

Stepwise Incorporation of Nonpolar Polymers within Polyelectrolyte Multilayers

Jason H. Rouse and Gregory S. Ferguson*

Departments of Chemistry and Materials Science & Engineering, Lehigh University, Bethlehem, Pennsylvania 18015-3172

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A method for incorporating uncharged, nonpolar polymers, polystyrene and poly[2-(6'-cyano-6'-methylheptyloxy)-1,4-phenylene] (CN-PPP), in the stepwise adsorption of polyelectrolyte multilayers is reported. Polystyrene and CN-PPP adsorbed irreversibly from toluene solution onto polyelectrolyte surfaces. The thickness of the adsorbed nonpolar layer was sufficient to cause the wettability of the surface to change from hydrophilic to hydrophobic but only attenuated subsequent polyelectrolyte adsorption and did not terminate it. Ultraviolet-visible spectroscopy provided evidence for the incorporation of the nonpolar polymers within the polyelectrolyte multilayers. The resultant composite film containing poly(styrene) displayed a reduced swellability by water vapor compared to a polyelectrolyte-only film, also consistent with the presence of the hydrophobic polymer within the film.

Introduction

The development of techniques that allow self-assembly of thin organic films is an area of considerable interest, given their potential use in applications ranging from organic light-emitting diodes (OLEDs),^{1–4} to perm-selective membranes,^{5,6} to conducting films.^{7–9} Methods that rely on molecular species to form such films, such as Langmuir–Blodgett (LB) transfer and self-assembly of molecular adsorbates,¹⁰ have been augmented by methods utilizing polymers, especially for films greater than one

monolayer in thickness. Many of the same interactions that govern small-molecule interactions, such as electrostatic interactions,^{3–5,8,9,11} hydrogen bonding,^{2,12} charge-transfer complexation,¹³ and stereocomplex formation,¹⁴ have been used to self-assemble polymeric films. Electrostatic interactions have been most widely used, allowing polymeric films to be built in a stepwise manner through the alternate adsorption of oppositely charged polyelectrolytes.

Although the absence of specific interactions, such as covalent bonding, in the electrostatic assembly process has allowed it to be used to prepare a wide variety of thin films, the requirement that the adsorbing species be charged has also limited the range of materials that could be prepared. As a result, applications of these films, for example, in light-emitting diodes,⁴ conducting films,⁹ or nonlinear optics,¹⁵ have required strategies for dealing with this limitation. Hence, existing polymers with useful properties have been modified to add charged units,^{4,9,16}

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or pendant groups of interest have been attached to an existing polyelectrolyte.¹⁵ The development of methods allowing the direct use of nonfunctionalized polymers (i.e., lacking charged or hydrogen-bonding groups, etc.) in a sequential adsorption process would greatly increase the adaptability of the method, as well as the diversity of film structures that could be prepared. In this paper, we demonstrate the incorporation of the uncharged, nonpolar polymers polystyrene (PS) or poly[2-(6'-cyano-6'-methylheptyloxy)-1,4-phenylene] (CN-PPP)¹⁷ in the stepwise adsorption of a multilayer film.

The sequential adsorption of oppositely charged polyelectrolytes from aqueous solution produces multilayers that are terminated, alternately, by polycation or by polyanion. Immersion of either of these surfaces into a toluene solution of PS or CN-PPP led to irreversible adsorption of the polymer onto the substrate. This adsorption resulted in an increase in the thickness of the film, measured ellipsometrically, and in its UV-vis absorbance, measured spectrophotometrically. These changes were accompanied by an obvious change in hydrophobicity of the surface, from hydrophilic for polyelectrolyte-terminated multilayers to hydrophobic for PS- or CN-PPP-terminated films. Subsequent treatment of the film with aqueous polyelectrolyte (of opposite charge to that adsorbed just prior to the PS or CN-PPP step) again led to adsorption, albeit of a smaller amount on average than if the uncharged polymer were not present. A sufficient amount adsorbed, however, to sustain renewed growth of the multilayer. This result indicates that the added PS or CN-PPP layer was sufficiently thick and/or complete to attenuate the electrostatic interactions that drive sequential polyelectrolyte adsorptions but not so thick and complete to render them ineffective.

Experimental Section

Materials. Poly(diallyldimethylammonium chloride) (20% w/w solution in water, MW 200 000–350 000) and poly(styrene sulfonate) (sodium salt, MW 70 000) were obtained from Aldrich and either diluted with or dissolved in Millipore Milli-Q water (15–16 M Ω) to obtain a 1% (w/w) solution. Polystyrene ($M_w \geq 1\,000\,000$, $T_g = 107\text{ }^\circ\text{C}$) was obtained from Dow Chemical Co. and diluted to the required concentration with toluene (EM Science). CN-PPP (MW = 5000, American Dye Source (ADS120BE)) was diluted to 0.1% (w/w) with toluene. The CN-PPP was a gift from Dr. Samson Jenekhe at the University of Washington.

Silicon (100) substrates (Si-Tech, Inc.) were cut into $\sim 1\text{ cm} \times \sim 4\text{ cm}$ pieces. To clean the cut pieces, they were first swabbed with absolute ethanol (McCormick) to remove any silicon dust and then placed in a piranha solution (1:2 (v/v) 30% H₂O₂ and concentrated H₂SO₄). *Caution: piranha solution reacts violently with organic materials and should be handled carefully.* The clean wafers were rinsed thoroughly with Milli-Q water and dried with nitrogen. The wafers had a native oxide thickness of 16–18 Å. Fused quartz slides (ChemGlass) were prepared in a similar way.

Analysis of Multilayers. The ellipsometric data were obtained using a Rudolph Auto-EL III nulling ellipsometer with a He-Ne laser ($\lambda = 632.8\text{ nm}$) at an angle of incidence of 70°. Three to four spots were measured at 7–10% relative humidity,¹⁸ unless otherwise noted, and averaged for each sample. The thickness of the multilayer was determined using a double-layer model and software supplied by the manufacturer (Program 222

on the Auto-EL III). This program utilizes the thickness and refractive index of the native oxide on silicon, as well as the refractive index of the silicon substrate, to determine the starting point for the calculation of the thickness and index of the sample film. For films thicker than 800 Å, the refractive index was also determined using the double-layer program.¹⁹

Ultraviolet-visible spectra were recorded on a Shimadzu UV-2101PC spectrophotometer at the “slow” scan speed setting, a slit width of 2 nm, and a sampling interval of 0.2 nm. Multilayered films were prepared on both sides of a fused quartz slide, and spectra were recorded by placing the coated slide in the sample beam and an identical uncoated slide in the reference beam. These samples were positioned diagonally in a 1.0 \times 1.0 \times 4.3 cm fused quartz cuvette so that the angle of incidence of the beams with the slides was 45°.

Contact angles of purified water (Millipore Milli-Q), buffered to pH 7, were recorded under ambient conditions using a Ramé-Hart 100-00 contact angle goniometer. All reported angles are an average of eight different measurements taken within 10–20 s of application of the drop.

Multilayer Formation. Clean, hydrophilic silicon or quartz substrates were sequentially dipped into aqueous solutions of poly(diallyldimethylammonium chloride) (PDDA, 1% w/w) and poly(styrene sulfonate) (PSS, 1% w/w), respectively. After 1 min in one of these solutions, the substrate was removed, rinsed with deionized water, and dried with nitrogen. Rinsing and drying were then repeated. Adsorptions were repeated to constitute a particular number of adsorption cycles. The polyelectrolyte film was then dipped into a 1% (w/w) polystyrene solution in toluene for 5 min, removed, rinsed with toluene, and dried with N₂. After a second rinsing with toluene and drying, the polyelectrolyte and PS adsorption treatments were repeated.

In this paper, treatment with both polyelectrolyte and uncharged polymer will be referred to as a complete “adsorption cycle” and will represent the repeat unit within the film. Depending on which polyelectrolyte was adsorbed immediately preceding the adsorption of the polystyrene, the composite films will be designated as either [(PDDA/PSS)_mPS]_n or [(PSS/PDDA)_mPS]_n, where *m* is the number of polyelectrolyte bilayers (2 or greater) and *n* is the number of complete adsorption cycles (repeat unit). Because of the need to initially treat the substrate surface with PDDA, an initial pretreatment of the substrate with the sequence PDDA/PSS/PDDA/PS preceded adsorption of films containing PS adsorbed onto a PDDA-terminated surface. For clarity, we have omitted this pretreatment in the film designation, but the number of complete adsorption cycles does include this first layer.

Composite films containing CN-PPP were prepared in a similar manner, except that a 20-min treatment with a 0.1% (w/w) solution was used. Films were prepared with CN-PPP adsorbed onto a PSS-treated surface and are designated as [(PDDA/PSS)_mCN-PPP]_n.

Swellability of Films in Humid Nitrogen. A 25-cycle (PDDA/PSS)₃PS film and a 17-cycle (PDDA/PSS)₃ film were exposed to nitrogen at various levels of relative humidity (RH). The RH was varied between $\sim 7\%$ and $\sim 71\%$, with ellipsometric measurements taken 5 and 10 min after the RH calibrator (Vaisala HMC 20) had equilibrated at each value of RH. The apparatus and this procedure have been described in more detail previously.¹⁸

Results and Discussion

Formation of Polystyrene-Containing Multilayers. Thin polyelectrolyte films were prepared by sequential adsorption from aqueous solutions of PDDA (1% w/w) and PSS (1% w/w) onto silicon or quartz substrates. After a given number of such alternating adsorptions, the film was dipped into a 1% (w/w) polystyrene solution in toluene for 5 min. Treatment with both polyelectrolyte and polystyrene will be referred to as a complete adsorption cycle and will constitute the repeating structural unit in the growing structure. Thus, the

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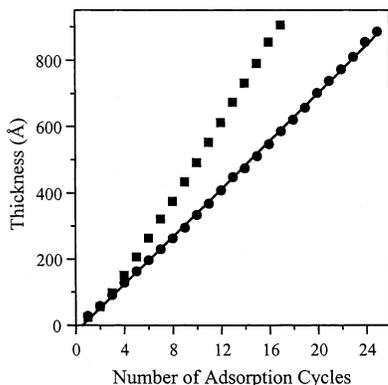


Figure 1. Increase in ellipsometric thickness for a (PSS/PDDA)₃PS multilayer film (circles) and a polyelectrolyte film prepared in an analogous manner without polystyrene (squares) as a function of the number of adsorption cycles. For the film containing PS, the substrate surface was initially treated by sequential treatments with PDDA, PSS, PDDA, and then PS prior to regular application of (PS/PDDA)₃PS adsorption cycles. The increase in thickness due to this pretreatment is included as the first adsorption step. For the film that did not contain PS, data are reported after each (PDDA/PSS)₃ treatment. The line is a least-squares fit to the data.

repeating structural unit will be designated as [(PSS/PDDA)_mPS]_n for films with polystyrene adsorbed onto a PDDA-terminated surface and [(PDDA/PSS)_mPS]_n for films with polystyrene adsorbed onto a PSS-terminated surface. The *m* refers to the number of polyelectrolyte bilayers (2 or greater) between polystyrene treatments, and *n* refers to the number of complete adsorption cycles (repeat units). For films having PS adsorbed onto a PDDA-terminated surface, the necessity of having to first treat the substrate surface with PDDA resulted in the need to pretreat the substrate with PDDA/PSS/PDDA/PS prior to beginning regular adsorption cycles. For clarity, we have omitted this pretreatment in the film designation, but the number of complete adsorption cycles does include this first layer.

A plot of the ellipsometric thickness of a film grown on a silicon wafer with (PSS/PDDA)₃PS adsorption cycles showed a linear increase in thickness as a function of the number of cycles (Figure 1). A linear fit to the data gave an average increase in thickness per cycle of 36 Å. After an initial adsorption of ~17 Å of PS onto the first polyelectrolyte layer, subsequent cycles resulted in 6 ± 2 Å of PS being adsorbed, and the average growth in each (PSS/PDDA)₃ step was 30 ± 3 Å. The growth in each polyelectrolyte and PS treatment over the first five complete adsorption cycles is shown in Figure 2 and demonstrates a high degree of uniformity in the amount of material added in each adsorption step (after the initial one). Increasing the PS concentration to 3% did not noticeably increase the average amount of PS adsorbed (7 ± 3 Å) after the first cycle but did result in a slightly reduced polyelectrolyte adsorption (26 ± 3 Å) for the (PSS/PDDA)₃ steps. The refractive index, determined ellipsometrically at a RH of 7–10%, of the composite film used to interpret the data in Figures 1 and 2 was 1.56. For comparison, the index of a PDDA/PSS film prepared in an analogous manner (though without PS) was also 1.56, and that of a dip-coated PS film was 1.58.

An expected effect of adsorbing a hydrophobic polymer onto the surface of a polyelectrolyte film would be a pronounced change in the wettability of that surface by water. Indeed, adsorption of PS onto a PDDA-terminated surface caused the advancing contact angle of water (pH 7) to increase from ~33° to ~91°, a value identical to that

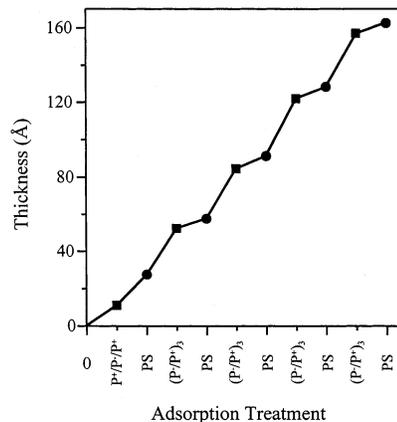


Figure 2. Ellipsometric thickness measured after each (PSS/PDDA)₃ treatment (squares) and PS treatment (circles) for the first five cycles of adsorption for the film shown in Figure 1. Again, the substrate surface was initially treated by sequential treatments with PDDA, PSS, PDDA, and then PS prior to regular application of (PSS/PDDA)₃PS adsorption cycles.

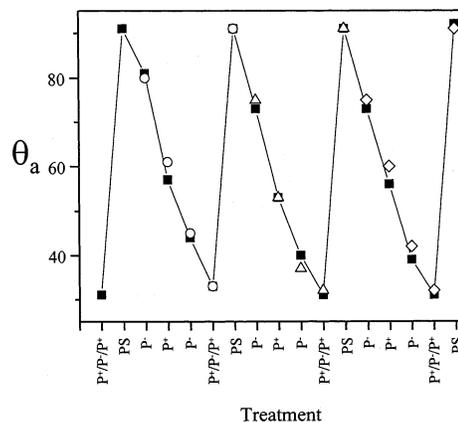


Figure 3. Advancing contact angles (θ_a) of water (pH 7) measured on polyelectrolyte/PS multilayer films versus surface treatment. The P⁺ labels on the abscissa refer to treatment with PDDA, and the P⁻ labels refer to treatment with PSS. Measurements taken during the preparation of a single [(PDDA/PSS)₃PS]₄ film are shown as squares connected by lines. For comparison, measurements were also taken only during the last cycle of three other films (other symbols).

measured on a compression-molded PS film.²⁰ Subsequent treatment of the PS-terminated surface with PSS resulted in a decrease in the contact angle to ~75°. The contact angle decreased further upon treatment of the PSS-terminated surface with PDDA (to ~55°) and then again with PSS (to ~39°). Measurements taken after the adsorption of three complete polyelectrolyte bilayers [i.e., (PSS/PDDA)₃] were indistinguishable for that on a pristine PDDA-terminated polyelectrolyte film [~32°, (PDDA/PSS)₂PDDA]. Figure 3 shows the oscillation of contact angles during the course of four complete adsorption cycles obtained on a single film [(PSS/PDDA)₃PS]₄. For comparison, identical measurements were also obtained on three additional films, each prepared with a different number of adsorption cycles (2, 3, or 4). These data demonstrate the reproducibility in the changes in wettability that accompany these adsorptions.

Although the above ellipsometric and wettability results show that polystyrene can be repeatedly adsorbed onto a

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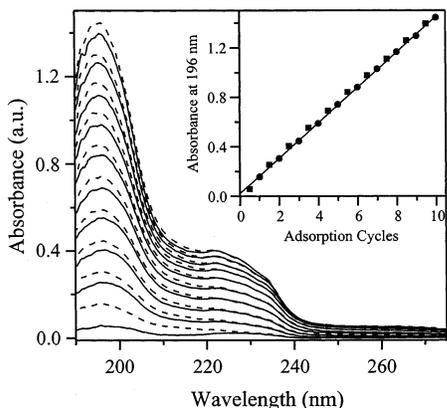


Figure 4. Ultraviolet absorbance measured after each (PDDA/PSS)₃ (solid line) and PS (dotted line) treatment for a 10-cycle film. The inset shows the absorbance at 196 nm plotted after each (PDDA/PSS)₃ (squares) and PS (circles) treatment; the line is a least-squares fit to the data obtained after the PS treatments.

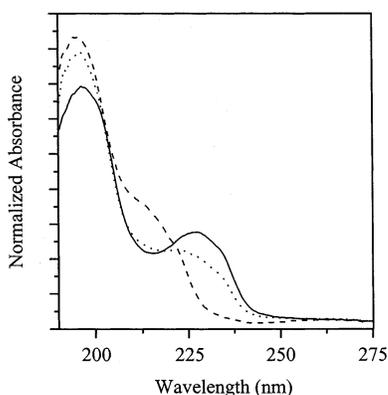


Figure 5. Ultraviolet absorbance spectra of the polyelectrolyte/PS multilayer film from Figure 4 after the adsorption sequence [(PDDA/PSS)₃PS]₉(PDDA/PSS)₃ (dotted line); of a polyelectrolyte film prepared in an analogous manner without PS (solid line); and of a dip-coated polystyrene film (dashed line).

polyelectrolyte surface, they do not prove that the initially adsorbed polystyrene was not at least partially removed during successive polyelectrolyte treatments. To address this question, we used ultraviolet spectrophotometry to monitor the growth of a composite film on a quartz slide. Spectra measured after each (PDDA/PSS)₃ sequence (solid line) and after each PS treatment (dashed line) are shown in Figure 4. Unfortunately, the overlapping spectra of the polystyrene and poly(styrene sulfonate) did not allow assignment of a unique adsorption band of the composite film solely to the polystyrene, but it was possible (i) to establish that the spectra of the composite film contained absorbance attributable to the polystyrene and (ii) to show that the polystyrene was not removed during the immediately subsequent polyelectrolyte treatment. The spectrum of polystyrene (Figure 5, dashed line) contains a shoulder centered at ~215 nm, a region in which a local minimum occurs in the spectrum of a PDDA/PSS film containing no PS (Figure 5, solid line). Since PDDA does not absorb in this region, this spectrum is associated with only the PSS. In the spectrum of a polyelectrolyte-terminated composite film (Figure 5, dotted line), [(PDDA/PSS)₃PS]₉(PDDA/PSS)₃, the local minimum observed in the polyelectrolyte film is nearly absent, and a PSS adsorption band centered at 230 nm has shifted to 223 nm, features consistent with the polyelectrolyte-poly-

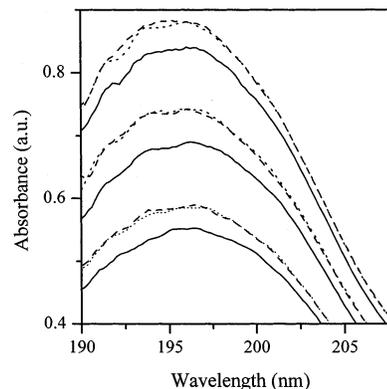


Figure 6. Ultraviolet absorbance spectra taken over three cycles after each: (PDDA/PSS)₃ treatment (solid lines); PS treatment (dashed lines); and immediately subsequent PDDA adsorption step after a PS treatment (dotted lines) for three complete (PDDA/PSS)₃PS cycles for the film shown in Figure 4.

styrene spectrum comprising a composite of PS and PSS spectra.

By preparing a film with the polystyrene adsorbed against PSS, it was possible to monitor both the increase in absorbance associated with the adsorption of PS and any loss in this absorbance upon subsequent PDDA treatment. In Figure 6, spectra obtained after a polystyrene treatment (dashed lines), the immediately subsequent PDDA treatment (dotted lines), and the full (PDDA/PSS)₃ treatment (solid lines) for three cycles of film growth are shown. The increase in absorption that occurs after each polystyrene adsorption step is clearly not affected by the subsequent PDDA treatment. As this indicates that polystyrene is not removed from the film, the linear increase in absorbance at 196 nm (Figure 4, inset) represents the regularity in both polyelectrolyte and polystyrene adsorption.

Although PS adsorption resulted in a measurable increase in film thickness and caused the surface hydrophobicity to change from hydrophilic to hydrophobic, subsequent polyelectrolyte adsorption was only attenuated, not terminated. The adsorption of the polyelectrolyte onto the PS-terminated surface could involve finite electrostatic forces that are attenuated by a uniform intervening layer of the low-dielectric PS or, more likely, occurs via intermingling of polyelectrolyte chains within the PS "layer." Significant mixing of adjacent layers in polyelectrolyte films is well documented.^{21,22} Moreover, in our case, segregation of the hydrophobic and hydrophilic components at the interface is also possible. Even if the PS layer were complete and uniform in the as-adsorbed state, upon subsequent treatment with the aqueous polyelectrolyte solution, the underlying polyelectrolyte should swell (vide infra),^{22,23} thus reducing the barrier to exposing the more hydrophilic component to the aqueous phase. Given that the amount of polyelectrolyte adsorbed was less than if the PS was not present, any swelling-induced reconstruction did not completely remove the PS

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from the surface but only exposed enough charged groups to the polyelectrolyte solution to allow some adsorption.

Consistent with swelling-induced reconstruction being involved in polyelectrolyte adsorption, the PS-terminated surface displayed a pronounced hysteresis in its wettability by water (the difference between advancing and receding contact angles). Surface inhomogeneities, mobility, and microscopic roughness have been identified as sources of contact angle hysteresis.²⁴ The first two factors may be important in this system, but roughness did not appear to be severe in these films. X-ray photoelectron spectroscopy (XPS) on a 205-Å thick composite film, [(PDDA/PSS)₃PS]₄(PDDA/PSS)_{2,5}, did not indicate the presence of any silicon photoemission from the substrate, which would be expected if the adsorbed material were present as "islands." Also, the films displayed a uniform interference color, indicating that this technique resulted in films of uniform thickness and refractive index, except where the film was held with tweezers, an effect displayed by other related systems.²⁵

While the amount of polyelectrolyte adsorbed onto the PS-terminated surface was small, the amount was sufficient to cause charge reversal, allowing the adsorption of a polyelectrolyte with a charge opposite to that initially adsorbed. Upon further treatment, the next polyelectrolyte layer would find the surface more highly charged than in the first polyelectrolyte adsorption, thus allowing a thicker layer to be added. Subsequent polyelectrolyte treatment would cause the number of charged surface groups to further increase, thus allowing even more polyelectrolyte to be adsorbed. As the number of polyelectrolyte layers added after a PS adsorption was increased, the amount of polyelectrolyte adsorbed eventually reached a value similar to that measured for films prepared under analogous adsorption conditions without PS, 58 ± 4 Å per (PSS/PDDA)₃ unit (Figure 1). After a PS adsorption, the amount adsorbed per (PDDA/PSS)₃ step increased from 35 Å in the first step to 47, 52, and 59 Å in the next three steps, respectively.

Another expected effect of incorporating a hydrophobic polymer within a polyelectrolyte film would be a reduction in the ability of that film to sorb water vapor.^{18,22,23,26} The amount of hydration occurring within the composite film was evaluated by measuring the changes in ellipsometric thickness (Figure 7a) and refractive index (Figure 7b) as a function of RH for a 25-cycle (PDDA/PSS)₃PS film. For comparison, a 17-cycle (PDDA/PSS)₃ film, having approximately the same thickness but containing no PS, was also measured. As the relative humidity was increased, the thickness of the composite film rose ~8.8%, and its refractive index decreased due to sorption of water having a lower index (1.333). In comparison, the changes in the thickness and index of the polyelectrolyte-only film were about twice as large.²⁷ Considering that the polystyrene makes up only 16% of the total film thickness of

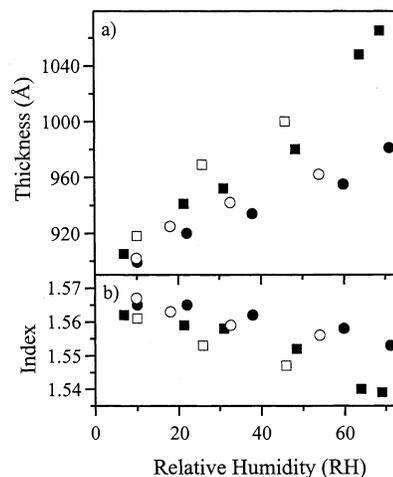


Figure 7. (a) Change in the ellipsometric thickness of a 25-cycle (PSS/PDDA)₃PS film (circles) and a 17-cycle (PDDA/PSS)₃ film (square) as a function of relative humidity (RH). Filled symbols represent data obtained with increasing RH, and open symbols were obtained with decreasing RH. (b) Corresponding change in refractive index of the films as a function of RH.

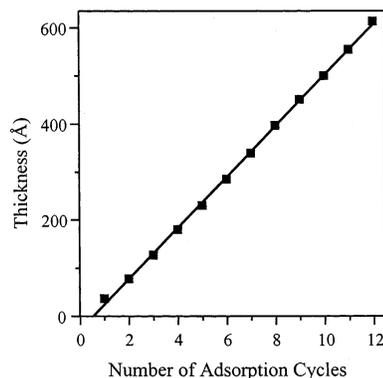


Figure 8. Increase in ellipsometric thickness versus the number of complete adsorption cycles for a 12-cycle (PDDA/PSS)₃CN-PPP multilayer film. The line is a least-squares fit to the data.

the composite film, the ~50% reduction in swellability demonstrates the dramatic effect it has on the hydrophobicity of the polyelectrolyte film.

Incorporation of a Conjugated, Nonpolar Polymer within a Polyelectrolyte Multilayer. To demonstrate that this method is applicable to other types of uncharged, nonpolar polymers and to provide further evidence for their incorporation into PDDA/PSS multilayers, films were prepared that included the conjugated polymer CN-PPP. The choice of CN-PPP was also motivated by its recent use as the electron-conducting layer in organic light-emitting diodes.¹⁷ Composite films containing CN-PPP were prepared in a manner analogous to that described for PS films, except that the low solubility of this polymer in toluene necessitated more dilute solutions (0.1% w/w) and longer adsorption times (20 min). A film prepared using (PDDA/PSS)₃CN-PPP adsorption cycles displayed a linear increase in thickness versus the number of treatments (Figure 8). The average increase in thickness for each complete cycle was 53 Å, with $44 + 4$ Å of growth in each (PDDA/PSS)₃ sequence and 9 ± 2 Å in each CN-PPP step. Similar changes in surface wettability to those reported for PS were seen in the preparation of polyelectrolyte-CN-PPP films.

Ultraviolet-visible spectrophotometric monitoring of film growth provided unequivocal evidence for the stepwise

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(27) The difference in swellability of these films is not the result of slower kinetics of water sorption in the composite film. Ellipsometric data obtained after allowing the RH to equilibrate at 71% for 30 min were nearly identical (to within ~1 Å) to those obtained after 5 min for the composite film.

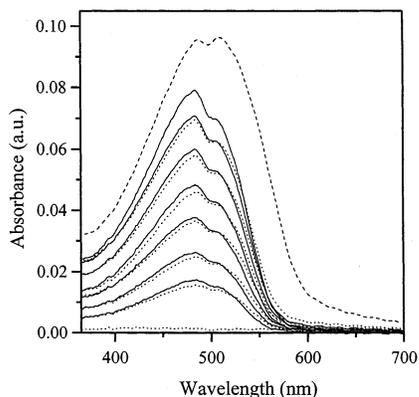


Figure 9. Visible absorbance spectra measured after each (PDDA/PSS)₃ (dotted line) and CN-PPP (solid line) treatment over seven adsorption cycles. The spectrum of a dip-coated CN-PPP film is shown for comparison (dashed line).

incorporation of CN-PPP within the composite film. Spectra measured after each CN-PPP treatment (solid line) and each (PDDA/PSS)₃ treatment (dotted line) through seven complete adsorption cycles are shown in Figure 9. The spectrum of a dip-coated film of only CN-PPP (dashed line) is shown for comparison. The polyelectrolyte multilayer does not absorb in this region (dotted line near the baseline), so the absorbance here is completely associated with the CN-PPP. Interestingly, the intensity of the CN-PPP absorbance decreased and shifted slightly to longer wavelength after treatment with the polyelectrolyte layer [(PDDA/PSS)₃]. We attribute this observation to a conformational change of the CN-PPP chains within the multilayer leading to a slight increase in its effective degree of conjugation, a "solvatochromic" shift due to the neighboring polyelectrolyte chains, or

differential aggregation of these chains before and after adsorption of the polyelectrolyte layers.

Conclusion

In summary, we have described a method that allows the direct incorporation of neutral, nonpolar polymers (polystyrene and CN-PPP) within sequentially adsorbed polyelectrolyte multilayers. The nonpolar polymers were irreversibly adsorbed onto polyelectrolyte surfaces, causing the wettability of those surfaces to change from hydrophilic to hydrophobic. Although the nonpolar polymer affected the wettability of the surface, it was not sufficiently thick and/or complete to terminate further polyelectrolyte adsorption, thus allowing film growth to continue. As expected, the presence of the hydrophobic polystyrene within the polyelectrolyte film resulted in a reduction in its swellability by water vapor, compared to a polyelectrolyte-only film. The potential applicability of this technique for the fabrication of films for use as OLEDs^{1-4,17} was demonstrated by the incorporation of the electron-conducting polymer, CN-PPP, within the polyelectrolyte multilayers.

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