Phenolic Polymer Interactions with Water and Ethylene Glycol Solvents

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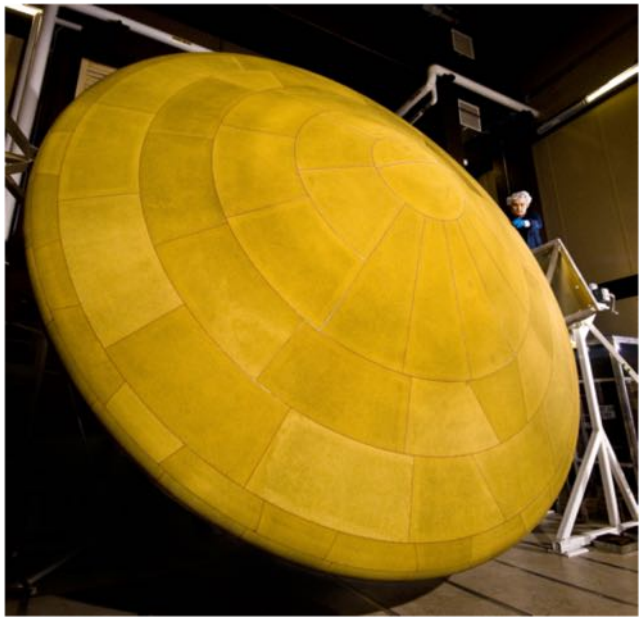
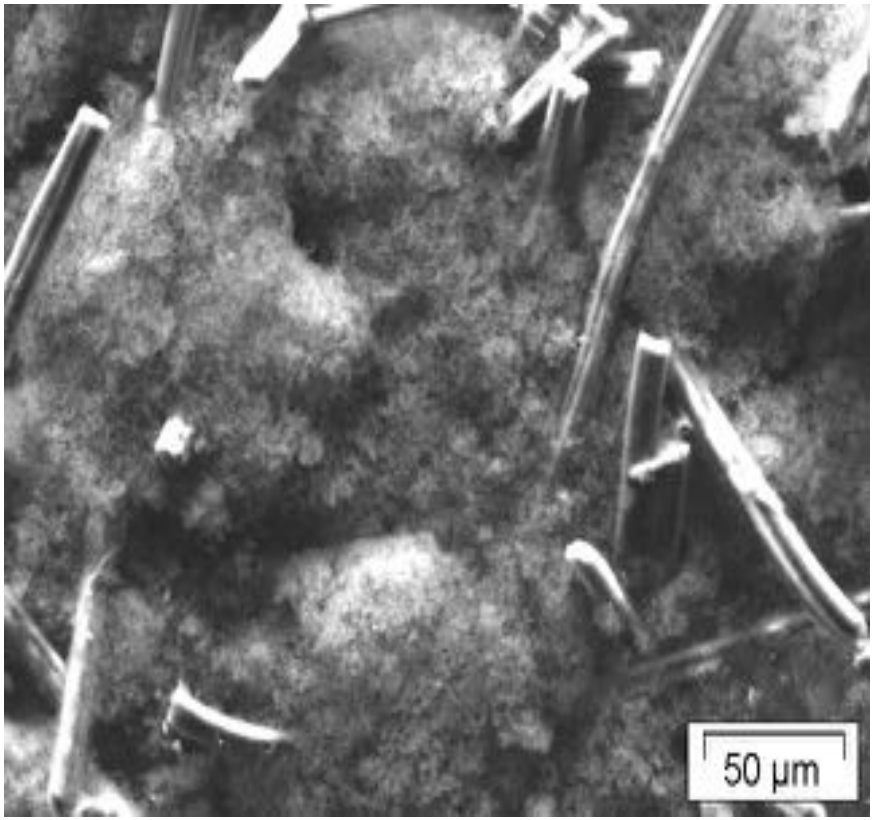
Ablative Heat Shields



Mars Science Lander

Stardust

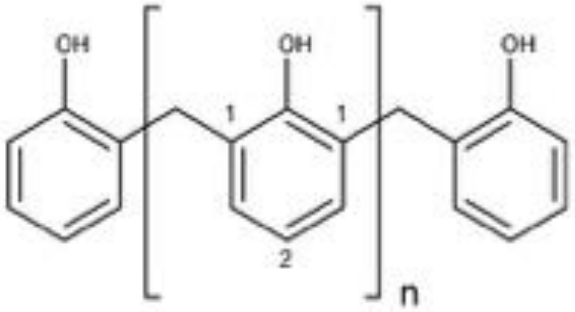


Ablative Composites for Re-entry
(carbon fiber/phenolic matrix)

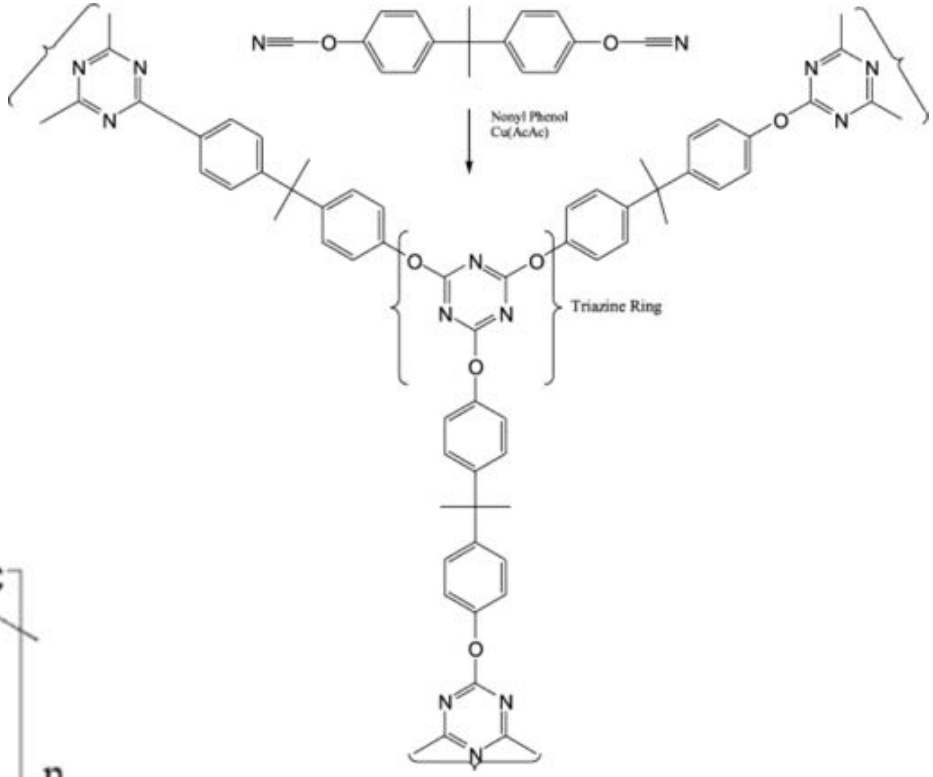
Stackpoole, et al. AIAA (2008)

Next Generation Resins for Heat Shields

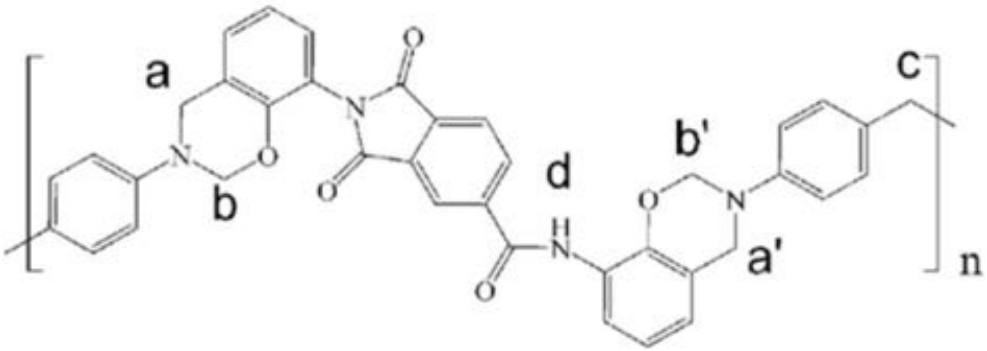
Phenolic (SOA)



Cyanate Esters



Polyimides

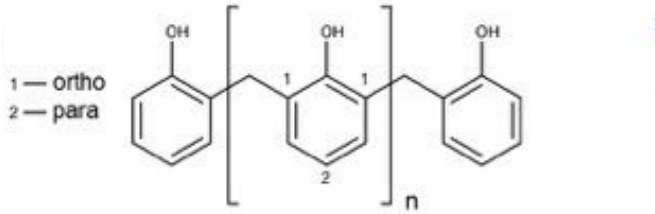


New resin chemistries for heat shields require different solvents for processing

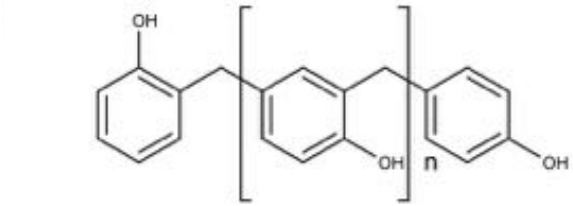
Phenolic Polymers

Polymers

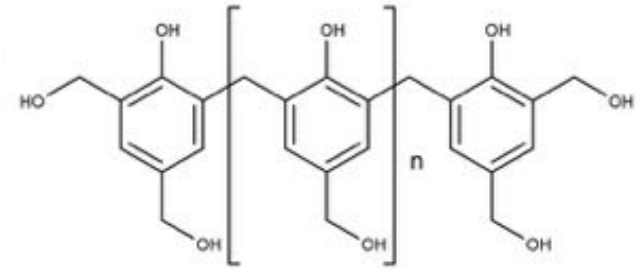
ortho-ortho novolac



ortho-para novolac

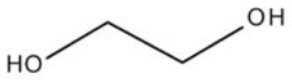


ortho-ortho resole



Solvents

ethylene glycol

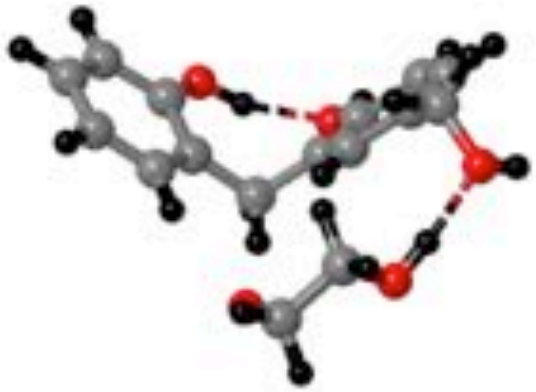


water

H_2O

Design rules for SOA polymer and solvents

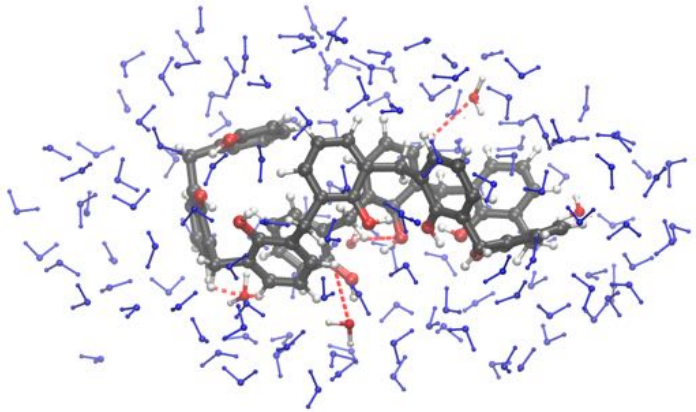
Outline



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

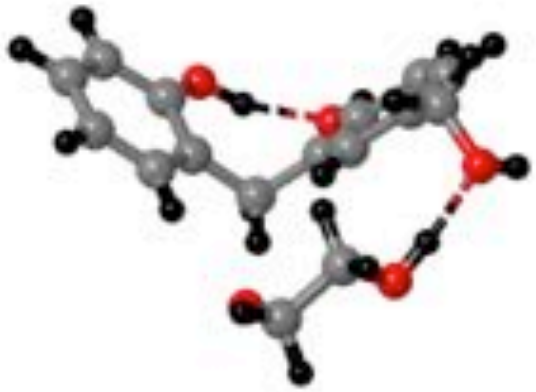


Phenolic in Water

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

Outline



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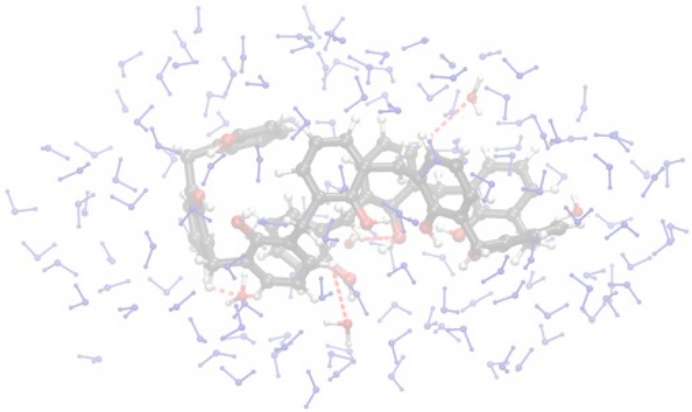

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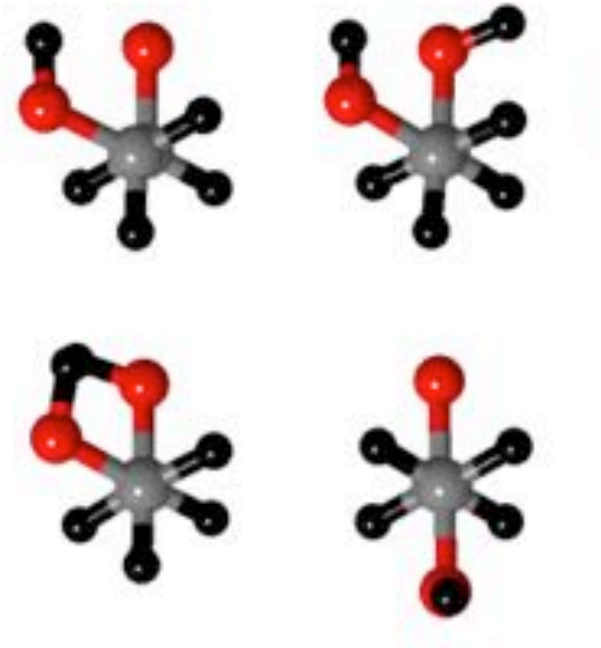
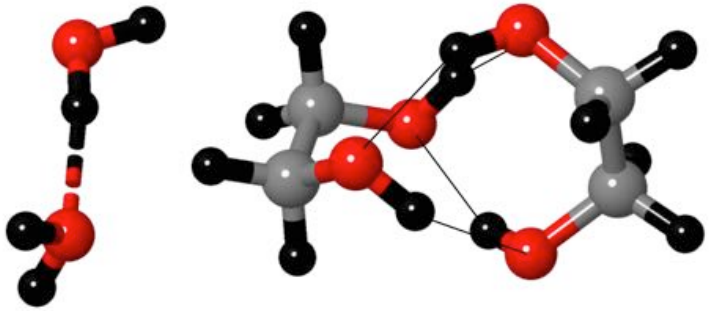
Water and Ethylene Glycol Interactions

Conformers of Ethylene Glycol



Water and Ethylene Glycol Dimers

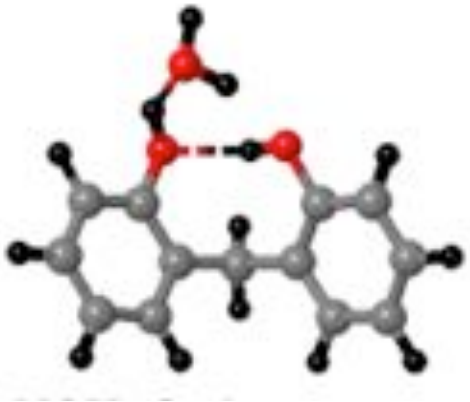


OPLS energetics within 2 kcal/mol of CCSD (T)

H = black; O = red; C = gray

Phenolic-Water Interactions

2 Unit Novolac



2 Unit Resole

3 Unit Novolac

OPLS interactions within 2 kcal/mol of MP2/CBS

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Phenolic-Ethylene Glycol Interactions

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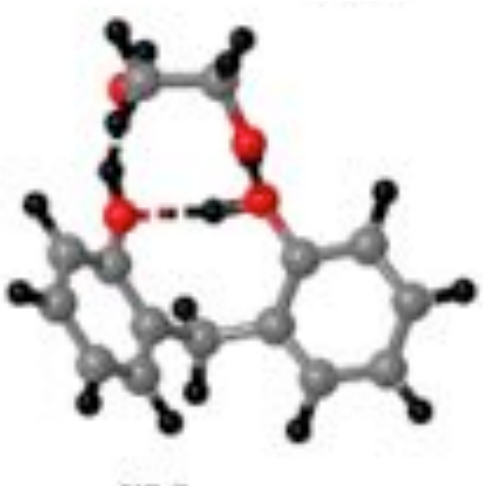
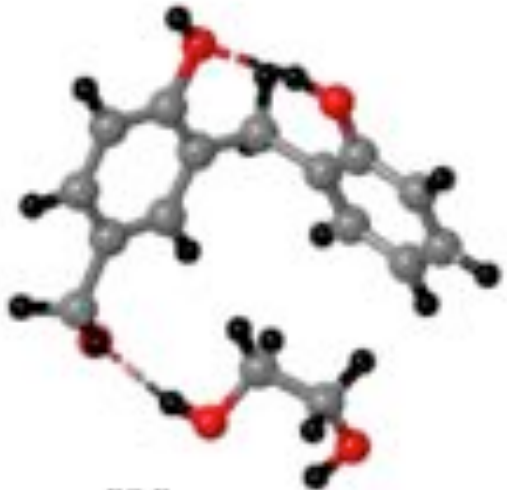


2 Unit Resole

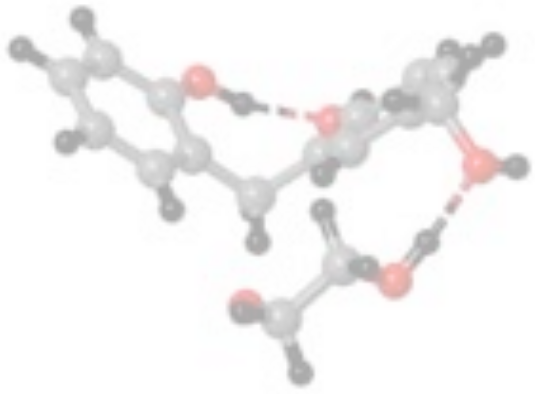


3 Unit Novolac

OPLS interactions within 3 kcal/mol of MP2/CBS

H = black; O = red; C = gray

Outline



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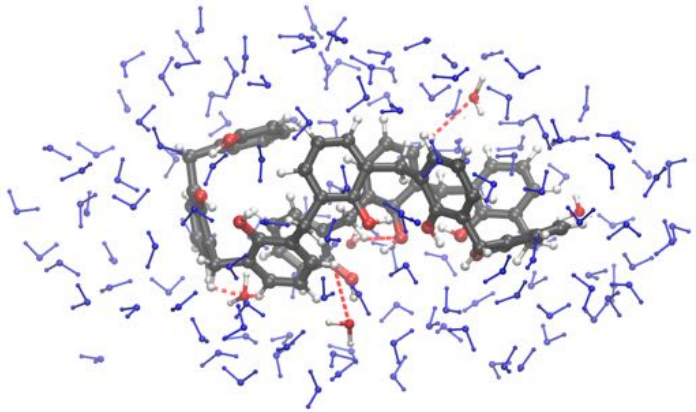

Phenolic in Water

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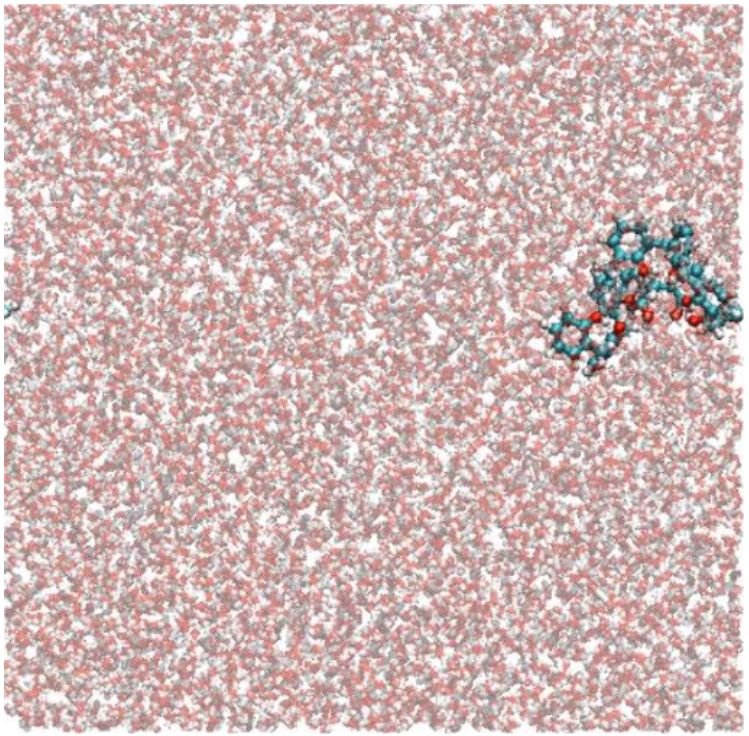
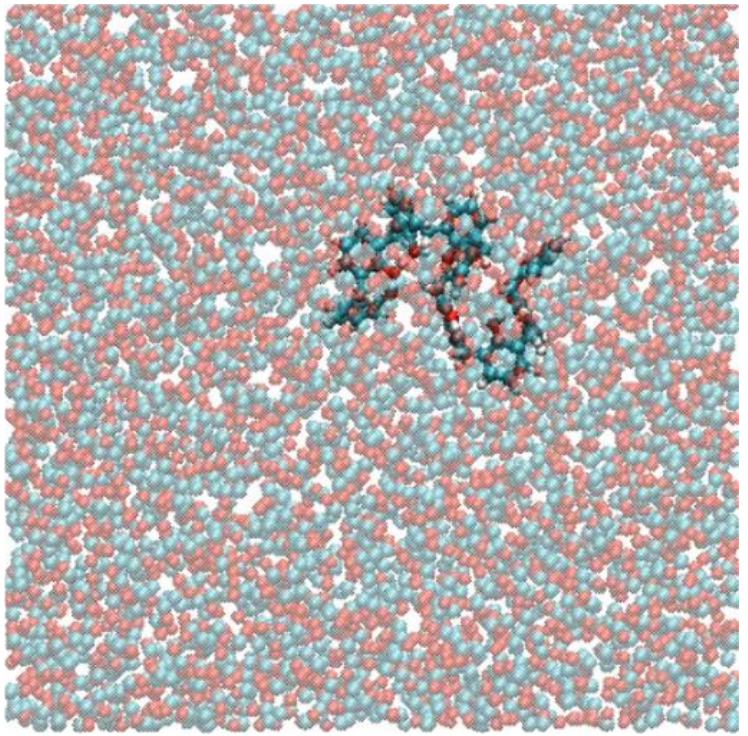
- polymers with 3-27 units

Dynamics of Solvated Phenolic

Phenolic in Water

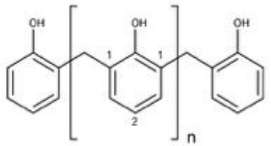


Phenolic in Ethylene Glycol

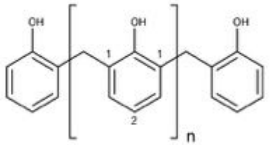


Diffusion and viscosity of solvent strongly affect polymer dynamics

Polymer Diffusion

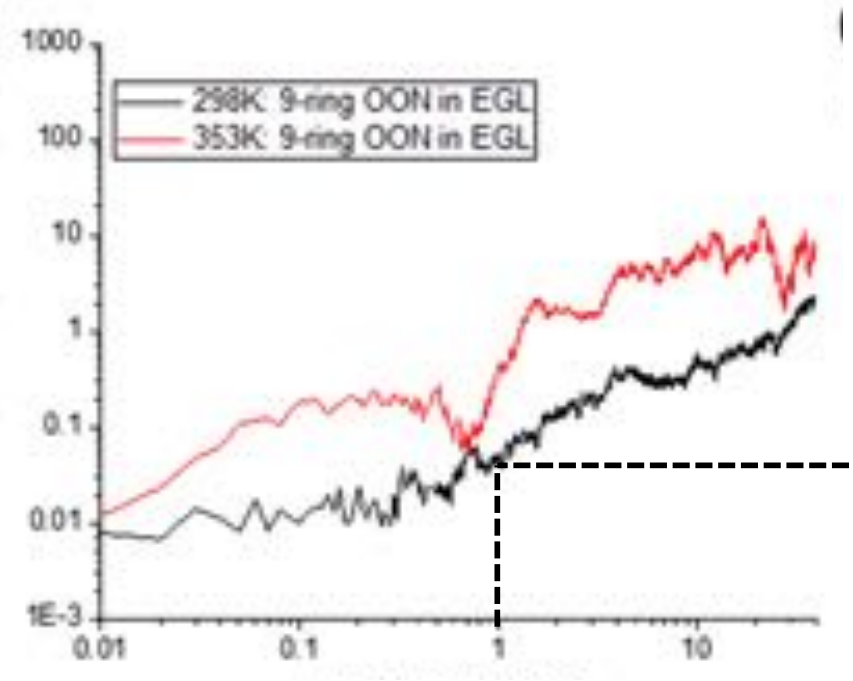


ortho-ortho novolac

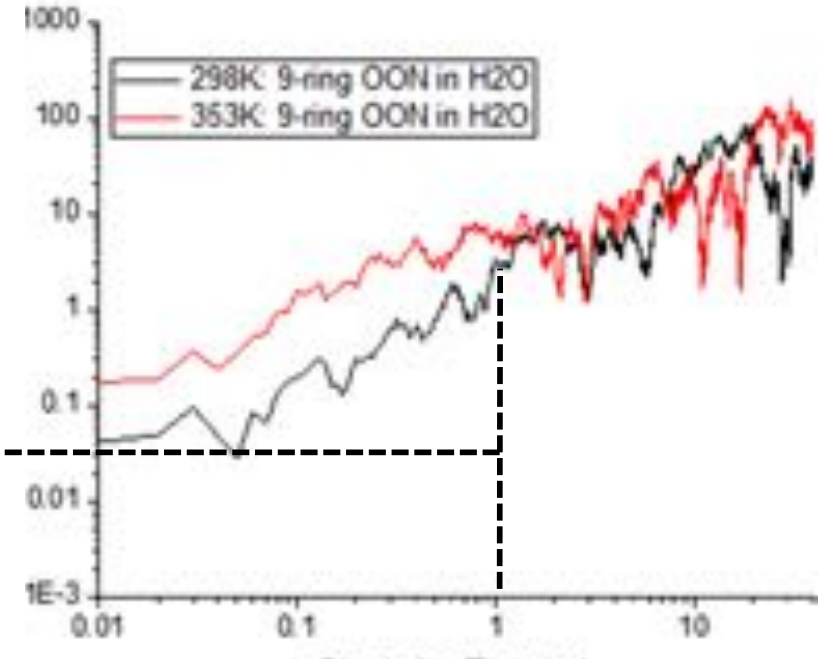


ortho-ortho novolac

Mean Square Displacement (nm^2)



Simulation Time (ns)



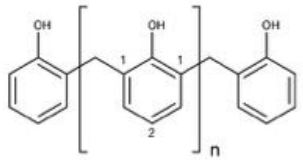
Simulation Time (ns)

Larger diffusion coefficients in water

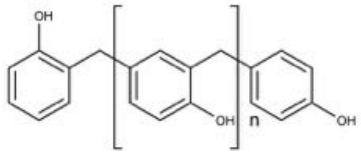
Solvation Free Energy

Solvation Free Energy (kcal/mol)

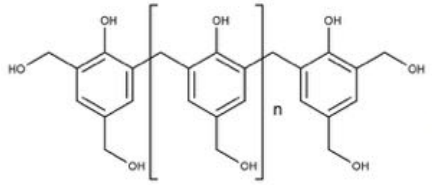
Ethylene Glycol	-27.1	-53.1	-84.0
Water	-8.5	-23.8	-46.5



ortho-ortho novolac



ortho-para novolac

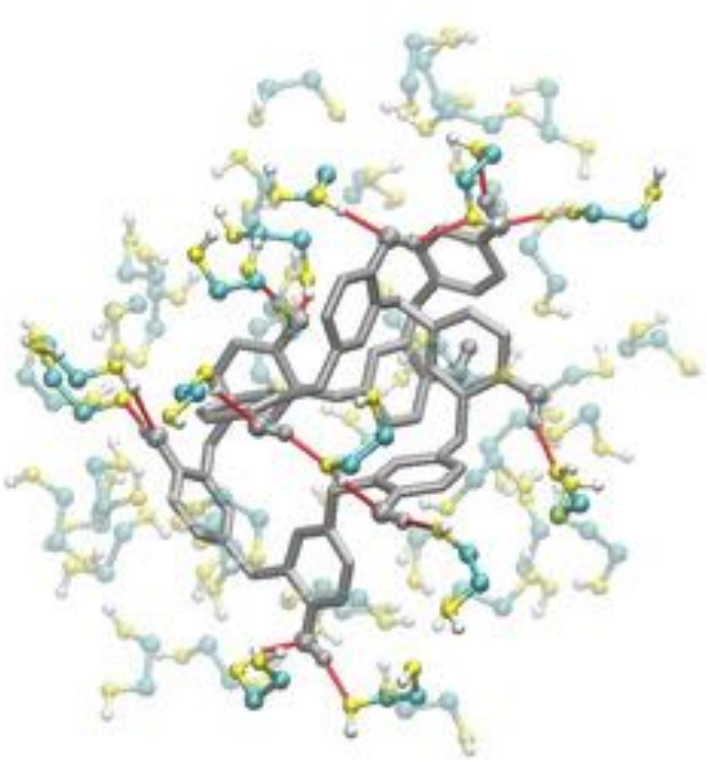


ortho-ortho resole

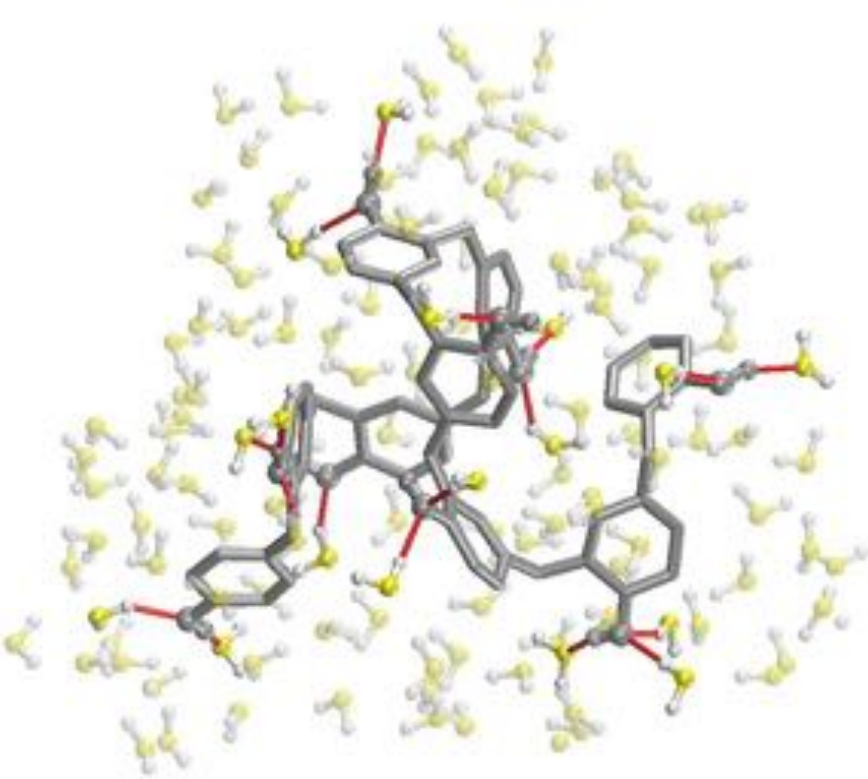
Polymers more soluble in ethylene glycol
Resole most soluble polymer

Solvation Shell of Polymer

Ethylene Glycol



Water

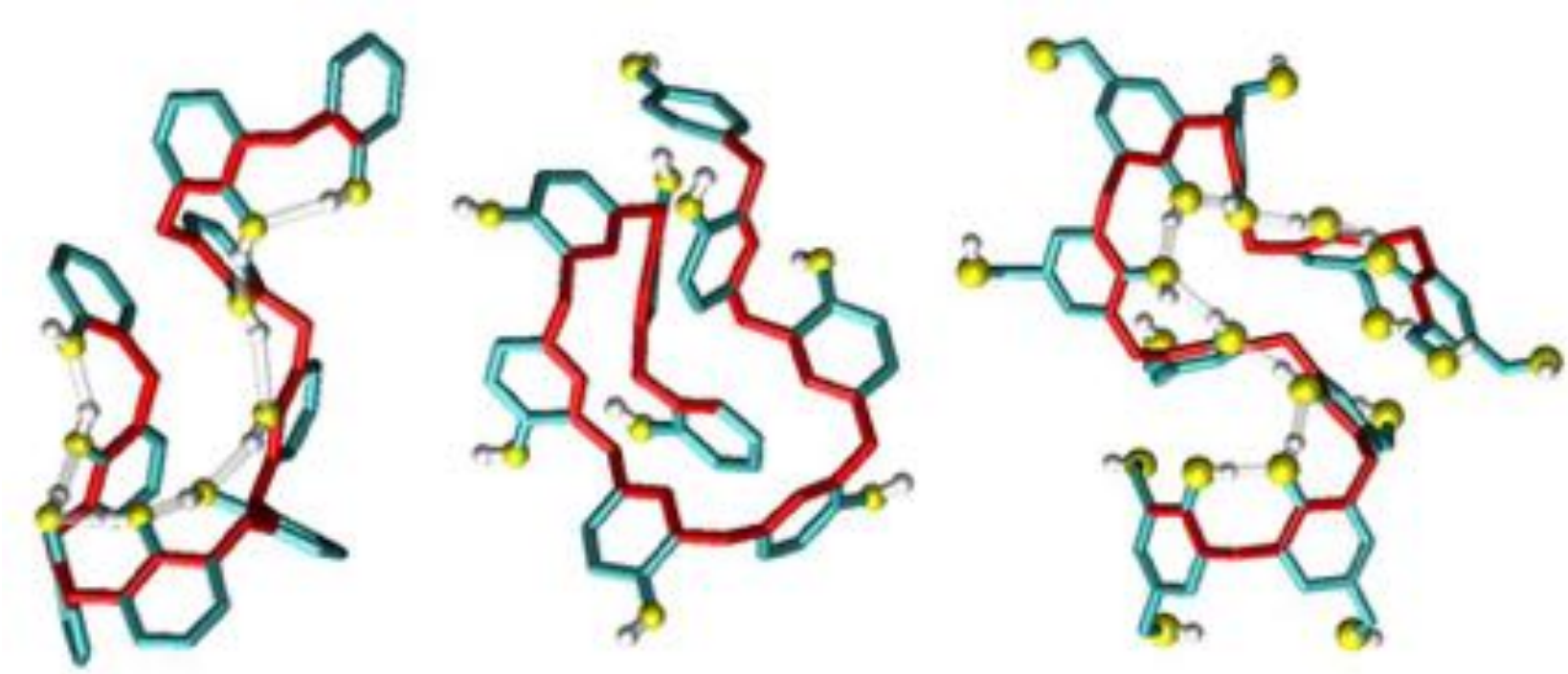


Solvation structure governs properties

polymer = gray; O = yellow; C = green; H = white

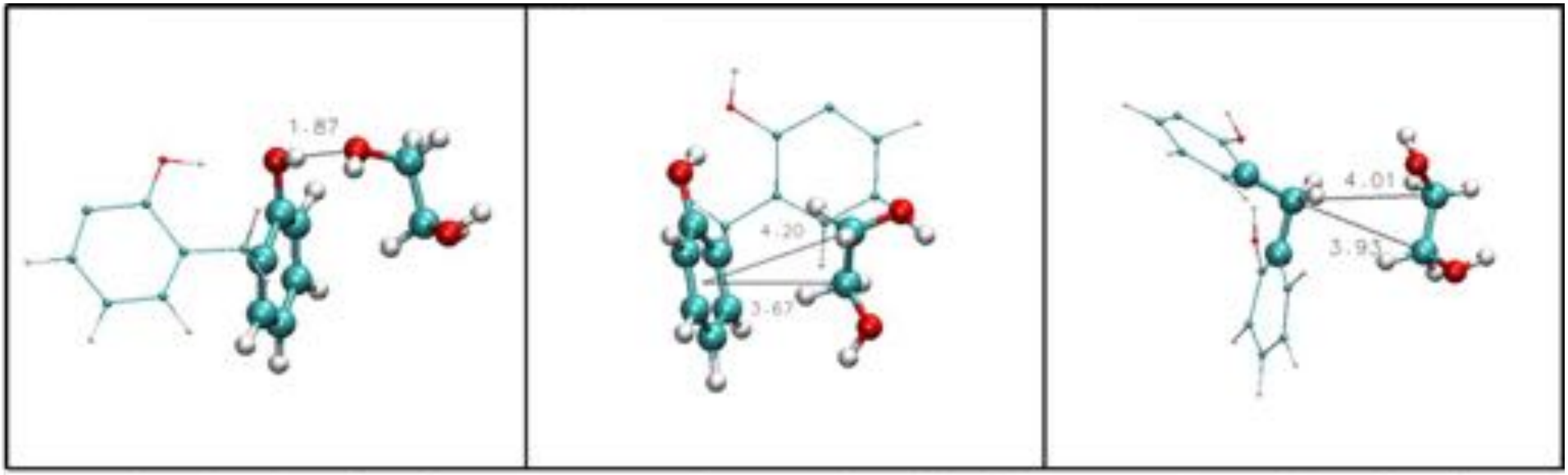
Solvated Polymer Structure

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

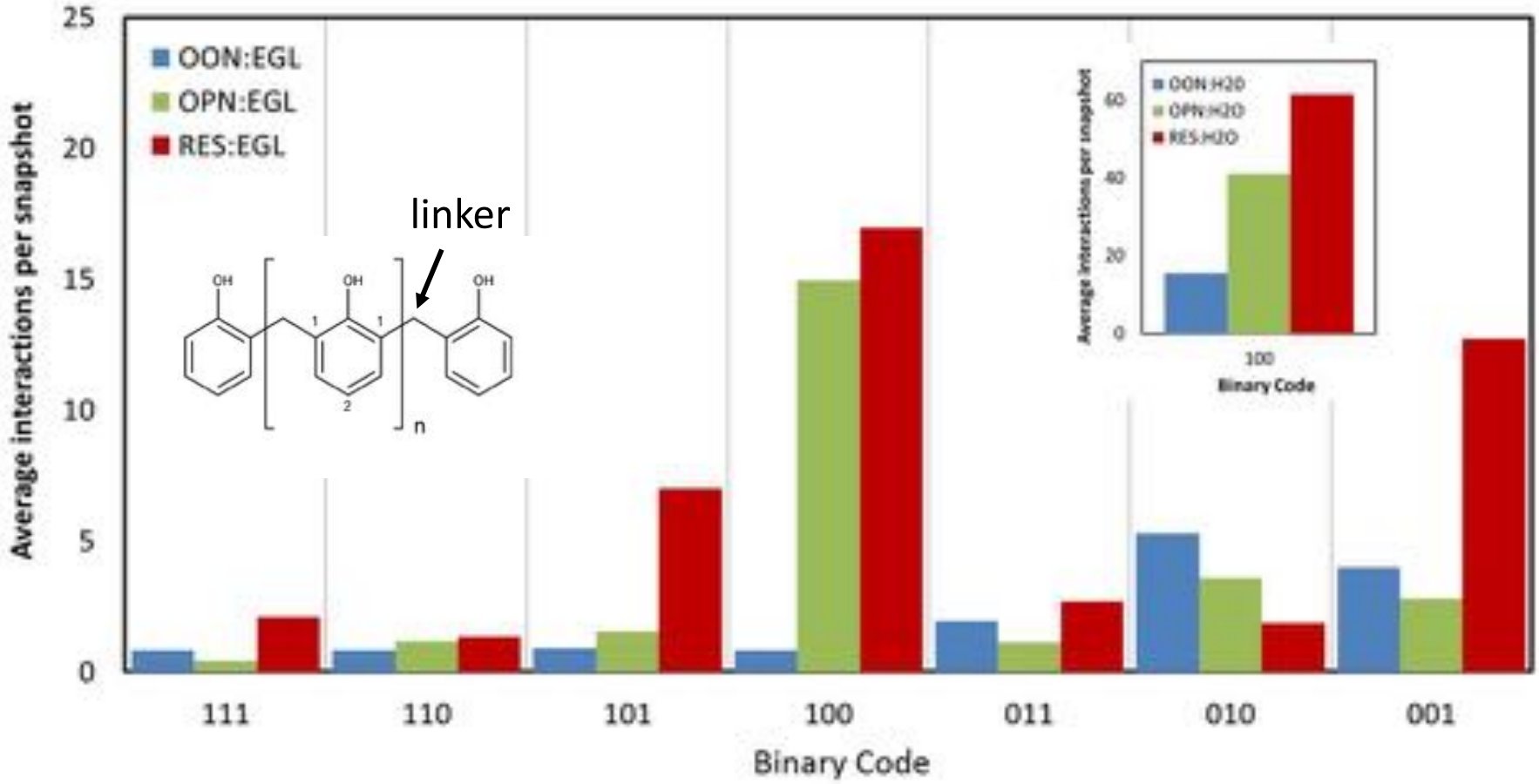


Hydroxyl:Solvent[EGL] Binary [100]	Center of Ring:Solvent[EGL] Binary [010]	Linker:Solvent[EGL] Binary [001]

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

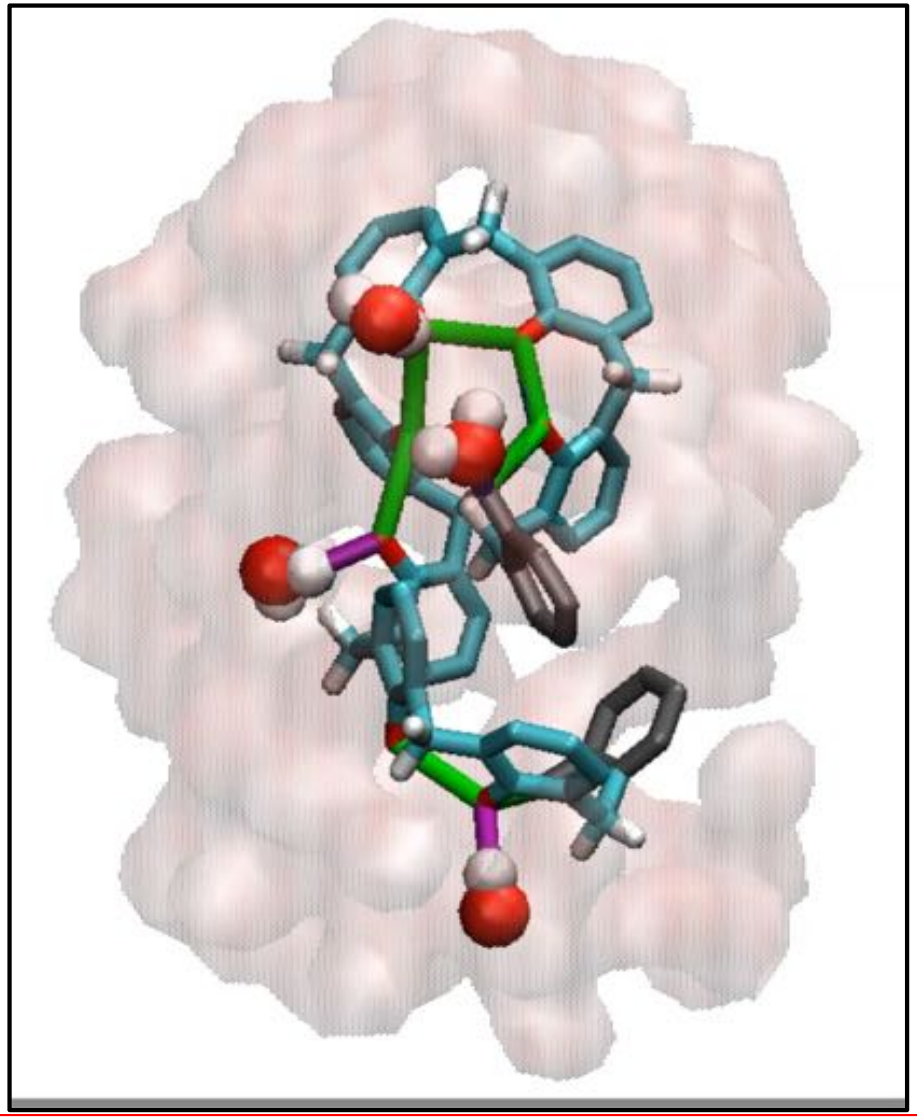
O = red; C = green; H = white

Specific Types of Polymer-Solvent Bonding



Hydrogen bonding and carbon linker interactions dominate

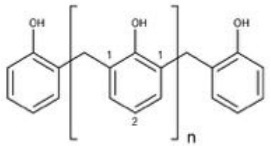
Hydrogen Bonding



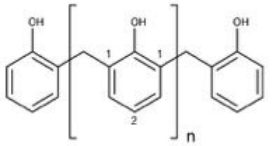
Hydrogen bonding common to both solvents and most prevalent bonding

O = red; C = green; H = white

Polymer-Solvent Hydrogen Bonds



ortho-ortho novolac



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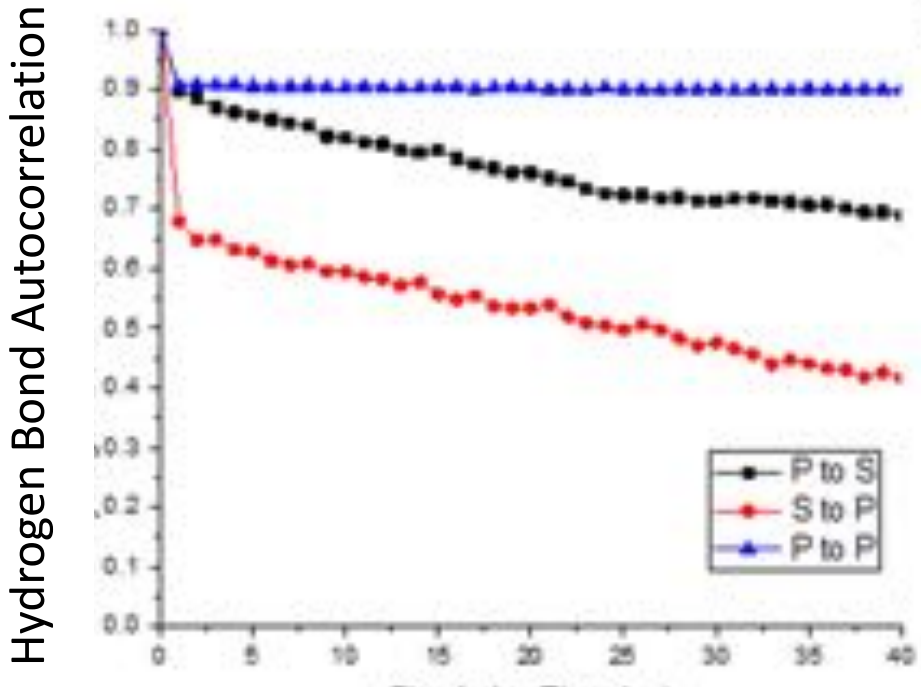

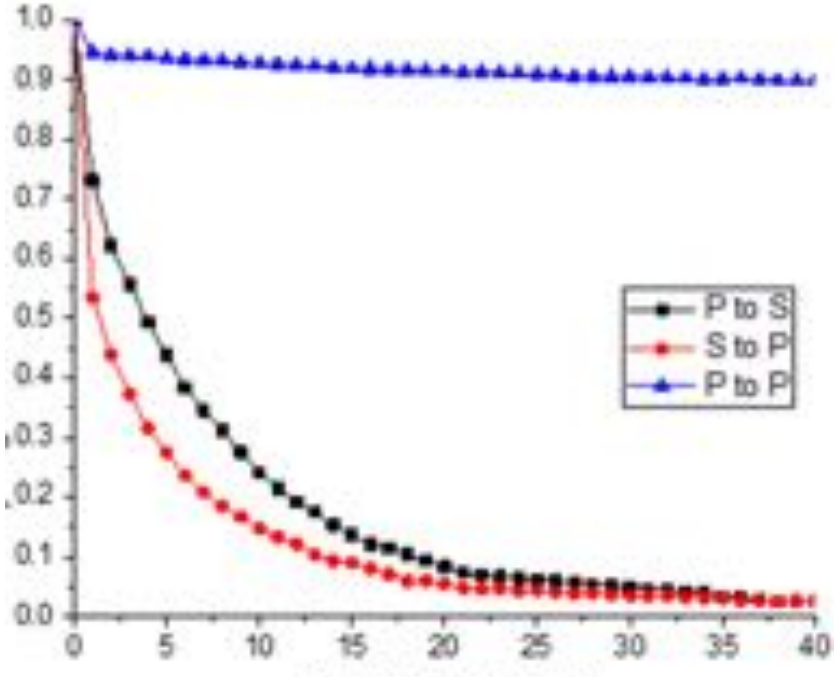

Hydrogen bonding more persistent in ethylene glycol

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)