

## Fabrication of Polyelectrolyte Multilayer Films Comprising Nanoblended Layers

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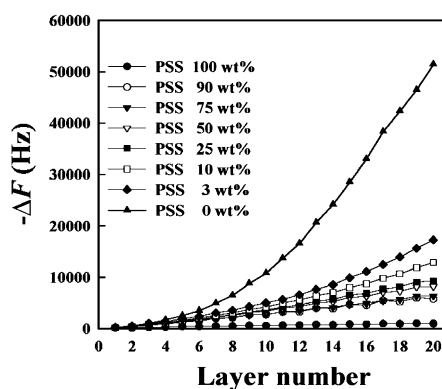
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Over the past decade the versatile layer-by-layer (LbL) assembly method has been widely utilized for the preparation of ultrathin polyelectrolyte (PE) films that show promise as light-emitting diodes, as electrochromic, membrane, and bioactive thin films, for selective area patterning, for particle surface modification, and the formation of capsular colloids.<sup>1</sup> Such films are typically prepared by the consecutive deposition of oppositely charged PEs from *single-component* solutions onto a solid support.<sup>1</sup> Few studies have examined the formation of thin films from solutions containing two or more components in each adsorption solution.<sup>2</sup> Such studies have employed species of opposite charge (e.g., PE–PE, PE–protein, and PE–dye), which complex in solution prior to adsorption.

Herein, we report the formation of multilayer films comprising nanoblended (i.e., mixed) layers of both weak (poly(acrylic acid), PAA) and strong (poly(styrene sulfonate), PSS) polyanions, alternately deposited with the polycation poly(allylamine hydrochloride) (PAH). This weak/strong PE combination was chosen because of the recent interest generated by multilayer films containing weak PEs, which is largely attributed to their pH-dependent characteristics.<sup>3–7</sup> The current work is significant because it demonstrates that nanoblended solutions comprising both weak and strong polyanions can be used to exert control over multilayer film properties, such as the film thickness (without the addition of salt), composition, morphology, and pH stability. Controlling these properties is important for many of the potential applications of PE multilayer films.<sup>1</sup>

PAH ( $M_w = 70\,000\text{ g mol}^{-1}$ ) was used as the cationic PE, and the anionic layers were deposited from a blend solution containing PAA ( $M_w = 30\,000\text{ g mol}^{-1}$ ) and PSS ( $M_w = 70\,000\text{ g mol}^{-1}$ ). Variations in adsorption behavior were induced by controlling the fraction of weak and strong PEs, the ionic strength of the solution, and the pH. Further, after exposure to an acidic solution the surface morphology of these blended multilayer films changes quite differently to films formed solely from PAH and PAA.

Initial studies were performed using a PAA/PSS blend solution pH of 3.5 and a PAH solution of pH 7.5, with no added salt. Multilayer formation was followed by quartz crystal microgravimetry (Figure 1). The frequency change,  $\Delta F$ , which is proportional to the mass deposited, shows that growth of the multilayer film increases markedly when the fraction of PAA in the blend is increased. The presence of only 10 wt % PAA in the blend solution dramatically increases the value of  $\Delta F$  for the (PAH/blend)<sub>10</sub> film (–5765 Hz, corresponding to 5015 ng) in comparison with that for the (PAH/PSS)<sub>10</sub> film (–1008 Hz or 877 ng). Conversely, the presence of only a small amount of PSS (10 wt %) in the PAA/PSS adsorption solution reduces the total film (i.e., 20 layers) mass deposited by about a factor of 3, compared with the corresponding film assembled from PAA and PAH. This trend is also observed at different salt concentrations and with varying molecular weight of PAA under the same pH conditions (see Supporting Information, S1).



**Figure 1.** QCM frequency changes for (PAH/blend)<sub>10</sub> multilayer films with varying blend compositions. Multilayer films were prepared from PAH solutions (pH 7.5) and PAA/PSS blend solutions (pH 3.5) without added salt.

**Table 1.** Film Thickness and PSS Content of PAH/(PAA/PSS) Multilayer Films Prepared at pH 7.5 (PAH) and pH 3.5 (PAA/PSS) and No Added Salt

| film composition (wt %) | film thickness (nm) <sup>a</sup> | PSS in film (%) <sup>b</sup> |
|-------------------------|----------------------------------|------------------------------|
| PAH/(PAA = 100)         | 810                              | 0                            |
| PAH/(PAA/PSS = 90:10)   | 210                              | 12                           |
| PAH/(PAA/PSS = 75:25)   | 160                              | 24                           |
| PAH/(PAA/PSS = 50:50)   | 140                              | 26                           |
| PAH/(PAA/PSS = 25:75)   | 130                              | 29                           |
| PAH/(PAA/PSS = 10:90)   | 92                               | 31                           |
| PAH/(PSS = 100)         | 18                               | 100                          |

<sup>a</sup> Determined by ellipsometry. <sup>b</sup> Determined by FTIR spectroscopy.

The total film thicknesses, as measured by ellipsometry, were also highly dependent on the composition of the blend solution (Table 1). The presence of 10 wt % PAA in the PSS solution led to a significant difference in thickness from the equivalent film prepared with only one polyanion (92 vs 18 nm). Further, it should be noted that the PAH/(PAA/PSS = 10:90)<sub>10</sub> film prepared with no added salt is significantly thicker (92 nm) than a (PAH/PSS)<sub>10</sub> film prepared from PE solutions with 0.5 M NaCl (~40 nm). The addition of salt to PE solutions is frequently used to obtain thicker layers.<sup>1</sup>

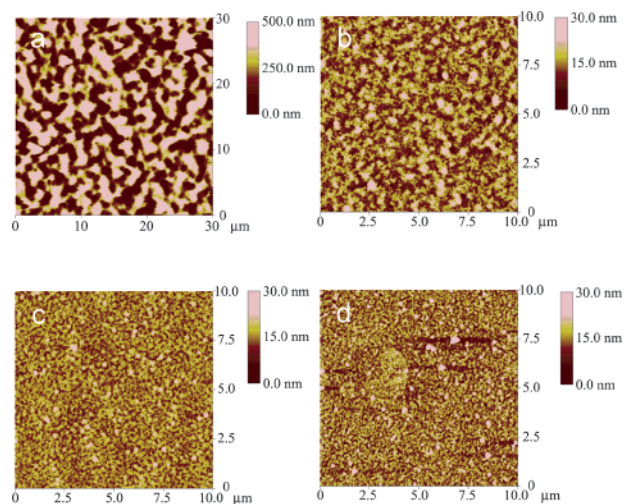
Fourier transform infrared spectroscopy (FTIR) was employed to monitor the infrared absorption peaks at 1007 and 1034  $\text{cm}^{-1}$ , which originate from the  $\text{SO}_3^-$  symmetric vibration mode of PSS in the multilayers (see Supporting Information, S2). The relative amount of PSS in the multilayer films could thus be calculated using the QCM  $\Delta F$  values for blended layers and the FTIR data (Table 1). These results demonstrate that the fraction of PSS in the film decreases with increasing PAA fraction in the adsorption solution, even though there is a general increase in the absolute amount of PSS in the film (see FTIR data). The large decrease in the total film adsorbed amount (and film thickness) when the PSS fraction is changed from 0 to 10 wt % may be attributed to several

factors. First, PSS may increase the total degree of ionization (and conformation) of the blend PEs, leading to deposition of thinner layers. The presence of PSS may also reduce H-bonding interactions between PAH and PAA, which also could result in thinner layers. Furthermore, it has been reported that PAA is virtually uncharged with a coiled chain conformation at pH 3.5.<sup>8</sup> In contrast, PSS is “stretched” due to the charge repulsion of adjacent sites at low ionic strength, and this stretching is largely independent of pH.<sup>3</sup> Consequently, PAA and PSS chains in a blend solution at pH 3.5 with low ionic strength will have different solution state conformations; PAA will be coiled and PSS stretched. As such, PAA chains in the blend may become entangled with PSS, thereby enhancing the adsorbed amount of PSS, compared to adsorption from a pure PSS solution.

The effect of PAA  $M_w$  on PSS adsorption was also investigated. When PAA of relatively high molecular weight ( $M_w \approx 30\,000\text{ g mol}^{-1}$ ) was added to the blended solution as 10 wt % of the total polyanion concentration, the adsorbed amount of PSS is significantly increased (as described earlier). However, the presence of 10 wt % of lower molecular weight ( $M_w \approx 2000$ ) PAA in the PSS solution decreases the adsorbed amount of PSS (see Supporting Information, S3). This molecular weight effect could indicate that, due to the lower  $M_w$  PAA providing fewer loops and coils per chain, there is less entanglement between the PAA and PSS chains. Thus, the PAA chains may be unable to enhance PSS adsorption. Alternatively, QCM data (Figure 1 and Supporting Information, S1b) suggest the formation of thinner films for the low  $M_w$  PAA/PSS blends, indicating lower adsorbed amounts of the components.

The effects of blend solution pH and ionic strength on the adsorbed amounts were also studied. UV–vis spectrophotometry was used to examine the influence of increasing the percentage of PAA in the blend adsorption solution on absorbance per PAH/blend bilayer at 226 nm (corresponding to the amount of PSS adsorbed). The experiments were conducted at both high and low degrees of PAA ionization (i.e., pH = 7.0 and 3.5, respectively) (see Supporting Information, S4). PSS and PAH are highly ionized at both pH values investigated. In the case of the blend pH = 3.5 and [NaCl] = 0 M, increasing the fraction of PAA in the blend to approximately 20 wt % increases the amount of PSS adsorbed. In contrast, when the blend contained a high salt concentration (0.5 M NaCl) at pH 3.5 (where both PAA and PSS have a coiled chain conformation), the adsorbed amount of PSS decreases slightly (ca. 15%) with increasing percentage of PAA. A decreasing trend was also observed at a blend pH of 7.0 for both salt concentrations (0 and 0.5 M), at which both PAA and PSS are highly ionized. Under these conditions PAA and PSS should adopt similar conformations with varying ionic strength.

Rubner and co-workers have previously shown that PAH/PAA multilayer films prepared by the alternate deposition of PAH (pH 7.5) and PAA (pH 3.5) can yield microporous films through the dissociation of electrostatic bonding (by acid treatment) and the rearrangement of adsorbed PAH/PAA chains (by water treatment).<sup>3b</sup> Figure 2 shows the surface morphology of blended multilayer films treated using the same methodology, as measured by atomic force microscopy (AFM). Films prepared from 100% PAA solution at pH 3.5 without added salt display a surface roughness of 153 nm after the treatment. Conversely, the PAH/(PAA/PSS) multilayer films assembled from the blend solution containing 10 wt % PSS were highly resistant to pH variation, as indicated by the relatively low surface roughness ( $\sim 4.7\text{ nm}$ ) obtained after treatment. This is probably due to PSS entanglement with PAA in the blend layer. As PSS has a fixed negative charge over the examined range of pH, it may prevent significant rearrangement of adsorbed PAA



**Figure 2.** AFM images of (PAH/blend)<sub>10</sub> multilayer films deposited from blend (PAA/PSS) solutions of different composition: (a) 0 wt % PSS, (b) 10 wt % PSS, (c) 25 wt % PSS, and (d) 50 wt % PSS. Film preparation conditions: pH (PAH) = 7.5 and pH (PAA/PSS) = 3.5. Films were then immersed in solutions of pH 2.5, followed by treatment with water.

chains and suppress changes in the surface morphology of PAH/blend films. This is also the case for the 25 and 50 wt % PSS films, which have surface roughness values of 4.3 and 4.5 nm, respectively.

In summary, the preparation of PE multilayer films with blended layers offers a new and general approach to construct thin films with tailored properties. In particular, we have shown that blended layers can be used to tailor film composition and thickness, as well as surface morphology and pH stability. We are currently studying a range of other blend combinations to prepare PE films with unique properties.

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**Supporting Information Available:** Material and experimental details, QCM graphs for varying ionic strength and molecular weight, FTIR spectra, and UV–visible data for varying pH, ionic strength and molecular weight (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) For a comprehensive book, see: *Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials*; Decher, G., Schlenoff, J. B., Eds.; Wiley-VCH: Weinheim, Germany, 2003.
- (2) (a) Das, S.; Pal, A. *J. Langmuir* **2002**, *18*, 458. (b) Caruso, F.; Schüler, C. *Langmuir* **2000**, *16*, 9595. (c) Schuetz, P.; Caruso, F. *Colloids Surf., A* **2002**, *207*, 33.
- (3) (a) Yoo, D.; Shiratori, S. S.; Rubner, M. F. *Macromolecules* **1998**, *31*, 4309. (b) Mendelsohn, J. D.; Barrett, C. J.; Chan, V. V.; Pal, A. J.; Mayes, A. M.; Rubner, M. F. *Langmuir* **2000**, *16*, 5017.
- (4) (a) Harris, J. J.; DeRose P. M.; Bruening M. L. *J. Am. Chem. Soc.* **1999**, *121*, 1978. (b) Balachandra, A. M.; Dai, J. H.; Bruening, M. L. *Macromolecules* **2002**, *35*, 3171.
- (5) (a) Xie, A. F.; Granick, S. *Macromolecules* **2002**, *35*, 1805. (b) Xie, A. F.; Granick, S. *J. Am. Chem. Soc.* **2001**, *123*, 3175.
- (6) (a) Mermut, O.; Lefebvre, J.; Gray, D. G.; Barrett, C. J. *Macromolecules* **2003**, *36*, 8819. (b) Burke S. E.; Barrett C. J. *Langmuir* **2003**, *19*, 3297.
- (7) (a) Fery, A.; Schöler, B.; Cassagneau, T.; Caruso, F. *Langmuir* **2001**, *17*, 3779. (b) Kato, N.; Schütz, P.; Fery, A.; Caruso, F. *Macromolecules* **2002**, *35*, 9780.
- (8) For adsorption of PE from single-component adsorption solutions, thinner layers are typically adsorbed for PEs with higher degrees of ionization. See for example: Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213.

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