Molecular-Level Processing of Conjugated Polymers. 3. Layer-by-Layer Manipulation of Polyaniline via Electrostatic Interactions

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Received January 17, 1997; Revised Manuscript Received March 4, 1997[⊗]

ABSTRACT: Multilayer thin films comprised of sequentially adsorbed layers of partially doped polyaniline and a polyanion, sulfonated polystyrene, were fabricated via the use of a simple layer-by-layer molecular-level processing scheme. Using this simple multilayer polymer adsorption process, uniform thin films of polyaniline in the 40−600 Å thickness range were readily fabricated onto a variety of different substrates. Doping of these films with strong acids such as HCl and methane sulfonic acid results in electrically conductive thin films with conductivities comparable to those obtained with spin cast films (0.5−1.0 S/cm). The adsorption process used to fabricate the films was found to be driven primarily by the electrostatic attractions developed between the partially doped chains of polyaniline (polycation) and the negatively charged chains of the polyanion.

Introduction

In this series of papers, we have been describing the application of a new layer-by-layer processing scheme[1] to the nanoscale manipulation both conjugated polyions[2] and in-situ polymerized electrically conducting polymers.[3] In this process, multilayer thin films are constructed one layer at a time via the alternating spontaneous adsorption of a positively charged polymer and a negatively charged polymer from dilute aqueous solutions. The charges can be in the form of delocalized charged defects along the backbone of a doped conjugated polymer (polarons etc.) or simple ionic charges on a pendant sidegroup. The manipulation of conductive conjugated polymers is particularly important as it provides an opportunity to fabricate ultrathin films of these materials with thicknesses that are controllable at the nanometer scale. Such films may find use as semitransparent thin film electrodes or as electrostatically dissipative coatings. Thin film heterostructures containing nanometer thick layers of conductive polymers may also be the source of new types of thin film devices that utilize the conductive layers to control the flow of electron and hole carriers. Although a layer-by-layer scheme involving the alternate deposition of in-situ polymerized conducting polymers has been previously described,[4] this approach is the first that allows true molecular-level manipulation of both in-situ polymerized and preformed conducting polymers with a variety of other electroactive or nonelectroactive polymers and, most importantly, is carried out with dilute aqueous solutions. This paper will describe the molecular level layer-by-layer processing of the important conducting polymer polyaniline.

Polyaniline is now regarded as one of the most technologically promising electrically conductive polymers due to its ease of synthesis, low cost, versatile processibility, and relatively stable electrical conductivity.[5] Most recently, for example, it has been demonstrated that thin films of this material can be used as semitransparent anodes in flexible polymer light-emitting devices[6] or to facilitate hole injection into various light-emitting polymers.[7] In the latter case, dramatic improvements in device efficiency and stability are realized when thin films of conductive polyaniline are placed at an anode surface. In these and other related thin film applications, it is important to be able to control film thickness and to create uniform, pinhole-free films of polyaniline. To achieve high levels of transparency in the visible region of the spectrum, for example, it is necessary to use as thin a film of polyaniline as possible due to its strongly absorbing nature. Thus, precise control over the thin film processing of polyaniline is clearly highly desirable in many of the applications currently envisioned for this very versatile conducting polymer. In this paper, we describe the molecular layer-by-layer manipulation of preformed, partially doped polyaniline. We have found[3a] that it is possible to create dilute aqueous-based solutions of partially doped polyaniline (>90% water) that are of sufficient stability to allow multilayer deposition with suitable polyanions. The process involves the repeated dipping of a substrate into the polyaniline solution followed by a solution of a polyanion with rinsing in between each polymer deposition step. In this case, the cationic nature of partially doped polyaniline promotes multilayer assembly via the electrostatic attractions developed with the polyanion. Using this simple polymer adsorption process, it is possible to fabricate uniform thin films of polyaniline in the 40−2000 Å range (or thicker). Further doping of these films with strong acids results in electrically conductive thin films with conductivities comparable to those obtained with spin cast films. Details concerning the electrostatic layer-by-layer manipulation of partially doped polyaniline and the polyanion, poly(styrenesulfonic acid), are described in this paper. In the next paper of this series, it will be shown that it is possible to manipulate polyaniline into multilayer thin films using hydrogen bonding interactions as opposed to electrostatic interactions.[8]

Experimental Section

Polyaniline, in its emeraldine base form, was prepared chemically by direct oxidation of aniline using the method

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[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

developed by MacDiarmid *et al.*[9] On the basis of the results from many similar syntheses,[10] the molecular weight (M_n) is estimated to be 20 000−25 000 with a polydispersity of about 2.5. Sulfonated polystyrene (SPS: obtained from Aldrich, MW = 70 000) was used without further purification.

Polyaniline Dipping Solutions. The emeraldine base form of polyaniline was dissolved in dimethylacetamide (DMAc) at a concentration of 20 mg/mL by first stirring the solution overnight and then sonicating it for about 8−10 h. The solution had some fine particulates (presumably crystalline polyaniline) which were removed by filtering the solution through a 0.7 μm glass filter. The polyaniline dipping solution was prepared by slowly adding one part (by volume) of the filtered polyaniline solution to nine parts of water that has had its pH adjusted to about 3.0−3.5 with methanesulfonic acid (MeSA) or HCl. The pH was then quickly lowered to 2.5−2.6 by adding drops of approximately 1 M MeSA or HCl solution. Care must be taken to not go below a pH of 2.5 or above a pH of 4.0 to avoid precipitation of the partially doped polyaniline. The solution was filtered through a 0.45 μm filter just before use. The polyaniline concentration was varied by adjusting either the amount of polyaniline in DMAc or the amount of water added. We believe that at least 5% DMAc is necessary to form a stable solution, although it may be possible to use even less DMAc. The molarity of the polyaniline solution (emeraldine base) was based on a repeat unit containing two aniline structural units i.e., the sum of a benzene ring, an amine unit, a quinoid ring, and an imine unit, giving a repeat unit molecular weight of $M_o = 181$. The polyaniline dipping solutions were typically used within 2 days of preparation.

Poly(styrenesulfonic acid) (SPS) Dipping Solutions: Solutions were made by stirring the SPS in MeSA or HCl aqueous solutions. The solutions were filtered with 4−10 μm filter paper before use: 0.01 M, pH 2.5 SPS solutions were used for all experiments. Fresh SPS solutions were prepared once every week.

All films were prepared on microscope glass slides that were treated to produce hydrophilic, hydrophobic, or positively charged surfaces. A detailed description of the various substrate treatments has been described previously.[2,3] Substrates defined as "charged" in this paper are glass slides that have been treated to create covalently bound positive charges on the surface followed by the adsorption of one layer of negatively charged SPS; i.e., the surfaces of these substrates have a net negative charge.

Multilayer films were made by alternately dipping substrates into the solutions of the cationic and anionic polymers. The substrates were dipped in each solution for 2−15 min and subsequently rinsed in pH 2.5 water baths for 15 s. After each deposition and rinsing step, the samples were dried with a gentle flow of filtered compressed air. Unless otherwise stated, the polyaniline multilayer films discussed in this paper were made from freshly prepared solutions at a pH of 2.5.

The polyaniline deposition process was examined primarily by monitoring the growth of the polyaniline excitonic absorption band centered at about 630 nm for neutral polyaniline or of the polaron band of doped polyaniline at 880 nm. In the former case, UV/visible spectra were recorded after the polyaniline films were dedoped by immersing the films in a 0.01 M sodium hydroxide (NaOH) solution for 30 s and subsequently rinsing with deionized Milli-Q water for 15 s and drying with compressed filtered air. In some cases, the visible absorption results were used to estimate the amount of polyaniline adsorbed per unit area. The conversion from visible absorption to mass adsorbed per area was accomplished using Beer's law. The molar absorption coefficient of dedoped polyaniline was determined from a series of polyaniline/DMAc solutions. A value of 1.4×10^4 (M cm)$^{-1}$ was obtained from this analysis. This ϵ value is in good agreement with that determined by Yamamoto et al.[11] Given the assumptions that are used to make the conversion from visible absorption to mass/area (solid state density of polyaniline etc.), these values are only presented as estimates and are best used for comparative purposes.

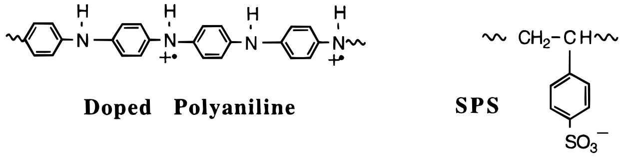

Figure 1. Chemical structures of polyaniline (shown in the fully doped form) and poly(styrenesulfonic acid).

Thicknesses of the multilayer assemblies were determined by profilometry using a Sloan Dektak 8000. Thickness per bilayer values were obtained by dividing the film thicknesses by the number of bilayers. This was done with films with a different number of total bilayers to obtain the most accurate thickness per bilayer value (a linear relationship between thickness and the number of deposited bilayers was always obtained). In-plane conductivities were measured by the standard four-point van der Pauw method for thin films. Prior to making contacts for electrical measurements, the films were doped with 1 M HCl for 2 min. All films were dried with compressed filtered air before measurements.

Results and Discussion

The layer-by-layer manipulation of doped polyaniline is accomplished via the use of dilute aqueous based solutions in which the polyaniline is only soluble over a rather limited pH range and for a limited duration. By diluting organic solutions of the nondoped emeraldine base form of this material with acidic aqueous solutions, it is possible to create a solvent system that is comprised almost entirely of water (90 vol % or more) and yet is sufficiently stable to allow reproducible adsorption onto substrates. During the dilution process, the polyaniline chains become partially doped thereby rendering them soluble in the final aqueous solution. The relatively "poor" nature of this final solvent system, however, creates a situation that favors the spontaneous adsorption of the polyaniline chains onto a variety of quite different substrate surfaces. In order to understand the adsorption behavior of the polyaniline chains from this relatively poor solvent system, the time dependent adsorption of a single layer of polyaniline onto different substrate surfaces was examined as a function of solution concentration. This was in turn followed by studies of the multilayer deposition characteristics of this new system and the electrical conductivity of the final multilayer thin films. The structures of the two polymers examined in this work are shown in Figure 1.

Single Layer Adsorption. Figure 2 displays the concentration/time dependent adsorption behavior of a single layer of polyaniline onto surfaces precoated with one adsorbed layer of SPS and four adsorbed bilayers of polyaniline/SPS with SPS at the outermost layer (the multilayer process will be described shortly). In both cases, it can be seen that the spontaneous adsorption of polyaniline onto a negatively charged surface occurs very rapidly, with the time to reach complete adsorption taking only about 5 min for the more concentrated solutions and about 25 min for the least concentrated solution (1×10^{-4} M). The observed relatively weak concentration dependence of the final adsorbed amount (increases with increasing concentration) is typical for polymers exhibiting "high affinity" type adsorption behavior[12] and reflects the fact that, in lower concentration solutions, the polymer chains have more time to spread out into thinner adsorbed layers (less competition for surface sites) and hence less polymer is adsorbed to the surface. This effect will become even more apparent when the multilayer adsorption studies are

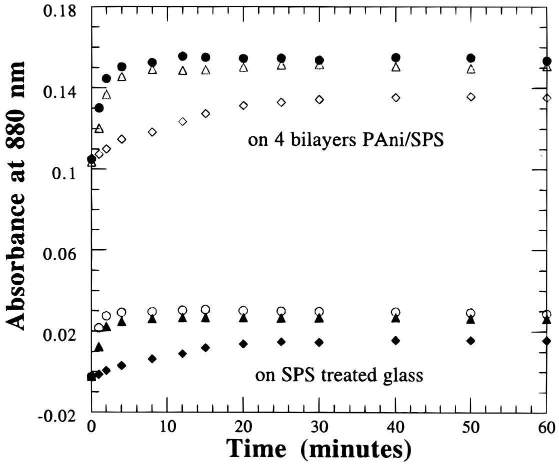

Figure 2. Time-dependent adsorption behavior of a single layer of polyaniline adsorbed onto a substrate precoated with a single SPS layer or four polyaniline/SPS bilayers as a function of polyaniline solution concentration (circles, 0.001 mol/L; triangles, 0.0005 mol/L; diamonds, 0.0001 mol/L).

presented. It should also be noted that no additional net adsorption was observed even when the time-dependent adsorption was monitored for as long as 24 h; i.e., this is a self-limiting adsorption process.

Using the data generated from the least concentrated solution in conjunction with the well-known Langmuir–Schaefer relationship, it is possible to estimate a diffusion coefficient for this adsorption process.[13] Such a coefficient would reflect the time for the macromolecules to diffuse to the surface and to adopt their kinetically imposed surface conformation. In both cases, adsorption from the lowest concentration solution (1×10^{-4} M) was found to give rise to a linear dependence of the adsorbed amount on the square root of time (Γ vs $t^{1/2}$) for the first 30 min of the adsorption process; i.e., the expected Langmuir–Schaefer relationship. An estimated diffusion coefficient of approximately 10^{-7} cm^2/s was obtained from this analysis. This value is similar to that estimated from adsorption studies of the conjugated polymer poly(thiopheneylacetic acid).[2b] Given the limited range of adsorption time over which the Langmuir–Schaefer relationship is valid for these polymers, this value should only be considered as a rough estimate.

The data in Figure 2 also show that the time-dependent adsorption of polyaniline onto a substrate previously coated with an adsorbed layer of SPS is essentially independent of how many bilayers of polyaniline/SPS have previously been deposited onto the substrate surface. This, of course, means that this system is well suited for reproducible layer-by-layer multilayer deposition. It has also been found that spontaneous polyaniline adsorption occurs readily on many different types of substrate surfaces including both hydrophilic and hydrophobic surfaces and on a variety of different materials such as platinum-coated glass, gold-coated glass, aluminum-coated glass, mica, graphite, silicon, glass pipettes, polystyrene culture dishes, poly(ethylene terephthalate) sheets, poly(methyl methacrylate) sheets, and plasticized poly(vinyl chloride) tubing. In general it has been found that, for the first polyaniline layer deposited directly on a substrate surface, negatively charged surfaces tend to adsorb 10–25% more material for a given solution concentration than both hydrophilic and hydrophobic surfaces. In all cases, however, the adsorbed layer of partially doped polyaniline is of sufficient uniformity and charge density to attract a polyanion layer and start the multilayer deposition process. The fact that polyaniline readily adsorbs onto many different surfaces is in part related to the "poor" nature of the aqueous solutions used for adsorption and the cationic nature of the doped polyaniline chains (most surfaces will readily adsorb a layer of a polycation). The poor solvent quality also means that the polyaniline solutions can only be used for about 1–2 weeks before significant aggregation of the polyaniline chains occurs (readily apparent by a very large increase in amount of polymer adsorbed per layer) and controllable multilayer deposition is no longer possible.

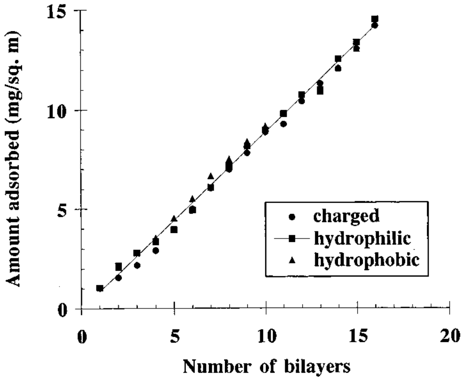

Figure 3. Amount of polyaniline adsorbed from 0.01 M, pH 2.5 polyaniline solutions on charged, hydrophilic, and hydrophobic glass as a function of the number of polyaniline/SPS bilayers deposited (dipping times of 5 min were used).

Multilayer Adsorption. The fact that polyaniline adsorbs readily onto negatively charged, hydrophilic, and hydrophobic surfaces suggests that it should be possible to use a variety of different substrates to fabricate multilayer thin films of polyaniline in a layer-by-layer manner. The multilayer process involves first adsorbing a layer of polyaniline, rinsing to remove excess, non-adsorbed material, and then dipping the substrate into a dilute aqueous solution of a polyanion. The adsorption of a negatively charged polymer onto the partially doped, positively charged polyaniline changes the net surface charge from positive to negative, thereby making it possible to adsorb another layer of polyaniline. This process can be repeated as many times as desired to create multilayer thin films comprised of semiinterpenetrated polyaniline/polyanion alternating layers (the level of layer interpenetration depends on many factors including solution concentration and charge density). Figure 3 shows plots of the amount of polyaniline adsorbed vs the number of polyaniline/SPS bilayers deposited in a layer-by-layer fashion onto three different substrates. The linear and equivalent growth observed in all three cases indicates that the multilayer deposition process is reproducible from layer to layer and independent of the type of substrate used to support the films. In other words, the same amount of polyaniline is deposited in each bilayer cycle and the amount deposited is independent of the substrate surface. The multilayer thin films formed in this manner are homogeneous and uniform down to at least the micrometer scale as observed by optical microscopy. Figure 4 illustrates the role that polyaniline solution concentration plays in the multilayer deposition process. In this case, a negatively charged substrate was used. Two important points are noteworthy. First, linear multilayer growth is observed over a wide range of polyaniline solution concentrations. Second, as indicated by the slopes of these curves, the amount of polyaniline deposited per bilayer increases with increasing solution

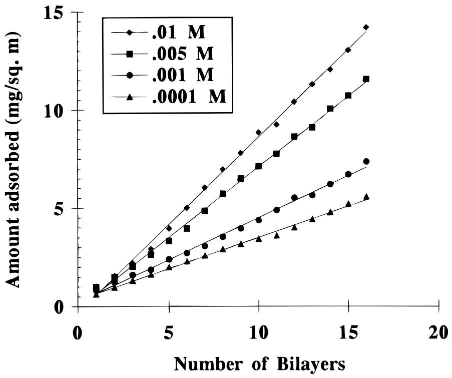

Figure 4. Amount of polyaniline adsorbed from different concentration polyaniline solutions as a function of the number of polyaniline/SPS bilayers deposited (dipping times of 5 min were used).

Table 1. Thickness and Optical Absorption per Bilayer Values of Polyaniline/SPS Films Fabricated with Different Polyaniline Solution Concentrations (5 min Dips)

concentration (M)	thickness per bilayer (Å)	absorption per bilayer (at 632 nm)
0.0001	12	0.0026
0.001	20	0.0034
0.005	28	0.0055
0.01	36	0.0067

concentration. This latter observation is consistent with the single layer adsorption results and shows that it is readily possible to vary the amount of polyaniline deposited in a multilayer film by simply changing solution concentration. As mentioned earlier, previous polymer adsorption studies[12] have also found that lower polymer concentrations tend to produce thinner adsorbed polymer layers due to kinetic effects.

Profilometry measurements were carried out to determine whether the increase in the amount of adsorbed polyaniline with increasing solution concentration also reflected an increase in the average bilayer thickness. The average thickness contributed per bilayer for the polyaniline/SPS system deposited with different polyaniline solution concentrations for a dipping time of 5 min are shown in Table 1 along with the optical absorbance per bilayer values measured at 630 nm (the peak of the polyaniline absorption band after dedoping; see experimental section). Both of these values were obtained by measuring the total thickness or absorbance of multilayer thin films and then dividing by the total number of bilayers. These results show that the average polyaniline/SPS bilayer thickness increases by a factor of about three (from about 12 to 36 Å) as the polyaniline solution concentration increases from 10^{-4} to 10^{-2} M. The fact that the optical absorbance per bilayer increases by a similar factor with increasing solution concentration suggests that the thickness increase is due primarily to an increase in the amount of polyaniline deposited per bilayer. This conclusion is supported by the observation that a linear plot of optical absorbance vs film thickness is obtained using the data derived from all of these different multilayer thin films. Thus, there is always a corresponding increase in polyaniline optical absorption with increasing film thickness.

It should be noted that the thickness per bilayer of the polyaniline/SPS system is independent of the molecular weight of the SPS used to fabricate the multilayer films. We have found, for example, that the thickness per bilayer of films fabricated from 0.01 M polyaniline solutions remains essentially the same (in the 35−40 Å range with 15 min dips) even when the SPS molecular weight is varied from 5 000 to 1 000 000. The details and significance of this observation are discussed in the following paper of this series which compares the electrostatic self-assembly of polyaniline with hydrogen bonding self-assembly.[8] Basically, it indicates that the SPS chains are adsorbing with highly extended conformations (i.e., a low segmental density of loops and tails).

Mechanism of Self-Assembly. A number of experiments were carried out to confirm that the driving force behind the polyaniline/SPS multilayer deposition process is in fact primarily electrostatic in origin. In one case, multilayer deposition was attempted with an undoped, neutral form of polyaniline. This was accomplished by adjusting the pH of the polyaniline solution to 7. Such a solution is stable only for a few hours so all experiments were carried out within this time period. As expected for an electrostatically driven process, no multilayer deposition was observed when substrates were alternately dipped into the neutral polyaniline solution and a SPS solution. A small amount of polyaniline was initially adsorbed on the substrates (about 10 times less than that obtained via adsorption from a pH 2.5 solution), but no additional polyaniline deposition was observed during the attempted multilayer deposition. Given the limited range of pH where the polyaniline solutions are stable, it is not possible to carry out detailed studies aimed at determining the influence of pH on polyaniline deposition. However, in the stable pH range of 2−4, we have found that the amount of polyaniline adsorbed per bilayer increases as pH decreases (by a factor of about 1.5). Thus, as the polyaniline backbone becomes more positively charged due to protonic acid doping, more polyaniline is adsorbed onto the negatively charged SPS layer.

In a second experiment, a substrate previously coated with an adsorbed layer of polyaniline was alternately immersed in a polycation solution of poly(allylamine hydrochloride) (pH 2.5) and a polyaniline solution (pH 2.5). Again, no multilayer deposition was observed, showing that the process will not work with two polymers that are positively charged. This observation in turn suggests that selective deposition of polyaniline may be possible on substrates patterned with negatively and positively charged regions. Recently, it has been shown that the patterned multilayer deposition of electrically conductive self-assembled polyaniline/SPS films is possible at the 400 μm level by using selectively plasma treated surfaces.[14] Selective deposition at the 2−4 μm level has also recently been accomplished with self-assembled layers of more conventional polyelectrolytes.[15] In both cases, selective deposition was facilitated by the different adhesion characteristics of polyelectrolytes on charged vs hydrophobic or hydrophilic surfaces. These different approaches open the door to the fabrication of patterned multilayer thin films for microelectronic applications.

Electrical Conductivity. Although the polyaniline used to fabricate multilayer thin films is in a partially doped form (needed for electrostatic self-assembly), it is not sufficiently doped to achieve a high level of electrical conductivity. It is therefore necessary to expose the completed multilayer thin films to a strongly acidic aqueous solution (pH = 0) to complete the doping

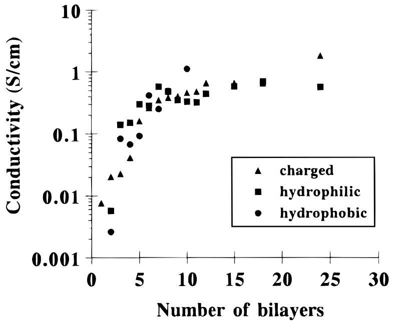

Figure 5. Dependence of in-plane conductivity on the number of polyaniline/SPS bilayers deposited on different substrates (dipping times of 5 min were used).

process. This has been accomplished with either HCl or MeSA solutions. Figure 5 shows how the in-plane conductivity of multilayer thin films of polyaniline/SPS varies with the number of bilayers deposited on three different substrates (charged, hydrophobic and hydrophilic). In this case, the films were fully doped by immersion in a 1 M HCl solution. Note that it takes about six bilayers (216 Å thick) to achieve the level of conductivity expected for a thick film of HCl doped polyaniline (0.5−1.0 S/cm); although conductivities of about 0.1 S/cm are reached with only three bilayers (108 Å thick). Also note that the level of conductivity for a given number of deposited bilayers is essentially independent of the type of substrate used in the deposition process. This is consistent with the previous conclusion that the multilayer deposition process is not appreciably influenced by the nature of the substrate surface.

The fact that near "bulk" levels of conductivity are not realized until greater than three bilayers have been deposited onto the substrate surface suggests that a fully continuous film of polyaniline is not formed until the multilayer film thickness is at least about 150 Å. We have previously found that self-assembled films of doped polypyrrole achieve near bulk levels of conductivity only after the film thickness reaches about 100 Å.[3] Thus, it appears that greater than at least 100 Å of film thickness is needed to overcome the effects of surface roughness and/or film morphology and create an electrically uniform thin film with properties similar to that observed in the bulk. This thickness effect may also reflect the fact that transport in these ultrathin films is governed by a different type of low-dimensional percolation behavior. Nevertheless, it is possible to create thin films with quite respectable conductivities (in the 10^{-1} S/cm range) with only three bilayers of the polyaniline/SPS system. It should also be noted that polyaniline/SPS multilayer thin films with slightly higher conductivities and much better environmental stability are obtained when methane sulfonic acid is used to carry out the final doping step. We are currently exploring the use of these ultrathin, electrically conductive films as semitransparent electrodes and hole transport layers in organic light-emitting diodes.

Acknowledgment. This work was supported in part by the National Science Foundation and by the MRSEC program of the National Science Foundation under Award No. DMR-9400334. We also thank Mr. Pradeep Sreekanthan, Mr. Johnathan Lai, and Dr. Marysilvia Ferreira of MIT for their contributions to this work.

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MA970047D