REACTER 2.0: Advanced Reaction Constraints and Automated Interaction Typing

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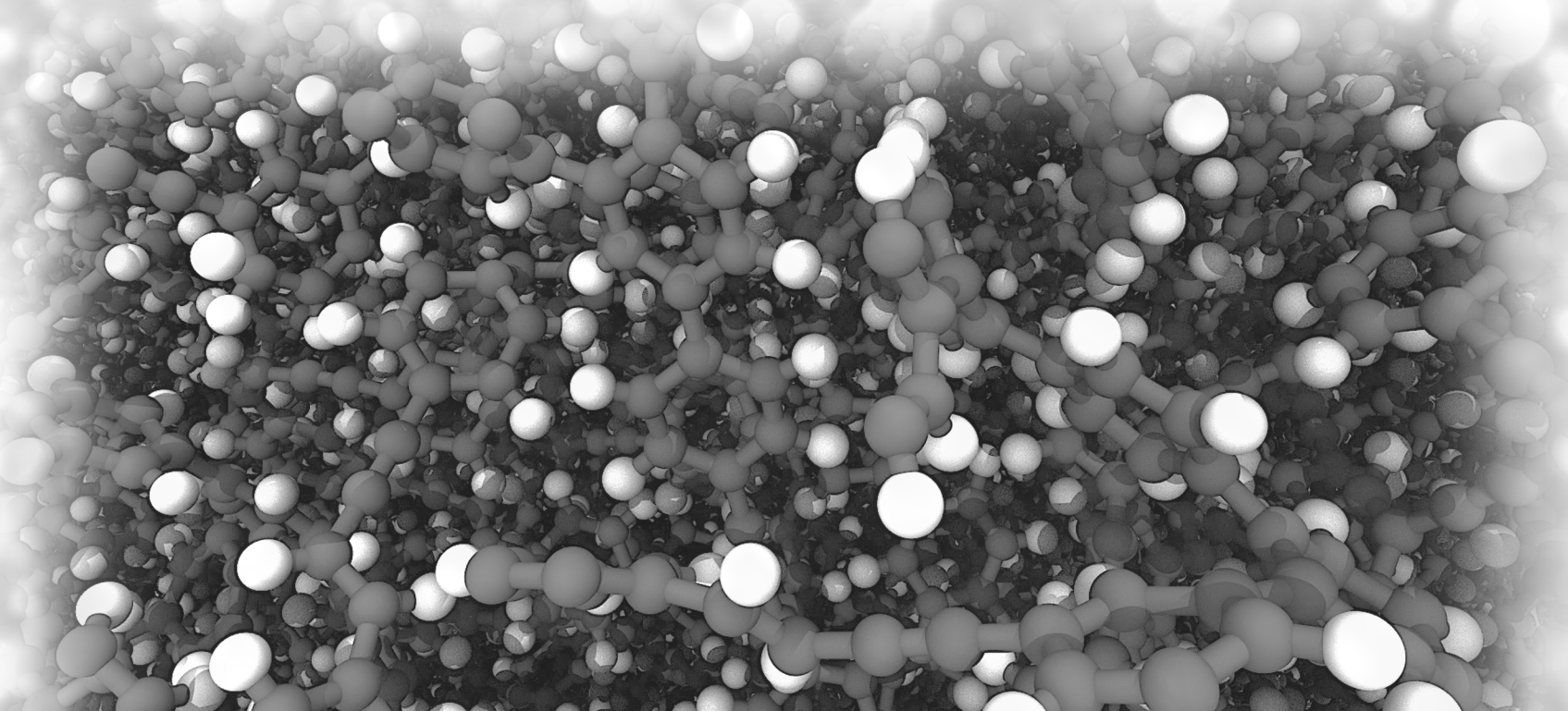


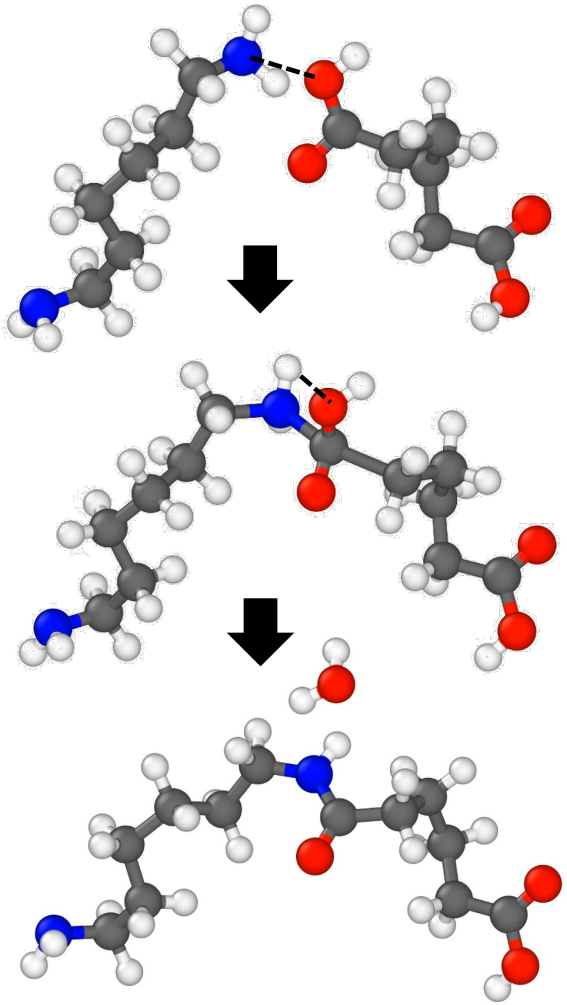
LAMMPS Workshop
Aug. 2021

Langley Research Center

What is REACTER?

- A protocol for adjusting topology during classical MD
  - Unique scale for reaction modeling (fast, atomistic simulations)
  - Add/remove specific bonds, angles, dihedrals, and impropers
  - Modify all force field types as well as atomic charges
  - Supports any fixed-valence force field (PCFF, OPLS, etc.)
  - Reaction stabilization

- Parallel implementation in LAMMPS as ***fix bond/react***
  - User inputs: molecule templates of pre- and post-reaction topology
  - A map file relating atoms before and after the reaction



REACTER: A Heuristic Method for Reactive Molecular Dynamics.
Gissinger, Jensen & Wise. Macromolecules 53, 22, 9953–9961 (2020).

www.reacter.org

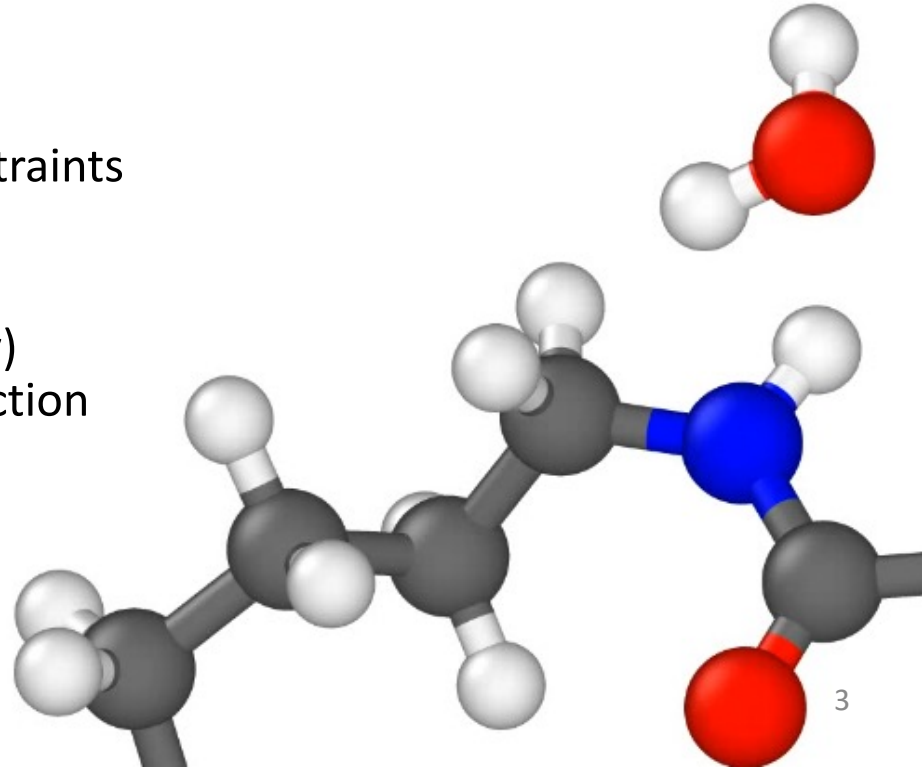
REACTER: Features added since 2019

1) Streamlined input/output formats for reaction templates and data files
   - String-based type labels allow easy creation of simulation-ready molecule templates
   - Eliminates need to match numeric types between data files and reaction templates

2) Automatic interaction typing
   - Enabled by alphanumeric type labels that encode atom types

3) Advanced reaction constraints
   - Arrhenius, root-mean-square deviation, and custom reaction constraints

4) General improvements/features:
   - Use variables for inputs (reaction cutoff, probability and frequency)
     - Use case: define reaction cutoff as a function of extent of reaction
   - Specify reaction as inter- or intramolecular
   - Update molecule IDs after reaction (default)
     - Makes *fix bond/react* compatible with other fixes, such as *fix gcmc*
   - Create new atoms/molecules



Beyond explicit reaction templates

- ‘Combinatorial explosion’ of templates needed when atoms surrounding reaction site are not constant
  - E.g., simple substitution of second and third neighbors required Kawagoe et al. to use 33 templates
  - Better solution needed than building a template for each possibility

Three-stage solution: Labels, wildcards, and autotyping

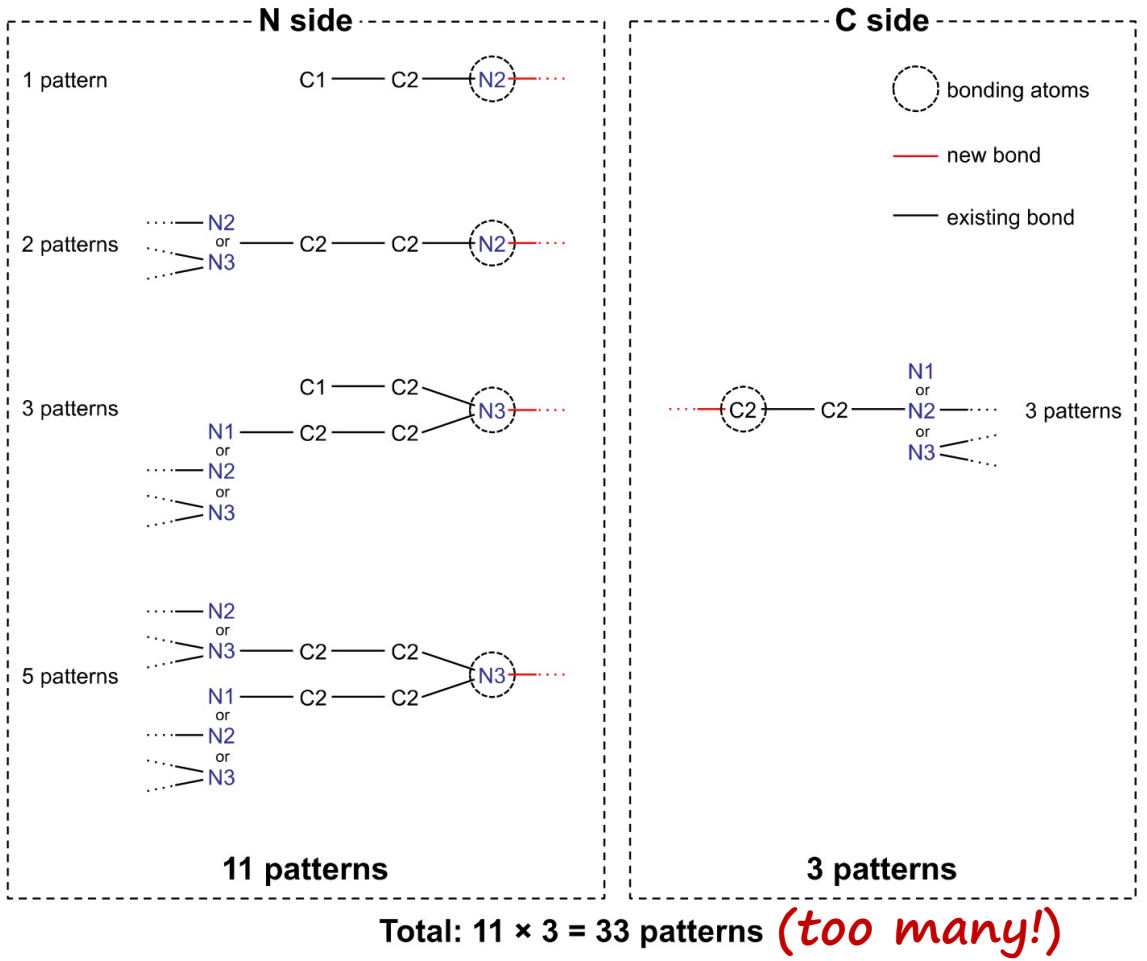
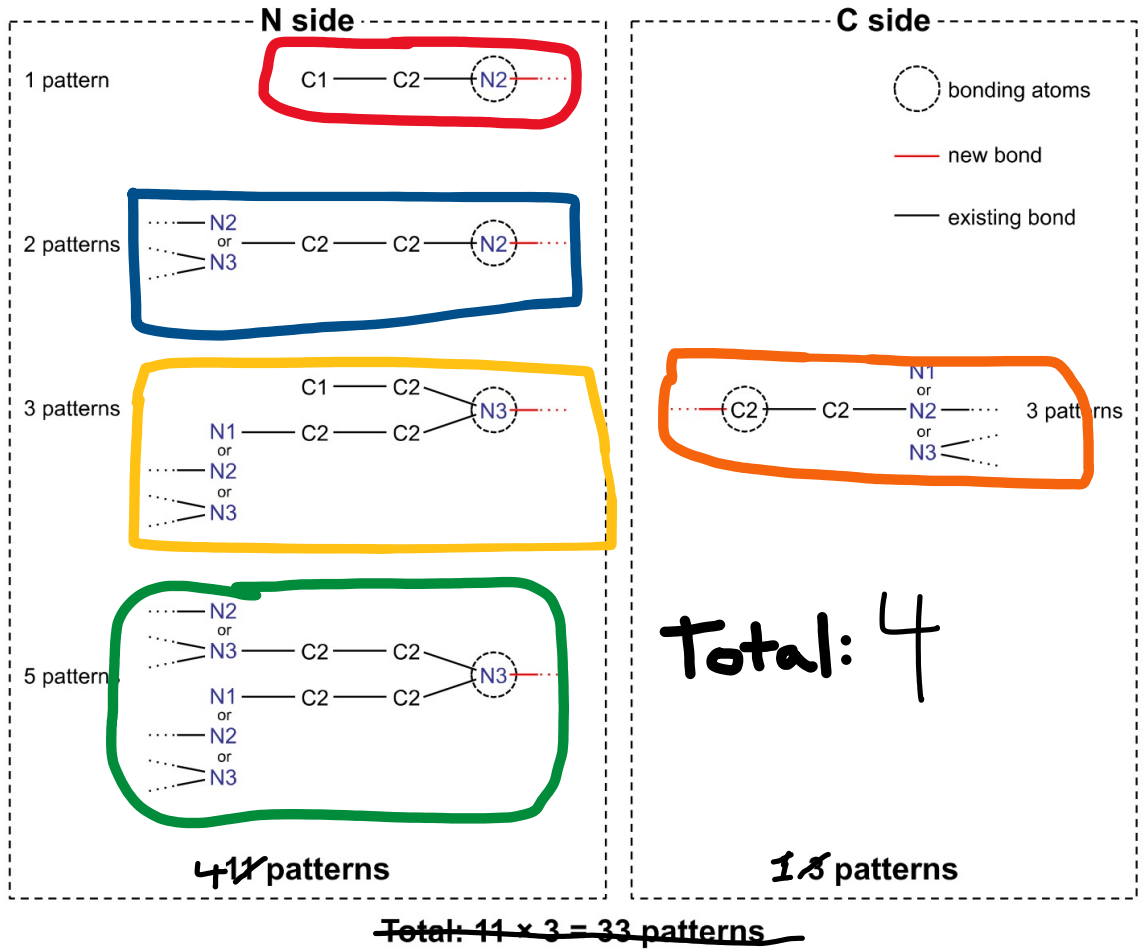


Fig. S2. Schematic of reaction patterns on the N (Nitrogen) side in the left panel and on the C (Carbon) side in the right panel.

Kawagoe, Yoshiaki, et al. "Construction of polydisperse polymer model and investigation of heat conduction: A molecular dynamics study of linear and branched polyethylenimine." *Polymer* 180 (2019).

Labels, wildcards, and autotyping

- Kawagoe et al. example can be reduced to four templates.
  - Type labels: mapping of each numeric type to an alphanumeric type
    - E.g., LAMMPS knows which atoms are ‘N1’
    - Similarly, LAMMPS knows which bonds are [N1][C2], etc.
  - Wildcards and autotyping:
    - E.g., use N* for {N1, N2 or N3}
    - Automatically determine the types of new bonds, angles, etc. that involve wildcard atoms



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Type labels: conventions and benefits

- Extra ‘Type Labels’ section in data file listing the type label mapping
  - Atom types in ‘Atoms’ section are not replaced directly, to minimize file size for large data files

- Molecule templates are small and benefit more from being human-readable
  - Atom, bond etc. types in ‘Types’, ‘Bonds’ etc. section are replaced directly

- Greatly simplifies/accelerates process of creating simulation-ready templates:
  - Automates task of coordinating types between templates and simulation

In data file

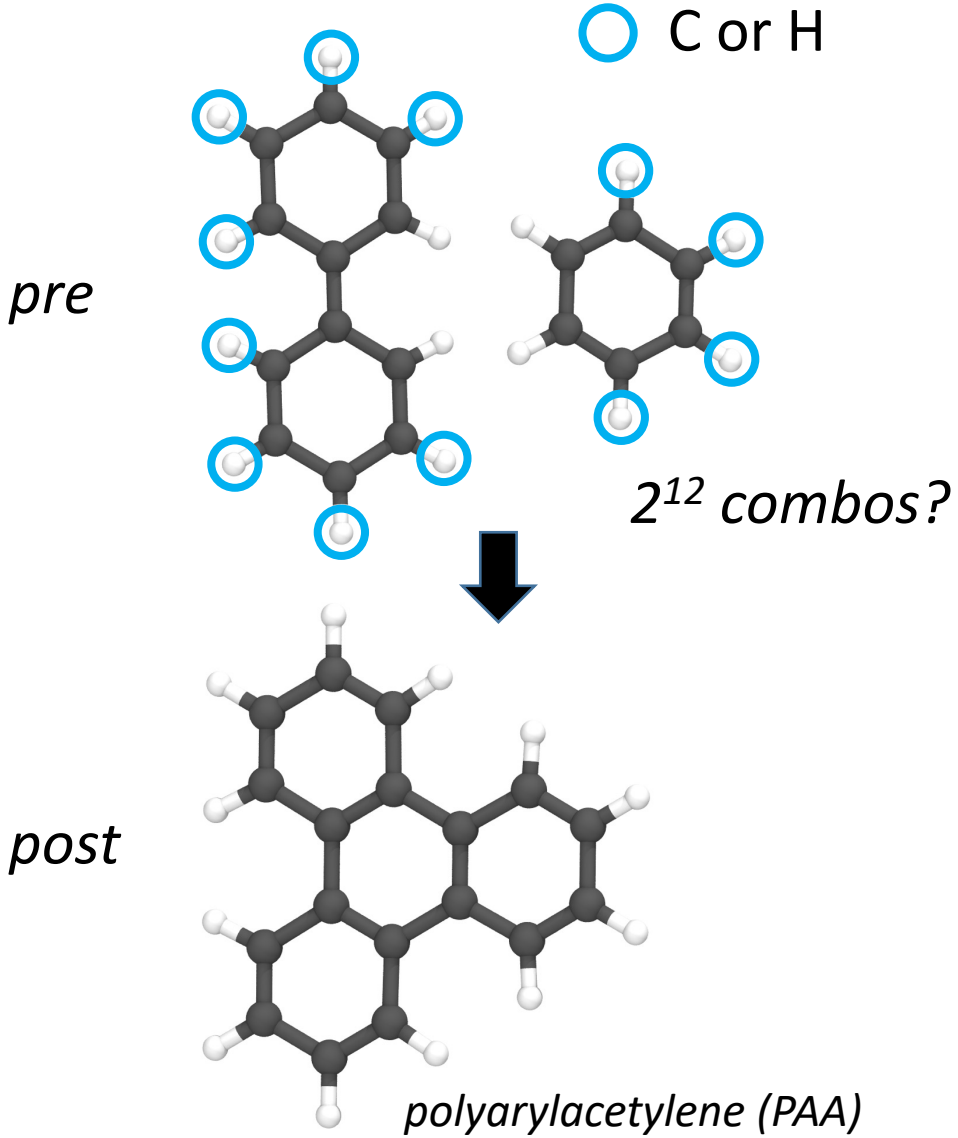
```
Atom Type Labels

1 cp
2 hc
3 ct
4 c=2
…
```

In molecule template

```
Types

    1 cp
    2 hc
    3 cp
    4 cp
    5 hc
…
```

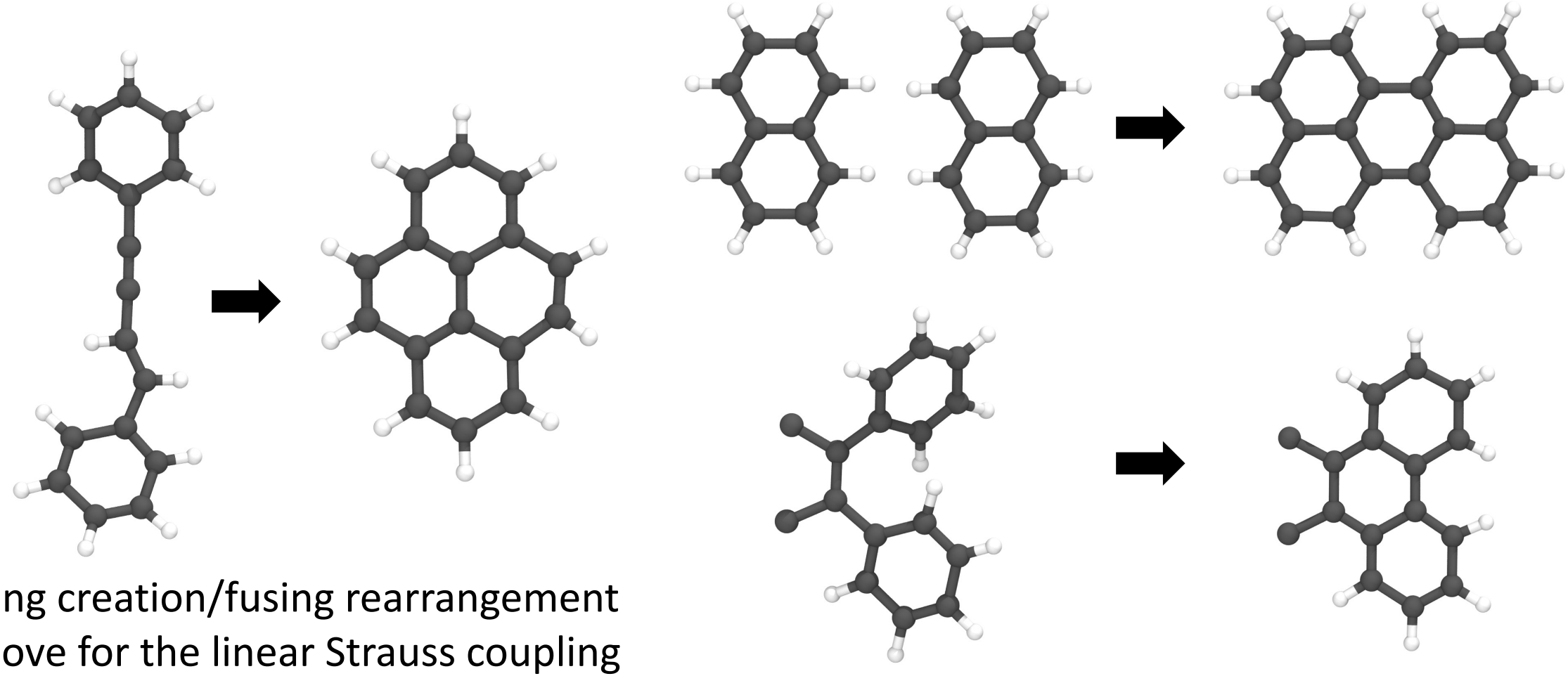
Case study: Carbonization reactions

- Starting point: diethynylbenzene polymerized via linear and cyclotrimerization reactions
- End goal: Approximate model of the carbonization and/or graphitization process
- The problem is not tractable using explicit reaction templates
  - Combinatorial explosion when atoms connected to ring may be C or H
- Only one template needed when atoms near edge of template are defined as wildcards



Case study: Nanoribbon formation

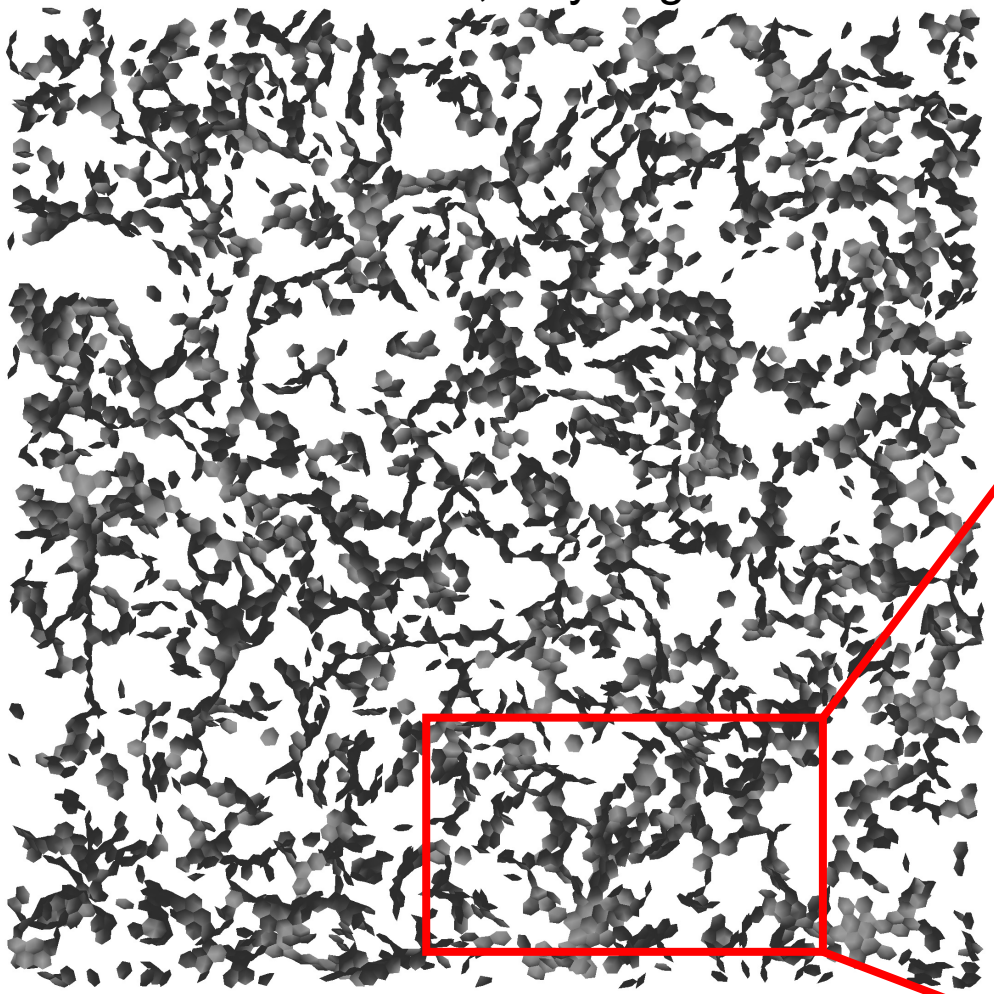
- Define carbonization moves from polymerized PAA motifs, as well as ring-closing and Diels-Alder reaction



Ring creation/fusing rearrangement move for the linear Strauss coupling

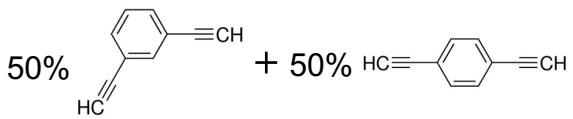
Case study: Nanoribbon formation

Slice is 7 Å thick; only rings shown



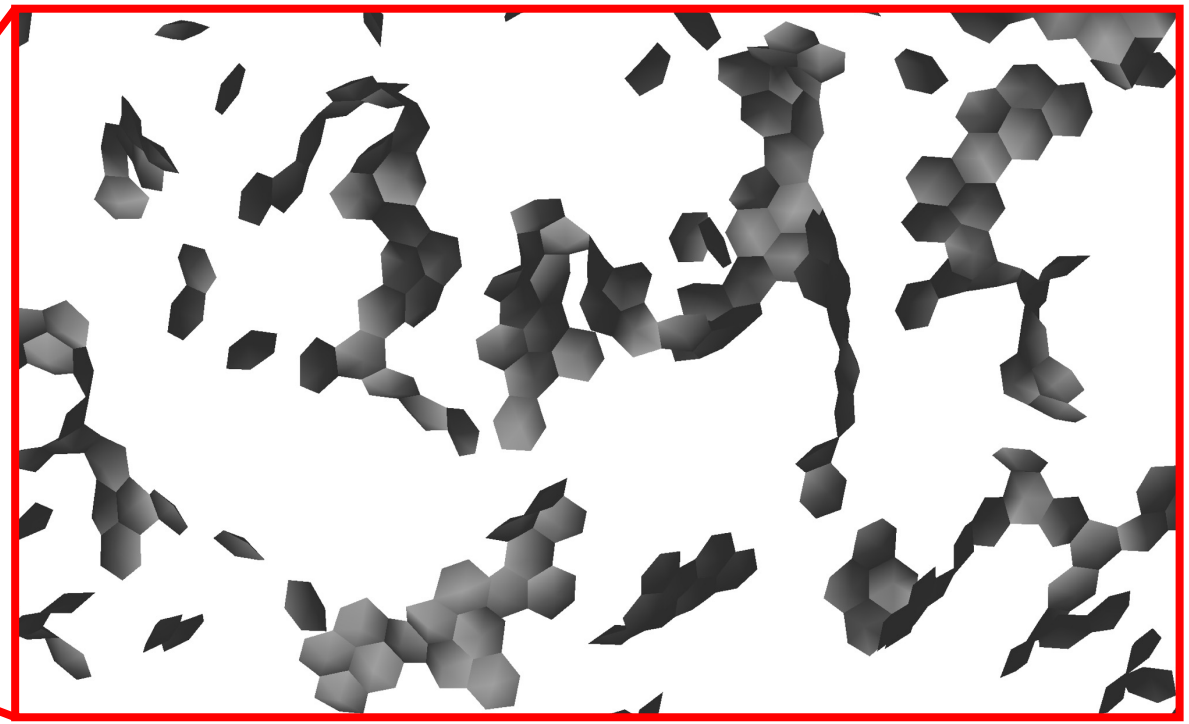
Density: 1.0 g/cm^3

Box Size: 13.8 nm



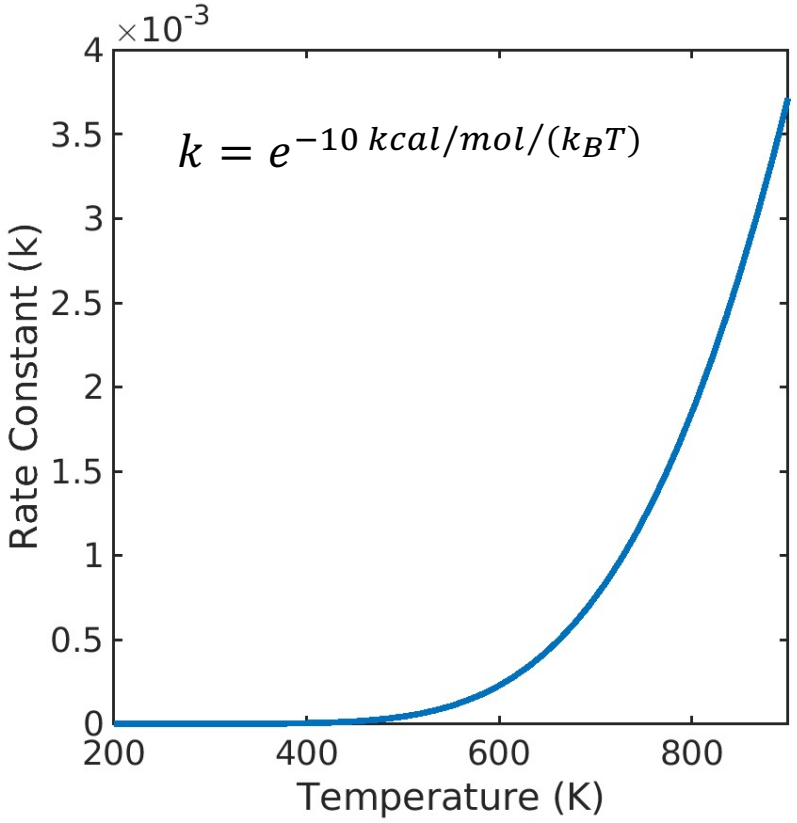
After ~99% polymerization and ~14.5K carbonization reactions

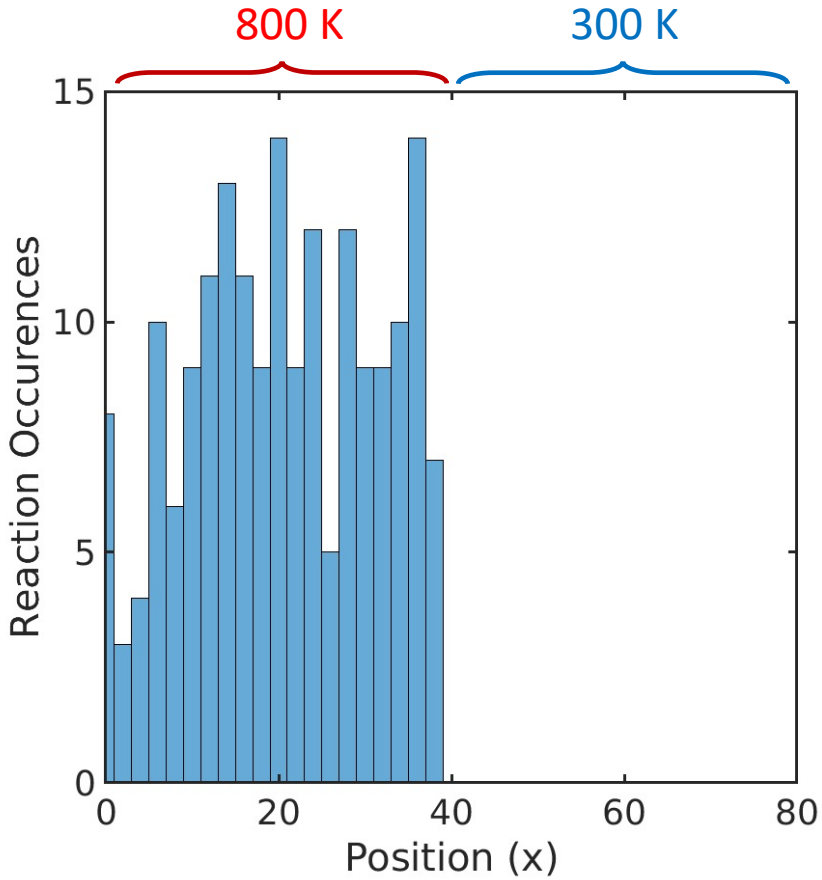
Expedient large-scale model for early-stage carbonization of polyarylacetylene (200K atoms)



Arrhenius Reaction Constraint

- Uses local temperature to enforce effective activation energy
  - Temperature-dependent Arrhenius equation: $k = AT^n e^{\frac{-E_a}{k_B T}}$
  - Reaction probability is proportional to calculated rate constant



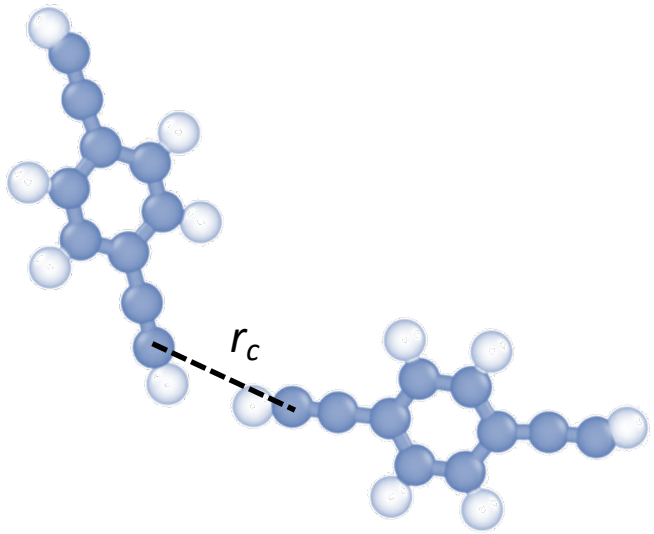


Nylon melt with Arrhenius constraint:
80x80x80 Å
35,000 atoms
10,000 fs
Reaction cutoff: 3.5 Å

Simulation box thermostated with a hot half and a cold half

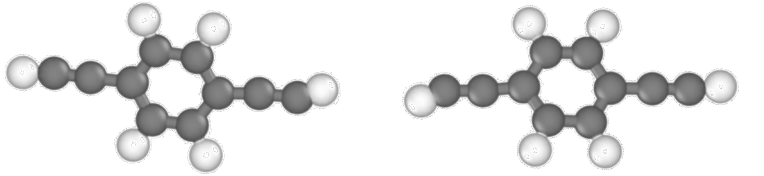
RMSD Reaction Constraint

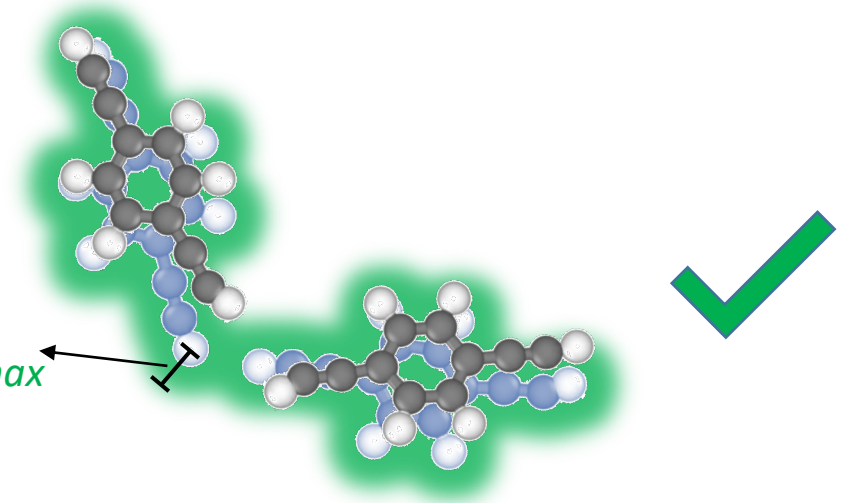
- Root-mean-square deviation (RMSD): a metric for similarity of molecular structures
- Enforce a maximum RMSD between template and local reaction site atoms
  - Calculated after optimal translation/rotation of pre-reaction template
- Orientation that allows reaction can be empirical or based off QM results
- A step toward more complex energy surfaces for reactive sites



Pre-reaction Template

Simulation Atoms

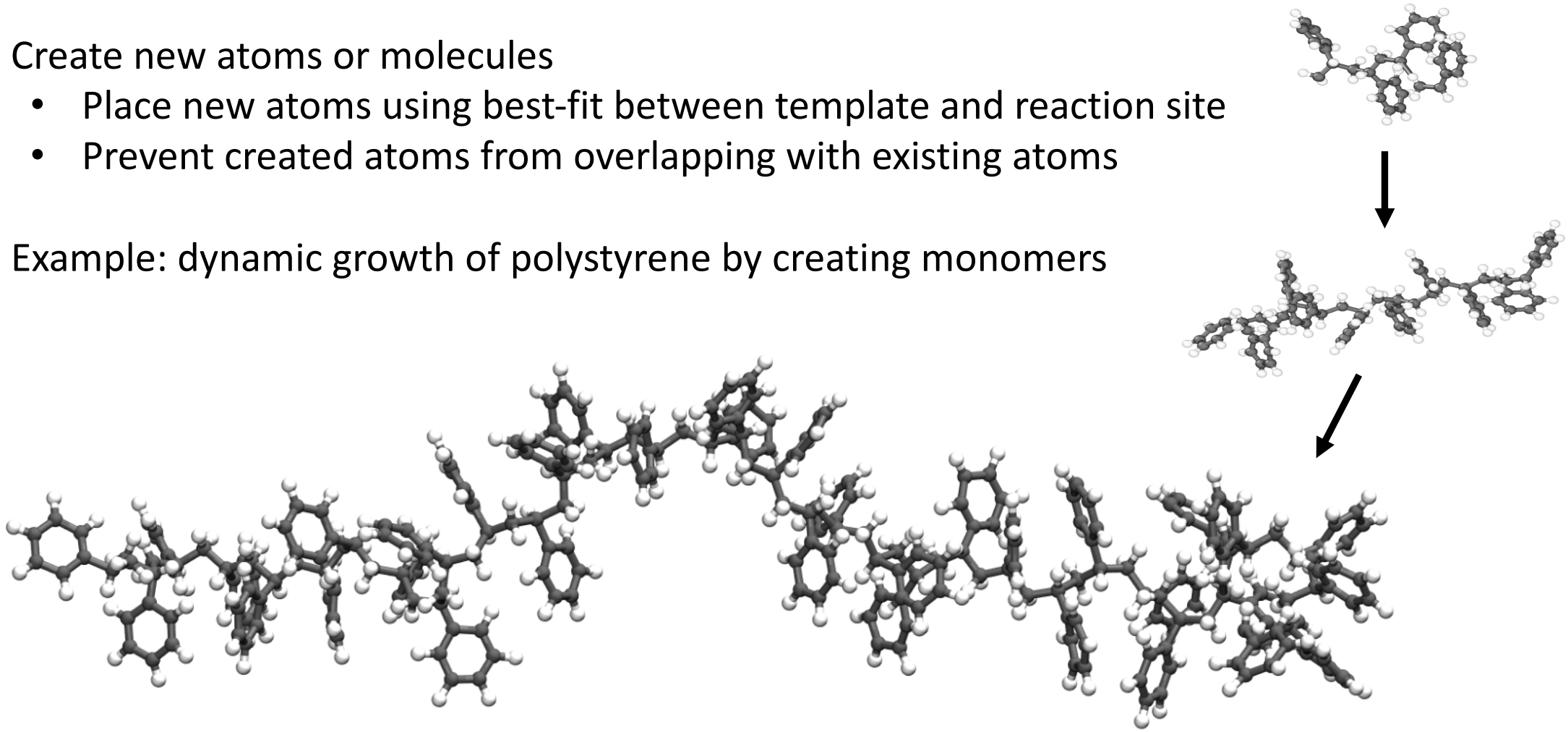




Create Atoms (and their Bonds, etc.)

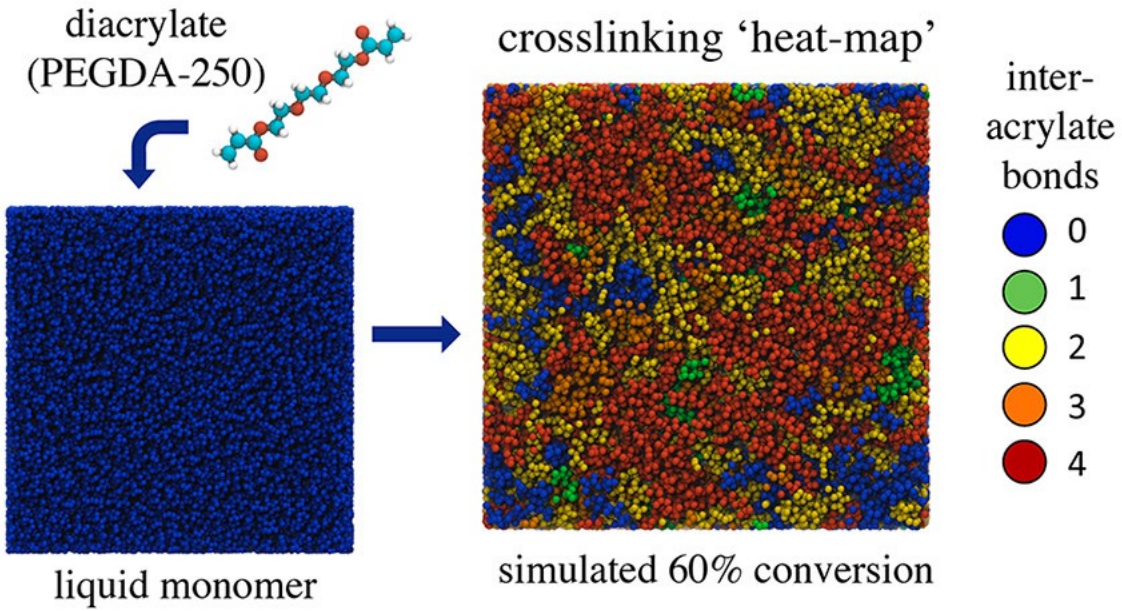
- Create new atoms or molecules
  - Place new atoms using best-fit between template and reaction site
  - Prevent created atoms from overlapping with existing atoms

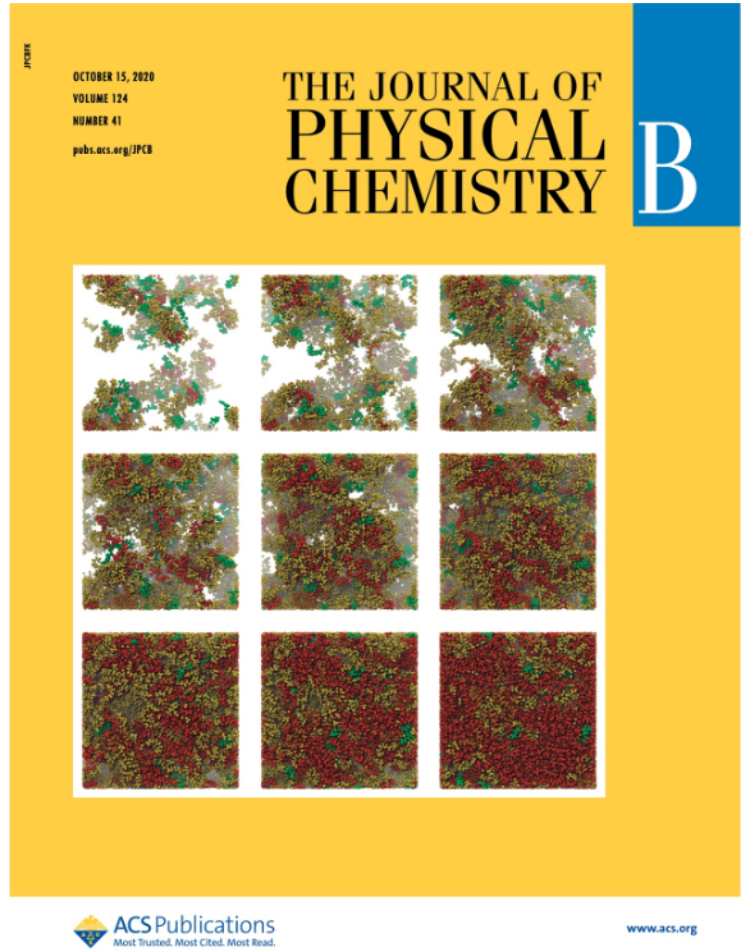
- Example: dynamic growth of polystyrene by creating monomers



What else can REACTER be used for?

- Modeling polymerization of photopolymer resins
- Reactive MD revealed the dependence of gel points and cyclic content on various poly- and difunctional acrylates

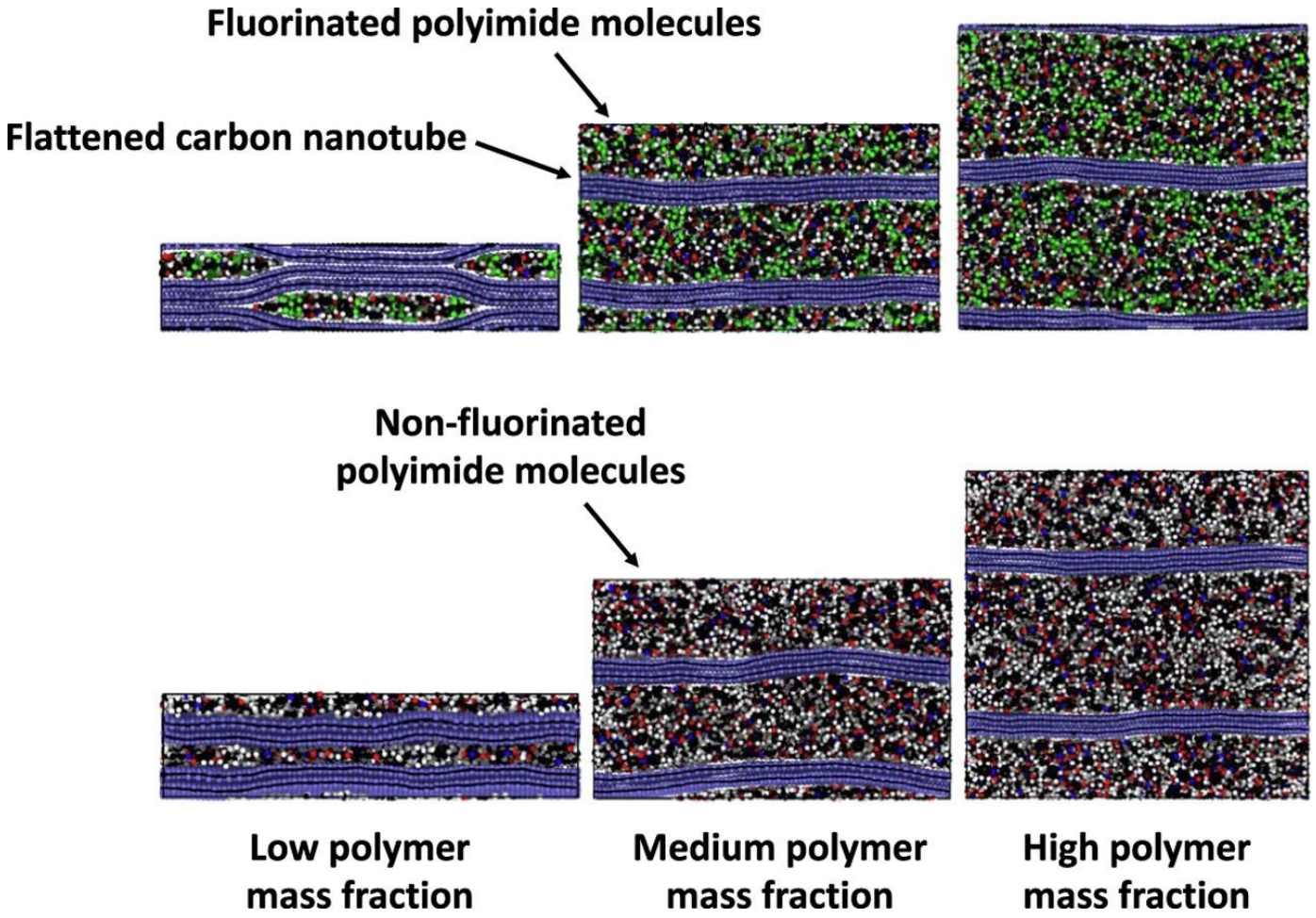




Karnes *et al.* On the network topology of cross-linked acrylate photopolymers: A molecular dynamics case study. *The Journal of Physical Chemistry B*, *124*(41), 9204-9215 (2020).

What else can REACTER be used for?

- *Fix bond/react* can act on a subset of the simulation, when nonreactive phases are present
- E.g., modeling the *in situ* polymerization of the matrix in nanocomposites
- The properties of the interface between polyimides and flattened CNTs depend on the polyimide chemistry (fluorinated vs non-fluorinated)



Patil *et al.* Interfacial characteristics between flattened CNT stacks and polyimides: A molecular dynamics study. *Computational Materials Science*, *185*, 109970 (2020).

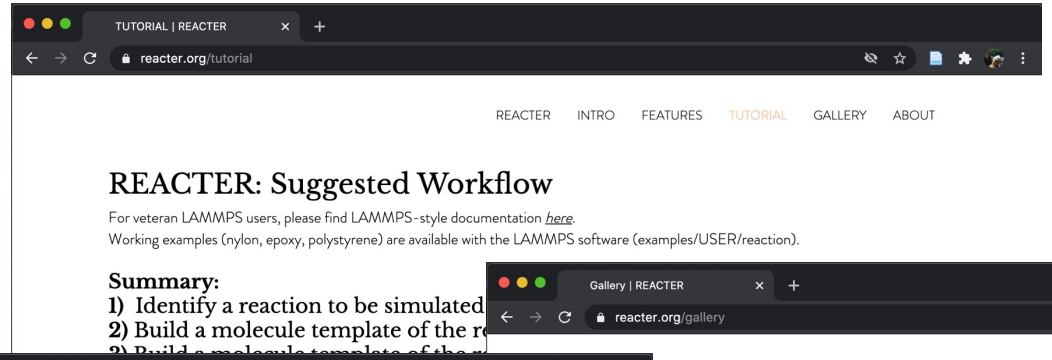
Where to learn more?

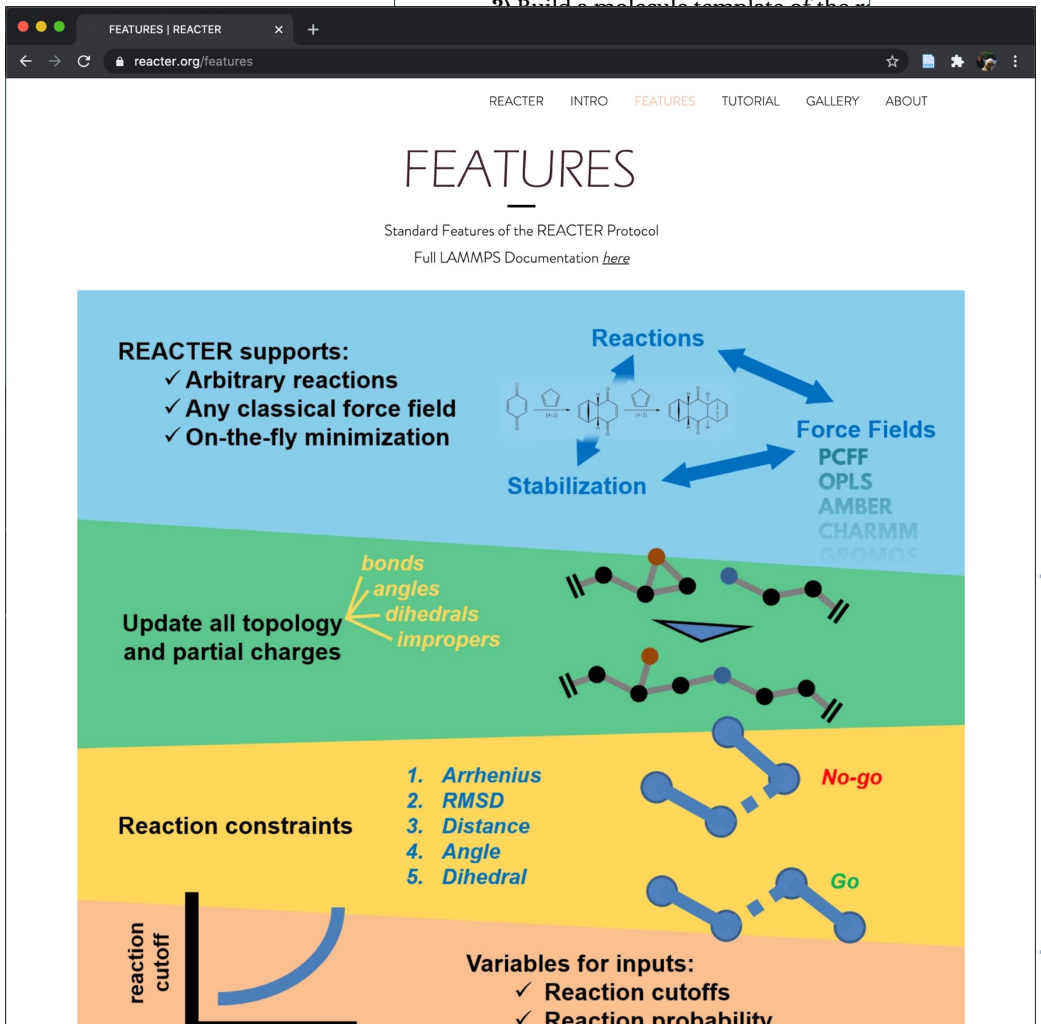
Visit ***www.reacter.org*** for:

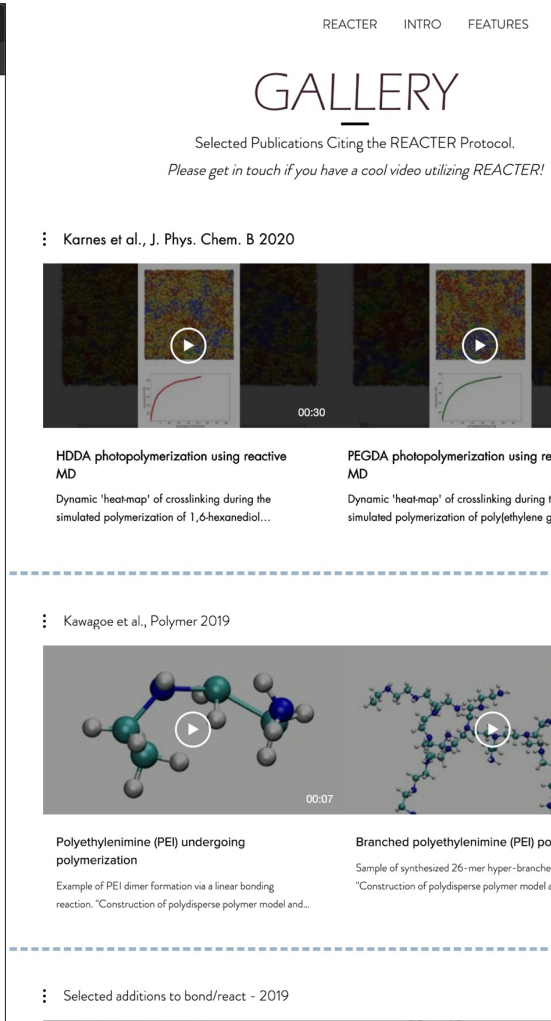
- Up-to-date features
  - Tutorials
  - Videos
- Links to related material

If you have a cool video or image that utilizes REACTER, send me an email to be added to the gallery

Also, check out the new AutoMapper tool
(Matt Bone, University of Bristol)
for a streamlined way to create reaction templates



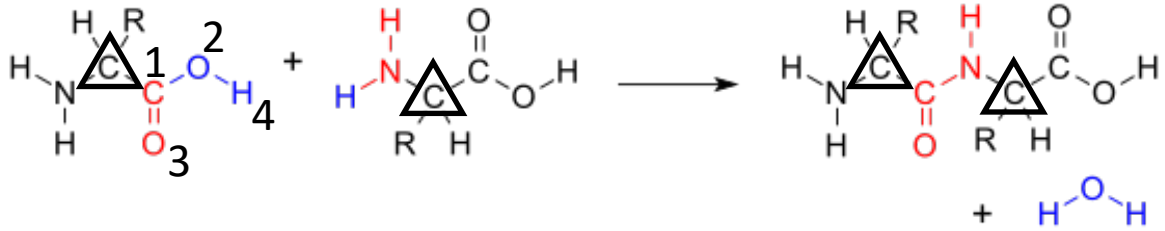




Outlook: The potential of type labels

- Type labels are invaluable for rapid creation of simulation-ready data files and reaction templates
- Library of reactions or classes of reactions
  - Templates could be applied directly to many force fields via type labels, wildcards and autotyping
- Existing databases, often expressed in SMILES or SMARTS format, can be converted into templates
- Incorporate reaction constraints such as RMSD if known (e.g., via DFT)

△ edge atoms



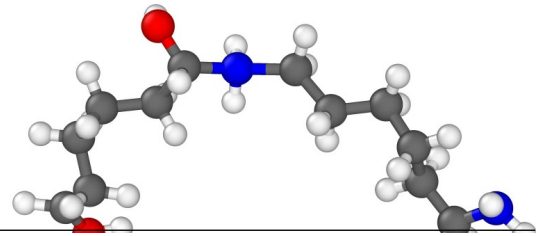
Molecule template in library: aa.pre

```
Types

    1 C*
    2 O*
    3 O*
    4 H*

...
```

In LAMMPS input script

```
fix 1 all fix bond/react &
    react rxn1 all 1 0.0 3.0 aa.pre aa.post aa.map
```

Thank You!



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