Photoresponsive Polymers

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Synergy Effect on Morphology Switching: Real-Time Observation of Photo-Orientation of Microphase Separation in a Block Copolymer**

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The dynamic motions of molecular assemblies are essential in biological systems and in some functional materials and devices. For technical applications, the liquid crystal (LC) display is a typical example; LC displays are based on the dynamic alignment switching of LC molecules driven by an electric field. Over the past two decades, significant research efforts have led to the establishment of a light-driven alignment method for LC materials.[1–6] When linearly polarized light (LPL) irradiates an LC polymer film that contains a rod-like photochromic unit such as azobenzene (Az), the mesogenic groups reorient in a cooperative way to a non-excitable direction, specifically, the direction orthogonal to the electric vector (E) of the actuating polarized light.[1–6] The mesogenic units can be further reoriented by irradiating with LPL from another E direction. On the other hand, macroscopic actuators consisting of photochromic LC polymers have recently become an active area of research. They show large and reversible shape deformations in response to light.[7–10] The cooperative motions of LC units within the aligned materials lead to macroscopic deformations. Some bending deformations reflect the direction of the LPL used for the irradiation.[8,9]

Despite the accumulated knowledge concerning the previously discussed light-driven materials, photoresponsive systems that have an intermediate "mesoscopic" feature size (typically 10–100 nm) remain an underexplored area. Such structures are readily available by the microphase separation (MPS) of block copolymers.[11] These size regions are expected to play important roles in the development of low-cost processes that exceed the limitations of ordinary photolithography.[12,13] Thus, numerous investigations have been conducted to manipulate the mesostructures of block copolymers.[12,13] However, the efforts to date have mostly been limited to the construction of static fixed structures attained by directed assembly using for example patterned surfaces,[14] mechanical flow,[15] electric fields,[16] or magnetic fields.[17] Only a few attempts have been made to alter the MPS structure by external stimuli.[18–22] Herein, the dynamic reorientation process of an MPS mesostructure was pursued under application of external electric fields[21,22] using in situ scanning probe microscopy and synchrotron X-ray scattering measurements. The elucidation of the light-induced reorientation processes of the MPS morphology of a block copolymer remains a challenging problem.

Our previous experiments have shown that a diblock copolymer, which consists of polystyrene and an LC Az-containing polymer block, is able to alter the orientation of an MPS cylinder structure (distance between the cylinders: ca. 32 nm) of coiled polystyrene domains in response to LPL.[19] Herein we report time-resolved in situ measurements of the photoinduced alignment changes of both smectic LC Az layers and a mesoscopic coiled polymer domain array by X-ray scattering from a synchrotron radiation source. The strong cooperative motions between the hierarchies of the constituents of photoresponsive molecules and mesoscopic MPS domains are revealed by this approach.

In our previous work on a polystyrene-based polymer (glass transition temperature (T_g) of polystyrene = 102 °C), the photoalignment procedure required both LPL irradiation and annealing followed by successive slow cooling; real-time monitoring was therefore not feasible.[19] In the present study, a newly synthesized Az LC block copolymer containing poly(butyl methacrylate) (PBMA, $T_g = 20\,°C$) instead of polystyrene was employed (Figure 1a; P5Az10MA$_{43}$-b-PBMA$_{70}$). This diblock copolymer formed the amorphous cylinders in the Az LC block matrix in the MPS structure, as determined by small-angle X-ray scattering measurements (Supporting Information, Section S3-3). The LC phases and thermal properties of P5Az10MA$_{43}$-b-PBMA$_{70}$ were evaluated using differential scanning calorimetry (DSC), thermal optical polarized microscopy, and X-ray diffraction measurements (Supporting Information, Section S3-2). P5Az10MA$_{43}$-b-PBMA$_{70}$ exhibited a T_g of 55 °C, which is identical to that of the P5Az10MA homopolymer. This result indicates that the PBMA and Az LC blocks were phase-separated from each

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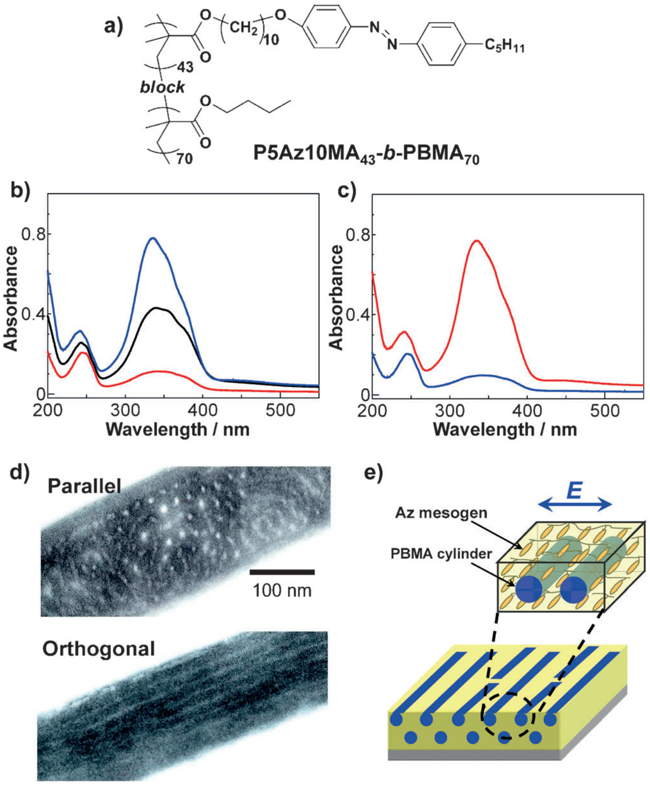

Figure 1. a) Molecular formula of P5Az10MA$_{43}$-*b*-PBMA$_{70}$. b) UV/Vis absorption spectra of a spin-cast film of P5Az10MA$_{43}$-*b*-PBMA$_{70}$ before illumination (black) and after illumination with 436 nm LPL, detected with the probing beam parallel (red) and orthogonal (blue) to *E* of the actuating LPL light. c) UV/Vis absorption spectra of the reoriented film attained by irradiation with 436 nm light set orthogonal to the initial alignment. The blue and red spectra were taken with the same probing beam used for (b). d) TEM images of cross-sections taken in directions parallel and orthogonal to *E* of the LPL used for irradiation. e) Depiction of the uniaxially aligned Az LC layer (yellow) and cylindrical domains of PBMA (blue) by LPL irradiation.

other. The P5Az10MA domain has a smectic C phase (ca. 55 to 90 °C), smectic A phase (90 to 115 °C), and isotropic phase at temperatures above 115 °C.

Thin films (ca. 200 nm in thickness) were prepared by spin coating from a chloroform solution and successive annealing of the films at 120 °C for 5 minutes for full evaporation of the solvent. The films were then slightly cooled to 95 °C, at which temperature P5Az10MA adopts a smectic A phase, and irradiated with LPL of 436 nm visible light at 1.0 mW cm^{-2} through an optical polarizer.

UV/Vis spectroscopic data and morphology observations are displayed in Figure 1 b–d. An as-annealed film exhibited no in-plane anisotropy of the Az mesogen orientation, which was confirmed by polarized absorption spectroscopy (black curve, Figure 1 b). This result suggests that a polydomained film was formed. After LPL irradiation for 300 s (300 mJ cm^{-2}), a large dichroism was induced at the π-π* transition band of the Az mesogen at about 340 nm (red and blue). Successive LPL (second LPL) irradiation from the orthogonal position at the same temperature switched the in-plane anisotropy to the orthogonal direction (Figure 1 c). In both cases, the absorbance band observed with a polarizer set orthogonal to the electric field vector *E* of the LPL became remarkably larger than that obtained with the polarizer in the parallel position. These results show that the Az mesogen was uniformly aligned (Figure 1 b) and then switched to align orthogonal to the LPL polarization direction (Figure 1 c) and both cases exhibited a highly ordered in-plane anisotropy of the Az–mesogenic groups.

Cross-sectional transmission electron microscopy (TEM) observations of the aligned film sliced in directions parallel and orthogonal to the LPL direction revealed uniaxially aligned MPS cylinders in the photoaligned film (Figure 1 d). Dot-like and stripe morphologies were observed in the cross-section when the films were sliced in the directions parallel and orthogonal, respectively, to the *E* vector of the LPL. Thus, the TEM images clearly demonstrate the uniaxial alignment of the PBMA cylinders directed orthogonal to the LPL direction. Based on these data, the LPL irradiation of the Az LC phase and the PBMA cylinders in the P5Az10MA$_{43}$-*b*-PBMA$_{70}$ film induces a hierarchical structure (Figure 1 e). These reorientations were possible when the temperature was within the range of the smectic A phase of P5Az10MA. Upon irradiation at temperatures below 80 °C, which corresponds to the smectic C phase, photoswitching of the dichroism became significantly slower and required more than 1000 mJ cm^{-2} (1000 s), even though the procedure was performed at temperatures above the T_g of both block segments. This result probably came from an unfavorably high order and viscosity of the Az layer domains in the smectic C phase.

We further evaluated the hierarchical structure by grazing incidence small-angle X-ray scattering (GI-SAXS) measurements at the BL-15A beam line of the Photonfactory (KEK-PF) in Tsukuba, Japan. A monochromated X-ray radiation source at a wavelength λ of 0.150 nm was used, and the detection was performed with an X-ray CCD detector with a 150 mm diameter X-ray image intensifier. The GI-SAXS measurement was conducted with sample-to-detector lengths of 1340 mm for the LC phase (0.5 nm^{-1} $< q <$ 3 nm^{-1}, $q = 4\pi(\sin\theta)/\lambda$, where q is the scattering vector and 2θ is the scattering angle) and 2250 mm for the MPS cylinder structure (0.06 nm^{-1} $< q <$ 0.7 nm^{-1}). The two-dimensional scattering images are shown in Figure 2. When the incident X-ray beam was set parallel to *E* of the first LPL irradiation (beam I), two diffraction spots corresponding to the Az smectic LC phase were observed in the in-plane position from the direct beam in the GI-SAXS pattern ($q = 1.87$ nm^{-1}, $d = 3.36$ nm, white arrows in Figure 2 a), and no scattering was seen with beam II. In contrast, the scattering peaks in the smaller region that correspond to the hexagonal PBMA cylinders appeared in the position above the in-plane line ($q = 0.22$ nm^{-1}, $d = 27$ nm)[23] only when the X-ray angle of incidence was set orthogonal to *E* (beam II, yellow arrows in Figure 2 b). The scattering spots that correspond to the MPS cylinder were detected near the edges of the beamstop to avoid the direct specular beam in the two-dimensional image of beam II in Figure 2 a.

After successive irradiation with the direction rotated by 90 degrees (second LPL, 436 nm, 1 mW cm^{-2} for 300 s), this scattering anisotropy was fully switched to the opposite direction (Figure 2 c, d). The scattering behaviors agree with

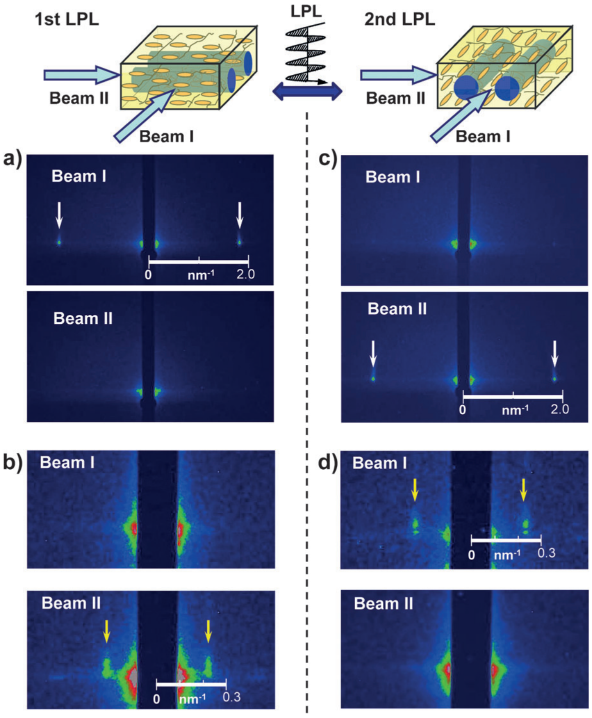

Figure 2. Charge-coupled device (CCD) camera images taken by GI-SAXS measurements with the BL-15A beam line at KEK-PF. In-plane diffractions corresponding to the LC Az layer taken with beam I or beam II (a) and in-plane scattering corresponding to the cylinder domain distance of PBMA (b) for the initially photoaligned film shown in the top-left scheme. The CCD images in the same setup configuration (c and d) taken after a second irradiation with LPL (436 nm, 300 mJ cm^{-2}) at 95 °C. Note that the in-plane scattering spots at wider (white arrows) and narrower (yellow arrows) angles are fully reversed with respect to the beam direction, which indicates the complete switching of the uniform alignment of both the LC Az layer of P5Az10MA and the direction of the PBMA cylinders.

the TEM images and the model in Figure 1 e. These results indicate that the macroscopic photoswitching of the Az smectic phase and the PBMA cylinders is attained over the whole film area by irradiation with LPL. The alignment change is induced simply by LPL irradiation, at a constant temperature of 95 °C, without the annealing and cooling procedures that were necessary for the polystyrene-based block copolymer.[19] This fact allows for the time-resolved monitoring of the X-ray profiles, as discussed below.

At the molecular level, time-resolved measurements have provided valuable information about the reorientation of LC molecules;[24,25] however, no information has been reported regarding the reorientation process of hierarchically structured LC block copolymer systems. Our efforts therefore focused on the acquisition of GI-SAXS profiles at the transient state of reorientation. Our setup, which combined the synchrotron radiation source with the CCD/intensifier system, enabled a highly sensitive GI-SAXS measurement to be attained in one second. The dynamic alternations in the two-dimensional scattering image were accumulated over time.[26] Figure 3 shows the timecourse changes of the extracted in-plane scattering profiles under LPL irradiation at 95 °C. For an initial photoaligned film, the film specimen was positioned such that the scattering peak intensity of the PBMA cylinders ($d = 27$ nm) became maximal (Figure 3 a, 0 s), at which the diffraction from the orthogonally formed smectic layer of the Az block was negligible (Figure 3 b, 0 s). Upon irradiation with 436 nm LPL with E set parallel to the Az chromophore (specifically, in the direction parallel to the PBMA cylinders) the scattering peak of the PBMA cylinders rapidly disappeared in the early 20 s. The increase of the scattering corresponding to the Az smectic layer ($q = 1.87$ nm^{-1}, $d = 3.36$ nm) started to appear after ca. 50 s and produced a saturated state after 200 s (Figure 3 b), which is overall a slower process. Next, the second LPL irradiation with the polarizer rotated in the direction orthogonal to the initial direction was performed, which led to the opposite transition behaviors. In this case, a rapid decay of the Az LC peaks (Figure 3 d) and a gradual increase in the peak from the cylinders (Figure 3 c) were detected in the larger (cylinder

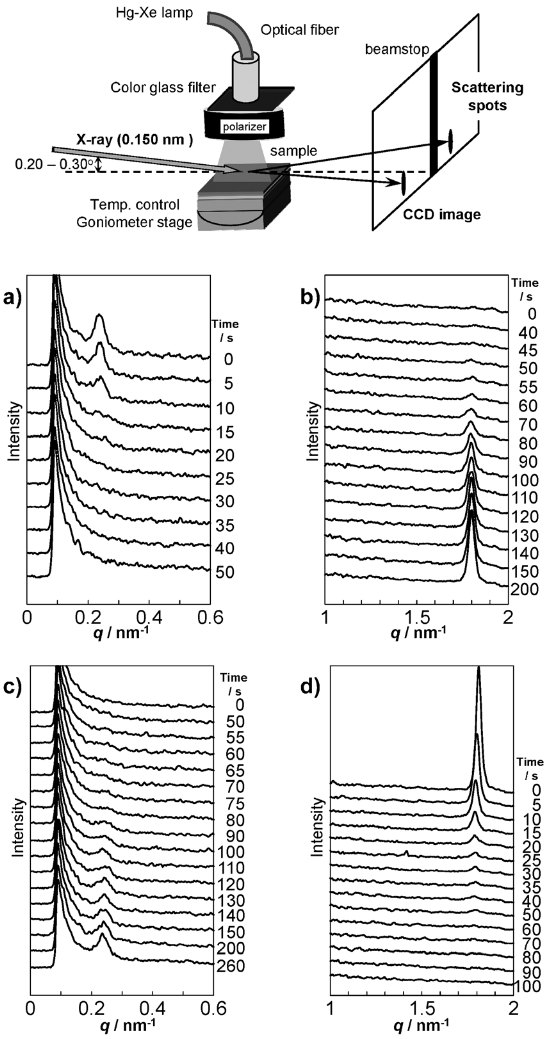

Figure 3. Time-resolved in-plane scattering profiles taken under irradiation with LPL, with E set parallel to the Az mesogenic group at 95 °C. a) Decay of the peak because of loss of order in the PBMA cylinder array. b) Enhancement of the peak because of ordering of the LC Az layer of P5Az10MA. c), d) The corresponding reversed process under irradiation with E set orthogonal to the initial direction of irradiation.

domain) and smaller (LC layer) regions. The scattering from the Az LC layer during the decay process exhibited a slight shift to a wider spacing (Figure 3 d, *d* from 3.36 to 3.53 nm), which suggests that the fluctuation of the smectic LC phase is enhanced by LPL irradiation because of a slight population increase of the *cis*-Az isomer. The molecular packing state of the Az mesogenic groups is probably somewhat loosened in the smectic A phase.

Using the above method, the enhancement and decay processes of the scattering peaks from the Az smectic layer and the PBMA cylinders were followed with satisfactory accuracy by the time-resolved synchrotron radiation setup. We expect that this method of time-resolved GI-SAXS measurements will be important for the evaluation of many other types of dynamic processes and molecular motions that occur in thin films. In Figure 4, time courses of the intensity changes in the normalized peaks of the decay (a) and enhancement (b) processes for the LC Az layer and the PBMA cylinders are compared. Most interestingly, the profiles of the intensity changes from the LC phase and the cylinder array essentially overlap each other in both processes. These data indicate that both events, at different hierarchies, occur simultaneously in a strongly cooperative manner. Peaks from both the LC layer and the PBMA cylinder array formations started to become enhanced about 50 s after the decay processes of the initial alignment was completed. In this experiment, the light intensity of the actinic LPL was changed from 0.5 to 2.0 mW cm^{-2}, but the dynamics of the peak enhancement (structure reformation) process were hardly affected. This result shows that the light-energy dose for the reformation is sufficient, as supplied by the photon doses of the above range. Thus, the rate of structure formation seen here reflects the intrinsic assembly dynamics of the block copolymer at the observed temperature.

The reorientation was performed by irradiation with visible light (436 nm) at 95 °C. This result shows that most of the Az units are in the *trans* form when adopting the smectic A phase. In fact, the polarized optical microscopy images revealed that the film shows a birefringent nature at the intermediate state. Thus, the orientation transition should occur with retention of the smectic A phase. The LPL irradiation for the orthogonal reorientation (*E* parallel to the MPS cylinder) probably first induces defects (dislocations/disclinations) in the initial MPS structure that correspond to the fast decay of the X-ray scattering. Such defects are then gradually diminished as the cylindrical MPS structure grows in the orthogonal direction, which is seen as the slower progression in the X-ray scattering profile. Schmidt et al.[27] conducted in situ synchrotron SAXS measurements and a computer simulation of data for the mechanism of the reorientation of a solvent-swollen block copolymer driven by an electric field. They proposed that the reorientation mechanism involves a domain nucleation and growth process or a grain rotation, either of which could also apply to our system. Other approaches, such as the molecular mass dependence of the block copolymer and microscopic morphological observations in the transient state, are urgently required. A precise understanding has not been acheived, and work to elucidate the mechanism is underway.

To date, various types of directed assembly procedures for block copolymer films have been demonstrated.[14–17] In such cases, the block copolymers themselves exhibit no ability to align their MPS patterns. Thus, the MPS alignment is achieved passively, and the resultant MPS morphologies are fixed. In contrast, the introduction of the photoresponsive Az to the LC domains allows the active control of the MPS alignment. In Figure 5, the MPS structure could be readily reoriented many times. Mesoscaled structures formed by block copolymers can be useful templates for the patterning and alignment

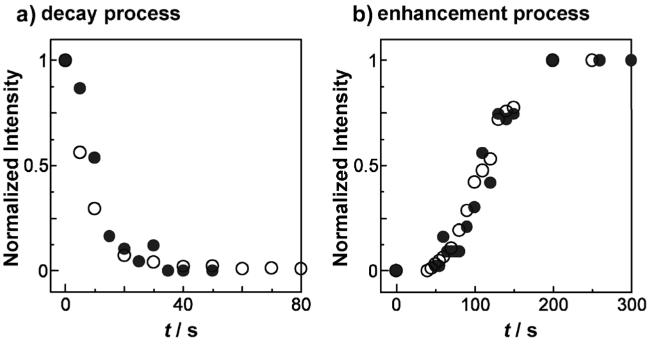

Figure 4. Time-course profiles of the scattering intensity normalized to the maximum of each peak in Figure 3. a) Decay processes from the loss of periodically ordered structures of both the smectic Az LC (open circle) and the PBMA cylinders (closed circle) examined with the appropriate X-ray beam direction (orthogonal with each other for the two hierarchical structures). b) Enhancement processes ascribed to the ordering of the periodicity of the two hierarchical structures.

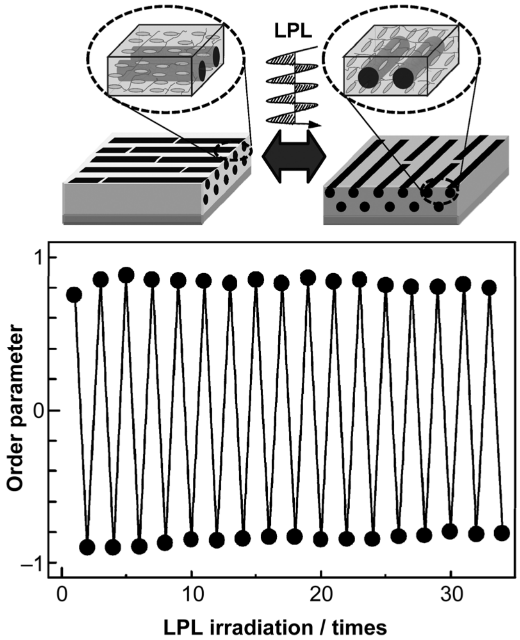

Figure 5. Orientational order parameter of the Az mesogenic group in the film altered by successive LPL irradiation with *E* orthogonal to the previous direction. The order parameter is defined as $(A_{\perp}-A_{\parallel})/(A_{\perp}+2A_{\parallel})$, where $A_{\perp}$ and $A_{\parallel}$ are the absorbance detected with the probing beam set orthogonal and parallel to *E* of the initial LPL used for irradiation, respectively. The alternation of negative and positive signs indicates the repeated orthogonal reorientation of the system.

of various functional materials. Light is a particularly versatile tool that allows noncontact and precisely addressable processing using simple, inexpensive equipment. The light-controllable dynamic mesostructures are anticipated to provide new possibilities in materials science, as well as technologies for device fabrication based on block copolymers.

Experimental Section

Materials and real-time GI-SAXS experiments: P5Az10MA$_{43}$-*b*-PBMA$_{70}$ ($M_n = 57000$ and $M_w/M_n = 1.08$) was synthesized by ATRP (atom-transfer radical polymerization) method. The P5Az10MA$_{43}$-*b*-PBMA$_{70}$ film was prepared on a fused silica substrate by the spincast method. Real-time GI-SAXS experiments were performed with a sample-to-detector distance of 2250 mm for the MPS structure and 1340 mm for the LC phase on the 15A beam line at the KEK Photon factory in Tsukuba, Japan. The scattering images were captured by a CCD detector (Hamamatsu C4880). Incidence angles were chosen between 0.2 and 0.3°, and the final images were the average of one-second exposures. Linearly polarized light (LPL) at 436 nm was obtained from the mercury/xenon light source (San-ei Electronics Supercure 203S) passing through glass filters (Y43, V44) and a polarizer. The sample film was pre-oriented by irradiation with LPL at 110°C.

The supporting information provides further experimental details of synthesis and characterization of the block copolymer, TEM detection, and real-time GI-SAXS measurement.

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