

Phenolic Polymer Interactions with Water and Ethylene Glycol Solvents



Justin B. Haskins,¹ Eric W. Bucholz,² Charles W. Bauschlicher,³ Joshua D. Monk,¹ John W. Lawson³

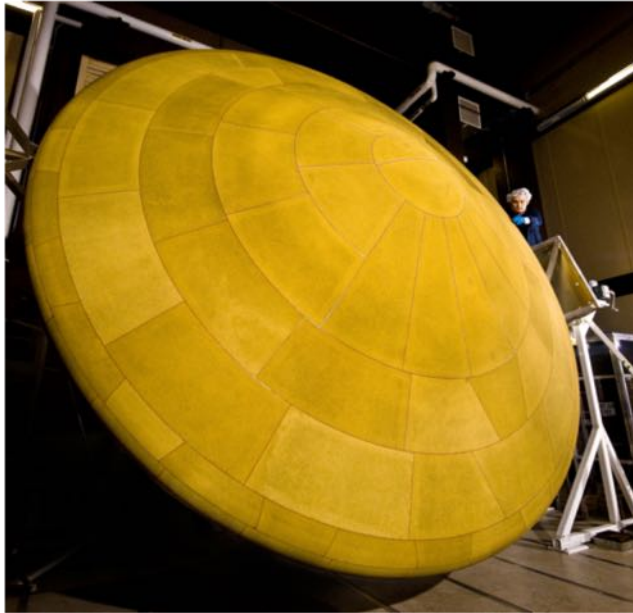
¹AMA, Inc., Thermal Protection Materials Branch, NASA Ames Research Center

²EAP, Thermal Protection Materials Branch, NASA Ames Research Center

³Thermal Protection Materials Branch, NASA Ames Research Center



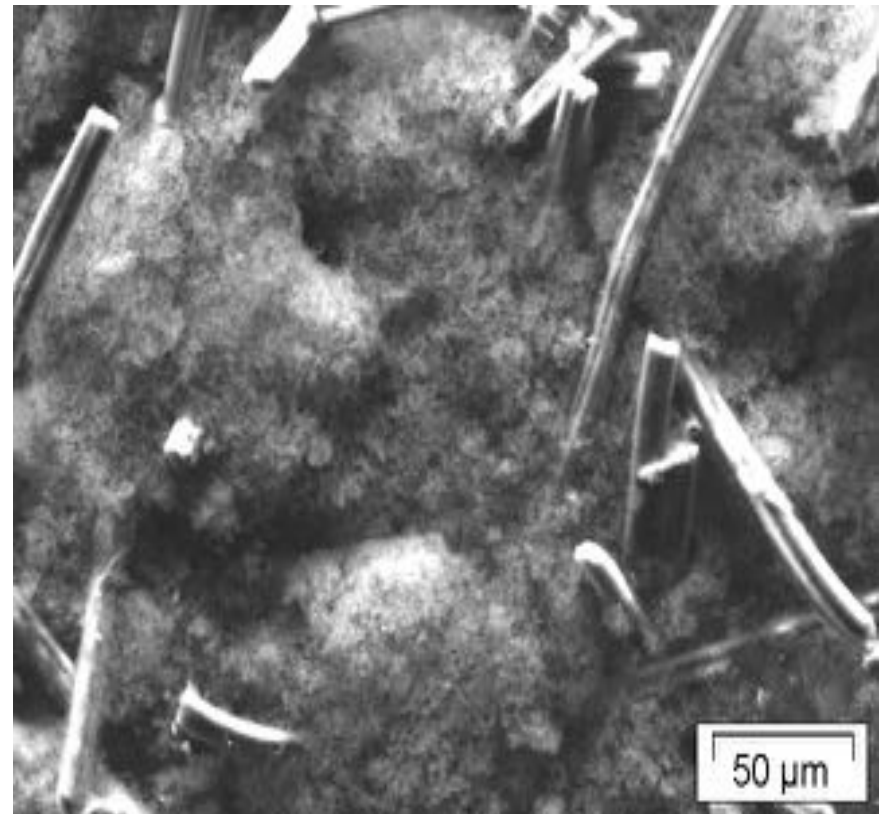
Ablative Heat Shields



Mars Science Lander



Stardust



Ablative Composites for Re-entry
(carbon fiber/phenolic matrix)

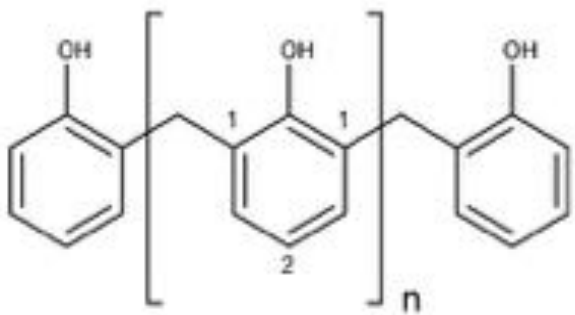
Stackpoole, et al. AIAA (2008)



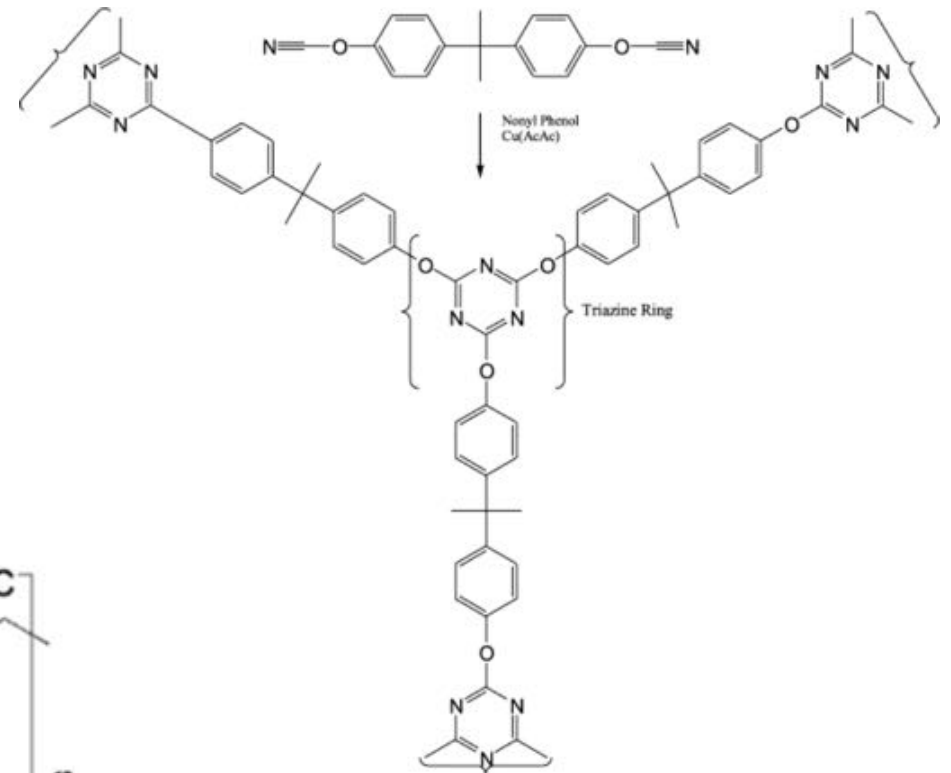
Next Generation Resins for Heat Shields



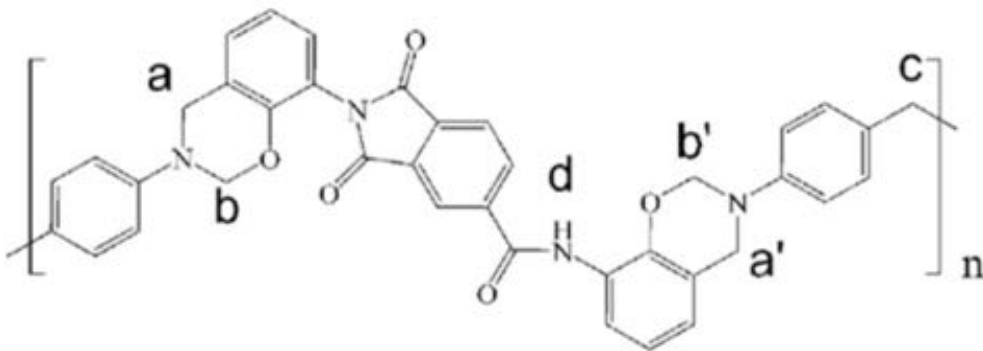
Phenolic (SOA)



Cyanate Esters



Polyimides



New resin chemistries for heat shields require different solvents for processing



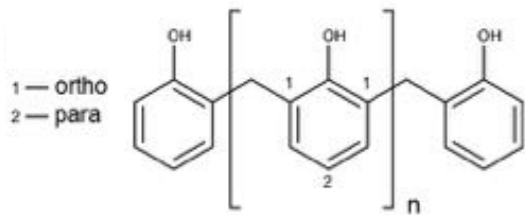
Phenolic Polymers



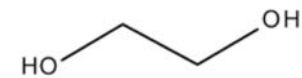
Polymers

Solvents

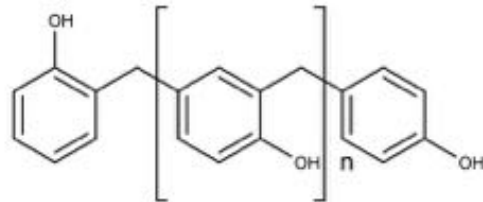
ortho-ortho novolac



ethylene glycol

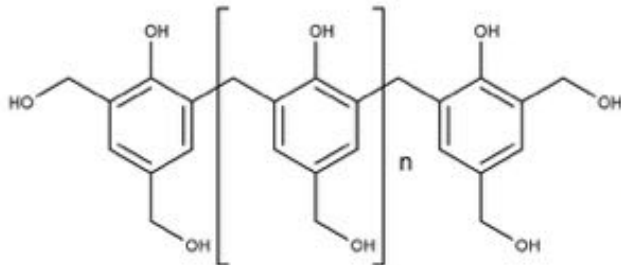


ortho-para novolac



water

ortho-ortho resole

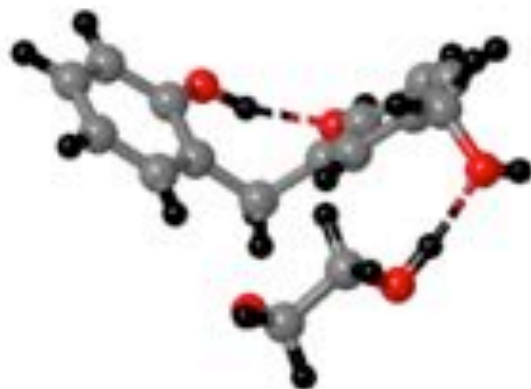


H₂O

Design rules for SOA polymer and solvents



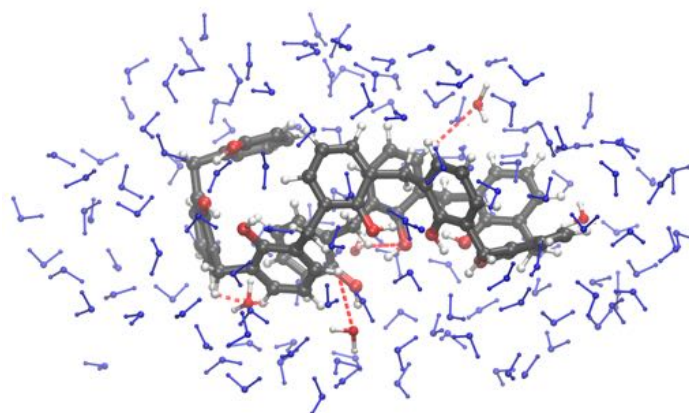
Outline



Ethylene glycol-phenolic dimer

Quantum Chemical Calibration: understand basic polymer-solvent interactions and benchmark MD models

- combination of DFT, MP2, CCSD(T)
- water and ethylene glycol dimers
- solvent-monomer dimers



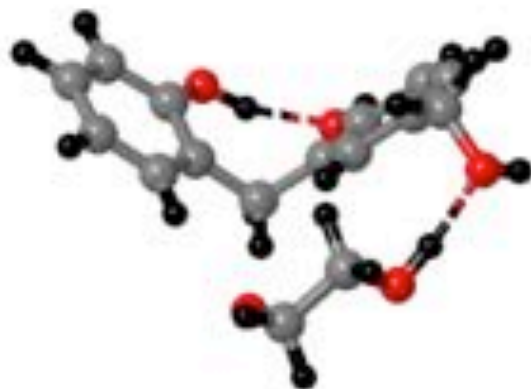
Phenolic in Water

Molecular Dynamics Simulation: characterize polymer solubility in solvents

- OPLS-AA-SEI force field
- single polymers in large solvent boxes
- 500-100,000 solvent molecules
- polymers with 3-27 units



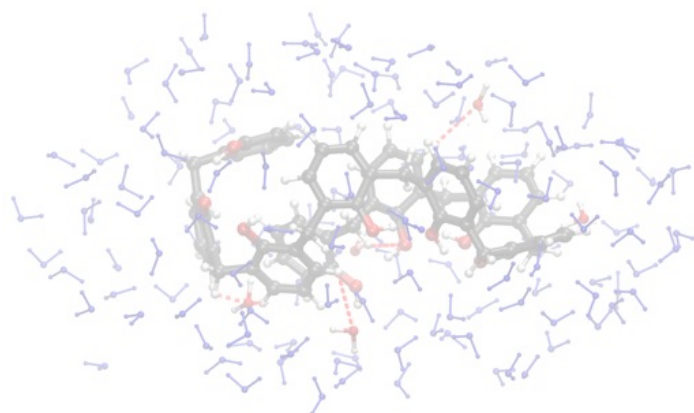
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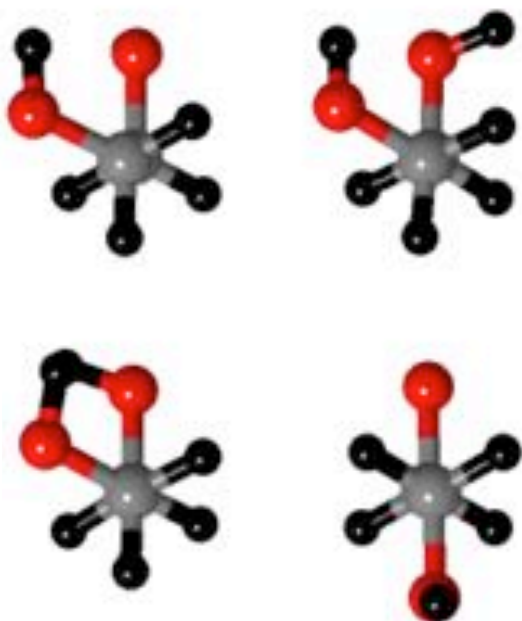
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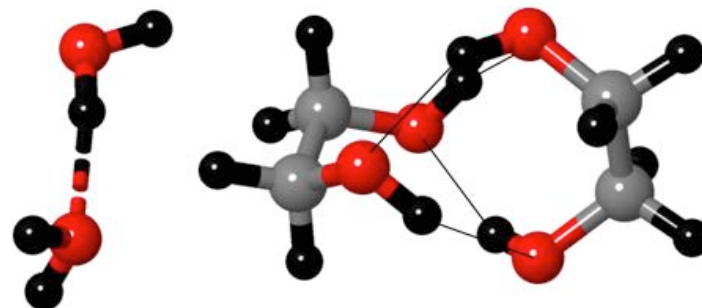
Water and Ethylene Glycol Interactions



Conformers of Ethylene Glycol



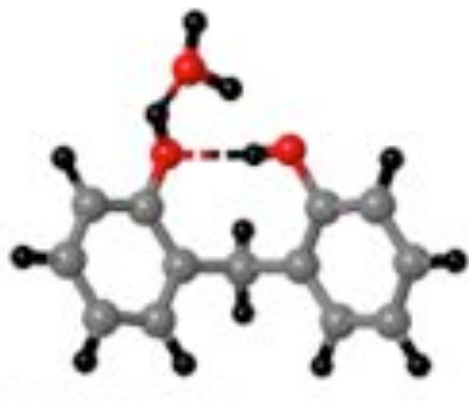
Water and Ethylene Glycol Dimers



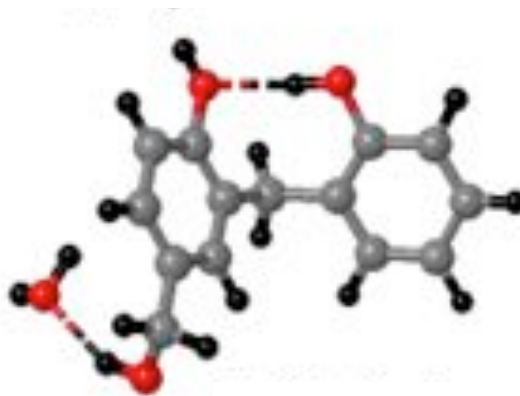
OPLS energetics within 2 kcal/mol of CCSD (T)

H = black; O = red; C = gray

2 Unit Novolac



2 Unit Resole



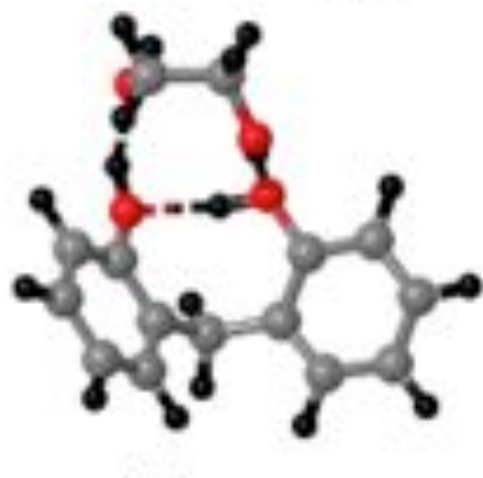
3 Unit Novolac



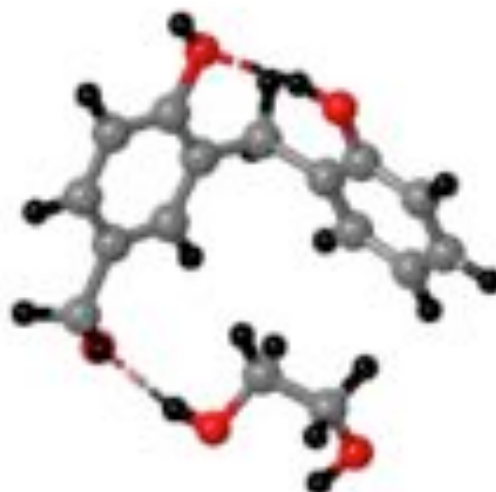
OPLS interactions within 2 kcal/mol of MP2/CBS

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2 Unit Novolac



2 Unit Resole



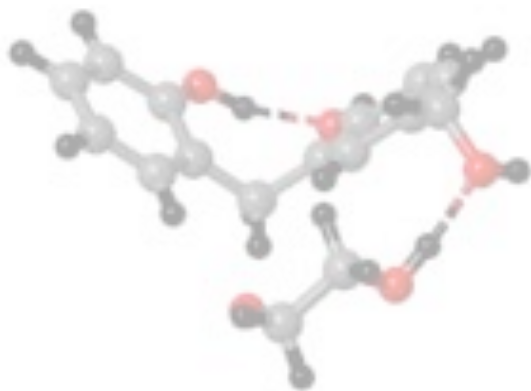
3 Unit Novolac



OPLS interactions within 3 kcal/mol of MP2/CBS



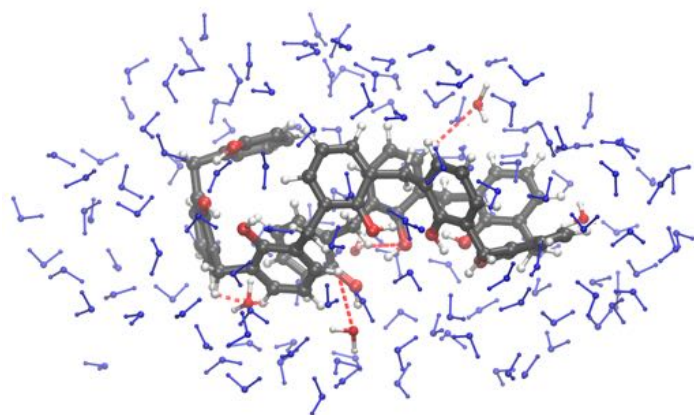
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Phenolic in Water

Molecular Dynamics Simulation: characterize polymer solubility in solvents

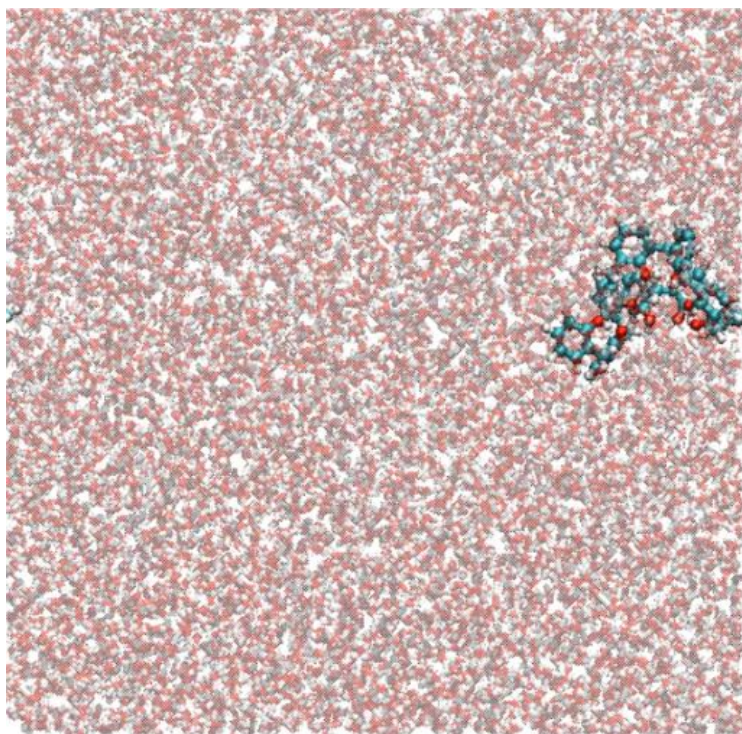
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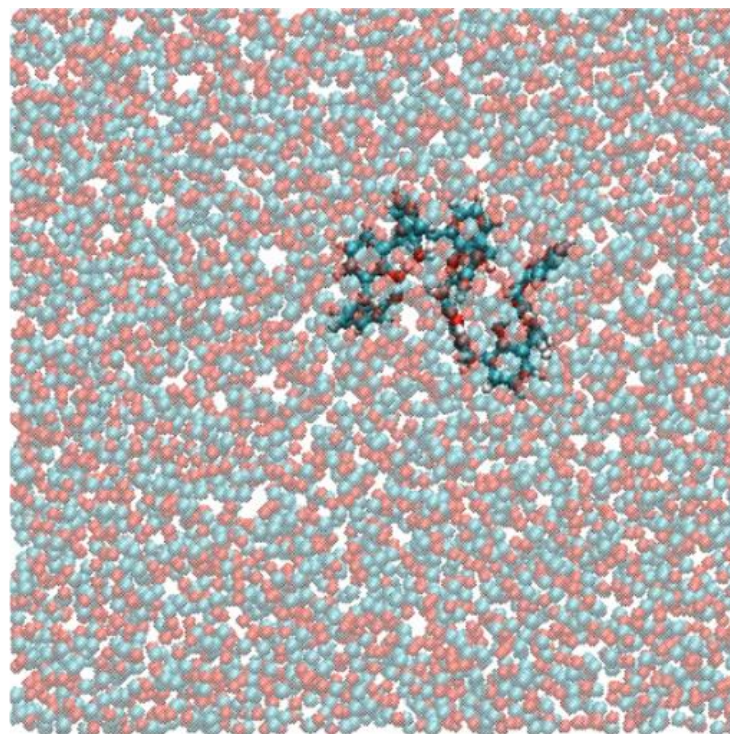
Dynamics of Solvated Phenolic



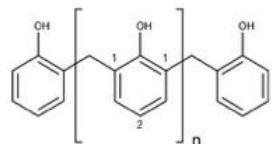
Phenolic in Water



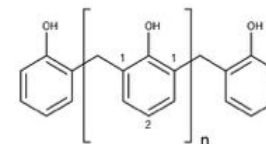
Phenolic in Ethylene Glycol



Diffusion and viscosity of solvent strongly affect polymer dynamics

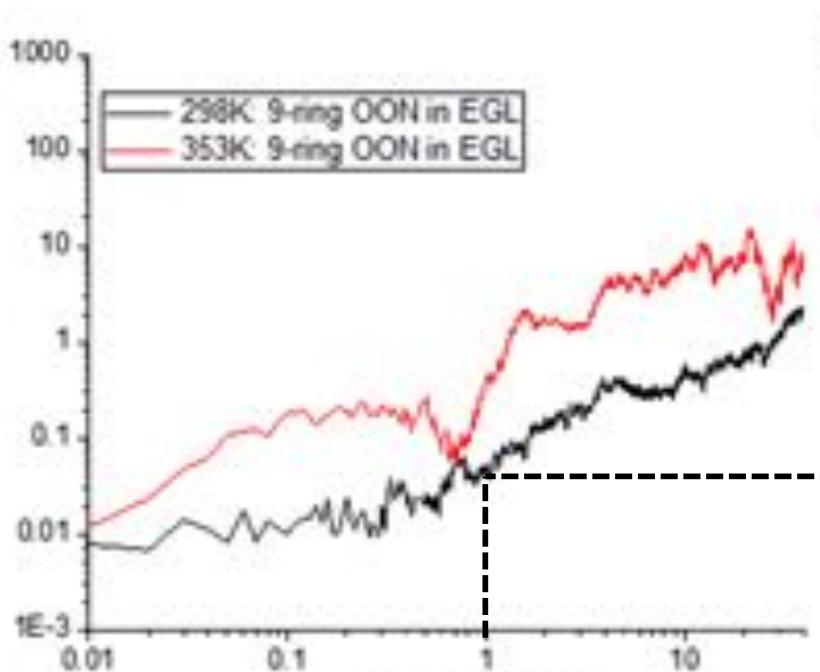


ortho-ortho novolac

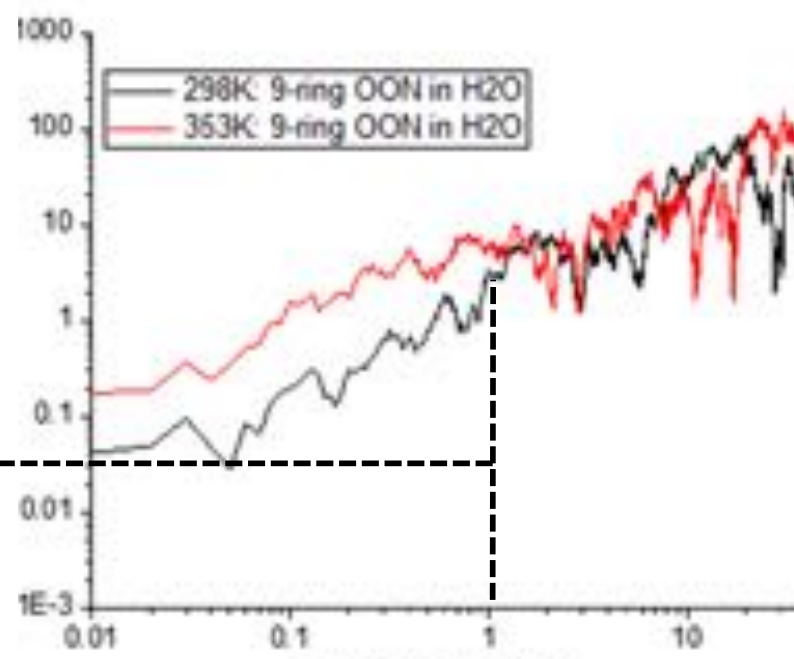


ortho-ortho novolac

Mean Square Displacement (nm²)



Simulation Time (ns)



Simulation Time (ns)

Larger diffusion coefficients in water

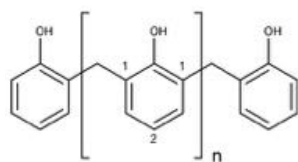


Solvation Free Energy

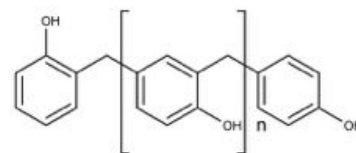


Solvation Free Energy (kcal/mol)

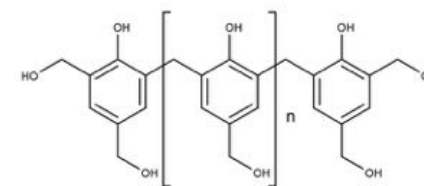
Ethylene Glycol	-27.1	-53.1	-84.0
Water	-8.5	-23.8	-46.5



ortho-ortho novolac



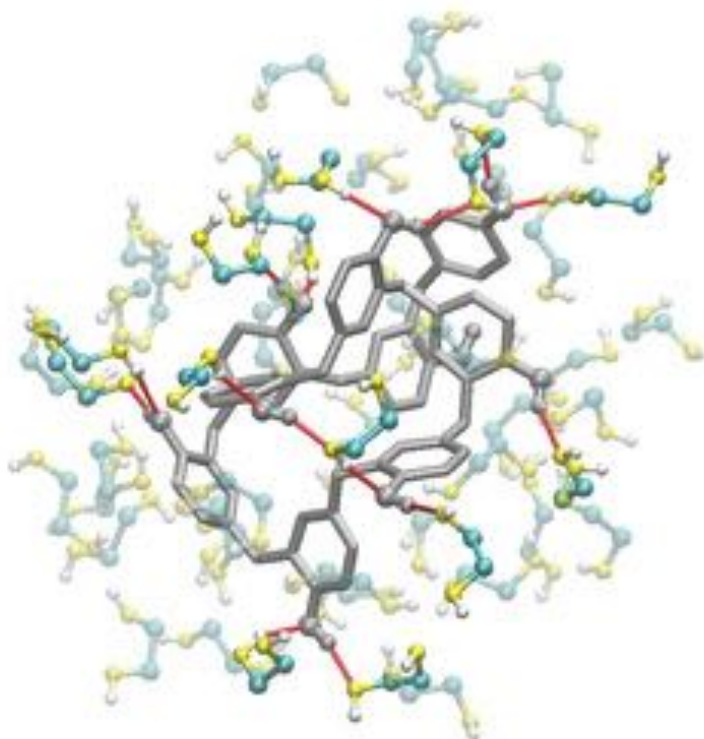
ortho-para novolac



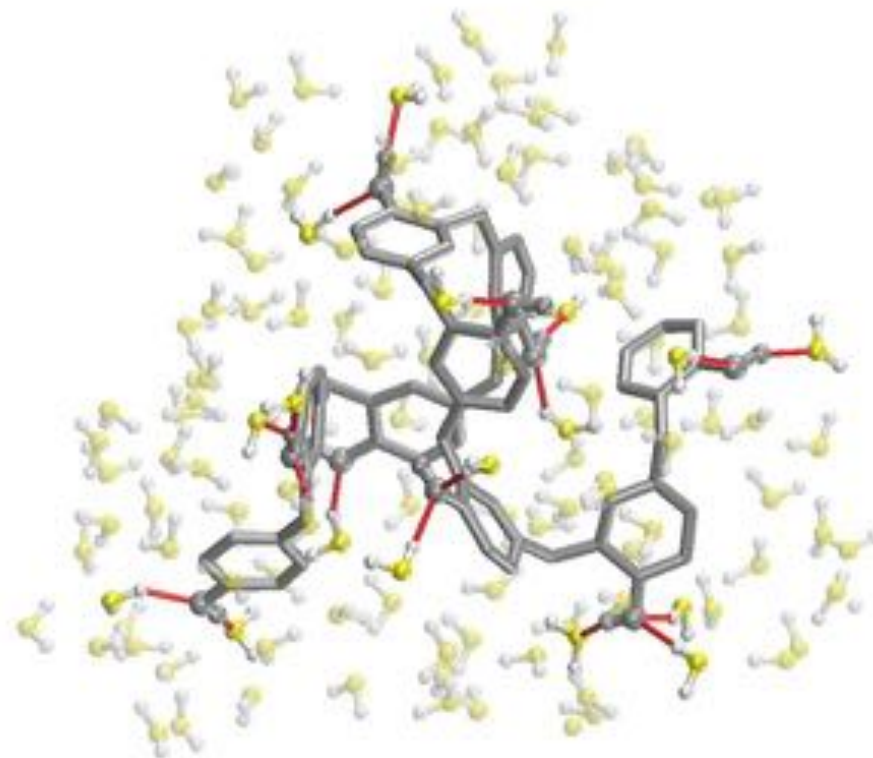
ortho-ortho resole

Polymers more soluble in ethylene glycol
Resole most soluble polymer

Ethylene Glycol

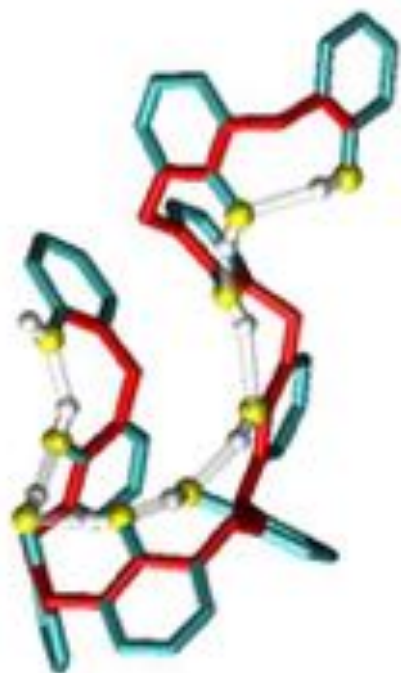


Water

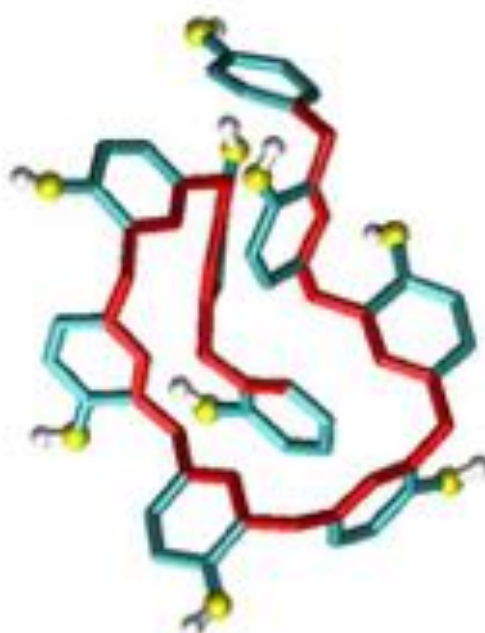


Solvation structure governs properties

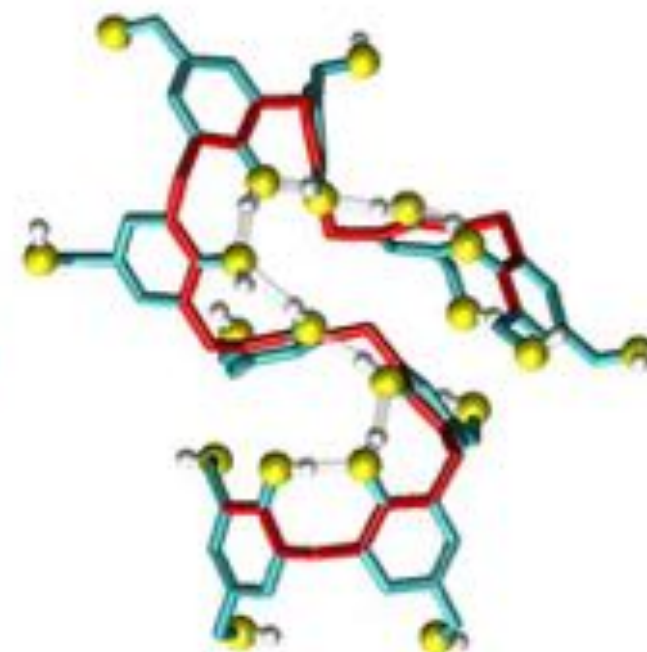
ortho-ortho novolac



ortho-para novolac



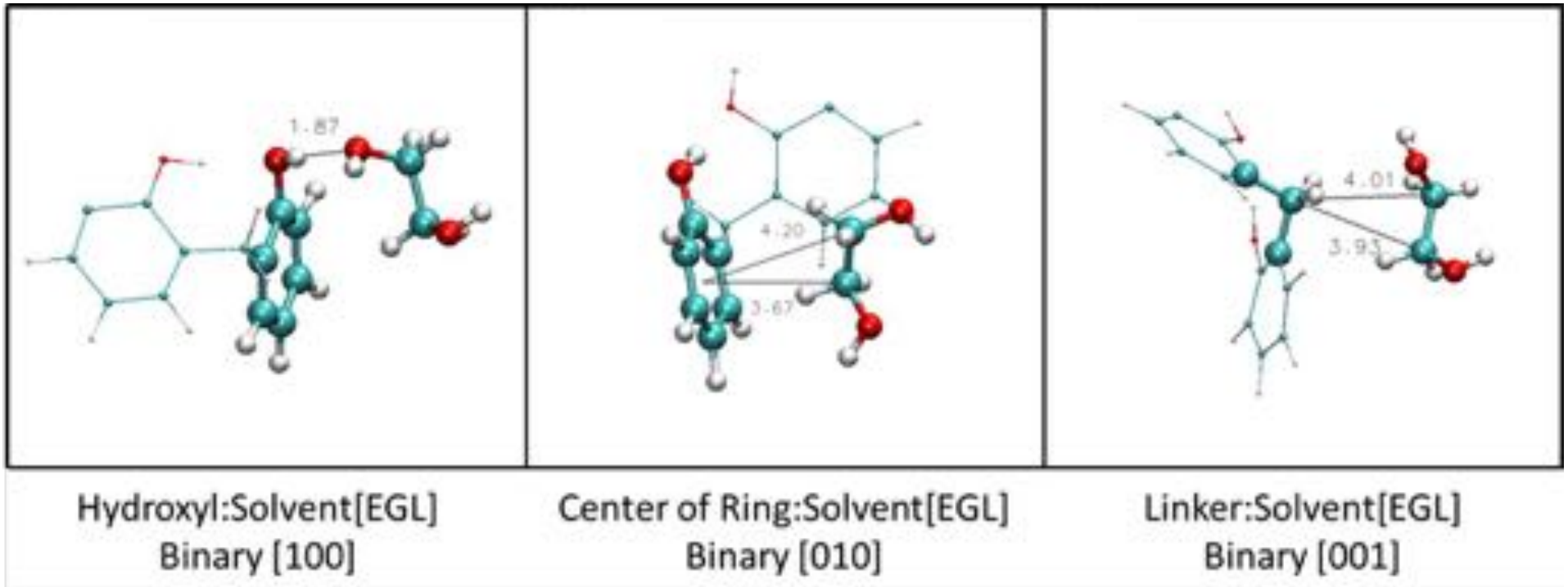
ortho-ortho resole



Self hydrogen bonding in ortho-ortho systems
Ortho-para novolac and ortho-ortho resole have free –OH groups



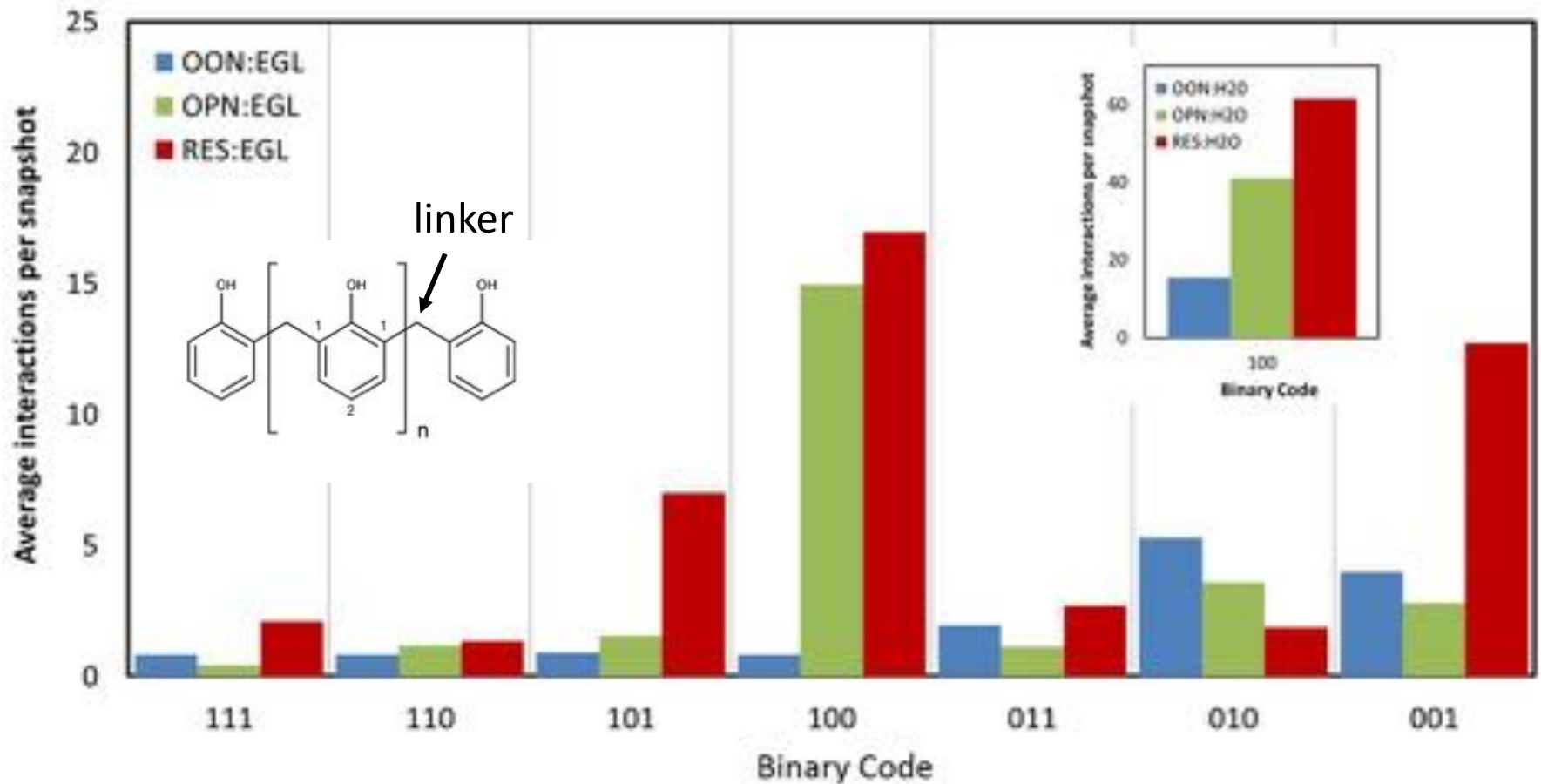
Specific Types of Polymer-Solvent Bonding



Three primary interactions found in polymer-ethylene glycol solvation; one type in polymer-water solvation



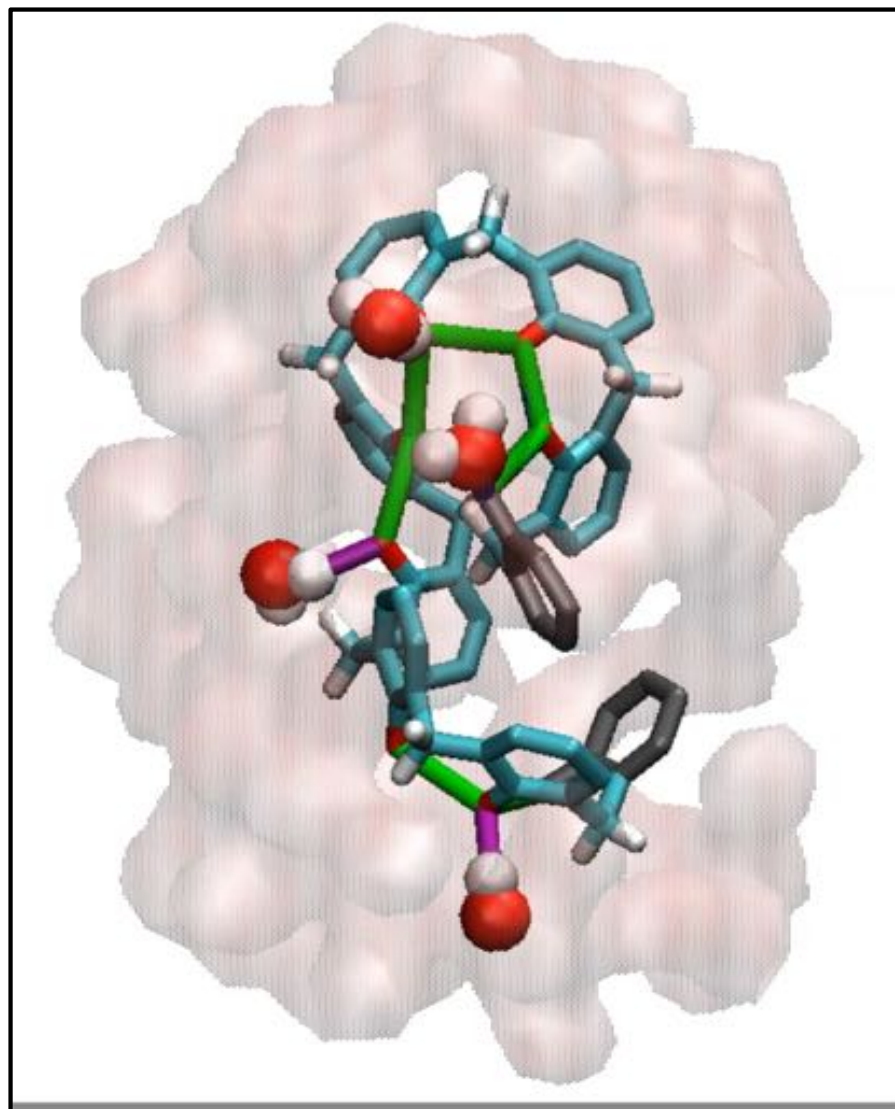
Specific Types of Polymer-Solvent Bonding



Hydrogen bonding and carbon linker interactions dominate

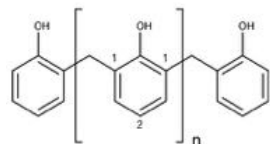


Hydrogen Bonding

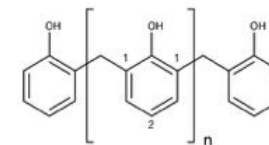


Hydrogen bonding common to both solvents and most prevalent bonding

O = red; C = green; H = white

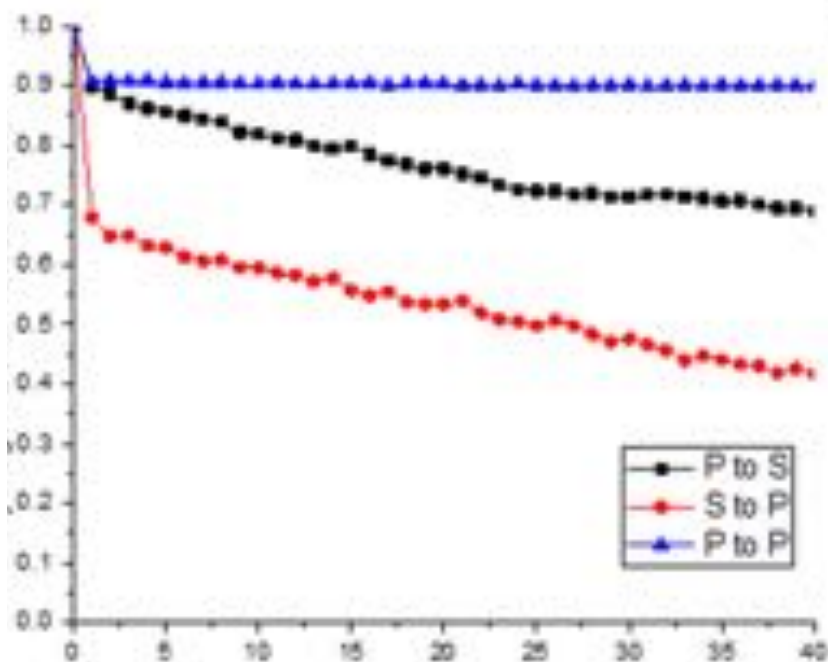


ortho-ortho novolac

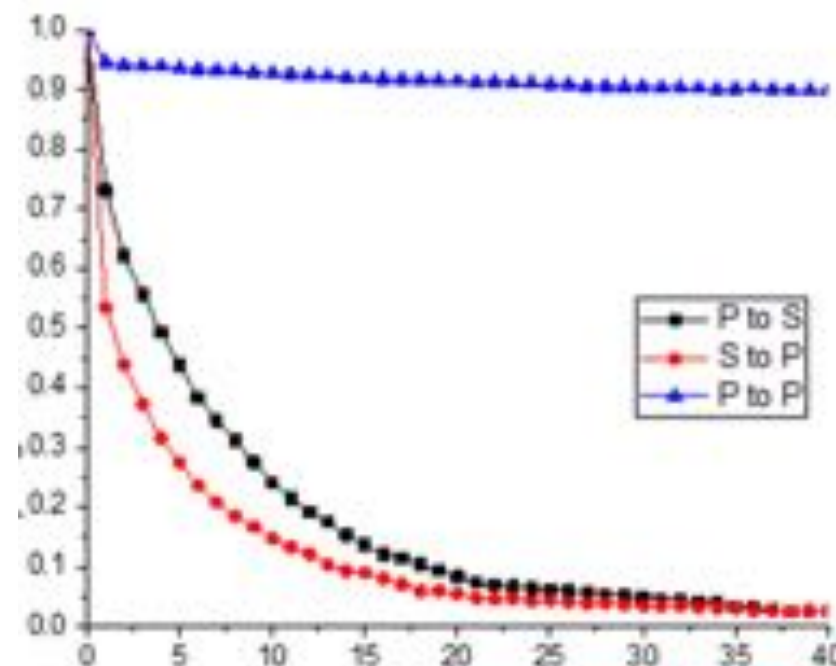


ortho-ortho novolac

Hydrogen Bond Autocorrelation



Simulation Time (ns)



Simulation Time (ns)

Hydrogen bonding more persistent in ethylene glycol



Conclusions



- **OPLS-AA-SEI energetics agree with high accuracy CCSD(T) solvent computations**
- **OPLS-AA-SEI polymer-solvent interactions within a few kcal/mol of MP2/CBS computations**
- **Ethylene glycol more readily solvates the polymers because of more, longer-lived hydrogen bonding than water**
- **Resole is more soluble than the novolac polymers: more hydrogen bonding and hydrophobic-hydrophobic interactions**

Bucholz, et al. *JPCB* **121**, 2839 (2017)

Bauschlicher, et al. *JPCB* **121**, 2852 (2017)



Questions?

Bucholz, et al. *JPCB* **121**, 2839 (2017)

Bauschlicher, et al. *JPCB* **121**, 2852 (2017)