Optical Control of Microphase Separated Nanostructures in Polystyrene-Based Liquid Crystalline Diblock Copolymer Thin Film

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Develop of alignment control methods of microphase separated nanostructures in copolymers has been a subject of great demand. This paper shows the novel optical process for alignment control of nanostructures in a diblock copolymer composed of polystyrene and polymethacrylate with a liquid crystalline azobenzene-side chain. The aligned nanostructures were formed by exposure to linearly polarized light and subsequent annealing at suitable temperature. Exposure to interferometic argon ion laser beam also led to uniform alignment of nanodomains involved in a surface relief structure via photo-triggered mass migration with assist of liquid crystal.

Key words: Block copolymer, Azobenzene, Photoalignment, Photo-triggered mass migration, Liquid crystalline polymer

1. INTRODUCTION

Diblock copolymers consisting of two different polymer segments provide microphase separated nanostructures of lamellar, cylinder or sphere at a nanometer scale, through selfassembly [1]. These structures have been noticed as the materials possessing large potential for performance devices [2]. Practical high applications to nanotechnology using such nanostructures require on-demand macroscopic and patterned alignment. Thus, several methods for alignment control of nanostructures have been investigated. The external field and [3] chemically or topologically surface patterned substrates [4-8] have been applied to fulfill the requirement to align the nanodomains. Quite recently, photoalignment [9] and 3D photopatterning [10] of nanocylinder structures has been demonstrated by using diblock copolymers consisting of poly(ethylene oxide) (PEO) and polymethacrylate with an azobenzene (Az) mesogenic group. This optical manipulation by linearly polarized light (LPL) irradiation is about by the angular selected brought photoreaction [11-13] of Az side chains and the cooperative orientation effect of liquid crystal mesogens. The resulting structure has a feature that Az mesogenic chromophores and PEO cylinders are oriented parallel with each other and perpendicular to the electric field vector of irradiated LPL. This indicates that the anisotropic motions of liquid crystal (LC) mesogens are reflected to the nanostructures.

For fabrication of thermally and mechanically stable materials, a diblock copolymer composed of photosensitive LC polymer and polystyrene (PS) bearing higher glass transition temperature (T_g) in comparison with PEO is an attracting target to be aligned [14]. To date the alignment control of microphase separated nanostructures by application of an external field has been performed [15,16].

We show herein the photoalignment control of PS nanostructures in a diblock copolymer connected with an Az-containing polymer, denoted as $p(S_{226}-Az_{56})$, where the indices indicates the number of each unit (Fig. 1). Furthermore, it is found here that flow induced alignment control of nanostructures is also available via phototriggered mass transport caused by holographic irradiation in thin film to $p(S_{226}-Az_{56})$.

2. EXPERIMENTAL

2.1 Materials

Tetrahydrofuran (THF) and anisole as solvents were distilled over sodium with a trace of benzophenone. Styrene was purified by distillation to remove an inhibitor for polymerization before use. Catalyst CuBr (Kanto Chem. Co., Japan) was washed with acetic acid containing a drop of HCl solution and diethyl ether for several times, and dried in vacuum. Other compounds were used without further purification.

2.1.2 Preparation of macroinitiator of polystyrene (PS-Br)

In the flask was charged with 34.0 mg of CuBr, degassed and filled with N₂ gas. An anisole solution (1 ml) dissolving 3.00 g of styrene, 17.6 μ m of 1-phenylethyl bromide and 75.0 mg of 2,2'-bipyridyl were degassed, filled with N₂ gas and added through a syringe. The mixture was degassed by freeze-pump-thaw procedure and

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Fig.1 Chemical structure of $p(S_{226}-Az_{56})$ and 5CB.

sealed under vacuum. The flask was placed in an oil bath at 110 °C for 20 h. The reaction mixture was dissolved in THF and passed through alumina column to remove Cu catalyst. After being concentrated, The THF solution was poured to methanol to remove styrene monomer. The final product was dried under vacuum. $M_n = 23500$ with $M_w/M_n = 1.07$.

2.1.3 Preparation of Az monomer

The synthesis of Az monomer was performed according to the following procedure. First, 4-[(4'-Pentylphenyl)azo]phenol (5AzOH) was synthesized by the diazo-coupling reaction of 4-pentylaniline with phenol in the presence of sodium nitrate and hydrochloric acid. Second, 4-(10-hydroxydecyloxy)-4'-pentylazobenzene

(5Az10OH) was synthesized by the Williamson ether synthesis of 5AzOH with 10-bromodecanol in the presence of potassium carbonate and potassium iodide. The product was reacted with methacryloyl chloride to obtain 4-(10-methacryloydecyloxy)-4'-pentylazobenzene (Az monomer). The Az monomer was obtained as a yellow solid. 2.1.4 Preparation of Az-containing diblock copolymer ($p(S_{226}-Az_{56})$)

Anisole (1 ml) dissolving 59.0 mg of PS-Br, 380 mg of Az monomer and 6.90 mg of 1,1,4,7,10,10-hexamethyltriethylenetetramine was charged into a ample tube. After freezepump-thaw cycles for several times, 4.30 mg of CuBr was immediately inserted in the ample tube. The mixture was degassed by freeze-pump-thaw procedure and sealed under vacuum. The flask was placed in 70 °C oil bath for 16 h. The solution was passed through an alumina column with chloroform. The solution was concentrated and precipitated in hexane, methanol and finally in hot hexane (60 °C). The precipitation process in each solvent was repeated twice. The final product was dried under vacuum. Yield: 50 mg. 2.2 Characterizations

Molecular weight and polydispersity were measured by gel permeation chromatography (GPC) using a liquid chromatograph (Shodex UV-41) with an appropriate combination of columns (Shodex KF-803L and Shodex KF-805L). THF was used as eluent, and polystyrene standards were used for calibration. Differential scanning calorimetric (DSC) measurements were performed with a Seiko Instrument DSC6200 /EXSTAR6000. ¹H-NMR spectrum was recorded



Fig.2 DSC chart of the $p(S_{226}-Az_{56})$ in a heating process. Heating rate: 10 °C/min.

on a JEOL 270GXS instrument spectrometer operating at 270 MHz. p(S226-Az56) thin films were prepared from a chloroform solution onto a hydrophilic quartz glass substrate and baked at 60 °C for 5 min to remove residual solvent. The thin hybrid films containing 4'-pentyl-4-cyanobiphenyl (5CB) were spin-coated from a chloroform solution at a given molar mixing ratio (f =[5CB]/[Az]) of unity. The surface morphologies and film thickness of the films were evaluated by atomic force microscopy (AFM) using a Seiko Instrument SPA400/SPI3800N system in the dynamic force mode (phase and topographic modes). UV light (365 nm) and lineally polarized light (436 nm, LPL) irradiation were performed with a San-ei Supercure-202S. Polarized UV-visible absorption spectra were recorded on a Hewlett Packard 8452A diode array spectrometer equipped with a polarizer unit.

2.3 Holographic irradiation

The experimental setup for the holographic recording has been described previously [17]. UV light (365 nm) irradiation was first performed to undergo the photoisomerization to the cis-rich state. Onto this film the holographic irradiation was performed with a coherent argon ion (Ar^+) laser using an Omnichrome 543R-AP-A01 (488 nm). The half of the beam was reflected by a mirror, and the interference state was attained by mixing with the direct beam at the film surface.

3. RESULTS AND DISCUSSION

3.1 Photoalignment of microphase separated structure

The block copolymer, p(S₂₂₆-Az₅₆), was synthesized according to the atom transfer radical polymerization (ATRP) method. The resulting polymer possessed the unit numbers of PS and Az polymer of 226 and 56, respectively, with polydispersity of 1.22 based on the GPC and NMR measurements. The weight fraction of Az polymer was 0.54. Figure 2 shows a DSC chart of the $p(S_{226}-Az_{56})$. This polymer exhibited the glass transition temperatures (T_g 's) at 43 °C and 102 °C for the Az polymer block and polystyrene block, respectively, indicating that the polymer formed a microphase-separated state. The transition temperatures of the Az-containing polymer were



Fig.3 UV/VIS absorption spectra of the LPL irradiated $p(S_{226}-Az_{56})$ films after annealing at 100 °C (a) and 107 °C (b). Spectra 1; as -cast film. 2 and 3 display polarized spectra taken with probing beam perpendicular and parallel to the polarization direction of the actinic irradiating 436 nm light. In c and d, phase mode AFM images (3.0 x 3.0 μ m) of the corresponding films annealed at 100 °C (c) and 107 °C (d) were shown. Fast Fourier transform spectrum is inserted in the each AFM image.

60 °C (Sm_X-to-Sm_A) and 115 °C (Sm_A-to-iso).

Two film samples of p(S₂₂₆-Az₅₆) having film thickness of ca. 300 nm were prepared by spin-coating. Onto these films without 5CB, the LPL exposure (436 nm) was performed at 2.0 mW cm⁻² for 50 min at 130 °C, followed by gradual cooling at 2 °C min⁻¹ to 30 °C. One of the irradiated films was annealed at 100 °C, below both T_{g} of PS block and the transition temperature of Sm_A to isotropic of the Az polymer block, for 12 h [16]. The other film was annealed at 107 °C above T_g of PS block and below the transition temperature of Sm_A to isotropic transition of the Az polymer block, in the same manner. Figures 3a and 3b show polarized UV-visible absorption spectra of the thin $p(S_{226}-Az_{56})$ films annealed at 100 °C and at 107 °C, respectively. Both LPL-irradiated films after annealing exhibited large in-plane anisotropy of Az mesogenic groups. The absorption band peaking at 338 nm became larger and smaller when observed with polarized light in orthogonal $(A\perp, 2)$ and parallel $(A_{ij}, 3)$ to the polarization direction of the pre-irradiated LPL, respectively, showing that Az chromophores are highly oriented orthogonal to the electric field



Fig.4 AFM image of the $p(S_{226}-Az_{56})$ film after interferometric irradiation with (p-: p-) mode Ar+ laser beam. Topographic AFM image (a, 10 x 10 µm) of a photogenerated relief and a magnified phase mode image (b, 3.0 x 3.0 µm) of hill to valley slope area. Fast Fourier transform spectrum is inserted in b.

vector of LPL.

Figures 3c and 3d display the surface morphologies $(3.0 \times 3.0 \mu m)$ of the corresponding films evaluated by the phase mode AFM measurements. Both films gave the periodic nanostructure of ca. 80 nm. The film annealed at 100 °C provided a randomly arranged fingerprint-like nanoscale periodic structure (c), whereas the periodic nanostructure was preferentially oriented perpendicular to the electric field vector of LPL (d). As shown, the annealing at 107 °C above T_g of polystyrene and in Sm_A phase of the Az polymer was required for the evolution of photoaligned structure. These results indicate that sufficient segmental motions in polystyrene are of essence for the modulations of microphase separated nanostructures. Comparisons with the spectral data and morphologies in Fig. 3 leads to important conclusions that the photoorientation of the Az mesogenic group by LPL irradiation is readily attained, but that the alignment of microphase structure of the larger hierarchical size is only attained when the light-inert polymer segment has sufficient flexibility above T_{g} . 3.2 Surface relief formation

Frenz et al. [18] demonstrated that the block architecture of copolymer severely hinders the surface relief formation via photoinduced mass transport in comparison with the behavior of a statistical copolymer of the same composition. Therefore, attempts for surface relief formation of $p(S_{226}-Az_{56})$ are a challenging subject. In this work, the mass transport of the film of $p(S_{226}-Az_{56})$ was examined by hybridization with 5CB since our previous work revealed that this method is quite effective to induce mass migration [19]. The addition of 5CB gives a decrease in the phase transition temperature, resulting in an increase in the segmental mobility of polymer chains [20]. A spin-cast film of ca. 100 nm thickness was prepared for a mixture of $p(S_{226}-Az_{56})$ and 5CB at f = 0.8, and holographic irradiation was performed as mentioned in the experimental section. The increase in 5CB content gave rise to enhancement of the

undulation height. The maximum hight was obtained at f = 0.8. Here, the interferometric Ar⁺ laser beam was subjected to the film at 2 mW cm⁻² for 2500 s. The electric field vector of the irradiated beam was parallel to the plane of incidence ((*p*-, *p*-) mode). As shown, the hybrid film provided clear undulations in accord with the interference periodicity (4 µm for this case). The hill-to-valley height difference was 35 nm.

Figure 4b show the phase-mode AFM images $(3.0 \ \mu m \ x \ 3.0 \ \mu m)$ taken at the slope area from a hill to valley. The microphase separated nanostructures were tend to be aligned perpendicular to the undulated structure of the micrometer level. Contrary to our expectation, the direction of the microphase separated structure was aligned parallel to the polarization direction of irradiated LPL, which is in contrast the result shown in Fig.3d. This contradicting data should suggest that the mass flow induces the orientation of nanostructures in this case. Yokoyama et al. [21] reported the macroscopic orientation of cylindrical nanodomains in relief structure of poly-(ethylene propyrene)-block-polystyrene film obtained by soft molding method. The microphase separated cylinders of this polymer is aligned after pressing a grating patterned poly(dimethylsiloxane) (PDMS) mold followed by annealing above T_g of this polymer. The nanocylinders are aligned perpendicular to the edge of hill. This phenomenon can be interpreted as the consequence of pressure induced flow of the film mass during the pressing. In our case, the same flow induced orientation effect seems to be observed, aligning the microphase separated structure along the mass flow. The present system is unique in that the mass flow is caused by light irradiation, and not by mechanical pressure.

4. CONCLUSIONS

In this study successful control of microphase separated nanostructures of the diblock copolymer film composed of PS block and Az polymer one was achieved. The nanostructure could be photoaligned in the conditions that the LPL irradiation was achieved at temperature above T_g of PS block and below the transition temperature of Sm_A to isotropic of the Az polymer block. The photo-triggered mass migration was observed for the polystyrene-containing block copolymer for the first time by hybridization with a lowmolecular-mass LC molecule. The microphase separated nanostructures are governed by the flow induced orientation in this case and not by the electric field of the actinic LPL. These optical manipulations for the block copolymer may open new opportunities for fabrication of nanostructured materials and devices.

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