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

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The behavior of polyelectrolyte brushes at salt solution interface is important for applications in medical materials, as these materials are in contact with blood and other body fluids containing salts. We investigated the dependence of swelling brush conformation on the ionic strength analyzed by neutron reflectivity (NR) of zwitterionic type polyelectrolyte and cationic polyelectrolyte brushes prepared by surface-initiated atom transfer radical polymerization of 2-(methacryloyloxy)ethyl phosphorylcho line (MPC) and 2-(methacryloyloxy)ethyltri methyl ammonium chloride (MTAC), respectively.

The polyelectrolyte brushes were prepared on quartz surface. NR was measured by a multilayer interferometer for neutrons (MINE) in JRR-3 at TOKAI, using wavelength λ = 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 polymer 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 $q = (4\pi/\lambda)\sin\theta$. The NR profiles were analyzed by fitting calculated reflectivity from model scattering length density profiles to the data using Parratt32 software.

Fig. 1 shows the NR curves and scattering length density (SLD) profiles of poly(MTAC) brush in D2O and 1.0 - 5.6 M NaCl/D2O. The SLD of poly(MTAC) brush in pure D2O was increased from 5.20 × 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. When the poly(MTAC) brush was immersed in the 5.6 M NaCl/D2O solution, the reduction in roughness and thickness of swelling brush layer was observed, as shown in Fig. 1(f). The brush layer height was 69 nm. The hydrated salt ions screened the repulsive interaction between quarternary ammonium groups of the brush, forming a more shrinked chain conformation.

On the other hand, no structural change was observed in swollen poly(MPC) brush even in a salt solution, although the NR profiles were not shown here. Poly(MPC) is a quite unique polyelectrolyte of which chain structure in a aqueous solution hardly changed by salt effect probably due to a weak intermolecular interaction of phosphorylcholine units[1].

References

(1) Matsuda Y, Kobayashi M, Annaka M, Ishihara K and Takahara A 2008, Langmuir 24 8772.

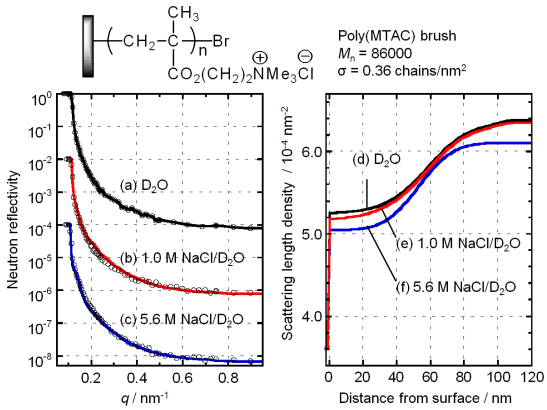

Fig. 1. Fig 1. NR curves of poly(MTAC) brush in (a) D2O, (b) 1.0 M NaCl, (c) 5.6 M NaCl in D2O, and (d)-(f) their corresponding neutron SLD profiles along with the distance from quartz surface, respectively. Scattering vector $q = 4\pi\sin\theta/\lambda$ at λ = 0.88 nm.