BL-15A2/2015G572

Frank-Kasper σ Phase observed in Block Copolymer / Homopolymer Blends

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1 Introduction

The microphase-separated structures observed in block copolymers have captivated researchers due to various nano-technological applications. The typical microphase-separated structures are spheres arranged in body-centered cubic (BCC) lattice, hexagonally packed cylinders (HEX), gyroid (Gyr) and lamellar structure (LAM).

Generally, spheres composed of block copolymers arranged in the BCC lattice. Since the Wigner-Seitz of BCC is relatively uniform polyhedron, packing frustration of block copolymer chain segments are lower than other lattices, such as face-centered (FCC) lattice and hexagonal close-packed (HCP) lattice. In other words, the Wigner-Seitz of both FCC and HCP has some vacancies. Thus, if these vacancies are filled by other components such as solvents or homopolymers, FCC and HCP lattice can be thermodymanically stable.

It is well known that there are two types of mixing state in block copolymer / homopolymer blends [1]. In a wet brush state, low molecular weight homopolymers tend to be selectively uniformly solubilized into the corresponding block copolymer microdomains. On the other hand, in a dry brush state, added homopolymers tend still to be solubilized selectively into the corresponding microdomains but to localize in the middle of it. The ñwet brushò or ñdry brushò conditions can be controlled by the chain length ratio of homopolymer to block copolymer.

In this study, we investigated the lattice in which spherical morphology arranges in block copolymer / homopolymer blends. It was found that Frank-Kasper σ phase was observed.

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 6,300 kg/mol and 1.05, respectively. The volume fraction of PCL was 0.27. The M_n of the synthesized PB homopolymer was 4,500, and the M_w / M_n was 1.03. Blend samples were prepared were obtained by solvent casting from toluene solution of the blend sample. The weight fraction of added homopolymer was 0.29.

The small angle X-ray scattering (SAXS) measurements were conducted at BL15A2 in PF. The detector was set at a position of 3.5 m apart from sample position. The energy of X-ray was 5.7 keV.

3 Results and Discussion

Figure 1 shows the SAXS profile of PB-PCL / PB blends obtained in heating process. In the temperature range from 60 to 100 °C, SAXS profiles show broad peak around q = 0.35nm^{-1} and shallow valley q = 0.80 nm^{-1}. These features are coincident with non-equilibrium disordered micelles observed only after melting of a crystalline-amorphous alternating lamellar structure [2]. Heating to 120 °C, a first order peak was divided into forth peaks, and additional new scattering peak near the low q side of the first order peak was observed. It can be seen easily that a lot of sharp peaks were observed at 140 °C. Finally, at 160 °C, the SAXS profile shows only one broad peak with small scattering intensity that is ascribed to the scattering from correlation hole in the disordered phase of block copolymers.

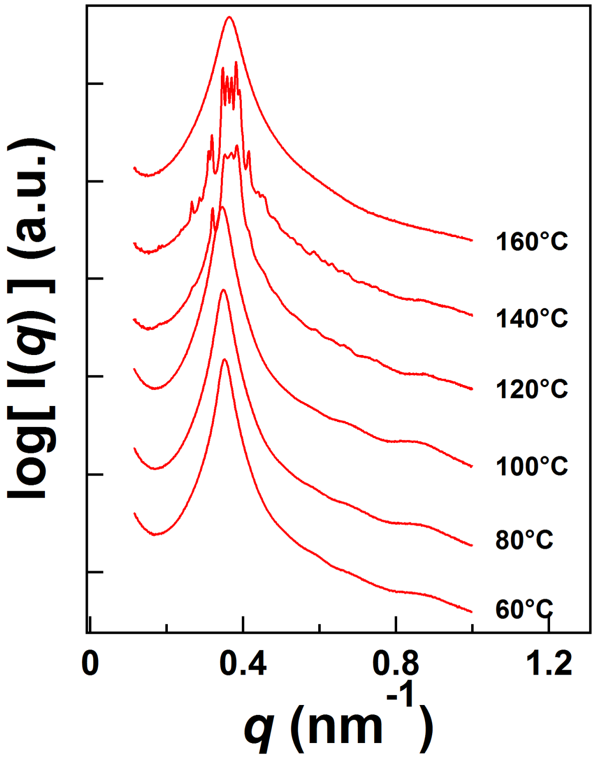

Fig. 1. The SAXS profile of PB-PCL / PB blends obtained in heating process.

Figures 2 (a) and (b) show the enlarged SAXS profiles obtained at 130 °C in the q-range from 0.27 to 0.45 nm^{-1} and high q-side ($0.44 < q < 1$ nm^{-1}), respectively. The thin arrows represent the predicted scattering peaks from Frank-Kasper σ phase. Frank-Kasper σ phase has 30 spheres in a unit cell, and these spheres are arranged into *P4₂/mnm* space group symmetry. It can be seen easily in Figure 2 that all diffraction peaks are excellently agreement with calculated ones. In addition, the ratio of unit cell size (*a* axis / *c* axis) is ca. 1.89 (a = 74.7 nm and c = 39.4 nm), which is also consistent with earlier reports in soft matter system [3]. Thus, these results indicate that the structure observed in the temperature range 120 < T < 140 °C is Frank-Kasper σ phase.

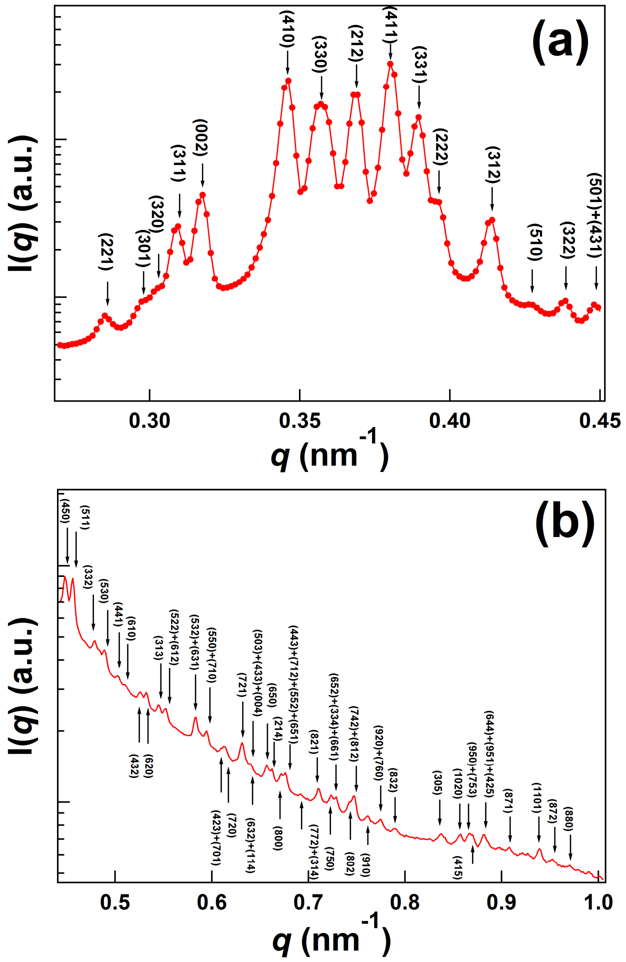

Fig. 2. (a) The enlarged SAXS profiles obtained at 130 °C in the q-range ($0.27 < q < 0.45$ nm^{-1})and (b) high q-side ($0.44 < q < 1$ nm^{-1}). Thin arrows represent calculated diffraction peaks from σ phase.

References

[1] M. W. Matsen, *Macromolecules* **28** 5765 (1995).
[2] H. Takagi *et al.*, *Colloid Polym. Sci.* **294**, 993 (2016).
[3] S. Lee et al., *Science* **330**, 349 (2010).

Research Achievement

1. 2nd Young Researcher Award of The Society of Fiber Science and Technology, Japan (2016)

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