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Micropatterning of Polymer Thin Films with pH-Sensitive and Cross-linkable Hydrogen-Bonded Polyelectrolyte Multilayers

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Layer-by-layer (LBL) assembled polyelectrolyte multilayers (PEMs) have received much attention in recent years as versatile nanostructured thin films for applications ranging from electronics to biomaterials.[1] Although electrostatic interactions between a polycation and a polyanion have been utilized as the main driving force of this novel assembly process, our work[2] and the work of others[3] demonstrated early on that hydrogen-bonding interactions can also be used for LBL processing. More recently, Granick and co-workers reported that hydrogen-bonded multilayers comprising weak polyacids could be assembled at low pH and subsequently dissolved at a higher pH as a consequence of increasing the degree of ionization of the weak polyacid.[4] This very interesting observation suggested to us intriguing new possibilities for patterning multilayer thin films. Key to these new patterning schemes was the development of strategies for stabilizing hydrogen-bonded multilayers to high pH environments, particularly physiological environments, thereby allowing their use in biomaterial applications (pH 7.4 with modest ionic strength). In this communication, we describe both thermal and photochemical approaches that can be used to render normally soluble hydrogen-bonded multilayers insoluble at high pH. The approaches described further enable the creation of micropatterned thin films using both ink-jet printing and photolithographic techniques. Compared with other additive patterning techniques for PEMs,[5,6] this represents the first water-based, subtractive patterning approach.

In this study, we used poly(acrylic acid) (PAA) ($M_w \sim 90\,000$), and polyacrylamide (PAAm) ($M_w \sim 5\,000\,000$) to construct multilayer films. The multilayers were deposited by the alternate dipping of a poly(allylamine hydrochloride) (PAH) (10 mM) coated substrate (silicon, glass, polystyrene or ZnSe slide) into dilute aqueous solutions of PAA and PAAm at pH 3.0. Both the dipping and rinsing solutions must be maintained at this low pH to avoid dissolution of the film.[4] The multilayer films fabricated with PAAm and PAA were uniform over large areas with rms surface roughnesses of less than 5% of the total film thickness, as measured by AFM. QCM studies show that about 75% of the mass of the multilayer is corresponding to PAAm.

FTIR measurements were made to confirm the hydrogen-bonding assembly process. Both PAA and PAAm can behave as both hydrogen bond donors and acceptors. In a film of neat PAAm, the amide I peak ($C{=}O$ stretching) and amide II peak ($N-H$ mixed mode) appear at 1661 and 1615 cm^{-1}, respectively. These peaks were found to shift to lower frequency (1659 and 1604 cm^{-1}) in the multilayer films due to hydrogen bonding between the amide and acid groups.[7] FTIR measurements also indicated that most of the acid groups of PAA are present in their nonionized form (Figure 1a). As expected, the PAA/PAAm multilayer films became completely soluble in water at a pH of about 5.0 or higher. Ionization of the PAA acid groups at high pH disrupts the hydrogen-bonded network and introduces electrostatic repulsive forces thereby rendering the multilayer soluble. We found, however, that heating the film at 175 °C for 3 h (or lower temperatures for longer times) introduces chemical cross-links that stabilize the multilayer assembly even at pH 7 in a buffered solution (0.15 M phosphate buffer). The heated multilayer film remained unchanged on the substrate even after 24 h of immersion in the pH 7 buffer solution. In contrast, the as-prepared multilayer film dissolved immediately when immersed in this solution.

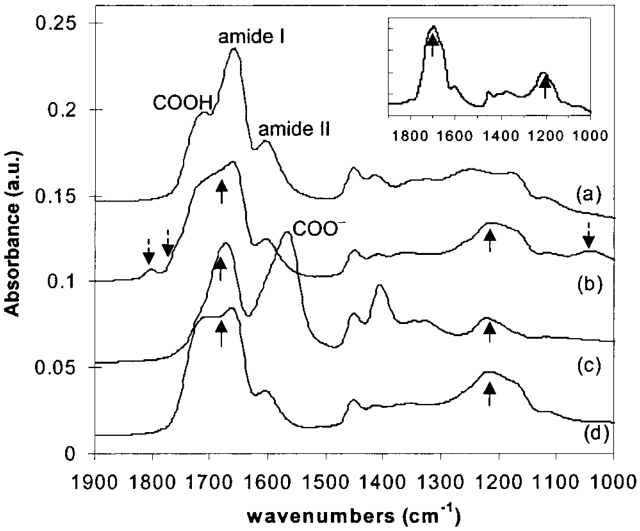

Figure 1. FTIR spectra of a (PAA/PAAm)$_{10}$ multilayer film on ZnSe (a) as-prepared, (b) after heating at 175 °C for 3 h, and (c) after heating and 1-day immersion in high pH solution (upward and downward arrows indicate imide and anhydride peaks, respectively). Spectrum d was sample c after a brief rinse with pH 3 water. The inset shows the spectrum of the multilayer film after 12 h of heating at 175 °C.

FTIR measurements indicate that the multilayer film is stabilized by a thermal imidization reaction[8] that produces imide cross-links between the PAA and PAAm chains. As shown in Figure 1b, new peaks, which correspond to imide groups, appear near 1700 (overlapping with the free acid peak), 1214, and 3099 cm^{-1} ($N-H$ stretching, not shown). FTIR suggests only a low level of cross-linking in this case. These changes are more clearly revealed by the FTIR spectrum of a film that was heated for 12 h at 175 °C (inset of Figure 1). The peak intensities of the amide and acid groups are decreased and a strong imide peak is clearly seen at 1698 cm^{-1}. Anhydride peaks also appeared at 1804, 1780, and 1042 cm^{-1} after heating; however, these peaks disappear after the heated film is treated with pH 7 buffer solution for 1 day (Figure 1c), suggesting that they are readily hydrolyzed and therefore not responsible for

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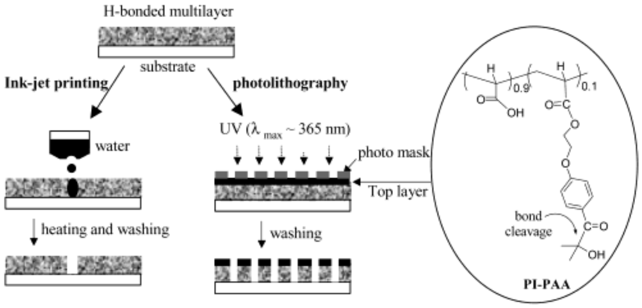

Figure 2. Patterning processes of H-bonded multilayers by ink-jet printing and photolithography. (Inside the circle is the chemical structure of PI-PAA.)

stabilizing the film. The peaks associated with the imide bonds, on the other hand, remain intact after this treatment as well as after a further rinsing in low pH water (Figure 1d).

Thermal imidization is known to occur when aromatic and aliphatic amic acid groups (amide−carboxylic acid bifunctional group) are heated.[8] In our case, the reaction appears to be facilitated by hydrogen bonding between the amide and acid groups (like amicacids): the anhydride groups may also facilitate the imidization reaction.[8a] Imidization is further supported by control experiments conducted on neat films of PAA and PAAm. In both cases, it was found that a heat-treatment sufficient to render the multilayers insoluble did not accomplish the same result with the neat PAA and PAAm films. Anhydride peaks observed in the FTIR spectrum of the heated PAA film disappeared after treatment in a pH 7 solution. In the case of PAAm, no changes were observed in the FTIR spectrum after heat-treatment. These results all support the idea that thermally induced chemical cross-links are formed between the amide groups of PAAm and the acid groups of PAA. We have further determined via ongoing mammalian cell studies that such cross-links are stable under physiological conditions for at least a month.[9] A thermally induced cross-linking reaction resulting in amide bonds has previously been reported for weak polyelectrolyte multilayers of PAA and PAH.[10]

In addition to thermal cross-linking, we have developed a simple means to photoinduce cross-linking within these multilayer films. In this case, we utilized a photoinitiator-labeled PAA copolymer (PI-PAA) to generate free radicals that are capable of cross-linking the PAA/PAAm multilayer film. A small portion of the carboxylic acid groups of PAA (about 10%) was modified with photoinitiator groups for this reaction. The structure of this polymer is shown in Figure 2; the synthesis of this material is described elsewhere.[11] This copolymer was deposited only as the final layer (about 80 Å in thickness) of a PAA/PAAm multilayer film. The PAA/PAAm multilayer film was then irradiated with UV light ($\lambda_{max} \sim 365$ nm, medium-pressure mercury lamp) for 20 min. We found that the radicals generated by the Norrish type I photocleavage reaction of the α-hydroxybenzoyl functional groups in the PI-PAA top layer are capable of rendering the film completely insoluble (without the PI-PAA top layer, the H-bonded multilayer still remained soluble after the same UV-treatment.) This suggests that the radicals are capable of diffusing into the multilayer film to promote cross-linking reactions.

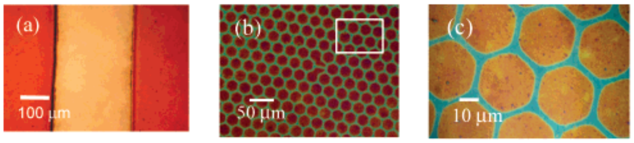

Figure 3. Optical microscope images of patterned PAA/PAAm films (a) by ink-jet printing (300 µm-width line) and (b) by UV-cross-linking through a TEM microscope grid. (c) A magnified image of the boxed area in part b.

The ability to stabilize the hydrogen-bonded multilayers via either thermal or photo-cross-linking reactions makes it possible to readily form patterns from these films by using water as a developing agent. Figure 2 illustrates two patterning methods that we have currently developed. In one case, we used an ink-jet printer to "print" pH 7.0 water onto the multilayer film followed by a thermal treatment at 95 °C for 8 h and rinsing with water. The regions "printed" with water are rendered non-cross-linkable due to ionization of the acid groups of PAA, whereas the nonprinted regions become cross-linked by the heat treatment. Figure 3 shows a 300 µm wide line of removed film created by this process. We have used this very simple approach to make patterned light emitting devices with feature sizes in the 100−300 µm range.[12] In the case of photolithography, we covered the PI-PAA-multilayer film with a TEM copper grid (used as a simple photomask) and irradiated it for 20 min with UV light, followed by a brief washing with neutral water. As shown in Figure 3, this process produced a pattern of isolated, 100 nm thick, 35 µm wide hexagons of PAA/PAAm.

In conclusion, we have demonstrated that hydrogen-bonded multilayers, composed of PAAm and the weak polyacid PAA, can be stabilized to neutral pH conditions by either thermal or photoinduced cross-linking reactions. This, in turn, makes it possible to use simple, water-based subtractive patterning techniques such as ink-jet printing or photolithography to create patterned multilayer thin films. Preliminary studies examining the ability of these patterned films to control spatially the adhesion of mammalian cells and to help fabricate patterned light emitting devices look promising.[9,12]

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Supporting Information Available: The full spectrum of the film shown in the inset of Figure 1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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