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SAXS Studies on Deformation of the BCC Lattice for Spherical Microdomains Formed in an Elastomeric Block Copolymer Film Along Several Cycles of Uniaxial Stretching (Loading and Unloading)

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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. In order to reveal structure-property relationship for this system, we conducted two-dimensional small-angle X-ray scattering (2d-SAXS) along several cycles of uniaxial stretching (loading and unloading processes).

The material used is a polystyrene-block-poly(ethylene-co-but-1-ene)-block-polystyrene (SEBS8) triblock copolymer, having the volume fraction of (PS) polystyrene of 0.084, Mn = 6.7 × 10^4, and Mw/Mn = 1.04 where Mn and Mw are the number- and weight-average molecular weight, respectively. It should be also noted that the glass transition temperatures (Tg), for PS and PEB (poly(ethylene-co-but-1-ene)) are 100 °C and −58 °C, respectively, indicating that the PS domains play a role of physical crosslinking in the rubbery PEB matrix.

The SAXS measurements were performed at SAXS beamline BL-10C in the Photon Factory of the High Energy Accelerator Research Organization, Tsukuba, Japan. The wavelength of the X-rays was tuned to 0.1488 nm. RAXIS-VII (Rigaku) was used as the area detector. The measured two-dimensional SAXS pattern was converted to the one-dimensional profile by conducting sector averaging in the direction parallel or perpendicular to the stretching 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 α in Figure 1. Note that the solid red lines and curves indicate the Affine deformation. It is surprisingly very nice that the data points fall down on the curves very well for the first stretching process. This means that the bcc lattice of the hard (spherical) domains (microscopic strain) are exactly deformed in the same magnitude of the macroscopic strain loaded externally. On the other hand, we found huge deviation for the first unloading process where the mechanical strain was gradually released from uniaxially-stretched sample. However, further close examination reveals that the slope of the behavior for $d_{//}$ vs. α is coincident with the Affine approximation. The deviation is considered to be due to the offset value of α at which the $d_{//}$ value becomes unchanged in the unloading (relaxing) process. Note here that the offset value of α should be referred to as the remaining strain. For the second loading (stretching) process, one can find a bit of the remaining strain, and the slope of the behavior for $d_{//}$ vs. α is coincident with the Affine approximation. Furthermore, almost identical behavior was detected for the second unloading process as compared to that observed for the first unloading process. For the third cycle of the loading-and-unloading process, almost similar behavior was found as compared to that for the second cycle.

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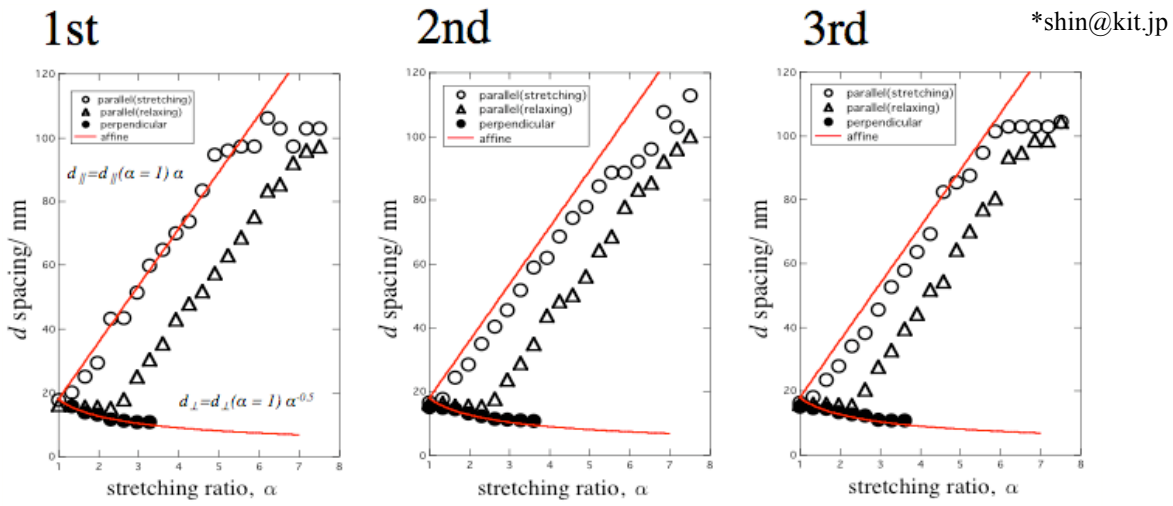

Figure 1. Changes in the domain spacing d with the stretching ratio α, along the cycles of uniaxial stretching (loading and unloading process). $d_{//}$ and $d_{//}$ stand for the $d_{\perp}$ values parallel and perpendicular to the stretching direction, respectively.