Stepwise Polymer Surface Modification: Chemistry−Layer-by-Layer Deposition

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ABSTRACT: The layer-by-layer assembly of polyelectrolytes (poly(allylamine hydrochloride) (PAH) and poly(sodium styrenesulfonate) (PSS)) was carried out using poly(chlorotrifluoroethylene) film that had been chemically modified to contain alcohol functionality (PCTFE−OH) as a substrate for the deposition. This neutral surface supports the layer-by-layer assembly when PAH is adsorbed as the first layer. The amount of PAH that adsorbs in the first layer deposition is a function of the pH of the adsorption solution and this was used to control the resulting surface charge density (ammonium ion concentration). Three types of multilayer assemblies were prepared using three experimental protocols. In protocol 1, PAH and PSS were deposited to PCTFE−OH at pH 4. In protocol 2, the first PAH layer was adsorbed at pH 11, and treated with water at pH 4, and subsequent PSS and PAH layers were deposited at pH 4. In protocol 3, the first PAH layer was adsorbed as in protocol 2, and subsequent PSS and PAH layers were deposited at pH 4 with 0.2 M $MnCl_2$ added to the PSS adsorption solutions. The assembly process was monitored using X-ray photoelectron spectroscopy (XPS) and contact angle analysis of isolated multilayer films. The thickness of the individual layers in the assemblies (determined using XPS) depends on both the charge density of the first layer and the ionic strength of the PSS adsorption solution. The stoichiometry of the assembly process (ammonium:sulfonate ratio) also depends on the ionic strength of the PSS adsorption solution. The average individual layer thicknesses for protocols 1,2, and 3, respectively, are 0.3, 0.8, and 4.1 Å thick, as assessed by XPS. Although the layers are extremely thin, XPS and contact angle data indicate that the layers are stratified. Peel tests using pressure-sensitive adhesive tape indicate cohesive failure within a few angstroms of the interface in both the adhesive and the multilayer assemblies.

Introduction

Layer-by-layer deposition of polyelectrolytes has been developed over the past several years[1−9] as a versatile method for preparing supported multilayer films. The process, in its simplest form, involves sequentially dipping a charged substrate into dilute aqueous solutions of oppositely charged polyelectrolytes and allowing the polymers to adsorb and reverse the charge of the substrate surface. The sequential adsorptions of anionic and cationic polyelectrolytes allow the buildup of multilayer film structures. The charge reversal occurs because the polyelectrolytes adsorb in excess over the surface charge. In individual adsorption steps, this leads to a charged surface in contact with a solution of a polyelectrolyte with the same charge and electrostatic repulsion limits the adsorption to a single polymer monolayer.

We have recently reported extensions of the layer-by-layer deposition technique to organic polymer substrates,[10,11] using it to prepare polyelectrolyte multilayer films supported on poly(4-methyl-1-pentene) (PMP) and poly(ethylene terephthalate) (PET). The studies using PMP and PET as substrates gave us new insight into the polyelectrolyte assembly process as well as insight into the structure and properties of the multilayer films supported on organic substrates, and a review of several features is warranted here. Our studies were largely confined to poly(allylamine hydrochloride) (PAH) and poly(sodium styrenesulfonate) (PSS) and the substrates were oxidized PMP (PMP−CO_2^-), virgin PET, hydrolyzed PET (PET−CO_2^-), and amidated PET (PET−NH_3^+); analysis was carried out principally using contact angle and X-ray photoelectron spectroscopy (XPS).

We emphasize six features of layer-by-layer deposition to organic substrates: One, the initial substrate surface chemistry defines the entire assembly process—the thickness of all the layers and the stoichiometry of the assembly (ammonium:sulfonate ratio) is predetermined by the substrate. The assembly process does not revert to a substrate-independent process after a certain number of layers is deposited. When we first envisioned using layer-by-layer deposition as a method for surface modification, we questioned whether dissimilar surfaces could be converted to identical surfaces by this process. This clearly is not the case for the organic substrates that we have studied; different surfaces can be made more similar, but the substrate profoundly influences the assembly process. Two, a particular assembly stoichiometry (NH_3^+:SO_3^- ratio) is not required and varies significantly, substrate-to-substrate. The self-assembly process exerts its own stoichiometric control and is quite forgiving—we found no limit to the number of layers that can be deposited on any substrate. Three, the layers can be extremely thin; for example, average layer thicknesses of 2.0, 2.8, and 4.1 Å were calculated from XPS data for PET, PET−CO_2^-, and PET−NH_3^+, respectively. We emphasize that these thicknesses are averages and individual layers must, by geometric considerations of repeat unit volumes, not be close-packed. It was not possible to accurately determine relative thicknesses of cationic vs anionic polyelectrolyte layers. Four, although the individual layers are not close-packed; the multilayer assemblies are quite dense as demonstrated by their gas barrier properties. Considering this property and the individual layer thicknesses, it must be concluded that the layers are inter-

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digitated and that the structures are rigidly cross-linked via ionic interactions. Stratification and interdigitation are observed in assemblies with thicker layers on silicon substrates.[12] Five, pronounced odd−even effects in both XPS and contact angle data indicate that the layers are significantly stratified, despite the interdigitation that is surmised from the considerations just mentioned. Surface properties (wettability) depend on which polyelectrolyte was deposited last. Six, counterions (sodium, manganese and chloride) either were not present as assessed by XPS or were present in very small amounts (less than should be present as indicated by the ammonium: sulfonate ratio). PAH was generally observed in higher molar concentration than PSS and chloride should have been observed, but rarely was; we rationalize its absence by assuming that HCl is lost from the excess ammonium ions to form the free base of PAH under the conditions of analysis (high vacuum).

We have had a long-term interest in the surface modification of fluoropolymers and have developed chemical methods for introducing functionality to the surfaces poly(chlorotrifluoroethylene) (PCTFE),[13−17] poly(vinylidene fluoride),[17−19] poly(tetrafluoroethylene-*co*-hexafluoropropylene),[17,20] and poly(tetrafluoroethylene).[21] We focused particular attention on one functionalized surface, PCTFE−OH, that contains a primary alcohol attached to the fluoropolymer chain by a three-methylene spacer. This surface exhibits versatile chemistry, and we have studied its structure and chemistry in considerable detail.[15] For the reason that we know more about the chemistry and structure of this functionalized surface than we do for any other (and can control its structure and chemistry), it was chosen as a substrate for further modification using layer-by-layer deposition. We chose PSS and PAH as polyelectrolytes for deposition because this system has been most widely studied, and direct comparisons of multilayer assembly processes and resulting structures on different substrates can be made. The techniques of contact angle analysis and X-ray photoelectron spectroscopy (XPS) were used for analysis, and the presence of nitrogen in the cationic polyelectrolyte and sulfur in the anionic polyelectrolyte proved to be effective XPS labels to indicate the structure and composition of the multilayer assemblies. The presence of fluorine in the substrate also proved to be an advantage for XPS analysis.

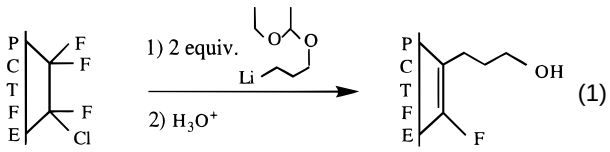
Experimental Section

General Data. PCTFE−OH was prepared from PCTFE film (Allied 5 mil Aclar 33C) and lithiopropyl ethyl acetaldehyde acetal as previously described at −15 °C in 50:50 heptane/THF.[15] Poly(allylamine hydrochloride) (PAH) (M_w = 50 000−65 000) and poly(sodium styrenesulfonate) (PSS) (M_w = 70 000) were obtained from Aldrich and used as received. Water was purified using a Millipore Milli-Q system that involves reverse osmosis, ion-exchange, and filtration steps. Solution pH for adsorption studies was adjusted with either HCl or NaOH solution using a Fisher 825MP pH meter. X-ray photoelectron spectra (XPS) were obtained using a Perkin-Elmer−Physical Electronics 5100 spectrometer with Mg Kα excitation (15 kV, 400 W). Spectra were recorded at two different takeoff angles, 15 and 75° between the plane of the sample surface and the entrance lens of the detector optics. Atomic concentration data were determined using sensitivity factors obtained from samples of known composition: C_{1s}, 0.201; O_{1s}, 0.540; F_{1s}, 1.0; N_{1s}, 0.385; S_{2p}, 0.440. Contact angle measurements were made with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Water (purified as described above) was used as the probe fluid. Dynamic advancing (θ_A) and receding angles (θ_R) were recorded while the probe fluid was added to and withdrawn from the drop, respectively. Peel tests were performed manually with an angle of 180° between the delaminated film surface and tape (3M #810).

Polyelectrolyte Depositions. Adsorptions were carried out at room temperature from unstirred polyelectrolyte solutions freshly prepared prior to use. The alternating layers were formed by sequential dipping of the PCTFE−OH substrates into 0.02 M PAH and 0.02 M PSS solutions (concentrations are based on repeat units and were varied from 0.02 M for concentration effect experiments) for generally 20 min. Substrates were rinsed with three 150 mL aliquots of water between each dipping and after the final adsorption. After the desired number of layers was deposited, the PCTFE−OH−supported multilayer assemblies were dried at room temperature under reduced pressure (<0.02 mm) for 24 h before analysis. These conditions were determined to be optimum based on a series of experiments described below.

Results and Discussion

Substrate Preparation. The substrate used for all of the experiments described in this report was 5 mil poly(chlorotrifluoroethylene) (PCTFE) film that had been chemically modified to incorporate alcohol functionality in its surface region (PCTFE−OH). This modification chemistry has been reported[13−15] and is reviewed only briefly here. PCTFE reacts with 2 equiv of acetaldehyde 3-lithiopropyl ethyl acetal to form an unsaturated surface containing protected alcohols (eq 1). Deprotection renders the alcohol-containing surface.



(1)

The depth of the modification reaction (thickness of the modified layer) can be conveniently controlled using solvent composition and temperature; conditions were chosen to yield a surface containing a ∼1000 Å thick modified layer.

First Layer Adsorptions. The general conditions for all polyelectrolyte adsorptions described here were modeled after those reported by Decher[1,2] for inorganic substrates modified by silanation to contain ammonium ions. A series of initial experiments (some are described below) were carried out to assess the tendencies of PAH and PSS to adsorb to PCTFE−OH from aqueous solution. As no charge exists on PCTFE−OH, the adsorption has to be driven by forces that are much weaker than electrostatic attraction: hydrogen bonding and interfacial free energy decreases. It was determined that PAH adsorbs under a variety of conditions and that PSS adsorbs only from solutions of high ionic strength. It was decided that PAH would be used as the polyelectrolyte for the first layer adsorptions. Neither PAH nor PSS adsorb to unmodified PCTFE under any of the conditions described.

Figure 1 shows the kinetics of adsorption of PAH to PCTFE−OH as monitored by XPS and contact angle. The PAH concentration was 0.02 M (based on repeat units, 1.4 mg/mL) and pH was adjusted to 4.0. XPS indicates that the adsorption is fast, reaching a final state in 5 min or less. We consciously use the term "final state" and not "equilibrium" because these adsorptions are irreversible; the PAH does not desorb upon rinsing with copious amounts of water at pH 4. The receding contact angle decreases initially and then

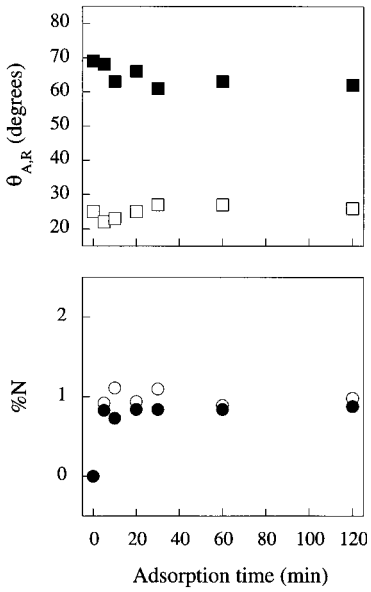


Figure 1. Kinetics of adsorption of PAH (0.02 M) to PCTFE−OH at pH 4. Nitrogen atomic concentration was determined using XPS at two takeoff angles, 15° (○) and 75° (●). Advancing (■) and receding (□) contact angles were determined using water as the probe fluid.

increases gradually over the first 30 min of adsorption and then levels at $\theta_R = 27°$. The advancing contact angle decreases during this 30 min and levels at $\theta_A = 61°$. Initial contact angles for PCTFE−OH are $\theta_A/\theta_R = 69/25°$.

Several comments concerning these data are in order: The adsorption involves a charged polyelectrolyte and a neutral surface; thus the surface becomes charged during adsorption, and at some point in the process (5 min or less as assessed by XPS), polyelectrolyte chains are repelled by the surface and further adsorption does not occur. The adsorption is fast relative to other neutral (and charged) substrates that we have studied,[10] and we surmise that the hydrogen-bonding interactions between ammonium ions and alcohols are strong. The wetting behavior of the isolated supported monolayers indicates that changes in the adsorbed polyelectrolyte structure continue after the adsorption is complete. The XPS data indicate that the nitrogen atomic concentration is ∼1%, and this value can be used to estimate the concentration of allylamine repeat units in the XPS sampling region of PCTFE−OH. The repeat unit structure of PCTFE−OH contains one fluorine atom; thus the N:F ratio is indicative of the PAH:PCTFE−OH repeat unit ratios. This indicates that approximately 1 PAH repeat unit is present per 12 PCTFE−OH repeat units in the 15° takeoff angle sampling depth and that ∼1 PAH repeat unit is present per 16 PCTFE−OH repeat units in the 75° takeoff angle sampling region. The 15 and 75° takeoff angle sampling regions are the outermost ∼10 and ∼40 Å, respectively; the attenuation of substrate photoelectron signals due to the adsorbed layers is discussed below in quantitative terms. The absence of a strong takeoff angle dependence in these data and, in particular, all of the data in Figure 1 suggests that the adsorbed PAH chains penetrate (at least) the outer few tens of angstroms of PCTFE−OH and may be more accurately described as "absorbed" chains. On the basis of these results, an adsorption time of 30 min was chosen for the first layer in the multilayer adsorption studies discussed below.

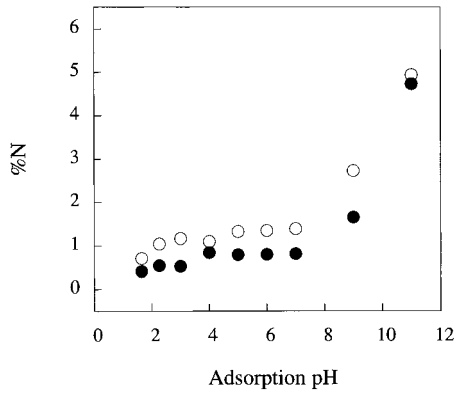


Figure 2. Effect of pH on the adsorbance of PAH (0.02 M) to PCTFE−OH. Nitrogen atomic concentration was determined using XPS at two takeoff angles, 15° (○) and 75° (●).

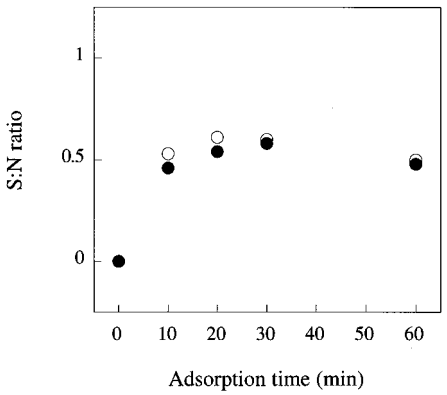


Figure 3. Kinetics of adsorption of PSS (0.02 M) to PCTFE−OH−PAH at pH 4. Sulfur:nitrogen atomic ratios were determined using XPS at two takeoff angles, 15° (○) and 75° (●).

The effect of pH on the adsorption of PAH to PCTFE−OH was assessed by carrying out 30 min adsorptions as a function of the pH of the PAH (0.02 M) solution. Figure 2 shows XPS atomic concentration (nitrogen) data for a range of solution pH values. The PCTFE−OH structure should not be pH sensitive over this range, but PAH has a reported pK_a of ∼10.6[22,23] and its degree of protonation should be pH dependent. At low pH values, all of the PAH repeat units are protonated and the low adsorbance (nitrogen content) is due to charge−charge repulsion of ammonium ions. There is a very gradual rise in adsorbance from pH 2 to pH 7 and a steeper rise from pH 7 to pH 11 as PAH becomes increasingly deprotonated and both charge−charge repulsion and polyelectrolyte solubility are diminished. Water contact angle data showed a slight dependence on the pH with θ_A increasing and θ_R decreasing with increasing pH (discussed below). We note without further comment that a greater takeoff angle dependence on nitrogen content is observed at pH values other than 4 and 11. Our first-layer adsorption experiments were confined to these pH values and the slight takeoff angle dependence was consistent (see data in Figures 1 and 5).

A second type of first layer substrate (PCTFE−OH−PAH) for multilayer formation, with a higher charge density and thicker adsorbed PAH layer, was devised from this pH dependence study: PAH was adsorbed to PCTFE−OH at pH 11 and then immersed in pH 4 solution to desorb any weakly attached polyelectrolyte that might desorb and reprecipitate as a polyelectrolyte complex in the subsequent adsorption of an oppositely

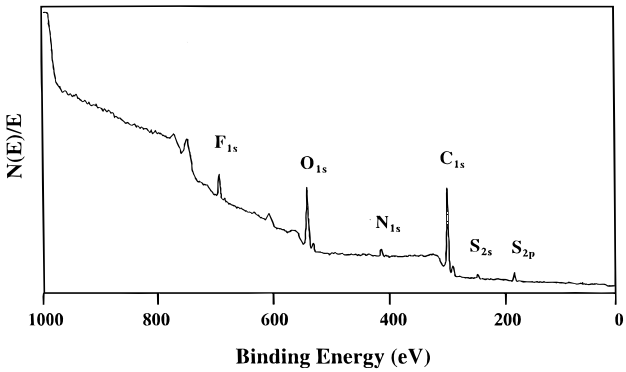


Figure 4. Survey XPS spectrum of a 22-layer polyelectrolyte film supported on PCTFE−OH prepared using protocol 1.

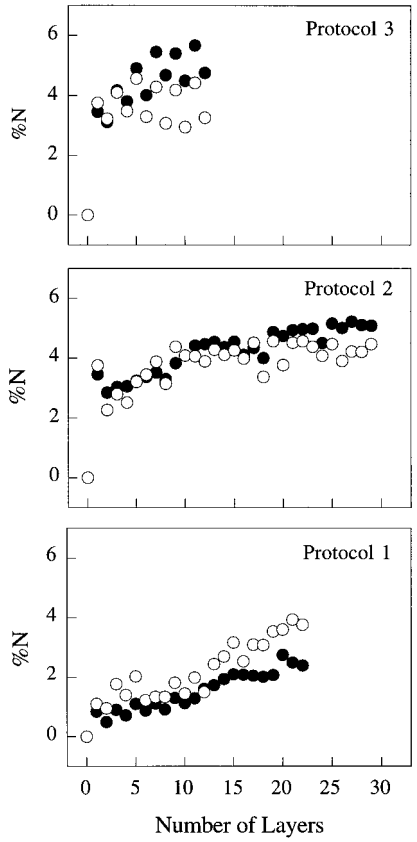


Figure 5. Nitrogen atomic concentrations determined at 15° (○) and 75° (●) takeoff angles as a function of the number of layers in the multilayer film.

charged polyelectrolyte. The kinetics for desorption were monitored by XPS and contact angle analysis. PCTFE−OH−PAH samples prepared at pH 11 (30 min adsorptions) were immersed in pH 4 water from 5 to 60 min. The desorption was rapid as indicated by XPS; nitrogen concentration decreased from ∼5% to ∼3.5% (there was little takeoff angle dependence—data in Figure 5) over the first 10 min and leveled at this value. Water contact angles did not change upon desorption and remained at $\theta_A/\theta_R = 70/14°$. This surface exhibits a higher contact angle hysteresis than the one prepared by adsorption at pH 4 ($\theta_A/\theta_R = 61/27°$) suggesting that this surface may be rougher and/or more chemically heterogeneous. Surfaces of this type that were used to prepare multilayers were prepared by adsorption at pH 11 for 30 min followed by desorption at pH 4 for 20 min. These surfaces were more concentrated in ammonium

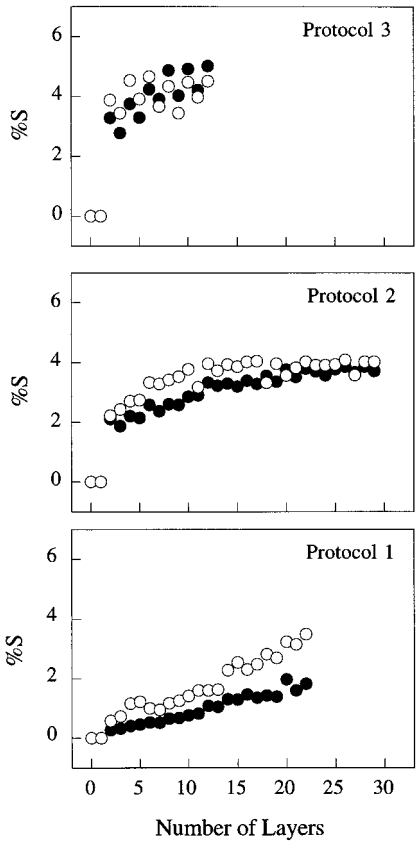


Figure 6. Sulfur atomic concentrations determined at 15° (○) and 75° (●) takeoff angles as a function of the number of layers in the multilayer film.

ions by a factor of ∼3.5 over those prepared by adsorption at pH 4.

The effects of PAH concentration and solution ionic strength were also assessed for the first PAH layer adsorption. Adsorbance (as assessed by nitrogen content of the PCTFE−OH-supported first layer) is essentially independent of PAH concentration from 0.005 to 0.2 M (indicating a high affinity concentration isotherm) and independent of $MnCl_2$ concentration from 0 to 1.5 M.

Second Layer Adsorptions. The adsorption of poly(sodium styrenesulfonate) (PSS) to PCTFE−OH−PAH (prepared by adsorption of 0.02 M PAH from pH 4 solution for 30 min) was studied with regard to kinetics and solution ionic strength.

Figure 3 describes the kinetics by plotting the XPS sulfur:nitrogen atomic ratio as a function of adsorption time. The data indicate that adsorption is complete within 20 min. The receding water contact angle decreases during the first 20 min of adsorption to 18° (from $\theta_R = 27°$ for PCTFE−OH−PAH) and remains constant at that value. The advancing contact angle remains unchanged. The absence of an XPS takeoff angle dependence indicates that the PSS (second) layer is not stratified over the PAH (first) layer but that ammonium and sulfonate ions are dispersed to the same extent throughout the XPS sampling depth (outermost ∼40 Å) of the sample. What is not apparent from this ratioed data is that both the PSS and the PAH become stratified in the XPS sampling region during the second layer adsorption. Both nitrogen and sulfur atomic concentrations are takeoff angle dependent (the data are present in Figures 5 and 6), indicating that both

polyelectrolytes are more concentrated near the surface than in the subsurface XPS sampling region. The first PAH layer thus restructures during the adsorption of PSS and the formation of the PAH−PSS polyelectrolyte complex. The S:N ratio of ∼0.6 indicates that the surface should have a net positive charge at pH 4, but apparently this is not the case: the adsorption of PSS ceases as indicated by the data in Figure 3, and PAH (the third layer) adsorbs to this surface, suggesting that it functions as a negatively charged or neutral surface. We emphasize that using XPS data (obtained at high vacuum) to analyze the structure or predict the behavior of surfaces in contact with liquids may lead to erroneous conclusions. The S:N ratio (which is also the sulfonate to ammonium ion ratio) of ∼0.6 also predicts that chloride should be present in significant concentration; this is not the case under high vacuum.

The effect of solution ionic strength for the second layer adsorption was studied by adding $MnCl_2$ to the PSS solution (0.02 M, pH 4) in concentrations ranging from 0.1 to 1.5 M. The adsorbed amount of PSS increases significantly at all $MnCl_2$ concentrations studied with a plateau above 0.2 M. The XPS data of these two-layer assemblies show a pronounced takeoff angle dependence as well, indicating that a thicker PSS layer is stratified above the PCTFE−OH−PAH substrate. S:N ratios of 2.8 and 1.8 are observed at 15 and 75° takeoff angles for a sample prepared with 1.0 M $MnCl_2$.

Multilayer Assembly. From these initial experiments, three protocols were chosen for multilayer assembly. In protocol 1, PAH and PSS were deposited at pH 4 without $MnCl_2$ added. In protocol 2, the first PAH layer was adsorbed at pH 11 and treated with water at pH 4, and subsequent PSS and PAH layers were deposited at pH 4 without $MnCl_2$ added. In protocol 3, the first PAH layer was adsorbed as in protocol 2, and subsequent PSS and PAH layers were deposited at pH 4 with 0.2 M $MnCl_2$ added to the PSS adsorption solutions. Polyelectrolyte concentrations were held at 0.02 M, and all adsorptions were carried out for 20 min except the first PAH layer adsorptions. The first layer adsorptions for protocols 2 and 3 were carried out for 30 min followed by 20 min treatments with water at pH 4 to desorb weakly bound PAH. Adsorptions were carried out at room temperature using freshly prepared unstirred polyelectrolyte solutions and samples were rinsed with three 150 mL aliquots of water after each adsorption. The polyelectrolytes were adsorbed in the same sequence for each protocol beginning with PAH as the first layer so in all cases multilayer assemblies with an even number of layers contain PSS as the top (outermost) layer and odd number-of-layer multilayers have PAH as the outermost layer.

The principal analytical tool used in analyzing the multilayer structures was XPS. A survey spectrum of a 22-layer film on PCTFE−OH prepared using protocol 1 is shown in Figure 4. All of the features of interest are present in this spectrum. The intensities of the N_{1s} (404 eV), and S_{2p} (169 eV) photoelectron lines can be used to assess the relative concentrations of PAH and PSS and degree of stratification (layer segregation) in the multilayers. The F_{1s} photoelectron line is due entirely to the PCTFE−OH substrate; this peak decreases in intensity and eventually disappears as more layers are deposited. We can estimate the thickness of the multilayer assemblies and individual layers from the decrease in intensity of this substrate peak.

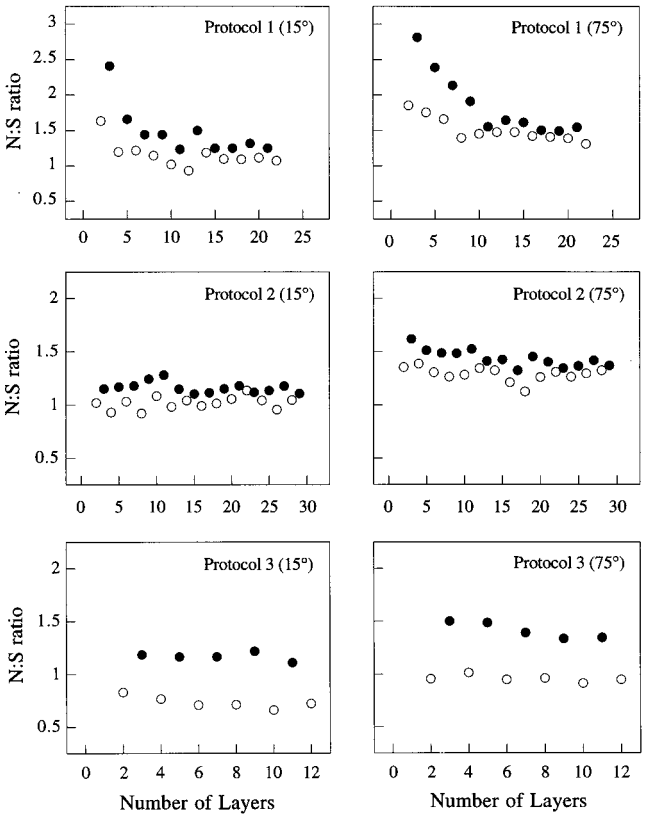


Figure 7. Nitrogen:sulfur atomic ratio data vs the number of layers for the 3 series of PAH/PSS multilayer assemblies: odd number of layers (●), even number of layers (○).

Protocol 1. As PAH and PSS polyelectrolytes are sequentially adsorbed to PCTFE−OH, photoelectron spectra of isolated samples show that nitrogen and sulfur atomic concentrations gradually increase and fluorine concentration gradually decreases, implying that PAH/PSS multilayer assemblies are being builtup and are covering the fluorine-containing substrate. As discussed above, the absence of a takeoff angle dependence in the N:S ratio of a two-layer sample (Figure 3) suggests that the layers are not individually stratified and that the two polyelectrolytes are distributed uniformly (with respect to one another) within the outer few tens of angstroms of PCTFE−OH. On the basis of these data they cannot be considered *layers*. Spectra of samples that have undergone more sequential adsorptions do provide evidence for layer formation and some degree of stratification of the layers. These layers are extremely thin, however (less than 1 Å average thickness—discussed below) and not close-packed so they are forced to interdigitate to fill space. Figures 5 and 6 (protocol 1) show plots of nitrogen and sulfur concentration as a function of the number of layers in the multilayer film for a series of samples prepared. The increasing takeoff angle dependence with number of layers indicates that the polyelectrolytes are concentrated in the outermost regions of the samples and must be adsorbing to the surface as opposed to being absorbed by the water-swollen PCTFE−OH layer, as was the case for the first two layers.

Nitrogen:sulfur atomic ratio data for the same series of multilayers are shown in Figure 7 (protocol 1). We make four points concerning these data: One, there is a pronounced odd−even trend at low layer numbers that

decreases in amplitude with increasing number of layers adsorbed. The large changes are due to the fact that an additional PSS or PAH layer significantly affects the multilayer assembly composition. The high ratios at low layer numbers are the result of the relatively large amount of PAH that adsorbs in the first adsorption. Two, the ratios level off after ~6 layers for 15° takeoff angle data and ~10 layers for 75° takeoff angle data, indicating that the composition is not greatly affected by the addition of one more PAH or PSS layer after this point; the stoichiometry of the assembly process (ammonium ion:sulfonate ion ratio) can be determined using this information. The 15° data converge on a N:S ratio of ~1.2 and the 75° data converge on a N:S ratio of ~1.5. These two values suggest ammonium ion:sulfonate ion ratios of 6:5 and 3:2, respectively. We believe that the 75° takeoff angle data is a better reflection of the stoichiometry (three ammoniums per two sulfonates) and expect that this discrepancy is due to the greater mean free path of the S_{2p} photoelectrons compared with the N_{1s} photoelectrons—this should bias the N:S ratios low, particularly at the grazing 15° takeoff angle. Three, The odd−even trend persists even at high layer numbers, with the nitrogen content relatively high when PAH is the last layer adsorbed and relatively low when PSS is the top layer. The trend is more apparent in the more surface-selective 15° data. This indicates that some degree of stratification occurs in the assembly. Four, the odd−even trends at higher layer numbers indicating stratification, as well as the takeoff angle dependence of the data, indicate that adsorption to a reasonably rigid interface is occurring after a few layers have more "absorbed into" rather than adsorbed to polymer surface.

Figure 8 (protocol 1) shows the fluorine atomic composition data vs number of layers for the same series of PAH/PSS multilayer assemblies supported on PCTFE−OH. The fluorine concentration decreases continually, indicating that the polyelectrolyte overlayer increases in thickness with increasing number of layers. Estimates of the thickness of individual polyelectrolyte layers are discussed below, but we point out here that the layers are extremely thin; the intensity of the fluorine signal at 75° takeoff angle is attenuated only by ~40% after greater than 20 layers have been adsorbed. We note that there is considerable scatter in the 15° takeoff angle data and variable takeoff angle dependence. Some degree of scatter in the data is expected due to the fact that separate samples prepared by multistep procedures were used for analysis of each thickness (number of layers) multilayer (samples were not used after analysis as substrates for further depositions). This degree of scatter, however, is greater than what we have seen in other systems, including data presented below. This, coupled with the fact that similar scatter is not observed in the 75° data for this series, suggests that the conversion from an absorption into the 1000 Å thick PCTFE−OH layer to an adsorption to a more rigid interface is gradual and occurs at different points in the multilayer assembly process in different individual experiments. In retrospect, this suggests to us that a reconstruction of the multilayer, similar to what was observed by receding contact angle changes in the first layer adsorption, may be occurring after the polyelectrolyte adsorption step. We have not carried out experiments to address this issue. We point out that the takeoff angle dependence is consistent for

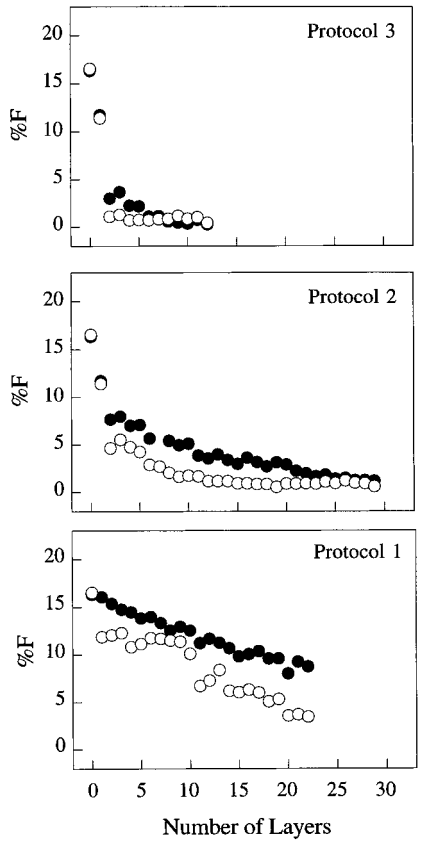


Figure 8. Fluorine atomic concentrations determined at 15° (○) and 75° (●) takeoff angles as a function of the number of layers in the multilayer film.

multilayer assemblies with 14 layers or more. Scatter in the receding contact angle data (Figure 9, protocol 1) reflect the scatter in the 15° takeoff angle data. The contact angle data is included for comparison with data presented below and we note that no odd−even effect is observed in the advancing contact angle data.

Protocols 2 and 3. The same series of experiments and analyses were carried out using protocols 2 and 3 and data analagous to that presented for protocol 1 is presented in Figures 5−9 for these conditions. Both of these protocols involve using a different procedure (described above) for adsorption of the first PAH layer that yields a surface that is more concentrated in ammonium ions. In protocol 2, subsequent layers are adsorbed in identical fashion as those using protocol 1; in protocol 3, $MnCl_2$ is added to the PSS adsorption solutions. These variations give rise to differences in multilayer assembly structure and these are discussed below.

The XPS data (nitrogen, sulfur, and fluorine concentrations) in Figures 5, 6, and 8 for samples prepared using protocol 2 indicate that the composition of the region of the samples assessed by XPS reaches a plateau after a sufficient number of layers has been adsorbed to form a multilayer assembly that is thick enough to effectively attenuate photoelectrons originating in the substrate. This occurs after ~9 layers have been deposited for the 15° takeoff angle data and after ~25 layers have been deposited for the 75° data. This is in contrast to the data for protocol 1, which does not reach plateau values, and this contrast indicates that the multilayer assemblies prepared using protocol 2 are thicker. This increased thickness is due, in large part, to the first two layers although the subsequent layers

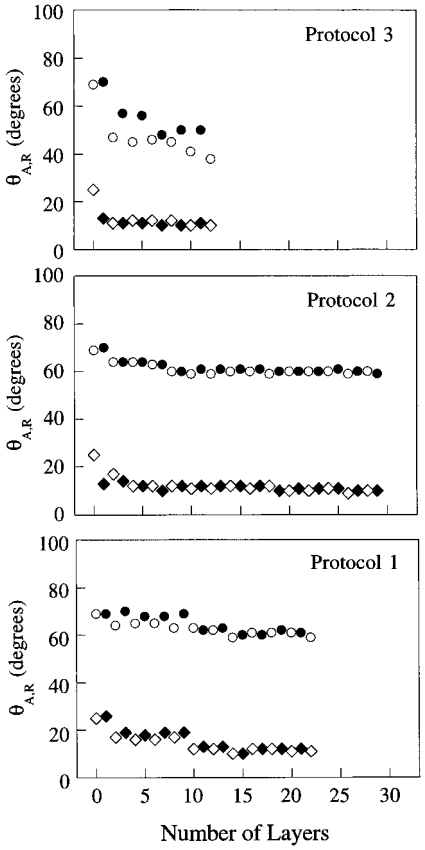


Figure 9. Advancing (●, ○) and receding (◆, ◇) contact angle data for each of the three series of samples: closed and open symbols indicate odd and even numbers of layers, respectively.

are thicker than those prepared using protocol 1 (see below). This can be seen most clearly in the fluorine composition data that decreases sharply after the first two layers have been adsorbed and more gradually with subsequent layers. This disparity in thickness can also be inferred from the nitrogen:sulfur ratios (Figure 7). A relatively thick second (PSS) layer is indicated by the depression of the N:S ratio after the second layer is adsorbed (compare with protocol 1—Figure 7). N:S ratios of 1.0 and 1.35 are observed for 15 and 75° takeoff angle data compared with 1.7 and 1.9 for protocol 1. The first layer in protocol 2 samples contains ~3 times the density of ammonium ions as that for protocol 1; thus the second layer in protocol 2 samples is greater than 3 times thicker than the second layer in protocol 1 samples. That the subsequent (third and higher) layers are not as thick as the first two (their thickness is discussed in quantitative terms below) is also indicated by the N:S ratio data. The amplitude of the odd−even effect is approximately the same as that for protocol 1. The increased surface charge (higher ammonium ion density) on protocol 2 first layers induces a greater adsorption of PSS, but the resulting increased surface sulfonate group concentration does not enhance the adsorption of the third layer. The layer-by-layer deposition process reverts to one very similar to that of protocol 1. We note that the stoichiometry of the assembly processes (ammonium ion:sulfonate ion ratio) are indistinguishable with N:S ratios of ~1.2 and ~1.5 for 15 and 75° takeoff angle data, respectively. Water contact angle data are consistent with this analysis (Figure 9, protocol 2). The receding contact angle data converges to the same value as that of protocol 1 samples ($\theta_R = 10°$), but this value is reached with fewer layers adsorbed.

The corresponding data for samples assembled with $MnCl_2$ added to the PSS adsorption solutions (protocol 3, Figures 5−9) indicate that much thicker layers are formed under these conditions. The atomic concentration data reach plateau values at a fewer number of layers. The N:S ratios for a two-layer sample are 0.8 and 0.95 (15 and 75° takeoff angle data), indicating that sulfonate ions are present in excess of ammonium ions. The increased surface anion concentration increases the adsorbance of the third (PAH) layer, and this enhancement propagates to higher layer numbers. The increased layer thickness is indicated by the amplitude of the odd−even effect in the N:S ratio (Figure 7). It is much higher than in the cases of protocols 1 and 2 and indicates that the layers are quite rigorously stratified. The layers are thick enough to cause an odd−even effect in the advancing water contact angle as well (Figure 9). Samples prepared using protocols 1 and 2 do not display this effect presumably because the technique samples two (or more) of the thinner layers. The stoichiometry of assembly for protocol 3 differs from protocols 1 and 2 with ammonium ion:sulfonate ion ratios of ~1.0 and ~1.2 for 15 and 75° takeoff angle data, respectively.

Estimates of Layer Thicknesses. We can estimate the thicknesses of the multilayer assemblies and the average thickness of individual layers from the XPS data. The F_{1s} peak intensity should decrease exponentially with the buildup of layers and the data (Figure 8) qualitatively fit the predicted decrease. If we knew the mean free path of the F_{1s} photoelectron in the multilayer assemblies, we could calculate the average thickness with no assumptions. We can calculate thickness in terms of photoelectron mean free paths, but we have to assume a value for the mean free path to estimate a dimensional thickness. We have calculated a mean free path of ~20 Å for Mg Kα excited Si_{2p} electrons in PAH/PSS multilayer assemblies supported on silicon wafers using XPS (75° takeoff angle) and X-ray reflectivity data,[11] and we can use this value to calculate[24] a mean free path of 11.5 Å for the F_{1s} photoelectron. This value is used below to calculate layer thicknesses.

We have previously[10] described eq 2, which relates the attenuation of a substrate photoelectron signal to the thickness of a polyelectrolyte multilayer assembly

$$-\ln(N/N_o)\sin\theta = nz/\lambda \qquad (2)$$

supported on that substrate. We use this expression here, where N is the atomic concentration of fluorine (data from Figure 8), N_o is the fluorine concentration of the substrate (PCTFE−OH), θ is the takeoff angle, n is the number of layers, z is the average thickness of the individual layers, and λ is the F_{1s} photoelectron mean free path. In Figure 10 are plots of $-\ln(N/N_o)\sin\theta$ vs n for the series of samples prepared using each protocol. The slopes of the lines indicate the average layer thickness divided by the photoelectron mean free paths. The fact that the 15 and 75° data yield different slopes indicates that the electron mean free path depends on takeoff angle. We have discussed this issue,[10] and it is not unexpected for an anisotropic system with thin stratified layers. Using a mean free path of 11.5 Å we calculate the average layer thicknesses from the 75° data to be 0.3, 0.8, and 4.1 Å for

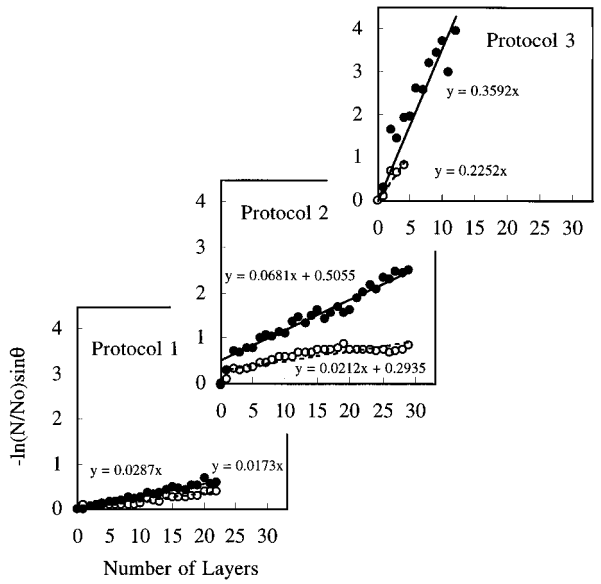


Figure 10. Plots of $-\ln(N/N_o)\sin\theta$ vs number of layers in the multilayer film for the 3 series of PAH/PSS multilayer assemblies. The slopes of the lines indicate the ratio of the average layer thickness to the F_{1s} photoelectron mean free path. The open (○) and closed (●) circles are for data recorded at 15 and 75° takeoff angles, respectively.

protocols 1, 2, and 3, respectively. The least-squares analysis that was used to determine the slopes included the origin for protocols 1 and 3. We have made the point that using protocol 2 causes the first two layers to be exceptionally thick; the origin and the first point for protocol 2 were not included in the slope determination for protocol 2. We emphasize that these values are only estimates, as we assume that the mean free paths are the same as that determined for the silicon-supported multilayer films.

Notwithstanding the assumption made in determining these thicknesses, the data indicate extraordinarily thin individual layers and the concept of stratified polymer monolayers of subangstrom thickness is counterintuitive and warrants additional comment. Close-packed monolayers of poly(allylammonium) and poly(styrenesulfonate) would have thicknesses of ~6 and ~9 Å, assuming a density of 1.0. The subangstrom thick monolayers must be far from close-packed with chain segments occupying only ~10% of the available surface area. We believe, however, based on gas permeability measurements,[11] that the multilayer assemblies are quite dense and thus the chains must be interdigitated. We have crudely modeled our mental image of these assemblies by applying alternating layers of red and yellow yarn on the floor. Upon compression, the layers interpenetrate, but clearly remain stratified.

Mechanical Properties of Multilayer Assemblies. We have carried out simple peel tests using pressure-sensitive adhesive tape (3M #810) to determine the locus of failure in PCTFE−OH/multilayer assembly/adhesive tape composites. Peel tests on samples prepared by all three protocols with both odd and even numbers of layers were performed: 39 and 40 layers for protocol 1, 29 and 30 layers for protocol 2, and 11 and 12 layers for protocol 3. The tape was applied and peeled from the samples, and XPS spectra (15° takeoff angle) of both surfaces were compared with spectra obtained before the adhesive joint was formed. The adhesive on the tape contains only carbon and oxygen, and the supported polyelectrolyte multilayer samples contain nitrogen and sulfur (each present in ~4 atom %—see Figures 5 and 6), so the analysis should be straightforward.

In all cases small amounts of sulfur and nitrogen (less that 0.5 atom %) were transferred to the tape upon peeling, indicating some cohesive failure in the multilayer assemblies; sulfur and nitrogen content in the supported multilayer assemblies remained high. Except for one case (protocol 1, 40 layers), the carbon concentration in the supported multilayer assembly increased (by 2−4%), indicating that some cohesive failure in the adhesive also occurs. These results indicate that the mechanical strength of the multilayer assemblies is approximately equal to the cohesive strength of the adhesive of the pressure sensitive tape (not very strong) and that failure occurs very near to (within a few angstroms of) the adhesive/multilayer assembly interface. That the adhesive strength between the multilayers and the PCTFE−OH substrate is stronger than this value is also indicated. These results contrast with the data for multilayer assemblies supported on other substrates[10] (PET, PET−CO_2^- and PET−NH_3^+), that indicate failure either exclusively in the pressure sensitive adhesive (PET−CO_2^- and PET−NH_3^+) or exclusively in the substrate (PET).

Summary

Poly(chlorotrifluoroethylene) film, chemically modified to contain alcohol functionality (PCTFE−OH) (a neutral surface), supports the layer-by-layer assembly of polyelectrolytes (PAH and PSS) when PAH is adsorbed as the first layer. The adsorbance of the first PAH layer can be controlled using pH; hence, the ammonium ion concentration of the first layer (charge density) can be controlled. Three different sets of conditions were used to prepare multilayer assemblies: protocols 1 and 2 differ by the charge density of the first layer. Protocol 3 differs from protocol 2 in that $MnCl_2$ was added to the PSS adsorption solutions. The thickness of the individual layers in the assemblies depends both on the charge density of the first layer and the ionic strength of the PSS adsorption solution. The stoichiometry of the assembly process (ammonium:sulfonate ratio) also depends on the ionic strength of the PSS adsorption solution. The average individual layer thicknesses for protocols 1, 2, and 3, respectively, are 0.3, 0.8, and 4.1 Å thick, as assessed by XPS. Although the layers are extremely thin, XPS data (and contact angle data for protocol 3) indicate that the layers are stratified. Peel tests indicate that the multilayer assemblies on PCTFE−OH exhibit poorer mechanical integrity than those on other substrates.

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