

PHENOLIC POLYMERIZATION USING Fe^{III} -TAML



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SUMMARY

Previous work has shown the effectiveness of the Fe^{III}-TAML (Iron Tetra Amino Macrocyclic Ligand) hydrogen peroxide (H₂O₂) system to degrade toxins.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^{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.² Previous observations with TAML have shown that this system will polymerize phenolic compounds.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.^{4,5,6} This work focuses on the use of the Fe^{III}-TAML® (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

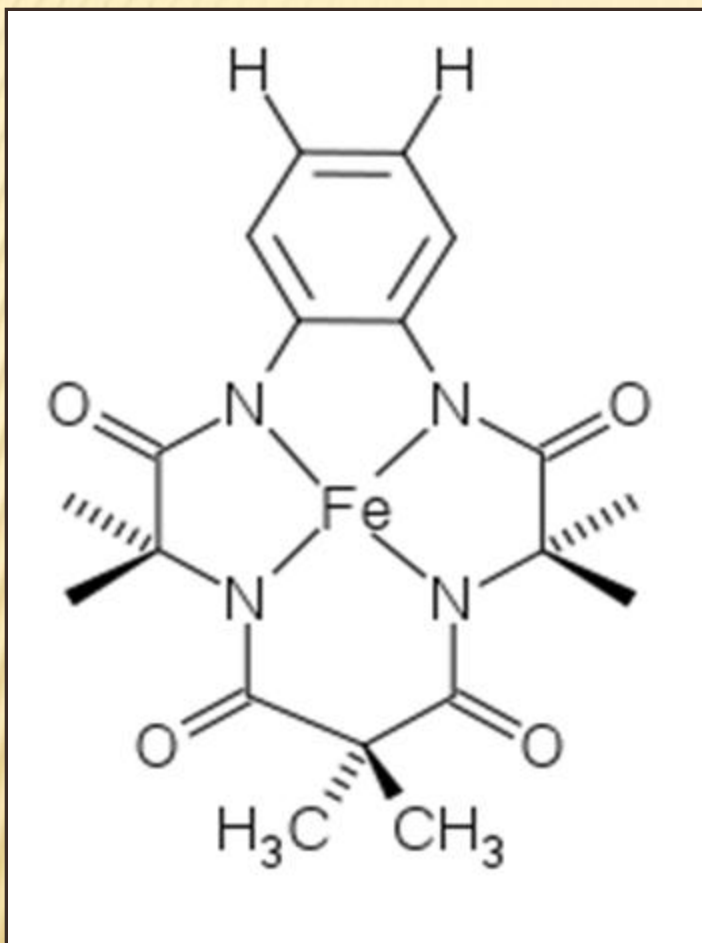


Figure 1
Fe-TAML

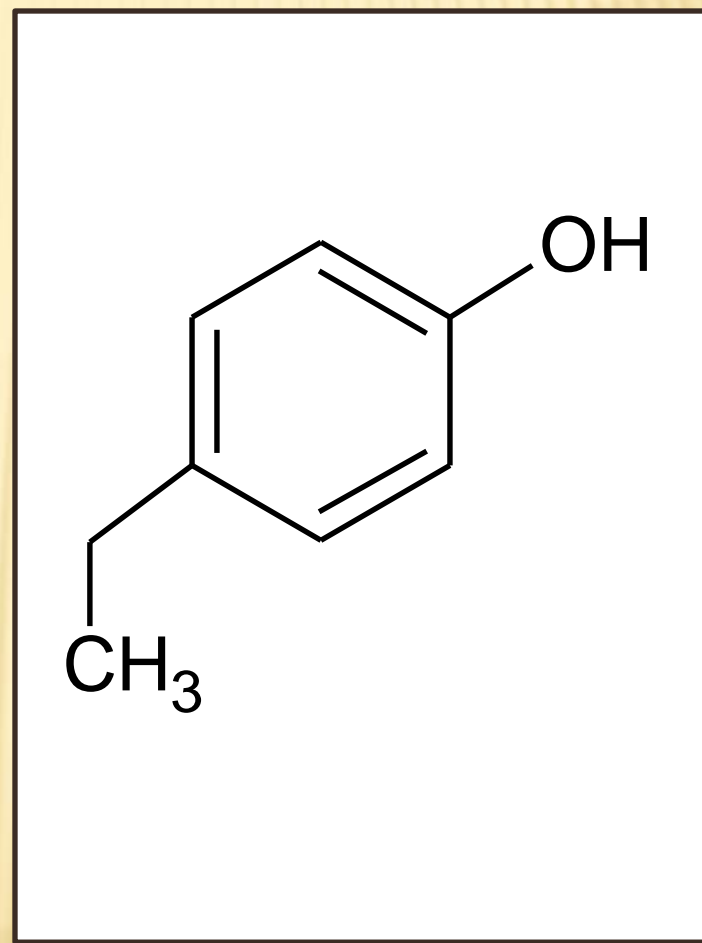


Figure 2
4-Ethylphenol

METHODS



Before addition of
hydrogen peroxide

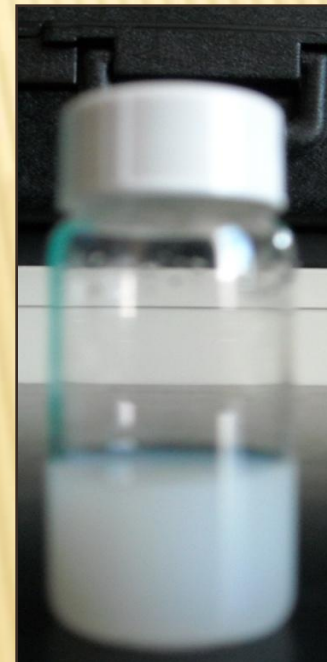
Example Reaction Conditions:

8.2 μmol 4-ethylphenol

20 μmol H_2O_2

0.032 μmol Fe^{III} TAML

pH 10 carbonate buffer



After addition of
hydrogen peroxide

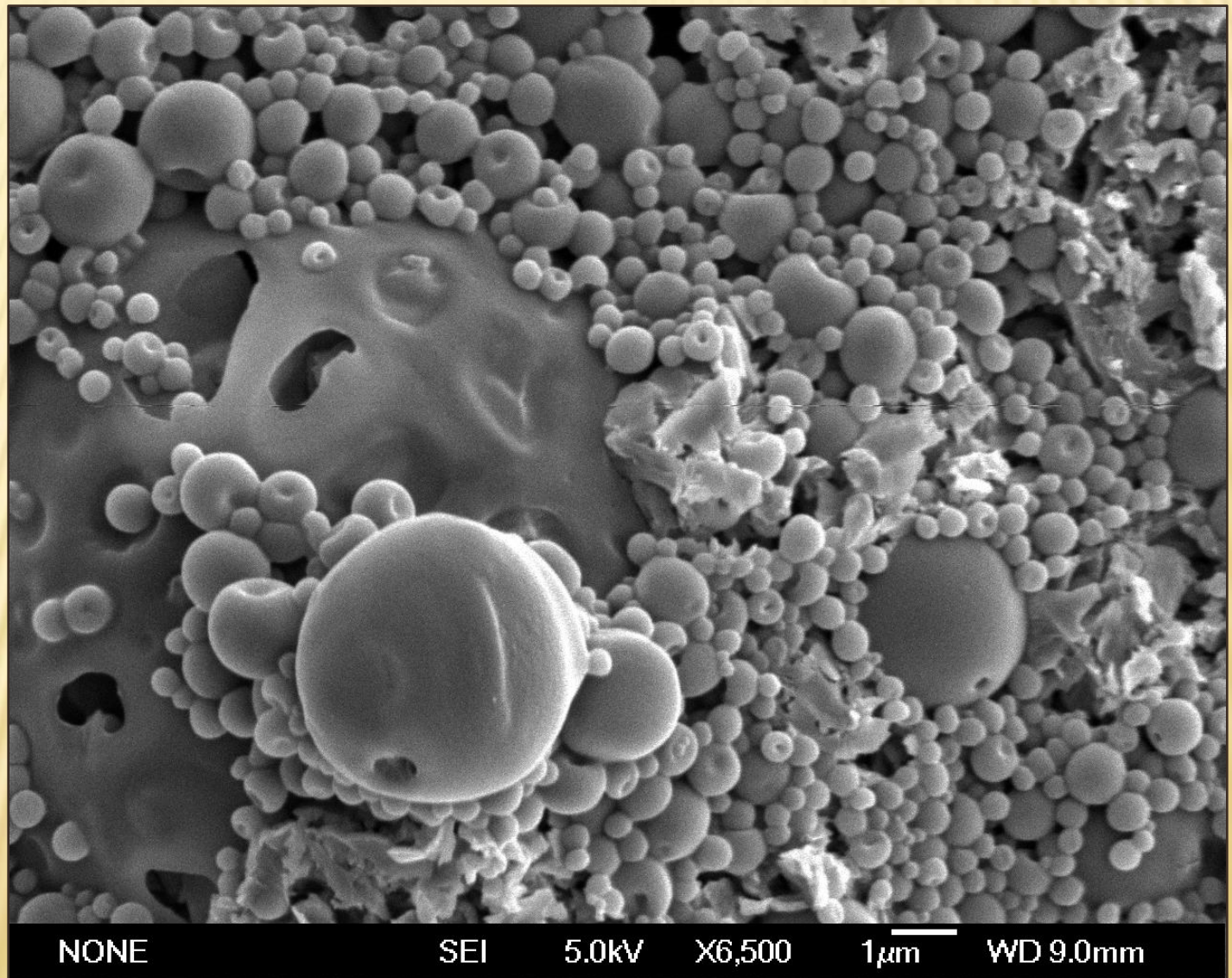
In general the hydrogen peroxide is approximately in a 2:1 molar ratio to 4-ethylphenol. The reaction takes place immediately.

RESULTS

The polymer reaction product is studied by:

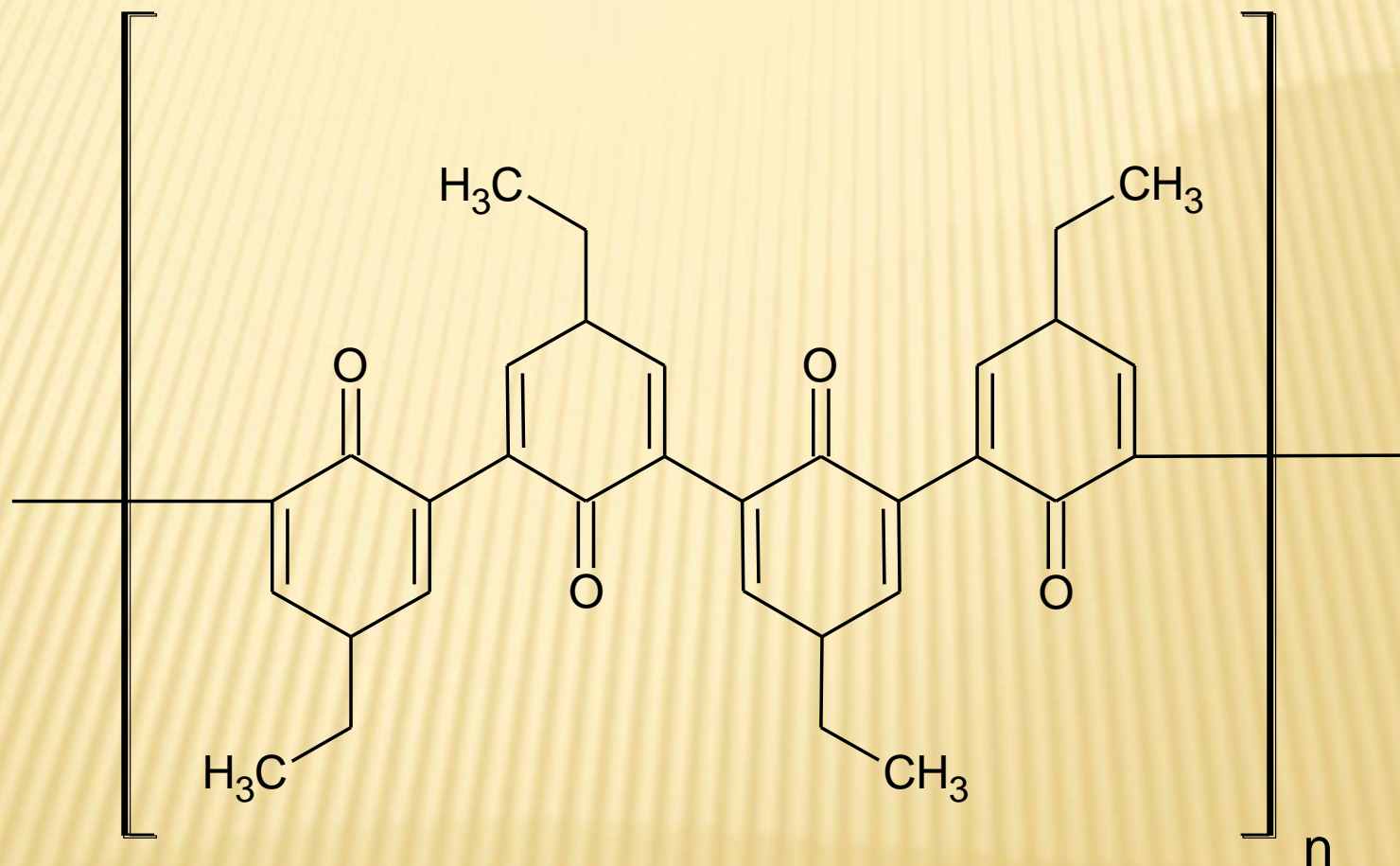
- ✖ NMR (Nuclear Magnetic Resonance) for molecular structure determination.
 - ^1H -NMR, ^{13}C -NMR
- ✖ FT-IR (Fourier Transform Infrared) for molecular structure determination.
- ✖ GPC (Gel Permeation Chromatography) for molecular weight determination.
- ✖ MALDI (Matrix Assisted Laser Desorption Ionization) mass spectrometry for molecular weight determination.
- ✖ SEM (Scanning Electron Microscopy) for study of the polymer.

SEM

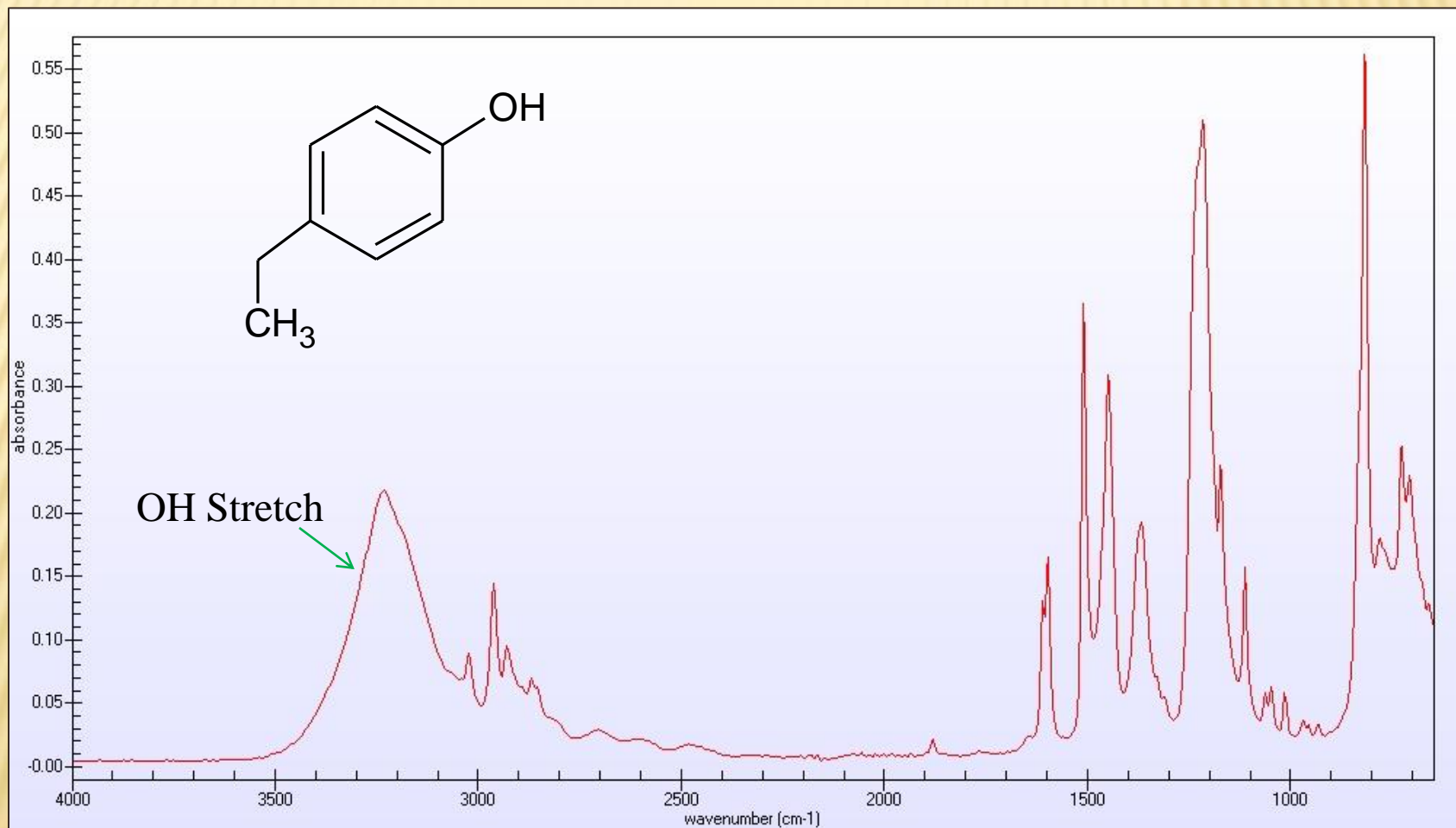


Spheres of polymerized 4-ethylphenol

PROPOSED STRUCTURE OF POLYMER

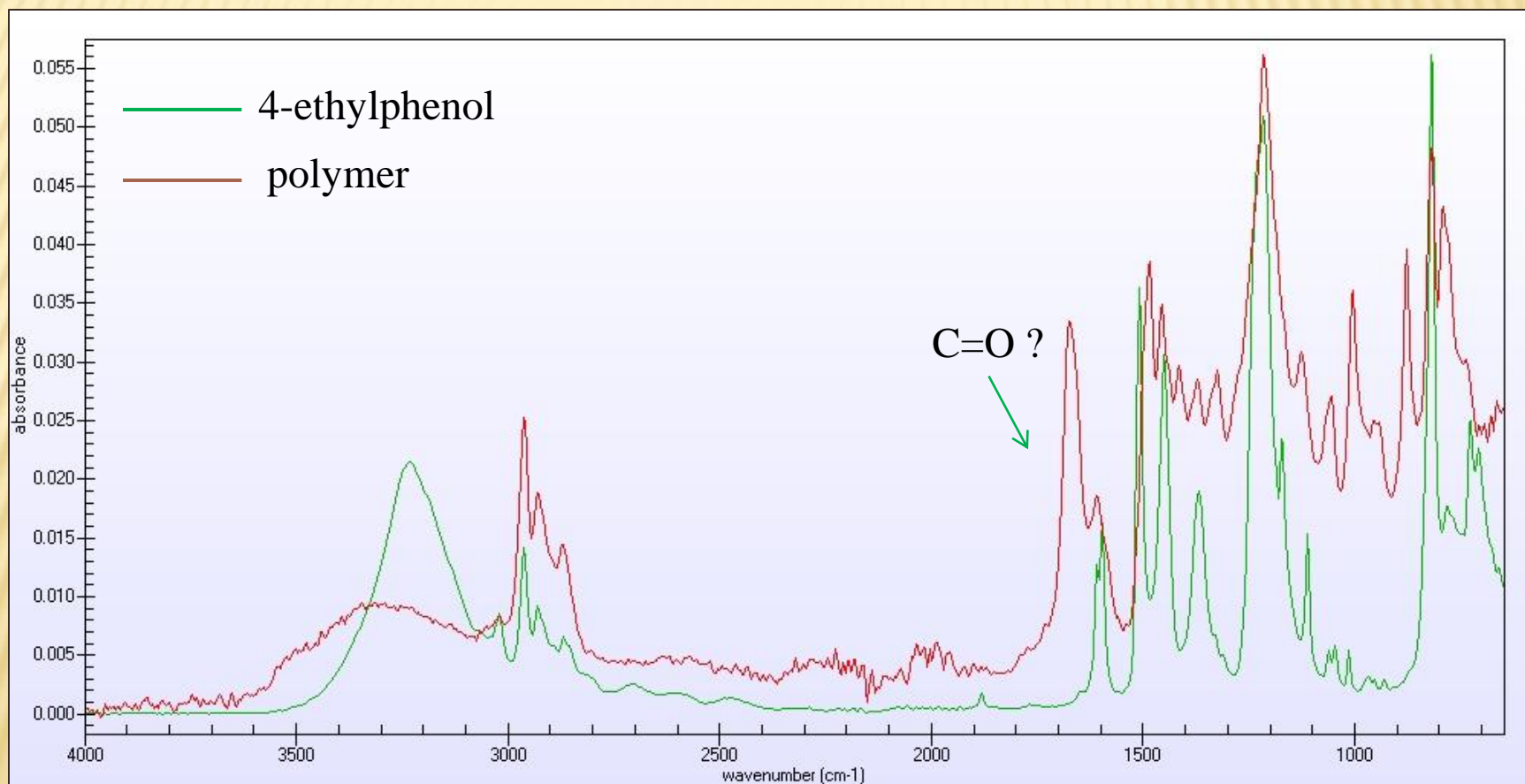


4-ETHYLPHENOL BY FT-IR



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

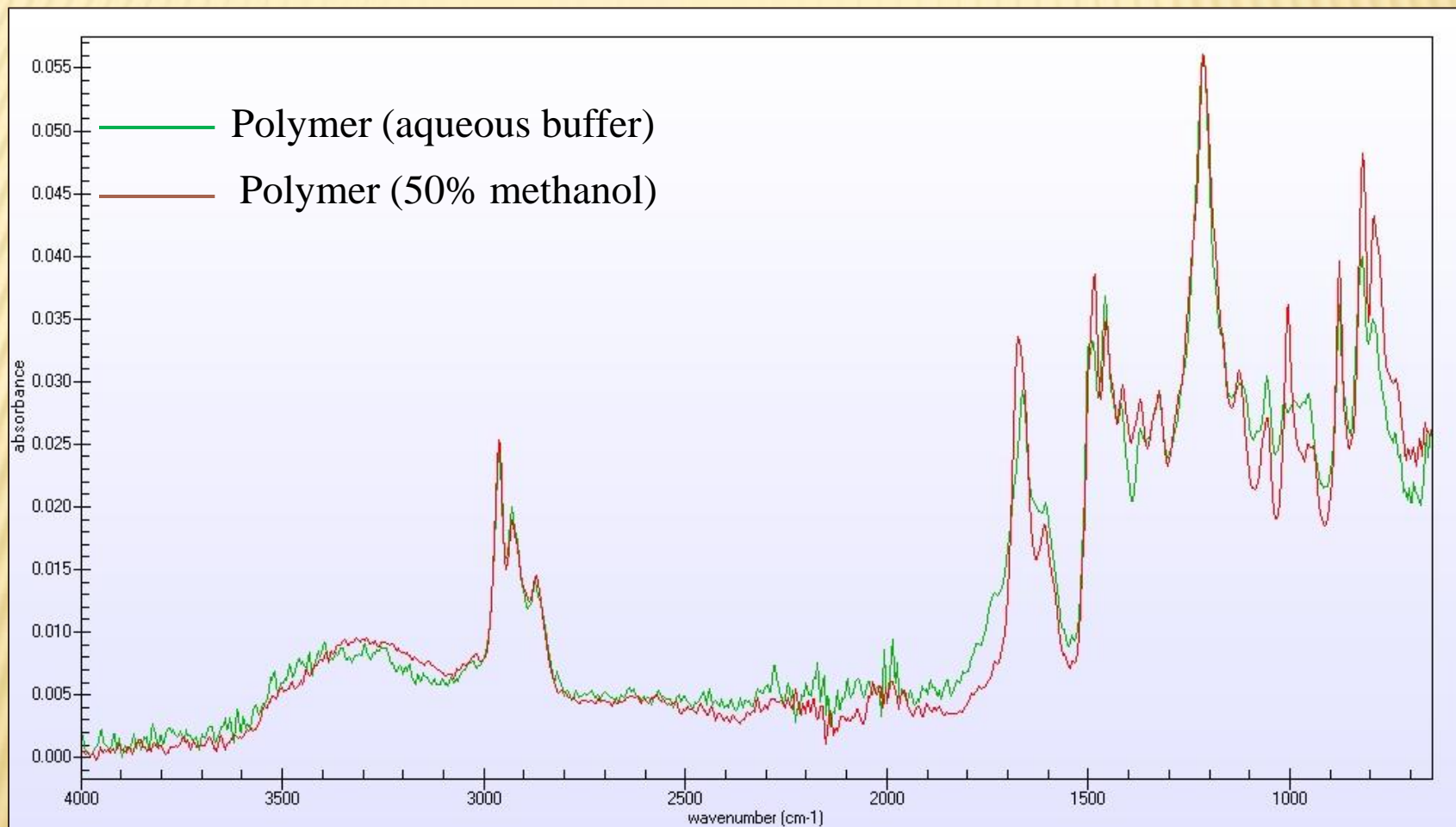
POLYMER AND MONOMER BY FT-IR



Polymer made in carbonate buffer only

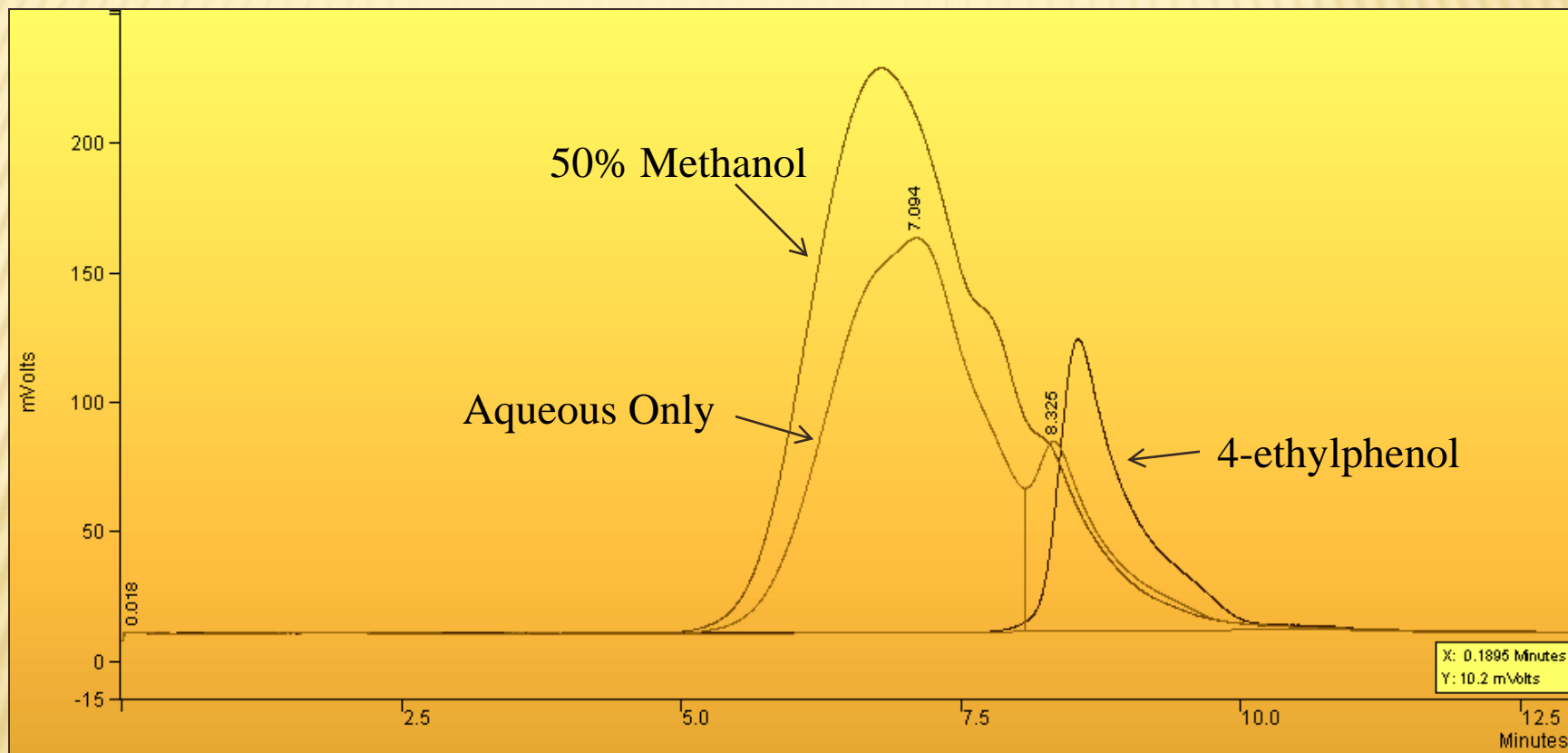
Smith detection FT-IR
4 cm⁻¹ resolution
number of scans 32

COMPARISON OF POLYMER BY FT-IR



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

GPC

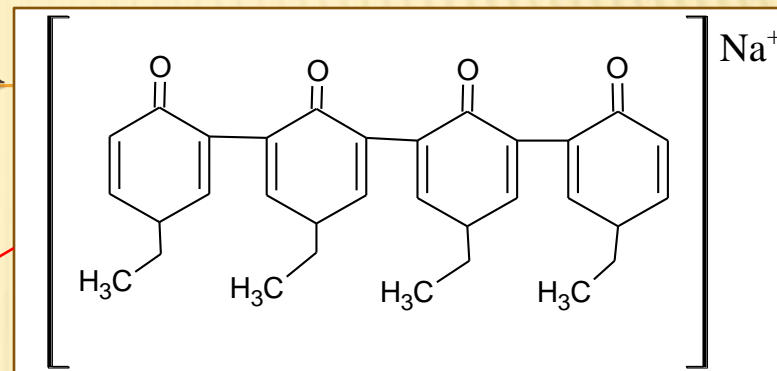


← Higher Molecular Weight

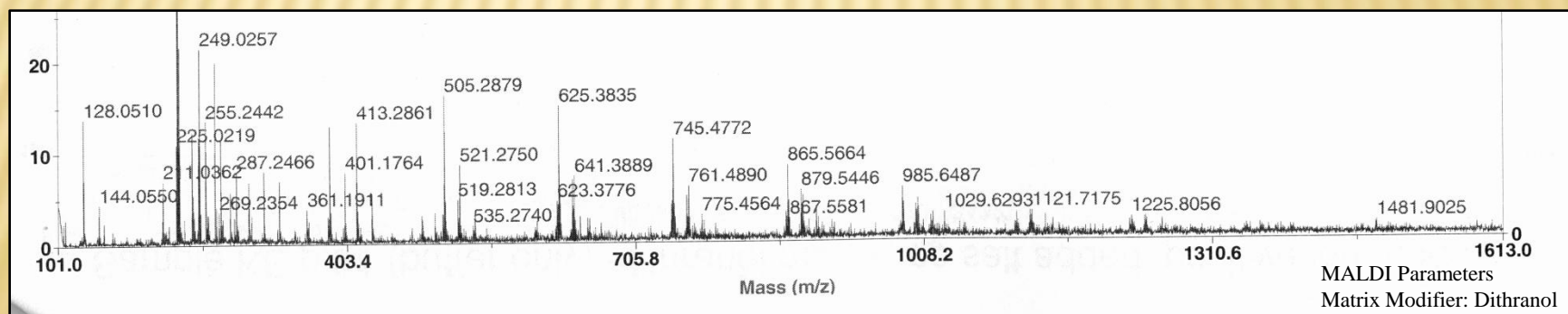
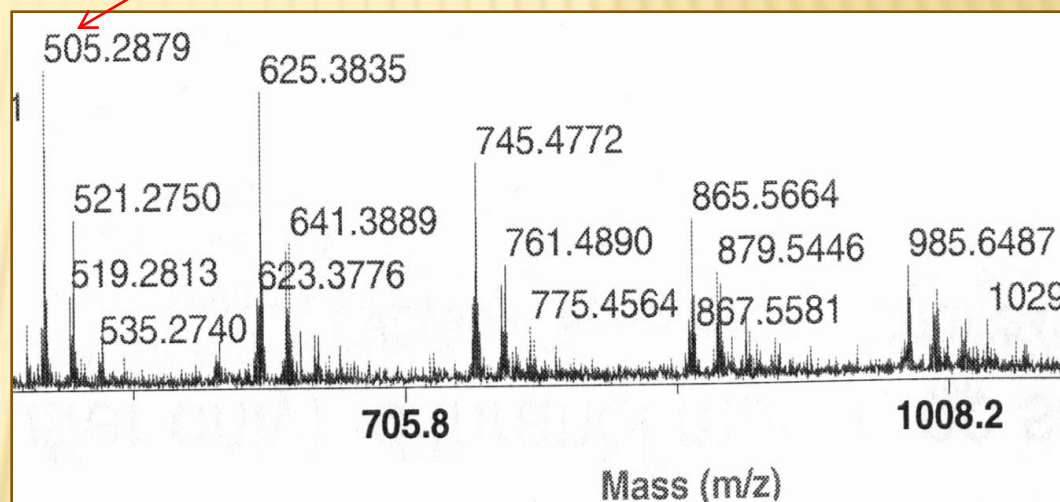
Lower Molecular Weight →

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



	oligomer length	Isotopic MW	(M+Na) ⁺
C ₈ H ₁₀ O	1	122.073	145.063
C ₁₆ H ₁₈ O ₂	2	242.131	265.120
C ₂₄ H ₂₆ O ₃	3	362.188	385.178
C ₃₂ H ₃₄ O ₄	4	482.246	505.236
C ₄₀ H ₄₂ O ₅	5	602.303	625.293
C ₄₈ H ₅₀ O ₆	6	722.361	745.350
C ₅₆ H ₅₈ O ₇	7	842.418	865.408
C ₆₄ H ₆₆ O ₈	8	962.476	985.466
C ₇₂ H ₇₄ O ₉	9	1082.533	1105.523
C ₈₀ H ₈₂ O ₁₀	10	1202.591	1225.581
C ₈₈ H ₉₀ O ₁₁	11	1322.648	1345.638
C ₉₆ H ₉₈ O ₁₂	12	1442.706	1465.696



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

FUTURE WORK

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

- ¹Collins, T. J.; Walter, C. Little Green Molecules. *Sci. Am.* **2006**, 294, 82-90.
- ²Global Phenolic Resins Association, A background to the Industry. <http://www.gpraweb.com/resins.html> (accessed February 22, 2010).
- ³Tshudy, D.; Wedell, M.; Collins, T. J. Carnegie-Mellon University, Pittsburgh, PA. Unpublished work, 2009.
- ³Curvetto, N. R.; Figlas, D.; Brandolin, A.; Saidman, S. B.; Rueda, E. H.; Ferreira, M. L. Efficiency of Enzymatic and Non-enzymatic Catalysts in the Synthesis of Insoluble Polyphenol and Conductive Polyaniline in Water. *Biochem. Eng. J.* **2006**, 29, 191-203.
- ⁵Nazari, K.; Esmaeili, N.; Mahmoudi, A.; Rahimi, H.; Moosavi-Moodahedi, A.A. Peroxidative Phenol Removal from Aqueous Solutions Using Activated Peroxidase Biocatalyst. *Enz. And Micr. Tech.* **2007**, 41, 226-233.
- ⁶Pang, Y.; Ritter, H.; Tabatabai, M. Cyclodextrins in Polymer Chemistry: Enzymatically catalyzed Oxidative Polymerization of Para-functionalized Phenol Derivatives in Aqueous Medium by Use of Horseradish Peroxidase. *Macromolecules.* **2003**, 36, 7090-7093.

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