

Strain-Induced Deformation of Glassy Spherical Microdomains Formed in Elastomeric Triblock Copolymer Films

Block copolymers are well-known polymeric materials forming a phase-separation structure in the order of several 10 nm with various kinds of morphology. In the case of ABA-type triblock copolymers, in which “A” and “B” are glassy and rubbery block chains, respectively, glassy nano-spheres tethered to each other by the rubbery chains can be formed. Since the glassy nano-spheres serve as physical crosslinking points for the rubbery matrix, the triblock copolymer film generates an elastomeric property. For industrial application of this material, deformation and fragmentation of glassy nano-spheres should not take place because these phenomena lead to loss of the crosslinking points and result in degradation of the elastomeric property. In this study, we showed that glassy nano-spheres are easily deformed by stretching of triblock copolymer films and the deformability significantly affects the elastomeric property of the films.

Block copolymer is a polymeric material composed of different kinds of polymer chains covalently bonded at each end of the block chains. In cases where the block chains are immiscible to each other, a phase-separation structure is formed in the order of 10 nm because macroscopic phase separation is prevented by a spatial restriction effect of the covalent bonding at the ends of the block chains. Furthermore, the morphology of the “microphase separation structure” varies such as sphere, cylinder and lamella, depending on the volume fraction, segregation power and degree of polymerization. When spherical microdomains are composed of glassy polymer chains and embedded in a rubbery matrix, the block copolymers can be utilized as thermoplastic elastomers because the glassy nano-spheres serve as physical crosslinking points for the rubbery

matrix, which imparts the elastomeric property, and the block copolymers become a viscous fluid at temperatures higher than the softening temperature of glassy block chains, which is the thermoplastic property. In order to utilize the block copolymer forming glassy nano-spheres for industry, nano-spheres must not deform and fragment, because this would result in loss of the physical crosslinking points and spoil the elastomeric property. However, deformation and fragmentation have been assumed not to occur because glassy polymers hardly deform under low stress, for instance 1–10 MPa. In our previous study [1], we examined the average shape and size of nano-spheres under cyclic stretching of block copolymer films by performing simultaneous measurements of two-dimensional small-angle X-ray scattering (2d-SAXS) images and stress-strain curves. Consequently, we found that nano-spheres can be easily deformed by stretching of block copolymer film and that the ease of deformation (deformability) changes with the initial size of nano-spheres before stretching. In this study [2], we examined the relationship between the deformability and mechanical properties of block copolymer films by conducting time-resolved 2d-SAXS measurements for a series of block copolymer films in the stretched state.

The samples used were polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene (SEBS) and polystyrene-*block*-polyisobutylene-*block*-polystyrene (SIBS) triblock copolymers, using two kinds of SEBS with volume fraction of polystyrene (PS) of 8% (SEBS-8) and 16% (SEBS-16). Although the equilibrium morphology for SEBS-16 is cylindrical, spherical microdomains can be formed from an SEBS-16 solution prepared with a solvent selectively good for the middle block, poly(ethylene-*co*-butylene). The time-resolved 2d-SAXS measurements in the stretched state were mainly conducted at BL-6A, where the X-ray energy and camera length were 8.3 keV and 1.5 m, respectively. Off-line measurements of stress relaxation curves in the stretched state were also conducted.

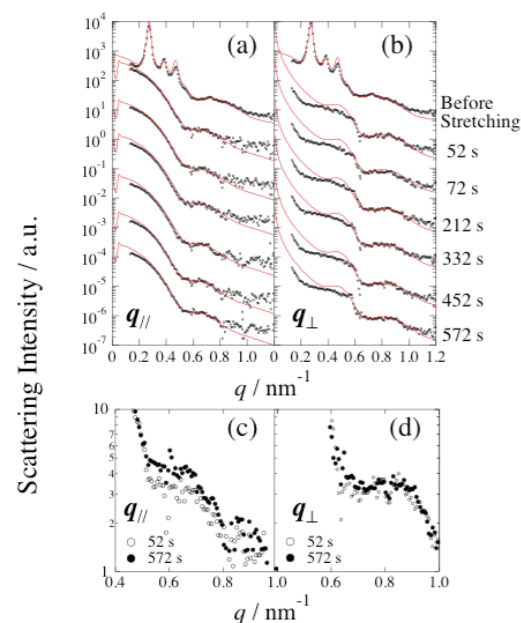


Figure 1: A series of 1d-SAXS profiles extracted from 2d-SAXS patterns measured at a given time elapsed from the quick elongation of the SEBS-8 specimen at strain of 4.0: (a), (c) parallel to SD; (b), (d) perpendicular to SD; (c), (d) highlighting the particle scattering peaks at 52 and 572 s in q_{\parallel} and q_{\perp} directions.

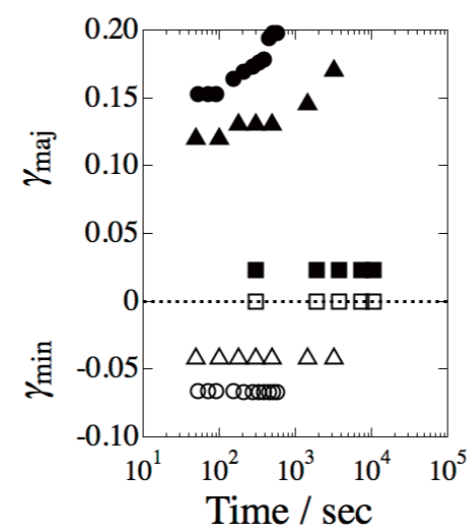


Figure 2: Change in strains of microdomains for major and minor axes, γ_{maj} and γ_{min} , respectively as a function of time for SEBS-8 (circles), SEBS-16 (triangles), and SIBS (squares).

Figure 1 shows 1d-SAXS profiles for the SEBS-8 specimen in directions parallel (q_{\parallel}) and perpendicular (q_{\perp}) to the stretching direction (SD), in which panels (c) and (d) highlight the change in the particle scattering peak as a function of time. Here, q is magnitude of scattering vector \mathbf{q} and is defined by $q = |\mathbf{q}| = (4\pi/\lambda)\sin(\theta/2)$, where λ and θ are wavelength of X-ray and scattering angle, respectively. In general, the position and shape of the particle scattering peak change depending on the size of particles, dispersion of size, and morphology of the particles. In case of the q -position of the particle scattering peak, it is inversely proportional to the size. Considering this relationship, the stretch-induced shifts of the particle scattering peaks shown in **Fig. 1** (a) and (b) can be understood as the stretch-induced deformation of glassy nano-spheres into prolate spheroids with the major axis parallel to SD. This stretch-induced deformation was also observed in our previous study, in which the deformation was attributed to stress concentration onto microdomains. **Figure 1** also shows that the shift of the particle scattering peak proceeded further while keeping the stretched state, which indicates that the deformation proceeded with time. The deformation behaviors of microdomains in the stretched state were similarly observed for SEBS-16 and SIBS specimens. In order to quantitatively discuss the deformation behavior, we assumed that the spherical microdomains were deformed into prolate spheroids with major axis parallel to SD and conducted model calculations of 1d-SAXS profiles (the results of the model calculations are shown as red curves in **Fig. 1** (a) and (b)). Finally, we obtained strains of microdomains for

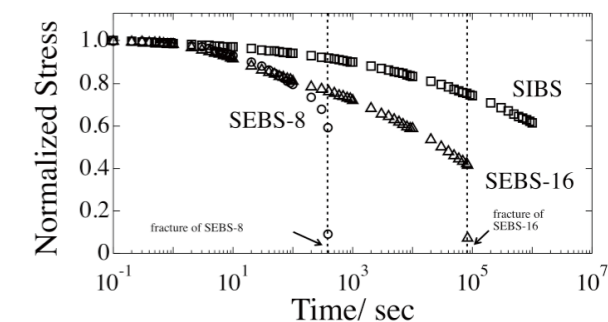


Figure 3: Stress relaxation curves for SEBS-8, SEBS-16 and SIBS stretched at strain of 4.0.

the q_{\parallel} and q_{\perp} directions, based on the radii of the major and minor axes of the prolate spheroids. In **Fig. 2**, the thus-obtained strain of microdomains is plotted as a function of time. It was found that the deformation proceeds faster for a specimen forming microdomains with a smaller radius before stretching. For further discussion about the difference in time scale of the microdomain deformation, the characteristic time for the deformation of microdomains was evaluated by fitting the plots in **Fig. 2** with an exponential function. The thus-evaluated characteristic times for each specimen were compared with those evaluated from stress relaxation curves shown in **Fig. 3**. Consequently, the characteristic times evaluated from the microdomain deformation and stress relaxation curves agreed closely within an order of magnitude. Based on these results, we concluded that 1) the deformation of nano-spheres caused fragmentation or damage of glassy microdomains, and 2) the fragmentation or damage increased the stress concentrated onto proximate spheres. Through the alternating occurrence of 1 and 2, the deformation of microdomains and stress relaxation accelerated on a similar time scale, resulting in macroscopic breakage of the film specimens.

REFERENCES

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BEAMLINE

BL-6A

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