

Microphase-Separated Structure of a Diblock Copolymer Blended with a Random Copolymer

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1 Introduction

A block copolymer with incompatible components self-assembles into regularly-ordered microphase-separated structure in bulk. So far, there have been many studies on microphase-separated structure, and it has been clarified that its morphology and size are dependent on the composition and molecular weight of block copolymer, respectively, that is, primary structure of the block copolymer [1]. Also, the morphology of a block copolymer can be controlled by blending the constituting homopolymer in place of synthesizing a block copolymer with specific composition. Unless molecular weight of homopolymer is higher than that of the block chain, it is soluble into the corresponding microdomain leading to morphological transition. In this study, effects of blending a random copolymer on the microdomain of a block copolymer are investigated.

2 Experiment

The samples used in this study are a diblock and three random copolymers composed of styrene and methyl methacrylate. The diblock copolymer has the molecular weight of 97×10^3 , and the volume fraction of a polystyrene block chain in a molecule of 0.54. The three random copolymers have almost the same molecular weight of about 10×10^3 , but different volume fractions, f_s , of styrene segments: 0.1, 0.5, and 0.8. The blend ratios, Φ , of the random copolymers were 0.2 and 0.52.

The film specimens were prepared by solvent-casting from dilute solutions in chloroform, and then annealed at 160°C for 24 hours in a vacuum.

Small-angle X-ray scattering (SAXS) measurement was conducted on BL-6A. The wavelength, λ , of X-ray was 0.15 nm, and the camera length was about 2.5 m using Pilatus as a two-dimensional position-sensitive detector. SAXS was measured at both through and edge views, in which X-ray is irradiated along the direction perpendicular and parallel to the film surface, respectively.

3 Results and Discussion

The two-dimensional scattering patterns obtained for all the samples at the through view were isotropic, and then the data were circularly averaged into scattering intensity profiles as a function of scattering vector, q , defined as $(4\pi/\lambda)\sin\theta$, in which 2θ is the scattering angle. The pure diblock copolymer shows several Bragg peaks at their relative q positions of $q_1:q_2:q_3: \dots :q_n=1:2:3: \dots :n$, in which

q_n is the position of n -th order peak, indicating formation of an alternating lamellar structure. The scattering intensity of the even-order peaks was weakened due to a form factor of a lamella formed by a symmetric diblock copolymer. The domain spacing, D , was estimated according to the Bragg equation: $D=2n\pi/q_n$, its value, D_0 , of the pure diblock copolymer was 48.8 nm.

All the blends with the random copolymers at Φ of 0.20 revealed several Bragg peaks attributed to a lamellar structure in their SAXS profiles irrespective of f_s . It was found that the random copolymer is soluble into the lamellar microdomain resulting in D increment when Φ is relatively low. At Φ of 0.52, the blends with the two random copolymers having relatively higher f_s experienced macrophase-separation, and their D values were almost unchanged from D_0 . On the other hand, the random copolymer with $f_s=0.1$ induced morphological change from lamellar to cylindrical structure. Fig. 1 represents ratios of D evaluated for the blends to D_0 for the pure diblock copolymer as a function of Φ . It was clarified that domain spacing for the random copolymer with $f_s=0.1$ was much increased with increasing Φ compared with the other two.

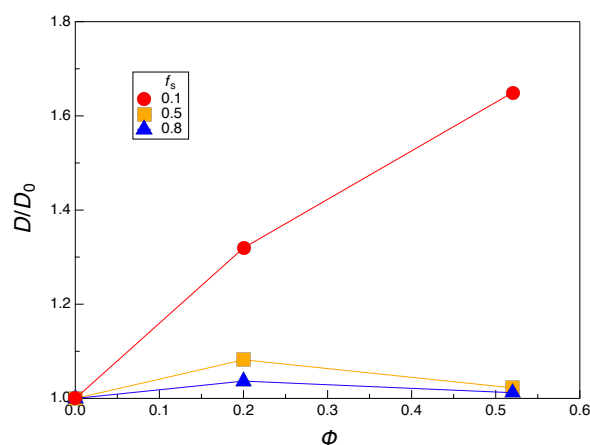


Fig. 1: The domain spacing ratio, D/D_0 , of the blend with the random copolymer having different f_s to the pure diblock copolymer as a function of Φ .

Reference

- [1] I. W. Hamley, "The Physics of Block Copolymers" Oxford University Press (1998).

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