Investigation of the Influence of Polyelectrolyte Charge Density on the Growth of Multilayer Thin Films Prepared by the Layer-by-Layer Technique

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ABSTRACT: We examine the influence of the charge density along a polyelectrolyte chain on the buildup of multilayer films formed by the sequential adsorption of alternating layers of polyanions and polycations (the layer-by-layer technique). Model random copolymers of diallyldimethylammonium chloride (DADMAC) and *N*-methyl-*N*-vinylacetamide (NMVA) having matched molecular weights and varying percentages (24−100%) of the cationic DADMAC component are alternated with polyanionic polystyrene sulfonate (PSS). Multilayer buildup is monitored by UV−vis and FTIR spectroscopies, and with a quartz crystal microbalance (QCM) and is correlated with structural information obtained using atomic force microscopy. When films are deposited from polyelectrolyte solutions containing added salt, a critical charge density limit (between 75% and 53%), below which no significant layer growth is possible, becomes apparent. Below the critical charge density, addition of the polyanion leads to almost complete removal of the previously deposited cationic copolymer and vice versa, and thus multilayers cannot grow. Above the critical charge density, the rate of film growth and the film morphology are strongly influenced by the solution structure of the adsorbing polyelectrolytes: thicker and rougher films are produced with increased salt concentration in the adsorption solutions.

Introduction

The buildup of multilayers by alternately adsorbing polyelectrolytes of opposite charge (the layer-by-layer technique) is a versatile method enabling the construction of ultrathin films with well-defined thickness, composition, and chemical functionalities.[1−5] This powerful technique has enormous potential for the fabrication of functional films for use in applications such as biosensing,[6] catalysis,[7] separations,[8−10] and optical devices,[11] and it has therefore witnessed explosive growth in the past decade. While films have been produced using a large variety of charged materials ranging from polyelectrolytes to proteins and inorganic and metallic nanoparticles, far less attention has been paid to the fundamental factors governing the structure and growth of the multilayer films.[12−15] Consequently, these issues remain less well understood.

The process of polyelectrolyte multilayer assembly is widely reported to be driven by electrostatic interactions.[5,15] In the simplest picture for polyelectrolyte multilayers, overcompensation by adsorbing polyelectrolytes leads to reversal of the surface charge, thus allowing the subsequent adsorption of oppositely charged polyelectrolytes to form the next layer. Multilayers are built up by sequential deposition in this manner. Although it is expected that the process of layer growth due to electrostatic interactions will be influenced by the charge density of the polyelectrolyte, the precise role of charge density is somewhat unclear. Several previous investigations have shown that there is a critical minimum charge density, below which no multilayer growth is possible.[16−18] However, other studies reveal that multilayer buildup with polyelectrolytes of very low charge density can also be achieved.[4,19,20] Thus, it is unclear whether a critical charge density for multilayer assembly exists in systems where the interactions are primarily electrostatic. Other reports suggest that factors other than a “critical” charge density might play a more important role in layer-by-layer assembly. Laschewsky and co-workers have suggested that, rather than a critical charge density, it is the matching of charge densities between the polyelectrolytes used to build up the film that determines layer growth.[4,20]

In systems that show a critical charge density, complicated trends have been observed for the variation in film growth with charge density.[16,17] Hoogeveen et al. found that for copolymers of charged and uncharged monomer units, the adsorbed amounts are nonmonotonic with charge density and show a maximum at intermediate values. This behavior was explained as a balance between two competing effects. With decreasing charge density more molecules adsorb at the surface to compensate the surface charge. However, when the charge density of the polyelectrolytes is too low, the attraction to the surface is weakened to such an extent that the adsorbed amounts decrease. The effect of charge density on polyelectrolyte multilayer growth has also been examined by Rubner and co-workers by employing *weak* polyelectrolytes and by using the pH of the adsorption solution to tune charge densities.[21,22] A comprehensive investigation of adsorption conditions (via pH) revealed a complicated but controllable dependence of layer thickness on pH and thus on charge density. Very thick layers were obtained when a fully charged chain was combined with a nearly fully charged chain. The trends observed with change in pH were explained by invoking different models for the adsorption behavior at different values of pH: the increase in adsorbed amounts at lower charge densities were explained using charge compensation arguments similar to Hoogeveen et al.,[16] while a thermodynamic model that accounts for the loss in entropy of the polyelectrolyte

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Table 1. List of the Polyelectrolytes with Different Charge Density, Including Their Molecular Weights and Their Notation in This Paper

charge density (%)	mol wt [g mol^{-1}]	notation
100	93 000	DDA100
75	107 000	DDA75
53	98 000	DDA53
24	92 000	DDA24

upon adsorption was used at higher charge densities.[22,23]

Recent studies have attempted to correlate adsorption behavior with the solution structure of the adsorbing polyelectrolytes.[24,25] The trends observed for film growth are similar when the charge density of the polyelectrolytes is decreased as when salt is added to the polyelectrolyte adsorption solution, since, in both cases, the stiffness of the polymer chain is reduced. Kolarik and co-workers investigated the structure of polyelectrolyte multilayers with high molecular weight (ca. 10^6 g mol^{-1}) copolymers of varying charge densities using atomic force microscopy and a quartz crystal microbalance and found increased adsorbed amounts and increasing film roughness with decreasing charge density.[24] Similarly, an increase in adsorbed amounts was observed with increased salt concentration in the adsorption solution.

Thus, while there are considerable data in the literature concerning the influence of charge density on multilayer formation, there is little consensus, and conflicting results have often been reported. Interpreting the results reported in the literature is further complicated by the different experimental systems and deposition protocols used. Thus, there is a need for detailed investigations that span a range of experimental conditions, using well-defined experimental model systems. In this work, we report investigations on the effect of polyelectrolyte charge density on multilayer film growth, using model copolymers of nearly equal molecular weight (ca. 10^5 g mol^{-1}). The copolymers used are diallyldimethylammonium chloride (DADMAC) and *N*-methyl-*N*-vinylacetamide (NMVA), with similar molecular weights and varying percentages (24−100%) of DADMAC. Steitz et al. have recently examined similar copolymer systems, but have only presented X-ray reflectivity data for *preassembled* 20-layer films; no measurements monitoring the formation of each layer were reported.[26] Here, we combine a range of techniques that probe the amounts of polyelectrolyte adsorbed with structural characterization methods to obtain details of the assembly process and to gain insight into the factors that govern polyelectrolyte self-assembly. Further, we explore multilayer formation for different salt concentrations in the adsorption solutions to obtain insight into the influence of solution structure of adsorbing polyelectrolytes on adsorbed amounts and film morphology.

Experimental Section

Materials. Poly(sodium 4-styrenesulfonate) (PSS), M_w = 70 000 gmol^{-1}, poly(ethyleneimine) (PEI), M_w = 25 000, and poly(diallyldimethylammonium chloride) (PDADMAC), M_w = 100 000−200 000, were purchased from Aldrich. Random copolymers of DADMAC and *N*-methyl-*N*-vinylacetamide (DADMAC−NMVA) with DADMAC contents (ratio of charged monomers to all monomers of the polymer) of 75% (DDA75), 53% (DDA53), and 24% (DDA24) were donated by H. Dautzenberg (Max Planck Institute of Colloids and Interfaces, Golm, Germany). The copolymers and their molecular weights are listed in Table 1. Structures of the polyelectrolytes used are shown in Figure 1. Information regarding the synthesis and characterization of these copolymers can be found elsewhere.[27,28] Sodium chloride was obtained from Merck and was used as obtained. The PSS and the DADMAC−NMVA copolymers were dialyzed against pure water. Quartz slides were obtained from Hellma Optik GmbH (Jena, Germany), the silicon wafers were purchased from Silchem Handelsgesellschaft mbH (Freiberg, Germany), and the QCM electrodes were obtained from Kyushu Dentsu (Nagasaki, Japan). The quartz slides and the silicon wafers were cleaned and hydrophilized using the RCA method (sonication in a 1:1 mixture of water and 2-propanol for 15 min), followed by heating at 70 °C for 10 min in a 5:1:1 mixture of water, H_2O_2, and 29% ammonia solution, while the QCM electrodes were cleaned by treatment with sulfuric acid/hydrogen peroxide (piranha solution: *CAUTION! Piranha solution should be handled with extreme care, and only small volumes should be prepared at any one time*.)[29] Water from a three-stage USF Purelab Plus purification system with a resistivity greater than 18 MΩ cm was used in all experiments.

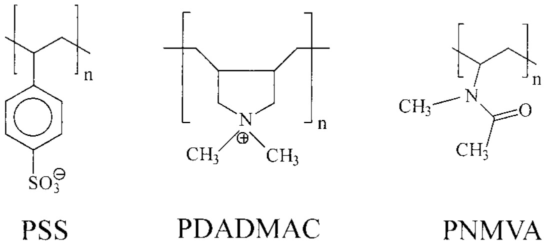

Figure 1. Chemical structures of the polyelectrolytes used. The copolymers used were composed of DADMAC and NMVA.

Preparation of Multilayer Films. For all experiments the concentration of the polymer solutions used was 1 mg mL^{-1}. Different concentrations of sodium chloride (0, 0.005, 0.05, 0.5, 1, and 2 M) were used in the adsorption solutions to obtain information about the influence of ionic strength on film growth. The salt concentration was always the same in the anionic and cationic adsorption solution. The prepared substrates (four samples at a time) were dipped at the first step for 20 min in PEI solutions. The samples were then washed by dipping three times in water (total washing time ca. 5 min), and blown dry with a stream of nitrogen or argon. The samples were then dipped in the anionic PSS solution for 20 min. The washing and drying procedure described above was repeated and the samples were then dipped in either the cationic PDADMAC or DADMAC−NMVA copolymer solutions for 20 min. This procedure was repeated to construct multilayers. Care was taken to ensure that each of the four samples with a different charge density had a separate beaker in every adsorption and washing step. UV−vis and QCM measurements were performed after each adsorption step. AFM measurements were performed on samples after the deposition of 10 layers.

UV−Vis Measurements. UV−vis spectra were taken after deposition of each layer with a HP5453 UV−vis spectrophotometer. While PDADMAC and the PDADMAC−NMVA copolymers show no absorption, PSS shows a peak at 227 nm. Data were evaluated after subtracting the spectrum of the RCA-treated quartz slide as a blank from each of the measured spectra.

QCM Measurements. A QCM device (Hewlett-Packard) was used to determine the deposited mass after each adsorption step. The resonance frequency of the QCM electrodes was ca. 9 MHz. The piezoelectric quartz crystal changes its fundamental oscillation frequency, F_o, as mass is deposited onto or depleted from the surface. According to the Sauerbrey equation, the resonant frequency shift, Δ*F*, of a QCM is proportional to the mass change, Δ*m*:[30]

$$\Delta F = -\frac{2F_0^{\,2}}{A(\mu_q\rho_q)^{1/2}}\Delta m \qquad (1)$$

where μ_q is the shear modulus of the quartz (2.947×10^{13} g m^{-1} s^{-2}), ρ_q is the density of the quartz (2.648×10^6 g m^{-3}), and A is the electrode area (1.59×10^{-5} m^2). Assuming the polyelectrolyte film density is 1.2×10^{-6} g m^{-3}, the polyelectrolyte film thickness, d, can be calculated from the following equation:[31,32]

$$\Delta d \text{ (nm)} = -0.017\Delta F \text{ (Hz)} \qquad (2)$$

AFM Measurements. AFM images were recorded with a Nanoscope IIIa multimode microscope (Digital Instruments Inc., Santa Barbara, CA). Measurements were performed in air on "dry films" using tapping mode. Silicon tips (Nanosensors, Wetzlar, Germany) with a resonance frequency of ca. 300 kHz and a spring constant of 32−41 N/m were used. Several images were recorded from different macroscopically separated areas. Measurements and processing (first-order image flattening and plane-fitting) of the AFM images were performed with Nanoscope 4.43r6 software.

FTIR Measurements. FTIR measurements were performed with a Bruker Equinox 55/S FTIR spectrometer operating in reflection mode. Glass slides coated initially with chromium and then with a 120 nm thick gold layer were used as substrates. Coating was performed with an evaporator in a vacuum chamber. The infrared reflection absorption spectroscopy (IR−RAS) spectra were taken with a modified reflection device (Harrick Co.) at an angle of 84°. Before each measurement nitrogen was streamed for 10 min through the measuring chamber to dry it.

Results

We first examine the formation of multilayers by the alternate adsorption of oppositely charged polyelectrolytes from solutions containing 0.5 M sodium chloride in both the anionic and the cationic solutions. These adsorption conditions are typical of the experimental protocol commonly followed for the formation of polyelectrolyte multilayers. Following a detailed investigation of the effect of charge density on layer growth, we then examine the effect of changing the ionic strength of the adsorption solution.

Adsorption from Polyelectrolyte Solutions Containing 0.5 M NaCl. Film growth was followed by UV−vis and QCM measurements (Figure 2). Evolution of the PSS absorption in the UV−vis signal was monitored, giving information on the adsorbed amount of PSS. The decrease in resonance frequency of the QCM provides a measure of the mass adsorbed for each deposition step. It should be noted that the QCM adsorbed mass includes residual water (even after nitrogen drying) and salt in the film. Water contents in multilayer films of up to 40% have been reported in the literature.[33−37] From the UV−vis data, it is clear that there is a difference in the manner in which films grow for polyelectrolytes with a high charge density (DDA75 and DDA100), compared with films of copolymers of lower charge density (DDA24 and DDA53) (Figure 2a). While 10-layer films from DDA100 and DDA75 show the formation of thicker multilayers ($d \approx 25-40$ nm, calculated from QCM data), 10-layer films fabricated from the lower charge density copolymers show no significant growth ($d \approx 5$ nm) (see Table 2). This indicates that there exists a critical charge density limit between 75% and 53%, below which no significant layer growth takes place. The QCM data are in good accord with the UV−vis data and provide additional confirmation of the trends observed (Figure 2b). No noticeable difference is observed between films from DDA75 and films from DDA100 up to seven layers. For higher layer numbers the DDA75 film shows increased adsorbed amounts in the UV−vis and QCM measurements, compared to the DDA100 film. This results in a very thick film after 24 layers (Figure 2a, inset). This film forms a gellike structure after 12 layers and scatters strongly when dried after 15 layers. Thus, reliable UV−vis data cannot be obtained beyond 15 layers for these films.

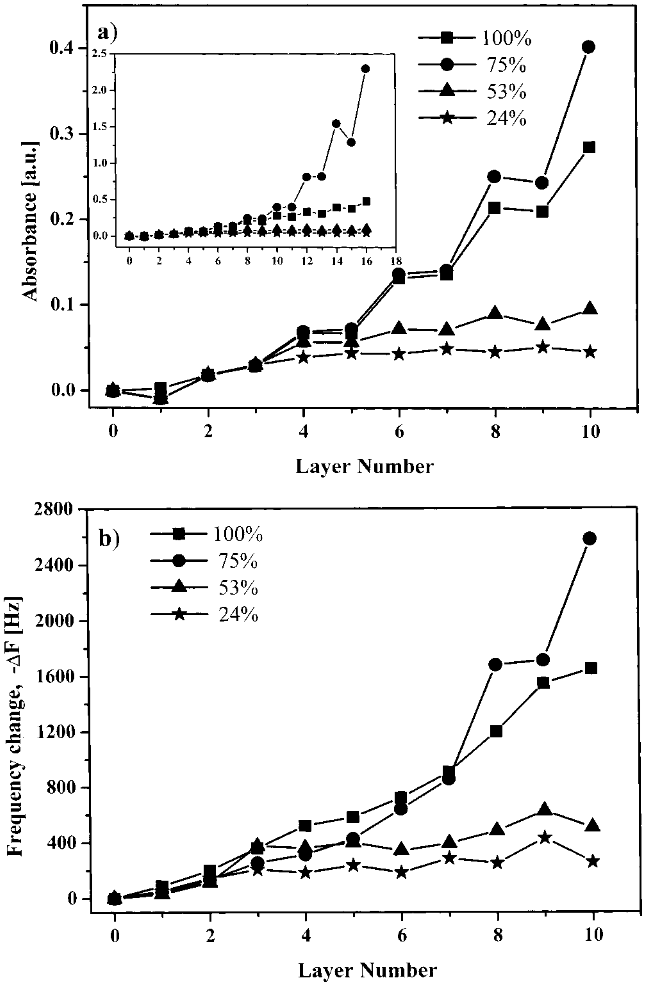

Figure 2. (a) UV−vis and (b) QCM measurements for the construction of multilayer films of PSS and DADMAC−NMVA copolymers prepared from solutions containing 0.5 M NaCl. The inset shows the UV−vis data for a larger range of layer numbers. Odd layer number: cationic polyelectrolytes. Even layer number: PSS.

Table 2. Thicknesses Calculated from QCM Data for 10-Layer PSS/DADMAC−NMVA Copolymer Films Assembled from Polyelectrolyte Solutions Containing 0.5, 1, and 2 M NaCl

	thickness [nm][a]			
salt concn (M)	DDA100	DDA75	DDA53	DDA24
0.5	25	39	8	4
1	47	32	12	3
2	83	44	8	2

[a] The error in these values is estimated as ±10%; this is arrived at from variations in the frequency values and errors in the assumed polyelectrolyte film density.

FTIR spectroscopy provides a means to simultaneously monitor the amounts of both PSS and copolymer adsorbed. Film growth was monitored by measuring the absorbance of the sulfonate group from PSS (at 1037 cm^{-1}) and the carbonyl group from the copolymers (at 1631 cm^{-1}). These measurements were used to confirm the QCM and UV−vis observations for adsorption from 0.5 M NaCl solutions, and to provide insight into the evolution of film composition with adsorption of multiple

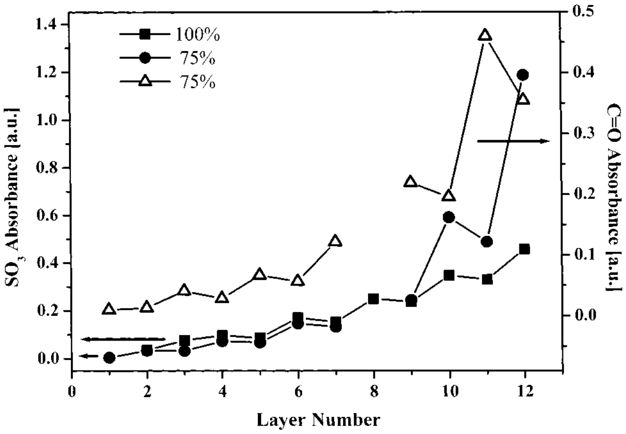

Figure 3. Formation of PSS and DADMAC–NMVA copolymer multilayers followed by FTIR spectroscopy. Odd layer number: cationic polyelectrolytes. Even layer number: PSS.

layers. We focused on multilayers comprising DDA75 copolymers and compared these with films of DDA100 since the DDA53 and DDA24 copolymers did not show regular film growth.

Figure 3 shows the absorbance of the sulfonate group of PSS and of the copolymer carbonyl group as a function of polyelectrolyte layer number. Films with DDA100 show a linear increase of the absorbance with each added bilayer. Films with DDA75 show a more complicated behavior: adsorption of polyelectrolyte leads to partial removal of the previously adsorbed layer, and the amount adsorbed per layer increases nonlinearly. The alternating increase and decrease of the absorbance for the sulfonate group indicates that adsorption of copolymer leads to partial removal of the previous PSS layer, and data for the carbonyl group indicate partial removal of copolymer upon adsorption of PSS. In the next adsorption step, more PSS adsorbs than is removed in the previous step; thus, layer growth takes place overall. A slight removal of material could also be observed from UV–vis measurements for this sample. Effects of molecular orientation within the film on the FTIR absorbance measurements using polarized radiation can be ruled out since we observe linear growth for the DDA100 film, which is in agreement with the UV–vis and QCM data.

To obtain structural information about the multilayer films composed of polyelectrolytes of different charge density, AFM measurements were performed after 10 layers were assembled from polyelectrolyte solutions containing 0.5 M NaCl. AFM images of the layers show clear differences in the surface morphology between the four samples containing polyelectrolytes of different charge densities (Figure 4). Films with DDA75 show a rougher surface and larger grain sizes compared to the DDA100 films. The two samples containing polyelectrolytes of charge densities below the critical limit (DDA24, DDA53) show a much smoother surface than the films with the high charge density polyelectrolytes.

Influence of Salt in the Adsorption Solution on Film Formation. Experiments with varying salt concentrations provide insight into the effect of solution structure of the polyelectrolyte chains on film formation. We performed experiments with concentrations of added salt (NaCl) of 0, 0.005, 0.05, 0.5, 1, and 2 M in both adsorption solutions. Initially, we examine the influence of salt concentration on the critical charge density limit by contrasting amounts adsorbed and the growth behavior for the different copolymers. We then examine details of how the multilayers are constructed at the different salt concentrations.

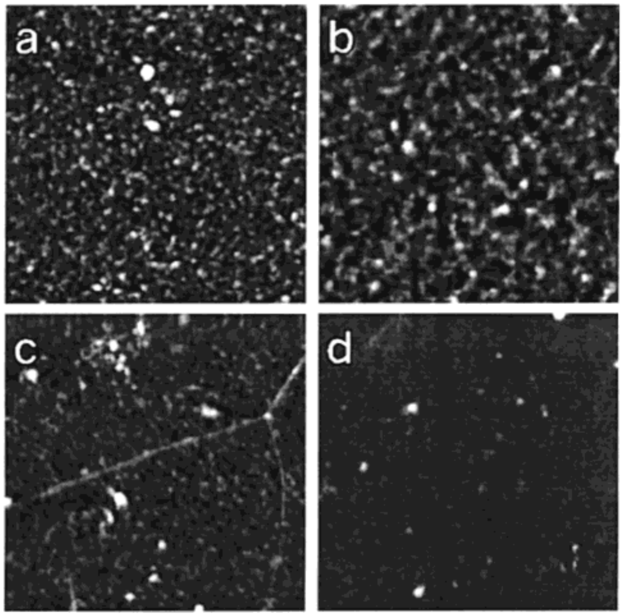

Figure 4. AFM images of 10-layer PSS/DADMAC–NMVA copolymer films prepared on Si substrates. Films use (a) DDA100, (b) DDA75, (c) DDA53, and (d) DDA24. The images are 1 × 1 μm^2. The vertical scale bar for all the images is 20 nm.

With increasing salt concentration, differences in film growth behavior between the high charge density polyelectrolytes (DDA100 and DDA75) and the low charge density copolymers (DDA53 and DDA24) become more apparent (Figure 5). While the films assembled from 0 M NaCl solutions show no clear differences in adsorbed amounts for the different charge densities, when films are assembled from 2 M NaCl solutions there is a large increase in adsorbed amount above the critical charge density. Thus, a “critical” charge density for film growth is not readily apparent when adsorbing from lower salt concentrations. In agreement with previous work,[31] layer growth proceeds linearly for the fully charged polyelectrolytes with layer number after about four layers, with the exception of films prepared from 2 M NaCl solutions. The number of layers required before linear growth is established depends on the nature of the surface, the polyelectrolyte type and the adsorption conditions.[31]

For the films from copolymers below the critical charge density limit (DDA53, DDA24), an increase in the salt concentration in the adsorption solution leads to only a very small increase in the adsorbed amounts in a 10-layer film (Figure 5). UV–vis measurements show that growth of the multilayers proceeds slowly, with most of the adsorbed PSS being removed from the surface when the film is exposed to copolymer solution. This removal of material from the surface becomes more pronounced with decreasing salt concentration in the adsorption solutions. In contrast to this, the higher charge density copolymers show very different behavior. For films with DDA75 and DDA100, an increase in salt concentration leads to a dramatic increase in the adsorbed amounts by about an order of magnitude (compared to 10-layer films from the lower charge density polyelectrolytes). Films with higher charge density polyelectrolytes also show a partial removal of PSS from

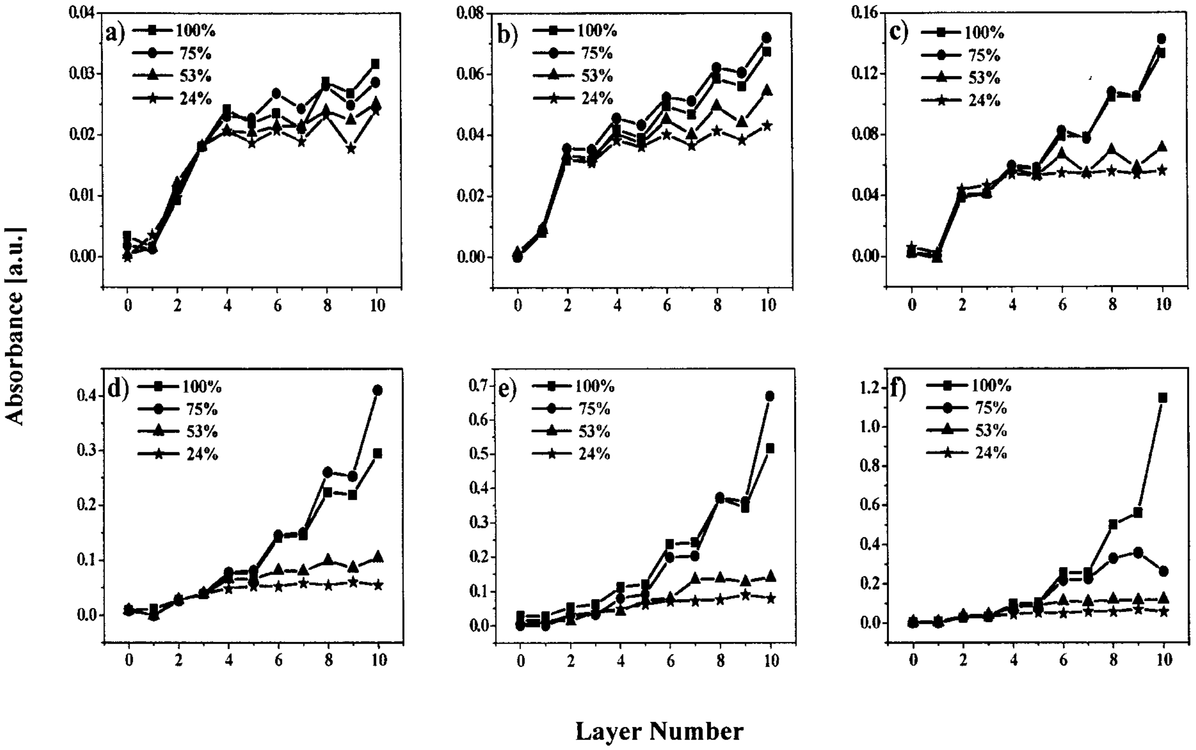

Figure 5. UV–vis data for the formation of films with PSS/DADMAC–NMVA copolymers adsorbed from (a) 0, (b) 0.005, (c) 0.05, (d) 0.5, (e) 1, and (f) 2 M NaCl in both adsorption solutions. Note that the scale for the absorbance is different for all the plots.

the surface when the film is exposed to copolymer solution. However this removal of material is much less pronounced than for the films with DDA24 and DDA53.

Contrasting films from DDA100 and DDA75, we see that for DDA100 films the adsorbed amounts after 10 layers increase continuously with salt concentration (Figure 6); this trend is in agreement with a previous report for similar polyelectrolytes.[33] In contrast, films from DDA75 show an increase in the adsorbed amounts only up to a salt concentration of between 0.5 and 1 M. Above this salt concentration, the adsorbed amount appears to saturate (UV–vis; Figure 6a). QCM data indicate that a “saturation” value is achieved for films with DDA75 at a salt concentration of about 0.5 M NaCl (Figure 6b). The DDA75 films are the only ones that show gelling—this becomes more prominent at higher salt concentrations and increases the uncertainty in the absolute values of the measurements reported. However, this does not affect the observed trends in amounts adsorbed.

AFM measurements were performed on 10-layer films assembled from polyelectrolyte solutions containing 0, 0.005, and 0.05 M NaCl (as well as 0.5 M; see earlier). The results of the measurements for the different salt concentrations are shown in Figure 7 and are summarized as follows. For the 0 M NaCl case, no significant differences in surface morphology and roughness between the multilayers prepared with polyelectrolytes of different charge density can be observed, in agreement with the UV–vis measurements, which reveal growth behavior independent of charge density. When 0.005 M NaCl is used, the surfaces for the low charge density samples (DDA24, DDA53) are marginally smoother than the DDA75 and DDA100 samples. This result also agrees with the UV–vis measurements for these samples, where differences between these two groups of samples

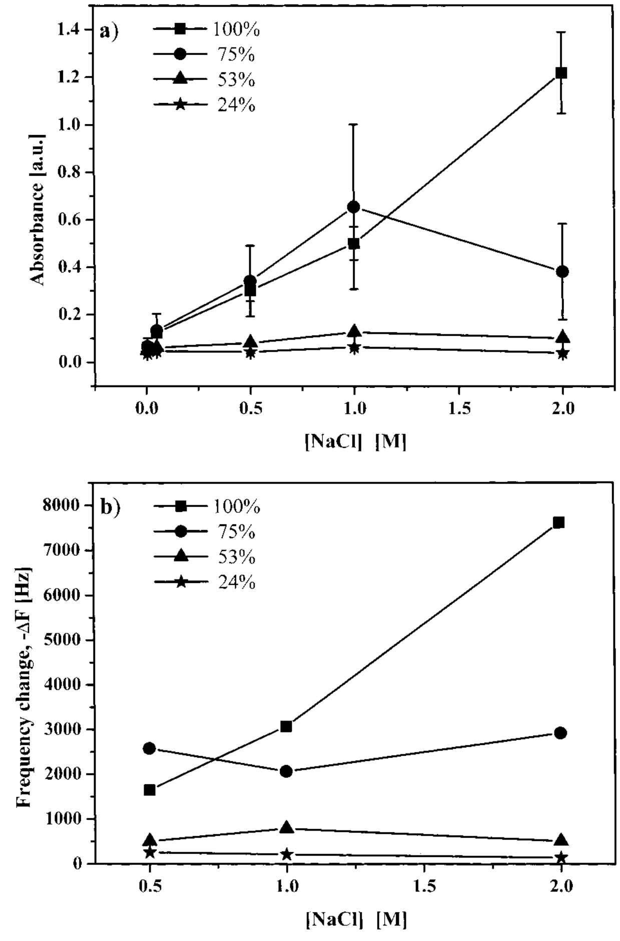

Figure 6. (a) UV–vis absorbance values and (b) QCM frequency shifts for 10-layer films prepared from copolymers of different charge density as a function of salt concentration.

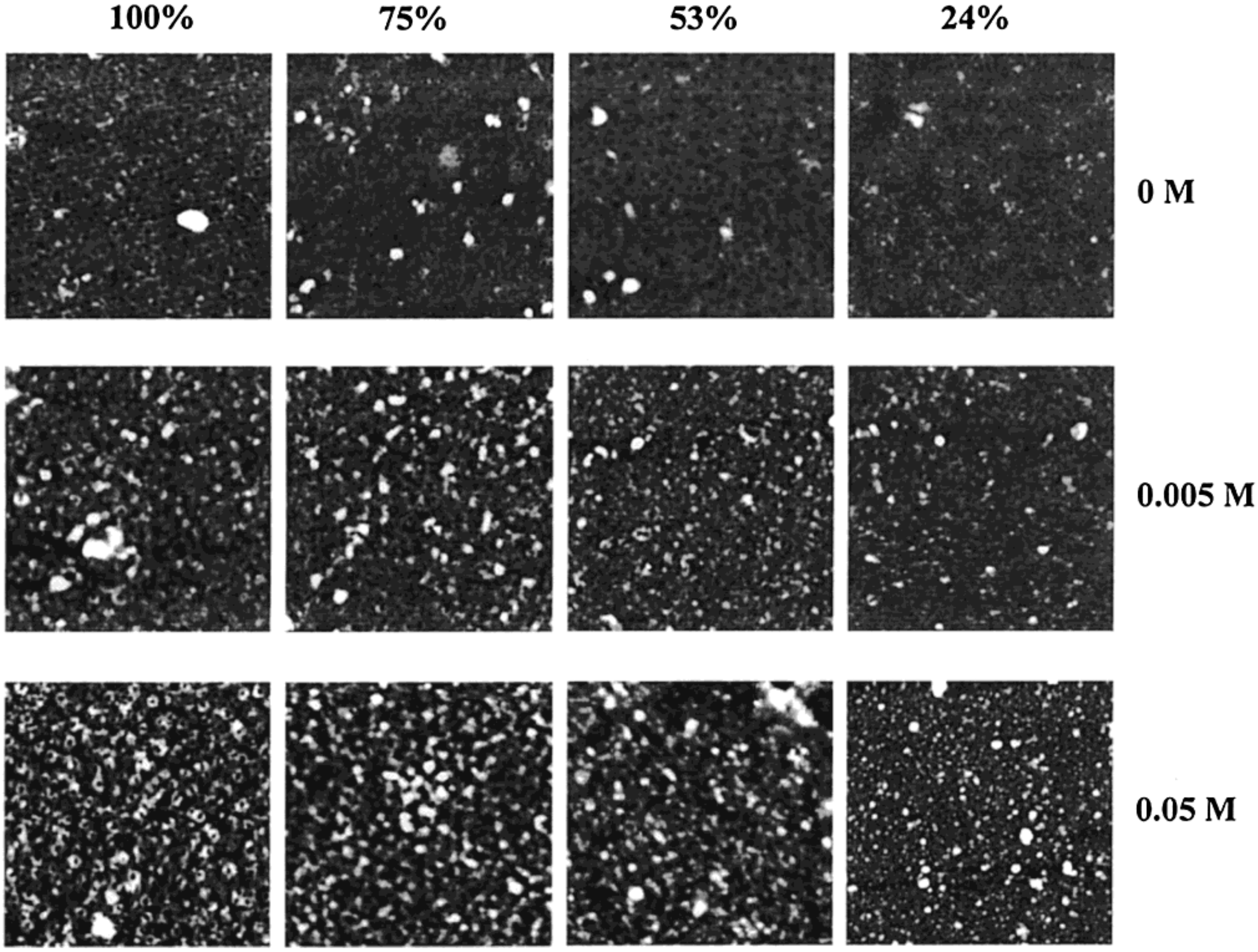

Figure 7. AFM images of 10-layer PSS/DADMAC−NMVA copolymer films prepared on Si substrates. From left to right, decreasing charge densities: 100, 75, 53, and 24%. From top to bottom, increasing salt concentration: 0, 0.005, and 0.05 M NaCl. The images are 1 × 1 μm^2. The vertical scale bar for all the images is 20 nm.

become visible (Figure 6a). For the 0.05 M NaCl system a difference in roughness between the surfaces of multilayers with copolymers above and below the critical charge density limit is observed again. The surfaces for the low charge density copolymers (below the critical charge density limit) appear smoother.

Discussion

We first focus on the critical charge density observed for multilayer formation, and propose a simple explanation for the role of charge density and contrast it with explanations in the literature. Then, we examine multilayer formation from the perspective of the solution structure of the adsorbing polyelectrolyte and discuss how film formation is influenced by the ionic strength of the adsorption solutions. The dependence of layer growth on charge density is next compared with data and mechanisms in the literature. We then discuss the formation of a gellike structure and the very thick layers observed for multilayers from DDA75. Finally, we explain how our nanoscale morphological characterization complements our other "macroscopic" measurements and provides further insight on the influence of charge density on multilayer assembly.

Critical Charge Density Limit and Influence of Salt Concentration. The results from both the UV−vis and QCM measurements for adsorption from 0.5 M salt concentration point to the existence of a critical charge density limit between 53% and 75%. The existence of a critical charge density limit has been debated extensively in the literature since polyelectrolyte multilayers have been constructed with polyelectrolytes of very low charge density[4,19,21] It is noteworthy that in all these systems, the polymers interact through further synergistic nonelectrostatic interactions (such as H-bonding,[38−40] hydrophobic,[41] and charge transfer[42]). In a forthcoming publication, we will present results on a copolymer system where nonelectrostatic interactions allow multilayer formation at charge densities of just 8%.[44] It is even possible to form multilayers with uncharged polymers using H-bonding interactions.[38−40] To further complicate the picture, it has been shown in previous work that an influence of molecular weight on multilayer growth cannot be excluded for polyelectrolytes with lower charge density.[22,25,42,43] The model system examined in this paper excludes such nonelectrostatic effects and further, excludes possible chain length effects since the copolymers have nearly equal molecular weight. Poly-NMVA is water-soluble—thus, the copolymer will also remain water-soluble even as the charge density is varied. This suggests that nonelectrostatic "hydrophobic" forces should not be significantly different for the different copolymers used and thus should not play an important role in multilayer assembly. Indeed, multilayer films cannot be formed from PSS and PNMVA.[26] The influence of some hydrophobic interaction, however, cannot be entirely ruled out.

Several explanations have been postulated in the literature to explain a critical charge density limit. We now examine these explanations and discuss our data in relation to them. A *critical* charge density for multilayer growth has been explained in terms of the charge overcompensation required for polyelectrolyte multilayer growth[16,17,25] When the charge density of the adsorbing polyelectrolytes decreases, more polyelectrolyte chains must adsorb to overcompensate and invert the surface charge to allow the adsorption of polyelectrolytes of the next layer.[16,17] When the charge density is too low, the polyelectrolyte chains that adsorb on the surface are insufficient to overcompensate the surface charge. This means that the surface charge is not reversed, and thus adsorption of the next layer is not possible. While this explanation predicts the existence of a critical charge density limit and the adsorption of increased amounts of polymer with decreasing charge density, it is not supported by our results. Our measurements suggest another mechanism for the inhibition of multilayer growth. The combination of spectroscopic techniques used in our investigations to quantify adsorption shows that weakly charged copolymers (below the critical charge density) adsorb readily on oppositely charged surfaces, but are desorbed when exposed to a PSS solution in the next “adsorption” step. UV−vis data show that PSS is removed from the surface upon copolymer adsorption. FTIR measurements show both removal of PSS upon copolymer adsorption and removal of copolymer upon PSS adsorption. This indicates that when polyelectrolyte copolymers below the critical charge density are adsorbed on oppositely charged surfaces, the individual copolymer chains are very weakly bound. In the following adsorption step, exposure to the oppositely charged, strong polyelectrolyte, PSS, results in removal of the weakly bound copolymer chains that probably form complexes with the PSS in solution (*rather* than the adsorption of the PSS required for multilayer growth). When the enthalpic gain from electrostatic interactions is small, as in the case of weakly charged materials, the formation of complexes is favored by entropic considerations: polyelectrolytes in complexes have more degrees of freedom than in a multilayer on a surface.[43] Such a model of removal of material from the surface has also been suggested by Hoogeveen et al.[16]

A recent study using similar copolymer systems as those employed in our work has concluded, based on film thickness determination using X-ray reflectivity measurements of films formed after 10 copolymer−PSS deposition cycles, that charge overcompensation is essential for multilayer formation.[26] The thicknesses measured (per bilayer) from the X-ray reflectivity study[26] are comparable to those obtained by QCM in our work. However, our multi-probe measurements of film formation after each adsorption step clearly demonstrate that the charge overcompensation arguments, as postulated, do not entirely explain the reasons for hindered film growth in this case, but rather indicate an alternative mechanism for the inhibition of multilayer formation. This underscores the importance of studying each adsorption step rather than the final film formed after several adsorption cycles, and illustrates the power of our multiple-technique measurements to shed light on the physical processes that govern multilayer film formation.

Instead of the existence of a critical charge density limit, Laschewsky and co-workers consider the matching of charge densities of the polyelectrolyte pair to be more important in determining film growth.[4,20] Their experiments show that a high concentration of ionic groups on the polyelectrolyte chain is not necessarily advantageous for good multilayer growth. For example when one of the polyelectrolytes used is rather hydrophobic, the combination with low charged polyelectrolytes allows regular growth while irregular growth takes place for the alternation with polyelectrolytes of high charge density. Dautzenberg and co-workers have examined the formation of complexes of PSS with copolymers with varying charge densities in solution[45] and explain their results by postulating a similar explanation as invoked by Laschewsky. With decreasing charge density, the distances between charges on the copolymer chains do not match those on the fully oppositely charged polyelectrolyte chain. Dautzenberg et al. found a decreasing packing density of the complexes with decreasing charge density resulting from incompatibility of charge−charge distances. These explanations suggest that the progressive mismatch between the charge−charge distances, as would apply to copolymers of decreasing charge density, could lead to weak binding of the lower charged copolymers to the surface so that they may be easily removed upon the next adsorption step. However, the existence of a critical charge density is not predicted by this theory.

We now examine the factors that govern the critical charge density. Previous work in the literature reveals that the critical charge density is not fixed, but depends on the specific architecture of the polyelectrolytes (the location of the charges—whether they are on the main chain or on pendant side chains—governs their accessibility) and on the salt concentration[46−48] of the adsorption solutions. With increasing salt concentration, the critical charge density limit shifts to higher charge density values: Hoogeveen et al. explain this shift by weakening of the electrostatic interaction between the polymer molecules, so that a higher polymer charge is needed to maintain a sufficiently strong attraction between the polyelectrolytes.[16] Such a shift of the critical charge density is not observed in our own measurements. However, such behavior might become apparent if copolymers with charge densities intermediate to DDA75 and DDA53 are examined.

The ionic strength of the polyelectrolyte solutions has a strong influence on the solution conformation of polyelectrolytes.[49] While polyelectrolytes adopt a stretched conformation in a salt-free solution due to the repulsion between charges along the chain, the screening of these electrostatic interactions due to counterions from added salt leads to a more coiled conformation.[49−51] A notable observation, viz. that the difference in growth behavior between the polyelectrolytes above and below the critical charge density becomes more pronounced with increasing salt concentration, has been brought to light by our UV−vis and AFM data. This result is initially unexpected as with increasing salt concentration the differences between the different copolymers would be reduced due to the screening of charges on the polylectrolytes. For example, Kolarik and co-workers related multilayer growth behavior to solution structure of polyelectrolytes and claimed that adsorption of polyelectrolytes of lower charge density is comparable to that of fully charged polyelectrolytes at higher salt concentration.[24] We rationalize our results by assuming that (a) below the critical charge density, the reduced charge density is insufficient to form stable multilayers (see earlier) and is not significantly affected by the addition of salt to the adsorption solution, while (b) above the critical charge density, the addition of salt changes the solution structure, making the chain more flexible by screening intrachain charge interactions, and thus facilitates the kinetics of the adsorption process leading to an increase in adsorbed amounts. This result suggests that the solution structure of the adsorbing polyelectrolyte governs the adsorption behavior: both the adsorbed amounts and (from the AFM data) the surface topography.

The extent of material removed from the films during multilayer formation was found to decrease with increasing salt concentration (Figure 5). This observation is in contrast to data reported in a previous study,[43] where a decreasing "stability" of polyelectrolyte multilayers with increasing salt concentration was found. This was rationalized by more extrinsically compensated surface charges as compared to intrinsically compensated charges (inside the multilayers). This intrinsic to extrinsic transition with increasing salt concentration leads to thicker but less "stable" layers. Extrinsic charge compensation results in more salt ions included inside the film. Since these salt ions carry a hydration shell with them, more water is included inside the film leading to swelling. Dautzenberg and co-workers found that PSS−copolymer complexes in solution swelled more with a decrease in the copolymer charge density. The increased swelling was explained by postulating that the incompatibility in charge separation along the polyelectrolytes led to a looser packing in the complex. The formation of thick gellike films for LbL multilayers using DDA75 in our work might be explained using the same hypothesis. Thus, a charge mismatch for the highly charged copolymer DDA75 does not lead to a disruption in multilayer formation but to the formation of loosely packed films.

Influence of Charge Density on Adsorbed Amounts. In addition to the occurrence of a critical charge density, the dependence of adsorbed amounts and surface topography with varying charge density was investigated. Films with copolymers above the critical charge density limit prepared from DDA75 show higher adsorbed amounts compared to films from DDA100 (starting after the seventh layer). The difference between these two samples increases further with increasing number of layers, leading to very thick layers after 16 layers are deposited. These thick layers show a gellike structure after washing and form opaque films after drying, scattering strongly in the visible region. This observation of very thick films when a fully charged chain is combined with a nearly fully charged chain has also been observed by Rubner and co-workers[22] and has been explained in a recent paper with a thermodynamic consideration of enthalpy and entropy contributions.[23] According to the theory, when the charge density is decreased, the polyelectrolyte cannot adsorb as a flat chain but must form loops and tails giving rough and thick layers. This is in agreement with our AFM measurements that show clear differences in the surface structures of films with DDA100 compared with DDA75.

In several studies, a continuous increase of the polyelectrolyte adsorbed amount with decreasing charge density was found.[24,25] Other studies showed a maximum in the adsorbed amount was observed at intermediate charge densities.[16,17,22] Our data show an increase in adsorbed amount as the charge density is decreased from DDA100 to DDA75. However, our data are limited to just these two copolymers, and we cannot exclude an intermediate maximum in adsorbed amount as the charge density is increased above the critical limit for multilayer formation.

Structural Characterization (AFM). Our AFM results accord well with the UV−vis and QCM data. The differences observed between multilayers with copolymers below and above the critical charge density limit are manifested in the AFM as differences in the surface morphology of the film: films below the critical charge density are very smooth while films above this limit are significantly rougher. The difference becomes more pronounced with increasing salt concentration and again, the AFM roughness is in accordance with the UV−vis and QCM results. For 0 M NaCl in the adsorption solutions no differences can be observed for the different charge densities, while this difference is most pronounced for 0.5 M NaCl. The AFM measurements suggest that below the critical charge density no significant layer growth takes place. Further, as we go from DDA100 to DDA75, the films are more loosely packed as discussed in the previous section. Accordingly, AFM reveals that the surface gets rougher. This result is also in agreement with literature data.[24]

Conclusion

In this study, the influence of the charge density of a polyelectrolyte chain on the formation of multilayers has been investigated. Model random copolymers of varying charge density but similar molecular weight have been adsorbed in alternation with a fully charged anionic polyelectrolyte. UV−vis, QCM, and AFM indicate the existence of a critical charge density limit between 75% and 53%, below which no significant layer growth is possible. While there is considerable debate in the literature about the existence of a critical charge density, and several mechanisms have been proposed for it, our data unambiguously show that the removal of the previously deposited (lowly charged) polyelectrolyte upon adsorption of the next layer is responsible for the critical charge density limit observed in our system. To obtain information about the influence of solution structure of the adsorbing polyelectrolytes on adsorbed amounts and surface topography, experiments with different salt concentrations in the adsorption solutions were performed. It was found that with increasing salt concentration the difference in growth behavior between polyelectrolytes above and below the critical charge density limit becomes more pronounced. Above the critical charge density limit, thicker and rougher films are produced with increasing salt concentration in the adsorption solutions. However, film thickness and roughness are not significantly influenced by salt concentration below the critical charge density limit.

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