Structure analysis of amphiphilic di-block copolymer monolayer by X-ray reflectivity

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Abstract. Monolayer of liquid crystalline amphiphilic di-block copolymer, PEO₄₀-b-PMA(Az)n, was investigated by a grazing incidence X-ray diffraction (GIXRD) and X-ray reflectivity. GIXRD results indicated the condensed ordered state of azobenzene moieties in the monolayer. The four-layer model considering the chemical structure and the Fourier transform analysis, and the five-layer model considering the molecular mobility of PEO₄₀-b-PMA(Az)n were used to analyze the X-ray reflectivity profiles. Both models gave the condensed state of trans azobenzene moieties, which aligned perpendicular to the silicon wafer surface.

1. Introduction

Various types of block copolymer form the nano-scale ordered structures, cubic micelle, hexagonally packed cylinders, lamella and gyroid as a result of micro-phase separation. These nano-scale structures give polycrystalline or multi-domain morphology, because the structure formation occurs under the phase separation kinetics. The liquid crystalline type amphiphilic di-block copolymer, consisted of hydrophilic poly(ethylene oxide) and hydrophobic poly(methacrylate) having mesogenic azobenzene moieties in an ester group, PEO-b-PMA(Az), forms hexagonally packed PEO cylinder structure [1, 2] due to the compensation effect of entropy loss caused by liquid crystal formation [3]. The orientation control of PEO cylinders were succeeded by controlling the orientation of mesogenic azobenzene moieties under photo irradiation [4] and an electric field [5]. We have proposed the orientation control method using the cooperative liquid crystal formation of PEO-b-PMA(Az) thin film on PEO-b-PMA(Az) monolayer in which azobenzene moieties aligned normal to the substrate [6].

Monolayer of amphiphilic polymers on water are investigated by X-ray reflectivity [7-9]. The thickness and the inverse area of molecule of Langmuir monolayer show a good linear relationship for sulfonate group end capped poly(isoprene) with various molecular weights [7]. The thickness of hydrophobic component of Langmuir monolayer on water depends on the surface pressure, however, the thickness of both hydrophilic and hydrophobic components of monolayer on the glass substrate depend on the surface pressure for amphiphilic di-block copolymer [8]. The conformational transition of azobenzene existed in the side chains of poly(vinyl alcohol) influences the Langmuir monolayer
structure [8]. In this study, the monolayer structure of PEO-b-PMA(Az) prepared on silicon wafer was investigated by X-ray reflectivity, especially the orientation of azobenzene moieties in monolayer was focused.

2. Experimental

Three block copolymers having same segment length of PEO and different segment length of PMA(Az), PEO₄₀-b-PMA(Az)₁₀, PEO₄₀-b-PMA(Az)₁₉ and PEO₄₀-b-PMA(Az)₃₉ (Scheme 1) were used in this study. The monolayer of PEOₙ-b-PMA(Az)ₙ was converted from water surface to silicon wafer at 23 mN m⁻¹ surface pressure, which corresponded to two-dimensional solid state [6].

Grazing incidence X-ray diffraction (GIXRD) and X-ray reflectivity measurements of monolayer were carried out by a Rigaku RINT-TTR III, operating at 300 mA and 50 kV. The wavelength of X-ray was 0.154 nm.

3. Results and Discussions

The in-plane XRD profile of PEO₄₀-b-PMA(Az)₁₉ monolayer on silicon wafer obtained by GIXRD showed two diffraction peaks at around 3 and 27 ° corresponded to the spacing 2.9 and 0.33 nm, respectively. The later diffraction peak was observed for the measurement in which the incident X-ray beam was parallel to the compression direction for monolayer, however, the former diffraction peak was observed for both case the parallel and the perpendicular direction of X-ray beam. From the surface pressure (π) – area per molecule (A) isotherm of PEO₄₀-b-PMA(Az)₁₉, the diameter of PMA(Az)₁₉ domain was evaluated 2.7 nm [10], which was smaller than the value estimated from the radius of gyration of PMA(Az)₁₉, however, the diffraction peak at 3 ° corresponded to the ordered alignment of PMA(Az)₁₉ domain consisted of single PEO₄₀-b-PMA(Az)₁₉ molecule [11]. The diffraction peak at 27 ° corresponded to the intermolecular distance between azobenzene moieties because the result of UV-vis spectrum revealed that azobenzene moieties formed the H-aggregation in PEO₄₀-b-PMA(Az)₁₉ monolayer [10].

The relative X-ray reflectivity profile of PEO₄₀-b-PMA(Az)₁₀, PEO₄₀-b-PMA(Az)₁₉ and PEO₄₀-b-PMA(Az)₃₉ monolayers were shown in figure 1 (A). The Fourier transform of the oscillation parts of the reflectivity curves were shown in figure 1 (B). Including the main peak at 4.2 and 5.0 nm corresponded to the total thickness of monolayer, four peaks were observed in the Fourier analysis. Considering to the Fourier transform and the chemical structure of PEO₄₀-b-PMA(Az)ₙ, the four-layer model as shown in scheme 1 divided to hydrophilic PEO (A), poly(methacrylate) (B), azobenzene (C) and n-butyl chain end (D) was used to analyze the reflectivity profile. The best fitted curve by four-layer model was shown in figure 2 (dotted line), described the shape of Kiessig fringe within 2.1 % error. The four-layer model was used to analyze the X-ray reflectivity profiles of PEO₄₀-b-PMA(Az)₁₀ and PEO₄₀-b-PMA(Az)₁₉ monolayer. The fitting error increased from 2 to 2.5 % for PEO₄₀-b-PMA(Az)₁₀ and PEO₄₀-b-PMA(Az)₁₉ monolayer.

Considering to the molecular mobility of PEO₄₀-b-PMA(Az)ₙ, poly(methacrylate) main chain had lower mobility comparing to alkyl ester chain, the five-layer model was used to analyze the reflectivity profiles. Poly(methacrylate) part was divided to main chain and alkyl ester chain in the five-layer model. The best fitted curve by the five-layer model showed a good agreement with the experimental
value within 1.5 % error as shown in figure 2 (solid line). The thickness of each layer obtained by the four-layer and five-layer models showed a good agreement. However the density of PEO and azobenzene parts evaluated by the four-layer model gave lower values than those obtained by the five-layer model. Comparing with the density profile and the Fourier transform, each FT peaks indicated the interface between layers except the peak at 1 nm. As all monolayer samples gave the FT peak at 1 nm, the half of PEO molecule absorbed strongly on the silicon wafer surface had higher density than another half of PEO molecule. The total thickness of monolayer of PEO\textsubscript{40-}b-PMA(Az)\textsubscript{10} was 0.7 nm thicker than those of PEO\textsubscript{40-}b-PMA(Az)\textsubscript{19} and PEO\textsubscript{40-}b-PMA(Az)\textsubscript{39} monolayer. The difference came from the thickness of PEO.

**Figure 1.** Refractivity profiles (A) and Fourier transforms (B) for PEO\textsubscript{40-}b-PMA(Az)\textsubscript{10}, PEO\textsubscript{40-}b-PMA(Az)\textsubscript{19} and PEO\textsubscript{40-}b-PMA(Az)\textsubscript{39} monolayer

**Figure 2.** Experimental and calculated results of reflectivity for PEO\textsubscript{40-}b-PMA(Az)\textsubscript{39} monolayer.

The obtained fitting parameters for PEO\textsubscript{40-}b-PMA(Az)\textsubscript{39} monolayer by the four-layer and the five-layer models were listed on Table. 1. The thickness of azobenzene part was 1.10 ± 0.05 nm for all samples, which was independence from models. However, the density of azobenzene was 1.23 ±0.05 and 1.3 ± 0.07 g cm\textsuperscript{-1} for the four-layer and the five-layer model, respectively. The former value
corresponded to the crystal density of cis azobenzene, and the later value was slightly higher than the crystal density of trans azobenzene. These fitted results for azobenzene parts were almost the same for three monolayers used in this study. As the length of trans azobenzene was 0.9 nm, H-aggregated azobenzene moieties aligned perpendicular to the silicon wafer surface. This XR result agreed with the UV-vis spectrum of monolayer on quartz surface in which the long axis of azobenzene moieties aligned perpendicular to the quartz surface. Both models gave the larger roughness for each interface reflecting high mobility of alkyl chains. The thickness of n-butyl group connected to azobenzene was 0.34 ± 0.05 nm with 0.4 nm roughness and 0.7 ± 0.1 g cm⁻¹ density, which was similar to the density of n-butane (0.601 g cm⁻¹). These results suggested that the surface of monolayer was covered with liquid like butyl groups. The root mean square roughness of PEO₄₀-b-PMA(Az)₁₉ monolayer by atomic force microscope (AFM) observation was 0.385 ± 0.03 nm for 3 x 3 µm². The surface roughness of monolayer evaluated by X-ray reflection and AFM were almost the same.

The coupling of FT analysis and model fitting gave the consistent results for the thickness profile, however, the obtained density and roughness included some extents of error. The model optimization was necessary to obtain the stack parameters of inter-layers.

| Table 1. Obtained fitting parameters for PEO₄₀-b-PMA(Az)₁₉. |
|-----------------|--------|--------|--------|--------|
|                | A      | B₁     | B₂     | C      | D      |
| Thickness / nm |        |        |        |        |        |
| Four-layer     | 1.61   | 1.59   | 1.15   | 0.35   |
| Five-layer     | 1.73   | 0.63   | 0.81   | 1.11   | 0.34   |
| Density / g cm⁻¹ |        |        |        |        |        |
| Four-layer     | 1.12   | 0.99   | 1.22   | 0.76   |
| Five-layer     | 1.16   | 0.96   | 0.89   | 1.29   | 0.70   |
| Roughness / nm |        |        |        |        |        |
| Four-layer     | 0.7    | 0.6    | 0.3    | 0.4    |
| Five-layer     | 0.8    | 0.1    | 0.5    | 0.3    | 0.4    |

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