Orthorhombic *Fddd* Network in Diblock Copolymer Melts

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ジブロックコポリマーにおいて初めて小角 X 線散乱法と電子顕微鏡によって Fddd 構造を見いだした。このブロックコポリマーは温度の低下に伴い、無秩序-Fddd-ラメラと構造転移することが確認された。

1 Introduction

Recently, a remarkable finding has been done by Bailey et al.[1]. They identified a noncubic network morphology, the *Fddd* (O^{70}) structure in poly(isoprene-*b*-styrene-*b*-ethyleneoxide) (ISO) triblock copolymers. Epps et al. confirmed that the O^{70} phase is an equilibrium phase in triblock copolymers[3, 4]. Tyler et al. studied the phase behavior of triblock copolymers by using SCFT[5]. The calculated phase diagram is quite similar to that of ISO and the O^{70} phase is found to be located between gyroid, lamellae, and alternating gyroid phases as an equilibrium phase. Tyler et al. also found the O^{70} phase between gyroid, lamellae, and cylinder phases with SCFT calculation although the region of the O^{70} phase is limited within quite a narrow temperature region[5]. We, thus, studied the phase behavior of poly(styrene-*b*-isoprene) by using small-angle X-ray scattering (SAXS) and transmission electron microscope (TEM) in detail.

2 Experimental

We studied an isoprene-rich S-I diblock copolymer. The S-I used here has volume fraction of isoprene f_{PI}=0.63$_8$, the weight–averaged molecular weight M_w=2.64×10^4 and the heterogeneity index M_w/M_n= 1.02. The S-I was synthesized by an anionic polymerization method. SAXS experiments were conducted on BL-15A at KEK, Japan. We observed the morphology of the S-I diblock copolymer with a transmission electron microscope (JEM-2000EX, JEOL Co., Ltd).

3 Results and Discussion

Figure 1 shows the temperature dependence of azimuthally-averaged SAXS profiles of the S-I. At 230°C, a broad peak is observed which corresponds to disordered phase. Below 170°C, several distinct peaks appear in the profiles, indicating that the S-I is in its ordered state. Except for T=160°C, and T=135°C, the peak positions at the other temperatures coincide each other. In the case of T=150°C, the SAXS peaks are located at q/q_m = 1, 1.22, 1.56, 1.72, 1.81, 1.94, 2, 2.18, 2.29, 2.49, 2.75, 2.93, 3. This series of peaks suggests that the lattice structure of the S-I is an orthorhombic. The peak positions of orthorhombic lattices are calculated by

$$q_{hkl} = 2\pi[h^2/a^2 + k^2/b^2 + l^2/c^2]^{1/2}, \quad (1)$$

where a, b, and c are unit cell parameters and h, k, and l are Miller indices for a, b, and c, respectively. We estimated (a:b:c) = (1:2.02:3.47) and the Miller indices indicated by arrows in Fig.1. These peaks agrees with those for O^{70} structures. These agreements suggest that the S-I diblock copolymer forms O^{70} structures. Although we do not show here, TEM observation also confirmed that the obtained

structure correspond to O^{70}. At 137.5°C, the peak positions ratio of the SAXS profile are 1, 2, and 3 suggesting that the S-I diblock copolymer melt forms lamellar structurse at this temperature. A strange feature appears in SAXS profiles at 165°C and 160°C. The second peak position splits into two peaks at q/q_m = 1.22 and 1.14, while the higher order peaks agrees with the peaks observed at 150°C, 170°C and 172°C. Since gyroid structures has a second peak at q/q_m = 1.15, the coexistence of gyroid and O^{70} structures is one of the possible reason of these peaks. However, we can not observe the higher order peaks originating from gyroid structures. Thus we can not identify definitively the structures present in this temperature region. This point will be addressed in future work. Finally, we plotted the points of O^{70} structures in the phase diagram obtained by Khandpur et al[2]. We used the following temperature dependence of χ parameter reported in their paper:

$$\chi = 71.4/T - 0.0857. \qquad (2)$$

The O^{70} region is located between Lamellar, Gyroid and HPL regions. This location of the O^{70} region agrees with the SCFT phase diagram obtained by Tyler et al[5]. According to the SCFT phase diagram, we anticipate that the S-I with f being slightly larger than 0.64 exhibits gyroid- O^{70}-lamellar transition with decreasing temperature. We will investigate the phase diagram around f=0.64 in detail and confirm the regions of the O^{70} structures and the order-order transition between the morphologies.

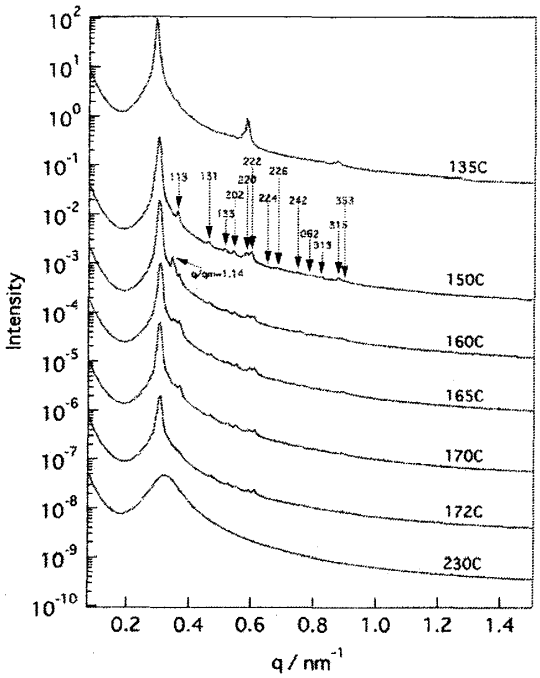

Figure 1. Azimuthally-averaged SAXS profiles for S-I at various temperatures. Indices of SAXS profile for 170°C are calculated for *Fddd* structures with unit lattice cell constant. The SAXS profiles are shifted vertically for clarity.

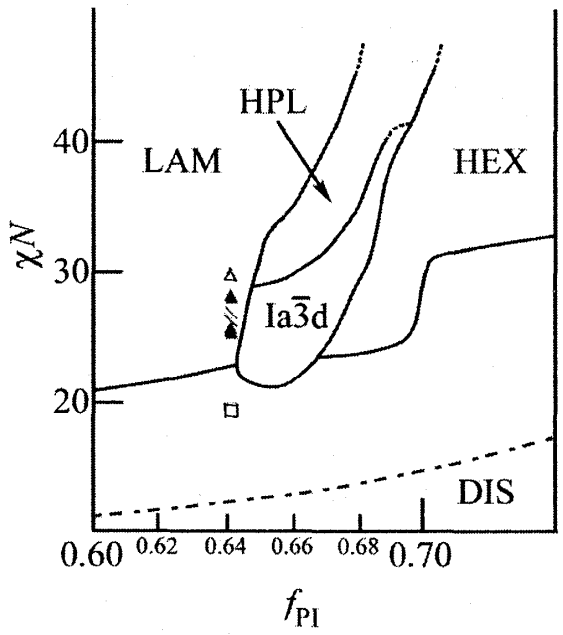

Figure 2. Phase diagram of S-I diblock copolymers. Open square, filled triangle, and cross symbols correspond to disordered state, O^{70} structure and lamellar structures, respectively. Open triangle, corresponds to the coexistence of gyroid and O^{70} structures. Adapted from Khandpur et al.[2]

References

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