Direct TEM Observation of Perpendicularly Oriented Nanocylinder Structure in Amphiphilic Liquid Crystalline Block Copolymer Thin Film

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Abstract   A series of amphiphilic liquid crystalline diblock copolymer consisting of poly(ethylene oxide) as hydrophilic segment **(pEO)** and poly(methacrylate) containing azobenzene moiety as hydrophobic liquid crystalline segment **(pMA(Az))** have been synthesized and characterized. Hexagonally arranged **pEO** dot structures of periodicity from 10 to 20 nm were observed on the surfaces of the annealed thin films on quartz and PET substrates by atomic force microscopy (AFM). Hexagonally arranged cylinder **(HAC)** structures perpendicular to the film plane in the annealed thin films were directly observed by transmission electron microscopy (TEM) in cross-sectional view. The **pEO** dot structures observed in AFM surface images correspond to (001) faces of the perpendicularly oriented **HAC**. Furthermore, small lamellar structures with a period of ca. 3.0 nm were observed inside the **pMA(Az)** domain. The lamellar structures were assigned to the smectic layers, independently confirmed by small-angle X-ray scattering (SAXS) measurements. The azobenzene mesogens in the **pMA(Az)** domain were aligned perpendicular to the smectic layers, verified by ultraviolet-visible absorption spectra (UV spectra) measurements. The alignment of the azobenzene mesogen in smectic layer looks to be correlated with the orientation of **pEO HAC** array found in the annealed thin film. These orientational correlations may provide significant information on the orientation control of the nanostructures.

Keyword: Block copolymer, Microphase separation, Cross sectional TEM image, Smectic layer, Perpendicular orientation

Introduction

In recent years, there have been intensive researches on block copolymer thin films due to their tremendous potential for nanostructures to be applied widely, since diblock copolymers form periodic structures on the tens of nanometer length scale[1,2]. In principle, the size and morphology of microphase-separated domains can be controlled by the volume fractions of the individual segments which the block copolymers consist of.

In addition to conventional studies of the microphase-separation, strong molecular interactions found in liquid crystal, π-conjugated polymer, and so on, have been introduced to realize a wide variety of nanostructures. Such molecular aggregates may play an important role in the phase-segregation to form the nanostructures, so that the resulting hierarchical structures, *i.e.*, *structure-within-structure* in different length scales, are formed as microphase separation[3,4,5,6]. For example, Mao et al. investigated the correlation between the microphase-separated structures and the liquid crystalline structure in a block copolymer polystyrene-*b*-isoprene containing azobenzene mesogen [3]. Ikkara et al. reported another hierarchical structure in the supramolecular block copolymer, *i.e.*, polystyrene-*b*-poly(4-vinylpyridine) hydrogen-bonded to nonadecylphenol [4,5,6]. Along with these studies, the

mesophase must adapt to various domain boundary conditions by embedding the liquid crystalline phase in a polymer matrix with different domain sizes and geometries.

We designed a series of amphiphilic liquid crystalline diblock copolymers, pEO_m-*b*-$pMA(Az)_n$, consisting of poly(ethylene oxide) as hydrophilic segment **(pEO)** and poly(methacrylate) containing azobenzene moiety as hydrophobic liquid crystalline segment **(pMA(Az))**. These multi-functions, i.e., amphiphilicity, liquid crystalline character, and photoisomerization of the azobenzene moiety, have would be exhibited in the individual domains specific to the phase-segregated structure of the block copolymers.

We have systematically synthesized a series of block copolymers, pEO_m-*b*-$pMA(Az)_n$ (m = 40, 114, n =
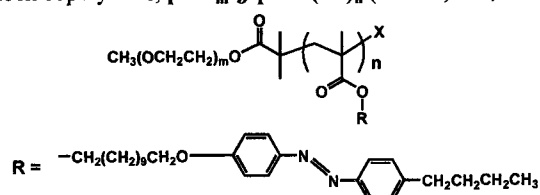

Figure 1   Chemical structure of diblock copolymer, pEO_m-*b*-$pMA(Az)_n$.

$10 \sim 92$), by using atom transfer radical polymerization (**ATRP**) (Figure 1)[7, 8]. The block copolymers were prepared with a range of number-average molecular weights from 12400 to 54200 with narrow polydispersities (ca. 1.1). Their thermal properties showed that the block copolymers exhibit the smectic A, smectic C and undefined smectic X phases in the order of decreasing temperature from the isotropic temperature around 120 °C. In the thin films of **pEO$_m$-b-pMA(Az)$_n$**, highly ordered **pEO** hexagonally arranged cylinder (**HAC**) structures were confirmed consistently by transmission electron microscopic (TEM) observation of thin films stained with RuO$_4$, atomic forced microscopic (AFM) images of the film surface, and small-angle X-ray scattering (SAXS) profiles of thin films and pellets[9]. Based on these observations lead the consistent structure of the **HAC**, the significant information on the nanostructures inside the thin films, *i.e.*, the **pEO** cylinder lengths cause our interest. The structural parameters of smectic layers, *i.e.*, the oriented direction of smectic layer, become important issues to be understood. In this paper, we report to directly verify the phase-separated structures of the thin films by TEM in cross-sectional view. The liquid crystal layer structures are investigated by TEM cross-sectional observations and ultraviolet-visible absorption spectra (UV spectra) measurements.

Experimental section
Materials

Diblock copolymer, **pEO$_{114}$-b-pMA(Az)$_{48}$** used in this study, was synthesized by **ATRP** method from the **pEO$_{114}$** macroinitiator[8]. The number average molecular weights of **pEO** and **pMA(Az)** segments were 5000 and 24000 respectively, evaluated by ^{1}H NMR. The polydispersity was 1.09 estimated by GPC[10], and the **pMA(Az)** weight fraction was 0.83.

The quartz and PET substrates were cleaned by successive immersion into pure ethanol and distilled water under sonication for 5 min each. The substrates were dried by nitrogen gas flow. The water contact angles of the cleaned quartz and PET substrates were ca. 40° and ca. 80°, respectively.

Small-angle X-ray scattering (SAXS)

The temperature-dependent SAXS measurements with DSC profiles were carried out at the beam line 10C, Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan. The wavelength of monochromator X-ray for SAXS was 0.1488 nm. The scattering X-ray was detected by a one-dimensional position sensitive proportional counter (PSPC, 512 channels, Rigaku Co. Ltd.). The distance between sample and PSPC was 980 mm, which covered $0.15 < q = 4\pi\sin\theta/\lambda < 3.00$ nm^{-1}. The pellet samples of the block copolymers were annealed at 140 °C in the isotropic phase for 24h.

Atomic force microscopy (AFM)

The spin-coated films of the block copolymer **pEO$_{114}$-b-pMA(Az)$_{48}$** were prepared from 2 wt% toluene solution onto the quartz and PET substrates. The samples were annealed at 110 °C (smectic phase) for 24 hour. Tapping mode AFM (SPM-9500 J2: Shimadzu Corporation) measurement was performed to image surface nanostructures of the block copolymer thin films
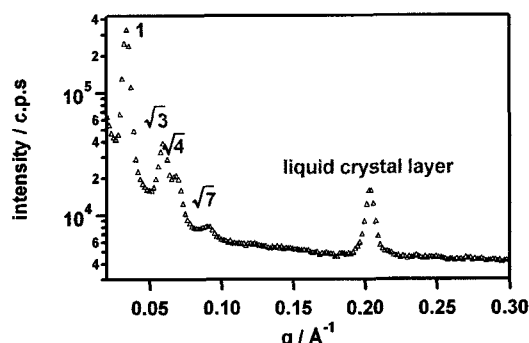

Figure 2   SAXS data for **pEO$_{114}$-b-pMA(Az)$_{47}$** obtained after cooling from isotropic phase to 25 °C.

with commercially available cantilevers (Nanodevice). The manufacturer's values for the probe tip radius and force constant are < 10 nm and 5 Nm^{-1}, respectively. Topographic images were obtained simultaneously using a resonance frequency of approximately 150 kHz for the probe oscillation.

Transmission electron microscopy (TEM)

For TEM in cross-sectional view, spin-coated films of the block copolymer **pEO$_{114}$-b-pMA(Az)$_{48}$** were prepared from 2 wt% toluene solution onto the PET substrates. The films were annealed at 140 °C (isotropic phase) for 24 hour and exposed to RuO$_4$ vapor at room temperature for 3 min to selectively stain the **pEO** block. The films with the PET substrate were embedded with epoxy resin (Technical Date Sheet 127, Polysciences, Inc.) after curing at 70 °C for 8 hour. Thin sections of the epoxy-embedded sample were obtained by using a Ultra Microtome (Ultracut UCT: Leica corporation) with a diamond knife. TEM observation was performed on a Hitachi H7000 operating at 100kV.

Ultraviolet-visible absorption spectra (UV-vis spectra)

The UV spectra of the spin-coated thin films onto quartz and PET substrates before and after annealing at 110 °C (smectic phase) for 24 hour were recorded on a Shimadzu UV-3100S spectrophotometer.

Results and discussion
Nanostructures in the bulk

The typical example of SAXS profiles of **pEO$_{114}$-b-pMA(Az)$_{47}$** after cooling from the isotropic phase to 25 °C was shown in Figure 2. A sharp peak from a microphase–separated structure appears at $q = 0.034327$ Å^{-1}, corresponding to 21.0 nm of the (001) periodicity (equivalent to 18.2 nm of lattice constant of the hexagonal cylinder). Weak higher-order peaks at $\sqrt{3}$, $\sqrt{4}$, and $\sqrt{7}$ indicate that the morphology should be the **HAC**. Another Bragg peak is observed at $q = 0.20284$ Å^{-1}, assigned to the spacing of the smectic layer in the **pMA(Az)** domain. The spacing of the smectic layer was $d = 3.10$ nm, consistent with the length (3.37 nm) of the fully extended conformer of the **pMA(Az)** side chain, calculated by MM2 force field method. The SAXS profiles indicated the **HAC** structures as the microphase-separated structures of other **pEO$_m$-b-pMA(Az)$_n$** diblock copolymers (e.g. m = 40, 114, n = 10 ~ 92)[9].

Figure 4 TEM cross sectional image of pEO₁₁₄-*b*-pMA(Az)₄₈ spin-coated film on PET substrates after annealing at 140 °C for 24 hour. The film was stained with RuO₄ before ultramicrotome cutting.

Figure 5 UV spectra of pEO₁₁₄-*b*-pMA(Az)₄₈ spin-coated films on the (A) quartz and (B)PET substrates (a) before annealing and (b) after annealing at 110 °C for 24 hour.

Figure 3 AFM topological images of pEO₁₁₄-*b*-pMA(Az)₄₈ spin-coated films after annealing at 110 °C for 24 hour (A) on quartz and (B) PET substrates.

Surface morphology of thin film

Thin films of pEOₘ-*b*-pMA(Az)ₙ were usually prepared on the Si wafer, mica, and quartz substrates. A PET substrate, which can be cut with the microtome, was used for the direct observation of cross sections in the thin films. The AFM topological images of the surface of the thin films after annealing on quartz and PET substrates were shown in Figure 3. Hexagonally arranged dark brown dot structures were observed in the thin films on either quartz or PET substrates (Figure 3A and 3B). The dot structure can be regarded as the (001) faces of the **pEO HAC** structures perpendicular to the substrates, as reported in our previous papers[7, 8, 9]. The distance between the nearest cylinders was ca. 20 nm, in good agreement with the value obtained from SAXS. The consistent nanostructures were reproducible in the spin-coated thin films on mica, quartz, and Si wafer, which should be noticed as the remarkable microphase-separated structures of the present block copolymers.

Cross-sectional TEM observation of nanostructures

Figure 4 shows a cross-sectional TEM image of the thin film on the PET substrate. The **pEO** domains as
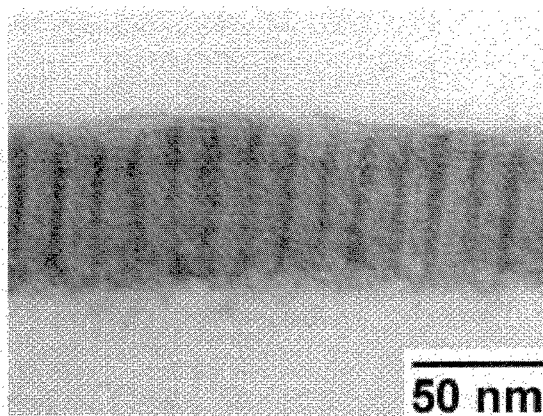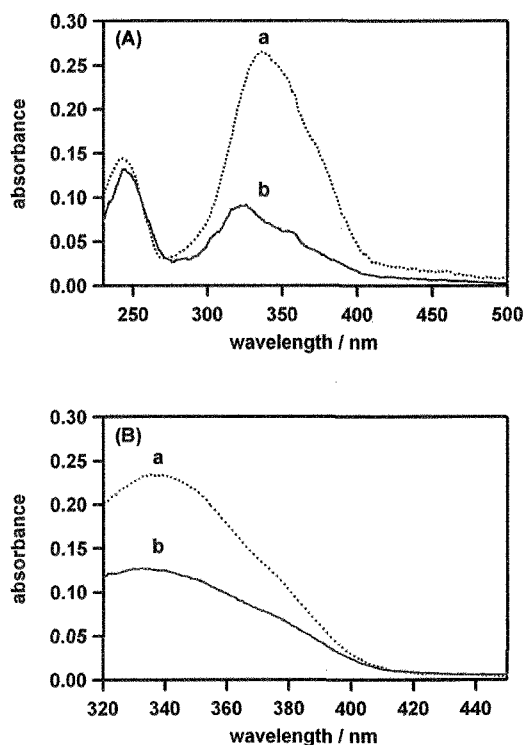
darker cylinders were selectively stained with RuO₄. The image clearly shows the perpendicular orientation of the **HAC** structures to the substrate, which run through over 70 nm of film thickness to both surfaces. In the **pMA(Az)** domains, the small lamellar structures with a period of ca. 3 nm are observed between the cylinders. The 3 nm periodicity of the lamellar structures is in good agreement with the spacing of the smectic layer from the SAXS measurements and the calculated length (3.37 nm) of the fully extended conformer of the **pMA(Az)** side chain. Therefore the small lamellar structures were assigned to the smectic

layer of the **pMA(Az)** domain. In other words, the homeotropic alignment of the azobenzene side-chains in the **pMA(Az)** domain was achieved in the smectic phase after annealing. As a result, the hierarchical structure is demonstrated in the present block copolymer thin film.

Alignment of azobenzene mesogen

Since the transition dipole moment of the lowest energy π-π^* transition (360 nm) of azobenzene lies in parallel with the longitudinal molecular axis, the 360 nm π-π^* absorbance of the azobenzene moiety in the film should be a good probe to reflect the direction of the longitudinal molecular axis in the films toward the incident monitoring light beam[11]. Figure 5 shows the UV spectra of the spin-coated films before and after annealing on quartz and PET substrates. An as-prepared thin film before annealing exhibited an absorption maximum at 337 nm assigned to the π-π^* long axis transition of the azobenzene mesogen on quartz substrate (Figure 5A). After annealing at 110 °C for 24h, the absorption maximum was 15 nm blue-shifted, implying a strong H-aggregation of the azobenzene mesogen[12]. During the annealing, the absorbance of thin film decreased down to about 30%, indicating homeotropic alignment of the azobenzene mesogen to the substrate. The similar spectral change after annealing was observed in the thin film on PET substrate, which is served for cross sectional TEM observation (Figure 5B). Compared with the degree of the decreasing absorbances of the π-π^* long axis transition, the azobenzene mesogen of the thin film on the PET substrate was less aligned perpendicular to the film plane than the film on quartz substrates. The homeotropic alignment of the azobenzene mesogen is consistent with the lamellar structure parallel to the film plane, in which the azobenzene mesogen is aligned perpendicular to the smectic layer.

Conclusion

We directly observed the **pEO HAC** structures of thin films by cross-sectional TEM and clearly verified the **pEO HAC** structures perpendicular to the film plane, which run through over 70 nm of film thickness to both surfaces. The cross-sectional TEM observations showed the smectic layer structures with a period of ca. 3 nm in **pMA(Az)** domains. The homeotropic alignment of the azobenzene mesogen to the film plane is confirmed by the UV spectral change after annealing, consistent with the smectic layer structure found in TEM cross sectional image. The correlation between the alignment of the azobenzene mesogen and orientation of the **pEO HAC** structures may provide significant information on the orientation control of nanostructures.

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