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Molecular-Level Processing of Conjugated Polymers. 2. Layer-by-Layer Manipulation of In-Situ Polymerized p-Type Doped Conducting Polymers

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ABSTRACT: A novel thin-film processing technique has been developed for the fabrication of ultrathin films of conducting polymers with angstrom-level control over thickness and multilayer architecture. As part 2 of this series, we present here the molecular self-assembly of p-doped conducting polymers (e.g., polypyrrole and polyaniline), a layer-by-layer process in which a substrate is alternately dipped into a chemically active aqueous solution of an in-situ polymerized conjugated polymer and a solution of a polyanion. In-situ oxidative polymerization produces continuously the highly conductive, underivatized form of the conjugated polymer, which is deposited in single layers of precisely controlled thickness as it is formed. The thickness of each layer, ranging from 20 to 60 Å, can be fine-tuned by adjusting the dipping time and the solution chemistry. The surface chemistry of the substrate (hydrophobic, charged, etc.) is key in determining the deposition characteristics and uniformity of the film. Widely different deposition characteristics onto different surfaces make it possible to selectively deposit conducting polymers onto certain, well-defined regions of a substrate by patterning the surface with different chemistries. Typical multilayer films exhibit conductivities in the range of 20–80 S/cm; however, ultrathin films with conductivities over 300 S/cm can be made with suitable adjustments to the solution chemistry.

Introduction

The processing of electrically conductive polymers into thin films is oftentimes extremely challenging since the highly conductive forms of many of these materials are completely insoluble, intractable, and infusible. The ability to work with the conducting forms of these materials is important as it avoids the need to chemically oxidize ("dope") the conjugated polymer after it has been manipulated into a thin film. In some cases, such as polypyrrole, it is only possible to work with the conducting form since the neutral polymer is not oxidatively stable. In these instances, the conducting polymer is typically formed by a chemical oxidative polymerization process. The polymerization of polypyrrole, for example, has been successfully carried out onto fabric fibers,[1] within preformed polymer matrices,[2] via "template synthesis" in microtubules,[3] and within LB films.[4] Thin films of polypyrrole can also be prepared by electrochemical polymerization onto a conducting substrate. In this latter case, it has been demonstrated that multilayer heterostructures can be fabricated by alternately electrochemically depositing layers of different conducting polymers.[5] This approach, however, is restricted to electrically conductive substrates and to a very limited number of materials. To date, none of these techniques has been developed to the point that they afford molecular-level control over film thickness and supermolecular architecture. In other words, no technologically useful and simple technique currently exists that can provide the level of molecular and supermolecular control needed to manipulate conducting polymers into thin films with controllable and complex multilayer heterostructures.

In this second paper of this series, we describe the solution chemistry and methodologies needed to utilize the layer-by-layer processing technique described in our previous papers[6] to manipulate conducting polymers such as polypyrrole and polyaniline into multilayer thin films with angstrom-level control over both film thickness and film architecture. It will be demonstrated that will proper control of solution chemistry and the substrate surface, in-situ polymerized polypyrrole (and polyaniline) can be self-assembled with suitable polyanions into multilayer thin films. In this case, the self-assembly process is based on the ionic attractions developed between the negatively charged polyanion and the positively charged, p-type doped, electrically conductive chains of polypyrrole (continuously formed in the active dipping solution); that is, the delocalized positive charges (polarons and bipolarons) of the doped conjugated polymer backbone provide the secondary forces that are required for layer-by-layer deposition with a polyanion. In contrast to the typical polymer adsorption process in which the thickness of the deposited film is self-limiting, the polypyrrole deposits in a continuous manner onto the surface as it is being formed in the dipping solution. The thickness of the deposited layer can therefore be controlled by dipping time and solution chemistry.

With this new approach, it is possible to controllably incorporate highly conductive, p-type doped conjugated polymers into multilayer heterostructure films by using the self-assembly technique. This is accomplished by simply controlling the sequence of dips into solutions of various polycations and polyanions. As long as the substrate to be coated is alternately dipped into polycationic and polyanionic solutions, any number of different polymer layers can be built into complex, multicomponent thin films. This new self-assembly process for in-situ polymerized conducting polymers therefore opens up new and exciting possibilities in applications that require uniform large-area, ultrathin films of conducting polymers and, more importantly, in applications that can take advantage of the unique interactions achievable only in the complex supermolecular architectures of multilayer films.

Experimental Procedure

Substrate Pretreatment. The substrates were ordinary glass microscope slides treated with one of the following

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procedures to create hydrophilic, hydrophobic, negatively charged, or positively charged surfaces. All were first cleaned with a 7:3 concentrated sulfuric acid/hydrogen peroxide solution and a 1:1:5 ammonium hydroxide/hydrogen peroxide/water solution for 1 h each. This rendered the surface hydrophilic. Some of these cleaned slides were then exposed to 1,1,1,3,3,3-hexamethyldisilazane (98%, Aldrich) in a static vacuum of 200 mTorr for 36 h to render the surface hydrophobic. The remaining slides were subjected to the following treatments to covalently anchor charges onto the surface. The cleaned slides were immersed for 10 min each into the following solvents: methanol (HPLC grade, Mallinckrodt), 1:1 methanol/toluene, and toluene (analytic reagent grade, Mallinckrodt). Then they were exposed to a 5 vol % solution of (*N*-2-aminoethyl-3-aminopropyl)trimethoxysilane (Huls America, Inc.) in toluene for 12 h. After silanization, the slides were immersed in fresh boiling toluene for 1 h. Then they were immersed for 10 min each in toluene, 1:1 methanol/toluene, and methanol, after which they were thoroughly rinsed with Millipore (ultrapure) water. This produced a surface with covalently anchored amine functionalities; these are protonated and thus positively charged in the low-pH solutions used in this study. To produce a negative surface, a single layer of sodium poly(styrene-4-sulfonate) was adsorbed onto some of these aminosilanized slides by immersing then in a 10^{-3} M solution of sodium poly(styrene-4-sulfonate) with the pH adjusted to unity by HCl. It was found that these slides are best stored under ultrapure water prior to use.

Molecular Self-Assembly Procedure. The dipping solutions used in this study for self-assembly were as follows. The solutions containing the negative polyelectrolyte were 0.001 M sulfonated polystyrene (SPS, 99% sodium poly(styrene-4-sulfonate), Aldrich) in Millipore water with the pH adjusted to unity by hydrochloric acid. The active dipping solutions of the p-doped, conducting polymer were made by dissolving an oxidizing agent, ferric chloride (≥98% anhydrous $FeCl_3$, Fluka Chemika), in Millipore water and then adjusting the pH to unity by adding HCl. A sulfonic acid such as *p*-toluenesulfonic acid (PTS, 99%, Aldrich) or anthraquinone-2-sulfonic acid (ASA, 97%, Aldrich) was then dissolved in the solution, followed by the addition of the pyrrole monomer (99% pyrrole, Aldrich). The specific concentrations utilized are discussed in the test; however, a typical dipping solution contained 0.006 M $FeCl_3$, 0.026 M PTS or 0.005 M ASA, and 0.02 M pyrrole monomer. After the addition of the pyrrole monomer, the solutions were allowed to stir for 15 min when PTS was used and for 2 min if ASA was used. The reaction kinetics of the PPY–ASA solution are faster than that of the PPY–PTS; therefore the solution is ready for dipping after a shorter "induction period". All active solutions were filtered through a 0.45 μm syringe filter just before dipping. The polypyrrole is continuously being formed during the lifetimes of the dipping solutions, which are typically up to 2 h.

The basic layer-by-layer molecular self-assembly process developed in this study is as follows. A substrate pretreated with a single layer of negatively charged sulfonated polystyrene on the surface was immersed into the polypyrrole dipping solution for a set amount of time (usually 5 or 10 min). A single layer of polypyrrole deposits onto the surface; the thickness of each layer depends on the solution chemistry and deposition time. The substrate was then removed and vigorously rinsed with pH-neutral Millipore water to eliminate any loosely bound material. After being briefly dried in a dream of compressed air, the sample was dipped into the polyanionic solution of sulfonated polystyrene for 10 min. A single layer was adsorbed, changing the surface charge to negative and thus priming it to attract more polypyrrole when immersed in the active polypyrrole (polycationic) solution again. This alternating dipping sequence was repeated to build up the multilayer film. Typical sample films of 10 bilayers of polypyrrole/sulfonated polystyrene were made for electrical and optical characterization. Polypyrrole was also deposited onto the various substrates by a single-dip, "free-growth" process in which the substrate was simply immersed in the polypyrrole dipping solution for a specific amount of time, rinsed, and dried.

In-situ polymerized polyaniline was self-assembled in a similar manner. The polyaniline active solution contained 0.004 M ammonium peroxysulfate (99%, Aldrich) in Millipore water with the pH adjusted to unity by hydrochloric acid. *p*-Toluenesulfonic acid was added to give 0.026 M PTS, and aniline monomer (99%, Aldrich) was added to a concentration of 0.02 M. The solution was allowed to stir for 30 min and then filtered through 0.45 μm syringe filters. Typical 10-bilayer sample films are built up with 5 min dips in the active polyaniline solution and 10 min dips into the SPS solution.

Electrical and Optical Characterization. The deposition of doped polypyrrole was monitored by visible absorption spectroscopy since polypyrrole is strongly absorbing in this region of the spectrum. A circular area of 1 cm in diameter was scanned with polychromatic light from 400 to 870 nm using an Oriel Instaspec 250. The thickness of sample films was determined by profilometry using a Sloan Dektak 8000. Several parallel scratches in the film were scribed by a razor blade, and a stylus with a pressure of 12 mg was traced perpendicularly across the series of scratches. An average step height was calculated and taken as the thickness of the film. In-plane conductivity measurements were done with the standard four-point, van der Pauw technique on a square area of 1 cm × 1 cm.[7] The original film on the glass slide was scraped down with a razor blade to leave the square centimeter area. Thin gold wire leads were contacted at each of the four corners with graphite Electrodag or silver paste. Voltages were measured with a Keithley Model 614 electrometer, and the current was generated by a Keithley Model 224 current source. The applied currents were adjusted such that the maximum current that could be supported by the film was used (typically 1–10 mA). The resulting voltage readings and a set of voltages using currents 1 order of magnitude smaller were averaged and used in the van der Pauw calculations. This particular method was used because it is applicable to films of any geometry (the four probes can be contacted at any four points at the edge of the film) as long as the thickness is uniform across the area measured. Preliminary atomic force and optical microscopy studies provided additional information about the ultrathin films.

In order to estimate total film thicknesses quickly, visible absorption data were directly correlated with the thickness of the film obtained by Dektak profilometry. The resulting linear correspondence between absorbance and thickness allows an accurate estimate of the thickness of the films simply by measuring the absorbance. It was found, however, that this method of estimating thickness was not completely universal for all polypyrrole thin films. Specifically, when substantially higher ferric chloride concentrations were used, the films showed greater absorbance per unit thickness. Therefore, it was necessary to generate new absorbance versus thickness plots for films made with solution chemistries containing different ferric chloride concentrations. Otherwise, the above method provided a quick and simple way of determining the thicknesses of these ultrathin films. Finally, it should be noted that the SPS accounts for about 15 Å of the thickness of each bilayer; this thickness contribution was determined by comparing the thickness of a self-assembled film of 10 bilayers with that of a film made by free growth with a dip time of 50 min, equivalent to 10 dips of 5 min each into the active polypyrrole solution.

Results and Discussion

The layer-by-layer molecular-level processing of polypyrrole via aqueous-based solutions is best accomplished with the use of an in-situ polymerization process. The in-situ chemical conversion of pyrrole monomer to electrically conductive polypyrrole is a well-established process that has previously been used to create a wide variety of electrically conductive coatings and composites.[1-4] Although this approach can be used to deposit uniform thin films of conductive polypyrrole onto various substrates, to date, an understanding of the factors required to provide molecular-level control over

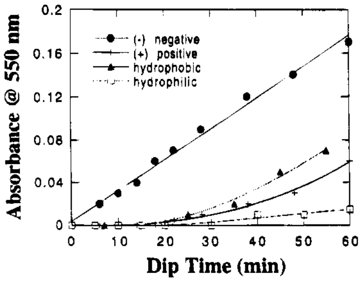

Figure 1. Time-dependent growth of polypyrrole thin films deposited by a single dip of the various substrates into a dipping solution of PPY−PTS (0.006 M $FeCl_3$, 0.026 M PTS, pH = 1, 0.02 M pyrrole).

the deposition process has not yet emerged. Without this level of control, it is simply not possible to fabricate heterostructure thin films with complex molecular architectures. As will become apparent shortly, we have found that the key to molecular-level control over the deposition of in-situ polymerized conducting polymers lies in the nature of the surface onto which they are deposited.

Figure 1 compares the time-dependent growth of in-situ polymerized polypyrrole onto four different surfaces as determined by monitoring the visible absorption of the film at 550 nm. In this case, the samples were made by immersing multiple substrates with the various surface treatments into the polypyrrole dipping solution. A substrate of each kind of surface was removed after the indicated amount of time, rinsed, and dried. The visible absorption spectra were taken immediately thereafter; the increase in absorption with each dip therefore traces the deposition of the polypyrrole. This type of deposition is labeled as "free growth" as opposed to self-assembly, since the substrate is simply immersed in the polypyrrole solution and the polypyrrole allowed to grow (deposit) onto the surface as it is being formed by the oxidative polymerization in the solution. This "free growth" of polypyrrole is contrasted to the self-limiting monolayer adsorption of preformed polymers described in part 1 of this series of papers on self-assembly.

Figure 1 clearly shows that the nature of the substrate surface plays an important role in the early stages of the polypyrrole deposition process. For surfaces fitted with negative charges (ionized sulfonate groups of poly(styrene-4-sulfonate)), it can be seen that there is a linear correspondence between dipping time and the amount of polypyrrole deposited onto the substrate. That is, in a dip time of up to 60 min the rate of deposition of newly formed polypyrrole is constant. This is in sharp contrast to surfaces that are hydrophobic, hydrophilic, or positively charged. In these cases, there is an apparent "induction period" of about 20 min, during which time no polypyrrole is deposited. After this induction period, the nonlinear growth of polypyrrole onto these surfaces is still significantly less than that observed on the negatively charged surface. The fact that polypyrrole deposits in a very controlled manner on negatively charged surfaces makes it possible to use this process to fabricate single layer and multilayer thin films with well-defined layer thicknesses. The film adhesion and uniformity were observed to be poor when polypyrrole was deposited onto hydrophobic, positively charged, and hydrophilic surfaces; the films were blotchy and could be easily rubbed off. On the other hand, films deposited onto negatively charged surfaces were exceptionally uniform and strongly adherent to the surface. The fact that virtually no deposition occurs onto the nonnegatively charged surfaces during the induction period can be also exploited in a selective deposition process to delineate a surface with adjacent conducting and insulating regions. For example, by modifying the surface of a substrate with adjacent positive and negative areas, one can attract the p-doped, conducting polymer to the negatively charged areas and "block" deposition in the positively charged areas by electrostatic repulsion.

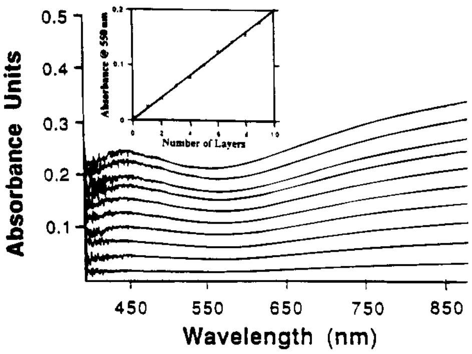

Figure 2. Overlaid absorption spectra of a PPY/SPS layer-by-layer deposition process with inset showing the linear relationship between absorbance at 550 nm and number of bilayers deposited (PPY active solution: 0.006 M $FeCl_3$, 0.02 M pyrrole, pH = 2.5).

For the single-layer "free-growth" deposition process, uniform films of polypyrrole with thicknesses in the range of 20−500 Å can be deposited by simply controlling the amount of time a negatively charged substrate is immersed in the dipping solution. The best control is achieved when the concentrations of the reactants in the polypyrrole dipping solution are very dilute (e.g., 0.006 M $FeCl_3$, 0.026 M PTS, and 0.02 M pyrrole). If concentrations comparable to those of standard chemical and electrochemical preparations are used, the polypyrrole tends to grossly precipitate out of solution within a short amount of time, thereby eliminating control over the deposition process. Since the in-situ polymerization of polypyrrole is a dynamic process, the thickness of the polypyrrole film increases linearly with time but gradually becomes sublinear as the solution is "exhausted"; that is, the polypyrrole that is not deposited onto the surface will gradually precipitate out of solution. Once this happens, it can no longer be controlled to deposit a uniform film on the substrate. Therefore, to maintain control over the deposition, fresh solutions are typically used for only 2−3 h and then discarded. The single-layer deposition process as described here has been used to create extremely uniform films of up to 500 Å in thickness with superior adhesion and uniformity on negatively charged surfaces. This simple, single-dip process is most useful when only the film thickness needs to be controlled.

When layer-by-layer control over the architecture of a multilayer thin film is desired, the substrate can simply be alternately dipped into the active polypyrrole solution and a dilute solution of a polyanion such as sulfonated polystyrene (SPS). Again, the thickness of each polypyrrole layer is determined by the chemistry and dip time in the polypyrrole active solution. By using the same dip time (typically 5 min) and same dipping solution, a highly reproducible thickness of polypyrrole is deposited with each dip. This is illustrated in Figure 2, which shows the overlaid absorption spectra of a self-assembled polypyrrole sample film

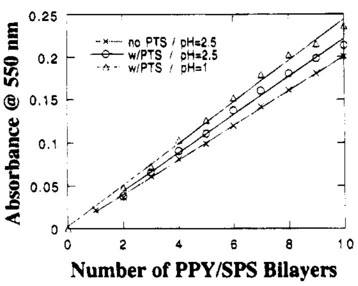

Figure 3. Absorbance versus number of deposited bilayers of PPY/SPS for various polypyrrole solution chemistries.

after each polypyrrole layer was deposited. The inset shows that the deposition is remarkably linear; that is, a reproducible amount (or thickness) of polypyrrole is deposited with each successive dip. In addition, as illustrated in Figure 3, this linear growth process holds for active solutions of various chemistries. In this case, each bilayer was made with a 5 min dip into the polypyrrole solution and a 10 min dip in the SPS solution. Since the SPS component of each bilayer is colorless and thus contributes nothing to the overall absorbance of the film, the visible absorbance only traces the deposition of the polypyrrole. The larger the slope of the lines in the figure, the greater the thickness per deposited layer of polypyrrole. For example, the addition of *p*-toluenesulfonic acid (PTS) is seen to slightly increase the per-layer thickness as does the addition of hydrochloric acid. This linear deposition characteristic occurs for a wide variety of polypyrrole solution chemistries. Although not shown here, the polyaniline system behaves similarly; that is, in-situ polymerized polyaniline also exhibits a linear deposition characteristic. For the conditions described above, the films are extremely uniform, highly adherent, and blue.

Table 1 summarizes the average conductivity and average per-bilayer thickness of representative polypyrrole sample films fabricated from dipping solutions with different reactant concentrations. All samples contained 10 bilayers of polypyrrole/sulfonated polystyrene made using 5 min dips in the polypyrrole active solution and 10 min dips in the SPS. The very low concentrations of reactants used in this study should be noted immediately. As mentioned earlier, the reason for using such low concentrations is that greater control over the deposition process and better uniformity of the resultant films are obtained with more dilute solutions. In general, there is a tradeoff between control of the deposition process and achieving higher conductivities by using greater reactant concentrations; that is, when greater concentrations are used to achieve higher conductivities, precipitation occurs more quickly in the active solution and precise control over the layer thickness is compromised. However, despite the low concentrations used in these experiments, the ultrathin films exhibit conductivities comparable to those of bulk polypyrrole samples. Clearly, the solution chemistry determines the conductivity and thickness of the deposited polypyrrole.

The first two rows in this table show that increasing the ferric chloride (oxidizing agent) concentration enhances the conductivity but does not significantly alter the average thickness of the bilayer building block of this film (polypyrrole/sulfonated polystyrene); for the 5 min dipping times utilized, it stays remarkably constant around 35 Å. An enhancement of the conductivity can also be achieved by adjusting the pH to unity or lower with hydrochloric acid. In general, the addition of a sulfonic acid was found to enhance the rate of reaction, thus producing thicker layers for a given dip time and also further increase the conductivity. An exception to this trend is seen in the films prepared from the pH = 0 solutions which deliver a thickness per bilayer that is independent of the presence of sulfonic acids. Consistent with the work of Kuhn and colleagues,[8] the use of anthraquinonesulfonic acid (ASA) as a conductivity enhancer results in higher conductivities than *p*-toluenesulfonic acid (PTS).

Various other processing conditions were also investigated in the attempt to achieve greater control over the deposition process or to enhance the conductivity of the deposited polypyrrole. For example, the temperature of the dipping solutions was lowered and held constant at 3 °C. This simply caused thinner layers of polypyrrole to be deposited per dip; the deposition remained linear, but with a reduced slope. No increase in conductivity was observed, despite previous findings for electropolymerized polypyrrole.[3a] Second, annealing of the samples in an oven at 90 °C was found to initially improve the room temperature conductivity by up to 50%, perhaps by removing excess water. Additional heating after two 15 min "anneals", however, caused a slow decrease in the conductivity, attributable to the normal degradation of the polymer in air at elevated temperatures. Thin films with significantly higher conductivities can be prepared by simply increasing the ferric chloride concentration to 0.06 M (10 g/L) and using the usual 0.005 M ASA and 0.02 M pyrrole concentrations. In this case, thin films could be readily prepared with conductivities over 300 S/cm. The higher oxidizer concentrations needed to produce these exceptionally high conductivities, however, make it possible to deposit only a few controlled layers before precipitation occurs in the bath. Increasing the concentration of the sulfonic acid additive close to fivefold (to 0.025 M) did not significantly enhance the conductivity of the films. It is generally known that higher oxidizer concentrations produce more highly conductive polypyrrole in in-situ polymerization processes.

It was found that "bulk" conductivities were achieved with films as thin as 100 Å. For example, films of 3 self-assembled bilayers or 15 min free growth showed conductivities between 60 and 80 S/cm. Figure 4 shows the linear increase in thickness with dip time and the associated thickness dependence of the conductivity for the PPY–ASA system in free growth mode. Multiple substrates were dipped into an active polypyrrole solution containing 0.006 M $FeCl_3$, 0.005 M ASA, and 0.02 M pyrrole at pH = 1.0; individual substrates were then removed after specific dip times. A substrate dipped for 5 min gives a film of around 20 Å, with an undetectable conductivity ($<10^{-6}$ S/cm). Therefore, no point is shown for the 5 min (20 Å) film. It should be noted that although the deposition is subsequently linear, it is always observed that the first layer is thinner than the average layer thickness for the film; that is, the thickness of the film after the first 5 min is less than the thickness deposited during subsequent 5 min intervals. Once the film reaches a thickness of about 60 Å, the conductivity is already around 10 S/cm and by 100 Å, a conductivity close to the plateau value (about 100 S/cm) is achieved. These observations demonstrate that by around 100 Å total thickness, the film of polypyrrole becomes completely coherent on the microscopic level, with all "island" domains interconnected, thus leading to the observed "bulk" conductivity. This is particularly

Table 1. Average Conductivity and Bilayer Thickness of Sample Films[a]

	pH = 2.5		pH = 1.0		pH = 0	
cell contents	conductivity (S/cm)	bilayer thickness (±5Å)	conductivity (S/cm)	bilayer thickness (±5Å)	conductivity (S/cm)	bilayer thickness (±5Å)
no PTS 0.003 M $FeCl_3$	0.003	26	2	35	1	35
no PTS 0.006 M $FeCl_3$	0.05−0.15	33	5−9	39	14−20	34
0.026 M PTS 0.006 M $FeCl_3$	12	44	18−27	47	34	36
0.005 M ASA 0.006 M $FeCl_3$	15	45	35−80	43	47	36

[a] All samples consist of 10 bilayers of PPY/SPS (5 min dips in PPY solution and 10 min dips in SPS solution). Single conductivity points represent average values of less than 5 measurements. Conductivity ranges represent the range of values observed in greater than 10 samples.

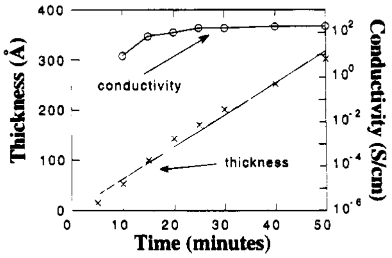

Figure 4. Conductivity/thickness relationship for a PPY−ASA free growth deposition process (0.006 M $FeCl_3$, 0.005 M ASA, 0.02 M pyrrole at pH = 1.0).

significant as it represents the first clear demonstration of the minimum film thickness required to achieve maximum "bulk" conductivity in in-situ polymerized films of polypyrrole. Thus, it can be inferred that a two-dimensional percolation threshold has been reached by as little as 100 Å in these self-assembled films. Furthermore, it was found that the conductivity of sample films prepared via the layer-by-layer self-assembly method was the same as that of the films prepared by the free growth process when corrected to account for the SPS contribution to the thickness. For example, the conductivity of the above film after a single dip of 15 min was nearly identical to that of a film made with three 5 min dips into the polypyrrole active solution (with 10 min dips into the polyanion, SPS, in between each polypyrrole layer). The SPS remains an inert component in the self-assembled film, accounting for about 15 Å of the average 45 Å thickness of each bilayer. These ultrathin films are at the same time extremely uniform optically and greater than 85% transparent, with a neutral gray tint. Currents of 1−10 mA are readily supported by these films, making them potential candidates to serve as one of the electrodes for organic light-emitting diodes.

Although a detailed investigation of the mechanism of deposition of in-situ polymerized electrically conductive polypyrrole onto negatively charged surfaces has not yet been completed, it is possible to make some preliminary comments about this process. Based on our observations, it appears that the polypyrrole chains are formed in solution and subsequently adsorbed onto the surface after achieving a critical molecular weight which depends on the nature of the substrate surface. For negatively charged surfaces, the ionic attractions developed between the growing polymer chains (positively charged due to delocalized bipolarons) and the substrate surface promote a uniform, continuous deposition process in which conducting polypyrrole chains or micro-aggregates of polypyrrole chains are adsorbed onto the surface at an essentially constant rate. For hydrophobic, hydrophilic, and positively charged surfaces, adsorption onto the surface is driven primarily by the poor solubility of the oxidized polymer in water. In this case, the polypyrrole chains, most likely in the form of larger sized aggregates, deposit onto the surface only after a relatively higher molecular weight or aggregate size is achieved, resulting in a nonlinear growth process and less uniform deposition. Recall that the films deposited onto these surfaces tend to be blotchy and exhibit poor adhesion. Thus, for these surfaces, the polypyrrole is essentially forced out of the dipping solution and onto the surface by solubility effects.

The above hypothesis is supported by the following general observations. The longer induction period (see Figure 1) observed with the hydrophilic, hydrophobic, and positively charged surfaces as compared to the negatively charged surface suggests that the polypyrrole chains must grow to a larger size (or aggregate more) before they deposit onto the surface. Once this critical size is reached, the polypyrrole tends to deposit more rapidly and uncontrollably onto the surface as indicated by the increasing slopes of the absorption versus time plots. Further, it has been found that a constant filtering of the polypyrrole dipping solution with 0.45 μm syringe filters effectively prevents deposition onto the "nonnegative" surfaces for approximately the first 45 min of dipping. This indicates that the critical size of the aggregates for deposition onto these surfaces is greater than 0.45 μm. In sharp contrast, filtering has no effect on the linear deposition observed with negative surfaces, indicating that the polypyrrole chains are indeed attracted to the surface at earlier stages of formation; that is, the delocalized positive charges of the polarons and bipolarons of nascent p-doped polypyrrole chains are attracted to the negative charges on the surface. In this way, the surface is key to the deposition characteristics of the in-situ polymerized polypyrrole.

Optical micrographs show that, without filtering, polypyrrole precipitates with sizes on the order of 1−5 μm will begin to attach and sparsely dot the surface of the film as the active solution ages. These precipitates do not appreciably influence the macroscopic deposition, uniformity, or conductivity of the ultrathin films but may adversely affect the performance of ultrathin film devices such as light-emitting diodes. Filtering between each polypyrrole dip is thus highly desirable when the microscopic level and size of defects within the film are of concern, e.g., in thin-film electronic devices. Preliminary atomic force microscopy (AFM) studies show that the surface of the ultrathin films produced both by "free growth" onto a negatively charged substrate or via layer-by-layer self-assembly with sulfonated polystyrene is highly uniform and resembles a plane of "mushroom caps" closely packed together to give an average RMS surface roughness of 20−40 Å. The "caps" themselves are roughly 100 Å in diameter. This surface morphology suggests a nucleation and growth mechanism for the deposition of in-situ polymerized polypyrrole. As the initial "layers" are deposited, "mushroom caps" stack on top of each other and form a coherent film, such that by 3 layers or 15 min free growth, a fully continuous film is formed, characterized by essentially "bulk" conductivity. More work is needed, however, to confirm the origin of this type of morphology and the nucleation and growth mechanism. In any event, it is clear that control over the deposition of in-situ polymerized polypyrrole is best achieved with negatively charged surfaces. It should also be noted that preliminary orientation studies using polarized visible spectroscopy indicate that the polypyrrole chains are preferentially oriented with their chain axes lying within the plane of the film as expected for a deposition process involving rigid polymer chains.

Finally, as mentioned earlier, since the deposition of in-situ polymerized polypyrrole is strongly dependent on the nature of the substrate, it is possible to delineate patterns comprised of electrically conductive and insulating regions on a substrate surface. This is accomplished by patterning a surface with positively and negatively charged areas and by keeping the dip times in the polypyrrole solution to under 20 min each. The polypyrrole will grow linearly onto negatively charged areas but will not deposit onto positively charged areas. To date, we have used this approach to create substrates with adjacent conducting and insulating areas with centimeter resolution. This was done by dipping a negatively charged substrate partially into a dilute aqueous solution of a polycation, poly(allylamine) hydrochloride. The polycation is absorbed onto the regions that were dipped. The resulting surface is then comprised of a negative and a positive region. The entire substrate was then dipped into the polypyrrole active solution. The polypyrrole selectively deposits onto areas with the negative sulfonated polystyrene and is selectively "blocked" by regions with the positive poly(allylamine) hydrochloride. The above "blocking" and "selective deposition" steps can be repeated to build up a multilayer film on the desired surface areas. Chemolithographic techniques which can pattern a surface with positive and negative charges, when combined with self-assembly of conducting polymers, will make it possible to pattern a surface with adjacent conducting and insulating regions with micron resolution.

Since self-assembly is a layer-by-layer deposition process, it gives us the freedom to build complex, multicomponent films simply by alternating between dipping solutions of a wide variety of different conjugated and nonconjugated polymer polyelectrolytes. As long as the substrate is alternately dipped into a solution containing a polycation and a solution containing a polyanion, it is possible to fabricate multilayer heterostructures in which layers of different materials are positioned within the multilayer film to create specific electrical and optical effects. To demonstrate this, workers in our group have fabricated highly anisotropic thin-film heterostructures containing blocks (multiple bilayers) of electrically conductive polypyrrole (PPY)/sulfonated polystyrene (SPS) alternating with blocks of insulating poly(thiophene-3-acetic acid) (PTAA)/poly(allylamine) (PAH).[9] Since the conductive blocks of PPY/SPS bilayers were isolated between the insulating PTAA/PAH blocks, highly anisotropic properties were observed. Films with 150 Å blocks, for example, exhibited in-plane conductivities ($\sigma_{\|}$) of 1−10 S/cm and transverse conductivities ($\sigma_{\perp}$) of about 10^{-10} S/cm, giving conductivity anisotropies ($\sigma_{\|}/\sigma_{\perp}$) on the order of 10^{10}. It was also demonstrated that the dielectric properties of these heterostructure films could be altered by changing the volume fractions of the PPY and PTAA blocks or by increasing the number of interfaces between the conducting and insulating blocks.[9]

Conclusions

We have developed and demonstrated a new method for processing p-type doped conducting polymers such as polypyrrole and polyaniline into ultrathin films. Layer-by-layer self-assembly of in-situ polymerized polypyrrole provides molecular-level control over the deposition of single layers of polymer. Along with the techniques presented in the other papers of this series, layer-by-layer self-assembly opens up vast new possibilities in the fabrication of complex, multicomponent heterostructure thin films of polymers.

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