Changes in two-dimensional small-angle X-ray scattering pattern by uniaxial stretching of a double-gyroid block copolymer

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We report an experimental observation of collapse of the Ia3d symmetry by stretching of an elastomeric block copolymer that forms a double-gyroid (DG) microdomain structure. The specimen used is polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) triblock copolymer with Mn = 8.5×10^4,Mw/Mn = 1.05, and ϕ_{PS} = 0.32 where Mn and Mwdenote the number- and weight-average molecular weights, respectively, and ϕ_{PS} is the volume fraction of polystyrene (PS) blocks. A toluene solution of this sample with ca. 5 wt% of the initial polymer concentration was cast at room temperature. After complete evaporation of the solvent for about 7 days, an as-cast film obtained was then thermallyannealed at 190 °C for about 24 h to form a well-ordered DG structure. The microphase-separated structures were analyzed by using the 2D SAXS technique with synchrotron X-rays at BL-10C SAXS beamline (PF, Tsukuba, Japan) and also at BL-45XU SAXS beamline (SPring-8, Nishi-Harima, Japan).

As shown in Figure 1, the stress-strain curve exhibited strong yielding in the first-step elongation, and then the second-step elongation it exhibited some rubbery-like behavior. The strong yielding suggests that the hard PS gyroid networks underwent fracture. According to the labeled position (a)-(h), the two-dimensional small-angle X-ray scattering (2d-SAXS) patterns were measured as shown in Figure 2. Two new diffraction spots were observed for a deformed DG structure. These spots were assigned to {110} and {200} reflections ($\sqrt{2}$ and $\sqrt{4}$). For the Ia3d symmetry, these reflections are prohibited by the extinction rule and therefore none of them appeared for the specimen before deformation. Appearance of these reflections indicates breakdown of the extinction rule and can be explained as a result of collapse of the symmetry of glide when three-dimensional DG networks are partially ruptured upon stretching [1].

[1] S. Sakurai et. al., *Phys. Rev. E,,* **63**, 061803 (2001).

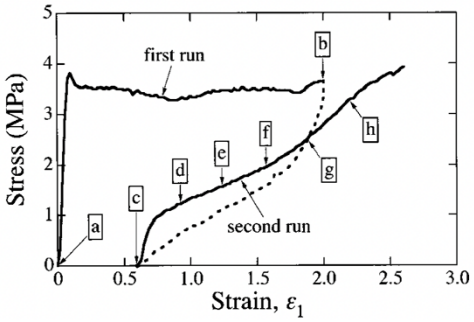

Figure 1 Stress-strain curve for a DG specimen measured at a strain rate of 0.056 sec^{-1}. The first run of the stretching of the virgin DG specimen is conducted up to $\varepsilon_1 = 2.0$. Here, ε_1 designates strain for the first run of stretching, as defined by $\varepsilon_1 = (l_0 - l)/l_0$, with l_0 (= 15 mm) and l being, respectively, longitudinal lengths of the virgin and stretched films. From $\varepsilon_1 = 2.0$, the strain was in turn reversed until the stress reached zero. The stress recorded during this process is shown in a dotted curve. Right after this process, the second run of the stretching was performed.

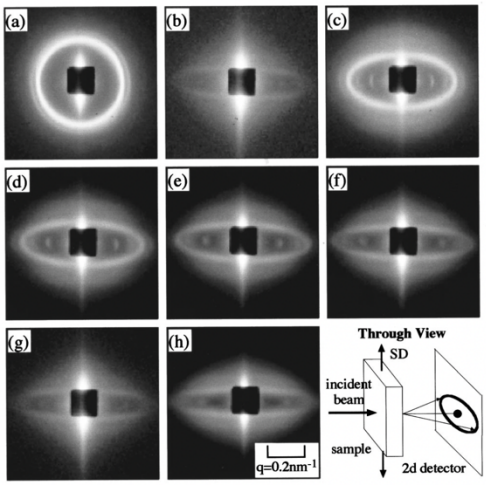

Figure 2 2D SAXS pattern (gray-scale displays logarithm of the scattering intensity) of the through view. (a) Virgin film, (b) at $\varepsilon_1 = 2.0$ from the virgin film, (c) relaxed from $\varepsilon_1 = 2.0$ (no load but with residual strain $\varepsilon_r = 0.8$), and (d) ~(h) restretching of the relaxed film at $\varepsilon_2 = = 0.2$, 0.4, 0.6, 0.8, and 1.0, respectively. The value of strain for the second run of stretching, ε_2, was defined with respect to the stretched-and-relaxed film [taking Fig. 2c at $\varepsilon_r = 0.8$ as a reference] and hence $\varepsilon_2 = (\varepsilon_1 - \varepsilon_r)/(\varepsilon_r + 1)$. Except in Fig. 2a, the SD is perpendicular to the equator.