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Control of Regular Nanostructures Self-Assembled in an Amphiphilic Diblock Liquid-Crystalline Copolymer

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An amphiphilic diblock liquid-crystalline copolymer consisting of poly(ethylene oxide) (PEO) and polymethacrylate containing an azobenzene moiety in the side chain was prepared by atom transfer radical polymerization (ATRP). The specifically-designed chemical constitution and the low molecular-weight polydispersity enable the block copolymer to form a regular microphase-separated nanostructure self-assembled in its bulk films, in which a hexagonal packing of the PEO cylinders normal to the substrates was dispersed in a continuous phase of azobenzene mesogens with out-of-plane alignment. Then a commercially available rubbing technique was first used to control the microphase-separated domains in the copolymer films. By introducing novel supramolecular cooperative motions between ordered azobenzene mesogens and PEO microphase domains, macroscopic array of PEO nanocylinders was regularly formed along the rubbing direction. Both the dotted and parallel stripe patterns of PEO nanocylinders were successfully obtained in the same block copolymer.

Keywords: amphiphilic diblock LC copolymer; dotted and parallel stripe array of nanocylinders; nanoscale phase separation; rubbing technique; supramolecular cooperative motions

INTRODUCTION

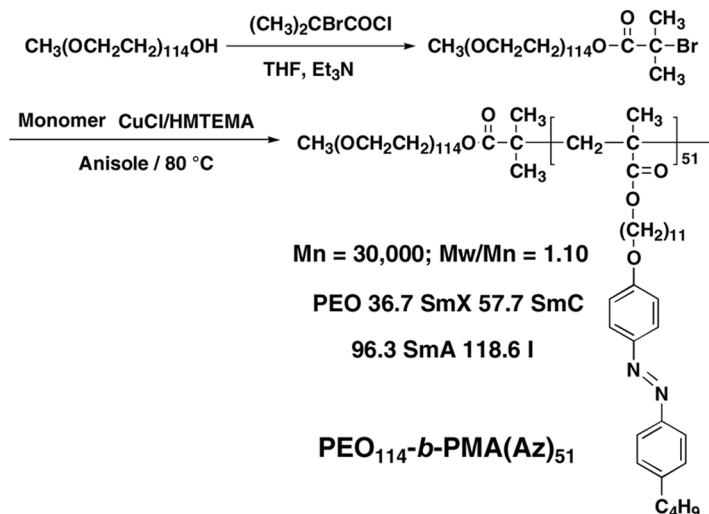
Block copolymers composed of two or more chemically immiscible polymers joined together are fascinating materials because of their excellent

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performances. Generally, they not only have the properties of their constituent homopolymers but also possess some novel features such as microphase separation [1]. Because an unfavorable mixing enthalpy and a very small mixing entropy drive the system into phase separation while the covalent bond between these two polymer chains prevents the system from undergoing microphase separation. Upon self-assembly of block copolymers in the process of microphase separation, the minority phase forms a variety of distinct nanostructures of sphere, cylinder, double gyroid, double diamond, and lamellae domains with an increase in its ratio up to about 50% [2].

Unfortunately, such ordered periodic nanostructures often extend to a molecular scale (5-50 nm) only by the self-assembly of block copolymers [3]. To be used as templates or scaffolds for fabricating nano-devices, well-defined ordered structures in bulk films should be controlled precisely. Recently, electric or magnetic field [4–7], temperature gradient [8], crystallization [9], modified substrate surface [10], shearing [11], solvent evaporation [12], roll casting [13], photo-control [14,15] and mixing with homopolymer [16] have been explored to control the microphase-separated domains. However, perfect dotted and parallel stripe patterns of such nanostructures in the same block copolymer are still remaining challengeable.

On the other hand, liquid-crystalline (LC) materials have been extensively studied owing to their inherent properties such as self-organizing nature, fluidity of long-range order, cooperative motions and anisotropy in various physical properties [17]. Attaching rigid mesogens as one segment of block copolymers would endow the obtained block LC copolymers with excellent features above-mentioned [18–24]. Furthermore, the LC ordering of the mesogenic block has mutual interference with the process of microphase separation, leading to novel supramolecular cooperative motions [23]. Most interestingly, the LC molecules can be elegantly orientated on the surface of rubbed polyimide films [25], which has been regarded as one of the key techniques in commercial assembly of LC display. This offers a novel method to control the nanostructures in LC block copolymers by combining the supramolecular cooperative motions. In this study, we prepared an amphiphilic diblock LC copolymer consisting of poly (ethylene oxide) (PEO) and polymethacrylate (PMA) containing an azobenzene (Az) moiety in the side chain by atom transfer radical polymerization (ATRP) [19,21]. The thermally-induced microphase-separated nanostructures in bulk films of the block copolymer was systematically studied. Then the industrialized rubbing technique to align LC was first used to control the nanoscale microphase domains.



SCHEME 1 The synthetic route and properties of the amphiphilic diblock liquid-crystalline polymer used in this article.

EXPERIMENTAL

Materials

As shown in Scheme 1, the amphiphilic diblock LC copolymer, PEO₁₁₄-*b*-PMA(Az)₅₁, was synthesized by a modified ATRP reaction with a bromo-terminated PEO₁₁₄-Br as a macroinitiator [19]. A number-average molecular weight (M_n) of 30,000 and a low polydispersity ($M_w/M_n = 1.10$) was obtained from GPC. About 51 repeated units of Az were estimated from ¹H NMR spectrum of the block copolymer based on the well-defined structures. Four transition peaks appeared at 36.7, 57.7, 96.3 and 118.6°C in its thermogram by differential scanning calorimetry (DSC), corresponding to PEO melting point, smectic X to smectic C to smectic A to isotropic phase, respectively. The maximum absorption band at 350 nm is observed in the UV-vis spectrum of the block copolymer in chloroform, owing to the π - π^* transition of Az chromophores [20–22].

Method

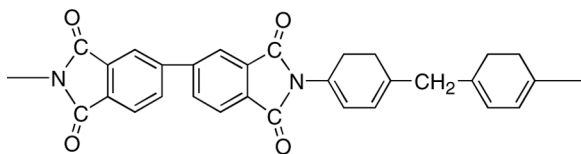
Annealing Without Rubbing Treatment

The block copolymer films with a thickness of about 200 nm were prepared by spin-coating their toluene solution on glass or silicon substrates. After the solvent was removed at room temperature, the

copolymer films were annealed at 140°C in a vacuum oven for 24 h. Both heating and cooling rates were controlled at 0.5°C/min. The microphase-separated nanostructures in the block copolymer films was explored at room temperature with a scanning probe microscope (Veeco Instruments Inc., Nanoscope IV) in tapping mode because of different modulus between the phase domains of PEO and the Az mesogens.

Rubbing Technique

The clean glass substrates were spin-coated with 3 wt% poly (amic acid) solutions in N,N-dimethylformamide (DMF) at 500 rpm for 5 s and 3000 rpm for 30 s. Then surface-treated glass substrates were soft-baked at 100°C for 1 h and hard-baked at 250°C for 2 h to remove the solvent and cure for imidization. The chemical structure of the polyimide used in this experiment is shown as below.



measured with a surface profiler (Veeco Instruments Inc., Dektak 3ST). Further experiments on conductive silicon wafers were carried out on a field-emission scanning electron microscope (FESEM, Hitachi S-5200 SEM) at a voltage of 3.0 kV.

RESULT AND DISCUSSIONS

Since the ATRP has been regarded as one of controlled/living radical polymerization [26], the obtained diblock copolymer, PEO₁₁₄-*b*-PMA(Az)₅₁, has a well-defined structure as shown in Scheme 1. The maximum absorption peak at 336 nm in its spin-coated film was observed in UV-vis absorption shown in Figure 1, with a blue shift of 14 nm comparing with its absorption in solution because of the H-aggregates of the Az chromophores in a film state. After annealing, the absorption peak deceased greatly, which might be attributed to the out-of-plane alignment of Az mesogens [21,22]. The transition moments of the Az mesogens were orientated perpendicular to the substrate because of the layer structures in smectic LC phase.

Upon annealing, regular nanostructures was clearly shown in the AFM topological and phase images of the block copolymer film without any treatment (Fig. 2). Considering the constituent of the block copolymer, PEO₁₁₄-*b*-PMA(Az)₅₁, although repeated units of PEO are almost twice of that of the Az block, the PEO block still constitutes the minority component in the self-assembly of the diblock copolymer films. One block of PEO is well known for its crystallization and strong intermolecular and intramolecular hydrogen bonds. Another block of Az mesogens has inherent properties of self-organization, fluidity of long-range order, and so on [17]. Therefore, strong molecular

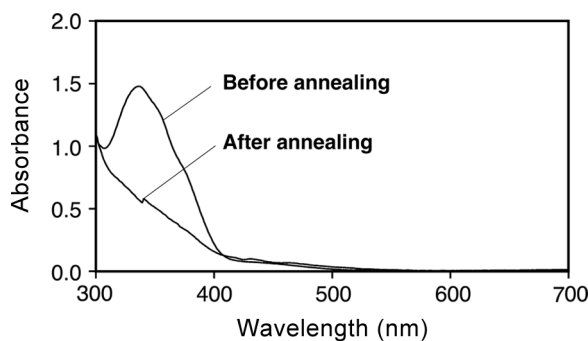


FIGURE 1 Change in the UV-vis spectra of the diblock copolymer films before and after annealing treatment.

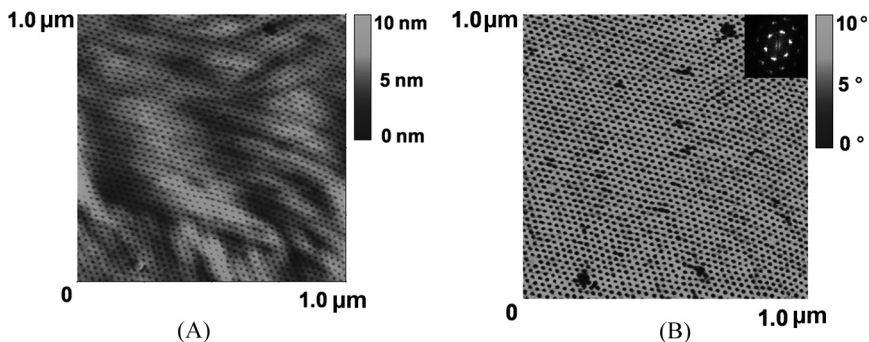


FIGURE 2 AFM topological (A) and phase (B) images of the diblock copolymer films. Inset of (B) is the fast Fourier transform (FFT) image.

interactions exist in both of the constituent segments of the present block copolymer, enabling its microphase separation different from the traditional block copolymers with relative weak molecular interactions. In fact, PEO blocks self-assemble into nanocylinders dispersed in the mesogenic substrates when the Az blocks have a volume fraction of 20–55%, and similar results have been published previously [21]. In Figure 2, PEO blocks self-assembled into nanocylinders with 10 nm in diameter and 24 nm in periodicity dispersed in the continuous phase of Az mesogens. The microphase-segregated PEO cylinders exhibited a perpendicular alignment to the substrates. A hexagonal packing of the PEO cylinders was indicated by the fast Fourier transform (FFT) shown in the inset of Figure 2 (B), in which not only six

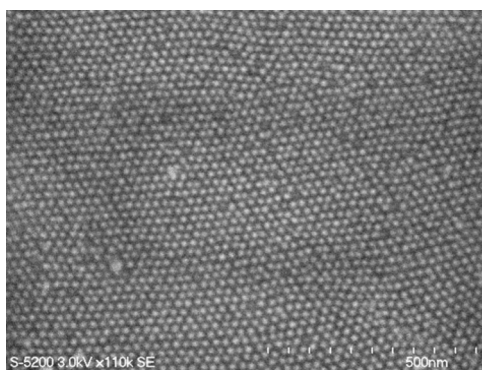


FIGURE 3 FESEM images of the diblock copolymer films. The bright dots are PEO blocks since they have been selectively stained by RuO_4 .

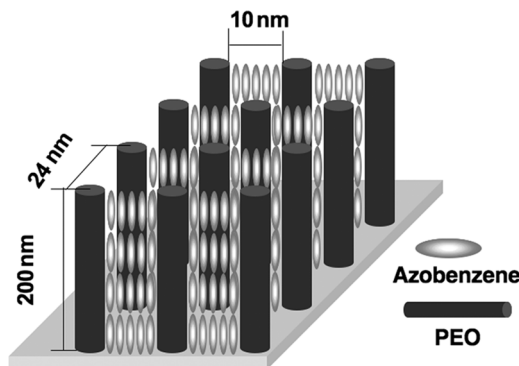


FIGURE 4 Model of microphase-separated structures in the diblock copolymer films without rubbing treatment.

sharp first-order reflections but also twelve clear second-order signals are observed, indicating the regular ordered nanostructures.

To obtain FESEM images of the nanostructures, a similar procedure was carried out to prepare the sample films with conductive silicon wafers. Before observation, the block copolymer films were exposed to ruthenium tetroxide (RuO_4) vapor at room temperature for 1 min to selectively stain the PEO blocks. A dotted pattern of PEO nanocylinders with a hexagonal packing was also obtained in Figure 3. Similarly, the PEO nanocylinders showed a preferential orientation normal to the silicon substrate, which might be assisted by the out-of-plane alignment of the Az mesogens. Accordingly, the plausible microphase-separated nanostructures of both the PEO cylinders and Az mesogens can be schematically illustrated in Figure 4.

For many diverse areas of nanotechnology, parallel processes for patterning densely packed nanostructures are often required [3]. The regular nanostructures self-assembled in bulk films of the present LC diblock copolymer might supply a good chance for preparing such parallel stripe pattern. To achieve that, a commercialized rubbing technique was chosen to homogeneously align the Az mesogens in the block copolymer films. The periodic ordering of oriented Az mesogens might be transferred to the microphase-segregated PEO cylinders by the supramolecular cooperative motions.

After the rubbing and annealing treatment, the LC alignment of Az mesogens was checked by measuring the transmittance (T), placing sample films between a set of two-crossed polarizer and analyzer, as a function of the rotation angle between the rubbing direction and the polarizer (Fig. 5 (A)). If the LC alignment is homogeneous, the

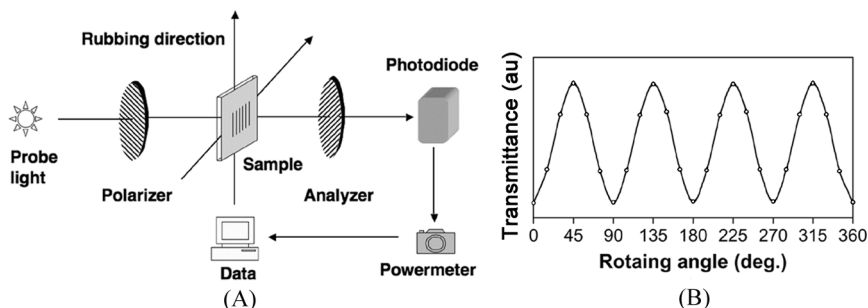


FIGURE 5 Optical setup (A) for transmittance measurement and the experimental result (B).

obtained T should be fitted by the following equation,

$$T = \frac{I}{I_0} = \sin^2(2\theta) \cdot \sin^2(\delta)$$

$$\delta = \frac{\pi d \Delta n}{\lambda}$$

where θ is the angle between the LC alignment and the polarization of the polarizer, d is the film thickness, Δn is the birefringence of the copolymer film, λ is the wavelength of the probe light. As shown in Figure 5 (B), T shows a sinusoidal-like curve, changing periodically with 90° for the rotation angle. Accordingly, the Az mesogens were in-plane aligned along the rubbing direction since T shows the maximum value when the sample film is tilted by 45° or 135° and so on, with respect to the rubbing direction and the polarizer, whereas it shows the minimum value at 0° or 90° and so on.

As we expected, the highly ordered Az LC aligned by the rubbing method exerted a great effect on the PEO nanodomains in the micro-phase-separated process. An almost perfect alignment of PEO nanocylinders, orientating along the rubbing direction was clearly observed in the AFM topological and phase images shown in Figure 6. The inset FFT image in the AFM phase image exhibited a parallel stripe patterning of the PEO nanocylinders in the plane of substrate. In theory, such patterning of PEO nanocylinders can be perfectly achieved in an area as large as the commercially available LC displays (about $2\text{ m} \times 2\text{ m}$ for the eighth generation), depending on the size of the substrates coated with rubbed polyimide films.

Similarly, a parallel stripe pattern of PEO nanocylinders was also obtained in the FESEM picture shown in Figure 7. Comparing with

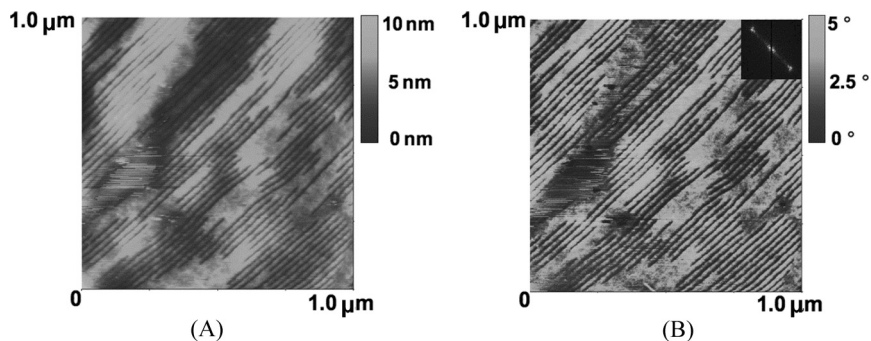


FIGURE 6 AFM topological (A) and phase (B) images of the diblock copolymer films after rubbing treatment. Inset of (B) is the FFT image.

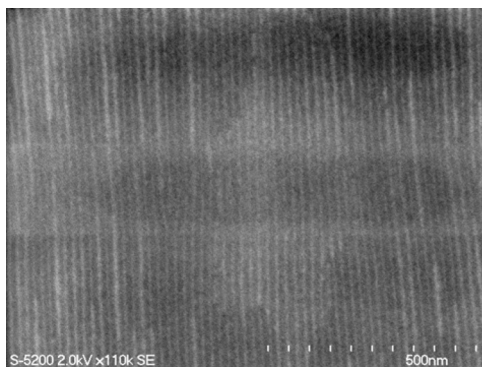


FIGURE 7 FESEM images of the diblock copolymer films after rubbing treatment. The bright lines of parallel stripes are PEO blocks.

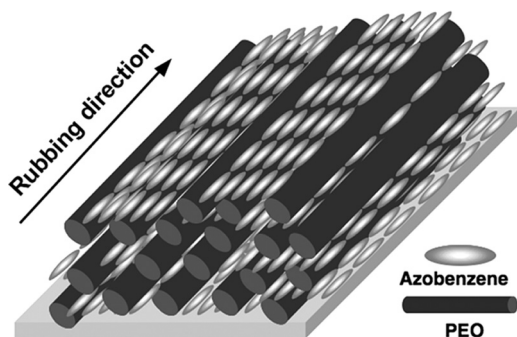


FIGURE 8 Model of microphase-separated structures in the diblock copolymer films after rubbing treatment.

other approaches to control nanostructures in block copolymer films [4–16], the present method by rubbing polyimide films and annealing treatment has advantages of simplicity, convenience and low costs. Finally, the plausible microphase-separated nanostructures of both the PEO cylinders and Az mesogens in the block copolymer films can be schematically illustrated in Figure 8.

CONCLUSION

We prepared an amphiphilic diblock liquid-crystalline copolymer consisting of poly(ethylene oxide) (PEO) and polymethacrylate containing an azobenzene moiety in the side chain by ATRP. The microphase-separated nanostructures self-assembled in the bulk films was systematically studied. By controlling the homeotropic and homogeneous alignment of Az mesogens, the out-of-plane and in-plane orientation of the PEO nanocylinders was successfully obtained under the supra-molecular cooperative functions. The plausible microphase-separated nanostructures of both the PEO nanocylinders and Az mesogens in the block copolymer films are proposed.

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