

Photoinduced 3D Ordering and Patterning of Microphase-Separated Nanostructure in Polystyrene-Based Block Copolymer

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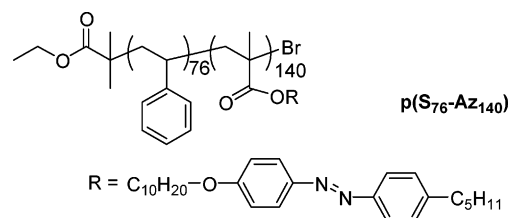
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The potential of block copolymers with incompatible blocks for nanotechnologies has been widely realized in the past decade, and an increasing number of applications has been described.^{1,2} Block copolymers provide highly ordered microphase-separated (MPS) nanostructures typically comprising sphere, cylinder, or lamella shapes through self-assembly. For practical applications toward nanotechnologies such as membrane separation and addressing of nanomaterials, the MPS structures should be homogeneously aligned over large macroscopic areas in the film; however, this is not attained for most block copolymer systems without aligning procedures. Therefore, many efforts have been made for fruition of macroscopic alignment of MPS structures. For example, applications of the external field³ and alignment via confinement of chemically or topologically surface patterned substrates^{4,5} have been performed.

Quite recently, photoalignment⁶ and 3D photopatterning⁷ of the MPS structure has been demonstrated by using diblock copolymers composed of poly(ethylene oxide) (PEO) and an azobenzene (Az)-containing polymethacrylate. This optical method is based on the angular selected photoreaction of azobenzene side chains and the collective molecular motions.⁸ The nanocylinders of PEO are aligned orthogonal to the direction of the electric field vector of irradiated polarized light. Here, the photoaligned Az mesogenic chromophores induce alignment of the PEO cylinder structure

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Az polymer : glass-43 °C-SmX-90 °C-SmA-118 °C-Iso

T_g of PS : 102 °C

Figure 1. Chemical structure and thermal transition properties of p(S₇₆-Az₁₄₀).

of the larger-sized hierarchy of the MPS structure. The key to the successful photoalignment control seems to be the use of the stimuli-responsive soft-block component of PEO exhibiting a low glass-transition temperature (T_g).

With regard to thermal and mechanical stability, polystyrene (PS)-based block copolymers possessing higher T_g are a fascinating target. The syntheses and characterizations of Az-containing block copolymer films have already been investigated. Ober's group⁹ first synthesized a series of block copolymers of PS connected with an Az-containing liquid crystalline (LC) polymer derived from polyisoprene, and structural characterizations were made in detail. Schmidt and co-workers¹⁰ observed the MPS structure of a diblock copolymer composed of PS and amorphous Az-containing polymer block. They found that the photoinduced mass migration was highly hindered by the block architecture in comparison with the behavior of a statistical random copolymer of the same composition, and applications in photoaddressing for optical information are demonstrated. Zhao and co-workers¹¹ discussed the confinement effects on the photoalignment of liquid-crystalline Az side chains. Within the MPS domains of PS, suppressed motions of the azobenzene mesogenic groups are manifested. In spite of the above efforts, no data on the on-demand photoalignment of the MPS structure of PS-containing block copolymers have been reported. We show herein the first example of photoalignment and realignment of the MPS structure in a PS-based block copolymer film attained via optimizations of the preparation conditions. The diblock copolymer used in this study is denoted as p(S₇₆-Az₁₄₀), where the indices indicate the number of each unit. (Figure 1).

The block copolymer p(S₇₆-Az₁₄₀) ($M_n = 77\,000$ and $M_w/M_n = 1.21$) was synthesized by an atom transfer radical polymerization method.¹² The polymer employed in this study exhibited two T_g values at 43 and 102 °C for the Az polymer block and PS block, respectively, indicating that the system is microphase-separated.

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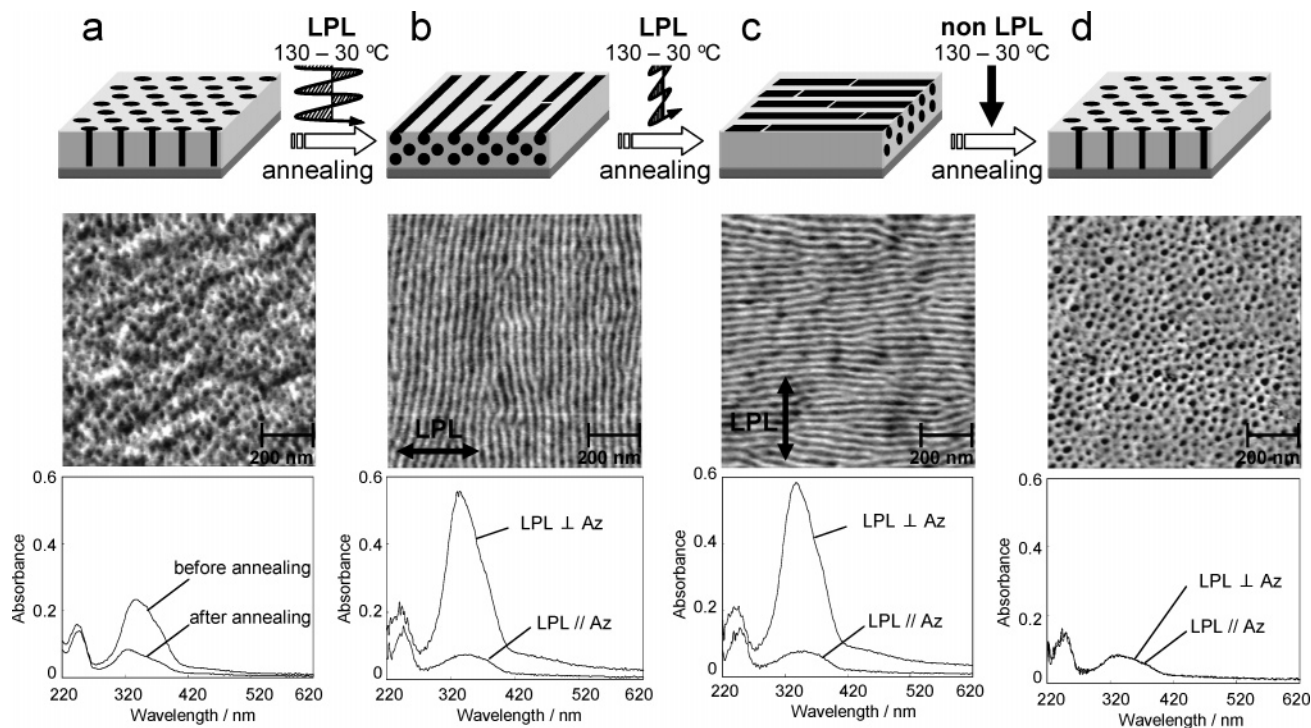


Figure 2. A series of optical orientational controls on the mesogenic Az groups and MPS nanocylinder domains of PS in the p(S₇₆-Az₁₄₀) film (thickness ≈ 100 nm) evaluated by phase-mode AFM and polarized UV-vis absorption spectroscopy, respectively. (a) Initial state. The annealing induces the perpendicular orientation to the substrate plane for both Az and PS cylinders. (b) After irradiation with LPL (436 nm) followed by annealing. (c) Successive irradiation with LPL (436 nm) at the orthogonal polarization angle followed by annealing. (d) After irradiation with nonpolarized light (436 nm) followed by annealing.

Figure 2 displays the surface morphologies ($3.0 \times 3.0 \mu\text{m}$) and UV-visible absorption spectra of light-irradiated p(S₇₆-Az₁₄₀) films of ~ 100 nm thickness evaluated by the phase-mode AFM measurements using a SPA40/SPI3200 (Seiko Instruments). For the irradiated film, the LPL exposure (436 nm) was performed at 2.0 mW cm^{-2} for 50 min at 130°C , followed by gradual cooling to 30°C at a rate of 2°C min^{-1} . For evolution of MPS structure, the films were successively annealed at 107°C , slightly above the T_g of the PS block and below the Sm_A transition to isotropic transition of the Az polymer block, for 12 h.

As shown, obvious effects of light irradiation on the molecular orientation and morphology of MPS were observed. These images indicate that the nanocylinder structure of PS were formed. Nonirradiated film provided PS cylinders in the upright orientation (a) after annealing. The spectral data also indicate that the annealing induces the Az orientation normal to the substrate plane. The reduction in absorbance of the $\pi-\pi^*$ band peaking at 338 nm whose transition moment is along the long axis of Az indicates this fact. A hypsochromic shift was also observed, indicative of further promotion of H-aggregation. The diameter of the cylinders was 14 ± 1 nm, with an average cylinder to cylinder distance of 32 nm. After LPL irradiation, a stripe morphology whose direction was highly controlled orthogonal to the direction of LPL was observed (b). The average line-to-line distance was 32 nm, which agrees with that evaluated above. The Az group showed a strong in-plane anisotropy with the orientational order parameter ($S = (A_{\perp} - A_{\parallel}) / (A_{\perp} + 2A_{\parallel})$), where A_{\perp} and A_{\parallel} denote the absorbance orthogonal and

parallel to the irradiated LPL, respectively) of 0.68. The photoalignment of Az mesogens in LC polymer films induced by directionally selective excitation with LPL is well-known.⁸ Here, such molecular alignment is reflected to the larger hierarchy of MPS morphology via collective and cooperative molecular motions.^{6,7} The same procedure was successively performed using LPL set at another angle, orthogonal to the previous irradiation (c). Essentially the same results on the MPS morphology and spectral data were obtained except for the direction of molecular orientation with $S = 0.68$ and MPS morphology. The cylinders aligned in the in-plane direction was again reverted to the out-of-plane (normal) mode by irradiation of nonpolarized light irradiation in the normal direction (d). The final state obtained exactly coincides with that of the initial state (a). These facts unequivocally indicates that 3D ordering, namely both in-plane and out-of-plane orientational control, of a nanocylinder of PS domain is achieved by light. Such realignment of MPS structure required irradiation at a temperature above the order-disorder transition temperature (118°C , i.e., above both T_g of PS and the smectic-to-isotropic transition temperature of Az LC polymer). In the series of present experiments, the samples were heated to 130°C and slowly cooled to 30°C , as described in the experimental procedures. It is thus assumed that the directed MPS structure evolved from a photooriented nucleation formed in a disordered state.

Next, photopatterning was achieved (Figure 3). The LPL irradiation was performed on a perpendicularly aligned film (a) through a line and space photomask ($10 \mu\text{m}$ period)

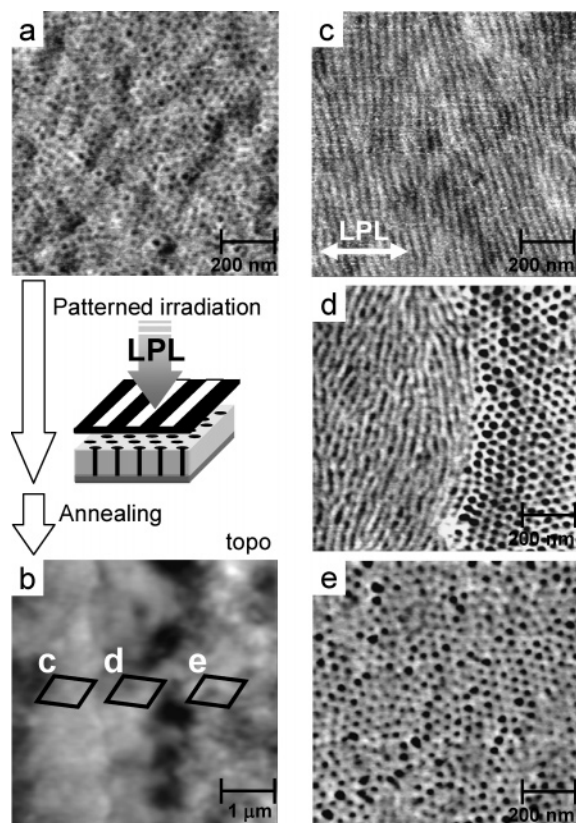


Figure 3. Orientational control of the PS cylinder by patterned irradiation of LPL (436 nm) in the p(S₇₆-Az₁₄₀) film (thickness \approx 100 nm). (a) Phase-mode AFM image of the initial annealed state, where all cylinders are aligned in the normal orientation. (b) Topographical AFM image after patterned irradiation with LPL. (c–e) Phase-mode AFM images taken at the (c) irradiated area, (d) boundary region, and (e) non-irradiated area.

followed by annealing. The topographical image of the resulting film indicated that the surface was flat within 4

nm (b). The phase-mode image (c–e) clearly indicated the patterned orientation of the nanocylinders. The LPL-irradiated area exhibited the horizontal orientation of the cylinders with orientation orthogonal to the direction of LPL (c), whereas the perpendicular orientation was maintained in the nonirradiated area (e). The observation of the boundary region indicated that there was no gradient region between the two in-plane and out-of-plane oriented areas (d).

In the above manner, we succeeded in on-demand 3D orientational alignment of the MPS structure of the PS-based block copolymer. We are now conducting further experiments with a lamella-forming block copolymer of the identical components. In this case, the continuous phase of PS domains impeded the reorientation of the MPS structure. An interesting aspect observed for the lamella-forming block copolymer is that clear memory effects on the orientation of Az-containing LC phase were observed. The details for the features of cylinder-forming and lamella-forming photoresponsive block copolymers will be presented in due course. We believe that the development of photoinduced 3D orientation and patterning of the MPS structure of block copolymers with relatively high T_g values will be particularly useful for fabrication of new information materials and devices.

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Supporting Information Available: Synthetic procedures for the block copolymer and its characterizations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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