with the theory which predicts a negligible susceptibility of the adhesion to charge density variations at high charge densities. The fourth case served as a control experiment and showed no substantial pH sensitivity of the adhesion. The values of the changes of the adhesion obtained for the various surface charge densities comply favorably with the theoretically expected data.

The results demonstrate that the electrostatic contribution to the interfacial adhesion between charged surfaces is substantial and thus relevant for the Langmuir-Blodgett transfer. The work of adhesion can be understood qualitatively and – to a certain degree - quantitatively with the double layer forces. The electrostatic interactions have been selected for the presented studies, because they can be modified easily via changes of the subphase pH.

Nevertheless, it is unquestionable that the other types of interactions mentioned in the introduction will also play an important role in the adhesion between hydrophilic surfaces. Of those interactions, the hydration forces and the acid/base-interactions offer themselves as a perfect choice for future investigations, because they can analogously to the presented studies be modified by parameters easily accessible.

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E 7712

Buildup of Ultrathin Multilayer Films by a Self-Assembly Process: 11. Consecutive Adsorption of Anionic and Cationic Bipolar Amphiphiles and Polyelectrolytes on Charged Surfaces

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Adsorption / Interfaces / Polymers / Supramolecular Assemblies / Ultrathin Films

We have recently reported on the consecutive physisorption of anionic and cationic bipolar amphiphiles onto charged surfaces, adsorbed out of aqueous solutions [1]. Here, we extend our previous concept to multipolar compounds such as polyelectrolytes. In contrast to the bipolar amphiphile system, it is not necessary to separate single charges by a rigid unit, when the polyelectrolyte is adsorbed from sufficiently concentrated solutions. In this case the physisorbed layer does not bind with all ionic groups to the surface and exposes free ionic groups at the new film/solution interface. Therefore a polyelectrolyte layer can replace a layer of bipolar amphiphiles in the consecutive buildup of a multilayered assembly. The buildup of multilayers can then be described as follows: A solid substrate with a positively charged planar surface is immersed in the solution containing the negatively charged bipolar amphiphile, a monolayer of the amphiphile is adsorbed and due to its bipolar structure the surface charge is reversed. After rinsing in pure water the substrate is immersed in the solution containing the positively charged 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 compounds are obtained. In the same way multilayer assemblies can be prepared by using negatively charged polyelectrolytes and positively charged bipolar amphiphiles. It is demonstrated that multilayer films composed of at least 39 consecutively alternating layers, which corresponds to a total film thickness of 151 nm, can be assembled.

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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. [2,3]). Most of these tasks require the preparation of well defined films composed of molecules with appropriate properties in a unique geometrical arrangement with respect to each other and to the substrate. Molecularly thin layers offer the possibility to construct multilayer assemblies in which the distance between two molecules can be controlled in the Ångstrom range.

We have recently introduced a new technique for the buildup of multilayer assemblies using the ionic attraction between opposite charges as the driving force [1]. In comparison to chemisorption techniques [4, 5] our approach has the advantage that no covalent bonds need to be formed and thus steric hindrance and the necessity of a reaction yield of 100%, in order to maintain surface functional density in each layer, are avoided. Additionally, an advantage over the classic Langmuir-Blodgett technique (e.g. [6]) is, that a solution process is independent of the substrate size and topology.

The adsorption of cationic and anionic amphiphiles by solids has been studied extensively as a function of concentration, pH, ionic strength and temperature (e.g. [7]). Reversible adsorption of a single monolayer of sodium dodecyl sulfate on a silicon single crystal surface, equipped with a positive surface charge by aminopropylsilanization, was reported by Haller in 1978 [8]. The adsorption of polyelectrolytes onto charged surfaces has also been studied (e.g. [9–11]).

In order to maintain a charged surface after the adsorption of each monolayer we have previously used bipolar amphiphiles with two identical charges at each end [1]. Presently we report on the replacement of layers of either the bipolar anionic amphiphile by a negatively charged polyelectrolyte or of the bipolar cationic amphiphile by a positively charged polyelectrolyte. This is feasible because at sufficiently high concentrations of polymer the polyelectrolytes adsorb in such a way that only a part of the ionic residues sticks to the charged surface but some of the ionic groups remain exposed at the solution interface. Therefore the adsorption of a polyelectrolyte also leads to a reversal of the surface charge which is the prerequisite for the assembly of multilayered films by consecutive adsorption [1].

The bipolar anionic amphiphile **1** and the bipolar cationic amphiphile **2** are the same materials as described in Ref. [1]. Although we believe that in principle all polyelectrolytes can be used for the adsorption, we have currently selected polystyrenesulfonate sodium salt **3**, polyvinylsulfate potassium salt **4**, poly-4-vinylbenzyl-(N,N-diethyl-, N-methyl-)-ammonium iodide **5**, and poly-l-lysine hydrobromide **6**. Most of the experiments reported here were carried out with the compounds **1** and **5**. The molecules and their graphic representations are depicted in Fig. 1.

At the bottom of Fig. 1 only two (3, 5) of the four chemical structures of the polyelectrolytes (**3–6**) are shown. For the sake of clarity they serve as examples for their corresponding schematic representations (**3–6**), which are meant to generally symbolize polyanions (3, 4) and polycations (5, 6). These symbols are not itended to describe the solution conformation of the polyelectrolytes, the graphic representa-

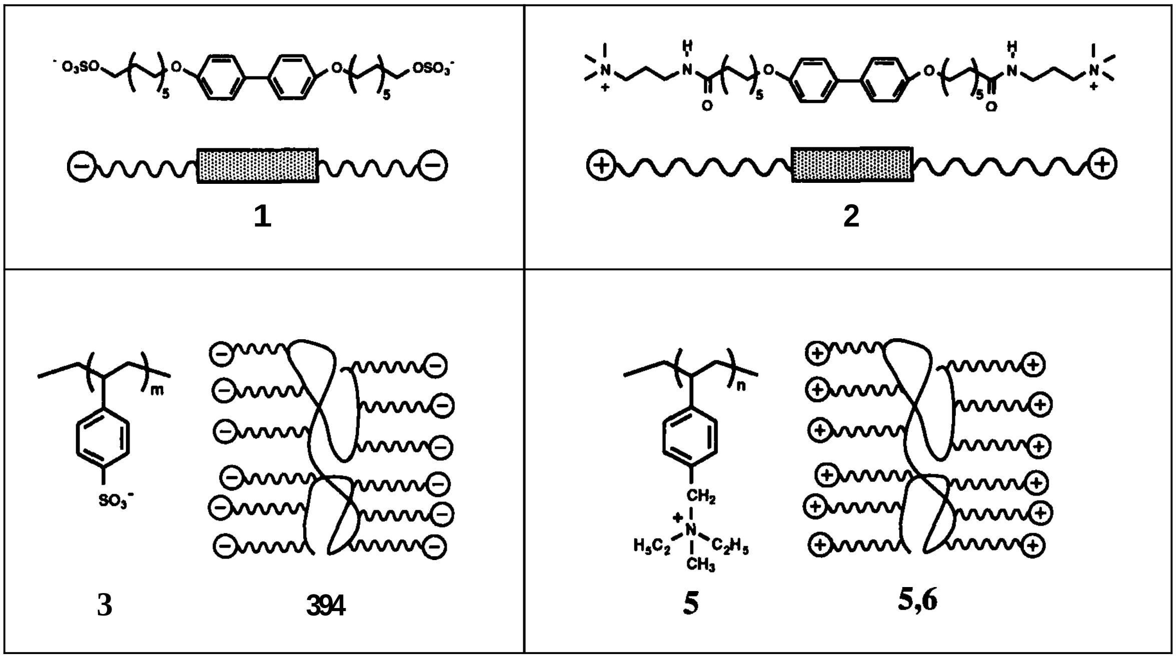

Fig. 1
Correlation of the molecular structures with their corresponding graphic representations as used in e.g. Fig. 2

tions should only help to conjecture the buildup of multilayer assemblies.

2. Materials and Methods

Compounds **1** and **2** were obtained as already described in Ref.[1]. Polystryrenesulfonate (sodium salt, M_r = 100.000) **3**, polyvinylsulfate (potassium salt, M_r = 245.000) **4** and poly-l-lysine (hydrobromide, M_r = 50.000–100.00) **6** were obtained from SERVA. All polyelectrolytes were used without further purification. Poly-4-vinylbenzyl-(N,N-diethly-, N-methyl-)-ammonium iodide **5** was synthesized using standard procedures. The monomer 4-vinylbenzyl-(N,N-diethyl-)-amine was synthesized from 1-bromo-2-phenylethane according to Ref. [12–14]. The monomer was then polymerized in tetrahydrofurane using n-butyllithium as initiator. Finally the aminogroups were quarternized with methyliodide according to Ref. [15].

Consecutively alternating multilayer assemblies of all materials were characterized by UV/Vis spectroscopy (Perkin Elmer Lambda 17, computer controlled, PECSS software) optical microscopy (Zeiss Axioplan) and small angle X-ray scattering (SAXS) (Siemens D-500, computer controlled via DACO-MP). The dependency of the UV/Vis spectra on layer numbers were 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. For optical microscopy the silicon surface was overlaid with a thermally grown 160 nm oxide coat and samples consisting of 10 and 20 layers were used. SAXS experiments were carried out with a multilayer sample consisting of 39 alternating layers on a substrate without additional oxide coating.

The ultrapure water used for all experiments and for all cleaning steps was obtained by reversed osmosis (Milli-RO 35 TS; Millipore GmbH) followed by ionexchange and filtration steps (Milli-Q; Millipore GmbH). The resistivity was better than 18.2 MΩ . cm and the total organic content was less than 10 ppb (according to manufacturer).

2.1. Functionalization of Substrates and Preparation of Multilayer Assemblies

Aminopropylsilanized fused quartz or silicon single crystal substrates were used for the adsorption experiments. The substrates were ultrasonically agitated in a hot H_2SO_4/H_2O_2 (7:3) mixture for 1 h and then washed with Milli-Q water. Further purification was carried out using the $H_2O/H_2O_2/NH_3$ (5:1:1) step of the RCA cleaning procedure [16]. After extensively washing with Milli-Q water, the substrates were immersed for two minutes 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-aminopropyldimethylethoxysilane (Petrarch Systems) in toluene and kept there for 15 h under an atmosphere of dry nitrogen. Afterwards the substrates were ultrasonically agitated for one minute in pure toluene, a toluene/DMSO (1:1) mixture and finally in pure DMSO. The freshly surface-modified substrates were used within two hours for the adsorption experiments.

For the adsorption of the first layer an acidic solution of compound **1** or **3** was used in order to protonate the aminogroups on the surface of the substrate. Therefore the substrate was immersed for 20 min. in a solution containing 4.5 mg **1** in a mixture of 0.3 ml 0.1 n HCI, 1.7 ml Milli-Q water and 6 ml DMSO (or 25 mg **3** in 10ml Milli-Q water) at 0°C. Afterwards the substrate was washed with water at 0°C and then rinsed with water at ambient temperature. 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 bipolar amphiphile **2** or of the cationic polyelectrolytes (**5**, **6**) were adsorbed from a solution containing 10 mg **2** (or 25 mg (**5**, **6**)) in 10 ml Milli-Q water. All following layers (odd layer numbers) of the anionic bipolar amphiphile **1** of the anionic polyelectrolytes (**3**, **4**) were adsorbed from a solution containing 4.5 mg **1** in a mixture of 2 ml Milli-Q water and 8 ml DMSO (or 25 mg (**3**, **4**) in 10 ml Milli-Q water). In all cases adsorption time was 20 min. at ambient temperature. In the case of the polyelectrolytes the results were not critically dependent on the polymer concentration. 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. After each adsorption step the substrates were washed three times with Milli-Q water.

3. Results and Discussion

3.1. Strategy for and Realization of Multilayer Buildup

The process of the consecutively alternating adsorption of low molecular weight compounds and polymers is schematically depicted in Fig. 2. The illustration shows the buildup of a multilayer assembly using an anionic bipolar amphiphile and a cationic polyelectrolyte. In the same fashion we have constructed assemblies composed of cationic bipolar amphiphiles and anionic polyelectrolytes.

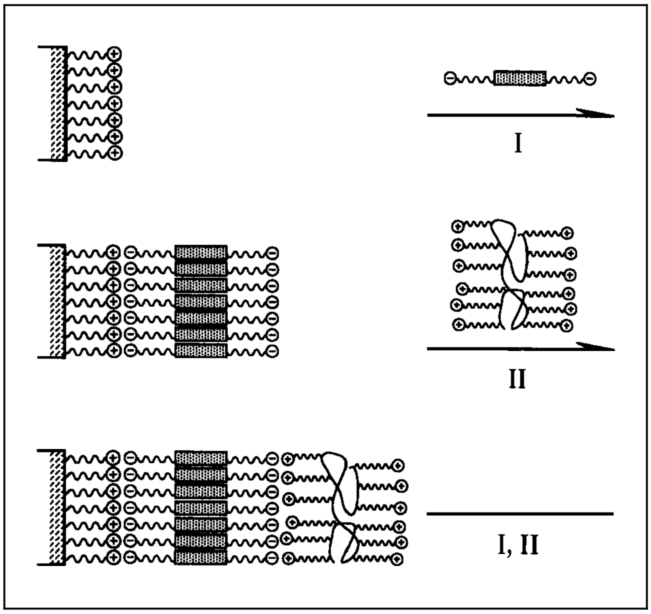

Fig. 2
Schematic for the buildup of multilayer assemblies by consecutive adsorption of bipolar amphiphiles and polyelectrolytes, exemplarily depicted for the case of anionic bipolar amphiphiles and cationic polyelectrolytes

In step **I** a substrate with a positively charged surface is immersed in the solution of the negatively charged amphiphile leading to the adsorption of one monolayer and to the reversal of the surface charge. Then the substrate is rinsed in pure water in order to remove adhering solution of the negatively charged amphiphile. In step **II** the substrate is dipped into the solution containing the positively charged polyelectrolyte. Again a monolayer is adsorbed but now the original positive surface charge is restored. After a second rinsing step the process (steps **I** and **II**) is carried out in a cyclic fashion, yielding multilayer assemblies of at least 39 layers in thickness. If the rinsing steps were omitted, an adhering layer of one solution would be left on the surface of the substrate. This would lead to a contamination of the next solution and eventually to co-precipitation of both compounds and to the undesired incorporation of precipitated particles into the following layer.

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 charged bipolar amphiphiles 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 classic 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.

3.2. Characterization of Multilayer Assemblies

With the bipolar amphiphile/polyelectrolyte system described here, it is possible to adsorb at least 39 consecutively alternating layers onto solid supports. As in the case of the low molecular weight compounds, the multilayer films were optically transparent.

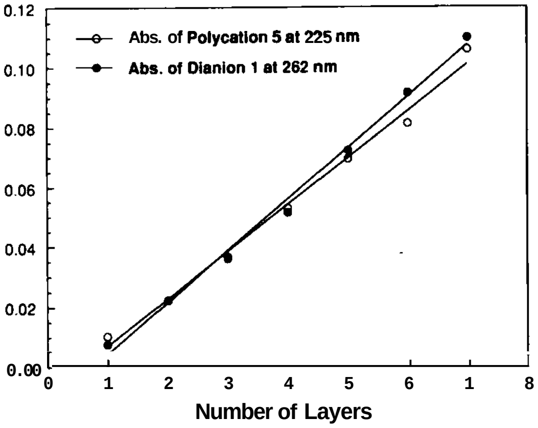

Fig. 3
Optical absorbance of poly-4-vinylbenzyl-(N,N-diethyl-, N-methyl-)-ammonium iodide **5** layers at *225* nm (open circles) and of layers of the anionic bipolar amphiphile **1** at 262 nm (full circles) depending on the number of layers deposited in each case

By UV/Vis spectroscopy we have also demonstrated that the consecutive adsorption of layers is a stepwise and regular process. Fig. 3 depicts the optical absorbance spectra up to a layer number of 14 (7 layers of each compound), composed of the bipolar anionic amphiphile **1** alternated with poly-4-vinylbenzyl-(N,N-diethyl-, N-methyl-)-ammonium iodide **5**. It shows a plot of the corrected optical densities of the biphenyl chromophore of **1** at 262 nm (full circles) and of the phenyl chromophore of **5** at 225 nm (open circles) versus the layer number. The correction of intensities at 225 nm is necessary since the absorptions of both chromophores overlap in this region as shown in spectra of a monolayer of **1** and **3** in Fig. 4. The spectrum of a monolayer of **5** cannot be measured directly since we have to start from a positively charged surface. However, the spectral characteristics of **3** and **5** are so similar that **3** serves perfectly to illustrate the necessity of the correction. In order to obtain the linear plot in Fig. 3 we have simply subtracted a value of 0.017 times the number of layers of **1** (fraction of absorbance due to the anionic bipolar amphiphile) from the measured optical densities at 225 nm. Fig. 3 also indicates that the first layers of each compound seem to be slightly different from the following ones since the linear fits do not go through zero.

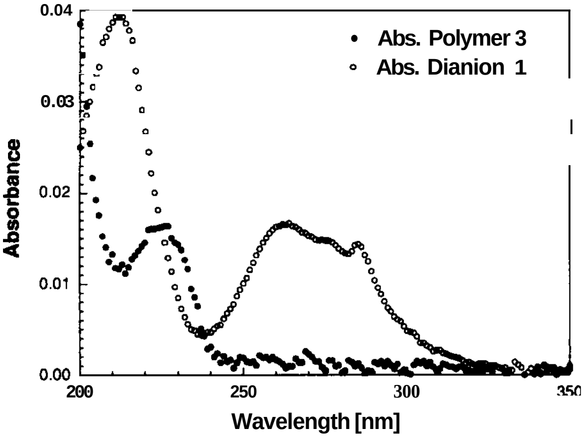

Fig. 4
Optical absorbance spectra of single monolayers of the anionic bipolar amphiphile **1** (open circles) and of polystyrenesulfonate **3** (full circles)

Both sets of points in Fig. 3 were fitted with a linear fit, yielding an average optical density of 0.017 ± 0.002 (at 262 nm) per layer of the bipolar anionic amphiphile **1** and 0.016 ± 0.002 (at 225 nm) per layer of the polycation **5**.

When samples were examined with optical microscopy under crossed polarizers no birefringence could be detected, indicating either a highly oriented (homeotropic) or isotropic structure of the multilayer assemblies. In all cases we observed that the mixed multilayers display a more homogeneous optical interference color than multilayers composed of bipolar amphiphiles (**1**, **2**) alone.

This enhanced film quality is further evidenced in small angle X-ray scattering. In contrast to the multilayers only composed of the bipolar amphiphiles (**1**, **2**), we have observed so called Kiessig fringes [17] in the X-ray diffractograms. Fig. 5 shows an X-ray scattergram of a 39-layer sample composed of a first layer of polystyrenesulfonate and of 38 consecutively alternating layers of the polycation **5** and the bipolar anionic amphiphile **1**. Nine fringes are observed between scattering angles 0.7 and 1.2 degrees. They results 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 a total film thickness of 151 nm is calculated, that agrees well with the observed blue interference color of the sample. From space-filling models we deduce the molecular

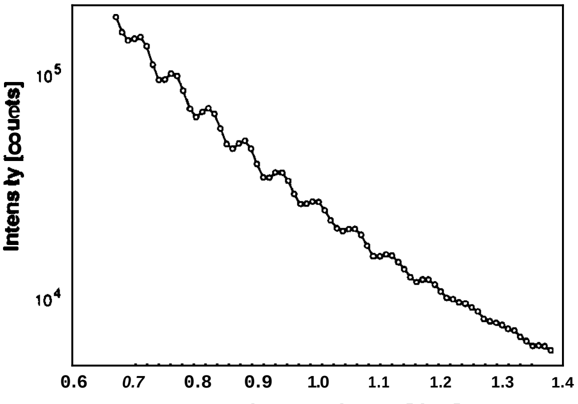

Fig. 5
Small angle X-ray scattergram of a multilayer assembly composed of a first layer of polystyrenesulfonate and of 38 consecutively alternating layers of the polycation **5** and the anionic bipolar amphiphile **1**. It shows 9 Kiessig fringes from which a total film thickness of 151 nm is calculated

lenght of compound **1** to be 4.46 nm in its maximum extended conformation. If it assumed that the molecules of **1** are not tilted with respect to the layer normal, the 19 layers of **1** account for 84.74 nm of the total film thickness. That leaves 66.26 nm of the total film thickness for the 20 polymeric layers or 3.31 nm for each polymeric layer. This value is in the same order of magnitude as values reported for polyelectrolytes adsorbed as monolayers on different surfaces [9, 11]. It further indicates that the polyelectrolyte must adsorb forming loops at the surface. Since the ionic groups are connected by the polymer backbone they cannot be separated more than approximately 0.5 to 1.0 nm. Therefore the ionic groups must also be present within each polymeric layer and not only at the two interfaces as oversimplified in Fig. **2**.

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E 7715

Scanning Tunneling Microscopy of the Initial Stages of Metal Condensation on Semiconductor Surfaces

Progress Report

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Crystal Growth / Nucleation / Semiconductors / Surfaces

After a brief description of the theoretical and experimental basis of scanning tunneling microscopy (STM) typical results from the initial stage of metal condensation on semiconductor surfaces will be presented. As substrates Si(111) and Si(100) are used. Their reconstruction is explained by the current atomic models and compared with STM images of the clean surfaces. While the 7 x 7 reconstruction of Si(111) can be prepared with a defect concentration in the order of 0.03% of a monolayer, Si(100) shows a higher density of imperfections by at least one order of magnitude. STM images from nonreactive systems (Ag/Si(111) and Ag/Si(100)) are described and from a reactive system (Fe/Si(111)), which forms well defined silicides. In case of Ag/Si and room temperature condensation the initial stage is characterized by a two-dimensional interface layer, which does not cover the substrates completely and the growth of rather regular three-dimensional Ag islands, whose shape is consistent with metallic character. After Fe deposition on Si(111) the surface is covered by islands, which due to their irregular size and shape indicate compound formation or intermixing with Si. After annealing Fe/Si(111) shows the development of well ordered Fe silicide layers.

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