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SELECTIVE ADSORPTION OF AMPHIPHILIC BLOCK COPOLYMERS ON WEAK POLYELECTROLYTE MULTILAYERS

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

In this study, an amphiphilic block copolymer, polystyrene-*block*-poly(acrylic acid) (PS-PAA), was adsorbed from tetrahydrofuran (THF) solution onto self-assembled weak polyelectrolyte multilayer surfaces of poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH). The short hydrophilic PAA block adsorbs to the multilayer surface as an anchor block and the long hydrophobic PS block then dangles out from the surface. Several different PAA/PAH multilayer systems generated by controlling the processing pH conditions were investigated in an attempt to find the optimal multilayer platforms for PS-PAA adsorption. We found that PS-PAA adsorption in this system is driven by mostly secondary interactions such as hydrogen-bonding. By regulating the nature of the multilayer surfaces, we were able to manipulate multilayer platform surfaces to be either highly promoting or highly blocking for PS-PAA adsorption. In the former case, contact angle measurements showed that, upon PS-PAA adsorption, a hydrophilic multilayer surface turned into a hydrophobic surface with contact angle values similar to those of a pure PS surface.

Key Words: Amphiphilic block copolymers; Polyelectrolyte multilayers

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INTRODUCTION

The development of the chemistry and processing needed to manipulate readily the molecular and supramolecular structure of multicomponent functionally active organic materials, both small molecules and polymers, has challenged researchers for many years. The desire to accomplish this task is motivated by the unique opportunities provided to control function and properties at the molecular level through the creation of complex materials combinations with precisely controlled supramolecular organizations. Nature, of course, has mastered this approach for quite some time and serves as an excellent model for conceptualizing and designing such complex systems. Although both the molecular and nanoscale manipulation of organic materials to control properties have become very common in recent years, some of the early studies and ideas of Tripathy and colleagues [1, 2] demonstrated the utility of this approach to realize enhanced electrical and optical properties in multilayered thin films. By combining uniquely elements of biology, supramolecular engineering and organo-electroactivity, the Tripathy group over the years has shown just how important this level of control can be for creating functionally active thin films and thin film devices [3]. This paper is dedicated to the pioneering work and inspiring personality of Sukant Tripathy, a great friend and colleague for eternity.

Of all the different approaches available to construct functional multilayer thin films, the layer-by-layer assembly of polyelectrolytes has emerged as one of the most versatile and technologically feasible processing routes [4-6]. In this process, alternate molecular-scale layers of oppositely charged materials are adsorbed onto a substrate to create highly uniform, multilayer thin films with readily controllable heterostructures. A wide variety of ionically charged, functionally active materials (conductive, luminescent, photo-responsive, anti-bacterial etc.) can be incorporated into the multilayers to create complex multilayer arrangements determined simply by the dipping sequence [5, 6]. In addition, by controlling such parameters as dipping solution pH and salt concentration, it is possible to control precisely the manner in which the oppositely charged polyions are blended together and hence the bulk and surface composition of the multilayer film. For example, using weak polyelectrolytes like poly(acrylic acid) (PAA) and poly(allyamine hydrochloride) (PAH), we have shown that by simply adjusting the pH of the dipping solutions, it is possible to dramatically alter the structure and properties of these films [7, 8]. Polyelectrolyte multilayers also can be applied to a variety of surfaces with, in most cases, excellent adhesion. This means that they are ideally suited for modifying and controlling surface properties including electrode surfaces [9] in thin film devices and biomaterial surfaces [10, 11].

In this paper, we show that the role of polyelectrolyte multilayers in modifying surface properties can be further expanded via the use of amphiphilic block copolymers. In this scheme, polyelectrolyte multilayers are used as platforms onto which amphiphilic block copolymers are physically grafted. The excellent adhesion of polyelectrolyte multilayers to many different surfaces combined with the ability to control the composition and functional group density of their surfaces makes them ideally suited for this task. The adsorption of a block copolymer designed to have one block that can anchor strongly to the multilayer surface via secondary forces (ionic, hydrogen bonding, etc.) and another that presents itself as a new functional surface provides a means to further modify the surfaces of these multilayer thin films. This is demonstrated in this paper with a polystyrene-poly(acrylic acid) block copolymer. In this case, the poly(acrylic acid) block grafts onto a multilayer surface via hydrogen bonding interactions and the polystyrene block renders the hydrophilic multilayer hydrophobic. In the future, we show how this approach can be used to create patterned surfaces comprised of selectively functionalized surface regions for biomaterials and electronic applications.

EXPERIMENTAL

Materials

Poly(allylamine hydrochloride) (PAH) (M_w = 70 000) and methylene blue dye were purchased from Aldrich. Poly(acrylic acid) (PAA) (M_w = 90 000) was purchased from Polysciences. All polyelectrolytes and methylene blue dye were used as received without further purification. Polyelectrolyte dipping solutions of PAA and PAH were prepared in a concentration of 10^{-2} M with respect to the molecular weight of each repeat unit in 18 MΩ Millipore water. The methylene blue dye solution was made with 18 MΩ Millipore water in 10^{-3} M. All of the aqueous solutions of polyelectrolytes and dye were pH-adjusted with either HCl or NaOH.

Polystyrene-*block*-poly(acrylic acid) (PS-PAA) (M_W of PS block = 66 500; M_W of PAA block = 4500) was purchased from Polymer Source Inc. All block copolymers and the solvent were used as received without further purification. PS-PAA was dissolved in THF at a concentration of 10^{-3} M based on the molecular weight of the repeat unit in the PAA block and was not pH-adjusted.

Glass slide substrates for multilayer deposition were ultrasonicated in detergent for 20 minutes and then ultrasonicated in fresh deionized water for 20 minutes, twice. After drying by air flushing, the glass substrates were plasma-cleaned for 2 minutes prior to the multilayer deposition process.

Polyelectrolyte Multilayer Formation

The layer-by-layer deposition of PAA and PAH was done automatically by a programmable dipping machine (HMS programmable slide stainer from Zeiss, Inc.) at room temperature. Cleaned glass slides were immersed into the polyelectrolyte solutions for 15 minutes for one layer deposition and rinsed with agitation in three fresh water baths for 2 minutes, 1 minute, and 1 minute before the next layer deposition. In the present study, a certain number of PAA/PAH bilayers were deposited onto the glass substrates with PAH as the first adsorbed layer and also as the outermost layer. Then the bottom half of the glass substrate with multilayers was dipped into the PAA solution for an additional PAA layer on top, making a sample that has regions with both PAA and PAH as the outermost layer. In some cases, PAA was deposited as the outermost layer of the multilayer film, and an additional PAH layer was deposited on the bottom half of the substrate. All polyelectrolyte multilayer samples were dried by air flushing for 2 minutes and further dried in ambient air for several hours before additional treatment or contact angle measurements.

Block Copolymer Adsorption

For block copolymer adsorption, polyelectrolyte multilayers prepared as indicated in the previous section were immersed into the PS-PAA solution for 15 minutes. Samples were taken out from the solution and rinsed in fresh THF for 2 minutes with agitation. After the samples were dried with air flushing, contact angles were measured on both PAA and PAH outermost layer surfaces with adsorbed PS-PAA block copolymers.

Characterization Methods

Contact angle measurements were carried out as described earlier [8] with the standard sessile drop technique by an Advanced Surface Technology (AST) device. All samples were dried by air flushing for 2 minutes right before contact angle measurements. In the present paper, the receding contact angles were measured as well as the advancing contact angles, so as to have a better understanding of the wetting characteristics and hysteresis of the multilayers. After adding several more water droplets onto the sample surface, the stage was vertically elevated up to the point that the syringe tip of the device was inserted into half the height of the water drop on the sample. Then, the water drop on the sample was withdrawn back into the syringe until the contact area of the water drop on the sample surface was decreased. At least four separate locations on each sample were measured to give a reliable average contact angle value.

Methylene blue staining was done by immersing the multilayers into the methylene blue solution at pH 7.0 for 5 minutes followed by rinsing in deionized water for 2 minutes. The amount of absorbed methylene blue into the films was determined by measuring the UV/Vis absorbance at λ_{max} by an Oriel Intraspec II. The absorbance values represent the dye amount in the multilayer films on both sides of the substrate.

Fourier transform infrared spectroscopy (FT-IR) spectra were acquired using a Nicolet FT-IR spectrophotometer with a DTGS detector. ZnSe was used as the substrate, instead of glass, following the multilayer deposition procedure described above. The thickness of multilayer films was determined using a

Gaertner ellipsometer at 633 nm, with polished silicon wafers as the substrate for the multilayer deposition. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra XPS with a monochromatic Al source. A low-resolution survey at a glancing take-off angle of 20° was obtained for each sample.

RESULTS AND DISCUSSION

In order to identify PAA/PAH multilayer films that could be used to either promote or resist the adsorption of a PS-PAA block copolymer, three different PAA/PAH multilayer systems were investigated. The three PAA/PAH multilayer systems were fabricated by controlling the pH of the PAA and PAH dipping solutions. Specifically, multilayers were fabricated with both the PAA and PAH solutions at a pH of 2.5 (hereafter denoted as 2.5/2.5), a pH of 6.5 (denoted 6.5/6.5), and with the PAA solution at a pH of 3.5 and the PAH solution at a pH of 7.5 (denoted 3.5/7.5). To investigate the role that the outermost layer plays in influencing block copolymer adsorption, the last polyelectrolyte layer adsorbed was only deposited onto the bottom half of the multilayer film. This creates a single film with both a PAA and a PAH outermost layer surface, thereby making it possible to compare directly in the same experiment the preference that these different surfaces have for block copolymer adsorption. Details concerning the assembly, composition and organization of these different PAA/PAH multilayer films can be found in previous publications [7, 8]. A brief summary of their key attributes is provided below and illustrated schematically in Figure 1.

In the case of the 2.5/2.5 PAA/PAH multilayer, the degree of ionization of the PAA chains is kept low during each polymer adsorption step, thereby produc-

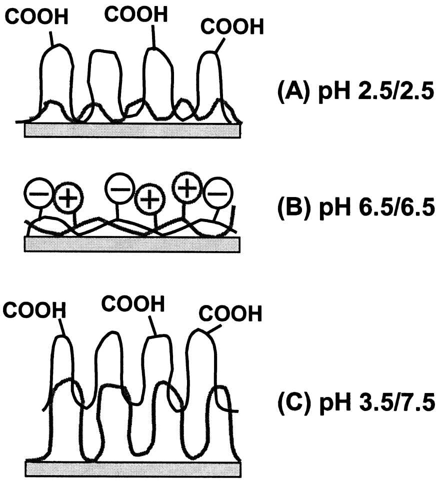

Figure 1. Schematic of the surface of PAA/PAH multilayers with PAA as the outermost layer at different assembly PAA/PAH pH's: (A) pH 2.5/2.5; (B) pH 6.5/6.5; (C) pH 3.5/7.5.

ing a film that is rich in PAA chains (approximate composition: 75% PAA, 25% PAH) with a low degree of ionization (about 30%). The net result is a multilayer film with a relatively low ionic crosslink density and a high concentration of accessible non-ionized acid groups on the surface regardless of whether PAA or PAH is the outermost layer. In contrast, the 6.5/6.5 PAA/PAH multilayer films are assembled with both polymer chains in their fully ionized state. This, in-turn, produces a nearly completely ion-paired multilayer film with a higher level of ionic crosslinking and a 50/50 PAA/PAH surface composition (independent of what layer is on top). In the 3.5/7.5 case, weakly ionized PAA chains are adsorbed at low pH onto a surface comprised of completely ionized PAH chains. During the adsorption of the PAH chains, however, the pH is increased and the remaining acid groups of PAA become fully ionized. This produces a multilayer thin film with an ion-paired internal structure but with a surface that is enriched in either PAA segments or PAH segments depending on the outermost layer. Thus, when PAA is the outermost layer, there is a significant fraction of free acid groups on the multilayer surface, whereas there are essentially no free acid groups on the surface when PAH is the top layer. At pH 7.5, it is likely that there are also some free amine groups on the PAH chains.

Figures 2 and 3 show how the wettability of PAA/PAH multilayer films changes after immersion in a THF solution containing a PS-PAA block copolymer. All of the multilayer films initially exhibited very low receding contact angles indicating that the surfaces became highly wettable after contact with water.

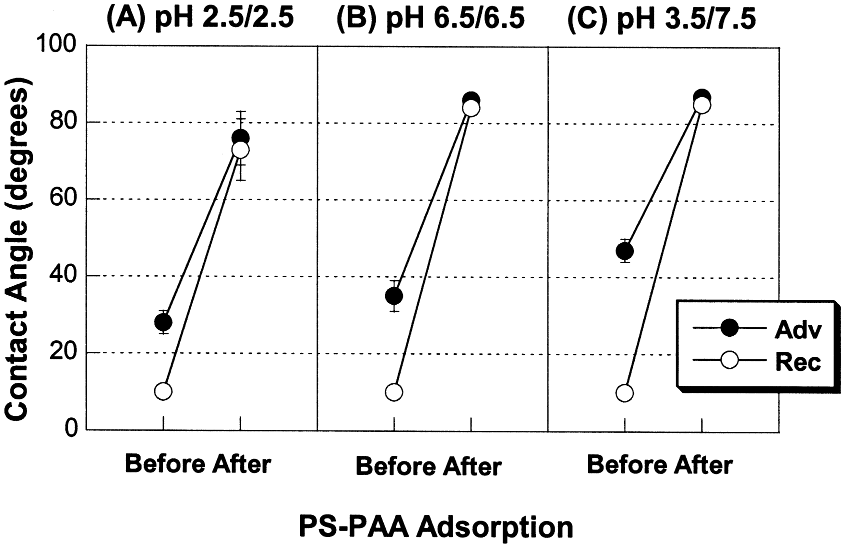

Figure 2. Contact angle values of multilayers with PAH as the outermost layer before/after PS-PAA adsorption. The solid circles represent the advancing contact angle and the open circles the receding contact angle: (A) pH 2.5/2.5, $(PAA/PAH)_{15.5}$ bilayers; (B) pH 6.5/6.5, $(PAA/PAH)_{24.5}$ bilayers; (C) pH 3.5/7.5, $(PAA/PAH)_{8.5}$ bilayers.

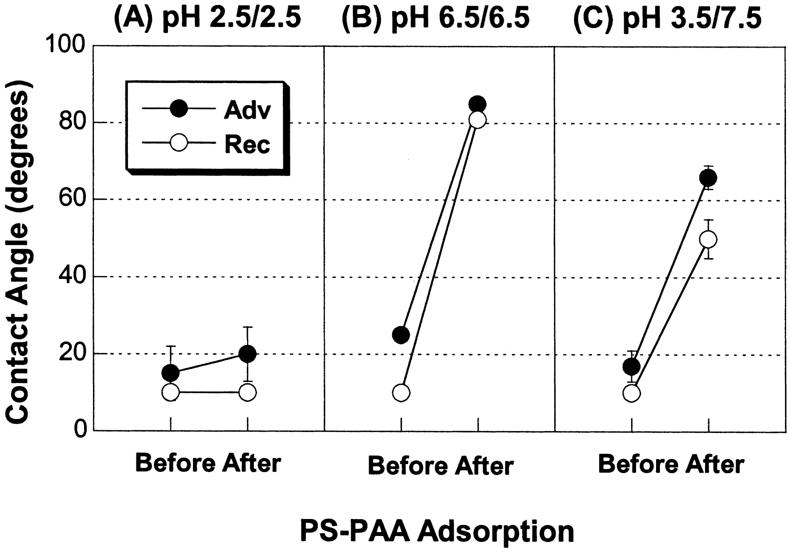

Figure 3. Contact angle values of multilayers with PAA as the outermost layer before/after PS-PAA adsorption. The solid circles represent the advancing contact angle and the open circles the receding contact angle: (A) pH 2.5/2.5, $(PAA/PAH)_{15}$ bilayers; (B) pH 6.5/6.5, $(PAA/PAH)_{25}$ bilayers; (C) pH 3.5/7.5, $(PAA/PAH)_9$ bilayers.

However, as presented in Figure 2, the contact angles of all films with PAH as the outermost layer increased significantly after adsorption of the PS-PAA block copolymer. Both the advancing (θ_{adv}) and the receding contact angles (θ_{rec}) increased to high values after these films were immersed in the block copolymer solution, which means that the surfaces have become significantly more hydrophobic. As a control test, bare glass slides with θ_{adv} and θ_{rec} of less than 10° were also immersed into the PS-PAA solution. In this case, no significant change in wettability was observed; the advancing contact angle increased at most to a value of 20° after immersion in the PS-PAA solution. Thus the significant increase in contact angle values only occurs when the glass slides are coated with PAA/PAH multilayers.

For the 6.5/6.5 and 3.5/7.5 multilayer films with PAH as the top layer, the advancing and receding contact angles increased to about 85° after adsorption of the PS-PAA block copolymer. In the 2.5/2.5 multilayer system with PAH as the top layer (Figure 2A), the advancing and receding contact angles increased to about 75°. Thus, in all cases, contact angle measurements show that the multilayer surface becomes hydrophobic after block copolymer adsorption with the 6.5/6.5 and 3.5/7.5 multilayer films showing the largest increase in hydrophobicity. It should also be noted that rinsing these films with fresh THF solution did not alter their wetting behavior. Both the advancing and receding contact angles maintained their values after the multilayer films were soaked in fresh THF for 100 minutes.

This shows that the adsorption of a PS-PAA block copolymer onto a PAA/PAH multilayer film with PAH as the outermost layer is stable and irreversible.

For multilayer films with PAA as the outermost layer, the situation was quite different. As seen in Figure 3, immersion of the 2.5/2.5 film in the block copolymer solution had very little effect on the wettability of this multilayer system. The very low contact angles exhibited by the highly wettable 2.5/2.5 multilayer film (θ_{adv} = 15 ± 5° and θ_{rec} <10) remained essentially unchanged after treatment with the block copolymer solution indicating that no block copolymer was adsorbed onto the PAA surface or the adsorbed amount was too little to affect the wettability of the surface. Thus, PAA/PAH multilayer films formed at pH 2.5/2.5 with PAA as the outermost layer appear to completely resist the adsorption of this block copolymer.

With PAA as the outermost layer, the 6.5/6.5 multilayers showed basically the same behavior after PS-PAA adsorption as the case with PAH as the outermost layer. As shown in Figure 3B, the multilayers became more hydrophobic after adsorbing PS-PAA, with θ_{adv} = 85 ± 1° and θ_{rec} = 81 ± 1°. In the 3.5/7.5 multilayer system with PAA as the top layer, the wettability of the multilayer film was also changed after immersion in the PS-PAA solution; θ_{adv} increased to 66 ± 3° and θ_{rec} increased to 50 ± 2°. However, from the large difference observed between the values of θ_{adv} and θ_{rec}, and the lower contact angles achieved, it is clear that block copolymer adsorption is less effective at modifying wettability when PAA is the outermost layer than when PAH is the outermost layer.

The above contact angle measurements suggest that the 3.5/7.5 multilayer system with PAH as a top layer is best used for promoting block copolymer adsorption whereas the 2.5/2.5 multilayer system with PAA as the outermost layer is best used for resisting block copolymer adsorption. In order to confirm the results observed from the contact angle measurements and to understand the PS-PAA adsorption mechanism, these two multilayer systems were examined by FT-IR spectroscopy. Figures 4 and 5 show the FT-IR spectra obtained from these multilayer platforms before and after block copolymer adsorption. To make sure that the absorbance peaks associated with any adsorbed PS-PAA chains were not obscured by the absorbance bands of the multilayer film, a small number of layers was used to construct the films in this case; 3 layers (1.5 bilayers) for the pH 3.5/7.5 multilayer and 8 layers (4 bilayers) for 2.5/2.5 multilayer.

Spectrum A in each figure is that of the multilayers before immersion into the PS-PAA block copolymer solution, and spectrum B is after immersion. As indicated by the arrows in Figure 4B, several strong peaks attributed to the polystyrene block of PS-PAA were detected after PS-PAA adsorption on the PAH surface of the pH 3.5/7.5 system. The strong peak at ν = 698 cm^{-1} is attributed to the out-of-plane aromatic ring deformation of PS, the peaks at ν = 1601 cm^{-1} and 1493 cm^{-1} are from the aromatic ring stretching of PS, and the peak at ν = 1453 cm^{-1} is due to the bending mode of $-CH_2$ groups along the block copolymer chain [12].

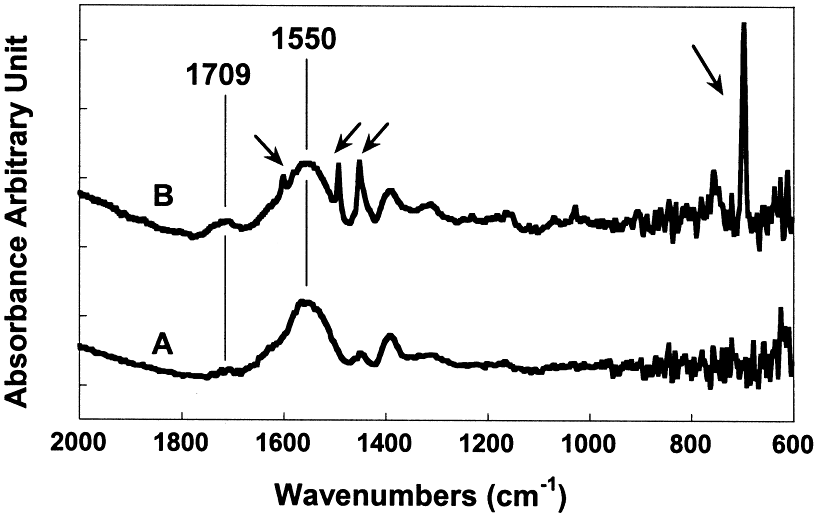

Figure 4. FT-IR spectra of $(3.5/7.5)_{1.5}$ bilayers with PAH as the top layer: (A) before and (B) after PS-PAA adsorption.

In Figure 4, the broad peak with strong intensity at ν = 1550 cm^{-1} is due to the asymmetrical stretching band of the carboxylate groups ($-COO^-$) in the PAA chains. The small peak at ν = 1709 cm^{-1} is from the C=O stretching of the carboxylic acid groups (–COOH) in the PAA chains. The peak height ratio of these two peaks ($COOH/COO^-$) changed from a value of 0.146, before PS-PAA adsorp-

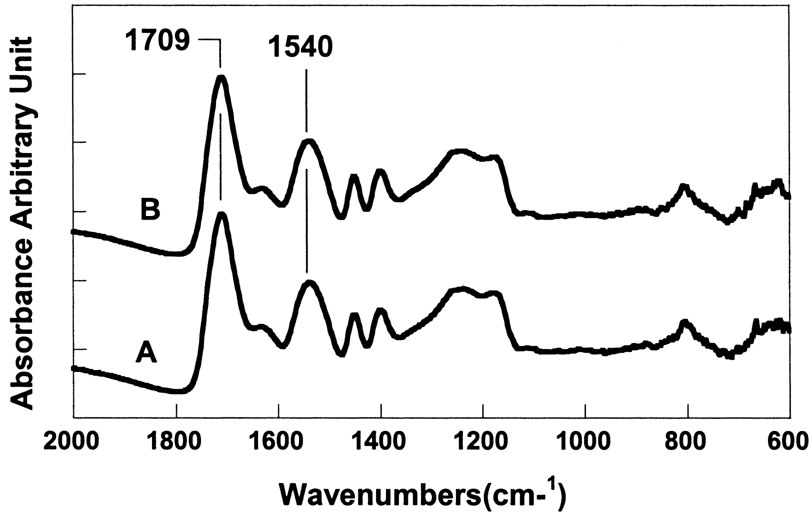

Figure 5. FT-IR spectra of $(2.5/2.5)_4$ bilayers with PAA as the top layer: (A) before and (B) after PS-PAA adsorption.

tion, to a value of 0.224, after PS-PAA adsorption. This implies that the PAA functional groups of the PS-PAA molecules are mostly non-ionized when they adsorb onto the multilayer surface, i.e. they adsorb mostly in the form of carboxylic acids (–COOH) rather than carboxylates ($–COO^-$). This further suggests that PS-PAA adsorption on the PAH surface is driven mainly by secondary bonding interactions such as hydrogen bonding as opposed to ionic attractions, although a small level of ionic bonding cannot be ruled from these experiments.

In sharp contrast, as seen in Figure 5, no significant change in the FTIR spectrum of the 2.5/2.5 multilayer system was observed after immersion in the block copolymer solution. Consistent with contact angle measurements, this suggests that the amount of PS-PAA taken up by the PAA outermost layer of the 2.5/2.5 multilayer is negligible.

To further probe the surfaces of these films, methylene blue was used as a staining agent for free acid groups. We have previously shown that this cationic dye will only bind to free acid groups within a PAA/PAH multilayer thin film. In addition, if the immersion time in the methylene blue solution is short, the adsorption process is essentially confined to the first few surface layers. Thus, by measuring the adsorbed amount of methylene blue, the relative amount of accessible unbound free acid groups on a multilayer surface can be quantitatively examined. Figure 6 shows the amount of methylene blue adsorbed on each outermost layer surface (PAA or PAH) for the 2.5/2.5 and 3.5/7.5 system before and after immersion into the PS-PAA solution. As expected for an assembly process carried out at pH 2.5/2.5, the resultant multilayers have a high population of free acid groups on

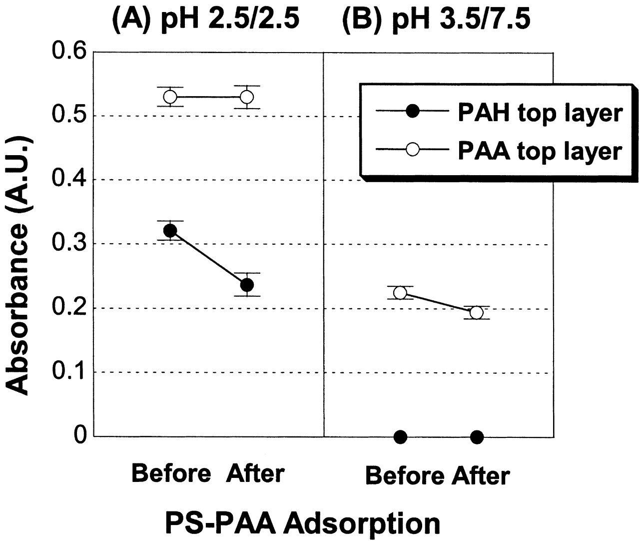

Figure 6. UV/Vis absorbance of methylene blue adsorbed on PAA/PAH multilayers before/after PS-PAA adsorption: (A) pH 2.5/2.5, $(PAA/PAH)_{15/15.5}$ bilayers; (B) pH 3.5/7.5, $(PAA/PAH)_{9/8.5}$ bilayers.

the surface as well as within the layers. The amount of methylene blue adsorbed onto the 2.5/2.5 multilayers (as indicated by UV/Vis absorbance measurements) with PAA as the outermost layer was therefore quite high at 0.53. The amount of methylene blue adsorbed remained the same after the multilayer film was immersed into the PS-PAA solution, suggesting that the amount of PS-PAA adsorbed to the surface was too small to affect the methylene blue staining. However, when PAH was the outermost layer, the methylene blue absorbance value was initially 0.32 and decreased to 0.24 for the film immersed in the PS-PAA solution. This implies that some PS-PAA was absorbed onto the surface in this case.

In the case of the 3.5/7.5 system, multilayers with PAH as the outermost layer do not contain any free acid groups on the surface. Thus, the amount of methylene blue adsorbed onto the film before immersion into the PS-PAA solution was non-detectable. No methylene blue adsorption was detected with the 3.5/7.5 film that was immersed in the block copolymer solution either, indicating that the PAA segments of the adsorbed block copolymer are attached to the surface and therefore shielded from methylene blue by the hydrophobic polystyrene segments. This observation is consistent with the high contact angle observed from the multilayer film after block copolymer adsorption. When PAA is the outermost layer, as expected from previous experiments, a large amount of methylene blue is absorbed onto the PAA rich surface (absorbance value of 0.23). After the multilayers were immersed in the block copolymer solution, the amount of methylene blue adsorbed onto the multilayer film decreased to 0.19. This is also consistent with the contact angle measurements which showed an increase in the contact angle of the 3.5/7.5 multilayers with PAA as the top layer after immersion into the block copolymer solution.

Preliminary XPS measurements on the 3.5/7.5 films before and after block copolymer adsorption further confirm that a uniform block copolymer adsorption occurs on the PAH outermost layer films. The atomic concentrations of the 3.5/7.5 multilayer surface with PAH as an outermost layer were found to be 74.68% for carbon, 9.19% for nitrogen and 16.13% for oxygen, before block copolymer adsorption. However, after PS-PAA adsorption, only carbon atoms were detected on the surface, with a 100% atomic concentration. This indicates that the PS blocks are localized to the top part of the adsorbed block copolymer layer, whereas the PAA blocks are attached to and in contact with the multilayer surface. Assuming that the surface is flat, the vertical penetration depth (d) of XPS is $d = 3\lambda \sin\alpha$ where α is the glancing take-off angle and λ is the inelastic mean free path of the emerging electron. Considering that λ is 30~40Å for Al K_α radiation ejecting C_{1s}, O_{1s} and N_{1s} electrons from organic polymers, the estimated penetration depth is in the range of 30~60 Å. The thickness increment we observed upon PS-PAA adsorption was in the range of 30-80Å as determined by ellipsometry. Thus, it is reasonable to conclude that the outermost surface of these films is dominated by at least a 30 Å thick layer of the PS block. In addition, the thickness measurements rule out the possibility of adsorption of the PS-PAA chains in the form of micelles, since micelle sizes are an order or more larger in magnitude than the thickness increment observed.

Our results show that it is possible to design PAA/PAH surfaces that effectively promote or resist the adsorption of an amphiphilic block copolymer. Contact angle and FTIR measurements reveal that block copolymer adsorption occurs readily on surfaces with PAH as the outermost layer, with the 3.5/7.5 multilayer films performing the best in this regard. In all cases, we observed a dramatic increase in contact angle after block copolymer adsorption. The net result is a transformation of a hydrophilic surface to a hydrophobic surface with wetting characteristics similar to polystyrene (pure PS exhibits an advancing contact angle value of 91-99° and a receding angle of 74-92° [13-17]). In contrast, block copolymer adsorption can be prevented with the use of PAA/PAH 2.5/2.5 multilayer films with PAA as the outermost layer.

The multilayer films examined in this study consisted of two coexisting surface regions with either PAA or PAH as the top layer. In specific cases such as pH 2.5/2.5 multilayers, contact angle measurements clearly showed a preference for the block copolymer to adsorb to the PAH rich surface. These results suggest that patterned surfaces can be designed to selectively direct the adsorption of a functionalized amphiphilic block copolymer to specific regions of a surface. This in turn provides a new means for selectively functionalizing surfaces with polyelectrolyte multilayers. This interesting capability will be explored in a future publication.

The preference for block copolymer adsorption onto surfaces containing PAH segments is clear. For example, a multilayer film built at pH 3.5/7.5 with PAH as the top layer has a large fraction of PAH segments on the surface. This multilayer film exhibited a highly hydrophobic surface with $\theta_{adv} = 87°$ and $\theta_{rec} = 85°$ after immersion into the PS-PAA block copolymer solution. This represents a dramatic change, particularly in the receding contact angle, which was originally a very low value of $\theta_{rec} < 10°$. The pH 3.5/7.5 multilayers with PAH as the outermost layer initially had an advancing contact angle of $\theta_{adv} = 47°$, which is close to the value estimated for pure PAH film (50°-55°). The fraction of PAH segments at the surface in this case was estimated using the Cassie's equation to be greater than 70%. Thus, a surface enriched with PAH segments has a strong affinity for the PAA blocks of the PS-PAA molecules in solution thereby enabling strong and irreversible block copolymer adsorption.

A small, but not insignificant change in wettability after block copolymer adsorption was observed with the 3.5/7.5 system when PAA was the outermost layer. In this case, some of the PAH segments from the underlying PAH layer must be penetrating into the PAA outermost layer. Thus, to completely prevent block copolymer adsorption, it is necessary to create a PAA outermost surface with essentially no accessible PAH segments.

In the case of the pH 6.5/6.5 system, regardless of whether PAH or PAA was the top layer, the multilayer film became quite hydrophobic (θ_{adv} = 85-86°) after immersion into the block copolymer solution. The surfaces of multilayers assembled at a pH of 6.5 consist of essentially the same fraction of segments from both polymers regardless of the outermost layer. With the PAH segments comprising about 50% of the multilayer surface, we again see a strong tendency for block copolymer adsorption. It is interesting to note that, in this case, the PAH and PAA segments are strongly ion paired resulting in a high level of ionic crosslinking. In other words, there are very few free PAA or PAH segments at the surface. It therefore appears that the way the PAH segments present themselves at the surface, i.e., as free segments associated with microions (3.5/7.5, PAH outermost layer case) or as polymer-polymer ionically bound segments, is less important than the fact that they are accessible to the block copolymer. Although both pH 6.5/6.5 and pH 3.5/7.5 multilayers with PAH as the top layer exhibited almost the same results in hydrophobicity after immersion in the block copolymer solution, the pH 3.5/7.5 multilayers seemed to be a better platform for promoting the PS-PAA adsorption, as indicated by their slightly higher reproducibility compared to films of pH 6.5/6.5.

For the multilayer surfaces assembled at pH 6.5/6.5 and pH 3.5/7.5 with PAH as the top layer, once they became highly hydrophobic after immersion in PS-PAA solution, they maintained their hydrophobicity even after long-term stability tests in water. After the multilayer films with PS-PAA molecules adsorbed were soaked in deionized water for 40 hours, any changes in the values of both advancing and receding contact angles were less than 5°. This reveals that the PS-PAA block copolymers adsorbed on the multilayer films do not undergo molecular rearrangement even when exposed to water for a long time, thus creating truly hydrophobic surfaces. It also confirms that the block copolymer chains are attached to the multilayers with the immobilized PAA blocks anchoring on the surface and buried under a thick layer of PS blocks.

In all of the multilayer films examined in this study, the PAH segments on the surface exist primarily in the form of charged ammonium groups ($-NH_3^+$). In the 3.5/7.5 case, however, it is likely that a small fraction of the PAH segments are not charged (i.e., $-NH_2$ groups). At pH 7.5, the PAH chains that were fully ionized at lower pH start losing protons as the *pKa* of this polymer is approached. Nevertheless, we surmise that the driving force for block copolymer adsorption is primarily hydrogen bonding interactions between the charged ammonium groups of PAH and the acid groups of the PS-PAA block copolymer. It is reported that charged ammonium groups readily form hydrogen bonds of moderate strength with carboxylic acids [18, 19].

The FTIR results confirm that the PAA groups of the adsorbed PS-PAA block copolymers remained in the carboxylic acid form (–COOH), suggesting that few, if any, of the adsorbing –COOH groups became ionized during adsorption. This indicates that an ionic interaction of the acid groups of the PAA block with the PAH segments was not a dominant factor in the PS-PAA adsorption mechanism. The possibility of the formation of some ionic bonds via a titration of the acid groups cannot be completely eliminated, although no definite evidence for electrostatic interactions has yet to be found.

In contrary to the other systems, the pH 2.5/2.5 multilayers with PAA as the top layer exhibited almost no change in wettability after immersion into the PS-PAA block copolymer solution. FTIR spectroscopy as well as methylene blue staining shows that the amount of adsorbed block copolymer on the multilayer surface is undetectable. These results are in good agreement with the previous explanation that the population of the PAH segments on the multilayer surface is the key factor that controls the adsorption of PS-PAA block copolymer from solution. The multilayer film assembled at pH 2.5/2.5 has many PAA segments dominantly residing within the multilayer and on the multilayer surface. Moreover, when PAA is the outermost layer of the film, PAH segments are buried underneath by the large number of PAA segments from the top layer, leaving almost no PAH segments on the surface. Thus, the access of the block copolymer to PAH segments in the multilayer is highly hindered, resulting in no significant adsorption of the PS-PAA block copolymer. The hydrogen bonding formation that easily occurs with carboxylic acid dimers in solution does not seem to happen in this case. The carboxylic acid groups in the PS-PAA molecules fail to form inter-molecular hydrogen bonding with the carboxylic acids in the PAA segments on the multilayer surface. Although it is known that the hydrogen bond of O–H···O=C in carboxylic acid dimers is stronger than that of N–H···O=C between amines and carboxylic acids [19], the inter-molecular attractions by hydrogen bonding, if any, between the free acid groups on the multilayer surface and the –COOH groups of the PAA block must not be strong enough to overcome solvent-polymer interactions.

The explanation above is also supported by the case where PAH, instead of PAA, is the outermost layer of the pH 2.5/2.5 multilayer film. In this case, although the multilayer composition is still dominated by PAA segments both inside the film and on the surface, the small portion of PAH segments from the top layer allow for block copolymer adsorption. This leads to a more hydrophobic surface with a contact angle of about 75° for both advancing and receding contact angles.

The adsorption of PS-PAA block copolymers from solution onto the multilayer surface occurs as a result of the competition between the PS block-solvent interaction and the PAA block-PAH groups (on the multilayer surface) interaction. There is a free energy decrease when the block copolymers adsorb by forming hydrogen-bonds between the –COOH groups of the PS-PAA molecules and the $-NH_3^+$ groups of the PAH segments on the surface. In order for the adsorption of PS-PAA to occur, this free energy decrease should be large enough to overcome the free energy of mixing of PS groups with THF and the entropic penalty of the block copolymer molecules being tethered onto the surface. Thus, the number of PAH groups on the surface plays the most important role in the adsorption of PS-PAA block copolymers. There should be a certain number of PAH groups available on the adsorbing surface so that the surface provides enough binding sites for the PS-PAA block copolymers. In that sense, the PAH outermost layer at pH 3.5/7.5 has the most PAH groups on the surface and thus, it promotes the greatest

PS-PAA adsorption. Conversely, the PAA outermost layer at pH 2.5/2.5 resists PS-PAA adsorption because there are few PAH groups on the surface and thus, the driving force of adsorption is too weak to draw PS-PAA molecules from the solution.

CONCLUSION

Amphiphilic block copolymers were successfully adsorbed onto weak polyelectrolyte multilayer surfaces and formed hydrophobic surfaces, depending on the multilayer platforms. The PAA/PAH multilayers assembled at pH 3.5/7.5 with PAH as the outermost layer highly promote the adsorption of PS-PAA block copolymer onto the multilayer surface. On the other hand, the multilayers built at pH 2.5/2.5 with PAA as the outermost layer are capable of preventing the adsorption of PS-PAA block copolymers from the THF solution onto the surface. We suggest that the main driving force for the PS-PAA adsorption is non-electrostatic secondary interactions such as hydrogen bonding.

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REFERENCES

1. Carter, G.M.; Chen, Y.J.; Tripathy, S.K. Intensity-Dependent Index of Refraction in Multilayers of Polydiacetylene. Appl. Phys. Lett. **1983**, *43* (10), 891-893.
2. Yang, X.Q.; Chen, J.; Hale, P.D.; Inagaki, T.; Skotheim, T.A.; Fischer, D.A.; Okamoto, Y.; Samuelsen, L.; Tripathy, S.; Hong, K.; Watanabe, I.; Rubner, M. F.; Denboer, M.L. Poly(Heterocycle) Langmuir-Blodgett Films. Langmuir **1989**, *5* (6), 1288-1292.
3. He, J.A.; Samuelson, L.; Li, L.; Kumar, J.; Tripathy, S.K. Oriented Bacteriorhodopsin/polycation Multilayers By Electrostatic Layer-By-Layer Assembly. Langmuir **1998**, *14* (7), 1674-1679.
4. Decher, G.; Hong, J.D.; Schmitt, J. Buildup of Ultrathin Multilayer Films By a Self-Assembly Process. 3. Consecutively Alternating Adsorption of Anionic and Cationic Polyelectrolytes on Charged Surfaces. Thin Solid Films **1992**, *210* (1-2), 831-835.
5. Decher, G. Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites. Science **1997**, *277* (5330), 1232-1237.
6. Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. Ultrathin Polymer Coatings by Complexation of Polyelectrolytes at Interfaces: Suitable Materials, Structure and Properties. Macromolecular Rapid Communications **2000**, *21* (7), 319-348.

7. Shiratori, S.S.; Rubner, M.F. pH-Dependent Thickness Behavior of Sequentially Adsorbed Layers of Weak Polyelectrolytes. Macromolecules **2000**, *33* (11), 4213-4219.
8. Yoo, D.; Shiratori, S.S.; Rubner, M.F. Controlling Bilayer Composition and Surface Wettability of Sequentially Adsorbed Multilayers of Weak Polyelectrolytes. Macromolecules **1998**, *31* (13), 4309-4318.
9. Ho, P.K.H.; Kim, J.S.; Burroughes, J.H.; Becker, H.; Li, S.F.Y.; Brown, T.M.; Cacialli, F.; Friend, R.H. Molecular-Scale Interface Engineering for Polymer Light-Emitting Diodes. Nature **2000**, *404* (6777), 481-484.
10. Elbert, D.L.; Herbert, C.B.; Hubbell, J.A. Thin Polymer Layers Formed By Polyelectrolyte Multilayer Techniques on Biological Surfaces. Langmuir **1999**, *15* (16), 5355-5362.
11. Mendelsohn, J.D.; Barrett, C.J.; Chan, V.V.; Pal, A.J.; Mayes, A.M.; Rubner, M.F. Fabrication of Microporous Thin Films from Polyelectrolyte Multilayers. Langmuir **2000**, *16* (11), 5017-5023.
12. Nakashima, K.; Ren, Y.; Nishioka, T.; Tsubahara, N.; Noda, I.; Ozaki, Y. Two-Dimensional Infrared Correlation Spectroscopy Studies of Polymer Blends: Conformational Changes and Specific Interactions in Blends of Atactic Polystyrene and Poly(2,6- dimethyl-1,4-phenylene ether). J. Phys. Chem. B **1999**, *103* (32), 6704-6712.
13. Jordan, R.; Ulman, A.; Kang, J.F.; Rafailovich, M.H.; Sokolov, J. Surface-Initiated Anionic Polymerization of Styrene by Means of Self-Assembled Monolayers. J. Am. Chem. Soc. **1999**, *121* (5), 1016-1022.
14. Kwok, D.Y.; Gietzelt, T.; Grundke, K.; Jacobasch, H.J.; Neumann, A.W. Contact Angle Measurements and Contact Angle Interpretation. 1. Contact Angle Measurements by Axisymmetric Drop Shape Analysis and a Goniometer Sessile Drop Technique. Langmuir **1997**, *13* (10), 2880-2894.
15. Zhao, B.; Brittain, W.J. Synthesis, Characterization, and Properties of Tethered Polystyrene-b-polyacrylate Brushes on Flat Silicate Substrates. Macromolecules **2000**, *33* (23), 8813-8820.
16. The contact angle values that we observed on a spin-coated PS film on glass were $\theta_{adv} = 95 \pm 1°$ and $\theta_{rec} = 92 \pm 1°$.
17. Petke, F.D.; Ray, B.R. Temperature Dependence of Contact Angles of Liquids on Polymeric Solids. J. Colloid. Interf. Sci. **1969**, *31* (2), 216-227.
18. Taylor, R.; Kennard, O.; Versichel, W. The Geometry of the N–H···O=C Hydrogen-Bond. 3. Hydrogen-Bond Distances and Angles. Acta Crystallogr. B **1984**, *40* (JUN), 280-288.
19. Vinogradov, S.N. Hydrogen-Bonds in Crystal-Structures of Amino-Acids, Peptides and Related Molecules. Int. J. Pept. Prot. Res. **1979**, *14* (4), 281-289.