Thermotropic Order-Order Transition between FCC and HCP Lattice in Sphere-forming Block Copolymer/Homopolymer blends

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1 Introduction

It is well known that block copolymers can form a spherical morphology when a composition asymmetry is significantly large. In many cases, spherical micelles composed of block copolymers are arranged into body-centered cubic (BCC) lattice. It was reported that the close-packed lattice exists outside theoretically as an ordered phase in the phase diagram [1]. The polybutadiene-poly(ethylene oxide) block copolymer was reported to exhibit a face-centered cubic (FCC) lattice [2].

Theoretical studies on thermodynamic stability of close-packed lattice show that the free energy of FCC is only slightly smaller than hexagonal close-packed (HCP) lattice; i.e., the Helmholtz free energies of FCC and HCP lattice differ by less than 0.05% [3].

Our research group has studied the phase behavior of binary mixtures of block copolymers and homopolymers by using small angle X-ray scattering (SAXS) techniques. In this report, we confirmed that thermotropic order-order transition form FCC to HCP was observed in block copolymer/homopolymer blends.

2 Experiment

Polybutadiene-poly(ε-caprolactone) block copolymer (PB-PCL) and polybutradiene (PB) homopolymer were synthesized by anionic polymerization under a high vacuum. The number -average molecular weight (M_n) and its heterogeneous index (M_w/M_n) of PB-PCL were 7,600 kg/mol and 1.04, respectively. The volume fraction of PCL was 0.41. The M_n of the synthesized PB homopolymer (PB2k) was 1,700, and the M_w/M_n was 1.06. Blend samples were prepared by solvent casting from toluene solution of the blend sample. The weight fraction of added homopolymer was 0.53.

SAXS measurements were conducted at BL-6A and BL-10C in PF. The detector was set at a position of 2.5 m at BL-6A and 3 m at BL-10C apart from sample position, respectively. The wavelength of X-ray was 1.5 Å at BL-6A and 1.77 Å at BL-10C, respectively.

3 Results and Discussion

Figure 1 shows the SAXS profiles for PB-PCL/PB2k obtained at 160 °C and 240 °C. Data are plotted as the logarithm of the relative scattered intensity log I(q) versus the magnitude of scattering vector $q = 4\pi\sin(\theta/2)/\lambda$, λ is the wavelength of the x-ray and θ is the scattering angle. The profiles are shifted vertically to avoid overlapping. At 160°C, the scattering peaks are observed at a relative q-peak position of 1:1.15:1.63:1.91:2:2.52:2.83:3.42 as marked thick arrows. Here, theoretical relative q-peak

positions and reflection indexes for FCC and HCP are shown in Table 1. It was found that scattering peaks observed at 160 °C are good agreement with that of FCC. When the temperature reaches 240 °C, the scattering profile was changed. The relativ q-peak position changes to the 1:1.06:1.13:1.46:1.73:1.87:2.07:2.12:2.56:2.65:2.75:2.84 position (thin arrows). From Table 1, a series of the peak positions was consistent with that predicted as HCP, indicating that a phase transition from FCC to HCP took place.
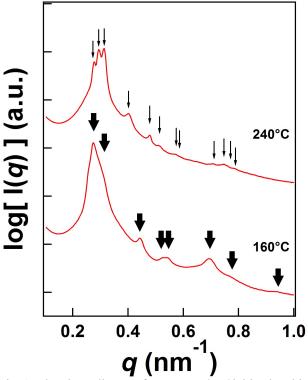

Fig. 1: The phase diagram for PB-PCL/PB2k blends. Thin arrows show scattering from HCP, and thick arrows represent scattering peaks from FCC.

Table 1: Calculated relative peak positions and reflection indexes of FCC and HCP

	(111)	(200)	(220)	(311)	(222)	(400)	(331)
FCC	1	1.15	1.63	1.91	2	2.31	2.52
	(100)	(220)	(101)	(102)	(110)	(103)	(112)
HCP	1	1.06	1.13	1.46	1.73	1.86	2.04

(420)	(422)	(333)	(440)	(531)	(442)	(533)	(444)
2.58	2.83	3	3.27	3.42	3.46	3.79	4
(201)	(004)	(202)	(104)	(203)	(210)	(211)	(114)
2.07	2.12	2.26	2.34	2.56	2.65	2.7	2.75

References
[1] M. W. Matsen,et al., *Macromolecules* **29**, 1091 (1996).
[2] Y. Y. Haung, et al., *Macromolecules* **40** 406 (2007).
[3] P. G. Bolhuis, et al A. *Nature* **388**, 235 (1997).

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