Influence of α-methyl group on molecular aggregation structure and surface physicochemical properties of fluoroalkyl side chain polymers

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Abstract: Influence of α-methyl group on molecular aggregation states and surface physicochemical properties of poly(fluoroalkyl acrylate)s [PFA-Cₙ, where y is fluoromethylene number in Rₚ group] and poly(fluoroalkyl methacrylate)s [PFMA-Cₙ] thin films were systematically investigated. Spin-coated PFA-Cₙ and PFMA-Cₙ thin films were characterized by dynamic contact angle measurements and grazing-incidence wide-angle X-ray diffraction (GIWAXD) measurements. GIWAXD data revealed that fluoroalkyl side chains of PFA-Cₙ and PFMA-Cₙ with y ≥ 8 formed regular structures in the surface region as well as the bulk one. However, the degree of orientation and ordering of the Rₚ groups of PFMA-C₈ thin films was low. Also, the receding contact angle (θ_r) of PFMA-C₈ thin films was lower than that of PFA-C₈ ones. By annealing treatment, the θ_r of PFMA-C₈ was increased. These results suggest that the Rₚ groups of PFMA-C₈ were disordered due to presence of the α-methyl group. The Rₚ groups became ordered to pack closely each other by annealing treatment, so that the water repellency was increased.

1. Introduction
Polymers with long fluoroalkyl (Rₚ) groups have high water and oil repellencies and they are widely used for surface modifiers. It is well known that the surface molecular aggregation states and physicochemical properties of these polymer depend on side chain Rₚ groups [1-4]. In this paper, The surface molecular aggregation structure and physicochemical properties of poly(fluoroalkyl acrylate) [PFA-Cₙ, where y is the fluoromethylene number of Rₚ groups] and poly(fluoroalkyl methacrylate) [PFMA-Cₙ] thin films were investigated, and influence of the α-methyl group on surface molecular aggregation state and water repellency was discussed.
2. Experimental

2.1. Material. The chemical structure of PFA-C_y and PFMA-C_y is shown in Figure 1. Polymers were prepared by free radical polymerization. PFA-C_y and PFMA-C_y thin films were prepared by the spin-coating method (2000 rpm, 30 s). The film thickness was estimated as approximately 100 nm by atomic force microscopy (AFM).

2.2. Wide-angle X-ray diffraction (WAXD) measurements. The WAXD measurements were carried out for powder samples on a RINT 2500V (Rigaku Co., Ltd.) with a Cu-K_a X-ray source (40 kV, 200 mA). The wavelength, \( \lambda \), of the incident X-ray was 0.1542 nm. The scattering vector, \( q \), was defined as \( (4\pi/\lambda) \sin \theta \).

2.3. Grazing-incidence wide-angle X-ray diffraction (GIWAXD) measurements. GIWAXD measurements were carried out at 300 K with a four-circle diffractometer installed at a BL-13XU beamline of SPring-8 (JASRI, Japan). The \( \lambda \) of incident X-rays used in this study was 0.1284 nm or 0.1025 nm. The data collection time was 1.5 sec per step, and the angular interval between steps was 0.05º. Figure 2 shows the schematic geometry of the in-plane and out-of-plane GIWAXD measurement. Bragg diffraction from the surface region of a sample was obtained at \( \alpha_i = 0.10º \) or 0.08º below the critical angle of total external reflection at the surface of the sample [5]. In the in-plane geometry, scattering vector (q_\text{xy}) is parallel to the sample surface, and the detected profiles show crystallographic regularity of the lattice plane being perpendicular to the film surface. On the other hand, information about crystallographic regularity of the lattice plane being parallel to the surface is obtained from out-of-plane geometry.

2.4. Dynamic contact angle measurement. Wetting properties were evaluated by dynamic contact angle measurements. The dynamic contact angle was measured using an inclinable plane [6]. A sample on a stage was tilted from an angle where the sample surface is level with the ground until a 50 \( \mu \)L water droplet began to slide down along the sample surface. Subsequently, an advancing contact angle (\( \theta_a \)), a receding contact angle (\( \theta_r \)), and a sliding angle (\( \theta_s \)) were determined.

![Fig.1](image1.png) Chemical structures of PFA-C_y and PFMA-C_y (x = 1 for 1 and 2, x = 2 for y \geq 4).

![Fig.2](image2.png) Schematic geometry of (a) in-plane and (b) out-of-plane GIWAXD measurement.

3. Result and Discussion

3.1. WAXD measurements. Fig.3 shows WAXD profiles of (a) PFA-C_y and (b) PFMA-C_y. PFA-C_y and PFMA-C_y with y \leq 6 had no sharp peak. For those with y \geq 8, Diffraction peaks were measured at \( q = 1.0 – 7.0 \text{ nm}^{-1} \) and ca. 12.3 nm\(^{-1}\). The peaks at \( q = 1.0 – 7.0 \text{ nm}^{-1} \) were explained as reflections from the lamellar structure in which R_f groups were ordered like a multilayered structure (the d-spacing [3.4 – 3.9 nm] was in good agreement with length of the two R_f groups) [7]. The other peaks at \( q = \text{ca. 12.3 nm}^{-1} \) were assignable to reflections from a regular packing structure of the R_f groups (\( d = \text{ca. 0.50 nm, which is close to the intermolecular distance of the PTFE crystal [}d = 0.49 \text{ nm}] \), which
shows pseudo-hexagonal packing of fluoroalkyl chains) [8]. Thus, PFA-C_y and PFMA-C_y with y ≥ 8 are in the crystalline state. Then, the molecular aggregation structure in the near-surface region of PFA-C_8 and PFMA-C_8 thin films was measured by GIWAXD measurements.

3.2. GIWAXD measurements. Fig.4 show the (a) in-plane and (b) out-of-plane GIWAXD profiles of PFA-C_8 and PFMA-C_8 thin film surfaces. In in-plane and out-of-plane GIWAXD profiles of PFA-C_8 and PFMA-C_8 samples, diffractions from packing structures of R_f groups and lamellar structures of these polymers were clearly observed, respectively. These results indicated that the R_f groups were oriented perpendicular to the film surface and stacked each other parallel to it. The lamellar domains were stacked perpendicular to the film surface. Then, the GIWAXD profiles were compared with annealed one (PFA-C_8: at 333 K and 348 K (T_m) for 6 h, PFMA-C_8: 333 K, 348 K, and 358 K (T_m) for 6 h). For PFA-C_8, the peak attributed to the lamellar structure was also observed in an in-plane GIWAXD profile before annealing. However, this peak became weaker in intensity for a PFA-C_8 annealed at 333 K and disappeared for one annealed at 348 K. Another peak attributed to the pseudo-hexagonal packing of the R_f groups became sharper with an increase in annealing temperature. By annealing treatment, some R_f groups changed their orientation from the random orientation to the perpendicular one against the film surface. In the case of out-of-plane GIWAXD, diffractions from the lamellar structure became sharper in peak profile with an increase in annealing temperature. In the case of PFMA-C_8, diffractions from the packing structures of the R_f groups and the lamellar structures also became sharper in peak profile and stronger in intensity by annealing treatment. However, diffractions attributed to pseudo-hexagonal packing of the R_f groups were broader in peak profile and weaker in intensity than those of PFA-C_8. This indicates that the small size or less ordered orientation of the packed R_f groups was formed for PFMA-C_8 compared with PFA-C_8. This structural disordering of R_f groups of PFMA-C_8 probably relates to the presence of the α-methyl group that restricted the orientation of R_f side chains. This behavior is similar to that observed for poly(alkyl methacrylate)s [9].

3.3. Dynamic contact angle measurement. To evaluate the effect of these molecular aggregation states on wetting properties, the dynamic contact angle measurement was carried out. Table 1 summarized the results of dynamic contact angle against water for PFA-C_8 and PFMA-C_8 thin film before and after annealing. For PFA-C_8, the value of θ_r was high and there were no differences in the dynamic contact angle before and after annealing. On the other hand, the θ_r of PFMA-C_8 before annealing was lower than that of PFA-C_8 and increased after annealing. In the case of PFA-C_8, the orientation and ordering of R_f groups before annealing was sufficiently high for achieving high water repellency. For the PFMA-C_8, the degree of orientation and ordering of R_f groups before annealing was extremely low. As a result, θ_r of PFMA-C_8 before annealing was lower than that of PFA-C_8. After annealing, the R_f groups became ordered closely and the water repellency was increased.
4. Conclusions

Influence of the $\alpha$-methyl group on molecular aggregation structure and surface physicochemical properties of PFA-C$_y$ and PFMA-C$_y$ thin films were systematically investigated as a function of the fluoromethylene number of side-chain R$_f$ groups, $y$. WAXD measurement revealed that the PFA-C$_y$ and PFMA-C$_y$ with $y \geq 8$ formed crystal structures. GIWAXD revealed that fluoroalkyl side chains of PFA-C$_y$ and PFMA-C$_y$ with $y \geq 8$ formed regular structures in the near-surface region as well as in bulk. However, the R$_f$ groups of PFMA-C$_8$ thin films formed less ordered small size crystallite. The $\theta_i$ of a PFMA-C$_8$ thin film was lower than that of a PFA-C$_8$ thin film. By annealing treatment, the $\theta_i$ of the PFMA-C$_8$ thin film became increased. These results indicated that crystallographic disordering of the R$_f$ groups of the PFMA-C$_8$ might relate to the aggregation state of $\alpha$-methyl group, and the R$_f$ groups became ordered and the water repellency was improved by annealing treatment.

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Table 1. Dynamic contact angle against water (50 $\mu$L) for PFA-C$_8$ and PFMA-C$_8$ thin films.

| Sample            | $\theta_i$/deg. | $\theta_l$/deg. | $\omega$/deg. |
|-------------------|-----------------|-----------------|---------------|
| PFA-C$_8$         | 124 $\pm$ 1.1   | 108 $\pm$ 0.6   | 12 $\pm$ 1.2  |
| PFA-C$_8$(annealed) | 124 $\pm$ 0.6   | 112 $\pm$ 0.5   | 11 $\pm$ 0.6  |
| PFMA-C$_8$        | 123 $\pm$ 2.1   | 90 $\pm$ 2.1    | 22 $\pm$ 3.1  |
| PFMA-C$_8$(annealed) | 122 $\pm$ 1.3   | 112 $\pm$ 1.1   | 7 $\pm$ 1.2   |

Fig.4 (a) in-plane and (b) out-of-plane GIWAXD profiles measured at surface region of PFA-C$_8$ (upper) and PFMA-C$_8$ (bottom) thin films. The $\lambda$ of incident X-ray was 0.100 nm.