

Neutron Reflectivity Studies of the Swelling States of Polysulfobetaine Brush at Water Interface

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Water-swollen states of hydrophilic polymer brushes have been paid great attention because they relate to biointerface performance and water lubrication. We studied the swollen structure of polymer brushes containing zwitter ionic and nonionic macromolecules in aqueous solution by neutron reflectivity (NR). This article describes a part of them, focusing on swelling behavior of polysulfobetaine brush prepared by surface-initiated radical polymerization of (3-dimethyl(methacryloxyethyl) ammonium propane sulfonate) (DMAPS). Poly(DMAPS) is insoluble in pure water due to the strong attractive electrostatic interaction between ammonium cations and sulfonate anions. In contrast, poly(DMAPS) is soluble in salt solution because of the screening of the inter- or intramolecular interaction by ions in aqueous solution [1,2]. The dependence of ionic strength on swelling behavior of poly(DMAPS) brush was investigated by NR.

The poly(DMAPS) brush on quartz was prepared by surface-initiated atom transfer polymerization of DMAPS. NR was measured by a multilayer interferometer for neutrons (MINE) in JRR-3 at TOKAI, using wavelength $\lambda = 0.88$ nm with an accuracy of 2.7 %. A neutron beam was irradiated from a quartz substrate to the interface between heavy water (D₂O) and the poly(DMAPS) brush on quartz glass. The incident slit width were adjusted to maintain a 55 mm footprint size on the sample surface. The scattering vector, q , in specular reflectivity is defined by $q = (4 / \lambda) \sin \theta$. The NR profiles were analyzed by fitting calculated reflectivity from model scattering length density profiles to the data using Parratt32 software.

Figure 1 shows the neutron reflectivity curves and scattering length density profiles of poly(DMAPS) brush in D₂O and 0.5 M NaCl/D₂O. The neutron scattering length density (SLD) of poly(DMAPS) brush in D₂O was dramatically increased from 4.80×10^{-4} to 6.32×10^{-4} nm⁻² along with the distance from the substrate, and was slightly increased up to 6.39×10^{-4} nm⁻² at the pure D₂O region. Volume fraction distribution of DMAPS segments in D₂O solution was evaluated from SLD curve, and was fitted by the parabolic function to estimate the brush thickness in solution, which was 130 nm in pure D₂O. On the other hand, the SLD profile in 0.5 M NaCl/D₂O 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. Polymer brush chains at the outermost region were stretched up to 260 nm from quartz surface. Hydrated salt ions screened the attractive electrostatic interaction of sulfobetaine groups to give an extended chain structure like as an osmotically swollen brush of an electrically neutral polymer.

References

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- (2) Kato T and Takahashi A 1996 Ber. Bunsenges. Phys. Chem. 100 784.

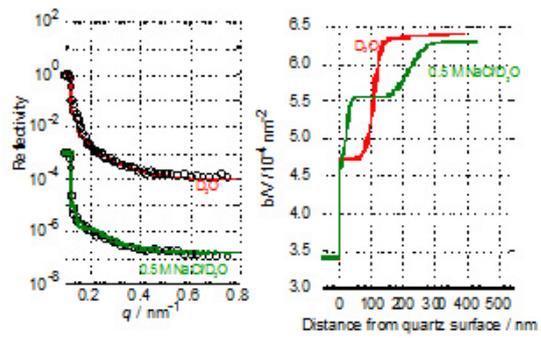


Fig. 1. Figure 1. NR of PDMAPS brush in D₂O and 0.5 M NaCl/D₂O solution and the corresponding fits (Left). The SLD profiles in D₂O and 0.5 M NaCl/D₂O solution to calculate the fitting curves for reflectivity (Right).