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Depth Dependence of Lattice Deformation of Cylindrical Microdomain of Polystyrene-*b*-poly(2-vinyl pyridine) Thin Film Revealed by GISAXS using Low Energy X-ray

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1 Introduction

Block copolymers (BCPs) are composed of two or more polymers connected by covalent bond. They can form a few tens nanometer scale periodic structure, which is called micro-phase separated structure, such as lamellae, cylinders and spheres, etc. In case of thin film, cylindrical and lamellar microdomains are preferentially aligned parallel to a substrate when one component of the block copolymer segregates the surface or the substrate to minimize the free energy at the surface and interface. The parallel orientation of the domains was analyzed by neutron reflectivity measurement (NR), TOF secondary ion mass spectroscopy (TOF-SIMS), X-ray photoelectron spectroscopy (XPS), and grazing incident SAXS (GISAXS). NR, TOF-SIMS, and XPS can allow us to reveal depth profiling of the microphase separated structures. On the other hand, GISAXS using hard X-ray is unsuited for the depth profiling because of penetration depth of the X-ray abruptly increases up to a thousand of nanometers at the critical angle. Below the critical angle, the penetration depth is a few nanometers.

Wide range 2.1 – 15keV of energy of X-ray at BL15A2 can be available. Using relatively low energy of X-ray for example 2.4 keV, the penetration depth is suited for depth profiling of the typical phase separated structure because of the shallower penetration depth even near the critical angle and mechanically ease control of the incident X-ray.[1,2]

In this study, we performed GISAXS measurement with low energy X-ray (2.4keV) in order to investigate depth profiling of lattice parameters of the parallel cylindrical structures in polystyrene-b-poly(2-vinyl pyridiene) (S2VP) thin film.

2 Experiment

GISAXS measurement with soft X-ray was performed at BL15A2 in Photon Factory, KEK, Tsukuba in Japan. This beam line offers a wide energy range from 2.1 to 15keV. In this research, the experiment was conducted at 2.4keV corresponding to wavelength, 5.16Å. Sample to detector distance (SDD) was about 830 mm. Pilatus 2M specified for use in vacuum was used as a detector of 2D scattering pattern. Exposure time was 300sec. GISAXS measurements with hard X-ray were performed (at BL10C in Photon Factory and) BL03XU in SPring-8, Harima, Japan. SDD and wavelength were 2 m and 1.0Å, respectively.

Block copolymer S2PV thin film was prepared by spin-casting on a silicon substrate (3000 rpm, 30s) from toluene solution (10 wt%). After drying the thin film in air, the S2VP thin film was thermally annealed at 443 K for 48 h to obtain parallel cylindrical microdoimains.

3 Results and Discussion

GISAXS measurement using soft X-ray was performed with various incident angles. Figure 1 shows typical GISAXS pattern at incident angle over the critical angle of the X-ray. Many scattering peaks can be obtained and assigned as hexagonally packed cylinders that were oriented parallel to the surface of the substrate. Figure 2 shows 1D scattering profiles along q_z direction vertically cut at q_y = 0.26 nm^{-1} with various incident angles. Here, the second order reflections (q_z = 0.6 – 0.7 nm^{-1}) were used for precise analysis of the lattice parameters of the cylindrical microdomains because of missing the first order peaks due to detector gaps. Scattering peaks became broad with a decrease in the penetration depth. This broadening can be explained with the reduction of measured region. That is, when the penetration depth of the X-ray is small, the number of reflected planes decreases.

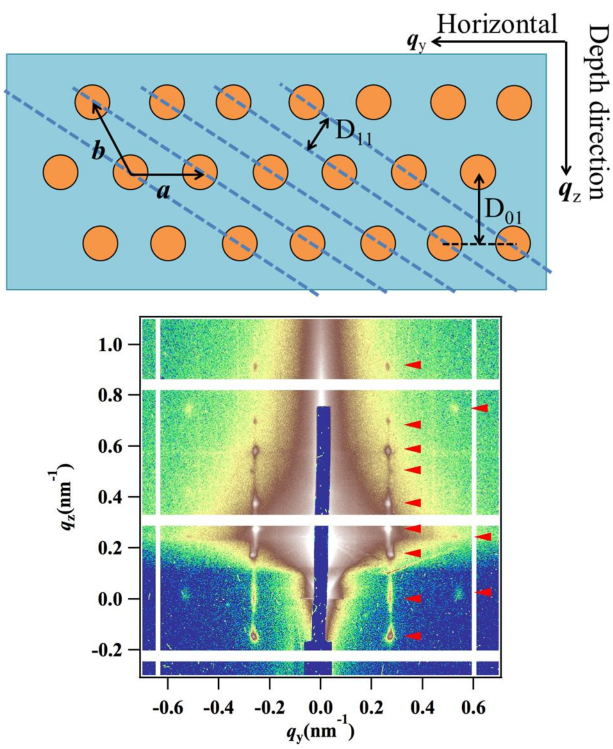

Fig. 1: GISAXS pattern and illustration of parallel oriented cylinder domains.

Full width at half maximum (FWHM) of the scattering peaks depends on the number of the layers according to the Laue function.

$$L(\boldsymbol{q_z}) = \sum_N \exp(iN\boldsymbol{q_z}\cdot\boldsymbol{b}) = \frac{\sin[(N+1)\boldsymbol{q_z}\cdot\boldsymbol{b}/2]}{\sin[\boldsymbol{q_z}\cdot\boldsymbol{b}/2]}$$

where N is the number of the (10) planes, D_{cyl} is the period of (10) plane. Herein, D_{cyl} was 20 nm that was the spacing obtained from the bulk sample. Taking into consideration an attenuation of the X-ray, the Laue function can be expressed as follows;

$$L(q_z) = \sum_N \frac{\sin[(N+1)q_z D_{01}/2]}{\sin[q_z D_{01}/2]} \exp\left[-\frac{\left(\frac{1}{2}+\frac{2}{3}N\right)D_{01}}{\Lambda}\right]$$

where Λ is the penetration depth.

Experimentally obtained FWHM was plotted against incident angles with open red circles in Figure 3. Simulated FWHM using above Laue function was also indicated with black marks and solid line. Experimental FWHM was in good agreement with the simulated ones.

When incident angle is beyond the critical angle, the lattice parameters can be calculated using DWBA. Lattice parameters of the cylindrical microdomains at each penetration depth were determined at various depth of the thin film. The cylinder lattices normal to the substrate and along lateral direction were found to be narrowed and elongated as compared with the value in the bulk state of S2VP-26k, respectively. Moreover, this deformation was relaxed as the depth was shallow (near the surface) except that the parameters in the lateral direction were almost unchanged as shown in Figure 3. This lattice relaxation behavior was associated with the mobility of polymer chains in the thin film, i.e., a higher mobility was expected near the surface, in contrast the mobility (diffusion) along the lateral direction was suppressed near the interface. In conclusion, a low energy GISAXS can provide precise analysis of depth dependence of the structure.

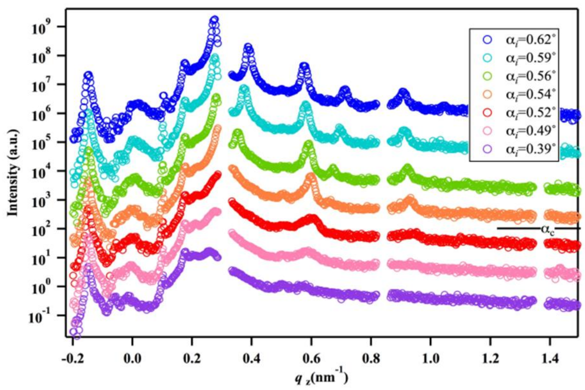

Fig. 2: 1D GISAXS profiles along q_z direction vertically cut at $q_y \sim 0.26$ nm^{-1}.

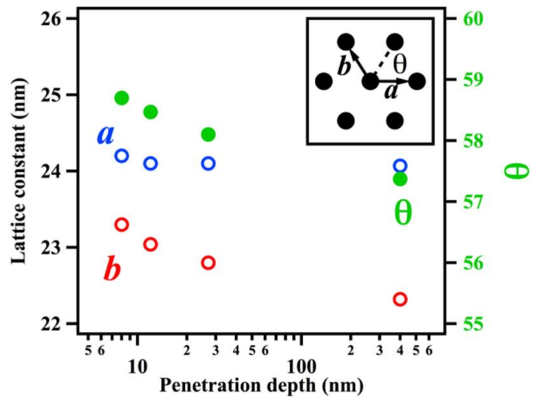

Fig. 3: Depth dependent of the lattice parameters.

References
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[2] J. Wernecke *et al.*, *Macromolecules* **47**, 5719 (2014).

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