

## Liquid Crystal- Assisted Photo-triggered Mass Migration in Liquid Crystalline Diblock Copolymer

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Photo-triggered mass migration in thin films of photoresponsive azobenzene (Az)-containing polymers leads to development-free formation of surface relief structure. This work shows that this method can be applied to a thin film of a diblock copolymer consisting of an Az-containing liquid crystalline segment and poly(ethylene oxide). A corrugated surface structure following the interference periodicity was efficiently formed with the assist of 4'-phenyl-4-cyanobiphenyl (5CB). The content of 5CB greatly influenced the migration efficiency which was evaluated by both the first-order diffraction and surface topology measurements.

Key words: Photoinduced massive migration, Surface relief, Block copolymer, Azobenzene, Liquid crystalline polymer

### 1. INTRODUCTION

The alignment control and micro-patterning of nanoscale periodic structures in thin films is significant technology for application to various nanodevices.<sup>1</sup> The nanostructure and patterns self-assembled in block copolymer thin films depend on film thickness in the range of several tens of nanometer levels.<sup>2,3</sup> Topographically patterned substrates made by photolithographic procedures provide corrugated surfaces for thin films and then induce alignment control and patterning of nanostructure due to thickness undulation.<sup>4,5</sup>

With respect to topological surface relief formation, photoresponsive polymers functionalized with an azobenzene (Az) chromophore have been attracting much attention.<sup>6-10</sup> Exposure to two interference coherent beams of argon ion laser leads to formation of surface relief structure without development or etching as a consequence of mass transport. Another feature of this process is the capability of erasure and regeneration of the pattern. Most of the polymers employed are homopolymers and random copolymers. In consideration of the fascinating functionalities of the block copolymers stated above, fabrication of light-driven mass transport of block copolymer systems should be of particular interest, where hierarchical nanoscale microdomain structure would be involved in the micrometer-scale topological patterns.

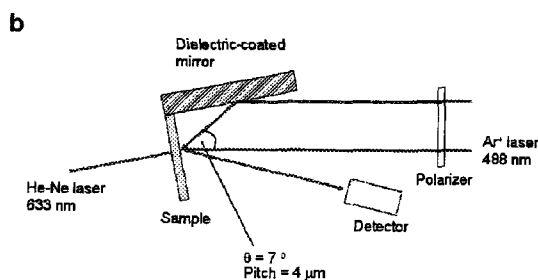
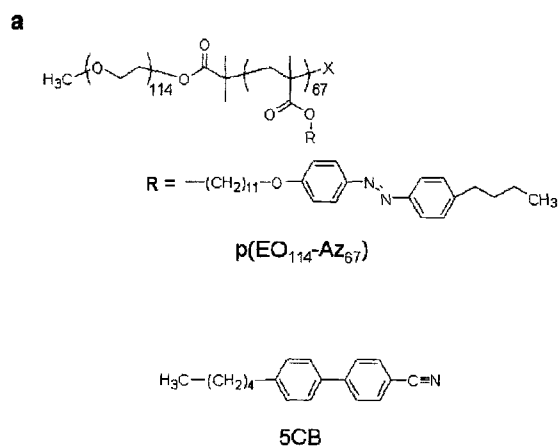
It is only recently that the Az-containing block copolymers have been targeted for the study of photoinduced mass transport. Frenz et al.<sup>11</sup> synthesized polystyrene-*block*-Az-containing polymer and compared the mass transport

behavior with that of a random copolymer or an Az-homopolymer. They found that the architecture of block copolymer severely impede the mass migration motions despite the fact that the mass transport is induced for the random copolymer of the same composition. Yu et al.<sup>12</sup> investigated poly(ethylene oxide)-*block*-liquid crystalline Az polymer. For their system, the mass transport is actually induced by light, however, interference beam of relatively high intensity (50 mW cm<sup>-2</sup>) is required. Furthermore, without annealing the surface relief modulation is at a few percent level of the total film thickness. We show herein that highly efficient photo-triggered mass migration is attained for a poly(ethylene oxide)-*block*-liquid crystalline Az polymer<sup>13,14</sup> when a low-molecular-mass liquid crystal, 4'-phenyl-4-cyanobiphenyl (5CB) is incorporated. The chemical structure of the materials are indicated in Figure 1. This method is formerly performed for an Az-containing random copolymer.<sup>9</sup> This paper shows the wider applicability and validity of this procedure.

### 2. EXPERIMENTAL

#### 2.1 Preparation of thin hybrid films

The diblock copolymer used in this study possesses the unit numbers of PEO and the Az polymer of 114 and 67, respectively ( $M_n = 34800$ ,  $M_w = 38400$ ,  $M_w/M_n = 1.10$ , smectic X 66.9 smectic C 95.9 smectic A 119 isotropic, denoted as p(EO<sub>114</sub>-Az<sub>67</sub>)). Synthesis and characterizations were described in the previous paper.<sup>13,14</sup> The thin hybrid films containing p(EO<sub>114</sub>-Az<sub>67</sub>) and 5CB were spin-coated from a



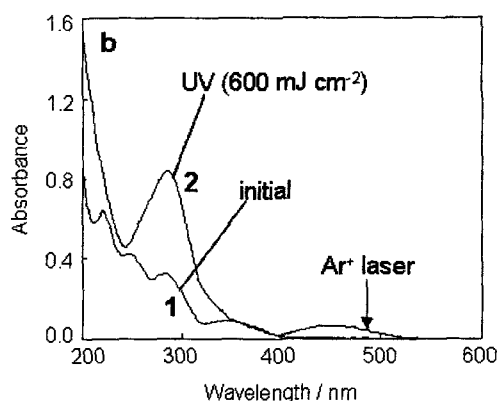
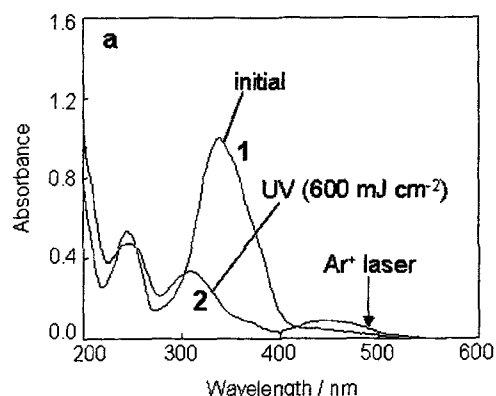
**Figure 1** a) Chemical structure of  $\text{p}(\text{EO}_{114}\text{-Az}_{67})$  and 5CB. b) Schematic illustration of the experimental setup for the holographic recording by the argon ion laser beam.

chloroform solution at a given molar fraction ( $f$ ) ( $f = [\text{5CB}]/([\text{Az unit}] + [\text{5CB}])$ ) onto a clean quartz glass substrate and baked at 60 °C for 5 min to remove the residual solvent. The film thickness of the films was measured by atomic force microscopy (AFM, Nanopics 2100, Seiko Instruments, Inc). The film was scratched with a needle, and the height difference between the exposed substrate surface and the film surface was estimated.

UV-visible absorption and transmission spectra were recorded on a Hewlett Packard 8452A diode array spectrometer.

### 2.2 Formation of surface relief structure

The set up for holographic recording experiment is sketched in Figure 1b. In advance of holographic recording, UV light (365 nm) irradiation was performed with a San-ei Supercure-202S to induce photoisomerization to the cis-rich state. Onto this film the holographic irradiation was performed with a coherent argon ion ( $\text{Ar}^+$ ) laser (Omnichrome 543R-AP-A01, 488 nm). The half of the beam was reflected by a dielectric-coated mirror, and the interference state was made with a direct beam at the film

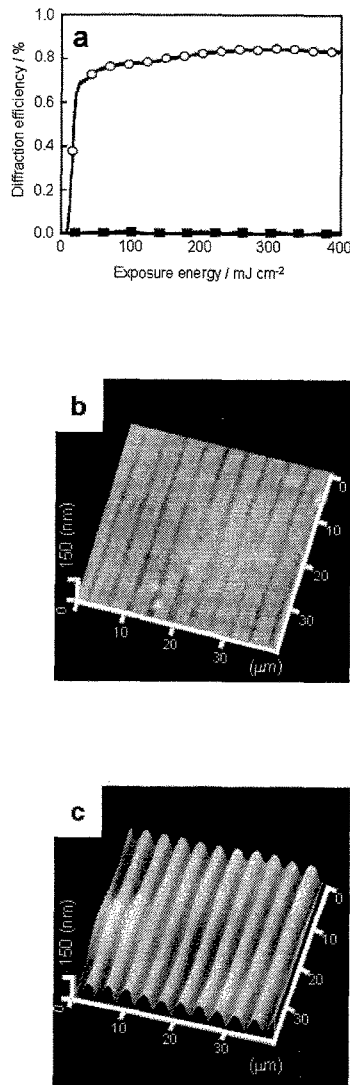


**Figure 2** UV-visible absorption spectra. a) the  $\text{p}(\text{EO}_{114}\text{-Az}_{67})$  film and b) the  $\text{p}(\text{EO}_{114}\text{-Az}_{67})/\text{5CB}$  hybrid film ( $f = 0.5$ ) before (1) and after UV light exposure (2).

surface. Formation of surface relief structure was confirmed by intensity measurement of the first-order diffraction of a He-Ne laser beam (NEC GLC 5700) on the transmittance mode with an optical power meter (Advantest TQ82190). The topographic image was also observed with a Nanopics 2100.

### 3. RESULTS AND DISCUSSION

A spin-cast films of pure  $\text{p}(\text{EO}_{114}\text{-Az}_{67})$  and  $\text{p}(\text{EO}_{114}\text{-Az}_{67})$  with 5CB at  $f = 0.5$  were prepared from chloroform solutions. The initial thickness of these hybrid films were ca. 180 nm. The exposure to the interferometric argon ion beam (488 nm) was performed after pre-irradiation of UV light (365 nm). Therefore, the photoreactivity was first evaluated by UV-visible absorption spectroscopy. Figure 2 shows the spectral changes of the pure  $\text{p}(\text{EO}_{114}\text{-Az}_{67})$  film (a) and the  $\text{p}(\text{EO}_{114}\text{-Az}_{67})/\text{5CB}$  hybrid film (b) before and after UV light exposure. In both cases, the  $n-\pi^*$  transition band around 440 nm was enhanced, indicative of the efficient proceeding of the trans-to-cis photoisomerization. The holographic irradiation described below was performed from

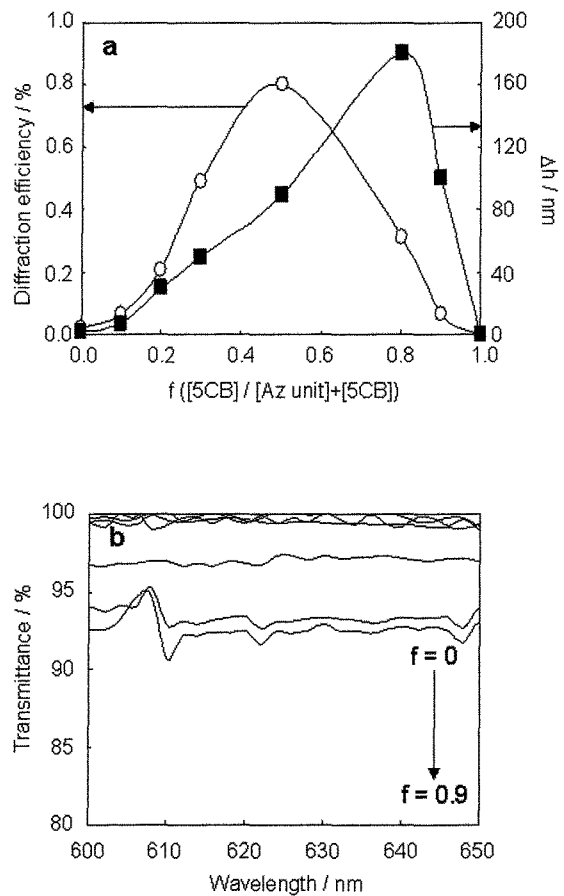


**Figure 3** a) First-order diffraction efficiency of the p(EO<sub>114</sub>-Az<sub>67</sub>) film (■) and the p(EO<sub>114</sub>-Az<sub>67</sub>)/5CB hybrid film (*f* = 0.5) (○) with exposure energy. b) and c) Topographic AFM images (40 × 40 μm) of photogenerated relief structure in the pure p(EO<sub>114</sub>-Az<sub>67</sub>) film and the p(EO<sub>114</sub>-Az<sub>67</sub>)/5CB hybrid film (*f* = 0.5).

the cis-rich photostationary state.

Figure 3a displays the enhancement of the first-order diffraction efficiency with exposure energy evaluated with a He-Ne laser beam, which monitors the surface relief structure formation. The effect of addition of 5CB was obvious. For the hybrid film (*f* = 0.5), diffraction efficiency reached up to 0.80 % at 220 mJ cm<sup>-2</sup>, corresponding to 110 s exposure at 2 mW cm<sup>-2</sup>. After this point the efficiency remained constant. In contrast, the enhancement of the diffraction efficiency for the film without 5CB was negligible (0.07 %).

Figure 3b and 3c show the topographical



**Figure 4** a) The first-order diffraction efficiency (○) and surface modulation depth (■, Δ*h*) of the p(EO<sub>114</sub>-Az<sub>67</sub>)/5CB hybrid films with various 5CB fractions (*f*). b) Visible transmission spectra of the p(EO<sub>114</sub>-Az<sub>67</sub>)/5CB hybrid films with various 5CB fractions (*f*).

AFM images of the pure (EO<sub>114</sub>-Az<sub>67</sub>) film and in the hybrid film (*f* = 0.5) exposed with the interferometric Ar<sup>+</sup> laser beam at 2 mW cm<sup>-2</sup> for 200 s. As shown, the pure film provided little undulation (b), and the hybrid one gave large undulation in accord with the interference periodicity (4 μm for this case) (c). The height from the top to valley reached 90 nm, clearly indicating that a very efficient mass transport took place seeing from the initial thickness of 180 nm. The marked enhancement of the mass transfer should be the result of strong synergy motions of the Az polymer and 5CB in the plasticized film.<sup>9</sup>

Figure 4a shows the first-order diffraction efficiency (○) and surface modulation depth (■, Δ*h*) of the films at various molar fractions (*f*) of 5CB. Starting from *f* = 0, the increase of 5CB content enhanced the diffraction efficiency. The maximum efficiency was obtained at *f* = 0.5 and above this point it was reduced. With respect to the undulation height (Δ*h*), on the other hand, the maximum value was observed at *f* = 0.8. These

results can be compared with those obtained for the random copolymer system<sup>9</sup>, where both profiles of the diffraction efficiency and undulation height coincided with each other. At present, we infer that this discrepancy is caused by light scattering of He-Ne laser beam in hybrid films. Figure 4b shows the transmission spectra of the hybrid films at 600 – 650 nm various fractions of 5CB. The transmittance of hybrid films decreased, i. e., the film became turbid with the increase of 5CB content. The light scattering can reduce the diffraction efficiency than the actual value. A phase separation of pure 5CB in the polymer matrix should occur at high  $f$ . Therefore, we regard that the optimal mixing ratio is  $f = 0.5$ , and this condition will be adopted for further investigation.

#### 4. CONCLUSIONS

For pure p(EO<sub>114</sub>-Az<sub>67</sub>) film, no surface relief formation is admitted. When a low molecular mass liquid crystal, 5CB, is incorporated, highly efficient mass migration occurred by cooperative motions of the constituents. The full mass migration is attained at a dose of 220 mJ cm<sup>-2</sup>, which is rather large but almost comparable to the random copolymer system.<sup>9</sup> By varying the molar fraction of 5CB, the optimal fraction is found to be  $f = 0.5$ . Based on the knowledge obtained here, our work is now underway for evaluation of microphase separation structure of the block copolymer film.

#### ACKNOWLEDGMENT

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