Interaction of Strong Polyelectrolytes with Surface-Attached Polyelectrolyte Brushes−Polymer Brushes as Substrates for the Layer-by-Layer Deposition of Polyelectrolytes

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ABSTRACT: The complex formation between a monolayer consisting of strong polyelectrolyte molecules covalently attached to a solid surface and an oppositely charged strong polyelectrolyte in solution is studied. The surface-attached polyelectrolyte molecules are grown in situ on the substrate using a surface-initiated polymerization ("grafting from") technique. The amount of oppositely charged polymer adsorbed by the polyelectrolyte monolayer on the surface ("brush") is measured as a function of salt concentration, deposition time, polymer concentration, and thickness of the surface-attached monolayer. When the oppositely charged polymer is added to the polyelectrolyte brush, which is swollen in salt-free water, the monolayer collapses rapidly due to formation of a nonstoichiometric, insoluble polyelectrolyte−polyelectrolyte complex. It is shown that polyelectrolyte brushes are an interesting substrate for the buildup of well-defined polyelectrolyte multilayers through a layer-by-layer deposition process.

Introduction

Since the introduction of polyelectrolyte multilayer architectures formed by the alternate deposition of polycations and polyanions from solution to a solid support by Decher et al. in 1991,[1] numerous papers have been published on different scientific and technological aspects using this very simple yet versatile technique to modify organic or inorganic solid surfaces.[2−17] Applications (or potential applications) of substrates modified by polyelectrolyte multilayers have been described or proposed in a variety of areas, ranging from the fabrication of optoelectronic modules to the surface biocompatibilization of medical devices.[18−30]

The driving force of the formation of polyelectrolyte multilayers through layer-by-layer deposition of polyelectrolytes[1] mainly originates from the electrostatic attraction between the oppositely charged polymer species. The preparation of polyelectrolyte multilayers using this method is very simple: A substrate having some surface charges is immersed into an aqueous solution of a polyelectrolyte (PEL) with the opposite charge sign to generate an adsorbed polyelectrolyte monolayer on the surface. It takes typically just a few minutes at most to establish a stable situation or equilibrium. After rinsing several times with water, the sample is again dipped into an aqueous solution of a polyelectrolyte, now with the opposite charge sign. This leads to adsorption of a second monolayer. In the standard model of the layer-by-layer deposition process it is presumed that the charge sign of the surface is reversed due to charge overcompensation.[3,10,31] The repetition of this deposition process then results in a polyelectrolyte multilayer formation. Accordingly, the conformation of the polymer chains in the layer and layer thicknesses of the attached polyelectrolyte layers are dominated by parameters of the medium, which is present during the dipping procedure. Typical examples for such parameters are pH value, ionic strength, charge density of the polymer chain, and the surface charge density.[4,10,31−34]

Polyelectrolyte multilayers built up by this process represent a simple pathway to fabricate a film with well-controlled film thickness. However, the stability of the multilayered system in different environments is generally of concern. Especially the adhesion of the first layer to the surface poses a problem which should not be neglected. Because the attachment of the first layer depends solely on the interaction of the polymers with surface charges, the whole multilayer assembly can be desorbed by either changing the sign of the surface charge of the substrate or by addition of competing low molecular weight electrolytes, which can displace the polymer molecules in the first monolayer. Several publications have theoretically dealt with the desorption of polymers due to reduction or inversion of the surface charge of the substrate and/or with the addition of low molecular weight electrolyte.[3,31,37] In a study by Dubas and Schlenoff it is explicitly described that *"For adsorption via a purely electrostatic mechanism, at some point the concentration of salt ions is sufficient to displace all the polymer from the surface*".[10]

This has led our attention onto polyelectrolyte layers, which are covalently attached to the surfaces of the substrates. We have recently reported that it is possible to generate polyelectrolyte monolayers in situ on solid substrates using a "grafting from" technique.[38−42] If the grafting density of such polyelectrolyte monolayers is high enough to induce chain stretching the term "polyelectrolyte brushes" is used to name such systems. Since the polyelectrolyte chains are covalently attached to the surface, they can only be removed from the surface by cleaving the chemical bonds that connect the polymer to the substrate. In addition, the polyelectrolyte monolayers generated using this technique can be easily controlled concerning layer thickness, graft density, charge density, and swelling behavior. They represent therefore an interesting approach to prepare surfaces with well-defined structure and surface charge.

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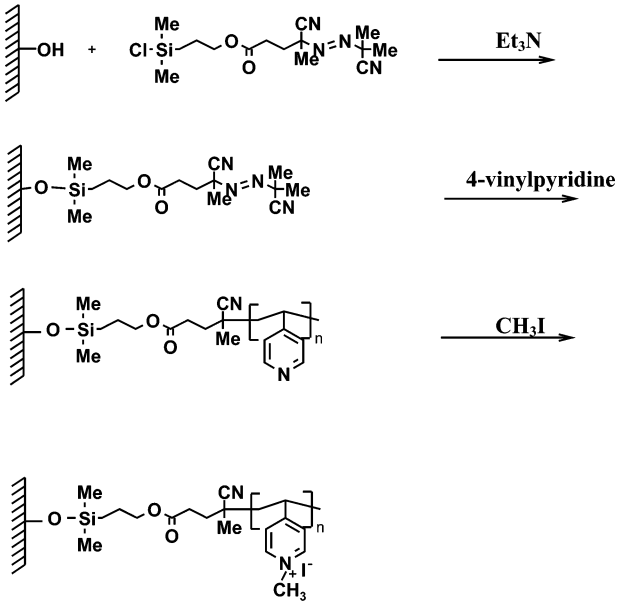

Figure 1. Chemical pathway for the formation of poly(4-vinyl-*N*-methylpyridinum) iodide monolayers covalently attached to solid substrates.

In this paper, we use monolayers of a covalently attached positively charged polymer, poly(4-vinyl-*N*-methylpyridinum) iodide (MePVP), formed as described in Figure 1 to generate a positively charged surface. Poly(styrenesufonate) sodium (PSSNa) is used as the negatively charged polymer in solution. Accordingly, both polymers involved in this study are strong polyelectrolytes. We study the polyelectrolyte−polyelectrolyte complex formation at the interface, how it depends on the conditions of the environment during film deposition, and investigate in how far the surface-attached PEL monolayers can be used for the generation of polyelectrolyte multilayers in a layer-by-layer process.

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 was 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}). Poly(styrenesulfonate) sodium salt (PSS, $M_w \sim$ 1 000 000, Aldrich) was used as received. Poly(4-vinyl-*N*-methylpyridinium) iodide (MePVP) was synthesized from 4-vinylpyridene using AIBN in benzene at 60 °C as the initiator. After isolation and purification it was quarternized with methyl iodide in nitromethane at 45 °C as described by Fuoss and Strauss.[43] The molecular weight of the MePVP was inferred as 1 060 000 g/mol from that of the free PVP (450 000 g/mol; polydispersity 1.78) generated in solution assuming 100% conversion. The molecular weight of the latter was determined using gel permeation chromatography (GPC system from Aglient with columns from PSS, Mainz, Germany) and narrow molecular weight distribution poly(2-vinylpyridine) standards purchased from PSS (Mainz, Germany). All the other solvents and chemicals were used as received.

The substrates used for attachment of the polymer layers were silicon wafers with a 2.5 nm silicon oxide layer (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.

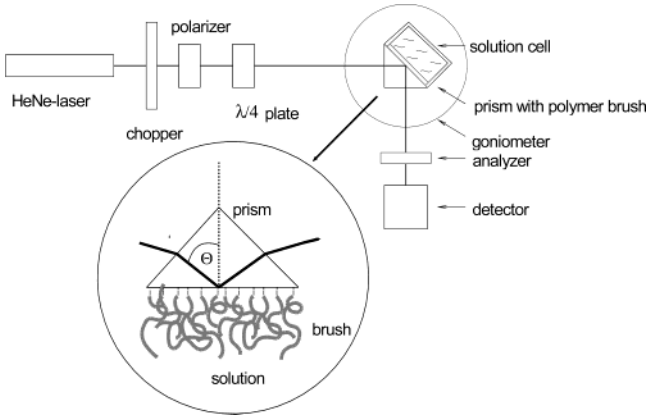

Figure 2. Schematic depiction of the setup of the multiangle null ellipsometer.

To determine the dry thickness of the PEL monolayers and multilayers, null ellipsometry measurement were carried out at an incident angle of 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, which is schematically shown in Figure 2, has been described elsewhere in detail.[44] 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 the first moment of the segment density profile will be referred to as "brush height". The data analysis of the ellipsometric spectra was discussed in detail in previous publications.[44,45]

The surface-attached poly(4-vinyl-*N*-methylpyridinium) iodide with the molecular weight of 600 000 g/mol was prepared as described in the literature in three steps:[46] immobilization of the silyl-functionalized azo initiator synthesized according to Prucker et al.,[41] bulk polymerization of 4-vinylpyridine at 60 °C for a chosen reaction time, extraction with methanol overnight in a Soxleht extractor, and quarternization of the poly(4-vinylpyridine) chains with methyl iodide in nitromethane at 45 °C for 6 h. PEL complexes and multilayers were fabricated by dipping the samples into aqueous solutions of the polyanions (PSSNa) or polycations (MePVP) for 30 min 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 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 to be 2 mmol/L with respect to repeat units of the polymer.

Results and Discussion

The positively charged polymer (MePVP) monolayers are generated on silicon substrates using the "grafting from" technique as described in Figure 1. Growing the polymer chains from the surface allows to generate much thicker monolayers than by attaching preformed polymers to surfaces.[47] The first step in such a surface-initiated polymerization reaction is the formation of a neutral polymer (PVP) monolayer through initiation of 4-vinylpyridine using the surface-attached azo initiator. After completion of the polymerization and extraction of the sample with methanol, which is a good solvent for PVP and which removes all physisorbed polymer, the quarternization of PVP monolayers was carried out under mild conditions to form a MePVP monolayer

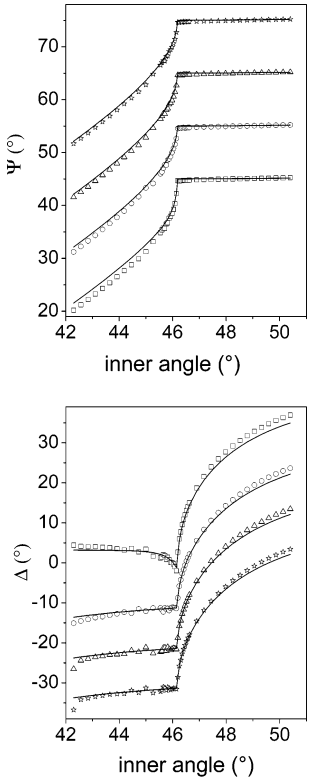

Figure 3. Ellipsometric spectra of a 13 nm MePVP monolayer in contact with pure water for 30 min (squares); after addition of a 2 mM PSS aqueous solution the sample was remeasured after 5 min (circles), 30 min (triangles), and 50 min (stars). The solid lines represent model calculations described in the text.

which is positively charged. We recently showed that the quarternization step can be carried out to quantitative conversion.[46]

To investigate how fast the adsorption of free polyelectrolyte from solution onto the surface-attached monolayer proceeds, the brush height of a 13 nm (dry film thickness) MePVP monolayer exposed to an aqueous solution was measured after 30 min equilibration by multiangle total internal reflection ellipsometry. After the spectrum in pure water was measured, the water was largely removed and an aqueous 2 mM PSSNa solution was added. Five minutes after the exchange another spectrum was taken. The measurement was repeated after 30 and 50 min. As each spectrum requires a very large number of nulling procedures, 10 min is with the current setup the time resolution of the experiment. The obtained ellipsometric spectra are shown in Figure 3.

Without any detailed modeling already the visual inspection of the measured spectra allows to draw some qualitative conclusions about what is happening in brush because the slope of the ellipsometric spectrum directly below the critical angle are closely related to the Fourier transform of the segment density profile as discussed in refs 45 and 48. From the strong change in the slope of the curve close to the critical angle when the polyanion is added, it is evident that the thickness of the MePVP monolayer has changed strongly already after only 5 min exposure to the oppositely charged polyelectrolyte and then remains more or less constant. The process might be even much faster. This, however, cannot be measured as it is below the time resolution of the current setup.

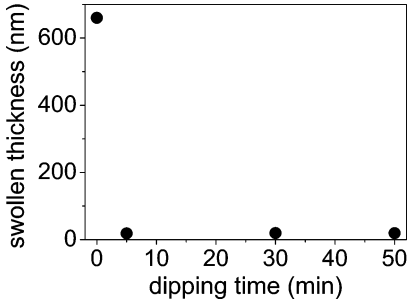

Figure 4. Layer thickness of a 13 nm MePVP brush in contact with a 2 mM PSS aqueous solution as a function of exposure time.

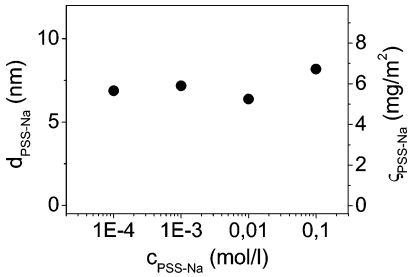

Figure 5. Thicknesses d of polyanion layers (PSS) adsorbed to ca. 41 nm thick MePVP brushes as a function of the concentration of the PSS solution.

The results of the quantitative evaluation with the model described above are shown in Figure 4. The calculated ellipsometric spectra are shown as solid lines in Figure 3. While the thickness of the brush in pure water is about 660 nm (degree of swelling $d_{swell}/d_{dry} \approx 50$) immediately after addition of the PSS solution the brush height collapses to about 19 nm, which is roughly the expected value for a dry double layer. As the collapse is quite rapid, 30 min is taken in the following experiments as immersion time to make sure that a stable situation of the formation of MePVP/PSS complex is achieved.

Another important parameter for polymer adsorption to surfaces in general is the concentration of the polymer in solution. To study the influence of the PSSNa concentration on the adsorbed amount several, very similar ca. 41 nm thick MePVP brushes were prepared on silicon wafers. The brushes, swollen in salt-free water, were exposed to PSSNa solutions with concentrations ranging from 10^{-4} to 1 mol/L. The film thicknesses d of the adsorbed polyanion (obtained after drying of the film) are shown in Figure 5. To allow a better comparison to results published on polyelectrolyte adsorption from solution, also the adsorbed amount ($\varsigma = \rho d$) is given. The density ρ of the PSS polymer was taken as 0.82 g/cm^3. Obviously, the amount of PSSNa adsorbed on the MePVP monolayers does not change significantly even when the concentration of the PSSNa in solution is changed by orders of magnitude.

As the electrostatic interaction between the polyelectrolyte molecules plays a major role in the adsorption process, it can be expected that the addition of low molecular weight electrolytes can influence the layer formation process strongly. We therefore studied the influence of the ionic strength of the surrounding medium on the formation of the MePVP−PSS complex. To this a series of identical adsorption experiments were carried out, where the ionic strength of the medium was varied by adding various amounts of sodium nitrate.

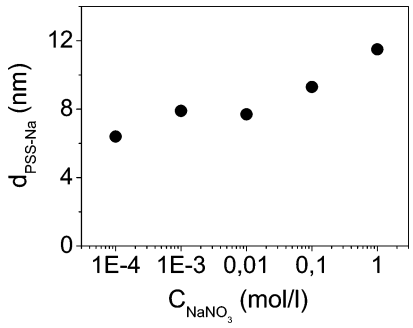

Figure 6. Layer thicknesses of the second layers (PSS) obtained by immersion of ca. 41 nm thick MePVP brushes into 2 mM PSSNa for 30 min as a function of the salt concentration ($NaNO_3$) of the solution.

Figure 6 shows that the adsorbed amount of PSS increases with increasing sodium nitrate concentration of the solution. Apparently, the enhanced screening of the electrostatic forces with increasing ionic strength of the solution from which the second polyelectrolyte is adsorbed results in an enhancement of polyelectrolyte adsorption. Thus, controlling this parameter is a favorable pathway to control the layer thickness of the adsorbed PEL. This behavior is in good agreement with the ionic strength dependence of the layer thickness in typical layer-by-layer processes.[2,10]

Another very important question is how the thickness of the first, surface-attached layer influences the thickness of the second layer. To this the (dry) film thickness of the brushes was varied between 10 and roughly 200 nm by varying the graft density of the surface-attached chains. To this MePVP monolayers were formed from bulk 4-vinylpyridine at 60 °C with different reaction times. Such a synthetic procedure leads to molecules that have approximately the same molecular weight but different grafting densities. Figure 7a shows that the adsorbed amount of the second layer changes only slightly with increasing thickness of the surface attached brush by increasing grafting density. While the brush thickness is varied by a factor of about 20, the maximum variation of the thickness of the adsorbed PSSNa layer is by a factor of about 1.5 (if the value at very low grafting density is not considered). In addition, it is also obvious (Figure 7b) that the PEL−PEL monolayer complex is far away from a 1:1 stoichiometry, even at the lowest graft density studied. For the calculation of the numbers in Figure 7b ρ_{MePVP} was taken as 1.40 g/cm^3.

The nonstoichiometry and the weak dependence of the adsorbed polyanion amount on the thickness of the polycation might be explained in such a way that the collapse of the brush, which results from the insolubility of the PEL−PEL complex in water, is the limiting step in the complex formation. Once the polymer in the monolayer is becoming collapsed, the diffusion of the PSS into the MePVP layer will essentially stop, and a strongly nonstoichiometric complex is formed. As the monolayer complexes have such a nonstoichiometric composition when they collapse, it is clear that the addition of more polymer segments (as present in the thicker films) does not change the collapse properties, and the absorbed amount is essentially independent of the thickness of the surface-attached monolayer. This is a behavior which is quite different than that of the formation of PEL−PEL complexes in solution where no diffusion barrier exists and accordingly more or less stoichiometric complexes are obtained.[49]

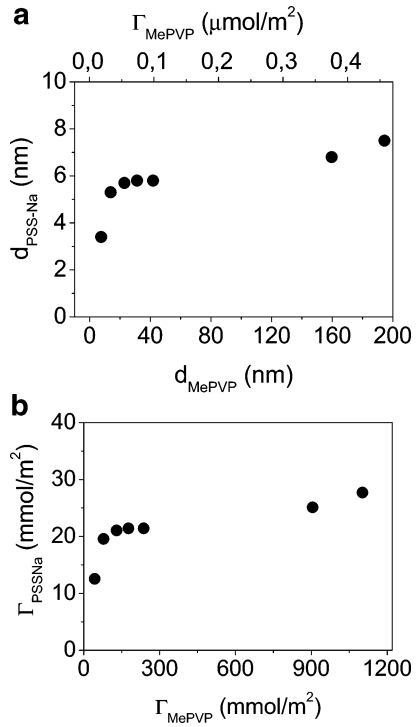

Figure 7. (a) Layer thickness of PSS layers absorbed to MePVP brushes as a function of the thickness and grafting density of the surface-attached monolayer. (b) Molar ratio of PSSNa vs surface-attached MePVP in respect to repeat units of the polymers. Details concerning sample preparation are given in the text. The grafting densities were calculated from the initiator decomposition kinetics.[40]

At very low and at high grafting densities, however, the situation is slightly different. At low grafting densities the diffusion of the PSS into the layer will be less of problem, and a significant dependence of the adsorbed amount with increasing number of charged moieties in the surface-attached monolayer is expected. This is in qualitative agreement with the experimental results.

On the other hand, if the polycation/polyanion composition ratio is studied at very high brush thicknesses, it might be hypothesized that an increase of the self-screening of the charges in the monolayer with increasing graft density leads to a weak increase of the PSS layer thickness at high film thicknesses of the surface attached monolayer. Here the argument for this increase of the layer thickness would follow exactly along the same lines as discussed above in connection with the dependence of layer thickness on the ionic strength of the medium during deposition.

We now move to polyelectrolyte multilayers builtup using the charged polymer brushes as substrates. To this the substrates were consecutively dipped into PSSNa and MePVP aqueous solutions with a rinsing procedure after each dipping step until the desired number of layers was reached. Figure 8a shows the results of X-ray reflectivity experiments (XRR) of such multilayers. The layer thickness can be determined from the Kiessig fringes and the roughness of the air/polymer interface from the general slope of the curve. It should be noted that the X-ray beam damages the MePVP-I monolayers due to the presence of iodide ions in the system. Therefore, for the XRR measurements each time new samples were used. The roughness of outmost layer of the monolayer system (total of 20 layers) was deter-

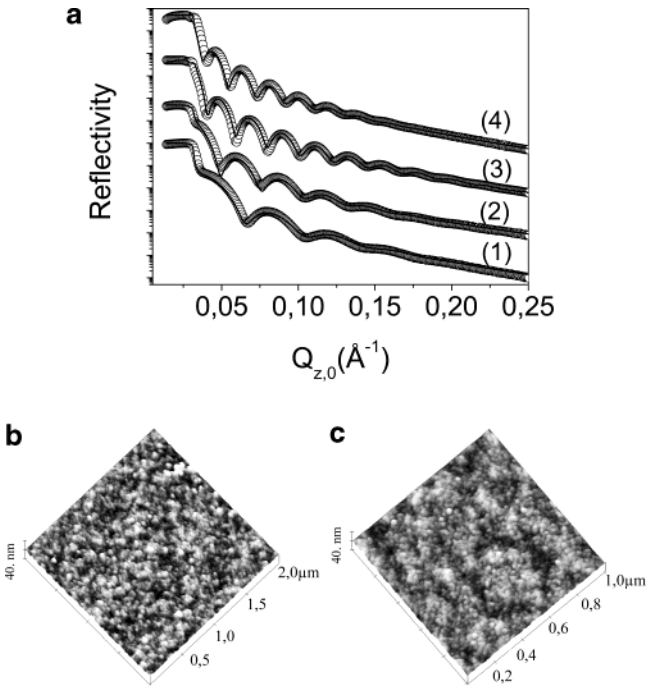

Figure 8. (a) X-ray reflectivity curves of a PVP layer (1), the corresponding MePVP layer (2), a MePVP/PSS bilayer (3), and a multilayer assembly after deposition of 20 layers of MePVP/PSS (4). (b) AFM image of a bilayer of MePVP/PSS using 22.9 nm MePVP as the first layer. (c) AFM image of a similar sample as in (b) after deposition of 20 layers of MePVP/PSS.

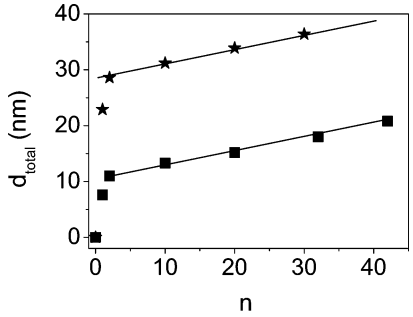

Figure 9. Film thickness as a function of the layer numbers for a MePVP/PSS multilayers deposited on silicon wafers from 2 mM salt-free polyelectrolyte solution using 7.6 nm (square) and 22.9 nm (star) MePVP covalently attached monolayers as the first layer. The additional layers were obtained by immersion of the substrate into a polyanion or polycation solution as described in the text. The solid lines show a linear fit of the dependence of the film thickness on the number of deposited layers.

mined by XRR to 1.3 nm, which is slightly larger than that of the unmodified substrate but similar to that of the brush monolayer. These results are in good agreement with AFM measurements which give for the bilayer system a rms roughness of 1.4 nm and for the sample with 20 layers 1.6 nm. The AFM images of such two samples are shown in Figure 8b,c.

The change of the thickness of the multilayers as a function of the layer number is shown in Figure 9. The deposition of all layers was carried out in salt-free solution, and 30 min was used as immersion time for each dipping step. It can be seen that the thickness increase due to adsorption of the second layer is larger than that of the following layers deposited on top of it. Starting from the third layer the thickness increases only about 0.5 nm per deposition cycle (i.e., deposition of two monolayers), and a linear relationship between the layer thickness and the number of deposited layers is observed. This behavior agrees well with that of the traditional layer-by-layer multilayers buildup.[10] Within the experimental error two subsequent monolayers in the multilayer assembly deposited here seem to have a 1:1 composition of polyanion and polycation. Furthermore, the slope of the layer thickness vs deposited layer is also independent of the thickness of the first, surface-attached polyelectrolyte monolayer. Figure 9 shows the thicknesses of multilayer assemblies deposited onto two samples which had a very different layer thickness of the brush monolayer. While the overall film thickness of the two samples is strongly different due to the difference in the first (and to a minor extend second) monolayer the subsequent multilayer buildup is essentially identical. Thus, after deposition of a total of three or four PEL layers no influence of the brush on the layer properties of the outer layers is visible anymore.

Conclusions

Brushes consisting of surface-attached strong polyelectrolyte molecules can be used as substrates for the adsorption of strong polyelectrolytes from solution and for the subsequent buildup of polyelectrolyte multilayers by a layer-by-layer deposition process. The generation of covalently attached polymer monolayers through a surface-initiated growth process seems to be an attractive pathway to such systems, as it allows strong adhesion of the layer system to the solid substrate and allows to control the properties of the first monolayer in great detail.

Because of the strong electrostatic forces between the surface attached and free polymer molecules and the low solubility of the PEL−PEL complex in aqueous solution, the polycationic brush, which is strongly swollen before addition of the polyanion, collapses rapidly upon addition of the oppositely charged polymer to almost the dry film thickness.

The adsorption of the oppositely charged polymer from solution onto a surface attached polyelectrolyte brush is a process, which is very robust against small changes of the parameters during film deposition. It is independent of the concentration of the free polymer in solution in a very wide concentration range and almost independent of the thickness of the surface-attached monolayer. However, the addition of low molecular weight salt during the PEL adsorption allows to control the film thickness to some extent. Nevertheless, because of the rapid collapse of the brush upon addition of the oppositely charged polymer the PEL−PEL systems studied here, are all far away from a 1:1 stoichiometry one might have intuitively expected.

After adsorption of one additional polyelectrolyte layer into the brush the obtained bilayer system can be used as a substrate for the layer-by-layer deposition of polyelectrolytes as it has been described for many other systems before.

It will be interesting to compare this system, which is based on two strong polyelectrolytes with the behavior of systems consisting of a weak and a strong or two weak polyelectrolytes. These experiments will be described in a subsequent publication.

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