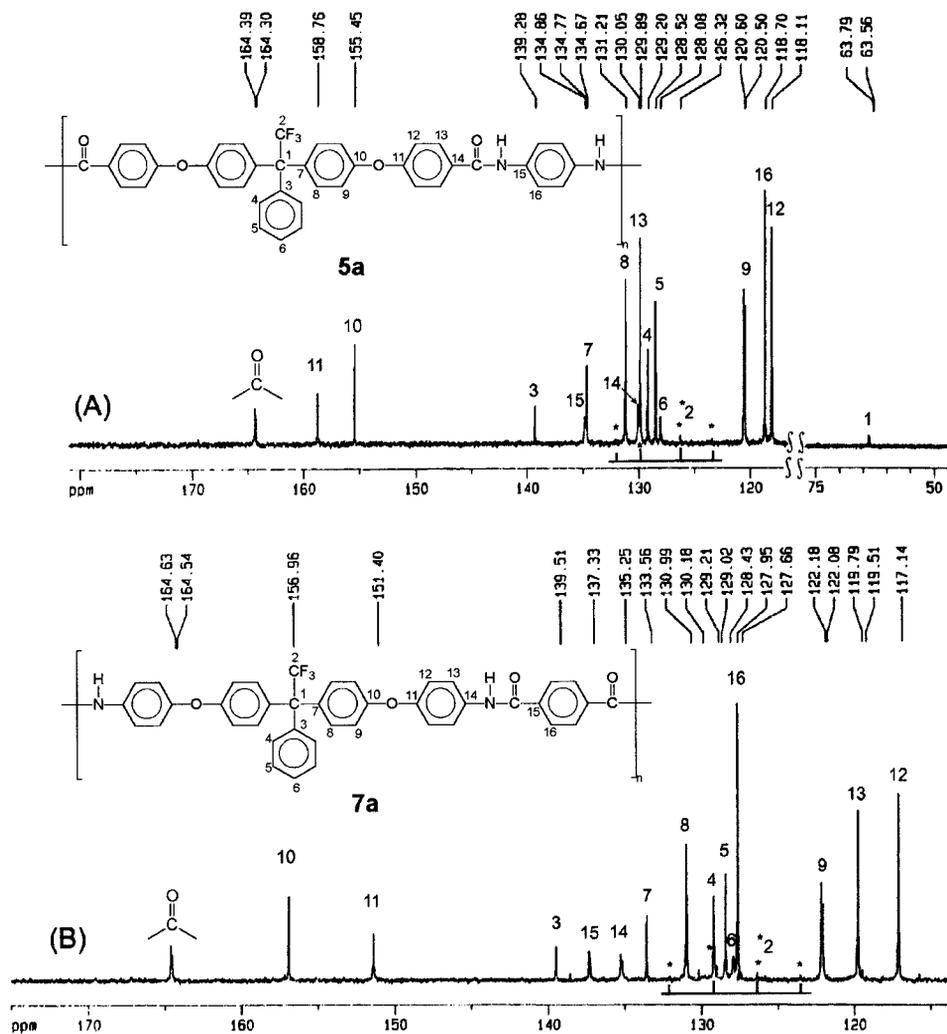


Figure 2. (A) ^{13}C NMR ($\text{DMSO-}d_6$) spectrum of polyamide **5a** and (B) ^{13}C NMR ($\text{DMSO-}d_6$) spectrum of polyamide **7a**.

azine monohydrate and Pd/C catalyst in refluxing ethanol. All the structures of the intermediates and monomers were identified by elemental analyses as well as FTIR and NMR spectroscopy.

Polymer Synthesis

The phosphorylation polyamidation technique developed by Yamazaki et al.²² was used to prepare fluorinated polyamides **5a–h** and **7a–i** from diacid **3a** with various aromatic diamines **4a–h** and diamine **3b** with various aromatic dicarboxylic acids **6a–i**, respectively. Structures and codes of the polymers prepared are outlined in Scheme 2. No attempts were made to maximize molecular weights. With the reaction conditions listed in Table 1, we generally obtained high-molecular-

weight polymers. In most cases, a higher initial reactant concentration and adding more solvent to the highly viscous reaction medium before the formation of the swollen gel yielded polymers with higher molecular weights. Viscosities of the polymerization mixtures were normally very high, and the nature of the precipitated polymers (as tough stringy precipitates) implied high-molecular-weight products. As shown in Table 1, the resulting polymers had inherent viscosities higher than 0.51 dL/g and up to 1.54 dL/g. GPC analysis revealed that the weight-average (M_w) and number-average (M_n) molecular weights of the THF-soluble polyamides range from 36,200 to 80,000 and 17,200 to 64,300, respectively. All the polyamides prepared could be solvent-cast into flexible, high-strength films. Structural features

Table 2. Solubility Behaviors and Thin-Film Tensile Properties of the Polyamides

Polymer	Solubility ^a						Tensile Properties of the Polymer Films ^b			
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
5a	+	+	+	+	+	–	95	93	69	2.03
5b	+	+	+	+	+	+	97	93	26	2.07
5c	+	+	+	+	–	–	97	89	16	2.22
5d	+	+	+	+	+	+	88	86	45	1.83
5e	+	+	+	+	+	+	87	79	23	1.87
5f	+	+	+	+	+	+	94	86	44	1.95
5g	+	+	+	+	δ	+	87	83	42	1.71
5h	+	+	+	+	+	+	83	76	26	1.81
7a	+	+	+	+	+h	–	85	83	36	1.92
7b	+	+	+	+	+	+	87	81	10	1.81
7c	+	+	+	+	–	–	93	87	13	2.10
7d	+	+	+	+	+	+	95	93	15	1.90
7e	+	+	+	+	+	+	85	82	14	1.77
7f	+	+	+	+	+	+	85	81	16	1.70
7g	+	+	+	+	+	+	89	88	9	1.91
7h	+	+	+	+	+h	+	96	94	13	2.10
7i	+	+	+	+h	+	+	83	82	6	2.12

^a Qualitative solubility was tested with 10 mg of sample in 1 mL of solvent. Symbol: +, soluble at room temperature; +h, soluble on heating at 100 °C; δ, partially 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, and THF: tetrahydrofuran.

^b Films were cast from slow evaporation of polymer solutions in DMAc. The cast films were dried under vacuum at 160 °C for 6 h prior to the tensile test.

of these polyamides were verified by FTIR and NMR spectroscopy. They exhibited characteristic absorption bands of the amide group around 3300 (N–H stretching) and 1650–1670 cm⁻¹ (C=O stretching), with strong absorptions of aryl ether and C–F stretching in the region of 1100–1300 cm⁻¹. ¹H NMR and ¹³C NMR spectra of a typical set of isomeric polyamides **5a** and **7a** are illustrated in Figures 1 and 2, respectively. Assignments of each carbon and proton are also given in the figures, and these spectra agree with the proposed polymer structures.

Polymer Characterization

The solubility behavior of these polyamides was tested qualitatively, and the results are summarized in Table 2. All the polyamides were readily soluble in amide-type polar aprotic solvents (such as NMP, DMAc, and DMF). Almost all the polymers were also soluble in DMSO and *m*-cresol. In addition, polyamides obtained from flexible diamines dissolved in less polar solvents like THF. Polymers **5c** and **7c** exhibited a slightly lower

solubility because of their symmetrical and rigid biphenylene segments; they were insoluble in *m*-cresol and THF. Similar to the results described previously,¹⁸ the two sets of analogous polyamides **5a–d** and **7a–d** showed a similar solubility behavior. The high solubility of these polyamides is apparently due in part to the presence of the packing-disruptive triphenyltrifluoroethane unit 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 the bulky triphenyltrifluoroethane core and flexible ether linkages.

X-ray diffraction patterns confirmed that all polyamides were amorphous. Transparent, tough, and flexible films of all polyamides could be obtained by casting their DMAc solutions. The tensile properties of the polyamide films are also summarized in Table 2. They exhibited tensile strengths of 76–94 MPa, elongations to break of 6–69%, and initial moduli of 1.7–2.22 GPa. Most of the polymer films necked during tensile testing

Table 3. Thermal Properties of Polyamides

Polymer	T_g (°C) ^a	T_s (°C) ^b	T_d (°C) ^c		Char Yield (%) ^d
			In N ₂	In Air	
5a	241 (212) ^e	245	531 (510) ^e	516 (509)	62
5b	217 (197)	217	509 (513)	521 (494)	62
5c	266 (260)	268	538 (504)	517 (511)	67
5d	229 (194)	229	524 (509)	514 (511)	62
5e	211 (201)	210	519 (511)	512 (502)	57
5f	190	194	516	509	61
5g	210 (218)	218	529 (527)	529 (498)	62
5h	185	190	530	502	62
7a	259 (216)	248	554 (496)	540 (475)	63
7b	230 (201)	232	542 (516)	511 (487)	63
7c	253	255	558 (475)	536 (496)	62
7d	240 (210)	237	562 (504)	530 (475)	64
7e	249 (224)	254	554 (489)	526 (491)	62
7f	260 (219)	255	563 (516)	544 (504)	57
7g	250 (224)	259	555 (502)	531 (489)	61
7h	259 (217)	255	561 (504)	548 (493)	67
7i	220 (220)	222	538 (467)	520 (473)	63

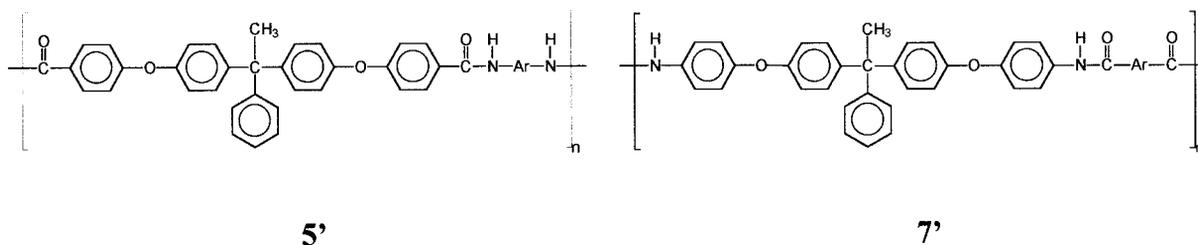
^a Midpoint temperature of baseline shift on the second DSC heating trace (scan rate: 20 °C/min) of the sample after quenching from 400 °C.

^b Softening temperature measured by TMA with a penetration method. The film samples were heated at 250 °C for 30 min prior to the TMA experiments.

^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 at a scan rate of 20 °C/min in nitrogen.

^e Data shown in the parentheses are those of the analogous nonfluorinated polyamides **5'** and **7'** (see ref. 18) with the same diamine (-Ar-) and diacid residue (-Ar'-) as those of **5** and **7**.



and had moderate elongations to break, indicating strong and tough materials.

DSC, TMA, and TGA were used to evaluate the thermal properties of all polymers. The thermal behavior data of the polyamides are summarized in Table 3. The T_g of these polyamides was obtained from the second DSC heating trace (heating rate: 20 °C/min) after rapid cooling from 400 °C (cooling rate: 100 °C/min). Polyamides **5a–h** and **7a–i** indicated clear T_g 's ranging from 185 to 266 and 220 to 260 °C, respectively. The lowest T_g of 185 °C was observed for polyamide **5h** derived from the multiring flexible diamine **4h**. In general, the T_g values depend on the structures of diamine and diacid moieties and decreased with

decreasing rigidity and symmetry of the polymer backbone. For comparison, the reported T_g values¹⁸ of the corresponding nonfluorinated analogues **5'** and **7'** are also included in Table 3. In most cases, the fluorinated polyamides exhibited T_g 's higher than the nonfluorinated counterparts. This result can be attributed to the increase of structural hindrance because of the bulky $-\text{CF}_3$ units. The T_s values of these polymer film samples were also measured with TMA by the penetration method. They were obtained from the onset temperature of the probe displacement on the TMA trace. Typical TMA thermograms for polymers **5a** and **7a** are illustrated in Figure 3. The T_s values of these polyamides were observed in the

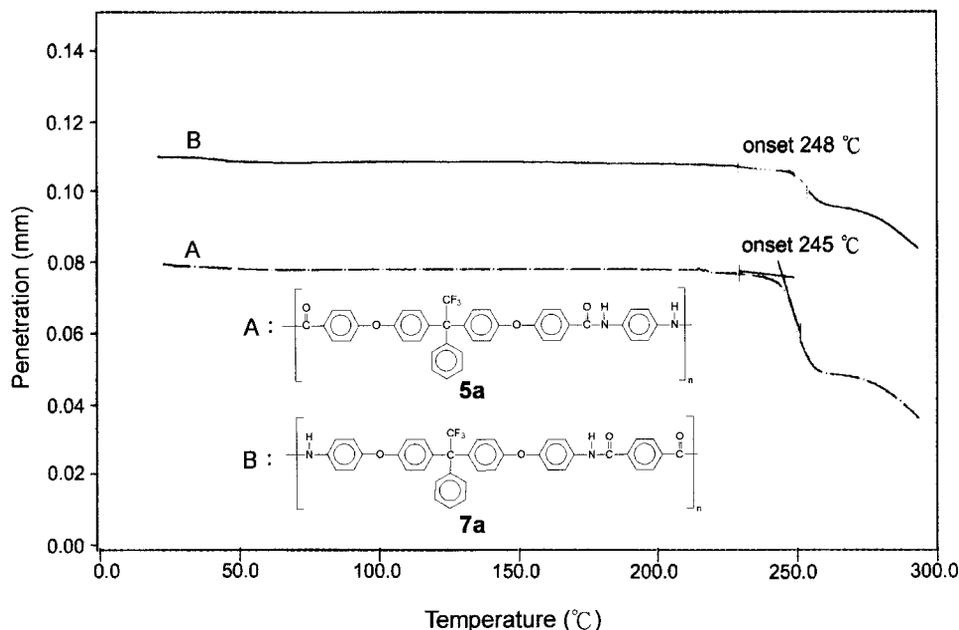


Figure 3. TMA thermograms of polyamides **5a** and **7a** at a heating rate of 10 °C/min.

range 190–268 °C. In most cases, the T_g values obtained by TMA are comparable to the T_g values measured by the DSC experiments.

The thermal and thermooxidative stability of the polyamides were examined by TGA. The temperatures of 10% weight loss in nitrogen and air atmospheres determined from the original thermograms are included in Table 3. All polymers exhibited good thermal stability with the decomposition temperatures (T_d 's) at 10% weight loss above 500 °C in both air and nitrogen atmospheres. The anaerobic char yield at 800 °C for all polymers was in the range of 57–67 wt %. The T_d values of the nonfluorinated polyamides reported previously¹⁸ are also displayed in Table 3 for comparison. As expected, the fluorinated polyamides generally revealed a higher thermal or thermooxidative stability than the nonfluorinated analogues because of the higher C–F bond strength.

CONCLUSIONS

Extended 3F-bis(ether-carboxylic acid) and 3F-bis(ether amine) monomers, **3a** and **3b**, were successfully synthesized in high purity and high yields. Two sets of fluorinated aromatic polyamides were prepared in high yields from various combinations of **3a** with aromatic diamines or **3b** with aromatic diacids, with the Yamazaki–Hi-

gashi phosphorylation technique. Because of the presence of bulky, three-dimensional, propeller-shaped triphenyltrifluoroethane cores in the main chain, all the polyamides were noncrystalline. Incorporation of the 3F groups in the polyamide backbones led to higher T_g 's and thermal stability as compared with nonfluorinated counterparts. Good solubility, moderate T_g values suitable for molding, and high thermal stability made these fluorinated polyamides promising high-performance polymeric materials.

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