pH-Dependent Thickness Behavior of Sequentially Adsorbed Layers of Weak Polyelectrolytes

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Received September 28, 1999

ABSTRACT: A detailed study of the role that solution pH plays in the layer-by-layer processing of the weak polyelectrolytes poly(acrylic acid) and poly(allylamine hydrochoride) was carried out. It was found that dramatically different polymer adsorption behavior is observed as one systematically increases (or decreases) the charge density of a weak polyelectrolyte including transitions from very thick adsorbed layers (ca. 80 Å) to very thin adsorbed layers (ca. 4 Å) over a very narrow pH range. By controlling pH, it is possible to vary the thickness of an adsorbed polycation or polyanion layer from 5 to 80 Å. In addition, control over the bulk and surface composition of the resultant multilayer thin films is readily achieved via simple pH adjustments. These studies have provided new insights into the polyelectrolyte sequential adsorption process and have already opened up some interesting technological applications.

Introduction

Polyelectrolyte complexes, formed by the mixing of dilute solutions of a polycation and a polyanion, have been extensively studied in past years and are known to exhibit a unique combination of physical properties due to their ionically cross-linked nature.[1] These interesting polymeric salts, however, are oftentimes insoluble and hence very difficult to manipulate into useable forms such as uniform thin film coatings. A novel layer-by-layer deposition process initially introduced by Decher and co-workers[2] has changed this situation. In this process, polyelectrolyte complexes are fabricated one molecular layer at a time via a simple sequential adsorption procedure. By repeatedly dipping a substrate into a dilute polycation solution followed by a dilute polyanion solution, it is possible to fabricate highly uniform polyelectrolyte multilayer thin films with precisely controlled thicknesses and molecular architectures. Currently, this approach has been utilized to assemble a wide variety of quite different materials into multilayer thin films.[2]

In general, most researchers have utilized strong polyacids and polybases to construct these multilayer thin films. With such materials, adding salt to the polyelectrolyte dipping solutions best controls the thickness of an adsorbed layer. Our approach has been to use weak polyelectrolytes such as poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) whereby control over the layer thickness and molecular organization of an adsorbed polymer chain can be achieved by simple adjustments of the pH of the dipping solutions.[3] In this case, pH controls the linear charge density of an adsorbing polymer as well as the charge density of the previously adsorbed polymer layer. As will be further demonstrated in this paper, the net result is an unprecedented ability to control the blending of a polycation and polyanion at the molecular level. In addition, these studies have revealed that dramatic changes in the thickness of an adsorbed layer can be

induced by very small changes in the pH of the dipping solutions. An understanding of the molecular origin of these thickness transitions is expected to provide new insights into the basic polymer physics of the sequential adsorption process as well as to provide new possibilities for their technological application. For example, soon we will show that it is possible to fabricate uniform, microporous thin films from these weak polyelectrolyte multilayers.

Experimental Section

Poly(acrylic acid) (M_w = 90 000) (PAA) was obtained from Polysciences. Poly(allylamine hydrochloride) (M_w = 55 000−65 000) (PAH) and the methylene blue dye were obtained from Aldrich. All polyelectrolytes and the dye were used as received without further purification. Polyelectrolyte dipping solutions of 10^{-2} M (based on the repeat unit molecular weight) were made from 18 MΩ Millipore water and pH adjusted with either HCl or NaOH.

Details concerning substrate preparation, thickness measurements, contact angle measurements, methylene blue staining, and the automated layer-by-layer dipping process can be found in a previous paper.[3] To avoid substrate effects, incremental thickness measurements were started on films containing a minimum of 10 bilayers. After the substrates were dipped into a polyelectrolyte solution, they were rinsed in three separate bins of pH neutral water (pH of 5.5−6.5). No drying step was used in the dipping procedure. All multilayer films were dried at 90 °C for 1 h prior to any measurements.

Surface roughness measurements were done on 20 layer films deposited on silicon wafers with a Dimension 3000 scanning probe microscope (Digital Instrument). A silicon cantilever was used for all measurements. The spring constant of the cantilever was 20−100 N/m. Typically, the surface morphology of three 10 × 10 mm spots near the center of each sample was observed by the tapping mode of the scanning probe microscope.

Results and Discussion

An automatic dipping method was used to fabricate a number of different PAH/PAA multilayer thin films on both silicon wafers and hydrophilic glass slides. The pH of the PAH and PAA dipping solutions was systematically varied from 2.5 to 9.0 in order to determine how

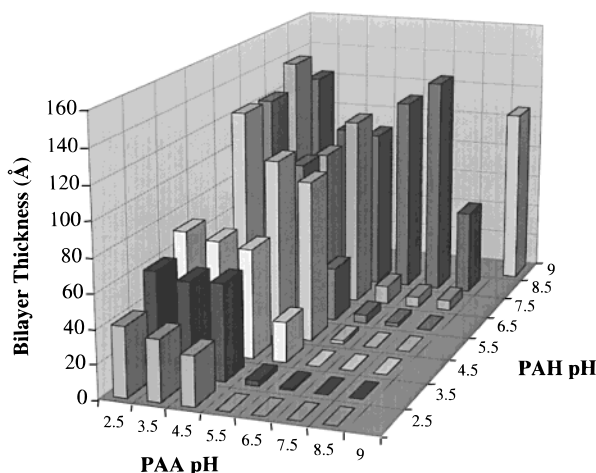† Keio University.
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Figure 1. Complete pH matrix showing the average incremental thickness contributed by a PAH/PAA bilayer as a function of dipping solution pH.
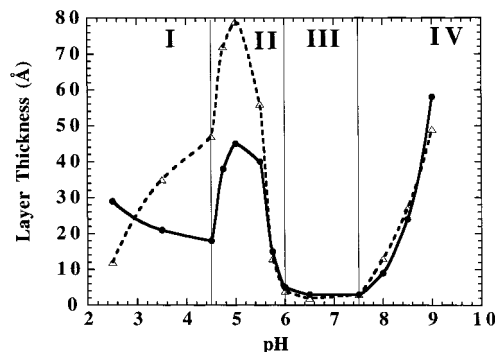

Figure 2. Average incremental thickness contributed by a PAA and PAH adsorbed layer as function of solution pH. Both the PAH and PAA dipping solutions in this case were at the same pH. Solid line represents the PAA layer thickness, and the dashed line is the PAH layer thickness.

dipping solution pH influences layer thickness and organization. Figure 1 shows the full pH matrix generated in this study. This figure displays the average incremental thickness contributed to each multilayer thin film by the bilayer building block (polycation plus polyanion: measured on dried films). A quick survey reveals that the deposition of this layer pair is dramatically influenced by the pH of the individual dipping solutions. By simply controlling pH, it is possible to deposit unusually thick bilayers (>120 Å) or very thin bilayers (<10 Å) or, in some cases, completely prevent the multilayer deposition process (for example, when the pH of the PAH solution is 3.5 and the pH of the PAA solution is 7.5).

What is not evident in this figure is the fact that the average incremental thickness contributed by the individual polycation and polyanion layers is also highly sensitive to dipping solution pH. To further explore this important observation, we will examine more closely different regions of the pH matrix including (1) the diagonal of the matrix, i.e., the case where multilayers are constructed with the PAA and PAH dipping solutions at the same pH, (2) the case where the pH of the PAA dipping solution is held constant and the pH of the PAH solution is varied, and (3) the case where the pH of the PAH dipping solution is held constant and the pH of the PAA solution is varied.

The Diagonal: Deposition with the PAA and PAH Solutions at the Same pH. Figure 2 displays the average incremental layer thickness contributed by PAH and PAA to a multilayer thin film over the pH range 2.5–9.0. In this pH range, the degree of ionization of an adsorbed PAA chain starts at about 20–30% at a pH 2.5 and reaches close to 100% at a pH of 6.5 (determined by FTIR). The PAH chains remain fully ionized over much of this range but start to lose protons (become less than fully ionized) above a pH of about 7.0.

In this figure, we have identified four different growth regions. In region I (pH 2.5–4.5), the thickness of a PAH-adsorbed layer increases with increasing pH whereas the thickness of an adsorbed layer of PAA decreases with increasing pH. These changes in thickness are both related to the increase in charge density of the PAA chains that occurs with increasing pH. Details concerning the adsorption behavior of PAH and PAA in this portion of the pH matrix have been described in a previous paper.[3] In short, the decrease

in PAA layer thickness results from the decreasing segmental population of loops and tails that occurs as the PAA chains become more highly charged with increasing pH. The increase in PAH layer thickness, on the other hand, results from the increasing surface charge density of a previously adsorbed PAA chain with increasing pH (more oppositely charged PAH is needed to neutralize the higher surface charge of the more highly ionized PAA surface chains). The pH-dependent adsorption behavior observed in region I is similar to what has been observed in single layer adsorption studies of weak polyelectrolytes onto oppositely charged surfaces.[4] An important conclusion of our previous work in this pH region[3] is that the thickness of an adsorbed layer of PAH and PAA depends primarily on the charge density of the adsorbing polymer and the surface and not on the thickness, conformation (segmental population of loops, tails, and trains), or free ionic binding sites of the previously adsorbed polymer layer. As will become apparent shortly, this does not hold true in other regions of the pH matrix.

When the pH of the dipping solutions is increased beyond 4.5, a remarkable thickness transition is observed. The thickness of an adsorbed layer of PAA, rather than continuing to decrease with increasing pH, increases abruptly to a value as large as about 45 Å before collapsing over a very narrow pH range to a thickness of about 3 Å/layer. The thickness of an adsorbed layer of PAH undergoes a similar abrupt thickness change in this pH region reaching a value as large as 80 Å before it also collapses to a very thin layer near a pH of 6.0.

A consideration of this thickness transition from the high pH side of region II provides an interesting insight into its origin. In region III, both PAH and PAA are adsorbing as fully charged polyelectrolytes and are deposited as very thin layers (in the 3–5 Å/layer range). This, in fact, is what is typically observed when the sequential adsorption process is carried out with any two fully charged vinyl-type polyelectrolytes from salt-free solutions.[5] When the pH of the dipping solutions is lowered below 6.0, the thickness of both the PAH and PAA layer increases dramatically over a very narrow pH range of only 0.5 pH units. In the pH range of 5.5–6, the PAH chains are fully ionized and the PAA chains are close to fully ionized. FTIR measurements, for example, indicate that the degree of ionization of the PAA chains in the multilayer film varies from about 80 to 90% over this range. Thus, the PAH chains are

adsorbing as fully ionized chains onto a PAA outermost adsorbed layer that is almost fully ionized. This condition, i.e, the alternate deposition of a fully charged chain onto a nearly fully charged chain, produces these unusually thick adsorbed layers.

A similar transition from very thin adsorbed layers (3−5 Å/layer) to unusually thick adsorbed layers (>40 Å/layer) is observed in region IV of the pH matrix. In this pH region, the PAA chains are always adsorbing in their fully ionized state whereas the degree of ionization of the PAH chains starts to decrease with increasing pH. Again, we have the situation that a fully charged chain is alternately adsorbed onto a nearly fully charged chain, the net result being the creation of unusually thick PAA and PAH layers. Clearly this thickness transition from very thin adsorbed layers to very thick adsorbed layers does not depend on which polyelectrolyte is in the fully charged state but only on the fact that a fully ionized chain and a nearly fully ionized chain are being alternately deposited. An exploration beyond pH 9 to determine if this region completely mirrors region I and II is not possible due to solubility and film quality/precipitation problems.

To our knowledge, a thickness transition of this type has not been previously reported in any single layer or multilayer adsorption studies on polyelectrolytes. To understand the driving force behind this behavior, Barrett et al. have recently carried out model studies involving the adsorption of fully charged PAA chains onto methoxysilane self-assembled monolayer surfaces (SAMs) with pH-controllable surface charge densities of cationic ammonium groups.[6] These studies also reveal an abrupt transition from a molecularly thin adsorbed layer (ca. 5 Å) to a much thicker adsorbed layer (ca. 25 Å) over a very narrow pH range of about a half a pH unit. A thermodynamic model that captures all of the features observed experimentally was put forth to explain this behavior.[6] In essence, the model indicates that, at a critical high surface charge density (modeled as neutral "stickers"), the entropic penalty for spreading a chain into a flat conformation on the surface (molecularly thin layer) is overcome by the enthalpic gain to the free energy of adsorption. As the surface charge density decreases below this point, however, the energy gain for spreading a chain over the surface is not sufficient to overcome the loss in configurational energy, and a sharp transition to a thicker layer with a high segmental population of loops occurs. As observed experimentally, this transition to a thick layer was predicted to occur when the surface charge density dropped somewhat below its fully charged state.

In the case of the multilayer thin films of PAH/PAA, the interaction between the two sequentially adsorbed polyions must also be considered. We surmise that two fully charged chains of this type in the absence of added salt will strive to form a cooperatively stitched 1:1 polyelectrolyte complex with extended sections of polycation/polyanion double-strand like units. Such "zipped-up" structures are known to occur in the water-insoluble, stoichiometric polyelectrolyte complexes formed by the mixing of solutions containing two oppositely and fully charged polyions.[1,7] In the layer-by-layer deposition process, these insoluble complexes are constructed one layer at a time. The net result in the case of fully charged chains is the deposition of very thin adsorbed layers that are highly interpenetrated and lying essentially flat within the multilayer. In support of this description, we have found that the thickness of an adsorbed polymer layer deposited when both macromolecules are fully charged (for example, when PAH and PAA are deposited at a pH of 6.5) is independent of the molecular weight of the adsorbing polymer over a range of at least $3000-10^6$ g/mol. Hence, larger molecular weight chains simply spread out and occupy more surface area without increasing the thickness of the adsorbed layer.

When a fully ionized chain and a nearly fully ionized chain are alternately deposited, this cooperative zipping process is frustrated somewhat and the chains cannot spread out flat over the surface but instead adopt a conformational arrangement of dense loops that extend away from the surface leading to the deposition of much thicker layers. The layers within the film are still highly interpenetrated but organized in a different fashion. As expected for a loopy conformational arrangement,[8] the thickness of an adsorbed layer deposited in region II (for example with the dipping solutions at a pH 5.0) is dependent on the molecular weight of the adsorbing polymer chain. Preliminary results indicate that the layer thickness in this case scales approximately as $T \propto M^{0.3}$.

The idea that the polycation/polyanion chains are still highly interpenetrated (as opposed to forming discrete layers) is supported by measurements of advancing water contact angles and methylene blue staining studies. We have previously shown[3] that such measurements provide complementary information about the composition of the multilayer surface. Contact angle measurements made on films fabricated with the dipping solutions set at pH 5.5−8.5 (regions II−IV) all indicate that the surface is comprised of an approximately equal volume fraction of segments from both polymers regardless of which polymer is the outermost layer. In all cases, an advancing water contact angle of 25 ± 6° is observed. Even at a pH of 5.0, where the thickest adsorbed layers are deposited, contact angle measurements indicate that the PAH and PAA outermost layers are well interpenetrated by segments from the previously adsorbed layer (contact angles: PAH as the outermost layer, 38°; PAA as the outermost layer, 24°). According to the well-known Cassie's equation,[9] a contact angle of about 30° for this polymer combination would indicate a 50/50 mixture of both segments (the contact angle measured from a thin film of pure PAA prior to dissolution is less than 5° whereas that of pure PAH is 50−55°).[3] If the surfaces of these multilayer thin films are well interpenetrated, it seems reasonable to conclude that the internal layers are also highly interpenetrated.

In the case of methylene blue surface staining measurements, we find that very little methylene blue is adsorbed onto a PAA or PAH outermost layer film when multilayers are fabricated from pH 5.0−6.0 solutions (absorbance at λ_{max} of about 0.04 when PAA is the outermost layer and less than 0.02 when PAH is the outermost layer). Essentially no methylene blue is adsorbed onto multilayers fabricated from solutions of pH 6.5 or higher (absorbance at λ_{max} of 0.02 or less). We have previously suggested[3] that, under the conditions employed, methylene blue will only adsorb onto a multilayer surface that contains free binding sites in the form of carboxylic acid or nonpolycation bound carboxylate groups. Thus, these measurements suggest that the interpenetrated surfaces of the multilayer films
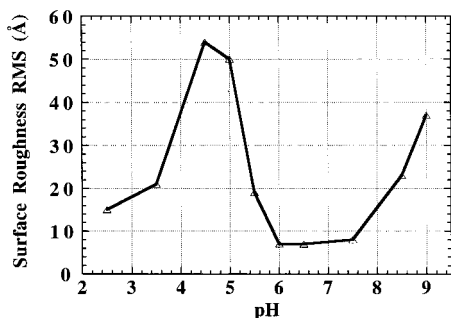
Figure 3. RMS surface roughness of 20 layer PAH/PAA films as a function of dipping solution pH. Both the PAH and PAA dipping solutions in this case were at the same pH.

Figure 4. Average incremental bilayer thickness of PAH/PAA layers deposited at pH 6.5/6.5 onto preformed PAH/PAA 20 layer films fabricated at (a) PAH/PAA 6.5/3.5 (solid line) and (b) PAH/PAA 3.5/3.5 (dashed line). The rms surface roughness of the preformed multilayers is shown before and after the deposition of the PAH/PAA 6.5/6.5 layers.

fabricated from solutions of pH 5.0 and higher are comprised primarily of polycation–polyanion ion pairs. The weak methylene blue absorption observed with PAA outermost layer films in the pH range of 5–6 is consistent with the fact that the PAA chains do not become fully ionized (i.e., not fully charged) until a pH of about 6.5.

The conformational state of a multilayer surface (i.e., whether it is dominated by loop and tail segments or train segments) can be explored indirectly via measurements of the surface roughness of dried films. A solvated surface comprised of a significant population of loops and tails, upon drying, will produce a molecularly rough surface whereas a surface dominated by flat, trainlike segments will produce a more molecularly smooth surface. Figure 3 shows the rms surface roughness of dried PAH/PAA multilayer films fabricated from dipping solutions covering the range of 2.5–9 as determined by AFM. For the most part, the shape of this curve maps onto the thickness data found in Figure 2; i.e., the large increase in thickness that occurs as one moves from region III to region II or IV is accompanied by a large increase in surface roughness. In the pH range of 6–7.5, it can be seen that the multilayer films exhibit very low surface roughness (<10 Å) as has been found in other studies[10] utilizing two fully charged polyions to assemble multilayers (no added salt). This very low surface roughness is a consequence of the flat, surface bound conformations adopted by the polymer chains during multilayer assembly. The surface roughness increases significantly, however, when the films are fabricated at lower or higher pH due to the establishment of a more loopy conformational arrangement.

To determine if the conformational state of a multilayer film (as inferred from surface roughness measurements of dried films) can influence the thickness of an adsorbed layer, we carried out the following experiments. First, two multilayer thin films containing 20 layers of PAH and PAA deposited at a PAH/PAA solution pH of 3.5/3.5 and 6.5/3.5 were fabricated. The multilayer film deposited at 3.5/3.5 exhibits a rms surface roughness of about 20 Å whereas the film deposited at 6.5/3.5 exhibits a higher surface roughness of about 85 Å. We then deposited onto these films PAH/PAA bilayers at a pH of 6.5/6.5. Recall that PAH and PAA layers deposited at a pH of 6.5 onto flat substrates such as silicon wafers are about 3–5 Å in thickness. The results of these experiments are found in Figure 4.

When the 6.5/6.5 PAH/PAA bilayers are deposited onto the multilayer thin film exhibiting the highest surface roughness (PAH 6.5/PAA 3.5), the first few bilayers deposited are clearly very thick (in the range
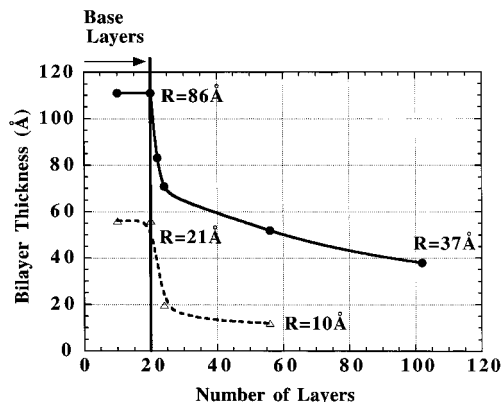
of 70–85 Å/bilayer). Even after 40 bilayers have been deposited onto the PAH/PAA 6.5/3.5 multilayers, the thickness contributed by a bilayer is still unusually large (about 40 Å/bilayer). Similar results are obtained when the PAH/PAA 6.5/6.5 bilayers are deposited onto the PAH/PAA 3.5/3.5 multilayers; i.e., the thickness per bilayer is much greater than that obtained when these layers are deposited onto flat substrates. In this case, the effect is less pronounced correlating with the lower surface roughness of the 3.5/3.5 multilayer film. It should also be noted that we have observed the same effect when bilayers based on the strong polyacid SPS are deposited onto these relatively high surface roughness multilayers (SPS/PAH bilayers are normally about 5–8 Å in thickness when deposited from salt-free solutions). Thus, when any two fully charged polyelectrolytes are deposited onto "conformationally" rough multilayers, the thickness contributed per bilayer increases significantly from what would be obtained on flat substrates. This effect is gradually damped out as more bilayers are deposited and the surface roughness decreases (i.e., the segmental population of loops decreases).

It is clear from the above experiments that the conformational state of a previously adsorbed polyelectrolyte layer (or layers) can strongly influence the thickness/conformation of an adsorbing polyelectrolyte layer. This effect helps to explain a number of important observations. First, in regions II and IV, it often takes about 8–10 bilayers to achieve the layer thicknesses presented in Figure 2; although the pH trends of Figure 2 are similar, the initial bilayers deposited are thinner and exhibit less surface roughness. After these initial bilayers are deposited both the thickness contributed per layer and the surface roughness plateau and remain constant to at least 25 bilayers. Second, as mentioned earlier, on the basis of single-layer adsorption studies of PAA, one would have expected the thickness of an adsorbed PAA layer to continuously decrease with increasing pH when moving from region I to region III. Instead, there is an abrupt increase in thickness in region II. Third, the layer thicknesses in regions II and IV are significantly larger than what has been observed (and predicted) in the single layer studies involving the adsorption of a fully charged PAA chain onto a smooth SAMs surface of controllable surface charge density.[6] All of the above observations can be attributed to the
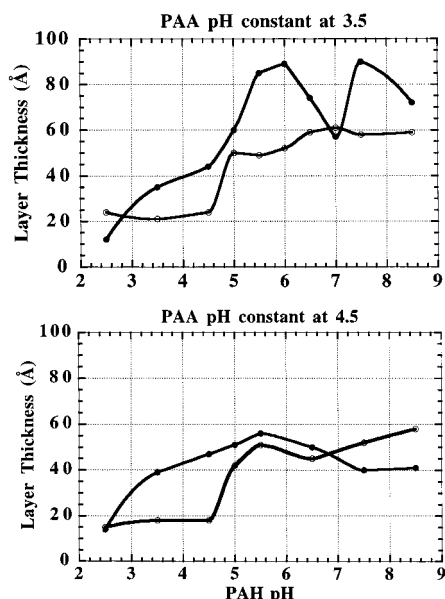
Figure 5. Average incremental thickness contributed by a PAA and PAH adsorbed layer as function of solution pH. In this case, the PAA dipping solution was at pH 3.5 or 4.5 and the pH of the PAH dipping solution was varied. Solid circles represent the PAH layer thickness and the open circles represent the PAA layer thickness.

increase in layer thickness that results when a polyelectrolyte is adsorbed onto a surface comprised of a high density of loops and tails.

In regions II and IV, the thickness of an adsorbed layer is strongly influenced by the conformational state of the previously adsorbed layers. Interestingly, we have not observed this effect in region I.[3] In this region (pH 2.5−4.5), the thickness of an adsorbed layer depends essentially only on solution pH. Insights into why this is the case are suggested by the following results.

Deposition at a Constant PAA pH. Figure 5 shows how the thickness contributed by a PAH and PAA layer varies when the pH of the PAA dipping solution is held constant at either pH 3.5 or 4.5 and the pH of the PAH solution is varied from 2.5 to 8.5. In the pH range 2.5−4.5, the PAA layer thickness remains essentially constant whereas the PAH layer thickness increases with increasing pH. As indicated above, in this pH range, the thickness of an absorbed layer depends primarily on pH. For example, the thickness of an adsorbed PAA layer deposited at pH 3.5 is about 20 Å even though the previously adsorbed PAH layer is increasing from about 10 to 45 Å over this range. Similarly, the thickness contributed by a PAH layer at, for example, a PAH pH of 3.5, is close to 40 Å when the PAA pH is either 3.5 or 4.5.

This situation changes dramatically, however, when the PAH solution pH is increased above 4.5. In both the PAA pH 3.5 and 4.5 cases, the PAA layer thickness increases abruptly to more than 40 Å at a PAH solution pH of 5.0 and continues to increase with increasing PAH pH, reaching about 60 Å at pH 8.5. The thickness contributed by a PAH layer continues to increase until a pH of about 6.0 and then either fluctuates about this maximum thickness (PAA pH 3.5 case) or drops to a somewhat lower thickness (PAA pH 4.5 case) with increasing pH. Thus, in sharp contrast to what was observed when the diagonal of the matrix was examined, the PAA and PAH layers remain thick over the entire pH 5.0−8.5 range.

The above pH trends can be rationalized in the following manner. When a PAA chain is adsorbed onto a PAH layer at a relatively low solution pH (2.5−4.5), the degree of ionization of the chains in solution is very low (less than 10% in all cases[11]). The degree of ionization of the adsorbed chain segments of PAA, however, is significantly higher as these segments will increase their charge in an attempt to neutralize/titrate the positively charged surface.[12] In other words, the adsorbed PAA chain segments have a lower effective pK_a than PAA chain segments in the solution. This means that an adsorbed PAA layer is comprised of charged segments that penetrate into the PAH surface layer and a population of loop and tail segments that are for the most part extending away from the surface and are essentially not charged. The thickness of a dried PAA layer therefore reflects the thickness contributed by the segments that intermingle with the PAH segments as well as a contribution from the collapsed loop and tail segments. As the pH of the PAA solution increases, more of the chain segments will become charged and the average size of the loop/tail segments will decrease. Assuming that the conformation of the previously adsorbed PAH layer does not influence this situation, one would expect the PAA layer thickness to decrease with increasing pH and remain about the same at constant pH and varying PAH pH. This is the behavior that is observed in the 2.5−4.5 pH range.

The idea that the effective pK_a of the acid groups is lowered when the PAA segments are in a PAH environment is supported by the following observation. In the pH range of 2.5−6.5, we find that whenever a PAH layer is deposited onto a PAA layer at the same pH as the PAA layer, the degree of ionization of the PAA chains increases by about 10% (determined by FTIR). This observation is consistent with the notion that the pK_a of PAA is very sensitive to local environment. The addition of more positively charged PAH segments further titrates some of the nonionized PAA segments by shifting the effective pK_a to a slightly lower value.

When a fully charged PAH chain is adsorbed onto a PAA surface, the pH of the PAH solution determines how many of the remaining acid groups contained within the PAA loops become ionized. As pH increases, more of the PAA loop segments become charged and more PAH is needed to neutralize this charge. The net result is an increase in the PAH layer thickness with increasing pH until the PAA chains become fully charged at about pH 6.5.

The above simple explanation works in the pH range of 2.5−4.5 but fails to explain the results obtained at higher pH. As indicated earlier, we know that the conformational state of a polyelectrolyte multilayer surface can dramatically influence layer thickness. It appears that this effect becomes important when the dipping solution pH is increased above pH 4.5. Apparently, above a pH of 4.5, the conformational arrangement of the PAH layer forces the PAA chains to adopt a more loopy conformation and hence produce a thicker layer. It is interesting to note that, in both deposition strategies, i.e., PAA and PAH at the same pH (the diagonal) and constant PAA pH/varying PAH pH, the transition to thicker PAA layers occurs after the PAH layer thickness reaches about 45 Å (at pH 4.5). This suggests that a critical density and size of loops are needed to trigger this effect.
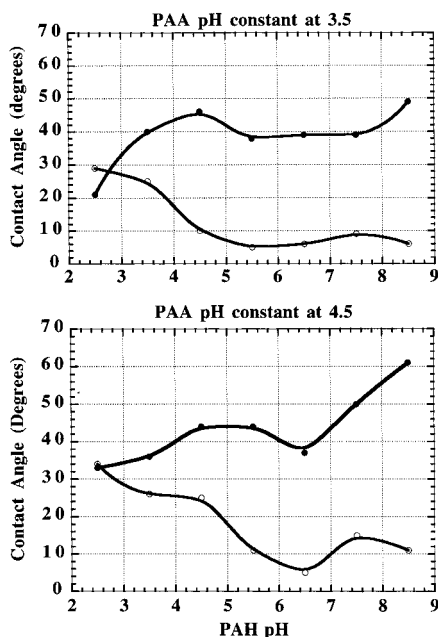
Figure 6. Advancing water contact angles measured on PAH/PAA multilayers fabricated with the PAA solution pH set at 3.5 or 4.5 and varying PAH solution pH. Solid circles represent PAH outermost layer films and the open circles represent PAA outermost layer films.

Figure 7. Methylene blue absorbance measured from PAH/PAA multilayers fabricated with the PAA solution pH set at 3.5 or 4.5 and varying PAH solution pH. Solid circles represent PAH outermost layer films, and the open circles represent PAA outermost layer films.

Figure 6 shows water droplet advancing contact angles measured on the series of multilayer films fabricated with the PAA pH at 3.5 and 4.5. In both cases, the contact angle measured on films with PAH as the outermost layer increases to a value greater than 40° as the pH of the PAH dipping solution increases from 2.5 to 5.0. Thereafter, the contact angle remains at about 40° and then increases to a higher value at the highest pH levels. The contact angle measured on films with PAA as the outermost layer, on the other hand, decreases to a value of 10° or less with increasing PAH pH and essentially remains at this low angle up to pH 8.5.

The observation that, above a PAH pH of about 5.0, the contact angle measured on PAH and PAA outermost layer films is ca. 40 and 10°, respectively, indicates that the surface layers of these films are dominated by segments of the outermost layer. This is in contrast to multilayer films fabricated along the diagonal where it was found that the contact angles measured from films made at pH 5.5 and higher were about 25° regardless of what layer was on top. Thus, these latter films have surfaces comprised of well-mixed PAH and PAA segments whereas the surfaces of films made at constant PAA pH are enriched in segments from the outermost layer (above pH 5.0).

Figure 7 displays the results of methylene blue surface staining experiments for films made at constant PAA pH. These data show that when PAA is the outermost layer, a large amount of methylene blue is adsorbed over the pH range of 2.5−7.5. In addition, on average, more methylene blue is adsorbed onto the PAA layers deposited at pH 3.5 than at 4.5. Over the pH range 2.5−6.5, the average methylene blue absorbance is about 0.19 for the PAA pH 3.5 films and about 0.13 for the PAA pH 4.5 films. At higher pH, the amount of methylene blue adsorbed drops to lower values. At these very high pH levels, this simple surface staining technique becomes more difficult to interpret due to the fact
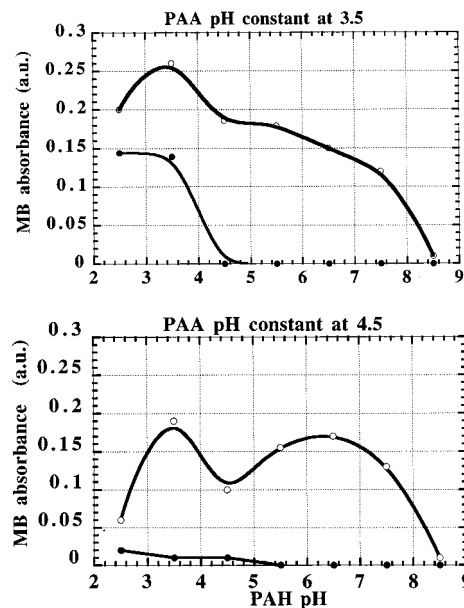
that the ammonium groups of PAH are losing protons. The reason for this decrease is currently not understood. When PAH is the outermost layer, methylene blue adsorption occurs over the pH range 2.5−4.5 (much less in the PAA 4.5 case than in the PAA 3.5 case) but then decreases to undetectable levels above a PAH pH of 5.0.

In combination, the contact angle and methylene blue staining data indicate that, in the pH range of 2.5−4.5, the surfaces of the multilayer films are comprised of both PAH and PAA segments; the extent of this mixing being determined by the specific PAH/PAA solution pH's (see ref 3). Above a pH of about 5.0, the thickness of the PAH and PAA layers increases to the extent that the surfaces are now dominated by segments of the outermost polymer layer. When PAA is the outermost layer, the surface contains a large number of free carboxylic acid groups (vide methylene blue data), the specific amount increasing with decreasing PAA solution pH. At a PAA pH of 2.5, for example, the measured amount of methylene blue absorbance is about 0.45. When PAH is the outermost layer, these acid groups become ionized during PAH deposition and form ion pairs with the cationic groups of PAH. The net result being that no acid groups are available for methylene blue adsorption.

It should be noted that the observation of thick, predominately PAA and PAH surface layers does not prove that the multilayer films fabricated under these conditions are comprised of noninterpenetrated layers. It simply means that the surface layers are enriched in segments from the outermost layer. Once the next layer is deposited, it can and will interpenetrate into the previously adsorbed layer.

Deposition at a Constant PAH pH. The layer thickness data obtained when the PAH solution pH was held constant at 2.5 and the PAA solution pH was varied are found in Figure 8. The thickness trends observed in the pH range 2.5−4.5 are as previously discussed. Above a pH of 4.5, we basically find that the deposition process stops after only a few layers have been adsorbed
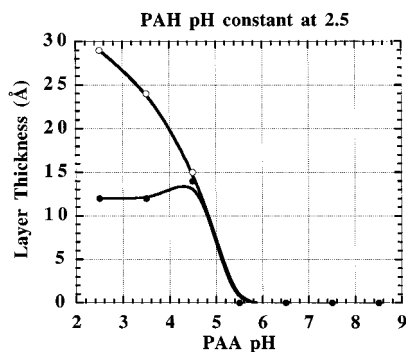
Figure 8. Average incremental thickness contributed by a PAA and PAH adsorbed layer as function of solution pH. In this case, the PAH dipping solution was at pH 2.5 and the pH of the PAA dipping solution was varied. Solid circles represent the PAH layer thickness, and the open circles represent the PAA layer thickness.

onto the surface. Similar results are obtained when the PAH pH is held constant at pH 4.5 (in this case no deposition occurs above a PAA solution pH of 5.5). Above a pH of 5.0, the PAA layer is adsorbed as a highly charged chain. The pH is then dropped to a lower value when the PAH layer is deposited. Under these conditions, the negative surface charge of the PAA layer is decreased to the point that the surface takes on a net positive charge from the previously adsorbed PAH layer. Since a positively charged PAH chain is attempting to adsorb onto a positively charged surface, the sequential adsorption process stops.

To confirm this explanation, the following experiment was carried out. A (PAH/PAA/SPS)$_x$ trilayer system was sequentially deposited with the SPS solution at pH 4.5, the PAA solution at a pH of 6.5, and the PAH solution at a pH of 4.5. Both SPS and PAH are adsorbing as fully charged polyelectrolytes in this experiment. Note also that the deposition procedure involves the sequential adsorption of a negatively charged SPS layer and a negatively charged PAA layer. Under these deposition conditions, multilayer thin films were fabricated containing up to 60 layers with an average thickness per layer of about 2−3 Å. The fact that a negatively charged SPS chain is able to adsorb onto the PAA layer at a pH of 4.5 and thereby facilitate the multilayer deposition process indicates that the PAA layer at this pH is in fact carrying a net positive charge. The very low layer thicknesses observed in this experiment indicate that some polymer desorption may be taking place.

Conclusions

The layer-by-layer processing of weak polyelectrolytes into multilayer thin films is highly sensitive to the pH of the polyion dipping solutions. Using two typical weak polyelectrolytes, PAA and PAH, it has been demonstrated that dramatic changes in the thickness of a sequentially adsorbed polyelectrolyte layer can be realized with very small changes in solution pH. Using this approach, it possible to (1) systematically vary the thickness of an adsorbed polymer layer over the range of approximately 5−80 Å, (2) control the bulk and surface composition of the multilayer film, and (3) control the number of nonionized carboxylic acid groups contained within the film and on its surface. To date, we have utilized our understanding of this new polyelectrolyte molecular-level blending approach to enhance the performance of thin film light emitting devices,[13] to synthesize inorganic nanoparticles within mutlilayers,[14] and to create microporous multilayer thin films.[15] Thus, in addition to providing an understanding of the factors that govern the adsorption of polyelectrolytes onto oppositely charged surfaces, the exploration of multilayers based on weak polyelectrolytes has already opened up new technological possibilities.

References and Notes

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