Macromolecules

Photoresponsive Liquid-Crystalline Polymers Containing a Block Mesogenic Side Chain: Systematic Studies on Structural Parameters for Nanophase-Separated Structures

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Supporting Information

ABSTRACT: A family of liquid-crystalline polymers (LCPs) containing a block mesogenic side group was synthesized by varying the hydrophilic moiety (oligooxyethylene) ratio. As the oligooxyethylene content increased, the range of the LC phase narrowed or vanished. The polymers were subjected to annealing and exposed on the surface of films, and their morphologies were observed using an atomic force microscope. While the annealed films prepared from the LCPs showed nanophase separation on the surface, the film of the amorphous polymer exhibited no phase separation. Under the optimized conditions, two types of irradiation procedures were adopted: (i) UV (365 nm) light illumination for a phase transition induced by trans-cis photoisomerization and (ii) linearly polarized visible (>436 nm) illumination



for a photoinduced alignment change. These results revealed that the photoresponsive behavior of the nanostructure is strongly coupled to the molecular alignments induced by annealing.

INTRODUCTION

During the past decade, bottom-up processes to construct nanosized structures have been progressed significantly because of the continuing demand for miniaturization of electronic devices and the creation of biomimetic materials. Studies of a phase separation in block copolymers (BCPs) have received attention for broad applications in nanotechnology because their size, shape, and periodicity of BCPs can be controlled by changes in structural parameters such as molecular weight, composition, and chain connectivity.^{1,2} Furthermore, the tuning of morphology by external stimuli has been attempted through solvent annealing,³ casting,⁴ electric-field alignment,⁵ and so on. To manipulate the morphology of phase separation by light, incorporation of an liquid-crystalline (LC) component into a polymer segment an effective approach given the cooperative change in molecular alignment by external stimuli.⁶ For example, the phase-separated structures in LC block copolymers (LCBCPs) containing an azobenzene moiety can be controlled by photoisomerization.⁷ Generally, photoisomerization induces a change in the molecular alignment of an azobenzene polymer, and the alignment can be fixed below a glass transition temperature (T_g) .⁸ Thus, the Weigert effect induced by polarized light⁹ can reversibly control the alignment of a nanostructure.

Recently, we proposed a novel molecular architecture of a polymer material exhibiting nanophase separation based on a framework of LCBCPs (Chart 1).¹⁰ The polymer contains a block mesogenic side chain in which a hydrophobic mesogen is directly attached to hydrophilic moieties. In addition, the block mesogen is composed of an azobenzene moiety exhibiting photochromism. The polymer system shows the following

characteristics based on its chemical structure. (i) The polymer, which exhibits nanophase separation, can be synthesized by conventional radical polymerization because of the amphiphilic nature of the block mesogen with a hydrophobic mesogenic core and hydrophilic oligooxyethylene moieties. (ii) Nanophase separations prepared from the polymer film are manipulated reversibly by combining photochemical and thermal processes. Analogous to BCPs,¹¹ the molecular architecture would create complex that exhibit photoresponsive properties. For example, mean-field theories of BCPs predict the morphology of phase separation depending on the degree of segregation of the system, the volume fraction occupied by one of the blocks, and the conformational asymmetry.¹¹ The theory prompted us to explore the effect of the position and number of the oligooxyethylene moieties in the block mesogenic system on phase-separated structures. Accordingly, in this study, we synthesized different polymers containing a block mesogen and investigated the relationship between their structures and surface morphologies.

EXPERIMENTAL SECTION

Unless otherwise noted, all commercial reagents were used as received. ¹H and ¹³C NMR spectra were recorded in CDCl₃ with a JNM ECP-500 spectrometer. Chemical shifts of ¹H and ¹³C NMR signals were quoted to internal standard CDCl₃ (δ = 7.24 and 77.0) and listed as chemical shifts in ppm (δ). High-resolution mass spectra were obtained with a JMS-SX102A spectrometer with fast atom

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bombardment (FAB). LC behavior and phase transition behavior were examined on an Olympus model BX-51 polarizing microscope equipped with Mettler hot-stage models FP-90 and FP-82. Thermotropic properties of compounds were determined with a differential scanning calorimeter (DSC) on a Seiko I&E SSC-5200 and DSC220C at a scanning rate of 10 °C/min. At least three scans were performed for each sample to verify the reproducibility. Wide-angle X-ray diffraction (WAXD) measurements of the sample films were carried out on a Rigaku Ultima using Cu K α radiation. AFM was performed in the tapping mode with a NanoNavi probe station and an S-image unit (SII NanoTechnology Inc., Tokyo, Japan).

4-(3,6-Dioxaoctyloxy)-2-ethynylbenzene (2)¹². Yield 3.5 g (68%) of yellow oil. ¹H NMR (CDCl₃, δ, ppm): 7.41 (2H, d, *J* = 8.6 Hz), 6.85 (2H, d, *J* = 8.8 Hz), 4.16–4.09 (2H, m), 3.87 (2H, t, *J* = 4.8 Hz), 3.73–3.71 (2H, m), 3.62–3.60 (2H, m), 3.54 (2H, q, *J* = 7.0 Hz), 2.99 (1H, s), 1.22 (3H, t, *J* = 7.1 Hz).

4-(4-(3,6-Dioxaoctyloxy)phenylethynyl)-4'-(10-hydroxydecyloxy)azobenzene (3). A mixture of 1 (4.2 g, 9.6 mmol), 2 (2.3 g, 9.6 mmol), PdCl₂(PPh₃)₂ (0.32 g, 4.6 mmol), CuI (0.30 g, 1.6 mmol), PPh₃ (0.64 g, 2.4 mmol), triethylamine (50 mL), and THF (50 mL) was refluxed at 60 °C for 6 h under a N₂ atmosphere. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with 1 N HCl and water and dried over anhydrous magnesium sulfate. The crude solid was purified by column chromatography (silica gel; eluent: ethyl acetate/hexane = 1:4) to yield 2.5 g (44%) of orange solid (mp 200 °C). ¹H NMR $(CDCl_3) \delta$: 7.91 (2H, d, J = 8.8 Hz), 7.86 (2H, d, J = 8.4 Hz), 7.62 (2H, d, J = 8.4 Hz), 7.48 (2H, d, J = 8.8 Hz), 7.00 (2H, d, J = 9.0 Hz), 6.91 (2H, d, J = 8.6 Hz), 4.17–4.13 (4H, m), 4.04 (2H, t, J = 6.5 Hz), 3.88 (2H, t, *J* = 4.8 Hz), 3.74–3.72 (2H, m), 3.66–3.63 (2H, m), 3.55 (2H, q, *J* = 7.0 Hz), 1.82 (2H, t, J = 7.2 Hz), 1.48–1.33 (14H, m), 1.22 (3H, t, J = 7.0 Hz).

10-[4-(4-{4-(3,6-Dioxaoctyloxy)phenylethynyl}phenylazo)phenoxy]decyl Methacrylate (4). A solution of methacryloyl chloride (0.59 g, 5.6 mmol) in THF (50 mL) was added dropwise at 0 °C to a mixture of 3 (1.1 g, 1.9 mmol), triethylamine (0.57 g, 5.6 mmol), and a trace amount of hydroquinone, and the reaction mixture was stirred at room temperature for 24 h. The solution was poured into saturated aqueous sodium hydrogen carbonate, and the product was extracted with ethyl acetate. After the organic layer was dried with anhydrous magnesium sulfate, the solvent was removed by evaporation. The crude solid was purified by column chromatography (silica gel, chloroform as eluent) and finally recrystallized from methanol to yield 0.42 g (33%) of an orange solid (mp 193 °C). ¹H NMR (CDCl₃) δ: 7.90 (2H, d, *J* = 9.0 Hz), 7.85 (2H, d, *J* = 8.6 Hz), 7.61 (2H, d, *J* = 8.6 Hz), 7.47 (2H, d, J = 9.0 Hz), 6.99 (2H, d, J = 9.0 Hz), 6.90 (2H, d, J = 8.8 Hz), 6.09 (1H, dd, J = 1.7, 1.0 Hz), 5.53 (1H, t, J = 1.6 Hz), 4.17–4.11 (4H, m), 4.02 (2H, t, J = 6.5 Hz), 3.86 (2H, t, J = 4.9 Hz), 3.73–3.71 (2H, m), 3.62–3.60 (2H, m), 3.53 (2H, q, J = 7.0 Hz), 1.94 (3H, dd, J = 1.6, 1.0 Hz), 1.85-1.25 (8H, m), 1.22 (3H, t, J = 7.0 Hz).¹³C NMR (CDCl₃) δ : 167.52, 161.90, 159.10, 151.79, 146.95, 136.58, 133.13, 132.16, 125.60,

125.10, 124.86, 122.63, 115.33, 114.76, 91.72, 88.19, 70.97, 69.86, 69.66, 68.36, 67.53, 66.69, 64.80, 29.79, 29.45, 29.42, 29.33, 29.22, 29.18, 28.61, 26.00, 25.97, 18.32, 15.16. MS (FAB) 655.3447 (MH⁺).

p-oxyAzo. Compound 4 (0.25 g, 0.32 mmol) and AIBN (5.0 mg, 3.2 μ mol) were dissolved in dry DMF (10 mL) and placed in a polymerization tube. After several freeze–pump–thaw cycles, the tube was sealed under high vacuum. Then, the tube was kept at 60 °C for 48 h. The resulting solution was cooled to room temperature and poured into 400 mL of methanol with vigorous stirring to precipitate the polymer. The polymer obtained was purified by repeated reprecipitation from DMF into a large excess of methanol and dried under vacuum for 48 h to yield 0.14 g of *p*-oxyAzo in 56% conversion.

3-(3,6-Dioxaoctyloxy)bromobenzene (5). Yield 3.5 g (68%) of an yellow oil. ¹H NMR (CDCl₃) δ : 7.21 (1H, t, *J* = 7.9 Hz), 7.08 (1H, dt, *J* = 7.6, 1.1 Hz), 7.03 (1H, t, *J* = 2.0 Hz), 6.92 (1H, ddd, *J* = 8.3, 2.6, 0.9 Hz), 4.13 (2H, t, *J* = 4.9 Hz), 3.86 (2H, t, *J* = 4.9 Hz), 3.72 (2H, t, *J* = 4.6 Hz), 3.61 (2H, t, *J* = 4.7 Hz), 3.54 (2H, q, *J* = 7.0 Hz), 3.05 (1H, s), 1.22 (3H, t, *J* = 7.0 Hz).

4-(3-(3,6-Dioxaoctyloxy)phenylethynyl)-4'-(10-hydroxydecyloxy)azobenzene (6). A mixture of 5 (2.0 g, 8.5 mmol), 1 (3.7 g, 8.5 mmol), PdCl₂(PPh₃)₂ (0.30 g, 0.43 mmol), CuI (0.29 g, 1.5 mmol), PPh₃ (0.60 g, 2.3 mmol), triethylamine (50 mL), and THF (40 mL) was refluxed at 60 °C for 6 h under a N₂ atmosphere. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with 1 N HCl and water and dried over anhydrous magnesium sulfate. The crude solid was purified by column chromatography (silica gel; eluent: ethyl acetate/chloroform = 1:5) to yield 3.2 g (64%) of orange solid (mp 126 °C). ¹H NMR (CDCl₃) δ: 7.92 (2H, d, J = 8.6 Hz), 7.87 (2H, d, J = 8.4 Hz), 7.65 (2H, d, J = 8.3 Hz), 7.26 (1H, t, J = 7.8 Hz), 7.15 (1H, d, J = 7.5 Hz), 7.10 (1H, s), 7.00 (2H, d, J = 9.0 Hz), 6.97 (1H, dd, J = 21.9, 8.5 Hz), 4.17 (4H, t, J = 4.7 Hz), 4.04 (2H, t, J = 6.4 Hz), 3.89 (2H, t, J = 4.8 Hz), 3.74 (2H, t, J = 4.6 Hz), 3.65 (2H, t, J = 6.1 Hz), 3.55 (2H, q, J = 7.0 Hz), 1.82 (2H, t, J = 7.1 Hz), 1.57–1.33 (14H, m), 1.22 (3H, t, J = 7.0 Hz).

10-[4-(4-{3-(3,6-Dioxaoctyloxy)phenylethynyl}phenylazo)phenoxy]decyl Methacrylate (7). A solution of methacryloyl chloride (0.63 g, 6.0 mmol) in THF (60 mL) was added dropwise at 0 °C to a mixture of 6 (1.2 g, 2.0 mmol), triethylamine (0.60 g, 6.0 mmol), and a trace amount of hydroquinone, and the reaction mixture was stirred at room temperature for 24 h. The solution was poured into saturated aqueous sodium hydrogen carbonate, and the product was extracted with ethyl acetate. After the organic layer was dried with anhydrous magnesium sulfate, the solvent was removed by evaporation. The crude solid was purified by column chromatography (silica gel, chloroform as eluent) and finally recrystallized from methanol to yield 0.82 g (63%) of an orange solid (mp 104 °C). ¹H NMR (CDCl₃) δ: 7.91 (2H, d, *J* = 8.8 Hz), 7.87 (2H, d, *J* = 8.4 Hz), 7.64 (2H, d, *J* = 8.4 Hz), 7.26 (1H, t, *J* = 7.9 Hz), 7.15 (1H, d, *J* = 7.5 Hz), 7.10 (1H, s), 7.00 (2H, d, *J* = 9.0 Hz), 6.94 (1H, d, J = 8.1 Hz), 6.10 (1H, s), 5.54 (1H, s), 4.18-4.12 (4H, m), 4.04 (2H, t, J = 6.5 Hz), 3.88 (2H, t, J = 4.8 Hz), 3.74 (2H, t, J = 4.7 Hz), 3.63 (2H, t, J = 4.7 Hz), 3.55 (2H, q, J = 7.0 Hz), 1.94 (3H, s),

1.82 (2H, t, J = 7.2 Hz), 1.70–1.33 (14H, m), 1.22 (3H, t, J = 7.1 Hz). ¹³C NMR (CDCl₃) δ : 167.56, 161.95, 158.61, 152.01, 146.89, 136.55, 132.41, 129.46, 125.17, 125.09, 124.91, 124.42, 123.99, 122.63, 117.15, 115.89, 114.75, 101.44, 91.46, 89.13, 70.96, 69.89, 69.70, 68.36, 67.55, 66.72, 64.81, 29.79, 29.53, 29.51, 29.46, 29.43, 29.34, 29.22, 29.18, 28.60, 26.00, 25.97, 21.45, 18.35, 15.17, 14.32. MS (FAB) 655.3756 (MH⁺).

m-oxyAzo. Compound 7 (0.25 g, 0.32 mmol) and AIBN (1.5 mg, 9.2 μ mol) were dissolved in dry DMF (10 mL) and placed in a polymerization tube. After several freeze-pump-thaw cycles, the tube was sealed under high vacuum. Then, the tube was kept at 60 °C for 48 h. The resulting solution was cooled to room temperature and poured into 400 mL of methanol with vigorous stirring to precipitate the polymer. The polymer obtained was purified by repeated reprecipitation from DMF into a large excess of methanol and dried under vacuum for 48 h to yield 0.20 g of *m*-oxyAzo in 68% conversion.

3,4,5-Tri(3,6-dioxaoctyloxy)bromobenzene (8)¹³. Yield 12 g (55%) of yellow oil. ¹H NMR (CDCl₃) δ: 6.74 (2H, s), 4.15–4.11 (6H, m), 3.86–3.78 (6H, m), 3.74–3.69 (6H, m), 3.60–3.58 (6H, m), 3.55–3.48 (6H, m), 1.21 (9H, t, *J* = 6.9 Hz).

3,4,5-Tri(3,6-dioxaoctyloxy)trimethylsilylethynylbenzene (9). A mixture of 8 (2.0 g, 8.5 mmol), trimethylsilylacetylene (2.8 g, 29 mmol), PdCl₂(PPh₃)₂ (0.77 g, 1.1 mmol), CuI (0.76 g, 4.0 mmol), PPh₃ (1.6 g, 6.0 mmol), triethylamine (50 mL), and THF (40 mL) was refluxed at 60 °C for 6 h under a N₂ atmosphere. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with 1 N HCl and water and dried over anhydrous magnesium sulfate. The crude solid was purified by column chromatography (silica gel; eluent: ethyl acetate/hexane = 1:2) to yield 7.1 g (57%) of yellow oil. ¹H NMR (CDCl₃) δ : 6.76 (2H, s), 4.17–4.12 (6H, m), 3.88–3.82 (6H, m), 3.77–3.71 (6H, m), 3.63–3.58 (6H, m), 3.58–3.51 (6H, m), 1.22 (9H, t, *J* = 6.9 Hz), 0.24 (9H, s).

3,4,5-Tri(3,6-dioxaoctyloxy)-2-ethynylbenzene (10). 9 (7.0 g, 12 mmol) and K₂CO₃ (0.3 g) were stirred in a mixture of THF (20 mL) and methanol (200 mL) for 3 h at room temperature. The mixture was extracted with ethyl acetate. After the organic layer was dried with anhydrous magnesium sulfate, the solvent was removed by evaporation. The product was purified by column chromatography (silica gel, ethyl acetate: hexane = 1:3 as eluent) to yield 4.9 g (81%) of brown oil. ¹H NMR (CDCl₃, δ , ppm): 6.66 (2H, s), 4.09–4.06 (6H, m), 3.81–3.72 (6H, m), 3.65–3.62 (6H, m), 3.53–3.51 (6H, m), 3.47–3.44 (6H, m), 2.93 (1H, s), 1.14 (9H, t, *J* = 6.9 Hz).

4-(3,4,5-Tri(3,6-dioxaoctyloxy)phenylethynyl)-4'-(10-hydroxydecyloxy)azobenzene (12). A mixture of 11 (2.0 g, 4.0 mmol), 1 (1.8 g, 4.2 mmol), PdCl₂(PPh₃)₂ (0.14 g, 0.20 mmol), CuI (0.50 g, 2.6 mmol), PPh₃ (0.30 g, 0.90 mmol), triethylamine (50 mL), and DMF (50 mL) was refluxed at 60 °C for 6 h under a N₂ atmosphere. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with 1 N HCl and water and dried over anhydrous magnesium sulfate. The crude solid was purified by column chromatography (silica gel; eluent: ethyl acetate/hexane = 1:1) to yield 1.6 g (48%) of yellow oil. ¹H NMR (CDCl₃) δ : 7.89 (2H, d, J = 9.2 Hz), 7.84 (2H, d, J = 8.2 Hz), 7.60 (2H, d, J = 8.7 Hz), 6.98 (2H, d, J = 8.7 Hz), 6.78 (2H, s), 4.17 (6H, q, J = 4.9 Hz), 4.11 (2H, t, J = 4.8 Hz), 4.02 (2H, t, J = 6.6 Hz), 3.84–3.81 (6H, m), 3.76–3.67 (6H, m), 3.61–3.56 (6H, m), 3.52–3.50 (6H, m), 1.79 (2H, t, J = 7.3 Hz), 1.50–1.34 (14H, m), 1.20–1.13 (9H, m).

10-[4-(4-{3,4,5-Tri(3,6-dioxaoctyloxy)phenylethynyl}phenylazo)phenoxy]decyl Methacrylate (13). A solution of methacryloyl chloride (0.21 g, 2.0 mmol) in THF (60 mL) was added dropwise at 0 °C to a mixture of **12** (0.54 g, 0.64 mmol), triethylamine (0.19 g, 1.8 mmol), and a trace amount of hydroquinone, and the reaction mixture was stirred at room temperature for 24 h. The solution was poured into saturated aqueous sodium hydrogen carbonate, and the product was extracted with ethyl acetate. After the organic layer was



Figure 1. Chemical structures and properties of polymers. M_{nn} numberaverage molecular weight; M_{wn} weight-average molecular weight.

dried with anhydrous magnesium sulfate, the solvent was removed by evaporation. The crude solid was purified by column chromatography (silica gel, chloroform as eluent) and finally recrystallized from methanol to yield 0.31 g (53%) of an orange solid. ¹H NMR (CDCl₃) δ : 7.89 (2H, d, *J* = 8.7 Hz), 7.84 (2H, d, *J* = 8.2 Hz), 7.60 (2H, d, *J* = 7.8 Hz), 6.98 (2H, d, *J* = 8.2 Hz), 6.78 (2H, s), 6.07 (1H, s), 5.52 (1H, s), 4.18–4.17 (6H, m), 4.13–4.08 (2H, m), 4.02 (2H, t, *J* = 6.4 Hz), 3.87–3.80 (6H, m), 3.71–3.69 (6H, m), 3.59–3.58 (6H, m), 3.54–3.50 (6H, m), 1.92 (3H, s), 1.80 (2H, t, *J* = 7.1 Hz), 1.48–1.36 (14H, m), 1.24–1.19 (9H, m). ¹³C NMR (CDCl₃) δ : 167.49, 161.86, 152.43, 151.86, 149.70, 146.81, 136.44, 132.20, 132.04, 131.96, 128.51, 128.42, 125.09, 125.04, 124.81, 122.55, 117.76, 115.98, 114.67, 111.17, 91.51, 88.37, 72.41, 70.81, 70.48, 69.82, 69.58, 68.80, 68.28, 66.61, 66.55, 64.73, 29.66, 29.35, 29.32, 29.22, 29.11, 29.07, 28.50, 25.90, 25.87, 18.23, 15.06. MS (FAB) 919.5320 (MH⁺).

3-oxyAzo. Compound **13** (0.30 g, 0.33 mmol) and AIBN (1.6 mg, 9.7 μ mol) were dissolved in dry DMF (10 mL) and placed in a polymerization tube. After several freeze–pump–thaw cycles, the tube was sealed under high vacuum. Then, the tube was kept at 60 °C for 48 h. The resulting solution was cooled to room temperature and poured into 400 mL of methanol with vigorous stirring to precipitate the polymer. The polymer obtained was purified by repeated reprecipitation from DMF into a large excess of methanol and dried under vacuum for 48 h to yield 0.18 g of 3-oxyAzo in 60% conversion.

RESULTS AND DISCUSSION

Thermal Properties. In an LCP containing a block mesogen, the hydrophilic moieties are oligooxyethylene units, whereas the hydrophobic segments are the polymer backbone, the hydrocarbon spacer, and the mesogenic core. To understand the effects of the position and volume of the hydrophilic moieties on nanophase-separated structures, various polymers (Figure 1) were designed and synthesized. The synthetic procedures and analytical data are reported in the Experimental Section.

ARTICLE

Scheme 1





⁽a) PdCl₂(PPh₃)₂, CuI, PPh₃, Et₃N; (b) Et₃N; (c) AIBN; (d) K₂CO₃, Me-OH

The thermal properties of the polymers were investigated by DSC, polarizing optical microscopy (POM), and WAXD. Figure 2 shows the DSC curves of the polymers on their second heating and cooling procedures. In the case of *p*-oxyAzo, two well-defined endothermic transitions at 142 and 183 °C, respectively, are observed upon heating. These transitions, which are reversible upon cooling with a slight supercooling effect of a few degrees, were attributed to two LC transitions identified by POM (Figure 3). Upon cooling *p*-oxyAzo showed a optical texture (Figure 3a). Below 101 °C, the texture was frozen to show the glassy state. The layer space of the smectic phase was measured by WAXD. At 125 °C, the diffraction pattern consists of two diffraction peaks $(d_{001} \text{ and } d_{002})$ in the small-angle regions (Figure 3d). The layer spacing of $d_{001} = 3.70$ nm is a little shorter than the length of the fully expanded molecular length (L =4.2 nm, calculated by CS Chem3DPro software). This seems to be due to the folding of the aliphatic spacers and reduced order of the azotolane cores. Moreover, at 155 °C, POM revealed a typical schlieren texture (Figure 3b), and WAXD showed no diffraction at the small-angle region (Figure 3e). This result indicates that the LC phase has a nematic phase structure. For *m*-oxyAzo, T_{σ} was observed at 76 °C, and an endothermic peak was also seen at 88 °C. As revealed by POM, the polymer adopted the isotropic

state above 88 °C. On the heating process, at 76–88 °C, a broken fan-shaped texture, which is a characteristic one for the smectic A phase, was observed (Figure 3c). As shown in Figure 3f, a small-angle diffraction peak at 5.88° attributable to $d_{001} = 3.01$ nm was observed. Though the spacing length is shorter than that of expanded side chain (L = 3.7 nm) due to the folding of aliphatic spacers, the LC phase is identified as SmA.

Surface Morphologies and Their Photoresponsive Behaviors. Figure 4 displays the surface morphologies and UV-vis absorption spectra of annealed and irradiated films in the polymers. Initially, to generate nanophase-separated structures in the polymer system, they were annealed above T_{g} . In the *p*-oxyAzo film (Figure 4A), the surface morphology of the film after annealing at 125 °C exhibited fiber-like structures whose width was about 30 nm. The significant decrease in an absorption band of the azobenzene unit indicates that homeotropic alignments of azobenzene moieties are formed during the phase separation. Furthermore, a hypsochromic shift was also observed, indicative of further promotion of H-aggregation.¹⁴ The homeotropic alignment of azobenzene moieties is inactive to a pumping light because of the small transition moment. Therefore, application of UV irradiation to the film causes little change in the absorption spectra for photoisomerization and in the



Figure 2. DSC curves of polymers during second heating and cooling at a rate of ± 10 °C/min. Profiles are for *p*-oxyAz (a), *m*-oxyAz (b), and 3-oxyAz (c). Inset of (c): polarized optical micrograph of 3-oxyAz at 70 °C.



Figure 3. Polarized optical micrographs of *p*-oxyAz at 125 °C (a) and 155 °C (b) as well as *m*-oxyAz at 84 °C (c). Temperature-dependent wide-angle X-ray diffraction of *p*-oxyAz at 125 °C (d) and 155 °C (e) as well as *m*-oxyAz at 84 °C (f).

morphology of the annealed surface. Upon irradiation with LPL, the polarized absorption spectra indicated a slight dichroism of azobenzene moieties induced by the Weigert effect. As shown in the AFM image, this also erased the surface morphology, presumably because the change in molecular alignment disrupted the phase separation. An order parameter *S* of 0.07 at 380 nm is calculated by

$$S = (A_{\perp} - A_{\parallel})/(A_{\perp} + 2A_{\parallel})$$

where A_{\perp} and A_{\parallel} are the absorbances perpendicular and parallel to the polarization, respectively.

In the case of *m*-oxyAzo, random cylinders with a diameter of about 20 nm were observed on the surface of the films after annealing (Figure 4B). In fact, the reduced absorbance of the $\pi - \pi^*$ band peaking at 357 nm indicates that the long axis of azobenzene adopts a homeotropic alignment. In the next test, we irradiated the annealed samples with a pumping beam to induce a change in the structure of the nanophase separation. Azobenzene aligns perpendicular to incoming polarized light (the Weigert effect),⁹ which means that polarized light induces some kind of order in the molecules. Therefore, in azobenzene LCBCPs, one can induce a change in morphology of nanophase-separated

surfaces accompanied by the Weigert effect because photoisomerization causes a supramolecular cooperative motion. After LPL irradiation, the azobenzene moiety showed in-plane anisotropy (S = 0.09), and its direction was perpendicular to that of the polarization of the pumping light. Despite the change in molecular order by the Weigert effect, the morphology of the annealed surface showed little change. On the other hand, UV irradiation erased the surface morphology because of the photochemical phase transition in azobenzene LCP¹⁵ that induces an order-disorder change by photoisomerization. That is, whereas a rod-like trans form stabilizes the LC phase, a bending cis form destroys the LC order. In a previous study,¹⁶ trans-cis photoisomerization changed the shape of microphase separation in an azobenzene BCP but did not destroy the phase-separated structure. This is probably because polymer segments in the BCP are separated covalently. That is, hydrophobic segments composed of azobenzene are poorly miscible with hydrophilic segments after photoisomerization. On the other hand, in this system, hydrophobic domains composed of azotolanes were miscible with the hydrophilic domains after photoisomerization, possibly because each mesogenic core is attached directly to hydrophilic moieties.



Figure 4. Optical orientational control of the block mesogenic core and surface morphologies of the *p*-oxyAz (A), *m*-oxyAz (B), and 3-oxyAz (C) (thickness ~100 nm) evaluated by phase-mode AFM, UV–vis, and polarized UV–vis absorption spectroscopy, respectively. A_{\parallel} and A_{\perp} indicate absorptions parallel and perpendicular, respectively, to the transition moment of the azotolane unit. (a) Irradiation with LPL (>436 nm, 200 mW/cm²) followed by annealing at 125 °C in *p*-oxyAz and at 75 °C in *m*-oxyAz for 6 h. (b) Initial state. Annealing induces the orientation perpendicular to the substrate plane for azobenzene moieties. (c) After irradiation of polymer films with nonpolarized light (366 nm, 20 mW/cm²) at room temperature.

In 3-oxyAz, which exhibits no LC phase (amorphous polymer), the film annealed at 70 °C for 5 h showed no phaseseparated structure (Figure 4C). This indicates that phase separation of the block mesogen occurs in an LC phase in the polymer system. Moreover, a phase-separated structure was not observed even though a change in azobenzene alignment was induced upon UV and LPL irradiation. In a previous study,¹⁰ we proposed a mechanism of phase separation, according to which an LCP consisting of a mesogenic core and attached hydrophilic chains (mutually incompatible in the LC phase) forms a phaseseparated structure, and the morphology is fixed below T_{g} . The results for 3-oxyAz in Figure 4C also support the view that an LC phase is necessary to induce a phase separation.

CONCLUSION

In summary, the work presented here shows the relationships between the chemical structures of an LCP system and its nanophase separations. By varying the position and volume of the hydrophilic moieties, different thermal properties were observed. Phase-separated structures generated by annealing are dependent on the chemical structures and can be fixed below $T_{\rm g}$. Despite containing a similar block mesogen, an amorphous polymer shows no phase-separated structures, suggesting that the cooperative effect of the amphiphilic mesogen in the LC phase is necessary for nanophase separation. Moreover, the molecular alignment strongly affects the photoresponsive behavior of the surface morphorogy. The polyphilic effect in LCs plays a role in several types of complex structure.¹⁷ By analogy with the previous studies of amphiphilic LCs, we believe the molecular architecture could represent more complex photoresponsive structures through an increased number of molecular segments of a block mesogen.

ASSOCIATED CONTENT

Supporting Information. NMR spectra of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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