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Surface "Priming" for Layer-by-Layer Deposition: Polyelectrolyte Multilayer Formation on Allylamine Plasma-Modified Poly(tetrafluoroethylene)

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ABSTRACT: Allylamine plasma polymerization is reported as a method to surface-modify PTFE and to prepare substrates that promote layer-by-layer assembly of polyelectrolytes. Two conditions for the plasma polymerization that differ in radiofrequency power were studied. Both conditions (10 and 50 W) produce substrates that support layer-by-layer assembly, and well-defined multilayer structures are apparent in samples with greater than ~10 layers. The substrates prepared at lower power yield more reproducible initial layer data; infrared spectra indicate a higher surface density of amine groups in the samples prepared at 10 W that likely leads to a higher surface charge density upon exposure to acidic aqueous solution. Poly(allylamine hydrochloride) and poly(sodium styrenesulfonate) were used to construct multilayer assemblies. XPS and contact angle data indicate stratified layers. XPS analysis also indicates that the stoichiometry of the assembly process is two ammonium ions per sulfonate group and that the average individual layer thickness is ~6.1 Å.

Introduction

Spontaneous assembly is widely used for preparing modified surfaces and supramolecular ordered structures.[1−3] The Langmuir−Blodgett (LB) and self-assembled monolayer (SAM) techniques have been the most widely used methods for preparing structures of this type, but each of these methods has limitations. Chief among these limitations are that the range of substances that are useful self-assembly components is limited for both LB and SAM techniques and that multilayer structures cannot be readily prepared using the SAM technique. The relatively recent reports by Decher *et.al.*[4−8] of layer-by-layer (L-by-L) deposition to prepare polyelectrolyte multilayer assemblies have added a new and versatile spontaneous assembly tool to the techniques of thin film synthesis. L-by-L deposition has several obvious advantages. (1) The process is simple and the composite supported films are obtained in a straightforward manner in simple glassware: the substrate is exposed alternately to aqueous solutions of polyelectrolytes of opposite charge, rinsing between deposition steps. (2) A wide variety of water-soluble polyions can be used as assembly components including a variety of linear polyelectrolytes,[4−8] proteins,[9] viruses,[10] dendrimers,[11] clays[12] and silica.[13] (3) Any substrate that can be modified to contain a charge can be used and it can be of any shape, topography or topology. (4) The individual layers have molecular thicknesses and this thickness can be controlled by experimental variables. The overall thickness of the assembly can be controlled simply by the number of deposition cycles. The utility of the method is demonstrated by the applications that have been reported including conducting thin films,[14,15] sequential enzyme reactors,[16] films for nonlinear optics,[17] light-emitting and electrochromic thin films,[18−20] lithographic development[21] and asymmetric gas separation membranes.[22] The incredibly short time between the initial reports of L-by-L deposition and the range of demonstrated applications is further evidence of the simplicity and practicality of the method.

We have recently[22−24] reported the extension of the L-by-L deposition technique to organic polymer substrates, preparing supported polyelectrolyte multilayers on surface-modified (and in one case, unmodified) polymer film samples. Poly(4-methyl-1-pentene) (PMP) was oxidized[22] to prepare a carboxylic acid-functionalized PMP surface (PMP$-CO_2^-$) that is negatively charged at sufficiently high pH and that adsorbs cationic polyelectrolytes. Poly(ethylene terephthalate)[23] (PET) was hydrolyzed (PET$-CO_2^-$) and amidated (PET$-NH_3^+$) to form surfaces that, respectively, cationic and anionic polyelectrolytes adsorb to and initiate L-by-L deposition. Poly(chlorotrifluoroethylene) (PCTFE) was modified to introduce alcohol functionality[25] and poly(allylamine hydrochloride) (PAH) was adsorbed to PCTFE−OH to promote L-by-L assembly.[24] Virgin PET (a neutral surface) also supports L-by-L deposition initiated with PAH and we suspect that hydrogen bonding is the primary interaction driving adsorption of the first layer with PET and PCTFE−OH substrates.

Our studies with each of these substrates used PAH and poly(sodium styrenesulfonate) (PSS) as polyelectrolytes, and direct comparisons can be made between the multilayer assemblies on the different substrates. We found no limit to the number of layers that can be deposited on any substrate, but the multilayer assemblies differ significantly on different substrates. Individual layer thicknesses vary from less than an angstrom to ~10 Å and the stoichiometry of the assembly process (ammonium ion:sulfonate ion ratio) varies from ~1:1 to ~1.6:1. The assembly process is remarkably forgiving, adapting to different substrates and exerting layer thickness and stoichiometry control. X-ray photoelectron spectroscopy indicates that the layers are stratified on all substrates, but the extremely small average thicknesses measured indicate that the individual layers are not close-packed and must be interdigitated at functional group dimensions. Stratification and interdigitation are observed in assemblies with thicker layers on silicon substrates.[26] Contact angle data indicate that wettability is controlled by the outermost layer when the layers are sufficiently thick, but by at least two layers when the layers are thinner.

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The mechanical integrity of the multilayer films on PET, PET$-CO_2^-$, and PET$-NH_3^+$ was assessed using a peel test with pressure-sensitive adhesive tape. The results indicate that PAH/PSS multilayer assemblies have significant mechanical strength: failures occur in the adhesive for PET$-CO_2^-$- and PET$-NH_3^+$-supported films and in the PET substrate for virgin PET-supported films.

Our previous studies indicate that L-by-L deposition can be used to modify polymer surfaces, however they also point out that the method is not generally applicable. Different surface modifications are required to initiate L-by-L deposition on different polymer substrates. In this paper we present a general method for priming polymer surfaces for L-by-L deposition: we report that allylamine can be plasma-polymerized onto poly(tetrafluoroethylene) (PTFE) and that this polymer layer initiates layer-by-layer deposition of PSS and PAH. PTFE was chosen as a substrate because it is difficult to surface-modify and is resistant to plasma modification,[27] thus it is a severe test of this method. Allylamine has been plasma polymerized on other polymer substrates[28] and the resulting plasma polymers have been shown to contain amine functionality. L-by-L deposition has been reported on an oxygen plasma-treated plasma-polymerized methane film supported on glass.[29]

Experimental Section

General Procedures. PTFE was obtained from Norton Performance Plastics as a 4 mil skived film (DuPont Teflon). Poly(allylamine hydrochloride) (PAH) (Aldrich, $M_n = 50\,000-65\,000$), and poly(sodium styrenesulfonate) (PSS) (Aldrich, $M_n = 70\,000$) were used as received. Allylamine (99+%, Aldrich) was degassed using freeze−pump−thaw cycles. Water was purified using a Millipore Milli-Q system that involves reverse osmosis followed by ion-exchange and filtration steps. Plasma modification reactions were carried out in a home-built inductively coupled Pyrex reactor in which flow rate, power (13.56 MHz—supplied by an Astron RS-35A power supply and a Yaesu FT-840 HF transceiver), and pressure can be controlled. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer-Physical Electronics 5100 spectrometer with Al Kα excitation (15 kV, 400 W) at a takeoff angle of 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}, 0.200; O_{1s}, 0.501; N_{1s}, 0.352; S_{2p}, 0.540; F_{1s}, 1.00. Attenuated total reflectance infrared (ATR IR) spectra were recorded using a Bio-Rad FTS 175C FTIR at 1 cm^{-1} resolution with a 10 × 5 × 1 mm 45° KRS-5 internal reflection element. Contact angle measurements were made with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Dynamic advancing (θ_A) and receding angles (θ_R) were recorded while the probe fluid (water, purified as described above) was added to and withdrawn from the drop, respectively. Interferometric microscopy was performed with a Zygo Maxim 3D Model 5800. Peel tests were performed manually with an angle of 180° between the delaminated film surface and the tape (3M no. 810).

Plasma Chemistry. PTFE film samples were inserted into the reactor which was then evacuated to ~0.05 mm. Air was introduced using a needle valve and the pressure was equilibrated to 0.2 mm by adjusting the needle valve. After equilibrium pressure was reached, radiofrequency at 50 W was applied for 30 min. The air inlet was then closed, and the reactor was evacuated to ~0.05 mm. The inlet to a vessel containing allylamine was then opened and the monomer pressure was adjusted to 0.3 mm. The flow rate was measured to be ~1.7 sccm. The allylamine plasma was operated at the desired power for the desired period of time. Most of the experiments were conducted at 10 W for 30 min or at 50 W for 5 min. After the radiofrequency was turned off, allylamine was allowed to flow through the system for 2 min before evacuating the chamber to ~0.05 mm for 15 min and isolating the PTFE film samples.

Polyelectrolyte Depositions. 0.02 M PAH and 0.02 M PSS (concentrations based on repeat units) deposition solutions were prepared and adjusted to pH 2.2 and 2.9, respectively, by adding small amounts of dilute HCl and NaOH solutions and using a Fisher 825MP pH meter. Alternating monolayers of PAH and PSS were deposited onto the plasma-treated PTFE substrate by alternating submersions of the film samples in the polyelectrolyte solutions to build multilayer structures of up to 30 layers. Between the 20-min depositions, the films were rinsed with three aliquots of water.

Results and Discussion

Plasma Chemistry. Our home-built plasma reactor was modeled after the one described by Morosoff[30] and consists of an 85 mm diameter Pyrex tube attached to a ballasted vacuum manifold with ports to introduce compressed gases and volatile liquids through needle valves. The stationary electrode is 10 turns of $^3/_{16}$ in. soft copper tubing around a 15 cm section of the tube and is powered by a radio transmitter that has been set to broadcast at 13.56 MHz. Samples are supported by a glass plate that rests in the center of the tube within the volume defined by the electrode.

Film samples of PTFE were cut to dimensions appropriate for our analytical techniques (generally 1 × 5 cm) and were exposed to an air plasma (50 W) for 30 min. X-ray photoelecton spectroscopy (XPS) of samples treated in this manner indicate the incorporation of small amounts of oxygen (~2 atom %) and no nitrogen. Gardella[27] has reviewed and discussed the chemical inertness of fluoropolymers toward air and other plasmas; our objective in using the air plasma was not to incorporate functionality but to clean the samples and remove any weak boundary layer that would adversely affect adhesion. The water contact angles of PTFE change from $\theta_A/\theta_R = 120/92°$ to $\theta_A/\theta_R = 131/49°$, and we attribute these changes to the incorporation of small amounts of hydrophilic oxygen-containing functionality that pin the drop during advancing or receding analysis, increasing the hysteresis. Normally the samples were not isolated from the plasma reactor after this treatment, but the system was evacuated and allylamine vapor was introduced. After equilibration of pressure/flow rate, the radiofrequency power was applied at the desired power for the desired period of time. After the RF power was turned off, allylamine vapor was allowed to flow through the system for two minutes before evacuating the chamber and isolating the samples. The majority of samples were prepared using two optimized conditions that were determined to be reasonably reproducible: one set of samples was prepared at low power (10 W) for 30 min and the other at high power (50 W) for 5 min. The power (and also the flow rate and pressure) affect the plasma chemistry. Low power plasmas retain the structure of the monomer more than do high power plasmas[31] and tend to be less highly crosslinked. Figure 1 shows ATR IR spectra of the two plasma-modified samples which we abbreviate ^{10}PTFE$-NH_3^+$ and ^{50}PTFE$-NH_3^+$, where the superscript indicates the radiofrequency power used in the synthesis. They are named as the ammonium ion because the amines present in the sample are protonated during the L-by-L depositions described below. Both spectra indicate the presence of primary amine groups (3400−3600 cm^{-1}), and clearly they are present in higher concentration on ^{10}PTFE$-NH_3^+$ than on ^{50}PTFE$-NH_3^+$. Also

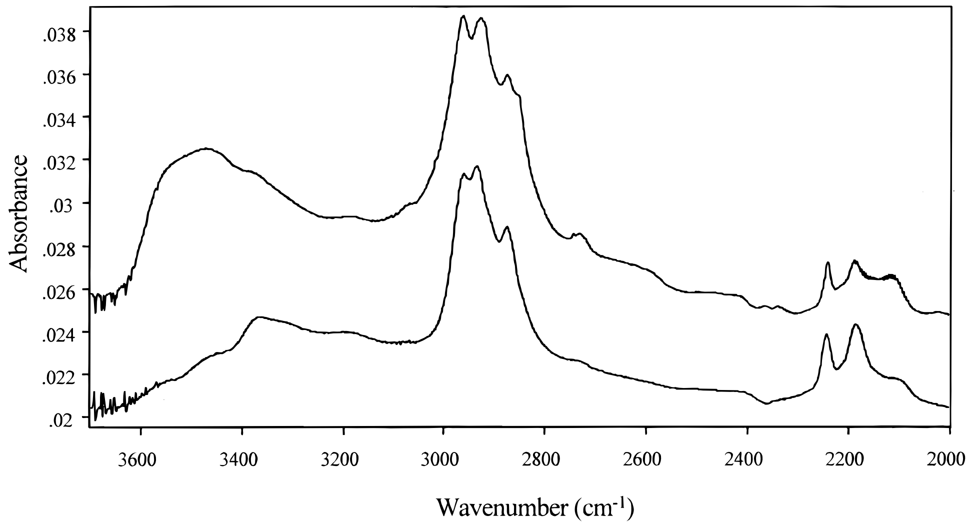

Figure 1. ATR IR spectra of allylamine plasma-modified PTFE samples: ^{50}PTFE−NH_3^+, lower spectrum; ^{10}PTFE−NH_3^+, upper spectrum.

indicated are secondary amines and/or imines (3300−3400 cm^{-1}), nitriles (2240 cm^{-1}) and isonitriles (2180 cm^{-1}). Other functionalities including C−C unsaturation as well as signals from the PTFE substrate are observed in portions of the spectra not shown. XPS spectra showed significant nitrogen concentration (discussed quantitatively below) and the disappearance of fluorine, indicating a continuous coating of plasma polymer. Interferometric microscopy was used to measure the thickness of the plasma polymers. Allylamine was plasma polymerized onto microscope slides with half the slide masked using the conditions for preparation of ^{10}PTFE−NH_3^+ and ^{50}PTFE−NH_3^+. The step height was measured indicating thicknesses of ∼720 and ∼120 Å for the 10 W, 30 min and 50 W, 5 min polymerizations, respectively. Water contact angles are significantly lower than PTFE and air plasma-treated PTFE: $\theta_A/\theta_R = 64/6°$ and 52/8° for ^{10}PTFE−NH_3^+ and ^{50}PTFE−NH_3^+, respectively. The mechanical integrity of the plasma-polymerized films and the adhesion of the plasma polymers to PTFE was assessed using a 180° peel test with a pressure-sensitive adhesive tape. For samples prepared using both plasma conditions, XPS analysis of the delaminated tape showed the absence of nitrogen. Analysis of the plasma-modified PTFE films after delamination showed increased carbon and oxygen content and decreased nitrogen content. These results indicate that failure occurs within the tape and that the plasma polymers have a higher cohesive strength than the adhesive and also that the adhesion between the plasma polymers and PTFE is quite good.

Polyelectrolyte Depositions. Both ^{10}PTFE−NH_3^+ and ^{50}PTFE−NH_3^+ were used as substrates for layer-by-layer deposition of PSS and PAH. Film samples were alternately placed in unstirred aqueous solutions of the two polyelectrolytes at room temperature, rinsing with pure water between deposition steps. The polyelectrolyte concentrations used were chosen, based on data for other substrates, to be well within the plateau region of concentration isotherms. The kinetics of the first layer (PSS) adsorptions were determined by XPS over 2 h and sulfur concentration values indicate that the adsorption is complete within 20 min. The first PSS layer in all multilayer assemblies was deposited using a 30 min adsorption time and subsequent layers were deposited using 20 min adsorption times. Adsorption solutions used for first-layer depositions were discarded and replaced by fresh solutions to ensure that the adsorption solutions were not contaminated by impurities that may desorb from the plasma polymer. A buildup of PSS and PAH layers by L-by-L deposition occurred on both ^{10}PTFE−NH_3^+ and ^{50}PTFE−NH_3^+ substrates; however, the data for multilayer films on ^{10}PTFE−NH_3^+ exhibited less scatter and are presented in detail here. The (more scattered) data for multilayer films on ^{50}PTFE−NH_3^+ have been presented[32] and are discussed comparatively below. We assume that the higher concentration of amine groups (and ammonium ions when in contact with acidic water) in ^{10}PTFE−NH_3^+ is responsible for its more consistent behavior as a substrate for L-by-L deposition. It may also be that more reproducible plasma polymers are formed at the lower power.

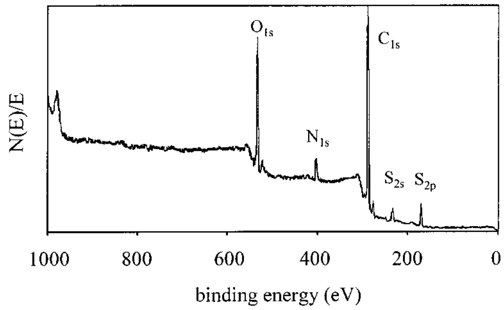

Figure 2. Survey XPS spectrum of an 11-layer polyelectrolyte film (^{10}PTFE−NH_3^+−$(PSS,PAH)_5$−PSS).

XPS analysis of ^{10}PTFE−NH_3^+ indicates that the plasma polymer contains ∼17 atom % nitrogen. Upon L-by-L deposition of PSS and PAH this value decreases and levels off at ∼6.5% after 6−10 layers (3−5 PSS/PAH bilayers) have been deposited. The polyelectrolyte layers build up on top of the plasma polymer and attenuate the strong nitrogen signal from ^{10}PTFE−NH_3^+. Figure 2 shows a representative XPS survey spectrum of a ^{10}PTFE−NH_3^+-supported multilayer assembly (11 layers) and Figure 3 shows the nitrogen content, determined by XPS at 75° takeoff angle, vs the number of layers deposited. A takeoff angle of 75° was used because we have measured a photoelectron mean free path in a series of $(PSS/PAH)_n$ samples at this angle and can use these data and this value to estimate individual layer thickness.[22−24] We have discussed the angular dependence of electron mean free paths in these

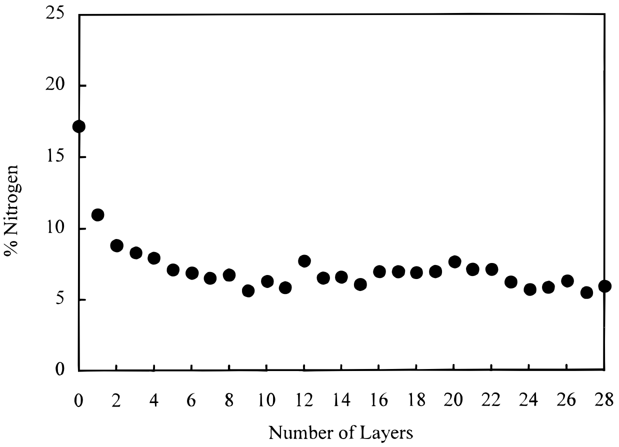

Figure 3. Nitrogen atomic concentrations determined by XPS as a function of the number of layers in the PSS/PAH multilayer film.

multilayer assemblies.[23] The sampling depth of XPS under these conditions is the thickness of the 6−10 polyelectrolyte layers; the scatter in the data precludes a more precise determination than 6−10, but other data (below) indicate that ~10 layers is a better estimate. Some degree of scatter in the data is expected due to the fact that separate samples (each prepared by multistep procedures) are used for analysis of each multilayer assembly; samples were not reused as substrates for additional layer adsorption after analysis. We emphasize, however, that the scatter is not great and is significantly less than that in individual samples of the $^{10}\mathrm{PTFE{-}NH_3^+}$ substrate: all of the nitrogen concentration values between 6 and 28 layers vary between 5.52% (27 layers) and 7.75% (12 layers). The sulfur content increases with the first 10−12 layer depositions and levels off at 3.3 ± 0.4% (the average and scatter of the data for all multilayer assemblies with 10−28 layers). The S_{2p} photoelectron has only a slightly longer mean free path that the N_{1s} photoelectron (20.5 vs 19.8 Å—- see below) so sulfur and nitrogen compositions are expected to level off with the same number of layers. From the sulfur and nitrogen data we estimate that the sampling depth of XPS under these conditions is the thickness of ~10 polyelectrolyte layers.

We can calculate the average thickness of the individual layers using the nitrogen XPS data (Figure 3) plotted according to eq 1.[23] This equation relates the

$$-\ln(N/N_o)\sin\theta = nz/\lambda \tag{1}$$

attenuation of a substrate photoelectron signal to the thickness of a multilayer assembly where N is the number of substrate photoelectrons that reach the detector through the assembly, N_O is the number of substrate photoelectrons detected without a L-by-L deposited overlayer, θ is the takeoff angle, n is the number of layers, z is the average thickness of the individual layers and λ is the photoelectron mean free path. We were able to observe the attenuation of the F_{1s} signal in PCTFE−OH and the carbonyl C_{1s} signal in PET derivatives as layers were deposited and determine average layer thicknesses.[23,24] The $^{10}\mathrm{PTFE{-}NH_3^+}$ substrate, however, does not contain an element that is not present in the polyelectrolytes (the F_{1s} signal from PTFE is completely attenuated by the plasma polymer layer), so the analysis is less straightforward. In this system we have to measure the attenuation of the nitrogen signal from the substrate as polyelectrolytes, one of which contains nitrogen (of lower concentration), are deposited. Figure 4 shows a plot of $-\ln(N/N_O)\sin\theta$ vs n where N and N_O are the observed nitrogen concentrations minus the final (leveled) nitrogen concentration. The slope of the line (z/λ-eq 1) is the average layer thickness divided by the N_{1s} photoelectron mean free path; this analysis indicates that the average layer thickness is ~0.3λ. This is the average thickness of layers 2−7; the first PSS layer was thicker than the others and was not included in the analysis because it would have biased the average high. We have measured a mean free path of 20Å for the Mg Kα-excited Si_{2p} electron in a $(\mathrm{PAH/PSS})_n$ assembly supported on a silicon wafer using XPS (75° takeoff angle) and X-ray reflectivity data[22] and we can use this value to calculate[33] a mean free path of 19.8 Å for the Al Kα-excited N_{1s} photoelectron. Assuming that the electron mean free path in $^{10}\mathrm{PTFE{-}NH_3^+}$-supported $(\mathrm{PAH/PSS})_n$ is the same as that determined for Si-supported $(\mathrm{PAH/PSS})_n$, the average layer thickness is 6.1 Å.

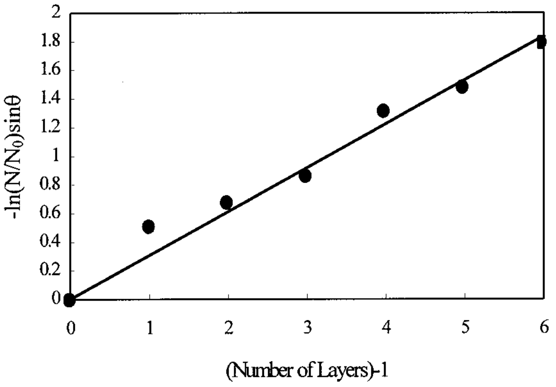

Figure 4. Plot of $-\ln(N/N_o)\sin\theta$ vs number of layers in the PSS/PAH multilayer film.

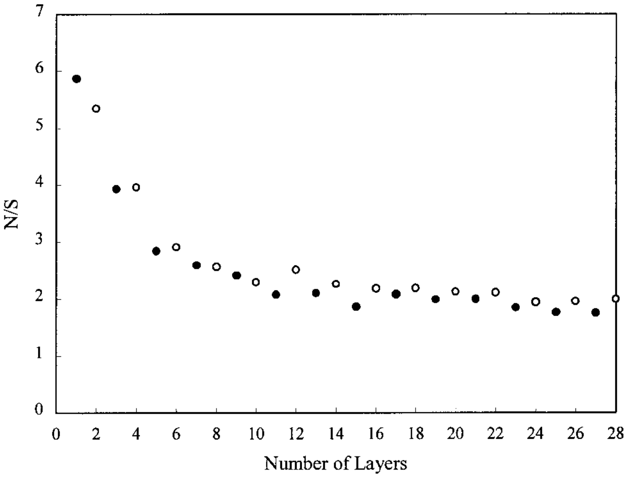

Figure 5. Nitrogen:sulfur atomic ratio data (XPS) vs the number of layers in the PSS/PAH multilayer film. Closed (●) and open (○) symbols indicate odd and even numbers of layers, respectively.

In other polymer-supported $(\mathrm{PAH/PSS})_n$ films,[22−24] pronounced odd−even effects are observed in the surface composition and in the wettability. Nitrogen:sulfur ratios oscillate between relatively high values when PAH is the outermost layer and relatively low values when PSS is topmost. The oscillations indicate that the layers are stratified and the amplitude of the oscillation is proportional to the thickness of the layers and their degree of stratification (vs interpenetration). Figure 5 shows the nitrogen:sulfur ratio (calculated from 75°

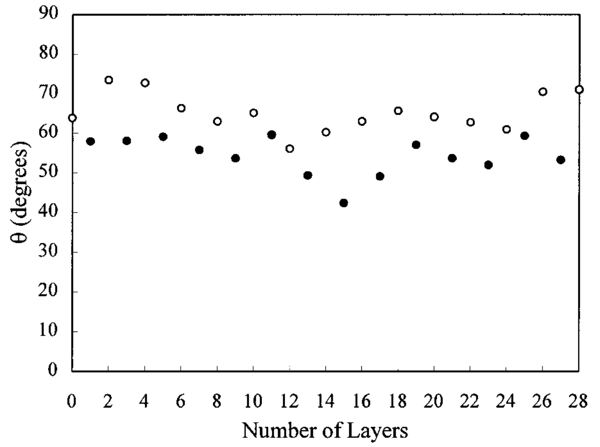

Figure 6. Advancing water contact angle data vs the number of layers in the PSS/PAH multilayer film. Closed (●) and open (○) symbols indicate odd and even numbers of layers, respectively.

takeoff angle and XPS atomic composition data) as a function of the number of layers deposited on ^{10}PTFE$-$NH$_3^+$. The ratio decreases with increasing number of layers and levels after ~10 layers have been deposited and the nitrogen signal from ^{10}PTFE$-$NH$_3^+$ is attenuated. For the samples with 10 or more layers, an odd$-$even effect consistent with the composition of the outermost layer is observed. There is not an obvious odd$-$even trend in the data for samples with fewer than 10 layers (we note that the decreases in N:S ratio between two and three layers and between four and five layers are consistent with the adsorption of a PSS layer) and this could be due to variability in the nitrogen content of the ^{10}PTFE$-$NH$_3^+$ substrate and/or to less well-defined layers being formed in the initial depositions. Water contact angle data (Figure 6) show a pronounced odd$-$even trend that is consistent across the series of samples (the 11-layer sample is anomalous) with samples containing PSS as the top layer exhibiting greater wettability than those with PAH as the outermost layer. The strong amplitude at low layer numbers suggests that the initial layers are stratified and well defined and that scatter in the N:S ratio data is due primarily to composition differences in ^{10}PTFE$-$NH$_3^+$ samples.

The N:S ratio data converge on a value of ~2 indicating that the stoichiometry of the assembly process is two ammonium ions per sulfonate ion. This suggests that chlorine (as chloride) should have been observed in XPS spectra, but it rarely was and only in very small quantities; 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). The stoichiometry also suggests that the multilayer assemblies have a net positive charge when in contact with acidic aqueous media and that this charge should increase with increasing number of layers deposited. This may be the case, but apparently chloride ions effectively screen this positive charge so that assemblies with PSS as the outermost layer have available sulfonate groups, function as negatively charged surfaces, and adsorb cationic polyelectrolytes. We must qualify these analyses by emphasizing that the XPS data were obtained on dry samples at high vacuum and the extent to which these data reflect the structure of the surfaces in contact with acidic polyelectrolyte solutions must be questioned.

Polyelectrolyte multilayer assemblies were also prepared using ^{50}PTFE$-$NH$_3^+$ samples as substrates and the results were qualitatively similar to those obtained using ^{10}PTFE$-$NH$_3^+$. A preliminary account of this work[32] discussed the ^{50}PTFE$-$NH$_3^+$ data. The data for the first ~10 layers had significantly more scatter and we suspect that the initial layers on this substrate are not as well-defined. A lower initial surface charge (fewer $-$NH$_3^+$ groups) may be the cause of this. The adsorptions become more well behaved after 10 layers have been adsorbed, and odd$-$even trends in XPS and contact angle data indicating layer stratification are apparent in samples with higher numbers of layers. The thickness of the individual layers is comparable to that of layers supported on ^{10}PTFE$-$NH$_3^+$ and the stoichiometry of the assembly is also ~2:1 ammonium:sulfonate ions.

Summary

PTFE can be surface-modified using an allylamine plasma polymerization to contain amine groups; the modified surfaces support layer-by-layer deposition of polyelectrolytes. The conditions of the plasma polymerization affect the chemical structure of the resulting polymer layer. In particular, a higher surface concentration of primary amines is formed at lower radiofrequency power and this translates to higher surface charge density and more reproducible polyelectrolyte adsorptions. Multilayer assemblies of PSS and PAH form by sequential polyelectrolyte adsorption, and XPS and contact angle data indicate stratified layers. XPS analysis also indicates that the stoichiometry of the assembly process is two ammonium ions per sulfonate group and that the average individual layer thickness is ~6.1 Å. The assembly stoichiometry is determined by the initial substrate chemistry and the adsorption behavior of the polyelectrolytes in the first few layer formation steps. The established stoichiometry is maintained throughout multiple polyelectrolyte adsorption steps and differs from that of different substrates. The successful surface modification of PTFE by this sequential protocol (plasma polymerization/layer-by-layer deposition) suggests that this is a general method for polymer surface modification.

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