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Nanostructure Observation of Block Copolymer Photonic Films Swollen with Nonvolatile Protic Solvent

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1 Introduction

Photonic crystal is a structural array where materials with different refractive indices are arranged periodically. The simplest photonic crystal is a one-dimensional photonic crystal, also referred to as an optical multilayer stack. Lamellar nanophase-separated structures of block copolymers (BCPs) can be such one dimensional photonic crystals. In this study, by immersing the BCP thin films into a nonvolatile protic solvent, we fabricate swollen photonic films with long-lasting photonic properties due to the nonvolatile nature of the solvent. The nanostructures of the films were evaluated by transmission electron microscopy (TEM) and ultra-small angle X-ray scattering (U-SAXS).

2 Experiment

Polystyrene-b-poly(2-vinylpyridine) (PS-P2VP, M_n = 121k, ϕ_{PS} = 0.6) thin films were fabricated on a polyimide substrate by the spin-coating method. The substrates coated with a PS-P2VP thin film were immersed into a nonvolatile protic solvent, tetraethyleneglycol (TEG) at 40°C for 12 hours, producing a light-reflecting photonic thin films. Ultra-thin sections prepared by a microtome were exposed to iodine vapor for 40 min to stain the P2VP phase for TEM observations. U-SAXS measurements were also performed at the BL-15A2 of the Photon Factory in Tsukuba, Japan. The camera length and X-ray wavelength were 3.6 m and 0.172 nm, respectively.

3 Results and Discussion

Since the P2VP phase was stained with iodine vapor, a phase with brighter contrast is a PS component while a phase with darker contrast is a P2VP component. A lamellar structure with approximately symmetrical composition was observed for neat or unswollen PS-P2VP (Fig 1a). From the TEM image, the average interdomain distance D, the average PS layer thickness d_S, and the average P2VP layer thickness d_P were estimated to be 59, 34 and 25 nm, respectively. In the PS-P2VP/TEG film prepared by addition of TEG, only the darker contrast layer clearly became larger than that of neat PS-P2VP; therefore, it is considered that only the P2VP layer was swollen with TEG (Fig 1b). Assuming that the brighter layer is attributed to the PS component and the darker layer is attributed to the mixture of P2VP/TEG, the values of D, d_S, d_P are 120, 37 and 83 nm, respectively, showing that the D value was approximately doubled after addition of TEG.

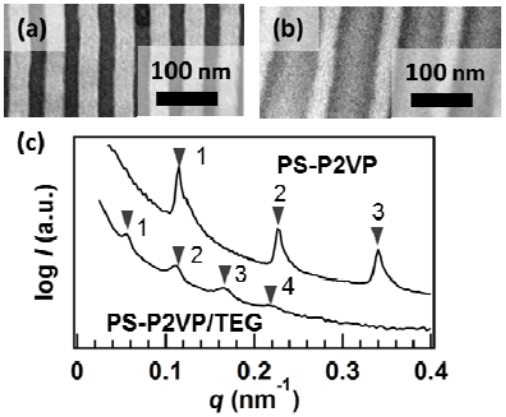

Fig 1. (a) TEM image of neat PS-P2VP. (b) TEM image of PS-P2VP/TEG. (c) U-SAXS profiles of neat PS-P2VP (top) and PS-P2VP/TEG (bottom) .

To determine D more quantitatively, U-SAXS measurements were performed (Fig 1c). In the U-SAXS profile of the neat PS-P2VP, integer order peaks were observed, suggesting formation of a lamellar structure, and D was estimated to be 55 nm from the relationship $D = 2\pi/q_1$. Integer order peaks were also observed in the U-SAXS profile of the PS-P2VP/TEG, which proves the lamellar structure is maintained even after TEG addition. However, peak positions are shifted to the lower q side, suggesting that D has become larger; D was estimated to be 114 nm, which means a 2.1-fold increase in the D value. The estimated D value was approximately the same as that estimated from TEM, which confirms consistency.

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References

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