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Analysis of Multilayer Structure of Amphiphilic Di-block Copolymer by X-ray Reflectivity

Takeshi Yamada1, Sunyoung Jung2,3, Hirohisa Yoshida2,3

1: Graduate School of Engineering, Tokyo Metropolitan University, 1-1 Minamiosawa Hachiouji 192-0397, Japan
2: Faculty of Urban Environmental Science, Tokyo Metropolitan University, 1-1 Minamiosawa Hachiouji 192-0397, Japan
3: CREST-JST

yamada-takeshi@ed.tmu.ac.jp

Abstract. The structure of Langmuir-Blodgett (LB) membranes of liquid crystal amphiphilic di-block copolymer, poly(ethylene oxide)-b-poly{11-[4-(4-butylphenylazo)phenoxy]-undecyl methacrylate, (PEO-b-PMA(Az)) was investigated by X-ray reflectivity (XR). XR results indicated that the structure of LB membranes below 6 layers was formed by the head to head type bilayer structure consisting of the extended hydrophilic PEO and the compressed hydrophobic PMA(Az) layers. In the case of 10 layers, the another type of bilayers consisting of the interdigitate PMA(Az) structure corresponding to the smectic C phase in the bulk state and the collapsed PEO layer were lapped on the bilayer structure of 6 layers. The structural transition from the head to head type bilayer to the interdigitate bilayer occurred around 6 to 10 layers.

1. Introduction
Polymer thin films are widely used in many products for protecting or improving optical properties. The structure of thin films differs from that in the bulk state because the ratio of surface and interface against substance volume becomes large with the decrease of thickness. Especially, the interactions between substances and substrates have an important role for the thin film structure. The structure of thin film is interesting from both scientific and industrial viewpoints. Langmuir-Blodgett (LB) technique is one of methods to make the ordered thin film on various substrates [1]. LB technique can easily control the aggregation states and the thickness of thin film by changing the surface pressure and the number of deposition layer on substrates, respectively.

On the other hand, block copolymers form ordered micro-phase separated structures such as lamellar, cylinder and sphere as an equilibrium structure. In the bulk state, the micro-phase separated structure is related with the degree of polymerization, the relative volume fraction and the interaction between block components [2]. LB film of block copolymer is expected to show the different structure in the bulk state.

We reported the phase transitions and the micro-phase separated structure of liquid crystal amphiphilic di-block copolymers, poly(ethylene oxide)-b-poly{11-[4-(4-butylphenylazo)phenoxy]-
undecyl methacrylate, (Scheme 1, PEO\textsubscript{m-}b-PMA(Az)\textsubscript{n}) where “m” and “n” were polymerization degrees of PEO and PMA(Az) sequences, respectively consisting of hydrophilic poly ethylene oxide (PEO) and hydrophobic poly methacrylate derivatives having azobenzene moieties as a liquid crystal mesogen (PMA(Az)) [3]. PEO-b-PMA(Az) forms highly ordered hexagonal packed PEO cylinder structure in the wide range of PEO volume fraction comparing with the linear block copolymers. In this report, PEO\textsubscript{40-b-PMA(Az)\textsubscript{39}} LB membranes with various layer numbers were analyzed by X-ray reflectivity.

![Scheme 1. Chemical structure of PEO\textsubscript{m-b-PMA(Az)\textsubscript{n}}.](image)

2. Samples and Experiments
PEO\textsubscript{40-b-PMA(Az)\textsubscript{39}} was synthesized by atom transfer radical polymerization described elsewhere [3]. The dispersion of molecular weight determined by gel permission chromatography was 1.13.

LB membranes of PEO\textsubscript{40-b-PMA(Az)\textsubscript{39}} having different number of layers (N = 2, 3, 4, 6 and 10) were prepared by the vertically deposition of Langmuir monolayer of PEO\textsubscript{40-b-PMA(Az)\textsubscript{39}} on water surface to the hydrophobic carbon coated glass plates using LB240-S-MWC (Filgen Ldt.) at 24 mN m\textsuperscript{-1} of surface pressure and 4 mm min\textsuperscript{-1} of dipper speed. Under this condition, the Y-type LB membrane was obtained and LB membrane with even layer number had the hydrophobic surface [4]. After preparation, the LB membranes were kept in a desiccator with phosphorus pentaoxide. X-ray reflectivity (XR) was performed by MX-24 (Mac Science Co Ltd) operating at 300 mA and 40 kV. The wavelength of X-ray (λ) was 0.154 nm (Cu Kα).

3. Results and Discussions
Figure 1 showed XR profiles of LB membranes of PEO\textsubscript{40-b-PMA(Az)\textsubscript{39}} having different number of layers. Fringes coming from the total thickness of LB membrane were observed for all LB membranes. The interval between fringes decreased with increasing the number of layers. The total thickness of LB membranes (D) was evaluated from the interval between fringes by following equation.

![Figure 1. XR profiles of LB membranes of PEO\textsubscript{40-b-PMA(Az)\textsubscript{39}} having 2, 3, 4, 6 and 10 layers from the top to the bottom. Each profile was magnified several decades for visualization.](image)
Here $\Delta q$ indicates the interval scattering vector ($q = \frac{\lambda}{4\pi \sin \theta}$) between fringes.

Figure 2. Relationship between total thickness and number of layers of PEO$_{40}$-b-PMA(Az)$_{39}$ LB membranes. The filled circle was PEO$_{40}$-b-PMA(Az)$_{19}$ LB membrane.

Figure 2 showed a relationship between $D$ and $N$ for PEO$_{40}$-b-PMA(Az)$_{19}$ LB membranes. Below 6 layers, $D$ and $N$ showed a good linear relationship. The intercept of the linear relationship to the Y-axis corresponded to the thickness of carbon coat on glass plate. The slope of linear relationship was 6.2 nm / layer. From the surface pressure ($\pi$) – molecular area (A) curve of PEO$_{40}$-b-PMA(Az)$_{39}$, the cross-sectional area was 0.32 nm$^2$. This value coincided with the cross-sectional area of azobenzene molecule in the similar liquid crystalline tri-block copolymer having azobenzene as a mesogen in the side-chain, which aligned normal to the water surface [5]. The UV-vis spectrum of PEO$_{40}$-b-PMA(Az)$_{19}$ monolayer prepared on quartz indicates the perpendicular alignment of azobenzene molecules to the quartz surface [6]. Therefore, the azobenzene molecules of side-chain of PMA(Az) domain in the LB membranes prepared at 24 mN m$^{-1}$ of surface pressure aligned normal to the glass surface. As the length of PMA(Az) side-chain was 3.4 nm calculated by MM2 method [3], the thickness of PEO layer was 2.8 nm, which was larger than the radius gyration of PEO$_{40}$ molecules ($R_g = 1.76$ nm). On water surface, the compressed side-chains in the PMA(Az) domain aligned normal to the water surface and PEO chains were extended in water at 24 mN m$^{-1}$ surface pressure. Therefore, the LB membrane below 6 layers formed the head to head type bilayer structure consisted of the extended hydrophilic PEO and the compressed hydrophobic PMA(Az) domains as shown in figure 3 (a).

In the case of 10 layers, the total thickness was 55.2 nm, which was smaller than the estimate value from the linear relationship below 6 layers. In the XR profile of 10 layers LB membrane in figure 1, two Bragg peaks appeared at around 2 and 4 nm$^{-1}$. These Bragg peaks are observed for the 20 layers PEO$_{40}$-b-PMA(Az)$_{19}$ LB membrane [4]. The distance evaluated from these peaks was 3.1 nm. This value agreed with the thickness of the smectic layers of PMA(Az) domain in the bulk state, where PMA(Az) domain formed the interdigitate structure with 3.1 nm thickness as same as the thickness of smectic layer in the smectic C phase. [7]. The thickness difference between the 6 layers and 10 layers LB membranes was 12.6 nm, which corresponded to the thickness of 4 smectic layers in the bulk state. For the 10 layers LB membrane, therefore, the ordered interdigitate PMA(Az)
bilayer structure, which gave the SAXS diffraction peaks, was piled up on the head to head type bilayer structure of 6 layers as shown in figure 3 (b). The PEO layer of 10 layers LB membrane seemed to become thinner than that below 6 layers because the interdigitate PMA(Az) structure collapsed the PEO layers. Grazing incident XRD analysis of PEO\textsubscript{40}-b-PMA(Az)\textsubscript{19} LB membrane with 20 layers suggests the perpendicular alignment of azobenzene molecules to the substrate surface [4]. These results indicated that the thickness of 3.1 nm came from the interdigitate PMA(Az) structure instead of the tilting of PMA(Az) side chains. The increase of layer number induced the structural transition from the meta-stable head to head type bilayer structure to the stable interdigitate bilayer structure between 6 and 10 layers.

The transfer ratio during downward deposition (0.9 – 0.95) was slightly smaller than that during upward deposition (1.05 – 1.15), however, the average transfer ratio for bilayer was around 1 for LB membranes below 6 layers. The transfer ratio during downward deposition increased gradually with the increase of layer number above 5 layers (1.2 – 1.3). The excess deposition enhanced the meta-stability of head to head type bilayer structure and induced the transition to the interdigitate structure during the drying process. The bilayer structure of LB membrane below 4 layers was stabilized by the interaction between the glass substrate and PEO\textsubscript{40}-b-PMA(Az)\textsubscript{39} and the deposition balance in the head to head type bilayer.

Figure 3. Schematic models of LB membranes below 6 layers (a) and 10 layers (b).

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