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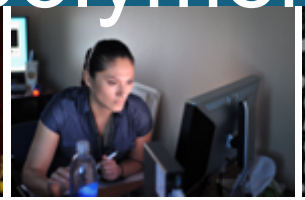
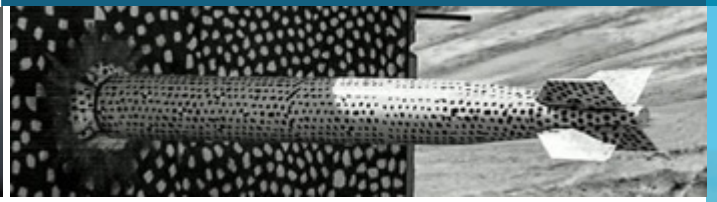
# Reactive molecular dynamics simulations of shock-induced chemistry in phenolic polymer





2021 APS GSCCM Early Career Symposium

Keith A. Jones, J. Matthew D. Lane, Nathan W. Moore

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# Motivation and background – Phenolic polymers under shock

## Background

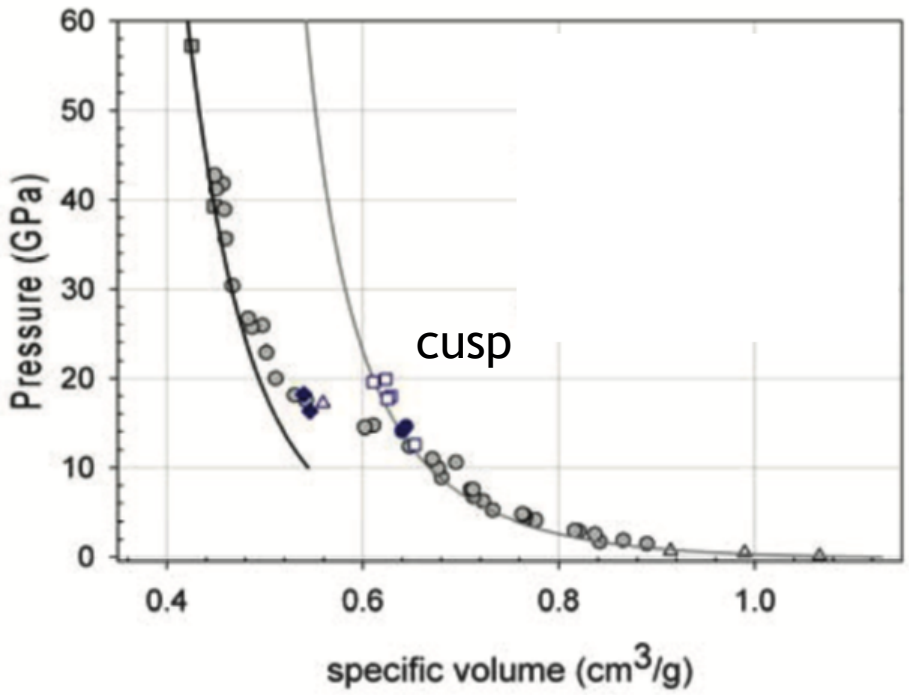
- Phenolic polymers commonly used in extreme environments – subjected to heating and shock.
  - Common material for NASA in thermal shields.
- Many polymers, and benzene undergo shock-induced chemical densification.

## Motivation

- Reliable equation of state (EOS) important for accurate continuum scale modelling.
- Shock-induced chemistry affects material properties.
- Chemical mechanisms during shock loading of phenolic not well understood.
  - Reactive MD can bridge the gap.

Rankine-Hugoniot energy equation

$$(E_1 - E_0) = \frac{1}{2}(P_1 + P_0)(V_0 - V_1)$$




Benzene Hugoniot. Image taken from Dattelbaum *AIP Conf. Proc.* **1979**, 020001 (2018).

Which chemical mechanisms account for densification behind the shock front in phenolic polymer?

W. J. Carter and S. P. Marsh, *Hugoniot Equation of state of polymers* (University of California Press, Berkeley, 1995).
J. M. Lang et al. *AIP Conf. Proc.* **1979**, 090008 (2018).
C. E. Morris et al. *J. Chem. Phys.* **80**(10), 5203-5218 (1984).
N. C. Dang et al. *J. Phys. Chem. A* **116**, 10301 (2012).

# Methodology - Hugoniostat simulations

Non-propagating, constant stress Hugoniostat method by Ravelo uniaxially compresses system until the final pressure is reached. Temperature is controlled to satisfy Rankine-Hugoniot conditions. Previous success with polyethylene in ReaxFF.

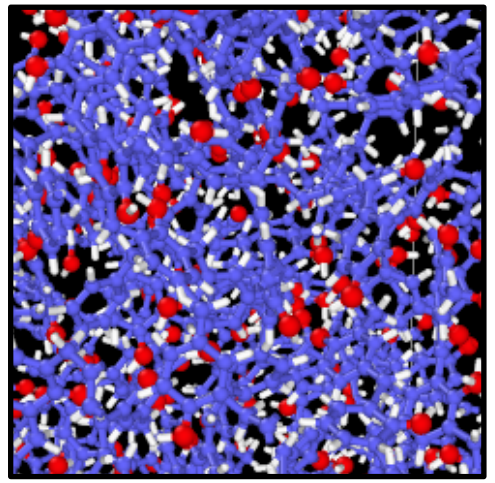
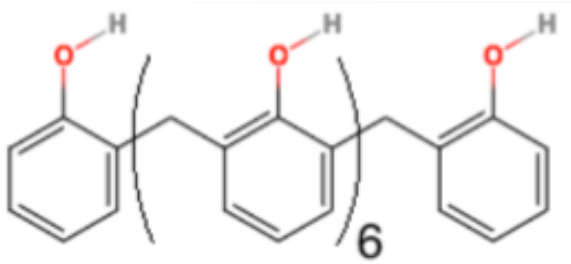


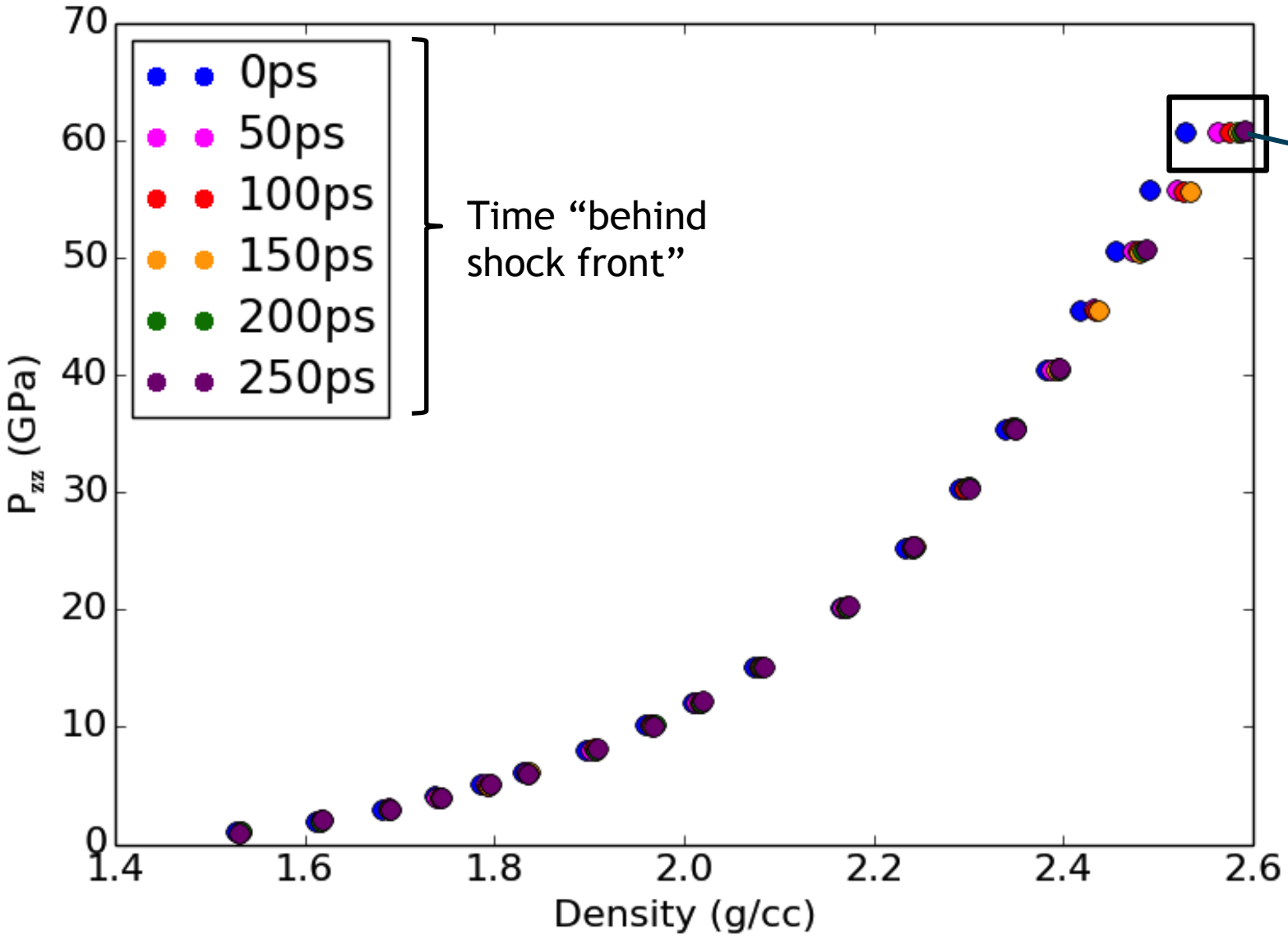
Image crated with OVITO software
A. Stukowski *Mod. Sim. Mater. Sci. Eng.* ***18****, 015012 (2010).*

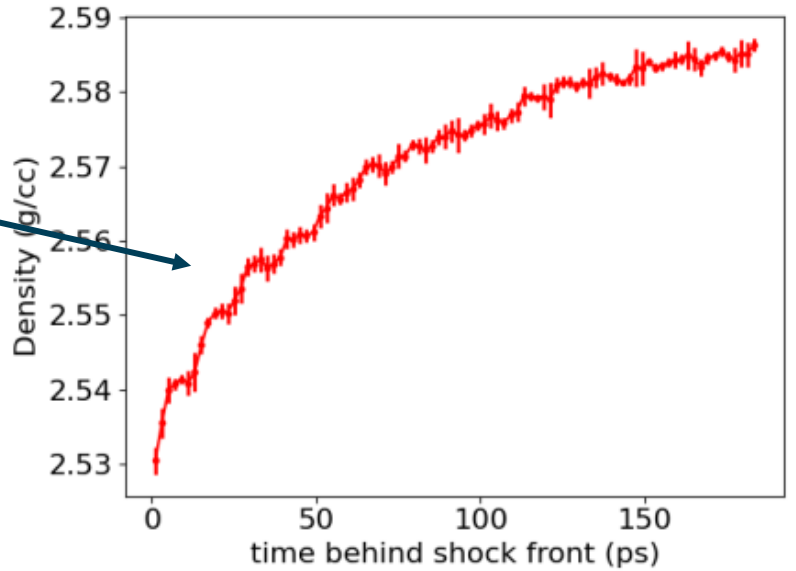
- Initial system: 432 linear phenolic chains at 1.4 g/cc
- Pressures studied: 1 to 60 GPa
- LAMMPS molecular dynamics 3D atomistic simulation code
- Periodic boundary conditions
- Equilibrated at ambient T, P for 150 ps
- ~48,000 atoms
- ReaxFF force field – CHO potential by Chenoweth et al.
- 0.05 fs timestep




R. Ravelo et al., *Phys. Rev. B* **70**, 014103 (2004).
T. R Mattsson et al., *Phys. Rev. B* **81**, 054103 (2010).
S. Plimpton, *J. Comput. Phys.* **117**, 1 (1995).
K. Chenoweth et al., *J. Phys. Chem.* **112**, 1040 (2008).

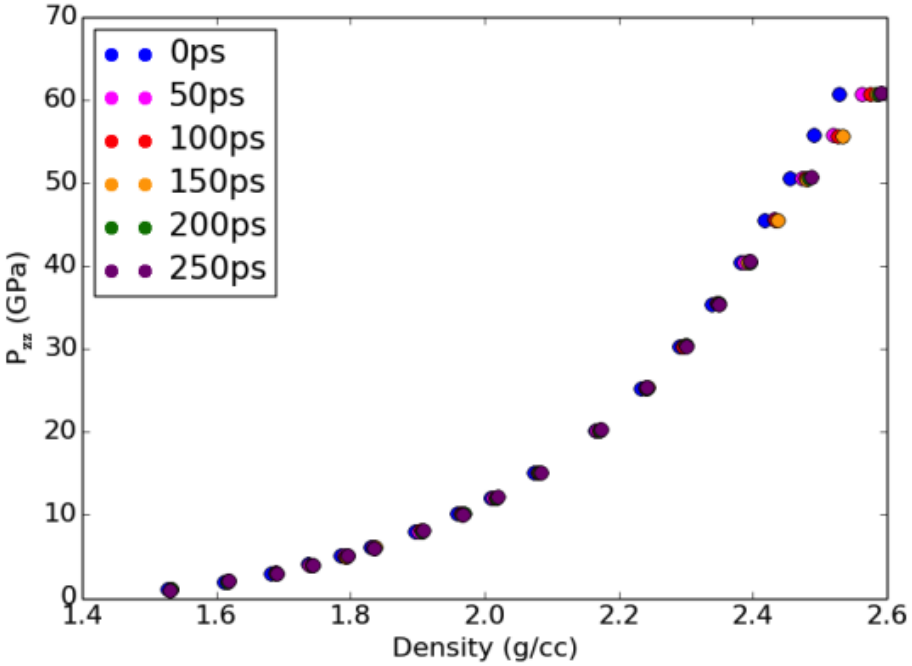
# Results - Hugoniot

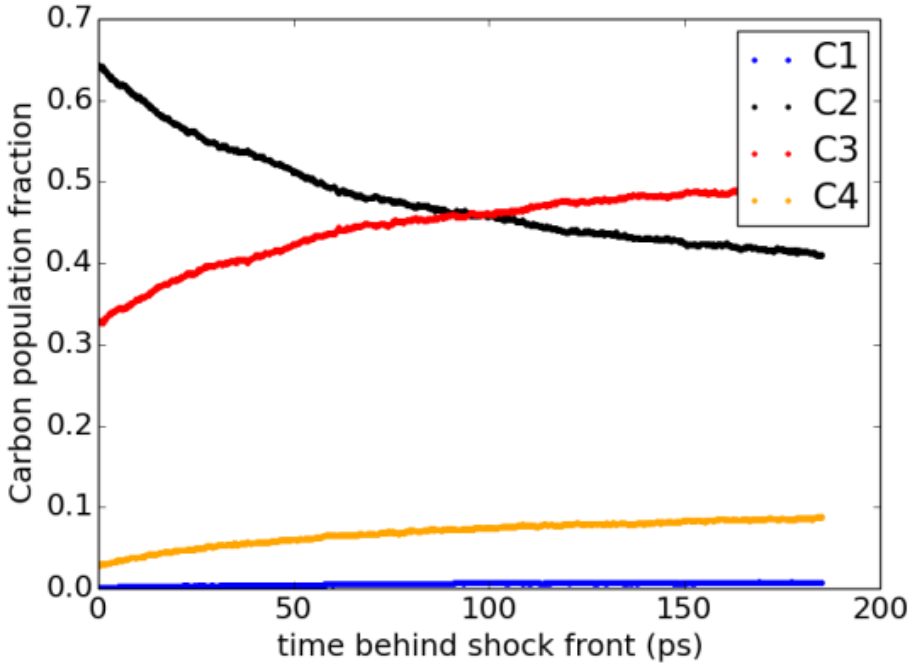


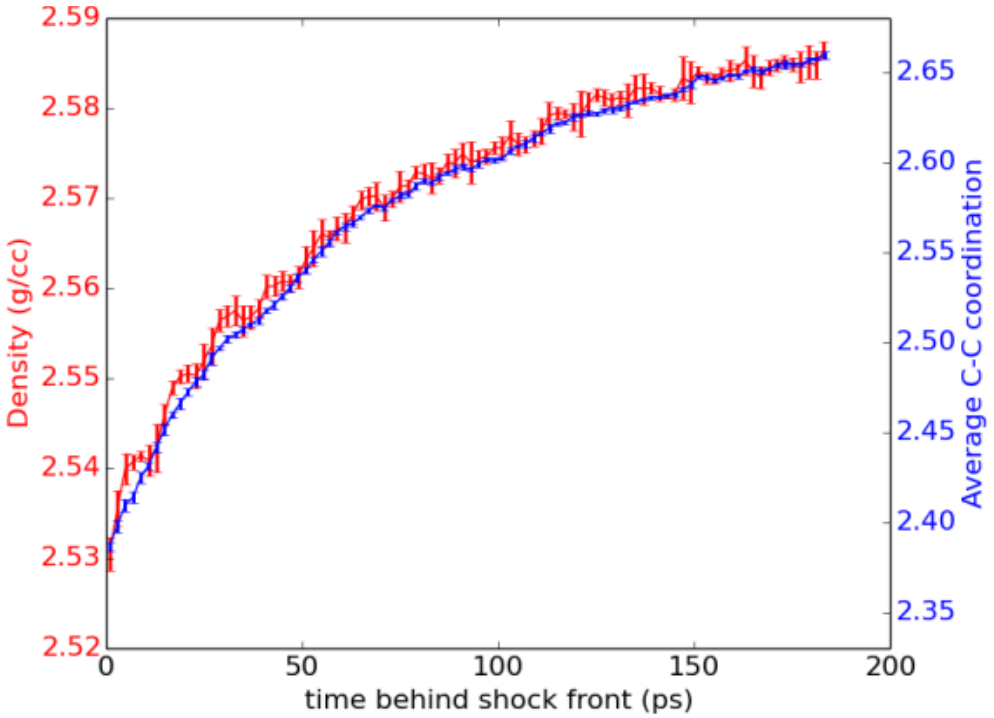



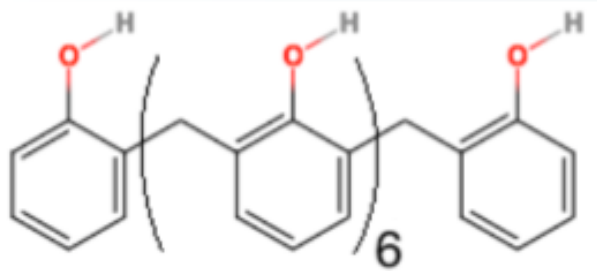

Densification behind the shock observed at high pressure, manifesting over 10s- 100s of ps.

# Results



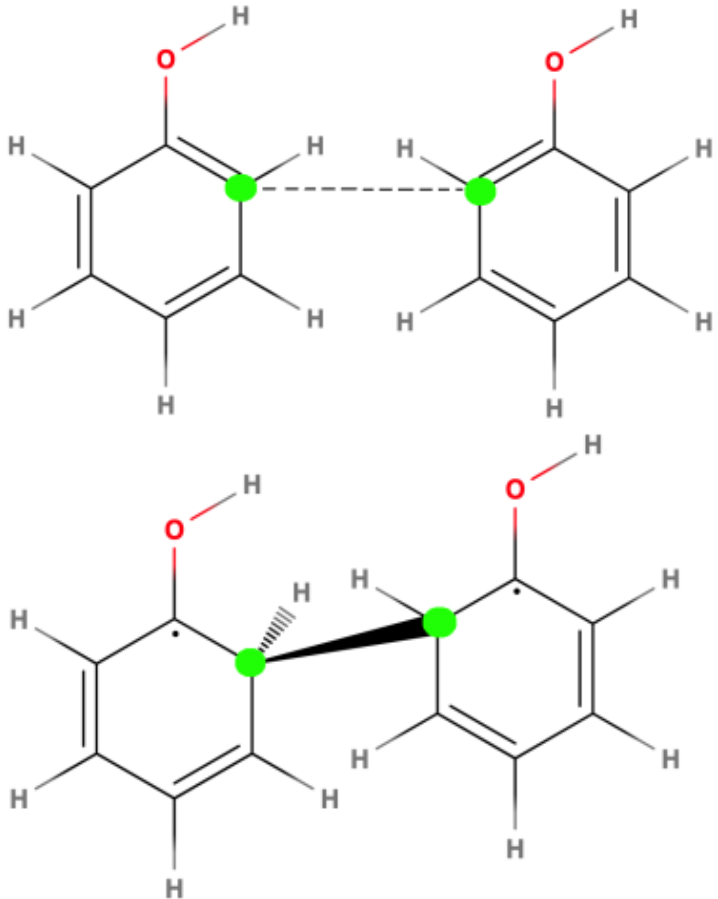

Increase in average carbon-carbon coordination number, correlated in time with the increase in density.

Carbon-carbon coordination number: Number of carbons that a carbon is bonded to.

# Results – densification mechanism

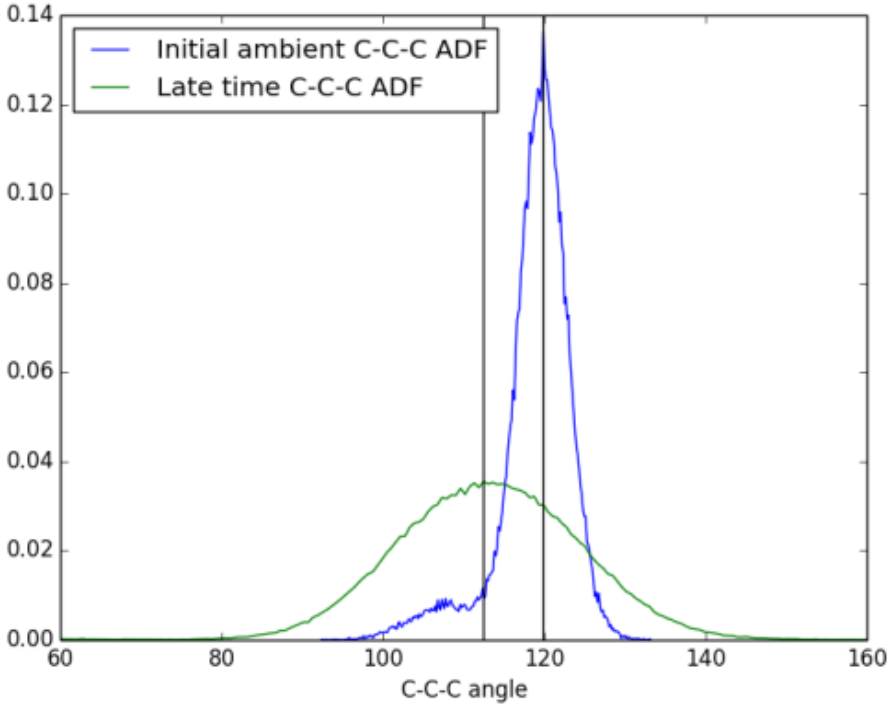
Majority **(>89%)** of C-C bonding events correspond to sp2 → sp3 conversion mechanism (illustrations below).

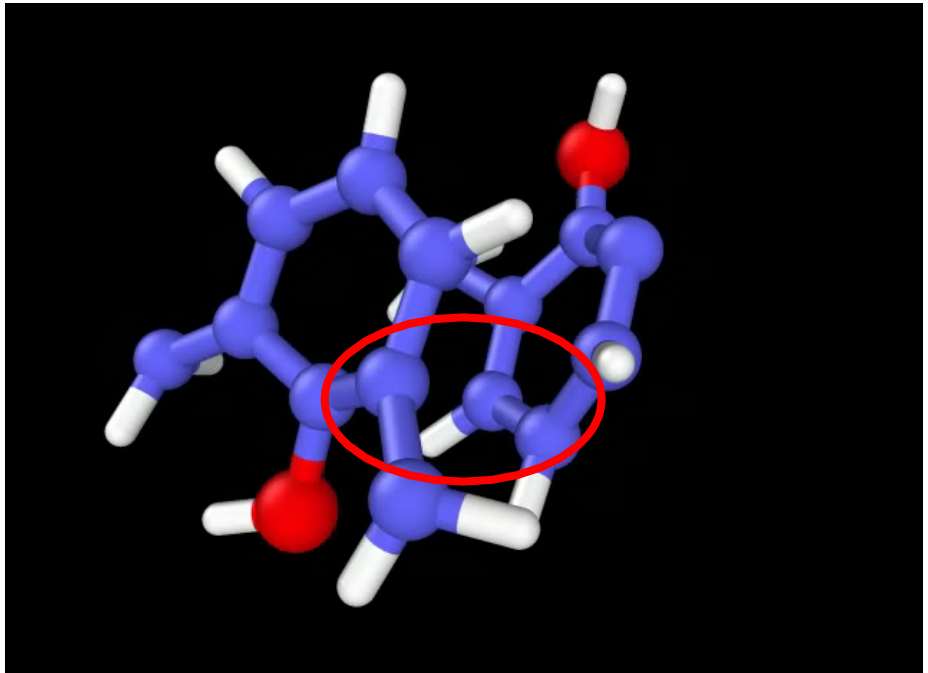
Transition captured in C-C-C angular distribution function comparison between initial and late time shocked systems.



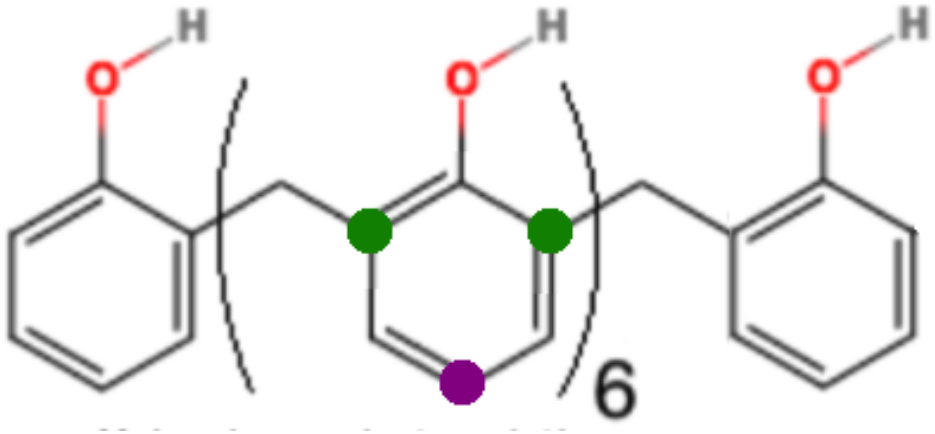
Sp2 carbon
Planar/aromatic
Average X-C-X angle = 120
Total coordination number = 3

Sp3 carbon
Tetrahedral
Average X-C-X angle = 109
Total coordination number = 4



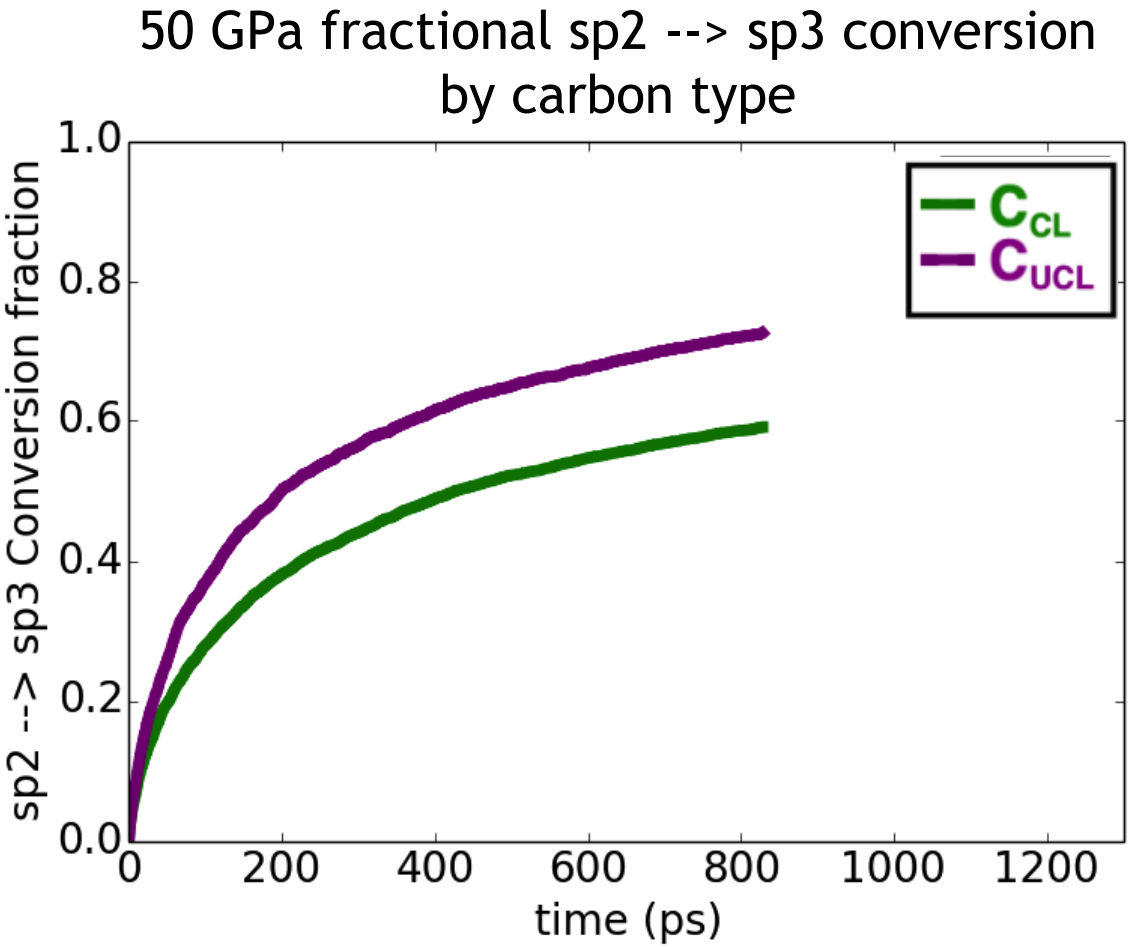



# Results - Selectivity




$C_{CL}$: Cross-linked. Bonded to 3 other C atoms. Located at ring's ortho position.

$C_{UCL}$: Uncross-linked. Bonded to 2 other C atoms. Located at ring's para position.



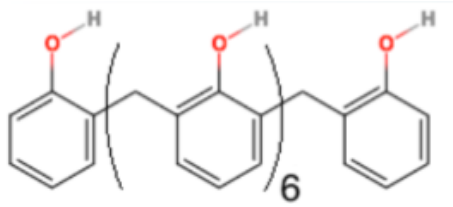
# Conclusions

- Shock-induced chemical densification in phenolics is captured with ReaxFF/Hugoniostat combination.
- This process is linked to an increase in C-C bonds under shock loading, forming a dense, highly crosslinked, carbonaceous solid.
- The primary mechanism for the increase in C-C bonds is inter-ring bonding, which converts newly bonded ring carbons from sp2 to sp3.
- This reaction is selective, more frequently targeting **uncrosslinked** ring carbons over **crosslinked** carbons, potentially due to local constraints.

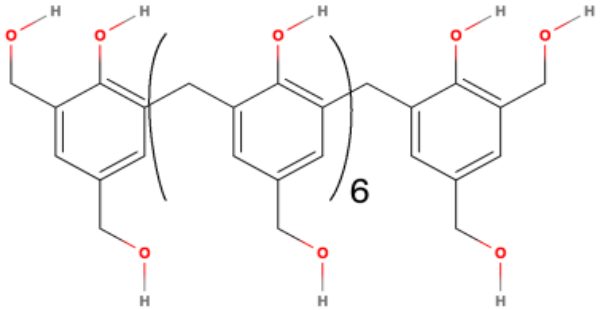
# Future work

Phenolics – complex polymers that are often not well-characterized in terms of molecular weight and degree of crosslinking. Would like to choose a variety of systems that ”run the gamut” from low to high crosslinking with different sidechains and linkers.

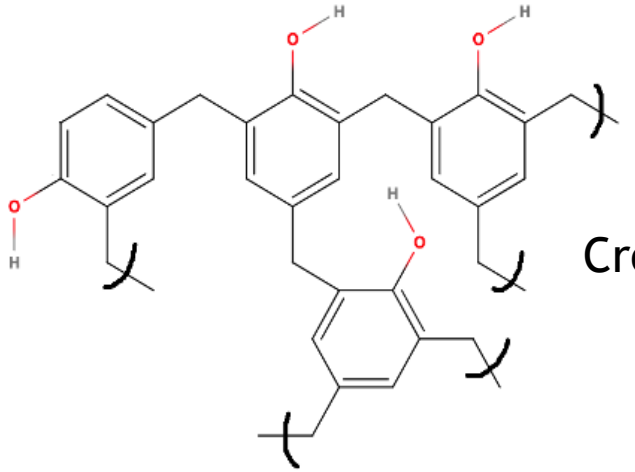
Relevant subset of systems - bracket possible structures



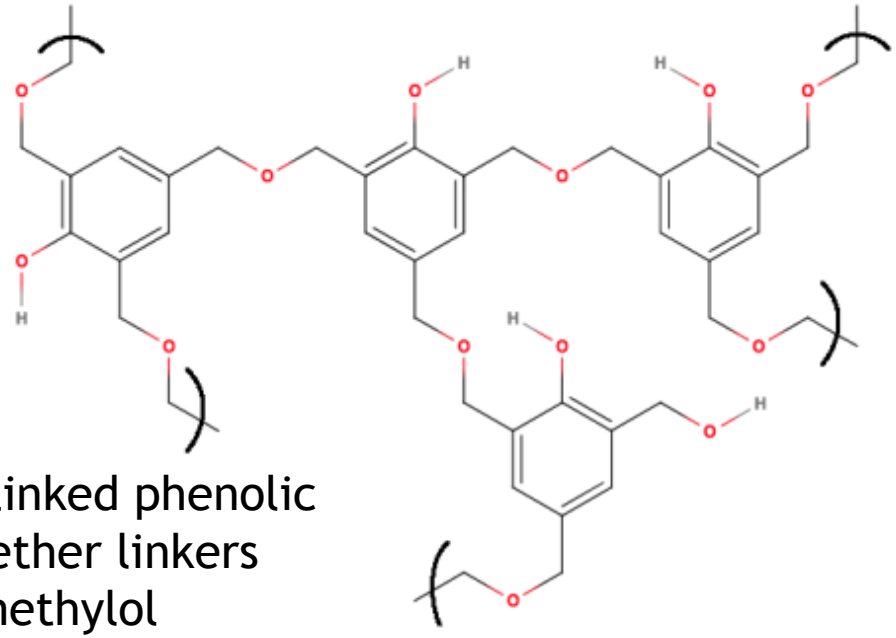

System of linear chains




System of linear chains with methylol sidechains



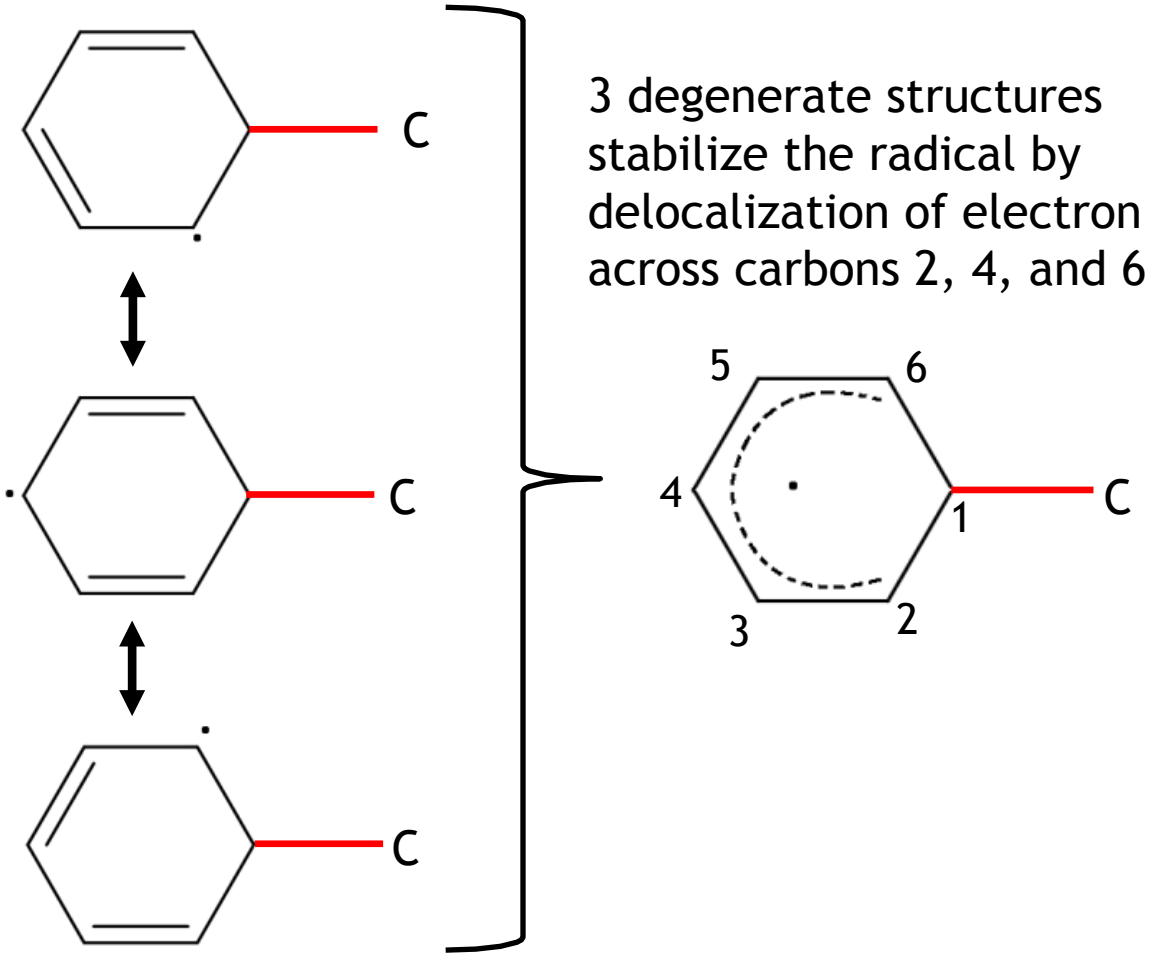
Crosslinked phenolic



Crosslinked phenolic with ether linkers and methylol sidechains

# Results – Qualitative observations

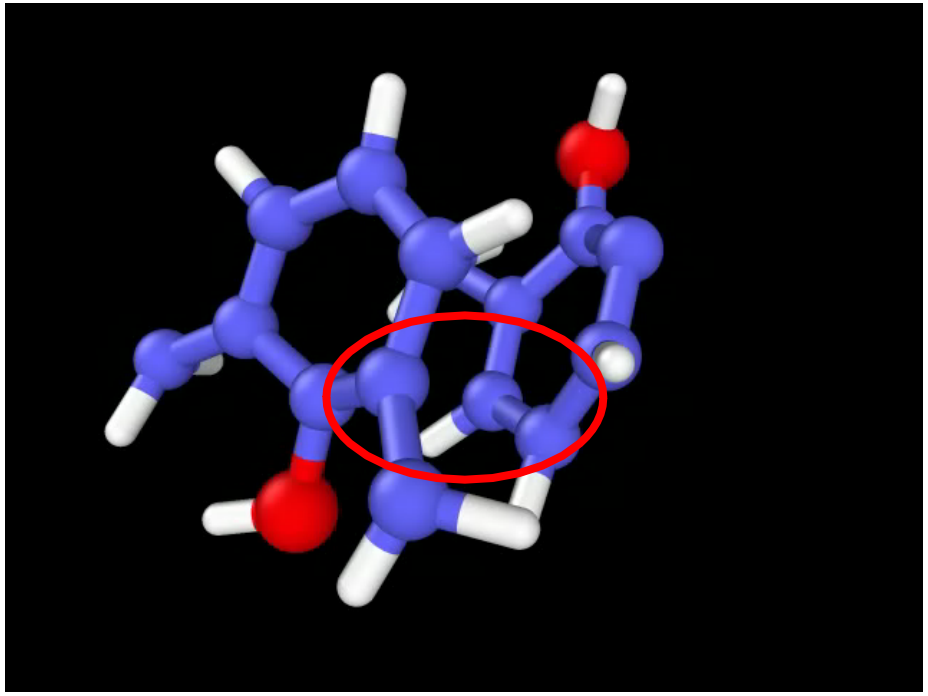
Due to resonance stabilization of radical, rings do not destabilize immediately upon new C-C bond formation.




3 degenerate structures stabilize the radical by delocalization of electron across carbons 2, 4, and 6.




ReaxFF/CHO has been shown to capture the resonance stabilization of radicals even without explicit inclusion of electronic degrees of freedom.



K. Chenoweth et al., *J. Phys. Chem.* **112**, 1040 (2008).