

Anomalous Small-angle X-ray Scattering Study on Distribution of Homopolymer in Block Copolymer / Homopolymer Blend

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1 Introduction

Block copolymers (BCPs) are composed of two or more polymers connected by covalent bond. They can form a few tens nanometer scale periodic structure, which is called micro-phase separated structure, such as lamellae, cylinders and spheres, etc. Distribution of homopolymer (HP) blended in a block copolymer (BCP) depends on the ratio of the molecular weight of HP to that of the BCP, which was revealed by SANS and SAXS methods previously. In case that the large homopolymer (LHP) was blended to BCP, most of the LHP was localized at the center of the microdomain with a wide distribution. In contrast, small homopolymer (SHP) was distributed uniformly in the BCP microdomain. We applied an anomalous small-angle X-ray scattering (ASAXS) technique to investigate the distribution of HP in HP/BCP blend system. ASAXS, which is SAXS depending on the energy of incident X-ray near adsorption edge of an element, enable to obtain scattering of a specific HP in BCP.

2 Experiment

Block copolymer polystyrene-*b*-polyisoprene (PSI1: $M_{n,PS} = 15,600$, $PDI = 1.06$, $\phi_{PS} = 0.31$) was synthesized by anionic polymerization. Partially brominated polystyrene (BrPS13k with $M_n = 13,100$ and BrPS4k with $M_n = 3,700$: 4-bromostyrene unit of 5 mol%) were synthesized by atom transfer radical polymerization and used as marker HP for ASAXS (X-ray energy of 13.484 keV which is the adsorption edge of K shell of bromine (Br)). BrPS was blended into a PSI1. Blend polymer films were obtained by solvent casting from toluene solution of the blend sample. After casting, the film was dried in air and annealed in vacuum at 423 K for a week. SAXS and ASAX measurements were conducted at BL-10C in PF or BL-40B2 in SPring-8.

3 Results and Discussion

Figure 1 shows X-ray energy-dependent SAXS profiles for blend sample PSI1/BrPS13k near K-edge of Br. The intensities of the third and second order peaks increased and decreased as X-ray energy came close the adsorption edge as shown in Figure 2. If BrPS is uniformly distributed in PS domain of PSI1, the energy dependent SAXS profile is never observed. Actually, SAXS profile for BrPS4k/PSI blend system showed no dependency on X-ray energy. The observed energy dependency of SAXS profiles in case of BrPS13k/PSI was attributed to the inhomogeneous distribution of BrPS. Simulation for resonant term of SAXS profile revealed the distribution of the BrPS in PS domain of PSI1.

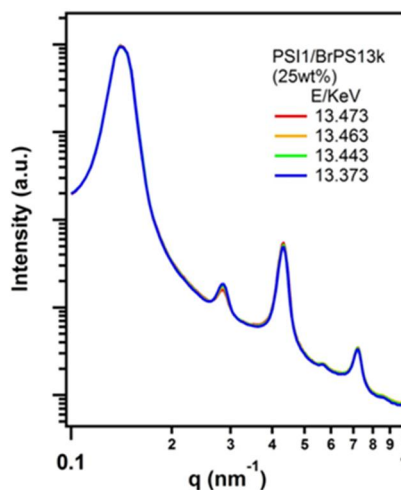


Fig. 1. X-ray energy dependent SAXS profiles of PSI1/BrPS13k.

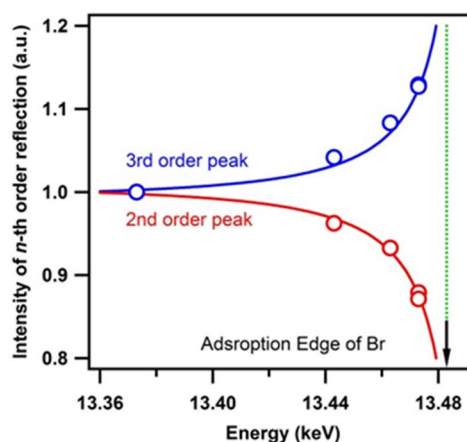


Fig 2. Relative intensity variation of the n -th order reflection peaks with X-ray energy

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