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Characterization of Swollen Structure of High-density Polyelectrolyte Brushes in Salt Solution by Neutron Reflectivity

Motoyasu Kobayashi1,2, Yuki Terayama3, Masahiro Hino4, Kazuhiko Ishihara5, Atsushi Takahara1,2,3
1 Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. 2 JST/ERATO, 3 Graduate School of Engineering, Kyushu University, 4 Reactor Research Institute, Kyoto University, 5 Graduate School of Engineering, The University of Tokyo
E-mail: takahara@cstf.kyushu-u.ac.jp

Abstract. Zwitterionic and cationic polyelectrolyte brushes on quartz substrate were prepared by surface-initiated atom transfer radical polymerization of 2-(methacryloyloxy)ethyl phosphocholine (MPC) and 2-(methacryloyloxy)ethyltrimethylammonium chloride (METAC), respectively. The effects of ionic strength on brush structure and surface properties of densely grafted polyelectrolyte brushes were analysed by neutron reflectivity (NR) measurements. NR at poly(METAC)/D2O and poly(MPC)/D2O interface revealed that the grafted polymer chains were fairly extended from the substrate surface, while the thickness reduction of poly(METAC) brush was observed in 5.6 M NaCl/D2O solution due to the screening of the repulsive interaction between polycations by hydrated salt ions. Interestingly, no structural change was observed in poly(MPC) brush even in a salt solution probably due to the unique interaction properties of phosphorylcholine units.

1. Introduction

The dimensions and hydrodynamic radius of the isolated polyelectrolytes bearing positive or negative charges in an aqueous solution strongly depend on the ionic strength of the solution [1,2]. It is generally accepted that polyanion or polycation chains in aqueous solution with low ionic strength form expanded chain structures due to the intramolecular repulsive interactions. Electrostatic repulsive interactions also enhance intermolecular repulsive interactions, resulting in a large second virial coefficient. In contrast, the polyelectrolyte dissolved in higher ionic strength in solution behaves like an electrically neutral polymer to give smaller dimension because the electric interactions are screened by salt ions. However, surface-grafted polymer chains are expected to exhibit different behaviors from those of the isolated polymers [3].

The dimension of nonionic polymer chains immobilized on solid surface largely depends on the graft density. Polymer chains sparsely immobilized on a flat surface form a coil structure such as a mushroom, whereas densely immobilized polymer chains on a flat surface in a good solvent stretch in a perpendicular direction against the substrate surface because of high osmotic pressure arising from the excluded volume effect by densely-grafted neighboring chains [4]. In the case of polyelectrolyte brush, repulsive electrostatic interaction would also afford a stretched chain conformation. Then, we are wondering whether screening of electrostatic interaction by salt ions could take place for the densely-grafted polyelectrolyte chains to change the extended chain structure or not. The behavior of
polyelectrolyte brushes in salt solution is important for applications in medical materials, as these materials are in contact with blood and other body fluids containing salts. Herein, we describe the dependence of swelling brush structure on the ionic strength analyzed by neutron reflectivity (NR) of zwitterionic type polyelectrolyte, as well as cationic polyelectrolyte brushes prepared by surface-initiated controlled polymerization of 2-(methacryloyloxy)ethyl phosphorylcholine (MPC) and 2-(methacryloyloxy)ethyltrimethylammonium chloride (METAC), respectively.

2. Experimental

Quartz plates (65 × 65 × 10 mm³) were cleaned by washing with piranha solution at 373 K for 1 h and subsequent exposure to vacuum ultraviolet-ray (λ = 172 nm) for 5 min under reduced pressure (30 Pa). The surface initiator, (2-bromo-2-methyl)propionyloxyhexyltriethoxysilane, was immobilized on the substrate by chemical vapour adsorption method.[5] Poly(MPC) brush was prepared by surface-initiated atom transfer radical polymerization in methanol using CuBr and 4,4'-dimethyl-2,2'-bipyridyl at 303 K for 12 h.[6] For METAC polymerization, 10% isopropanol aqueous solution was used as a solvent.[7] The number-average molecular weights (Mₐ) and molecular weight distribution of the unbound polymers were determined by size-exclusion chromatography recorded on a JASCO instrument equipped with a JASCO 2031plus RI detector and TSK-gel column Super H6000, H4000, and H2500 using 0.01 M LiBr aqueous solution for poly(MPC) and acetonitrile/water (1/1, v/v) solution with 0.5 M of acetic acid and 0.2 M sodium nitrate for poly(METAC) as the eluents at a rate of 0.5 mL/min at 313 K. The thickness of the polymer brushes on the silicon substrate were determined using an imaging ellipsometer (Nippon Laser & Electronics Lab.) equipped with a YAG laser (532.8 nm). The polarizer angle was fixed at 50°, and a refractive index of 1.48 was assumed for calculations of the film thickness. NR measurements were carried out using a multilayer interferometer for neutrons (MINE) in JRR-3 at TOKAI, using wavelength λ = 0.88 nm. A neutron beam was irradiated from quartz to the interface between D₂O and the poly(MPC) brush on quartz glass. The incident slits were adjusted to maintain a 55 mm footprint size on the sample surface. The NR profiles were analyzed by fitting calculated reflectivity from model scattering length density profiles to the data, using Parratt32 software.

3. Results and Discussion.

Figure 1 shows the NR curves of D₂O/poly(METAC) brush interface and the corresponding neutron scattering length density (SLD) profile normal to the interface. A critical angle was clearly observed at q = 0.11 nm⁻¹ attributed to the difference in SLD between quartz and deuterium oxide. The neutron SLD profiles of the poly(METAC) brush in D₂O formed in a smooth upward curve from 5.2 × 10⁻⁴ to 6.36 × 10⁻⁴ nm⁻² along with the distance from the substrate. The gradient profile indicated that the polymer chains in D₂O were stretched up to ca. 80 nm, which is larger than the brush thickness under the air (humidity = 50%) estimated to be 46 nm by ellipsometer. Therefore, the polymer chains immersed in D₂O were considerably extended to perpendicular direction against the substrate. High osmotic pressure caused by high concentration of quarternary ammonium ions in the brush layer would have made an extended chain conformation. The gradual change in SLD was appeared by the molecular weight distribution of polymer brush. Large polydispersity index of brush, Mₘ/Mₙ = 1.5, afforded a thick boundary zone to make unclear fringes in reflectivity curve.

In general, an increase in ionic strength leads to the reduction of the electrostatic repulsion. The polyelectrolyte chains in a salt solution may undergo a transition toward a more coiled state and show a volume reduction. However, quite similar reflective curve was observed from the interface of the poly(METAC) brush in the 1.0 M NaCl/D₂O solution, indicating that the extended structure of the swelling brush chains did not change, even in a salt solution. It is a quite contrast to the fact that the unbound polyelectrolyte would shrink in salt solution. We estimated the swollen brush thickness by volume fraction (φ) curve of METAC segments as a function of the distance from substrate (z) and the corresponding parabolic-type profile assuming a brush layer height (h°). A pure parabola equation of φ = φ₀{(1-z/h°)²} is theoretically predicted by Cates et al. for polymer brush in the limit of strong
stretching.[8] Actual volume fraction curve as shown in Figure 2 requires the parabolic function and an additional exponential tail at larger $z$ region to obtain better fit due to a roughness at the brush/solution interface. We regard $h^*$ as thickness of the swollen brush. Let us assume the swollen poly(METAC) thickness in 1.0 M NaCl solution was 83 nm, the $M_n$ was 86,000, and grafting density was 0.36 chains/nm$^2$, the apparent concentration of METAC monomers in the brush layer can be estimated to be 3.1 M, which is much higher than salt concentration in the external solution. Therefore, hydrated salt ion could not diffuse into a high-density polymer brush layer due to the high local charge density, and then polyelectrolyte brush could keep an extended chain structure in solution. Similar results have been reported by Matsuoka [9, 10], Kurihara [11], and Tran.[12] Huck et al. reported the swelling behavior of the poly(METAC) brush in solution observed by AFM.[13] They suggested that thickness of brush decreased at much lower external salt concentrations than the concentration of chemically charged monomers of the chains. Unfortunately, our NR profiles could not detect the apparent change in the swollen structure of brush between at 0 ~ 1 M NaCl/D$_2$O solution probably due to the large roughness and nonuniform thickness of the brush along the neutron-irradiated footprint as long as 50 mm.

When the poly(METAC) brush was immersed in the 5.6 M NaCl/D$_2$O solution, the reduction in roughness and thickness of swelling brush layer was observed, as shown in Figure 1(f). The brush layer height $h^*$ was 69 nm. The hydrated salt ions in the adjacent solution with higher ionic strength than the brush layer must have screened the repulsive interaction between quaternary ammonium groups of the brush chain to moderate highly extended chain conformation. The graft area occupied with a tethered chain was 2.7 nm$^2$ given by graft density. Considering the molecular volume per monomer unit $v_0$ (= 0.28 nm$^3$) estimated from bulk density of METAC and the chain contour length per monomer unit $l_0$ ($l_0=0.25$ nm for vinyl monomers), the cross-sectional area per monomer unit $a^2 = v_0/l_0$ is 1.1 nm$^2$. Therefore, the distance between the tethered chains on the substrate surface is around 1.0 nm, which is larger than size of hydrated ions. Apparent hydration radius of equivalent hydrated sphere of Na$^+$ and Cl$^-$ are reported to be 0.18 and 0.20 nm.[14] Once the concentration of added ions in solution reaches the concentration of the free counterions inside the brush, hydrated ions can enter the polyelectrolyte brush layer to screen the electric interactions forming relatively smaller dimension and thickness. The solvent quality of saturated NaCl aqueous solution for poly(METAC) has not been well-studied yet, although poly(METAC) quickly dissolves in 5.6 M NaCl aqueous solution. The second virial constant of poly(METAC) in NaCl solution should be given by light scattering measurement.

Independency on salt concentration was also observed between the swelling structure of poly(MPC) facing a pure D$_2$O and a NaCl/ D$_2$O solution, as shown in Figure 3(a) and (b). Swollen thickness $h^*$

**Figure 1.** (a) NR curves of poly(METAC) brush/D$_2$O, (b) poly(METAC) brush/ 1.0 M NaCl in D$_2$O, (c) poly(METAC) brush/5.6 M NaCl in D$_2$O, and (d)-(f) their corresponding neutron SLD profiles along with the distance from quartz surface, respectively. Scattering vector $q = 4 \pi \sin \theta / \lambda$ at $\lambda = 0.88$ nm.

**Figure 2.** (a: open circle) Volume fraction distribution ($\phi$) for poly(METAC) brush in 1.0 M NaCl/D$_2$O calculated by Figure 1(e), and (b: filled circle) the corresponding fit based on a Parabolic function using $\phi = \phi_0 \{(1-z/h^*)^2\}$.
was estimated to be around 90 nm. As mentioned before, higher ionic strength in densely grafted poly(MPC) layer than that in outer solution might be one of the reason for a negligible change in swollen brush structure. In this case, however, additional mechanism based on a specific property of MPC should be also contributed. We previously carried out dynamic light scattering measurement of unbound free poly(MPC) dissolved in an aqueous solution to find out that the dimension of poly(MPC) was independent on the ionic strength of the salt solution.[15] Poly(MPC) can be regarded as a quite unique zwitter-type polyelectrolyte of which chain structure in an aqueous solution hardly changed by salt effect, although its reason has not been cleared, yet.

4. Conclusion
NR of the swollen poly(METAC) and poly(MPC) brushes revealed that the extended chain structure formed in pure water as well as in aqueous NaCl solution with low concentration (1.0 M). We suppose that the hydrated ions of sodium and chloride in the external solution could not diffuse into the swollen brush layer due to the high osmotic pressure and high charge density of the densely packed polyelectrolyte chains. At the higher salt concentration (5.6 M), the screening of repulsive interaction took place to reduce the thickness of poly(METAC) brush. Negligible dependency of hydrated poly(MPC) behavior on salt concentration is supposed based on the unique interaction of phosphorylcholine and water molecule, however, further investigation using various derivatives of MPC and analysis at higher salt concentration will be required to discuss the details.

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