

## The Labyrinth of Block Copolymers with Nanometer Scale: Conditions for Forming Ordered Bicontinuous Double-Diamond Structures

Block copolymers can easily form highly ordered and labyrinth-like bicontinuous morphologies. In this study, the conditions necessary for forming ordered bicontinuous double-diamond (OBDD) structures were investigated by small-angle X-ray scattering (SAXS) in polystyrene-rich polystyrene-polyisoprene block copolymer (PS-PI) and polyisoprene (PI) blends. Our findings reveal that three conditions are needed to form OBDD phases: (i) The volume fraction of PI ( $f_{PI}$ ) is within the range of  $f_{PI} = 31\text{--}35$ ; (ii) The chain length of PI homopolymer is longer than that of the same constituent chain in PS-PI; and (iii) A threshold homopolymer amount (11 wt.%) may be required.

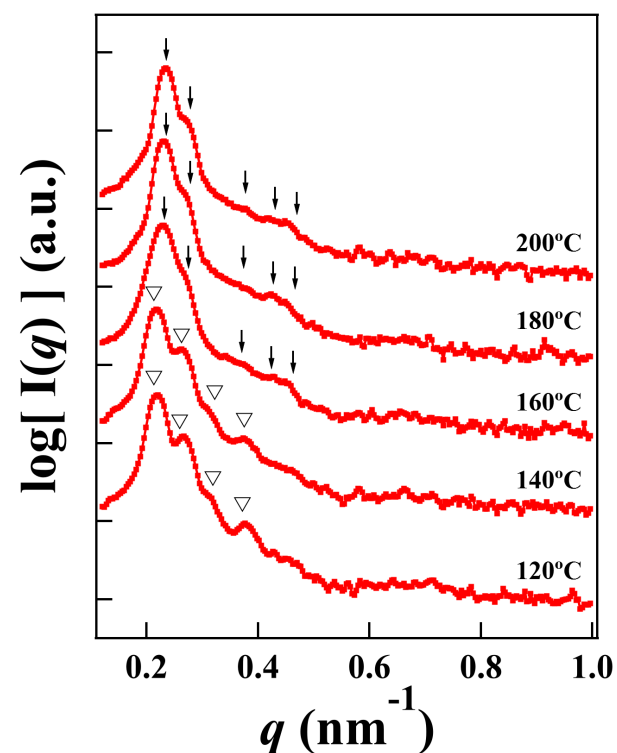
Block copolymer self-assembly can result in periodic structures with long-range order and nanoscale features. It is well known that there are two types of highly ordered bicontinuous morphologies—gyroid (Gyr) and *Fddd*—as equilibrium structures in linear diblock copolymer systems. Gyr is a double network-type morphology constructed from 3-fold nodes connected by *la3d* symmetry while *Fddd* is a non-cubic single network in an orthorhombic unit cell and is constructed from 3-fold nodes.

The ordered bicontinuous double-diamond (OBDD) structure is another type of bicontinuous morphology, consisting of 4-fold nodes connected by *Pn3m* symmetry. Theoretical works predict that OBDD is not in the equilibrium state in a simple linear diblock copolymer system due to the existence of high packing frustration in 4-fold nodes of OBDD [1]. However, theoretical calculations suggest that OBDD exists as an equilibrium

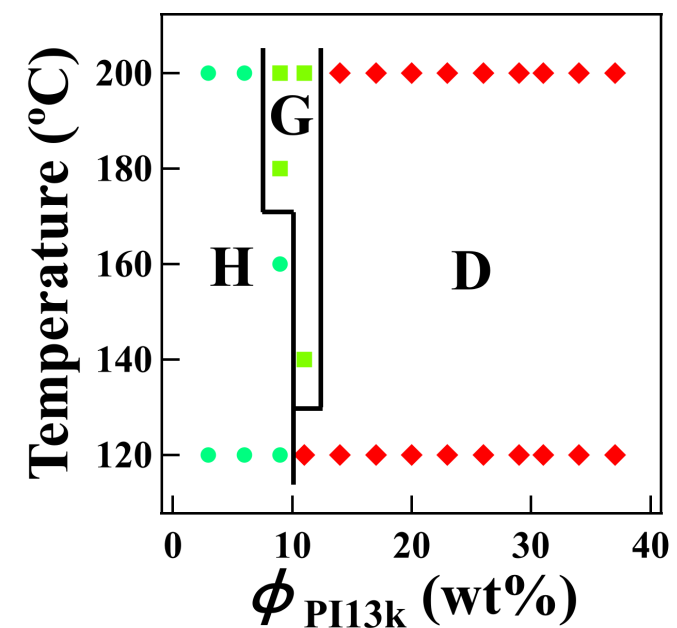
phase in A-B diblock copolymer and A homopolymer blends. By controlling the homopolymer distribution, the packing frustration inside 4-fold-node-connected OBDD can be relaxed as the homopolymer is localized to the middle region of the nodes.

Previously, we investigated the phase behavior in blends of block copolymer and homopolymer and found that OBDD structures appeared as a stable phase in binary mixtures of block copolymer and homopolymer [2, 3]. The objective of the present study was to investigate the effect of block copolymer composition and chain length of the homopolymer on OBDD stability in blends of PS-rich PS-PI/PI and to analyze the conditions necessary for OBDD formation.

PS-rich PS-PI diblock copolymers and PI homopolymers were synthesized by anionic polymerization under high-vacuum conditions. The degree of polymerization



**Figure 1:** SAXS profiles of a representative blend of PS-PI and PI during the heating process. Triangles indicate the scattering peak positions of OBDD and arrows represent the peak positions of Gyr.



**Figure 2:** Phase diagram of blends of SI33 and PI13k. ●, HEX; ■, Gyr; ◆, diamond, OBDD. The gray shaded regions represent macro-phase separation and solid lines represent phase boundaries.

of PS-PIs used in this study was  $\sim 320$  and the volume fraction of PI ( $f_{PI}$ ) was in the range of  $31 \leq f_{PI} \leq 40$  vol.%; meanwhile, in the homopolymers, the homopolymer chain length ( $N$ ) was in the range of  $57 \leq N \leq 312$ . Laboratory-scale SAXS measurements were conducted using a Nano-Viewer instrument (Rigaku), and synchrotron SAXS experiments were performed at the BL-6A beamline.

The SAXS profiles of a representative PS-PI/PI blend are shown in Fig. 1. The profiles were vertically shifted to avoid overlapping and to facilitate analysis. At 120 and 140°C, scattering peaks were observed at relative  $q$ -peak ratios of  $1:(3/2)^{1/2}:(4/2)^{1/2}:(6/2)^{1/2}$ , as marked by triangular symbols. These scattering peak ratios are in good agreement with the theoretical positions of OBDD, indicating that OBDD was formed at 120 and 140°C. When the sample was heated to 160°C, the scattering peak positions changed to  $1:(8/6)^{1/2}:(16/6)^{1/2}:(20/6)^{1/2}:(22/6)^{1/2}$ . This means that OBDD was transformed into Gyr as the temperature was increased. Thus, order-order transition (OOT) from OBDD to Gyr occurred upon further heating.

Figure 2 shows the phase diagrams of binary blends of SI33 and PI13k, indicating various phases, such as hexagonally packed cylinders (HEX), Gyr, and OBDD. The ratio ( $\alpha$ ) of homopolymer chain length ( $N$ ) and total chain length of the block copolymer ( $N_{block}$ ) is defined as  $\alpha = N/N_{block}$ . Meanwhile,  $\alpha_{PI}$ , which is the ratio of PI chain length to that of the PI component in the block copolymer ( $N_{PI,block}$ ), is defined as  $\alpha_{PI} = N/N_{PI,block}$ . The gray shaded region in Fig. 2 indicates macro-phase separation. The phase notation is as follows: ●, HEX; ■, Gyr; ◆, OBDD. The molecular weights of SI33 and PI13k are

29,400 and 13,400 g/mol, respectively. The values of  $\alpha$  and  $\alpha_{PI}$  are calculated to be 0.6 and 1.53, respectively.

In SI33/PI13k blends, HEX was observed in the entire tested temperature range when  $\phi_{PI13k} \leq 6$  wt.%. HEX was transformed into Gyr when the temperature was increased and  $\phi_{PI13k} = 9$  wt.%. An OOT from OBDD to Gyr occurred at  $\phi_{PI13k} = 11$  wt.% but only OBDD could be observed when  $\phi_{PI13k} \geq 14$  wt.%. Thus, in SI33/PI blends, OBDD was observed only when  $\alpha_{PI}$  was at least 11 wt.% and the homopolymer chain length was greater than that of its counterpart in the diblock copolymer.

By comparing with other phase diagrams of PS-PI and PI blends, we concluded that OBDD emerges as a stable phase when the following requirements are satisfied: (1) volume fraction of PI in PS-PI is  $31 \leq f_{PI} \leq 35$  vol.%, (2) the molecular weight of PI is larger than that of the PI component of PS-PI, and (3) homopolymer content is at least 11 wt.% [4].

### REFERENCES

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### BEAMLINE

BL-6A

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