Molecular Aggregation Structure of Poly(fluoroalkyl acrylate) Thin Films Evaluated by Synchrotron-sourced Grazing-incidence X-ray Diffraction

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Molecular aggregation structure of poly(fluoroalkyl acrylate) [PFA-C_y, where y is the fluoromethylene number of the fluoroalkyl (R_f) groups] thin films was characterized by grazing-incidence X-ray diffraction (GIXD). In-plane diffractions corresponding to the hexagonal packing of the R_f groups were measured for PFA-C_y with $y \geq 8$ in the surface and bulk regions. This result indicated that the R_f groups were oriented almost perpendicular to the film surface.

It is well-known that polymers with fluoroalkyl (R_f) groups have surface characteristics that differ greatly from those of comparable hydrogenated structures: for example, excellent chemical and thermal stability, nonadhesive properties, low friction coefficients, low surface free energies,[1] and non-fouling behavior.[2] Most of them are poly(fluoroalkyl acrylate)s with long R_f groups.[3–5]

The thermal stability and mechanical characteristics of poly(fluoroalkyl acrylate)s depend on the properties of the hydrocarbons of main chain, whereas the surface properties depend on the chemical structures of the R_f groups at the side chain. In the previous report, the authors clarified the water repellent mechanism of poly(fluoroalkyl acrylate) [PFA-C_y, where y is the fluoromethylene number of the R_f groups] thin films.[6] This water repellent mechanism which seems to reflect the crystalline states of the R_f side chains at the surface region is important for stable surface properties.[1] However, there is no direct evidence on the surface crystalline states of PFA-C_y films. As it has been reported in our previous study, in-plane grazing-incidence X-ray diffraction (GIXD) is a powerful technique which can directly characterize the surface crystalline state of polymeric materials.[7] In this paper, the authors report the molecular aggregation structures of PFA-C_y thin films evaluated by in-plane GIXD.

The chemical structure of PFA-C_y is shown in Figure 1. Fluoroalkyl acrylate monomers and 1,1,1,4,4,4-hexafluoro-2,2,3,3-tetrachlorobutane (CFC-316) were provided by Daikin Industries Co., Ltd. PFA-C_y's were prepared by radical polymerization under nitrogen atmosphere in 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225) at 323 K for 18 h for $y = 1$, 2, 4, 6, and 8, and in CFC-316 at 363 K for 18 h for $y = 10$, using azobisisobutyronitrile (AIBN) as an initiator.[8] The polymers, except for PFA-C_1, were purified by precipitation in methanol. PFA-C_1 was precipitated in hexane. PFA-C_1, C_2, C_4, and C_6 were obtained as rubbery solids and PFA-C_8 and C_{10} were obtained as a white powder.

PFA-C_y's, except for PFA-C_{10}, were dissolved in HCFC-225 (concentration; 1 wt %), and a Si-wafer was coated with the PFA-C_y solution by the spin-coating method (2000 rpm, 30 s). PFA-C_{10} was dissolved in CFC-316 (concentration; 1 wt %) by heating at 373 K, and a Si-wafer was coated with the PFA-C_{10} solution at 373 K by the same method, as this polymer could not be dissolved in HCFC-225 and CFC-316 at room temperature. The film thickness was estimated as approximately 100 nm by atomic force microscopy (AFM).

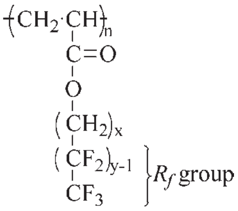

Figure 1. Chemical structure of poly(fluoroalkyl acrylate)s [PFA-C_y, where y is the fluoromethylene number of the R_f group] ($x = 1$ for $y = 1$ and 2, $x = 2$ for $y = 4$, 6, 8, and 10).

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 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan).[9] The wavelength, λ, of monochromatized incident X-rays used in this study was 0.1284 nm. The data collection time was 1.5 s per step, and the angular interval between steps was 0.05°. Figure 2 shows the schematic geometry of the in-plane GIXD measurement. When the incident angle of X-ray, α_i, is equal to, or smaller than, the critical angle, α_c, the incident angle X-rays undergo total external reflection and penetrate into the sample as evanescent waves. In the case of the present experimental condition, the α_c is calculated to be 0.128°. Thus, Bragg diffractions from crystallographic planes perpendicular to the film surface were obtained from the surface and bulk regions at the incident angle of X-rays, α_i, of 0.10° and 0.20°, respectively.[10]

Figure 3 shows the in-plane GIXD profiles measured at $\alpha_i = 0.10°$ and 0.20° for PFA-C_y thin films. Each PFA-C_y with

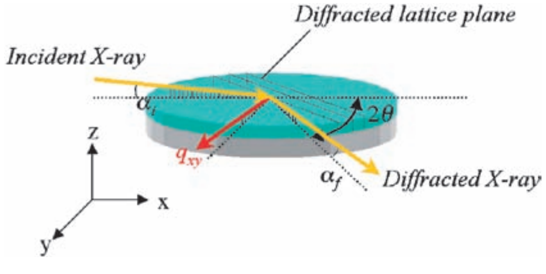

Figure 2. Schematic geometry of the in-plane GIXD measurement.

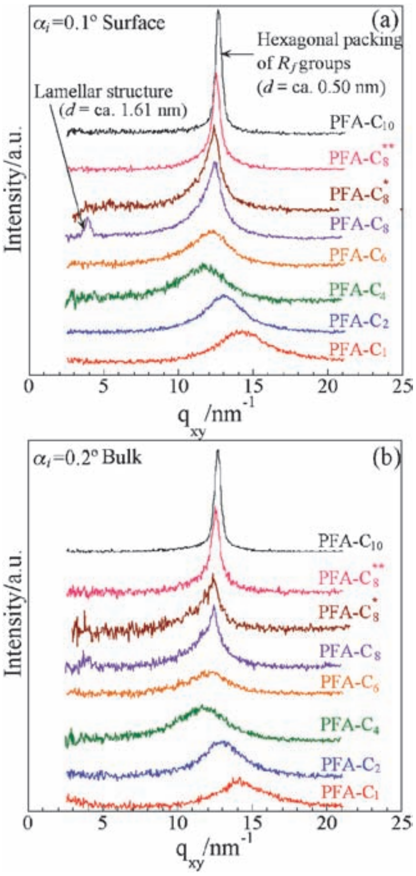

Figure 3. In-plane GIXD profiles measured at $\alpha_i = 0.10°$ (a) and 0.20° (b) for PFA-C$_y$ thin films (* and ** indicate samples annealed at 333 K and 348 K for 6 h, respectively). The λ of incident X-ray was 0.1284 nm.

$y \leq 6$ had a broad and weak peak around q_{xy} = ca. 12–14 nm^{-1} in the profiles. On the other hand, a sharp and strong peak was measured for each PFA-C$_y$ with $y \geq 8$ at q_{xy} = ca. 12.5 nm^{-1}. The d-spacing calculated from the peak position was ca. 0.50 nm, that was closed to the intermolecular distance between helical chains of poly(tetrafluoroethylene) (PTFE) hexagonal ($d = 0.49$ nm).[11–14] Therefore, it was suggested that the rigid rod-like R_f groups formed hexagonal packing in the films of PFA-C$_y$ with $y \geq 8$, and the d-spacing of PFA-C$_y$ with $y \geq 8$ (0.50 nm) was larger than that of PTFE (0.49 nm), indicating that slightly tilted R_f groups might be oriented almost perpendicular to the film surface. It was revealed that highly oriented and hexagonally packed fluoroalkyl chains at the surface of PFA-C$_y$ with $y \geq 8$ led to the high water repellency of their films.

In-plane GIXD profiles for PFA-C$_8$ were also compared with annealed ones at 333 K and 348 K for 6 h. Before annealing, sharp and strong diffractions were measured for PFA-C$_8$ at peak positions of $q_{xy} = 12.4$ nm^{-1} and 3.9 nm^{-1}. A peak at $q_{xy} = 3.9$ nm^{-1} was explained as a reflection from the lamellar structure in which the R_f groups were ordered like bilayer lamellar.[15–17] This peak became weak in intensity for PFA-C$_8$ annealed at 333 K (PFA-C$_8$*) and disappeared for one annealed at 348 K (PFA-C$_8$**). Another peak corresponding to the 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 parallel direction to the perpendicular one to the film surface, so that crystallographic orientation and regularity of the R_f groups of PFA-C$_8$ were improved. In the case of PFA-C$_{10}$, the R_f groups were highly oriented perpendicular to the film surface even for its original films before annealing. In addition, a comparison of the in-plane GIXD profiles between the surface (Figure 3a) and bulk (Figure 3b) regions were also carried out. The peak position and half-value width of the diffractions do not show large difference between the surface and bulk regions. It indicates that the orientation and the order of the R_f groups in the surface and bulk regions are almost the same.

In summary, molecular aggregation structure of PFA-C$_y$ thin films was evaluated by in-plane GIXD measurements. An in-plane diffraction for PFA-C$_y$ with $y \geq 8$ suggested the hexagonal packing of R_f groups in the films. This result indicated that the R_f groups oriented perpendicular to the film surface. The crystallographic orientation and regularity of the R_f groups were improved by annealing treatment.

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