Effect of Annealing on the Perfection of Ordered Structure of Highly Asymmetric Diblock Copolymer

Daisuke Yamaguchi and Takeji Hashimoto*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

Nitin Y. Vaidya and Chang Dae Han*

Department of Polymer Engineering, The University of Akron, Akron, Ohio 44325-0301

Received June 28, 1999

Revised Manuscript Received August 31, 1999

Today it is well accepted by the block copolymer community that the classical microdomain structures, namely spheres in body-centered cubic lattice (bcc-sphere), hexagonally packed cylinders (hex-cyl), and lamellae, are equilibrium morphologies. In the past there was confusion as to whether other types of equilibrium microdomain structures might exist in block copolymers. Using transmission electron microscopy (TEM), some investigators[1,2] reported that an ordered bicontinuous double diamond (OBDD) morphology existed in some polystyrene-*block*-polyisoprene (SI diblock) copolymers in a narrow range of block compositions, between the block compositions that gave rise to the hexagonally packed cylindrical morphology and the lamellar morphology. Using small-angle X-ray scattering (SAXS) and TEM, Hajduck et al.[3] found a bicontinuous cubic morphology with $Ia\bar{3}d$ space group symmetry, referred to as double gyroid network, when an SI diblock copolymer having 37 wt % polystyrene (PS), which had lamellar morphology at low annealing temperature, was annealed at elevated temperatures approximately 50 °C below the order−disorder transition temperature (T_{ODT}). They claimed that the gyroid microdomain structure is an equilibrium morphology. Subsequently, Hajduck et al.[4] reported that the earlier identification of the OBDD morphology in the literature was incorrect and that the OBDD microdomain structure should be identified as the double gyroid network.

More recently, Bates and co-workers[5−8] claimed that two additional equilibrium microdomain structures, hexagonally modulated layered (HML) microdomain structure and hexagonally perforated layered (HPL) microdomain structure, also existed in a narrow range of block compositions, between the block compositions that gave rise to the hexagonally packed cylindrical morphology and the lamellar morphology. However, recent theoretical studies[9,10] indicate that both HML and HPL microdomain structures are *not* equilibrium morphologies, and subsequently Bates and co-workers[11] retracted their earlier claims.[5−8] It then becomes very clear that experimental determination of an equilibrium morphology of *neat* block copolymer requires extreme caution. We wish to point out that other types of microdomain structure (mesh, strut, catenoid-lamellar phase) have been reported in mixtures of a block copolymer and a homopolymer.[12−15] Despite the many research activities described above, relatively little attention has been paid to the effect of annealing on the perfection of ordered structure of highly asymmetric block copolymers.

Very recently, we found that annealing of a *highly asymmetric* SI diblock copolymer has a profound influence on the determination of order−order transition (OOT) temperature (T_{OOT}) when conducting isochronal dynamic temperature sweep experiment. In this Communication we report the highlights of our findings: a minimum in the dynamic storage modulus (G') observed at a temperature lower than T_{ODT} in the isochronal dynamic temperature sweep experiment does not necessarily signify OOT for highly asymmetric block copolymers; instead, the minimum in G' sometimes reflects ordering of initially imperfect bcc-spheres toward more perfect bcc-spheres with annealing of a specimen. Here we report our recent findings that a minimum in G', observed for an *unannealed* specimen in the isochronal dynamic temperature sweep experiment, disappeared completely when the specimen was annealed for a sufficiently long time at an elevated temperature below the lattice-disordering transition temperature (T_{LDT})[16] of an SI diblock copolymer (SI-7/29) having a number-average molecular weight of 3.56×10^4 determined by membrane osmometry, a polydispersity index of 1.03 determined by gel permeation chromatography, and a 0.18 volume fraction of PS (f_{PS}) determined by NMR spectroscopy. That is, we observed a remarkable annealing effect on the perfection of ordered structure, as determined by SAXS and TEM, of a highly asymmetric SI diblock copolymer. Full details of our results and interpretation will be described elsewhere.[17]

The sample preparation procedures and the experimental procedures employed for SAXS and TEM of this study are the same as described in our forthcoming paper[17] or previous papers,[16,18] except for the annealing conditions employed after the drying in a vacuum oven.

Figure 1 gives 2-dimensional (2D) SAXS patterns of the SI-7/29 measured with an imaging-plate detector system[19] (a) before annealing and (b) after annealing at 90 °C for 15 days, where $q = (4\pi/\lambda) \sin(\theta/2)$ is the magnitude of scattering vector $\mathbf{q}$ with λ and θ being the wavelength of X-ray and scattering angle, respectively. In Figure 1a,b we observe distinctly different SAXS diffraction patterns between the two specimens. Specifically, in the *unannealed* specimen (Figure 1a) we observe a diffuse ring, suggesting that the specimen consists of a large number of small, randomly oriented grains of bcc-spheres composed of PS block chains in the matrix of PI block chains, so that the first-order diffraction from (110) becomes a diffraction ring. On the other hand, in the *annealed* specimen (Figure 1b) we clearly observe several very bright diffraction spots, suggesting the existence of large grains composed of highly ordered bcc-spheres. Only a limited number of grains are seen to give (110) and (200) diffraction spots on the 2D detector plane, and other large grains give their corresponding diffraction spots in the space other than the 2D detector plane. In Figure 1c we observe a considerable difference in the azimuthal-angle dependence of the first-order peak between the two specimens (the symbol ● for an unannealed specimen and the symbol ○ for an annealed specimen), reflecting the difference between the diffraction pattern composed of a diffraction ring and the diffraction pattern composed of the discrete diffraction spots, respectively, shown in Figure 1, a and b.

10.1021/ma991034y CCC: $18.00 © 1999 American Chemical Society
Published on Web 10/13/1999

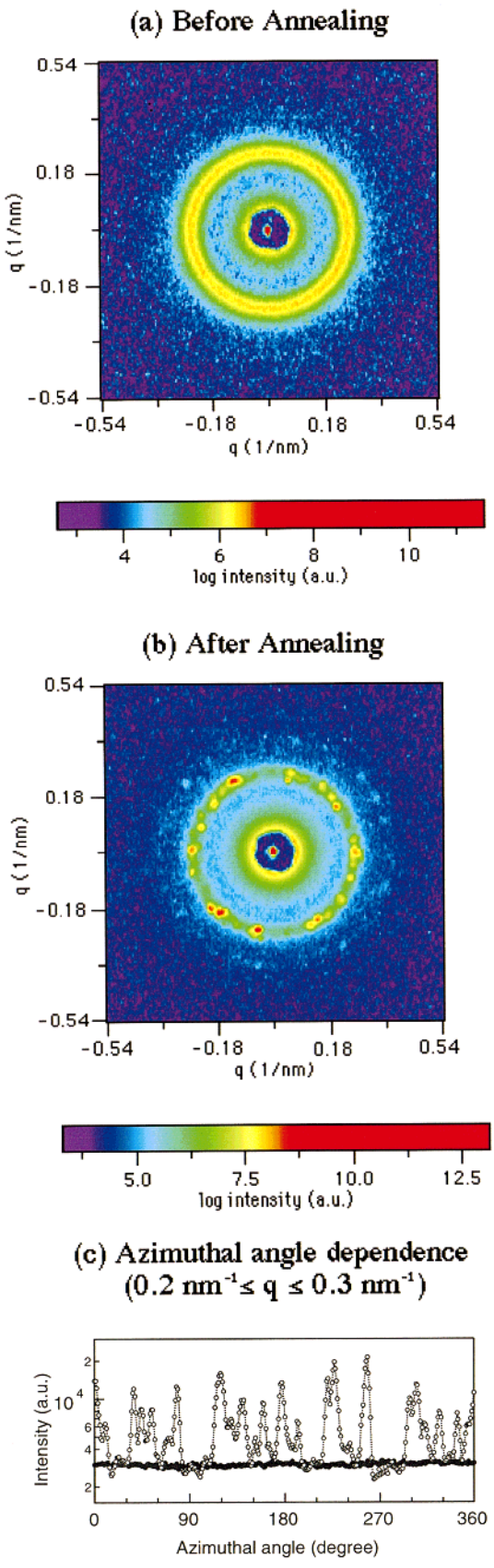

Figure 1. (a) 2D SAXS patterns before annealing, (b) 2D SAXS patterns after annealing at 90 °C for 15 days, and (c) the corresponding intensity distributions of the first-order peak with respect to azimuthal angle before annealing (●) and after annealing at 90 °C for 15 days (○) for the SI-7/29.

Figure 2 gives desmeared SAXS profiles with values of q that were obtained using slit collimation and a 1D

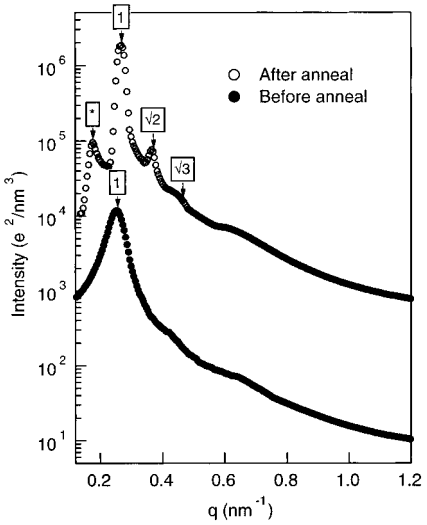

Figure 2. Desmeared SAXS profiles for the SI-7/29 before annealing (●) and after annealing at 90 °C for 15 days (○).

position-sensitive detector. These results are consistent with the 2D diffraction pattern given in Figure 1. In the SAXS profiles of the annealed specimen we observe three diffraction peaks located at ratios of $1:\sqrt{2}:\sqrt{3}$ in the reciprocal space, which originate from the interdomain interference, and one broad peak located at ca. $q = 0.6$ nm^{-1} from the particle scattering of the isolated sphere. Moreover, we observe an extra peak (designated with an asterisk) inside the first-order scattering maximum. This is due to an "artifact" encountered by detecting a (110) diffraction spot as shown in Figure 1b, existing at a position within a window of the 1D detector, using the 1D detector. Note that once the intensity of the spot was detected with the 1D detector, the corresponding scattering peak remained even after desmearing. The extra peak does reflect the diffraction spots in the 2D SAXS pattern. In contrast, in the SAXS profile of the unannealed specimen we observe a broad first-order peak, a very weak second-order shoulder, and a broad maximum from the particle scattering, suggesting a less ordered bcc lattice.

Figure 3 gives TEM images of SI-7/29 specimens (a) before annealing and (b) after annealing at 90 °C for 15 days, the same annealing condition as employed in the SAXS experiments described above. It is very clear from Figure 3 that a prolonged annealing made the bcc lattice of the SI-7/29 very distinct with very sharp grain boundaries.

Figure 4 gives the temperature dependence of G' during the isochronal dynamic temperature sweep experiment at $\omega = 0.01$ rad/s in the heating process for SI-7/29 specimens before and after annealing at 90 °C for 15 days. It can be seen in Figure 4 that the value of G' of the specimen before annealing went through a minimum at ca. 84 °C before beginning to decrease precipitously at a critical temperature (T_c) of ca. 96 °C, whereas a minimum in G' disappeared completely when the specimen had been annealed at 90 °C for 15 days.

The SAXS profiles $I(q)$ for SI-7/29 were measured as a function of q at various temperatures. The results revealed that the block copolymer after annealing at 90 °C for 15 days had bcc-spheres up to T_{LDT} (lattice-disordering temperature above which bcc lattice is destroyed and spheres exist with a short-range liquid-like order),[16,18] which was 93 °C. In other words, the SAXS results revealed *no* evidence of OOT taking place

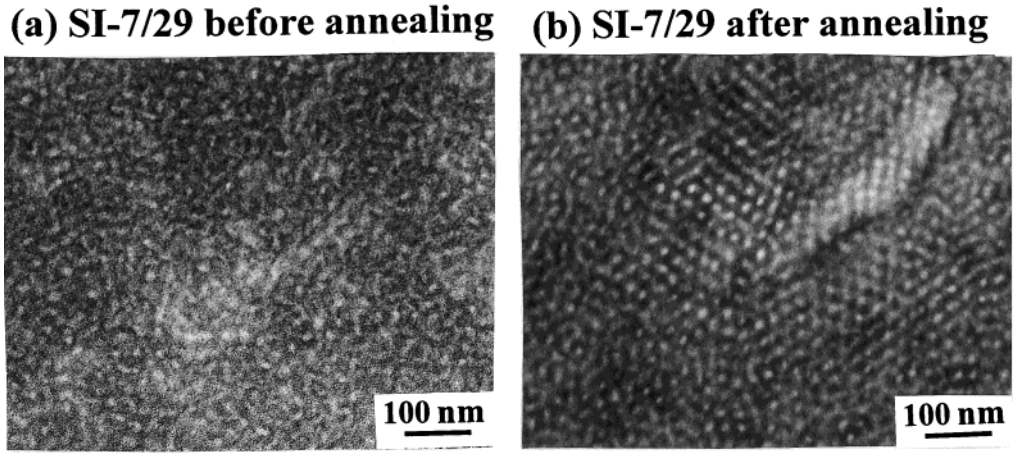

Figure 3. TEM images of the SI-7/29 (a) before annealing and (b) after annealing at 90 °C for 15 days.

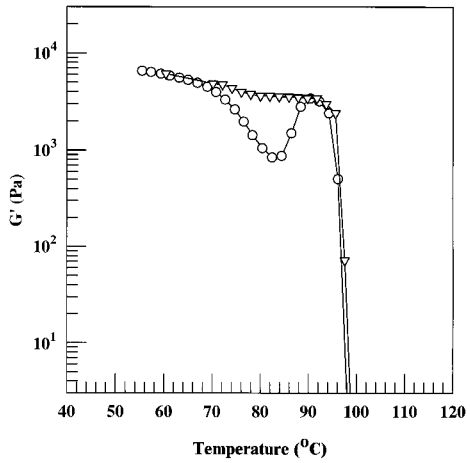

Figure 4. Dynamic temperature sweep experiment for the SI-7/29 under isochronal condition at $\omega = 0.01$ rad/s during heating: (○) before annealing and (▽) after annealing at 90 °C for 15 days.

below T_{LDT}, from hex-cyl of PS in the matrix of PI to the bcc-spheres of PS in the matrix of PI at ca. 84 °C, which may be inferred[16,20] from the minimum in G' in the isochronal dynamic temperature sweep experiment for an *unannealed* specimen (the symbol ○ in Figure 4). Instead, the SAXS results, as will be shown in detail elsewhere,[17] showed (i) a narrowing of the first-order peak in the *unannealed* specimen upon annealing at $T > T_{g,PS} \cong 58$ °C, glass transition temperature of PS spherical microdomains, indicating improved perfection of bcc lattice that was promoted by an increased mobility of PS block chains at $T > T_{g,PS}$, and (ii) a sharp first-order peak from the beginning in the *annealed* specimen at low temperatures followed by a broadening of the peak with increasing temperature toward T_{LDT}, indicating the presence of highly perfected bcc-spheres in the beginning and an increasing thermal distortions of bcc lattice with increasing temperature.

Thus, we can conclude that a minimum G' observed at ca. 84 °C in Figure 4 has nothing to do with the OOT but rather reflects the remarkable annealing effect as described above. If we did not have SAXS results, we could have drawn an erroneous conclusion that the apparent minimum in G' at ca. 84 °C in Figure 4 might signify, in accordance with the previous studies of Almdal et al.[20] and Sakamoto et al.,[16] the onset of OOT in SI-7/29.

From the SAXS results presented above we conclude that long-time annealing of the highly asymmetric SI diblock copolymer, SI-7/29, increased the grain size and hence decreased the grain-boundary area and made a more perfect bcc lattice within the grains. For such specimen, the value of G' monotonically decreases, due to a steady softening of PS spherical microdomains and their lattices, with increasing temperature toward T_{LDT}. Such a conclusion is supported by the TEM images (see Figure 3), showing that a prolonged annealing made the diffuse grain boundary very sharp, giving rise to highly ordered bcc lattice. On the other hand, the value of G' for an *unannealed* specimen first decreases, due to softening of PS spheres, with increasing temperature toward $T_{g,PS}$. G' then increases, due to the increased perfection of the long-range order promoted by an enhanced mobility of PS chains above $T_{g,PS}$, with increasing temperature to T_{LDT}. The increase of G' with increasing temperature above ca. 84 °C is a consequence of the increase of G' due to the increased long-range order that outweighs the decrease of G' due to the softening effect.

The results presented above should draw the attention of those who wish to investigate, by means of oscillatory shear rheometry alone, phase transitions in a highly asymmetric block copolymer without a sufficiently long annealing.

References and Notes

(1) Alward, D. B.; Kinning, D. J.; Thomas, E. L.; Fetters, L. F. *Macromolecules* **1986**, *19*, 215.
(2) Hasegawa, H.; Tanaka, H.; Yamasaki, K.; Hashimoto, T. *Macromolecules* **1987**, *20*, 1651.
(3) Hajduk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Kim, G.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1994**, *27*, 4063.
(4) Hajduk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1995**, *28*, 2570.
(5) Hamley, I. W.; Koppi, K. A.; Rosedale, J. H.; Bates, F. S.; Almadal, K.; Mortensen, K. *Macromolecules* **1993**, *26*, 5959.
(6) Förster, S.; Khandpur, A. K.; Zhao, J.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W. *Macromolecules* **1994**, *27*, 6922.
(7) Khandpur, A. K.; Förster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. *Macromolecules* **1995**, *28*, 8796.
(8) Schulz, M. F.; Khandpur, A. K.; Bates, F. S.; Almdal, K.; Mortensen, K.; Hajduk, D. A.; Gruner, S. M. *Macromolecules* **1996**, *29*, 2857.
(9) Laradji, M.; Shi, A.-C.; Noolandi, J.; Desai, R. *Macromolecules* **1997**, *30*, 3242.
(10) Qi, S.; Wang, Z.-G. *Macromolecules* **1997**, *30*, 4491.

(11) Hajduk, D. A.; Takenouchi, H.; Hillmyer, M. A.; Bates, F. S.; Vigild, M. E.; Almdal, K. *Macromolecules* **1997**, *30*, 3788.
(12) Hashimoto, T.; Koizumi, S.; Hasegawa, H.; Izumitani, T.; Hyde, S. T. *Macromolecules* **1992**, *25*, 1433.
(13) Disko, M. M.; Liang, K. S.; Behal, S. K.; Roe, R. J.; Jeon, K. J. *Macromolecules* **1993**, *26*, 2983.
(14) Spontak, R. J.; Smith, S. D.; Ashraf, A. *Macromolecules* **1993**, *26*, 956.
(15) Spontak, R. J.; Smith, S. D.; Ashraf, A. *Macromolecules* **1993**, *26*, 5118.
(16) Sakamoto, N.; Hashimoto, T.; Han, C. D.; Kim, D.; Vaidya, N. Y. *Macromolecules* **1997**, *30*, 1621.
(17) Han, C. D.; Vaidya, N. Y.; Kim, D.; Shin, G.; Yamaguchi, D.; Hashimoto, T. Submitted to *Polymer*.
(18) Sakamoto, N.; Hashimoto, T.; Han, C. D.; Kim, D.; Vaidya, N. Y. *Macromolecules* **1997**, *30*, 5321.
(19) Hashimoto, T.; Okamoto, S.; Saijo, K.; Kimishima, K.; Kume, T. *Acta Polym*. **1995**, *46*, 463.
(20) Almdal, K.; Koppi, K. A.; Bates, F. S.; Mortensen, K. *Macromolecules* **1992**, *25*, 1743.

MA991034Y