Synthesis and Characterization of New Polyquinolines Containing 9,9′-Spirobifluorene Units

Chi-Long Chiang and Ching-Fong Shu*

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

Received July 5, 2001. Revised Manuscript Received October 24, 2001

Polyquinolines, which contain 9,9′-spirobifluorene units in the main chain, were synthesized via the acid-catalyzed Friedländer condensation reactions of bis(*o*-aminoketone) with bisacetyl monomers. In the spiro-fused bifluorene moiety, the two mutually perpendicular fluorene rings were connected via a common tetracoordinated carbon atom. This structural feature leads to polymers that possess high thermal stability and good solubility in common organic solvents. The polyquinolines have similar lowest energy transitions that can be attributed to a $\pi-\pi^*$ transition with $\lambda_{\max}$ values in the 363−385 nm range and exhibit blue emission. A model compound was synthesized to demonstrate that the tetrahedral bonding carbon at the center of the spiro moiety could serve as a conjugation interrupt to effectively control the conjugation length of the polymers. The electrochemical behaviors of these polymers were investigated by cyclic voltammetry. The reversible reduction and low-lying LUMO energy level suggest that some of the polyquinolines might have potential for use as materials for electron injection and transport in polymer LEDs.

Introduction

Polyquinolines, which were developed by Stille et al. in the 1970s,[1] are synthesized by the acid-catalyzed Friedländer condensation reaction between monomers containing bis(*o*-aminoketone) and bis(ketomethylene) functional moieties.[2] The high thermal and oxidative stability, good mechanical and electrical properties, and eminent processability of such polymers make them useful as high-performance polymer materials.[1,3] Based on their optical and electronic properties,[4] these polymers have recently been investigated as potentially useful materials in optoelectronic applications such as electroluminescent[5−8] and nonlinear optical devices.[9,10]

Although rigid-rod polyquinolines generally exhibit high strength and possess excellent thermal properties, they have limited solubility in organic solvents, thus making fabrication difficult.[11,12] Attempts have been made to enhance the solubility of polyquinolines by incorporating flexible ether linkages or cardo units into the polymer backbone.[13] In this paper, we report on the synthesis of polyquinolines containing 9,9′-spirobifluorene in the polymer main chain via the acid-catalyzed Friedländer quinoline synthesis. In the spiro-segment, the bifluorene rings are orthogonally arranged and connected via a common tetracoordinated carbon.[14,15] This structural feature would be expected to reduce the probability of interchain interactions and prevent the close packing of the polymer chains, resulting in good solubility of polymers. In addition, the spiro-annulated segment would be expected to enhance the rigidity of the polymer backbone, leading to a significant increase in both T_g values and thermal stability. Moreover, the tetrahedral bonding carbon at the center connects conjugated moieties via a σ-bonded network, which serves as a spacer and a conjugation interrupt, thus effectively controlling the conjugation length of the polymers. Polyquinolines and copolymers have been

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* To whom correspondence should be addressed.

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10.1021/cm010665f CCC: $22.00

proposed as electron transport materials (or emitters) for LED devices[5−8] because of the electron-deficient nature of the quinoline ring.[16] In light of these observations, we also studied the optical, luminescent, and electrochemical properties of these new polyquinolines.

Experimental Section

Materials. Compounds **1**,[17] **2**,[18] **5**,[19] **6**,[20], **7**,[2c] and **9**[21] were prepared as described in the literature. Compound **8** was prepared from 9,9-dipropyl-2-nitrofluorene[21] according to reported procedures.[2c] Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl, and *m*-cresol was purified by distillation under reduced pressure. Tetrabutylammonium hexafluorophosphate was purified by recrystallization from ethyl acetate and dried in vacuo at 60 °C. All other chemicals were used as received unless otherwise stated.

9,9-Spirobifluoreno-bis-3-phenyl[2,3-*c*]isoxazole (3). To an ice-cooled mixture of sodium hydroxide (4.93 g, 122 mmol), methanol (20 mL), and tetrahydrofuran (30 mL), benzyl nitrile (2.85 mL, 24.6 mmol) was added dropwise. After stirring for 5 min, 2,2′-dinitro-9,9′-spirobifluorene (**2**) (5.00 g, 12.3 mmol) was slowly added and the mixture was then heated at 80 °C for 20 h. The reaction mixture was then cooled in an ice-bath, and the resulting precipitate was isolated by filtration and washed with cold methanol until the methanol washings were clear. The crude product was purified by column chromatography (CH_2Cl_2) to give **3** (5.00 g, 73.8%). ^{1}H NMR ($CDCl_3$): δ 6.85 (d, 2 H, $J = 7.6$ Hz), 7.01 (d, 2 H, $J = 1.1$ Hz), 7.22 (dd, 2 H, $J = 7.5, 7.5$ Hz), 7.43 (dd, 2 H, $J = 7.5, 7.5$ Hz), 7.51 (t, 2 H, $J = 7.1$ Hz), 7.60 (dd, 4 H, $J = 7.0, 7.0$ Hz), 7.98 (d, 2 H, $J = 7.7$ Hz), 8.08 (d, 4 H, $J = 7.1$ Hz), 8.21 (d, 2 H, $J = 1.1$ Hz). ^{13}C NMR ($CDCl_3$): δ 63.8, 109.9, 110.8, 115.1, 120.7, 124.8, 126.6, 128.5, 128.6, 129.3, 129.6, 130.2, 139.1, 139.5, 149.5, 154.7, 158.5, 164.2. HRMS [M^+]: 550.1665. Calcd for $C_{39}H_{22}N_2O_2$: 550.1681.

2,2′-Diammo-3,3′-dibenzoyl-9,9′-spirobifluorene (4). Iron powder (0.38 g, 6.7 mmol) and water (0.5 mL) was added to a stirred suspension of compound **3** (0.50 g, 0.90 mmol) in acetic acid (15 mL) at 95 °C. The reaction mixture was heated at 95 °C for 1 h, cooled, and filtered to remove the iron powder. The filtrate was poured into water (100 mL). The resulting precipitate was collected by filtration and purified by column chromatography (EtOAc/hexane/$CHCl_3$ 1:5:45) to give **4** (0.48 g, 95.7%). ^{1}H NMR ($CDCl_3$): δ 6.08 (s, 2 H), 6.15 (s, 2 H), 6.73 (d, 2 H, $J = 7.5$ Hz), 7.03 (dd, 2 H, $J = 7.5, 7.5$ Hz), 7.27 (dd, 2 H, $J = 7.5, 7.5$ Hz), 7.47−7.61 (m, 4 H), 7.73 (d, 4 H, $J = 6.6$ Hz), 7.87 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 65.4, 112.3, 117.6, 118.9, 124.1, 125.5, 126.8, 128.0, 128.2, 129.2, 129.8, 131.2, 140.2, 147.1, 147.5, 151.5, 156.1, 198.7. HRMS [M^+]: 554.1999. Calcd for $C_{39}H_{26}N_2O_2$: 554.1994.

Preparation of Polyquinoline (PQ1). A mixture of **4** (1.000 g, 1.804 mmol), **6** (0.458 g, 1.804 mmol), diphenyl phosphate (DPP) (11.3 g, 45.2 mmol), and freshly distilled *m*-cresol (3.0 mL) was flushed with nitrogen with stirring for about 20 min and heated in an oil bath from room temperature to 140 °C over about a 30 min period. It was maintained at this temperature for 72 h under a nitrogen atmosphere. After cooling, the resulting viscous solution was diluted with chloroform (10 mL) and added dropwise into an agitated solution of 330 mL of methanol containing 10% v/v of triethylamine. The collected polymer was purified by precipitating from chloroform (15 mL) into a solution of 330 mL of methanol containing 10% v/v of triethylamine three times. The polymer was then continuously extracted in a Soxhlet extractor for 24 h with a methanol solution containing 10% v/v of triethylamine and then dried at 100 °C under vacuum to give **PQ1** (1.25 g, 94.0%). ^{1}H NMR ($CDCl_3$): δ 6.83 (d, 2 H, $J = 7.4$ Hz), 7.00 (d, 4 H, $J = 8.2$ Hz), 7.11 (dd, 2 H, $J = 7.5, 7.5$ Hz), 7.34 (dd, 2 H, $J = 7.5, 7.5$ Hz), 7.49−7.68 (m, 14 H), 7.85 (d, 2 H, $J = 7.5$ Hz), 7.99(d, 4 H,.$J = 8.1$ Hz), 8.27 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 65.0, 115.7, 118.7, 119.0, 121.0, 124.7, 125.0, 125.9, 128.2, 128.5, 128.7, 128.8, 128.9, 129.6, 134.8, 138.7,140.3, 140.7, 149.0, 149.2, 149.5, 152.0, 155.2, 157.9.

Preparation of Polyquinoline (PQ2). PQ2 was synthesized using a procedure similar to that described for polymer **PQ1** (yield: 92.4%). ^{1}H NMR ($CDCl_3$): δ 6.74 (d, 2 H, $J = 7.5$ Hz), 7.09 (dd, 2 H, $J = 7.5$ Hz), 7.24−7.42 (m, 16 H), 7.49 (s, 2 H), 7.54 (s, 2 H), 7.88 (d, 2 H, $J = 7.5$ Hz), 8.00 (d, 2 H, $J = 8.0$ Hz), 8.07 (d, 2 H, $J = 7.8$ Hz), 8.30 (d, 2 H, $J = 7.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 66.3, 112.3, 119.8, 120.6, 120.7, 122.8, 123.2, 124.2, 126.5, 127.90, 127.98, 128.50, 128.51, 128.6, 129.3,131.9, 137.8, 139.1, 141.2, 143.4, 145.5, 148.4, 149.0, 149.5, 154.5, 155.5.

Preparation of Polyquinoline (PQ3). PQ3 was synthesized using a procedure similar to that described for polymer **PQ1** (yield: 90.0%). ^{1}H NMR ($CDCl_3$): δ 6.50−6.80 (br, 4 H), 6.85−6.71 (br, 4 H), 7.15−7.33 (br, 4 H), 7.34−7.60 (br, 14 H), 7.63−7.90 (br, 8H), 8.00−8.23 (br, 4 H). ^{13}C NMR ($CDCl_3$): δ 65.0, 66.1, 115.6, 119.1, 120.1, 120.3, 120.8, 122.9, 123.1, 124.0, 124.2, 124.6, 125.1, 126.0, 127.7, 128.1, 128.3, 128.6, 128.8, 129.6, 138.6, 139.1, 140.3, 140.6, 141.0, 143.1, 148.7, 148.8, 148.9, 149.4, 149.7, 151.6, 155.7.

Synthesis of Model Compound 10. A mixture of **8** (0.150 g, 0.406 mmol), **9** (0.119 g, 0.406 mmol), DPP (2.10 g, 8.16 mmol), and freshly distilled *m*-cresol (0.3 mL) was flushed with nitrogen with stirring for about 20 min and heated at 140 °C for 12 h under nitrogen. After cooling, the reaction mixture was added dropwise into an agitated solution containing methanol (30 mL), triethylamine (3 mL), and water (15 mL). The precipitate was collected by filtration and purified by column chromatography (EtOAc/hexane 1:10) to give **10** (0.23 g, 90.5%). ^{1}H NMR ($CDC1_3$): δ 0.67 (br, 20 H), 1.99−2.20 (m, 8 H), 7.28−7.40 (m, 6 H), 7.56−7.72 (m, 6 H), 7.74−7.78 (m, 1 H), 7.83 (d, 1 H, $J = 7.9$ Hz), 7.84 (s, 1 H), 8.10 (s, 1 H), 8.16 (d, 1 H, $J = 1.1$ Hz), 8.18 (d, 1 H, $J = 0.4$ Hz), 8.23 (dd, 1 H, $J = 1.6, 7.9$ Hz). ^{13}C NMR ($CDCl_3$): δ 14.40, 14.45, 17.2, 17.3, 42.8, 43.6, 55.2, 55.5, 114.9, 119.1, 120.00, 120.02, 120.5, 121.7, 122.9, 123.1, 123.5, 125.5, 126.6, 126.8, 127.0, 127.3, 128.2, 128.4, 128.6, 129.7, 138.7, 139.0, 140.0, 140.5, 140.6, 142.3, 149.06, 149.10,151.2, 151.33, 151.34, 153.1, 156.4. HRMS [M^+]: 625.3693. Calcd for $C_{47}H_{47}N$: 625.3708.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 300 MHz or a Bruker-DRX 300 MHz spectrometer using $CDCl_3$ as solvent. Mass spectra were obtained on a JEOL JMS-SX/SX 102A mass spectrometer. Size exclusion chromatography (SEC) was carried out on a Waters chromatography unit interfaced to a Waters 410 differential refractometer. Three 5-μm Waters styragel columns (300 × 7.8 mm) connected in series in the decreasing order of pore size (10^4, 10^3, and 10^2 Å) were used with THF as eluent, and standard polystyrene samples were used for calibration. Wide-angle X-ray diffraction patterns were obtained at room temperature on a Material Analysis and Characterization M18XHF using Ni filtered Cu Kα1 radiation (50 kV, 200 mA) with a sampling step of 0.02° and a scan rate of 4° min^{-1}. Differential scanning calorimetry (DSC) was performed on a SEIKO SSC 5200 DSC unit using a heating/cooling rate of 20 °C min^{-1}. Samples were scanned from 30 to 400 °C and then cooled to 30 °C and scanned for second time from 30 to 400 °C. Glass transition temperatures (T_g) were determined from the second heating scan. Thermogravimetric analysis (TGA) was made on a Du Pont TGA2950 instrument. The thermal stability of the samples was determined in nitrogen, by measuring weight loss while heating at a rate of 10 °C min^{-1}. UV−vis spectra were measured with a HP 8453 diode array spectrophotometer. Photoluminescence spectra were obtained on an Acton Research Spectra Pro-150 luminescence spectrometer. Cyclic voltammetry measurements of the polymer films were performed on a BAS 100 B/W electrochemical analyzer in

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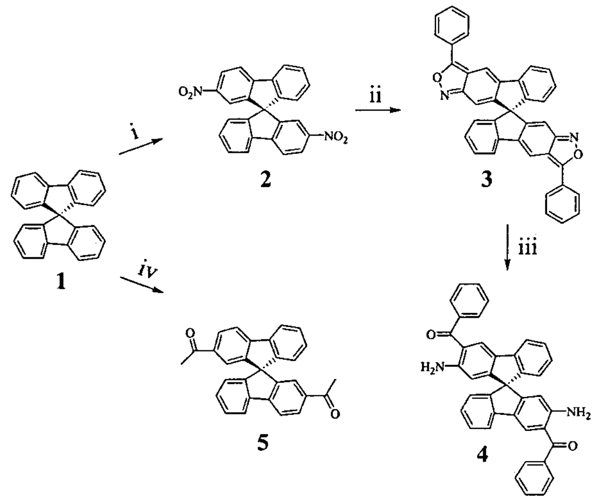
Scheme 1[a]



[a] Reagents: (i) HNO_3/CH_3COOH; (ii) $NaOH/CH_3OH/THF$, benzyl cyanide; (iii) Fe, CH_3COOH/H_2O; (iv) CH_3COCl, $AlCl_3/CS_2$.

acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte at a scan rate of 100 mV/s. The potentials were measured against an Ag/AgCl reference electrode with ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram.

Results and Discussion

Synthesis of Monomer. To introduce 9,9′-spirobifluorene units into the polyquinoline backbone, bis(*o*-aminoketone) and bisacetyl monomers containing 9,9′-spirobifluorene moiety were synthesized. The precursor, 9,9′-spirobifluorene (**1**), was prepared by following the Clarkson and Gomberg method,[17] which involves coupling of a Grignard reagent prepared from 2-iodobiphenyl with 9-fluorenone, followed by dehydrative ring closure of the resulting carbinol in acetic acid. The conversion of compound **1** to the bis(*o*-aminoketone) monomer **4** and the bisacetyl monomer **5** is shown in Scheme 1. The nitration of **1** with nitric acid in an acetic acid medium gave the dinitro derivative **2**.[18] The reaction of compound **2** with benzyl nitrile in the presence of base yielded the bisbenzisoxazole **3**, which was then transformed into the bis(*o*-aminoketone) monomer **4** by hydrogenation with an iron powder/acetic acid mixture. The structures of compounds **3** and **4** were verified by ^1H and ^{13}C NMR spectroscopy as well as mass spectroscopy. Figure 1 shows the ^1H NMR spectra of compounds **3** and **4**. Based on the reported ^1H NMR data of 2,2′-disubstituted-9,9′-spirobifluorene[19] and supplementing these data with 2D (H,H)-correlated NMR spectroscopy, the positions of the chemical shift for protons of compounds **3** and **4** could be readily assigned as shown in Figure 1. The bisacetyl monomer **5** was synthesized according to a reported procedure via the Friedel−Crafts acylation of compound **1** with acetyl chloride in CS_2.[19] The other two monomers, which have an ether linkage and contain no spirobifluorene moiety, bisacetyl **6**[20] and bis(*o*-aminoketone) **7**[2c] were prepared using previously described literature methods.

Synthesis of Polyquinolines. PQ1−3 were synthesized using a condensation scheme based on the acid-catalyzed Friedländer reaction,[10] as shown in Scheme 2. An equimolar mixture of the appropriate bisacetyl monomer and the bis(*o*-aminoketone) monomer was reacted in an acidic medium of diphenyl phosphate and *m*-cresol at 140 °C for 72 h under nitrogen. The resulting viscous polymer solution was diluted with $CHCl_3$ and precipitated into methanol containing 10% triethylamine, followed by Soxhlet extraction with the same solution to give the polyquinolines **PQ1−3** in high yields. The structures of these polymers were characterized by ^1H and ^{13}C NMR spectroscopy. The molecular weights of the polyquinolines were determined by SEC analysis in a THF solution calibrated against polystyrene standards and the results are listed in Table 1. These values, however, should be taken as being only indicative, since the backbone rigidity of the polymers studied may deviate strongly from that of polystyrene.[22]

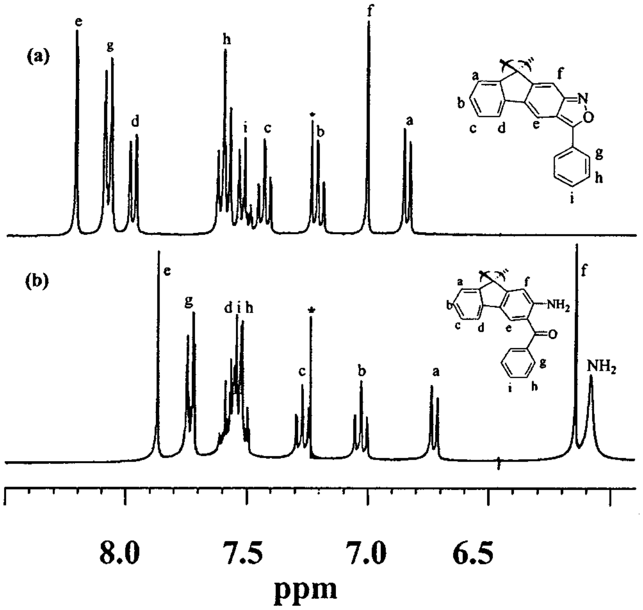
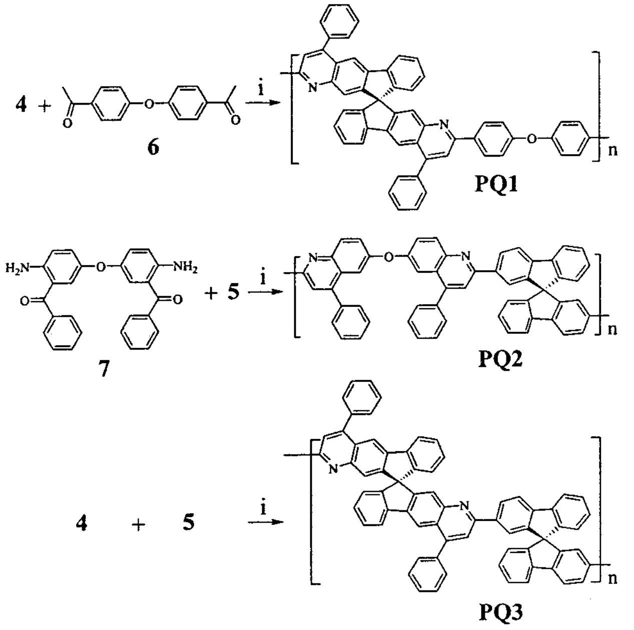


Figure 1. ^1H NMR spectra of compounds (a) **3** and (b) **4** in $CDCl_3$. * indicates a signal arising from $CHCl_3$.

Scheme 2[a]



[a] Reagents: (i) DPP/*m*-cresol.

Table 1. Molecular Weight and Thermal Properties of Polyquinolines PQ1−3

			DSC (°C)	TGA^c (°C)	
polymer	$M_n{}^a \times 10^4$	$M_w{}^a \times 10^4$	$T_g{}^b$	5%	10%
PQ1	1.5	2.0	*d*	600 (534)^e	618 (558)^e
PQ2	2.1	3.8	342	577 (529)^e	599 (560)^e
PQ3	1.8	2.8	*d*	657 (546)^e	859 (562)^e

[a] Molecular weight was determined by GPC in THF based on polystyrene standards. [b] T_g was determined by DSC at a heating rate of 20 °C min^{-1} under nitrogen. [c] Temperature at which 5% and 10% weight loss was determined at a heating rate of 10 °C min^{-1} under nitrogen. [d] Phase transitions were not observed in the temperature range of 30 to 400 °C. [e] Weight loss was determined at a heating rate of 10 °C min^{-1} in air.

Table 2. Solubility of Polyquinolines[a]

	solvent^b								
polymer	CH_2Cl_2	$CHCl_3$	Py	THF	*m*-cresol	DMF	NMP	Cyho	DMSO
PQ1	−+	++	++	++	++	−+	+−	++	−−
PQ2	++	++	++	++	++	−+	++	+−	−−
PQ3	++	++	++	++	++	−+	++	++	−−

[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; NMP, *N*-methyl-2-pyrrolidinone; Cyho, cyclohexanone; DMSD, dimethyl sulfoxide.

The crystallinity of the polyquinolines was evaluated by wide-angle X-ray diffraction experiments. All the polymers display amorphous diffraction patterns owing to the kinked 9,9′-spirobifluorene structure. In the spiro-segment, the two fluorene rings were orthogonally arranged and connected via a common tetracoordinated carbon. This structural feature minimizes the intermolecular interaction between the polymer chains and prohibits chain packing, leading to a reduction in crystallinity. The amorphous character of the polyquinolines was also reflected in their high solubility.

Properties of Polyquinolines. The solubility of these polyquinolines was tested in a variety of organic solvents and the results are summarized in Table 2. All of the polyquinolines exhibited good solubility in a variety of solvents such as chloroform, pyridine, tetrahydrofuran, and *m*-cresol. **PQ1** is only partially soluble in methylene chloride and *N*-methyl-2-pyrrolidinone, whereas **PQ2** and **PQ3** are soluble. In the case of cyclohexanone, **PQ1** and **PQ3** are soluble, while **PQ2** is soluble at elevated temperature. The good solubility nature of polyquinolines **PQ1** and **PQ2** can be attributed to the presence of the spiro-fused, orthogonal bifluorene units, along with flexible ether linkages in the polymer backbone. It is noteworthy that **PQ3** is soluble in a wider variety of organic solvents than **PQ1** and **PQ2**. The solubility of **PQ3** is significant in that it does not arise from flexible main linkages or flexible side chains; but rather, its solubility appears to result from the incorporation of rigid 9,9′-spirobifluorene groups. This result demonstrates that the introduction of the orthogonal spirobifluorene unit into the polymer main chain is highly effective in enhancing the solubility of the polyquinolines.

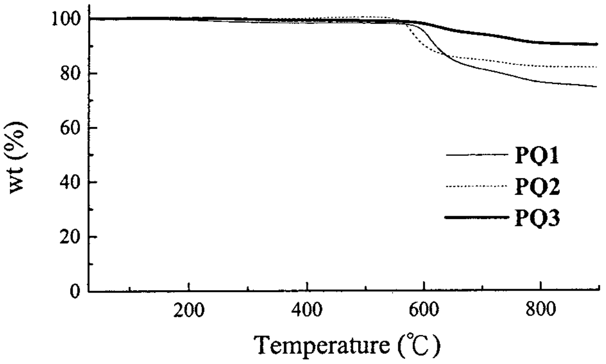


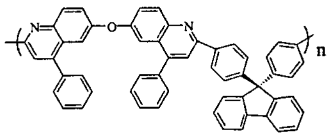
Figure 2. TGA curves for polyquinolines **PQ1−3** with a heating rate of 10 °C min^{-1} in N_2.

Table 3. Optical Properties of Polyquinolines PQ1−3

		photoluminescence, λ_{max} (nm)	
polymer	absorption^a λ_{max} (nm)	solution^b	film^c
PQ1	378	398	420
PQ2	363	395	401
PQ3	385	403	432 (485)

[a] In $CHCl_3$. [b] In $CHCl_3$, excited at 350 nm. [c] Spin-coating from their $CHCl_3$ solution, excited at 350 nm.

The thermal properties of the polyquinolines were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the results are tabulated in Table 1. DSC was performed in the temperature range from 30 to 400 °C. Phase transitions were not observed for either **PQ1** or **PQ3**. This is probably due to the chain stiffness of these polymers. However, a distinct glass transition temperature was observed for **PQ2** at 342 °C, which is higher than that of a similar polymer, **PQ4** ($T_g = 310$ °C) which contains fluorene cardo units.[13a]



PQ4

Thus, the incorporation of rigid 9,9′-spirobifluorene units into the polymer backbone increased the chain stiffness and resulted in a higher glass transition temperature (T_g). All the polyquinolines that contain spirobifluorene units have excellent thermal stability, as evidenced by thermogravimetric analysis. Figure 2 shows typical TGA curves for these polyquinolines. Their 5% and 10% weight loss temperatures in nitrogen were in the range of 577−657 and 599−859 °C, respectively. **PQ3**, which contains two spirobifluorene units in each polymer repeating unit, exhibits the highest thermal stability of the three polyquinolines synthesized. These results reflect the high thermal stability of the spirobifluorene unit in the polymer backbone.

Figure 3 presents the absorption and emission spectra of **PQ1−3** and the spectral properties are summarized in Table 3. The polyquinolines have similar lowest energy transitions attributed to a π−π* transition with a λ_{max} at 363−385 nm. The absorption spectra of solutions and corresponding films are nearly identical, while the emission from films is red-shifted compared to diluted solutions, which is due to the π−π interaction

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Table 4. Electrochemical Properties of Polyquinolines PQ1−3

polymer	$E_{\text{onset}}^{\text{ox}}$ (V)[a]	$E_{\text{onset}}^{\text{red}}$ (V)[a]	HOMO[b] (eV)	LUMO[c] (eV)	E_g^{el} (eV)[d]	E_g^{opt} (eV)[e]
PQ1	1.10	−2.08	−5.90	−2.72	3.18	3.13
PQ2	0.98	−2.24	−5.78	−2.56	3.22	3.16
PQ3	1.05	−2.01	−5.85	−2.79	3.06	3.04

[a] Potential values are versus Fc/Fc^+. [b] Determined from the onset oxidation potential. [c] Determined from the onset reduction potential. [d] Electrochemical band gap estimated using $E_g^{\text{el}} = E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}$. [e] Optical band gap, calculated from the absorption edge of the UV−vis spectrum.

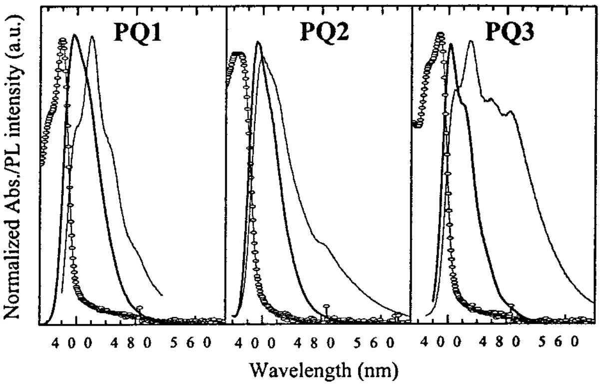
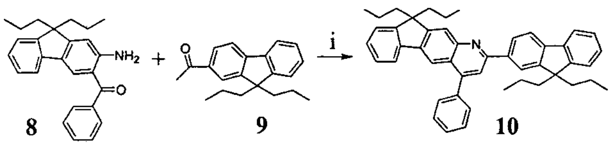


Figure 3. UV−vis absorption spectra of a film (circle), PL spectra of solution in $CHCl_3$ excited at 350 nm (bold line), and PL spectra of a film excited at 350 nm (solid line) for polyquinolines **PQ1**−**3**.

Scheme 3[a]



[a] Reagents: (i) DPP/*m*-cresol.

of the chromophores in the solid state.[23] The absorption maximum of **PQ2** appears at 363 nm, which is blue-shifted by 15 nm compared to **PQ1**, probably resulting from the decrease in chain rigidity and a reduction in electron delocalization. **PQ3** showed an absorption maximum at 385 nm, which is red-shift by 7 nm, compared to **PQ1** because of the increase in conjugation length. The PL spectrum of a dilute solution of **PQ3** has an emission maximum at 403 nm, while that for the thin film shows an emission maximum at 432 nm with a broad shoulder around 485 nm, which probably results from the interchain excimer emission.[24] These data reveal that chain stacking in the film of **PQ3** was not sufficiently suppressed by the spiro groups because of the rigid main-chain structure. For **PQ1** and **PQ2**, the problem of excimer emission in the thin film state is less serious, since the flexible ether linkage may aid in suppressing the chain stacking in the solid state.

To demonstrate that the tetrahedral bonding carbon at the center of the spiro moiety could serve as a conjugation interrupt to control the conjugation length of the polymers, a model compound **10** was synthesized (Scheme 3) as the repetitive conjugated unit of polymer **PQ3**. As shown in Figure 4, the solution UV−vis absorption and PL spectra of compound **10** in $CHCl_3$ and those obtained from **PQ3** are almost superimposable. This result implies that the effective conjugation length of **PQ3** is the same as that of compound **10** and that the tetrahedral bonding carbon at the center of the spiro moiety is efficient for interrupting the conjugation length of the polymer.

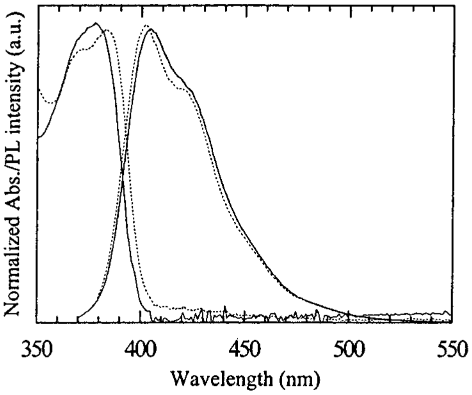


Figure 4. UV−vis absorption and PL spectra in $CHCl_3$ of model compound **10** (solid lines) and polyquinolines **PQ3** (dashed lines).

The electrochemical behaviors of the polyquinolines were investigated by cyclic voltammetry and the data are tabulated in Table 4. Upon cathodic sweep, **PQ1** and **PQ3** exhibited a reversible reduction with a formal reduction potential ($E°'$) at −2.22 and −2.12 V vs Fc/Fc^+ (FOC) couple, respectively, while the reduction of **PQ2** is irreversible and occurred in a more negative region with a peak potential at −2.36 V vs FOC couple. The shift of the reduction potential of **PQ2** toward a more negative value could be the result of the push−pull structure[25] of the quinoline ring presented in the polymer backbone. The oxidation processes of all three polymers were irreversible. Based on the onset potentials for the oxidation and reduction, the HOMO and LUMO energy levels of the polyquinolines were estimated regarding the energy level of the FOC reference (4.8 eV below the vacuum level).[26] The LUMO energy levels of the polymers are similar to those reported for other polyquinolines.[4a,6b] It is likely that the low-lying LUMO level of polyquinolines may originate from the electron-deficient nature of the quinoline ring. The band gaps of the polymers were estimated from electrochemical measurements, which are in good agreement with the results determined from the threshold of the optical absorption. From the reversible reduction and high electron affinity, it would appear that **PQ1** and **PQ3** have potential for use in electron-transporting materials in polymer LEDs.[27,28]

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Summary

A series of polyquinolines containing 9,9′-spirobifluorene moieties in the main chain have been synthesized via the acid-catalyzed Friedländer quinoline synthesis and their properties investigated. In the case of the spiro-segment, the two fluorene rings were orthogonally arranged and are connected via a common tetracoordinated carbon. The incorporation of the 9,9′-spirobifluorene unit provides good solubility due to 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. The optical, and electrochemical properties of these polyquinolines were also examined. As revealed from the PL spectra, the spiro segment is insufficient to completely suppress chain stacking in the solid state. The low-lying HOMO energy level and reversible electrochemical reduction of **PQ1** and **PQ3** suggest that they have potential for use as materials for electron injection and transport in polymer LEDS.

Acknowledgment. We wish to thank the National Science Council of the Republic of China for financial support.

CM010665F

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