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Photoinduced Alignment of Nanocylinders by Supramolecular Cooperative Motions

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Molecular and supramolecular orderings have attracted much attention because of their potential applications in multidisciplinary fields of nanotechnology.[1−12] At a molecular level, chromophore molecules such as azobenzenes (AZs) are well-known for photoinduced alignment with their transition moments almost perpendicular to the polarization of the actinic light by repetition of the trans−cis−trans isomerization cycles,[1] and such ordering can be transferred to other photoinert mesogens by molecular cooperative motions coinciding with the AZs.[2] On the other hand, supramolecular ordered nanostructures self-assembled in block copolymer films have been widely used as templates or scaffolds to prepare nanomaterials.[3,4] In the microphase-separated processes, the supramolecular function between incompatible phases plays an important role in the formation of diverse nanostructures such as sphere, cylinder, double gyriod, and lamellae.[3] The orderings of one phase domain might endow the other microphase-separated domain with some kind of regularity by the supramolecular cooperative motions, which gives hints to incorporate the photoresponsive AZs into block copolymers and transfer the molecular ordering to the supramolecular level. Therefore, well-ordered nanostructures in the AZ-containing block copolymers might be obtained by the photocontrol method.

Generally, the ordered periodic structures in block copolymers are formed at 5−50 nm scale only by the supramolecular self-assembly.[3] In the past two decades, electric or magnetic field,[5] temperature gradient,[6] crystallization,[7] modified substrate surface,[8] shearing,[9] solvent evaporation,[10] roll casting,[11] photoinduced mass transfer upon holographic irradiation,[12] and mixing with homopolymer[13] have been explored to control the nanostructures. However, a perfect parallel pattern of such nanostructures by noncontacted approaches is still remaining challengeable. Although the introduction of AZs into well-defined block copolymers has given the designed materials some interesting properties,[14] photocontrol of the microphase-separated nanostructures by the supramolecular cooperative motions has never been tried. In this paper, we communicate a noncontacted optical method by using a polarized laser beam to control poly(ethylene oxide) (PEO) nanocylinders in an amphiphilic diblock liquid−crystalline (LC) copolymer consisting of flexible PEO as a hydrophilic block and poly(methacrylate) containing an AZ moiety in the side chain as a hydrophobic LC segment.

Figure 1 shows the chemical structure of the amphiphilic diblock LC copolymer used in this paper, which was prepared by a typical atom transfer radical polymerization.[14d] When the copolymer was heated, two phase-transition peaks appeared at 40.1 and 158.4 °C in its thermogram by differential scanning calorimetry (Figure S4), corresponding to PEO melting point−smectic phase−isotropic phase, respectively. A T_g of 79.6 °C was obtained on cooling. Upon being annealed at 140 °C, the PEO block self-assembled into nanocylinders with a diameter of about 7 nm dispersed in the AZ LC matrix with a periodicity of 15 nm. Although multigrain was observed in Figure 1, the fast Fourier transform (FFT) image in a small area indicated a hexagonal packing of the PEO cylinders perpendicular to the substrates in each grain.

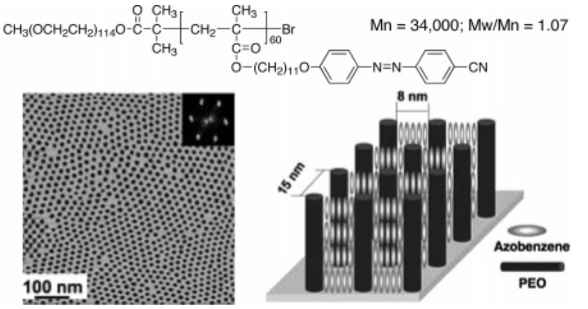

Figure 1. Chemical structure and microphase-separated scheme of the block copolymer. Inset of the AFM phase image is the FFT of a small area. Both azobenzenes and PEO cylinders are perpendicular to the substrate.

The block copolymer films with a thickness of about 100 nm were prepared by spin-coating their toluene solution on glass substrates. After the solvent was removed at room temperature, the films were irradiated with a linearly polarized beam from an Ar^+ laser (488 nm) at an intensity of 100 mW/cm^2. The transmittance (T) of a He−Ne laser at 633 nm with weak intensity as a probe beam was measured simultaneously during irradiation through two crossed polarizers with the sample films between them (Figure S6). Generally, T is defined by $T = \sin^2(\pi d\Delta n/\lambda)$, where d is the film thickness, Δn is the photoinduced birefringence, and λ is the wavelength of the probe light. The Δn of 0.26 was obtained after irradiation for 1000 s. Such a film exhibited intensive anisotropy in its polarized UV−vis spectra (Figure S8), indicating that the homogeneous LC alignment was achieved perpendicular to the polarization of the actinic light.[1] The order parameter (S) of 0.19 at 350 nm is calculated by $S = (A_\perp - A_\parallel)/(A_\perp + 2A_\parallel)$, where $A_\perp$ and $A_\parallel$ are the absorbance perpendicular and parallel to the polarization direction of the actinic laser beam, respectively. Upon the film being annealed at 140 °C, the S increased to 0.56 owing to the improvement of LC alignment by lowering viscosity of the smectic LC phase. No homogeneous alignment in the unirradiated area was observed in the polarized UV−vis spectra ($S = 0$).

The highly ordered AZs showed great influence on the PEO domains by the supramolecular cooperative motions upon annealing at an LC temperature, and a perfect regular array of PEO nanocylinders, corresponding to the photoinduced alignment direction of the AZs, was indicated as shown in the AFM images (Figure 2a,b). The inset FFT demonstrated a parallel patterning of the PEO cylinders in the plane of substrate. The periodic nanostructures might be achieved by the interplay process between the photoinduced ordering of AZs and the self-assembly of block copolymers,[15] leading to a parallel array of 40 nanocylinders aligned perpendicu-

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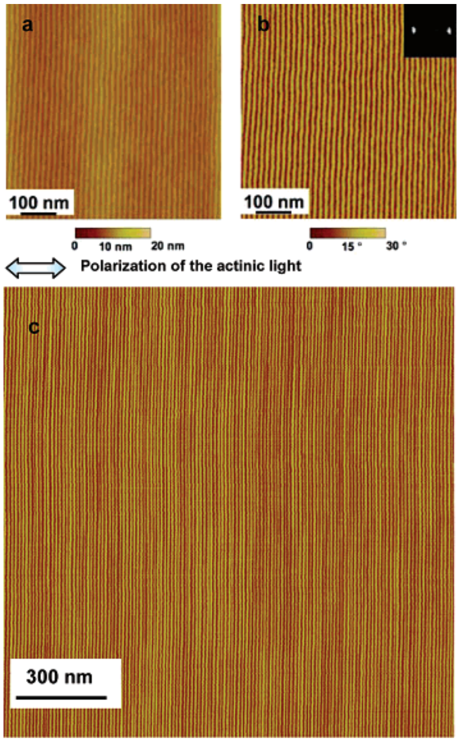

Figure 2. AFM images of the annealed block copolymer films in irradiated area: (a) AFM topological; (b) phase images. Inset of panel b shows the FFT image. Panel c is the AFM phase image in an area of 1.5 μm × 1.5 μm.

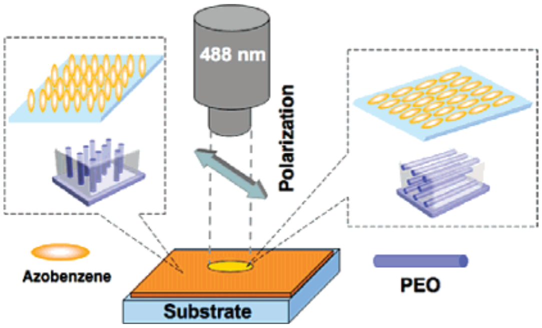

Figure 3. Scheme of LC alignment and microphase-separated structures in the irradiated and unirradiated area of the block copolymer films.

larly to the polarization direction of the actinic light in an area of 600 × 600 nm^2. Similar to other PEO-based block copolymers,[16] the sample films exhibited a regular surface relief of about several nanometers with a periodicity of 15 nm (Figure S9), possibly due to the confined crystallization of the PEO blocks among the ordered LC phases.[16]

Limited by the AFM resolution, a parallel array of the nanocylinders only in an area of 1.5 × 1.5 μm^2 is provided in Figure 2c. Actually, such parallel patterning of PEO nanocylinders can be perfectly achieved in an arbitrary area, depending on the size of the actinic light. In the unirradiated area, the AZs were out-of-plane because of the smectic layer structures, resulting in the perpendicular alignment of PEO nanocylinders.[14b] The alignment of the LC and PEO nanocylinders in the irradiated and unirradiated area of the block copolymer films can be schematically illustrated in Figure 3.

In summary, we proposed an optical method to control a parallel patterning of PEO nanocylinders in an amphiphilic diblock LC copolymer. The PEO nanocylinders are aligned perpendicular to the polarization direction of the actinic light by the supramolecular cooperative motions between the ordered AZ LCs and the microphase separation. By the simple and convenient way of photocontrol, the macroscopic parallel array of nanocylinders can be easily obtained in an arbitrary area. Furthermore, the noncontacted method might provide a novel opportunity to control the nanostructures even on curve surfaces.

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Supporting Information Available: Synthesis and characterization of monomer and the block copolymer; optical setup for photoinduced alignment. This material is available free of charge via the Internet at http://pubs.acs.org.

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