Structural analysis of a thin film of an SBS triblock copolymer forming double-gyroid morphology.

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Introduction

Various different kinds of supermolecular structures have been found in microphase-separated structures of block copolymers. We report here an experimental result of the transformation of surface morphology of double gyroid structures in block copolymer thin film.

Experimental

The sample used is polystyrene-block-polybutadiene-block-polystyrene triblock copolymer (SBS) having Mn = 4.56×10^4, \( \phi_{PS}=0.67, M_W / M_n=1.02 \). Thin films were prepared by spincoating from a 5.0wt% w/v solution of the SBS in toluene on a cover glass. All samples were annealed under vacuum at 190°C for 2h.

Results and Discussion

Atomic force microscopy (AFM) revealed that a randomly oriented double-gyroid structure (Fig. 1(a)) transformed into a well-ordered one (Fig. 1(b)), which looks similar to lamellar catenoid (or perforated lamellar) structure, upon thermal annealing of the thin film on a cover glass at 190°C for 2h.

Fig. 1 AFM tapping mode phase images showing transformation from a randomly oriented double-gyroid structure (a) into an well-ordered one (b) upon thermal annealing of the thin film on a cover glass at 190°C for 2h.

Fig. 2 shows the results of small-angle X-ray scattering (SAXS) experiments for thin films spin-cast on the cover glass and compares change in structures upon the thermal annealing. Both of the SAXS profiles exhibit a single diffraction peak and no higher-order peaks. Thus, it is not possible to conclude the double-gyroid morphology. An important finding here is that the peak position does not change upon the thermal annealing. This indicates that the bulk structure does not change while the surface morphology change upon the thermal annealing. The Bragg spacing was evaluated to be 22.1nm. In order to rationalize the structures between surface and bulk state, computer Fourier transformation (FFT) was conducted on the AFM images. As a result, Fig. 1(a) image gives similar spacing, while Fig. 1(b) image exhibits about 20% larger spacing. Therefore, it is reasonable to conclude that the surface morphology exhibiting perforated lamellar image does not necessarily indicate structural (morphological) transformation and rather reasonable to ascribe the change of AFM images to orientational transformation (ordering) in the double-gyroid structures.

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Fig. 2 SAXS profiles for thin films spin-cast on the cover glass and further annealed one.