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Controlling Bilayer Composition and Surface Wettability of Sequentially Adsorbed Multilayers of Weak Polyelectrolytes

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ABSTRACT: Variations in the linear charge density of a weak polyacid brought about by controlling solution pH in a layer-by-layer sequential adsorption process were used to systematically control the layer thickness, level of layer interpenetration, and surface wettability of sequentially adsorbed layers of poly(acrylic acid) (PAA) and poly(allylamine) (PAH). The thickness contributed by an individual polyion layer was found to depend primarily on the pH of the polymer's dipping solution and, within the pH range examined, was not influenced by the thickness or level of interpenetration of the previously adsorbed layer. Contact angle and methylene blue adsorption measurements revealed that the deposited layers are typically highly interpenetrated and that the deposition process is a surface charge dominated adsorption process. Using this simple molecular-level blending approach, it is possible to create surfaces with advancing water contact angles that vary from essentially zero (completely wettable surfaces) to as high as 50°, all using the same simple polycation/polyanion combination.

Introduction

The processing of polyelectrolytes into thin films one molecular layer at a time has now been clearly established as one of the most versatile means available to control structure and properties at the nanoscale level.[1] In a typical process, oppositely charged polymers are alternately adsorbed onto a substrate from dilute aqueous solutions to produce multilayer thin films comprised of sequentially adsorbed layers of polycations and polyanions. This approach has the advantages that it is environmentally sound (all water based processing), is readily amenable to automation and integration with current technologies, and can be easily used to fabricate complex multilayer heterostructures with excellent control over molecular architecture. Over the past few years, it has been demonstrated that the sequential adsorption approach can be used to manipulate many different types of materials including conducting polymers,[2−4] light emitting polymers,[5−8] molecular dyes,[9−12] fullerenes,[13,14] precursor polymers,[5,15] nonlinear optical polymers,[16,17] biomaterials,[18−21] and various inorganic systems.[22−26]

A basic understanding of some of the fundamental issues that need to be considered in order to control the structure, molecular organization, thickness, and properties of the multilayer thin films that are produced via this process is now starting to slowly emerge.[1,27,28] To date, most of this fundamental work has been carried out with fully charged polyelectrolytes such as poly(styrenesulfonate) and poly(allylamine). The primary means evaluated for controlling molecular organization with these polymers has been adjustment of the ionic strength of the dipping solutions. Through ionic strength adjustments, it has been clearly demonstrated that the thickness of the adsorbed layers can be fine-tuned at the molecular level.[29] This approach, however, is limited to a certain extent by the poor solubility of high molecular weight polyelectrolytes in solutions of high ionic strength (adding salt makes water a poorer solvent for polyelectrolytes). The net result is that ionic strength adjustments, although clearly an important processing parameter, provide a relatively narrow window of opportunity regarding the control over bilayer thickness and composition. To overcome this limitation and to provide a higher level of versatility in the layer-by-layer sequential adsorption process, we have been exploring the use of weak polyelectrolytes. The organization and thickness of sequentially adsorbed layers of weak polyelectrolytes are extremely sensitive to dipping solution pH, primarily due to the fact that the linear charge density of a weak polyelectrolyte can vary considerably with change in pH when operating near the pK_a of the polymer. With weak polyelectrolytes such as poly(acrylic acid), it is therefore possible to systematically vary the linear charge density of the polymer via simple adjustments of dipping solution pH (controls the degree of functional group ionization). This means that it is possible to controllably alter the charge of the polyacid both during its adsorption onto a polycation layer and after it has been deposited and is adsorbing a polycation layer. This provides a rich but complex parameter space within which molecular organization can be manipulated.

In this paper, we explore in detail the role that processing parameters play in determining the organization, layer thickness, and surface properties of multilayer thin films fabricated from bilayers of the weak polyacid poly(acrylic acid) and poly(allylamine). Specifically, important issues such as determining and controlling the level of interlayer interpenetration and the polyanion/polycation composition and thickness of both the internal bilayers and the outermost surface layer will be discussed. In addition, it will be demonstrated that control of this type makes it possible to systematically alter the wettability of surfaces. Our group[30] and McCarthy's[31] have previously shown that the surface wettability of sequentially adsorbed polyelectrolyte lay-

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ers is controlled primarily by the outermost surface layer. Thus, by simply changing the nature of the outermost layer, is it possible to create surfaces with molecularly tunable wetting characteristics. As will be demonstrated in this paper, this can be accomplished via the use of surface layers with different chemical structures or by controlling the surface composition of a single bilayer combination. The latter case represents a new type of molecular level blending process achieved simply by controlling the charge densities of polyelectrolytes in a layer-by-layer adsorption process.

Experimental Section

Materials. poly(methacrylic acid) (sodium salt, MW = 15 000) (PMA), poly(acrylic acid) (MW = 90 000) (PAA), and poly(styrene-4-sulfonate) (MW = 75 000) (SPS) were obtained from Polysciences. Poly(allylamine hydrochloride) (MW = 55 000) (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. Polyaniline (PAN) was manipulated into aqueous solutions as previously described.[4]

Dipping Procedures. The layer-by-layer deposition technique involves the repeated sequential dipping of a substrate into dilute polycation and polyanion solutions with rinsing between each deposition step. Hand dipping procedure. In this case, substrates were dipped in a polyelectrolyte solution for 15 min and subsequently rinsed with pure water that was adjusted to be the same pH as the polyelectrolyte dipping solution. After each deposition and rinsing, the samples were blown dry with a flow of compressed, filtered air. Substrates were then dipped in the oppositely charged solution for an equal amount of time followed by the same rinsing and drying procedures. The deposition was performed at room temperature. Automatic dipping procedure: In this case, the layer-by-layer deposition process was carried out via the use of an automatic dipping machine in the form of a programmable slide stainer (HMS programmable slide stainer from Zeiss Inc.). This dipping machine can be programmed to immerse substrates into a series of up to 20 different solutions. The substrates were dipped into a polyelectrolyte solution followed by three agitated rinses in three separate bins of pH neutral water (pH of 5.5−6.5). The substrates were then dipped into the oppositely charged polyelectrolyte solution followed by the same rinsing procedure. The dipping time in the polyion and water rinse solutions was 15 and 2 min, respectively (the final water rinse was for only 1 min). No drying step was used in the automatic dipping procedure.

Contact Angle Measurement. An Advanced Surface Technology (AST) video contact angle measuring device was used to measure the contact angle of water on films. The contact angles presented in this paper are advancing contact angles which were measured with the standard sessile drop technique. A water drop was made on the tip of a syringe and placed on a sample by moving the substrate vertically until contact was made between the water drop and the sample. The subsequent addition of a small amount of water to the water drop on the surface produced the static advancing angle with the surface in a few seconds. An image of the droplet was taken though a CCD camera and enlarged. The right and left contact angles of the droplet were then measured by using an enlarged image transmitted to a computer screen. The volume of the water droplets was maintained constant at 1 μL. Before measurement of the contact angle, the samples were dried at 90 °C for 1 h and stored in ambient air for 1 day. When the contact angles of consecutively deposited layers were measured, 12 separate samples were prepared where the total number of layers per sample varied from 1 to 12. Four separate locations (two measurements each) on each sample were measured to ensure a representative value of the contact angle. The average value of the measured contact angles was used to represent the wetting characteristics of the sample.

Thickness Measurements. Multilayer films were built up on silicon wafers and cleaned glass slide substrates. The films on the silicon wafers were used to measure the total thickness of the films via ellipsometry. Films on glass slides were scratched with a razor blade to form lines. By profiling the scored line, the depth of the line was measured. An average value of five measurements was chosen to represent the thickness of the film. A Sloan Dektak 8000 profilometer was used and the stylus was set to a pressure of 10 mg to minimize error and noise. The profilometer was used to measure films of 200 Å and thicker. Incremental thickness measurements were made on a Geartner ellipsometer operating at a wavelength of 633 nm. Films with 20−26 deposited layers were used for this work. All samples were dried at 90 °C for 1 h and stored in ambient air for 1 day prior to measurement.

Methylene Blue Studies. The amount of methylene blue absorption was determined by UV/vis spectroscopy (absorbance values represent a contribution from films on both sides of the substrate). PAH/PAA films with different numbers of layers were immersed in 10^{-3} M, pH 7.0 methylene blue solutions for 10 min. After immersion in the dye solution, the multilayer films were soaked in water (pH = 7.0) for 1 min and dried with a mild air flow. Measurements of the amount of methylene blue adsorbed as a function of film thickness indicate that methylene blue adsorption is, for the most part, confined to the outermost surface layer with only a limited diffusion of the dye deeper into the bulk of the multilayer film (the amount of methylene blue adsorbed for a particular outermost layer film was found to be independent of the total number of layers deposited from 8 up to at least 24 layers). The amount of methylene blue adsorbed typically did not reach saturation until 6−8 layers were deposited (approximately 80% of the final value occurred by 6 layers). This reflects the fact that it takes about 3 bilayers to fully establish the bilayer organization and eliminate the influence of the substrate.

Results

Layer-by-Layer Surface Modification. The wettability of an insoluble polymer film as measured by an advancing water contact angle is determined, in most cases, by the first 5−10 Å of the polymer's outermost surface.[32−34] This fact suggests that sequentially adsorbed polyelectrolyte layers can be used to systematically alter and control the wettability of any substrate surface by simply changing the nature of the polymer adsorbed as the outermost layer. The change in wettability that occurs as the outermost layer is changed will depend on a number of factors including the chemical composition of the adsorbed polymer, the hydrophilicity of its functional groups, and the level of interpenetration of the outermost layer by segments of the previously adsorbed polymer layer. Thus, by monitoring the changes that occur in wettability during the layer-by-layer processing of different polymers, it is possible to establish the basic understanding needed to controllably alter surface wettability in this manner as well as to gain fundamentally important information about the level of interlayer interpenetration present in sequentially adsorbed polyelectrolyte layers.

To explore the influence that the outermost polymer layer has on water wettability, sequentially adsorbed layers of various polycations and polyanions were deposited onto hydrophilic glass microscope slides. The sequential adsorption process in all cases was begun by first depositing a polycationic layer of either polyaniline (PAN) or poly(allylamine hydrochloride) (PAH) onto the surface. Various polyanions were then adsorbed as an outermost layer to modify surface properties. The structures of the polycations and polyanions used in this study are shown in Figure 1. The surface wettability of these single bilayer combinations was determined by measuring the advancing contact angle of water drops on the surface. The advancing water contact angle of the uncoated hydrophilic glass slide was determined to be 10° ± 2°.

The data in Table 1 show that the advancing water contact angle changes dramatically when the outermost polyanionic

Table 1. Contact Angles of Single Bilayer Films on Glass with the Polyanion as the Outermost Layer

bilayer combinations	contact angle, (deg)
PAH as Cationic Layer	
1. PAH/poly(acrylic acid) pH 2.5, autodipping	<5
2. PAH/poly(acrylic acid) pH 2.5, hand-dipping	18 ± 5
3. PAH/poly(methacrylic acid) pH 2.5, autodipping	11 ± 2
4. PAH/poly(methacrylic acid) pH 2.5, hand-dipping	20 ± 4
5. PAH/poly(3-thiophene acetic acid) pH 4.3	50 ± 3
6. PAH/poly(styrene sulfonate) pH 2.5	55 ± 2
7. PAH/PMDA-ODA (unconverted) pH 3.8	37 ± 6
8. PAH/PMDA-ODA (converted) pH 3.8	72 ± 3
PAN as Cationic Layer	
1. PAN/poly(methacrylic acid) pH 2.5, hand-dipping	23 ± 3
2. PAN/poly(vinyl pyrrolidone)[a] pH 5.3	34 ± 3
3. PAN/poly(vinyl alcohol)[a] pH 5.3	35 ± 3
4. PAN/poly(3-thiophene acetic acid) pH 4.3	51 ± 2
5. PAN/poly(sulfonate styrene) pH 2.5	51 ± 2
polyaniline (PAN) solution	concn 10^{-3} M, pH 2.5
poly(allylamine) (PAH) solution	concn 10^{-2} M, pH 2.5
polyanion solutions	concn 10^{-2} M (pH indicated in table)

[a] See ref 16 for information on the sequential adsorption of the hydrogen bonding polymers with PAN.

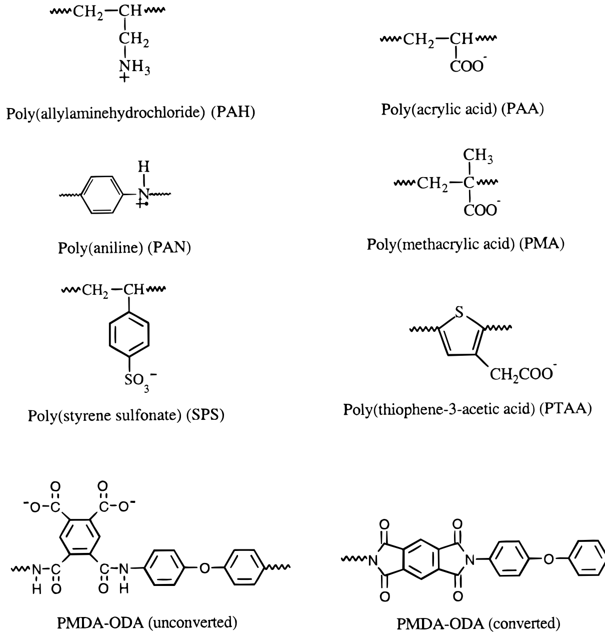

Figure 1. Structures of the polycations and polyanions described in this paper (counterions are not shown).

layer is changed. Using these simple single bilayer combinations, it is possible to systematically vary the surface from a completely wettable surface ($\theta < 5°$) to a hydrophobic surface ($\theta = 72°$). The most wettable surfaces ($\theta < 20°$) are created when the outermost layer is an aliphatic polyacid such as poly(acrylic acid), whereas aromatic polyacids such poly(styrene sulfonate) and poly(thiophene acetic acid) produce contact angles in the 50−60° range. The most hydrophobic surfaces ($\theta > 70°$) are created by converting the outermost polyelectrolyte layer into a noncharged macromolecule as in the case of the thermal imidization of the polyamic acid form of PMDA-ODA to its fully imidized form. In fact, if a precursor polycation such as the polycationic precursor to poly(*p*-phenylenevinylene) and polyamic acid are used to construct the bilayer, it is possible to create surfaces with water contact angles close to 100°.[15] Also note that these general trends are essentially independent of the nature of polycationic base layer as indicated by the fact that similar results are obtained when polyaniline is used as the polycation as opposed to poly(allylamine). However, as will become apparent when issues of layer interpenetration are discussed, this result may be quite fortuitous. The results in Table 1 also show that significant differences in surface wettability can be observed when hand-dipping versus autodipping methods are used. This suggests that the drying step and different pH adjustments of the rinsing baths used in the hand-dipping process (pH 2.5 versus 6.0) creates a surface layer that is different from that obtained in the all-wet, autodipping process.

It should be noted that the completely wettable surfaces created via the use the PAH/PAA bilayer combination ($\theta < 5°$) exhibit the very useful property of being antifogging. Thus, it is possible to create antifogging mirrors, eyeglasses, etc., by simply adsorbing a few bilayers of this system onto a surface with PAA as the outermost layer. The stability of this effect is also quite good. For example, the stability of these completely wettable surfaces was monitored as a function of time in laboratory air and in a 90 °C oven (in this case, 1 and 3 bilayers were deposited on both hydrophilic and hydrophobic glass substrates). The PAH/PAA layers retained their high level of wettability at room temperature for more than 1 month and only slowly started to lose some of their hydrophilic character after 2 months (still <10°). At a temperature of 90 °C, samples retained their hydrophilicity ($\theta < 5°$) for more than 1 week. Compared with modified polymer surfaces created via more conventional techniques, the layer-by-layer deposited films show excellent stability. Plasma-treated polymer surfaces, for example, often lose their hydrophilic nature after a few days due to a reorganization of the functional groups created on the polymer surface.[33,34]

These results clearly show that only a single bilayer of these sequentially adsorbed polyelectrolytes is needed to effectively modify the surface properties of a noncharged, hydrophilic substrate and that the surface properties can be systematically controlled by simply changing the nature of the outermost layer. It should also be noted that we have found that similar results are obtained with glass slides that have been chemically treated to render their surfaces hydrophobic ($\theta = 70°$). For example, a single bilayer of autodipped PAH/PAA (same conditions as in Table 1) was also found to produce a completely wettable surface ($\theta < 5°$) when deposited onto the more hydrophobic surface. Thus, under conditions that produce uniform, high quality adsorbed bilayers, the surface wettability only depends on the nature of the outermost polymer layer and not on the starting substrate. This is quite amazing considering that the thicknesses of these adsorbed bilayers are typically in the range of only 10−50 Å.

To determine how surface wettability changes in a layer-by-layer manner, samples having from 1 to 12 layers of the PAH/PAA bilayer combination were builtup and the wettability measured. In this case, samples with an odd number of layers have PAH as the outermost layer, whereas samples with an even number of layers have PAA as the outermost layer. Figure 2 displays the results of films fabricated with both the PAH and PAA dipping solutions at a pH of 2.5 (polymer

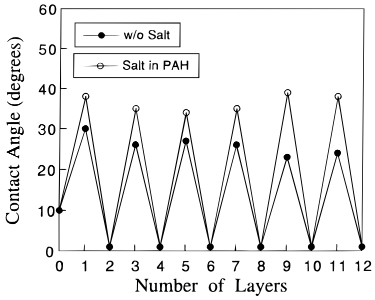

Figure 2. Contact angles measured from films containing a different number of adsorbed layers of PAH/PAA. Even numbers represent films with PAA as the outermost layer whereas odd number films have PAH as the outermost layer.

concentration: 10^{-2} M) with and without 0.4 M of $MgCl_2$ added to the PAH solution. This figure shows that the contact angle systematically and reproducibly alternates from a value less than 5° to a value of around 28° as the outermost layer is changed from PAA to PAH (no salt added). This oscillation in the contact angle continues to the same degree up to at least 12 layers. These results further support the notion that under suitable conditions, the outermost adsorbed layer distinctly influences the wettability of the surface and that it takes only one bilayer to achieve the surface modification provided by the bilayer. Note, however, that the very first layer of adsorbed PAH gives rise to a contact angle that is slightly higher than that measured from PAH outermost layer films with more than one PAH/PAA bilayer (no salt case). Thus, it takes one complete bilayer to firmly establish the contact angle oscillation. This first layer effect reflects the different deposition characteristics expected when PAH is deposited directly onto the hydrophilic glass substrate and, perhaps more importantly, the fact that it is not influenced by the presence of an underlying adsorbed layer of PAA. When $MgCl_2$ is added to the PAH solution, the oscillation in the contact angle is observed to be even more dramatic; films with PAH as the outermost layer in this case exhibit a contact angle of about 36°.

It is clear from the above results that the surface wettability of sequentially adsorbed polyelectrolyte layers is sensitive to a number of processing factors including the type of dipping process used and the addition of salt to a dipping solution. This, in turn, reflects that fact that important parameters such as the thickness and conformation of an adsorbed layer and its level of interpenetration with neighboring layers can vary dramatically when changes are made in processing conditions. Thus, it is important to understand how variations in solution conditions influence layer thickness and interpenetration. To accomplish this goal, we have carried out detailed studies on the PAH/PAA bilayer system with a particular emphasis on the role that solution pH plays in determining layer thickness and organization. Since PAA (pK_a about 4.5) and PAH (pK_a about 10) are weak polyelectrolytes with a level of functional group ionization that is highly sensitive to pH, this bilayer combination provides a rich parameter space within which to explore variations in processing conditions.

Detailed Studies of the PAH/PAA Bilayer Combination. The automatic dipping method was used to build up a number of PAH/PAA layers on hydrophilic glass slides. The pH of the PAH and PAA dipping solutions was systematically varied from 2.5 to 4.5 in order to determine how dipping solution pH influences layer thickness and organization. Layer thicknesses were measured primarily by profilometry but were confirmed through the use of ellipsometric measurements made on films deposited onto silicon wafers (in all cases, profilometry and ellipsometry gave thickness values that were within a 5−15% error of each other).

Figure 3 displays the thickness versus number of deposited layers curves for some representative pH combinations. Also included in this figure are data generated from a bilayer combination in which 0.4 M of $MgCl_2$ was added to the PAH solution. In all cases examined, we have found that the layer-by-layer deposition process proceeds in a linear and reproducible manner up to at least 30 bilayers. The only exception to this trend was the PAH (pH 4.5) and PAA (pH 2.5) combination in which the film growth turned nonlinear after 10 deposited bilayers and the films became slightly cloudy. From the slopes of curves of this type it can be determined that the average thickness deposited per bilayer can be varied from about 30 Å to more than 70 Å by independently varying the pH of the PAH and PAA dipping solutions over the indicated 2.5−4.5 pH range. It is interesting to note that linear and reproducible layer-by-layer deposition can be achieved even under conditions that the PAA chains have a very low degree of functional group ionization (at pH 2.5, the degree of carboxylic acid group ionization of PAA in solution is estimated to be less than 0.1%[35]). As expected, the thickness of the PAH/PAA bilayer building block is highly sensitive to solution pH.

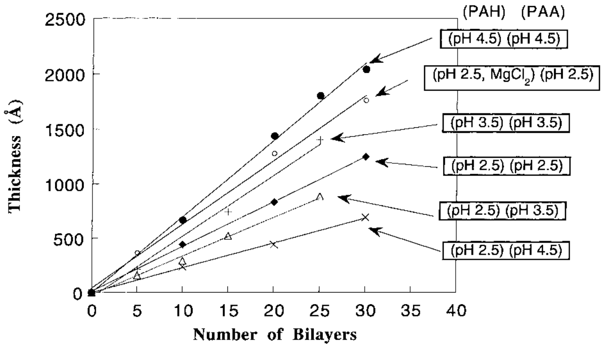

Figure 3. Thickness versus number of deposited bilayer plots of PAH/PAA films deposited from solutions with different pH adjustments. All solution concentrations were 10^{-2} M.

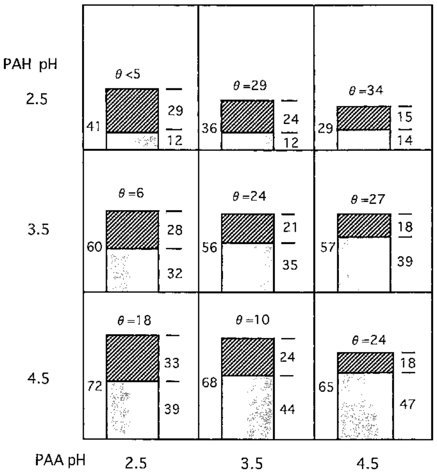

Figure 4. Average incremental thickness contributions of PAH/PAA layers deposited from solutions with different pH adjustments. Static water contact angles (θ) from films with PAA as the outermost layer (8 layer films) are also shown. The dark regions represent the PAA thickness contribution to the bilayer; the light regions PAH. All thickness values are in angstrom units.

To better understand the influence that solution pH has on bilayer thickness, measurements of the contribution that each individual layer makes to the thickness of the bilayer were made. This was accomplished via ellipsometric measurements made on films deposited onto silicon wafers. Figure 4 shows the results obtained from these measurements. The thicknesses reported in this figure represent the average incremental increase in thickness that occurs when an individual layer of either PAH or PAA is adsorbed onto a multilayer film and the film is dried (see Experimental Section for details) to remove excess water (all values are ±2−4 Å). The bilayer thickness obtained by adding these two values (PAH+PAA incremental layer thickness) is essentially the same as that obtained from the slopes of the curves shown in Figure 3 (within an error of 5−10%). Also included in Figure 4 are the contact angles measured on 8 layer films with PAA as the outermost layer.

A number of very interesting observations can be made from the data presented in Figure 4. First, it can be seen that the thickness contribution of both the PAA and the PAH layer systematically changes in a very specific manner as the pH of the PAA and PAH dipping solutions is varied from 2.5 to 4.5. In the case of PAA, the adsorbed layer thickness decreases from about 30 Å to about 17 Å as the pH of the PAA dipping solution increases from 2.5 to 4.5. The layer thickness contributed by PAH, on the other hand, increases from about 12 Å to about 43 Å as the pH of the PAH dipping solution increases from 2.5 to 4.5. Second, the thickness contributed by each individual layer is, within experimental error, independent of the thickness of the previously adsorbed layer and only depends on the pH of the dipping solution. Note, for example, that the PAA layer thickness contribution is 30 ± 3 Å when the PAA dipping solution is at pH 2.5, 22 ± 2 Å when the PAA dipping solution is at pH 3.5, and 16 ± 2 Å when the PAA dipping solution is at pH 4.5, all regardless of the thickness contributed by the previously adsorbed PAH layer (which varies from about 12 to about 43 Å with increasing solution pH). The PAH layer thickness contribution, on the other hand, remains essentially constant at 13 ± 2 Å when the pH of the PAH solution is 2.5, 35 ± 4 Å at pH 3.5, and 43 ± 4 Å when it is 4.5, again regardless of the thickness contribution of the previously adsorbed PAA layer (there appears to be a slight increase in the thickness of the PAH layer at a constant pH with increasing PAA pH). Thus, the thickness contributed by both the polycation layer and the polyanion layer depends essentially only on the pH of the PAH and PAA dipping solutions and not on the thickness of the previously adsorbed layer. This is a most remarkable observation as it suggests that the thickness contributed by a sequentially adsorbed layer is determined solely by the relative charge densities of the adsorbing and previously adsorbed polyelectrolyte and not by the segmental distribution of loops, tails, and trains of the previously adsorbed polymer chain. This phenomena will be discussed in greater detail at the end of this paper.

It should be pointed out that the simple illustrations in Figure 4 are somewhat misleading as they suggest that the bilayer is comprised of discrete polyanion and polycation layers. As will become apparent shortly, a high level of layer interpenetration clearly occurs in these systems. The data shown in Figure 4 simply show the overall increase in thickness that is observed when an individual layer is adsorbed onto a multilayer thin film and dried. Nevertheless, they clearly illustrate that the amount of polycation and polyanion adsorbed onto an oppositely charged surface can be readily controlled via suitable adjustments in dipping solution pH.

As mentioned earlier, information about the level of layer interpenetration can be obtained through measurements of advancing contact angles. Since the advancing contact angle of a water droplet is very sensitive to the composition of the surface layer, it is possible to determine if segments of the previously adsorbed layer have penetrated into the surface of the outermost adsorbed layer. The PAA outermost layer contact angles (eighth deposited layer) presented in Figure 4 show that the surface wettability of these various bilayer compositions is highly sensitive to the relative layer thicknesses of the polycation and polyanion with contact angles varying from values as high as 34° to values less than 5°. The lowest contact angle ($\theta < 5°$) occurs when the PAA layer thickness is large compared to the PAH layer thickness (PAH pH 2.5/PAA pH 2.5). In this case, the surface properties of the film are determined exclusively by the more hydrophilic PAA outermost layer (thick films of pure PAA exhibit completely wettable surfaces prior to dissolution). In general, as the PAA layer thickness decreases (increasing PAA solution pH), or the thickness of the previously adsorbed PAH layer increases (increasing PAH solution pH), the contact angle increases, suggesting that segments of the underlying PAH layer are now able to influence the surface properties. Note, for example, that even when the PAA layer thickness is held constant at its thickest value of about 30 Å (PAA dipping solution pH 2.5), the contact angle increases from its completely wettable value of less than 5° to 18° as the thickness of the previously adsorbed PAH layer increases from 12 to 39 Å. The highest contact angle measured for a PAA outermost layer film ($\theta = 34°$) occurs when both layers are thin (PAH pH 2.5/PAA pH 4.5). This suggests that the PAA and PAH layers in this case are highly interpenetrated. As a reference, the contact angle of a thick film of pure PAH is in the range 50−55° (measured before film dissolution).

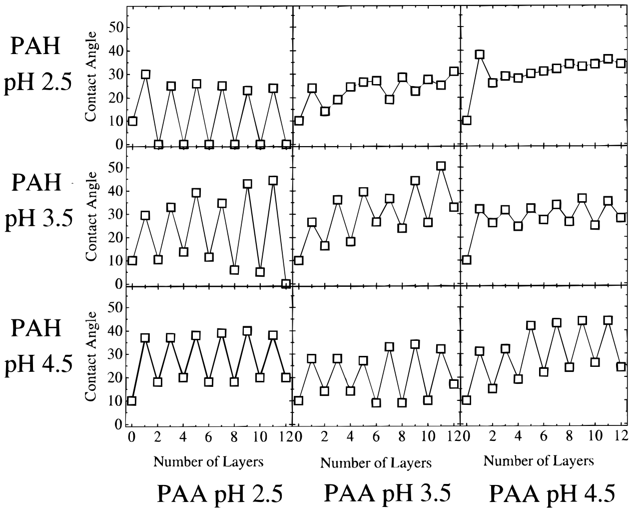

Figure 5. Contact angles measured from films containing a different number of adsorbed layers of PAH/PAA as a function of variations in the pH of the polyion dipping solutions. Even numbers represent films with PAA as the outermost layer whereas odd number films have PAH as the outermost layer.

It is clear that as the PAH layer thickness increases or the PAA layer thickness decreases, a larger fraction of PAH segments penetrate into the outermost PAA surface layer relative to what is observed with the PAH pH 2.5/PAA pH 2.5 combination. To examine if similar effects occur when PAH is the outermost layer and to see how these trends vary in a layer-by-layer manner, we measured contact angles for each bilayer composition on films containing from 1 to 12 layers. As before, samples with an odd number of layers have PAH as the outermost layer, whereas samples with an even number of layers have PAA as the outermost layer. The results of these measurements are found in Figure 5.

As indicated in Figure 5, most of these different bilayer compositions give rise to a distinct contact angle oscillation as the outermost layer changes from PAA to PAH etc. The largest contact angle oscillations are observed for the PAA pH 2.5 and PAH pH 2.5 and 3.5 combinations. The smallest oscillations, on the other hand, occur when the PAH and PAA layers are both very thin (PAH pH 2.5/PAA pH 3.5 and 4.5). In this case, no consistent difference is observed when PAH and PAA are interchanged as the outermost layer. This indicates the existence of a highly interpenetrated bilayer. Variations in the magnitude of these contact angle oscillations as well as specific outermost layer values reflect the different levels of layer interpenetration that occur as the bilayer composition is changed. As was seen in the PAA outermost layer case, the contact angle of films having PAH as the outermost layer is most characteristic of pure PAH when the PAH layer thickness is large compared to the PAA layer thickness (PAH pH 4.5/PAA pH 4.5; $\theta = 45°$). In this case, the contact angle measured when PAA is the outermost layer is as large as 26°, indicating that the PAA surface layer is interpenetrated by the underlying PAH layer. When the PAA layer is thick and the PAH layer thickness small (pH 2.5/2.5), the contact angle of the PAH outermost layer is about 25°, again suggesting that it is interpenetrated by the underlying PAA layer.

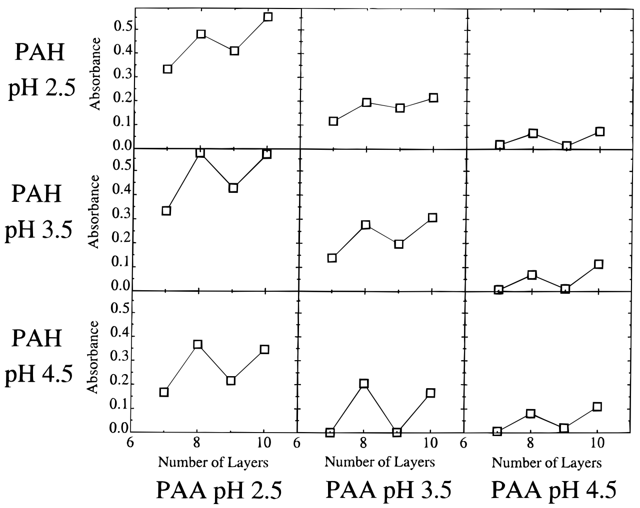

Figure 6. Methylene blue absorption (measured at 600 nm) of films containing a different number of adsorbed layers of PAH/PAA as a function of variations in the pH of the polyion dipping solutions. Even numbers represent films with PAA as the outermost layer whereas odd number films have PAH as the outermost layer.

In short, all of these bilayer combinations are interpenetrated to a certain extent. Typically, whenever a thin layer is deposited onto a thicker layer, a large number of chain segments from the underlying thicker layer penetrate into the surface layer. When the thicker layer is the outermost layer, the surface properties are dominated by the outermost layer, indicating that much fewer chain segments from the underlying thin layer penetrate into the surface of the thicker layer. As the thickness of the underlying thinner layer increases, more chain segments penetrate into the surface layer and the contact angle changes in response to this change in surface composition (consider, for example, the PAA pH 2.5 column). When both layers are thin, a high level of interpenetration within both the PAH and PAA surface layers is found. For intermediate thickness combinations, penetration of chain segments from the underlying layer occurs in both surface layers (PAH and PAA) with the amount of penetration being determined by the relative thicknesses of the two layers. Thus, by controlling the relative thicknesses of these sequentially adsorbed layers and the type of outermost layer, it is possible to systematically control the contact angle from a value less than 5° (a completely wettable surface) to as high as 50° using only this simple bilayer combination.

An important question to ask at this point is to what extent are the interpenetrated segments forming polycation/polyanion contact ion pairs? To address this question and to further explore the level of layer interpenetration in these films, we used a simple surface dying technique[36] to estimate the relative number of carboxylic acid groups available as binding sites on the surface. The procedure simply involved adsorbing a positively charged dye (methylene blue) onto the surface and measuring the amount of dye adsorbed via visible spectroscopy. The methylene blue dye was adsorbed at a fixed pH (pH 7.0) to ensure that the amount of dye adsorbed was not varying due to changes in the degree of ionization of the PAA chains (at this pH, the PAA chains are fully ionized). Similar trends were also revealed when the dye was adsorbed at a pH of 4.0, albeit with lower amounts of methylene blue adsorption for each sample (data not shown). Under the conditions utilized, no detectable amount of methylene blue was adsorbed onto the hydrophilic glass slides used to construct the multilayer films. The amount of methylene blue adsorbed was measured on films containing from 7 to 10 layers with the odd number of layers having PAH as the outermost layer and the even numbers having PAA as the outermost layer. The results of this study are present in Figure 6.

As was the case for most of the contact angle measurements, a clear oscillation in the data is evident as the outermost layer is changed from PAA to PAH via the sequential adsorption process. As expected, the larger amount of methylene blue adsorption occurs when the negatively charged PAA is the outermost layer, although it is clear that in many cases it is also possible to detect a significant amount of methylene blue adsorption onto the positively charged PAH layer. At this point, it will be assumed that the amount of methylene blue adsorbed onto a surface depends primarily on the number of available carboxylate groups not forming contact ion pairs with the cationic groups of PAH. The reason for this assumption will become apparent as the results are presented.

With the above assumption in mind, it can be seen first of all that the amount of methylene blue adsorbed onto a PAA or PAH outermost layer film systematically decreases as the pH of the PAA solution increases (moving across the rows of Figure 6). This indicates that the additional carboxylate groups created when the PAA solution pH is increased are not available as binding sites for methylene blue and are therefore predominately forming contact ion pairs with the cationic groups of the previously adsorbed PAH chains. This, in turn, shows that there is a strong tendency for all of the carboxylate groups created at a given pH to form partners with the cationic groups of the PAH chains during the adsorption of a PAA layer. The decreasing amount of methylene blue adsorption with increasing PAA solution pH therefore simply reflects the fact that there are fewer carboxylic acid groups available that can be ionized to free carboxylate groups during methylene blue adsorption. Consistent with this interpretation is the fact that essentially no methylene blue adsorption is detected when multilayer layer films are created with the pH of the PAA and PAH solutions set at values of 6.5 or higher (results to be published). In this pH range, the PAA chains are fully ionized during adsorption, thereby producing all polyanion−polycation contact ion pairs and leaving no free carboxylic acid/carboxylate groups available for methylene blue adsorption.

It is clear that the amount of methylene blue adsorbed onto a sequentially adsorbed film is directly related to the number of nonionized carboxylic acid groups remaining in an adsorbed surface layer. When PAA is the outermost layer, this value basically depends on the pH of the PAA dipping solution which, in combination with surface charge effects (influence the effective pK_a of the adsorbed PAA segments), determines the degree of ionization of the adsorbed PAA chains. A similar trend is found for PAH outermost layer films, however in this case, it can also be seen that the amount of methylene blue adsorbed depends on the ability of PAA segments to penetrate into the PAH surface layer. For example, the amount of methylene blue adsorbed is observed to decrease when the thickness of the PAH layer reaches its thickest value at a PAH pH of 4.5 for both the PAA pH 2.5 and 3.5 films (moving down the first two columns of Figure 6). In fact, for the PAH 4.5/PAA 3.5 film, no methylene blue is detected when PAH is the outermost layer. Methylene blue measurements therefore clearly indicate that, for the thinner PAH layers, a large fraction of carboxylic acid groups have penetrated into the PAH surface layer and are available as potential binding sites for methylene blue and that the level of PAA segmental penetration is less in the thickest PAH outermost layer films. For the PAA pH 4.5 column, the higher degree of ionization of the PAA chains and the concomitant formation of a larger fraction of PAH based contact ion pairs limits the amount of methylene blue adsorption that is possible. This means, however, that the thinner PAA surface layers created at this pH must be well penetrated by PAH segments. The high PAA outermost layer contact angles measured on these films (20−30°) are consistent with this conclusion.

As indicated earlier, the amount of methylene blue adsorption is determined primarily by the availability of free carboxylate groups within the surface layer, i.e., those not bound to ammonium groups of PAH (polycation/polyanion contact ion pairs). This, in turn, implies that, unlike PAH adsorption, the amount of methylene blue adsorbed is not determined by the net surface charge of a film. The validity of this assumption is further supported by the fact that there is no correlation found between the amount of PAH adsorbed and the amount

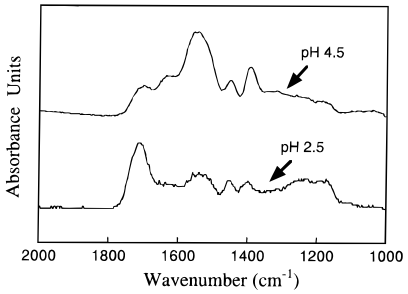

Figure 7. FTIR spectra of 5 bilayer films of PAH/PAA. Top spectrum: PAH/PAA solutions at a pH of 4.5. Bottom spectrum: PAH/PAA solutions at a pH of 2.5.

of cationic dye adsorbed onto a PAA layer. For example, films created with a constant PAH pH exhibit a significant decrease in the amount of methylene blue adsorption with increasing PAA pH (moving across the rows of Figure 6). The thickness of an adsorbed PAH layer at a constant PAH pH, however, remains essentially the same. Also note that the PAA pH 4.5 films all adsorb only a very small amount of methylene blue. This 18 Å thick surface layer of PAA, however, is capable of adsorbing a very large amount of PAH, ultimately producing a 47 Å thick PAH layer in the PAH pH 4.5 case and about a 40 Å thick layer in the PAH pH 3.5 case. These results all point to the fact that the amount of polycation adsorbed is determined essentially by the overall surface charge density of a film whereas the amount of dye adsorbed is determined primarily by the availability of suitable surface sites. It can therefore be concluded that the thickness of an adsorbed layer of PAH at a given pH depends primarily on the overall surface charge density and is not influenced to any great extent by the population of “free” versus PAH bound negative charges, which changes significantly, for example, across the bottom two rows of Figure 6.

Figure 7 shows infrared spectra (carbonyl region) of two 5 bilayer PAH/PAA films deposited onto ZnSe plates. The top spectrum was obtained from a film fabricated with a PAH and PAA dipping solution pH of 4.5, whereas the bottom spectrum was obtained from a film fabricated with the PAH and PAA solutions at a pH of 2.5. The films were rinsed with deionized water (pH 5.5) for 1 min before infrared measurements were made. The two carbonyl peaks of interest in these spectra are the carboxylic acid ($-$COOH) and carboxylate peaks ($-$COO$^-$) at 1700 and 1560 cm^{-1} respectively. For the sample made with the pH of both dipping solutions at 2.5, it can be seen that about 70% of the functional groups of PAA are still in the carboxylic acid form. When the pH of both dipping solutions is set at 4.5, about 70% of the functional groups exist in the ionized carboxylate form. As expected, the degree of ionization of the acid groups of PAA increases with increasing solution pH. If it is assumed that the brief water rinsing did not appreciably alter the degree of ionization, then it is possible to estimate that the effective surface pK_a of the PAA chains is around 4.0. The solution pK_a of PAA in the absence of added salt has been determined to be about 5.5 but can drop to about 4.5 when salt is added to the solution.[35,37] In addition, it has been noted in the literature[38] that at high surface charge densities (positive charge), the degree of ionization of a weak polyacid will increase to more effectively neutralize the surface charge. This would explain why the PAA chains in the multilayer films exhibit a higher degree of ionization (lower effective pK_a) than would be expected in the PAA solution and underscores the importance of surface charge effects in determining the degree of ionization of an adsorbed layer of PAA.

Discussion

The literature is replete with theoretical and experimental studies focusing on the single layer adsorption behavior of polyelectrolytes onto oppositely charged surfaces.[37−43] In the case of weak polyelectrolytes such as poly(acrylic acid), it is generally understood that the polymer chains tend to adsorb as thin layers with flat chain conformations when they are highly charged (high pH) and thicker, more loopy type structures when they are less charged (low pH). In addition, it has been established that the amount of polyelectrolyte adsorbed to a surface increases with increasing surface charge density since more material is needed to balance and overcompensate the higher charge density of the oppositely charged surface. Thus, as might be expected, the two most important parameters governing the adsorption of polyelectrolytes onto oppositely charged surfaces in the absence of added salt are the linear charge density of the adsorbing polymer chain and the surface charge density. This, in turn, provides an opportunity to systematically control the amount of polyelectrolyte adsorbed onto a surface and the resultant organization/conformation of the adsorbed chains. Since the degree of ionization of a weak polyelectrolyte can be controllably varied via pH changes, it is possible to systematically control both the linear charge density of an adsorbing polymer chain and the surface charge density. This type of control is particularly useful during a layer-by-layer sequential adsorption process as it provides a very powerful means to control bilayer composition, thickness, and organization. As demonstrated in this paper, the amount of polyacid adsorbed during deposition can be controlled by adjusting the pH of the polyacid solution, whereas the amount of polycation adsorbed during deposition can be independently controlled by adjusting the pH of the polycation solution. In the former case, the pH of the polyanion dipping solution determines the linear charge density of the polyacid and therefore the amount of polyacid adsorbed. In the latter case, the pH of the polycation solution determines the charge density of the previously adsorbed outermost polyacid layer. The amount of fully charged polycation adsorbed (in the pH range of this study, the PAH polycation is fully protonated) should therefore increase as the charge density of the previously adsorbed polyacid surface layer increases (increasing pH). Thus, by controlling the degree of ionization of the polyacid, both as an adsorbing layer and as a previously adsorbed layer, it is possible to systematically control the total bilayer thickness as well as the bilayer composition (amount of polyanion and polycation per bilayer). To our knowledge, this is the first time that bilayer thickness and composition have been systematically controlled through variations in the degree of ionization of a weak polyelectrolyte in a sequential adsorption process.

As indicated above, it has previously been established that the amount of weak polyacid adsorbed onto an oppositely charged surface increases as the linear charge density of the chain decreases with decreasing pH (decreasing degree of functional group ionization).[37,38,40] The increase in adsorbed amount with decreasing pH is believed to be due to a reduction in segmental repulsion effects and the concomitant formation of an adsorbed polymer layer with a larger fraction of chain segments in the form of loops and tails. For a fully charged polyelectrolyte such as PAH, it has been suggested that the amount of polymer adsorbed should increase linearly with increasing surface charge density.[37] Consistent with these expectations, over the pH range examined in this study (2.5−4.5), it has been found that the thickness of an adsorbed layer of PAA increases with decreasing pH and the thickness of an adsorbed layer of PAH increases with increasing pH. In both cases, these changes in incremental layer thickness with pH are approximately linear in nature. Recent calculations by Böhmer et al.[38] suggest that the degree of ionization of a surface layer of a weak polyacid with a pK_a similar to PAA on a highly charged surface varies in a near linear manner in the pH range of 2.5–4.5. Assuming this to be true in this case, the change in thickness observed with change in solution pH for both the PAH and PAA layers appears to be related directly to changes in the linear charge density of PAA, both as an adsorbing layer and as a previously adsorbed layer.

It should be noted that it has been theoretically predicted that a maximum in the amount of weak polyacid adsorbed onto an oppositely charged surface should occur about 1–1.5 pH units below pK_a.[38,41] Experimentally, it has been found that this maximum occurs at a pH of about 2.0 for PAA (lower than theoretically predicted) and that the amount of PAA adsorbed onto a positively charged latex increases in an approximately linear manner with decreasing pH over the pH range 2.5–4.5.[37] In our study, no maximum was observed in the amount of PAA adsorbed at low pH, although no attempt was made to sequentially adsorb PAA layers at a pH of less than 2.5. In any event, the results of this study with regard to the behavior of PAA are very consistent with those obtained from studies of PAA adsorption onto a highly charged cationic latex, i.e., a near linear increase in the amount adsorbed over the pH range 2.5–4.5.

It is clear that the pH dependent thickness behavior of the two sequentially adsorbed polyelectrolytes examined in this study is very similar to what has been observed in single-layer adsorption studies involving charged polymers adsorbing onto oppositely charged surfaces. Remarkably, however, it has been found that the changes in thickness that occur with changes in pH are essentially independent of the thickness of the previously adsorbed polymer layer. This observation, which could only be made easily using a sequential adsorption process, suggests that the thickness contributed by an adsorbed layer depends primarily on the relative charge densities of the adsorbing and previously adsorbed polymer. In other words, the thickness contribution of an adsorbed layer is not influenced to any great extent by the segmental distribution of loops, trains, and tails of a previously adsorbed layer nor by the number of "free" ionic binding sites capable of creating polymer contact ion pairs. The same thickness contribution is observed at a given dipping solution pH regardless of whether the previously adsorbed layer is very thin (presumably with a large fraction of train segments) or very thick (with a large fraction of loops and tails) and regardless of its level of interpenetration with the underlying layer.

Recently, Lowack and Helm[28] have suggested that the electrostatic barrier established by the like charges of an adsorbing polymer ultimately limits the adsorbed amount and determines the thickness of an adsorbed layer in a sequential adsorption process. They further suggested that the thickness of an adsorbed layer is therefore not determined by the number of available surface binding sites. Our results fully support their conclusions, at least in the pH range examined in this work (2.5–4.5). For example, the thickness contributed by a PAH layer at a given pH remains the same even though methylene blue adsorption measurements show that the number of free carboxylate binding sites changes significantly as the pH of the PAA dipping solution is increased from 2.5 to 4.5 (moving across the rows of Figure 6). Thus, it appears that the two critical parameters that control layer thickness are the linear charge densities of the previously adsorbed polymer (determines the net surface charge) and the adsorbing polymer. These parameters combined determine how much adsorbing polyelectrolyte is required to neutralize the surface charge and eventually establish the electrostatic barrier that inhibits further adsorption.

It should be pointed out that based on studies that we have made with PAA and other polycations containing visible chromophores,[44,45] we have found that the total amount of polymer adsorbed, as determined by optical spectroscopy, does, in some cases, depend on the thickness of the previously adsorbed layer, with higher adsorbed amounts typically being found with thicker layers. Thus, it is only the incremental layer thickness that is independent of the previously adsorbed layer thickness. During the adsorption step, segments from the adsorbing polymer penetrate into the previously adsorbed layer in an attempt to neutralize the surface charge via the formation of polymer–polymer contact ion pairs. The extent that all possible polymer-based contact ion pairs will be satisfied will be determined by a number of factors including the relative charge densities of the two polymers, the existence of previously established polymer contact ion pairs formed by interpenetration, kinetic effects, and conformational restrictions due to entanglements etc. The number of adsorbing segments penetrating into the previously adsorbed layer could therefore depend on the thickness and segmental distribution of loops, trains, and tails of the previously adsorbed layer. Thus, caution must be exercised when comparing the total amount of polymer adsorbed to the incremental layer thicknesses reported in this paper, as these values may vary in a different manner depending on the particular circumstances.

In the many different cases that we have used PAA as the polyanion and polycations other than PAH, the general pH dependent thickness trends described in this paper (increasing PAA thickness with decreasing pH and increasing polycation thickness with increasing pH) have always been observed in the pH range 2.5–4.5. In some of these other cases, however, we have found that the incremental thickness contributed by an adsorbed layer (particularly the polycationic layer) can be influenced to a certain extent by the thickness of the previously adsorbed layer. This may reflect the fact that the polycations used in these other studies typically have more complex repeat unit structures such as the cationic precursor to poly(*p*-phenylenevinylene),[45] which we use in a very high molecular weight form (10^6 g/mol) at low solution concentrations, and a new dicationic ruthenium(II) containing polyester.[44] For the PAH/PAA bilayer combination, however, we consistently and reproducibly find that the thickness contributed by an adsorbing layer in the pH range 2.5–4.5 depends only on the pH of the polymer's dipping solution.

The observation that the bilayer thickness as determined from the slope of a plot of thickness versus number of deposited bilayers is essentially the same as that determined by adding the incremental layer thicknesses (obtained from dried surface layers) indicates that the thickness contributed by an internal layer is essentially the same as that contributed by the same polymer as an outermost surface layer. In other words, the thickness established by an adsorbing layer either as a collapsed surface layer or an internal layer is essentially the same. This suggests that the conformation and organization of an adsorbed polymer layer (segmental distribution of trains, loops, and tails) ultimately determines its thickness regardless of whether it is an internal layer penetrated by segments from the surrounding layers or a collapsed surface layer. The adsorbed layer is therefore acting as a template with a thickness that is determined by the density distribution of its chain segments nearest to the surface. It is to be expected that the segmental density of an adsorbed layer would be the highest at the surface and decay to much lower values as one moves away from the surface. The more dense surface layer must therefore establish the final layer thickness, whereas any loops and tails that extend far from the surface, although important in influencing the spatial extent of segmental penetration into adjacent layers, play a lesser role in determining thickness.

Regarding the important issue of layer interpenetration, it is clear from this work that all of the sequentially adsorbed PAH/PAA bilayer compositions examined exhibit a high level of segmental interpenetration in at least one or both of the alternating layers. Contact angle and methylene blue adsorption measurements both show that, in all cases, a significant number of chain segments of the previously adsorbed layer penetrate into the outermost surface layer when either the polyanion or the polycation is the outermost layer or in both cases. This, in turn, means that the internal bilayers of multilayer films of this bilayer combination are quite interpenetrated. In those cases where a thick surface layer is deposited onto a much thinner (and highly interpenetrated) previously adsorbed layer, the contact angle is clearly dominated by the wettability characteristics of the outermost layer. This would suggest that a very low level of segmental penetration from the underlying layer is taking place. However, it must be kept in mind that the surface characteristics may not always reflect the true nature of the internal structure of a sequentially adsorbed multilayer thin film. After drying, the surface layer collapses into a more dense layer; i.e., the loops and tails that extend from the surface in the dipping solution collapse onto the surface when the water is removed. A thick surface layer deposited on top of a thin previously adsorbed layer would therefore produce a surface that is enriched in segments from the outermost adsorbed layer. This, by the way, is the ideal situation for producing surfaces with properties that are controlled primarily by the nature of the outermost layer such as the highly wettable surfaces described in this paper. During multilayer formation, however, the surface layer is in a hydrated, expanded form and is thereby readily penetrated by the next adsorbing layer. The net result is a multilayer film with a surface whose composition is dominated by the thick outermost layer but an internal structure that is more interpenetrated.

It remains to be determined if any of the different PAH/PAA combinations examined in this work produce an internal bilayer structure with a clearly defined compositional gradient or, at the other extreme, a completely homogeneous bilayer composition. It seems reasonable to conclude that both possibilities are possible with more homogeneous bilayer compositions occurring as the polymer pairs attain equal charge densities and are thereby able to form 1/1 stoichiometric complexes. Nevertheless, we conclude that all of the various bilayer compositions examined in this study are characterized by a high level of polycation/polyanion interpenetration.

We have recently carried out other experiments that also suggest a high level of interpenetration in sequentially adsorbed layers based on weak polyacids. Using Förster energy transfer schemes involving sequentially adsorbed donor and acceptor polymers separated by spacer layers of weak polyelectrolytes such as PAH and poly(methacrylic acid), we estimate that segments from a particular polymer layer can penetrate into as many as one to three of their surrounding bilayers.[46] It has also previously been reported[1] that sequentially adsorbed layers constructed from fully charged polyanions exist in a highly interpenetrated state. This work has been carried out with polymers that are capable of forming 1/1 polyanion/polycation complexes such as poly(styrenesulfonate) and PAH (fully protonated form). Thus, there is mounting evidence that suggests that the sequential adsorption of both fully charged and partially charged polyelectrolytes invariably results in a high level of layer interpenetration. It should be noted, however, that a recent neutron reflectivity study involving the deposition of a cationic poly(*p*-phenylenevinylene) precursor and poly(styrenesulfonate)[47] suggests that it is possible to prepare films with a much lower level of segmental interpenetration than is typically observed. In this case, the authors use a drying step between dipping that involves the high speed spinning of the substrate. It is currently unclear what role this added spinning step plays in influencing the resultant internal structure of the adsorbed layers.

Finally, an interesting question to ask is what happens when the pH range is extended beyond 4.5, i.e., the PAA chains are allowed to approach and attain their fully charged state (expected at about pH 6.5). In a future publication,[48] we will show that the thicknesses of the sequentially adsorbed layers of PAA and PAH undergo dramatic, charge density induced conformational transitions that initially drive the PAH layer thickness to about 80 Å and the PAA layer thickness to about 40 Å before both polymer layers collapse over a very narrow pH range to thicknesses of about 5 Å. Thus, the relatively simple behavior observed in the 2.5−4.5 pH range of this study changes in a most remarkable manner as the PAA chains approach their fully ionized state, resulting in some very interesting and previously unreported behavior.

Conclusions

It has been demonstrated that key characteristics of the basic bilayer building block of sequentially adsorbed layers of weak polyelectrolytes can be systematically varied over a wide range by simply controlling the pH of the dipping solutions. Through this type of control it is possible to vary the composition of the bilayer, the surface wettability, the level of layer interpenetration, and the thickness contributed by each individual layer. Surprisingly, it was found that the thickness contributed by an individual layer depends only on the pH of the polymer's dipping solution and, within the pH range examined, is not influenced by the thickness of the previously adsorbed layer. Using this approach, it is possible to create surfaces with advancing water contact angles that vary from essentially zero (completely wettable surfaces) to as high as 50, all using the same simple polycation/polyanion combination. Finally, we have already found that control over bilayer composition at this nanoscale level can result in dramatic improvements in the device characteristics of the light emitting multilayer thin films that we fabricate from sequentially adsorbed PAA/light emitting polymer systems.[44,45] Thus, this approach appears to have far reaching consequences with regard to the molecular level tuning of the properties of sequentially adsorbed polymer layers.

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