

Structure of Polyelectrolyte Brushes in the Presence of Multivalent Counterions

Jing Yu,^{†,‡} Jun Mao,[†] Guangcui Yuan,^{||,⊥} Sushil Satija,^{||} Zhang Jiang,[§] Wei Chen,^{*,†,‡} and Matthew Tirrell^{*,†,‡}

[†]Institute for Molecular Engineering, University of Chicago, Chicago, Illinois 60637, United States

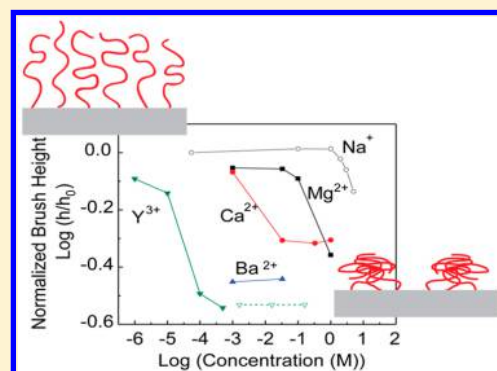
[‡]Materials Science Division and [§]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, United States

^{||}NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, United States

[⊥]Department of Polymer Engineering, The University of Akron, Akron, Ohio 43250, United States

S Supporting Information

ABSTRACT: Polyelectrolyte brushes are of great importance to a wide range of fields, ranging from colloidal stabilization to responsive and tunable materials to lubrication. We synthesized high-density polystyrenesulfonate (PSS) brushes using surface initiated atom transfer radical polymerization and performed neutron reflectivity (NR) and surface force measurements using a surface forces apparatus (SFA) to investigate the effect of monovalent Na⁺, divalent Ca²⁺, Mg²⁺, and Ba²⁺, and trivalent Y³⁺ counterions on the structure of the PSS brushes. NR and SFA results demonstrate that in monovalent salt solution the behavior of the PSS brushes agrees with scaling theory well, exhibiting two distinct regimes: the *osmotic* and *salted* brush regimes. Introducing trivalent Y³⁺ cations causes an abrupt shrinkage of the PSS brush due to the uptake of Y³⁺ counterions. The uptake of Y³⁺ counterions and shrinkage of the brush are reversible upon increasing the concentration of monovalent salt. Divalent cations, Mg²⁺, Ca²⁺, and Ba²⁺, while all significantly affecting the structure of PSS brushes, show strong ion specific effects that are related to the specific interactions between the divalent cations and the sulfonate groups. Our results demonstrate that the presence of multivalent counterions, even at relatively low concentrations, can strongly affect the structure of polyelectrolyte brushes. The results also highlight the importance of ion specificity to the structure of polyelectrolyte brushes in solution.



1. INTRODUCTION

Surface tethered polyelectrolyte brushes are scientifically interesting and technologically relevant to many applications, including colloidal behavior,^{1–5} lubrication,^{6–8} drug and therapeutic delivery,⁹ biological interactions,^{10–12} coatings,^{13,14} and adhesives.^{15–20} Recently, stimuli-responsive polyelectrolyte brushes have also drawn great attention.^{21,22} Understanding the structure of polyelectrolyte brushes under various solution ionic conditions has a significant impact in various applications involving polyelectrolytes.

The polymer brush structure is formed when polymer chains are anchored to surfaces at high tethering densities.²³ With polyelectrolyte brushes, the charge of the monomer segments brings another level of complexity to the system due to not only the long-range electrostatic interactions but also the counterions, which directly interact with the charged monomer segments and play a crucial role in polyelectrolyte chain behaviors. The structure and properties of polyelectrolyte brushes are dramatically influenced by the surrounding environment, e.g., ionic strength, pH, and counterions. For weak (so-called annealed) polyelectrolyte brushes, the degree

of ionization is a function of the solution pH and salt concentration, and a nonmonotonic behavior is observed by both experiments and theory.^{13,14,24}

For (so-called quenched) brushes formed by strong polyelectrolytes, the height of polyelectrolyte brushes is determined from the balance between the osmotic pressure of the counterions and the polyelectrolyte chain elasticity.²⁵ Scaling theory shows that for relatively dense and strongly charged brushes in relatively low ionic strength, the thickness of the brushes is independent of the grafting density and solution ionic strength. This regime is called the *osmotic* regime. In the *osmotic* regime, the thickness of the brush in θ -solvent is given by $h \sim Nf^{0.5}$, where N is the degree of polymerization of the polyelectrolyte chain and f is the fraction of charged monomers. At higher salt concentration, the brushes enter the so-called *salted brush* regime, in which the thickness of the brush follows Alexander Scaling form of the brush thickness in a good

Received: May 20, 2016

Revised: July 10, 2016

Published: July 20, 2016

solvent, $h \sim Nf^{2/3}\sigma^{1/3}C_s^{-1/3}$, where σ is the grafting density and C_s is the solution salt concentration. The existence of the *osmotic* and *salted brush* regimes has been validated experimentally.^{26–28} Scaling theory predicts that the crossover of the two regimes occurs when the solution salt concentration C_s equals the inner concentration of counterions C_i in the brush; however, experimental results show that the transition from the *osmotic* to the *salted brush* regime required addition of only about 15–35% of C_i to the solution due to the phenomenon of counterion condensation.^{27,29}

Besides the ionic strength, the valency of the counterions also plays a critical role in the structure of polyelectrolyte brushes. Polyelectrolyte brushes experience a rapid shrinkage in brush height in the presence of multivalent counterions, which can greatly impact the functionality of the brushes.^{30,31} Considering the common existence of multivalent ions in biological systems and industrial formulations, a deep understanding of this collapsing behavior is of great importance to the field. We have previously shown by surface force apparatus (SFA) measurements on sparsely tethered polystyrenesulfonate (PSS) brushes^{30,32} and by neutron reflectivity (NR) on densely tethered PSS brushes³³ that adding multivalent counterions to the solution, even at very low concentration, induces abrupt shrinkage of the PSS brushes. Strong adhesion force was also measured in our previous SFA experiments between two PSS brushes as a result of multivalent electrostatic bridging between chain segments.^{30,32} Many theoretical works have suggested that entropy is the driving force for the collapse of polyelectrolyte brushes in the presence of multivalent counterions, as the replacement of the monovalent counterions to trivalent counterions reduces the osmotic pressure of the counterions.^{1,31,34} While providing an important contribution to lower the brush height, the osmotic pressure difference is insufficient to fully explain some brush behaviors in the presence of multivalent ions, such as the adhesion force between two brush-coated surfaces measured in our previous SFA experiments.^{1,32} These observations, however, can be explained by introducing a bridging contribution of the polyelectrolyte chains by the multiple charges on the multivalent counterions to a mean field model.³⁵

In this work we used the surface initiated atom transfer radical polymerization method to generate densely tethered PSS brushes. We investigated the structure of PSS brushes in the presence of multivalent counterions, including divalent Ca^{2+} , Mg^{2+} , and Ba^{2+} and trivalent Y^{3+} ions, using a combination of NR and SFA techniques.

2. EXPERIMENTAL SECTION

2.1. Materials. Sodium 4-vinylbenzenesulfonate (SSNa, technical, $\geq 90\%$), (3-aminopropyl)triethoxysilane (APTES, 99%), α -bromoiso-butyl bromide (BIBB, 98%), triethylamine (TEA, $\geq 99\%$), 2,2-bipyridyl (bpy, $\geq 99\%$), Cu(I)Br (99.999%), THF (anhydrous, 99.8%), methanol ($\geq 99.9\%$), sodium nitrate (99%), magnesium nitrate hexahydrate (99%), calcium nitrate tetrahydrate (99%), barium nitrate (99%), and yttrium nitrate hexahydrate (99.8%) were purchased from Aldrich and used without further purification. Single-sided polished silicon wafers (100-oriented, 3 in. diameter, 5 mm thickness) were purchased from University Wafer (Boston, MA). Deionized water was prepared from a Millipore Milli-Q system with a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$.

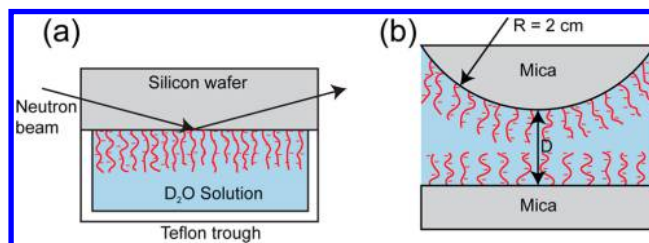
2.2. Synthesis of PSSNa Brushes. The synthesis of PSSNa polymer brush was performed via surface initiated atom transfer radical polymerization (SI-ATRP) using a reported procedure.³³ For silicon surface, a layer of APTES was first deposited onto a piranha cleaned

silicon wafer via vapor deposition. For mica surfaces, the mica surfaces were treated using argon/water vapor plasma for 30 min to create hydroxyl groups on the mica surfaces before the APTES deposition. After annealing, an ATRP initiator, BIBB, was grafted to the APTES monolayer via solution phase deposition using THF as the solvent. SI-ATRP grafting of PSSNa was carried out in a 1:1 mixture of methanol and water solution (50 mL) with SSNa (5 g, 24.2 mmol), Cu(I)Br (35 mg, 0.24 mmol), and bpy (75 mg, 0.48 mmol) dissolved. The SI-ATRP method can give densely tethered PSS brushes with well-controlled brush height. X-ray reflectivity measurements show that the dry thickness of two PSS brushes used in our neutron reflectivity study are 24 and 25 nm (S Figure 1 and S Figure 2). The total dry thickness of two PSS brushes on mica surface is around 7 nm. The grafting density of the PSS brush is estimated to be about 0.1 chain/ nm^2 on silicon surfaces and 0.025 chain/ nm^2 on mica surfaces (Supporting Information). Mica is significantly more inert than silicon, and therefore the difference in polymer grafting density is expected.

2.3. X-ray Reflectivity. X-ray reflectivity measurements were conducted to measure the thickness of dry PSSNa films using a Bruker, D8 Advance X-ray reflectometer employing Cu $K\alpha$ radiation at National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) (Gaithersburg, MD). The copper source was operated at 40 kV and 40 mA, and the wavelength was 0.154 nm. The beam width was 10 mm, and the beam height was 0.1 mm.

2.4. Neutron Reflectivity. Neutron reflectivity (NR) measurements were performed at NCNR NIST on the NG7 horizontal reflectometer using an in-house-designed sample chamber, as shown in Scheme 1a. The reflected intensity was measured as a function of

Scheme 1. Geometries of (a) Neutron Reflectivity and (b) Surface Forces Apparatus Measurements on PSS Brushes



momentum transfer vector $[q_z = (4\pi \sin(\theta))/\lambda]$, where θ is the incident angle and $\lambda = 0.475$ nm is the neutron wavelength. D_2O was used in all the NR experiments. The statistical error bars for reflectivity curves correspond to one standard deviation.

2.5. Reflectivity Data Analysis. Fitting of the neutron reflectivity data was achieved using a box model using MatLab. A custom model was developed for data analysis, whereby the PSS brush is split into three regions for the data sets from NaNO_3 , $\text{Mg}(\text{NO}_3)_2$, and $\text{Ca}(\text{NO}_3)_2$ solutions and five regions for the data sets from $\text{Ba}(\text{NO}_3)_2$ and $\text{Y}(\text{NO}_3)_3$ solutions. A subphase and an incident medium are also required. Each of these regions is described by a thickness, roughness, and scattering length density (SLD) parameter.

2.6. Surface Forces Apparatus. The interaction between two PSS brushes grafted on mica surfaces was measured using a surface forces apparatus 2000 (SFA2000, SurForce LLC). Freshly cleaved mica sheets ($\sim 2\text{--}5\ \mu\text{m}$) were glued to cylindrical glass disks ($R = 2$ cm) using UV-curable optical glue. The synthesis of PSS brush on mica surface is described in section 2.2. Interaction between two PSS brushes in solution was measured as a function of the distance between apposing mica surfaces in a cross-cylinder geometry (Scheme 1b), which is equivalent to a spherical surface on a flat surface. The approach and separation speed of our SFA measurements is about 4 nm/s. Upon changing solutions, the old solution in the SFA chamber was completely drained, and the SFA chamber was then flushed with the new solution three times to fully remove the old solution. All solutions were prepared using Milli-Q water with a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$.

3. RESULTS

3.1. Shrinkage of PSS Brushes in Monovalent Salt Solution. We employed neutron reflectivity (NR) to investigate the structures of PSSNa brushes with different concentrations (pure D₂O, 1 mM, 100 mM, 1 M, 2 M, 3 M, and 5 M) of monovalent NaNO₃ salt in D₂O solution. Here 1 M = 1 mol/L. For all the conditions measured, none of the NR spectra show clear interference fringes due to a diffused interface.³³ The almost identical NR spectra (Figure 1a and S

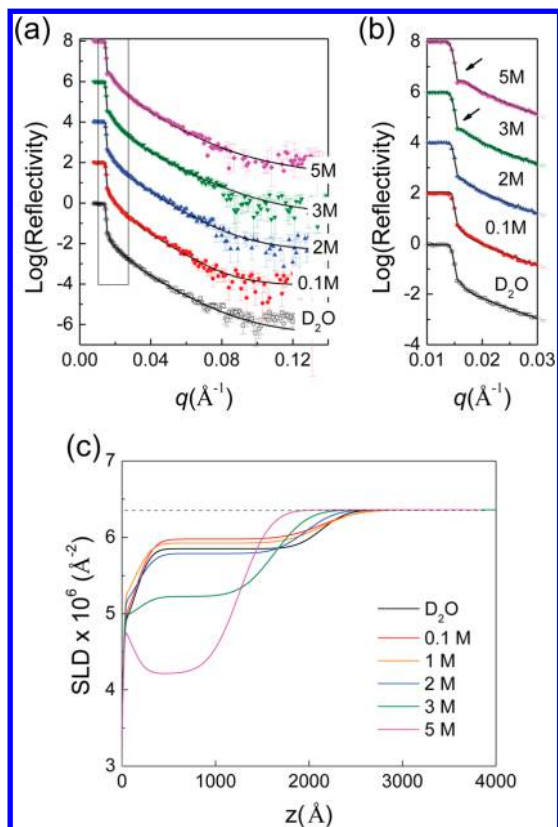


Figure 1. Neutron reflectivity of PSS brushes in the presence of monovalent salt, NaNO₃. (a) NR spectra of a PSS brush (dry film thickness 25 nm) in D₂O and in NaNO₃ solutions with different salt concentrations. The reflectivity profiles are shifted for the clarity of the presentation. (b) Enlarged NR spectra at the low q range. The arrows indicate the changes observed only at very high salt concentrations, 3 and 5 M. (c) Scattering length densities (SLDs) of the PSS brush in D₂O and in NaNO₃ solutions obtained from the best fittings of the NR data presented.

Figure 3) measured at different salt concentrations indicate that the structure of the PSS brushes does not change significantly up to a salt concentration of 2 M. A noticeable change at the low q range of the NR spectra is measured on the NR spectra upon increasing the salt concentration to 3 M, and the change became more pronounced in 5 M NaNO₃ solution, as shown by the arrows in Figure 1b. The best-fitted scattering length density (SLD) profiles (Figure 1c) of the brush reveal that the brush height remains as a constant in NaNO₃ solutions with up to 2 M monovalent salt. Above 2 M, the brush height decreases upon further increasing salt concentration.

The SLD obtained from fitting is a function of the solvent (D₂O), the PSS polymer, and the added salt: $\rho = \rho_s V_s + \rho_p V_p + \rho_c V_c$ in which ρ_s , ρ_p , and ρ_c are the scattering length density of D₂O, PSS, and Na⁺, respectively. V_s , V_p , and V_c are the volume

fraction of D₂O, PSS, and Na⁺, respectively. We are not able to unambiguously obtain the volume fraction profile of the PSS polymer due to (1) the strongly coupled density profiles of the PSS brush and the counterions and (2) nonideal mixture of three components in solution, which renders the additivity relationship of the scattering length density inaccurate. The latter factor becomes more pronounced upon adding multivalent counterions, which we will discuss in later sections. We therefore plot the SLD profiles obtained from fittings instead of the volume fraction of the polymer in this paper. Despite not being able to extract the volume fraction of the PSS brush, the SLD can still give quantitative information on the PSS polymer volume fraction in the brush, which is critical for resolving the structure of PSS brushes in different solution conditions. All the SLDs have a parabolic form, indicating that the volume fraction profiles of the PSS brush in monovalent NaNO₃ solutions are also parabolic. This agrees with the density profile of a polymer brush given by the self-consistent field theory.³⁶

We performed surface force apparatus (SFA) experiments to measure the interactions between two PSS brushes in NaNO₃ solutions with different salt concentrations to further explore the effect of monovalent salt to the structure change of the PSS brushes.³⁷ The dry thickness of the two PSS brushes is about 7 nm, which means that the thickness of each PSS brush is around 3.5 nm. The measured forces between two PSS brushes are purely repulsive for both compression and separation (Figure 2). At each particular salt concentration, the

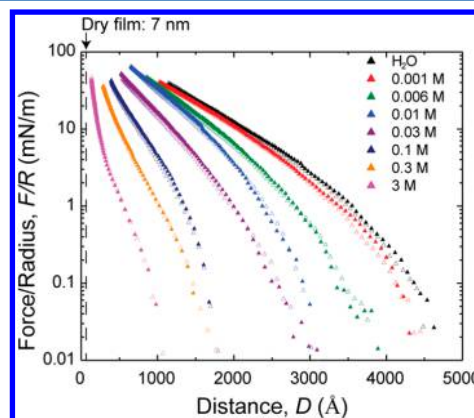


Figure 2. SFA force–distance profiles measured during compressing and separating two identical PSS brushes in D₂O and in NaNO₃ salt solutions with different salt concentrations. Solid data points represent forces upon compression, and open data points were measured upon separation (this is the same for all surface force figures).

compression curve overlaps the separation curve very well, indicating that no appreciable hysteresis is observed in any of these experiments. The force profiles clearly show the influence of the external salt on the conformation of the PSS brush. The range of repulsion is almost a constant (~400 nm) at very low NaNO₃ concentration (below 1 mM), evident of the *osmotic* regime. As the NaNO₃ concentration increases, the interaction range decreases, which is a sign of the shrinkage of PSS brushes in solutions of high NaNO₃ concentrations. The grafting density of the PSS chain on the mica surface is much lower than on the silicon surface, and therefore the *osmotic* to *salted brush* transition happens at a much lower salt concentration.

To examine the scaling relationship between brush height and salt concentration, we plot the brush height versus NaNO₃ concentration measured by both NR and SFA in a log–log plot.

For NR data, we take the distance at which the SLD value is $6.2 \times 10^{-6} \text{ \AA}^{-2}$ as the brush height; for the SFA data, we take the distance at which a significant amount of repulsion (1 mN/m) is measured as the thickness of two PSS brushes, and the brush height is half of this distance. Figure 3 clearly demonstrates that

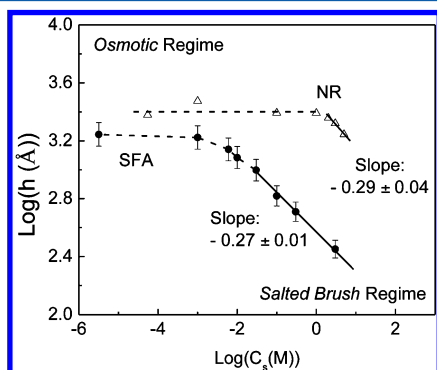


Figure 3. Salt concentration dependence of the brush height measured by both NR and SFA. The data are plotted in a log–log scale.

both NR and SFA data sets show the *osmotic* brush and *salted* brush regime. The brush height is nearly a constant and independent of the bulk NaNO_3 concentration in the *osmotic* brush regime at low salt concentration. While in the *salted* brush regime, above 0.03 M for the brushes used in SFA measurements and 2 M for the brush used in NR study, the

brush height shrinks linearly upon the addition of NaNO_3 in the log–log plot. The slope of the linear regime is -0.29 ± 0.04 for brush heights obtained from NR fitting and -0.27 ± 0.01 for SFA results. Both values are close to the $-1/3$ value given by the scaling law.

3.2. Effect of Trivalent Counterions. The presence of multivalent counterions can cause abrupt change in the structure of polyelectrolyte brushes. We performed a series of titration experiments to investigate the effect of trivalent cation, Y^{3+} , to the structure of the PSS brush using NR. We fixed the total ionic strength and varied the Y^{3+} content by adjusting the mixing ratio of Y^{3+} and Na^+ .³² We first measured the NR in 6 mM NaNO_3 as the reference (Figure 4a). The NR spectra do not show interference fringes due to a diffused interface. After adding 0.001 and 0.01 mM Y^{3+} to the solution, few changes in the NR are measured. Clear neutron interference fringes appear in the reflectivity spectra upon increasing the Y^{3+} concentration to 0.1 mM, indicative of the brush structure becoming less diffused. The interference fringes stayed almost the same when further increasing Y^{3+} concentration to 0.5 mM.

The best-fitted SLD profiles of the titration experiment (Figure 4b) show that the thickness of the PSS brush shrinks continuously with increasing the Y^{3+} concentration in solution. In solutions of 0.001 and 0.01 mM Y^{3+} , SLDs indicate that the volume profiles of the PSS brush have a parabolic form. However, the structure of the PSS brush undergoes an abrupt change upon increasing the Y^{3+} concentration from 0.01 to 0.1 mM. The brush height collapses from about 300 to 80 nm, and

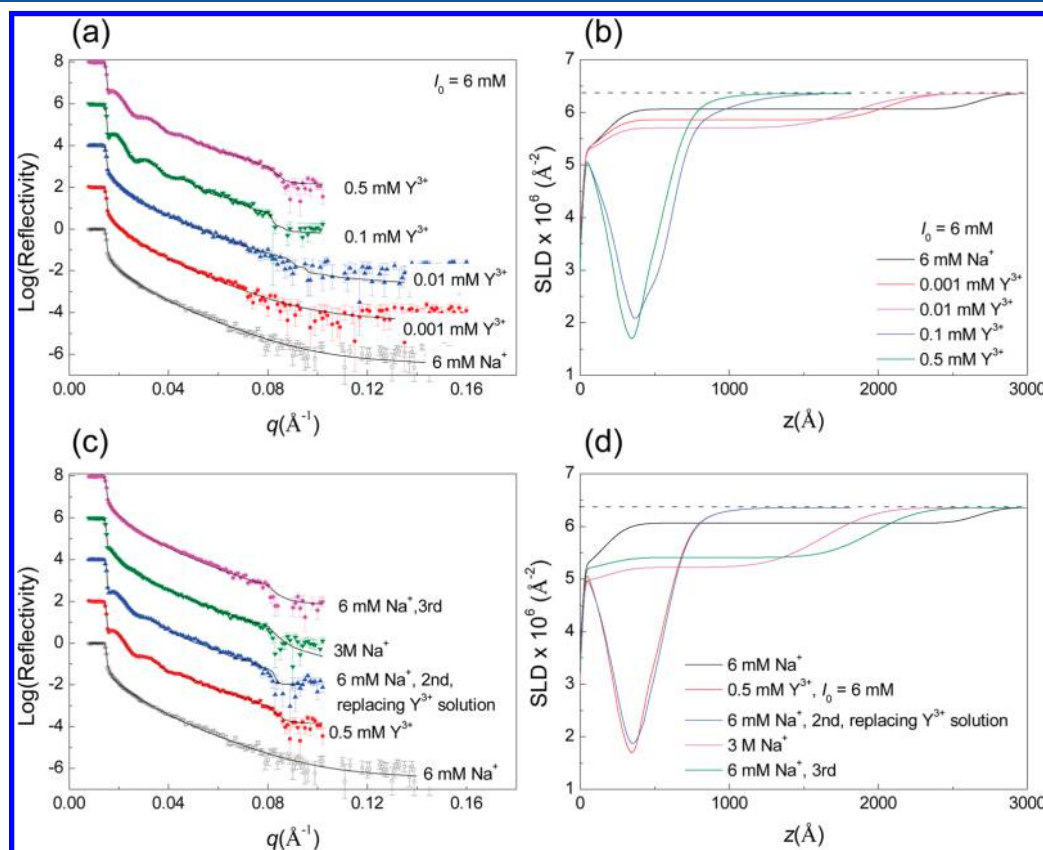


Figure 4. NR measurements on PSS brushes in the presence of Y^{3+} . (a) NR of a PSS brush in the presence of different concentrations of trivalent Y^{3+} ions at a fixed solution ionic strength $I_0 = 6 \text{ mM}$. (b) SLD profiles obtained from the best fittings of NR data presented in (a). (c) NR of the PSS brush before and after the reversible uptake and release of Y^{3+} . (d) SLD profiles obtained by the best fittings of Y^{3+} reversible uptaken NR data presented in (c).

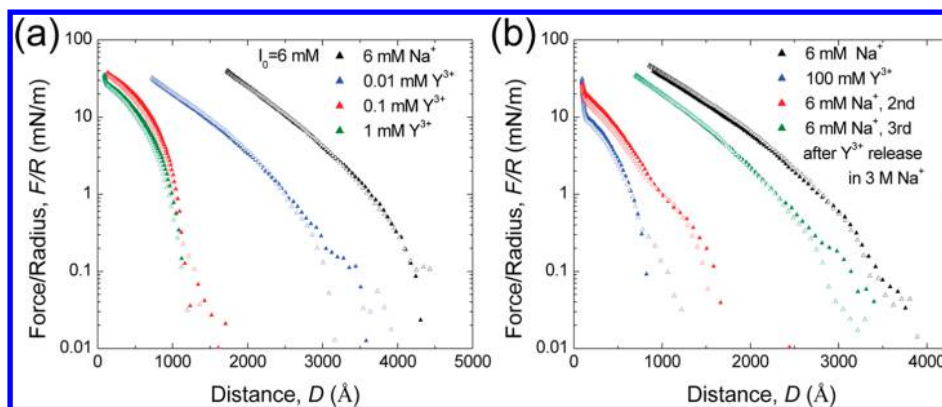


Figure 5. Surface forces apparatus measurements on interactions between two PSS brushes in the presence of Y^{3+} cations. (a) Force–distance profiles of two PSS brushes in 6 mM Na^+ , 0.01 mM Y^{3+} , 0.1 mM Y^{3+} , and 1 mM Y^{3+} solutions. The total ionic strength of the solutions is fixed to 6 mM by adding an additional amount of NaNO_3 . (b) Force–distance profiles of two PSS brushes before and after the release of Y^{3+} cations.

the shape of the SLD profile is not parabolic anymore. A peak of the scattering length density arises near the middle of the film, demonstrating that the concentration of PSS segment is the highest near the center. The SLD of the PSS brush in 0.5 mM Y^{3+} solution becomes more Gaussian-like with a peak value roughly at the center of the collapsed film.

The structural change of PSS brush introduced by Y^{3+} is reversible. After introducing the collapse of the brush by adding 0.5 mM Y^{3+} , the brush stayed in the collapsed state even when removing the Y^{3+} in bulk solution by replacing the bulk solution with a 6 mM NaNO_3 solution (Figure 4c). However, after immersing the collapsed brush in a solution of 3 M NaNO_3 for 30 min, the NR measured is almost identical to that from a PSS brush in a solution of 3 M NaNO_3 without any Y^{3+} exposure (S Figure 4). Upon lowering the NaNO_3 concentration to 6 mM, the brush returns to its extended state as indicated by NR. SLD profiles reveal that the PSS brush shrinks from 250 to 80 nm after adding 0.5 mM Y^{3+} (Figure 4d). Again, the SLDs show Gaussian-like profiles (Figure 4d), indicative of a Gaussian-like profile of the PSS density in the collapsed state. Upon immersing the collapsed brush into a 3 M NaNO_3 solution, the brush height increases to 180 nm. Further decreasing the NaNO_3 concentration to 6 mM increases the brush height to about 200 nm.

Introducing trivalent Y^{3+} cations dramatically changes the interactions between the PSS brushes in solution. Figure 5a shows that at a fixed ionic strength, $I_0 = 6$ mM, a repulsive force is measured at a distance of about 400 nm between two PSS brushes in NaNO_3 solution. After replacing the NaNO_3 solution with a solution containing 0.01 mM $\text{Y}(\text{NO}_3)_3$ and 5.94 mM NaNO_3 , the repulsion range decreases to 260 nm. The repulsion range further decreases upon increasing the concentration of Y^{3+} in solution to 0.1 mM. In contrast to the sparsely tethered PSS brushes, the measured forces between two PSS brushes in the presence of Y^{3+} are purely repulsive during the compression–separation cycle. However, in the presence of 0.1 and 1 mM Y^{3+} , small hysteresis is measured between the compression and separation force curves. This small hysteresis is an indication of attractive interactions between the sulfonate groups and Y^{3+} ions, possibly due to bridging introduced by Y^{3+} . The lack of adhesion measured during the separation is possibly due to the effect of a high grafting density of the PSS brushes generated via SI-ATRP used in this study. The grafting density is of great importance to the interaction between two polyelectrolyte brushes and their functionality. At high grafting

densities, it becomes more difficult for the interpenetration of the polyelectrolyte chains from two brushes. This chain interpenetration can increase the chance of multivalent counterion-mediated interchain bridging between two brushes and therefore gives rise to adhesion.^{38,39}

Surface force measurements also reveal the reversible uptake and release of Y^{3+} ions by PSS brushes in solution (Figure 5b). Upon adding 100 mM $\text{Y}(\text{NO}_3)_3$ into the solution, the repulsion range of the force profile decreases from 350 to 80 nm. The repulsion range increases to about 150 nm after removing the Y^{3+} from the bulk solution by replacing the $\text{Y}(\text{NO}_3)_3$ solution with a 6 mM NaNO_3 solution, indicating that a certain portion of the Y^{3+} ions taken up by the PSS brushes stays within the brushes even when removing the free Y^{3+} in the solution. However, after immersing the two PSS brushes in a 3 M NaNO_3 solution for half an hour and then repeating the same measurement in a 6 mM NaNO_3 solution, the repulsion range was shifted out to about 300 nm, which is very close to the range of repulsion measured from two PSS brushes without exposure to Y^{3+} (350 nm). The recovery of the brush height indicates that the trivalent yttrium counterions taken up by the PSS brush are mostly released to the bulk solution when immersing the brush into a solution containing high concentration of monovalent salt.

3.3. Effect of Divalent Counterions. We compared the effect three divalent cations, Mg^{2+} , Ca^{2+} , and Ba^{2+} , with the same anion, NO_3^- , to the structure of PSS brushes. NR of the PSS brush is first measured in a 3 mM NaNO_3 solution as a reference. Dramatic differences are observed on the reflectivity spectra of the PSS brush in solutions of the three cations. For Mg^{2+} (Figure 6a), no significant changes in NR are measured in Mg^{2+} concentrations of 1, 33, and 100 mM. Noticeable changes are only measured at the highest concentration investigated, 1000 mM Mg^{2+} . Best-fitted SLD profiles show that brush height decreases with increasing Mg^{2+} concentration with a trend similar to that measured in NaNO_3 solutions (Figure 6d). During the shrinkage of the brush in $\text{Mg}(\text{NO}_3)_2$ solutions, the PSS density profiles have parabolic forms. Ca^{2+} in solution causes more pronounced changes to PSS brushes at the same concentrations. Interference fringes on NR spectra are measured in a solution of 33 mM Ca^{2+} . The fringes become clearer at higher Ca^{2+} concentrations (333 and 1000 mM) (Figure 6b). SLD profiles (Figure 6e) suggest that the PSS brush undergoes a structural change from a swollen state to a collapsed state. The peak in the SLD profiles at collapsed state

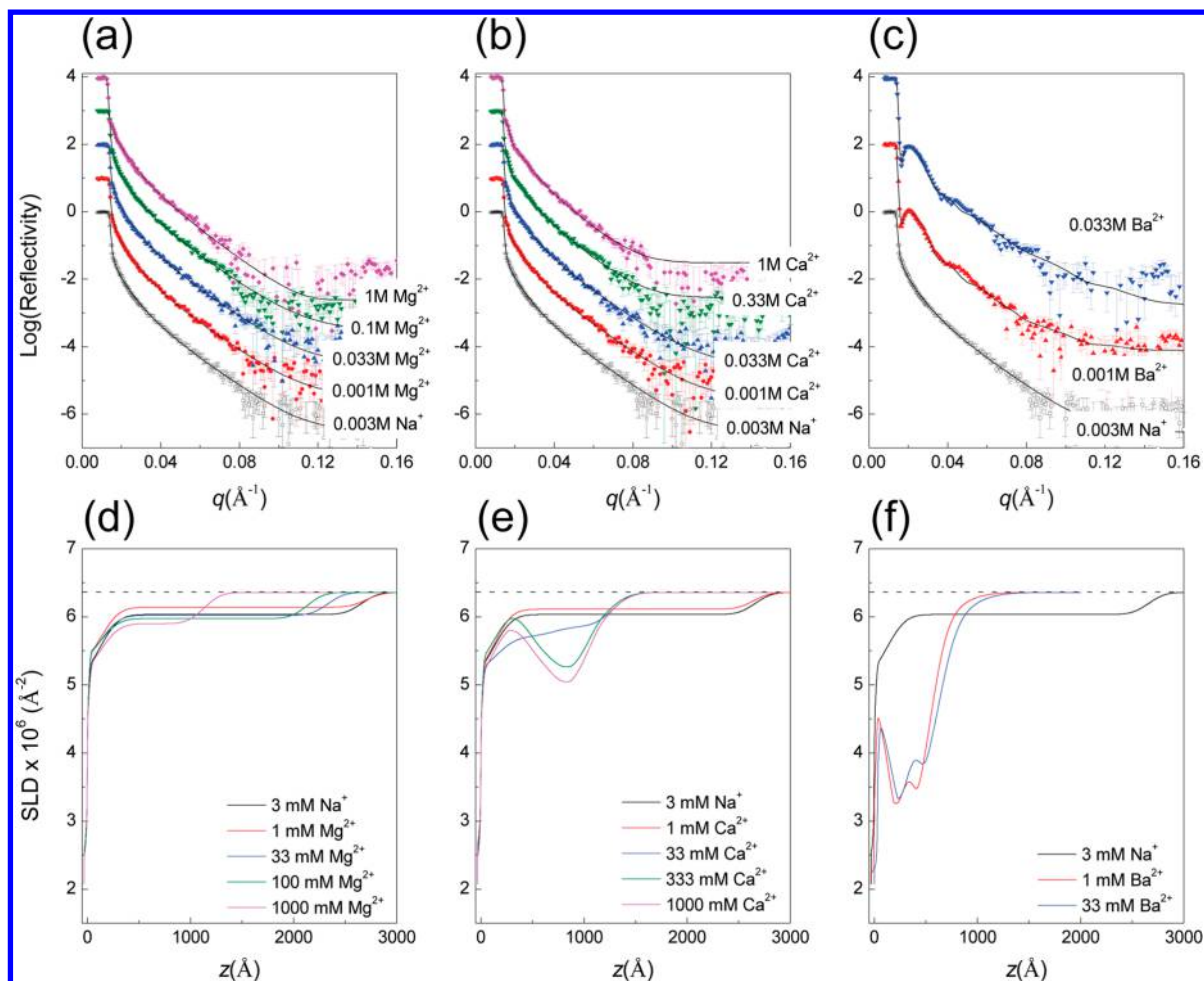


Figure 6. NR of a PSS brush (28 nm dry film thickness) in the presence of divalent cations Mg^{2+} , Ca^{2+} , and Ba^{2+} at different concentrations. NR of the PSS brush in in D_2O solutions of (a) 3 mM NaNO_3 , 1 mM, 33 mM, 100 mM, and 1000 mM $\text{Mg}(\text{NO}_3)_2$; in solutions of (b) 3 mM NaNO_3 , 1 mM, 33 mM, 333 mM, and 1000 mM; and in solutions of (c) 3 mM NaNO_3 , 1 mM, and 33 mM $\text{Ba}(\text{NO}_3)_2$. (d), (e), (f) SLD profiles of the PSS brush obtained from fitting the data presented in (a), (b), and (c), respectively.

suggests that the volume fraction of PSS in the brush is not uniform after the collapse induced by Ca^{2+} . The shapes of the SLDs are very similar to these from the collapsed PSS brush in the presence of Y^{3+} . Ba^{2+} has the most dramatic effect on inducing the structural change of the PSS brush (Figure 6c). Interference fringes are measured immediately upon adding 1 mM Ba^{2+} into the solution. Increasing the Ba^{2+} concentration to 33 mM does not significantly change the reflectivity spectra. Because of the relatively low solubility of $\text{Ba}(\text{NO}_3)_2$ (less than 100 mM), we did not conduct NR measurements at higher Ba^{2+} concentrations. SLD profiles (Figure 6f) again suggest that the PSS brush collapses into a denser layer, and the volume fraction of a collapsed PSS does not have a parabolic form. For the Ba^{2+} data, we had to include two additional layers in our fitting model to get an excellent fitting of the NR spectra, which gives two peaks in the best-fitted SLD profile. We are not sure about the physical meaning of the two peaks in the SLD profile, but in any sense, it does not affect the overall conclusion that the structure of the PSS brush in the presence of Ba^{2+} is very different from the structures of a PSS in Mg^{2+} and Ca^{2+} solutions.

4. DISCUSSION

4.1. Effect of the Multivalent Counterions. We summarize the normalized PSS brush height h/h_0 versus the concentration of all the multivalent counterions investigated in this work and in our previous NR work³³ using the same type of PSS brush in a log–log scale in Figure 7. The concentration required to induce the shrinkage of PSS brushes is reduced by 5 orders of magnitude as the valency of the counterions goes from monovalent to trivalent, emphasizing the role of multivalent counterions on the structure of polyelectrolyte brushes. The three divalent counterions show a more complicated picture, which highlights the importance of ion specificity, as less than 1 mM Ba^{2+} can cause the collapse of a PSS brush, whereas the value for Mg^{2+} is between 0.1 and 1 M, differing by at least 2 orders of magnitude. We will come back to this ion specificity later.

The SLD profiles of collapsed PSS brushes reveal that multivalent counterions can lead to two different collapse structures. In the presence of Mg^{2+} , the brush shrinks as a function of salt concentration. This is very similar to the height change of a PSS brush in monovalent NaNO_3 solutions. In solutions of both salts, the SLD profiles (Figures 1 and 6d) indicate that the polymer density profile has a parabolic form, which agrees with the self-consistent field theory.³⁶ However, in

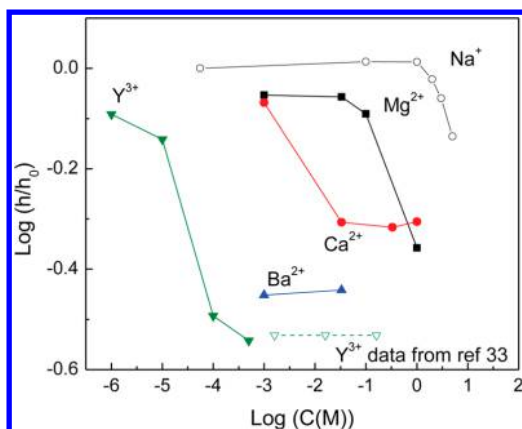


Figure 7. Normalized brush height h/h_0 measured by NR plotted against the concentration of cations with different valencies, Na^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , and Y^{3+} , in a log–log scale. The open triangle Y^{3+} data are taken from ref 33. The solid lines are guides to the eye. The brush heights are normalized by (1) brush height of the PSS brush in D_2O for the data taken in NaNO_3 solutions, (2) brush height of the PSS brush in 3 mM NaNO_3 solutions for the data taken in $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, and $\text{Mg}(\text{NO}_3)_2$ solutions, and (3) the height of the PSS brush in 6 mM NaNO_3 solution for data taken in $\text{Y}(\text{NO}_3)_3$ solutions.

the presence of Ca^{2+} , Ba^{2+} , and Y^{3+} , the SLD profiles (Figures 4 and 6e,f) point to a very different structure for the collapsed brushes. Instead of a parabolic form, the shape of the SLD is close to a Gaussian function. The presence of multivalent counterions leads effectively to a decrease of the solvent quality.⁴⁰ Zhulina et al. have suggested that in poor solvents polymer brushes can collapse into pinned micelles, which have a density profile similar to the one suggested by the SLD profiles of our measurements.^{41,42} Similar polymer density profiles have also been observed in molecular dynamics (MD) simulations^{43,44} and density functional theory (DFT) calculations³⁴ for polyelectrolyte brushes in the presence of trivalent counterions. We believe this uneven shrinkage of the PSS brush is due to a combined effect of the diffusion of multivalent counterions into the PSS brush layer and the cross-linking of the PSS segments induced by the multivalent counterions. As the Y^{3+} ions diffuse into the brush layer, they start to introduce

electrostatic cross-linking among the nearby PSS segments. The cross-links give rise to geometric constraints to the PSS chains, which can lead to the pinned micelle structure, as shown in Figure 8b.

4.2. Reversal Uptake and Release of Multivalent Counterions. Our NR and SFA results unambiguously show that the reversible change of the PSS brush structure is caused by a reversible uptake and release of multivalent counterions upon changing solution ionic environment, as shown in Figure 8. When the ionic strength of the solution environment is low, the PSS brush takes up the Y^{3+} ions (and other multivalent cations), causing the collapse of the brush. At high concentrations of monovalent salt, the Y^{3+} ions get released from the PSS brush, and the PSS brush recovers its height, as shown in Figure 8c. Although we mainly used Y^{3+} to demonstrate this reversible uptake, the general conclusion also holds for Ca^{2+} (S Figure 5) and other divalent cations investigated in this work. Previously, we have shown other trivalent ions, including $\text{Ru}(\text{NH}_3)_6^{3+}$ and La^{3+} , can also be reversibly taken up and released by physisorbed, sparsely tethered PSS brushes.³² This reversible uptake mechanism not only shows the importance of multivalent counterions to the structure of polyelectrolyte brushes but also demonstrates the potential of creating multivalent counterion mediated stimulate-responsive materials.

4.3. Importance of Ion Specificity. We observed strong ion specific effects with the divalent cations to the structure of PSS brushes. SLD profiles shown in Figure 9 reveal that the PSS brush is in the swollen state in 33 mM Mg^{2+} , whereas the brush is in the collapsed state in 33 mM Ba^{2+} . The dramatic differences in the NR spectra (Figure 6a–c) and SLD (Figure 9) profiles of the PSS brush in Mg^{2+} , Ca^{2+} , and Ba^{2+} solutions with the same concentration strongly suggest that the collapse of PSS brushes in the presence of divalent cations is not purely entropic. While the ion exchange process between the monovalent counterions and divalent counterions is driven entropically, the enthalpic binding strength between the sulfonate group and the divalent cation is of great importance to the structural change of the PSS. The significance of the binding strength between cations and anions is often ignored in many polyelectrolyte models based on Poisson–Boltzmann or

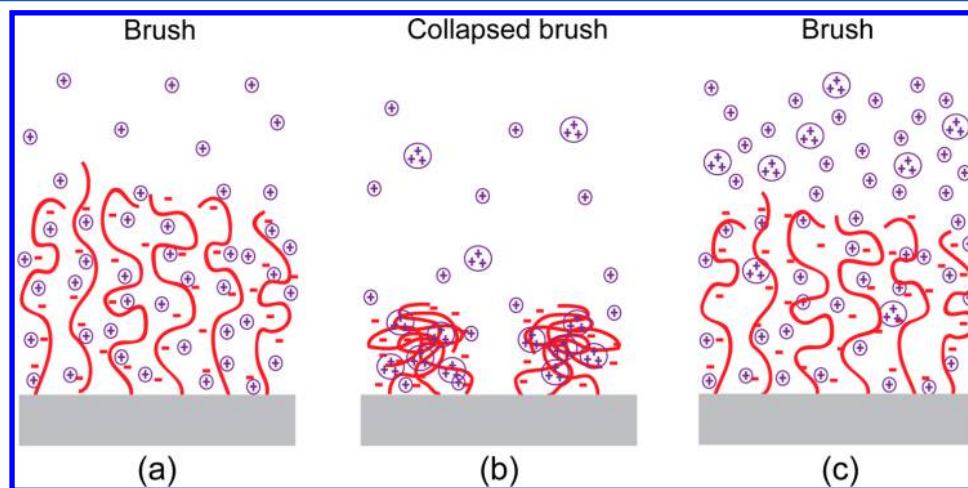


Figure 8. Through adjusting the external salt environment surrounding end-tethered polyelectrolyte chains, a polyelectrolyte brush can transition from an extended brush structure (a) to a pinned micelle-like structure (b) and to an extended brush again at high concentration of monovalent salt (c).

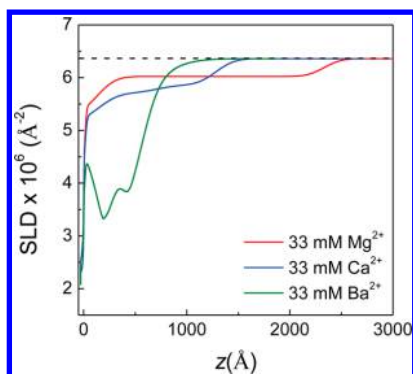


Figure 9. Comparisons between SLD of the PSS brush in 33 mM Mg^{2+} , Ca^{2+} , and Ba^{2+} .

Debye–Hückel theories, which treat ions as point charges and only take into account the electrostatic interactions between the ions.^{24,31,45}

Naturally, the valence state of the counterions plays a significant role in behaviors of polyelectrolytes. There are however, other factors that come into play, such as the sizes and charge densities of the counterions as well as their corresponding hydration radii.⁴⁶ The tendency of the three divalent cations in introducing structural change of the PSS brushes follows the trend of ionic radii: $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Ba}^{2+}$. Specific ion effects are ubiquitous in chemistry and biology. Ions in the Hofmeister series exhibit different ability to dissolve or precipitate proteins.^{47,48} Anomalous X-ray reflectivity measurements have shown the different divalent cations can adsorb on mineral surfaces very differently.⁴⁹ Surface force measurements by SFA and atomic force microscopy (AFM) have also observed ion specific effects on mica surfaces, phospholipid membranes, and DNAs.^{50–53} Many of these effects are related to the size of the ions, and the ion hydration that may strongly influence the cation–anion interaction.^{47,49,53} Our NR results clearly show the importance of ion specificity, yet our understanding on the specific ion effect on the structure of polyelectrolyte brushes is in its infancy. There still remains a great deal to be learned from this important subject.

5. CONCLUSION

We have systematically investigated the effects of monovalent, divalent, and trivalent counterions on the structure of densely tethered PSS brushes generated from SI-ATRP. Our NR and SFA results unambiguously show that PSS polyelectrolyte brushes are able to reversibly change from an extended state to a collapsed state in the presence of multivalent counterions. Divalent cations, including Mg^{2+} , Ca^{2+} , and Ba^{2+} , show strong ion specific effects that relate to the specific interactions between the positively charged cations and the negatively charged sulfonate groups. Our results demonstrate that the structure of polyelectrolyte brushes can be tuned by the reversible uptake and release of different multivalent counterions and highlight the importance of ion specificity to the structure of polyelectrolyte brushes in solution. We believe that this work can have a significant impact in a wide range of applications involving polyelectrolytes, ranging from colloidal systems to responsive and tunable materials to drug delivery, especially in media containing multivalent ions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b01064.

S Figure 1 to S Figure 5 (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail wchen@anl.gov (W.C.).

*E-mail mtirrell@uchicago.edu (M.T.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Science, Program in Basic Energy Sciences, Division of Materials Science and Engineering. The identification of commercial products does not imply endorsement by the National Institute of Standards and Technology nor does it imply that these are the best for the purpose.

■ REFERENCES

- (1) Mei, Y.; Lauterbach, K.; Hoffmann, M.; Borisov, O. V.; Ballauff, M.; Jusufi, A. Collapse of spherical polyelectrolyte brushes in the presence of multivalent counterions. *Phys. Rev. Lett.* **2006**, 97, 158301.
- (2) Schneider, C.; Jusufi, A.; Farina, R.; Li, F.; Pincus, P.; Tirrell, M.; Ballauff, M. Microsurface potential measurements: Repulsive forces between polyelectrolyte brushes in the presence of multivalent counterions. *Langmuir* **2008**, 24, 10612.
- (3) Schneider, C.; Jusufi, A.; Farina, R.; Pincus, P.; Tirrell, M.; Ballauff, M. Stability behavior of anionic spherical polyelectrolyte brushes in the presence of La(III) counterions. *Phys. Rev. E* **2010**, 82, 011401.
- (4) Schaller, C.; Schauer, T.; Dirnberger, K.; Eisenbach, C. D. Synthesis and stabilizing properties of amphipolar polyelectrolytes. *Eur. Phys. J. E: Soft Matter Biol. Phys.* **2001**, 6, 365.
- (5) Guenoun, P.; Argillier, J. F.; Tirrell, M. End-tethered charged chains at surfaces. *C. R. Acad. Sci., Ser. IV: Phys., Astrophys.* **2000**, 1, 1163.
- (6) Chen, M.; Briscoe, W. H.; Armes, S. P.; Klein, J. Lubrication at Physiological Pressures by Polyzwitterionic Brushes. *Science* **2009**, 323, 1698.
- (7) Klein, J. Repair or replacement-A joint perspective. *Science* **2009**, 323, 47.
- (8) Klein, J.; Kamiyama, Y.; Yoshizawa, H.; Israelachvili, J. N.; Fredrickson, G. H.; Pincus, P.; Fetters, L. J. Lubrication Forces between Surfaces Bearing Polymer Brushes. *Macromolecules* **1993**, 26, 5552.
- (9) Yu, Y. C.; Berndt, P.; Tirrell, M.; Fields, G. B. Self-assembling amphiphiles for construction of protein molecular architecture. *J. Am. Chem. Soc.* **1996**, 118, 12515.
- (10) Tugulu, S.; Arnold, A.; Sielaff, I.; Johnsson, K.; Klok, H.-A. Protein-Functionalized Polymer Brushes. *Biomacromolecules* **2005**, 6, 1602.
- (11) Andruzzi, L.; Senaratne, W.; Hexemer, A.; Sheets, E. D.; Ilic, B.; Kramer, E. J.; Baird, B.; Ober, C. K. Oligo(ethylene glycol) Containing Polymer Brushes as Bioselective Surfaces. *Langmuir* **2005**, 21, 2495.
- (12) Senaratne, W.; Andruzzi, L.; Ober, C. K. Self-assembled monolayers and polymer brushes in biotechnology: Current applications and future perspectives. *Biomacromolecules* **2005**, 6, 2427.
- (13) Gong, P.; Wu, T.; Genzer, J.; Szeleifer, I. Behavior of surface-anchored poly(acrylic acid) brushes with grafting density gradients on solid substrates: 2. Theory. *Macromolecules* **2007**, 40, 8765.

- (14) Wu, T.; Gong, P.; Szeleifer, I.; Vlcek, P.; Subr, V.; Genzer, J. Behavior of surface-anchored poly(acrylic acid) brushes with grafting density gradients on solid substrates: 1. Experiment. *Macromolecules* **2007**, *40*, 8756.
- (15) Stuart, M. A. C.; Huck, W. T. S.; Genzer, J.; Muller, M.; Ober, C.; Stamm, M.; Sukhorukov, G. B.; Szeleifer, I.; Tsukruk, V. V.; Urban, M.; Winnik, F.; Zauscher, S.; Luzinov, I.; Minko, S. Emerging applications of stimuli-responsive polymer materials. *Nat. Mater.* **2010**, *9*, 101.
- (16) Ito, Y.; Nishi, S.; Park, Y. S.; Imanishi, Y. Oxidoreduction-sensitive control of water permeation through a polymer brushes-grafted porous membrane. *Macromolecules* **1997**, *30*, 5856.
- (17) Park, Y. S.; Ito, Y.; Imanishi, Y. pH-controlled gating of a porous glass filter by surface grafting of polyelectrolyte brushes. *Chem. Mater.* **1997**, *9*, 2755.
- (18) Ayres, N.; Boyes, S. G.; Brittain, W. J. Stimuli-responsive polyelectrolyte polymer brushes prepared via atom-transfer radical polymerization. *Langmuir* **2006**, *23*, 182.
- (19) Kumar, S.; Dory, Y. L.; Lepage, M.; Zhao, Y. Surface-grafted stimuli-responsive block copolymer brushes for the thermo-, photo- and pH-sensitive release of dye molecules. *Macromolecules* **2011**, *44*, 7385.
- (20) Mei, Y.; Lu, Y.; Polzer, F.; Ballauff, M.; Drechsler, M. Catalytic activity of palladium nanoparticles encapsulated in spherical polyelectrolyte brushes and core-shell microgels. *Chem. Mater.* **2007**, *19*, 1062.
- (21) Tagliazucchi, M.; Szeleifer, I. Stimuli-responsive polymers grafted to nanopores and other nano-curved surfaces: structure, chemical equilibrium and transport. *Soft Matter* **2012**, *8*, 7292.
- (22) Borisova, O. V.; Billon, L.; Richter, R. P.; Reimhult, E.; Borisov, O. V. pH- and Electro-Responsive Properties of Poly(acrylic acid) and Poly(acrylic acid)-*block*-poly(acrylic acid-*grad*-styrene) Brushes Studied by Quartz Crystal Microbalance with Dissipation Monitoring. *Langmuir* **2015**, *31*, 7684.
- (23) de Gennes, P. G. Conformations of Polymers Attached to an Interface. *Macromolecules* **1980**, *13*, 1069.
- (24) Zhulina, E. B.; Borisov, O. V. Poisson-Boltzmann Theory of pH-Sensitive (Annealing) Polyelectrolyte Brush. *Langmuir* **2011**, *27*, 10615.
- (25) Pincus, P. Colloid stabilization with grafted polyelectrolytes. *Macromolecules* **1991**, *24*, 2912.
- (26) Li, F.; Balastre, M.; Schorr, P.; Argillier, J. F.; Yang, J.; Mays, J. W.; Tirrell, M. Differences between Tethered Polyelectrolyte Chains on Bare Mica and Hydrophobically Modified Mica. *Langmuir* **2006**, *22*, 4084.
- (27) Balastre, M.; Li, F.; Schorr, P.; Yang, J.; Mays, J. W.; Tirrell, M. V. A Study of Polyelectrolyte Brushes Formed from Adsorption of Amphiphilic Diblock Copolymers Using the Surface Forces Apparatus. *Macromolecules* **2002**, *35*, 9480.
- (28) Ahrens, H.; Forster, S.; Helm, C. A. Charged polymer brushes: Counterion incorporation and scaling relations. *Phys. Rev. Lett.* **1998**, *81*, 4172.
- (29) Manning, G. S. Limiting Laws and Counterion Condensation in Polyelectrolyte Solutions. I. Colligative Properties. *J. Chem. Phys.* **1969**, *51*, 924.
- (30) Farina, R.; Laugel, N.; Pincus, P.; Tirrell, M. Brushes of strong polyelectrolytes in mixed mono- and tri-valent ionic media at fixed total ionic strengths. *Soft Matter* **2013**, *9*, 10458.
- (31) Mei, Y.; Hoffmann, M.; Ballauff, M.; Jusufi, A. Spherical polyelectrolyte brushes in the presence of multivalent counterions: The effect of fluctuations and correlations as determined by molecular dynamics simulations. *Phys. Rev. E* **2008**, *77*, 031805.
- (32) Farina, R.; Laugel, N.; Yu, J.; Tirrell, M. Reversible Adhesion with Polyelectrolyte Brushes Tailored via the Uptake and Release of Trivalent Lanthanum Ions. *J. Phys. Chem. C* **2015**, *119*, 14805.
- (33) Yu, J.; Mao, J.; Yuan, G.; Satija, S.; Chen, W.; Tirrell, M. The effect of multivalent counterions to the structure of highly dense polystyrene sulfonate brushes. *Polymer* **2016**, DOI: 10.1016/j.polymer.2016.02.053.
- (34) Jiang, T.; Wu, J. Z. Ionic effects in collapse of polyelectrolyte brushes. *J. Phys. Chem. B* **2008**, *112*, 7713.
- (35) Brettmann, B. K.; Laugel, N.; Hoffmann, N.; Pincus, P.; Tirrell, M. Bridging contributions to polyelectrolyte brush collapse in multivalent salt solutions. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 284.
- (36) Zhulina, E. B.; Borisov, O. V.; Pryamitsyn, V. A.; Birshtein, T. M. Coil Globule Type Transitions in Polymers 0.1. Collapse of Layers of Grafted Polymer-Chains. *Macromolecules* **1991**, *24*, 140.
- (37) Israelachvili, J.; Min, Y.; Akbulut, M.; Alig, A.; Carver, G.; Greene, W.; Kristiansen, K.; Meyer, E.; Pesika, N.; Rosenberg, K.; Zeng, H. Recent advances in the surface forces apparatus (SFA) technique. *Rep. Prog. Phys.* **2010**, *73*, 036601.
- (38) Maeda, N.; Chen, N. H.; Tirrell, M.; Israelachvili, J. N. Adhesion and friction mechanisms of polymer-on-polymer surfaces. *Science* **2002**, *297*, 379.
- (39) Klein, J. Shear, friction, and lubrication forces between polymer-bearing surfaces. *Annu. Rev. Mater. Sci.* **1996**, *26*, 581.
- (40) Schiessel, H.; Pincus, P. Counterion-condensation-induced collapse of highly charged polyelectrolytes. *Macromolecules* **1998**, *31*, 7953.
- (41) Zhulina, E.; Singh, C.; Balazs, A. C. Behavior of tethered polyelectrolytes in poor solvents. *J. Chem. Phys.* **1998**, *108*, 1175.
- (42) Zhulina, E. B.; Birshtein, T. M.; Priamitsyn, V. A.; Klushin, L. I. Inhomogeneous Structure of Collapsed Polymer Brushes under Deformation. *Macromolecules* **1995**, *28*, 8612.
- (43) He, G. L.; Merlitz, H.; Sommer, J. U. Molecular dynamics simulations of polyelectrolyte brushes under poor solvent conditions: Origins of bundle formation. *J. Chem. Phys.* **2014**, *140*, 104911.
- (44) Carrillo, J. M. Y.; Dobrynin, A. V. Morphologies of Planar Polyelectrolyte Brushes in a Poor Solvent: Molecular Dynamics Simulations and Scaling Analysis. *Langmuir* **2009**, *25*, 13158.
- (45) Delacruz, M. O.; Belloni, L.; Delsanti, M.; Dalbiez, J. P.; Spalla, O.; Drifford, M. Precipitation of Highly-Charged Polyelectrolyte Solutions in the Presence of Multivalent Salts. *J. Chem. Phys.* **1995**, *103*, 5781.
- (46) Israelachvili, J. N. *Intermolecular and Surface Forces*, 3rd ed.; Academic Press: Burlington, MA, 2011.
- (47) Zhang, Y. J.; Cremer, P. S. Interactions between macromolecules and ions: the Hofmeister series. *Curr. Opin. Chem. Biol.* **2006**, *10*, 658.
- (48) Parsons, D. F.; Bostrom, M.; Lo Nostro, P.; Ninham, B. W. Hofmeister effects: interplay of hydration, nonelectrostatic potentials, and ion size. *Phys. Chem. Chem. Phys.* **2011**, *13*, 12352.
- (49) Lee, S. S.; Fenter, P.; Park, C.; Sturchio, N. C.; Nagy, K. L. Hydrated Cation Speciation at the Muscovite (001)-Water Interface. *Langmuir* **2010**, *26*, 16647.
- (50) Pashley, R. M.; Israelachvili, J. N. DLVO and Hydration Forces between Mica Surfaces in Mg-2+, Ca-2+, Sr-2+, and Ba-2+ Chloride Solutions. *J. Colloid Interface Sci.* **1984**, *97*, 446.
- (51) Pashley, R. M. DLVO and Hydration Forces between Mica Surfaces in Li+, Na+, K+, and Cs+ Electrolyte-Solutions - a Correlation of Double-Layer and Hydration Forces with Surface Cation-Exchange Properties. *J. Colloid Interface Sci.* **1981**, *83*, 531.
- (52) Marra, J.; Israelachvili, J. Direct Measurements of Forces between Phosphatidylcholine and Phosphatidylethanolamine Bilayers in Aqueous-Electrolyte Solutions. *Biochemistry* **1985**, *24*, 4608.
- (53) Hansma, H. G.; Laney, D. E. DNA binding to mica correlates with cationic radius: Assay by atomic force microscopy. *Biophys. J.* **1996**, *70*, 1933.