Swelling Dynamics of Multilayer Films of Weak Polyelectrolytes

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The swelling behavior of thin polyelectrolyte multilayers assembled from poly(acrylic acid) and poly(allylamine hydrochloride) under various pH conditions was characterized in real time by in situ single wavelength ellipsometry. Both the rates and extent of swelling were found to be independent of the solution environment, yet they depended strongly on the pH conditions under which the layers were fabricated. The transport mechanism could be determined by analyzing the rate of swelling and was also observed to vary significantly with the initial assembly conditions of the multilayer films. The swelling behavior was non-Fickian for films constructed with a deposition pH of 3.5, 5.0, and 6.5 for both polyelectrolytes. The time scales to reach maximum swelling depended strongly on pH assembly conditions and varied over at least 3 orders of magnitude from seconds to tens of minutes. Swelling of the films was also observed to depend strongly on the ambient humidity to which the films were exposed before measurement; for example, when equilibrated at 45% relative humidity prior to swelling, films assembled at pH = 3.5 required ~1800 s to reach equilibrium, while the same films reached maximum swelling in ~3 s when pre-exposed to an environment of 20% relative humidity.

Introduction

Polymer multilayers can be prepared by the sequential electrostatic adsorption of oppositely charged polyelectrolytes onto a substrate. Through control of various assembly parameters one can gain good control over the thickness, internal structure, and surface roughness of the multilayer.[1] Thin polyelectrolyte multilayer (PEM) films fabricated by this layer-by-layer (LbL) adsorption technique have been extensively studied and have been demonstrated to have potential applications as sensors,[2,3] membranes,[4] and drug delivery agents,[5−7] and in some polyelectrolyte systems biocompatibility was observed.[8,9] It is important to note that for many of these more interesting applications water transport plays a key role, and hence, the conformation and behavior in an aqueous environment must be well understood for systems to be tailored and optimized. Some of the most interesting systems reported to date are PEMs of weak polyelectrolytes. Unlike strong polyelectrolytes that remain fully charged over a wide range of pH, the charge fraction of weak systems can be regulated with assembly pH, affording great control over many final film properties. Two of the most well studied weak polyelectrolytes are poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH), which can exhibit many anomalous properties. For example, Shiratori and Rubner have found that PAH/PAA systems can undergo a large thickness transition depending on assembly conditions.[10] Measuring the swelling in situ is key to the understanding of the structural and physical properties of multilayers in response to the local environmental in many applications. For instance, the swelling behavior of PEMs in air at different relative humidites has been used to determine a Flory−Huggins parameter for a fully charged PAH/PSS system and to suggest a mechanism for vapor water permeation.[11]

When a thin polymer film is brought into contact with a penetrating liquid, the penetrant diffuses into the polymer matrix and the polymer swells. The solvent enters the polymer through pre-existing voids or through spaces that are formed by local segmental motion in the polymer network, which is followed by local relaxation of polymer segments. The swelling mechanism is then characterized by diffusion and relaxation times of the polymer. The process can be described as Fickian (case I) diffusion when the rate of permeant diffusion is much less than the polymer segment mobility. In this process there is a continuous concentration profile in the film and a steady transport of the penetrant.[12] When the rate of diffusion is much faster than the swelling-induced

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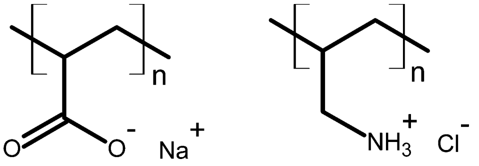

Figure 1. Structures of polyelectrolytes: PAA and PAH.

polymer relaxation, the diffusion process is classified as case II. Case II swelling is characterized by a sharp interface between the swollen polymer and unswollen polymer that moves at a constant rate.[12] The diffusion process is termed super case II when a late-stage acceleration in the permeation rate occurs.[12−15] Generally, with super case II swelling there is an induction period where a concentration profile has been established across the film. Super case II diffusion has been reported in polymer systems such as polystyrene swollen with *n*-hexane.[14] Finally, anomalous or non-Fickian swelling is a combination of Fickian and case II swelling, and it occurs when the rate of permeant diffusion and the rate of polymer relaxation are comparable.[12]

While swelling has been well studied in many hydrophobic polymer films, the kinetics and environmental factors that affect the swelling mechanism of PEMs in water have not been studied. In this paper, the swelling of PAH/PAA multilayers assembled under various conditions was studied as a function of various aqueous bath conditions by in situ null- and off-null ellipsometery, to record swelling behavior in real time and to determine the mechanism. The effect of humidity preexposure of the dry films on subsequent water transport through the multilayer films was also investigated, as this variable was found to be highly influential to the resulting swelling behavior.

Experimental Section

Materials and Film Assembly. Poly(acrylic acid) (MW = 90 000) (PAA) and Poly(allylamine hydrochloride) (MW = 60 000) (PAH) were obtained from Polysciences and Aldrich, respectively, with structures detailed in Figure 1.

Polyelectrolyte solutions of 10^{-2} M were prepared on the basis of repeat unit molecular weight using 18.2 MΩ cm Millipore water. The pH of the polyelectrolyte solution was adjusted with HCl or NaOH, and solutions were then filtered though a 0.7 μm filter. Polished Si⟨100⟩ silicon slides were cleaned in concentrated chromium(III) oxide/sulfuric acid for a minimum of 12 h and then first thoroughly rinsed with distilled water and then rinsed with Millipore water. Multilayer films were fabricated on the basis of the usual layer-by-layer technique using an automated dipper.[10,16] The silicon substrate was first immersed into the PAH solution for 15 min. This was followed by a rinsing procedure, where the substrate was successively immersed into three rinse baths of Millipore water (pH ~ 5.5−6.5) for 1, 2, and 2 min, respectively. The substrate was then immersed into the oppositely charged polyanion (PAA) solution for 15 min, followed by the same rinsing procedure to complete one bilayer. The process was repeated until the desired layer thickness was achieved (15, 25, and 60 bilayers for matched assembly, pH = 5.0, 3.5, and 6.5, respectively). After the films were assembled, excess water was removed with compressed air, and then the films were oven-dried under vacuum at 65 °C overnight. PAH/PAA films assembled at pH = 6.5 were autodipped with light agitation.

Table 1. Dependence of Assembly Conditions and Layer Number on the Dry Thickness[a]

assembly pH	layer no.	av dry thickness (Å)
3.5	50	1153
4.0	50	1325
5.0	20	668
5.0	26	1357
5.0	30	1739
6.5	120	402

[a] The average dry thickness was obtained at ~45% RH. Errors associated with the average dry thickness are ~4%.

Swelling Experiments. The thickness and refractive index of the PAH/PAA films were measured using a Multiskop (Optrel, Germany) single wavelength (633 nm) null-ellipsometer at a fixed angle of 70° with respect to the normal. In situ measurements were conducted in a home-built liquid sample cell that has two fixed BK7 windows aligned perpendicular to the incident and reflected beam. Film thickness was measured dry and then swelling measurements were subsequently made by the addition of solution of pH = 4.0, 7.0, 8.0, 9.0, and 10.0 by adjusting the pH with HCl or NaOH, and an ambient refractive index for water of 1.332 was assumed. The accuracy of the cell was tested through the nonswelling of a hydrophobic test film of polystyrene spin-coated onto a Si wafer, to confirm that the instrument was correctly calibrated for the liquid cell. Ellipsometric measurements were performed first in air and then in solution. The error associated with the thickness and refractive index measurements were determined to be ±1% and ±0.2% respectively. For studies of the effect of salt on swelling, solutions of 1−6 mM NaCl were used. For the determination of the percent swelling of the PAH/PAA film, 15 separate ellipsometric measurements were conducted in a 1.2 × 0.5 cm area around the center of the film. Experiments were preformed on multiple samples. The percent swelling is defined as

$$\left(\frac{\text{swollen thickness} - \text{dry thickness}}{\text{dry thickness}}\right) \times 100\% \qquad (1)$$

In cases where the swelling rate approached the time scale of sampling, off-null ellipsometry was used.[17,18]

Controlled humidity environments for the dry films prior to measurement were established by using the equilibrium water vapor over saturated salt solutions.[19] The PAH/PAA films were dried in a cell with a dry nitrogen purge. After the film was dried, the film was exposed to a constant purge of nitrogen at specific percent humidity until equilibrium was reached. The film was then hydrated with water.

Results and Discussion

Extent of Swelling. Polyelectrolyte multilayers consisting of (PAH/PAA), with PAA as the top capping layer, were assembled under different conditions as indicated in Table 1. In this study the layer number was varied to ensure similar film thickness was being compared between different assembly pH conditions. A typical swelling profile and corresponding refractive index change is shown in Figure 2; after the dry layer thickness was determined in air to be 1200 Å, water was added to the cell at time 0, and the thickness of

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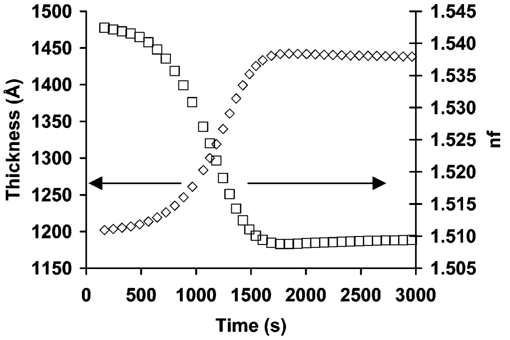

Figure 2. Typical swelling curve for assembly pH = 3.5 (25 bilayers), when exposed to bath pH = 4.0, showing swelling of 20% and a corresponding reduction in refractive index. Prior to solution exposure the film was equilibrated at ~45% RH.

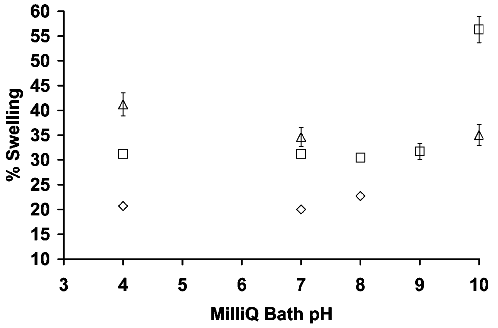

Figure 3. The effect of assembly pH on the degree of swelling when exposed to various MilliQ bath pH. The symbols ◇, □, and △, correspond to assembly pH = 3.5 (25 bilayers), 5.0 (15 bilayers), and 6.5 (60 bilayers), respectively. The films were equilibrated at ~45% RH prior to solution exposure.

the swelling film was recorded every ~2 s until saturation of 1440 Å is reached at ~2000 s. From this, an equilibrium swelling extent could be estimated as 20% by eq 1. The validity of the final swollen thickness was verified through a simple conservation-of-mass mixing approximation, to check that the refractive index measurement returned by the ellipsometer agreed with the corresponding water dilution of the swollen polymer. The final equilibrium swelling extent and reduced refractive index was within 1% of the calculated conservation-of-mass value. Equilibrium swelling extents for similar films constructed and measured in a range of pH solutions are presented in Figure 3.

Film assembled at pH = 3.5 (25 bilayers) exhibited only a modest extent of swelling (~20%) when immersed in solutions of pH = 4.0, 7.0, and 8.0, as shown in Figure 3. The films assembled at pH = 3.5 were not stable in water beyond pH = 8.0, as the original film thickness could not be recovered reversibly. The apparent low level of swelling of the pH = 3.5 assembled films may be due to the films being preswollen at ~45% relative humidity.

At an assembled pH of 5.0 (15 bilayers), the films swelled to a greater extent than those assembled at pH = 3.5. No great change in the extent of swelling was observed when the assembly pH = 5.0 films were exposed to bath pH = 4.0−9.0; in all cases the films swelled ~30%. However, the films swelled to ~56% when exposed to bath pH = 10.0. At pH = 10.0, the free amine groups in PAH are less charged (~20% free NH_3^+ groups) as compared to that of the assembly conditions, and the free carboxylic acid groups of the PAA are completely charged (100% COO^- groups).[20] At this solution pH, there would be a low amount of available ionic cross-links expected, and the increase in the repulsion of the negative charges of the free carboxylic acid groups on the PAA chains could facilitate a larger extent of swelling.

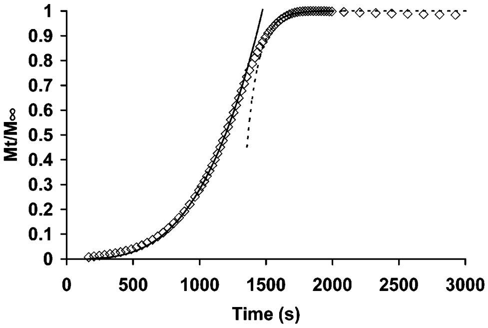

Figure 4. Swelling curve for assembly pH = 3.5 (25 bilayers), when exposed to MilliQ bath pH = 4.0. Prior to solution exposure the film was equilibrated at ~45% RH. The solid line corresponds to a fit with eq 2 and the dashed line was fit with eq 3.

Films assembled at pH = 6.5 (60 bilayers) swelled to a greater extent than those assembled at pH = 3.5 and 5.0; however, this may be an artifact of the greater preswollen thickness. The extent of swelling was ~40% upon exposure to a bath pH of 4.0. The films swelled to ~35% when immersed in bath pH = 7.0 and 10.0. Although one might expect an increase in swelling at pH = 10.0, the nature of the assembly condition might play a key role. The highly compact networked structure and lack of free amine and carboxylic acid groups may impair greater swelling when exposed to bath pH = 10.0. In general, the PAH/PAA system swells to the same extent (20−40%), regardless of the bath conditions used in this study, over a wide range of pH. It thus appears that the swelling properties of the polyelectrolyte multilayers are governed largely by the pH conditions under which they are assembled and not by their pH environment.

Dynamic Swelling and Kinetics. The dynamic swelling behavior of the polyelectrolyte multilayer films was analyzed with the following equation[21]

$$\frac{M_t}{M_\infty} = kt^n \qquad (2)$$

where M_t is the amount of water absorbed at time t, M_∞ is the amount of solution absorbed at equilibrium, k is a characteristic constant dependent on the structure of the polymer network, and n is the exponent that describes the type of diffusion into the polymer. Equation 2 is valid only when the fraction of water (M_t / M_∞) uptake is less than 0.60.[21] From the slopes and intercepts of $\ln(M_t/M_\infty)$ versus ln t, the constants n and k were calculated. A typical such fit is shown in Figure 4. From the evaluation of n, the diffusion type for the system can be obtained. For a thin film, $n = 0.5$ implies Fickian diffusion, $0.5 < n < 1.0$ indicates anomalous diffusion, and $n = 1.0$ describes case II transport, and when $n > 1.0$, the transport mechanism is super case II.[12,21] For volume fractions greater than 60%, the swelling process

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Table 2. Assembly pH Dependence on A and k_2 at Various MilliQ Bath pH[a]

	A			k_2 (s^{-1})		
bath pH	pH = 3.5	pH = 5.0	pH = 6.5	pH = 3.5	pH = 5.0	pH = 6.5
4.0	2×10^6	8×10^{10}	1.7	0.01	0.5	0.6
7.0	2×10^{10}	3×10^6	1.6	0.02	0.1	0.8
8.0	7×10^8	6×10^7		0.03	0.2	
9.0	1×10^5	2×10^5		0.04	0.2	
10.0		4×10^5			0.3	

[a] Errors on k_2 are approximately 10%. The pre-exponential factor A is accurate to within an order of magnitude. Prior to solution exposure the films were equilibrated at ~45% RH.

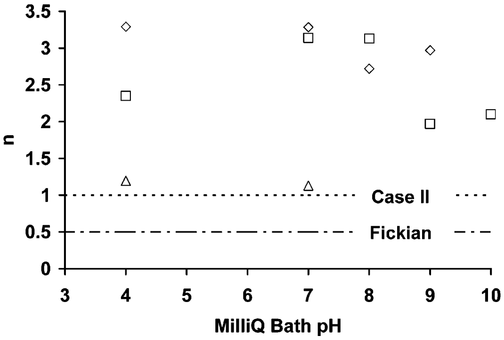

Figure 5. The dependence of assembly pH on the transport mechanism at various MilliQ bath pH. The symbols ◇, □, and △ correspond to assembly pH = 3.5 (25 bilayers), 5.0 (15 bilayers), and 6.5 (60 bilayers), respectively. Errors associated with n are 14%. The films were equilibrated at ~45% RH prior to solution exposure.

was assumed to be dominated by the relaxation of the polymer network. The first-order sorption process was fit with the following equation[22,23]

$$\frac{M_t}{M_\infty} = 1 - A \exp(-k_2 t) \qquad (3)$$

where A is a vertical scaling constant and k_2 is the relaxation constant. The pre-exponential factor and k_2 were calculated from the slopes and intercepts of the plot of $\ln(1 - M_t/M_\infty)$ versus time t. The constants n, k, k_2, and A under various film assembly conditions and solution pH were similarly determined and are shown in Figures 5 and 6 and in Table 2.

From Figure 5 it is apparent that the transport mechanism is highly dependent on assembly pH. Films assembled at pH = 6.5 exhibited case II behavior with $n \sim 1$ when exposed to bath pH = 4.0 and 7.0. Although the extent of swelling of assembly pH = 6.5 films when exposed to bath pH = 10.0 was recorded, the dynamics of the swelling was beyond the sampling rate of the off-null technique. The transport mechanism for assembly pH = 3.5 was determined to be super case II with $n \sim 3.2$ at solution pH = 4.0 and 7.0. With increasing solution pH, no significant change in the exponent was observed (n varies from just 2.8 to 3.0).

Assembly pH = 5.0 films also appear to swell by a super case II process. When exposed to pH = 4.0, n was ~2.4. With increasing pH, n increased to approximately 3.2. At bath pH = 9.0 and 10.0, n decreased to ~2.0.

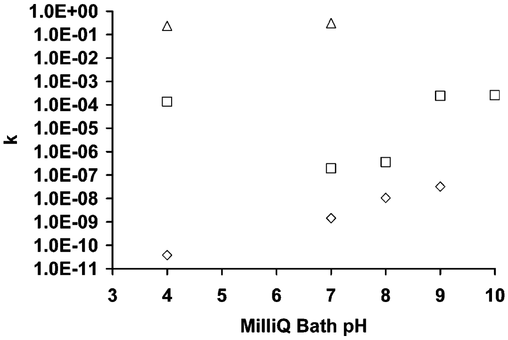

Figure 6. Dependence of k on solution pH, for films assembled under various pH conditions. The symbols ◇, □, and △, correspond to assembly pH = 3.5 (25 bilayers), 5.0 (15 bilayers), and 6.5 (60 bilayers), respectively. Errors associated with k are within an order of magnitude. Prior to solution exposure the films were equilibrated at ~45% RH.

The dependence of swelling mechanism on assembly conditions is related to the amount of ionic-linking in the multilayer film. The films assembled at pH = 3.5 and 5.0 have a complex nature due to the "loopy" structure of the multilayer. The availability of counterions, free acid/base groups, increased water content, and the highly entangled structure can greatly influence chain dynamics, which will affect the transport mechanism and rates. Films assembled at pH = 3.5 have a highly convoluted internal structure and this therefore probably leads to the late stage exponential rate enhancement once the initial entanglements are overcome. Therefore, the "loopy" structure with fewer ionic links of films assembled at pH = 3.5 might be expected to facilitate an enhanced relaxation-controlled transport mechanism with the largest value of $n \sim 3.2$. Films assembled at pH = 5.0 also exhibited super case II transport. However, the mechanism is generally less relaxation controlled with a lower value of $n \sim 2.5$. At assembly pH = 6.5, the multilayer forms with a "zipper type" mechanism, since both PAH and PAA are fully charged.[10] The highly ionic-linked polymer network, free from these impeding considerations, should be expected to exhibit an enhanced rate of permeation as observed, relative to a more diffusion controlled mechanism, where $n \sim 1$, even though the process is still relaxation controlled.

Assembly pH also has a significant effect on k, as time scales are many orders of magnitude different. As depicted in Figures 6 and 7, films assembled at pH = 6.5 undergo fast swelling with values of k in the range of 0.23−0.31 s^{-n} when swelled with solutions of pH = 4.0 and 7.0. The swelling was completed within 5 s. Films assembled at pH = 5.0 underwent slower swelling; 60% sorption is generally complete in 40 s to 2 min. When exposed to solution pH = 4.0, the value of k is 1.4×10^{-4} s^{-n}; at a higher bath pH (7.0 and 8.0) k decreases to 1.9×10^{-7} and 3.6×10^{-7} s^{-n}, respectively. At higher pH conditions of 9.0 and 10.0, k decreases to the same order of magnitude found when exposed to a bath pH of 4.0. Films assembled at pH = 3.5 have characteristic swelling times that are much slower than films assembled at pH = 6.5 and 5.0. Complete swelling generally takes approximately 5−30 min. The values of k increased with increasing solution pH. At low pH,

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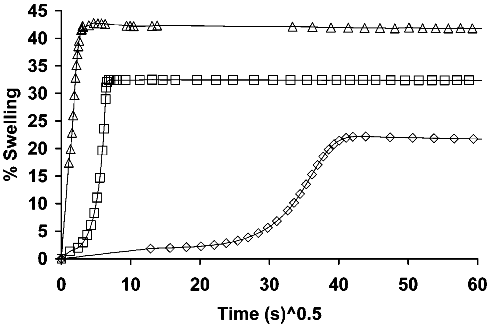

Figure 7. Swelling curves for different assembly pH values when exposed to bath pH = 4.0: assembly pH = 3.5 (25 bilayers), ◇; 5.0 (15 bilayers), □, and 6.5 (60 bilayers), △. Prior to solution exposure the films were equilibrated at ~45% R. H. The time scales of maximum swelling are drastically different depending on assembly conditions (note the % swelling is plotted versus $t^{0.5}$ for clarity).

the value of k was 3.8×10^{-11} s^{-n} and increased to 3.2×10^{-8} s^{-n} at a bath pH = 9.0.

The dependence on humidity to which the dry films were exposed prior to swelling on the onset of swelling is related to the amount of ionic cross-links and thus the number of free carboxylic acid groups associated with PAA. As will be shown later, the dependence of k on humidity is most prevalent with films assembled at pH = 3.5. It is known that water clusters can form around the free carboxylic acid groups of PAA, and that the amount of water clusters associated with PAA is dependent on the humidity.[24] It may also be possible for water clusters to form around counterions within the multilayer. It is further known that for the PSS/PAH system water is a bad solvent for the system with $\chi \sim 0.91$.[11] It is not unrealistic to assume that the water/water association is much stronger than the association of water/polymer for PAH/PAA. The Flory−Huggins parameter for our systems was experimentally determined to be ~1.6 for films assembled at pH = 3.5. This strong association of water ($\chi > 0.5$) within the multilayer may lead to the impedance of bulk liquid water through the film. Contact angle measurements for PAH/PAA systems indicated a hydrophilic surface,[10] but it is still possible that the internal polymer matrix is much more hydrophobic than the surface layer. Blockage of accessible microchannels in the film, through the formation of hydrogen-bonded water clusters or through hydrogen-bonding interactions with entangled loops, would lead to a longer time needed to establish a Fickian or case II front before the autocatalytic plastization of the film occurs, resulting in super case II swelling. Therefore, at a given humidity, films assembled at pH = 3.5 will take longer to reach maximum swelling than those assembled at pH = 5.0 and 6.5.

The first-order relaxation process also appears to be strongly dependent on assembly conditions, as shown in Table 2. The relaxation process was substantially faster for films assembled at pH = 6.5 than those assembled at pH = 5.0 and 3.5. Films assembled at pH = 5.0 displayed a slower relaxation process than those assembled at pH = 6.5. The relaxation rate of the multilayers is also related to the amount of ionic linking in the multilayer. The first-order relaxation (k_2) is much faster with films assembled at pH = 6.5. The high degree of ionic linking of the network would result in a high elastic restoring force.[25] Values of k_2 decrease as the ionic linking of the multilayer network decreases, because the elastic restoring force decreases. The lowest values of k_2 were seen with films assembled at pH = 3.5, which have the lowest amount of ionic linking groups.

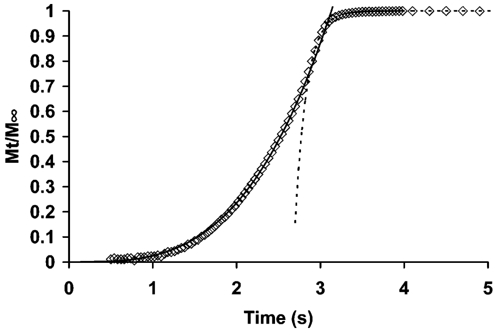

Figure 8. Swelling curve for assembly pH = 3.5 (25 bilayers) when exposed to MilliQ bath pH = 4.0. Prior to solution exposure the film was equilibrated at ~20% RH. The solid line corresponds to a fit with eq 2 and the dashed line was fit with eq 3.

Other factors that were investigated for their influence on the swelling dynamics were the ionic strength of the solution, the identity of the capping layer, and the layer number. Only minor swelling changes were observed when assembly pH = 4.0 (25 bilayers) films were exposed to various salt concentrations up to a 6 mM NaCl solution, with only a ~5% increase in swelling seen when compared to that of pure unadjusted (pH 5.5−6.0) water. Similarly, little dependence of the transport mechanism was observed on the nature of the capping layer for films assembled at pH = 3.5 (25 and 25.5 bilayers). The water transport mechanism was super case II for both PAA- and PAH-capped multilayers, with similar dynamics. The effect of layer number was also studied for assembly pH = 5.0 films (10, 13, and 15 bilayers), with dry film thicknesses of approximately 670, 1360, and 1780 Å, respectively. The extent of swelling in pure water for this thickness series was found to be 23 ± 2%, 28 ± 4%, and 29 ± 3% for 10, 13, and 15 bilayers, respectively. The water transport mechanism was super case II for all the films, with $n \sim 1.5$, (10 bilayer) and $n \sim 1.8$ for the 13 and 15 bilayer films at ~45% RH. Values for k and k_2 were of the same order of magnitude and did not vary significantly. Overall, little dependence of the transport mechanism was seen with layer number.

Effect of Humidity on Swelling Dynamics. Ambient humidity levels (prior to swelling with bulk water), however, were observed to have a strong effect on the swelling dynamics of PAH/PAA films. The most pronounced effects are seen with films assembled at pH = 3.5 (compare Figures 4 and 8). The initial swelling behavior is super case II at both low and high humidity. At low and high humidity, the values of n are comparable: 3.2 and 3.3, respectively. However, the onset of swelling was orders of magnitude different, with the

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swelling process being completed in ~3 s when films were equilibrated at low humidity prior to solution swelling, as compared to 1800 s at high humidity. This behavior is also indicated by k, which was determined to be 2.5×10^{-2} and 3.8×10^{-11} s^{-n} when pre-equilibrated at ~20% and ~45% RH. respectively, when swollen with pH = 4.0 solution. A large difference in the relaxation process was also observed. At low humidity the k_2 was determined to be 7.25 s^{-1}, indicating a very fast relaxation. At high humidity the relaxation process was substantially slower and k_2 was found to be 0.017 s^{-1}. These trends were also seen at higher bath pHs. One might naively expect that higher water vapor content in the film would plasticize the film and therefore increase the rate of swelling. However, the rate of swelling decreases with pre-exposure at high humidity. Previous investigations have shown that water adsorbed from a humid atmosphere into a hydrophobic polymer matrix (such as that under consideration here, with $\chi > 0.5$) forms tightly associated water clusters.[24] Furthermore, it has been suggested that the low mobility of these water clusters could explain the lower diffusion rates at higher ambient humidity, at least with regard to sorption from the gas phase.[12] It is conceivable that a similar argument might apply here. At low humidity, the polymer network is free of bound water, and as a result the first-order relaxation is unhindered. At high humidity, the highly organized water within the polymer network would slow the dynamics.

Conclusions

PAA/PAH polyelectrolyte films swell in water to 20−50% of their dry thickness at 45% RH, but at vastly different rates depending on the pH of their assembly. It has been demonstrated that the extent of swelling is largely independent of the environmental pH, salt concentration, and number of layers. It was found, however, that the assembly conditions of the polyelectrolyte multilayers strongly influence both swelling mechanism and kinetics. Our results suggest that the swelling mechanisms can be tuned through the assembly pH. Unexpectedly, it was found that ambient humidity strongly influences the rate of swelling. The time scales to reach maximum swelling varied from a few seconds to tens of minutes, depending on the pre-exposed humidity conditions. This anomalous swelling behavior should be considered by research groups who use polyelectrolyte multilayers for aqueous applications such as membrane coatings and drug delivery.

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