

Nanostructure Evaluation of Block Copolymer Photonic Films by Ultra-Small Angle X-ray Scattering

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1 Introduction

Photonic crystals are periodic structures composed of components with different refractive indices. An alternating layer stack with multiple refractive components reflects the light with a specific wavelength depending on the layer thicknesses and refractive indices of components. Lamellar nanophase-separated structures of block copolymers (BCPs) can be applied as such one dimensional photonic crystals; however, large molecular weight ($M_n > 300$ kg/mol) BCPs are normally required to reflect visible light with a wavelength larger than 400 nm, which are not easy to synthesize. Here we report preparation of BCP photonic films swollen with a nonvolatile ionic liquid (IL), where the molecular weight of the BCP used for photonic film preparation is less than 100 kg/mol. [1]

2 Experiments

Thin films of neat polystyrene-*b*-poly(2-vinyl pyridine) (PS-P2VP, $M_n = 78k$, $\phi_{PS} = 0.5$) were prepared on glass or polyimide substrates by spin-coating of the polymer solutions, which were followed by solvent vapor annealing. Photonic films reflecting blue visible light (wavelength ~ 400 nm) were prepared by depositing several drops of IL onto the neat PS-P2VP films. Nanostructures of the films were observed by transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and ultra-small angle X-ray scattering (U-SAXS).

3 Results and Discussion

An TEM image of the cross-sections of a neat PS-P2VP film was shown in Fig 1a, where symmetric lamellar nanophase-separated structure with domain periodicity (D) of approx. 33 nm was seen. On the other hand, asymmetric lamellar structure with D of approx. 106 nm was observed in a TEM image of an IL-deposited PS-P2VP film (Fig 1b), suggesting swelling of the film with the IL occurred at the nanoscopic scale.

To estimate D of the IL-deposited PS-P2VP film more quantitatively, both conventional SAXS and U-SAXS were measured at Photon Factory. The beamlines used for SAXS and U-SAXS were BL-10C and BL-15A2, respectively. SAXS provided multiple peaks on the profile (bottom profile in Fig 1c), but the first order peak was not observed in the SAXS profile. On the other hand, U-SAXS profile (top profile in Fig 1c) showed multiple integer order peaks including the first order peak. D was determined to be 135 nm from the relationship of $D =$

$2\pi/(q_n/n)$, where q_n is the scattering vector of the n th order peak and n is the integer number of the relative q value of the peak.

In summary, U-SAXS was found to be very useful and effective for measuring nanostructures with D of over 100 nm, which is usually difficult to measure by SAXS.

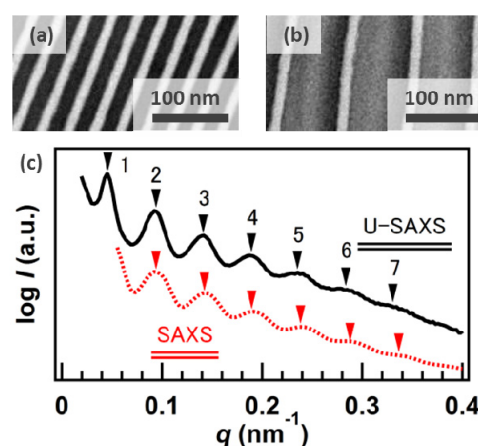


Fig 1. (a) TEM image of neat PS-P2VP. (b) TEM image of IL-deposited PS-P2VP. (c) U-SAXS (top) and SAXS (bottom) profiles of IL-deposited PS-P2VP.

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References

- [1] A. Noro, Y. Tomita, Y. Shinohara, Y. Sageshima, J. J. Walsh, Y. Matsushita, E. L. Thomas, *Macromolecules* **47**, 4103-4109 (2014)

Research Achievements

1. Patent (WO/2014/185426) pending.
2. The research about block copolymer photonic films was featured in the Chemical Daily newspaper (20-June-2015 issue), "Scientific News" of Kobunshi (Sep-2014 issue), "Topics" of Ceramics Japan (Nov-2014 issue).

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