

Synthesis and Characterization of Liquid Crystalline Side-Chain Block Copolymers Containing Luminescent 4,4'-Bis(biphenyl)fluorene Pendants

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ABSTRACT: A series of new liquid crystalline homopolymers, copolymers, and block copolymers were polymerized from styrene-macroinitiator (**SMi**) and methacrylates with pendent 4,4'-bis(biphenyl)fluorene (**M1**) and biphenyl-4-ylfluorene (**M2**) groups through atom transfer radical polymerization (ATRP). The number-average molecular weights (M_n) of polymers **P1-P4** were 10,007, 14,852, 6,275, and 10,463 g mol^{-1} with polydispersity indices values of 1.21, 1.15, 1.31, and 1.22, respectively. All polymers exhibit the nematic phase. The thermal, mesogenic, and photoluminescent properties of all polymers were investigated. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 4564–4572, 2007

Keywords: atom transfer radical polymerization; block copolymers; liquid crystalline polymer; photoluminescence

INTRODUCTION

During the past decade, there are several types of liquid crystalline (LC) block copolymers produced by living free-radical polymerizations.^{1–5} Matyjaszewski and coworkers⁶ and Sawamoto and Kamigaito⁷ independently developed transition metal catalyzed living free radical polymerization known as atom transfer radical polymerization (ATRP), which is typically initiated by an alkyl halide ($R-X$) and catalyzed by a transition metal complex, such as CuX/bpy . ATRP has been demonstrated to provide controlled polymerizations of styrenes, methacrylates, and acrylonitriles with variations of compositions and architectures.

Recently, ATRP were also used in the synthesis of side-chain LC block copolymers,^{8–12} in

which mesogenic pendent groups were grafted onto polymer backbones to form side-chain LC blocks. The interest in this type of materials resides in the cohesive properties of two (or more than two) completely different polymers that are chemically bonded to each other. The macrophase separation takes place because of the segregation of different polymer chains. To introduce luminescent properties into LC polymers, the combination of long conjugation rigid cores with flexible chains is required for the molecular design of luminescent LCs.^{13–15} However, the microphase structures of side-chain LC polymers were influenced by the mesogenic groups, such as azobenzene^{16–18} and biphenyl^{19–24} units, which were frequently used in LC monomers.

In our previous studies,^{25,26} main-chain block copolymers containing conjugated fluorene, thiophene, and biphenyl backbones as well as side-chain block copolymers containing biphenyl-4-ylthiophene or cyanoterphenyl pendants possess the smectic A and columnar (Col_h ,

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and Col.) phases, but side-chain block copolymers consisting of biphenyl-4-ylfluorene pendants possess the nematic phase. Herein, a series of a new mesogenic homopolymer and block copolymer (**P1** and **P2**), which were composed of styrene-macroinitiators (**SMi**) and methacrylates with pendent 4,4'-bis(biphenyl)fluorene (**M1**) groups, were synthesized through ATRP. In addition, random copolymer **P3** and block copolymer **P4** consisting of pendent 4,4'-bis(biphenyl)fluorene units (**M1**) and biphenyl-4-ylfluorene units (**M2**) were also prepared by ATRP. Furthermore, thermal, mesogenic, and PL properties of all polymers were also investigated in this study.

EXPERIMENTAL

Measurements

^1H NMR spectra were recorded on a Varian unity 300 MHz spectrometer using CDCl_3 and d_6 -DMSO solvents. Elemental analyses were performed on a HERAEUS CHN-OS RAPID elemental analyzer. Transition temperatures were determined by differential scanning calorimetry (DSC) (Perkin-Elmer, model: Diamond) with a heating and cooling rate of $5\text{ }^\circ\text{C}/\text{min}$. The mesogenic properties were studied using a polarizing optical microscope (POM) (Leica, model: DMLP) equipped with a hot stage. Thermogravimetric analysis (TGA) was conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen. Gel permeation chromatography (GPC) analysis was conducted on a Waters 1515 separation module with chloroform as the eluant against a polystyrene calibration curve. High-resolution electron impact mass data were obtained on a Finnigan-MAT-95XL. UV-visible absorption spectra were recorded in dilute THF solutions (10^{-6} M) on a HP G1103A spectrophotometer. Photoluminescence (PL) spectra were obtained on a Hitachi F-4500 spectrophotometer.

Materials

Chemicals and solvents were reagent grade and purchased from Aldrich, ACROS, TCI, and Lancaster Chemical. Dichloromethane and THF were distilled to keep anhydrous before use. Pyridine was dried by refluxing over calcium

hydride. The other chemicals were used without further purification.

Synthesis

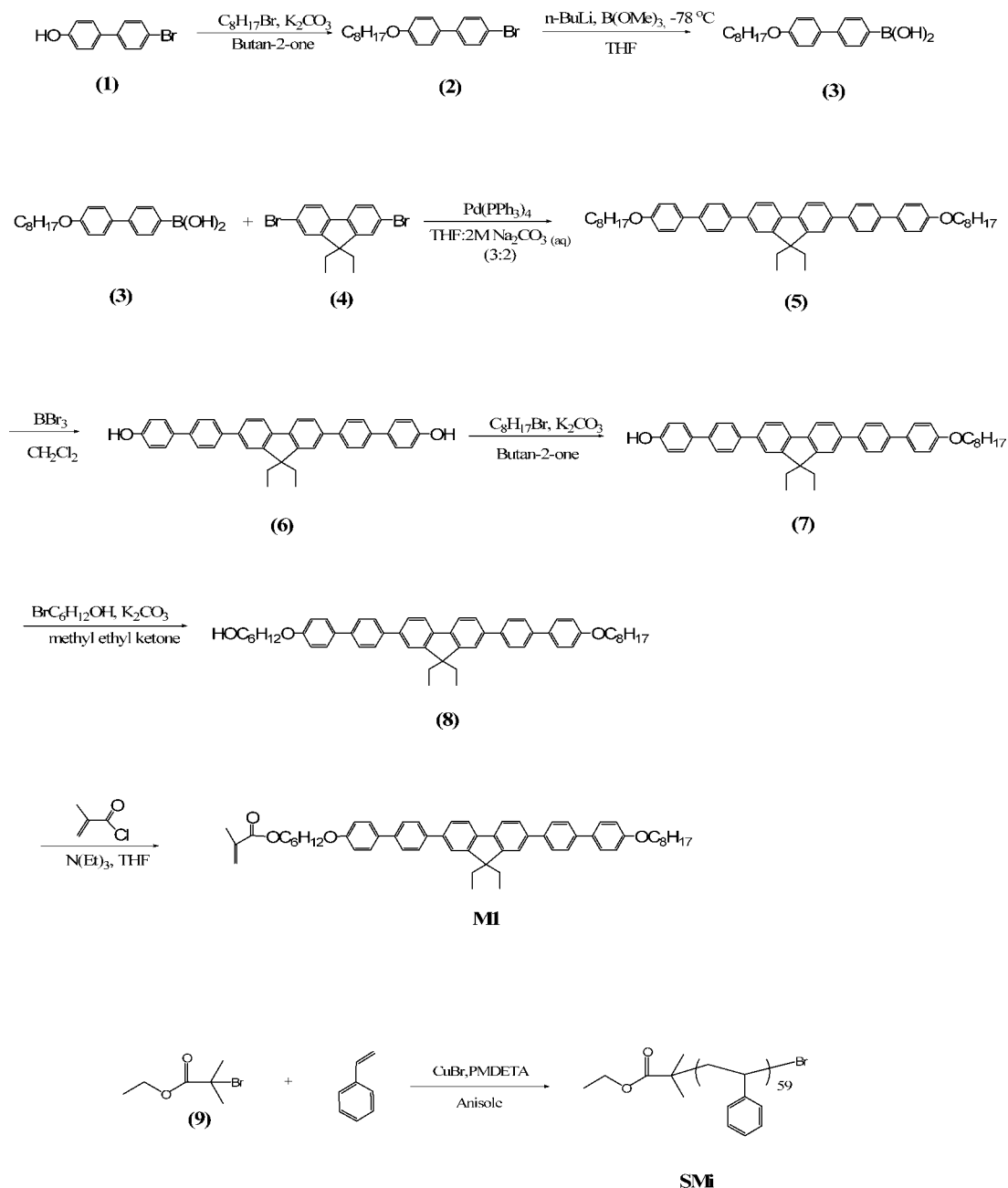
ATRP is very versatile and is tolerant for a wide range of functional groups present either in the monomers, solvents, or initiators.^{25,27,28} Schemes 1 and 2 summarize the steps involved in the syntheses of the macroinitiator (**SMi**), monomers (**M1** and **M2**), and polymers (**P1–P4**), and the details of each step are given below.

4-Bromo-4'-octoxybiphenyl (**2**)

1-Bromooctane (11.6 g, 60 mmol), 4-bromo-4'-hydroxybiphenyl (10 g, 40 mmol), and potassium carbonate (16.6 g, 120 mmol) were dissolved in butan-2-one (100 mL) and reacted under reflux for 24 h. After cooling to room temperature, the potassium salt was filtered off. The solvent was removed by rotavapor and the crude product was recrystallized from petroleum ether (bp: $35\text{--}60\text{ }^\circ\text{C}$) to yield a white solid (13.5 g, 93%). ^1H NMR (ppm, CDCl_3), δ : 0.89 (t, $J = 6.9\text{ Hz}$, 3H), 1.29–1.47 (m, 10H), 1.80 (quintet, $J = 6.6\text{ Hz}$, 2H), 3.98 (t, $J = 8.6\text{ Hz}$, 2H), 6.99 (d, $J = 8.8\text{ Hz}$, 2H), 7.40–7.54 (m, 6H).²⁵

4'-Octoxybiphenyl-4-ylboronic Acid (**3**)

4-Bromo-4'-octoxybiphenyl (**2**) (5 g, 13.8 mmol) was dissolved in THF (200 mL) and then *n*-butyllithium (8.9 mL, 2.5 M, 22.1 mmol) was added dropwise to react at $-78\text{ }^\circ\text{C}$. The reaction mixture was maintained under this condition for 1 h. Furthermore, it was added dropwise to trimethyl borate solution (3.5 g, 33.2 mmol) at $-78\text{ }^\circ\text{C}$. The solution was allowed to cool to room temperature overnight. The final solution was acidified with 100 mL of 10% HCl solution and stirred for 45 min at room temperature. The solution was washed with saturated sodium carbonate solution and water, and then THF was removed. The crude product was extracted by diethyl ether and the organic layer was dried over magnesium sulfate. After removing the solvent by rotavapor, the resulting solid was washed with petroleum ether and briefly dried on filter to obtain a white solid (6.0 g, 80%). ^1H -NMR (ppm, d_6 -DMSO), δ : 0.85 (t, $J = 7.2\text{ Hz}$, 3H), 1.24–1.41 (m, 10H), 1.71 (quintet, $J = 6.6\text{ Hz}$, 2H), 3.98 (t, $J = 6.6\text{ Hz}$, 2H), 6.99 (d,



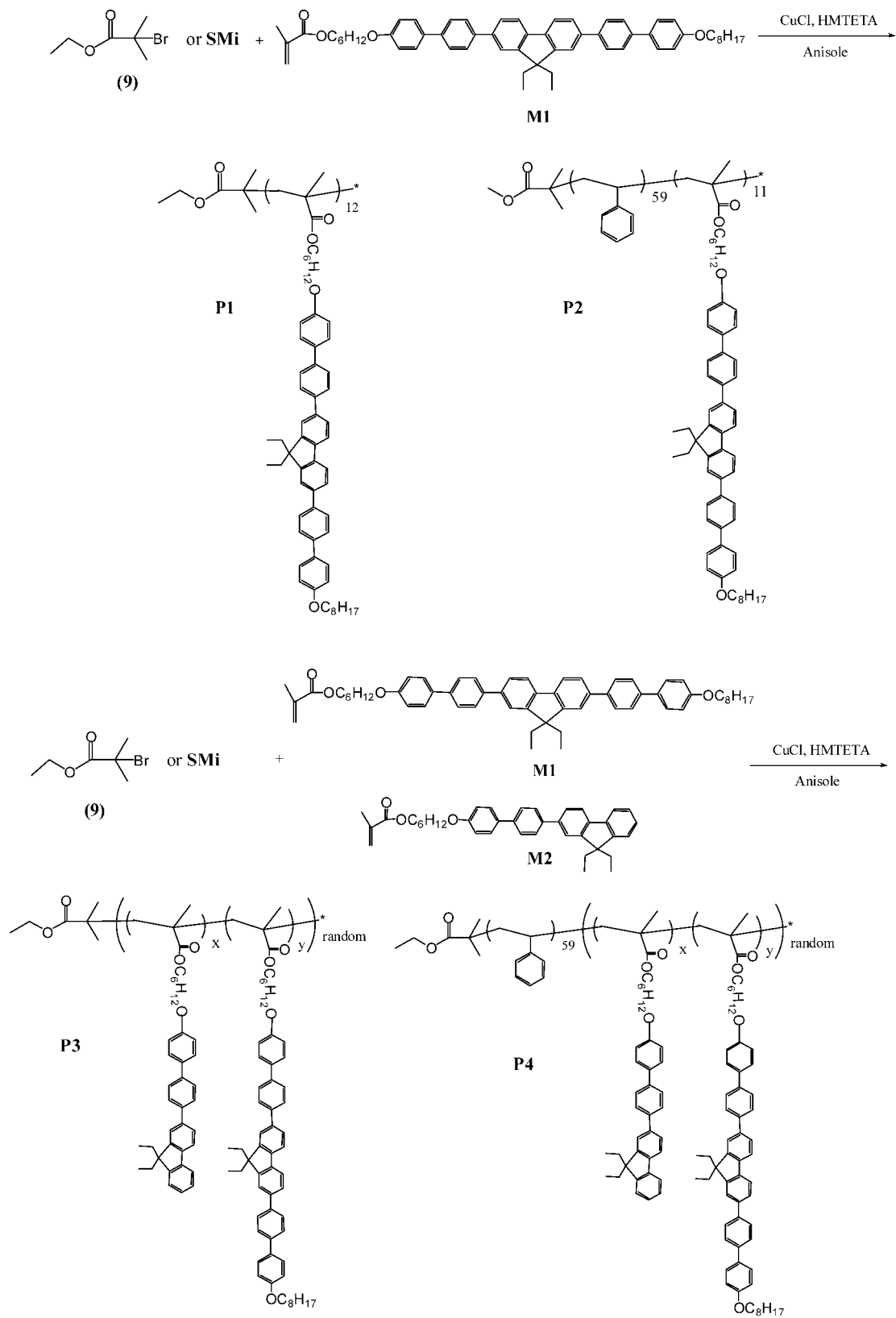
Scheme 1. Synthetic routes of the monomer (**M1**) and the macroinitiator (**SMi**).

$J = 8.8$ Hz, 2H), 7.56–7.62 (m, 4H), 7.83 (d, $J = 8.8$ Hz, 2H), 8.03 (s, 2H).²⁵

Compound 5

Compound **4** (2.0 g, 5.3 mmol), compound **3** (4.0 g, 12.3 mmol), and tetrakis(triphenylphosphine)-palladium(0) (307 mg, 0.27 mmol) were reacted in THF (120 mL) for 10 min, and then 80 mL of 2 M aqueous Na_2CO_3 solution was added. The mixture was reacted and refluxed for 48 h. After

reaction, the cooled solution was washed with dilute hydrochloric acid (10%) and water, and dried over magnesium sulfate. The final solution was purified by column chromatography (silica gel, CH_2Cl_2 /hexane 1:1) to yield a white solid (3.3 g, 87%). 1H NMR (ppm, $CDCl_3$), δ : 0.42 (t, $J = 6.9$ Hz, 6H), 0.89 (t, $J = 6.9$ Hz, 6H), 1.31–1.61 (m, 20H), 1.84 (m, 4H), 2.14 (q, $J = 7.3$ Hz, 4H), 4.01 (t, $J = 6.0$ Hz, 4H), 6.98 (d, $J = 7.8$ Hz, 4H), 7.57–7.80 (m, 18H).



Compound 6

Compound **5** (3.3 g, 4.5 mmol) was dissolved in dry chloroform (150 mL) under nitrogen and then boron tribromide (3.4 g, 13.6 mmol) was added dropwise to react at $-78\text{ }^{\circ}\text{C}$. The mixture was allowed to warm up to room temperature and reacted for 24 h. The solution was washed with sodium hydroxide (1 M, 50 mL), and then the solution was acidified with 10% HCl and stirred for 4 h. Finally, the suspension was filtered off and purified by column chromatography (silica gel, ethyl acetate) to yield a white solid (2.4 g, 94%). $^1\text{H-NMR}$ (ppm, d_6 -DMSO), δ : 0.29 (t, $J = 7.2$ Hz, 6H), 2.16 (q, $J = 7.2$ Hz, 4H), 6.87 (d, $J = 8.4$ Hz, 4H), 7.5 (d, $J = 8.7$ Hz, 4H), 7.70 (m, 6H), 7.79 (m, 6H), 7.91 (d, $J = 7.8$ Hz, 2H), 9.63 (s, 2H).

Compound 7

Compound **6** (2.2 g, 3.94 mmol) and potassium carbonate (1.09 mg, 7.88 mmol) were dissolved in 50 mL of DMF and then 1-bromooctane (760 mg, 3.94 mmol) was added in solution to react for 24 h by reflux. After cooling to room temperature, the solution was extracted with dichloromethane and water, and the organic layer was dried over magnesium sulfate. The final solution was purified by column chromatography (silica gel, CH_2Cl_2) to yield a white solid (1.3 g, 54%). $^1\text{H-NMR}$ (ppm, CDCl_3), δ : 0.43 (t, $J = 7.2$ Hz, 6H), 0.90 (t, $J = 6.6$ Hz, 3H), 1.25–1.48 (m, 10H), 1.82 (m, 2H), 2.14 (q, $J = 6.9$ Hz, 4H), 4.01 (t, $J = 6.6$ Hz, 2H), 4.90 (s, 1H), 6.92–7.01 (m, 4H), 7.53–7.67 (m, 12H), 7.73–7.80 (m, 6H).

Compound 8

Compound **7** (1.2 g, 1.80 mmol), 6-bromo-1-hexanol (421 mg, 2.33 mmol), K_2CO_3 (740 mg, 5.4 mmol), and KI (20 mg) were dissolved in 80 mL of DMF to reflux overnight. The reaction mixture was then cooled and poured into 200 mL of water and stirred for 2 h. The crude product was extracted with ethyl acetate and the organic layer as washed with a saturated aqueous solution of NaCl and water, and then the organic layer was dried over magnesium sulfate. After removing the solvent by rotavapor, the residue was recrystallized from absolute ethanol to give a colorless solid (1.1 g, 80%). $^1\text{H-NMR}$ (ppm, CDCl_3), δ : 0.43 (t, $J = 7.2$ Hz, 6H), 0.88 (t, $J = 6.0$ Hz, 3H), 1.31–1.86 (m, 20H), 2.15 (m, 4H),

3.67 (m, 2H), 4.01 (m, 4H), 7.00 (m, 4H), 7.57–7.80 (m, 18H).

M1: Compound **8** (1.1 g, 1.4 mmol), triethylamine (1.4 g, 14.3 mmol), and 2,6-ditertbutyl-4-methylphenol (30 mg, as a thermal inhibitor) were dissolved in 100 mL of anhydrous THF under a nitrogen atmosphere and then methacryloyl chloride (448 mg, 4.3 mmol) was added dropwise. The reaction mixture was heated under reflux overnight and then cooled to pour into 200 mL of aqueous NH_4Cl solution (10%). The crude product was extracted with CH_2Cl_2 . The resulting organic layer was washed with a saturated solution of NaCl and water, and the organic layer was dried over magnesium sulfate. After removing the solvent by rotavapor, the resulting solid was purified by column chromatography using dichloromethane as an eluant to yield a colorless solid (1.1 g, 92%).

$^1\text{H-NMR}$ (ppm, CDCl_3), δ : 0.41 (t, $J = 7.2$ Hz, 6H), 0.88 (t, $J = 6.9$ Hz, 3H), 1.31–1.82 (m, 20H), 1.94 (s, 3H), 2.12 (m, 4H), 3.98 (m, 2H), 4.15 (m, 4H), 5.54 (s, 1H), 6.09 (s, 1H), 6.98 (m, 4H), 7.55–7.79 (m, 18H). Elemental analysis for $\text{C}_{59}\text{H}_{66}\text{O}_4$: Calc. C, 84.45; H, 7.93; Found C, 84.12; H, 7.74. LRMS (EI) m/z : Calc. 838.4; Found 838.4.

M2: The synthetic route has been reported in our previous study.²⁶ Yield: 83%.

$^1\text{H-NMR}$ (ppm, CDCl_3), δ : 0.36 (t, $J = 6.9$ Hz, 6H), 1.45–1.56 (m, 4H), 1.67–1.83 (m, 4H), 1.94 (s, 3H), 2.06 (m, 4H), 4.01 (t, $J = 6.3$ Hz, 2H), 4.16 (t, $J = 6.6$ Hz, 2H), 5.54 (s, 1H), 6.09 (s, 1H), 6.98 (d, $J = 8.7$ Hz, 2H), 7.32–7.36 (m, 3H), 7.55–7.77 (m, 10H). Elemental analysis for $\text{C}_{39}\text{H}_{42}\text{O}_3$: Calc. C, 83.83; H, 7.58; Found C, 83.52; H, 7.54. HRMS (EI) m/z : Calc. 558.3134; Found 558.3126.

Polymerization of Macroinitiator SMI

In a Schlenk flask, N,N,N',N',N'' -pentamethyldiethylenetriamine (PMDETA, 3.46 mg, 0.5 mmol), CuBr (14.3 mg, 0.25 mmol), and styrene (6.8 g, 65 mmol) were added and stirred for 30 min. Ethyl 2-bromo-2-methylpropanoate (195 mg, 1 mmol) was added, and the mixture was immediately frozen in liquid nitrogen under vacuum. After several freeze-thaw cycles, the flask was sealed under vacuum and put in an oil bath at $100\text{ }^{\circ}\text{C}$ for 20 h. After the reaction, the content was dissolved in chloroform. After being concentrated, the chloroform solution was precipitated into methanol and the precipitation was repeated for three times. The final product

was dried at 50 °C under vacuum. Yield: 75%. The number-average molecular weight measured by GPC is $M_n = 6196 \text{ g mol}^{-1}$ with PDI (M_w/M_n) = 1.11.

General Synthetic Procedures of All Polymers

According to analogous procedures as shown in Scheme 2, **P1–P4** were synthesized by utilization of different initiators.

An Example of Polymerization for Polymer P2

Four milligram (0.04 mmol) of CuCl, 63 mg (0.01 mmol) of **SMi**, and 251 mg (0.3 mmol) of **M1** were mixed under nitrogen. 27 μL (22.9 mg, 0.1 mmol) of 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) in 3 mL of anisole was added through a syringe. The mixture was degassed three times using the freeze-pump-thaw procedure and sealed under vacuum. After stirring for 30 min at room temperature, the mixture was reacted at 100 °C in a preheated oil bath for 12 h. The solution was passed through a neutral Al₂O₃ column with THF as an eluant to remove the catalyst. The white filtrate was concentrated under reduced pressure and reprecipitated twice into methanol. The white product of polymer was collected by filtration and dried under vacuum. Yield: 125 mg (40%).

¹H-NMR (ppm, CDCl₃), δ : 0.35 (broad), 0.88 (broad), 1.28–1.78 (broad), 2.01 (broad), 3.94 (broad), 6.56 (broad), 6.98 (broad), 7.55 (broad). The number-average molecular weight measured by GPC is $M_n = 14,852 \text{ g mol}^{-1}$ with PDI (M_w/M_n) = 1.15.

P1: Yield: 85 mg (34%). ¹H-NMR (ppm, CDCl₃), δ : 0.36 (broad), 0.88 (broad), 1.28–1.94 (broad), 2.03 (broad), 3.97 (broad), 6.94 (broad), 7.57 (broad). The number-average molecular weight measured by GPC is $M_n = 10,007 \text{ g mol}^{-1}$ with PDI (M_w/M_n) = 1.21.

P3: (**M1/M2/initiator** = 15/15/1). Yield: 75 mg (30%). ¹H-NMR (ppm, CDCl₃), δ : 0.36 (broad), 0.86 (broad), 1.24–1.94 (broad), 2.04 (broad), 3.99 (broad), 6.96 (broad), 7.30 (broad), 7.62 (broad). The number-average molecular weight measured by GPC is $M_n = 6275 \text{ g mol}^{-1}$ with PDI (M_w/M_n) = 1.31.

P4: (**M1/M2/initiator** = 15/15/1). Yield: 121 mg (39%). ¹H-NMR (ppm, CDCl₃), δ : 0.35 (broad), 0.87 (broad), 1.28–1.79 (broad), 2.03 (broad), 3.96 (broad), 6.55 (broad), 6.94 (broad), 7.29 (broad), 7.55 (broad). The number-average molecular

weight measured by GPC is $M_n = 10,643 \text{ g mol}^{-1}$ with PDI (M_w/M_n) = 1.22.

RESULTS AND DISCUSSION

Synthesis and Characterization

In this study, the styrene-macroinitiator (**SMi**),⁶ was used to copolymerize with methacrylate monomers containing luminescent 4,4'-bis(biphenyl)fluorene units (**M1**) to produce diblock copolymer **P2** by ATRP. In addition, random copolymer **P3** and block copolymer **P4** containing pendent 4,4'-bis(biphenyl)fluorene units (**M1**) and biphenyl-4-ylfluorene units (**M2**) were synthesized by similar (ATRP) procedures. The number-average molecular weights (M_n) and PDI values of all polymers (**P1–P4**) containing mesogenic 4,4'-bis(biphenyl)-fluorene units and biphenyl-4-ylfluorene units are shown in Table 1. The number-average molecular weight (M_n) of macroinitiators (**SMi**) is 6196 g mol^{-1} with a PDI value of 1.11. Comparing NMR spectra of random copolymer **P3** and block copolymer **P4**, a broad peak of **P4** at 6.56 ppm belonged to the chemical shift of polystyrene block and a broad peak at 6.98 ppm incorporated chemical shifts of **M1** and **M2** with that of polystyrene block, so **P4** could be recognized as a diblock copolymer. However, because of the overlapped proton peaks around phenyl and alkyl groups of **M1** and **M2** in NMR spectra of polymers **P3** and **P4**, the molar ratio of **M1** and **M2** in random copolymer **P3** and block copolymer **P4** could not be distinguished, so the values of x and y in the chemical structures of random copolymer **P3** and block copolymer **P4** in Scheme 2 are undetermined.

Thermal and Mesogenic Properties

The thermal stability of polymers (**P1–P4**) under an atmosphere of nitrogen was evaluated

Table 1. Molecular Weights and Polydispersity Indexes of Polymers **P1–P4**

Polymer	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	PDI (M_w/M_n)
P1	10,007	12,108	1.21
P2	14,852	17,137	1.15
P3	6275	8220	1.31
P4	10,463	12,984	1.22

Table 2. Thermal Properties of Polymers **P1–P4**^{a,b,c}

Polymer	Transition Temp. (°C) ^{b,c}	T_d (°C) ^a	T_g (°C)
P1	N 299.5 (1.78) I	392.0	60.1
P2	N 316.1 (0.76) I	367.3	88.2
P3	N 308.4 (4.54) I	351.0	56.4
P4	N 298.2 (4.34) I	362.3	89.7

Transition temperatures (measured by DSC) of M1 and M2—M1: K 104.4 °C (31.5 kJ/g) N 266.0 °C (1.86 kJ/g) Ti and M2: K 60.4 °C (3.4 kJ/g) N 98.0 °C Ti (Ti was characterized by POM).

^aTemperature of 5% weight loss measured by TGA under nitrogen.

^bTransition temperatures (°C) and enthalpies (in parentheses, kJ/g) were determined by DSC (with heating rates of 5 °C/min).

^c**N** = nematic phase; **I** = isotropization temperature.

by TGA, which indicates that T_d (the degradation temperature of 5% weight loss in nitrogen) ≥ 350 °C for all polymers (shown in Table 2). The mesogenic properties were characterized by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The phase transition temperatures and enthalpies of all polymers are summarized in Table 2. Regarding their mesomorphism, all polymers exhibit the nematic phase with mesophasic ranges wider than 200 °C. In our previous studies,^{25,26} block copolymers containing conjugated main-chain fluorene, thiophene, and biphenyl blocks as well as block copolymers containing side-chain biphenyl-4-ylthiophene or cyanoterphenyl blocks possess the smectic A and columnar (Col_h and Col_r) phases, but block copolymers consisting of side-chain biphenyl-4-ylfluorene blocks possess the nematic phase. Compared with the smectic A phase of the polymers in our previous studies, the side-chains of the rigid cores in polymers **P1–P4** composed of pendent 4, 4'-bis(biphenyl)-fluorene and biphenyl-4-ylfluorene units were separated by the diethyl groups on 9th position of fluorene units which cause the reduction of lateral interaction among rigid rods and thus to favor the nematic phase. To avoid thermal decomposition, these polymers were only heated up to about 320 °C (with a heating rate of 5 °C/min) and all polymers (**P1–P4**) revealed isotropization temperatures (T_i) around 299–316 °C. Figure 1 showed that a schlieren texture of the corresponding nematic phase of **P1** observed by POM at 280 °C (cooling).

Because of the unclear glass transition temperatures (T_g) of these block copolymers, T_g val-

ues were detectable in the first heating scans of DSC measurements (with a heating rate of 5 °C/min) by quenching of polymers (from 200 °C) in liquid nitrogen. By this quenching process, the DSC results can reveal T_g values of all polymers more clearly (in the range of 56–90 °C as shown in Table 2). In Table 2, polymers **P1** and **P3** exhibit the glass transition temperatures (T_{gs}) at 60 and 56 °C, respectively. T_{gs} of **P2** and **P4** (around 90 °C) were mostly contributed from the polystyrene block.^{29,30}

To elucidate the structures of the mesophases, X-ray diffraction (XRD) measurements were carried out at the temperature ranges of mesophases, which were determined by DSC and POM, for polymers **P1–P4**. The nematic phase of all polymers characterized by the schlieren texture of POM is further confirmed by the results of no refraction peaks observed in the XRD patterns.

Photophysical Properties

The photophysical properties of polymers **P1–P4** including UV-visible absorption spectra and PL spectra in THF solutions are summarized in Table 3. Because of to identical rigid cores of luminescent 4,4'-bis(biphenyl)fluorene pendants (**M1**), the synthesized polymers **P1** and **P2** have almost the same maximum absorption wavelength around 343 nm in solutions and solid films. In addition, the maximum PL wavelengths ($\lambda_{max,PL}$) were around 396 nm in solutions and 425 nm in films, respectively. Polymers **P3** and

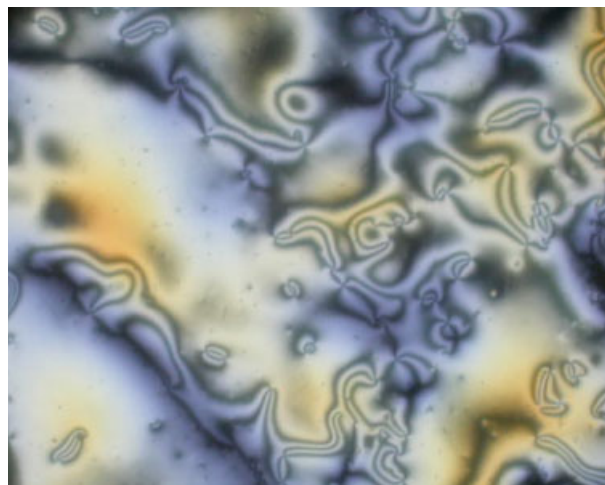


Figure 1. The schlieren texture (the nematic phase) of **P1** observed by POM at 280 °C (cooling).

Table 3. UV-Visible Absorption and Photoluminescence Spectral Data of Monomers **M1-M2** and Polymers **P1-P4**

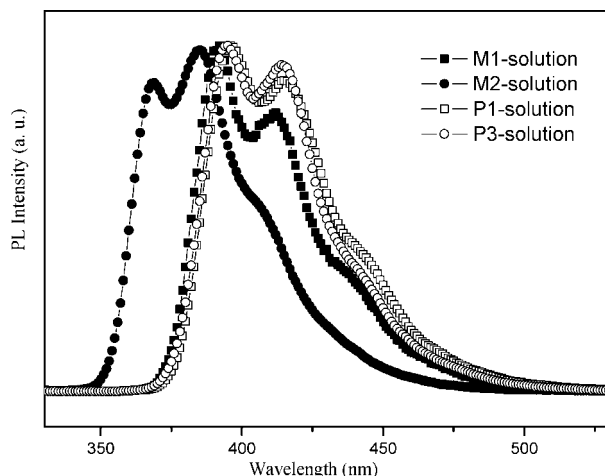
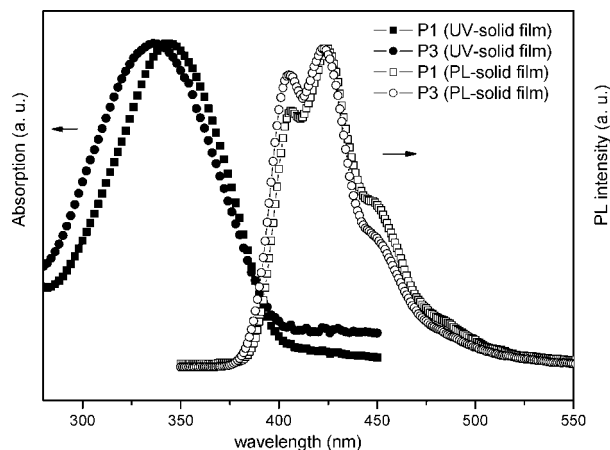
Sample	$\lambda_{\max, \text{Abs}}$ (nm)		$\lambda_{\max, \text{PL}}$ (nm)		$\phi(\%)^b$
	Solution ^a	Film	Solution ^a	Film	
M1	344	–	392	–	74
M2^c	322	–	385	–	23
P1	344	343	396	425	73
P2	344	340	397	424	70
P3	338	336	395	422	70
P4	337	336	394	423	72

^a Absorption and PL emission spectra were recorded in dilute THF solutions at room temperature.

^b 9,10-Diphenylanthracene in THF is used as the reference of the quantum yield.

^c UV-visible absorption and PL data of **M2** in solutions was reported in our previous study.²⁶

P4 both possess the biphenyl-4-ylfluorene pendants (**M2**), therefore, they had the same maximum absorption wavelength around 336 nm in solutions and films. Figure 2 shows an example of PL spectra of the monomers (**M1** and **M2**) and polymers (**P1** and **P2**) in solutions. Compared with **M2** (which was reported in our previous study),²⁶ **M1** consisting of an additional biphenyl unit results in the longer conjugation lengths than **M1**. Hence, the maximum absorption wavelengths and PL wavelengths of **M1** are more red-shifted than **M2**. In Figure 3, because of the biphenyl-4-ylfluorene pendants of **P3**, the

**Figure 2.** PL spectra of monomers (**M1** and **M2**) and polymers (**P1** and **P3**) in solutions.**Figure 3.** UV-visible absorption and PL spectra of **P1** and **P3** in solid films.

maximum absorption wavelength of **P3** was more blue-shifted than that of **P1** (around 343 nm) in films and solutions. However, the $\lambda_{\max, \text{PL}}$ values of **P1** and **P3** were almost the same (396 nm in solutions and 423 nm in films). This phenomenon may be originated from the energy transfer of biphenyl-4-ylfluorene pendants to 4,4'-bis(biphenyl)fluorene pendants which can be confirmed by the overlapped UV-visible spectra of **M2** and PL spectra of **M1**. However, Intermolecular aggregation of luminescent pendants could cause shoulders of **P1** and **P3** around 440 nm in Figure 3. In addition, the quantum yields of all polymers consist of 4,4'-bis(biphenyl)fluorene groups (70%) were better than other analogous polymers (around 20%) in our previous studies.^{25,26}

CONCLUSIONS

Polymers (**P1** and **P2**) containing 4,4'-bis(biphenyl)fluorene pendants (**M1**) and random copolymers (**P3** and **P4**) composed of 4,4'-bis(biphenyl)fluorene pendants (**M1**) and biphenyl-4-ylfluorene pendants (**M2**) are polymerized by ATRP. Thermal and XRD investigations indicate that polymers exhibit the nematic phases which have little relationship with respect to the flexible polystyrene block, but the glass transition temperatures (T_{gs}) of block copolymers **P2** and **P4** containing polystyrene blocks are higher than those of polymers **P1** and **P3** without the polystyrene block. In terms of PL and absorption wavelengths of all polymers in dilute solutions,

P1 and **P2** are a little red-shifted than **P3** and **P4**, which might be due to longer conjugation lengths of the 4,4'-bis(biphenyl)fluorene pendants (**M1**) in polymers **P1** and **P2**.

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