

NMR Studies of PAH/PSS Polyelectrolyte Multilayers Adsorbed onto Silica

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ABSTRACT: Solid-state NMR spectroscopy is used to monitor the layer-by-layer (L-B-L) growth of polyelectrolyte multilayers on colloidal silica. The dynamics and conformation of polyelectrolyte multilayers comprised of the weak polycation, poly(allylamine) hydrochloride, and the strong polyanion, poly(sodium-4-styrene sulfonate), assembled at pH 7 and pH 10 were studied by a combination of ¹H and ¹³C NMR measurements. NOESY spectra detect the association of water to the polyanion, while relaxation measurements show that the outermost layer and the water content influence the mobility of the polyelectrolytes and the adsorbed water. Differences in mobility for films assembled at high and neutral pH are explained by the conformation of the polycation during the assembly process. Finally, the strong–weak polyelectrolyte multilayers are compared to a previous NMR study of strong–strong polyelectrolyte multilayers.

Introduction

Polyelectrolyte multilayers (PEMs) are of current interest because of potential applications as pH sensors, drug delivery vehicles, and selective membranes among others.^{1–4} Strong polyelectrolytes such as poly(diallyldiammonium) chloride (PDADMAC) and poly(sodium-4-styrene sulfonate) (PSS) are often used because of their ability to be charged over a large pH range, while weak polyelectrolytes, such as poly(allylamine) hydrochloride (PAH) and poly(acrylic acid) (PAA), are pH dependent with their degree of ionization depending on the local electrostatic environment.⁵ Because of their ability to respond to changes in the local environment, multilayers of weak polyelectrolytes with many different architectures or properties can be prepared by changing the pH of the assembly solution.

The current system under investigation consists of a colloidal silica substrate and the polyelectrolytes PAH and PSS (Figure 1). The weak polycation PAH, having a pK_a in dilute solution of 8.7, is half ionized at this value, becoming fully charged as the pH is lowered and neutral at a pH value above ten. The strong polyanion, PSS, remains fully charged throughout a large pH range. The interactions of these two polyelectrolytes during multilayer formation are of interest since varying the polymer charge (i.e., pH) of the adsorption solutions leads to differences in multilayer growth.

Several groups have studied the properties of multilayers consisting of a weak and strong polyelectrolyte. Most of these studies have involved examining differences in multilayer behavior by post-assembly pH changes. Hoogeveen et al. showed that the stability of multilayers comprised of a weak and strong polyelectrolyte to changes in pH depended on the nature of the

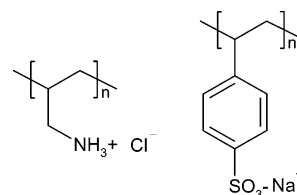


Figure 1. Structures of PAH (polycation) and PSS (polyanion).

terminal layer.⁶ Termination with a weak polyelectrolyte poly(dimethylamino)ethyl methacrylate (PAMA) made for unstable multilayers whereas when the final layer was a strong polyelectrolyte (PSS) a stable film was observed. This is in contrast to what was seen with multilayers formed from highly charged polyelectrolytes in which stable multilayers resulted regardless of the identity of the terminal layer. Rubner et al. showed that PAH/PSS multilayers have different molecular architectures based on differences in assembly pH, which rendered them relatively sensitive or insensitive to post-assembly pH changes.⁷ Shenoy et al. examined the pH-dependent permeability of PAH/PSS hollow capsules finding that permeability of the shells increased the further away from neutral pH, suggesting that post-assembly changes in pH resulted in conformational changes of the multilayers.⁸

Thus, while some studies have been undertaken to look at the properties of films composed of a weak and strong polyelectrolyte, many fundamental questions remain unanswered. The aim of this paper is to provide insight into the dynamics and conformation of strong–weak polyelectrolyte multilayer systems through solid-state NMR spectroscopy. A detailed study of the layer growth and mobility of strong polyelectrolyte multilayer pairs (PDADMAC/PSS)^{9,10} revealed striking differences in the mobility of the polyanion versus the polycation as well as the water associated with the film. An alternation in both polymer and water mobilities with

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layer number was observed. It is of interest to see whether these properties extend to other types of PEMs. The layer growth and dynamics of PAH/PSS multilayers assembled under various pH conditions are characterized using the same ^{13}C CP/MAS and ^1H fast MAS NMR techniques as employed in the earlier study. The mobility of the polyions as well as the associated water of multilayers assembled at different pH values is expected to vary, yielding information on the film structure in terms of the polymer conformation and the location of the associated water, a major component of PEMs.

Experimental Section

Materials. Poly(allylamine hydrochloride) (PAH), $M_w = 60\,000$ g/mol and poly(sodium-4-styrene sulfonate) (PSS), $M_w = 70\,000$ g/mol were purchased from Aldrich. Snowtex silica colloids (nominal diameter 70–100 nm) were provided by Nissan Chemical Corporation. Millipore Milli-Q water (18 M Ω resistivity) was used for all sample preparations. The molecular structures of the polymers are shown in Figure 1.

Sample Preparation. Five-hundred milliliters of a 0.02 M PAH, 0.2 M NaCl (pH 7 or 10) solution was added to 1 g (2.5 mL) of silica colloid suspension. The samples were sonicated and the adsorption solution was left to stand for a minimum time of 30 min. The solution was then centrifuged at 4300 rpm and the supernatant was removed. Five-hundred milliliters of water (pH 7 or 10) was added to the sample and the solution was sonicated and left to stand for a minimum of 30 min. The supernatant was then removed to rinse the unadsorbed polyelectrolyte from the colloids. A total of three 500-mL washings were performed, after the adsorption of each polyelectrolyte layer. A small amount of sample was then removed and dried overnight at 70 $^\circ\text{C}$ for characterization studies. To the remaining colloidal solution was added 500 mL of a 0.02 M PSS, 0.2 M NaCl (pH 7 or 10) solution. Similar adsorption and washing steps were performed, until a total of four or seven PAH–PSS bilayers for assembly at pH 7 and 10 had been prepared, respectively.

Electrophoretic Mobility (EPM) Measurements. Zeta potential (ζ -potential) values of the bare and multilayered silica nanoparticles were measured on a Zeta Plus zeta potential analyzer (Brookhaven Instruments Corporation, New York). Approximately 30 mg of each dried colloid sample was suspended in 15 mL of 1 mM NaCl solution. The pH of each solution was adjusted to a value of 4.0, 7.0, or 10.0. Ten mobility measurements were performed on each sample and the averages were converted to ζ -potentials.

NMR Measurements. ^{13}C Spectra were recorded on a Chemagnetics CMX-300 spectrometer for the multilayer samples. A total suppression of sidebands (TOSS) sequence with background suppression, a spinning speed of 4 kHz, and a contact time of 1 ms were used. The ^1H 90 $^\circ$ pulse widths were 4 μs and an average of 30 000 scans were taken. ^{13}C $T_{1\rho}$ measurements were performed by applying a 90 $^\circ$ pulse for cross-polarization, followed by a variable spin-lock time in which the carbon magnetization decays by dipolar coupling. A total of 5000 scans were acquired for ^{13}C $T_{1\rho}$ spectra of the multilayers while 1000 scans were acquired for the bulk complex. All measurements were performed at a spinning speed of 4 kHz. The ^{13}C T_1 measurements were carried out by means of a modified inversion–recovery

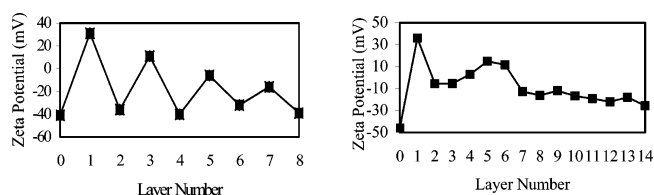


Figure 2. Zeta potential values for PAH/PSS multilayers assembled at pH 7 (on the left) and at pH 10 (on the right), measured at pH 7 in 1 mM NaCl.

T_1 experiment, in which the 180 $^\circ$ pulse was replaced with a 90 $^\circ$ pulse for cross-polarization. A total of 900 scans were acquired for all ^{13}C T_1 spectra. All measurements were performed at a spinning speed of 4 kHz.

^1H spectra were recorded on a Bruker asx500 spectrometer. Samples were placed in 2.5-mm rotors and were spun at 25 kHz. Proton Hahn echo experiments were acquired under MAS conditions with a total of 512 scans. ^1H T_1 were measured using an inversion–recovery sequence with 16 scans and 10-s recycle delay. One-dimensional double-quantum-filtered back-to-back (1D DQF BABA)¹¹ experiments allowed for the probing of rigid parts of the multilayer film by reintroducing dipolar coupling normally removed by MAS, selecting for nuclei which can form double-quantum coherences because of dipolar coupling. A total of 512 scans were taken. Two-dimensional double-quantum back-to-back (2D DQ BABA)¹¹ experiments were performed to probe spatial proximity of nuclei by revealing which protons are dipolar coupled to each other. NOESY spectra were also taken to observe the proton correlations within the multilayer system with a total of 32 scans.

Results

Electrophoretic Mobility. As seen in Figure 2, which shows the zeta potential as a function of layer number for the PAH/PSS multilayers assembled at pH 7, the alternation between positive and negative values as PAH and PSS are added is apparent. Surface charge reversal is not seen after layer five. However, this reversal is not always observed during the buildup of polyelectrolyte multilayers and the trend in the ζ -potential still suggests the stepwise growth of the multilayer.^{8,12} Electrophoretic mobility measurements were also performed on the PAH/PSS multilayers assembled at pH 10. A plot of the zeta potential as a function of layer number does not display the typical alternation between positive and negative charge as layers are added (Figure 2). The lack of alternation seems to indicate that no multilayer growth has occurred. However, since zeta-potential measurements are indirect measurements of multilayer growth, solid-state NMR spectroscopy was employed to determine if this was indeed the case. Some flocculation occurred during the assembly of pH 10 films. This instability of the colloidal dispersion would also lead to the lack of alternation in the zeta potentials. However, the colloids were not completely flocculated, and some multilayer growth in addition to polyelectrolyte complex globule formation occurred, as discussed below.

^{13}C Chemical Shifts. ^{13}C CP/MAS NMR was performed on the multilayers and the 1D ^{13}C spectra (Figure 3) reflect the layer-by-layer (L-B-L) growth of the PAH/PSS multilayers assembled at pH 7. The peak at 33 ppm arises from the methine carbon in the PAH, while the two peaks at 127 ppm (CH aromatic carbons)

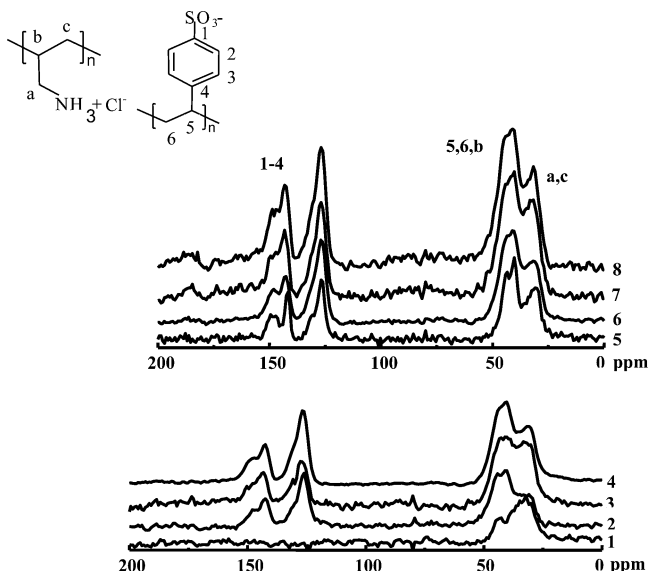


Figure 3. ^{13}C CP/MAS spectra of PAH/PSS multilayers (assembled at pH 7) as a function of layer number. The numbers on the right correspond to number of layers adsorbed.

Table 1. Peak Area for PAH/PSS Multilayers Assembled at pH 7 and pH 10

layer number	PSS/PAH pH 7 ratio	PSS/PAH pH 10 ratio
1	n/a	n/a
2	1.2	0.78
3	0.8	0.87
4	1.0	0.51
5	0.9	0.27
6	1.6	0.48
7	0.7	0.30
8	1.0	0.41
9		0.41
10		0.64
11		0.34
12		0.47
13		0.30
14		0.53

and 146 ppm (quaternary carbons) are assigned to PSS. The peak at 40 ppm corresponds to overlapping peaks of the PAH and PSS backbone carbons. Examining the relative intensities for the peak at 33 ppm (PAH) versus that of the peak at 40 ppm (PAH/PSS), it is apparent that when PAH is adsorbed this difference in peak height decreases. While after the addition of PSS, an increase in the difference of peak intensity between these two resonances occurs. As shown in the earlier NMR study of the strong PEMs, quantitative information can be determined by peak integration of the adsorbed polyelectrolytes with the results being in good agreement to elemental analysis.⁹ The integrated intensities of the four CH aromatic carbons, which resonate at 127 ppm for PSS, and the two methylene carbons at 33 ppm for PAH were used to calculate the stoichiometric ratios which are listed in Table 1.

The films adsorbed at pH 7 have three resolved peaks in the aromatic region (Figure 3). There is a resonance at 146 ppm for the phenylene carbon attached to the PSS backbone and a resonance at 140 ppm because of the sulfonated carbon at the para position of the ring in addition to the peak at 127 ppm.¹³ This splitting is not as apparent in either the samples assembled at pH 10 or the strong-strong PDADMAC/PSS multilayers.⁹ This is presumably due to increased mobility in the quaternary carbon next to the sulfonate group in the multilayers assembled at pH 7.

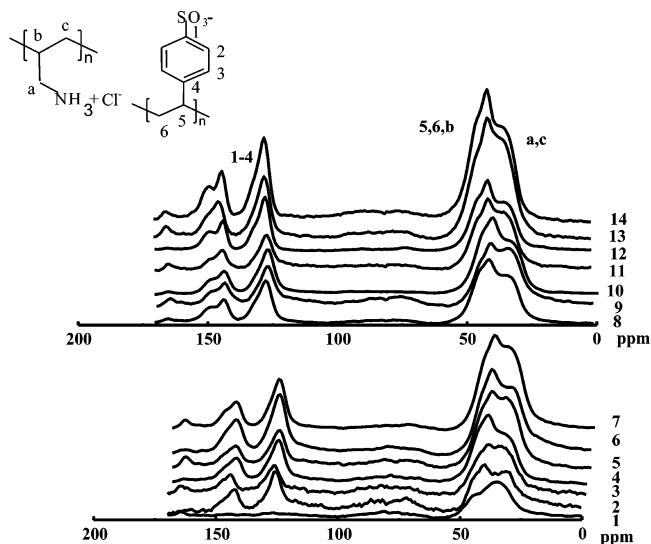


Figure 4. ^{13}C CP/MAS spectra of PAH/PSS multilayers (assembled at pH 10) as a function of layer number. The numbers on the right correspond to number of layers adsorbed.

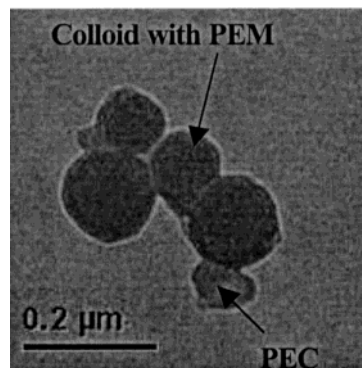


Figure 5. TEM image of PAH/PSS films assembled at pH 10.

^{13}C CP/MAS NMR was also used to determine whether multilayer growth occurred for PEMs assembled at pH 10. Figure 4 illustrates the layer-by-layer (L-B-L) growth of a PAH/PSS multilayer system assembled at pH 10 comprised of 14 layers. By examining the alternation in relative intensities between the peaks that arise solely to PAH (33 ppm) versus the peak at 40 ppm, which arises because of both PAH and PSS, multilayer growth is observed. Once again when PAH is adsorbed the signal at 33 ppm increases relative to the peak at 40 ppm, while the differences between these two peaks decrease when PSS is the terminating layer. The adsorption of polyelectrolyte is supported by peak area integration for PAH and PSS and is given in Table 1. The growth is not linear in terms of the amounts adsorbed and deviates significantly from the 1:1 stoichiometry normally observed. The PAH peak area for films assembled at pH 10 is on average 2 times larger than for films assembled at pH 7. This increase in amount adsorbed is responsible for the improved signal-to-noise (S/N) relative to the films assembled at pH 7. The instability of the multilayers assembled at pH 10 can also be seen in the transmission electron microscope images (TEM) (Figure 5) of these samples. The images show that the polyelectrolytes do not form true multilayers; instead, globules of polyelectrolyte complex form on the surface of the silica colloids.

^1H Chemical Shifts. The ^1H NMR spectra of the multilayers were acquired using Hahn spin-echo mea-

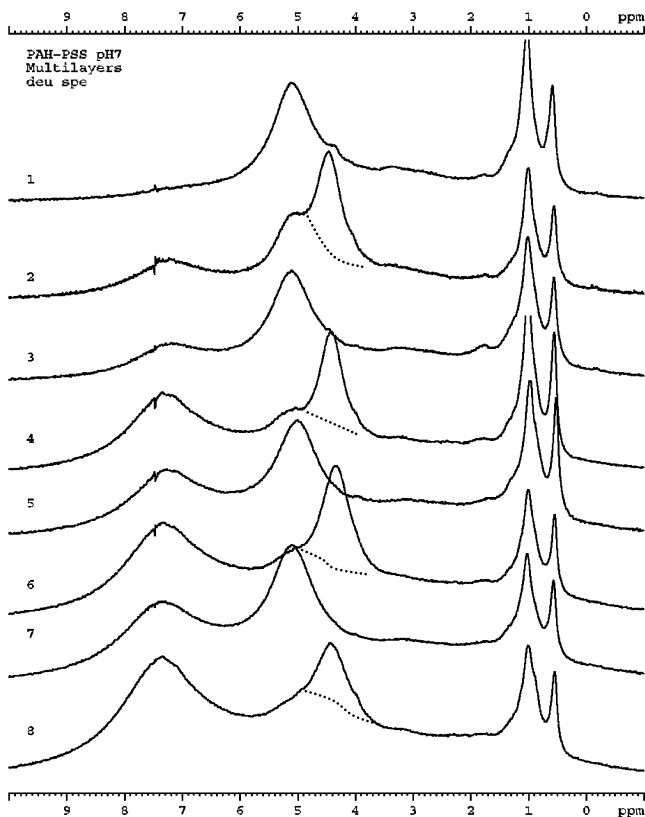


Figure 6. Hahn spin-echo of multilayers assembled at pH 7 (deuterated water has been used). Layer numbers are given to the left. Dashed lines are guides to the eye only and indicate substrate water peaks.

measurements. The Hahn spin-echo is used to reveal information on the chemical environment of the components of the films through the observed chemical shift. The water peak at 5.0 ppm dominates the spectra because of the large amount of water that is associated with the polyelectrolytes and the silica substrate (Figure 6). To suppress the water signal and observe the polyelectrolyte peaks, the samples were dried and then rehydrated with D_2O . For the first layer, the broad peak at 1–3 ppm is due to the CH and CH_2 protons of PAH. Dry PAH has an NH_3 peak at 8 ppm, which vanishes upon adsorption. The absence of the peak for the amino group is attributed to broadening because of exchange with the water protons. The peak at 5.0 ppm because of water associated with the substrate and the polycation is still observed after treatment with D_2O . After adsorption of the second layer (PSS), additional peaks from the aromatic protons at 7.0–7.4 ppm appear and the water peak shifts upfield from 5.0 to 4.3 ppm. All the odd layers (PAH terminated) contain a single water peak at 5.0 ppm, while the even layers (PSS terminated) display two water peaks at 4.3 and 5.0 ppm. The peak for the water associated with the polyelectrolyte film coincides with that of the water associated with the silica substrate when PAH forms the outer layer. The relative intensities between water associated with the substrate and water associated with the film can be seen in the even-numbered layers in Figure 6. It is apparent that as film growth proceeds, the ratio of substrate water to film water decreases. The alternation in the chemical shift of the water associated with the film, shown in Figure 7, has been observed in the strong polyelectrolyte PDADMAC/PSS system and indicates that the nature of the water environment within the

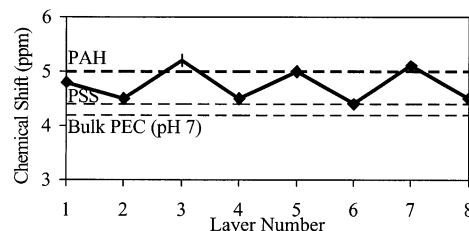


Figure 7. A plot of the chemical shifts of the water adsorbed in PEM films. In addition, the shifts of the water associated with the PEC, PSS, and PAH are indicated.

film is different depending on the outermost layer. The chemical shift of water associated with PSS capped multilayers (4.3 ppm) is close to that of the water peak of bulk PAH/PSS polyelectrolyte complex (4.2 ppm), indicating that the environment of the water associated with complete bilayers is similar to that of the bulk PEC.

The spin-echo experiments for the PAH/PSS multilayers assembled at pH 10 both prior to and after treatment with D_2O showed the same polymer resonances as well as a water peak at 5.0 ppm. Unlike the PEMs assembled at pH 7, no alternation of the water chemical shift is observed. Upon raising the temperature to 90 °C, the single water peak at 5.0 ppm separates into three water peaks. These three types of water environments may be due to the silica substrate, the polyelectrolyte film, and the formation of some bulk PEC as revealed by the TEM images.

1H Double-Quantum (DQ) MAS NMR. 1H double-quantum (DQ) MAS NMR experiments were used to selectively observe the proton signals of the polyelectrolytes. These experiments were carried out using the back-to-back (BABA) pulse sequence, which reintroduces the dipolar coupling that is removed by magic-angle spinning.¹¹ Protons with strong dipolar couplings recouple in a short period of time while protons that are weakly coupled, because of larger internuclear distances or enhanced molecular mobility, require longer recoupling periods. When a short recoupling time is applied to the PAH/PSS multilayers, the resonances attributed to the polyelectrolytes survive while the mobile (weakly coupled) water signal vanishes. After adsorption of the first layer, two peaks in the 1H DQ MAS NMR spectra are observed (data not shown). The peak at 1.8 ppm is due to the CH and CH_2 protons of the PAH, the peak at 3.0 ppm is assigned to the CH_2N protons, and no signal for the NH_3 group is observed, as in the Hahn spin-echo spectra. The second layer, which has PSS as the terminating layer, has the same spectra as the first layer with the addition of a broad peak at ~7.0 ppm because of the aromatic protons. No change in the 1H chemical shifts of the polymers is observed as layers are added.

2D 1H DQ MAS NMR experiments are commonly used to probe the dipolar couplings between various protons within a system and thus the spatial proximity of different chemical groups. Under the conditions of this experiment, a double-quantum signal should appear if the dipolar coupled protons are separated by less than ~3.5 Å.¹¹ Long recoupling times (in terms of an integral number of rotor cycles) were used to detect weakly dipolar coupled spins. As seen in Figure 8, for PSS the autocorrelation peak of the aromatic protons appears at (14.8 ppm, 7.4 ppm), while the autocorrelation peak for PAH is at (6.0 ppm, 3.0 ppm). Cross-peaks due to

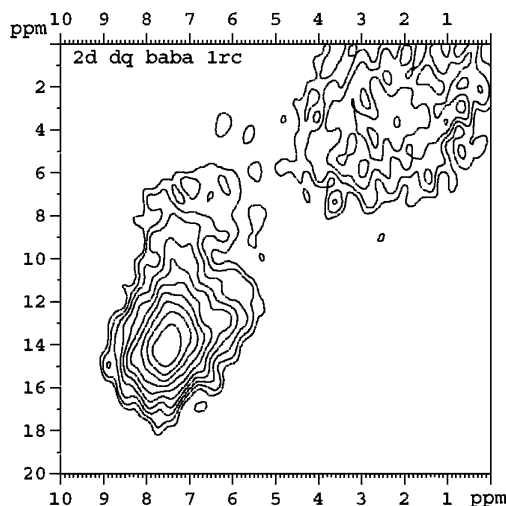


Figure 8. 2D DQ BABA with one rotor cycle for PAH/PSS PEC.

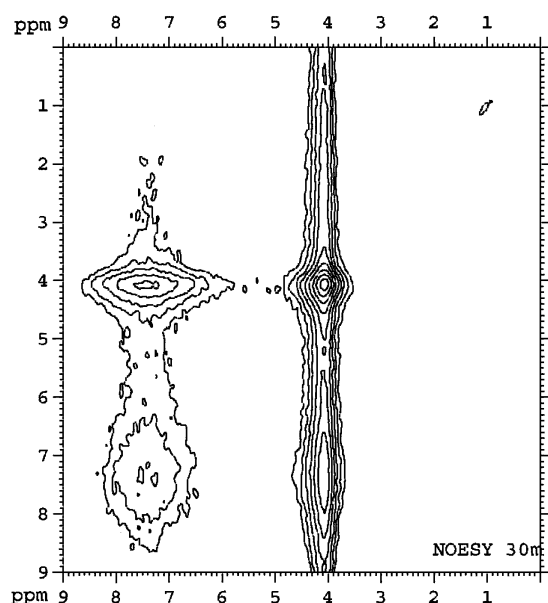


Figure 9. NOESY spectra of PAH/PSS PEC prepared at pH 7.

dipolar couplings between the PAH and PSS protons would occur at (10.4 ppm, 7.4 ppm) and (10.4 ppm, 3.0 ppm). However, there are no such cross-peaks even for long recoupling periods regardless of layer number or assembly conditions (i.e., pH 7 and pH 10). This contrasts the situation in the strong-strong polyelectrolyte system studied earlier,^{10,14} where the corresponding cross-peaks are observed in both the bulk complex and in the multilayers. The CH and CH₂ DQ signals decay very fast and are much weaker than the aromatic PSS DQ signal. This would make cross-peaks difficult to detect even in the bulk complex (Figure 8).

NOESY DATA. NOESY spectra allow for the determination of correlations between protons within the multilayer without suppression of some signals, unlike the DQ 2D BABA experiments. As was done for all proton measurements, treating the samples with D₂O allowed for the simplification of the spectrum. The bulk PAH/PSS complex shows cross-peaks between the water and PSS (Figure 9). No correlations between PAH and water nor between the polyelectrolytes is observed. The adsorption of the first layer of PAH results in the

appearance of autocorrelation peaks belonging to the backbone protons (~1.0 ppm) and the methylene protons (~3.0 ppm) of the polycation as well as the water (5.0 ppm) (Figure 10). The adsorption of layer two (PSS) results in two additional peaks along the diagonal at 7.4 ppm because of the protons on the aromatic ring and a peak at 4.5 ppm because of water that is associated with the film. In addition, cross-peaks between the PSS aromatic protons and the film water are observed (Figure 10). As additional layers are added, no additional correlations arise. In general, when PSS is the terminating layer, two water peaks occur at 5.0 and 4.3 ppm. For films terminated with PAH, there is only one water peak at 5.0 ppm.

The NOESY spectra for layers 12–14 were performed for the multilayers assembled at pH 10. Unlike the pH 7 multilayers, no alternation of the chemical shift of the film-associated water with layer number occurs; there is a single water peak at 5.0 for all layers. For both layers 12 and 14 (PSS terminated layers), the appearance of cross-peaks between the substrate/film water at 5.0 ppm and the PSS aromatic protons (7.4 ppm) is observed (data not shown). However, when the terminating layer is PAH, no cross-peaks for PAH and water are observed and the PSS–water cross-peaks remain, indicating that the water remains associated with the PSS.

Relaxation Measurements. The mobility of the polyelectrolytes and the water associated with the film was probed by relaxation measurements. Spin–lattice relaxation measurements probe motions in the megahertz (MHz) frequency range. Both proton and carbon T₁ measurements were performed. The ¹³C T₁ measurements have the advantage of selectively probing the polycation and polyanion, while ¹H T₁ measurements allow for the study of the motion of the associated water.

The proton T₁ values of the resonances at 7.4 and 5.0 ppm for PSS and the water are shown in Figure 11. The T₁ values for PAH could not be determined conclusively because of overlapping peaks. Within experimental error, little change in the relaxation times for PSS is seen as layers are added; however, there is a slight decrease in the T₁ values of the water. From variable temperature (VT) measurements, it was found that PSS is in the slow motion regime of the T₁ versus autocorrelation time curve, while the water lies on the fast motion regime. Therefore, the decrease in T₁ would indicate that the mobility of the water decreases as layers are added.

Films assembled at pH 7 which had been swollen by exposure to D₂O vapor and then stored at ambient humidity (rather than oven-dried) displayed an alternation in relaxation time as a function of layer number for the film water (Figure 12). The mobility of the water increases and then decreases when PAH and PSS are the outermost layers, respectively. This is similar to the PDADMAC/PSS system in which the water for the polyanion-terminated films experienced a decrease in mobility when the multilayers were sufficiently hydrated.¹⁰

The proton T₁ measurements for the multilayers assembled at pH 10 are given in Figure 11. Unlike the films assembled at pH 7, the ¹H T₁ values of PSS experience an alternation between low and high values when PSS versus PAH is the outermost layer, respectively, implying that the polymer mobility increases when PSS forms the outer layer. The T₁ relaxation data

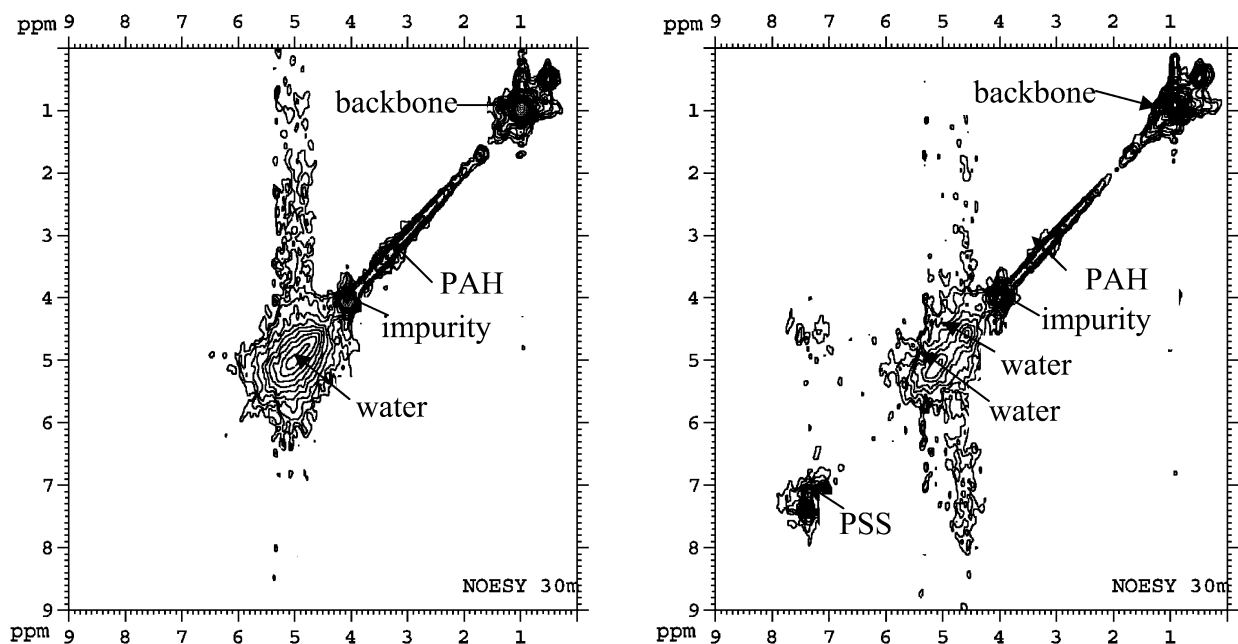


Figure 10. NOESY spectra of layer 1 (left) and layer 2 (right) assembled at pH 7 (30-ms mixing time).

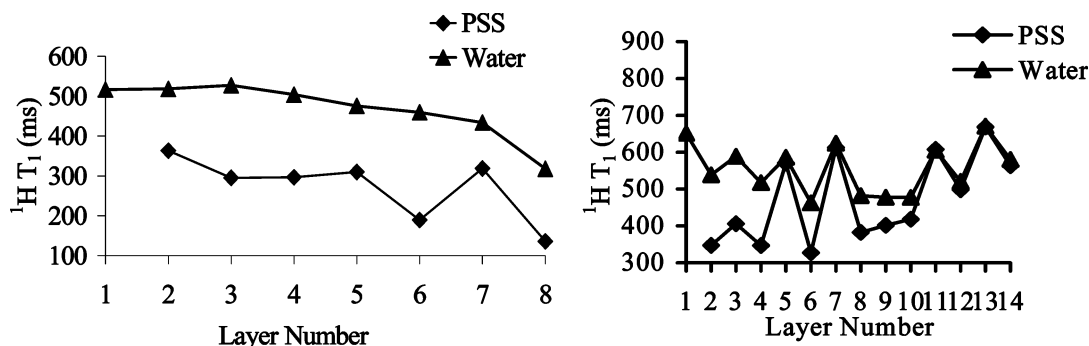


Figure 11. PAH/PSS PEM assembled at pH 7 (on the left) and at pH 10 (on the right) ^1H T_1 values as a function of layer number.

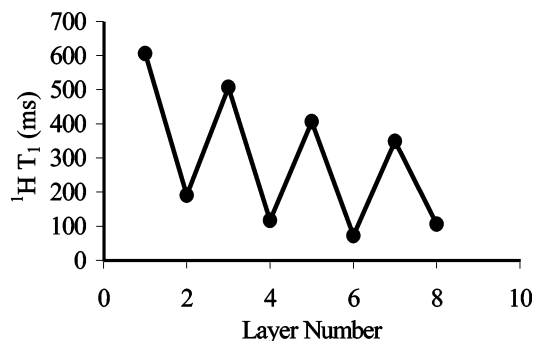


Figure 12. ^1H T_1 values as a function of layer number for the water peak for films assembled at pH 7 after being swollen and dried by exposure to the atmosphere.

for the water peak (Figure 11) shows the same trend as the sufficiently hydrated pH 7 films.

The measurement of ^{13}C $T_{1\rho}$ can be used to characterize motions in solid polymers and to evaluate chain dynamics in the 10–1000 kHz frequency range.¹⁵ ^{13}C $T_{1\rho}$ relaxation is not influenced by spin diffusion because of the small dipolar coupling due to the low natural abundance of ^{13}C and large separation of the nuclei. While ^{13}C $T_{1\rho}$ measurements are useful in providing information on mobility, the interpretation of the data

is influenced by the fact that the static ^1H – ^1H spin–spin processes contribute to the relaxation, reducing the observed ^{13}C $T_{1\rho}$ values. If there is an exponential static-field dependence, this is an indication that the spin–spin mechanism dominates, while a weaker dependence suggests that molecular motion is important.¹⁵ A non-exponential dependence of the ^{13}C $T_{1\rho}$ values (data not shown) was observed and indicates that proton spin–spin relaxation is not a predominate mechanism. The ^{13}C $T_{1\rho}$ values of the two polyelectrolytes of the multilayer are slightly different, but the values for a given polyelectrolyte does not change as layers are added, indicating that there is little variation in the chain motion in the kHz range.

The ^{13}C T_1 measurements as layers are added are given in Figure 13 for the PEMs assembled at pH 7 and pH 10. The slightly larger values for ^{13}C T_1 for the bulk PAH/PSS complex indicate that the mobility of the individual components within the bulk complexes is more restricted than within the multilayers. In the multilayers assembled at pH 7, the oscillating ^{13}C T_1 values indicate that there is a decrease in mobility upon PAH adsorption and a subsequent increase when PSS is adsorbed. The ^{13}C T_1 values of the multilayers assembled at pH 10 show little variation with layer number.

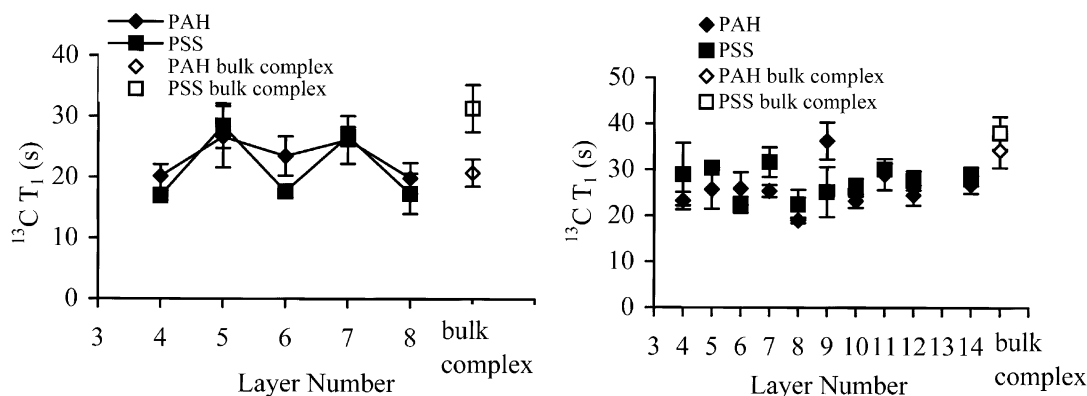


Figure 13. ^{13}C T_1 measurements for PAH/PSS multilayers assembled at pH 7 (on the left) and pH 10 (on the right).

Discussion

L-B-L Growth of PEMs. Zeta potential measurements are typically used as an indirect method of measuring the layer-by-layer growth of polyelectrolyte multilayers deposited on colloidal substrates. The direct monitoring by NMR was important for films assembled at pH 10 since electrophoretic mobility suggested that no multilayer growth had occurred. From the relative peak areas for these films, it is apparent that while films assembled at pH 7 exhibit the often seen 1:1 stoichiometry as layers are added, this is not the case for films assembled at pH 10. Multilayers assembled at pH 7 have both the polyions in a fully charged state and thus behave as strong polyelectrolytes.¹⁶ However, for films assembled at higher pH values, the polycation is no longer fully charged and the adsorption behavior in this system deviates from the typical 1:1 stoichiometry, making the films unstable. The instability of the multilayers assembled at pH 10 can be seen in the transmission electron microscope images (TEM) of these films. The images show that the polyelectrolytes do not form true multilayers; instead, globules of polyelectrolyte complex form on the colloid surface. This is predicted theoretically for films in which the polycation–polyanion complex interaction is large compared to the substrate–polycation electrostatic attraction.¹⁷

At higher pH values, PAH adsorbs in a coiled conformation because of the lower charge density. Adsorption of the coiled polyelectrolyte allows for more chains to interact with the fully charged surface, resulting in an increase in the overall adsorbed amounts.⁶ In the present study, twice as much PAH adsorbed than PSS at pH 10. By ellipsometry, Riegler et al. also found that PAH adsorbed in larger amounts than PSS, with PAH exceeding PSS by typically 50% up to 100% in high ionic concentrations at pH 5.5.¹⁸ They attributed this excess to salt screening, which necessitates an increase in the amount of PAH adsorbed in order to have charge compensation.

Polyelectrolyte Complexation and Dynamics. The 2D spectra (2D BABA, NOESY), which probe the packing of the two polyelectrolytes, show no cross-peaks in either the multilayers or the bulk complex. In contrast, correlations between polyelectrolyte components were observed in the PDADMAC/PSS multilayers for every layer.¹⁰ For the PAH/PSS films assembled at pH 7, the PAH is fully charged and should behave similarly to a strong polycation such as PDADMAC. The lack of cross-peaks could be attributed to an enhanced mobility as compared to the PDADMAC/PSS multilayers or the amount of water associated with these films. However,

these reasons can be ruled out since cross-peaks were also not observed for the bulk PAH/PSS complex. Furthermore, the NMR data indicates that PDADMAC is more mobile than PAH when complexed to PSS in the PEMs. Another reason for the lack of cross-peaks may be due to the different structures of the polycations PAH and PDADMAC. In the PDADMAC/PSS complex, the cross-peak is observed between the $\text{N}-\text{CH}_3$ protons of PDADMAC and the aromatic protons of PSS. The CH_2N protons of PAH may be located too far away (> 3.5 Å) from the aromatic PSS protons for sufficient dipolar couplings to excite a double quantum signal. Finally, the lack of cross-peaks may be simply due to the weakness of the broad PAH signals.

The mobility of the adsorbed polyelectrolytes was studied by ^1H and ^{13}C T_1 measurements. For films assembled at pH 7, ^1H T_1 measurements show relatively small changes in mobility for PSS as multilayer growth occurred, while multilayers assembled at pH 10 show some alternation in the proton relaxation times for PSS as a function of layer number. The trend indicates that the polymer mobility increases when PSS forms the outer layer. Because of the poor resolution of PAH, ^1H NMR could not be used to directly detect mobility changes of this polyelectrolyte. Furthermore, proton spin diffusion should lead to common T_1 values for the two complexed polyelectrolytes. However, these problems were circumvented by ^{13}C T_1 measurements. In the pH 7 multilayers, an alternation between low and high ^{13}C T_1 values occurs when PSS and PAH are the outermost layers, respectively. Since the polyelectrolytes are in the slow motional regime with respect to T_1 , the mobility of both polyelectrolytes increases when PSS is the outermost layer. This alternating behavior may be the result of changes in conformation, changes in hydration within the film as layers are adsorbed, or differences in the intrinsic mobility of the polyelectrolytes. The first situation has been previously suggested; the addition of a new layer produces changes in the conformation of the underlying layers⁶ which in turn causes changes in mobility. The second idea is supported by previous studies whereby the mobility of the films is seen to be dependent on the presence of water.¹⁰ If when PSS is adsorbed the multilayer “swells”, an increase in polymer chain mobility is expected. The subsequent addition of PAH could cause the multilayer to “shrink” and would result in a decrease in mobility.¹⁹ However, this behavior was proposed for PEMs deposited on colloids that were suspended in water whereas our studies were conducted for dried samples. The final suggestion is that the variation in mobility is a result

of the differences in the intrinsic mobilities of the bulk polyelectrolytes. The mobilities of the bulk polyelectrolytes increase in the following order: PAH > PSS > PDADMAC. This is supported by variable temperature NMR spectra of water-plasticized PDADMAC, PSS, and PAH which demonstrate motional narrowing at 70 °C, 100 °C, and >100 °C, respectively (T_g not available). The polyanion that forms the outer layer will be partially complexed with free loops and tails, which are charge compensated with small counterions. When PAH forms the outer layer, its noncomplexed segments are less mobile than those of PSS when it forms the outer layer.

Behavior of Water in the Film. For films assembled at pH 7, an alternation in the adsorbed water chemical shift can be seen as a function of layer number. For polycation terminated films, only one peak at 5.0 ppm is observed and corresponds to the overlapping signal of the water associated with both the film and the substrate, while for polyanion terminated films a separate peak for the film water appears at 4.3 ppm. 2D correlations are seen between only PSS and the water peak at 4.3 ppm, confirming the assignment of this peak. On the other hand, films assembled at pH 10 show one water peak at 5.0 ppm for both PAH and PSS terminated films, reflective of the unstable multilayer growth. However, upon heating a polycation terminated multilayer (layer 13) assembled at pH 10, the resonances for the water associated with the substrate, multilayer, and bulk complex were resolved.

^1H T_1 measurements show that the mobility of the water decreases with increasing layer number. However, T_1 measurements are averages of the entire water in the sample (water in the bulk of the film, the film's surface layer, and water associated with the silica substrate). The decrease in water mobility may be explained by the increasing restriction of the bulk water in the underlying layers. The alternation in the water relaxation times with layer number is only seen for films with sufficient water content. Films with less water present to swell the multilayer are relatively more constrained, making changes in mobility difficult to observe.

This alternation in the water mobility, also observed indirectly from NMR solvent relaxation measurements by Schwarz et al. for colloidal samples suspended in water, was proposed to be the result of reversible swelling as a consequence of the outermost layer.¹⁹ The observed alternation of the solvent relaxation times of PAH/PSS multilayers led to the conclusion that the water mobility decreased when the polycation formed the outer layer. However, in the present study, the water mobility in films capped with the polycation is higher. The differences in mobility between our system and that studied by Schwartz may be because in the latter study the overall water mobility is the combination of bulk water, water associated with free polymer chains, water associated with the substrate, as well as water associated with bound polymer. In the current study, the water associated with the substrate and the bound polymer determines the overall water mobility and is directly observed. Furthermore, in Schwartz's study the alteration observed is thought to arise from changes in surface potential and such a mechanism would apply only to films in contact with solvent, which is not the case in the present study. The mechanism by which this variation in water mobility occurs for films in the absence of solvent is unknown at this point.

Polyelectrolyte Conformation. The differences seen for films assembled at pH 7 and pH 10 can be explained by the manner in which the multilayers form. It has been proposed that PAH/PSS films assembled at high pH (9.5) have a relatively low degree of ionic cross-linking and a high extent of chain loopiness, which creates sufficient flexibility for the system to access various conformational states.⁷ These conformational differences between PAH/PSS films assembled at high versus low pH have also been observed in swelling experiments, where it was found that films assembled at high pH exhibited pH sensitive swelling behavior in contrast to films assembled at neutral pH.⁷

If PAH at pH 7 adsorbs in a more planar fashion, the presence of added layers would simply decrease the overall mobility of the film components. On the other hand, films assembled at pH 10 would adsorb in less planar fashion (because of the coiled nature of the PAH at this pH value), producing a film in which the polymer chains and associated water should have inherently greater motional freedom. The interpretation of the data for films assembled at pH 10 is complicated by the presence of bulk complex. While the ^1H T_1 data indicates an alternation in polymer mobility as a function of layer number, the ^{13}C T_1 data does not. This apparent discrepancy may be rationalized by considering that for the ^1H T_1 measurements the narrow component (i.e., more mobile component) is represented to a greater degree than the less mobile component. Since the polymer in the multilayer is more mobile than in the bulk complex, the ^1H T_1 values may more strongly reflect the mobility of the adsorbed polyelectrolytes. ^1H – ^{13}C cross polarization, which favors the less mobile component, was used for the ^{13}C T_1 measurements and would have the opposite effect. The presence of the bulk complex damps the oscillation in the ^{13}C T_1 values in the multilayers assembled at high pH.

Conclusions

As far as the properties of the adsorbed water, the weak–strong PAH/PSS polyelectrolyte films assembled at pH 7 behave similarly to the previously studied strong–strong (PDADMAC/PSS) polyelectrolyte films since both PAH and PSS are fully charged at this pH. The overall mobility of the water in films assembled at pH 7 decreases with added layers and strong oscillations in the adsorbed water mobility are observed for films with sufficient water content. The stronger association of water with PSS is responsible for the increase in water mobility for PAH terminated films. Relaxation studies of PAH/PSS films detect an alternation in polymer mobility, with an increase in mobility when the polyanion forms the outer layer. The opposite pattern was observed for the PDADMAC/PSS films. This difference is attributed to the trends in the intrinsic mobilities of the pure bulk polymers (PDADMAC > PSS > PAH) since the polymer chains at the outermost layer form loops and tails which are charge compensated by small counterions, similar to the pure bulk polymers. The films assembled at pH 10 do not show the usual 1:1 stoichiometry. Instead, PAH is adsorbed in large excess because of the coiled state of the chains at this high pH. Interpretation of the dynamic behavior of films assembled at pH 10 was complicated by the formation of some bulk polymer complex that dampened the oscillations in the adsorbed water chemical shift and the polymer relaxation times.

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References and Notes

- (1) Burke, S. E.; Barrett, C. J. *Langmuir* **2003**, *19*, 3297.
- (2) Yu, A.; Caruso, F. *Anal. Chem.* **2003**, *75*, 3031.
- (3) Caruso, F.; Yang, W.; Trau, D.; Renneberg, R. *Langmuir* **2000**, *16*, 8932.
- (4) Krasemann, L.; Tieke, B. *Langmuir* **2000**, *16*, 287.
- (5) Xie, A. F.; Granick, S. *Macromolecules* **2002**, *35*, 1805.
- (6) Hoogeveen, N. G.; Cohen-Stuart, M. A.; Fleer, G. J.; Boehmer, M. R. *Langmuir* **1996**, *12*, 2, 3675.
- (7) Hiller, J.-A.; Rubner, M. F. *Macromolecules* **2003**, *36*, 4078.
- (8) Shenoy, D. B.; Antipov, A. A.; Sukhorukov, G. B.; Möhwald, H. *Biomacromolecules* **2003**, *4*, 265.
- (9) Smith, R. N.; Reven, L.; Barrett, C. J. *Macromolecules* **2003**, *36*, 1876.
- (10) McCormick, M.; Smith, R.; Graf, R.; Barrett, C. J.; Reven, L.; Spiess, H. W. *Macromolecules* **2003**, *36*, 3616.
- (11) Brown, S. P.; Spiess, H. W. *Chem. Rev.* **2001**, *101*, 4125.
- (12) Caruso, F.; Möhwald, H. *J. Am. Chem. Soc.* **1999**, *121*, 6039.
- (13) Kwei, T. K.; Dai, Y. K.; Lu, X.; Weiss, R. A. *Macromolecules* **1993**, *26*, 6583.
- (14) Rodriguez, L. N. J.; De Paul, S. M.; Barrett, C. J.; Reven, L.; Spiess, H. W. *Adv. Mater.* **2000**, *12*, 1934.
- (15) Koenig, J. L. *Spectroscopy of Polymers*; ACS Professional Reference Book; American Chemical Society: Washington, DC, 1992; pp 260–261.
- (16) Farhat, T.; Yassin, G.; Dubas, S. T.; Schlenoff, J. B. *Langmuir* **1999**, *15*, 6621.
- (17) Messina, R.; Holm, C.; Kremer, K. *Langmuir* **2003**, *19*, 4473.
- (18) Riegler, H.; Essler, F. *Langmuir* **2002**, *18*, 6694.
- (19) Schwarz, B.; Schönhoff, M. *Langmuir* **2002**, *18*, 2964.

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