Electrochemical Alignment of Amphiphilic Block Copolymer Domain

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Introduction

Self-organization ordering into periodic nanostructures has potential use in applications ranging from optics to microelectronics, leading to developments on bottom-up nanotechnologies. Block copolymer is one of the foremost examples due to its micro/nanophase separated structure with high scalability based on the polymer synthesis, *i.e.*, polymer compositions. Fabrication of the block copolymer film materials with well-aligned nanostructures, however, is still challenge. External stimuli such as electric fields controlled interfacial interactions and solvent evaporation effect have been used to control the alignment in the block copolymer materials.[1] These techniques are still required to apply for various kinds of film shapes and thicknesses and to extend to the nanotemplates hybridizing with electronic, magnetic, or photonic functional components. Herein, we demonstrate the electrochemical control of microdomain alignments in amphiphilic block copolymer film consisting of hydrophilic polyethylene oxide (pEO) and hydrophobic polymethacrylate with azobenzene-based liquid crystalline side-chain (pMA(Az)) as shown in **Figure 1**. The pEO-based hexagonal nanocylinder structure resulted from the self-organization in the microdomains has been revealed by small angle x-ray scattering. The AFM study was carried out to observe the microdomain alignments of the hexagonal nanocylinders.

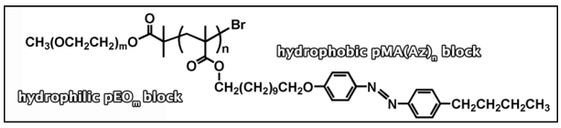

Figure 1 Amphiphilic block copolymer, $pEO_mpMA(Az)_n$

Experimental The diblock copolymer (m = 114, n = 47) was synthesized by a previously published procedure.[2] A 2 wt% toluene solution of the diblock copolymer was cast onto the silicon wafer. The resulting wafer was kept in an oven preheated at 50 ˚C for 48 hrs. Sandwich type cell was set with the ITO glass substrate as working electrode and Teflon spacer. A 0.5 M KBr aqueous solution was injected therein and an electrolytic potential was applied in rectangular wave function mode (-1.0 V for 1 min and +1 V for 1 min) using Hokuto HZ-3000 with Pt counter electrode and Ag/AgCl reference electrode.

Results and discussion

The cast film annealed above isotropic temperature overnight has shown hexagonal pEO dot pattern with a characteristic period of 20 nm. Microtome cutting has demonstrated the normal orientation of pEO cylinder microdomain to the substrate over a range of several micrometers, leading to the assignment of dot pattern in the AFM image as (001) face of the cylinder microdomain. However, a significant limitation of this technique was found as a lack of reproducibility, leading us to realize the potential of the external stimuli inducing the complete alignment.

The electrochemical treatments can be utilized to control the orientation for repeatable preparation of nanocylinderical surface patterns. The AFM observations

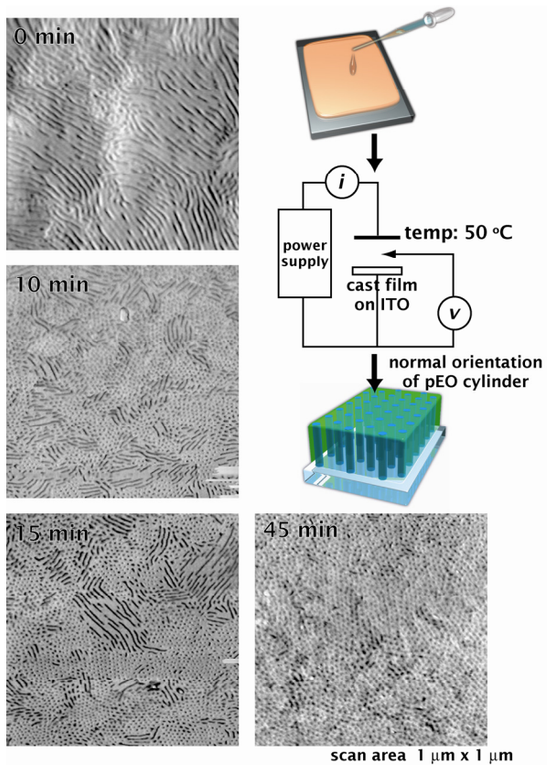

Figure 2 Tapping mode AFM phase images of the cast polymer film at different stages of pEO cylinder orientation.

were carried out to examine the electrochemical processing (**Figure 2**). When the cast film was annealed at 50 ˚C 48 hrs, the cylinders were mainly laid in a plane parallel to the ITO substrate. To this film the application of rectangular wave function at 50 ˚C yields the cylinder orientation essentially perpendicular to the substrate. The surface areas corresponding to (001) face of hexagonal cylinder array, $A_\perp/(A_\perp+A_\parallel)$, were obtained by the AFM images to estimate the effective charge passed through the film for the alignment under the potentiostatic rectangular wave mode, yielding 5 % at 0 min, 48 % at 10 min, 59 % at 15 min, 96 % at 45 min. It has been reported that the self-organized nanocylinder microdomains align parallel to the electrolytic field as the lowest energy orientation.[1b] Additionally in our system, the ionic diffusion locally induced in the vicinity of the electrode could function as making passage of hydrophilic pEO cylinder normal to the substrate, leading to the control of cylinder microdomains.

Conclusion

The highly aligned nanocylinders were fabricated using the cast film of pEOpMA(Az) diblock copolymer. It has been shown that rectangular wave function is an effective means of orientating cylinder microdomain normal to the substrate. This technique could be promising candidates to tailor various cylinder orientations over areas of many square centimeters as well as decorating with conducting organic polymers and metals.

References

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[2] Tian, Y.; Watanabe, K.; Kong, X.; Iyoda, T. *Macromolecules* **2002**, *35*, 3739.