13C Solid-State NMR Study of Polyelectrolyte Multilayers

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ABSTRACT: Polyelectrolyte multilayers have been prepared by consecutively adsorbing poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium 4-styrenesulfonate) (PSS) from aqueous solution onto colloidal silica (70–100 nm in diameter), with a total of five bilayers being prepared. The multilayer growth was followed by electrophoretic mobility as well as solid-state NMR spectroscopy. The electrophoretic mobility measurements show the expected reversal in the z-potential with the alternate adsorption of the polycation and polyanion. The alternation in the relative intensities observed in the 13C solid-state NMR spectra was used to qualitatively follow the layer-by-layer growth. Relaxation measurements show that the mobility of the polyanion is found to remain constant throughout the layer-by-layer assembly, while the mobility of polycation decreases with increasing numbers of layers.

Introduction

The layer-by-layer (L-b-L) method of preparing polyelectrolyte multilayer (PEM) films has attracted much interest in recent years, since the early development by Decher.1,2 This self-assembly technique allows for the formation of multilayers on a wide range of charged solid supports by the sequential adsorption of oppositely charged polyelectrolytes from dilute aqueous solutions. The ability to tailor the film properties by varying the preparation conditions (ionic strength, pH, and polyelectrolyte concentrations) makes the L-b-L technique especially attractive.3 With the alternate adsorption of anionic and cationic polymers becoming an increasingly important method for producing uniform thin films, these materials have promising futures in the areas of electrooptics, coatings, catalysis, separations, diagnostics, and drug delivery.2,4,5 The L-b-L method most recently has been extended from macroscopically flat surfaces of silicon, glass, and gold to particle substrates ranging from inorganic colloids to enzymes and blood cells.3,6,9 The encapsulation of colloidal particles by polyelectrolytes has been studied by electrophoresis, dynamic light scattering, particle sizing, and fluorescence intensity measurements.3,6,10 Transmission, scanning electron, and atomic force microscopies have also been employed to characterize PEMs on colloidal substrates.11

Although there has been some effort to understand the microscopic structure of these films, very little experimental work using techniques that directly probe the dynamics and conformation of the polyelectrolyte chains has appeared in the literature. The theoretical understanding of the growth mechanism of PEMs is at a very early stage, and the dependence of the film structure on various preparative parameters is usually rationalized in terms of their effect on chain conformation and mobility. The charge overcompensation is attributed to the presence of dangling loops and tails at the surface, and this fluidity of the outermost layer allows interpenetration of the next polyelectrolyte layer, resulting in a nonstratified film. The nonlinear growth of the first few layers is interpreted in terms of a roughening of the polymer/polymer interface which creates a progressively larger number of adsorption sites for subsequently deposited layers.12–14 The formation of thick layers at high ionic strength is attributed in part to the adsorption of polymer coils rather than extended chains.15,16 However, direct measurements of the variation in the chain mobility and conformation with preparative parameters and the number of layers are needed before these assumptions about the microscopic properties of PEMs can be validated.

Solid-state nuclear magnetic resonance (NMR) spectroscopy, well suited to probe these variables, is routinely used to characterize the structure and dynamic properties of polymers in the bulk state.17 Recently, Rodriguez and co-workers reported the direct observation of the complexation between PDADMAC and PSS in a PEM system comprised of two bilayers adsorbed onto silica colloids using high-resolution solid-state 1H NMR techniques.18 These experiments demonstrated the feasibility of using solid-state NMR to study the interaction of the polyelectrolytes adsorbed onto silica colloids. While the high sensitivity of 1H NMR is advantageous for surface studies, the resolution is poor in the solid state, thus limiting the amount of information that can be obtained. Quantitative studies are complicated by the large 1H signals of the adsorbed water and the silica substrate. Furthermore, proton spin diffusion prevents separate observation of the dynamic behavior of the polyanion vs the polycation via relaxation measurements. Alternatively, 13C NMR gives higher resolution spectra without interference from the substrate, but there is the problem of low sensitivity due to the low natural abundance of this isotope. The combination of magic angle spinning (MAS) and 1H–13C cross-polarization (CP) partially circumvents the obstacles of low sensitivity and long relaxation times, permitting 13C spectra of organic adsorbates to be acquired within reasonable time periods.

In an extension of our earlier work, solid-state 13C CP MAS NMR spectroscopy is used here to characterize a polyelectrolyte multilayer comprised of five bilayers. Our initial samples only consisted of two bilayers were deposited on colloidal silica,18 which proved insufficient for 13C relaxation measurements. The resolution provided by 13C NMR allows the signals of the polycation and polyanion to be monitored separately for direct
observation of the layer-by-layer growth. Relaxation measurements as a function of layer number reveal the differing chain dynamics of PSS and PDADMAC with increasing number of layers. Finally, variable-temperature NMR studies of the multilayers were used to provide an estimate of the motional frequencies of the polymer chains and dynamic properties of the PEMs.

Experimental Section

Materials. Poly(diallyldimethylammonium chloride) (PDADMAC), $M_w = 400000–500000$ g/mol, and poly(sodium 4-styrenesulfonate) (PSS), $M_w = 70000$ g/mol, were purchased from Aldrich. Snowtex silica colloids (nominal diameter 70–100 nm) were provided by Nissan Chemical Corp. Millipore Milli-Q water (18 MΩ resistivity) was used for all sample preparations. The molecular structures of the polymers and the sample preparation scheme are shown in Figure 1.

Sample Preparation. 500 mL of a 0.02 M PDADMAC, 0.2 M NaCl 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. 500 mL of water (pH 10) was then added to the sample, and the solution was sonicated and left to stand for a minimum of 30 min. The supernatant was then removed and rinsed overnight at 70 °C for characterization studies. To the remaining colloidal solution was added 500 mL of a 0.02 M PSS, 0.4 M NaCl solution. Similar adsorption and washing steps were performed, until a total of five PDADMAC–PSS bilayers had been prepared.

A relatively large amount of sample is required for the solid-state NMR studies, and there is considerable loss of sample as layers are added due to the centrifugation steps. A salt concentration of 0.4 M was found to make the centrifugation of the even layer colloids (PSS outer layer) easier, thus allowing a greater amount of sample to be recovered for NMR studies. However, a salt concentration of 0.4 M resulted in poorer adsorption of the PDADMAC. Therefore, different salt concentrations of 0.2 and 0.4 M were used to adsorb the PDADMAC and PSS, respectively, to maximize both the amount adsorbed and the amount recovered after the washing and centrifugation steps. A second set of samples were prepared in which the salt concentration was kept at 0.2 M for both PSS and PDADMAC adsorption. The elemental analyses for these samples were similar to those shown in Table 1 (data not shown), indicating that this particular difference in ionic strength is not a major factor in the relative the amounts of polyanion and polycation adsorbed.

Electrophoretic Mobility (EPM) Measurements. Electrophoretic mobilities of the bare and multilayered silica nanoparticles were measured on a Microelectrophoresis Apparatus Mk II (Rank Brothers, Botttingham) and were converted to $\zeta$-potentials using the Smoluchowski equation. 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 10.0. Twenty mobility measurements were performed on each sample, and the averages were converted to $\zeta$-potentials.

NMR Measurements. 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 $^1$H 90° pulse widths were 4 $\mu$s, and an average of 30 000 scans were taken. The $^1$H measurements were achieved via $^1$H CP-MAS and were carried out by applying $^1$H 90° pulses that were left on (spin-locked) for various values of $t_1$, while cross-polarization with the carbons was achieved. Subsequent proton decoupling allowed for carbon detection with a total of 512 scans acquired for each $t_1$ evolution period. The $^1$C $T_1$ measurements were carried out by means of a modified inversion–recovery $T_1$ experiment, in which the 180° pulse was replaced with a 90° pulse for cross-polarization. A total of 900 scans were acquired for all $^1$C $T_1$ spectra. All measurements were performed at a spinning speed of 4 kHz.

Results and Discussion

Electrophoretic Mobility. EPM measurements were performed to monitor multilayer formation as the polyelectrolytes were adsorbed onto the colloid. While EPM measurements are an indirect method of investigating multilayer formation, they are useful in giving a preliminary indication of polymer adsorption through changes in the surface charge. Figure 2 demonstrates the expected reversal in the sign of the $\zeta$-potential from positive to negative as the polycation and polyanion are adsorbed, respectively. Even though the $\zeta$-potential measurements suggest the continued growth of the multilayer, it is not unambiguous proof since it is not possible to discern between the growth of the multilayer vs the alternate adsorption and desorption of the polyanion.

Elemental Analysis. The elemental analysis confirmed the layer-by-layer growth of the multilayers on the colloidal silica. Figure 3 shows that the total amount adsorbed, as monitored from the total carbon content, increases in a linear fashion after the deposition of several bilayers. The amounts of PDADMAC vs PSS adsorbed, given in Table 1, were calculated from the nitrogen and sulfur contents. With the exception of the first layer, it is apparent that no PDADMAC desorbs when a PSS layer is added. For some layers, PSS decreases slightly after adsorption of a polycation layer. The amount of polymer adsorbed increases from ~1.3 mol of monomer per layer for the first layers to ~3.0 mol of monomer for last layers. The stoichiometry of the polyanions in the first few bilayers shows significant deviations from the 1:1 ratio found in the bulk PSS–PDADMAC polyelectrolyte complex. For even numbers of layers, where PSS is the outer layer, PSS is present in excess whereas the reverse is true for the odd number of layers. However, the stoichiometry appears to be tending toward the 1:1 ratio of the bulk complex with increasing number of layers as expected.

NMR Chemical Shifts and Intensities. The solid-state $^{13}$C CP-MAS NMR spectra of the 10-layer PEM adsorbed on the silica colloids are shown in Figure 4. Six $^{13}$C resonances of the two polymers of the complex are resolved in the spectra. The peaks with chemical shift values of 71, 55, and 27 ppm are assigned to the polycation (PDADMAC), while the peaks with chemical shifts of 140 and 127 ppm are due to the aromatic carbons of the polyanion (PSS). PSS and PDADMAC also have overlapping peaks at 40 ppm. By examining
the increase in relative intensity between the peaks arising solely from the PDADMAC vs those that arise from the PSS, it is possible to qualitatively see the layer-by-layer growth of the PEM as more layers are adsorbed. The first layer is comprised entirely of PDADMAC and has only its four characteristic peaks, while in the spectrum of the second layer comprised of PDADMAC and PSS all six peaks attributed to the two polyelectrolytes are visible. By the examination of the spectrum for three layers, it is evident that the PDADMAC has adsorbed onto the PSS layer rather than desorbing the PSS. This can be seen by the increase in intensity of the PDADMAC peak at 71 ppm relative to the PSS peak at 127 ppm for layer 3, which contains two layers of PDADMAC and one layer of PSS. This alternation in relative peak intensity between the PDADMAC and PSS occurs during each adsorption step.

Integration of $^{13}$C CP MAS NMR signals is not strictly quantitative due to variations in the relaxations parameters and the number of attached protons, which influence the cross-polarization efficiency. The cross-polarization efficiency is determined by the CP rate constant, $T_{\text{CH}}$, and the spin–lattice relaxation time in the rotating frame, $T_{\text{1p}}$. As discussed below, the $T_{\text{1p}}$ values of the two polymers do not differ greatly, so this parameter should not be a large source of variation in cross-polarization efficiency with layer number. $T_{\text{CH}}$ depends on the number of attached protons and should

Table 1. Amount of Polyelectrolyte (mg) Adsorbed/1 g of Silica as a Function of Layer Number and Stoichiometric Ratios Calculated from Elemental Analysis and NMR

<table>
<thead>
<tr>
<th>Layer</th>
<th>PDADMAC/1 g of silica</th>
<th>PSS/PDADMAC ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol of monomer (increment) ($\times 10^{-4}$)</td>
<td>mg</td>
</tr>
<tr>
<td>1</td>
<td>1.3 (±1.3)</td>
<td>24.6</td>
</tr>
<tr>
<td>2</td>
<td>0.9 (±0.4)</td>
<td>27.7</td>
</tr>
<tr>
<td>3</td>
<td>2.6 (±1.8)</td>
<td>56.5</td>
</tr>
<tr>
<td>4</td>
<td>2.7 (±0.1)</td>
<td>49.1</td>
</tr>
<tr>
<td>5</td>
<td>4.9 (±2.2)</td>
<td>105.0</td>
</tr>
<tr>
<td>6</td>
<td>4.7 (±0.2)</td>
<td>86.9</td>
</tr>
<tr>
<td>7</td>
<td>7.4 (±2.7)</td>
<td>136.7</td>
</tr>
<tr>
<td>8</td>
<td>7.2 (±0.2)</td>
<td>133.3</td>
</tr>
<tr>
<td>9</td>
<td>10.2 (±3.0)</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

*$^a$ S % weight not available for these samples. The moles of PSS monomer was estimated from the total C % and the moles of PDADMAC monomer calculated from the N % weight for these samples.

Figure 2. $\zeta$-potential measurements as a function of layer number for multilayer.

Figure 3. Elemental analysis of PDADMAC/PSS multilayer as a function of layer number.

the increase in relative intensity between the peaks arising solely from the PDADMAC vs those that arise from the PSS, it is possible to qualitatively see the layer-by-layer growth of the PEM as more layers are adsorbed. The first layer is comprised entirely of PDADMAC and has only its four characteristic peaks, while in the spectrum of the second layer comprised of PDADMAC and PSS all six peaks attributed to the two polyelectrolytes are visible. By the examination of the spectrum for three layers, it is evident that the PDADMAC has adsorbed onto the PSS layer rather than desorbing the PSS. This can be seen by the increase in intensity of the PDADMAC peak at 71 ppm relative to the PSS peak at 127 ppm for layer 3, which contains two layers of PDADMAC and one layer of PSS. This alternation in relative peak intensity between the PDADMAC and PSS occurs during each adsorption step.

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Figure 4. L-b-L growth of polyelectrolytes on silica obtained by solid-state $^{13}$C CP/MAS NMR. The corresponding layer numbers are given next to each spectrum. Odd layers correspond to PDADMAC-terminated layers, while even layers correspond to PSS-terminated layers.
be shorter for the methylene carbons at 70 ppm as compared to the aromatic carbons of the PSS, giving rise to a more efficient cross-polarization rate for the PDADMAC peak, but this should not be a large effect. The main parameter influencing the integrated intensities in this case is the large chemical shift anisotropy of the aromatic carbons, which spreads the signal intensity out over an array of spinning sidebands. The TOSS sequence suppresses the sidebands of the PSS aromatic signal, leaving only the center band at 127 ppm. The corrections due to the loss in the sideband contribution were calculated by running a PSS sample with and without the TOSS sequence. The integrated intensities of the four CH aromatic carbons, which resonate at 127 ppm for PSS, and the two methylene carbons at 71 ppm for PDADMAC were used to calculate the stoichiometric ratios which are listed in Table 1. The trends in the stoichiometric ratios are consistent with those calculated from the elemental analyses. The amount of PDADMAC is larger for odd numbers of layers, while PSS is larger for the even numbers of layers. The deviations from a 1:1 stoichiometric ratio are somewhat smaller than those calculated from the elemental analysis, decreasing with number of layers from 1.35 for PSS outer layer and 0.73 PDADMAC outer layer to 1.1 and 0.83, respectively.

Relaxation Measurements. 1. Spin–Lattice Relaxation in the Rotating Frame (T_1\text{H}) Measurements. Relaxation measurements were used to study the dynamics and conformation of the polyelectrolyte layers as the multilayers are built up. Since spin–lattice relaxation of protons in the rotating frame (T_1\text{H}) probes motion in the kilohertz range, this relaxation parameter is useful for dynamic studies of large molecules such as polymers. In the case of multicomponent systems, such as polymer blends, T_1\text{H} measurements also provide a crude assessment of the degree of phase separation due to proton spin diffusion. Spin diffusion, the spatial migration of magnetization, is very efficient for rigid organic solids which have an extended network of strongly dipolar coupled protons. Spin diffusion thus will lead to common proton spin–lattice relaxation times for glassy or crystalline polymers that are mixed at the chain level. The same T_1\text{H} value for the different components is indicative of domain sizes less than ~20 Å. Whereas T_1\text{H} values for dried samples of pure PSS and PDADMAC were 7 and 4 ms, respectively, a single T_1\text{H} of 7 ms was measured for the PSS and PDADMAC components in the bulk polyelectrolyte complex. In addition to providing mixing at the chain level, the polymer–polymer complexation will couple the motions of the PSS and PDADMAC chains. The T_1\text{H} values of PSS/PDADMAC multilayers as a function of layer number are presented in Figure 5. Within experimental error, there is very little change in the T_1\text{H} values as polyurea layers are added to the silica. Any variation in the mobility as detected by proton relaxation measurements may be masked by efficient proton spin diffusion since 1H double quantum NMR experiments showed that the two polymers in the multilayers are strongly associated as in the bulk polyelectrolyte complex. Another possibility is that there is little variation in the chain motion in the kilohertz frequency range as the layers are added.

13C Spin–Lattice (T_1\text{C}) Relaxation Measurements. 13C detection allows for the selective probing of the polycation and the polyanion as well as the side groups vs polymer backbone. Carbon relaxation measurements are a more selective probe of molecular motion due to the absence of spin diffusion, which is often problematic in 1H detection. 13C spin–lattice relaxation times in the laboratory frame, T_1\text{C}, are sensitive to motional frequencies in the megahertz range. In the case of polymers, rapid reorientation of side chain groups is often the main contributor to carbon spin–lattice relaxation. Carbon spin–lattice relaxation times in the rotating frame, T_1\text{H}, are used to detect the slower main chain motions in the 5–100 kHz range. T_1\text{H} measurements avoid the problem of spin diffusion, but coupling of the 13C spins to the proton dipolar system during the spin lock period often complicates interpretation.

To measure the relative mobilities of the polymers, it is necessary to determine whether the system is in the so-called fast- vs slow-motional limit. When the molecular motion is in the slow limit, an increase in the spin–lattice relaxation time, T_1, indicates a decrease in the motional frequencies, and the reverse is true for the fast limit. At the T_1 minima, the motional frequencies are on the order of the Larmor frequency of the nucleus under observation. Variable temperature measurements allow determination of which side of the T_1 vs correlation time curve the system lies on. Table 2 lists the variable temperature T_1\text{C} values for the ring methylene carbons of PDADMAC (71 ppm) and the aromatic carbons of PSS (127 ppm) for a multilayer containing six layers along with the bulk polyelectrolyte complex. The magnitudes of the changes in the carbon T_1 times with temperature are relatively small. A slow variation in T_1 with temperature is commonly observed for glassy polymers due to a low density of chain motions in the megahertz frequency range. A broad distribution of correlation times, also frequently observed for glassy polymers, will give rise to a shallow T_1 vs correlation time curve. Examination of the values in Table 2 shows that at room temperature the motional frequencies of PDADMAC and PSS in both the multilayers and the bulk complex are in the slow limit or near the T_1 minima.
Figure 6. $^{13}$C $T_1$ measurements for the multilayers as a function of layer number. Diamonds represent the PDADMAC component, and the squares represent the PSS component. Also shown are the values for the individual components of the bulk complex.

where the motional frequencies are close to the Larmor frequency (~75 MHz). The increase in $T_{1C}$ when the multilayer is heated above room temperature may be due to the system exceeding the $T_{1C}$ minima temperature. There is also the possibility that some water is lost during the long acquisition times, which would decrease the chain mobility and increase $T_{1C}$. However, the values of $T_{1C}$ were also found to vary with field strength, confirming that the systems are in the slow motion limit at room temperature.

Modulation of the heteronuclear C–H dipolar coupling is normally the main relaxation mechanism for carbons in organic solids. Since the size of the dipolar coupling drops off rapidly with distance, the relaxation of a particular carbon will depend on its distance from the reorienting group. For PDADMAC, the rapid rotation of the methyl groups is possible source of spin–lattice relaxation of the ring methylene carbons at 71 ppm but may be a weak contribution given that the methyl group is not directly attached to these carbons. Backbone motion, such as rotation about the backbone methylene carbon bonds, would produce more efficient relaxation if rapid enough since such motions would cause reorientation of the ring methylene C–H bonds. In the case of PSS, small angle reorientations or ring flips of the aromatic side groups would produce the most effective relaxation of the aromatic carbons at 127 ppm. The polymer–polymer complexation may both hinder and couple the possible motions responsible for the relaxation of the carbons of the two polynions.

The $T_{1C}$ values for the PSS and PDADMAC in the multilayers on the colloidal silica as a function of layer number are shown in Figure 6. Only samples with more than four layers provided sufficient sensitivity for $^{13}$C relaxation measurements. Assuming that the systems remain in the slow limit or close to the $T_{1C}$ minimum as layers are added, the increase in the $T_{1C}$ values of PDADMAC indicates a decrease in mobility with increasing numbers of layers. By contrast, little change is observed in the carbon spin–lattice relaxation times of PSS. Also plotted in Figure 6 are the $T_{1C}$ values for the PSS and PDADMAC components in the bulk complex, which were prepared under similar conditions to the multilayer. It is apparent that as multilayer growth continues, the $T_{1C}$ values of the PEM approach those of the bulk complex. This is not surprising since as the layers are added, the substrate has less of an effect on the polyelectrolyte layers, allowing the PDADMAC and PSS to behave similarly to the bulk complex. Other researchers have argued that it is appropriate to compare PEMs and PECs since the polyelectrolyte multilayer film formation process is similar to the formation of the polycation/polyanion bulk complex in solution. Given the extensive interpenetration of the polymers, the final structure is not a true 2-D structure but is rather more similar to the “scrambled egg” structure of bulk polyelectrolyte complexes. The bulk complex is motionally restricted due to the strong complexation between these polynions. This is expected since both PDADMAC and PSS are strong polyelectrolytes and are therefore charged completely along the length of the polymer chain.

The differences observed in the mobility of PDADMAC and PSS in the polyelectrolyte multilayers may be due to the differences in the intrinsic mobility of the bulk polymers or differences in the average surface chain conformations. In the bulk state, the mobility of PDADMAC is higher than that of PSS. The glass transition temperature of dry PDADMAC (~70 °C) is much lower than that of bulk PSS (~150 °C). Both polymers are plasticized by the adsorption of water with the $T_{g}$ of PDADMAC being lowered to below room temperature when the water content exceeds 20%. Whereas water plasticized PDADMAC shows a well-resolved $^1$H NMR spectrum under slow MAS at room temperature, PSS with a similar water content must be heated by 70 °C to see the onset of motional narrowing. The polyelectrolyte which forms the outer layer is only partially complexed with the lower layers, leaving more mobile segments forming loop and tails which are charge compensated by small counterions. When PDADMAC forms the outer layer, its noncomplexed segments are more mobile than those of PSS when it forms the outer layer. As more layers are added, this surface effect gradually diminishes due to the decrease in the fraction of mobile chains segments that are located at the surface, and the $^{13}$C spin–lattice relaxation times approach those of the bulk complex. Another contribution may be due to the different average conformations assumed by PSS vs PDADMAC upon adsorption. If PDADMAC adsorbs with a more mobile, loopy conformation as compared to PSS, the addition of subsequent layers will lead to a greater decrease in the mobility of PDADMAC as compared to PSS. However, at the high ionic strengths used to prepare these multilayers, both polymers should be in a celled state and are expected assume similar conformations upon adsorption. Because of the large molecular weights of PDADMAC (500 000 g/mol) and PSS (70 000 g/mol), differences in molecular weight should not have a significant effect upon the adsorbed conformations. The differences in the mobility of PDADMAC and PSS observed here by $^{13}$C NMR are strongly corroborated by recent measurements of the $^1$H dipolar couplings which also demonstrate that the changes in mobility during multilayer growth is strongly associated with the presence of water within the polyelectrolyte films. Measurements of the $^1$H dipolar couplings of dried multilayers show that the mobility of neither PSS nor PDADMAC varies with the number of layers in the absence of adsorbed water.

Summary

The use of colloidal silica allows the layer-by-layer growth to be followed quantitatively through elemental analysis and $^{13}$C NMR spectroscopy. The alteration of the PSS/PDADMAC stoichiometry shows that the poly-
ion constituting the outer layer is in excess ranging from 30% to 50% for the first few layers. The stoichiometry tends gradually to the 1:1 ratio observed for the bulk polyelectrolyte complex since increasing amounts of both the polycation and polyanion are adsorbed. The amount adsorbed increases from ~1.4 mol of monomer/g of silica for the first layers to ~3 mol of monomer/g of silica for the layers above five layers. Such nonlinear growth has been observed for a number of polyelectrolyte systems and is attributed to a roughening of the polymer/polymer interface and a corresponding increase in the number of accessible adsorption sites as layers are added. The extent of this nonlinear growth behavior depends on the particular polyanion/polycation combination as well as the substrate.

The similar $T_1^H$ values for the polyanion and polycation as well as the lack of variation with number of layers reflect the strong complexation between the polyelectrolytes in the multilayer film, which allows for efficient proton spin diffusion. However, the $^{13}$C spin–lattice relaxation measurements reveal that the mobility of PDADMAC in the multilayers (in the megahertz frequency range) is enhanced as compared to the bulk complex and becomes increasingly restricted as layers are added. In contrast, the mobility of PSS in the multilayers shows little variation from the bulk complex. One rationalization for this variation in the mobility of the two polyions in the multilayers is to assume that the mobility of the noncomplexed segments of PSS or PDADMAC at the outer layer should reflect the intrinsic differences in the dynamic properties of the bulk polymers ($T_0$(PSS) $\gg$ $T_0$(PDADMAC)). Ongoing solid-state NMR studies using different polyion combinations should help clarify the factors that influence these dynamic properties of polyelectrolyte multilayers.

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**References and Notes**

(25) Reven, L. Unpublished data.