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Small-angle X-ray scattering characterization on lamellar microdomains comprising binary blends of anti-symmetric diblock coplymers

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Introduction

For a UCST (upper critical solution temperature) type neat diblock copolymer, the repeat period of lamellar microdomains decreases with an increase of temperature. This originates from the fact that the interaction parameter between two types of segments decreases with an increase of temperature namely weakening of the segregation. The scaling relationship, $D \propto T^{\alpha}$ (α= -1/3), has been found between the lamellar repeat period (D) and the absolute temperature (T). On the other hand, it has been reported that lamellar microdomains formed in binary blends of asymmetric diblock copolymers exhibited anomalous temperature dependence of D. In some cases, D increased with increasing temperature, which is quite contrary to the usual behavior [1]. In this current study, based on this result, we aimed at preparing lamellar microdomains of which spacing does not change even if temperature is changed.

Experimental

Various asymmetric diblock copolymers, poly (methyl acrylate)-*block*-polystyrene (PMA-*b*-PS), were synthesized by atom transfer radical polymerization. The characteristics of three typical samples are listed in Table 1. We

Table 1. Characteristics of Diblock Copolymer Samples

code	M_n	M_w/M_n	ϕ_{PS}
MS5	20900	1.14	0.31
MS11	17300	1.10	0.50
MS17	20600	1.11	0.70

φ_{PS} : volume fraction of polystyrene

prepared a blend sample (B5/17-50) by mixing MS5 and MS17 with the total volume fraction of PS φ_{PS} being equal to 0.5. For comparison, the neat diblock copolymer (MS11) was used. For those samples, small-angle X-ray scattering (SAXS) measurements were conducted at BL-10C of the Photon Factory in the High Energy Accelerator Research Organization, Japan. To discuss the temperature dependencies of D, we evaluated it from the position of the first-order peak in a SAXS profile as a function of temperature.

Results and Discussion

Double logarithmic plots of D vs T are shown in Figure 1. For the neat diblock copolymer (MS11), D decreased with an increase of T, which is a usual behavior of the UCST diblocks. On the other hand, for B5/17-50, D hardly changed with T. Thus, it is confirmed that we can prepare lamellar microdomains having invariant spacing against temperature change. We further discuss dependencies of the scaling exponent α on the deviation in φ_{PS} for two different diblock copolymer samples in the blend. For this purpose, we introduce the degree of asymmetry as;

$$\tau = [\, x_{\alpha}(\phi_L^{\alpha}/\phi_S^{\alpha}) + x_{\beta}(\phi_L^{\beta}/\phi_S^{\beta}) \,] - 1$$

where ϕ_L^K and ϕ_S^K are, respectively, the volume fractions of longer and shorter block chains which compose K diblock copolymer (K =α or β). x_{α} and x_{β} are the mol fractions of the respective diblock copolymers. Plots of the scaling exponent α in the heating process for the neat diblock copolymer (circle) and blend samples (triangles) as a function of the degree of asymmetry are shown in Figure 2. It is confirmed that the scaling exponent linearly increased withτ.

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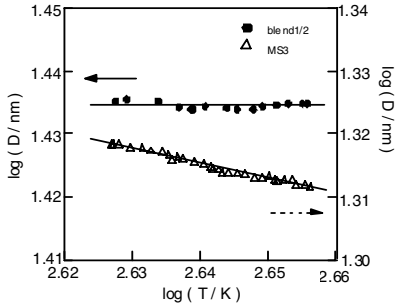

Figure 1. Double logarithmic plots of the lamellar repeat period, D, and the absolute temperature, T, in the heating process.

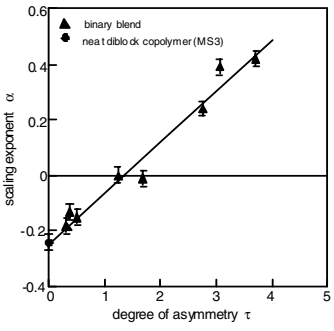

Figure 2. Plots of the scaling exponent α as a function of the degree of asymmetry,τ.