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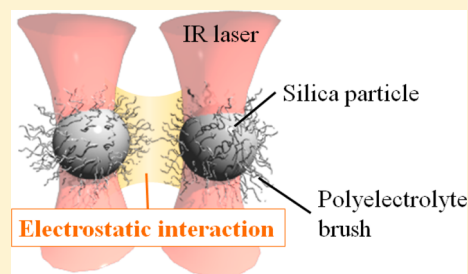
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Measurement of the Electrostatic Interaction between Polyelectrolyte Brush Surfaces by Optical Tweezers

Daiki Murakami,[†] Ai Takenaka,[†] Motoyasu Kobayashi,[†] Hiroshi Jinnai,^{†,‡} and Atsushi Takahara^{*,†,‡}

[†]Japan Science and Technology Agency (JST), ERATO, Takahara Soft Interfaces Project, and [‡]Institute for Materials Chemistry and Engineering, CE80, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

ABSTRACT: We demonstrated an optical tweezers method to measure the electrostatic interaction between the strong polyelectrolyte brushes, poly(2-(methacryloyloxy)ethyltrimethylammonium chloride) (PMTAC), grafted on silica particles in aqueous media. The weak electrostatic interaction was successfully detected with a resolution of less than $0.1 \mu\text{N m}^{-1}$. The apparent Debye length, including the charge distribution in the polymer brush and the surface potential, decreased as the salt concentration in the medium increased. The experimentally obtained surface charge density was much smaller than that estimated from the amount of polyelectrolyte on the surface. Furthermore, the dissociation of ionic groups was enhanced by decreasing the grafting density of the polyelectrolyte brush. The results suggest that the majority of chloride counterions was immobilized in the dense polyelectrolyte brush layer to neutralize the high charge density.



INTRODUCTION

Polymers chemically grafted to the surface of substrates are known as polymer brushes. Surfaces formed from polyelectrolyte brushes, which are polymer brushes consisting of a polyelectrolyte, are particularly attractive because of their potential in applications, including adhesion, antifouling, and water lubrication systems.^{1–7}

Numerous techniques, such as X-ray and Neutron reflectivity,^{8,9} Fourier transform infrared (FTIR) spectroscopy,¹⁰ ellipsometry,¹¹ and theoretical and computational studies,^{12–16} have been used to determine the distribution of the polyelectrolyte brush counterions in aqueous media. The properties of the polyelectrolyte brushes strongly depend upon the experimental conditions, such as the grafting density, molecular weight, salt concentration, and pH of the medium. The counterions are immobilized inside the polyelectrolyte brush layer in the salt-free and low-salt concentration regimes. In this osmotic brush regime, the grafting density has a negligible effect on the brush height, because of the balance between the osmotic pressure of the counterions and the elastic energy of the polymer chains. As the salt concentration, c_s , increases further in the salted brush regime, the brush height decreases according to a scaling law of $c_s^{-1/3}$, which results from the screening of the electrostatic interactions inside the brush layer. Eventually, the salt concentration becomes uniform, inside and outside the brush layer, and the polyelectrolyte chains behave as neutral brushes at sufficiently high c_s .^{14,17}

The mechanical properties of polymer brushes can be evaluated by measuring the surface force. Surface force measurements are usually conducted using a surface force apparatus (SFA) and atomic force microscopy (AFM) with a colloidal probe, which has a typical detection range of 10–1000 pN.^{18–21} These methods are suitable for strong interactions, such as the short-range steric interactions of polymer chains,

where the polymer brush surfaces are in contact with each other. In the case of polyelectrolyte brush surfaces, however, it is difficult to examine the electrostatic and steric interactions separately when polymer brushes come into contact. In addition, an increase in the counterion adsorption to the polyelectrolyte brush layer, through the charge regulation effect,²² occurs when the two surfaces are close enough. Thus, it is necessary to determine the long-range electrostatic interactions before the two brush surfaces touch to analyze the contribution of the electrostatic interactions separately. However, the long-range force is less than or similar to the detection limit of the conventional apparatus.^{18,19}

Optical tweezers are an experimental tool for optically trapping and manipulating tiny objects on a sub-micrometer to micrometer scale with no physical contact, using a laser.²³ The trapping force conserves the momentum of the laser against refraction at substance surfaces by maintaining its position at the laser focus. The intensity of the trapping force is proportional to the distance between the center of the material and the laser focus (Δx). Therefore, the external force, F , on the trapped substance can be estimated using Hooke's law: $F = k\Delta x$. The force (spring) constant, k , of the laser trapping is typically in the range of 10^{-5} – 10^{-4} N m^{-1} , whereas the spring constants normally used in SFA or AFM are 10^{-3} N m^{-1} . The resolution in determining Δx is less than 1 nm using the quadrant photodiode detector. Thus, optical tweezers are a powerful instrument for detecting much weaker forces (0.1–100 pN) with a sufficiently small experimental error of 0.1 pN.^{24–26} The resolution in normalized force F/R (R is the radius of sphere probe) is less than $0.1 \mu\text{N m}^{-1}$, which

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substantiates the high performance of the optical tweezers method for the force measurement. Detailed comparisons to AFM, SFA, and other techniques,²⁷ such as total internal reflection microscopy (TIRM) or bioforce probe (BFP) are found elsewhere.

Kremer et al. have used optical tweezers to measure a steric interaction of less than 20 pN between polymer brushes and clarified the entropic (osmotic) contribution of the counterions in the brush layers.^{28,29} The electrostatic force contribution was neglected because of the high counterion concentration in the brush layer and the small dissociation constants of the acid polymers. In this work, we demonstrated the high performance of optical tweezers to examine the long-range electrostatic interaction outside the brush layer rather directly. The cationic polyelectrolyte, poly(2-(methacryloyloxy)-ethyltrimethylammonium chloride) (PMTAC), was used because its monomer unit (MTAC) almost fully dissociates in water, and therefore, a strong interaction among well-dissociated ionic groups was expected. Consistency between obtained force curves and theoretical calculation of the electrostatic interaction between charged spheres was fairly good, verifying the prominent performance of the optical tweezers method. Immobilization of counterions in the polyelectrolyte brush near the substrate was suggested also in the method as the same as above-mentioned previous works.

EXPERIMENTAL SECTION

Materials. Silica particles (radius $R = 1.5 \mu\text{m}$) were purchased from Ube Nitto Kasei Co., Ltd. The size distribution of the particles was within 2.5%. Copper(I) bromide (CuBr, Wako Pure Chemical) was purified by successive washing with acetic acid and ethanol and dried under vacuum. 2,2'-Bipyridine (bpy, Aldrich) and 2,2,2-trifluoroethanol (TFE, Acros) were used as received. The cationic monomer, MTAC, was obtained from a commercially available aqueous solution (Aldrich, 80%) by removing the water and was then dissolved in TFE. The MTAC/TFE solution was purified by alumina column chromatography and membrane filtration.

Preparation of the Polymer Brush. The PMTAC brushes were prepared on the surface of silica particles (Figure 1) by the grafting-from and the grafting-to methods to achieve different surface grafting densities.

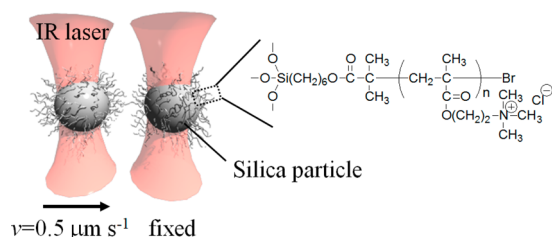


Figure 1. Optical trapping of the PMTAC-grafted silica particle.

Grafting-from Method (Si-from-PMTAC). The grafting-from method is also called surface-initiated atom transfer radical polymerization. The surface initiator, (2-bromo-2-methyl)propionyloxyhexyl triethoxysilane (BHE), was synthesized from 5'-hexenyl (2-bromo-2-methyl)propionate and trimethoxysilane in the presence of Karstedt's catalyst³⁰ and immobilized on silica particles (Si-BHE) as follows.^{31,32} The silica particles (1.0 g) were dispersed in ethanol (35 mL). A mixture of aqueous NH_3 (28%, 1.8 g) and ethanol (40 mL) was added dropwise to the suspension of silica particles over 3 h with stirring at 40 °C. BHE (0.50 g, 1.2 mmol) diluted with ethanol (2.5 mL) was added to the suspension, and the reaction mixture was stirred for another 18 h at 40 °C. The resulting Si-BHE was washed with ethanol and dispersed in TFE to obtain a 10 wt % suspension. The Si-BHE/

TFE suspension (2.6 g) and 2.0 M MTAC/TFE solution (7.4 mL) were mixed and degassed with three freeze-pump-thaw cycles. A TFE solution of CuBr (0.022 mmol) and bpy (0.045 mmol) was injected. The resulting mixture was degassed again and stirred at 333 K for 65 h. The PMTAC-grafted silica particles were purified by centrifugation in ethanol and redispersion in water.

Grafting-to Method (Si-to-PMTAC). In the grafting-to process, the PMTAC chains were polymerized from unfixed BHE (PMTAC-BHE) in the TFE solution. MTAC/TFE solution (2.0 M, 7.0 mL) and BHE/TFE solution (0.50 M, 0.14 mL) were mixed. After three freeze-pump-thaw cycles, a TFE solution of CuBr (0.0142 mmol) and bpy (0.030 mmol) was injected. The mixture was degassed and stirred at 60 °C for 24 h. The resulting PMTAC-BHE was purified by reprecipitation from methanol, mixed with 1,4-dioxane, and freeze-dried. The silica particles (0.3 g) were treated with aqueous NH_3 (28%, 2.0 mL) in ethanol (75 mL), as described above. PMTAC-BHE (0.030 g) diluted with ethanol (2.0 mL) was added to the suspension, and the mixture was continuously stirred for another 16 h at 40 °C. The samples were purified using the same method as for Si-from-PMTAC.

Estimation of the Amount of Grafted Polymers. The amount of polymer on the particles was evaluated by thermogravimetric analysis (Pyris 1 TGA, Perkin-Elmer). The samples were dried at 60 °C in a vacuum for 3 h before measurement. The weight of the samples was monitored from 100 to 800 °C (heating rate of 10 °C/min) on a platinum pan. The mass of the PMTAC brushes determined from the weight loss was 2.93×10^{-13} g/particle for Si-from-PMTAC and 9.58×10^{-14} g/particle for Si-to-PMTAC. These values corresponded to surface charge densities of 4.83 and 1.58 C m^{-2} , respectively, assuming full dissociation of the ionic groups.

Force Measurement with Optical Tweezers. The force measurements were performed with optical tweezers (NanoTracker, JPK Instruments, Germany). The apparatus was equipped with an IR laser source (3 W, 1064 nm). The laser was split into two beams by a beam splitter, and each laser position was controlled separately with a Galvano mirror and a moving lens. The beams were guided into the sample cell through the trapping objective in the attached microscope (ECLIPS Ti, Nikon, Co., Ltd.). The glass plates used in the sample cell were chemically modified with a silane coupling coating of (3-(2-aminoethyl)aminopropyl)trimethoxysilane to prevent the adsorption of particles onto the cell surface.

The particles were dispersed in water or aqueous NaCl and placed in the sample cell. Two particles were randomly picked up with the two independently focused lasers. One of the particles was held in the same position, and the other was moved toward the laser-stabilized particle at a rate of 0.5 $\mu\text{m/s}$. The shift in the center position from the laser focus was caused by the interaction between the particles. The displacement, Δx , was determined by detecting the scattering of the laser with the quadrant photodiodes behind the sample cell with the resolution of less than 1 nm. The sensitivity of the detectors and the force constant, k , of the laser trapping, typically $2.0\text{--}3.5 \times 10^{-5} \text{ N m}^{-1}$, were determined by power spectrum analysis.³³

RESULTS AND DISCUSSION

Figure 2 shows the force curves measured in water for Si-from-PMTAC and the uncoated silica particles. F was divided by the radius, R , of the particle to convert the force into the interaction energy between two planes based on the Derjaguin approximation.³⁴ F/R was in the range of a few $\mu\text{N m}^{-1}$, whereas many previous polymer-polymer interaction studies have been carried out for F/R on the order of mN m^{-1} . For uncoated particles, the interaction force was zero in the long-range region and increased rapidly at $D = 3.0 \mu\text{m}$ when the two particles came into contact with each other. This could be explained to the steric repulsion of the hard spheres and the absence of long-range forces in the system because the surfaces of the particles were covered with a thin layer of SiO_2 . Small negative inclination of the curve at $D = 3.0 \mu\text{m}$ may be due to

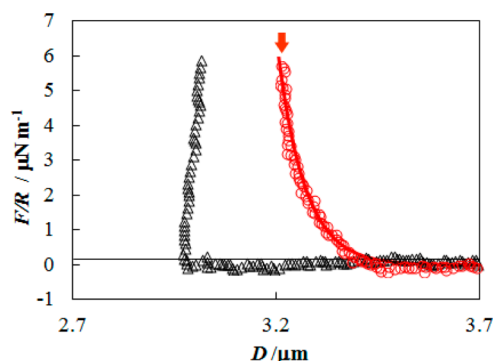


Figure 2. F/R versus D curves in water for Si-from-PMTAC (red open circles) and uncoated silica particles (black open triangles). The solid line indicates the fit with eq 1, and the arrow represents the distance of D_0 .

the minor error in the detector calibration. In contrast, for the PMTAC-coated particles, the increase in force was gradual and occurred at much longer distances.

The electrostatic interaction between two particles of radius R with surfaces homogeneously covered with charged polymer brushes of height H is expressed as^{34,35}

$$F \approx 2\pi R \epsilon \epsilon_0 \kappa \psi_0^2 \exp(-\kappa(L - 2H))$$

$$= \frac{2\pi R \sigma^2 \exp(-\kappa(L - 2H))}{\epsilon \epsilon_0 \kappa} \quad (1)$$

Here, ϵ_0 and ϵ are the permittivities of a vacuum and the medium, and L is the distance between two surfaces. The surface charge density, σ , is related to the Debye length, $1/\kappa$, and the surface potential, ψ_0 , by $\sigma = \epsilon \epsilon_0 \kappa \psi_0$ (Grahame's equation³⁶) under the condition of low surface potential, $\psi_0 < 25$ mV. The fit of eq 1 to the force curve of the PMTAC brush surfaces with the fitting parameters κ , ψ_0 , and H is indicated by a solid line in Figure 2. The experimental and theoretical results showed excellent agreement, demonstrating that the repulsive force at long distances was caused by the electrostatic interaction between polyelectrolyte brush surfaces. When the particles further approached each other ($D < 3.2$ μm), the force between the brush surfaces increased sharply. This probably corresponds to the contact distance of the polymer brushes, D_0 (corresponding to $L - 2H = 0$ in eq 1; see the arrow in Figure 2). The origin of the interaction at $D < D_0$ is complex because, in addition to the electrostatic interactions, the excluded volume effect of polymer chains and counterions becomes dominant. Furthermore, the electrostatic interactions cannot be expressed by eq 1 at this distance, because the charge regulation effect in the brush layer is not negligible.²² Therefore, we focus on distances of $D > D_0$, and the particle–particle distance (x axis) in the force curves is normalized to D_0 to compare the electrostatic interaction without other contributions and to regulate the small particle size distribution.

Figure 3 shows the surface force measurements for Si-from-PMTAC in aqueous NaCl solutions. The gradual increase in the force curves was smaller at higher salt concentrations. The force curves were successfully fitted with eq 1 with the fitting parameters in Table 1. The Debye length obtained from the fitting was larger than that calculated by the Gouy–Chapmann model. For example, according to the model, $1/\kappa = 9.6$ nm at $[\text{NaCl}] = 1$ mM. The difference might reflect the fact that the experimental value of $1/\kappa$ included the charge distribution in

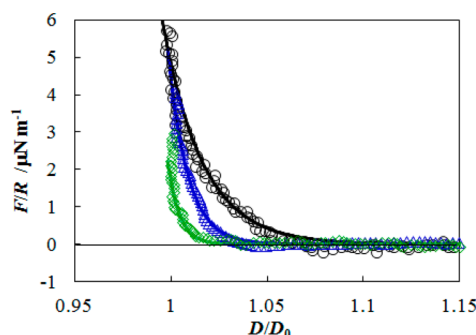


Figure 3. F/R versus the normalized distance D/D_0 for Si-from-PMTAC in aqueous NaCl: (black open circles) $[\text{NaCl}] = 0$ mM, (blue open triangles) $[\text{NaCl}] = 1$ mM, and (green open diamonds) $[\text{NaCl}] = 2$ mM. Solid lines represent the fit by eq 1

Table 1. NaCl Concentration Dependence of the Fitting Parameters for Si-from-PMTAC

	[NaCl] (mM)		
	0	1	2
Debye length, $1/\kappa$ (nm)	66.7	38.5	20.0
surface potential, ψ_0 (mV)	18	12	5.3
surface charge density σ (C m^{-2})	0.19	0.22	0.19

the brush layer as well as the length of the diffusion layer outside the brush. Therefore, we defined it as the apparent Debye length. The apparent Debye length and the surface potential, ψ_0 , decreased with an increasing NaCl concentration because of the screening of the electrostatic interaction by the added salt. The σ values did not depend upon the NaCl concentration, indicating that the change in the brush structure itself was small in this concentration regime. A large decrease in the brush height, from the osmotic brush to the salted brush regime, was observed over $[\text{NaCl}] = 0.1$ M in the Neutron reflectivity measurements.⁸ The σ value was ca. 0.2 C m^{-2} , which was much smaller than that estimated from the TGA measurements. In comparison to 4.8 C m^{-2} , assuming full dissociation of all ionic groups, the degree of dissociation was limited to only 4.0% in the dense polymer brush layer of Si-from-PMTAC. Thus, the majority of chloride counterions were immobilized in the dense polyelectrolyte brush layer to neutralize its high charge density.

Finally, we used dilute Si-to-PMTAC to verify our conclusions more quantitatively. The amount of PMTAC on Si-to-PMTAC was about $1/3$ of that of Si-from-PMTAC. However, only a small difference in the force curves was observed (Figure 4). The values of $1/\kappa$ and ψ_0 obtained from the fitting were 74.1 nm and 11 mV, respectively. The σ value was 0.11 C m^{-2} , which also implies that a large amount of counterions were localized in the brush layer. The degree of dissociation was estimated as 7.0% by comparison to full dissociation and was larger than that of Si-from-PMTAC. The degree of ionic dissociation increased as the grafting density of the polymer at the surface decreased. Our electrostatic force measurements with optical tweezers quantitatively demonstrated that the counterions were immobilized to neutralize the high charge density in the polyelectrolyte brush layer.

CONCLUSION

The electrostatic interactions between the PMTAC brushes grafted to the surface of silica particles were measured in the

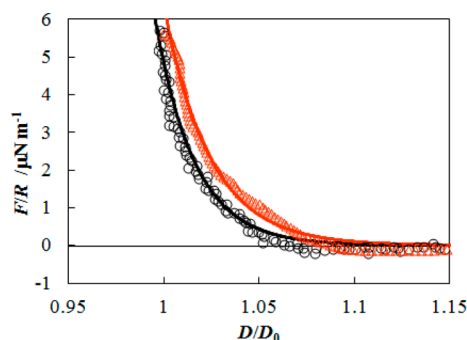


Figure 4. F/R versus the normalized distance D/D_0 in water for Si-from-PMTAC (black open circles) and Si-to-PMTAC (red open triangles).

aqueous media by optical tweezers. The weak electrostatic interactions were successfully detected in the range of a few $\mu\text{N m}^{-1}$. The apparent Debye length and the surface potential obtained by fitting the force curves decreased with an increasing NaCl concentration because of the screening of the electrostatic interaction by the added salt. The surface charge density was estimated to be only 4.0% by comparison to that assuming full dissociation of the polyelectrolyte. Furthermore, an increase in the degree of ionic dissociation was observed when the grafting density of the polymer at the surface was decreased. Thus, our force measurements with optical tweezers quantitatively demonstrated that the majority of the chloride counterions were immobilized in the dense polyelectrolyte brush layer to neutralize its high charge density.

AUTHOR INFORMATION

Corresponding Author

*E-mail: takahara@cstf.kyushu-u.ac.jp.

Notes

The authors declare no competing financial interest.

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