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Molecular Aggregation States of Poly{2-(perfluorooctyl)ethyl acrylate} Polymer Brush Thin Film Analyzed by Grazing Incidence X-ray Diffraction

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Abstract. Fluoropolymer brush with crystalline side chains was prepared by surface-initiated atom transfer radical polymerization of 2-(perfluorooctyl)ethyl acrylate (FA-C₈) from a flat silicon substrate. The crystallization and the molecular aggregation structures of polymer side chain at the outermost surface and internal region in the brush film were characterized by grazing incidence X-ray diffraction (GIXD) measurement using two different incident angles of X-ray. At the air interface of PFA-C₈ brush film, the rod-like Rf group was oriented perpendicular to the surface forming a hexagonal packing structure to reduce surface energy. In contrast, the oriented Rf groups parallel to the substrate coexisted at the internal region in the brush. This unique depth dependence of crystalline state of the fluoropolymer brush was observed by surface-sensitive GIXD measurement.

1. Introduction

Surface-initiated polymerization from a solid surface gives a tethered polymer with high graft density and controlled molecular weight, a so-called "polymer brush" [1]. Recent development of "grafting-from" method supported by living polymerization made it possible to prepare the highly dense brush [2]. In general, the graft density of the polymer chains is so high that the polymer chains are forced to stretch along the direction normal to the graft surface [3]. Therefore, the molecular mobility and chain conformation of brush are restricted to form a unique molecular aggregation structure [4].

The long perfluoroalkyl (Rf) chains of poly(perfluoroalkyl acrylate) also favor to form an aggregated structure aligning perpendicular direction to the substrate to reduce the surface energy [5]. It is known that the molecular aggregation state of the Rf groups strongly affects the surface wettability and water repellency of the polymer films [6]. Previously, the authors prepared poly{2-(perfluorooctyl)ethyl acrylate} (PFA-C₈) brushes with thicknesses of 4 and 11 nm on silicon wafer by surface-initiated atom transfer radical polymerization (ATRP) to analyze the molecular aggregation structure of Rf groups by
wide-angle X-ray diffraction, X-ray reflectivity (XR), and grazing incident X-ray diffraction (GIXD) measurements [7]. The diffraction pattern attributed to the crystalline and ordered structure of the \( R_f \) groups, including a lamellar structure, was observed from the thicker brush film, while the thinner PFA-C\(_8\) film showed only an amorphous hallow without any sharp diffraction peaks. The \( R_f \) groups located near to the brush/substrate interface could not diffuse enough to form an ordered packing structure due to the immobilization of main chain.

In this paper, we tried to characterize the depth profile of the molecular aggregation structure of PFA-C\(_8\) brush with thickness of 41 nm by GIXD in order to elucidate the relationship between the brush thickness and the molecular aggregation state of crystalline side chains to show the structure along with the distance from the outermost brush surface to the substrate interface.

2. Experimental

2.1. Materials. Copper (I) bromide (CuBr, Wako Pure Chemicals, 98%) was purified by washing with acetic acid and ethanol and was dried under vacuum. Ethyl 2-bromoisobutylate (EB) (TCI, 99%), 2,2'-bipyridyl (Wako, 98 %) and 4,4'-dinonyl-2,2'-bipyridyl (C\(_9\)Bpy, Aldrich, 98 %) were used as received. FA-C\(_8\) monomer (Daikin Industry Ltd.) was purified by distillation from calcium hydride under reduced pressure. The silicon (111) wafers (diameter = 1 inch, thickness = 3 mm) were cleaned by washing with piranha solution and by exposure to vacuum ultraviolet-ray (VUV, \( \lambda = 172 \) nm) for 10 min under reduced pressure. Surface initiator, (2-bromo-2-methyl) propionyloxyhexyltriethoxysilane (BHE) [8,9] was immobilized on the silicon wafers by the chemical vapor adsorption method to form a monolayer as reported previously [10].

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\text{Si Wafer} \quad \text{Surface initiator} \quad \text{CuBr / C}_9\text{Bpy} \quad \text{FA-C}_8 \quad \text{PFA-C}_8 \text{ Brush} \quad \text{R}_f \text{ group}
\]

Scheme 1. Preparations of PFA-C\(_8\) brush by surface-initiated ATRP.

2.2. General procedure for surface-initiated ATRP. Preparation procedure of PFA-C\(_8\) brush was described elsewhere [7]. As shown in Scheme 1, surface-initiated ATRP of FA-C\(_8\) from the initiator-immobilized silicon wafers was carried out in the presence of CuBr, C\(_9\)Bpy, and EB at 383 K for 72 h under argon. The resulting silicon wafer was washed with piranha solution and by exposure to vacuum ultraviolet-ray (VUV, \( \lambda = 172 \) nm) for 10 min under reduced pressure. Sample was annealed at 373 K for 1 h and gradually cooled to room temperature at 10 K/min.

2.3. Measurements. XR and GIXD measurement were carried out on a BL13XU beam line of SPring-8 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan) using an incident X-ray with a wavelength \( \lambda \) of 0.100 nm [11]. The scattering vector, \( q \), in specular reflectivity is defined by \( q = (4\pi/\lambda) \sin \theta \). The incident and reflection angles of XR were kept at same magnitude for specular condition. Model calculation and data analysis for the XR were carried out using a software, XRR, a program provided by Rigaku Corp. GIXD data were obtained from the surface and deeper regions at \( \alpha_i \) of 0.08 and 0.16, respectively [12,13]. Diffractions from the sample were detected in the in-plane and out-of-plane directions. The information about the structure perpendicular to the surface is obtained from in-plane geometry because scattering vector (\( q_{||} \)) is parallel to the surface. On the other hand, the detected profiles reflect information on crystalline states parallel to the film surface in the out-of-plane geometry. XR and GIXD observations were carried out at room temperature.

3. Results and Discussion

3.1. X-ray reflectivity of PFA-C\(_8\) brush. Figure 1(a) shows a reflectivity profile of PFA-C\(_8\) brush film, and corresponding fit which was calculated by the density distribution of the thin film as shown in
Figure 1(b). The thickness of the brush film can be roughly estimated from the intervals of the Kiessig fringes in the XR curve. The bulk density of silicon and SiO$_2$ are 2.33 and 2.65 g cm$^{-3}$, respectively. As can be seen from Figure 1(b), the bulk density inside the brush layer near the tethered point at the silicon substrate was relatively low and the density gradually increased along with the distance from the substrate. The outermost area facing air revealed the highest density of 2.3 g cm$^{-3}$, which is close value to the density of poly(tetrafluoroethylene) (PTFE). Thus, the density distribution of the PFA-C$_8$ brush thin film is not homogeneous. In other words, molecular chains seem to form ordered state at the outermost surface of PFA-C$_8$ thin films.

![Figure 1](image_url)

**Figure 1.** XR curve of PFA-C$_8$ brush (circle plot) and the corresponding (solid line) (a). The assumed density profile is shown in right side (b).

3.2. GIXD measurement of PFA-C$_8$ brush. Figure 2(a) shows the in-plane GIXD profiles of PFA-C$_8$ brush film. Sharp and strong peaks were appeared for PFA-C$_8$ brush thin films at 12.6 nm$^{-1}$. Hence, the side chains of the PFA-C$_8$ are oriented perpendicular to the surface. The d-spacing calculated from the peak position was ca. 0.50 nm, which was close to the intermolecular distance between R$_f$ chains of PTFE hexagonal (d = 0.49 nm) [14]. Therefore, it was suggested that the rigid rod-like R$_f$ groups underwent hexagonal packing at the outermost surface of PFA-C$_8$ brush film. Figure 2(b) represents the out-of-plane GIXD profile of PFA-C$_8$ brush film. The strong diffraction peaks were observed at $q_z$ = 2.2, 3.9, and 5.8 nm$^{-1}$ correspond to the d-spacings of 2.84, 1.56, and 1.05 nm, respectively. These peaks are assignable to the lamellar structure of R$_f$ group. These Bragg diffractions indicate that the (001) crystallographic planes are oriented almost parallel to the substrate.

Interestingly, a broader diffraction peak at $q_z$ = 12.5 nm$^{-1}$ was observed from out-of-plane measurement with higher incident angle $\alpha_i = 0.16^\circ$, while no peak appeared at the same $q_z$ range in the diffraction pattern obtained by lower $\alpha_i$ (0.08$^\circ$). This result suggested that the hexagonal packing structure of R$_f$ groups at the deeper region in the brush thin film was oriented parallel to the substrate. In addition, in-plane diffraction pattern in the case of $\alpha_i = 0.16^\circ$ showed a peak at $q_{xy} = 3.9$ and 5.9 nm$^{-1}$ attributed to lamellar structure.

Considering these X-ray diffraction patterns, the R$_f$ aggregation states seem to be different between the outermost surface and internal region in the brush film, as shown in Figure 2(c). At the air interface of PFA-C$_8$ brush, the rod-like R$_f$ groups oriented perpendicular to the substrate forming a hexagonal packing structure, which contribute to the reduction of surface energy. In contrast, the oriented R$_f$ groups parallel to the substrate coexisted at the internal region in the brush. We suppose that the densely immobilized polymer backbones were forced to stretch at perpendicular direction to the silicon wafer, resulting in a parallel orientation of R$_f$ side chains to the substrate. However, the brush/substrate interface region of brush seems to contain an amorphous structure of R$_f$ groups because broader diffraction peak was observed by GIXD at higher $\alpha_i$. 

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4. Conclusion
Semicrystalline polymer brushes having $R_f$ groups was prepared by surface-initiated ATRP on silicon substrate. The surface- and bulk-sensitive GIXD measurements of polymer brushes film showed the different aggregation state of the $R_f$ groups at the air/brush and the brush/substrate interfaces. On the outermost surface of PFA-C$_8$ brush film, $R_f$ groups formed a hexagonal packing structure due to the low surface free energy, and were oriented almost perpendicular to the substrate to afford a lamellar structure. On the other hand, the $R_f$ groups were partially oriented parallel to the substrate at the deeper layer in the brush. The anchoring effect of polymer backbone restricted the available chain conformation and molecular mobility of $R_f$ groups at the brush/substrate interface to form different molecular aggregation structure from that of the air/brush interface.

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