Influence of the Degree of Ionization on Weak Polyelectrolyte Multilayer Assembly

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ABSTRACT: The effects of charge density on weak polyelectrolyte multilayer growth were investigated by assembling several strong polyelectrolytes with either poly(allylamine hydrochloride) (PAH) or poly(acrylic acid) (PAA) to keep one polymer fully charged while varying the degree of ionization of the other. The degree of ionization of the weak polyelectrolytes in solution and in a multilayer film was controlled by pH adjustment and quantified by Fourier transform infrared spectroscopy analyses. In all cases, the bilayer thickness exhibited a dramatic change from molecularly thin bilayers (case of two fully charged polymers) to much thicker bilayers when the degree of ionization of the weak polyelectrolyte decreased below 70−90% charged units. We also confirmed and quantified earlier observations that both the charge density and the effective pK_a of a weak polyelectrolyte can change substantially from solution-state values when the polymer is incorporated into a multilayer film. In addition, it was found that the degree of ionization of PAA in a multilayer film is also influenced strongly by the type of polycation used in the assembly process.

Introduction

Polyelectrolyte multilayers assembled in a layer-by-layer fashion from aqueous solutions have been extensively explored over the past decade and show promise in numerous applications.[1,2] While several solution processing variables including salt concentration[3] and temperature[4] play important roles in controlling molecular organization with strong (pH-independent) polyelectrolyte systems, pH becomes a key factor in the case of weak polyelectrolytes whose charge densities are pH-dependent. Previously, we have investigated the multilayer assembly of weak polyelectrolytes such as poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH).[5,6] With suitable adjustment of solution pH, the degree of ionization of these polymers can be altered substantially, thereby making it possible to precisely tune at the molecular level the structure and properties of the resultant multilayer thin films. The fundamental understanding gained from these studies has led to the development of nanoreactor schemes,[7,8] pH-gated micro- and nanoporosity transitions,[9,10] discontinuous reversible swelling transitions,[11] selectively responsive surfaces for block copolymer adsorption,[12] and strategies for controlling the adhesion of cells.[13]

The ability to systematically vary the linear charge density of weak polyelectrolytes makes it possible to study the influence of charge density on the multilayer assembly process. In previous work with PAA and PAH,[6] we discovered that dramatic changes in the thickness of an adsorbed polymer layer can take place with only a very small change in the charge density of an adsorbing polymer. Specifically, it was found that the thickness of the fundamental building block of a multilayer film, the bilayer (combination of polycation plus polyanion), undergoes a dramatic increase when the charge density of one of the weak polyelectrolytes is reduced by only a small amount from its fully charged state. It was argued from a theoretical standpoint[14,15] that a thickness transition of this type may occur when the surface charge density (determined primarily by the outermost polymer layer) drops below the critical value needed to maintain a fully charged adsorbing polymer chain in a flattened conformation; the net result being the adoption of a more loopy conformation and hence thicker layers. An important conclusion of these studies was that very thick layers can be formed when a fully charged polymer is assembled with a nearly fully charged polymer.

A potential complication of working with weak polyelectrolytes is that the polymer chains can adjust their local charge density to accommodate different molecular environments. To eliminate this effect, a number of researchers have recently synthesized random copolymers with fixed charge densities and assembled these polymers with fully charged strong polyelectrolytes. Using polycation copolymers of this type, von Klitzing and co-workers[16,17] found that a maximum bilayer thickness occurred when a copolymer with 75% charged units was assembled with a fully charged polymer. Using similar copolymers, Caruso and co-workers[18] have also reported that a maximum bilayer thickness occurs when a fully charged polymer is assembled with a copolymer with 75% of its repeat units in a charged state. Kolarik et al.[19] examined various copolymers and found that the adsorbed mass of a multilayer increased as the fraction of charged units decreased from 75% to 40%. Laschewsky and co-workers,[20] on the other hand, reported that a transition from very thin bilayers to thicker bilayers only occurred when the charge density of a copolymer dropped below about 30%. In many of these studies, salt was added to the polymer solutions and the number of deposited layers (can influence thickness) was small, making it difficult to compare results directly. In all cases, however, the magnitude of the thickness change that was observed when the charge density of the copolymer was decreased from 100% (fully charged homopolymer) to 70−80% was small compared to what is observed with weak polyelectro-

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lytes. It has been suggested that this difference is associated with the fact that when weak polyelectrolytes are assembled under optimum conditions, the surface charge of a previously adsorbed polymer layer will vanish during the adsorption of the next oppositely charged layer.[16] While this is not correct, it is possible for both the charge density of the surface and that of the adsorbing polymer to change during each adsorption step.[5,6]

In this paper, we demonstrate that the same pH-dependent bilayer thickness behavior reported for the PAH/PAA multilayer system is observed when a strong polyelectrolyte is assembled with a weak polyelectrolyte. Specifically, PAH was assembled with the strong polyanions poly(vinylsulfonic acid) (PVS) and sulfonated polystyrene (SPS), and PAA was assembled with the strong polycations poly(diallyldimethylammonium chloride) (PDAC) and poly(4-vinylbenzyltrimethylammonium chloride) (PVTAC). With these polymer pairs, only the charge density of the weak polyelectrolyte can vary with changes in solution pH, thereby eliminating the more complicated situation presented with the assembly of two weak polyelectrolytes. Again it is found that a dramatic change in the adsorbed layer thickness occurs (compared to the assembly of two fully charged polymers) when a fully charged polymer is assembled with a nearly fully charged polymer. Fourier transform infrared spectroscopy measurements show that the onset of the transition from molecularly thin layers to much thicker layers occurs when the charge density of the weak polyelectrolyte in the multilayer film drops below 70−90% charged units (the onset point for most of the polymers examined in this study occurred in the range of 80−90%). During the process of quantifying the pH-dependent degree of ionization of the weak polyelectrolyte in solution and in a multilayer film, we also confirmed and quantified earlier observations that (1) at a given pH the charge density of an adsorbing weak polyelectrolyte can increase substantially from its solution-state value when it is incorporated into a multilayer film and (2) the effective pK_a of a weak polyelectrolyte in a multilayer film shifts dramatically from its solution-state value. It will also be demonstrated that the degree of ionization and pK_a of PAA in a multilayer film are influenced strongly by the type of polycation used in the assembly process.

Experimental Section

Poly(allylamine hydrochloride) (PAH) ($M_w \sim 70\,000$), poly(diallyldimethylammonium chloride) (PDAC) ($M_w = 100\,000-200\,000$), poly(sodium 4-styrenesulfonate) (SPS) ($M_w \sim 70\,000$), and poly(vinylsulfonic acid, sodium salt) (PVS) ($M_w \sim 4000-6000$) were purchased from Aldrich. Poly(acrylic acid) (PAA) ($M_w \sim 90\,000$) and poly(4-vinylbenzyltrimethylammonium chloride) (PVTAC) ($M_w \sim$ unknown) were purchased from Polysciences. The chemical structures of these polyelectrolytes are shown in Figure 1. The pH-dependent ionic characteristics of the polymers are listed in Table 1. All polyelectrolytes were used as received without further purification. Dipping solutions of all polyelectrolytes were prepared with a concentration of 10^{-2} M (with respect to the molecular weight of each repeat unit) in 18 MΩ Millipore water and further pH-adjusted with either HCl or NaOH. No additional salt was added to any of the polymer or rinse solutions. Polished ⟨100⟩ silicon wafers for multilayer deposition were ultrasonicated in a 0.1 N aqueous solution of NaOH for 2 min to promote formation of an oxide layer on the surface prior to the multilayer deposition processing.

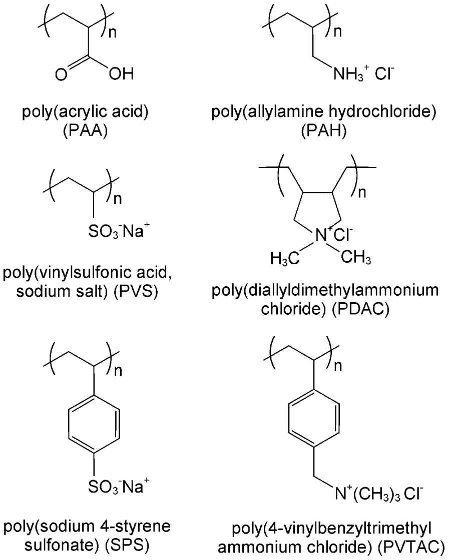

Figure 1. Chemical structures of polyelectrolytes.

Table 1. Ionic Characteristics of Polyelectrolytes in pH Range 2−9

polymer	charge density	polymer	charge density
PAH	(+) variable	PAA	(−) variable
PDAC	(+) fully charged	PVS	(−) fully charged
PVTAC	(+) fully charged	SPS	(−) fully charged

The layer-by-layer deposition of polyelectrolytes was done automatically by a programmable dipping machine (HMS programmable slide stainer from Zeiss Inc.) at room temperature. Cleaned substrates were immersed into the polyelectrolyte solutions for 15 min for one layer deposition and rinsed with agitation in three freshwater baths (pH about 5.6) for 2, 1, and 1 min before the next layer deposition. Polyelectrolyte multilayer samples were dried by air flushing for 2 min and further dried in ambient air for several hours before characterization. All of the multilayers were fabricated from polymer solutions set to the same pH unless indicated otherwise. For example, pH 3.5/7.5 PAA/PAH multilayers refer to films alternately assembled with the PAA layers deposited at a pH of 3.5 and the PAH layers at a pH of 7.5. The average bilayer thickness of multilayer films was determined using a Gaertner ellipsometer at 633 nm with polished silicon wafers as the substrate for the multilayer deposition. Average bilayer thicknesses were obtained by dividing the total film thickness by the number of bilayers.

Fourier transform infrared spectroscopy (FTIR) spectra were acquired using a Nicolet FTIR spectrophotometer with a DTGS detector. For determination of solution pK_a values of PAA and PAH, aqueous solutions of PAA and PAH were prepared in the same manner as the multilayer dipping solutions and pH-adjusted by adding HCl or NaOH. Then, each pH-adjusted solution was cast onto a ZnSe substrate and evaporated in a vacuum to leave a pure polymer film for FTIR characterization. For FTIR analyses of polymer components within the multilayers, 20-bilayer multilayer films were deposited on cleaned ZnSe substrates in the same manner as mentioned above.

For the FTIR analysis of PAA in the form of a dried cast film, two distinct adsorption bands of the carboxylic acid functional groups of PAA were considered; $\nu = 1565-1542$ cm^{-1} (asymmetric stretching band of COO^-) and $\nu = 1710-1700$ cm^{-1} (C=O stretching of COOH). A straightforward deconvolution of each vibrational band was possible by assuming a Gaussian distribution and by using Microcal Origin software. The band intensity was estimated by using the maximum peak height of each adsorption band. Assuming the same extinction coefficients for both bands,[21] the degree of ionization of PAA (α) at a given pH was calculated from $\alpha = [\nu(COO^-)]/[\nu(COOH) + \nu(COO^-)] \times 100$ (%).

As for the degree of ionization of PAA in multilayers, in the case of PAA/PDAC and PAA/PVTAC multilayers, there was no significant overlapping of absorbance bands from PDAC or

PVTAC with the COOH band ($\nu = 1707-1709$ cm^{-1}) or the carboxylate band ($\nu = 1557$ cm^{-1}). Therefore, a straightforward deconvolution of the carboxylate and carboxylic acid bands was possible in the same way as in the dried cast film of PAA. In the case of PAA/PAH multilayers, we had to take into account the fact that PAH presented absorbance bands that overlapped with the PAA bands. In this case, only a simplified deconvolution of the representative absorbance bands was possible. To accomplish this, the intensity of PAH peaks (one centered at 1626 cm^{-1}, asymmetric NH_3^+ bending mode, and the other at 1517−1523 cm^{-1}, symmetric NH_3^+ bending)[22] collected from a pH 1.97 PAH dried film was used to determine the intensity contribution the PAH peaks made to the multilayer film. For multilayers assembled at pH 6.5, a newly emerging broad peak from deprotonated amine groups centered at 1586 cm^{-1} was additionally considered for subtraction. (Original curve fittings for this band were obtained from a PAH dried film at pH 6.5.)

To perform the analysis of the degree of PAH ionization in the form of a dried cast film of PAH, the intensity of the broad band centered around $\nu = 3016$ cm^{-1} (asymmetric NH_3^+ stretching band) was normalized to the intensity of the band at $\nu = 2919$ cm^{-1} (asymmetric CH_2 stretching). In this case, the extent of peak overlap was significant, and a clean deconvolution was not possible in this spectral regime. We assumed that at a very low pH (pH = 1.97) the amine groups of PAH are in the fully charged NH_3^+ form, whereas at high pH (pH = 12), the amine groups are fully deprotonated in the NH_2 form. Thus, the ratio of $[\nu(NH_3^+)/\nu(CH_2)]_{pH=1.97}$ is considered as the state of 100% ionization, and that of $[\nu(NH_3^+)/\nu(CH_2)]_{pH=12}$ is considered as the state of 0% ionization, and the value of ionization (α) is defined as

$$\text{degree of PAH ionization } (\alpha) = \frac{[\nu(NH_3^+)/\nu(CH_2)]_{pH} - [\nu(NH_3^+)/\nu(CH_2)]_{pH=12}}{[\nu(NH_3^+)/\nu(CH_2)]_{pH=1.97} - [\nu(NH_3^+)/\nu(CH_2)]_{pH=12}} \times 100(\%)$$

Results and Discussion

Determination of the Solution pK_a of PAA and PAH. As has been well documented in the literature,[6,10,21,23−27] the degree of ionization of a weak polyelectrolyte can change significantly from its solution value when it is incorporated into a multilayer environment. To establish the relationship between multilayer film growth and the charge density of a weak polyelectrolyte, it is therefore prudent to determine the degree of ionization (α) of the polymer in solution as well as in the multilayer film. To accomplish this goal, we analyzed dry films by Fourier transform infrared (FTIR) spectroscopy. By analyzing for the amount of ionized vs nonionized functional groups, FTIR analysis enables the direct detection of the degree of ionization of a polymer within a multilayer film. In addition, solution values can be estimated by FTIR measurements on cast films of the pure polymer. As will become apparent, this approach provides data that are in good agreement with solution state values determined by more conventional titration methodologies. Since the pK_a of a weak polyelectrolyte can be a complex function of the degree of ionization,[28] we are using the term "pK_a" to indicate the pH at which 50% of the polymer's functional groups are ionized.

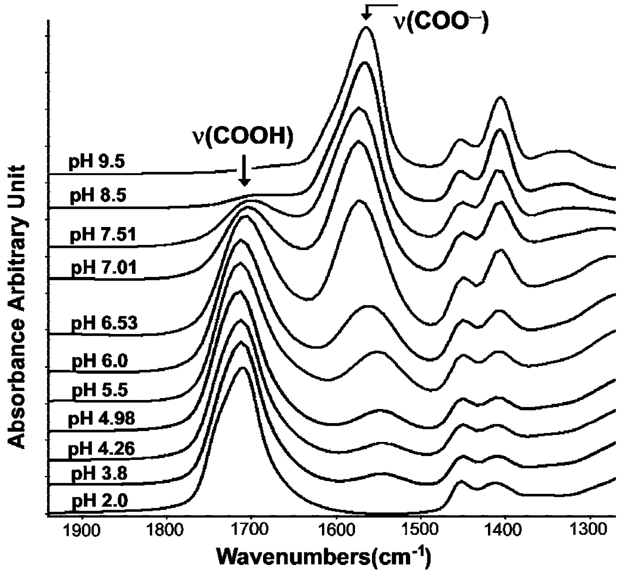

Figure 2. FT-IR spectra of PAA films cast from aqueous solutions of various pH. Spectra are intentionally overlaid with arbitrary offset for clarity.

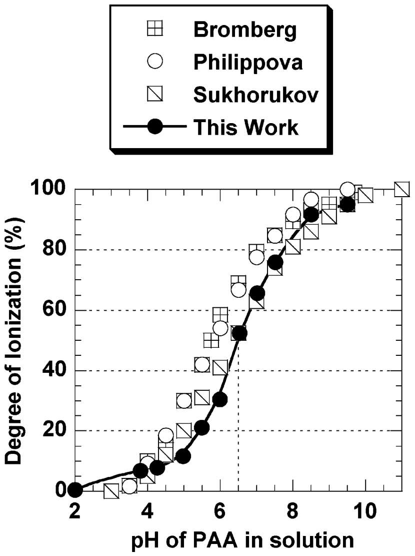

Figure 3. Estimated degree of ionization of PAA in solution as a function of pH. Data from other studies are also plotted for comparison. Broken line indicates the pH at which 50% of the PAA units are charged (pH ≅ 6.5) in our work.

Figure 2 displays the FTIR spectra of dry films of PAA that were cast from aqueous solutions of various pH. Two distinct peaks of the carboxylic acid functional groups of PAA are highlighted: one at $\nu = 1565-1542$ cm^{-1} that is associated with the asymmetric stretching band of the ionized carboxylate (COO^-) group and the other at $\nu \sim 1710$ cm^{-1} which is attributed to the C=O stretching of the carboxylic acid (COOH) groups. In the acidic regime at pH 2.0, only the COOH acid peak was detected which indicates that essentially 100% of the functional groups of PAA exist in the nonionized form. With increasing solution pH, the peak intensity of the COOH band decreased and the intensity of the COO^- band increased as the acid groups became ionized. At pH 9.5, most of the COOH groups were transformed into the COO^- form, with almost no trace of the COOH peak. Since the extinction coefficients of these two absorption bands are about the same,[21] the degree of ionization of PAA at various pH values can be directly represented by the ratio of the peak intensity of $\nu(COO^-)$ to the intensity sum of $\nu(COO^-)$ and $\nu(COOH)$. Figure 3 shows the results of this analysis as well as degree of ionization data reported by others[25,29,30] that were generated by titration methods. Literature values for the solution pK_a (p$K_{1/2}$) of PAA in the absence of added salt range from about 5.5 to 6.5 (for example, ~5.7,[29] ~5.8,[30] and ~6.4[25]). Our analysis of dry films of PAA suggests a pK_a of about

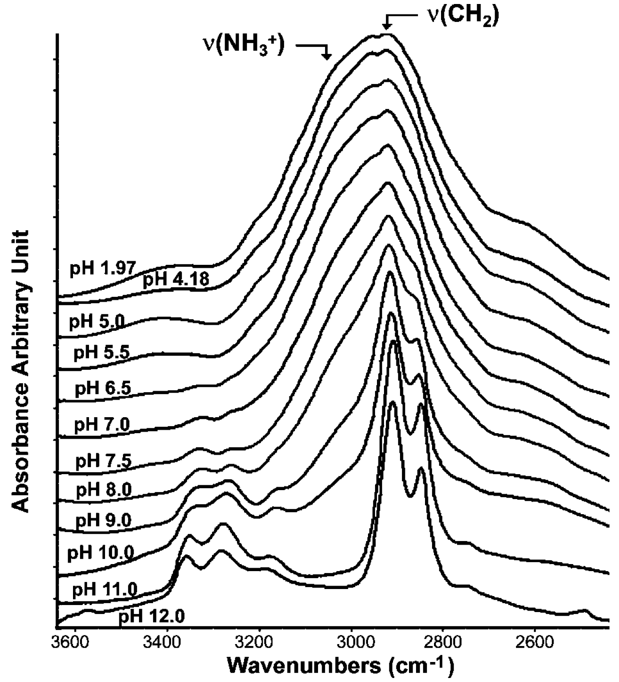

Figure 4. FT-IR spectra of PAH films cast from aqueous solutions of various pH. Spectra are intentionally overlaid with arbitrary offset for clarity.

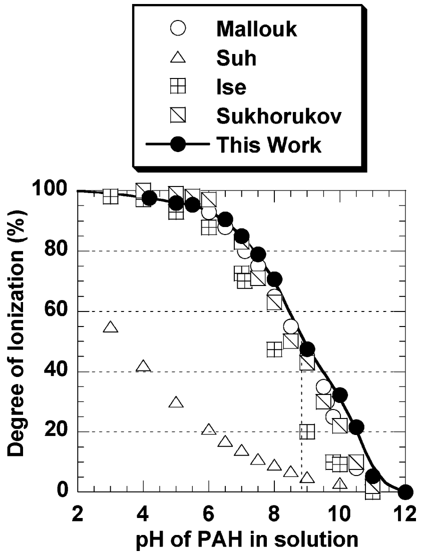

Figure 5. Estimated degree of ionization of PAH in solution as a function of pH. Data from other studies are also plotted for comparison. Broken line indicates the pH at which 50% of the PAH units are charged (pH ≅ 8.8) in our work.

6.5, a value that is in good agreement with solution titration values, especially the solution pK_a value of about 6.4 for PAA from a very recent report by Sukhorukov and co-workers.[25]

The degree of ionization of PAH as a function of solution pH was estimated by using a similar approach. To limit as much as possible the complications of overlapping bands, we analyzed the region of the spectrum that includes the N−H and C−H stretching bands (4000−2000 cm^{-1}). FTIR spectra are presented in Figure 4, whereas the degree of ionization data extracted from these curves can be found in Figure 5. The calculation method used to estimate the degree of ionization is explained in the Experimental Section in detail.

Reported solution pK_a (p$K_{1/2}$) values for PAH obtained by solution methods include ∼3.3,[31] ∼8.0,[32] ∼8.2,[33] and ∼8.7.[25,34] Figure 5 compares some of the PAH degree of ionization data reported in the literature with the results we obtained from FTIR analysis (closed circles). In our study, the solution pK_a (p$K_{1/2}$) of PAH was estimated to be between 8.0 and 9.0 (see end of paragraph). This range is consistent with solution pK_a values reported by many researchers using solution state methods. A notable exception is the report of Suh et al.,[31] which concluded that PAH has a pK_a of ∼3.3. This large discrepancy may reflect the fact that of Suh et al. utilized poly(allylamine) in their acid−base titration studies whereas we and others utilized poly(allylamine hydrochloride) as the starting material. As will be noted later, hydrophobic effects can make it more difficult to ionize functional groups in weak polyacids and bases. More likely than not, the nonionized chains of PAH used as the starting point in the Suh work were aggregated into a pearl-necklace-type structure with hydrophobic regions. Such structures have been theoretically predicted[35] and recently experimentally imaged[36] in the weak polybase poly(vinylamine). Unlike the PAA FTIR analysis where it was possible to cleanly isolate the absorption bands associated with the ionized and nonionized forms of the acid group, in the PAH case, a strong overlap between the amine and methylene group peaks made it difficult to easily deconvolute the intensity of these peaks. Given the error introduced by this problem, we are only able to state that the solution pK_a of PAH is in the range of 8−9.

Determination of the pK_a of PAA and PAH in Multilayer Films. As mentioned in the previous section, an important issue with weak polyelectrolytes like PAA and PAH is that their degree of ionization is subject to change when the polymer chain is incorporated into a multilayer system.[5,6,10,11] For example, ionization of the carboxylic acid groups of PAA can be more favorable in a multilayer environment compared to an aqueous solution.[21,25,26,37] This in turn results in a shift of the apparent pK_a value of PAA to lower pH values. Figure 6 presents clear evidence of the change in the degree of ionization of PAA that can occur when this polymer is adsorbed from an aqueous solution at a given pH into a multilayer film. The degree of ionization of PAA within a multilayer film was estimated by analyzing the FTIR spectra of three different multilayer systems: PAA/PAH, PAA/PDAC, and PAA/PVTAC. FTIR analysis revealed that in all three multilayer systems the degree of ionization of PAA increased significantly from the solution value in the pH range of 2 to 7. This effect is most dramatic when PAA is assembled with PAH. For example, at an assembly pH of 4.0, the degree of ionization of PAA increased from ∼7% in solution to ∼63% in the multilayer. In contrast, at this same pH, the degree of ionization of PAA increased to only about ∼30% when assembled with either PDAC or PVTAC.

The dissociation behavior of a weak functional group can be influenced by its local environment through a number of effects including electrostatic, hydrophobic, and chemical/titration effects. Electrostatic effects are observed when a polymer of opposite charge is added to form a complex or when salt is added to water solutions of a polyelectrolyte. Such effects have been reported for polyelectrolyte complexes[38,39] as well as polyelectrolyte multilayers[21,23−26,37] including our previ-

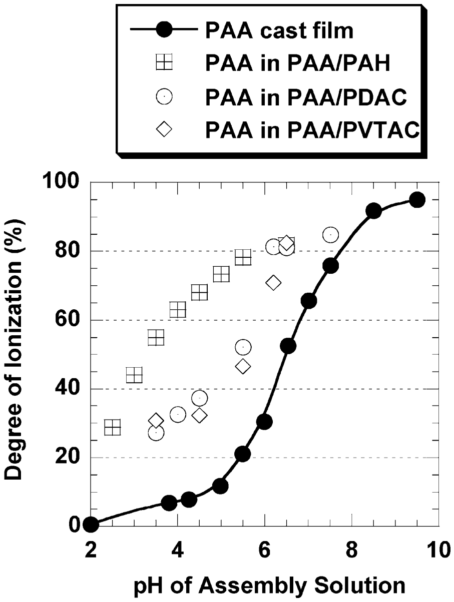

Figure 6. Estimated degree of ionization of PAA within multilayers of PAA/PAH, PAA/PDAC, and PAA/PVTAC as a function of assembly pH. The degree of ionization of PAA in solution from Figure 3 is also plotted for comparison.

ous results.[5,6,10,11] In essence, the presence of positive charges lowers the barrier to ionization of a carboxylic acid group. Hydrophobic effects occur when a weak polyelectrolyte experiences hydrophobic moieties/regions that can alter the dielectric environment (decrease the dielectric constant) of the weak ionic group. The association of hydrophobic elements can also increase the density of weak functional groups, thereby making it more difficult to induce ionization due to unfavorable electrostatic effects. In both cases, changes in the local electric field of a weak functional group induced by the surrounding media are believed to inhibit the ability of both acid and base groups to achieve an ionized state.[40] Such effects, for example, have been reported in copolymer gel studies[40−42] where it has been found that the apparent pK_a of a weak polyacid component can be increased[40] and that of a weak polybase reduced[41,42] in hydrophobic environments. We speculated that a similar effect was responsible for the interesting molecular memory and discontinuous reversible swelling behavior exhibited by an assembly pH 9.0/9.0 SPS/PAH multilayer system.[11] Recently, FTIR measurements (results to be published) have confirmed that these properties are associated with a significant decrease in the apparent pK_a of the PAH chains due to the hydrophobic environment created during assembly at this high pH. It should be noted that a different type of hydrophobic effect has also been reported in polyelectrolyte multilayers.[23] In this work, a chromophore modified poly(carboxylic acid) (PAZO) was assembled with a highly hydrophobic cationic polymer from ethanol solutions. The effective pK_a of the polyacid in this case was observed to shift to lower values.

In the case of multilayers, the presence of an abundance of oppositely charged cationic groups (electrostatic effect) would be expected to increase the degree of ionization of PAA (relative to the solution value) regardless of the type of polycation used to create the multilayer film. The magnitude of this effect, however, appears to be mediated by the hydrophobic nature of the polycation and possibility to a lesser extent by an acid/base reaction between the polyacid and polybase. In the former case, the more hydrophobic nature of the PDAC and PVTAC chains appears to limit the change in degree of ionization possible at a given pH. The fact that the acid groups of PAA can undergo an acid−base reaction with free amine groups of PAH may also facilitate a higher degree of ionization in PAA/PAH multilayers, although this effect becomes much less important as the degree of ionization of PAH in solution increases at lower pH. The quaternary ammonium groups of PDAC and PVTAC cannot support this type of reaction. Interestingly, at an assembly pH of about 6.5 or higher, the degree of ionization of the PAA chains within all multilayers reaches essentially the same value. This must be because shifts in the pK_a of a weak polyelectrolyte become more difficult (i.e., further "induced" ionization becomes more difficult) as the degree of ionization of the chain increases due to unfavorable electrostatic effects from ionized neighboring sites of similar charge.[43,44]

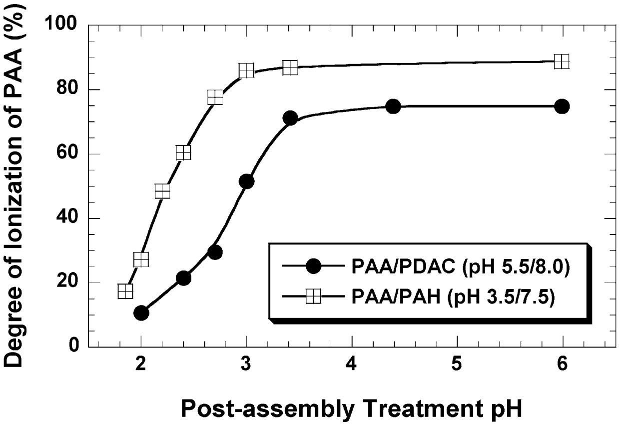

Figure 7. Degree of ionization of PAA in pH 5.5/8.0 PAA/PDAC and pH 3.5/7.5 PAA/PAH multilayers as a function of post-assembly pH treatment (1 min).

The consequences of all of these environmental effects can be exploited in a number of useful and technologically important ways. For example, we have previously shown that porosity transitions can be induced in specific PAA/PAH multilayers (for example, pH 3.5/7.5 PAA/PAH) by exposing the film to low-pH acidic water.[9,10] These transitions are triggered by a dramatic decrease in the degree of ionization of the PAA chains, which in turn occurs at a pH determined by the effective pK_a of the PAA chains. Thus, the above results suggest that by changing the nature of the polycation, it should be possible to shift the pH at which these transitions occur. In addition, since the degree of ionization of the PAA chains in a multilayer film depends on both assembly pH and the type of polycation used in the assembly process, it is possible to create heterogeneous multilayers comprised of discrete domains within which the PAA chains exhibit different ionization values. We are currently exploring structures of this type as a means to control the size distribution of nanoparticles[7,8] grown selectively within complex multilayer heterostructures.

To illustrate these points, Figure 7 shows how the degree of ionization of the PAA acid groups changes as a function of pH (after assembly) for pH 3.5/7.5 PAA/PAH and pH 5.5/8.0 PAA/PDAC multilayer films. Both of these films undergo phase transitions at low pH. In both cases, the degree of ionization of the PAA acid groups remains essentially unchanged until the pH drops below pH 3.5. This shows the dramatic influence that a multilayer environment can have on suppressing the protonation of acid groups. These results indicate that the effective pK_a of the PAA chains in the PAA/PDAC multilayer is higher by about 0.8 pH units than that of the PAA chains in a PAA/PAH multilayer. This translates to a multilayer pK_a value for PAA of ~2.2 for the PAA/PAH multilayer compared to ~3.0 for the PAA/PDAC multilayer. In other words, the apparent pK_a of PAA shifts from its solution value by about 4.3 pH units in PAA/PAH multilayers and by about 3.5 pH units in the case of the PAA/PDAC multilayers. A recent report from Sukhorukov and co-workers[25] is consistent with this shifting pK_a trend. These authors also observed a larger shift of the pK_a of PAA in the case of PAA/PAH multilayers compared to that of PAA/PDAC multilayers. For example, for PAA/PAH multilayers, the apparent pK_a shift of PAA was reported to be as much as about 4.5 pH units, whereas for PAA/PDAC multilayers, it was about 2.8 pH units. The large shift in pK_a observed in PAA/PAH multilayers was previously reported by us[5,6,10] and more recently confirmed by Barrett and co-workers[26] (pK_a shift of about 4 units). In the Sukhorukov and Barrett work, pK_a values of PAA and PAH were estimated by either potentiometric titrations of hollow PAA/polycation multilayer shells[25] or zeta potential measurements of colloidal particles coated with multilayers.[26]

Because of the difficulties associated with performing an FTIR analysis of PAH chains in a PAA/PAH multilayer film (multiple overlapping peaks from PAA), it was not possible to use this type of analysis to estimate the degree of ionization of PAH within a multilayer. Thus, unlike the case of PAA, where the degree of ionization both in solution and within the multilayer was obtained from FTIR analyses, for PAH, we were only able to estimate with any degree of certainty, the degree of ionization of PAH in solution. Instead, we take advantage of the above-mentioned recent results reported by Sukhorukov[25] and Barrett.[26]

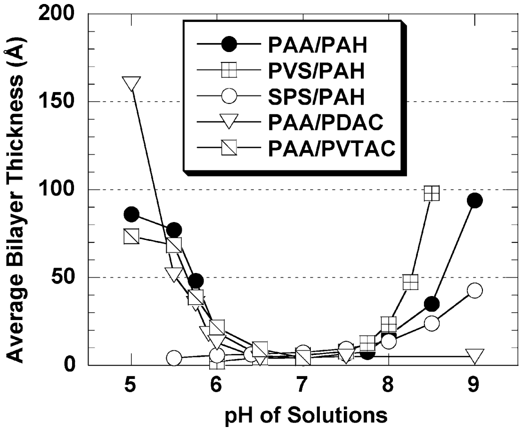

Figure 8. Average bilayer thickness of polyelectrolyte multilayers assembled at different solution pH (both polycation and polyanion solution at the same pH).

Influence of Weak Polyelectrolyte Charge Density on Film Growth. With an understanding of how the degree of ionization of PAA and PAH in solution and in multilayer films varies with assembly pH, we set out to determine how the charge density of a weak polyelectrolyte influences average bilayer thickness. This was accomplished by assembling a weak polyelectrolyte (either PAA or PAH) with a strong polyelectrolyte and comparing the results to the well-studied PAA/PAH system. The charge densities of the fully charged strong polyelectrolytes examined in this work are independent of pH over the range studied. Thus, by eliminating the pH sensitivity of one of the assembly polyelectrolytes, it was possible to focus only on the effects of variable charge density of a single weak polyelectrolyte. Specifically, PDAC and PVTAC were assembled as polycations with PAA, and PVS and SPS were assembled as polyanions with PAH. The chemical structures and the ionic characteristics of the polymers used in this study are presented in Figure 1 and Table 1, respectively. Figure 8 shows the multilayer growth trends of the five different assembly pairs over the full pH range examined (pH 5−9). Expanded views of these results that focus on either the low-pH region or the high-pH region are featured in parts A and B of Figure 9, respectively. The average bilayer thickness of the multilayers was determined from the total thickness of 20-bilayer films, except for the case of PAA/PDAC. In this latter case, 10-bilayer films were used to determine bilayer thickness because of problems with aggregation and nonuniformity in films with more assembled bilayers. In our previous study of PAA/PAH multilayers,[6] we obtained bilayer thicknesses by averaging the incremental layer thickness values of films containing from 20 layers (10 bilayers) up to 26 layers (13 bilayers). Given the fact that average bilayer thickness values can depend on the total number of layers deposited, there are some differences in the values of the bilayer thickness reported in this work compared to our previous paper. However, the trends of how bilayer thickness varies with assembly pH are the same and very reproducible.

The thickness of bilayers assembled from fully charged, strong polyelectrolytes in the absence of any added salt is known to be quite small (about 5 Å). As seen in Figure 8, all of the polymer pairs assembled into very thin layers (4−8 Å per bilayer) near neutral pH, which indicates that in this pH regime (pH 6.5−7.5) PAA and PAH behave essentially like fully charged strong polyelectrolytes.[6] In those cases where the weak polyelectrolyte remains in a highly charged state with either decreasing (PAH) or increasing pH (PAA), assembly with a strong polyelectrolyte continues to produce films with very thin bilayers. For example, PAA/PDAC multilayers in the pH 7−9 range and SPS/PAH multilayers in the pH 5−7 range. In sharp contrast, if the weak polyelectrolyte begins to lose charge density with either increasing (PAH) or decreasing pH (PAA), a dramatic increase in bilayer thickness occurs over a very narrow pH range (less than 1 pH unit). The same behavior is observed when two weak polyelectrolytes are assembled (PAA/PAH) and when a weak polyelectrolyte is assembled with a strong polyelectrolyte. Thus, whenever a fully charged polymer (either weak or strong polyelectrolyte) is assembled with a polymer with a pH variable charge density, the bilayer thickness undergoes a dramatic increase when the assembly pH decreases the charge density of the weak polyelectrolyte from its fully charged state. As we have reported earlier for PAA/PAH,[6] this transition from very thin layers to very thick layers occurs after only a small amount of charge has been removed from the polymer with the varying charge density.

To show the relationships between the degree of ionization of the weak polyelectrolyte, both in solution and in the multilayer, and bilayer thickness, Figure

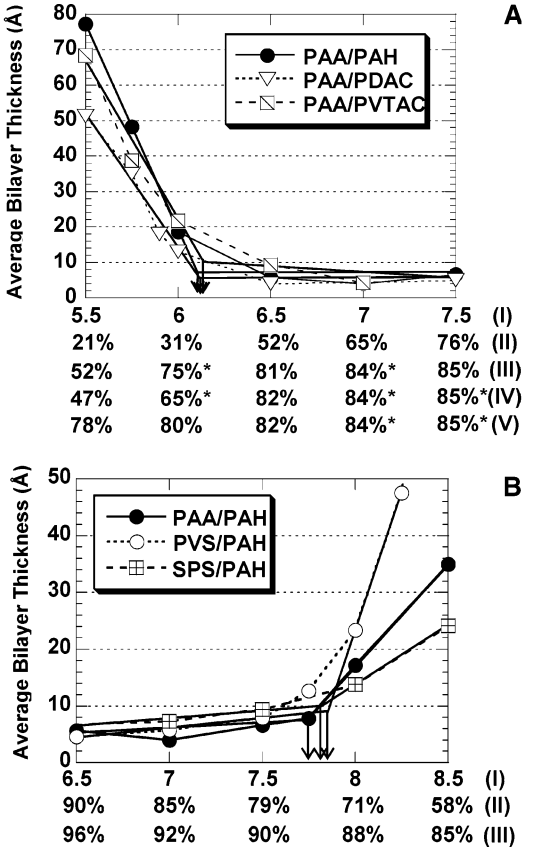

Figure 9. (A) Expanded view of the bilayer thickness of multilayers of PAA with PAH, PDAC, and PVTAC in the low-pH region of Figure 8. The *x* axes are (I) assembly solution pH, (II) degree of PAA ionization in the cast film, (III) degree of PAA ionization in PAA/PDAC multilayers, (IV) degree of PAA ionization in PAA/PVTAC multilayers, and (V) degree of PAA ionization in PAA/PAH multilayers. Vertical arrows indicate the onset of the thickness change as determined by the intersection of the indicated tangent lines (* interpolated values). (B) Expanded view of the bilayer thickness of multilayers of PAH with PAA, PVS, and SPS in the high-pH region of Figure 8. The *x* axes are (I) assembly solution pH, (II) degree of PAH ionization in the cast film, and (III) degree of PAH ionization in SPS/PAH multilayers adapted from the work of Sukhorukov and co-workers[25] (assembled at pH 7.0/7.0). Vertical arrows indicate the onset of the thickness change as determined by the intersection of the indicated tangent lines.

9A,B displays the results obtained from FTIR studies and thickness studies. Multiple *x*-axes are presented in these figures. In Figure 9A, the bilayer thickness is plotted as a function of (I) assembly pH, (II) the degree of ionization of PAA in a cast film, (III) the degree of ionization of PAA within PAA/PDAC multilayers, and (IV) the degree of ionization of PAA within PAA/PVTAC multilayers. The degree of ionization of PAA within PAA/PAH multilayer films (V) is also included in this figure. In Figure 9B, the bilayer thickness is plotted as a function of (I) assembly pH, (II) the degree of ionization of PAH in a cast film, and (III) the degree of ionization of PAH within SPS/PAH multilayers as reported by Sukhorukov and co-workers.[25]

Figure 9A,B shows that strong polyelectrolyte-like behavior is maintained by both PAA and PAH until the degree of ionization of the polymer in the multilayer film drops to less than about 70−80% in the PAA case (about 80% for PAH and PDAC and 70% for PVTAC) and less than about 89% in the PAH case. As the degree of ionization of these polymers drops below these trigger points, the average thickness per deposited bilayer increases dramatically, reaching values after a one unit pH change from the trigger point in the range of 20−80 Å per bilayer depending on the particular polymer pair. The fact that the onset of this change from molecularly thin assembled layers to much thicker assembled layers is similar for all polymer pairs examined (80−90% degree of ionization for four out of the five polymer pairs) implies that the thickness change was triggered primarily by a change in the degree of ionization of PAA (low-pH region with PAH, PDAC, and PVTAC) or PAH (high-pH region with PAA, PVS, and SPS). In other words, the chemical structure of the polymer maintained in the fully charged state does not strongly influence the pH at which the thickness change starts to occur. On the other hand, the chemical structure of the polymer maintained in its fully charged form clearly influences the magnitude of the change in bilayer thickness that occurs as the degree of ionization of the weak polyelectrolyte drops below a critical charge density value. Factors such as the presence of hydrophobic interactions, chain flexibility, ability to form hydrogen bonds, and polymer molecular weight and molecular weight distribution are all expected to play a role in determining the bilayer thickness in this regime.

The degree of ionization of the weak polyelectrolyte in the solution state appears to be less important than the degree of ionization of the polymer in the multilayer. At the very least, there is no obvious correlation between this value and the critical charge density below which the bilayer thickness increases. For example, in the case of PAA as the charge varying weak polyelectrolyte, the onset for change in bilayer thickness occurs when the degree of ionization of PAA in solution is about 50%. In the case of PAH as the charge varying weak polyelectrolyte, the onset for change in bilayer thickness occurs when the degree of ionization of PAH in solution is about 75%. On the basis of this observation, we hypothesize that the dramatic change in bilayer thickness that occurs when the charge density of the weak polyelectrolyte drops below a critical level is driven primarily by the layer deposition step involving the adsorption of the fully charged polymer onto the less charged, previously adsorbed polymer. In this scenario, when a weak polyelectrolyte of low charge density is adsorbed onto a multilayer film with a fully charged polymer as the outermost layer, the degree of ionization of the adsorbing polymer increases in response to the environment provided by the oppositely charged polymer. If this process produces an adsorbed polymer chain with a degree of ionization that is below a critical charge density value, then the next adsorbing layer of the fully charged polymer[45] encounters a thermodynamic frustration as described by Mayes and co-workers.[14,15] Basically, below a critical charge density, the enthalpic energy required to maintain the chain in a more extended, flat conformation is no longer able to overcome the entropic penalty associated with this conformational state. The net result is that the adsorbing chains form a larger number of tails and loops which in turn promotes thicker layers. Note that even though the degree of ionization change that occurs when PAA is adsorbed into a PAH multilayer at low pH (<6) is much larger than the change observed in PDAC and PVTAC multilayers, in all of these systems, the degree of ionization of PAA in the multilayer goes to ~80% at pH 6.5.

This work suggests that the critical charge density below which the change from molecularly thin adsorbed layers to thicker adsorbed layers starts to occur is observed at a degree of ionization in the range of 70–90%. We note that the Sukhorukov data[25] used for estimating the PAH degree of ionization were obtained by titration of a multilayer with a fixed composition (SPS/PAH assembled at pH 7.0/7.0). Since the degree of ionization of a weak polyelectrolyte chain depends on the assembly conditions, the actual degree of ionization of the PAH chains assembled at higher pH may be different. In the PAH case, however, the difference between the solution-state degree of ionization and the multilayer-state degree of ionization is less than in the PAA case. For example, at the trigger point (about pH 7.8), the degree of ionization of PAH in solution is about 73%, whereas an estimate of the multilayer-state value from the Sukhorukov work is 89%. Therefore, it is safe to assume that the degree of ionization of the PAH chains at the trigger point is greater than 73% and as high as 90%. Further, it should be noted that ongoing FTIR studies that are focusing on the discontinuous swelling transitions exhibited by high-pH assembled PAH-containing multilayers (PAH assembled with SPS or poly(vinyl sulfate)) also suggest that the degree of ionization of PAH in a multilayer assembled at pH 8 or lower is about 90% or higher (results to be published).

In many of the studies utilizing copolymers with different amounts of fixed charges to explore charge density effects, it has been found that a maximum in bilayer thickness occurs when the fraction of charged monomer units is about 75%.[17,18] In one study, however, it was found that a significant thickness increase was not observed until the fraction of charged monomer units dropped to about 30%.[20] The unusually large increase in bilayer thickness that we observe with weak polyelectrolytes (greater than an order of magnitude in many cases) when the charge density drops from the trigger point to the range of 50–85% has not been reported in any of the copolymer studies. In many of the copolymer studies, salt was added to the dipping solutions making a direct comparison more complicated. In addition, thickness effects of this type often become more dramatic as more bilayers are added to the film.[18] Many of the studies with fixed charged copolymers only examined films with 14 layers (7 bilayers) or less. Nevertheless, it is clear that weak polyelectrolytes exhibit behavior that is unique to their ability to dynamically adjust their charge density in response to local environmental variations. It has recently been demonstrated that the distribution of charges along a chain may be just as important as charge density in determining adsorption behavior and stable multilayer assembly.[46] The charge adjusting behavior of weak polyelectrolytes makes it possible for the polymer chains to adopt a charge distribution that promotes maximum multilayer stability and cooperativity with the oppositely charged partner in the multilayer assembly process. Thus, although some studies with fixed charge density copolymers find a maximum bilayer thickness in the 70–80% range, the dramatic changes we observe in thickness from very thin layers to very thick layers with only a small drop in charge density from the essentially fully charged state may be a unique consequence of weak polyelectrolyte behavior.

Conclusions

The influence of the charge density of a weak polyelectrolyte on multilayer growth was investigated by assembling PAA and PAH with strong polyelectrolytes and comparing the results to the well-studied PAA/PAH multilayer system. In all cases, a transition from thin flat layers to much thicker adsorbed layers occurred when the charge density of the weak polyelectrolyte decreased from its fully charged state to 70–90% charged units. Additionally, FT-IR analyses of the pH-dependent degree of ionization of the weak polyelectrolyte in solution and in a multilayer film quantitatively verified earlier observations that the ionization behavior of a weak polyelectrolyte can differ substantially from the solution state when it is incorporated into a multilayer film.

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