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Layer-by-layer Assembly of Thick, Cu²⁺-Chelating Films

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Abstract

Layer-by-layer adsorption of protonated poly(allylamine) (PAH) and deprotonated poly(*N,N*-dicarboxymethylallyl amine) (PDCMAA) yields thick films with a high density of iminodiacetic acid (IDA) ligands that bind metal ions. When film deposition occurs at pH 3.0, PAH/PDCMAA bilayer thicknesses reach 200 nm, and Cu²⁺ binding capacities are ~2.5 mmoles per cm³ of film. (PAH/PDCMAA)₁₀ films deposited at pH 3.0 are 4- to 8-fold thicker than films formed at pH 5.0, 7.0, or 9.0, presumably because of the low charge density on PDCMAA chains at pH 3.0. However, with normalization to film thickness, all films bind similar amounts of Cu²⁺ from pH 4.1 solutions of CuSO₄. In μm-thick films, equilibration of binding sites with Cu²⁺ requires ~4 h due to a low Cu²⁺ diffusion coefficient (~2.6×10⁻¹² cm²/sec). Sorption isotherms determined at several temperatures show that Cu²⁺ binding is endothermic with a positive entropy (binding constants increase with increasing temperature), presumably because metal-ion complexation involves displacement of both a proton from IDA and water molecules from Cu²⁺. (PAH/PDCMAA)₁₀ films retain their binding capacity over 4 absorption/elution cycles and may prove useful in metal-ion scavenging, catalysis, and protein binding.

Introduction

Thin organic films that bind metal cations are attractive for applications such as ion capture and separation,¹⁻³ protein binding,^{4,5} catalysis,^{6,7} and fluorescence sensing.⁸ Some films containing metal-ion complexes also exhibit antimicrobial properties.⁹ This paper reports a simple layer-by-layer (LBL) method for depositing polymeric films that contain metal-ion-binding iminodiacetic acid (IDA) ligands. The LBL technique allows coating of surfaces with a wide range of geometries,¹⁰ and remarkably 10-bilayer protonated poly(allylamine) (PAH)/poly(*N,N*-dicarboxymethylallyl amine) (PDCMAA) films (Figure 1) have thicknesses as high as 1 μm and bind 2–3 mmol of Cu²⁺ per cm³ of film. This high metal-ion-binding capacity is potentially useful for scavenging metal ions,¹¹ creating highly active catalysts,^{6,7,12,13} increasing protein binding in metal-affinity chromatography,⁴ or enhancing lifetimes for antimicrobial applications.⁹

A number of papers describe the incorporation of metal-ion complexes in LBL films. One form of LBL assembly directly employs metal-ion coordination to connect neighboring polymers.^{8,14-17} However, the thicknesses of such films are typically <3 nm/per bilayer,¹⁵ and elution of the metal ion delaminates the film unless it is cross-linked. In a second LBL

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†Professor Baker passed away unexpectedly on October 17, 2012. We dedicate this work as a memorial to him.

Supporting Information

Description of PDCMAA synthesis, NMR and IR spectra of PDCMAA, titration curves, water and ethylene glycol contact angles on various films, detailed ellipsometric data including a discussion of swelling and refractive indices, reflectance IR spectra of multilayer films, AFM images with line scans, and sorption isotherms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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method for creating metal-ion-containing films, functional groups in the film, e.g. carboxylates, bind metal ions after film formation.^{4,7,18} Subsequent reduction of these ions leads to metal nanoparticles.¹⁹ Polymer-metal ion complexes can also serve as the polyelectrolytes for LBL assembly.²⁰ However, metal-ion binding to carboxylates and amines is often weak, and the film thickness per layer is still relatively low. Strong binding is important to prevent metal-ion leaching in applications such as metal-affinity chromatography where proteins bind to immobilized metal ions.⁴

Several recent studies introduced polyanion/polycation complexes as building blocks for multilayer assembly, including the formation of films containing metal ions.^{6,21} Compared to LBL assembly with conventional polyelectrolytes, deposition of polyanion/polycation complexes leads to thick films and high metal-ion loadings with only a few deposition steps. Nevertheless, metal-ion-binding is still relatively weak because the polyelectrolyte complexes typically contain conventional carboxylate- and amine-based polyelectrolytes.

Another approach to obtaining thick LBL films employs alternating assembly where one of the polyelectrolytes diffuses throughout the film, which leads to an exponential growth in film thickness with the number of deposited layers.²² Typically, exponential growth occurs with polyelectrolytes that have a low charge density. In some cases such films undergo an exponential to linear growth transition because the depositing electrolyte cannot diffuse throughout the entire film, but the thickness per layer is still very high.^{23,24}

This work describes LBL adsorption of PAH and PDCMAA to give films with unusually high thicknesses (up to 200 nm per bilayer), presumably because of an exponential growth-type mechanism. We chose to employ PDCMAA because its IDA-containing side chains form stable complexes with metal ions such as Cu^{2+} . IDA is also a well-known ligand for immobilized metal affinity chromatography.^{25,26} Equally important, at low pH PDCMAA has a relatively low charge density per atom, which leads to rapid film growth. Controlling the deposition pH during assembly of $(\text{PAH/PDCMAA})_n$ films affords tunable bilayer thicknesses up to 200 nm. Moreover, μm -thick films are stable over at least 4 cycles of Cu^{2+} binding and elution. This paper examines growth of $(\text{PAH/PDCMAA})_n$ films at several pH values and the thermodynamics and kinetics of Cu^{2+} binding to the thickest films.

Experimental Section

Materials

Poly(allylamine hydrochloride) was purchased from Alfa Aesar (molecular weight 120,000 ~ 200,000 Da, used for LbL deposition) or from Aldrich (molecular weight ~58,000 Da, employed for PDCMAA synthesis). The supporting information describes the synthesis of PDCMAA and provides NMR and IR spectra of the polymer (Figures S1 and S2) along with a titration curve (Figure S3). (Figure numbers beginning with “S” refer to the supporting information.) Sodium chloroacetate (98%) and 3-mercaptopropionic acid (MPA, 99%) were received from Aldrich and used without further purification. Aqueous solutions of 0.02 M PAH and 0.01 M PDCMAA (polymer concentrations are given with respect to the repeating unit) were prepared in deionized water (18.2 M Ω cm, Milli-Q). PDCMAA-containing solutions with various pH values (3.0, 5.0, 7.0 and 9.0) were obtained by first dissolving the polymer with the addition of 6 M NaOH to achieve a pH 9.0 solution and then adjusting the pH with 6 M HCl. Gold-coated wafers prepared by sputter coating of 200 nm of gold on 20 nm of Cr on Si(100) wafers (coating was performed by LGA Thin Films, Santa Clara, CA) were cleaned in a UV/O₃ chamber for 15 min just before use. A stock solution of Cu^{2+} was obtained by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 20 mM phosphate solution. For binding studies, the stock solution was diluted with 20 mM phosphate solution to give the desired concentration of Cu^{2+} ions.

Preparation of (PAH/PDCMAA)_n films

To immobilize a monolayer of –COOH groups on a substrate, Au-coated Si wafers (24 mm × 11 mm) were immersed in 5 mM MPA in ethanol for 12 h, rinsed with ethanol and dried with N₂. Subsequent adsorption of PAH occurred during substrate immersion for 5 min in a 0.02 M PAH solution adjusted to pH 3.0, 5.0, 7.0, or 9.0. After rinsing with flowing deionized water for 1 min and drying with N₂, the Au-MPA(PAH) substrates were immersed in a 0.01 M PDCMAA solution (adjusted to the desired pH of 3.0, 5.0, 7.0, or 9.0) for 5 min and again rinsed with deionized water and dried with N₂. This process was repeated to obtain the desired number of PAH/PDCMAA multilayers.

Quantitation of Cu²⁺ binding to (PAH/PDCMAA)_n films

Au-coated wafers modified with (PAH/PDCMAA)_n films ($n = 1$ to 10) assembled at different pH values (pH 3.0, 5.0, 7.0 or 9.0) were separately immersed in vials containing 10 ml of 1.40 mM CuSO₄ (20 mM phosphate solution adjusted to pH 4.1 with HCl) and incubated for 15 h. Before the Cu²⁺-sorption experiments but after film deposition, the back sides of the Au-coated wafers were covered with Scotch transparent duct tape to limit Cu²⁺ sorption to the front side of the film-coated wafer. (This reduced the Cu²⁺ sorption nearly 50%.) After rinsing the wafers with deionized water from a squirt bottle for 1 min, the Cu²⁺ was eluted from the films by immersing the substrates in 5.0 mL of 20 mM EDTA (adjusted to pH 7.4) for 12 h. Using atomic absorption spectroscopy (Varian Spectra AA-200 atomic absorption spectrophotometer), the amount of Cu²⁺ in the stripping solution was calculated from its absorbance using a calibration curve. Both the standard and sample solutions contained 20 mM EDTA (pH 7.4). To examine the effect of the Cu²⁺ solution pH on sorption, Au-coated wafers modified with (PAH/PDCMAA)₁₀ films (assembled at various pH values) were separately immersed in vials containing 10 ml of 1.40 mM CuSO₄ at pH 4.0, 5.0 and 6.0 (20 mM phosphate solutions adjusted to the desired pH), and incubated for 15 h. Elution of Cu²⁺ ions and sample analysis to determine the amount of Cu²⁺ bound to each film occurred as described above. When establishing the equilibration time for maximum Cu²⁺ sorption and evaluating the sorption kinetics of Cu²⁺ binding, (PAH/PDCMAA)₁₀-coated wafers were separately immersed in 10 mL of 1.40 mM Cu²⁺ (pH 4.0, 20 mM phosphate) for various times prior to determination of Cu²⁺ binding following the above procedure.

To obtain isotherms for Cu²⁺ sorption in (PAH/PDCMAA)₁₀ films deposited at pH 3.0, a series of Au-coated wafers modified with (PAH/PDCMAA)₁₀ films were immersed separately in 10 mL of 0.007–1.40 mM Cu²⁺ (pH 4.0, 20 mM phosphate) and incubated at five different temperatures (4, 16, 25, 31 or 37 °C) for 15 h. Then (PAH/PDCMAA)₁₀-Cu²⁺-coated wafers were rinsed with deionized water for 1 min, and Cu²⁺ ions were eluted and analyzed as described above. For all ellipsometric thicknesses, refractive indices, and Cu²⁺ sorption data, uncertainties and error bars represent the standard deviations of measurements with at least 3 different films. In the case of isotherms, each point represents sorption in a different film, but these data were not repeated due to the large number of measurements.

Characterization of monomers, polymers, and (PAH/PDCMAA)_n films

A Varian UnityPlus-500 spectrometer was used to record ¹H and ¹³C NMR spectra at room temperature for synthesized and purchased polymers. The chemical shifts are reported in ppm and referenced to residual signals from deuterated solvents. The “dry” thicknesses for multilayer polyelectrolyte films were determined with a rotating analyzer spectroscopic ellipsometer (model M-44, J. A. Woollam) using WVASE32 software. Both refractive index

and thickness were fitting parameters. A Cauchy model, $n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4}$ was employed to fit the refractive index as a function of wavelength. In situ ellipsometry in aqueous

solutions was performed using a home-built cell described previously.²⁷ After the dry layer thickness was determined in air, water was added to the cell, and the thickness of the swollen film was recorded after 10 min. Reflectance Fourier Transform Infrared (reflectance FTIR) spectra of films were obtained with a Thermo Nicolet 6700 FTIR spectrometer that contained a mercury-cadmium telluride detector and a PIKE grazing angle (80°) attachment. Typically, 128 scans were collected for each spectrum. The AFM morphology images (Cypher™ atomic force microscope) of (PAH/PDCMAA)₁₀ films on Au-coated wafers were recorded in tapping mode (amplitude ratio = 0.90–0.99) using a silicon nitride tip. AFM images are shown in height mode without any image processing except flattening. Scanning rates were between 1.0 and 2.0 Hz. SEM images were obtained with a Hitachi S-4700 II field-emission scanning electron microscope. The samples were coated with 5 nm of sputtered gold prior to imaging. For cross sectional images, the samples were soaked in liquid nitrogen before fracturing to expose the cross section.

Results and discussion

Adsorption of μm -thick (PAH/PDCMAA)_n films

Alternating adsorption of PAH and PDCMAA on Au-coated substrates modified with MPA provides a simple method for preparing films with metal-ion-binding groups. Remarkably the ellipsometric thicknesses of (PAH/PDCMAA) films reach values as high as 1 μm after adsorption of only 10 bilayers (Figures 2b and 2d), creating films with high metal-binding capacities (see below). However, film thickness is a complicated function of the number of adsorbed layers and deposition pH.

For weak polyelectrolytes the pH of adsorption solutions controls the degree of ionization and hence the charge density along the polymer chain. This in turn greatly affects both the polymer conformation and the amount of polyelectrolyte that adsorbs on a surface.²⁸ In aqueous solutions the pK_a values of free IDA, the metal-binding group in PDCMAA repeating units, are $pK_{a1} = 1.8$, $pK_{a2} = 2.5$ and $pK_{a3} = 9.1$ (Scheme 1).^{29,30} Titration of PDCMAA with HCl (Figure S3) suggests fully protonated amine groups in the polymer below pH 8.0, whereas protonation of carboxylic acid groups occurs primarily below pH 4.0. Moreover, on going from pH 4.0 to 10.0, the fraction of protonated amines in PAH decreases from 96 to 30%.³¹ Therefore, solution pH controls the charge densities on both PAH and PDCMAA.

Figure 2 shows that as a function of adsorption pH the thicknesses of (PAH/PDCMAA)_n films increase in the order pH 5.0, 7.0 < pH 9.0 < pH 3.0, and films deposited at pH 3.0 are especially thick. At adsorption pH values of 5.0 and 7.0 PAH is more than 80% protonated,³¹ and PDCMAA should carry a net charge of ~ -1 per repeating unit (Figure S3). These relatively high charge states likely lead to the most extended polymers and the thinnest films. When the deposition pH increases to 9.0, PAH becomes less protonated whereas PDCMAA should carry a net negative charge < -1 (Figure S3). The decreased ionization of PAH at pH 9.0 likely yields a less extended polymer that leads to a small (<2-fold) increase in thickness with respect to films formed at pH 5.0 or 7.0. In contrast, at pH 3.0 the net charge per repeat unit of PDCMAA is > -1 (Figure S3), and film thickness increases dramatically compared to assembly at other pH values, probably because of increased loops in the polymer and more penetration of PDCMAA into the film. Prior studies show that the rate of polyelectrolyte diffusion into multilayer films increases with decreasing charge density and affects the film growth mechanism.³²

With adsorption at pH 3.0, film thickness initially increases exponentially with the number of bilayers (Figure 2a) and then becomes linear (Figure 2b). Models for such growth suggest that at first one of the polyelectrolytes deposits throughout the film, but subsequent changes

in films structure restrict penetration of the polyelectrolyte to only an outer region of the film, albeit a large outer region.^{24,33} For the linear region in Figure 2b, the growth rate is about 200 nm per bilayer. Although this rate is much larger than that for polyelectrolyte films prepared with strong electrolytes,^{34,35} there are a few examples of films with μm thicknesses prepared from weak polyelectrolytes via exponential growth.^{36,37}

Deposition pH also affects film structure. The AFM images in Figure 3 show clear variations in surface morphologies of (PAH/PDCMAA)₁₀ films as a function of adsorption pH. Films deposited at pH 5.0 and 7.0 (Figures 3b and 3c) have surface roughnesses of 7 and 4 nm, respectively. In these coatings extended polyelectrolytes give rise to a relatively smooth surface. In contrast, PAH/PDCMAA deposition at pH 3.0 and 9.0 yields coatings with surface roughnesses of 74 and 24 nm, respectively (Figures 3a and 3d). Loops and tails in these films likely lead to the high roughness.³⁸ Such high roughnesses may cause errors in ellipsometric determinations of film thickness, because the models for ellipsometric data typically assume flat surfaces. However, even for the very rough films deposited at pH 3.0, thicknesses determined from SEM images are consistent with those from ellipsometry (see Figure 2d). Moreover, the surface roughness of 74 nm is only ~6% of the total film thickness.

Water contact angles on (PAH/PDCMAA)₁₀ films increase dramatically from 5° to 80° when the assembly pH increases from 3.0 to 9.0. Films deposited at pH 5.0 and 7.0 show intermediate water contact angles of 50° and 58°, respectively. Deposition of PDCMAA at pH 3.0 results in many –COOH groups, and subsequent deprotonation of these groups in water (see Figure S12a) probably leads to the very hydrophilic surface. Moreover, the high surface roughness and sorbed water in films deposited at pH 3.0 (see the supporting information) should contribute to the low contact angles. In contrast, the high water contact angles on coatings formed at pH 9.0 indicate a surface dominated by polymer backbones³⁹ or perhaps lightly protonated PAH. In films adsorbed at pH 9.0, either most –COO[–] groups form ion pairs with ammonium groups of PAH, or PDCMAA is buried within the film even though PDCMAA adsorption is the last step in film formation. This is consistent with an exponential growth mechanism where PDCMAA either diffuses into the film or PAH diffuses out of the film to form PDCMAA/PAH complexes. Similar phenomena may occur at deposition pH values of 5.0 and 7.0 to give the intermediate contact angles, but a more protonated PAH could lead to higher surface energies. The supporting information discusses measurements of ethylene glycol contact angles to examine polar and nonpolar surface tensions (see Figure S5).

Sorption of Cu²⁺ ions in (PAH/PDCMAA)_n films

After immersion in a 1.40 mM CuSO₄ solution for 15 h and rinsing with deionized water, changes in the reflectance IR spectra of a (PAH/PDCMAA)_n film provide evidence for Cu²⁺ coordination to carboxylate groups. Upon Cu²⁺ binding, the spectrum shows a –COO[–] asymmetric stretching peak at 1641 cm^{–1} (see Figure S2a), presumably due to the formation of a Cu²⁺-iminodiacetate complex. Prior to complexation the spectrum of the film contains an asymmetric –COO[–] stretching peak at 1652 cm^{–1} and a shoulder due to the acid carbonyl stretch (1724 cm^{–1}). Spectral interpretation is difficult, however, because the degree of ionization depends on pH, and in a resin containing IDA functionalities, the Cu²⁺-carboxylate stretch appeared around 1620 cm^{–1}.⁴⁰

To quantify the amount of Cu²⁺ strongly sorbed in (PAH/PDCMAA)₁₀ films, we immersed film-coated substrates in 1.40 mM CuSO₄ (pH 4.1), rinsed the films with water, eluted the bound Cu²⁺ with 20 mM EDTA (pH 7.4) and determined the amount of Cu²⁺ in the eluate using atomic absorption spectrophotometry. The excess EDTA relative to the amount of immobilized IDA should ensure elution of essentially all of the Cu²⁺ ions from the film.

Moreover, EDTA has a higher binding constant for Cu^{2+} than IDA.⁴¹ Figure 4a shows the Cu^{2+} binding capacities per unit area for coatings deposited at different pH values. For all films, the Cu^{2+} binding capacity increases with the number of bilayers, and the trends in Cu^{2+} -binding capacities as a function of film deposition pH are similar to trends in film thickness (compare Figure 4a and Figure 2).

Using the ellipsometric thicknesses of “dry” films, we estimated the concentrations of Cu^{2+} inside the different coatings (Figure 4b). For films with more than 4 or 5 bilayers, the concentrations of Cu^{2+} in the films are essentially constant, showing that the Cu^{2+} binds throughout the film. Figure 4b suggests that for films with more than one bilayer, coatings deposited at pH 3.0 contain the lowest concentrations of Cu^{2+} . However, as discussed in the supporting information (see Figures S7 and S8) “dry” $(\text{PAH/PDCMAA})_n$ films deposited at pH 3.0 have a lower refractive index than films deposited at other pH values, probably because of some water sorption at ambient conditions. Thus the “dry” ellipsometric thicknesses of coatings adsorbed at pH 3.0 likely overestimate the true thickness of a dehydrated film, which will lead to an underestimation of the Cu^{2+} concentration in the film.

For films with 5 or more bilayers, the Cu^{2+} concentrations vary between 2.4 and 4.6 mmol/cm³ (Figure 4b). If a film contains pure PDCMAA with a density of 1 g/cm³, the Cu^{2+} binding capacity should be 5.8 mmol/cm³. Given that the coatings also contain PAH and some water, the binding capacities between 2.4 and 4.6 mmol/cm³ are reasonable. Measurements of film thicknesses after deposition of each PDCMAA and PAH layer (see Figures S10 and S11) suggest that coatings deposited at pH 5.0, 7.0, and 9.0 are predominantly PDCMAA. (Swelling after deposition of PDCMAA prevents estimation of the contributions of PDCMAA and PAH to the thicknesses of films deposited at pH 3.0.)

Effect of solution pH on Cu^{2+} sorption

Decreased competition between protons and Cu^{2+} for IDA binding sites may lead to increased Cu^{2+} binding at high pH.⁴² Figure 5 shows how Cu^{2+} sorption in $(\text{PAH/PDCMAA})_{10}$ films varies with the pH of both the film deposition and the Cu^{2+} solutions. The concentrations of Cu^{2+} sorbed from the pH 4.0 solutions range from 2.1 ± 0.1 to 3.0 ± 0.2 mmol/cm³, consistent with saturation of the IDA binding groups. (The isotherms below show that the Cu^{2+} concentration in solution is sufficient to essentially saturate binding sites.) After increasing the Cu^{2+} solution pH from 4 to 5, the Cu^{2+} sorption capacities increase 5- to 7-fold for $(\text{PAH/PDCMAA})_{10}$ films prepared at pH 5.0, 7.0, and 9.0 (Figure 5). The increase in binding capacity suggests that at pH 5.0, amine groups of PAH may coordinate with Cu^{2+} .⁴³ Previous studies of Cu^{2+} binding to amine-containing polymers also show large increases in binding at solution pH values ranging from 4.0 to 6.0.^{3,44} With PAH at pH 5.0, Cu^{2+} can likely effectively compete with protons for binding sites. However, the binding capacities at pH 5.0 are sometimes higher than we would expect. For a film containing 50 wt% PAH and 50 wt% PDCMAA with a composite density of 1 g/cm³, the binding capacity would be 10 mmol Cu^{2+} /cm³ if each amine and IDA functional group bound one Cu^{2+} ion. The even higher binding capacities for films deposited at pH 5.0 and 7.0 might suggest binding multiple Cu^{2+} ions per IDA group, where each carboxylate group binds to a different Cu^{2+} ion. Based on electron spin resonance data, Kinast et al. suggest that in some cases IDA-like ligands may bind to Cu^{2+} via only one carboxylate group.⁴⁵ Water or hydroxide should fill additional coordination sites.

In contrast, the films deposited at pH 3.0 show only a moderate Cu^{2+} sorption increase from 2.4 ± 0.0 mmol/cm³ to 3.0 ± 0.4 mmol/cm³ on going from a pH 4.0 to a pH 5.0 binding solution. This might indicate a higher pK_a of ammonium groups in these films compared to films deposited at other pH values and hence minimal binding of Cu^{2+} to PAH. The higher ammonium pK_a could stem from a high negative charge in these films, as $-\text{COOH}$ groups

present during deposition will deprotonate as the pH increases to add negative charge to the film and stabilize ammonium groups. We also attempted to examine binding at pH 6.0, but $\text{Cu}(\text{OH})_2$ precipitates were clearly visible.

The following sections examine kinetics and sorption isotherms for Cu^{2+} binding to (PAH/PDCMAA)₁₀ films deposited at pH 3.0. We decided to investigate films formed at this deposition pH because they have the highest thickness and Cu^{2+} sorption for a 10-bilayer film. Moreover most of the binding likely occurs through IDA units in these films.

Kinetics of Cu^{2+} sorption

To establish the equilibration time needed for maximum Cu^{2+} sorption and evaluate the binding kinetics in (PAH/PDCMAA)₁₀ films, we measured Cu^{2+} binding as a function of time. As Figure 6a shows, sorption approaches a maximum value after about 4 h of exposure to the 1.40 mM Cu^{2+} solution. When diffusion limits the sorption rate, at least initially the amount of sorption should be proportional to the square root of time with an intercept at the origin.⁴⁶ Figure 6b shows that this is the case, so diffusion into the film must be slow compared to the rate of Cu^{2+} binding to ligands. In fact, diffusion may involve hopping between Cu^{2+} binding sites.⁴⁷

If Fickian diffusion controls the rate of Cu^{2+} entry into a coating, equation (1) will describe the total amount of Cu^{2+} , $M(t)$, in the film at a given time t , where $M(\infty)$ is the amount of Cu^{2+} in the film at equilibrium, l is the film thickness, and D is the diffusion coefficient.⁴⁸

$$\frac{M(t)}{M(\infty)} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-\frac{D(2n+1)^2 \pi^2 t}{4l^2}\right) \quad (1)$$

Figures 6a and 6b show fits to the experimental data with equation (1) when using a swollen film thickness of 2 μm and a diffusion coefficient of $2.6 \times 10^{-12} \text{ cm}^2/\text{s}$. This diffusion coefficient is 6–7 orders of magnitude lower than the diffusion coefficient in aqueous solution,⁴⁹ implying that the film greatly hinders ion movement. This low diffusion coefficient is consistent with slow transport of divalent ions through some polyelectrolyte multilayer membranes.⁵⁰

Sorption isotherms

After demonstrating that 4 h of exposure to a Cu^{2+} solution is sufficient to achieve equilibrium binding, we determined the equilibrium Cu^{2+} sorption capacity in (PAH/PDCMAA)₁₀ films as a function of the solution Cu^{2+} concentration. Figure 7 and Figures S15–S17 show the sorption isotherms that result from these data, and at 25 °C binding reaches ~90% of saturation at solution Cu^{2+} concentrations of 0.3 mM. Using a non-linear fitting method, we examined whether the data correspond well with Langmuir⁵¹ or Sips⁵² isotherms. Equation (2) describes the Langmuir isotherm

$$q_e = \frac{q_m K_L C_e}{1 + (K_L C_e)} \quad (2)$$

where q_m is the maximum adsorption capacity; K_L is the Langmuir constant, which is a measure of the binding free energy; q_e is the amount of Cu^{2+} sorbed at equilibrium, and C_e is the concentration of Cu^{2+} in solution. Importantly, this model implies a fixed number of sorption sites with similar affinities for Cu^{2+} . In contrast, the Sips isotherm (the

Freundlich⁵³ isotherm is a special case of the Sips model) described in equation (3) allows for a distribution of binding energies or accessibilities for the sorption sites.⁵⁴

$$q_e = \frac{q_m (K_s C_e)^n}{1 + (K_s C_e)^n} \quad (3)$$

In equation (3) K_s is the median association constant and n is the exponent of the Sips model. If the value of n is one, the Sips isotherm reverts to the Langmuir isotherm. In the case of Cu^{2+} sorption to $(\text{PAH/PDCMAA})_{10}$ films at 4 °C, the Sips and Langmuir models gives essentially the same fit to the data, and the value for n in the Sips isotherm is 1.02. Thus, these films most likely have homogeneous binding sites.⁵⁵ However, at 25 and 37 °C, the values of n increase to 1.4 and 1.7, respectively. At the higher binding temperatures, the Langmuir model overpredicts the amount of sorption at low Cu^{2+} concentrations. Such an effect might stem from changes in the accessibility of binding sites with the amount of binding, or a distribution of binding site energies at the higher temperatures. All the temperatures give similar values of q_m , consistent with well-defined binding sites, presumably the IDA functionalities.

Table 1 presents the values of free energy of association, ΔG_a^o and binding constants at different temperatures. Both K_L and K_s increase by a factor of ~6 on going from 4 to 37 °C, and at 37 °C binding approaches saturation at Cu^{2+} concentrations of only 0.1 mM. Increased binding at higher temperatures indicates that entropic factors affect the spontaneity of the Cu^{2+} sorption.

We determined ΔG_a^o for Cu^{2+} sorption, along with the enthalpy (ΔH_a^o) and the entropy (ΔS_a^o) of sorption using equations (4) and (5) and the plot of $\ln K_L$ vs $1/T$ in Figure 8.

$$\Delta G_a^o = -RT \ln K_L \quad (4)$$

$$\ln K_L = \frac{\Delta S_a^o}{R} - \frac{\Delta H_a^o}{RT} \quad (5)$$

In these equations R is the gas constant (8.314 J/mol K) and T is temperature (K).^{56,57}

The ΔH_a^o and ΔS_a^o values for the Cu^{2+} sorption were 39 ± 5 kJ/mol and 213 ± 15 J/mol K, respectively, similar to values obtained for Cu^{2+} binding (pH 5.0) to IDA ligands immobilized on polystyrene beads.⁵⁸ The positive enthalpy change indicates an endothermic reaction, which likely results from exchange of a proton for a Cu^{2+} ion (Scheme 2). Binding constants and pK_a values for the free IDA ligand (not immobilized to a polymer) also show a positive enthalpy and negative entropy for the exchange of a proton for Cu^{2+} .⁵⁹ The positive ΔS_a^o value probably results from liberation of water molecules in the metal-ion absorption process,⁵⁸ and the relatively large magnitude of ΔS_a^o leads to negative ΔG_a^o values and spontaneous metal chelation, especially at higher temperatures.⁶⁰

Repetitive Cu^{2+} binding and elution in $(\text{PAH/PDCMAA})_{10}$ films

Figure 9 illustrates the sorption capacities of $(\text{PAH/PDCMAA})_{10}$ films during four cycles of Cu^{2+} binding followed by elution with EDTA. For this set of films, which were all prepared from the same polyelectrolyte adsorption solutions, the Cu^{2+} sorption capacity increases from 2.46 ± 0.02 mmol/cm³ to 2.64 ± 0.12 mmol/cm³ after the first cycle and then remains constant. The 7% increase in binding capacity after the first cycle may stem from film

rearrangement in the pH 7.4 EDTA solution. Despite the possible rearrangement, (PAH/PDCMAA)₁₀ films are clearly stable over several absorption/elution cycles, and presumably many more cycles of binding and elution are possible. This stability should allow reuse of the films in applications such as metal scavenging or protein binding.

Conclusions

This study describes fabrication of polyelectrolyte multilayer films with remarkably high thicknesses and Cu²⁺ binding capacities. When assembled at pH 3.0, (PAH/PDCMAA)₁₀ films have “dry” thicknesses of ~1.2 μm and Cu²⁺ binding capacities of 2–3 mmol/cm³. The low deposition pH decreases the charge on PDCMAA during adsorption and increases film thicknesses 8-fold compared to assembly at pH 5.0 or 7.0. For μm-thick films, saturation of binding sites requires ~4 h, and the Cu²⁺ diffusion coefficient in these coatings is 6–7 orders of magnitude lower than that in aqueous solutions. Sorption is endothermic with a positive entropy, presumably because of an endothermic exchange between Cu²⁺ and H⁺ with release of waters of hydration to increase entropy. Sorption capacities are stable over at least four cycles of Cu²⁺ binding and elution, suggesting possible applications in metal ion scavenging or protein binding.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Schematic representation of the assembly of (PAH/PDCMAA)_n-Cu²⁺ films on Au-coated substrates modified with a monolayer of 3-mercaptopropionic acid (MPA). The layering of polymers represents the number of depositions steps, but is likely not present in the film structure.

Figure 2.

Thicknesses of (PAH/PDCMAA) _{n} films adsorbed from solutions with different pH values. (a,b) Adsorption at pH 3.0 leads to an exponential increase in ellipsometric film thickness with the number of adsorbed layers for $n=1$ to 5 and a linear increase in film thickness for $n = 5$ to 10. (c) Adsorption at pH 5.0, 7.0 or 9.0 gives an exponential increase in ellipsometric film thicknesses for $n=1$ to 10. Curves show exponential or linear fits to the data. (d) Cross-sectional SEM image of a (PAH/PDCMAA)₁₀ film deposited at pH 3.0.

Figure 3. AFM topography images of (PAH/PDCMAA)₁₀ films adsorbed at (a) pH 3.0, (b) pH 5.0, (c) pH 7.0 and (d) pH 9.0.

Figure 4.

Cu^{2+} -binding capacities (a) per unit area and (b) per unit volume of $(\text{PAH/PDCMAA})_n$ films deposited at various pH values. During Cu^{2+} sorption $C_{\text{Cu}^{2+}} = 1.40 \text{ mM}$, $\text{pH} = 4.1$, and $T = 25 \text{ }^\circ\text{C}$. Film volumes were calculated using ellipsometric thicknesses of “dry” films without sorbed Cu^{2+} .

Figure 5. Cu^{2+} -binding capacities of $(\text{PAH/PDCMAA})_{10}$ films in 1.40 mM CuSO_4 solutions adjusted to pH 4.0 and 5.0. Film assembly occurred at pH 3.0, 5.0, 7.0 or 9.0, and the legend refers to assembly pH.

Figure 6.

Cu^{2+} sorption in $(\text{PAH/PDCMAA})_{10}$ films as a function of time (a) and the square root of time (b). Films were assembled at pH 3.0, and during Cu^{2+} adsorption $C_{\text{Cu}^{2+}} = 1.40$ mM, pH = 4.0, and $T = 25$ °C. The curves show fits to the data using equation (1) with $D = 2.6 \times 10^{-12}$ cm²/sec and $l = 2.0$ μm .

Figure 7.

Sorption isotherms for Cu^{2+} binding to $(\text{PAH/PDCMAA})_{10}$ films at different temperatures. Fits to the data (curves) result from Langmuir isotherms. Films were assembled at pH 3.0, and binding was allowed to occur for 15 h in pH 4.0 solution (20 mM phosphate). In the supporting information Figure S15 shows fits of the data to the Sips isotherm, and Figures S16 and 17 shows sorption isotherms at 16 and 31 °C.

Figure 8. Plot of $\ln K_L$ versus $1/T$ for equilibrium Cu^{2+} sorption in $(\text{PAH/PDCMAA})_{10}$ films. Films were assembled at pH 3.0, and sorption occurred at pH =4.0 for 15 h.

Figure 9.

Cu^{2+} Sorption capacities of $(\text{PAH/PDCMAA})_{10}$ coatings (formed at pH 3.0) over four cycles of binding and elution on the same films. Sorption occurred from 1.40 mM CuSO_4 solutions (pH 4.0, 20 mM phosphate solution) for 15 h, and Cu^{2+} was eluted with 20 mM EDTA (pH 7.4).

Scheme 1.

Protonation states of the IDA groups of PDCMAA. The pK_a values are those of IDA that is not attached to a polymer.³⁰

Scheme 2.

Cu^{2+} chelation to IDA functional groups via exchange with a proton.

Table 1

Fitting parameters from Langmuir and Sips isotherm models of Cu²⁺ sorption in (PAH/PDCMAA)₁₀ films.

Langmuir isotherm				
Temperature (°C)	ΔG_a^o (kJ/mol)	q_m (mmol/cm ³)	K_L (L/mmol)	R^2
4	-20.7	2.44 ± 0.09	7.75 ± 1.15	0.987
16	-23.3	2.60 ± 0.02	15.9 ± 0.7	0.999
25	-24.7	2.77 ± 0.09	20.4 ± 3.7	0.980
31	-26.9	2.50 ± 0.11	41.0 ± 9.5	0.944
37	-27.6	2.83 ± 0.12	43.2 ± 10.9	0.948
Sips isotherm				
Temperature (°C)	n	q_m (mmol/cm ³)	K_s (L/mmol)	R^2
4	1.02 ± 0.18	2.42 ± 0.19	7.96 ± 1.84	0.985
16	0.98 ± 0.04	2.62 ± 0.04	15.6 ± 0.9	0.998
25	1.36 ± 0.15	2.62 ± 0.07	23.3 ± 2.5	0.990
31	1.41 ± 0.10	2.43 ± 0.08	24.6 ± 10.5	0.967
37	1.71 ± 0.19	2.67 ± 0.05	49.5 ± 4.6	0.991