

Frank-Kasper σ Phase Boundary of Polybutadiene-poly(ϵ -caprolactone)/homopolymer Blends

Hideaki Takagi^{1,*}

¹Photon Factory, 1-1 Oho, Tsukuba, 305-0801, Japan

1 Introduction

Recently, quasicrystals have been discovered in soft matter system, such as dendrimers, multi block copolymers and block copolymer solutions [1]. The all quasiperiodic structure observed in dendritic and polymeric materials has 12-fold symmetry, while the temperature-induced transition from the face-centered cubic phase to the 12-fold and 18-fold symmetry phases occurred in block copolymer solutions. Frank-Kasper σ phase which is well known as a crystalline approximant of a dodecagonal quasicrystal have been also observed in such systems. The Frank-Kasper σ phase has $P4_2/mnm$ symmetry and 30 spheres in a unit cell.

Theoretical studies on thermodynamic stability of the σ phase in block copolymers have been studied intensively in the last few years. Self-consistent field theory (SCFT) predicts that the appearance of the σ phase is the conformational asymmetry $\varepsilon = v_A a_A^2 / (v_B a_B^2)$, where v and a are the molecular volume and the statistical segmental length, respectively [2]. The σ phase as a stable phase appears in a narrow region between the body-centered cubic (BCC) and hexagonally packed cylinders (HEX) at $\varepsilon > 1.5$.

In a pure polymer system without any solvents, the σ phase was observed in a novel linear or miktoarm multi block copolymer composed of three or more blocks. Recently, we reported that the σ phase was found in block copolymer/homopolymer blends [3]. In this report, in order to investigate the concentration effect of added homopolymer to the appearance of the σ phase, the phase diagram of block copolymer/homopolymer blends was constructed.

2 Experiment

Polybutadiene-poly(ϵ -caprolactone) block copolymer (PB-PCL) and polybutadiene (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 6,400 kg/mol and 1.02, respectively. The volume fraction of PCL was 0.27. The M_n of the synthesized PB homopolymer (PB5k) was 4,500, and the M_w/M_n was 1.03. Blend samples 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 BL-15A2 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 phase diagram for PB-PCL/PB5k blends. The horizontal axis represents the weight fraction of added PB5k (ϕ_{PB5k}) and the vertical axis represents the morphology observed at each temperature. The ordered structures observed were HEX (triangles), coexisting of BCC and HEX (squares), BCC (circles), Frank-Kasper σ phase (pluses) and disordered state (crosses). Filled diamonds represent non-equilibrium lattice disordered micelles, which is observed after melting of the crystalline-amorphous alternating lamellar structure [4]. As depicted in Figure 1, HEX was seen in the lower ϕ_{PB5k} region ($\phi_{PB5k} \leq 17$ wt%). On the other hand, at higher ϕ_{PB5k} region ($\phi_{PB5k} \geq 41$ wt%), BCC phase was only observed. Frank-Kasper σ phase appeared between BCC and HEX phase in the narrow range $29 \leq \phi_{PB5k} \leq 33$. Theoretical studies predict that σ phase is observed in a narrow region between HEX and BCC [2]. Thus, our results were in good agreement with theoretical ones.

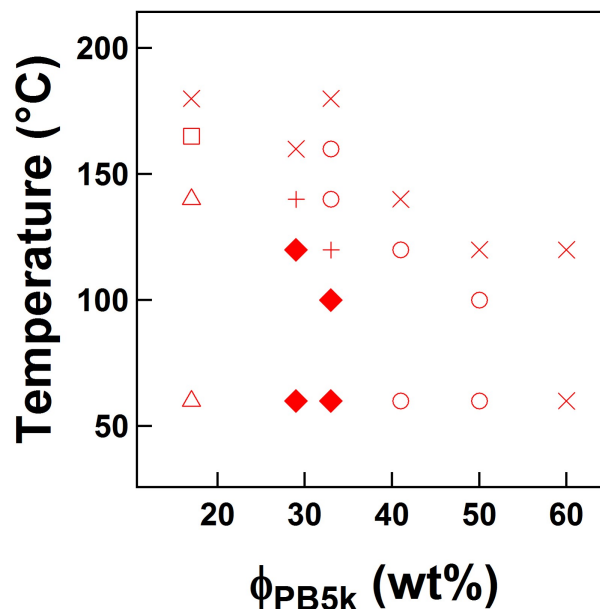


Fig. 1: The phase diagram for PB-PCL/PB5k blends. Phase notation is as follows: triangles (HEX), squares (coexisting of HEX and BCC), circles (BCC), pluses (σ phase), diamonds (transient disordered micelles) and crosses (disordered state).

References

[1] T. Dotera, *J. Polym. Sci. Part B* **50**, 155 (2012).

- [2] N. Xie, et al., *ACS Macro Lett.* **3** 906 (2014).
- [3] H. Takagi, et al., *J. Phys: Condens. Matter* **29**, 204002 (2017).
- [4] H. Takagi, et al., *Colloid Polym. Sci.* **294**, 993 (2016).

* takagih@post.kek.jp