Surface molecular aggregation structure and surface physicochemical properties of poly(fluoroalkyl acrylate) thin films

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Abstract. Effect of side chain length on the molecular aggregation states and surface properties of poly(fluoroalkyl acrylate)s [PFA-Cy, where y is fluoromethylene number in Rf group] thin films were systematically investigated. Spin-coated PFA-Cy thin films were characterized by static and dynamic contact angle measurements, X-ray photoelectron spectroscopy (XPS), and grazing-incidence X-ray diffraction (GIXD). The receding contact angles showed small values for PFA-Cy with short side chain (y ≤ 6) and increased above y ≥ 8. GIXD revealed that fluoroalkyl side chain of PFA-Cy with y ≥ 8 was crystallized and formed ordered structures at the surface region as well as bulk one. These results suggest that water repellent mechanism of PFA-Cy can be attributed to the presence of highly ordered fluoroalkyl side chains at the outermost surfaces. The results of XPS in the dry and hydrated states and contact angle measurement in water support the mechanism of lowering contact angle for water by exposure of carbonyl group to the water interface through reorientation of short fluoroalkyl chains. The surface nanotextured PFA-C8 through imprinting of anodic aluminum oxide mold showed extremely high hydrophobicity as well as high oleophobicity.

1. Introduction
Poly(fluoroalkyl acrylate)s with long fluoroalkyl (Rf) groups have high water and oil repellency and they are widely used for surface modifiers. It is well known that the surface property of poly(fluoroalkyl acrylate)s depends on side chain Rf groups. However, its detailed mechanism has not yet been clarified. In this paper, The water repellent mechanism of poly(perfluoroalkyl acrylate)s [PFA-Cy, where y is carbon number in Rf group] [1,2] was discussed based on the surface ordered structure of Rf groups and surface reorganization. Moreover, nanoimprinting for PFA-C8 film was applied in order to improve hydrophobicity and oleophobicity.

2. Experimental

2.1. Material. The chemical structure of PFA-Cy is shown in Figure 1. PFA-Cy’s were prepared by free radical polymerization. PFA-C1, C2, C4, and C6 were obtained as rubbery states and PFA-C8 and C10 were obtained as a white powder at room temperature. PFA-Cy 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). The films were not annealed, unless it is mentioned otherwise.

2.2. Dynamic Contact Angle (DCA) Measurement. Wetting properties were evaluated by DCA measurement. The DCAs were measured using an inclinable plane [3]. In an inclinable plane, a sample on a stage was tilted until a 50 \( \mu \)L water droplet began to slide down onto the sample. Subsequently, an advancing contact angle \( \theta_a \), a receding contact angle \( \theta_r \), and a sliding angle \( \theta_s \) were determined.

2.3. Grazing-Incidence X-ray Diffraction (GIXD). GIXD measurements were carried out for the films at 300 K with a six-axis diffractometer installed at a BL-13XU beamline of SPring-8 (JASRI, Japan). The wavelength, \( \lambda \), of incident X-rays used in this study was 0.1284 nm (in-plane) or 0.1025 nm (out-of-plane). The data collection time was 1.5 sec per step, and the angular interval between steps was 0.05°. Figure 2 shows the schematic geometry of the in-plane and out-of-plane GIXD measurement. Bragg diffraction was obtained from surface regions at \( \alpha_i = 0.10° \) or 0.08° below their critical angles [4]. In the in-plane geometry, scattering vector \( (q_{xy}) \) is parallel to the surface, and the detected profiles reflect information on crystalline states perpendicular to the film surface. On the other hand, information about the structure parallel to the surface is obtained from out-of-plane geometry.

2.4. X-ray Photoelectron Spectroscopy (XPS). Surface reorganization of PFA-C\( y \) thin film was evaluated by XPS. The XPS measurements were carried out with an Al-K\( \alpha \) X-ray source. Take-off angles of photoelectron were kept constant at 45°. The samples were measured in the hydrated state to characterize the suspected surface chemical composition in water. In the hydrated state, the samples were hydrated by immersion in water (T = 300 K) for 120 min, then dried under vacuum (60 Pa) for 120 min, after which their XPS spectra were immediately measured.

3. Result and Discussion

3.1. Contact Angle Measurements. Figure 3 shows the dependence of the dynamic contact angle against water and sliding angle on the fluoromethylene number of the R\( f \) groups. \( \theta_o \) were very high (above 100°), independent of the fluoromethylene number of the R\( f \) groups. On the other hand, \( \theta_r \) showed a small value for the PFA-C\( y \) with \( y \leq 6 \) and increased drastically for \( y \geq 8 \). It has been known that \( \theta_r \) reflects the occurrence of surface reorientation. This result therefore suggests that the surface reorientation occurred by exposure of the PFA-C\( y \) (\( y \leq 6 \)) surface to water. These phenomena may be explained by an enhanced mobility of the R\( f \) groups with \( y \leq 6 \).

3.2. GIXD measurement. Figure. 4 show the in-plane and out-of-plane GIXD profiles of surface region measured for PFA-C\( y \) thin films (\( y = 1,2,4,6,8, \) and 10 for in-plane GIXD, \( y = 8 \) and 10 for out-of-plane GIXD). The scattering vector \( (q) \) was defined as \((4\pi/\lambda)\sin \theta \). In in-plane and out-of-plane GIXD profiles, sharp and strong peaks were observed for each PFA-C\( y \) with \( y \geq 8 \) at \( q_{xy} = \) ca. 12.5 nm\(^{-1} \) and \( q_z = 1-7 \) nm\(^{-1} \), respectively. These peaks was assignable to the hexagonal packing of R\( f \) groups.
and the lamellar structure in which Rf groups are ordered like multilayer (the spacing \( d = 3.2 \text{ nm} \) [PFA-C8] and 3.6 nm [PFA-C10], with these values being in good agreement with the length of the two Rf groups) [6], indicating that the Rf groups and lamellar structure is oriented perpendicular and parallel to the film surface, respectively. It was revealed that highly oriented and hexagonally packed fluoroalkyl chains at the surface of PFA-C_y with \( y \geq 8 \) contributed to the high water repellency of their films. In-plane and out-plane GIXD profiles for PFA-C8 were also compared with annealed one at 333 K and 348 K for 6 h. As shown in Figure 4(a), the peak attributed to the lamellar structure was also observed in an in-plane GIXD profile of the PFA-C8 sample before annealing. However, this peak became weak in intensity for PFA-C8 annealed at 333 K and disappeared for one annealed at 348 K. Another peak corresponding to the hexagonal packing of the Rf groups became sharper with an increase in annealing temperature. By annealing treatment, some Rf groups changed their orientation from the parallel direction to the perpendicular one against the film surface. In the case of out-of-plane GIXD, peaks corresponding to the lamellar structure also became sharper with an increase in annealing temperature.

![Figure 3](image3.png)

**Figure 3.** Dependence of the dynamic contact angle against water on the fluoromethylene number of the Rf groups.

![Figure 4](image4.png)

**Figure 4.** (a) In-plane and (b) out-of-plane GIXD profiles measured at surface region for PFA-C_y thin films (* and ** indicated samples annealed at 333 K and 348 K for 6 h, respectively)

### 3.3. Surface Reorganization
Based on the above results, the following water repellent mechanism of PFA-C_y is proposed. In the case of PFA-C_y with \( y \geq 8 \), the mobility of the molecular chains is low because of the crystallization of Rf groups; therefore, lowering of the contact angle against water by reorientation of the Rf groups is very difficult. To evaluate the reorientation of the Rf groups, X-ray photoelectron spectroscopy in both dry and hydrated states were carried out. Figure 5 shows the results of \( F_{1s}/C_{1s} \) and \( O_{1s}/C_{1s} \) values of spin-coated PFA-C_y thin films in the dry and hydrated states. \( F_{1s}/C_{1s} \) and \( O_{1s}/C_{1s} \) values represent the relative magnitude of fluorine and oxygen concentrations at the surface. In the hydrated state, the \( F_{1s}/C_{1s} \) and \( O_{1s}/C_{1s} \) values did not change for PFA-C_y with \( y \geq 8 \); the \( F_{1s}/C_{1s} \) value decreased and the \( O_{1s}/C_{1s} \) value increased for PFA-C_y with \( y \leq 6 \). Low values of \( F_{1s}/C_{1s} \) and high values of \( O_{1s}/C_{1s} \) for PFA-C_y with \( y \leq 6 \) are probably derived from the reorientation of Rf groups and the exposure of carbonyl groups to the water interface, and the constant values for PFA-C_y with \( y \geq 8 \) are derived from the inhibition of reorientation due to crystallization of the Rf groups. It is likely that this reorientation of Rf chains with \( y \leq 6 \) at the surface is the greatest contributive factor to the observed decrease in the receding contact angle.

### 3.4. Nano-imprinting for PFA-C8 film
Nano-imprint lithography (NIL) has excellent features, such as being able to create lithographic printing that is sub-10 nm in over a large area [7]. We examined that fabrication of super-hydrophobic and oleophobic surface by NIL. The NIL process is as shown in Figure 6. Anodic aluminum oxide (AAO) mold with a pore diameter of 200nm (Figure 6 (a)) was pressed onto a cast film of PFA-C8. During the pressing, the film was heated at 348 K that is the
melting point of PFA-C₈. Then, the film was cooled at room temperature and AAO mold was removed. The nano-textured PFA-C₈ (Figure 6 (c)) exhibited super hydrophobicity as well as high oleophobicity (Figure 6 (f), (g)). This super hydrophobicity was explained by the notion of heterogeneous wetting proposed by Cassie [8]. In this case, the space between the solid surface and probe liquid was occupied by air and consequently the contact angle was increased.

**Figure 5.** Dependence of F₁s/C₁s and O₁s/C₁s values in XPS spectra on the fluoromethylene number of the R₈ groups in the dry and hydrated states.

**Figure 6.** Schematic preparation of nano-imprinted PFA-C₈ film and SEM images of (a) as cast film of PFA-C₈, (d) AAO film, and (e) nano-imprinted film of PFA-C₈. Inset shows micrographs of water and n-hexadecane (HD) droplets on the surface of as cast film and nano-imprinted film of PFA-C₈ ((b),(f) : water, (c),(g) : n-HD).

4. Conclusion

The relationship between surface properties and the fluoromethylene chain length of the R₈ groups of PFA-C₈ was investigated. Results of dynamic contact angle and GIXD measurements suggest that the water repellent mechanism of PFA-C₈ could be attributed to the presence of highly ordered R₈ chains with low mobility at the surface. XPS in dry and hydrated states showed that a reduced contact angle was caused by reorientation of the R₈ chains and exposure of the carbonyl groups. Moreover, nanoimprinted PFA-C₈ surface showed extremely super hydrophobicity as well as high oleophobicity.

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