

## Study on Structural Response of Glassy Spherical Microdomains Upon Uniaxial Stretching of Triblock Copolymer Films

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### 1 Introduction

Block copolymer is a polymeric material forming self-assembled structures with a variety in morphology, for instance sphere, cylinder, lamella and double-gyroid structure. A lot of reports were devoted on the relationship between self-assembled structure and physical properties upon stretching of block copolymer films forming cylindrical and lamellar structures. However, there have been limited number of the reports focusing on deformation behavior of spherical microdomains during elongation. While the deformation of lattice composed of the spheres has been discussed deeply, an argument about deformability of the glassy spheres dispersed in a rubbery matrix upon drawing the block copolymer film remains in an issue. Orientation of molecular chains forming glassy spheres toward the stretching direction has been detected via polarized FT-IR measurements, which indicates the deformation of the glassy spheres upon stretching. However, no direct evidence of the sphere deformation was reported. In this study, we show definite deformation of the glassy spheres into prolate ellipsoidal shape.

### 2 Experiment

The samples used in this study were polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene (SEBS) triblock copolymers. We have two different kinds of SEBS samples with respect to the volume fraction of polystyrene (PS), which are referred to as SEBS8 and SEBS16 whose volume fractions of PS were 0.08 and 0.16, respectively. We prepared solutions of these polymers with a concentration of 5wt%, using toluene for SEBS8 and a mixture of dichloromethane and the *n*-heptane for SEBS16. The reason of using *n*-heptane is to form non-equilibrium morphology in the film prepared by solution casting. For SEBS8, number-average molecular weight ( $M_n$ ), the polydispersity index of molecular weight ( $M_w/M_n$ ), where  $M_w$  is weight-averaged molecular weight, and volume fraction of PS ( $\phi_{ps}$ ) were  $6.5 \times 10^4$ , 1.05 and 0.08, respectively and for SEBS16,  $M_n = 6.6 \times 10^4$ ,  $M_w/M_n = 1.03$  and  $\phi_{ps} = 0.16$ . Thus obtained as-cast film of SEBS16 was cut into rectangles and was stretched to a strain of 4. Two-dimensional small-angle X-ray scattering (2d-SAXS) measurements were conducted for the stretched SEBS16 film at BL-6A, Photon Factory.

### 3 Results and Discussion

Fig. 1 shows SAXS profiles obtained at the time elapsed from the onset of stretching for the stretched SEBS16 at the strain of 4. The change of the SAXS profiles is displayed in Fig. 1(a) for the direction of the scattering vector  $q$  perpendicular to the stretching direction, where  $q (= |q|)$  is the magnitude of  $q$ , as defined by  $q = (4\pi/\lambda)\sin(\theta/2)$  with  $\lambda$  and  $\theta$  being the wavelength of X-ray and the scattering angle, respectively. Fig. 1(b) shows the change of the SAXS profiles in the  $q$ -direction parallel to the stretching direction. Before the stretching of the film, a broad peak was observed at  $q = 0.73 \text{ nm}^{-1}$  for both SAXS profiles in Figs. 1(a) and 1(b). This is the first-order peak of the particle scattering (not the lattice peak). From the peak position, the radius of the sphere was evaluated as  $R = 7.05 \text{ nm}$ . Upon stretching, it was found that the peak shifted toward higher  $q$  and lower  $q$  in Figs. 1(a) and 1(b), respectively. This fact indicates that the initially isotropic spheres deformed into prolate ellipsoids with the major axis parallel to the stretching direction.

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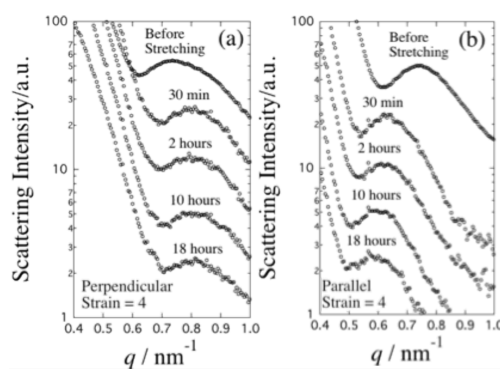


Figure 1 A series of SAXS profiles extracted from 2d-SAXS patterns measured for the stretched SEBS16 film at the strain of 4, as a function of time elapsed from the onset of stretching. The SAXS profiles were shown for the  $q$  directions (a) parallel and (b) perpendicular to the stretching direction.