PHENOLIC POLYMERIZATION USING Fe$^{III}$-TAML

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Previous work has shown the effectiveness of the Fe\textsuperscript{III}-TAML (Iron Tetra Amino Macrocyclic Ligand) hydrogen peroxide ($\text{H}_2\text{O}_2$) system to degrade toxins.\textsuperscript{1} There have also been observations that the TAML system will also cause polymerization of phenolic compounds. It is reported in the literature that peroxidases along with hydrogen peroxide can be used to polymerize phenols, but little work has been done in characterization of the TAML polymerization process. As an initial study, 4-ethylphenol is being evaluated as a model compound to study this reaction mechanism. Hydrogen peroxide concentration, pH, Fe\textsuperscript{III}-TAML concentration, co-solvent composition and time are being studied in order to understand the reaction space. Infrared spectroscopy, liquid chromatography, gas chromatography, UV/Vis absorbance and size exclusion chromatography and MALDI mass spectrometry are utilized to study both the reaction products and the starting materials.
INTRODUCTION

Phenolic based resins have been around since the introduction of ‘Bakelite’ in the 1920’s and 30’s. Today there are numerous formulations covering products such as thermosetting resins to fire resistant materials.\textsuperscript{2} Previous observations with TAML have shown that this system will polymerize phenolic compounds.\textsuperscript{3} The polymerization of phenolic compounds using peroxidases (such as horseradish peroxidase) and hydrogen peroxide have been reported as a way to create a “greener” process for making phenolic resins.\textsuperscript{4,5,6} This work focuses on the use of the Fe\textsuperscript{III}-TAML\textsuperscript{®} (Figure 1) hydrogen peroxide system as the process to complete the polymerization. The initial monomer chosen to study this polymerization is 4-ethylphenol (Figure 2).
MATERIALS

Figure 1
Fe-TAML

Figure 2
4-Ethylphenol
METHODS

Example Reaction Conditions:
- 8.2 µmol 4-ethylphenol
- 20 µmol H₂O₂
- 0.032 µmol Fe³⁺TAML
- pH 10 carbonate buffer

In general the hydrogen peroxide is approximately in a 2:1 molar ratio to 4-ethylphenol. The reaction takes place immediately.
RESULTS

The polymer reaction product is studied by:

- NMR (Nuclear Magnetic Resonance) for molecular structure determination.
  - $^1$H-NMR, $^{13}$C-NMR
- FT-IR (Fourier Transform Infrared) for molecular structure determination.
- GPC (Gel Permeation Chromatography) for molecular weight determination.
- MALDI (Matrix Assisted Laser Desorption Ionization) mass spectrometry for molecular weight determination.
- SEM (Scanning Electron Microscopy) for study of the polymer.
Spheres of polymerized 4-ethylphenol
PROPOSED STRUCTURE OF POLYMER
4-ETHYLPHENOL BY FT-IR

Smith detection FT-IR
4 cm$^{-1}$ resolution
number of scans 32

OH Stretch
Polymer made in carbonate buffer only

Smith detection FT-IR
4 cm\(^{-1}\) resolution
number of scans 32
COMPARISON OF POLYMER BY FT-IR

Polymer (aqueous buffer)

Polymer (50% methanol)

Smith detection FT-IR
4 cm⁻¹ resolution
number of scans 32
50% Methanol

Aqueous Only

4-ethylphenol

LC: varian prostar
Detection: 275 nm
Phenomenex Phenogel 5 100 A column
300 x 7.80 mm, 5 micron
Mobile phase: 100% THF 1.0 mL/min
MALDI MASS SPECTRA

MALDI Parameters
Matrix Modifier: Dithranol
Mode: positive ion
Applied Biosystems Voyager DE STR

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Spectra by Linda Prengaman at Center for Molecular Analysis at Carnegie Mellon University
The work completed so far has provided evidence that the TAML system is able to be used for polymerization. We plan on being able to characterize the reaction in more detail as we study the analytical information that we have and as we obtain more information about the polymer structure and its properties. Additional work includes better understanding of the reaction mechanism, studying the reaction conditions, and looking for the primary factors for controlling average molecular weight and molecular weight dispersity.
REFERENCES


I would like to thank Dr. Terrence Collins for supplying the Fe-TAML and for approving this research, Dr. Dwight Tshudy for his guidance throughout the course of this research, and Andrew Worth for all of the techniques and instrumentation that he has helped me learn how to use. A special thanks to Linda Prengaman at the Center for Molecular Analysis at Carnegie Mellon University for the MALDI data. Thanks to Seth Gerard for his help with the SEM data.