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Characterization of Swollen States of Polyelectrolyte Brushes in Salt Solution by Neutron Reflectivity

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Abstract. Cationic and zwitterionic polyelectrolyte brushes on quartz substrate were synthesized by surface-initiated atom transfer radical polymerization of 2-(methacryloyloxy)ethyltrimethylammonium chloride (MTAC) and 2-(methacryloyloxy)ethyl phosphorylcholine (MPC). The effects of ionic strength on brush structure are investigated by neutron reflectivity (NR) in NaCl deuterium oxide (D₂O) solutions. We observed that poly(MTAC) chains were drastically shrunk at concentrations above 0.1 M NaCl/D₂O, which may be the change in charge-screening effect against ions on poly(MTAC). On the other hand, effect of salt concentration on a swollen state of poly(MPC) brush was negligible, even at the high concentration (5.0 M) close to saturation. The behaviour of poly(MPC) in salt aqueous solution is completely different from that of poly(MTAC), which may arise from the unique interaction properties, neutral nature, and hydrated water structure of phosphorylcholine units.

1. Introduction

Polyelectrolyte brushes consist of polymer chains that are densely tethered one end to a surface while the other end is free, and their repeating units contain positive or negative charges [1]. In general, polyelectrolyte brushes have relatively stretched conformation in aqueous solution of low ionic strength, because of the intra- and intermolecular repulsive interactions and a higher osmotic pressure caused by the high ionic concentration inside the brush layer compared to outer bulk solution [2,3]. With increase in ionic strength, the electrostatic repulsion is screened by hydrated salt ions, and the difference in osmotic pressure of brush layer and bulk solution becomes smaller. As a result, polyelectrolyte brush behaves like an electrically neutral polymer forming a more coiled conformation, and the thickness of brush decreases. One of the typical examples is poly(2-(methacryloyloxy)ethyltrimethylammonium chloride) (poly(MTAC)) brush, whose conformational transition in aqueous NaCl solution was observed by Huck et al. using quartz crystal microbalance and scanning force microscopy [6]. On the contrary, phosphorylcholine-containing polyampholytes, such as poly(2-(methacryloyloxy)ethyl phosphorylcholine) (poly(MPC)), present an unusual phenomenon in salt solutions. Poly(MPC) is a super hydrophilic polyampholyte, which shows good blood compatibility, low friction, and anti-protein adsorption due to its cell membrane-like surface [7]. Recent dynamic light scattering study revealed that relatively expanded chain dimension of poly(MPC) in aqueous solution was hardly affected by salt concentration up to 1 M of NaCl [8], although the precise
mechanism of this swollen behavior is still unknown. In this study, neutron reflectivity (NR) measurements were carried out to characterize the swollen structure of densely-grafted zwitterionic poly(MPC) brush on a flat substrate in aqueous solutions with much higher NaCl concentration than 1 M. The effect of salt concentration on the volume and thickness of cationic poly(MTAC) brush was also investigated as well as poly(MPC) brush by using 0 - 5 M of aqueous NaCl solution.

2. Experimental

Quartz plates (65 × 65 × 10 mm³) were washed with piranha solution at 373 K for 1 h and subsequently exposed to vacuum ultraviolet-ray (∆ = 172 nm) for 5 min under reduced pressure (30 Pa). The surface initiator, (2-bromo-2-methyl)propionyloxyhexyltrimethoxysilane, was immobilized on the substrate in toluene. 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 [9]. For MTAC polymerization, 2,2,2-trifluoroethanol was used as a solvent [10]. The number-average molecular weights (Mn) and molecular weight distribution of the free polymers simultaneously obtained with polymer brushes 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 0.5 M of acetic acid aqueous solution containing 0.2 M sodium nitrate for poly(MTAC) as the eluents at a rate of 0.6 mL min⁻¹ at 313 K. NR measurements were carried out by a time-of-flight (TOF) type reflectometer ARISA-II at BL16 in MLF/J-PARC providing 25 Hz-pulsed neutron radiation at 120 kW. Wavelength of the incident neutrons is tuned at 0.2 - 0.88 nm by a disk chopper. The neutron beam was irradiated through quartz at the interface between D₂O/ poly(MPC) brush on quartz glass and reflected neutrons were collected by a 2-D scintillation detector. The incident slits were adjusted to maintaining a 50 mm footprint size on the sample surface at all incident angles (typically 0.30, 0.75, 1.20 deg). The NR profiles were analyzed by fitting calculated reflectivity from the model scattering length density profiles to the data, using Parratt32 software.

3. Results and Discussion

We prepared poly(MTAC) with Mₙ = 94,300 in Mₙ/Mₘ = 1.17, and poly(MPC) with Mₙ = 137,000 in Mₙ/Mₘ = 1.85. The thickness under air (50% relative humidity at 25 °C) of the poly(MTAC) and poly(MPC) brushes on quartz substrates were 22.5 nm and 7.5 nm, respectively.

Figure 1 shows NR curves of poly(MTAC) brush interfaces in contact with D₂O solutions at several NaCl concentrations and the corresponding neutron scattering length density (SLD) profiles along with distance from the quartz surface. The volume fraction profiles in D₂O and 0.1 M D₂O solution against distance from the substrate are also represented in Figure 1 (g) and (h), respectively. In the case of D₂O/ poly(MTAC) interfaces, a critical angle was clearly observed at q = 0.11 nm⁻¹ due to the difference in SLD between quartz and D₂O. The SLD profile of the poly(MTAC) brush in D₂O was a smooth upward curve from 4.6 × 10⁻⁴ to 6.3 × 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. 70 nm, which is thicker than 22.5 nm, the brush thickness in the air estimated by a NR measurement. Therefore, the polymer chains immersed in D₂O were extended significantly in the direction normal to the substrate. On the other hand, the volume fraction profile of poly(MTAC) in D₂O shows relatively high content of D₂O (volume fraction = 0.7) at the substrate, and polymer content decreased with distance from the substrate. It indicates that D₂O molecules deeply penetrated into the brush layer, resulting from the high osmotic pressure inside the brush. According to the self-consistent field theory, volume fraction (φ) of polymer brush with uniform chain length in a good solvent at a position (z) apart from the substrate is represented by parabolic function φ(z) = φ₀(1-(z/h)²) [11], where φ₀ is the volume fraction at z = 0, and h is the cut-off thickness of the swollen brush layer. In our case, the volume fraction profile in D₂O was in good agreement with a parabolic function with h = 75 nm. The estimation with the theoretical prediction indicates D₂O worked as a good solvent for poly(MTAC) brush, which resulted in the highly expanded brush structure.
In the case of NaCl concentration of 0.1 M in D\(_{2}\)O, the SLD profile showed a similar feature to that in D\(_{2}\)O, that is, a gradual upward curve from 4.4 \(\times 10^{-4}\) to 6.2 \(\times 10^{-4}\) nm\(^{-2}\). The volume fraction profile also suggests that a high content (65 % at the substrate) of D\(_{2}\)O exists in the brush layer. Additionally, the volume fraction is described well by the parabolic equation with \(h = 64\) nm. These features are quite similar to that in D\(_{2}\)O, which indicates that the brush structure in 0.1 M NaCl/D\(_{2}\)O was still in a swollen state. In contrast, the SLD profile in [NaCl] = 1.0 M shows a significant reduction of SLD value at the substrate to 2.2 \(\times 10^{-4}\) nm\(^{-2}\) and thickness of the brush layer to c.a. 45 nm, in comparison with those in D\(_{2}\)O and [NaCl] = 0.1 M. These facts suggest the shrinkage of the poly(MTAC) brush. We obtained a similar result in case of salt concentration of 5.0 M to that in [NaCl] = 1.0 M and confirmed that the brush had a shrunk conformation in such a concentrated condition.

Generally, the shrinkage or reduction of hydrodynamic radius of a free polyelectrolyte with positive or negative charges in an aqueous solution containing salt is thought as a transition from a swollen state to a more coiled state. The transition, which is resulted from screening of electrostatic repulsion between the monomer units by addition of salt, occurs at a critical point called “theta point”, where the second virial coefficient is negligibly small. The brush’s shrinkage observed in the poly(MTAC) brush system also took place by the same mechanism as shrunk behavior in the free polyelectrolyte system. Thus, a theta point should be also defined in the brush system and estimated between 0.1 -1.0 M in our experiment.

Figure 2 shows the NR curves of poly(MPC) in D\(_{2}\)O and 5.0 M NaCl/D\(_{2}\)O solution, and the corresponding SLD profiles. The volume fraction profile in D\(_{2}\)O was also shown in Figure 2(e). The SLD profile of the brush in D\(_{2}\)O monotonically increases with the distance from the substrate and intersects with the SLD of the solvent at c.a. 60 nm. Taking dry thickness (7.5 nm at 50 % relative humidity at 25\(^{\circ}\)C) into account, it indicates that the poly(MPC) brush has a stretched conformation in a D\(_{2}\)O medium. However, in contrast to poly(MTAC) brush, the volume fraction profile of poly(MPC) brush in D\(_{2}\)O did not describe by simple parabolic function representing swollen brush structure in a good solvent. This discrepancy could be explained by molecular weight distribution of the polymer brush since the parabolic expression does not include the effect of heterogeneity of chain length. Indeed, poly(MPC) has a larger polydispersity index (\(M_w/M_n = 1.85\)) than that of poly(MTAC) (\(M_w/M_n = 1.17\)), the disagreement with the theoretical prediction was dominant in the case of poly(MPC). The monotonically decreasing volume fraction as shown in Figure 2(e) does not conflict with another theoretical prediction considering the molecular weight distribution effect reported by other groups, where an exponential-like decay appears in a volume fraction profile of polymer brush with large molecular weight distribution in a good solvent [12].

On the other hand, in the case of poly(MPC) brush in [NaCl] = 5.0 M (near saturation at 25 \(^{\circ}\)C), the SLD profile was almost the same as that in D\(_{2}\)O (see Figure 2(c) and (d)). A similar result was also obtained in more concentrated condition at 1.0 M. These facts suggest the swollen states of poly(MPC)
The brush is independent of salt concentration, in contrast to the poly(MTAC) brush, which indicates that the poly(MPC) should have no transition, i.e., it has no theta salt concentration point. The origin of this characteristic behavior of poly(MPC) brush in aqueous solutions of NaCl is not clear but might come from its unique interaction among the brush side chains, its neutral nature or structure of hydration around the brush.

4. Conclusion

In this work, we have investigated on swelling behaviors of poly(MTAC) and poly(MPC) brushes in NaCl D_2O solutions using neutron reflectometry. It was revealed that the brush of poly(MTAC) shrunk drastically at NaCl concentration between 0.1 and 1.0 M, which corresponds to theta point. We also found that the brush structure of poly(MPC) is not affected by the NaCl aqueous solutions contacting with the brush. The unique behavior of poly(MPC) brush in a D_2O solution of NaCl might be closely related with its properties in tribology, anti-fouling, and wettability.

Acknowledgments

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References