Structural Determination of a Synthetic Polymer by Gaussian Computational Modeling Software and Nuclear Magnetic Resonance Spectroscopy

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Summary

Previous research[1] has used the Iron-Tetraamido macrocyclic ligand system (Fe^{III}–TAML with hydrogen peroxide[2]) to polymerize the model monomer of 4-ethylphenol. The resulting polymer is thought to be phenolic, but structure has not yet been definitively confirmed with analytical measurements. This portion of the research focuses on the structural determination of this polymer using Gaussian Computational Modeling, Nuclear Magnetic Resonance (NMR) Spectroscopy, and Fourier Transform Infrared (FT-IR). Proton NMR (^{1}H-NMR), Carbon NMR (^{13}C-NMR), and two-dimensional NMR (2D-NMR) are employed for this study using an Anasazi Eft 60 Megahertz (MHz) NMR. The experimental (NMR and FTIR) and computational results from Gaussian 03W Software[3] are compared and predicted structure of the polymer is proposed. Computational and experimental data are used in conjunction with each other to better understand the polymer structure.

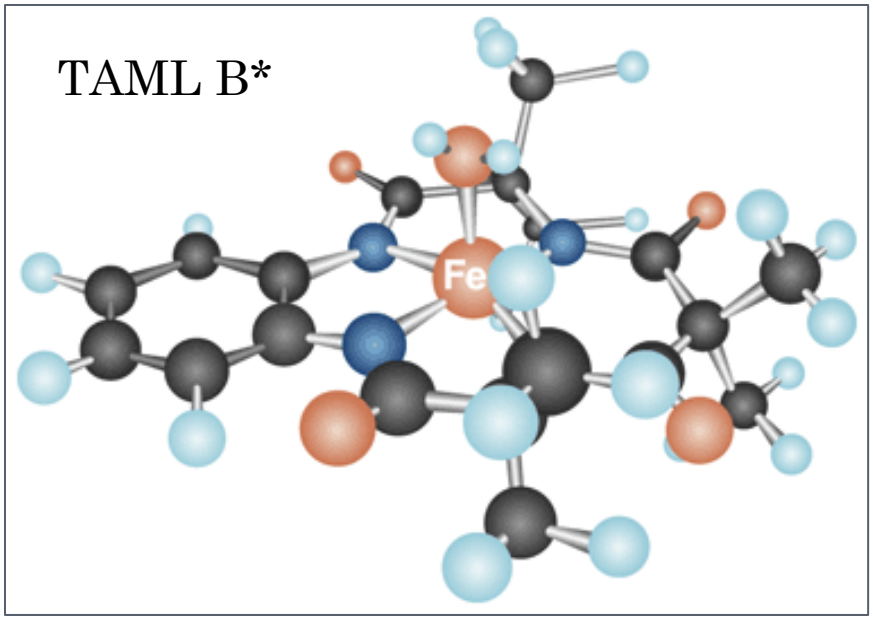
Introduction

The polymer that has been discovered through other research is hypothesized to be an aromatic monomer, but the linkage of the aromatic rings are less clear. NMR is a commonly used way to determine the structure of unknown compounds as well as polymers[4] . NMR shows the different types of the particular atom in question (^{1}H, ^{13}C) in a compound, each peak relative to the number of atoms that are alike of that type. Two dimensional NMR is also very useful (Correlation spectroscopy - COSY and Heteronuclear correlation - HETCOR) to combine the results of proton-proton and proton-carbon data to help understand near neighbor relationships in the structure.

Materials and Methods

Polymer Reaction Matrix

136 µmol 4-ethylphenol
599 µmol H_2O_2
0.0439 µmol Fe^{III}–TAML
Ethanol
pH 10 carbonate buffer



http://www.chem.cmu.edu/groups/collins/images/taml-web.gif

* The 4-ethylphenol is prepared in ethanol. The reaction is completed in a solution that is 83% ethanol. The reaction is stopped after one hour with 5 M HCl which will destroy the TAML making it in-active.

Preparing the Polymer for NMR

- The polymer is
  - Washed
  - Centrifuged
  - Dried
  - Dissolved

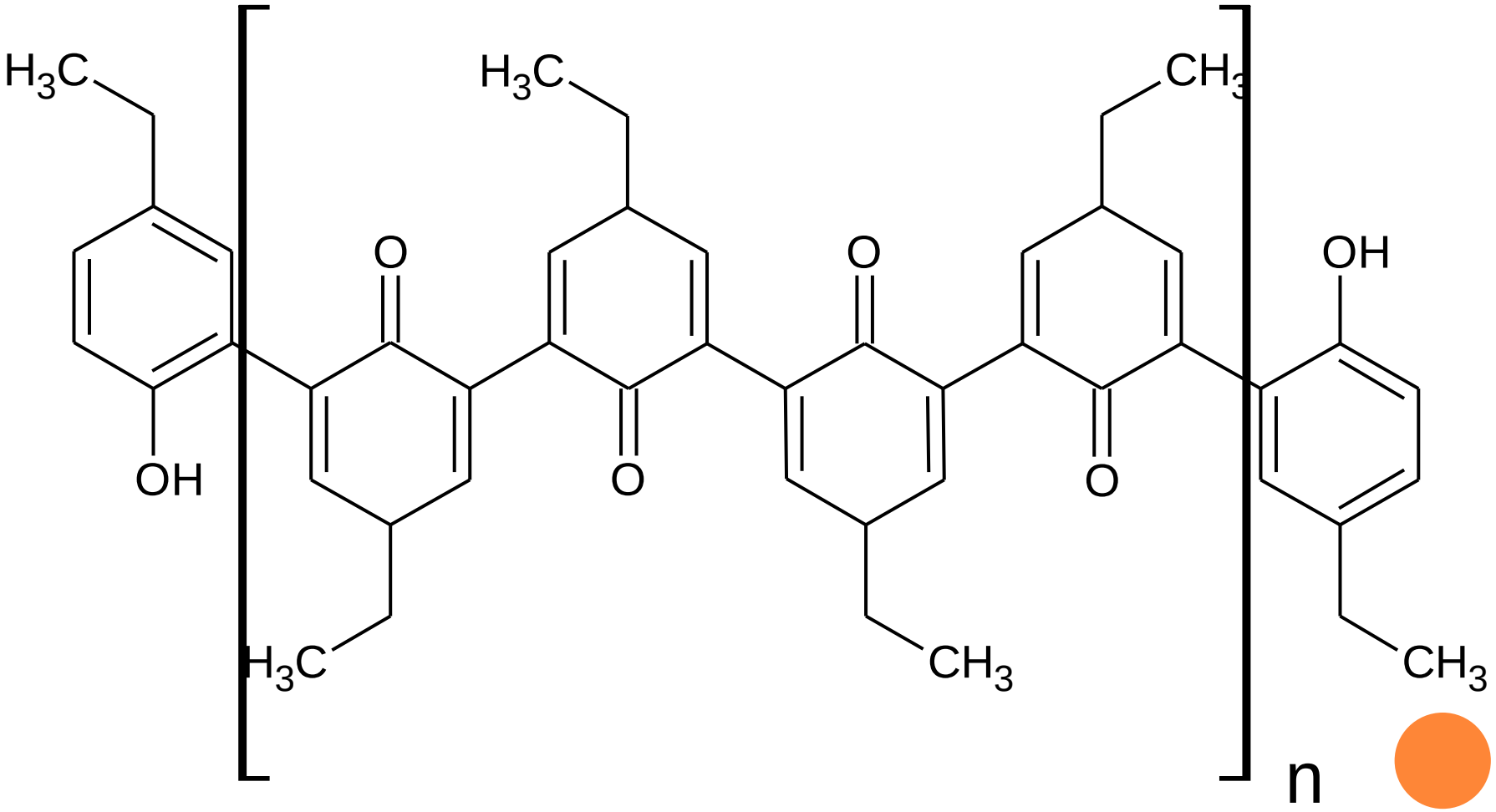
Eft60

http://www.aiinmr.com/products/

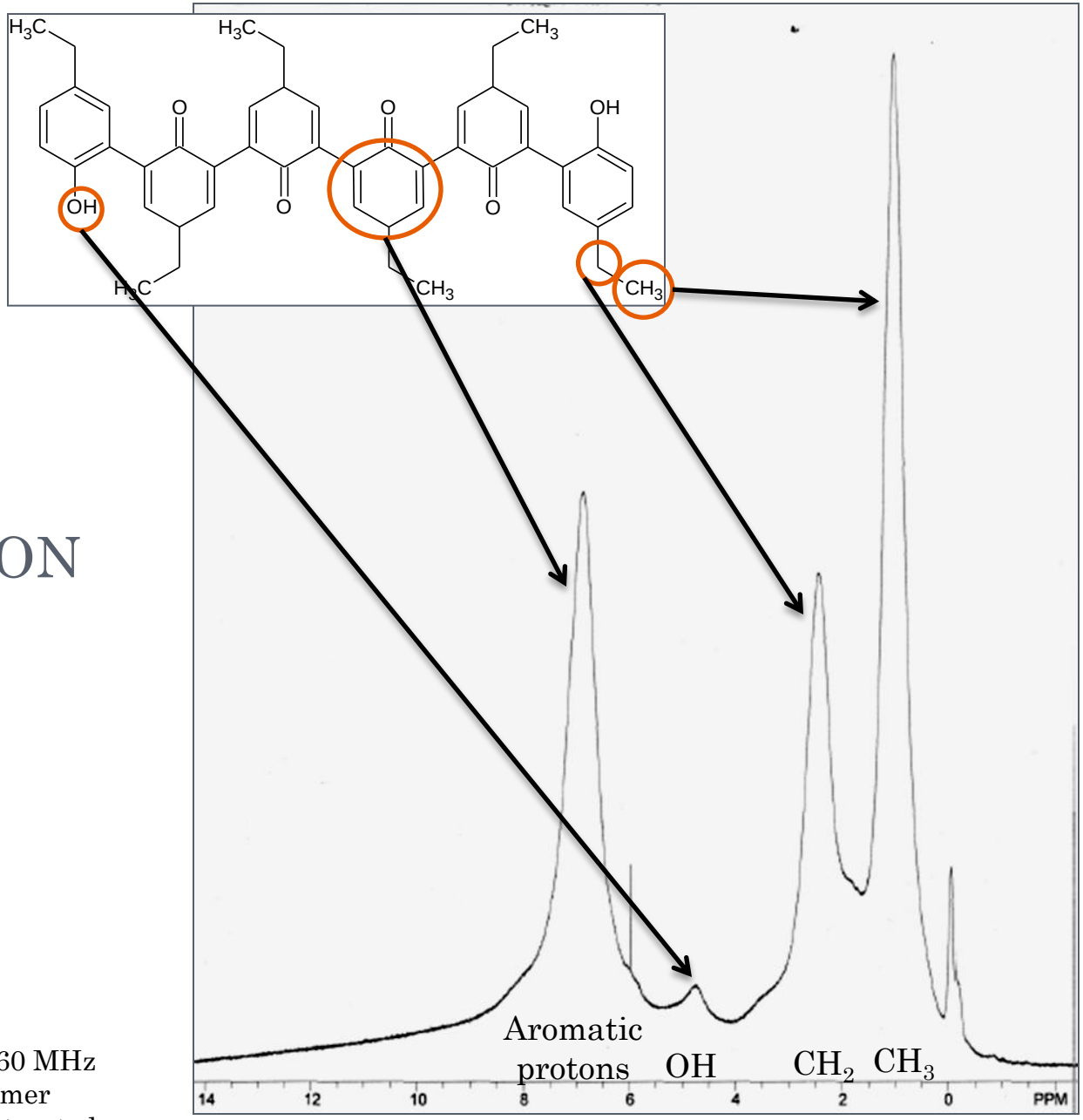
Instrumentation

- Anasazi Instruments Eft 60 Megahertz Nuclear Magnetic Resonance Spectrometer
- Gaussian 03W Software
- Smith's Detection ATR-FTIR

Structure of Proposed Polymer



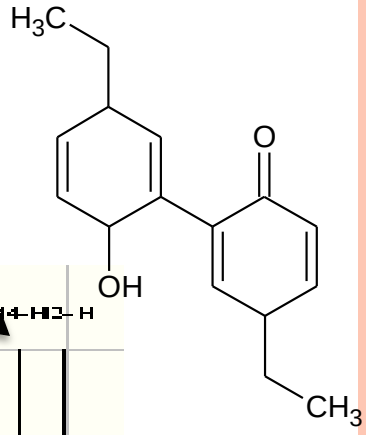
Proton NMR (^{1}H)



Anasazi Eft60 MHz
200 mg polymer
Solvent: deuterated chloroform

^{1}H-NMR

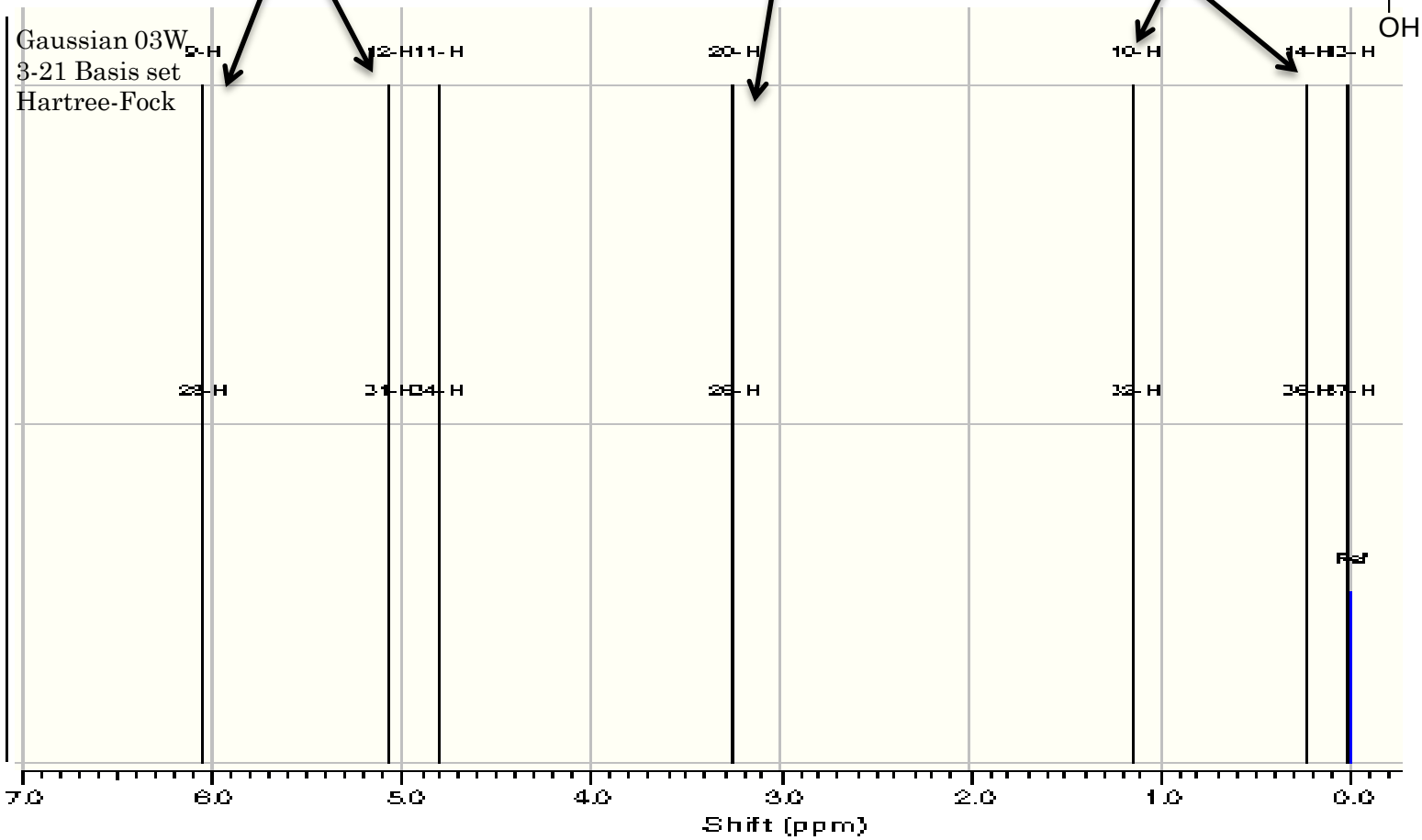
Model Dimer A
1-OH, 1-ketone

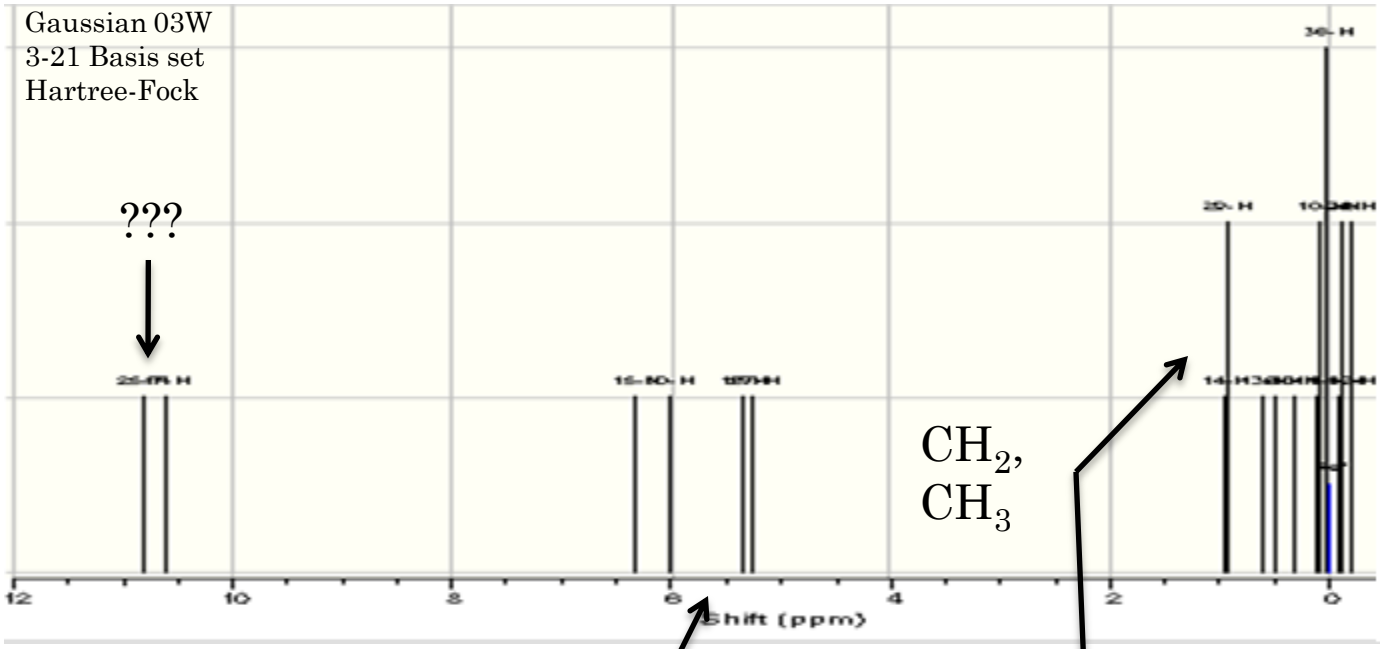


Aromatic and
Aliphatic protons

OH

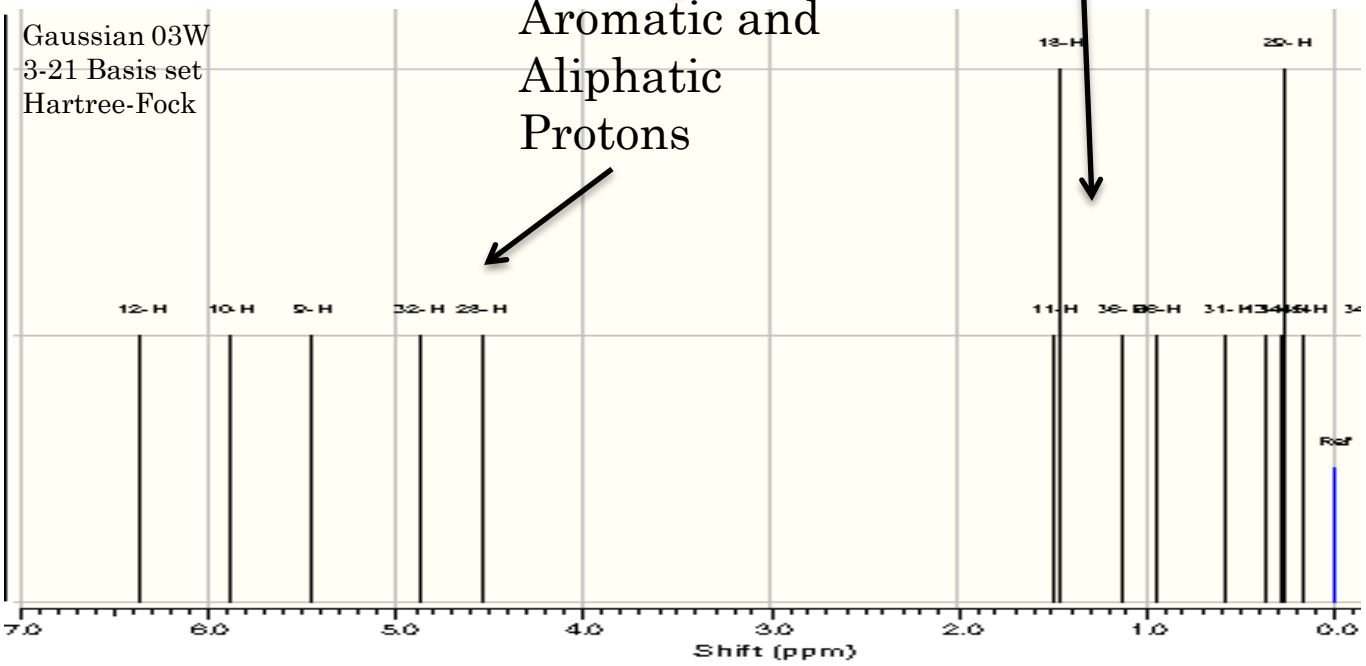
CH_2, CH_3





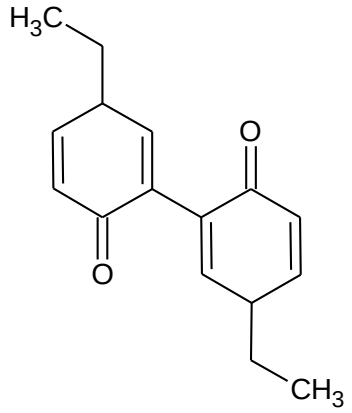
CH_2, CH_3

Aromatic and Aliphatic Protons



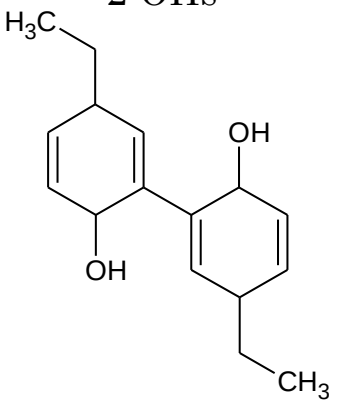
Model Dimer B

2-ketones

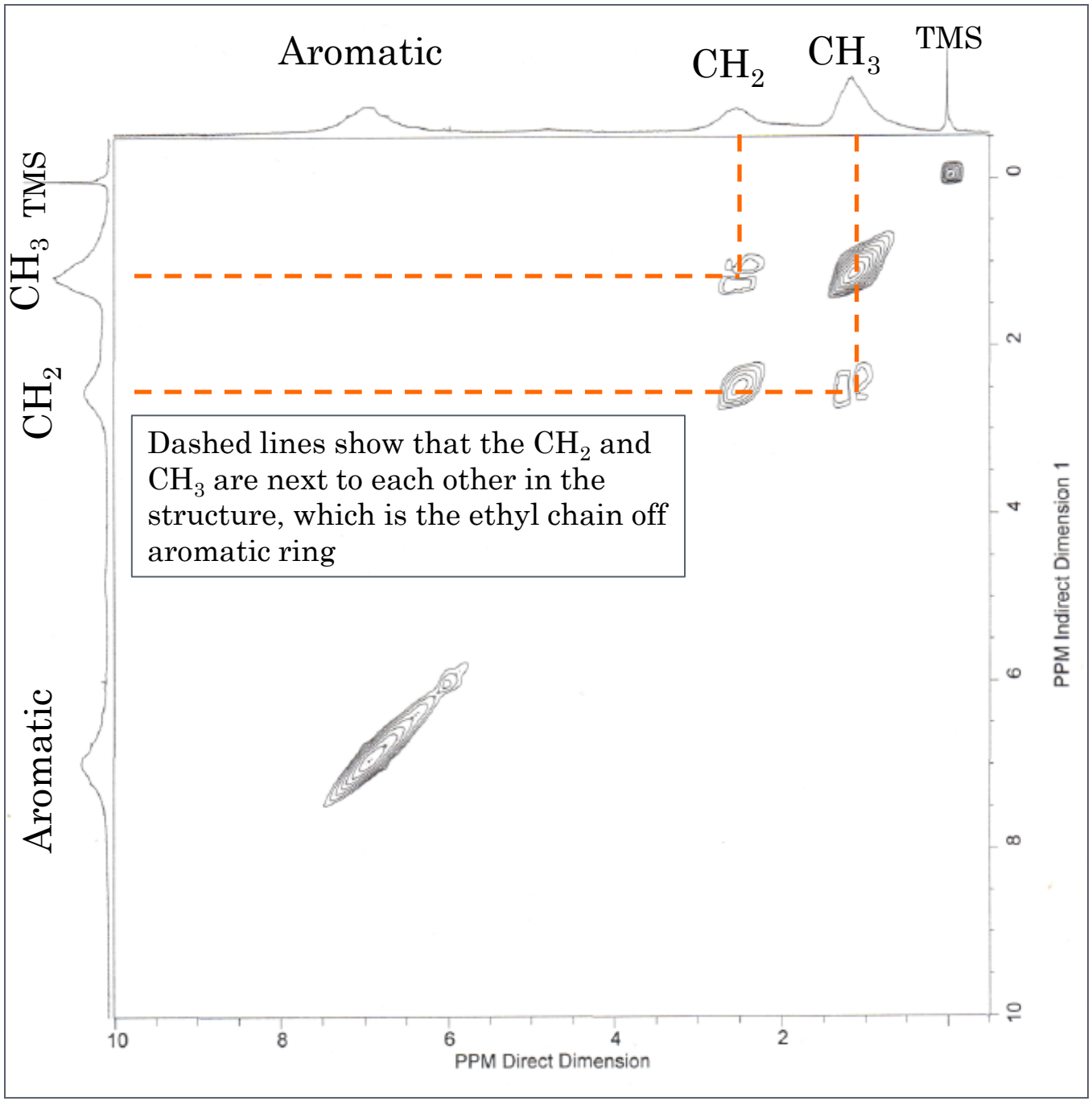


Model Dimer C

2-OHs

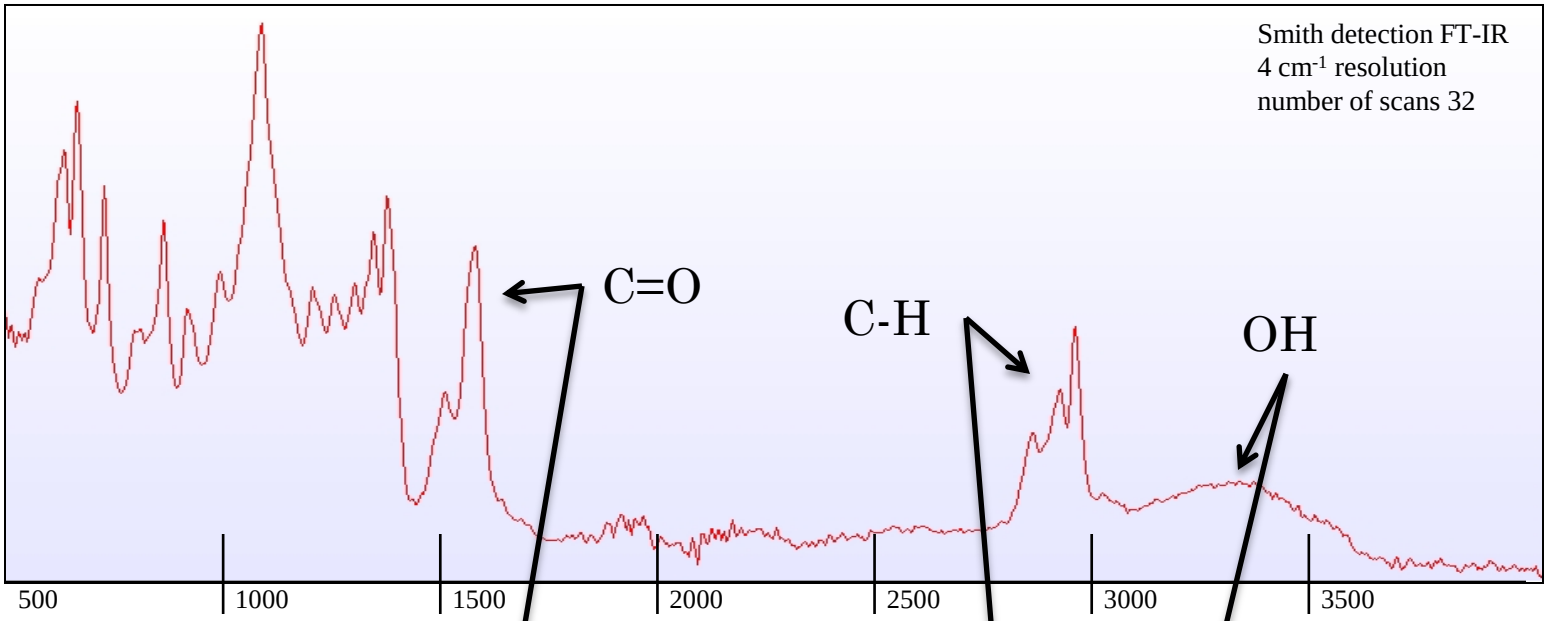


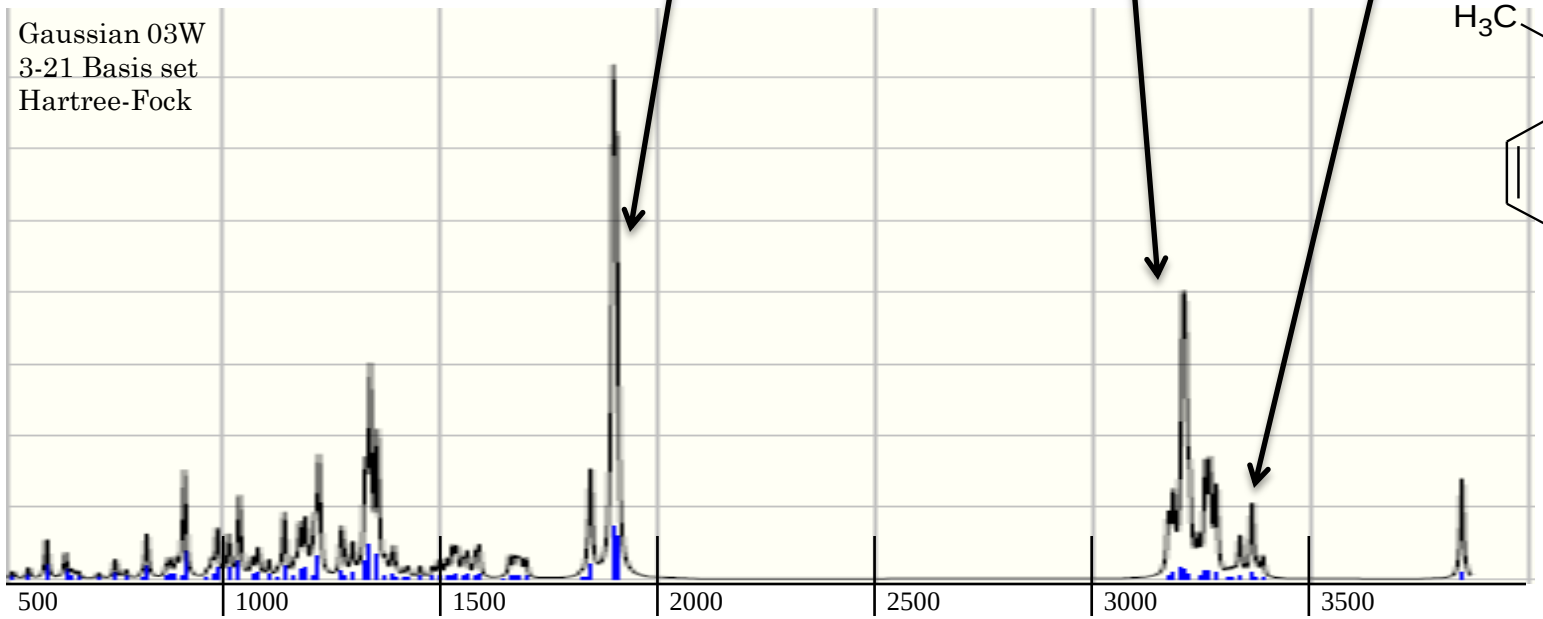
COSY SPECTROSCOPY

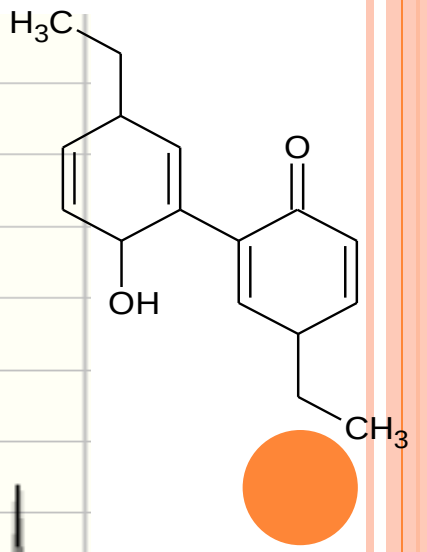


COSY 2D NMR (^1H x ^1H) of polymer

Infrared Spectroscopy

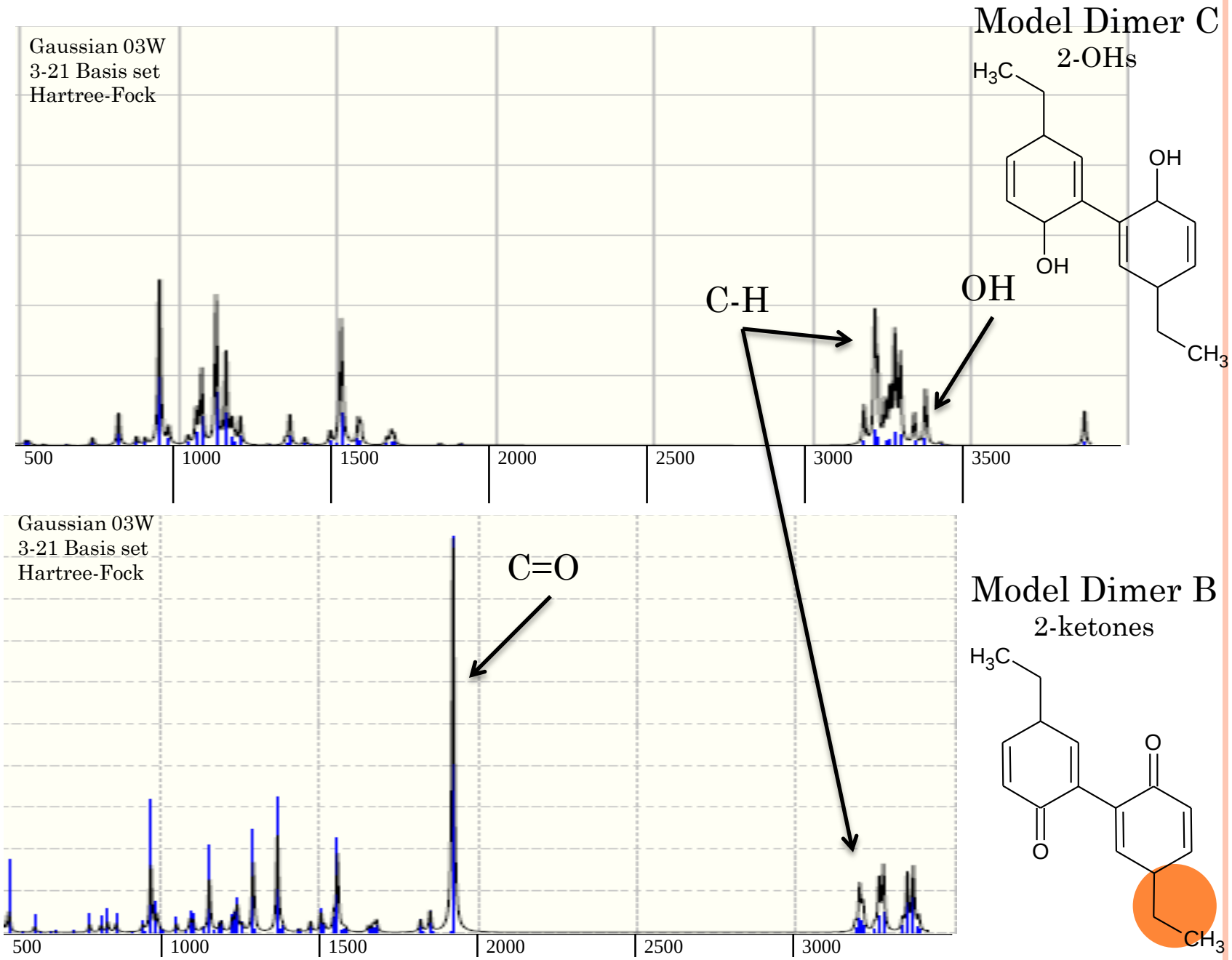






Model Dimer A

1-OH, 1-ketone


Gaussian 03W
3-21 Basis set
Hartree-Fock
Model Dimer C
2-OHs
H3C
OH
OH
CH3
C-H
OH
500
1000
1500
2000
2500
3000
3500
Gaussian 03W
3-21 Basis set
Hartree-Fock
C=O
Model Dimer B
2-ketones
H3C
O
O
CH3
500
1000
1500
2000
2500
3000

Conclusions

The polymer is primarily the ketone form with alcohols on the end group due to acidification. The preliminary Gaussian work confirms this assumption. The IR spectrum also lines up quite well with this assumption. The IR data obtained from this work is very similar to that found by Uyama et. al in their polymerization work using horseradish peroxidase[5].

Future Work

The structure of the polymer needs to be determined with more certainty, particularly as it relates to the Carbon NMR. Future work in this project includes sending out samples to for solid state NMR and/or analysis on an NMR with higher resolution than our 60 MHz instrument. Running similar calculations on Gaussian 09, which has updated basis sets specifically for NMR, may result in more accurate NMR frequency determination. Reaction reproducibility will be studied by molecular weight and molecular weight distribution using mass spectrometry and gel permeation chromatography.

Acknowledgements

The author would like to thank Dr. Tshudy for his continued guidance with this research and Dr. Collins for supplying the Fe^{III}–TAML and for allowing this research to move forward.

Please also see the poster (P-01) titled "Phenolic Polymerization using Fe^{III} – TAML" which highlights more of the experimental work on these polymers.

References

1. Entwistle, K.; Tshudy, D.; Collins, T. J., Phenolic Polymerization using FeIII–TAML. Gordon College, Carnegie Mellon University: 2010.
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5. Uyama, H.; Kurioka, H.; Siugihara, J.; Komatsu, I.; Kobayashi, S., Oxidative Polymerization of p-Alkylphenols Catalyzed by Horseradish Peroxidase. *Journal of Polymer Science, Part A Polymer Chemistry* **1996,** *35* (8), 1453-1459.