Predicting Char Yield of High-Temperature Resins

Jacob Gissinger* and Kristopher Wise
NASA Langley Research Center

*jacob.gissinger@nasa.gov
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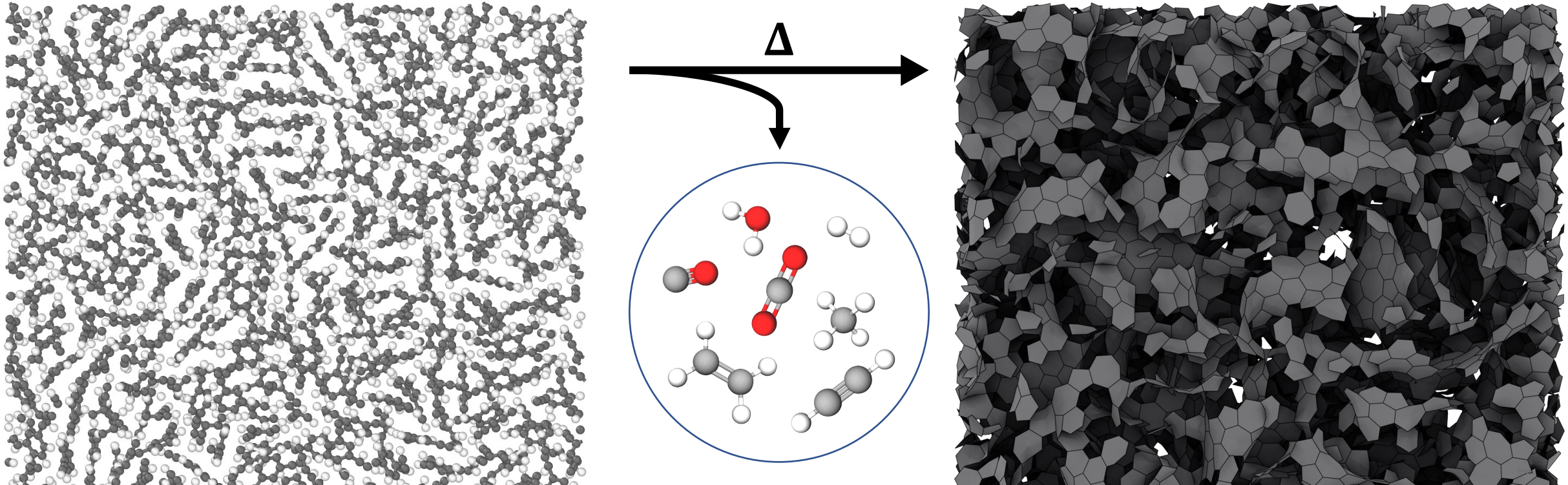
Langley Research Center

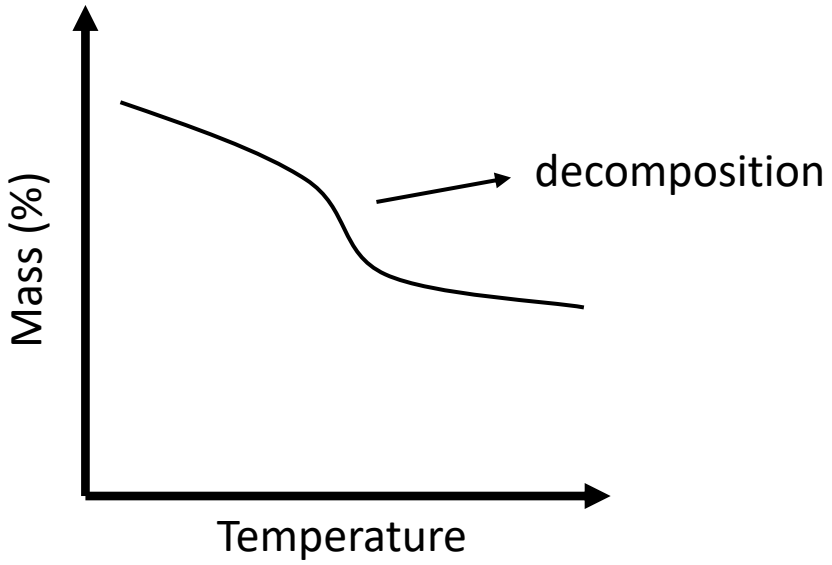


Composites are Pervasive in Aerospace

- Composites have replaced many components of aircraft and spacecraft
- Huge design space: the efficacy of new chemistries is difficult to predict
- Computational screening can help guide us toward next-generation high-temperature resins

Why is Char Yield Important?

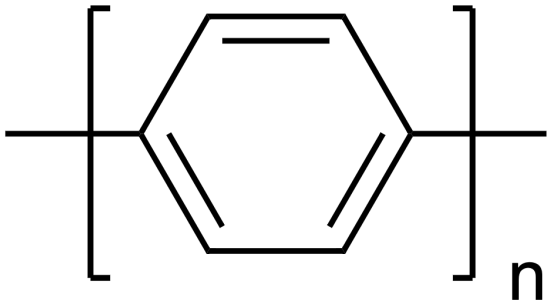
- Char yield is the amount of material left over after subjecting it to high temperature pyrolysis
  - Thermogravimetric analysis (TGA) is used to obtain plots of mass vs time and/or temperature (typically ramped up to 800°C - 1000°C)
- High char materials require fewer cycles of carbonization and resin infiltration to achieve desired properties



Typical TGA plot

Prior Efforts to Predict Char Yield

- Correlate existing literature data with empirical formulas
  - Element ratios, molecular group analysis, quantitative structure-property relationships (QSPR)
  - Achieves reasonable correlations with low-char yield resins
- Not useful for materials substantially different from training set



$M_i \approx 76$ g/mol (mass of group)
$X_i = 35$ g/mol (molar group contribution)

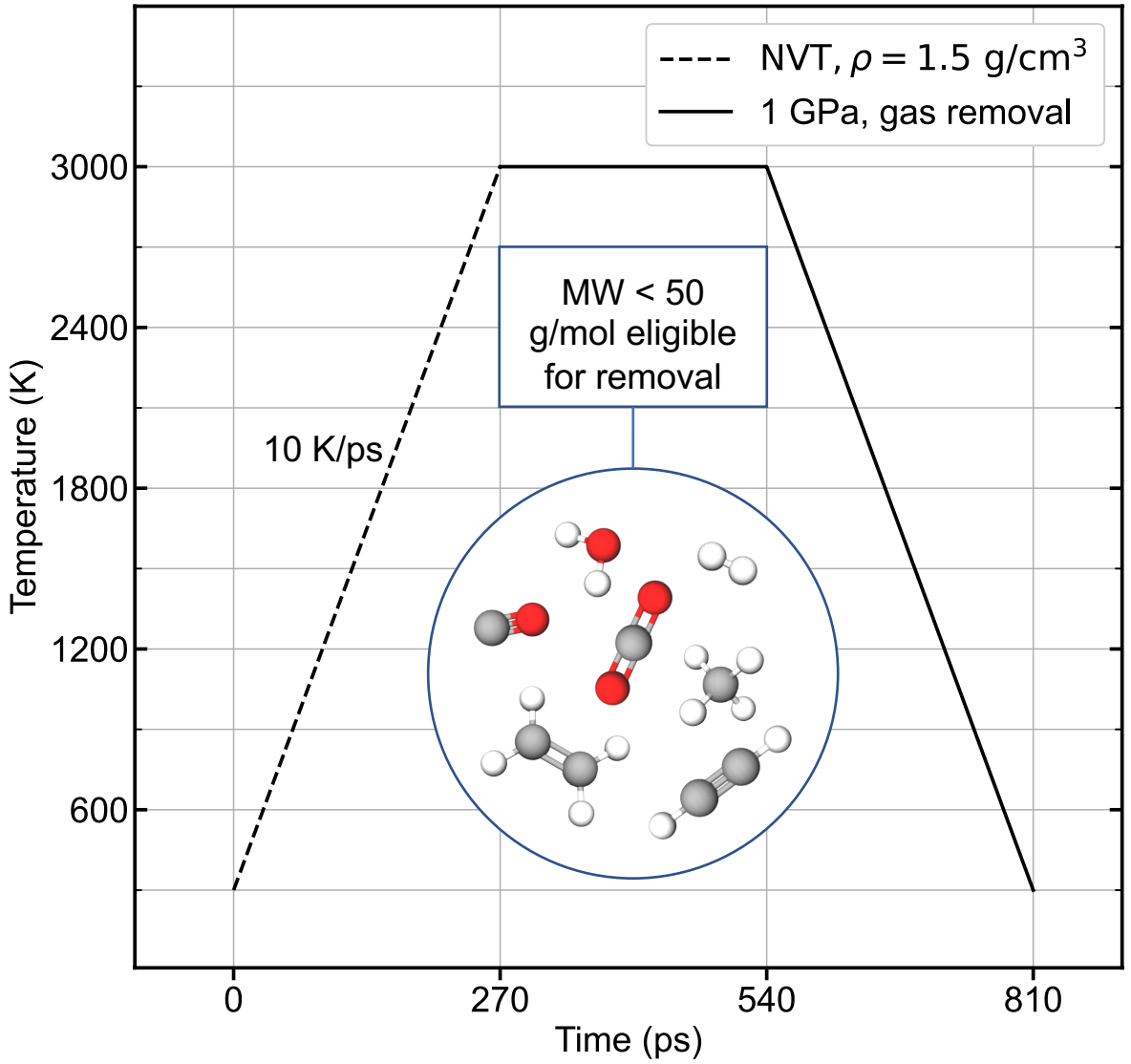
Predicted char yield: $X_i/M_i \approx 46\%$

Example of molecular group analysis for phenyl group in polymer backbone

Lyon, Richard E., et al. “A Molecular Basis for Polymer Flammability.” *Polymer* 50, no. 12, 2608–17 (2009).

Char Yield Simulation Protocol

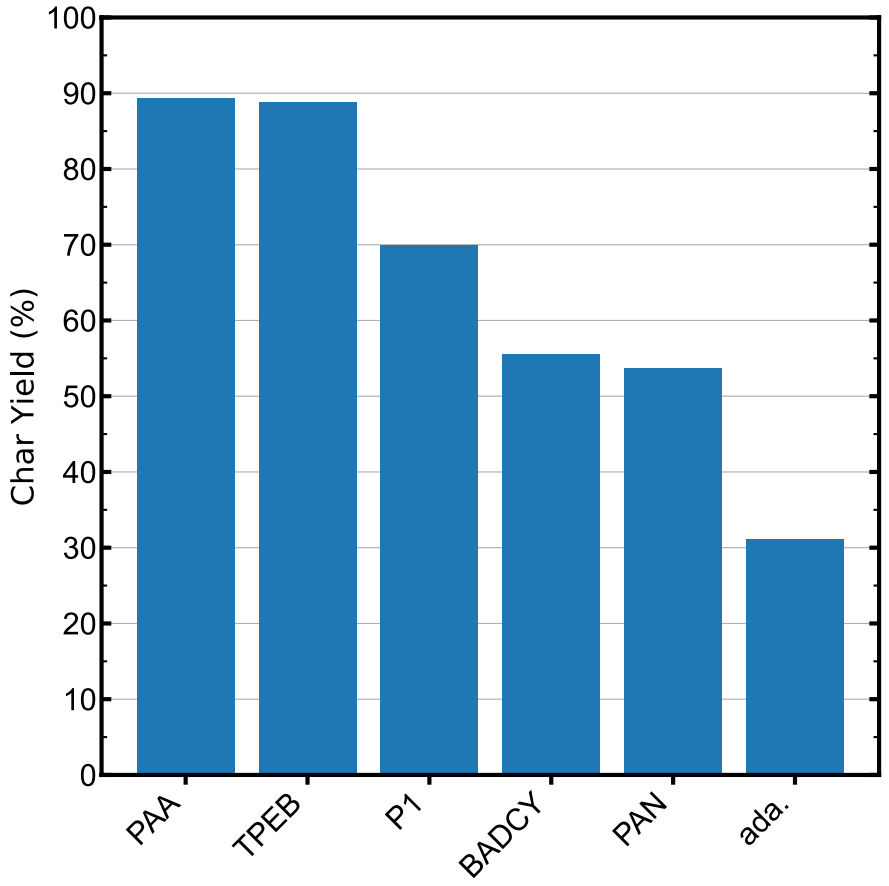
- Temperature ramp cycle
  - 300K – 3000K at 10 K/ps
  - High temperatures/rates to accelerate reactions
- Anneal at high pressure (1 GPa) to achieve final densities of 1.8 g/cm^3 - 2.0 g/cm^3
- ReaxFF with periodic removal of outgassing products to allow for carbonization and densification
- Initial system size: 36000 atoms

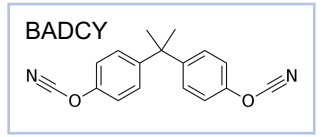


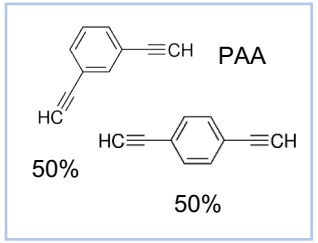
Char Yield Results

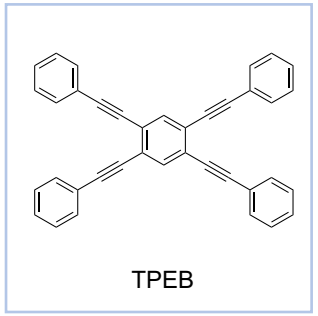
- Simulation protocol able to accurately predict char yield trends
  - Expected values (literature)*:
    - PAA and TPEPB: ~90%
    - P1: ~80%
    - BADCY: ~45%
    - PAN: ~55%
    - Adamantane: ~33%

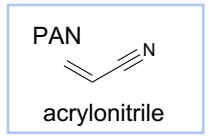
- Chemically specific method
- No assumptions or fitting of experimental results

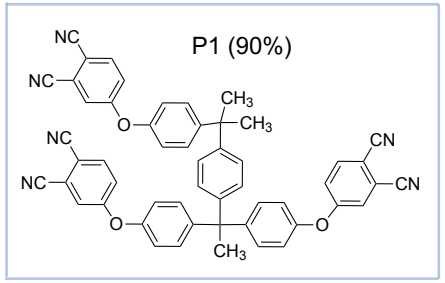








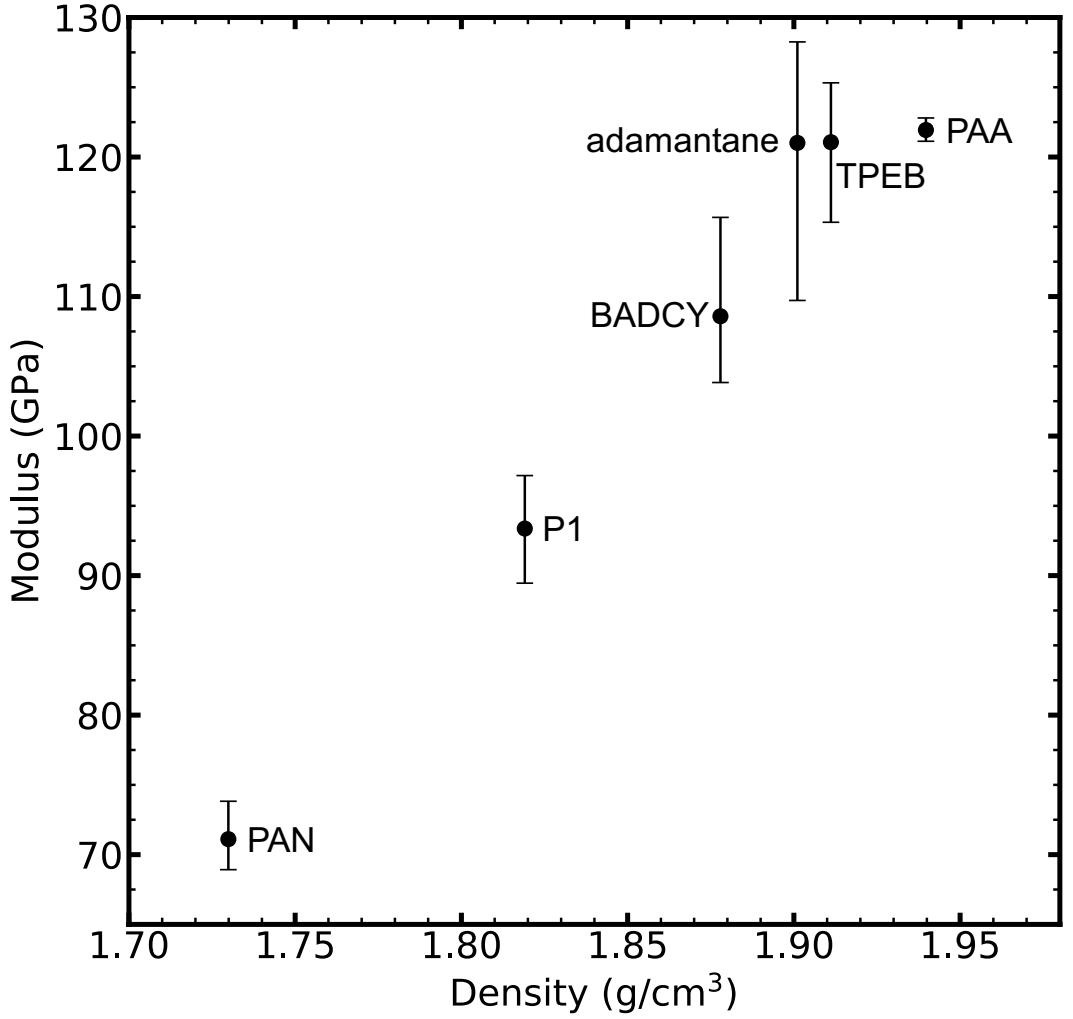




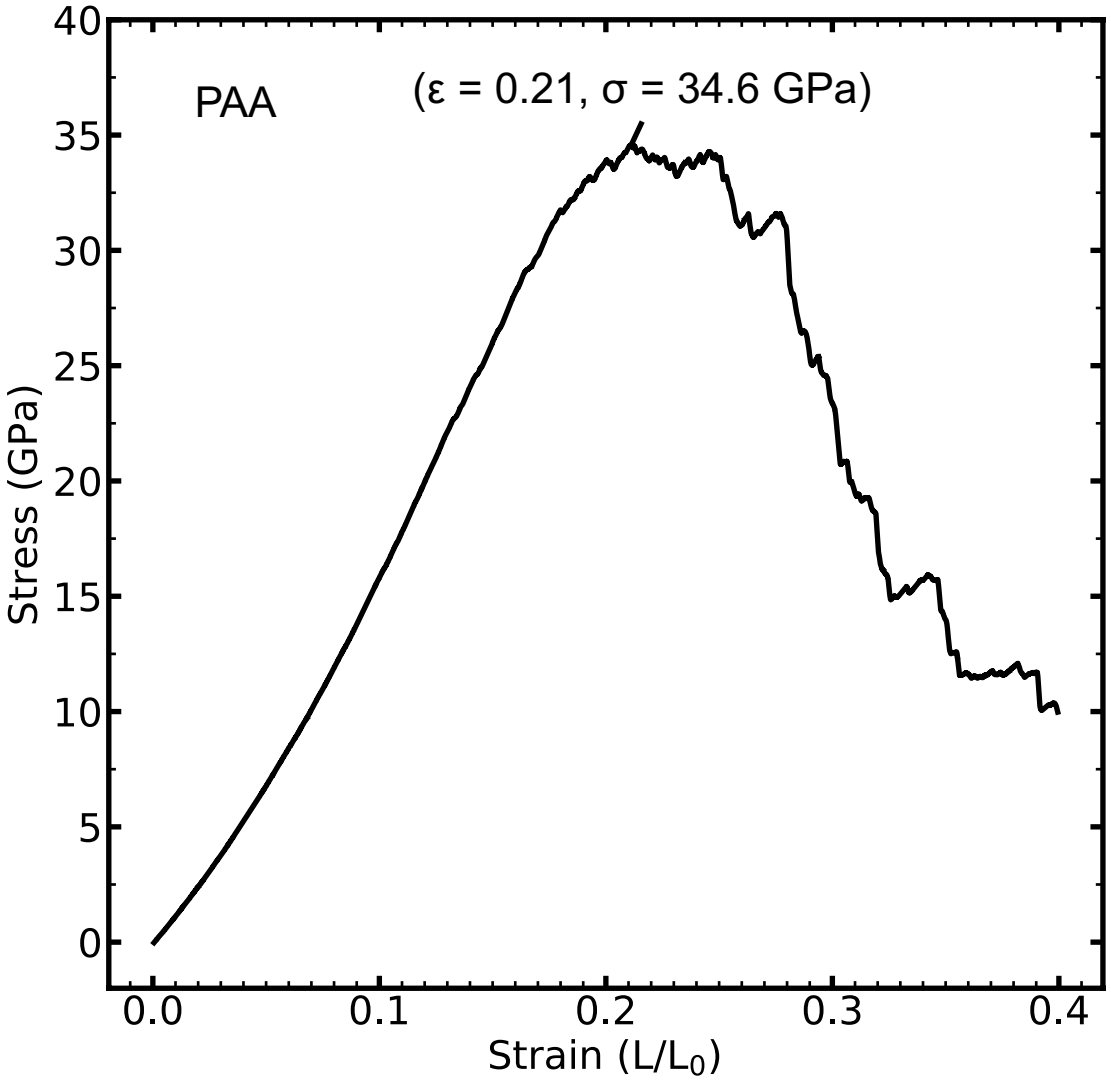
* Full names and literature citations provided on Chart 19

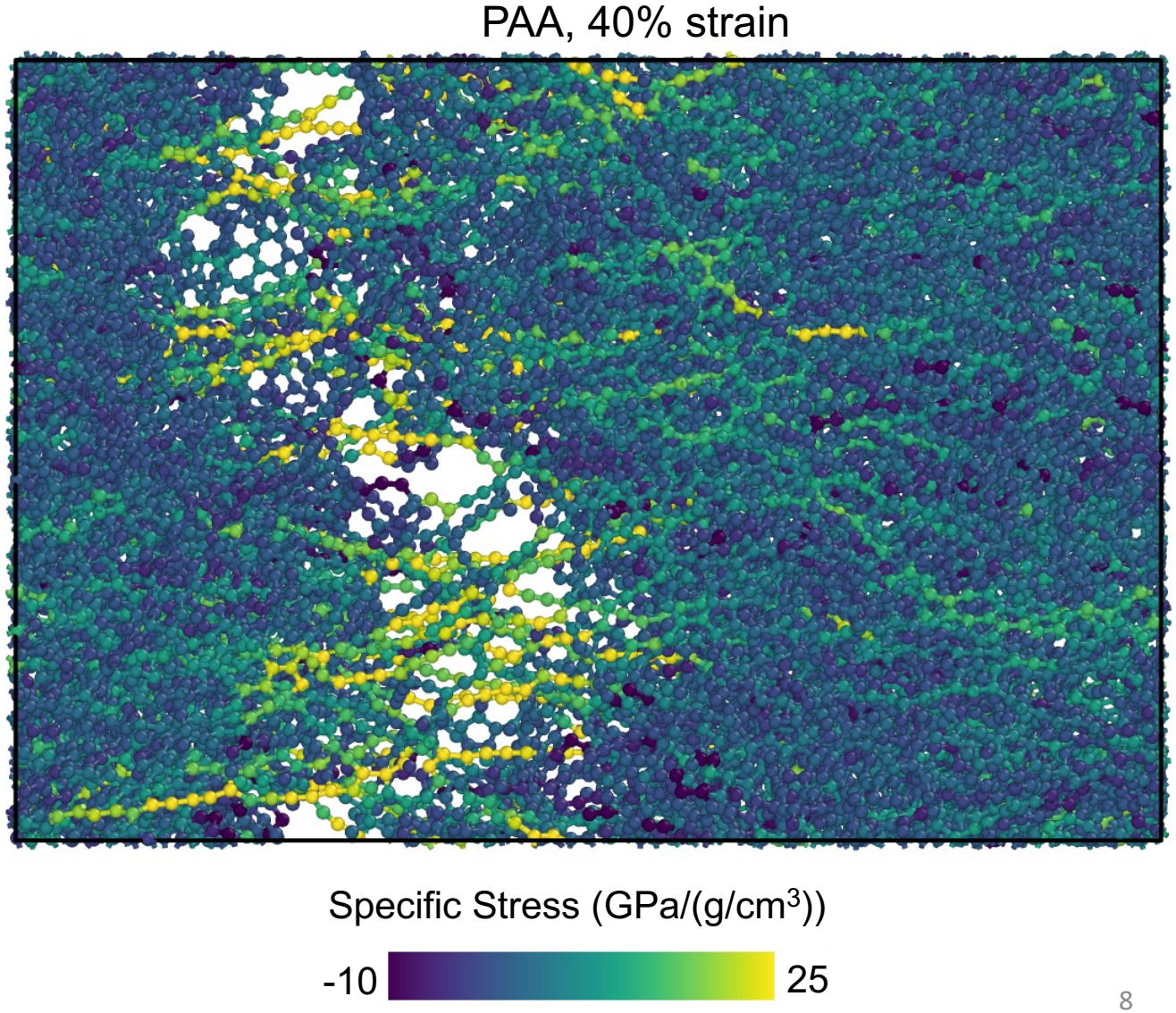
Mechanical Properties

- Nonporous char morphology results in high predicted elastic moduli
- Predicted values in expected range for glassy carbon (~30 GPa @ 1.5 g/cm^3), but far lower than high modulus carbon fibers
- Highlights importance of achieving structures with high density and low defects, porosity

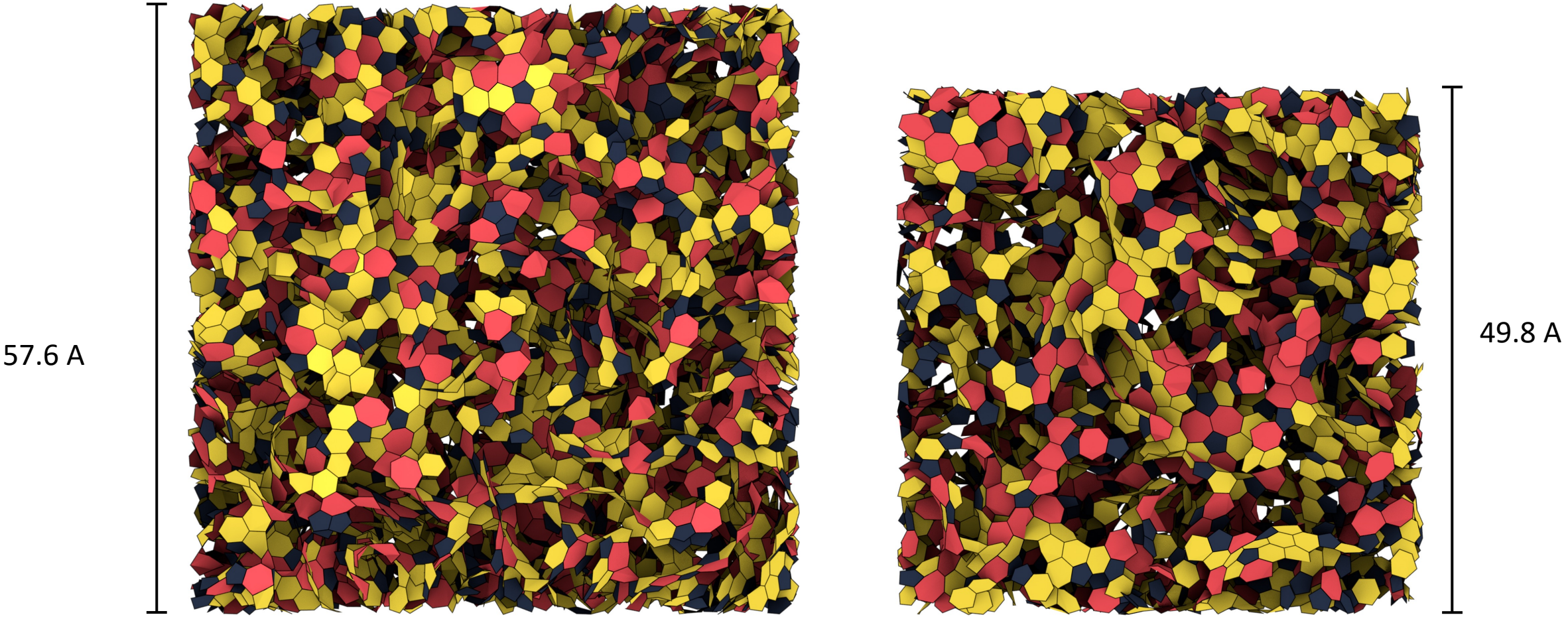


Strain to Failure



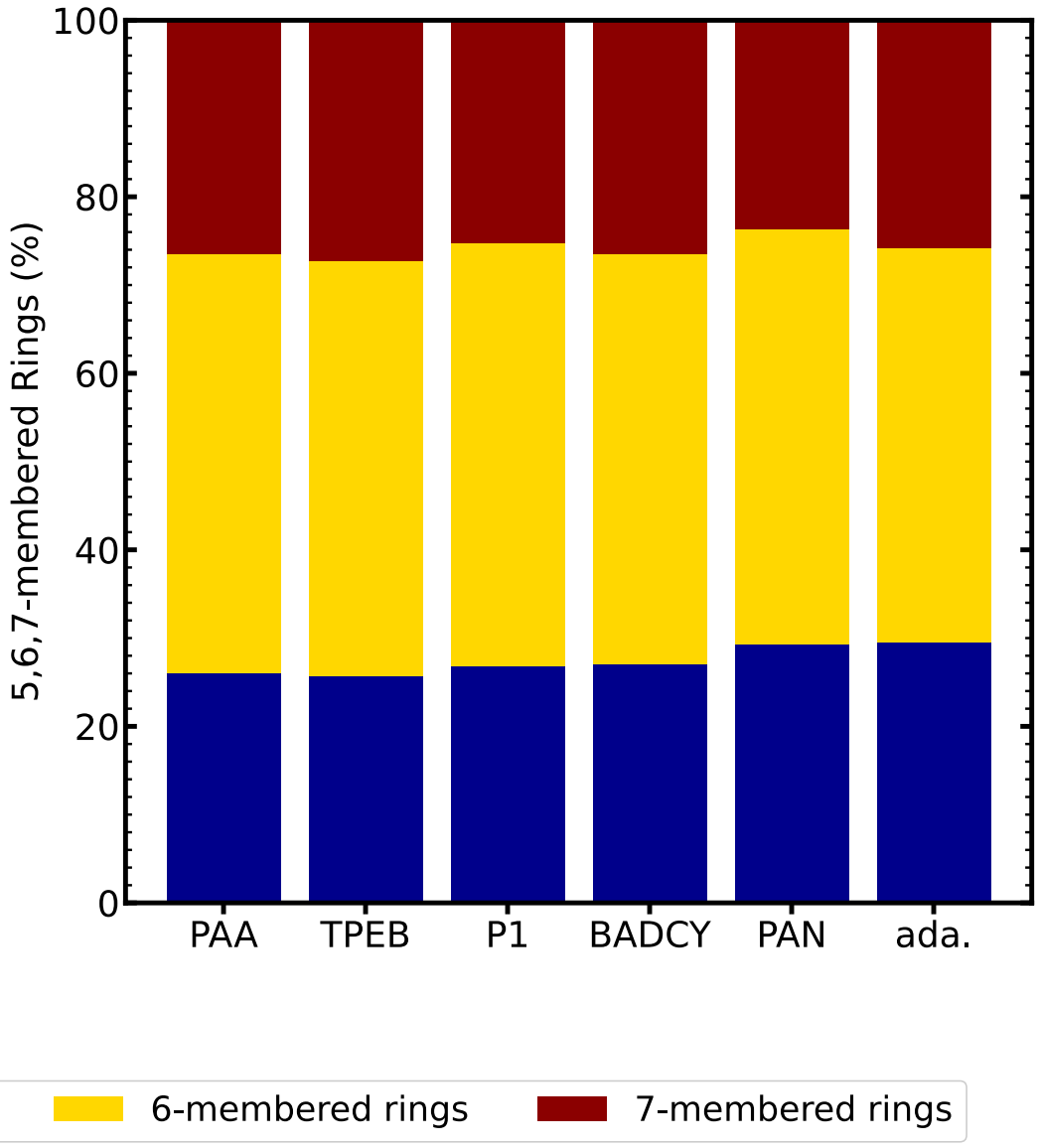


Final Morphology: Ring Distribution

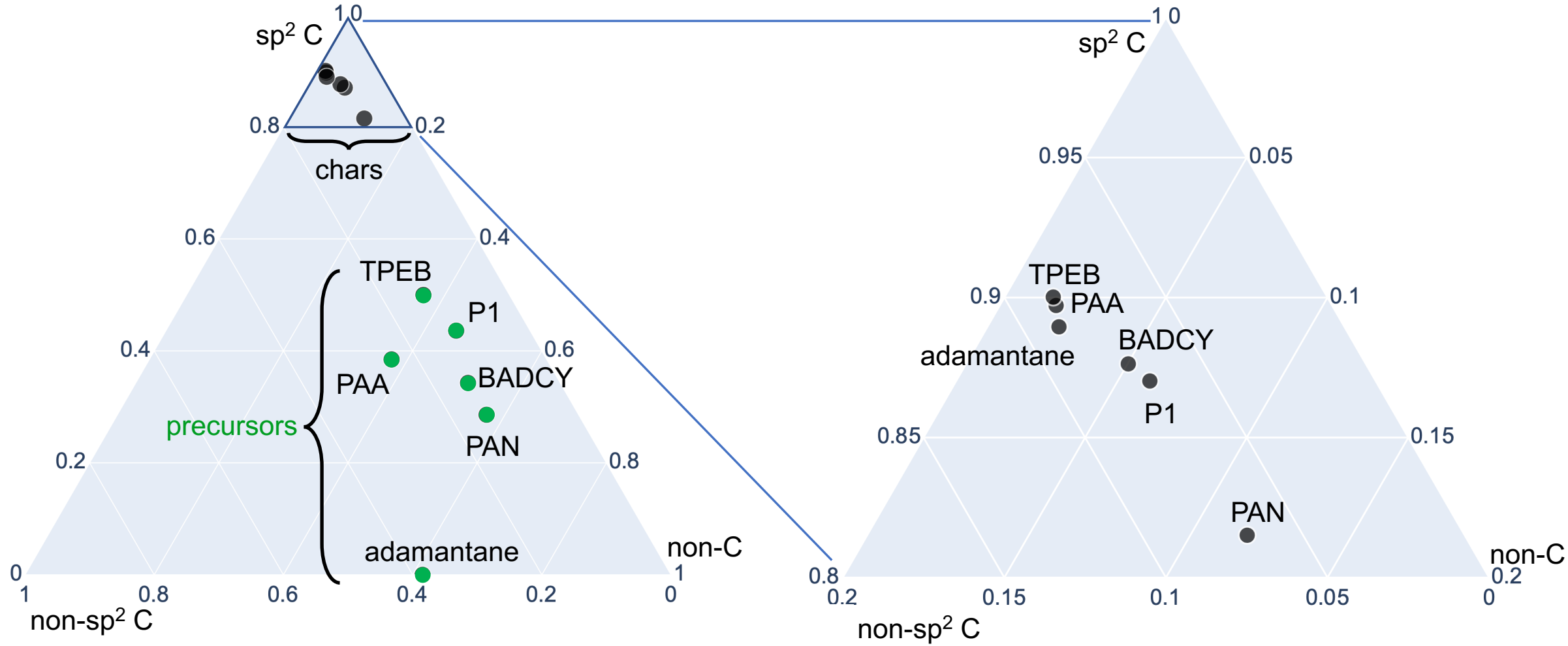


Final Ring Morphology

- Ratios of 5-, 6- and 7-membered rings consistent across chemistries
- Little dependence on char yield or final density
- Relatively large number of 5- and 7-membered rings remain
- Further annealing affects ring structure but not char yield



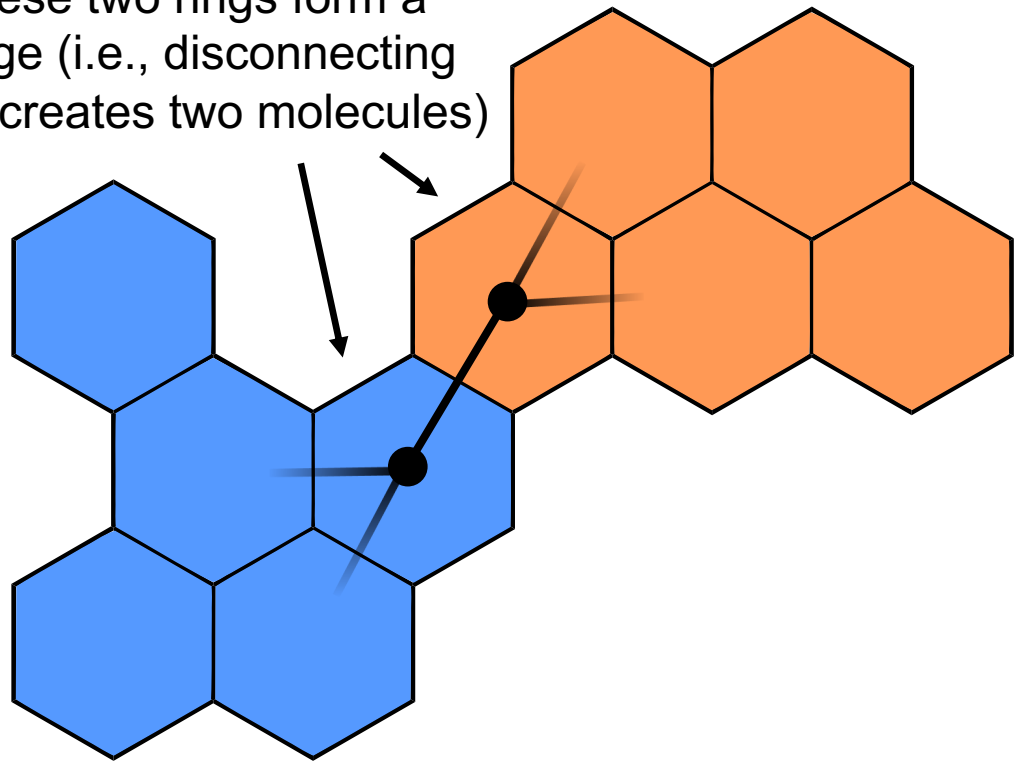
Carbon Hybridization/Heteroatoms Evolution



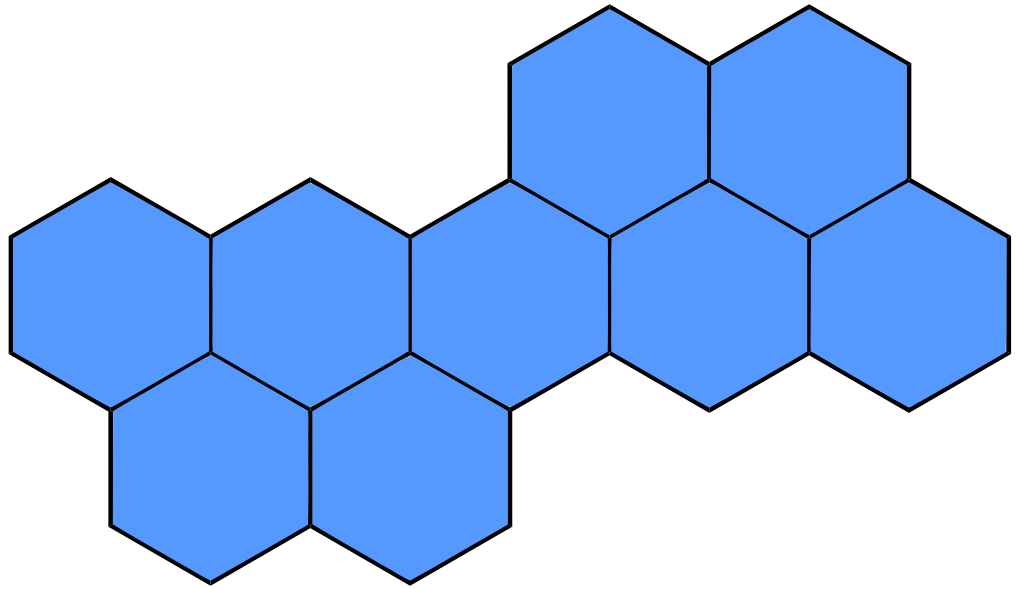
Ternary ‘glassy carbon’ phase diagram
axes = fractional number of atoms

Topological Analysis: Cluster Definition

These two rings form a bridge (i.e., disconnecting them creates two molecules)



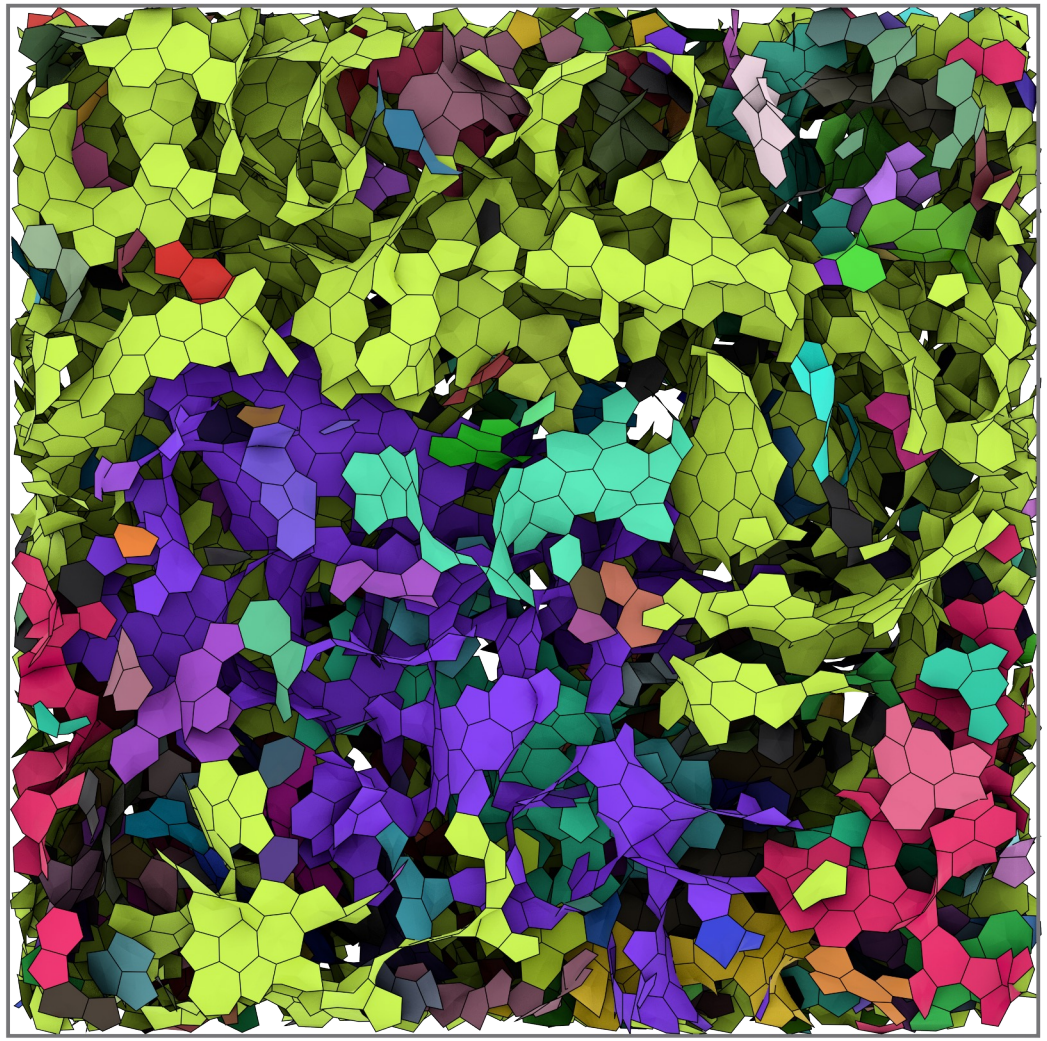
Two clusters



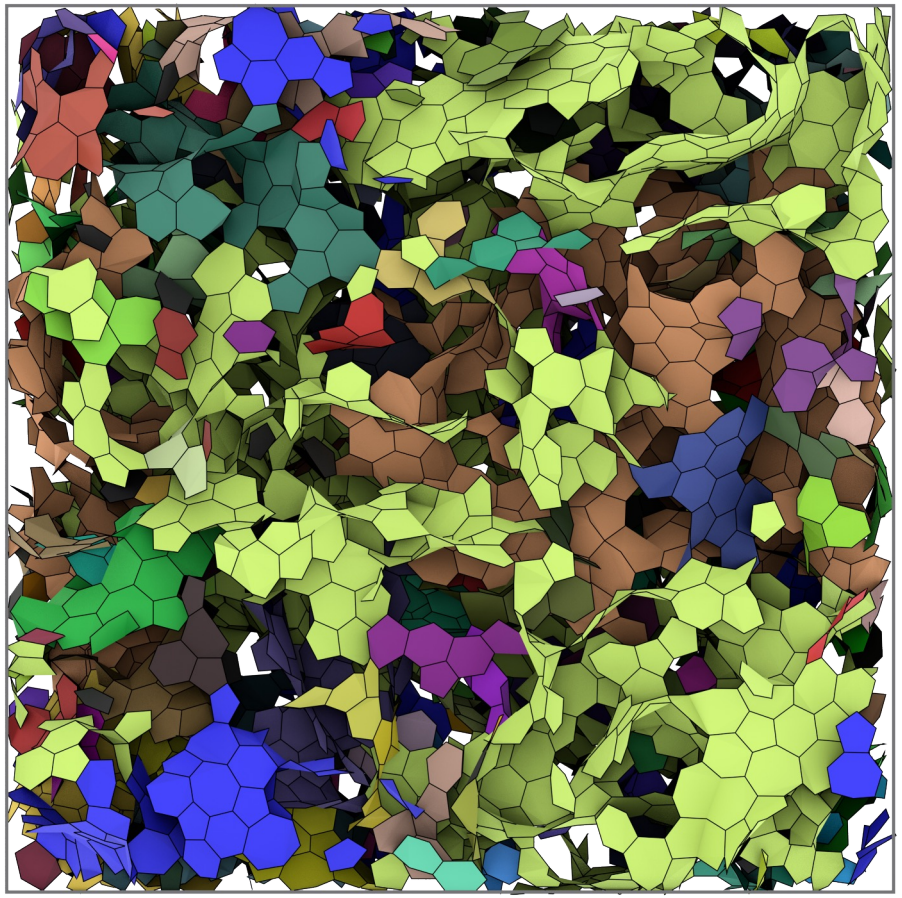
One cluster (no bridges, i.e., each fused ring pair shares at least one other ring)

Final Morphology: Cluster Distribution

57.6 A

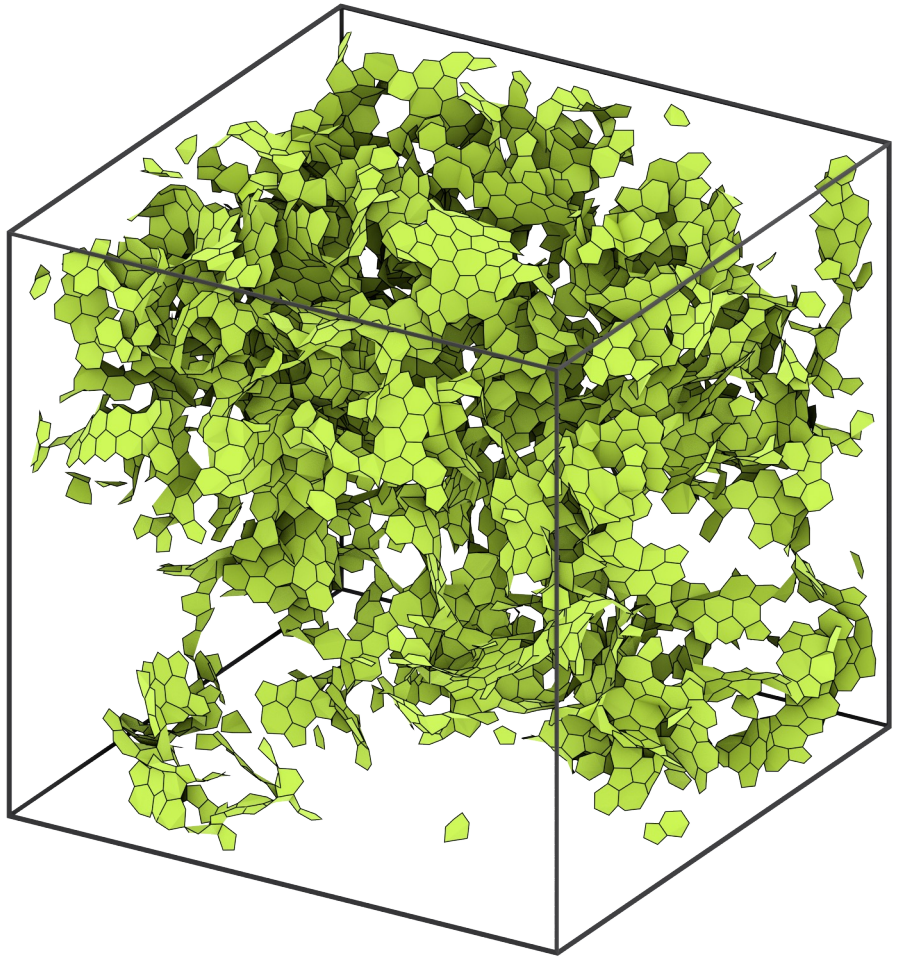


PAA

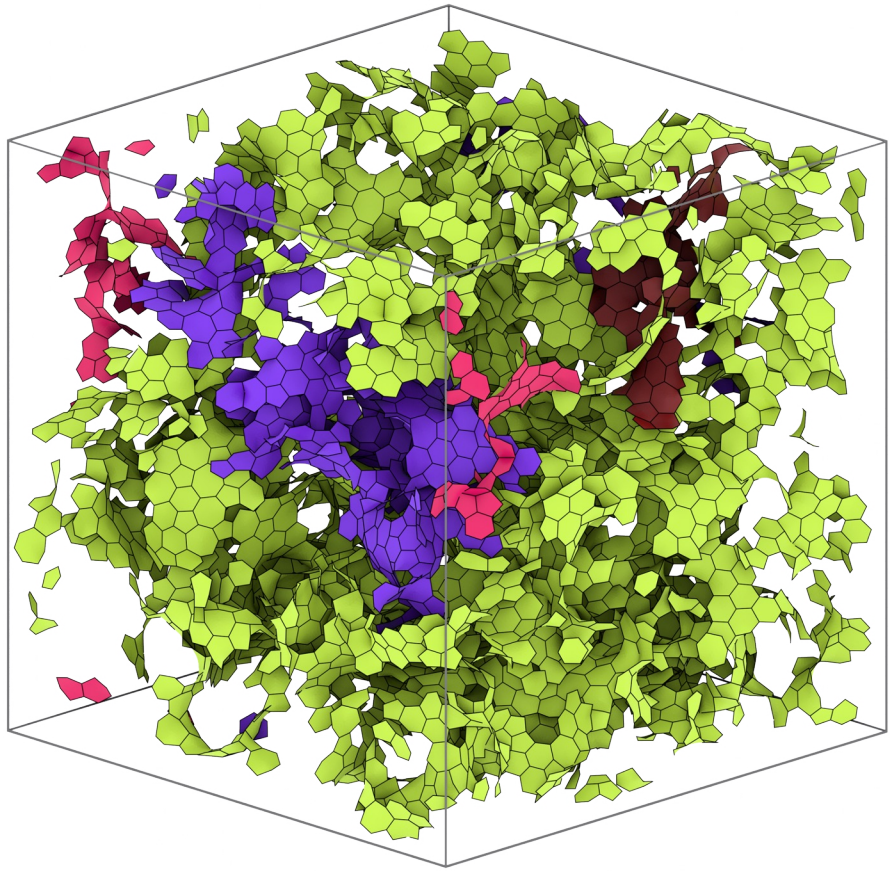


BADCY

Final Morphology: Cluster Distribution



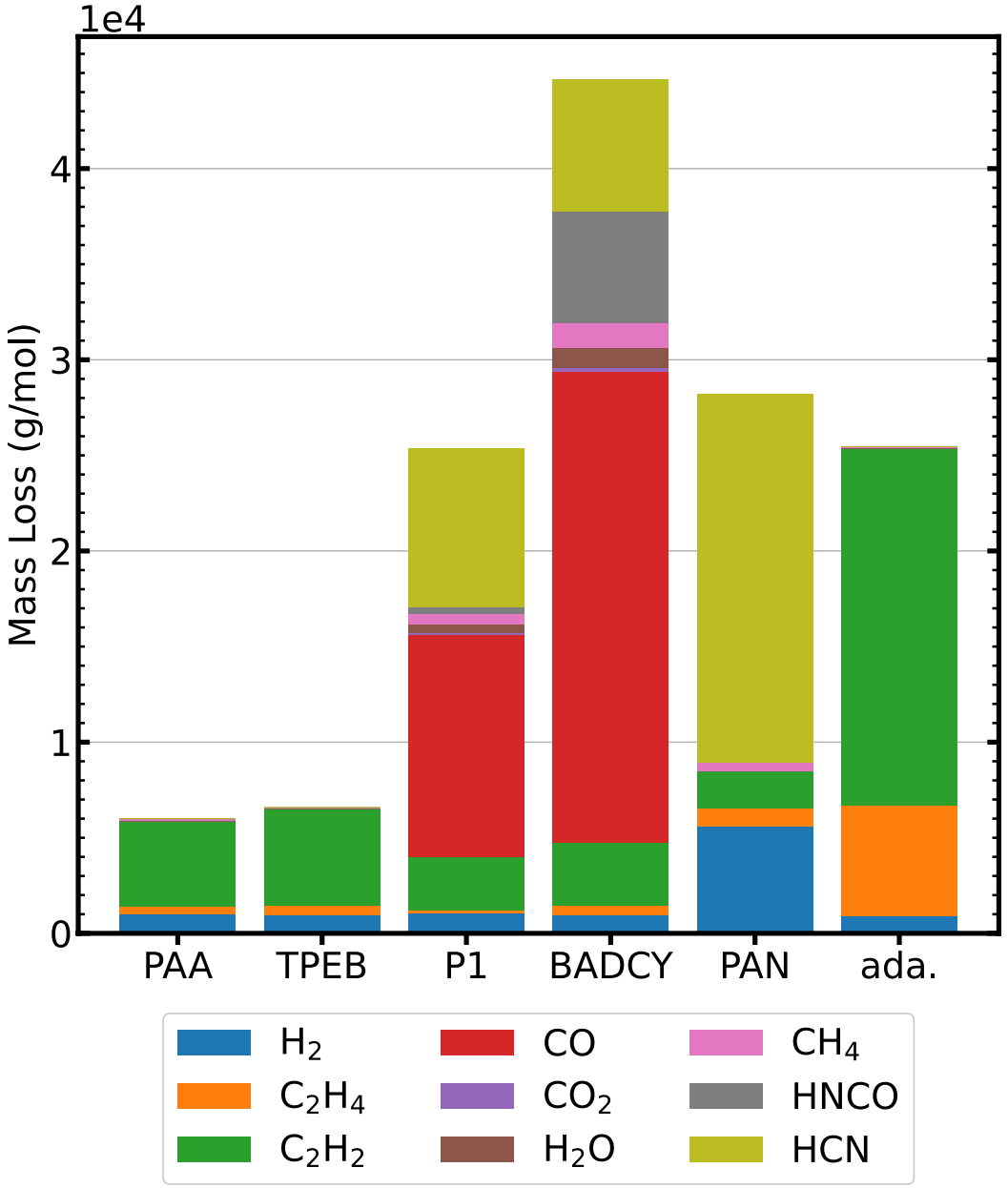
PAA, largest cluster



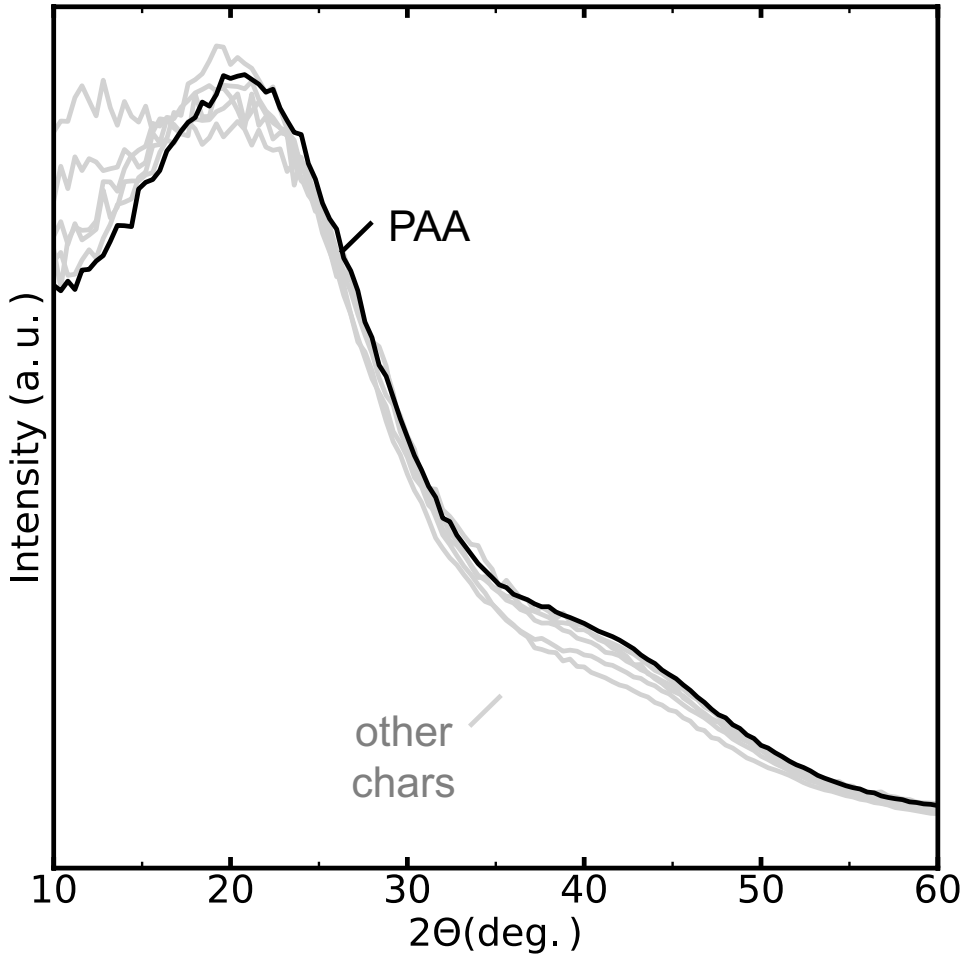
PAA, top four largest clusters

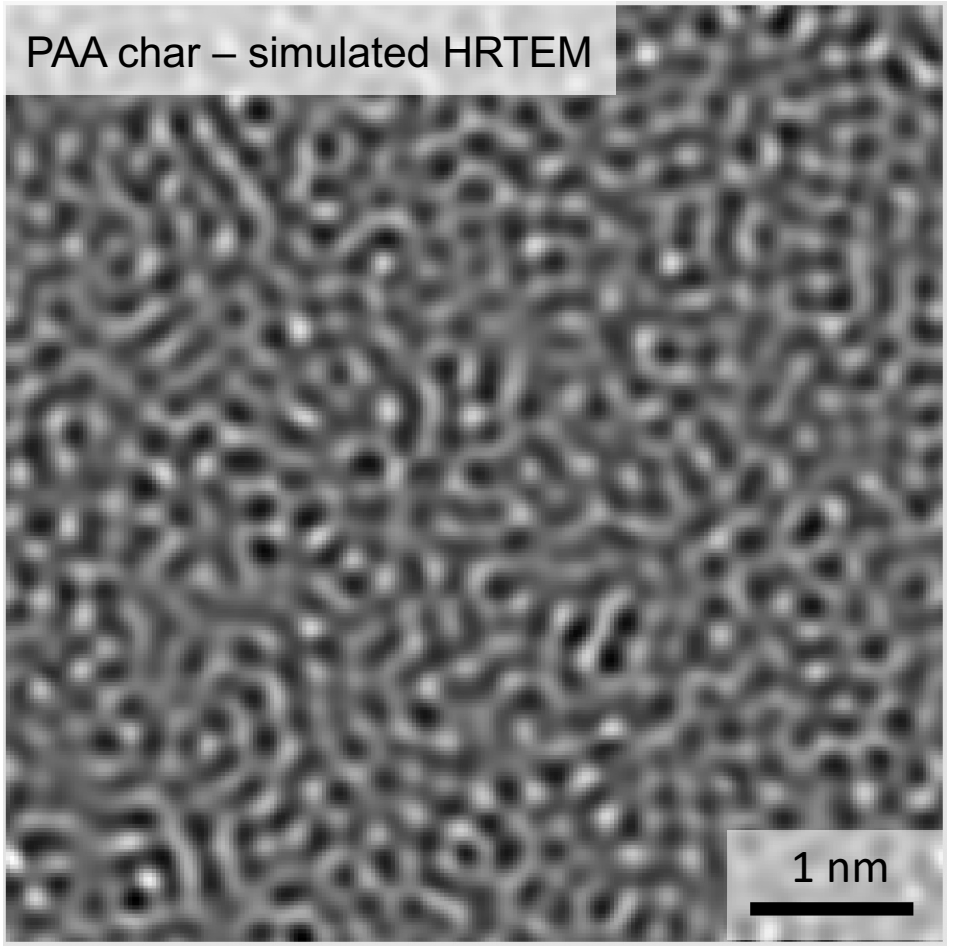
Outgassing Products

- Protocol keeps track of molecules removed from the system to mimic outgassing
- Primarily carbon monoxide (CO) for oxygen-containing resins (highly stable bond)
- Useful metric to compare to experiment, to confirm correct chemistry



Tools for Direct Experimental Comparison

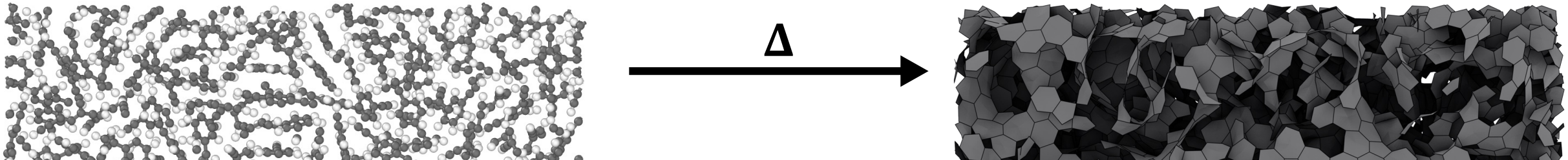




Simulated X-ray Diffraction and microscopy consistent with non-graphitized glassy carbon

A Promising Method for Predicting Char Yield

- A chemically specific protocol was developed to predict char yield for high temperature resins
  - No prior knowledge of high-temperature behavior required
- Validated for low, medium and high char yield resins with various chemical structures and number of heteroatoms
- Additional outputs include atomistic structure, composition, morphology, mechanical properties, chemical pathways, outgassing products
- Currently being used to investigate and screen new chemistries



Thank You!

Email: jacob.gissinger@nasa.gov

References (experimental char yield values):

PAA (Polyarylacetylene)
Katzman, H. A. et al. DTIC Accession Number ADA302053, 1995.

TPEB (Tetraphenylethynylbenzene)
Jones, K. M. et al. Polymer, 36, 187, 1995.

P1 (4-[4-[2-[4-[1,1-bis[4-(3,4-dicyanophenoxy)phenyl]ethyl]phenyl]propan-2-yl]phenoxy]benzene-1,2-dicarbonitrile)
Hu, Y. et al. RSC Advances, 8, 32899, 2018.

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Wang, Y. et al. Polymer, 77, 354, 2015.

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Song, C. et al. J Porous Materials, 16, 197, 2009.

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Kazanskii, B. A. et al. Russian Chemical Bulletin, 17, 2506, 1968.