

Synthesis and Characterization of Spirobifluorene-Based Polyimides

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ABSTRACT: The synthesis and properties of organosoluble aromatic polyimides, containing spiro-skeletal units in the polymer backbone on the basis of the spiro-diamine monomer, 2,2'-diamino-9,9'-spirobifluorene, are described. In the case of the spiro segment, the two fluorene rings are orthogonally arranged and connected through a tetrahedral bonding carbon atom, the spiro center. As a consequence, the polymer chain is periodically zigzagged with a 90° angle at each spiro center. This structural feature minimizes interchain interactions and restricts the close packing of the polymer chains, resulting in amorphous polyimides that have good solubility in organic solvents. Compared with their fluorene-based cardo analogues, the spirobifluorene-based polyimides have an improved solubility. Furthermore, the main-chain rigidity of the polyimide appears to be preserved because of the presence of the spiro structure, which restricts the free segmental mobility. As a result, these polyimides exhibit a high glass-transition temperature (T_g 's) and good thermal stability. The T_g 's of these polyimides were in the range of 287–374 °C, and the decomposition temperatures in nitrogen for a 10% weight loss occurred at temperatures above 570 °C. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 40: 3615–3621, 2002

Keywords: organosoluble; polyimides; spirobifluorene; amorphous; thermal properties

INTRODUCTION

Aromatic polyimides possess outstanding thermal, mechanical, and electrical properties as well as excellent chemical resistance.^{1,2} However, their poor processability poses limitations to their use in practical applications.³ Considerable research efforts have been focused on the synthesis of soluble polyimides that maintain the excellent properties of this class of compounds.⁴ Typical approaches include the introduction of bulky lateral groups,^{5–12} flexible linkages,^{13,14} kinked^{15–20} or unsymmetrical structures^{21,22} into the polymer backbone.

Previous studies have shown that the introduction of a spirobifluorene linkage into the structure of small molecules led to the reduction in crystallization tendency, an enhancement in solubility, and an increase in glass-transition temperature (T_g).^{23–27} Such spiro structures have also been applied to polymeric materials, and both T_g and thermal stability are enhanced in the case of alternating 2,7-polyfluorene copolymers.²⁸ We have synthesized amorphous aromatic polyquinolines and poly(ether imide)s, containing spirobifluorene units, that have an improved solubility and thermal stability.^{29,30} In light of these observations, the goal of this research is to synthesize organosoluble polyimides with spiro-skeletal units in the polymer backbone on the basis of a spiro-fused diamine monomer. The spirobifluorene monomer 3 consists of two identical amino-

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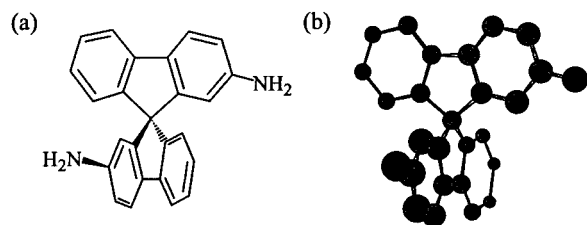


Figure 1. (a) Chemical structure and (b) the AM1 optimized molecular structure of the spiro-diamine monomer.

fluorene moieties connected through an sp^3 carbon atom, the spiro center. Figure 1 illustrates a computer-generated three-dimensional structure of the spiro-diamine monomer using AM1 calculations and MOPAC for energy minimization (Chem 3D software). In the spiro segment, the rings of the connected bifluorene entities are orthogonally arranged.^{25,31} The resulting polyimides would be expected to have a polymer backbone that is periodically twisted with an angle of 90° at each spiro center. We anticipated that this structural feature would restrict the close packing of the polymer chains and reduce the probability of interchain interactions, resulting in more highly soluble polymers. In addition, the rigidity of the main chain of the polyimide would be preserved because of the spiro structure, leading to a significant increase in both T_g and thermal stability. This article reports on the synthesis of aromatic polyimides containing 9,9'-spirobifluorene moieties in the main chain via the one-step polymerization of 2,2'-diamino-9,9'-spirobifluorene (**3**) with a variety of dianhydrides. The solubility, crystallinity, and the thermal properties of the obtained polyimides are reported herein.

EXPERIMENTAL

Materials

The dianhydrides, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (**4a**), bisphenol-A dianhydride (**4b**), 4,4'-oxydiphthalic anhydride (**4c**), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (**4d**), and 3,3',4,4'-biphenyltetracarboxylic dianhydride (**4e**) were recrystallized from acetic anhydride. *m*-Cresol was purified by distillation under reduced pressure prior to use. Other common organic solvents were used as received unless otherwise stated.

Characterization

^1H and ^{13}C NMR spectra were recorded on a Varian Unity 300-MHz or a Bruker-DRX 300-MHz spectrometer with CDCl_3 or dimethyl sulfoxide- d_6 ($\text{DMSO-}d_6$) as solvents. IR spectra were obtained on a Nicolet 360 FT-IR spectrometer. Differential scanning calorimetry (DSC) was performed with a DuPont TA 2000 instrument, with a heating/cooling rate of $20^\circ\text{C min}^{-1}$. Samples were scanned from 30 to 400°C and then cooled to 30°C and scanned a second time from 30 to 400°C . The T_g was determined from the second heating scan. Thermogravimetric analyses (TGAs) were made on a DuPont TGA 2950 instrument. The thermal stability of the samples was determined in nitrogen by measuring weight loss during heating at a rate of $10^\circ\text{C min}^{-1}$. Size exclusion chromatography was carried out on a Waters chromatography unit, interfaced with a Waters 410 differential refractometer. Three $5\ \mu\text{m}$ Waters Styragel columns ($300 \times 7.8\ \text{mm}$), connected in series in decreasing order of pore size (10^5 , 10^4 , and $10^3\ \text{\AA}$), were used with *N,N*-dimethyl formamide (DMF) as the eluent, and standard samples of Poly(methyl methacrylate) (PMMA) were used for calibration. Wide-angle X-ray diffraction patterns were obtained at room temperature on a Rigaku DMX2B (Cu $K\alpha$, 20 mA, 30 kV) with a sampling step of 0.02° and a scan rate of $2^\circ\ \text{min}^{-1}$.

9,9'-Spirobifluorene (**1**)³²

A mixture of dry magnesium turnings (6.00 g, 0.25 mol) and 2-iodobiphenyl (63.0 g, 0.23 mol) in dry ether (250 mL) was refluxed gently for 1 h. After this period, 9-fluorenone (44.6 g, 0.25 mol) was added dropwise over 30 min. The mixture was then heated under reflux overnight. The solution was cooled to room temperature, and ammonium chloride (*aq*) (10%, 400 mL) was added. The aqueous layer was extracted with ether ($3 \times 50\ \text{mL}$), and the combined organic layers were washed with brine and dried over magnesium sulfate. The crude product was recrystallized from ethanol to afford the desired carbinol as colorless plates (37.0 g, 57%). The carbinol obtained was cyclized by refluxing with glacial acetic acid (120 mL) in the presence of two drops of concentrated hydrochloric acid over a period of 1 h. The solid solidified upon cooling was filtered and recrystallized from ethanol to give **1** (33.0 g, 94%).

^1H NMR ($\text{DMSO-}d_6$): δ 7.99 (d, 4H, $J = 7.8\ \text{Hz}$), 7.36 (dd, 4H, $J = 7.5, 7.5\ \text{Hz}$), 7.07 (dd, 4H, J

= 7.5, 7.5 Hz), 6.57 (d, 4H, J = 7.5 Hz). ^{13}C NMR (DMSO- d_6): δ 148.1, 141.2, 127.9, 127.8, 123.4, 120.5, 65.4.

2,2'-Dinitro-9,9'-spirobifluorene (**2**)³³

A mixture of concentrated nitric acid (80 mL) and glacial acetic acid (60 mL) was added dropwise to a boiling solution of **1** (8.00 g, 25.3 mmol) in acetic acid (90 mL) over 1 h, and the contents were refluxed for a further 4 h. The reaction mixture was then cooled, and ice cold water (100 mL) was added under stirring. The precipitated yellow solid was filtered and washed with excess water. Recrystallization of the crude dinitro compound from acetic acid afforded **2** (7.19 g, 70%) as yellow crystals.

^1H NMR (CDCl_3): δ 8.32 (dd, 2H, J = 8.4, 2.1 Hz), 7.98 (d, 2H, J = 8.4 Hz), 7.96 (d, 2H, J = 7.5 Hz), 7.53 (d, 2H, J = 2.1 Hz), 7.47 (dd, 2H, J = 7.5, 7.5 Hz), 7.25 (dd, 2H, J = 7.5, 7.5 Hz), 6.76 (d, 2H, J = 7.5 Hz). ^{13}C NMR (CDCl_3): δ 148.3, 148.2, 148.1, 147.6, 139.4, 130.3, 129.0, 124.6, 124.3, 121.8, 120.6, 119.5, 65.6.

2,2'-Diamino-9,9'-spirobifluorene (**3**)³³

Concentrated hydrochloric acid (5 mL) was added dropwise into a boiling suspension of **2** (2.03 g, 5.00 mmol) and iron powder (2.15 g, 38.5 mmol) in ethanol (85 mL). After refluxing for 4 h, the excess iron was filtered off. Activated charcoal (0.51 g) was added to the filtrate, heated, and again filtered through Celite. The solvent was evaporated, and the residue was purified by column chromatography over silica gel (ethyl acetate/hexane 1:3) to yield **3** (1.11 g, 64%) as colorless prisms.

^1H NMR (DMSO- d_6): δ 7.67 (d, 2H, J = 7.5 Hz), 7.57 (d, 2H, J = 8.1 Hz), 7.24 (dd, 2H, J = 7.5, 7.5 Hz), 6.92 (dd, 2H, J = 7.5, 7.5 Hz), 6.54 (dd, 2H, J = 8.1, 1.8 Hz), 6.50 (d, 2H, J = 7.5 Hz), 5.86 (d, 2H, J = 1.8 Hz), 5.12 (s, 4H). ^{13}C NMR (DMSO- d_6): 150.9, 149.1, 148.0, 142.4, 129.0, 127.3, 125.1, 123.2, 120.8, 118.2, 113.3, 108.6, 64.9.

Polymerization

A typical polymerization procedure is as follows. To a solution of **3** (173 mg, 500 μmol) in 1.0 mL of freshly distilled *m*-cresol, was added **4a** (222 mg, 500 μmol) and isoquinoline (two to three drops) as the catalyst, followed by stirring at room temperature under a nitrogen atmosphere for 1 h. The reaction mixture was stirred at 80 °C for an ad-

ditional 2 h and then slowly heated to 200 °C with stirring for 6 h. After cooling, the viscous solution was added dropwise to an agitated methanol solution (100 mL), and the fibrous solid was collected by filtration, washed thoroughly with methanol, and dried under vacuum at 120 °C to afford the corresponding polyimide **5a**. The polymer was further purified by reprecipitating from DMF into methanol.

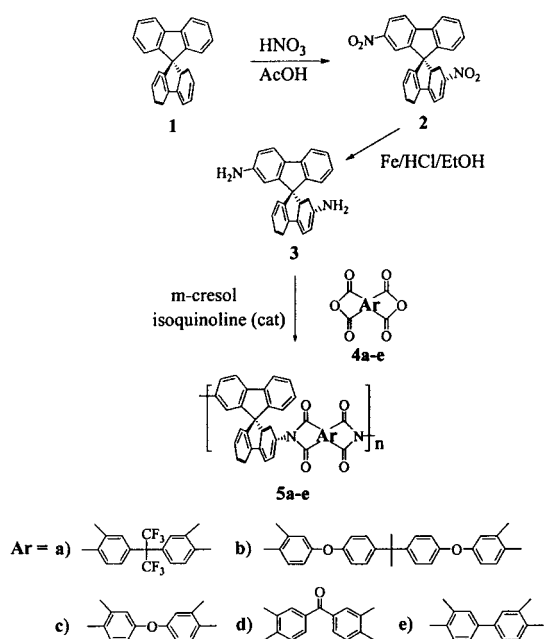
5a: yield 87%. ^1H NMR (CDCl_3): δ 7.90 (d, 2H, J = 8.1 Hz), 7.85 (d, 2H, J = 8.1 Hz), 7.81 (d, 2H, J = 7.8 Hz), 7.77 (s, 2H), 7.67 (d, 2H, J = 8.1 Hz), 7.39 (dd, 2H, J = 8.1, 1.8 Hz), 7.33 (dd, 2H, J = 7.8, 7.8 Hz), 7.12 (dd, 2H, J = 7.8, 7.8 Hz), 6.79 (d, 2H, J = 1.8 Hz), 6.77 (d, 2H, J = 7.8 Hz). ^{13}C NMR (CDCl_3): δ 166.1, 166.0, 149.2, 148.6, 142.2, 140.8, 139.2, 136.0, 132.7, 132.4, 130.8, 128.8, 128.4, 126.6, 125.4, 124.5, 124.2, 122.7, 120.8, 120.6, 66.2.

5b: yield 90%. ^1H NMR (CDCl_3): δ 7.90 (d, 2H, J = 8.1 Hz), 7.81 (d, 2H, J = 7.8 Hz), 7.75 (d, 2H, J = 8.1 Hz), 7.42 (dd, 2H, J = 8.1, 1.8 Hz), 7.35 (dd, 2H, J = 7.5, 7.5 Hz), 7.28–7.23 (m, 8H), 7.13 (dd, 2H, J = 7.5, 7.5 Hz), 6.95 (d, 4H, J = 8.1 Hz), 6.84 (d, 2H, J = 1.5 Hz), 6.78 (d, 2H, J = 7.5 Hz), 1.67 (s, 6H). ^{13}C NMR (CDCl_3): δ 166.5, 163.6, 152.6, 148.8, 148.5, 147.4, 141.5, 140.7, 134.1, 131.1, 128.6, 128.3, 128.1, 126.2, 125.5, 124.9, 124.2, 122.8, 122.4, 120.33, 120.25, 119.9, 111.6, 65.9, 42.5, 30.9.

5c: yield 86%. ^1H NMR (CDCl_3): δ 7.87 (d, 2H, J = 8.1 Hz), 7.82–7.75 (m, 4H), 7.39 (d, 2H, J = 7.8 Hz), 7.36–7.30 (m, 4H), 7.26–7.21 (m, 2H), 7.10 (dd, 2H, J = 7.8, 7.8 Hz), 6.82 (s, 2H), 6.75 (d, 2H, J = 7.8 Hz). ^{13}C NMR (CDCl_3): δ 166.0, 165.8, 160.9, 148.8, 148.4, 141.7, 140.6, 134.4, 130.8, 128.5, 128.1, 127.0, 126.3, 126.0, 124.5, 124.2, 122.4, 120.4, 120.3, 113.8, 65.9.

5d: yield 94%. ^1H NMR (CDCl_3): δ 8.12 (s, 2H), 8.09 (d, 2H, J = 7.5 Hz), 7.98–7.88 (m, 4H), 7.82 (d, H, J = 7.5 Hz), 7.43 (d, 2H, J = 7.5 Hz), 7.36 (dd, 2H, J = 7.5, 7.5 Hz), 7.14 (dd, 2H, J = 7.5, 7.5 Hz), 6.86 (s, 2H), 6.78 (d, 2H, J = 7.5 Hz). ^{13}C NMR (CDCl_3): δ 192.7, 165.8, 148.9, 148.4, 141.9, 141.6, 140.5, 135.7, 134.8, 131.9, 130.6, 128.6, 128.2, 126.3, 124.6, 124.2, 124.1, 122.4, 120.5, 120.4, 66.0.

5e: yield 86%. ^1H NMR (CDCl_3): δ 8.00 (s, 2H), 7.96–7.78 (m, 8H), 7.42 (br, 2H), 7.34 (br, 2H), 7.12 (br, 2H), 6.86 (s, 2H), 6.76 (br, 2H). ^{13}C NMR (CDCl_3): δ 166.5, 148.9, 148.5, 145.3, 141.8, 140.6, 133.3, 132.8, 131.4, 130.9, 129.7, 128.5, 128.2, 126.4, 124.4, 124.2, 123.2, 122.3, 120.5, 118.9, 66.0.



Scheme 1

RESULTS AND DISCUSSION

Monomer Synthesis

To introduce the spiro-skeletal units into the polyimide backbone, the novel spiro-diamine monomer, **3**, was synthesized (as shown in Scheme 1). The precursor, 9,9'-spirobifluorene (**1**), was prepared by reacting of 9-fluorenone with the Grignard reagent prepared from 2-iodobiphenyl followed by dehydrative ring closure of the resulting carbinol in acetic acid.³² The nitration of **1** with nitric acid in an acetic acid medium gave the dinitro derivative **2**, which subsequently on reduction using an iron powder/HCl mixture afforded the desired monomer **3**.³³ The structures of compounds **1**, **2**, and **3** were verified by ¹H and ¹³C NMR spectroscopies.

Preparation of Polyimides

For the synthesis of polyimides **5a–e**, a one-step polymerization method was used. This method is useful for the preparation of high-molecular-weight polyimides even from diamines or dianhydrides with low reactivity.³⁴ However, the disadvantage of the one-step method is that insoluble polyimides cannot further react to form high-molecular-weight polymers because of premature precipitation. The one-step solution method was chosen on the basis of the hypothesis that the

polyimides resulting from **3** would be soluble in *m*-cresol. As shown in Scheme 1, the polymerization of spiro-diamine **3** with a variety of dianhydrides **4a–e** was carried out in *m*-cresol with isoquinoline as a catalyst (Scheme 1). In all these reactions, homogeneous solutions were obtained throughout the polymerization. The polymers were isolated in high yields by precipitation into methanol and dried under vacuum. The structures of the synthesized polyimides **5a–e** were characterized by IR and NMR spectroscopies. The IR spectra of these polyimides showed characteristic imide-ring absorptions near 1775 (C=O asymmetric stretching), 1720 (C=O symmetric stretching), and 1365 (C–N stretching) cm⁻¹. DSC and TGA measurements, which did not show any transition corresponding to imidization, are also consistent with the obtained polyimides being fully imidized. With the supplementing of two-dimensional (H,H)-correlated NMR spectroscopy, the positions of the chemical shift for protons of polymers **5a–e** could be readily assigned as depicted in Figure 2. In addition to the distinct features associated with the spirobifluorene diamine moiety, resonances corresponding to the aromatic protons of the dianhydride component are clearly present. Thus, the ¹H NMR spectra are consistent with the assigned structures of polyimides **5a–e**. ¹³C NMR spectra provided complementary information. Resonances associated with the carbonyl carbons of the imide ring appeared in the relatively downfield region (δ 166).³⁵ Polyimides **5a–e** had an inherent viscosity ranging from 0.40 to 0.77 dL/g in DMAc at 30 °C (Table 1). The molecular weights of the polymers were determined by gel permeation chromatography (GPC) with DMF as the eluent, calibrated against PMMA standards. GPC analysis indicated that the weight-average molecular weights and polydispersities (M_w/M_n) of the polyimides are in the range of $(2.3–5.5) \times 10^4$ and 1.5–1.9, respectively, as summarized in Table 1.

Properties of the Polyimides

The crystallinity of the polyimides was evaluated by wide-angle X-ray diffraction experiments. All the polymers display amorphous diffraction patterns as a result of the kinked 9,9'-spirobifluorene structure. The amorphous character of the polyimides was also reflected in their high solubility. The solubility of polyimides **5a–e** was tested in a variety of organic solvents, and these results are summarized in Table 2. Although these polyim-

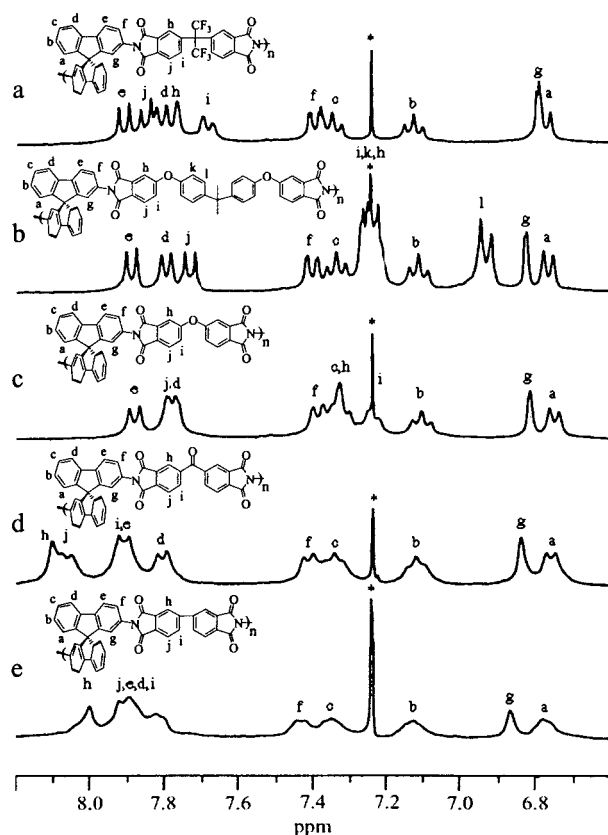


Figure 2. ^1H NMR spectra in CDCl_3 of polyimides (a) **5a**, (b) **5b**, (c) **5c**, (d) **5d**, and (e) **5e** (* signal arising from CHCl_3).

ides do not have a flexible aryl ether linkage in the diamine component as an auxiliary group for enhancing solubility, all the polyimides exhibited good solubility in polar aprotic solvents such as

Table 2. Solubility of Aromatic Polyimides

Solvent ^b	Solubility ^a						
	5a	5b	5c	5d	5e	6d	6e
CH_2Cl_2	+	+	+	+	±	+	-
CHCl_3	+	+	+	+	±	+	-
Py	+	+	+	+	+	+	+
THF	+	+	+	+	-	-	-
DMF	+	+	+	+	+	+	-
DMAc	+	+	+	+	+	+	-
NMP	+	+	+	+	+	+	±
Acetone	-	-	-	-	-	-	-
<i>m</i> -cresol	+	+	+	+	+	+	+
Cyho	+	+	+	+	-	±	-

^a Solubility: (+) soluble at room temperature; (±) soluble on heating; (-) partially soluble on heating; (-) insoluble.

^b CH_2Cl_2 methylene chloride; CHCl_3 , chloroform; Py, pyridine; THF, tetrahydrofuran; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; Cyho, cyclohexanone.

NMP, DMF, DMAc and pyridine, and the phenolic solvent *m*-cresol as well as chlorinated solvents, including chloroform and methylene chloride, except for polymer **5e** that was soluble in chloroform and methylene chloride only on heating. These polyimides, except for polyimide **5e**, were also soluble in less polar solvents such as tetrahydrofuran (THF) and cyclohexanone. The poor solubility of **5e** in THF, cyclohexanone, and chlorinated solvents is possibly due to the rigid nature of the biphenylene moiety. Transparent, flexible films of the polyimides could be obtained by solution casting.

Table 1. Molecular Weight, Inherent Viscosity, and Thermal Properties of Polyimides **5a-6e**

Polymer	$M_w^a \times 10^4$	M_w/M_n	η_{inh}^b (dL/g)	DSC T_g^c	TGA ^d		$Y_c(\%)^e$
					5%	10%	
5a	2.3	1.5	0.40	364	542	573	63
5b	3.6	1.6	0.62	287	563	593	63
5c	4.2	1.7	0.55	362	606	652	70
5d	5.5	1.8	0.77	371	602	626	68
5e	3.9	1.9	0.61	374	587	647	69
6d	3.7	1.9	—	357	576	602	64
6e	—	—	—	362	566	593	64

^a Molecular weight was determined by GPC in DMF on the basis of PMMA standards.

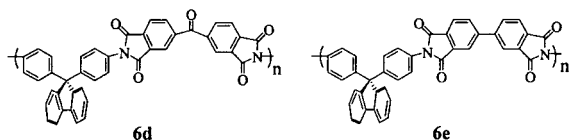
^b Measured at 0.5 g/dL in DMAc at 30 °C.

^c T_g was determined by DSC at a heating rate of 20 °C min⁻¹ under nitrogen.

^d Temperature (± 5 °C) at which a 5 and 10% weight losses were detected at a heating rate of 10 °C min⁻¹ under nitrogen.

^e Char yields at 900 °C in nitrogen.

The highly amorphous nature and good solubility of these polyimides can be attributed to the presence of the kinked spirobifluorene units along the polymer backbone. In the case of the spiro-fused bifluorene moiety, the two fluorene rings are mutually perpendicular and connected via a common tetracoordinated carbon atom,^{25,31} and consequently the polymer chain is repeatedly zig-zagged with an angle of 90° at each spiro center. This structural feature, which minimizes inter-chain interactions and restricts the close packing of the polymer chains, resulted in polyimides possessing low crystallinity and high solubility. It has been demonstrated that the incorporation of a cyclic cardo side group, such as fluorene, into the polymer backbone affords aromatic polyimides with good solubility and high thermal stability.^{36–38} For comparison, fluorene-based cardo polyimides **6d** and **6e** were prepared by polymerization from 9,9'-bis(4-aminophenyl)fluorene with dianhydrides **4d** and **4e**. When comparing the solubility of polyimides **5d** and **5e** with their analogues **6d** and **6e**, **5d** and **5e** were more soluble than **6d** and **6e** (Table 2). This observation clearly demonstrates the important role of the orthogonal arrangement of each bifluorene moiety in the polymer chain for enhancing the solubility of the polyimides.



The thermal properties of the polyimide were investigated by DSC and TGA, and the results are presented in Table 1. The incorporation of rigid spirobifluorene units into the polymer backbone led to polyimides exhibiting a high T_g . The T_g 's of polyimides **5a–e** were in the range of 287–374 °C, depending on the structure of the dianhydride monomer moiety. Polyimides **5d** and **5e** with a stiffer dianhydride moiety in the polymer backbone had higher T_g values. The polyimide with a flexible linkage, such as the 4,4'-isopropylidene-diphenoxy (**5b**) group, exhibited a lower T_g . In a comparison of T_g 's of polymers **5d** and **5e** with **6d** and **6e**, the spirobifluorene-based polymers possessed higher T_g 's, which were about 12–14 °C higher than the corresponding fluorene-based cardo polymers. This result demonstrates the role of the incorporated spiro-fused bifluorene moiety in increasing the rigidity of the polymer back-

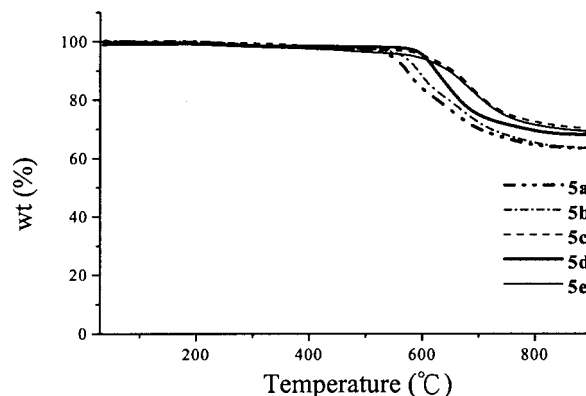


Figure 3. TGA curves for polyimides **5a–e** at a heating rate of 10 °C min⁻¹ in N₂.

bone. As evidenced by TGA, all the spirobifluorene-based polyimides have excellent thermal stability. Figure 3 shows typical TGA curves for these polyimides. The 5 and 10% weight-loss temperatures in nitrogen were in the range of 542–606 and 573–652 °C, respectively. The char yields for these polyimides were in the range of 63–70% in nitrogen at 900 °C. As shown in Table 1, polyimides **5d–e** also displayed a higher thermal stability than their fluorene-based cardo analogues. These results are indicative of the high thermal stability of the spirobifluorene unit in the polymer backbone.

In conclusion, a series of aromatic polyimides containing 9,9'-spirobifluorene moieties in the main chain have been synthesized via the polycondensation of **3** with a variety of dianhydrides. In the case of the spiro segment, the two fluorene rings are mutually perpendicular and are connected via a common tetracoordinated carbon. This structural feature confers an enhanced solubility on the polyimides because of a decrease in the degree of molecular packing and crystallinity while imparting a significant increase in both T_g and thermal stability by restricting segmental mobility. Further studies on the incorporation of spirobifluorene units into the polymer backbone achieving soluble polymeric materials that are amenable for use as light-emitting polymers are now in progress.^{39–41}

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