Influence of Salt Concentration on Swelling States of Poly(sulfobetaine) Brush at Aqueous Solution Interface

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Abstract. Swelling states of poly(3-dimethyl(methacryloyloxyethyl)ammonium propane sulfonate) (DMAPS) brush in aqueous solutions with different salt concentrations were investigated by atomic force microscopy (AFM) and neutron reflectivity measurement. The thickness of swollen poly(DMAPS) brush evaluated by AFM was increased from 212 nm up to 352 nm with an increase in salt concentration from 0 to 0.5 M. Poly(DMAPS) brush chains formed shrunk structure in a pure water due to the attractive electrostatic inter- and intra-chain interaction of sulfobetaine groups, while the brush chains in NaCl aqueous solution were stretched up because the hydrated salt ions screened the attractive interaction.

1. Introduction

Polysulfobetaine, such as poly(3-dimethyl(methacryloyloxyethyl)ammonium propane sulfonate) poly(DMAPS), is one of the zwitterionic polymers, which has attracted much attention due to its unique solution properties and applications. For instance, poly(DMAPS) cannot be dissolved in pure water due to the strong attractive electrostatic interaction between ammonium cations and sulfonyl anions of the side chains. Salt ions added into the poly(DMAPS) aqueous solution screen the inter- or intramolecular interaction among side chains to give a greater chain expansion [1], higher intrinsic viscosity [2], and lower upper critical solution temperature (UCST) [3]. Not only solution properties but also surface-tethered poly(DMAPS) on substrates was investigated by several groups. Kato et al. estimated the thickness of adsorbed poly(DMAPS) layer on silica surfaces as function of salt concentration [4]. Very low non-specific protein adsorption was observed on the surface of poly(DMAPS)-immobilized substrate prepared by surface-initiated atom transfer radical polymerization (ATRP) [5]. The wettability control of the substrate surface has been also achieved by using poly(DMAPS) brush with various ranges of graft density [6]. They described that the wettability of poly(DMAPS) brush switched from hydrophilic to hydrophobic at UCST. The switching temperature became higher by increasing the graft density. In general, the high-density polymer brush chains are extended to perpendicular direction from a substrate in good solvent due to the osmotic pressure by excluded volume effect [7]. In the case of polyelectrolyte brush, the repulsive or attractive interaction among the ionic groups of polymer chains also affects the swelling structure of the brush in the solution [8]. In particular, poly(DMAPS) brush chains would form a relatively extended conformation in a salt water, while the chains would shrink in pure water attributed to the strong
attractive interaction among side chains. In this report, the dependence of ionic strength on swelling behavior of poly(DMAPS) was investigated by atomic force microscopy (AFM) and neutron reflectivity (NR) measurement.

2. Experimental

2.1. Materials. The surface initiator, (2-bromo-2-methyl)propionyloxyhexyltriethoxysilane (BHE) [9,10] and DMAPS monomer [11] were synthesized using previous reported procedures. Silicon wafer and quartz plates (65 × 65 × 10 mm³) were washed with piranha solution at 373 K for 1 h and subsequently exposed to the vacuum ultraviolet-ray for 15 min under 30 Pa. The BHE monolayer was immobilized on the substrates using the chemical vapour adsorption (CVA) method [12].

2.2. Surface-initiated ATRP. A few sheets of BHE-immobilized silicon wafers and quartz plate, CuBr (0.088 mmol), and 2,2’-dipyridyl (0.168 mmol) were introduced into a glass tube equipped with a stopcock under argon atmosphere. A methanol/water (1/1 = v/v) solution of DMAPS (215 mmol) was added to the catalyst in glass tube, and was degassed three times by repeated freeze-pump-thaw cycles. Polymerization reaction was carried out at 303 K for 12 h under dry argon to generate a poly(DMAPS) brush from the substrate (Figure 1), and was quenched by opening the vessel to air. The substrates were washed with hot water using a Soxhlet apparatus for 12 h.

2.3. Measurements. The thickness of the polymer brushes on the silicon substrate in air (the relative humidity = 19%) were determined by an imaging ellipsometer (Nippon Laser & Electronics Lab.) equipped with a YAG laser (λ = 532.8 nm). The polarizer angle was fixed at 50°, and a refractive index of 1.50 was used for calculations of the film thickness. Topographic imaging and force measurement were performed by AFM (SI Nanotechnology Inc., E-Sweep). The curvature radius of the used cantilever (Sphere Tips CONT, Nanosensors) made of SiO₂ was 1000 nm. The bending spring constant of the cantilever tip was 0.24 N/m. The cantilever surface was covered with n-propyltriethoxysilane (Sigma Aldrich Co.) monolayer by CVA method. A liquid cell was used for the measurement in pure water and 0.5 M NaCl aqueous solution at 298 K. NR measurements were carried out by a multilayer interferometer for neutrons (MINE) in JRR-3 at TOKAI, using wavelength of λ = 0.88 nm. The scattering vector, q, in specular reflectivity is defined by q = (4π/λ) sinθ. The fitting curves of NR profiles were calculated by using Parratt32 software.

3. Results and Discussion.

The swollen thicknesses of poly(DMAPS) brush (Mₙ ~ 3.2 × 10⁵, Mₚ/Mₙ ~ 1.8) in aqueous solution were evaluated by AFM [7]. The interaction force of poly(DMAPS) brush compressed by a cantilever with radius R of probe head was measured in a pure water and in 0.5 M NaCl aqueous solution. The measured force F was converted to the force F/R. As shown in Figure 2, the F/R value increased with compressing the brush layer and with decreasing the distance from the substrate surface D. However, absolute distance from the substrate surface cannot be given directly by the force curve measurement. Let us define the gap D’ as a distance between the position at the beginning of repulsive force detection and the constant compliance region in the force curve where the cantilever deflection was proportional to the piezo displacement. The offset distance D₀ was determined by scanning the scratched sample across the boundary of a scratched and an unscratched region. In this study, D₀ was obtained as a height of the brush layer from the scratched surface by AFM image taken under a constant force mode by applying the force corresponding to the constant compliance region in the force curve measurement. The equilibrium thickness Lₑ of the swollen polymer brush was defined by Lₑ = D₀ + D’. The thickness of poly(DMAPS) brush in air (relative humidity = 19%) was 147 nm, which was agreed with the value estimated by ellipsometry. The Lₑ values in pure water and in 0.5 M NaCl aqueous solution were 212 nm and 352 nm, respectively. We supposed that poly(DMAPS) formed relatively shrunk structure in pure water due to the attractive electrostatic interactions based on ammonium cations and sulfonyl anions, while these electrostatic interactions were screened by hydrated salt ions in 0.5 M NaCl aqueous solution. Poly(DMAPS) brush immersed in a salt solution

![Figure 1. Poly (DMAPS) brush.](image-url)
behaves like an electrically neutral polymer to give relatively stretched chain structure due to the osmotic pressure. In the strict sense, the $L_e$ estimated in this method cannot describe the true thickness of swollen brush, because the electrostatic interaction between the probe head and the outermost polyelectrolyte brush should be considered, especially in the case of a low ionic strength solution. Then, we tried to estimate the swollen thickness of poly(DMAPS) brush by NR, too.

Figure 3 shows the NR curves and scattering length density (SLD) profiles of poly(DMAPS) brush in D$_2$O and 0.5 M NaCl/D$_2$O. The neutron SLD of poly(DMAPS) brush in D$_2$O was dramatically increased from 4.75 × 10$^{-4}$ to 6.32 × 10$^{-4}$ nm$^{-2}$ along with the distance from the substrate ($z$), and was slightly increased up to 6.39 × 10$^{-4}$ nm$^{-2}$ at the pure D$_2$O region. Theoretically, the SLD profiles are described by a parabolic function and an additional exponential tail at larger $z$ region [13]. Figure 4 represents volume fraction ($\varphi$) curve of DMAPS segments as a function of $z$ and the corresponding parabolic-type profile $\varphi = \varphi_0/(1-z/h^*)^2$ assuming a brush layer height ($h^*$).

In this study, we regard $h$ as thickness of the swollen brush. The tail part in a volume fraction curve at $z > h^*$ region was caused by a roughness at the interface of brush and solution. The $h^*$ for poly(DMAPS) brush in D$_2$O solution was 130 nm in pure D$_2$O. This result indicated that the brush chains were shrunk due to the attractive electrostatic interaction. On the other hand, the SLD profile in 0.5 M NaCl/D$_2$O drastically increased to 5.50 × 10$^{-4}$ in 50 nm region from the substrate, and gradually increase to 6.29 × 10$^{-4}$ nm$^{-2}$ at the external solution interface. The $h^*$ for poly(DMAPS) brush in 0.5 M NaCl/D$_2$O was estimated to be 280 nm. The moderate increment from 5.50 × 10$^{-4}$ nm$^{-2}$ to 6.29 × 10$^{-4}$ nm$^{-2}$ in SLD profile of 0.5 M NaCl/D$_2$O indicated that the brush chain was further extended from the quartz substrate because hydrated salt ions screened the attractive electrostatic interaction. The steep increment 4.30 × 10$^{-4}$ nm$^{-2}$ to 5.50 × 10$^{-4}$ nm$^{-2}$ was observed at $z = 0 ~ 40$ nm. We supposed that the brush chains located near the quartz substrate was not completely extended. Dimension of poly(DMAPS) brush in 0.5 M NaCl solution has been studied by Kato et al. using a light scattering. They reported that $R_H$ of unbound poly(DMAPS) chain was continuously enlarged along with NaCl salt concentration from 0.06 M to 1.0 M [1]. Similar results were also obtained in the case of poly(DMAPS) chains adsorbed on a silica surface [4]. Therefore, 0.5 M of NaCl aqueous solution was not high concentration enough for free poly(DMAPS) to screen the intra or inter molecular electrostatic interaction completely. In addition, large molecular weight distribution of grafting polymer gives the gradient distribution of polymer concentration in the swollen brush layer with lower polymer density at the outermost surface and higher at the bottom region. The screening of electrostatic interaction would effectively take place at the external solution/brush interface forming relatively extended chain conformation, while the brush chains near the substrate surface remained shrinking.

Polymer chains at the outermost region were stretched up to $h^* = 280$ nm from the substrate. The thickness of brush layer was clearly increased with NaCl concentration in D$_2$O. We have to point out here that the $h^*$ values determined by NR measurement were not agreed with the $L_e$ values estimated by AFM. One of the reasons is supposed to be attributed to the molecular weight distribution. Considering the polymer chains with various molecular weights and/or length tethered on a flat substrate, the local concentration of polymer in the outermost surface region of the swollen brush must be much lower than that in the deeper region. The probe for the force curve measurement is so sensitive that the repulsive force can be detectable from the longest-length chain in the brush in spite of the low concentration at the outermost brush/solution interface region. Meanwhile, it is hard for NR measurement to determine the neutron SLD curve of the low polymer-concentration layer at the
outermost brush/deuterated solvent interface because of the low H/D contrast. Therefore, we suppose that the larger thickness $L_e$ was obtained from AFM compared with $h^*$ estimated by NR measurement.

4. Conclusion.

This is the first report on the analysis of the swollen poly(DMAPS) brush structure in aqueous solution with different salt concentrations by AFM and NR measurement. The equilibrium thickness $L_e$ of the swollen polymer brush in pure water evaluated by force curve measurement was increased from 212 to 352 nm by addition of salt to the solution. The hydrated salt ions screened the strong attractive electrostatic interaction of sulfobetaine groups to give the structure change of the brush from shrunk to relatively stretched state. Similar swelling state was observed by NR measurement, too. The neutron SLD profile represented the gradient structure of swollen brush due to the large molecular weight distribution.

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