SAXS, SANS and Spectroscopy Study on High Tunability of a Block Copolymer by Strongly Selective Solvents

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ABSTRACT

Block copolymer copolymers (BCPs) generally form periodic structures on the order of tens of nanometers. The morphology and the dimension are determined by the volume fractions of the blocks, the segregation power described by the Flory-Huggins interaction parameter (χ), the molecular weight, and the molecular architecture.

The aim of this study is to control dimensions of microphase-separated structures, i.e., domain spacings for potential application of BCPs to photonic crystals with high tunability of wavelengths. BCPs are expected to play an important role in the development along this strategy because they form structures by self-assembly at less energy cost. Many researches on controlling domain spacings have been conducted by temperature change, constructive or destructive change of hydrogen bonding, compositional change in blend systems of BCPs.

In this study, we demonstrate the control of domain spacings by exposing diblock copolymers to solvents with selectivity to one or both constituent blocks; lamella-forming symmetric polystyrene-b–polyisoprene, PS-b-PI, diblock copolymers and three kinds of solvents were employed: dimethyl phthalate (DMP) selective for PS, n-tetradecane (C14) selective for PI, and dioctyl phthalate (DOP) as a neutral solvent. DMP and C14 selectively swell PS and PI, respectively, resulting in the enhancement of the segregation power between PS and PI and the increase in the domain spacing, while DOP shields the segregation power resulting in the decrease in the domain spacing[1-4].

METHODS AND MATERIALS

Two kinds of polystyrene-b-polyisoprene (PS-b-PI), designated SI-60 and SI-655, were synthesized by anionic living polymerization. SI-60 has weight averaged molecular weight (M_w) of 60.1k with M_w/M_n =1.03, where M_n is number averaged molecular weight, and has f_{PS} of 46.7 vol.%. SI-655 has M_w of 655k with M_w/M_n =1.09, and f_{PS} of 37.9 vol.%. DMP, C14 and DOP were used as described above. Small-angle X-ray scattering (SAXS) was measured with in-house apparatus, Nanoviewer (Rigaku), and at BL-40B2 at SPring-8. Reflection spectra measurement was conducted with Multispec-1500 (Shimadzu corp.), measurement wavelength of which ranges from 190nm to 800nm.

A diblock copolymer used for Small-angle Neutron Scattering was poly(styrene)-block-poly(methyl meth-acrylate) with a molecular weight of 2.4×10^5 g/mol. The volume fraction of PS was 0.43. We used two combinations of solvent mixtures ((i)tetrahydrofuran (THF) / water and (ii)toluene / methanol as a good and non-solvent, respectively). Small-angle Neutron

Scattering (SANS) measurement was conducted at 40M SANS Beamline in HANARO, Korea to evaluate the spatial distribution of the solvent molecules by the contrast variation method using the mixtures of protonated and deuterated solvents.

RESULTS AND DISCUSSION

By combination of protonated and deuterated solvents, the scattering length densities of block copolymer solutions were varied for the SANS experiments. From the primary peak intensities, the spatial distributions of the solvents were evaluated. THF and Toluene were mainly distributed into PS phase. However, Toluene was slightly selective for PS chain. From theoretical calculation on the basis of SCFT, THF and water were mainly distributed into PMMA phase and behaved as a single solvent. In the case of toluene and methanol mixture, however, toluene was mainly distributed into PS phase and methanol was inversely distributed into PMMA phase. These phenomena resulted in the increase in the segregation power in solutions.

We prepared various ratios of SI/DOP/DMP/C14 mixtures of SI-60 and SI-655. Each solution has different concentrations of the polymers and/or different ratios of DOP in the solvent mixture (DOP, DMP and C14). The volume ratios of DMP to C14 are fixed at 47:53 for SI-60 solutions, and 39.2:60.8 (50:50 by weight) for SI-655 solutions. Solutions at the volume ratio of DOP from 0 to 100% were prepared for SI-60. However, as for SI-655, at least ca. 28 vol.% of DOP was required to dissolve the polymer into the mixture. In Figure 1, the domain spacing of SI-60 solutions are shown as a function of the DOP ratio. We studied the solutions at the polymer concentration of 20, 30, 40 vol.%. Domain spacing was calculated from the first SAXS peak position by $2\pi/q_{max}$, where q_{max} is the first peak position. The SAXS profiles of the solutions at the lower ratio (0 to 40%) of DOP showed multiple scattering peaks. The ratios of the peak positions confirmed that the structure is lamella. The solutions at the higher ratios (50 to 100%) of DOP showed only one peak, from which it is difficult to identify the morphology. However, the morphology is most probably lamella in the weak segregation regime, because volume ratio of PS:PI and DMP:C14 are nearly 50:50. As shown in Figure 1, we successfully controlled domain spacing by adjusting the ratio of the selective solvents to the neutral solvent. As for the solution at the polymer concentration of 20 vol.%, the domain spacing varied from 28.8 to 107.9 nm, while that of neat SI-60 is 34.8 nm. In Figure 2, the reflection peaks of SI-655 is 34.8 nm.

In Figrue 2, the reflection peaks from the SI-655 solutions are shown. We observed the reflection peaks varying from 342.2 to 770.9 nm. In the past study, Urbas et al. conducted reflection wavelength control by blending PS and PI into SI. In their report[5], the reflection peak was ranged from c.a. 340 to 610 nm, and the full width at half maxima of those were ca. 70 nm at narrowest. In our study, the use of solvent mixture successfully yielded wider range and narrower peak width. From Figures 1 and 2, we can see the different behavior of the shift of domain spacing against the polymer concentration, e.g. SI-60 at 30% of DOP and SI-655 at 29% of DOP. They have almost the same concentration of DOP, although the rise of polymer concentration increase the domain spacing of SI-655 solution, while it decreases that of SI-60 solution. We consider that SI with the larger molecular weight (SI-655) has higher segregation power that was shielded in the solvent mixture with 29% of DOP by a so-called dilution effect while it increases for the lower molecular weight one (SI-60). As a conclusion, the effect of solvent mixture depends on the magnitude of the segregation power of the diblock copolymers.

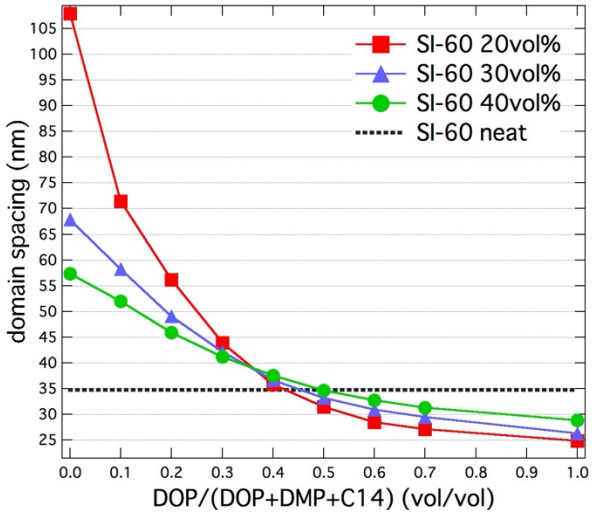

Figure 1: Domain spacing as a function of DOP ratio of SI-60 solutions at the polymer concentration of 20, 30 and 40 vol.%

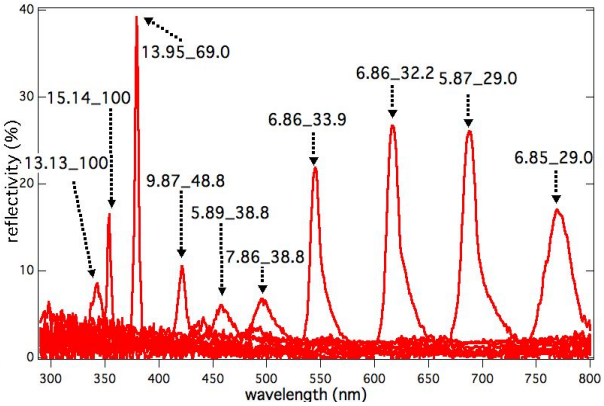

Figure 2 Reflection peaks from SI-655 solutions as a function of wavelength. Attached numbers represent polymer concentrations and DOP ratios in the solutions.

CONCLUSIONS

We prepared solutions of SI-60 and SI-655 with various ratio of PS-selective solvent (DMP), PI-selective solvent (C14) and a neutral solvent (DOP). In the SI-60 solution, we obtained lamella structure with the domain spacing varied from 28.8 to 107.9 nm by adjusting the neutral solvent ratio, while that of neat polymer is 34.8nm. The reflection peaks of SI-655 solutions shifted over the whole range of visible wavelength (342.2 to 770.9 nm). In brief, we found that domain spacing can be controlled over quite a large range by using solvent mixture.

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