PhD Proposal Defense

Molecular Simulation and Prediction of Mechanical Properties of High-performance Polyamide Crystals

Quanpeng (Sam) Yang,

Advisor: Prof. Ashlie Martini

Department of Mechanical Engineering

University of California - Merced,

Merced, California, USA

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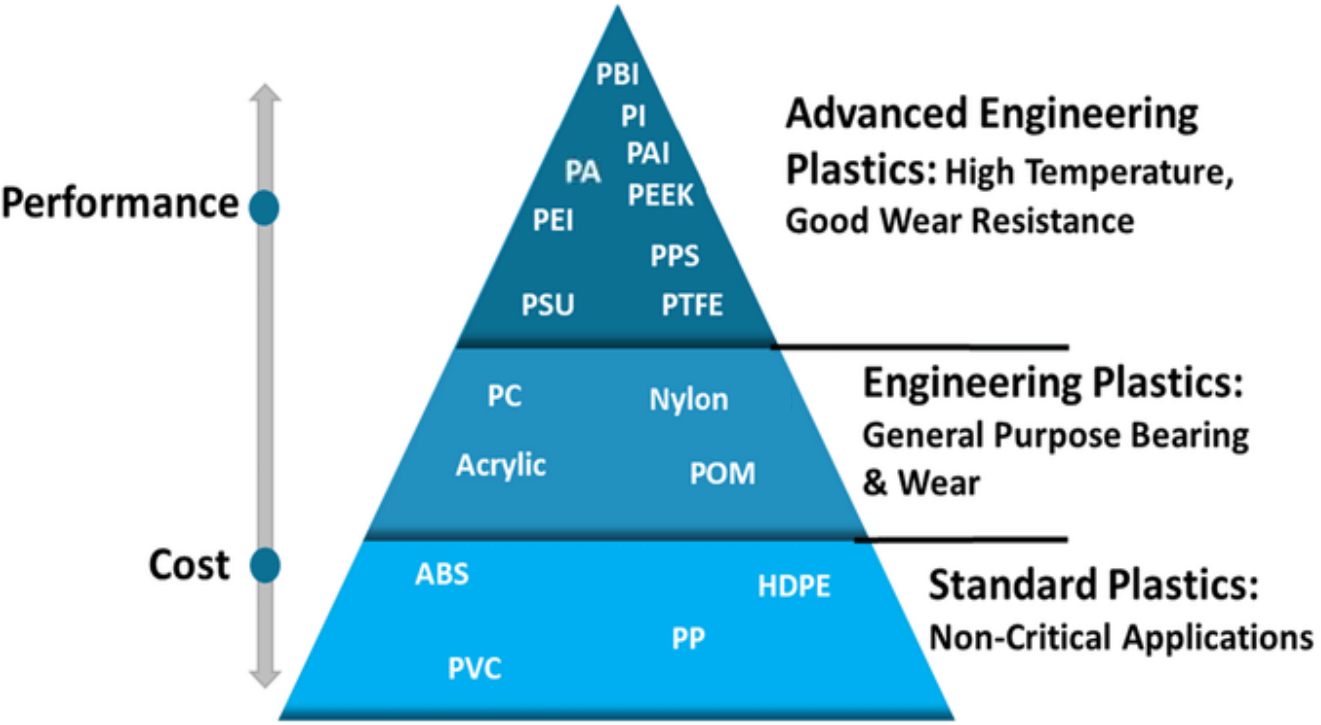
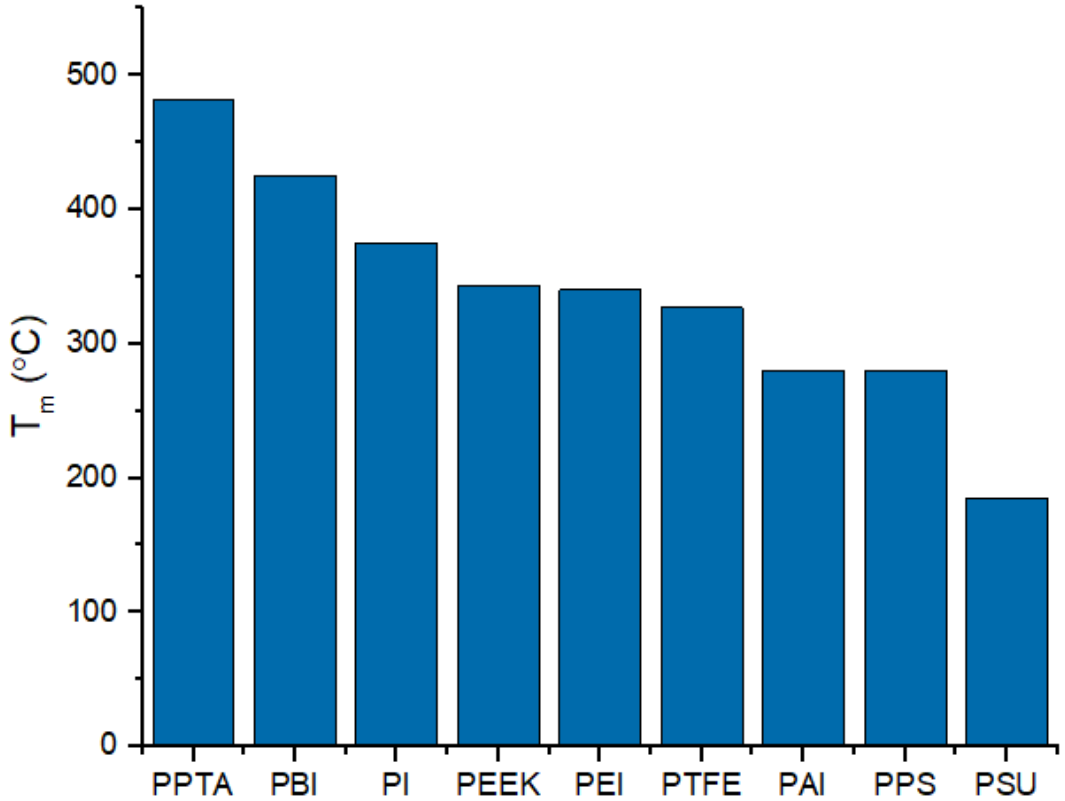
Content

Introduction

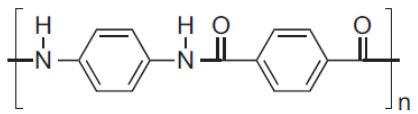
- Today, life without polymers is unimaginable
- Polymers have become the major synthetic materials of the 21st century
- High-performance polymers are particularly desirable
- High performance plastics typically have a permanent operating temperature of more than 150°C



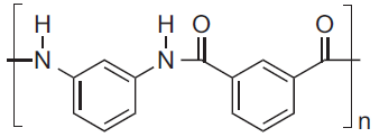
"Advanced polymeric coatings and their applications: Green tribology." (2019): 1-14.



Aromatic polyamide

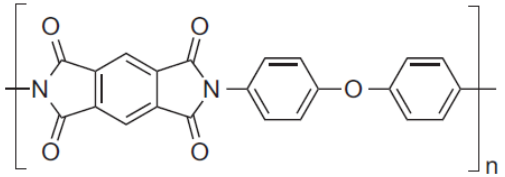


Kevlar

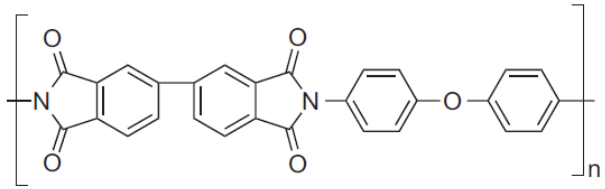


Nomex

Aromatic polyimide

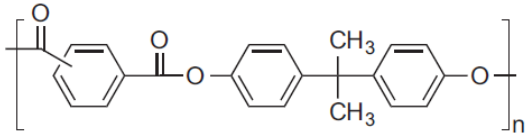


Kapton



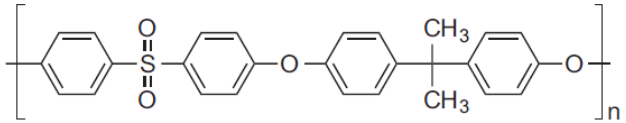
Upilex R

Aromatic polyester



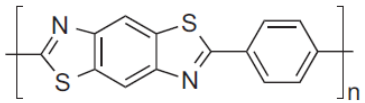
U-polymer

Aromatic polysulfone



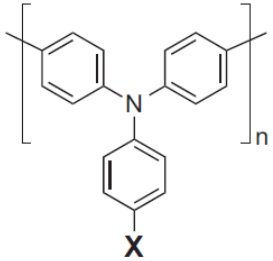
PST

Aromatic heterocyclic polymer



PBT

Aromatic polytriphenylamine

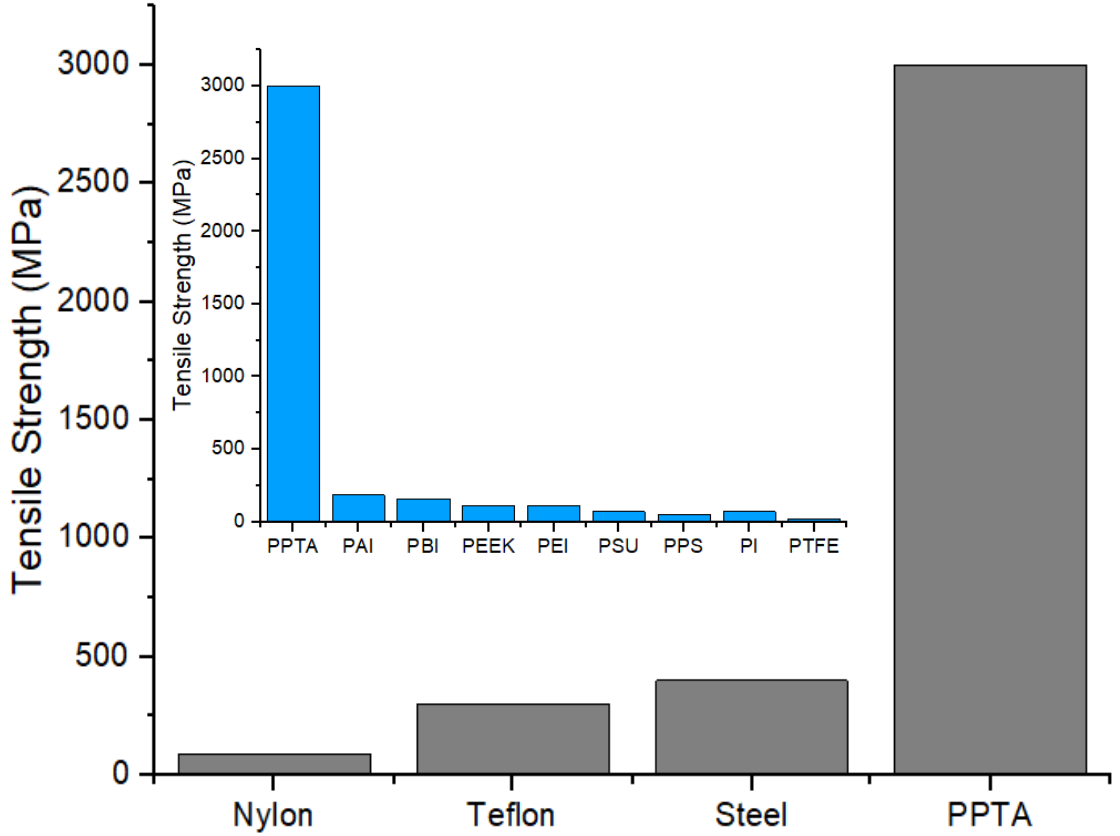


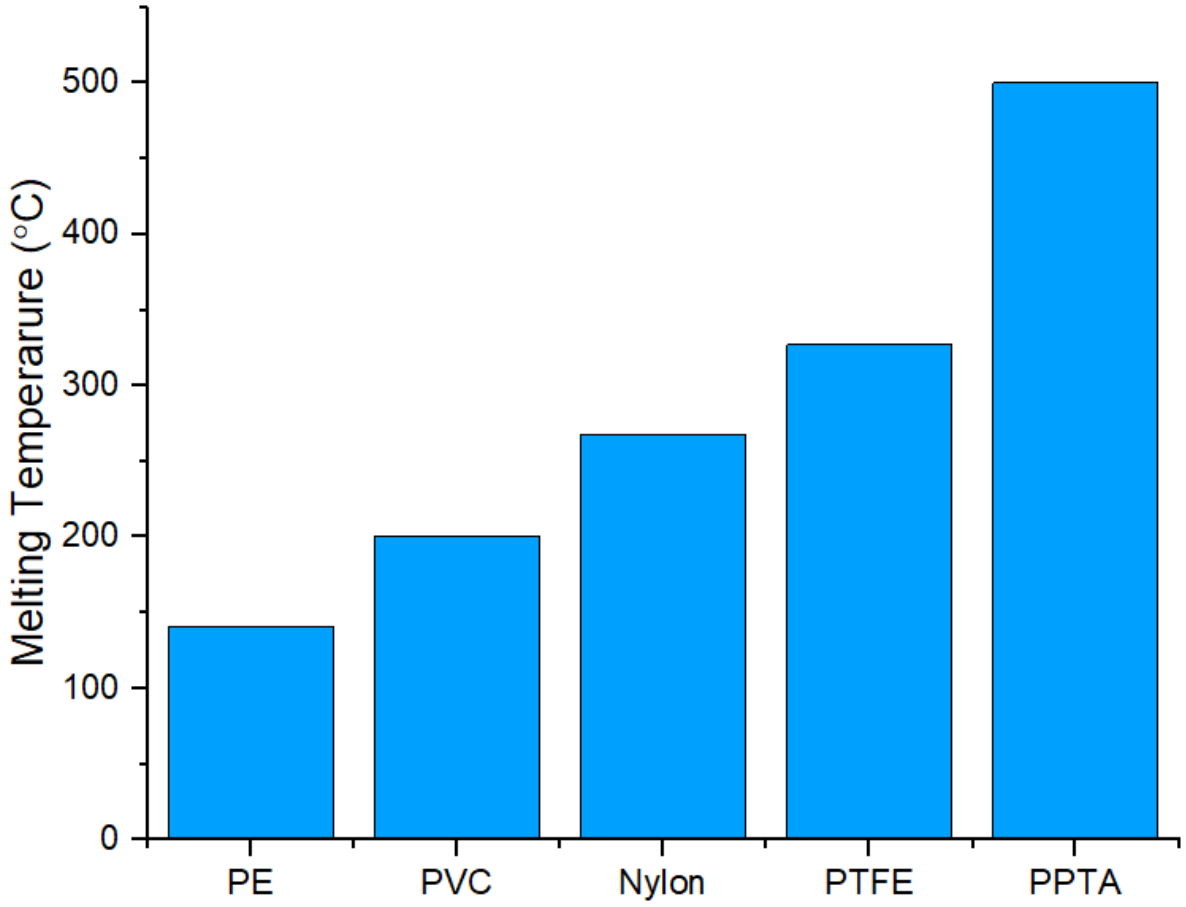
X

- Incorporation of aromatic segments into a polymer generally results in a notable increase in its thermal stability
- For this reason, much of the research work has been directed toward aromatic compositions
- Hence, high-performance polymers usually contain large numbers of aromatic units in their structures.
- Aromatic high-performance polymers examples: **aromatic polyamides, polyimides, polyesters, polysulfones, polytriphenylamine and heterocyclic polymers**

- Aromatic polyamides (aramids), such as poly(*p*-phenylene terephthalamide) (PPTA), which is also trademarked as Kevlar® and Twaron®
- Excellent thermal and oxidative stability, high mechanical strength, low flammability and good chemical and radiation resistance.

- Tensile strength of PPTA is much higher than other commonly seen polymers and even 5 times higher than steel

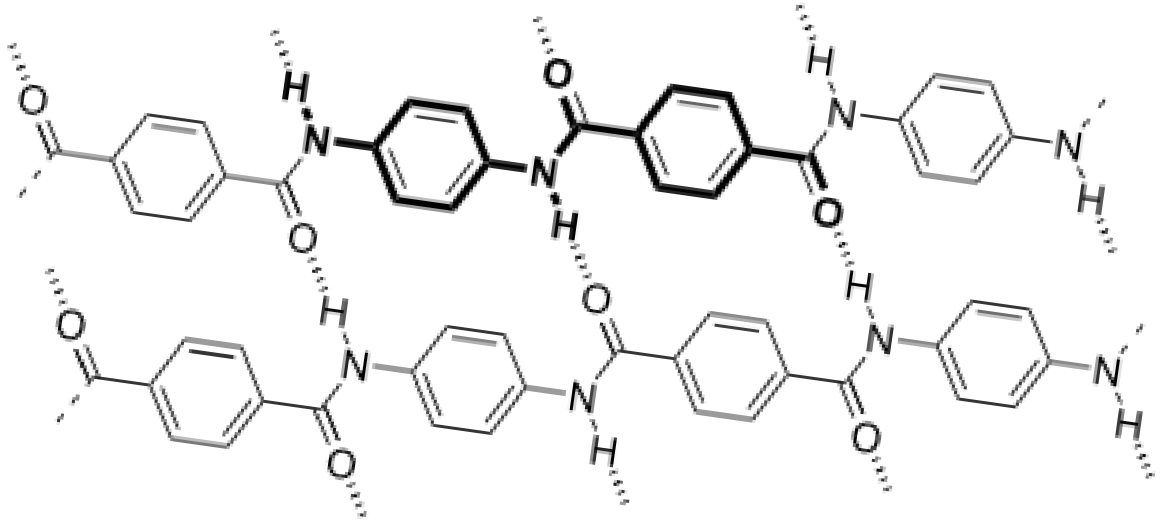




- High melting temperature (500 Celsius), therefore it is hard to process (injection, extrusion, and 3D printing)
- Degrades before melted
- Only soluble in strong acids such as sulfuric acid, which is not economically or environmentally friendly

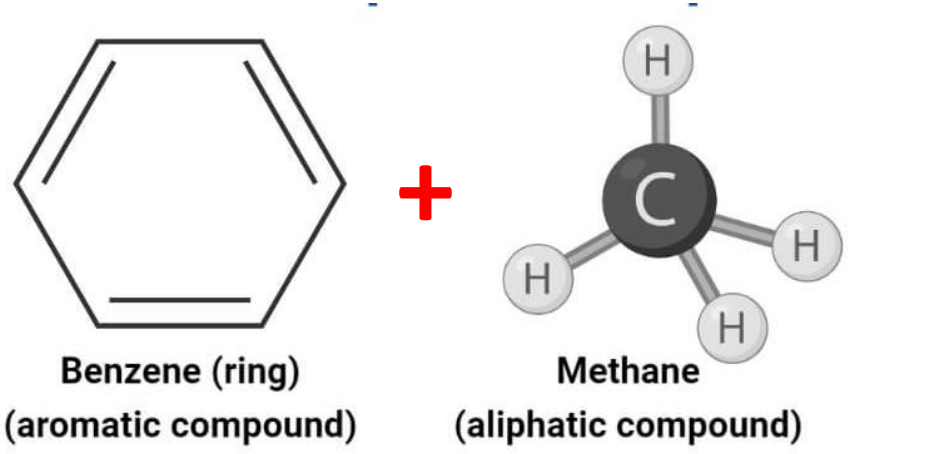
Reasons for high melting temperature:

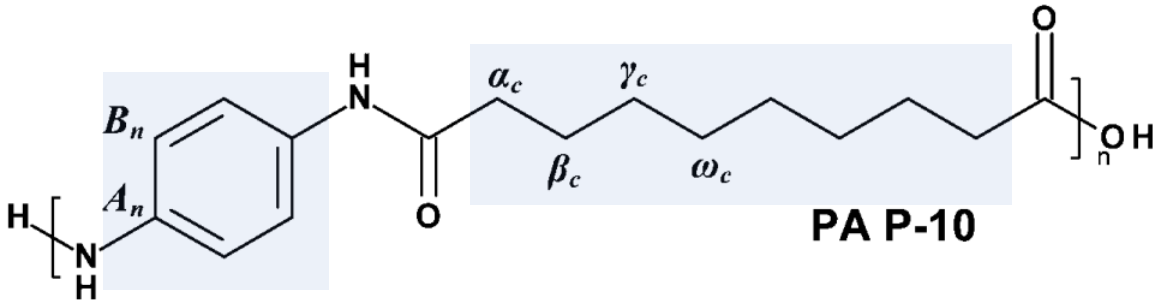
- rigid structure of aromatic moieties
- low flexibility of the chains (no rotation)
- strong intermolecular interactions



Solution:

- Increase flexibility of the structure
  - Introducing flexible aliphatic compound to be aromatic-aliphatic polyamide
  - PAPX, X is depending on how many methylene units are included





Macromolecules 49.3 (2016): 950-962.

Small

- Difficult to apply tensile strain in the transverse direction of single fiber

Sensitive

- Minor changes in the molecular structure of the aromatic-aliphatic polyamides might significantly affect mechanical behavior

Crystallinity

- Obtaining large single crystal materials is challenging, and the morphology of the polymers is complicated due to the presence of amorphous contributions

Effects

- Difficult with experimental techniques to distinguish the relative contributions of intramolecular (e.g., covalent bonds) interactions and intermolecular interactions (e.g., H-bonding and π-stacking) to bulk mechanical properties.

Density Functional Theory (DFT)

- The quantum mechanical wavefunction contains, in principle, all the information about a given system
- A method of obtaining an approximate solution to the Schrödinger equation of a many-body system
- Prediction and calculation of material behavior based on quantum mechanics
- Widely used in physics, chemistry, and material science

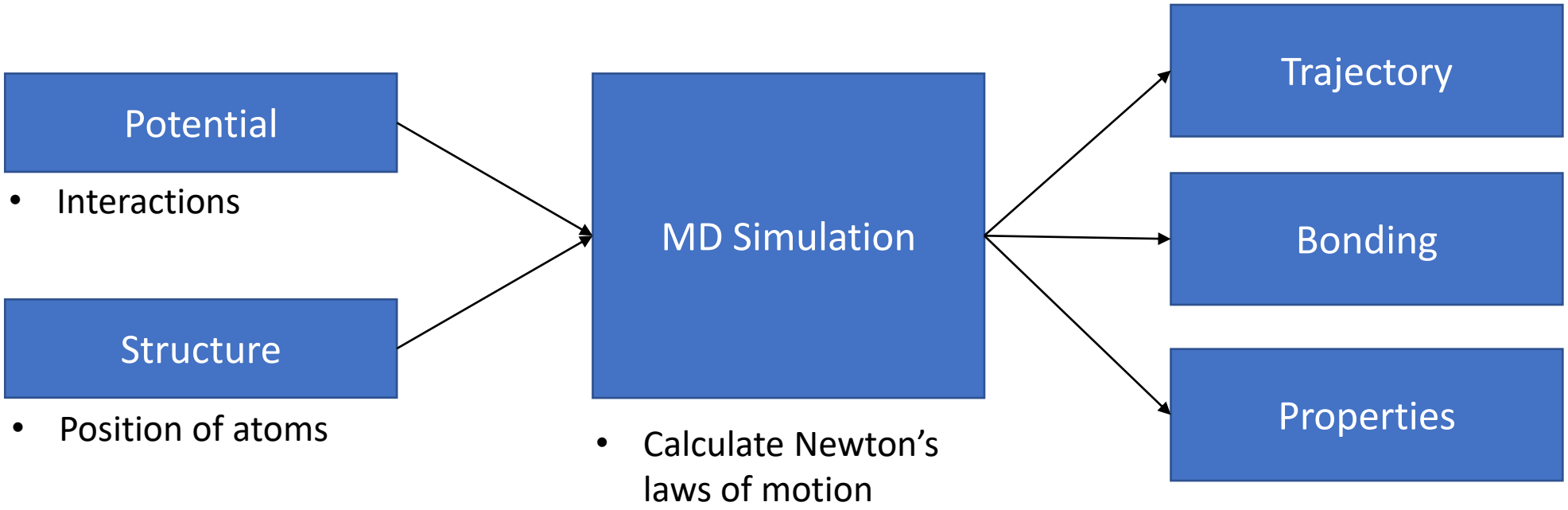
Schrödinger equation → Approximation → **DFT**

Exact solution:
- 2-D square potential
- 1 Hydrogen atom

Impossible:
- Many-body system

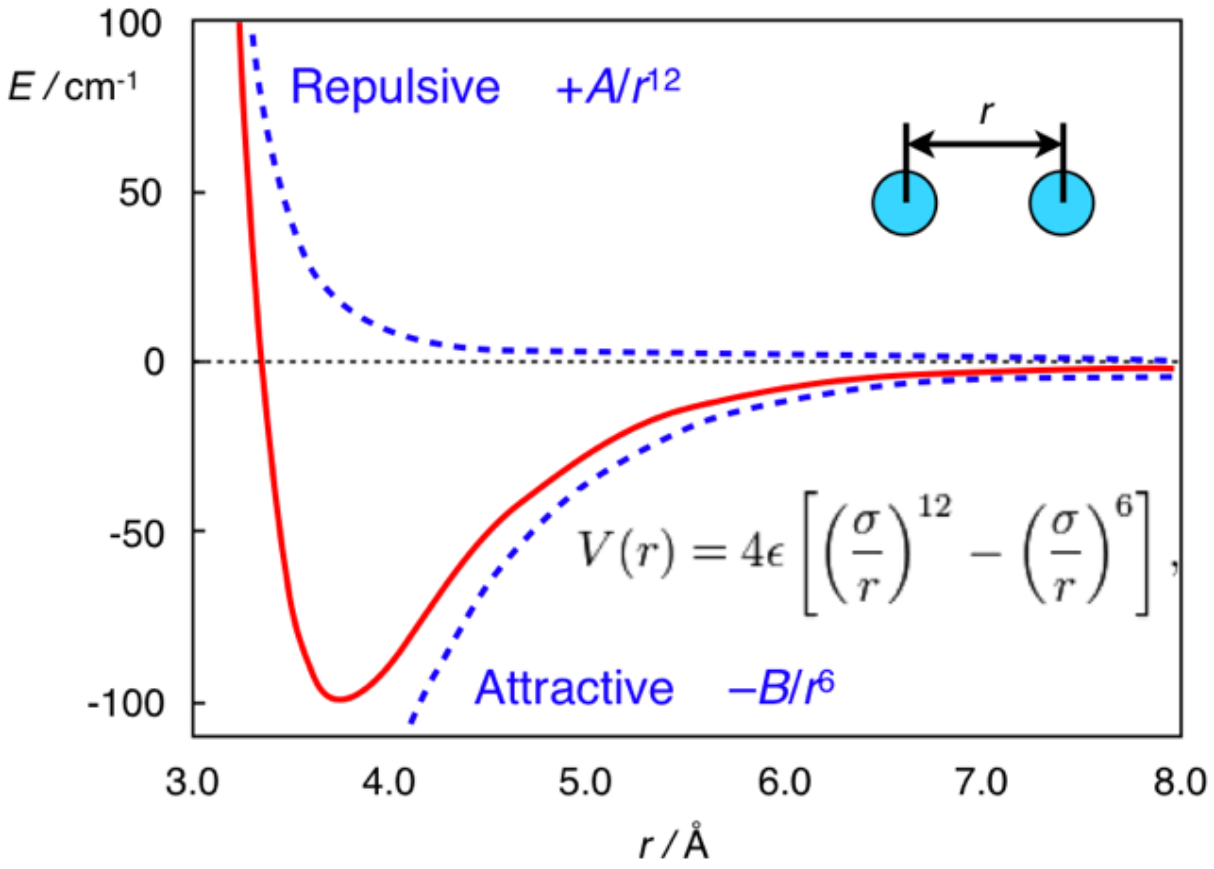
- Approximate solution
- Kohn–Sham theorem
- Density of electrons determines the properties of the system
- Only hundreds of atoms

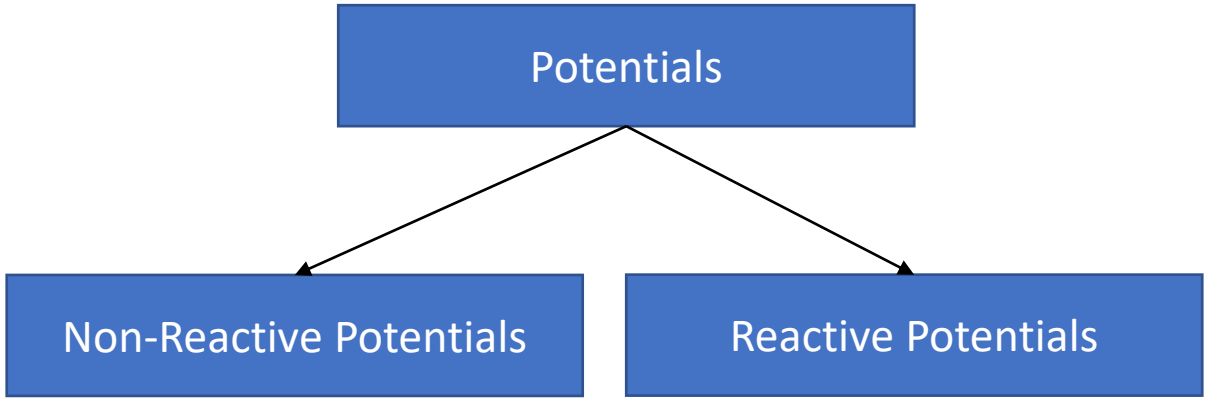
- DFT simulations are accurate but computationally expensive (only restricted to a few hundreds of atoms)
- MD simulations use potentials either fitting from experiments or DFT calculations
- MD simulations can handle much larger models (easily handle over 10,000 atoms)



- Potentials are used to describe the interactions between the atoms in the model system
- Example: Lennard-Jones potential

Lennard-Jones Potential

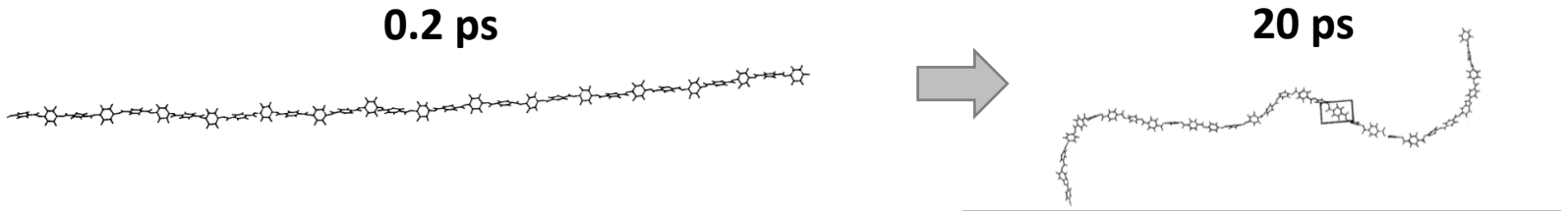




- Static bonds
- No bond breaking/formation

- Dynamic bonds
- Bond breaking/formation

- MD has been previously recognized as a useful tool for studying the behavior of crystalline PPTA
- Studies have been performed to:
  - Predict the ideal molecular geometry and chain conformations [1]



  - Thermal expansion coefficient and elastic moduli [2,3]

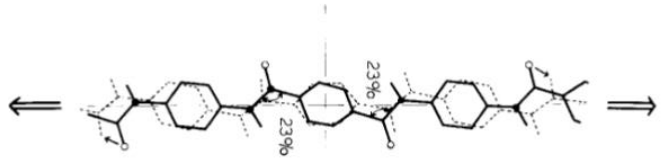
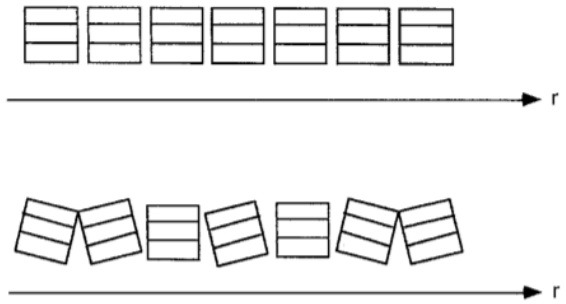


Table 1. Average Thermal Expansion between 300 and 500 K

	PPTA		PBA	
	calculated	experimental[a]	calculated	experimental[a]
α_1 (10^{-5} K^{-1})	7.9	8.3	7.7	7.0
α_2 (10^{-5} K^{-1})	2.9	4.7	4.6	4.1
α_3 (10^{-5} K^{-1})	−0.57	−0.29	−0.84	−0.77

[a] Ii *et al.*, ref 24.

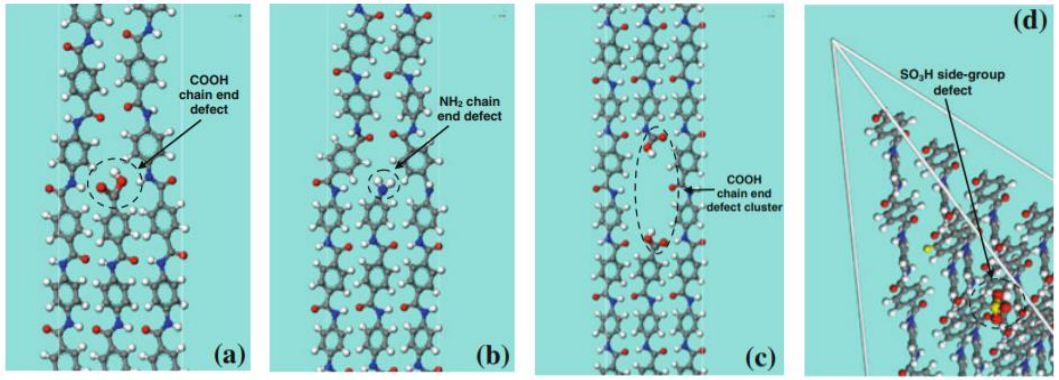
  - Compressive failure due to chain buckling [4]



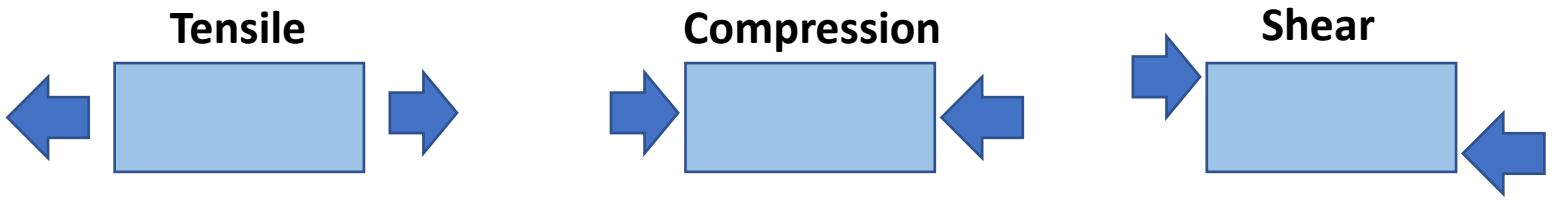
[1] *Polymer* 33.2 (1990), pp. 398-404.
[2] *Macromolecules* 27 (1994), pp. 7197-7204.
[3] *Polymer* 25 (1984), pp. 147164.
[4] *Journal of Materials Science* 31.22 (1996), pp. 5885-5889.

- More recent work [1-6] on PPTA MD simulations:
  - **Various defect patterns and impurities,**

Defects



  - **Tensile, torsion, and compressional loading**

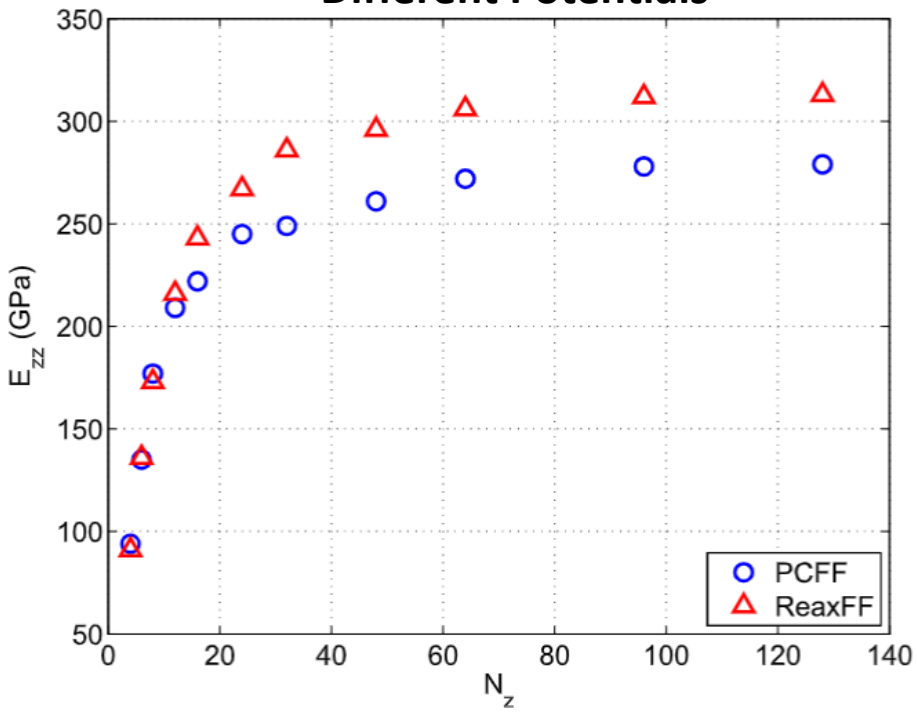


  - **Elastic moduli and strength**

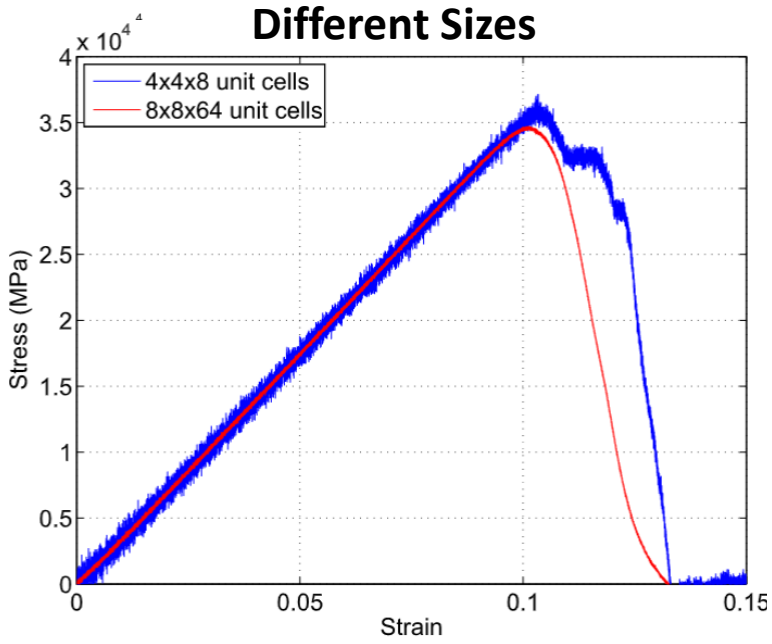
[1] *Journal of Materials Engineering and Performance* 20 (2011), pp. 1401-1413
[2] *Journal of Materials Science* 46.14 (2011), pp. 4787-4802.
[3] *Journal of Materials Engineering and Performance* 22.3 (2013), pp. 681695.
[4] *Advances in Materials Science and Engineering* 2013 (2013), pp. 115.
[5] *Journal of Materials Engineering and Performance* 22.11 (2013), pp. 3269-3287.
[6] *Journal of Materials Science* 49.24 (2014), pp. 82728293.

- The most recent work PPTA MD simulations [1-2]:
- Two potentials (PCFF and ReaxFF Liu) were evaluated for their ability to model PPTA structure and mechanical response to strain
- PCFF and ReaxFF Liu Potentials give similar results, except that PCFF can only be used for situations where primary bonds are not expected to rupture

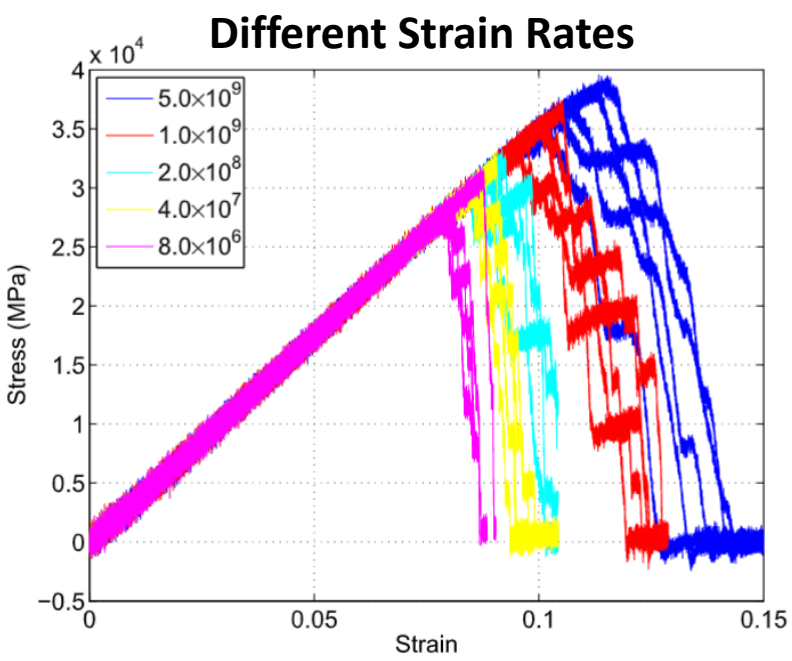
Different Potentials



Different Sizes

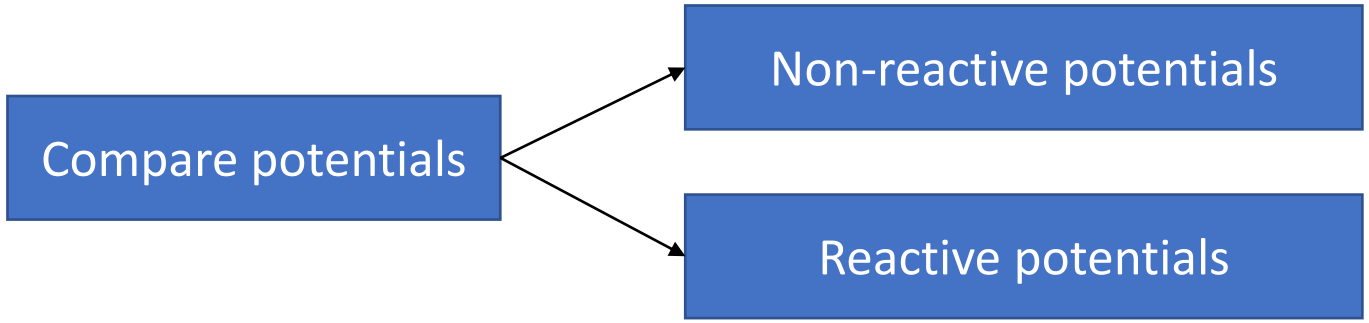


Different Strain Rates

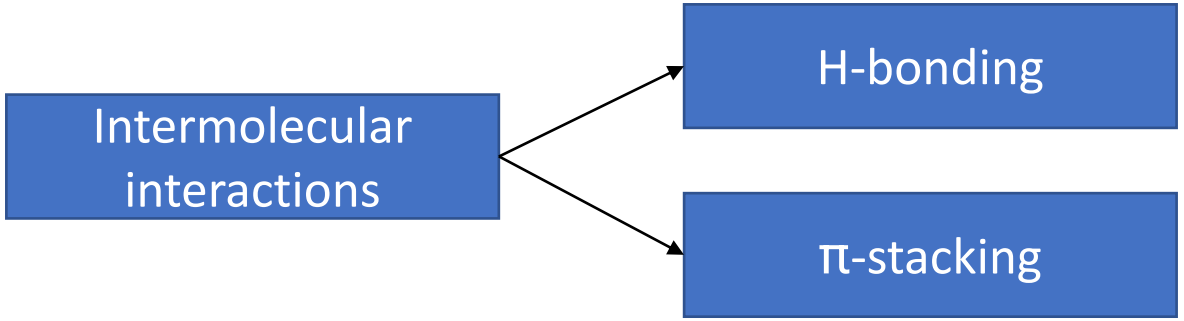


[1] *Polymer* 114 (2017): 329-347.
[2] *Polymer* 129 (2017): 92-104

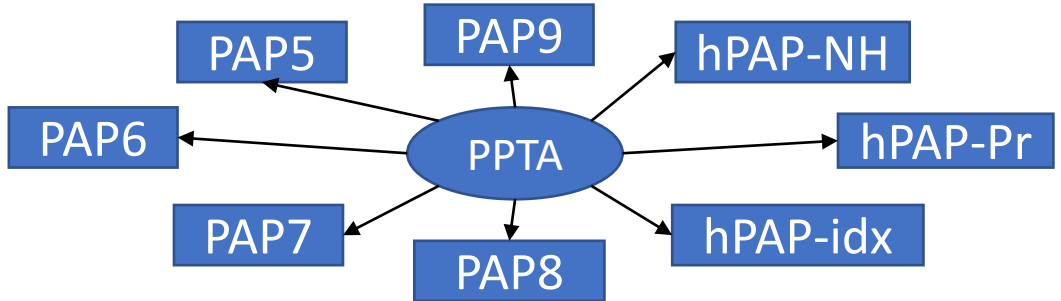
- No comparison of a comprehensive set of potentials, including multiple reactive and non-reactive models

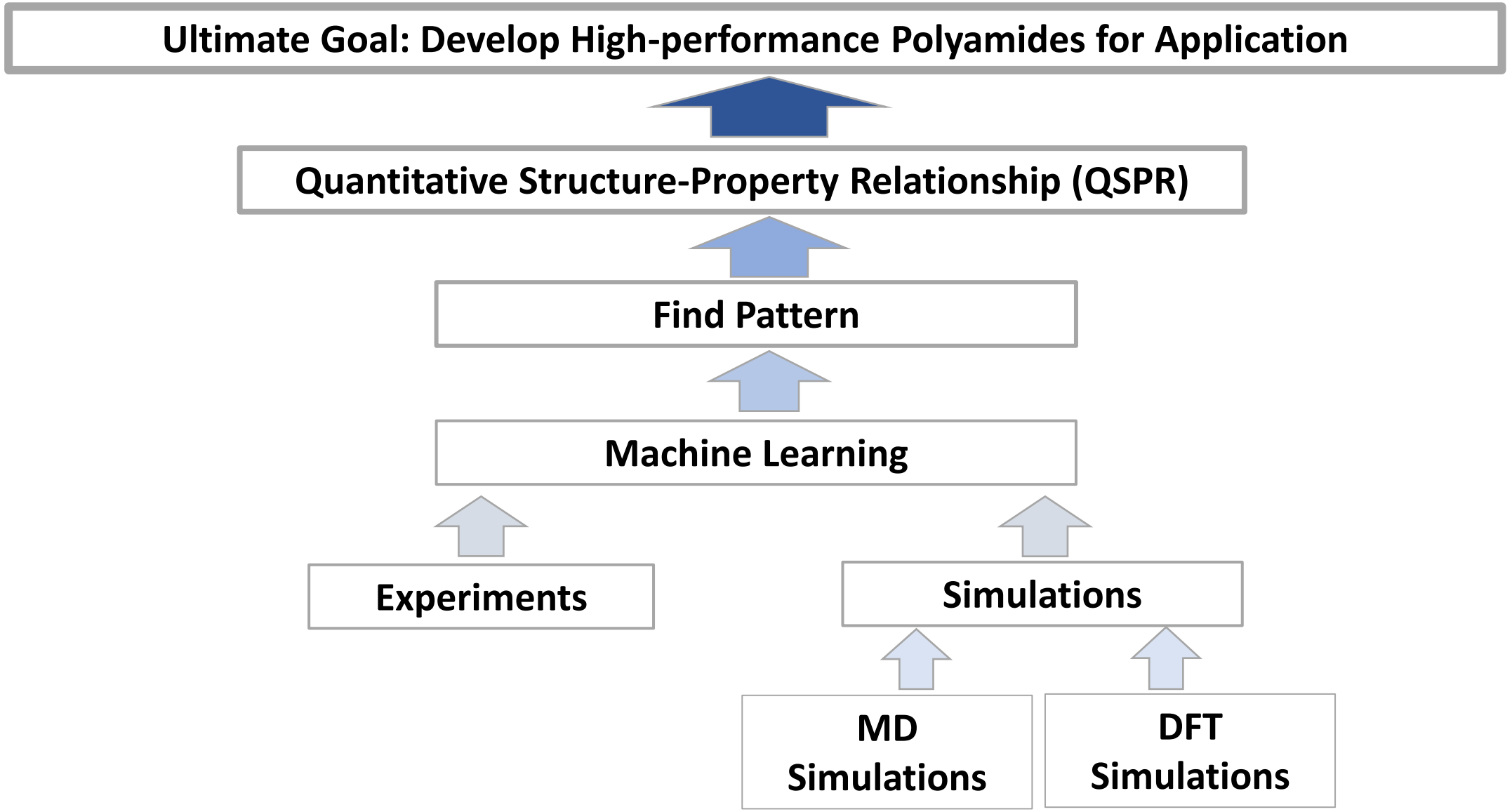


- No evaluation of the ability to model H-bonding and π-stacking patterns



- No generalizability assessed by evaluating homologous material systems

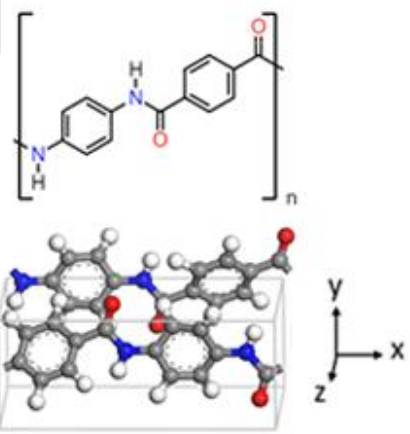



Ultimate Goal: Develop High-performance Polyamides for Application
Quantitative Structure-Property Relationship (QSPR)
Find Pattern
Machine Learning
Experiments
Simulations
MD Simulations
DFT Simulations

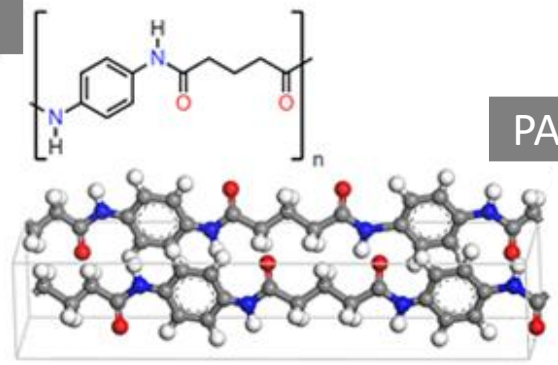
Methods

- PPT5 to PAP8 are four example aromatic-aliphatic polyamides
- They both have aromatic and amide groups
- The difference among them is the number of carbons between the benzene rings

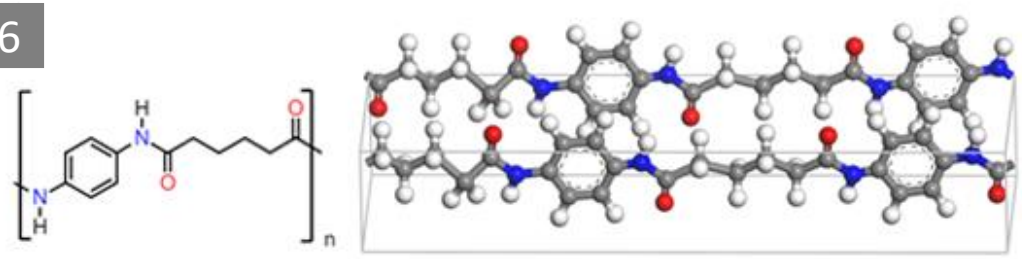
PPTA



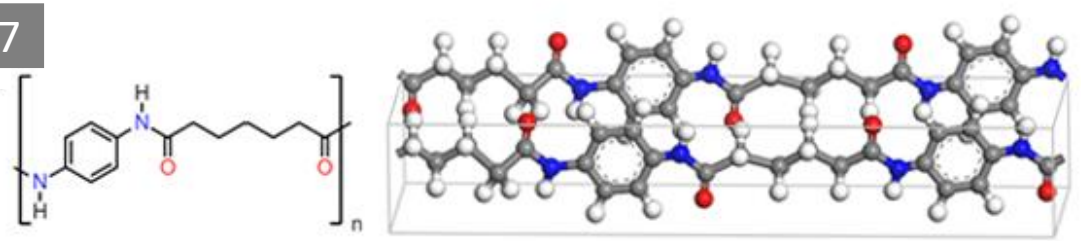
PAP5



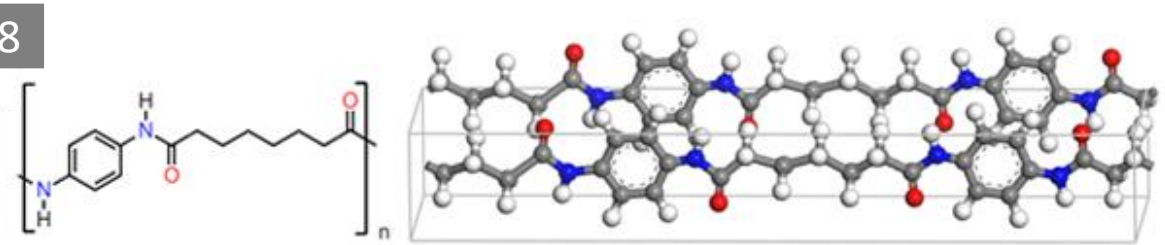
PAP6

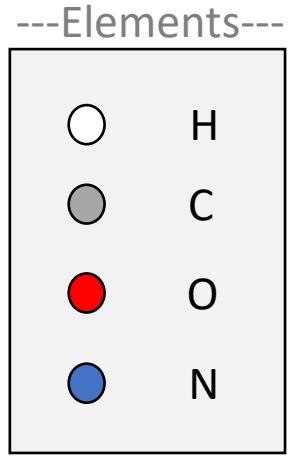


PAP7



PAP8





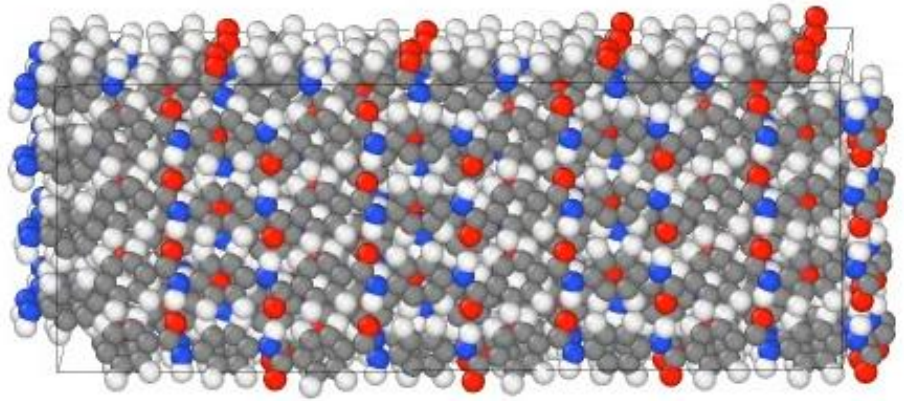
1. Create 1x1x1 unit cell model in Material Studio

2. Replicate unit cell to 4x4x4 in LAMMPS

3. Energy minimization

4. NPT at 300 K and 1 atm for 125 ps

5. Stress-strain simulation

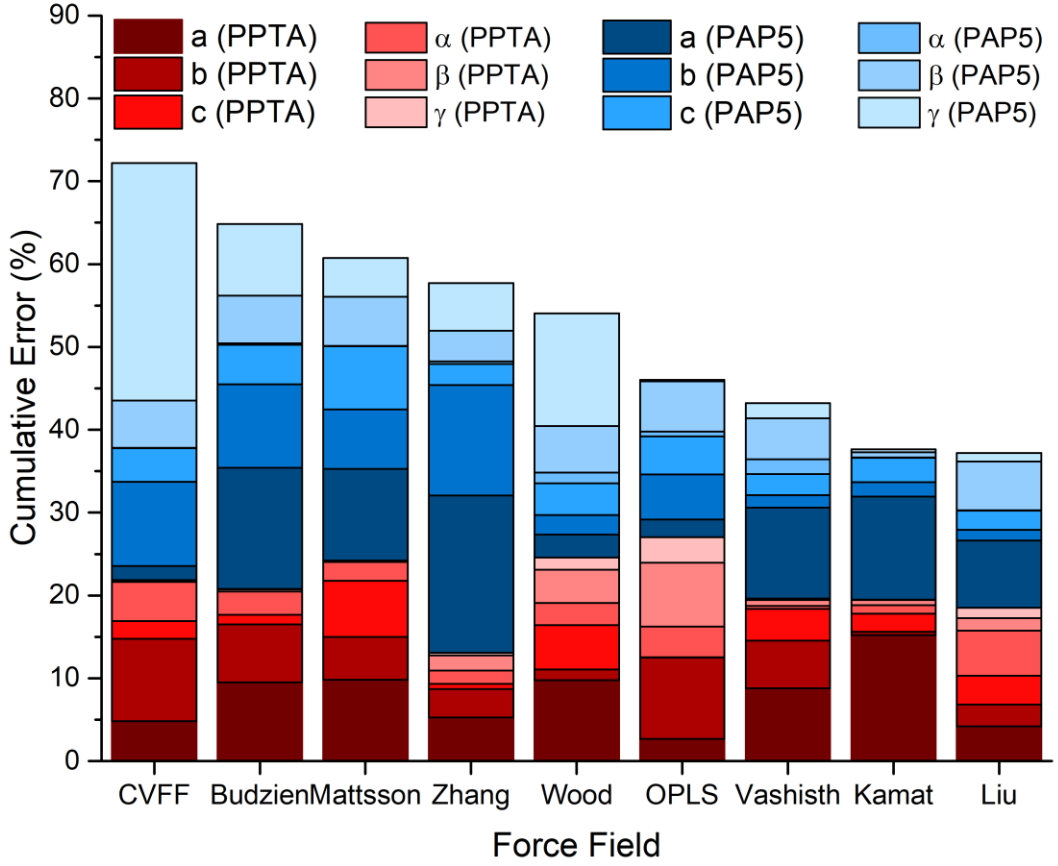


Preliminary Results

Preliminary Results >> Potential Selection – Lattice

Polyamide	Unit Cell Lattice Parameters					
	a (nm)	b (nm)	c (nm)	α (˚)	β (˚)	γ (˚)
PPTA	0.787	0.518	1.29	90	90	90
PAP5	0.850	0.470	2.48	90	85	90

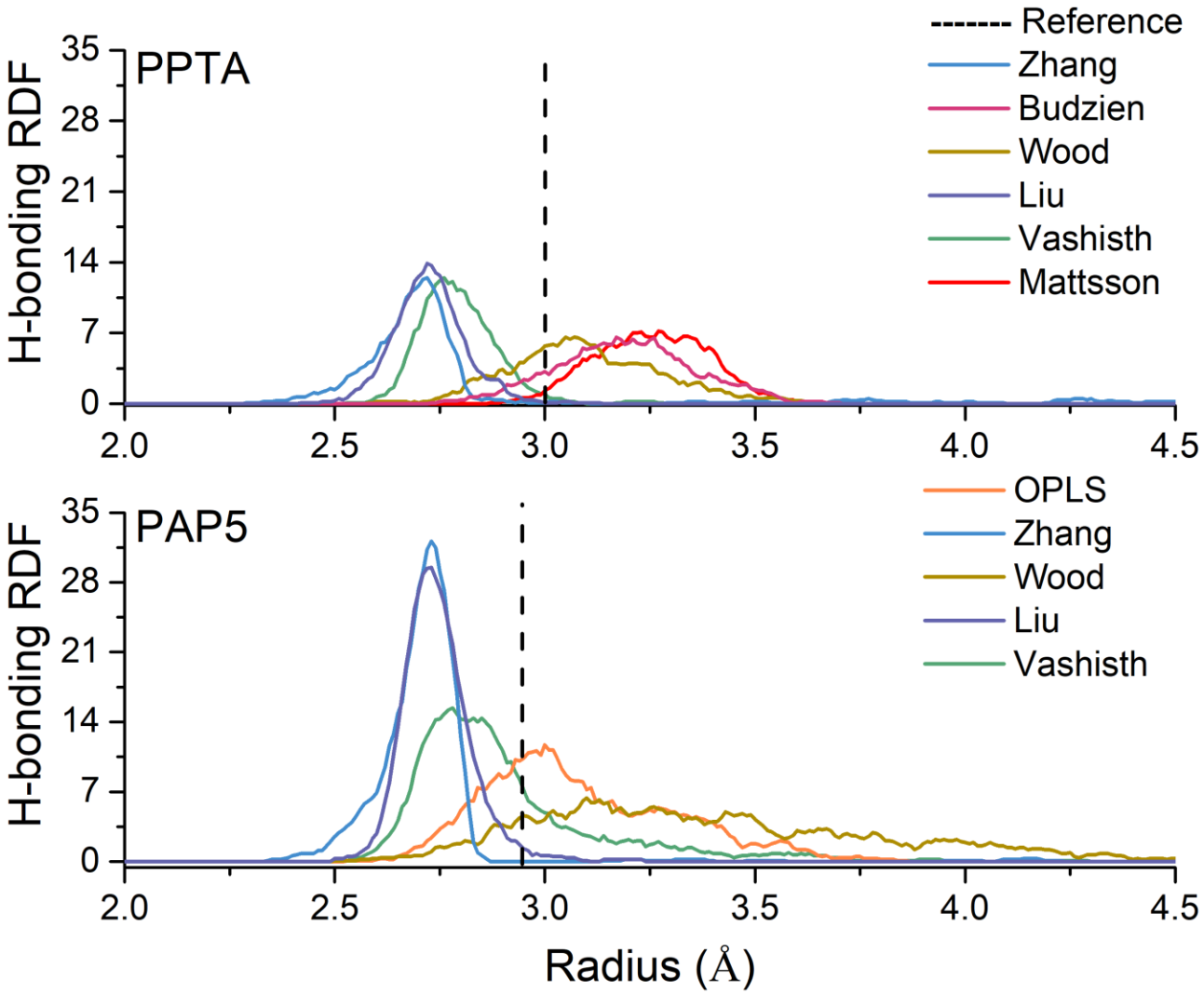
Macromolecules 49 (2016): 950-962



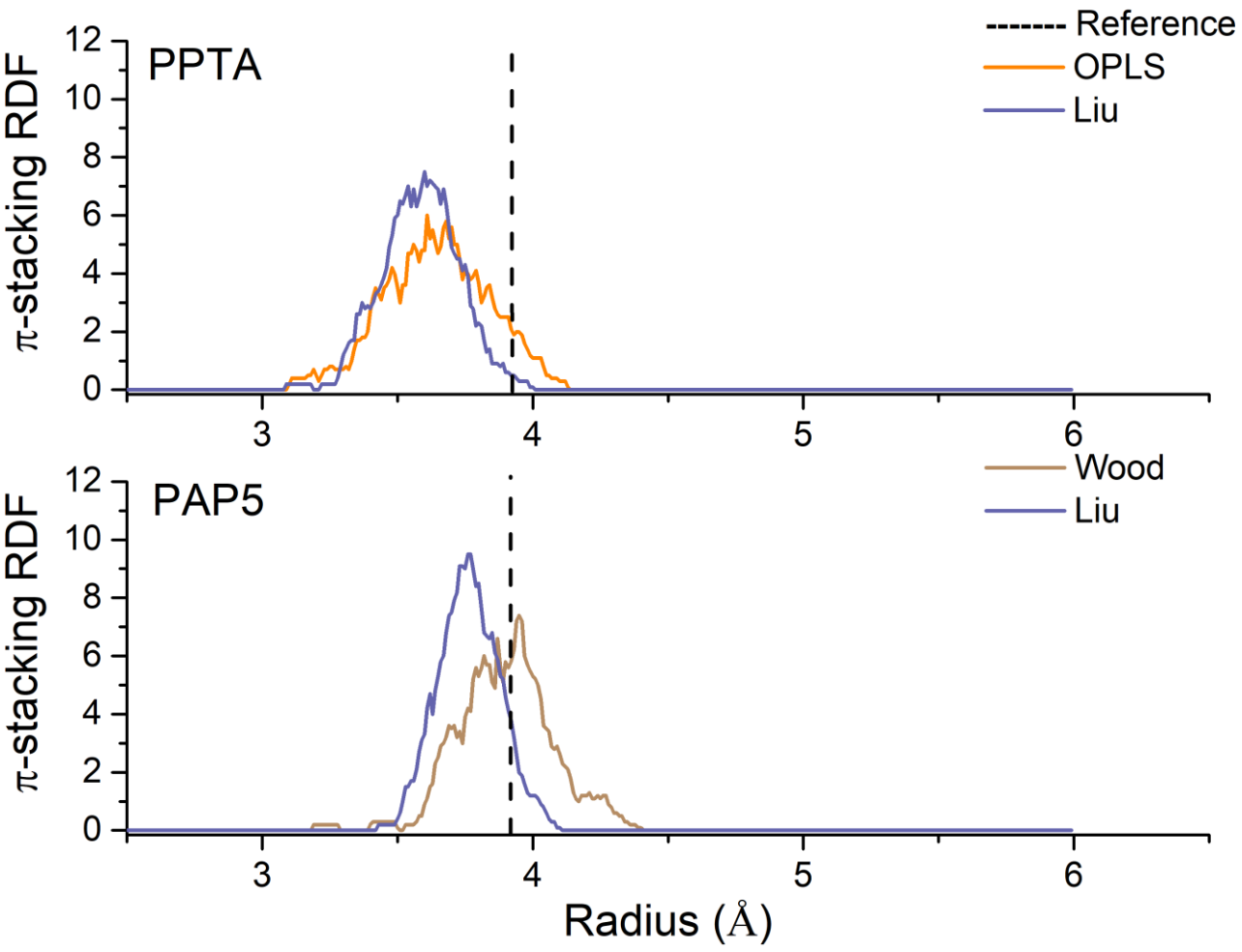
- Comparison of the accuracy (error) and stability (deviation) of seven reactive potentials and two non-reactive potentials.
- CVFF has the largest error and especially large error in γ of PAP5

Reactive ReaxFF Potentials:

Mattsson et al. Phys. Rev. B 2010, 81, 054103.
Zhang et al. J. Phys. Chem. B 2009, 113, 31, 10770-10778.
Kamat et al. J. Phys. Chem. A 2010, 114, 48, 12561-12572.
Wood et al. J. Phys. Chem. A 2014, 118, 5, 885-895.
Vashisth et al. *J. Phys. Chem. A* 2018, 122, 32, 6633-6642.
Liu et al. *J. Phys. Chem. A* 2011, 115, 11016-11022.
Budzien et al. *J. Phys. Chem. B* 2009, 113, 13142-13151.



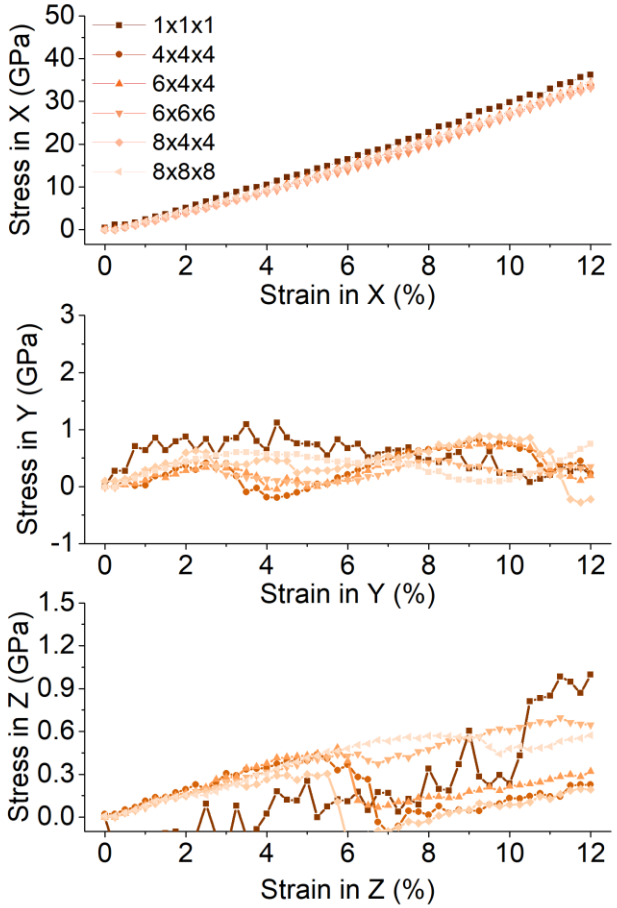
- Comparison of O-N radial distribution functions calculated for PPTA and PAP5
- For PPTA, the best potentials are Wood, Budzien, Mattsson, Zhang, Vashisth, and Liu
- For PAP5, the best are OPLS, Wood, Zhang, Vashisth, and Liu



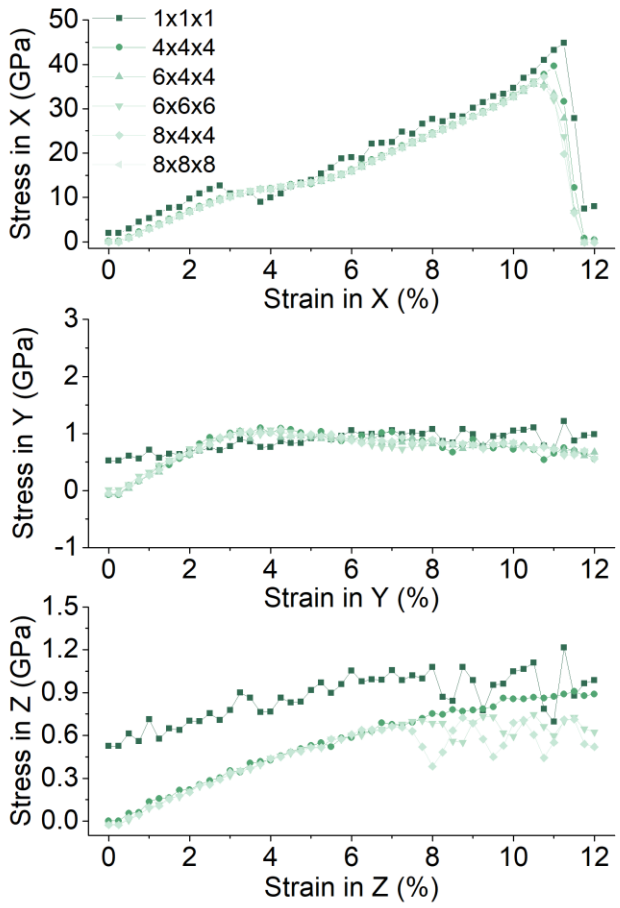
- Comparison of O-N radial distribution functions calculated for PPTA and PAP5.
- For PPTA, the RDF peaks of Liu and OPLS are the closest to the reference value.
- For PAP5,Wood and Liu are the most accurate, with relatively narrow peaks.

- Identify the smallest model that can be used (to maximize computational efficiency) without simulation artifact
- OPLS doesn't break at all
- Vashisth shows fluctuations between 7-12% strain
- Size 4x4x4 and the ReaxFF Liu potential are suitable for the stress-strain response of PPTA and PAP5

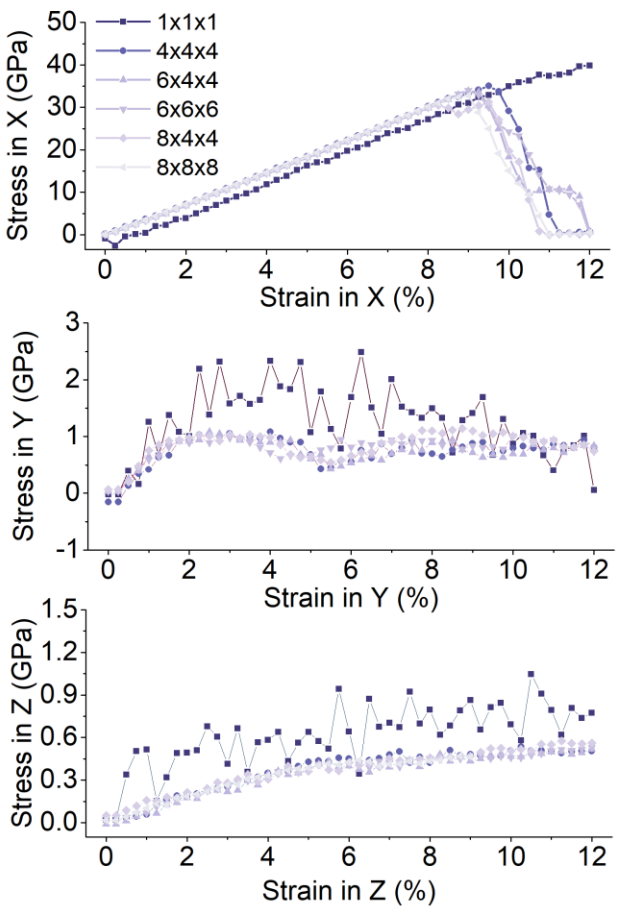
Non-reactive OPLS



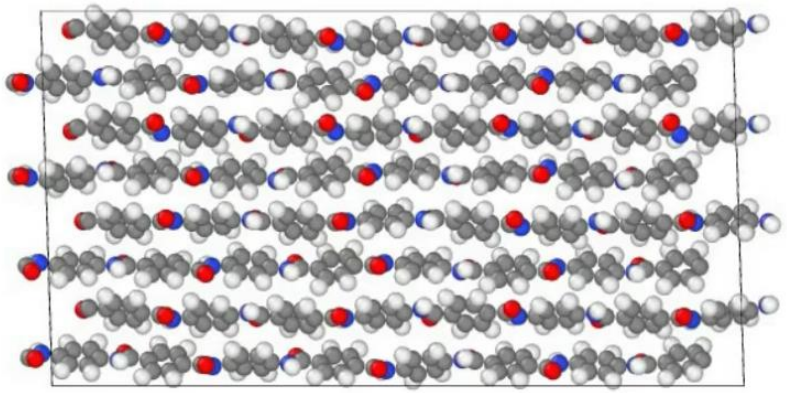
ReaxFF Vashisth



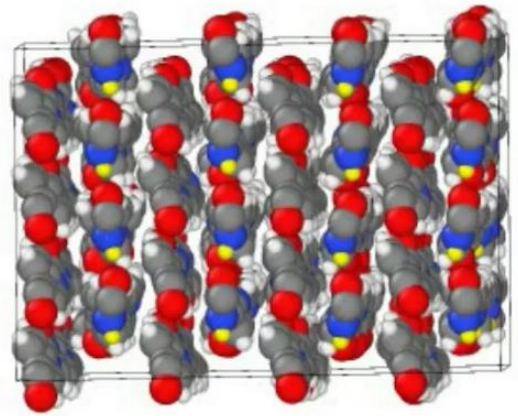
ReaxFF Liu



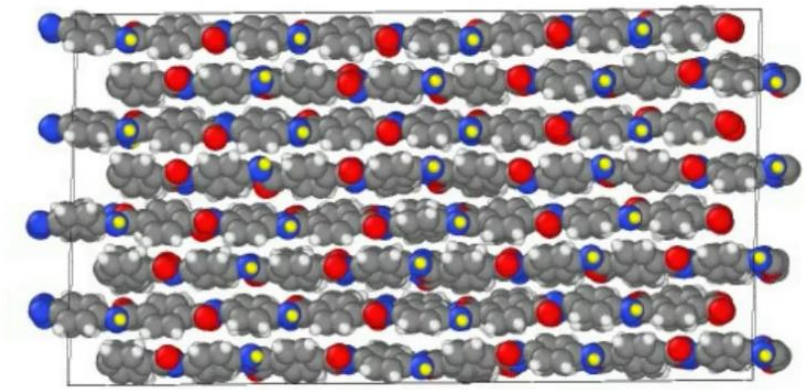
PPTA



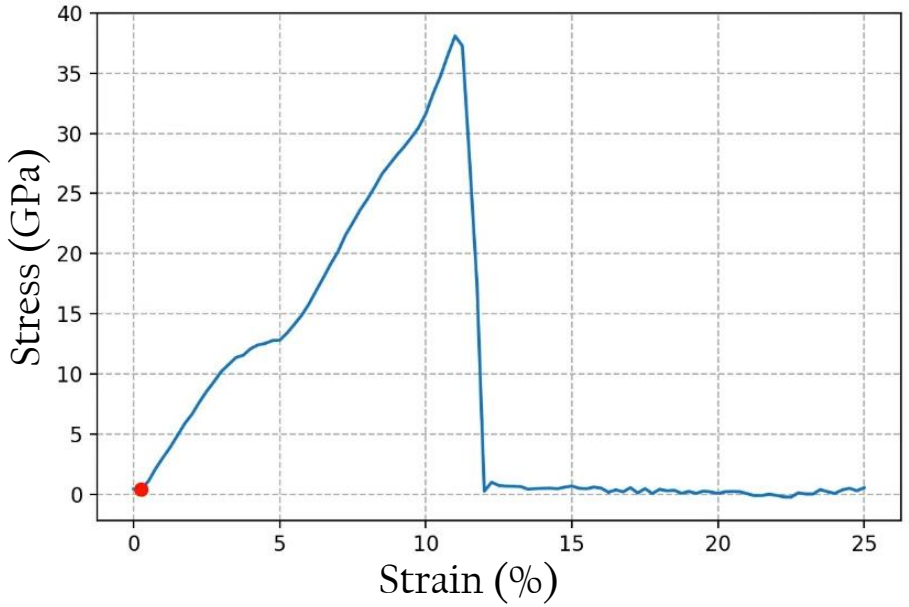
Top View



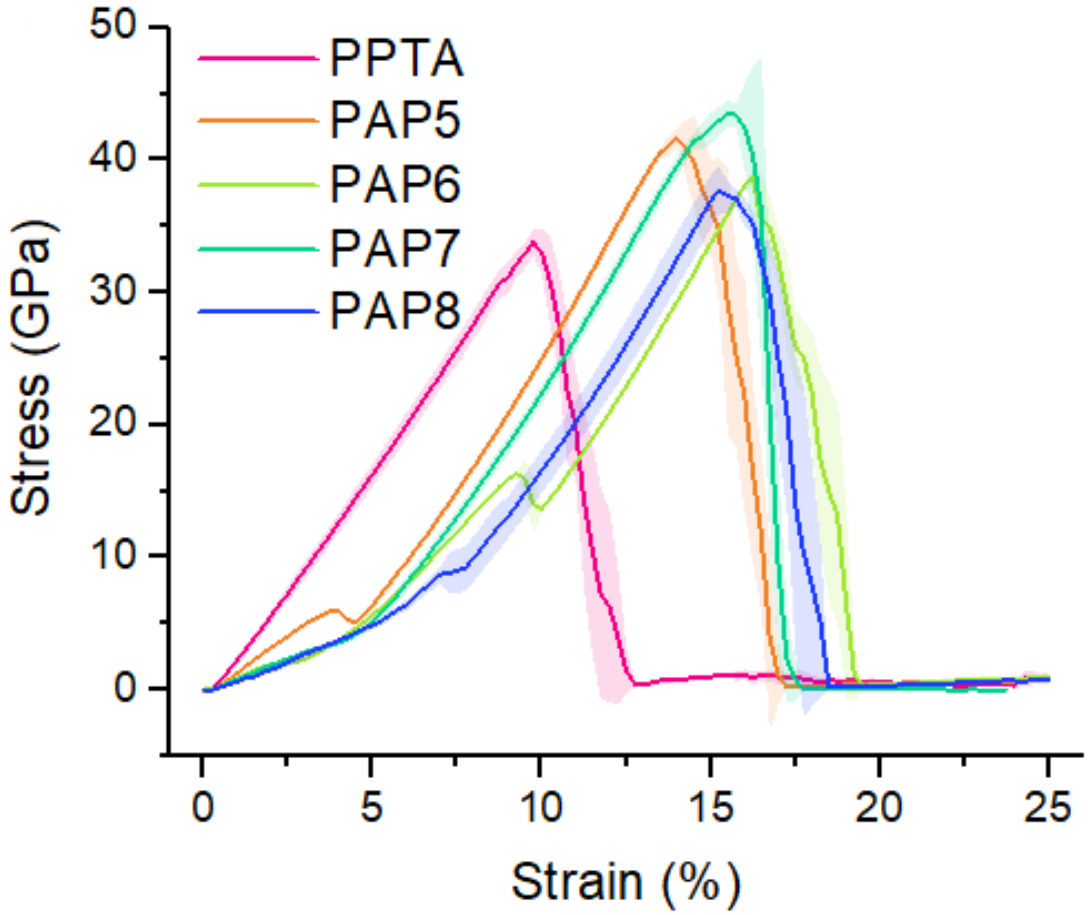
Side View

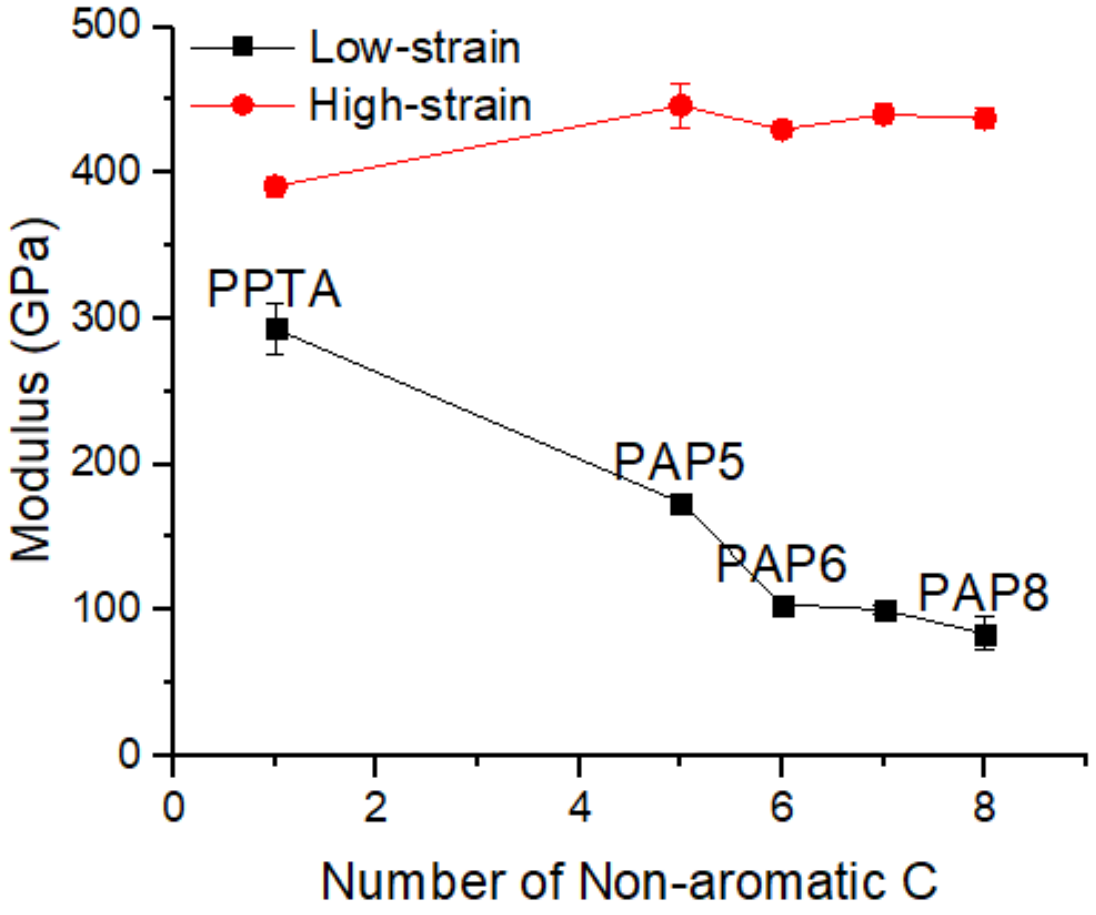


Front View



- Low strain modulus lower than high strain modulus
- Low strain modulus decreases with increasing number of non-aromatic C atoms
- High-strain modulus is essentially independent of the number of non-aromatic C atoms

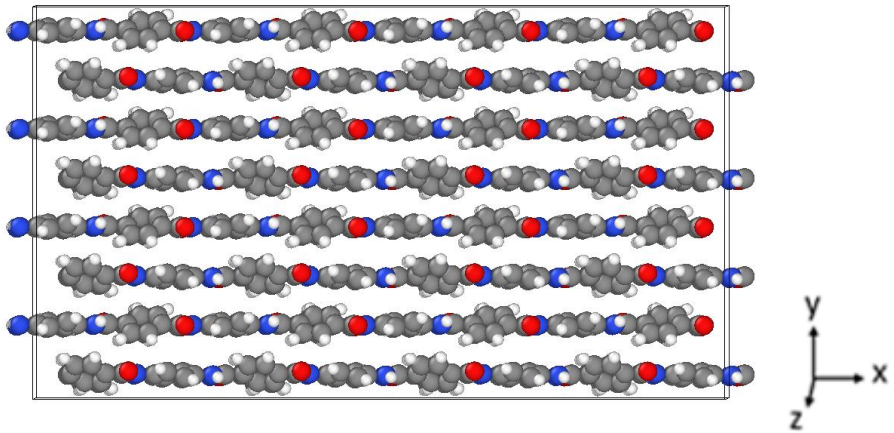




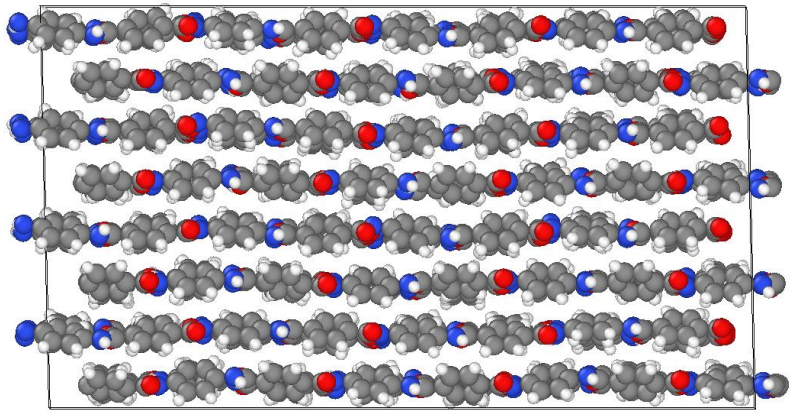
- After equilibration, the chains become wavy, especially for polymers with more non-aromatic C

PPTA

Initial Structure

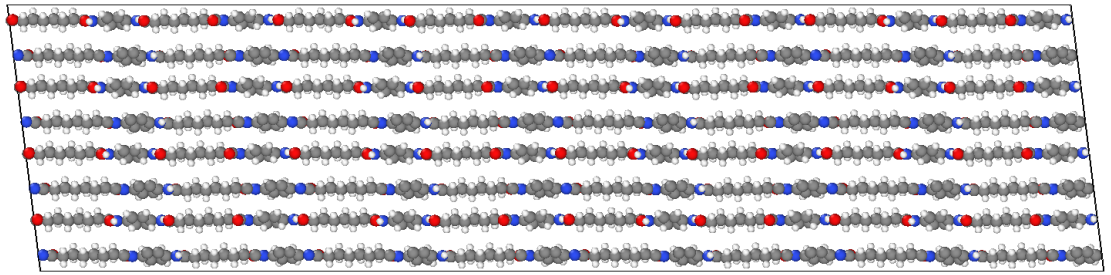


After Equilibration

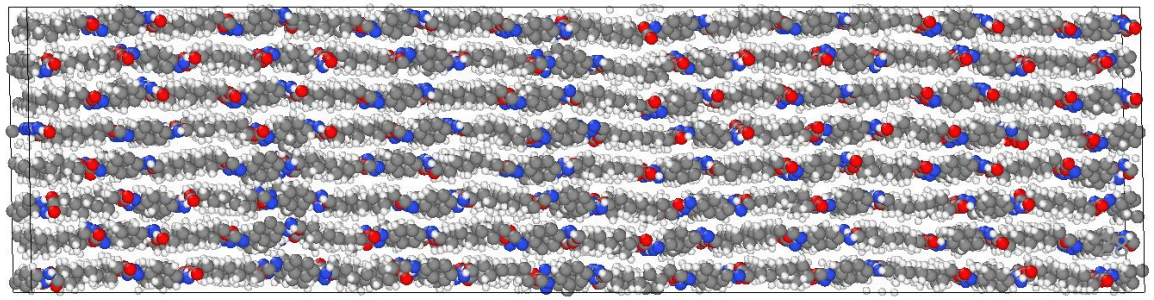


PAP8

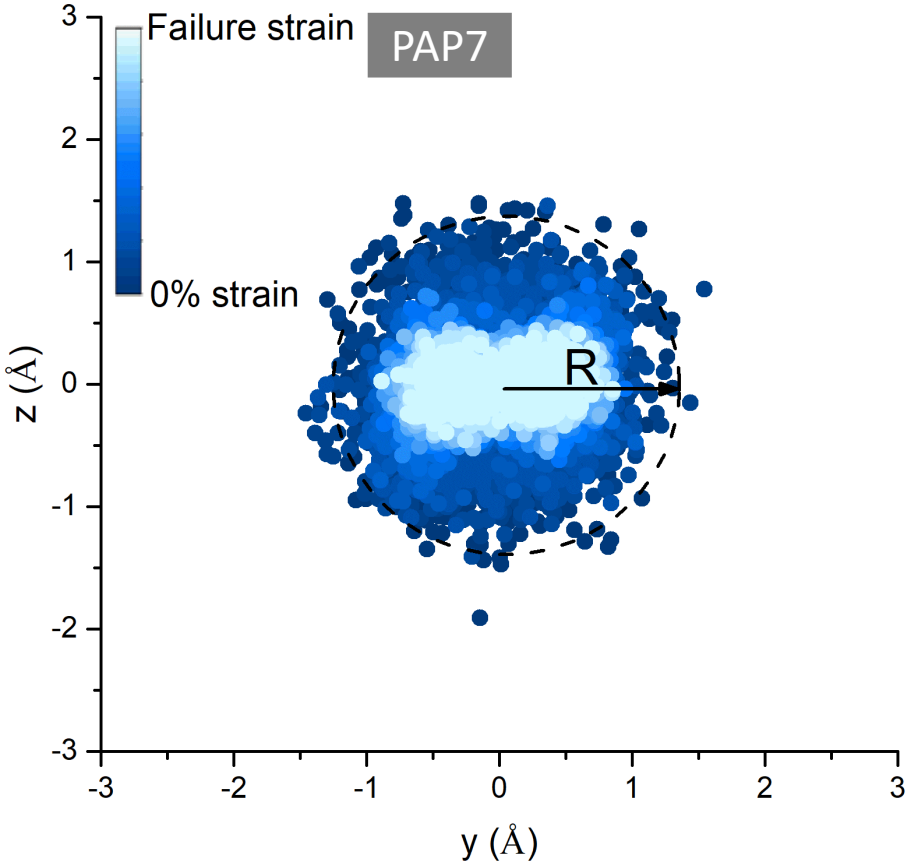
Initial Structure

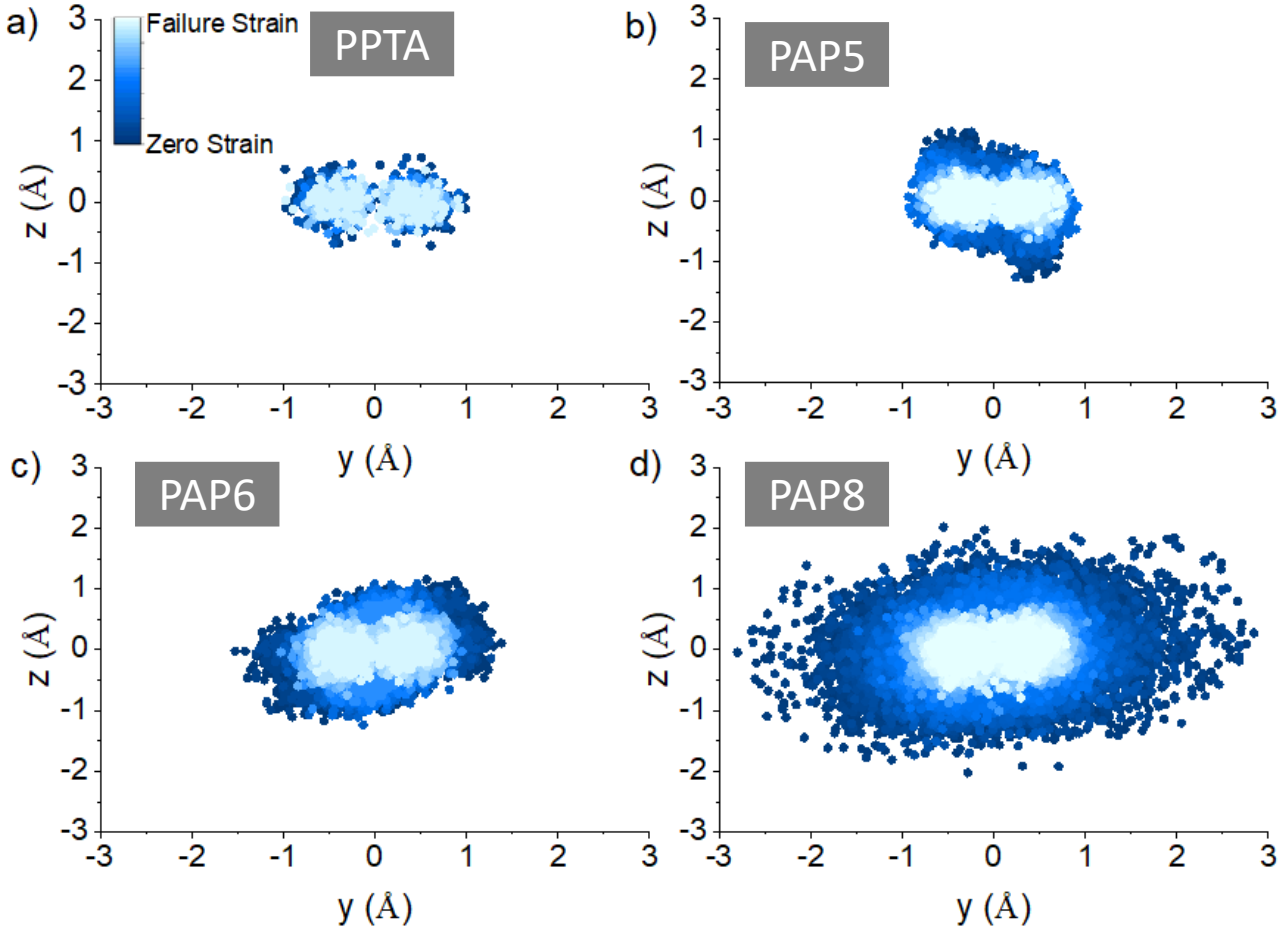


After Equilibration

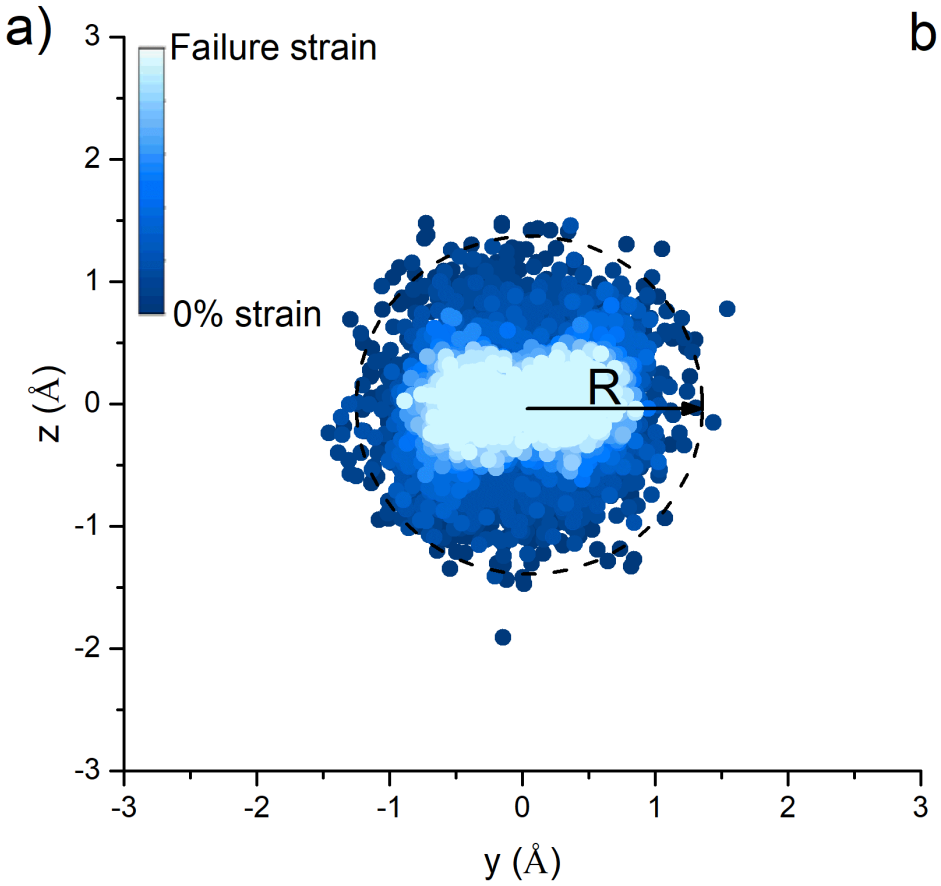


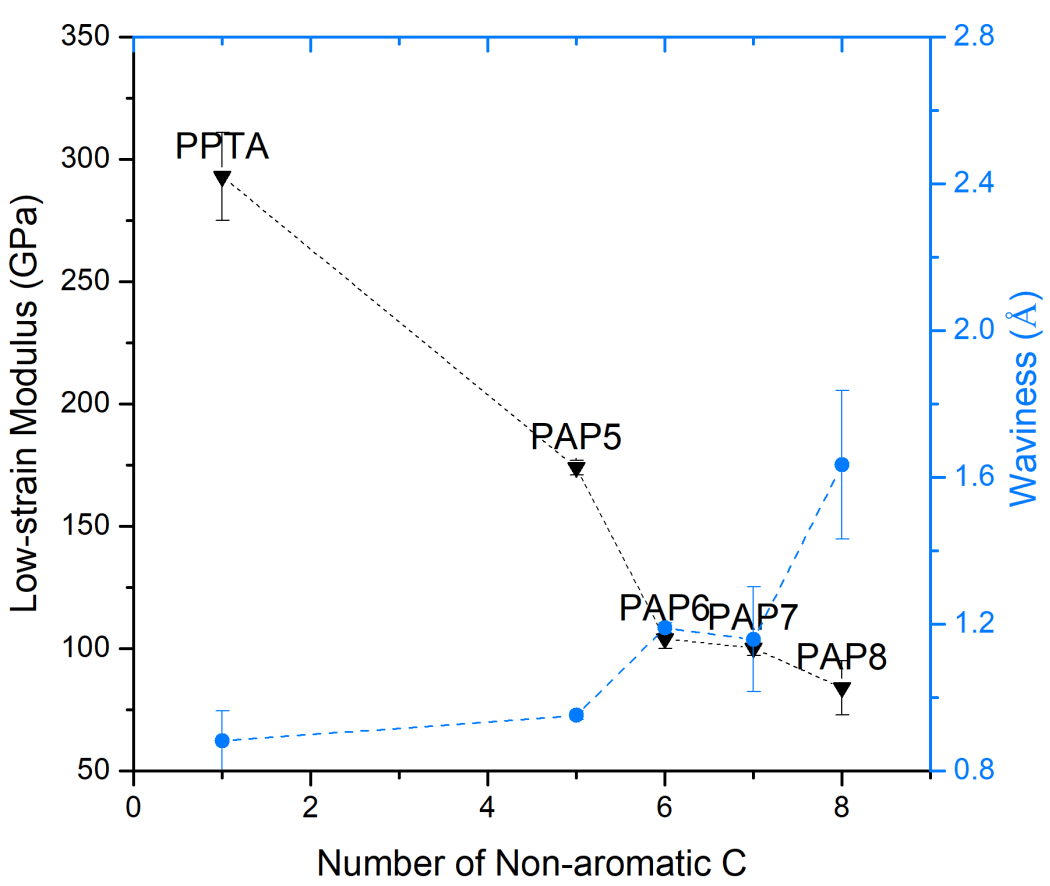
- Side view (yz-plane) of the polymers (only backbone C and N are shown)
- As the number of non-aromatic C increases, the atom cloud spreads out more (more wavy chains)





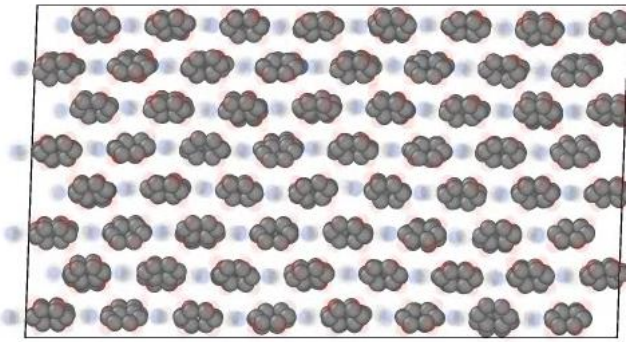
- The decrease in modulus with chain length is due to increasing waviness of the polymers
- Waviness is due to the methylene groups acting as spacers between the hydrogen-bonded amide groups, which increases the conformational freedom of the polymer chains
- More waviness decreases stiffness because force resistant to stretch has less components in the chain direction



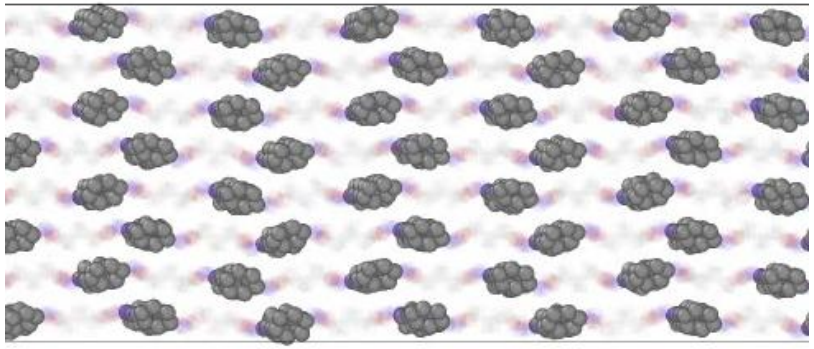


- Movies of strain simulations shown from the y-direction where all atoms except the aromatic rings are faded. Only even polymers (PAP6 and PAP8) exhibit interchain slip.

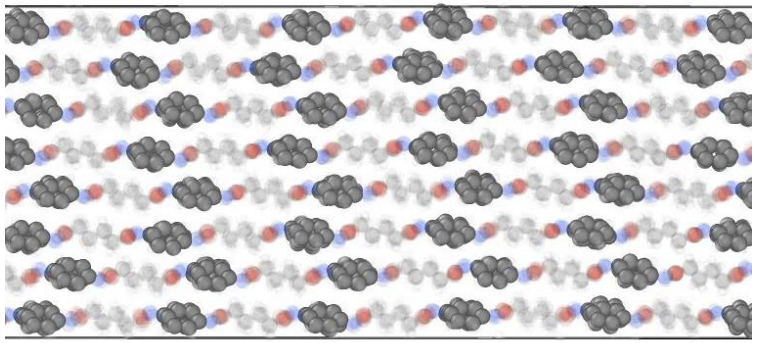
PPTA



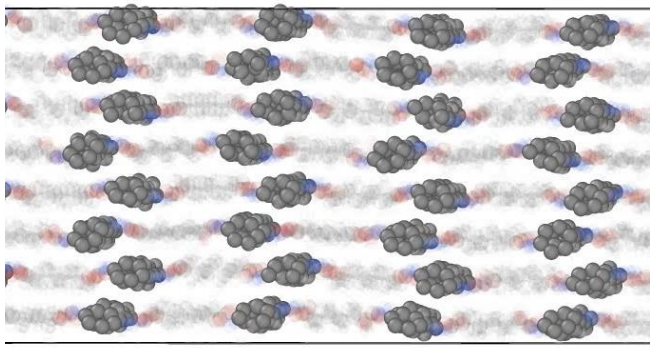
PAP5



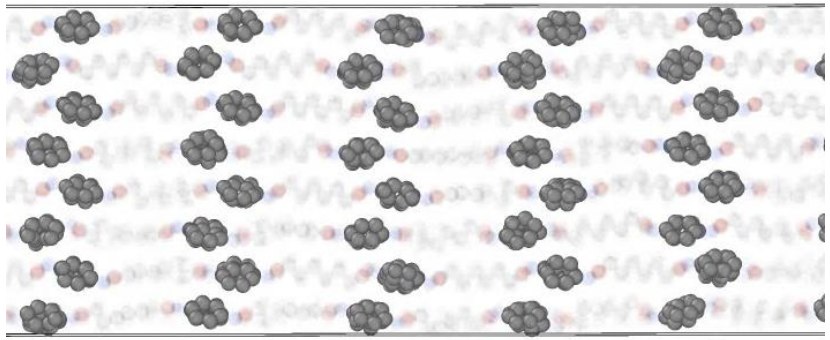
PAP6

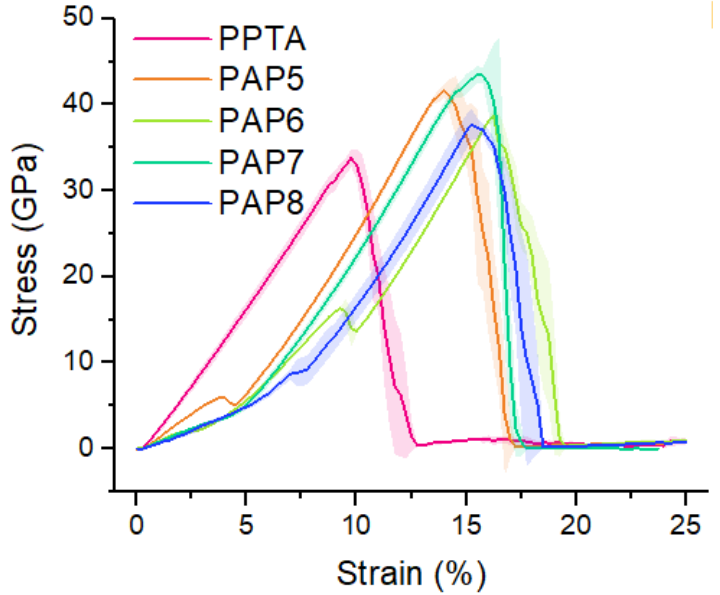


PAP7

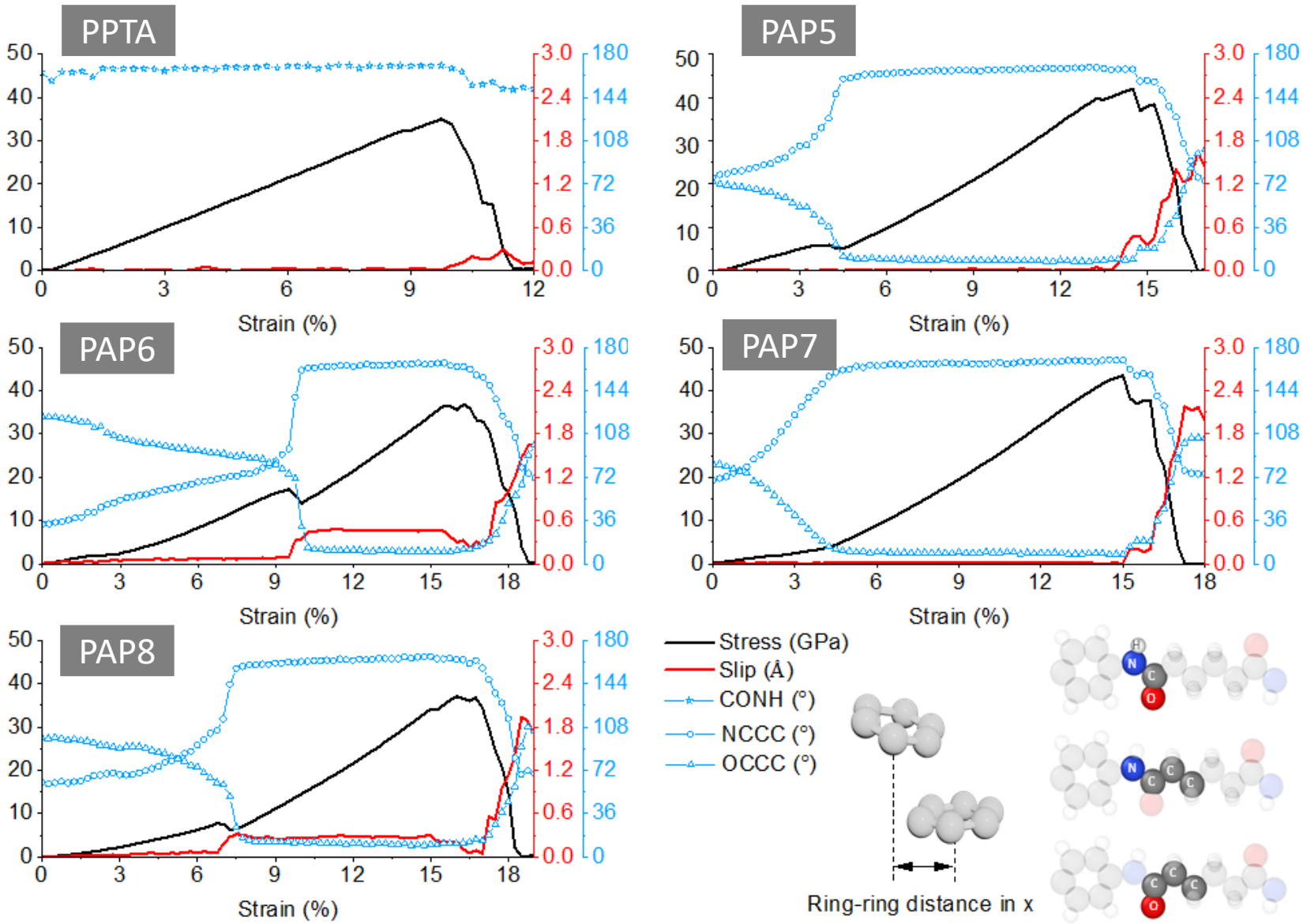


PAP8

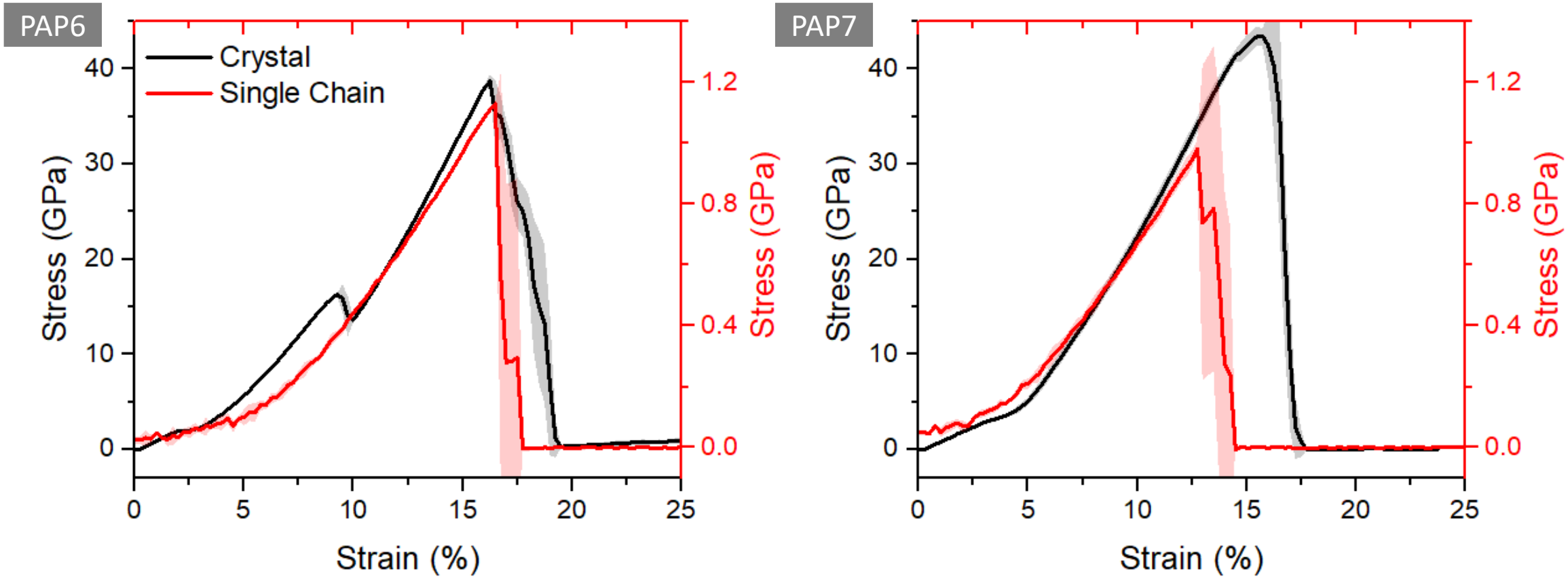




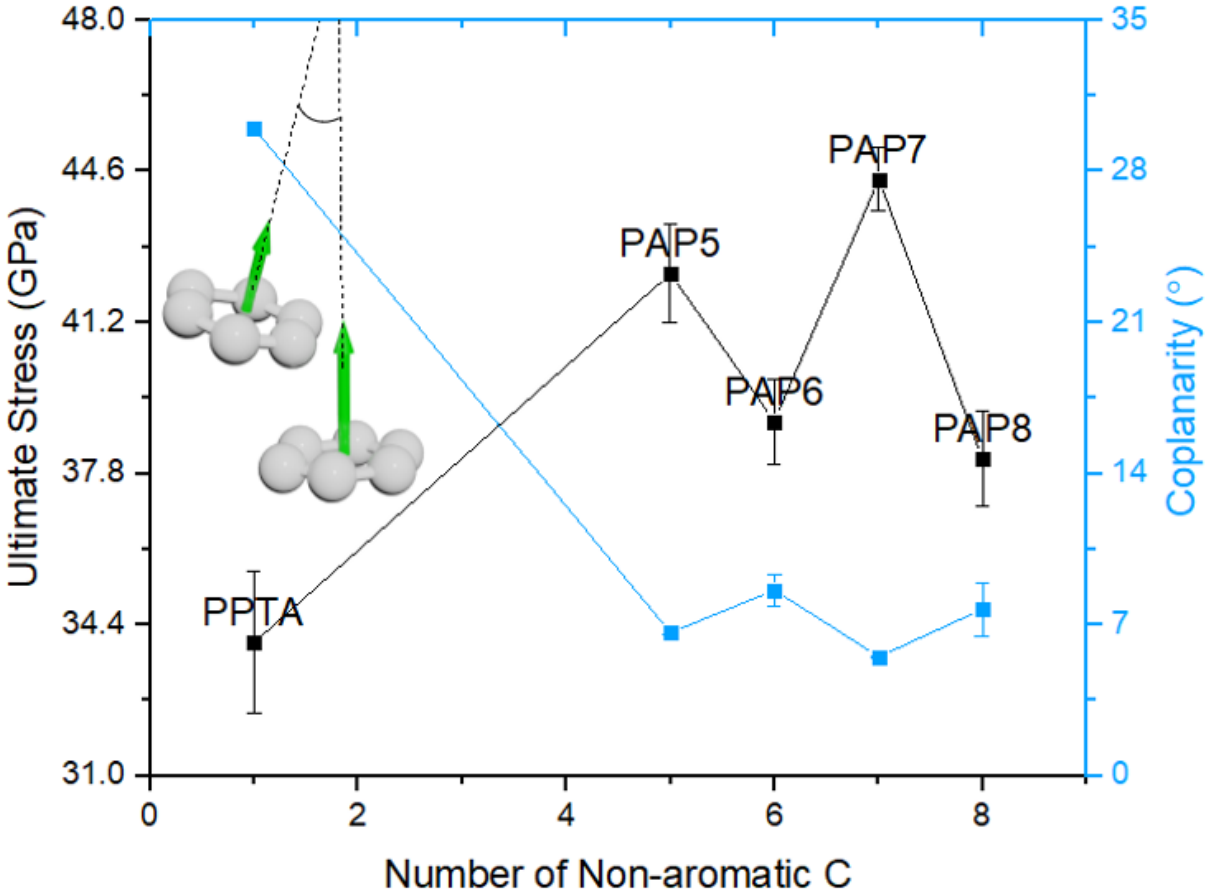
- The gradual increase in stiffness exhibited by all polymers (except PPTA) correlates well with changes in the dihedral angles, indicating the low strain is accommodated by elongation/rotation of wavy chains
- The sharp transition exhibited by PAP6 and PAP8 correlates with intra chain slip, quantified by ring-ring distance
- These even polymers slip because they have the less stable trapezoidal structure



- Both single chain and crystals exhibit lower stiffness at low strain than high strain and a gradual increase in stiffness around 5% strain; this indicates the behavior is due to intrachain processes
- For the PAP6 crystal only, there is a sharp transition from low to high strain behavior observed around 10% strain
- This suggests there are odd-even effects and that they are due to interchain processes

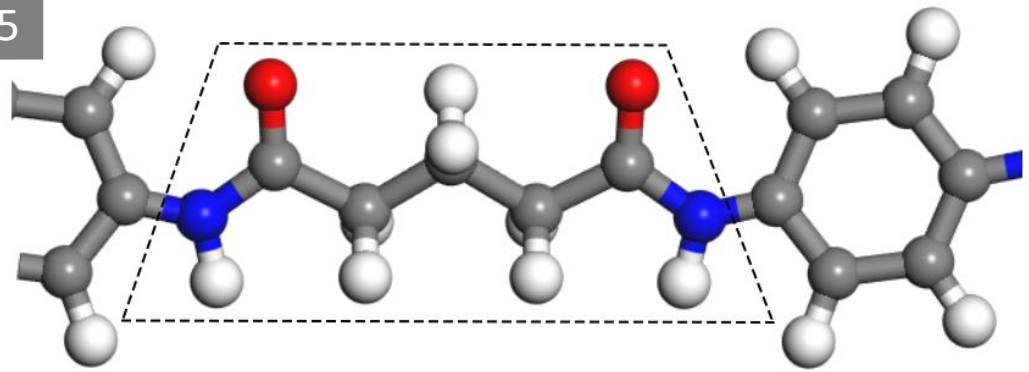


- The ultimate stress exhibits odd-even behavior where odd numbers of carbon atoms have larger strength
- Since the chains are extended at this point, and Spence showed the bond strength is the same for all polymers using DFT, this must be an interchain effect
- Interchain strength is determined by the coplanarity of the rings, quantified by ring-ring angle, which is lower (more aligned rings) for the polymers with odd numbers of carbon atoms, explaining their strength

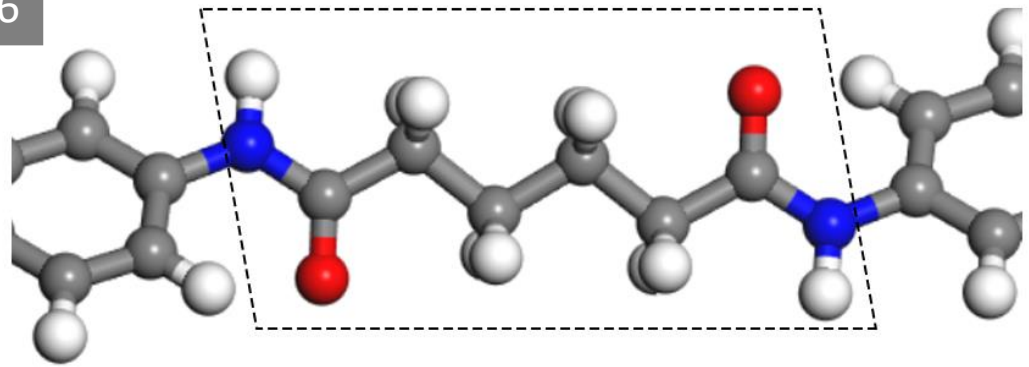


- Representative snapshots of trapezoidal and parallelogrammatic structures in the backbones of odd (PAP5) and even (PAP6) polymers.

PAP5

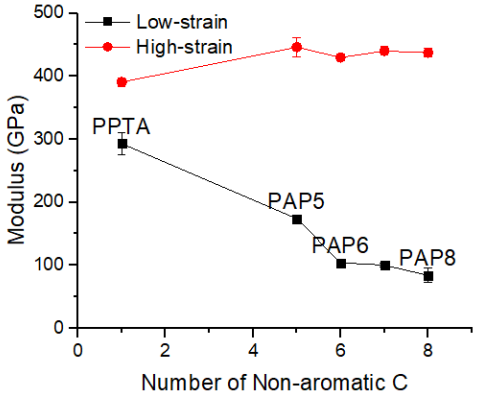


PAP6

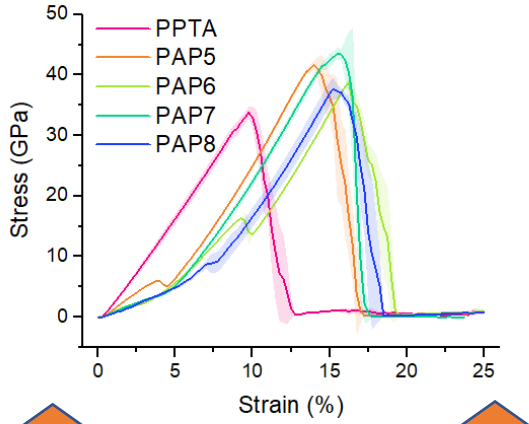


- It is an important origin of odd-even effect

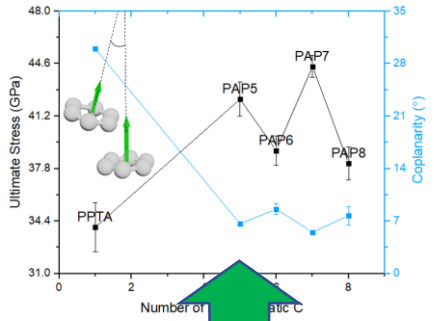
Modulus



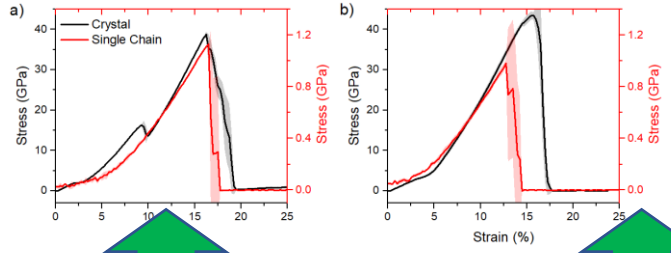
Transition



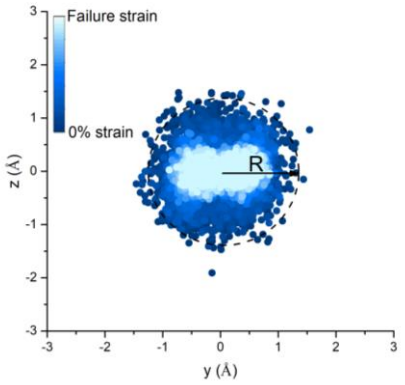
Ultimate Stress



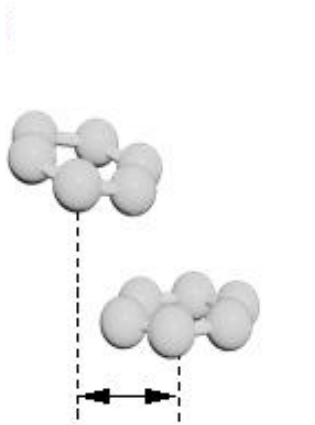
Intermolecular interactions



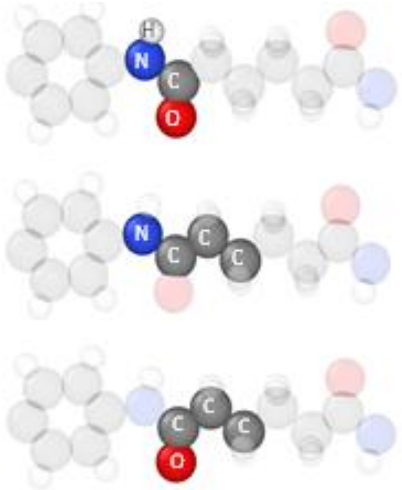
Waviness



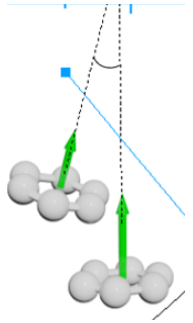
Slip



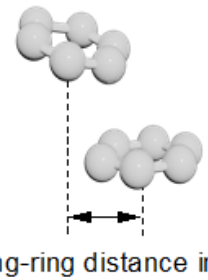
Rotation



Ring-ring coplanarity



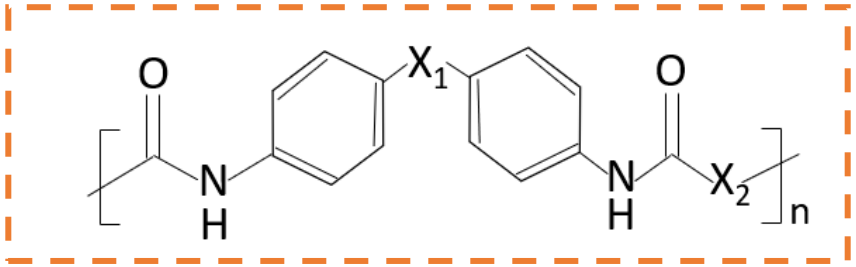
Slip

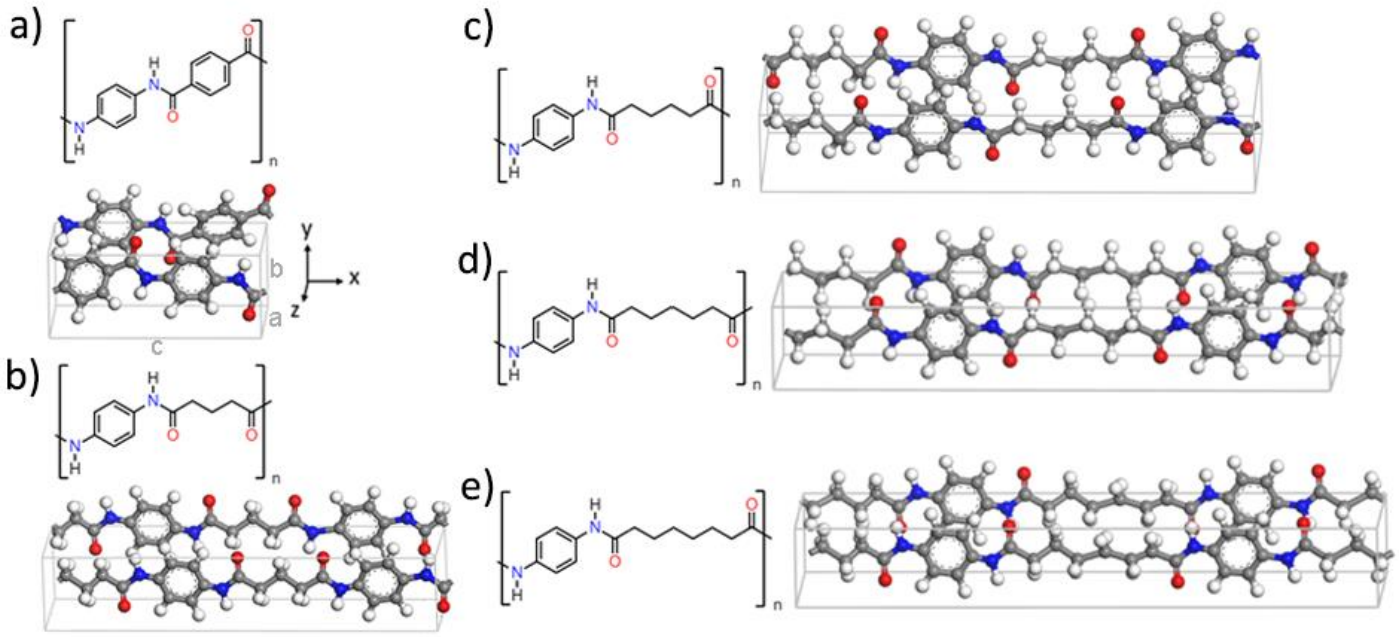


Proposed Work

Examples of polyamides

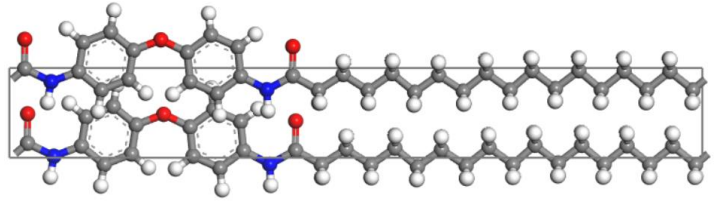
- All can be written as a formular:



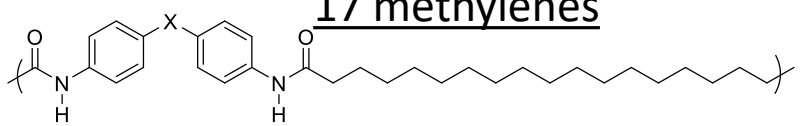


Macromolecules 49.3 (2016): 950-962.

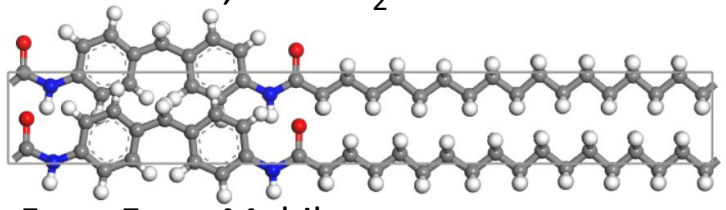
h2-PAP-16, X = O



17 methylenes

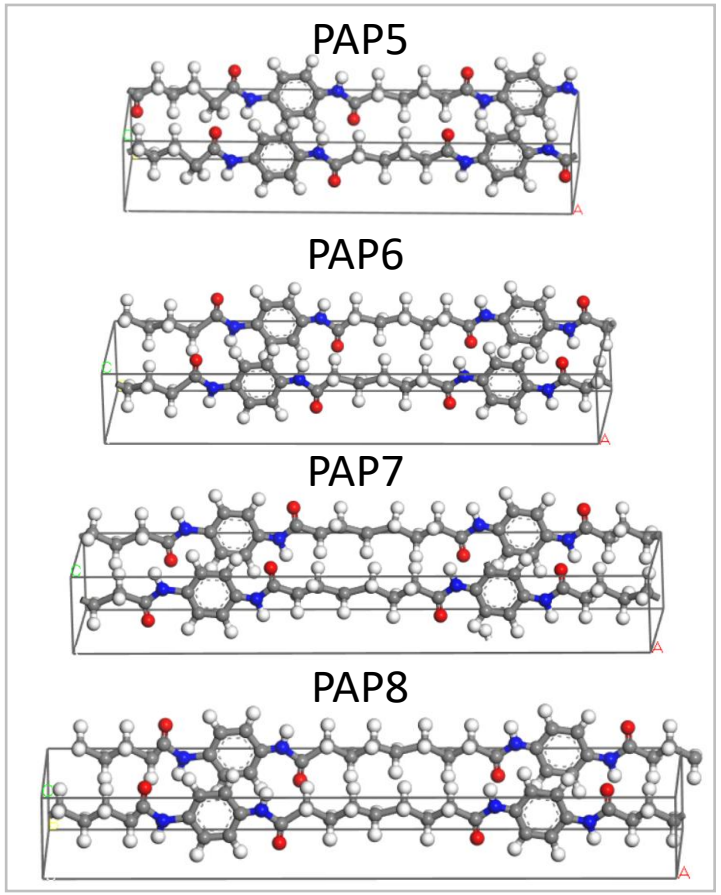


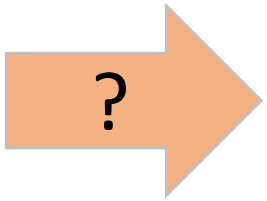
h2-PAP-23, X = CH_2

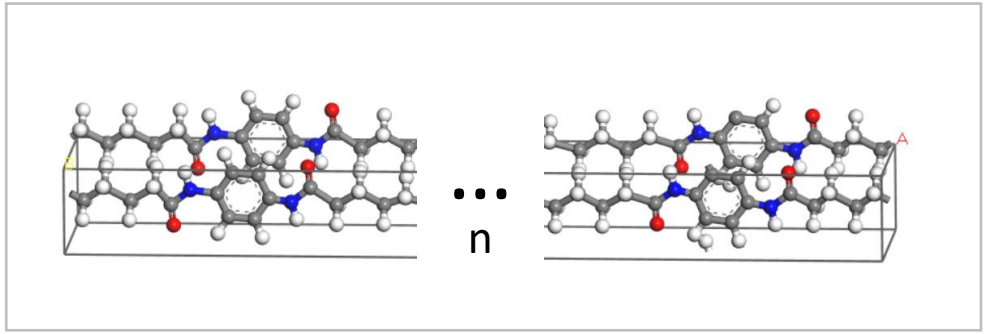


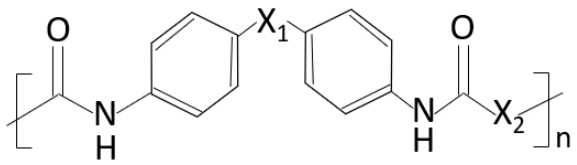
From ExxonMobil

- From our preliminary results, we have seen that increasing aliphatic chain length can increase waviness of polyamides at equilibrium
- This results in a smaller low-strain modulus and higher failure strain for polyamides with longer aliphatic chains
- This is what we observed from increasing the chain from three to
- However, what if the length of the aliphatic chain keeps increasing? Is it still true?

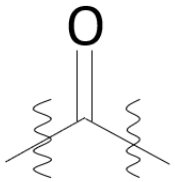
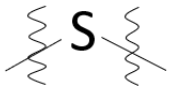
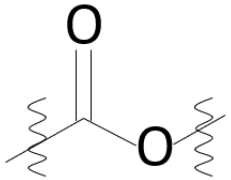
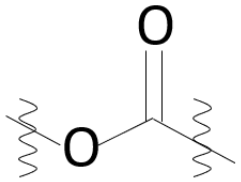
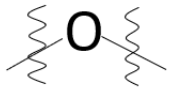
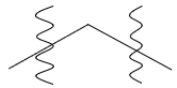


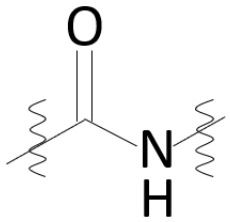
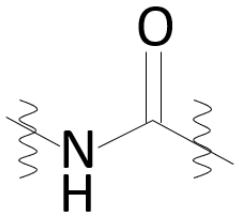
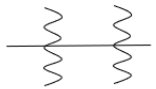
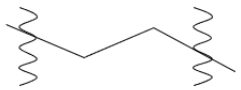
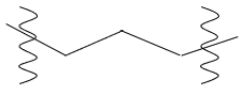
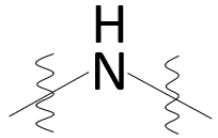


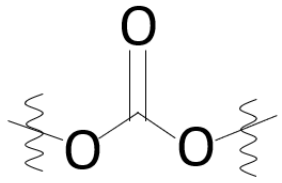
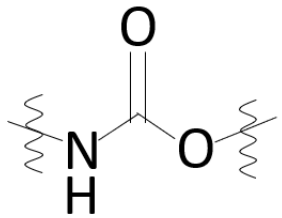
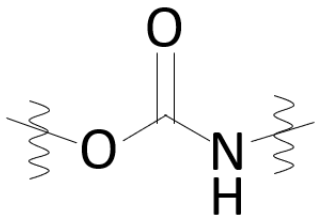
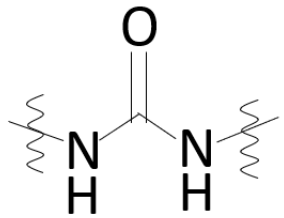
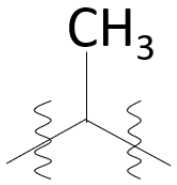
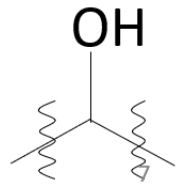




Functional Groups:

hPAP-2	hPAP-12	hPAP-14	hPAP-14-f	hPAP-16	hPAP-23
					

hPAP-idx1	hPAP-idx1-f	hPAP-biphenyl	hPAP-Et	hPAP-Pr	hPAP-NH
					

hPAP-carbonate	hPAP-urethane	hPAP-urethane-f	hPAP-urea	hPAP-X6	hPAP-X7
					

Proposed work >> Machine Learning

Polyamide Information

- Molecular weight?
- # of atoms?
- Bonds?
- Chain length?

input

Machine Learning

output

Mechanical Properties

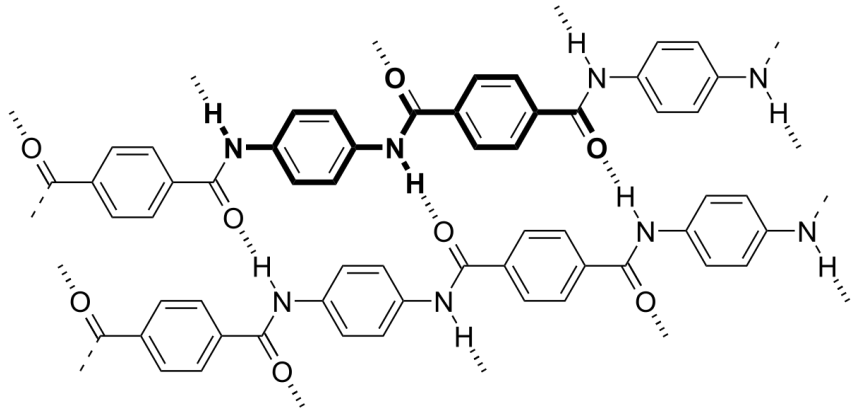
- Low-strain modulus
- High-strain modulus
- Ultimate strain
- Ultimate stress

ML Models

- Linear Regression
- Polynomial Regression
- Artificial Neural network (ANN)
- Support Vector Machines (SVM)
- Deep Learning

Thank you!

Q&A

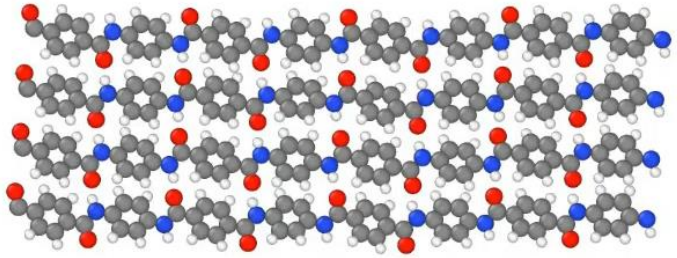


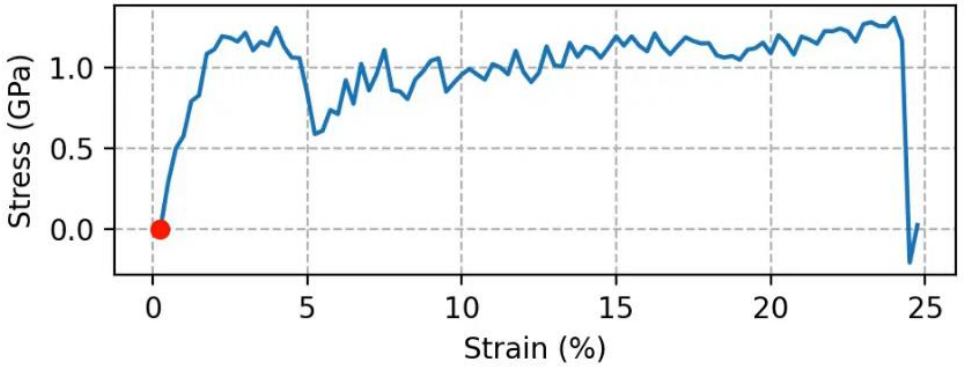
Appendix

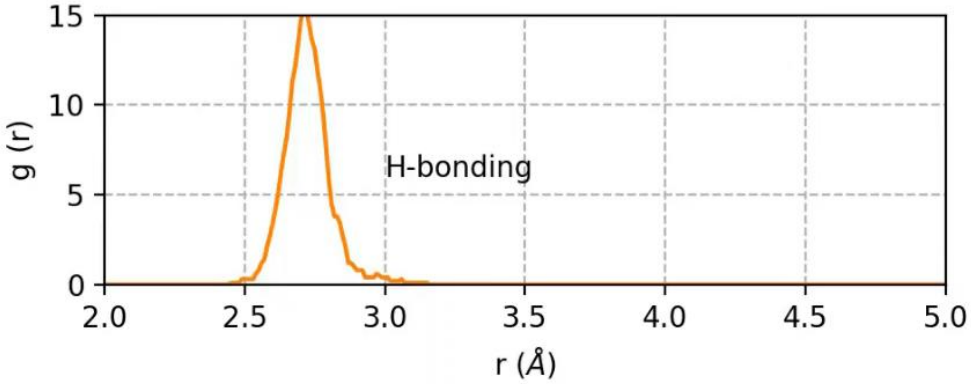
H-bond

Chain

Pi-Pi



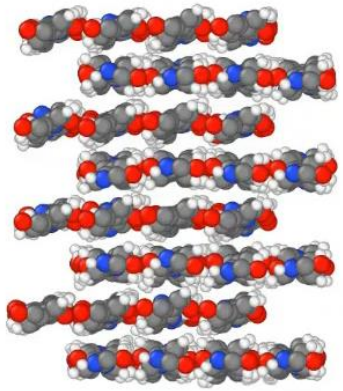


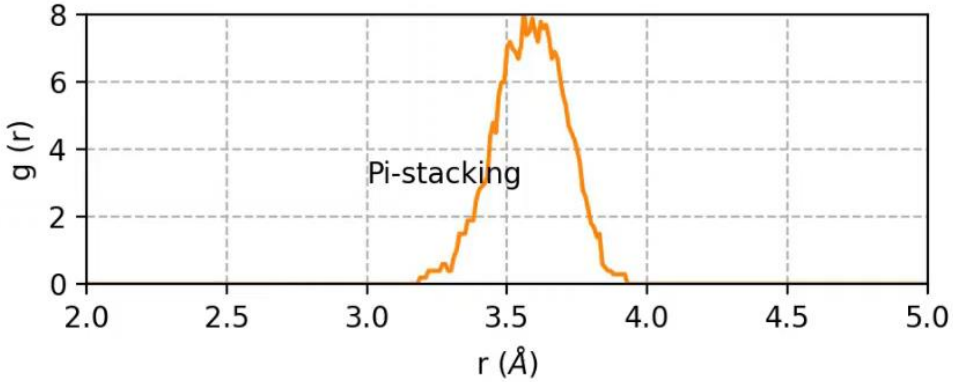


Pi-Pi

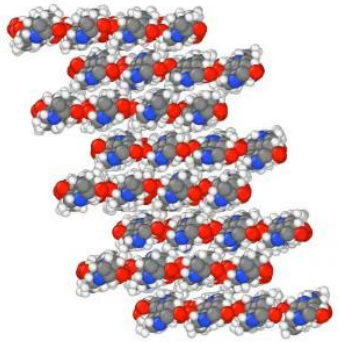
Chain

H-bond





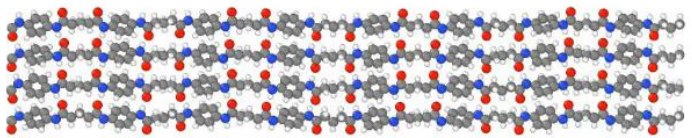
- Only part of the model is shown to reflet the detailed changes in structure



H-bond

Chain

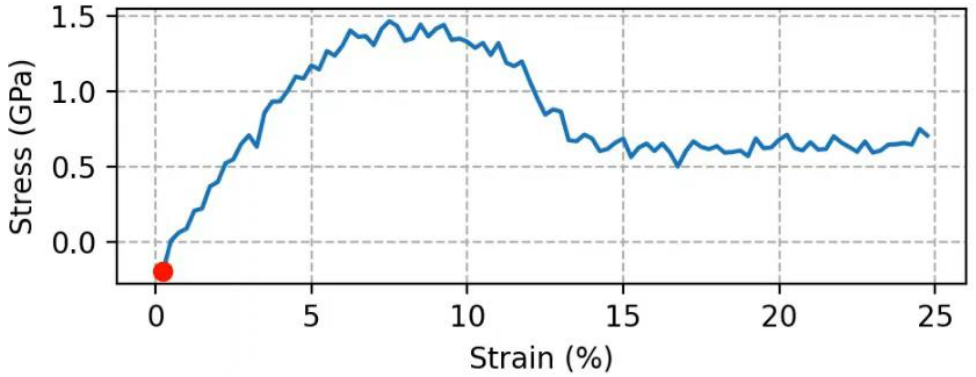
Pi-Pi

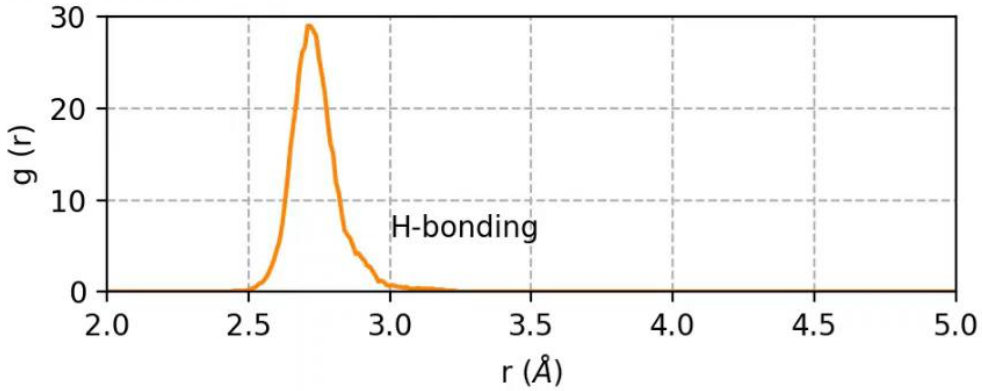


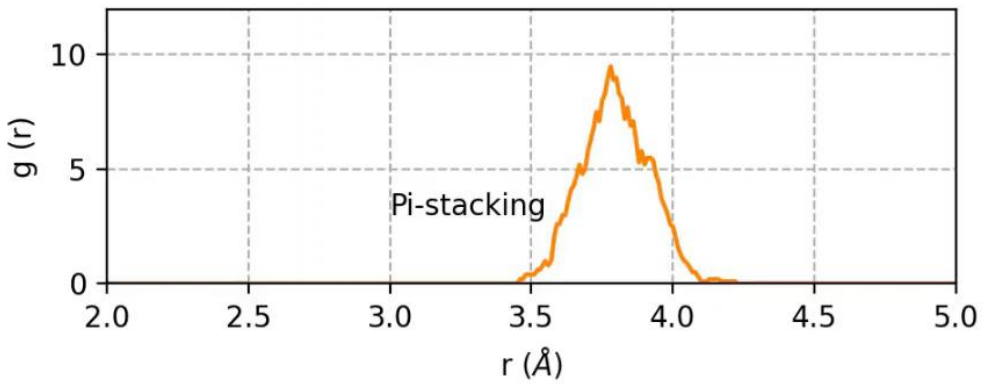
Pi-Pi

Chain

H-bond

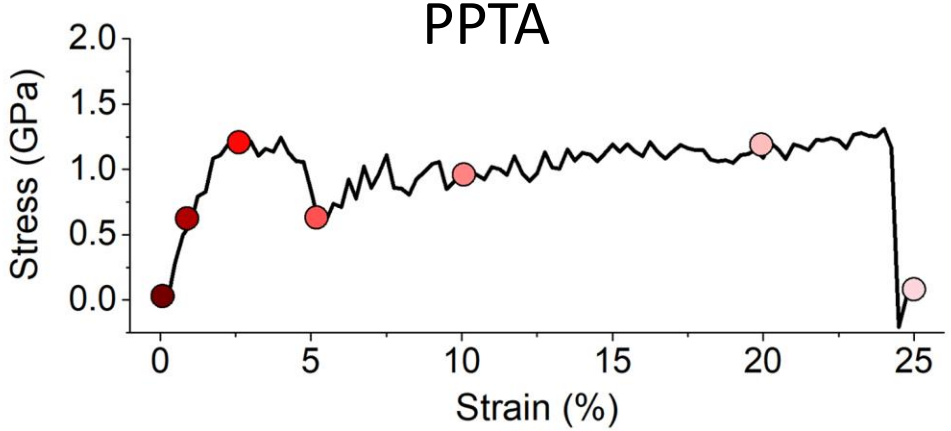




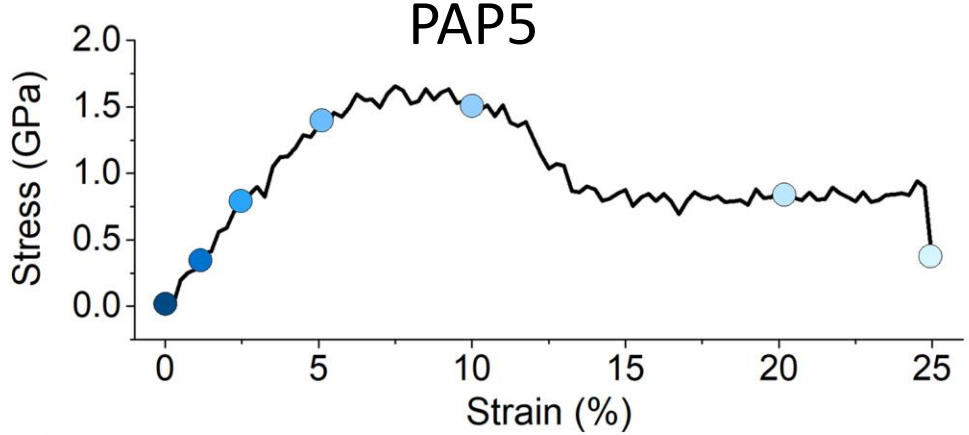


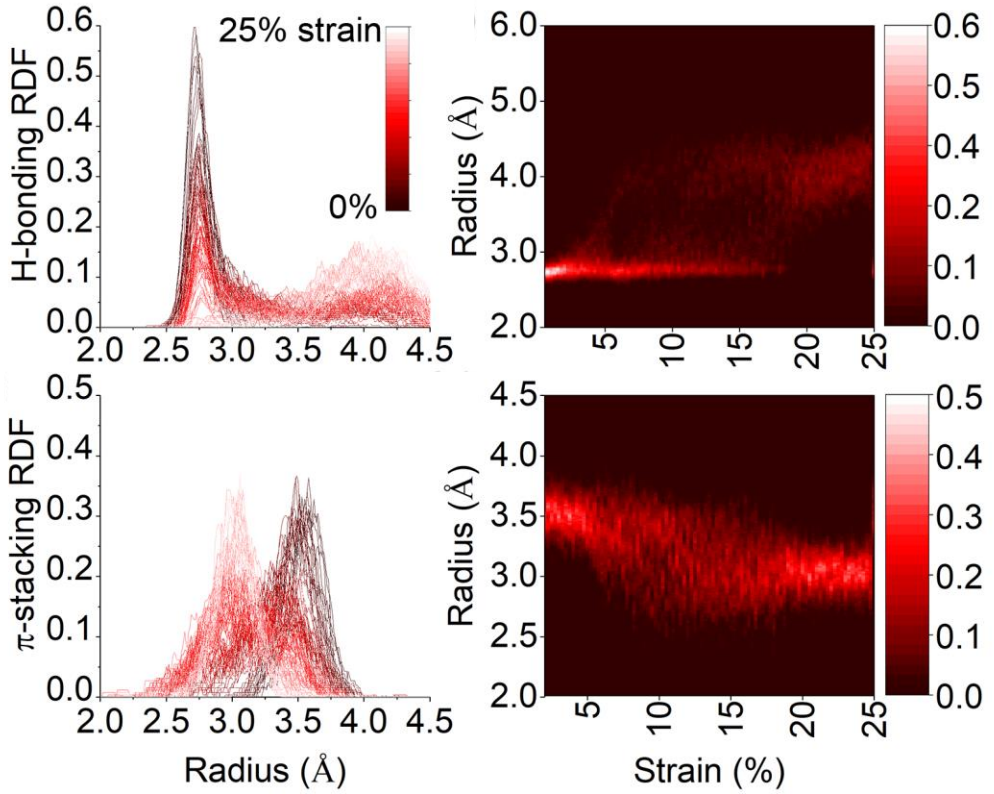
- Only part of the model is shown to reflet the detailed changes in structure

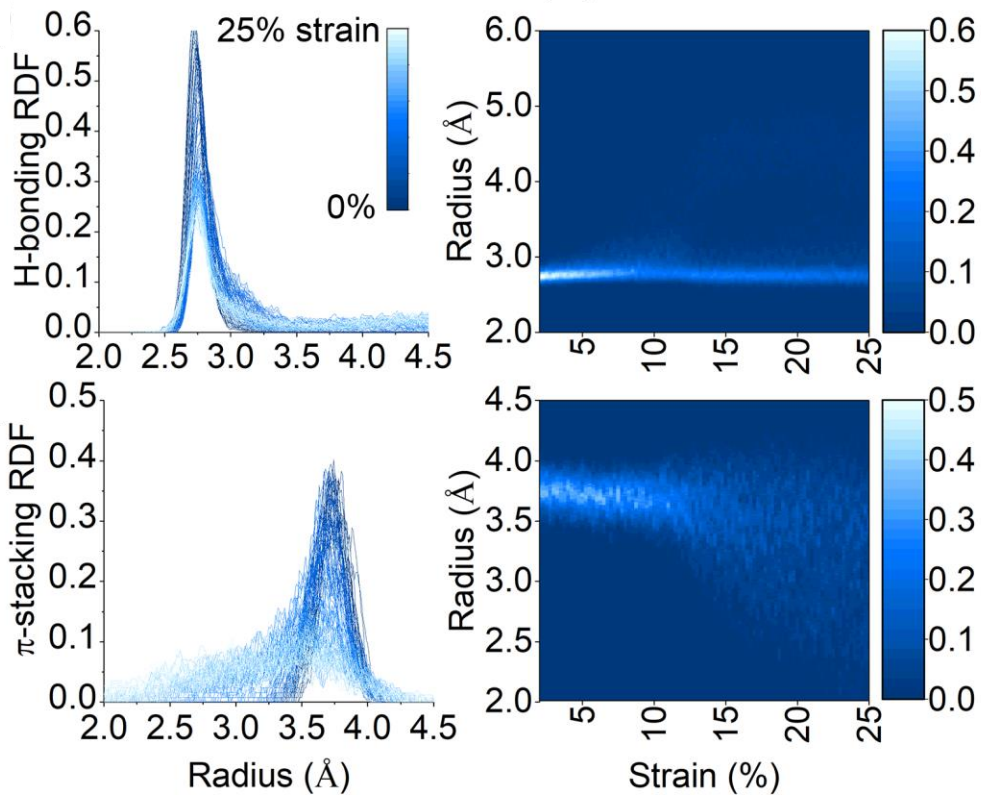
PPTA

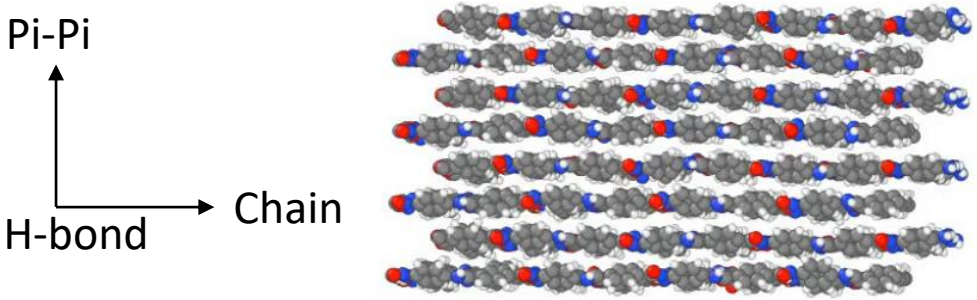

Stress (GPa)
Strain (%)

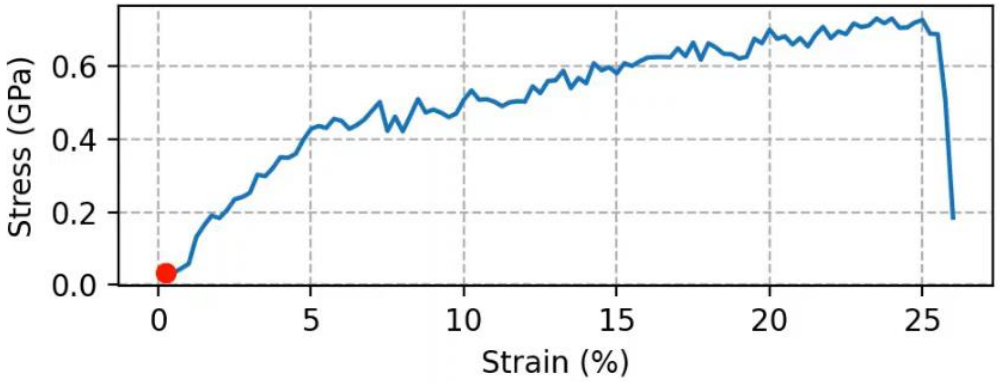
PAP5

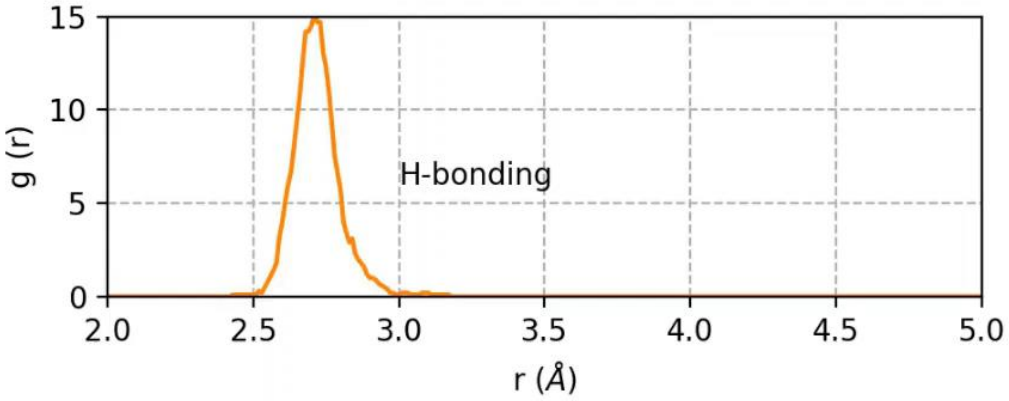

Stress (GPa)
Strain (%)

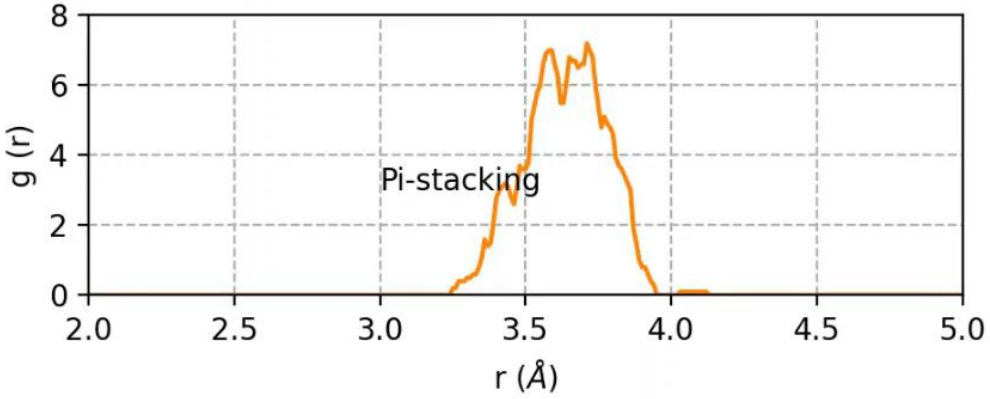

H-bonding RDF
25% strain
0%
Radius (Å)
π-stacking RDF
Radius (Å)
Strain (%)

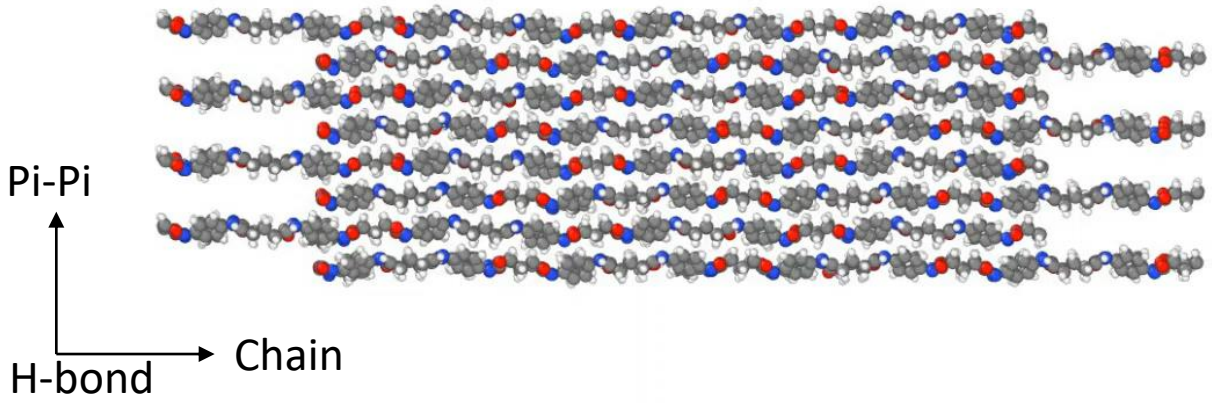

H-bonding RDF
25% strain
0%
Radius (Å)
π-stacking RDF
Radius (Å)
Strain (%)

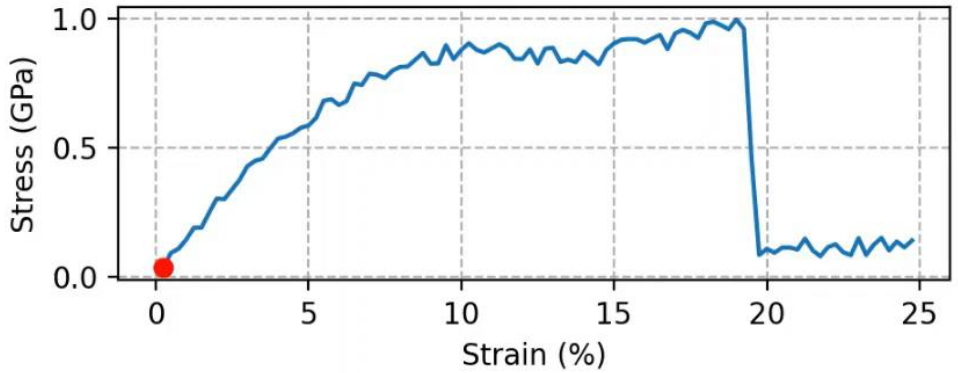

Pi-Pi
Chain
H-bond

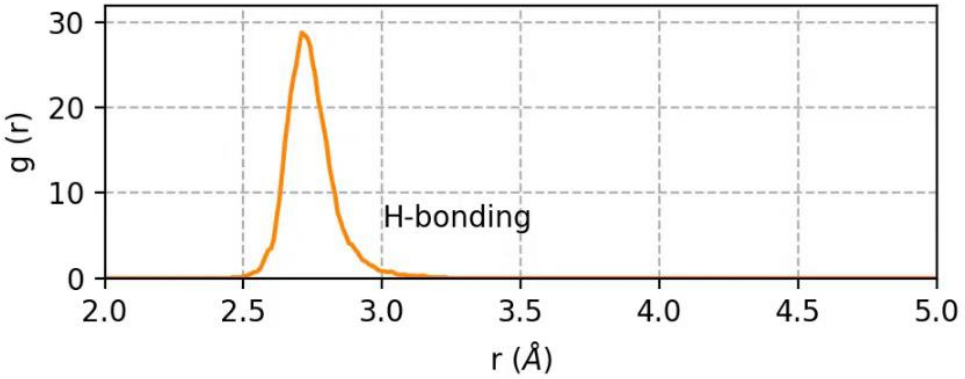

Stress (GPa)
0.0
0.2
0.4
0.6
0
5
10
15
20
25
Strain (%)

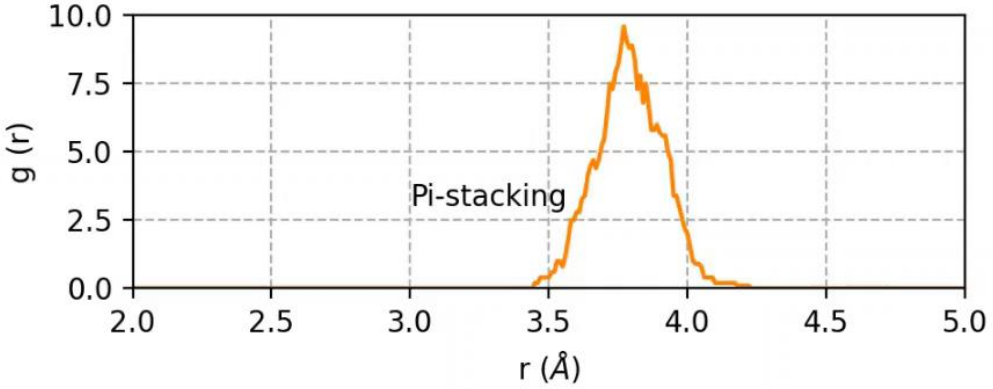

g (r)
0
5
10
15
H-bonding
2.0
2.5
3.0
3.5
4.0
4.5
5.0
r (Å)


g (r)
0
2
4
6
8
Pi-stacking
2.0
2.5
3.0
3.5
4.0
4.5
5.0
r (Å)

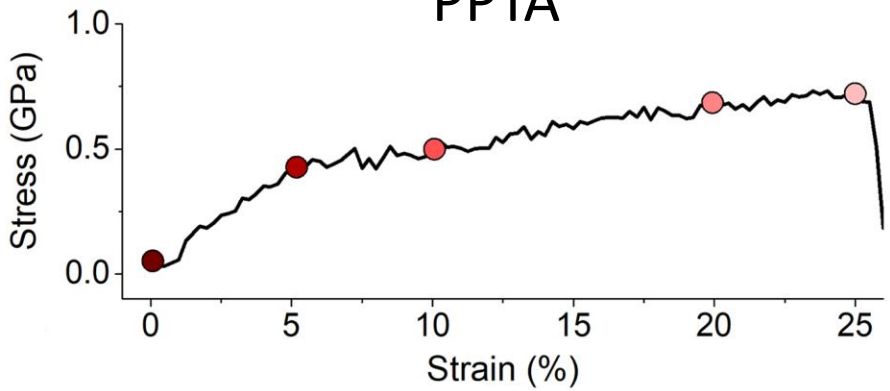

Pi-Pi
Chain
H-bond


Stress (GPa)
Strain (%)
1.0
0.5
0.0
0
5
10
15
20
25

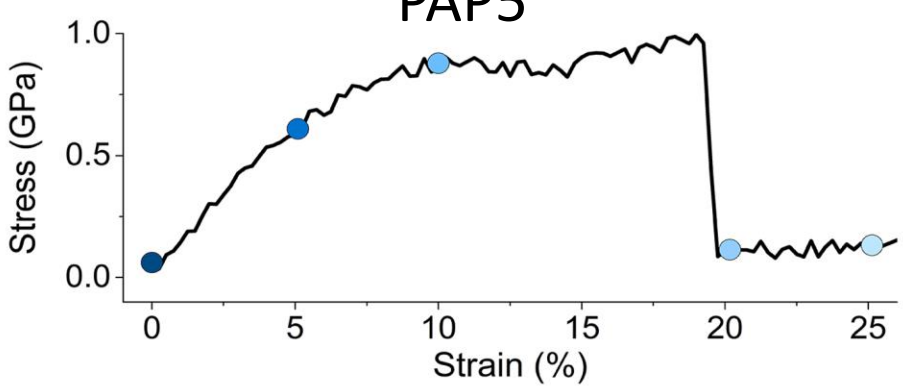

g (r)
r (Å)
H-bonding
30
20
10
0
2.0
2.5
3.0
3.5
4.0
4.5
5.0

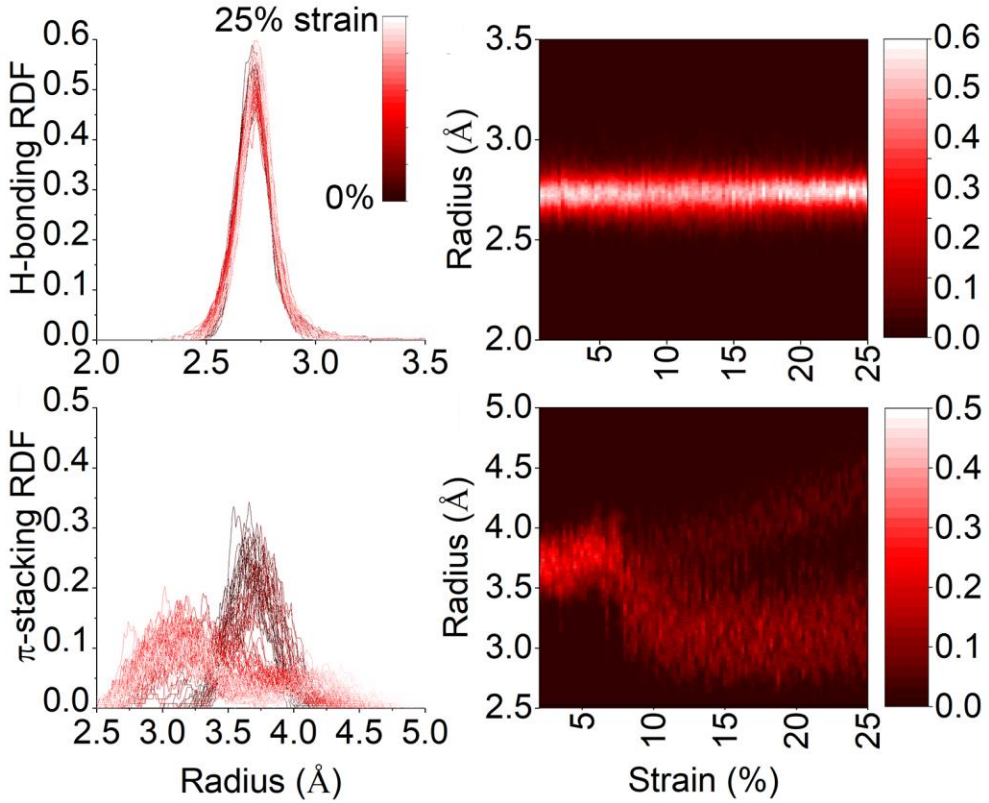

g (r)
r (Å)
Pi-stacking
10.0
7.5
5.0
2.5
0.0
2.0
2.5
3.0
3.5
4.0
4.5
5.0

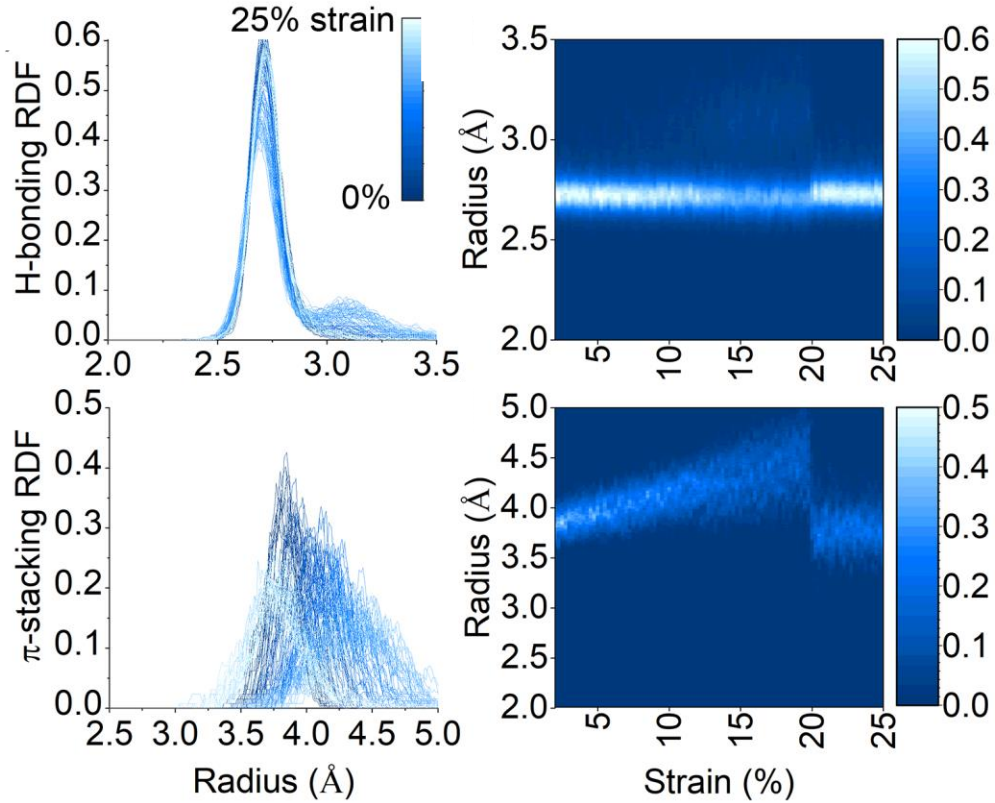
PPTA


Stress (GPa)
Strain (%)

PAP5


Stress (GPa)
Strain (%)


25% strain
0%
H-bonding RDF
Radius (Å)
π-stacking RDF
Radius (Å)
Strain (%)


25% strain
0%
H-bonding RDF
Radius (Å)
π-stacking RDF
Radius (Å)
Strain (%)