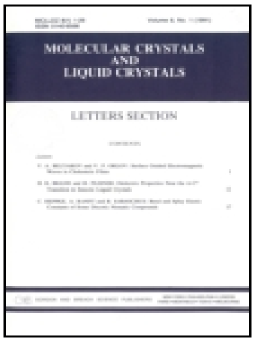

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Photo-switching Behavior of Microphase Separated Structure in Liquid Crystalline Azobenzene Block Copolymers Possessing Different Poly(alkyl methacrylate) Blocks

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We have recently reported the photo-switching process of hierarchical structures of microphase separated (MPS) cylindrical structures embedded in a liquid crystalline (LC) phase in a film of a diblock copolymer composed of amorphous poly(butyl methacrylate) (PBMA) and a light responsive LC azobenzene (Az) blocks. In the present work, homologous poly(alkyl methacrylate) of poly(hexyl methacrylate) (PHMA) and poly(octadecyl methacrylate) (PODMA) are introduced as the cylinder forming polymer block. The Az mesogens and MPS cylinders in these polymers were aligned in the in-plane direction, and the alignments were photo-switched by changing LPL irradiation direction. The PODMA containing block copolymer exhibited a different reorientation behavior from PHMA or PBMA contained block copolymer. It was suggested that the viscosity or fluidity of cylindrical polymer affect the photoswitching alignment behavior.

Keywords azobenezene; liquid crystalline diblock copolymer; photoalignment; photoswitching; real-time GI-SAXS measurement; microphase separation structure

I. Introduction

The alignment methods for microphase separated (MPS) structure [1–6] have been extensively studied toward applications of block copolymer films for nanopatterning and nanotemplating materials [7–13]. Several studies have demonstrated that the liquid crystalline block copolymer exhibited highly ordered MPS structures [12–17]. Our recent work has shown the photoalignment [16, 17] and orientational photo-switching [18] of the MPS structure in diblock copolymers composed of an amorphous polymer block and liquid crystalline (LC) polymer containing photoreactive azobenzene (Az) mesogene (PAz) using

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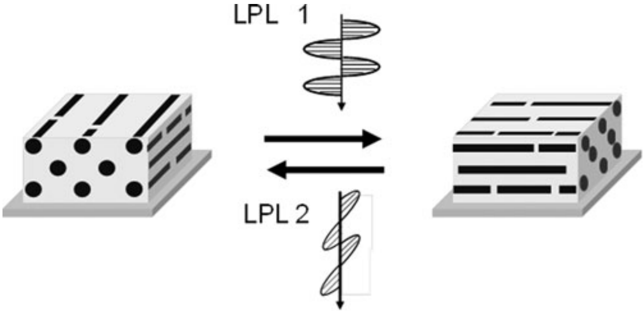

Figure 1. Schematic illustration of the photoswitching process of MPS cylinder structure of block copolymer films.

lineally polarized light (LPL). In the case of the amorphous polystyrene cylinder block polymer, the photoalignment was performed by LPL irradiation during a slow cooling process from a high temperature above the glass transmission temperature (T_g) of polystyrene (PS, $T_g =$ ca. 100°C) and the isotropization temperature of the Az LC block [17]. On the other hand, the LC Az block copolymer film with MPS cylinders consisting of lower T_g poly(butyl methacrylate) (PBMA, $T_g =$ ca. 20°C) provide continuous orientational photoswitching of MPS cylinder structure in the smectic LC phase at ca. 95°C without temperature alternations (Figure 1) [18]. Therefore, the thermal properties of the amorphous cylinder forming polymers greatly affect the photoalignment process. The controllable temperature and orientation modes can be influenced by T_g of the cylinder forming polymer block. Another important aspect in the PBMA case is that this amorphous block was segregated to the free surface, which led to the persistent in-plane orientation of the mesogenic group and MPS structure [19,20].

In the above contexts, we attempted to introduce homologous amorphous poly(alkyl methacrylate) blocks with different T_gs in the LC Az block copolymers to explore the role of the thermal properties. In this work, LC Az diblock copolymers with poly(hexyl methacrylate) (PHMA), poly(octadecyl methacrylate) (PODMA) and PBMA (Figure 2) are systematically synthesized and their dynamic aspects in the photo-switching behavior of the LC and MPS cylinder domain are investigated by time-resolved grazing incidence small angle X-ray scattering (GI-SAXS) measurements using a synchrotron X-ray beam.

2. Experimental Section

Synthesis of LC Az Diblock Copolymer

The block copolymers, PBMA-*b*-PAz, PHMA-*b*-PAz, and PODMA-*b*-PAz were synthesized by the atom transfer radical polymerization method [19]. Number-averaged molecular weight (M_n) and polydispersity index (PDI) were estimated by gel permeation chromatography (GPC) using tetrahydrofuran as eluent, using a UV detector (UV-41), a RI detector (RI-101) and pump operated at 0.3 mL/min (DS-4, Shodex). Molecular weights and PDI are quoted with respect to monodisperse polystyrene standards (Tosoh). ^{1}H NMR spectra were recorded with a GSX-270 (JEOL) spectrometer using tetramethylsilane as the standard signal.

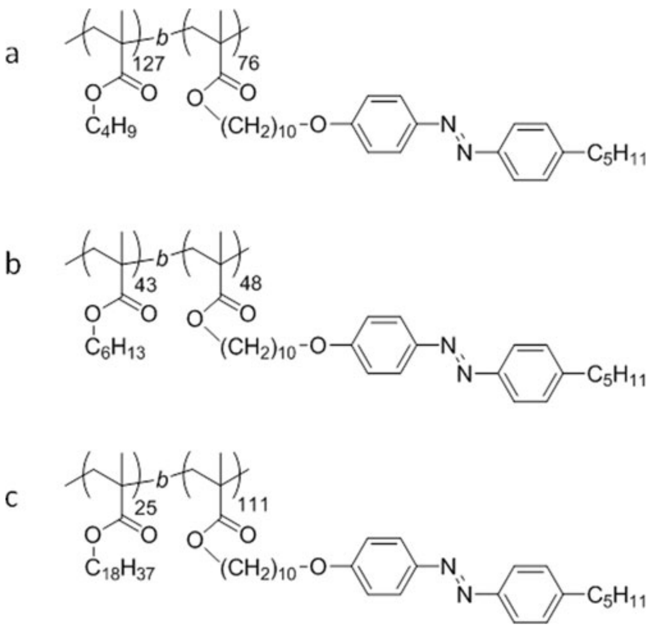

Figure 2. Chemical structures of PBMA-*b*-PAz (a), PHMA-*b*-PAz (b), and PODMA-*b*-PAz (c) used in this work.

Characterizations

Differential scanning calorimetic (DSC) measurements were carried out using a DSC Q200 MO-DSC-UV (TA Instruments Japan). The scanning rate was 2°C min^{-1}. SAXS measurements to evaluate the microphase-separated structures in the bulk state were performed with a NANO-Viewer X-ray diffractometer (Rigaku) equipped with an imaging plate (FUJIFILM) as the detector. CuKα radiation ($\lambda = 0.154$ nm) was used as the X-ray beam source. The diameters of the X-ray beams were $0.3 - 0.6$ mm which were collimated by pinhole slits. The camera length was 960 mm.

Photoalignment Procedures

Thin films of the synthesized diblock copolymers were prepared on quartz plates by spin-casting (2000 rpm) from a 2% by weight chloroform solution. The film was first annealed at 130°C (isotropic state of PAz) on a thermostated stage before photoalignment, and then the initial alignment was performed by irradiating with LPL at 95°C (SmA state of PAz). Film thickness was evaluated by surface profiles obtained by atomic force microscopy (Nanopics 2100, Seiko Instruments). The film was partly scratched by spatula and the height difference between the film surface and substrate surface was measured. The typical film thickness was ca. 200 nm. LPL irradiation at 436 nm was performed with a mercury lamp source (REX-250, Asahi Spectra) at 1 mW cm^{-2} with a 436 nm band-pass filter (Asahi Spectra).

Time Resolved GI-SAXS Measurements

Time resolved GI-SAXS measurements were performed on the BL(beamline)-6A system at the KEK Photon factory in Tsukuba, Japan. A monochromated X-ray radiation source at the

Table 1. Characterizations of the polymers

Polymer	Unit Alkyl methacrylate	Az	Φ_{LC}	$M_n/10^4$	PDI	d spacing/ nm	Phase transition temperature/°C
PBMA-*b*-PAz	127	76	0.68	4.8	1.18	29.2	20^a
PHMA-*b*-PAz	43	48	0.77	2.7	1.16	31.5	-5^a
PODMA-*b*-PAz	25	101	0.82	3.5	1.21	31.0	35^b

ϕ_{LC}: volume fraction of LC domain, a: glass transition temperature, b: melting temperature,

wavelength λ of 0.150 nm with the beam size of ca. 250 μm × 500 μm, and the detection was performed with an X-ray CCD detector (PILUTUS 300HK detectors, DECTRIS). The detailed procedures and analyses were described in the previous paper [18]. The peak intensities in the time resolved GI-SAXS measurements were monitored for the in-plane peaks at $q_y =$ ca. 0.2 nm^{-1} corresponding to the MPS cylinder arrays which were extracted from the 2D images.

3. Results & Discussions

Thermal Properties and MPS Structure of LC Az Diblock Copolymers

The diblock copolymers synthesized in this work, PBMA-*b*-PAz, PHMA-*b*-PAz and PODMA-*b*-PAz, were characterized by GPC and ^{1}H-NMR measurements. Their volume fractions of PAz matrix (ϕ_{LC}) estimated from molecular weight ranged from 0.68 to 0.82, which infer that these polymers exhibit the MPS cylinder domain [21]. Actually, formation of the MPS cylinders structure in the PAz matrix was confirmed in the bulk by small-angle X-ray scattering measurement (SAXS). Table 1 summarizes spacing values (d) of the MPS cylinders estimated from the first order peak of the SAXS data. The d values for the three polymers were almost the same ranging from 29.2 to 31.5 nm.

The thermophysical properties of the LC Az block copolymers with the homologous poly(alkyl methacrylate) blocks were evaluated by DSC. The thermal transitions due to the poly(alkyl methacrylate) blocks could not be detected by DSC for all the block copolymers. This should be attributed to small volume fractions of the cylindrical polymer domains. Therefore, we examined the thermal properties for these poly(alkyl methacrylates)s by using homopolymers. PHMA and PBMA of the amorphous polymers exhibited a T_g at −5 and 20°C, respectively. The PODMA homopolymer was crystalline at room temperature and melted at 35°C (T_c) [22]. On the other hand, the PAz matrix domains in all diblock copolymers clearly exhibited T_g around 56°C, despite the fact that each poly(alkyl methacrylate) has different T_g or T_c. The matrix PAz domain adopted a smectic C phase (from 55°C to 90°C) and smectic A phase (from 90°C to 115°C), and became isotropic above 115°C.

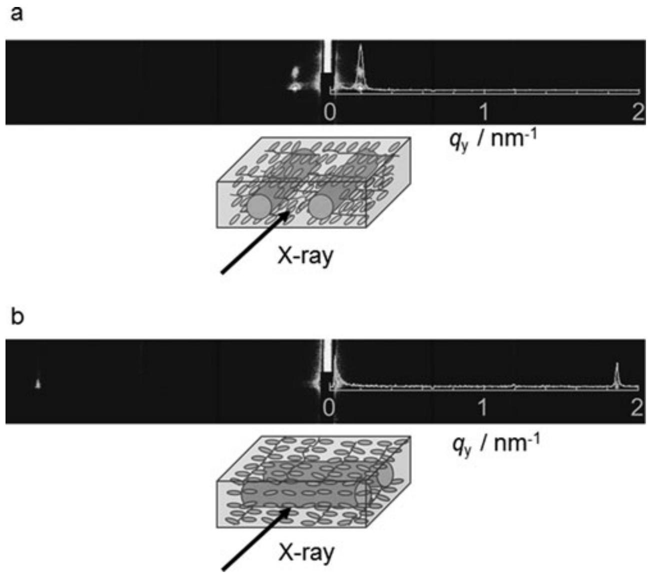

Figure 3. Two-dimentional GI-SAXS images of PHMA-*b*-PAz. The X-ray was introduced orthogonal (a) and parallel (b) to the irradiated LPL electric vector. The inserted line indicates one-dimentional intensity profiles in the in-plane direction. The peaks at $q_y = 0.20$ nm^{-1} in (a) and $q_y = 1.87$ nm^{-1} in (b) correspond to the scatterings from the MPS cylinder array LC smectic A layers, respectively.

Photoreorientation of LC Az Block Copolymer Thin Films

The spincast films of the diblock polymers were prepared and annealed above the isotropization temperature of PAz. Then, the films were irradiated with LPL at 436 nm in the smectic A phase at 95°C. After LPL irradiation, these films exhibited a large dichroic nature in the $\pi-\pi^*$absorption band of Az chromophore, indicating that the Az mesogens were photoaligned by LPL irradiation. Significantly larger light absorption was observed in the perpendicular direction of the electric field of the irradiating LPL. Optical order parameter S for each polymer films reached 0.70, 0.57, 0.52, for PBMA-*b*-PAz, PHMA-*b*-PAz, and PODMA-*b*-PAz, respectively, indicating that the mesogens in all these polymers were well aligned to the orthogonal directions of irradiated LPL electric vector (initial aligned state). Here, S are defined as $S = (A_\perp - A_\parallel)/(A_\perp + 2A_\parallel)$, where $A_\parallel$ and $A_\perp$ denote absorbances at the peak of the π–π^* transition band (around 336 nm) measured with polarized probing light set parallel and perpendicular to the irradiated LPL light, respectively. When we successively irradiated to the pre-aligned film with LPL in the orthogonal direction of the initially irradiated LPL at 95°C, the films then gave high order parameter S corresponding to the second irradiating LPL direction (realigned state). The realignment could be repeated at the smectic A temperature of PAz (95°C) without changing to the homeotropic state. This fact suggests that the poly(alkyl methacrylate) blocks were commonly segregated to the free surface [19,20] irrespective of the alkyl length, in contrast with the results for the diblock copolymer with a polystyrene block [17, 20].

To determine the orientation of both smectic phase of PAz and MPS cylindrical structures in the aligned and realigned films, we conducted GI-SAXS measurement for the three block copolymer films. Figure 3 displays two dimensional GI-SAXS images for the aligned film of the PHMA-*b*-PAz as typical examples. When the X-ray incidence was set parallel

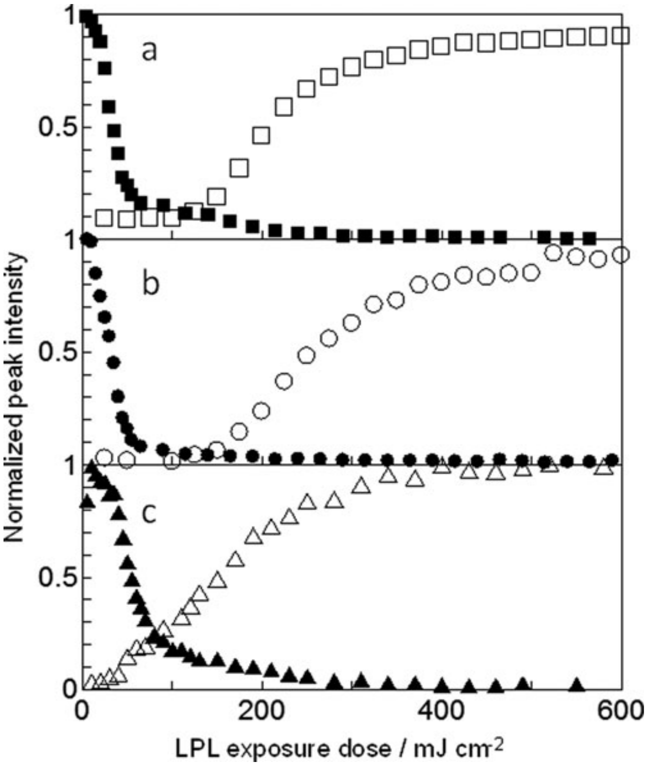

Figure 4. Normalized peak intensity of GI-SAXS with LPL exposure dose for the decay (close symbols) and enhancement (open symbols) processes. Figures a – c correspond to data for PHMA-*b*-PAz (a, $T_g = -5°C$), PBMA-*b*-PAz (b, $T_g = 20°C$), and PODMA-*b*-PAz (c, $T_c = 35°C$), respectively.

to the electric field of irradiating LPL, the in-plane scattering peaks were observed at $q_y = 1.87$ nm^{-1}, which correspond to the spacing of smectic A phase of PAz. After the second LPL irradiation process, on the other hand, the in-plane scattering was not observed. Instead, the scattering peaks appeared in a smaller angle region at $q_y = 0.20$ nm^{-1}. This small angle scattering was attributed to the mesoscopic MPS cylinder array structures. These in-plane angle dependent scatterings were alternatively observed by alternating irradiation of orthogonal LPL. These results suggest that the LC phase and MPS cylinder phase were monoaxially aligned and realigned by LPL irradiation. Essentially the same results were obtained with PBMA-*b*-PAz and PODMA-*b*-PAz films. For these diblock copolymers, the small angle scatterings were observed at 0.22 and 0.20 nm^{-1} for PBMA-*b*-PAz and PODMA-*b*-PAz, respectively.

Real Time Monitoring of the Photo-switching

To gain more insight into the orientational switching behavior, we carried out real time observations for the MPS cylinder domains by time-course analysis of GI-SAXS measurements using a synchrotron X-ray beam. The measurement setup was already reported in our previous paper [18].

Figure 4 shows the time course profiles of the normalized peak intensity for the orientational photoswitching of MPS cylinders in PHMA-*b*-PAz (a, $T_g = -5°C$), PBMA-*b*-PAz (b, $T_g = 20°C$), and PODMA-*b*-PAz (c, $T_c = 35°C$) thin films at 95°C. The peak intensities were monitored at $q_y = 0.20$, 0.22 and 0.20 nm^{-1} for PHMA-*b*-PAz, PBMA-*b*-PAz, and PODMA-*b*-PAz, respectively. The open symbols indicate peak intensities observed from orthogonal direction of the irradiated LPL electric vector, and the close symbols depicts the data measured from the parallel direction of the LPL. Changes in the scattering peak intensity were obviously observed for all the block copolymer thin films with the LPL irradiation dose. In this temperature condition, the poly(alkyl methacrylate) blocks should adopt a fluid amorphous state because the LC temperature is 75 and 100°C higher than T_g of PBMA-*b*-PAz and PHMA-*b*-PAz, and 60°C higher than T_c of PODMA-*b*-PAz.

In the peak decay process (disturbance of the regular array structure in one direction, close symbols in Figure 4), PBMA-*b*-PAz and PHMA-*b*-PAz showed rapid peak decays below ca. 60 mJ cm^{-2} of the second LPL irradiation. On the other hand, the decay for the PODMA-*b*-PAz film required apparently larger light doses to ca. 125 mJ cm^{-2}. The intensity enhancement process (formation of the regular array structure in the other (orthogonal) direction, open symbols in Figure 4), the initial uprises of the peak in PBMA-*b*-PAz and PHMA-*b*-PAz films were observed at ca. 120 mJ cm^{-2} via an induction period. The intensity enhancement curves showed a sigmoidal feature and saturated at 400 mJ cm^{-2}. In the case of PODMA-*b*-PAz film, however, the peak uprise was observed at an earlier stage of 50 mJ cm^{-2} of irradiation dose. In this case, the sigmoidal feature was poor and saturated at 400 mJ cm^{-2} irradiation. In the decaying process, the irradiating LPL is set parallel to the initial monoaxial alignment of the Az chromophore. The initial alignment state of PAz block instantly led to efficient trans-cis photoisomerization motions of Az unit by LPL irradiation. Thereby, MPS cylinders undergo disarrangement by fluctuations of Az chromophores. In the enhance process the cylindrical domains are reconstructed in the other direction.

The different behavior of PODMA-*b*-PAz from PHMA-*b*-PAz or PBMA-*b*-PAz should stem from the difference in the fluidity of the poly(alkyl methacrylate) block parts. These amorphous domains would be more fluid for PHMA-*b*-PAz or PBMA-*b*-PAz because T_g is lower to larger extents. Thus, efficient disarrangement could occur in the PBMA-*b*-PAz and PHMA-*b*-PAz films. In these two systems, the cylinder domains quickly become highly disordered and random orientation state by the second LPL irradiation. The existence of the induction period should reflect this situation. On the other hand, the PODMA having the long alkyl side chain exhibiting crystalline state at room temperature could be more viscous compared with the other two polymers. The more viscous nature of PODMS will delay the randomizing process. The lack of clear induction time in the peak enhancement process for can also be attributed to the higher viscosity of PODMA block. Only in this case, the MPS scattering were observed with both X-ray incidence directions, i. e., parallel and perpendicular to the LPL direction, in the range from 50 to 300 mJ cm^{-2}. It is thus suggested that the reorientation mechanism may be changed between PODMA-*b*-PAZ and PHMA-*b*-PAz or PBMA-*b*-PAz.

As indicated in this work, the thermal properties of the cylinder polymer domain play a great role in orientational photoswitching behavior of the LC Az block copolymer thin films. The MPS reorientation mechanism of the system can involves a domain nucleation and growth process and or a grain rotation process. To explain the precise mechanisms of the reorientation process, other experimental approaches such as microscopic morphology and LC domain size estimation in the transient state by transmission electron microscope observation are required. Investigations to understand the mechanisms are in progress.

4. Conclusion

In this work, we introduced the homologous poly(alkyl methacrylate) block, PBMA, PHMA and PODMA, to the MPS cylinder phase in Az-containing LC block copolymers. Through this approach, three issues are proposed. First, the Az mesgens and cylinder MPS separation structures are commonly aligned in the in-plane direction at the smectic A LC temperature for the all three block copolymer films. This should be ascribed to the free-surface segregation of the poly(alkyl methacrylate) blocks. Second, all the diblock copolymer films showed the orientatinal photoswiching of the MPS domains by alternative orthogonal LPL irradiation at the temperature examined where the poly(alkyl methacrylate)s adopt amorphous fluid state. And third, the reorientation behavior is modified by the difference in the fluidity of the poly(alkyl methacrylate) domain. The diblock copolymers with highly fluid PHMA and PBMA exhibited a highly cooperative alignment switching, whereas the cooperativity becomes poor for the copolymer with more viscous PODMA. These results will provide useful guidelines for the design of photoresponsive LC block copolymers.

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