

**BUILDUP OF ULTRATHIN MULTILAYER FILMS
BY A SELF-ASSEMBLY PROCESS, 1
CONSECUTIVE ADSORPTION OF ANIONIC AND CATIONIC
BIPOLAR AMPHIPHILES ON CHARGED SURFACES**

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Abstract: An anionic and a cationic bipolar amphiphile containing rigid biphenyl cores were synthesized. The compounds were dissolved in a mixture of dimethylsulfoxide (DMSO) and water and pure water, respectively. When 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 bipolar amphiphile. 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. It is demonstrated that multilayer films, composed of at least 35 consecutively alternating layers, which corresponds to a total film thickness of 170 nm can be assembled.

INTRODUCTION TO ULTRATHIN FILMS

Ultrathin organic films are currently gaining interest in many areas such as integrated optics, sensors, friction reducing coatings or surface orientation layers. (e. g. Ref. 1). 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.

Today there exist four principal methods for the preparation of ultrathin multilayered films. The method of solution casting of preformed bilayer aggregates yields layered structures, but the alignment of the layers and the positioning of molecules with respect to each other is limited (Ref. 2). The latter also applies to the production of layered structures by annealing of spin coated films of copolymers which was recently introduced (Ref. 3). In the now classical Langmuir-Blodgett (LB) technique a film is prepared on the surface of water and then transferred onto solid substrates (Ref. 4). This method is a straightforward approach to the tailor-made construction of multilayered ultrathin films, but rather inconvenient for automation and large scale application. The fourth

method based on chemisorption is very similar to the Merrifield peptide synthesis. Each layer is grafted onto the previous one (Refs. 5-6), requiring chemical reactions with a yield of exactly 100% in order to preserve the surface density of functional groups in each layer. Since this task is very difficult to fulfill, the respective investigations seem to be limited to maximum layer numbers of 8 to 12.

FROM ADSORBED MONOLAYERS TO ADSORBED MULTILAYERS

Our approach avoids this problem by using electrostatic attraction between the surface and the molecules which are adsorbed (Ref. 7). This way an exact positional matching of the charged groups is not required. The adsorption of cationic and anionic amphiphiles by solids has been studied extensively as a function of concentration, pH, ionic strength and temperature (Ref. 8). Reversible adsorption of a single monolayer of sodium dodecyl sulfate on a silicon single crystal surface, equipped with a positive surface charge by aminopropylsilylation, was reported by Haller in 1978 (Ref. 9).

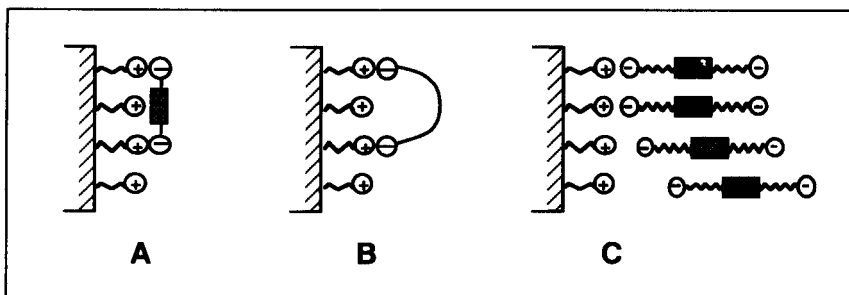


Fig. 1: Schematic representation of the adsorption of bipolar molecules on a charged surface. (A) flat adsorption (undesired); (B) adsorption as a loop (undesired); (C) end-on adsorption (desired)

In order to maintain a charged surface after the adsorption of the first monolayer we have used bipolar amphiphiles with two identical charges at each end. As depicted in Fig. 1, three principle ways how such molecules may adsorb onto a charged surface can be envisioned. If the molecule is too short, that is if the charges are only separated by a small distance, the molecule will adsorb flat on the surface (Fig. 1a). As a consequence the ionic groups that stick to the solid substrate are solvent accessible and the first monolayer is completely desorbed when the second layer is to be put on top of the first one. This was observed when 4,4'-terphenyldisulfonic acid is used as dianionic amphiphile. When the molecular length is increased the molecule might adsorb as a loop, which would lead to a reduction of charged groups on the surface (Fig. 1b).

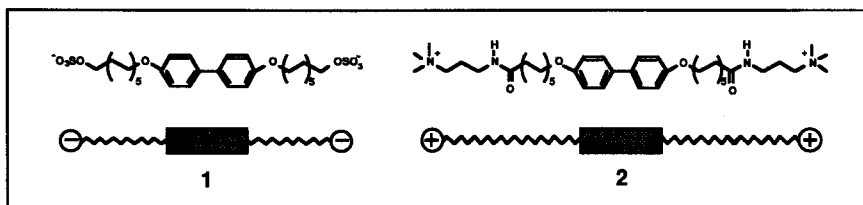


Fig. 2: Materials used in this study and their respective graphic representations. 1 Boladianion; 2 Boladikation

In order to avoid the formation of loops and to facilitate the possibility of the end-on adsorption (Fig. 1c), we have designed amphiphiles with a central biphenyl unit as a rigid core, connected to the ionic end groups by alkyl chains containing 11 carbon atoms each. The molecules and their graphic representations are depicted in Fig. 2. With these two bipolar amphiphiles it is possible to construct multilayer assemblies by consecutively alternated physisorption.

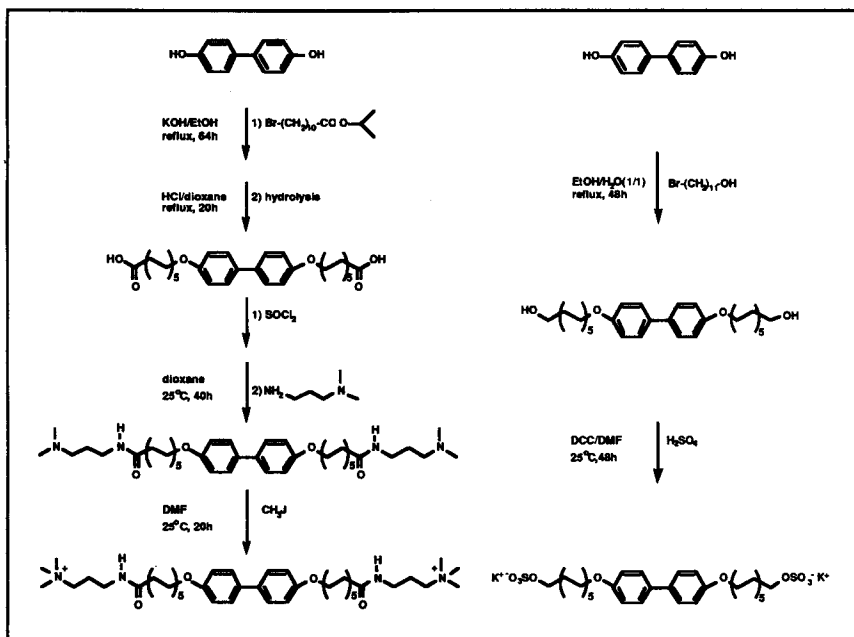


Fig. 3: Synthetic routes to compounds 1 and 2

MATERIALS AND METHODS

Compounds **1** and **2** were obtained via synthetic routes as shown in Fig. 3. Consecutively alternating multilayer assemblies of these 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. Optical microscopy and SAXS measurements were performed with multilayer assemblies on single silicon crystals overlaid with a thermally grown 1600 Å oxide coat. In both experiments samples consisting of 10 and 20 layers were used.

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 H₂SO₄/H₂O₂ (7:3) mixture for 1 h and then washed with Milli-Q water. Further purification was carried out using the H₂O/H₂O₂/NH₃ (5:1:1) step of the RCA cleaning procedure (Ref. 10). 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-aminopropyltrimethoxysilane (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** 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**, 0.3 ml 0.1 n HCl, 1.7 ml Milli-Q water and 6 ml DMSO 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** were adsorbed from a solution containing 10 mg **2** in 10 ml Milli-Q water. All following layers (odd layer numbers) of the anionic bipolar amphiphile **1** were adsorbed from a solution containing 4.5 mg **1** in a mixture of 2 ml Milli-Q water and 8 ml DMSO. In both cases adsorption time was 20 min. at ambient temperature. Between adsorption cycles the substrates were washed three times with water.

STRATEGY FOR AND REALIZATION OF MULTILAYER BUILDUP

The process of sequential adsorption of monolayers is graphically described in Fig. 4. 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 bipolar amphiphile. Again a monolayer is adsorbed but now the original positive surface charge is restored. After a second rinsing step the process can be carried out in a cyclic fashion, yielding multilayer assemblies of at least 35 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 incorporation of precipitated particles into the following layer.

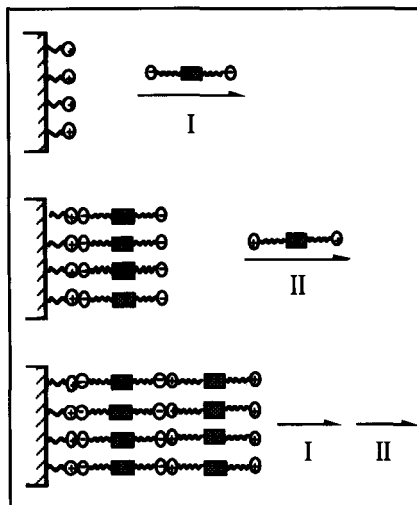


Fig. 4: Schematic representation of the adsorption process

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 classical 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.

CHARACTERIZATION OF MULTILAYER ASSEMBLIES

With the newly developed technique it is possible to adsorb at least 35 consecutively alternating layers onto solid supports. It is currently not clear if the molecules adsorb from solution as monomers or already as a preformed monolayer (lamellar micellar aggregate), which have been observed for rigid amphiphiles

carrying hydrophilic groups at both ends (Ref. 11). In UV/Vis spectroscopy one observes changes from the solution spectrum to that of the adsorbed layer, indicating molecular rearrangements upon adsorption. On the other hand NMR-spectra of an aqueous solution of compound **2** exhibit the typical signal broadening observed in micellar solutions.

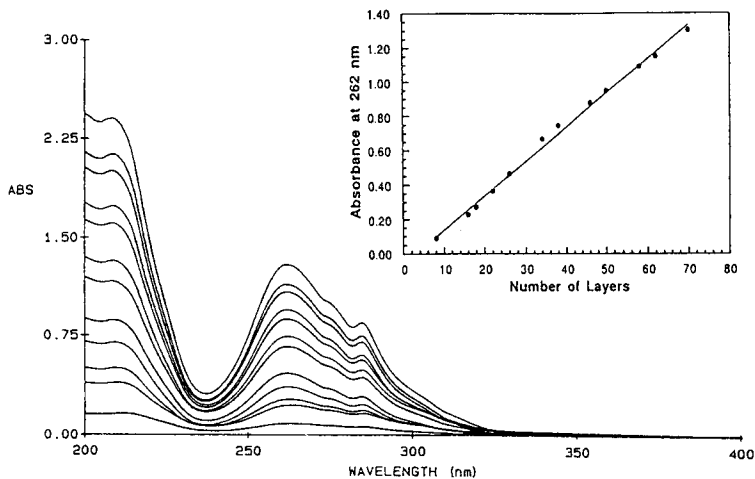


Fig. 5: UV/Vis absorption spectra of multilayer assemblies in dependence of layer numbers

By UV/Vis spectroscopy we have also demonstrated that the consecutive adsorption of layers is a stepwise and regular process. Fig. 5 depicts the optical absorbance spectra for the layer numbers 1, 4, 8, 9, 11, 13, 17, 19, 23, 25, 29, 31 and 35. The inset shows a plot of the optical density at the main absorption band of the biphenyl chromophore (262 nm) versus the layer number. The points can be fitted with a linear fit, yielding an average optical density of 0.018 ± 0.002 per layer. Similar values are obtained from LB-films of biphenyl amphiphiles indicating a reasonable monolayer coverage in each layer (Ref. 12). Slight deviations of some data points from the straight line may be explained by inhomogeneities in some of the layers, possibly induced by the drying of the substrate, which was necessary for the UV/Vis measurements. Similar imperfections are also occasionally observed in samples that were not dried during multilayer buildup and seem to depend on the quality of the aminopropyl surface functionalization. When present they are easily visualized by the occurrence of more than one interference color in different regions of the substrate or by observation of some opaqueness in the interference colors. Typically defects appear within a 2 mm margin around the edges of the substrate. However, the results reported here were obtained from central areas of samples which did not display visible imperfections.

When samples were examined with optical microscopy under crossed polarizers no birefringence could be detected, indicating either a highly oriented (homeotropic) or completely isotropic structure of the multilayer assemblies. However, when mechanically scratched a bright zone appeared simultaneously around the forming groove. In the moment it cannot be decided, whether this birefringence originates from reorienting the previously homeotropic layers or from inducing order in the formerly isotropic film.

In small angle X-ray scattering no Bragg peaks are observed, which might indicate the absence of order or the inadequacy of our instrument. From space-filling models we deduce the molecular length of compound **2** to be 52.6 Å and of compound **1** to be 44.6 Å, yielding a repeating unit of the multilayer assembly of 97.2 Å. This spacing corresponds to an angle of 0.908 degrees in 2θ at which the Bragg peak would be observed using Copper K_{α} irradiation. However, with the D-500 diffractometer a peak in the region below 1.0 degree cannot be detected and higher order peaks are not observed.

Up to now the only indication for the formation of a regularly layered assembly is deduced from the stepwise adsorption as seen in UV/Vis spectroscopy. Together with the maximum extended length of the molecules, as derived from the space filling models, a maximum film thickness can be predicted for a given number of adsorbed layers. For example, a 35 layer sample in which the molecules are neither tilted with respect to the substrate normal nor partially interdigitated would have a maximum total layer thickness of approximately 1700 Å.

ACKNOWLEDGEMENTS

We thank the Bundesministerium für Forschung und Technologie for financial and K. Bach for technical support.

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