DisARMMD: Distance-Actuated Reaction Mechanisms in Molecular Dynamics

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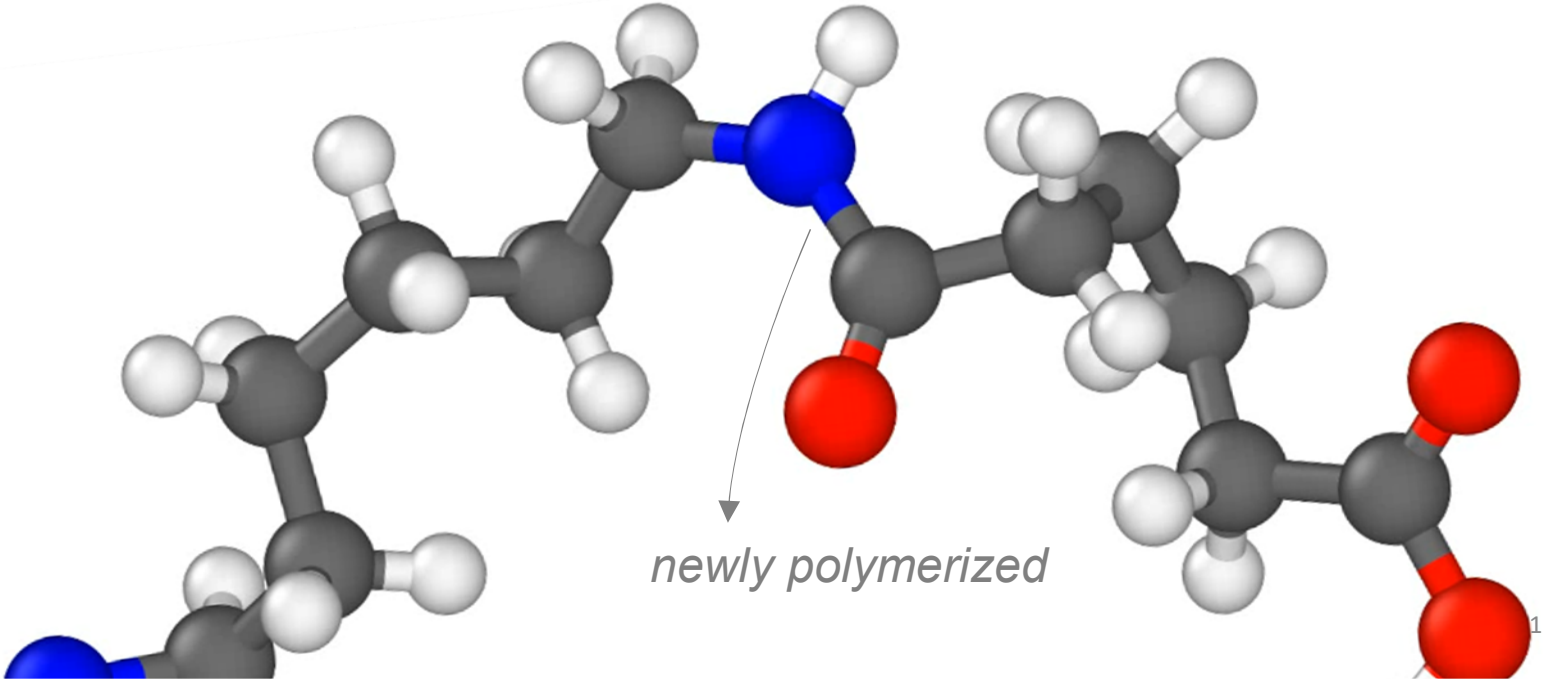
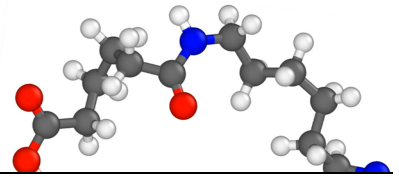


What is the DisARMMD protocol?

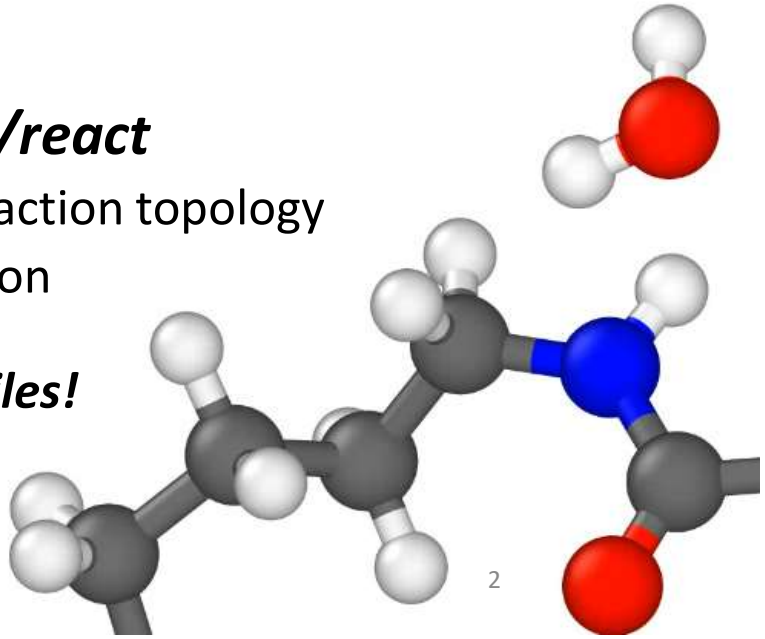


- A general, user-friendly method for adjusting topology during classical MD
  - Add and remove specific bonds, angles, dihedrals, and impropers
  - Modify all force field types as well as atomic charges
  - Supports any fixed-valence force field
  - Reaction stabilization options

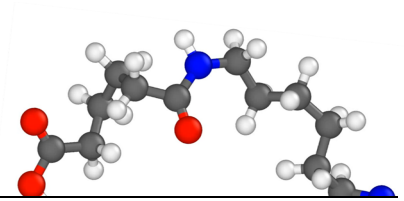
- Parallel implementation in LAMMPS as ***fix bond/react***
  - User inputs: molecule templates of pre- and post-reaction topology
  - A map file relating atoms before and after the reaction

Molecule templates are simple! And quite similar to data files!

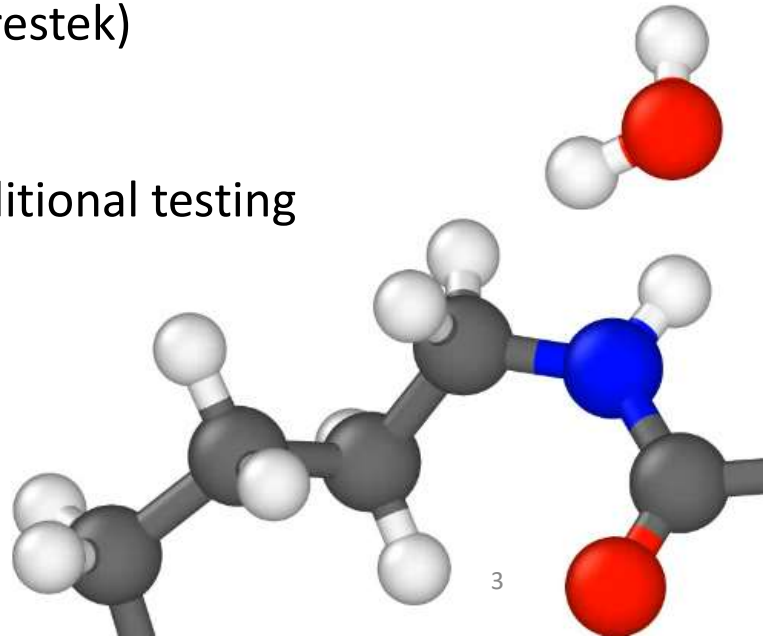
www.disarmmd.org



What's new?

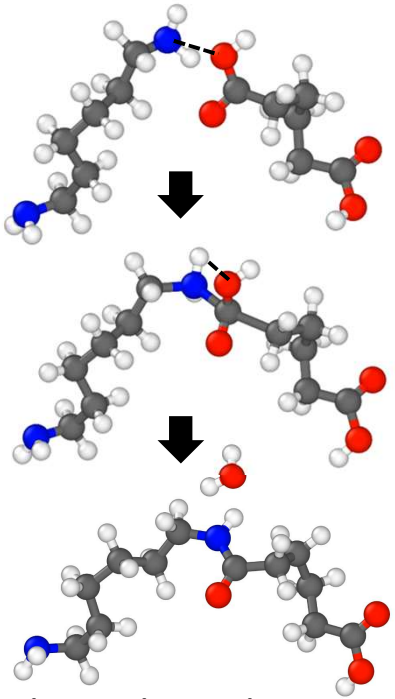


- Recently-Added Options/Extensions to *fix bond/react*:
  - Support for coarse-grained systems (Mark Stevens, Amulya Pervaje)
  - Limit on total occurrences of a given reaction (Wolfgang Verestek)
    Use case: Halt reactions after an certain percentage of crosslinking
  - Customizable behavior of edge atoms (Wolfgang Verestek)
    For example, specify which atomic charges are updated
  - Thanks to Axel Kohlmeyer for multiple bug fixes
  - Thanks to Yoshiaki Kawagoe, Doug Pratt, etc. for additional testing
- Major updates:
  - Delete user-specified atoms based on topology
  - Reactions triggered by bond-breaking
  - Reaction constraints

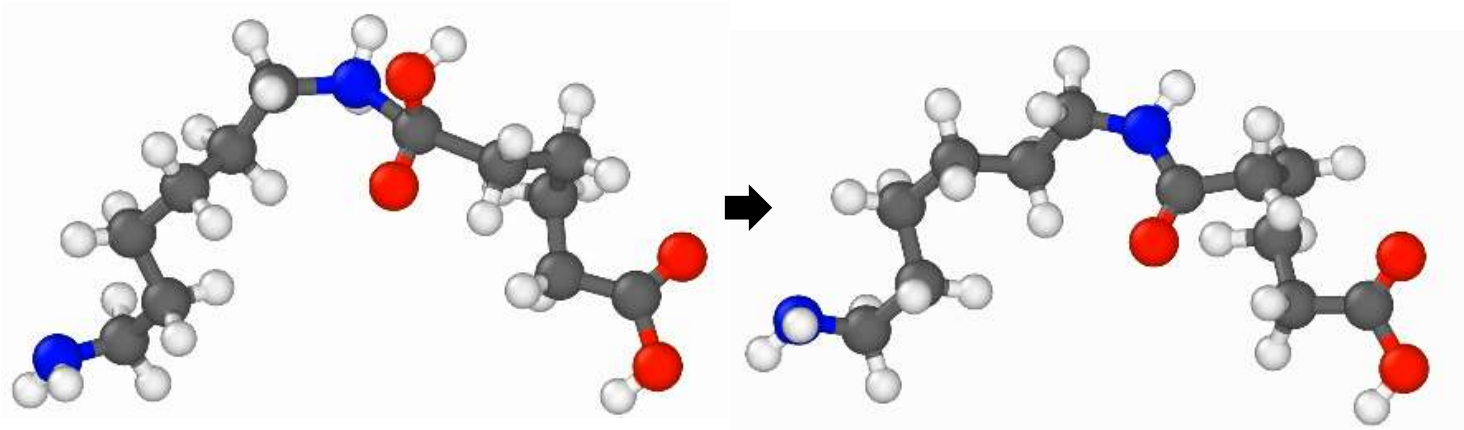


Delete atoms based on topology

1) Delete unwanted reaction by-products
2) Remove specific molecules based on topology (such as small rings)



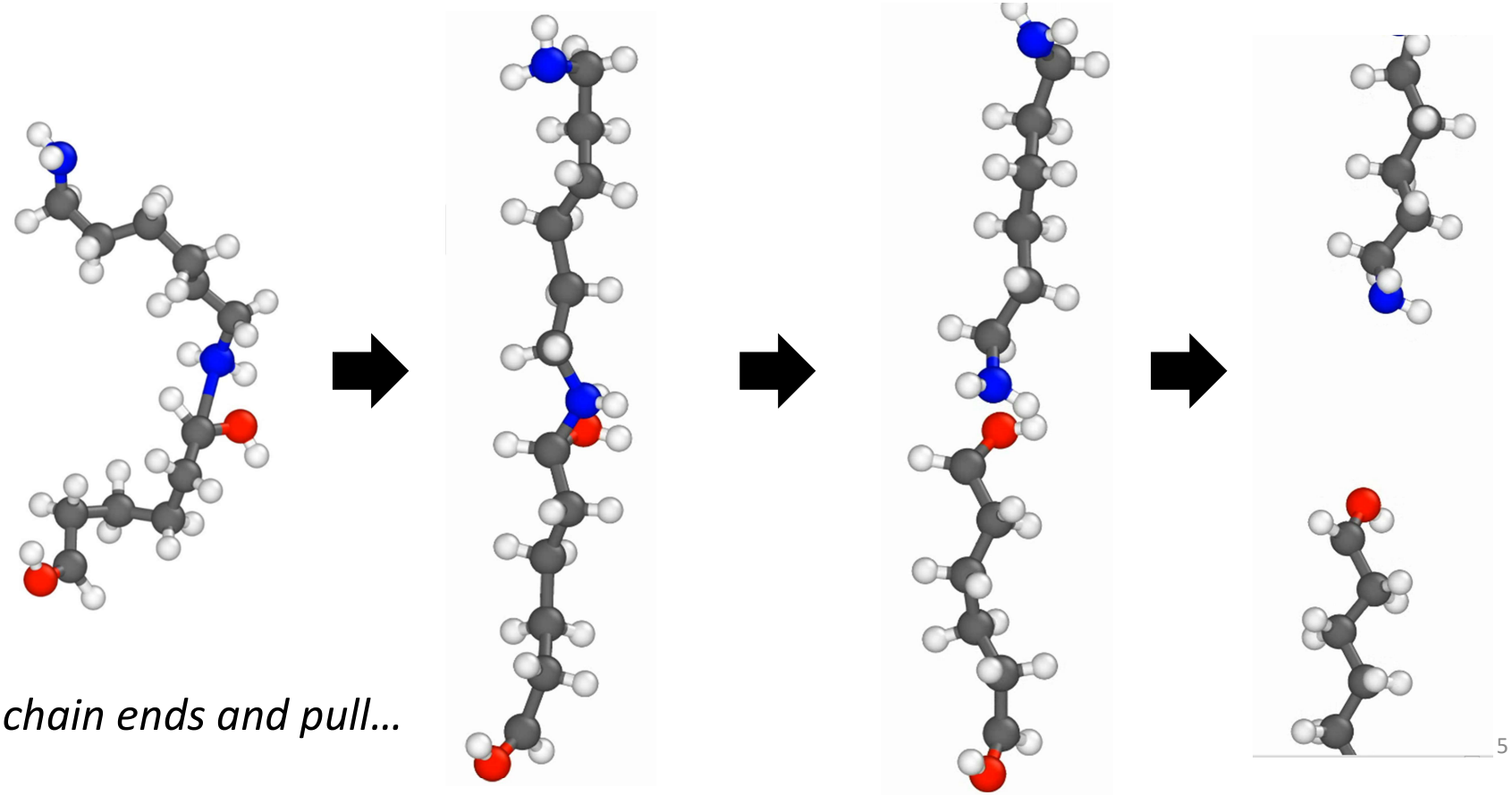
nylon polycondensation



deletion of condensed water molecule

Bond-breaking reaction trigger

- Simple bond-length criterion for mechanically-induced chain scission

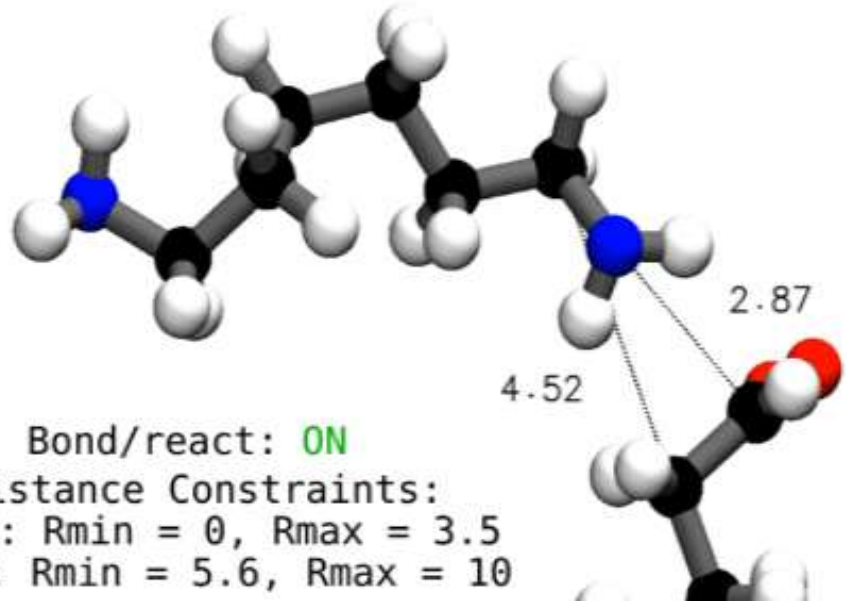


grab chain ends and pull…

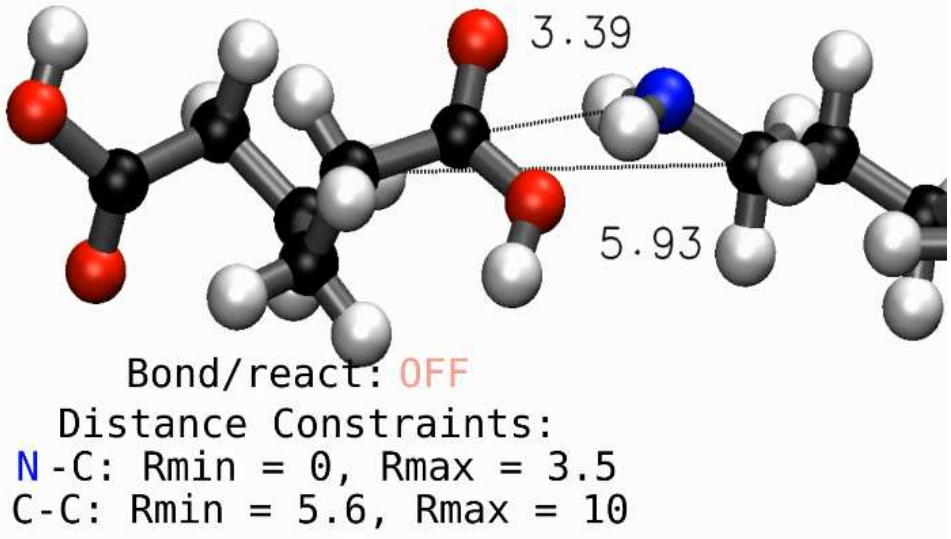
Reaction constraints

- Currently one option: distance constraints between any two atoms
  - Can be used to enforce a relative orientation between reacting molecules
- Other ideas: angle constraint, energy criteria, others?

Reaction Constraints Unsatisfied



Reaction Constraints Satisfied *(will react)*

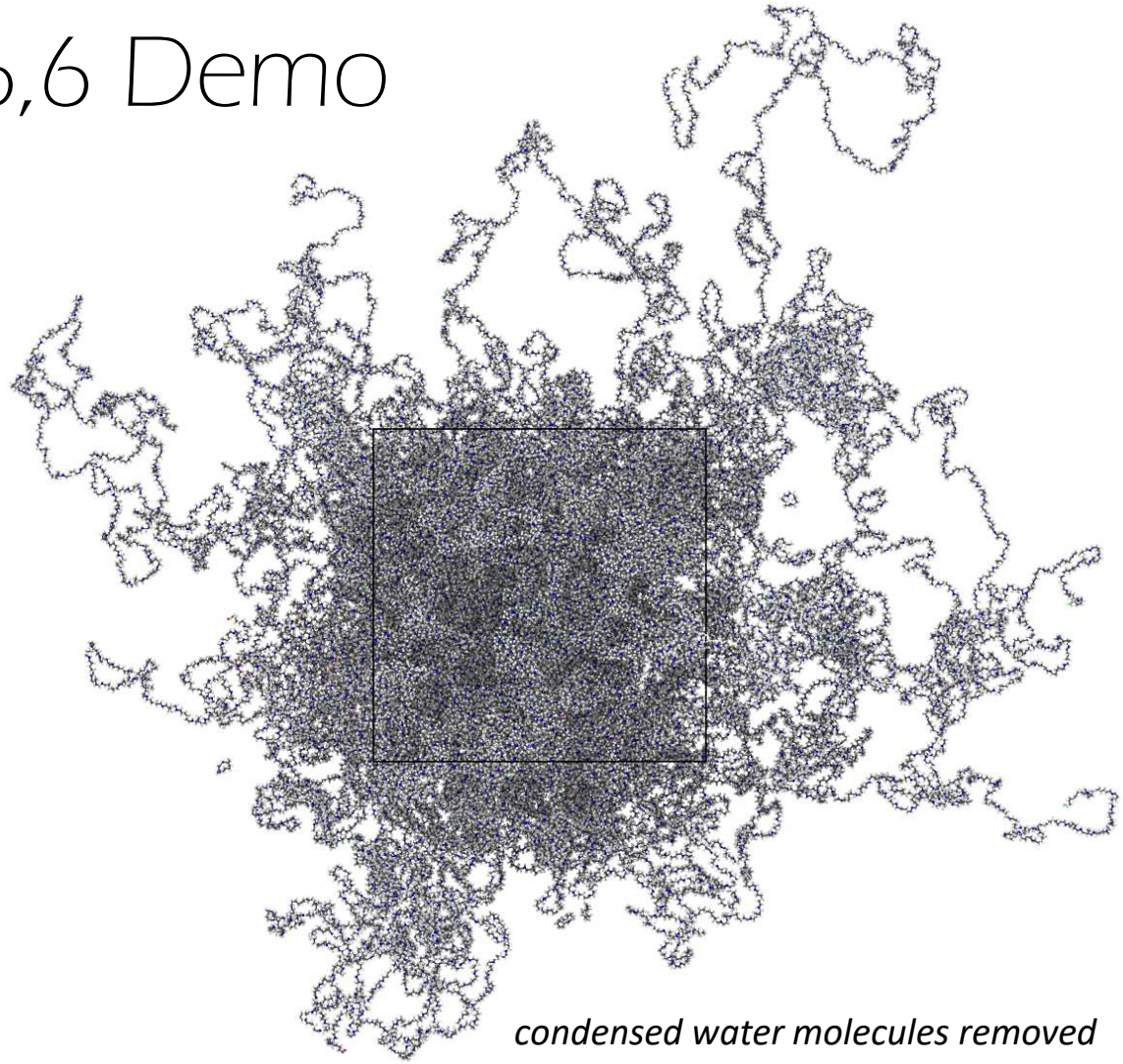


Large-scale Nylon 6,6 Demo

Setup: 5,000x adipic acid
5,000x hexamethylenediamine

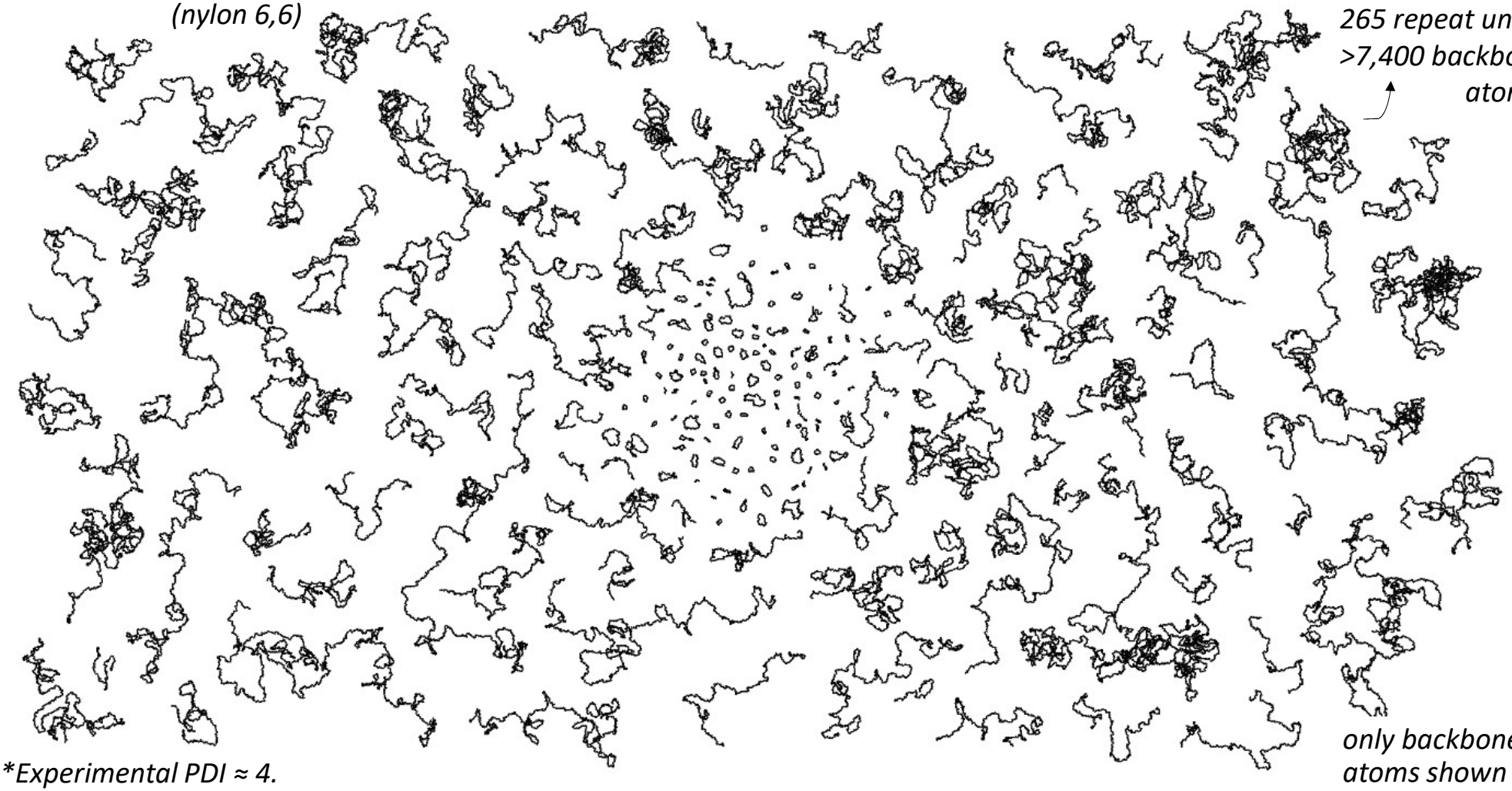
220,000 atoms
Temperature: 530 K
(actual synthesis temp)
Final density: 0.9 g/cm^3
Side length: 13.3 nm
3-5 Å reaction cutoff

>99% polymerized



condensed water molecules removed

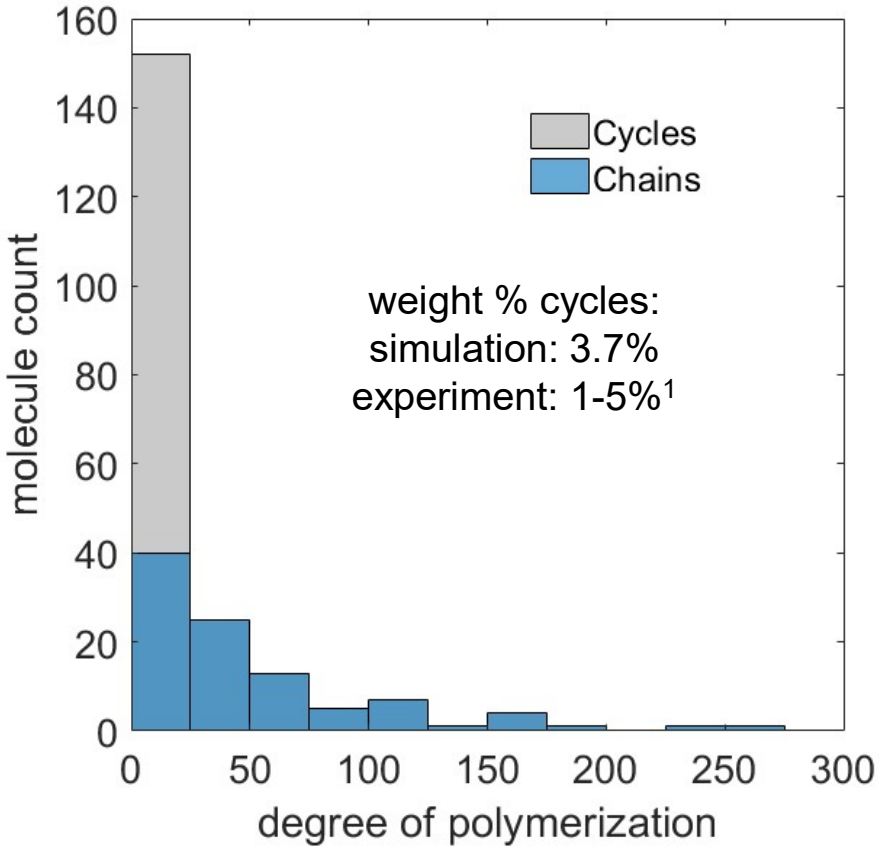
Chain PDI ≈ 2 Overall PDI (with cycles) ≈ 3.9*

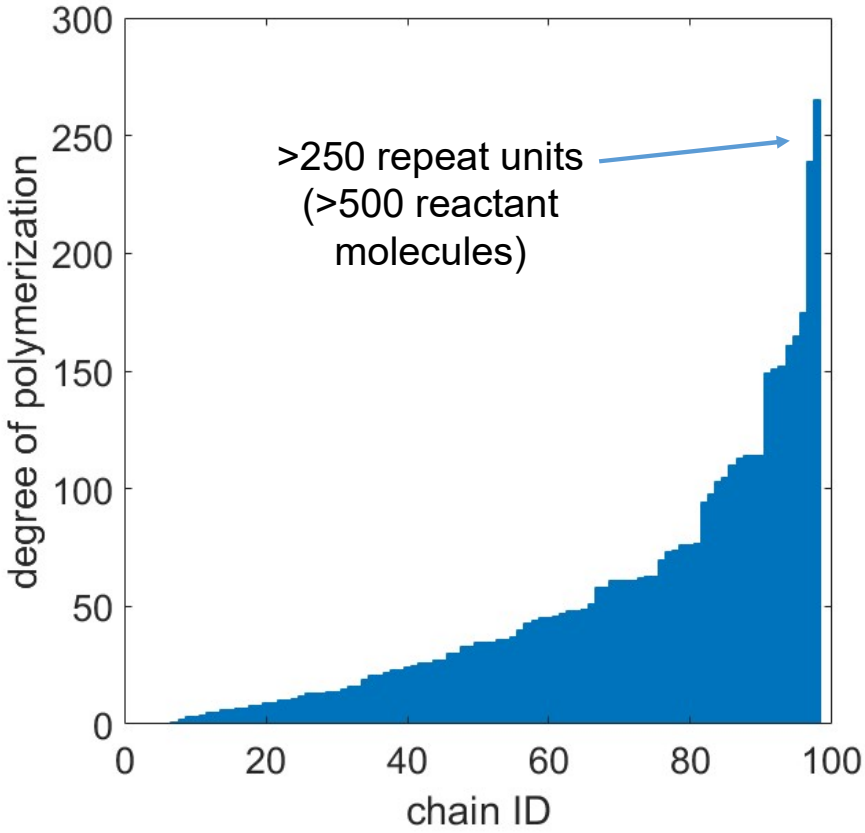


**Experimental PDI ≈ 4.*

Jeyakumar, A. (2012). Solid-state modification of polyamide-6,6 Eindhoven: Technische Universiteit Eindhoven.

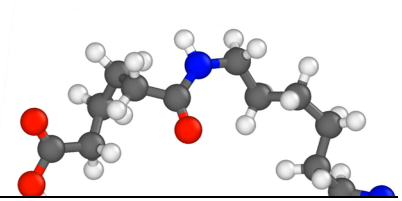
>99% polymerized Nylon 6,6: Chains *vs.* Cycles





[1]Endgroup-based separation and quantitation of polyamide-6,6 by means of critical chromatography. Mengerinka, et al. Journal of Chromatography A, 949 (2002).

Nylon 6,6: chain morphology



$$\langle r^2 \rangle^{1/2} \approx 10 \text{ nm}$$

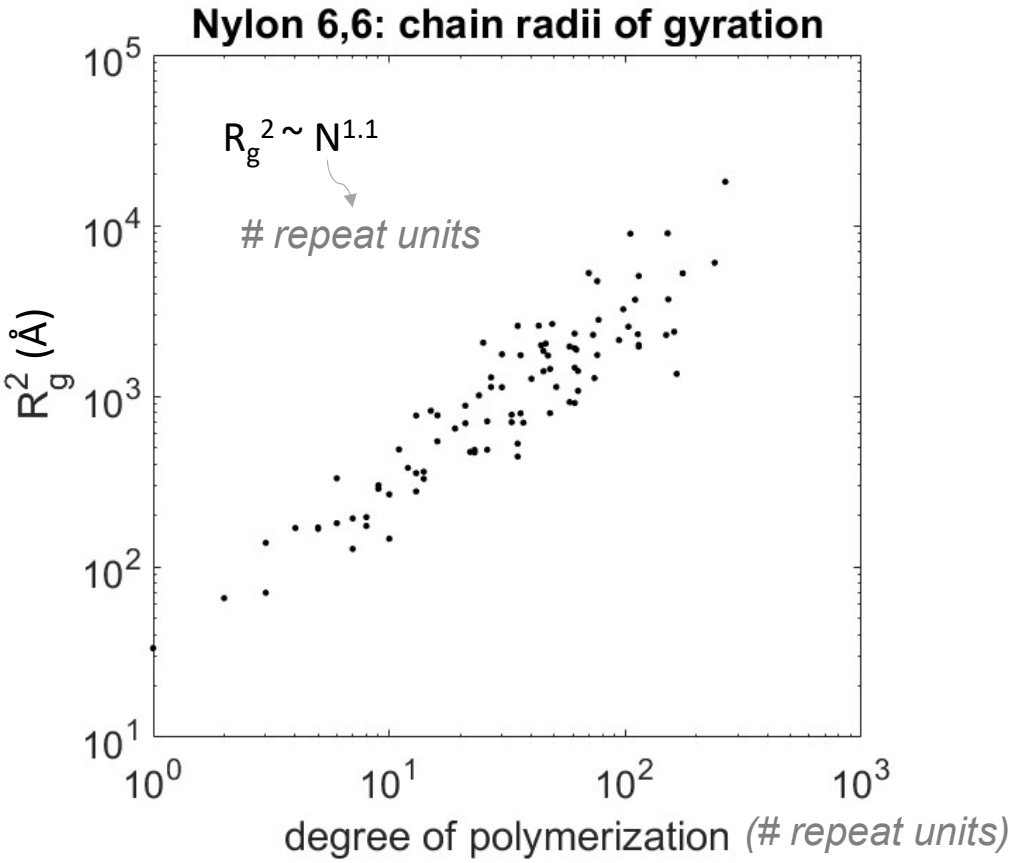
end-to-end distance

$$\langle R_g^2 \rangle^{1/2} \approx 4 \text{ nm}$$

radius of gyration

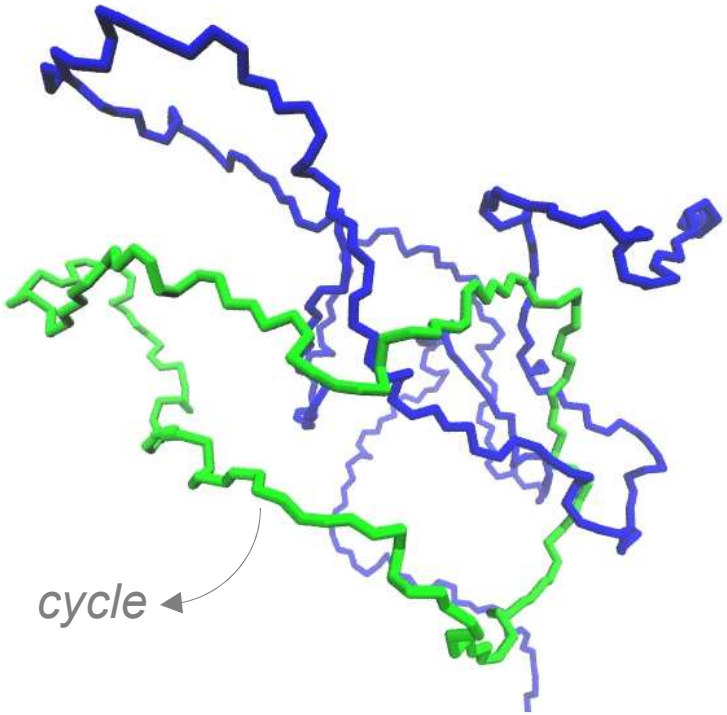
$$\left\langle \frac{r^2}{R_g^2} \right\rangle = 6.07$$

Value for a Gaussian chain: 6

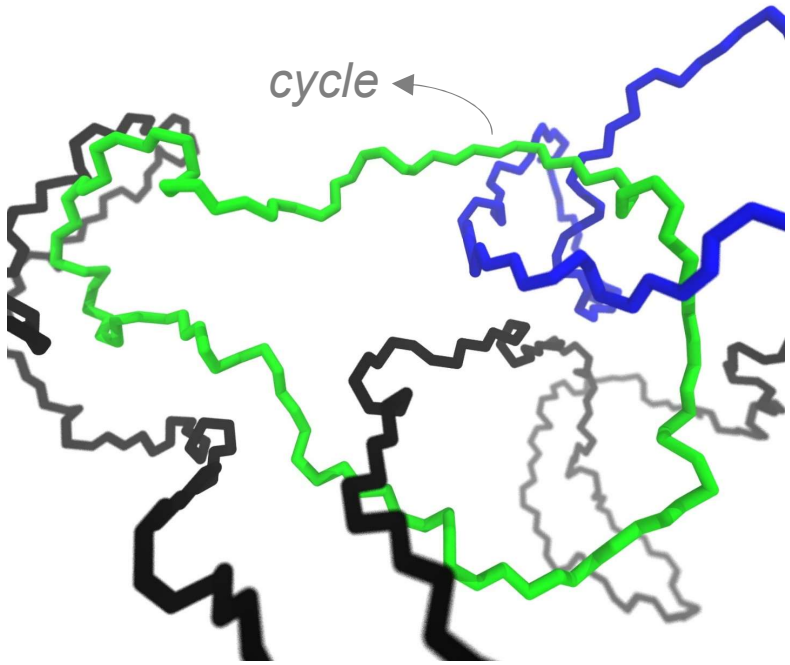


Chain growth *vs.* ring formation

Nylon 6,6

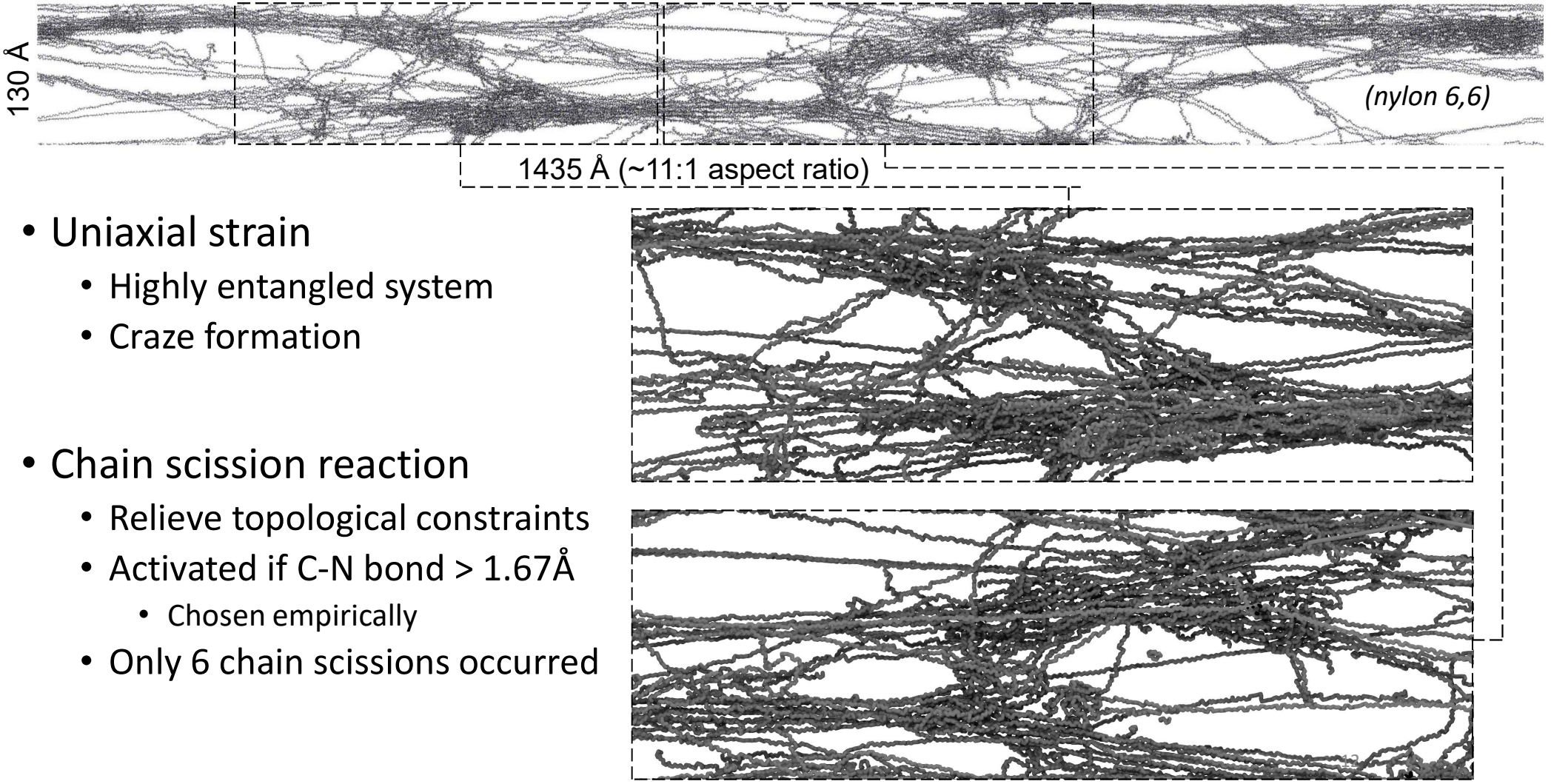


single topologically-constrained cycle



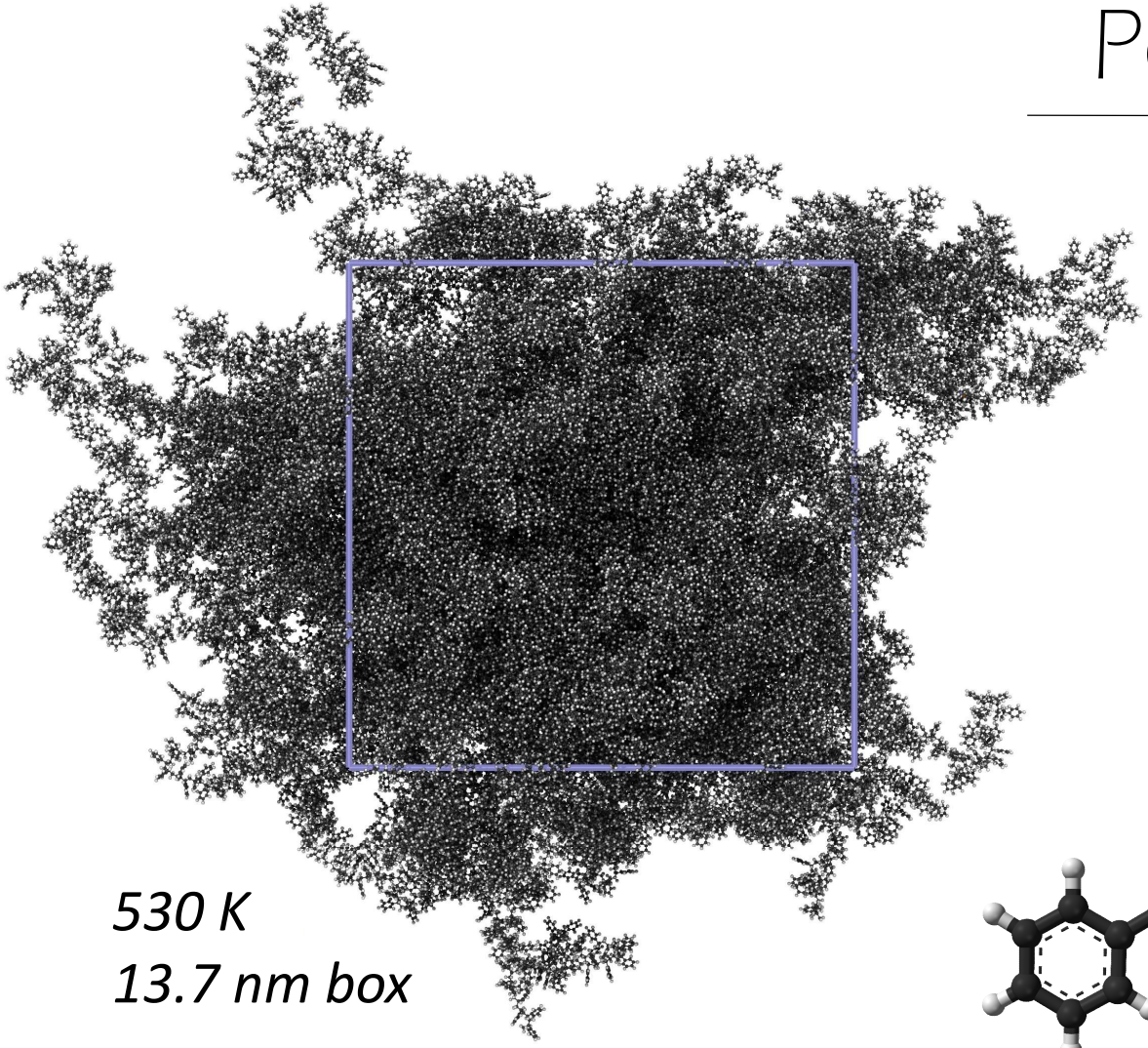
cycle constraining two chains: physical 'slip-link'

Uniaxial extension with chain scission:



- Uniaxial strain
  - Highly entangled system
  - Craze formation
- Chain scission reaction
  - Relieve topological constraints
  - Activated if C-N bond > 1.67Å
    - Chosen empirically
  - Only 6 chain scissions occurred

Polystyrene demo

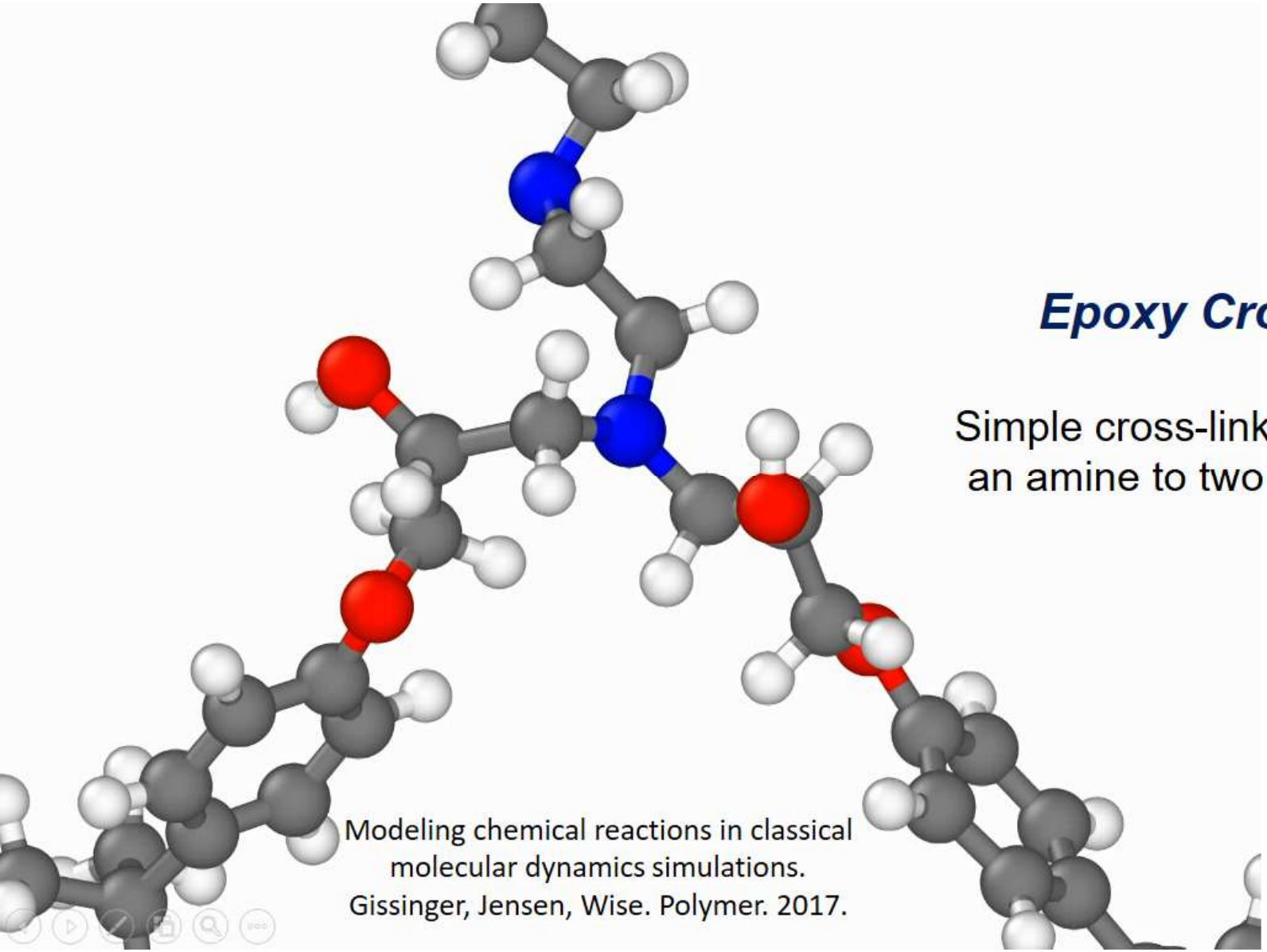


530 K
13.7 nm box

>99% polymerized polystyrene
200,000 atoms (12,500x styrene)

>98.5% polymerized with 3.0 Å distance cutoff, before switching to 3.5 Å

Conclusion: DisARMMD can handle small monomers with bulky side groups

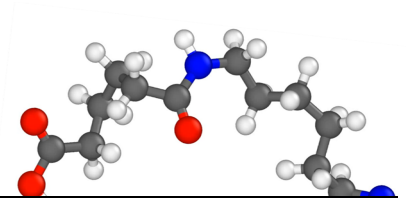


Epoxy Cross-linking

Simple cross-linking mechanism of an amine to two epoxy molecules

Modeling chemical reactions in classical molecular dynamics simulations.
Gissinger, Jensen, Wise. Polymer. 2017.

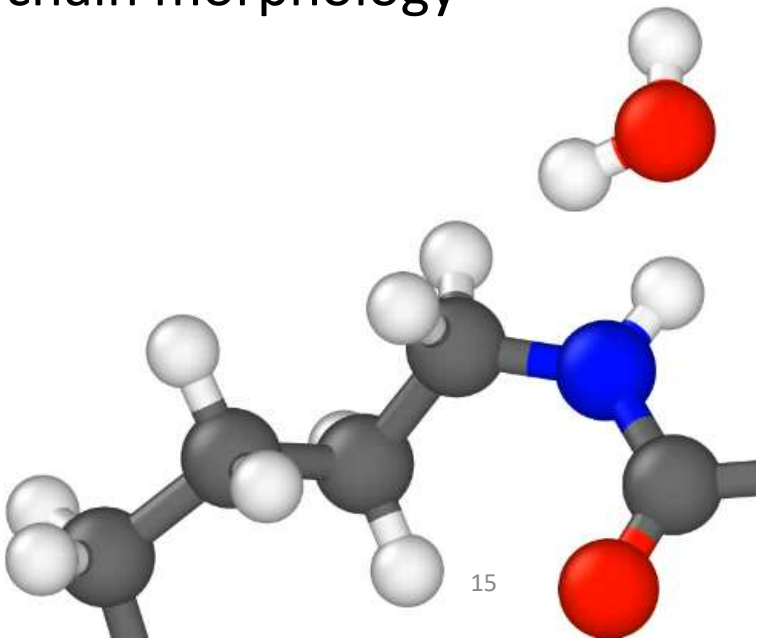
Summary and Outlook



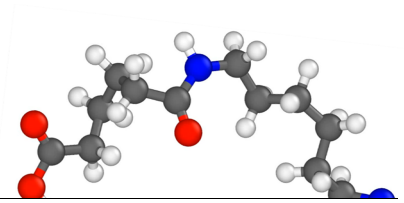
- The DisARMMD protocol scales well
  - 10,000 nylon precursors
  - 12,500 styrene molecules

  } true temp. (≈260 C)
  low cutoff 3-5 Å

  } >99% polymerization
- Correctly predicts cyclic content, dispersity and chain morphology
- What's next?
  - More predictive reaction constraints
    - Potential energy surfaces?
  - Large-scale bio applications
    - See Andrew Jewett's talk tomorrow
  - Features in progress
    - Additional reaction constraints
    - Option to create atoms



Thank you!



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