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Control of surface ordering of spherical microdomains of block copolymers by utilizing the order-disorder transition in bulk

Shinichi Sakurai*, Hidekazu Yoshida, Yoshihiro Tsuji

Department of Polymer Science & Engineering,
Kyoto Institute of Technology, Sakyo-ku, Kyoto 606-8585, JAPAN

Surface ordering of spherical microdomains were thoroughly examined by atomic force microscopic (AFM) observations using polystyrene-b-polyethylenebutylene-b-polystyrene (SEBS) triblock copolymers with glassy polystyrene (PS) spheres embedded in the rubbery polyethylenebutylene (PEB) matrix. It was found that PS spheres regularly order to form a hexagonal array on the free surface when they regularly order in bulk, and viceversa. We quantitatively confirmed that the sphere ordering in bulk affects regularity of sphere ordering on the free surface.

The SEBS sample has a number-avergae molecular weight (M_n) of 6.7×10^4, volume fraction of PS blocks (ϕ_{PS}) of 0.084 and polydispersity index (M_w / M_n) of 1.04. The PEB mid-blocks were obtained by conducting hydrogenation of polybutadiene midblocks in a precursory polystyrene-b-polybutadiene-b-polystyrene (SBS) triblock copolymers. The content of a butylene moiety in the PEB block is 50 mol%. The film sample was obtained by evaporating the solvent (toluene) from a 5 wt% polymer solution at room temperature. After the solvent was completely removed, an as-cast film obtained was further annealed for 10 hours at 140˚C and 150˚C that are above the glass transition temperature (Tg) of the PS blocks, followed by quenching into ice water.

Fig. 1 displays small-angle X-ray scattering (SAXS) profiles for SEBS samples cast from 5-wt% polymer solutions in toluene; (a) as-cast sample, (b) sample annealed at 140˚C for 10 hours, and (c) sample annealed at 150˚C for 10 hours. The profile (b) exhibits multiple diffraction peaks from the bcc lattice, as indicated by arrows with 1, $2^{1/2}$, $3^{1/2}$, while profile (a) or (c) shows a single main peak with a shoulder, which is a signature of disordered arrangement of spherical microdomains. The SEBS sample has been found to undergo the order-to-disorder transition (ODT) at 150˚C. In the present work, we have utilized these characteristic samples with and without regularity of spherical arrangement in bulk to examine effects of bulk structure on surface ordering of spherical microdomains.

The results of the AFM observation to examine the surface morphology and the surface ordering are presented together in Fig. 1. The brighter region specifies a higher altitude and the extent of height is expressed by the brightness. Thus, it was found that round-shaped domains consist of PS blocks and they are protrudent at the free surface of the sample film. Panels (a), (b) and (c) are images of the free surface for an as-cast sample, a sample annealed at 140˚C for 10 hours, and a sample annealed at 150˚C for 10 hours, respectively. Note here that those films were all obtained by casting 5-wt% polymer solutions in toluene, and then the thermal annealing was conducted with the condition specified. The thickness of the films is in the range of 0.3~0.5 mm. It is clearly seen that regularly arranged spheres were only observed in panel (b), whereas disorder of the packing of spheres was found in panel (a) or (c). These results are well correlated to the SAXS results, indicating that spheres also regularly order on the free surface when the spheres regularly order in bulk, and viceversa.

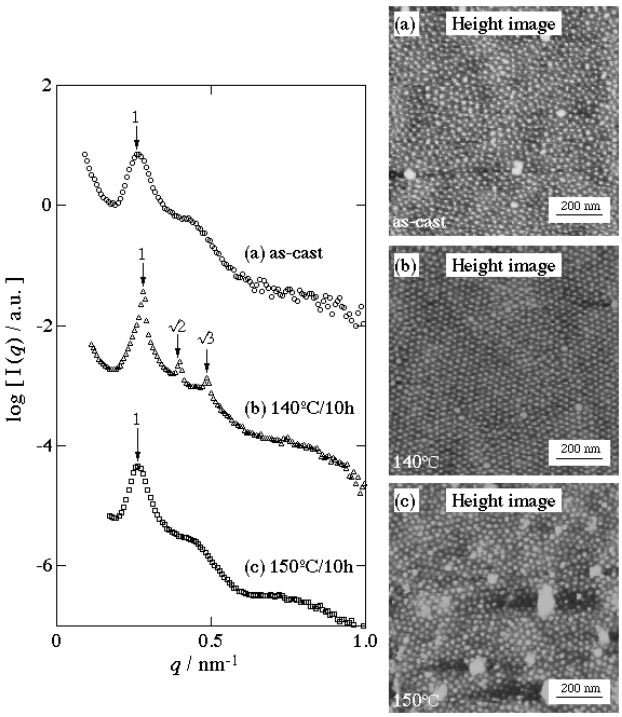

Fig.1 1d-SAXS profiles and corresponding AFM height images on the free surface of SEBS samples cast from 5-wt% polymer solutions in toluene; (a) as-cast sample, (b) sample annealed at 140˚C for 10 hours, and (c) sample annealed at 150˚C for 10 hours.

* shin@kit.jp