Laboratory-GISAXS Measurements of Block Copolymer Films with Highly Ordered and Normally Oriented Nanocylinders

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Highly ordered microphase separated films with hexagonally arranged nanocylinders yielded distinct scattering peaks even in laboratory grazing incidence small-angle X-ray scattering measurements. Hierarchical structures with perpendicularly oriented nanocylinders and parallel aligned liquid crystalline layers sustaining highly ordered nanostructures were revealed.

Block copolymers give periodic morphologies with well-defined size and spacing having nanodomains with characteristic length scales of a few to tens of nanometers and have been extensively studied because of their potential use as nanolithographic templates[1,2] for the generation of quantum electronic structures, catalytic surfaces, and separation membranes. For these applications, reliably ordered structures in a large region are crucial, and methods for proving the reliability are indispensable. Microscopic methods such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) are strong tools to image such microphase-separated structures of block copolymers. While grain structures, boundaries, defects, and so on can be visualized well, the information on the images is limited within a microscopic view. Grazing incidence small-angle X-ray scattering (GISAXS) provides both diffraction patterns and alignments of periodic structures of microphase-separations as averaged structural information,[2–5] which is necessary to insure reliable structures for applications. Moreover, GISAXS has an advantage of effective data acquisition from a large irradiated area with neither absorption nor scattering by a substrate. A number of GISAXS studies of microphase-separated structures of polymer alloy have been reported by using high-intensity synchrotron radiation,[2–5] but to our best knowledge, no reports of laboratory-GISAXS have appeared because of inefficient data acquisition, resulting from microphase separations generally showing too low X-ray scattering intensity to obtain distinct peaks owing to small electron density difference between two domains of microphase separation.[4]

Recently, we found an anomalously regular nanostructure of thin amphiphilic liquid-crystalline diblock copolymer film through microphase separation. The polymer consists of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic polymethacrylate with azobenzene–mesogen in the side-chain (PMA(Az)), and the PEO cylindrical microdomains are arranged hexagonally and oriented perpendicular to the film plane (Figure 1).[6] Moreover, such films can be obtained on several types of substrates such as a silicon wafer, glass, mica, and poly(ethylene terephthalate) (PET) by casting, spin-coating, bar-coating, and dipping methods. The perpendicular orientation of the cylinders has been confirmed by cross-sectional TEM and cross-sectional AFM observations in a microscopic scale.[7] The perpendicular orientation and highly ordered arrangement of microphase-separated cylinders originate from parallel alignment of liquid-crystalline Az (LC) layers identical to homeotropical alignment of Az mesogen in smectic phase (Figure 1). Such high regular nanostructure motivated us to examine practical validity of a laboratory-GISAXS for possible real-time and simultaneous measurements coupled with spectroscopy.

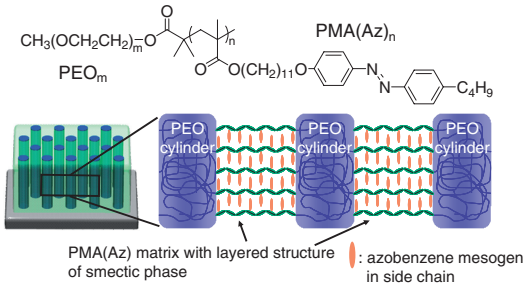

Figure 1. Structural formula of an amphiphilic liquid-crystalline block copolymer PEO_m-*b*-$PMA(Az)_n$ and schematic figures showing periodic structures of the microphase-separated film.

Herein, we report that the highly ordered nanostructures of microphase-separated PEO-*b*-PMA(Az) films yielded distinct peaks even in laboratory-GISAXS measurements.

The microphase-separated films were prepared by spin-coat or bar-coat methods from chloroform or toluene solutions of PEO_{114}-*b*-$PMA(Az)_{51}$ on silicon substrates and annealing at 140 °C for one hour under vacuum. The laboratory-GISAXS instrument used in this study was a Nano-Viewer with a CCD camera (Rigaku corp. Japan). The X-ray experiment was performed by using a Cu Kα radiation beam ($\lambda = 1.541$ Å) which was converged and monochromatized by a Confocal Max Flax (CMF) mirror. The X-ray generator was a Rigaku Micro7 rotating anode generator (40 kV, 30 mA). The diameter of the X-ray beam controlled by a three-slit optical system was set to 250 µm. Incidence angle of the X-ray was set to 0.20–0.21° near the critical reflection angle of a Si wafer to effectively obtain in-plane signals.

Figure 2a shows a GISAXS CCD image of a 3-µm thickness film with 60 min of data acquisition. A couple of peaks appeared in the out-of-plane region for 10 s and four peaks did in the in-plane region for 30 min. There was no signal in the case of as-prepared film with partly ordered micelle-like nanostructure. Figure 2b shows an in-plane intensity profile having four peaks with $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$ in q-scale indicating a hexagonally arranged structure. Distance between the cylinders is calculated to be 23.5 nm, consistent with that obtained by AFM measurements 23.4 nm. There is neither a peak nor Debye ring originating from

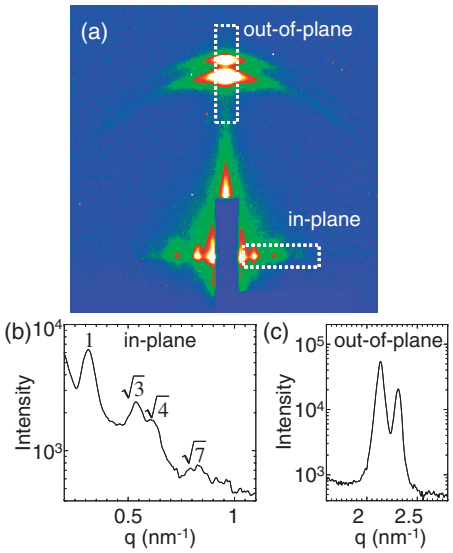

Figure 2. (a) A GISAXS CCD image of a microphase-separated PEO_{114}-*b*-$PMA(Az)_{51}$ film with perpendicularly oriented hexagonal cylinders. X-ray incidence angle was set to 0.2° near the critical total reflection angle of a Si wafer. Intensity profiles in regions labeled as in-plane and out-of-plane in (a) are shown in (b) and (c), respectively. The in-plane profile has four peaks indicating hexagonally arranged cylinders. A pair of peaks in the out-of-plane profile indicates A layered structure of smectic phase of PMA(Az). The lower and the higher peaks originated from scattering of transmitted X-rays and X-rays reflected on a Si substrate, respectively.

parallel or randomly aligned microphase-separated cylinders in Figure 2a.[5] The perpendicularly oriented cylinders were formed in the whole film. Such clear peaks obtained by laboratory-GISAXS of which X-ray power (ca. 1.3×10^7 cps) is much weaker by three orders than that of synchrotron-GISAXS imply quite high regularity of the microphase-separated nanostructure film beyond conventional block copolymer films. Furthermore, it should be mentioned that the first in-plane peak was obtained even in a 60-nm film after one hour and that a 1-μm film which showed the highest scattering intensity of the cylinder structure showed the first peak with only 30 s of data acquisition time. These results suggest an extremely high "crystallinity" of the present microphase-separated nanostructure.

Figure 2c shows an out-of-plane profile having two peaks indicating the LC Az layers. The lower and higher peaks originated from scattering of the original X-ray beam and X-ray beam reflected on a Si substrate, respectively. An LC periodicity of 2.95 nm calculated from the lower peak from the original X-ray beam was not the correct value owing to refraction of X-rays at the film surface.[5,8] Although a 2θ difference between the two peaks in the out-of-plane should have been 0.4° equal to twice the value of incidence angle 0.2°, it was 0.24° owing to the refraction effect. We obtained an angle change of incidence X-ray beam as 0.08° (=(0.4° − 0.24°)/2), which leads to a refraction index of the block copolymer, 0.9999961 (= $\cos 0.2°/\cos(0.2° - 0.08°)$), according to Snell's law. The LC layer periodicity corrected with the refraction index resulted in 3.07 nm. In this correction procedure, we can neglect the refraction effect of X-rays exiting from the sample because the angle change difference between the two scattered X-rays with ca. 3° of the outgoing angle from the surface were quit small, compared with the resolution of the CCD camera, and was cancelled in the subtraction process of 0.4–0.24°.

In conclusion, we have investigated microphase-separated PEO-*b*-PMA(Az) film with perpendicularly oriented cylinders sustained by parallel aligned LC Az layers by laboratory-GISAXS. It was found that the highly ordered periodic nanostructures enabled the laboratory-GISAXS to afford sufficient scattering intensity and that the scattering signal can be obtained with short acquisition times and real time measurements of phase transition and simultaneous measurements comparable to UV–vis and Raman spectroscopies, etc., and is now under investigation. The present result encourages us to monitor selective doping processes with various substances into the cylindrical PEO microdomains and selective etching under vacuum UV and electron beam irradiation since the scattering signals should be enhanced.[9] Setups of such in situ measurements optimized in the laboratory-GISAXS will enable a synchrotron-GISAXS to conduct them with quite short time resolution.

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