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Humidity Swelling/Deswelling Hysteresis in a Polyelectrolyte Multilayer Film

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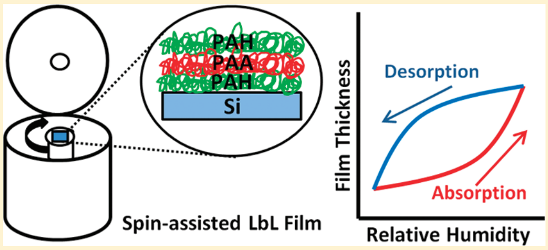
S *Supporting Information*

ABSTRACT: We demonstrate that polyelectrolyte multilayer film (PEM) systems constructed using layer-by-layer (LbL) assembly of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) exhibit significant swelling/deswelling hysteresis in humid air environments, swelling less upon absorption of water from a dry state than upon deswelling from a hydrated (≈100% RH) state. The hysteretic swelling, measured utilizing in-situ reflectometry, is reproducible over multiple absorption−desorption cycles and is essentially absent in spin-coated films of either pure polyelectrolyte. Kinetic swelling measurements support the notion that the structural response to humidity in PEMs can occur over two distinct regimes: an initial swelling response on the order of seconds to minutes as water enters the film and a longer time scale structural relaxation on the order of hours to days. While the structural relaxation appears to influence the magnitude of the hysteresis effect, it cannot account for it entirely; rather, upon long-term storage at an intermediate humidity, the internal structure of a PEM retains some "memory" of its humidity exposure history, similar to some biologically derived textile and food materials. We propose that the mechanism of hysteresis in PEM systems is tied to a combination of internal molecular restructuring in response to ambient moisture and the frustration of structural relaxations by the internal electrostatic cross-link network within the film. Our results suggest that factors such as the drying technique and the manner in which films are equilibrated to ambient humidity may subsequently affect PEM properties as well as the performance of these systems in applications such as environmental sensing.



INTRODUCTION

Polyelectrolyte multilayers (PEMs) are thin films formed from the alternating layer-by-layer (LbL) adsorption of polycationic and polyanionic polymers from dilute solutions. Ease of fabrication, conformability, and the environmental friendliness of this aqueous-based "green" technology are a just a few of many reasons for the recent popularity of the field. Among the possible application areas that have been suggested for PEMs, sensing is one of the more promising due in part to the sensitivity of PEM films to various chemical environments and their ability to be assembled to precise nanoscale dimensions.[1] Such films afford, for example, ease of measuring even slight dimensional or refractive index changes using well-established optical techniques as well as fast response times due to limited transport resistance to the diffusion of chemical species within the film. Although practical demonstrations of sensing have been reported for some nonpolar solvents,[2] PEMs are particularly well-suited to sensing in aqueous and humid environments due to their natural sensitivity to water; they have been previously utilized in humidity-sensing devices,[3−10] and a number of studies have examined the influence of humidity on PEM structure.[11−16] Overall, the body of research suggests that the response of a PEM to ambient moisture can be quite subtle, and the film properties can be highly sensitive to the film chemistry and assembly conditions.[11−13,17] Moreover, the film hydration state has been shown to be an important consideration when PEMs are used in applications such as organic thin-film transistors[18] and lithographic contact printing.[19] A more thorough understanding of how PEMs respond to changes in humidity would thus further both the theoretical understanding and practical utilization of these systems.

In this paper, we report the observation of swelling hysteresis in PEMs stored in ambient air and subjected to changes in relative humidity (RH), comparing the humidity-dependent swelling and deswelling of the PEMs to single-component spin-coated films of each polyelectrolyte. Both PEMs and single-component polyelectrolyte film thicknesses appeared to stabilize quickly (within minutes) to changes in RH, but PEMs exhibited a smaller relative film thickness upon the absorption of water vapor (increasing humidity) than during desorption (decreasing humidity). This swelling/deswelling hysteresis was reproducible over several absorption−desorption cycles and was essentially absent in both of the single-component polyelectrolyte films. Prior reports on swelling/deswelling hysteresis phenomena in PEMs have almost

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exclusively focused on aqueous-based, fully hydrated films stimulated by changes in pH.[20−22] The mechanism for hysteresis in these latter systems is thought to be due to a competing interplay between cohesive hydrophobic interactions and repulsive forces due to increasing ionization of polyelectrolyte chains. Our observations suggest that the hysteresis mechanism for *humidity-swollen* films is tied to both the ability of a film to restructure upon exposure to increasing water activity as well as the frustration of chain movements due to the presence of electrostatic cross-linking. We initially focused our hysteresis study on PEMs grown utilizing solutions of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) with pH values of 7.5 and 3.5, respectively, since this system was known to grow in relatively thick deposition increments and previous humidity swelling results were available for comparison.[13] In the following, however, we demonstrate that the hysteresis effect is present in (PAH/PAA) systems assembled at other pH values as well.

This is, to our knowledge, the first detailed report of significant *humidity-induced* swelling hysteresis in PEMs. Although the qualitative shapes of the hysteresis curves in this study suggest a more general connection to previously known polymer−solvent vapor hysteretic systems (such as poly(methyl methacrylate) (PMMA)/toluene)[23] as well as previous studies on naturally derived polymeric materials,[24−26] hysteresis effects are measurably absent for certain other PEMs[12] and ionomers[27] and as we demonstrate below are absent in single-component films of either PAH or PAA. Overall, our results serve to illustrate that the presence of swelling hysteresis in certain PEM systems necessitates a careful approach to how such materials are stored, handled, and tested, as the humidity exposure history of a PEM can have a persistent impact on the material properties and structure.

EXPERIMENTAL SECTION

All films were created using spin-coating (Laurell Technologies Inc., model WS-400BZ-6NPP/Lite) onto (100) p-type single-crystal polished silicon wafers (University Wafer). Prior to film deposition the wafers were treated for 30 min using a Novascan Digital UV ozone system in order to remove residual organic contaminates. Aqueous solutions of PAH (M_w = 56 000 Sigma-Aldrich) and PAA (25% solids in water, M_w > 200 000, Polysciences, Inc.) were prepared in deionized water (Millipore, 18.2 MΩ·cm) to a concentration of either 10 wt % (used for spin-coating single-component polyelectrolyte films) or 0.02 M by repeat unit (used for multilayer assembly). Solutions for multilayer assembly were adjusted to the desired pH using 0.02 M solutions of either NaOH or HCl. The 10 wt % solutions were adjusted to pH 7.0 for PAH (higher pH values yielded precipitation at this concentration) and pH 3.0 for PAA, which was close to the unadjusted pH of the solution. Single-component polyelectrolyte films were spin-coated at 2000 rpm for 2 min. PEMs were constructed using 2000 rpm spin steps with durations of 20 s. PAH was deposited first, followed by two separate rinse steps of pure water; PAA was then deposited, followed by two more rinse steps. This completed one bilayer of film deposition and the above steps were repeated until the desired film thickness was reached. Films are denoted as $(\mathrm{PAH}X/\mathrm{PAA}Y)_Z$, where X and Y are the respective pH values of the PAH and PAA solutions and Z is the number of bilayers, with a half-integer bilayer designating an additional PAH capping step.

The effect of humidity on film thickness was studied for both single-component polyelectrolyte films and cross-linked PEMs using a reflectometer (Filmetrics, F20). Measurements were taken in a humidity-controlled glovebox (Electro-Tech Systems, Inc.) and are reported in this paper as relative film thicknesses (normalized to the thickness of each sample at 10% RH). The Supporting Information contains detailed information about the relative swelling measurement technique. The dry-state thicknesses of 20- and 20.5-bilayer samples of (PAH7.5/PAA3.5) were ≈150 nm, and the thickness of the $(\mathrm{PAH3.0/PAA3.0})_{50.5}$ sample was ≈260 nm. The thicknesses of the PAA and PAH single-component films were ≈410 and ≈120 nm, respectively. The average temperature during experimentation was 26.1 ± 2.6 °C unless otherwise indicated. The systematic uncertainties in relative humidity and temperature readings were 0.25% RH and 1 °C, respectively. Films were equilibrated at 10% RH for 2−5 min, and when the thickness reading stabilized a measurement was recorded. The RH was then increased ≈10%, and the film thickness was again recorded after another 2−5 min equilibration period. Data collected during this period of swelling upon increasing humidity are referred to as absorption data. After reaching ≈100% RH, measurements were collected in the same manner while deswelling the film by decreasing the humidity in 10% increments (desorption) until again reaching 10% RH. The absorption and desorption measurement cycles were then repeated on the same film an additional two times.

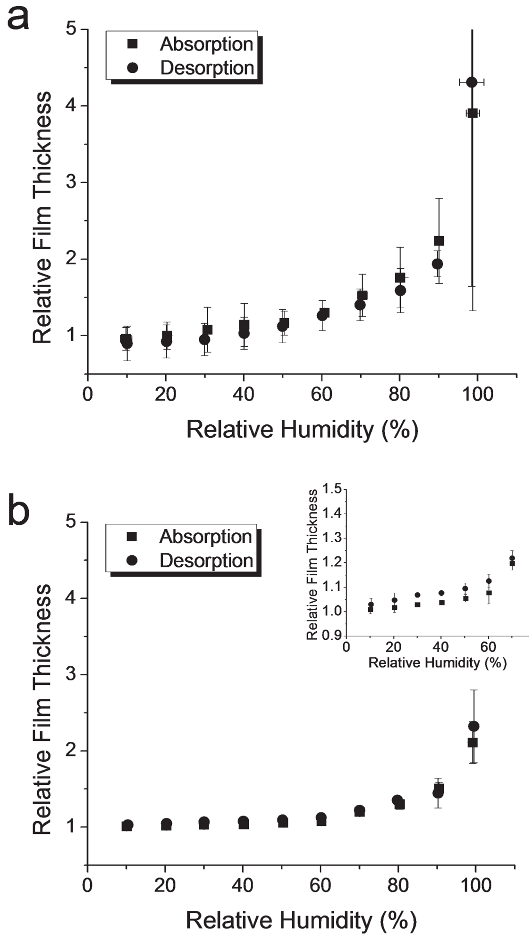

Figure 1. Humidity-dependent swelling and deswelling of (a) PAH and (b) PAA films. The squares and circles indicate measurements during absorption and desorption, respectively.

To examine the stability of the hysteresis phenomenon, a $(\mathrm{PAH7.5/PAA3.5})_{20.5}$ sample was split and both halves were equilibrated at 10% RH, after which the humidity was raised to 60% RH. One half of the sample was then removed to room conditions (62% RH, 23 °C) while the second portion of the film was brought to ≈100% RH, equilibrated for several minutes, and then returned to 60% RH. The first piece was then placed back in the glovebox, and both samples were held at 60% RH for ≈8 days. Thickness measurements were initially taken every 10 min, eventually decreasing in frequency to two measurements per day.

To determine the effect of drying technique on film thickness, a $(PAH7.5/PAA3.5)_{20.5}$ sample was submerged in a beaker of water and swirled for 45 min. Excess water was shaken from the film, and it was allowed to dry at room conditions (58 ± 4% RH, 22.7 ± 2.0 °C) for ≈5 min before taking a thickness measurement. The film was then reimmersed in the water for 20 min, excess water was shaken from the slide, and low-humidity (<10%) compressed air was swept across the slide surface for ≈5 min. The sample thickness was then measured again in the laboratory air. This process was repeated an additional five times on the same sample.

All uncertainties and error bars in this work represent the 95% confidence interval on the measurement.

RESULTS AND DISCUSSION

Single-Component Polyelectrolyte Films. The relative thickness for single-component (not multilayer) films of PAH and PAA are shown in Figure 1, parts a and b, respectively. Both films exhibited limited swelling at low humidity, with swelling increasing substantially between 80% and 100% RH. PAA was observed to approximately double in film thickness near 100% RH, while the PAH film swelled on average to 4 times of its original film thickness, though we note that there was a large error associated with this value possibly due to uneven swelling in the highly solvated film. Increased swelling at high humidity has been observed before for polyelectrolyte multilayer films,[11−13,28] particularly in (PAH/PAA) films assembled at low pH, where the PEM is enriched in the anionic polyelectrolyte and the film chemistry is expected to bear a strong similarity to lightly cross-linked PAA.[13]

The general shape of the humidity graph can be attributed to the increased availability of additional adsorption sites for water as the polyelectrolyte structure swells. In certain multilayer systems, the swelling curve can be seemingly divided into two distinct regimes, with a transition to increased swelling at higher humidity that is attributed to the percolation of adsorbed water within the film and the concomitant rapid swelling and reorganization of the multilayer structure.[12,13] In some cases, the transition between swelling regimes is less pronounced, and Flory−Huggins solution theory provides a reasonable fit to the data.[11,28] We note that our data in Figure 1 for single-component polyelectrolytes can only be reasonably explained by a modified Flory−Huggins theory where the χ-parameters for both systems are allowed to decrease as the films swell (see Supporting Information). In other words, in both systems the polyelectrolyte−water interaction appears to become more favorable as the film swells. This observation has precedent in the swelling of hydrophilic polymer gels in aqueous solutions[29] and suggests that it is energetically favorable for the polymer structure to reorganize in response to the presence of solvent in the system.

Fits of our swelling data to a quadratic model[29] for χ (see Supporting Information) suggest that χ for PAH decreases from 0.3 at 10% RH to −0.9 at ≈100% RH. The crossover from positive to negative χ represents the point where the polymer begins preferring interactions with water molecules over interchain interactions. This point occurred between 60% and 70% RH for PAH and is consistent with the transition to increased swelling shown in Figure 1a. The ability of PAH to exhibit a negative χ at high humidity is also consistent with the large uncertainties in the film thickness that were recorded near 100% RH (where the film was imbibing large quantities of water). In addition, visual observations of PAH films that had been subjected to high-humidity conditions revealed a high degree of film thickness nonuniformity. We presume that the affinity of PAH for water allows for significant structural rearrangements in the film at high humidity; this latter case would not be true for PAA, for which (according to our fit) χ decreased from 1.3 at 10% RH to 0.3 at ≈100% RH. The large χ at lower humidity is reflective of the surprisingly low swellability of PAA at RH values up to ≈60% and can be physically explained by strong interchain H-bonding between COOH groups. At higher humidity, however, water penetrates the structure, mitigates interchain H-bonding, and permits rapid swelling as the COOH groups ionize and are forced apart.[13] Nevertheless, χ remains positive for PAA over the entire range of humidity, consistent with the overall lesser degree of swelling and lower uncertainties in film thickness over multiple cycles (due in part to a lesser degree of film restructuring at high humidity).

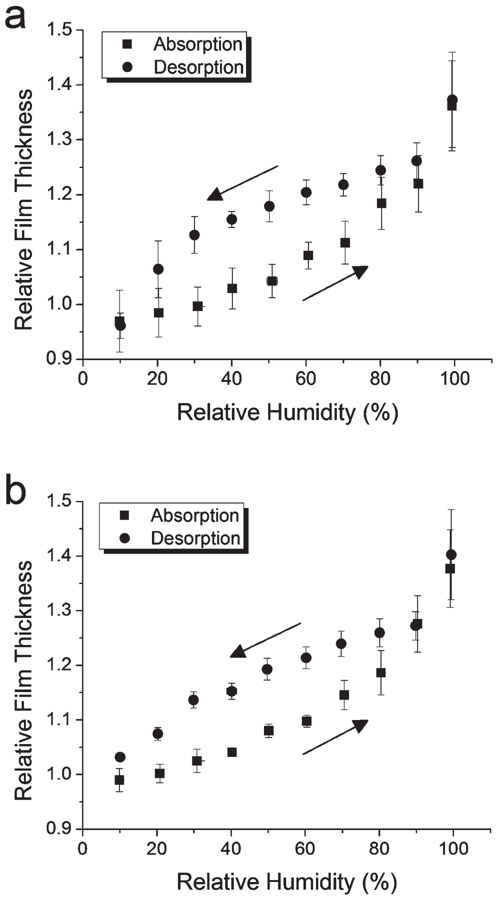

Figure 2. Humidity-dependent swelling and deswelling of (a) 20-bilayer and (b) 20.5-bilayer (PAH7.5/PAA3.5) polyelectrolyte multilayer films. The squares and circles indicate measurements during absorption and desorption, respectively.

In general, both PAH and PAA film thicknesses at given humidity values were reproducible within error, regardless of cycle number or direction of humidity change. PAH single-component films displayed essentially no swelling/deswelling hysteresis; relative film thicknesses were reproducible within measurement error at a given humidity during both absorption and desorption. PAA appeared to exhibit a slight but measurably higher (≈3−4% between 20% and 50% RH) film thickness on desorption over the 20−50% RH range (see inset of Figure 1b), but otherwise was similarly hysteresis-free. This behavior is in marked contrast to the clear swelling/deswelling hysteresis observed for PEMs comprised of PAH and PAA, as described in the following section.

Polyelectrolyte Multilayer Films. Three cycles of increasing and decreasing humidity were applied successively to both 20-bilayer and 20.5-bilayer (PAH7.5/PAA3.5) films. Both systems were tested to ascertain the effect of the outermost layer on the swelling behavior; these data are shown in Figure 2. Both films exhibited reproducible, hysteretic swelling/deswelling behavior, with the relative film thickness at any value of RH between 20% and 80% RH dependent upon whether the sample was absorbing or desorbing moisture. The desorption data point at 10% RH in the 20.5-bilayer system (Figure 2b) was not hysteretically stable, and its thickness would collapse back to the initial film thickness if given several more minutes to equilibrate; this could possibly be due to decreased chain mobility in the PEM at the lowest humidity value, as water is known to be a good plasticizer for this system.[13] This difference in thickness was not observed at 10% RH for the 20-bilayer film (Figure 2a), and the relative thickness curves for both films appeared otherwise identical within error, indicating that the choice of polyelectrolyte capping layer provided little influence on the subsequent swelling/deswelling behavior of the (PAH7.5/PAA3.5) system.

Above 90% RH the PEMs exhibited a significant increase in swelling, presumably as the system entered a more solvated-like state as the external water activity approached unity. This notion is supported by the fact that upon desorption from ≈100% RH to 90% RH the films quickly reestablished their 90% RH absorption film thicknesses, suggesting that water that entered the films above this humidity value was not tightly bound. Below 90% RH, however, the film began to exhibit hysteresis upon desorption, suggesting that the process of fully hydrating the PEM allowed for a rearrangement of the film structure that permitted more specific binding interactions with water molecules and discouraged the desorption of water from the film. Upon further desorption, these specific interactions impeded the film from forming the same interchain interactions that were present upon absorption; in addition, electrostatic cross-linking in the film hindered the chain rearrangements necessary for the adoption of a more collapsed state. These factors resulted in a more swollen structure until the external water activity was sufficiently low to drive enough bound water from the film and allow the polyelectrolytes to adopt a more collapsed molecular architecture.

The foregoing framework offers a reasonable hypothesis for the mechanism of humidity-based hysteretic swelling in PEMs and was in fact proposed decades ago to explain sorption hysteresis phenomena in biologically derived hydrophilic polymer systems such as textiles and foodstuffs.[24−26] In some previous cases the hysteresis phenomenon decreased with successive absorption−desorption cycles,[24,30] but for the PEMs tested here there was no change in either the absorption or the desorption curves over three measurements cycles. We speculate that this could be due to the large number of strong electrostatic cross-links in PEMs compared to the mostly secondary interactions found in natural materials. The necessity of cross-linking to stabilize the hysteresis effect is further supported by the lack of hysteresis in the un-cross-linked, single-component polyelectrolyte films. While PAH exhibited no measurable hysteresis, the slight hysteresis in PAA at low humidity might be explainable on the basis of weak cross-linking through H-bonding of COOH groups on the chains. This bonding would be expected to diminish with humidity as water would begin to disrupt the H-bonded network and possibly permit ionization of the acids; correspondingly, we observed the disappearance of a measurable hysteresis in PAA above ≈60% RH, concurrent with an increase in swelling of that system (inset Figure 1b). A slight (≈ 2%) swelling/deswelling hysteresis has also been noted in certain polyelectrolyte−clay composite films, where clay platelets were used as the electrostatically negative component in assembling the film.[31] Such systems would be expected to have significantly fewer cross-links than a PEM comprised of interpenetrating polyelectrolyte chains.

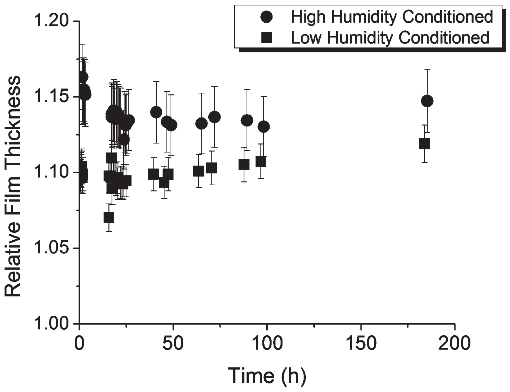

Figure 3. Stability of swelling/deswelling hysteresis for $(PAH/PAA)_{20.5}$ films stored at 60% RH. Both films were conditioned at 10% RH. The "low humidity conditioned" film (squares) was swollen directly from 10% RH to 60% RH, while the "high humidity conditioned" film (circles) was swollen from 10% RH to ≈100% RH before being deswelled back to 60% RH. Both films were then stored and tested in the same 60% RH environment.

The above considerations are consistent as well with the current understanding of hysteretic vapor solvent uptake in some nonionic polymer systems. Recent studies on PMMA/toluene, for example, have demonstrated vapor solvent mass uptake curves with qualitative similarity to the swelling curves we have obtained for the (PAH/PAA) system.[23] In the case of PMMA (un-cross-linked), the observed desorption hysteresis emerged when the solvent activity was decreased relatively quickly from a value above the glass transition solvent activity (a_g), where the PMMA was in a rubbery state, to a value *below* a_g, where the PMMA was glassy. Thus, impeded chain relaxations were again a necessary prerequisite for the emergence of hysteresis upon solvent desorption. Indeed, for solvent desorption below a_g the incorporation of an appropriate term to the Flory−Huggins activity model to account for mechanical stresses in the glassy matrix produced good fits to the experimental data; incorporation of glassy relaxation kinetics (following a stretched exponential function) could further explain nontrivial dependencies of the polymer softening time on the solvent activity at which the sample was aged.[23]

In order to test the kinetic stability of the two different swollen states within the hysteresis region for our system, we subjected a sample, one part of which had been previously conditioned at low humidity and the other at high humidity, to prolonged aging at 60% RH for ≈8 days, as detailed in the Experimental Section. The results of this test are shown in Figure 3. The sample initially showed a difference in thickness of ≈6%, which was observed to decay to ≈3% over approximately the first 2 days of testing. After that time the difference in thickness between the two samples was remarkably stable, persisting during the remainder of the ≈8 days that we ran the test.

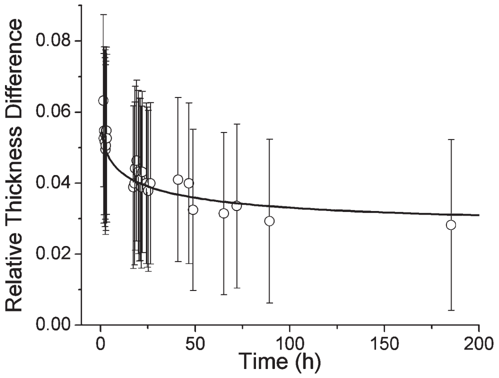

Figure 4. Relative thickness difference between the high humidity- and low humidity-conditioned sample measurements from Figure 3. The solid line is the best fit to the stretched exponential function given in eq 1, with $\beta = 0.36 \pm 0.06$ and $\tau = 16 \pm 11$ h. The R^2 value for the fit was 0.83. Five outlying data points falling more than two standard deviations from the fit curve have been removed in Figure 4 according to the method of Montgomery et al.[34]

In an effort to more clearly visualize the data shown in Figure 3, we produced a separate plot showing the difference in relative film thickness between the high and low humidity conditioned samples versus relative humidity; these data are shown in Figure 4. As with the PMMA/toluene study discussed previously,[23] our data exhibited a stretched exponential dependence (solid line in Figure 4) given by

$$\frac{d - d_\infty}{d_0 - d_\infty} = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \qquad (1)$$

where d is the difference in film thicknesses, d_∞ is the difference between the film thicknesses at long times (in our case ≈180 h), d_0 is the initial difference in film thicknesses (at time $t = 0$), τ is a time constant, and β is a stretching exponent. Equation 1 has been previously applied to diffusion processes in PEMs[32] but is also well-known to apply generally to structural relaxation processes in glassy polymer systems, where β ($0 < \beta < 1$) is typically treated as a fitting parameter that encapsulates relaxation events occurring in the system over a spectrum of time scales.[23,33] For the data in Figure 4, we found $\beta = 0.36 \pm 0.06$ (a value that agrees well with results for other systems where $\beta = 0.3-0.34$)[23] and $\tau = 16 \pm 11$ h. Inspection of the data in Figure 3 seems to indicate that this structural relaxation is happening primarily in the film conditioned at high humidity, and the large time constant indicates that deswelling is happening on a much longer time scale than the change in film thickness that immediately accompanies a humidity change, which we estimated to be complete within a couple of minutes.

On the basis of the above observations, we hypothesize that humidity swelling in this PEM system happens over two distinct time scales. The shortest time scale involves the diffusion of water into or out of the film and the relatively fast swelling/deswelling response of the polyelectrolyte network, occurring on the order of seconds to minutes. At longer time scales of hours to days, gradual changes in the film thickness may continue to be observed, a phenomenon that is more evident upon the desorption of moisture. This longer time-scale deswelling effect presumably reflects kinetically difficult structural relaxations of the polymer chains from a more to a less water-favorable configuration, due to both interchain cross-linking and increased vitrification of the PEM structure at relative humidity values less than ≈90%, where the swelling curves were observed to bifurcate.[23] The near absence of hysteresis in either PAH or PAA homopolymer films suggests particularly that electrostatic cross-linking plays a prominent role in the emergence of hysteresis in (PAH/PAA) PEMs.

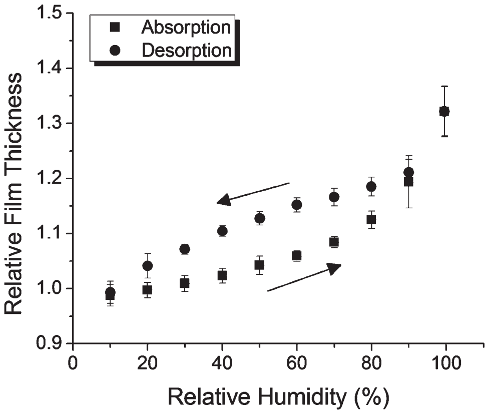

Figure 5. Humidity-dependent swelling and deswelling of a (PAH3.0/PAA3.0)$_{50.5}$ film. The squares and circles indicate measurements during absorption and desorption, respectively.

Our observation of two time scales during humidity swelling/deswelling is consistent with previous surface plasmon spectroscopy studies by Kugler et al. on PEM systems comprised of PAH and poly(4-sodium styrenesulfonate); these authors observed that final equilibration times could take 8−15 h.[28] When utilizing PEM films for compression printing applications, Gong et al. have reported that the mobility of PEM films depends upon the drying time, a process that can take several hours (they observed differences in patterning between films dried 6 h vs 12 h). In addition, Lutkenhaus et al. have reported that impedance spectroscopy measurements of PEM systems under controlled humidity can take up to a week to completely stabilize, which agrees in magnitude with the longer time scale relaxation times that we have observed.[35] In our experiment, we saw essentially no change in the relative film thickness difference after a few days, although we continued the experiment for over a week. Even at these long times, however, the systems exhibited a measurable difference of a few percent, indicating that some degree of internal structural difference was persistently trapped in the films at intermediate humidity values, possibly due to electrostatic cross-linking within the PEM.

To assess the generality of the hysteresis phenomenon to (PAH/PAA) films assembled under different conditions, we tested the humidity-dependent swelling and deswelling of a 50.5-bilayer film of (PAH3.0/PAA3.0); the results are shown in Figure 5. This system, similar to films of (PAH7.5/PAA3.5), exhibited a pronounced hysteresis loop between approximately 10% and 90% RH, indicating that the hysteresis effect is not limited to the pH 7.5/3.5 assembly conditions. In comparison to (PAH7.5/PAA3.5) films, the (PAH3.0/PAA3.0) system showed less swelling upon absorption at low (<60% RH) humidity, consistent with previous reports for (PAH/PAA) assembled at low pH.[13] Thus, while changing the pH assembly conditions appeared to affect certain characteristics of the swelling curve, the overall response remained qualitatively very similar in both the (PAH7.5/PAA3.5) and (PAH3.0/PAA3.0) systems.

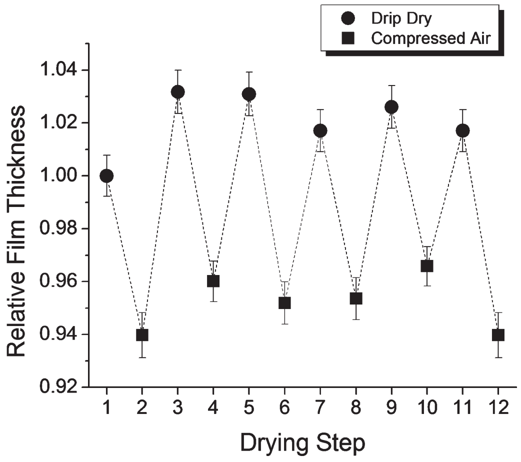

Figure 6. Relative film thickness of a $(PAH7.5/PAA3.5)_{20.5}$ film as measured in laboratory air (58 ± 4% RH, 22.7 ± 2.0 °C) after allowing the film to either "drip dry" (odd steps, circles) or after drying with compressed air (even steps, squares).

As a demonstration of the practical importance of the hysteresis effect to routine PEM film processing, we subjected a $(PAH7.5/PAA3.5)_{20.5}$ film to an alternating succession of immersion and drying steps; after each drying step the thickness was measured in the ambient laboratory air (≈60% RH) after a few minutes had elapsed. The film was either allowed to "drip dry" in laboratory air (reflecting desorption of water to the ambient humidity) or was blown with compressed, dry air (necessitating absorption back to the ambient humidity); the results are shown in Figure 6, in which the film thicknesses have all been normalized to the first "drip dry" step.

The data in Figure 6 indicate that the choice of drying technique affected the film thickness of a $(PAH7.5/PAA3.5)_{20.5}$ film in laboratory air by ≈5%. Normalized to the first "drip dry" step, subsequent compressed air steps showed lower relative thicknesses between 0.94 and 0.96. Overall, there was a slight variability in the relative film thickness of the "drip dry" versus the compressed air-dry steps, which is perhaps expected given the nature of the experiment. Nevertheless, the hysteresis effect is apparent and reproducible. In addition, the effect does not seem to be diminished by successive cycling, in agreement with the reproducibility of the swelling measurements in Figures 2 and 5.

CONCLUSIONS

We have demonstrated that polyelectrolyte multilayer films comprised of PAH and PAA can exhibit significant swelling/deswelling hysteresis when subjected to changes in relative humidity. The hysteretic behavior was essentially absent in the swelling and deswelling of spin-coated films of the individual component polyelectrolytes, which showed good agreement with a modified Flory–Huggins solution theory allowing for a decreasing χ to reflect restructuring of the films to a more water-favorable configuration upon humidity absorption (see Supporting Information). This restructuring was largely reversible upon desorption in the individual component un-cross-linked polyelectrolyte films due to high chain mobility. Upon desorption in PEM systems, however, the presence of electrostatic cross-linking hindered reversible deswelling of the restructured film, resulting in hysteresis. Following the initial relatively fast deswelling that accompanied a decrease in relative humidity, further structural relaxations appeared to continue over a time scale of several hours to days, but a measurable thickness hysteresis remained even in systems equilibrated for over a week. Although changing the pH of the PAH and PAA solutions upon assembly affected the shape of swelling curve, the hysteresis effect was still apparent and qualitatively similar, indicating that the phenomenon is not limited to the (PAH7.5/PAA3.5) system. Because of the hysteresis effect, PEM films were shown to be sensitive to the choice of drying technique; the thickness of a film dried in compressed air was consistently ≈5% less than the thickness of the same film when allowed to "drip dry" in the same environment. This effect was repeatable over multiple drying–rehydration cycles.

In future work we plan to examine the generality of the hysteresis phenomenon by studying a wider range of assembly conditions and by considering different types of polyelectrolytes as well as other charged species that may be incorporated using LbL assembly. In this work, we utilized spin-assisted LbL deposition, which could also conceivably have an effect on film properties as opposed to, for example, the typical dipping technique used for constructing LbL films.[36] We note, however, that the growth increment of our films created using spin-assisted LbL assembly was in reasonable agreement with the values obtained in previous work for dipped systems.[13] The results of Doumenc for swelling of PMMA in toluene vapor[23] suggest that the relaxation kinetics of the PEM could be a function of the humidity at which the film is equilibrated—this will be a topic for future investigation. We additionally plan to determine the extent to which a modified Flory–Huggins theory may be useful for describing hysteretic swelling/deswelling in PEMs. Previous studies appear to have only examined swelling (absorption) behavior;[11,28] we plan to explore the extent to which polymer solution theories may also be useful in describing desorption behavior in PEM systems.

Our results indicate that the choice of drying technique and the manner in which a PEM is equilibrated to the ambient environment may have a measurable effect on film properties. Furthermore, in cases where, for example, the swellability of a PEM may be of interest in an application such as an environmental sensor or an electronic device, the humidity exposure history of a film postassembly could potentially impact the intended performance. From a more fundamental standpoint, we expect that future studies of humidity swelling/deswelling hysteresis in PEMs may lead to a better understanding of the internal order and dynamics in this rapidly growing class of materials.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed information on relative swelling calculations and Flory–Huggins fits to single-component polyelectrolyte swelling data. This material is available free of charge via the Internet at http://pubs.acs.org.

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