

**Supporting Information for**

**Metal Chelating Polymer Thin Films by Surface Initiated**

**ROMP and Modification**

Xuanli Deng, Liudmyla Prozorovska, and G. Kane Jennings\*

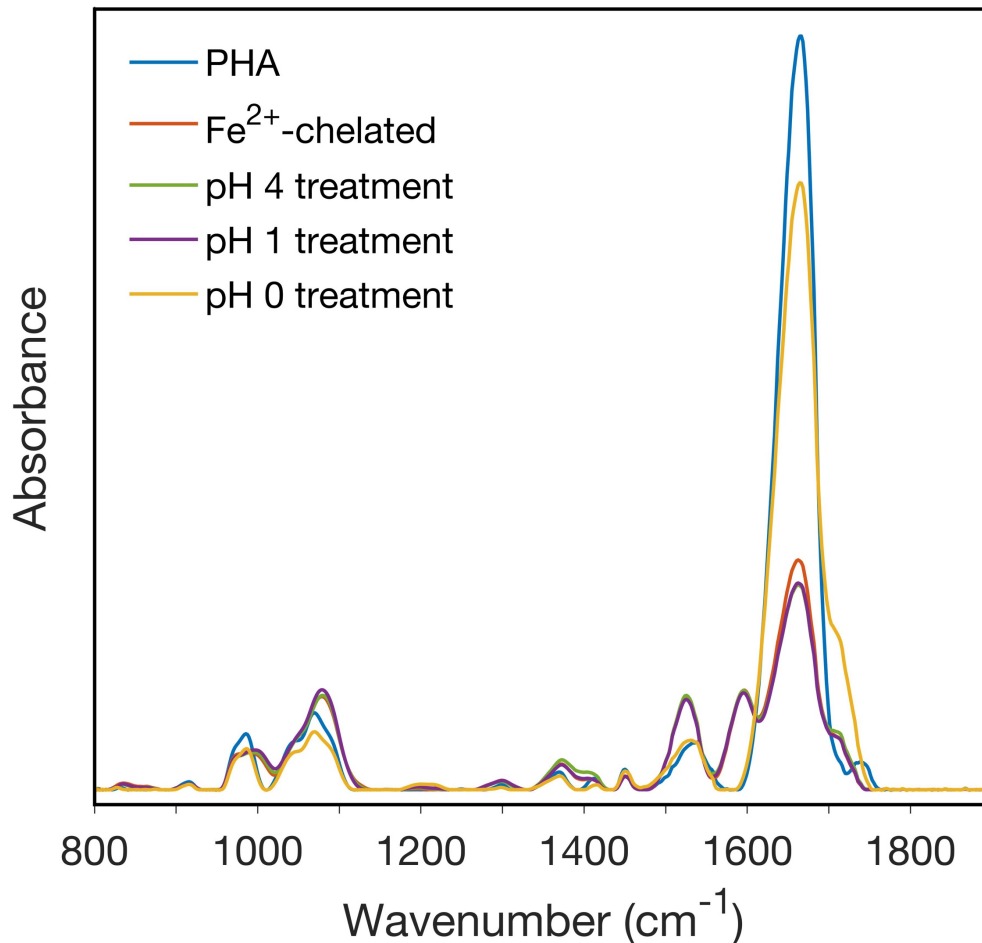
Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville,  
Tennessee, 37235

E-mail: [kane.g.jennings@vanderbilt.edu](mailto:kane.g.jennings@vanderbilt.edu)

Phone: +1 615 322 2707

### **Stability of Fe Chelated Film at Different pH Levels**

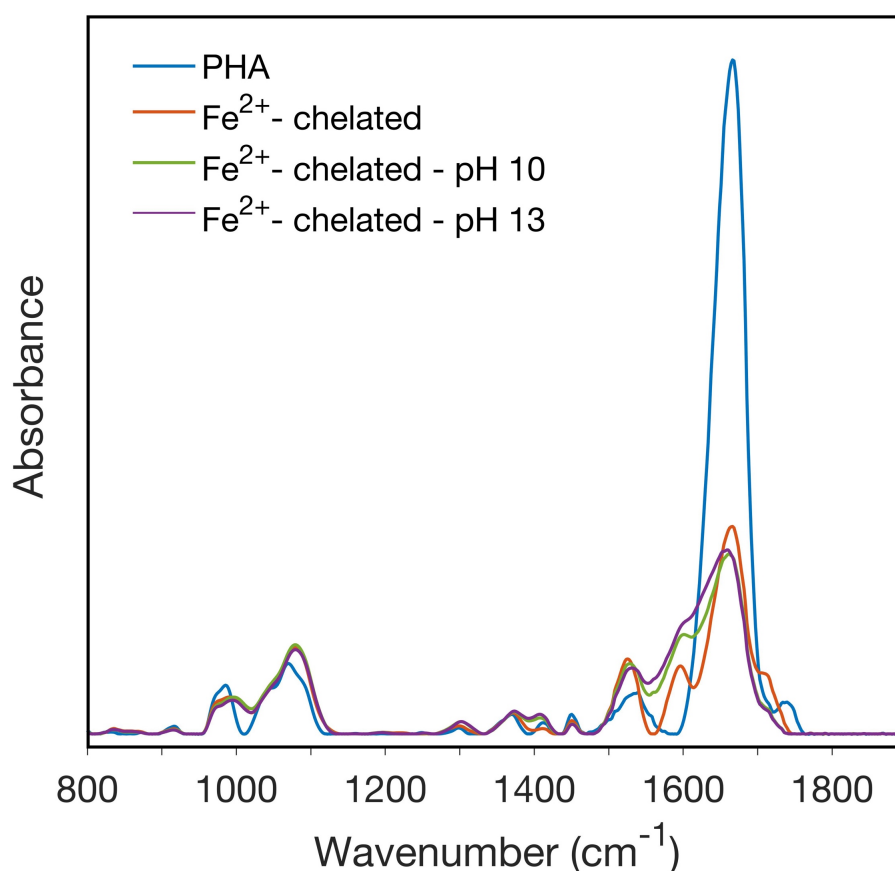
Chelated bonds are generally stable and metal-chelated polymers usually exhibit high stability to environmental changes.<sup>1</sup> However, in many chelation applications, such as heavy metal removal, the polymer matrices are expected to be reusable for many cycles, even after repeated liberation of metal ions that were bound to the polymer chains. In addition, the stability of metal-chelated polymers is important if the chelated film is actually the final product. Acid treatment is a feasible method to break the ligand-metal bond and remove the chelated metal ions from the polymer. Therefore, we soaked the PHA films in pH 4 standard buffer solution, 0.1 M HCl (pH 1), and pH 0 for 1 h and recorded IR spectra both before and after the acid treatment (Figure S.1). The IR spectra after treatment at pH 4 and pH 1 are almost the same as in the chelated polymer film, which shows that the ligand-metal chelation exhibits a high stability even in pH 1 acidic solutions. When we further increase the acidity of the solution to pH 0 (1 M HCl), the IR spectrum shows dramatic change, as the absorption band due to C=O ( $1666\text{ cm}^{-1}$ ) stretching in the chelated structure disappears and the absorption band due to C=O stretching in the hydroxamic acid is reobtained. Upon comparing the spectrum of the pH 0 treated film to that of the original unchelated PHA film, the intensity of the hydroxamic acid peak slightly decreases and a peak due to carboxylic acid C=O stretching ( $1710\text{ cm}^{-1}$ ) appears. The appearance of carboxylic acid groups are possibly due to the hydrolysis of a small portion of hydroxamic acid. Therefore, when we apply strong acid to regenerate the PHA from the chelated polymer, the strong acid also may not only break the chelation bond but may also catalyze the hydrolysis of hydroxamic acids in the aqueous solution.



**Figure S.1.** IR spectra of a PHA film, an Fe-chelated film, and resulting films after different acidic pH treatments for 1 h.

To examine the film stability in basic solutions, the metal-chelated film was placed in pH 10 and pH 13 solutions. The IR spectra of the original PHA film, the film after chelation, and chelated films after pH 10 and pH 13 treatments are shown in Figure S.2. The IR spectra of the films after basic solution treatments show the same peak positions but different peak shapes as compared with the spectrum after chelation. The overall intensities of the spectra remain the same, which indicates that there is no film loss after the basic solution treatments. The

broadening in the carbonyl peak shape at  $1666\text{ cm}^{-1}$  and its gradual shift to lower wavenumber upon exposure to basic solutions is due to the deprotonation of the non-chelated hydroxamic acid groups in the chelated film. In the manuscript, we estimate that  $\sim 30\%$  of the hydroxamic acid groups are non-chelated based on IR and QCM-D analyses. Roman et al.<sup>2</sup> has reported that the pKa of these hydroxamic acid groups within a grafted film is 9.65 and that the deprotonated groups exhibit carbonyl stretching at  $1612\text{ cm}^{-1}$ . Thus, at pH 10 and 13, some of these non-chelated groups will become deprotonated, which broadens and shifts the carbonyl peak to lower wavenumbers. Nonetheless, the metal-chelated film remains stable to these basic conditions.



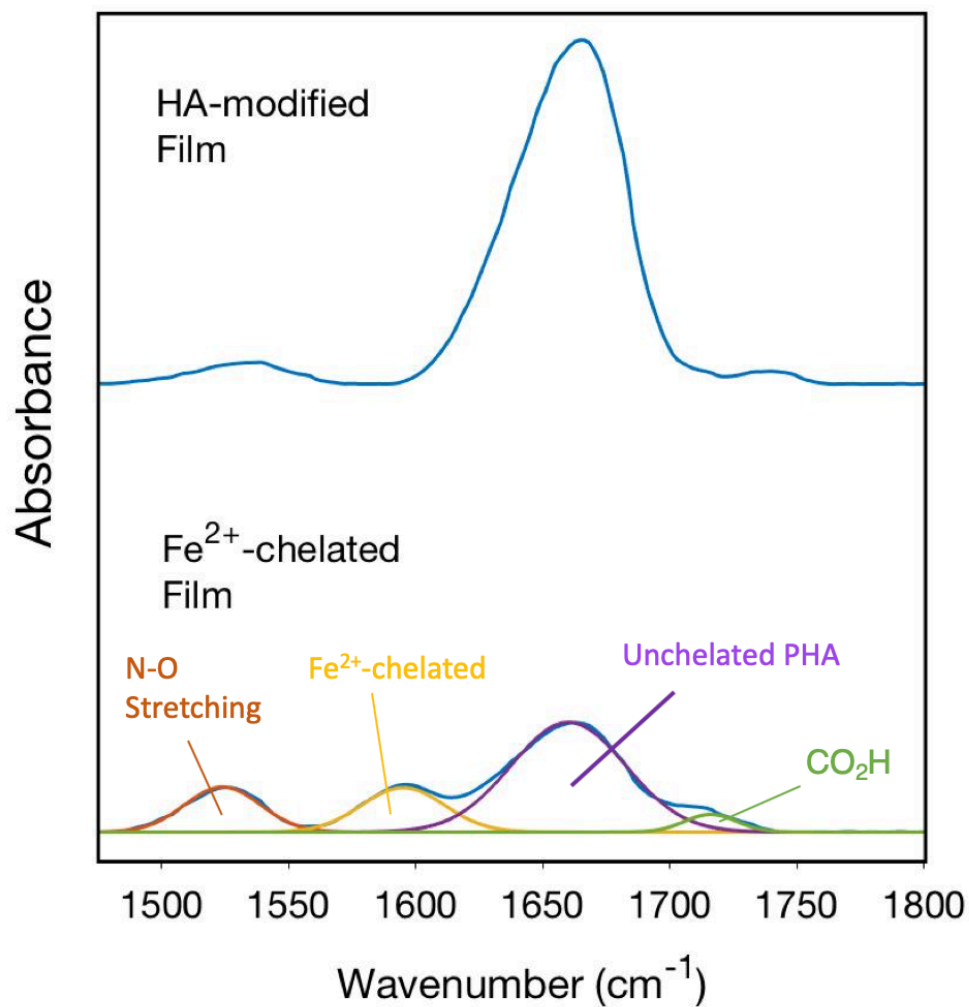
**Figure S.2.** IR spectra of the original PHA film and Fe-chelated films before and after exposure to basic environments for 1 h.

### IR Analysis of Metal Chelation within the PHA Films

The IR spectrum shows that not all the hydroxamic acid groups in the film are chelated with  $\text{Fe}^{2+}$ . The incomplete conversion is consistent with previous literature on chelation. Considering that two center-symmetric hydroxamic acid groups are required to chelate  $\text{Fe}^{2+}$ , not all the hydroxamic acid groups would be positioned or oriented to form such a center-symmetric structure, and thus, a portion of unchelated hydroxamic acid groups remain after the exposure to the metal salt solution. By peak deconvolution (shown in Figure S.3), the area of the unchelated PHA in the film can be obtained, and the molar percentage of the chelation can be calculated as

$$\text{chelation percentage} = \left(1 - \frac{\text{area of unchelated PHA}}{\text{area of original PHA}}\right) \times 100 \quad (5.1)$$

Other noticeable changes are the disappearance of the absorption band due to C=O stretching ( $1739 \text{ cm}^{-1}$ ) and newly formed absorption band at  $1710 \text{ cm}^{-1}$  due to C=O stretching in carboxylic acid. The C=O stretching shifting from  $1739$  to  $1710 \text{ cm}^{-1}$  is most likely due to the hydrolysis of the ester, as catalyzed by the divalent metal ions.



**Figure S.3.** Illustration of the peak deconvolution used to calculate peak areas of the original PHA film and the chelated PHA film. The yellow, purple and green deconvoluted peaks demonstrate C=O stretching absorption bands in different molecular structures.

### Effect of Chelation on Shear Moduli

The shear loss moduli before and after chelation with iron are 67.8 kg/m s and 36.1 kg/m s, respectively, showing that the film has dramatically reduced viscous energy dissipation after chelation. The shear storage moduli before and after chelation with iron are 11.3 MPa and 18.5 MPa, respectively, consistent with less deformation for the chelated film. Both results are consistent with a more cross-linked and solid-like film after chelation.

### References

- (1) Martell, A. E. Chelation: Stability and Selectivity, *Ann. N. Y. Acad. Sci.* **1960**, 88 (2), 284–292.
- (2) Roman, M. J.; Decker, E. A.; Goddard, J. M. Fourier Transform Infrared Studies on the Dissociation Behavior of Metal-Chelating Polyelectrolyte Brushes. *ACS Appl. Mater. Interfaces* **2014**, 6, 5383–5387.