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Layer-by-Layer Assembly of Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate)

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ABSTRACT: Ultrathin films of the conducting polymer system PEDOT:PSS, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate), were fabricated through layer-by-layer assembly with PAH, poly(allylamine hydrochloride). A variety of grades of PEDOT:PSS were used to study the effects of the PEDOT to PSS weight ratio and particle size on the assembly behavior. All systems studied exhibited linear film-growth behavior as indicated by film thickness and UV−vis absorption measurements. Assembly of grades with a relatively small proportion of PEDOT to PSS behaved similarly to PSS/PAH bilayer films fabricated from pristine components. Grades with a higher proportion of PEDOT resulted in thicker bilayers, primarily due to the incorporation of more PEDOT into the film. When compared to their spin-coated analogues, layer-by-layer assembled films incorporated a smaller amount of PEDOT with respect to the PSS. This is highly suggestive of partial decomplexation of the PEDOT from the PSS during the assembly process. Surprisingly, the percent of decomplexation is estimated to be just over 50% for all of the grades studied. That is, slightly less than half of the PEDOT originally present in solution is incorporated into the layer-by-layer film, independent of both the PEDOT:PSS particle size and weight ratio. The combination of this depressed level of PEDOT together with the incorporation of PAH into the film results in the conductivity of the layer-by-layer films being ∼1 order of magnitude less than that for spin-coated films of the same grade.

Introduction

Conjugated polymers have been studied in detail as thin films for an array of applications including electrochromic devices,[1,2] sensors,[3] light-emitting diodes (LEDs),[4,5] transistors,[6,7] and photovoltaics.[8,9] The polythiophene derivative poly(3,4-ethylenedioxythiophene), PEDOT, is of particular interest due to its high conductivity, transparency, and stability.[10,11] By polymerizing PEDOT in the presence of a water-soluble polyelectrolyte, poly(styrenesulfonic acid) (PSS), a homogeneously dispersed polymer complex (PEDOT:PSS) is formed.[12] Suspensions of PEDOT:PSS are now commercially available from a variety of sources, including H.C. Starck under the trade name of Baytron P. This material has found extensive utility as interfacial modification layers and flexible transparent conductive electrodes in organic devices as well as antistatic agents.[13−15] By varying the PEDOT to PSS ratio and the average particle size in solution, films with a wide range of conductivities and dramatically different properties can be fabricated. The ability to subsequently control film parameters such as surface topography and interfacial interactions[16,17] could provide a means of directly influencing device performance.

Layer-by-layer assembly is a polymer thin film deposition technique developed by Decher,[18] Rubner,[19] and others that affords molecular-level control over polyelectrolytes deposited from solution.[20] Alternately dipping a substrate between a polycation and a polyanion solution results in linear film growth with the ultimate thickness being controlled by the number of bilayers deposited. Solution properties such as pH and salt concentration can directly influence the individual bilayer thickness by modifying the polymer chain conformation in solution, the degree of ionization, and the subsequent electrostatic interactions between the polyelectrolytes.[21]

This deposition technique has commonly been used with simple polyelectrolytes such as poly(acrylic acid) (PAA), poly(styrenesulfonate) (PSS), and poly(allylamine hydrochloride) (PAH). Complexed polymer systems such as PEDOT:PSS have also been studied, though less extensively, in electrochromic devices by Hammond[22,23] and Reynolds[24] as well as in light-emitting devices by Friend.[25] In this study, the layer-by-layer assembly characteristics of select grades of PEDOT:PSS with PAH are investigated. The PEDOT to PSS weight ratio and the particle size in solution were varied with the goal of providing a more complete, fundamental understanding of how these complex systems behave.

Experimental Section

Poly(allylamine hydrochloride) (PAH, $M_w = 60\,000$ g/mol) was obtained from Polysciences, Inc., and used without further purification. Baytron P, Baytron P AG, Baytron P VP AI 4083, and Baytron P VP CH 8000 (H.C. Starck) were filtered prior to use. UV−vis spectra were obtained using a Varian Cary 5000 UV−vis−NIR spectrophotometer. Conductivity values were determined from four-point Van der Paaw resistivity measurements using a Keithley 4200 semiconductor characterization unit. Thickness measurements were obtained using a KLA Tencor P-10 surface profiler. Solutions of PAH (5.0 mM based on the repeat unit) with NaCl (50.0 mM) and Baytron P solutions (0.08−0.10 g/L based on percent solids from certificates of analysis) were made with deionized water (Millipore, resistivity of 18 MΩ·cm), were pH adjusted to 3.5 ± 0.02 with either HCl or NaOH, and were vacuum-filtered prior to use. Glass and quartz slides were cleaned by ultrasonication sequentially in

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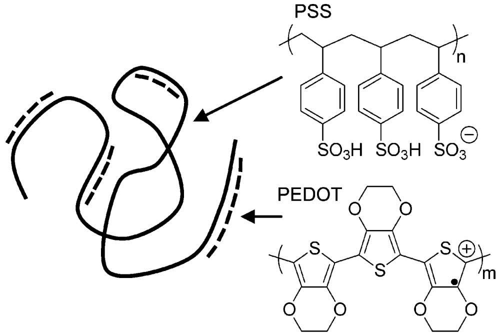

Grade of Baytron P	PEDOT:PSS[a] Weight Ratio	Avg. Particle[a] Size (nm)	σ[b] (S/cm)
AG	1:2.5	110	2
Standard	1:2.5	90	0.1
4083	1:6	42	5×10^{-3}
8000	1:20	22	6×10^{-5}

[a] Data obtained from H. C. Starck.
[b] Measured conductivity values for spin-coated films.

Figure 1. Schematic representation of the polymer complex between PEDOT and PSS and key properties for the four specific grades of commercially available aqueous dispersions of PEDOT:PSS used in this study.

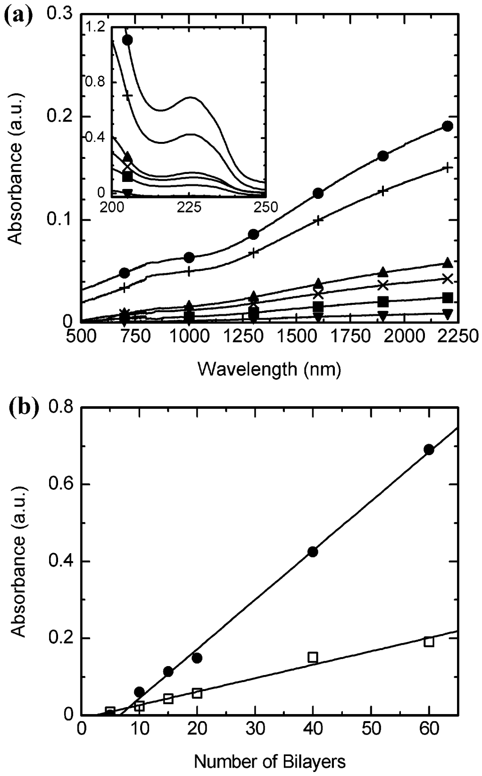

Figure 2. (a) UV−vis−NIR spectra of AG grade layer-by-layer films with 5 (▼), 10 (■), 15 (×), 20 (▲), 40 (+), and 60 (●) bilayers. The presence of doped PEDOT is evidenced by the broad absorption out to 2200 nm. The inset shows the absorption peak at 225 nm, which is associated with PSS. (b) UV−vis−NIR absorbance values at 225 nm (●) and 2200 nm (□) as a function of the number of bilayers for the films described in (a).

detergent, water, 1,1,1-trichloroethane, acetone, and methanol at 15 min intervals, followed by treatment in a low-power air plasma for several minutes using a Harrick PDC-32G plasma sterilizer.

The electrostatic self-assembly process was carried out using a Zeiss HMS series programmable slide stainer. Slides were alternately immersed in two polyelectrolyte solutions for 15 min intervals followed by three separate water rinse steps for 2, 1, and 1 min. Neat films of each Baytron P grade were fabricated by spin-coating filtered solutions onto glass slides at 500 rpm for 10 s and then 3000 rpm for 30 s.

Results and Discussion

A schematic representation of the polymer complex formed between PEDOT and PSS chains in solution is shown in Figure 1. Relatively small, oligomeric PEDOT chains (average DP = 5−15 repeat units) are electrostatically bound to longer PSS chains. The PEDOT is oxidized (i.e., doped) to the level such that, on average, there is one positive charge for every three EDOT repeat units. The counterions are provided by anionic sulfonate groups on the PSS, and the remaining unassociated sulfonic acid groups permit the PEDOT:PSS polymer complex to act as a polyanion during layer-by-layer assembly.

The four grades of PEDOT:PSS used in this study are also listed in Figure 1 along with some key physical properties. The four types are Baytron P AG (hereafter referred to as “AG”), Baytron P (hereafter referred to as “standard”), Baytron P VP AI 4083 (hereafter referred to as “4083”), and Baytron P VP CH 8000 (hereafter referred to as “8000”). The observed differences in both the weight ratio of PEDOT to PSS and the average size of the suspended particles are a result of employing different synthetic methods for the preparation of each grade. These property differences in turn give rise to a very wide range of conductivities when different grades are used to spin-coat thin films.

Layer-by-layer films comprised of PEDOT:PSS and PAH were deposited on quartz slides using each of the four grades described above. UV−vis−NIR absorption spectra were taken at various intervals to monitor the deposition process for each grade. Representative spectra for PAH/AG assembled films are shown in Figure 2a, and the general features observed hold true for all PEDOT:PSS grades studied. The broad absorbance out to 2200 nm corresponds to the metallic peak of doped PEDOT, while the absorbance at 225 nm (see inset) is due to the substituted phenyl groups in PSS.[26] The monotonic increase in both features with an increasing number of bilayers indicates that both PEDOT and PSS chains get incorporated into the layer-by-layer films. Since PEDOT itself has no electrostatic attraction to PAH (both are cationic), it is incorporated simply because of its complexation with PSS. The absorbance values at 225 and 2200 nm are shown in Figure 2b as a function of the number of bilayers deposited. The observed linear growth for each peak illustrates the fact that both PEDOT and PSS are incorporated into the film in a relative proportion that is independent of the film thickness (i.e., the number of bilayers). It should also be noted that linear fits of the data do not pass through the origin due to anomalous deposition characteristics for the first few bilayers. This is a commonly observed effect and is possibly a result of limited charge overcompensation caused by interfacial interactions with the substrate.[27]

The overall film thickness for each grade of PEDOT:PSS (measured using profilometry) is shown in Figure 3 as a function of the number of bilayers deposited. As observed for the absorbance characteristics in Figure 2, all four systems exhibited linear growth behavior based on these film thickness measurements. Both the AG and standard grades of PEDOT:PSS exhibited an average thickness of 28 Å per bilayer when assembled with PAH (given by the slope of the fitted line). This result is consistent with the fact that both grades have the same PEDOT to PSS weight ratio with only slightly different particle sizes (see Figure 1). The 4083 and 8000 grades, on the other

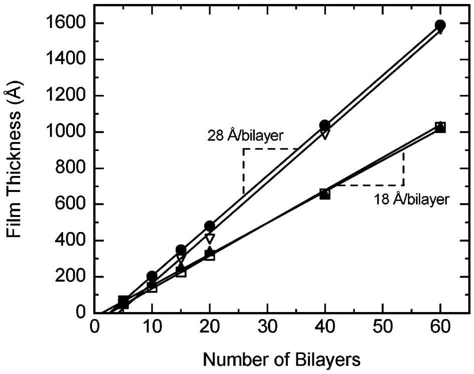

Figure 3. Film thickness as a function of the number of bilayers for AG (●), standard (▽), 4083 (□) and 8000 (▲) grades of PEDOT:PSS.

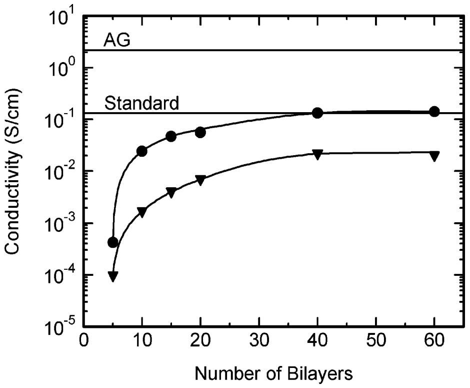

Figure 4. Conductivity of AG (●) and standard (▼) grade bilayer films. Horizontal lines correspond to the conductivity of the spin-coated films.

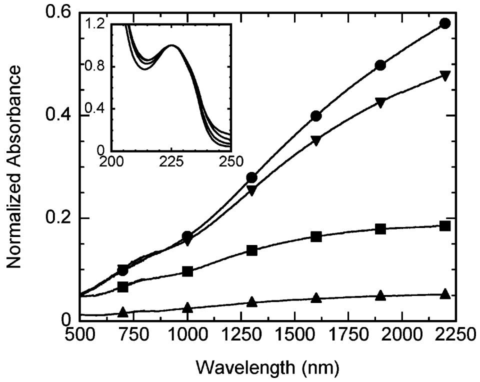

Figure 5. Normalized absorbance as a function of wavelength for spin-coated films of AG (●), standard (▼), 4083 (■), and 8000 (▲) grades of PEDOT:PSS.

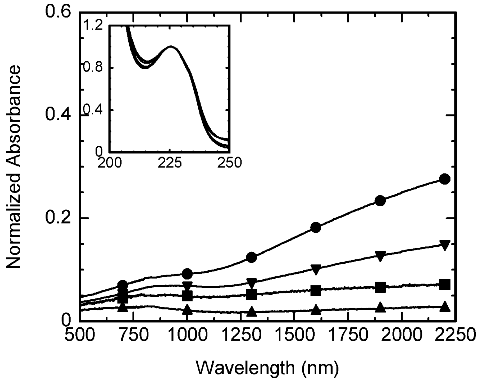

Figure 6. Normalized absorbance as a function of wavelength for 60 bilayer films of AG (●), standard (▼), 4083 (■), and 8000 (▲) grades of PEDOT:PSS.

hand, exhibited a thickness of 18 Å per bilayer. For these two systems, the relative proportion of PEDOT to PSS is much lower. It is also instructive to realize that the simple polyelectrolyte system of PAH assembled with pristine PSS has been reported to produce a thickness of 17 Å per bilayer.[28] Consequently, it appears that the 4083 and 8000 grades of Baytron P are behaving much like that of a pure polyelectrolyte when assembled with PAH, and the small amount of PEDOT that becomes incorporated into the film does not significantly affect the assembly characteristics.

To quantify the effect of PEDOT:PSS grade on thin film conductivity, in-plane Van der Paaw resistivity measurements were performed on both layer-by-layer assembled films and spin-coated films. Results for the AG and standard grades of PEDOT:PSS are shown in Figure 4. The results for the 4083 and 8000 grades are omitted due to measurement difficulties associated with the very low conductivities of these films. The conductivity values observed for spin-coated films of the AG and standard grades are lower than those provided by H.C. Stark (10−20 S/cm for AG grade and 1 S/cm for standard grade). These variations are likely a result of differences in processing and testing conditions;[29] however, since all solutions and films are treated similarly in this study, the measured conductivity values provide a valid point for comparison.

The layer-by-layer films for both grades of PEDOT:PSS exhibited a conductivity which changed greatly over the first 10 bilayers and then slowly approached a saturation value. Lower conductivity values for the first few bilayers in layer-by-layer films are consistent with observations made by Decher et al.,[27] where it was determined that these initial bilayers have a structure different from that of the bulk of the film due to their proximity to the substrate. As the number of bilayers increases, the influence of the first few layers on the measured conductivity decreases. Thus, as the film becomes thicker, the measured conductivity approaches that of the bulk. A comparison of conductivity values for spin-coated films to those for layer-by-layer films shows that the saturation conductivity value for a given layer-by-layer film is ~1 order of magnitude less than that of the corresponding spin-coated film. Factors contributing to this result could include film morphology, PAH content, or the relative proportion of PEDOT to PSS. It should be noted that the conductivities for both standard and AG grade spin-coated films exhibited little variation from the reported values for films ranging in thicknesses from approximately 70 to 110 nm.

To clarify the observed trends in conductivity, the absorption spectra of both spin-coated films and layer-by-layer assembled films for all four grades of PEDOT:PSS are compared in Figures 5 and 6, respectively. In both figures, the PSS absorbance at 225 nm is normalized to a value of one for all spectra (see insets). Consequently, a change in the relative intensity at 2200 nm reflects a change in the relative proportion of PEDOT to PSS. Note that while a change in the PEDOT doping level and the associated charge carrier density could also give rise to a change in the relative intensity at 2200 nm, this would be accompanied by the PEDOT $\pi \rightarrow \pi^*$ transition near 600 nm.[30] Because this absorption is not present in any of the spectra, the doping level of the PEDOT in these films is assumed to be constant, and the change is attributed to differences in the relative proportion of PEDOT to PSS present in the films. Examination of the spectra for the spin-coated films in Figure 5 illustrates this fact by showing that the absorbance value at 2200 nm decreases in going from films of high conductivity and relatively high PEDOT content (AG grade) to films of low conductivity and relatively low PEDOT content (8000 grade).

It is interesting to note that although the PEDOT to PSS weight ratio is reported to be the same for the AG and the standard grade (see Figure 1), it is observed here that in fact the AG grade has a slightly higher relative proportion of PEDOT in a spin-coated film.

An analogous comparison of absorption spectra for 60 bilayer assembled films (again for all four grades of PEDOT:PSS) is provided in Figure 6. It should first be noted that for each grade the layer-by-layer film has a reduced amount of PEDOT relative to the amount of PSS as compared to the corresponding spin-coated film shown in Figure 5. This suggests that during the assembly of the layer-by-layer film partial decomplexation of the PEDOT:PSS occurs such that a lower relative proportion of the PEDOT originally present in solution gets incorporated into the film. Furthermore, it can be seen that the reduction factor is ∼2.5, regardless of the grade of PEDOT:PSS used. This points to the fact that even though the different grades of PEDOT:PSS have different particle sizes in solution, the amount of decomplexation that occurs is independent of that particle size. It is thus estimated that slightly less than half of the PEDOT originally present in solution is incorporated into the layer-by-layer film, regardless of the grade of PEDOT:PSS used. These effects, combined with the presence of PAH in the assembled films, are likely the primary factors contributing to the significantly lower conductivities for layer-by-layer films when compared with corresponding spin-coated films.

Conclusions

The assembly behavior of PAH with select grades of PEDOT:PSS, each with varying PEDOT to PSS ratios and particle sizes, was investigated. All four systems exhibited a linear film growth response and incorporated both PEDOT and PSS into layer-by-layer films as indicated by absorption and film thickness measurements. Assembled films of both the AG and standard grades of PEDOT:PSS had an average thickness of 28 Å per bilayer, while the 4083 and 8000 grade layer-by-layer films exhibited a thickness of only 18 Å per bilayer and contained a much lower relative proportion of PEDOT to PSS. This suggests that the 4083 and 8000 grades of PEDOT:PSS behave very much like that of the pure polyelectrolyte, PSS, when assembled with PAH.

Because the layer-by-layer films have a reduced amount of PEDOT (relative to PSS) incorporated into the film when compared to the corresponding spin-coated films, it is apparent that during the assembly of the layer-by-layer film partial decomplexation of the PEDOT:PSS particles occurs. As a result, a significantly lower proportion of the PEDOT originally present in solution gets incorporated into the assembled film. This, coupled with the incorporation of insulating PAH into the layer-by-layer films, results in an overall lower conductivity of ∼1 order of magnitude when compared to the corresponding spin-coated film.

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