Swelling of Poly(methacrylic acid) Brushes: Influence of Monovalent Salts in the Environment

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ABSTRACT: The swelling behavior of poly(methacrylic acid) (PMAA) brushes covalently attached to solid planar surfaces in aqueous solutions containing different monovalent salts was investigated with multiangle null ellipsometry. The polymer chains were grown in situ from the surface by surface-initiated polymerization using a surface-attached initiator ("grafting from" method). The swelling of the PMAA brushes was measured as a function of pH value, concentration of added low molecular weight salt, and the grafting density of the surface-attached polymer brushes. At pH values between 4 and 10, the brush thickness initially increases and then decreases with increasing concentration of added salt; i.e., a maximum of brush thickness appears at a medium salt concentration. The influence of the chemical nature of different monovalent co- and counterions on the swelling behavior of the brushes is studied.

Introduction

Polyelectrolyte (PEL) brushes constitute an interesting model case for soft, water-swellable, charged surfaces.[1−3] Such brush systems consist of monolayers of polymer chains formed by tethering polyelectrolyte molecules with one end to a solid surface with such a high grafting density of the surface-attached chains so that the chains significantly overlap and stretch away from the surface.[4−6] These systems pose good models for the elucidation of the interactions of biological molecules with solid surfaces. An especially interesting case is weak polyelectrolytes as the number of charges varies in response to the environmental conditions, especially to the pH value of the environment. In such systems charges can be reversibly placed on the chains and removed again under other conditions. These changes in the degree of charging of the chains have a strong influence on the conformation of the surface-attached polymer molecules and accordingly lead to strong changes in the physical properties of the film. In contrast to purely physisorbed systems the extent of charging of the chains can be altered without the danger of loosing chains from the film.

Theoretical studies predict that the swelling behavior of weak PEL brushes in salt solution is rather complicated.[13−17] At sufficiently high added salt concentration c_s, weak PEL brushes behave in a very similar way as strong PEL brushes: the brush thickness decreases with increasing ionic strength of the solution (i.e., increasing salt concentration) due to screening of the charges on the chains, which strongly reduces electrostatic repulsion between the individual segments. In this region the brush height L follows a similar scaling relationship $L \propto c_s^{-1/3}$ as that of a strong PEL brush system. This regime is known as the "salted brush" regime.

At low salt concentration, the ionic environment in a weak PEL brush is different from that in the bulk solution. For a polyacid brush, the proton concentration inside the brush is considerably higher than that in the bulk phase as long as the concentration of salt added to the system is low. Addition of salt to the contacting solution leads to substitution of protons by salt counterions. This results in an increase of the degree of ionization of the polymer chains. As a consequence, the swelling of the brush increases with increasing salt concentration. This regime is called the "osmotic brush" regime as the osmotic pressure of the ions in the brush monolayer is responsible for the extent of swelling of the brush. Note that in the theoretical predictions mentioned above all steric interactions of the polymer chains, the binding equilibrium between immobilized charges, and salt counterions as well as any formation of a complex between the charged groups and the polymer chains are neglected.

So far only few experimental papers have been published on the swelling behavior of very thin weak PEL brushes in aqueous solution, especially in contact with solutions containing low molecular weight electrolytes.[18−21] For example, Currie et al. and Wesley et al. have reported on the salt-induced swelling behavior of weak polyacid and polybase brushes and investigated features of the osmotic brush regime.[18,19] Ballauf et al.[21] have studied the hydrodynamic radius of spherical particles with surface-attached strong and weak polyelectrolytes using scattering techniques and have found a nonmonotonic behavior of the swelling of a thin spherical poly(acrylic acid) (PAA) brush with increasing salt concentration.

However, no report has been published so far on the conformation of very thick weak polyelectrolyte layers with controlled grafting densities on simple, planar surfaces as a function of conditions of the surrounding environment.

We recently reported that the preparation of polymer brushes using a "grafting from" technique[22−27] and studied the swelling of the weak PEL brush attached to silicon substrates.[23] The thickness of the polymer layer in the dry state can be controlled by adjusting the molecular weight and the grafting density of the surface-attached polymer chains.

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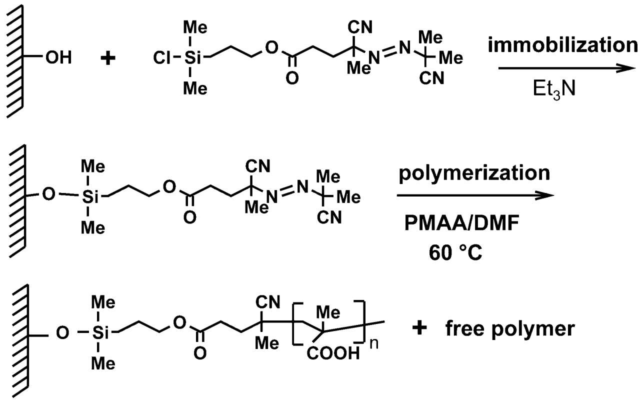

Figure 1. Chemical pathway for the formation of poly(methacrylic acid) brushes covalently attached to a solid substrate.

In this paper, poly(methacrylic acid) (PMAA) brushes were prepared on solid planar surface as schematically described in Figure 1. The swelling behavior of such a system in aqueous solutions was studied as a function of the concentration of added monovalent salt, the pH value of the solution, the chemical nature of the added salt, and the grafting density of the attached polymer chains using angle-dependent ellipsometry. The results of these measurements are compared with the theoretically predicted swelling behavior of a weak PEL brush.

Experimental Section

High refractive index LaSFN9 prisms, which were used as substrates in the ellipsometric experiments ($n = 1,845$, Hellma, Jena), were pretreated for 3×1 min with 2 N sulfuric acid and subsequently rinsed with water and ethanol and then dried under vacuum. Silicon wafers (Crystec) were used as obtained. The synthesis of the PEL monolayers followed the "grafting from" technique[22,29] as depicted in Figure 1. First, a self-assembled monolayer of an initiator which is a derivative of azobis(isobutyronitrile) (AIBN) is formed on the substrates via a monochlorosilyl anchor group. The immobilization of the initiator was carried out under nitrogen in dry toluene at room temperature. The concentration of the initiator solution was about 0.5 mmol/L in all cases. Several drops triethylamine were used as catalyst for the attachment reaction. After immobilization, noncovalently attached initiator and other byproducts were removed by rinsing with toluene, methanol, and acetone. Unless otherwise indicated, the polymerization of methacrylic acid with the surface attached initiator was performed in *N,N′*-dimethylformamide at a concentration of 1:1 (v/v). After removal of all oxygen traces from the solution through five freeze−thaw cycles under vacuum, the Schlenk flasks containing the samples and the polymerization solutions were placed in a thermostat at 60 °C. The reaction was allowed to proceed for a given reaction time and then quenched by cooling rapidly to room temperature. After that, the prisms were extracted with DMF for 15 h and additionally with methanol for 15 h to remove all physisorbed polymer remaining on the substrate. Both DMF and methanol are good solvents for PMAA. Finally, the samples were dried under vacuum. The free polymer, which is generated in the process of the polymerization reaction, was extracted and precipitated several times, carefully washed with solvent, and analyzed with regard to its molecular weight.

The molecular weight of the covalently attached polymers is a priori unknown. However, it can be estimated from gel permeation chromatography (GPC) of the free polymer which was formed from the nonattached part of the initiator. According to our previous work on similar systems, the molecular weight and its distribution in the brush are about the same as those of the free polymers.[30] The free polymer had a molecular weight of $M_n \sim 2 \times 10^6$ g/mol with a polydispersity of $M_w/M_n \sim 1.8$ for the monomer concentration of 50% (v/v). From the molecular weight M_n and the dry thickness L_{dry}, the grafting density Γ can be derived as $\Gamma = (\rho L_{dry})/M_n$, where $\rho = 1.12$ g/cm^3 is the substance density of PMAA.

To determine the swollen thickness of the surface-attached polyelectrolyte monolayers, multiangle null ellipsometry was used. The experimental setup and ellipsometric data analysis have been described elsewhere.[22,28] Briefly, the ellipsometric parameters Ψ and Δ were measured as a function of the angle of incidence in an ATR geometry. The refractive index profile is inferred from the angle dependence of the complex reflectivities r_p and r_s for p- and s-light. To fit the experimental data, a complementary error function was taken:

$$\varphi_{fit}(z) = \varphi_0 \frac{1}{2}\left(1 - \mathrm{erf}\left(\frac{z - d}{w}\right)\right)$$

where φ is the polymer volume fraction, d is the brush thickness, w is the "interface width" which determines to what extent the profile is boxlike or not, and φ_0 is a normalization constant.[22,28]

For strongly swollen brushes, the parameter w is comparable with d. In this case, the point of inflection d in the error function is no longer a good measure of the brush thickness and can obtain values which can even be zero or negative. Therefore, we defined a model-independent parameter d^* which is twice the first moment of the segment density profile $2\int z\varphi(z)\,dz$. Although the parameter d^* is defined independently from the error function, it is numerically equal to the parameter d in the error function as long as w is smaller than d. The "brush thickness" in this article signifies d^*.

The different salt solutions were pumped into the measurement cell by means of a homemade robotic system. To avoid any problems due to dissolution of CO_2 from the ambient in the aqueous solutions, which would, especially at high pH values, cause changes in the pH value of the system which are strongly depending on pH value and exposure time, all swelling experiments were carried out und inert gas conditions. To this all solutions were carefully purged with argon and kept under argon in flasks sealed with a septum, from which they were withdrawn with a syringe and pumped automatically directly into the measurement cell, which was hermetically sealed.

Results and Discussion

Dependence of the Brush Height on the Concentration of Added Salt. The influence of added salt on the swelling behavior of a PMAA brush attached to the base of a high refractive index prism was investigated at different pH values by multiple angle ellipsometry in an ATR geometry as described above. The pH of the contacting solution was adjusted by adding small amounts of HCl or NaOH. As the amount of acid or base was small compared to the amount of added salt during the experiments, the amount of ions thus added to the system was neglected in the following discussions. A significant contribution by these ions to the total ion concentration of the system occurs only at very low or very high pH values and at extremely low salt concentrations. In these cases it is taken into account, and these cases are discussed separately. Sodium nitrate ($NaNO_3$) was chosen as added salt because it is inert and consists only of monovalent ions. Figure 2 shows one example of ellipsometric spectra of a sample exposed to aqueous $NaNO_3$ solutions of different concentrations at pH = 4.2.

As discussed previously,[22,28] the visual inspection of the measured ellipsometric spectra alone already allows to draw qualitative conclusions. The slope of Δ at the critical angle becomes steeper for increasing salt concentrations up to 0.001 M (Figure 2). This observation

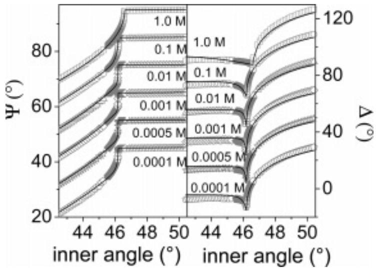

Figure 2. Ellipsometric spectra of a 36 nm thick PMAA brush on a LaSFN9 prism prepared by surface-initiated polymerization of MAA in DMF (1:1 v/v; 60 °C; 2 h). The sample was swollen in aqueous solutions at different added $NaNO_3$ concentrations as given in the figure. The pH value was set to pH = 4.2. The solid lines represent the results of model simulations using a complementary error function to describe the segment density profile.

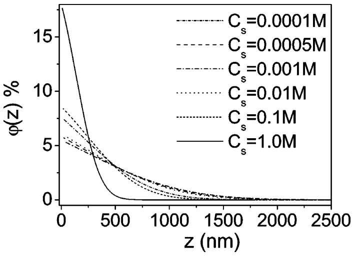

Figure 3. Segment density profiles of the same brushes as in Figure 2 in contact with aqueous solutions with different added $NaNO_3$ concentration as noted in the figure. The profiles were obtained from model simulation based upon the ellipsometric spectra from Figure 2 according to calculations described in the text.

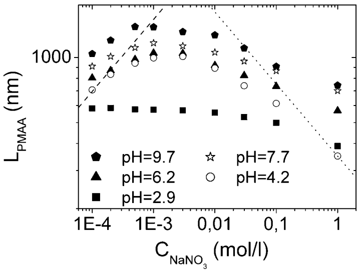

Figure 4. Swollen thickness of a 36 nm PMAA brush on a LaSFN9 prism as a function of the added salt concentration in aqueous solutions with different pH values. The dashed line at low salt concentration and the dotted line at high salt concentration represent the theoretically predicted scaling behavior.[11,15]

alone suggests that the swollen thickness of the brush increases with increasing added salt concentration and then decreases with further addition of salt. This view of the data is supported by the quantitative evaluations, which are shown as solid lines in the figure.

Figure 3 shows the segment density profiles of this PMAA brush derived from these quantitative evaluations. At relative high salt concentration ($c_s \approx 1.0$ M), the brush shrinks strongly, however, remains swollen over the whole range of added salt concentrations studied. At an added salt concentration of about 0.001 M, a maximum of the swollen thickness is reached.

The average swollen thickness of the brush can be obtained from the Fresnel calculations as described earlier. The results of such calculations are shown as a function of added salt concentration at different pH values in Figure 4. For comparison, the theoretically predicted scaling behavior[11,15] for weak PEL brushes at low added salt concentrations ($L \propto c_s^{1/3}$, OsB regime) and at high salt concentrations ($L \propto c_s^{-1/3}$, SB regime) are shown in the same graph as well.

At pH = 2.9 the brush height is almost independent from the concentration of added salt. Only at high salt concentrations the height of the brush decreases with increasing salt concentration. The observation that under these conditions the addition of salt has only very limited influence on the layer thickness can be easily understood when it is taken into account that the brush is almost completely neutral at this low pH value. If almost all carboxylic acid moieties are protonated, the addition of salt has accordingly little or no influence on the brush height. The slight decrease in brush height, however, at high salt concentrations indicates that even under these rather acidic conditions not all charges have been removed. This finding is corroborated by the IR experiments where in all samples a both vibration bands which can be assigned to COOH and COO^- groups were observed. Experiments at lower pH values than 2.9 were not feasible as the lanthanum oxide substrate starts to degrade at pH values significantly lower than pH = 3.

At higher pH values the brush height first increases with increasing salt concentration and then decreases. This is well understood on the basis of a shift in the protonation/depronation equilibrium at low salt concentration, which leads to the generation of more charges on the chains and thus a stronger chain stretching, and the screening of charges at high salt concentrations, which leads to a decrease of the electrostatic repulsion. The crossover between the two regimes appears to be in all cases around 10^{-3} mol/L. This aspect will be discussed in further detail below. When the film thicknesses at the lowest salt concentrations are compared, it is evident that with increasing pH value the brush height increases. This is due to the fact that with increasing pH the brush becomes more and more deprotonated, and the additional charges increase the electrostatic repulsions/confine more ions to the brush and accordingly increase the brush height as discussed above. As far as the scaling behavior of the brush height with the salt concentration of the contacting solution is concerned, it is evident that the exponents both in the osmotic and in the salted brush regime are much smaller than the exponents expected from theoretical calculations. This might be due to the influence of nontrivial three-body interactions caused by the high grafting density of the system, the polydispersity of the chains, or the hydrophobicity of the polymer backbone, which were not taken into consideration in the theoretical calculations. Such a nonmonotonic behavior and a lower exponential power have also been observed in thinner planar PAA brush systems by Currie et al.[19] and spherical systems by Ballauf et al.[21]

At high pH values all concentration vs brush height curves look rather similar, as far as the general behavior is concerned. However, if absolute values are considered, which is easily possible as all curves shown in Figure 4 have been obtained from the same brush, it is evident that with increasing pH value much higher salt concentrations are required to obtain the same degree of charge screening and accordingly brush height.

Theory states that the crossover in the swollen thickness should occur when the external salt concentration matches the concentration of free ions in the brush and accordingly predicts the concentration $c_{s,\max}$ at which the maximum in the swollen thickness should

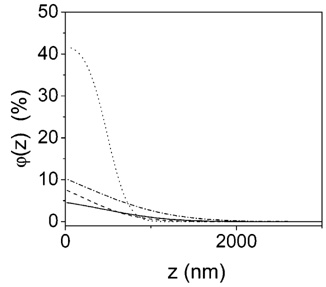

Figure 5. Segment density profiles of PMAA brushes with graft density of 0.018 (23 nm, solid line), 0.036 (36 nm, dotted line), 0.10 (120 nm, dash-dotted line), and 0.26 μmol/m^2 (41 nm, dashed line) on LaNSFN9 prism in contact with 0.0001 M NaNO$_3$ solution (pH = 4.2). The profiles were obtained from model simulations as described in the text. The profile of the sample with the highest grafting density was normalized by normalizing the molecular weight.

Table 1. Summary of the Conditions Used for the Preparation of the PMAA Brushes[a]

t (h)	0.5	1	2	6	18
C_m (%, v/v)[b]	70	50	50	50	10
d (nm)	30	23	36	160	41
Γ (μmol/m^2)[c]	0.009	0.018	0.036	0.10	0.26

[a] All samples were by obtained by polymerization in DMF at 60 °C using an immobilized azo initiator on the substrate. [b] Ratio between MAA monomer volume and the total volume of the solution. [c] Graft densities of the samples were calculated from the initiator decomposition kinetics as described in ref 31.

occur to be $c_{s,max} \propto \sigma[\alpha_b(1 - \alpha_b)]^{1/2}$.[11,14] From the fact that the crossover is located at all pH values at concentrations of around 10^{-3} mol/L it can be concluded that the number of mobile ions in the brush is also of the same magnitude, and accordingly only 2−3% of all ions in the brush are osmotically active. Decreasing the pH value apparently does not increase the number of osmotically active ions as at all pH values measured the same value for $c_{s,max}$ was observed. To improve the understanding of the system, brushes with different graft densities were studied.

Influence of the Grafting Density on the Salt Sensitivity of the Brush. As described previously,[29] the graft density of the brush can be controlled by varying the polymerization time during the brush formation. The molecular weight of the brushes on the other hand can be controlled by choosing the appropriate monomer concentration during the brush growth. To allow a comparison of the segment density profiles of PMAA brushes in contact with added salt solutions, both polymerization parameters, monomer concentration, and polymerization time were varied simultaneously in the following, so that the brushes had more or less the same thickness, while the graft density of the chains was strongly varied. Sodium nitrate was again chosen as external salt and the pH value of the solutions was set to pH = 4.2. The polymerization conditions and the characteristics of the brushes are shown in Table 1. It should be noted that the graft densities of the brushes are calculated from the initiator decomposition kinetics as shown in our previous publications.[31]

Figure 5 shows some segment density profiles calculated from the ellipsometric spectra obtained from different brushes. It can be seen that brushes with a higher graft density exhibit a segment density profile that resembles more closely a box model. Also, brushes with similar molecular weight show a similar swollen thickness.

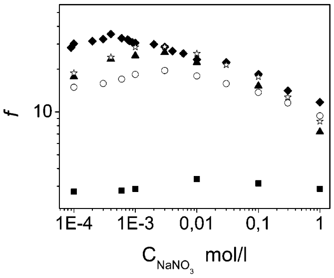

Figure 6. Swelling factor of PMAA brushes with different graft densities (0.009 (◆), 0.018 (☆), 0.036 (▲), 0.10 (○), and 0.26 μmol/m^2 (■)) as a function of the added NaNO$_3$ concentration (pH = 4.2).

Since both the graft density and the molecular weight are varied in this study, it is difficult to directly see the influence of graft density on the swelling behavior when the swollen thickness is plotted as a function of the added salt concentration for different brushes. Therefore, a parameter f, the swelling factor, is introduced and defined as the ratio between the swollen thickness and the dry brush thickness:

$$f = \frac{\text{swollen thickness}}{\text{dry thickness}}$$

In Figure 6 the swelling factor f is plotted as a function of the concentration of added salt at pH = 4.2 for different graft densities. It is clearly visible that higher graft densities lead to a lower degree of swelling.This is in good agreement with expectations, as for osmotic brushes the swollen brush height is independent from the graft density while the dry film thickness is (trivially) directly proportional to the graft density.

An important feature which can be seen in Figure 6 is that the swollen thickness of the brushes shows a maximum of the brush height at an intermediate salt concentration for all grafting densities as expected. However, with increasing grafting density the influence of salts onto the swelling behavior of the brushes becomes less pronounced, and at the highest grafting density (Γ = 0.26 μmol/m^2) only a very weak influence of the addition of salt onto the brush height can be detected.

In addition, the salt concentration $c_{s,max}$, at which the crossover from the OsB to SB regime occurs, increases with increasing the graft density. For example, $c_{s,max}$ changes from roughly 0.0005 M to around 0.015 M when the graft density increases from 0.009 to 0.26 μmol/m^2. This is easily understood as a higher graft density leads to a lower dissociation of PMAA molecules through self-screening.[15] Accordingly, more external counterions are required to reach the transition between OsB and SB regime, where the concentration of mobile counterions inside the brush equals that in the bulk solution. Or to put it in other words, the higher grafting density leads to a broader OsB regime. To demonstrate this effect, $c_{s,max}$ (extracted from Figure 6 by linearly fitting the data in both the OsB and SB regime) is plotted as a function of the graft density in Figure 7. The added salt concentration $c_{s,max}$ increases almost linearly with increasing graft density. This observation agrees very well with SCF theoretical predictions[15] for weak PEL brushes, in which the added salt concentration $c_{s,max}$ has been predicted as

$$c_{s,max} \propto \sigma[\alpha_b(1 - \alpha_b)]^{1/2}$$

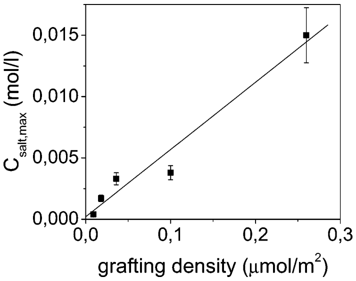

Figure 7. Added salt concentration c_{max}, at which the PMAA brush has a maximum swollen thickness, as a function of graft density. The data were extracted from Figure 6. The solid line represents a linear fit.

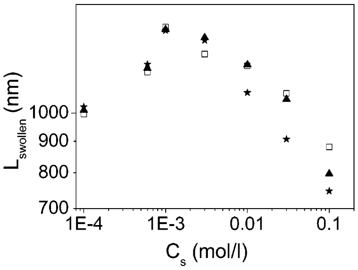

Figure 8. Swollen thickness of a 36 nm PMAA brush on a LaSFN9 prism as a function of the concentration of NaCl (□), NaBr (▲), and NaI (★) at pH = 6.9. The preparation of the sample is described in the text.

To obtain a more complete understanding of the influence of salts onto the swelling of surface-attached weak polyelectrolyte brushes, also the influence of the chemical nature of counterions and co-ions onto the swelling properties of such films needs to be studied.

Influence of the Co-ions onto the Swelling of the PMAA Brushes. The effect of different co-ions onto the swelling behavior of PMAA brush in aqueous solution is shown in Figure 8. NaCl, NaBr, and NaI were chosen as added salts because all of them consist of the same counterion for the carboxylate group, namley sodium, but different monovalent co-ions. The solutions to which the brush was exposed to were almost neutral with a pH value of 6.9.

As expected, the swollen thickness of the brush as a function of the concentration of added salt shows a maximum thickness at an added salt concentration of around 0.001 M for all three compounds. At lower salt concentration ($c_S < 0.001$ M), i.e., in the OsB regime, it is observed that the chemical nature of the co-ions does not affect the swelling of the brush, and in this regime all curves coincide. This is expected as the osmotic pressure inside the brush depends only on the degree of dissociation and the number of ions, not on the type of the ion. In the salted brush regime largely the extent of charge screening by the external salt determines the brush height. This, however, depends only on the activity of the given salt, which is slightly different for the different salts so that in this concentration range the slope of the height vs concentration curve depends on the chemical nature of the salt and accordingly on the nature of the co-ion.

Influence of the Counterions onto the Swelling of the PMAA Brushes. The influence of the nature of the (monovalent) counterions on the swollen thickness of a PMAA brush has also been investigated. To allow for an easy comparison, the alkaline metal ions Li^+, Na^+, K^+, and Cs^+ were used as counterions while the co-ion, namely Cl^-, remained the same. The solutions used for the swelling of the PMAA brush were again almost neutral with a pH value of 6.9.

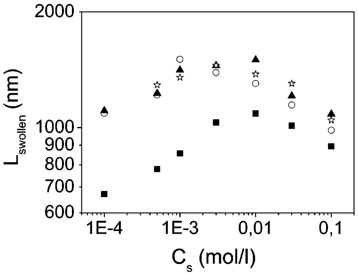

Figure 9. Swollen thickness of a 40 nm PMAA brush on a LaSFN9 prism as a function of the concentration of LiCl (■), NaCl (○), KCl (▲), and CsCl (☆) solutions (pH = 6.9).

Figure 9 shows the swollen thicknesses of the PMAA brush in contact with neutral aqueous solutions of alkaline chloride salt having different concentrations. It can easily be seen that the brush shows qualitatively the same behavior for all brushes. However, while NaCl, KCl, and CsCl give within the experimental error the identical thickness over the entire range of salt concentrations and the crossover always occurs at roughly 0.001 M independently of the nature of alkaline ion, LiCl solutions show a quantitatively quite different behavior. The Li ion contacting brush is much less strongly swollen as it is in contact with the other ions, and the crossover appears to occur only at around 0.01 M. This might be attributed to the high binding constant between Li^+ and COO^-, which leads to strong association according to

$$Li^+ + COO^- \rightleftarrows COOLi$$

It is well-known that chemical bonds in lithium salts are much less ionic in nature compared to their homologues with higher order numbers (Na^+, K^+, and Cs^+) and that these bonds have a considerable covalent contribution. Thus, the degree of dissociation, the electrostatic repulsion between the segments of the PMAA chains, and the concentration of mobile ions in the brush are much lower if lithium is the counterion compared to the cases where the other alkaline ions are employed. As a direct consequence, also the brush height is much lower if the brush is exposed to lithium ion containing solutions compared to the other cases. The covalent contribution of the lithium carboxylate bond is, however, still a little smaller than that of the same system when H^+ is the counterion, so that the brush height still increases with increasing lithium ion concentration in the osmotic brush regime. This relatively strong association also requires addition of a higher Li^+ concentration to reach the maximum swollen thickness of the brush as the effective ionic strength of the system decreases.

Conclusions

The swelling behavior of PMAA brushes grown on a solid surface through a surface-initiated polymerization process was studied by using multiangle null ellipsometry. The samples were exposed to a variety of solutions containing monovalent low molecular weight ions. At higher pH values the swollen thickness of the PMAA brushes first increases and above a certain critical concentration decreases with increasing concentration of small, monovalent ions in the environment. The obtained results are in qualitative agreement with theoretical predictions of such systems. It is, however, obvious that the scaling of the brush height with increasing salt concentration is in all investigated samples weaker than the exponents of $+^1/_3$ and $-^1/_3$ which have been predicted for the osmotic and salted polyelectrolyte brushes. However, to allow for a quantitative comparison, the influence of the chemical nature of the polymer backbone onto the swelling behavior of the brush needs to be elucidated, as the solvent quality of the aqueous solution strongly changes with changing degree of charge neutralization on such a weak polyelectrolyte system.

The graft density of the brushes has a very profound influence on how strongly the addition of external salt influences the swellability of the brush and at what added salt concentration the brush reaches a maximum thickness. If the grafting density of the surface-attached chains becomes too high, strong self-screening of the ions inside the monolayer occurs, and the layers become rather insensitive to the presence of external salt. Only at low grafting densities a strong response of the brush height to changes in the salt contents of the environment can be observed.

A very interesting aspect will be to vary the number of charges on the counterions and move from monovalent to di- and trivalent ions, as then bridging between different chains in the monolayer can occur, leading to physically cross-linked polyelectrolyte brushes. In addition, it will be important to study systems in which the metal ions not only exhibit purely ionic interactions with the surface-attached polymer brush but also form specific polyelectrolyte−metal complexes. Such studies are currently under way.

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