Synthesis, Nanostructures, and Functionality of Amphiphilic Liquid Crystalline Block Copolymers with Azobenzene Moieties

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ABSTRACT: A series of liquid crystalline (LC) homopolymers of poly{11-[4-(4-butylphenylazo)phenoxy]undecyl methacrylate}containing an azobenzene mesogen with different degrees of polymerization were synthesized by using the atom transfer radical polymerization (ATRP) method. The homopolymers were prepared with a range of number-average molecular weights from 6100 to 23 500 with narrow polydispersities of less than 1.17. Thermal investigation showed that the homopolymers exhibit monolayer smectic A, smectic C, and an unknown smectic X phases. The transition temperatures increase slightly with the increase of the molecular weights and level off at around 21 500. Novel amphiphilic LC-coil diblock copolymers with a defined length of a flexible poly(ethylene glycol) segment as the hydrophilic coil were also prepared by the ATRP method. The LC-coil diblock copolymers were investigated by using transmission electron microscopy (TEM). Microphase separation with small size in the range of 10-20 nm (nanoseparated structures) was observed. Different photophysical and photochemical behaviors were observed between annealed homopolymer and block copolymer films, which is thought to be caused by the formation of nanostructures of the block copolymers.

Introduction

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Block copolymers can produce numbers of microphaseseparated nanostructures with cylinder, lamellar, sphere morphologies, etc, which are of wide scientific and technological interests.¹⁻³ If any functional groups/ properties are well assembled into the block copolymers, the functionality might act as a probe to elucidate relationship of nanostructures with functionality, i.e., both nanostructures controlled by functionality and nanostructure-specific functionality. Some of the recent studies in the fields are shifting their gravities to the function-directed polymer materials utilizing the nanostructures. For example, Jenekhe et al. revealed that different morphologies of a rod-coil diblock copolymer exhibited quite different photoluminescence emissions.⁴ Mao et al. pointed out that the formed cylinder structures of a series of liquid crystalline (LC) block copolymers may stabilize the mesophases, resulting in the increase of isotropic transition temperatures.⁵ Schneider et al. found that not only the nanoseparated morphologies but also the domain sizes could be controlled by using different thermal treatment conditions of a LC block copolymer.⁶ Along this line, we have set our object more clearly to explore new type of functional materials based on the microphase-separated nanostructures.

To further understand the nanostructure-functionality correlation based on functional block copolymers, we design a novel series of multifunctional block copolymers, which contain both a defined length of poly-(ethylene glycol) (PEG) as the hydrophilic block and different length of poly(methacrylate) with an azobenezene unit as the hydrophobic, liquid crystalline, and photoisomerization block. The combination of LC with

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amphiphilic properties in the block copolymers not only provides novel LC block copolymers but also opens the opportunities to investigate reproducible nanostructure formation under the influence of polymer structures, thermal treatment, and the driving force by selfassembly. Additionally, azobenzene chromophore is one of the typical functional units which can undergo reversible trans-cis isomerization under photoirradiation and can be applied in the fields of information storage, waveguide switching, optical memories, etc. Based on the microphase separation of block copolymers with different morphologies, the azobenzene group will act as a probe to study whether the photoisomerization has influence on the microphase separation and whether the above-mentioned morphologies have some influence on the photochromism of the azobenzene unit. Though some studies on nanostructures affected by polymer sequences and LC properties of the azobenzene block copolymers⁵⁻⁷ have been reported, the investigation of the relationship of the photophysical and photochemical properties of azobenzene block copolymers with the nanostructures⁸ has just started.

For the preparation of the new functional block copolymers, we chose the recently developed polymerization technique—atom transfer radical polymerization (ATRP) method—because the ATRP method can be handled easily and can be applied to a wide variety of monomers and lead to interesting polymer architectures with narrow polydispersity.^{9–17} Different from many reports describing the synthesis of amphiphilic block copolymers and LC block copolymers, ^{5,6,18–21} we adopted the ATRP method for the first time to the synthesis of amphiphilic thermotropic functional LC block copolymers.

Therefore, in this paper, we will describe the synthesis of a new series of LC homopolymers of $poly{11-[4-(4-butylphenylazo)phenoxy]undecyl methacrylate} (P1)$

Chart 1



and their amphiphilic block copolymers with a defined poly(ethylene glycol) as the hydrophilic block (**P2**) by using the ATRP method and the investigation and comparison of their LC properties, nanostructures, and the relationship of nanostructures with their photophysical and photochemical properties (see Chart 1).

Experimental Section

Characterization. ¹H NMR spectra were measured by using a JEOL 270 instrument spectrometer operating at 270 MHz with TMS internal standard as a reference for chemical shifts. FT-IR spectra were recorded on a Bio-Rad FTS 3000 spectrophotometer. UV-vis absorption spectra were recorded on a Shimadzu UV-3100S spectrophotometer. Polymer films for photoreactions were spin-coated from 1 wt % toluene solutions onto quartz glass plates. Trans-cis photoisomerizations of azobenzene units were carried out by using a Xe lamp with cut filters of UV34 and U340 (the light intensity was about 1.2 mW/cm² at 365 nm). Cis-trans photoisomerizations were carried out by the Xe lamp using an L42 and a Y50 cut filter. Molecular weights of polymers were determined by using a JASCO 860 GPC (Japan Spectroscopic Co., Ltd.) equipped with UV and RI detectors in reference of a series of standard polystyrenes with THF as eluent.

Thermal behaviors were determined by using a SII Extra 6000 DSC system (Seiko Instruments Inc.) at a scanning rate of ± 10 °C/min. Liquid crystalline textures were observed under a Nikon Microphot-UFX polarized optical microscope (POM) with a Mettler FP-82 hot stage and a FP-80 central processor. Wide-angle X-ray diffraction (WAXD) was measured on a MAC Science MPX 3 X-ray diffractometer equipped with a thermal controller model 5310.

Transmission electron microscopy (TEM, JEOL 1200 EXII) experiments were carried out at an acceleration voltage of 200 kV. TEM samples for the observation of nanostructures of the block copolymers were prepared by spreading 0.5–2 wt % toluene solutions onto water surface and then transferring the thin films onto a copper TEM grid. The thin films on the grids were annealed at 105 °C for 24 h and then exposed to RuO₄ vapor at room temperature for 2 min to selectively stain the PEG block.²²

Materials. Anisole as the solvent for solution polymerization was purified by distillation from sodium with benzophenone. Catalyst Cu(I)Cl (Kanto Chem. Co., Japan) was washed successively with acetic acid and ether, then dried, and stored under nitrogen. 2-Bromo-2-methylpropionyl chloride, 11-bromo-1-undecanol, 4-butylaniline, methacrylic acid, and dicyclohexylcarbodiimide (DCC), commercially available from Kanto Chem. Co (Japan), were used without further purification. Poly(ethylene glycol) methyl ether with number-average molecular weight of about 2000 (Aldrich) was dried by azeotropic distillation with toluene before use. The ligand 1,1,4,7,10,10hexamethyldiethylenetriamine (HMTETA, Aldrich) was used as received without further purification.

Preparation of Azobezene Monomer. The synthesis of the monomer is illustrated in Scheme 1 according to the normal organic synthetic procedure.²³ The purity of the monomer 11-[4-(4-butylphenylazo)phenoxy]undecyl methacrylate (1) was guaranteed by IR, NMR, and elemental analysis.²⁴

Preparation of Homopolymers. Homopolymers, **P1a**–**P1e**, were synthesized by using Cu(I)Cl complexed with HMTETA as the catalyst and ethyl 2-bromoisobutyrate as the



initiator as shown in Scheme 1. The polymerizations were carried out under vacuum in degassed and sealed ampules at 80 $^\circ\mathrm{C}.$

Example of the Preparation of P1b. 10 mg (0.1 mmol) of Cu(I)Cl and 492 mg (1.0 mmol) of the monomer 1 were mixed in a 10 mL ampule bottle, degassed and filled with nitrogen. 11 μ L (14.7 mg, 0.1 mmol) of HMTETA and 7.3 μ L (9.75 mg, 0.05 mmol) of ethyl 2-bromoisobutyrate in 5 mL of anisole were added through a syringe. The mixture was degassed by three cycles of freeze-pump-thaw procedures and sealed under vacuum. After 30 min stirring at room temperature, the ampule was placed in the preheated 80 °C oil bath for 20 h. A solution was taken for ¹H NMR measurement. Conversion was 87%, determined on the basis of the intensity of the peak at 2.66 ppm $(I_{2.66})$ corresponding to the two methylene protons of the butyl group at the para position of the phenyl group and that at 6.08 ppm ($I_{6.08}$) representative of a vinyl proton of the methacrylate group by eq 1.

conv (%) =
$$(I_{2.66} - 2I_{6.08})/I_{2.66} \times 100\%$$
 (1)

The solution was passed through a neutral Al_2O_3 column with THF as eluent to remove the catalyst. The yellow filtrate was concentrated under reduced pressure and reprecipitated twice into methanol. The yellow polymer was collected by filtration and dried under vacuum. Yield: 270 mg (54%). M_n (GPC) = 8300, $M_w/M_n = 1.10$.

Preparation of PEG Macroinitiators (5). The synthesis of the macroinitiator is shown in Scheme 2.

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 PEG methyl ether with an M_n of 2000 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 PEG macroinitiator was precipitated into cold ether. After dissolution in ethanol, the solution was stored in refrigerator to recrystallize the product. Yield: 60%. ¹H NMR (CDCl₃), δ (ppm): 4.33 (dd, 2H, $-OCH_2COO-$), 3.73 (m, 158H, $-CH_2-$), 3.38 (s, 3H, $-OCH_3$), 1.94 (s, 6H, (CH₃)₂CBrCOO-). M_n (GPC) (RI detector) = 3500, $M_w/M_n = 1.03$, and M_n (NMR) = 1900.

Preparation of the Block Copolymers. Block copolymers were synthesized by using the analogous procedure of the homopolymers of **P1** except for a use of **5** as the macro-initiator.

Example of the Synthesis of P2d. A 4 mg (0.04 mmol) of Cu(I)Cl, 19 mg (0.01 mmol) of **5**, and 570 mg (1.15 mmol) of the monomer **1** were mixed in a 10 mL ampule bottle,

Table 1. Experimental Conditions^a and Properties of the Polymers Synthesized by the ATRP Method

sample	$[M]_0/[I]_0^b$	time ^c	$\operatorname{conv}^d(\%)$	$M_n(GPC)^e$	$M_{\rm n}$ (calc)	$M_{\rm n}({ m NMR})^h$	$M_{\rm w}/M_{\rm n}{}^i$	LC content (%)	yield (%)
P1a	10	18	90	6 100	4 600 ^f		1.12	100	66
P1b	20	20	87	8 300	8 800 ^f		1.10	100	54
P1c	40	20	88	13 600	17 500 ^f		1.13	100	62
P1d	60	20	90	21 500	23 800 ^f		1.16	100	68
P1e	80	20	80	23 500	31 700 ^f		1.17	100	64
P2a	115	2	20	15 900	13 200 ^g	13 700	1.08	86 ^j	10
P2b	115	4	32	18 700	20 000g	21 600	1.09	91 ^j	24
P2c	115	8	60	27 800	35 800g	34 400	1.09	94 ^j	45
P2d	115	12	80	35 600	47 200 ^g	53 600	1.11	96 ^j	63

^{*a*} [Initiator]:[HMTETA]:[Cu(I)Cl] = 1:2:2. Initiators for **P1** and **P2** are ethyl 2-bromoisobutyrate and **5**, respectively. Polymerization temperature is 80 °C. ^{*b*} Feed molar ratio of the monomer [M]₀ to initiator [I]₀. ^{*c*} Polymerization time in hours. ^{*d*} Conversion determined by ¹H NMR from eq 1 in the text. ^{*e*} Number-average molecular weight, M_n (GPC), determined by GPC. ^{*f*} M_n (calc) calculated according to M_n (calc) = 195 + [M]₀/[I]₀ × conv × 492, where 195 and 492 are the molecular weights of initiator and monomer, respectively. ^{*g*} M_n (calc) calculated according to eq 3. ^{*h*} M_n (NMR)determined by ¹H NMR according to eq 2. ^{*i*} Polydispersity determined by GPC. ^{*j*} LC weight fraction determined by ¹H NMR.

degassed, and filled with nitrogen. An 11 μ L (15 mg, 0.1 mmol) of HMTETA in 6 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 30 min stirring at room temperature, the ampule was placed in the preheated 80 °C oil bath for 12 h. A solution was taken for ¹H NMR measurement. Conversion was 80%. The solution was passed through a neutral Al₂O₃ column with THF as eluent to remove the catalyst. The yellow filtrate was concentrated under reduced pressure and reprecipitated twice into acidic methanol. The yellow polymer was collected by filtration and dried under vacuum. Yield: 365 mg (63%). M_n (GPC) = 35 600, $M_w/M_n = 1.11$.

Results and Discussion

Synthesis. For the study of the influence of the degree of polymerization on the liquid crystalline properties, five homopolymers with azobenzene units, P1a-Ple, were synthesized by using ethyl 2-bromoisobutyrate as the initiator and CuCl complexed by HMTEMA as the catalyst. Detailed experimental conditions and results are given in Table 1. For all of the polymerizations, the initial monomer concentration $([M]_0)$ was kept constant ($[M]_0 = 0.2 \text{ M}$), whereas the monomer/initiator molar ratio, $[M]_0/[I]_0$, was systematically changed from 10 for P1a to 80 for P1e, to control their molecular weights by the $[M]_0/[I]_0$. The molar mass characteristics were determined by using GPC. All of the homopolymers, P1a-P1e, show monomodal GPC curves that shift toward lower values along the elution volume scales as the increases of the [M]₀/[I]₀. Number-average molecular weights (Mn(GPC)) from 6100 to 23 500 g/mol and narrow polydisperisties (M_w/M_n) in the range of 1.10–1.17 were evaluated, which implied the polymerization of 1 could be controlled well under the above conditions.

Four amphiphilic LC-coil diblock copolymers, P2a-P2d, were synthesized from 5 as the hydrophilic coil macroinitiator by controlling the degree of polymerization of 1 as a function of time. Detailed experimental conditions and the measured average molecular weights are also given in Table 1. Figure 1 shows the GPC profiles of the four block copolymers P2a-P2d and their starting macroinitiator 5. The GPC curves corresponding to the block copolymers P2a-P2d shifted to high molecular weights with the increase of polymerization time, implying a well-controlled living polymerization. No residual precursor 5 was detected, suggesting that the macroinitiator 5 work efficiently to initiate the copolymerizations. Figure 2 gives the kinetic plot of polymerization of the azobenzene monomer 1 with 5 as the macroinitiator in anisole solution. A nearly linear



Figure 1. GPC curves of the macroinitiator **5** (a) and its diblock copolymers **P2a** (b), **P2b** (c), **P2c** (d), and **P2d** (e). For **5**, M_n (GPC) = 3500, $M_w/M_n = 1.03$. For **P2a**, M_n (GPC) = 15 900, $M_w/M_n = 1.08$. For **P2b**, M_n (GPC) = 18 700, $M_w/M_n = 1.09$. For **P2c**, M_n (GPC) = 27 800, $M_w/M_n = 1.09$. For **P2d**, M_n (GPC) = 35 600, $M_w/M_n = 1.11$.



Figure 2. First-order kinetic plots for the ATRP of azobenzene monomer **1** initiated by **5** mediated by HMTETA and copper-(I) chloride in anisole at 80 °C.

relationship was observed, implying the controlled living character of the block copolymerization by using the ATRP method. Figure 3 gives the dependence of molecular weight and polydispersity on monomer conversion. It can be seen clearly that the block copolymers exhibit narrow polydispersities in the range from 1.08 to 1.11, and the molecular weight of the block copolymers increases regularly with the increase of the conversion of the azobenzene monomer **1**, indicating the living character of the block copolymerization. Estimation of the relative compositions of **1** to **5** in the block copolymers was derived from the integration of the oxymethylene protons at 3.9 ppm ($I_{3.9}$) (c and e in Figure 4) of the azobenzene block to that of the oxyethylene protons of PEG block at 3.7 ppm ($I_{3.7}$) (b in Figure 4). The



Figure 3. Dependence of molecular weight (M_n (GPC)) of **P2a–P2d** and polydispersity (M_w/M_n) on the conversion of azobenzene monomer **1**.



Figure 4. Typical ¹H NMR spectrum of block copolymer **P2c** in CDCl₃.

calculated molecular weight based on NMR ($M_n(NMR)$) is given by eq 2:

$$M_{\rm p}({\rm NMR}) = 1900 + 40 \times (I_{3.9}/I_{3.7}) \times 492$$
 (2)

where 1900 and 492 are the molecular weights of PEG initiator and the azobenzene monomer, respectively. The theoretical molecular weight (M_n (calc)) is given by the conversion and feed ratio of the monomer to initiator by using eq 3:

$$M_{\rm p}({\rm calc}) = 1900 + [{\rm M}]_0 / [{\rm I}]_0 \times {\rm conv} \times 492$$
 (3)

When the conversion is lower than 60%, the M_n (calc) and M_n (NMR) are in accordance well based on the controlled living character.

Thermal Properties. Thermal properties of the polymers were investigated by using differential scanning calorimetry (DSC), polarized optical microscopy (POM), and wide-angle X-ray diffraction (WAXD).

The azobenzene monomer **1** melted at 80 °C on heating and crystallized at 72 °C on cooling with no indication of LC character. However, all of the polymers exhibit LC properties. Figure 5 shows the DSC curves of the polymer **P1a**–**P1e** on their second heating and first cooling procedures. In the case of **P1e**, on heating, two well-defined endothermic transitions at 74 and 123 °C and a very small transition (transition enthalpy around 0.2 J g⁻¹) around 109 °C are observed, respectively, which are reversible on cooling with a few degree of supercooling effect. These transitions were attributed to three LC transitions. POM was used to identify the mesophases. On cooling of **P1e**, focal conic-fan shaped textures (Figure 6A) were observed in the temperature range 122–101 °C, suggesting a smectic A (SmA) phase.



Figure 5. DSC curves of the homopolyers **P1** on the first cooling (A) and second heating (B) process with a heating/ cooling rate of ± 10 °C/min. Curves a, b, c, d, and e are for **P1a**, **P1b**, **P1c**, **P1d**, and **P1e**, respectively.

On further cooling below 100 °C, slight texture change but clear birefringence change were observed as shown in Figure 6B, suggesting a smectic C phase (SmC). On the further cooling below 74 °C, the color caused by the birefringence changed and the textures (Figure 6C) became obscure, indicating an other kind of smectic phase (SmX).²⁵ Results of WAXD also confirmed the smectic phases. Figure 7 shows the typical temperaturedependent WAXD patterns of **P1e**. At room temperature the diffraction pattern is constituted by three diffraction peaks (d_{001} , d_{002} , and d_{003}) in the small-angle regions at a periodicity of $d_{001} = 3.10$ nm. The layer spacing of d_{001} is a little shorter than the length of the fully extended monomer molecular length (L = 3.37 nm, calculated by MM2 force field method), thus suggesting a tilted monosmectic layer (SmX) of the side group with a tilted angle of 23° to the layer normal. On heating to 90 °C, the layer spacing d_{001} changed to 3.21 nm, suggesting the slightly tilted SmC phase with an angle of 15° to the layer normal. Actually, the tiled angles decrease from 23° to 0° with the increasing of the temperature from 70 to 115 °C, confirming the tilted SmC phase. On heating to 115 °C, the small-angle Bragg diffraction shifts to $d_{001} = 3.39$ nm, suggesting the monolayer SmA phase. It can also be seen that on heating to SmA and SmC phases the wide-angle diffusion at $2\theta \approx 20^\circ$ becomes much broader, which suggested a loss of the lateral correlation among the molecular side groups within the SmA and SmC phases. The strong lateral correlation among the LC segment at room temperature suggested the SmX is a high-order smectic phase; however, we did not do further research of its nature. Hence, the mesophase sequence of polymers 1 can be summarized as follows: SmX-SmC-SmA-I. A possible schematic representation of molecular orientation in the LC phases is given in Figure 8. The transition temperatures and transition enthalpies of the homopolymers are collected in Table 2. The transition temperatures increase with the increase of molecular weights and level off at an M_n (GPC) less than 21 500, while the transition enthalpies level off at an $M_{\rm n}({\rm GPC})$ less than 13 600.

Figure 9 gives the DSC curves of the block copolymers **P2a**–**P2d** on the second heating process. Two clear endothermic transitions at about 70 and 120 °C and a very small transition at about 100 °C were observed, which should be associated with the SmX–SmC, SmC–



Figure 6. Typical polarized optical micrographs of **P1e** at 115 (A), 90 (B), and 30 $^{\circ}$ C (C) (magnification: $\times 200$).



Figure 7. Temperature-dependent wide-angle X-ray power diffraction of **P1e** at 30 (a), 90 (b), and 115 °C (c).

SmA, and SmA–I transitions based on the thermal properties of **P1**. The temperature-dependent WAXD

results also confirmed the transitions and mesophases. For example, in the case of **P2c**, the layer spacing (d_{001}) at 30, 90, and 110 °C are 3.12, 3.17, and 3.38 nm, respectively, which are in accordance with those of homopolymers. The melting point of the PEG segment in the block copolymers was not detected by thermal analysis. It may be attributed to the high weight fraction of the LC block as shown in Table 1 and/or the enthalpy loss caused by the disordered interface between the PEG and LC blocks.^{5,19–21,26}

Based on the thermal investigations, their phase transitions and transition enthalpies of the block copolymers are also shown in Table 2. According to Figure 9 and Table 2, it can be seen that the transition temperatures and enthalpies of **P2a**–**P2d** increase with the increase of LC fractions. However, the enthalpies associated with the LC transitions are lower than that expected on the basis of the weight compositions of the LC blocks in the block copolymers. The phenomenon becomes much clearer if we consider the molecular weights of the azobenzene blocks, as shown in Figure 10. Such a kind of phenomenon was observed in several kinds of LC-coil block copolymers, 5.19-21.26 which was explained as resulting from the disordering of the LC structures near the microphase interface.

TEM Observation of Nanostructures. The nanostructures were imaged by TEM observation of their thin films. Figure 11 gives the typical TEM images of P2a-P2d. For all of the four block copolymers, PEG blocks exhibit as cylinders and/or spheres with a width/ diameter about 2-3 nm dispersed into the LC matrix. For P2a (Figure 11A), the PEG cylinders have a perpendicular orientation to the surface, and the cylinders exhibit several different directions on the surface. The orientation of the cylinders within the film can be nicely illustrated by tilting the sample in the electron microscope. The boundaries of the different directions of the cylinders on the surface before tilting become much clearer after the samples were tilted to 10° (Figure 11B) and 25° (Figure 11C); meanwhile, the parallel oriented cylinders become visible when the samples are tilted. Therefore, the above results clearly illustrated the PEG domains are perpendicularly oriented cylinders. For P2b, PEG cylinders with orientations parallel and perpendicular to the surface (Figure 11D) were observed. For P2c, the morphologies become much simpler; only uniform aligned hexagonal cylinders with perpendicular orientation to the surface (Figure 11E) were observed. With the further increase of the LC fraction to 96 wt % (P2d, Figure 11F), the PEG block exhibits as spheres dispersed into the LC matrix, because no morphological change was observed after the sample was titled. The cylinder structures in the present thin films with high LC fractions (86-94 wt %) are unusual, different from the widely accepted correlation between LC fraction and nanostructure in the bulk. A further investigation to explain it is still required, but the following two issues are added here: At high LC fractions the smectic alignment of the side chain plays a great effect on the nanostructures of the LC-coil block copolymers.²⁷ Very recently, during the reviewing process of the paper, Anthamatten et al. reported a block copolymer with 85 wt % of LC fraction exhibiting hexagonal coil polystyrene domains dispersed into bilayer LC structures.²⁷ The morphology of the thin film may be different from that of bulk film because the surface free energy also plays an important role for the



Figure 8. A possible schematic illustration of the layer structures of the LC phases. L: extended molecular length, 3.37 nm, calculated by the MM2 force field method. d_{001} : the layer spacing elucidated from the X-ray patterns of Figure 7. θ : tilt angle of the smectic phases to the layer normal. The closed and open ellipsoids show the mesogenic groups directed upward and downward, respectively.

Table 2.	Thermal	Properties ^a	of the S	ynthesized	Polymers
				./	./

		transition temp (<i>T</i> /°C)			enthalpies (ΔH /J g ⁻¹)			
sample	$T_{\rm m}/^{\circ}{\rm C}$	T _{SmX-SmC}	T _{SmC-SmA}	$T_{\rm SmA-I}$	$\Delta H_{\rm SmX-SmC}$	$\Delta H_{\rm SmC-SmA}$	$\Delta H_{\rm SmA-I}$	
P1a		65		105 ^b	1.99		8.00	
P1b		69	104	113	2.20	pprox0.2	8.42	
P1c		72	106	117	2.27	pprox0.2	8.53	
P1d		74	108	122	2.47	pprox0.2	8.48	
P1e		74	109	123	2.40	pprox0.2	8.49	
5	52							
P2a		70	100	116	0.53 (2.06) ^c	d	6.50 (7.30) ^e	
P2b		70	102	118	1.00 (2.18) ^c	d	7.51 (7.73) ^e	
P2c		74	107	122	1.00 (2.26) ^c	d	7.52 (7.98) ^e	
P2d		74	109	124	1.00 (2.30) ^c	d	7.98 (8.15) ^e	

^{*a*} Transition temperatures and enthalpies on the second heating process were determined by DSC at 10 °C/min. ^{*b*} Mixed transitions of SmC–SmA and SmA–I. ^{*c*} The $\Delta H_{SmX-SmC}$ shown in parentheses was calculated from the weight fraction of LC block and the $\Delta H_{SmX-SmC}$ of homopolymer **P1e**. ^{*d*} Not detected. ^{*e*} The ΔH_{SmA-I} shown in parentheses was calculated from the weight fraction of LC block and the ΔH_{SmA-I} of the homopolymer **P1e**.



Figure 9. DSC curves of the macroinitiator **5** (a) diblock copolymers **P2a** (b), **P2b** (c), **P2c** (d), and **P2d** (e) on the second heating process. Heating rate is 10 °C/min.

nanostructures in the thin film state.²⁸ The distances between PEG domains of **P2a**, **P2b**, **P2c**, and **P2d** are about 10, 12, 15, and 19 nm, respectively, increasing with the increase of the LC fractions as expected. Therefore, the influence of the LC fractions in the block copolymers on the size and arrangement of the nanostructures were observed clearly by using the four amphiphilic block copolymers. The successful controllability of the nanostructures provides the possibility of the investigation of nanostructure-specific functionality by using photophysical and photochemical properties as the probe.

Nanostructure-Specific Photochemical Function of Azobenzene Chromophore. To obtain information about the relationship between the nanostruc-



Figure 10. Relationship of the transition enthalpies at SmA–I transitions of homopolymers (\bullet) and block copolymers (\bullet) with the degrees of the polymerization (DP) of the azobenzene units derived from the M_n (calc).

tures with functionality, homopolymers and block copolymers were compared. As a typical example, the results of homopolymer **P1e** and diblock copolymer **P2c** with close molecular weights of the azobenzene units (M_n (calc) as shown in Table 1) were described. Figure 12 illustrates the UV–vis spectra of the as-cast films and annealed films. It can be seen that the as-cast films of the two polymers exhibited similar absorption maxima at 337 nm due to the π – π * long axis transition of the azobenzene unit. After being annealed at 105 °C in its smectic phase, the homopolmyer **P1e** film exhibited an 18 nm blue shift, implying a strong H-aggregation (faceto-face) of the azobenzene chromophore in LC state; meanwhile, the absorbance of the fresh as-cast **P1e** film



Figure 11. TEM micrographs of the block copolymers **P2a** (A), **P2a** (B, tilted angle is 10°), **P2a** (C, tilted angle is 25°), **P2b** (D), **P2c** (E), and **P2d** (F). PEG block appeared as dark. The solid lines in A, B, and C represent the domain boundaries.



Figure 12. UV–vis spectra of the as-cast (a) and annealed films (b) of homopolymer **P1e** (A) and block copolymer **P2c** (B). The fresh film was cast from 1 wt % solution in toluene onto quartz glass. Annealing condition is at 105 °C (smectic phase) for 24 h.

decreased more than 60% after annealing, indicating homeotropic alignment of the chromophores to the substrate plan. However, only a slight decrease of absorbance and no blue shift were observed in the case of block copolymer **P2c**. The other block copolymers exhibited consistent results with that of **P2c**. These differences might be attributed to the formed microphase-separated structures between the PEG block and azobenzene side-chain LC block in the nanoseparated thin film. Probably, the formed nanostructures hinder the formation of larger LC domain and further chromophore aggregation within the small LC domain of the microphase-separated block copolymer films, which caused the different photophysical behavior between the homopolymers and block copolymers.⁸

The as-cast **P1e** and **P2c** films exhibit a similar simple trans-cis photoreactive process with successive

decrease of the absorbance maximum at 337 nm and the increase of the absorbance maximum at 460 nm, with the irradiation of 340 nm light. However, their photoreactive processes are quite different between their annealed films as shown in Figure 13. A complicated photochemical procedure was observed in the case of the annealed **P1e** film with the irradiation of $\lambda \approx 340$ nm. In the early stage of the irradiation for 0.5 min, the absorbance at 338 nm decreased successively, indicating simple trans-cis isomerization. However, with further irradiation (0.5-2 min), the absorbance increased smoothly, and the spectra became much broader. (The shoulder at 354 nm was assigned to the isolated monomeric absorption.) These processes might be related with the reorganization of the azobenzene chromophores during the trans-cis isomerization due to insufficient free volume caused by the strong H-ag-



Figure 13. Photochemical processes of the annealed films of homopolymer **P1e** (A and C) and block copolymer **P2c** (B and D) with the irradiation of 340 nm light (A and B) and 440 nm light (C and D), respectively. For A and B: (a) initial spectrum before irradiation; (b) 0.5 min irradiation; (c) 2 min irradiation; (d) 8 min irradiation corresponding to the photostationary state. For C and D: the irradiation times of a, b, c, d, e, f, g, and h are 0 s, 10 s, 20 s, 30 s, 1 min, 2 min, 4 min, and 8 min, respectively.

gregation and perpendicular alignment of the chromophores.⁸ With further irradiation to 8 min, the reaction reached its photostationary state. However, simple photochemical process was observed in the case of the annealed film of block copolymer **P2c**, similar to its fresh as cast film, implying its simple trans-cis isomerization process. These findings are analogous to the results reported by Moriya et al.⁸ by using polystyrene-*b*-poly{6-[4-(4-cyanophenylazo)phenoxy]hexyl methacrylate}.

The back-reaction processes of the two polymer films with the irradiation by using visible light at 440 nm are also given in Figure 13. For each of the two polymers isolated monomer absorption with a maximum at 354 nm was observed clearly during the cis-trans procedure. The absorbance of the final state of **P1e** is much higher than the original annealed film, showing that the homeotropic alignment and the H-aggregation of the azobenzene chromophores formed by annealing in its smectic state were broken by the photoisomerization process. However, the absorbance of the photostationary state of block copolymer, **P2c**, is about 90% of its original annealed film.

Therefore, the above results clearly show that the homopolymers and block copolymers exhibit quite different photophysical and photochemical properties. Such different behaviors might relate with the formed nanostructrures of the block copolymers. Further investigations of the effect of photochemical process on nanostructures are in progress, which will be reported in another paper.

Conclusions

We have synthesized a new series of well-defined LC homopolymers and amphiphilic LC-coil diblock copolymers with functional azobenzene units and narrow polydispersities in the range of 1.08–1.11 by using the newly developed ATRP method. Thermal investigation shows that each of the polymers exhibits monolayer SmA, SmC, and SmX phases. For the block copolymers,

cylinder and/or spherical morphologies of PEG block dispersed into LC block were clearly observed after annealing at 105 °C (smectic phase) for 24 h. The sizes of nanoseparated structures are in the range of 10-20nm, increasing with the increase of LC fraction. Photophysical and photochemical investigations revealed the annealed homopolymer thin films exhibited strong H-aggregations of the azobenzene chromophores and complicated trans-cis photochemical processes; however, the annealed block copolymers did not show the obvious H-aggregations and exhibited simple photochemical processes. The significant different behaviors among block copolymers and azobenzene homopolymers are considered to be attributed to the formed nanostructures of the block copolymers. Such findings may provide the opportunities of new application of azobenzene block copolymers as for new optical storage and holography materials.

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