

Fabrication of Microporous Thin Films from Polyelectrolyte Multilayers

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A simple process has been developed to create large area, highly uniform microporous thin films. Multilayers of weak polyelectrolytes were assembled onto silicon substrates by the sequential adsorption of poly(acrylic acid) and poly(allylamine) from aqueous solution. These multilayers were then immersed briefly into acidic solution ($\text{pH} \approx 2.4$) to effect a substantial and irreversible transformation of the film morphology. The resulting microporous structures are 2–3 times the thickness of the original films, possess a correspondingly reduced relative density of $1/2$ to $1/3$, and are stable against further rearrangement under ambient conditions. In addition, the microporous films may undergo a secondary reorganization in neutral water, leading to a morphology with more discrete throughpores. A mechanism is proposed for these transformations based on interchain ionic bond breakage and reformation in this highly protonating environment, leading to an insoluble precipitate on the substrate which undergoes spinodal decomposition with the solvent. FTIR (Fourier transform infrared spectroscopy) analysis supports the underlying chemical basis of this pH-induced phase separation, and AFM (atomic force microscopy), in situ ellipsometry, and SEM (scanning electron microscopy) have been used to monitor the morphological changes. The unique combination of properties exhibited by these microporous films makes them potential candidates for microelectronic and biomaterial applications.

Introduction

The fabrication of polyelectrolyte multilayer thin films has received much attention recently as a simple yet versatile technique for assembling various thin film optoelectronic devices and nanostructured thin film coatings.^{1–6} This new layer-by-layer deposition process provides a means to create polycation–polyanion polyelectrolyte complexes one molecular layer at a time, thereby allowing an unprecedented level of control over the composition and surface functionality of these interesting materials. Typically, alternate layers of positively and negatively charged polymers are sequentially adsorbed onto a substrate from dilute solution to build up interpenetrated multilayer structures. Most studies have focused on polyelectrolytes in their fully charged state, such as the strong polyelectrolytes poly(styrene sulfonate) (SPS) and poly(dimethyldiallylammonium chloride) (PDAC), and poly(allylamine hydrochloride) (PAH) deposited at pH values < 7.0 . Recently, however, attention has been paid to multilayers of weak polyelectrolytes, where the charge density along the chain can be readily controlled by adjusting the pH values of the polyelectrolyte solutions.^{6,7} With this class of systems, exemplified by poly(acrylic acid) (PAA) and PAH, one is afforded greater control over the physical state of the assembled polymers, such as their linear charge density, thickness, and conformation and the degree of interchain ionic bonding.

Whereas strong polyelectrolytes typically deposit (in the absence of salt) as molecularly thin ($\sim 5 \text{ \AA}$) layers, weak polyelectrolytes can be deposited with a high percentage of segments comprising loops and tails by adsorbing under pH conditions of incomplete charge. In fact, layer thicknesses $> 80 \text{ \AA}$ have been reported in weak PAA/PAH multilayers by depositing at a pH near the solution $\text{p}K_a$ of the polyelectrolytes.^{6,7}

Polyelectrolyte complexes, typically formed by the mixing of solutions containing oppositely charged polymers, are established biomaterials finding application as drug delivery systems, enteric coatings for drugs, dental adhesives, blood-compatible implant coatings, membranes for artificial kidney dialysis, contact lenses, and scaffold materials for tissue regeneration, among others.^{8,9} Due to their ionic nature, hydrogel structure, and permeability to bodily fluids, polyelectrolyte complexes possess many features similar to those of proteins.⁹ This protein resemblance and their low toxicity, hydrophilicity, good mechanical strength, and inherent ability to bind with molecules of opposite charge have made polyelectrolyte complexes attractive candidates for biomedical use.⁹ The unique complexation and phase separation behavior of polyelectrolytes have also made them candidate materials for ultrafiltration membranes, flocculation agents, and thin film coatings.^{9,10}

Perhaps one of the most studied applications of polyelectrolyte complexes is for encapsulating cells (or cell products, drugs, or enzymes) for novel therapeutic purposes, such as cell-based internal artificial organs and as a potential treatment for many ailments, including

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diabetes, neurological conditions, and chronic pain.¹¹ Much of this immunoisolation technology has been based on the complex coacervation of alginate and poly-L-lysine. Recently, the layer-by-layer approach has been used to improve the biocompatibility, mechanical integrity, and permeability properties of capsule membranes by depositing alternating layers of PAA and various polycations, for example poly(ethylene imine) (PEI), onto enzyme- or islets-containing alginate microcapsules.^{12,13} Furthermore, it has been demonstrated that alginate-poly-L-lysine multilayers assembled onto highly cell-adherent biological surfaces, for example extracellular matrix and type I collagen, could render such surfaces bioinert, thus preventing cell and protein adhesion.¹⁴ The ability to form porous morphologies from such multilayer coatings is clearly desirable, as it provides further control over the immunoisolation process.

In this paper, we report the assembly of multilayer films of the weak polyelectrolytes PAA and PAH and demonstrate that microporous thin films can be created simply by immersing the multilayers briefly in a bath of low-pH water. This pH-induced phase separation, although similar to phase transitions exhibited by polyelectrolyte complexes in solution, is unique in that it occurs in a uniform thin film of polyelectrolyte multilayers supported on a substrate. A mechanism for this microporosity transformation is proposed, whereby the low-pH environment of the transformation bath cleaves interchain ionic bonds by protonation of carboxylate groups, allowing a large scale reorganization and phase separation from the acidic water solvent. The resulting interconnected network morphology exhibits a high (up to 66%) volume of pores, a density of only $1/2$ to $1/3$ that of the original film, and an associated reduction in refractive index and dielectric constant. As this technique is rapid (on the time scale of seconds), requires no other processing steps, and can be localized on a surface, it appears to hold promise as a novel fabrication approach for reduced dielectric or low-refractive-index coatings and a wide variety of biomaterial applications. For example, it may be feasible to utilize multilayer-produced microporous membranes as an alternative to the conventional complex coacervation materials routinely used to encapsulate cells or drugs for biomedical applications.

Experimental Methods

Poly(acrylic acid) (PAA) (MW = 90 000) was obtained from Polysciences as a 25% aqueous solution. Poly(allylamine hydrochloride) (PAH) (MW = 70 000) was purchased from Aldrich Chemical. The polyelectrolytes were used without any further purification. Both polyelectrolyte deposition baths were prepared as 10^{-2} M (based on the repeat unit molecular weight) solutions using 18 M Ω Millipore water pH adjusted with either HCl or NaOH. Polished (100) silicon substrates ~ 10 cm² in area were cleaned in a concentrated chromium(III) oxide/sulfuric acid solution for a minimum of 4 h and then rinsed thoroughly with Millipore water. Water standards of pH 1.00 and pH 7.00 were obtained from Aldrich.

As detailed previously,⁶ the layer-by-layer deposition technique to prepare the multilayer thin films was completed via an automatic dipping procedure using an HMS programmable slide stainer from Zeiss, Inc. Clean silicon substrates were immersed in a polyelectrolyte solution (PAH first) for 15 min followed by rinsing in three successive baths of water (pH ≈ 5.5 –6.5) with

light agitation, for 2, 1, and 1 min, respectively. The substrates were then immersed into the oppositely charged polyelectrolyte solution for 15 min and subjected to the same rinsing procedure. After the desired number of layers (from 10 to 40) had been built on silicon, the substrates were removed from the automatic dipping machines, blown dry with filtered compressed air, and subsequently oven dried at 80 °C for 1 h.

To effect the porosity transformation, a series of low-pH solutions ($1.00 \leq \text{pH} \leq 3.00$) was prepared by addition of a variable volume of a pH 1.0 standard to a pH 7.0 standard solution using a buret. The pH of the samples was confirmed with an Orion pH meter. Multilayer substrates were immersed into one of these acidic solutions typically for 60 s, rinsed with neutral water for about 15 s, blown dry, and then oven dried at 80 °C for 1 h. Alternately, rather than immersing the substrate, individual drops of acidic water were deposited onto the films using a pipet. The neutral water rinsing step was varied from no rinse to minutes. Both the nonporous and porous multilayer thin films were stored under ambient conditions prior to measurement.

Pore volumes were estimated from thickness measurements in the following manner: % pore volume = $100((H - H_0)/H)$, where H_0 and H are the film thickness before and after the pH transformation, respectively. This approach assumes a conservation of mass in the films during the porosity transformation. The observed decrease in the refractive index of the porous films is consistent with the notion that the films increase in thickness and fill with air ($n_{\text{air}} \approx 1.0$) after the pH treatment.

The thickness and refractive index of the films were measured using a Gaertner ellipsometer at 633 nm, and values reported represent an average of at least 10 separate measurements on each film. Some thickness measurements were confirmed by profilometry. For surface microscopy, an atomic force microscope (Digital Instruments Dimension 3000 Scanning Probe Microscope, Santa Barbara, CA) was used in tapping mode. Scanning electron microscopy was performed on a JEOL 6320 FESEM after the surface of the polymer films had been coated with 100 Å of Au/Pd by vapor deposition. Advancing contact angles with water were measured as previously described.⁶

Infrared absorbance spectra were recorded with a Nicolet FT-IR spectrophotometer after layering the polyelectrolytes onto ZnSe windows following the multilayer deposition procedure described above. Absorbance values for the COO⁻ and COOH peaks of the PAA were estimated by examining the absorbance bands at ~ 1550 and ~ 1710 cm⁻¹, respectively, and assuming approximately equal extinction coefficients. Each peak height was also assumed to be the maximum of a Gaussian absorbance curve for its respective chemical species.

For dielectric constant measurements, PAA/PAH films were sequentially adsorbed onto patterned indium-tin oxide (ITO)-coated glass substrates and made porous following the same procedure as that for films assembled onto silicon wafers. Some films were further annealed up to 350 °C in an argon atmosphere, so that an amidization reaction occurred between the carboxylate ions (COO⁻) of PAA and the ammonium groups (NH₃⁺) of PAH to form stable nylon-like cross-links within the multilayers. An aluminum electrode was thermally evaporated on the film surface at a pressure of 10^{-6} Torr. Each device had an area of 6 mm², which was defined by a mechanical mask during aluminum evaporation. All the device measurements were performed in a glovebox with a dry nitrogen environment. Impedance measurements at different frequencies were performed with a Hewlett-Packard 4284A LCR meter with an applied bias of 10 mV rms. LabVIEW (National Instruments, Austin, TX) programs were used to automate testing via a GPIB interface.

Results and Discussion

PAA/PAH multilayer thin films deposited under the conditions of pH 3.5 for the PAA deposition bath and pH 7.5 for the PAH deposition bath (hereafter denoted 3.5/7.5) were prepared for this study. Under these conditions, 3.5/7.5 multilayers are assembled with weakly ionized PAA chains depositing onto nearly fully charged PAH molecules. A previous survey⁷ of the dependence of layer thickness on the pH of the polyelectrolyte solutions found the 3.5/7.5 system to produce some of the thickest layers

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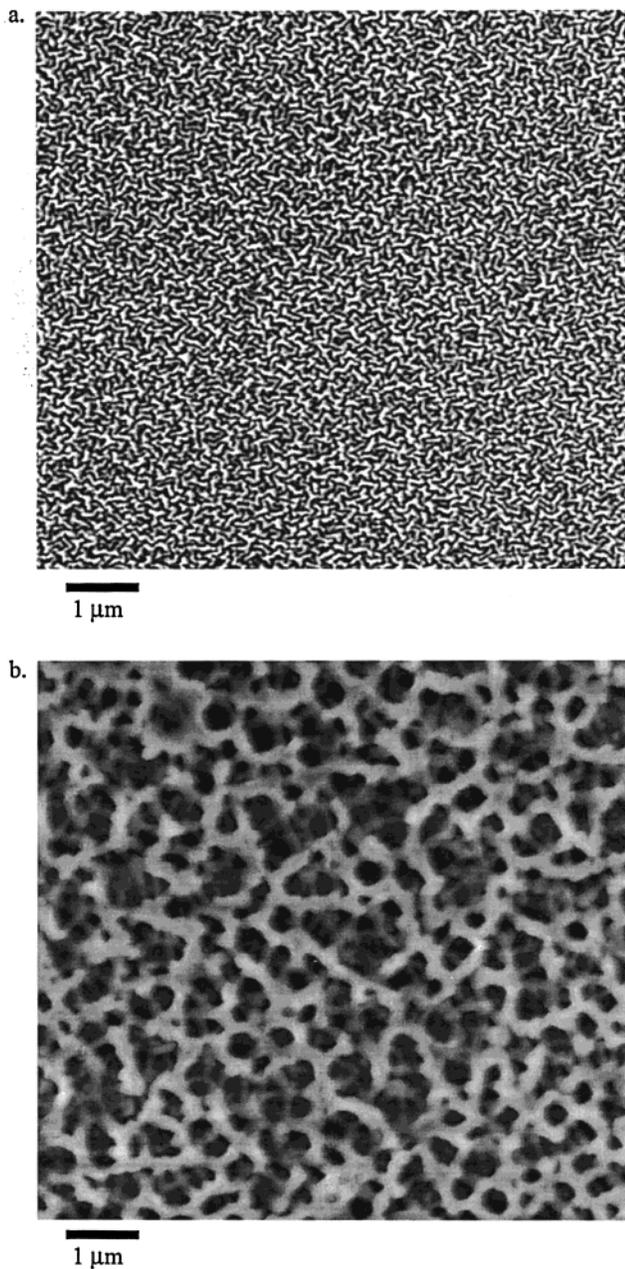


Figure 1. AFM image of the surface of a 21-layer 3.5/7.5 polyelectrolyte multilayer film before (a) and after (b) immersion in a transition bath of pH 2.50. The film thickness and refractive index of these films are 950 Å and 1.54, and 2790 Å and 1.18, respectively.

and roughest films of all the pH combinations examined; the individual dried layer thicknesses (beyond the first 10 layers) of these multilayers are in the range 50–80 Å, indicative of an adsorbed layer conformation rich in loops and tails.⁷ The rms surface roughness of these films is similarly quite high, reaching up to 100 Å for a typical 21-layer film. These results contrast with those obtained from multilayers fabricated from the same polymers in their fully charged state (e.g., pH 6.5/6.5), where molecularly thin (<5 Å) layers yield rms roughness levels of ≤10 Å. Despite the high surface roughness of the 3.5/7.5 system, the surface is dominated by chain segments from the outermost polymer layer, as demonstrated by water contact angle measurements made after each successive layer is deposited. Contact angles alternated reproducibly between 10–20° (PAA on top) and 50–60° (PAH on top) for 10–20 layers. As depicted in Figure 1a, atomic force

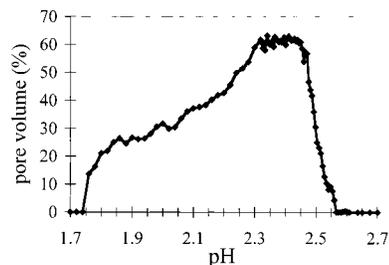


Figure 2. Plot of the resulting pore volume in 3.5/7.5 films induced by the pH of the transition bath. Here, the pore volume is defined as $100((H - H_0)/H)$, where H_0 and H are the film thickness before and after the pH transformation, respectively. There is no change in thickness from pH 7 to pH 2.6, and with baths below pH 1.75, the film is completely removed from the substrate.

microscopy (AFM) characterization reveals that the 3.5/7.5 films exhibit an interesting surface texture (regardless of the outermost layer identity); this morphology is unique to these and a few closely related pH conditions (e.g., PAA/PAH 4.5/7.5 films). Furthermore, the 3.5/7.5 multilayer films are stable over time in air, moderate heat, and extended immersion in water over a wide range of pH conditions from $3 \leq \text{pH} \leq 9$.

The molecular organization of the 3.5/7.5 multilayers, however, can be altered dramatically to a microporous morphology through a simple and irreversible transformation involving only exposure to acidic water ($\text{pH} \leq 2.5$). Upon exposure to water of $\text{pH} \leq 2.5$, these films almost instantaneously undergo a significant increase in thickness, as indicated by a substantial change in the film's interference color. Measured by ellipsometry, the dry layer thickness of such films has increased nearly 3-fold, and the refractive index has decreased correspondingly, suggesting that the polymer mass is conserved. This change in thickness is coupled to the emergence of a highly porous structure due to an extensive rearrangement and phase separation of the multilayer film in the acidic water. Figure 1b depicts the AFM image of the surface of the same 21-layer film as that in Figure 1a, after a 60-s immersion in an aqueous bath of pH 2.50. A highly interconnected, porous microstructure is observed, with a characteristic pore length scale in the range 100–500 nm. Generally, porosity of this type is observed to occur only with those precursor PAA/PAH multilayers exhibiting the rough surface texture that is characteristic of the 3.5/7.5 system.

The development of porosity in these films depends strongly on the pH of the transition bath, as presented in Figure 2. The figure plots the pore volume (given by $100((H - H_0)/H)$, where H_0 and H are the film thickness before and after the pH transformation, respectively) as a function of pH for 100 identical 21-layer PAA/PAH 3.5/7.5 multilayers exposed to 100 different transition solutions ranging in pH from 1.70 to 2.70. The experimental uncertainties in Figure 2 are $\text{pH} \pm 0.01$ and pore volume $\pm <4\%$ (thickness ± 30 Å). The 3.5/7.5 films exposed to solutions of $\text{pH} \geq 2.6$ underwent no discernible changes in thickness, refractive index, or morphology, and appeared indistinguishable from reference multilayers by ellipsometry and AFM. Upon exposure to solutions of $\text{pH} \leq 2.5$, however, irreversible changes to the films were observed. Using the pH 2.40 bath, multilayers were observed to increase in thickness by nearly 200% (from 950 to 2790 Å), and the refractive index was observed to decrease correspondingly from $n = 1.54 \pm 0.01$ to $n = 1.18 \pm 0.01$. All 3.5/7.5 multilayer thin films containing from 15 to 30 layers exhibit a similar thickness expansion of $185\% \pm 10\%$ and a corresponding reduction of n to

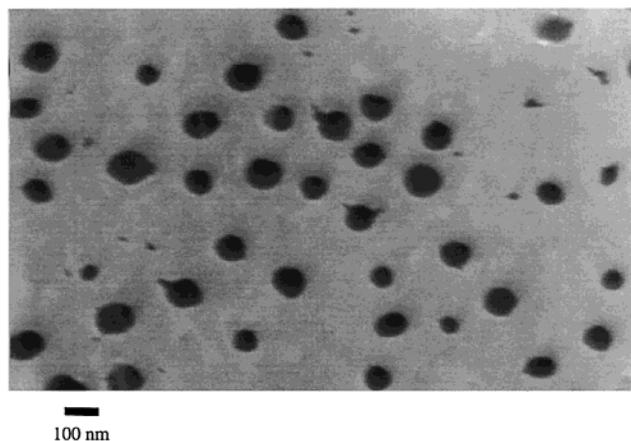


Figure 3. SEM image of the surface of a porous 3.5/7.5 multilayer film (created by immersion in a pH \sim 2.4 bath) after treatment in neutral water for 10 h.

1.20 ± 0.03 using the pH 2.40 transformation bath. For all 3.5/7.5 multilayer films examined, there was no change in thickness upon exposure to pH 2.60 and higher solutions (as tested up to 24 h), and the greatest change was induced with a transition solution of pH 2.40. Below a pH of 2.30, the effect is somewhat diminished, with thickness increases of \sim 50% observed at pH 1.80. At a pH of 1.75 or lower, the multilayers are dissolved/removed entirely from the substrate to reveal bare silicon. It is possible that the apparent diminished effectiveness of the transformation baths below pH 2.30 is due to the increasing influence of this competing effect of removing material from the substrate. Thus, given the possibility of material being lost at very low pH, the pore volumes indicated for pH values $<$ 2.30 in Figure 2 should be regarded only as rough estimates.

Perhaps most remarkable is the abruptness of the onset of this morphological change as the pH of the transition bath is lowered. Over only 1/10 of a pH unit (from pH 2.55 to pH 2.45), immersed films go from no discernible change in properties to the most substantial morphological transformation that can be effected under any solution conditions. This entire pH-induced phase separation and the emergence of a microporous structure occurs on the time scale of seconds. The resultant microporous films are stable for at least 18 months in air. However, it has been observed that these porous multilayers will undergo a secondary rearrangement when immersed in neutral water, particularly if the films are immersed for \geq 1 h, for example, overnight (following the neutral water conditioning, the films were blown dry with compressed air). Exposure to neutral water for extended times compacts and redensifies the porous multilayers, leading to thinner films with discrete rounded throughpores ranging in diameter from 50 to 200 nm. While a rinse of only a few seconds is too short to reduce the film thickness, a 1-h exposure to neutral water results in a thickness close to that of the original multilayer thin film. A SEM image of a 21-layer 3.5/7.5 film that was initially exposed to a pH \sim 2.4 bath and then to neutral water overnight is presented in Figure 3. In this case, the thickness has diminished to 1030 Å, which is within 10% of the original film thickness of 950 Å. After this neutral water conditioning, the refractive index of the 3.5/7.5 films increases from $n \approx 1.2$ to essentially the original value of $n \approx 1.5$, consistent with the notion that a densification process has occurred.

Dielectric measurements made on 3.5/7.5 films sandwiched between a conductive indium tin oxide (ITO) and an aluminum electrode confirm that the pores of the

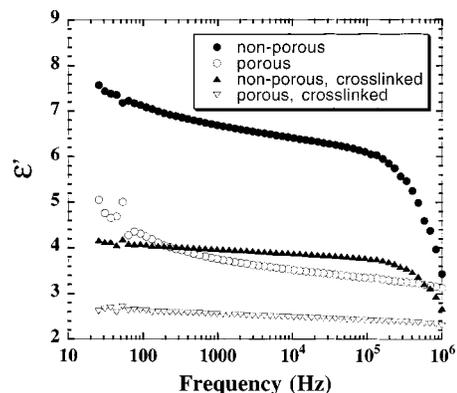


Figure 4. Plot of dielectric constant versus frequency for 3.5/7.5 films before and after transformation to a porous morphology and for their cross-linked counterparts.

densified films extend from the surface to the substrate. As expected for such a morphology, all devices were shorted out after thermal evaporation of the top aluminum electrode. The films with the interconnected microporous morphology, on the other hand, behave as conventional dielectrics when sandwiched between the same electrodes, demonstrating a percolating 3-D network that lacks direct throughpores. Figure 4 displays the frequency dependent behavior of the dielectric constant of a 3.5/7.5 film in the “as-prepared” state and as a microporous thin film. The dielectric response of cross-linked 3.5/7.5 films is also presented in this figure (to be discussed). The low-frequency dielectric constant (at 25 Hz) of the as-prepared 3.5/7.5 film is about 7.5 and drops to about 6.0 over the indicated frequency range. A low-frequency dielectric constant in the range 4–8 is what would be expected for a dried polyelectrolyte complex with a very low concentration of low-mobility small ions.¹⁵ The low-frequency dielectric constant of the microporous 3.5/7.5 film drops to about 5.0 and displays a similar frequency dependence to that of the original 3.5/7.5 film. This significant drop in dielectric constant is consistent with the fact that the 3.5/7.5 film is now comprised of about 40–60% air (the dielectric constant of air is 1.0). The low-frequency dielectric loss (ϵ'' data not shown) is about 2.5 for the original 3.5/7.5 film and about 1.2 for the microporous film. In both cases, the dielectric loss drops to about 0.2 at a frequency of 10^4 Hz. The frequency dependent behavior of the dielectric constant and dielectric loss of these films is characteristic of polyelectrolyte complexes with very limited ionic conductivity.¹⁵ The fact that a relatively high dielectric loss is observed at low frequencies suggests that some local ion movement is occurring in the films.

As suggested above, it is possible to cross-link multilayer thin films based on PAA/PAH. This simple chemical cross-linking approach can be used to effectively lock in either one of the different microporous morphologies. Heating a multilayer to >200 °C causes an amidization reaction between the COO^- groups of PAA and the NH_3^+ groups of PAH to form amide ($-\text{NHCO}-$) cross-links that rigidify the multilayers.¹⁶ Microporous films that are cross-linked resist the secondary rearrangement induced by the neutral water treatment and retain their 3-D interconnected porosity. As might be expected, amidization of the 3.5/7.5 multilayers before the acidic pH bath prevents porosity formation.

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Returning to the dielectric data presented in Figure 4, it can be seen that the dielectric constant of the cross-linked 3.5/7.5 films is much lower than those of their non-cross-linked counterparts. In addition, as was the case with the non-cross-linked films, the dielectric constant of the cross-linked microporous film is approximately 60% lower than that of the cross-linked, as-prepared film. In this latter case, the dielectric constant drops from about 4 to about 2.5 as a result of the introduction of a microporous network. The dielectric constant of the cross-linked films is also less frequency dependent than that of the non-cross-linked films, and they exhibit a very low dielectric loss of about 0.04 over the entire frequency range examined. Thus, the conversion of ionic bonds to covalent bonds has the effect of lowering the dielectric constant and further limiting the already low ionic mobility of these films. The low dielectric constant and loss of the cross-linked microporous multilayers coupled with their ability to be formed into highly uniform, large area thin films suggest their use as low dielectrics in semiconductor device applications. Employing precursor polyelectrolytes such as the polyamic acid precursor to polyimides¹⁷ should allow a further reduction of the dielectric constant of these microporous thin films to values below 2.0.

It is important to note that of the many pH combinations of PAA and PAH surveyed⁷ (from pH 2.5 to 9 for each polyelectrolyte) there appears to be only a narrow window of opportunity for creating microporous films. Specifically, the pH-induced porosity occurs most substantially with those multilayers assembled under PAA/PAH pH conditions of 3.5/7.5 or 4.5/7.5. While the 3.5/7.5 system results in the highest porosity, 4.5/7.5 multilayers also exhibit a pH dependence similar to that of Figure 2. Multilayers assembled with polyelectrolyte deposition pH conditions near 3.5/7.5 (e.g., 3.5/6.5 films) also exhibit some microporosity. In contrast, fully charged PAA/PAH systems (e.g., pH 6.5/6.5) do not appear to be suitable precursors to large scale microporosity. While most studies on the optimal 3.5/7.5 system have been performed on films in the range 15–30 layers, the development of microporosity does not appear to be restricted to that range; a film with just a few (e.g., 5) layers also becomes porous at pH ~ 2.4, although the most substantial morphological changes occur on films having at least 10–15 layers.

Investigations into the mechanism responsible for this process focused on the chemical changes that are induced in the interchain ionic bonds as the pH of the multilayer environment is lowered. As a measure of the degree of ionization of the PAA acid groups in multilayer thin films, we used FTIR to determine the ratio of COOH to COO⁻ groups. In the initially prepared 3.5/7.5 multilayers, the percentage of carboxylic acid groups present as the charged COO⁻ species (carboxylate ions) is observed by FTIR spectroscopy to be in the range 80–90% after assembly. In their charged state, the carboxylate ions of PAA are readily able to bind to the NH₃⁺ groups of PAH to form COO⁻-NH₃⁺ ionic intermolecular cross-links. Figure 5 presents a plot of the COOH/COO⁻ absorbance peak ratios measured from spectra collected on a series of multilayers exposed to different pH transition baths down to pH 2.0. These films were not rinsed but just blown dry, so as to estimate as accurately as possible the ratios of COOH/COO⁻ groups present in situ in the transition bath. In the lowest pH solutions, it is highly likely that a smaller fraction of ionized COO⁻ groups exists than is estimated by this approach. It is clear from the data obtained from

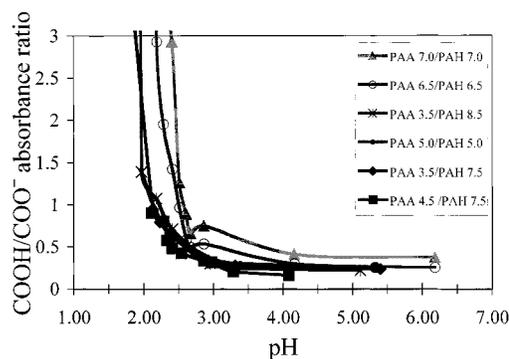


Figure 5. Plot of the FTIR-determined absorbance ratio of COOH to COO⁻ in multilayer films as a function of the pH of the transition bath, for 3.5/7.5, 4.5/7.5, 3.5/8.5, 7.0/7.0, 6.5/6.5, and 5.0/5.0 PAA/PAH multilayer thin films.

the 3.5/7.5 multilayers that there is not much change in the acid–base equilibria of the carboxylic acid groups from neutral pH down to pH ~ 3.0, with the vast majority (>80%) of these groups existing as COO⁻. Below a pH of about 2.5, a sharp increase in the protonated COOH fraction is observed, so that at pH 2.40, where the film structure reorganizes to a porous morphology, approximately 60% of the groups remain charged. At pH 2.0, this fraction is further decreased to ≤35%. The films are removed from the substrate at pH values not much below 2.0, preventing further exploration of this regime of protonation. It should also be noted that immersion in neutral water for any amount of time recharges most of the COOH groups back to the COO⁻ species; these rinsed, porous films generally have >70% of the carboxylic acid groups present as COO⁻.

Figure 5 suggests the underlying chemical basis for the unique pH-induced porosity observed in 3.5/7.5 multilayer thin films. Essentially, the acidic pH protonates a substantial portion of the COO⁻ ions, thus cleaving interchain ionic cross-links to enable a rapid spinodal decomposition to a microporous morphology. The abrupt transition in the COOH/COO⁻ absorbance ratio of the 3.5/7.5 multilayers at pH ~ 2.5 coincides nicely with the sharp transition also observed at pH ~ 2.5 in the thickness or pore volume, as depicted in Figure 2. The FTIR results also help explain why conditions above pH 2.6 fail to activate the phase separation; essentially, not enough ionic bonds are cleaved to initiate large-scale rearrangement.

As indicated in Figure 5, FTIR measurements of PAA/PAH multilayer films built with different pH combinations (such as 7.0/7.0, 6.5/6.5, 3.5/8.5, 4.5/7.5, and 5.0/5.0) display a pH dependent behavior very similar to that of the 3.5/7.5 multilayers. In all cases, the degree of ionization of the PAA chains remains essentially unchanged until the pH drops below 2.5, at which point there is a significant increase in the fraction of protonated acid groups. From these measurements, it appears that the pH at which the PAA chains achieve a degree of ionization of 50% is between 2 and 2.5. Thus, the effective pK_a of the PAA chains in a multilayer thin film is quite low compared to what is observed in dilute solution (PAA pK_a in the range 4.5–5.5). Similar shifts in the apparent pK_a values of polyelectrolytes within multilayer films have previously been reported.^{6,18} Since the COOH/COO⁻ absorbance ratio trends displayed in Figure 5 are characteristic of all the different PAA/PAH systems examined, the observed porosity transition is clearly not due to a substantially different acid–base equilibrium in the 3.5/7.5 and 4.5/7.5

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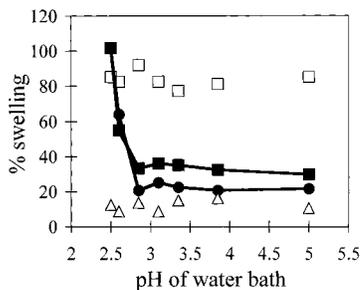


Figure 6. Plot of the degree of swelling versus pH for 21-layer films of 7.0/7.0 (Δ) and 5.0/5.0 (\square) showing swelling percentages of $\sim 10\%$ and $\sim 90\%$, respectively, independent of the pH. Swelling of 21-layer films of 3.5/7.5 (solid line) is shown both for lowering the pH from 5.0 to 2.5 (\bullet) and for the return curve back to pH 5 (\blacksquare) with a 10% irreversible increase in thickness after drying.

systems. In the other PAA/PAH films (such as 6.5/6.5, 7.0/7.0, and 5.0/5.0), decreasing the number of PAA ionic bonding sites by 50% or more does not result in a large scale porosity transition whereas a similar reduction with the 3.5/7.5 multilayers appears to be sufficient to allow the polymer chains to reorganize and phase separate from the acidic solution. Hence, the breaking of a critical number of ionic bonds is not sufficient in itself to induce the transition. This in turn suggests that the manner in which the polymer bilayers are assembled, and thus ionically linked together, is equally as important.

Figure 6 displays measurements by in situ ellipsometry of the swelling of multilayers in water baths of various pH values. Included here are 21-layer PAA/PAH thin films assembled under 5.0/5.0, 7.0/7.0, and 3.5/7.5 pH conditions. The degree of swelling of the 5.0/5.0 and 7.0/7.0 multilayers appears independent of pH in the range $2.5 \leq \text{pH} \leq 5.0$, at $\sim 90\%$ and $\sim 10\%$, respectively. The swelling of these films is completely reversible, as the original dried layer thickness is recovered after removal from the baths and drying. Thus, even though FTIR measurements show that the number of ionic bonds has decreased significantly at and below pH 2.5 (for example, in the 7.0/7.0 case), the basic swelling behavior of these different multilayer films does not change. This observation suggests that this process does not significantly perturb the regions or domains acting to ionically cross-link the multilayers. In other words, the basic morphological arrangement remains unchanged. In sharp contrast, for the 3.5/7.5 multilayers, the degree of swelling is strongly dependent on the pH in a manner analogous to that for the PAA degree of ionization observed by FTIR. With these films, a swelling of $\sim 30\%$ is seen for baths of pH 5.0–2.8 (\bullet symbols in Figure 6). As the pH of the porosity transition is approached, a dramatic increase in the extent of swelling is observed to 65% at pH 2.60 and $>100\%$ just above pH 2.50. Decreasing the pH any further induces the irreversible morphological transformation with an accompanied swelling of $\sim 200\%$. If the films approaching pH 2.50 are sequentially exposed to the series of higher pH baths, however, the swelling behavior is nearly reversible (\blacksquare symbols in Figure 6); the original thickness of the dry film is recovered within 10% in this case, and no porous morphology is observed by AFM.

A possible explanation for all of the above observations is as follows. It has been suggested^{9,10,19} that the polyanion/polycation chains of polyelectrolyte complexes can adopt two extreme molecular organizations: a “ladder-like” architecture in which two polyelectrolytes form coopera-

tively stitched chain segments and a “scrambled salt” architecture in which the chains adopt a more statistical distribution of ion pairs with many different chains. These two types of ionic pairing can have a marked effect on the properties of polyelectrolyte complexes in solution.^{9,10} In the multilayer process, polyelectrolyte complexes are generated one molecular layer at a time. Given the very low surface roughness, the low degree of swelling, and the molecularly thin layers observed when multilayers are assembled from fully charged polyelectrolytes (e.g., 7.0/7.0 PAA/PAH multilayers), it is reasonable to conclude that the polymer chains in this case are linked together with a large fraction of cooperatively stitched chain segments. Although exposure to low pH may reduce the number of ionic linkages in such fully charged films to less than half, it is not sufficient to free large segments of chains from their oppositely charged partners, and the structure remains largely intact. In contrast, in the thick and loop-rich 3.5/7.5 layers, the ionic stitching must be substantially more random and multichain in nature, possibly resembling more of a scrambled salt type arrangement. Consequently, for the 3.5/7.5 system, a reduction to 50% of the COO^- groups linking its loopy and highly intermingled structure together might be sufficient to allow large segments of the polymer chains to release from the surrounding layers. Still partially tethered to adjacent layers and to the substrate, the increased chain mobility leads to a reorganization on the surface as chains explore more energetically favorable conformations. If a more highly stitched organization resulted, the low water solubility of such a complex^{9,10} would promote phase separation via a spinodal decomposition process.

Clearly, more work is needed to confirm this hypothesis and to further understand why the thick and presumably loop-rich layers deposited at PAA/PAH 5.0/5.0 do not undergo a similar pH-induced porosity transition. It is known from previous work that these multilayers exhibit more highly interpenetrated surfaces than the 3.5/7.5 multilayers.⁷ This, coupled with the fact that the PAA chains are deposited with a higher degree of ionization, suggests that the 5.0/5.0 multilayers may form domains of cooperatively stitched chains. These domains would serve to cross-link the multilayers in a manner similar to that for the hard domains of segmented polyurethanes but still allow a high degree of swelling with limited sensitivity to pH changes. In any event, it is clear that dramatically different chain organizations can be obtained in multilayers of weak polyelectrolytes when the pH of the processing solutions is systematically controlled.

Conclusion

We have demonstrated that microporous thin films can be readily fabricated from layer-by-layer assembled multilayers of the weak polyelectrolytes PAA and PAH. This transition to a 3-D interconnected microporous network is induced by a brief exposure to acidic aqueous solutions at $\text{pH} \approx 2.3\text{--}2.5$. Such a treatment results in a thickness increase of nearly 200%, the formation of interconnected pores ranging in size from 100 to 500 nm, and a corresponding reduction of the density to $1/3$ that of the original film. Subsequent exposure to neutral water initiates a further reorganization that creates films with more discrete, rounded pores with sizes ranging from about 50 to 200 nm. Either of these porous morphologies can be locked in place by chemical cross-linking via a thermally induced amidization reaction. This new microporosity transition is associated with a partial breaking of the ionic interchain pairs formed during the original layer-by-layer assembly process. The resultant reorganization of the polymer

chains produces an insoluble polyelectrolyte complex that phase separates from the solution, yielding a classical spinodally decomposed morphology. Characterization by FTIR and in situ ellipsometry supports the concept of bond breaking and reformation during the porosity development. This process is exemplified by PAA/PAH multilayers assembled at a pH of PAA-3.5/PAH-7.5 and a few neighboring pH deposition conditions, indicating that a specific molecular organization is needed to create the microporous structure. The novel electrical properties of these microporous thin films make them attractive as low-refractive-index and low-dielectric-constant materials, while the pH dependent transition and resultant porous

morphology point to their potential application in drug delivery or other biomaterial applications.

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