Distribution of Additives in Ordered-Bicontinuos-Double-Network Structure Formed in Block Copolymer Systems Revealed by Small Angle Neutron Scattering

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Introduction. It is well known that block copolymer forms several periodic network structures due to phase-separation with nanoscale features. Well-defined network nanostructures have been expected to be utilized as hybrid porous filtration membranes, photonic crystals, and optical metamaterials, etc. There are two types of defined bicontinuous network structure in a block copolymer: gyroid (Gyr) and Fddd. Gyr is constructed from 3-fold nodes connected with Ia3d symmetry, whereas Fddd also has 3-fold nodes but has an orthorhombic unit cell. Recently, an ordered-bicontinuous- double-diamond (OBDD) structure which is constructed by 4-fold nodes connected with Pn3m symmetry was discovered in syndiotactic polypropylene(sPP)-polystyrene(PS) block copolymer [1,2]. The reason why the OBDD in this copolymer was thermodynamically stabilized was that the higher packing frustration of block copolymer chains in nodes was relaxed due to the existence of the population of helical segments of sPP. We also discovered OBDD structure in PS-b-polyisoprene(PI) (PS-b-PI) blended with PI. OBDD structures in Block copolymer (BCP)/HP systems was theoretically predicted [3,4] and experimentally observed [5]. Pure BCP melt never forms OBDD except for those with a favored helical conformation of sPP as mentioned above. However, in a BCP/HP system, the addition of the HP may reduce the frustration due to localization of the HP in the nodes, which is likely to occur when HP is longer than the identical chain in a BCP. The localization of the HP at the specific site is the key to understand the stabilization of OBDD. We aim to elucidate this point experimentally. SAXS experiment for such a system gives only morphological information, i.e., emergence of the OBDD. On the other hand, SANS expectedly gives not only morphology but also information of the distribution of the HP added when deuterated HP is used. We expect that the SANS profile will be very different from SAXS one if the added deuterated HP is located in specific sites.

Experimental. PS-b-PI (Mn,PS = 32800, Mn,PI = 18500, Mw/Mn = 1.03, volume fraction of PS = 38.6 vol%, NMR) synthesized by anionic polymerization. Fully deuterated PI (dPI) (Mn = 20,000) was purchased from Polymer Source Incorporation. Block copolymer PS-b-PI and homopolymer dPI were mixed in toluene and blended film samples were made from slow casting at 25 degree C for a week. Dried film samples were further dried at 140 degree C in a vacuum oven for 72 h. The films were cut into diameter of 1.5 cm and thickness of 0.5 mm. Blend ratios of dPI relative to PS-b-PI was 15, 20, and 25 wt%. Chain length ratio of BCP to dPI and the blend ratio was chosen to be form ordered double diamond network structure, which was predicted in literature [3,4] and our previous work [5]. SAXS and SANS measurements were conducted at BL10C (wave length of X-ray 0.1nm, camera length 3 m) in Photon Factory KEK (Tsukuba) and at BILBY (time-of-flight) in ANSTO (Australia), respectively.

Result and Discussion. Figure 1 shows SAXS and SANS profiles of PS-b-PI/dPI with a blend ratio of 25wt%. SAXS profile of the original PS-b-PI was also indicated in Figure 1. Original PS-b-PI indicates a hexagonally packed cylindrical morphology. As dPI was blended in PS-b-PI, the morphology changed to others depending

on the blend ratio of dPI. When the blend ratios of 15 and 20 wt%, the microphase separated structure was Gyr. At higher the blend ratio, the morphology was the cylinders with a larger lattice constant. (the periodicity became large). SANS profiles also indicated the identical structures observed in SAXS. In the case of blend ratio of 15 and 20 wt%, the difference in scattering profile between SAXS and SANS was small, indicating dPI was distributed uniformly PI domain. On the other hand, the significant difference was clearly observed at blend ratio of 25 wt%, e.g., the intensity of the first order peak in SANS was relatively smaller than that in the SAXS. This difference can be interpreted by taking into account for homopolymer distribution in the PI domain. Chain length of dPI was larger than that in BCP, meaning the"dry-brush" system. The dPI can be distributed preferentially in the core-region of the PI domain. SAXS and SANS profile were fitted with calculation (paracrystal distortion theory) of cylindrical model as shown in Figure 1 for the PS-b-PI/dPI (25wt%) sample. As for pure BCP, the estimated volume fraction of cylindrical domain was 33.3 vol% that is slightly deviated from the value estimated from NMR because of a larger error in NMR. In the blend system, the radius of the cylinder obtained in SANS fitting was found to be smaller than that in SAXS. Based on the volume fraction (40 vol%) of cylinder obtained from SAXS after blending, added dPI was mostly dissolved in PI domains. In the SANS measurement, the scattering contrast between deuterated region and hydrogenated materials is enhanced. Thus dPI distributed region was shown up. Thinner cylinder indicates the dPI should distribute in the core of the PI cylinder. From the value of the volume fraction of thin cylinder, most of the dPI was located in the core-region. Unfortunately, we did not get morphology of OBDD. This may be caused by inappropriate chain length ratio of dPI to BCP for forming the OBDD.

References
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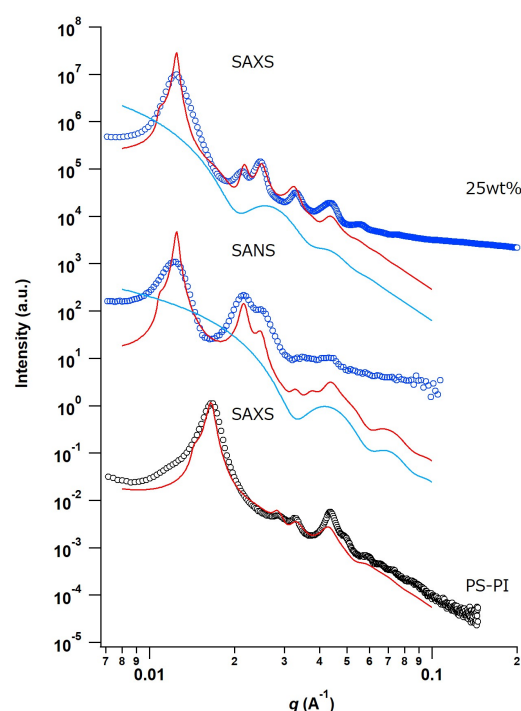[5]H.Takagi, et al. EPL 110 (2015), 48003.

Fig. 1. SAXS (symbols) and SANS (lines) profiles of PS-b-PI/dPI with dPI blend ratio of 25wt% and PS-b-PI. The solid lines were obtained from the calculation. Blue lines indicate the form factor of the cylinder.