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Synthesis and characteristics of novel azo-based diblock copolymers and their self-assembly behavior via solvents and thermal annealing

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Abstract: A series of azo-based diblock copolymers (DBC)s with various compositions were successfully synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization in anisole with PCAEMA-CTA (macro-CTA), DOPAM (new acrylamide monomer) and AIBN (initiator). Kinetic studies on diblock copolymerization manifested a controlled/living manner with good molecular weight control. Structures and properties of monomers and DBCs were determined by ^1H nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC) and gel permeation chromatography (GPC). Liquid crystalline (LC) phases and morphological properties were investigated using optical polarizing microscope (OPM), atomic force microscopy (AFM), scanning electron microscopy (SEM) and small-angle X-ray scattering (SAXS). Experimental results demonstrated that the prepared PCAEMA-CTA and DBCs possessed low polydispersity index (≤ 1.37). All DBCs revealed sharp endothermic transition peaks corresponding to the smectic-to-nematic phase. DBCs with high azo contents showed batonnet textures of the smectic phase whereas DBCs of low azo segments displayed threaded textures of the nematic phase. DBC with 49 wt% of azo side-chains generated a lamellar compared to DBCs with low azo block (≤ 41 wt%) or non-azo block (≤ 38 wt%) which produced hexagonal-type nanostructures. In addition, all DBCs exhibited reversible trans-cis photoisomerization behavior under UV irradiation and dark storage at different intervals of time.

Keywords: azobenzene moiety; azo diblock copolymers; phase transitions; photoresponsive property; self-assembly.

1 Introduction

In recent years, considerable attention has been paid to azobenzene-containing polymer materials including homopolymers and block copolymers due to the valuable combination of liquid crystals' anisotropy within attractive bulk properties of polymers (1, 2). Polymers containing azo-chromophores exhibit anisotropic absorption behaviors with the primary absorption dipole along the molecular long axis and the secondary absorption dipole along the molecular short axis, as a result of alignment of azo dyes which is the same as the nematic liquid crystal host by cooperation motion (3). In addition, block copolymers (BCs) having the interplay between the microphase separation and the elastic deformation of liquid crystal ordering which is defined as supramolecular cooperative motion (SMCM), exhibit more hierarchical structures with photoresponsive features. Generally, such an SMCM is regarded as one of the most effective approaches to control supramolecularly self-assembled nanostructures in liquid crystalline (LC) BCs (4, 5).

The BCs tend to microsegregate into ordered micro- or nanometer-sized domains because of two or more chemically different polymer segments (6). Especially, the BC with a LC block gives rise to microphase separated morphologies and fast self-assembly into diverse nanostructures such as spheres, cylinders and lamellae by the solvent vapor annealing (SVA) process or thermal treatment of an LC block. Likewise, the azobenzene-based BC has an advantage of changing its thin film's morphology by the trans-cis photoisomerization of azo chromophores in the BC under alternating irradiation of UV and visible light (7, 8). This photoinduced transformation from one isomer to another by UV-visible light can also cause large changes in the size, the polarity and the shape of the polymers (9, 10). Thus, it has long been noted that azobenzene-containing polymers are very widely used for applications such as optical data storage media (ODSM) for digital data (11), liquid crystal displays (LCD), photo-switching, sensors (12), nanotechnology (13), holographic surface relief gratings and photonic memories through the photoinduced trans-cis isomerization of the light-sensitive azobenzene chromophore (14).

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As few scientific research papers are available on the synthesis of crystalline (hard)-crystalline (hard) diblock copolymers (DBC), this article reveals the synthesis and the characterization of a series of novel LC hard-hard DBCs from the new polyacrylamide with a long alkyl chain, poly(*p*-dodecylphenyl-*N*-acrylamide) (PDOPAM) and the side-chain liquid crystalline polymer (SCLCP) containing azobenzene mesogenic side groups, poly(2-[2-(4-cyanoazobenzene-4'-oxy)ethylene-oxy]ethyl methacrylate) (PCAEMA). The article also describes the thermal behavior and morphology of the prepared DBCs having different compositions.

Moreover, these AB-type DBCs are of particular scientific interest because they can generate microphase separation and form well-ordered microdomain nanostructures including sphere, cylinder, lamellar, and cubic structures. The perfect formation of well-ordered nanostructures through self-assembly is based on the selection of the proper structure of polymer, solvent and thermal annealing treatment (15).

The last decade has seen an increase in the current state-of-the-art reviews for LC polymers such as the capability of self-assembly for nanofabrication, photoalignment in LC polymers (16, 17), photoinduced chirality (18) and photoinduced orientation of meso-azobenzene groups in polymer films (19, 20). This photoinduced orientation allows systems possessing azo-chromophore to be employed as photoswitches that could rapidly and reversibly control the material properties. Besides, the photoinduced orientation of azo groups in LC DBC is much more stable than other materials (21, 22). Therefore, the azobenzene-containing DBC is believed to be a material that exhibits optical storage properties (23).

Herein, we will expand our involvement in this emerging area of research especially the molecular design of azobenzene-based DBCs with well-defined phase transitions and their morphologies with various compositions. Lastly, we highlight our findings for the basic understanding of the polymer chemistry of these phenomena.

2 Materials, measurements and methods

2.1 Materials

4-Aminobenzonitrile (98%, Sigma-Aldrich, Seoul-Korea) was recrystallized from a mixture of water and ethanol (9/1, v/v) (24). Sodium nitrite (97+%, Sigma-Aldrich, Seoul-Korea), potassium carbonate (97+%, Sigma-Aldrich,

Seoul-Korea), diglyme (99%, Sigma-Aldrich, Seoul-Korea), phenol (99+%, Sigma-Aldrich, Seoul-Korea), 2-cyanoprop-2-yl dithiobenzoate (CPDB, 97%, Sigma-Aldrich, Seoul-Korea), *p*-dodecylaniline (97%, Sigma-Aldrich, Seoul-Korea) and 2-(2-chloroethoxy) ethanol (99%, Sigma-Aldrich, Seoul-Korea) were used as received. Tetrahydrofuran (THF, 98%, Samchun Chemical, Seoul-Korea) was dried over CaH₂ and distilled under a nitrogen atmosphere before use. Methacryloyl chloride (97+%, Sigma-Aldrich, Seoul-Korea) was purified by vacuum distillation to remove an inhibitor. Azoisobutyronitrile (AIBN, Merck Chemicals, Seoul-Korea) was used after recrystallization from methanol, and anisole was used as received (99%, Sigma-Aldrich, Seoul-Korea).

2.2 Measurements

The following instruments were used: a 400 MHz nuclear magnetic resonance (NMR) spectrometer (Bruker, Seoul-Korea) using tetramethylsilane (TMS) as a reference solvent. A gel permeation chromatograph (GPC) instrument (Waters, Seoul-Korea) equipped with four waters columns (Styragel HR 0.5, 2, 4 & 5) and a Waters 2414 refractive index detector using THF as an eluent (flow rate of 1 ml/min). A differential scanning calorimeter (DSC-Q 100, TA Instruments, Seoul-Korea). Atomic force microscopy (AFM, Park Systems, Seoul-Korea) using an XE-100 system (advanced scanning probe microscopy) operating in non-contact mode with a 910-NCHR cantilever (force constant; 42 N/m, resonance frequency; 330 KHz). A Hitachi-4800 scanning electron microscopy (SEM, Hitachi, Seoul-Korea) with a field emission at 1 kV. An optical polarizing microscope (OPM-DMRXP-MPS 60, Leica, Seoul-Korea) equipped with a hot stage. Small-angle X-ray scattering (SAXS, conducted on 4C2 beamline, Pohang-Korea) and grazing incidence small angle X-ray scattering (GISAXS, conducted on 3C1 beamline, Pohang-Korea) equipped with an monochromatized X-ray ($\lambda = 1.1747 \text{ \AA}$) with grazing incident angles ranging from 0.10 to 0.23° and the SCX (4300-165/2 CCD detector, Princeton Instruments). A Cary 50 Bio UV-Visible spectrophotometer (Varian, Seoul-Korea).

2.3 Synthesis of new monomer, *p*-dodecylphenyl-*N*-acrylamide (DOPAM)

A (12 g, 0.046 mol) amount of *p*-dodecyl-aniline was dissolved in methylene chloride (MC) solvent (100 ml). The solution was poured into a 250 ml 2-neck round flask, and triethylamine (20% excess) was added dropwise through a dropping funnel for 10 min (25). A solution containing

acryloyl chloride (3.8 ml, 0.047 mol) in MC (30 ml) was gradually added dropwise to the mixed solution for 20 min under a nitrogen atmosphere. Meanwhile, the solution was cooled in an ice bath to prevent the temperature of the reaction mixture from rising above 5°C. After 6 h of reaction time under 0°C, the solution was kept at room temperature for a further 10 h of reaction. Upon completion of the reaction, the solution was passed through a filter paper to eliminate the precipitated salt, and then the solvent was evaporated from the filtrate on an evaporator. The obtained solid was dissolved in MC (100 ml) and added to a separatory funnel with 10% aqueous NaHNO₃ solution (50 ml). The funnel was shaken vigorously and set aside to allow complete separation of the aqueous phase and thereby to remove the unreacted acryloyl chloride. Magnesium sulfate (1.0 g) was added to the separated MC solution. After being stirred for 5 h, the solution was subjected to filtration to remove the trace amount of water dissolved in the solvent. The MC solution thus obtained was kept on the evaporator, and n-hexane (100 ml) was added. The solution was stirred for 2 h and the unreacted p-dodecyl aniline was filtered from the solution. The resulted product was recrystallized from methanol to yield a white solid DOPAM monomer (Scheme 1). Yield: 89%, m.p: 101°C differential scanning calorimetry (DSC), ¹H nuclear magnetic resonance (NMR) (CDCl₃, 400 MHz, ppm): 7.5 (d, 2H), 7.2 (s, 1H), 7.15 (d, 2H), 6.4 (d, 1H), 6.2 (q, 1H), 5.8 (d, 1H), 2.6 (t, 2H), 1.25–1.35 (m, 20H), and 0.93 (t, 3H) (see supporting information, Figures 4 and 8B).

2.4 Synthesis of the macromolecular chain-transfer agent (PCAEMA-CTA)

The successful synthesis of poly(2-[2-(4-cyano-azobenzene-4'-oxy)ethylene-oxy]ethyl methacrylate) (PCAEMA-CTA) was carried out in anisole using AIBN as initiator and CPDB as starting chain transfer agent (Scheme 2). For the reaction,

CAEMA (6.0 g, 0.0158 mol), AIBN (8.6 mg, 0.0526 mmol), CPDB (35 mg, 0.1579 mmol) and 18 ml of anisole were added into a 25 ml Schlenk flask. After 15 min nitrogen purge under stirring, the flask was sealed and placed into a preheated oil bath at 75°C for 24 h. The reaction solution was quenched from liquid nitrogen, diluted by 12 ml of THF and dropped into 500 ml of methanol to precipitate the PCAEMA-CTA. The precipitation was repeated three times. The obtained PCAEMA-CTA (orange powder) was dried in a vacuum oven at room temperature 24 h. The conversion of CAEMA monomer into PCAEMA was 40%. Mn = 13,800 g/mol, Mw/Mn = 1.14 (GPC), ¹H NMR (CDCl₃, 400 MHz): 0.8–1.15 (d, 3H, main chain CH₃), 3.8–4.25 (t, 8H, OCH₂CH₂O), 1.7–2.0 (CH₃-CCN-CH₃ and main chain CH₂), 6.90 (s, 2H, o-Ar H to OCH₂), 7.41–7.74 (t, 9H, o,m-Ar H to CN, m-Ar H to OCH₂ and p,o-Ar to SCS), 7.84 (s, 2H, m-Ar H to SCS).

2.5 Preparation of the azo-based diblock copolymer (PCAEMA-b-PDOPAM)

A typical reversible addition-fragmentation chain transfer (RAFT) polymerization was employed to fabricate DBCs using the PCAEMA-CTA (Scheme 2). (DOPAM) (280 mg, 0.898 mmol), AIBN (1.85 mg, 0.0112 mmol) and PCAEMA-CTA (Mn = 13,800 g/mol, 310 mg, 0.0224 mmol) were added into a 10 ml Schlenk flask. Then anhydrous anisole (2.8 ml) was added to the mixture. After a 30 min nitrogen purge, the flask was flame-sealed and placed in an oil bath. The reaction was held at 70°C for 72 h. After a while, the reaction solution was diluted with THF (3 ml) and precipitated into (250 ml) methanol. The precipitation procedure was repeated twice and the light orange DBC was dried in a vacuum oven for 24 h at (40°C). The conversion of the DOPAM into block was 48% after 72 h of polymerization time. Mn = 19,800 g/mol and Mw/Mn = 1.19 (GPC). Other DBCs of various compositions were prepared using similar procedures (26, 27).

Scheme 1: Synthesis of a new long alkyl chain acrylamide monomer (DOPAM).

Scheme 2: Synthetic route to the macromolecular chain transfer agent (PCAEMA-CTA) and diblock copolymers.

2.6 Thin films preparation

Thin films of the prepared DBCs were prepared by spin coating the 1.0 wt% polymer solution in THF onto silicon wafer at 3000 rpm for 1 min (28). Then the thin films were either thermally annealed in the vicinity of 110°C or solvent vapor annealed under the mixed solvent vapor of THF/cyclohexane (70/30, v/v) in a covered Petri dish for 24 h (29). The surface morphology of the annealed thin films was investigated by AFM and SEM.

3 Results and discussion

3.1 Synthesis and characterization

RAFT polymerization has proved to be a powerful technique to synthesize the macromolecular chain transfer agent (PCAEMA-CTA) from the LC monomer with azobenzene moiety (CAEMA) and prepare diblock copolymers with two hard blocks built up from the azo block and the long alkyl chain polyacrylamide block (PDOPAM). The PCAEMA-CTA with a well-controlled number-average molecular weight ($M_n = 13,800$ g/mol) and a narrow polydispersity index (PDI, $M_w/M_n = 1.14$), was first prepared by carefully adjusting the feed molar ratio of 2-(4-cyanoazobenzene-4'-oxy)ethylene-oxy]ethyl methacrylate (CAEMA) monomer, 2-cyanoprop-2-yl-1-dithionaphthalate (CPDN) RAFT agent and azoisobutyronitrile (AIBN) initiator in anisole solution at 75°C for 24 h ($[\text{CAEMA}]_0 : [\text{CPDN}]_0 : [\text{AIBN}]_0 = 300:3:1$).

In order to investigate the influence of molecular weight on phase-transition temperatures, a series of

azobenzene-containing side-chain liquid crystalline DBCs of different compositions were synthesized by changing the molar ratio of monomer/maco-CTA ($[\text{DOPAM}]_0 / [\text{PCAEMA-CTA}]_0$) in the presence of fixed AIBN concentration in anisole solution at 70°C for 3 days (Table 1). The number-average molecular weight and the polydispersity index of the resulting DBCs increased with increasing DOPAM monomer concentration. This indicates that the diblock polymerization via RAFT is a controlled/living process.

Figure 1A and B displays the ^1H NMR spectrum for the macromolecular chain transfer agent PCAEMA-CTA and the DBC-2 as an example. The chemical constitution of the designed DBCs was estimated from the ratio of the indicated characteristic peaks in their ^1H NMR spectrum. The M_n values and the contents of azobenzene in the DBCs are summarized in Table 1.

Figure 2 shows typical GPC curves of the PCAEMA-CTA and the resulting DBCs. The GPC curves signify successful initiation and growth of the second block PDOPAM. All the GPC traces for the designed DBCs shifted linearly to high molecular weights with increasing the second monomer DOPAM feed ratio from 20 to 140 mol (molar ratios) versus PCAEMA-CTA, indicating a well-controlled/living manner of RAFT polymerization. All obtained DBCs have a narrow molecular weight distribution and a unimodal peak, proving that the PCAEMA-CTA performed as a chain extender to form the second block with no significant amounts of free polymer as a side reaction. Additionally, the conversion of acrylamide monomer DOPAM for RAFT polymerization reached the highest value of 71% at high monomer concentration (supporting information, Figure 7). Obviously, the molecular weights $M_n(\text{GPC})$ s of the obtained DBCs were very close to the theoretical values

Table 1: Experimental conditions and characteristics of the synthesized polymers.

Polymer (Azo. %)	[DOPAM] ₀ /[PCAEMA-CTA] ₀ /[AIBN] ₀ ^c	Reaction time (h)	Solvent (anisole) w. % ^d	Conversion (%) ^e	Mn (GPC) ^f	Mn (¹ H NMR) ^g	Mn (calcd) ^h	Mw/Mn (GPC) ⁱ	Azo. % ^j
Macro-CTA ^a	100: 1: 1/3	24	25	40	13,800	—	14,100	1.14	100
DBC 1 (81) ^b	20: 1: 1/2	72	10	42	16,900	18,100	16,800	1.15	81
DBC 2 (69)	40: 1: 1/2	72	10	48	19,800	20,100	19,900	1.19	69
DBC 3 (62)	50: 1: 1/2	72	10	50	21,900	21,900	21,600	1.21	62
DBC 4	80: 1: 1/2	72	10	54	27,200	26,700	27,700	1.23	49
DBC 5 (41)	100: 1: 1/2	72	10	63	33,700	32,900	33,600	1.33	41
DBC 6 (28)	140: 1: 1/2	72	10	71	48,600	45,000	48,500	1.37	28

^amacro-CTA, macromolecular chain transfer agent (PCAEMA-CTA); ^bDBC, diblock copolymer; ^cFeed molar ratio: [DOPAM]₀, monomer; [AIBN]₀, azoisobutyronitrile; [PCAEMA-CTA]₀, macro-chain transfer agent; ^dPCAEMA-CTA concentration vs. solvent. ^{e,f}and ⁱDetermined by GPC on the basis of polystyrene standards. ^gDetermined by ¹H NMR. ^hCalculated from the equation (Eq. 1). ^jDetermined by GPC. AIBN was used as initiator. Block copolymerization temperature = 70°C.

[Mn(th)s]. The theoretical molecular weight [Mn(th)] was calculated according to the following equation.

$$M_{n(th), DBC} = M_{n(th), PCAEMA-CTA} + \frac{[DOPAM]_0}{[PCAEMA-CTA]_0} \times M_{w, DOPAM} \times \text{Conversion} \quad [1]$$

$M_{n(th)}$ is the theoretical molecular weight of the macromolecular chain transfer agent PCAEMA-CTA, whereas M_w is the molecular weight of the DOPAM monomer. [DOPAM]₀ and [PCAEMA-CTA]₀ were the initial concentrations of DOPAM and PCAEMA-CTA, respectively. The PDI values of the prepared DBCs were relatively narrow as 1.15–1.37 in all cases (Table 1).

3.2 Phase transition behaviors and LC textures

The phase-transitions and LC textures of the prepared polymers were determined by means of DSC and OPM. In Figure 3, typical second heating DSC scans of the homopolymer (PCAEMA-CTA) and its corresponding azo diblock copolymers are well highlighted. As marked in Figure 3A, PCAEMA-CTA exhibited a glass transition temperature (T_g) in the vicinity of 43°C and two endothermic and exothermic peaks during both heating and cooling. The sharp and strong peak at 99°C (3.1 J/g) was assigned to smectic-to-nematic phase transition (T_{S-N}), while the weak transition at 176°C is attributed to nematic-to-isotropic transition (T_{N-I}). On the other hand, all DBCs displayed a single glass transition temperature (T_g) around 73°C and different LC phase transitions as compared to the homopolymer PCAEMA-CTA. The first three DBCs (Figure 3B–D) exhibited relatively strong and sharp endothermic transition peaks (T_{S-N}) at 114°C, 116°C and 117°C,

respectively. In contrast, the DBCs (Figure 3E–G) with low composition of LC block displayed weak endothermic peaks (T_{S-N}) at 120°C, 121°C and 123°C, especially the DBC with the lowest LC content of 28 wt% (Figure 3G) that had a very weak feature. Indeed, all the designed DBCs showed a broad melting temperature (T_m) between 223°C and 240°C. As revealed in the DSC spectrum, the endothermic transitions for the diblock systems moved slightly upwards and decreased its strength as the content of the LC block decreases from 81 wt% to 28 wt% (Table 2). From recorded data in Table 2 with supporting information in Figure 9, the phase transition enthalpies of LC decreased and the melting point (T_m) enthalpies increased with an increase of the second block content (PDOPAM). This result was in good agreement with our expectation.

To investigate the optical textures of the LC phases for the obtained polymers, the photomicrographs under crossed polarizers for the LC monomer CAEMA, homopolymer PCAEMA-CTA and DBCs were taken at different temperatures during the first heating and cooling cycle using OPM, as shown in Figure 4. As observed, the CAEMA exhibited nematic texture with fine thread-like fibrils at 116°C upon cooling the monomer from the isotropic phase without any thermal annealing (Figure 4A). Further cooling to 45°C and annealing for 2 h, the threaded texture is transformed into the smectic phase with a typical fan-shaped focal conic texture (Figure 4B). This proved that the rate of the developing LC phase is very slow. In the case of PCAEMA-CTA, nematic texture with the appearance of thread-like fibrils was the first LC phase that appeared at 112°C by cooling the sample from the isotropic phase after 1 h of thermal annealing at 140°C (Figure 4C). In addition, a significant increase in the number of fibrils was observed upon cooling to 45°C (OPM image not shown). Subsequently, annealing the PCAEMA-CTA at 45°C for 1 h transformed the fibrils into the smectic structure with a typical rod-like texture (Figure 4D).

Figure 1: ^1H NMR spectrum of (A) the macromolecular chain transfer agent (PCAEMA-CTA) and (B) the diblock copolymer (DBC-2) in CDCl_3 solvent.

On the contrary, the DBCs were annealed for several hours to develop their LC textures. The annealing times for the DBC-5 and DBC-6 with low LC content block (41 wt% and 28 wt%) were longer than annealing times for those with high LC content. The DBCs with 81 wt%, 69 wt%, 62 wt% and 49 wt% of LC blocks exhibited the batonnet textures of the smectic phase by annealing the samples for 3 h at 240°C and slow cooling to the lower temperature ranging from 112°C to 47°C . This indicates that the temperature range for

the formation of LC phase is very wide. The optical texture of DBC-2 (Figure 4E) shows an example. Subsequently, annealing the diblock copolymers DBC-1, -2, -3 and -4 at 47°C for 1 h changed the batonnet textures, smectic phase to another more ordered smectic phase, suggesting smectic-C phase (Figure 4F). This remarkable result indicates that the transformation of isotropic phase into smectic phase takes place in a unique fashion. In contrast, the DBCs with the low concentrations of the LC segments, DBC-5 and DBC-6

Figure 2: GPC traces for the macromolecular chain transfer agent (PCAEMA-CTA) and diblock copolymers Poly (CAEMA-b-DOPAM) (see Table 1).

Figure 3: DSC thermograms of the second heating scan for the macromolecular chain transfer agent (PCAEMA-CTA) and diblock copolymers with different contents of the azo block: (A) PCAEMA-CTA, (B) DBC-1-81%, (C) DBC-2-69%, (D) DBC-3-62%, (E) DBC-4-49%, (F) DBC-5-41% and (G) DBC-6-28%.

displayed threaded texture typical of nematic phase after 6 h annealing at 240°C to develop their texture and then slow cooling to 121°C (Figure 4G). On further cooling to lower temperatures, the texture becomes a highly threaded texture (Figure 4H). These results imply that the LC texture of the DBC-5 and DBC-6 is hard to develop. This shows consistency with DSC measurements (Figure 3F and G).

Table 2: Thermal properties^a of the prepared azo diblock copolymers.

Sample	Phase transition temp (T, °C), 2nd heating			Enthalpy change (ΔH, J/g)	
	T _g	T _{lc}	T _m	ΔH _{lc}	ΔH _{Tm}
(Azo.%/PDOPAM.%)					
DBC-1 (81/19)	72	114	223	2.6	0.9
DBC-2 (69/31)	72	116	225	1.46	1.4
DBC-3 (62/38)	72	117	228	1.35	6.3
DBC-4 (49/51)	73	120	232	0.42	9.6
DBC-5 (41/59)	73	121	238	0.23	11.3
DBC-6 (28/72)	74	123	240	0.13	11.9

^aTransition temperatures and enthalpies on the second heating scan were determined by DSC at 10°C/min. T_g = glass transition temperature; T_{lc} = liquid crystal temperature; T_m = melting temperature; ΔH_{lc} and ΔH_{Tm} are phase change enthalpy of liquid crystals and enthalpy change of melting, respectively.

3.3 Morphology of thin films

Commonly, the chemical incompatibility between the two blocks in the DBC system can form microphase segregated nanostructures (spheres, cylinders, gyroids and lamellae) depending on the relative volume fractions of different segments and the extent of their incompatibility. Besides, LC molecules in the DBC system can be used as ordering actuators to control the alignment of

Figure 4: Liquid-crystalline textures of the monomer CAEMA and the synthesized polymers: (A) CAEMA-116°C, (B) CAEMA-annealed-45°C-2 h, (C) PCAEMA-CTA-112°C, (D) PCAEMA-CTA-annealed-45°C-1 h, (E) DBC-2-108°C, (F) DBC-2-annealed-47°C-1 h, (G) DBC-6-121°C and (H) DBC-6-annealed-61°C-4 h. (A and B: magnification $\times 400$); (C, D, E and F: magnification $\times 200$); (G and H: magnification $\times 100$).

Figure 5: Tapping-mode AFM images (scan size = $2 \times 2 \mu\text{m}$ and scale bar = 400 nm) of diblock copolymer thin films with different LC block contents: (A) DBC-2-THF-SC (3000 rpm)-110°C, (B) DBC-4-THF-SC (3000 rpm)-110°C, (C) DBC-6-THF-SC (3000 rpm)-110°C, (D) DBC-2-THF-SC (3000 rpm)-solvent-annealing (THF-70%/cyclohexane-30%), (E) DBC-4-THF-SC (3000 rpm)-solvent-annealing (THF-70%/cyclohexane-30%), (F) DBC-6-THF-SC (3000 rpm)-solvent-annealing (THF-70%/cyclohexane-30%).

microphase separated nanostructures by supramolecular cooperative motion.

Morphological investigation of the DBCs containing mesogenic side chain segments is of particular interest. The morphology of thin films of the prepared DBCs with different ratios of azo dye contents are studied with the aid of tapping-mode AFM and SEM. Thin films were prepared by the spin coating method with thermal annealing or the SVA process. The spin coated films were annealed in the vicinity of the T_{S-N} temperature at 110°C or annealed under the mixed solvent vapor of THF/cyclohexane for 24 h. The obtained morphologies of poly(CAEMA-*b*-DOPAM) block copolymer thin films with thickness ranging from 2.7 nm to 3.2 nm were easily distinguished from each other.

In the case of thermal annealing treatment, the DBCs (DBC-1, -2 and -3) with high concentration of LC block in the range between 81 wt% and 62 wt%, exhibited morphology that is consistent with hexagonal-type nanostructures (Figure 5A). In contrast, the AFM image of the DBC-4 (Figure 5B) revealed microphase separated lamellar morphology, as was expected from the volume fraction of LC block content of 49 wt%. The lamellar domain spacing (d spacing) determined by AFM was 36 nm. The DBC-5 and DBC-6 also displayed hexagonal morphology which is consistent with the composition ratios of LC block of 41 wt% and 28 wt%. The hexagonal d spacing and pore size obtained from AFM were 53 nm and 34 nm, respectively (Figure 5C). Generally, the self-assembly of these DBCs can be explained by interplay processes between regular periodicity of LC ordering and thermally controlled microphase separation caused transfer of ordering of mesogens to nanostructures inside them, which leads to periodically ordered nanostructures (30, 31). Such a supramolecular cooperative motion in azo-based DBC thin films is responsible for the formation of microphase separated nanostructures.

On the other side, the nanostructures can be more clearly observed in the solvent vapor annealed films, mainly because of the effect of the mixed solvent vapor of THF/cyclohexane on the degree of swelling of the two different polymer blocks. After annealing the thin films under the mixed solvent vapor of THF/cyclohexane (70/30, v/v) in a covered Petri dish for 24 h, similar transitions with thermal annealing have been recorded for all DBCs (Figure 5D–F). The SEM micrographs, Figure 6A and B, also show huge similarity in the observation of block copolymer thin film morphologies and revealed nearly equivalent microphase separated domain size to that determined by AFM. These results indicate that the designed DBCs can self-assemble into a variety of nanostructures, depending on the volume fractions of both LC block and non-LC block in the diblock systems. Thus, these polymers can promise to find their diverse applications in advance technologies.

3.4 Morphology identification via SAXS and GISAXS

SAXS and GISAXS [monochromatized X-ray ($\lambda = 1.1747 \text{ \AA}$): 10–0.23°; the SCX: 4300-165/2 CCD detector] experiments were conducted on 4C2 and 3C1 beamlines at the Pohang Accelerator Laboratory (Korea) in order to study the microphase separation and the self-assembly of the prepared azo DBCs with different compositions. Figure 7 shows in-plane intensity profiles of SAXS and GISAXS patterns as a function of scattering vector for the PCAEMA-*b*-PDOPAM with three different molecular weights. The d spacing and microdomain structures for the DBCs were estimated from the scattering peaks in their SAXS and GISAXS diffraction patterns (Figure 7A–F). The scattering profiles of DBC-2 (Figure 7A–D) and DBC-6 (Figure 7C–F) suggested hexagonally ordered cylinder nanostructure that is consistent with the characteristic peak ratios of $q/q^* = \sqrt{3}$ and $\sqrt{7}$ (Figure 7A–F), where q denotes the length of scattering

Figure 6: Top-view SEM images of diblock copolymer thin films with different contents (or volume fractions) of azo block: (A) DBC-4-THF-SC (3000 rpm)-solvent-annealing (THF-70%/cyclohexane-30%) and (B) DBC-6-THF-SC (3000 rpm)-solvent-annealing (THF-70%/cyclohexane-30%).

Figure 7: A-B-C; SAXS and D-E-F; GISAXS diffraction patterns for three diblock copolymers (DBC-2, DBC-4 and DBC-6) with different compositions.

vector and q^* denotes the position of the first diffraction peak. In contrast, the scattering profiles of DBC-4 (Figure 7B–E) exhibited a scattering vector of ($\sqrt{1}=1$) and ($\sqrt{4}=2$) times relative to the first-order reflection, suggesting lamellar morphology.

3.5 Photoresponsive property

It is well known that azobenzene-containing polymers exhibit reversible trans-cis photoisomerization by irradiation of light with appropriate wavelength and when a

Figure 8: UV-Vis absorption spectra of DBC-2 in chloroform solution under UV light exposure at 365 nm (A) and in darkness (B). (A): (a) before irradiation; (b) 20 s irradiation; (c) 40 s irradiation; (d) 60 s irradiation; (e) 80 s irradiation; (f) 100 s irradiation. (B): (f) 5 min in darkness; (e) 10 min in darkness; (d) 15 min in darkness; (c) 20 min in darkness; (b) 25 min in darkness; (a) 30 min in darkness for stability.

chiral azobenzene molecule is doped in cholesteric liquid crystals. The photoresponsive property of the resulting azo-based DBC-2 was investigated by UV-Vis absorption spectra in chloroform solution (Figure 8). As can be seen in Figure 8A, the intensity of the absorption band corresponding to the π - π^* transition ($\lambda_{\max} = 362$ nm) slightly decreased with its small rise in the n - π^* transition absorption ($\lambda_{\max} = 451$ nm) after 20 s, 40 s, 60 s, 80 s, and 100 s UV light exposure time. On the other hand, Figure 8B shows the stability of the DBC-2 in darkness after 365 nm UV light exposure. As recorded, the absorption band π - π^* is increased significantly in intensity with its small decrease in the absorption band n - π^* . Thereby this UV-induced trans-cis isomerization caused variations on the

configurational structure, the polarity, and the surface tension of the DBC.

4 Conclusion

A well-controlled macromolecular chain transfer agent and a novel series of well-defined azo DBCs were prepared from a monomer with LC p-cyanoazobenzene moiety as both a mesogen and a photoresponsive chromophore, via RAFT polymerization. The newly designed LC DBCs were successfully synthesized from 2-[2-(4-cyano-azobenzene-4'-oxy)ethylene-oxy]ethyl methacrylate (CAEMA) and p-dodecylphenyl-N-acrylamide (DOPAM) by RAFT polymerization using CPDB as the starting chain transfer agent and AIBN as the initiator. The molecular weights of the LC DBCs increased linearly with conversion, indicating a controlled/living manner of RAFT polymerization. All the DBCs displayed narrow PDI, $M_w/M_n \leq 1.37$, and showed different features due to their varied LC contents. The DBCs with high LC contents displayed strong and sharp endothermic peaks as compared to those of lower LC contents. Thermal investigation revealed that both the PCAEMA-CTA homopolymer and the DBCs have a smectic structure. The DBCs self-assembled into different nanostructures (hexagonal cylinder and lamellar), depending on the azobenzene content and the volume fraction of PDOPAM in the DBC thin films. However, the morphologies of DBC thin films were also related to the solvent and thermal annealing treatment. This result appears to be superior to those of LC DBCs. Furthermore, the prepared LC DBCs exhibited reversible trans-cis photoisomerization behavior under UV light exposure at 365 nm and in darkness at different intervals of time.

5 Highlights

- RAFT polymerization produced DBCs with blocks of well-defined length and narrow molar mass distribution.
- Combination of a mesogenic unit with a long alkyl chain enhanced the microphase separation in DBCs.
- Self-assembly of azo DBC thin films generated via solvent vapor annealing or thermal annealing.
- LC textures are varied depending on composition of azo content in DBCs.

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