

## Perpendicularly Oriented Cylinder Nanostructure of Liquid Crystalline Block Copolymer Film on Si Substrate with Various Surface Wettability

Hideaki Komiyama,<sup>1</sup> Tomokazu Iyoda,<sup>\*1</sup> and Kaori Kamata<sup>1,2</sup>

<sup>1</sup>Division of Integrated Molecular Engineering, Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8503

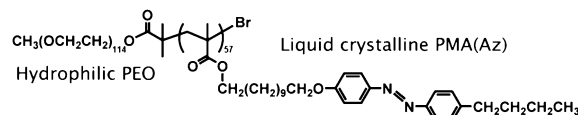
<sup>2</sup>JST-PRESTO, 4-1-8 Hon-cho, Kawaguchi, Saitama 332-0012

(Received October 3, 2011; CL-110812; E-mail: iyoda.t.aa@m.titech.ac.jp)

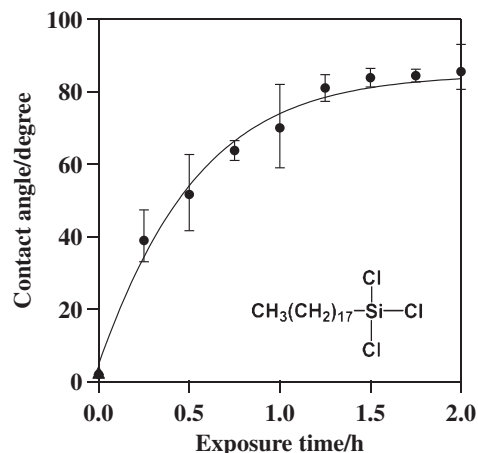
Hexagonally arranged PEO cylinders in the PEO<sub>m</sub>-*b*-PMA(Az)<sub>n</sub> thin film were perpendicularly oriented on Si wafer substrates with a wide range of water contact angle (<5° to 85°) by controlled modification with octadecyltrichlorosilane (OTS). Additionally, the film was stiffly adhered on the modified substrate due to an anchoring effect of partly covered monolayer of OTS.

The use of block copolymer templating to provide nano-scaled materials has been growing due to its simplicity, low cost, and high throughput.<sup>1</sup> In order to use the block copolymer template, it is important to control the orientation of its periodic nanostructures. Over the past few decades, a considerable number of studies have been conducted on this subject in block copolymer template thin films.<sup>2–4</sup> The perpendicular orientation to the substrate of the poly(methyl methacrylate) (PMMA) microdomain in the poly(styrene)-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) thin film, which is a very conventional diblock copolymer, requires precise adjustment of surface energy between the film and a substrate. Surface neutralized substrate, which balances interaction energies of PS or PMMA with the substrate, can be prepared by covalent anchoring of OH-terminated random copolymer (PS-*r*-PMMA) to the oxide layer on Si wafer substrate.<sup>5</sup> The neutralization can be also achieved by modifying the substrate surface with self-assembled monolayer (SAM).<sup>6</sup> Typically, gold and Si substrates were modified with alkythiol and alkylsilane, respectively. Nealey et al. reported defect-free lamellar nanostructures in the PS-*b*-PMMA thin film, which was prepared by registration of individual microdomains along with line-patterned phenylethyltrichlorosilane monolayer on a Si wafer substrate.<sup>7</sup> It has been concluded that these pretreatments of the substrate surface should be crucial for well-oriented microphase-separated nanostructures. Block copolymer templating processes require versatility of various substrates such as a Si wafer, ITO, glass, and so on. Therefore, such delicate pretreatment may be omitted with respect to engineering applications.

Our research group has reported a series of liquid crystalline block copolymers consisting of hydrophilic poly(ethylene oxide) and hydrophobic polymethacrylate bearing azobenzene mesogen in the side chain (PEO<sub>m</sub>-*b*-PMA(Az)<sub>n</sub>) (Scheme 1).<sup>8</sup> Just thermal annealing without any pretreatment of a wide variety of substrates affords the perpendicularly oriented and hexagonally arranged PEO nanocylindrical microdomain array surrounded by PMA(Az) matrix, confirmed by cross-sectional TEM observation with ultrathin microtome and cross-sectional AFM obser-



**Scheme 1.** Chemical structure of PEO<sub>114</sub>-*b*-PMA(Az)<sub>57</sub> block copolymer with 0.85 of weight fraction on PMA(Az) segment.

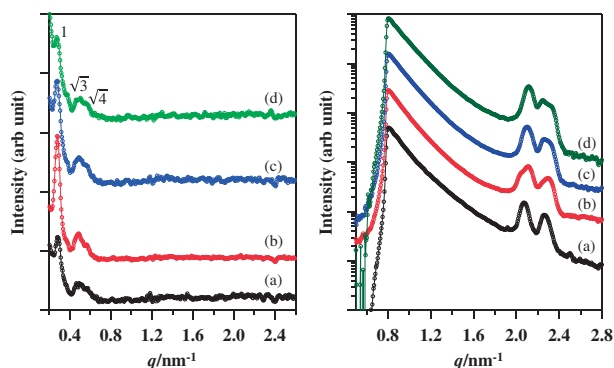


**Figure 1.** Static water contact angle of OTS-modified Si substrates by exposure of VUV-treated Si substrates with OTS vapor at 140 °C in an autoclave reaction vessel (CVD method). The contact angle of a bare Si substrate just after VUV treatment was <5° (denoted as ▲). Inset is chemical structure of OTS.

vation under ambient atmosphere.<sup>9</sup> A simple question arises about the effect of surface energy of the substrate on the orientation of the hexagonal cylindrical phase.

Here we demonstrated surface-independent perpendicular orientation of the PEO cylinders in the PEO<sub>m</sub>-*b*-PMA(Az)<sub>n</sub> thin film by using a series of SAM-modified substrates with various surface wettability. Additional advantage to stiffly adhere the film onto a substrate was achieved.

The SAM-modified Si substrate was prepared by chemical vapor deposition (CVD)<sup>10</sup> with *n*-octadecyltrichlorosilane (OTS), of which chemical structure was shown in the inset of Figure 1. The as-purchased Si wafer (SUMUCO Corp., Sb-doped N-type (100), 0.0–0.02 Ω cm of resistivity) was 48° in static water contact angle. Vacuum ultraviolet (VUV, λ = 172 nm) irradiation for 30 min caused the surface hydrophilic (<5°). CVD of OTS was carried out at 140 °C. Unreacted excess OTS was removed from the surface by rinsing with toluene.

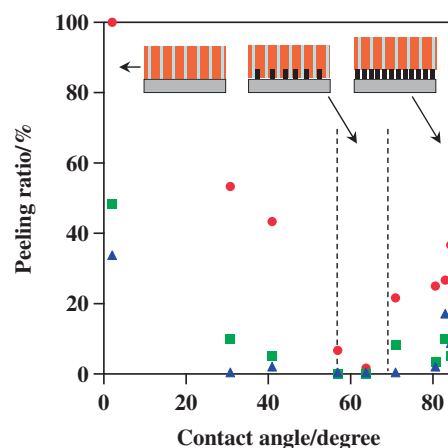


**Figure 2.** (left) In-plane and (right) out-of-plane profiles of GISAXS CCD image of PEO<sub>114</sub>-*b*-PMA(Az)<sub>57</sub> thin film on (a) as-purchased Si substrate with the contact angle of 48°, (b) VUV-treated Si substrate (<5°), and OTS-modified Si substrates with the contact angles of (c) 65 and (d) 85°. Signal below 0.8 nm<sup>-1</sup> in the out-of-plane profile was not collected due to a direct beam stopper. In the out-of-plane direction there are two peaks at low and high scattering vectors, both of which are assigned to the layered structure of smectic phase of the PMA(Az) microdomains as two kinds of scattering from the incident and reflected X-ray beams on the silicon wafer substrate. Details are described in our previous report.<sup>12</sup>

Figure 1 shows the static water contact angle of the OTS-modified Si substrates as a function of the CVD reaction time. The contact angle increased rapidly during the first 1 h and then was saturated up to 85° over 2 h.<sup>11</sup>

The PEO<sub>114</sub>-*b*-PMA(Az)<sub>57</sub> was synthesized according to our previous report.<sup>8</sup> A toluene solution (4 wt%) of PEO<sub>114</sub>-*b*-PMA(Az)<sub>57</sub> was spin-coated onto the OTS-modified Si wafer substrates with various contact angles. Then, the PEO<sub>114</sub>-*b*-PMA(Az)<sub>57</sub> thin films on the substrates were thermally annealed at 140 °C for 6 h so as to induce the microphase-separation. The thickness of the PEO<sub>114</sub>-*b*-PMA(Az)<sub>57</sub> thin film was 120 nm.

Figure 2 shows the in-plane and out-of-plane intensity profiles of the laboratory-GISAXS (2D images are shown in Figure S1<sup>15</sup>). The PEO<sub>114</sub>-*b*-PMA(Az)<sub>57</sub> thin films on the OTS-modified Si substrates with 65° and 85° of contact angles gave three peaks at 0.28, 0.48, and 0.57 nm<sup>-1</sup> in *q*-vector, corresponding to 1:√3:√4 in ratio, which indicates perpendicular orientation of the hexagonal cylindrical nanostructure with 26 nm of center-to-center distance of the adjacent PEO cylindrical microdomains. The identical profiles were given in the PEO<sub>114</sub>-*b*-PMA(Az)<sub>57</sub> thin film on both the VUV-treated and the as-purchased Si substrates with contact angle of <5° and 48°, respectively. AFM images indicate that all the PEO<sub>114</sub>-*b*-PMA(Az)<sub>57</sub> thin films on the various substrates with a contact angle range from <5° to 85° give a consistent hexagonal dot structure as the (001) face of the perpendicularly oriented cylinder structure (Figure S2<sup>15</sup>). The center-to-center distance of the PEO cylinders from the AFM images is 26 nm, in good agreement with the values from GISAXS measurement. Baker et al. reported that the perpendicularly oriented hexagonal cylinder nanostructure in PS-*b*-PMMA thin film was achieved on the Si substrate modified with octadecyldimethylchlorosilane monolayer (contact angle of 65° to 75°), on the basis of the similar surface neutralization.<sup>13</sup> On the other hand, the PEO<sub>114</sub>-*b*-



**Figure 3.** Peeling ratio of PEO<sub>114</sub>-*b*-PMA(Az)<sub>57</sub> film from the substrates by the modified peeling test, which is described in the text. ●, the films with immersion in acetonitrile; ■, the films with immersion in water; ▲, the films without immersion process. Inset is schematic illustration of PEO<sub>114</sub>-*b*-PMA(Az)<sub>57</sub> film on Si substrates (left) without SAM modification and with SAM modification (middle) in amorphous state and (right) in crystalline state.

PMA(Az)<sub>57</sub> thin film showed the perpendicular orientation of the hexagonal cylinder phase in a wide range of contact angle (<5° to 85°) of the OTS-modified Si substrate. Such perpendicular orientation, independent of surface energy and therefore suitable for practical use, could be driven by the homotropic orientation of the side chain mesogen of PMA(Az) segment (Figure 2 (right)).<sup>9,12</sup>

Adhesion of the coated PEO<sub>114</sub>-*b*-PMA(Az)<sub>57</sub> thin film on the OTS-modified Si substrate could be improved due to an anchoring effect of the OTS monolayer. The adhesive property was evaluated by modifying a peeling test (JISK 5600-5-6, cross-cut method) authorized by Japanese Industrial Standards (JIS).<sup>14</sup> The film on the substrate was scratched like a checkered flag pattern with a knife, as is shown in Figures S3, S4, and S5.<sup>15</sup> Then, the films on the substrates were immersed in acetonitrile or water for 1 h. The commercial adhesive tape (NICHIBAN Corp. Ltd., Japan. NW-PK15SF) adhered on the film under dried condition was peeled out, and then the peeling ratio of the pieces was evaluated with an optical microscope. Figure 3 shows the relationship between the peeling ratio and the contact angle of the OTS-modified Si substrates. All the pieces of the film on the VUV-treated Si substrate (contact angle of <5°) were peeled out after immersion in acetonitrile. The peeling ratio was gradually decreased with the increasing contact angle (31°, 41°, and 57°) of the OTS-modified substrate. At 65° of the contact angle, very few pieces of the film were peeled out. However, the film was peeled out in a larger contact angle region (71°, 81°, 83°, and 85°). The similar tendency was obtained in the peeling tests on both the film without immersion in acetonitrile and the film after immersion in water. Mao et al. mentioned that OTS monolayers with <75° of contact angle, prepared by the similar CVD process, should be amorphous state, while it becomes crystalline at contact angle of 90°. That is to say, the OTS would become closely packed to be crystalline. The loosely packed OTS monolayer would anchor the side chains in

PMA(Az) segment, while the closely packed OTS monolayer would not, as is shown in inset of Figure 3. Thus, the thin film on the modified substrate with the contact angle of  $65^\circ$  showed the most stiffly adhesive property even after immersion in acetonitrile and water. We therefore demonstrated an electropolymerization of 3,4-ethylenedioxythiophene (EDOT, 10 mM) in acetonitrile containing 0.1 M NaClO<sub>4</sub> as a supporting electrolyte by using the film on OTS-modified substrate with contact angle of  $65^\circ$  as a working electrode (Figure S6<sup>15</sup>), which will be reported elsewhere. It should be noticed here that the film on the electrode was never peeled out during the electropolymerization. The present partial modification of OTS on a substrate will provide a useful technique for further wet processing of the microphase-separated PEO<sub>m</sub>-b-PMA(Az)<sub>n</sub> template film, including electrochemical application.

In conclusion, we have successfully fabricated the PEO<sub>114</sub>-b-PMA(Az)<sub>57</sub> thin film with perpendicular orientation of the hexagonal cylindrical nanostructure in a wide range of contact angle ( $<5^\circ$  to  $85^\circ$ ). The film coated on the loosely packed OTS monolayer can be durable in wet processes as a stable template to fabricate nanoscaled materials.

The present work was partly supported by a Grand-in-Aid for Scientific Research (S) (No. 18101005) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. H.K. thanks a Japan Society for the Promotion of Science for a research fellowship for young scientists. K.K. thanks a Grant-in-Aid for Science Research in a Priority Area "Super-Hierarchical Structures" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

#### References and Notes

- 1 a) K. W. Guarini, C. T. Black, Y. Zhang, H. Kim, E. M. Sikorski, I. V. Babich, *J. Vac. Sci. Technol., B* **2002**, *20*, 2788. b) R. Watanabe, K. Kamata, T. Iyoda, *J. Mater. Chem.* **2008**, *18*, 5482. c) J. Li, K. Kamata, S. Watanabe, T. Iyoda, *Adv. Mater.* **2007**, *19*, 1267.
- 2 T. Thurn-Albrecht, J. Schotter, G. A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen, T. P. Russell, *Science* **2000**, *290*, 2126.
- 3 D. E. Angelescu, J. H. Waller, R. A. Register, P. M. Chaikin, *Adv. Mater.* **2005**, *17*, 1878.
- 4 R. A. Segalman, H. Yokoyama, E. J. Kramer, *Adv. Mater.* **2001**, *13*, 1152.
- 5 a) P. Mansky, Y. Liu, E. Huang, T. P. Russell, C. Hawker, *Science* **1997**, *275*, 1458. b) P. Mansky, T. P. Russell, C. J. Hawker, J. Mays, D. C. Cook, S. K. Satija, *Phys. Rev. Lett.* **1997**, *79*, 237. c) P. Mansky, T. P. Russell, C. J. Hawker, M. Pitsikalis, J. Mays, *Macromolecules* **1997**, *30*, 6810. d) E. Huang, T. P. Russell, C. Harrison, P. M. Chaikin, R. A. Register, C. J. Hawker, J. Mays, *Macromolecules* **1998**, *31*, 7641.
- 6 a) J. Heier, E. J. Kramer, S. Walheim, G. Krausch, *Macromolecules* **1997**, *30*, 6610. b) R. D. Peters, X. M. Yang, T. K. Kim, P. F. Nealey, *Langmuir* **2000**, *16*, 9620. c) R. D. Peters, X. M. Yang, T. K. Kim, B. H. Sohn, P. F. Nealey, *Langmuir* **2000**, *16*, 4625. d) X. Yang, S. Xiao, C. Liu, K. Pelhos, K. Minor, *J. Vac. Sci. Technol., B* **2004**, *22*, 3331.
- 7 S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. de Pablo, P. F. Nealey, *Nature* **2003**, *424*, 411.
- 8 a) Y. Tian, K. Watanabe, X. Kong, J. Abe, T. Iyoda, *Macromolecules* **2002**, *35*, 3739. b) K. Watanabe, H. Yoshida, K. Kamata, T. Iyoda, *Trans. Mater. Res. Soc. Jpn.* **2005**, *30*, 377.
- 9 M. Komura, T. Iyoda, *Macromolecules* **2007**, *40*, 4106.
- 10 J. Dong, A. Wang, K. Y. S. Ng, G. Mao, *Thin Solid Films* **2006**, *515*, 2116.
- 11 The saturated value of contact angle ( $85^\circ$ ) in this study was smaller than that of  $110^\circ$  reported by Ulman and co-workers. Our VUV treatment was adopted to introduce OH group on Si substrate prior to OTS modification. The amount of the OH group could be insufficient for full coverage of OTS. N. Tillman, A. Ulman, J. S. Schildkraut, T. L. Penner, *J. Am. Chem. Soc.* **1988**, *110*, 6136.
- 12 M. Komura, K. Watanabe, T. Iyoda, T. Yamada, H. Yoshida, Y. Iwasaki, *Chem. Lett.* **2009**, *38*, 408.
- 13 A. Niemi, K. Bandyopadhyay, E. Tan, K. Cha, S. M. Baker, *Langmuir* **2006**, *22*, 11092.
- 14 <http://www.jisc.go.jp>.
- 15 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.