Macromolecules **2005,** *38,* 4345−4354

Interaction of Poly(methacrylic acid) Brushes with Metal Ions: Swelling Properties

Rupert Konradi and Jürgen Rühe*

Institute for Microsystem Technology, University of Freiburg, D-79110 Freiburg, Germany

Received June 30, 2004; Revised Manuscript Received January 12, 2005

ABSTRACT: The swelling behavior of poly(methacrylic acid) (PMAA) brushes in contact with aqueous solutions of sodium, silver, alkaline-earth metal, copper, and aluminum nitrate was studied by multiple angle null ellipsometry. Fundamentally different swelling behavior were found for the interaction of the polyacid brush with metal cations of increasing valency or when going from a main group to a transition metal ion at constant valency. The different cations were classified with respect to the nature of their interaction with the surface-attached poly(carboxylic acid), and the findings were compared to theoretical predictions as well as to experimental investigations of related systems, such as free polyacids in solution or polyacid gels interacting with different metal cations.

1. Introduction

Polyelectrolyte brushes can be readily prepared by a surface-initiated free radical polymerization which allows for the use of a broad range of functional monomers such as methacrylic acid to obtain a weak polyacid brush, poly(methacrylic acid) (PMAA), in a one step procedure. The synthesis and characterization of polyelectrolyte brushes has recently been reviewed.[1−3] Polyelectrolyte brushes have been investigated with respect to their application as (bio)lubricants.[4] In addition to the massive reduction in sliding friction due to the resistance of polymer brushes to mutual interpenetration, hydrated ions at the interface of polyelectrolyte brushes can act as extremely efficient lubricants between sliding charged surfaces. Furthermore, polyelectrolyte brushes find application for the steric and electrostatical stabilization of colloids, both in technology and in nature.[5,6] As an example, casein micelles in milk are stabilized in that way.

Weak polyelectrolyte brushes, moreover, can be readily and reversibly tuned in their swelling behavior via an adjustment of external parameters like the pH value or the presence of different kind of ions as schematically illustrated in Figure 1. This system offers a new route toward the fabrication of soft hydrophilic and stimulus-responsive surface architectures. An example for the application of such systems has been reported by Ito et al.[7] The authors used PMAA brushes to control the liquid permeation through a porous membrane by changes in the pH value. The use of poly(carboxylic acid)s as templates for the preparation of metal nanoparticles has attracted much attention recently.[8−10] The size of so-formed silver nanoparticles has been controlled through variations of the pH value.[10] Furthermore, the potential application of synthetic weak polyacids for the fabrication of biomaterials has attracted much attention since a long time. The interaction of PMAA with proteins has already been studied in the early 1950s.[11] Further examples comprise the use of PMAA for the retardation of tumor metastasis[12] and biomaterials for the growth of artificial bone[13] and for controlled drug release[14] as well as bioinert multilayer thin films.[15] It is the stimulus-responsive swelling behavior that controls the function of weak polyelectrolytes in biological systems. Signaling processes like nerve excitation, muscle contraction, and cell locomotion often involve the interaction with small metal ions like calcium.[16,17] It is therefore crucial to develop a fundamental understanding of the interaction of weak polyacids with the different kind of ions. The role that the pH value plays on the swelling of weak polyacid brushes has recently been investigated.[18] In the present article, we will discuss the influence of small metal ions. The role that valency, polarizability, and complex formation play will be elucidated and summarized in a classification of the various ions that relates their influence on the swelling behavior of the brush and the type of interaction between the ion and the brush.

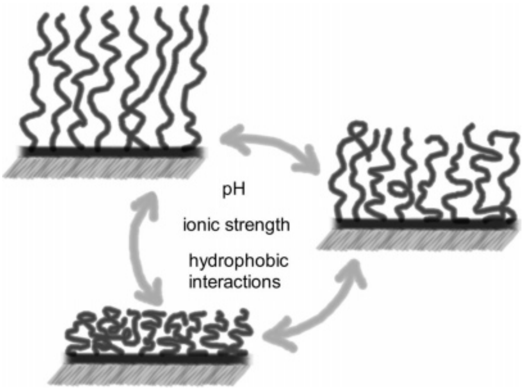


Figure 1. Schematic representation of a swollen weak polyacid brush. External parameters like the pH value of the solution or the ionic strength strongly influence the degree of swelling.

2. Experimental Section

2.1. Materials. High refractive index lanthanum glass prisms (LaSFN9, $n_D = 1.845$; Fa. Hellma, Germany) were used as substrates. They were activated prior to the initiator deposition by repeated dipping into 1 mol/L H_2SO_4 and subsequent rinsing with deionized water and methanol (p.a. grade). Methacrylic acid (Fluka, Germany) was purified by vacuum distillation over a Vigreux column and stored under nitrogen at −20 °C. Water was deionized with a Millipore system (resistivity ≥18.2 MΩcm^{-1}) immediately prior to use.

---

* Corresponding author. E-mail: ruehe@imtek.uni-freiburg.de.

10.1021/ma0486804 CCC: $30.25

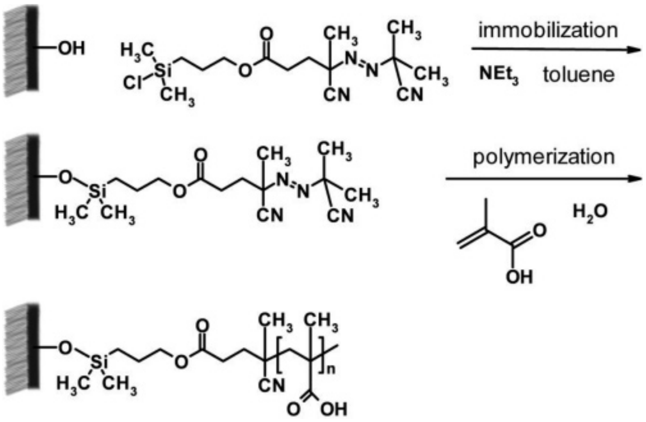


Figure 2. Schematic depiction of the "grafting-from" approach. A free radical polymerization is surface-initiated by a covalently attached self-assembled monolayer of azo initiators.

All salts were of p.a. grade (Merck, Germany) and solutions were prepared with water of Millipore quality.

2.2. Synthesis of the PMAA Brushes. PMAA brushes were synthesized via a surface-initiated free radical chain polymerization ("grafting from") as depicted in Figure 2.

The procedure was described in detail by Prucker and Rühe.[19−21] First, a self-assembled monolayer of an initiator bearing an azo and a monochlorosilane moiety was covalently attached to the surface of LaSFN9-glass prisms. The glass surface was activated with 1 mol/L H_2SO_4 in order to generate hydroxyl groups as described in section 2.1. In a second step, the surface-bound azo function was thermally cleaved to initiate the radical polymerization of methacrylic acid. The polymerizations were carried out in either pure methacrylic acid or in a solution of 50 vol % methacrylic acid in water. In every case the reaction mixture was carefully degassed by repeated ultrasonication and the application of vacuum before the initiator-functionalized substrates were added under nitrogen. The polymerization reactions were carried out in a thermostat at 60.0 ± 0.1 °C. The technique allows for an independent control over both, the graft density and the molecular weight. The graft density can be controlled by varying the conversion of the surface attached initiator through adjustment of the polymerization time. The molecular weight of the surface-attached polymer chains can be controlled via the monomer concentration. To remove free polymer chains, the PMAA-grafted substrates were extracted in methanol and water for approximately 15 h, respectively. The molecular weight of the surface-attached polymer molecules could not be precisely measured by gel permeation chromatography (GPC) since the higher molecular weight fraction of the polymer was beyond the exclusion limit of available GPC columns and also beyond the limits of available GPC standards. However, from the film thickness data (brush thickness d as a function of the graft density $\Gamma(t)$ for different polymerization times and the number-averaged molecular weight M_n: $d = \Gamma(t)M_n$) and from a comparison to experiments, which were almost identical although using a lower monomer concentration, the molecular weight of the surface-attached polymer can be estimated to be around $(4 \pm 1) \times 10^6$ g/mol. Note that the exact molecular weight does not affect the interpretation of the experimental findings. From the dry layer thicknesses, the molecular weight, and the polymerization time (3 h) we estimate the graft density of the PMAA brushes to be on the order of 0.01 μmol/m^2, corresponding to an anchoring distance D of approximately 12 nm so that all polymer layers were well in the brush regime.

2.3. Instrumentation. Ellipsometric spectra were recorded on a home-built multiple angle null ellipsometer in an attenuated total reflection geometry. The light was coupled into a high refractive index glass prism (see section 2.1) from the backside and was reflected at the base of the prism where the polymer brush was grown. The light source was a He−Ne laser with a wavelength of 632.8 nm and an intensity of 3 mW. Automated minimizations were performed at predefined angles. An angular scan took approximately 30 min and was needed to determine the swollen brush volume fraction profile (see section 3.1). To obtain a better time resolution for kinetic measurements, continuous minimizations were performed at a fixed angle and the ellipsometric parameters Δ and Ψ were recorded as a function of time. The angle was chosen so that the Δ value was most sensitive to a change in the swollen brush thickness (close to the critical angle). The setup was described in detail previously.[22,23]

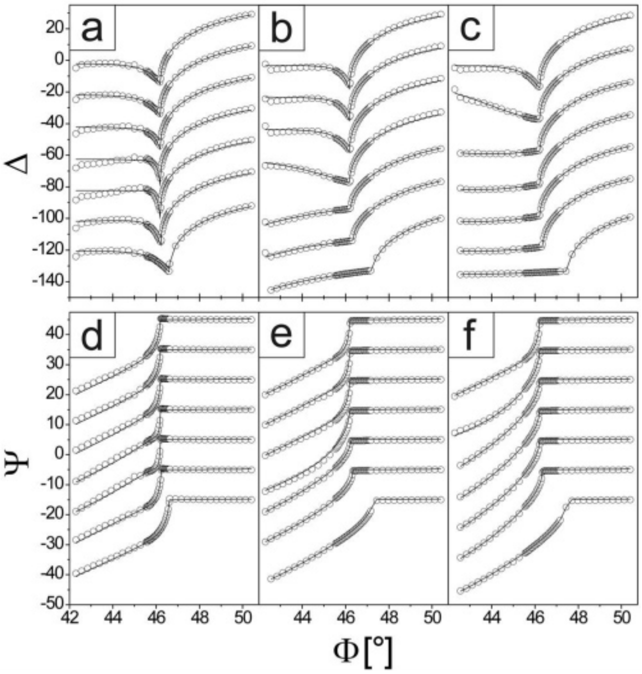


Figure 3. Representative ellipsometric spectra (Δ and Ψ as a function of the incidence angle) of PMAA brushes (d_{dry} = 42 and 46 nm) swollen in aqueous solutions of $NaNO_3$ (a and d), $Ca(NO_3)_2$ (b and e), and $Cu(NO_3)_2$ (c and f). The spectra at the very top of each graph correspond to brushes swollen in deionized water. From the second spectrum to the bottom, the concentrations were 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, and 1 mol/L, respectively. Δ- and Ψ-traces were offset by 20 and 10°, respectively. The solid lines represent model calculations using a complementary error function to describe the refractive index profile at the interface.

3. Results and Discussion

3.1. Characterization of the Swelling Behavior. All salts were dissolved in neutral water (pH = 7). Some of the used ions (Mg^{2+}, Cu^{2+}, Al^{3+}) react slightly acidic in aqueous solution, depending on the nature and the concentration of the respective ion. We did not adjust the pH by adding a base in order to avoid the presence of monovalent counterions which would lead to competitive adsorption of mono- and multivalent cations.

Figure 3 compares typical ellipsometric spectra and the corresponding model fits for a PMAA brush in the presence of sodium (Figure 3a,d), calcium (Figure 3b,e) and copper ions (Figure 3c,f).

Parts a−c and d−f of Figure 3 represent the Δ- and Ψ-traces, respectively. The refractive index profile at the interface was modeled by using a complementary error function. This function was chosen as the simplest mathematical description of what one would qualitatively expect for the volume fraction profile of a swollen polydisperse polymer brush. The model calculations are represented in Figure 3 as solid lines. Although an exact evaluation of the data relies on the fitting procedure, a

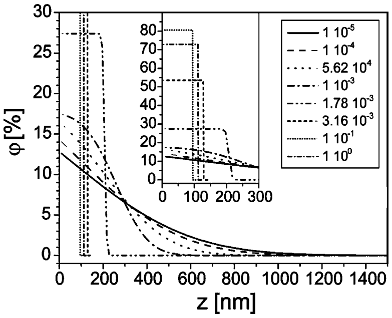


Figure 4. Representative volume fraction profiles of a PMAA brush ($d_{\text{dry}} = 46$ nm) swollen in aqueous solutions of $Ca(NO_3)_2$. The salt concentrations are denoted in the figure. The profiles were derived from model calculations based on the ellipsometric spectra of Figure 3, parts b and e. The inset shows an enlargement.

visual inspection of the Δ- and Ψ-traces already allows us to qualitatively track the major features concerning the swelling behavior of the brush in the course of a series of measurements. Below the critical angle, the ellipsometric spectra are related to the Fourier transform of the segment density profile. In this region, the slope of both the Ψ- and the Δ-trace, are related to the swollen brush thickness with a steeper slope beeing indicative of a higher brush thickness for both functions. This aspects have been discussed in more detail previously.[18,23] One can now analyze the qualitative trends from the raw data of Figure 3. The brush in the presence of sodium ions is swollen at all concentrations. Moreover, at intermediate concentrations, the swelling becomes even more pronounced. In the presence of both calcium and copper ions, one can see, that the swelling dramatically decreases with increasing salt concentration. This behavior starts at lower concentrations for copper in comparison to calcium ions.

The volume fraction profiles which were obtained through an iterative modeling of the experimentally found Δ- and Ψ-traces with the complementary error function are represented in Figure 4.

Exemplarily, the profiles of the PMAA brush in contact with aqueous solutions of increasing calcium ion concentration are shown. These profiles were derived from the model calculations shown in Figure 3, parts b and e. At low salt concentrations, the brush is highly swollen and shows an almost exponential profile extending far into solution. The polymer volume fraction close to the surface is only ≈10 vol %. With increasing salt concentration, the profile becomes more and more box-like and correspondingly, the brush more and more contracts and the polymer segments accumulate at the surface. At a concentration of 10^{-1} mol/L the polymer volume fraction close to the surface is ≈80 vol %. In the following, we define the swollen brush thickness as twice the normalized first moment of the volume fraction profile.[22] This thickness is equal to a box-profile with the same integrated area and the same first moment and will be used throughout this article to describe the swelling behavior of the polymer brushes.

3.2. Monovalent Cations. In Figure 5, the thickness of a PMAA brush swollen in aqueous solutions of sodium and silver nitrate of neutral pH is shown as a function of the respective salt concentration.

It should be noted that the identical brush was used for the examination of both ions. Therefore, the difference in the influence of the two monovalent counterions on the swelling behavior of the brush should become directly visible. In this investigation, the brush was first swollen in pure water of neutral pH and then treated with increasingly concentrated silver ion solutions. Reaching a maximum concentration of 1 mol/L, the silver ion concentration was again gradually decreased and finally exchanged for pure water. The same brush was then equilibrated with sodium ion solutions of increasing concentrations.

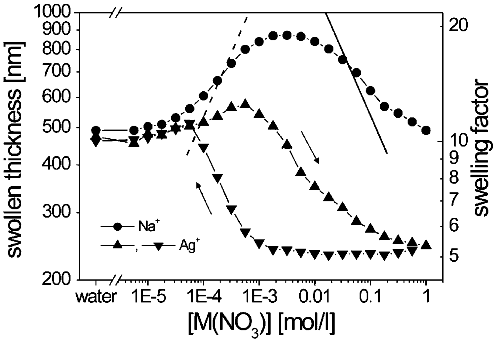


Figure 5. Swollen thickness of a PMAA brush ($d_{\text{dry}} = 42$ nm) in contact with aqueous solutions of $NaNO_3$ (●) and $AgNO_3$ (▲) of neutral pH as a function of the external salt concentration. In the case of silver ions, the brush was equilibrated with increasing (▲) and decreasing (▼) concentrations of silver nitrate. The dashed line (slope $m = +1/3$) and the solid line (slope $m = -1/3$) correspond to theoretical scaling predictions for a weak polyacid brush in contact with aqueous solutions of monovalent ions in the osmotic and the salted brush regime.

Sodium. The qualitative trend of the swollen brush thickness as a function of the sodium ion concentration as estimated from an inspection of the raw data (compare section 3.1) was confirmed by the quantitative evaluation of the ellipsometric spectra. The brush is in a highly swollen state at all salt concentrations. In the intermediate concentration range the swelling is even more pronounced so that the brush thickness passes through a maximum at 3 ± 1 mmol/L. On the basis of simple considerations, the general trend can be well understood, although it might be somewhat counterintuitive at a first sight. At infinitely low salt concentrations (the experimentally accessible region is limited by the self-dissociation of water), the protons are confined within the brush in order to keep the surface-attached polymer layer electroneutral. The dissociation of the carboxylic acid groups is therefore at a minimum. The addition of low amounts of sodium ions facilitates the dissociation of the acid groups as sodium ions can now replace protons which in turn can leave the brush without violating the electroneutrality condition. This way increasing the charge density along the chains, electrostatic repulsion leads to an increase in the swelling of the brush. As a consequence, at sufficiently low salt concentrations, the brush thickness increases with increasing salt concentration. This is called the osmotic brush regime. However, above a critical ionic strength (in the salted brush regime), further addition of salt leads to an increased electrostatic screening of the charged groups leading to a decreasing brush thickness with increasing salt concentration.

The swelling behavior of weak polyacid brushes as a function of the external salt concentration has also been subject to a number of theoretical investigations.[24−28] In these studies, the polyelectrolyte brush metal ion interactions are assumed to be purely ionic. The predicted scaling laws are included in Figure 5. At low salt concentrations, in the osmotic brush regime, the brush thickness is expected to increase with the ion concentration with a slope of $m = +^1/_3$ (dashed line). At high salt concentrations, in the salted brush regime, the brush thickness is expected to decrease with the ion concentration with a slope of $m = -^1/_3$ (solid line). Although the experimental data indicates smaller exponents, the qualitative behavior is correctly seized by the theory. Discrepancies may stem from the nontrivial segment density profile and the polydispersity of the real brush system. Furthermore, the steric repulsion between the monomeric units was neglected in the scaling approach although the influence of this effect becomes evident if one considers the influence of the graft density on the swelling behavior of such systems.[29] A detailed comparison of the influence of the nature of the alkaline metal and the halogen ion as well as that of the graft density of the PMAA brush on the swelling behavior has been recently published.[29] The results of Ballauff et al.[30] and Currie et al.,[31] who studied similar systems, are qualitatively in good agreement with our findings.

Silver. The theoretical descriptions of a weak polyacid brush in contact with monovalent cations do not differentiate between chemically different ions. In principle, all monovalent cations should therefore behave similar. It is interesting to see whether the underlaying assumption that the brush metal cation interactions are exclusively of ionic nature still holds true when going to a monovalent transition metal ion. We have chosen silver ions to test this case. The swollen thickness of a PMAA brush in contact with first increasingly and then decreasingly concentrated solutions of silver nitrate is shown in Figure 5. As mentioned above, the swelling behavior in the presence of silver and sodium ions was studied on the very same brush so that a direct comparison can be made. Note that all silver ion solutions were freshly prepared from analytical grade salt and that all measurements were performed in an automated setup directly one after the other. It is therefore very unlikely that elementary silver particles have formed. In contrast to the theoretical predictions, a completely different behavior was found for the silver ions in comparison to the sodium ions: First, the maximum in the swollen brush thickness is much less pronounced and shifted to lower ion concentrations (≈0.5 mmol/L). Second, the decrease of the brush height upon addition of salt was much more pronounced as in the sodium case when the silver ion concentration was further increased up to 1 mol/L. The brush shrank to only half of the thickness it had before the addition of salt in pure water. Upon decreasing the ion concentration, a reswelling started indicating the removal of the silver ions only at concentrations below 1 mmol/L. While swelling and deswelling with increasing and decreasing salt concentration followed essentially the same curve in the sodium case, the reswelling occurred in the silver case only at a several orders of magnitude lower concentration. In addition, in the silver case, no maximum in the brush height could be observed when the salt concentration decreased. Regardless of this it should be noted that the silver ions were gradually completely removed and the initial swollen brush thickness in pure water was recovered again indicating that no silver remained in the brush. Clearly, the behavior of the PMAA brush in the presence of silver ions is fundamentally different from the behavior in the presence of sodium ions and strongly deviates from theoretical predictions. As these are based on ionic interactions alone, we ascribe the observed behavior to a significant contribution of specific interactions between the carboxylic acid groups and the silver ions to the polymethacrylate silver ion complex formation. Specific interactions of silver ions with polyacids were also observed for other systems. For instance, Pohl and Kuhn observed a shrinkage of a poly(acrylic acid) (PAA) gel upon addition of silver ions with a concurrent change in the UV spectrum.[32] Ikegami and Imai investigated the precipitation of bulk PAA on addition of different kind of ions, including silver ions.[33] They explained the precipitation with a dehydration of both the metal cations and the carboxylate groups as a result of the specific binding and a thus increased hydrophobicity of the polymer. Accordingly, it seems likely that the carboxylate groups in the PMAA brush become more and more hydrophobic with increasing silver ion loading due to charge recombination and concurrent dehydration as a result of specific binding. This leads to an increase in hydrophobic interactions within the brush and eventually to major conformational changes causing a shrinkage of the brush. Now, when the silver ion concentration is decreased, the redissolution of the complex is very difficult as water molecules have to penetrate into the hydrophobic patches and hydrophobic interactions have to be broken up, what is probably associated with a high activation barrier. We do not know whether such a process is just slow, i.e., the system is then in a metastable state, or a new thermodynamic equilibrium is obtained. In the latter case, the polymer is after ion addition much more strongly associated with specifically interacting counterions and adopts a conformation that is very different from the conformation prior to salt addition.

In a way, the silver case represents a transition of the binding behavior between the fully reversible situation when sodium couterions are employed and the situation if a PMAA brush was exposed to multivalent counterions and then immersed into water. As will be discussed in section 3.3, in the latter case a completely irreversible swelling behavior was observed; i.e., the strongly shrunken brush could not be reswollen in pure water.

3.3. Divalent Alkaline-Earth Metal Ions. We have seen that the swelling behavior of a PMAA brush in the presence of monovalent cations was fundamentally altered when going from an alkaline to a transition metal ion. The question arises how an increase in the valency of the metal cation would influence the swelling behavior. To answer this question, we have replaced the monovalent cations by divalent alkaline-earth ions. Figure 6 shows the swelling behavior of a PMAA brush in aqueous solutions of alkaline-earth metal nitrates as a function of the divalent salt concentration at neutral pH.

Strikingly, for all alkaline-earth ions, the PMAA brush exhibits a collapse at intermediate concentrations (around 10^{-3} mol/L) and displays no maximum in the brush swollen thickness as it was found in the case of sodium ions. The differences between the various alkaline-earth ions, i.e., the influence of the polarizability of the cation, are much less pronounced. Note that the influence of the different alkaline-earth ions on the swelling behavior of the PMAA brush was studied on the very same brush for all ions. Once the brush was collapsed in concentrated salt solution a reswelling with water was impossible. However, the brush could be

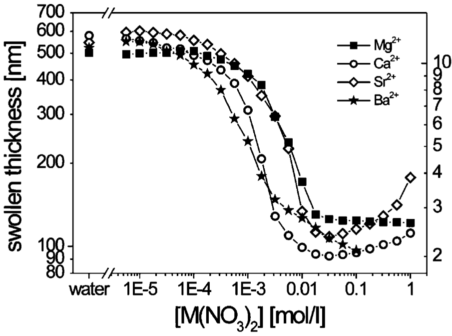


Figure 6. Swollen thickness of a PMAA brush ($d_{\mathrm{dry}} = 46$ nm) in contact with aqueous solutions of $Mg(NO_3)_2$ (■), $Ca(NO_3)_2$ (○), $Sr(NO_3)_2$ (◇), and $Ba(NO_3)_2$ (★) of neutral pH as a function of the external salt concentration.

reswollen upon multiple exchange of the medium for 0.1 mol/L sodium nitrate solutions indicating that all alkaline-earth ions could be replaced by sodium ions. The sodium ions in turn could be replaced by protons upon multiple exchange of the solution for water of neutral pH. Finally, the initial swollen brush thickness was obtained, and the influence of another ion could be studied.

At a first glance, one might expect a more gradual shrinkage of the brush rather than a collapse at a critical calcium ion concentration as the calcium ion concentration in solution is gradually increased. To exclude the possibility that a kinetically slow shrinkage at low calcium ion concentrations was missed in our measurements due to too short exposure, we performed kinetic studies on a PMAA brush in contact with increasingly concentrated calcium ion solutions. This investigation is summarized in Figure 7.

Figure 7a shows the equilibrium swollen thickness as a function of the calcium ion concentration. The values at each concentration were taken only after the brush thickness had reached an equilibrium and only then, the calcium ion concentration was increased and a kinetic measurement on the next higher concentration was performed. The corresponding kinetic measurements are represented in Figure 7, parts b and c. Figure 7b shows kinetic measurements at 10^{-5} and 10^{-4} mol/L under steady-flow conditions. To obtain a time resolution in the range of a few seconds, these measurements were performed at a fixed angle of incidence and Δ was recorded as a function of time as described in section 2.3. Δ levels off at constant values within approximately 15 and 35 min after the brush was placed in contact with calcium ion solutions of 10^{-5} and 10^{-4} mol/L, respectively. The equilibration of the PMAA brush with the calcium ion solution of 10^{-3} mol/L was slower and could be studied with successive angular scans. The respective swollen brush thicknesses as a function of time are depicted in Figure 7c. The solution was not added in a steady-flow manner but was instead renewed three times prior to each angular scan, and each time, the system was allowed to equilibrate for 20 min. The swollen thickness reaches an equilibrium after approximately 10 h. The fact that the equilibrium was reached faster for the lower concentrations indicates that diffusion is not the rate-limiting step. It is rather likely, that the conformational reorganization of the polymeric chains in the course of shrinking is rate limiting. At 10^{-3} mol/L, the swollen brush thickness changes by approximately a factor of 2. At 10^{-2} mol/L, the equilibrium was reached after three cycles (not shown), at all following concentrations, the first and the second cycle were almost identical. The overall curve in Figure 7a is well in accordance with the one shown in Figure 6. This confirms, that the brush in contact with the different salt solutions was in (quasi-)equilibrium at all concentrations. Furthermore, the collapse was found at the exact same concentrations, between 10^{-3} and 10^{-2} mol/L in both experiments. This again confirms that a slow, gradual decrease in the swollen brush thickness at low calcium concentrations can be firmly excluded.

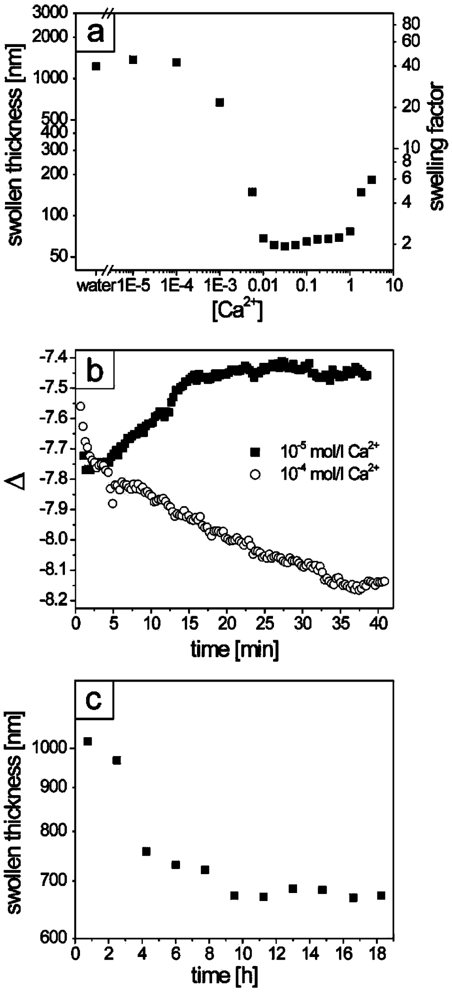


Figure 7. Kinetic study of the interaction of a swollen PMAA brush ($d_{\mathrm{dry}} = 31$ nm) with Ca^{2+} ions of increasing concentration. (a) Equilibrium swollen brush thickness as a function of the $Ca(NO_3)_2$ concentration. (b) △ as a function of time at a fixed angle of incidence (46.15°). The swollen brush was in contact with a 10^{-5} mol/L (■) and a 10^{-4} mol/L (○) solution of $Ca(NO_3)_2$ under steady flow conditions. The flow rate was approximately 3 mL/min c) Swollen brush thickness in the presence of a 10^{-3} mol/L solution of $Ca(NO_3)_2$ as a function of time. Three times prior to each angular scan, the solution was renewed and the system was allowed to equilibrate for 20 min.

To address the question how we can understand the tremendous shrinkage of the brush at a critical concentration of alkaline-earth metal ions, a comparison of the experimental findings with theoretical predictions was made. On the basis of a scaling model, Zhulina and Birshtein theoretically described the equilibrium structure of an annealed brush interacting with multivalent cations.[34,35] As compared to the theoretically predicted behavior for the interaction with monovalent cations, a maximum in the swollen brush thickness with increasing ion concentration is also expected and should be shifted to lower ion concentrations for multivalent salts. Accordingly, a higher charge of the salt counterion should only lower the exponents in the scaling dependences of the degree of neutralization and the swollen brush thickness on the salt concentration. A strong shrinkage of the brush, however, is not predicted. This theoretically predicted behavior is clearly contradictory to our experimental observations. Again, the scaling approach was based on the assumption, that electrostatic interactions would dominate, i.e., that the binding of the calcium ions to the carboxylate groups would be mainly ionic. This suggests that the binding between the PMAA brush and the alkaline-earth ions is dominated by specific interactions.

The complex formation of polycarboxylates with multivalent cations such as alkaline-earth ions has also been studied for bulk polyacids[33,36−45] and for polyacid gels.[46−49] It is commonly discussed in terms of a specific binding and it is generally accepted that a partial dehydration of both the polyanion and the cations leads to an increased hydrophobicity of the polymer. A contraction of the polymer is accordingly assigned to increasing hydrophobic interactions within the polymer and a decreasing solvation power of the solvent. The dehydration phenomenon was investigated in detail by Ikegami and Imai.[33,37] They performed refractive index measurements on poly(acrylic acid) (PAA) solutions in the presence of multivalent cations, including alkaline-earth ions. They found, that the binding of these ions, unlike the interaction with sodium ions, destroys the first “intrinsic” hydration region of the polyanion leading to partial dehydration. Huber et al. investigated the shrinkage of PAA chains in the presence of calcium ions by light scattering.[44] They also observed a reduction of the coil dimensions and a characteristic precipitation behavior upon increasing the Ca^{2+} concentration and attribute this to an increasing hydrophobicity of the chains. Finally, interesting conclusions can be drawn by a comparison with the work of Horkay et al., who investigated the contraction of fully neutralized PAA gels upon the interaction with a variety of cations.[46−48] In the case, of sodium ions interacting with the PAA gel, only a slight contraction due to screening effects was observed. However, in the presence of divalent cations, they found that, at a critical salt concentration, a sudden volume transition occurs. The critical concentration was depending on the chemical identity of the cation and was significantly lower for transition metal ions than for alkaline-earth ions. They could experimentally separate different contributions to the free energy of the gel interacting with the different cations and found that the mixing free energy was not altered in the presence of sodium, but in the presence of divalent cations. Furthermore, a distinct difference was found for PAA gels interacting with alkaline-earth ions and for those interacting with divalent transition metal cations, such as copper, or with trivalent cations: only the latter ones were causing a change in the elastic properties of the gel in addition to the change in the mixing free energy. In conclusion, this strongly suggests that divalent cations do specifically interact with the gel, whereas sodium ions, as expected, only interact ionically. Furthermore, to account for the different findings for alkaline-earth ions and transition metal or trivalent ions, the authors suggest the promotion of a weak aggregation of the chains in the swollen gel in the former case, and only in the latter case they assign the sudden volume change to the formation of additional more permanent cross-links. This strongly indicates that the collapse of the PMAA brush interacting with calcium ions is due to dehydration and accordingly a reduced solubility of the complex and not due to a cross-linking of the brush by the ions.

We have studied the complexation behavior of PMAA brushes with a number of different cations, including calcium ions, by infrared spectroscopy previously.[50] The degree of dissociation of the carboxylic acid groups and accordingly the concentration of calcium ions inside the brush could be determined. In this context, two observations from this study shall be mentioned. First, we found that the increase in complex formation with increasing external salt concentration is monotonic and smooth, which implies that the collapse is not related to an abrupt change in the calcium concentration in the brush. This is in accordance with Horkay et al.[47] Despite the discontinuous change in the gel volume, they measured a smooth and continuous increase of the calcium concentration in the gel by flame atomic absorption spectroscopy. Second, the degree of dissociation did strongly depend on both the external salt concentration in solution and the graft density of the brush. In all cases, however, the degree of dissociation was less than unity; i.e., the brush was not fully deprotonated in the concentration range where the collapse with calcium ions occurs. For instance, the degree of dissociation of a PMAA brush having a similar graft density than the one used in Figure 6 was determined to be less than 0.3 and 0.4 after equilibration with calcium ion solutions of 10^{-3} and 10^{-2} mol/L, respectively. This is remarkably different from the behavior of free polycarboxylate in solution. When calcium ions are added to this system it has been found, that a precipitation occurs close to the isoelectric point, i.e., at Ca^{2+}/COO^{-}-ratios of approximately 0.5, in a L-type precipitation according to Ikegami and Imai.[33,38,40] For instance, Sabbagh and Delsanti reported a value of $Ca^{2+}/COO^{-} = 0.36$ for the precipitation of sodium polyacrylate with calcium ions.[40] The different behavior of the polymer brush system is likely to be a consequence of the surface confinement of the polymer chains.

We finally want to address the reswelling phenomenon which was found at high concentrations of $Sr(NO_3)_2$ and $Ca(NO_3)_2$ (compare Figure 6 and Figure 7a), where the collapsed brush experiences again an increase in the swollen thickness with increasing salt concentration to a certain extent. At 1 mol/L (Figure 6), this effect was most pronounced for strontium ions (the reswelling was ≈60% compared to the minimum swelling at ≈0.03 mol/L). The reswelling was less pronounced in the case of calcium ions (≈20%) and absent in the case of magnesium ions. Unfortunately, if barium ions were employed, this concentration region was not experimentally accessible due to the limited solubility of barium salts. At extremely concentrated calcium nitrate solutions (Figure 7a) of up to more than 3 mol/L, a value close to the solubility limit, the brush reswells quite strongly by approximately a factor of 3.

A small linear increase in the swollen brush thickness as it was found for calcium ions in the range from 0.03 to 1 mol/L could be simply due to a mass uptake from salt penetrating into the brush. However, the strong changes at high concentrations in the strontium and calcium case cannot be explained by such an effect.

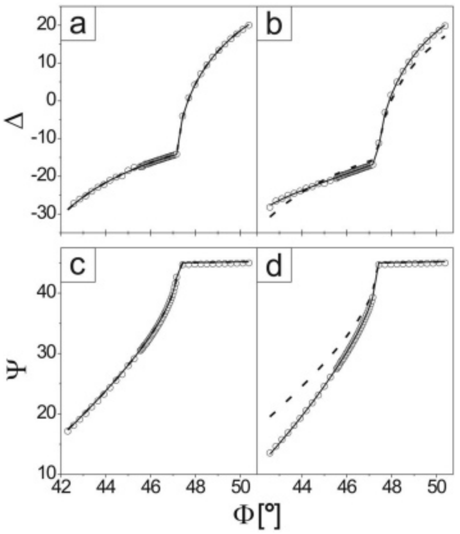


Figure 8. Ellipsometric spectra (Δ and Ψ as a function of the incidence angle) of a PMAA brush ($d_{\mathrm{dry}} = 46$ nm) in contact with 1 mol/L aqueous solutions of $Mg(NO_3)_2$ (a and c) and $Sr(NO_3)_2$ (b and d). The solid lines represent best fits using a box-model for the refractive index profile at the interface. The dashed lines show corresponding fits with the brush thickness fixed at the value of minimum swelling at 0.03 mol/L.

Although the absolute values of the changes of the film thickness in this regime where the film is almost collapsed should not be overemphasized, as the accuracy of the fitting procedure in this thickness regime is limited, the general trend is undoubtedly clear. This is illustrated in Figure 8, where the Δ- and Ψ-traces of a PMAA brush in contact with 1 mol/L aqueous solutions of $Mg(NO_3)_2$ (parts a and c) and $Sr(NO_3)_2$ (parts b and d) are shown together with best fits using a box-model for the refractive index profile at the interface (solid lines) and with fits where the brush thickness was fixed at the value of minimum swelling at 0.03 mol/L (dashed lines).

In the case of strontium, a good fit was only obtained when the swollen brush thickness was increased from 103 to 177 nm, whereas in the case of magnesium, a value of 119 nm gave identically good fits for both concentrations. As the reswelling is quite strong and as a simple mass uptake would only lead to minor changes in the film thickness, it seems obvious that this effect is due to a change in the hydrophilicity of the polymer. Furthermore, it is known, that alkaline-earth ions can form both mono- (mc) and dicomplexes (dc) with the carboxylic acid moieties of polycarboxylates.[51,52] Monocomplexes and dicomplexes are formed when the divalent cation binds to only one or to two carboxylic acid moieties, respectively. The formation of the two complex species is interconnected via the equilibrium $2\mathrm{mc} \rightleftharpoons \mathrm{dc} + \text{free ion}$ (see Scheme 1).

For free polyacids in solution, it has been predicted that the polymer should redissolve due to strong charge inversion, if monocomplexation is favored.[51] Precipitation and redissolution of a free polymer in solution correspond to the collapse and reswelling of the surface confined polymer brush. Accordingly, upon addition of large amounts of calcium ions the aforementioned equilibrium could be shifted toward the monocomplexes, and the reswelling would be the result of a charge inversion of the brush. The subtle differences in the swelling behavior of a PMAA brush in the presence of the different alkaline-earth ions as shown in Figure 6 may also be attributed to differences in the complex formation constants of mono- and dicomplexes for the different ions. With increasing ion radius of the bivalent ions, the polarizability and monocomplex formation and accordingly the reswelling at high ion concentration increases. As a result, the tendency to reswell at high ion concentration increases in the order Mg^{2+} (no reswelling) < Ca^{2+} (slight reswelling) < Sr^{2+} (strong reswelling).

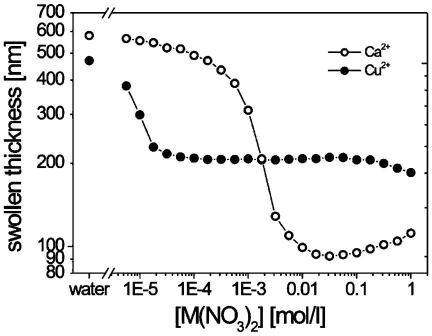
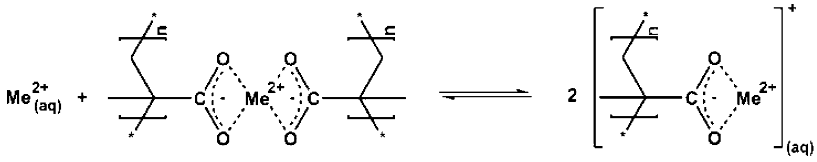


Figure 9. Swollen thickness of a PMAA brush ($d_{\mathrm{dry}} = 46$ nm) in contact with aqueous solutions of $Ca(NO_3)_2$ (○) and $Cu(NO_3)_2$ (●) of neutral pH as a function of the external salt concentration.

3.4. Copper. A Divalent Transition Metal Ion. We have seen distinct differences in the interaction of the PMAA brush with a monovalent main group and a monovalent transition metal ion (compare section 3.2). How would an exchange of the divalent alkaline-earth ions for a divalent transition metal ion affect the swelling behavior of the PMAA brush? To answer this question, we have placed a PMAA brush in contact with copper nitrate solutions of increasing concentrations. Figure 9 shows a comparison of the swelling behavior in the presence of calcium and copper ions.

Again, the brush was reswollen after calcium complexation through multiple exchanges of the medium first for sodium nitrate solution and then for water and the very same brush was used to study the interaction with copper ions. Hence the two curves are directly comparable. As for the monovalent ions, an exchange of the main group metal ion for a transition metal ion at constant valency leads to a conspicuously different swelling behavior of the PMAA brush. In contact with copper ions, the brush already collapses at extremely low concentrations $<10^{-5}$ mol/L which is more than 2 orders of magnitude lower than in contact with calcium ions. However, with further increasing copper ion concentration, the swollen brush thickness remains

Scheme 1. Equilibrium between Mono- and Dicomplexes of Alkaline-Earth Metal Ions and Polycarboxylates



constant at a level that is elevated in comparison to the alkaline-earth case.

The difference in the behavior of the two metal ions can be related to the different geometries of the calcium and copper polycarboxylate complexes. The structure of polycarboxylate copper complexes has been described by François and Heitz.[43] Both ions can form chelating bidentate complexes where the central ion is coordinated to both oxygen atoms of the carboxylate ligand. Either mono- or dicomplexes with one or two ligands attached can be formed as discussed in section 3.3. Only the copper ions, however, can in addition form binuclear complexes through the association of two copper ions with two pairs of adjacent carboxylate groups. The carboxylate ligand binds in a bridging bidentate configuration with the two oxygen atoms of the ligands being coordinated to different copper ions. The two central copper ions are bridged by four carboxylate groups with two additional solvent ligands along the central copper−copper axis. Interestingly, the chelating bidentate and the bridging bidentate coordination of the polycarboxylate ligand are reflected in separate carbonyl absorption bands in the infrared spectra of the respective complexes. We have studied the PMAA brush complexes with calcium and copper ions previously.[50] For calcium ions only one absorption band of the carboxylate ion due to a chelating bidentate coordination was found. In contrast to this, for PMAA brushes interacting with copper ions, two carboxylate absorption bands were found, corresponding to both chelating and bridging bidentate complexes. These findings strongly suggest that the collapse of the PMAA brush at very low copper ion concentrations is caused by a bridging of the polymeric chains by the copper ions. This explanation is well in accordance with the work of Horkay et al. on the interaction of a PAA gel with alkaline-earth and transition metal cations. When transition metal ions were used, the gels collapsed at lower concentrations compared to alkaline-earth metal ions and only transition metal ions caused a change in the elastic properties of the gel indicating an additional bridging of the polymeric chains. The fact that the brush shrinks upon exposure to copper ions much less compared to the calcium exposed brush could be due to the increased steric demands of the binuclear complex. Moreover, it is likely that the binuclear complex, which in solution includes two water molecules along the copper−copper axis, is more hydrophilic than the chelating bidentate complex, which causes a dehydration of the polymer.

The PMAA brush in contact with copper nitrate solutions already shrank at the lowest concentration used (5.6×10^{-6} mol/L). At this concentration, however, the number of ions in the total cell volume was calculated to be less than the number of surface bound carboxylic acid groups. We therefore performed a kinetic measurement under steady-flow conditions in the very same manner as with the calcium ions (see Figure 10).

A PMAA brush was treated with a copper nitrate solution of a concentration as low as 10^{-6} mol/L. The angle of incidence was fixed at a position where Δ is most sensitive to a change in the swollen brush thickness and the ellipsometric parameters were recorded as a function of time. The Δ-trace is shown in Figure 10a. In addition, angular scans before the addition of copper ions, when the brush was swollen in pure water and after the adsorption of the copper ions, at the end of the kinetic measurement were taken and are shown in Figure 10, parts b and c, respectively. Δ immediately starts to fall when the brush is exposed to the copper ion solution and reaches an equilibrium value after approximately 8 h. The swollen brush thicknesses before and after addition of copper ions were obtained from the angular scans. The brush shrank to only one-fourth of its original thickness in the course of the kinetic measurement. This proves that the PMAA brush is indeed sensitive to trace concentrations of copper ions. Such a behavior cannot be expected if only a reduction in hydrophilicity of the brush was caused by the copper ion complexation. Much more realistic, this can be ascribed to a bridging of the polymeric chains by the copper ions.

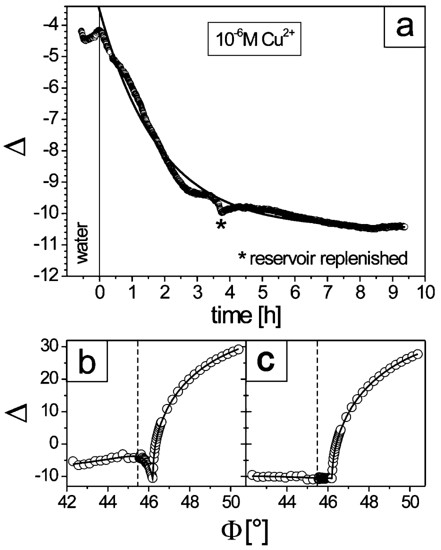


Figure 10. (a) Kinetic ellipsometric measurement of the collapse of a PMAA brush (d_{dry} = 28 nm) in contact with a 10^{-6} mol/L solution of $Cu(NO_3)_2$ under steady flow conditions. The flow rate was approximately 3 mL/min. △ was recorded as a function of time at a fixed angle of incidence (45.54°). The solid line is a guide to the eye. (b) Angular scan (only the Δ-trace is shown, Ψ is omitted for clarity) of the brush swollen in deionized water before the addition of $Cu(NO_3)_2$ solution. The angle at which the kinetic measurement was performed is marked with a dashed line. The swollen thickness was determined by a model fit (solid line) as 809 nm. c) Angular scan of the brush at the end of the kinetic experiment (9.3 h). The brush swollen thickness had shrunk to 200 nm.

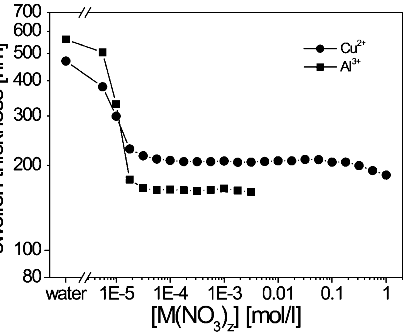


Figure 11. Swollen thickness of PMAA brushes in contact with aqueous solutions of $Cu(NO_3)_2$ (●; d_{dry} = 46 nm) and $Al(NO_3)_3$ (■; d_{dry} = 45 nm) of neutral pH as a function of the external salt concentration.

3.5. Aluminum. A Trivalent Cation. In Figure 11, the swelling behavior of a PMAA brush in the presence of increasingly concentrated solutions of $Al(NO_3)_3$ is compared to that of a PMAA brush in contact with $Cu(NO_3)_2$ solutions.

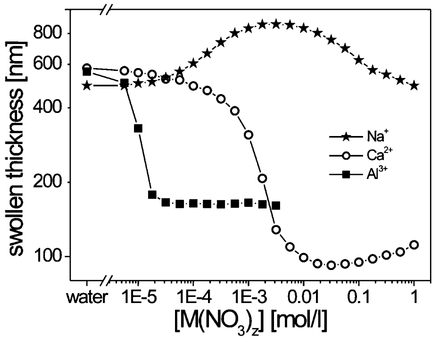


Figure 12. Swollen thickness of PMAA brushes in contact with aqueous solutions of $NaNO_3$ (★; $d_{\mathrm{dry}} = 42$ nm), $Ca(NO_3)_2$ (○; $d_{\mathrm{dry}} = 46$ nm) and $Al(NO_3)_3$ (■; $d_{\mathrm{dry}} = 45$ nm) of neutral pH as a function of the external salt concentration.

The aluminum nitrate solutions were not concentrated to more than 3 mmol/L since the acidic reaction of the hydrated aluminum ions would then cause a change in the pH value of the solutions. The influence of a change in the pH value and that of a change in the aluminum ion concentration on the swelling behavior of the PMAA brush cannot be separated. The use of a buffer, on the other hand, would change the ionic strength and the behavior of the brush would also be altered. The two brushes in contact with aluminum and copper ion solutions, respectively, show a very similar behavior: Both undergo a strong deswelling at extremely low salt concentrations. As in the copper case, the brush treated with aluminum ions remains at an elevated degree of swelling as compared to the calcium case once the brush was collapsed.

The similarity of the interactions of PMAA brushes with copper and aluminum ions was also found in the infrared spectra.[50] Both complexes were characterized by two carboxylate vibrational bands, corresponding to chelating and bridging bidentate complexation. It therefore seems rational to assume a bridging of the polymeric chains of the PMAA brush by the aluminum ions similar to that found for the interaction with copper ions. The exact geometry of the aluminum PMAA brush complex is unknown but may differ form that of the respective copper complex. This could account for the slightly lower swelling factor of the former complex.

4. Conclusions: A Classification

We summarize our findings on the swelling behavior of PMAA brushes in the presence of different kinds of metal ions in a classification of the ions with respect to the nature of their interaction with the PMAA brushes and the related influence on the swelling behavior of these brushes. In Figure 12, a typical representative of each class is shown.

We have discussed essentially three mechanisms that govern the swelling of PMAA brushes.

Mainly Ionic Interactions. Ionic interactions dominate the swelling behavior of PMAA brushes in the first class. Ions like sodium and other alkaline ions fall into this class. Typically, the swollen brush thickness passes through a maximum with increasing salt concentration and the addition of salt is fully reversible. This class is the only one where the experimental observations are qualitatively in agreement with theoretical investigations.

Specific Interactions. Dehydration. The second class is characterized by specific interactions leading to a dehydration of both the ions and the polymeric chains. Typical representatives of this group are the alkaline-earth metal ions, but also silver is best represented by this class. With increasing ion loading, the brush becomes less hydrophilic and typically a collapse of the swollen brush is observed at intermediate concentrations between 0.001 and 0.01 mol/L when the solvation power of the aqueous solution is surpassed by hydrophobic interactions within the polymer brush metal ion complex. The formation of the complex is irreversible, i.e., the brush cannot be reswollen in low concentrated solutions of the same ion or in pure water after being collapsed with this type of ion (with the exception of silver ions). However, ions of this class can be replaced by ions of the first class which in turn can be removed by water.

Specific Interactions. Bridging. In the third class, specific interactions involve a bridging of the carboxylate groups by the metal ions via strong complexation. This behavior was found on one hand for the trivalent aluminum ion and on the other hand for the divalent transition metal ion copper. Typically, the brush strongly deswells already at trace concentrations of these ions due to a bridging of the polymeric chains by the metal ions. However, the brush remains at a higher degree of swelling after exposure to this kind of ions than after being collapsed by ions of the second class. This is probably due to the higher hydrophilicity of the PMAA brush complexes with ions of the third class.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft, DFG (Schwerpunkt: Polyelektrolyte mit definierter Molekülarchitektur), under Grant No. Ru 489/6-3, is gratefully acknowledged. D. Johannsmann is thanked for the development of the ellipsometry software.

References and Notes

(1) Rühe, J.; et al. *Adv. Polym. Sci.* **2004**, *165*, 79−150.
(2) Biesalski, M.; Rühe, J.; Kügler, R.; Knoll, W. Polyelectrolytes at solid surfaces: multilayers and brushes. In *Handbook of Polyelectrolytes and Their Applications*; Tripathy, S. K., Kumar, J., Nalwa, H. S., Eds.; American Scientific Publishers: Stevenson Ranch, CA, 2002; Vol. 1.
(3) Kurihara, K.; Murase, Y. Polyelectrolyte brushes. In *Handbook of Polyelectrolytes and Their Applications*; Tripathy, S. K.; Kumar, J.; Nalwa, H. S., Eds.; American Scientific Publishers: Stevenson Ranch, CA, 2002; Vol. 1.
(4) Raviv, U.; Giasson, S.; Kampf, N.; Gohy, J.-F.; Jerome, R.; Klein, J. *Nature* **2003**, *425*, 163−165.
(5) Napper, D. H. *Steric Stabilization of Colloidal Dispersions;* Academic Press: New York, 1983.
(6) Tuinier, R.; de Kruif, C. G. *J. Chem. Phys.* **2002**, *117*, 1290−1295.
(7) Ito, Y.; Park, Y. S.; Imanishi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 2739−2740.
(8) Schuetz, P.; Caruso, F. *Chem. Mater.* **2004**, *16*, 3066−3073.
(9) Zhang, M.; Drechsler, M.; Müller, A. H. E. *Chem. Mater.* **2004**, *16*, 537−543.
(10) Wang, M.-C.; Liao, J.-D.; Weng, C.-C.; Klauser, R.; Frey, S.; Zharnikov, M.; Grunze, M. *J. Phys. Chem. B* **2002**, *106*, 6220−6226.
(11) Morawetz, H.; Hughes, W. L., Jr. *J. Phys. Chem.* **1952**, *56*, 64−69.
(12) Franchi, G.; Garattini, S.; Kram, K. J.; Van Putten, L. M. *Eur. J. Cancer* **1973**, *9*, 383−385.
(13) Stupp, S. I.; Ciegler, G. W. *J. Biomed. Mater. Res.* **1992**, *26*, 169−183.
(14) Akerman, S.; Viinikka, P.; Svarfvar, B.; Jarvinen, K.; Kontturi, K.; Nasman, J.; Urtti, A.; Paronen, P. *J. Controlled Release* **1998**, *50*, 153−166.
(15) Mendelsohn, J. D.; Yang, S. Y.; Hiller, J.; Hochbaum, A. I.; Rubner, M. F. *Biomacromolecules* **2003**, *4*, 96−106.

(16) Iwasa, K.; Tasaki, I.; Gibbons, R. C. *Science* **1980**, *210*, 338−339.
(17) Tasaki, I.; Byrne, P. M. *Biopolymers* **1994**, *34*, 209−215.
(18) Biesalski, M.; Johannsmann, D.; Rühe, J. *J. Chem. Phys.* **2002**, *117*, 4988−4994.
(19) Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 592−601.
(20) Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 602−613.
(21) Prucker, O.; Rühe, J. *Langmuir* **1998**, *14*, 6893−6898.
(22) Habicht, J.; Schmidt, M.; Rühe, J.; Johannsmann, D. *Langmuir* **1999**, *15*, 2460−2465.
(23) Biesalski, M.; Rühe, J.; Johannsmann, D. *J. Chem. Phys.* **1999**, *111*, 7029−7037.
(24) Israels, R.; Leermakers, F. A. M.; Fleer, G. J. *Macromolecules* **1994**, *27*, 3087−3093.
(25) Fleer, G. J. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 936−942.
(26) Lyatskaya, Y. V.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1995**, *28*, 3562−3569.
(27) Zhulina, E. B.; Birshtein, T. M.; Borisov, O. V. *Macromolecules* **1995**, *28*, 1491−1499.
(28) Zhulina, E. B.; Borisov, O. V. *Macromolecules* **1996**, *29*, 2618−2626.
(29) Zhang, H.; Rühe, J. Submitted for publication.
(30) Guo, X.; Ballauff, M. *Phys. Rev. E* **2001**, *64*, 051406/1−9.
(31) Currie, E. P. K.; Sieval, A. B.; Fleer, G. J.; Stuart, M. A. C. *Langmuir* **2000**, *16*, 8324−8333.
(32) Pohl, W. G.; Kuhn, H. J. *Kolloid, Z. Z. Polym.* **1966**, *212*, 1−12.
(33) Ikegami, A.; Imai, N. *J. Polym. Sci.* **1962**, *56*, 133−152.
(34) Zhulina, E. B.; Borisov, O. V.; Birshtein, T. M. *Macromolecules* **1999**, *32*, 8189−8196.
(35) Birshtein, T. M.; Zhulina, E. B. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 929−935.
(36) Ikeda, Y.; Beer, M.; Schmidt, M.; Huber, K. *Macromolecules* **1998**, *31*, 728−733.
(37) Ikegami, A. *J. Polym. Sci., Part A* **1964**, *2*, 907−921.
(38) Michaeli, I. *J. Polym. Sci.* **1960**, *48*, 291−299.
(39) Sabbagh, I.; Delsanti, M.; Lesieur, P. *Eur. Phys. J. B* **1999**, *12*, 253−260.
(40) Sabbagh, I.; Delsanti, M. *Eur. Phys. J. E* **2000**, *1*, 75−86.
(41) Miyajima, T.; Mori, M.; Ishiguro, S.-i.; Chung, K. H.; Moon, C. H. *J. Colloid Interface Sci.* **1996**, *184*, 279−288.
(42) Miyajima, T.; Mori, M.; Ishiguro, S.-i. *J. Colloid Interface Sci.* **1997**, *187*, 259−266.
(43) Francois, J.; Heitz, C.; Mestdagh, M. M. *Polymer* **1997**, *38*, 5321−5332.
(44) Schweins, R.; Huber, K. *Eur. Phys. J. E* **2001**, *5*, 117−126.
(45) Rivas, B. L.; Pereira, E. D.; Moreno-Villoslada, I. *Prog. Polym. Sci.* **2002**, *28*, 173−208.
(46) Horkay, F.; Basser, P. J.; Hecht, A.-M.; Geissler, E. *Macromolecules* **2000**, *33*, 8329−8333.
(47) Horkay, F.; Tasaki, I.; Basser, P. J. *Biomacromolecules* **2000**, *1*, 84−90.
(48) Horkay, F.; Tasaki, I.; Basser, P. J. *Biomacromolecules* **2001**, *2*, 195−199.
(49) Horkay, F.; Hecht, A.-M.; Grillo, I.; Basser, P. J.; Geissler, E. *J. Chem. Phys.* **2002**, *117*, 9103−9106.
(50) Konradi, R.; Rühe, J. *Macromolecules* **2004**, *37*, 6954−6961.
(51) Wittmer, J.; Johner, A.; Joanny, J. F. *J. Phys. II (Paris)* **1995**, *5*, 635−654.
(52) Ermoshkin, A. V.; Olvera de la Cruz, M. *Phys. Rev. Lett.* **2003**, *90*, 125504/1−4.

MA0486804