

Surface Structure Analysis of Monolayer and Its Application for Nano-structure Control

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Introduction

It is well known that di-block copolymers form ordered structure in nano-scale, such as body centered cubic, hexagonal packed cylinder and lamellar, as a result of micro-phase separation of block components.[1,2] We have reported that the liquid crystalline

amphiphilic di-block copolymers consist of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(methacrylate) derivative containing azobenzene (Az) moieties, PEO_m-*b*-PMA(Az)_n (scheme 1) form hexagonal packed PEO cylinder structure in wide ranges of both copolymer content and temperature.[3,4] Thin films of block copolymers has paid recently many attentions because of their potential of nano-fabrications. [5] In these applications, the morphology control of block copolymer thin films, particularly the orientation and the order of phase-separated microdomains, are essentially important. We have evaluated the in-plane structure of LB film of PEO₄₀-*b*-PMA(Az)₁₉ by grazing incidence X-ray scattering (GISAXS) method [6]. In Langmuir monolayer of PEO_m-*b*-PMA(Az)_n, Az moieties is expected to align perpendicular to the substrate surface.

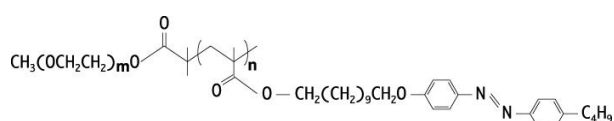
In this study, the PEO_m-*b*-PMA(Az)_n monolayer structure and the cylinder orientation of PEO_m-*b*-PMA(Az)_n which was spin-coated on silicon (Si) wafer modified by monolayer was analyzed by AFM, GISAXS and SAXS.

Experimental

PEO_m-*b*-PMA(Az)_n di-block copolymers used in this study were synthesized by the atom transfer radical polymerization method. The monolayer and multilayer of PEO₄₀-*b*-PMA(Az)₁₉ was deposited on Si wafer at 23 mN m⁻¹ of surface pressure, corresponding to two-dimensional solid state [LB240-S-MWC, Filgen Ltd.]. PEO_m-*b*-PMA(Az)_n was dissolved in toluene, and was spin-coated on Si wafer modified by PEO₄₀-*b*-PMA(Az)₁₉ monolayer. PEO_m-*b*-PMA(Az)_n thin films were annealed in vacuum oven at 140 °C for 24 hrs. The monolayer and multilayer structures were analyzed by GISAXS [RINT-TTR III, Rigaku] operating at 50 kV and 300 mA with a fixed incident angle ($\theta_i = 0.5^\circ$). The nano-scale ordered structures were analyzed by SAXS [BL-10C, PF, High Energy Acceleration Organization, Tsukuba], GISAXS [nano viewer, Rigaku] and AFM [SPM 9500-J3, Shimadzu Co. Ltd].

Results and Discussion

GISAXS technique is powerful to determine internal morphologies of both in-plane and out-plane of thin film because the X-ray beam pass through the film plane, there is no unfavorable scattering from the substrate for in-plane structure. Fig 1 shows the in-plane structure of PEO₄₀-*b*-PMA(Az)₁₉ LB film(20 layers) GISAXS profiles obtained by the incidence X-ray beam parallel (A) and perpendicular (B) to the compression direction. The GISAXS profiles (Fig 1 A) showed two diffraction peaks corresponding to plane spacing of 0.4 and 2.17 nm, caused by the perpendicular structures to the LB surface. The diffraction peak corresponding to 2.17 nm was due to the closed packed single PEO₄₀-*b*-PMA(Az)₁₉ molecule domain, which was aligned



Scheme 1. Molecular structure of PEO_m-*b*-PMA(Az)_n di-block copolymer.

perpendicular to the compression direction. The peak corresponding to 0.4 nm was due to the intermolecular distance between Az moieties orientated perpendicular to substrate surface. This value showed a good agreement with the intermolecular distance obtained from the cross section area of Az molecule of PEO₄₀-*b*-PMA(Az)₁₉ at surf ace pressure (23 mN m⁻¹) of solid state. This peak (0.4 nm) was observed similarly for both A and B, indicating that Az molecule was randomly orienting in in-plane direction.

Fig 2 shows AFM topo images for the hexagonal packed cylinder structure of PEO₁₁₄-*b*-PMA(Az)₄₆ thin film on Si substrate without monolayer (a) and with monolayer (b). The vertical orientation of PEO cylinder (black spots and lines) was only observed in AFM image (b). These results suggested that the orientation of PEO cylinder was controllable by the existence of monolayer on Si substrate.

The effect of monolayer on the cylinder orientation was also observed by SAXS. Film A spin-coated on Si wafer with monolayer showed only diffraction peaks from hexagonal cylinder structure. Film B prepared on Si wafer without monolayer showed the broad diffraction peak from the smectic A layer at 1.8 nm⁻¹, instead of the diffraction peaks from hexagonal structure. These results suggested that the alignment of cylinder was perpendicular and of smectic A layer of Az molecules was parallel to the substrate surface, respectively, for Film A. However, SAXS profile of Film B indicated the parallel orientation of PEO cylinder to substrate surface.

In this study, we succeeded to control the orientation of hexagonal cylinder using monolayer. PEO cylinders in spin-coated PEO_m-*b*-PMA(Az)_n thin film on monolayer were aligned perpendicular to the substrate surface, as results of orientation of Az molecules in spin-coated film, which were determined by the orientation direction of Az moieties in monolayer.

References

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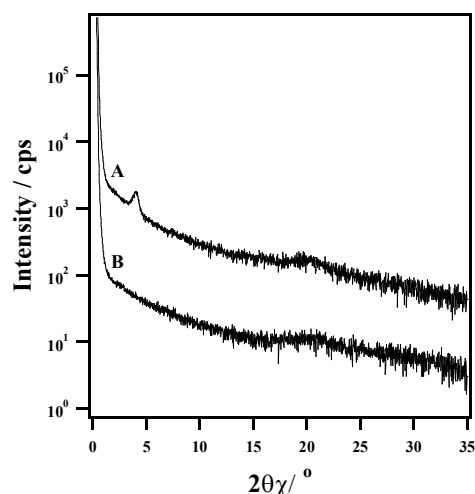


Fig 1. In-plane X-ray diffraction patterns for multi-layer of amphiphilic di-block copolymer PEO₄₀-*b*-PMA(Az)₁₉.

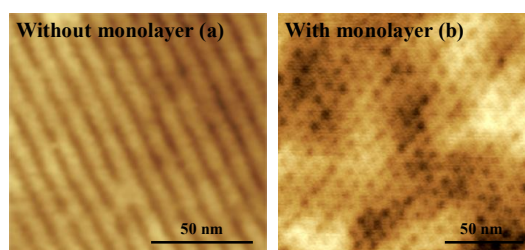


Fig2. Atomic force microscopy (AFM) images for thin film of PEO₁₁₄-*b*-PMA(Az)₄₆ prepared with and without monolayer.

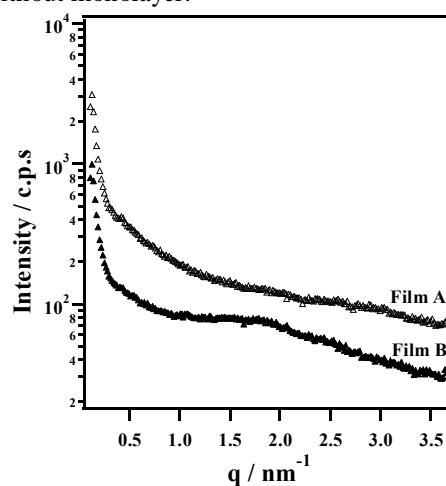


Fig 3. SAXS profiles of PEO₁₁₄-*b*-PMA(Az)₄₆ thin film prepared with (Film A) and without monolayer (Film B)