AFM Cross-Sectional Imaging of Perpendicularly Oriented Nanocylinder Structures of Microphase-Separated Block Copolymer Films by Crystal-like Cleavage

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Periodically ordered nanostructures arising from the microphase separation of block copolymers, as one of the self-assembling processes, have driven one to fabricate nanoporous materials, membranes, lithographic nanotemplates, and scaffolds as fundamental technology of the coming electronic and photonic materials.[1−13] Of particular interest are block copolymers that form cylindrical nanodomains oriented perpendicularly and spanning to both the topmost surfaces, which should be crucial for mass transport through the cylindrical channels across the film as membrane function. Transmission electron microscopy (TEM) of microtomed specimen, small-angle X-ray scattering of bulk samples, and atomic force microscopy (AFM) of the surface morphology have been used so far to complementarily analyze the periodic nanostructures. The AFM is a powerful tool to easily image the surface morphology under ambient atmosphere, but the imaging has been limited only on the surface, which can be untied in this study to open the possibility for both surface and inside imaging of the microphase-separated nanostructures.

Recently, we reported that the thin films of a series of newly designed amphiphilic block copolymer consisting of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic polymethacrylate with azobenzene−mesogen in side-chain (PMA(Az)) (Figure 1) show highly ordered microphase separation with hexagonally arranged cylinders.[14] Especially, the PEO nanocylinders are perpendicularly oriented to the surface and a substrate when the films were prepared on a silicon wafer, glass, mica, and poly(ethylene terephthalate) (PET) substrates by casting, spin-coating, bar-coating, and dipping methods. The perpendicular orientation of the cylinders has been confirmed by cross-sectional TEM observation using a staining technique with RuO_4 and ultrathin microtomy in the similar manners reported previously.[15−23] However, the structural analysis inside the film samples has been limited to the films of which domains are selectively stained beforehand, adequate film thickness below ca. 500 nm, and soft substrates such as PET. There has been no direct imaging of such perpendicularly oriented cylinders under ambient atmosphere. Herein, in order to solve these problems, we selected atomic force microscopy (AFM) as a method for evaluating cross sections without staining, quite different from the conventional usage to image surface morphology. We report the first successful demonstration of the AFM cross-sectional imaging of the perpendicularly oriented and hexagonally arranged PEO cylinder structures under ambient atmosphere with a simple sample preparation as a new technique for evaluating inside structures.

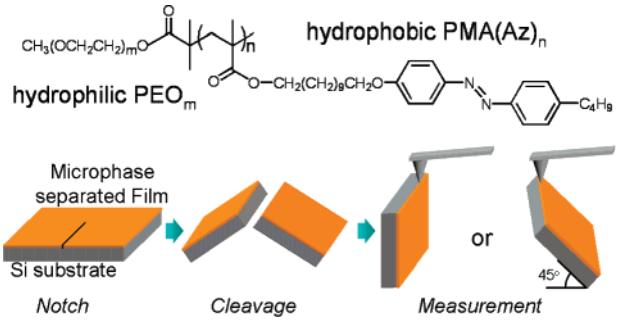

Figure 1. Structural formula of an amphiphilic PEO_m-*b*-$PMA(Az)_n$ and schematic figures showing a procedure for preparing cross sections of microphase-separated films.

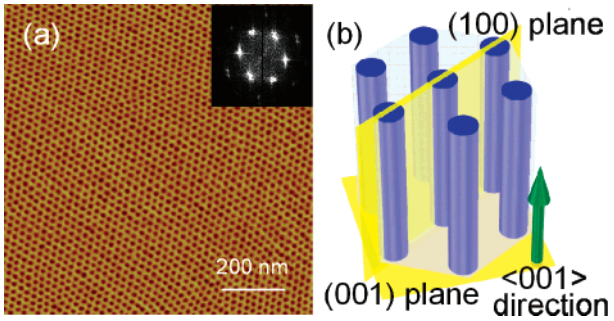

Figure 2. (a) AFM phase-shift image of a surface of a PEO_{114}-*b*-$PMA(Az)_{51}$ film. Inset is a 2D Fourier transformed image. (b) Schematic figure showing planes with periodicity of a microphase-separated structure with hexagonally arranged cylinders.

The PEO-*b*-PMA(Az) microphase-separated films were prepared on a silicon wafer (see Supporting Information). The cross sections of the microphase-separated films were prepared just by cleaving films together with the notched silicon substrate, as Figure 1 illustrates. The cleaved film on the substrate put up on an AFM sample stage with fixative was measured by AFM. The measurements were made by a Multi Mode scanning probe microscope, Nanoscope IV (Digital Instruments). We used Tapping Mode silicon cantilevers with a nominal resonance frequency of 300 kHz (NanoDevices).

A typical phase-shift image of a surface of the PEO_{114}-*b*-$PMA(Az)_{51}$ film bar-coated from a 2 wt % toluene solution is shown in Figure 2a. The large-area scanned image and its partly zoomed ones are shown in the Supporting Information. A hexagonally arranged dot pattern observed in the whole surface corresponding to a (001) plane of the microphase-separated hexagonal cylinder structure (Figure 2b), where the dots are PEO cylindrical domains and the surrounding media are PMA(Az) domains. A clear hexagonal spot in the fast Fourier transformed (FFT) image (Figure 2a, inset) of the phase-shift image indicated high regularity of the dot pattern with ca. 23 nm of periodicity.

The authors have challenged to cleave the films like crystalline materials and image their cross sections so as to visualize the perpendicularly oriented PEO cylinder array under ambient atmosphere. It should be noted that the cleavage of the as-coated film before annealing always afford rough and disordered cross sections with little nanostrucutre, as is shown in the Supporting Information. Figure 3 shows (a) three-dimensional (3D) topo-

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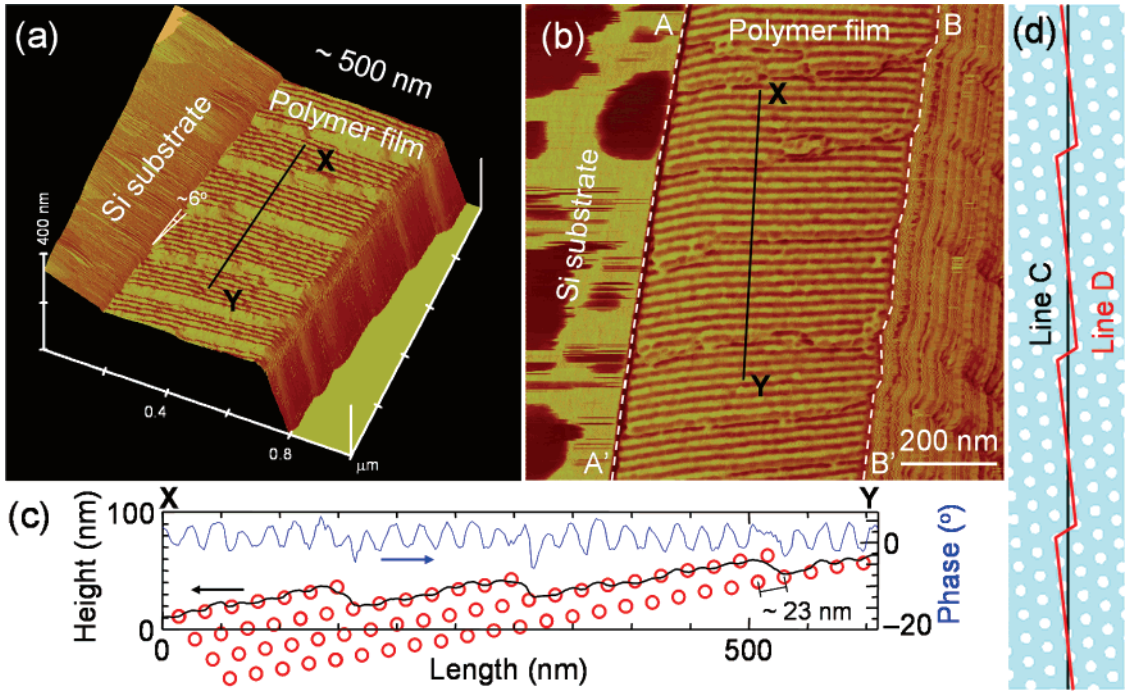

Figure 3. AFM topographic (a) and phase-shift (b) images of a cross section of a PEO_{114}-*b*-$PMA(Az)_{51}$ film with the film thickness of 500 nm. The dashed lines between A and A′ and between B and B′ indicate the interfaces between the film and a Si substrate and between the film and air, respectively. (c) The profile identical to a black line drawn in (a). Red circles indicate the ideal hexagonal pattern with the cylinder period of 23 nm consistent with that of surface images. (d) The cleavage lines of a Si substrate (line C) and a microphase-separated film with hexagonally arranged cylinders (line D) on a (001) plane of the ideal microphase-separated structure.

graphic and (b) phase-shift images of the cross section cleaved with the substrate of the same annealed films as the surface morphology was imaged in Figure 2. The cross section of the 500 nm thick film with both boundaries to the substrate and air could be clearly imaged to have dark stripes (PEO cylinders) spanning to both edges with 500 nm length and a consistent periodicity (23 nm) with that of the dot pattern in the surface morphology. The regular stripe patterns observed in most of the area in the cleaved cross sections of the annealed films indicated that the microphase-separated film was cleaved selectively along the aligned cylinders. Another long-periodic structure with a periodicity of 7−10 stripes was found in both topographic and phase-shift profiles (Figure 3c) along the lines X−Y in the both images. The long-periodic structure can be explained by a slight discrepancy of angle (ca. 6°) between a ⟨110⟩ cleavage direction of the edge of the silicon wafer as the substrate and a (100) plane of the hexagonal cylinder structure of the film (Figure 3d), where the film cross section to be cleaved along the ⟨001⟩ direction tends to exhibit as much of a (100) plane as possible. Here, we should note that there is elastic modulus difference between the PEO cylinder domains in melting state and the PMA(Az) domains in semicrystalline state at room temperature (see Supporting Information). Along the topographical profile, the PEO cylinders slightly sink in due to tip indentation of the softer PEO domains, consistent with the periodic contrast along the phase-shift profile. Red circles drawn as a (001) plane with the consistent periodicity with that derived from the surface morphology could be well fitted to both the periodic profiles. Such morphological feature of the cross sections is found as a step and terrace structure in cleaved surfaces of crystals or clean surfaces of the crystalline films prepared by ultrahigh-vacuum deposition methods. When the film was subjected to a stress for cleavage, the stress would concentrate at the interfaces between the PEO and PMA(Az) domains with different elastic moduli, and therefore, the film must be cleaved on the (100) plane which includes the interfaces most densely. Furthermore, one can realize through the cleavage nature mentioned above that the present microphase-separated structures should be ranked literally as a crystal with the 2-order larger lattice constant of common crystalline substances.

Our next challenge of AFM observation is to simultaneously image both the surface and the cross section of the film in one scanned frame. The film cleaved with substrate was set on the AFM stage with 45° of tilting angle, as Figure 1 illustrates. Figure 4 shows 3D topographic (a) and phase-shift (b) images, and their zoomed images, (c) and (d), corresponding to a position of a square drawn in (b), respectively. The normally aligned hexagonal cylinder structure with fine ridgeline was clearly visualized in both images. Our success in the simultaneous imaging led us to the conclusion that the present microphase-separated film should behave as a crystal to be cleaved with little damage around the ridgeline. Unexpected interesting features were revealed of bent structures along the PEO cylinders in the cross-sectional surface of the 1.0 μm thick film, while few bends were found in the case of thin films with $<$500 nm thickness. At the same depth from the surface (ca. 250 nm), all the cylinders are bent to the identical direction with ca. 30° angles but can be traced through the bends without breaks. Such bent structures were observed among many cross sections of the thick films with ca. 30 $\pm$ 10° angle, which sounds not like an artifact on the cleavage but inherent possibly due to the liquid crystalline structure. Although a detailed mechanism of the bent structures has not been elucidated, it would be originated from a kind of conflict between the perpendicularly oriented PEO cylinders and a tilting structure of the mesogens in liquid crystalline state.[11] This disagreement of the directions between the cylinders and the mesogens would induce the bent structures, which will be verified through careful multilateral analyses with temperature-dependent AFM, WAXRD, and UV spectral measurements and be reported elsewhere.

In conclusion, we succeeded in imaging the cross sections of the cylindrical microphase-separated films under ambient

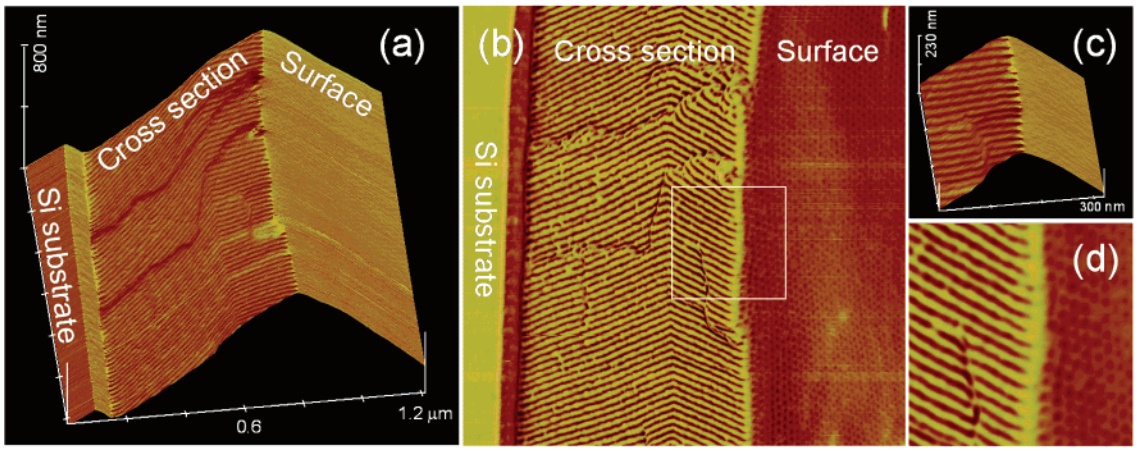

Figure 4. AFM simultaneous observation of both a surface and a cross section of a PEO_{114}-*b*-$PMA(Az)_{51}$ microphase-separated film with hexagonally arranged cylinders. A 45° tilted sample with a 1 μm thickness film was observed. A topographic and a phase-shift images are shown in (a) and (b), respectively, and also their zoomed images identical to a position of a white square drawn in (b) are shown in (c) and (d), respectively.

atmosphere by AFM, through such a simple sample preparation by just cleavage. The cross-sectional AFM imaging demonstrated in this study provides a new analytical technique to visualize the detailed inside structures of such highly ordered microphase-separated nanostructures including defects, which has little been discussed by conventional structural analyses such as SAXS and TEM. While the cleavage nature of high-quality microphase separated films should be required for clear images, the technique will be easily applied for other materials.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Harrison, C.; Park, M.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *J. Vac. Sci. Technol. B* **1998**, *16*, 544.
(2) Spätz, J. P.; Herzog, T.; Mössmer, S.; Ziemann, P.; Möller, M. *Adv. Mater.* **1999**, *11*, 149.
(3) Lopes, W. A.; Jaeger, H. M. *Nature (London)* **2001**, *414*, 735.
(4) Haupt, M.; Miller, S.; Ladenburger, A.; Sauer, R.; Thonke, K.; Spätz, J. P.; Riethmuller, S.; Möller, M.; Banhart, F. *J. Appl. Phys.* **2002**, *91*, 6057.
(5) Templin, M.; Franck, A.; Chesne, A. D.; Leist, H.; Zhang, Y.; Ulrich, R.; Schädler, V.; Wiesner, U. *Science* **1997**, *278*, 1795.
(6) Boontongkong, Y.; Cohen, R. E. *Macromolecules* **2002**, *35*, 3647.
(7) Fahmi, A. W.; Braun, H.-G.; Stamm, M. *Adv. Mater.* **2003**, *15*, 1201.
(8) Ribbe, A. E.; Okumura, A.; Matsushige, K.; Hashimoto, T. *Macromolecules* **2001**, *34*, 8239.
(9) Yeh, S. W.; Wei, K.-H.; Sum, Y.-S.; Jeng, U. S.; Liang, K. S. *Macromolecules* **2003**, *36*, 7903.
(10) Kim, D. H.; Kim, S. H.; Lavery, K.; Russell, T. P. *Nano Lett.* **2004**, *4*, 1841.
(11) Haryono, A.; Binder, W. H. *SMALL* **2006**, *2*, 600.
(12) Lodge, T. P. *Macromol. Chem. Phys.* **2003**, *204*, 265.
(13) Segalman, R. A. *Mater. Sci. Eng. R.* **2005**, *48*, 191.
(14) Tian, Y.; Watanabe, K.; Kong, X.; Abe, J.; Iyoda, T. *Macromolecules* **2002**, *35*, 3739.
(15) Senshu, K.; Kobayashi, M.; Ikawa, N.; Yamashita, S.; Hirao, A.; Nakahama, S. *Langmuir* **1999**, *15*, 1763.
(16) Whitea, H.; Pua, Y.; Rafailovicha, M.; Sokolova, J.; Kingb, A. H.; Giannuzzic, L. A.; Urbanik-Shannonc, C.; Kempshallc, B. W.; Eisenbergd, A.; Schwarze, S. A.; Strzhemechnye, Y. M. *Polymer* **2001**, *42*, 1613.
(17) Radzilowski, L. H.; Carvalho, B. L.; Thomas, E. L. *J. Polym. Phys. Sci. B* **1996**, *34*, 3081.
(18) Xu, T.; Goldbach, J. T.; Leiston-Belanger, J.; Russell, T. P. *Colloid Polym. Sci.* **2004**, *282*, 927.
(19) Chen, X.; Gardella, J. A., Jr.; Kumler, P. L. *Macromolecules* **1993**, *26*, 3778.
(20) Fukunaga, K.; Hashimoto, T.; Elbs, H.; Krausch, G. *Macromolecules* **2002**, *35*, 4406.
(21) Fukunaga, K.; Hashimoto, T.; Elbs, H.; Krausch, G. *Macromolecules* **2003**, *36*, 2852.
(22) Sivaniah, E.; Hayashi, Y.; Matsubara, S.; Kiyono, S.; Hashimoto, T.; Fukunaga, K.; Kramer, E. J.; Mates, T. *Macromolecules* **2005**, *38*, 1837.
(23) Xu, T.; Hawker, C. J.; Russell, T. P. *Macromolecules* **2005**, *38*, 2802.

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