Notes

Layer-by-Layer Adsorption of Identically Charged Polyelectrolytes

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The alternating adsorption of oppositely charged polyelectrolytes has evolved recently as a facile and powerful method to fabricate thin polymer films.[1,2] The method is particularly versatile with respect to the detailed chemical nature of the polymers adsorbed, therefore enabling the preparation of coatings containing various functionalities. The simplicity of the equipment needed and of the procedure has risen considerable interest in this technique for tailoring model surfaces (e.g., for wetting, adhesion, or molecular recognition), replacing more demanding thin-film methods such as the Langmuir−Blodgett technique, or the chemisorption of thiols on gold, etc.

The observed film growth relies on charge overcompensation by the newly adsorbed polyions, the reasons for which are not fully clear yet.[2,3] But the success of the method is attributed to the electrostatic interaction of the complementary cation−anion pairs formed in successive adsorption steps. In agreement with this point of view, the amount of adsorbed polyelectrolyte is self-limiting, i.e., approaching asymptotically a maximal value upon prolonged adsorption times. Also, the reimmersion of a substrate that is freshly coated by a polyelectrolyte layer into a solution of the same polyelectrolyte does not lead to a further uptake of polymer. Only when the coating was subject to more or less severe drying is the adsorption of a small additional amount of the polyelectrolyte observed upon reimmersion.[4] This has been attributed to a rearrangement of the last adsorbed layer[4,5] which creates some extra space for additional material to be adsorbed.

In agreement with this general perception, attempts to adsorb layers of identically charged polyions onto each other, e.g., various polycations onto cationic protein layers,[6] have failed. But recently, the successful adsorption of up to four subsequent polycation layers on top of thick alternating layer-by-layer assemblies was reported, when using two different polycations, namely protonated poly(allylamine) with poly(2-vinylpyridine) and protonated poly(allylamine) with polylysine.[7] The adsorption stopped after four layers and was attributed to a gain of entropy in the mixed polycation systems. However, as protonated polyamines were employed in all examples, but protonation is probably not complete, hydrogen bonding between protonated and residual free amine groups could be responsible for film growth, too.

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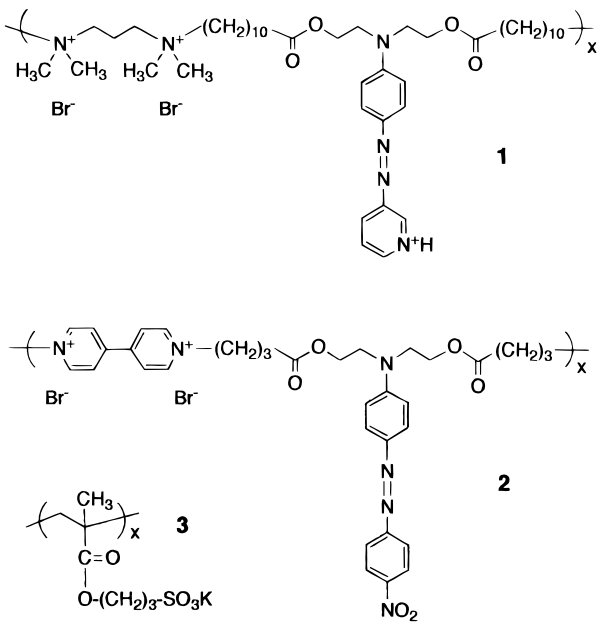

Figure 1. Chemical formulas of the colored polycations studied.

Strong hydrogen bonding was already proposed in the past to be responsible for alternating multilayers made of polyaniline and noncharged polymers,[8] or of poly(4-vinylpyridine) and poly(acrylic acid),[9] or for the binding of various species to such adsorbed polyion layers, in molecular recognition studies.[10]

To verify whether the use of two different polycations, instead of one type only, poses an advantage for the preparation of polyelectrolyte multilayers of identical charge, we have studied alternating adsorption of two quaternized polycations **1** and **2** (Figure 1). The chemical structure of the polymers excludes notable H-bonding interactions between them. Both polycations bear a strong chromophore to facilitate the recording of adsorption. Also, they are susceptible to marked solvatochromic spectral shifts in normal, alternating polyelectrolyte multilayers.[11]

Experimental Section

The synthesis of polymers **1**−**3** is described elsewhere.[11] Water was purified by an ELGASTAT water purification system (resistivity 18 MΩ/cm). Polyelectrolytes were adsorbed from 0.02 M solutions (based on the repeat unit) onto quartz plates. Whereas polymer **2** was adsorbed from pure aqueous solutions, the pH was adjusted to 1 by added HCl in the case of polymer **1**. The supports were cleaned by immersion for 20 min in freshly prepared "piranha" solution (1:1 H_2SO_4/35% H_2O_2) at 80 °C prior to use and rinsed extensively with water. (WARNING: *Piranha solution is very corrosive and must be handled with extreme caution; it reacts violently with organic materials and may not be stored in tightly closed vessels.*) After each adsorption step, samples were extensively rinsed with water, to remove adhering polymer solution. UV/vis spectra

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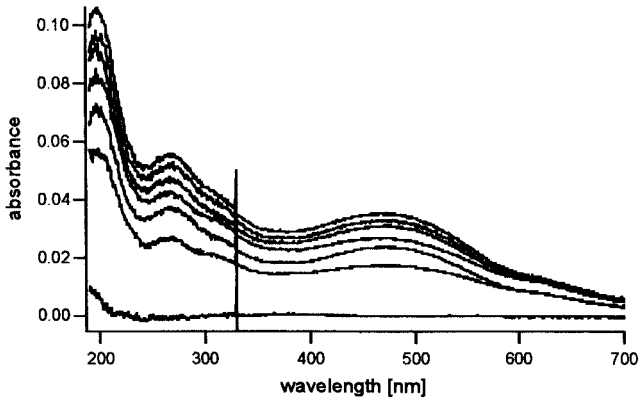

Figure 2. UV−vis spectra of attempted multilayer growth of polycations **1** and **2** on quartz slides precoated with a cushion of poly(ethylenimine) and polyanion **3**. From bottom to top: PEI/**3**/**1**, PEI/**3**/**1**/**2**, PEI/**3**/**1**/**2**/**1**, PEI/**3**/**1**/**2**/**1**/**2**, PEI/**3**/**1**/**2**/**1**/**2**/**1**/**2**, PEI/**3**/**1**/**2**/**1**/**2**/**1**/**2**/**1**/**2**.

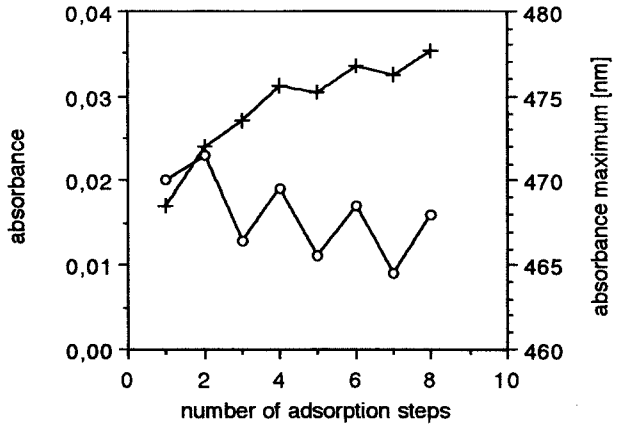

Figure 3. Multilayer growth of polycations **1** and **2** on quartz slides precoated with a cushion of poly(ethylenimine) and polyanion **3**: (+) maximum absorbance, (○) wavelength of absorbance maximum. Polycation **1** is the top layer after an odd number of adsorption steps, and polycation **2** is the top layer after an even number of adsorption steps.

were recorded in the double beam mode using a clean quartz plate as reference.

Results and Discussion

In the experiments, a cleaned quartz slide is precoated by one layer of cationic poly(ethylenimine) and one subsequent layer of anionic poly(sulfopropyl methacrylate) (**3**) to improve the adsorption of the functional polycations. These cushion layers are not visible in the vis−UV spectrum. On top of the polyanion layer, the alternating adsorption of the colored polycations was attempted. Between each adsorption step, the films were allowed to dry in the air. Note that the immersion of normal alternating polyelectrolyte films of these polycations and poly(sulfopropyl methacrylate) (**3**) into the aqueous solution of the identical polymer does not result in a notable uptake of additional polymer under the conditions chosen, neither for polycation **1** nor for polycation **2**. Monolayers of **1** adsorbed on top of polyanion **3** exhibit an absorbance maximum at 470 nm, whereas the absorbance maximum of a monolayer of **2** adsorbed on top of **3** is at 461 nm.

The evolution of the absorbance of the films obtained with a number of adsorbed layers is shown in Figure 2. A notable increase of the absorbance is observed for the first four layers. However, from the fifth layer on, the absorbance levels strongly off, approaching a limiting value. The colored coatings obtained are homogeneous within optical resolution. The additionally adsorbed amount of polymer is well bound, as samples stored in pure water do not leach material. A closer look at the spectra reveals a slight oscillation of the value of maximal absorbance. In parallel, the wavelength of the absorbance maximum exhibits a slight overall shift to smaller values with the number of adsorption cycles, but oscillates by a few nanometers, between the adsorption of **1** and **2** (Figure 3).

These results confirm that indeed thin coatings of mixed polycation layers can be made. However, extended multilayer growth is not possible. According to the absorbance values, the maximal adsorbed amount of all polycations does not exceed twice that of a single polycation layer. The limiting amount of polyelectrolyte uptake upon repeated short drying/reimmersion resembles the previous findings of Decher et al. studying the repetitive adsorption/forced drying of poly(styrenesulfonate) on a polyelectrolyte film terminated with poly(allylamine hydrochloride).[4] The use of two different polyelectrolytes of identical charge does not seem to provide a particular advantage, as hypothesized.[7] As withdrawal and reimmersion of the supports into the polyelectrolyte solutions after drying are essential to observe the effect of polycation growth, inhomogeneous adsorption of the polycations is excluded. This would also lead to continuous adsorption of the polycations just with increasing adsorption time, which is not observed. Obviously, a rearrangement of the adsorbed polymers must take place upon withdrawal from the dipping solutions and drying, but the reasons for that are not clear. It may be speculated that the rearrangement liberates some sulfonate groups in the underlying polyanion layer for binding, as proposed recently to explain the binding of charged fluorescent probes to alternating polyelectrolyte multilayer.[12] Alternatively, hydrophobic fragments could accumulate at the interface by the drying procedure as discussed before,[5] thus at least contributing to the adsorption of some additional polymer by hydrophobic interactions. But we have no experimental evidence for any of such mechanisms.

Furthermore, the slight but notable oscillation of the absorbance for a high number of adsorption cycles, together with the parallel oscillating spectroscopic shifts, suggests that a dynamic exchange of some polycations of the topmost layer takes place with the second type of polycation in solution. The extent of the oscillation does not level off with the increasing number of adsorption cycles but stays nearly constant. Therefore, the smaller and smaller increase of absorbance does not seem to reflect simply less and less adsorption of polycation from the solution. Rather, a certain portion of the last deposited material is exchanged against a slightly higher amount of the newly offered polycation. The resulting small surplus makes the overall value of absorbance grow. A similar dynamic exchange of some polyions from the top layers with the identical polyion in solution had been suggested before[13] and had been demonstrated by fluorescence labeling in the past.[7,14] Also, radiolabeling showed some partial exchange of material from the topmost layer with the solution.[15] Molar mass effects were invoked as an explanation. In our case, however, this argument does not seem to be valid, as this should lead to the preference of one type of polycation and not to an oscillating exchange between both polymer species. The oscillation might result from

a reversible binding of polymers at some relatively weak adsorption sites, but this is speculative.

In conclusion, the limited successive adsorption of different polycations could be confirmed by a system that excludes hydrogen bonding as a major driving force. A dynamic exchange of some polyions from the topmost layer and from the solution is apparently correlated to this phenomenon. But the adsorption of identically charged polyions seems far from being useful as an alternative method of film growth. Nevertheless, these findings underline once more the dynamic character of polyelectrolyte layer-by-layer assemblies.

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