Characterization of Norbornene–Carbon Monoxide Copolymers

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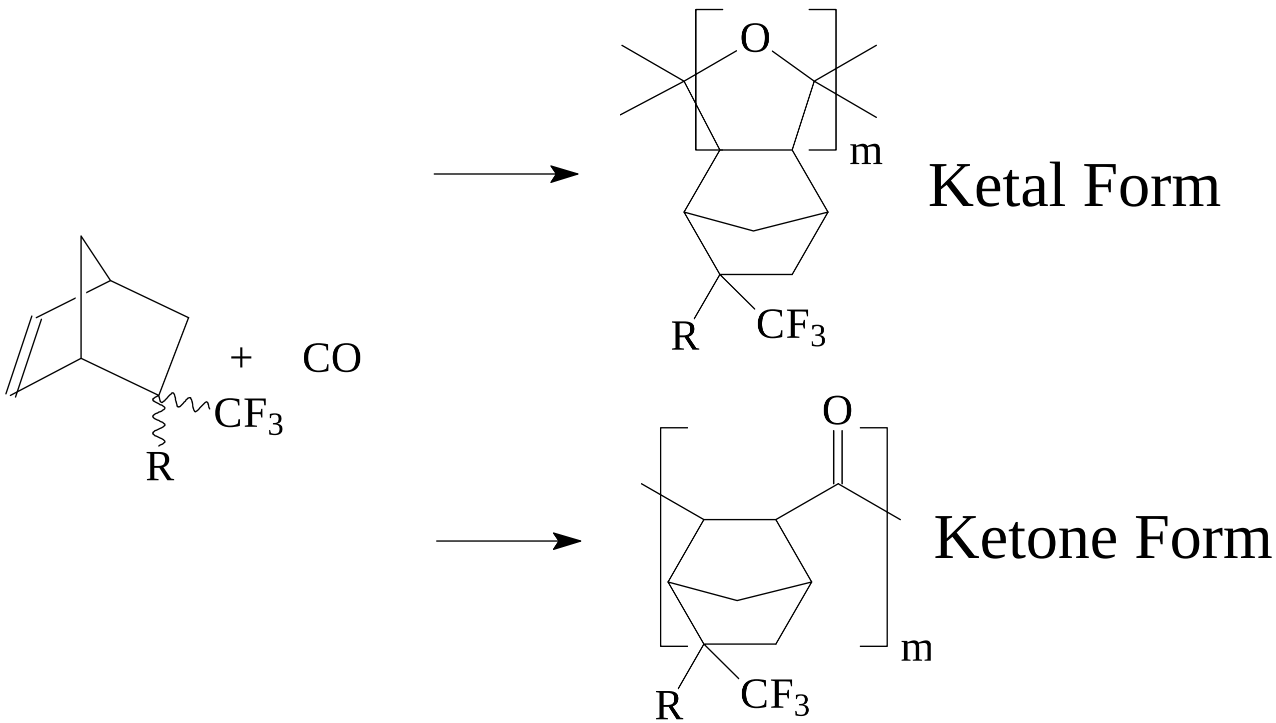
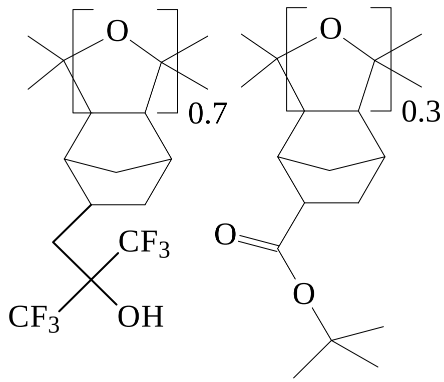
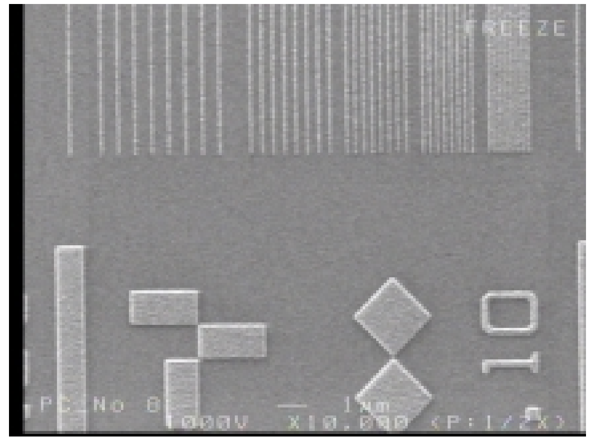
Carbon Monoxide Copolymerization

- Successful co-polymerization of various transparent geminal disubstituted norbornene monomers ($-CF_3$)
- Introduces polar nonacidic groups



First Imaging Experiments





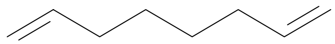
High contrast, High resolution,
No swelling, No residues

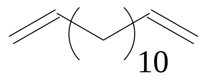
Severe line edge roughness

Mw 1600 → We need higher molecular weight !!

Addition of Cross Linker to Increase Mw

Terminal Olefins

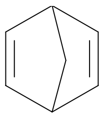




No cross linking

Too slow to react

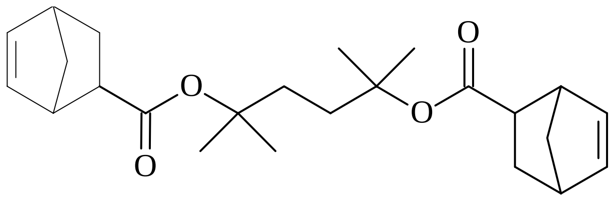
Cyclic Diene



Hard to control Mw

Too much cross linking

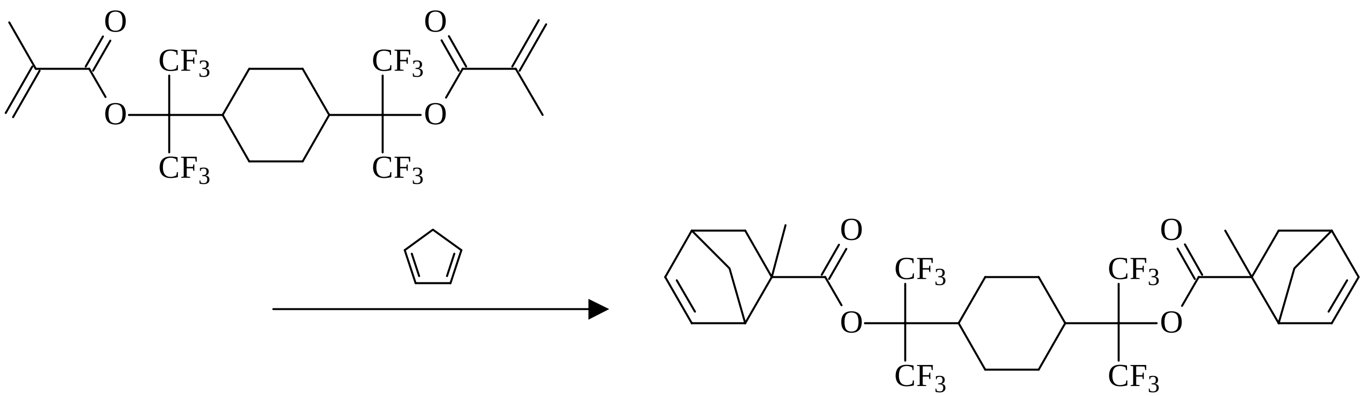
Linked norbornene



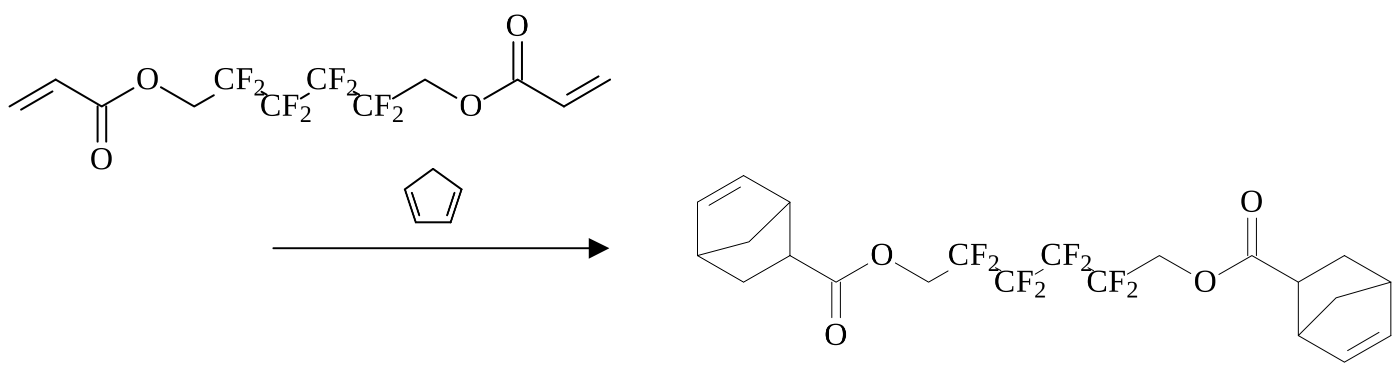
Mw 6000

Just Right !

Synthesis of Crosslinkers



Insoluble?

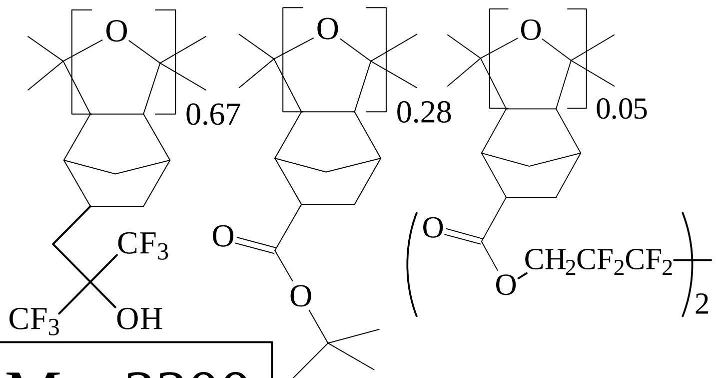


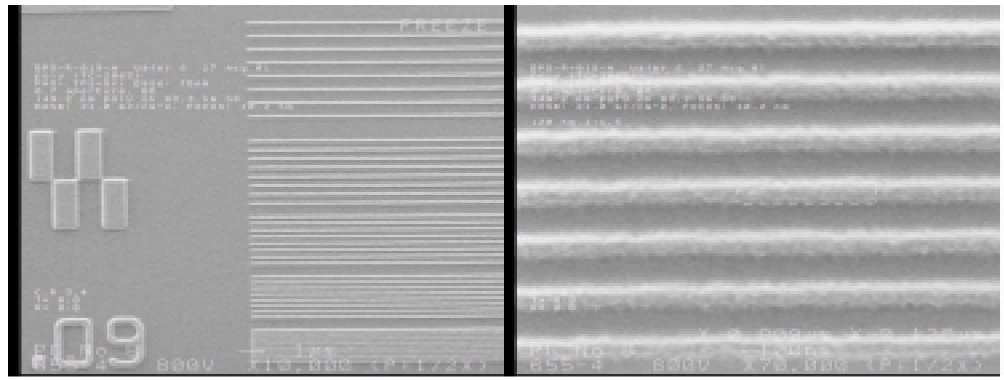
Liquid

Imaging Results

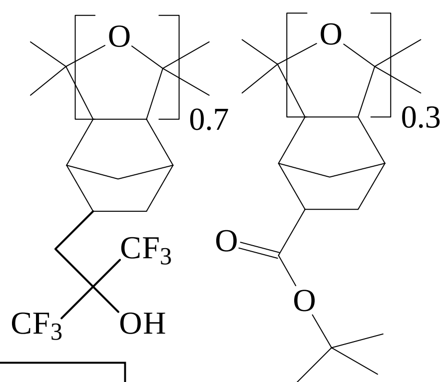
Resist Polymer

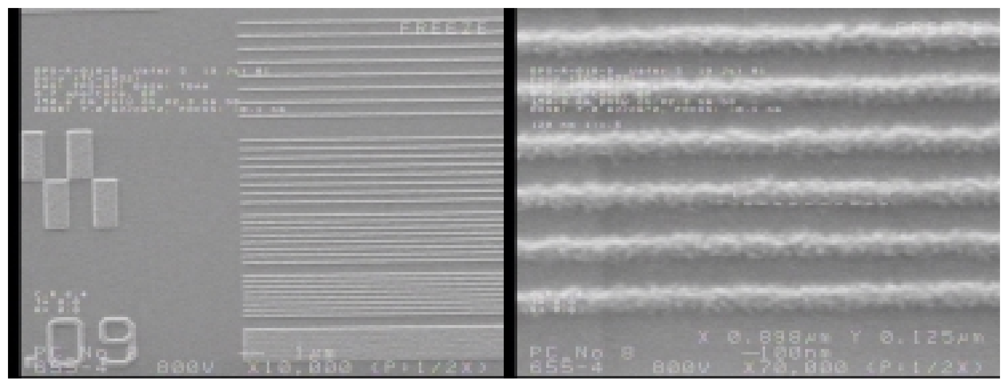
90nm Binary mask 120nm 1:1.5





Mw 3300



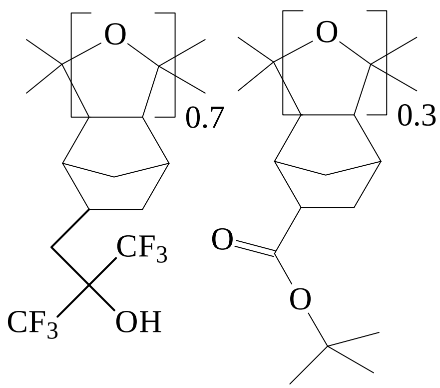


Mw 1600

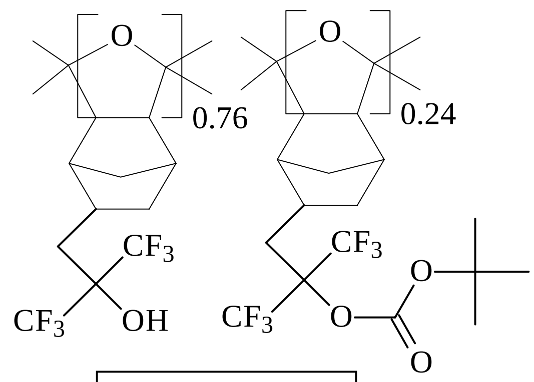
Increasing molecular weight improves LER

Absorbance of Polymers

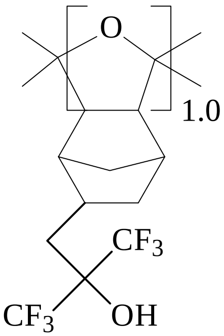
CO Polymer



3.7 μm^{-1}

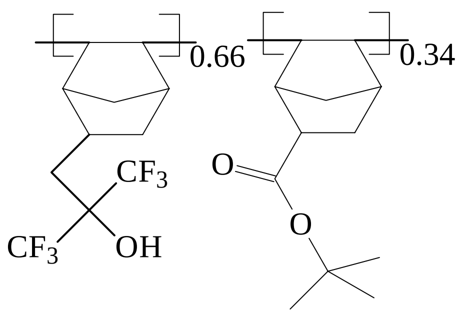


2.8 μm^{-1}

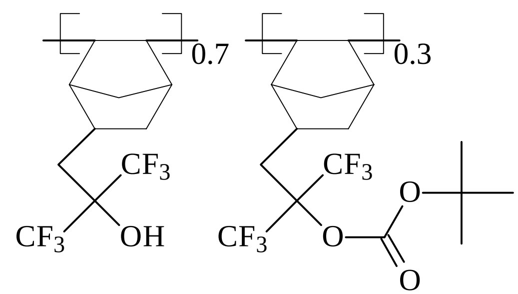


2.6 μm^{-1}

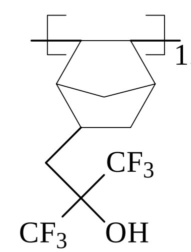
Metal Cat. Vinyl Add.



2.7 μm^{-1}



2.2 μm^{-1}

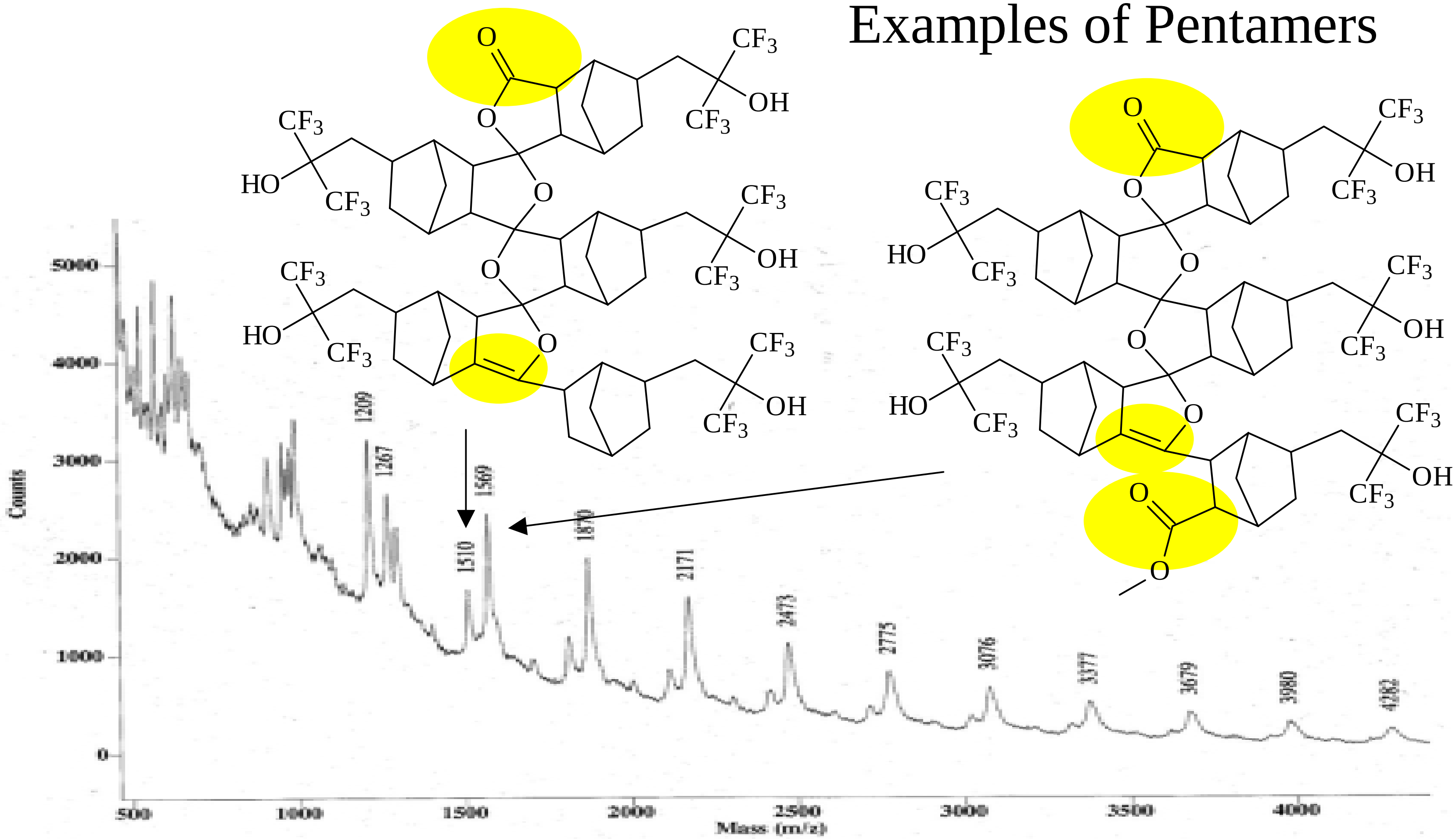


1.5 μm^{-1}

What is the reason for this difference??

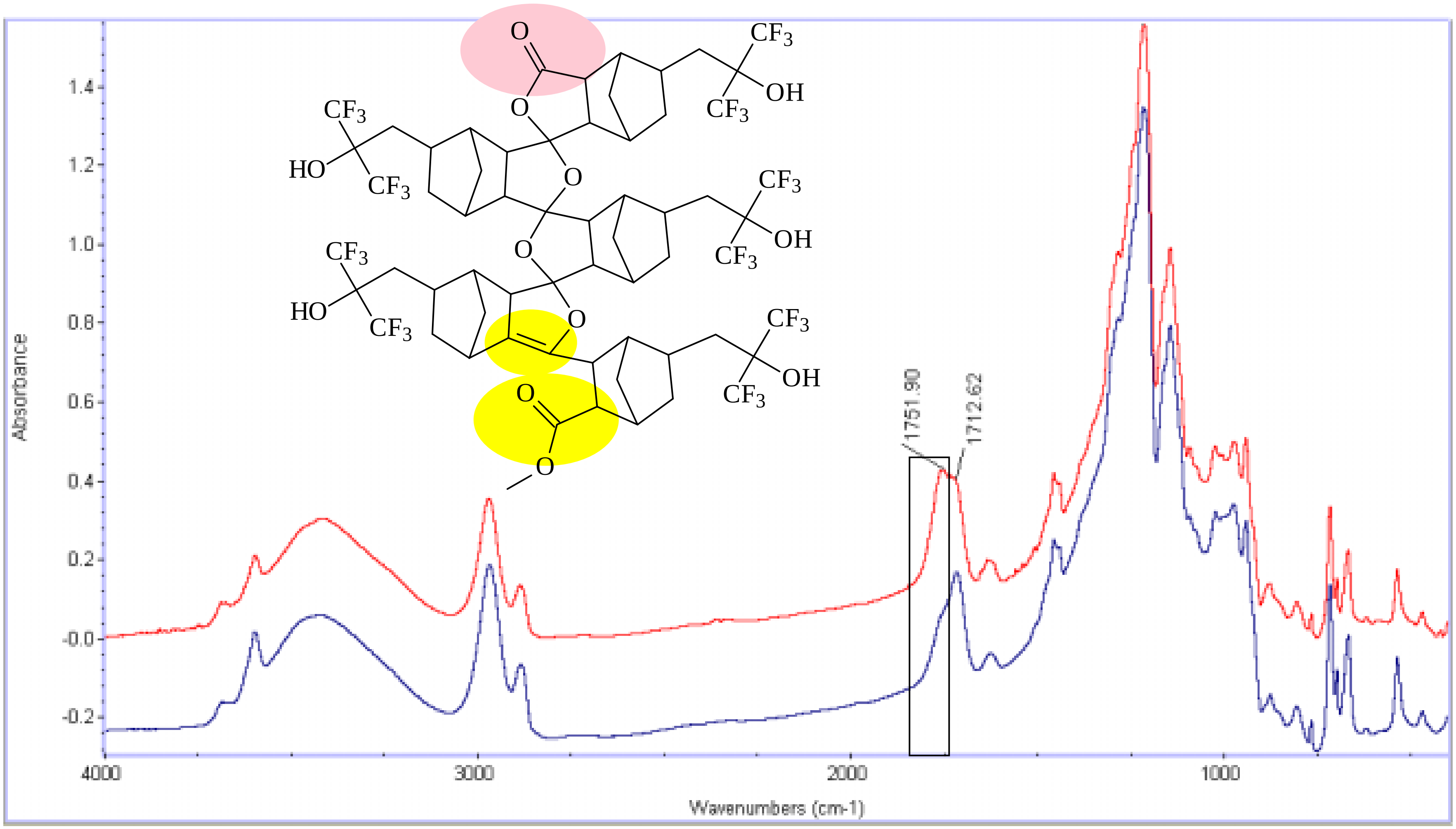
Plausible Polymer Structure

Examples of Pentamers



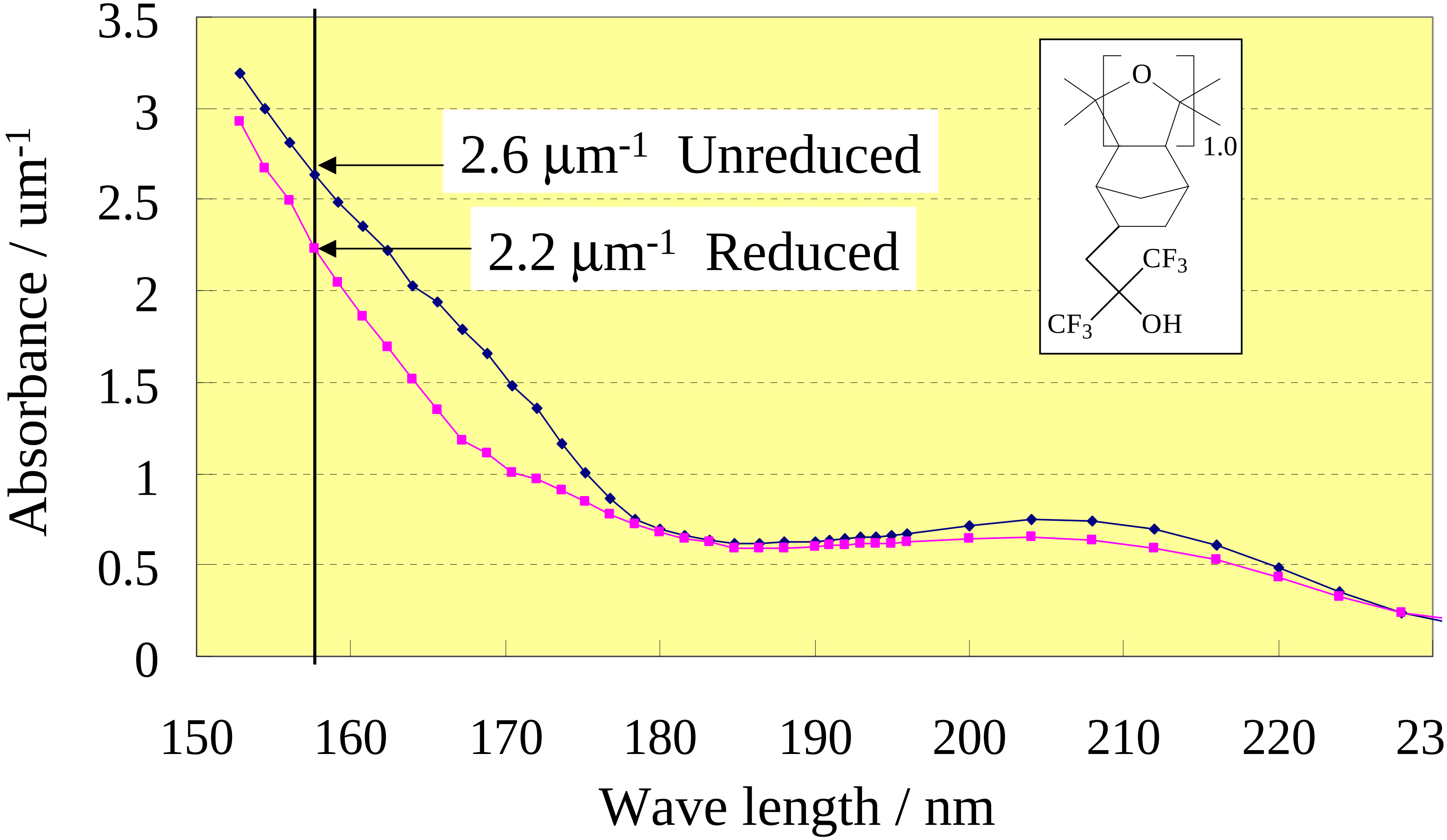
Lactone and ester groups are absorbing !!

Polymer End Group Modification



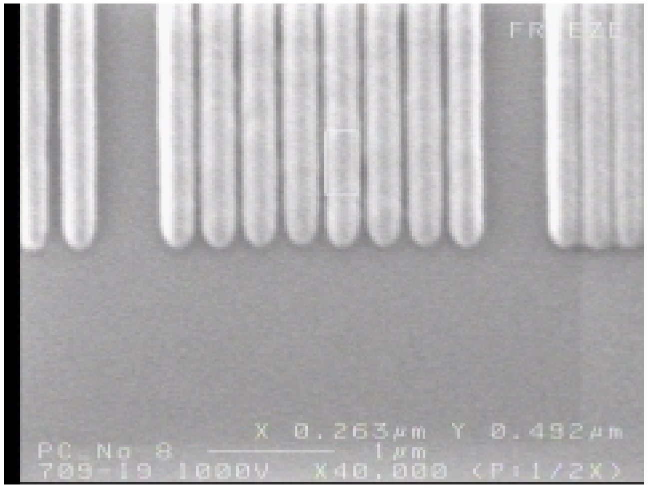
Absorbance of Modified Polymer

- Reduction of lactone improves transparency!!

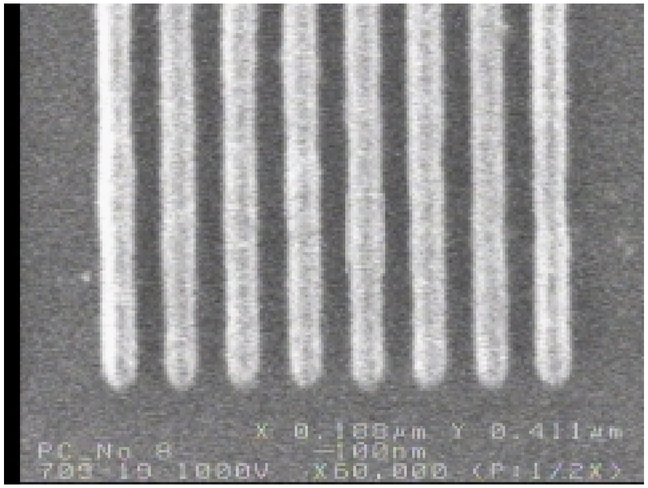


CO Copolymer as DI

- Interesting platform as imaging polymer.
- Valuable as DI.



130 nm 1:1.5
without DI



130 nm 1:1.5
with DI

Conclusion (CO Polymer)

- Absorbance improved by end group modification.
- Feature roughness improved by increasing Mw.

Future Work

- Optimization of crosslinker structure and feed.
  → Lower roughness.
- Reduce both end groups.
  → Higher transparency.
- Continue to explore as DI.

Acknowledgement

- Brian Trinque
- Brian Osborn
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- Clariant
- Central Glass
- SEMATECH

Dissolution Inhibitor Studies

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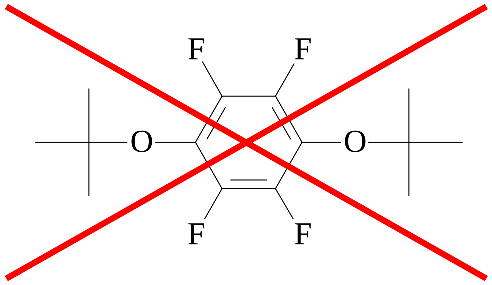
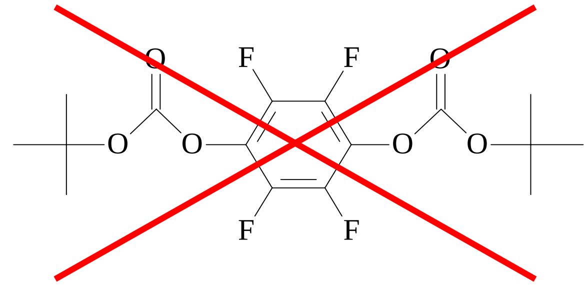
Required properties of DI

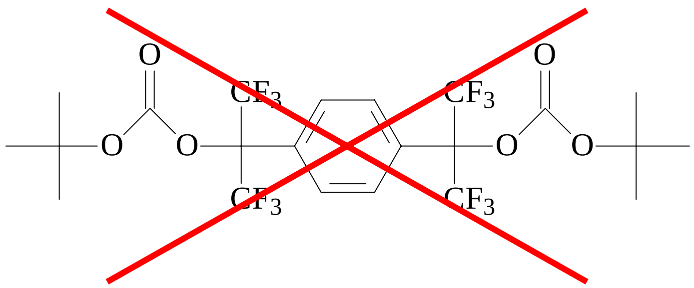
- ✓ Inhibit base polymer
- ✓ Switchable
- ✓ Transparent
- ✓ Soluble in casting solvent
- ✓ Low volatility
- ✓ Etch resistant
- ✓ Phase compatible with base polymer
- ✓ Synthetic access
- ✓ Reproducibility
- ✓ Cheap, non-toxic, etc.

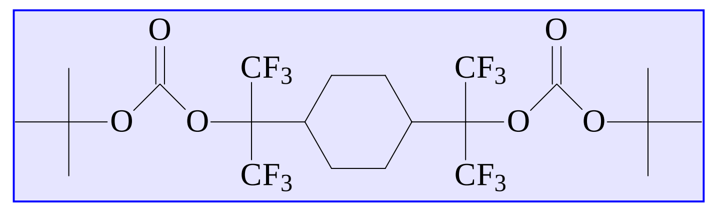
- CO copolymer works, but monomeric DI is an attractive alternative.

Monomeric DIs





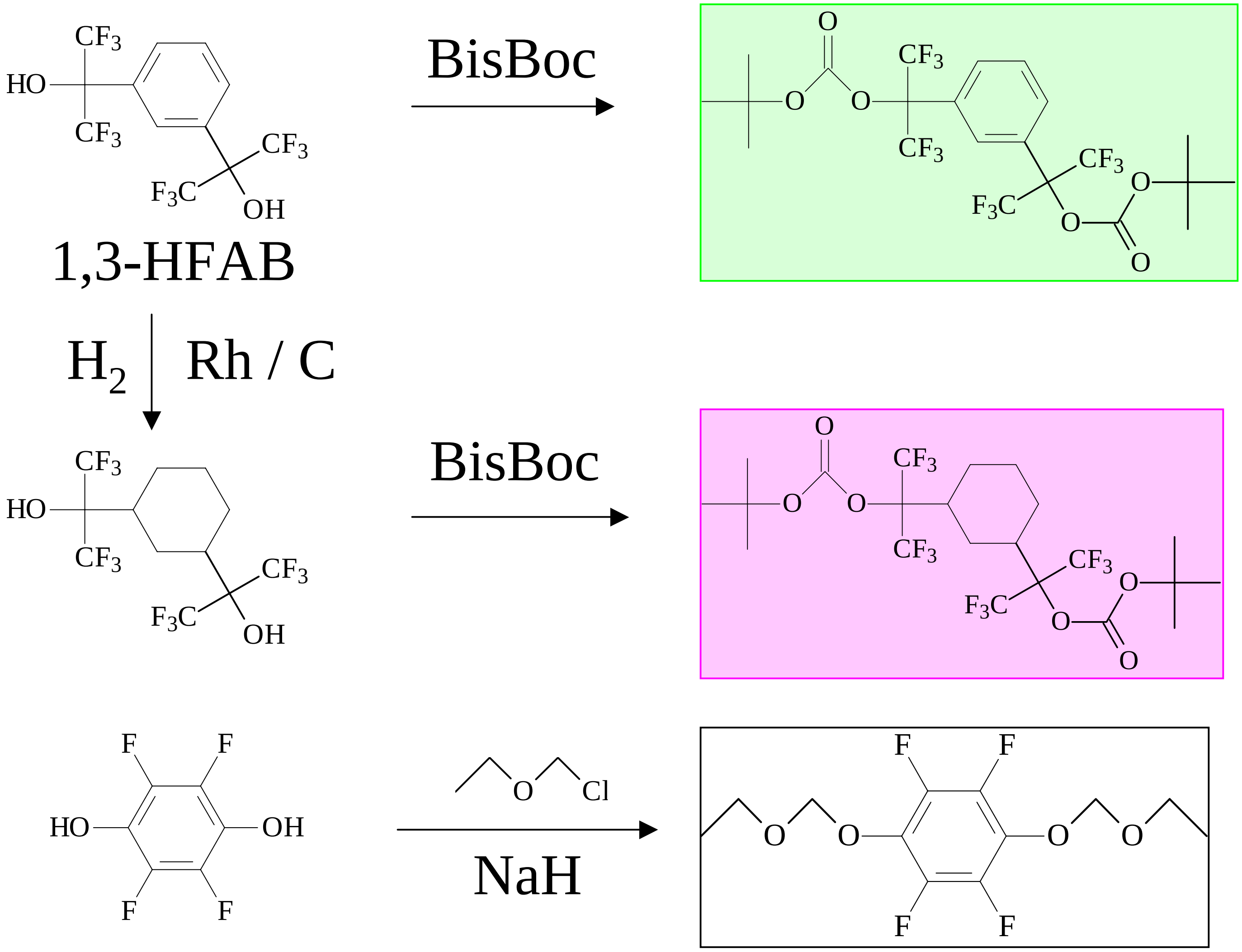




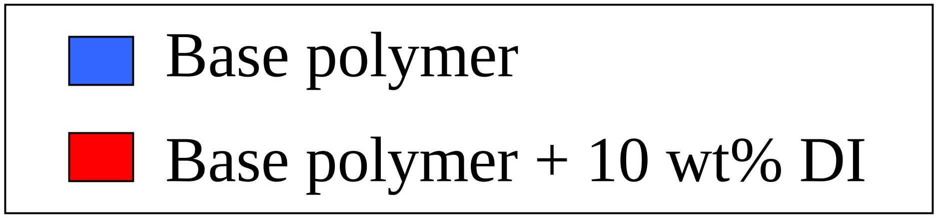
Solubility Test   Inhibition Test

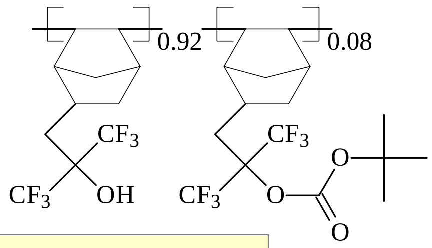
More DIs !!

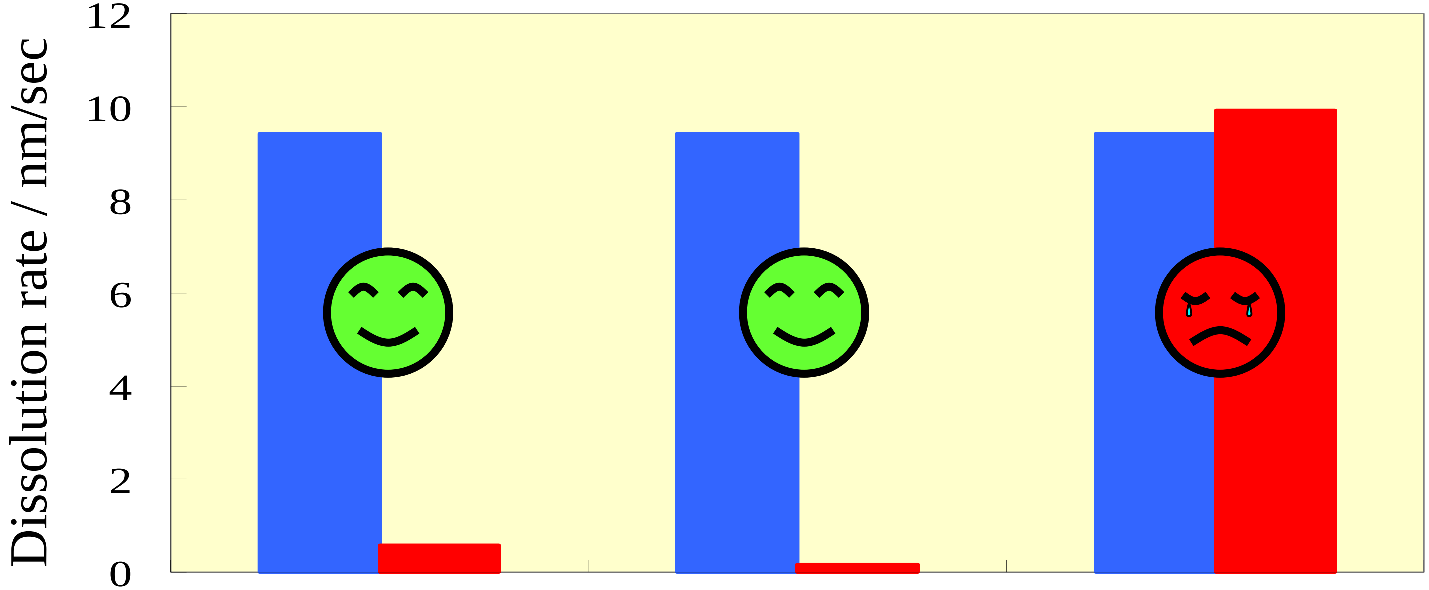
Synthesis of Alternative DIs

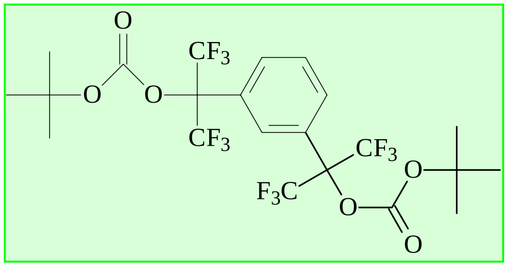


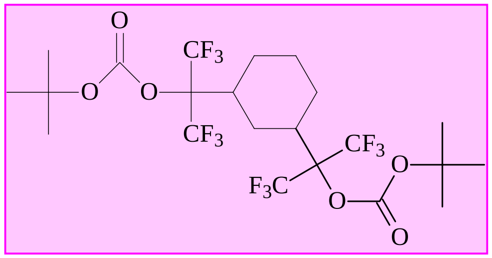
Dissolution Inhibition Test

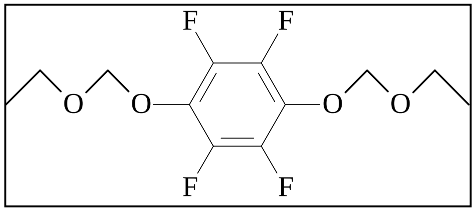












Estimating the Absorbance of DIs

Absorbance measurement technique

- VASE: The sample must be a film.

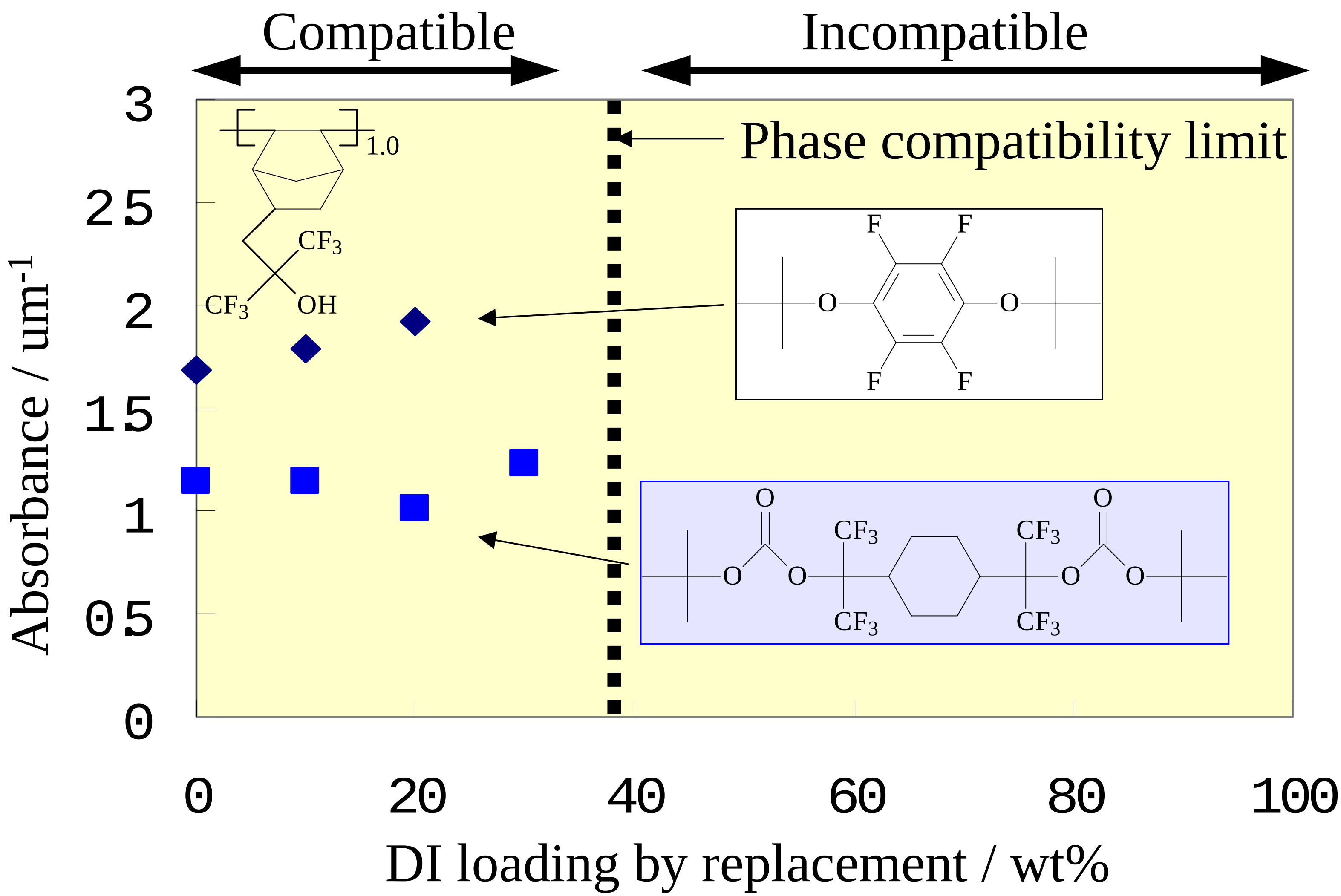
  → Monomeric materials do not form films.
- Gas phase: The sample must be volatile.

  → Useful DIs must be non-volatile !
- Solution: No solvent is transparent enough at 157 nm.

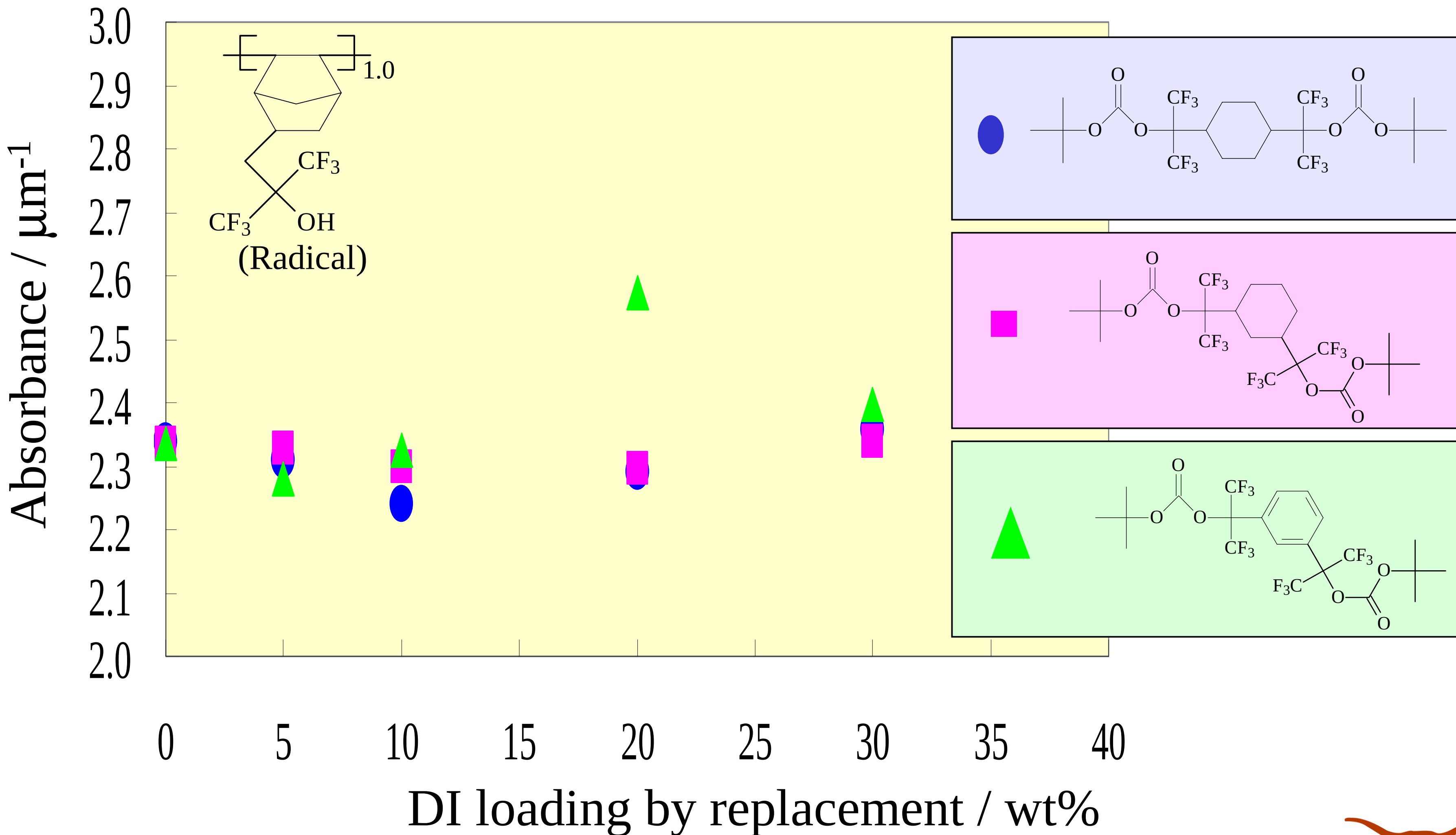
  → Not realistic.

There is no straightforward measurement technique!!

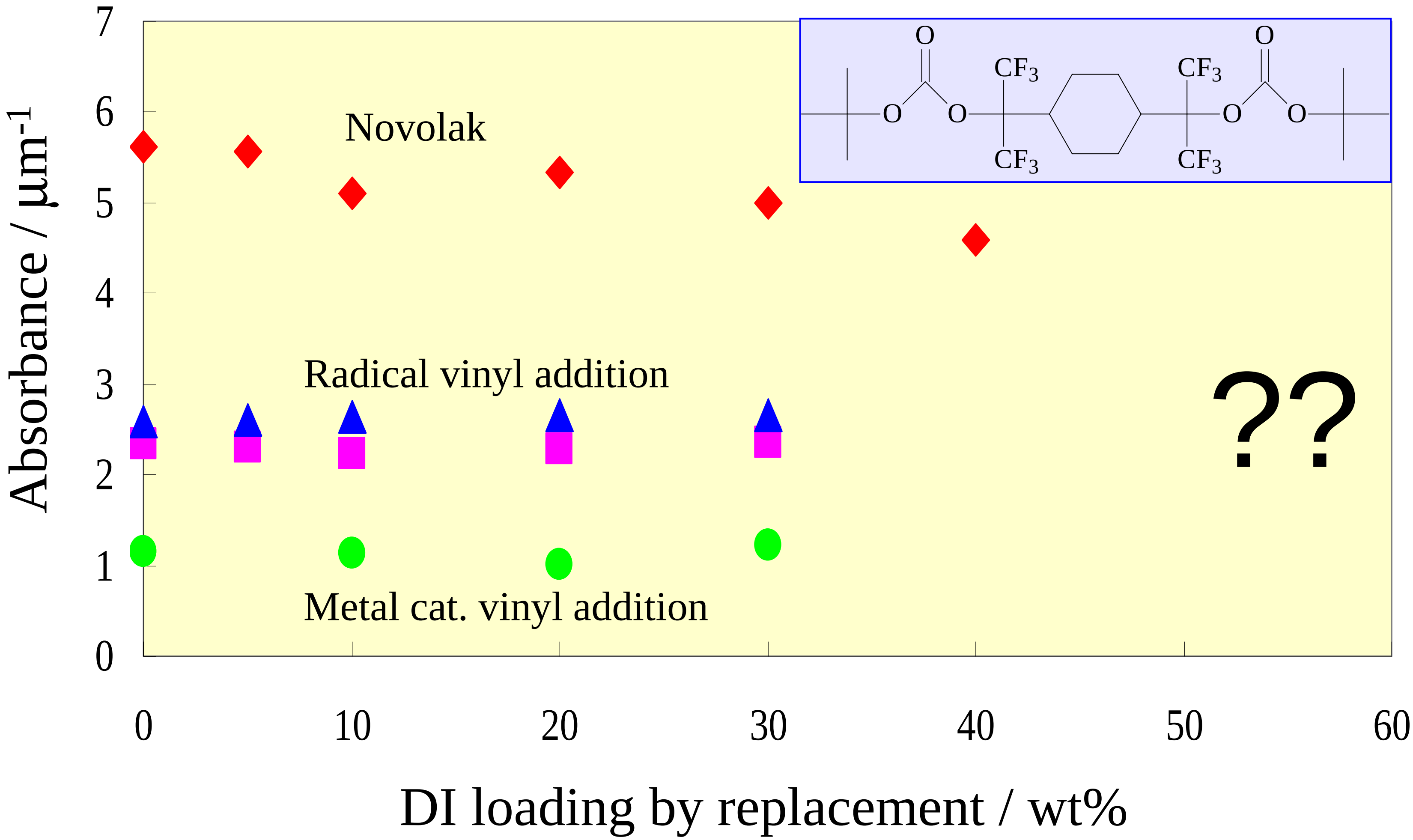
Dilution Experiment



DIs in a Polymer Matrix



DI in Various Matrices



Conclusions (DI)

- We have 3 powerful DIs.
- Attempted to quantify absorbance
  - – Dilution method requires more work.
  - – Considering alternatives.
    - Solution cell?
    - Polymer analogs?
- Continuing DI synthesis activities.
  - – High priority for the next quarter

Acknowledgements

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