Synthesis and Characterization of Thermally Stable Blue Light-Emitting Polyfluorenes Containing Siloxane Bridges

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ABSTRACT: The first novel polyfluorene copolymers containing siloxane bridges were synthesized by Ni(0)-mediated copolymerization between 2,7-dibromo-9,9′-dihexylfluorene and a bridged fluorene monomer containing siloxane linkages. Two such bridged copolymers were prepared: PSiloBg1 (containing 1 mol % siloxane-bridged fluorene unit) and PSiloBg3 (containing 3 mol % siloxane-bridged fluorene unit). PSiloBg1 and PSiloBg3 exhibited good solubility in common organic solvents, thermal stability up to 420 °C, and facile film formation. The glass transition temperatures of the bridged polymers (106 and 110 °C, respectively) were higher than that of the homo poly(dihexylfluorene) (PDHF). In particular, PSiloBg3 exhibited a polymerization yield (96%) and a molecular weight (MW = 185 000) higher than those of PDHF (polymerization yield = 62%, MW = 82 000). Interestingly, after the bridged polymers had been annealed at 150 °C for 4 h in air, their PL spectra showed no significant increase in vibronic structures at 450 and 475 nm and no evidence of aggregation formation and excimers at wavelengths of >500 nm. In addition, the full width at half-maximum (fwhm) of the bridged polymers was very small (fwhm = 51−52 nm) compared to that of PDHF (fwhm = 85 nm). Collectively, the results show that the polyfluorenes with siloxane bridges exhibit thermally stable almost pure blue emission, making these polymers promising candidate materials for device applications.

Introduction

Since the first use of conjugated polymers in electroluminescence devices by Friend and co-workers,[1] such polymers have attracted great attention as candidate light-emitting materials for display applications.[2−4] π-Conjugated polymers such as poly(p-phenylenevinylene), polythiophene, poly(p-phenylene), and their derivatives are easily fabricated as light-emitting diode (LED) devices via solution processing, and can be used in large area light-emitting displays.[2−6,11−13] In 1989, Fukuda et al.[7] reported the synthesis and optical properties of novel polyfluorenes in which the two benzene rings of the biphenyl in each monomer are made coplanar by linking them with a methylene group. Subsequent work has established polyfluorenes as promising candidates for applications requiring blue light-emitting materials. Polyfluorenes have many properties that favor their use over other conjugated polymers in blue light-emitting applications.[6,8−10] They exhibit high photoluminescence (PL) and electroluminescence efficiencies, offer facile functionalization at the C-9 position of fluorene, and have good solubility in common organic solvents such as chloroform, toluene, and tetrahydrofuran (THF).[13−18]

The utility of polyfluorenes for polymer light-emitting diode (PLED) applications has been limited because of their tendency to undergo interchain aggregation when the solid-state films of the polymers are maintained for several hours at temperatures above T_g. This aggregation gives rise to various undesirable characteristics, including excimer formation and a tailed emission band at long wavelengths (>500 nm). A number of solutions to this problem have been proposed, most of which involve the suppression of interchain aggregation and therefore of excimer formation. These solutions, outlined below, have led to the synthesis of polymers whose optical properties are more thermally stable.[8,9,13] Miller et al.[12,13] demonstrated that the introduction of bulky groups (e.g., substituted fluorene or anthracene) as end cappers or introduction of cross-linkable moieties such as the styryl group tends to suppress excimer emission and to enhance color stability. Huang et al.[14] reported that the inclusion of spirofluorene-functionalized bifluorene moieties into polyfluorenes prevented the polyfluorene from undergoing molecular aggregation, and that the spectral properties of these polyfluorenes were not degraded by treatment at higher temperatures. Introduction of dendron side groups into the C-9 position of polyfluorenes is also known to inhibit interchain aggregation of polyfluorenes and to improve the thermal stability in PL spectra.[15] Other trials of cross-linking or networking polyfluorenes were carried out by the groups of Carter and Advincula.[12] Carter et al. synthesized amorphous networked polyfluorenes using a spirobifluorene with a tetrareactive site and a cross-linkable styryl end group. These networked polyfluorenes exhibited good color stability and luminescence stability even after being heated to 150 °C.[12b] Advincula et al. prepared partially cross-linked polyfluorenes by reacting precursor-type polymers with tethered fluorene units. The PL spectra of these polyfluorenes from the oxidative cross-linking reaction with $FeCl_3$ were more or less broadened compared to the spectra of other poly(dialkylfluorene)s due to the presence of the partially oligomerized fluorene units in the polymer networks.[12c] As shown above, it is important to prepare polyfluorene derivatives that, even after thermal treatment, stably emit blue light without an increased level of excimer formation or a spectral tail at long wavelengths.

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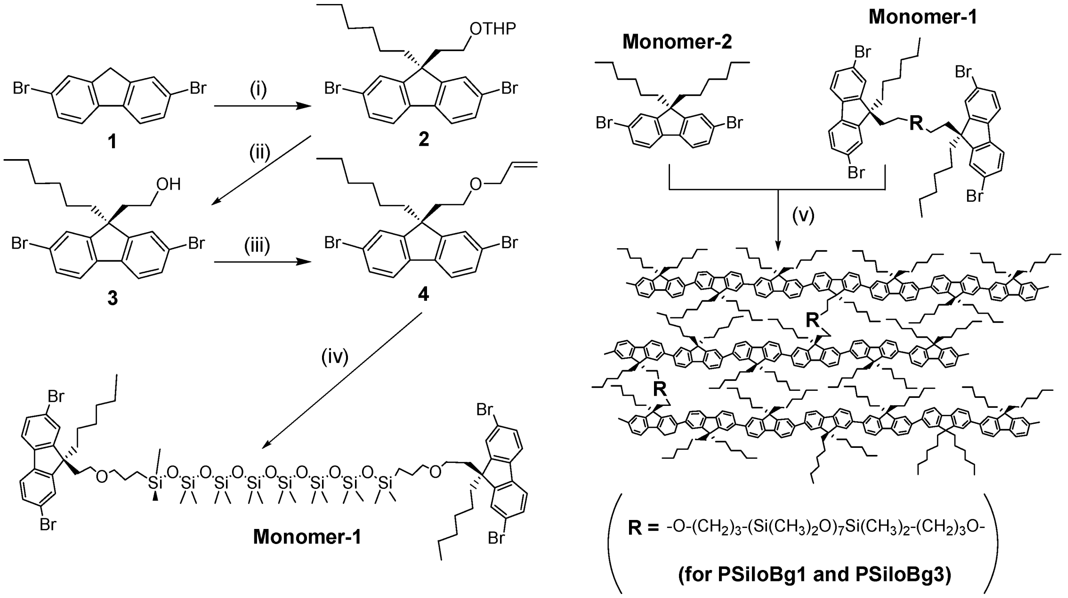
Scheme 1. Synthetic Routes to the Monomers and Polymers[22] [a]



[a] (i) NaOH (50 wt % aqueous solution), toluene, TBAB, bromohexane, 2-(2-bromoethoxy)tetrahydro-2*H*-pyran, 100 °C, 8 h; (ii) HCl (several drops), ethanol, 80 °C, 20 min; (iii) NaOH (50 wt % aqueous solution), toluene, TBAB, allyl bromide; (iv) hydride-terminated siloxane (MW ~ 580), toluene, Pt on activated carbon, 60 °C, 24 h; (v) (a) Ni(COD)$_2$, COD, DMF, 2,2′-bipyridyl, toluene, 80 °C, 3 days; (b) bromopentafluorobenzene, 80 °C, 24 h.

In this paper, we report a novel method for preparing soluble, bridged polyfluorenes in which poly(dihexylfluorene) chains are interconnected by siloxane linkages. To our knowledge, this is the first report of polyfluorenes containing siloxane moieties. Siloxane moieties are well-known as the materials which show the oxidative, thermal, and chemical stability and exhibit low dielectric constants. In addition, the dimethylsiloxane unit of poly(dimethylsiloxane) (PDMS) linkages occupies a larger volume than the methylene unit of the hydrocarbon linkage, and sufficiently long siloxane linkages separate the interchains of the polymers at some distance. These properties of siloxane linkages can effectively hinder the aggregation and excimer formation of polyfluorene chains. The PL spectra of these bridged polyfluorenes showed no evidence of excimer formation at ambient temperature, indicating that the polymers had not aggregated with the siloxane linkage. In addition, after thermal treatment in the solid state, the PL spectra of the bridged polyfluorenes showed no significant increase in excimer formation at wavelengths of >500 nm or the appearance of strong vibronic structures; as a result, the polyfluorenes continued to show almost pure blue emission even after being annealed at temperatures well above T_g. In the study presented here, the preparation of a bridged fluorene monomer provides a facile method for asymmetric substitution of functional groups at the C-9 positions of the fluorene units in the polyfluorene backbones. The molecular structures and synthetic procedures for the novel bridged polyfluorenes containing siloxane interchain bridges are shown in Scheme 1. In a few of the fluorene units of 9,9′-dihexylfluorene polymers, one hexyl chain at the C-9 position of dihexylfluorene was replaced with a siloxane bridge, which then connected the polyfluorene chains.

Experimental Section

Measurements. 2,7-Dibromofluorene, 1-bromohexane, 2-(2-bromoethoxy)tetrahydro-2*H*-pyran, tetrabutylammonium bromide, 2,2′-dipyridyl, and 1,5-cyclooctadiene were obtained from Aldrich Chemical Co. and used without further purification. Bis(1,5-cyclooctadienyl)nickel(0) was purchased from STREM Chemicals, and hydride-terminated siloxane (MW ~ 580) was obtained from ShinEtsu Chemical Co. Sodium hydroxide was purchased from Junsei Chemical Co., and all other reagents and solvents were purchased commercially, were analytical-grade quality, and were used without further purification.

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 300 and 400 spectrometers, respectively, with tetramethylsilane as an internal reference. For the NMR measurements, chloroform-*d* (CDCl$_3$) was used as the solvent. FTIR spectra were obtained using a Nicolet model 800 spectrometer with samples prepared as KBr pellets. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters GPC-150C instrument, using THF as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of the polymers were performed under a nitrogen atmosphere at a heating rate of 10 °C/min using a Dupont 9900 analyzer. UV−vis spectra were recorded on a Jasco V-530 UV−vis spectrometer, and PL spectra of the polymers were recorded at room temperature on a Spex Fluorolog-3 spectrofluorometer (model FL3-11) using spin-coated films. Cyclic voltammetry was performed on an AUTOLAB/PG-STAT12 model system with a three-electrode cell in a solution of Bu$_4$NBF$_4$ (0.10 M) in acetonitrile at a scan rate of 50 mV/s. A film of each polymer was coated onto a Pt wire electrode by dipping the electrode into a solution of the polymer (0.5 wt % in chloroform). A Pt wire was used as the counter electrode, and an Ag/AgNO$_3$ (0.10 M in acetonitrile) electrode was used as the reference electrode.

Syntheses of Monomers and Polymers. (1) Preparation of 2-[2-(2,7-Dibromo-9-hexylfluoren-9-yl)ethoxy]perhydro-2*H*-pyran (2). To a solution of 29.18 g (90 mmol) of 2,7-dibromofluorene, 11.95 g (72 mmol) of 1-bromohexane, 24.39 g (117 mmol) of 2-(2-bromoethoxy)tetrahydro-2*H*-pyran, 50 mL of toluene, and 1.2 g of tetrabutylammonium bromide (TBAB) as a phase-transfer catalyst was added 50 mL of a 50 wt % NaOH aqueous solution. The reaction mixture was then refluxed at 100 °C for 10 h, after which the reaction mixture was cooled to ambient temperature. The resulting solution was extracted with 200 mL of ethyl acetate from 200 mL of saturated sodium bicarbonate, washed with water, dried over anhydrous magnesium sulfate, and then concentrated in vacuo. The crude oily product was chromatographed on silica gel with a mixture of ethyl acetate and *n*-hexane (1/30) as the eluent to give 27.85 g (57.7% yield) of the product as a viscous oil: ^{1}H NMR (CDCl$_3$) δ 0.58 (br s, 2H), 0.74 (t, 3H), 0.98−1.18 (m, 6H), 1.20−1.65 (m, 6H), 1.92 (m, 2H), 2.32 (t, 2H), 2.73−3.15 (m, 2H), 3.23−3.47 (m, 2H), 4.10 (t, 1H), 7.41−7.50 (m, 6H); ^{13}C NMR (CDCl$_3$) δ 13.94, 19.29, 22.53, 23.32, 25.30, 29.44, 30.42, 31.41, 39.38, 40.68, 53.89, 61.88, 63.60, 98.68, 121.15, 121.47, 126.49, 130.35, 138.86, 151.71. Anal. Calcd for $C_{26}H_{32}Br_2O_2$: C, 58.22; H, 6.01. Found: C, 58.34; H, 6.17.

(2) Preparation of 2-(2,7-Dibromo-9-hexylfluoren-9-yl)-ethan-1-ol (3). To 16.21 g (30 mmol) of the THP-protected fluorene compound, **2**, in a single-necked 250-mL round-bottom flask was added 100 mL of acidified ethanol (containing 5 mL of a 10% HCl aqueous solution). The reaction mixture was then refluxed for 30 min, after which it was cooled to room temperature, and the ethanol was removed by rotoevaporation in vacuo at 60 °C. The reaction solution was extracted with chloroform and washed with a saturated aqueous sodium bicarbonate solution and two 100 mL portions of water. The combined chloroform solutions were then dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was column chromatographed on silica gel using a mixture of ethyl acetate and *n*-hexane (1/10) as the eluent, yielding 10.34 g (87.6% yield) of the viscous oily product: ^{1}H NMR (CDCl$_3$) δ 0.52 (br s, 2H), 0.75 (t, 3H), 1.00−1.10 (m, 6H), 1.92 (t, 2H), 2.27 (t, 2H), 2.96 (t, 2H), 7.42−7.51 (m, 6H); ^{13}C NMR (CDCl$_3$) δ 14.09, 22.61, 23.03, 29.49, 31.45, 40.43, 42.25, 53.76, 58.46, 121.38, 121.77, 126.33, 130.56, 138.71, 151.67. Anal. Calcd for $C_{21}H_{24}Br_2O$: C, 55.77; H, 5.35. Found: C, 55.91; H, 5.38.

(3) Preparation of 1-[2-(2,7-Dibromo-9-hexylfluoren-9-yl)ethoxy]prop-2-ene (4). The deprotected compound (**3**) (9.05 g, 20 mmol), allyl bromide (12 g), and tetrabutylammonium bromide (1.4 g) were dissolved in 30 mL of toluene over the course of 10 min. To this solution was added 100 mL of a 50 wt % NaOH aqueous solution, and the reaction mixture was stirred at 120−140 °C for 24 h. After being cooled to room temperature, the resulting solution was extracted with chloroform from brine and a saturated aqueous sodium bicarbonate solution, and finally distilled water. The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo to give an oily product. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and *n*-hexane (1/30) as the eluent, yielding 8.64 g (87.7% yield) of the oily product: ^{1}H NMR (CDCl$_3$) δ 0.63 (br s, 2H), 0.76 (t, 3H), 1.02−1.09 (m, 6H), 1.93 (m, 2H), 2.30 (t, 2H), 2.73 (t, 2H), 3.58 (d, 2H), 5.04 (m, 2H), 5.63 (m, 1H), 7.43−7.51 (m, 6H); ^{13}C NMR (CDCl$_3$) δ 14.00, 22.58, 23.33, 29.47, 31.46, 39.30, 40.55, 53.71, 66.20, 71.63, 116.71, 121.23, 121.61, 126.39, 130.46, 134.44, 138.77, 151.68. Anal. Calcd for $C_{24}H_{28}Br_2O$: C, 58.55; H, 5.73. Found: C, 58.46; H, 5.89.

(4) Preparation of 1-[2-(2,7-Dibromo-9-hexylfluoren-9-yl)ethoxy]-3-{1-[1-(1-{1-[1-(1-{4-[2-(2,7-dibromo-9-hexylfluoren-9-yl)ethoxy]-1,1-dimethyl-1-silabutoxy}-1-methyl-1-silaethoxy)-1-methyl-1-silaethoxy]-1-methyl-1-silaethoxy}-1-methyl-1-silaethoxy)-1-methyl-1-silaethoxy]-1-methyl-1-silaethoxy}-3-methyl-3-silabutane (Monomer-1). A total of 0.87 g (2.0 mmol) of the vinylfluorene compound (**4**) and 0.56 g (0.98 mmol) of hydride-terminated siloxane (MW ∼ 580) were dissolved in 30 mL of toluene, and 0.2 g of Pt on activated carbon was dispersed in the solution. The resulting solution was stirred at 60 °C for 24 h and then filtered through a medium-size glass filter packed with Celite-545. After the mixture had been filtered, the toluene was evaporated in vacuo and the concentrated crude product was purified by column chromatography using a mixture of ethyl acetate and *n*-hexane (1/30) as the eluent, yielding 1.21 g (86.25% yield) of the oily product: ^{1}H NMR (CDCl$_3$) δ −0.10 to 0.16 (m, 48H), 0.35 (m, 4H), 0.60 (b, 4H), 0.76 (t, 6H), 0.93−1.19 (m, 12H), 1.35 (m, 4H), 1.93 (m, 4H), 2.28 (t, 4H), 2.73 (t, 4H), 2.98 (t, 4H), 7.37−7.56 (m, 12H); ^{13}C NMR (CDCl$_3$) δ 0.11, 1.1, 1.2, 14.0, 14.1, 22.6, 23.3, 23.4, 29.5, 31.4, 39.4, 40.5, 53.8, 66.5, 73.6, 121.2, 121.6, 126.4, 130.4, 138.8, 151.8. Anal. Calcd for $C_{63}H_{104}Br_4O_9Si_8$: C, 48.82; H, 6.76. Found: C, 48.27; H, 6.49.

Table 1. Physical Properties of the Polymers

polymer	feed ratio (*x*/*y*)	content ratio (*x*/*y*)[a]	yield (%)	M$_W$ ($\times 10^4$)	PDI	T_g (°C)	T_d (°C)[b]
PDHF	100/0	100/0	62	8.2	2.3	75[c]	421
PSiloBg1	99/1	98.7/1.3	78	7.5	2.2	106	425
PSiloBg3	97/3	96.9/3.1	96	18.5	2.4	110	427

[a] Content ratios were calculated by NMR assignment of the polymers, and *x*/*y* indicates the ratio of 2,7-dibromo-9,9′-dihexylfluorene to the siloxane-bridged fluorene.[21] [b] Temperature resulting in a 5% weight loss based on the initial weight. [c] From ref 12b.

(5) Preparation of 2,7-Dibromo-9,9′-dihexylfluorene (Monomer-2). To a solution of 24.92 g (76.9 mmol) of 2,7-dibromofluorene, 26.05 g (157.8 mmol) of 1-bromohexane, 50 mL of toluene, and 1.4 g of tetrabutylammonium bromide as a phase-transfer catalyst was added 50 mL of a 50 wt % NaOH aqueous solution. The reaction mixture was then refluxed at 100 °C for 10 h, after which it was cooled to ambient temperature. The resulting solution was extracted with 200 mL of methylene chloride from 200 mL of saturated sodium bicarbonate, washed with water, dried over anhydrous magnesium sulfate, and then concentrated in vacuo. The crude product was purified by recrystallization with *n*-hexane several times, yielding 34.75 g (91.8% yield) of the solid product: ^{1}H NMR (CDCl$_3$) δ 0.58 (br s, 4H), 0.74 (t, 6H), 1.02−1.12 (m, 12H), 1.90 (m, 4H), 7.42−7.51 (m, 6H); ^{13}C NMR (CDCl$_3$) δ 14.00, 22.58, 23.66, 29.59, 31.46, 40.21, 55.70, 121.13, 121.49, 126.20, 130.17, 139.08, 152.58. Anal. Calcd for $C_{25}H_{32}Br_2$: C, 60.99; H, 6.55. Found: C, 61.05; H, 6.64.

All the copolymers were synthesized by the nickel(0)-mediated polymerization method (commonly called the Yamamoto coupling reaction).[13]

(6) Preparation of PSiloBg-3. A mixture of 0.735 g of bis(1,5-cyclooctadienyl)nickel(0), 0.417 g of 2,2′-dipyridyl, 0.2 mL of 1,5-cyclooctadiene, and 5 mL of anhydrous DMF was kept at 80 °C for 30 min under an argon atmosphere. To this solution was added dropwise a total of 1.8 mmol of monomers, comprising a mixture of 2,7-dibromo-9,9′-dihexylfluorene (monomer-2) and siloxane containing bridged fluorene (Monomer-1) in a molar ratio of 97/3, dissolved in 15 mL of toluene. The resulting solution was stirred at 80 °C for 3 days. Then, 0.1 g of bromopentafluorobenzene (the end capper) in 5 mL of anhydrous toluene was added to the polymer solution, and the resulting solution was stirred at 80 °C for a further 24 h. The polymer was precipitated in 400 mL of a mixture of HCl, acetone, and methanol (1/1/2, v/v). The filtered crude polymer was extracted with chloroform from an NaHCO$_3$ aqueous solution, washed with distilled water, and dried over anhydrous magnesium sulfate. The organic layer was concentrated in vacuo, dissolved in chloroform, and precipitated in methanol again. The resulting polymer was purified by Soxhlet extraction in methanol (80 °C, 3 days) and dried under vacuum. Finally, the dried polymer was dissolved in chloroform, precipitated in methanol, and dried in vacuo to give 0.617 g (96% yield) of a slightly yellow polymer: ^{1}H NMR (CDCl$_3$) δ 0 (m), 0.58 (m), 0.78 (t), 1.12 (m), 2.09 (m), 7.66−7.83 (m); FTIR (KBr) 2954, 2927, 2856, 1458, 1402, 1377, 1250, 1107, 1033, 999, 885, 813, 758 cm^{-1}. Anal. Calcd for PSiloBg-3: C, 89.44; H, 9.67. Found: C, 87.67; H, 9.84.

(7) Preparation of PSiloBg-1 and Poly(dihexylfluorene) (PDHF). The polymerization and purification procedures for PSiloBg-1 and PDHF were the same as those used for PSiloBg-3; the polymerization yields are listed in Table 1. The ^{1}H NMR and FTIR spectra of PSiloBg-1 and PDHF were similar to those of PSiloBg-3. Anal. Calcd for PSiloBg-1: C, 90.01; H, 9.69. Found: C, 89.47; H, 9.83. Anal. Calcd for PDHF: C, 90.30; H, 9.70. Found: C, 90.42; H, 9.96.

Results and Discussion

Synthesis and Characterization. We first synthesized 2-[2-(2,7-dibromo-9-hexylfluoren-9-yl)ethoxy]perhydro-2*H*-pyran (**2**) having different substituents at the

9 position of fluorene by alkylation of 2,7-dibromofluorene, and then deprotected **2** under acidic conditions to obtain 2-(2,7-dibromo-9-hexylfluoren-9-yl)ethan-1-ol (**3**). To synthesize compound **2**, at first we mixed three starting reagents [2,7-dibromofluorene, 1-bromohexane, and 2-(2-bromoethoxy)tetrahydro-2*H*-pyran] at a feeding ratio of 1/1/1. With regard to the feeding ratio of the reagents, the products were predicted to be in a ratio of 1/1/1 (33.3/33.3/33.3, mol %) for 2,7-dibromo-9,9′-dihexylfluorene, 2-{2-[2,7-dibromo-9-(2-perhydro-2*H*-pyran-2-yloxyethyl)fluoren-9-yl]ethoxy}perhydro-2*H*-pyran, and 2-[2-(2,7-dibromo-9-hexylfluoren-9-yl)ethoxy]-perhydro-2*H*-pyran, respectively. But, unexpectedly the yield of 2-[2-(2,7-dibromo-9-hexylfluoren-9-yl)ethoxy]-perhydro-2*H*-pyran (compound **2**) was 43 mol %. The higher yield of compound **2**, compared to the yields of the other two products, probably occurs because the reaction is accomplished in a two-phase solution of water and toluene, and the phase-transfer reaction is advantageous for the substitution of 2-(2-bromoethoxy)-tetrahydro-2*H*-pyran which has both a hydrophilic ethoxytetrahydro-2*H*-pyran moiety and a hydrophobic bromoethoxy moiety compared to 1-bromohexane which is a very hydrophobic material. Also, the substitution of two 2-(2-bromoethoxy)tetrahydro-2*H*-pyrans into the 9 position of a fluorene compound is shown to be difficult because of the sterically bulky size of 2-(2-bromoethoxy)-tetrahydro-2*H*-pyran compared to 1-bromohexane.

Therefore, we used the higher feeding ratio of 2-(2-bromoethoxy)tetrahydro-2*H*-pyran to obtain the higher yield of compound **2**. Moreover, we used the overdose of two alkyl bromides on the whole to prevent the formation of 9-monoalkylated fluorene derivatives which generate the keto defect sites of fluorene derivatives.[20] The resulting yield of compound **2** was ~58 mol %. Compounds **2** and **3** were clearly isolated from the reactants and other byproducts at the respective synthetic steps by column chromatography, as judged from the evident separation of their spots on the TLC plate. After allylation of **3** under basic conditions, the siloxane oligomer-bridged fluorene monomer (Monomer-1) was prepared by hydrosilation between 1-[2-(2,7-dibromo-9-hexylfluoren-9-yl)ethoxy]prop-2-ene (**4**) and the H-terminated siloxane (MW ~ 580). 2,7-Dibromo-9,9′-dihexylfluorene (Monomer-2) was synthesized by alkylation of 2,7-dibromofluorene. The new siloxane-bridged fluorene monomer (Monomer-1) was successfully synthesized and confirmed by elemental analysis, the ^{1}H NMR spectrum, and the ^{13}C NMR spectrum, and the ^{1}H NMR spectrum of Monomer-1 is shown in Figure 1. Monomer-1 and Monomer-2 were polymerized via the Ni(0)-mediated coupling reaction to give PSiloBg1 and PSiloBg3. The crude polymers were purified using a previously specified procedure.[11a] The polymerization yields are reported in Table 1. The polymerization yield of PSiloBg3 (96%) was higher than that of PSiloBg1 (78%), but the polymerization yield of PSiloBg1 exceeded that of PDHF (62%). The molecular structures of PSiloBg1 and PSiloBg3, shown in Scheme 1, were confirmed by ^{1}H NMR and FTIR spectroscopy. Both the ^{1}H NMR and FTIR spectra of the copolymers (Figures 2 and 3, respectively) exhibited characteristics of PDHF due to the similarity of the molecular structures of the copolymers and PDHF, and additionally exhibited peaks due to the siloxane groups. For PSiloBg1 and PSiloBg3, proton peaks characteristic of Si−C$\underline{H}_3$ groups in siloxane units appear in the ^{1}H NMR spectrum near 0 ppm (Figure 2), and the FTIR spectra contain Si−O stretching bands at 1107 and 1033 cm^{-1} and a Si−C stretching band at 1250 cm^{-1} (Figure 3). The spectral features associated with the siloxane groups, proton peaks near 0 ppm in the ^{1}H NMR spectra and Si−O stretching bands near 1107 and 1033 cm^{-1} in the FTIR spectra, were more intense in the PSiloBg3 spectra than in those of PSiloBg1. The content ratio of a siloxane-bridged

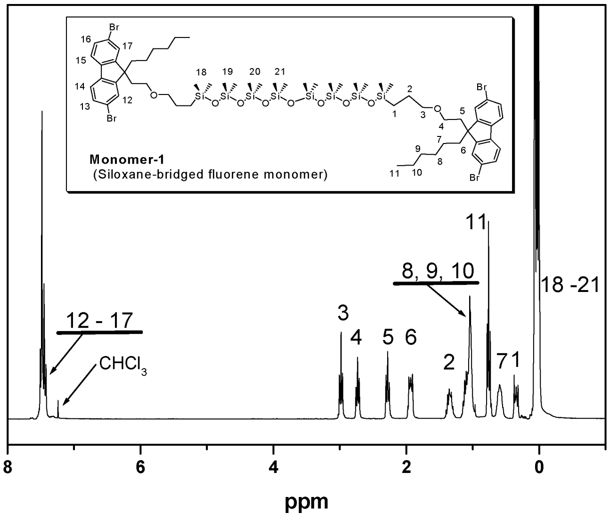


Figure 1. ^{1}H NMR spectrum of Monomer-1 in the range of −1 to 8 ppm (in CDCl$_3$).[22]

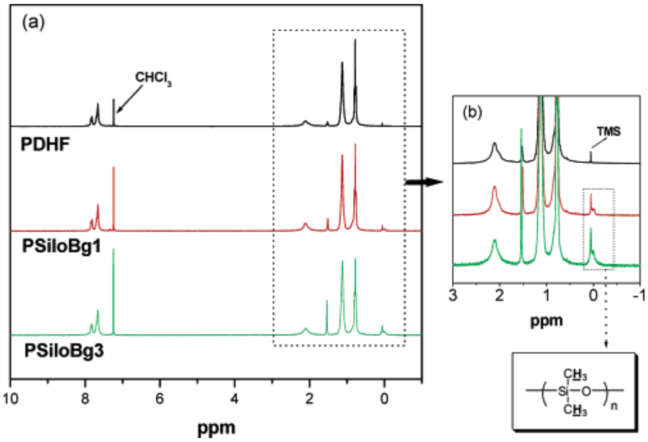


Figure 2. ^{1}H NMR spectra of the polymers (in CDCl$_3$): (a) ^{1}H NMR spectra of the polymers in the range of −1 to 10 ppm and (b) ^{1}H NMR spectra of the polymers in the range of −1 to 3 ppm.

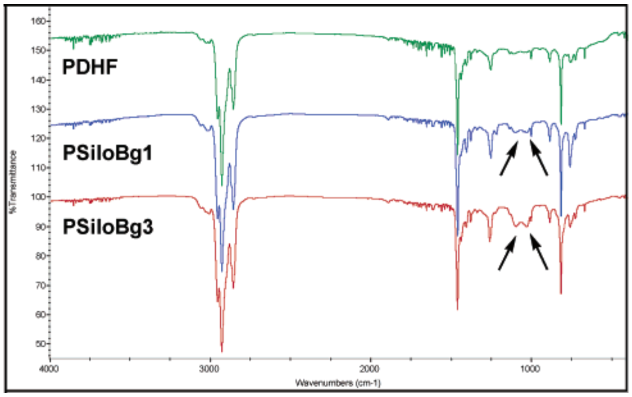


Figure 3. FTIR spectra of the polymers: first spectrum, homo-PF; second spectrum, PSiloBg1; and third spectrum, PSiloBg3 in a descending series.

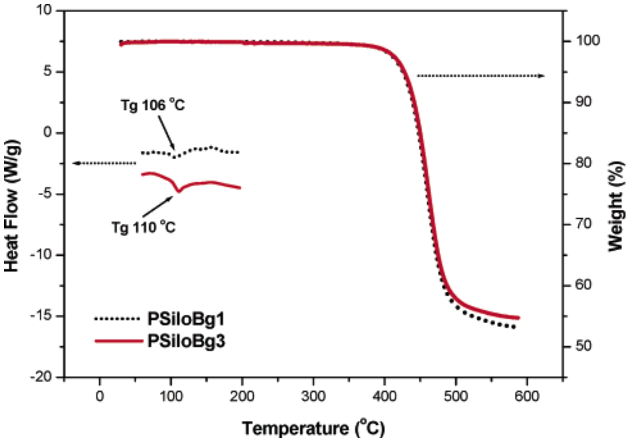


Figure 4. TGA traces and DSC thermograms of the polymers.

fluorene monomer in the polymers was calculated from the ratio of the integrals of the ^{1}H NMR spectral features corresponding to aromatic protons and siloxane unit protons (near 0 ppm).[22] The calculated content ratios were similar to the polymerization feed ratios; the content ratios of the monomers in the polymers and the higher polymerization yields of the bridged polymers compared to those of PDHF show that the network systems of the bridged polymers were successfully fabricated.[12b]

PSiloBg1 and PSiloBg3 exhibited good solubility in common organic solvents such as chloroform, tetrahydrofuran, toluene, *p*-xylene, and chlorobenzene without any gel formation. It seems that the low levels of the flexible siloxane bridges do not reduce the solubility of the copolymers. All the copolymers easily formed films when solutions of the polymers in chloroform were cast on a glass substrate and the solvent was evaporated under air. The molecular weights of the synthesized polymers were determined by gel permeation chromatography (GPC) against polystyrene standards with tetrahydrofuran (THF) as the eluent. The molecular weights and polydispersity indices of the polymers are reported in Table 1. The molecular weight of PSiloBg3 (M_n = 76 000, M_W = 185 000) was higher than that of PSiloBg1 (M_n = 34 000, M_W = 75 000) or PDHF (M_n = 35 000, M_W = 82 000). Moreover, PSiloBg3 exhibited molecular weights higher than those previously reported for networked or cross-linked polyfluorenes.[12] The reason behind the higher molecular weights of PSiloBg3 is likely that this polymer contains the highest siloxane bridge content of the polymers, which presumably leads to the creation of larger network systems in PSiloBg3 than in PSiloBg1 and PDHF. The polydispersity indices of the polymers equaled 2.2−2.4.

The glass transition temperatures (T_g) of the bridged polyfluorenes were determined by DSC (heating rate of 10 °C/min) and are reported in Table 1. The glass transition temperatures increase with increasing siloxane content, and the T_g values for PSiloBg1 and PSiloBg3 (106 and 110 °C, respectively) are higher than that of PDHF (75 °C). The observation of a higher T_g for PSiloBg3 is attributed to that polymer having a more extensive network system. In addition, the observation of a higher T_g for the bridged polymers than for PDHF provides further evidence that PSiloBg1 and PSiloBg3 are the network systems of bridged polymers. The thermal stabilities of the polymers were measured by TGA (heating rate of 10 °C/min). The copolymers exhibited good thermal stability. As shown in Figure 4, the decomposition temperatures for 5% weight loss (T_d) of the copolymers were above 420 °C,[17] and the copolymers exhibited no significant weight loss upon being heated to ~400 °C (see Table 1 for T_d values).

Table 2. Optical Properties of the Polymers

polymer	λ_{max} (UV, nm) solution	λ_{max} (UV, nm) film	λ_{max} (PL, nm) solution	λ_{max} (PL, nm) film	E_g (eV, UV/nm)[a]	Φ_{PL} [b]
PDHF	385	391	415	425	2.91	0.82
PSiloBg1	385	392	415	425	2.91	0.83
PSiloBg3	386	391	415	424	2.91	0.86

[a] E_g, calculated from the onset values of the absorption spectra of the spin-coated film on quartz. [b] Solution fluorescence quantum yields measured in chloroform relative to quinine sulfate (ca. 1 × 10^{-5} M) in 0.10 M H_2SO_4 as a standard.

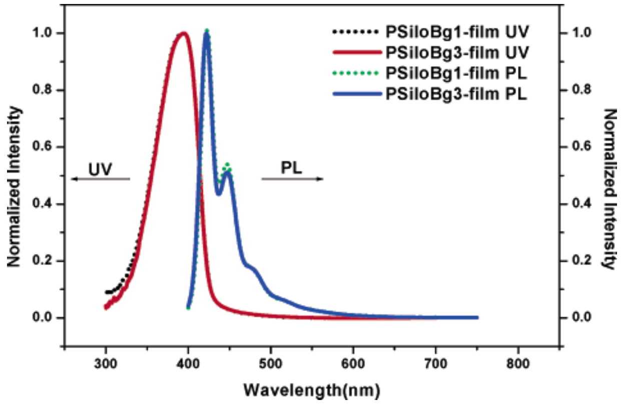


Figure 5. UV−visible absorption and photoluminescence spectra of the polymers as spin-coated films (2000 rpm, *p*-xylene).

Optical and Photoluminescence Properties. The key features of the UV−vis and PL spectra of the bridged polyfluorenes in *p*-xylene are listed in Table 2. The maximum absorption wavelengths of PSiloBg1 and PSiloBg3 in *p*-xylene were 385 and 386 nm, respectively. The maximum absorption wavelengths and spectral patterns of the polymers in *p*-xylene are not significantly different from those of PDHF.[14] The PL spectra of the polymers in *p*-xylene exhibit a maximum emission wavelength of 415 nm for both PSiloBg1 and PSiloBg3. Moreover, the onsets and shapes of the emission spectra in *p*-xylene are the same for PSiloBg1, PSiloBg3, and PDHF. This result is consistent with the findings of Huang et al.,[14] who reported that substitution of the 9 position of fluorene units of a polyfluorene does not remarkably change the electronic structure of the polyfluorene.

The UV−vis and PL spectra of thin films of PSiloBg1 and PSiloBg3 on quartz plates prepared by spin casting at 2000 rpm of a 1 wt % polymer solution in *p*-xylene are shown in Figure 5. The UV−vis absorption patterns of the two bridged polyfluorenes are similar, showing absorption maxima in the range of 391−392 nm, and these absorption patterns are the same as that of PDHF. The PL spectra of the polymer thin films (Figure 5) are also similar to each other and to those of PDHF in onset and shape, with a PL maximum of ~425 nm. In previous studies, the aggregation peak of PDHF was observed at ~525 nm;[16] however, in our experiments, this peak was indistinct. This discrepancy is attributed to the end capping of the copolymers and the higher molecular weight (MW = 8.4 × 10^4), compared to that of PDHF, used in the study presented here.[13] Miller et al.[13a] found that high-molecular weight fluorene copolymers may not

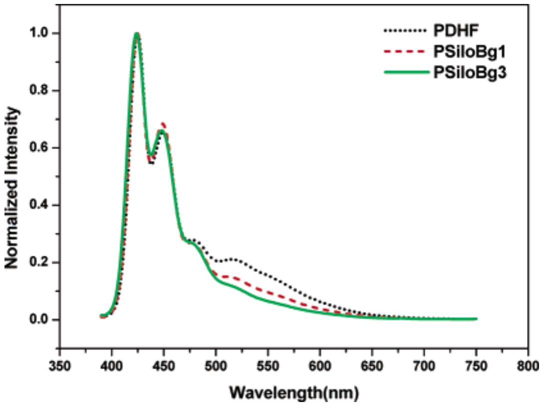


Figure 6. Photoluminescence spectra of PDHF (···), PSiloBg1 (- - -), and PSiloBg3 (—) as spin-coated films (1500 rpm, *p*-xylene) and annealed at 150 °C for 30 min.

exhibit any emission at longer wavelengths. The photoluminescent quantum yields of PSiloBg1 and PSiloBg3, which are listed in Table 2, are similar to those of PDHF.[17] The PL quantum yields of PSiloBg1 and PSiloBg3 in solution were 0.83 and 0.86, respectively.[17]

Spin-coated thin films of PSiloBg1 and PSiloBg3 on quartz plates were used to examine the thermal stability of the optical properties of the bridged copolymers. The films were maintained at 150 °C for 30 min in air, and then cooled to room temperature.[12,14] The PL spectra of the annealed copolymer films are shown in Figure 6. The PL spectrum of the annealed PSiloBg3 film exhibits no additional peaks at wavelengths of >500 nm due to aggregation or excimer formation, and no increased vibronic peak intensities. In contrast, under the same experimental conditions, the PL spectrum of PDHF annealed at 150 °C exhibits peaks characteristic of aggregation and excimer formation at wavelengths of >500 nm. Thus, the introduction of siloxane bridges into polyfluorenes seems to restrict aggregation of the polymer chains. Previous studies have found that the polymer chains of polyfluorenes heated to a temperature above their T_g pack more closely with each other because of increased diffusive motion and that PDHF annealed at >100 °C shows an additional emission peak above 500 nm due to the formation of interchain excimers.[14] The reduced levels of excimer formation and aggregation in the bridged copolymers are probably due to the siloxane bridges preventing the free rearrangement of the polyfluorene chains. This property of siloxane-bridged polyfluorenes can potentially be exploited to create polyfluorene derivatives with thermally stable spectral features. For example, the copolymer PSiloBg3 prepared in this work does not exhibit an increase in the magnitudes of vibronic peaks and aggregation peaks after annealing at temperatures well above its glass transition temperature, most likely because the bridging system in this polymer lowers the mobility of the polymer chains and the flexible siloxane linkages occupy sufficient volume to prevent efficiently the aggregation of the polymer chains.

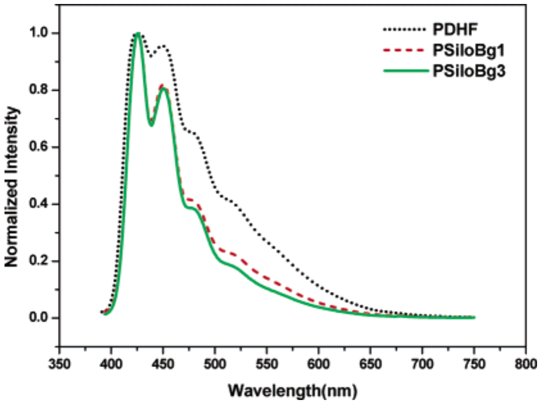


Figure 7. Photoluminescence spectra of PDHF (···), PSiloBg1 (- - -), and PSiloBg3 (—) as spin-coated films (1500 rpm, *p*-xylene) and annealed at 150 °C for 4 h.

Table 3. Normalized Peak Intensity and Full Width at Half-Maximum of the Polymers

	annealed at 150 °C, 30 min				annealed at 150 °C, 4 h			
polymer	0−0[a]	0−1[a]	0−2[a]	fwhm[b] (nm)	0−0[a]	0−1[a]	0−2[a]	fwhm[b] (nm)
PDHF	1.00	0.65	0.28	43	1.00	0.96	0.65	85
PSiloBg1	1.00	0.68	0.27	43	1.00	0.82	0.41	52
PSiloBg3	1.00	0.66	0.27	44	1.00	0.81	0.39	51

[a] Columns denoted 0−1 and 0−2 give the relative peak intensity of the resolved peaks at 448 and 476 nm, respectively, in the standards of the peak at 424 nm (0−0).[18] [b] fwhm means full width at half-maximum.

Additional experiments in which the polymer films were annealed at 150 °C for 4 h yielded very interesting results. As shown in Figure 7, after PDHF had been annealed for 4 h, its PL spectra exhibited a very broad fwhm (full width at half-maximum) (85 nm) as well as more intense vibronic peaks at 450 and 478 nm, aggregation peaks, and excimer formation at >500 nm. In contrast, after 4 h at 150 °C the PL spectrum of PSiloBg3 exhibited remarkably suppressed vibronic peaks and aggregation peaks, and a small fwhm (51−52 nm) compared to that of PDHF. Thus, the inclusion of a bridging system in the polyfluorene structure seems to restrict the various vibronic bands of the polymer chains, aggregation, and the formation of excimers, even after thermal treatment at high temperatures, thereby ensuring the spectral stability of the bridged polymers.[14] For purposes of comparison, the fwhm values and relative peak intensity around 425, 450, and 475 nm of the thin films of PSiloBg1, PSiloBg3, and PDHF annealed at 150 °C for 30 min and 4 h are listed in Table 3.[19]

Electrochemical Properties. To investigate the electrochemical properties of the copolymers and estimate the HOMO and LUMO energy levels, cyclic voltammetry (CV) was carried out using a copolymer-coated platinum electrode as the working electrode, a platinum wire as the counter electrode, and an Ag/AgNO$_3$ (0.10 M) electrode as the reference electrode. CV was performed with these three electrodes immersed in a solution of 0.1 M tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_3$) in anhydrous acetonitrile at room temperature under nitrogen with a scan rate of 50 mV/s. The measurements were calibrated using ferrocene as the standard. Figure 8 exhibits the oxidation wave of the copolymers induced by p-type doping. From the first oxidation process, the HOMO energy levels of PSilo1Bg1 and PSilo3Bg3 were estimated to be 5.85 and 5.86 eV, respectively; these values coincide with the HOMO energy level (5.85 eV) of PDHF.[17] The LUMO energy levels of the polymers were estimated from the onset of the absorption spectra of the copolymer films. The LUMO energy levels of PSiloBg1, PSiloBg3, and PDHF were estimated to be 2.94, 2.95, and 2.94 eV, respectively. The band gap energies of the bridged copolymers

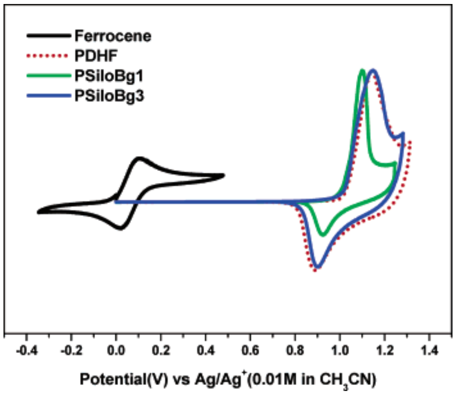


Figure 8. Cyclic voltammograms of PSiloBg1 and PSiloBg3.

Table 4. Electrochemical Properties and Energy Levels of the Polymers

polymer	p-doping (V vs SCE) E_{pa}	E_{pc}	$E_{1/2}$	E_g (eV, UV/nm)	HOMO (eV)[a]	LUMO (eV)[b]
PDHF	1.14	0.89	1.02	2.91	5.85	2.94
PSiloBg1	1.10	0.93	1.02	2.91	5.85	2.94
PSiloBg3	1.15	0.90	1.03	2.91	5.86	2.95

[a] Determined from $E_{1/2}$ (energy level of ferrocene of 4.8 eV under vacuum).[17] [b] Calculated from the HOMO and E_g.

and PDHF were obtained from the onset of the UV spectrum of each polymer; all the polymers exhibited a band gap energy of 2.91 eV.[17] Thus, within the errors of the experimental measurements, PSilo1Bg1, PSilo3Bg3, and PDHF have the same HOMO and LUMO energy levels and band gap energies. This result indicates that the siloxane linkages of the bridged copolymers are not involved in the oxidation of the polymers, and that the siloxane linkages do not affect the redox properties of the fluorene copolymers compared to those of PDHF. The HOMO−LUMO energy levels and band gap energies of the polymers are listed in Table 4.

Summary

We have synthesized a novel type of bridged fluorene copolymer containing siloxane linkages via Ni-mediated polymerization. This work is related to the first reported polyfluorene derivatives containing siloxane units. The bridged polyfluorenes exhibited higher polymerization yields, molecular weights (for PSiloBg3), and glass transition temperatures than PDHF. Additionally, in contrast to PDHF, the bridged polyfluorenes exhibited almost pure blue PL emission. Importantly, even after being annealed at 150 °C for 30 min, the bridged polyfluorenes exhibited structureless PL spectra and a narrow fwhm (43−44 nm). Moreover, the PL spectra of the bridged polyfluorenes showed no increase in the magnitudes of vibronic peaks and excimer peaks above 500 nm and exhibited very small fwhm values (51 nm) even after being annealed at 150 °C for 4 h in air. In contrast, the PL spectra of PDHF annealed at 150 °C for 4 h exhibited strong vibronic bands at ∼450 and ∼478 nm and more intense excimer peaks above 500 nm, and the PL spectral fwhm of PDHF was very large (85 nm). These results highlight the promise of polyfluorenes with siloxane bridges as candidates for pure blue light-emitting materials. In future work, we intend to focus on the improvement of the electroluminescent properties of bridged polyfluorenes.

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References and Notes

(1) Bourroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackey, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
(2) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Eng.* **1998**, *37*, 402.
(3) Shim, H. K.; Jin, J. I. *Adv. Polym. Sci.* **2002**, *158*, 194.
(4) (a) Hwang, D. H.; Shim, H. K.; Lee, J. I.; Lee, K. S. *Chem. Commun.* **1994**, 2461. (b) Kim, S. T.; Hwang, D.; Li, X. C.; Gruner, J.; Friend, R. H.; Holmes, A. B.; Shim, H. K. *Adv. Mater.* **1996**, *8*, 879. (c) Ko, S. W.; Jung, B. J.; Ahn, T.; Shim, H. K. *Macromolecules* **2002**, *35*, 6217.
(5) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.
(6) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686.
(7) Fukuda, M.; Sawada, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1989**, *28*, 1433.
(8) Yu, W.-L.; Pei, J.; Cao, Y.; Huang, W.; Heeger, A. J. *Chem. Commun.* **1999**, 1837.
(9) Pei, J.; Yu, W.-L.; Huang, W.; Heeger, A. J. *Chem. Commun.* **2000**, 1631.
(10) Ego, C.; Marsitzky, D.; Becker, S.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; MacKenzie, J. D.; Silva, C.; Friend, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 437.
(11) (a) Cho, N. S.; Hwang, D. H.; Lee, J. I.; Jung, B. J.; Shim, H. K. *Macromolecules* **2002**, *35*, 1224. (b) Hwang, D. H.; Cho, N. S.; Lee, J. I.; Shim, H. K. *Opt. Mater.* **2003**, *21*, 199. (c) Jung, B. J.; Lee, J. I.; Chu, H. Y.; Do, L. M.; Shim, H. K. *Macromolecules* **2002**, *35*, 2282. (d) Lim, E. H.; Jung, B. J.; Shim, H. K. *Macromolecules* **2003**, *36*, 4288.
(12) (a) Klärner, G.; Lee, J. I.; Lee, V. Y.; Chan, E.; Chen, J. P.; Nelson, A.; Markiewicz, D.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800. (b) Marsitzky, D.; Murray, J.; Scott, J. C.; Carter, K. R. *Chem. Mater.* **2001**, *13*, 4285. (c) Inaoka, S.; Advincula, R. *Macromolecules* **2002**, *35*, 2426.
(13) (a) Lee, J. I.; Klärner, G.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1083. (b) Klärner, G.; Lee, J. I.; Davey, M. H.; Miller, R. D. *Adv. Mater.* **1999**, *11*, 115.
(14) (a) Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 828. (b) Zeng, G.; Yu, W.-L.; Chua, S.-J.; Huang, W. *Macromolecules* **2002**, *35*, 6907.
(15) (a) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946. (b) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965. (c) Tang, H. J.; Fujiki, M.; Zhang, Z. B.; Torimitsu, K.; Motonaga, M. *Chem. Commun.* **2001**, 2426. (d) Chou, C. H.; Shu, C. F. *Macromolecules* **2002**, *35*, 9673.
(16) Xia, C.; Advincula, R. *Macromolecules* **2001**, *34*, 5854.
(17) Suh, Y. S.; Ko, S. W.; Jung, B. J.; Shim, H. K. *Opt. Mater.* **2002**, *21*, 109.
(18) Wu, F. I.; Reddy, S.; Shu, C. F.; Liu, M. S.; Jen, A. K. Y. *Chem. Mater.* **2003**, *15*, 269.
(19) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1365.
(20) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477.
(21) The calculation equation of x/y is $x/y = (48A - 12B)/6B$, where A denotes the integral of peaks at 7.5−8.0 ppm of ^{1}H NMR spectra of the copolymers, B denotes the integral of near 0 ppm of ^{1}H NMR spectra of the copolymers, 48 is derived from the H number of the siloxane linkages in Monomer-1, 12 is derived from the H number of the fluorene moieties in Monomer-1, and 6 is derived from the H number of the fluorene moieties in Monomer-2.
(22) Because the siloxane linkage is a polydisperse material, the accurate expression of the siloxane linkage is $[Si(CH_3)_2O]_7$-$Si(CH_3)_2$.

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