Characterization of the Interface Structure of Hydrophilic and Hydrophobic Polymer Brushes by Neutron Beam and Synchrotron Radiation

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Abstract:
Soft interfaces such as polymer brush have played important roles in various technological applications. Neutron reflectivity (NR) is a powerful tool for the characterization of liquid/amorphous polymer and amorphous polymer/inorganic solid interfaces. In contrast, X-ray reflectivity (XR) and grazing incidence X-ray diffraction (GIXD) can characterize the crystalline state on the outermost surface and the electron density profile along the thickness direction, respectively. In this presentation, recent progresses in the characterization of polymer brushes by NR, XR, and GIXD is introduced.

1. Introduction

Surface-initiated polymerization from a solid surface is a promising method for modifying wettability, adhesion behavior, and frictional properties on the surface of inorganic or organic films, particles, and fibers to give a "soft interface". During past decades, a controlled radical polymerization technique has been applied to a surface-initiated polymerization system, giving a tethered polymer with high graft density and controlled molecular weight, a so-called "polymer brush.[1] However, it is indeed difficult to measure the thickness of the swollen brush in solution because a continuous layer of solvated chains will be formed. Neutron reflectivity (NR) measurements are, therefore, appropriate for the study of the influence of solvent on polymer brush structure. X-ray refractivity (XR) is also quite useful for analyzing the electron density profile along the thickness direction and for investigating the migrated interface structure of polymer brushes. The purpose of this paper is to reveal the structure of polymer brush at various interfaces by utilizing neutron and X-ray beams. In this study, hydrophilic and hydrophobic polymer brushes with 20 ~ 40 nm thickness were prepared on the Si-wafer and quartz plate by surface-initiated atom transfer radical polymerization (ATRP) of vinyl monomers with different functional groups. We demonstrate here the analysis of the hydrophilic polyelectrolyte brush/water interface structure by NR, and characterization of the molecular aggregation structure of hydrophobic poly(fluoroalkyl acrylate) brush by XR and grazing incidence X-ray diffraction (GIXD) measurements, which has attracted much attention as a technique for investigating the transformation of the molecular aggregation state of organic ultrathin films, because we can directly obtain a

great deal of information about the two-dimensional molecular aggregation states of the surface of materials. In the case of spin-cast films of poly(fluoroalkyl acrylate)s with long perfluoroalkyl (R_f) groups, it has been reported that the molecular aggregation and crystalline state of R_f groups at the side chains affect the surface wettability and water repellency.[2-3] Therefore, further analysis of the molecular aggregation structures of R_f groups in the polymer brush are carried out in this work.

2. Experimental

Materials: Copper(I) bromide (CuBr, Wako Pure Chemicals) was purified by successive washing with acetic acid and ethanol, and was dried under vacuum. Ethyl 2-bromoisobutylate (EB), purchased from Tokyo Chemical Inc., was distilled before use. 4,4'-Dimethyl-2,2'-bipyridine (Me$_2$bpy) and 4,4'-dinonyl-2,2'-bipyridyl (C$_9$bpy, Aldrich) were used as received. 2-(Perfluoro octyl)ethyl acrylate (FA-C$_8$) was donated by Daikin Industry Ltd., and was repeatedly purified by distillation under reduced pressure. 2-Methacryloyloxyethyl phosphorylcholine (MPC) was prepared using a previously reported procedure.[4]
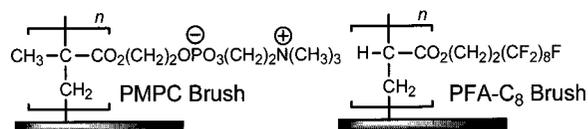

Figure 1. Chemical structure of PMPC and PFA-C$_8$ brushes.

Surface initiator, (2-bromo-2-methyl)propionyloxy-hexyltriethoxysilane (BHE),[5] was immobilized on a purified silicon wafer and quartz plate by the chemical

vapor adsorption method. An unbound initiator as a sacrificial initiator is necessary to control the degree of polymerization and to estimate the number-average molecular weights (M_n) of the resulting polymer. The chemical structures of PMPC and PFA-C_8 brushes are shown in Figure 1. A typical surface-initiated ATRP of FA-C_8 was performed as follows; a few sheets of the initiator-immobilized silicon wafers, CuBr (0.075 mmol), and C_9bpy (0.150 mmol) were introduced into a glass vessel with a stop cock and were dried by repeating a degas and argon purge. FA-C_8 (25.7 mmol) and EB (0.075 mmol) were added to the catalyst. Oxygen was removed by the freeze-pump-thaw cycles. The polymerization reaction was conducted at 383 K for 72 h under argon to simultaneously generate PFA-C_8 brush from the silicon substrate and free PFA-C_8 from EB. The reaction was quenched by opening the glass vessel to air at 273 K. The reaction mixture was diluted with AK-225 (Asahi Glass Co.), which is a mixture of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,1,2,2,3-penta fluoropropane, and poured into THF to precipitate the free polymer. The silicon wafers were washed with AK-225 using a Soxhlet apparatus for 8 h to remove the free polymer absorbed on their surface, and were dried under reduced pressure at 373 K for 1 h. All the sample were annealed at 373 K for 1 h and gradually cooled to room temperature at 10 K/min. PMPC brush was synthesized in a similar manner using CuBr and Me$_2$bpy in methanol at 303 K for 12 h.[6]
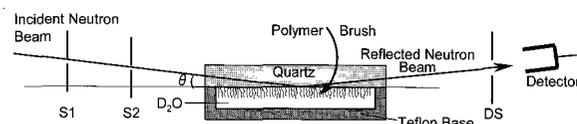

Figure 2. Schematic view of the liquid cell used in NR experiment.

Measurements: The number-average molecular weight (M_n) and molecular weight distribution of unbound PMPC were estimated by size-exclusion chromato graphy (SEC) recorded on a JASCO LC system using PMPC standards calibration,[7] which runs through two directly connected polystyrene gel columns (TOHSO super AW3000 and super AW4000, 0.5 mL/min) using water containing 0.01 M LiBr as an eluent at 313 K. SEC measurements for PFA-C_8 were carried out using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as an eluent. Calibration curves were constructed based on a series of PMMA standards. The thickness of the polymer brushes immobilized on a silicon wafer in air (the relative humidity was ca. 45%) was determined by an imaging ellipsometer (Nippon Laser & Electronics Lab.) equipped with a YAG laser (the wavelength was 532 nm). The thickness was also measured by AFM of a partially scratched brush film under a vacuum condition

to avoid the influence of moisture. The contact angles were recorded with a drop shape analysis system DSA10 Mk2 (KRÜSS Inc.) equipped with a video camera using an inclinable plane.

NR measurements were performed on the ARISA reflectometer using white neutrons with wavelengths of 0.12 - 0.16 nm at the KENS pulsed-neutron source.[8] As shown in Figure 2, a neutron beam was irradiated from quartz glass to the interface between D$_2$O and immobilized PMPC brush. Incident angles were fixed at 0.3 and 0.6° that covered a q range of 0.11~0.55 nm^{-1} and 0.2~1.1 nm^{-1}, respectively. The incident slits (S1 and S2) were adjusted to maintain a 55 mm of footprint size on the sample surface as well as an angular resolution, $\Delta\theta/\theta$, of 5%. The NR profiles were analyzed by fitting calculated reflectivities from model scattering length density profiles to the data using Parratt32 software.

XR and GIXD measurements were carried out for the PFA-C_8 brush 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). The wavelength, λ, of monochromatized incident X-rays used in this study was 0.10 nm. The data collection time was 3.0 sec per step, and the angular interval between steps was 0.05°. Bragg diffraction was obtained from surface regions at α_i = 0.08°. In the case of in-plane geometry, the scattering vector (q_{xy}) was parallel to the surface, and was defined as $q = (4\pi/\lambda)\sin\theta$. In contrast, the information perpendicular to the surface was obtained by out-of-plane geometry.

3. Results and discussion

Analysis of the Polyelectrolyte Brush/Water Interface by NR: PMPC is known as a specially designed hydrophilic polymer with excellent biocompatibility. The behavior of PMPC brushes under aqueous conditions is important for the medical applications such as artificial joints[9] and catheters.

The PMPC brush was prepared by simultaneous surface-initiated ATRP of MPC from the BHE-immobilized surface of a quartz plate (65 mm × 65 mm× 10 mm) and from a silicon wafer (10 mm× 40 mm× 0.5 mm). The M_n of the obtained polymer was estimated to be 59500 (degree of polymerization was ca. 200) by SEC analysis of linear polymer, which was simultaneously grown from co-existed sacrificial initiator during surface-initiated polymerization. The thickness of polymer brush on a silicon wafer in the dry state was found to be 25 nm by an imaging ellipsometer. Polymer brush on a quartz plate should have the same thickness. The grafting density was calculated to be 0.22 chains/nm^2 from the thickness, the molecular weight of brush, and the bulk density of PMPC.
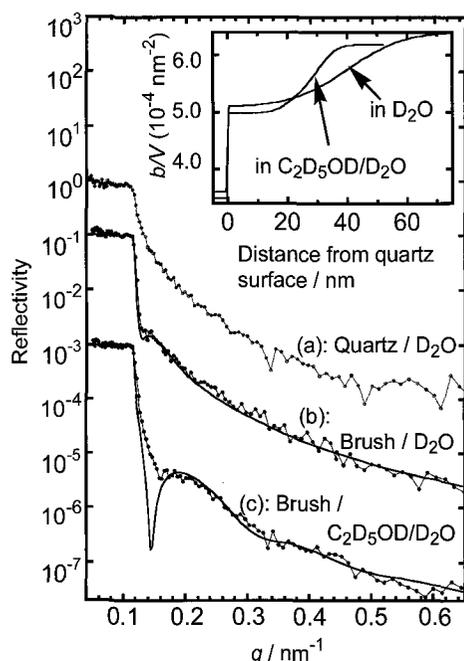
Figure 3. Experimental NR profiles of (a) bare quartz, (b) PMPC brush in D_2O, (c) PMPC brush in a mixture of deuterated ethanol / D_2O (68/32, v/v), and their corresponding fits. Assumed scattering length density profiles for (b) and (c) are shown in the inset.

NR at the interface of PMPC brush/D_2O is shown in Figure 3. A critical angle was clearly observed at q = 0.11 nm^{-1} in Figure 3 due to the difference in the scattering length density between quartz (3.80×10^{-4} nm^{-2}) and D_2O (6.4×10^{-4} nm^{-2}). The reflective profile arising from polymer brush interface (Figure 3(b)) shifted downward compared with that from bare quartz (Figure 3(a)). This result indicates that the PMPC chains were stretched up to 60~70 nm and formed a concentration gradient of D_2O under swelling states. The full length of the graft chain in the all-trans conformation is calculated to be 50 nm, assuming a length per monomer unit of 0.25 nm and 200 repeating units. The observed thickness by NR is an acceptable value, since polymer brush has a chain length distribution corresponding the molecular weight distribution (M_w/M_n = 1.5).[10] Therefore, the tethered polymer chains would have fairly extended conformation along the direction normal to the quartz surface.

On the other hands, a thickness of PMPC brush decreased to 30~40 nm in deuterated ethanol/D_2O (68/32, v/v), as shown in Figure 3(c). Ishihara and his coworkers have already reported that PMPC is soluble in pure water and pure ethanol, while it is insoluble in a water/ethanol mixture containing 70~90% ethanol. [11-12] This is called cononsolvency behavior. Hence the polymer brush is shrunk in a mixture of deuterated ethanol and D_2O.

Surface-initiated ATRP of PFA-C_8 on a silicon wafer: Surface-initiated ATRP of FA-C_8 was carried out from the BHE-immobilized silicon wafer in the presence of EB as a free initiator at 383 K. The M_n of the corresponding free polymer was estimated to be approximately 28,000 by PMMA-standard calibration on a SEC using HFIP as an eluent. The thickness of the polymer brush was determined to be ca. 39 nm by ellipsometer. The graft density was estimated to be ca. 0.15 chains/nm^2 if the reflective index is uniform in brush thin layer. AFM observation revealed that a homogeneous polymer layer was formed on the substrate, and the surface roughness was 0.8-1.5 nm in a dry state in a 5×5 μm^2 scanning area.

The water contact angle of the PFA-C_8 brush surface was 120°, which is the same as that of spin cast film. The surface free energy for PFA-C_8 brush thin film was estimated to be 11.5 mN/m by Owens and Wendt's equation [13] based on static contact angles of water and methylene iodide.
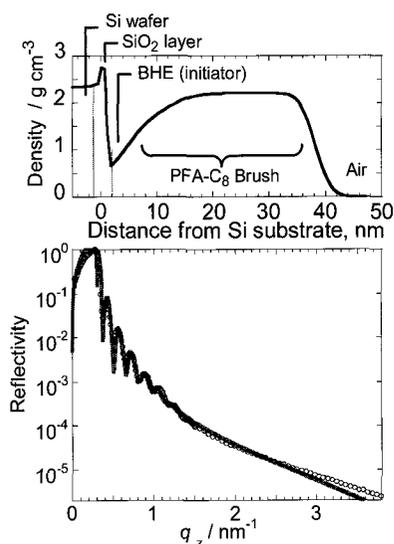

Figure 4. XR profiles of PFA-C_8 brush with 39 nm thick (dot line) and the corresponding fitting curve (solid line). Assumed density profile along with the distance from silicon wafer is shown above.

XR of PFA-C_8 brush: The specular reflectivity of X-rays provides information regarding electron-density variations normal to the surface with angstrom resolution. Figure 4 shows a reflectivity profile of PFA-C_8 brush film with a thickness of 39 nm, and a corresponding fit that was calculated by the density distribution of the thin film.The thickness of the brush film can also be roughly estimated based on the intervals of Kiessig fringes in the XR curve as well as on ellipsometry, the XR curve, however, seemed to overlap some of the Bragg diffraction peaks. This film consists of a PFA-C_8 brush layer, a surface initiator layer, and a SiO_2 layer on silicon substrate, but the best-fitting curve

required five layers. As is easily seen from Figure 4, the bulk density inside the brush layer near the tethered point at the silicon substrate was relatively low, and the density gradually increased from 0.7 to 2.1 g cm^{-3} along with the distance from the substrate. The outermost area facing air was found to have a higher density than the substrate interface. The fitting curve corresponded to the XR profile, which was fitted by XRR software using step functions. This density distribution indicates that R_f groups at the side chains aggregate with each other to form an assembled structure on the outermost surface. As a result, the density distribution of the PFA-C$_8$ brush thin films was not homogeneous. In other words, molecular chains seem to form an ordered structure on the outermost surface of PFA-C$_8$ thin films.
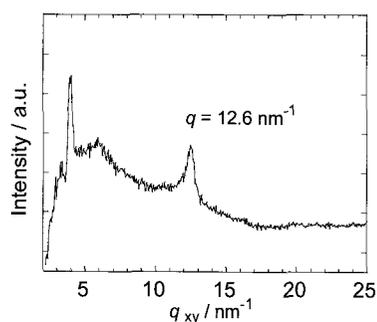

Figure 5. In -plane GIXD profile measured at $\alpha_i = 0.08°$ for PFA-C$_8$ brush thin film with 39 nm thick.
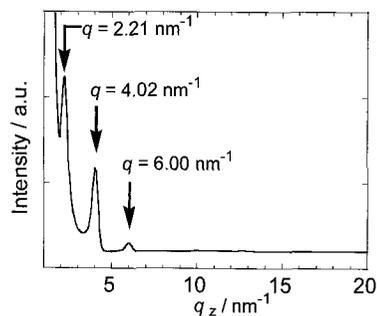

Figure 6. Out-of-plane GIXD profile measured at $\alpha_i = 0.08°$ for PFA-C$_8$ brush thin film with 39 nm thick.

GIXD of PFA-C$_8$ Brush: GIXD is a powerful tool to characterize the crystalline state of polymer thin films. Figure 5 shows the in-plane GIXD profile of PFA-C$_8$ brush film measured at an incident angle of 0.08°. Sharp and strong peaks were measured at ca. 12.6 nm^{-1}. Hence, there must be an ordered structure oriented normal to the surface. The d-spacing calculated from the peak position was ca.0.50 nm, which was close to the intermolecular distance between helical chains of poly(tetrafluoroethylene) (PTFE) in hexagonal packing ($d = 0.49$ nm),[14-17] and was almost the same as the intermolecular distance between R_f groups at the side chains of PFA-C$_8$ spin cast films ($d = 0.50$ nm).

These results suggest that the rigid rod-like R_f groups

underwent hexagonal packing in the brush film. However, the d-spacing of PFA-C$_8$ brush thin films was slightly larger than that of PTFE, indicating that slightly tilted R_f groups might be oriented almost perpendicular to the silicon wafer. The out-of-plane GIXD profiles are shown in Figure 6. The strong peaks were clearly observed at 2.21, 4.02, and 6.00 nm^{-1}, corresponding to d-spacings of ca. 2.84 nm, 1.56 nm, and 1.05 nm, respectively. These peaks are assignable to the lamellar structure of the R_f group. These Bragg diffractions indicate that the *(00l)* crystallographic planes are parallel to the substrate. Diffraction peaks due to lamellar structure were also observed by symmetric wide-angle X-ray diffraction measurements.
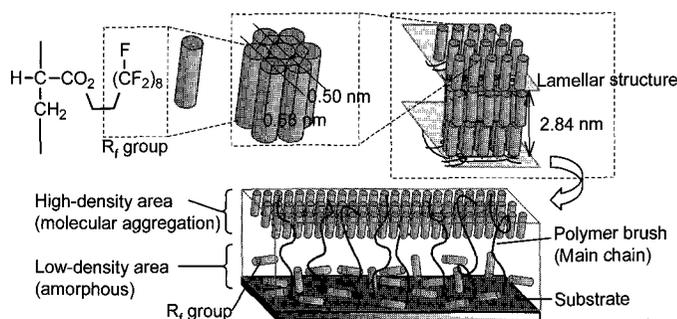

Figure 7. Schematic representation of molecular aggregation structure for the PFA-C$_8$ brush on silicon substrate.

Molecular Aggregation Structure in PFA-C$_8$ Brush Thin Films: Considering these X-ray diffraction patterns, the R_f groups aggregate to form hexagonal packing on the outermost surface and are oriented almost perpendicular to the substrate. Moreover, the assembly of R_f groups fabricates a lamellae structure that is oriented parallel to the substrate. In contrast, R_f groups closely located around the substrate in the present study could not diffuse sufficiently to form an aggregate structure because the conformation of the main chain was restricted by covalent bonding with the substrate. As a result, an amorphous structure with low density formed at the substrate interface in the brush layer. Figure 7 provides a schematic representation of the molecular aggregation structure of R_f groups speculated from XR and GIXD profiles. These highly ordered structures of the R_f groups at the outermost surface might create a surface with higher water repellency.

4. CONCLUSION

In the present study we have carried out analyses of the interface structures of both hydrophilic and hydrophobic polymer brushes by NR, XR, and GIXD. NR is a suitable technique for characterizing the interface structure due to the semi-transparency of the substrate against the neutron beam as well as the

scattering contrast obtained by utilizing heavy water. NR at the polyelectrolyte brush/aqueous solution revealed that the gradient chain density at the interface solvated polymer brush depends on the solvent quality. A fairly extended structure of high-density brush chain was observed in D_2O due to osmotic pressure and chain density, while the interface thickness was reduced in poor solvent because of the shrunken structure of the polymer brush. A combination of XR and GIXD measurements also contributed to the analysis of PFA-C_8 brush thin film to show the different aggregation states of the R_f groups at the air/brush interface and the substrate/brush interface. On the outermost surface, R_f groups at the side chains formed a hexagonal packing structure due to the low surface free energy, and were oriented almost perpendicular to the substrate resulting in a lamellar structure and a high-density area. In contrast, the conformation and molecular motion of polymer chains at the brush/substrate interface were restricted by an anchoring effect to prevent the ordered structure formation of R_f groups, producing an amorphous layer with low density. The heterogeneous depth profile in the PFA-C_8 brush was confirmed by XR.

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