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Dynamics of the order-order transition in SI diblock copolymer melts

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Introduction

Block copolymers that are composed of chemically different polymers connected by a covalent bond can self-assemble into various microstructures via microphase separation. Typically, the microstructures of block copolymer depend on several parameters such as the copolymer composition (f), the Flory-Huggins interaction parameter (χ), and the total number of the statistical segments (N). The phase behavior in block copolymers has also been studied extensively, both theoretically and experimentally [1]. Recently we reported a new bicontinuous microdomain morphology with the symmetry of *Fddd* space group found in a polystyrene-*block*-polyisoprene (SI) diblock copolymer with number–average molecular weight M_n = 2.67 x 10^4 g/mol, polydispersity index M_w/M_n =1.02, and volume fraction of polyisoprene f_{PI} = 0.629 [2]. And we confirmed the stability of *Fddd* structure and found *Fddd* structure exists as an equilibrium structure in SI diblock copolymer [3]. In this study, we performed time-resolved SAXS experiments on the order-order transition (lamella-*Fddd*-gyroid) induced by temperature jump in SI diblock copolymer to investigate the ordering mechanism.

Experimental

We synthesized SI diblock copolymer with M_n = 2.57 x 10^4 g/mol, M_w/M_n=1.02 and f_{PI} = 0.635 via living anionic polymerization in benzene at 50˚C using *sec*-butyl lithium (Kanto Chemical Co.) as initiator. SI diblock copolymer were prepared by casting 5wt% toluene solution with 0.2 wt% Irganox and obtained by solvent casting at room temperature. Time-resolved SAXS experiments were performed at BL-15A in KEK, Japan by temperature jump of the sample. The X-ray wavelength and the sample-to-detector distance were, respectively, 0.154nm and 2000mm. Imaging plate was used as the detector.

Experimental

The microdomain structures of SI diblock copolymer were investigated as a function of temperature in situ by SAXS. It exhibited lamellar structure at 120˚C, *Fddd* structure at 145˚C, and gyroid structure at 155˚C. Therefore it showed two types of order-order transitions (lamella-*Fddd* and *Fddd*-gyroid) with increasing temperature. The temperature jump measurements were conducted by rapid heating SI diblock copolymer from 120˚C where we observed lamellar structure to 155˚C where we observed gyroid structures. Figure 1 shows the time-evolution of SAXS profiles after the T-jump from 120˚C to 155˚C. Before the T-jump to 155˚C, we found the peaks at q/q_m = 1, 2, and 3, where q_m is q at the first order peak, indicating that lamellar structure was formed. After the T-jump in 5 min we found the several peaks at q/q_m =1, 1.22, 1.55, 1.72, 1.81, 1.95, and 2 thus, SI diblock copolymer exhibited *Fddd* structure. *Fddd* structure was sustained until 15min. From 30 min, the peaks appeared at q/q_m =1 and 1.15, which means gyroid structure started to appear but we also observed the characteristic peaks of *Fddd* structure indicating *Fddd* and gyroid structures coexists. After 40 min from the T-jump *Fddd* structure disappeared and gyroid structure exists as a stable phase at 155˚C. As a result, we found when the phase is transformed from lamella to gyroid, it pass through *Fddd* structure.

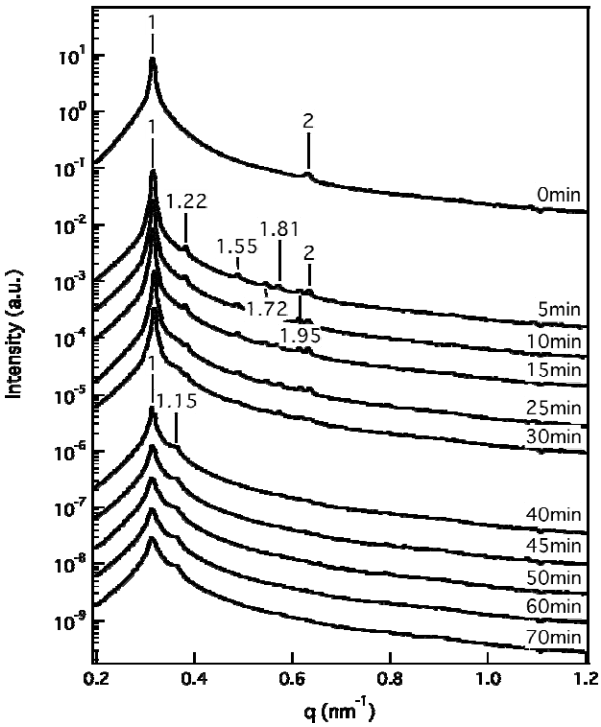

Figure 1 Time changes in SAXS profiles during OOT.

References

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