# Application of polyelectrolytes to novel adhesion system

Adhesion utilizing the ionic interaction between oppositely charged polyelectrolytes is a simple adhesion system as an organic solvent-free adhesion system. To realize this adhesion system, it is necessary to understand the solution characteristics of polyelectrolytes because the chain dimension is an important parameter for adhesion and debonding. However, little is known on the chain dimension of a polyelectrolyte in aqueous media, which is used for adhesion and debonding solvents. In the present research, the chain dimension of the polyelectrolyte was characterized by small angle X-ray scattering (SAXS). The adhesion, debonding and reversible adhesion between the ionic polymer brush substrates were demonstrated using a deionized water as an adhesion solvent and an aqueous salt solution as a debonding solvent [1].

To characterize the effect of ionic strength on chain dimension, the authors prepared poly(2-(methacryloyloxy)ethyltrimethylammonium chloride) (PMTAC) and studied their chain dimension by synchrotron radiation SAXS at **BL03XU** beamline using an incident X-ray wavelength λ of 0.10 nm with a sample-to-detector distance of 2180 mm. The weight-average molecular weight of PMTAC was 73000. Figure 1(a) shows SAXS profiles of PMTAC of various concentrations (C_p, g·cm^{-3}) dissolved in an aqueous NaCl solution (1.0 mol·L^{-1}). The experimental excess scattering intensity $\Delta I(q)$ versus scattering vector q (nm^{-1}) was well simulated by Debye function fitting, which gave the radius of gyration $<S^2>_z^{1/2}$ (nm) of PMTAC of 4.3 nm. The radius of gyration is the average distance from the center of the gravity to the chain segment, which tells us the dimension of PMTAC in the solution. The

$<S^2>_z^{1/2}$ of PMTAC in 3.0 mol·L^{-1} NaCl solution was also determined to be 4.2 nm using a similar protocol. In addition, SAXS curves showed similar slopes around the $q = 10^0$ nm^{-1} region, indicating that PMTAC maintained similar random coil conformations at various C_p when the salt concentrations were 1.0 and 3.0 mol·L^{-1}.

On the other hand, the second virial coefficient A_2 of PMTAC in the aqueous NaCl solution was obtained using the proportional relationship between the inverse of $\Delta I(0)$ and the polymer concentration C_p, as shown in Fig. 1(b). $\Delta I(0)$ was obtained using the intercept of $\Delta I(q)/C_p$ in Fig. 1(a). The A_2 values of PMTAC in the aqueous NaCl solution with 1.0 and 3.0 mol·L^{-1} were 2.0×10^{-4} and 6.3×10^{-5} g^{-1}·cm^3·mol, respectively. In this case, the decrease in A_2 with increasing NaCl concentration indicates the reduction in electrostatic repulsive interaction among the ammonium cations of PMTAC. In general, the electrostatic interactions among the ionic functional groups are screened by hydrated ions in the aqueous salt solution. The dependence of electrostatic interaction of ion-containing polymers on the ionic strength in the solution can be utilized for the reversible adhesion system.

The authors prepared 100-nm-thick polyelectrolyte brushes by the surface-initiated atom transfer radical polymerization of MTAC [2], 3-sulfopropyl methacrylate potassium salt (SPMK), and 3-(N-2-methacryloyloxyethyl-N,N-dimethyl) ammonatopropanesulfonate) (MAPS) [3] on the silicon wafers. As shown in Fig. 2, 2 μL of deionized water was placed on a brush-immobilized silicon substrate and then another substrate was pressed onto it under a constant load of 4.9 N at 298 K. The contact area
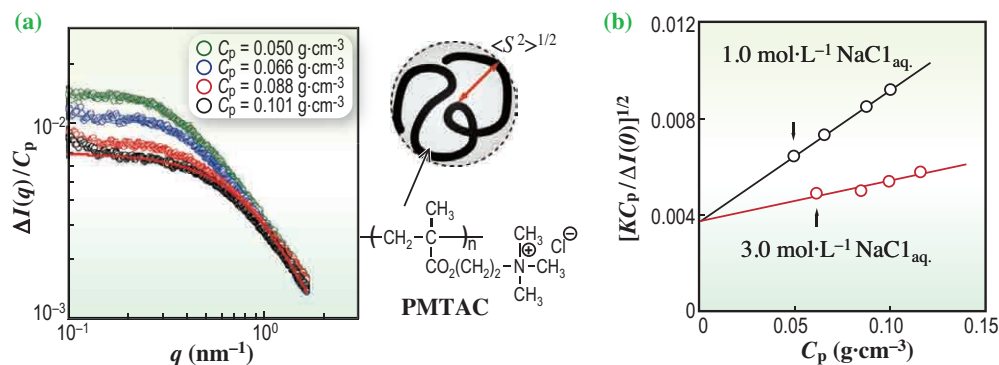
Fig. 1. **(a)** SAXS profiles of PMTAC with various polymer concentrations (C_p, g·cm^{-3}) in aqueous NaCl solution at 1.0 mol·L^{-1} (open circles) and the corresponding fit based on Debye function (red solid line), and **(b)** dependence of $[KC_p/\Delta I(0)]^{1/2}$ on C_p for PMTAC in aqueous NaCl solutions at 1.0 and 3.0 mol·L^{-1}. $\Delta I(q)$ is the experimental excess scattering intensity at q. Scattering vector $q = 4\pi \sin\theta/\lambda$.
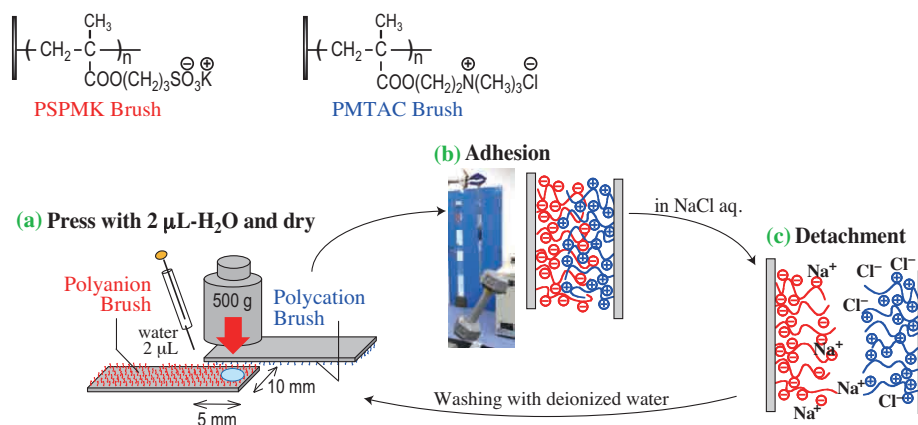
Fig. 2. Schematic view of **(a)** adhesion process of cationic PMTAC and anionic PSPMK brushes, **(b)** the bonded substrate hanging a 5 kg dumbbell, and **(c)** detachment of oppositely charged polyelectrolyte brushes in 0.5 mol·L^{-1} NaCl aqueous solution.

of the substrates was maintained at 5×10 mm^2. After 2 h of drying, the adhesion strength was measured using the lap shear adhesion force in an ambient atmosphere.

In the case of the PMTAC and poly(SPMK) (PSPMK) brush pair, the average adhesion strength reached about 1.52 MPa, as shown in Fig. 3. This strength was lower than the typical adhesion strength of commercially available adhesives (10−30 MPa); however, it would be a sufficiently useful adhesion strength for many applications because the adhered brush substrates with 1 cm^2 adhesion area could lift up a weight of *ca.* 15 kg. The lap shear adhesion strength between the poly(sodium methacrylate) (PMANa) brush and PMTAC brush substrates was 1.08 MPa. The sulfonate anion group of PSPMK interacted strongly with the ammonium cation group in PMTAC compared with carboxylic acid of PMANa. This result indicates that the electrostatic interaction contributed to the adhesion of anionic/cationic polymer brushes.

Since the polymer brushes remained on the substrate even after the lap shear test, a specimen combined with PMTAC and PSPMK brushes was rebonded several times by repeating the swelling with water and debonding in air, although the adhesive

strength decreased in a stepwise fashion from 1.52 to 0.85 MPa.

To measure the debonding time, a specimen prepared by the adhesion of oppositely charged polymer brushes was attached to a hanging weight of 100 g and slowly immersed in deionized water at 298 K. The debonding did not occur in deionized water for over 24 h because of the formation of a polyion complex between brushes. On the other hand, the specimen was separated within 10−60 min in the aqueous NaCl solution with 0.5−5.0 mol·L^{-1}, because the hydrated salt ions permeated the adhesion interface to reduce the electrostatic interaction between brushes. After the debonded substrates were washed with deionized water to remove the salt, they readily adhered to each other again. The lap shear adhesion strength of the re-adhered substrates was 1.23 MPa, which was close to the initial adhesion strength. In this case, adhesion and debonding can be repeated without damages to the brushes by using deionized water as an adhesion solvent and salt aqueous solution as a debonding solvent.
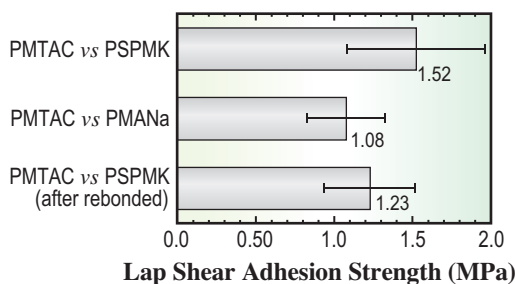
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Fig. 3. Lap shear adhesion strengths of pairs of polyelectrolyte brushes at 298 K in an ambient atmosphere and 55% relative humidity.

References
[1] M. Kobayashi *et al.*: Soft Matter **7** (2011) 5717.
[2] M. Kobayashi *et al.*: Macromolecules **43** (2010) 8409.
[3] *Y. Terayama, M. Kikuchi, M. Kobayashi, A. Takahara: Macromolecules* **44** *(2011) 104.*