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Molecular-Level Processing of Conjugated Polymers. 1. Layer-by-Layer Manipulation of Conjugated Polyions

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ABSTRACT: The layer-by-layer molecular-level manipulation of conjugated polyions has been successfully utilized to fabricate ultrathin multilayer films and multilayer heterostructures. Through a process involving the alternate spontaneous adsorption of oppositely charged polymers from dilute aqueous solutions, multilayer thin films were fabricated from a variety of different bilayer combinations including conjugated/nonconjugated polyion bilayers, conjugated/conjugated polyion bilayers, and precursor polymer/conjugated polyion bilayers. UV–vis absorbance measurements revealed that in all cases the bilayer deposition process was linear and highly reproducible from layer to layer. Kinetic studies showed that the equilibrium adsorption of a polyion layer is reached within about 10 min and the process can be carried out onto different substrate surfaces. The typical bilayer thickness ranges from approximately 10 to 25 Å and can be readily controlled by variations in such parameters as solution concentration, pH, doping level, and ionic strength.

Introduction

The development and utilization of conjugated polymers as the active elements of thin-film electronic and optical devices continue to be a highly pursued area of research. These materials are generally manipulated into thin films via simple spin-casting techniques. However, it is becoming increasingly more apparent that more control over the molecular and supramolecular organizations of these materials is needed to fully exploit their novel optical and electrical properties. For example, multilayer thin films comprised of separate hole and electron transport layers are currently being considered for use in light-emitting diodes based on conjugated polymers.[1] The ultimate realization of this particular approach would be the ability to manipulate conjugated polymers into layers with molecular dimensions in a highly controlled manner. Although the Langmuir–Blodgett processing technique provides such control,[2] it is generally considered most useful for studying model systems of limited technological utility. Recently, a new layer-by-layer processing technique involving the alternate deposition of adsorbed layers of oppositely charged polyelectrolytes from dilute solutions has emerged[3,4] as a viable means to manipulate polymers into multilayer thin films. This approach provides molecular-level control over the thickness and architecture of multilayer thin films, is remarkably simple to use, and is readily extended to a wide variety of polymers including many different electroactive polymers.

The basic process involves dipping a substrate into a dilute aqueous solution of a positively charged polymer, rinsing the substrate with water, and subsequently dipping it into a dilute aqueous solution of a negatively charged polymer (for suitably treated substrates, it is also possible to start the process with a polyanion). Multilayer thin films are prepared by simply repeating this basic bilayer deposition process. As long as the substrate is alternately dipped into a polycation solution and a polyanion solution, multilayer thin films with precisely controlled thicknesses and molecular architectures can be readily fabricated. In this series of papers, it will be demonstrated that this new process can be successfully carried out with a wide variety of quite different materials including conjugated and nonconjugated polycations and polyanions,[4] conjugated polymer precursors,[5] p-type doped conducting polymers,[6] polyimide precursors,[7] polyion molecular dyes,[8] and fullerenes ("Bucky Balls") fitted with ionizable surface groups.[5]

Experimental Section

Poly(thiophene-3-acetic acid) (PTAA) was prepared by the ferric chloride polymerization of ethyl thiophene-3-acetate (Lancaster Synthesis) followed by acid hydrolysis of the ester group.[9] Sulfonated polyaniline (SPAn) was synthesized using the procedure described by Epstein et al.[10] Poly[(*N*-methylpyridinium-2-yl)acetylene] (PMPA) was provided by Dr. Blumstein and co-workers,[11] and the poly(*p*-phenylenevinylene) (PPV) precursor was supplied by Dr. Hsieh of Xerox Corp.[12] Poly(allylamine) hydrochloride (PAH) (MW = 28 000) was used without further purification (from Aldrich Chemical Co.).

Solutions containing PTAA were prepared by dissolving the polymer in a 0.1 M solution of sodium hydroxide, converting the polymer to its salt form. The solution was then acidified with HCl to a pH of 4.8 unless otherwise specified. The ionic strength was adjusted to approximately 0.5 M by adding sodium chloride. The solutions were then filtered through 0.8 μm followed by 0.45 μm filters. The SPAn solutions were prepared following a similar procedure using HCl or $MeSO_3H$ to render a pH 3.0 solution, unless otherwise stated. The ionic strength was adjusted to approximately 0.1 M by adding sodium chloride, and in this case the solutions were filtered through 0.8 μm filters. The polycation solutions were prepared by simply dissolving the polymer in acidic aqueous solutions. In all cases the pH was chosen to be the same as that of the polyanion solution.

Glass slides with hydrophilic, hydrophobic, or positively charged surfaces were used as substrates for all of the adsorption experiments. These substrates were cleaned by first placing them in a hot H_2SO_4/H_2O_2 (7:3) bath for about 1 h and then in a $H_2O/H_2O_2/NH_3$ (5:1:1) bath at 40 °C for 30 min. The substrates were extensively rinsed with Milli-Q water after each cleaning step. The above procedure produces hydrophilic substrates. Hydrophobic surfaces were created by gas-phase treatment of these slides with 1,1,1,3,3,3-hexamethyldisilazane (HMDS from Aldrich). A few drops of the HMDS were placed in a desiccator containing the substrates

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and then evacuated and maintained at a static vacuum (200 μTorr) for 36 h. The treatment was completed by rinsing with hexane and Milli-Q water to remove any residual HMDS. The positively charged surfaces were made by treating the hydrophilic slides with (*N*-2-aminoethyl-3-aminopropyl)trimethoxysilane (TMS) solution. The precleaned surfaces were first conditioned by successive rinses in methanol, methanol/toluene (1:1), and pure toluene. They were then immersed in a 5% TMS in toluene solution for 15 h. The TMS gel-coated substrates were then heated in a warm toluene bath for 1 h and rinsed in toluene, methanol/toluene (1:1), and methanol for 2 min. Finally, they were extensively rinsed with Milli-Q water to remove residual TMS and dried. To produce a negatively charged surface, a single layer of a polyanion was adsorbed onto some of these aminosilanized slides by immersing them in a dilute solution of the polyanion.

Multilayer films were fabricated by alternately dipping glass slides in solutions containing the polycations and polyanions. The substrates were typically dipped for 10 min, washed with acidic solution to remove residual polymer, and dried with an air stream. The pH of the washing solution was set according to the dipping solutions. For hydrophilic and hydrophobic surfaces, the substrates were first immersed in the polycation solutions since the reverse order results in a poor deposition process. For PTAA it is of particular importance to filter the solutions before dipping as this procedure was found to essentially eliminate the formation of polymer aggregates and their consequent effect of increasing the amount of material delivered to the substrate during the adsorbing process.

A Sloan Dektak 8000 profilometer with a stylus pressure of 12 mg was used to determine the thickness of multilayer films (typically on films that contained at least 25 bilayers). Ultraviolet–visible absorption spectra were used to monitor the layer-by-layer deposition process of the optically active material in the system. After each deposited layer a regular increment in the absorption spectrum could be easily observed. Polarized visible light was used to determine the preferential orientation of the polymer chains relative to the substrate. From the visible absorption data it was also possible to estimate the amount of polymer adsorbed per unit area (Γ). This estimation was carried out by initially generating a calibration curve of the visible absorbance maximum versus concentration for a set of very dilute PTAA solutions. Beer's law was then used to determine the molar absorption coefficient (ϵ) for the material. Assuming that the conformation of the short polymer chains in dilute solution is approximately similar to that in the solid state, one can use ϵ to calculate a factor for converting visible absorption values into values of Γ. For PTAA this value was found to be 270 mg/m^2 per absorption unit. An Oriel Instaspec Model 77200 multichannel analyzer was used for all of the optical experiments.

Results

Figure 1 displays the chemical structures of some of the various polycations and polyanions that we have used to fabricate self-assembled multilayer thin films containing conjugated polymers. In all cases, a linear deposition pattern is observed with respect to the amount of polymer deposited per bilayer combination. This is illustrated in Figure 2, which shows how the visible absorbance associated with the $\pi-\pi^*$ electronic transition of the conjugated polymer component varies with the number of layers deposited for selected examples. As can be seen in this figure, the deposition process is linear, indicating that the amount of material deposited per bilayer is completely reproducible from layer to layer regardless of the nature of the polycation/polyanion combination. Thus, multilayer thin films can be readily fabricated from polycation/polyanion combinations that include conjugated/nonconjugated polyions (Figure 2B,D), conjugated/conjugated polyions (Figure 2C), and precursor polymer/conjugated polyions (Figure 2A). In the case of the precursor films, thermal treatment of the multilayer film converts the precursor into its fully conjugated form (PPV precursors)[5] or its fully imidized form (polyimide precursors).[7] It should also be noted that the conjugated polyions used to fabricate multilayer films need not be of high molecular weight as illustrated by the fact that PTAA, an oligomer with only 8–12 repeat units, is readily manipulated into multilayer thin films with as many as 100 layers. As will be discussed shortly, the multilayer deposition process can be successfully carried out with a variety of different substrates including hydrophilic, hydrophobic, and charged substrates. The process is also not limited by the shape or size of the substrate.

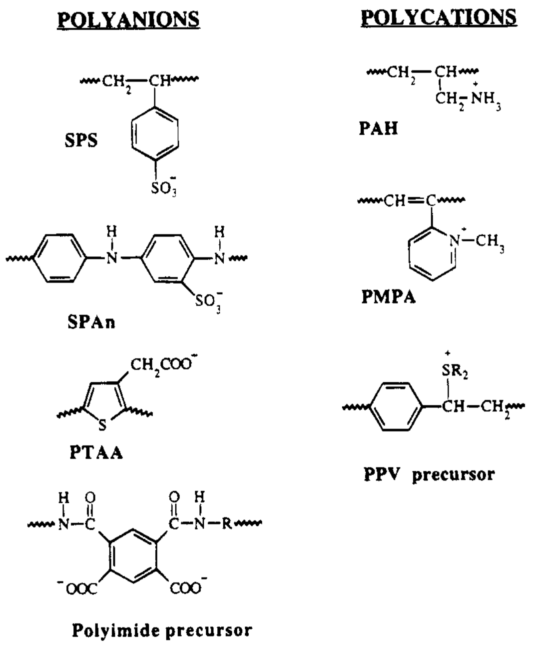

Figure 1. A selection of conjugated and nonconjugated polyions that have been successfully used to fabricate multilayer thin films via the self-assembly process.

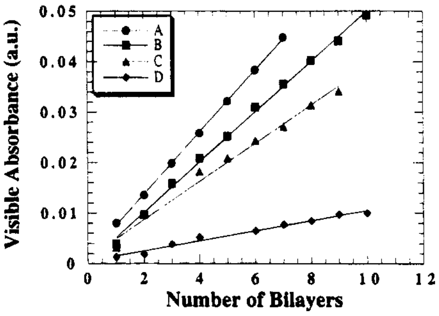

Figure 2. Dependence of the visible absorption on the number of bilayers deposited for different polycation/polyanion combinations: (A) PTAA/PPV precursor, (B) PTAA/PAH, (C) PTAA/PMPA, and (D) SPAn/PAH (PTAA systems measured at 420 nm, SPAn at 630 nm).

In order to establish the adsorption behavior of the relatively rigid conjugated polymers used in this work, we have examined in detail the single and multilayer deposition of the PTAA/PAH and SPAn/PAH systems. The former bilayer combination represents a system that utilizes a low molecular weight conjugated polyion fitted with weak carboxylic acid groups whereas the latter bilayer combination represents a system that utilizes a higher molecular weight conjugated polymer fitted with strong sulfonic acid groups. Since the sulfonated polyaniline backbone can be protonated (doped) in acidic solutions, this polymer is actually an

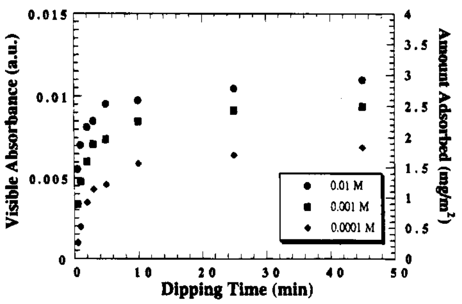

Figure 3. Time-dependent adsorption behavior for a single adsorbed layer of PTAA deposited onto a positively charged surface as a function of solution concentration (visible absorption measured at 420 nm).

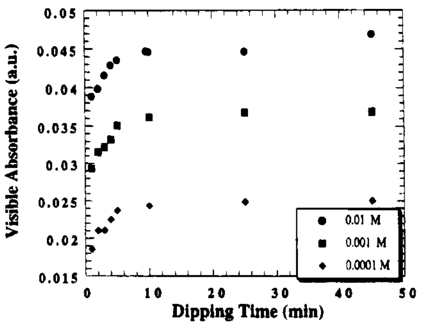

Figure 4. Time-dependent adsorption behavior for a single adsorbed layer of PTAA deposited onto a 5-bilayer PTAA/PAH film as a function of solution concentration (visible absorption measured at 420 nm).

amphoteric polyelectrolyte as it is capable of supporting both negative and positive charges.

Poly(thiopheneacetic acid)/Poly(allylamine) Bilayer Deposition. In order to understand the deposition behavior of the PTAA/PAH system, we first studied the adsorption of one single layer of the conjugated polyanion onto different substrates. Three different concentrations of the PTAA solution were used: 1×10^{-4}, 1×10^{-3}, and 1×10^{-2} M. These solutions were operated at a pH of 4.8 and at an ionic strength of approximately 0.5 M (adjusted with NaCl). Two basic experiments were performed. In one case, adsorption was carried out on chemically treated slides and on hydrophilic and hydrophobic glass slides that were precoated with a single adsorbed layer of PAH (1×10^{-3} M dipping solution). The chemically treated slide was positively charged due to the presence of covalently bound protonated amino groups whereas the hydrophobic and hydrophilic glass slides carried a net positive charge due to the presence of a single adsorbed layer of PAH. In the second case, adsorption was carried out on hydrophilic, hydrophobic, and chemically treated substrates that had been precoated with 5 bilayers of self-assembled PTAA/PAH. Comparison of the adsorption behavior of PTAA onto these various substrates provides insights into the bilayer deposition process at different stages of the multilayer film's growth. It should be noted that it was not possible to deposit PTAA directly onto hydrophilic or hydrophobic surfaces; the deposition was limited and very nonuniform. Thus, quality multilayer deposition in this case can only be started by first depositing a polycation layer or by using a positively charged substrate.

Figure 3 shows the time-dependent growth of a single adsorbed layer of PTAA onto a positively charged surface (chemically treated slide). For each curve, all points correspond to the same substrate which was taken out of the solution, washed, dried, measured, and put back into the solution. The total measured absorbance of one layer obtained by this method and one layer adsorbed without interruption are essentially the same. This figure shows that, for the conditions used, the deposition of one PTAA layer onto a flat, nonporous, positively charged substrate is more than 85% complete within the first 5 min of dipping and reaches a pseudoplateau after 10 min. Measurements made on samples immersed for longer times (up to 24 h) show that no significant additional adsorption occurs beyond the first 45 min of deposition. Also note that the amount of polymer adsorbed is strongly dependent on the concentration of the dipping solution, with higher concentrations resulting in a greater amount of adsorbed PTAA at equilibrium. The estimated amount of PTAA adsorbed at equilibrium is in the range typically found in polymer adsorption studies, i.e., 1–10 mg/m^2.[13]

Very similar results were obtained for the adsorption of one layer of PTAA onto hydrophilic and hydrophobic substrates that were precoated with a single PAH base layer. For these substrates, the amount of polymer adsorbed at equilibrium was essentially identical to that observed on chemically treated slides for the two higher concentration solutions and about 40% less for the most dilute solution. These results show that a single adsorbed layer of PAH of sufficient charge density can be successfully deposited onto both hydrophilic and hydrophobic substrates, thereby making it possible to deposit a subsequent layer of PTAA and start the multilayer deposition process. The adhesion of the PTAA/PAH bilayer to the substrate as determined by a simple tape–peel test was found to be outstanding for both the chemically treated and hydrophilic slides but very poor for the hydrophobic slides (the faint yellow color of PTAA was removed with the tape). The initially deposited PAH base layer therefore appears to adhere well to hydrophilic substrates (adhesion comparable to chemically treated slides) but exhibits only a weak affinity for hydrophobic substrates.

Figure 4 shows the time-dependent growth of a single adsorbed layer of PTAA onto a chemically treated slide precoated with 5 bilayers of PTAA/PAH. Again a strong concentration dependence is observed as well as a very fast adsorption process. In this case, however, the adsorption process is much better defined as indicated by the obtainment of a true equilibrium plateau after 10 min of deposition. Thus, although a single adsorbed layer of PAH is sufficient to start the multilayer deposition process, the surface coverage and charge density appear to be more uniform after a number of bilayers have been deposited, thereby eliminating any effects that the substrate itself may have on the adsorption process. Water contact angle measurements of multilayer thin films fabricated from this bilayer combination indicate that two bilayers are required to totally eliminate the effects of the substrate.[14]

As might be expected, all of the different substrates precoated with 5 bilayers of PTAA/PAH displayed essentially the same behavior with regard to the time-dependent adsorption of a single layer of PTAA. In other words, the deposition process is not influenced by the nature of the substrate once a few bilayers have been successfully deposited. This is best illustrated by Figure 5, which shows how the visible absorbance (measured at 420 nm) varies with the number of deposited bilayers of PTAA/PAH for the three different substrates examined in this work. In this case, the

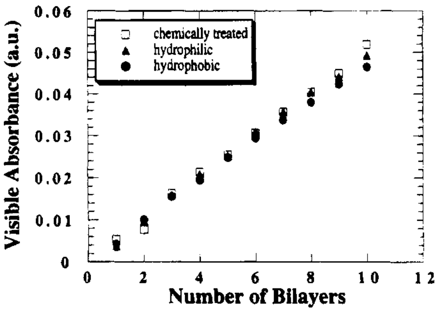

Figure 5. Visible absorption (measured at 420 nm) versus the number of PTAA/PAH bilayers deposited onto different surfaces.

PTAA layers were adsorbed from a 1 × 10^{-3} M solution with 10 min dipping times. It can be seen that in all cases the amount of PTAA adsorbed during multilayer buildup per bilayer is essentially the same for all substrates and is remarkably reproducible from layer to layer. For the multilayer thin films it was again observed that the best adhesion was found for treated and hydrophilic substrates. Hydrophobic substrates consistently exhibited very poor adhesion. Similar results were obtained with both the lower and higher concentration PTAA solutions; i.e., for a given solution concentration, the amount of PTAA adsorbed per bilayer was the same for all three of the substrates evaluated.

Using the kinetic data discussed above, an attempt was made to fit the PTAA results to the well-known Langmuir–Schaefer (LS) relationship[15] which is appropriate for a diffusion-controlled adsorption process at low surface coverage. According to this relationship, at a given adsorbate concentration, a plot of the amount adsorbed (Γ) against the square root of the adsorption time should yield a straight line that passes through the origin. The slope for these lines determines the effective diffusion coefficient, which typically reflects both the time to diffuse to the surface and the time required for the adsorbate to relax to its surface conformation. This approach is only valid when the polymer concentration at the boundary of the solution and substrate is essentially zero, which means its use may only be appropriate for a very small segment of the entire adsorption time.[16] At very short times, the polymer concentration at the interface is the same as the solution concentration and adsorption onto the uncovered surface proceeds very quickly. This results in a rapid depletion of the polymer concentration near the surface and sets up the necessary conditions for Langmuir–Schaefer type adsorption. As the surface becomes progressively more covered with polymer, however, the rate of adsorption decreases and a plateau is observed in the adsorption/time curves. Thus, depending on the details of the adsorption process (diffusion time versus the time it takes for the polymer to adopt its surface conformation, level of surface coverage, etc.), the Langmuir–Schaefer relationship may only be valid over a limited range of adsorption time.

For the PTAA system only the first 3 min of adsorption can be represented by an apparent diffusion-limiting process (linear relationship in Γ versus $t^{1/2}$), after which surface coverage is essentially complete and a plateau is reached for all of the concentrations. The diffusion coefficients obtained for the PTAA/PAH system for the adsorption of a PTAA layer onto a chemically treated substrate and onto a substrate precoated with 5 bilayers of PTAA/PAH were all found to be about the same for a given solution concentration. However, the diffusion coefficients varied over 4 orders of magnitude (from 10^{-11} to 10^{-7} cm^2/s) with decreasing solution concentration. The fact that similar values are obtained for the single layer and multilayer adsorption process shows that the kinetics of PTAA adsorption are similar at all steps in the multilayer deposition process; i.e., the time dependence of PTAA adsorption is independent of how many bilayers have been deposited onto the substrate. This is not too surprising given the similar surface that the polymer is adsorbing onto during deposition, the low molecular weight of this material, and its conformationally restrictive rigid-rodlike nature. What is surprising is the fact that the calculated effective diffusion coefficient varies over 4 orders of magnitude from the lowest to highest solution concentration. This reflects the fact the slopes of the Γ versus $t^{1/2}$ plots were essentially the same for all concentrations. We attribute this large variation in diffusion coefficient with concentration to the fact that the PTAA adsorption process is very fast, thereby providing a limited range of useful data to determine the diffusion coefficient; i.e., the plots are linear over a very narrow range of times. In other words, the Langmuir–Schaefer relationship is simply not valid for this particular system in the time regime accessible by this type of experiment. A rough estimate of the effective diffusion coefficient of the PTAA system is therefore best obtained from the lowest concentration solution, which provides at best a lower limit for the diffusion coefficient of about $D = 10^{-7}$ cm^2/s. It most probably is even larger than this value.

Table 1. Average Thickness and Optical Absorbance per Bilayer of PTAA/PAH Multilayer Films Fabricated with a Dipping Time of 10 min onto Positively Charged Surfaces

PTAA concn (M)	thickness/bilayer (Å)	absorption/bilayer (420 nm)
1 × 10^{-4}	10 ± 3.2	0.0039
1 × 10^{-3}	16 ± 2.5	0.0060
1 × 10^{-2}	23 ± 1.6	0.0079

The thicknesses contributed per bilayer for the PTAA/PAH system deposited from different concentration PTAA solutions for an immersion time of 10 min are listed in Table 1. Also included in this table are the visible absorption per bilayer values obtained at 420 nm. These thickness and absorption per bilayer values were obtained by measuring the total thickness or optical absorption of multilayer films comprised of at least 30 bilayers and then dividing by the total number of bilayers. They therefore represent an average contribution per bilayer. It can be seen that the average thickness per bilayer and average optical absorption per bilayer both essentially increase by a factor of 2 from the most dilute to the most concentrated PTAA solution. In fact, for the PTAA/PAH system, a plot of the optical absorbance of multilayer films fabricated from different concentration PTAA solutions versus measured film thickness reveals an essentially linear relationship, indicating that an increase in the optical absorption per bilayer corresponds directly to an increase in the thickness of the PTAA layer.

Based on work carried out in our group with other PAH-based bilayer systems and the work of Decher and colleagues,[3] we estimate the thickness contributed per bilayer by the PAH used in this study to be in the range of 4–8 Å. If it is assumed that the thickness contributed per bilayer by PAH is not influenced appreciably by the concentration of the PTAA dipping solution, it can be

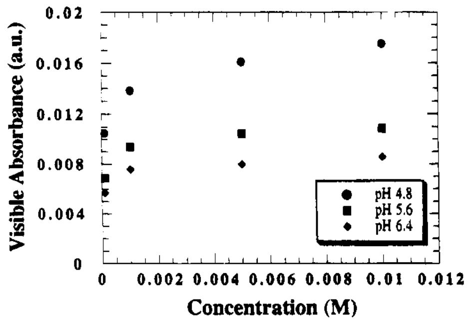

Figure 6. pH dependence of the visible absorption versus concentration isotherms of multilayer films fabricated from different concentration PTAA solutions. All points were generated from 1-bilayer films deposited onto charged substrates.

estimated that the thickness contributed per bilayer by PTAA increases from about 5 to about 18 Å as the concentration of the PTAA dipping solution increases from 10^{-4} to 10^{-2} M. This is a reasonable assumption considering the fact that the same concentration PAH dipping solution was used throughout this work. The significance of this thickness increase will be examined in the Discussion.

pH Effects. The adsorption of PTAA onto positively charged surfaces was also found to be dependent on solution pH as is shown in Figure 6. In this case, PTAA adsorption was carried out on substrates previously coated with one PTAA/PAH bilayer. The isotherms presented in this figure show that the equilibrium amount of PTAA adsorbed for a given PTAA solution concentration increases as the pH decreases. The isotherms in this figure are of the high-affinity type, which is the usual behavior observed in polymer adsorption studies. This type of pH dependence is typical for weak polyelectrolytes, such as PTAA, in which the degree of chain ionization α depends upon the pH of the solution (increases with increasing pH). Previous workers, for example, have shown that the amount of weak polyelectrolyte adsorbed onto a charged surface is maximum at pH values about 1 pH unit below the pK_0 of the polyacid.[17] If it is assumed that the pK_0 value of PTAA is similar to those of acetic acid and related polyacids (pK_0 = 4.3–4.9), the maximum adsorption of PTAA should occur below this value. Experimentally, the minimum useful pH level for a PTAA solution is 4.8. Below this level the solution tends to precipitate and cannot be used for multilayer assembly. Thus, for this system, it is not possible to ascertain where the maximum in adsorption occurs at lower pH levels. In the case of the weak polyelectrolyte poly(acrylic acid)[18–20] the maximum occurs around pH = 3.

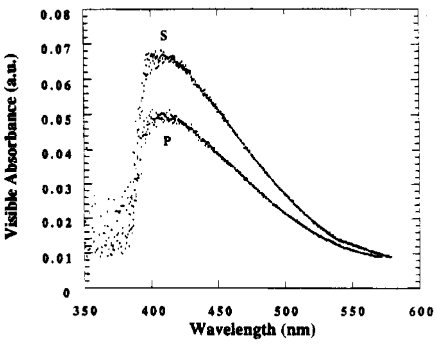

Figure 7. P- and S-polarized UV–vis spectra of a 9-bilayer PTAA/PAH multilayer film deposited from a 1 × 10^{-3} M PTAA solution.

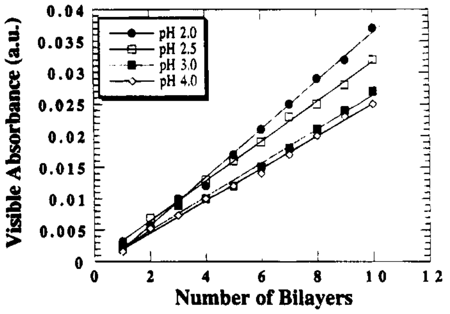

Figure 8. Influence of pH on the visible absorption (measured at 630 nm) versus number of deposited bilayers curves of SPAn/PAH. All SPAn solutions were 5 × 10^{-4} M with the pH adjusted with HCl, and the films were fabricated onto positively charged substrates.

Orientation Studies. The orientation of the PTAA chains within the multilayer thin films was probed by polarized UV–vis spectroscopy: a technique commonly used to determine whether conjugated chains have a preference to lie within the plane of the substrate or perpendicular to the substrate plane.[21] This was accomplished by comparing the intensities of spectra recorded with light polarized parallel to (S-polarized) and with a component perpendicular to (P-polarized) the surface of a substrate placed at a 45° angle with respect to the polarized beam. An example of a typical pair of S- and P-polarized spectra is shown in Figure 7, which shows a PTAA/PAH film with 9 bilayers fabricated from a 1 × 10^{-3} M solution using the conditions specified earlier in this paper. This figure illustrates the general trend observed for films fabricated from different solutions onto different substrates, all of which revealed that the absorption in the S-polarized mode is always higher than that of the P-polarized mode. The ratio of S/P absorbance at peak maximum was found to be 1.4 ± 0.1 regardless of solution chemistry or substrate type. This type of polarization dependence indicates that, on average, the PTAA chains are lying preferentially in the plane of the substrate.

Multilayer Deposition of the SPAn/PAH System. In contrast to the weak polyelectrolyte PTAA, SPAn is a strong polyelectrolyte due to the presence of sulfonic acid groups on approximately every other benzene ring. This polymer, however, can also be acid doped by protonation of the nitrogen amine groups. The degree of acid doping depends on the pH level of the solution, increasing with lower pH. These two effects confer to SPAn an amphoteric character that makes the SPAn/PAH system more complex compared to the PTAA/PAH system.

Preliminary multilayer deposition studies with this bilayer system were carried out on solutions in which HCl was used to control pH and doping level. Figure 8 shows plots of the absorbance of SPAn (measured at 630 nm) versus the number of bilayers deposited onto positively charged glass slides for SPAn solutions at various pH levels (all SPAn solutions were 5 × 10^{-4} M and adjusted to an ionic strength of 0.1 M with NaCl, the PAH solution was 5 × 10^{-4} M at a pH of 3.0, and films were rinsed between dips with pH 3.0 HCl solutions). In this case, 2 min dipping times were used as it was found that the pH of the HCl-adjusted solutions was not stable over long periods of time, thereby producing results that were difficult to reproduce. A linear relationship was observed at all pH levels, indicating that even for this more complex system, the self-assembly technique allows a high level

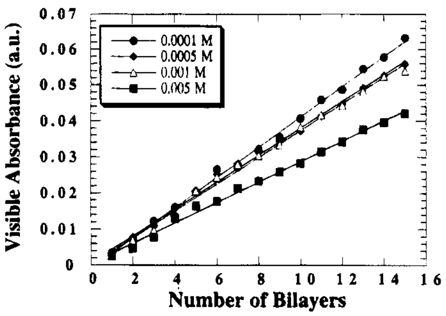

Figure 9. Influence of concentration on the visible absorption (measured at 630 nm) versus number of deposited bilayers curves of SPAn/PAH. The pH of the SPAn solutions was adjusted to 3.0 with $MeSO_3H$.

of control over the multilayer deposition process. Over this particular pH range, it can be seen that there is a weak pH dependence, with the amount of SPAn adsorbed per bilayer increasing with decreasing pH. At lower pH levels, the polyaniline backbone takes on a greater positive charge, thereby neutralizing some of the negative charge associated with the sulfonic acid groups and decreasing the overall negative charge of the polymer. The net result appears to be similar to what is observed with weak polyelectrolytes, i.e., pH changes that reduce the level of segmental electrostatic repulsion favor the adsorption of more polymer. It is not possible to explore this phenomenon over a wider pH range because there is only a narrow window of pH over which the SPAn solutions are stable (best results are obtained in the pH range of 3–4.5; solutions with lower pH levels are only stable for about a day and for higher pH levels only a very limited amount of material was adsorbed).

Although HCl can be used to adjust the pH and doping level of the SPAn solutions, we have found that its use results in solutions with limited stability and difficult to reproduce results. Significantly improved stability of the SPAn solutions, however, can be achieved by using methanesulfonic acid ($MeSO_3H$) to control pH and the doping level. With this acid, the lower concentration solutions were found to be stable without precipitation for more than 3 weeks while with HCl, polymer precipitation was typically observed within a few days.

Figure 9 shows how the visible absorbance (measured at 630 nm) varies throughout the multilayer deposition process for films fabricated from SPAn solutions with different concentrations. All of the SPAn solutions were adjusted to an ionic strength of 0.1 M with NaCl and a pH of 3.0 with $MeSO_3H$; the PAH solution was 1×10^{-3} M at a pH of 3.0, and the films were rinsed between dips with pH 3.0 $MeSO_3H$ solutions. Dipping times of 10 min were used since a preliminary time dependence study showed, as observed for the PTAA/PAH combination, that more than 95% of the adsorption process is completed within this time. In this case, it can be seen that the amount of SPAn deposited per dip actually decreases with increasing polymer concentration. This is in sharp contrast to what was observed with the PTAA system and is in fact different from what was observed with SPAn solutions whose pH was adjusted with HCl (the amount of polymer deposited per dip increased with increasing solution concentration).

Table 2. Average Thickness and Optical Absorbance per Bilayer of SPAn/PAH Multilayer Films Fabricated from pH 3.0 $MeSO_3H$ Solutions onto Positively Charged Substrates with a Dipping Time of 10 min

SPAn concn (M)	thickness/bilayer (Å)	absorption/bilayer (630 nm)
1×10^{-4}	19 ± 2.4	0.0040
5×10^{-4}	20 ± 1.7	0.0038
1×10^{-3}	19 ± 2.1	0.0038
1×10^{-2}	19 ± 2.5	0.0028

Thickness measurements were carried out to determine if this change in the amount of SPAn deposited per dip also reflected changes in the average bilayer thickness. Table 2 lists the average thickness and absorbance per bilayer values obtained from films fabricated from these different SPAn solution concentrations. It can again be seen that the amount of SPAn adsorbed per dip as determined by visible absorption measurements increases with decreasing solution concentration. The largest increase, however, occurs between concentrations of 5×10^{-3} and 1×10^{-3} M and thereafter only a very modest increase in the average bilayer absorption is observed with decreasing concentration. The average thickness per bilayer, on the other hand, remains essentially the same over the entire concentration range (about 20 Å). Thus, within experimental error, the three lowest concentration solutions actually deliver essentially the same visible absorption and thickness per bilayer, indicating a nearly concentration-independent deposition process in this range. The highest concentration solution (5×10^{-3} M) also results in an average bilayer thickness of about 20 Å but produces multilayer films with less visible absorption per bilayer. Assuming a constant thickness contribution from the PAH molecules, Table 2 suggests that the SPAn molecules are less densely packed in each bilayer. It is not entirely clear why this would be the case, although it could simply reflect the fact that this and higher concentration solutions of SPAn are more prone to precipitation on standing even when $MeSO_3H$ is used to adjust pH.

These preliminary results show that SPAn is a more complex polyion than PTAA. More systemic studies are therefore necessary to understand the adsorption behavior of this material. Nevertheless, under suitably controlled conditions, it is possible to carry out well-behaved layer-by-layer processing of this material and fabricate uniform, high optical quality multilayer thin films.

Multilayer Heterostructures. The ability to process conjugated polymers in a layer-by-layer fashion makes it possible to fabricate complex multilayer heterostructures in which layers of electronically dissimilar materials are stacked in a controlled sequence within the film. This is illustrated in Figure 10, which shows the visible spectrum of a multilayer thin film comprised of a total of 40 alternating bilayers of PTAA/PAH and SPAn/PAH. The conjugated polymers and PAH were deposited from 5×10^{-4} M solutions at a pH of 4.5 (HCl) using 2 min dip times.

For this bilayer combination, the absorption spectrum is a simple superposition of the spectra of the two conjugated polymers; λ_{max} for PTAA is about 440 nm and about 600 nm for SPAn at this doping level. The inset shows the absorption of the film measured at wavelengths of 470 nm after each deposition of a PTAA/PAH bilayer and 650 nm after each deposition of a SPAn/PAH bilayer as a function of the number of deposited bilayers. Linear growth at both of these wavelengths demonstrates that the amount of each conjugated polymer deposited in the multilayer is the same from bilayer to bilayer.

Through the construction of such heterostructure thin films, it is possible to systematically study electronic

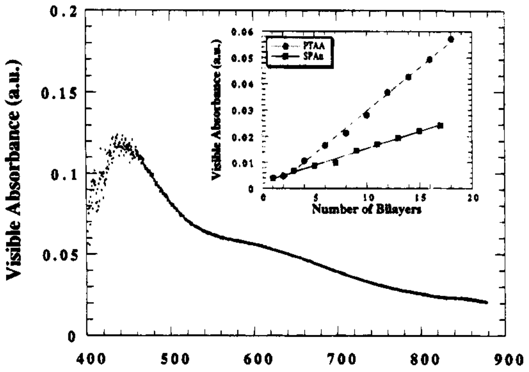

Figure 10. Visible absorption spectrum of a 40-bilayer heterostructure film, (PTAA/PAH/SPAn/PAH)$_n$, fabricated from 5×10^{-4} M solutions. The inset shows the dependence of the visible absorption with the number of bilayers.

interactions between conjugated polymers in interface-rich structures. For example, we are currently investigating photoinduced charge transfer interactions in multilayer heterostructures comprised of electron-accepting and electron-donating conjugated polymers and electroluminescence in self-assembled multilayer heterostructures comprised of electron transport, hole transport, and emitter layers. The details of this work will be published separately.

Discussion

Each step in this new multilayer deposition process involves the adsorption of a charged polymer onto an oppositely charged surface from a dilute aqueous solution. Control over important structural parameters such as the thickness of each deposited layer and the orientation and conformation of the deposited polymer chains therefore requires a fundamental understanding of the factors that control the adsorption of a single charged polymer layer onto a surface. The adsorption of polyelectrolytes onto charged and noncharged surfaces has been studied in great detail over the years.[13,18,22,23] For relatively flexible polymer chains, it has been found that the thickness and conformation of the adsorbed polymer chain depend primarily on the substrate/polymer affinity as mediated by the level of the effective intrasegmental repulsion of the ions distributed along the chain. High levels of intrasegmental repulsion, for example, tend to produce thin adsorbed layers with the chain adopting a more extended conformation on the surface (frequently referred to as extended trains), whereas lower levels of intrasegmental repulsion tend to produce thicker layers due to the existence of a greater fraction of polymer segments present in loops and tails. The level of intrasegmental repulsion of a polyelectrolyte can be manipulated by changes in the ionic strength of the polymer solution (shielding effect) and/or by changes in the charge density along the polymer chain (such as by changing the pH of a solution supporting a weak polyelectrolyte). The nature and charge density of the substrate surface also influence the thickness and conformation of the adsorbed polymer chain.

To date, the adsorption behavior of all of the conjugated polyions that we have used to construct multilayer thin films in general appears to be similar to what has been observed with more conventional polyelectrolytes. In the case of PTAA, a low molecular weight conjugated polymer fitted with a weak acid pendant group, the amount of polymer adsorbed to a surface during a single dip depends strongly on pH and solution concentration. The strong pH dependence is related to changes in the degree of ionization of the carboxylic acid groups with changing pH (as pH increases, the net negative charge of the polymer increases). As has been found with many weak polyelectrolytes, highly ionized polymers produce thinner layers due to stronger intrasegmental repulsion effects. Although a systematic ionic strength study was not undertaken, adding salt to the PTAA solutions to partially neutralize the net charge of the chain and decrease its solubility has also been found to enhance the adsorption of this polymer onto surfaces.

It is difficult to ascribe the differences observed in the amount of PTAA adsorbed from solutions with different pH and concentration levels to changes in the population of chain segments present as trains, loops, and tails. The PTAA oligomers used in this study are only comprised of 8−12 repeat units and are quite rigid. It is therefore not appropriate to discuss this adsorbed polymer in terms of loops and trains. A more fruitful basis for interpreting these data is to consider the PTAA used in this work to behave more as a rigid ionic dyelike molecule than as a high molecular weight, flexible polyelectrolyte. In this scenario, the rodlike PTAA molecules can adsorb either with a flat or edgewise orientation with respect to the substrate surface. Visible dichroism results indicate that in all cases examined the PTAA molecules have a tendency to preferentially orient with their long axes within the plane of the substrate (independent of solution concentration). This would support the notion that the different layer thicknesses obtained with different solution concentrations are associated primarily with the tendency of the PTAA molecules to lie with the thiophene rings either flat to the surface or in an edgewise manner as opposed to in-plane versus out-of-plane changes in the orientation or the existence of loops and tails. This technique unfortunately cannot distinguish between an edgewise versus facewise orientation as both orientations absorb light in the same manner (absorption is polarized along the chain axis). Molecular models indicate that the thickness of a PTAA adsorbed layer is about 4 Å when the molecules lie flat on the surface and about 14 Å when they lie in an edgewise orientation. The thickness contributed per bilayer for the PTAA/PAH system changes from about 10 to 23 Å from the lowest to highest solution concentrations examined. Assuming that the thickness contributed by the PAH molecules remains essentially constant at a value of about 5 Å, it seems reasonable to conclude the thickness change that occurs with increasing PTAA solution concentration is in fact associated with a change from a flat to an edgewise orientation of the PTAA molecules. The doubling of the optical absorbance per bilayer that was observed on increasing the PTAA solution concentration is also consistent with this proposal as molecular models show that an edgewise orientation results in a more densely packed adsorbed layer with approximately twice as many molecules per unit area. The change in the amount of PTAA adsorbed from solutions with different pH levels may also be related to changes in the orientation of the PTAA molecules although more work is needed to confirm the origin of this effect.

Similar behavior has been observed when dye molecules are adsorbed onto surfaces.[24] At low dye concentrations with suitable substrate/adsorbate interactions, the molecules can assume an energetically favorable facewise orientation but the more severe competition for available surface sites that takes place at higher concentrations (faster kinetics) forces the molecules to adopt an edgewise orientation. In other words, with the faster kinetics associated with higher concentrations, edgewise orientation is preferred over facewise orientation due to the limited surface space available to the adsorbing molecules.

The adsorption of amphoteric SPAn molecules onto positively charged surfaces presents a rather interesting case of polymer adsorption. Kamiyama et al.[25] have studied amphoteric materials such as gelatin and found the adsorption behavior of these materials to depend strongly upon the pH of the solution, with enhanced polymer adsorption occurring near the isoelectric point (IEP). At pH levels above and below the IEP, the polymer molecules assume a net positive (below the IEP) or a net negative charge (above the IEP) and adsorption behavior is governed by the more complex interplay between ionic strength and polymer charge. Unfortunately, it is not possible to examine this type of behavior with SPAn due to its rather limited pH and concentration window of solubility. For the narrow range of pH and concentration levels that form stable solutions, the SPAn solutions deliver approximately the same amount of material during each dip, resulting in a thickness per bilayer for the SPAn/PAH system of about 20 Å. Nevertheless, under the proper conditions, this material can be used to form highly reproducible multilayer thin films with potentially interesting electrical and optical properties.

Conclusions

In summary, it has been demonstrated that facile layer-by-layer deposition of a wide variety of conjugated polyions can be successfully carried out using only dilute aqueous solutions of these materials. Preliminary studies of the adsorption behavior of these novel electroactive polymers indicate that, as has been found in single-layer adsorption studies of conventional polyelectrolytes, variations in parameters such as solution concentration, pH, and ionic strength can be used to readily control the deposition process. The demonstration of multilayer heterostructures using this new technique opens the door to the fabrication of novel thin-film molecular architectures with electrical and optical properties that can be turned at the molecular and supermolecular level.

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