3. *Thermoreversible Morphology Transition of Block Copolymers*^{†)}

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Abstract: Thermoreversible morphological transition of a poly(styrene-*block*-isoprene) (SI) block copolymer was studied by small-angle X-ray scattering and transmission electron microscopy (TEM). Although block copolymers are theoretically predicted to exhibit a reversible morphological change between lamellae and disordered state via cylinders and spheres with temperature, this thermoreversibility in morphology transition has not been experimentally confirmed yet. In order to study this thermoreversible transition, the SI diblock copolymer may have to have a biased composition and sufficient mobility. To meet these requirements, we used the SI with the weight fraction of polystyrene (PS) 0.16 and with a relative low number-average molecular weight 8.2×10^4 . Heat treatments of the specimen were carefully conducted. Moreover, the ultrathin sectioning was performed by cryo-ultramicrotomy at -85°C for TEM studies. The cylindrical and spherical microdomains of PS which are embedded in the polyisoprene matrix were thermoreversibly observed at 150 and 200°C , respectively.

Key words: Block copolymer; SI diblock copolymer; morphology transition; spherical microdomain; cylindrical microdomain.

Introduction. Thermally induced morphological transition in a block copolymer has potentiality to promote kinetic control of morphology in various ways. This has a similar concept of the kinetic control of morphology of polymer blends via spinodal decomposition.¹⁾ Although the phase-separated structure in the block copolymers is considerably smaller than that in the polymer blends, physical properties of the block copolymers also strongly depend on their morphologies.²⁾ The use of a selective solvent for the solution casting of the block copolymer has promoted the morphology control and the thermally induced morphology transition.³⁾ In this case kinetically locked morphology can be formed in the as-cast specimen and the thermally induced transition from such kinetically locked morphology to an equilibrium morphology in melts has been definitely elucidated.³⁾

Control of thermodynamically equilibrium morphology is another important aspect. The recent theories⁴⁾⁻⁸⁾ predict that the morphology reversibly changes with the

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segregation power and therefore with temperature. According to Leibler's theory,⁴⁾ in which the so-called finite size effect^{5)–8)} was not included, with increasing temperature the equilibrium morphology changes from lamellae to disordered state via cylinders and spheres, except for $f = 0.5$, and this morphological changes should be thermoreversible. The quantity f denotes the fraction of one of the block chain in the copolymer. However, the thermoreversible transition has not yet been experimentally confirmed. This may be due to narrow temperature ranges for cylinders and spheres when $f \approx 0.5$. As f approaches to 0 or 1, the possible morphology in the cast film at room temperature (or in the strong segregation limit) is cylindrical or spherical. In the case of cylinders, the transition from cylinders to spheres should be necessarily detected with increasing temperature, prior to observation of the disordered state. However, this kind of observation has also never been confirmed.

A poly(styrene-*block*-isoprene) (SI) block copolymer was used in order to study the thermoreversible morphological transition by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). Since the copolymer was required to have sufficient mobility and the biased composition f , the SI with the small weight fraction of polystyrene (PS) (0.16) was utilized. Moreover, the specimens were sufficiently heat-treated at 150 and 200°C so as to improve regularity in the packing of the microdomains and the ultra-thin sectioning was performed by cryoultramicrotomy at -85°C so as to prevent the microdomain structure from deformation by the sectioning. The cylindrical and spherical microdomains of PS in the polyisoprene (PI) matrix were thermoreversibly observed at 150 and 200°C, respectively.

Experimental. The SI specimen coded as SI-16/82 was living-anionically synthesized in benzene at 30°C with *sec*-butyllithium as the catalyst. The details of the synthesis is described elsewhere.⁹⁾ The number-average molecular weight, M_n , and the heterogeneity index, M_w/M_n were determined to be 8.2×10^4 and 1.05 by membrane osmometry and GPC, respectively, where M_w designates the weight-average molecular weight. The weight fraction of polystyrene (PS), w_{PS} , was analyzed by $^1\text{H-NMR}$ to be 0.16. The volume fraction of PS, f_{PS} , was calculated to be 0.15 using the densities 0.970 g/cm^3 for PS at 398K and 0.899 g/cm^3 for PI at 298K, respectively.¹⁰⁾ The microstructures in the PI blocks characterized by $^1\text{H-NMR}$ were 93 and 7% for 1,4- and 3,4-linkages, respectively. The film specimens were obtained by evaporating the solvent from *ca.* 5 wt% polymer solution using toluene as a solvent. Since the solubility parameter values¹¹⁾ are 7.9–8.4, 8.6–9.7 and $8.9 \text{ [cal/cm}^3\text{]}^{1/2}$ for PI, PS and toluene, respectively, toluene can be approximated as a

Fig. 1. Temperature diagrams for the heat treatment of Samples A, B, and C.

neutral solvent for SI.

The as-cast specimen was subjected to the thermal annealing at 150 and 200°C under vacuum. The temperature diagrams for the heat treatments used in this work are shown in Fig. 1. First, the as-cast specimen was heated up to 150°C and then held at this temperature for 30 min. Then the specimen designated as Sample A was obtained by immediately quenching it in iced water. For the other specimens, temperature was further raised to 200°C and kept for 30 min. Then the specimen designated as Sample B was obtained by immediately quenching the sample in iced water. For Sample C, temperature was cooled down again to 150°C, kept for **40 hours** and then quenched in iced water. These specimens were subjected to SAXS and TEM experiments. It is noted here that the kinetically locked morphology in the as-cast specimen,³⁾ if any, may be erased by the first annealing at 150°C for 30 min.

TEM was conducted in order to confirm the morphology analyzed by SAXS. The ultra-thin sectioning was performed by cryo-ultramicrotomy at -85°C, below T_g of PI (T_g = -68°C¹⁰⁾), to attain the rigidity of the specimen, using a Reichert Ultracut E low-temperature sectioning system. A Hitachi H-600 transmission electron microscope operated at 100 kV was used for the TEM of ultra-thin sections of the specimens stained with osmium tetroxide (OsO₄).

Results and discussion. Figs. 2 to 4 show TEM photographs for Samples A to C where the dark domains correspond to the PI microdomains stained with OsO₄, and the bright ones to the unstained PS microdomains. Generally speaking, the cylindrical microdomain structures of PS in the PI matrix phase were observed for Sample A (Fig. 2) and C (Fig. 4), while PS spheres in the PI matrix were seen for Sample B (Fig. 3).

The hexagonally packed PS-cylinders are observed everywhere in Sample A in Fig. 2. In some regions, the orientation direction of the cylinder axes is approximately parallel to and in other regions perpendicular to the thin section. For Sample B, PS spheres in the PI matrix are clearly seen in Fig. 3. While the ordering of the spheres is obviously seen, the micrograph shows a grain structure with its orientation changing from place to place. Fig.

Fig. 2. Transmission electron micrograph of Sample A.

4 clearly shows hexagonally packed PS-cylinders for Sample C which was annealed at 150° for 40 hours. Owing to the long annealing time, the degree of ordering of the cylinders seems to be better than that of Sample A, or in other words, the cylinders seem to be packed in larger grains. Thus TEM definitely revealed the thermoreversible morphological transition between cylinders and spheres at temperatures between 150 and 200°C.

Although the SAXS results are not presented in this report, let us describe the important findings.¹²⁾ For Sample A and C, the SAXS profiles are almost same and the scattering maxima can be detected at the relative q -values of 1, $\sqrt{3}$ and $\sqrt{4}$. These are the diffraction peaks from hexagonally packed cylinders. On the other hand, the maxima at the relative q -values of 1, $\sqrt{2}$ and $\sqrt{3}$ are detected for Sample B. These can be ascribed to the spheres arranged in a body-centered cubic (B.C.C.) lattice. The values of the Bragg's spacing d are evaluated from the positions of the first-order lattice scattering peak. In the SAXS profile, at least one scattering maximum due to the isolated particle can be clearly seen for every sample. In some cases even the second order maximum of the particle structure factor can be discerned. From the position of the particle scattering maxima, the average value of radius of the cylinders or spheres, R , is estimated. The values ϕ , which denotes the volume fraction of the particle, were estimated by assuming respective morphology from d and R values. It was found that the values ϕ assuming the hexagonally packed cylinders for Samples A and C are consistent with the f_{PS} value (0.15). On the other hand the spheres in B.C.C. lattice give the best result for Sample B among the four types of morphology, i.e., hexagonally packed cylinders, the spheres in simple cubic (S.C.) lattice, those in B.C.C. lattice and those in face-centered cubic (F.C.C.) lattice, respectively. Thus SAXS also revealed the thermoreversible morphological transition between cylinders and spheres at temperatures between 150 and 200°C.

Finally, it is noted that the thermoreversible morphological transition between spheres and cylinders is governed by balance of the following physical factors: (i) The free energy associated with the conformational entropy and (ii) that associated with the interfacial energy, both of which are a function of the interfacial curvature.¹²⁾

Fig. 3. Transmission electron micrograph of Sample B.

Fig. 4. Transmission electron micrograph of Sample C.

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