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.
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. NMR shows the different types of the particular atom in question ($^1\text{H}$, $^{13}\text{C}$) 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 H₂O₂
0.0439 μmol Fe³⁺–TAML
Ethanol
pH 10 carbonate buffer

* 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

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
Aromatic and Aliphatic protons

$^1$H-NMR

Model Dimer A
1-OH, 1-ketone

Gaussian 03W
3-21 Basis set
Hartree-Fock
Gaussian 03W
3-21 Basis set
Hartree-Fock

Model Dimer B
2-ketones

CH$_2$, CH$_3$

Aromatic and Aliphatic Protons

Model Dimer C
2-OHs
Dashed lines show that the CH$_2$ and CH$_3$ are next to each other in the structure, which is the ethyl chain off aromatic ring.

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

Smith detection FT-IR
4 cm⁻¹ resolution
number of scans 32

Gaussian 03W
3-21 Basis set
Hartree-Fock

Model Dimer A
1-OH, 1-ketone
Gaussian 03W
3-21 Basis set
Hartree-Fock

Model Dimer C
2-OHs

Model Dimer B
2-ketones

C-H

OH

C=O

H3C

CH3

C

H

O

H

O

CH3

C

H

O

H

O

CH3

C

H

O

H

O

CH3

C

H

O

H

O

CH3
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\textsuperscript{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.
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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


