

# Fourier Transform Infrared Studies on the Dissociation Behavior of Metal-Chelating Polyelectrolyte Brushes

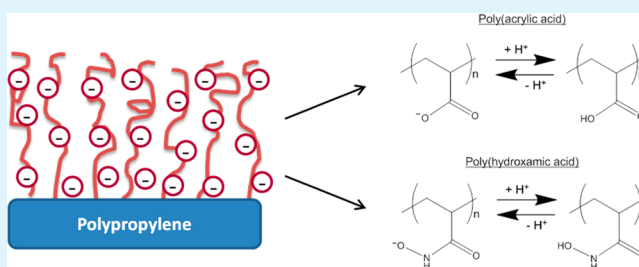
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## S Supporting Information

**ABSTRACT:** The dissociation behavior of surface-grafted polyelectrolytes is of interest for the development of stimuli-responsive materials. Metal-chelating polyelectrolyte brushes containing acrylic acid (PAA) or hydroxamic acid (PHA) chelating moieties were grafted from the surface of polypropylene (PP). Fourier transform infrared (FTIR) spectroscopy was used to determine the effective bulk  $pK_a$  of the polyelectrolyte brushes ( $pK_a^{\text{bulk}}$ ) and to characterize metal-chelating behavior. The  $pK_a^{\text{bulk}}$  values of PP-g-PAA and PP-g-PHA were 6.45 and 9.65, respectively. Both PP-g-PAA and PP-g-PHA exhibited bridging bidentate and chelating bidentate iron chelation complexes. This is the first reported determination of the  $pK_a^{\text{bulk}}$  of surface-grafted poly(hydroxamic) acid.

**KEYWORDS:** polymer brushes,  $pK_w$  dissociation, metal chelation, poly(acrylic acid), poly(hydroxamic acid), FTIR



The attachment of polyelectrolytes onto solid supports enables the synthesis of stimuli-responsive functional surfaces that have numerous applications in water treatment,<sup>1</sup> colloidal stabilization,<sup>2</sup> protein immobilization,<sup>3</sup> drug delivery,<sup>4</sup> and biosensors.<sup>5,6</sup> The functionality of these surfaces, which often relies on charge and ligand-specific interactions, depends on the microenvironment at the interface. The microenvironment of surface-grafted polyelectrolytes not only is influenced by solvent conditions, such as the pH and ionic strength, as in the case with their solution-based analogues, but also is influenced by the properties of the surface and surrounding grafted polymers. Because of the steric restrictions associated with the attachment of polyelectrolytes to a surface, the dissociation behavior of surface-grafted polyelectrolytes may be very different from that corresponding to polyelectrolytes in solution.<sup>7</sup> For example, Dong et al. reported a  $pK_a^{\text{bulk}}$ , which characterizes the dissociation behavior of the surface-grafted polyelectrolytes, of PAA brushes that was 2 units higher than the previously reported  $pK_a$  values of PAA in solution.<sup>8,9</sup>

The dissociation behavior of polyelectrolytes in solution as a function of the pH, salt concentration, or metal chelation is quantifiable by well-established titration techniques. However, these methods are not applicable to polymers grafted onto a solid support because of the inability of the equipment used to collect data, such as pH meters and isothermal titration calorimeters, to directly monitor the charge fraction within the surface-grafted polyelectrolyte layer. There have been studies that generate titration curves of surface-grafted polyelectrolytes, mainly carboxylate-containing polymers such as PAA and PMAA, from data collected by the contact-angle,<sup>8,10</sup> reflectometry,<sup>11,12</sup> ellipsometry,<sup>6,10,13,14</sup> and FTIR spectroscopy<sup>6,8,15,16</sup> techniques. Titration curves generated by contact-

angle measurements reflect the ionization properties of only the top few nanometers of surface-grafted polyelectrolytes ( $pK_a^{\text{surface}}$ ), while titration curves generated by reflectometry, ellipsometry, and FTIR measurements can be used to examine the dissociation behavior of the entire surface-grafted polyelectrolyte layer ( $pK_a^{\text{bulk}}$ ).<sup>8</sup> Of the techniques that characterize the  $pK_a^{\text{bulk}}$ , FTIR is the only technique that enables direct quantification of the charge fraction to characterize the dissociation behavior by measuring the absorbance bands of specific bonds. FTIR may also be used to characterize the absorption of charge species, such as proteins and metal ions, to polyelectrolyte-modified surfaces.

We recently developed metal-chelating polymer films for antioxidant packaging applications, wherein either PAA or PHA brushes were grafted from the surface of PP via photoinitiated graft polymerization.<sup>17</sup> Herein, we report the characterization of the dissociation and iron chelation behavior of these surface-grafted polyelectrolyte brushes using FTIR-based characterization techniques. Particularly,  $pK_a^{\text{bulk}}$  values and possible metal coordination complexes were determined. This is the first reported determination of the  $pK_a^{\text{bulk}}$  of surface-grafted PHA.

A more detailed experimental section is available in the Supporting Information (SI). In brief, PAA grafted from PP (PP-g-PAA) and PHA grafted from PP (PP-g-PHA) were prepared using modification of a previously reported work.<sup>17–19</sup> PP-g-PAA films were prepared by photoinitiated graft polymerization of acrylic acid. PP-g-PHA films were prepared by photoinitiated graft polymerization of methyl acrylate followed

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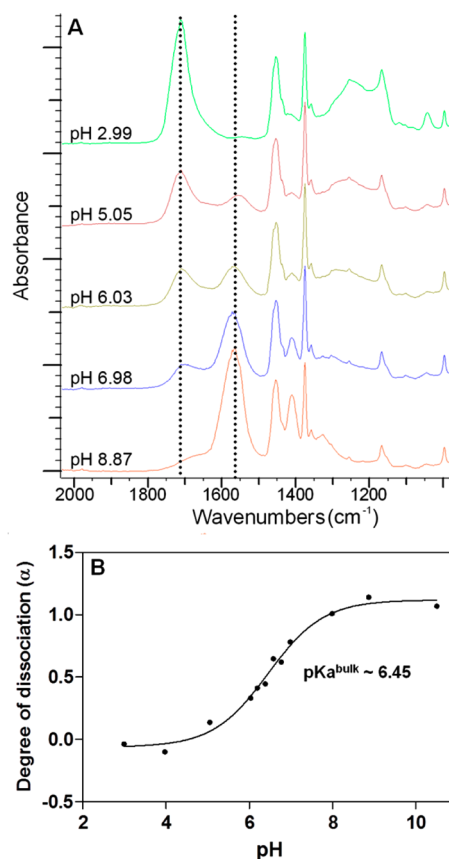
by conversion of methyl acrylate to hydroxamate via reaction with a basic hydroxylamine solution. A FTIR titration was adapted from a previously reported work to determine the  $pK_a^{\text{bulk}}$  of carboxylate ligands of PP-g-PAA and hydroxamate ligands of PP-g-PHA.<sup>8</sup> PP-g-PAA was incubated in 0.1 M 2-morpholinoethanesulfonate (MES) buffers of different pH values, ranging from 3 to 10. PP-g-PHA was incubated in buffers of different pH values, with the 0.1 M MES buffer ranging from pH 5 to 7 and the 0.1 M sodium carbonate buffer ranging from pH 8 to 13. FTIR spectra were collected on an IRPrestige FTIR spectrometer (Shimadzu Scientific Instruments, Inc., Kyoto, Japan) with a diamond ATR crystal. For iron chelation studies, PP-g-PAA and PP-g-PHA films were incubated in 0.08 mM ferric chloride in 0.05 M sodium acetate/imidazole, pH 5.0, for 24 h and then rinsed with copious amounts of deionized water to remove unbound iron. FTIR spectra collected before and after iron chelation assay were compared and interpreted based on previously published research on metal chelation by PMAA brushes.<sup>20</sup>

The synthesis of PP-g-PAA and PP-g-PHA by the described techniques for iron chelation applications has been confirmed by FTIR, contact-angle, scanning electron microscopy, atomic force microscopy, and colorimetric assays.<sup>17,19</sup> For this study, ATR-FTIR spectra of the PP-g-PAA and PP-g-PHA films were used to characterize the chemistry of surface-grafted polyelectrolytes. Spectra were collected at wavenumbers ranging from 4000 to 600  $\text{cm}^{-1}$ . At wavenumbers above 1800  $\text{cm}^{-1}$ , the only absorbance bands attributed to the surface-grafted PAA and PHA brushes were broad bands corresponding to the O–H and N–H bonds, which were easily influenced by the presence of water. Therefore, FTIR analysis was restricted to absorbance bands present in the range of 1800–600  $\text{cm}^{-1}$ . Absorbance bands were assigned based on analysis by KnowItAll(R) Informatics System 9.5 (Bio-Rad Laboratories, Inc., Informatics Division, Philadelphia, PA) and a comparison to previously published research.<sup>8,17,19–25</sup> Tables S1 and S2 in the SI show the absorbance band assignments for PP-g-PAA and PP-g-PHA, respectively.

FTIR studies on the dissociation behavior of surface-grafted polymers with carboxylate ligands, such as PAA and PMAA, were previously conducted by monitoring the C=O absorbance band.<sup>6,8,15,16</sup> Deprotonated and protonated carboxylate ligands absorb at different wavelengths. Representative FTIR spectra of PP-g-PAA after incubation in buffers of different pH values are shown in Figure 1a. C=O absorbance bands at  $\sim 1710$  and  $\sim 1564$   $\text{cm}^{-1}$  corresponded to protonated carboxylic acid and deprotonated carboxylic acid, respectively. As the pH increased, the intensity of the deprotonated C=O band increased and the intensity of the protonated C=O band decreased, which illustrated dissociation of the carboxylate groups as a function of the solution pH. The degree of dissociation,  $\alpha$ , was calculated using the following equation:

$$\alpha = [\text{COO}^-]/[\text{COO}^-] + [\text{COOH}]\epsilon(\text{COO}^-)/\epsilon(\text{COOH})$$

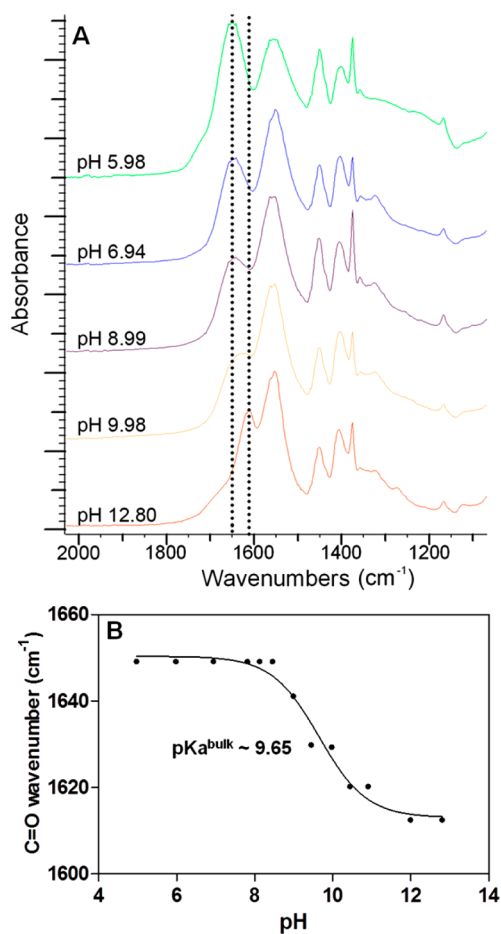
where  $[\text{COO}^-]$  and  $[\text{COOH}]$  correspond to the integrated area of deprotonated and protonated carboxylic acid absorbance bands and  $\epsilon(\text{COO}^-)$  and  $\epsilon(\text{COOH})$  are the extinction coefficients of deprotonated and protonated carboxylic acid.<sup>8</sup> A previously determined  $\epsilon(\text{COO}^-)/\epsilon(\text{COOH})$  value of 1.8 was used in the calculations.<sup>20</sup> The degree of dissociation and their corresponding pH values were fitted to a sigmoidal dose-response function (GraphPad Prism 6.0, La Jolla, CA) to generate a titration curve that was used to



**Figure 1.** (a) ATR-FTIR spectra of PP-g-PAA treated with buffer solutions of varying pH. Protonated and deprotonated IR bands are marked at 1710 and 1566  $\text{cm}^{-1}$ , respectively. (b) FTIR titration curve for PP-g-PAA. The  $pK_a^{\text{bulk}}$  calculated at the midpoint of the titration curve is 6.45.

determine the  $pK_a^{\text{bulk}}$  (Figure 1b). The  $pK_a^{\text{bulk}}$  was defined as the solution pH value corresponding to the midpoint of the titration curve and calculated as 6.45 for PP-g-PAA. This value is in agreement with a previous FTIR study of the dissociation behavior of PAA brushes on gold substrates.<sup>8</sup> The  $pK_a$  of PAA in solution has been reported as  $\sim 4.7$ , which is approximately 2 units lower than the  $pK_a^{\text{bulk}}$  of PAA brushes.<sup>9</sup> The  $pK_a^{\text{bulk}}$  values of PAA brushes are hypothesized to be greater than the  $pK_a$  values of PAA in solution because of the influence of the surface and surrounding grafted PAA on the charge distribution within the modified surface.<sup>8,26</sup> Electrostatic interactions between surface-grafted carboxylate ligands dictate the distribution of charges within the grafted layer, wherein it is energetically unfavorable to ionize ligands closer to the surface because of the energy cost of repulsion between surface-grafted PAA that occurs upon deionization.<sup>8,16</sup> Therefore, it is hypothesized that the solution pH may be higher than the local pH within the grafted PAA layer as the surface is approached. This phenomenon would have brought about an increase in the  $pK_a^{\text{bulk}}$  of the surface-grafted PAA compared to PAA in solution. This shift of the  $pK_a^{\text{bulk}}$  of surface-grafted carboxylate polyelectrolytes of approximately 2 pH units higher has been reported many times in the literature.<sup>8,13,16,26</sup> The  $pK_a^{\text{bulk}}$  values of polyelectrolyte brushes as a function of the solution pH are important when determining applications of such surface-modified materials.

FTIR spectroscopy investigations on the dissociation behavior of hydroxamate-containing compounds in solution have demonstrated that deprotonation of hydroxamic acids most notably results in a downshift of the C=O absorbance band, which is likely attributed to the weakened C=O bond strength of deprotonated hydroxamic acids due to the delocalization of  $\pi$  electrons to C–N and N–O bonds.<sup>21–23</sup> Therefore, for this study, deprotonation of the hydroxyl group of PHA brushes grafted from PP was monitored by quantifying the shift in the C=O absorbance band from  $\sim 1650$  (protonated) to  $\sim 1612$   $\text{cm}^{-1}$  (deprotonated) as dependent on the pH (Figure 2a). The shift of the C=O absorbance band

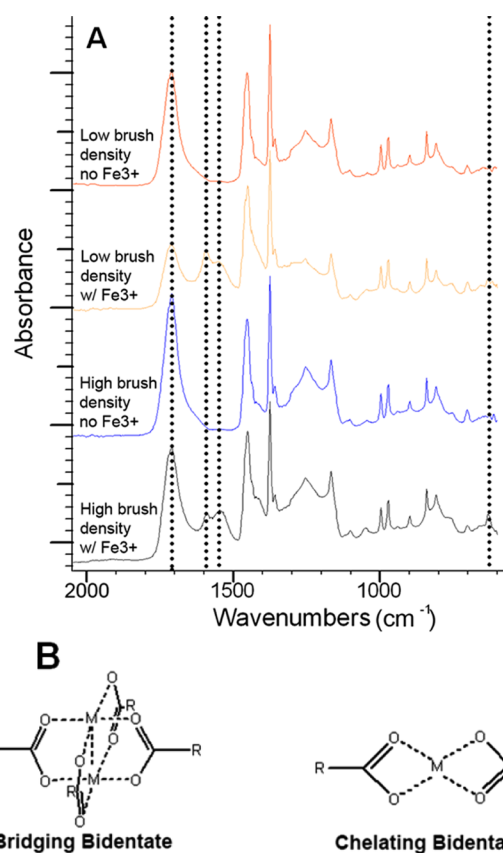


**Figure 2.** (a) ATR-FTIR spectra of PP-g-PHA treated with buffer solutions of varying pH. The absorbance band C=O shift caused by deprotonation, from 1649 and 1612  $\text{cm}^{-1}$ , is marked. (b) FTIR titration curve for PP-g-PHA. The  $pK_a^{\text{bulk}}$  calculated at the midpoint of the titration curve is 9.65.

as a function of the solution pH was fitted to a sigmoidal function to generate a titration curve from which the  $pK_a^{\text{bulk}}$  could be estimated (Figure 2b). As with PP-g-PAA, the  $pK_a^{\text{bulk}}$  was defined as the solution pH value corresponding to the midpoint of the titration curve. The  $pK_a^{\text{bulk}}$  of PHA brushes grafted from PP estimated from the titration curve, 9.65, was in the range for the  $pK_a$  of hydroxamic acids in solution. Desferoxamine B, a chelator that contains three hydroxamate ligands, has three  $pK_a$  values ranging from 8.35 to 9.71.<sup>27</sup> Unlike PAA brushes, the  $pK_a^{\text{bulk}}$  values of the hydroxamate ligands of PHA brushes were not strongly affected by attachment to a solid support. It is hypothesized that because

hydroxamate ligands are much weaker acids than carboxylates, as indicated by their high  $pK_a$  values, electrostatic interactions between grafted PHA chains may not be strong enough to have a significant effect on the charge distribution of the micro-environment close to the surface. Therefore, the PHA-grafted layer, especially closer to the surface, may not greatly influence the local pH, as was suggested in the case with carboxylate ligands. However, further investigations on the effect of the polyelectrolyte acidity on  $pK_a$  shifts caused by solid support attachment are necessary to confirm the proposed hypothesis. For the case of surface-grafted PHA, the reduced impact of the surface microenvironment on the dissociation behavior of hydroxamate ligands as well as the specificity of its reactivity with certain metals, such as iron, may be useful for broadening the working pH range of stimuli-responsive surface applications.

Previous studies of metal chelation by polyelectrolyte brushes with carboxylate binding groups have demonstrated that the nature of the coordination complex influences the wavelength at which the binding groups absorb.<sup>20,25</sup> The two primary coordination complexes observed from carboxylate ligands are bridging bidentate and chelating bidentate (Figure 3b). The C=O absorbance bands of bridging bidentate and chelating complexes have been previously observed at 1610 and 1552  $\text{cm}^{-1}$ , respectively, for PMAA brushes.<sup>20</sup> Figure 3a shows the FTIR spectra of high and low brush density PP-g-PAA before



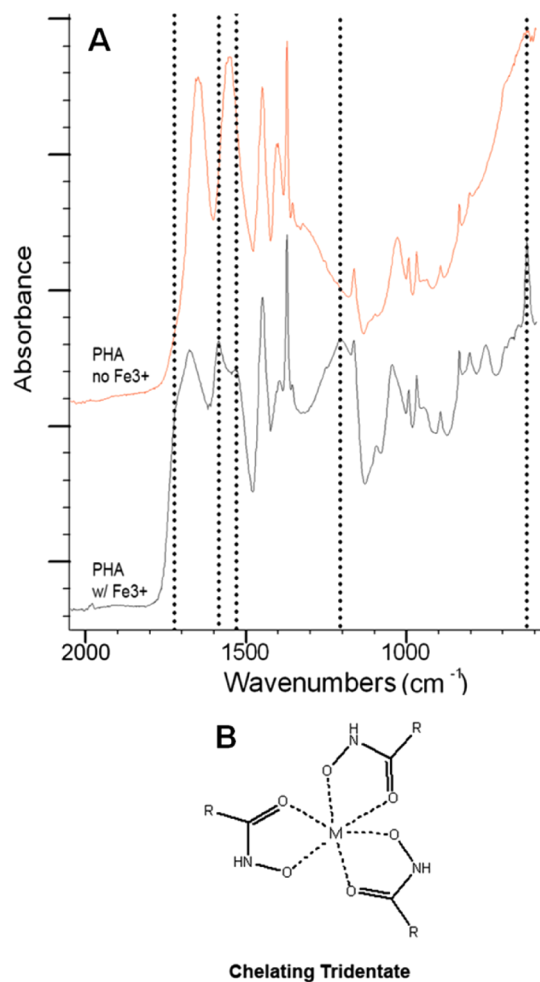
**Figure 3.** (a) ATR-FTIR spectra of PP-g-PAA before and after iron chelation performed at pH 5 at low and high brush density. The marked absorbance peaks were affected by iron chelation. The absorbance bands at 1589 and 1547  $\text{cm}^{-1}$  correspond to bridging bidentate and chelating coordination complexes, respectively. (b) Known coordination complexes for carboxylate and metal ions.



and after iron chelation. A low graft density brush was synthesized by adjusting the parameters for attachment of the photoinitiator (see the SI). The FTIR spectra of the high and low brush density PP-g-PAA before chelation show that C=O absorbance bands were present at  $1710\text{ cm}^{-1}$ , the characteristic absorbance band for protonated carboxylate groups. After iron chelation at pH 5, the intensity of the absorbance band at  $1710\text{ cm}^{-1}$  decreased and new bands were present at  $1589$  and  $1547\text{ cm}^{-1}$ . It was hypothesized that these new bands corresponded to bridging bidentate and chelating bidentate, respectively. Furthermore, the relative intensity of these absorbance bands may be indicative of which chelating coordination complex was favored under the given conditions. At low brush density, the absorbance band at  $1589\text{ cm}^{-1}$  had a higher intensity than the absorbance band at  $1547\text{ cm}^{-1}$ , which suggested that bridging bidentate was favored. At high brush density, the absorbance band at  $1589\text{ cm}^{-1}$  had an intensity similar to that of the absorbance band at  $1547\text{ cm}^{-1}$ , which suggested that both bridging bidentate and chelating bidentate were equally favored. The lower brush density graft may have allowed for improved chain flexibility by minimizing cross-linking reactions during surface-initiated polymerization that allowed for more bridging bidentate coordination complexes.<sup>28</sup> Although the chelating and bridging complexes are both bidentate structures, the bridging complex may be thermodynamically favorable through additional stabilization that results from interaction between metals in the complex. Konradi et al.<sup>20</sup> analyzed FTIR spectra of PMAA brushes of varying graft densities after incubation with  $0.1\text{ M}$  solutions of  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ , or  $\text{Al}(\text{NO}_3)_3$  and noted that complex geometries can be influenced by the brush density as well as the chelated metal ion. In order to corroborate the proposed hypothesis on the relationship between the PAA brush density and ferric iron coordination complex geometry, the study of the coordination complex as a function of the graft density will be the subject of future work. Additionally, a new absorbance band was observed at  $631\text{ cm}^{-1}$  after the chelation of iron and was attributed to Fe–O stretching vibrations based on previous analysis of IR spectra of iron oxides.<sup>29</sup>

Changes in the FTIR spectra of PHA grafted from PP before and after chelation resembled those observed in PP-g-PAA (Figure 4a). As with PP-g-PAA, an Fe–O absorbance band was observed at  $631\text{ cm}^{-1}$  after chelation. The C–NH absorbance band split into  $1587$  and  $1531\text{ cm}^{-1}$ . In addition, the C=O absorbance band split into  $1720$  and  $1678\text{ cm}^{-1}$ , the N–O absorbance band shifted to  $1049\text{ cm}^{-1}$ , and a C–NH absorbance band shifted to  $1207\text{ cm}^{-1}$ . FTIR spectra of deferoxamine B, a solution-based analogue of PHA, have exhibited shifts of the C=O and N–H absorbance bands after iron chelation, and these band shifts were attributed to the formation of a chelating tridentate coordination complex (Figure 4b).<sup>21,30</sup> The FTIR spectra collected in this study exhibited a combined shifting and splitting of the C=O and C–NH absorbances into two bands. Based on similarities between the absorbance band splitting observed in the FTIR spectra of PP-g-PAA and PP-g-PHA, it is suggested that after chelation of ferric iron at pH 5, two coordination complexes of the hydroxamate ligand may be present when PHA brushes chelate iron due to the steric restrictions of surface-grafted PHA. Further studies that examine the effect of graft density on the intensity of these bands could possibly clarify these findings.

In summary, the dissociation and metal chelating behavior of surface-grafted PAA and PHA brushes were characterized by



**Figure 4.** (a) ATR-FTIR spectra of PP-g-PHA before and after iron chelation performed at pH 5. Marked absorbance bands were affected by iron chelation. (b) Known coordination complex of hydroxamate and metal ions.

simple and rapid FTIR-based analysis that directly monitored changes in the absorbance bands of carboxylate and hydroxamate ligands responsible for metal chelation. This investigation of polyelectrolyte brushes has demonstrated the underlying importance of steric restrictions of the surface-grafted polyelectrolytes on electrostatic interactions that dictate the local pH at the surface and its impact on the  $\text{pK}_a^{\text{bulk}}$  as a function of the solution pH. The effect of steric restrictions on the microenvironment within a grafted layer may be influenced by the chemical nature of the ionizable ligands because a weaker acid, PHA, did not exhibit significant differences between  $\text{pK}_a^{\text{bulk}}$  and  $\text{pK}_a$  of solution-based analogues as observed for PAA. Additional research to create a more complete understanding of the effect of the pH, salt concentration, and metal chelation on the dissociation behavior of surface-grafted polyelectrolytes may be useful in optimizing of the applications of these stimuli-responsive materials.

## ■ ASSOCIATED CONTENT

### Supporting Information

A detailed experimental section and ATR-FTIR band assignments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

ATR-FTIR = attenuated total reflectance Fourier transform infrared

PAA = poly(acrylic acid)

PHA = poly(hydroxamic acid)

PMA = poly(methyl acrylate)

PMAA = poly(methacrylic acid)

PP = polypropylene

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