Molecular-Level Processing of Conjugated Polymers. 4. Layer-by-Layer Manipulation of Polyaniline via Hydrogen-Bonding Interactions

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Received January 17, 1997[⊗]

ABSTRACT: The molecular-level layer-by-layer processing of polyaniline with a variety of different nonionic water soluble polymers has been demonstrated. This new type of layer-by-layer adsorption process is driven by hydrogen-bonding interactions and has been accomplished with poly(vinylpyrrolidone), poly(vinyl alcohol), poly(acrylamide), and poly(ethylene oxide). FTIR spectroscopy measurements confirm a high level of hydrogen bonding between polyaniline and the nonionic polymer in the multilayer films. The effects of solution pH and polymer molecular weight on the deposition process were investigated. Comparisons with polyaniline films assembled via an electrostatic mechanism with sulfonated polystyrene indicate that the nonionic polymers adsorb onto polyaniline with a greater density of loops and tails and form highly interpenetrated bilayers with a high polyaniline content. The conductivities of these self-assembled multilayer films were found to be on the order of 1−4 S/cm for films doped with methane sulfonic acid. It was also demonstrated that the deposition process could be carried out with mixed solutions of polyaniline and a nonionic polymer.

Introduction

In the preceding paper of this series, we described the molecular-level layer-by-layer processing of partially doped polyaniline via the use of electrostatic interactions.[1] Over the past few years, it has become very apparent that polyaniline is capable of forming strong complexes with a variety of different solvent and dopant molecules.[2,3] In many cases, the strong interactions developed between polyaniline and these other small molecule systems have been attributed to hydrogen-bonding interactions at the amine or imine sites of the polyaniline backbone. Strong interactions of this type also appear to promote a high level of phase mixing in blends of polyaniline and specific hydrogen-bonding polymers such as poly(vinyl pyrrolidone).[4] Hydrogen-bonding interactions are also believed to play an important role in determining the level of aggregation of polyaniline in solution.[5] The strong propensity of polyaniline to form hydrogen bonds suggested to us that it may be possible to use these relatively strong secondary forces to self-assemble polyaniline in a layer-by-layer manner. In this paper it will be demonstrated that it is indeed possible to fabricate multilayer thin films of polyaniline via a hydrogen-bonding-based self-assembly process. We believe that this represents the first demonstration of molecular-level layer-by-layer polymer processing via a spontaneous adsorption process driven by hydrogen-bonding interactions.

We have previously shown that polyaniline can be self-assembled with a number of different nonionic, water-soluble polymers including poly(vinylpyrrolidone), poly(vinyl alcohol), poly(acrylamide), and poly(ethylene oxide).[6] Each of these polymers contains functional groups that are capable of forming hydrogen bonds with polyaniline. The resultant multilayer films are comprised of interpenetrating layers of polyaniline and a nonionic, hydrogen-bonding polymer with the thickness of the basic bilayer building block of these systems being controllable at the molecular level (in the range 10−125 Å). The ability to fabricate multilayer thin films and thin film heterostructures containing nonionic polymers opens up new possibilities for self-assembled films of conjugated polymers. For example, since poly(ethylene oxide) is an ion-conducting polymer, it is now possible to create multilayer thin films that are both electronically and ionically conductive. These films may be of use in thin film devices that are based on electrochemical processes such as the light-emitting devices recently described in the literature.[7]

This paper will describe the basic hydrogen-bonding self-assembly process as well as how parameters such as molecular weight, solution pH, and polymer type influence the bilayer thickness and electrical conductivity of the resultant multilayer thin films. Comparisons will also be made between the polyaniline films fabricated via the electrostatic self-assembly process and the films made with this new hydrogen-bonding process.

Experimental Section

The layer-by-layer assembly of polyaniline via electrostatic interactions is described in detail in the preceding paper of this series.[1] The polyaniline solutions used in the adsorption process described in this paper were prepared in the same manner. In forming the dipping solutions of the other polymers examined in this study, all polymers were used as-received and dissolved in water to form 0.01 M solutions (molar in terms of one monomer repeat unit). Using calculated radius of gyration values (R_g) for the water soluble polymers,[8] it was determined that a 0.01 M concentration is below the calculated critical overlap concentration in all cases. Thus, adsorption of the hydrogen-bonding polymers is from nonoverlapping chains in solution. Milli-Q deionized water (18 MΩ) was used for all solutions and rinses. For the pH study, the pH was adjusted by using either methane sulfonic acid (MeSA) or ammonium hydroxide. The solutions were all filtered through a 0.2 μm filter.

Solutions of different molecular weight poly(vinylpyrrolidone) (PVP) were prepared by dissolving the polymers in water at a concentration of 1.11 mg/mL (1 000 000 and 10 000 g/mol materials were from Polysciences, whereas the narrow molecular weight series was from American Polymer Standards).

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[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1997.

S0024-9297(97)00048-X CCC: $14.00

These solutions have a pH of about 4.5. Poly(vinyl alcohol) (PVA) (M_w = 86 000, from Scientific Polymer Products) was dissolved in water at a concentration of 0.44 mg/mL. The resulting solution has a pH of 6.25. Poly(acrylamide) (PAAm) (M_w = 5 500 000, from Polysciences) was dissolved in water at a concentration of 0.71 mg/mL, with a resulting pH of 6.2. Poly(ethylene oxide) (PEO) (M_w = 5 000 000, from Aldrich) was dissolved in water at a concentration of 0.44 mg/mL and had a pH of 6.3. Solutions of sulfonated polystyrene (SPS) were prepared by dissolving SPS in water at a concentration of 2.06 mg/mL: the pH was adjusted to 2.6 with MeSA (all SPS samples were obtained from Polysciences).

Multilayer films were deposited on a variety of substrates, including glass, plastics, metal, and silicon. In the case of glass and silicon, the slides or wafers were acid cleaned in a sulfuric acid/hydrogen peroxide bath (piranha), and then hydroxylated in an ammonium hydroxide/hydrogen peroxide bath. Adhesion could be further enhanced by surface treatment of the clean substrate to render the surface charged. Glass slides and silicon wafers were rendered charged by one of two types of surface treatments described previously[9,10] and briefly outlined here. The surface was either silanized with an amine-terminated trifunctional silane ((*N*-(2-aminoethyl)-3-aminopropyl)trimethoxysilane) or coated by adsorption of a single layer of poly(ethyleneamine) (PEI). In either case, this renders the surface positively charged through the protonation of the amine groups. The final step involved coating the surface with a single layer of a polyanion such as SPS by immersion into a SPS solution at a pH of 2.5. This gives the surface a net negative charge.

The multilayer deposition process was as follows. The treated substrates were first immersed into the polyaniline solution for 15 min, followed by rinsing with water at pH = 2.5 (MeSA), then drying with a gentle flow of compressed air. The films were then immersed in the nonionic polymer solution for 15 min, followed by rinsing with neutral water, and compressed air drying. A multilayer structure was formed by simply dipping the substrate alternately into the polyaniline and the nonionic polymer solutions. Fully doped polyaniline for conductivity measurements was obtained by immersion in a 1 M MeSA solution, followed by a quick rinse in a 1 M HCl solution to remove any residual surface MeSA.

The layer-by-layer buildup was monitored by visible spectroscopy at 630 nm. UV−visible spectra were taken directly from glass slides using an Oriel Multispec spectrophotometer. Dichroic ratios (the ratio of absorbance for S-polarized light to that for P-polarized light) were measured at a 45° angle of incidence and interpreted following the procedures outlined in.[11−13] IR spectra were taken on films built up on ZnSe plates, using a Nicolet 510P FTIR. All spectra were recorded after dedoping the films by rinsing with 0.1 M ammonium hydroxide and then rinsing with water. Examination of dedoped films avoids the complications associated with the sensitivity of the absorption of doped polyaniline to doping level. Atomic force microscopy (AFM) was performed using a Digital Instruments Nanoscope III operating in tapping mode. Film thicknesses were measured by both profilometry (using a Sloan Dektak 8000) and by ellipsometry (for films on reflective surfaces, using a Gaertner three-wavelength ellipsometer). A Zeiss light microscope with a maximum magnification of 1000× was used for light microscopy. All conductivities of fully doped films were measured in air by the van der Pauw four-probe method.

The average thickness per bilayer values were measured on films containing from 8 to 16 bilayers using profilometry and/or ellipsometry. An approximate estimate of the volume percent polyaniline per bilayer was obtained via the use of an absorbance per thickness calibration curve. This curve was generated by measuring the thickness and absorbance (at 630 nm) of a series of known concentration spin-coated thin films of polyaniline/PVP. The absorbance per unit thickness was determined to be 7.155×10^{-4} absorption units/Å. This analysis gives an extinction coefficient, ϵ, at 630 nm of about 1.3×10^4 (M cm)$^{-1}$ for dedoped polyaniline (where a mole is defined for two aniline structural units in the emeraldine base form). This compares quite favorably to the value of ϵ reported in the previous paper of 1.4×10^4 (M cm)$^{-1}$, which was determined by using polyaniline solutions and Beer's law.[1] Using this calibration value and an absorbance per bilayer value, the contribution of polyaniline per bilayer was estimated. The volume percent of polyaniline reported in this paper is simply this contribution divided by the thickness per bilayer.

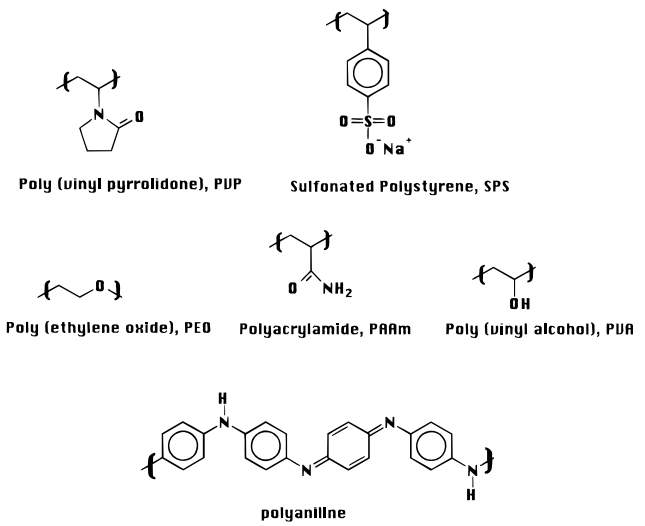

Figure 1. Chemical structures of the polymers used in this study.

Films have also been deposited from polyaniline solutions made with NMP (*N*-methylpyrrolidone) rather than dimethylacetamide (DMAc) in the water/solvent solution. The films assembled from DMAc were found to be about five times more conductive (after doping) than those assembled from NMP solutions. This suggests that there is residual NMP, which acts to hinder doping by loosely binding or complexing the dopant protons. There is likely less residual DMAc, since polyaniline retains NMP more tightly than DMAc. Similar results were seen for polyaniline/PVP blends.[4]

Results and Discussion

The ability of polyaniline to form strong hydrogen bonds at both the amine and imine sites along its polymer backbone suggests that it may be possible to utilize these relatively strong secondary forces to assemble multilayer thin films in a layer-by-layer manner. We have previously demonstrated that partially doped polyaniline can be manipulated into multilayer thin films via the use of polyanions such as poly(styrenesulfonic acid), polyamic acid and poly(methacrylic acid).[1,14] The self-assembly process in this case is driven by the electrostatic interactions established between the acid-doped, positively charged polyaniline backbone and the negatively charged polyanion. In order to determine whether hydrogen-bonding interactions can be utilized to facilitate the layer-by-layer self-assembly of polyaniline, sequential multilayer adsorption was attempted with a number of different types of nonionic, water-soluble hydrogen-bonding polymers. The structures of these various polymers are shown in Figure 1.

To start the multilayer adsorption process, a bilayer of poly(styrenesulfonic acid)/polyaniline was first deposited onto the substrate surface to promote good adhesion and to place the first polyaniline layer on the surface. This was typically accomplished by first dipping a positively charged substrate into an SPS solution, rinsing the substrate with acidic water (pH = 2.5), and then dipping the substrate into the polyaniline solution. Thus, the first polyaniline bilayer is assembled onto the surface via electrostatic forces. After these "prep layers" were deposited, the substrate was alternately immersed

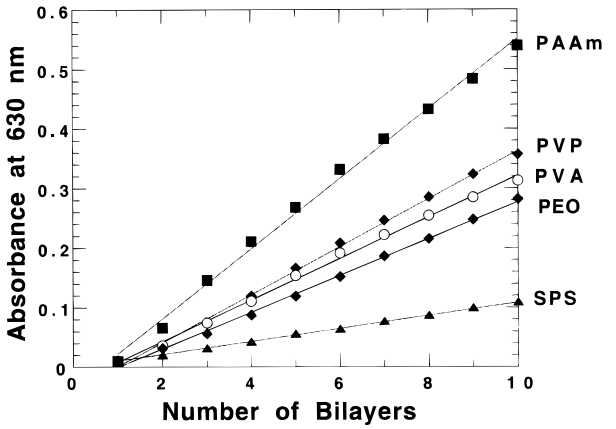

Figure 2. Absorbance vs the number of deposited bilayers for various polyaniline/hydrogen-bonding polymer combinations (the type of hydrogen-bonding polymer assembled with polyaniline is indicated in the figure). Data from the polyaniline/SPS bilayer system are also included.

into a solution containing the hydrogen-bonding polymer and the polyaniline solution (with a rinsing step in between). Multilayer thin films were fabricated by simply repeating this latter process. Since the pH of the solutions of the nonionic polymers was in all cases greater than 4.5, adsorption of the hydrogen-bonding polymer is taking place onto a layer of polyaniline that is essentially dedoped, i.e., electrically neutral. Adsorption of the polyaniline layer onto a layer of the hydrogen-bonding polymer, on the other hand, occurs with the polyaniline in a partially doped state (dipping solution maintained at pH = 2.5 for stability reasons).

The multilayer deposition process was monitored by UV−visible spectroscopy; the absorbance of a film at 630 nm was typically measured after the deposition of each bilayer. At this wavelength, dedoped polyaniline exhibits a strong excitonic absorption band. The other polymers examined in this work do not absorb light in this wavelength range. The multilayer deposition process was therefore monitored by examining the increase in polyaniline absorption with increasing bilayer deposition. Figure 2 shows such results for four different polyaniline/hydrogen bonding polymer bilayer systems (the molecular weights of these polymers can be found in Table 1). For comparison, the multilayer buildup of polyaniline with SPS via electrostatic self-assembly is also included in this figure. The linear relationship observed between absorbance and the number of deposited bilayers indicates that the deposition process in all cases is reproducible from layer to layer. In other words, for each bilayer system, the amounts of polyaniline adsorbed in each bilayer cycle are the same. These results clearly demonstrate that the layer-by-layer self-assembly of polyaniline can be successfully carried out with a wide variety of different nonionic polymers including polymers with amide, ether, and hydroxyl functional groups. The multilayer films obtained from this process are optically uniform down to at least the micrometer scale as determined by light microscopy.

Note that the amount of polyaniline adsorbed per bilayer (as indicated by the slopes of the curves in Figure 2) is actually greater when hydrogen-bonding interactions are used to drive the self-assembly process as opposed to electrostatic interactions. Generally speaking, we have found that the hydrogen-bonding self-assembly process typically delivers more polyaniline per bilayer than the electrostatic self-assembly process, particularly when electrostatic self-assembly is carried out with low ionic strength polyanion solutions. The fact that all of the curves generated from the polyaniline/hydrogen-bonding polymer bilayer combinations do not pass through the origin simply reflects the fact that the polyaniline/SPS bilayer used to start the deposition process contains less polyaniline.

Some of the important characteristics of these new polyaniline/hydrogen bonding polymer self-assembled multilayer films are outlined in Table 1. In this case, the numbers presented represent the range of values obtained from measurements made on samples fabricated from a number of different batches of the polyaniline solution. The variability observed with different batches of the polyaniline solution is associated with the fact that each solution has a slightly different polyaniline concentration after filtering due to the tendency of this material to partially aggregate in the starting DMAc solution of the emeraldine base. Multilayer films made from the same polyaniline solution, however, consistently give very similar values. Also included in this table are values generated from the polyaniline/SPS system using two different molecular weight SPS samples. All polymer concentrations were 0.01 M, and no pH adjustment was made to the water-soluble polymer solutions. Details concerning the various measurements used to generate these values can be found in the Experimental Section.

It can be seen from Table 1 that the average thickness and optical absorbance per bilayer of the multilayer thin films fabricated with the hydrogen-bonding polymers are greater than the values obtained when polyaniline is self-assembled with SPS. This is not simply due to the fact that most of the hydrogen-bonding polymers are of much higher moleculear weight than the SPS as indicated by the fact that the thickness and absorbance per bilayer of the polyaniline/SPS system are not sensitive to the molecular weight of the SPS used in the fabrication process. Indeed, similar results are obtained with either 70 000 or 500 000 molecular weight SPS. Using these hydrogen-bonding polymers, it is possible to deposit quite thick polyaniline bilayers, in the range of 50−125 Å per bilayer, that are comprised of a relatively large volume fraction of polyaniline (50−70 vol % of the bilayer is estimated to be polyaniline). This is in contrast to the polyaniline/SPS system, which only delivers about 35 Å per bilayer.

The electrical conductivity values generated from methanesulfonic acid doped films show that all of these self-assembled multilayers can be doped to conductivity levels comparable to spin cast films of polyaniline (0.5−1 S/cm). The conductivities of the polyaniline/hydrogen-bonding polymer systems, however, are typically about 1 order of magnitude larger that what is obtained from the polyaniline/SPS multilayer system (1−4 vs 0.1−0.5 S/cm). The higher conductivity of the polyaniline/hydrogen-bonding polymer multilayers is in part due to the fact that more polyaniline is present on average per bilayer, although it may also reflect differences in the ordering and conformation of the polyaniline chains.[15] It is to be expected that charge transport is better facilitated when the doped polyaniline chains form a more continuous, less isolated network. This would suggest that the polyaniline/hydrogen-bonding polymer multilayers are more highly interpenetrated than the polyaniline/SPS multilayer system and/or that they are comprised of more continuous domains of polyaniline.

Table 1. Selected Characteristics of Polyaniline/Hydrogen-Bonding Polymer Multilayer Films

polymer system w/PAn	Å/bilayer	σ(S/cm)	absorbance/bilayer (at 630 nm)	est. vol % PAn	dichroic ratio
PAAm (5 500 000)	90−125	1.9−4.0	0.042−0.054	53−76	1.11−1.12
PVP (1 000 000)	65−85	1.3−3.7	0.032−0.045	64−74	1.21−1.25
PEO (5 000 000)	50−70	0.4−2.2	0.021−0.028	49−60	1.21−1.26
PVA (86 000)	55−65	1.1−3.6	0.020−0.031	52−72	1.22−1.24
SPS-low (70 000)	28−41	0.1−0.5	0.007−0.013	26−62	1.19−1.21
SPS-hi (500 000)	27−42	0.1−0.4	0.011−0.013	43−65	1.20

[a] Molecular weights of the polymers are found in column 1.

The dichroic ratios (S-polarized/P-polarized absorbance ratio) listed in column 6 of Table 1 give relative information about the level of preferred orientation of the polyaniline chains. The larger this value is, the greater the tendency of the polyaniline chains to adopt a preferential in-plane orientation. Using the approach outlined in refs 11−13 and assuming a refractive index of 1.6 for the polyaniline films,[16,17] we estimate that a dichroic ratio of about 1.10 corresponds to a random chain orientation. Thus, any ratio greater than 1.10 suggests that the polyaniline chains exhibit a tendency to orient within the plane of the film. If all of the polyaniline structural units were extended and oriented in the plane of the surface, the calculated dichroic ratio would be about 1.50. There are some difficulties in determining the absolute dichroic ratio (such as problems with baseline interpretation and variability of the ratio with wavelength), as well as with the assumption about the refractive index of the multilayers, so these values are best used to provide a relative comparison of chain orientation. With the exception of the polyaniline/PAAm system, the polyaniline present in all of the bilayer systems gives rise to a dichroic ratio of about 1.2. Although this indicates a slight preferred in-plane orientation of the polyaniline chains, it suggests that the polyaniline chains are oriented in an essentially random manner within the multilayers.

The fact that self-assembly with the hydrogen-bonding polymers produces thicker bilayers with a larger amount of polyaniline deposited per bilayer can be explained as follows. It is well-known that the amount of a charged polymer adsorbed onto a surface depends, among other things, on the level of segmental repulsion of the ions distributed along the chain. High levels of segmental repulsion tend to produce thin adsorbed layers with the chains adopting a more extended conformation on the surface. As ionic repulsion effects are reduced, adsorbed polymer chains tend to produce thicker layers with a greater fraction of the polymer chain present as loops and tails.[18] Segmental repulsion effects can be reduced by increasing the ionic strength of the polymer solution (shielding effect) and/or reducing the charge density along the chain by structural or pH changes. The limiting case of this effect would be the adsorption of a completely neutral polymer which will generally adsorb with a high concentration of loops and tails. The neutral, hydrogen-bonding polymers examined in this study must adsorb onto the preceding adsorbed layer of polyaniline with a high density of chain segments extending from the surface (in the wet state). This provides a large effective surface area for the next adsorbing layer of polyaniline. The net result is the adsorption of a large amount of polyaniline that is presumably highly interpenetrated with the hydrogen-bonding polymer. In contrast, the highly charged SPS chains are adsorbed as thinner layers with more extended chain conformations. Such a surface layer is capable of adsorbing less polyaniline. In this latter case, the polyaniline chains are presumably forming a layered polyaniline/SPS complex in which the polyaniline chains are, for the most part, sandwiched between chains of SPS (this may explain the lower conductivity of the polyaniline/SPS system).

Implicit in the above argument is the assumption that the interchain interactions developed between polyaniline and the hydrogen-bonding polymers are driving the reproducible layer-by-layer polymer deposition. The different amounts of polyaniline adsorbed per bilayer with the different kinds of hydrogen-bonding polymers are related to differences in molecular weight and in the strength and types of hydrogen bonds formed with polyaniline. It is clear that the amine/imine groups of polyaniline form sufficiently strong hydrogen bonds with ether, amide, and alcohol groups to enable reproducible multilayer deposition. The nitrogen-containing polymers, such as PVP and PAAm, tend to form thicker bilayers with polyaniline most likely due to the opportunity to form hydrogen bonds via both the electron pairs on the nitrogen atoms and the carbonyl groups of the amide linkage. Apparently, thicker films (more deposited polyaniline) are obtained with hydrogen-bonding polymers that have the most "binding" interactions. This effect is illustrated by comparing the polyaniline/PAAm system to the polyaniline/PEO system (only amine−ether hydrogen bonds possible). The use of PAAm results in a much thicker bilayer than the use of PEO of comparable molecular weight. Also note that the dichroic ratio of the PAAm bilayer system is lower than that of the other bilayer systems and that the PAAm bilayer system delivers the thickest bilayer. This is consistent with the notion that thicker bilayers are developed by the adsorption of polyaniline onto a polymer layer with a high surface density of loops and tails, thereby producing less oriented chains of polyaniline. It is not too surprising that polyaniline will readily adsorb onto a number of different hydrogen-bonding polymers. We have previously shown that partially doped polyaniline will adsorb onto many different substrate surfaces including hydrophilic, hydrophobic, and negatively charged substrates.[1,10a] It is quite amazing however that these highly water soluble polymers will readily and reproducibly adsorb onto a layer of undoped polyaniline. This again attests to the fact that polyaniline is capable of forming strong hydrogen bonds with a variety of different functional groups and that the strength of these interactions is sufficient to promote layer-by-layer deposition.

Molecular Weight Effects. To further explore the idea that the hydrogen-bonding polymers tend to adsorb onto a polyaniline layer with a higher fraction of segmental loops and tails than what is obtained with a negatively charged polymer, we examined the role that molecular weight plays in determining the average thickness per bilayer. For a highly charged polymer adsorbing in a more extended conformation, one would expect that increasing the molecular weight of the polymer would not appreciably influence the thickness

Table 2. Selected Properties of Polyaniline/PVP Multilayer Films (10 Bilayers) As a Function of Molecular Weight

sample (M_w)	Å/ bilayer	abs/ bilayer	dichroic ratio	est. vol % PAn	σ (S/cm)
a. Polyaniline/PVP Films: PVP Molecular Weight					
PVP (1M)[a]	77	0.0403	1.14	73	1.2
PVP (350K)	80	0.0370	1.17	65	1.6
PVP (125K)	56	0.0272	1.26	68	1.1
PVP (35K)	17	0.0072	1.38	59	0.07
PVP (25K)	11	0.0040	1.47	51	0.10
PVP (10K)[a]			1.49[b]		
PVP (9K)			1.45[b]		
b. Polyaniline/SPS Multilayer Films: SPS Molecular Weight					
SPS (990K)	42	0.0143	1.19	48	0.11
SPS (500K)	42	0.0127	1.20	43	0.11
SPS (350 K)	41	0.0138	1.20	47	0.11
SPS (77K)	40	0.0128	1.17	45	0.09
SPS (70K)[c]	41	0.0125	1.19	43	0.11
SPS (35K)	41	0.0122	1.18	41	0.06
SPS (5K)	41	0.0131	1.14	45	0.06

[a] Indicates very polydisperse PVP (branched as well); all others are relatively narrow MW distribution ($M_w/M_n \approx 3$). [b] Represents a single polyaniline layer on SPS. [c] Indicates polydisperse SPS, all others are essentially monodisperse ($M_w/M_n = 1.10$)

of the adsorbed layer.[18] The polymer chains simply spread out to occupy more area on the surface as molecular weight increases. In sharp contrast, one would expect a polymer that tends to absorb with a high fraction of segmental loops and tails to show a pronounced dependence of layer thickness on molecular weight. Since a much larger fraction of the polymer chain is not bound to the surface, the larger loops and tails of higher molecular weight chains would produce thicker layers than those of lower molecular weight chains. As will become apparent shortly, this is exactly what is observed with the hydrogen bonding polymers.

Table 2 shows how the average bilayer thickness varies with increasing molecular weight for a representative polyaniline/hydrogen-bonding bilayer system (polyaniline/PVP) and the polyaniline/SPS bilayer system. Also included in these tables are the dichroic ratios and conductivities measured on these various samples. In order to minimize the effects of molecular weight distribution, polymers with the lowest available molecular weight distributions were used in these particular studies. All of the SPS polymers used with the exception of the 500K and 70K samples (both of these polymers were of higher polydispersity) have a molecular weight distribution, $M_w/M_n = 1.10$. The PVP samples used were more polydisperse with $M_w/M_n \approx 3$. Two of the PVP samples (PVP-1M and PVP-10K) were of a higher polydispersity. Molecular weights covering the range 5 000−1 000 000 were examined in this study.

A quick review of Table 2 reveals that the average thickness per bilayer is strongly dependent on molecular weight for the polyaniline/PVP bilayer system and independent of molecular weight for the polyaniline/SPS bilayer system. The polyaniline/PVP bilayer system therefore clearly behaves in a manner that is consistent with the PVP chains adsorbing with a high segmental density of loops and tails whereas the polyaniline/SPS system behavior is more consistent with the SPS chains adsorbing with a much more extended chain conformation. In the case of the polyaniline/PVP bilayer system, there appears to be a minimum PVP molecular weight (<25 000) below which no multilayer deposition occurs. Above this molecular weight, the average bilayer thickness increases dramatically with increasing molecular weight reaching an apparent plateau at a molecular weight of 350 000. Similar plateau behavior has been observed in more conventional PVP adsorption studies.[18c] In sharp contrast, the average thickness per bilayer of the polyaniline/SPS bilayer system remains the same even though the molecular weight of the SPS has been changed from 5 000 to 990 000.

The fact that layer-by-layer deposition is not possible with low molecular weight PVP but works fine with low molecular weight SPS suggests that the weaker hydrogen-bonding interactions of PVP are more prone to deadsorption effects than are the stronger ionic interactions developed with SPS. We suspect that the lower molecular weight chains of PVP deadsorb during the dipping process, thereby preventing multilayer deposition. With fewer direct secondary bonding sites to the surface (more loops and tails), the probability of polymer deadsorption would be expected to increase as the molecular weight of the polymer chain decreases. The stronger ionic bonds associated with electrostatic self-assembly coupled with the tendency of the charged SPS chains to adopt a more surface-anchored, extended chain conformation, on the other hand, make it possible to use much low molecular weight polymers in the self-assembly process. In fact, we have found that both charged oligimers[9b] and small ionic dye molecules[19] can be successfully utilized to fabricate multilayer thin films via the electrostatic self-assembly process.

A few other comments are worth making about the data in Table 2. First, it can be seen with the polyaniline/PVP bilayer system that the dichroic ratio increases (more in-plane orientation of the polyaniline chains) with decreasing PVP molecular weight and that the conductivity of doped films drops to lower values below a PVP molecular weight of 125 000. Both of these effects suggest that the very low molecular weight PVP chains tend to adopt more extended chain conformations (fewer loops and tails) and possibly become less interpenetrated with the polyaniline chains as the PVP molecular weight decreases; i.e., they move in the direction of behaving conformationally more like the SPS chains. The drop in conductivity may also reflect the fact that the molecular level continuity of the polyaniline chains in the very thin polyaniline/PVP bilayers is not very high.

The low dichroic ratio consistently obtained from the polyaniline/SPS bilayer system regardless of SPS molecular weight would seem to suggest that the polyaniline chains are not adopting a high level of chain elongation at the surface or that the films are relatively rough and wavy. A high level of surface roughness would act to lower the dichroic ratio, even if the polyaniline chains were elongated along the surface. Note that the dichroic ratio of the two lowest molecular weight PVP films presented in Table 2 (PVP-10K and -9K) is actually obtained from a single layer of polyaniline adsorbed onto an SPS "prep" layer (recall that no polyaniline/PVP deposition occurs with these molecular weights). The high dichroic ratios obtained in this case show that the chains in the first polyaniline layer deposited onto SPS do exhibit a strong tendency to align along the substrate surface. Thus, the multilayer thin films of polyaniline/SPS exhibit lower dichroic ratios presumably due to an increase in surface roughness with increasing number of bilayers.

Surface roughness measurements by AFM (for 10 × 10 μm areas) on the films discussed here indicate that the root mean square (RMS) roughness of the polyaniline/SPS bilayer system is at least 70 Å by the time

Table 3. Selected Properties of Polyaniline/ Hydrogen-Bonding Polymer Multilayer Films (Eight bilayers) As a Function of pH Conditions

system (pH)	Å/ bilayer	abs/ bilayer (630 nm)	est vol % Pan	dichroic ratio
PEO (3.0)	34	0.0124	52	1.23
PEO (6.0)	52	0.0210	57	1.19
PEO (9.0)	50	0.0222	63	1.22
PVA (3.0)	67	0.0263	55	1.20
PVA (5.0)	55	0.0204	52	1.23
PVA (7.0)	46	0.0174	53	1.24
PAAm (3.0)	146	0.0688	66	1.09
PAAm (5.0)	91	0.0494	76	1.12
PAAm (7.0)	75	0.0430	80	1.29
PVP (4.0)	84	0.0446	74	1.19
PVP (5.0)	74	0.0430	81	1.20
PVP (6.0)	71	0.0412	81	1.20

the sixth polyaniline/SPS bilayer is deposited. It should also be noted that while the RMS roughness for polyaniline/SPS multilayer films ranges from about 60 to 70 Å, the polyaniline/PVP bilayers (PVP: $M_w = 10^6$) have a slightly lower RMS roughness of about 50−55 Å. This may explain why it is possible to observe more variation in the dichroic ratios of the polyaniline/PVP bilayer system, although we have not examined the surface roughness of the polyaniline/PVP bilayers containing the lower molecular weight PVP. Surface roughness values in the 50 Å range have also been observed (using neutron reflectivity measurements) in multilayer thin films fabricated from sulfonated polyaniline/poly(allylamine) bilayers.[20] The relatively high surface roughness associated with all of these polyaniline-based bilayer systems compared to bilayers of more conventional polyelectrolytes (typically in the range of 10−30 Å[21]), is most likely due to the tendency of the polyaniline chains to form nanoaggregates in the water-based dipping solutions used in the multilayer deposition process. It may be possible to reduce or eliminate these nanoaggregates by adding LiCl to the starting polyaniline DMAc solution, as has been recently demonstrated by Angelopoulous and co-workers.[5] Systems that favor more loopy chain organizations may also give rise to higher surface roughness.

pH Effects. The pH of the hydrogen-bonding polymer solution can be varied over a wide range and still allow for successful multilayer deposition with polyaniline. The polyaniline solution, on the other hand, must be maintained at a pH close to 2.5 due to the limited stability of this solution. Thus, polyaniline is adsorbed as a partially positively charged polymer whereas the hydrogen-bonding polymers can be adsorbed onto a polyaniline layer that is either partially doped or electrostatically neutral. Studies were carried out to determine how the pH of the hydrogen-bonding polymer solution influences the deposition process. It is known that pH can influence a nonionic polymer's ability to hydrogen bond; OH^- ions, for example, can act to dissociate hydrogen bonds at high pH.[22,23] Table 3 summarizes results from a series of multilayer films built up from solutions with different pH values for the nonionic, hydrogen-bonding polymer.

With the exception of poly(ethylene oxide), it can be seen that lowering the pH of the hydrogen bonding polymer solution tends to result in an increase in the average thickness per bilayer. This is a weak effect with poly(vinyl alcohol) and poly(vinylpyrrolidone) and a quite pronounced effect with poly(acrylamide). In the PEO case, there is a weak pH dependence in the opposite manner; i.e., higher pH produces slightly thicker bilayers. For all of these quite different hydrogen-bonding polymers, it can be seen that multilayer deposition is possible over a wide range of pH values including pH levels that completely and rapidly dedope the previously adsorbed layers of polyaniline (6.0−9.0). Thus, the adsorption of the hydrogen-bonding polymers onto polyaniline appears to be primarily driven by hydrogen-bonding interactions. Also note that no significant changes in the orientation of the polyaniline chains were detected with change in pH as indicated by the very similar dichroic ratios reported in Table 3 (the polyaniline/PAAm system does show a weak pH/ dichroic ratio dependence).

It is difficult to determine the origin of these pH effects. Possibilities include the developement of partial charges on the hydrogen-bonding polymers due to a weak ionization (−OH groups) or protonation ($-CONH_2$ groups) of functional groups, the development of weaker hydrogen bonds at high pH levels due to the presence of OH^- ions and, most importantly, changes in the number and nature of polyaniline hydrogen-bonding sites due to changes in doping level. Any combination of these effects may be contributing to the observed changes in bilayer thickness with solution pH. In any event, the important point is that these highly water soluble polymers will readily adsorb onto polyaniline surface layers over a wide pH range.

FTIR Determination of Hydrogen Bonding. Direct evidence for hydrogen bonding with polyaniline was obtained using FTIR spectroscopy. The N−H stretch of the amine group of dedoped polyaniline was used to estimate the level of hydrogen bonding. It has been well-established that the peak intensity and position of the N−H stretching vibration are very sensitive to hydrogen-bonding effects.[24] Both the polyaniline/PVP bilayer system and the polyaniline/PEO bilayer system were examined by FTIR. Both of these hydrogen-bonding polymers are not able to form hydrogen bonds with themselves, thereby making the analysis more straightforward (they both would be considered hydrogen-bonding proton acceptors). Four spectra were compared in each case, the two pure homopolymers, a solution-cast blend of the two polymers (approximately 50/50) and a self-assembled multilayer thin film (10 bilayers). For the multilayer thin films, the 10 bilayers were deposited directly onto an untreated ZnSe substrate, starting with the polyaniline layer first. The blends and all three homopolymers were solution cast from NMP. All films were thoroughly dried before taking the IR spectra. In all cases, the polyaniline was in a completely dedoped state.

The four FTIR spectra (N−H stretch region only) for the polyaniline/PVP system are shown in Figure 3. Since polyaniline can hydrogen bond with itself,[25] one would expect to see two major bands in the N−H stretching region (3200−3500 cm^{-1}). The non-hydrogen-bonded N−H stretch of pure undoped polyaniline appears at about 3380 cm^{-1}, whereas the lower energy hydrogen-bonded N−H stretch occurs at about 3310 cm^{-1}. It can be seen that the solution cast film of polyaniline is comprised of both hydrogen-bonded and free N−H groups, with a larger fraction of the N−H groups being present in the non-hydrogen-bonded form. The smaller peak near 3050 cm^{-1} is attributed to the aromatic ring stretching in polyaniline. For comparative purposes, the absorbances of all of the spectra shown in Figure 3 were normalized to this peak. In this

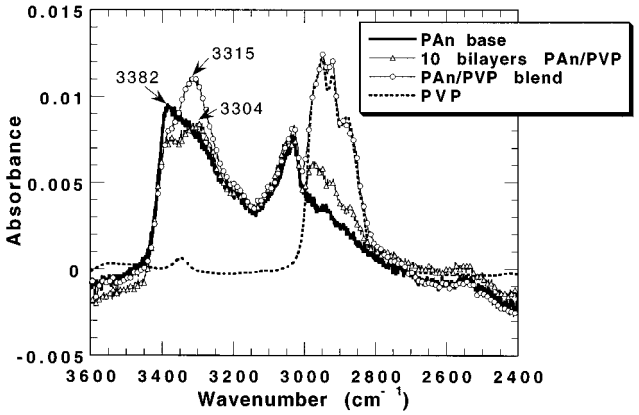

Figure 3. FTIR spectra showing the N−H stretching region of a solvent cast polyaniline film (emeraldine base form), a 10 bilayer film of polyaniline/poly(vinyl pyrrolidone), and a 50/50 polyaniline/poly(vinyl pyrrolidone) blend.

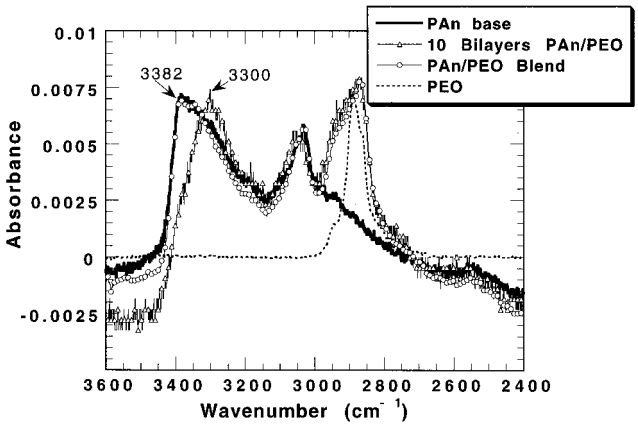

Figure 4. FTIR spectra showing the N−H stretching region of a solvent cast polyaniline film (emeraldine base form), a 10 bilayer film of polyaniline/poly(ethylene oxide), and a 50/50 polyaniline/poly(ethylene oxide) blend.

spectral region, pure PVP only exhibits a strong C−H symmetric and asymmetric stretch between about 2800 and 3000 cm^{-1}.

The FTIR spectrum of the polyaniline/PVP blend shows a pronounced hydrogen-bonded N−H stretching peak at 3315 cm^{-1} and a weaker free N−H peak at 3382 cm^{-1}. Thus, in the blended state, polyaniline exhibits a higher level of hydrogen bonding than it does in its nonblended state. We have previously found that polyaniline and PVP form compatible, highly phase mixed blends.[4] It is therefore not too surprising that a large fraction of polyaniline/PVP hydrogen bonds are observed in the blend; hydrogen bonding most likely drives the mixing process. In the multilayer system of polyaniline/PVP, the hydrogen bonded N−H stretching peak (at 3304 cm^{-1}) is also more pronounced than the peak associated with free N−H groups. This increase in polyaniline hydrogen bonding is particularly evident when one compares the spectrum of pure polyaniline with the multilayer film. Given the fact that a hydrogen-bonded N−H stretching vibration is known to absorb more strongly than the free N−H stretching vibration, without knowledge of the magnitude of this difference, it is difficult to carry out a quantitative analysis of the fraction of bonded vs nonbonded N−H groups in these various systems. It seems reasonable to conclude, however, that polyaniline/PVP hydrogen bonds are being formed in both the blend and multilayer thin film.

A similar series of four FTIR spectra for the polyaniline/PEO system is shown in Figure 4. The C−H symmetric and asymmetric stretching vibrations of pure PEO are observed around 2900 cm^{-1}. Again, all peaks were normalized to the aromatic stretching peak at about 3050 cm^{-1}. In this case, it can be seen that, in contrast to the polyaniline/PVP blend, there is no significant difference observed in the population of free and hydrogen-bonded N−H groups when pure polyaniline is compared to the polyaniline/PEO blend. The polyaniline present in the blend maintains the same low level of hydrogen bonding found in unblended polyaniline. The lack of any observable hydrogen-bonding interactions in this case suggests that polyaniline and PEO form a phase-separated blend system. This conclusion was confirmed by observing the polyaniline/PEO blend under a light microscope at 1000×. The polyaniline/PEO blend is clearly highly phase separated whereas samples of the polyaniline/PVP blend appear completely phase mixed at this magnification.

Turning to the spectrum of the polyaniline/PEO multilayer film, it is evident that there is a significant increase in the intensity of the hydrogen-bonded N−H peak (in this case at 3300 cm^{-1}) relative to what is observed in pure polyaniline or the polyaniline/PEO blend. The free N−H peak, in this case, only appears as a weak shoulder on the high-energy side of the hydrogen-bonded peak; i.e., almost all of the N−H groups are participating in hydrogen bonds in the polyaniline/PEO bilayer system. The spectrum of the polyaniline/PEO multilayer film therefore indicates the formation of a high level of polyaniline/PEO hydrogen bonds.

It is interesting that the hydrogen-bonding interactions developed between polyaniline and PVP and polyaniline and PEO are sufficient to promote multilayer assembly but only result in compatible blends in the polyaniline/PVP case. Apparently, for polyaniline/PEO, hydrogen bonds are readily formed during the adsorption process (even though water is a good solvent for PEO) but are not as readily formed during a typical blending process from NMP. Although not fully investigated, we have evidence that polyaniline also forms compatible blends with PAAm. Recall that the polyaniline/PAAm bilayer system delivers the thickest bilayers of the hydrogen-bonding polymers. It has been observed that the imine nitrogen atoms in polyaniline chains can act as proton acceptors, forming interchain NH−H hydrogen bonds in pure polyaniline.[25] PVP and PAAm both contain nitrogen sites that may promote these types of additional strong interactions with polyaniline. This, in turn, may account for the fact that both of these polymers form relatively thick bilayers and compatible blends.

The FTIR spectra in Figures 3 and 4 can be used to estimate the fraction of polyaniline present in the polyaniline/PVP and polyaniline/PEO multilayer films. This can be accomplished by comparing suitable polyaniline to PVP or PEO peak ratios in both the 50/50 blends and the multilayer thin films. Using the 3050 cm^{-1} polyaniline peak and the 2950 cm^{-1} PVP or 2900 cm^{-1} PEO peak, we estimate that the polyaniline/PVP multilayer is about 70% polyaniline and the polyaniline/PEO multilayer is about 50% polyaniline. Using visible spectroscopy in combination with thickness measurements, values of 65−75% polyaniline were obtained for the polyaniline/PVP system and 50−60% for the polyaniline/PEO system. Given the different substrates used in these various experiments and some of the assumptions made to get these number, they compare quite well.

Hydrogen-Bonding Self-Assembly: General Comments. To explore the general utility of using nonionic, water-soluble hydrogen-bonding polymers for layer-by-layer deposition, a variety of combinations of nonionic and ionic polymers was examined for ability to fabricate multilayers. Attempts were made to form the following types of bilayer combinations involving a charged polymer (negatively charged SPS or positively charged poly(allylamine)) and a nonionic, hydrogen-bonding polymer: PEO/SPS, PVP/SPS, PEO/poly(allylamine), and PVP/poly(allyl amine). In all cases, no layer-by-layer deposition was observed (SPS-based depositions were tested in the pH range of 2.5−6.5; poly(allylamine) was tested in the pH range of 2−3). Thus, multilayer fabrication does not seem to be possible with hydrogen-bonding polymers and either polycations or polyanions. Bilayer combinations involving two polymers with hydrogen bonding capabilities such as such as PVP/PVA, PAAm/PVP, PAAm/PVA, and PAAm/PEO were also attempted. Preliminary results, although not exhaustive, show that multilayer deposition is also not possible with any of these various combinations.

All of these results combined attest to the fact that polyaniline is a rather unique polymer in its ability form strong hydrogen bonds with a variety of different functional groups. They also show that the electrostatic contribution to adsorption processes involving polyaniline and hydrogen-bonding polymers is much less significant than the hydrogen-bonding contribution (as indicated by the fact that other charged polymers will not form multilayers with the hydrogen-bonding polymers). It is therefore clear that self-assembly via hydrogen-bonding interactions requires the use of polymers that are capable of forming very strong hydrogen bonds.

Mixed Layer Deposition from Polyaniline Solutions. A unique advantage of using hydrogen-bonding interactions to assemble multilayer thin films of polyaniline is that it is possible to actually utilize mixed solutions that contain both the hydrogen-bonding polymer and polyaniline. This is not possible with electrostatic self-assembly since a polycation and a polyanion will quickly form a salt that precipitates out of solution.

Dipping solutions containing polyaniline and either PAAm or PVP were prepared by mixing equal volume portions of 0.01 M polyaniline (pH = 2.6) and either 0.01 M PAAm (pH = 2.6) or 0.01 M PVP (pH = 2.6) to form a 50/50 mixture 0.005 M in both polymers. The solutions are quite miscible in both cases, as no particulates formed upon mixing or after standing for 2 weeks. Adsorption from these solutions onto an SPS-treated glass slide was monitored as a function of time. In both cases, a mixed layer containing both polymers was quickly deposited (90% deposition in 30 min) with the deposition process reaching its self-limiting value in about 45 min. Thickness values of 60 Å for the polyaniline/PVP mixed layer and 50 Å for the polyaniline/PAAm mixed layer were estimated using a spectroscopic calibration. In addition, these single mixed layers were estimated (using FTIR) to contain about 50−60 vol % polyaniline. It is also possible to form multilayers with these mixed layers by simply carrying out an alternate deposition process with polyanions such as SPS. Thus, alternation with SPS can be used to fabricate more complex multilayer thin films in which the mixed layers are assembled via electrostatic interactions with SPS. Multilayer formation is not possible via alternate deposition with polyaniline or PVP, however, indicating that no additional deposition is possible using the individual components of the mixed layer (the deposition process becomes self-limiting).

The advantage of this approach is that relatively thick, highly uniform mixed layers of polyaniline are deposited in a single dip. The conductivity after doping of these single mixed layers is about 0.1 S/cm. In the case of the alternate deposition of polyaniline/SPS or polyaniline/PVP, it typically takes at least two bilayers (four dips) to reach this same level of conductivity. Thus, it is possible to render surfaces electrically conductive by using a single dip process as opposed to a multiple dip process. The mixed layer approach also provides new opportunities for fabricating more complex multicomponent bilayer systems.

Conclusions

It has been demonstrated that a wide variety of hydrogen-bonding interactions can be used to assemble multilayer thin films of polyaniline in a layer-by-layer manner. The use of hydrogen-bonding forces to assemble these multilayers results in relatively thick, high polyaniline content bilayers due to the tendency of the hydrogen-bonding polymers to adsorb with a high segmental density of loops and tails. This is in contrast to films formed via an electrostatic mechanism in which charge repulsion effects more severely limit the amount of polyaniline adsorbed per deposition cycle. The polyaniline films formed via hydrogen-bonding self-assembly also exhibit conductivities about 1 order of magnitude larger that those obtained from films assembled via electrostatic interactions.

Acknowledgment. This work was supported in part by the National Science Foundation and by the MRSEC program of the National Science Foundation under Award No. DMR-9400334. The authors also thank Mr. Wade Samec and Mr. Anand Raghunathan of MIT for assistance.

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MA9700486