

Synthesis of Passivating, Nylon-Like Coatings through Cross-Linking of Ultrathin Polyelectrolyte Films

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This paper describes cross-linking of layered poly(allylamine hydrochloride) (PAH)/poly(acrylic acid) (PAA) films via heat-induced amide formation. Unlike many layered polyelectrolyte films, these cross-linked, nylon-like films are stable over a wide pH range and highly impermeable. Fourier transform infrared external reflection spectroscopy (FTIR-ERS) and X-ray photoelectron spectroscopy (XPS) confirm the conversion of carboxylate and ammonium groups into amide bonds, while electrochemical impedance spectroscopy shows that 11–13-nm thick cross-linked films have resistances as high as $10^5 \Omega\text{-cm}^2$.

Layered polyelectrolyte films are relevant to sensing,^{1–3} separations,^{4,5} and electronics applications^{6–10} because of their simple layer-by-layer synthesis and wide variability. Additionally, these films can naturally cover defects¹¹ and coat substrates having unusual geometries. Decher and co-workers demonstrated the synthesis of ultrathin polyelectrolyte films using poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS).^{12,13} A number of recent studies show that systems as diverse as DNA,^{14,15} redox-active polymers,^{6,7} charged viruses,¹⁶ semiconductor particles,⁸ conducting polymers,^{9,10} and inorganic sheets^{11,17–19} can be included in polyelectrolyte films. The feasibility of applying these films will depend on their permeability and stability under relevant conditions. We report that the stability and permeability of PAH/PAA films can be controlled simply by heating these films to form amide bonds as is done in a common procedure for the synthesis of nylon.²⁰ This stabilization strategy resembles that used by other groups when forming layered polymer films with

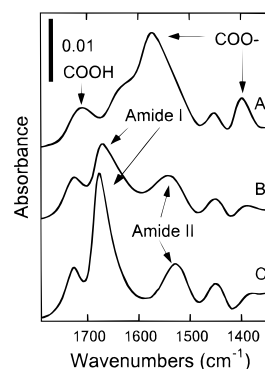


Figure 1. FTIR-ERS spectra of nine-bilayer PAH/PAA films before heating (A), after heating at 130 °C (B), or after heating at 215 °C (C).

covalent linkages.^{21–23} However, postdeposition cross-linking of polyelectrolytes preserves the advantages inherent in synthesis by simple electrostatic adsorption (e.g., no need for organic solvents and minimal deposition times).

To synthesize PAH/PAA films on gold, we first form a monolayer of mercaptopropionic acid (MPA) by immersing a gold-coated silicon wafer (Si(100) wafers coated with 20 nm Ti and 200 nm of Au by electron beam evaporation) in 1.5 mM MPA in ethanol for 30 min. (Use of MPA, rather than of a longer molecule such as mercaptoundecanoic acid, avoids possible blocking of the electrode by the monolayer.) Upon deprotonation, the monolayer provides a negatively charged surface. Immersion of the MPA-modified gold slide in PAH (0.02 M with respect to the monomer unit, pH adjusted to 5.1 with NaOH) for 5 min yields a layer of positively charged polymer on the substrate. Subsequent immersion in PAA (0.01 M with respect to the monomer unit, pH adjusted to between 5.6 and 5.7 with NaOH) for 5 min results in deposition of the first negatively charged layer. Repetition of this procedure allows synthesis of films with a large number of polyelectrolyte layers. The inability of previous XPS studies to detect counterions in layered polyelectrolyte films shows that electrostatic deposition occurs with nearly complete charge compensation by subsequent layers.^{7,24} We rinsed samples with Milli-Q water (18 M Ω -cm) for one minute after the deposition of each layer, and we dried with N₂ only after deposition of the desired number of layers. Optical ellipsometry indicates nonlinear bilayer growth. The thickness increase for 1–5 bilayers is 1.0 ± 0.5 nm/bilayer and for bilayers 6–9 the increase is 5.5 ± 1.1 nm/bilayer. Note that small fluctuations (± 0.10) in the pH of the deposition solutions result in drastic changes in film thickness.²⁵ We used two methods for cross-linking after the deposition of nine bilayers: heating “dry” films at 130 °C or at 215 °C for 2 h under N₂.

FTIR-ERS verifies that cross-linking between ammonium groups of PAH and carboxylate groups of PAA occurs by formation of an amide bond. Figure 1 shows spectra of nine-bilayer PAH/PAA films (ellipsometric thickness of ~ 13 nm) on gold before (A) and after heating (B and C). Before heating, the most notable peaks are due to the $-\text{COOH}$ carbonyl and $-\text{COO}^-$ asymmetric and symmetric stretches (1709, 1572, and 1399 cm^{-1} ,

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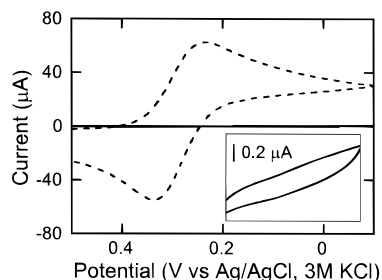


Figure 2. Cyclic voltammograms (0.005 M $\text{Fe}(\text{CN})_6^{3-}$ in 0.025 Na_2HPO_4 , 0.025 NaH_2PO_4 , 1 M Na_2SO_4 , pH 6.3) for a gold electrode coated with a nine-bilayer PAH/PAA film before (dashed line) and after heating the film at 130 °C for 2 h (solid line and inset). Scan rate of 0.1 V/s and electrode area of 0.1 cm^2 . The electrode was immersed for 2 min prior to data acquisition.

respectively).^{25,26} Both carboxylate groups and a small fraction of protonated acid are present because the deposition was performed at pH 5.6–5.7. After the slide is heated at 130 °C, the carboxylate peaks are no longer present, and amide peaks appear at ~ 1540 and 1670 cm^{-1} as seen in spectrum B. Some protonated acid remains, but its absorbance peak shifts to higher wavenumbers, indicating a change in hydrogen bonding or environment. Similar spectral changes occur when a PAH/PAA film is heated at 215 °C (spectrum C), but the amide to acid peak–height ratio is larger, suggesting more extensive cross-linking. Heating solvent cast PAH or PAA films at 130 °C does not produce the amide peaks seen in Figure 1. XPS also demonstrates the formation of amide bonds (N_{1s} spectrum) in heated PAH/PAA films (see Supporting Information).

Cyclic voltammetry demonstrates the dramatic decrease in film permeability that occurs upon cross-linking. Figure 2 shows cyclic voltammograms of a nine-bilayer PAH/PAA film-coated gold electrode before and after heating at 130 °C for 2 h. Cross-linking reduces the peak current to about 1% of its initial value (Figure 2 inset). Heating at 215 °C has an even more dramatic effect on permeability. The voltammogram for this system shows an additional 85% decrease in peak current from that of a film heated at 130 °C. The decreased permeability shown by PAH/PAA films heated at 215 °C is probably due to the higher degree of cross-linking suggested by FTIR-ERS, but there could also be some decrease due to annealing.

Impedance spectroscopy allows quantitative comparison of the permeability of films before and after cross-linking. Figure 3 shows typical plots of impedance for electrodes coated with nine bilayers of PAH/PAA before and after heating at 215 °C. In the case of the unheated film (Figure 3A), we see a small semicircle at high frequencies and the beginnings of a straight line at low frequencies that would be characteristic of semi-infinite linear diffusion.²⁷ The diameter of the semicircle is approximately equal to the charge-transfer resistance, R_{ct} , which is indicative of the accessibility of the electrode. The impedance plot for a film after cross-linking at 215 °C (Figure 3B) contains only $1/8$ of a circle, showing that the reaction is completely kinetically controlled.²⁷ Using the modified Randles' equivalent circuit²⁸ shown in Figure 4, we modeled the electrode–film interface and calculated values for R_{ct} , film resistance (R_f), film capacitance (C_f), double-layer capacitance (C_{dl}), and the diffusion impedance (Z_w). The equivalent circuit provides an excellent fit to the experimental data (see Supporting Information). R_{ct} increases by a factor of 200 upon

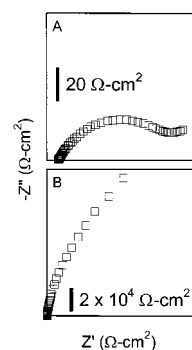


Figure 3. Impedance plots (0.005 M $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.025 Na_2HPO_4 , 0.025 NaH_2PO_4 , 1 M Na_2SO_4 , pH 6.3) for gold electrodes coated with nine-bilayer PAH/PAA films before heating (A) and after heating at 215 °C (B). Scale bars apply to both x- and y-axes. Frequency range 1–10⁵ Hz. Sinusoidal voltage: 5 mV about E^0 . The electrode was immersed for 5 min prior to data acquisition.

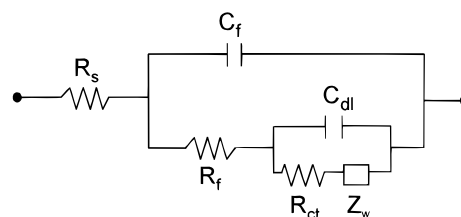


Figure 4. Modified Randles' equivalent circuit used to model impedance data.

cross-linking at 130 °C ($8 \times 10^3 \text{ } \Omega\text{-cm}^2$), and the R_f value is $6.5 \times 10^3 \text{ } \Omega\text{-cm}^2$. Heating of films at 215 °C has an even more dramatic effect on the electrode system. R_f and R_{ct} values for these systems (8×10^4 and $1 \times 10^5 \text{ } \Omega\text{-cm}^2$, respectively) are 1–2 orders of magnitude higher than for films heated at 130 °C. These results are in good agreement with cyclic voltammetry.

Cross-linking of PAH/PAA films dramatically increases their stability at high pH values. Prior to cross-linking, immersion of a PAH/PAA film in a pH 10-buffered solution (0.025 M $\text{Na}_2\text{CO}_3/0.025 \text{ M NaHCO}_3$ in 1 M Na_2SO_4) for 20 min followed by a water rinse results in an $\sim 30\%$ decrease in ellipsometric thickness. We observe similar instability at high pH when working with PAH/PSS films. At pH 10, a large fraction of the amine groups in these films are deprotonated, and many of the electrostatic bonds linking the layers are no longer present. In contrast, cross-linked PAH/PAA films show no decrease in film thickness after immersion in pH 10 buffer. As a control, we immersed PAH/PSS films (heated at 130 °C for 2 h) in pH 10 buffer for 20 min. These films still show an $\sim 30\%$ decrease in ellipsometric thickness.²⁹

In conclusion, heat-induced cross-linking between PAH and PAA occurs via formation of amide bonds and stabilizes these films over a wide pH range. Cyclic voltammetry and impedance spectroscopy show that film permeability decreases dramatically after cross-linking and depends on heating conditions. We are investigating using these nylon-like, cross-linked films as ultrathin membranes or corrosion-resistant coatings.

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Supporting Information Available: XPS spectra and impedance plot, two figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(29) FTIR-ERS spectra suggest that heating PAH/PSS films at 215 °C stabilizes these films, which may be due to annealing of the polymer film.

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