Collapse of the $Ia\bar{3}d$ cubic symmetry in a double-gyroid block copolymer

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Introduction

Various different kinds of supermolecular structures have been found in microphase-separated structures of block copolymers. Recently, a new type of bicontinuous structure was found. The minor component of a block copolymer aggregates in three-armed continuous rods that form a three-dimensionally interconnected network with the $Ia\bar{3}d$ symmetry in the matrix of the major component of the block copolymer. Since two independent sets of the 3d-network were found to be interwoven, the morphology is referred to as double gyroid (DG; see Fig. 1).

We report here the first experimental observation of collapse of the $Ia\bar{3}d$ symmetry by the uniaxial stretching, as revealed by the two-dimensional small-angle X-ray scattering (2d-SAXS) [1]. Although transformation of packing symmetry of crystals is well known in inorganic crystals or metallic alloys that undergo transformation from the NaCl arrangement to the CsCl type under high pressure, collapse of symmetry due to fracture is a rare case for a supermolecular structure in soft matter.

Experimental

The SBS (polystyrene-*block*-polybutadiene-*block*-polystyrene) triblock copolymer with $M_n = 8.5 \times 10^4$, $M_w/M_n = 1.05$, and $\phi_{PS} = 0.32$ was used where M_n and M_w denote 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 the room temperature. After complete evaporation of the solvent for about 7 days, an as-cast film obtained was then thermally annealed 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.

Results and Discussion

Fig. 2 shows change in 2d-SAXS patterns along with the uniaxial stretching. The uniaxial stretching direction (SD) is perpendicular to the equator. The virgin sample exhibits an isotropic pattern with two intense diffraction rings, indicating a randomly-oriented polygrain structure. The ratio of radii of these two rings was found to be v6 : v8. These are assigned to {211} and {220} reflections of the DG structure. Upon the uniaxial stretching of the virgin film, the main {211} reflection was significantly distorted and the {220} reflection completely disappeared (Fig. 2(b)). Fig. 2(c) is a result obtained after release of a load from Fig. 1(b) (elongation at $\varepsilon_1 = 2.0$). Note here that residual strain was $\varepsilon_r = 0.8$. It is interesting to observe that the elliptic diffraction ring that was disconnected near the equator in Fig. 2(b) is now reconnected. This fact implies that ordering regularity of the {211} planes in the equatorial direction is recovered upon release of a load. Here, it should be noticed that new diffraction spots (more or less arcs) showed up on the equator in Fig. 2(c). It is suggested that the new peaks are ascribed to distorted DG structure that may be composed of partially-ruptured 3d-networks of glassy PS.

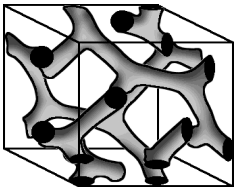

Fig. 1. Schematic drawing of the DG structure.

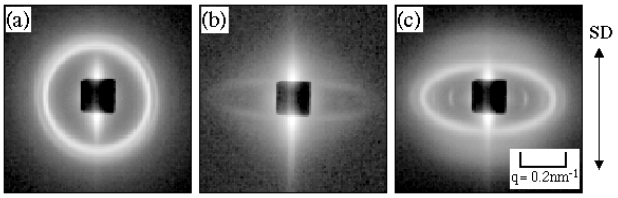

Fig. 2 2d-SAXS pattern (gray-scale displays for logarithm of the scattering intensity) of the through view. (a) Virgin film, (b) at strain 2.0 from the virgin film, (c) relaxed from (b) (no load but with 0.8 residual strain).

References

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

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