

# Aqueous Solvation and Functionalization of Weak-Acid Polyelectrolyte Thin Films

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A combination of in situ and ex situ ellipsometric studies and infrared spectroscopy was used to evaluate the extent of solvation of a thin covalently assembled, hyperbranched poly(acrylic acid) (PAA) graft on a gold substrate. The results show that these thin films swell reversibly by up to 300% upon immersion in a pH 1.7 buffer and by more than 500% at pH 10.7. This change in thickness, which is centered at pH 4.3, results from acid-group ionization. Covalent modification of the PAA thin films can be used to control both the extent of film swelling and the pH range over which the films undergo protonation/deprotonation reactions. For example, partial fluoramidation of the PAA carboxyl groups raises the pH where ionization occurs to 6.7 and reduces the extent of swelling (compared to the dry film) to 130% and 150% at pH 1.7 and 10.7, respectively. Solvated poly(sodium acrylate) films also serve as polyvalent ion-exchange substrates for immobilization of polyvalent cations including dendrimers, poly-L-lysine, and poly(allylamine). This immobilization technique yields self-assembled nanocomposites of the polyanionic surface graft with polycationic guests. pH modulation allows the guests to be released.

## Introduction

This paper describes solvation of weak-acid polyelectrolyte thin films, how such solvation depends on the degree of polymer ionization, and how polymer swelling of such films can be used to prepare nanocomposites. Using in situ ellipsometry,<sup>1-3</sup> we show that a "dry" film of hyperbranched poly(acrylic acid) (PAA) prepared by three sequential grafting steps (3-PAA)<sup>4-8</sup> swells reversibly by 300% upon immersion in a pH 1.7 buffer and by more than 500% at pH 10.7 buffer. The change in swelling results from acid-group ionization. As a consequence of this pH-dependent swelling and film-charge modulation, polyanionic 3-PAA films can act as polyvalent ion-exchange sorbents. Deprotonated films reversibly sorb fourth generation (G4), amine-terminated PAMAM dendrimers, and polycationic electrolytes such as poly-D-lysine at pH 7. Therefore, these brush-like polyelectrolytes are generally useful for ionic self-assembly of homogeneous nanocomposite films.

The type of ionic self-assembly described here is complementary to horizontal ionic self-assembly methods. Using techniques first reported by Iler,<sup>9</sup> several groups later demonstrated the utility of alternating adsorption

of polyanionic and polycationic materials to form composite films one layer at a time. In particular, Decher and co-workers showed that alternating adsorption of polycationic poly(allylamine) and polyanionic poly(styrene sulfonate) leads to the formation of alternatively stacked oppositely charged layers.<sup>10-13</sup> Polyelectrolyte materials amenable to this method include macromolecules as diverse as DNA, viruses, and redox polyelectrolytes.<sup>14-16</sup> In related studies, Mallouk<sup>17-19</sup> and Ferguson<sup>20,21</sup> have developed inorganic multilayer films based on this layer-by-layer adsorption strategy and shown that they yield interesting and useful architectures.<sup>21-24</sup>

In contrast to the horizontally layered polymers described above, polymer brushes are typically anchored to the surface or interface at one end of the polymer chain such that the polymer can extend away from the

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surface.<sup>25–29</sup> Polymer brushes comprised of uncharged polymers<sup>30–33</sup> and of polyelectrolytes have both been the object of significant recent attention.<sup>31,34–37</sup> Theoretical studies and computer simulations predict that these brushes will extend in the direction normal to the surface upon exposure to suitable solvents.<sup>38–46</sup> Such solvent-dependent morphological changes should be useful in constructing new types of chemical interfaces.

Thin films and brushes are of broad interest for many applications in interfacial materials science including tribology, membrane chemistry, biocompatibility, and adhesion.<sup>35,36,47–50</sup> Several groups have employed techniques such as neutron scattering,<sup>51,52</sup> X-ray fluorescence,<sup>53</sup> atomic force microscopy,<sup>35,54,55</sup> surface forces analysis,<sup>56</sup> ellipsometry,<sup>57,58</sup> and quartz crystal-based gravimetry<sup>57</sup> to study neutral polymer brushes. Fewer reports describe polyelectrolyte brushes.<sup>34,59,60</sup> The lack of experimental data results largely from difficulties in preparing dense, grafted polyelectrolyte films and from problems associated

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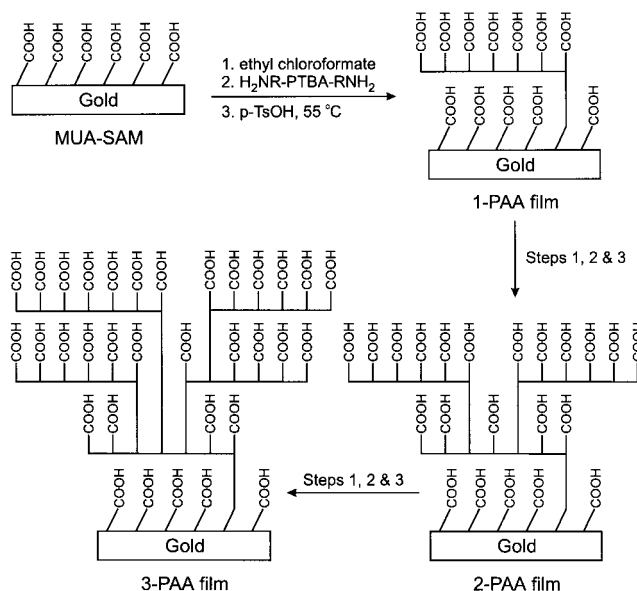
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### Scheme 1



with in situ analysis of solvated thin films. Mir and co-workers have, however, directly examined solvation of a polystyrene-*c*-polystyrene sulfonate sodium salt graft on porous silica using small-angle neutron scattering to determine its density profile.<sup>60</sup>

The experiments we describe examine solvation, pH behavior, and ionic assembly within thin hyperbranched films of PAA prepared as illustrated in Scheme 1. These hyperbranched films are brushlike in that they are grown from the surface into solution. The results we describe are important because they quantitatively show the dramatic extent of swelling that these films undergo in water. Moreover, they demonstrate that PAA thin films undergo significant pH-dependent changes in swelling due to their acid/base behavior. Such changes cannot be observed with the aforementioned aryl sulfonic acid grafts because of the high acidity of the  $-\text{SO}_3\text{H}$  group.<sup>61</sup>

## Experimental Section

**Buffer Solutions.** Buffer solutions were prepared in a 0.1 M NaCl solution using 18 M $\Omega$ ·cm deionized water (Milli-Q, Millipore) to provide a nearly constant refractive index and ionic strength. pH measurements were taken before each experiment using a pH meter (Beckman). The composition and measured pH values of the buffers are as follows: 0.01 M  $\text{Na}_2\text{SO}_4$  + 0.02 M HCl (pH = 1.7), 0.018 M  $\text{Na}_2\text{SO}_4$  + 0.004 M HCl (pH = 2.6), 0.002 M  $\text{CH}_3\text{COONa}$  + 0.018 M  $\text{CH}_3\text{COOH}$  (pH = 3.7), 0.005 M  $\text{CH}_3\text{COONa}$  + 0.015 M  $\text{CH}_3\text{COOH}$  (pH = 4.0), 0.01 M  $\text{CH}_3\text{COONa}$  + 0.01 M  $\text{CH}_3\text{COOH}$  (pH = 4.5), 0.015 M  $\text{CH}_3\text{COONa}$  + 0.005 M  $\text{CH}_3\text{COOH}$  (pH = 5.0), 0.002 M  $\text{Na}_2\text{HPO}_4$  + 0.018 M  $\text{NaH}_2\text{PO}_4$  (pH = 5.7), 0.01 M  $\text{Na}_2\text{HPO}_4$  + 0.01 M  $\text{NaH}_2\text{PO}_4$  (pH = 6.7), 0.015 M  $\text{Na}_2\text{HPO}_4$  + 0.005 M  $\text{NaH}_2\text{PO}_4$  (pH = 7.2), 0.018 M  $\text{Na}_2\text{HPO}_4$  + 0.002 M  $\text{NaH}_2\text{PO}_4$  (pH = 7.7), 0.02 M  $\text{Na}_2\text{B}_4\text{O}_7$  + 0.02 M HCl (pH = 9.0), 0.002 M  $\text{Na}_2\text{CO}_3$  + 0.018 M  $\text{NaHCO}_3$  (pH = 9.0), 0.01 M  $\text{Na}_2\text{CO}_3$  + 0.01 M  $\text{NaHCO}_3$  (pH = 9.9), and 0.018 M  $\text{Na}_2\text{CO}_3$  + 0.002 M  $\text{NaHCO}_3$  (pH = 10.7).

**Other Chemicals.** Amine-terminated, G-4 Starburst PAM-AM dendrimers (Dendritech, Inc., Midland, MI), ethylenediamine (Aldrich, 99%), ethanolamine (Aldrich, 99+%), pentadecafluorooctylamine (PCR, 97%), poly-D-lysine hydrobromide (Aldrich,  $M_n$ : 4000–15000), and poly(allylamine hydrochloride) (Aldrich,  $M_n$ : 8500–11000) were used as received. *O,O*-Bis(2-aminoethyl)poly(ethylene glycol) ( $M_n$  ca. 4600) was synthesized from

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poly(ethylene glycol) (Aldrich,  $M_n$  ca. 4600) analogous to a literature procedure.<sup>62</sup>

**Substrate Preparation.** Au-coated substrates were prepared by electron-beam deposition of 100 Å of Ti followed by 2000 Å Au onto Si(100) wafers. Before each experiment all wafers were cleaned in a low-energy ozone cleaner for 10 min (Boekel Industries, Inc., model 135500).

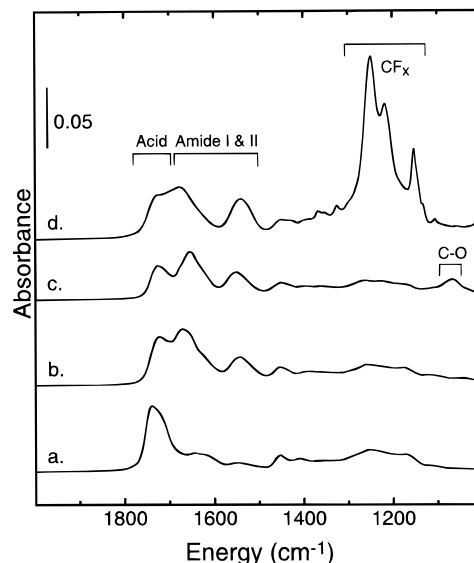
**Preparation of  $\alpha,\omega$ -Diaminopoly(*tert*-butyl acrylate) (PTBA).** PTBA was synthesized as previously described with only minor modifications.<sup>5</sup> At the diacid polymer step, the product was twice precipitated from methanol/distilled water (1:1) yielding a polymer dispersity of 1.9 ( $M_n = 15\ 000$ , GPC). The final diamino-terminated polymer had a polymer dispersity of 2.0 ( $M_n = 18\ 000$ , GPC).

**Preparation and Derivatization of Poly(acrylic acid) (PAA) Films.** Hyperbranched PAA films on Au-coated Si wafers were prepared by first grafting  $\alpha,\omega$ -diaminopoly(*tert*-butylacrylate) (PTBA) onto an ethyl chloroformate activated mercapto-undecanoic acid (MUA) self-assembled monolayer (SAM). Hydrolysis of the *tert*-butyl ester groups followed by two additional stages of activation, grafting, and hydrolysis yielded a grafted hyperbranched 3-PAA film (Scheme 1).<sup>5</sup> The 3-PAA films prepared in this way were  $230 \pm 30$  Å thick. Prior reports of such 3-PAA films prepared by using a more polydisperse PTBA oligomer yielded films whose thickness was somewhat higher (ca. 350 Å). The physical and chemical properties of 3-PAA films are largely independent of the polydispersity of the starting materials.

Amidation of the carboxylic groups of the 3-PAA films with pentadecafluorooctylamine, ethanolamine, or ethylenediamine after ethyl chloroformate activation followed our previously described procedure.<sup>4</sup> After preparation, all covalently modified 3-PAA films were dipped in a pH  $\sim 2$ /ethanolic solution for 10 min, to protonate unfunctionalized acid groups and remove salts, and finally rinsed with ethanol and dried under flowing  $N_2$ . 3-PAA salt films were prepared by a 15 min soaking in pH 7 buffered solutions containing 6.4 mequiv/L of amine groups. Following this the samples were washed with water and ethanol and then dried with flowing  $N_2$ . The aqueous solutions of G4 PAMAM dendrimer, poly(allylamine hydrochloride), poly-D-lysine hydrobromide, and *O,O'*-bis(2-aminoethyl)poly(ethylene glycol) were prepared by dissolving 14.2, 6.0, 13.4, and 147.2 mg, respectively, of the compounds in 10 mL of the buffer solution.

**Spectroscopic Analysis.** FTIR-ERS measurements were made using a Bio-Rad FTS-40 spectrometer equipped with a Harrick Scientific Seagull reflection accessory and a liquid- $N_2$ -cooled MCT detector. Spectra were obtained using *p*-polarized light at an 85° angle of incidence with respect to the Au substrate. Spectra were measured at 4- $cm^{-1}$  resolution using between 100 and 256 scans.<sup>63</sup> FTIR-ERS spectra of PAA films as a function of pH were obtained by immersing the films in the appropriate buffer solution for 5 min, rinsing with ethanol, and drying under flowing  $N_2$ .

**Ellipsometry.** Ellipsometric measurements were performed using a Gaertner L2W26D ellipsometer employing a 488.0 nm  $Ar^+$  laser and a  $70.00 \pm 0.02^\circ$  angle of incidence. Refractive index ( $n$ ) and film thicknesses were calculated assuming a standard homogeneous film model using Gaertner software. To calculate the thickness of dry PAA films a refractive index of 1.54 was used.<sup>4,64</sup> This refractive index value was determined using ellipsometry on thicker, protonated PAA films where such measurements are more accurate. In the case of the thicker 3-PAA/poly-D-lysine, poly(allylamine), and G4 PAMAM dendrimer salt films both refractive index and thickness were measured; the refractive indices of these films were 1.55, 1.56, and 1.58, respectively. Ex situ thickness measurements of all dry polyelectrolyte-intercalated 3-PAA salt films were compared with those of a 3-PAA film dipped in a pH 7 buffer solution for 15 min, rinsed with ethanol, and then dried. In situ ellipsometry



**Figure 1.** FTIR-ERS spectra of a (a) 3-PAA film and 3-PAA films derivatized with (b) ethylenediamine, (c) ethanolamine, and (d) pentadecafluorooctylamine.

was performed using a trapezoidal-prism-shaped cell, having glass windows oriented perpendicular to the incident laser beam. The refractive index of the 0.1 M buffer solutions was calculated to be 1.338 and the refractive index of pure water at 488 nm is 1.337.<sup>65,66</sup> For the in situ measurements, it was possible to determine both the refractive index and thickness of the films using ellipsometric data.

The uncertainty of the in situ film thickness measurements is  $\pm 30$  Å while the uncertainty in the film refractive index is  $\pm 0.01$ . These errors are larger than those for measurements in air because of the similarity of the refractive indices of the buffer solutions and the swollen films. We determined the uncertainties by estimating the maximum error in  $\psi$  and  $\delta$  and calculating the corresponding values for thickness and refractive index (Woollam M44 VASE software, J. A. Woollam Company, Lincoln, NE). For all ellipsometric measurements, it was assumed that refractive index did not vary within the film. Thus, thickness values and refractive indices reported are effective values that reflect the average of the density gradient of the polyelectrolyte films. In some previous studies, ellipsometric thicknesses were corrected to reflect a Gaussian density distribution.<sup>67,68</sup> Because the form of the density distribution is not known here and because such a correction would contribute little to the conclusions of this work, which mainly rely on changes in film thicknesses rather than absolute values, we simply report the effective ellipsometric thicknesses calculated using the homogeneous film model.

**Contact-Angle Measurements.** Contact angles were measured with a FTÅ 200 goniometer using doubly distilled water. The contact-angle values reported are the average of four measurements obtained at different spots on the same film. The estimated error is  $\pm 3^\circ$ .

## Results and Discussion

Figure 1a shows the spectrum of an unmodified 3-PAA surface where the dominant feature is an acid carbonyl peak at  $1735\ cm^{-1}$ . Reaction of the activated acid groups with ethylenediamine (Figure 1b), ethanolamine (Figure 1c), or pentadecafluorooctylamine (Figure 1d) leads to a large increase in the amide I and II peaks at  $1680\text{--}1670$  and  $1560\text{--}1550\ cm^{-1}$ , respectively.<sup>4-8</sup> Comparing the

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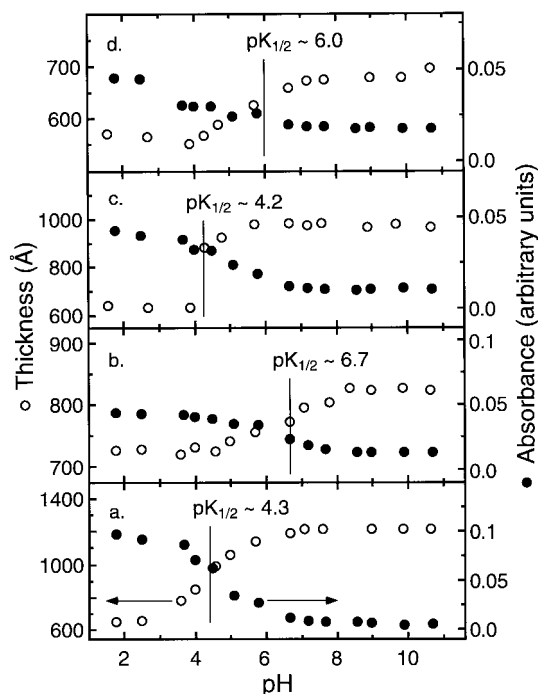
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**Figure 2.** Plots of in situ ellipsometric thickness and FTIR-ERS acid carbonyl peak height versus pH for a (a) 3-PAA film and 3-PAA films derivatized with (b) pentadecafluorooctylamine, (c) ethanolamine, and (d) ethylenediamine.

areas of the acid carbonyl peaks before and after amidation, we estimate that about 35% of the acid groups within the 3-PAA films reacted with the amine species, which is consistent with previous findings.<sup>4</sup> Other absorption peaks, such as a characteristic C–O mode at 1063  $\text{cm}^{-1}$  arising from the primary alcohol group of ethanolamine (Figure 1c) and the characteristic  $\text{CF}_x$  stretching modes (1250–1150  $\text{cm}^{-1}$ ) resulting from the presence of pentadecafluorooctylamine  $-\text{NHCH}_2(\text{CF}_2)_6\text{CF}_3$  moieties (Figure 1d), are also present, further confirming the derivatization chemistry.

Figure 2a shows the in situ measured ellipsometric thickness of a 3-PAA film as a function of pH. In this particular case, the thickness of the dry film was 230 Å. The PAA film swells by 430 Å upon immersion for 5 min in a pH 1.7 buffer solution. Removal of this film from solution, washing with ethanol, and drying under a  $\text{N}_2$  stream yields a “dry” film having a thickness unchanged from the original value of 230 Å indicating that solvent swelling is reversible. In situ analysis of film thickness as a function of buffer pH indicates a thickness increase of 560 Å as the pH increases from 2.6 to 7.2. The halfway point for this thickness increase ( $pK_{1/2}$ ) occurs at pH 4.3, which is comparable to the  $pK_a$  of PAA in solution.<sup>69</sup> Further thickness changes do not occur as the pH is increased above 7.2 or below 2.6. We titrated the 3-PAA film twice between pH 2 and pH 11 with a series of buffer solutions, and the results showed that the thickness changes are completely reversible and that there is no hysteresis associated with swelling and deswelling. Ex situ FTIR-ERS confirms that the thickness changes correlate with deprotonation of the  $-\text{COOH}$  groups in the film. Figure 2a also shows that the absorbance due to the  $-\text{COOH}$  carbonyl peak (1735  $\text{cm}^{-1}$ ) decreases rapidly after exposure to solutions whose pH is between pH 3.6 and 7.6.

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**Table 1.** Thickness,  $pK_{1/2}$ , and Water Contact Angles for 3-PAA and Derivatized 3-PAA films

	thickness (Å)			$pK_{1/2}$	contact angle $\theta_a$ (deg)
	dry	wet (pH 1.7)	wet (pH 10.7)		
3-PAA	230	660	1220	4.3	25
3-PAA/ $\text{H}_2\text{NCH}_2(\text{CF}_2)_6\text{CF}_3$	570	730	830	6.7	120
3-PAA/ $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$	295	640	970	4.2	34
3-PAA/ $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	320	580	680	6.0	62

The large increase in PAA film thickness in solution at high pH is consistent with a film comprised of approximately 80% water. This fractional composition is also in agreement with the measured values of the refractive indices. If the refractive index of the solvent-swollen films is considered to be a linear combination of the refractive indices of water (1.338) and the polymer (1.54)<sup>4</sup> times their respective volume fractions, the refractive index of extended PAA should be 1.38. The Bruggeman effective medium approximation also predicts a refractive index of 1.38.<sup>70</sup> Within experimental error, this is consistent with the measured value of 1.39. Thus, ellipsometry provides a consistent picture of the effective thickness and volume fraction of 3-PAA.<sup>71</sup>

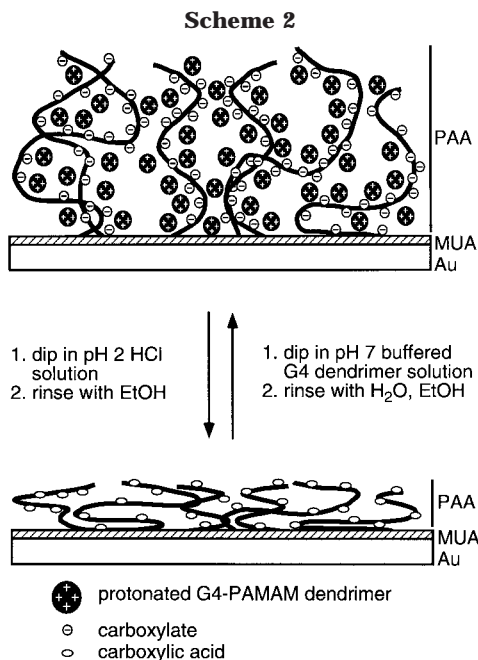
It is possible to control the extent of film swelling and the  $pK_{1/2}$  by derivatizing the  $-\text{COOH}$  groups of hyperbranched PAA films. Amidation of a 225-Å-thick (dry) 3-PAA film with pentadecafluorooctylamine (3-PAA/ $\text{H}_2\text{NCH}_2(\text{CF}_2)_6\text{CF}_3$ ) results in an increase of dry-film thickness to 570 Å (thickness data for all films are collected in Table 1).<sup>4,6–8</sup> The 3-PAA/ $\text{H}_2\text{NCH}_2(\text{CF}_2)_6\text{CF}_3$  film has ca. 65% remaining  $-\text{COOH}$  groups. It swells to 730 Å upon immersion in pH 1.7 buffer solution and further to 830 Å at elevated pH. The  $pK_{1/2}$  of the perfluorinated film occurs around pH 6.7 (Figure 2b) rather than at pH 4.3 as for the 3-PAA film (Figure 2a). Ex situ FTIR-ERS spectra confirm that deprotonation of the residual  $-\text{COOH}$  groups occurs 2–3 pH units higher in the fluorinated film than it does in underivatized PAA films (Figure 2a).

To determine whether the enhanced hydrophobicity of the fluorinated groups or the amide linkages in the fluorinated film change  $pK_{1/2}$ , we also derivatized 3-PAA films with ethanolamine to form partially amidated hydrophilic films. After amidation of a 250-Å-thick 3-PAA film with ethanolamine, the dry film had a thickness of 295 Å. Contact-angle measurements show that derivatization of a 3-PAA film with ethanolamine instead of pentadecafluorooctylamine results in a more hydrophilic film. The measured advancing water contact angle ( $\theta_a$ ) for 3-PAA/ $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$  and 3-PAA/ $\text{H}_2\text{NCH}_2(\text{CF}_2)_6\text{CF}_3$  films were 34 and 120°, respectively. The 3-PAA/ $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$  film swells to 640 Å upon immersion in pH 1.7 buffer solution and to 970 Å at high pH. The  $pK_{1/2}$  of 3-PAA/ $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$  occurs around pH 4.2 (Figure 2c). Figure 2c also shows that the absorbance due to the  $-\text{COOH}$  carbonyl peak (1735  $\text{cm}^{-1}$ ) decreases rapidly between pH 3.7 and 7.7, similar to the 3-PAA film. The results indicate, therefore, that the  $pK_{1/2}$  of these films is a strong function of their hydrophobicity. This is a reasonable and expected result based on the energetic consequences of placing a charged carboxylate group within a low-dielectric fluorinated film.<sup>72</sup> Similarly, the

(70) Tompkins, H. G. *A User's Guide to Ellipsometry*; Academic: San Diego, CA, 1993.

(71) The measured refractive index of a “dry”, ionized film is 1.51 (see ref 4), which is slightly lower than for the protonated PAA films. However, when this value and the corresponding thickness are used for the calculations discussed in this paragraph, the results are identical.

(72) Lewis, G. N.; Randall, M. *Thermodynamics*; McGraw-Hill: New York, 1961.



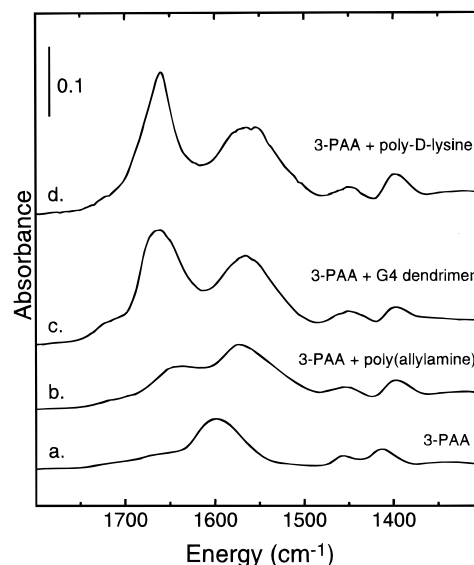
more hydrophobic film absorbs less water than the ethanolamine-derivatized film and therefore swells less as a function of its degree of ionization.

Cross-linking should produce a more rigid hyperbranched film whose thickness should not vary greatly as a function of pH. Reaction of a 3-PAA film with ethylenediamine results in a "dry" thickness increase from 250 to 320 Å. Upon immersion in pH 1.7 buffer solution, the film swells to 580 Å, slightly less than a 3-PAA/H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH film. However the ethylenediamine cross-linked film thickness change between pH 2 and 11 (100 Å) is much smaller than that for the 3-PAA/H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH film (Figure 2d). Ex situ FTIR-ERS spectra confirm that deprotonation of the underivatized -COOH groups occurs in the same pH region (Figure 2d). As for the 3-PAA film, the swelling behavior for the three derivatized 3-PAA films is reversible.

Since self-assembly of alternating layers of cationic and anionic polyelectrolytes to form layered thin films has proven to be a highly successful synthetic procedure<sup>10-13,18,19,21-24</sup> and since these hyperbranched polyelectrolytes swell so much in water, we explored the ion-exchange behavior of PAA grafts. The results show that insertion of cationic polyelectrolytes into PAA films does indeed occur and that such an ionic assembly is a general route to thin films of complementary charged polyelectrolytes at surfaces.

The ellipsometric thickness of a dry 3-PAA film before and after treatment with a pH 2 buffer solution is 260 Å. However, if the same film is immersed in a pH 7 buffer, rinsed with ethanol, and dried it is found to have a thickness of 340 Å. FTIR-ERS indicates this 80 Å (31%) thickness change is a result of the formation of carboxylate groups.<sup>4</sup> Exposure of the same film to a pH 7 solution containing either a mono- or diamine, like ethanolamine or ethylenediamine and *O,O'*-bis(2-aminoethyl)poly(ethylene glycol) ( $M_n$  ca. 4600), respectively, results in little (<5%) change in dry-film thickness compared to one prepared in an amine-free pH 7 buffer. FTIR-ERS spectroscopy confirms that little of the mono- and diamines sorb into the PAA films (vide infra).

In contrast to the mono- and diamines, which do not sorb into PAA films, polyvalent amines do. Exposure of a 3-PAA film to a pH 7 solution of a G4 PAMAM dendrimer



**Figure 3.** FTIR-ERS spectra of a (a) 3-PAA and 3-PAA salt films intercalated with (b) poly(allylamine), (c) G4-PAMAM dendrimer, and (d) poly-D-lysine.

(Scheme 2) results in a dry-film thickness increase of 230%. When a 3-PAA film is exposed to linear polycations such as poly(allylamine) ( $M_n = 8500-11000$ ) the dry thickness increases by 170%. Finally, exposure of 3-PAA to the hydrophilic poly-D-lysine ( $M_v = 4,000-15,000$ ) results in a dry-film thickness increase of 180%. These dry-film thickness increases, which are unaffected by copious rinsing with water or ethanol, are due to the presence of multiple electrostatic interactions between protonated groups on the polyvalent amines and the polyanionic 3-PAA films. The bulkiness of these intercalated counterions compared to Na<sup>+</sup> is responsible for the large thickness increases.

FTIR-ERS confirms the binding of polyamines to deprotonated PAA films. Figure 3a shows the FTIR-ERS spectra of a 3-PAA film taken after exposure to a pH 7 buffer. The most prominent peaks in the spectrum correspond to the asymmetric and symmetric carboxylate modes at 1600 and 1415 cm<sup>-1</sup>, respectively, which reflect the deprotonated state of the film. The spectrum shown in Figure 3b was prepared identically to that in Figure 3a, except the pH 7 buffer solution contained poly(allylamine). There are prominent peaks corresponding to the symmetric and asymmetric carboxylate modes at 1640 and 1400 cm<sup>-1</sup>. The shift to higher energy of the asymmetric carboxylate mode relative to that shown in the 3-PAA spectrum reflects the presence of R-NH<sub>3</sub><sup>+</sup> in the film. The 1570 cm<sup>-1</sup> peak in Figure 3b corresponds to the superposition of the symmetric and asymmetric -NH<sub>3</sub><sup>+</sup> modes, which arise from the poly(allylamine) and are observed for monomers at 1580 and 1550 cm<sup>-1</sup>.<sup>73</sup> Parts c and d of Figure 3 correspond to the G4-dendrimer- and poly-D-lysine-intercalated films, respectively. They reveal the same salt peaks as observed for poly(allylamine) intercalation, as well as amide I and II bands at 1660 and 1565 cm<sup>-1</sup>, respectively, arising from the G4 dendrimer branches and poly-D-lysine polymer backbones. Finally, the 3-PAA/polyamine interactions are reversible. Soaking any of the composite 3-PAA films in a pH 2 HCl solution for 15 min releases intercalants from the films.

(73) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic: San Diego, CA, 1990.

### **Summary and Conclusion**

In summary, in situ ellipsometry shows that thin, hyperbranched PAA films undergo dramatic thickness changes as a function of pH. Covalent modification of these films can be used to control the extent of swelling and the pH range over which swelling occurs. In their swollen polyanionic state, the PAA hyperbranched grafts reversibly sorb polyvalent cationic polyelectrolytes leading to ionic self-assembly of nanocomposite, polyelectrolyte thin films.

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