Alignment of Self-Organized Nanocylinder Array Structure in Amphiphilic Liquid Crystalline Block Copolymer 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) with azobenzene liquid crystalline side chains as hydrophobic segment **(PMA(Az))** was synthesized for the phase-separated nanostructure. By atomic forced microscopy (AFM) and transmission electron microscopy (TEM), hexagonally-arranged PEO cylinder **(HAPC)** structures were observed with perpendicular alignment to the substrate in the annealed thin films at 110 °C for 24 hrs. The azobenzene mesogens forming the smectic layers in the PMA(Az) domain were aligned perpendicularly to the substrate, verified by UV-vis absorption spectral measurements. The alignment of azobenzene mesogen was found as parallel to HAPC orientation in the thin film. In this paper, we reported the systematical analysis of HAPC orientation in the PEO-*b*-PMA(Az) thin film after annealing in the various kinds of film preparations, using multilateral observations with AFM, TEM, and UV measurements. In the case of a thick film with > 1 μm thickness, the unidirectional orientation was not achieved because of multi-domain structures. The thinner film with 20-60 nm-thickness produced the HAPC parallel to the substrate. In 60-1000 nm-thickness film, the perpendicular orientation of HAPC structure as thermodynamic equilibrium was successfully fabricated by only annealing treatment.
Key words: Block copolymer, Cylinder structure, Orientation, Film preparation

Introduction

The nanometer-scale architectures in thin films of self-assembling block copolymers evince great interest due to their nanodomain structures with the uniform size and shape in the films. The properties of microphase-separation make the block copolymer films attractive for potential applications in nanolithography[1], nanoparticle synthesis[2], and high-density information storage media[3]. The nanostructures in the film, however, lack the orientation of the nanodomains against the substrate as well as the long-range orderness. Most of these practical applications require well-aligned nanostructures with long-range positional order in the film.

We have synthesized a series of amphiphilic liquid crystalline diblock copolymers, **PEO-*b*-PMA(Az)**, consisting of poly(ethylene oxide) as hydrophilic segment **(PEO)** and poly(methacrylate) containing azobenzene liquid crystalline moiety as hydrophobic segment **(PMA(Az))**[4,5] **(Fig. 1)**. The hexagonally-arranged PEO cylinder **(HAPC)** structure can be fabricated in the thin film after annealing at 110 °C for 24 hrs. Additionally, the **PEO-*b*-PMA(Az)** can produce the reliable **HAPC** phase structure in a wide range of the **PMA(Az)** volume fraction, while the typical block copolymers only show hexagonal cylindrical phases in narrow regions[5,6]. The amphiphilic block copolymer can be expected as an attractive nano-template, which is utilized for the selective doping of the metal, ion, and polymerizable monomer and so on. In this work, we developed the fabrication method of well-aligned **HAPC** structure in **PEO-*b*-PMA(Az)** thin film by varying kind of substrates and the film thickness.

The **PEO-*b*-PMA(Az)** formed **HAPC** structure, which gave hexagonal dot pattern on the film surface as (001) face of perpendicular alignment. But the parallel alignment of **HAPC** was rarely observed, when the film preparation was changed. It has been known that kinds of substrate and solvent, solvent evaporation rate, and evaporation process have a strong effect on the alignment of block copolymer phase structures[7,8,9]. Especially, the solvent evaporation is used for controlling the phase structure to the substrate[8]. Only a few studies have reported the multilaterally direct nanostructure analyses, using AFM, TEM, and UV measurement. The systematic
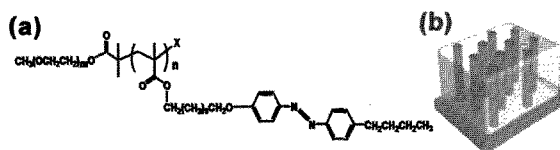
Figure 1 (a) Chemical structure of PEO$_m$-*b*-PMA(Az)$_n$ and (b) illustration of phase-separated PEO cylindrical structure in the thin film.

Table 1 Experimental conditions for film preparation

Run number	Method	Substrate	Film thickness (nm)	Measurement
1	Spin coating	Si	100	AFM
2	Bar coating	Si	500	AFM
3	Casting	Si	1000	AFM
4	Spin coating	Carbon	20-50	TEM
5	Water surface	Water/carbon	20-100	TEM
6	Spin coating	PET	20-100	TEM cross section

analyses of the nanostructures in the thin film are essential for addressing the origin, which results in the phase structures and the alignment. For this purpose, we prepared the thin film of the PEO-*b*-PMA(Az) block copolymer by using (1) spin-coating, (2) bar-coating, (3) casting on the substrate and (4) on the water surface. The observations of nanostructures were carried out by the atomic force microscope (AFM) and transmission electron microscope (TEM).

Experimental section (Table 1)
Materials: Diblock copolymer, PEO_{114}-*b*-$PMA(Az)_{42}$, used throughout this study was synthesized by the atom transfer radical polymerization method from the PEO_{114} macroinitiator[4, 5]. The number average molecular weights of **PEO** and **PMA(Az)** segments were 5,000 and 21,000, respectively, obtained by ^1H NMR. The 1.10 of polydispersity was estimated by GPC, and the **PMA(Az)** weight fraction was 0.80. A 2 wt% of the polymer toluene solution was used for every film preparation.
Substrate: Si wafers, PET film, and quartz plates as substrates were cleaned by successive immersion into pure ethanol and distilled water with ultrasonication for each 5 min. The substrates were dried by nitrogen gas flow. Water contact angles of the cleaned substrates were ca. 20°, 35°, and 80°, respectively. Mica substrates with carbon films were prepared by vacuum vapor deposition method. A copper TEM grid with carbon supporting film (Okenshoji Co., Ltd.) was used as received.
**Film preparation:** (1) The spin-coating was carried out with 2000 rpm for 30 sec. The Si wafer, PET film, quartz, and carbon-coated mica substrates were used for AFM, cross sectional TEM, and TEM, respectively. (2) The bar-coating was conducted by casting the solution to Si wafer and then sliding the substrate surface with wire-bar. (3) The casting film onto Si wafer was prepared by slowly placing the droplet of toluene solution. (4)The casting film onto water surface was prepared by developing the toluene solution and then the resulting thin film was transferred to a copper TEM grid with carbon supporting film. The films on the substrates were annealed at 140 °C (isotropic phase) for 24 hrs. TEM samples were exposed to RuO_4 vapor at room temperature for 3 min in order to selectively stain the **PEO** domains.
Nanostructure Observation: Tapping mode AFM (Nanoscope IV: Digital Instruments Corporation)

measurement was performed to image surface nanostructures of the block copolymer thin films with commercially available cantilevers (TAP300, Nanodevice). Probe tip radius and force constant are < 10 nm and 5 Nm^{-1}, respectively. Both topographic and phase images were obtained simultaneously. TEM observation was performed by a Hitachi H7000 with an acceleration voltage of 100kV. For the preparation of cross-sectional TEM observation, the films on the PET substrate were annealed and stained by RuO_4. The small pieces of the samples were embedded into epoxy resin (Technical Date Sheet 127, Polysciences, Inc.) and then cured at 70 °C for 8 hrs. Thin sections with 60 nm thickness of the epoxy-embedded sample were obtained by using a Ultra Microtome (Ultracut UCT: Leica) with a diamond knife (Diatome 40°). UV spectra of the spin-coated thin films onto quartz substrates were recorded on a Shimadzu UV-3100S spectrophotometer before and after annealing at 110 °C (smectic phase) for 24 hrs.

Result and Discussion
AFM phase images showed characteristic HAPC structures in the surfaces of the spin-coated, bar-coated, and cast film before and after annealing (Fig. 2). The cylinder diameters of 10 ± 3 nm and the periodicity (*L*) of 20 ± 2 nm were found in all films. As-prepared films exhibited dot surface structures (15 ± 4 nm diameter) with poor regularity (Fig. 2a). The similar features were observed in all of as-prepared films. S. Y. Heriot et al. reported that microstructures in spin-coated polymer-blend films of polystyrene and poly(methyl methacrylate) resulted from both phase segregation and dissipative processes[10]. Therefore, nanostructures far from thermodynamical equilibrium state were formed because the evaporation of the solvent in polymer solution takes place in too fast. By SAXS measurements, no diffraction peak assigned to phase-separated structure was detected[11]. After annealing at 140 °C for 24 hrs., the AFM phase images clearly showed highly ordered dot structures in the spin- and bar-coated films, implying perpendicular orientation of HAPC structures (Fig. 2b, c). The dot structures observed reproducibly could be assigned as (100) face of perpendicular aligned HAPC structures in these films. Line structure partly observed in the cast film indicates that the HAPC structure was laid parallel to the substrate surface, i.e., (100) face of HAPC structure. Both the line and dot structures were observed in the cast film after annealing, implying the parallel and perpendicular orientations of HAPC to the substrate as multi-grain structures, respectively (Fig. 2d, e).
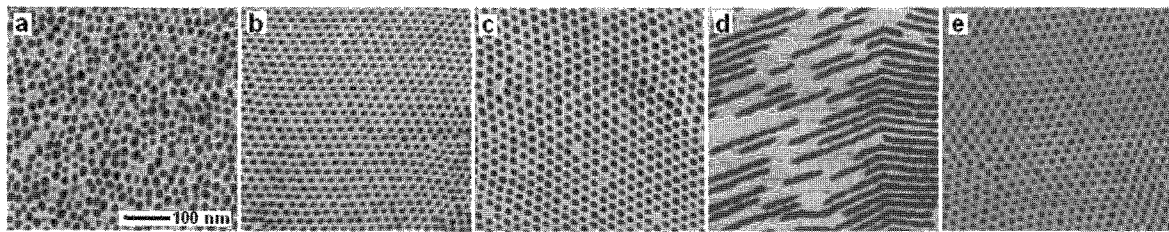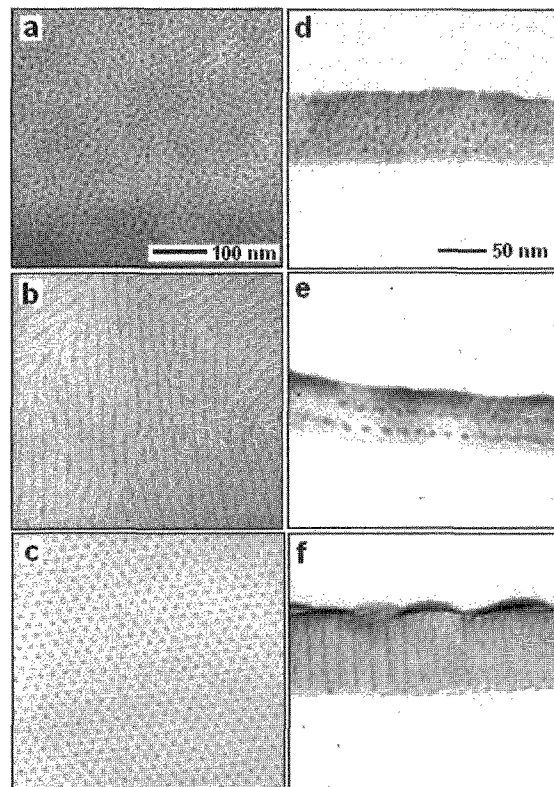
Figure 2   AFM phase images of PEO_{114}-b-$PMA(Az)_{42}$ thin films prepared by (a), (b) spin coating, (c) bar coating, (d), (e) casting the toluene solution. The samples were annealed (a) at r.t. for 24 hrs. and (b)-(e) at 140 °C for 24 hrs.

TEM top view of the spin-coated film before annealing was shown in **Fig. 3a**. The disordered dot structure was observed, supporting AFM results. After annealing, both parallel and perpendicular cylinder structures were observed in 0.2~10 μm grain structures (**Fig. 3b**). The population of the grains with perpendicular and parallel **HAPC** was almost same. In contrast, a perfect perpendicular cylinder structure was observed everywhere in the cast film on water surface (**Fig. 3c**).

These poor reproducibility of the alignment in block copolymer thin film prepared by spin-coated film has been regarded as difficulty for any application, even though the regularity is high in a microscopic view. The discussion on relationship between the sample procedures and the observed nanostructures should be worthwhile significant information for reliable nanostructures. According to the AFM height images, the cast film has a large roughness over the film surface. Remarkably, the perpendicular cylinder structures were observed in relatively thinner films and oppositely the parallel alignment appeared in thicker films. These results suggested that the **HAPC** orientation depends on the film thickness.

We focused here on the cross-sectional TEM images of spin-coated films on PET substrates to reveal the relationship between the film thickness and the **HAPC** alignment through the films. The large grain structure with over 10 μm region was observed throughout the cross-sections. The film thickness was very flat and found as 60 nm in most of the region, except for the area close to edge of substrate. Interestingly, the grains with thinner thickness of 20 nm in the edge of substrate exhibited the parallel **HAPC** alignment, which appeared (100) face of hexagonal cylinder phase structure (**Fig. 3e**). The thick film had cylinder array structures perpendicular through the film direction (**Fig. 3f**). The perpendicular **HAPC** structure was reproducibly observed in 100 nm-thick films. In contrast, both perpendicular and parallel **HAPC** structures were observed in 60 nm-thick films.

R. Magerle et al. showed that the cylinder orientation was parallel to the substrate when the film thickness (H) is equal to nL, where n is an integer[12, 13]. Since the L of **HAPC** is 20 nm in the case of PEO_{114}-b-$PMA(Az)_{42}$, the thickness of 60 nm exactly matches $3L$. **Figure 4** shows brief summary with the illustration for the correlation between cylinder alignments and film thickness. With thickness of 20~60 nm, the cylinder structure parallel to the substrate is formed as thermodynamically stable structure based on strong interaction between substrate and film, consistent with the theory, i.e., $H = nL$ (**Fig. 4a**). The 60 nm-thickness may be a critical point for **HAPC**

Figure 3   TEM top view and cross-sectional images of PEO_{114}-b-$PMA(Az)_{42}$ thin films prepared by (a), (b), (d), and (e) spin coating and (c), (f) casting onto water surface. The annealing conditions: (a), (d) at r.t. for 24 hrs, and (b), (c), (e), and (f) at 140 °C for 24 hrs.

alignment in the PEO_{114}-b-$PMA(Az)_{42}$ films. As a critical point of film thickness, the film with thickness of 60 nm < H <1000 nm forms perpendicular **HAPC** structure, which is more stable state as thermodynamic equilibrium. Large χ parameter (segment-segment interaction parameter), which is easily accepted in the present block copolymers consisting of crystalline **PEO** and LC segments, may be also key to the perpendicular alignment to the substrate. In case of H > 1000 nm, the orientation can not be well-controlled by the present procedure. Because the anisotropic **HAPC** inside of the thick film can not be affected by the interfaces, which is the similar behavior to the bulk sample.

Our previous work suggested that the alignment of the azobenzene LC mesogen in **PMA(Az)** matrix were parallel to the orientation of the **HAPC** structures[11]. Once the azobenzene orientation is evaluated by UV-vis measurement, the cylinder orientation can be statistically predicated without the AFM or TEM observation. **Figure**
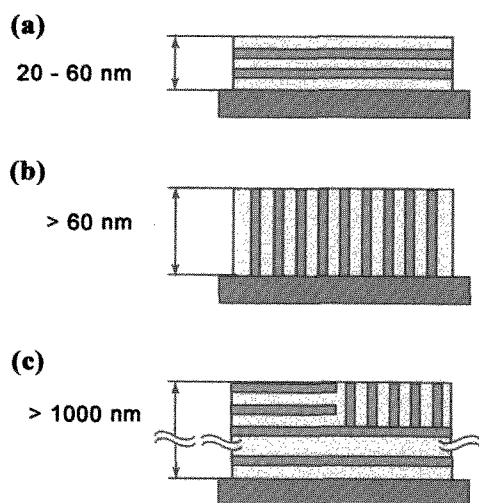
Figure 4 Illustration of **PEO** cylindrical orientation in thin films. The grey line indicates **PEO** cylinder and white region shows **PMA(Az)** matrix. The cylindrical orientation depends on film thickness. Film thickness of (a) 20-60 nm **(Fig. 3b)** and (b) > 60 nm **(Fig. 2b, 2c, 2e, and Fig. 3c)** generates parallel and perpendicular **HAPC** alignment. Film with > 1000 nm thickness **(Fig. 2d)** of mainly exhibited multi-grain structure with size of several ten μm.

5 shows the UV spectra of the spin-coated films on quartz substrates with different film thicknesses before and after annealing. An as-prepared film before annealing exhibited an absorption maximum at 337 nm assigned to the π-π^* long axis transition of the azobenzene mesogen. After annealing at 110 °C for 24h, the absorption maximum 70 nm-thick film was blue-shifted by 15 nm, implying a strong H-aggregation of the azobenzene mesogen **(Fig. 5a)**[14]. During the annealing, the absorbance of this film decreased down to 60%, indicating homeotropic alignment of the azobenzene mesogen and also the **HAPC** structure perpendicular to the substrate. In the case of a 20 nm-thick film, no spectral change was observed before and after annealing. From our prediction of the orientations of **HAPC** and the azobenzene long axis, the **HAPC** structures would be assigned as multi-grain structure whose alignment direction is not fixed in the film **(Fig. 5b)**. The UV spectral analysis strongly supported the relationship between the alignment and nanostructure alignment and
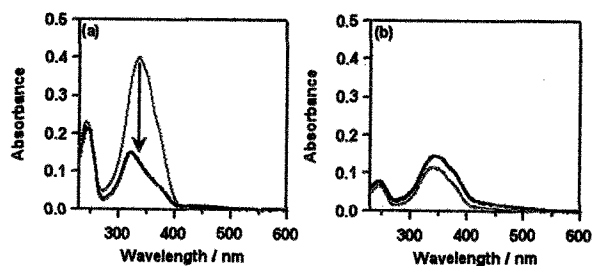
also nanostructure alignment demonstrated in the microscopic study.

Conclusion

We demonstrated that the **HAPC** structure in the **PEO$_m$-b-PMA(Az)$_n$** thin film was aligned perpendicularly and/or parallel to the substrate, as a function of the film thickness. In particular, we successfully controlled the perfect perpendicular orientation of **HAPC** in the wide region of thickness 60 nm < H < 1000 nm. The systematic observation could lead to fabrication of film with the complete alignment in large area. The alignment control by utilizing external field like a photo-irradiation or electric field is undergoing especially in the region of the thickness showing uncontrollable alignment. The study can be expected to apply for the highly reliable nanocylinder template as the coming future materials.

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Figure 5 UV-vis spectra of **PEO$_{114}$-b-PMA(Az)$_{48}$** thin films prepared by spin coating from (a) 2.6 wt% toluene solution and (b) 0.7 wt% toluene solution before and after annealing at 140 °C for 24 hrs.