

Thermoreversible Order-Order Transition between Spherical and Cylindrical Microdomain Structures of Block Copolymer

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ABSTRACT: The thermoreversible transition between spherical and cylindrical microdomains of a polystyrene-*block*-polyisoprene diblock copolymer was studied using small-angle X-ray scattering (SAXS). At a low temperature cylindrical microdomains on a hexagonal lattice were observed. They transformed to spherical microdomains packed in a body-centered cubic (bcc) lattice at a high temperature. The transition was thermally reversible. By examining the SAXS pattern from a large grain that was developed by a slow cooling of the specimen, it was found that spheres formed by dividing cylinders laid in the [111] direction of the bcc lattice without changing the grain structure. The dynamic behavior of the transition was also investigated.

I. Introduction

Block copolymers show a variety of morphologies such as lamellar, cylindrical, and spherical microdomains due to the segregation between the constituents. In a strong segregation limit the morphology basically depends on the volume fraction of one of the constituents ("block composition")¹ In a weak segregation limit, Leibler² predicted that the order-order transitions (OOT) between different kinds of morphologies occur by changing the temperature for the block copolymer with a given constant block composition other than 0.5. Though such experimental results were not reported for a while, recently some experimental results on OOTs were reported.³⁻⁵ However, the mechanism and the dynamics of the OOT has not been thoroughly understood yet. Here we focus on a thermoreversible OOT between spherical and cylindrical microdomain structures of a block copolymer and try to elucidate the transition mechanism and the dynamic behavior.

II. Experimental Methods

The sample used in this study was a polystyrene-*block*-polyisoprene (PS-PI) diblock copolymer having a number-averaged molecular weight of 4.39×10^4 and a weight fraction of PS of 0.204. The morphology in the block copolymer were investigated by small-angle X-ray scattering (SAXS). The SAXS profiles were taken using a one-dimensional position sensitive proportional counter (PSPC) with line focus optics and were corrected for the absorption of the sample, background scattering, and the thermal diffuse scattering arising from acoustic phonons.

SAXS patterns were also measured with a two dimensional imaging plate (IP⁶).

III. Results and Discussion

Figure 1 shows the SAXS profiles of the block copolymer taken at various temperatures. Measurement was carried out in a cooling process from a high temperature. The profiles obtained at 177.4 and 157.7°C (profiles a and b) show a broad first order scattering maximum (marked by a black arrow) and a shoulder at around $q=0.45\text{nm}^{-1}$ (marked by a white arrow) due to the inter-particle interference, indicating the structure at these temperatures was lattice-disordered spherical microdomain structure (LDS), at where spherical microdomains with well defined interface exist with only short-range order. At temperatures from 138.2 to 118.7°C (profiles c and d) higher-order scattering maxima were observed at the positions of $\sqrt{2}q_m$ and $\sqrt{3}q_m$ with q_m being the position of the first-order scattering maximum, indicating spherical microdomains packed on a body-centered cubic lattice (bcc-sphere). The positions of the higher-order scattering maxima changed to $\sqrt{3}q_m$, $\sqrt{4}q_m$, and $\sqrt{7}q_m$ below 99°C (profiles e and f), indicating the microdomains changed to cylindrical microdomains on a hexagonal lattice (hex-cylinder). Furthermore the measurements with a small temperature change were carried out in both heating and cooling processes and the transitions between the bcc-sphere and the hex-cylinder were occurred between 114.7 and 116.7°C in both processes. The order-order transition temperature, T_{OOT} , was centered at 115.7°C.

In conventional X-ray scattering experiments, the size of the incident X-ray on the sample is quite large compared with the size of the grains within which the ordered microdomain structure exists in a coherent orientation. If the orientation of the grains is perfectly random, the scattering pattern should be circularly symmetric with respect to the incident beam. However, if the size of the grain becomes large enough and comparable to the beam size, the Bragg's scattering peaks are observed as diffraction spots. By determining the corresponding

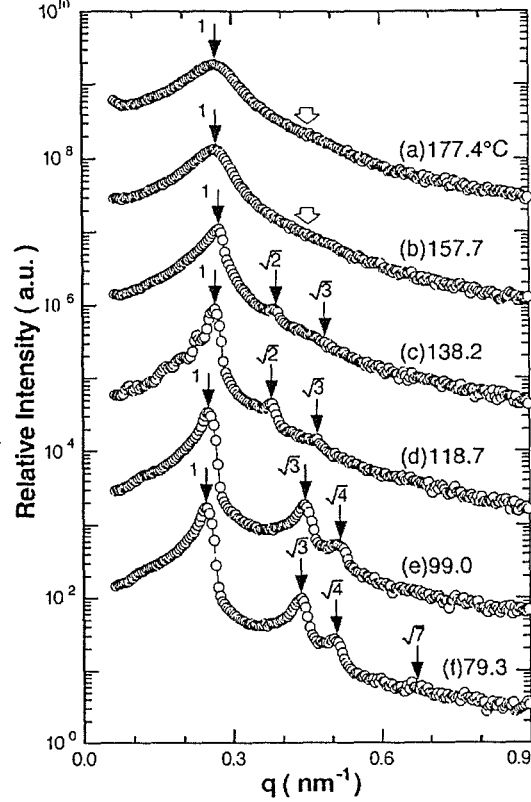


Figure 1. SAXS profiles of the block copolymer plotted against the magnitude of the scattering vector q , defined by $q=(4\pi/\lambda)\sin(\theta/2)$, with λ and θ being the wavelength of the incident X-ray and the scattering angle, respectively. The LDS structure (a and b) changed to the bcc-sphere (c and d), and the hex-cylinder (e and f) with decreasing the temperature.

lattice places of the diffraction spots, one is able to know the orientation of the microdomain structures in the grain that one is focusing on. If one is able to trace the change in the diffraction pattern from the grain during the OOT, one is able to know the transition mechanism in the grain. Though there are many previous works which are concerned with developing of large grains by shear flow, we tried to develop a large grain with a slow cooling of the specimen.

Figure 2a shows a SAXS pattern of the diblock copolymer taken with the IP at 119.6°C where the bcc-sphere was observed. The sample giving rise to figure 2a was obtained by cooling the sample from the temperature where the LDS structure was observed with cooling rate of 2.4K/hour. The first and second-order

scattering peaks at q_m and $\sqrt{2}q_m$ appeared as many spots, indicating a limited number of large grains composed of the bcc-sphere were developed in the volume irradiated by incident X-ray. We note that the SAXS pattern was circular ring for the same sample which was cooled down from the same temperature with cooling rate of over 100K/hour. Next the temperature was lowered to 111.8°C which is below T_{OOT} (part b). The position of the second-ordered scattering peaks changed from $\sqrt{2}q_m$ to $\sqrt{3}q_m$, indicating that the microdomain structure changed from the bcc-sphere to the hex-cylinder. The scattering peaks were also observed as spots, elucidating the grain structures existed even after the OOT. Furthermore the temperature was raised again to 119.6°C (part c) and lowered back to 111.8°C (part d). The diffraction spots in the scattering patterns observed at the same temperatures were almost identical (compare between parts a and c, and between parts b and d) in terms of their spot size and their position in q -space, indicating the grain structure did not change before and after the OOT in terms of not only the size but also the orientation of the microdomains in the grain.

With using a sample having thin thickness (0.3mm) and a small size of the incident X-ray (0.5mm in diameter) the number of the grains irradiated by X-ray was decreased. By scanning the sample with respect to the incident X-ray, a 6-fold pattern was obtained at 111.8°C

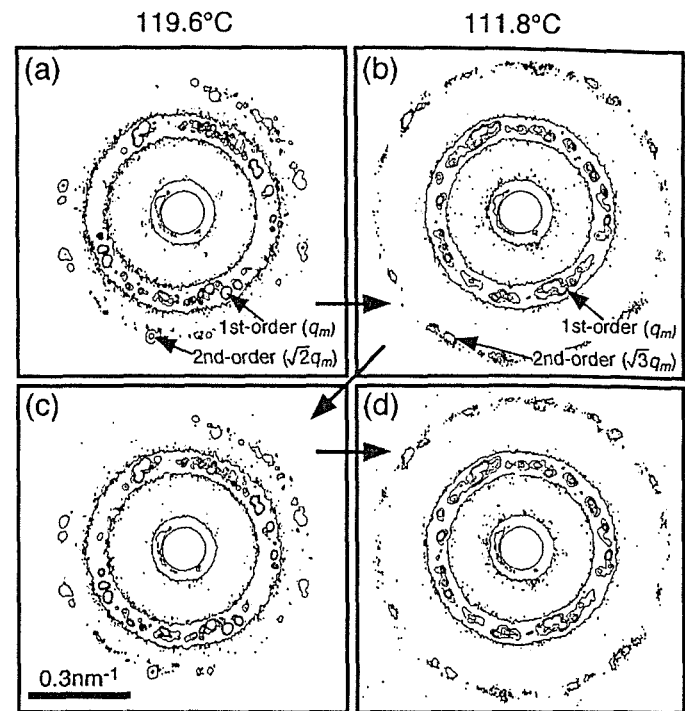


Figure 2. SAXS patterns taken with IP at (a and c)119.6°C for the bcc-sphere and (b and d)111.8°C for the hex-cylinder. The measurement was carried out in the order of (a), (b), (c), and (d). The patterns obtained at the same temperature are almost identical, showing the conservation of the grain structures before/after the OOT.

where the hex-cylinder was observed. Figure 3a shows the SAXS pattern thus obtained. The first-order peaks appeared in a hexagonal pattern at q_m and the second-order peaks also appeared in a hexagonal pattern at $\sqrt{3}q_m$ at different azimuthal angle. The former is the Bragg reflection from the (10) plane of the hexagonal lattice and the latter is that from (11) plane. In this situation the incident X-ray was parallel to the cylindrical axes as illustrated in part b of the figure. Next the temperature was raised to 119.6°C, where the bcc-sphere was observed, without changing the sample position. The hexagonal pattern of the first-order peaks was kept (see figure 3c). To observe such

a pattern from the bcc-sphere, the incident X-ray beam should be parallel to the [111] direction of bcc lattice as illustrated in part d. This result strongly indicates that spheres formed by dividing a cylinder laid in the [111] direction of the bcc lattice without changing the grain structure. Furthermore the detailed process and the kinetics of the OOT were investigated with an use of ultra-angle-X-ray scattering, which will be presented in the symposium.

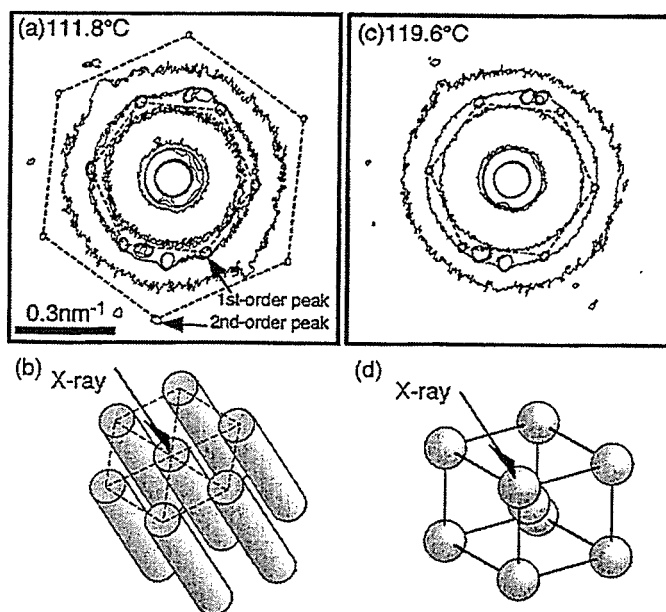


Figure 3. SAXS patterns taken with IP from a single grain at (a)111.8°C for the hex-cylinder and at (b)119.6°C for the bcc-sphere without changing the sample position. Bottom two figures shows the relation the direction of the incident X-ray and the orientation of the lattice.

References

- (1) Hashimoto, T; Shibayama, M.; Fujimura, M.; Kawai, H. In *Block Copolymers, Science and Technology*; Meier, D. J., Eds.; Harwood Academic Publishers: London, New York, 1983; pp 63-108.
- (2) Leibler, L. *Macromolecules*, **1980**, *13*, 1602.
- (3) Hajduk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Thomas, E. L.; Fetters, L. J. *Macromolecules*, **1994**, *27*, 4063.
- (4) Khandpur, A. K.; Forester, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen K. *Macromolecules*, **1995**, *28*, 8796.
- (5) Sakurai, S.; Hashimoto, T.; Fetters, L. J. *Macromolecules*, **1996**, *29*, 740.
- (6) Hashimoto, T.; Okamoto, S.; Saijo, K.; Kimishima, K.; Kume, T. *Acta Polymerica*, **1995**, *46*, 463.