Synthesis and Characterization of Soluble Polyimides Derived from 2,2′-Bis(3,4-dicarboxyphenoxy)-9,9′-spirobifluorene Dianhydride

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ABSTRACT: The synthesis of aromatic poly(ether imide)s containing spirobifluorene units in the polymer backbone is described. 2,2′-Bis(3,4-dicarboxyphenoxy)-9,9′-spirobifluorene dianhydride, which was used as a new monomer, was synthesized with 2,2′-dihydroxy-9,9′-spirobifluorene as the starting material. In the spiro-segment, the rings of the connected bifluorene were orthogonally arranged. This bis(ether anhydride) monomer was employed in reactions with a variety of aromatic diamines to furnish poly(ether imide)s, involving an initial ring-opening polycondensation and subsequent chemically induced cyclodehydration. Excellent solubility in common organic solvents at room temperature, good optical transparency, and high thermal stability are the prominent characteristic features of these new polymers, which can be attributed to the presence of spiro-fused orthogonal bifluorene segments along the polymer chain. The glass-transition temperatures of the polyimides were 240–293 °C, and the 5% weight-loss temperatures were greater than 500 °C. © 2001 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 40: 262–268, 2002

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

INTRODUCTION

The excellent mechanical and electrical properties, thermal stability, and chemical resistance of polyimides recommend them for use in high-performance polymer materials.[1,2] However, applications of these polyimides have, in the past, been limited because of their poor solubility in typical organic solvents. This led to modifications in the mode of fabrication, in which the poly(amic acid) precursors are first subjected to fabrication, which is followed by a rigorous thermal treatment. However, this process has several drawbacks, which include the emission of volatile by-products (e.g., H_2O) that create strength-weaken-ing voids in thick parts and a storage instability of poly(amic acid) intermediates.[3] To overcome these limitations, a considerable amount of research has been focused on the synthesis of soluble and processable polyimides without deterioration of their excellent innate properties.[4] Several approaches involving structural modifications of the polymer backbone, such as the introduction of bulky lateral groups,[5–11] flexible linkages,[12,13] and kinked monomers,[14–19] have been reported.

In light of these observations, our goal was the synthesis of highly soluble polyimides and an examination of their properties. Our strategy involved the incorporation of spirobifluorene units into the polymer backbone with ether linkages in the main chain. In the spiro-segment, the rings of the connected bifluorene were orthogonally arranged and connected via a common tetracoordinated carbon,[20–22] and the polymer chains were

twisted at an angle of 90° at each spiro-center. This structural feature was predicted to restrict the close packing of the polymer chains, thereby reducing the probability of interchain interactions, resulting in higher polymer solubility. Moreover, for the spiro-annulated segment, the rigidity of the polyimide backbone would be preserved. Therefore, a novel bis(ether anhydride) monomer, 2,2′-bis(3,4-dicarboxyphenoxy)-9,9′-spirobifluorene dianhydride (**4**), was synthesized, starting from 2,2′-dihydroxy-9,9′-spirobifluorene (**1**),[23] and then polymerized with various aromatic diamines. The characteristics of these new poly(ether imide)s, such as the solubility, thermal behavior, and optical properties, are discussed.

EXPERIMENTAL

Materials

1 (mp = 285–287 °C) was prepared as described in the literature.[23] *p*-Phenylenediamine was purified by sublimation. *m*-Phenylenediamine was vacuum-distilled before use. 4,4′-Methylenedianiline and 4,4′-oxydianiline were recrystallized from ethanol. 3,3′-(Hexafluoroisopropylidene)dianiline was used without further purification. The anhydrous solvents *N*-methyl-2-pyrrolidone (NMP; Aldrich) and pyridine (Aldrich) were stored over 4-Å molecular sieves before use.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 300-MHz or Bruker-DRX 300-MHz spectrometer with $CDCl_3$ or dimethyl sulfoxide-d_6 (DMSO-d_6) as a solvent. IR spectra were obtained on a Nicolet 360 Fourier transform infrared (FTIR) spectrometer. Differential scanning calorimetry (DSC) was performed on a Seiko SSC 5200 DSC with heating and cooling rates of 20 °C min^{-1}. Samples were scanned from 30 to 400 °C, cooled to 30 °C, and scanned for a second time from 30 to 400 °C. The glass-transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was performed on a Seiko TG/DTA 200 instrument. The thermal stability of the samples was determined in nitrogen by measurement of the weight loss during heating at a rate of 10 °C min^{-1}. Mass spectra were obtained on a JEOL JMS-SX/SX 102A mass spectrometer. Size exclusion chromatography was carried out on a Waters chromatography unit interfaced with a Waters 410 differential refractometer. Three Waters 5-μm Styragel columns (300 × 7.8 mm) connected in series in decreasing order of pore size (10^4, 10^3, and 10^2 Å) were used with tetrahydrofuran (THF) as the eluent, and polystyrene standard samples were used for calibration. Ultraviolet–visible (UV–vis) spectra were obtained with an Agilent 8453 spectrophotometer. Wide-angle X-ray diffraction patterns were obtained at room temperature on an M18XHF material analysis and characterization instrument with Ni-filtered Cu Kα 1 radiation (50 kV, 200 mA) with a sampling step of 0.02° and a scanning rate of 4° min^{-1}.

2,2′-Bis(3,4-dicyanophenoxy)-9,9′-spirobifluorene (2)

A mixture of **1** (3.48 g, 10.0 mmol) and 4-nitrophthalonitrile (3.48 g, 20.1 mmol) was dissolved in anhydrous dimethylformamide (DMF; 20 mL), potassium carbonate (2.80 g, 20.3 mmol) was added, and the mixture was stirred at 60 °C for 14 h. The resulting solution was slowly poured into 120 mL of water to give a colorless, solid precipitate, which was collected by filtration and dried *in vacuo*. The crude product was recrystallized from ethyl acetate/acetonitrile (1:1 v/v) to afford the pure bis(ether dinitrile) **2** (5.67 g, 94.5%).

mp: 286–288 °C. IR (KBr, cm^{-1}): 2234 (C≡N), 1246 (C—O—C). ^{1}H NMR (DMSO-d_6, δ): 6.54 (d, 2H, J = 2.1 Hz), 6.66 (d, 2H, J = 7.5 Hz), 7.15 (dd, 2H, J = 7.5, 7.5 Hz), 7.23 (dd, 2H, J = 8.7, 2.1 Hz), 7.26 (dd, 2H, J = 8.9, 2.4 Hz), 7.41 (dd, 2H, J = 7.5, 7.5 Hz), 7.62 (d, 2H, J = 2.4 Hz), 7.97–8.03 (m, 4H), 8.12 (d, 2H, J = 8.3 Hz). ^{13}C NMR (DMSO-d_6, δ): 161.1, 153.6, 150.2, 147.9, 140.2, 139.0, 136.1, 128.2, 128.0, 123.4, 122.5, 122.3, 121.8, 120.7, 120.4, 116.5, 115.9, 115.3, 108.1, 65.4. HRMS: calcd for $C_{41}H_{20}N_4O_2$, 600.1586; found, 600.1572.

2,2′-Bis(3,4-dicarboxyphenoxy)-9,9′-spirobifluorene (3)

Sodium hydroxide (13.5 g) was dissolved in a mixture of water and methanol (30 mL/30 mL) and added to compound **2** (5.4 g, 9.0 mmol). The mixture was refluxed for 36 h, at which time a clear solution was obtained. The resulting hot solution was filtered for the removal of insoluble impurities. The filtrate was diluted with distilled water

and acidified with concentrated HCl (pH 2–3). The precipitated product was filtered and washed thoroughly with water until the washings were neutral and was dried to give the bis(ether diacid) **3** (5.3 g, 87.1%).

mp: 155–158 °C (decomposition). IR (KBr, cm^{-1}): 2500–3400 (br, OH), 1712 (C=O), 1261 (C—O—C). ^{1}H NMR (DMSO-d_6, δ): 6.37 (d, 2H, J = 2.3 Hz), 6.65 (d, 2H, J = 7.5 Hz), 6.98–7.02 (m, 4H), 7.11–7.16 (m, 4H), 7.39 (dd, 2H, J = 7.6, 7.6 Hz), 7.67 (d, 2H, J = 8.9 Hz), 7.97 (d, 2H, J = 7.6 Hz), 8.05 (d, 2H, J = 8.3 Hz). ^{13}C NMR (DMSO-d_6, δ): 168.3, 167.4. 158.9, 155.1, 150.2, 147.8, 140.5, 137.9, 136.4, 131.4, 128.3, 127.9, 126.0, 123.4, 122.3, 120.6, 119.6, 118.8, 116.8, 114.9, 65.4.

2,2′-Bis(3,4-dicarboxyphenoxy)-9,9′-spirobifluorene dianhydride (4)

Acetic anhydride (6 mL) was added to bis(ether diacid) **3** (3.2 g, 4.7 mmol), and the suspension was stirred under reflux for 45 min, during which time a white solid precipitated. After cooling, the solid was collected by filtration, washed with a small amount of glacial acetic acid, and dried *in vacuo* at 140 °C for 12 h to yield the colorless, pure dianhydride (2.6 g, 86%).

mp: 202–203 °C. IR (KBr, cm^{-1}): 1849, 1777 (C=O), 1283 (C—O—C). ^{1}H NMR (DMSO-d_6, δ): 6.52 (d, 2H, J = 2.2 Hz), 6.68 (d, 2H, J = 7.5 Hz), 7.16 (dd, 2H, J = 7.5, 7.5 Hz), 7.24 (dd, 2H, J = 8.4, 2.4 Hz), 7.31 (d, 2H, J = 2.1 Hz), 7.38–7.44 (m, 4H), 7.97 (d, 2H, J = 8.4 Hz), 8.01 (d, 2H, J = 7.5 Hz), 8.13 (d, 2H, J = 8.4 Hz). ^{13}C NMR (CDCl$_3$, δ): 164.9, 162.4, 162.0, 153.7, 150.9, 147.9, 140.4, 139.6, 133.8, 128.3, 127.6, 124.8, 124.2, 124.0, 121.8, 120.4, 120.1, 116.5, 112.0, 65.8. HRMS: calcd for C$_{41}$H$_{20}$O$_8$, 640.1158; found, 640.1150.

Poly(ether imide)s (6a–6e)

A typical polymerization procedure was as follows. The dianhydride **4** (320 mg, 500 μmol) was added in one portion to a stirred and clear solution of 4,4′-methylenedianiline (99 mg, 500 μmol) in NMP (2.8 mL) under N$_2$ at ambient temperature. The stirring was continued for 12 h, resulting in a viscous solution. Chemical cyclodehydration of the resulting poly(amic acid) solution was performed by the slow addition of a mixture of acetic anhydride (1.5 mL), pyridine (0.75 mL), and NMP (1.5 mL), which was followed by heating
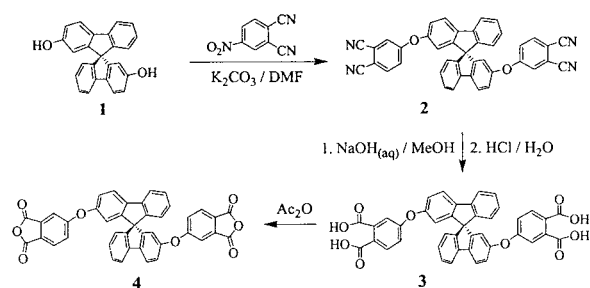
Scheme 1

at 80 °C for 2 h. The polymer solution was poured into methanol (80 mL), and the colorless, fibrous solid was collected by filtration, washed thoroughly with methanol, and dried *in vacuo* at 100 °C to afford the corresponding polymer **6a**. The polymers were purified by reprecipitation from THF into methanol.

RESULTS AND DISCUSSION

Synthesis of the Monomer

The new dianhydride (**4**) was synthesized in three steps, starting from **1**, as shown in Scheme 1. Compound **1** was prepared according to the reported literature.[23] Nucleophilic substitution of the nitro function of 4-nitropthalonitrile with diol **1** in an anhydrous DMF/K$_2$CO$_3$ medium furnished **2** in quantitative yields. Alkaline hydrolysis of the bis(ether dinitrile) **2** with aqueous sodium hydroxide in methanol resulted in **3**, which was subsequently dehydrated with acetic anhydride to afford the desired monomer **4**. The structures of the synthesized compounds were verified by FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopy, as well as mass spectroscopy. The presence of the C≡N function in **2** is evident from the IR spectrum (2234 cm^{-1}). However, compound **3** was characterized by the presence of carboxyl groups (2500–3400 broad and 1712 cm^{-1}) in the IR spectrum, and in the ^{13}C NMR spectrum, the carbonyl carbon signals were observed at δ = 168.3 and 167.4. When the tetracarboxylic acid **3** was dehydrated to the bis(ether anhydride) **4**, the absorptions due to the carboxyl groups disappeared, and characteristic C=O stretching absorptions of the cyclic anhydride unit appeared at 1849 and 1777 cm^{-1}. In addition, the carbonyl carbon peak in the ^{13}C NMR spectrum was shifted upfield (δ = 164.9). Based on reported ^{1}H NMR data of 2,2′-disubstituted-9,9′-spirobifluorene[24] and aux-
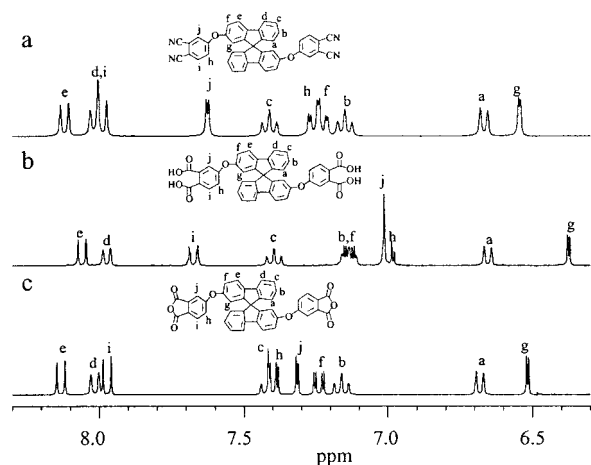
Figure 1. ^{1}H NMR spectra of compounds (a) **2**, (b) **3**, and (c) **4** in DMSO-d_6.

Scheme 2

iliary two-dimensional (H,H)-correlated spectroscopy, the positions of the chemical shifts for protons of compounds **2**–**4** were readily assigned, as shown in Figure 1. The area of integration for the protons is consistent with the assignment. Therefore, the ^{1}H NMR spectra are consistent with the assigned structures of compounds **2**–**4**.

Synthesis of the Poly(ether imide)s

Polyimides **6a**–**6e** were synthesized in NMP solutions with the conventional two-stage procedure, involving ring-opening polycondensation and cyclodehydration, in which the bis(ether anhydride) **4** was reacted with stoichiometric amounts of diamine monomers **5a**–**5e** to form poly(amic acid) intermediates (Scheme 2). The poly(amic acid)s were subsequently chemically imidized to poly-(ether imide)s by treatment with a mixture of acetic anhydride and pyridine.[25] The polymers were isolated in quantitative yields by precipitation into methanol and dried *in vacuo*. The formation of poly(ether imide)s **6a**–**6e** was confirmed by IR spectroscopy. The absence of amic acid absorptions [~3350 (NH and OH) and 1650 cm^{-1} (amide, C=O)] and the presence of cyclic imide carbonyl absorptions (1778 and 1724 cm^{-1}) in the IR spectra of poly(ether imide)s confirmed the complete cyclodehydration of the corresponding amide intermediate. In addition, DSC and TGA measurements, which did not show any transitions corresponding to imidization, indicated that the resultant polyimides were fully imidized. The structure of the poly(ether imide)s was characterized by ^{1}H NMR. Figure 2 shows the ^{1}H NMR
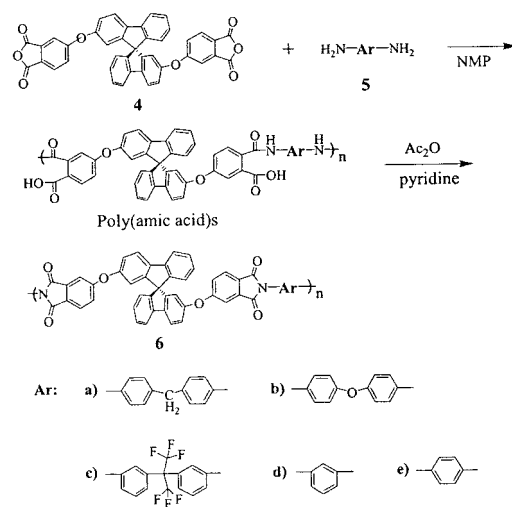
spectra of polymers **6a**–**6e**. In addition to the distinct features associated with the spirobifluorene dianhydride component, resonances corresponding to the aromatic protons of the diamine component are clearly present. ^{13}C NMR provided complementary information. The resonances as-
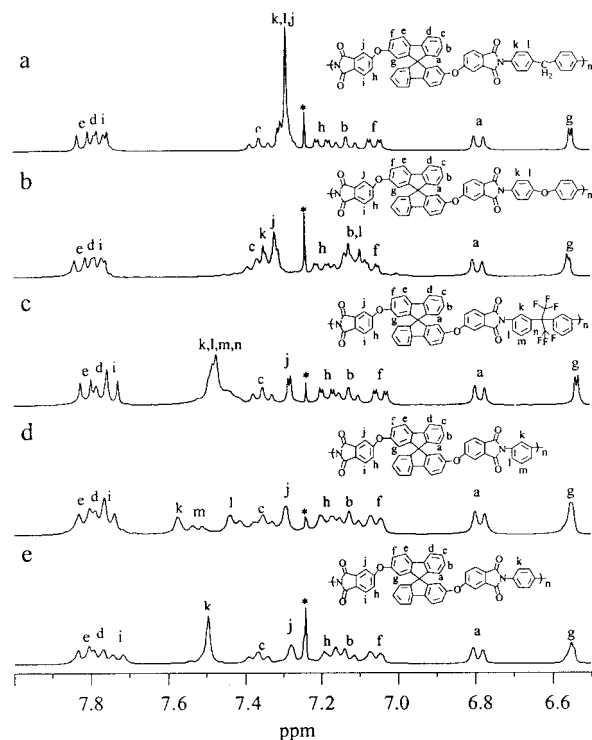

Figure 2. ^{1}H NMR spectra of poly(ether imide)s (a) **6a**, (b) **6b**, (c) **6c**, (d) **6d**, and (e) **6e** in CDCl$_3$. * indicates a signal arising from CHCl$_3$.

Table I. Molecular Weights, Inherent Viscosities, and Optical and Thermal Properties of Poly(ether imide)s **6a–6e**

Polymer	M_w $(\times 10^4)^a$	M_w/M_n	η_{inh} (dL/g)^b	Transparency (%)^c	DSC T_g^d	TGA^e 5%	10%
6a	5.0	1.7	0.63	97	280	516	554
6b	2.7	1.5	0.47	92	279	550	571
6c	3.8	1.6	0.57	98	240	528	548
6d	2.8	1.5	0.42	94	265	553	574
6e	—^{f}		0.44	94	293	545	570

^{a} Determined by GPC in THF based on polystyrene standards.
^{b} Measured at 0.5 g/dL in DMAc at 30 °C.
^{c} Average transmittance in the visible region (400–780 nm) for poly(ether imide) solutions in NMP at a concentration of 5 $\times$ 10^{-3}M with a 1.0-cm path length.
^{d} Determined by DSC at a heating rate of 20 °C min^{-1} under nitrogen.
^{e} Temperatures at which 5 and 10% weight losses were determined at a heating rate of 10 °C min^{-1} under nitrogen.
^{f} Partially soluble in THF.

sociated with the carbonyl carbons of the ether-linked phthalic ring appeared in a relatively downfield region (δ = 166).[26] The molecular weights of the polymers, except for the poly(ether imide) **6e**, which was only partially soluble in THF, were determined by gel permeation chromatography (GPC) with THF as the eluent and with calibration against polystyrene standards. The molecular weights and polydispersities [weight-average molecular weight/number-average molecular weight (M_w/M_n)] are shown in Table I.

The crystallinity of the poly(ether imide)s was evaluated by wide-angle X-ray diffraction experiments. All the polymers displayed amorphous diffraction patterns due to the kinked 9,9′-spirobifluorene structure. For spiro-fused bifluorene, the two mutually perpendicular fluorine rings are connected via a common tetracoordinated carbon atom. This structural feature minimizes intermolecular interactions between the polymer chains and inhibits chain packing, leading to the observed reduction in crystallinity. The amorphous character of the polyimides is also reflected in their high solubility.

Solubility

The solubility of the poly(ether imide)s was determined in a variety of organic solvents. All the polyimides exhibited good solubility in polar aprotic solvents such as NMP, DMF, dimethylacetamide (DMAc), and pyridine and in *m*-cresol, a phenolic solvent, as well as chlorinated solvents such as chloroform and methylene chloride. The poly(ether imide)s, except for polyimide **6e**, were

also soluble in the less polar THF. The poor solubility of **6e** in THF was possibly due to the rigid nature of its diamine moiety. The highly soluble nature of these poly(ether imide)s can be attributed to the presence of kinked spirobifluorene units (as discussed previously), with flexible aryl ether linkages along the polymer backbone. It has been reported that poly(ether imide)s derived from 9,9′-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorine dianhydride (**7**) have poor solubility in organic solvents.[27] This observation reveals the important role of the orthogonal arrangement of each bifluorene moiety in the polymer chain, as this affects the enhanced solubility of poly(ether imide)s **6a–6e**:

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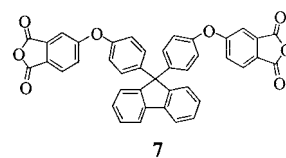
Transmittance

UV–vis spectra of the poly(ether imide)s at a concentration of 5 $\times$ 10^{-3} mol/L in NMP solutions are shown in Figure 3. All the polymers except **6b** showed transmittances above 90% in the wavelength range 450–600 nm. Polymer **6b** exhibited a transmission in excess of 80% in the visible region. The transparency of the polymer solution in the visible region was evaluated by the averaging of the transmittances from 400 to 780 nm in the UV–vis spectra, and the results are presented in Table I. The colored nature of the polyimides
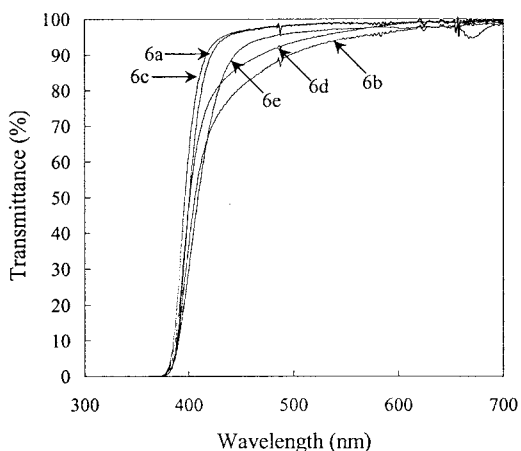
Figure 3. UV–vis spectra of polyimide solutions in NMP at a concentration of 5×10^{-3} mol/L with a 1.0-cm path length.

was due to the presence of intramolecular and intermolecular charge-transfer interactions and electron conjugation.[28–30] The favorable optical transparency of the polymers can be attributed to the suppression of intermolecular interactions by the spiro-structure, which possesses a mutually perpendicular arrangement of the bifluorene moiety. Moreover, the tetrahedral spiro-junction serves as a conjugation interrupter, thereby preventing extended conjugation along the polymer backbone.

Thermal Properties

The thermal properties of the poly(ether imide)s were investigated by DSC and TGA, and the results are tabulated in Table I. The incorporation of rigid spirobifluorene units in the polymer backbone resulted in poly(ether imide)s with higher T_g's. The T_g's of polyimides **6a**–**6e** were 240–293 °C, depending on the structure of the diamine component. The poly(ether imide) with a hexafluoroisopropylidene linkage (**6c**) or the less symmetric m-phenylene unit (**6d**) tended to have a lower T_g. Because of the symmetry and stiffness of the p-phenylene moiety in the polymer backbone, the T_g of **6e** was higher than that of the other polymers. The thermal stability of the poly(ether imide)s was evaluated with TGA. All the polyimides were stable up to approximately 500 °C and showed a similar pattern of decomposition. Their 5 and 10% weight-loss temperatures in nitrogen were 516–553 and 548–574 °C, respectively. These results are indicative of the high

thermal stability of the spirobifluorene unit in the polymer backbone.

SUMMARY

Spirobifluorene units with ether linkages were successfully introduced into the polymer backbone for the first time via the polycondensation of **4** with a variety of diamines. The new dianhydride monomer was prepared from **1** and 4-nitrophthalonitrile. The obtained poly(ether imide)s possess excellent solubility in common organic solvents and good transparency to visible light, which can be attributed to the presence of spirofused orthogonal bifluorene segments along the polymer chain. DSC and TGA experiments also demonstrated the high thermal stability of the spiro-structure in the polymer backbone. Further studies on the incorporation of the spirobifluorene unit into a polymer backbone for the purpose of identifying new candidates for soluble and processable high-performance polymeric materials are currently in progress.

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