

Meta-stable Structures Observed Prior to Formation of Gyroid Phase in Poly(ϵ -caprolactone) -*block*-polybutadiene

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Introduction

Many studies on order-order transition (OOT) of block copolymers have been reported. During the phase transition including OOT, intermediated structures are often observed, which has been revealed by small angle X-ray scattering (SAXS) and transmission electron microscopy. In some cases, when transitions of hexagonally packed cylinder phase (HEX) to gyroid phase (Gy), lamellar phase (LAM) to Gy, and Gy to LAM occurred, it was reported that a perforated layer (PL) structure as a meta-stable structure appeared.¹⁻³

Here, we observed meta-stable structure of poly(ϵ -caprolactone)-*block*-polybutadiene (PCL-b-PB) during the phase transition from crystalline phase to Gy and disordered state to Gy. The observed meta-stable structure varied with sample composition.

Result and Discussion

Block copolymer PB-b-PCL was synthesized by anionic polymerization. The characteristics of the samples are listed in Table 1. The upper SAXS profiles of both samples BCL34 and BCL39 showed primary peak at q^* and higher-order peaks at $\sqrt{4/3}q^*$, indicating Gyroid phase. At room temperature, the crystalline-amorphous alternative structure was formed as shown in Figure 1. Figure 2 shows SAXS profile of BCL34 measured in a heating process at a rate of 10°C/min. Before the Gy phase forms, HEX phase appeared at 57 °C. As for BCL39, a process of gyroid formation was observed at 65 °C as shown in Figure 3.

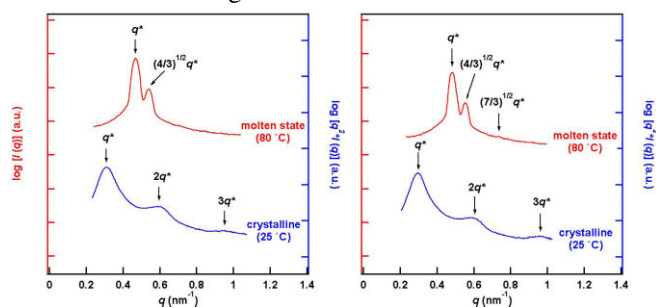


Figure 1. SAXS profiles of BCL34 (left) and BCL39 (right) observed at 80 and 25 °C.

Table 1: Characteristics of PCL-b-PB

Sample	M_n	M_w/M_n	ϕ_{PCL}	T_m (°C)
BCL34	6400	1.16	34 vol%	55
BCL39	5600	1.19	39 vol%	57

With increasing aging time, it was found that LAM phase decreased and Gy phase grew. We also examined transition from disordered state. Even in that case, HEX and LAM phase were observed prior to the formation of gyroid for BCL34 and BCL39, respectively.

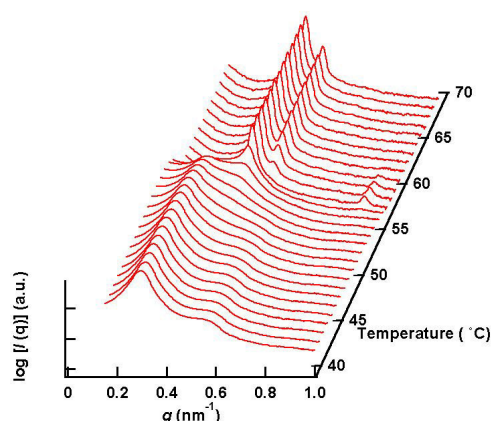


Figure 2. SAXS profile of BCL34 in a heating process at a rate of 10°C/min.

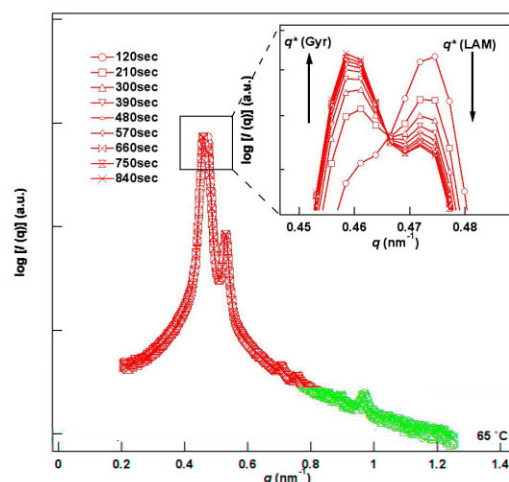


Figure 3. Time resolved SAXS measurement for BCL 39 during formation of Gy at 65°C.

References

- [1] M. E. Vigild et al., *Macromolecules*. 31, 5702 (1999).
- [2] I. W. Hamley et al., *J. Biol. Chem.* 1, 2097 (1999).
- [3] D. A. Hajdul et al. *J. Phys. Chem. B.* 102, 1356 (1998).

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