Synthesis and Characterization of Liquid-Crystalline Block Copolymers with Cyanoterphenyl Moieties by Atom Transfer Radical Polymerization

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Received 11 April 2006; accepted 18 May 2006
DOI: 10.1002/pola.21556
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of new mesomorphic block copolymers composed of different macroinitiators, including poly(ethylene oxide), polystyrene, and poly(ethylene oxide)-*b*-polystyrene, and polymethacrylate with a pendent cyanoterphenyl group were synthesized through atom transfer radical polymerization. The number-average molecular weights of the three diblock copolymers, determined by gel permeation chromatography, were 10,254, 9,772, and 15,632 g mol^{-1}, and their polydispersity indices were 1.17, 1.28, and 1.34. The mesomorphic and optical properties of all the block copolymers were investigated, and they possessed a smectic A phase with mesophasic ranges wider than 100 °C. Moreover, X-ray diffraction patterns provided evidence of the smectic A phase and the corresponding interdigitated packing of all the polymers.

Keywords: atom transfer radical polymerization (ATRP); block copolymers; liquid-crystalline and photoluminescence properties; X-ray

INTRODUCTION

In recent years, many research groups have concentrated on the synthesis of liquid-crystalline (LC) block copolymers and the characterization of their phase behavior and morphology.[1–6] These kinds of LC block copolymers are synthesized via different types of living free-radical polymerizations.[7–10] The interest in these types of materials resides in the combined properties of two (or more than two) completely different polymers that are chemically bonded to each other. Macrophase separation takes place because of the segregation of different polymer chains. Regarding LC properties, the combination of rigid cores and flexible chains is required for the LC molecular design. In general, there are two kinds of LC block copolymers: main-chain and side-chain LC block copolymers. Mesogenic groups are connected along the polymer backbones as main-chain copolymers, and pendent mesogenic groups are attached to the polymer backbones via flexible spacers as side-chain copolymers.

Side-chain LC polymers are often used in electro-optical applications; different kinds of rigid cores, including azobenzene[11–13] and biphenyl units,[14–19] are used in the mesogenic monomers. In previous studies, aromatic cores in conjugation with a terminal cyano group had high values of birefringence and reasonable viscosities. Moreover, they were chemically and photochemically stable. Cyanoterphenyl derivatives have been used in a wide range of nematic mixtures possessing high thermal, chemical, and photochemical stabilities.[20] Therefore, a series of novel side-chain LC block copolymers consisting of different flexible macroinitiators, including poly(eth-

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ylene oxide) (PEO), polystyrene (PS), and PEO-*b*-PS, and polymethacrylate with a pendent cyanoterphenyl group were synthesized through atom transfer radical polymerization (ATRP). Furthermore, the thermal, mesomorphic, and PL properties of all the polymers were investigated in this study.

EXPERIMENTAL

Measurements

^{1}H NMR spectra were recorded on a Varian Unity 300-MHz spectrometer with $CDCl_3$ and dimethyl sulfoxide-d_6 (DMSO-d_6) as solvents. Elemental analyses were performed on a Heraeus CHN-OS Rapid elemental analyzer. The transition temperatures were determined by differential scanning calorimetry (DSC; Diamond model, PerkinElmer) with a heating and cooling rate of 5 °C/min. The mesophases were studied with a polarizing optical microscope (DMLP model, Leica) equipped with a hot stage. Thermogravimetric analysis (TGA) was conducted on a DuPont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen. Gel permeation chromatography (GPC) analysis was conducted on a Waters 1515 separation module with chloroform as the eluant against a PS calibration curve. Ultraviolet–visible (UV–vis) absorption spectra were recorded in dilute chloroform solutions (10^{-6} M) on an HP G1103A spectrophotometer. Photoluminescence (PL) spectra were obtained on a Hitachi F-4500 spectrophotometer. Polymer solid films were spin-coated on quartz substrates from chloroform solutions with a concentration of 1 mg/mL.

Materials

The chemicals and solvents were reagent-grade and were purchased from Aldrich, Acros, TCI, and Lancaster Chemical Co. Dichloromethane and tetrahydrofuran (THF) were distilled to keep them anhydrous before use. Pyridine was dried via refluxing over calcium hydride. The other chemicals were used without further purification.

Synthesis

Scheme 1 summarizes the steps involved in the synthesis, with the details of each step given next.

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 the mixture cooled to room temperature, the potassium salt was filtered off. The solvent was removed by a rotavapor, and the crude product was recrystallized from petroleum ether (bp = 35–60 °C) to yield a white solid (13.5 g, 93%).

^{1}H NMR (ppm, $CDCl_3$, δ): 0.89 (t, J = 6.9 Hz, 3H), 1.29–1.47 (m, 10 H), 1.80 (quintet, J = 6.6 Hz, 2H), 3.98 (t, J = 8.6 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 7.40–7.54 (m, 6H).[21]

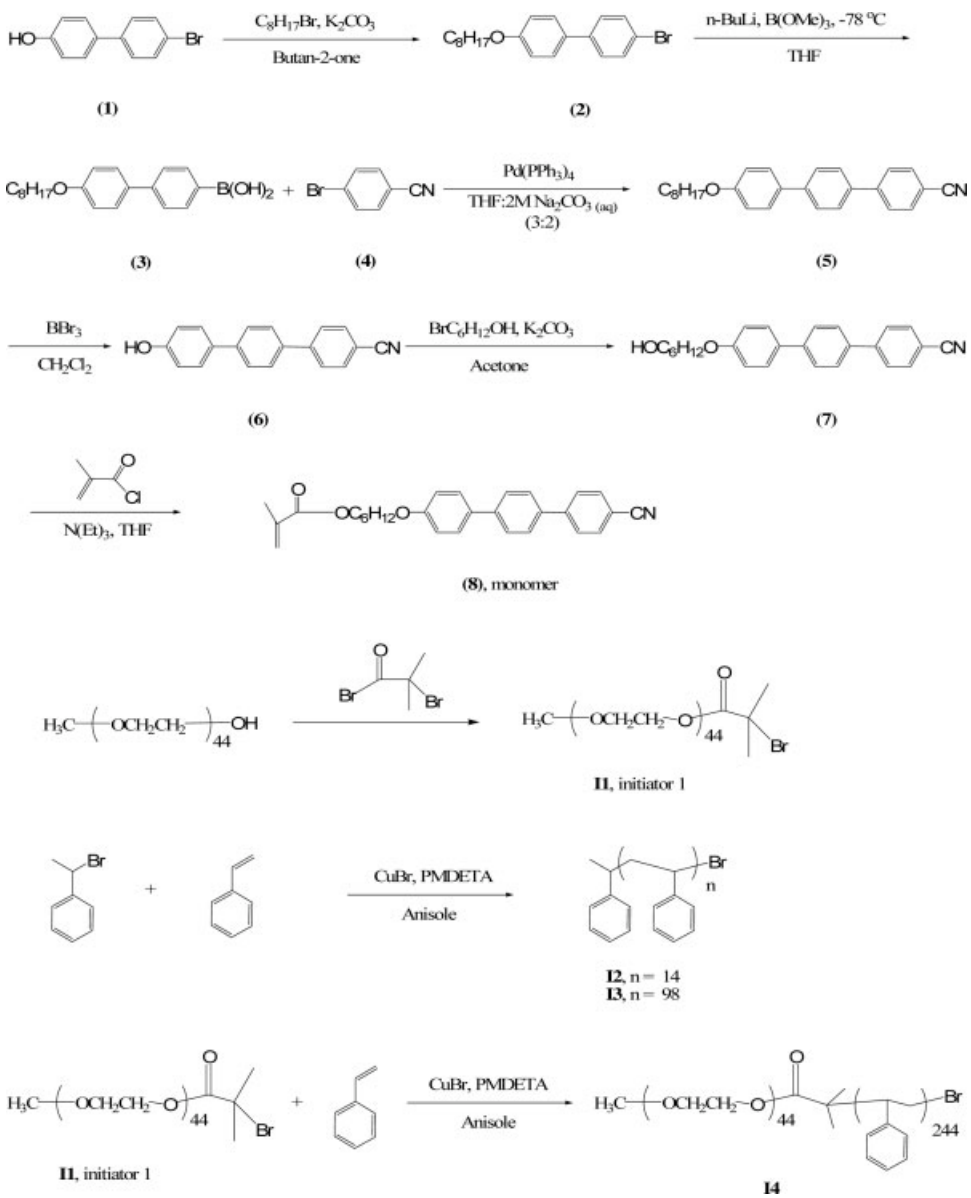
4′-Octoxybiphenyl-4-ylboronic Acid (3)

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 at −78 °C to react. The reaction mixture was maintained under these conditions for 1 h more. Furthermore, it was added dropwise to a trimethyl borate solution (3.5 g, 33.2 mmol) at −78 °C. The solution was allowed to cool to room temperature overnight. The final solution was acidified with a 10% HCl solution (100 mL) and stirred for 45 min at room temperature. The solution was washed with a saturated sodium carbonate solution and water, and THF was removed. The crude product was extracted by diethyl ether, and the organic layer was dried over magnesium sulfate. After the solvent was removed by a rotavapor, the resulting solid was washed with petroleum ether and briefly dried on a filter to obtain a white solid (6.0 g, 80%).

^{1}H NMR (ppm, DMSO-d_6, δ): 0.85 (t, J = 7.2 Hz, 3H), 1.24–1.41 (m, 10H), 1.71 (quintet, J = 6.6 Hz, 2H), 3.98 (t, J = 6.6 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 7.56–7.62 (m, 4H), 7.83 (d, J = 8.8 Hz, 2H), 8.03 (s, 2H).[21]

4-Octoxy-4″-cyanoterphenyl (5)

Compound **4** (2.3 g, 12.8 mmol), compound **3** (5.0 g, 15.3 mmol), and tetrakis(triphenylphosphine)palladium(0) (740 mg, 0.64 mmol) were reacted in THF (100 mL) for 10 min, and then 100 mL of a 2 M aqueous Na_2CO_3 solution was added. The mixture was reacted and refluxed for 48 h. After the reaction, the cooled solution was washed with dilute hydrochloric acid (10%)



Scheme 1. Synthetic routes of the monomers and macroinitiators.

and water and dried over magnesium sulfate. The final solution was purified by column chromatography (silica gel, 1:1 CH_2Cl_2/hexane) to yield a white solid (4.7 g, 83%).

^{1}H NMR (ppm, $CDCl_3$, δ): 0.87 (t, J = 6.6 Hz, 3H), 1.26–1.46 (m, 10 H), 1.80 (quintet, J = 6.9 Hz, 2H), 3.99 (t, J = 6.6 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 7.54 (d, J = 9.0 Hz, 2H), 7.62 (m, 4H), 7.71 (m, 4H).

4-Hydroxyl-4″-cyanoterphenyl (6)

5 (3.7 g, 9.5 mmol) was dissolved in dry chloroform (150 mL) under nitrogen, and then boron tribromide (4.8 g, 19.1 mmol) was added dropwise and reacted at −78 °C. The mixture was allowed to warm to room temperature and reacted for 24 h. The solution was washed with sodium hydroxide (1 M, 50 mL). 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 (2.37 g, 92%).

^{1}H NMR (ppm, DMSO-d_6, δ): 6.86 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.7 Hz, 2H), 7.91 (m, 4H), 9.63 (s, 1H).

4-(6-Hydroxyhexyloxy)-4″-cyanoterphenyl (7)

6 (2.4 g, 8.7 mmol), 6-chloro-1-hexanol (2.1 g, 11.3 mmol), K_2CO_3 (3.6 g, 26.1 mmol), and less KI (20 mg) were dissolved in 200 mL of DMF and refluxed overnight. The reaction mixture was then cooled and poured into 200 mL of water and was stirred for 2 h. The crude product was extracted with ethyl acetate, and the organic layers were washed with a saturated aqueous solution of NaCl and water; then, the organic layer was dried over magnesium sulfate. After the solvent was removed by a rotavapor, the residue was recrystallized from absolute ethanol to give a colorless solid (2.6 g, 80%).

^{1}H NMR (ppm, DMSO-d_6, δ): 1.28–1.70 (m, 8H), 3.44 (m, 2H), 3.99 (t, J = 6.6 Hz, 2H), 4.32 (t, J = 5.0 Hz, 1H), 7.00 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.71(d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.90 (m, 4H).

4-(6-Methacryloyloxyhexyloxy)-4″-cyanoterphenyl (8)

7 (2.6 g, 7.0 mmol), triethylamine (2.1 g, 21 mmol), and 2,6-di-tertbutyl-4-methylphenol (200 mg; used as a thermal inhibitor) were dissolved in 150 mL of anhydrous THF under a nitrogen atmosphere, and then methacryloyl chloride (2.2 g, 21 mmol) was added dropwise. The reaction mixture was heated under reflux overnight and then was cooled and poured into 200 mL of an aqueous solution of NH_4Cl (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 the solvent was removed by a rotavapor, the resulting solid was purified by column chromatography with hexane/ethyl acetate (7:3) as an eluant to yield a colorless solid (2.3 g, 75%).

^{1}H NMR (ppm, $CDCl_3$, δ): 1.46–1.53 (m, 4H), 1.62–1.74 (m, 2H), 1.82 (m, 2H), 1.93 (s, 3H), 4.00 (t, J = 6.3 Hz, 2H), 4.15 (t, J = 6.6 Hz, 2H), 5.53 (m, 1H), 6.09 (m, 1H), 6.97 (d, J = 8.7 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.64 (m, 4H), 7.71 (m, 4H). ELEM. ANAL. Calcd. for $C_{29}H_{29}NO_3$: C, 79.24%; H, 6.65%; N, 3.19%. Found: C, 79.30%; H, 6.71%; N, 3.05%.

Macroinitiator I1

A solution of 1.8 g (7.7 mmol) of 2-bromo-2-methylpropionyl chloride in 10 mL of dry THF was added to a mixture of 1.1 g (10 mmol) of triethylamine and 10 g (5 mmol) of poly(ethylene glycol) methyl ether with a number-average molecular weight (M_n) of 2000 g mol^{-1} in 30 mL of THF at 0 °C, and then the mixture was stirred for 18 h. After the mixture was filtered, half of the solvent was evaporated, and the poly(ethylene glycol) macroinitiator was precipitated into cold ether. After dissolution in ethanol, the solution was stored in a refrigerator to recrystallize to yield a white solid.

Yield: 55%. ^{1}H NMR (ppm, $CDCl_3$, δ): 1.94 (s, 6H), 3.38 (s, 3H), 3.54–3.76 (m, 174H), 4.33 (dd, 2H).

Preparation of Macroinitiators I2, I3, and I4

Polymerization of Macroinitiator ***I3***. To a Schlenk flask, 3.46 mg of *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA; 0.02 mmol), 14.3 mg of CuBr (0.1 mmol), and 5.5 g of styrene (52.8 mmol) were added, and they were stirred for 30 min. 1-(1-Bromoethyl)benzene (74 mg, 0.4 mmol) was added, and the mixture was immediately frozen in liquid nitrogen *in vacuo*. After several freeze–thaw cycles, the flask was sealed *in vacuo* and put in an oil bath at 100 °C for 20 h. After the reaction, the content was dissolved in chloroform. After being concentrated, the chloroform solution was precipitated into methanol. The precipitation was repeated three times. The final product was dried at 50 °C *in vacuo*. M_n was 10,337 g mol^{-1}, and the polydispersity index [PDI; i.e., weight-average molecular weight/number-average molecular weight (M_w/M_n)] was 1.28 (by GPC).

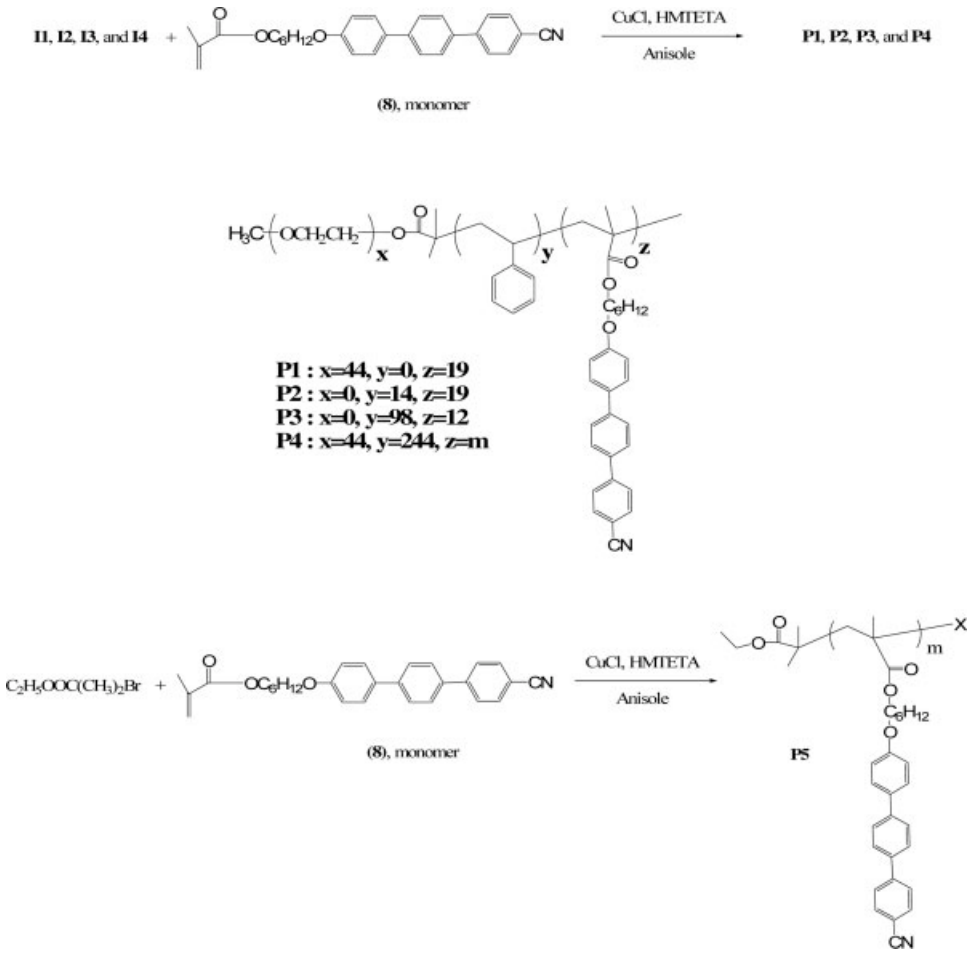
The macroinitiators (**I2** and **I4**) were synthesized with analogous procedures via ATRP, and the M_n and PDI values for **I2** and **I4** are given next.

Macroinitiator ***I2***. M_n was 1016 g mol^{-1}, and PDI (M_w/M_n) was 1.11 (by GPC).

Macroinitiator ***I4***. M_n was 27,474 g mol^{-1}, and PDI (M_w/M_n) was 1.35 (by GPC).

Preparation of the Homopolymer and Block Copolymers

The block copolymers (**P1–P4**) and homopolymer (**P5**) were synthesized with an analogous procedure, except for the utilization of different initiators (see Scheme 2).



Scheme 2. Synthetic routes of the polymers m means undetermined value.

*Preparation of Polymer **P1** (Polymerization of Monomer **8** with Macroinitiator **I1**).* CuCl (4 mg, 0.04 mmol), 20 mg (0.01 mmol) of **I1**, and 440 mg (1 mmol) of monomer **8** were mixed under nitrogen. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA; 11 μL, 23 mg, 0.1 mmol) in 6 mL of anisole was added through a syringe. The mixture was degassed three times with the freeze–pump–thaw procedure and sealed *in vacuo*. After stirring for 30 min at room temperature, the mixture was reacted in a preheated 80 °C oil bath for 12 h. The solution was passed through a neutral Al_2O_3 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 the polymer was collected by filtration and dried *in vacuo*. The yield was 150 mg (34%). M_n was 10,258 g mol^{-1}, and PDI (M_w/M_n) was 1.17 (by GPC).

P2. The yield was 158 mg (33%). M_n was 9772 g mol^{-1}, and PDI (M_w/M_n) was 1.28 (by GPC; the soluble part of the polymer).

P3. The yield was 206 mg (32%). M_n was 15,632 g mol^{-1}, and PDI (M_w/M_n) was 1.34 (by GPC; the soluble part of the polymer).

P4 and P5. No data were obtained because of the poor solubilities of the longer cyanoterphenyl blocks.

RESULTS AND DISCUSSION

Synthesis and Characterization

ATRP has proven to be a very powerful polymerization technique for the preparation of block

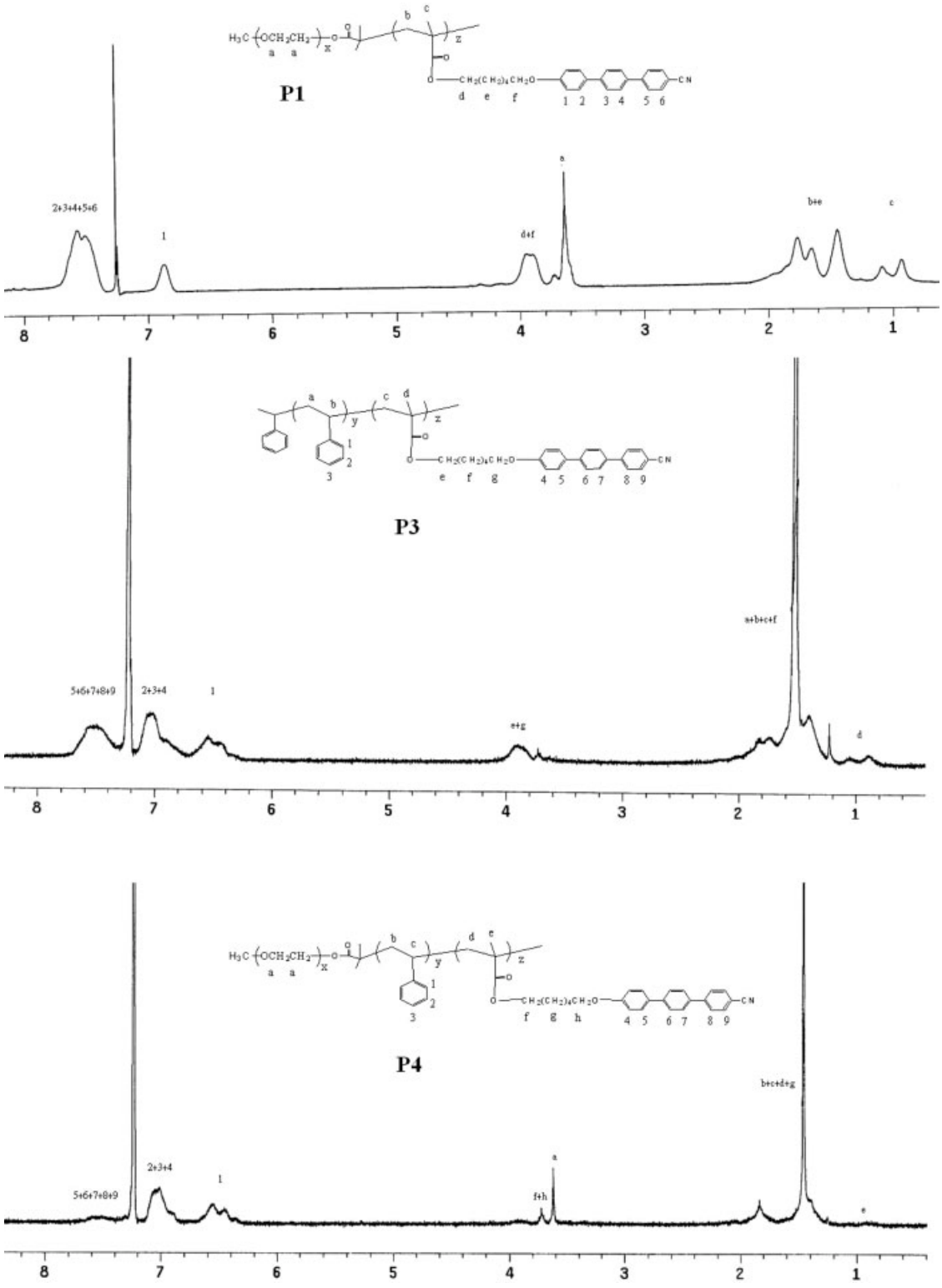


Figure 1. ^{1}H NMR spectra of block copolymers **P1**, **P3**, and **P4**.

copolymers from a wide variety of monomers.[22,23] In this work, macroinitiators, including PEO (**I1**),[11] PSs (**I2** and **I3**),[6] and PEO-*b*-PS (**I4**), were used to copolymerize cyanoterphenyl methacrylate monomers to produce LC cyanoterphenyl block copolymers. GPC measurements

Table 1. Molecular Weights and Thermal Properties of Block Copolymers **P1–P4**

Sample	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI (M_w/M_n)	T_d (°C)[a]	T_g (°C)[b]
P1	10,258	11,996	1.17	325.0	162.9
P2	9,772	11,308	1.28	347.5	111.7
P3	15,632	18,110	1.34	341.6	98.4
P4	—	—	—	326.3	82.7 and 153.7

[a] Measured by TGA under nitrogen.
[b] Determined by DSC (with a heating and cooling rate of 5 °C/min).

indicated that all macroinitiators (**I1–I4**) and the diblock copolymers (**P1–P3**) with extended molecular weights had narrow polydispersities. Because of the poor solubilities of the longer cyanoterphenyl blocks in **P4** and **P5**, no GPC data were obtained for these polymers. The M_n values of the macroinitiators (**I2**, **I3**, and **I4**) determined by GPC were 1016, 10,337, and 27,474 g mol^{-1} with PDIs of 1.11, 1.28, and 1.35, respectively. The precursor of **I1** was procured from commercially available PEO (M_n = 2000 g mol^{-1}) with PDI = 1.04. The cyanoterphenyl homopolymer (**P5**) exhibited poor solubility in conventional organic solvents and so was not characterized and processed into films.[24] Figure 1 shows the NMR spectra of block copolymers **P1**, **P3**, and **P4**; the NMR spectrum of **P2** is omitted because of its similarity to that of **P3**. Table 1 shows the M_n values of the diblock copolymers containing LC cyanoterphenyl blocks (**P1–P3**) as determined by GPC, for which chloroform was used as an eluant. Triblock copolymer **P4** also exhibited poor solubility in conventional organic solvents. Although the flexible chains of the PEO and PS blocks were longest in **P4**, this suggested that the molecular weight of the LC cyanoterphenyl block might be polymerized to such a high degree of polymerization as to induce poor solubility.

Table 2. Phase Behavior of Block Copolymers **P1–P4**[a]

Sample	Temperature (°C)[b]	T^c (°C)[c]
P1	K 173.8 (9.8) S_A	~300
P2	K 152.5 (4.1) S_A	~300
P3	K 181.6 (7.0) S_A	~275
P4	K 191.1 (4.7) S_A	~300

[a] The transition temperatures and enthalpies (shown in parentheses; kJ/mol) were determined by DSC (at a heating rate of 5 °C/min).
[b] K = crystalline; S_A = smectic A.
[c] Observed by POM.

Thermal Properties and X-Ray Investigation

The average molecular weights and PDIs of these macroinitiators (**I1–I4**) and block copolymers (**P1–P3**) were obtained by GPC. The thermal stability of the polymers (**P1–P4**) under an atmosphere of nitrogen was evaluated by TGA, which indicated that the degradation temperature of 5% weight loss (T_d) in nitrogen was greater than or equal to 325 °C for all the polymers (shown in Table 1). The mesomorphism was characterized with polarizing optical microscopy (POM) and DSC. The phase-transition temperatures and enthalpies of all the polymers are summarized in Table 2. Regarding these results, all block copolymers (**P1–P4**) possessed a smectic A phase, which also existed in the cyanoterphenyl homopolymer (the same structure as **P5**) in a previous study.[24] The DSC thermograms are displayed in Figure 2. To avoid thermal decomposition, these polymers were heated to about 250 °C (at a heating rate of 5 °C/min), and their melting temperatures were not observed even over 250 °C. All the block copolymers revealed clearing (isotropization) tempera-

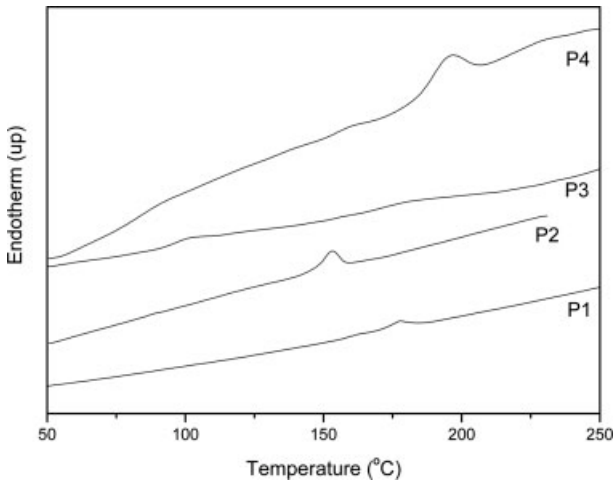


Figure 2. DSC thermograms of block copolymers **P1–P4** during the first heating scan at 5 °C/min.

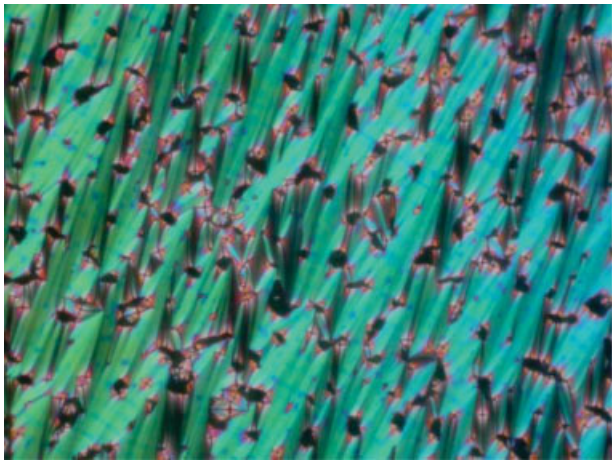


Figure 3. Optical texture of the mesophase (smectic A) of **P1** observed by POM at 270 °C (cooling).

ture (T_c) values around 275–300 °C at which thermal decomposition occurred. Figure 3 shows a fan-shaped texture of the corresponding smectic A phase of **P1** observed by POM at 270 °C (cooling).

Because it was not easy to observe the glass-transition temperatures (T_g's) of these block copolymers, the T_g values were detectable by liquid nitrogen quenching of the polymers in the first heating scans of DSC measurements (at a heating rate of 5 °C/min). At this rate, the DSC results indicated T_g values of all the block copolymers more clearly, and the T_g values were in the range of 82–163 °C (see Table 1). As shown in Figure 2, T_g for **P3** and **P4** was easily revealed, but the T_g values of **P1** and **P2** could not be observed because of the low T_g value of the PEO block in **P1** and the short block of PS in **P2**. T_g of **P3** (at 98 °C) was mostly contributed by the PS block with PS repeating units of 98.[25,26] However, two T_g values (at 83 and 154 °C) were present in **P4**, which were attributed to the immiscibility between the more extended PS block (with PS repeating units of 244 and T_g = 83 °C) and the LC cyanoterphenyl block (with T_g = 154 °C). The lower T_g value of the more extended PS block (with PS repeating units of 244 and T_g = 83 °C) in **P4** in comparison with the higher T_g value of the shorter PS block (with PS repeating units of 98 and T_g = 98 °C) in **P3** was due to the plasticizer effect of the PEO block in triblock copolymer **P4**. Hence, this situation may serve as evidence for the microphase-separation morphology of triblock copolymer **P4**.[27]

To elucidate the structures of the mesophases, X-ray diffraction (XRD) measurements were carried out at the temperature ranges of the mesophases for polymers **P1–P5**. As shown in Figure 4, the XRD patterns of polymers **P1–P5** are almost identical, and their layer *d*-spacing values are around 37 Å. In addition, the layer *d*-spacing values in the ratio of 1:1/2 indicate a lamellar order in the mesophases, and the XRD data are summarized in Table 3. Furthermore, a fan-shaped texture can be clearly observed by POM, as shown in Figure 3, which is a characteristic texture of the smectic A phase. According to the molecular modeling calculation, the layer *d*-spacing value of the coplanar structure in monomer **8** is around 35.6 Å (the layer *d*-spacing value is ca. 37 Å by XRD patterns). Therefore, a possible layer structure of block copolymers **P1–P5** is suggested to be interdigitated packing of rods. From this evidence,

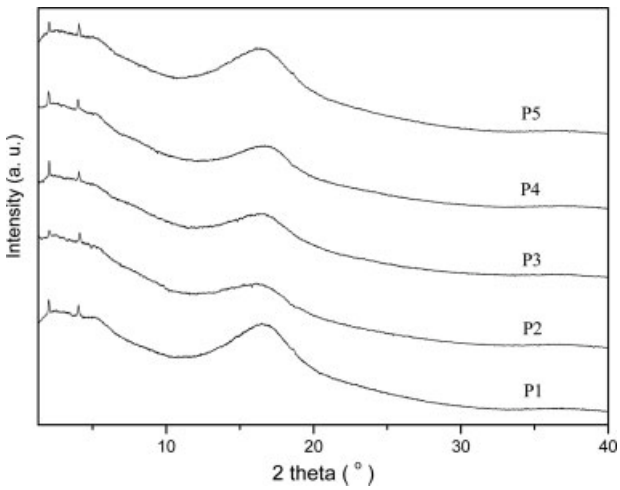


Figure 4. X-ray diagrams of polymers **P1–P5**.

Table 3. XRD Diffraction Data of Polymers **P1–P5** at 190 °C

Sample	*d*-Spacing (Å)[a]
P1	d_{001} = 37.45
	d_{002} = 18.82
P2	d_{001} = 36.70
	d_{002} = 18.45
P3	d_{001} = 37.27
	d_{002} = 18.73
P4	d_{001} = 38.03
	d_{002} = 18.91
P5	d_{001} = 36.90
	d_{002} = 18.45

[a] The theoretical *d*-spacing was 35.6 Å for polymers **P1–P5**.

Table 4. Absorption and PL Spectral Data of Block Copolymers **P1–P4**

	$\lambda_{max,Abs}$ (nm)[a]		$\lambda_{max,PL}$ (nm)[a]	
Sample	Solution[b]	Film	Solution[b]	Film
P1	310	309	403	427
P2	312	314	416	435
P3	310	308	404	434
P4	312	310	431	438

[a] $\lambda_{max,Abs}$: the maximum absorption wavelength. $\lambda_{max,PL}$: the maximum photoluminescence wavelength.
[b] Absorption and PL emission spectra were recorded in dilute $CHCl_3$ solutions at room temperature.

the layer structures of all the polymers, **P1–P5**, have little relationship with respect to the flexible blocks, such as the PS and PEO blocks.

Optical Properties

The photophysical properties of block polymers **P1–P4** containing luminescent cyanoterphenyl blocks were studied by photoluminescence (PL) and UV–vis absorption spectra in dilute chloroform solutions and solid films. The optical properties of all the polymers are summarized in Table 4. Because of the identical rigid cores of the luminescent cyanoterphenyl blocks, all the synthesized polymers in solutions had almost the same maximum absorption wavelength around 310 nm and emitted blue light at approximately $\lambda_{max,PL}$ (the maximum photoluminescence wavelength) = 435 nm in solid films.

Figure 5 shows an example of UV–vis and PL spectra of diblock copolymer **P1**. In comparison

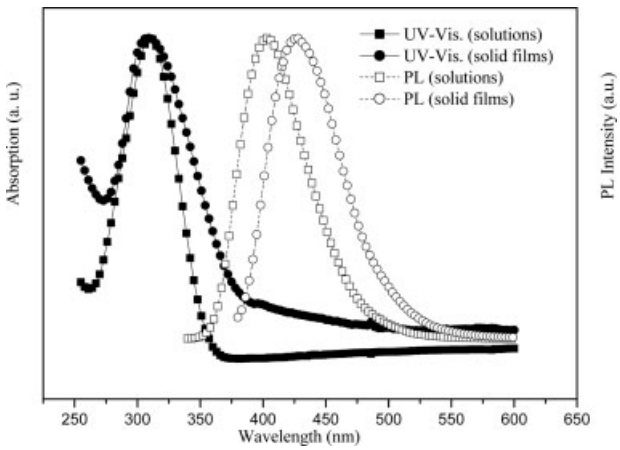


Figure 5. (—) Absorption and (- - -) PL spectra of **P1** in solutions ($CHCl_3$ as the solvent) and solid films.

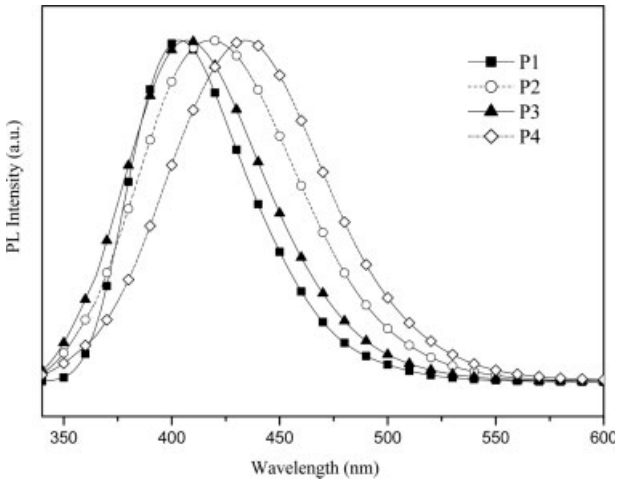


Figure 6. PL spectra of block copolymers **P1–P4** in solution ($CHCl_3$ as the solvent).

with the maximum PL wavelength in solutions, the materials in solid films exhibited a redshifted PL emission because of the π–π^* aggregation of the rigid cores (luminescent cyanoterphenyl blocks). In terms of the PL wavelengths of all the block copolymers in dilute solutions, Figure 6 indicates that **P2** and **P4** were more redshifted than **P1** and **P3**. The redshifted PL emission in **P4** might have resulted from a large molecular weight of the LC cyanoterphenyl block with higher aggregation of emitting cyanoterphenyl moieties. In contrast to **P1**and **P3**, **P2** had shorter flexible PS chains resulting in a stronger π–π^* aggregation effect of the cyanoterphenyl blocks.

CONCLUSIONS

ATRP was employed to fabricate block copolymers composed of different macroinitiators and LC cyanoterphenyl-based polymethacrylate blocks. Thermal and XRD investigations indicated that all the polymers exhibited the interdigitated packing smectic A phase and had little relationship with respect to the flexible PS and PEO blocks. In terms of the PL wavelengths of all the block copolymers in dilute solutions, **P2** and **P4** were more redshifted than **P1** and **P3**, and this might have been due to the π–π^* aggregation effect of the cyanoterphenyl blocks in block copolymers.

The powder X-ray diffraction measurements were supplied by the BL17A beam line (charged by Jey-Jau Lee) of the National Synchrotron Radiation Research

Center in Taiwan. The instruments for the gel permeation chromatography measurements were provided by Prof. Yun Chen (Department of Chemical Engineering, National Cheng Kung University).

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