Weak Polyelectrolyte Brushes as Substrates for the Formation of Surface-Attached Polyelectrolyte−Polyelectrolyte Complexes and Polyelectrolyte Multilayers

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ABSTRACT: Monolayers of polyelectrolyte complexes are generated at solid surfaces using covalently attached monolayers of weak polyelectrolyte molecules ("polyelectrolyte brushes") exposed to aqueous solutions of oppositely charged polyelectrolytes. The adsorption of the charged polymers onto the brush-coated substrate is measured as a function of deposition time, pH value, salt concentration, and concentration of the polymer solution as well as the thickness of the surface-attached monolayer. It is shown that the adsorbed amount depends critically on the pH value of the solution and shows a pronounced maximum at intermediate salt concentrations. Upon exposure to an oppositely charged polyelectrolyte solution, the brush adsorbs large amounts of the polyelectrolyte and form thick layers in the same range as the thickness of the brush layer. Additionally, the thus-obtained layers are used as substrates for the formation of polyelectrolyte multilayers following a standard layer-by-layer approach. It is shown that the total film thickness scales linearly with the number of dipping cycles and that even the outermost layer is strongly correlated to the thickness of the brush layer which is used as the substrate.

Introduction

The interaction of soft, swollen interfaces with charged macromolecules in solution is so far not well understood. Knowledge about such interactions, however, is crucial for the understanding of the interaction of proteins with soft surfaces, as proteins carry a significant number of charges in an aqueous environment. A first step in this direction is to study a simple model system in which polyelectrolyte molecules (PEL) that are covalently attached to a surface interact with charged polymer molecules in solution. So far almost all studies carried out in this direction have been concerned with PEL monolayers physically adsorbed to surfaces.[1−5] It is well-known, however, that PEL molecules adsorbed to charged surfaces obtain a rather flat conformation due to the strong electrostatic interactions between the polymer and the solid substrate. However, such a strong confinement of the molecules to a layer, which is much thinner than the radius of gyration of an unperturbed coil, has a strong influence on their physical properties and might under some circumstances even totally dominate their behavior. In addition, the situation is complicated by the fact that the sign and density of surface charges are very important parameters in such systems. The number of surface charges, however, is sometimes difficult to reproduce and depends strongly on the experimental conditions.[6−11] Under certain circumstances, the sign of the surface charge might become reversed and the whole polyelectrolyte assembly might leave the surface.[12,13]

To avoid these problems, we use polymer brushes as substrates for such studies. In these systems one chain end is covalently attached to the surface. We have recently shown that such systems can be obtained with high graft densities, high molecular weights of the tethered chains, and accordingly high film thicknesses through surface-initiated polymerization processes.[14−18] The layers reach easily film thicknesses in the swollen state of several hundred nanometers, so that a direct investigation of the swollen films by ATR ellipsometry is possible.[19,20]

For the understanding of surface-attached polyelectrolyte complexes it is useful to compare them with those formed free in solution. Because of their interesting materials properties, the formation of PEL−PEL complexes (PEC) in solution has been the subject of a vast number of studies.[21−30] A complete review of this field is beyond the scope of this article, and just a few remarks should be made on the properties of such compounds. Since the driving force for the complex formation is mainly the strong Coulombic interaction between the opposite charges, the complex formation is governed by the chemical nature and charge density of the polyelectrolytes, the concentration of the polyelectrolyte solution, and among other parameters,the ionic strength and pH value of the solution. In general, PEL−PEL complexes can be classified according to their solubility into water insoluble/highly aggregated complexes[28−30a] and water-soluble complexes, which are, by definition, even after complex formation, molecularly dispersed in the aqueous solvent.

Highly aggregated structures of PECs are always formed by two strong, oppositely charged polyelectrolytes with high charge density in salt-free solution. In this case, most of the complexes are more or less stoichiometric, and directly after mixing of the two compounds they form colloidal particles and/or precipitate due to their insolubility in water. Water-soluble or quasi-soluble PECs can be prepared by different methods mostly involving at least one weak polyelectrolyte. Kabanov[21] and Dautzenberg et al.[22,23] have described for example the formation of soluble complexes which are highly nonstoichiometric and thus still soluble in an aqueous environment. In addition, highly aggregated PECs can be dissolved under certain conditions in aqueous solutions with high ionic strength.[25−27] A detailed description of the theory of PECs consisting of

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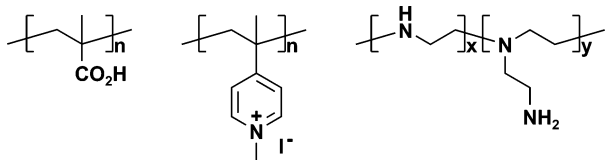

Figure 1. Chemical structure of the polyelectrolytes used in this study for the formation of the PEL complexes and multilayers at the surface.

polyacids and polybases has been recently published by Biesheuvel and Cohen-Stuart.[30b] The authors discuss the stability boundaries for polyacid−polybase complexation under different environmental conditions, especially the pH value in relation to the pK_a value of the polyions and the salt concentration. Depending on these conditions, either soluble PECs are formed or macroscopic phase separation and precipitation occur.

We have recently reported that it is possible to generate polyelectrolyte complexes and PEL multilayer systems by using a solid surface to which a PEL monolayer has been covalently attached.[31,32] A PEL brush monolayer, which is grown on the substrate in situ through a surface-initiated polymerization reaction, can be used as a charged substrate for the generation of surface attached polyelectrolyte complexes or PEL multilayers during the deposition process of strong PEL molecules.[31] In such a strong PEL−PEL system, the complex between a surface attached monolayer and an oppositely charged polymer chain is far away from the 1:1 stoichiometry. This is more or less due to the insolubility of the complex in water. The insolubility drives the system rapidly into a state, where the polyelectrolyte brush collapses completely, and after collapse of the layer no further molecules can be adsorbed.

In this paper we describe a system in which a brush consisting of weak PEL molecules is generated and exposed to solutions of an oppositely charged polyelectrolyte. The chemical structures of the polyelectrolytes used in this study are shown in Figure 1. The height of the surface-attached brushes is measured in situ during formation of the polyelectrolyte complex. The amount of polyelectrolyte adsorbed from solution is studied as a function of the parameters during complex formation.

Experimental Section

Toluene was distilled under nitrogen after refluxing overnight with sodium using benzophone as an indicator. Triethylamine was refluxed over calcium hydride and distilled under nitrogen. 4-Vinylpyridine and methacrylic acid were purified by chromatography on a silica column, distilled under vacuum from copper(I) chloride, and stored under nitrogen at 0 °C. Water was deionized through a Milli-Q system (Millipore, resistivity = 18.2 MΩ·cm^{-1}). Polyethylenimine (PEI, branched polymer from Aldrich, $M_w \sim 25\,000$) was used as received. Poly(methacrylic acid) (PMAA) was synthesized from methacrylic acid in *N,N′*-dimethylformamide (DMF) at 60 °C using AIBN as the initiator and purified by repeated precipitation in diethyl ether. The molecular weight was determined by gel permeation chromatography (GPC, Aglient, with columns from PSS, Mainz, Germany) to $M_n = 500\,000$ g/mol using narrow distribution PMAA-Na polymers as standards. The polydispersity was determined to $M_w/M_n = 1.98$. Poly(4-vinyl-*N*-methylpyridinium) iodide (MePVP) was synthesized from 4-vinylpyridine by radical polymerization at 60 °C using AIBN as the initiator. After isolation and purification it was quaternized with methyl iodide in nitromethane at 45 °C, as described by Fuoss and Strauss.[33] According to infrared and NMR measurements, the quaternization reaction proceeded quantitatively. The molecular weight of the MePVP was inferred as $M_n = 600\,000$ g/mol from that of the PVP precursor ($M_n = 254\,000$ g/mol; polydispersity $M_w/M_n = 1.70$) as no suitable standards were available for direct measurement of the molecular weight of the MePVP. All other solvents and chemicals were used as received.

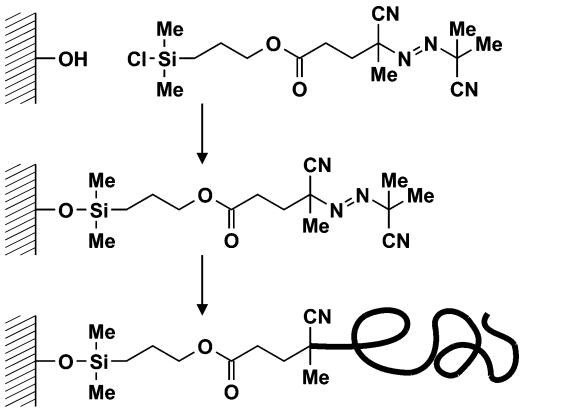

Figure 2. Synthesis of a charged polymer brushes covalently attached to a solid surface by a "grafting from" approach.

The substrates used for the attachment of the polymer layers were silicon wafers with a 2.5 nm silicon oxide layer (one side polished for general experiments and both sides polished for FTIR measurements, CrysTec, Germany) and lanthanum prisms (LaSFN9, $n = 1.844$, Helma, Germany). The LaSFN9 prisms were activated before immobilization of the initiator layer by dipping into a 2 N sulfuric acid for 1 min and rinsing carefully with water and ethanol. Silicon wafers were used without further surface treatment.

To investigate the formation of weak PEL complexes, transmission Fourier transform infrared spectra (FTIR, Bio-Rad FTS 3000; resolution 4 cm^{-1}) were recorded after rinsing and drying the sample. To determine the dry thickness of the PEL monolayers and multilayers, null ellipsometry measurements were carried out an incident angle 70° using an ELX-2 ellipsometer (He−Ne laser, $\lambda = 632.8$ nm, Riss, Germany). The roughness of the PEL layers was determined by X-ray reflectivity (Cu Kα, $\lambda = 0.154$ nm, Bruker AXS D5000) and atomic force microscopy (AFM, Nanoscope III, Digital Instruments) measurements. The swelling of the brushes in aqueous solution was determined with a home-built multiangle null-ellipsometer using a He−Ne laser ($\lambda = 632.8$ nm) as a light source. The setup has been described elsewhere in detail.[19] To model the spectra, a complementary error function was chosen, and the brush height and interface width were adjusted until a good fit between the measured and calculated spectra was obtained. In the following two times the first moment of the segment density profile will be referred to as "brush height". Details of the data analysis of the ellipsometric spectra were discussed in previous publications.[19,20]

The surface-attached PEL brushes were prepared as described in the literature:[14−18] immobilization of the silyl-functionalized azo initiator[14] and radical polymerization of 4-vinylpyridine in methanol (1:1 v/v) or methacrylic acid in DMF (1:1 v/v) at 60 °C for a chosen reaction time were followed by extraction with good solvents overnight in a Soxleht extractor (Figure 2). The MePVP monolayer chains were obtained by quaternization of the surface-attached poly(4-vinylpyridine) chains with methyl iodide in nitromethane at 45 °C for 6 h. PEL complexes and multilayers were fabricated by consecutively dipping the samples into oppositely charged PEL aqueous solutions for 1 h per immersion step. After each dipping step the sample was extracted three times by immersion into pure water for 2 min and then dried under nitrogen flow and later in a vacuum. The polymer solutions were prepared by freshly dissolving the polymers in pure water. Unless otherwise indicated, the concentration of the polymers was chosen as 2 mmol/L with respect to repeat units of the polymer.

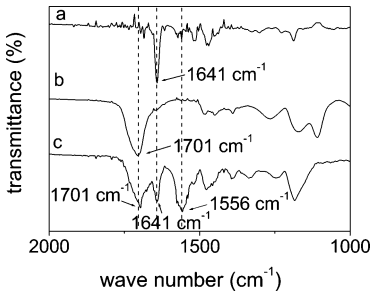

Figure 3. Transmission FTIR spectra through a 900 μm double-side polished silicon wafer with (a) a spin-cast layer of MePVP, (b) with a 58 nm PMAA brush attached to both sides of the substrate, and (c) after dipping of the sample of (b) into MePVP solution as described in the text. The PMAA brush was prepared by polymerizing methacrylic acid in DMF solution (50%, v/v) for 3 h at 60 °C.

Results and Discussion

In the following we will first discuss the complex formation using PMAA brushes as substrates and only in later parts of the paper return to the inverse case, where MePVP was used as the brush component. To characterize the formed surface-attached PMAA/MePVP complexes, FTIR spectra were taken (Figure 3). For comparison, also FTIR spectra of a spun-cast thin MePVP layer and an as obtained PMAA brush without any further surface treatment are shown. The FTIR spectrum of the complex monolayer was recorded after exposure of the PMAA brush to an aqueous solution of MePVP for 1 h, followed by washing and drying. The IR spectrum of the sample clearly shows the appearance of two new adsorption bands for the $-COO^-$ symmetric stretching vibration (1556 cm^{-1}) and for the C=C stretching vibration from the pyridinium ring (1641 cm^{-1}) accompanied by a decrease of the relative intensity of the absorption band of the −COOH asymmetric stretching vibration (1701 cm^{-1}). The spectral changes clearly prove the formation of the PEL−PEL complex. However, it should be explicitly noted that the band due to the COOH vibration does not completely disappear, even when high PEL concentrations and long exposure times are employed. Thus, upon complex formation a significant number of carboxylic acid groups remain unaffected. To determine the stability of the polyelectrolyte complexes, different extraction times in pure water were used (data not shown). It was observed that the layer thickness of the formed PEL complex does not change significantly whether the sample is rinsed for 3×2 min or extraction times of 15 h are employed. In all cases, only a slight reduction of the film thickness (0−10%) was observed if the film was treated with water overnight.

To obtain reproducible conditions for the complex formation, a number of brushes with approximately the same film thickness were prepared and exposed for 1 h to MePVP solutions having different concentrations (Figure 4). The obtained data show that the adsorbed amount is in a wide range independent of the concentration of the polymer solution. Only at the lowest concentrations (smaller than 10^{-3} mol/L) the amount of adsorbed oppositely charged polyelectrolyte was lower than expected from the other experiments. To check whether the adsorption times were chosen sufficiently long to allow for completion of the diffusion process of the oppositely charged polymer into the film, the same process was carried out as described above with a fixed

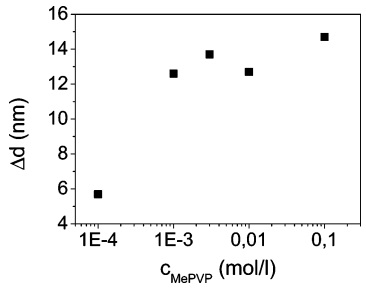

Figure 4. Time for establishing (quasi-)equilibrium for the formation of PMAA−MePVP complexes on a PMAA monolayer as a function of concentration of MePVP. The thickness of the PMAA monolayer formed during polymerization of MAA in DMF (1:1, v/v, 60 °C, and 1 h) is 15 nm.

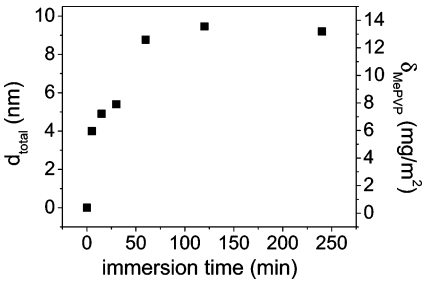

Figure 5. Adsorption of MePVP onto 15 nm PMAA brushes as a function of immersion time. The adsorbed amount of MePVP was calculated from the increase in film thickness (directly measured) according to the formula for adsorption $\delta = \rho\Delta d$, where ρ is the polymer density (1.40 g/cm^3 for MePVP) and Δd is the change of thickness.

concentration of 2×10^{-3} mol/L; however, the adsorption experiments were allowed to proceed for different periods of time (Figure 5). All samples shown in Figure 5 were prepared independently and had roughly the same dry film thickness. It is clear that at this concentration after roughly 1 h no more changes of the adsorbed amount occurred.

To obtain a more detailed picture, in-situ experiments were carried out in which a number of brushes were generated at the surfaces of lanthanum glass prisms and exposed to solutions of the oppositely charged PEL. During the immersion the film thickness of the surface-attached layer was followed by multiple angle total internal reflection ellipsometry. After the spectrum in pure water was measured, the water was removed and a salt-free aqueous solution of MePVP was added. Five minutes after the exchange of the solution another spectrum was recorded. It can be seen that upon addition of the PEL the brush layers starts to shrink slowly, even though the experiments show that more mass has been added to the layer. To follow this process, the measurements were repeated until no further changes in the ellipsometric spectra were observed, indicating a constant swollen film thickness. As an example, Figure 6 shows the measured ellipsometric spectra and the calculated spectra of a 30 nm PMAA brush in contact with 2×10^{-3} mol/L MePVP solutions after different times of exposure to this solution. Direct evidence of the shrinking of the surface-attached swollen layer are the changes in the slope of the spectra close to the critical angle (Figure 7). The experiments also show that the rate of thickness decrease becomes smaller with time and eventually a constant thickness is reached. It should be noted that the swollen thickness of all samples in the plateau region was very similar. In the case of the films shown in Figure 7 it was 160

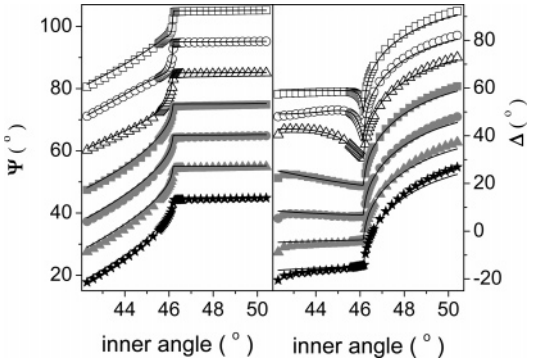

Figure 6. Ellipsometric spectra of a 30 nm PMAA brush, prepared by polymerization of MAA in DMF (1:1 v/v, 60 °C, 2 h), in contact with pure water for 30 min (open squares); after addition of a 2 mM MePVP aqueous solution the sample was remeasured after 5 min (○), 20 min (△), 40 min (■), 1 h (●), 2 h (▲), and 5 h (☆). The solid lines represent model calculations described in the text.

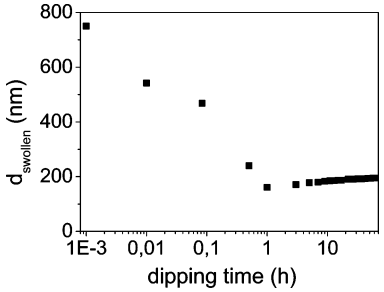

Figure 7. Layer thickness of a 30 nm PMAA brush in contact with a 2 mM MePVP aqueous solution as a function of exposure time.

nm ($d_{swollen}/d_{dry} \sim 5.3$), whereas the swollen thickness of the as-obtained brushes in pure water was around 750 nm ($d_{swollen}/d_{dry} \sim 25$). This shows on the one hand that formation of the complex leads to a significant compaction of the layer; however, on the other hand, the data also clearly show that even after very long exposure to oppositely charged polyelectrolyte the films remain in a significantly swollen state. Even in the plateau region, where the polymer layer is most strongly contracted, the average segment density is below 20%, and accordingly more than 80% of the volume of the brush is taken up by water. This behavior is very different from that of a system where a strong PEL (MePVP) is exposed to another strong PEL (PSSNa).[31] In the latter case the PEL brush collapsed completely within a few minutes, and the resulting surface-attached PEL−PEL complex is only weakly swollen.

The time to reach such a plateau in the adsorption kinetics as a function of the concentration of the MePVP solution is shown in Figure 8. The in-situ experiments show that the time to reach equilibrium for weak PEL complexes strongly depends on the polyelectrolyte concentration. For example, for 10^{-5} mol/L solution roughly a minimum time of 25 h is required while for a 2×10^{-3} mol/L solution the brush height does not change after about 1 h. At this point no detailed investigation of the kinetics of the complex formation was carried out. It is expected that the rate of complex formation will depend strongly on the graft density of the surface-attached polymer chains and on the strength of the electrostatic interactions and thus on the pH value and salt concentration of the system.

The results shown in Figure 8 demonstrate that the ex-situ experiments, in which only the amount of

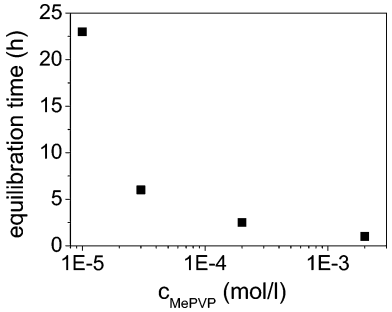

Figure 8. Time for establishing an equilibrium for the formation of PMAA−MePVP complex at solid surfaces as a function of concentration of MePVP.

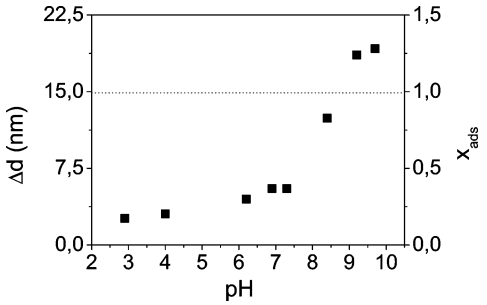

Figure 9. Layer thickness of adsorbed MePVP layers onto 10 nm PMAA brushes as a function of pH value of the contacting solution. x represents the molar ratio of adsorbed to grafted monomeric units.

adsorbed oppositely charged polyelectrolyte is measured, give roughly the same results as the in-situ measurements where the brush height is followed directly. In addition, it shows that the data point in Figure 4 at 10^{-4} mol/L, where a strong deviation of the adsorbed amount from the expected result observed, is not the result of an experimental error, but rather that the low observed thickness is caused by a too short adsorption time.

To study the influence of the pH value of the solution onto the complex formation, we carried out a set of the adsorption experiments at different pH values and measured the adsorbed amount of MePVP (Figure 9). Because PMAA is a weak polyacid, the charge density along the polymer chains strongly depends on the pH value of the surrounding environment. For MePVP as a strong polyelectrolyte, however, the degree of charging is independent from the pH value of the contacting solution. At low pH values the PMAA is mostly protonated and thus carries only a relatively small number of charges on the polymer backbone. As a result, the adsorbed amount of MePVP is rather low. At high pH value, PMAA is more strongly dissociated, and the number of charges along the polymer backbone is high. Thus, under these conditions the amount of adsorbed MePVP is accordingly also high. For example, at pH = 3, the increase in film thickness Δd due to PEL adsorption is only 2.5 nm while at pH = 10 a roughly 8 times higher ($\Delta d \cong 20$ nm) amount of PEL is becoming adsorbed. At this point it is interesting to view not only the changes in the film thickness d but also the molar ratio x between the two components in the film. This conversion information can be readily obtained from the thickness measurements according to equation 1. The calculation, however, is based on the assumption that the low molecular weight counterions (Na^+ and J^-) leave the brush during/after complex formation. The molar ratio x between the two components of the polyelectro-

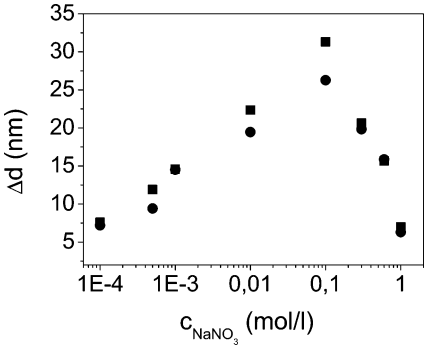

Figure 10. Layer thickness of adsorbed MePVP layers onto 12 nm thick PMAA brushes as a function of added salt ($NaNO_3$) concentration with different extraction time 3 × 2 min (■) and 15 h (●) from pure water.

lyte complex can then be calculated according to

$$x = \frac{d_{\mathrm{MePVP}}\rho_{\mathrm{MePVP}}M_{\mathrm{PMAA}}}{d_{\mathrm{PMAA}}\rho_{\mathrm{PMAA}}M_{\mathrm{MePVP}}} \quad (1)$$

If the low molecular weight counterions do not leave the brush appropriate corrections need to be made. According to this, the molar ratio of adsorbed repeat units to surface-attached repeat units varies between $x = 0.18$ and $x = 1.28$. The observed increase in Δd (and accordingly x) is in qualitative agreement with simple titration experiments where the brush height has been measured as a function of the pH value of the solution.[20] In the latter case stronger charging is equivalent to stronger electrostratic repulsion, stronger confinement of the ions to the brush, and accordingly stronger stretching of the brush.

Since the driving force for the formation of the PEL complex mainly originates from the attractive electrostatic interaction between the oppositely charged polymers, addition of low molecular weight electrolyte (salt) should play an important role in the complexation process. To elucidate this, the adsorption of MePVP onto PMAA brushes was investigated at different $NaNO_3$ concentrations (Figure 10). $NaNO_3$ was chosen as it strongly dissociates in water, contains only monovalent ions, and is inert under the given conditions. It can be seen that the adsorbed amount at first increases with increasing salt concentration, but then eventually decreases again, so that at a certain salt concentration $c_{\mathrm{ads,max}}$ a clear maximum of the adsorbed amount can be obtained.

To explain this behavior, first the behavior of a polyelectrolyte brush in the presence of low molecular weight salt, but in the absence of the oppositely charged polyelectrolyte, is described, which has been analyzed in detail in a previous publication.[34] At low salt concentration, the weak PMAA brush is in the so-called osmotic brush regime. In this regime, the addition of the salt leads to a shift of the protonation /deprotonation equilibrium and increases the degree of dissociation of the carbonyl groups. Thus, the number of charges on the surface attached polymer chains is increased, and the chains become more strongly stretched.[34−37] With further addition of salt, however, the PMAA brush approaches the "salted brush regime", in which the salt concentration in the brush is identical to or larger than that in solution.[34−37] In this regime, the added salt screens the charges on the polymer chain, which decreases the electrostatic interactions. This increase, the screening induced decrease of the brush height, and the observed maximum, $c_{\mathrm{s,max}}$, can be described, following simple theoretical considerations, according to

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

Here σ denotes the graft density of the system and α_b the degree of dissociation of the polyion.[36]

As the degree of dissociation of the macroions is strongly influenced by the added salt and the degree of dissociation of the macroions determines the amount of PEL adsorbed from solution, an increase in the salt concentration of the contacting solution will accordingly also cause first an increase and eventually, at high external salt concentration where strong charge screening sets in, a decrease of the adsorbed amount of polymer. Therefore, it is not surprising that the dependence of the adsorbed amount of polyelectrolyte on the concentration of added salt follows essentially the same pattern as the increase in brush height upon addition of salt.[34,37]

Despite the general similarity of the two curves, however, it should be noted that $c_{\mathrm{s,max}}$, where the brush height reaches its maximum, and $c_{\mathrm{ads,max}}$, where the adsorbed amount of polyelectrolyte is highest, strongly differ in their absolute values. While in the low molecular weight electrolyte case the maximum is already reached at concentrations of around 10^{-3} mol/L,[34,37] the maximum in the polyelectrolyte complex formation process is located close to 0.1 mol/L.

That the observed 2 orders of magnitude difference of $c_{\mathrm{s,max}}$ and $c_{\mathrm{ads,max}}$ is caused by differences in the grafting density can be firmly excluded as this parameter is rather similar for the samples studied. The reason for the observed difference becomes much more clear if two systems are considered that for both processes the most important question is how many charges reside on a chain. In the case of the swelling experiments, which monitor the brush height as a function of sodium concentration, the increase is caused by an exchange of a proton on the carboxylic acid for sodium. The sodium salt of the carboxylic acid dissociates more strongly, adding more charges to the brush.

In the case of the uptake of oppositely charged polyelectrolyte, we have to consider two equilibria (eqs 2 and 3)

$$-\mathrm{COOH} + \mathrm{Na}^+ \rightleftharpoons -\mathrm{COONa} + \mathrm{H}^+ \quad (2)$$

$$-\mathrm{COOMeVP} + \mathrm{Na}^+ \rightleftharpoons -\mathrm{COONa} + \mathrm{MeVP}^+ \quad (3)$$

Here MeVP indicates a repeat unit of the MePVP polymer.

The maximum in both curves is reached at a concentration where the brush is fully charged and addition of further salt just screens charges. This concentration, however, depends on the type of counterion as shown in eqs 2 and 3 which are obviously different from each other. That PEC brushes are much less charged compared to the brushes without the oppositely charged polyelectrolyte at the same salt concentration can already be seen when the in-situ experiments of PEC formation are viewed, where it is evident that the PEC layers are much less strongly swollen compared to the brush before the adsorption.[34,37]

At very low salt concentration the brush contains almost no charges, and the uptake of polyelectrolyte from solution is weak. With increasing salt concentration the brush becomes more charged and adsorbs more

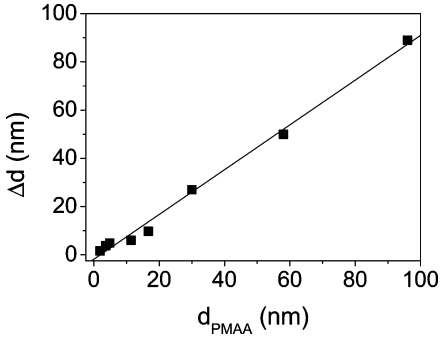

Figure 11. Layer thickness of adsorbed MePVP layers onto PMAA brushes as a function of the thickness of the PMAA brush. The solid line represents a linear fit to the obtained data.

oppositely charged PEL. At very high salt concentration, however, the PEC becomes unstable and starts to dissociate. As the underlying basic reason for the decrease in the decline of the number of taken up polymer is different from that of the decrease of the film thickness in swelling experiments, it is not surprising that the concentration at which the maximum is positioned is also different.

Another important question for the understanding of the systems is how the brush thickness influences the adsorbed amount of the oppositely charged PEL. To this, PMAA brushes with dry film thickness ranging from 4 to 100 nm were grown on the substrate by varying the grafting density while keeping the molecular weight constant. These brushes were then exposed to MePVP solutions (Figure 11). It can be clearly seen that the layer thickness increase caused by the PEL adsorption strongly depends on the film thickness of the first, covalently attached monolayer. It is interesting to note that this behavior is completely different from that of a very similar system which uses MePVP brushes as substrates and a strong polyelectrolyte (polystyrenesulfonate) in solution. In the strong−strong PEC layer system formed this way, the thickness increase due to the adsorbed polyelectrolyte is almost completely independent of the brush thickness. The reason for this very interesting difference between the different systems is most likely attributed to the solubility/swellability of the formed polyelectrolyte complexes. Whereas the data shown in Figure 7 indicate that the complex formed by weak/strong or weak/weak systems in the swollen state at all times, it is know that for the strong−strong system already after addition of smallest amounts of oppositely charged polyelectrolyte the system collapses to almost the dry film thickness, and accordingly strongly nonstoichiometric complexes are formed.

It is further interesting to note that, although its exact value depends of course on the deposition conditions, the thickness of the adsorbed PEL layer was in all cases roughly equivalent to the film thickness of the brush layer. Thus, in one absorption step easily about 100 nm of polyelectrolyte can be adsorbed. This is insofar quite remarkable as in typical adsorption experiments, where polyelectrolytes are directly physisorbed to solid surfaces, layers of only very few nanometers (i.e., 0.3−5 nm) film thickness can be deposited under similar conditions.[38−40]

To study whether the adsorbed behavior was specific for the studied PMAA bushes also the inverse situation was investigated (Figure 12). To this MePVP brushes of different graft densities and same molecular weight

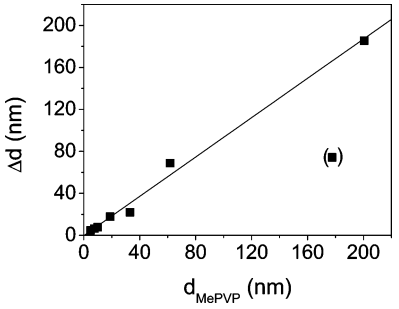

Figure 12. Layer thickness of adsorbed PMAA layers onto MePVP brushes as a function of the thickness of MePVP monolayers. The MePVP brushes were formed by quaternization of PVP brushes with methyl iodide prepared by bulk polymerization of 4-vinylpyridine using surface-attached initiator monolayers with different reaction time at 60 °C. The solid line is a linear fit for the measured data excluded the sample of the 170 nm thick brush.

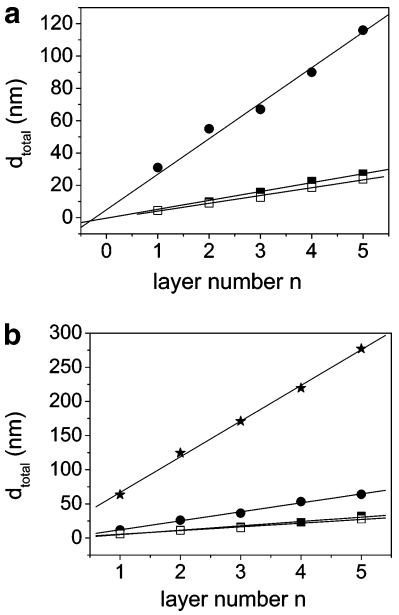

Figure 13. Film thickness as a function of the number of layers for PEL/PEL multilayers deposited from 2 mM salt-free polyelectrolyte aqueous solution: (a) for a PMAA/MePVP system using 5 nm (■, ellipsometry; □, X-ray reflectivity data) and 31 nm (●) PMAA brushes as substrates; (b) for a PMAA/PEI system using 6 nm ((■, ellipsometry; □, X-ray reflectivity data), 12 nm (●), and 63 nm (★) PMAA brushes as substrates. Solid lines represent a linear fit to the experimental data.

(with accordingly strongly varying film thicknesses) were generated. The extracted monolayers were first swollen in water and then exposed to PMAA solutions. Again a linear relation between the brush height and the amount of adsorbed PEL was observed. Thus, the situation seems to be symmetric and does not depend on which of the two components is surface-attached and which is free in solution.

The surface-attached PEL−PEL complexes obtained by exposure of PEL brushes to oppositely charged PELs can now be used as substrates for the formation of PEL multilayers in a layer-by-layer process.[38] To this, substrates were consecutively dipped into 2 mM MePVP and 2 mM PMAA solutions with a rinsing and drying step in between. The deposition of all layers was carried out in salt-free solution, and 1 h was used for the immersion time. The layer thickness was measured by ellipsometry or X-ray reflectivity after every new monolayer was adsorbed. Figure 13a,b shows the dependence

of the multilayer thicknesses on the number of immersion steps for two series of samples, both starting from a PMAA brush. One is, however, using PEI and the other MePVP as the cationic polyelectrolyte. It can be seen that in both cases the film thickness increases linearly with the number of dipping cycles. In addition, it is evident that the thickness of multilayers strongly depends on the thickness of the brush layer and is again more or less the same as the thickness of the initial brush monolayer.

Conclusions

Polyelectrolyte brushes can be used as substrates for the absorption of polyelectrolytes from solution to form surface-attached PEL−PEL complexes and for the subsequent buildup of multilayers of weak polyelectrolytes by a layer-by-layer deposition process. As the adsorbed amount depends only on the degree of charging of the brush, the system is independent from the peculiarities of the surface chemistry of the substrate.

The formation of the weak PEL complexes on the solid substrate is based on attractive electrostatic interactions between the charged brush and the oppositely PEL molecules and can be controlled by varying the medium environment, especially through control of the pH value and addition of low molecular weight electrolytes. The amount of adsorbed polyelectrolyte is linearly connected to the initial brush height. This can be well understood as the complexes generated between the weak and the strong PEL molecules remain swollen throughout the whole adsorption process, even in what appears to be the equilibrium state. Such a behavior is strongly different from that of a system in which the resulting PEL−PEL complexes are insoluble in the contacting medium and brush and aqueous solvent strongly phase-separate. In the latter case the adsorbed amount is not or only very weakly correlated to the number of charged segments in the brush. It is quite remarkable that, by using systems in which polymer brushes serve as substrates and at least one component, either the one at the surface or the one in solution, consists of a weak polyelectrolyte, very large amounts of oppositely charged PEL can be removed from solution and attached to the surface.

Even more remarkable is that, if the brush-coated substrates are used for the generation of PEL multilayers following a layer-by-layer deposition scheme, all layers of the multilayer assembly show a strong templating effect. Even the thicknesses of the outer layers seem to be strongly correlated to the initial brush thickness. The latter is yet not well understood and is currently being investigated.

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