

Changes of Structures in an Elastomeric Block Copolymer Film Upon Strip-Biaxial Stretching -Analyses by Two-Dimensional Small-Angle X-ray Scattering-

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In block copolymers comprising rubbery and glassy chains with the glassy minor component, spherical microdomains are formed due to microphase separation, which are dispersed in the rubbery matrix. Such a microphase-separated structure imparts elastomeric properties to the material since the glassy spherical microdomains play the role of a crosslinker. Meanwhile, they can be melt-processed above the glass transition temperature of the glassy component. Thus, they are referred to as a thermoplastic elastomer. The microphase-separated structures in block copolymers have been studied for many decades and much has been uncovered, such as that spherical microdomains regularly order in the body-centered cubic (bcc) lattice. We recently reported that the bcc lattice achieved enhanced packing regularity in the direction parallel to the uniaxial stretching. This fact seems to imply that mechanical stretching can play the role of an external field. However, the ability to enhance the packing regularity of spherical microdomains is exclusive to the mechanical stretching, bearing in mind that other external fields are generally effective for alignment or orientation of microdomains. It should be further mentioned that a cycle of stretching-and-releasing plays an important role from analogy of densification of packing in granules upon shaking. In this study, we quantify the enhancement of packing regularity of spherical microdomains in the bcc lattice upon uniaxial stretching of the same elastomeric triblock copolymer by conducting small-angle X-ray scattering (SAXS) measurements using high brilliant synchrotron radiation.

The material used is a polystyrene-block-poly(ethylene-co-but-1-ene)-block-polystyrene (SEBS) triblock copolymer, having the volume fraction of (PS) polystyrene of 0.084, $M_n = 6.7 \times 10^4$, and $M_w/M_n = 1.04$ where M_n and M_w are the number- and weight-average molecular weight, respectively. It should be also noted that the glass transition temperatures (T_g), for PS and

(poly(ethylene-co-but-1-ene)) are 100 °C and -58 °C, respectively, indicating that the PS domains play a role of physical crosslinking points in the rubbery PEB matrix.

The SAXS measurements were performed at SAXS beamline BL-15A in the Photon Factory of the High Energy Accelerator Research Organization, Tsukuba, Japan. The wavelength of the X-rays was tuned to 0.150 nm. Imaging plates of 250 × 200 mm size and 100 × 100 mm resolution were used as detectors. The measured two-dimensional SAXS pattern was converted to the one-dimensional profile by conducting sector averaging in the direction where diffraction peaks were most prominent.

Figure 1 shows the 1d-SAXS profiles for the SEBS sample uniaxially stretched at room temperature. It was clearly found the similar tendency that the packing regularity in the direction parallel to the uniaxial stretching was enhanced while it was spoiled in the perpendicular direction. Based on the position of the first-order peak, the domain spacing d was evaluated, and shown in the plot against the stretching ratio in Figure 2. Note that the solid curves indicate the Affine deformation. It is surprisingly very nice that the data points fall down on the curves very well.

Figure 3 shows 2d-SAXS patterns obtained from the sample under the strip-biaxial stretching state at room temperature, from which the 1d-SAXS profiles shown in Figure 4 were obtained. Now it is clearly confirmed that only in the parallel direction, the packing regularity was enhanced while no change in the 1d-SAXS profile in the direction where the sample size was fixed (was not compressed). Thus, we can conclude that the enhancement of the packing regularity is ascribed to the stretching.

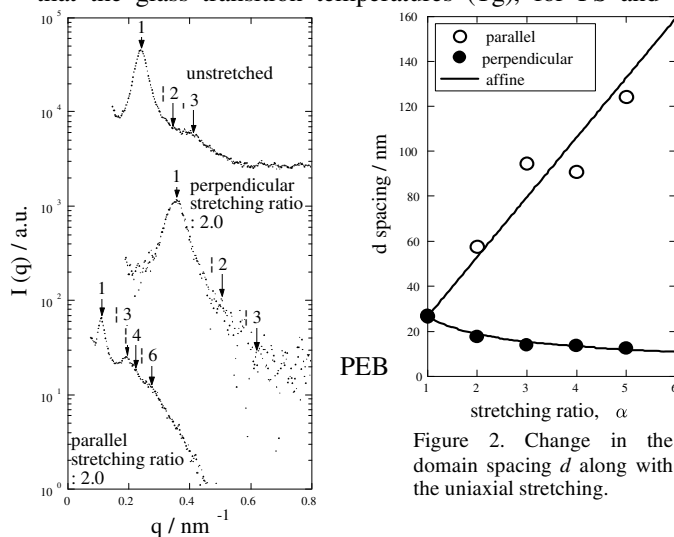


Figure 1. 1d-SAXS profiles for the SEBS sample uniaxially stretched at room temperature.

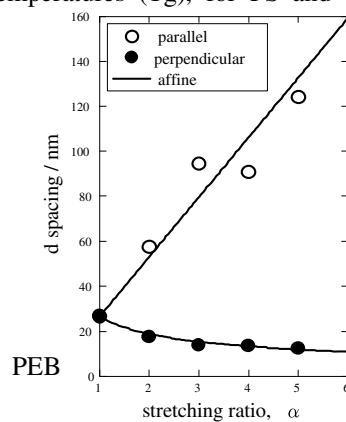


Figure 2. Change in the domain spacing d along with the uniaxial stretching.

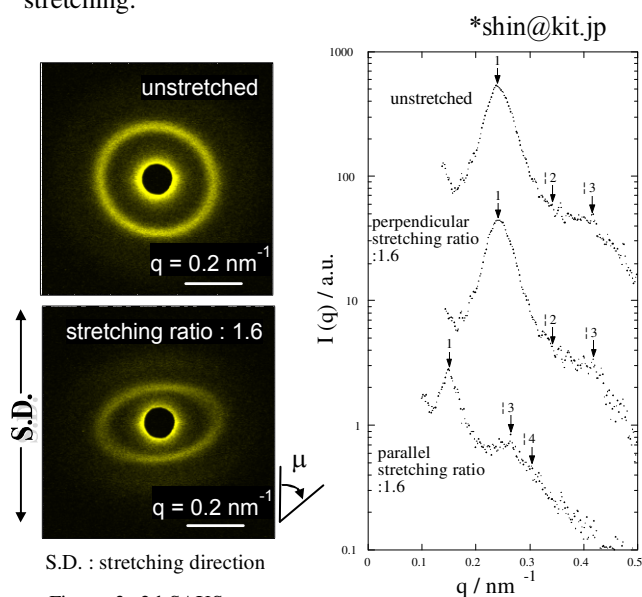


Figure 3. 2d-SAXS patterns obtained from the sample under the strip-biaxial stretching state at room temperature.

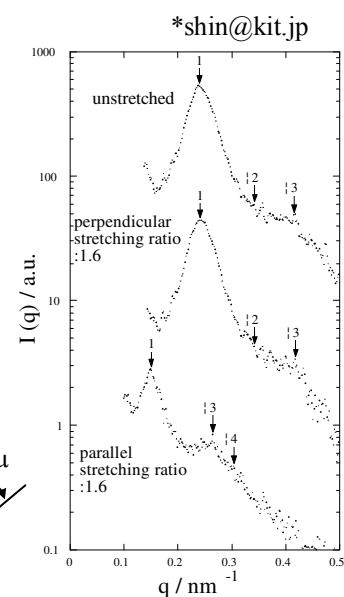


Figure 4. 1d-SAXS profiles converted from 2d-SAXS patterns shown in Figure 3.