Growth of Multilayer Films of Fixed and Variable Charge Density Polyelectrolytes: Effect of Mutual Charge and Secondary Interactions

Bjoern Schoeler,[†] **Evgeni Poptoshev,**[†] **and Frank Caruso***[,‡]

Max Planck Institute of Colloids and Interfaces, D-14424 Potsdam, Germany, and Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia

Received January 6, 2003; Revised Manuscript Received March 26, 2003

ABSTRACT: We report on the effect of mutual polyelectrolyte charge and secondary interactions on the formation of polyelectrolyte multilayer films of a lowly charged copolymer of acrylamide and [3-(2-methylpropionamido)propyl]trimethylammonium chloride, AM-MAPTAC 10 (10 mol % of cationic monomers), and poly(acrylic acid) (PAA). These multilayer films were constructed on planar substrates by the sequential adsorption of AM-MAPTAC 10 and PAA at different pH conditions. Surface plasmon resonance spectroscopy (SPRS), quartz crystal microbalance (QCM), and atomic force microscopy (AFM) were employed to follow the film formation process. While AM-MAPTAC 10 is permanently charged, the ionization of PAA is adjusted by changing the pH of the adsorption solutions. In contrast with previous studies, it is shown that multilayer formation with one polyelectrolyte with a charge density of 10 mol % is possible. However, the multilayer growth follows a different pattern depending on the relative charge density of PAA. At low pH, where PAA is only lowly ionized, the films show an exponential-like growth, with a gradual increase of the thickness and adsorbed mass per layer with increasing layer number. At neutral to alkaline pH, where PAA approaches full ionization, multilayer growth proceeds via a series of adsorption−desorption steps, with immersion in PAA solutions leading to partial removal of the underlying AM-MAPTAC 10 layer. The obtained results are discussed in terms of an interplay between electrostatic and secondary interactions within the films and matching of the charge density of the polyelectrolytes employed to construct the films.

Introduction

The layer-by-layer (LbL) technique, which entails the alternate adsorption of oppositely charged species onto solid supports, provides a versatile means to construct ultrathin films of well-defined thickness, composition, and chemical functionality.[1−6] Electrostatic interactions are widely reported to be the main driving force for the multilayer formation process between two oppositely charged polyelectrolytes.[4,7] Charge overcompensation by adsorbing polyelectrolytes, which leads to a reversal of the net surface charge, is considered to be a prerequisite for polyelectrolyte multilayer formation, as it allows the subsequent adsorption of oppositely charged polyelectrolytes through electrostatic association.[8] Thus, it is apparent that the process of multilayer growth will be heavily influenced by the charge density of the polyelectrolytes used to assemble LbL multilayered thin films. The intercharge distance along the polymer backbone determines to a large extent not only the polyelectrolyte conformation in solution but also its adsorbed layer structure,[9] the degree of charge reversal upon adsorption to an oppositely charged surface,[10] and ultimately the structure of the resulting multilayer films.

In several previous investigations, the existence of a polyelectrolyte critical minimum charge density was observed, below which no multilayer growth is possible.[8,11−13] In these studies, copolymers composed of charged and uncharged monomer units were sequentially adsorbed with a highly charged polyelectrolyte. For the poly(styrenesulfonate) (PSS)/diallyldimethylammonium chloride−*N*-methyl-*N*-vinylacetamide copolymer (DADMAC−NMVA) system, the critical charge density necessary for multilayer formation was determined to be between 53 and 75 mol % for the DADMAC−NMVA copolymer.[8,12] However, the present study shows multilayer formation with lowly charged polyelectrolytes (charge density of 10 mol %), and even in the case where one of the polyelectrolytes is uncharged under the conditions of film preparation, multilayer formation is possible. This suggests that in the present case formation of the multilayers is not solely governed by electrostatic interactions. Numerous studies have shown that secondary (nonelectrostatic) interactions, such as hydrogen-bonding and hydrophobic interactions, play a significant role in the formation of polyelectrolyte multilayers.[4,14−18] On the other hand, Laschewsky and co-workers have reported that, rather than a critical minimum charge density, the matching of charge densities between the polyelectrolytes used is important in determining multilayer growth.[19,20] It has been shown that regular and stable layer growth can be achieved when two lowly charged polyelectrolytes are combined, while the alternate adsorption of a lowly charged and a highly charged polyelectrolyte leads to irregular or no layer growth. These studies[19,20] suggested that stable growth could be achieved when the intercharge distances of both polyions are matched.

For polyelectrolytes with pH ionizable groups, the magnitude of electrostatic (and secondary interactions) in polyelectrolyte multilayer films can be tuned through variation of the polyelectrolyte charge densities by altering the solution pH. To this end, Rubner and co-workers investigated the multilayer formation of two weak polyelectrolytes, poly(acrylic acid) (PAA) and poly(allylamine) (PAH), at various pH conditions.[21,22] It was shown that control over the layer thickness, composition

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[†] Max Planck Institute of Colloids and Interfaces.

[‡] The University of Melbourne.

* To whom correspondence should be addressed: Fax +61 3 8344 4153; e-mail fcaruso@unimelb.edu.au.

10.1021/ma034018g CCC: $25.00 © 2003 American Chemical Society
Published on Web 06/20/2003

of the layers, degree of layer interpenetration, and surface wettability is possible for the PAA/PAH system by adjusting the pH of the adsorption solutions. It has also been reported that nanoporous films can be obtained from multilayers composed of PAA/PAH by pH-induced[23] or salt-induced[24] structural changes of preformed PAA/PAH multilayers.

In this work, we examine the transition from predominantly electrostatically formed multilayer films to those prepared mainly as a result of secondary interactions. By utilizing one low, but permanently charged, copolymer composed of positively charged [3-(2-methylpropionamido)propyl]trimethylammonium chloride (MAPTAC) and acrylamide (AM) with a MAPTAC content of 10 mol % (AM-MAPTAC 10) and the weak polyacid, PAA, we show that it is possible to adjust the ratio between electrostatic and secondary interactions simply by varying the degree of dissociation of PAA, which is achieved by adjusting the pH of the adsorption solutions. Acrylamide containing polymers are expected to form multilayers with polycarboxylic acids via hydrogen bonding.[25] Thus, by varying the degree of protonation of PAA, the strength of the secondary interactions can also be regulated. In the two limiting cases, the interactions are expected to be mainly electrostatic (at high pH where PAA is fully charged) and, on the other hand, predominantly based on secondary interactions (at low pH where PAA is uncharged). Variation of the pH of the adsorption solutions also allows qualitative investigation of the degree of charge matching between the polyelectrolytes used to form the layers.

The current study is different to previous investigations that involve the use of PAA in preparing multilayer films: in the current work, we use a partner polyelectrolyte species that is permanently charged with a low linear charge density (as opposed to a weak polyelectrolyte);[21-24,26] thus, the degree of dissociation of AM-MAPTAC 10 in the films will not be affected by the changes in the adsorption solution pH. This should influence not only the film formation behavior but also the final film structure (porosity, thickness, etc.), giving rise to multilayer films with different properties.

Experimental Section

Materials. Poly(acrylic acid) (PAA) with a molecular weight (M_w) of 450 000 g mol^{-1} was obtained from Polysciences. To determine the pK_a value of the PAA, 0.5 mg mL^{-1} solutions of PAA in 0.1 M NaCl were titrated with 0.01 M NaOH. A pK_a value of 5.4 was obtained. Poly(diallyldimethylammonium chloride) (PDADMAC), M_w = 100 000−200 000 g mol^{-1}, and mercaptoundecanoic acid (MUA) were purchased from Aldrich, and sodium chloride was from Merck. The random copolymer of positively charged [3-(2-methylpropionamido)propyl]trimethylammonium chloride (MAPTAC) and acrylamide (AM) with a MAPTAC content of 10 mol % (AM-MAPTAC 10), M_w = 1 000 000 g mol^{-1}, was kindly donated by Per Claesson (Royal Institute of Technology, Stockholm, Sweden). The structures of the monomer units of the polyelectrolytes used are shown in Figure 1. All polyelectrolytes were used as 0.5 mg mL^{-1} aqueous solutions in 0.1 M NaCl. All chemicals and polyelectrolytes were used as supplied. Microscope glass slides were obtained from Hellma Optik GmbH (Jena, Germany), oxidized silicon wafers were purchased from Silchem Handelsgesellschaft GmbH (Freiberg, Germany), and QCM electrodes were from Kyushu Dentsu (Nagasaki, Japan). Water from a three-stage USF Purelab Plus purification system (Millipore) with a resistivity >18 MΩ cm was used in all the experiments.

Substrate Preparation. Glass slides and silicon substrates were sonicated for 15 min in a water/2-propanol (1:1) mixture, followed by cleaning according to the RCA protocol (heating at 70 °C for 10 min in a 5:1:1 mixture of water, H_2O_2, and 29% ammonia solution). QCM electrodes were cleaned by treatment with a sulfuric acid/hydrogen peroxide (3:1) mixture (piranha solution) (*CAUTION: Piranha solution should be handled with extreme care, and only small volumes should be prepared at any one time.*) SPRS substrates were prepared by metal vapor deposition of Cr (1.5 nm) and Au (45 nm) on glass microscope slides. An Edwards Auto 306 evaporation unit operated at 1.8×10^{-6} Pa and a deposition rate of 10 nm min^{-1} was used for metal deposition. A monolayer of MUA was first assembled on the QCM electrodes and gold-coated glass slides in order to obtain a uniformly, negatively charged surface. This was achieved by dipping the substrates for 10 h in a 10^{-3} M solution of MUA in dried 2-propanol, followed by several rinsings with 2-propanol, ethanol, and water. Silicon wafers were directly used after RCA treatment for multilayer preparation.

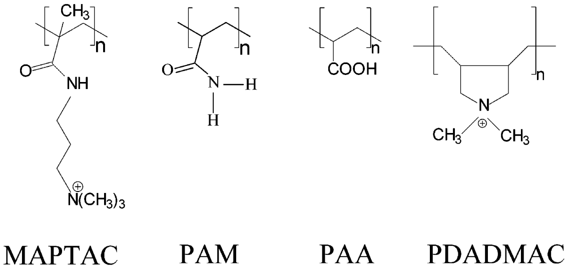

Figure 1. Chemical structures of the polyelectrolytes used.

Preparation of Multilayer Films. Polyelectrolyte multilayer films were prepared by dipping the substrates in 0.5 mg mL^{-1} polyelectrolyte solutions containing 0.1 M NaCl for 20 min, followed by rinsing three times in water, and drying in a gentle stream of nitrogen. The pH of both adsorption and rinsing solutions was adjusted to ±0.03 units by adding HCl or NaOH. The adsorption of the first AM-MAPTAC 10 layer was always performed from solutions with pH = 6.0 to ensure a sufficient and reproducible charge density of the underlying MUA layer.[27] QCM and SPRS measurements were performed in ambient air after each adsorption step to follow film formation. AFM images were collected on samples after the deposition of 6, 7, 8, 9, and 10 layers.

QCM Measurements. An in-house built QCM device with a frequency counter from Hewlett-Packard was used to determine the deposited mass after each adsorption step. QCM electrodes with a resonance frequency of ca. 9 MHz were used. Details of the method can be found in a previous publication.[12] According to the Sauerbrey equation,[28] the following direct relationship exists between frequency and mass change for the quartz resonators used in this study:

$$\Delta F\ (\mathrm{Hz}) = -1.15\Delta m\ (\mathrm{ng}) \qquad (1)$$

AFM Imaging. To examine the surface morphology of the polyelectrolyte multilayer films, AFM images were recorded with a Nanoscope IIIa multimode microscope (Digital Instruments Inc., Santa Barbara, CA). Measurements were performed in Tapping Mode using silicon tips (Nanosensors, Wetzlar) with a resonance frequency of ca. 300 kHz and a spring constant of 32−41 N m^{-1}. Several images were recorded from different macroscopically separated areas of the air-dried films.

Surface Plasmon Resonance Spectroscopy (SPRS). A commercially available plasmon resonance spectrometer (Multiscope, Optrel) was used. Details concerning the SPRS technique and experimental setup can be found elsewhere.[29,30] The total dielectric film thickness was obtained by fitting Fresnel theory to the resonance spectra. At least three SPRS curves were recorded for each sample from different areas of the surface. This method does not allow simultaneous determination of both the thickness and refractive index of the dielectric films studied here. Only film thickness was used as a fitting parameter, assuming a constant refractive index of

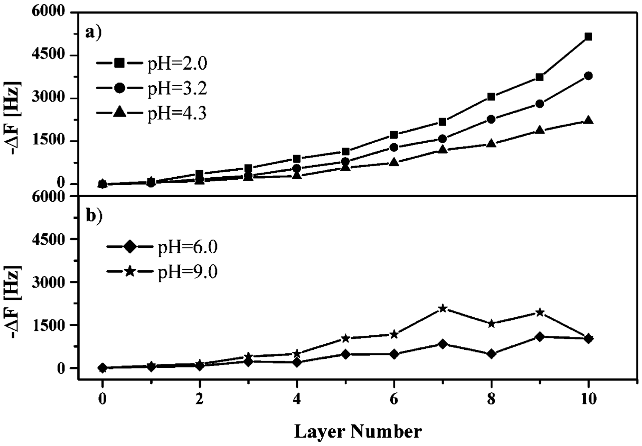

Figure 2. QCM frequency shift vs layer number for PAA/AM-MAPTAC 10 multilayers constructed at different pH: (a) pH = 2.0, pH = 3.2, pH = 4.3; (b) pH = 6.0, pH = 9.0. Odd layer number: AM-MAPTAC 10. Even layer number: PAA.

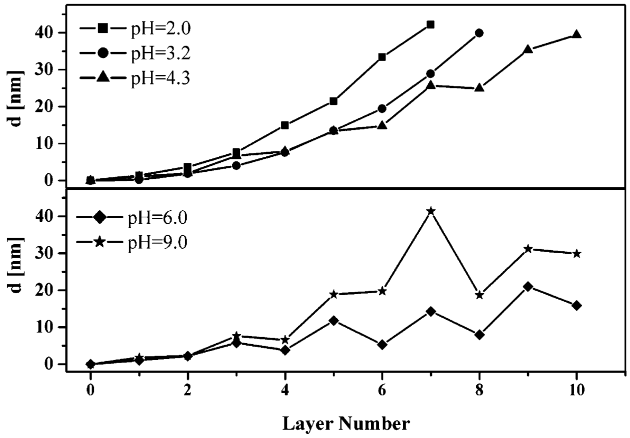

Figure 3. SPRS optical thickness vs layer number for PAA/AM-MAPTAC 10 multilayers constructed at different pH: (a) pH = 2.0, pH = 3.2, pH = 4.3; (b) pH = 6.0, pH = 9.0. Odd layer number: AM-MAPTAC 10. Even layer number: PAA.

1.47 for all films.[31,32] However, SPRS is fairly insensitive to small changes in the refractive index of the adsorbed films, especially for thicker films:[31]an uncertainty of no more than 5−7% in the determined optical thickness is estimated due to refractive index variations of ±0.05.

Titration of PAA. To determine the pK_a value of PAA and thus to obtain the degree of dissociation of PAA as a function of pH, PAA was titrated under conditions identical to the adsorption conditions used for its deposition (0.5 mg mL^{-1} PAA; 0.1 M NaCl). The pK_a value was determined from the titration curve from the point, where half of the amount of the base necessary for reaching the equivalence point was added. The pK_a value of 5.4 obtained for our sample differs from that reported for PAA/PAH multilayers (pK_a = 4.5).[21,22] However, previous work on the titration of polyelectrolytes in solution showed that the pK_a value depends on factors such as polyelectrolyte concentration, molecular weight, and ionic strength. Our value falls within the range 4.3−6 for the pK_a of PAA reported in the literature.[33] It should be pointed out that the actual pK_a of PAA would be different in solution and in the film. Schlenoff et al. showed that the pK_a value of a weak polyacid within a multilayer can be decreased by 1 or 1.5 units compared to the pK_a in solution.[34] As this decrease depends on several factors such as strength of the ion pair formation between the polycation and polyanion, chemical composition of the polyelectrolytes, and ionic strength of the adsorption solution, calculation of the apparent pK_a of PAA within or close to the multilayer from the value in solution is difficult. Additionally, the local pH within the multilayer film might be different from the solution pH, leading to a different degree of ionization compared to that in solution. For these reasons, an investigation of the influence of charge matching on polyelectrolyte multilayer formation using weak polyelectrolytes is performed qualitatively.

Results

Figures 2 and 3 show the buildup of AM-MAPTAC 10/PAA multilayers at different pH followed by QCM and SPRS, respectively. The overall mass loading, expressed as a change in QCM resonance frequency (Figure 2), and optical film thickness (Figure 3), are shown as a function of the number of deposited polyelectrolyte layers. To improve readability, measurements at low and high pH are plotted separately. It can be easily seen that a change of pH has a dramatic effect on the multilayer formation behavior. At pH below 4.3, where PAA is lowly charged, rather thick films are formed. Furthermore, as indicated by both the SPRS (thickness) and QCM (mass) measurements, the amount of polyelectrolyte deposited in each adsorption step gradually increases with increasing layer number. Thus, the multilayer growth follows an exponential-like pattern rather than the usually observed linear dependence of thickness on the number of deposited layers.[3] This is especially well pronounced after about four layers have been assembled. The upper two curves of Figures 2a and 3a (pH = 2.0 and pH = 3.2) become progressively steeper. Since the total film thickness also increases considerably, reliable SPR data could not be obtained for more than 6 or 7 layers at pH = 2.0 and pH = 3.2, respectively. However, QCM data indicate that the exponential-like growth continues until at least 10 layers have been deposited. Deposition from solutions of pH = 4.3 (lower curves of Figures 2a and 3a) yields overall thinner films and lower mass loadings. On average, the mass and thickness increments for films prepared from solutions of pH ≥ 4.3 are larger for the AM-MAPTAC 10 adsorption step.

Figures 2b and 3b show the growth of AM-MAPTAC 10/PAA films at pH = 6.0 and pH = 9.0, i.e., where PAA is highly ionized. Both QCM and SPR data show irregular film growth. The mass deposited and film thickness both increase upon AM-MAPTAC 10 adsorption. However, after the first few layers, typically a decrease of the total mass and thickness is observed when PAA is adsorbed as an outermost layer. Despite this adsorption−desorption trend the overall film thickness increases with layer number. This adsorption−desorption behavior was further examined by employing PDADMAC (homopolymer, 100% charged) as a polycation in alternation with PAA. In this case, the multilayer assembly was conducted at pH = 2.0 in order to induce charge mismatch (essentially uncharged PAA vs fully charged PDADMAC). The QCM results are presented in Figure 4. Similar to the behavior observed at pH = 6.0 with AM-MAPTAC 10 and PAA, irregular film growth was found; however, an increase in mass loading occurred upon PAA adsorption, and desorption was observed when PDADMAC was sequentially adsorbed.

The stability of AM-MAPTAC 10/PAA multilayer films in solutions of different acidity was also examined by using a QCM (Figure 5). Two QCM crystals coated with 10 polyelectrolyte layers (assembled at pH = 3.2) were immersed in water at pH = 3.2 (filled squares) and pH = 6.5 (filled circles). Periodically, the crystals were withdrawn and dried, and their resonance frequency was recorded. The *x*-axis thus represents the total

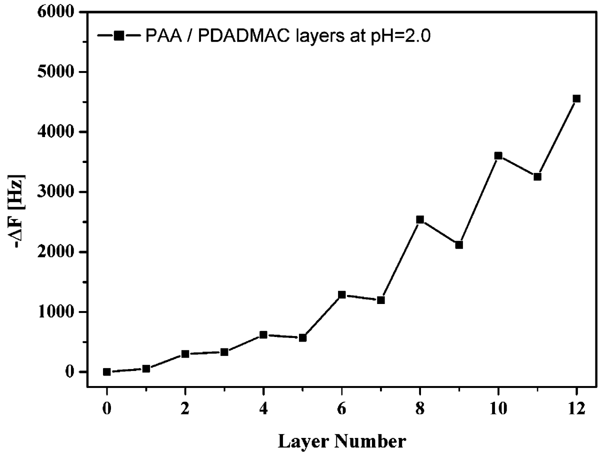

Figure 4. QCM frequency shift vs layer number for PAA/PDADMAC multilayers prepared at pH = 2.0. Odd layer number: PDADMAC. Even layer number: PAA.

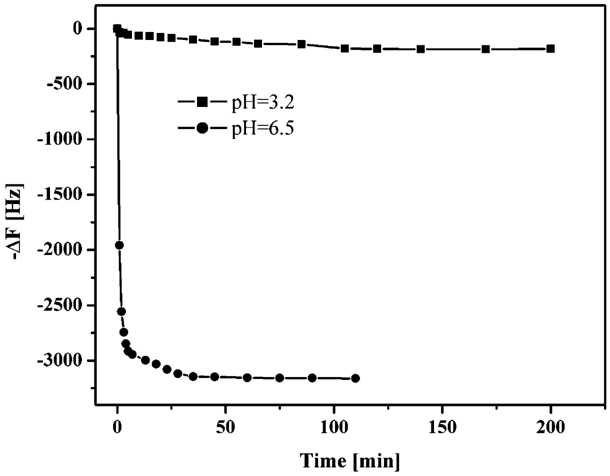

Figure 5. QCM frequency shift vs total immersion time for PAA/AM-MAPTAC 10 multilayers (10 layers) constructed at pH = 3.2. The different symbols represent incubation of the films at different pH.

immersion time. The overall frequency change of these films recorded for their formation was about 3000 Hz, corresponding to a film mass of $\sim$2600 ng/area. Exposure to water at pH = 3.2 leads to a small loss of material from the electrode surface. The increase in frequency (about 200 Hz) of the QCM after 200 min, indicating desorption, accounts for only about 7% of the total mass of the film. Experiments conducted at pH = 6.5 yield a strikingly different result. Rapid deconstruction of the film occurs with virtually the entire film being desorbed within approximately 50 min.

Figure 6 shows AFM images recorded during the buildup of AM-MAPTAC 10/PAA multilayers at pH = 6.0. These images reveal the different morphology of the surfaces bearing AM-MAPTAC 10 or PAA as an outermost layer. When PAA is the outermost layer (Figure 6a,c), smooth and homogeneous films are obtained. In contrast, films with a topmost AM-MAPTAC 10 layer (Figure 6b,d) exhibit much larger grain sizes and height variations. The results of root-mean-square (rms) roughness analyses of these images recorded after 6, 7, 8, 9, and 10 layers are presented in Figure 7. For comparison, the optical film thickness data from Figure 3b are also replotted. It can be seen that the oscillations in the film thickness data are well correlated with the rms roughness oscillations; i.e., during the step at which material is removed from the film (deposition of PAA), the rms roughness does not exceed 0.3 nm, whereas the sharp increase of film thickness upon AM-MAPTAC 10 adsorption is accompanied by a large increase in the rms roughness.

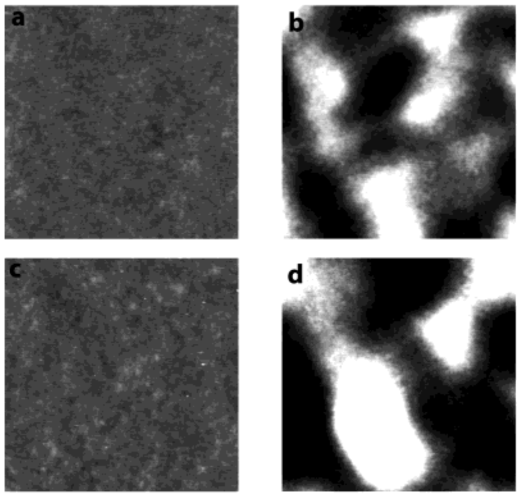

Figure 6. AFM images recorded after deposition of a different number of PAA/AM-MAPTAC 10 layers at pH = 6.0: (a) 6 layers; (b) 7 layers; (c) 8 layers; (d) 9 layers. The images are 1 × 1 μm^2. The vertical scale bar for all the images is 8 nm.

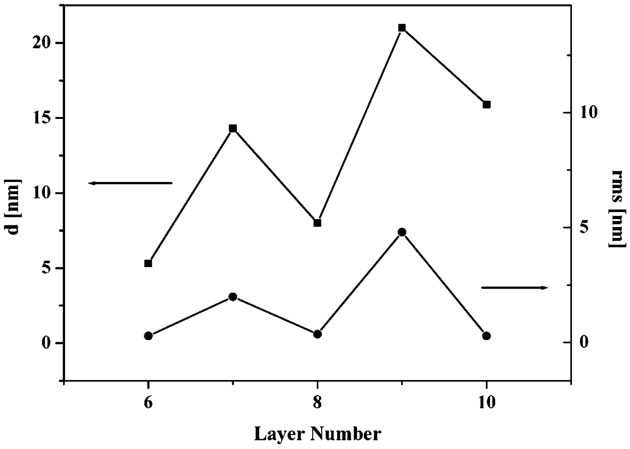

Figure 7. AFM root-mean-square roughness vs layer number for PAA/AM-MAPTAC 10 multilayers constructed at pH = 6.0. The SPRS optical thickness data is also shown. Odd layer number: AM-MAPTAC 10. Even layer number: PAA.

A similar investigation of the surface morphology was performed for films constructed at pH = 2.0. The dependence of rms roughness and peak-to-valley distance on the number of deposited layers obtained from 1 μm^2 scans is shown in Figure 8. Both parameters increase with increasing layer number. Compared to values reported for multilayers composed of highly charged polyelectrolytes,[35] the rms roughness of these films is 2−3 times higher, and the films show a more significant increase in the rms roughness with increasing the number of deposited layers.

Discussion

From the set of results presented in the previous section it becomes apparent that the charge density of PAA plays a key role for the growth behavior and stability of the multilayers. At constant ionic strength, variation of the charge density along the polymer backbone results in a change of the strength of *intramo-*

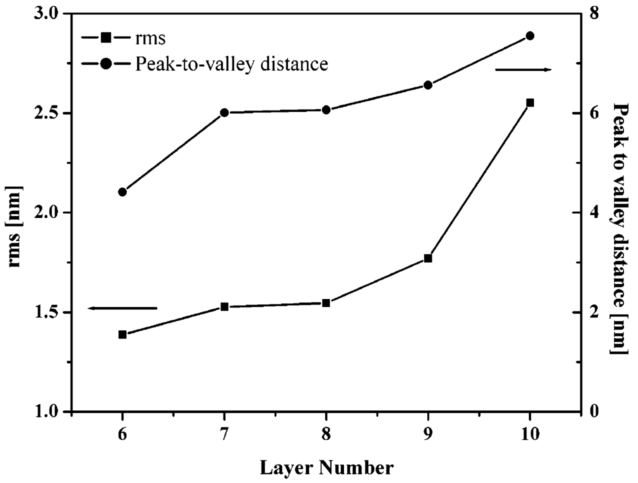

Figure 8. Peak-to-valley distance and AFM root-mean-square roughness vs layer number for PAA/AM-MAPTAC 10 multilayers constructed at pH = 2.0. Odd layer number: AM-MAPTAC 10. Even layer number: PAA.

Table 1. Degree of Dissociation and Charge Distance between PAA Charged Groups *in Solution* as a Function of pH, as Determined by Titration of PAA in 0.1 M NaCl Solution

pH	degree of dissociation in solution [α][a]	intercharge distance for PAA in solution [nm][b]
9.0	0.99	0.25
6.0	0.80	0.31
4.3	0.07	3.6
3.2	0.01	40.4
2.0	≈ 0	

[a] The degree of dissociation was calculated using the following relation between pH and α:[33] $\text{pH} = \text{p}K_a + \log[\alpha/(1 - \alpha)]$. [b] The intercharge distances were calculated assuming a fully stretched chain, a uniform distribution of the charges along the chain, and a distance between the carboxyl groups of PAA of 0.25 nm.

lecular and *intermolecular* electrostatic interactions. The intramolecular interactions affect the polyelectrolyte conformation in solution as well as the adsorbed amount and layer structure.[9,36,37] Decreasing the charge density leads to a more compact, coiled conformation.[37] The intermolecular interactions are related to a variety of association and complexation phenomena in bulk solution and at interfaces.[38] In our case, complexation within the polyelectrolyte multilayer film is of particular importance. It is instructive to discuss the behavior of the AM-MAPTAC 10/PAA system on the basis of the charge density of PAA and its relation to the charge of the oppositely charged polyelectrolyte used to build the films.

PAA at Low Charge Densities. At pH = 2.0–3.2, PAA is virtually uncharged or has a very low charge density (see Table 1). Thus, electrostatic attraction between PAA and the lowly charged AM-MAPTAC 10 cannot be solely responsible for the observed growth of the multilayers. It can therefore be inferred that secondary interactions are the main driving force for the polyelectrolyte association, in this case with hydrogen bonding suggested as the dominant attraction. It is known from previous work that the protonated carboxyl group of PAA and the amide group of poly(acrylamide) (uncharged component of AM-MAPTAC 10) interact strongly by hydrogen bonding, and thus the two chains form complexes in bulk solution.[25] In several earlier reports on the subject,[8,11–13] it has been found that multilayer growth cannot be sustained below a certain critical charge density. This also points out the importance of secondary interactions in these systems. It therefore appears that the presence of hydrogen bonds within the film is essential for the formation of multilayers between lowly charged polymers.

Another point that deserves closer attention is the growth pattern of the films. Both at pH = 2.0 and pH = 3.2, the multilayers follow an exponential-like growth. Similar behavior has been reported for several systems[12,39] constructed from lowly charged polyelectrolytes. It is usually attributed to a gradual increase of surface roughness with the number of deposited layers, which in turn increases the surface area available for adsorption.[40] An alternative explanation has been proposed by Lavalle et al.,[39] who did not observe a roughness increase for films with exponential growth behavior. In that case, the superlinear growth was attributed to polyelectrolyte diffusion in and out of the film core during adsorption. The results in Figure 8, however, seem to support the surface roughness mechanism; i.e., in our case, the surface roughness increases with the number of deposited layers. Furthermore, the diffusion model of Lavalle et al. is based on electrostatic complexation between the polyelectrolytes, while in our case at pH = 2.0 we deal with almost purely nonelectrostatic interactions.

Results from the stability experiments (Figure 5) are also in accord with the proposed dominance of hydrogen bonding in the AM-MAPTAC 10/PAAfilms constructed at low pH. At pH = 3.2, where high stability is observed, the majority of PAA monomers are protonated and thus available to form hydrogen bonds.

The low charge density also ensures the high flexibility necessary for PAA to maximize its contact with the AM monomers. If the pH is increased to around 6, about 80% of the ionizable groups of PAA in solution are deprotonated. Although the degree of charge within the films is expected to be somewhat different,[18] significant charging is expected to occur upon increasing the pH leading to a decrease of the number of hydrogen bonds within the film, since only protonated groups can take part in hydrogen bonding. Parallel to this, upon PAA ionization, the chain expands due to electrostatic intramolecular repulsions, and intermolecular repulsions are also generated. This disrupts the internal film structure and leads to rapid decomposition of the film, a finding that is in accordance with previous work in the literature.[18]

Multilayer Formation with PAA and PDADMAC. The buildup of multilayers from PDADMAC/PAA polyelectrolyte pairs (Figure 4) at pH = 2.0 was examined. The experiments were conducted, on one hand, to gain further understanding about the irregular film growth observed for the AM-MAPTAC 10/PAA multilayers prepared at pH = 6.0 and 9.0 (which will be discussed in the following paragraph) and, on the other hand, to examine the role of hydrogen bonding. Since PDADMAC cannot form hydrogen bonds, and in the absence of electrostatic attraction at pH = 2.0, it was expected that no growth or very thin films would be observed. Intriguingly, however, the film growth, although somewhat irregular, could be sustained for at least 12 layers with considerable mass loadings observed. This suggests that there is another attractive interaction responsible for the observed layer growth. In previous work in the literature multilayer formation has been described considering an ion-exchange mechanism between the salt counterion and the polyelectrolyte upon complexation.[41,42] It is not very probable that ion exchange of the proton of the carboxyl group against the tertiary ammonium group of the PDADMAC takes place because the pH = 2.0 used for adsorption is more than 2 units below the pK_a of PAA. This effect, which can also be attributed to a charge regulation mechanism, could result in some electrostatic attraction. Depending on the local environment, a weak polyelectrolyte can adjust its ionization in order to maximize the charge compensation within the film. Such effects have indeed been observed for films containing polycarboxylic acids.[18,26] However, since our experiment was conducted at very low pH, this effect is expected to be small. It is possible that hydrophobic attraction is the primary driving force for the assembly in this case. As suggested in the literature,[17] hydrophobic attraction can, under certain circumstances, play an important role for multilayer buildup.

Formation of PAA/AM-MAPTAC 10 Multilayers at pH 4.3. Multilayer deposition experiments from solutions of pH = 4.3 were aimed at examining qualitatively the effect of charge matching on the multilayer growth. Laschewsky et al. proposed that the charge density matching of the building polyelectrolytes, rather than their absolute charge, determines the growth behavior of the films.[19] As can be seen from Table 1, at pH = 4.3 about 7% of the PAA monomers carry a negative charge in solution, while AM-MAPTAC 10 has a 10% charge density. The intercharge distances (assuming fully stretched chains) are thus similar; i.e., the system is not far away from its charge matching point. However, as mentioned before, a different degree of ionization of PAA inside the multilayer as compared to in solution has to be considered. Despite the uncertainty of the exact degree of ionization of PAA within the multilayer, better charge matching at pH = 4.3 is expected as compared to the *two extreme situations*, where PAA is nearly fully charged (pH = 6.0/9.0) or nearly uncharged (pH = 2.0). Instead of an exponential-like growth, the mass and thickness of the films assembled at pH 4.3 exhibit more of a stepwise increase with increasing layer numbers. Both QCM and SPRS show that larger deposited amounts are realized upon AM-MAPTAC 10 adsorption. The SPRS data even indicate some small desorption upon deposition of layer 8. This case can be viewed as a transition from exponentially to irregularly growing films. Here, it is likely that both electrostatic and secondary interactions are operational. It was expected that, in this case a more stable, linear film growth would be obtained due to better matching of the charge densities of AM-MAPTAC 10 and PAA. The water retained in the films after air-drying may also play a role in determining film structure. Comparing the QCM frequency change of these multilayers at ambient humidity and after drying over silica gel revealed that a considerable amount of water could be drawn out of the films (about 30%), particularly for more than six layers. Water contents in polyelectrolyte multilayer films of up to 40% have been reported in the literature.[43,44] It was found that the frequency shift became progressively more sensitive to humidity changes. Thus, the small desorption step between the seventh and the eighth layers for assembly from pH = 4.3 adsorption solutions, evident from SPRS data (Figure 3a) and not in the QCM data (Figure 2a), can be attributed to a small variation in the ambient humidity at which the two measurements were performed. The two techniques, however, agree qualitatively, showing the trend toward thinner, stepwise growing films and the departure from the superlinear construction pattern characteristic for films assembled at pH = 2.0−3.2.

PAA at High Charge Densities. Multilayer construction from solutions with pH > 4.3 results in a situation where highly charged PAA is adsorbed in alternation with lowly charged AM-MAPTAC 10. The different solution conformation and adsorbed layer structure of the two polyelectrolytes account for the observed adsorption−desorption multilayer growth at pH = 6.0−9.0. Let us first consider the AM-MAPTAC 10 adsorption step, which corresponds to an increase in both the QCM film mass and SPR optical thickness. Because of its low charge density, the polymer forms thick and irregular adsorption layers, where the number of attachment points to the surface is much lower as compared to a highly charged polyelectrolyte. Figure 6b,d illustrates this particularly well. When highly charged PAA arrives at the surface during the next adsorption step, PAA molecules can wrap around the coiled AM-MAPTAC 10 structures on the surface and the PAA/AM-MAPTAC 10 complexes are liberated into solution. This accounts for the observed mass and thickness decrease during the PAA adsorption step. AFM imaging of the film surface confirms this mechanism. Both the surface roughness and the grain size are greatly reduced (Figure 7). Some (small) amount of AM-MAPTAC 10 should remain in the film, however, to promote the growth of consecutive layers. It appears that this growth mechanism is largely independent of the type of the polyelectrolytes used and whether the highly/lowly charged polyelectrolyte is the negatively or positively charged one, as long as there is a large difference in the charge densities, as illustrated by the PAA/PDADMAC pair in Figure 4. In the PAA/PDADMAC case, PAA is the coiled polymer, which is subsequently removed by adsorption of the highly charged PDADMAC. We note that similar behavior has been detected in several other systems, where multilayer films were constructed from polyelectrolytes with strongly differing architecture[45] or charge density.[12,40] We also note that the growth of dendrimer/polyelectrolyte multilayers, which initially showed similar irregular growth, can be improved by the use of fresh solutions for each adsorption step.[45] However, in the present work, using fresh adsorption solutions had no effect on the growth pattern; i.e., the adsorption of previously formed complexes appears to play a relatively minor role.

Conclusion

We have examined the construction pattern of multilayers comprising one lowly but permanently charged polyelectrolyte, AM-MAPTAC 10, and a weak polyacid PAA, under conditions where PAA is lowly or highly charged. The charge density of PAA was varied by altering the pH of the deposition solutions. Under conditions where PAA is uncharged or very lowly charged (pH = 2.0−4.3), thick films were formed and exponential growth of the multilayers was observed. Nonelectrostatic attractive interactions predominantly drive the assembly under these conditions. The film surface roughness increases with the number of deposited layers, which is also considered to be the main reason for the exponential-like construction pattern. Systems with a large degree of charge mismatch (at high pH (6.0 or 9.0), where PAA is highly charged) show an irregular, adsorption−desorption type of growth due to different conformation of the building polyelectrolytes. In this case, the buildup process proceeds through removal of the lowly charged polyelectrolyte by the subsequent adsorption of the highly charged polyelectrolyte.

The current study provides new insights into the importance of nonelectrostatic, secondary attractive interactions in the formation of polyelectrolyte multilayers. By tuning the pH of the adsorption solutions, a transition from electrostatic interactions to hydrogen bonding in the multilayer film assembly can be achieved. The type of interaction responsible for the multilayer growth, in turn, has a dramatic influence on the construction pattern and stability of these films.

Acknowledgment. A. Heilig is thanked for technical assistance. P. Claesson is acknowledged for donating the AM-MAPTAC 10 copolymer. H. Möhwald is thanked for the support within the Max Planck Institute and helpful discussions. P. Hammond, R. v. Klitzing, and P. Schütz are also acknowledged for helpful discussions. This work was supported by the BMBF and the DFG.

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MA034018G