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Orthorhombic *Fddd* Network in Diblock Copolymer Melts

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Soft materials such as block copolymers, surfactant, and liquid crystals exhibit a variety of ordered microstructures. Among them, the phase diagrams of diblock copolymers have been extensively investigated both experimentally and theoretically. Matsen and Schick[1] calculated the phase diagram of diblock copolymer melts by using self-consistent-field theory (SCFT) and predicted that the phase diagram contains four types of microdomain structures: spheres packed in a body-centered-cubic lattice, cylinders packed in a hexagonal lattice, alternating lamellae and double-gyroid networks. Khandpur et al.[2] investigated the phase diagram of poly(styrene-*block*-polyisoprene) diblock copolymer (S−I) in detail and showed a good agreement between their experimental results and the phase diagram calculated by SCFT. Then, in order to seek more variety of ordered structures, several researches on the phase behaviors of triblock copolymers have been done.[3−11] Among these studies a remarkable finding has been done by Bailey et al.[3] They identified a noncubic network morphology, the *Fddd* structure in poly(isoprene-*b*-styrene-*b*-ethylene oxide) (ISO) triblock terpolymer melts. Epps et al. confirmed that the *Fddd* phase is an equilibrium phase in triblock copolymers.[6−8] Tyler et al. studied the phase behavior of triblock copolymers as a function of composition at given conditions, where the Flory−Huggins interaction parameters, polymerization index, and statistical segment length are fixed, by using SCFT.[12] The calculated phase diagram is quite similar to that of ISO, and the *Fddd* phase is found to be located between gyroid, lamellae, and alternating gyroid phases as an equilibrium phase. Tyler et al.[12] also predicted the *Fddd* phase which is a 3-dimensional network morphology in an orthorhombic unit cell with *Fddd* space group symmetry, existing as an equilibrium phase surrounded by gyroid, lamella, and cylinder phases from a SCFT calculation for diblock copolymer melts although the *Fddd* phase was limited within a quite narrow temperature region. Yamada et al.[13] and Ranjan et al.[14] also found the *Fddd* phase in diblock copolymer melts by using a mode expansion method. Since two different theoretical approaches successfully predicted the phase diagram for the known morphologies of diblock copolymer melts, we can also anticipate the existence of the *Fddd* phase. We, thus, investigated the phase behavior of S−I melts in detail by using small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The SCFT calculation showed that the *Fddd* phase of diblock copolymer melts has a slightly asymmetric volume fraction f ($0.42 < f < 0.5$), and Khandpur et al.[2] found that the S−I with the composition rich in polyisoprene exhibits a variety of unusual ordered structure such as gyroid and hexagonally perforated layer (HPL). Therefore, we studied the S−I with a slightly asymmetric composition rich in polyisoprene. S−I-1, the S−I used here, has the volume fraction of polyisoprene $f_{PI} = 0.638$, the number-average molecular weight $M_n = 2.64 \times 10^4$ g/mol, and the heterogeneity index $M_w/M_n = 1.02$. S−I-1 was synthesized by a living anionic polymerization method. SAXS experiments with synchrotron radiation were conducted at BL-15A in KEK, Japan, and at BL45XU in SPring-8, Japan. At BL-15A, the X-ray wavelength and the distance from sample to detector were respectively 1.5 Å and 2000 mm. Imaging plates were used as the detector. At BL45XU,[15] the wavelength and the distance from sample to detector are respectively 1.5 Å and 3300 mm. A CCD camera was used as the detector. In-situ SAXS measurements were performed at particular temperatures, 120, 135, 145, 150, 160, 170, and 230 °C. Prior to each measurement we first annealed the samples at 230 °C for 30 min and then kept the samples at each temperature at least for 8 h in a N_2 gas atmosphere to attain the equilibrium structure. It should be noted that the samples are in their disordered state at 230 °C and that the anneal for 30 min is long enough to erase the morphologies formed previously. We also observed the morphology of S−I-1 at 135, 150, and 170 °C with TEM (JEM-2000FX, JEOL Co., Ltd.) at an acceleration voltage of 200 kV. We annealed S−I-1 sample specimen at 135, 150, and 170 °C for 8 h and then quenched them into liquid nitrogen to freeze the structures at each temperature. Ultrathin sections of ca. 50 nm thickness were obtained by cryo-ultramicrotoming with a Reichert-Nissei

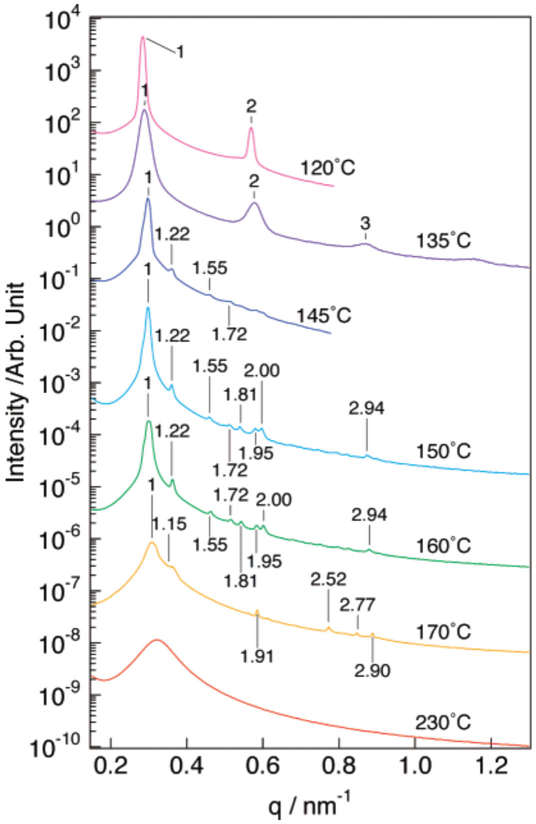

Figure 1. Azimuthally averaged SAXS profiles for S−I-1 obtained at designated temperatures. The SAXS data at 120 and 145 °C were measured with BL45XU while the others were measured with BL-15A. The samples were first annealed at 230 °C and then at each temperature of measurement at least for 8 h prior to the SAXS measurements. The SAXS profiles are vertically shifted for clarity. The number at each peak position indicates the ratio of the wavenumber q of the peak to that of the first-order peak.

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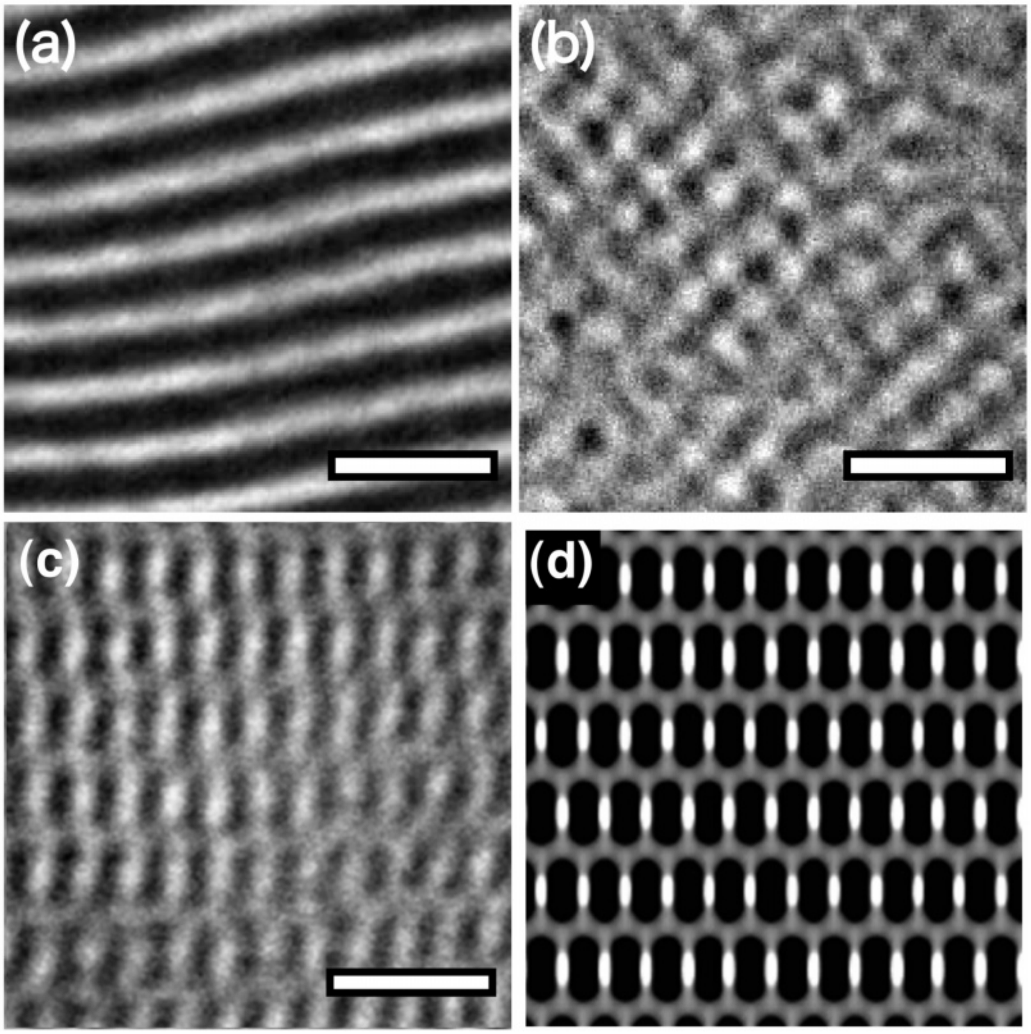

Figure 2. (a) TEM image of S−I-1 at 135 °C. The striped pattern indicates a lamellar structure. (b) TEM image of S−I-1 at 170 °C. The 4-fold gridlike pattern suggests a gyroid structure. (c) TEM image of S−I-1 at 150 °C. The pattern of the staggered rows of bright areas suggests a network structure interconnected with trivalent junctions. (d) Simulated TEM image of the projection in ⟨100⟩ direction obtained from the *Fddd* structure calculated with a Fourier synthetic method.[8] Scale bars in a, b, and c represent 50 nm.

Ultracut S ultramicrotome, stained with O_SO_4 vapor before TEM observation. Consequently, the dark part in the TEM images corresponds to polyisoprene domains.

Figure 1 shows the temperature dependence of the SAXS profiles of S−I-1 obtained from the 2D SAXS patterns by azimuthal averaging. The scattered intensity in arbitrary units is plotted as a function of the wavenumber q ($q = (4\pi/\lambda)\sin(\theta/2)$; θ is the scattering angle and λ is the wavelength) for each profile. At 230 °C, a single broad peak suggests that S−I-1 is in the disordered state. Although we do not show the data here, we also performed the experiment to determine the order−disorder transition temperature,[16] which was estimated to be 190 °C from the temperature dependences of the intensity and width of the first-order peak. Below 170 °C, several distinct peaks appear in the profiles, indicating that the S−I-1 is in its ordered state. At 120 and 135 °C, we found that the peaks in the SAXS profiles appeared at q with integer multiples of q_m, where q_m is q at the first-order peak. This indicates that S−I-1 has the lamella phase at 120 and 135 °C. The lamellar spacing estimated from the first-order peak was 22.1 and 21.7 nm for 120 and 135 °C, respectively. The striped pattern in TEM image at 120 °C (Figure 2a) also suggests the lamella structure. At 170 °C, the SAXS profile has the peaks at $q/q_m = 1$, 1.15, 1.91, 2.52, 2.77, and 2.90 with $q_m = 0.306$ nm^{-1}. These ratios agree with that of a double-gyroid structure. The TEM image at 170 °C exhibits a 4-fold gridlike pattern, which is typical of the projection of a double-gyroid structure onto the (001) plane, in agreement with the SAXS result. At 150 and 160 °C, the ratios q/q_m are different from those of gyroid at 170 °C. An enlarged SAXS profile at 150 °C is shown in Figure 3. The SAXS peaks are located at $q/q_m = 1$, 1.22, 1.55, 1.72, 1.81, 1.94, 2.00, 2.49, 2.65, 2.75, and 2.93 with $q_m = 0.297$ nm^{-1}. This series of peaks agrees with those of the *Fddd* structures of ISO triblock terpolymer melts,[8] and we found that this series of peaks originated from the lattice structure with the orthorhombic unit cell having the *Fddd* space group symmetry.[17] The peaks can be indexed as 111 ($q/q_m = 1$), 113 (1.22), 131 (1.55), 133 (1.72), 202 (1.81), 220 (1.94), 222 (2.00), 242 (2.49), 062 (2.65), 313 (2.75), and 315 (2.93) as indicated in Figure 3. We estimated $(a{:}b{:}c) = (1{:}2.00{:}3.51)$ with $a = 24.4$ nm by using

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

where a, b, and c are unit cell parameters and h, k, and l are Miller indices for a, b, and c, respectively. In order to check that the *Fddd* structure appears irrespective of the thermal history, we annealed the S−I-1 at 120 °C for 8 h and then annealed the S−I-1 at 145 °C for 1 h. After annealing at 120 °C for 8 h, the SAXS profile appeared at q with integer multiples of q_m, indicating that lamellar structure was formed

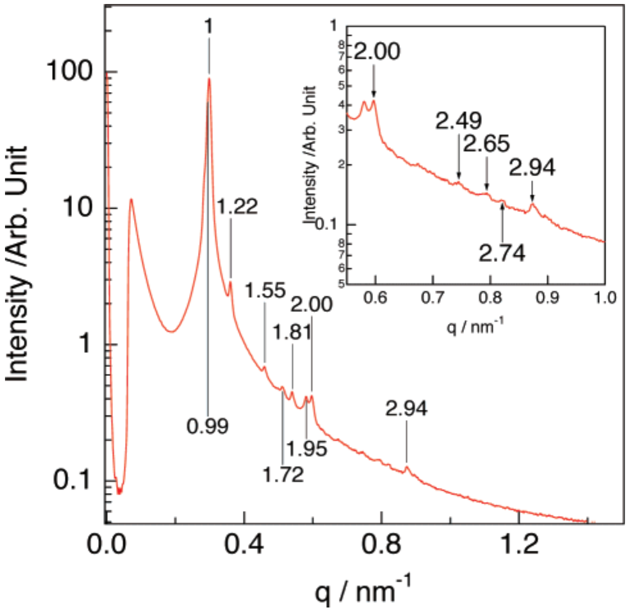

Figure 3. SAXS profile of S−I-1 at 150 °C. Indices are calculated for the *Fddd* structure with the unit cell parameters of (a:b:c) = (1:2.00:3.51). Inset corresponds to the enlarged profile at higher q region.

in the S−I-1. As the result of subsequent annealing at 145 °C, the peak at $q/q_{\mathrm{m}} = 1.22$ was developed, and the lamellar structure changed into the *Fddd* structure by the annealing at 145 °C. This fact suggests that the *Fddd* structure is formed at 145 °C irrespective of the thermal history applied previously.

Figure 2c shows the representative TEM image of S−I-1 annealed at 150 °C. Three different contrasts, bright, gray, and dark, are seen in the image, suggesting a complex structure with bright polystyrene domains (minor component) and dark polyisoprene domains (major component) overlapping in the thickness of the ultrathin section. The 2-fold symmetry in Figure 2c agrees with the *Fddd* symmetry. The stripes consisting of alternating bright and dark regions are separated by the gray lines, and the bright regions in the adjacent stripes are staggered by a half repeat distance, suggesting the trivalent junctions of polystyrene network in polyisoprene matrix as reported for the *Fddd* structure.[12,13] These features also agree with those obtained for *Fddd* structures of ISO triblock terpolymer melts.[8] However, it is not possible to elucidate the 3D structure from the 2D image. Therefore, we compared the TEM image with the simulated projection obtained from *Fddd* structure calculated with a Fourier synthetic method,[8] as shown in Figure 2d. The features of the simulated projection agree with those in the TEM image, indicating that S−I-1 has the *Fddd* structure at 150 °C.

In Figure 4, we plotted our data points of observed morphologies including the *Fddd* structure in the same phase diagram as obtained by Khandpur et al.[2] We used the following temperature dependence of χ parameter reported in their paper:

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

In the χN vs f_{PI} phase diagram where N is the degree of polymerization, the *Fddd* phase was observed as the thermodynamically stable phase surrounded by lamellae, gyroid, and HPL phases. This location of the *Fddd* phase agrees with the SCFT phase diagram obtained by Tyler et al.,[12] although the *Fddd* phase obtained experimentally is shifted to a higher f_{PI} region than that obtained by SCFT due to the conformational asymmetry between PS and PI.[2] Moreover, the gyroid−*Fddd*−lamellae transition sequence with increasing χN or decreasing temperature observed in our experiment also agrees with the sequence of order−order transition obtained by Tyler et al.[12] However, we did not find the cylinder and spheres regions between gyroid and disorder as Tyler et al. predicted. The thermal fluctuations effects may suppress the cylinder and spheres regions.[18]

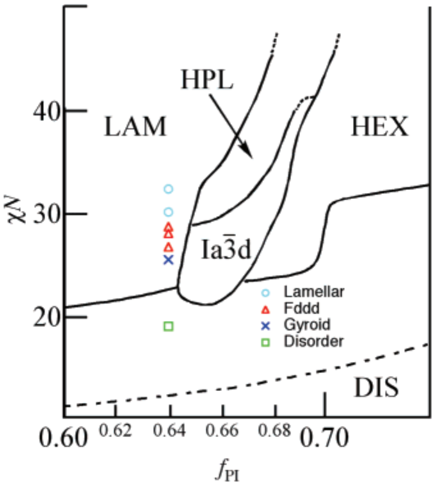

Figure 4. Observed microdomain morphologies in this study (symbols) are superposed on the phase diagram of S−I adapted from Khandpur et al.[2] Open circle, open triangle, cross, and open square symbols correspond to lamellar, *Fddd*, gyroid, and disordered state, respectively. The solid lines are the phase boundaries reported by Khandpur et al.:[2] LAM = lamellae, $Ia\bar{3}d$ = gyroid, HPL = hexagonally perforated layers, HEX = hexagonally packed cylinder, and DIS = disordered state.

Let us discuss the origin of the stability of the *Fddd* structure in diblock copolymer melts. Tyler et al.[12] suggested that the particular ratio of the unit cell parameters causes the near coincidence of 004, 111, and 022 reflections, which contributes to the stability of the *Fddd* structure. We calculated the positions of 022 and 004 reflections with (a:b:c) = (1:2.00:3.51), a = 24.4 nm, and eq 1. q_{022}/q_{111} and q_{004}/q_{111} for S−I-1 are respectively 1.00 and 0.99 (indicated in Figure 3) so that the near coincidence of 004, 111, and 022 reflections occurs in the S−I-1.

Yamada et al.[13] determined that the phase diagram of diblock copolymer melts by using a mode expansion method and also found the *Fddd* phase. According to their result, the *Fddd* structure did not become an equilibrium structure in their phase diagram when they calculated it with only 18 modes which were the minimal number of modes to express lamellae, cylinder packed in a hexagonal lattice, sphere packed in a body-centered-cubic lattice, gyroid, and *Fddd*. However, if 15 higher modes including 004 mode are added in the calculation, the *Fddd* region appears as an equilibrium structure in the phase diagram. Ranjan et al.[14] have shown that the Landau theory can explain the stability of the *Fddd* phase within the contest of a single wavenumber approximation where the primary set of reflections includes 111, 022, and 004. These facts also suggest that the higher modes play an important role in the stability of the *Fddd* structure.

As already mentioned above, *Fddd* structures have been found in ISO triblock terpolymer melts by Epps et al.[7,8] They observed the *Fddd* structures in significantly wider region in terms of both composition and temperature. In contrast, the diblock copolymer melts exhibit the *Fddd* structure in a much narrower compositional region in the phase diagram. The wider *Fddd* region of ISO may originate from the difference in the asymmetry of block copolymers. According to the results by Epps et al., the *Fddd* phase in the ISO triblock terpolymer melts was observed when the volume fractions of polyisoprene (I) and polystyene (S) were similar but that of poly(ethylene oxide) (O) was different, i.e., $f_S = f_I > f_O$, with f_j being the volume fraction of the jth (I, S, or O) component. In such triblock terpolymers, a flat interface is preferred between I and S domains while the interface between S and O tend to curve due to the finite spontaneous curvature. The formation of the three-dimensional network structure could minimize the frustration caused by this conflict. Thus, the ISO triblock terpolymers can stabilize the *Fddd* structure in wider region in terms of both composition and temperature since the structure formation is driven by the interfacial energy.

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