

Buildup of ultrathin multilayer films by a self-assembly process: III. Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces

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Abstract

A solid substrate with a positively charged planar surface is immersed in a solution containing an anionic polyelectrolyte and a monolayer of the polyanion is adsorbed. Since the adsorption is carried out at relatively high concentrations of polyelectrolyte, a large number of ionic residues remain exposed to the interface with the solution and thus the surface charge is effectively reversed. After rinsing in pure water the substrate is immersed in the solution containing a cationic polyelectrolyte. Again a monolayer is adsorbed but now the original surface charge is restored. By repeating both steps in a cyclic fashion, alternating multilayer assemblies of both polymers are obtained. The buildup of the multilayer films was followed by UV/vis spectroscopy and small angle X-ray scattering (SAXS). It is demonstrated that multilayer films composed of at least 100 consecutively alternating layers can be assembled.

1. Introduction

Ultrathin organic films are currently gaining interest in many areas such as integrated optics, sensors, friction reducing coatings or surface orientation layers [e.g. 1, 2]. Most of these tasks require the preparation of well defined films composed of molecules with germane properties in a unique geometrical arrangement with respect to each other and to the substrate. We have already reported on the consecutive physisorption of anionic and cationic bipolar amphiphiles onto charged surfaces, adsorbed out of aqueous solutions [3, 4]. Recently we have described the replacement of either the anionic or the cationic layers by layers of physisorbed polyelectrolytes [3, 5]. Currently we present the buildup of multilayer assemblies by consecutively alternating adsorption of anionic and cationic polyelectrolytes alone.

Our approach has the advantage that ionic attraction between opposite charges is the driving force for the multilayer buildup. In contrast to chemisorption techniques [6–8] that require a reaction yield of 100% in order to maintain surface functional density in each layer, no covalent bonds need to be formed. Additionally, an advantage over the classic Langmuir–Blodgett technique is that a solution process is independent of the substrate size and topology.

Although we believe that in principle all polyelectrolytes can be used for the adsorption, we have currently selected polystyrenesulfonate sodium salt **1**, polyvinylsulfate potassium salt **2**, poly-4-vinylbenzyl-

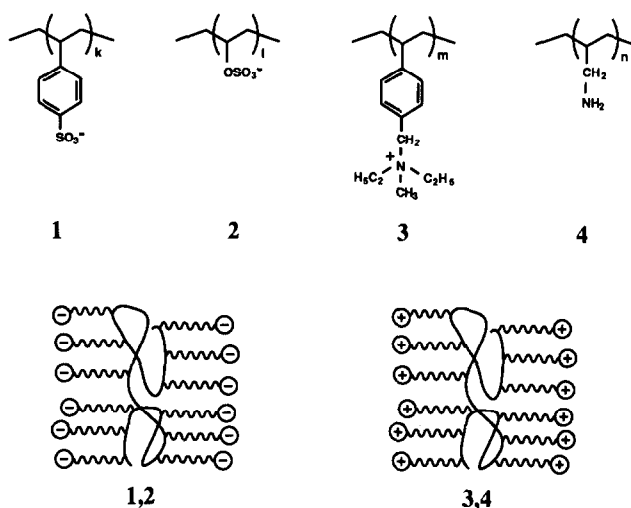


Fig. 1. Correlation of the molecular structures with their corresponding graphic representations as used in Fig. 2. For reasons of simplicity the counter-ions were omitted in both the chemical structures of the polyelectrolytes and in their oversimplified graphic representations. It is not implied that the symbols used for the polyelectrolytes represent their actual structure in solution.

(*N,N*-diethyl-*N*-methyl)-ammonium iodide **3**, and polyallylamine hydrochloride **4**. The molecular structures and their graphic representations are depicted in Fig. 1.

The buildup of multilayer films is shown in Fig. 2 and is described as follows. A solid substrate with a

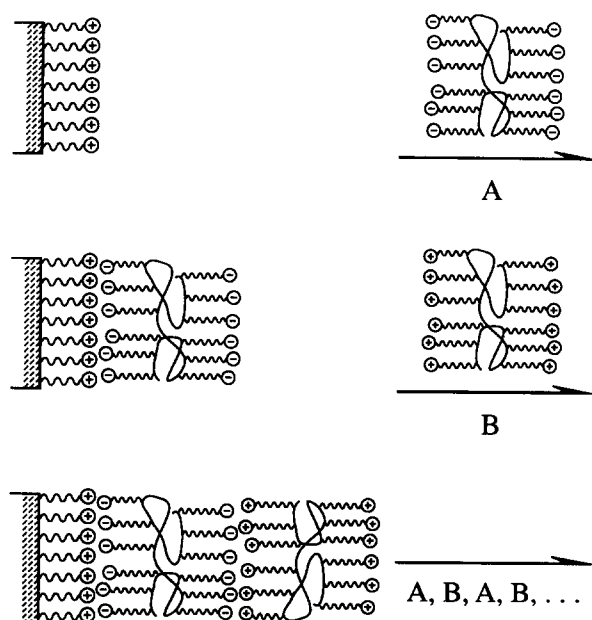


Fig. 2. Schematic for the buildup of multilayer assemblies by consecutive adsorption of anionic and cationic polyelectrolytes. The drawing is over-simplified. Again, it is not implied that the symbols used for the polyelectrolytes represent their actual structure in solution or after the adsorption.

positively charged planar surface is immersed in the solution containing the anionic polyelectrolyte and a monolayer of the polyanion is adsorbed (step A). Since the adsorption is carried out at relatively high concentrations of polyelectrolyte, a number of ionic groups remain exposed to the interface with the solution and thus the surface charge is reversed (a similar “non-flat” adsorption has also been observed by others [9, 10]). After rinsing in pure water the substrate is immersed in the solution containing the cationic polyelectrolyte. Again a monolayer is adsorbed but now the original surface charge is restored (step B). By repeating both steps in a cyclic fashion (A, B, A, B, . . .), alternating multilayer assemblies of both polymers are obtained.

This process of multilayer formation is based on the attraction of opposite charges, and thus requires a minimum of two oppositely charged molecules. Consequently, one is able to incorporate more than two molecules into the multilayer, simply by immersing the substrate in as many solutions of polyelectrolytes as desired, as long as the charge is reversed from layer to layer. Even aperiodic multilayer assemblies can easily be prepared. In this respect the new technique is more versatile than the Langmuir–Blodgett technique which is rather limited to periodically alternating layer systems. Another advantage is that the immersion procedure does not pose principal restrictions as to the size

of the substrate or to the automatization in a continuous process.

2. Materials and methods

Polystyrenesulfonate (sodium salt, $M_r = 100,000$) **1** and polyvinylsulfate (potassium salt, $M_r = 245,000$) **2** were obtained from Serva, polyallylamine (hydrochloride, $M_w = 50,000–65,000$) **4** was obtained from Aldrich. All polyelectrolytes were used without further purification. Poly-4-vinylbenzyl-(*N,N*-diethyl-*N*-methyl)-ammonium iodide **3** was synthesized as described in ref. 5.

Consecutively alternating multilayer assemblies of all materials were characterized by UV/vis spectroscopy (Perkin–Elmer Lambda 17, computer controlled, PECSS software) and small angle X-ray scattering (SAXS) (Siemens D-500 powder diffractometer using copper $K\alpha$ radiation with a wavelength of 1.541 \AA , data acquisition via a DACO-MP interface connected to a personal computer). The dependency of the SAXS and UV/vis spectra on layer numbers was recorded from a single multilayer specimen on fused quartz that was dried in a stream of nitrogen in between deposition cycles. Direct-light microscopy and SAXS measurements were performed with multilayer assemblies on silicon single crystals.

The ultrapure water used for all experiments and for all cleaning steps was obtained by reversed osmosis (Milli-RO 35TS; Millipore GmbH) followed by ion-exchange and filtration steps (Milli-Q; Millipore GmbH). The resistivity was better than $18.2 \text{ M}\Omega \text{ cm}$ and the total organic content was less than 10 ppb (according to the manufacturer). The toluene was dried by distillation from sodium.

For most experiments aminopropylsilanized fused quartz or silicon single crystal substrates were used. These substrates were ultrasonically agitated in a hot $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (7:3) mixture for 1 h and then washed with Milli-Q water. Further purification was carried out using the $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_3$ (5:1:1) step of the RCA cleaning procedure [11]. After extensively washing with Milli-Q water, the substrates were immersed for 2 min in pure methanol, a methanol/toluene (1:1) mixture and finally in pure toluene. From the last solution the substrates were directly transferred to a 5% solution of 3-aminopropyl-dimethylethoxysilane (Petrarch Systems) in toluene and kept there for 15 h under an atmosphere of dry nitrogen. Afterwards the substrates were immersed for 1 h in pure toluene under a nitrogen atmosphere. Finally, the substrates were immersed for 1 min each in toluene, toluene/methanol (1:1), methanol and Milli-Q water. The freshly surface-modified substrates were stored in water and used within 2 h for the adsorption experiments.

For the adsorption of the first layer an acidic solution of compound **1** or **2** was used in order to protonate the amino groups on the surface of the substrate. Therefore the substrate was immersed for 20 min in a solution containing 20 mg of **1** in a mixture of 0.5 ml of 0.1 N HCl and 9.5 ml of Milli-Q water at 0 °C. Afterwards the substrate was rinsed three times with water. After the adsorption of the first layer the substrates could be stored for some weeks without noticeable deterioration of the surface, but were usually used immediately for the deposition of additional layers. All following layers (even layer numbers) of the cationic polyelectrolyte **3** were adsorbed from a solution containing 20 mg **3** in 10 ml Milli-Q water. In the case of the non-quarternized polyallylamine **4** the polycation was always adsorbed from an acidic solution, containing 12.5 mg **4** in a mixture of 1.0 ml of 0.1 N HCl and 9.0 ml of Milli-Q water. All following layers (odd layer numbers) of the anionic polyelectrolytes (**1**, **2**) were adsorbed from a solution containing 20 mg (**1**, **2**) in 10 ml of Milli-Q water. In the case of samples containing polyallylamine **4** as the previously adsorbed layer (e.g. the X-ray measurements in Fig. 5), the polystyrenesulfonate layers were adsorbed from an acidic solution containing 30.0 mg of **1**, 1.0 ml of 0.1 N HCl, 2.03 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (E. Merck, p. A.) and 10.0 ml of Milli-Q water. In all cases adsorption time was 20 min at ambient temperature. The results were not critically dependent on the polymer concentration. In the case of polystyrenesulfonate **1**, an adsorption time of 20 min worked well for polymer concentrations in the range between 20 mg and 30 mg/10 ml Milli-Q water. Between adsorption cycles the substrates were washed three times with Milli-Q water.

3 Results and discussion

With polystyrenesulfonate **1** as a polyanion and poly-4-vinylbenzyl-(*N,N*-diethyl-*N*-methyl)-ammonium iodide **3** as a polycation, it is possible to adsorb at least 100 consecutively alternating layers onto solid supports. Figure 3 shows an optical micrograph of a 100 layer film on a silicon single crystal. It displays a homogeneous interference color in the central region of the substrate. At its top and bottom edges there is a well-defined 3 mm margin in which the interference color is not homogeneous. The same is true for the left and right edges of the sample where this margin has a width of less than 1 mm. These areas of poor film quality are definitively restricted to the edges of a given sample and are not even observed in all cases. X-Ray and UV/vis data were always taken from defect-free central areas or from samples without visible defects.

By UV/vis spectroscopy we have demonstrated that the consecutive adsorption of layers is a stepwise and

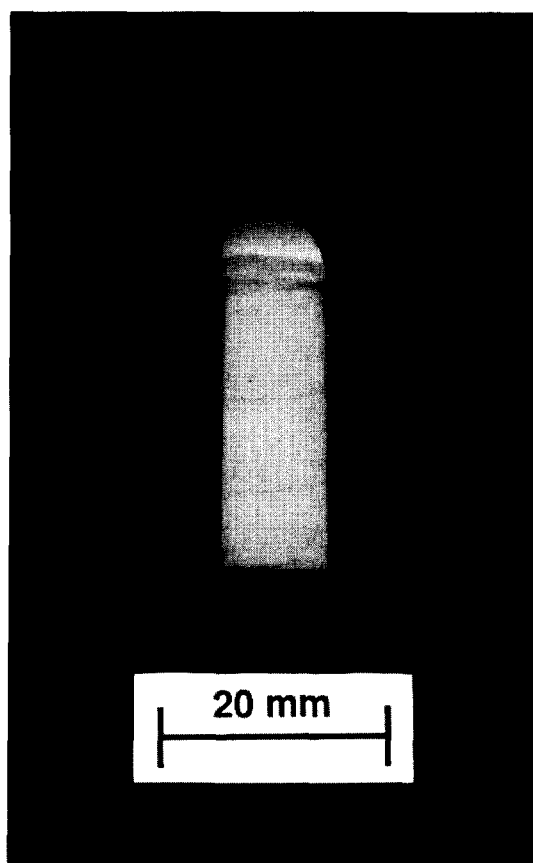


Fig. 3. Optical micrograph of a 100 layer sample consisting of consecutively alternating layers of polystyrenesulfonate **1** and poly-4-vinylbenzyl-(*N,N*-diethyl-*N*-methyl)-ammonium iodide **3** on a silicon single crystal wafer. Note that 7 mm at the top of the substrate are not covered by the film and show the native surface of the wafer.

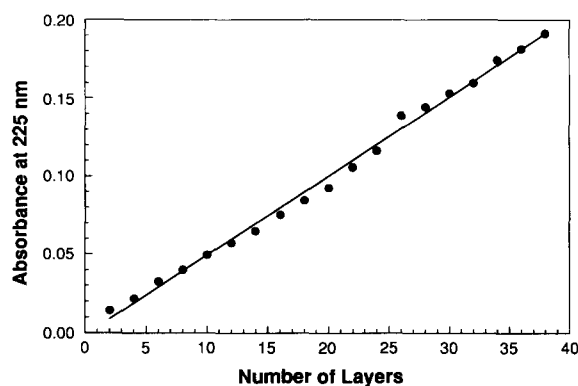


Fig. 4. Buildup of an assembled multilayer film of polystyrenesulfonate **1** and poly-4-vinylbenzyl-(*N,N*-diethyl-*N*-methyl)-ammonium iodide **3** monitored by optical absorbance of the phenyl chromophores at 225 nm.

regular process. Figure 4 depicts the optical absorbance of the phenyl chromophores at 225 nm up to a layer number of 38 (19 layers of **1** and **3** each). A linear fit yields an average increase of the optical density of 0.005 (correlation coefficient $R = 0.997$) per layer. This is a

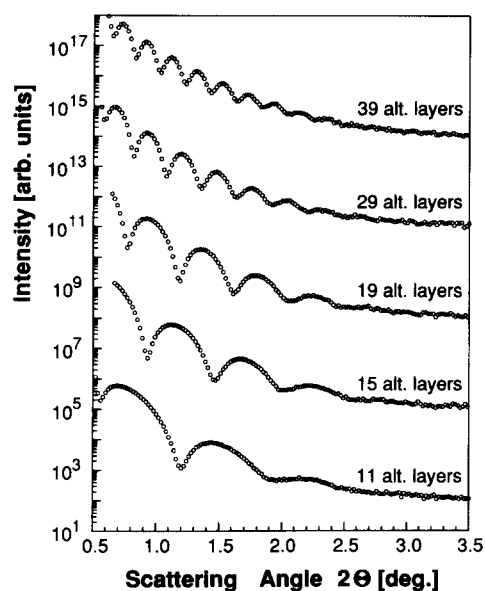


Fig. 5. Buildup of an assembled multilayer film of polystyrenesulfonate **1** and polyallylamine **4** monitored by small angle X-ray scattering. The well-developed Kiessig-fringes indicate that the film stays relatively smooth during multilayer buildup. The values for the absolute film thickness, as plotted in Fig. 6, are calculated from the distance between two neighboring fringes.

good approximation for both polyelectrolytes. Despite the different substitution of the benzene rings, the solution spectra and also the spectra of the adsorbed monolayers are almost identical for both compounds.

We have previously reported on the measurement of the absolute film thickness by small angle X-ray scattering for the case of an alternating multilayer film of a bipolar anionic amphiphile and of the polycation **3** [5]. In the case of a consecutively alternating film of polystyrenesulfonate **1** and polyallylamine **4**, we were able to follow the buildup of the multilayer by SAXS. Figure 5 shows the Kiessig fringes that were observed in dependence of the number of adsorbed layers. The so-called Kiessig-Fringes [12] result from interference of X-ray beams reflected at the substrate-film and film-air interfaces. Their occurrence points to the fact that the assembled film is relatively smooth.

From their distance, the total film thickness is calculated and plotted versus the number of adsorbed layers (Fig. 6, open circles). Additionally the optical absorbance of the benzene chromophores in the polystyrenesulfonate **1** was monitored at 225 nm (Fig. 6, full circles). The polyallylamine **4** does not absorb above 200 nm and therefore its adsorption could not be assessed. Both measurements show a linear increase in film thickness in dependence of the number of adsorbed layers. From the slope of the linear fit of the X-ray data a bilayer thickness of 2.27 nm is calculated for each adsorbed pair of anionic and cationic polyelectrolytes. This value is in the same range as values reported for

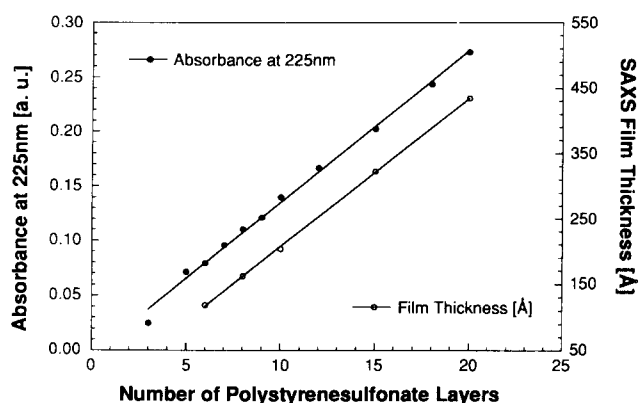


Fig. 6. Dependence of total film thickness and the optical absorbance at 225 nm on the layer number. The sample is an assembled multilayer film of polystyrenesulfonate **1** and polyallylamine **4** monitored on a substrate of fused quartz. For convenience, the layer number is given as numbers of polystyrenesulfonate layers, because the optical absorbance is entirely due to the benzene chromophores. The final thickness of the sample is 39 layers.

polyelectrolytes adsorbed as monolayers on different surfaces [9, 13]. Currently we are only able to calculate this bilayer thickness since we do not know if the single layers of both types of polyelectrolyte possess the same thickness. The total thickness of this 39 layer sample was 43.5 nm.

4. Summary and conclusions

We have demonstrated the buildup of optically transparent multilayer films of anionic and cationic polyelectrolytes on solid supports. The layered assemblies are fabricated by adsorption from solution and therefore the process is independent of substrate size and topology. We have established that at least 100 consecutively alternating layers can be adsorbed without noticeable changes in adsorption behavior. The linear increase of film thickness with the number of adsorption steps was demonstrated up to 39 layers or 43.5 nm as monitored by X-ray reflectivity. We are currently working on the fabrication of films with a thickness that will allow the evaluation of waveguiding properties.

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