Synthesis and Properties of Soluble Aromatic Polyamides Derived from 2,2′-Bis(4-carboxyphenoxy)-9,9′-spirobifluorene

SHEN-CHANG WU, CHING-FONG SHU

Department of Applied Chemistry, National Chiao Tung University, 1001 Ta Hsueh Road, Hsin-Chu, Taiwan 30035, Republic of China

Received 24 November 2002; accepted 29 January 2003

ABSTRACT: The synthesis of a new bis(ether carboxylic acid), 2,2′-bis(4-carboxyphenoxy)-9,9′-spirobifluorene, in which two orthogonally arranged carboxyphenoxyfluorene entities are connected through an sp^3 carbon atom (the spiro center), is reported. The direct phosphorylation polycondensation of this diacid monomer with various aromatic diamines yields aromatic polyamides containing 9,9′-spirobifluorene moieties in the main chain. The presence of the spiro segment restricts the close packing of the polymer chains and decreases interchain interactions, resulting in amorphous polyamides with enhanced solubility, and high glass-transition temperatures and good thermal stability are maintained through controlled segmental mobility. The glass-transition temperatures of these polyamides are in the range of 234–306 °C, with 10% weight losses occurring at temperatures above 530 °C. © 2003 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 41: 1160–1166, 2003

Keywords: amorphous; polyamides; spirobifluorene; solubility; thermal properties

INTRODUCTION

Aromatic polyamides are well known as high-performance polymers because of their combination of excellent thermal, mechanical, and chemical properties.[1–5] Despite their outstanding properties, the infusibility and limited solubility of aromatic polyamides restrict their areas of application. Therefore, much research effort has been directed at improving their processability without compromising their other desired properties. The strategies that have been employed to enhance the solubility of polyamides include the introduction of flexible linkages,[6–11] alkylphthalimido pendant groups,[12] bulky lateral groups,[13–17] and kinked or noncoplanar structures[18–25] into the polymer backbone.

It has been demonstrated that incorporating a spirobifluorene linkage into defined, low molecular weight structures leads to amorphous materials with an improvement in both solubility and thermal stability.[26–32] Such spiro structures have also been applied to polymeric materials such as polyfluorenes,[33–35] polyquinolines,[36] and polyimides[37,38] to enhance their solubility, glass-transition temperature (T_g), and thermal stability. In a continuation of our studies on spirobifluorene-based polymers, we herein report on the synthesis of organosoluble aromatic polyamides containing 9,9′-spirobifluorene (**1**) moieties along with flexible ether linkages in the polymer main chain, based on a novel diacid monomer: 2,2′-bis(4-carboxyphenoxy)-9,9′-spirobifluorene (**6**). In this spiro-fused monomer, the two identical carboxyphenoxyfluorene moieties are orthogonally arranged and are connected through a common sp^3 carbon atom, the spiro center.[39,40] The resulting polyamides are anticipated to have a polymer

Correspondence to: C.-F. Shu (E-mail: shu@cc.nctu.edu.tw)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 41, 1160–1166 (2003)

backbone periodically twisted by an angle of 90° at each spiro center. This structural feature would restrict interchain interactions and decrease hydrogen bonding between the amide groups. As a result, the packing efficiency and crystallinity of the polymers are reduced to yield soluble polyamides. In addition, the rigidity of the main chain would be preserved because of the presence of the spiro structure, with both high T_g's and good thermal stability maintained. The solubility, crystallinity, and thermal properties of the obtained polyamides have been examined.

EXPERIMENTAL

Materials

2,2′-Dihydroxy-9,9′-spirobifluorene (**4**) was prepared as described in the literature.[41] 3,3′-Methylenedianiline (**7a**), 4,4′-oxydianiline (**7b**), and 9,9-bis(4-aminophenyl)fluorene (**7e**) were recrystallized from ethanol. 4,4′-(Hexafluoroisopropylidene)dianiline (**7c**) and 1,4-phenylenediamine (**7f**) were purified by vacuum sublimation. 1,3-Phenylenediamine (**7d**) was vacuum-distilled before use. *N*-Methyl-2-pyrrolidinone (NMP) and *N,N*-dimethylformamide (DMF) were distilled over CaH_2 under reduced pressure. Pyridine (Py) was dried by distillation after being refluxed with KOH. Triphenylphosphite (TPP) was purified by distillation under reduced pressure. LiCl was dried at 120 °C *in vacuo*. All other reagents and solvents were used as received from commercial sources unless otherwise stated.

Characterization

^1H and ^{13}C NMR spectra were recorded with a Varian Unity 300-MHz or Bruker-DRX 300-MHz spectrometer. IR spectra were taken with a Nicolet 360 FTIR spectrometer. Mass spectra were obtained with a JEOL JMS-SX/SX 102A mass spectrometer. Gel permeation chromatography (GPC) was carried out with a Waters chromatograph connected to a Waters 410 differential refractometer. Three 5-μm Waters Styragel columns (300 × 7.8 mm) were connected in series and in decreasing order of pore size (10^5, 10^4, and 10^3 Å), with DMF as the eluent; poly(methyl methacrylate) (PMMA) standard samples were used for calibration. Differential scanning calorimetry (DSC) was performed with a DuPont TA 2000 instrument at a heating/cooling rate of 20 °C min^{-1}. Samples were scanned from 30 to 350 °C and then cooled to 30 °C and scanned for a second time over the same range. T_g was determined from the second heating scan. Thermogravimetric analysis (TGA) was made with a DuPont TGA 2950 instrument. The thermal stabilities of all the samples were determined in nitrogen by the measurement of the weight loss during heating at a rate of 20 °C min^{-1}. X-ray crystal structure determination was performed with a Bruker Smater Apex diffractometer with graphite monochromated Mo Kα radiation (λ = 0.7107 Å). Structure analyses were performed with the SHELXTL/PC program. Wide-angle X-ray diffraction patterns were obtained at room temperature with a Rigaku XRD-RU 200 (Cu Kα, 40 mA, 30 kV) at a sampling step of 0.02° and at a scan rate of 5° min^{-1}.

2,2′-Bis(4-cyanophenoxy)-9,9′-spirobifluorene (5)

A mixture of **4** (5.00 g, 14.4 mmol), 4-fluorobenzonitrile (3.83 g, 31.7 mmol), potassium carbonate (4.38 g, 31.7 mmol), and anhydrous DMF (30 mL) was heated at 100 °C for 24 h under nitrogen. After cooling, the resulting solution was slowly added into water (300 mL). The precipitate obtained was collected by filtration, washed repeatedly with water and hexane, and dried *in vacuo*. The product was recrystallized from methanol to afford **5** (7.20 g, 90.9%).

^1H NMR [dimethyl sulfoxide-d_6 (DMSO-d_6), δ]: 8.08 (d, 2H, J = 8.4 Hz), 7.99 (d, 2 H, J = 7.5 Hz), 7.75 (d, 4H, J = 8.7 Hz), 7.40 (dd, 2H, J = 7.5, 7.5 Hz), 7.17 (dd, 2H, J = 8.4, 2.1 Hz), 7.14 (dd, 2H, J = 7.5, 7.5 Hz), 6.97 (d, 4H, J = 8.7 Hz), 6.65 (d, 2H, J = 7.5 Hz), 6.41 (d, 2H, J = 2.1 Hz). ^{13}C NMR (DMSO-d_6, δ): 160.9, 154.3, 150.1, 147.8, 140.4, 138.3, 134.4, 128.2, 127.9, 123.3, 122.3, 120.6, 120.1, 118.5, 117.8, 115.4, 105.1, 65.4. IR (KBr): 2223 (C≡N), 1250 cm^{-1} (C—O). High-resolution mass spectrometry (HRMS): [M^+], 550.1677. Calcd. for $C_{39}H_{22}N_2O_2$, 550.1681. ELEM. ANAL. Calcd.: C, 85.07%; H, 4.03%; N, 5.09%. Found: C, 85.14%; H, 4.41%; N, 5.00%.

2,2′-Bis(4-carboxyphenoxy)-9,9′-spirobifluorene (6)

To a solution of potassium hydroxide (5.0 g) in a mixture of water and ethanol (20 mL/40 mL) was added compound **5** (1.00 g, 1.81 mmol). The mixture was then refluxed for 54 h. The resulting solution was cooled and acidified with 6 N HCl (aqueous). The precipitate was filtered, washed thoroughly with water, and dried. The product

was purified by recrystallization from acetic acid to give **6** (0.92 g, 86.5%).

^{1}H NMR (DMSO-d_6, δ): 12.62 (s, 2H), 8.05 (d, 2H, J = 8.7 Hz), 7.97 (d, 2H, J = 7.5 Hz), 7.86 (d, 4H, J = 8.7 Hz), 7.39 (dd, 2H, J = 7.8, 7.5 Hz), 7.14 (dd, 2H, J = 7.8, 6.6 Hz), 7.13 (dd, 2H, J = 8.4, 2.1 Hz), 6.92 (d, 4H, J = 8.7 Hz), 6.66 (d, 2H, J = 7.8 Hz), 6.35 (d, 2H, J = 2.1 Hz). ^{13}C NMR (DMSO-d_6, δ): 166.7, 160.8, 155.2, 150.2, 147.9, 140.6, 137.8, 131.6, 128.2, 127.8, 125.4, 123.5, 122.2, 120.5, 119.7, 117.2, 115.0, 65.4. IR (KBr): 2500–3400 (broad, O—H), 1685 cm^{-1} (C═O). HRMS: [M$^+$], 588.1564. Calcd. for $C_{39}H_{24}O_6$, 588.1573. ELEM. ANAL. Calcd.: C, 79.58%; H, 4.11%. Found: C, 79.22%; H, 4.34%.

Polymerization

A typical polymerization procedure was as follows. A mixture of diacid **6** (472 mg, 800 μmol), diamine **7a** (159 mg, 800 μmol), LiCl (70 mg, 1.6 mmol), TPP (0.70 mL, 2.7 mmol), Py (0.75 mL), and NMP (3.0 mL) was heated at 150 °C under nitrogen for 8 h. After cooling, the reaction mixture was added dropwise to an agitated methanol solution (100 mL). The precipitate was collected by filtration, washed thoroughly with methanol and hot water, and dried *in vacuo* to give polyamide **8a**, which was purified by reprecipitation from tetrahydrofuran (THF) into methanol twice.

8a

Yield: 93.1%. ^{1}H NMR (DMSO-d_6, δ): 10.08 (s, 2H), 7.98 (d, 2H, J = 8.1 Hz), 7.91–7.85 (m, 6H), 7.57 (d, 2H, J = 7.8 Hz), 7.56 (s, 2H), 7.32 (dd, 2H, J = 7.2, 6.9 Hz), 7.18 (dd, 2H, J = 7.2, 7.2 Hz), 7.12–7.02 (m, 4H), 6.91 (d, 6H, J = 7.2 Hz), 6.60 (d, 2H, J = 7.5 Hz), 6.31 (s, 2H), 3.83 (s, 2H). ^{13}C NMR (DMSO-d_6, δ): 164.5, 159.4, 155.6, 150.1, 147.8, 141.5, 140.5, 139.3, 137.5, 129.9, 129.6, 128.6, 128.2, 127.8, 124.1, 123.4, 122.2, 120.6, 120.4, 119.3, 118.2, 117.3, 114.5, 65.4. IR (KBr): 3309 (N—H), 1655 (C═O), 1255 cm^{-1} (C—O).

8b

Yield: 94.0%. ^{1}H NMR (DMSO-d_6, δ): 10.15 (s, 2H), 8.03 (d, 2H, J = 8.1 Hz), 7.95 (d, 2H, J = 7.8 Hz), 7.90 (d, 4H, J = 8.4 Hz), 7.71 (d, 4H, J = 8.4 Hz), 7.37 (dd, 2H, J = 7.8, 6.9 Hz), 7.17–7.07 (m, 4H), 7.01–6.89 (m, 8H), 6.65 (d, 2H, J = 7.5 Hz), 6.34 (s, 2 H). ^{13}C NMR (DMSO-d_6, δ): 164.4, 159.5, 155.6, 152.8, 150.2, 147.9, 140.5, 137.5, 134.7, 129.8, 129.6, 128.2, 127.8, 123.4, 122.1, 120.4, 119.3,118.5, 117.4, 114.5, 65.4. IR (KBr): 3314 (N—H), 1655 (C═O), 1260 cm^{-1} (C—O).

8c

Yield: 93.1%. ^{1}H NMR (DMSO-d_6, δ): 10.35 (s, 2H), 8.03 (d, 2H, J = 8.4 Hz), 7.96–7.89 (m, 6H), 7.83 (d, 4H, J = 8.4 Hz), 7.36 (dd, 2H, J = 7.5, 7.5 Hz), 7.28 (d, 4H, J = 8.4 Hz), 7.11–7.06 (m, 4H), 6.96 (d, 4H, J = 8.1 Hz), 6.64 (d, 2H, J = 7.5 Hz), 6.35 (s, 2H). ^{13}C NMR (DMSO-d_6, δ): 164.9, 159.7, 155.5, 150.2, 147.9, 140.5, 140.1, 137.6, 130.0, 129.3, 128.2, 127.8, 126.9, 123.4, 122.2, 120.5, 119.9, 119.4, 117.3, 114.6, 65.4. IR (KBr): 3304 (N—H), 1675 (C═O), 1244 cm^{-1} (C—O).

8d

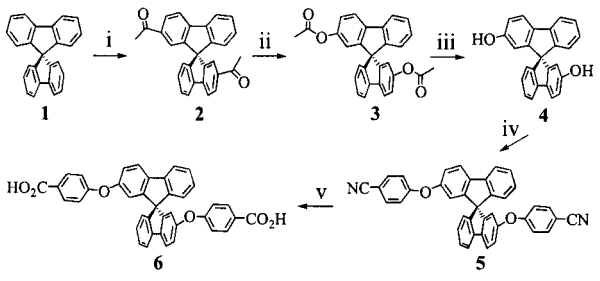
Yield: 92.3%. ^{1}H NMR (DMSO-d_6, δ): 10.17 (s, 2H), 8.23 (s, 1H), 8.01 (d, 2 H, J = 8.1 Hz), 7.94–7.89 (m, 6H), 7.42 (d, 2H, J = 8.4 Hz), 7.35 (dd, 2H, J = 6.9, 6.6 Hz), 7.21 (t, 2H, J = 8.4 Hz), 7.15–7.05 (m, 4H), 6.95 (d, 4H, J = 8.1 Hz), 6.63 (d, 2H, J = 7.2 Hz), 6.34 (s, 2H). ^{13}C NMR (DMSO-d_6, δ): 164.6, 159.5, 155.6, 150.2, 147.9, 140.6, 139.4, 137.5, 130.0, 129.7, 128.5, 128.2, 127.8, 123.4, 122.2, 120.5, 119.3, 117.4, 116.0, 114.5, 112.9, 65.4. IR (KBr): 3324 (N—H), 1669 (C═O), 1250 cm^{-1} (C—O).

8e

Yield: 93.0%. ^{1}H NMR (DMSO-d_6, δ): 10.12 (s, 2H), 7.99 (d, 2H, J = 7.5 Hz), 7.92–7.84 (m, 8H), 7.59 (d, 4H, J = 8.4 Hz), 7.40–7.24 (m, 8H), 7.14–7.01 (m, 8H), 6.93 (d, 4H, J = 7.2 Hz), 6.61 (d, 2H, J = 6.6 Hz), 6.31 (s, 2H). ^{13}C NMR (DMSO-d_6, δ): 164.5, 159.4, 155.6, 150.8, 150.1, 147.9, 140.7, 140.5, 139.5, 137.8, 137.5, 129.9, 129.6, 129.4, 128.2, 127.8, 126.0, 123.4, 122.2, 120.3, 119.2, 117.4, 114.5, 65.4, 64.2. IR (KBr): 3303 (N—H), 1669 (C═O), 1255 cm^{-1} (C—O).

8f

Yield: 94.2%. ^{1}H NMR (DMSO-d_6, δ): 10.10 (s, 2H), 8.02 (d, 2H, J = 8.1 Hz), 7.94 (d, 2H, J = 7.8 Hz), 7.89 (d, 4H, J = 8.1 Hz), 7.66 (s, 4H), 7.37 (dd, 2H, J = 6.9, 6.9 Hz), 7.17–7.04 (m, 4H), 6.94 (d, 4H, J = 8.1 Hz), 6.64 (d, 2H, J = 6.9 Hz), 6.34 (s, 2 H). ^{13}C NMR (DMSO-d_6, δ): 164.4, 159.4, 155.6, 150.1, 147.8, 140.5, 137.5, 134.9, 129.8, 129.7, 128.2, 127.8, 123.4, 122.2, 120.7, 120.4, 119.3,117.3, 114.5, 65.4. IR (KBr): 3313 (N—H), 1654 (C═O), 1239 cm^{-1} (C—O).



Reagents: (i) CH_3COCl, $AlCl_3/CS_2$; (ii) *m*-chloroperoxybenzoic acid/$CHCl_3$; (iii) NaOH(*aq*)/MeOH; (iv) 4-fluorobenzonitrile, K_2CO_3/DMF; (v) KOH(*aq*)/EtOH, HCl(*aq*).

Scheme 1

RESULTS AND DISCUSSION

Synthesis of the Monomer

Scheme 1 outlines the synthetic route for the preparation of the new dicarboxylic acid monomer **6** containing a 9,9′-spirobifluorene skeleton along with two flexible ether linkages. The precursor **1** was prepared according to the literature procedures.[42] On acylation and oxidation, followed by alkaline hydrolysis, **1** gave **4**.[41] The aromatic nucleophilic substitution reaction of **4** with 4-fluoronitrobenzene in DMF/K_2CO_3 medium yielded **5**, which subsequently, on hydrolysis in KOH (aqueous)/ethanol, afforded the desired product **6**. The structures of compounds **5** and **6** were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, as well as HRMS and elemental analysis. Figure 1 shows the ^{1}H NMR spectra of compounds **5** and **6**. With the reported ^{1}H NMR data of 2,2′-disubstituted **1**[43] and auxiliary two-dimensional ^{1}H–^{1}H correlation spectroscopy, the positions of the chemical shifts for protons in compounds **5** and **6** were readily assigned. In the ^{13}C NMR spectra, the relevant change from the dicyano compound

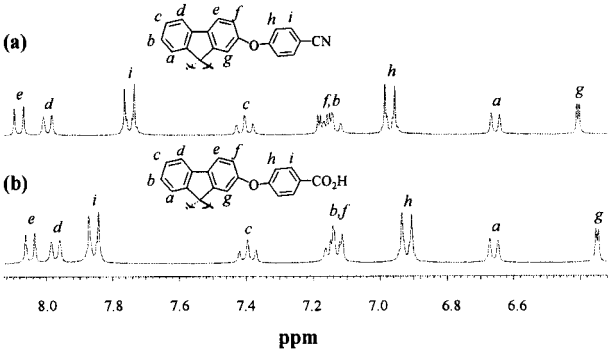


Figure 1. ^{1}H NMR spectra for the aromatic regions of compounds (a) **5** and (b) **6** in DMSO-d_6.

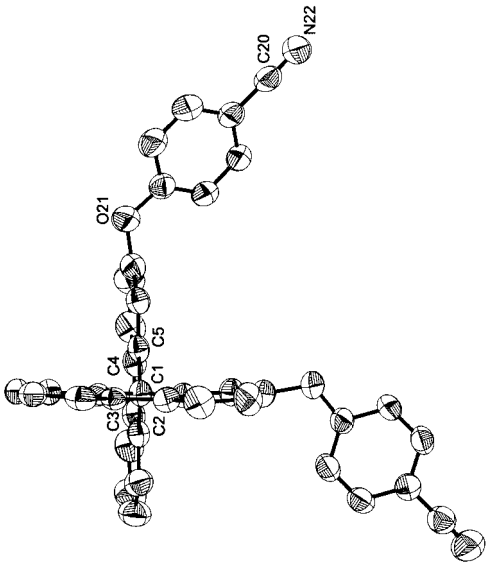
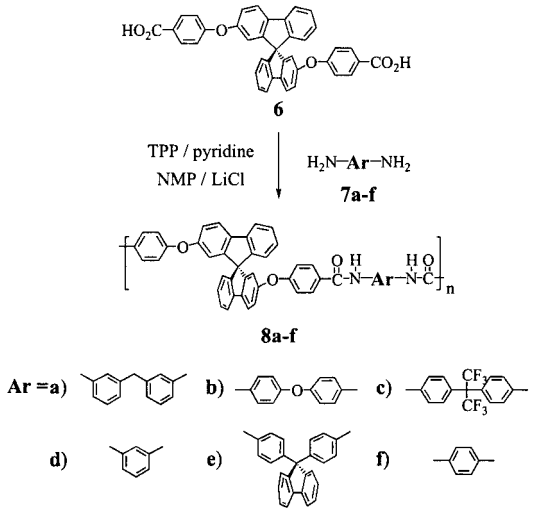


Figure 2. ORTEP diagram of compound **5** determined by X-ray crystallography. All hydrogens have been omitted for clarity.

to the dicarboxylic acid monomer is the disappearance of the signal at 118.5 ppm, assigned to the cyano carbon, and the appearance of the resonance for the carbonyl carbon at 166.7 ppm. The central spiro carbons (C-9) of both compounds resonate at 65.4 ppm, indicating the presence of a spiro skeleton in **5** and **6**. In the IR spectrum, the presence of the cyano function (C≡N) in **5** is evident from the peak at 2223 cm^{-1}. In compound **6**, the cyano stretching vibration disappears, and absorption bands associated with the carboxylic group appear at 2500–3400 (O—H stretching) and 1685 cm^{-1} (C═O stretching). The molecular structure of compound **5**, in the solid state, was elucidated by X-ray crystallography analysis. Single crystals of **5** were obtained by careful crystallization from methanol solutions. Figure 2 displays the Oak Ridge thermal ellipsoid plot (ORTEP) of **5**, calculated by X-ray diffraction at 295 K. The spiro molecule consists of two identical 2-(4-carboxyphenoxy)fluorene moieties connected through a common tetracoordinate carbon atom (the spiro center). In the spiro segment, the rings of the connected bifluorene entities are orthogonally arranged (dihedral angle = 89.9°), and this agrees nicely with the proposed structure.

Preparation of the Polyamides

As shown in Scheme 2, aromatic polyamides were prepared from the spiro-fused dicarboxylic acid monomer **6** and various aromatic diamines **7a–7f**



Scheme 2

with the Yamazaki phosphorylation polycondensation procedure, with TPP/Py as a condensing agent and LiCl as a solubility enhancer.[44] All of the polycondensations proceeded in homogeneous solutions, and the polyamides were isolated as fibrous solids by precipitation into methanol and drying *in vacuo*. The structures of the obtained polyamides were verified by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. Figure 3 shows the ^{1}H NMR spectra of polymers **8a**–**8f**, where all the peaks are readily assigned to the aromatic protons of the repeating unit. In addition to the distinct features associated with the spirobifluorene diacid component, resonances corresponding to the aromatic protons of the diamine component are clearly present. ^{13}C NMR data provide complementary information. Resonances associated with the carbonyl carbons of the amide group appear in the relatively downfield region (164.4–164.9 ppm). Polyamides **8a**–**8f** again have the central spiro carbon (C-9) signal at 65.4 ppm, which indicates the presence of a spirobifluorene moiety. Polyamide **8e**, which contains a diphenylfluorene component, has a cardo carbon (C-9) signal at 64.2 ppm. In the IR spectra, these polymers show characteristic amide group absorptions at 3303–3324 (N—H) and 1654–1675 cm^{-1} (C═O), which support the formation of polyamides. The molecular weights of the polyamides were determined by GPC with DMF as the eluent, calibrated against PMMA standards, with the results presented in Table 1.

Properties of the Polymers

The crystallinity of the polyamides was evaluated by wide-angle X-ray diffraction experiments. Each polymer was found to produce an amorphous diffraction pattern. It appears that the presence of the kinked **1** moiety, together with flexible aryl ether linkages in the diacid component, results in poor chain packing. The amorphous nature of the polyamides is also reflected in their high solubility. The solubility of polyamides **8a**–**8f** was tested in a variety of organic solvents, and these results are summarized in Table 2. All of the polyamides exhibit good solubility in THF and in polar aprotic solvents such as DMF, *N,N*-dimethylacetamide (DMAc), NMP, DMSO, and Py, despite the fact that some of them were derived from diamines with a rigid structure, such as **7e** and **7f**. Flexible films of the polyamides can be obtained by solution casting. The highly amorphous nature and good solubility of these polyamides can be attributed to the incorporation of kinked spirobifluorene units into the polymer backbone. In the case of the spiro-fused bifluorene moiety, the two mutually perpendicular fluorene rings are connected via a common tetracoordinated carbon atom.[39,40] As a result, the resulting polymer chain repeatedly zigzags with an angle of 90° at each spiro center. This structural feature, which minimizes interchain interactions and restricts the close packing of the polymer chains, leads to a reduction in crystallinity and an enhancement in solubility.

The thermal properties of the polyamides were investigated by DSC and TGA, and the results are

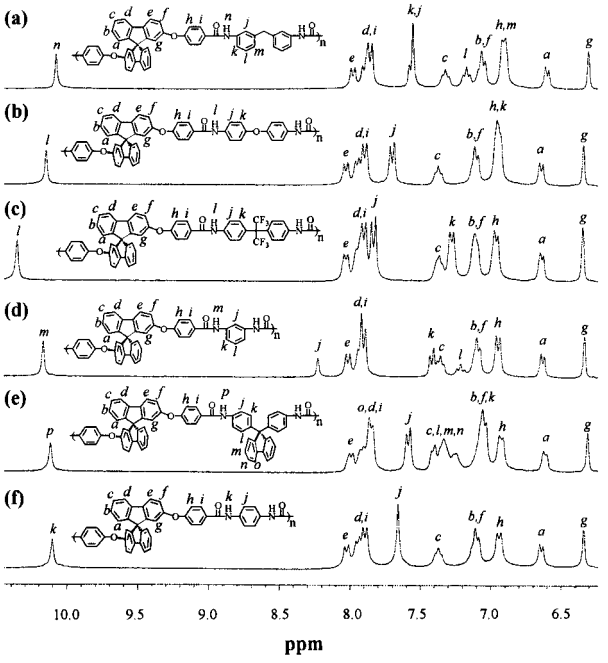


Figure 3. ^{1}H NMR spectra of polyamides (a) **8a**, (b) **8b**, (c) **8c**, (d) **8d**, (e) **8e**, and (f) **8f** in DMSO-d_6.

Table 1. Molecular Weights and Thermal Properties of Polyamides **8a–8f**

Polymer	$M_w \times 10^{4}$[a]	$M_n \times 10^{4}$[a]	DSC T_g[b]	TGA 10%[c]	Y_c (%)[d]
8a	6.8	2.6	234	570	77
8b	12.0	4.6	268	587	73
8c	6.1	2.8	265	535	66
8d	6.5	2.7	277	586	75
8e	8.3	3.6	306	585	76
8f	5.9	2.1	298	593	78

[a] The molecular weight (g mol^{-1}) was determined by GPC in DMF based on PMMA standards.
[b] T_g (°C) was determined by DSC at a heating rate of 20 °C min^{-1} under nitrogen.
[c] Temperature (±5 °C) at which a 10% weight loss was detected at a heating rate of 20 °C min^{-1} under nitrogen.
[d] Char yields at 900 °C in nitrogen.

presented in Table 1. The presence of rigid spirobifluorene units in the polymer backbone results in polyamides with high T_g's. All exhibit T_g's in the range of 234–306 °C, depending on the structure of the diamine component. The T_g order is related to the increasing order of stiffness of the polymer backbone. The comparatively lower T_g value of polymer **8a** can be attributed to the presence of flexible 3,3′-methylenediphenyl units in its polymer chain. Polyamide **8f**, containing a stiff 1,4-phenylene group, exhibits a higher T_g value. The cardo polymer **8e** exhibits the highest T_g value. In general, the chain rigidity of the polymer increases because of the presence of bulky pendent groups, which restrict rotation of the polymer chain. It has been demonstrated that the incorporation of a cyclic cardo side group,[45] such as fluorene, into the polymer backbone affords aromatic polyamides and polyimides high T_g's and good thermal stability.[20,46,47] These spirobifluorene-based polyamides possess T_g values comparable to those of the structurally related cardo-type polyamides derived from 9,9-bis[4-(4-carboxyphenoxy)phenyl]fluorine, as reported previously.[20] This observation reveals the effectiveness of incorporating spiro-fused bifluorene moieties for increasing the rigidity of the polymer backbone.

As shown by TGA, all of the polyamides show similar patterns of decomposition and have good thermal stability, with more than 65% char yields in nitrogen at 900 °C. The temperatures corresponding to a 10% weight loss in nitrogen are in the range of 535–593 °C, about 50 °C higher than the temperature range of the corresponding fluorene-based cardo polyamides. The high thermal stabilities of these polyamides reflect the rigid nature of the spiro-segment unit in the polymer main chain.

Table 2. Solubility of Aromatic Polyamides

	Solubility[a]					
Solvent	**8a**	**8b**	**8c**	**8d**	**8e**	**8f**
THF	+	+	+	+	+	+
DMF	+	+	+	+	+	+
DMAc	+	+	+	+	+	+
NMP	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
Py	+	+	+	+	+	+
m-Cresol	+	+	+	±	±	±

[a] + = Soluble at room temperature; ± = soluble on heating.

CONCLUSIONS

A series of organosoluble aromatic polyamides have been synthesized via the direct polycondensation of a novel diacid, which contains a 9,9′-spirobifluorene moiety along with two flexible ether linkages, with aromatic diamines with the phosphorylation method. The introduction of 9,9′-spirobifluorene units into the polymer backbone enhances the polyamides solubility because of a decrease in the degree of molecular packing and crystallinity. The high T_g's (234–306 °C) and good thermal stabilities (temperature of 10% weight loss = 535–593 °C) of the polyamide indicates that the presence of these units does not impair the thermal properties of these polymers. Further studies concerning the incorporation of the spirobifluorene unit into the polymer backbone to produce novel and processable high-performance polymeric materials are in progress.

The authors thank the National Science Council of the Republic of China for its financial support. They also

thank Gene-Hsiang Lee (Instrumentation Center, College of Science, National Taiwan University) for the X-ray crystal structure determination.

REFERENCES AND NOTES

1. Cassidy, P. E. Thermally Stable Polymer; Marcel Dekker: New York, 1980.
2. Preston, J. In Encyclopedia of Polymer Science and Technology; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley-Interscience: New York, 1988; Vol. 11, p 381.
3. Vollbracht, L. In Comprehensive Polymer Science; Allen, G.; Bevington, J., Eds.; Pergamon, Wheaton & Co.: Exeter, England, 1989; Vol. 5, p 375.
4. Yang, H. H. Aromatic High-Strength Fibers; Wiley-Interscience: New York, 1989; p 202.
5. Lin, J.; Sherrington, D. C. Adv Polym Sci 1994, 111, 177.
6. Bellomo, M. R.; Di Pasquale, G.; La Rosa, A.; Pollicino, A.; Siracusa, G. Polymer 1996, 37, 2877.
7. Hsiao, S. H.; Huang, P. C. J Polym Sci Part A: Polym Chem 1997, 35, 2421.
8. Liaw, D. J.; Liaw, B. Y.; Su, K. L. J Polym Sci Part A: Polym Chem 1999, 37, 1997.
9. Espeso, J. F.; Ferrero, E.; De La Campa, J. G.; Lozano, A. E.; De Abajo, J. J Polym Sci Part A: Polym Chem 2001, 39, 475.
10. Hsiao, S. H.; Chang, C. F. J Polym Sci Part A: Polym Chem 1996, 34, 1433.
11. Takeichi, T.; Suefuji, K.; Inoue, K. J Polym Sci Part A: Polym Chem 2002, 40, 3497.
12. Ferrero, E.; Espeso, J. F.; De La Campa, J. G.; De Abajo, J.; Lozano, A. E. J Polym Sci Part A: Polym Chem 2002, 40, 3711.
13. Carter, K. R.; Furuta, P. T.; Gong, V. Macromolecules 1998, 31, 208.
14. Spiliopoulos, I. K.; Kikroyannidis, J. A.; Tsivgoulis, G. M. Macromolecules 1998, 31, 522.
15. Spiliopoulos, I. K.; Kikroyannidis, J. A. Macromolecules 1998, 31, 1236.
16. Liaw, D. J.; Liaw, B. Y.; Chung, C. Y. Macromol Chem Phys 1999, 200, 1023.
17. Liaw, D. J.; Hsu, P. N.; Chen, J. J.; Liaw, B. Y.; Hwang, C. Y. J Polym Sci Part A: Polym Chem 2001, 39, 1557.
18. Chern, Y. T. Polymer 1998, 39, 4123.
19. Liaw, D. J.; Liaw, B. Y.; Yang, C. M. Macromolecules 1999, 32, 7248.
20. Hsiao, S. H.; Yang, C. P.; Lin, W. L. Macromol Chem Phys 1999, 200, 1428.
21. Liaw, D. J.; Liaw, B. Y.; Yu, C. W. J Polym Sci Part A: Polym Chem 2000, 38, 2787.
22. Liaw, D. J.; Liaw, B. Y.; Yang, C. M.; Hsu, P. N.; Hwang, C. Y. J Polym Sci Part A: Polym Chem 2001, 39, 1156.
23. Liaw, D. J.; Liaw, B. Y.; Lai, S. H. Macromol Chem Phys 2001, 202, 807.
24. Liu, Y. L.; Tsai, S. H. Polymer 2002, 43, 5757.
25. Liou, G. S.; Hsiao, S. H.; Ishida, M.; Kakimoto, M.; Imai, Y. J Polym Sci Part A: Polym Chem 2002, 40, 2810.
26. Salbeck, J.; Yu, N.; Bauer, J.; Weissörtel, F.; Bestgen, H. Synth Met 1997, 91, 209.
27. Salbeck, J.; Bauer, J.; Weissörtel, F. Macromol Symp 1997, 125, 121.
28. Johansson, N.; Salbeck, J.; Bauer, J.; Weissörtel, F.; Bröms, P.; Andersson, A.; Salaneck, W. R. Adv Mater 1998, 10, 1136.
29. Steuber, F.; Staudigel, J.; Stössel, M.; Simmerer, J.; Winnacker, A.; Spreitzer, H.; Weissörtel, F.; Salbeck, J. Adv Mater 2000, 12, 130.
30. Kim, Y. H.; Shin, D. C.; Kim, S. H.; Ko, C. H.; Yu, H. S.; Chae, Y. S.; Kwon, S. K. Adv Mater 2001, 13, 1690.
31. Katsis, D.; Geng, Y. H.; Ou, J. J.; Culligan, S. W.; Trajkovska, A.; Chen, S. H.; Rothberg, L. J. Chem Mater 2002, 14, 1332.
32. Wong, K. T.; Chien, Y. Y.; Chen. R. T.; Wang, C. F.; Lin, Y. T.; Chiang, H. H.; Hsieh, P. Y.; Wu, C. C.; Chou, C. H.; Su, Y. O.; Lee, G. H.; Peng, S. M. J Am Chem Soc 2002, 124, 11576.
33. Yu, W. -L.; Pei, J.; Huang, W.; Heeger, A. J. Adv Mater 2000, 12, 828.
34. Marsitzky, D.; Murray, J.; Scott, J. C.; Carter, K. R. Chem Mater 2001, 13, 4285.
35. Wu, F.-I.; Dodda, R.; Reddy, D. S.; Shu, C.-F. J Mater Chem 2002, 12, 2893.
36. Chiang, C.-L.; Shu, C.-F. Chem Mater 2002, 14, 682.
37. Reddy, D. S.; Shu, C.-F.; Wu, F.-I. J Polym Sci Part A: Polym Chem 2002, 40, 262.
38. Chou, C.-H.; Reddy, D. S.; Shu, C.-F. J Polym Sci Part A: Polym Chem 2002, 40, 3615.
39. Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. J Org Chem 1996, 61, 6906.
40. Johansson, N.; dos Santos, D. A.; Guo, S.; Cornil, J.; Fahlman, M.; Salbeck, J.; Schenk, H.; Arwin, H.; Brédas, J. L.; Salenek, W. R. J Chem Phys 1997, 107, 2542.
41. Prelog, V.; Bedekovic, D. Helv Chim Acta 1979, 62, 2285.
42. Weisburger, J. H.; Weisburger, E. K.; Ray, F. E. J Am Chem Soc 1950, 72, 4250.
43. Haas, G.; Prelog, V. Helv Chim Acta 1969, 52, 1202.
44. Yamazaki, N.; Matsumoto, M.; Higashi, F. J Polym Sci Polym Chem Ed 1975, 13, 1373.
45. Korshak, V. V.; Vinogradova, S. V.; Vygodskii, Y. S. J Macromol Sci Rev Macromol Chem 1974, 11, 45.
46. Yang, C. P.; Lin, J. H. J Polym Sci Part A: Polym Chem 1993, 31, 2153.
47. Hsiao, S. H.; Li, C. T. J Polym Sci Part A: Polym Chem 1999, 37, 1403.