Layer-by-Layer Assembly of Nanoblended Thin Films: Poly(allylamine hydrochloride) and a Binary Mixture of a Synthetic and Natural Polyelectrolyte

John F. Quinn, Johnny C. C. Yeo, and Frank Caruso*

Centre for Nanoscience and Nanotechnology, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia

Received May 12, 2004; Revised Manuscript Received June 16, 2004

ABSTRACT: Nanoblended multilayer thin films were formed by the layer-by-layer assembly of poly(allylamine hydrochloride) (PAH) and a binary mixture of single-stranded deoxyribonucleic acid (DNA) and poly(sodium styrenesulfonate) (PSS). UV−vis spectrophotometry was used as a facile means to determine the proportion of DNA and PSS in the films. Films assembled from solutions containing sodium chloride (NaCl) were found to contain predominantly PSS, while the presence of ethanol in the adsorption solution favored the incorporation of DNA into the film. The thickness of the films was determined by using surface plasmon resonance, which revealed increasing film thickness with a larger proportion of DNA in the film. This result was confirmed with quartz crystal microbalance studies, which showed a larger frequency increment for increasing DNA percentage in the film. The suppression of DNA adsorption under conditions of high ionic strength (high NaCl concentration) was shown to be a result of DNA displacement by PSS, which is favored when NaCl is present in the adsorption solution. Atomic force microscopy was used to examine the surface morphology, with films assembled without added salt having rougher surfaces than those prepared from solutions containing NaCl. Increasing the molecular weight of the PSS was shown to increase the proportion of DNA in the film, possibly due to increased chain entanglement between the two species. The reported results are significant in that they demonstrate that film composition can be tuned by adjusting the blend solution composition, adsorption conditions, and polyanion molecular weight to favor the adsorption of a particular species.

Introduction

The layer-by-layer technique is an important and versatile method for the fabrication of thin films with tailorable thickness and morphology.[1−3] The technique typically employs the sequential deposition of oppositely charged polyelectrolyte materials from dilute aqueous solutions to construct thin, multilayered films. Polyelectrolyte multilayer (PEM) film formation has been shown to depend on the chemical structure of the polyelectrolytes used,[4−8] the ionic strength of the deposition solution,[9] the type of supporting electrolyte,[10] the molecular weight of the polyelectrolytes,[11] the deposition procedure,[12] the solvent polarity,[13] and the pH at which deposition takes place.[14,15] To date, the vast majority of reports in the area have utilized systems in which there is only one polyelectrolyte in each solution. However, recent studies have demonstrated that by having two polyelectrolytes in one of the adsorption solutions (i.e., a blend of two polyanions or two polycations), film properties such as thickness, composition, and pH response can be tailored to meet specific applications. For instance, this approach was used by Leporatti et al. to demonstrate the generality of temperature annealing of polyelectolyte multilayer capsules[16] and by Schlenoff and Sui to modify the pH response of certain polyelectrolytes in controlling electroosmotic flow.[17] The first systematic study of blend composition in PEM film formation from blended polyelectrolyte solutions was performed by Schaaf and coworkers in late 2003.[18] In that work, poly(L-lysine) (PLL) was deposited in alternation with a binary mixture of poly(L-aspartic acid) (PLA) and poly(L-glutamic acid) (PGA), and it was shown that the presence of PGA augmented the formation of β-sheets of PLL and PLA. A further study by the same group examined the effect of using poly(allylamine hydrochloride) (PAH) in alternation with a mixture of PGA and PSS (poly(styrenesulfonate, sodium salt)).[19] This combination is interesting insofar that PAH/PSS films build up linearly, while PAH/PGA films grow exponentially. Using a different approach, Johal and co-workers examined the construction of films using the polycation polyethylenimine (PEI) in alternation with a blend of azo functional polyanion and a surfactant, sodium dodecyl sulfate (SDS).[20] In this case, increasing the proportion of SDS was shown to lead to a commensurate decrease in the adsorption of polyanion (up to the critical micelle concentration). It was postulated that the origin of this effect is the preferential adsorption of surfactant, which diminishes the number of sites available for polyanion adsorption. Recently, we reported the construction of multilayer films assembled from binary polyanion solutions and termed these "nanoblended" layers.[21] In particular, we examined the construction of multilayer thin films using a polyanion solution containing *both weak and strong polyelectrolytes* and demonstrated facile tailoring of the film properties (thickness, composition, pH stability) by varying the proportion of each polyanion in the adsorption solution.

In the current article, we report the preparation of multilayer thin films from a binary solution of *two strong polyelectrolytes* and demonstrate that film morphology, composition, and thickness can be tuned by variation of the blend composition and adsorption conditions. To study these aspects, films were con-

* To whom correspondence should be addressed. E-mail: fcaruso@unimelb.edu.au.

10.1021/ma0490698 CCC: $27.50
Published on Web 07/31/2004

structed from PAH adsorbed alternately with a blend of single-stranded deoxyribonucleic acid (DNA) oligonucleotides and PSS. The different UV−vis spectra of DNA and PSS allow determination of the film composition. In addition, a suite of techniques, including surface plasmon resonance (SPR), quartz crystal microgravimetry (QCM), and atomic force microscopy (AFM), were used to examine the film properties.

Experimental Section

Materials. PSS (M_w = 70 000 g mol^{-1}), PAH (M_w = 70 000 g mol^{-1}), and PEI (M_w = 25 000 g mol^{-1}) were obtained from Aldrich. Sodium chloride (NaCl) was obtained from Merck, absolute ethanol from BDH, and single-stranded DNA oligonucleotides (herring testes, <50 bases) from Sigma. All materials were used as received without further purification. Deionized water was obtained by using a Millipore RiOs/Milli-Q system and had a resistivity greater than 18 MΩ cm. Quartz slides were purchased from Hellma Optik GmbH (Jena, Germany) and were initially cleaned with piranha solution to remove any organic residues from the slide surface. ***Caution!*** *Pirahna solution is highly corrosive. Extreme care should be taken when handling pirahna solution, and only small quantities should be prepared*. Following this treatment, the slides were treated with RCA solution (5:1:1 water:hydrogen peroxide (30%):ammonia (28%)) to impart a hydrophilic surface to the quartz slides. QCM electrodes (frequency = 5 MHz, AT-cut) were obtained from Q-Sense Corp. (Q-Sense AB, Göteberg, Sweden) and prepared in the same manner as the quartz slides. Silicon wafers (Silchem Handelgesellschaft mbH, Germany) were cleaned initially with 2-propanol and then treated with RCA solution to hydrophilize the wafer surface. SPR slides were prepared by coating an RCA-cleaned glass slide with a thin layer of chromium (1−2 nm) using an Edwards Xenosput sputter coater, followed by a layer of gold (ca. 45 nm) using a sputter coater (Edwards).

Multilayer Film Formation. The substrate (silicon wafer, SPR slide, or quartz slide) was initially exposed to an aqueous solution of PEI (1 mg mL^{-1} in 0.5 M NaCl) for 15 min and then rinsed by three sequential dips into water (1 min duration each). The substrate was then exposed to the blend solution of DNA and PSS (total weight concentration = 1 mg mL^{-1}) for 15 min, followed by the same rinsing protocol as before. Multilayer films were then constructed by continuing this sequential adsorption process, alternating between positive (PAH) and negative (PSS/DNA) polyion solutions until the desired layer number was reached. Films prepared using three different supporting electrolyte concentrations were examined (0, 0.05, and 0.5 M NaCl as well as three different blends of ethanol/water (0, 5% (v/v), and 20% (v/v)). The polyanion compositions studied were DNA/PSS (w/w) = 90/10, 75/25, 50/50, 25/75, and 10/90. In the case of 0.5 M NaCl, DNA/PSS (w/w) = 95/5, 97.5/2.5, and 99/1 were also studied. After each deposition and washing cycle the films were dried under a gentle stream of high-purity nitrogen. The films are described as (DNA/PSS)/PAH multilayers, though it should be noted that each film is constructed on a precursor PEI layer.

UV−Vis Spectrophotometry. UV−vis spectra were collected from multilayer films assembled on quartz substrates using an Agilent 8453 single-beam UV−vis spectrophotometer. An air blank was taken for all measurements.

Surface Plasmon Resonance. A Multiskop SPR spectrometer was used for collecting surface plasmon resonance spectra. The experimental setup has been previously described.[22] SPR spectra were obtained as reflectivity vs angle of incidence curves, and the optical thickness of the dielectric film was extracted by fitting Fresnel theory to these curves. Only film thickness was used as a fitting parameter, assuming uniform film thickness with a refractive index of 1.47. It is noted that fits to Fresnel theory are relatively insensitive to minor variations in the refractive index of the dielectric material. In our measurements it is estimated that these variations could account for deviations of up to 10% in the calculated thickness of the adsorbed films.

Table 1. Absorbance per Bilayer for PEI-[DNA/PAH]$_{5.5}$ and PEI-[PSS/PAH]$_{5.5}$[a]

	absorbance (×10^3)		
system	pure water	0.5 M NaCl	20% (v/v) ethanol
PAH/PSS	2.4	35.6	2.5
PAH/DNA	14.2	111.6	19.9

[a] Values shown are calculated from the average of the first five layers (i.e., excluding the initial PEI-(DNA/PSS) bilayer). λ_{max}(DNA) = 260 nm; λ_{max}(PSS) = 226 nm.

Quartz Crystal Microgravimetry. A QCM with dissipation measurement was used to determine the rate of adsorption of the PSS/DNA blends onto the substrate. In each case the adsorption step analyzed was the third polyanionic adsorption,[23] and the data were collected from the fifth overtone of the resonant frequency. The adsorption solution was introduced to the measurement chamber for 15 min, after which the chamber was flushed with Milli-Q water for 15 min. The sample chamber was maintained at a constant temperature of 19.85 ± 0.10 °C for all measurements.

Atomic Force Microscopy. AFM images were taken of multilayer films on silicon wafers by using a Nanoscope 3A atomic force microscope in tapping mode. The scan area was 1 μm × 1 μm.

Results and Discussion

To examine the effect of varying adsorption conditions on the buildup of (DNA/PSS)/PAH multilayers, initial studies were conducted on PAH/PSS and PAH/DNA multilayers. The absorbance per bilayer (at 226 nm (PSS phenyl ring) for PAH/PSS and 260 nm (DNA bases) for PAH/DNA) was determined for three different adsorption solutions: pure water or aqueous solutions containing 0.5 M NaCl or 20% (v/v) ethanol. The results are given in Table 1. In the case of PAH/PSS multilayers, conducting the adsorption from solutions that contain a supporting electrolyte concentration of 0.5 M NaCl led to a 15-fold increase in the absorbance per bilayer when compared to adsorption from a solution of PSS in pure water. Conversely, constructing the PAH/PSS multilayer from aqueous solutions that are 20% (v/v) in ethanol led to no significant increase in the adsorbed amount of PSS (an observation that is consistent with that previously reported by our group).[13] For the PAH/DNA layers assembled from solutions with 0.5 M NaCl the absorbance per bilayer at 260 nm was 8-fold greater than those assembled from pure water, while assembly from 20% (v/v) ethanol led to a 40% increase in the adsorbed amount of DNA compared with adsorption from pure water. Therefore, considering solutions where *both* DNA and PSS are present in the polyanion solution and assuming there is no interaction between the polyelectrolytes, it is expected that added salt will lead to a greater proportion of PSS than DNA in the film, while added ethanol should favor the adsorption of DNA over PSS. Therefore, it may be possible to tune the composition of these films simply by varying the adsorption conditions.

Before examining this hypothesis, it was first necessary to develop a protocol for estimating film composition. Both DNA and PSS have chromophores that absorb in the UV−vis region, and therefore it is possible to extract an estimate of the film composition directly from the UV−vis spectrum of mixed films. We chose to examine the full range of wavelengths between 190 and 350 nm, considering the spectra of nanoblended films as a set of absorbance values each corresponding to a different wavelength. Each of these absorbance values

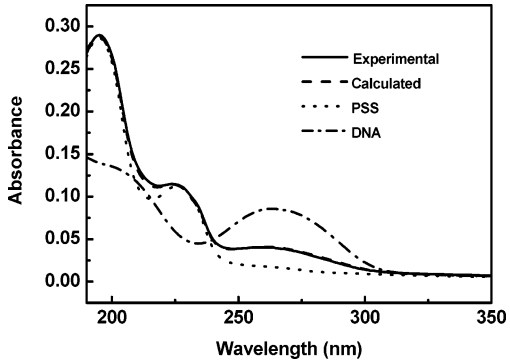

Figure 1. Comparison of calculated and experimental UV−vis spectra for (DNA/PSS)/PAH multilayers. Experimental spectrum is for PEI-$[(DNA/PSS)/PAH]_{5.5}$ assembled at 0 M NaCl, PAH concentration = 1 mg mL^{-1}, DNA and PSS concentrations = 0.5 mg mL^{-1}. Measured spectra obtained from $(PAH/DNA)_2$ assembled with PAH concentration = 1.0 mg mL^{-1}, DNA concentration = 1.0 mg mL^{-1} and NaCl concentration = 0.5 M, and $(PAH/PSS)_3$ assembled with PAH concentration = 1.0 mg mL^{-1}, PSS concentration = 1.0 mg mL^{-1}, and NaCl concentration = 0.5 M.

is treated as the sum of the absorbance contributions from DNA and PSS according to the equation:

$$A_i = A_i(\text{DNA}) + A_i(\text{PSS}) \quad (1)$$

where A is the absorbance and i indicates the specific wavelength. Using the Beer−Lambert law, this may be rewritten as

$$A_i = [\epsilon(\text{DNA})_i \times b \times c(\text{DNA})] + [\epsilon(\text{PSS})_i \times b \times c(\text{PSS})] \quad (2)$$

Since b is the path length, it is assumed to be the same for both the DNA and PSS contributions. The calculated spectrum can then be compared with that measured simply by normalizing and analyzing the residuals between the calculated and measured spectra. The values of c(DNA) and c(PSS) were varied systematically until the optimum fit was obtained between the calculated and measured spectra. This was when the condition

$$\sum_{i=190}^{350} |R_i| \rightarrow 0 \quad (3)$$

was satisfied (i.e., where the sum of the residual differences between calculated and measured absorbance values was at a minimum). Figure 1 demonstrates that the agreement between the calculated and measured spectra is quite good: the spectra are effectively superimposed. This technique was thereafter used to determine the composition of films assembled under a variety of adsorption conditions, allowing facile examination of changes in polyanion composition within the film.

Initially, studies on (DNA/PSS)/PAH multilayers were conducted using polyanion solutions that were 0.5 mg mL^{-1} in PSS and 0.5 mg mL^{-1} in DNA. To examine the effect of ionic strength, three different NaCl concentrations were employed: 0, 0.05, and 0.5 M. The ionic strength was the same in both polycation and polyanion solutions. The composition of PEI/$[(DNA/PSS)/PAH]_{5.5}$ films assembled under these conditions is given in Figure 2a. (It should be noted that %DNA refers to the percentage as a fraction of the polyanion component

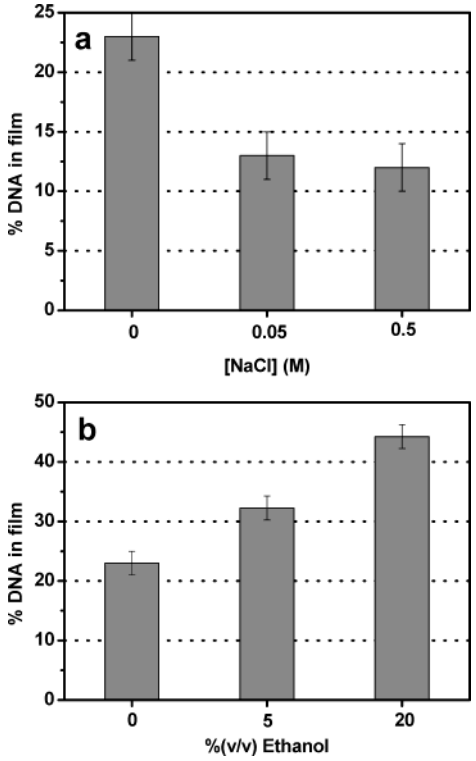

Figure 2. %DNA in PEI-$[(DNA/PSS)/PAH]_{5.5}$ multilayer films assembled under different conditions. PAH concentration = 1.0 mg mL^{-1}. DNA concentration = PSS concentration = 0.5 mg mL^{-1}. (a) 0, 0.05, and 0.5 M NaCl. (b) 0, 5% (v/v), and 20%-(v/v) ethanol/water.

only: at this stage no determination has been made of the fraction of the total film.) The %DNA in the film is clearly dependent on the ionic strength at which the film was assembled. In particular, an increase in the ionic strength of the adsorption solution leads to a decrease in the fraction of DNA in the polyanion layers. The difference is most notable when comparing the 0 and 0.05 M cases, while the difference between 0.05 and 0.5 M is considerably smaller. Importantly, it should be noted that the data presented are for films comprising 12 layers. Nevertheless, these results can be generalized as little compositional variation was seen for films comprising between 4 and 12 layers. Only the first binary layer (which is adsorbed onto PEI rather than PAH) was significantly different, with a larger %DNA in the layer (19%, cf. 12%).

An equally dramatic trend is evident when examining the effect of added ethanol on the assembly of layers from binary polyanion mixtures. Again, the same solvent conditions were employed in both the PAH and DNA/PSS solution. Figure 2b shows clearly that as the fraction of ethanol in the adsorption solution increases, the proportion of DNA in the anionic fraction of the film also increases. This can be reconciled by examining the effect of added ethanol on the buildup of multilayers from each individual pair. While adding 20% (v/v) ethanol to the PSS solution leads to no appreciable increase in the adsorbed amount of PSS (see Table 1 and ref 13), the addition of the same fraction of ethanol led to a 40% increase in the adsorbed amount of DNA when compared to film assembly from pure water. This indicates that the addition of ethanol to a mixed solution favors the adsorption of DNA over PSS, as observed in Figure 2b. Importantly, there has been a considerable amount of work on the effect of adding alcohols (includ-

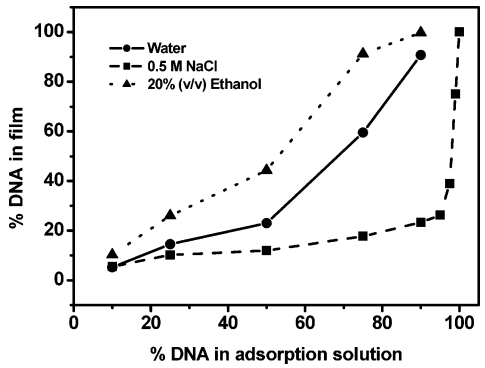

Figure 3. %DNA in PEI-[(DNA/PSS)/PAH]$_{5.5}$ multilayer films assembled under different conditions. PAH concentration = 1.0 mg mL^{-1}. Total DNA and PSS concentration = 1.0 mg mL^{-1}. PAH and DNA/PSS were adsorbed under the same conditions.

ing ethanol) to solutions of double-stranded DNA, particularly with regard to the effect on the helical structure of DNA and the hydrodynamic radius of the DNA molecules in solution.[24−29] It has been reported that the addition of ethanol to a DNA solution affects hydrogen-bonding and hydrophobic interactions within the molecule, thereby compacting DNA molecules in solution. While in the current study we have used single-stranded rather than double-stranded DNA, the addition of ethanol to the adsorption solution could be expected to affect the solution state conformation of these molecules by changing the water structure around the solvated polyions. This solution state change could be expected to influence the adsorbed amount incorporated into the multilayer film.

Further studies were conducted to probe the effect of varying the composition of the blend as well as the solvent conditions. In each case, increasing the amount of DNA in the adsorption solution leads to an increase in the amount of DNA incorporated into the film (Figure 3). Further, as described above, it is clear that adding ethanol to the adsorption solution increases the amount of DNA in the final film: in each of the five polyanion compositions studied, the films prepared from ethanolic solutions have a higher fraction of DNA in the film. Again, these results are consistent with what might be predicted by examining the individual responses of DNA and PSS to the presence of ethanol in the adsorption solutions. However, a more dramatic result is obtained for the case where the adsorption solutions contain 0.5 M NaCl. In this case, the amount of DNA in the final film is remarkably low considering the amount of DNA in the adsorption solution: only when the %DNA in the adsorption solution is increased to 95% is an appreciable amount of DNA (>20%) incorporated into the film. This is a much more dramatic effect than might be expected if only considering the different responses of the polymers to changes in the adsorption conditions. To explain this behavior, the possibility of adsorption/displacement rather than simple competitive adsorption was explored. Voegel and co-workers have previously observed substitution of PGA chains by PSS when PGA/PLL multilayer films were exposed to solutions containing PSS.[30] Therefore, we postulated that the adsorption of DNA may indeed take place on a short time scale but that displacement effects may override this adsorption. If the interaction between PSS and PAH is much stronger than the DNA/PAH case, then the initially adsorbed DNA chains may be displaced almost immediately by PSS, even at low PSS concentrations.

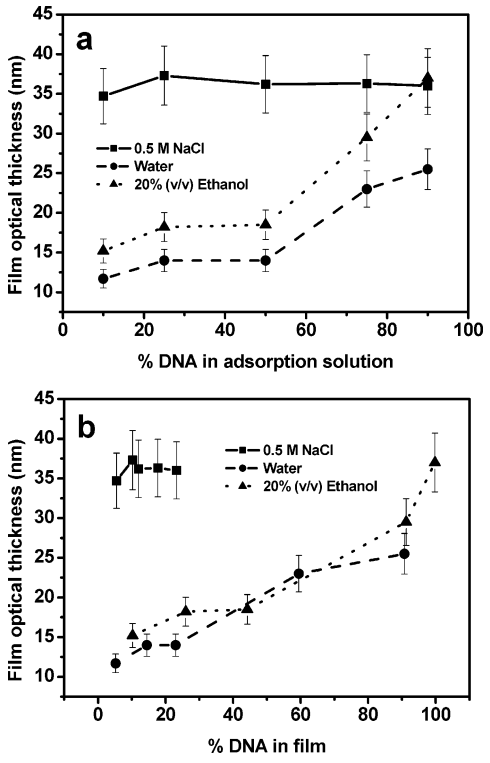

Figure 4. Optical thickness of PEI-[(DNA/PSS)/PAH]$_{5.5}$ multilayer films assembled under different conditions, as measured by using surface plasmon resonance. PAH concentration = 1.0 mg mL^{-1}, total DNA and PSS concentration = 1.0 mg mL^{-1}. PAH and DNA/PSS were adsorbed under the same conditions. (a) Variation of thickness with polyanion composition of adsorption solution. (b) Variation of thickness with polyanion composition of thin film.

To further investigate this possibility, studies were conducted using a single layer of DNA adsorbed onto a PAH-coated quartz slide. This slide was exposed to a solution of PSS (1 mg mL^{-1}) in 0.5 M NaCl for 15 min and then rinsed thoroughly. After this time almost complete displacement of the DNA takes place, as observed by UV−vis spectrophotometry (see Supporting Information). However, if a similarly prepared DNA monolayer is exposed to a solution of PSS (1 mg mL^{-1}) in the absence of any added sodium chloride (i.e., 0 M), no displacement takes place (see Supporting Information). This accounts for the result that when adsorption takes place at high ionic strength (0.5 M NaCl) in the presence of both DNA and PSS, the adsorption of PSS will be greatly favored. Therefore, it should be noted that displacement effects may be significant in the assembly of multilayers from binary polyion solutions, depending on the specific polyion pair chosen.

The thicknesses of films prepared from solutions containing 0.5 M NaCl, water, and 20% (v/v) ethanol were examined by using SPR. The optical thicknesses vs the amount of DNA in the adsorption solution are given in Figure 4a. In the cases of film assembly from water and 20% (v/v) ethanol, increasing the amount of DNA in the adsorption solution increases the optical thickness of the film. However, in the case where the adsorption solutions contain 0.5 M NaCl, there is little variation in the obtained film thicknesses. These data are in agreement with those in Figure 3: 0.5 M NaCl leads to very little variation in the film composition or thickness across the range of compositions analyzed, while using pure water or 20% (v/v) ethanol adsorption solutions lead to a change in both the film composition

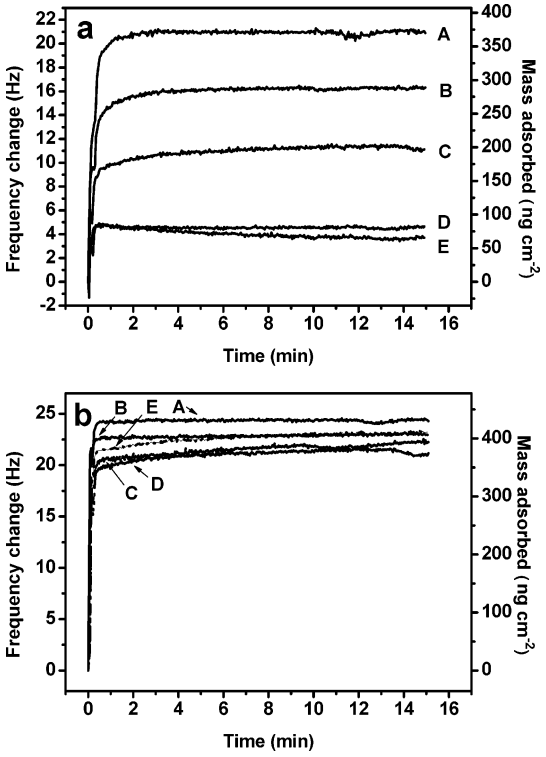

Figure 5. Adsorption kinetics of the third polyanion layer under different adsorption conditions, as measured by QCM. PAH concentration = 1.0 mg mL^{-1}, total DNA and PSS concentration = 1.0 mg mL^{-1}: (a) 0 M NaCl (pure water); (b) 0.5 M NaCl. (A) DNA:PSS = 90:10; (B) DNA:PSS = 75:25; (C) DNA:PSS = 50:50; (D) DNA:PSS = 25:75; (E) DNA:PSS = 10:90. All ratios are (wt/wt%).

and the thickness. As such, one may expect to find a relationship between the %DNA in the film and the optical thickness (Figure 4b). Clearly, the increase in thickness correlates with a linear increase in the proportion of DNA incorporated into the film. A plausible reason behind this thickness variation is conformational differences between DNA and PSS under different solution conditions. However, in the case of high ionic strength (0.5 M NaCl) DNA incorporation into the film is suppressed by the displacement effects mentioned above, and therefore there is no observable thickness variation across the film compositions (10−90 wt % DNA) studied.

To examine the variation of rate of adsorption with changes in the solution composition, studies were undertaken using a Q-Sense QCM with dissipation capability. The third polyanion adsorption step was chosen for examination, similar to a previous investigation of the adsorption step.[23] Two cases were examined: 0 M NaCl and 0.5 M NaCl (Figure 5a,b). Under both conditions and across the full range of examined compositions adsorption is fast, with the adsorbed amount reaching a plateau within the first 5 min. In the case where adsorption occurs from solution with no added supporting electrolyte, there is a considerable variation in the observed step size: when there is a low amount of DNA in the adsorption solution, this results in a correspondingly small frequency change. However, as the amount of DNA in the adsorption solution increases, the mass adsorbed (proportional to frequency change) also increases. This is consistent with results obtained from the thickness measurements: as the amount of DNA increases, the thickness (and therefore the mass adsorbed) also increases. In the case of adsorption from high ionic strength solutions, there is little variation between the five compositions studied, and all appear to be close to a frequency change of approximately 22 Hz (corresponding to ca. 390 ng cm^{-2}).

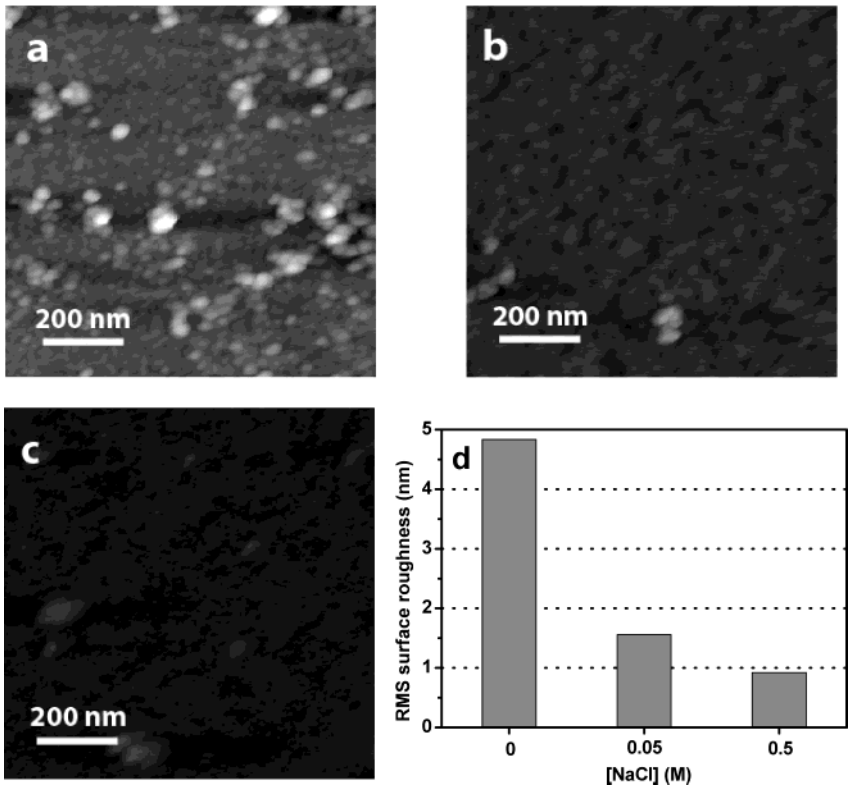

Figure 6. AFM images of PEI-[(DNA/PSS)/PAH]$_{5.5}$ multilayer films assembled under different conditions. PAH concentration = 1 mg mL^{-1}. DNA concentration = PSS concentration = 0.5 mg mL^{-1}. (a) 0 M NaCl; (b) 0.05 M NaCl; (c) 0.5 M NaCl; (d) rms surface roughness as a function of NaCl concentration.

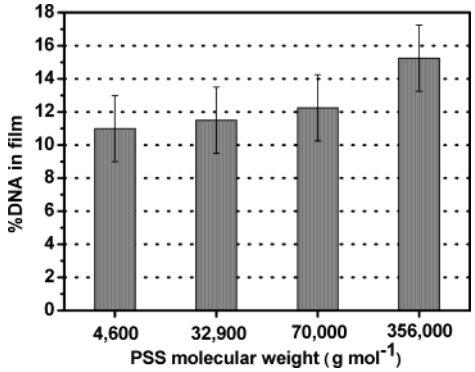

Figure 7. %DNA in PEI-[(DNA/PSS)/PAH]$_{5.5}$ multilayer films prepared using solutions containing PSS with different molecular weights. PAH concentration = 1.0 mg mL^{-1}. DNA concentration = PSS concentration = 0.5 mg mL^{-1}. PAH and DNA/PSS were adsorbed from solutions containing 0.5 M NaCl.

Again, this can be explained by relatively low amounts of DNA in the final film and the fact that the DNA proportion in the film correlates with thickness of the multilayer film formed (Figure 4b).

AFM images were collected from [PEI-(PSS/DNA)/PAH]$_{5.5}$ films prepared at 0, 0.05, and 0.5 M NaCl (Figure 6a−c, respectively). The root-mean-squared (rms) surface roughness of the films (Figure 6d) is largest when the film was prepared at low ionic strength. Close inspection of Figure 6a reveals that there are small circular domains present in the film when prepared at 0 M NaCl. These circular domains are consistent with other studies on multilayer films of DNA[31,32] and reflect an increased amount of DNA incorporated into the film (Figure 2a). Films prepared at higher salt concentration have a significantly lower surface roughness (by a factor of 4), and the films appear substantially smoother. These films (Figure 6b,c), which contain predominantly PSS in the polyanion layer, resemble films assembled from PSS and PAH, with an associated rms roughness of approximately 1 nm.[33]

The molecular weight of the PSS used in the film assembly was also shown to influence the composition of the films formed. Increasing the molecular weight of the PSS in the blend led to an increase in the amount of DNA in the final film (Figure 7). There is not a significant difference between the compositions of films assembled from 4600, 32 900, and 70 000 g mol^{-1} PSS blends, as the determined compositions are effectively within experimental error of each other. However, the increase to 356 000 g mol^{-1} introduces an increase in the adsorbed amount of DNA in the film. There are two possible reasons for this behavior. First, lower molecular weight PSS may be able to diffuse faster to the surface, thereby occupying sites that would otherwise be taken by DNA chains. Alternatively, longer PSS chains may be more substantially entangled with the DNA, meaning that adsorption of the PSS actually augments further adsorption of DNA. In view of the important displacement effects that were discussed above, the second explanation is probably more likely.

Conclusions

We have demonstrated that the composition, thickness, and morphology of multilayered films of (DNA/PSS)/PAH can be varied by changing (a) the composition of the blend adsorption solution and (b) the adsorption conditions employed. UV−vis spectrophotometry was used to determine the composition of films assembled from PAH adsorbed in alternation with a binary mixture of DNA and PSS. Films prepared using a blend solution that contained 0.5 mg mL^{-1} of both DNA and PSS and 0.5 M NaCl were found to contain predominantly PSS (ca. 88%), while adsorption from ethanol/water (20/80 v/v) yielded films that contained an increased proportion of DNA (ca. 45%). The thickness of the films was determined using SPR and shown to correlate with an increasing proportion of DNA in the film. Further, the low proportion of DNA in the films assembled at high NaCl concentration was shown to be a result of DNA displacement with PSS, which is favored when the salt concentration is high. Increasing the molecular weight of the PSS was shown to slightly increase the proportion of DNA in the final film (from 12 to 15%), possibly due to increased chain entanglement. The significance of this work lies in the demonstrated ability to tailor overall film composition by altering the polyanion solution composition and adsorption conditions to promote adsorption of a particular species. This approach is potentially applicable to any polymer pair that respond differently to changes in the specific adsorption conditions.

Acknowledgment. The authors acknowledge funding from the Australian Research Council under the Federation Fellowship and Discovery Project schemes and from the Victorian State Government under the STI Initiative. F. Meiser and E. Tjipto are thanked for AFM analysis and B. Radt for assistance with SPR measurements.

Supporting Information Available: Figures showing displacement of DNA by PSS under different ionic strength conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0490698