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Thin Film Thickness Gradients and Spatial Patterning via Salt Etching of Polyelectrolyte Multilayers

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ABSTRACT: We demonstrate the time- and concentration-dependent dissolution (etching) of polyelectrolyte multilayer (PEM) films comprised of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) immersed in NaCl solutions. PEM thickness decreases to a reproducible unchanging value that depends upon the initial film thickness and the concentration of NaCl. As opposed to a “top-down” removal of PEM chains from the film, the dissolution mechanism involves the diffusion and association of chains throughout the PEM that leave the film in the form of polyelectrolyte complexes (PECs). The PEC phase diagram is invoked to explain the observations presented in this paper and work by previous researchers. We demonstrate the straightforward application of PEM salt etching to pattern films where the spatial position and amount of dissolved material are controlled, resulting in a multicolor reflector and a gradient-thickness film. In addition to providing a more comprehensive picture of PEM stability, these results may help to advance the technological impact of PEMs in biology and other fields where the ability to create gradients in film thickness could be advantageous.

Introduction

The ability to create finely controlled patterns in thin polymer films by subtractive means has been instrumental in the development of many important modern technologies, having significant impact in fields such as semiconductor fabrication[1] and biotechnology.[2] While the spatial resolution of lithographic technologies continues to improve, controlling the thickness change at specific locations on the substrate (e.g., creating a gradient-thickness film) remains a challenging problem. Such films could be particularly useful, for example, in fields such as biology where recent research has suggested that cell adhesion mechanisms can be influenced by both the mechanical properties and the thickness of a substrate coating.[3] In this paper we propose a route toward such coatings via controlled salt etching of polyelectrolyte multilayer (PEM) films.

PEM assembly has recently emerged as a facile route to build up thin polymer films with precise film thicknesses and chemical functionalities on a variety of surface types and geometries.[4−6] This technique involves the layer-by-layer assembly of oppositely charged polyelectrolytes from aqueous solutions; controlling parameters such as the deposition pH of the polyelectrolyte baths and the total number of layers deposited allows one to tune the thickness and structure of the resulting film.[7] Several previous researchers have reported the loss of PEM material upon exposure to salt-containing solutions. The research in particular of Cohen Stuart et al.,[8−10] Sukhishvili et al.,[11−15] and Schlenoff et al.[16−19] has sought to quantify and describe this phenomenon in more detail. These and other researchers have highlighted the fact that a PEM is essentially a large, surface-bound insoluble polyelectrolyte complex (PEC); knowledge of the solution-phase behavior of PECs can therefore elucidate analogous processes encountered in the study of PEMs. For example, it is well-established that both the ionic strength of the solution and the ratio of positively to negatively charged polyelectrolyte repeat units help determine whether PECs will be soluble or insoluble.[10,19,20] In a similar manner, PEM films have been shown to undergo dissolution as a result of altering the ionic strength of the solution as well as by changing the molar ratio of polycations to polyanions in the system.[8]

With a few notable exceptions,[8,11,21] most literature reports have approached PEM etching as an “all or nothing” phenomenon, whereby a given film is expected either to remain more or less intact or dissolve completely. In this paper, we examine the controlled etching of films comprising poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) and films composed of PAH and poly(styrenesulfonate) (PSS). When immersed in solutions of NaCl, these films undergo a controlled loss of material and reestablish a new unchanging film thickness that depends upon the concentration of the NaCl solution. We provide evidence that salt etching of PEMs involves structural rearrangements of the entire film leading to ejection of nearly equal amounts of polycation and polyanion species (on a repeat unit basis) into solution. We also demonstrate that the strength and extent of polyelectrolyte interactions, as well as the molar mass distribution of the polyelectrolytes, are important factors in determining the etching behavior of a given system. We propose a general model for understanding the controlled dissolution of PEM films in solutions of salt and discuss its ability to explain our results and those of previous researchers. Spatial patterning of PEMs with control over both the location and amount of film removal is demonstrated through a straightforward surface screening technique. We also demonstrate how this technique can be used to generate a film with a continuous gradient in film thickness. Such films could be useful for applications such as controlling cell attachment and migration at biointerfaces.

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Experimental Section

PAH ($M_w = 70\,000$, Sigma-Aldrich), PSS (sodium form, $M_w = 70\,000$, Sigma-Aldrich), and two types of PAA ("high-PDI" (25% aqueous solution, $M_w = 90\,000$, Polysciences, PDI = 6.2) and "low-PDI" (solid, $M_w = 96\,400$, Polymer Source, PDI = 1.12)) were used without further purification to create polymer solutions of 0.01 M concentration by repeat unit (PDI = polydispersity index = M_w/M_n). PAH and PSS solutions additionally contained 0.1 M NaCl (Mallinckrodt Chemicals). Milli-Q deionized water (Millipore) with a resistivity of 18.2 MΩ cm was used for preparations of all solutions and rinse baths. Polymer solutions were pH-adjusted using either 1.0 M HCl or NaOH immediately prior to PEM assembly.

Single-crystal polished silicon wafers (p-type, 1−50 MΩ cm, [100] orientation, WaferNet) were used as substrates, except where the use of poly(dimethylsiloxane) (PDMS) was required as indicated in the text. Silicon substrates were sonicated for 15 min in a dilute detergent solution, followed by 10 min in pure water. They were treated for 8 min in an air plasma (Harrick Scientific PDC-32G plasma cleaner/sterilizer, 100 W, 400 mTorr) directly prior to PEM assembly. PDMS (Sylgard 184, Dow Corning) was prepared as previously described.[22]

PEMs were assembled using an automated programmable slide stainer (HMS slide stainer, Zeiss) according to methods described previously.[22] PEMs are represented by the standard nomenclature as ("polycation" X/"polyanion" Y)$_Z$, where X and Y are the pH values of the respective polyelectrolyte solutions and Z is the number of bilayers deposited.

Etching baths consisted of NaCl solutions prepared at the appropriate concentration. Samples were immersed in the salt solution with mild agitation and upon removal were immediately rinsed with agitation in pure water for 1 min, after which they were blown dry with air. Etching times are indicated for samples in the kinetic tests; all other samples were etched for 1 h, except for those shown in Figure 3 (10 min etch times) and Figure 4 (3 min etch times).

The gradient density salt column was prepared in a small glass vial, which was initially filled with a few milliliters of DI water. An equal amount of saturated NaCl solution was delivered to the bottom of the vial using a pipet; this step was performed slowly to ensure minimal mixing of the DI water and the denser NaCl solution. The vial was then tipped at a ≈45° angle and rotated a few times to generate a graded mixing of the NaCl solution layer and the DI water layer. Samples were inserted and removed very carefully to minimize disturbances to the concentration gradient in the vial.

Thickness characterization was performed using spectroscopic ellipsometry (M-2000D, J.A. Woollam Co.) according to a method we have previously described.[23] Ellipsometer fits for the roughness of the samples were used as indicated in the text to estimate uncertainties in the thickness measurements when multiple samples could not be measured to obtain an average and standard deviation. Except where indicated in the text, the thickness uncertainty was taken to be the larger of the modeled sample roughness or 1 nm.

Results and Discussion

Etching experiments were conducted on PAH7.5/PAA3.5 multilayers exposed to NaCl solutions of different concentrations. Three films of increasing number of bilayers (film thickness) were tested; the thickness changes for these films are displayed in Figure 1.

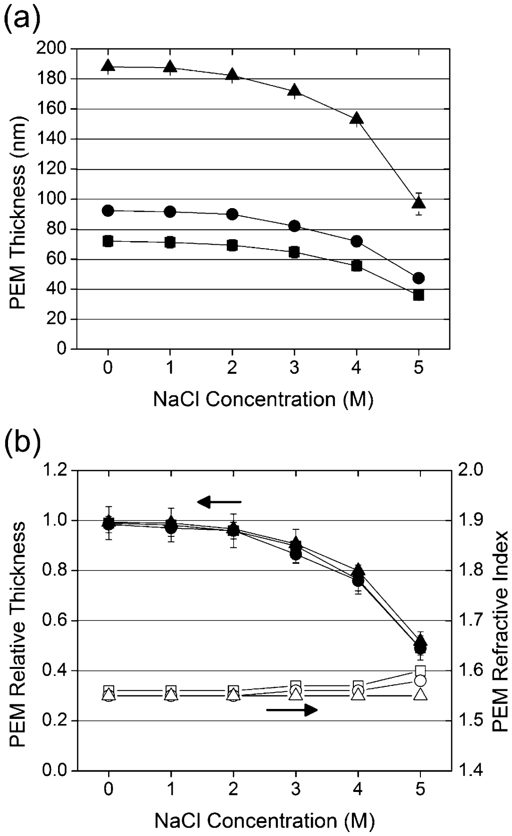

Figure 1. Salt etching of (PAH7.5/PAA3.5)$_z$ films of various thicknesses (etch time = 1 h). Films prior to etching had dry-state thicknesses of 70 nm (z = 7.5, squares), 90 nm (z = 9.5, circles), and 190 nm (z = 16.5, triangles). (a) Absolute film thicknesses as a function of salt concentration during etching. (b) Normalized film thicknesses (solid symbols) and the refractive indices of the dried films (open symbols) as a function of salt concentration during etching.

Figure 1 highlights some important characteristics involved in PEM salt etching. Figure 1a shows the absolute film thickness of three samples as a function of the NaCl concentration during etching. For all film thicknesses, higher salt concentrations led to increased thickness losses. Normalizing the thicknesses by their original values revealed essentially identical changes in the relative thicknesses for all samples (Figure 1b). These results indicate that salt etching does not involve polyelectrolytes simply being removed from the surface of the PEM without interaction with the rest of the film material—the entire bulk of the film must be sampled, as the film thickness decreases in proportion to the total thickness of PEM. Furthermore, the nearly constant refractive indices of the etched films (Figure 1b) support the notion that the decrease in film thickness in these samples is due to actual loss of material, and not shrinking or densification of the films, for which increased refractive indices would be expected. Figure 1b actually shows that a small increase in the refractive index was recorded for the two thinnest samples tested. This effect may in fact be an artifact, as less accurate model fits were obtained from the ellipsometer software for these thinner (<50 nm) samples; a corresponding increase was not observed with the thickest sample, for which a more confident data fit was obtained.

In order to determine whether the film thicknesses remained unchanging at the values indicated in Figure 1 rather than being simply interrupted during a kinetically slow dissolution process, we conducted time studies on two films comprising PAH7.5/PAA3.5 multilayers with initial thicknesses of 120 and 270 nm. An NaCl concentration of 4 M was used for the kinetic tests. The films to be tested were divided into multiple smaller samples, and each piece was immersed in the NaCl solution for the indicated time. All samples were washed for 1 min in water following the salt immersion. The absolute and relative PEM thickness vs time plots for these samples are shown in parts a and b of Figure 2, respectively.

Figure 2 suggests that the data follow a relationship at least qualitatively similar to an exponential function. The exact functional form followed by these data provides information

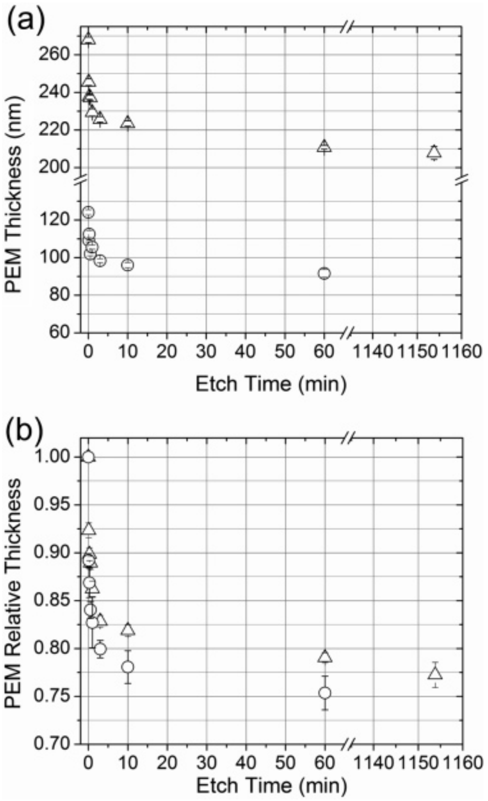

Figure 2. Absolute (a) and relative (b) PEM thickness vs time plots for two $(PAH7.5/PAA3.5)_z$ films with initial thicknesses of 120 nm (z = 10.5, circles) and 270 nm (z = 21.5, triangles). The films were etched in a 4 M NaCl solution.

concerning the mechanism of the etching process and will be examined at greater depth later in the paper. With only a cursory glance at the data, however, one can gather that etching happens quickly at relatively small times, with the film thickness eventually leveling off at an unchanging value. These data confirm that films reestablish a new value of thickness relative to the initial thickness of the PEM. The relative thicknesses of 0.75 (measured after 1 h) and 0.77 (measured after ≈19 h) reached at long times by the 120 and 270 nm thick films were equal within error. The data suggest slower kinetics in the case of the thicker film, which provides another argument against the notion that etching could be due to a top-down loss of polyelectrolyte chains from the surface, as the kinetics of such a process would presumably be unaffected by the film thickness.

One explanation for why a film might only dissolve partially is that the PEM establishes an exchange equilibrium with the dissolved polyelectrolyte material in solution, forbidding further thickness decrease. This hypothesis was tested by subjecting a single $(PAH7.5/PAA3.5)_{16.5}$ film (190 nm thickness) to multiple etch steps at the same concentration, exchanging the etching bath with fresh solution after every step. The film was taken through three etch steps at 0 M NaCl (water with no added salt), followed by three successive steps in each of 1, 2, 3, 4, and 5 M NaCl baths. All etch steps lasted for 10 min. The results from this experiment are displayed in Figure 3.

The thickness of the film displayed in Figure 3 did not begin to decrease until the 10th etch step, which was the first immersion in a 3 M solution. The two following steps at 3 M produced very little further change in film thickness, but a jump to a smaller thickness was again observed at the 13th etch step when the salt concentration was increased to 4 M. Another abrupt change in thickness is noticeable at the 16th step, which represented the first immersion into the 5 M NaCl solution. The thickness decreased relatively slightly for the two subsequent immersions into 5 M NaCl solutions.

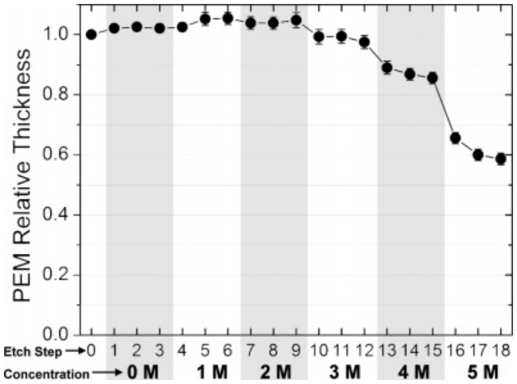

Figure 3. Relative thickness change of a $(PAH7.5/PAA3.5)_{16.5}$ film subjected to multiple etching steps at increasing concentrations. Each etch step consisted of a 10 min immersion in a fresh NaCl solution of the indicated concentration, followed by a 1 min rinse in water. The concentration of the etch solution was incremented 1 M following three successive steps at a given concentration.

The results in Figure 3 demonstrate that chains in the film are not establishing an exchange equilibrium with dissolved polyelectrolyte material in solution, thus prohibiting further dissolution. If this were the case, then the film would have been expected to reestablish a decreased thickness value for each successive etch step in fresh salt solutions (e.g., steps 14−15 and 17−18). Instead, only minimal thickness decreases are observed following the first immersion in a higher concentration solution; these small changes can be explained by noting that the films had not yet attained an unchanging thickness value after 10 min of etching.

Thus, successive immersion steps into fresh salt solutions will not result in total film dissolution; a given film will dissolve only partially even when immersed into an essentially infinite reservoir of solution. Izumrudov and Sukhishvili have previously demonstrated that hydrogen bonding between protonated carboxylate groups could result in the increased stabilization of multilayers exposed to solutions of NaCl at low values of pH,[11] and recently Jaber and Schlenoff have demonstrated that PEMs constructed from PAH and PSS can exhibit pH-controlled partial dissolution in basic solutions near the pK_a of PAH in the PEM.[21] The results presented in this work, however, were obtained in pH neutral NaCl solutions with measured pH in the range of 6.2−6.8. Furthermore, it has been established that strong preferential binding between PAA and PAH groups leads to a shift of the PAA pK_a from its solution value of 6.5 to a value of ∼2.2 when assembled with PAH.[24] These considerations suggest that under the conditions utilized in this work PAA groups in the film remain nearly fully ionized.

Partial dissolution of PEMs has also been reported by Kovačević and co-workers, who observed a similar phenomenon for PEMs subjected to an essentially infinite reservoir of salt and polyelectrolyte.[8] They explained the lack of total film dissolution in terms of the “three zone model” of Ladam et al.,[25] suggesting that the majority of the PEM will be lost when dissolution is favored, but a small fraction of PEM chains near the substrate will remain because they are “vitrified” by their proximity to the solid substrate. This explanation does not satisfactorily account for our observations, however, as we see only small fractional losses of material over the majority of salt concentrations tested. Furthermore, the zone model proposes that the size of the region of less mobile polymer chains is not dependent upon the total film thickness, whereas we observe changes in film thickness relative to the initial film thickness.

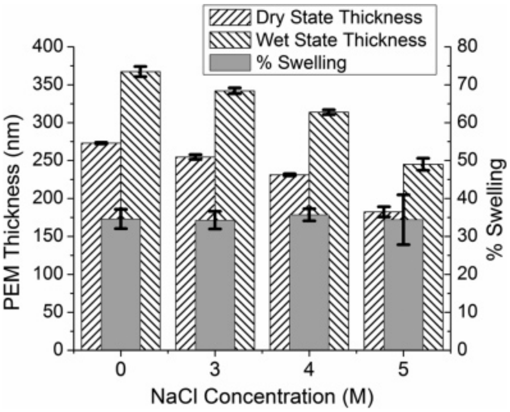

Figure 4. Dry- and wet-state thicknesses of (PAH7.5/PAA3.5)$_{20.5}$ films following etching in NaCl baths of concentration 0, 3, 4, and 5 M (etch time = 3 min). Wet-state thickness values were obtained from films swollen in water (unadjusted pH ≈ 6.2) with no added salt. The swelling percentage of each film is given. Error bars represent the standard deviation of measurements on three similar samples at each concentration value.

The data in Figure 3 show a slight increase in film thickness for immersions in the 0, 1, and 2 M concentration solutions. The cause of this increase is believed to be due to the fact that at low salt concentrations the polyelectrolyte chains in the hydrated PEM still have enough freedom to reorganize at low salt concentrations where the ionic strength is not yet high enough to induce etching.[26] Upon drying, the film is unable to collapse to the same dry-state thickness due to the reorganized chain structure. We have previously reported a similar observation with a PAH/poly(styrenesulfonate) (PSS) multilayer which was exposed to 1 M NaCl solution.[23]

To elucidate any changes in the structure of the film with exposure to increasing salt concentration, we examined the dry- and wet-state thicknesses of four (PAH7.5/PAA3.5) films following etching at increasing concentrations. The results of this study are shown in Figure 4.

The dry-state thicknesses of the etched films shown in Figure 4 exhibit the same decreasing trend that was observed in Figure 1. The same films were allowed to swell in pure water (no added salt) for ~4 h, after which time their thicknesses were measured using in-situ ellipsometry.[23] These wet-state measurements are shown along with the calculated swelling percentage, which is taken as the difference between the wet- and dry-state thicknesses, divided by the dry-state value. The lack of discernible change in the swelling percentage implies that there is little change in the ionic cross-link density with increased etching. These results are not immediately surprising, as previous researchers have shown that PEMs, even when assembled from or annealed in solutions with salt, tend to exhibit a strong preference for pairing with one another,[27,28] leaving very little residual salt in the bulk of the PEM. In our case, however, we were uncertain whether this same result would hold true for etched films that had lost a considerable portion of film material. The lack of change in cross-link density suggests that etching leads to the loss of charged polycation and polyanion repeat units in approximately equimolar amounts. According to the stoichiometric principles suggested by Schlenoff and coworkers,[26,29] the alternative option, that one polyelectrolyte is ejected preferentially to the other, would require inclusion of salt ions into the multilayer to balance the resulting unpaired charge groups, leading to broken ionic cross-links and a presumably more swollen film. The conclusion that neither the composition nor the cross-link density of the films is altered upon etching is further supported by buckling instability measurements on dry-state films using the SIEBIMM method,[23,30] which established no change in Young's modulus for PAH7.5/PAA3.5 films which had been treated over the range of 0−5 M.[31]

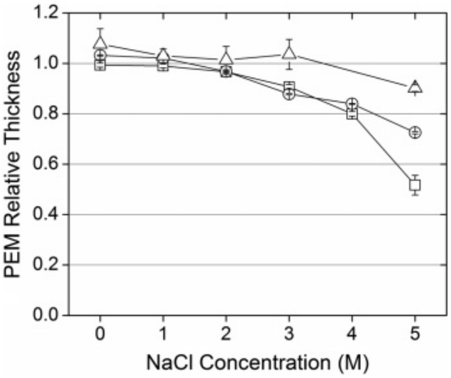

Figure 5. Relative thickness change for PAH7.5/PAA3.5 (squares), PAH6.5/PAA6.5 (circles), and PAH3.0/PSS3.0 (triangles) multilayer films exposed to NaCl etching solutions (etch time = 1 h). The 5 M data point for the PAH3.0/PSS3.0 system was obtained from a different batch of films assembled on PDMS substrates (see text for further explanation).

We conducted additional tests on (PAH6.5/PAA6.5)$_{100.5}$ and (PAH3.0/PSS3.0)$_{100.5}$ multilayers to see how other PEM systems would respond to the etching treatment. These results are shown in Figure 5.

Figure 5 demonstrates that the etching amount is affected not only by the selected polyelectrolytes, which determine the strength of the ionic cross-links, but also by the ionic cross-link density within the PEM assembly. PAH6.5/PAA6.5 multilayers have a fully ionically cross-linked internal structure;[7] this system therefore allowed us to measure the effect of a high degree of electrostatic cross-linking without changing the chemical nature of the cross-links themselves. Alternatively, the PAH/PSS system allowed us to test the effect of changing the chemical nature of the ionic cross-links while retaining nearly complete internal cross-linking within the film, as both PAH and PSS are fully charged at pH 3.0.[32]

The PAH6.5/PAA6.5 system displayed very similar behavior to the PAH7.5/PAA3.5 system for all salt concentrations less than 3 M. At 4 and 5 M concentrations, the PAH6.5/PAA6.5 films showed an increased resistance to film loss for the 1 h etching times used in this experiment. The PAH3.0/PSS3.0 system, however, showed no loss of material at all for NaCl concentrations up to 3 M. At etching concentrations of 4 and 5 M, the film was removed completely from the silicon substrate. Uncertain of whether the film had delaminated or dissolved, we repeated a 5 M etch of the PAH3.0/PSS3.0 system for a film that had been assembled on a poly(dimethylsiloxane) (PDMS) substrate, for which good adhesion of PAH/PSS multilayers has been previously observed.[23] The 5 M etch of PAH3.0/PSS multilayers on PDMS resulted in the loss of only 10% the original film thickness, demonstrating that substrate adhesion was the cause of the total loss of the film for the 4 and 5 M experiments conducted on silicon substrates.

The data presented in Figure 5 suggest that the PAH/PAA system is significantly more susceptible than the PAH/PSS system to etching in NaCl over the range of concentrations tested. To probe interactions within the PAH/PAA films in more detail, we examined the effect of changing the molar mass distribution of one of the polyelectrolyte species. Two sets of films comprised of (PAH7.5/PAA3.5)$_{10.5}$ were constructed. In one batch, PAA with a wide molar mass distribution (Poly-

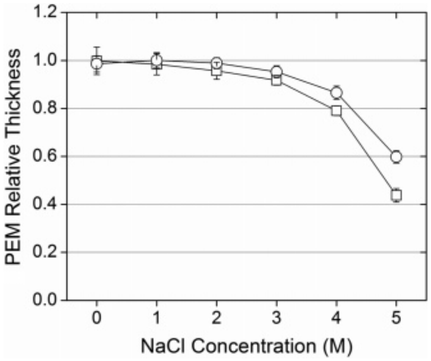

Figure 6. Relative thickness change for $(PAH7.5/PAA3.5)_{10.5}$ multilayer films exposed to NaCl etching solutions (etch time = 1 h). Films were assembled using PAA with either a narrow (circles, PDI = 1.12) or wide (squares, PDI = 6.2) molar mass distribution. The same PAH was used in both cases.

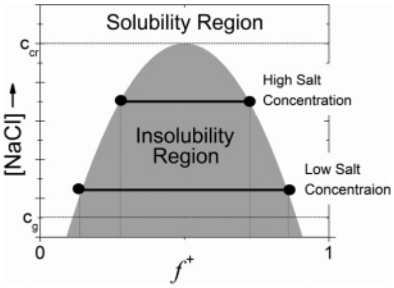

Figure 7. Illustration of a phase diagram for polyelectrolyte complexes (PECs) in solution.[8] NaCl concentration is shown along the vertical axis, while f^+, the mole fraction of positively charged polymer repeat units within the PEC, is given along the horizontal axis. The darkened area indicates the region of insolubility. Tie lines are shown to illustrate the required fractional composition of PECs that can be removed from the PEM film; soluble PECs are favored for f^+ values less than or greater than the values indicated by the bold points on the left and right sides of the darkened insolubility region, respectively.

sciences, $M_w = 90\,000$, PDI = 6.2) was used, and in the other system PAA with a similar value of M_w but a much narrower molar mass distribution was employed (Polymer Source, $M_w = 96\,400$, PDI = 1.12). Only the type of PAA differed between films; the same PAH was used in each case. Both sets of films were subjected to identical etching treatments, the results of which are displayed in Figure 6.

Figure 6 indicates that changing only the molar mass distribution of one of the polyelectrolytes can alter the etching characteristics of PAH/PAA films. The PAA with a low PDI resulted in films that possessed a greater resistance to etching than films assembled under the same conditions with PAA possessing a high PDI. A comprehensive mechanism for salt etching must include a means by which this result and all of the above data can be understood.

A Mechanism for PEM Salt Etching. Thus far, it has been established that a PAH/PAA film immersed in a given concentration of salt reestablishes a decreased thickness that is dependent upon the concentration of NaCl used. Films actually attain a new, unchanging thickness and are not simply interrupted during a complete dissolution process. Furthermore, the new thickness is relative to the initial thickness of the film; i.e., films of different thicknesses lose the same fraction of material, precluding an etching mechanism that only involves material at the surface of the film. In addition, films maintain this thickness in an effectively infinite reservoir of NaCl, indicating that some intrinsic property of the film has changed, and it has not simply established an exchange equilibrium with dissolved species in the etching solution. This change of film property does not seem to be linked to a change in the degree of electrostatic cross-linking, as in-situ ellipsometry studies have indicated no major change in the swelling percentage of postetched films immersed in pure water, indicating that PAH and PAA units must leave the film in an approximately equimolar ratio. The amount of etching in the PAH/PAA system can be controlled by varying the ionic cross-link density of the film, as well as the molar mass distribution of one of its components, indicating the apparent relevance of both of these parameters to the etching mechanism. Finally, studies of the PAH/PSS system indicate that it too displays etching behavior, although substantially less so than PAH/PAA films.

Previous researchers have been successful in correlating observed properties of PEMs with the phase behavior of free polyelectrolyte complexes in solution.[8,33] A schematic phase diagram for PECs, reproduced on the basis of the schematic given by Kovačević et al.,[8] is shown in Figure 7.

In Figure 7, increasing NaCl concentration is shown along the vertical axis, while f^+, the mole fraction of positively charged polymer repeat units within the PEC, is given along the horizontal. Kovačević suggests that for salt concentrations below some critical value ($[NaCl] < c_g$) PECs exist in a "glassy" phase for which the salt concentration is not high enough to allow for polyelectrolyte chain mobility. As the salt concentration is increased and chains become mobile, solubility is favored for polyanion-rich ($f^+ \approx 0$) and polycation-rich ($f^+ \approx 1$) complexes. At higher salt concentrations, soluble PECs are possible at a greater range of values of f^+. For sufficiently high salt concentrations ($[NaCl] > c_{cr}$), PECs are soluble for all molar ratios of cationic to anionic groups.

Figure 7 can help to explain the dissolution behavior of films of PAH/PAA immersed in solutions of increasing salt concentration, if film loss is understood as the formation of water-soluble PECs (WPECs) from chains comprising the multilayer film. Formation of WPECs, however, would presumably require mobility of polyelectrolytes within the film to permit for association of chains and detachment of the WPEC from the PEM surface. In films immersed in solutions with very little or no added salt, the polyelectrolyte chains are essentially immobile, and this process cannot take place, explaining why we see essentially no loss of film for NaCl concentrations less than ≈1 M (see Figure 1). As the solution concentration of salt is increased, increased "doping" of the PEM by salt ions leads to increased chain mobility within the film, and WPECs can be formed from polyelectrolytes comprising the PEM. The WPECs are expected to be rich in repeat units of either PAA or PAH, with concentrations of f^+ given by the bold points on the tie line marked "low salt conditions" in Figure 7. As the solution concentration of salt is increased, the formation of WPECs is favored over a broader range of f^+ values, and more of the PEM can dissolve.

The above mechanism explains a number of our reported observations, including why film dissolution seems to only begin at a certain salt concentration (c_g) where the film presumably loses its "glassy" nature and the polyelectrolytes become sufficiently mobile. This concentration will necessarily be larger for stronger interpolyelectrolyte interaction energies, explaining why we observe essentially no dissolution of the PEM for concentrations less than 1 M NaCl in the PAH/PAA system, while for other systems complete film dissolution has been reported at even lower concentrations.[11,16] These results are consistent with the reportedly strong favorability of PAH−PAA interactions.[24] Previous work would seem to indicate that even stronger interactions should exist between repeat units in the PAH/PSS system.[26] These findings are also consistent with our results, as Figure 5 illustrates that the PAH/PSS system resisted loss of material in solution concentrations up to 3 M NaCl.

Explaining salt etching of PEMs using the PEC phase diagram also answers the question of why films maintain an unchanging thickness when exposed to an infinite reservoir of solvent. Figure 7 indicates that at a given salt concentration WPECs can only be formed for a limited range of ratios of polycation to polyanion repeat units. Given that WPECs are expected to contain only one chain of the longer polyelectrolyte,[33] a sufficiently wide distribution of polyelectrolyte chain lengths is needed to allow formation of WPECs over a broad range of f^+ values. In addition, Figure 7 implies that formation of both negatively ($f^+ \approx 0$) and positively ($f^+ \approx 1$) charged WPECs should happen simultaneously, explaining how the overall ratio of polycation to polyanion repeat units in the PEM could remain constant, as is implied by Figure 4. It is proposed that the combination of broad polyelectrolyte molar mass distributions and the relatively high strength of PAH−PAA ionic cross-links leads to dissolution of PAH/PAA films over a wide range of relatively high NaCl concentrations. Alternatively, cases in which abrupt dissolution of other systems have been reported at low salt concentrations[16] could be due to the converse scenario, i.e., narrow molar mass distributions and relatively weaker ionic cross-links. When we assembled films with PAA possessing the same M_w but a much lower PDI, increased resistance to etching at low salt concentrations was observed. Etching of the film containing the low-PDI PAA proceeded in a qualitatively similar manner to the high-PDI PAA film, but with less film removal for all salt concentrations, possibly pointing to the inability of the system to form WPECs as readily due to the lack of availability of PAA chains much longer or shorter than the average length.

Kinetic Analysis of PEM Salt Etching. In order to elucidate the process of salt etching further, we attempted to develop a model to analyze in more detail the kinetic data presented in Figure 2. Our basic line of argument follows treatments from previous researchers who studied the absorption and desorption of uncharged polymer species from solution.[34] We consider a polyelectrolyte film with time-dependent thickness $h(t)$ immersed in a salt solution containing sufficient ionic strength to mobilize the chains within the film. Let $c(t)$ represent the average concentration of diffusing polymeric material in a film with a surface of area A exposed to a solution of salt where the concentration of polymer is effectively zero. The thickness of the film, $h(t)$, decreases with time due to the diffusion of polyelectrolytes to the surface of the film and their detachment as WPECs. This loss of material from the film, expressed in terms of the flux of moles of polyelectrolyte repeat units away from the surface, can be represented by

$$\frac{\mathrm{d}c(t)}{\mathrm{d}t}\frac{V(t)}{A} = \frac{\mathrm{d}c(t)}{\mathrm{d}t}h(t) \tag{1}$$

where $V(t) = Ah(t)$ is the film volume. Because the surface of the PEM is expected to possess comparatively more extrinsic charge (polyelectrolyte chains compensated by solution ions) than the interior of the multilayer,[29] it is assumed that the loss of PECs from the film is diffusion-limited; i.e., the diffusion of polyelectrolytes to the film surface is the rate-limiting step of material loss. If this is true, then the flux from the surface can be expressed as[34]

$$\frac{\mathrm{d}c(t)}{\mathrm{d}t}h(t) = -c(t)\sqrt{\frac{D}{\pi t}} \tag{2}$$

where D is the diffusion constant of the diffusing polyelectrolyte chain within the film. The concentration of the diffusing polyelectrolyte can be expressed in terms of the thickness of the film as

$$c(t) = \frac{\rho A}{V(t)}(h(t) - h_\infty) = \rho\left(1 - \frac{h_\infty}{h(t)}\right) \tag{3}$$

where ρ is the molar density (assumed to be constant throughout the film) and h_∞ is the unchanging film thickness at long times, i.e., $h(t) \to h_\infty$ as $t \to \infty$. Equation 2 can be rewritten using eq 3 to yield

$$\frac{\mathrm{d}h(t)}{\mathrm{d}t} = -\sqrt{\frac{D}{h_\infty^{\,2}\pi t}}(h(t) - h_\infty) \tag{4}$$

Equation 4 can be solved by separation of variables to yield

$$\frac{h(t) - h_\infty}{h_0 - h_\infty} = \frac{f(t) - f_\infty}{1 - f_\infty} = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right]; \quad \beta = \frac{1}{2}, \quad \tau = \frac{\pi h_\infty^{\,2}}{4D} \tag{5}$$

where h_0 is the initial film thickness and $f(t) = h(t)/h_0$ is the fractional thickness change.

A major limitation of the theoretical treatment so far has been the assumption that D is a constant. According to the mechanism for PEM etching presented above, WPEC formation at the surface of the film would require polyelectrolytes of very different molecular weights, and thus a wide spectrum of time constants (τ) would presumably enter into the kinetic response of the film. Such problems have been previously considered for the so-called "stretched exponential function" in eq 5, with the result that β in eq 5 takes on a value less than 1/2.[34] By performing linear regression on the data shown in Figure 2, the results shown in Table 1 are obtained:[31]

The values of β for both films were found to be ~0.25. The deviation in β from the expected value of 1/2 points to a process taking place at a spectrum of time scales, which is expected since polyelectrolytes of different lengths should possess different diffusion coefficients within the film.[29] Thus, the diffusion constants calculated using eq 5 and given in Table 1 are not true diffusion constants, but rather a type of average over all the mobile chains in the PEM contributing to the dissolution phenomena. Still, these calculations are expected to give a reasonable estimate for the diffusivity of the average chain throughout a PAH7.5/PAA3.5 film at 4 M NaCl. A value on the order of 10^{-16} m^2/s seems reasonable on the basis of previously reported literature values. Jomaa et al., for example, estimated a diffusion coefficient on the order of 10^{-17} m^2/s for poly(diallyldimethylammonium chloride)/PSS multilayers when annealed in 0.8 M NaCl solution.[29] The time constant, τ, is expected to increase with film thickness (see eq 5), with the result that thicker films take longer to reach an unchanging thickness value. This is indeed seen in the data in Figure 2,

Table 1. Results of Linear Regression Performed on the Data Given in Figure 2[31]

initial film thickness (nm)	β	τ (min)	D (m^2/s)
120	0.26	0.80	1.4×10^{-16}
270	0.25	1.9	2.9×10^{-16}

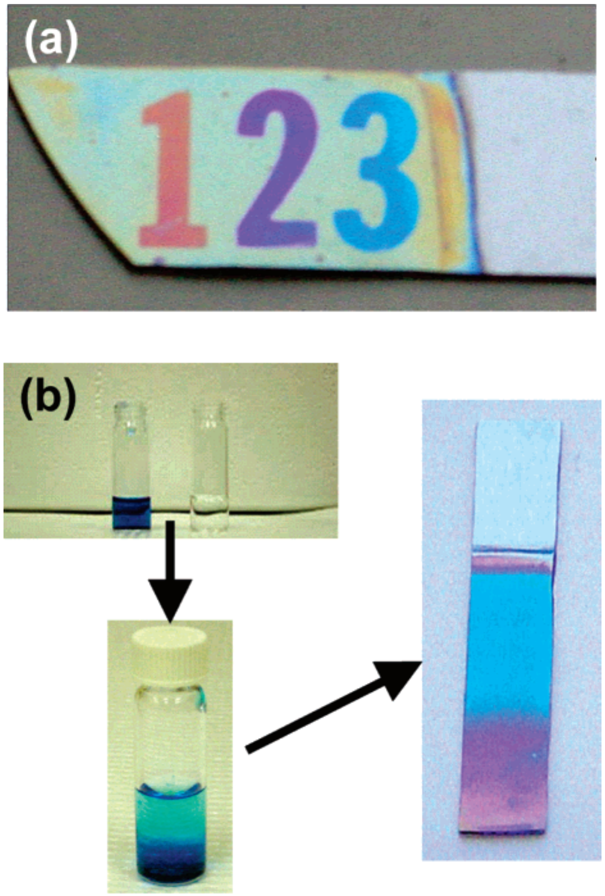

Figure 8. Application of salt etching to create thickness patterns within a PAH7.5/PAA3.5 film that has been deposited on silicon. (a) Masking combined with immersion into etching baths of decreasing concentration can create regions with discrete thickness increments. (b) Films with gradients in surface thickness can be created by employing a gradient density salt column.

with values of τ calculated by regression to be 0.80 and 1.9 min for the 120 and 270 nm thick films, respectively.

Applications. We have conducted preliminary work demonstrating how the etching technique described in this paper can be employed to create, from an initial PEM of uniform thickness, a patterned film with spatially distributed areas of different height. A multicolor reflector was fabricated by masking the areas of a PAH7.5/PAA3.5 film deposited on a silicon substrate with adhesive tape numerals. The "1", "2", and "3" were applied before subjecting the film to a short (3 min) immersion in a solution of 5.5 M NaCl, followed by rinsing with water and drying. The "1" mask was removed, and the substrate was treated in 5 M NaCl solution, after which the "2" mask was removed. The substrate was then treated in 4 M NaCl solution, before removing the "3" mask to uncover a region of untreated film. The completed reflector is shown in Figure 8.

Because of the different film thicknesses in the four regions in Figure 8a, different interference colors are observed. PEM films can also be created with continuous spatial gradients in the film thickness. By carefully combining a denser, saturated NaCl solution (shown in Figure 8b on the left, colored with methylene blue for clarity) with a solution of pure water (shown on the right), a gradient density salt column can be created, which has an increasing NaCl concentration from the liquid surface to the bottom of the vessel (see Experimental Section). Etching a film in such a column will produce a film possessing a spatial gradient in film thickness as demonstrated by the continuous color changes observed in the rightmost image in Figure 8b.

Conclusions

In conclusion, we have discussed the controlled etching of PEMs in solutions of NaCl. Relative changes in film thickness stabilized to an unchanging value that depended upon the NaCl concentration. Previous explanations for such a phenomenon that have invoked arguments about chain mobility[8] or secondary bonding restrictions[11] cannot be applied to our system. Instead, we suggest a mechanism whereby film reorganization leads to the release of water-soluble polyelectrolyte complexes (WPECs) and causes a reduction in film thickness. The thickness loss at a particular salt concentration is understood by considering the PEC phase diagram (see Figure 7), which suggests that WPECs can only be formed for particular ratios of polycation to polyanion repeat units at a given salt concentration; increasing the salt concentration in turn widens the composition range for WPEC formation and thus results in further film dissolution. Our kinetic data support the argument that etching involves the diffusion of polyelectrolyte species throughout the film (film rearrangement). In addition, our data support the notion that the molar mass distributions of the polyelectrolyte species are important in controlling the extent of film etching.

These results suggest that salt etching may be an attractive method to produce spatially patterned PEM films with a good degree of control over the amount of film removed. In addition to advancing the understanding of the internal dynamics and stability of PEM films, the results presented in this paper suggest ways to expand the technological importance of PEMs. In particular, the ability to controllably remove PEM material in different amounts and even to create gradients in film thickness across the substrate surface suggests a particular advantage this technique may have for certain biological applications. PEMs have already been shown to function as useful platforms for controlling cell attachment and function;[35−40] the added ability to control the adhesion and migration of cells via thickness patterning[3] could be an interesting and potentially useful functionality.

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Supporting Information Available: Mechanical properties of etched $(PAH7.5/PAA3.5)_{20.5}$ films and linear regression of kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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