

Nanopattern Transcription on the Surface of Microphase-Separated Structure of Block Copolymer through Domain-Selective Staining with RuO₄ Vapor

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Abstract We have developed a series of amphiphilic block copolymers (BCs), PEO_m-*b*-PMA(Az)_n, to form highly ordered phase-separated nanostructures. To apply the nanostructures for reliable templates, their reproducible formation on the surfaces and the high quality of the regularity are required. Here, we employed a handpress method to prepare thick films, which are called as pellets here, since free-standing samples can be easily prepared with no use of organic solvents. Tapping mode AFM image of the pellet after annealing at 140 °C clearly showed a hexagonally arranged array or pattern of the PEO domains, which made dimples with 1 nm depth in the surrounding PMA(Az) matrix surface. SAXS profiles completely supported the hexagonally arranged cylinder structures in the pellet. Conventional TEM staining technique with RuO₄ vapor was utilized to demonstrate the PEO domain-selective hybridization with RuO_x. As a result, the PEO domains were selectively stained to generate metallic RuO_x-hybrid convex arrays higher than the surrounding surface. The convex was 3 nm in height and 10 nm in diameter, and the periodicity of the hexagonal arrangement was about 20 nm, consistent with those of the nanostructured templates. We successfully transformed the hexagonally arranged PEO dimple pattern into the metallic RuO_x hybrid convex arrays on the pellet surface.

Key words: Block Copolymers, Microphase Separation, Template, RuO₄ Vapor

1. INTRODUCTION

Microphase-separated structures of BCs are of great interest because their feature sizes from several nanometers to one hundred nanometers are smaller than the resolution limits of conventional lithography techniques [1, 2]. Additionally, the self-organization producing the nanostructure can lead to the mass productivity with simple procedure and low cost performance. Therefore, BCs have been expected as one of the promising candidates for novel polymer materials such as nanotemplates and nanofilters [3]. Preparation of a BC film on various substrates is one of the most fundamental steps commonly employed to construct the phase-separated nanostructures and also to utilize them for possible applications. For instance, thin films are prepared by spin-coating, dip-coating, and casting BC solutions onto the substrates, where hydrophobic interactions as well as interfacial interactions are important factors for formation of thermodynamically stable nanostructures in desired film processing. Comparatively, a BC pellet mechanically compressed with a die set generates the reproducibly stable nanostructures on the thick film surface without serious interfacial interactions, while inside of the film should have bulk characters and multi-grain structures. The BC film surface afford not only physical concavo-convex patterns but also chemical contrastive patterns with nanodomains consisting of incompatible polymer segments, although conventional nano-imprint molds give only the physical patterns. Domain-selective modification with metal/metal oxide, ceramics, and organic functional monomers through chemical reaction or chemical adhesion on the BC film

surface, therefore, can be novel nanotemplating process to fabricate ultra-fine structured hybrid materials [4, 5, 6].

Here we demonstrated BC nanopattern hybridized with RuO_x, using the pellet prepared by the handpress method, whose procedure is quite simple. The BCs we used throughout this study were a series of amphiphilic BCs, PEO_m-*b*-PMA(Az)_n, consisting of crystalline poly(ethylene oxide) (PEO) and liquid crystalline poly(methacrylate) bearing azobenzene mesogen in the side chain, PMA(Az), to fabricate highly ordered hexagonal cylinder array nanostructures. The PEO_m-*b*-PMA(Az)_n shows strong molecular interactions in each domain, implying reproducible formation of the nanostructures with the high regularity unlike conventional BCs with weak molecular interaction. The pellet samples of PEO_m-*b*-PMA(Az)_n can provide us free-standing thick film and the inherent morphologies on the surface, based on the aggregated structures just prior to the reprecipitation in the synthetic process. We selected RuO₄ staining technique established for transmission electron microscopy (TEM) observation [7]. Since we have realized that RuO_x domain-selectively deposited in BC nanostructure shows electric conductivity as good as common metals, the RuO₄ staining technique can be applied for the domain-selective modification under optimized condition. The PEO_m-*b*-PMA(Az)_n pellets were exposed to RuO₄ vapor for several seconds to selectively dope RuO_x in the PEO domains, leading to isolated RuO_x convex pattern on the surface. The nanostructure transcription on BC film combined with RuO₄ staining technique can offer unique function such as anisotropic

segment in the BC (19 wt%). Strictly, the **SmA** phase should appear below 116 °C, once both of PEO and PMA(Az) domains are melted, the thermal vibrations of polymer chains become vigorous, so that the **I** phase should predominantly appeared here. At 105 °C the PEO₁₁₄-*b*-PMA(Az)₄₅ with **SmA** of PMA(Az) showed the first peak of **bcc** in **I** phase, and the scattering pattern was totally consistent with hexagonally arranged cylinder structure (**hac**) at relative positions of 1, 3^{1/2}, and 4^{1/2}. This mixed scattering pattern at 105 °C indicates that the phase transition of BC nanostructure, **bcc** to **hac**, took place in the **SmA** phase or at **I-SmA** transition in PMA(Az). After cooling to 90 °C, the polymer with the **SmC** phase showed the peaks located at relative positions of 1, 3^{1/2}, 4^{1/2}, and 7^{1/2}, indicating pure **hac** structure. Further cooling to room temperature affords no specific changes in SAXS profiles though the PMA(Az) LC phase showed the transition from **SmC** to **SmX** at 75 °C. After the measurements in the cooling process, the same sample was cooled by liquid nitrogen to sufficiently crystallize PEO domain, which caused the significant difference in the electron densities between the PEO and PMA(Az) domains. The resulting peak intensity was relatively strong to be assigned to the **hac**. The temperature-dependent SAXS analyses revealed that the PEO₁₁₄-*b*-PMA(Az)₄₅ formed the phase-separated nanostructure with high regularity, leading to the distinct scattering peaks. It is worthwhile mentioning that the nanostructure formation is strongly related to the PMA(Az) LC phase and PEO crystallinity. Especially, the annealing at 140 °C sufficiently higher than the isotropic transition could yield the microphase separation with large grain structures because of high fluidity of polymer chain.

3.3 Surface morphology of the pellets

The surface morphologies of the pellet samples before and after annealing were observed by AFM phase images to show strongly contrastive viscoelastic properties between the PEO and PMA(Az) domains (Fig. 4a and 4b), while the height images can only depict small height differences (< 1 nm) between the domains on considerable surface roughness resulted from the handpressed process. The AFM cantilever detects an elastical difference in tapping vibration, which can clearly image dark PEO domain and bright PMA(Az) domain. The randomly arranged PEO dot structure with approximately 10 nm in diameter was observed on the pellet surface before annealing. The disordered PEO-domain structure indicated the self-aggregated structure based on the initial BC structure formed in reprecipitation from methanol at the last step in the working-up process of polymer synthesis. Comparatively, the highly ordered PEO domain array structure with hexagonal arrangement in the PMA(Az) matrix was observed after the annealing with 8 nm in PEO diameter and 20 nm in periodicity (distance between the closest neighboring PEO domains).

While the non-annealed sample exhibited no significant scattering peak in the SAXS profile due to the poor regularity, clear scattering peaks corresponding to **hac** were detected after annealing (Fig. 4c). From the scattering pattern, the periodicity was estimated to be 20 nm from the q value of the first scattering peak,

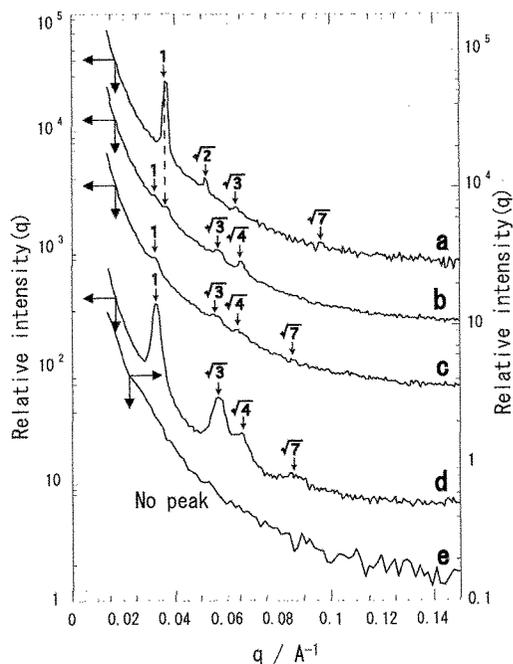


Figure 3 SAXS profiles of PEO₁₁₄-*b*-PMA(Az)₄₅ at different temperatures: (a) cooling from 140 °C to 105 °C, (b) 105 °C, (c) 90 °C, (d) 20 °C, and (e) the as-prepared sample at room temperature.

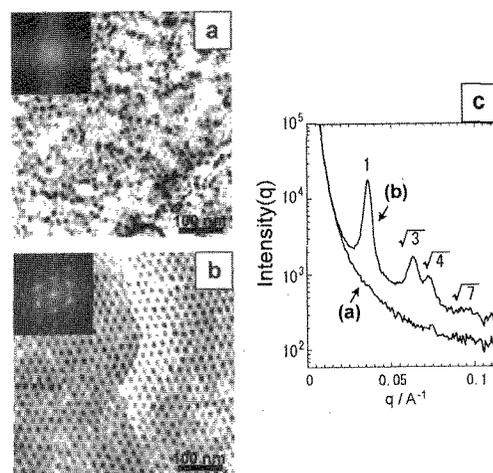


Figure 4 Tapping AFM phase images of the pellet surfaces of PEO₁₁₄-*b*-PMA(Az)₄₇ (a) before and (b) after annealing at 140 °C for 24 h, with their FFT images in insets and (c) their SAXS profiles.

which was consistent with the periodicity derived from the AFM observations. The multilateral analyses using AFM and SAXS lead one to the conclusion that the PEO domain observed on the pellet surface can be assigned as (001) face of **hac**, indicating the PEO nanocylinders perpendicular to the pellet surface without distortion. The hexagonally arranged PEO cylinder array structures in the pellet were successfully obtained on various kinds of substrates such as Si wafer and PET film. This substrate-independent surface morphology could be quite reasonable, since the pellets are too thick to be influenced by the interfacial interaction.

3.4 Nanopattern transcription via RuO₄ staining

The annealed pellet was exposed to RuO₄ vapor to demonstrate the PEO domain-selective hybridization with RuO_x. The AFM observations revealed the

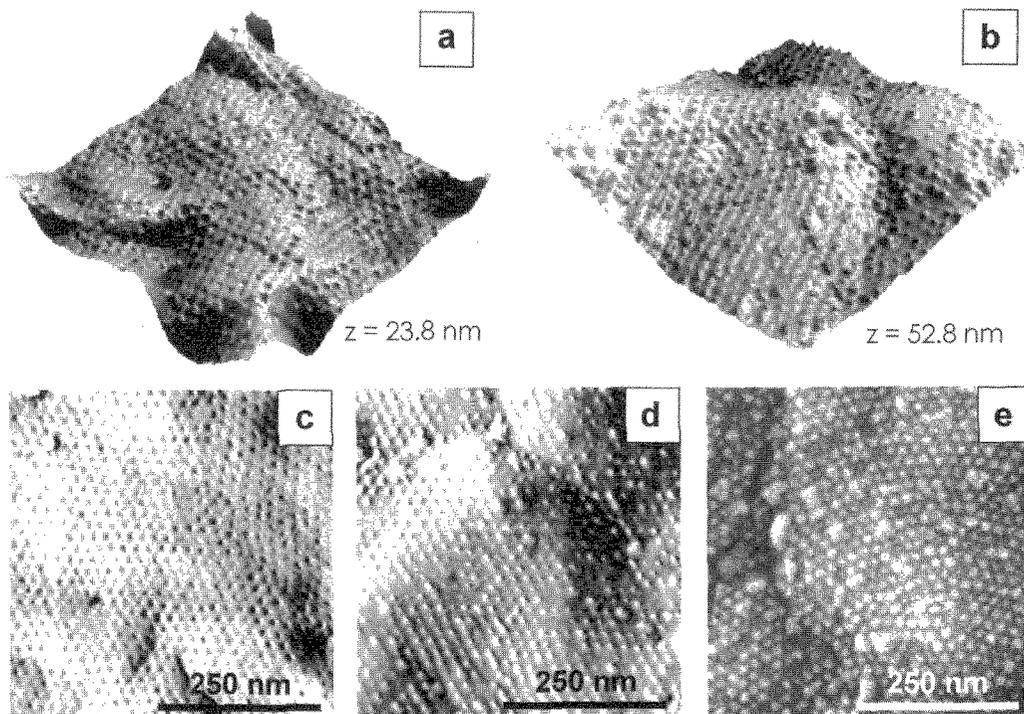


Figure 5 Tapping AFM images of the pellet surfaces of PEO₁₁₄-*b*-PMA(Az)₄₇ (a) (c) before and (b) (d) after exposure to RuO₄ vapor for 8 s at room temperature: (a), (b) height and (c), (d) phase images. The scan size is 500 nm x 500 nm. (e) FESEM image of the exposed pellet used for AFM observation (b) and (d).

morphological changes of hexagonally arranged PEO cylinder array structure on the pellet surface (Fig. 5). Figures 5a and 5c confirmed the surface structure of the annealed pellet sample. After the RuO₄ exposure for 8 s, the morphology of the pellet surface was considerably changed, where the PEO dimples as dark areas in AFM phase image became the convex as bright ones with a height of 3 nm (Fig. 5b and 5d). These changes were resulted from the hybridization of the PEO domain with RuO_x, which led to the lower viscoelasticity and the surface deposition on/in the PEO domains. Figure 5e indicated the FESEM image of RuO_x-deposited pellet. Consistently, the hexagonally arranged convexes were observed without any metal spattering pretreatment to avoid the electric charging. The brighter contrast gave the PEO pattern hybridized with RuO_x producing back scattering or reflected electrons, characteristic to heavy atom. The structural parameters after RuO₄ exposure with 10 nm of convex diameter and the 20 nm of periodicity were completely the same as those of the as-prepared BC nanostructures. Brighter islands were found, which covered two or three convexes as over-stained regions. The process of PEO domain-selective hybridization can be presumed as follows: the convexes grew and spread over the surface, and then the PEO/RuO_x hybrid domains were connected each other to form the islands. In a prolonged exposure, these islands finally covered an entire surface of the BC to form an over-stained layer. The RuO₄ staining technique was efficiently applied for the nanopattern transcription, which offered PEO domain-selective hybridization with electric-conductive RuO_x.

4. SUMMARY

We have achieved the highly ordered hexagonal arrays of the PEO nanocylinders surrounded by the

PMA(Az) matrix in the pellet samples by annealing at temperature above the isotropic transition. Domain-selective staining of the nanostructured film with RuO₄ vapor resulted in successful transcription of the PEO dimple arrays into PEO/RuO_x hybrid convex arrays with the highly ordered hexagonal arrangement. This transcription process could be effectively extended to provide electric nanodevices and optoelectronic materials with nanoscale regularity.

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6. REFERENCES

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