Materials Science

9C, 10C/2005G186

Anomalous temperature dependence of spacing of lamellar microdomains in binary blends of asymmetric diblock copolymers

Junji Fukuhara[1], Akifumi Yasui[1], Katsuhiro Yamamoto[2], Shigetaka Shimada[2], and Shinichi Sakurai[1,*]
[1)] Graduate School of Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto, Kyoto 606-8585, Japan,
[2)] Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Japan

Block copolymers form lamellar microdomains when the composition is around 0.5. It has been also found that the lamellar structure was formed when two asymmetric diblock copolymers were mixed with the overall composition being adjusted around 0.5. At a first glance, it might be considered that there is no difference in these lamellar structures. However, very peculiar character was found in the temperature behavior of the lamellar repeating distance, D, for the blends of asymmetric diblock copolymers with an individual composition differing much from each other. D is a monotonic decreasing function with temperature for a neat block copolymer (for the case of the upper critical solution temperature type system) as $D \sim T^{-1/3}$ (T: absolute temperature). On the other hand, for the blends of two asymmetric block copolymers, the exponent was much smaller than –1/3 for a moderate asymmetry in their composition, while D even increased for a very large asymmetry [ref. 1]. In this current study, we intended to find an appropriate blend of which lamellar repeat distance D is temperature independent.

The diblock copolymer sample, poly(methyl acrylate)-block-polystyrene, was prepared by ATRP (atom transfer radical polymerization) method. Three different samples were synthesized for this study, as shown in Table 1, where M_n and M_w denote number-average and weight-average molecular weights, respectively. We prepared a blend sample of MS1 and MS2, which are asymmetric diblock copolymers, with a 1:1 blend ratio (by weight). On the other hand, MS3 is a symmetric diblock copolymer to be compared with the blend.

In order to evaluate the lamellar repeat distance D as a function of temperature, temperature-dependent small-angle X-ray scattering (SAXS) experiments were conducted at BL-10C and BL-9C. From the first-order peak position, q*, D can be evaluated as $D = 2\pi/q^*$ where q denotes the magnitude of the scattering vector as $q = (4\pi/\lambda) \sin(\theta/2)$, with λ and θ being the wavelength of X-ray and the scattering angle, respectively.

Fig. 1 displays the temperature dependence of thus evaluated D values for the blend of MS1 and MS2 and for the neat diblock copolymer MS3 for comparison. These values were obtained in the heating process from 120ºC to 180ºC. It is found that D decreases with temperature for MS3, as expected. Although not shown here, the exponent is found –0.33. On the other hand, the blend exhibits almost invariant value of D, irrespective of temperature. Thus, we confirmed that it is possible by using this kind of the blend to produce such a characteristic film material that the thickness does not change with heating and cooling.

Reference

1. S.Sakurai et al., *Macromolecules* **30**, 7614 (1997)

*shin@kit.jp

Table 1. Characteristics of Samples.

	M_n	M_w/M_n	PS vol%
MS1	15300	1.09	30
MS2	16800	1.06	86
MS3	17300	1.10	50

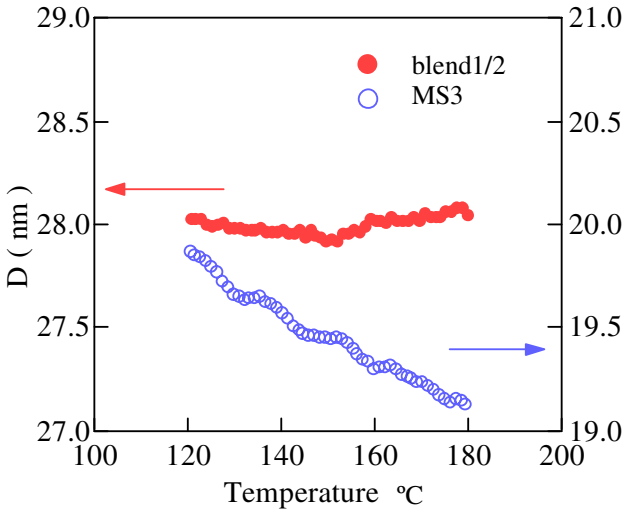

Figure 1. Plots of the lamellar repeating distance, D as a function of temperature, T in heating process.