

A novel class of organosoluble and light-colored fluorinated polyamides derived from 2,2'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl or 2,2'-bis(4-amino-2-trifluoromethylphenoxy)-1,1'-binaphthyl

Sheng-Huei Hsiao ^a, Chin-Ping Yang ^a, Che-Yu Tsai ^b, Guey-Sheng Liou ^{b,*}

^a Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Section, Taipei 104, Taiwan, ROC

^b Department of Applied Chemistry, National Chi Nan University, Nantou Hsien 545, Taiwan, ROC

Received 31 October 2003; received in revised form 5 January 2004; accepted 6 January 2004

Available online 27 February 2004

Abstract

Two series of novel fluorinated aromatic polyamides 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 dicarboxylic acids using the phosphorylation polycondensation technique. The polyamides had inherent viscosities ranging from 0.43 to 0.62 dl/g and 0.36 to 0.74 dl/g, respectively. All the fluorinated polyamides were soluble in many polar organic solvents such as *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone, and afforded transparent, light-colored, and flexible films upon casting from DMAc solvent. These polyamides showed glass-transition temperatures in the ranges of 190–240 °C (for the **6** series from diamine **2**) and 247–255 °C (for the **7** series from diamine **4**) by differential scanning calorimetry, softening temperatures in the ranges of 196–230 °C (**6** series) and 241–291 °C (**7** series) by thermomechanical analysis, and decomposition temperatures for 10% weight loss above 420 °C in both nitrogen and air atmospheres.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Fluorinated polyamides; Light-colored; Solubility; Thermal properties

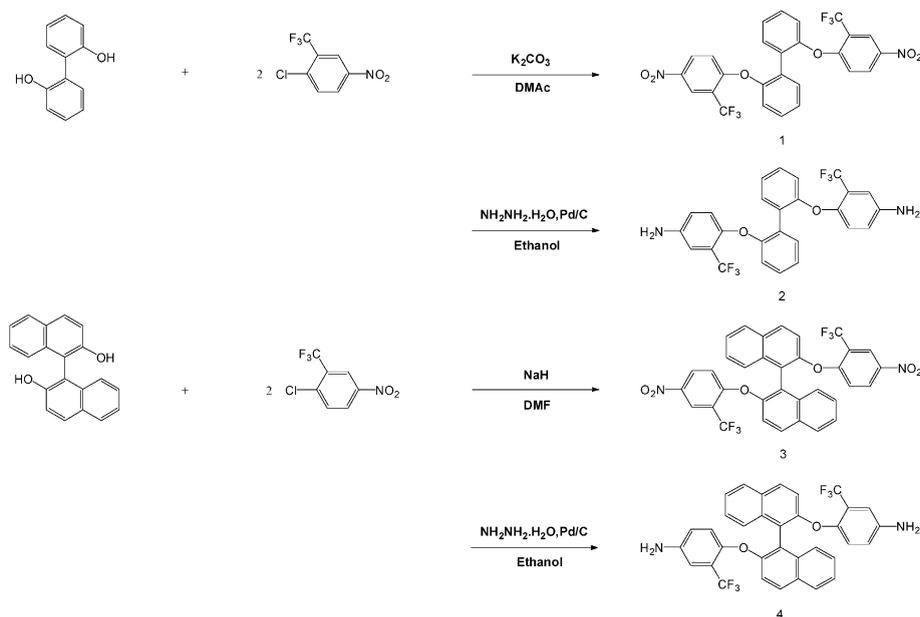
1. Introduction

It is well known that wholly aromatic polyamides (aramids) are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties [1,2]. However, these polymers are generally intractable and lack the properties essential for successful fabrication because of their high melting or glass transition temperatures and their limited solubility in common organic solvents. Therefore, a great deal of effort has been expended to improve the processing

characteristics of the relatively intractable polymers [3–12]. These studies include introducing flexible segments into the polymer chain; replacing symmetrical aromatic rings with unsymmetrical ones, which leads to a reduction in crystallization; introducing bulky pendant groups to minimize crystallization; and forming a non-coplanar structure, thereby making crystallization impossible. It has been demonstrated that the highly kinked and cranked bulky aromatic diamines, 2,2'-bis(4-aminophenoxy)biphenyl and 2,2'-bis(4-aminophenoxy)-1,1'-binaphthyl, were effectively used to prepare soluble aromatic polyamides and polyimides with various aromatic diacids and aromatic tetracarboxylic dianhydrides, respectively [5,13]. Structurally similar aromatic dicarboxylic acids, 2,2'-bis(4-carboxylphenoxy)biphenyl and 2,2'-bis(4-carboxylphenoxy)-1,1'-binaphthyl, were

* Corresponding author. Tel.: +886-49-2910962x4946; fax: +886-49-2917956.

E-mail address: gsliou@ncnu.edu.tw (G.-S. Liou).

Scheme 1. Synthesis of CF_3 -substituted diamines **2** and **4**.

also prepared for the production of aromatic polyamides [14], and it was found that the 1,1'-binaphthyl-2,2'-diyl-containing polymers had higher glass transition temperatures (T_g) by about 50 °C and better solubility as compared to the biphenyl-2,2'-diyl-containing polymers. This phenomenon is due to the fact that 1,1'-binaphthyl-2,2'-diyl has a larger dihedral angle (68.6° or 103.1°) [15,16] than that of 1,1'-biphenyl-2,2'-diyl (21°); the former should be able to further lower the interchain interactions or prevent the polymer chains from close packing. Furthermore, by virtue of restricted rotation about the bond joining the aromatic ring systems, the binaphthyl-based polymers should have higher glass transition temperatures (T_g s) than the biphenyl-based analogues. It is known that the introduction of ether linkages into the polymer backbone imparts processability and solubility to polymers without much loss of thermal stability, and the incorporation of fluorine-containing substituents is also known to enhance the solubility of aromatic polymers such as polyimides [17]. It is also well known that the incorporation of fluorinated substituents into polymers reduces the dielectric constant because of the low electronic polarizability of the C–F bond and the increase in the fractional free volume, which accompanies the replacement of methyl groups by trifluoromethyl (CF_3) groups [18,19].

The present study deals with the synthesis and basic characterization of novel fluorinated polyamides derived from 2,2'-bis(4-amino-2-trifluoromethylphenoxy)biphe-

nyl (diamine **2**, as shown in Scheme 1) and 2,2'-bis(4-amino-2-trifluoromethylphenoxy)-1,1'-binaphthyl (diamine **4** in Scheme 1) with various aromatic dicarboxylic acids. The attachment of bulky CF_3 groups would decrease polymer interchain interactions such as hydrogen bonding and generally disturb the coplanarity of aromatic units to reduce packing efficiency and crystallinity, thus being expected to lead to enhanced solubility and optical transparency.

2. Experimental

2.1. Materials

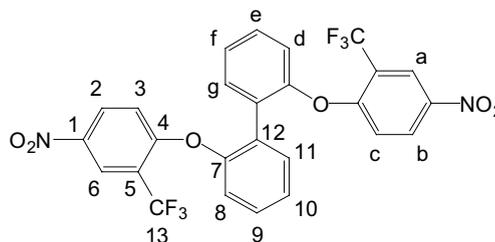
2,2'-Biphenol (Acros), 2,2'-dihydroxy-1,1'-binaphthyl (Acros), potassium carbonate (K_2CO_3) (Showa), sodium hydride (Aldrich), 2-chloro-5-nitrobenzotrifluoride (Aldrich), 10% palladium on carbon (Pd/C) (Lancaster), and hydrazine monohydrate (Tokyo Chemical Industry; TCI) were used as received. DMAc (TEDIA), NMP (TEDIA), *N,N*-dimethylformamide (DMF) (Acros), pyridine (Py) (TEDIA), and triphenyl phosphite (TPP) (Acros) were also used as received. The commercially available aromatic dicarboxylic acids such as terephthalic acid (**5a**) (Aldrich), isophthalic acid (**5b**) (Aldrich), 2,6-naphthalenedicarboxylic acid (**5c**) (TCI), 4,4'-diphenyldicarboxylic acid (**5d**) (TCI), 4,4'-dicarboxydiphenyl ether (**5e**) (TCI), 4,4'-dicarboxydiphenyl sulfone (**5f**)

(TCI), and 2,2'-bis(4-carboxyphenyl)hexafluoropropane (**5g**) (TCI) were used as received. Calcium chloride (CaCl_2) (Showa) was dried under vacuum at 180 °C for 8 h prior to use.

2.2. 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 *N,N*-dimethylacetamide (DMAc) in a 250-ml round-bottomed 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 poured into 800 ml of methanol/water (1:1) to give a yellow solid, which was collected, washed repeatedly with methanol, and dried. The crude product was recrystallized from DMF/methanol to give light-yellow needles 30.9 g (85%); mp 142–144 °C (onset to the peak top temperature), by differential scanning calorimetry (DSC) at a scan rate of 10 °C/min. IR (KBr): 1527, 1336 ($-\text{NO}_2$), 1288, 1252 (C–O), 1139, 1117 cm^{-1} (C–F). ^1H NMR (DMSO- d_6) δ : 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). ^{13}C NMR (DMSO- d_6) δ : 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, $^3J_{\text{C-F}} = 5$ Hz, C⁶), 121.99 (q, $^1J_{\text{C-F}} = 271$ Hz, C¹³), 121.07 (C¹⁰), 118.02 (q, $^2J_{\text{C-F}} = 33$ Hz, C⁵), 116.35 (C⁸). Anal. calcd for $\text{C}_{26}\text{H}_{14}\text{F}_6\text{N}_2\text{O}_6$ (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** (16.35 g, 0.029 mol) and 10% Pd/C (0.2 g) were suspended in 100 ml ethanol in a 250-ml flask. The suspension solution was heated to reflux, and hydrazine monohydrate (8 ml) was added

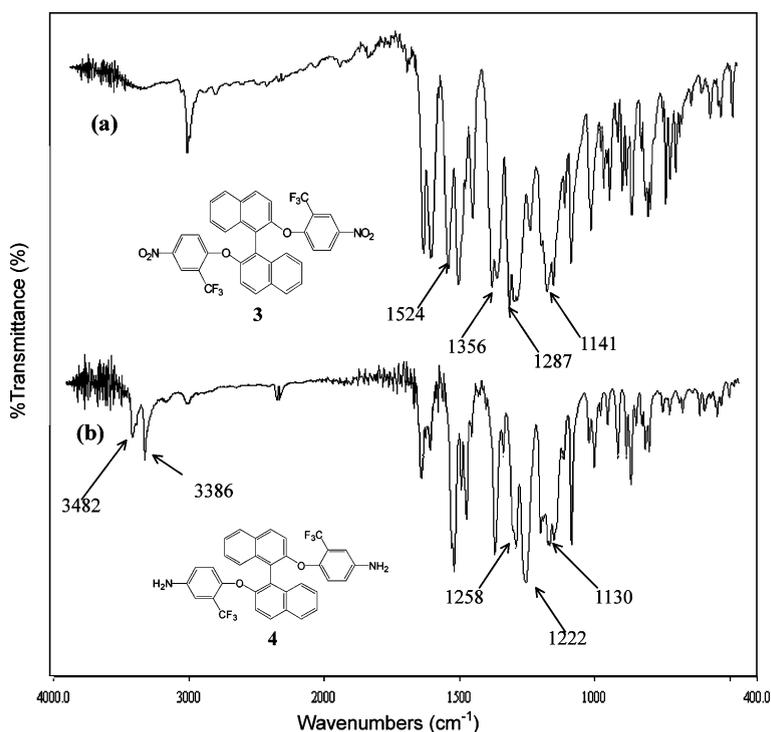


Fig. 1. IR spectra of (a) dinitro compound **3** and (b) diamine **4**.

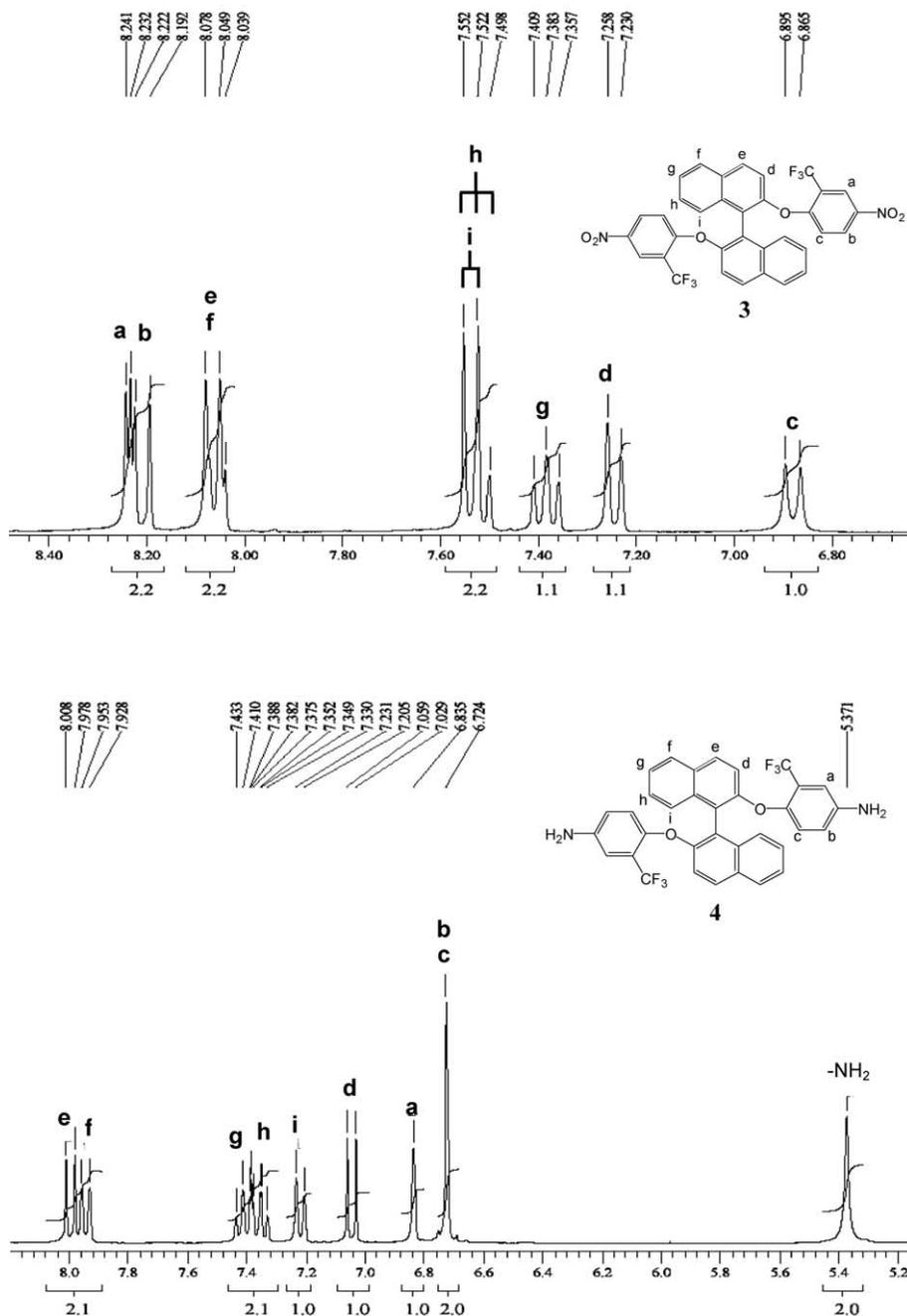
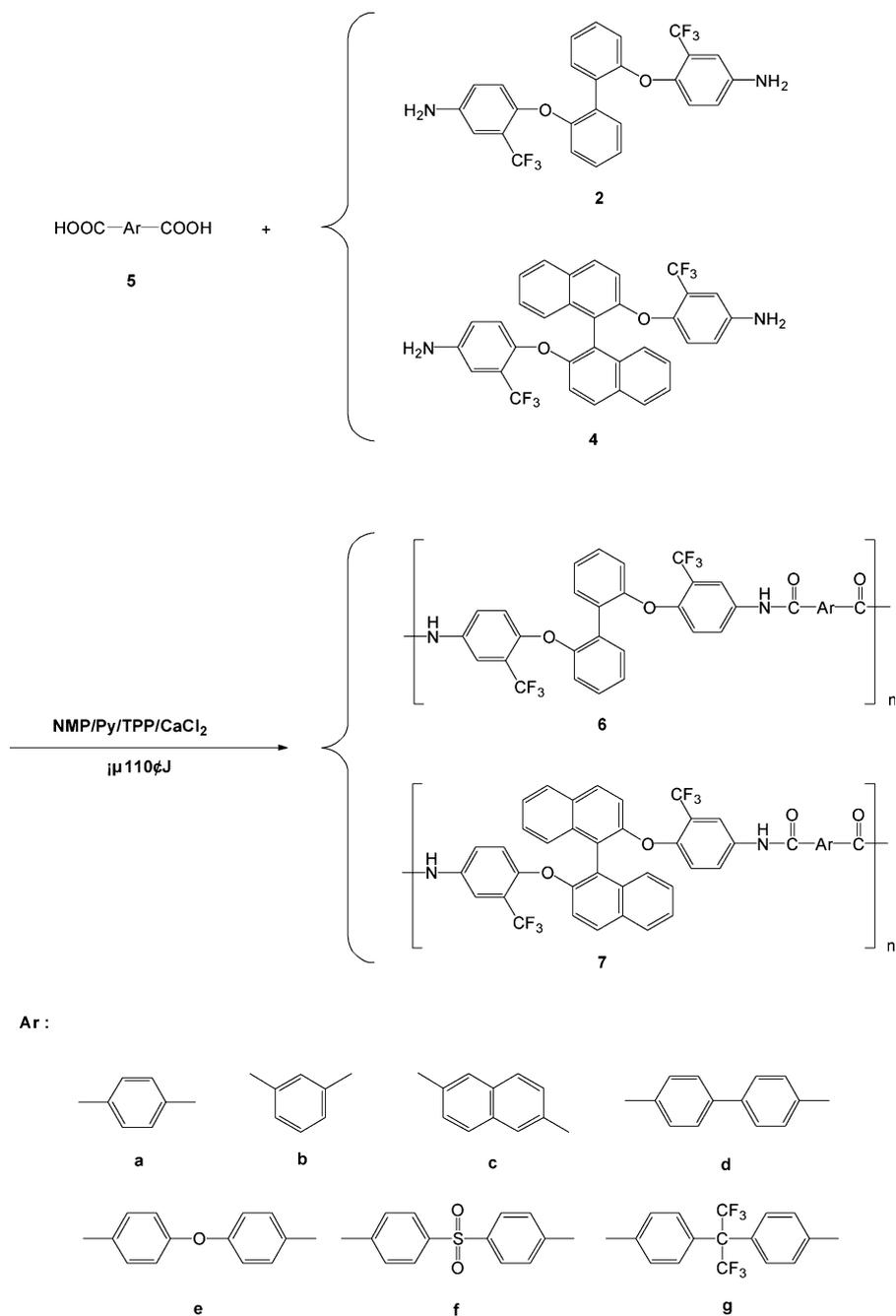


Fig. 2. ^1H NMR spectra of binaphthyl compounds 3 and 4 in DMSO- d_6 .

dropwise to the mixture. After a further 4 h reflux, the resultant clear, darkened solution was filtered hot to remove Pd/C, and the filtrate was then cooled to precipitate white-lump crystals (13.1 g, 90%); mp 194–195 °C (onset to the peak top temperature), by DSC at a

scan rate of 10 °C/min. IR (KBr): 3484, 3395 (N–H stretching), 1258, 1225 (C–O stretching), 1157, 1124 cm^{-1} (C–F stretching). ^1H NMR (DMSO- d_6) δ : 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,



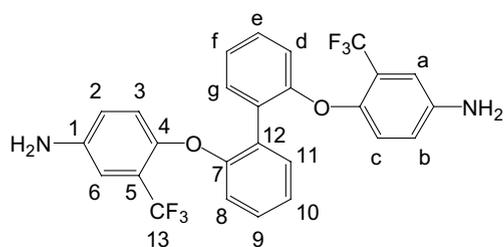
Scheme 2. Synthesis of polyamides.

$J = 7.5$ Hz, 2H, Hd), 6.64–6.72 (m, 6H, Ha,b,c), 5.34 (s, 4H, $-\text{NH}_2$). ^{13}C NMR (DMSO- d_6) δ : 155.27 (C^7), 145.19 (C^4), 143.24 (C^1), 131.79 (C^9), 128.99 (C^{11}), 128.04 (C^{12}), 123.05 (q, $^1J_{\text{C-F}} = 271$ Hz, C^{13}), 122.45 (C^2), 121.97

(C^{10}), 120.82 (q, $^2J_{\text{C-F}} = 33$ Hz, C^5), 118.53 (C^3), 116.65 (C^8), 110.65 (C^6). Anal. calcd for $\text{C}_{26}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_2$ (504.43): C, 61.91%, H, 3.60%, N, 5.55%. Found: C, 62.01%, H, 3.65%, N, 5.46%.

Table 1
Inherent viscosity and elemental analysis of polyamides

Polyamides		Elemental analysis (%) of polyamides				
Code	η_{inh}^a (dl/g)	Formula (formula weight)	C	H	N	
6a	0.50	(C ₃₄ H ₂₀ F ₆ N ₂ O ₄) _n	Calcd	64.30	3.15	4.41
		(634.56) _n	Found	62.54	3.12	4.47
6b	0.43	(C ₃₄ H ₂₀ F ₆ N ₂ O ₄) _n	Calcd	64.30	3.15	4.41
		(634.56) _n	Found	63.61	3.97	4.24
6c	0.46	(C ₃₈ H ₂₂ F ₆ N ₂ O ₄) _n	Calcd	66.60	3.21	4.09
		(684.62) _n	Found	65.66	3.88	4.61
6d	0.62	(C ₄₀ H ₂₄ F ₆ N ₂ O ₄) _n	Calcd	67.54	3.38	4.00
		(710.66) _n	Found	66.08	3.91	4.12
6e	0.57	(C ₄₀ H ₂₄ F ₆ N ₂ O ₅) _n	Calcd	66.06	3.30	3.85
		(726.66) _n	Found	64.49	3.71	3.86
6f	0.47	(C ₄₀ H ₂₄ F ₆ N ₂ O ₆ S) _n	Calcd	62.00	3.10	3.61
		(774.72) _n	Found	59.65	3.01	3.59
6g	0.51	(C ₄₁ H ₂₄ F ₁₂ N ₂ O ₄) _n	Calcd	60.00	2.79	3.25
		(860.68) _n	Found	58.62	3.05	3.04
7a	0.46	(C ₄₂ H ₂₄ F ₆ N ₂ O ₄) _n	Calcd	68.60	3.27	3.81
		(734.67) _n	Found	65.84	3.49	3.66
7b	0.36	(C ₄₂ H ₂₄ F ₆ N ₂ O ₄) _n	Calcd	68.60	3.27	3.81
		(734.67) _n	Found	65.26	3.78	3.53
7c	0.69	(C ₄₆ H ₂₆ F ₆ N ₂ O ₄) _n	Calcd	70.34	3.31	3.57
		(784.73) _n	Found	67.45	3.19	3.51
7d	0.74	(C ₄₈ H ₂₈ F ₆ N ₂ O ₄) _n	Calcd	71.04	3.45	3.45
		(810.77) _n	Found	69.95	3.39	3.67
7e	0.53	(C ₄₈ H ₂₈ F ₆ N ₂ O ₅) _n	Calcd	69.70	3.39	3.39
		(826.77) _n	Found	67.40	3.17	3.72
7f	0.49	(C ₄₈ H ₂₈ F ₆ N ₂ O ₆ S) _n	Calcd	65.84	3.20	3.20
		(874.83) _n	Found	62.97	3.04	3.54
7g	0.43	(C ₄₉ H ₂₈ F ₁₂ N ₂ O ₄) _n	Calcd	63.70	2.91	2.91
		(960.79) _n	Found	61.39	3.03	3.12



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 (14.3 g, 0.05 mol) and 2-chloro-5-nitrobenzotrifluoride

(23.3 g, 0.1 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 poured into 1.5 l of methanol/water (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 orange yellow-lump crystals (24.9 g, 75%); mp 164–168 °C (by DSC) (lit. [20] 165–167 °C). IR (KBr) (see Fig. 1): 1524, 1356 (–NO₂ stretching), 1287 (C–O stretching), 1141 cm⁻¹ (C–F stretching). ¹H NMR (DMSO-*d*₆) (for the assignment of peaks, see Fig. 2) δ : 8.24 (d, *J* = 2.7 Hz, 2H, Ha), 8.21 (d, *J* = 9.0 Hz, 2H, H,b), 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,

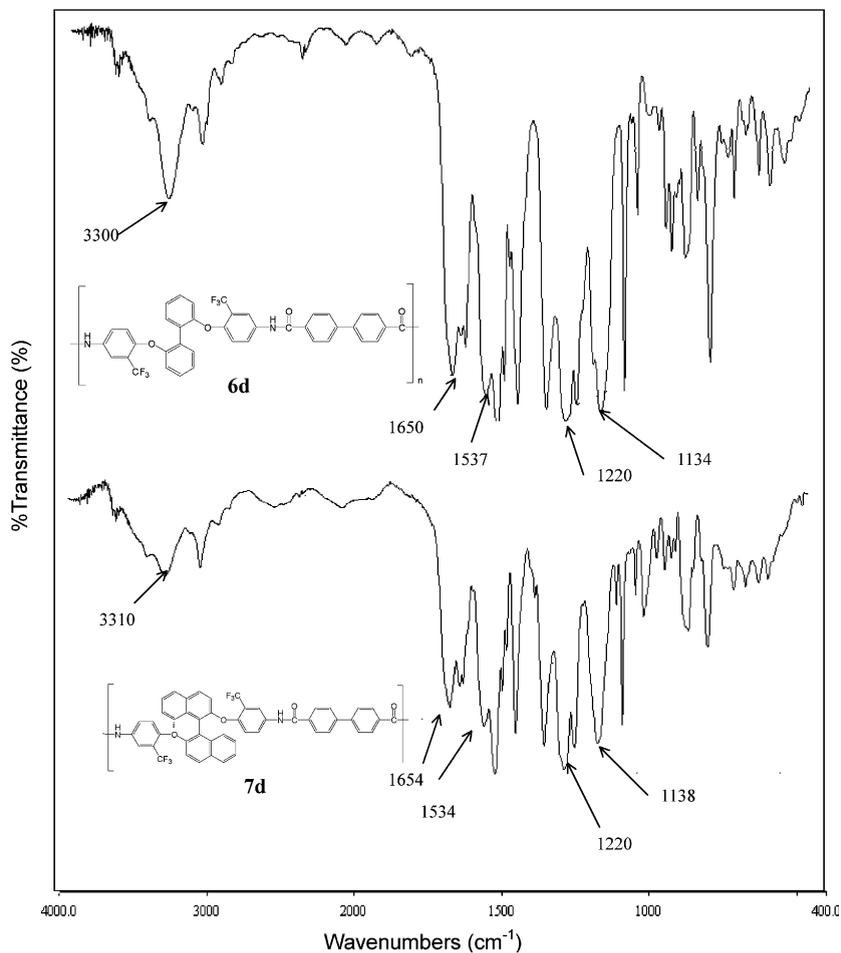


Fig. 3. IR spectra (film) of polyamides **6d** and **7d**.

$J = 9.0$ Hz, 2H, Hc). Anal. calcd for $C_{34}H_{18}F_6N_2O_6$ (664.54): C, 61.45%, H, 2.56%, N, 4.22%. Found: C, 61.78%, H, 3.00%, N, 4.56%.

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 ethanol in a 250-ml flask. The suspension solution was heated to reflux, and hydrazine monohydrate (10 ml) was added dropwise to the mixture at reflux temperature for about 6 h. After cooling, about 100 ml of tetrahydrofuran (THF) was added to dissolve the precipitated product during the refluxing. The 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. [20] 264–266 °C). IR (KBr): 3482, 3386 (N–H stretching), 1258 (C–O stretching), 1130 cm^{-1} (C–F stretching). 1H NMR (DMSO- d_6) (for the assignment of

peaks, see Fig. 2) δ : 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). Anal. calcd for $C_{34}H_{22}F_6N_2O_2$ (604.54): C, 67.55%, H, 3.67%, N, 4.63%. Found: C, 67.34%, H, 4.17%, N, 5.07%.

2.3. Polymer synthesis

A typical synthetic procedure for polyamide **7d** is described as follows. A mixture of 0.7254 g (1.2 mmol) of CF₃-diamine **4**, 0.2907 g (1.2 mmol) of 4,4'-diphenyldicarboxylic acid (**5d**), 0.2 g of calcium chloride, 4.5 ml of *N*-methyl-2-pyrrolidinone (NMP), 1.1 ml of pyridine (Py), and 0.9 ml of triphenyl phosphite (TPP) was heated with stirring at 110 °C for 4 h. As the polycondensation proceeded, the reaction mixture became viscous gradually. The resultant solution of the polymer

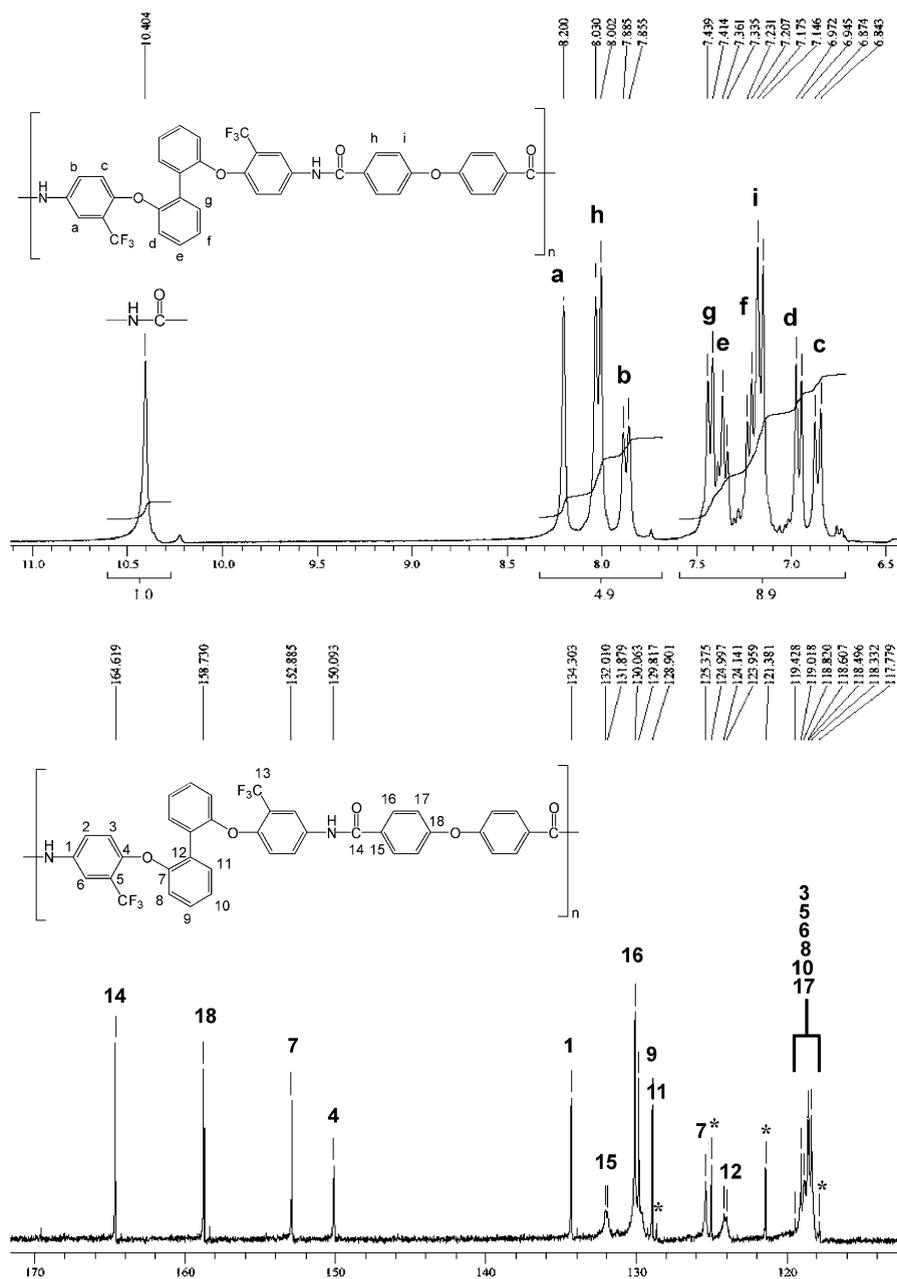


Fig. 4. The ¹H NMR and ¹³C NMR spectra of polyamide **6e** in DMSO-*d*₆.

was poured slowly into 300 ml of stirred methanol giving rise to a tough, fiber-like polymer precipitate. The product was collected by filtration, thoroughly washed by methanol and hot water, and dried. The inherent viscosity of the polyamide (**7d**) was 0.74 dl/g, as measured at concentration of 0.5 g/dl in DMAc at 30 °C.

2.4. Preparation of the polyamide films

A solution of polymer was made by dissolving about 0.8 g of the polyamide in 8 ml of DMAc to afford an approximate 10% solution. The homogeneous solution was poured into a 9-cm diameter glass culture dish,

which was placed in a 120 °C oven for one day for the slow release of the solvent. The polyamide film was released from the glass substrate and further dried in vacuo at 160 °C for 10 h. The obtained films were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

2.5. Measurements

Infrared spectra were recorded on a PerkinElmer RXI FT-IR spectrometer. Elemental analyses were in a Heraeus CHN-OS rapid element analyzer. ¹H and ¹³C NMR spectra were measured on a Varian Unity Inova-300WB spectrometer. The inherent viscosities were determined at 0.5 g/dl concentration using a Tamson TV-2000 viscometer at 30 °C. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-7000

X-ray diffractometer (40 kV, 20 mA), using graphite-monochromatized CuK α radiation. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Varian Cary 50 Probe spectrometer. An Instron universal tester model 4400R with a load cell of 5 kg was used to study the stress–strain behavior of the polyamide 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 scan rate of 20 °C/min in flowing nitrogen (20 cm³/min). Glass transition

Table 2
Solubility behavior of polyamides

Polymer code	Solvents ^a								
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Pyridine	THF	Chloroform	H ₂ SO ₄
6a	++	++	++	++	++	++	++	–	++
6b	++	++	++	++	++	++	++	–	++
6c	++	++	++	++	++	++	++	–	++
6d	++	++	++	++	++	++	++	–	++
6e	++	++	++	++	++	++	++	–	++
6f	++	++	++	++	++	++	++	–	++
6g	++	++	++	++	++	++	++	–	++
7a	++	++	++	++	++	++	++	–	++
7b	++	++	++	++	++	++	++	–	++
7c	++	++	++	++	++	++	++	–	++
7d	++	++	++	++	++	++	++	–	++
7e	++	++	++	++	++	++	++	–	++
7f	++	++	++	++	++	++	++	–	++
7g	++	++	++	++	++	++	++	+–	++
6a'	++	++	++	++	++	++	– ^b	– ^b	++
6b'	++	++	–	–	–	–	–	–	++
6c	++	++	–	–	–	–	–	–	++
6d'	++	–	–	–	–	–	–	–	++
6e'	++	++	–	–	–	–	–	–	++
6f'	++	++	++	++	++	++	–	–	++
7a'	++	++	++	++	++	++	–	–	++
7b'	++	++	++	++	–	–	–	–	++
7c'	++	++	++	++	+	+	–	–	++
7d'	++	–	–	+	–	–	–	–	++
7e'	++	++	++	++	++	++	–	–	++
7f'	++	++	++	++	++	++	–	–	++

^a The solubility was determined by using 2 mg sample in 2 mL of solvent. ++ = soluble at room temperature; + = soluble on heating; +– = partial soluble on heating; – = insoluble even on heating. NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran. The solubility behavior data of the referenced **6'** and **7'** series polyamides are those reported previously (see Ref. [5]).

^b The solubility was measured from methanol and acetone in Ref. [5].

Table 3
Mechanical properties and optical transparency of polyamide films

Polymer code	Tensile strength (MPa)	Elongation to break (%)	Initial modulus (GPa)	Cutoff wave length ^a (λ_0 , nm)
6a	58	6	1.9	365
6b	49	9	1.7	348
6c	58	7	1.9	382
6d	59	7	1.9	375
6e	71	8	1.9	336
6f	51	5	1.7	389
6g	66	7	1.9	352
7a	62	6	2.1	367
7b	48	5	1.4	347
7c	73	14	2.0	380
7d	61	21	1.8	375
7e	72	15	1.4	347
7f	57	9	1.7	380
7g	60	8	1.7	360

^a Absorption edge from the UV–vis spectra of the polyamide films.

temperatures (T_g s) were read at the middle of the transition in the heat capacity. Thermomechanical analysis

(TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted from 50 to 300 °C at a scan rate of 10 °C/min with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (T_s) were taken as the onset temperatures of probe displacement on the TMA traces.

3. Results and discussion

3.1. Monomer synthesis

The two main monomers including CF_3 -bis(ether amine)s **2** and **4** were prepared in two steps according to a well-developed method [5,13], as shown in Scheme 1. The first step was a Williamson etherification of 2,2'-biphenol and 2,2'-dihydroxy-1,1'-binaphthyl with 2-chloro-5-nitrobenzotrifluoride in the presence of potassium carbonate and sodium hydride in DMAc and DMF, respectively. The diamines **2** and **4** were readily obtained in high yields by the catalytic reduction of intermediate dinitro compounds **1** and **3** with hydrazine monohydrate using Pd/C as the catalyst in refluxing

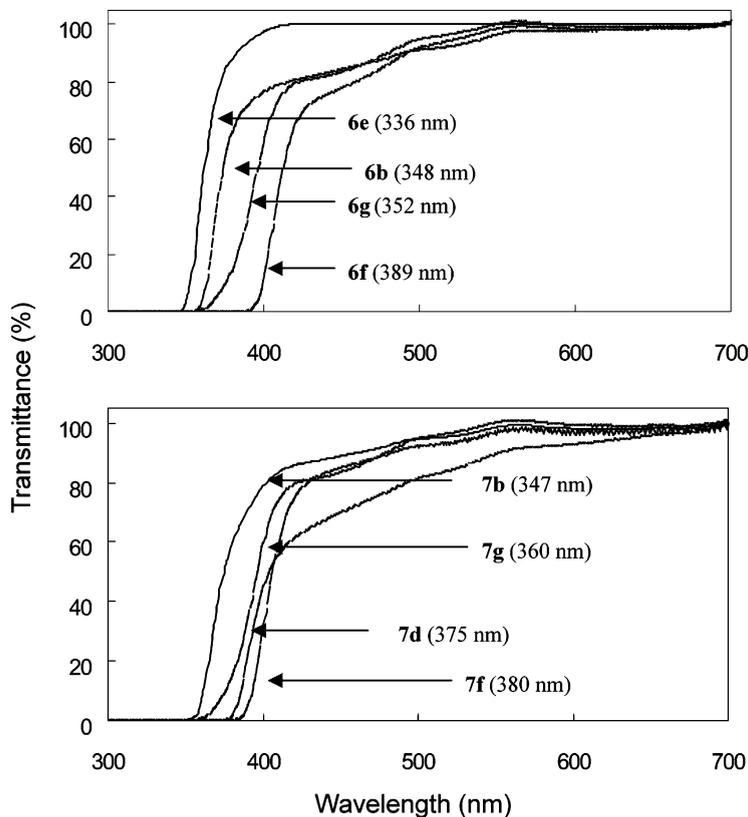


Fig. 5. Transmission UV–visible absorption spectra of some polyamide films. The value indicated in the parentheses is the cutoff wave length.

ethanol. The structures of **1–4** were confirmed by FTIR, NMR, and elemental analysis. A typical set of FTIR spectra of dinitro compound **3** and diamine **4** is illustrated in Fig. 1. Absorption bands representative of the nitro functionality were identified in the FTIR spectrum. The nitro group of compound **3** gave two characteristic bands at 1524 and 1356 cm^{-1} (NO_2 asymmetric and symmetric stretching). After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed the typical N–H stretching bands at 3482 and 3386 cm^{-1} . Fig. 2 displays the ^1H NMR spectra of binaphthyl compounds **3** and **4**. The ^1H NMR spectra confirm that the nitro groups have been completely transformed into the amino groups by the upfield shift of the aromatic protons and by the signal at 5.37 ppm peculiar to the amino protons. The structures of the synthesized compounds were also confirmed by ^{13}C NMR spectroscopy. As described in the experimental section, the ^{13}C NMR spectrum of the CF_3 -diamine **2** shows two clear quartets because of the heteronuclear ^{13}C – ^{19}F coupling. The large quartet centered at about 123.5 ppm is due to the $-\text{CF}_3$ carbons. The one-bond C–F coupling constant in this case is about 271 Hz. The CF_3 -attached carbon also shows a clear quartet centered at about 120.8 ppm with a smaller coupling constant of about 33 Hz due to two-bond C–F coupling. These quartet signals corroborate the presence of CF_3 group in the synthesized compounds. Thus, all the spectroscopic data obtained were in good agreement with the expected chemical structures.

3.2. Polymer synthesis

According to the phosphorylation technique first described by Yamazaki et al. [21,22], two series of new aromatic fluorinated polyamides **6a–g** and **7a–g** were synthesized from the trifluoromethylated diamines **2** and **4** with various aromatic dicarboxylic acids **5a–g** (Scheme 2). The polymerization was carried out via solution polycondensation using triphenyl phosphite (TPP) and pyridine (Py) as condensing agents in the NMP solution containing dissolved calcium chloride. All polymerization reactions proceeded homogeneously throughout the reaction and gave clear and viscous polymer solutions. As shown in Table 1, the resulting **6** and **7** series polyamides had inherent viscosities in the range of 0.43–0.62 dl/g and 0.36–0.74 dl/g, respectively. All of the polyamides could be fabricated into transparent and flexible films, indicating medium to high molecular weight polymer formation. FTIR, NMR, and elemental analysis confirmed the chemical structures of these polyamides. They showed characteristic FTIR absorption bands of the amide group around 3300 (N–H stretching), 1654 (C=O stretching), 1537 cm^{-1} (N–H bending), and 1134 cm^{-1} (C–F stretching), along with the characteristic absorption bands of aryl ether

Table 4
Thermal behavior data of polyamides^a

Poly- mer code	T_g^b (°C)	T_s^c (°C)	T_d^d (°C)		Char yield ^e (%)
			In N_2	In air	
6a	– ^f (–) ^g	199	460	450	56
6b	190 (215)	196	426	420	55
6c	233 (–)	210	488	462	59
6d	– (–)	221	490	442	59
6e	215 (200)	209	473	433	56
6f	237 (240)	227	474	440	56
6g	240	230	505	463	55
7a	– (300)	291	500	476	51
7b	255 (277)	260	500	462	56
7c	255 (290)	258	484	478	61
7d	251 (–)	–	549	476	66
7e	253 (266)	258	501	460	61
7f	248 (290)	241	513	458	59
7g	254	257	520	485	58

^a The samples were heated at 250 °C for 1 h prior to DSC, TMA, and TGA experiments.

^b Midpoint temperature of baseline shift on the DSC heating trace at a scan rate of 20 °C/min.

^c Softening temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C/min.

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

^e Residual weight % at 800 °C in nitrogen.

^f No discernible transition.

^g Data in the parentheses are the reported data of the non-fluorinated **6'** and **7'** polyamides (see Ref. [5]).

stretching near 1220 cm^{-1} . A typical set of IR spectra for the thin films of polyamides **6d** and **7d** are illustrated in Fig. 3. As a typical example, the structure of polyamide **6e** was also confirmed by solution NMR in $\text{DMSO}-d_6$ (Fig. 4). The formation of amide groups was verified by the resonance signals of amide protons at δ 10.4 in the ^1H NMR spectrum and amide carbons at δ 164.6 in the ^{13}C NMR spectrum. The results of elemental analysis are also reported in Table 1. Elemental analyses are generally in good agreement with the proposed structures, missing only the values found for the C-percentages that are always lower than the theoretical ones. That certainly can be attributed to the very aromatic nature of these polyamides, which commonly leave a small coal residue in the standard conditions of micro-analysis.

3.3. Polymer properties

All the polymers were characterized by WAXD studies in the film form. As expected, all the polyamides displayed a nearly completely amorphous pattern. When comparing the WAXD patterns of the **6** series polyamides with those of analogous counterparts of the **6'** series [5], the introduction of the pendent CF_3 groups

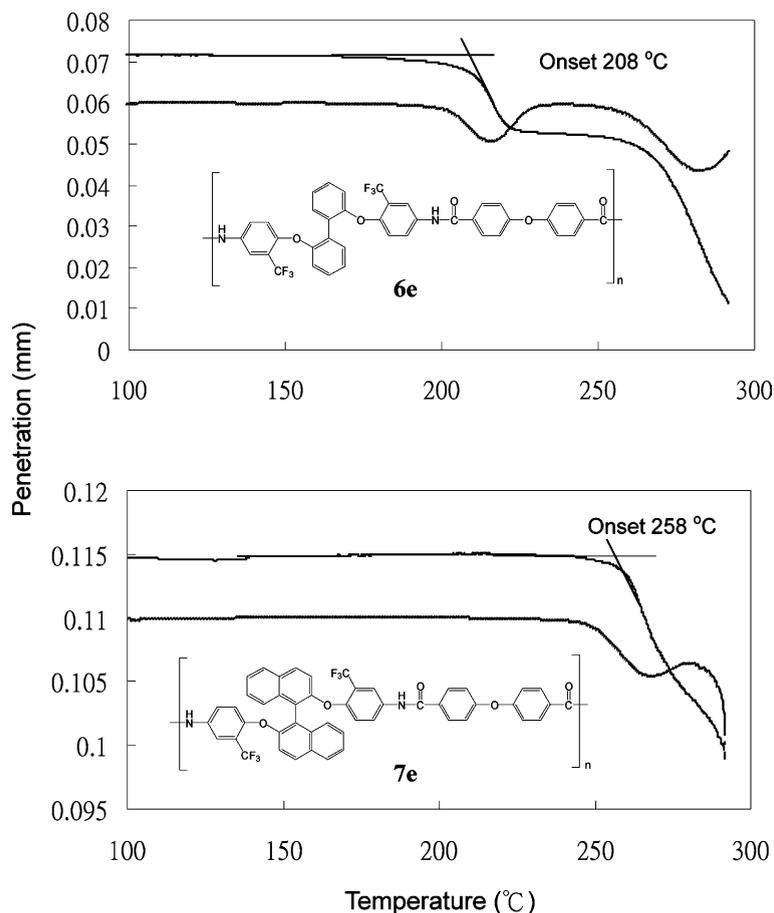
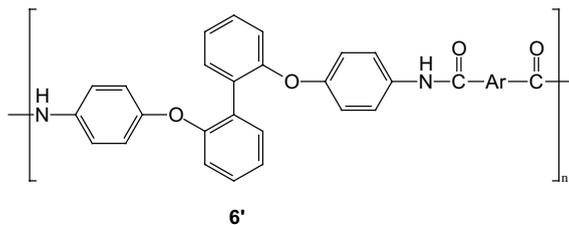


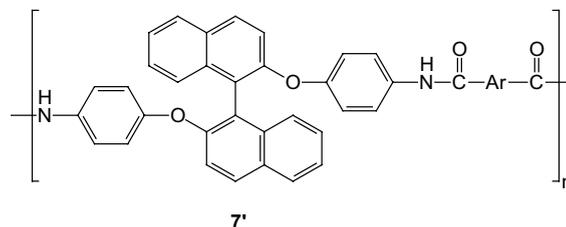
Fig. 6. Typical TMA thermograms for polyamides **6e** and **7e** (heating rate = 10 °C/min; applied force = 10 mN).

revealed an obvious effect on decreasing the crystallinity of these polyamides. The incorporation of bulky side groups produces wider separation of polymer chains, weakening intermolecular hydrogen bonding, and a lowering of chain packing efficiency with a gain of free volume, thus resulting in a decrease in crystallinity.



The solubility behavior of polyamides was tested qualitatively, and the results are presented in Table 2. Due to the amorphous nature and the decreased chain-chain interactions, all the **6** and **7** series polyamides were highly soluble in polar solvents such as NMP, DMAc,

DMF, dimethyl sulfoxide (DMSO), *m*-cresol, and even in less polar pyridine and tetrahydrofuran (THF). For comparison, the solubility behavior of the corresponding non-fluorinated **6'** and **7'** series polyamides reported previously [5] was also included in Table 2. Polyamides **6b'** to **6e'** were insoluble in many solvents such as DMF, DMSO, *m*-cresol, and pyridine. In contrast, the CF₃-containing polyamides **6b** to **6e** were soluble in these solvents. It is evident that the incorporation of the CF₃ substituents improves the solubility of these polyamides. The reason is similar to that cited above.



All polyamides could be readily processed to flexible, creasable, and essentially colorless films by casting from solutions in DMAc. The tensile properties of the polyamide films are summarized in Table 3. Their tensile strengths, elongations at break, and initial moduli of polymer films of the **6** series were in the range of 49–71 MPa, 5–9%, and 1.7–1.9 GPa, and polymer films of the **7** series were 48–72 MPa, 5–12%, and 1.4–2.1 GPa, respectively. Diamines **2** and **4** contain the twisted 2,2'-disubstituted biphenyl and binaphthyl units and a bulky pendent group and thus provide a highly irregular structure to the polyamide. This was expected to disrupt the dense packing of molecular chains and lead to low color polymer films. The thin films were measured for optical transparency using UV-vis spectroscopy. Fig. 5 depicts the UV-vis spectra of the typical polyamide films and the cutoff wave lengths (absorption edge, λ_0). The λ_0 values of all the fluorinated polyamides are also reported in Table 3. All the polyamides had λ_0 shorter than 400 nm and most of them exhibited high optical transparency higher than 80% transmittance at 500 nm.

DSC, TMA, and TGA were used to evaluate the thermal properties of these polyamides. Their thermal behavior data are compiled in Table 4. The occurrence of thermal transitions in the polyamides was investigated by DSC on samples being preheated at 250 °C for 1 h. All the polyamides, except for **6a**, **6d**, and **7a**, displayed well-defined slope changes arising from second-

order transitions in the temperature range of 190–240 °C (for the **6** series) and 247–255 °C (for the **7** series), generally following the increasing order of chain rigidity. Polyamides **6a**, **6d**, and **7a** did not show discernible T_g on their DSC curves possibly due to the rigid-rod structure of the diacid components. The T_g s of the **7** series polyamides derived from **4** were higher than those of the corresponding **6** series polyamides derived from **2** due to the higher bulky effect of the 1,1'-binaphthyl units. The T_g data of structurally similar polyamides **6'** and **7'** that reported in a previous publication [5] are also presented in Table 4. The lower T_g values of the **6'** and **7** series polyamides in comparison to the corresponding **6'** and **7'** counterparts may be explained in terms of the decreased intermolecular interactions caused by the CF₃ side groups. The softening temperatures (T_s) of the polymer film samples were measured by TMA using the penetration method, and the data were obtained from the onset temperature of the probe displacement on the TMA trace. Typical TMA thermograms for polymers **6e** and **7e** are illustrated in Fig. 6. All polymers showed well-defined T_s on the TMA traces except **7d**. In most cases, the T_s values obtained by TMA are comparable to the T_g values observed by DSC, and the **6** series polyamides also exhibited lower T_s values compared with the corresponding **7** series ones.

The thermal and thermo-oxidative stability of the polyamides was evaluated by TGA in both nitrogen and

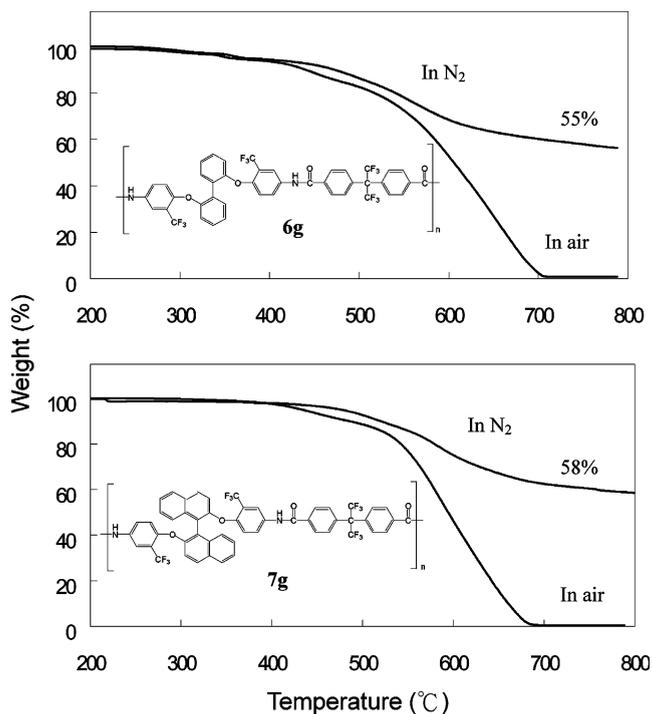


Fig. 7. TGA curves of polyamides **6g** and **7g** (heating rate = 20 °C/min).

air atmospheres. For illustration, two typical sets of TGA curves for polyamides **6g** and **7g** are reproduced in Fig. 7. The decomposition temperatures at a 10% weight loss determined from the original TGA curves are listed in Table 4. All polymers exhibited good thermal stability with insignificant weight loss up to temperature of approximately 400 °C in both air and nitrogen atmospheres, and the anaerobic char yield at 800 °C for all polymers were in the range of 55–59 wt.% (**6** series) and 51–66 wt.% (**7** series). In general, the polyamides **7** series showed higher thermal stability in comparison with the **6** series analogues.

4. Conclusions

Aromatic diamines having the CF₃ group and a kinked and cranked structure, 2,2'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (**2**) and 2,2'-bis(4-amino-2-trifluoromethylphenoxy)-1,1'-binaphthyl (**4**), were successfully synthesized in high purity and high yields. Two sets of novel fluorinated aromatic polyamides were prepared by the direct polycondensation of these two diamines and various aromatic dicarboxylic acids using the Yamazaki–Higashi phosphorylation technique. The introduction of the bulky trifluoromethyl group could disturb the coplanarity of aromatic units in chain packing while increasing the spacing or free volume between polymer chains. All the polyamides displayed significantly increased solubility in common organic solvents and decreased crystallinity when compared to analogous non-fluorinated polyamides, and could be cast to transparent, light-colored, and flexible films with moderately high glass transition temperatures and thermal stability.

Acknowledgements

The authors are grateful to the National Science Council of the Republic of China for financial support of this work (Grant NSC 92-2216-E-260-001).

References

- [1] Cassidy PE. Thermally stable polymers. New York: Dekker; 1980.
- [2] Yang HH. Aromatic polyamides, in aromatic high-strength fibers. New York: Wiley; 1989. p. 66–289.
- [3] Oishi Y, Takado H, Yoneyama M, Kakimoto M, Imai Y. J Polym Sci A: Polym Chem 1990;28:1763.
- [4] Yamashita M, Kakimoto M, Imai Y. J Polym Sci A: Polym Chem 1993;31:1513.
- [5] Liou GS, Maruyama M, Kakimoto M, Imai Y. J Polym Sci A: Polym Chem 1993;31:2499.
- [6] Yang CP, Lin JH. J Polym Sci A: Polym Chem 1993; 31:2153.
- [7] Maglio G, Palumbo R, Vignola MC. Macromol Chem Phys 1995;196:775.
- [8] Chern YT, Lin KS, Kao SC. J Appl Polym Sci 1998; 68:315.
- [9] Hsiao SH, Yang CP, Chuang MH, Hsiao HC. J Polym Sci A: Polym Chem 2000;38:247.
- [10] Espeso JF, Ferrero E, de la Campa JG, Lozano AE, de Abajo J. J Polym Sci A: Polym Chem 2001;39:475.
- [11] Liou GS, Hsiao SH. J Polym Sci A: Polym Chem 2003; 41:94.
- [12] Wu SC, Shu CF. J Polym Sci A: Polym Chem 2003; 41:1160.
- [13] Liou GS, Maruyama M, Kakimoto M, Imai Y. J Polym Sci A: Polym Chem 1993;31:3273.
- [14] Liou GS, Kakimoto M, Imai Y. J Polym Sci A: Polym Chem 1993;31:3265.
- [15] Kress RB, Duesler EN, Etter MC, Paul IC, Curtin DY. J Am Chem Soc 1980;102:7709.
- [16] Gao JP, Wang ZY. J Polym Sci A: Polym Chem 1995; 33:1627.
- [17] Xie K, Zhang SY, Liu JG, He MH, Yang SY. J Polym Sci A: Polym Chem 2001;39:2581.
- [18] Hsiao SH, Yang CP, Chung CL. J Polym Sci A: Polym Chem 2003;41:2001.
- [19] Vora RH, Krishnan PSG, Goh SH, Chung TS. Adv Funct Mater 2001;11:361.
- [20] Mi Q, Ma Y, Gao L, Ding M. J Polym Sci A: Polym Chem 1999;37:4536.
- [21] Yamazaki N, Higashi F, Kawabata J. J Polym Sci Polym Chem Ed 1974;12:2149.
- [22] Yamazaki N, Matsumoto M, Higashi F. J Polym Sci Polym Chem Ed 1975;13:1375.