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# The effect of polymer charge density and charge distribution on the formation of multilayers

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## Abstract

Polyelectrolyte multilayers which are built up by alternating adsorption of polyanions and polycations from aqueous solutions at a solid interface are investigated by reflectometry and ellipsometry. Below a degree of charge of about 70% the adsorption stops after a certain number of dipping cycles and no multilayer formation occurs. This indicates an electrostatically driven adsorption process. Below a charge density of 70% an adsorption can take place if the charged segments are combined as a block of the polymer.

## 1. Introduction

During the last ten years polymer films of a new kind formed by the alternating adsorption of polyanions and polycations from aqueous solutions [1] have been investigated intensively. The general opinion is that the formation of such multilayers is electrostatically driven [2]. But results of former studies on the effect of the ionic strength seem to disagree with this assumption. To solve this paradox, the effect of polymer charge density is investigated in the present study.

The film thickness *increases* with increasing salt concentration due to a change in chain conformation from a rather extended to a more coiled chain due to electrostatic screening of the charges along one chain [3]. On the other hand, for a certain ionic strength one would expect a *decrease* in film thickness caused by electrostatic screening of the attraction between the polyelectrolyte and oppositely charged surface. But contrary to this prediction, the film thickness increases even at a high salt concentrations (e.g. 3 mol l<sup>-1</sup>) [4, 5] where the Debye length is smaller than the diameter of a hydrated counterion and, as a consequence, electrostatic attraction should completely vanish. This could lead to a first conclusion that

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besides electrostatic forces, *non*-electrostatic forces are also important for the formation of multilayers.

To check whether electrostatic attraction between the polyelectrolyte chain and the surface is required for the polyelectrolyte adsorption, the effect of the polyelectrolyte charge density on the multilayer formation is studied. The polyelectrolytes are strong and their charge density is changed by varying the ratio between charged and neutral monomer units. Furthermore, the effect of charge distribution is investigated using statistical copolymers and block copolymers each consisting of a neutral and a charged block.

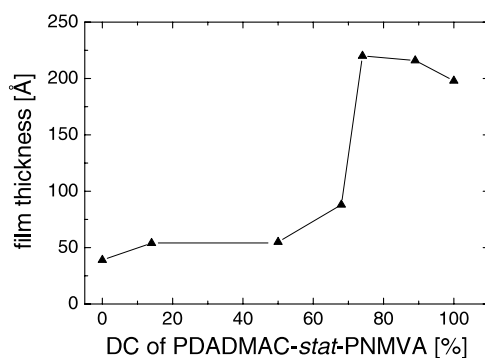
## 2. Materials and sample preparation

One of the statistical copolymers used in the present study is the polycation PDADMAC-*stat*-PNMVA which consists of positively charged diallyl-dimethyl-ammonium chloride (DADMAC) monomers and neutral *N*-methyl-*N*-vinylacetamide (NMVA) monomers. The other statistical copolymer consists of DADMAC monomers and neutral *N*-isopropyl-acrylamide (NIPAM) units. The diblock copolymers contain a charged block and a neutral PNIPAM block. As charged monomer units DADMAC, styrene sulfonate and diethylaminoethylmethacrylate (DEAEM) are used. A diblock copolymer is indicated as P(electrolyte)(*x*%)-*b*-PNIPAM and a statistical copolymer as P(electrolyte(*x*%)-*stat*-NIPAM). The percentage corresponds to the ratio of charged monomer units with respect to the number of monomers of the whole copolymer. The silicon wafers were provided by Wacker Siltronic AG, Burghausen (Germany). The polyelectrolyte films were deposited on the silicon wafers by immersion for 20 min into aqueous solutions containing  $10^{-2}$  monomol l<sup>-1</sup> (concentration of monomer units) of the respective polyelectrolyte and by rinsing with Milli-Q water after each deposition step. A complete *deposition cycle* in the following concerns to the sequence PSS/water/polycation/water. The first layer is a PEI layer adsorbed directly on the substrate.

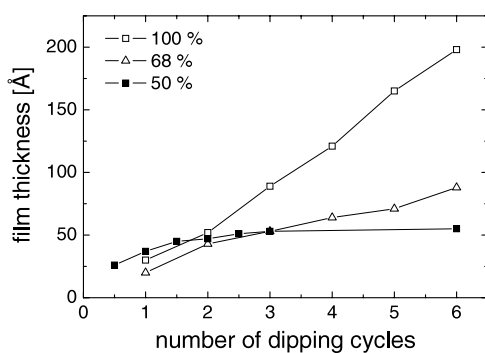
For the thickness measurements a Multiscopie from Optrel (Berlin, Germany) was used in the ellipsometry mode, and measurements were carried out using a home-made x-ray reflectometer.

## 3. Results

Figure 1 shows the thickness after six dipping cycles for PSS/P(DADMAC-*stat*-NMVA) as a function of the degree of charge (DC) of P(DADMAC-*stat*-NMVA). Depending of the DC of the cationic copolymer, two regimes can be distinguished: above a DC of 68% the films are thicker (between 200 and 220 Å) and a maximum in thickness is observed at a DC of 75%. This maximum can be explained by a change in polyelectrolyte conformation from a more stretched chain at a DC of 100% to a more coiled chain at a DC of 75% due to a decrease in electrostatic repulsion between different chain segments of the same or of different chains. AFM and x-ray measurements show an increasing roughness from 10 to 40 Å [6, 7]. Below a DC of 68% the films are thin (around 50 Å) and the thickness is almost independent of the DC. Only for the neutral polymer PNMVA is the film even thinner (35 Å). This result raises the question of whether below a DC of 68%, thin multilayers of six double layers are formed, or whether the multilayer formation stops after a certain number of layers. Figure 2 shows the multilayer formation at three different DCs. The thickness of the film containing fully charged PDADMAC increases quite linearly. In the case of the film containing 53% charged polycation, from the second PSS layer on no further polyelectrolyte is adsorbed. The multilayer formation of a film built up with 68% charged polycation is in between these two



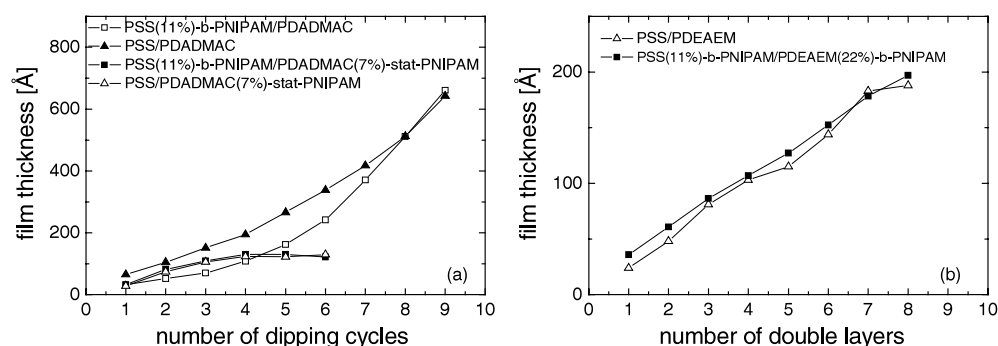
**Figure 1.** Film thickness as a function of the DC of the polycation PDADMAC-*stat*-PNMVA after six dipping cycles for PSS/PDADMAC-*stat*-PNMVA prepared from solutions containing  $10^{-1} \text{ mol l}^{-1}$  NaCl at a fixed polyelectrolyte concentration of  $10^{-2} \text{ monomol l}^{-1}$ .



**Figure 2.** Film thickness as a function of the number of dipping cycles for PDADMAC-*stat*-PNMVA.

groups of films. The thickness increases slightly after each deposition cycle. This suggests a multilayer formation but with very thin layers. Also the neutral PNMVA adsorbs slightly at the interface coated with PSS, but it forms a thinner layer (10–15 Å) than the charged polymers and no further polyelectrolyte can be deposited in a subsequent dipping step. These results lead to the conclusions that a minimum charge density of about 70% is required for the formation of multilayers.

Up to now, polyelectrolytes where the charge is more or less homogeneously distributed along the chain have been used. The question arises of whether the charge distribution also has an influence on the adsorption behaviour. Therefore the formation of multilayers which are built up from statistical copolymers or block copolymers is compared in figure 3. As a reference curve, that for a film built up from fully charged PSS and PDADMAC is shown (figure 3(a)). The other films are built up from polyelectrolytes where at least one of them carries an average charge density which is well below the minimum charge density of 70% required for the multilayer formation. If the fully charged PSS is replaced by a diblock copolymer where 11% of the monomer units are negatively charged styrene sulfonate units, the thickness increases monotonically and it is of the same order of magnitude as for PSS/PDADMAC. But if the PDADMAC is replaced by a 7% charged PDADMAC, the multilayer formation stops after the deposition of the third double layer. Then, the replacement of fully charged PSS by the corresponding 11% charged version has no additional influence on the thickness. In figure 3(b)



**Figure 3.** Film thickness as a function of number of dipping cycles, for films built up from different statistical and diblock copolymers where the charge is distributed in a different way. The polymer concentration was fixed at  $10^{-2}$  monomol  $l^{-1}$  and the NaCl concentration was  $0.1$  mol  $l^{-1}$ . (a) Derivatives of PSS and PDADMAC. (b) Derivatives of PSS and PDEAEM.

a multilayer is formed from two diblock copolymers of average charge density not more than 22%. The thickness increases monotonically and it is of the same order of magnitude as for the multilayer built up from the corresponding fully charged polyelectrolytes PSS/PDEAEM.

#### 4. Discussion

The fact that a minimum charge density is required for the multilayer formation leads to the conclusion that electrostatic attraction between the polyelectrolyte and the surface dominates the process. It is assumed that charge overcompensation is a stringent condition for the adsorption of the oppositely charged polyelectrolyte in the next adsorption step. If the sign of the net surface charge does not change, the polyelectrolytes in the next deposition step will be charged identically to the surface. This would avoid adsorption. But the interdigitation of oppositely charged polyelectrolytes adsorbed in former adsorption steps will be strong enough to lead to locally opposite charges. This again could induce adsorption. But after several adsorption steps the interdigitation is not efficient enough to induce polyelectrolyte adsorption and the multilayer formation stops.

On the other hand, the adsorption takes place if the charge is compressed within a block, even at an average charge density well below the minimum polycation charge density of 70%. This means that it is not the average polymer charge density that is the decisive factor for the formation of a multilayer but the charge distribution. The results indicate that a relatively short anchor (with respect to the whole polymer) is sufficient to induce a charge reversal and to induce multilayer formation. But this block has to have a charge density higher than the minimum charge density required for charge reversal. The film thickness is quite similar to the case where the fully charged corresponding polyelectrolyte is used. On the other hand, if one of the polyelectrolytes is a statistical copolymer of charge density below this minimum charge density, the multilayer formation stops after a certain number of dipping cycles and the film thickness does not change any more.

Such a charge threshold has been also observed by other authors [8, 9]. For different polyelectrolyte pairs, Hoogeveen *et al* [10] observed that a minimum charge density of 20% was required to form stable multilayers. This means that the thresholds can be different for different systems. It is assumed that there is no absolute value for the charge threshold, but that the ratio between the charge densities of the two polyelectrolytes is important for an optimized multilayer formation.

A non-electrostatic contribution to the formation of multilayers could derive from hydrogen bonding. It is believed to be decisive for the formation of multilayers consisting of poly(aniline) and neutral polymers [11] and of films consisting of poly(acrylic acid) (a hydrogen bonding donor) and poly(4-vinylpyridine) (a hydrogen bonding acceptor) [12]. It has been shown that multilayer formation via hydrogen bond interactions requires polymers that are capable of forming very strong hydrogen bonds. This is not the case for PSS and PDADMAC. Another indication for non-electrostatic contributions to the formation process of polyelectrolyte multilayers has been given by the fact that polyelectrolytes can be adsorbed on top of a polyelectrolyte surface of equal charge, as is already known from the literature [13–15]. These results can be explained by strong interdigitations between adjacent layers which lead finally to an electrostatic driving force for the polyelectrolyte adsorption. This effect is well pronounced after drying the films which indicates that the interdigitation is enhanced by drying. The adsorption of the neutral PNMVA layer on top of the PEI/PSS layer can be explained by the interdigitation of PEI and PSS and following hydrogen bonding between PEI and PNMVA.

If the multilayer formation is electrostatically driven, why does the film thickness increase up to high ionic strengths as mentioned in the introduction? An explanation of this paradox could be that mean-field theories like the Gouy–Chapman theory are insufficient for describing the electrostatic field in front of the polyelectrolyte surface for our purposes. In addition, density fluctuations in the cloud of counterions, which make surface charges ‘visible’ for a polyelectrolyte in front of the film surface, seem also to be important.

## 5. Conclusions and outlook

The present study gives a first insight into the effect of polymer charge density and charge distribution on multilayer formation. A highly charged short anchor seems to be sufficient for polyelectrolyte adsorption and for the reversal of surface charges. But the internal structure is still unclear. This is of special interest in the case of the multilayers containing diblock copolymers. The uncharged PNIPAM block is quite large and it is concluded from adsorption experiments using pure PNIPAM that it does not adsorb at the surface. That would mean that the uncharged PNIPAM block forms a kind of mushroom or brush in front of the surface and that the adsorbing chain has to penetrate into this PNIPAM layer. Measurements on this topic are under way. To get information about the importance of the ratio between polyanions and polycations, the polyanion charge should also be changed.

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