SAND2007-3874C

Mechanistic aspects of gel formation and degradation in BMI (octamethyltetrasiloxane-di-4,1-phenoxy bismaleimide)

Mat Celina, **Jim Aubert, Sarah Leming, Jim McElhanon**

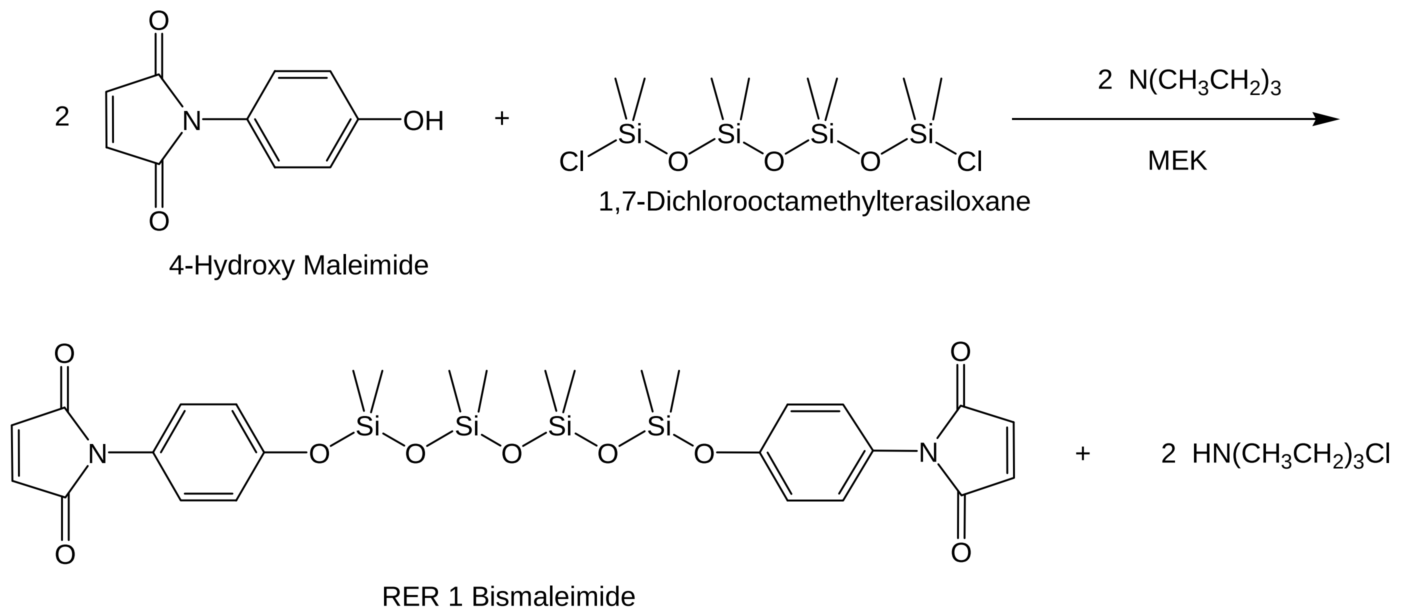
Organic Materials Dept. 1821
Sandia National Laboratories, Albuquerque, NM, 87185-1411

PolyMac conference 2007, Kansas City, MO

Our challenge: To further improve the production of BMI and removable foam processing

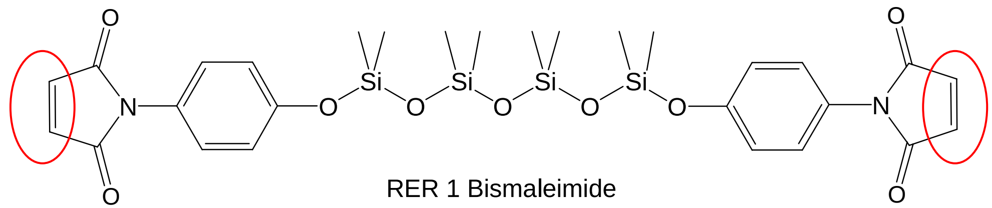
Production of BMI:

hydroxyl- chloro-siloxane condensation



Materials are in solvents (MEK, THF, EAc) and see elevated T

Removable epoxy foam:



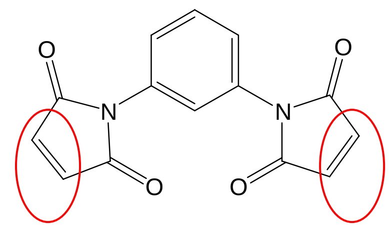
RER 1 Bismaleimide

4 main components in Part A:

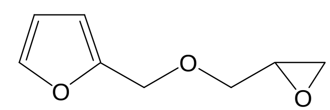
- RER 1 BMI
- N, N’-1,3-Phenylenedimaleimide (PDM)
- Furfuryl Glycidyl Ether (FGE)
- EPON 8121

EPON 8121 contains:

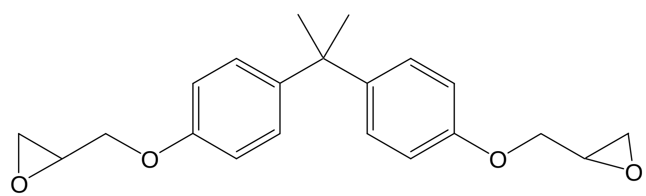
- Bisphenol A Diglycidyl Ether
- Pentaerythritol tetraacrylate



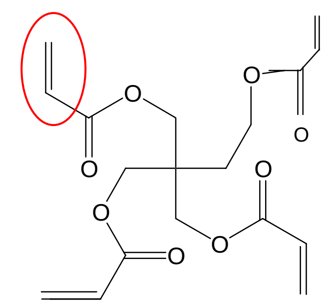
N,N'-1,3-Phenylenedimaleimide



Furfuryl Glycidyl Ether



EPON 8121 - Bisphenol A Diglycidyl Ether



EPON 8121 - Pentaerythritol Triacrylate

Constitutents have double bonds and epoxy groups to react

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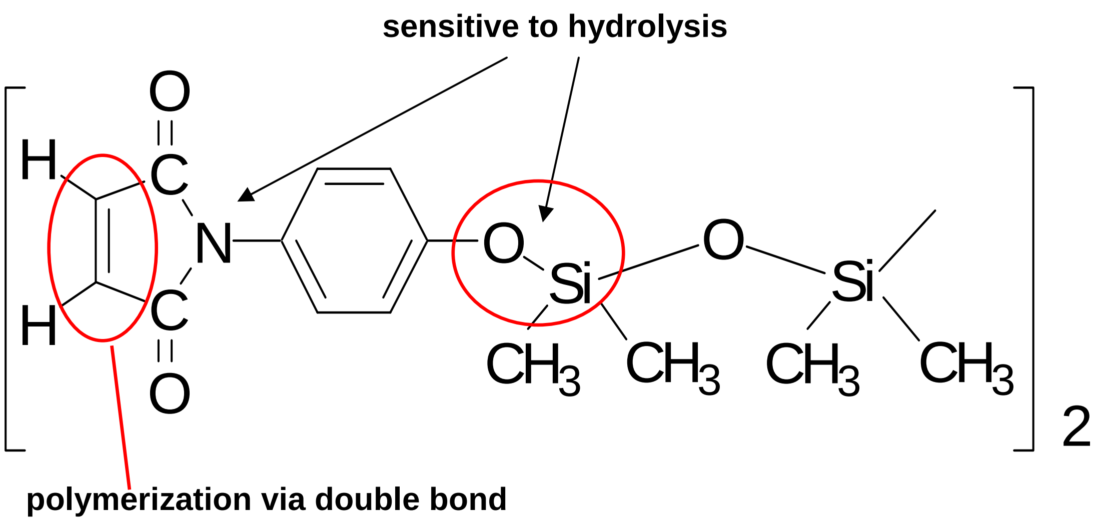
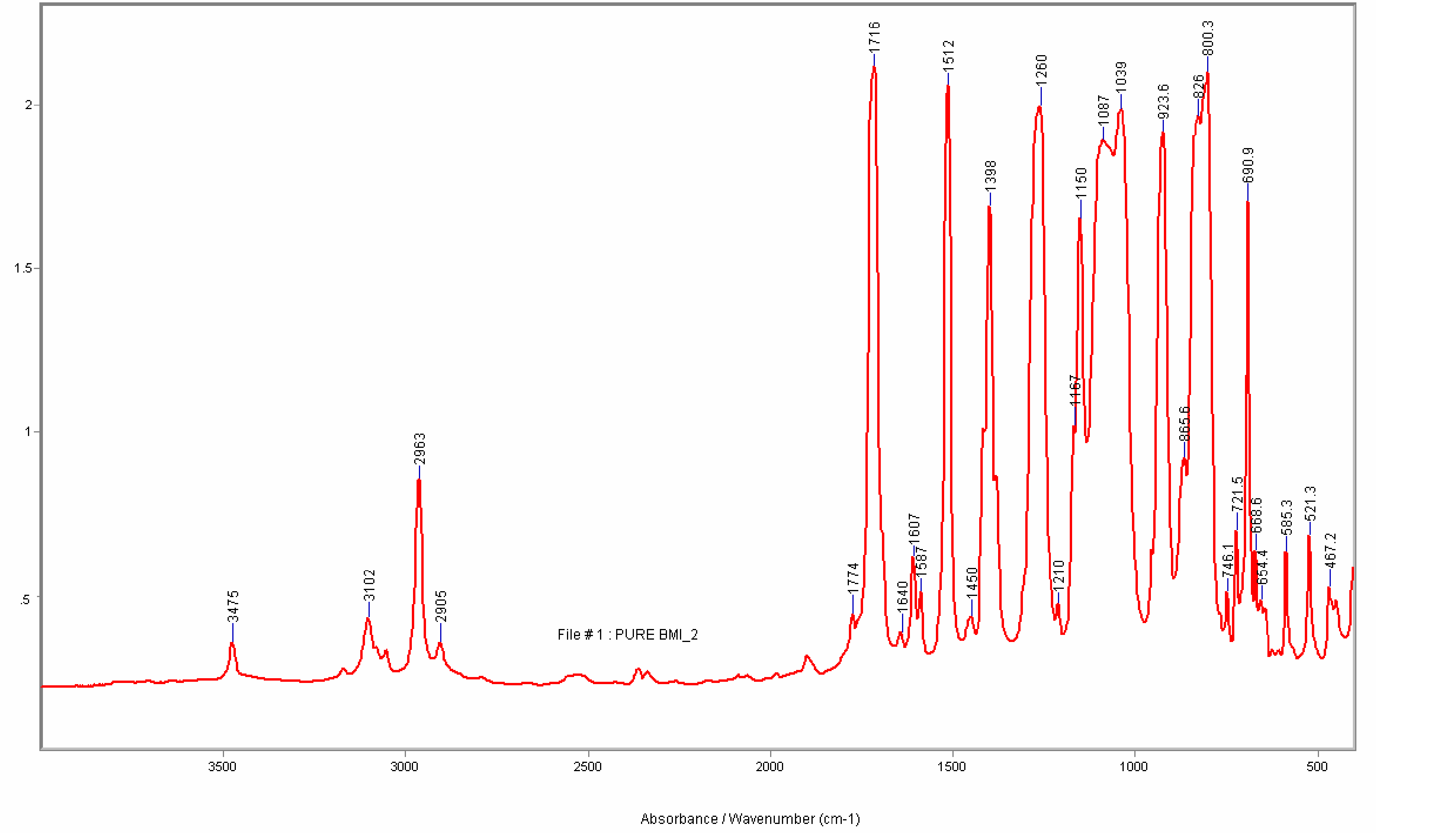
Bismaleimide with a siloxane bridge (BMI)

A reactive intermediate with a flexible linkage
A dienophile for Diels-Alder adducts
Unfortunately, also a molecule that can self-polymerize and hydrolyze

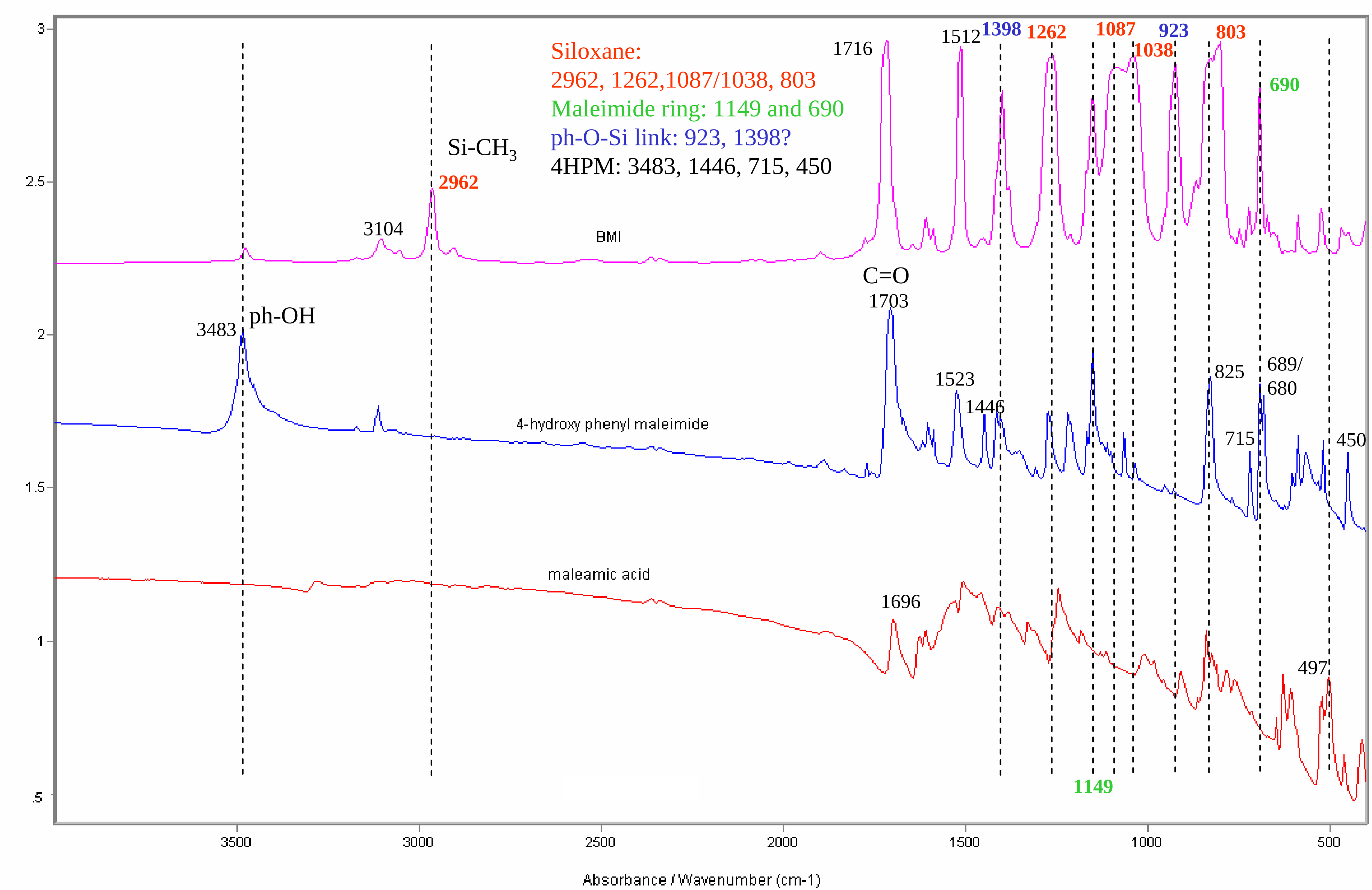


IR spectroscopy of BMI



Many signature bands, perfect for IR study

IR constituents of BMI



Nearly every band can be assigned

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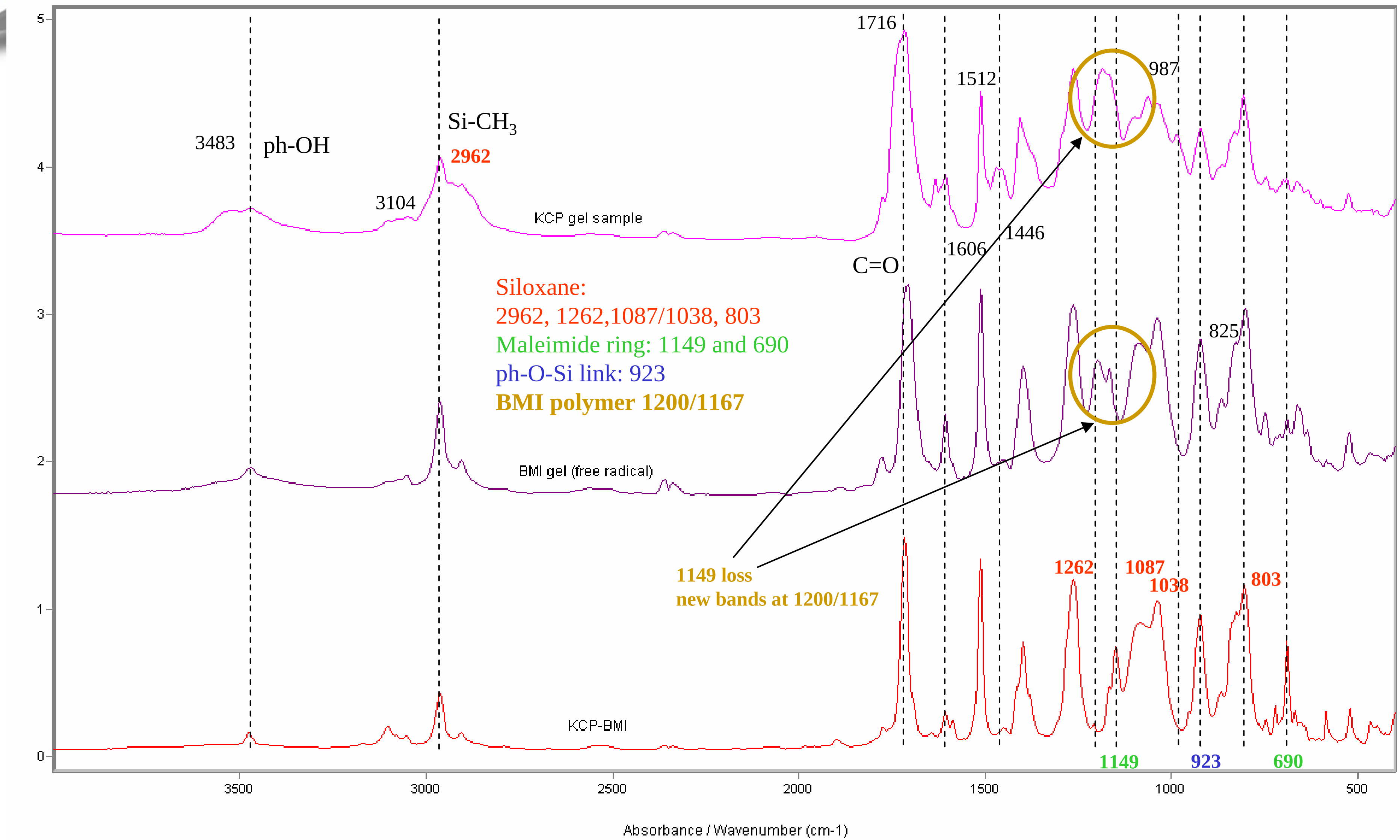
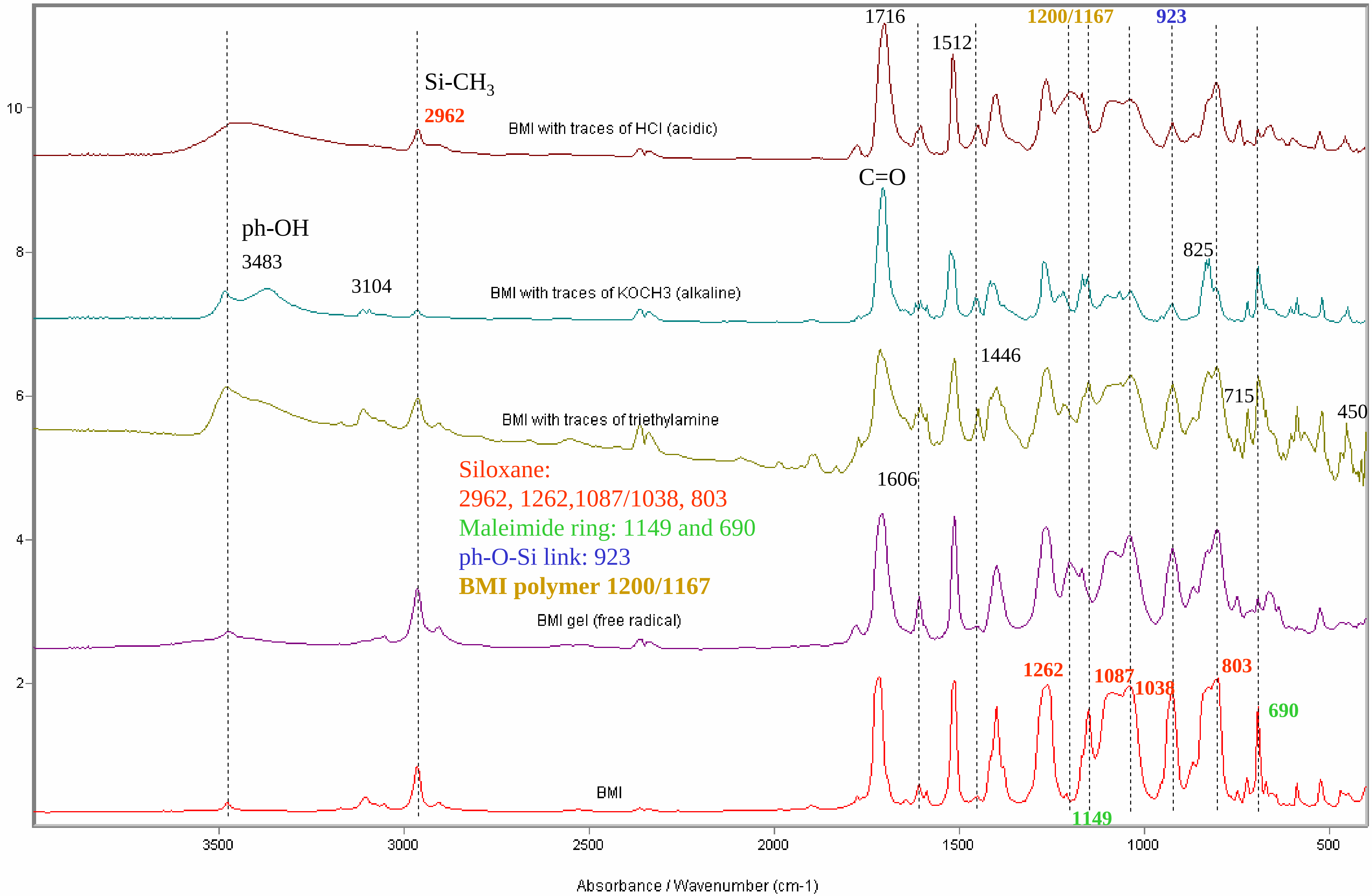
Key markers of polymerized BMI



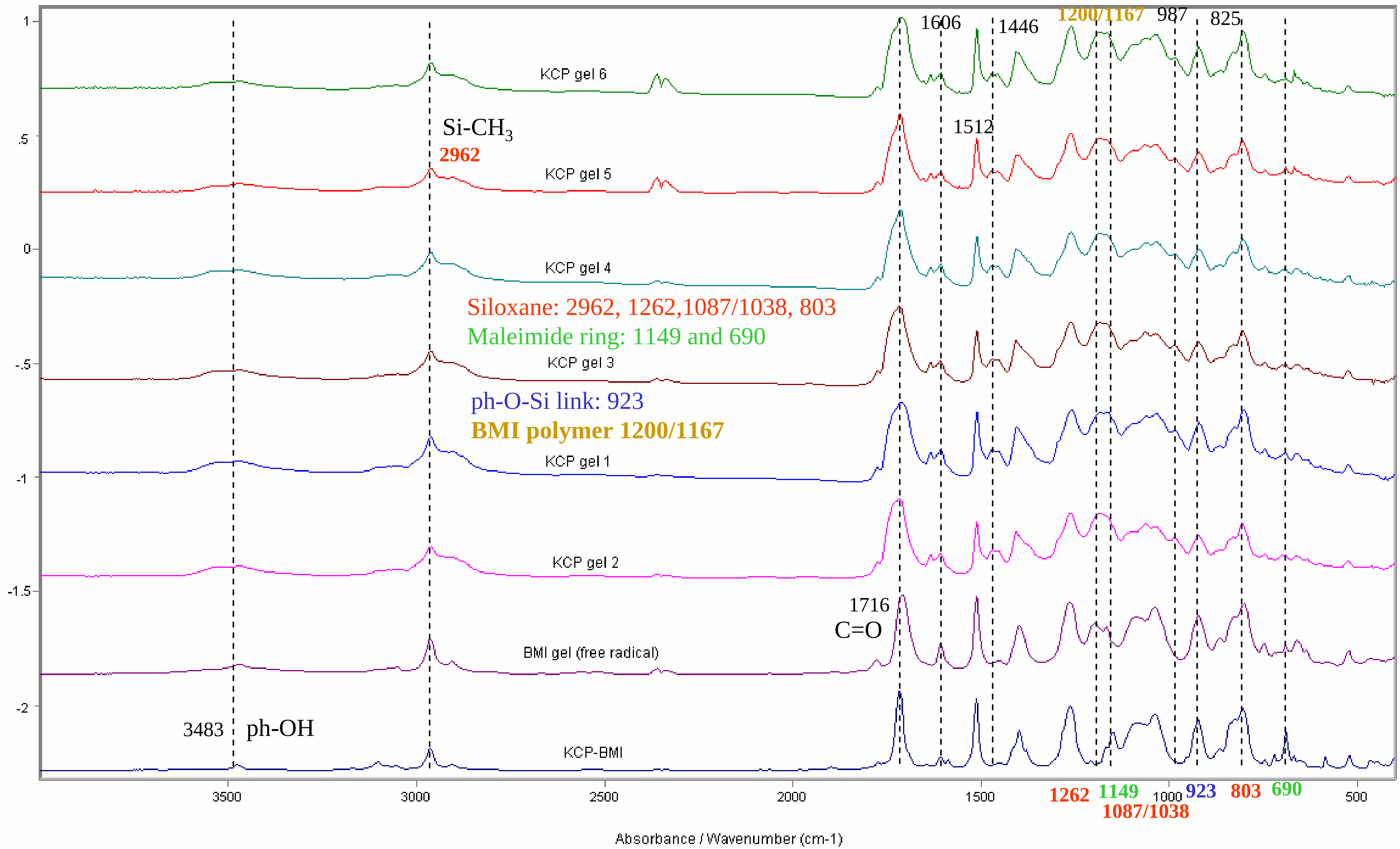
Important: Double bond, maleimide and succinimide ring

BMI stability under different chemical conditions



Acidic is worse than alkaline, hydrolytic and free radical damage

Various KCP samples



All samples show polymerization with double bond and hydrolysis, also some variation in silicone levels

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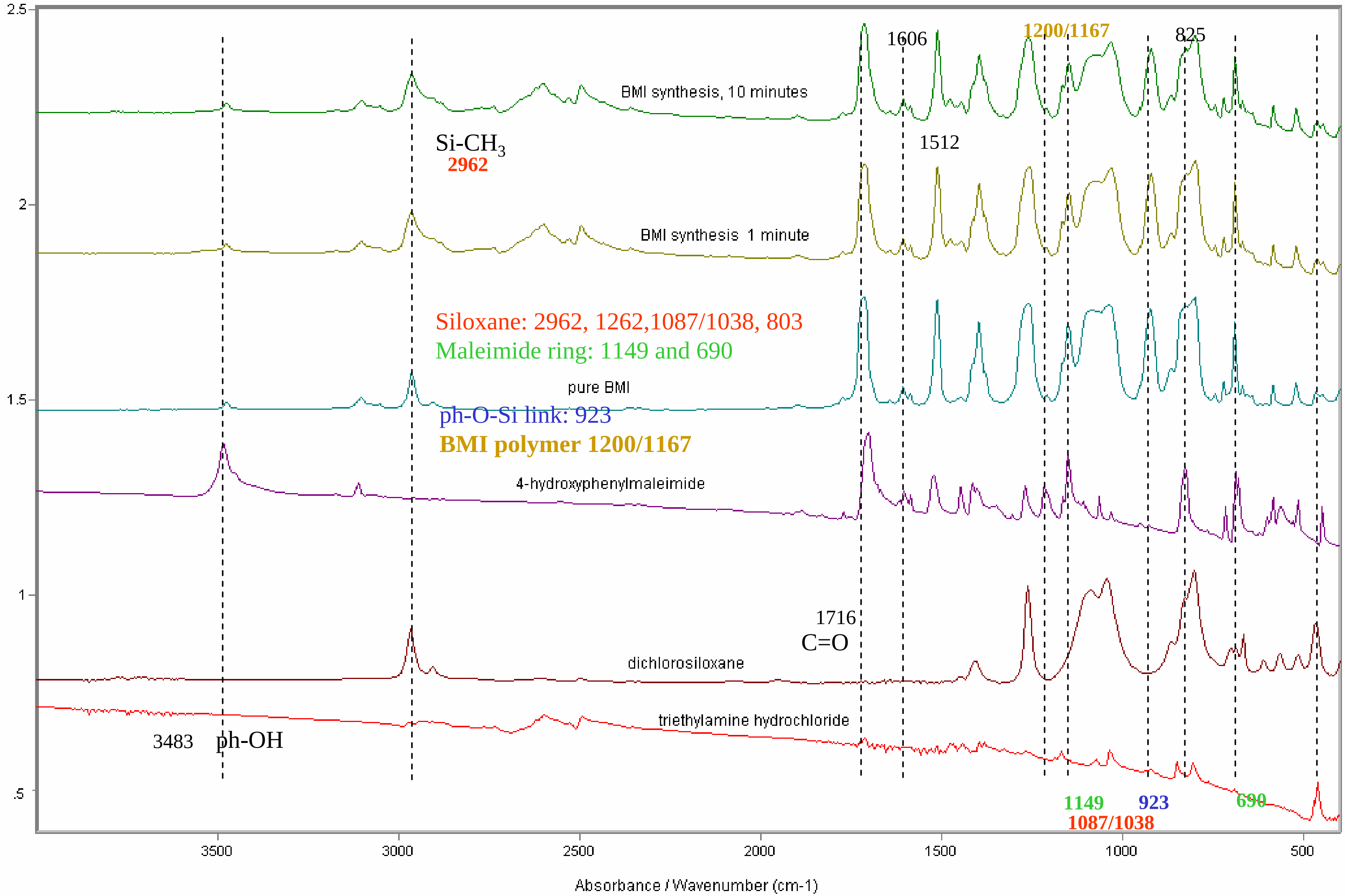
BMI synthesis, speed of chlorosiloxane addition?



Good news, reaction is fast and quantitative within minutes

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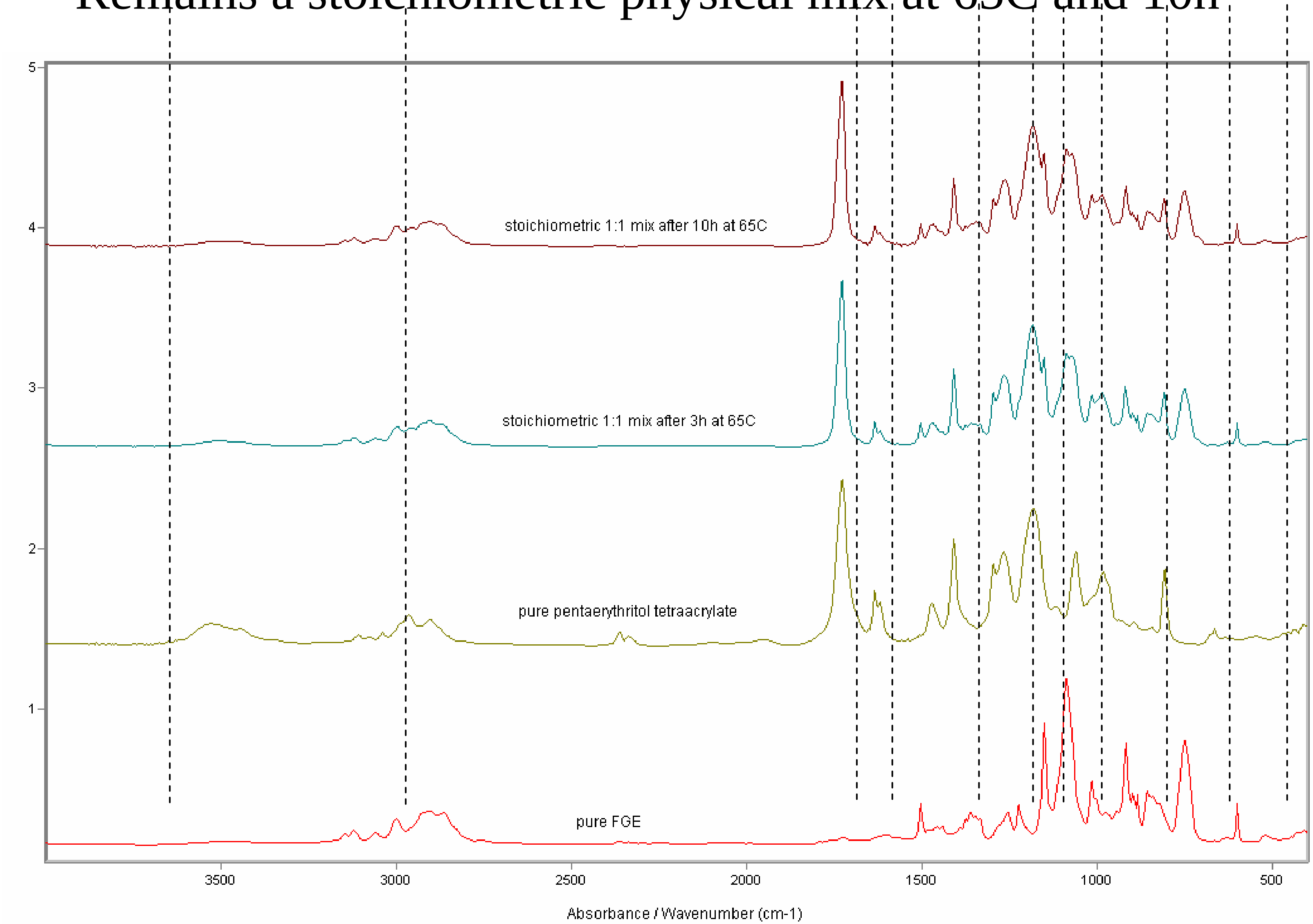
Tetra-acrylate reaction with FGE, Diels-Alder competition?

Part A, BMI+FGE versus Tetra-acrylate +FGE ?

Good news, reaction is very slow and likely not an issue

Remains a stoichiometric physical mix at 65C and 10h



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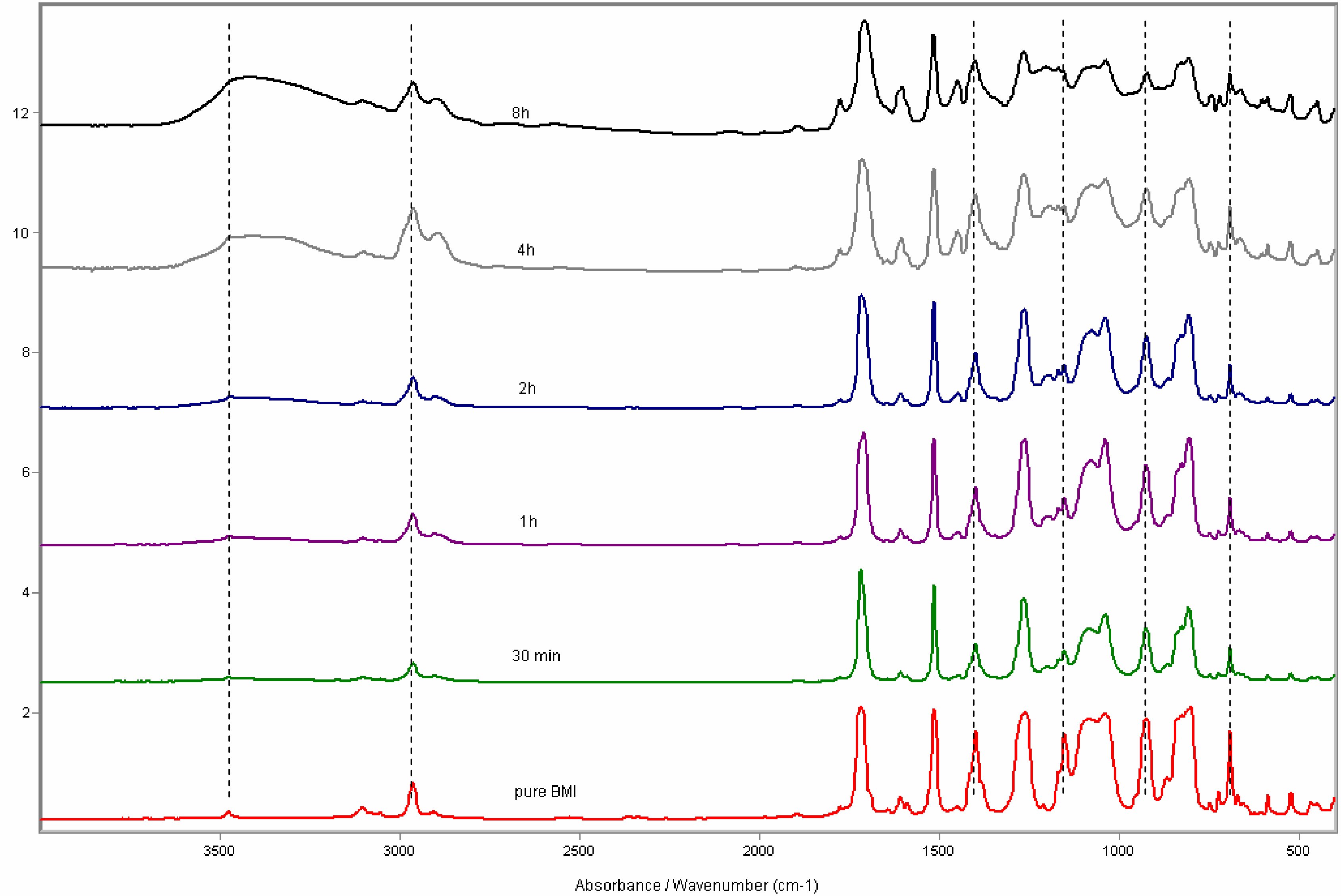
How do we prevent BMI gelation?

- Need reproducible initiation to explore counter measures
- Traces of HCl in MEK sometime lead to polymerization
- Small amounts of H2O appear to retard polymerization

- Simple system, BMI in solvent, under mild reflux, drop of HCl

- THF appears to be more consistent than MEK
- Controlled experiments allow mechanisms to be studied

BMI stabilization in THF, no antioxidant



fast polymerization

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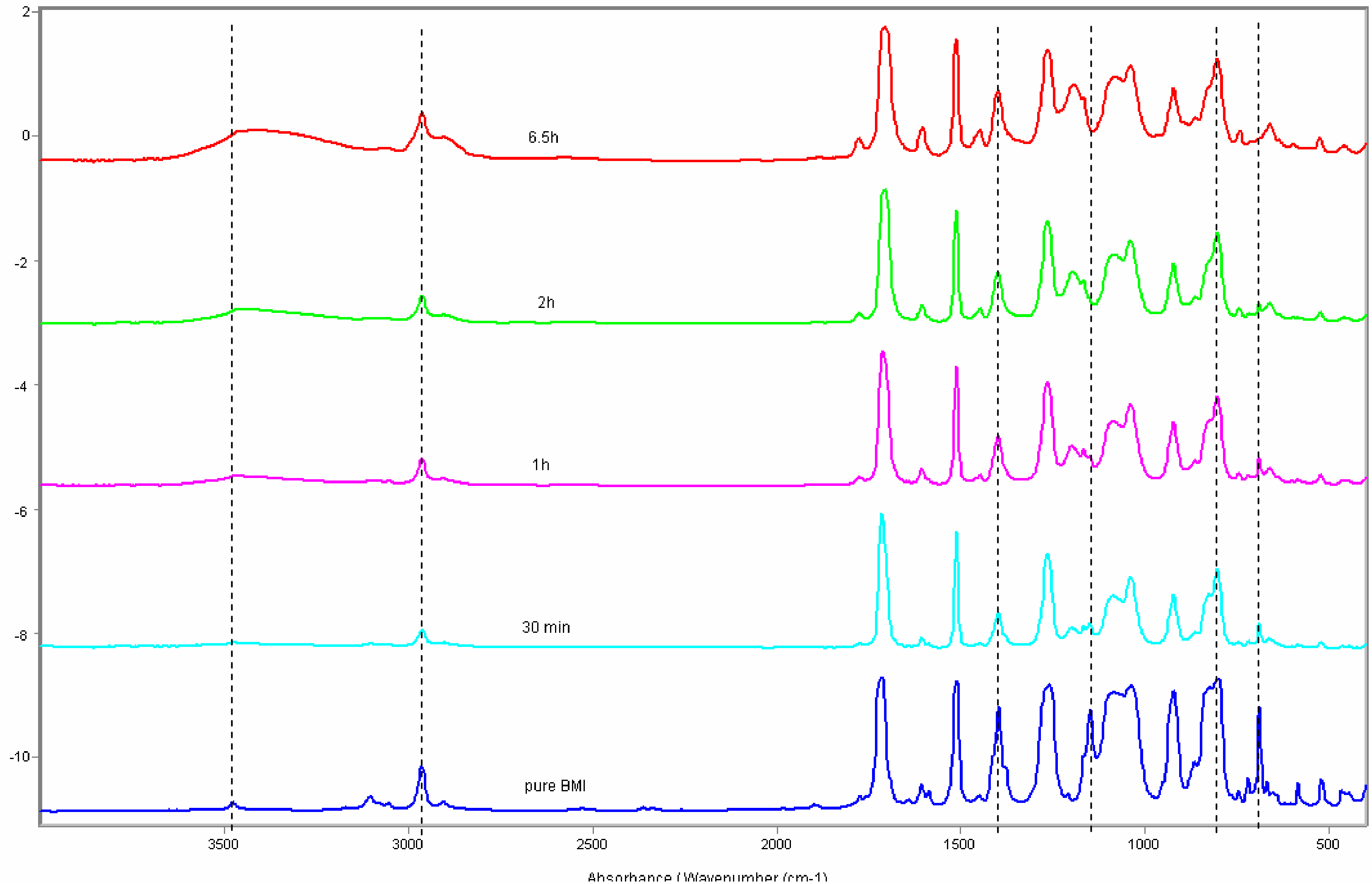
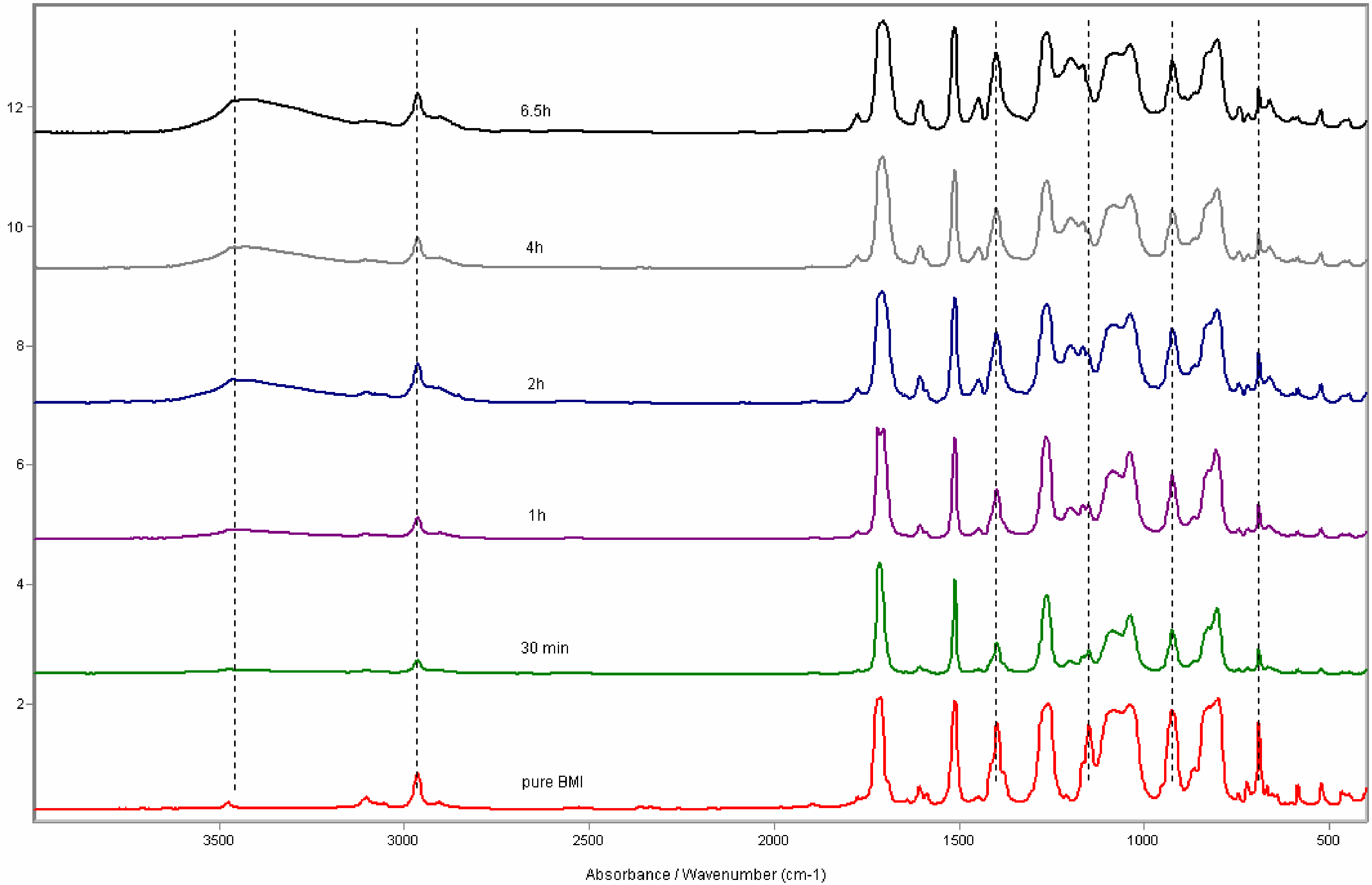
BMI stabilization in THF with 0.2% phosphite antioxidant



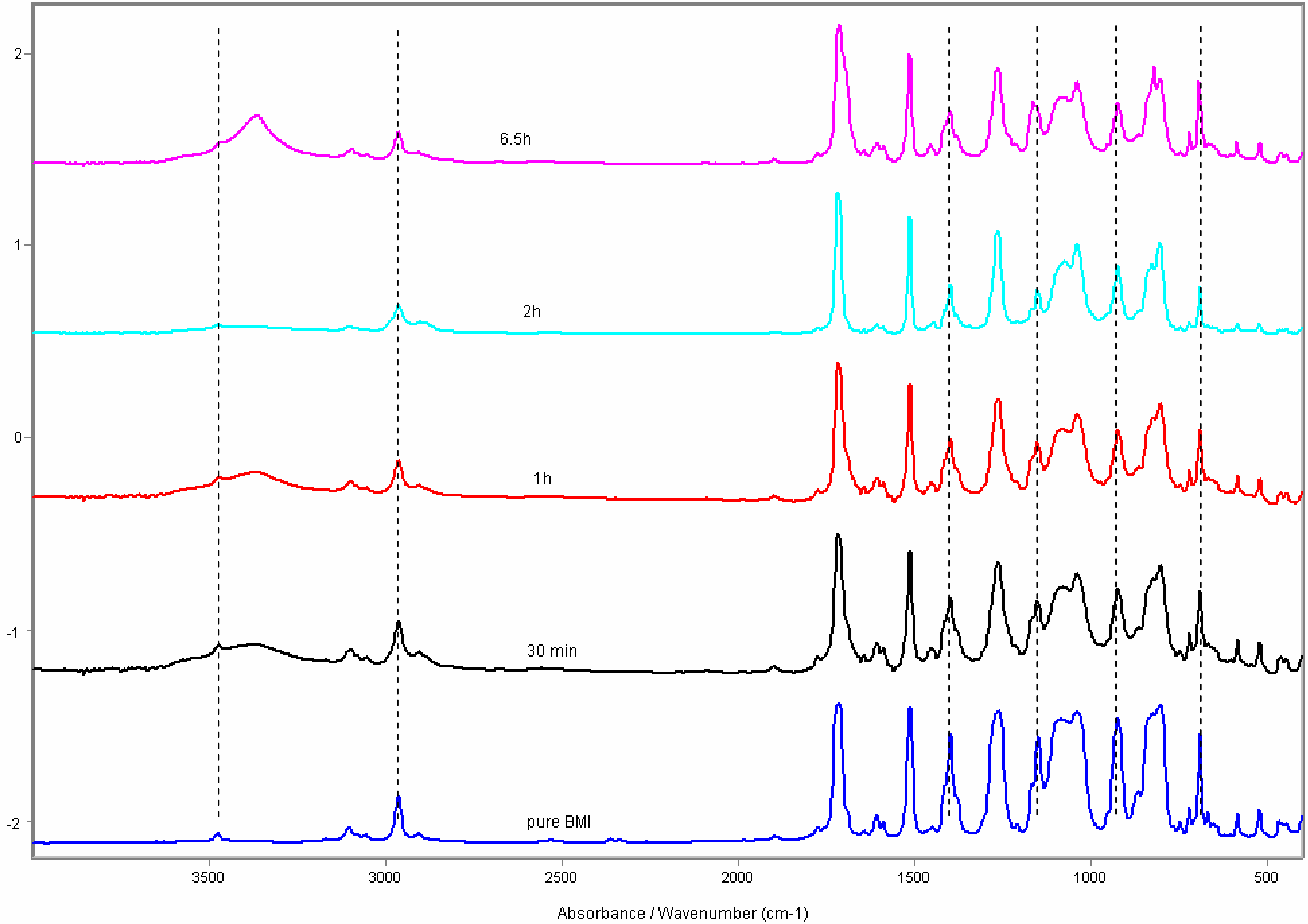
no effect, fast polymerization

BMI stabilization in THF with 0.2% BHT phenolic antioxidant



Some retardation

BMI stabilization in THF with 0.3% BHT phenolic antioxidant



Seems to be stable for some time

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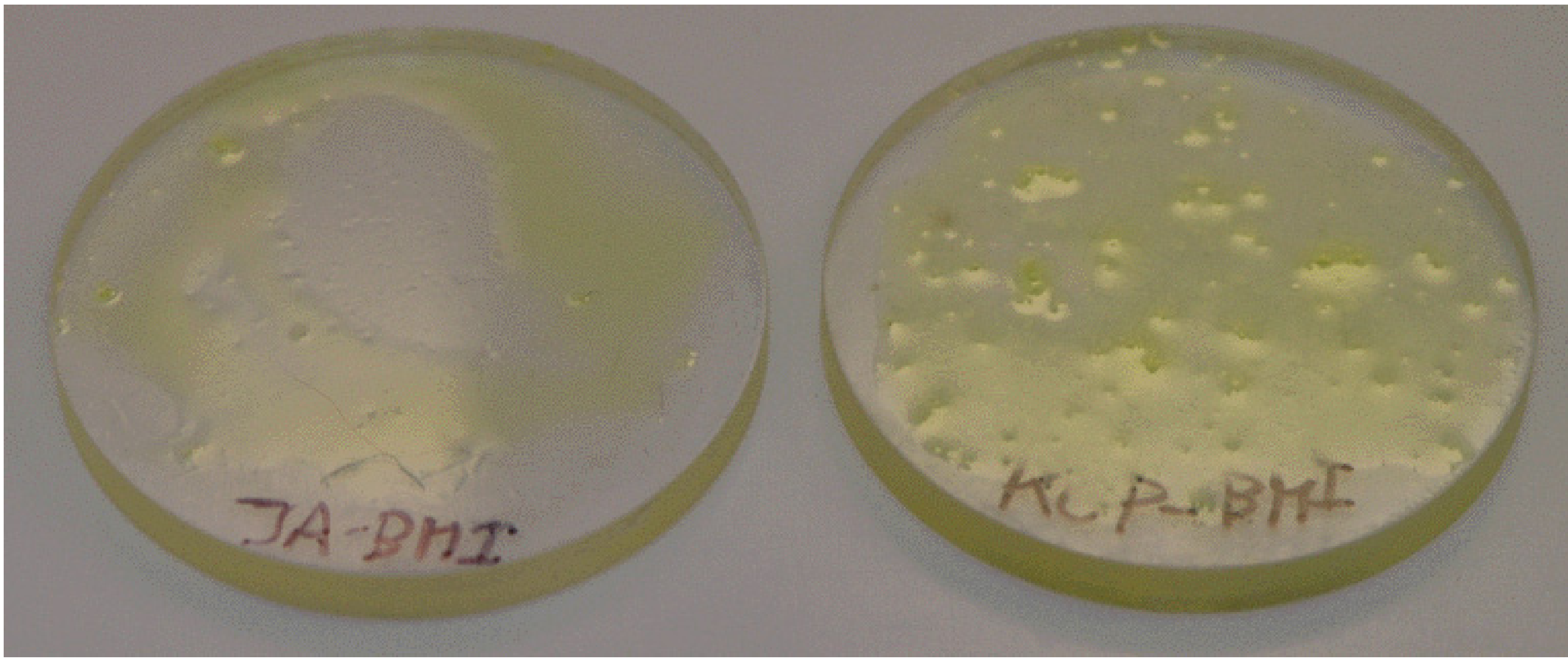
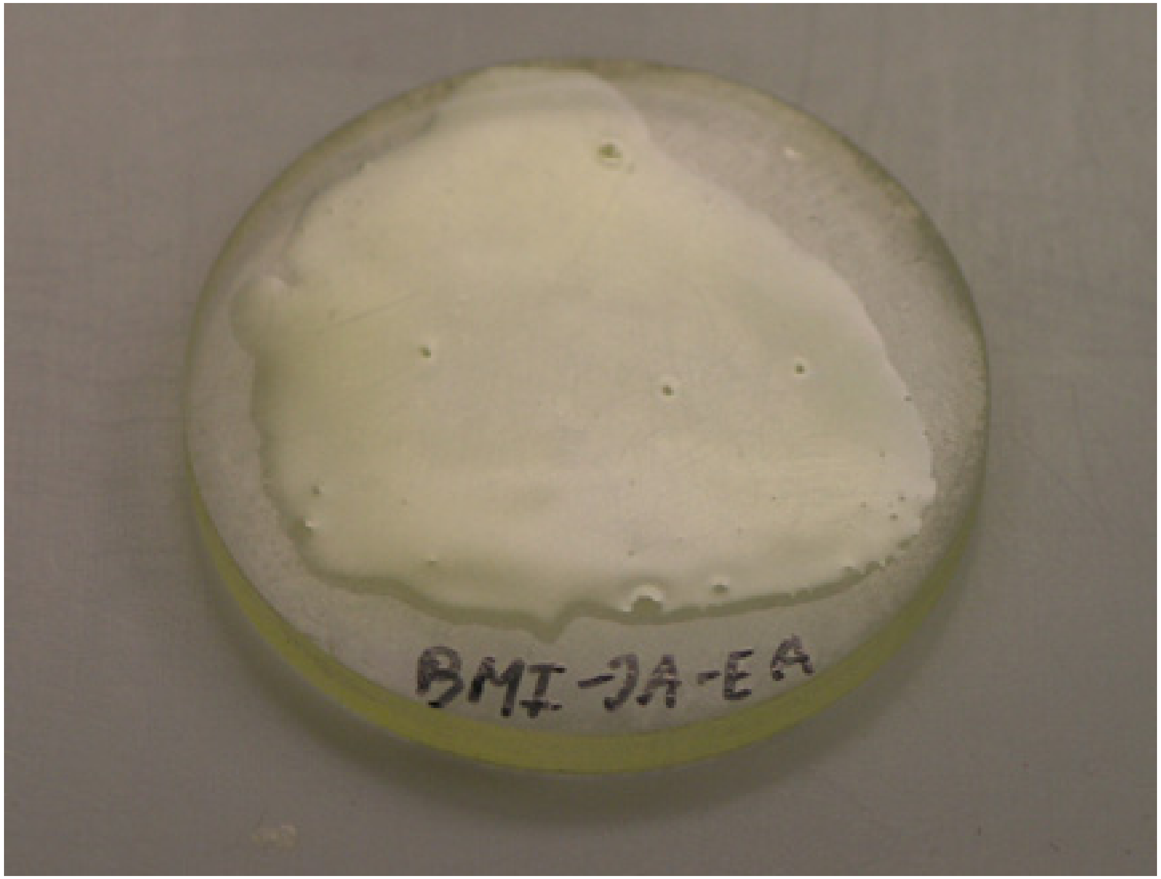
- Visual inspection for gelled particles in BMI
- Very few batches show visual evidence of gelation

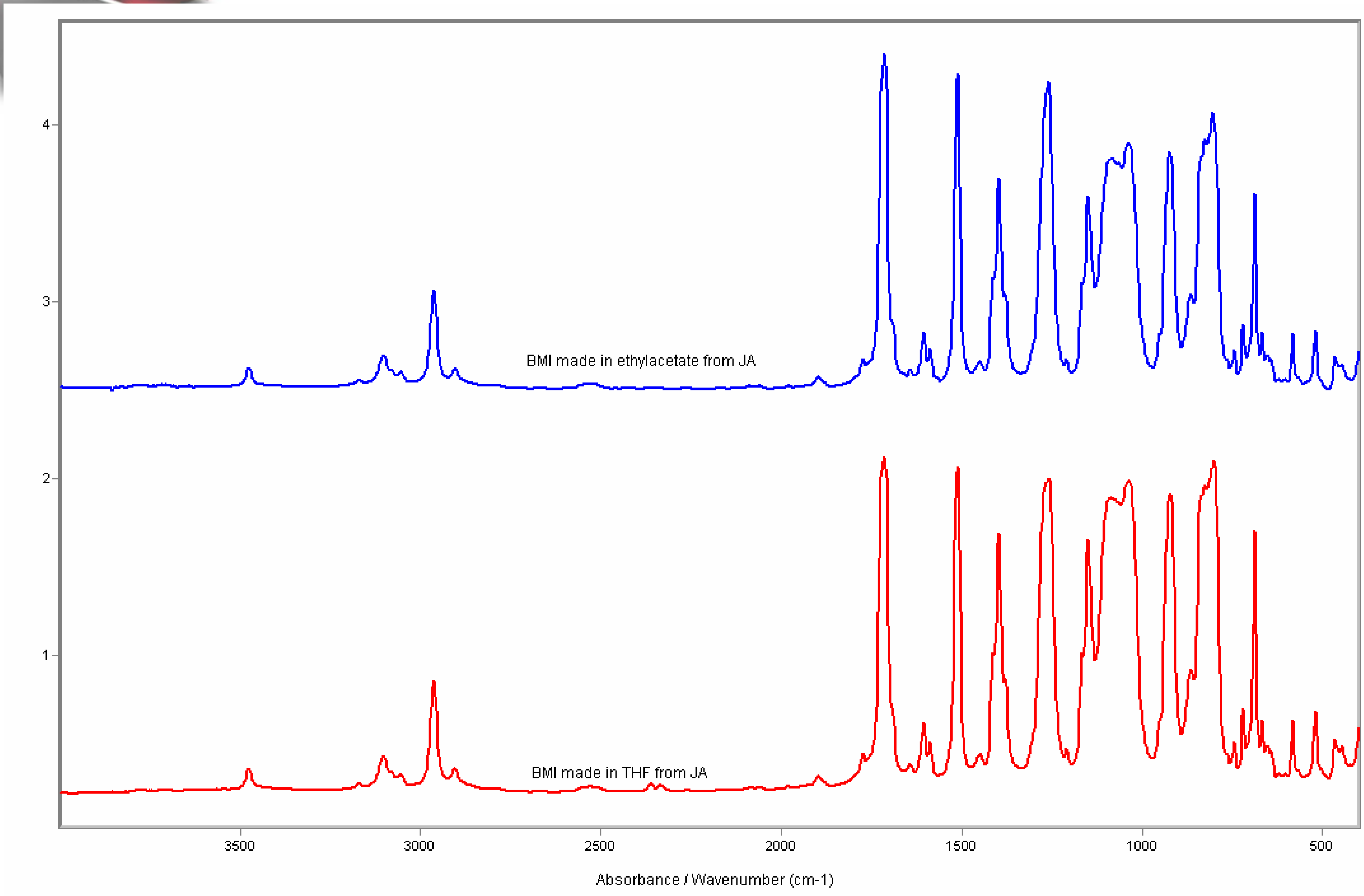


For comparison:

- BMI synthesized in ethylacetate as an alternative solvent
- Nice amorphous film formation



BMI synthesis in ethylacetate



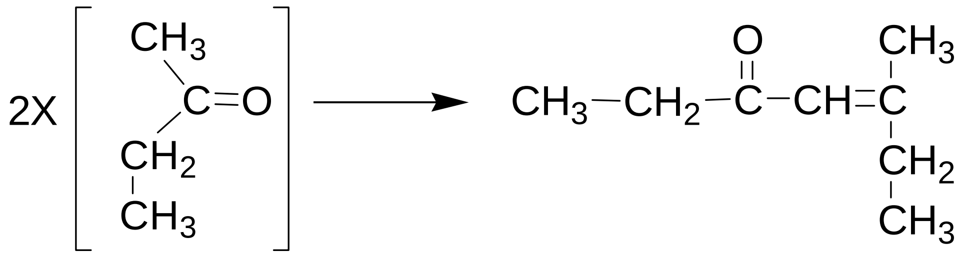
Identical features

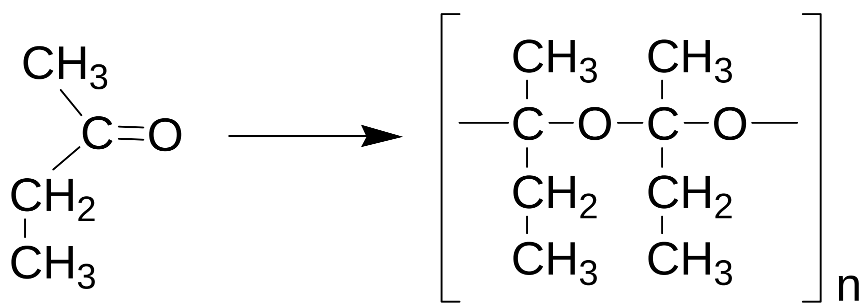
MEK, a reactive solvent?

High mutual solubility with H2O in binary system 28/12%

Self-condensation of MEK to mesityloxide equivalents

Formation of reactive double bonds





Ketone opening to polyether segments

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BMI gelation can continue even at RT when catalysis is present, 88% MEK solvent !

Conclusions

• BMI and other reagents in the Part A can potentially pre-react
• IR is a very suitable technique to probe for reactions of BMI
• Nearly all bands have been assigned, specific bands for bridge linkage and ring vibrations, double bonds
• NMR could be used, but longer acquisition and some peak overlap
• All observed gels involve double bond reactions
• BMI also is very sensitive to hydrolysis
• Remedies: AO's appear to retard polymerization, but minimum concentrations are required
• Solvent change can be beneficial as it reduces self-initiation, will also improve yields
• Goal: Improve production purity and material consistency from 96% to 100%

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