Using FT-IR Spectroscopy to Elucidate the Structures of Ablative Polymers

Wendy Fan

The composition and structure of an ablative polymer has a multifaceted influence on its thermal, mechanical and ablative properties. Understanding the molecular level information is critical to the optimization of material performance because it helps to establish correlations with the macroscopic properties of the material, the so-called structure-property relationship. Moreover, accurate information of molecular structures is also essential to predict the thermal decomposition pathways as well as to identify decomposition species that are fundamentally important to modeling work. In this presentation, I will describe the use of infrared transmission spectroscopy (FT-IR) as a convenient tool to aid the discovery and development of thermal protection system materials.

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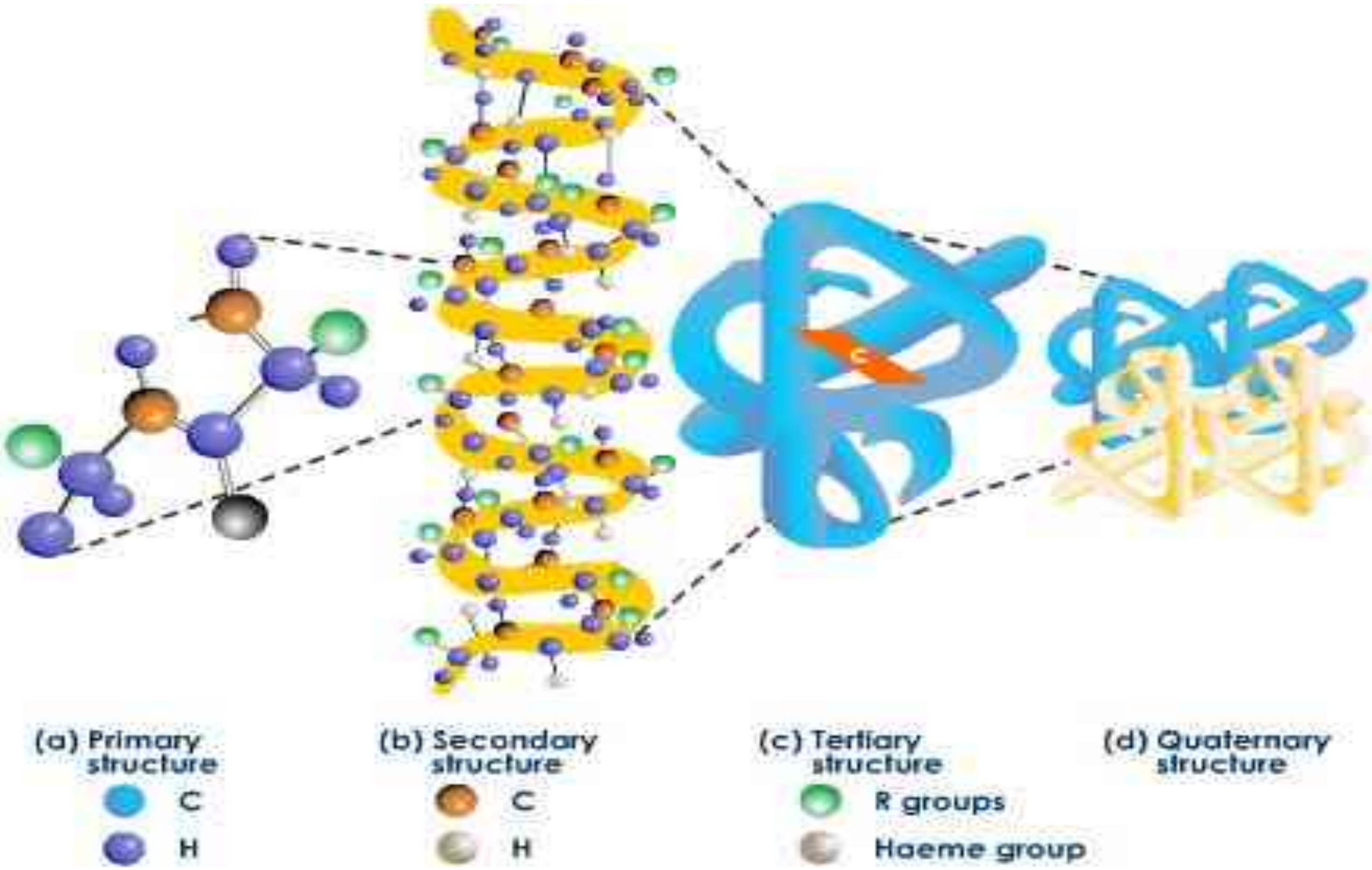
Outline

1. Introduction
   - Importance of polymer structure (Motivation)
   - FT-IR principle and technique
2. Applications
   - Detailed structural analysis of a phenolic polymer
   - Correlation among cure condition - crosslinking - thermal stability/char yield
   - Correlation between crosslinking - thermal oxidative decomposition mechanism
   - Diagnostic of a thermal decomposition product
3. Conclusion

Structure of Hemoglobin – How Nature Designs Its Materials



Unique sequence of amino acids

Held together by hydrogen bonding

Held together by hydrogen, ionic, sulfide bonding

Several peptide chains joined together

http://alevelnotes.com

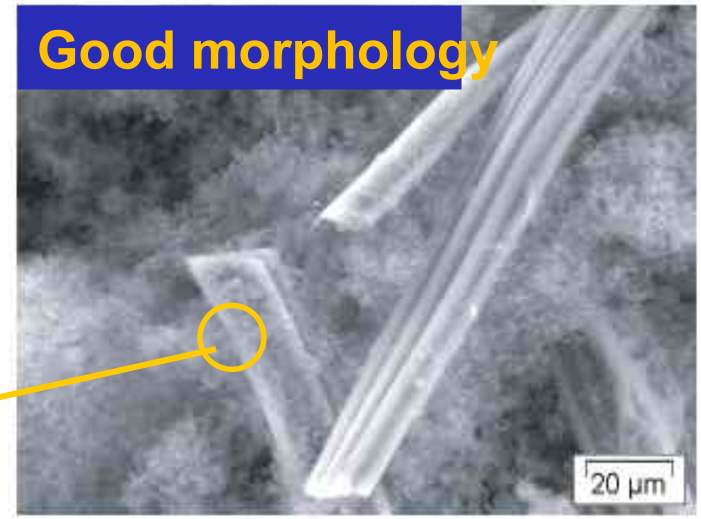
Polymer Structure and Morphology

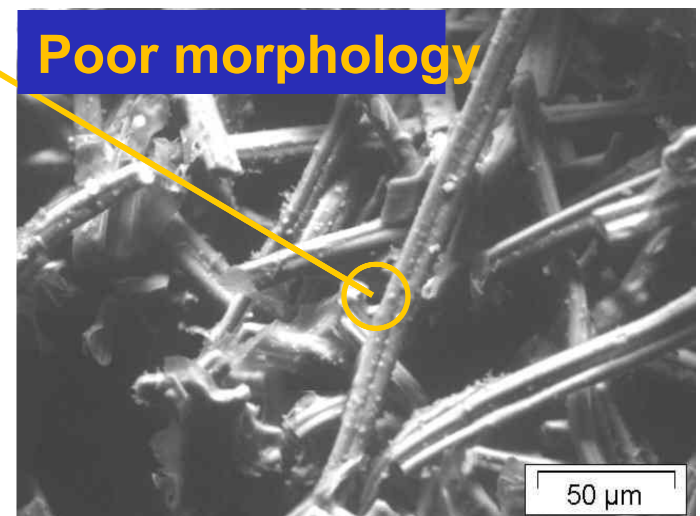
...influence key thermal, mechanical and ablative properties

Polymer matrix | Inter-face | Reinforcing fiber

Polymer structure and morphology (shape of a polymer)

How the polymer distributes around the fiber

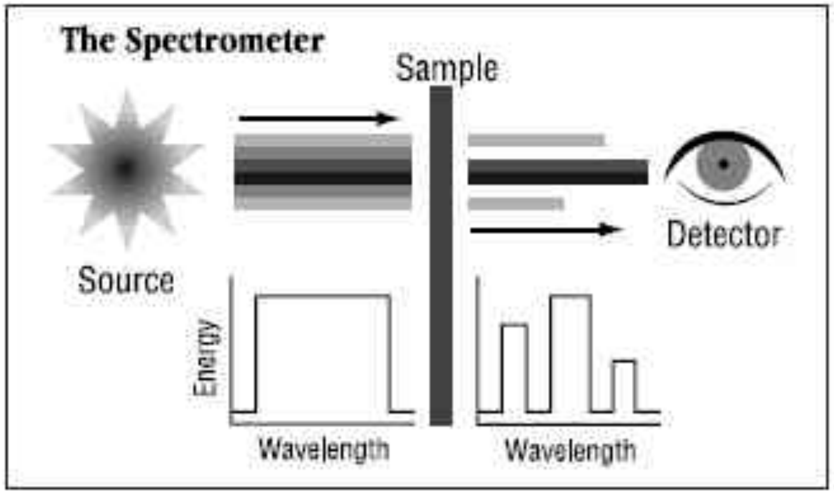




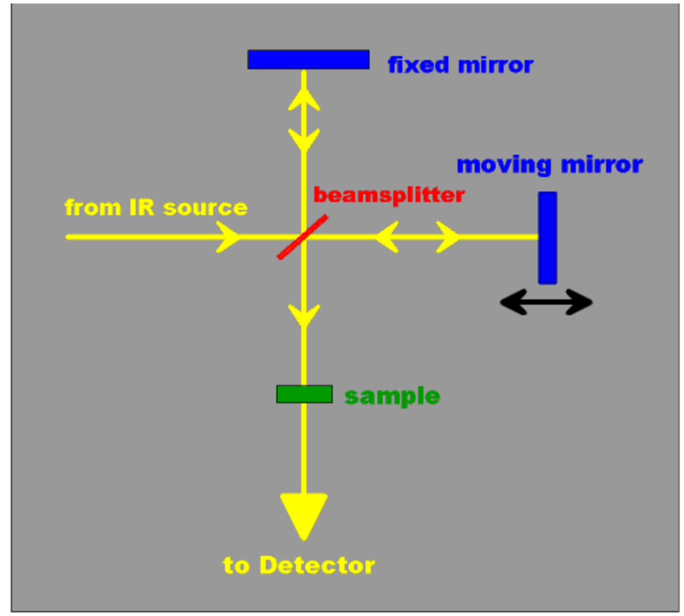
Techniques to Identify Polymer Structures

1. Nuclear Magnetic Resonance (NMR, both liquid and solid state)
   - Precise information of how atoms are bonded
2. FT-IR (Fourier Transform Infrared) transmission spectroscopy
   - Identify polymer structures, in particular polar functional groups, crosslink degree, crystalline region
3. Raman spectroscopy
   - Identify non-polar groups, such as olefinic groups (as in graphitic species)
4. Mass spectrometry
   - Information about fragments/groups, fragmentation modes
5. XPS (x-ray Photoelectron Spectroscopy)
   - Information about elements and functional groups on a surface

FT-IR – An Introduction



http://www.biophysik.uni-freiburg.de/Spectroscopy/FTIR/spectroscopy.html

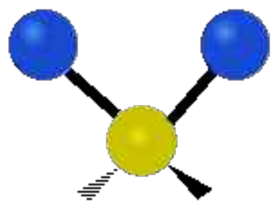


Main advantages of FT-IR
- Speed
- Sensitivity
- High spectral accuracy and resolution
- Internally calibrated
- Mechanical simplicity
- Easy sample preparation and operation

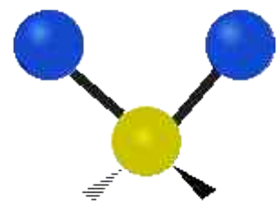
andersonmaterials.com

FT-IR spectroscopy: Theory

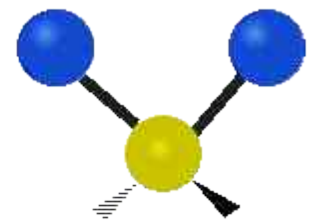
Vibrational modes of a -CH2 group



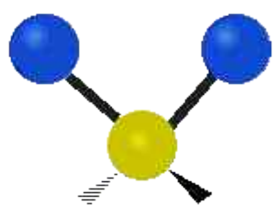
Symmetrical stretching



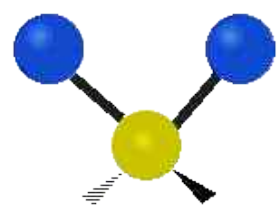
Twisting



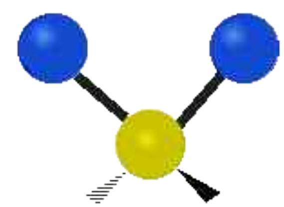
Wagging



Scissoring



Rocking

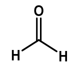


Asymmetric stretching

Vibrational transitions absorb discrete energy levels unique to a molecule

http://en.wikipedia.org/wiki/Fourier_transform_infrared_spectroscopy

FT-IR Spectrum of Formaldehyde



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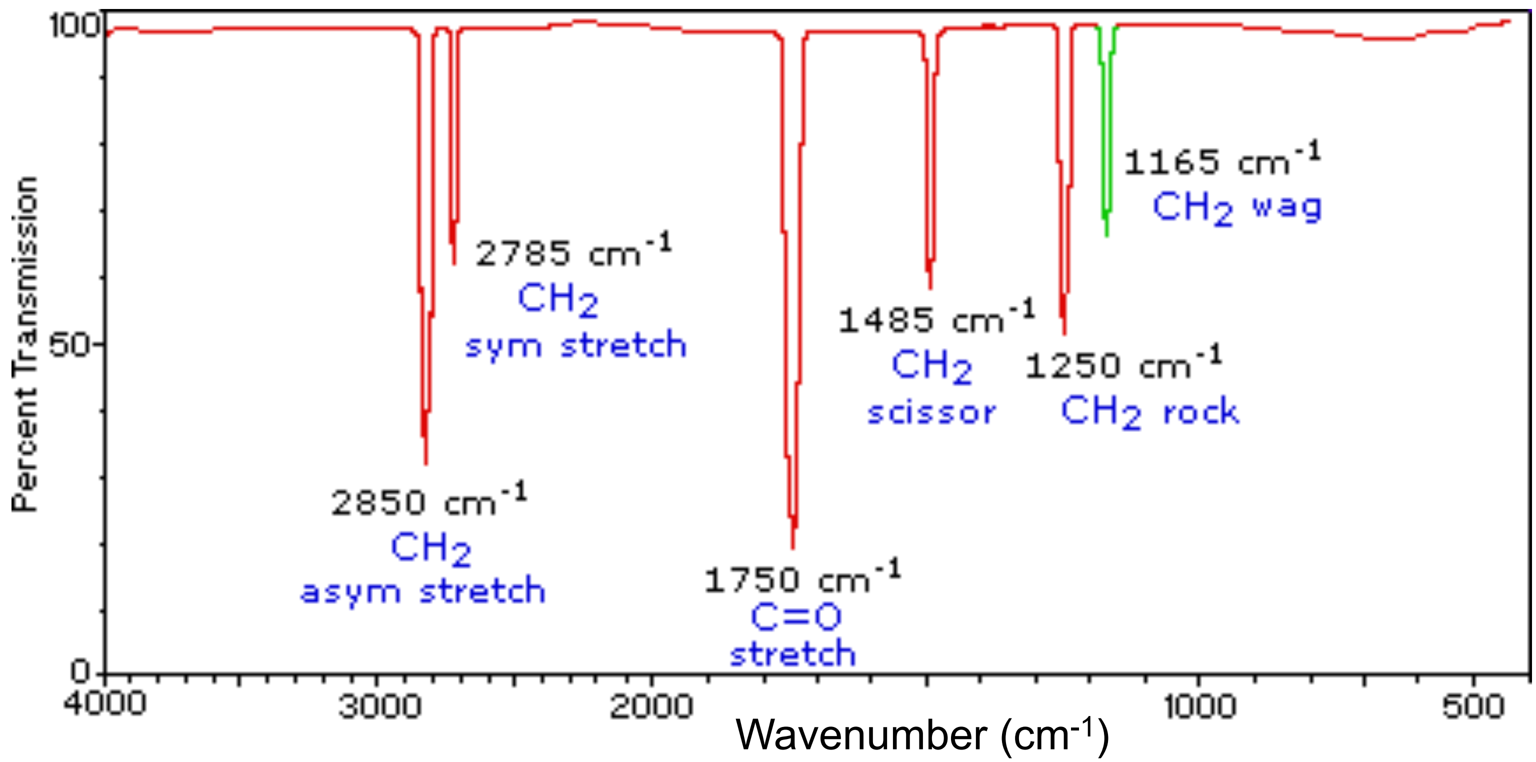
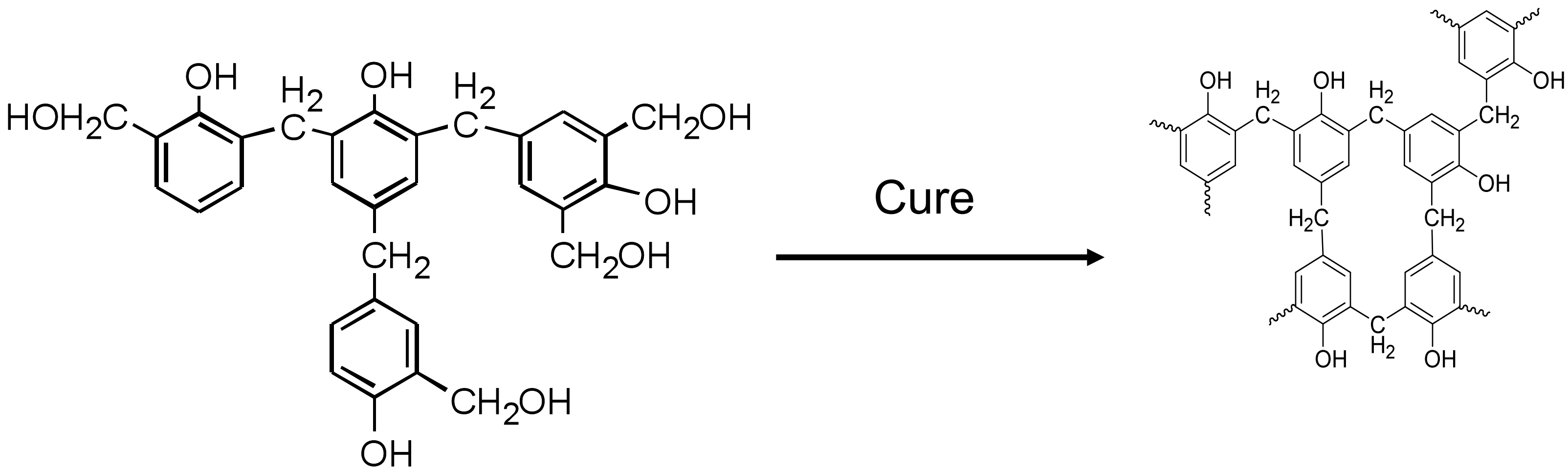


- To chemists, a FT-IR spectrum is like a pair of eyes looking into a molecule
- The intensity, shape, width and location of a peak all reflect the specific local environment the group is in

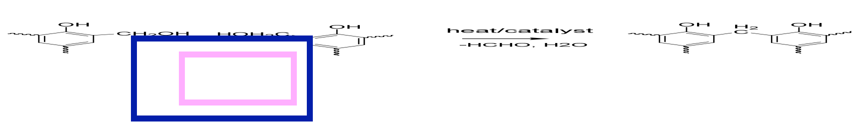
Curing Chemistry of Phenolic Resin

Phenolic resin (resole)

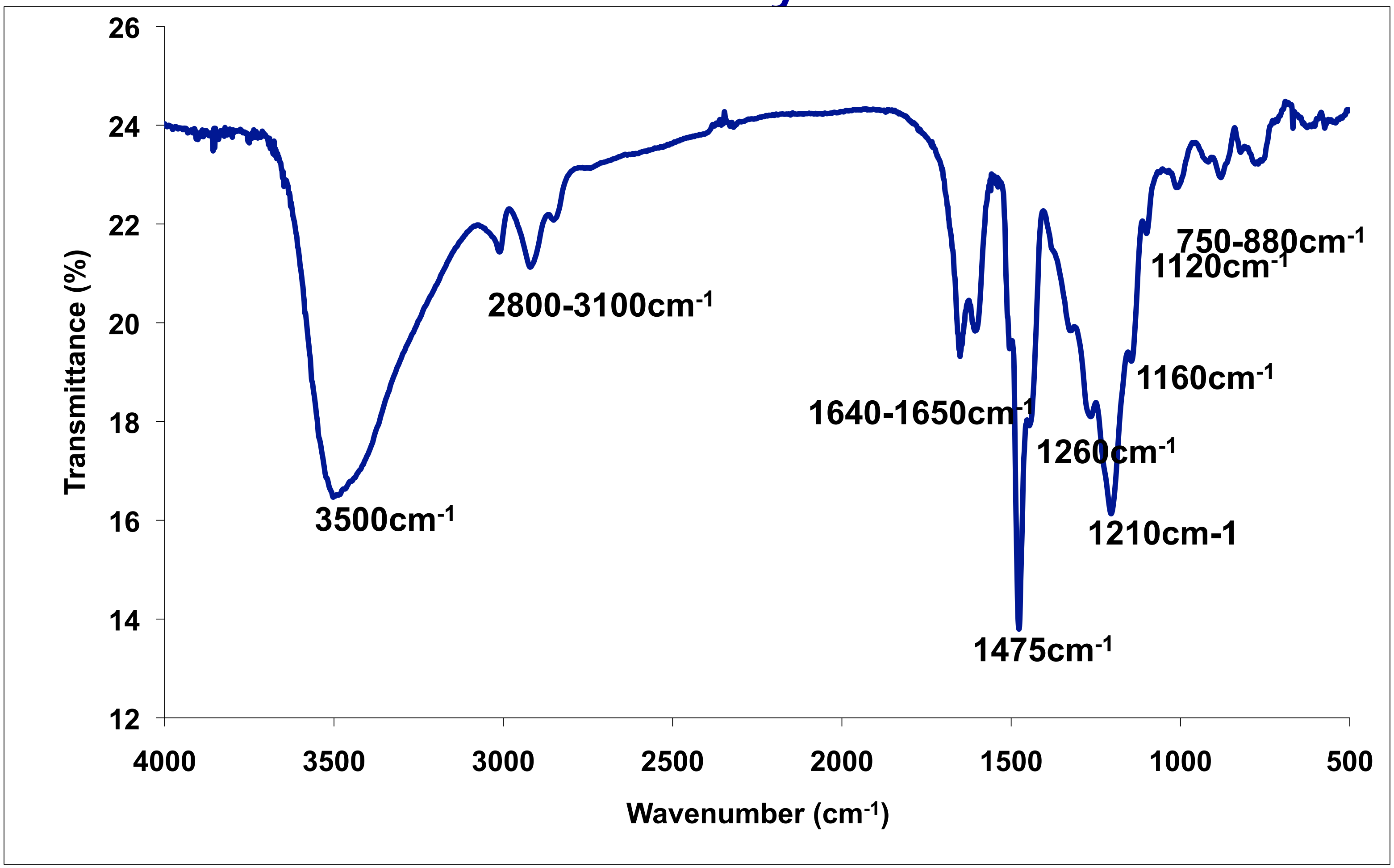
Phenolic Network polymer



A typical reaction in network formation

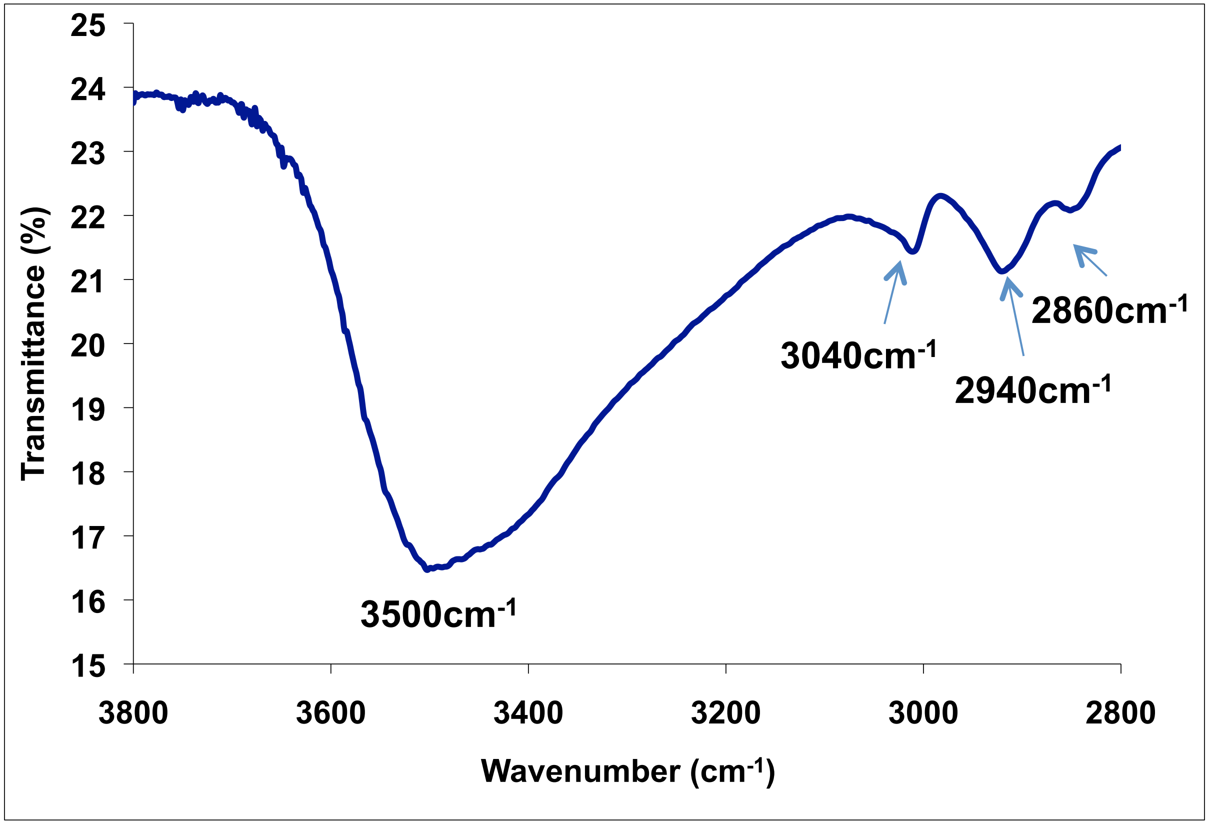


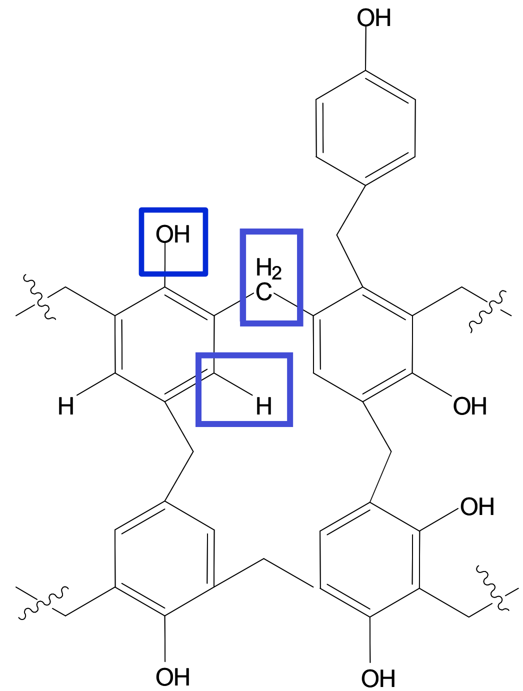
FT-IR of a Fully Crosslinked Phenolic Polymer



- Textbook example and extremely informative
- Absorption peaks can be easily assigned to corresponding groups
- Quantitative estimation of the degree of crosslinking is possible.

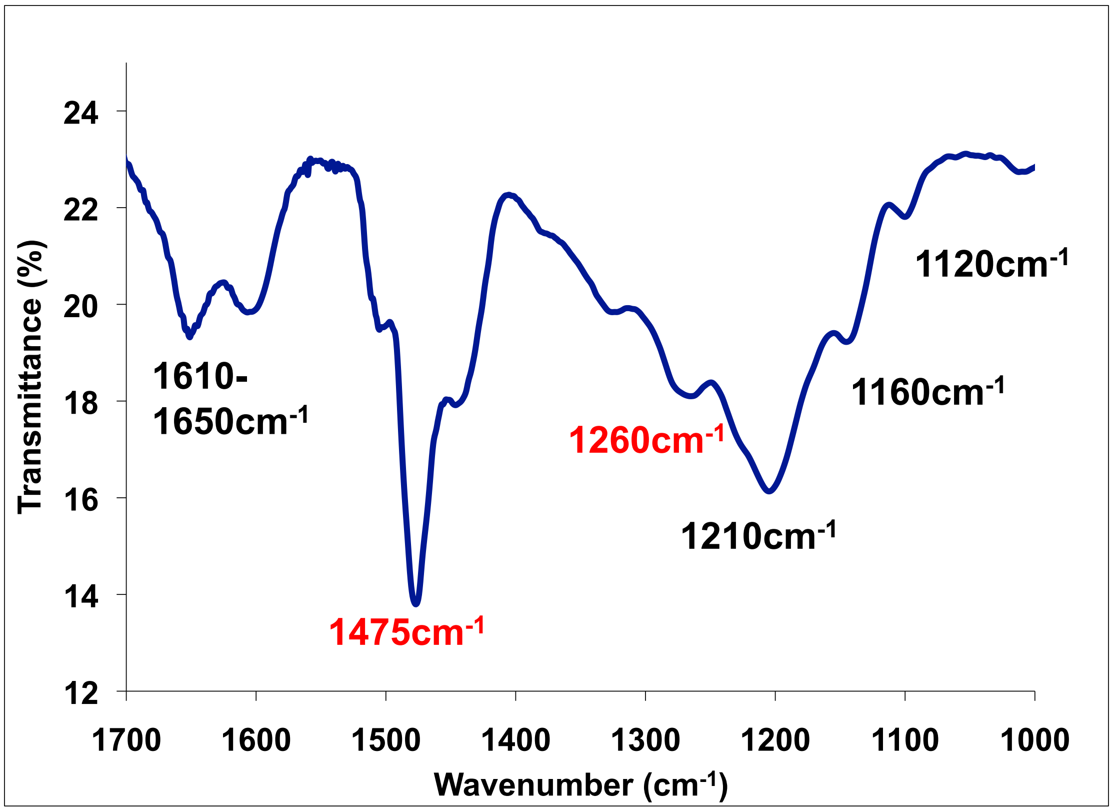
Region 1: $4000cm^{-1}$ - $2700cm^{-1}$

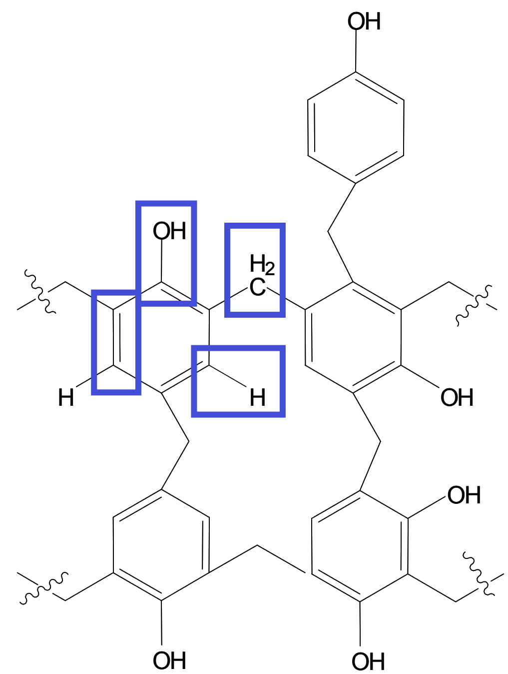




$3500cm^{-1}$: Phenolic OH
$3040cm^{-1}$: aromatic *sp2* C-H
$2940cm^{-1}$: Aliphatic *sp3* CH_2 asym. Stretch
$2860cm^{-1}$: Aliphatic *sp3* CH_2 sym. stretch

Region 2: $1700cm^{-1}$ - $1000cm^{-1}$

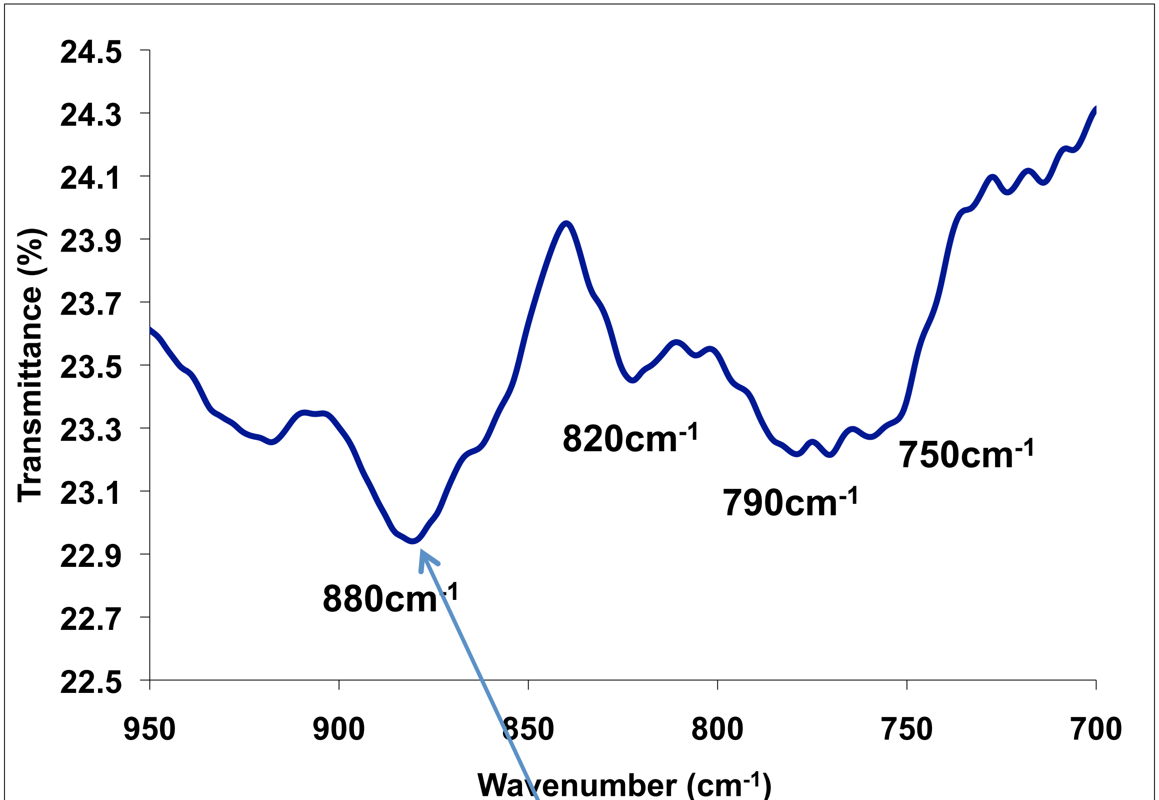


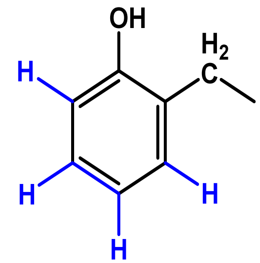


1610-$1650cm^{-1}$: Benzene C=C
$1475cm^{-1}$: CH2 scissor
$1260cm^{-1}$: CH2 rocking
$1210cm^{-1}$: *sp2* C-O
$1160cm^{-1}$: CH2 wagging
$1120cm^{-1}$: *sp2* C-H

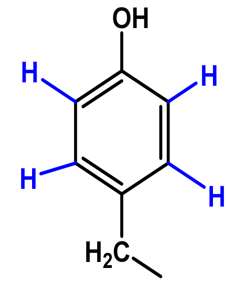
$I_{CH2} / I_{C=C}$ can be used to semi-quantitatively measure the crosslinking degree

Region 3: 900cm^{-1} - 700cm^{-1}

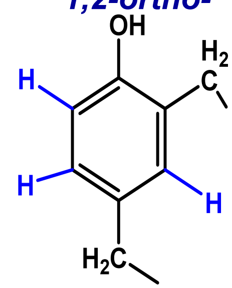




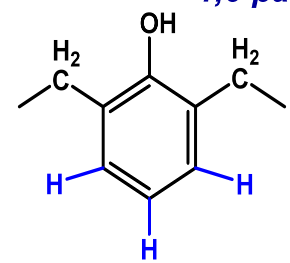
1,2-ortho-



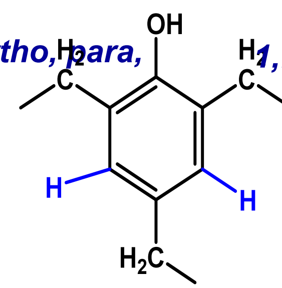
1,6-para



1,2,4-ortho, para,



1,2,6-ortho, ortho,



Most highly crosslinked

1,2,4,6-ortho, para, ortho-

Application

Cure conditions → **Phenolic network density & structure** → **Thermal and oxidative stability**

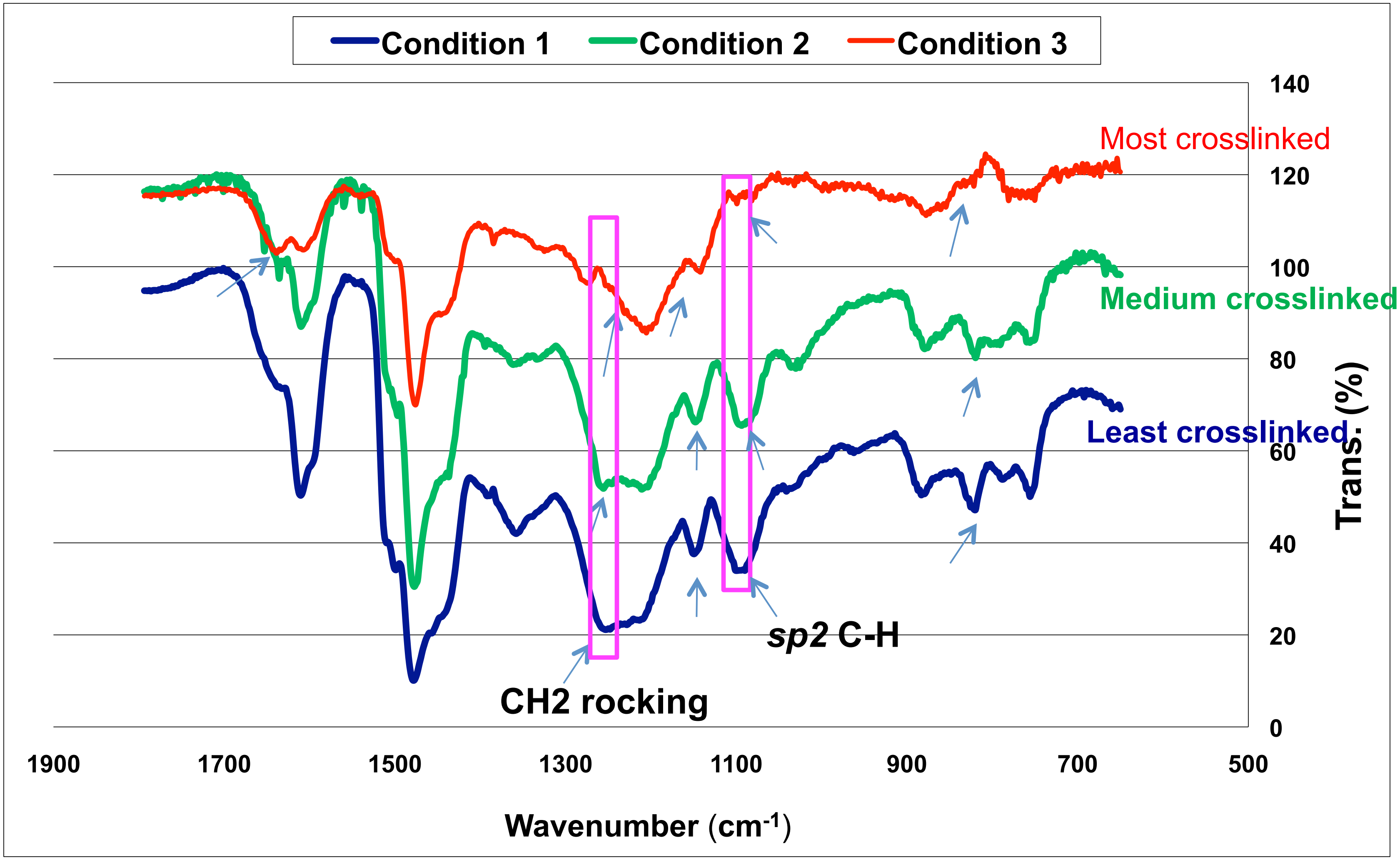
Experiments: phenolic resin was cured under three different conditions, each with increasing temperature and cure time.

Condition 1, Condition 2, Condition 3

→

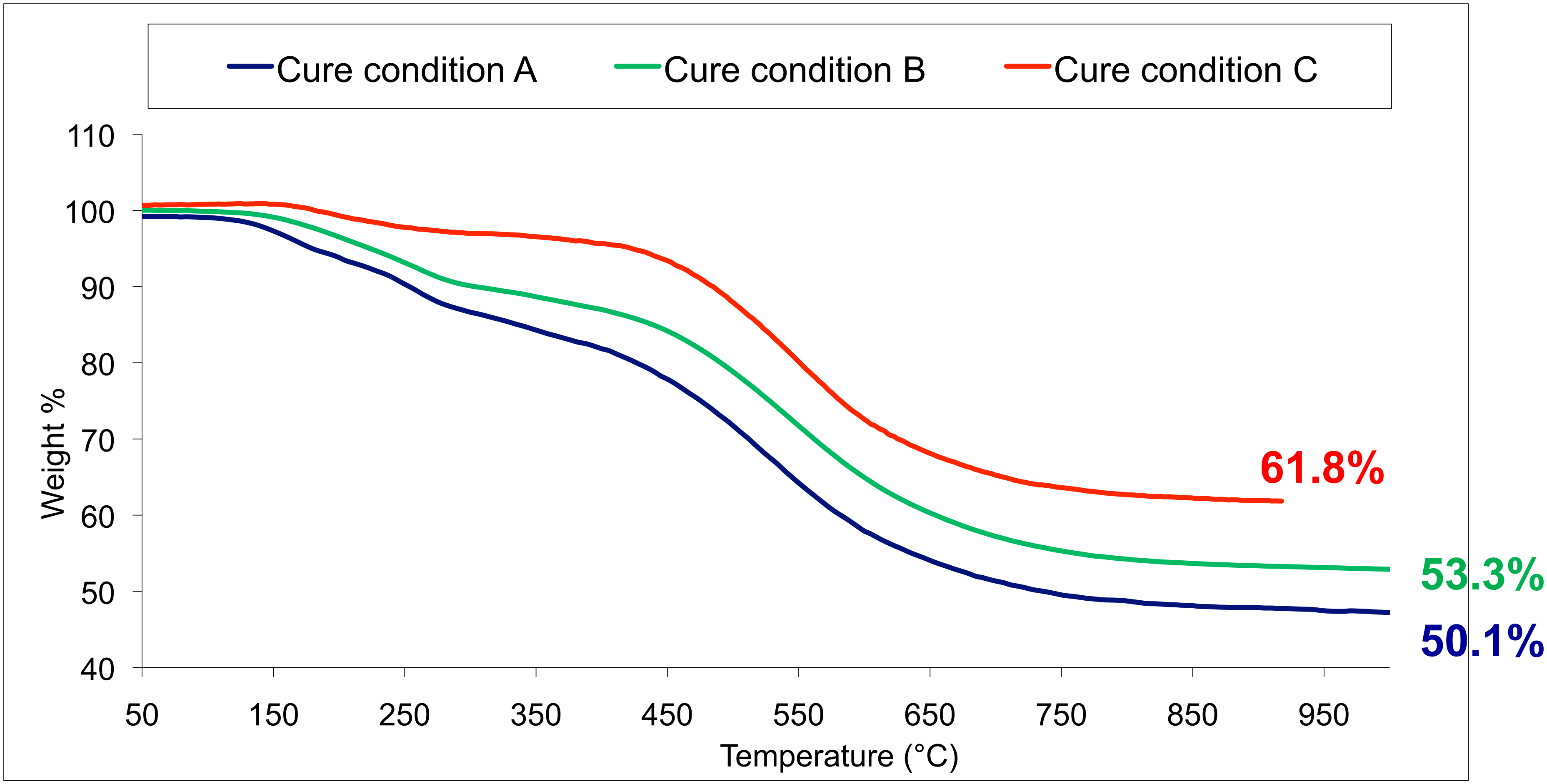
Temperature and cure time increases

FT-IR of Cured Phenolic Polymers



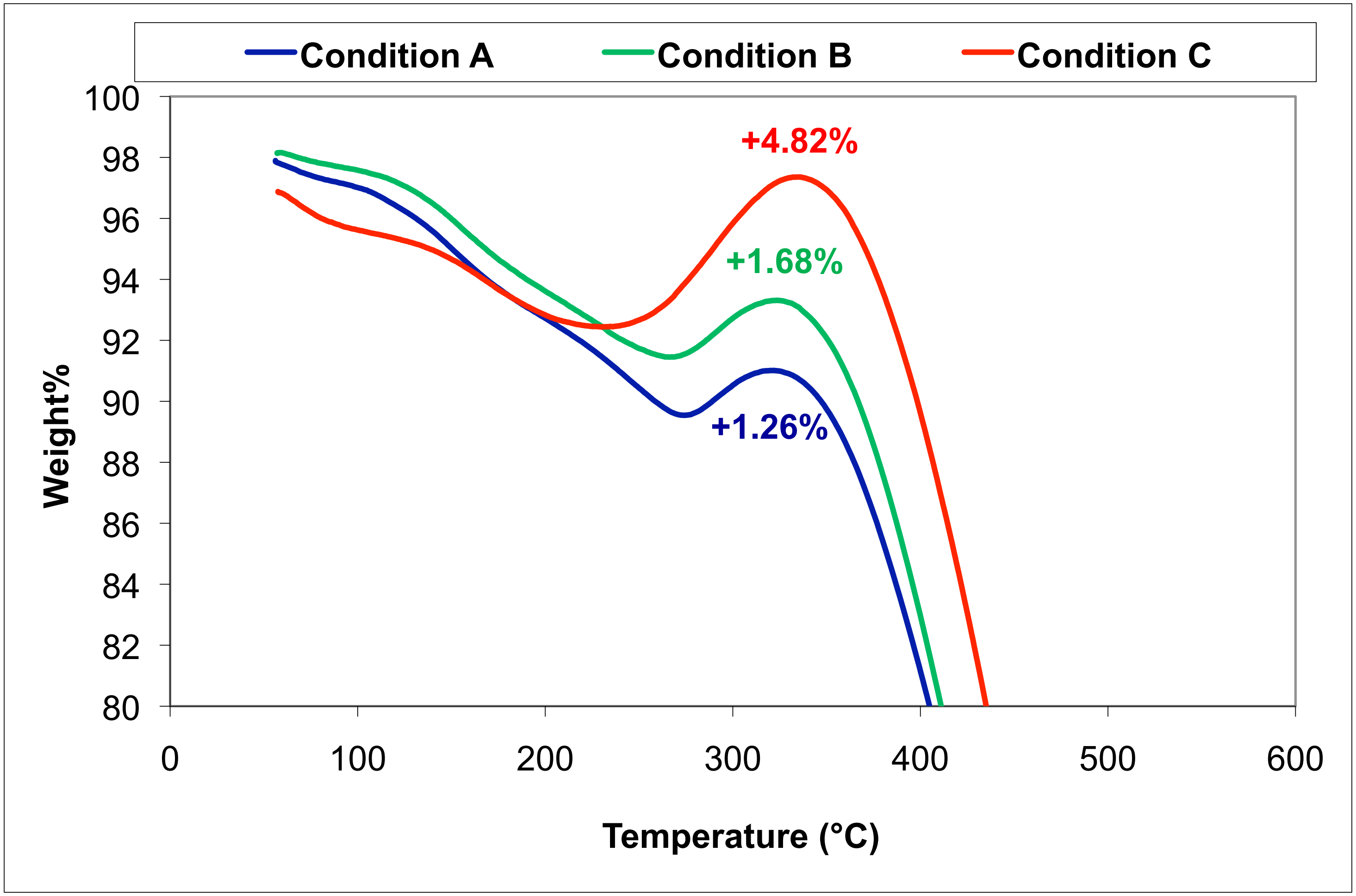
Change of intensity in multiple peaks indicates the progress of curing (more crosslink

Thermogravimetric Analysis (TGA) (in Nitrogen, 20°C/min.)



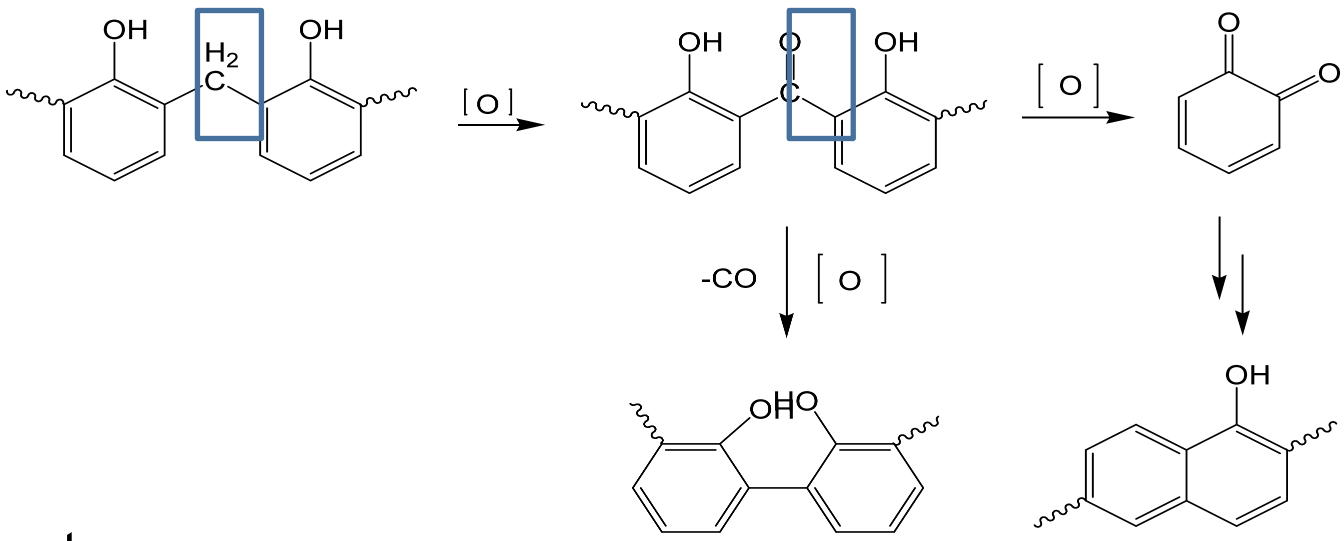
Char yield correlates with degree of polymer crosslinking

TGA in Air 20°C/min.



Weight% increases with increased crosslinking

Decomposition of Phenolic – Char Forming Mechanism



Char structures were characterized by solid state ^{13}C NMR

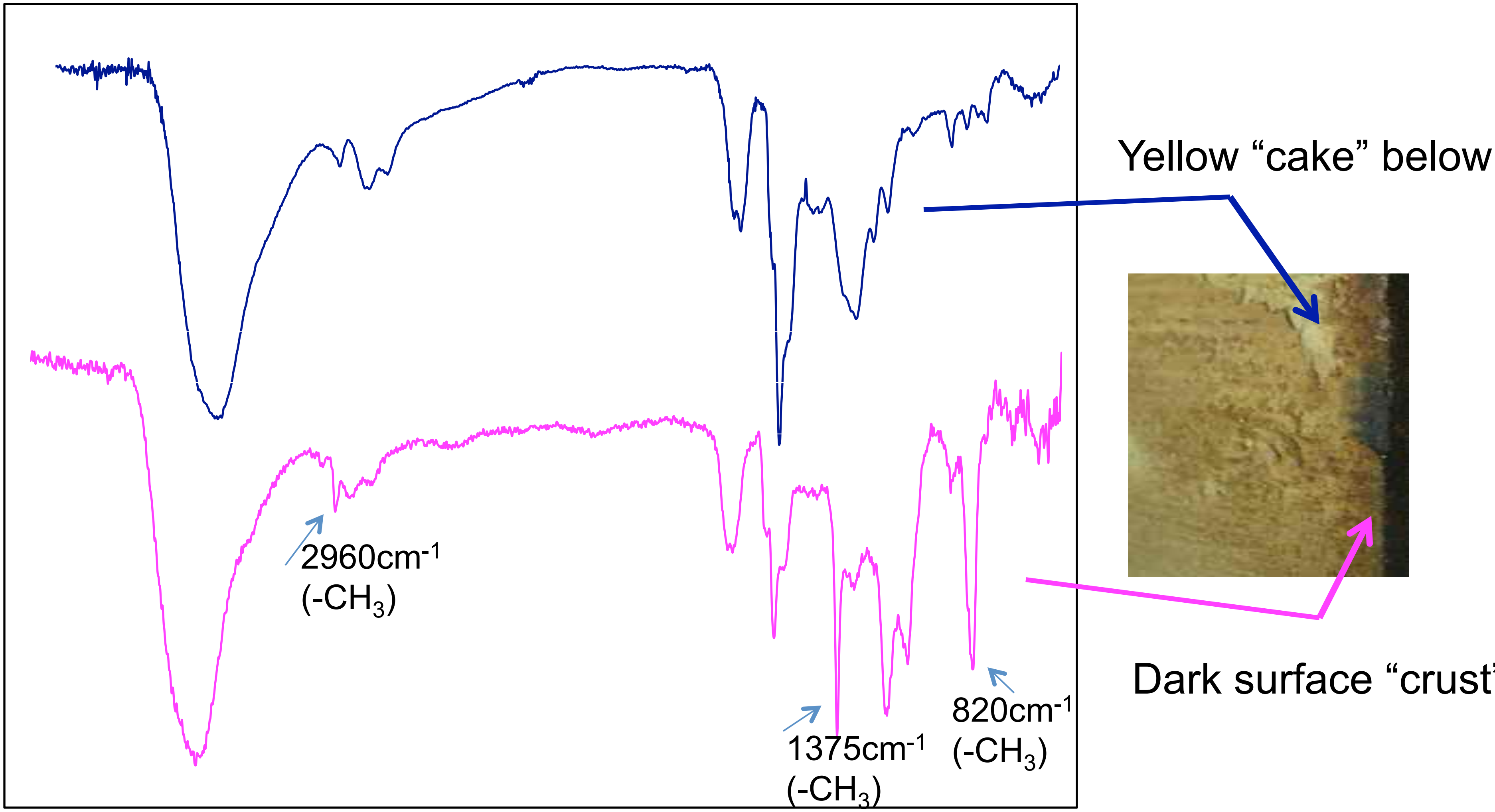
Substructures of graphitic/carbon char

↓

Amorphous carbon char

Virgin polymer structure dictates the decomposition pathways and char yield

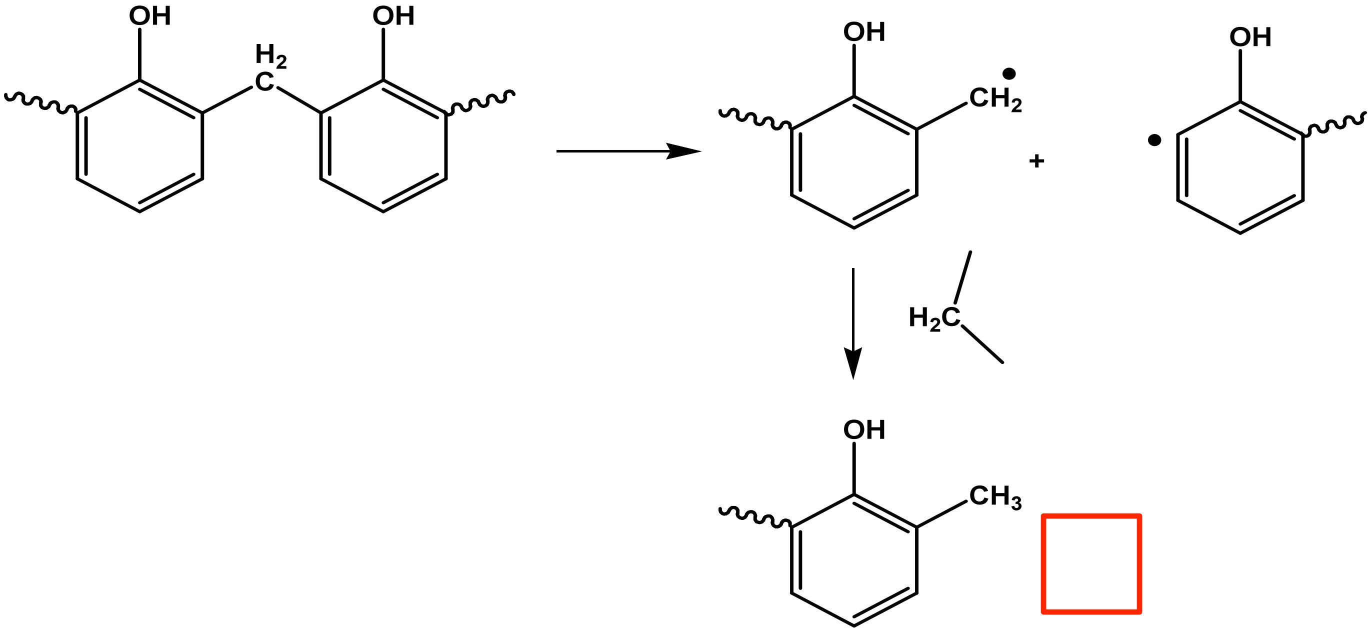
Application 2:
Identifying a Decomposition Process



- –CH_3 group formed
- Lower degree of crosslinking

Thermal Decomposition in Vacuum

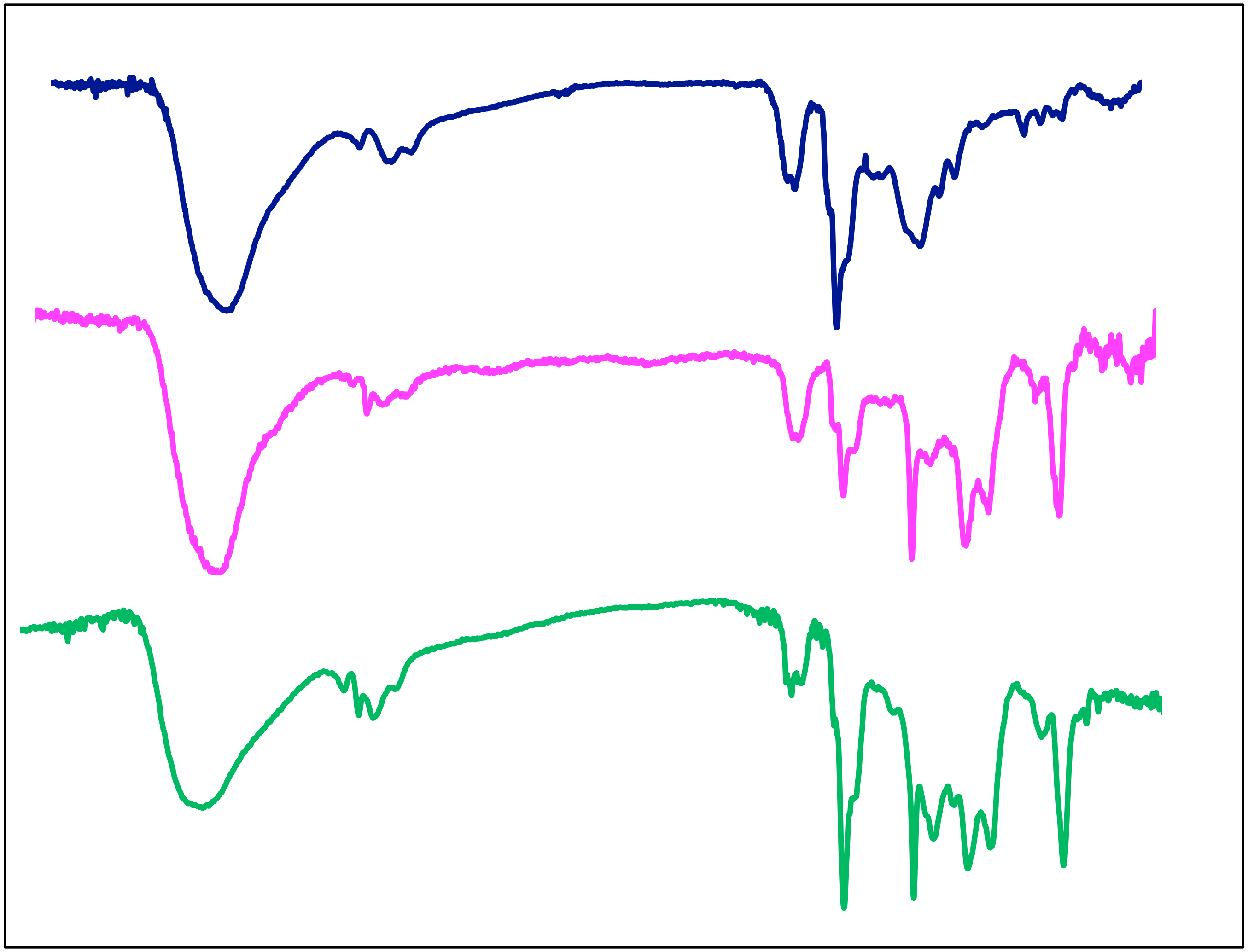
Likely Pathway



- Lower degree of crosslinking
- $–CH_3$ group formed

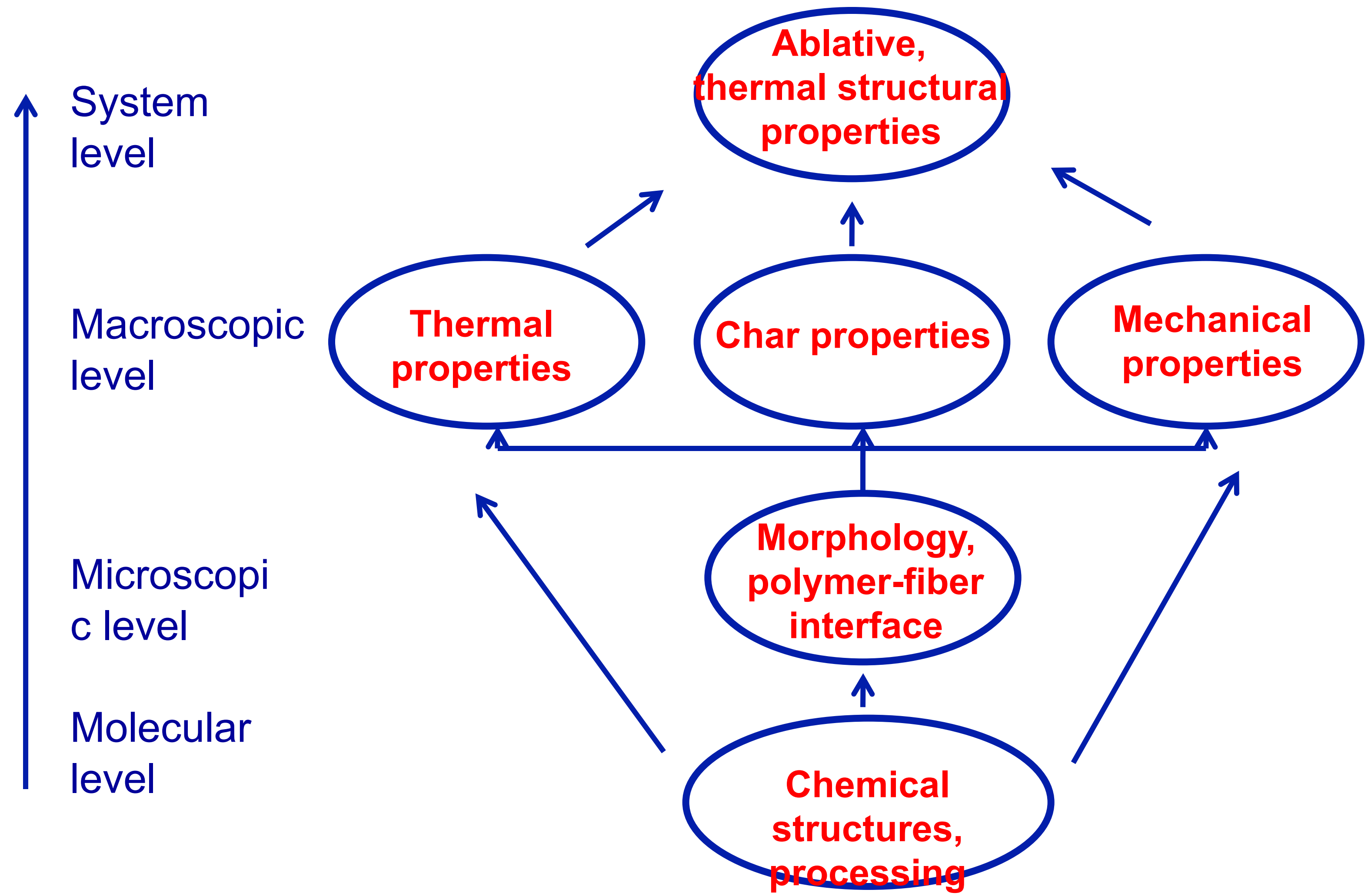
G. E. Maciel and I.-S. Chuang, Macromolecules, 1984, 17, 1081-1087
Fyfe, C. A. et al, Macromolecules, 1983, 16, 1216-1219
Zinke, A. J. Appl. Chem., 1951, 1, 257.

FT-IR Spectrum of a Model Polymer



Model polymer was cured in nitrogen and at an elevated temperature (close to the oven condition)

Bottom Up Approach to TPS Materials Discovery



- **A thorough understanding of chemistry/molecular structure is key**
- **Most of these correlations have been obtained by experiments**

Advantages and Limitations

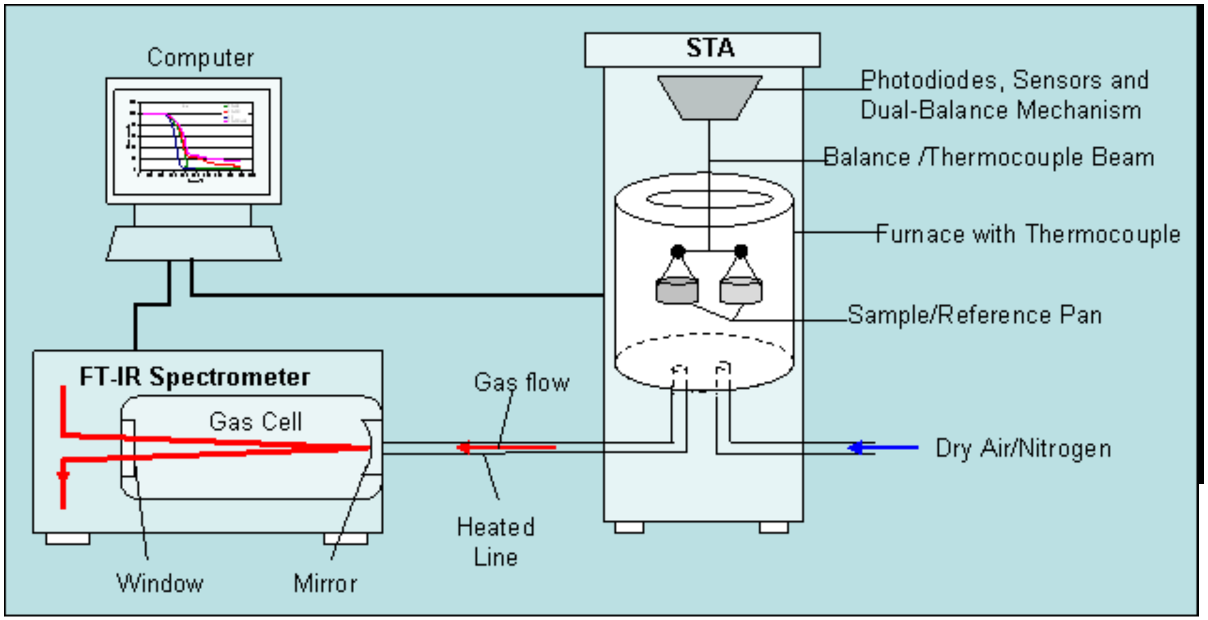
Advantages:

1. Convenient, low cost, speedy
2. Excellent tool for first screening of polymer structures and identification of unknowns
3. Useful for predicting reactivity and physicochemical properties, as well as interpreting decomposition mechanisms and products
4. Routinely used at Ames for qualitative determination of new polymer structures as well as analyzing curing products
5. Can be coupled with TGA to study thermal decomposition products (TGA-IR)

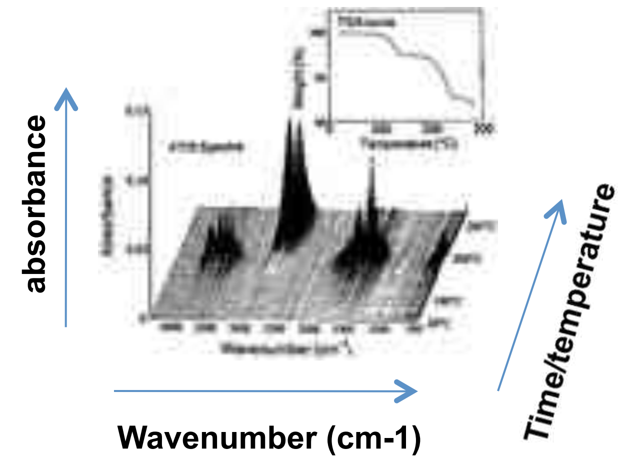
Limitations:

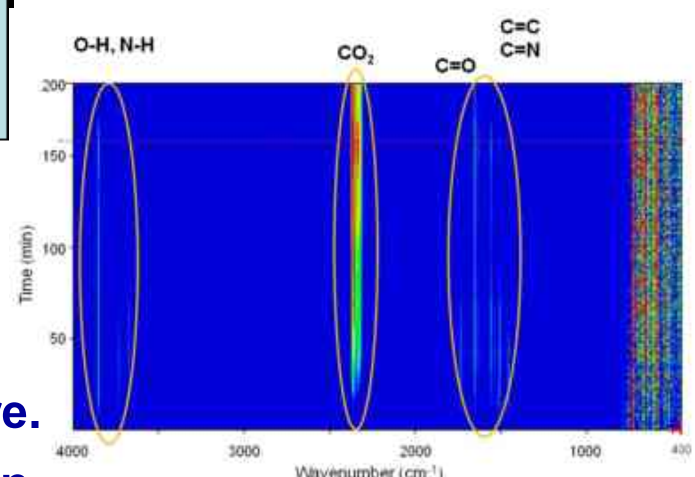
1. Mostly qualitative, does not provide precise molecular structures
2. Can be semi-quantitative with the right software
3. Not all polymers have well-resolved absorption peaks in the IR region (overlaps, weak absorptions)

Using TGA-FT IR to Monitor Gas Phase Products



http://www.uclan.ac.uk/schools/forensic_investigative/
fire_hazards_science/equipment_tests/tga_ftir_magna.php





http://cnx.org/content/m23038/latest/

- **TGA-IR allows the gas phase products to be collected continuously as a function of temperature.**
- **Gas phase infrared spectra are much sharper than condensed phase spectra, and recognition of the individual molecules is possible.**

Contributors

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