Mechanism of the pH-Induced Discontinuous Swelling/Deswelling Transitions of Poly(allylamine hydrochloride)-Containing Polyelectrolyte Multilayer Films

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ABSTRACT: The mechanism of the discontinuous swelling/deswelling transitions exhibited by polyelectrolyte multilayers containing poly(allylamine hydrochloride) (PAH) was examined by FT-IR spectroscopy, in-situ atomic force microscopy (AFM), and in-situ ellipsometry. Assembly pH was found to play a critical role in determining the postassembly pH-dependent swelling behavior of multilayers containing PAH. Multilayer films assembled at pH < 8.5 were found to exhibit pH-independent swelling behavior over the pH range of 2.0−10.5, whereas dramatic discontinuous swelling transitions were observed when the assembly pH was greater than 8.5. FT-IR spectroscopy was used to demonstrate unequivocally that the pH-triggered, discontinuous swelling/deswelling transitions of PAH/sulfonated polystyrene (SPS) multilayers assembled at high pH (>8.5) are driven by changes in the degree of ionization of free amine groups of PAH that are established during multilayer assembly. The pH trigger points of these swelling/deswelling transitions are determined by the elimination/reestablishment of hydrophobically associated PAH chain segments. Such hydrophobic interactions are responsible for shifting the pK_a of the free amine groups of PAH to unusually low values (ca. pH 4.0). The kinetics of deswelling were found to be strongly influenced by the type of polyanion assembled with PAH.

Introduction

The level of swelling of polyelectrolyte multilayers in aqueous environments is a critically important parameter when considering their use as functional biomaterial coatings and/or vehicles for controlled drug delivery. Multilayers designed to exhibit high levels of swelling under physiological conditions, for example, exhibit excellent resistance to the attachment and spreading of cells.[1] In contrast, multilayers constructed from the same polymers that swell to a much less extent promote the attachment and spreading of specific cell lines.[1] The release of drug molecules from or across a multilayer thin film is also determined by, among other things, the level of swelling of the film.[2,3] In all of these situations, it is desirable to be able to control the swelling level through the use of a specific stimulus such as a change in pH, temperature, or ionic strength. Such a capability would make it possible, for example, to use the physical state of a thin film coating to control drug release or to culture and release cells on demand.[4] Multilayer thin films with pH-tunable levels of swelling are possible when weak polyelectrolytes are used to construct the films under controlled pH assembly conditions. Examples of the pH-controlled swelling of multilayers continue to emerge and include reversible pH-triggered nano- and microporosity,[5−7] pH-triggered discontinuous swelling/deswelling transitions,[8] pH-controlled drug release,[2,9,10] and pH-induced capsule swelling.[11]

In a previous paper,[8] we reported that multilayers assembled from poly(allylamine hydrochloride) (PAH) and sulfonated polystyrene (SPS) under specific pH conditions undergo abrupt, pH-triggered discontinuous swelling/deswelling transitions similar to those exhibited by some polymer gels fabricated with weak polyelectrolytes.[12,13] In addition, it was found that after drying from the swollen state the film retained a “molecular memory” of its previous swelling state and returned to this specific level of swelling when immersed into deionized (DI) water. Thus, depending on postassembly processing history, a PAH/SPS multilayer film assembled at high pH (all solutions at pH 9.5 in this case) would swell in DI water to a low level (about 15%) or a very high level (about 400%). We suggested that the unique swelling behavior of this multilayer system was associated with a pH-driven change in the degree of ionization of the weak polyelectrolyte (PAH) and the elimination/reestablishment of hydrophobic interactions of the SPS chains. In this paper, we use FT-IR spectroscopy to demonstrate unequivocally that the pH-triggered, discontinuous swelling/deswelling transitions of PAH/SPS multilayers assembled at high pH (>8.5) are driven by changes in the degree of ionization of free amine groups of PAH. We further show that without these free amine groups (for example, PAH/SPS films assembled at pH < 8.5) pH-independent swelling behavior is observed over the pH range of 2.0−10.5. Finally, by examining the pH-dependent swelling behavior of a PAH-containing multilayer assembled with a less hydrophobic polyanion (poly(vinyl sulfate)), we suggest that the hydrophobic effects responsible for the pH-dependent swelling behavior are in fact primarily associated with hydrophobically associated segments of PAH.

Experimental Section

Materials. Poly(allylamine hydrochloride) (PAH) (M_w = 70 000) and poly(diallyldimethylammonium chloride) (PDAC) (M_w = 100 000−200 000, 20% aqueous solution) were used as polycations and poly(sodium 4-styrenesulfonate) (SPS) (M_w = 70 000) and poly(vinyl sulfate) potassium salt (SPV) (M_w = 170 000) were used as polyanions. All polyelectrolytes were purchased from Aldrich and used as received without further

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purification. Note, to avoid confusion with our previous work in which we used poly(vinylsulfonic acid) (PVS),[14] we are designating poly(vinyl sulfate) as SPV.

Multilayer Preparation. Polyelectrolyte dipping solutions of 10^{-2} M (based on the repeat unit molecular weight) were prepared from deionized water (18 megohm Millipore), and the pH of both polyelectrolyte solutions and the rinse water were adjusted to the same pH. For example, in PAH/SPS 8.5/8.5 multilayers, the pH of both polyelectrolyte dipping solutions and the rinse water was adjusted to pH 8.5. Solution pHs covering the range of pH 6.5−9.5 were created with either 1 M HCl or 1 M NaOH. The pH of both the assembly solutions and swelling solutions was monitored to ensure that a significant drift in pH did not occur during experiments. The drift in pH was typically less than 0.2 units. If the drift exceeded this amount, the solution was replaced with fresh solution. Polyelectrolyte multilayers were assembled onto polished ⟨1,0,0⟩ Si wafers and ZnSe substrates at room temperature by using an automated HMS programmable slide stainer (Zeiss, Inc.). Polyelectrolyte multilayers were deposited by dipping into a polycation solution and a polyanion solution alternatively (for 15 min each) with pH-adjusted water rinsing in between (for 2, 1, and 1 min with agitation before the next dip into a polyelectrolyte solution). Dipping and rinsing steps were repeated until the desired dry thickness was obtained (typically ~50 nm).

Multilayer Film Characterization. The thicknesses of multilayer films were measured by a Gaerter ellipsometer equipped with a He−Ne source at 633 nm (70° angle of incidence). Contact angle measurements were carried out with the standard sessile drop technique by a VCA 2000 (Advanced Surface Technology). X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS Ultra Imaging XPS with an Al Kα source. Atomic force microscopy (AFM) images and the surface roughness of the multilayer films were obtained with a Dimension 3000 scanning probe microscope (Digital Instrument). A 5 μm square area of the assembled film was scanned by tapping mode, and a Si cantilever was used for all dried multilayer films. Fourier transform infrared spectroscopy (FT-IR) spectra were acquired using a Nicolet FT-IR spectrophotometer with a DTGS detector. In the FT-IR measurements, ZnSe substrates were used, and films were assembled to produce thicknesses of ~120 nm in the dry state to obtain strong signals. FT-IR and dry-state AFM measurements of postassembly-treated multilayer films were performed after immersion in the treatment solutions (pH-adjusted water in the range of pH 2.0−10.5—adjusted with either 1 M HCl or 1 M NaOH) for typically 5 min followed by drying in a vacuum for 30 min or more. The treatment steps including dipping in various pH adjusted water solutions and drying were repeated up to 10 times. All measurements described above were performed at room temperature.

Swelling Studies. In-situ ellipsometry measurements to determine film swelling in solution were carried out with a self-built fluid cell based on a design described in the literature.[15] As was the case for dry state measurements, a Gaerter ellipsometry was used for the in-situ measurements. More details of the fluid cell can be found in a previous paper.[6] The accuracy of the cell design was verified by measurements of spin-coated polystyrene films. The error in the thickness measurements was determined to be within ±3% in pH-adjusted water over the range of pH 2.0−10.5. The percent swelling of the multilayer films is defined as

$$\% \text{ swelling} = 100 \times (T_{\text{in-situ}} - T_{\text{as-prepared}})/T_{\text{as-prepared}} \qquad (1)$$

where $T_{\text{as-prepared}}$ is the dry thickness of an as-prepared film and $T_{\text{in-situ}}$ is the film thickness obtained from the in-situ measurement. Note that this is a different way to present the swelling level compared to what was used in our previous PAH/SPS swelling paper.[8] (In that case, 100% was used to represent the thickness of the dry film.)

In-situ AFM images and surface roughness values of the multilayer films were obtained under pH-adjusted water by a Dimension 3000 scanning probe. Contact mode with a Si_3N_4 cantilever was used to scan a 5 μm square area of the film in fluid. Ellipsometry measurements and AFM scanning in fluid were performed typically 3 min after dipping in pH-adjusted water, and the immersion was continued for 5 min before the next pH treatment. Each pH treatment was carried out after drying the film with blown air. The thickness of multilayer films after storage under various conditions was also investigated to evaluate the stability of the swelling behavior. In this case, prior to measurement, films were preconditioned in pH 2.0 water for 5 min followed by drying, and then the film thickness was measured 3 min after dipping into a pH 2.0 solution by in-situ ellipsometry.

Estimation of the Degree of Ionization of PAH in Multilayer Films. The degree of ionization of PAH in multilayer films was estimated from FT-IR spectra recorded in the dry state.[14] To avoid the complications associated with overlapping bands due to the CH_2 asymmetric and symmetric stretching modes of both PAH and SPS in the 2800−3250 cm^{-1} region of the spectrum, we analyzed the absorption bands in the 1450−1650 cm^{-1} region of the spectrum. Peak assignments for this region are provided in the Results section. Spectra generated from films of neat PAH cast from solutions ranging in pH from 2 to 10 were used to generate a calibration curve. The calibration curve was prepared by plotting the ratio of the absorbance at 1512 and 1549 cm^{-1} vs the degree of ionization of PAH determined from these spectra using methods as described in a previous paper.[14] It should be noted that very similar values for the degree of ionization of PAH in solution as a function of pH were obtained by Sukorokov and co-workers by using more traditional titration methods,[16] thereby validating the assumption that the degree of ionization of PAH chains in the dry state is essentially the same as the solution state degree of ionization at a given pH. Since the relevant absorption bands shift from their pure state values when PAH is incorporated into a multilayer film (see Supporting Information), the ratio of the absorbance at 1522 and 1564 cm^{-1} was used in conjunction with the above calibration curve for multilayer films. Because of problems with overlapping bands, this calibration curve is only useful when the degree of ionization of PAH in a multilayer film is greater than 50%, which fortuitously is the case for all multilayers described in this paper. A comparison of the spectra of pure PAH films cast from pH 2.0 (fully ionized) and pH 7.0−9.0 (degree of ionization comparable to that found in multilayers) solutions and specific multilayer films in this paper can be found in the Supporting Information. These spectra show that a high level of confidence in results is possible when PAH chains in multilayers are essentially fully ionized (>90%), but more error is possible in the estimation of the degree of ionization when the chains are in the range of 65−80%. Thus, a value reported in this range carries with it an error of about ±10%.

Results

Swelling Behavior of PAH/SPS Films. Multilayer films assembled from PAH and SPS under specific pH conditions exhibit unique swelling behavior. To demonstrate the importance of assembly conditions, PAH/SPS multilayer films assembled with the dipping solutions covering the pH range of 6.5−9.5 were fabricated and characterized. To compare swelling behavior, the films were first examined 3 min after immersion in each treatment solution. Figure 1 shows the change in swelling that occurs when the multilayer films are conditioned sequentially in different treatment solutions: pH 2.0 and pH 10.5 with a treatment in deionized water (pH 5.5) between each low- and high-pH solution. In this case, the films were dried between each swelling step to examine whether swelling influences the dry-state thickness and to determine whether a “molecular memory” of the previous swelling treatment was re-

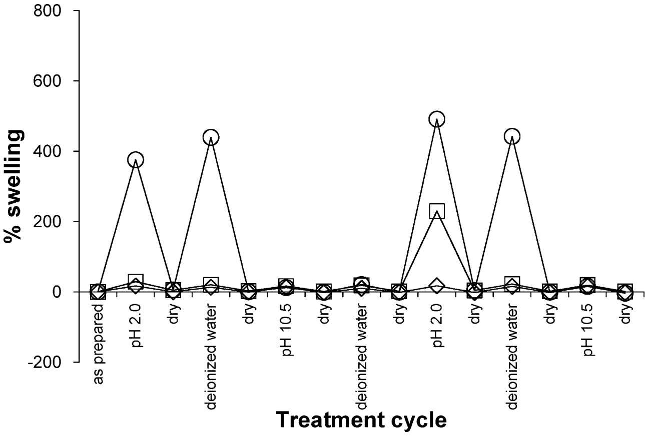

Figure 1. Swelling level of PAH/SPS multilayer films during and after pH treatments. The circles, squares, and diamonds represent the films assembled at pH 9.3, pH 8.5, and pH 7.5, respectively. Each measurement in solution was carried out 3 min after immersion, and the immersion continued 5 min before drying. The pH of deionized water is ∼5.5. All films started with a dry thickness of 50 ± 5 nm.

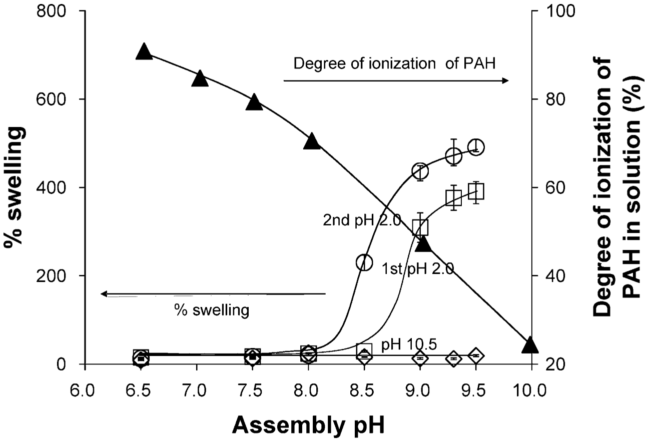

Figure 2. Summary of the swelling level of PAH/SPS multilayer films assembled at various pH conditions in the range of pH 6.5−9.5. The squares, circles, and diamonds represent the swelling level during the first immersion in pH 2.0 water, the second immersion in pH 2.0 water, and immersion in pH 10.5 water, respectively (%). The triangles represent the degree of ionization of PAH in solution (%). Lines are drawn to guide the eye. All films started with a dry thickness of 50 ± 5 nm.

Table 1. Bilayer Thickness, Contact Angle, and mol % of PAH of PAH/SPS Multilayer Films Assembled in Various pH Conditions[a]

assembly pH	bilayer thickness[b] (Å)	contact angle[c] (deg)	mol % of PAH[d]
6.5	5	47	
7.5	8	50	61
8.0	12	50	
8.5	25	56	66
9.0	40	57	
9.3	46	62	72
9.5	49	64	

[a] All data were obtained from about 50 nm thick films with PAH as the outermost layer. [b] The bilayer thickness was calculated by average. [c] The advancing contact angle was measured. [d] The mol % of PAH in films was obtained by XPS.

tained by the film. As previously reported,[8] multilayer films assembled with the dipping solutions of both polymers at a high pH (PAH/SPS 9.3/9.3 in this case) attain a highly swollen state (more than a 380% increase of the as-prepared film thickness in the dry state) when exposed to a pH 2.0 solution. After drying from this highly swollen state, the film retains a molecular memory of this low-pH treatment and swells to a similar level after immersion into deionized water. Treatment in a pH 10.5 solution, on the other hand, produces a phase that can only swell to a level of about 15%. Again it is found that after drying and immersion into DI water the films retains a memory of this treatment and swells to a similar low level. This pH treatment cycle can be repeated reproducibly many times.

In contrast to PAH/SPS 9.3/9.3 films, the swelling behavior of multilayer films assembled at a pH of 7.5 (PAH/SPS 7.5/7.5) is essentially insensitive to the pH of the treatment solutions over the pH range of 2.0−10.5. In this case, the multilayer film swells to a level of about 15% regardless of the solution pH. The PAH/SPS multilayers assembled at pH 8.5 (PAH/SPS 8.5/8.5) exhibit a hint of the existence of a highly swollen state during the second treatment in a pH 2.0 solution but essentially behave more like the PAH/SPS 7.5/7.5 multilayer film in these cycling experiments. These observations suggest that a transition in swelling behavior is taking place between an assembly pH of 7.5 and 9.0. It should be noted that no significant differences in swelling behavior have been observed when the outermost layer of these films is either SPS or PAH.

Figure 2 summarizes the swelling behavior of PAH/SPS multilayer films assembled at various pH conditions in the range of 6.5−9.5 (above pH 9.5, reproducible film formation is not possible). This figure also shows how the degree of ionization of PAH in solution varies with pH.[14] These data confirm that all films assembled at a pH of 8.0 or lower do not exhibit the ability to access the highly swollen state (low-pH treatment) that is possible with films assembled at pH 9.0 or higher. The transition between these two very different swelling profiles occurs in films assembled with a pH between 8.0 and 9.0. PAH/SPS multilayer films assembled at a pH of 9.0 or higher all exhibit the reversible and repeatable transition from the highly swollen state (low-pH treatment) to the less swollen state (high-pH treatment) as well as the previously described molecular memory effects. The degree of ionization data displayed in Figure 2 indicate that the reversible swelling transition of PAH/SPS multilayer films becomes possible when the linear charge density of PAH in solution drops below a degree of ionization of about 50%. The implications of this observation are presented in the Discussion section. The importance of a weak polyelectrolyte in facilitating these novel swelling transitions is also underscored by the fact that multilayer films of SPS assembled with the strong polyelectrolyte PDAC do not exhibit any pH-sensitive swelling behavior in the pH range between 2 and 10.5 even when the films are assembled at pH 9.3. Such films only swell to a level of about 30% across this entire pH range.

Table 1 shows the bilayer thickness and water droplet advancing contact angles (PAH outermost layer) of PAH/SPS films assembled at different solution pH. As previously reported,[14,17] the bilayer thickness of multilayer films containing the weak polyelectrolyte PAH undergoes a dramatic change from molecularly thin layers to much thicker layers when the degree of ionization of the polymer within the multilayer films drops below 80−90%. The water droplet contact angle data show that PAH/SPS films become progressively more hydrophobic when the assembly pH is 8.5 or higher. This reflects the fact that the outermost PAH layer contains a larger fraction of free amine groups, which, in turn, promotes the development of hydrophobic clusters (to be discussed). XPS experiments (Table 1) indicate that the composition of the PAH/SPS multilayer changes from about 60 mol % PAH for films assembled at pH 7.5 to about 70 mol % PAH at an assembly pH of 9.3. In other words, the films become slightly more enriched in PAH at the higher assembly pH. The mol % of PAH in these films was estimated from the atomic ratio of nitrogen (PAH) to sulfur (SPS), which was essentially independent of the outermost polymer layer for films assembled at pH 7.5. In the case of multilayers assembled at pH 8.5 and 9.3, films with SPS as the top layer indicated less of an increase in PAH content, suggesting that the surface composition more strongly influences results as the bilayer thickness increases (pH 8.5−41 layers with PAH on top: 66% PAH, 40 layers with SPS on top: 61% PAH, pH 9.3−21 layers with PAH on top: 72% PAH, 20 layers with SPS on top: 62% PAH). The XPS result obtained at pH 7.5 is consistent with previous XPS studies on PAH/SPS multilayers assembled with PAH in the essentially fully charged state. For example, McCarthy and co-workers[18] found that PAH/SPS multilayers assembled at pH 2.2, 4.0, and 8.0 without added salt contain about $\sim$60% PAH. Similarly, Riegler and Essler[19] reported that PAH/SPS multilayers assembled from non-pH-adjusted water with no salt added contain 60% PAH.

To determine whether any of the differences observed in swelling behavior as a result of assembly pH were kinetic in origin, we examined the time-dependent swelling behavior of select films. Figure 3 compares the time-dependent swelling behavior of PAH/SPS 9.3/9.3 and 8.5/8.5 films. In the case of the 9.3/9.3 film, 90% of the steady-state swelling behavior is achieved in about 20 min during the first low-pH treatment and in only about 10 min during the second. After an immersion time of about 60 min, each treatment results in a steady-state swelling level of about 560% (Figure 3a). As shown in Figure 3a, reswelling in DI water occurs very fast after drying from a pH 2.0 treatment, but the film undergoes a collapse to the less swollen state ($\sim$30%) if it is left in this solution for more than 60 min. The origin and implications of this transient swelling behavior in DI water will be considered later. For the 8.5/8.5 film (Figure 3b), a 60 min immersion in the first pH 2.0 treatment solution is still not capable of inducing a transition to the highly swollen state. Only during the second low-pH treatment does the film swell quickly (about 1 min) to a more swollen state. In addition, long time immersions in DI water after either of these treatments and drying are not capable of producing the more swollen phase. PAH/SPS films assembled at pH 7.5 or lower (data not shown) have been found to maintain their low level of swelling during extended immersions (at least 16 h) in solutions covering the range of pH 2.0−10.5. These results show that the significant differences in swelling behavior observed with films assembled at pH > 8.5 as well as the more complicated swelling behavior of the 8.5/8.5 film are not the result of simple kinetic effects: i.e., longer immersion times do not induce higher levels of swelling in films that did not access the highly swollen state during shorter immersion times.

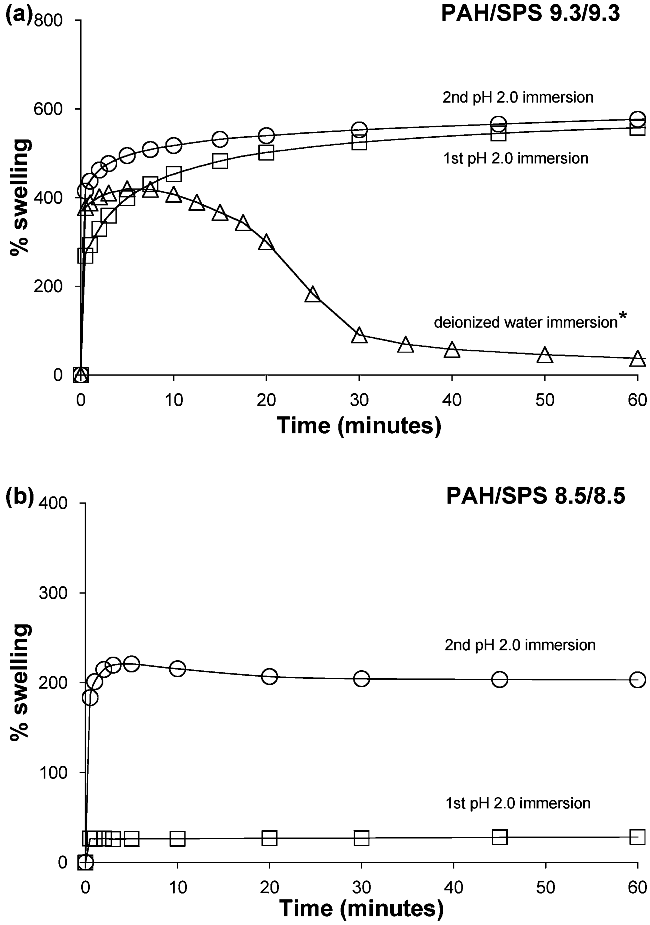

Figure 3. Time dependence of swelling level during immersion steps: (a) PAH/SPS 9.3/9.3 films and (b) PAH/SPS 8.5/8.5 films. The triangles in (a) show immersion in deionized water after a pH 2.0 treatment. Lines are drawn to guide the eye. All films started with a dry thickness of 50 ± 5 nm.

Although PAH/SPS 8.5/8.5 films show more complicated swelling behavior than the others when cycled through drying and DI water steps, Figure 4b shows that a reproducible transition between a more swollen and less swollen state can be realized when a 8.5/8.5 multilayer film is cycled directly between a pH 2.0 and pH 10.5 solution (immersion time 3 min). Similar data (Figure 4a) for a PAH/SPS 9.3/9.3 film are presented for comparison. In both cases, after the first cycle, a reversible and repeatable change in the swelling level and refractive index is observed for at least four cycles. Thus, once activated by the first immersion in a pH 2.0 solution, PAH/SPS 8.5/8.5 films display swelling behavior very similar to PAH/SPS 9.3/9.3 films, albeit with a much lower level of swelling in the more swollen state. Thus, this assembly pH produces a molecular organization that is clearly in transition from what is obtained at lower pH (pH-insensitive swelling behavior) to what is obtained at higher pH (discontinuous, pH-dependent swelling behavior).

In-Situ AFM Characterization. To understand the origin of the discontinuous, pH-dependent swelling behavior observed with films assembled at pH 9.0 or higher, we examined both the physical (AFM) and chemical (FT-IR) changes that take place during these transitions. Figure 5 displays in-situ AFM images of PAH/SPS 9.3/9.3 films recorded during treatment cycles of pH 2.0 and pH 10.5. The as-prepared dry film is relatively featureless with a low rms roughness of 1 nm. Upon immersion of the as-prepared film in a pH 10.5 solution (Figure 5b), the film morphology and roughness

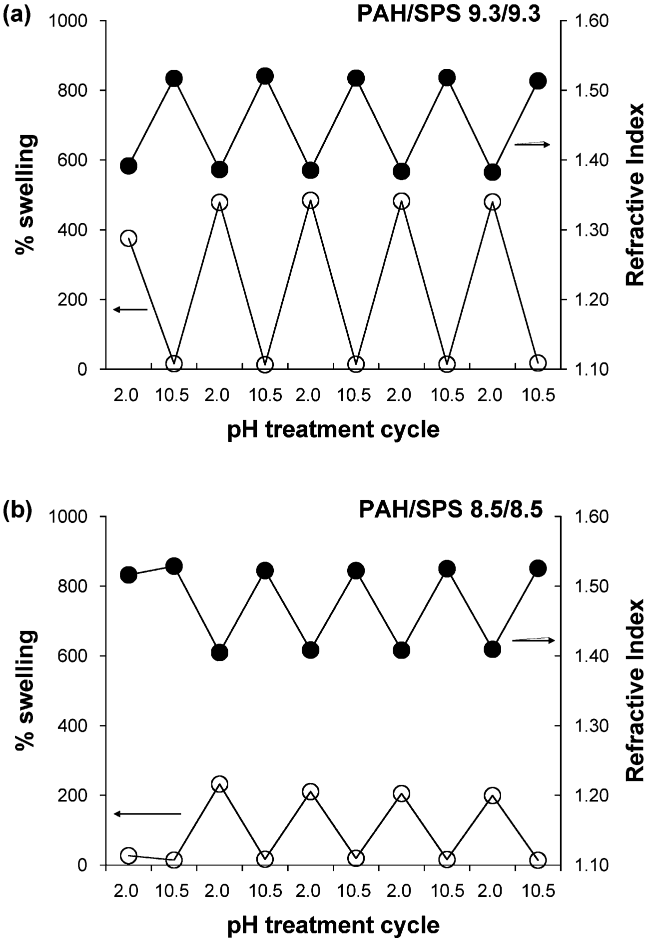

Figure 4. Swelling level and refractive index of films during different immersion steps: (a) PAH/SPS 9.3/9.3 films and (b) PAH/SPS 8.5/8.5 films. Each measurement in solution was carried out 3 min after immersion, and the immersion was continued 5 min before drying. All films started with a dry thickness of 50 ± 5 nm.

remain essentially unchanged. Immersion into the first pH 2.0 solution, however, produces a new more globular morphology with a rms roughness that is more than an order of magnitude larger than the as-prepared film. When the pH 2.0 treated film is immersed in a pH 10.5 solution, the film reverts back to a low roughness state with a slightly larger rms roughness and the appearance of a more textured morphology with relatively small domain features. Repeated cycling in the 2.0 and 10.5 solutions reveals a similar trend; i.e., the roughness of the film in the pH 2.0 solution is always more than an order of magnitude larger than in the pH 10.5 solution. In addition, a progressive coarsening of the globular morphology of the pH 2.0 state and the evolving worm-like morphology of the pH 10.5 state occurs with each additional cycle. For example, after the film has experienced the third pH 2.0 immersion, domain sizes on the order of 1−2 μm are observed, and the rms roughness increases from 22 nm (first pH treatment) to ~70 nm (Figure 5(a-3)). These coarsening effects appear to be leveling off after the first two pH cycles. In should be noted that estimates of the thickness/level of swelling of the films obtained from these in-situ AFM studies were essentially the same as those obtained from the in-situ ellipsometry method, thereby providing a high level of confidence of the reported swelling values. In summary, the AFM images clearly show a reversible morphology change during each treatment cycle that coincides with the dramatic change in swelling level. As suggested by the data in Figure 4a and the AFM images, after a few treatment cycles, it appears that the transition from the highly swollen state to the less swollen state with change in pH becomes essentially repeatable in terms of both swelling level and morphology.

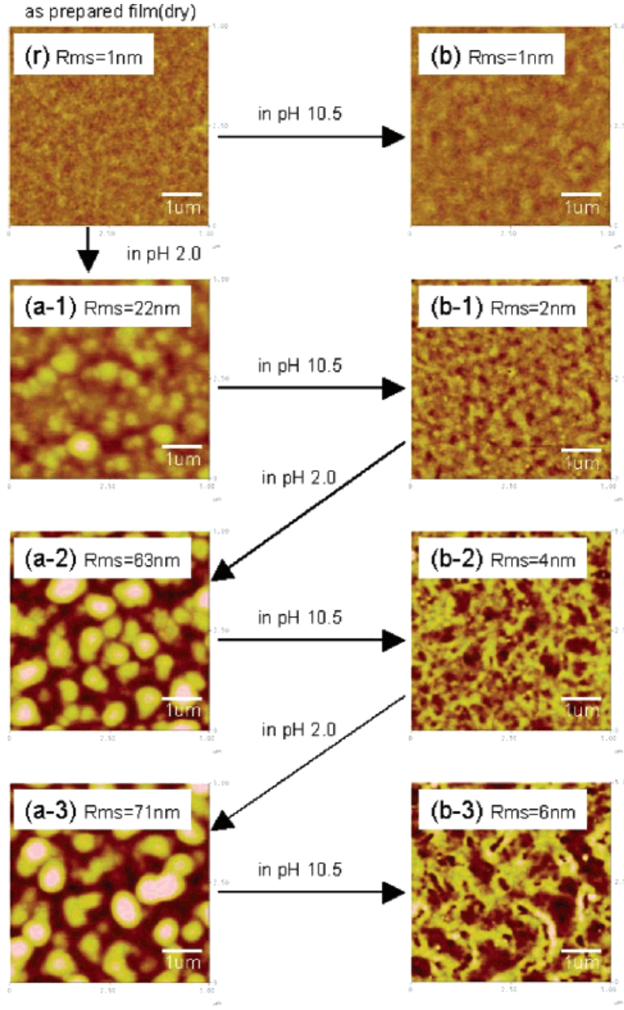

Figure 5. In-situ AFM images of PAH/SPS 9.3/9.3 films during treatment cycles of pH 2.0 and pH 10.5: (r) the as-prepared film in the dry state, (b) a pH 10.5 immersion of the as-prepared film, (a-1) the first pH 2.0 immersion, (b-1) the first pH 10.5 immersion, (a-2) the second pH 2.0 immersion, (b-2) the second pH 10.5 immersion, (a-3) the third pH 2.0 immersion, and (b-3) the third pH 10.5 immersion. AFM images were recorded 3 min after immersion. All films started with a dry thickness of 50 ± 5 nm.

FT-IR Analysis. The presence of a weak polyelectrolyte (PAH) with a pH changeable degree of ionization is one of the key design elements for creating multilayer films that exhibit a discontinuous swelling transition. FT-IR spectroscopy is an excellent tool for determining how the degree of ionization of PAH within a multilayer film changes with different pH treatments. Measurements in this case were made on dried films after specific pH treatments. Figure 6a−c displays the FT-IR spectra of PAH/SPS 9.3/9.3, 8.5/8.5, and 7.5/7.5 films as-prepared and after cyclic treatment in pH 2.0 and pH 10.5 solutions. The important PAH absorption bands that indicate the degree of ionization of this polymer are found in the wavelength range of 2800−3600 and 1450−1650 cm^{-1}.[20] The strong broad absorption band in the range of 2800−3250 cm^{-1} is associated with the stretching mode of the $-NH_3^+$ group (centered around 3045 cm^{-1}). Overlapping bands associated with the CH_2 asymmetric and symmetric stretching modes also occur in this region of the spectrum. In the range of 1450–1650 cm^{-1}, the peaks around 1603 and 1522 cm^{-1} are assigned to the asymmetric and symmetric bending vibrations of $-NH_3^+$, respectively. A broad absorption band associated with the $-NH_2$ bending mode emerges between the peaks of the two bending vibrations of $-NH_3^+$ as the protonated amine groups of PAH lose their protons.

In the case of PAH/SPS 9.3/9.3 films (Figure 6a), which exhibit a reversible swelling transition, the $-NH_2/-NH_3^+$ absorption bands in the range of 2800–3250 cm^{-1} and in the range of 1450–1650 cm^{-1}, undergo clearly reversible intensity changes that show a change from a more ionized state (low pH) to a less ionized state (high pH). For the PAH/SPS 8.5/8.5 films (Figure 6b), similar spectral trends are observed but of a significantly lower change in intensity. It is interesting to note that no significant difference is observed between the FT-IR spectrum recorded after the first pH 2.0 treatment and the spectrum recorded after the second pH 2.0 treatment. Recall that the swelling levels of PAH/SPS 8.5/8.5 films are quite different during these treatments (Figure 3b). In contrast to the 9.3/9.3 and 8.5/8.5 films, the FT-IR spectra of PAH/SPS 7.5/7.5 films reveal no significant changes in the intensity of any of the key vibrational bands during pH cycling.

To quantify the changes in the degree of ionization of PAH observed in PAH/SPS 9.3/9.3 films as a function of postassembly pH, we analyzed the absorption bands in the 1450–1650 cm^{-1} region of the spectrum (see Experimental Section and Supporting Information for details). From an analysis of this type, we estimate that the degree of ionization of PAH is ~70% (±10%) in the as-prepared PAH/SPS 9.3/9.3 films and 90% or higher in the as-prepared PAH/SPS 8.5/8.5 and 7.5/7.5 films. In addition, the degree of ionization of PAH within the 9.3/9.3 film increases to 90% or higher after a pH 2.0 treatment and returns to essentially the same level as the as-prepared film after a pH 10.5 treatment. Note that the degree of ionization of PAH in a multilayer film is significantly higher than its solution-state value at a given pH (see Figure 2 for comparison). For example, the degree of ionization of PAH in solution at pH 9.3, 8.5, and 7.5 is ~40%, ~55%, and ~80%, respectively, compared to ~70% and ~90% or higher for PAH/SPS 9.3/9.3 and the 8.5/8.5 and 7.5/7.5 films, respectively. The fact that the degree of ionization of a weak polyelectrolyte increases substantially from its solution-state value when the polymer is incorporated in a multilayer film has been well documented in the literature[5,17,21] and is associated with the fact that the ionized state is more easily achieved in the presence of oppositely charged polymers (SPS in this case). Consistent with our analysis, a recent paper by Sukhorukov and co-workers[16] reports that the degree of ionization of PAH in PAH/SPS films assembled at pH 7.0 is about 94% (determined by titration of hollow capsules).

Figure 7a shows how the degree of ionization of PAH in PAH/SPS 9.3/9.3 multilayer films changes as a function of postassembly pH treatments. Figure 7b shows the corresponding pH-dependent swelling data for this multilayer system. These figures combined clearly and unequivocally demonstrate that the discontinuous swelling transition observed in PAH/SPS films assembled at a pH greater than 9.0 is driven by a abrupt change in the degree of ionization of PAH. Note that the degree of ionization of PAH remains unchanged at about 70% from a pH of 10.5 to 4.5, at which point it increases rapidly to about 95% over a range of about 1 pH unit. The film, in turn, undergoes a dramatic change in swelling level at this pH trigger point from about 35% to about 680%. The deswelling transition at higher pH and the large hysteresis loop observed with this multilayer system are also seen to be intimately linked to abrupt changes in the degree of ionization of PAH.

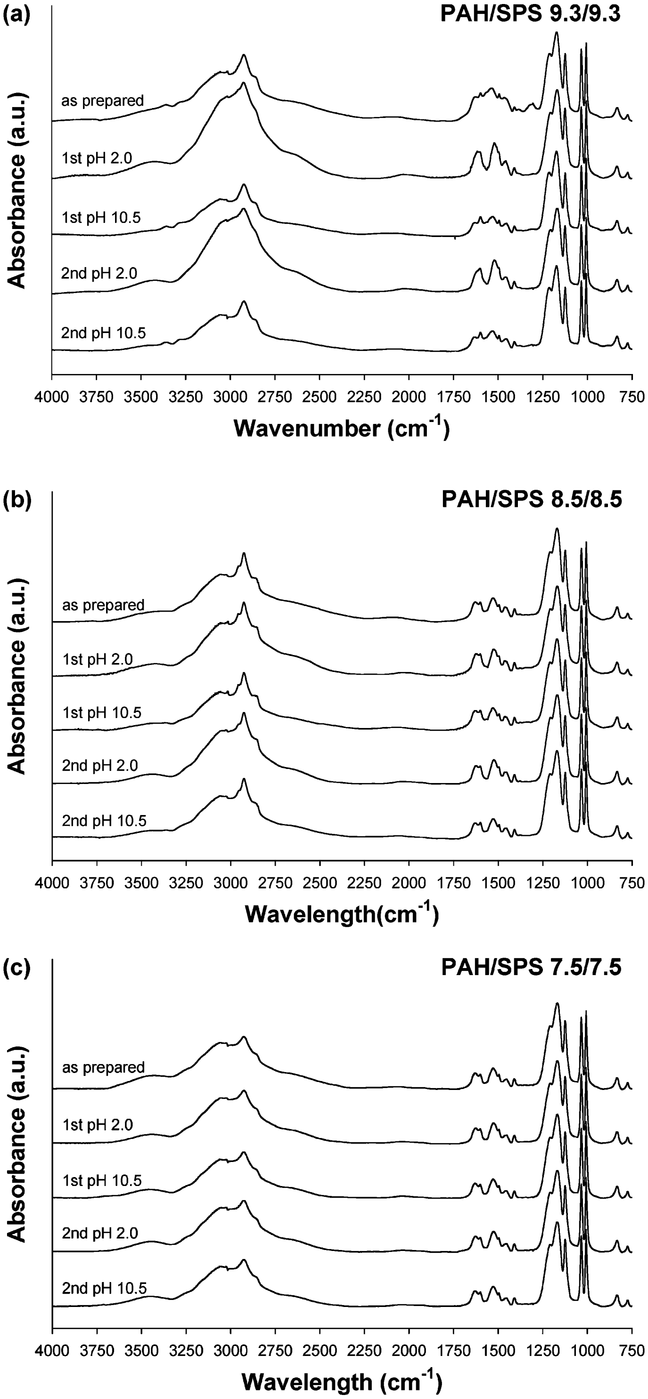

Figure 6. FT-IR spectra of PAH/SPS multilayer films after each step of a treatment cycle of pH 2.0 and pH 10.5: (a) PAH/SPS 9.3/9.3 films, (b) PAH/SPS 8.5/8.5 films, and (c) PAH/SPS 7.5/7.5 films. The immersion time of each step is 5 min. All films started with a dry thickness between 100 and 130 nm.

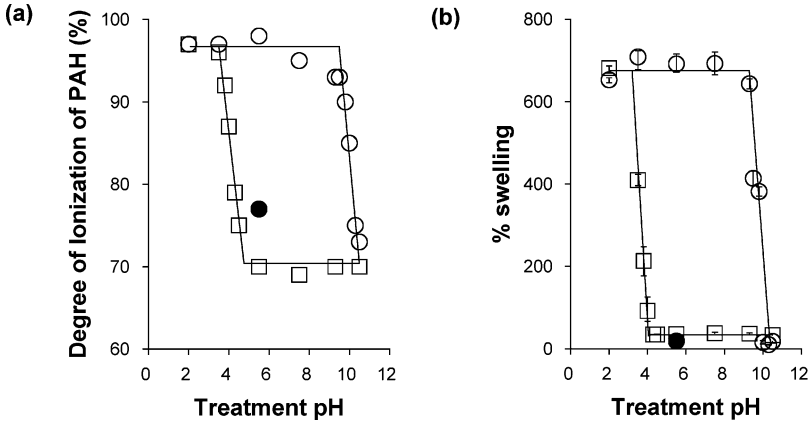

Figure 7. (a) Estimated degree of ionization of PAH in PAH/SPS 9.3/9.3 multilayer films obtained by FT-IR measurements after various pH treatments. (b) Swelling level of PAH/SPS 9.3/9.3 multilayer films as a function of immersion pH. The squares, open circles, and filled circles represent data generated after a pH 10.5 treatment (swelling cycle), after a pH 2.0 treatment (deswelling cycle), and after a 16 h treatment in deionized water (pH ~5.5) after a pH 2.0 treatment, respectively. Lines are drawn to guide the eye. The immersion time of each step is 5 min. Dry film thickness = ca. 130 nm.

Deswelling only occurs when the degree of ionization of PAH returns to its as-assembled level near a pH of 10.0. The existence of a large hysteresis loop is responsible for the molecular memory effects observed with this system.[8] Note, however, that the hysteretic behavior is clearly a kinetic effect as indicated by the fact the degree of ionization of PAH decreases with a corresponding deswelling of the film if it is left in DI water for 16 h after the pH 2.0 treatment (black circles in Figure 7a,b). This result is consistent with the data presented in Figure 3a, which also show that extended treatments in DI water cause a film previously activated to the highly swollen state to deswell.

Swelling Behavior of PAH/SPV Films. It is clear that the pH-dependent nature of PAH plays a critical role in the discontinuous swelling behavior of PAH/SPS multilayers assembled at high pH. To better understand the role of SPS in facilitating the observed discontinuous swelling transitions and associated memory effects, we also examined the pH-dependent swelling behavior of multilayers containing a less hydrophobic strong polyanion, namely poly(vinyl sulfate) (SPV). Figure 8a,b shows how the level of swelling of this multilayer system varies as a function of postassembly solution pH as well as how the degree of ionization of PAH is changing during this process. The degree of ionization of PAH in the as-assembled multilayer (ca. 73%) is about the same as that found in films containing SPS that were assembled at this same high pH (PAH/SPV 9.3/9.3). In addition, as was found for PAH/SPS 9.3/9.3 multilayers, the degree of ionization of PAH and the level of swelling of the film undergo an abrupt increase near a solution pH of 4.0. Thus, during the first low pH cycle of the as-prepared film, PAH/SPV and PAH/SPS multilayers behave very similarly. During the cycling from low pH to higher pH, however, the behavior is quite different. The degree of ionization of PAH in this case does not undergo an abrupt transition but rather gradually decreases and only to a value of about 83%. Recall that in the case of the SPS-containing film the degree of ionization undergoes an abrupt transition back to the original as-prepared value in this same pH cycle. Deswelling of the PAH/SPV multilayer also occurs at a much lower pH (about pH 6 compared to about pH 10 in the PAH/SPS case), and this abrupt deswelling transition occurs even though the degree of ionization of PAH is still quite high (>90%). Given this type of swelling−deswelling hysteresis behavior, it is not surprising to find that the PAH/SPV multilayer films do not exhibit the memory effects found in PAH/SPS multilayers. Films treated at pH 2.0 followed by drying do not reswell to the highly swollen state when placed into DI water as was found for SPS containing films (see Figure 1). Regardless of the previous pH treatment (pH 2.0 or 10.5), dried films only swell to the lower level state when placed in DI water (pH 5.5), consistent with the much tighter hysteresis swelling loop exhibited by this multilayer system. In short, the low-pH swelling transitions of these two different multilayer systems appear to be very similar in origin, whereas the higher pH deswelling transitions are quite different.

Stability of Swelling Behavior. We have previously mentioned[8] that the reversibility of the swelling transitions of PAH/SPS multilayers assembled at high pH can change significantly if the films are stored in water at neutral pH for long times. Specifically, films stored under these conditions for more than 10 h begin to lose their ability to reswell to the highly swollen state when treated at low pH. To better understand this irreversible change in swelling behavior, we examined the swelling behavior of PAH/SPS 9.3/9.3 films after the films were stored under various environmental conditions. Figure 9 shows the swelling levels of PAH/SPS 9.3/9.3 films achieved in a pH 2.0 solution[22] after as-prepared (no postassembly pH treatments) films were stored under different conditions as a function of storage time. When films are stored in air at room temperature at either 60% relative humidity (RH) or 20% RH, the level of swelling they can achieve in a pH 2.0 solution decreases with storage time with the film conditioned at 60% RH displaying a faster rate of decline in swelling level than the film conditioned at 20% RH. A film conditioned in water more rapidly loses its ability to achieve a high level of swelling at pH 2.0, whereas a film stored in a vacuum or in dry nitrogen maintains its ability to undergo a transition to the highly swollen state at pH 2.0. Note that films stored after a pH 2.0 treatment within the first few days of multilayer assembly exhibit a slower rate of decay of swelling amount compared to nontreated films (in this case stored at 24 °C/60% RH). This suggests that the presence of the electrostatically repulsive ionized amine groups formed during the low-pH treatment inhibits the molecular rearrangements that occur during storage. In any event,

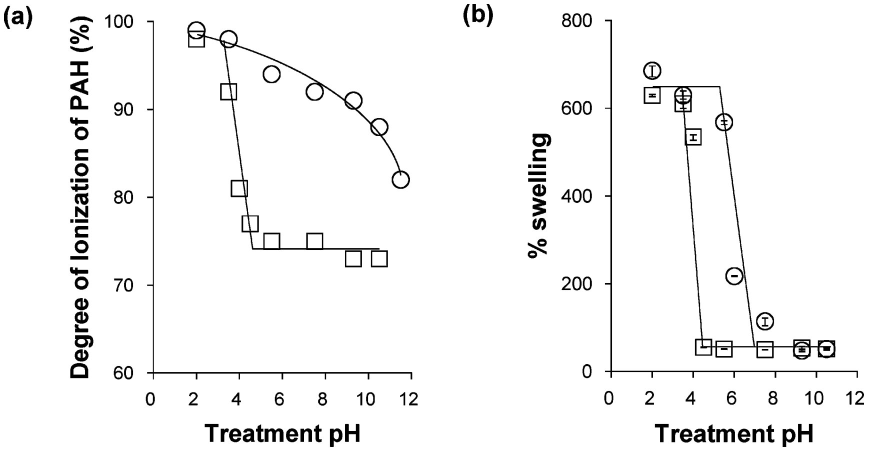

Figure 8. (a) Estimated degree of ionization of PAH in PAH/SPV 9.3/9.3 multilayer films obtained by FT-IR measurements after various pH treatments. (b) Swelling level of PAH/SPV 9.3/9.3 multilayer films as a function of immersion pH. The squares and open circles represent data generated after a pH 10.5 treatment (swelling cycle) and after a pH 2.0 treatment (deswelling cycle), respectively. Lines are drawn to guide the eye. The immersion time of each step is 5 min. Dry film thickness = ca. 130 nm.

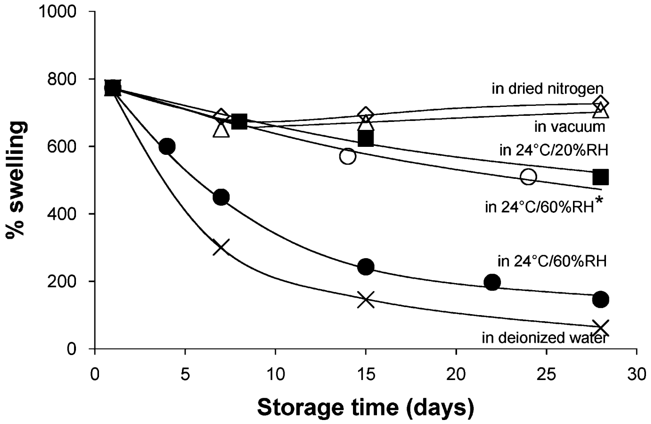

Figure 9. Swelling level of PAH/SPS 9.3/9.3 multilayer films during a second pH 2.0 immersion after storage in various conditions. The open circles represent a film stored in 24 °C/60% RH after a pH 2.0 treatment. Lines are drawn to guide the eye. All films started with a dry thickness of 50 ± 5 nm.

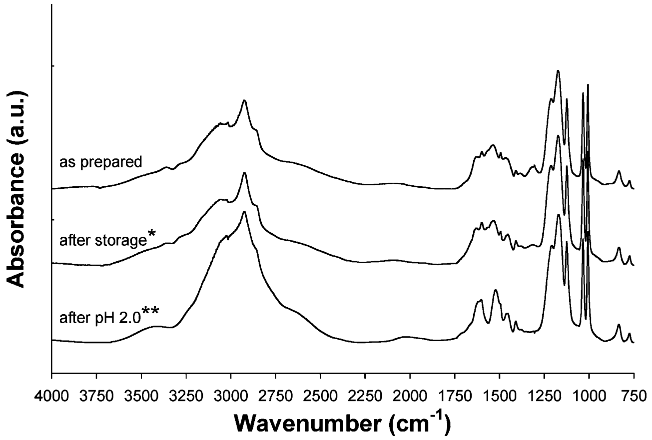

Figure 10. FT-IR spectra of PAH/SPS 9.3/9.3 multilayer films: (*) after storage in deionized water (pH ~5.5) for a month; (**) after storage in deionized water (pH ~ 5.5) for a month followed by a pH 2.0 treatment. Dry film thickness = ca. 130 nm.

these results clearly indicate that the swelling behavior of PAH/SPS 9.3/9.3 films can change substantially during storage and that the amount of moisture present during storage affects the rate at which a film loses its ability to access the highly swollen state. The drive toward a new molecular organization with less swelling ability is clearly facilitated by the higher chain mobility expected in a multilayer film plasticized with water.

To determine whether PAH/SPS 9.3/9.3 films lose their ability to swell because molecular reorganizations create an environment that suppresses the ability of the amine groups of PAH to become ionized in low pH solutions, we examined the FT-IR spectra of films stored for 1 month in deionized water. As seen in Figure 10, only minor changes were detected in the FT-IR spectrum of the stored film as compared to the as-prepared film. In addition, the FT-IR spectrum of a film stored for 1 month in DI water and then immersed in a pH 2.0 solution shows that the degree of ionization of the PAH chains increases to essentially the same high level that is achieved by a low-pH treatment of a freshly prepared film. This result indicates that, in this case, a change in the degree of ionization of PAH is not in itself sufficient to induce a swelling transition. Hence, extended storage in water produces a molecular organization with virtual cross-links (most likely hydrophobic in nature) that cannot be disassociated by the electrostatic repulsive forces created by the ionized amine groups.

Contact angle measurements provide some indirect evidence to support the hypothesis that during storage the multilayer film is building more strongly associated hydrophobic regions that act to cross-link the film and prevent high swelling levels. Advancing contact angles obtained from as-prepared films and those stored at room temperature at 60% RH for a month remain essentially unchanged (62° to 62°) whereas the receding contact angle increases significantly after storage (11° to 21°). This result indicates that the surface composition of the film is not changing but the ability of the polymer chains to reconfigure in response to a water droplet is becoming restricted.

Discussion and Conclusions

General Comments. The pH-induced swelling transitions in polymer networks based on weak polyelectrolytes are well documented in the literature.[12,13] The mechanisms of such transitions often involve a complex interplay between changes in the degree of ionization of the weak polyelectrolyte component(s) and the formation or elimination of weak attractive forces such as those developed by the physical association of hydrophobic elements of the network or hydrogen bonds. Highly swollen states are typically achieved when the electrostatic repulsive forces and/or osmotic pressure effects of pH-activated charged groups overcome weakly associated hydrophobic elements. Hydrophobic effects can also cause large shifts in the effective pK_a of the weak polyelectrolyte, thereby giving rise to discontinuous swelling transitions, pH hysteresis loops, and swelling–deswelling trigger points that occur at unexpected solution pHs. We earlier hypothesized[8] that the discontinuous swelling–deswelling transitions exhibited by specific PAH/SPS multilayer films were associated with changes in the degree of ionization of the PAH chains and that hydrophobic interactions were responsible for shifting the low-pH-induced swelling transition to a pH much lower than expected given the known pK_a of PAH. The results of this present study confirm clearly that the discontinuous swelling transitions and related hysteresis behavior of PAH/SPS multilayer films assembled at high pH (>8.5) are intimately connected to discontinuous changes in the degree of ionization of PAH.

Molecular Environment Influences Degree of Ionization. To create PAH/SPS multilayers that exhibit discontinuous swelling transitions and molecular memory effects, the polymer chains should be assembled at a pH greater than 8.5. As the assembly pH increases above this value, PAH chains with nonionized amine groups are incorporated into the multilayer film. (The degree of ionization of the PAH chains is about 70% at an assembly pH of 9.3.) In addition, assembly at high pH produces a multilayer film that is slightly more enriched in PAH since, as a less ionized chain, more PAH is needed to neutralize the charge of the SPS chains. Ionization of the free amine groups within the multilayer film ultimately triggers the transition to the highly swollen state at lower pH. The molecular environment of the free amine groups established during multilayer assembly, in turn, has a profound effect on the pH trigger points of the swelling–deswelling transitions of this multilayer system.

The solution pK_a for PAH is about 8.5, and the pK_a shifts to an even higher pH when PAH is incorporated into a multilayer. Note, for example, that the FT-IR spectra of PAH/SPS films assembled with essentially fully ionized PAH chains such as PAH/SPS 7.5/7.5 films (Figure 6) indicate that the PAH chains maintain their highly ionized state up to a pH of at least 10.5, suggesting a multilayer pK_a greater than 10.5. Recent reports describing titration studies of PAH/SPS multilayers in the form of hollow capsules[16] (assembled at pH 7.0) and zeta potential measurements of PAH/PAA multilayers assembled on colloidal particles[21] (assembled at pH 9) estimated the multilayer pK_a of PAH to be approximately 11. The fact that the free amine groups of PAH in PAH/SPS 9.3/9.3 multilayers do not become ionized until the pH is lowered to about 4 (a pH well below the solution and multilayer pK_a of PAH) indicates that their as-assembled molecular environment has shifted the effective pK_a of these groups to a much lower pH. Large shifts in the pK_a of a weak polyelectrolyte are often attributed to hydrophobic effects.[23] The association of hydrophobic elements of a polymer chain or polymer network can increase the local density of weak functional groups and/or decrease the local dielectric constant experienced by weak functional groups. In both cases, it becomes more difficult to ionize the weak functional group due to an unfavorable local electric potential.

Hydrophobic effects appear to play a key role in the swelling–deswelling behavior of specific PAH/SPS multilayer films. The broad swelling–deswelling hysteresis loop (and related changes in the degree of ionization of PAH) displayed by PAH/SPS 9.3/9.3 multilayer films indicates that the hydrophobic environment created during multilayer assembly and eliminated at low pH is not reestablished until a pH of about 10.5, at which point the degree of ionization of the amine groups returns to the as-assembled level. Longer immersion times in the treatment solutions show that this is clearly a kinetic effect: with a longer treatment time of the low-pH-activated film in DI water (pH about 5.5), for example, the degrees of ionization and swelling level both decrease to values at or near those observed at pH 10.5. The deswelling transition, which heralds a return to the as-assembled, hydrophobically associated molecular organization, is therefore influenced by the time it takes for the hydrophobic interactions to be reestablished.

We originally suspected that the hydrophobic elements responsible for shifting the pK_a of the nonionized amine groups within PAH/SPS 9.3/9.3 multilayers were the aromatic rings of SPS. The fact that PAH multilayers assembled with the less hydrophobic polyanion SPV exhibit a dramatic discontinuous swelling transition (at about the same pH) that is also associated with a abrupt increase in the degree of ionization of free amine groups created during assembly, however, suggests that the origin of the hydrophobic effects may in fact be PAH. In solution, weak polyelectrolytes can undergo a transition from an extended coil conformation to a more associated globular state as the charge density of the chain decreases. Further, it has been predicted theoretically[24] that such a transition may involve the formation of an intermediate pearl-necklace-type structure comprised of associated globular regions along the chain. Direct experimental evidence for the pearl-necklace structure has recently been reported[25] for the weak polybase poly(vinylamine) adsorbed onto mica surfaces from solutions of varying pH: elongated globular structures were clearly observed near the solution pK_a of the polymer. We hypothesize that at and above the solution pK_a of PAH (about 8.5) the PAH chains are adsorbing with regions comprised of hydrophobically associated segments rich in nonionized amine groups. These hydrophobic domains in turn create a local environment that suppresses the ability of the amine groups to ionize down to a pH as low as about 4.0. The rising water droplet advancing contact angle observed when the assembly pH increases above pH 8 is a clear indication that the multilayer is becoming more hydrophobic. We have previously reported that the water droplet advancing contact angle of PAH/poly(acrylic acid) multilayers increases dramatically when the PAH assembly pH increases above 7.[17] In addition, previous papers have mentioned the hydrophobic nature of PAH,[26,27] including the fact that PAH/SPS multilayers are more hydrophobic (swell less) than PDAC/SPS films.[26] Thus, multilayers based on PAH, particularly those assembled at high pH, exhibit clearly observable hydrophobic characteristics that are essentially independent of the polyanion partner.

Mechanism of Swelling–Deswelling Transitions. The mechanism driving the abrupt, swelling–deswelling transitions of PAH containing multilayers assembled at high pH (9.3/9.3 for example) appears to be the disruption/re-formation of hydrophobically associated PAH domains. Although the swelling transition looks to be independent of the type of polyanion assembled in the mutlilayer, the deswelling transition is strongly influenced by this polymer. Manifestations of this influence include the ability of a multilayer to exhibit a "molecular memory" effect, which is a simple consequence of a broad, well-defined swelling–deswelling hysteresis loop. In the case of PAH/SPS multilayers, the SPS chains inhibit kinetically the re-formation of the hydrophobic domains established during assembly, and as a result, over short time periods, the deswelling transition takes place at a pH much higher than the swelling transition. The SPV chains, on the other hand, allow the multilayer to revert back to the low swelling state at a lower pH (about pH 6.2 vs 10.5). In addition, PAH/SPV multilayers do not exhibit the molecular memory effect, presumably due to a more rapid reestablishment of the hydrophobic domains during film drying.

On the basis of its strongly time-dependent nature, it is reasonable to conclude that the deswelling kinetics are controlled primarily by chain dynamics. As previously reported,[8] the swelling–deswelling hysteresis loop of PAH/SPS multilayers becomes much less broad if measurements are made at a higher temperature (45 °C) or after longer immersion times. The swelling–deswelling hysteresis loop in this case in fact looks very similar to the PAH/SPV hysteresis loop presented in Figure 8b. The low-pH trigger point occurs at about pH 4, but the deswelling trigger point decreases from 10.5 to about pH 6.2. Thus, given enough time or energy to overcome kinetic effects, the swelling–deswelling behavior of multilayers containing PAH is essentially the same. The fact that the deswelling transition in PAH/SPV multilayers occurs with a much smaller decrease in the degree of ionization of PAH compared to PAH/SPS multilayers shows, however, that the delicate balance between ionization level and the association of hydrophobic elements is strongly influenced by the type of polyanion present in the multilayer. Clearly, more studies are needed to sort out the complicated role that different polyanions play in influencing the kinetics of deswelling.

Stability of Swelling–Deswelling Transitions. Finally, it should be noted that the molecular organization created during assembly at high pH is not stable to storage over long times. Given the chain mobility needed to reorganize (high humidity or water immersion), PAH/SPS multilayers assembled at a high pH lose their ability to access the highly swollen state even though the degree of ionization of the free amine groups still changes with changes in solution pH. In the absence of any evidence to suggest that chemical cross-links are being formed, this observation suggests that the hydrophobic interactions are become stronger with storage time and eventually reach a state that cannot be overcome by changes in the degree of ionization of the amine groups. Dubas and Schlenoff[26] noted that SPS-containing multilayers not used immediately after preparation exhibited an induction period before salt solution induced "smoothing effects" were realized and attributed this effect to aggregation of hydrophobic domains. Thus, it appears that multilayers whose properties are influenced by strong hydrophobic interactions may be prone to time-dependent behavior that needs to be considered when designing experimental investigations.

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Supporting Information Available: Spectra of pure PAH films cast from pH 2.0 (fully ionized) and pH 7.0–9.0 solutions and specific multilayer films. This material is available free of charge via the Internet at http://pubs.acs.org.

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