

# Reflectometric Investigation of Monolayers of Copolymers with Dendritic and Perfluoroalkyl Side Chains

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The structural investigation of monolayer consisting of homologs of block copolymer at air/water interface and on solid substrate has been performed by using neutron and X-ray reflectometry. Homologous polymers are constructed by poly(perfluoroalkyl acrylate), poly(methacrylic acid) and poly(dendron methacrylate) blocks, polymerization degree of which are different. The arrangement of these copolymers varied depending on fraction of poly(dendron methacrylate) block both at air/water interface and on solid surface. A copolymer with low fraction of poly(dendron methacrylate) block lies on water subphase and Si substrate. With the fraction increase of poly(dendron methacrylate) block, copolymer is normally oriented to the interfaces. Key Words: block copolymer, neutron reflectometry, X-ray reflectometry, dendritic side chain, fluorinated side chain, monolayer

## 1. INTRODUCTION

Many studies of molecular arrangement of block copolymers at interfaces have been done [1]. Their orientation and stability at the interfaces are varied depending on components of the blocks, that is, chemical structure, property, size and shape of each block [2]. From this view, we have synthesized block copolymers, poly(3,5-bis(3,5-bis(benzyloxy)benzyl-oxy)benzyl methacrylate-random-methacrylic acid)-*block*-poly(2-perfluorooctylethyl acrylate) (P(D<sub>3</sub>MA, MAA)-*b*-PFA) (Chart 1) [3], which have both rigid dendritic and fluorinated side chains [4,5]. By the way, PD<sub>3</sub>MA blocks with benzyloxy type dendritic side chains are oleophilic and PFA blocks with perfluoroalkyl side chains are oleophobic. Then these copolymers could arrange in monolayer at air/water interface.

For investigation of molecular orientation within thin films, neutron reflectometry (NR) and X-ray reflectometry (XR) have been utilized [6,7]. As one of some advantages of these methods, NR and XR can be applied for thin films not only at gas/solid interface but also at gas/liquid and liquid/liquid interfaces [8,9]. According to these methods, the atom or electron density profile within a thin film is obtained. Consequently, the components of each layer within the film can be estimated, and the molecular orientation is determined [10].

In this study we investigated the orientation of P(D<sub>3</sub>MA,MAA)-*b*-PFA at air/water and air/solid interfaces. Depending on the fraction of blocks in copolymer, the orientation of the polymer at the interface is expected to change. Consequently oleophilicity or oleophobicity of surface can be controlled.

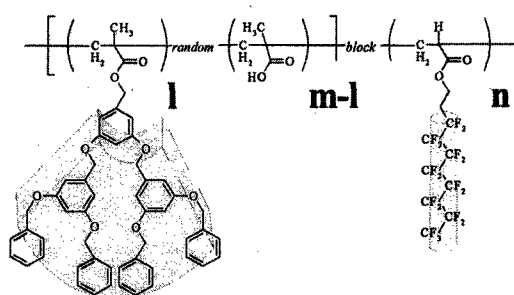
## 2. EXPERIMENTAL

Poly(methacrylic acid)-*block*-poly(2-perfluoro-octyl ethyl methacrylate) (PMAA-*b*-PFA) (M2:  $l = 0$ ,  $m-l = 123$ ,  $n = 29$ ) and P(D<sub>3</sub>MA,MAA)-*b*-PFA (M2den2:  $l = 24$ ,  $m-l = 12$ ,  $n = 11$  and M2den3:  $l = 28$ ,  $m-l = 2$ ,  $n = 8$ ) were previously synthesized and used [3]. D<sub>2</sub>O (99 %) and chloroform were purchased from Wako Pure Chemical Industries, Ltd. and Aldrich, respectively.

Nikon COOLPIX950 digital camera was used for contact angle measurement of 0.02 cm<sup>3</sup> water and decane droplet on films at room temperature (~25°C). Since vertical cross-section of water droplet is approximated to be an arc of circle, contact angle  $\theta$  was calculated from an equation,  $\theta = 2\text{tan}^{-1}(h/x)$ , where  $h$  and  $x$  are height and radius of the arc, respectively.

NR measurements were carried out on ARISA (Advanced Reflectometer for Interface and Surface Analysis) of High-energy Accelerator Research Organization (KEK) in Tsukuba, Japan, which is equipped with a Langmuir-Blodgett (LB) trough (37 cm × 12 cm). The details of the operation of ARISA and the trough were described elsewhere [11]. An aliquot of a chloroform solution (1.0 mg/cm<sup>3</sup>) of polymer was spread on D<sub>2</sub>O subphase in the trough, and 30 minutes were allowed for solvent evaporation. Surface pressure was compressed up to 25mN/m for M2 and 13mN/m for both M2den2 and M2den3. The measurements were performed under a specular condition: The range of wave vector  $Q (=4\pi\sin\theta/\lambda)$ ,  $\theta$ : incident angle,  $\lambda$ : wavelength) was 0.006 ~ 0.63 Å<sup>-1</sup>. The data were analyzed by the program "mlayer" with the 7% error of the  $Q$ .

XR measurements were carried out on Rigaku RINT 2500 X-ray reflectometer with Cu/K $\alpha$  X-ray source (200mA / 40kV) and the X-ray beam ( $\lambda=0.154$  nm),

Chart 1. Chemical structure of P(D<sub>3</sub>,MAA)-b-PFA.

which was monochromized by multi-layered mirror. The divergence and receiving slits were 0.05 and 0.1 cm, respectively, in width. The sample stage was adjusted by a goniometer. The scan rate was 0.04°/min and angle step was 0.001°. The X-ray reflection curves were analyzed by using the equation described elsewhere [12]. The electron density, thickness and roughness of each layer can be calculated. LB film deposition for contact angle and XR measurements was performed using a Nippon Laser & Electronics LB deposition system at the same surface pressure as NR measurement. The Z-type and ZX type LB films were prepared by one upstroke transfer and additional downstroke transfer to the Z-type film, respectively, at a rate (dipper speed) of 2 mm/min. After the transfer, the LB films were dried in vacuo for 8 hours.

### 3. RESULTS

#### 3.1 Depth profile and orientation of copolymers in Langmuir films at air/D<sub>2</sub>O interface

Figure 1 shows NR curves of M2, M2den2 and M2den3 at air/D<sub>2</sub>O interface. The surface areas of M2, M2den2 and M2den3 were 51, 910 and 650 Å<sup>2</sup>/molecule, respectively, at surface pressures that examined NR [3]. These values indicate monolayer formation. Then the computer simulation was carried out on the basis of four layer models (air, solvophobic block, solvophilic block and water) and optimum fitting curves were included in Figure 1. The depth-scattering length density (SLD) profile is shown in Figure 2.

According to the model estimation, SLDs of fluorocarbon and dendron in the closest packing were  $\sim 3.5 \times 10^{-6} \text{ \AA}^{-2}$  and  $\sim 2.0 \times 10^{-6} \text{ \AA}^{-2}$ , respectively, which were evaluated from the mass density of the typical C<sub>8</sub> fluorocarbon and benzyloxy dendron compounds [13]. These values were taken into account on the determination of the position of blocks in the layers.

As seen in Figure 2, two layers were distinguished in the monolayer of M2 at the air/water interface. Since the SLD of the upper layer was calculated to be  $3.0 \times 10^{-6} \text{ \AA}^{-2}$ , it is assumed that the upper layer consists of the fluorocarbon blocks. The SLD of the lower layer was close to that of D<sub>2</sub>O (theoretically  $6.3 \times 10^{-6} \text{ \AA}^{-2}$ ) due to the inter-diffusion or hydration of D<sub>2</sub>O into hydrophilic PMAA block [14].

The best-fit model of M2den2 monolayer was also double layer. SLDs of two layers were  $1.95 \times 10^{-6} \text{ \AA}^{-2}$  (upper layer) and  $2.25 \times 10^{-6} \text{ \AA}^{-2}$  (lower layer). The

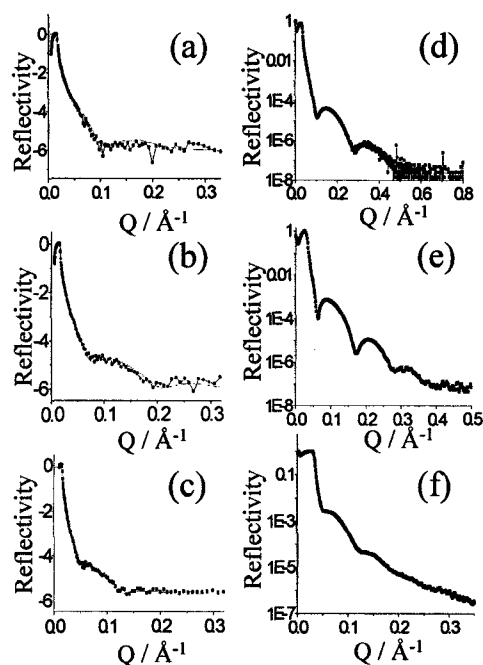


Figure 1. NR and XR curves of M2, M2den2 and M2den3 at air/D<sub>2</sub>O and air/Si interfaces, respectively. Solid lines are the optimum fitting curves. (a) NR, M2; (b) NR, M2den2; (c) NR, M2den3; (d) XR, M2; (e) XR, M2den2; (f) XR, M2den3.

relatively smaller contrast of SLD between upper and lower layers and the SLD close to it of dendron but far low from it of fluorocarbon indicate that the fluorocarbon blocks were unlikely to specially localize in the either layer. Further, while the cross-sectional diameter of the M2den2 molecule was calculated to be  $\sim 50 \text{ \AA}$ , the total monolayer thickness resulted from NR was 45 Å (upper layer = 30 Å, lower layer = 15 Å). These results indicate that the molecules should be laid down completely at air/D<sub>2</sub>O interface.

The best-fit NR curve of the M2den3 monolayer at the air/D<sub>2</sub>O interface was a triple layer model but not a double layer model, as seen in the Figure 2. The first layer consisted of the dendron-rich layer, the second layer mainly comprised from the fluorocarbon blocks and the component of the third layer was the dendron's again. This assignment was derived from the comparison of the evaluated SLD with the appropriate theoretical values referred above. From such a fitting result, the most probable model of M2den3 monolayer was estimated to be the pseudo-micelle model. The fluorocarbon blocks were located in rather D<sub>2</sub>O side than airside, and dendron blocks were in the film surface.

#### 3.2 Depth profile and orientation of copolymers in LB film on hydrophilic solid substrate

Figure 1 includes XR curves of the LB (Z) films of M2, M2den2 and M2den3 on the silicon substrate. The result of the optimum fitting calculation for XR curve of M2 indicates that the LB film is constructed by double layers of the fluorocarbon blocks (upper layer) and hydrophilic PMAA blocks (lower layer) (see

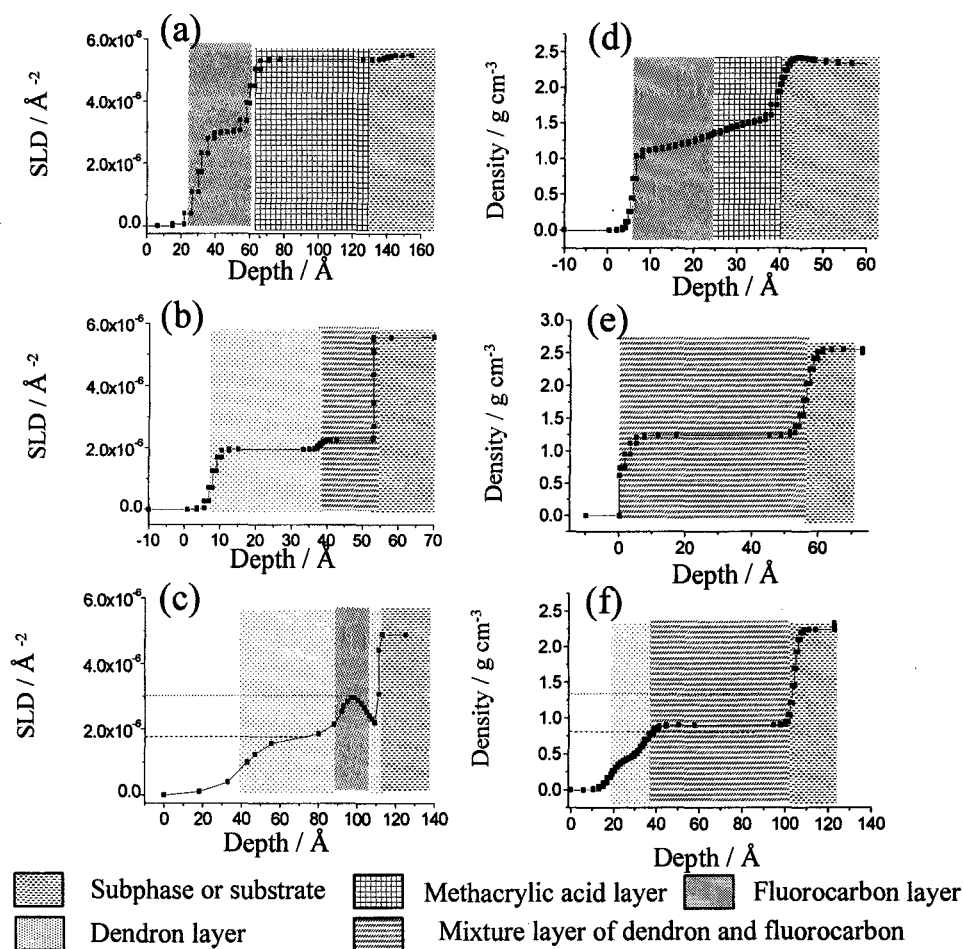


Figure 2. SLD vs. depth profile of M2, M2den2 and M2den3 at air/D<sub>2</sub>O and air/Si interfaces. Notation (a)-(f) have the same meaning as Figure 1.

Figure 2). This means that the fluorocarbon chain existed on the airside. The PMAA chain was highly compressed. This was shown from that the density of the lower layer was larger than that of the upper layer. Since the molecular size is evaluated to 220 Å but the total monolayer thickness is 35 Å, the molecule must be tilted. The water and decane contact angles were 60-70° and 20-30° for both LB (Z) and LB (ZX) films, respectively. This result does not support that PFA blocks are exposed to the surface of both LB films. The reason is that the PMAA blocks were highly compressed and penetrated into the layer of PFA blocks.

Figure 2 indicates that the LB film of M2den2 consists of the mixture of dendron and fluorocarbon blocks, since the best-fit model displayed only one layer in spite of the high contrast of densities between dendron and fluorocarbon blocks. Incidentally, in the closest packing, the typical density of fluorocarbon (C<sub>8</sub>) is ~ 3.5 g/cm<sup>3</sup> and that of benzyloxy type dendron is 1.13 g/cm<sup>3</sup>. If the dendron or fluorocarbon blocks localized at somewhere in this LB film, the optimum structure must be two or more layers. In addition, the water contact angle was ~80° for both LB (Z) and LB (ZX) films. This value is unlikely that only PFA blocks

have to be exposed to the surface due to lower contact angle than that of typical fluorinated compound [15]. The monolayer thickness (50 Å) is close to its simulated cross-sectional diameter of M2den2. Thus the molecules have to lie down completely on the substrate.

In the case of M2den3, the fitting shows that the layer of the substrate side was denser than that of the airside. It was assumed that the upper layer is dendron-rich, since the dendron moiety is less dense than the fluorocarbon moiety. In addition to XR result, the contact angle measurement also supported this. The water contact angle was ~80° and the decane contact angle was ~10° for both LB (Z) and LB (ZX) films. It is indicated that the surface profile is similar to that of M2den2, that is, the contact angle reflects the presence of dendron blocks at the monolayer surface. Totally, it was suggested that the lower layer was comprised with the mixture of the dendron and fluorocarbon blocks and the upper layer was mainly dendron blocks. Thus, the most of the dendron blocks must occupy the surface in the monolayer LB (Z) film.

#### 4. DISCUSSION

The location of block copolymers (M2, M2den2 and

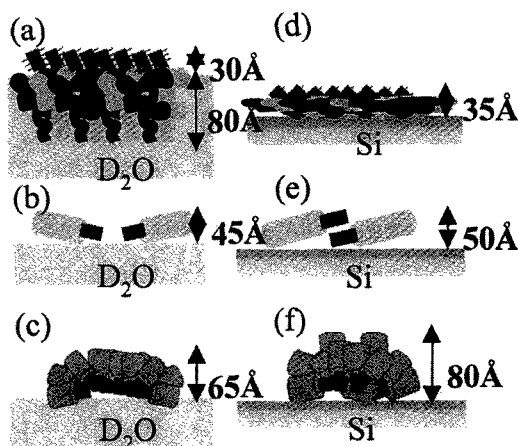


Figure 3. Schematic illustration of molecular location at air/water and air/solid interfaces. Notation (a)-(f) have the same meaning as Figure 1.

M2den3) in Langmuir film at air/water interface and LB film at air/solid interface, which was determined by NR and XR, respectively, is illustrated in Figure 3. Although each polymer existed similarly both on water subphase and on Si surface, there were slightly the differences. The monolayer of M2 on the water subphase was thicker than that on the solid substrate, since PMAA chains of M2 can diffuse into the water subphase and PFA chains can be closely packed by the solvophobic interaction at the air/water interface. The removal of solvent, water, from the monolayer makes such molecular arrangement shrunk and modified, as seen in Figure 3.

On the other hand, monolayers of M2den2 and M2den3 on the solid substrate are rather slightly thicker than on the water subphase. In addition, the density contrast of each layer of fluorinated block and non-fluorinated block at the air/solid interface was less definite than that obtained at air/water interface. Those are due to the stability of the monolayer and the mobility on each substrate, depending on the preparation condition, for example, the compression rate and the dipper speed. Consequently, when the solvent was removed, the loss of the affinity between copolymer and solvent supposed to increase the thickness of the monolayers of M2den2 and M2den3 and increase the density contrast of each layer.

The difference of aggregation activity and aggregate structure between M2, M2den2 and M2den3 at the interfaces should be due to the ratio of fluorocarbon block to dendron block and the substitution fraction of dendron on PMAA block. Although both fluorocarbon and dendron blocks have the hydrophobicity, the former is oleophobic but the latter is oleophilic. Thus, the concept of "solvophobicity-to-solvophilicity balance" can be introduced in order to discuss the location of fluorocarbon block at the interface. Since M2den3 consists of longer dendron block than fluorocarbon block, the hydrophobicity or oleophilicity of dendron block is superior to the solvophobicity of fluorocarbon block. Thus, the dendron block of M2den3 prefers to arrange at the monolayer surface, and the fluorocarbon block is enforced to exist close to water subphase at

air/water interface, as shown in Figure 3. The substitution degree of hydrophilic PMAA by hydrophobic dendron is low in the case of M2den2, although the polymerization degree of P(D<sub>3</sub>MA,MAA) block against PFA block is equivalent in ratio between M2den2 and M2den3. Then, M2den2 tends to take the "lying" structure at the interface (see Figure 3), because the solvophobicity-to-solvophilicity is balanced.

As advantageous point, the information about the internal interface between the polymer and water or solid substrate could be obtained by NR or XR profile, different from the AFM images, which display the information of the outermost surface on solid substrate. Figure 2 shows that the roughness at the polymer/water or polymer/Si interface of M2den2 and M2den3 was very low, that is, the SLD changes sharply between polymer layer and water or silicon phase. This indicates the high hydrophobicity of the polymers. On the other hand, the PMAA block of M2 is so hydrophilic that a large amount of D<sub>2</sub>O molecules penetrate into the PMAA layer, as shown in Figure 3, although PMAA blocks are shrunk at the dried state on solid substrate due to loosely solvated water.

#### ACKNOWLEDGEMENTS

Authors are grateful to the experimental support from Prof. H. Matsuoka, Dr. N. Torikai, and Dr. E. Mouri.

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