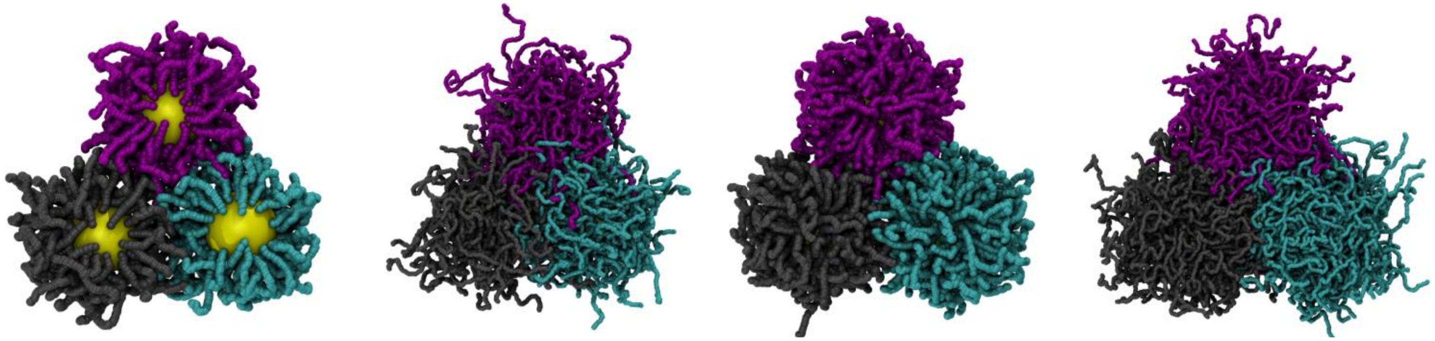


Coarse-Grained Simulations of Polymer-Grafted Nanoparticle Monolayers

Lisa M. Hall

The Ohio State University

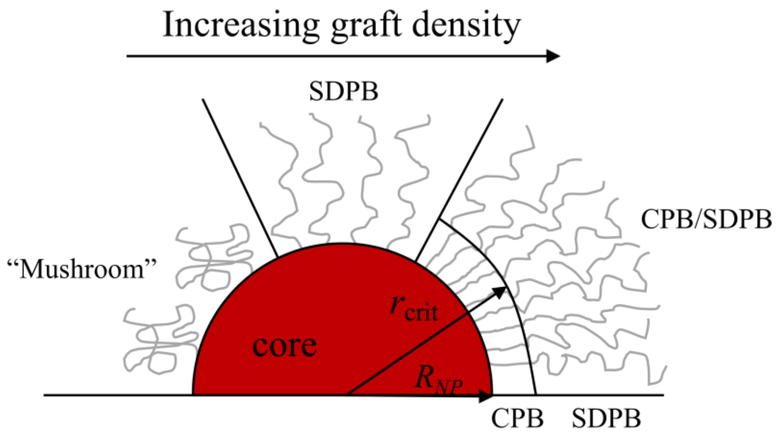
Polymer-Grafted Nanoparticles (PGNs)

Traditional Polymer Nanocomposites

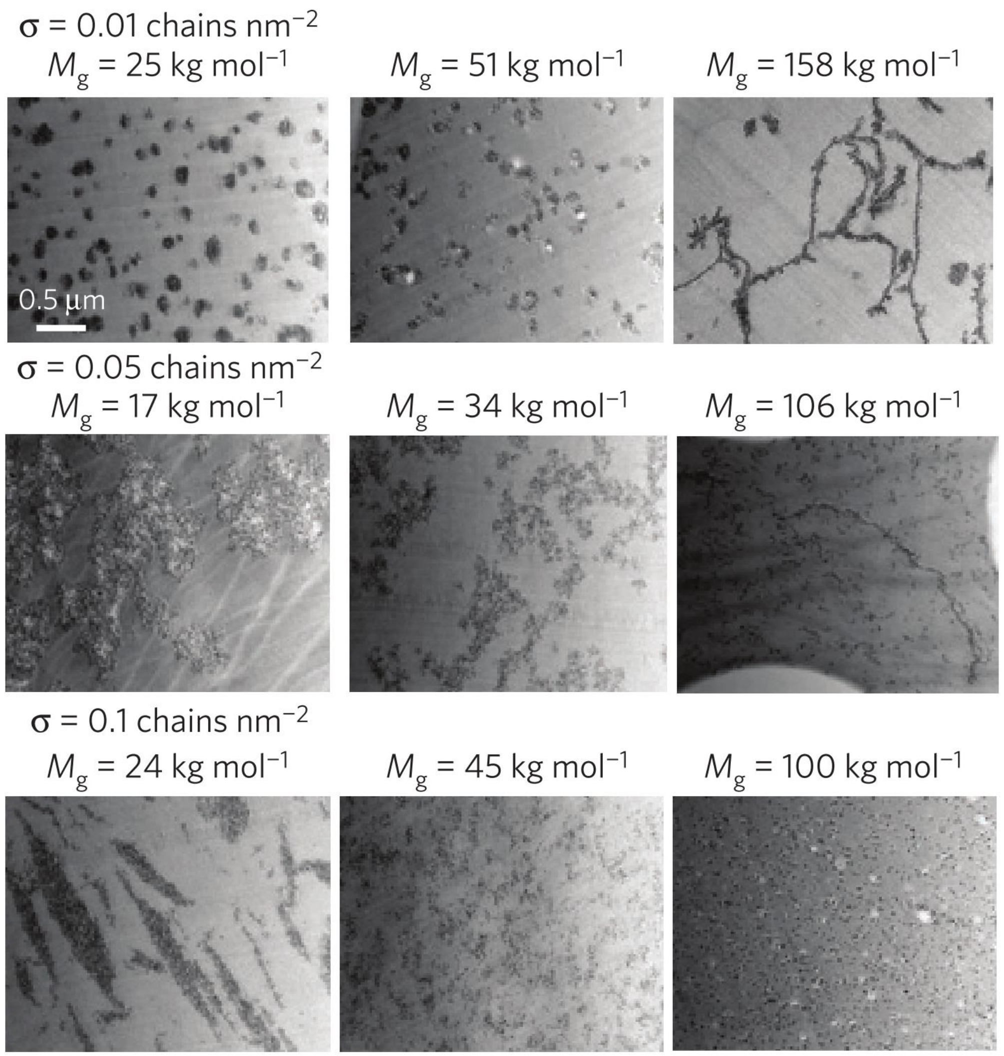
- ❑ Inorganic nanoparticle (NP) fillers often added to polymer matrices to enhance optical, electrical, and mechanical properties
- ❑ Key challenges: controlling and predicting particle dispersion

Polymer-Grafted Nanoparticles (PGNs)

- ❑ Can improve dispersion in composites
- ❑ Can be **<u>used neat</u>** (our focus; cannot demix macroscopically)
- ❑ Polymer conformation modified by constraint of NP surface



Ohno *et. al. Macromolecules* **2007,** *40,* 9143-9150

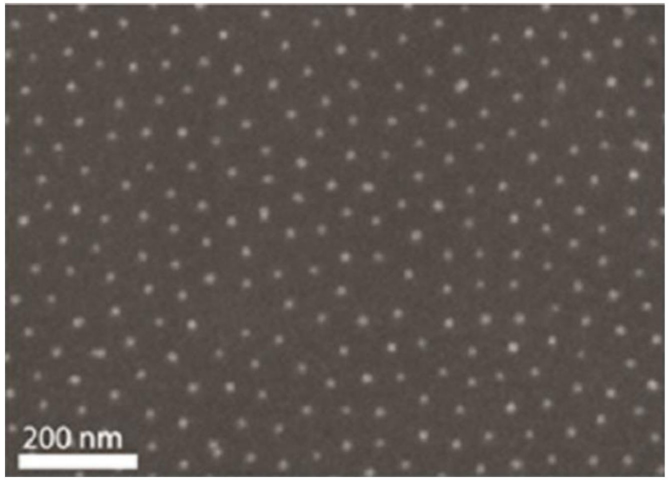


Akcora, Liu, Kumar, *et al. Nature Materials*, **2009**, *8*, 354-359

Polymer-Grafted Nanoparticle (PGN) Assemblies

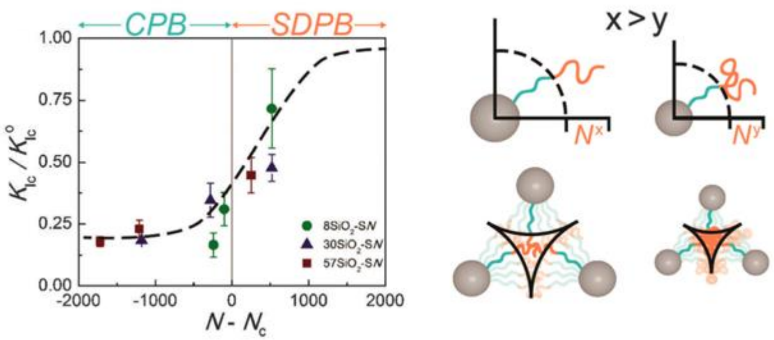
- Structure depends on NP size, graft density, chain length

- On surfaces, NPs can form hexagonal arrays



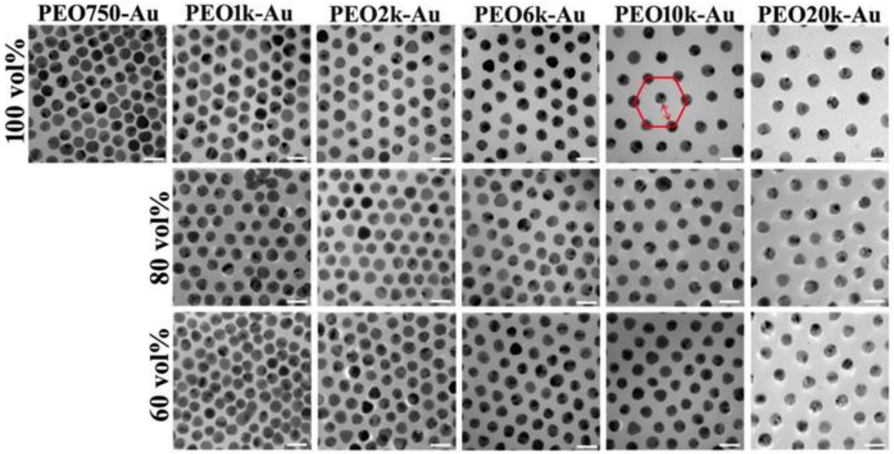
Che, Park, Grabowski, *et al*., *Macromolecules*, **2016**, *49*, 1834–1847

Toughness changes with graft length



Schmitt, Michael, *et al. Soft Matter* **2016**, 12, 3527-3537

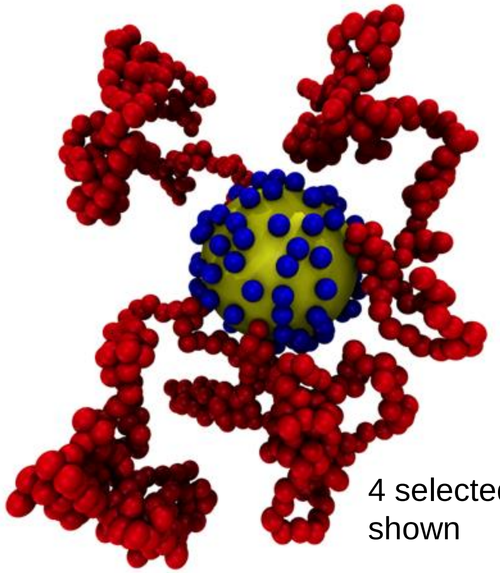
Particle spacing changes with graft length



Yang, Guang, *et al. Macromolecular Chemistry and Physics* **2018**, 1700417

Molecular Dynamics Simulations

- Coarse-grained bead-spring chains
- Randomly grafted to spherical nanoparticle
- LJ units (monomer diameter=1σ)



4 selected grafts shown

Bonds:
Finitely Extensible Nonlinear Elastic (FENE)

$$u = -kR_0^2 \ln\left(1 - \left(r / R_0\right)^2\right)$$

Monomer-monomer interactions:
Lennard-Jones (LJ) potential

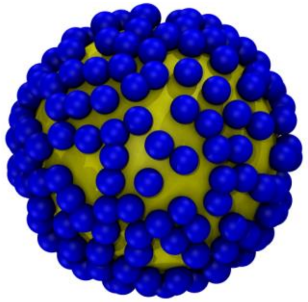
$$U_{LJ}\left(r\right) = 4e_{ij}\left[\left(\frac{s}{r}\right)^{12} - \left(\frac{s}{r}\right)^{6}\right]$$ cut off at $r_c = 2.5$

NP-monomer interactions:

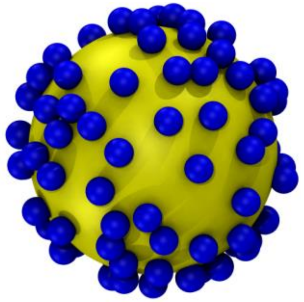
LJ with r shifted by 4.5 (particle diameter 10σ)

Wall-monomer interactions:
9-3 LJ potential

$$U_{LJ,W}\left(r\right) = e_{wp}\left[\frac{2}{15}\left(\frac{s}{r}\right)^{9} - \left(\frac{s}{r}\right)^{3}\right]$$



(0.6 chains/σ^2)



(0.3 chains/σ^2)

Systems Simulated

12 hexagonally packed polymer-grafted NPs

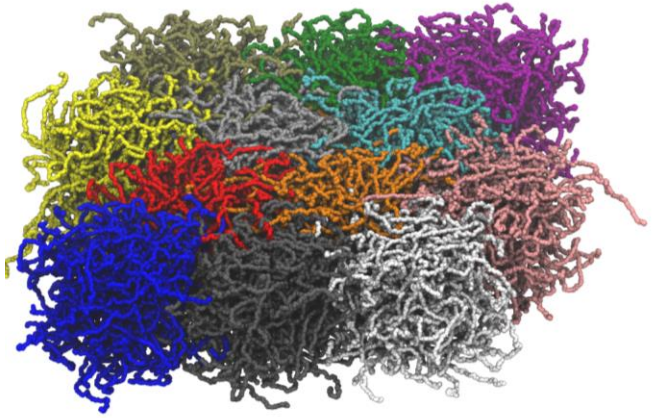
- ❑ 35 (unentangled) or 160 (entangled) beads/chain
- ❑ Graft density 0.3 – 0.6 chains/σ^2
- ❑ System names: PGN(graft density*10)-chain length

- ❑ Periodic in *x* and *y* directions, wall at *z* = 0
- ❑ $\varepsilon_{w\text{-}p}$ = 3.5 (stable monolayer)
- ❑ Equilibrate in melt state on surface

- ❑ (later) Cooled (glassy) films with wall removed

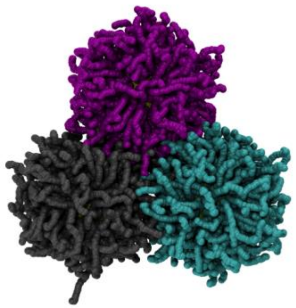
Homopolymer films (without NPs)

- ❑ Chain lengths *N* = 160, 240, and 320
- ❑ Area set to match thickness of PGN3-160 film

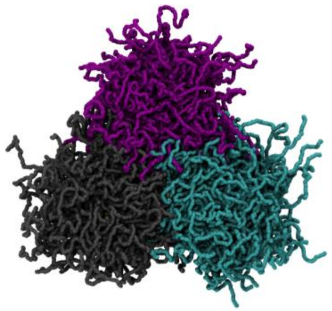


Tilted view, entire film

Time-averaged snapshots, unwrapped (grafted chain shown in same image as its nanoparticle)

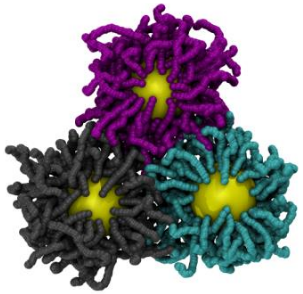


PGN6-35

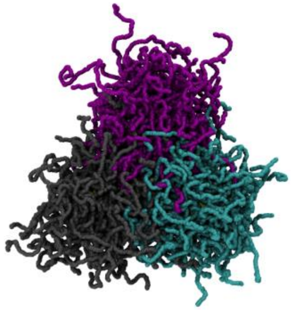


PGN6-160

Top view of three selected particles for various systems



PGN3-35



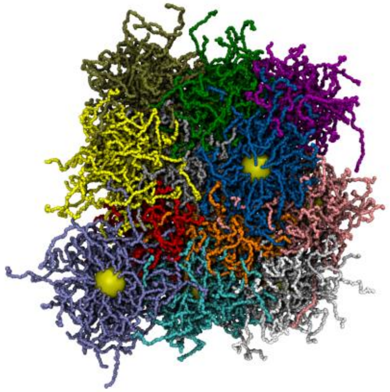
PGN3-160

Film Structure, N=160

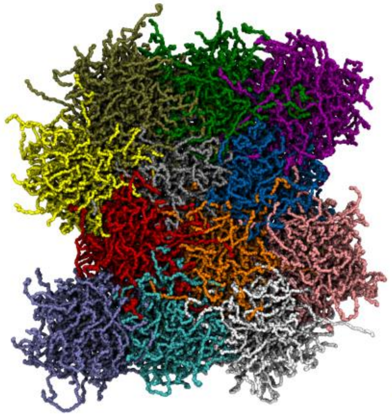
- ❑ Volume fraction effect: Higher graft density means larger spacing
- ❑ Degree of hexagonal ordering increases with graft density

Time-averaged snapshots, unwrapped (grafted chain shown in same image as its nanoparticle)

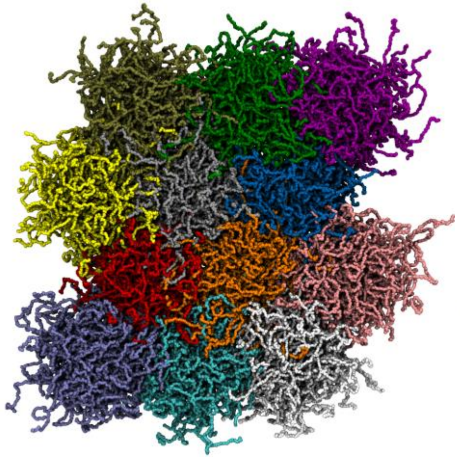
Averaging time 5500 τ



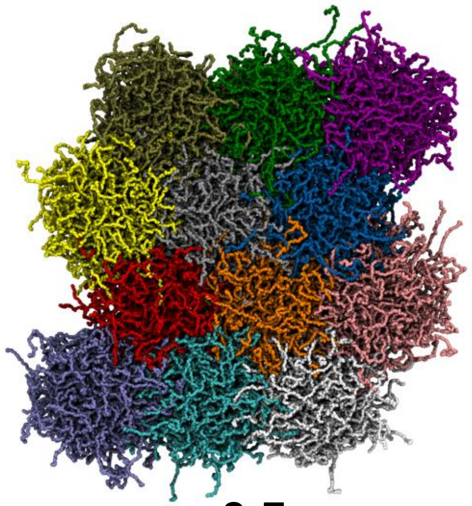
Graft density (chains/σ^2): 0.2



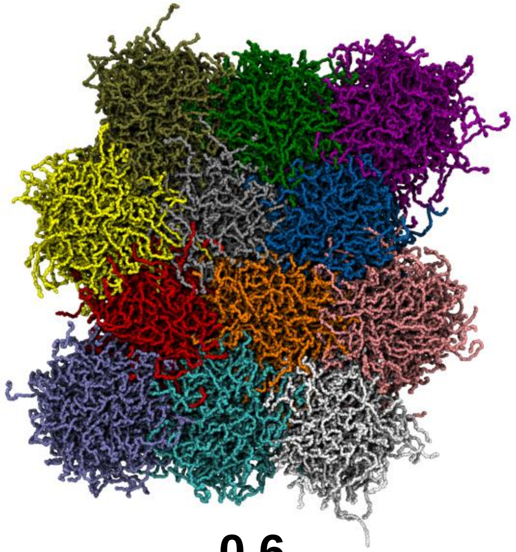
0.3



0.4



0.5

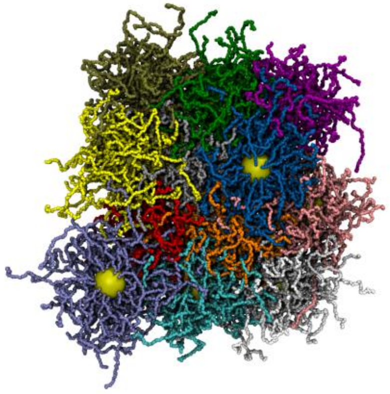


0.6

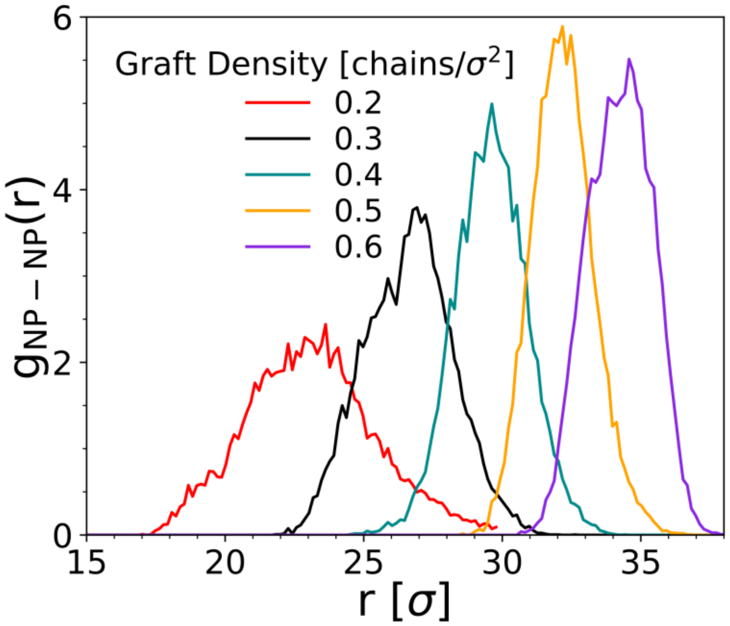
Film Structure, N=160

- Volume fraction effect: Higher graft density means larger spacing
- Degree of hexagonal ordering increases with graft density
- Increasing graft density decreases interpenetration

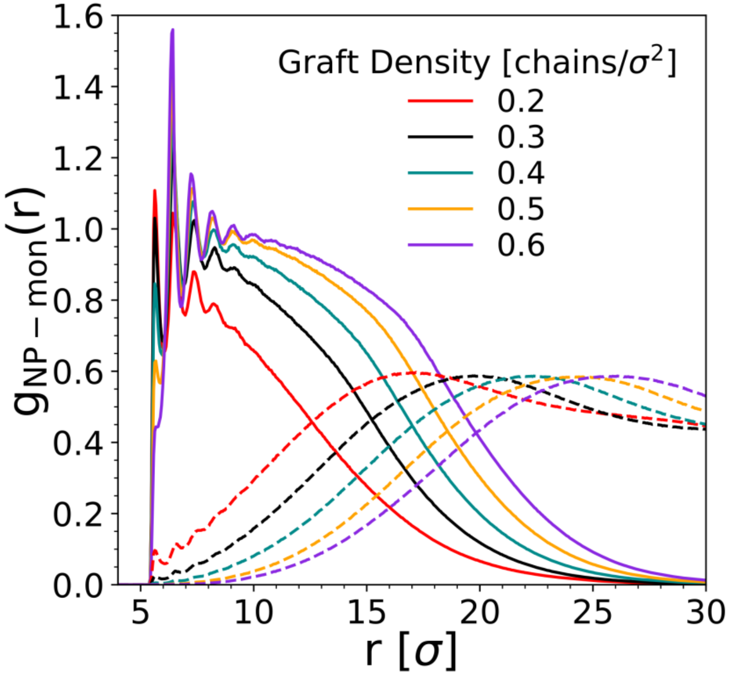
NP-NP pair correlation functions

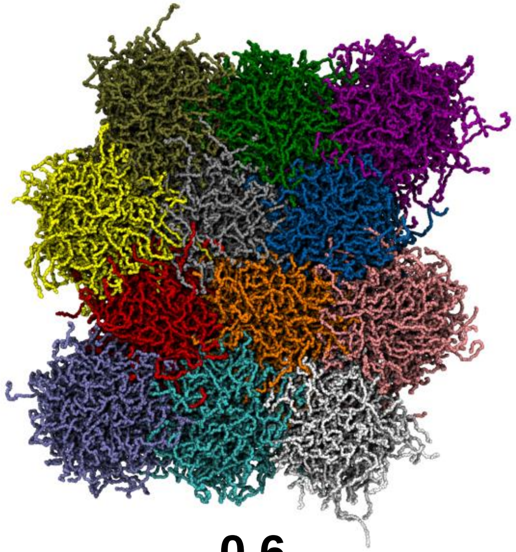


0.2



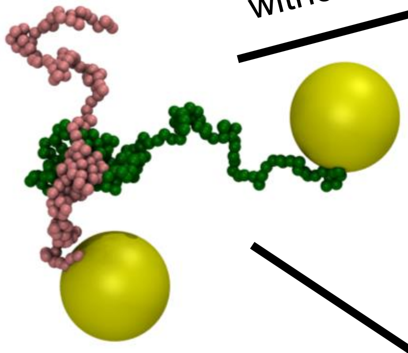
NP-monomer pair correlation functions
Solid lines: attached monomers
Dashed lines: other monomers





0.6

Entanglement Analysis (Two Types)

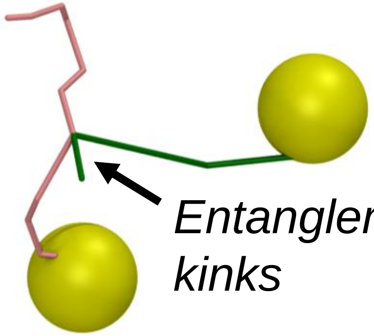


Instantaneous Coordinates

Iteratively straighten without crossing; Z1*

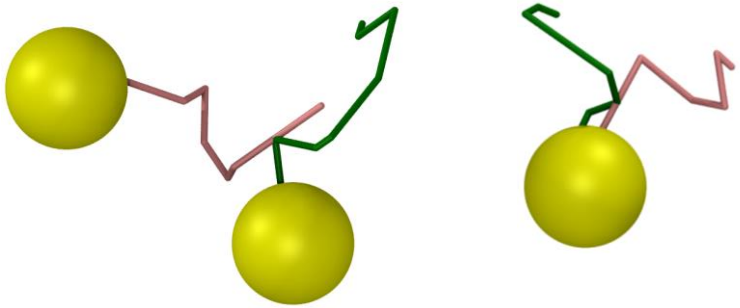
Time average

Primitive Paths

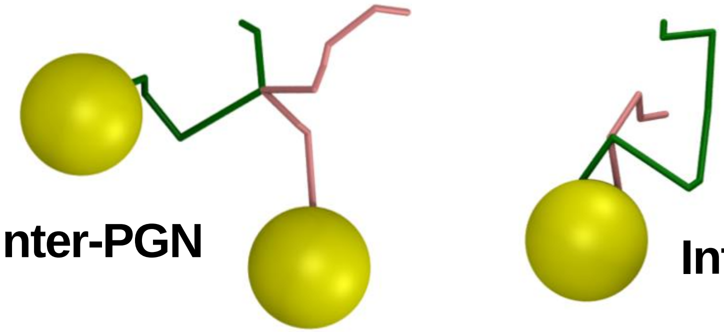


Entanglements: kinks

Single kink
kink forms against a straight region

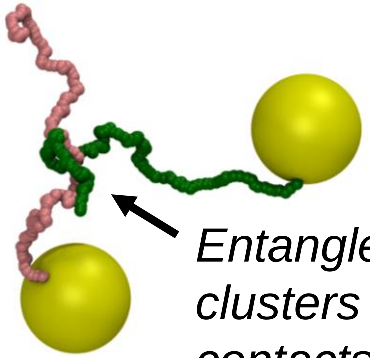


Double kink
chains both kink against each other



Inter-PGN **Intra-PGN**

Mean Paths



Entanglements: clusters of close contacts

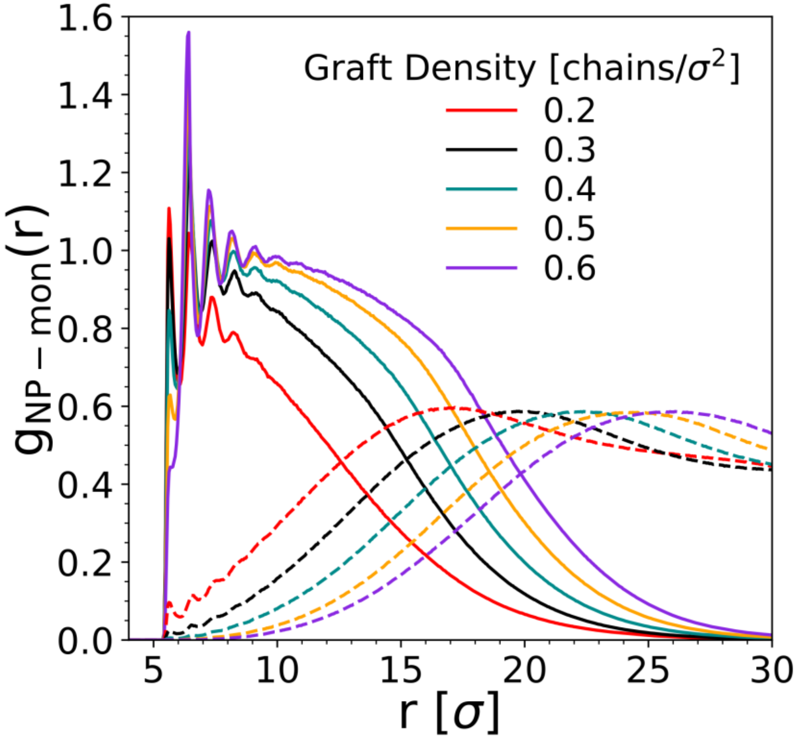
a la Likthman (*e.g. Macromolecules* **2008**, *41*, 6843-6853)

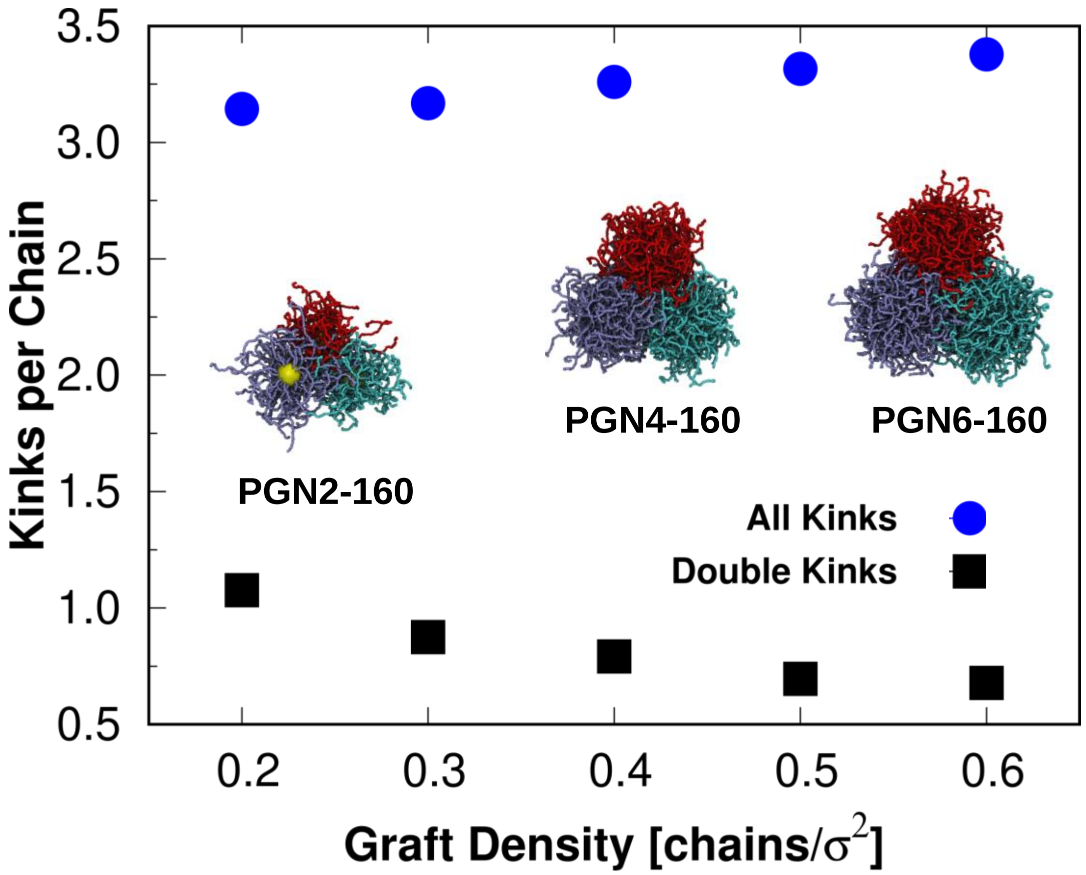
Longevity, strength analyzed by timescale of continuous contact and distance

Also of interest, isoconfigurational ensemble method: Cao, Qin, Milner *Macromolecules* **2015**, *48*, 99-110

Entanglements Per Chain

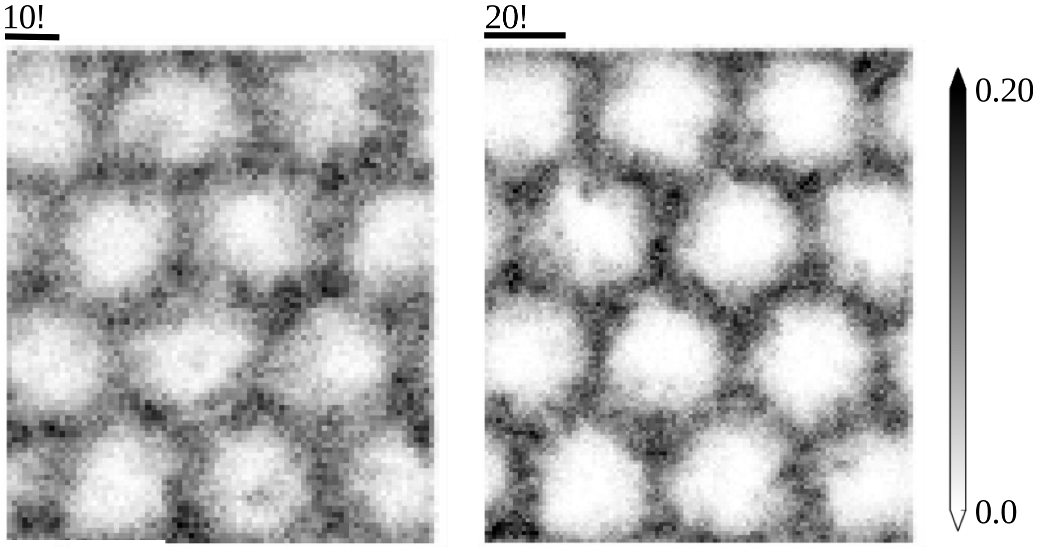
- ❑ Overall (mostly single) kinks per chain increase with graft density
- ❑ Double kinks per chain decrease with graft density

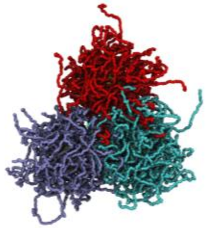




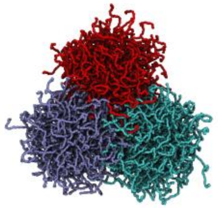
Entanglement Locations: Heat Maps

Interparticle double kinks: top view





PGN3-160
Moderate graft density

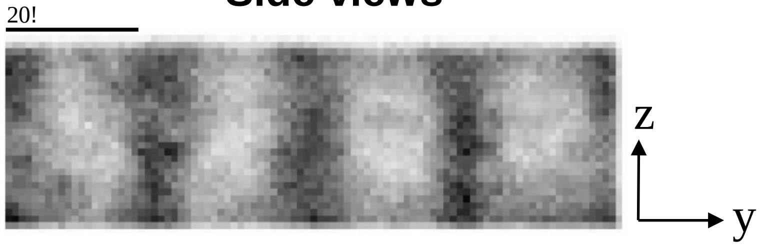


PGN6-160
High graft density

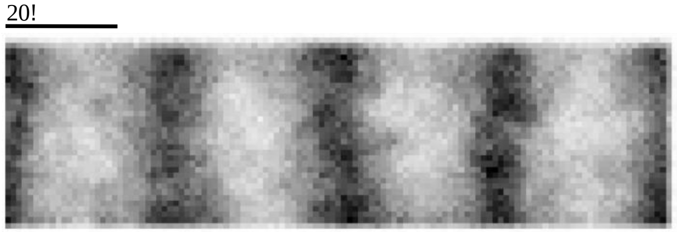
- ❑ Double kinks localized in interstitial areas at high graft density
- ❑ Lowering graft density increases entanglements above and below particles

Side views

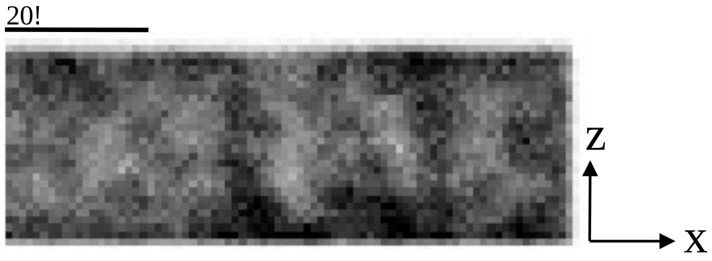
PGN3-160



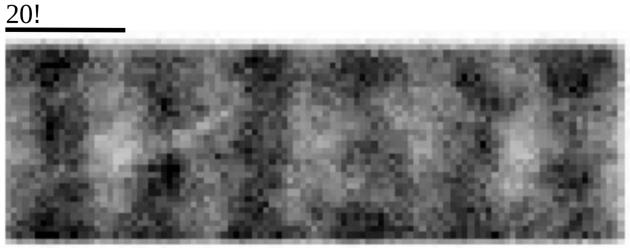
PGN6-160



PGN3-160



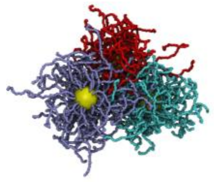
PGN6-160



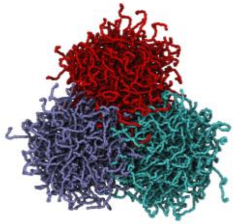
Ethier, Hall, *Macromolecules*, 2018, *51*, 9878–9889

Entanglement Locations

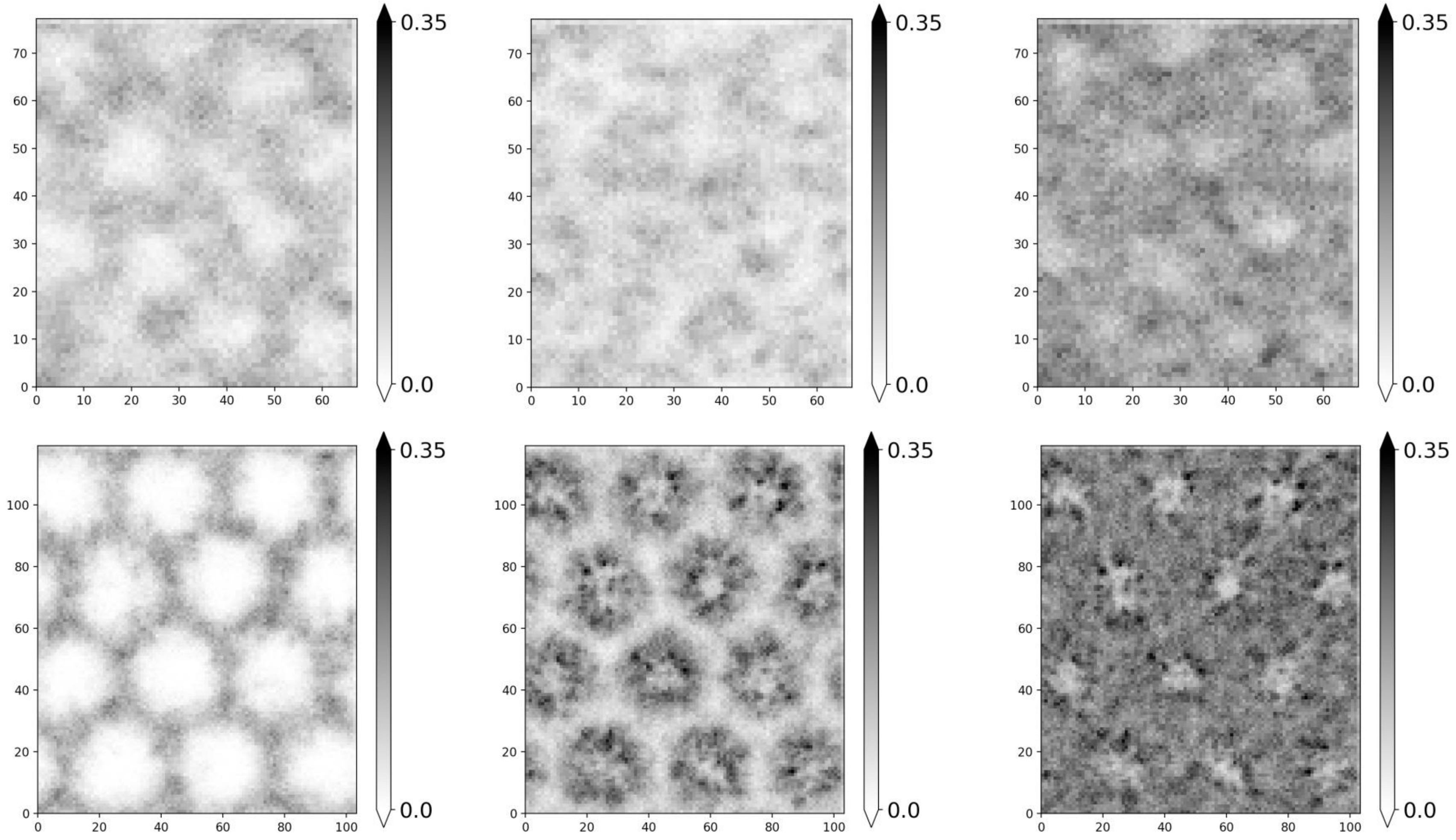
Inter-PGN **Intra-PGN** **All Double Kinks**



PGN2-160

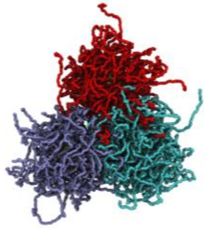


PGN6-160



- ❑ Increased intraparticle kinks near particle surface
- ❑ Increase near surface pronounced at high graft density (local chain stretching)

Entanglement Locations

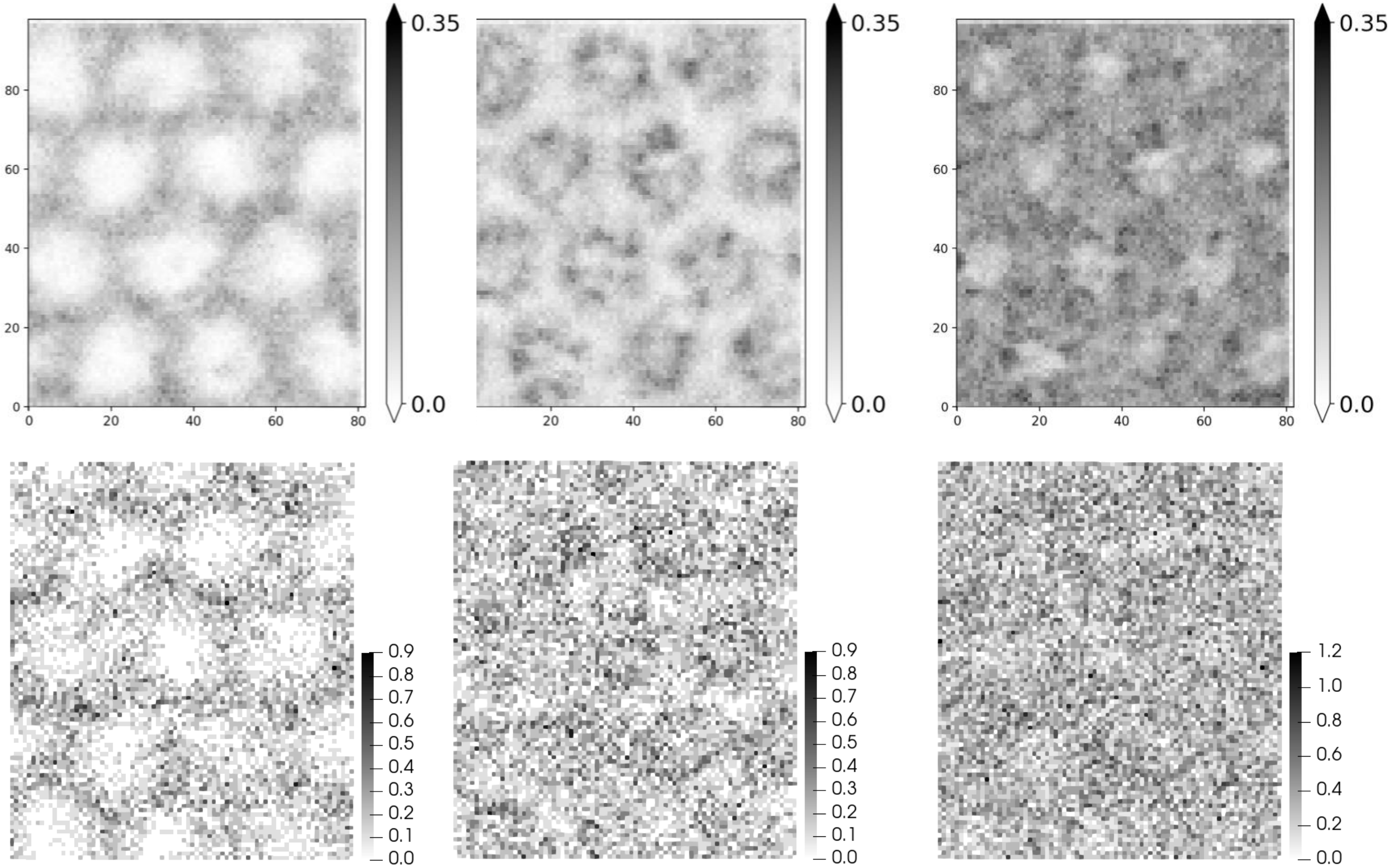


PGN3-160 Moderate graft density

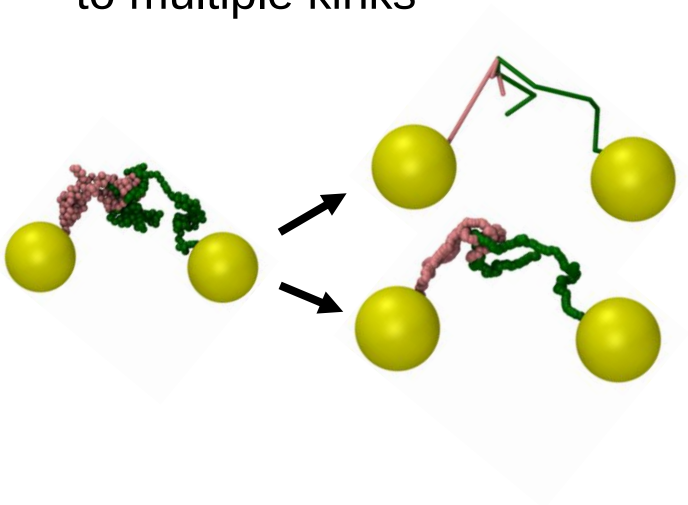
	Inter-PGN	Intra-PGN	All Double Kinks

Double Kinks (Z1)

Mean Path Closest Contacts (Preliminary)



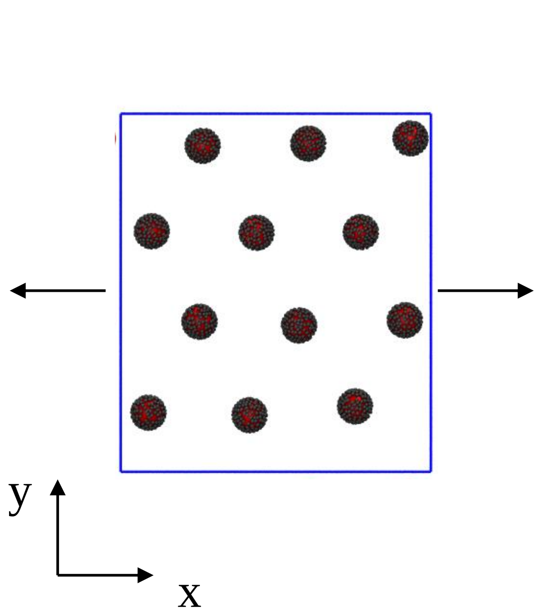
- ❑ Mean path, primitive path analyses qualitatively similar
- ❑ Mean path analysis yields tightness and timescale of contact
- ❑ Some long held mean path contact clusters correspond to multiple kinks

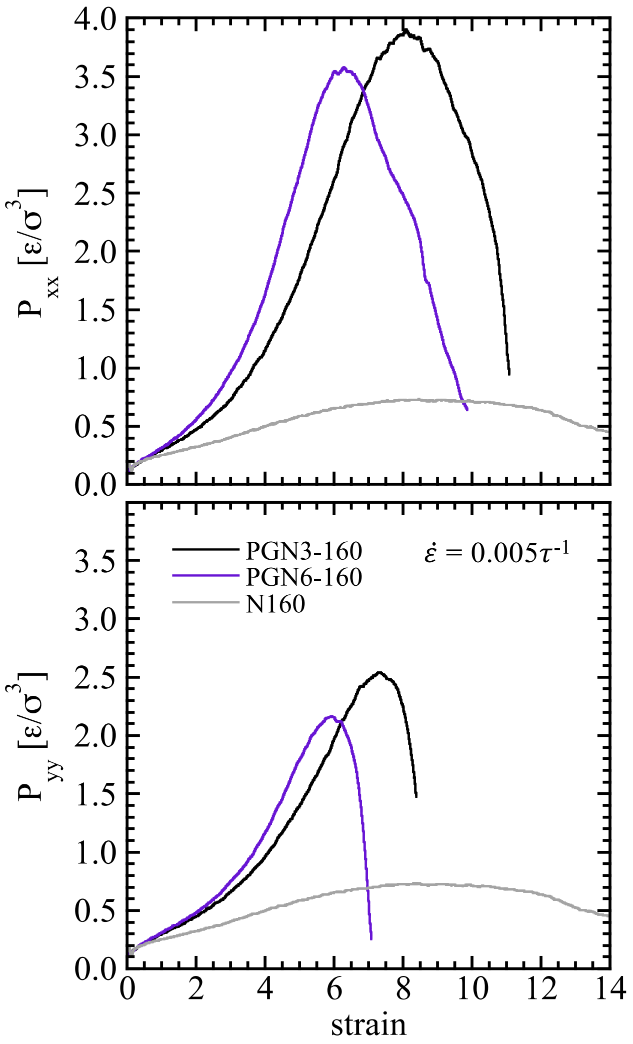


Mechanical Properties Depend on Graft Density (Melt State)

Deformation behavior: melt state, on surface

- Strain rate of 0.005 τ^{-1} in x or y, constant P in other direction
- Stress recorded in direction of pull





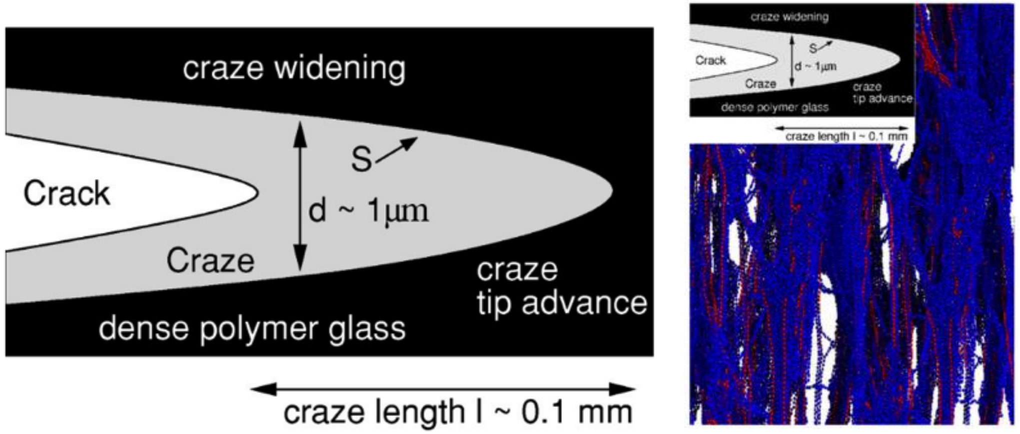
Higher graft density particles fail at lower strain due to less interparticle interaction and entanglements

Mechanical Behavior in Glassy State: Background

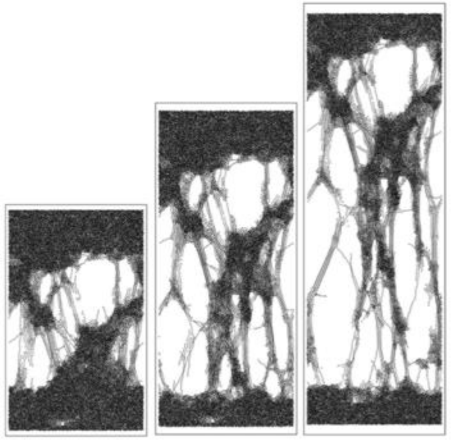
Molecular Dynamics Simulations

- During plastic flow, polymer is drawn into an intricate network of fibrils, or “craze”

- Significantly increases the fracture energy of the material

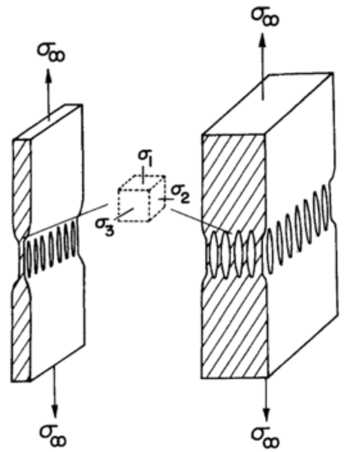


Baljon, Robbins, *Macromolecules* **2001**, *34,* 4200



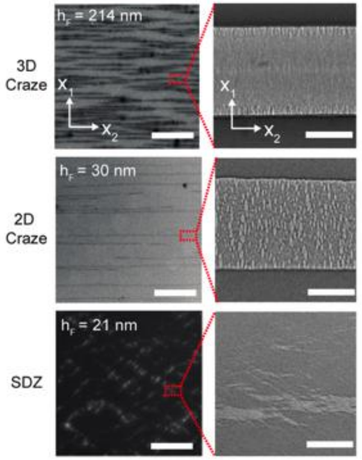
Rottler, Robbins, *Phys. Rev. E* **2003**, *68*, 011801

Thin Films vs. Bulk



Chan, Donald, Kramer, *J. Mat. Sci.* **1981**, *16*, 676

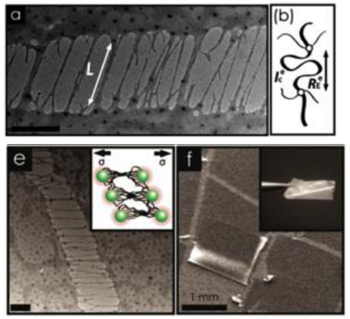
- Crazes observed in films with thickness > 30nm



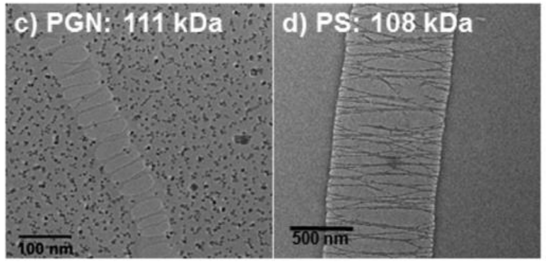
Bay, Shimomura, Liu, Ilton, Crosby, *Macromolecules* **2018**, *51*, 3647–3653

Crazing in Glassy PGN Assemblies

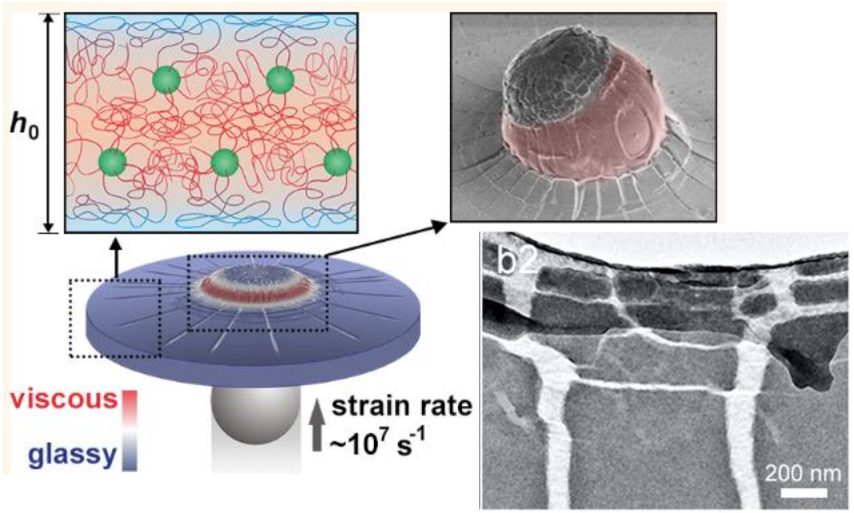
Neat Polymer-Grafted Nanoparticles (PGNs), Experiments

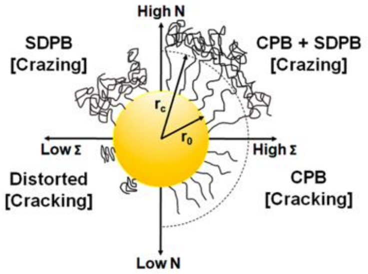


Choi, Dong, Matyjaszewski, Bockstaller,
J. Am. Chem. Soc. **2010**, *132*, 12537–12539



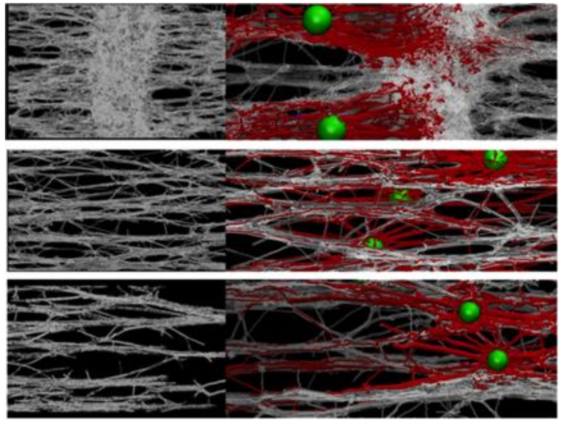
Jiao, Tibbits, Gillman, Hsiao, Buskohl, Drummy, Vaia, *Macromolecules* **2018**, *51*, 7257–7265

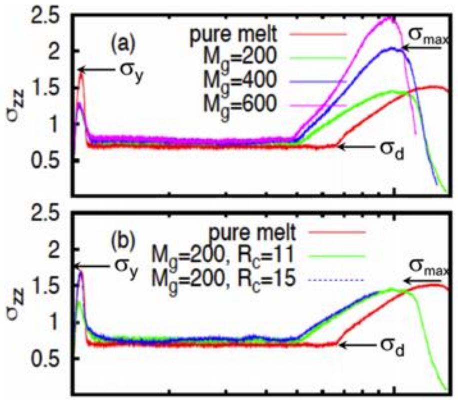




Hyon, Gonzales, Streit, Fried, Lawal, Jiao, Drummy, Thomas, Vaia, *ACS Nano* **2021**, *15*, 2439–2446

MD Simulations in Bulk PGN blends

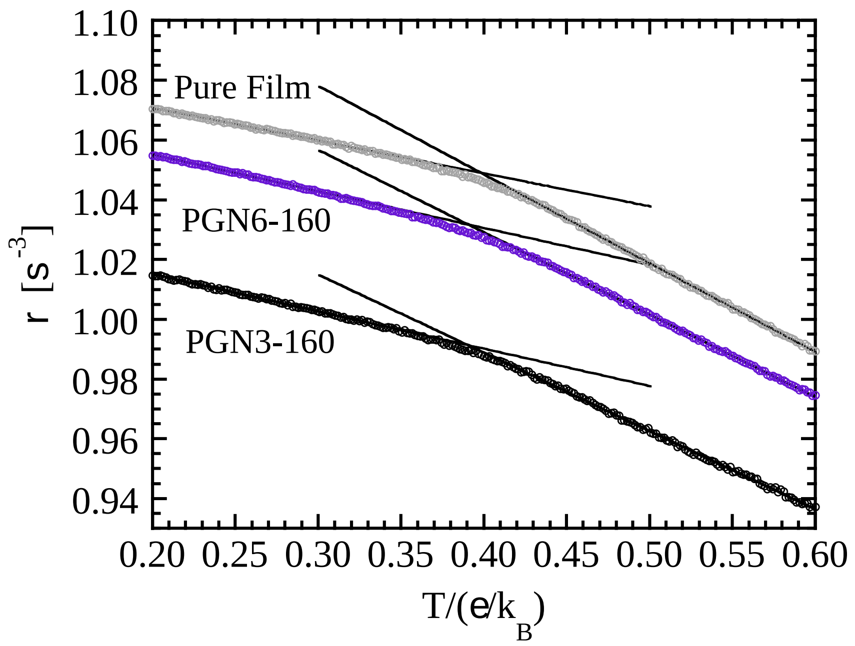




Meng, Kumar, Ge, Robbins, Grest, *J. Chem. Phys.* **2016**, *145*, 094902

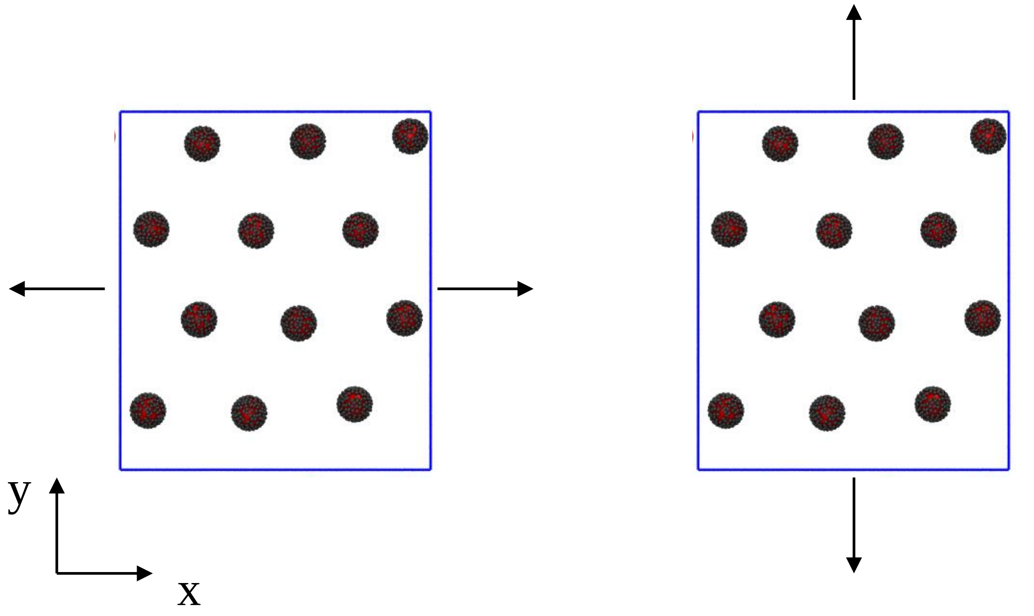
Creating Glassy Monolayer Films

- Switch to a quartic bond potential (to allow bonds to break during deformation)
- Cool monolayers to T* = 0.2 (T_g = 0.39-0.40) and remove the surface

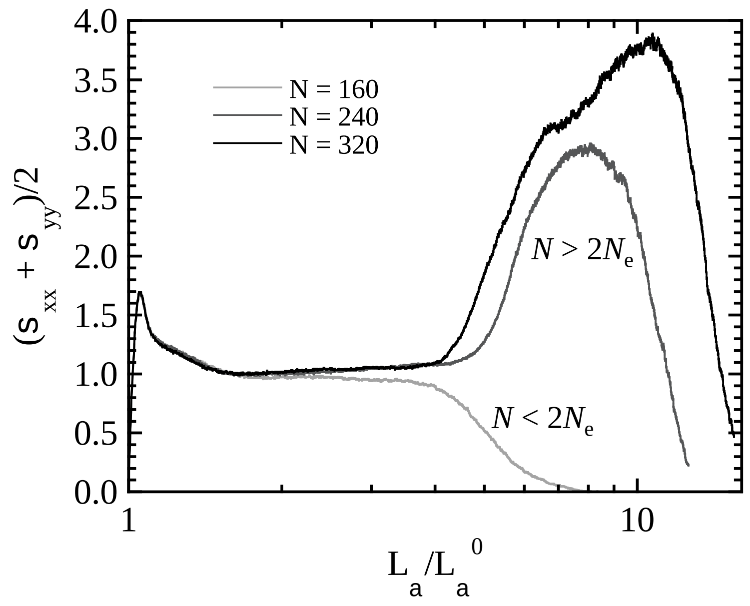


Deformation

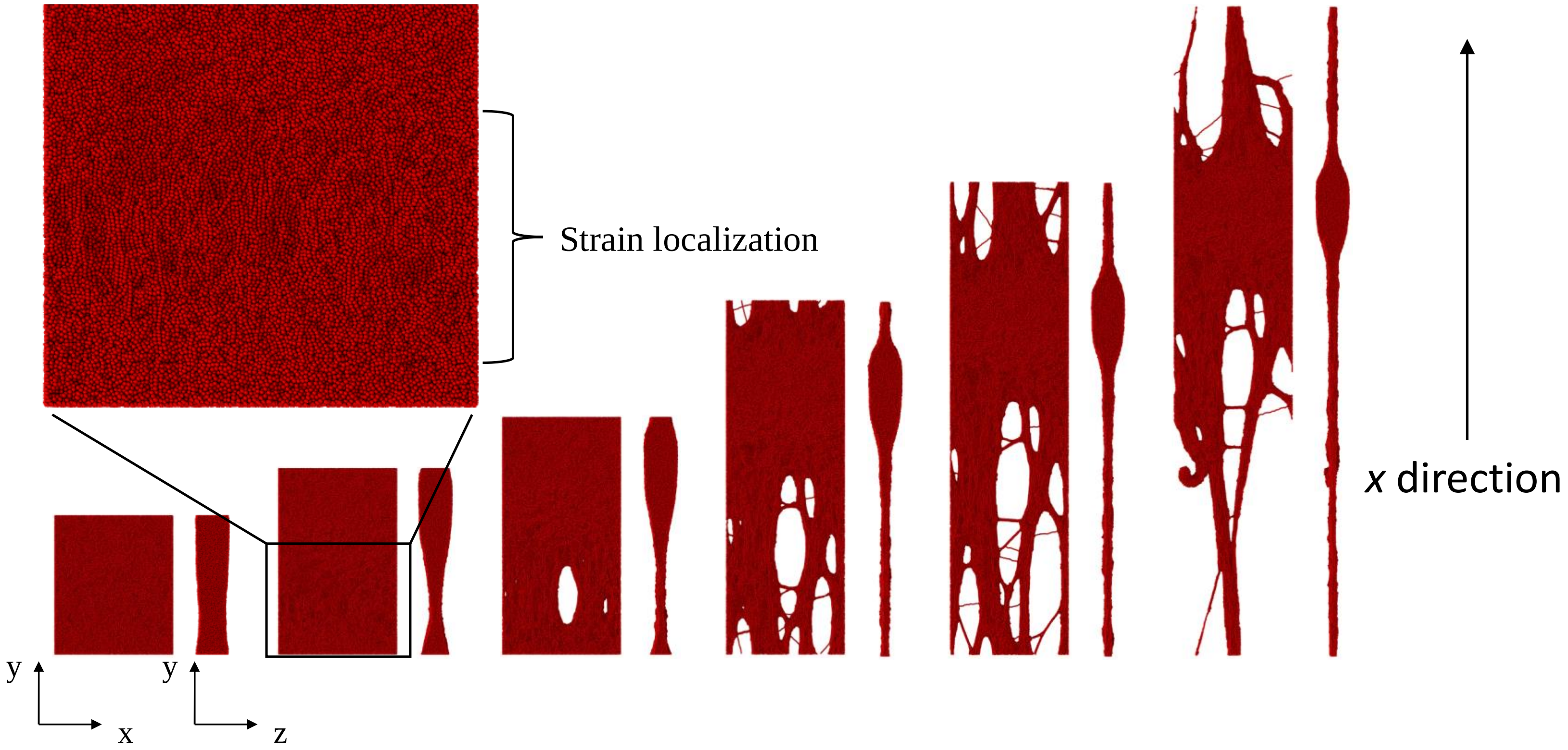
- Deform uniaxially at constant deformation rate of 0.03 σ/τ
- Keep non-deformed side length constant
- Record stress in direction of pull



Homopolymer Films – Uniaxial Deformation

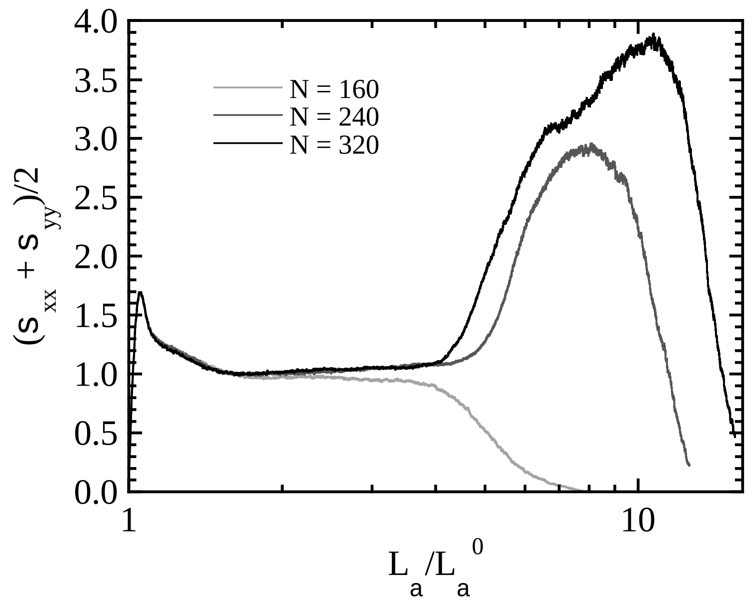


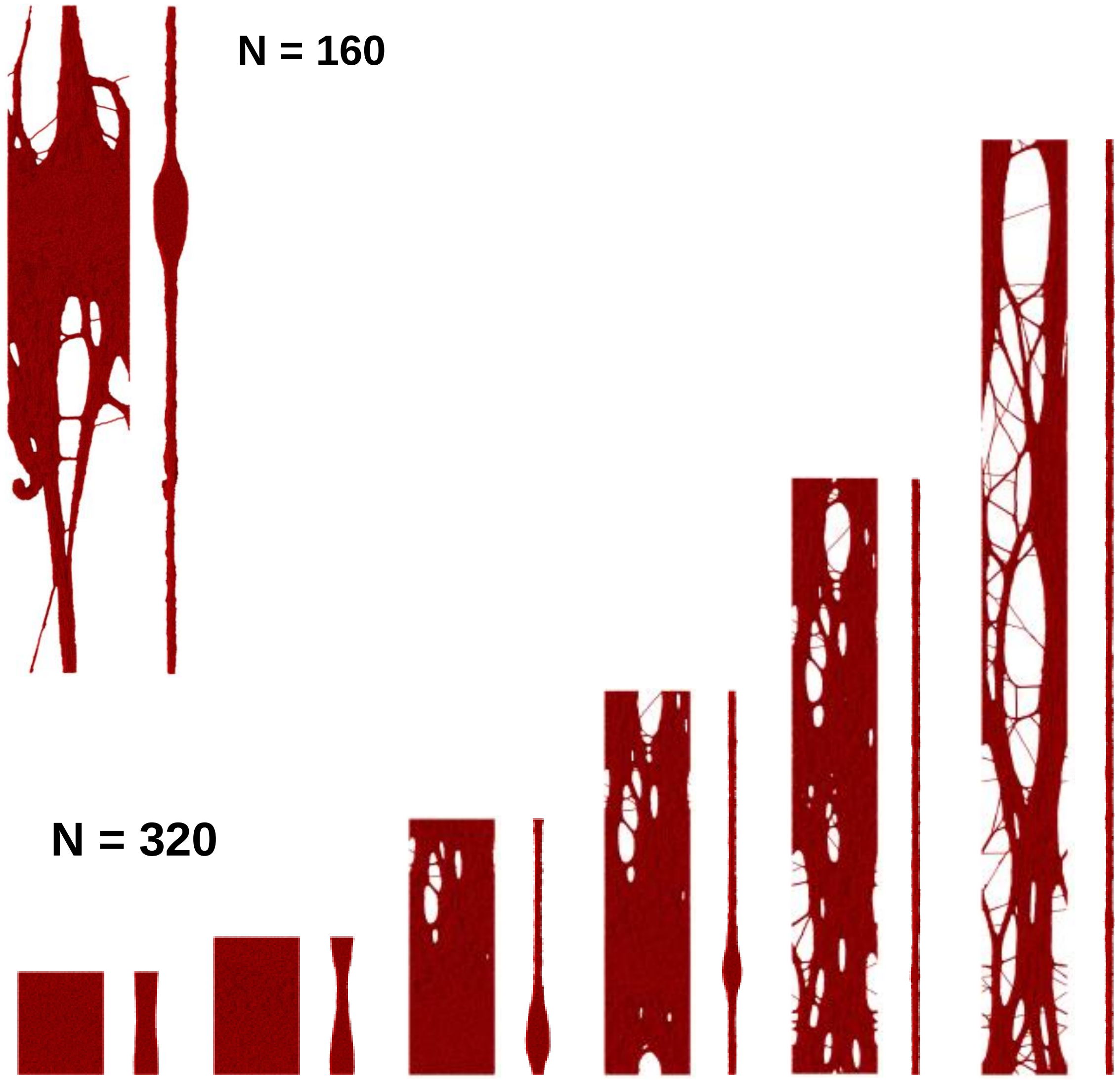
N = 160



Stress-strain curves similar to expectations for bulk polymer

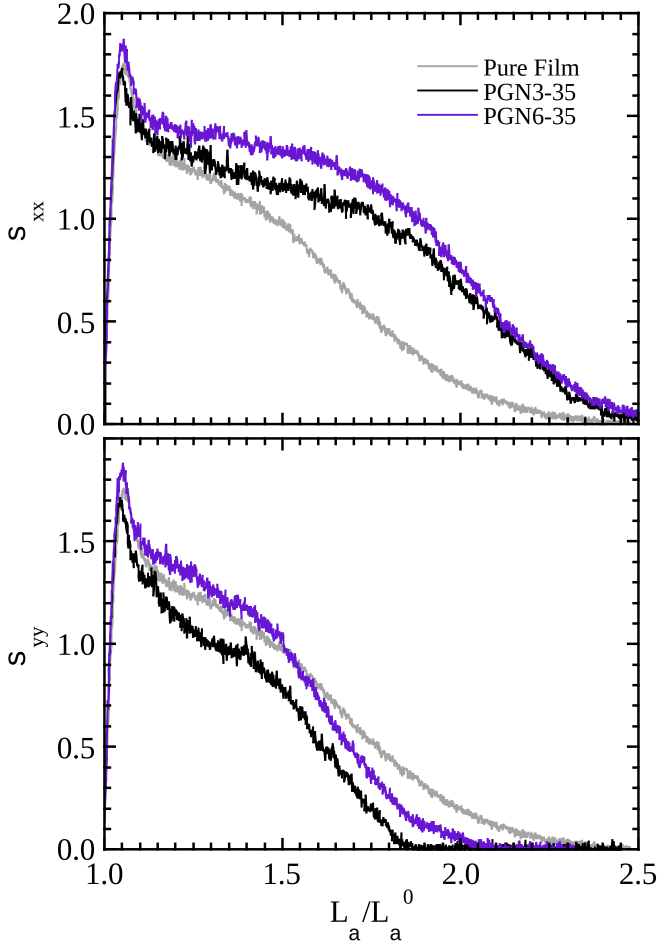
Homopolymer Films – Uniaxial Deformation

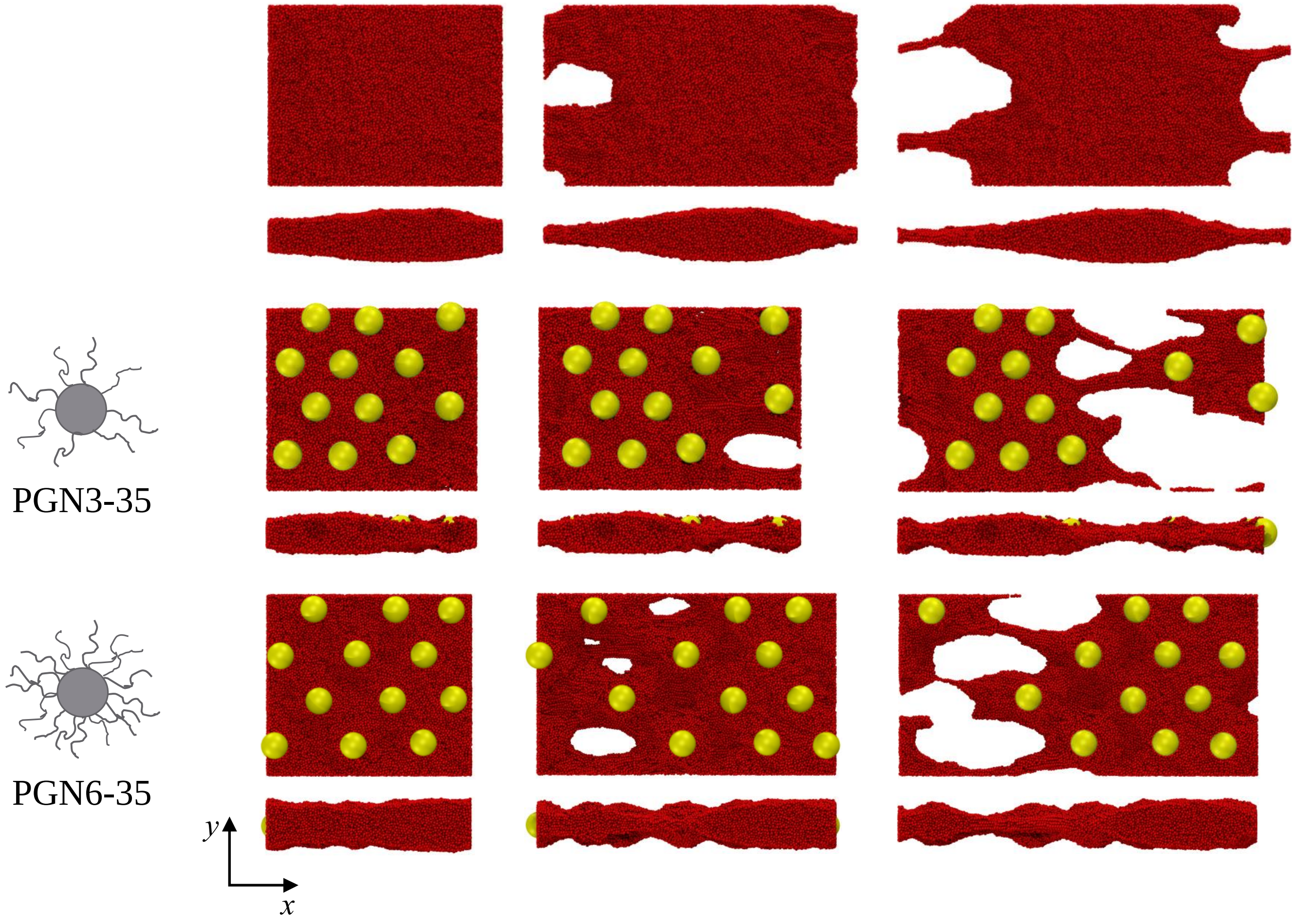




Glassy Monolayer Films – Uniaxial Deformation

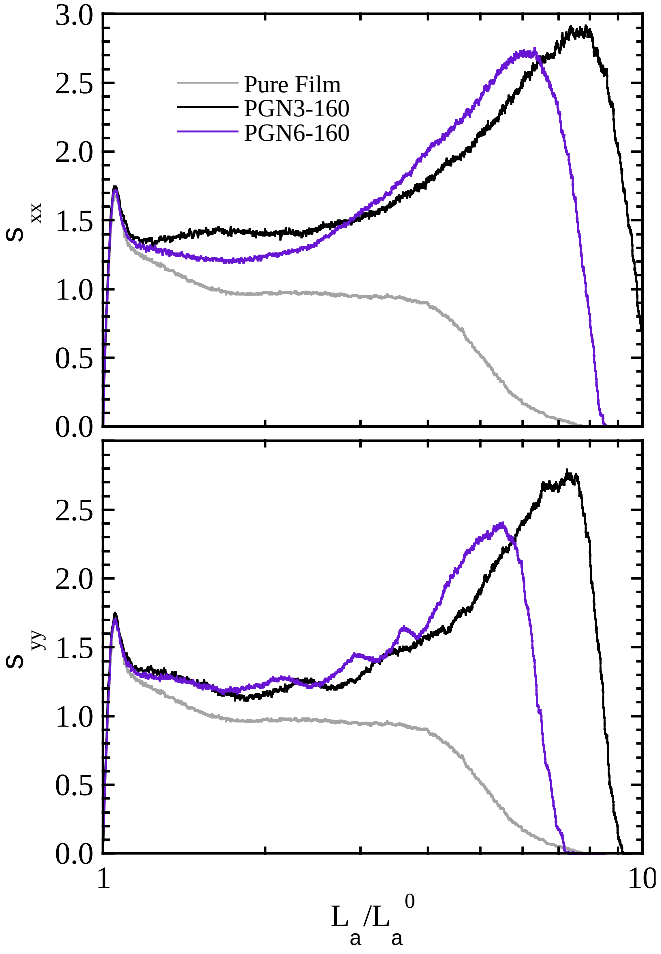
Short Chains (*N* = 35 beads/chain)

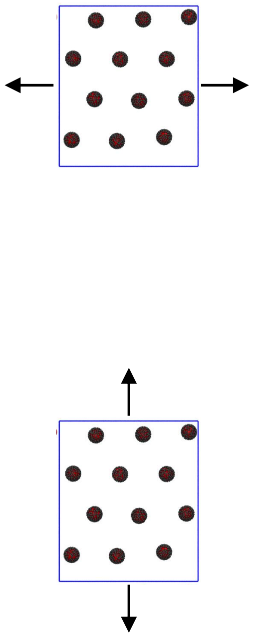


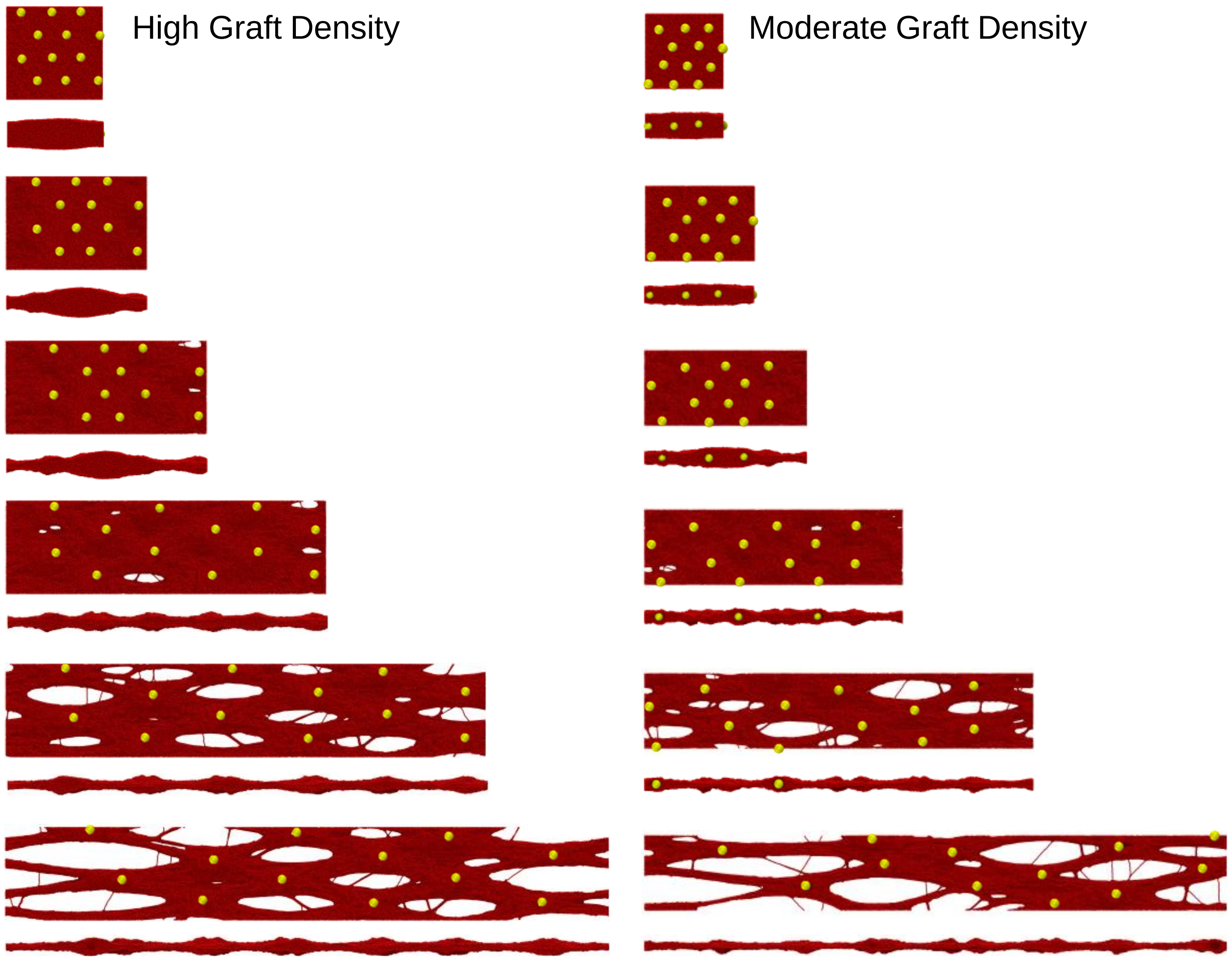


Glassy PGN Monolayer Films – Uniaxial Deformation

Long Chains (N = 160 beads/chain)

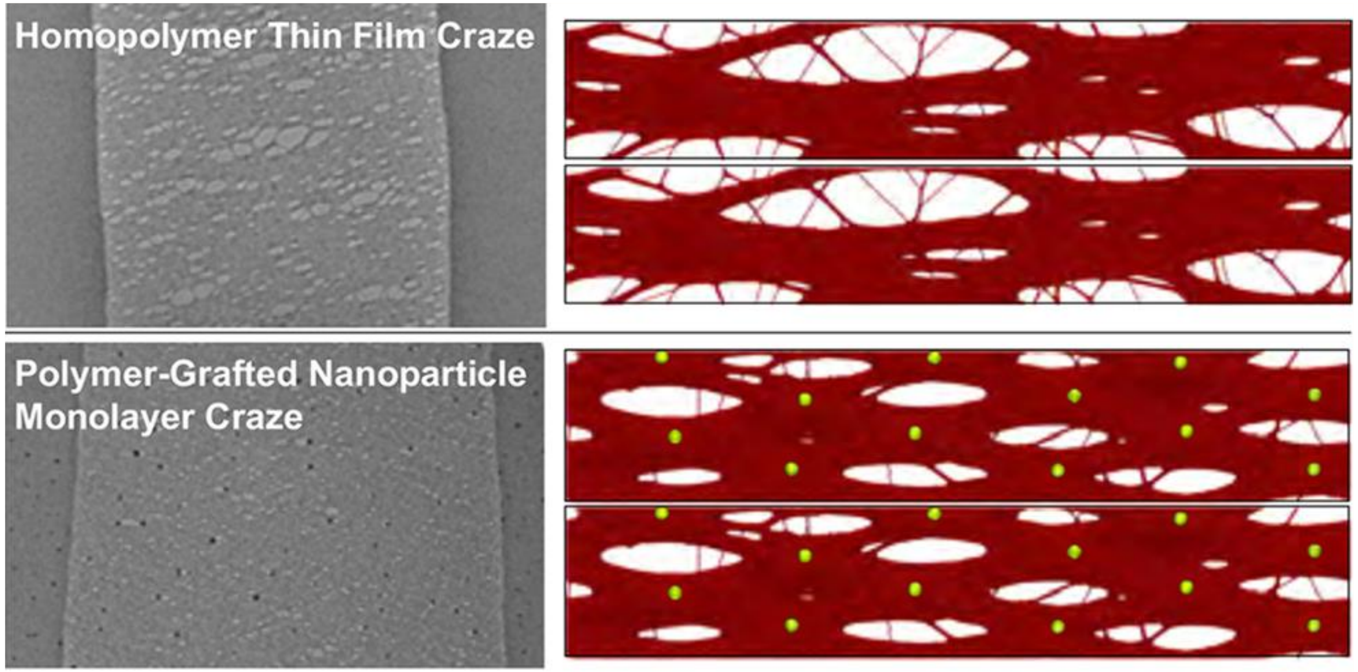






Comparison with Experiment

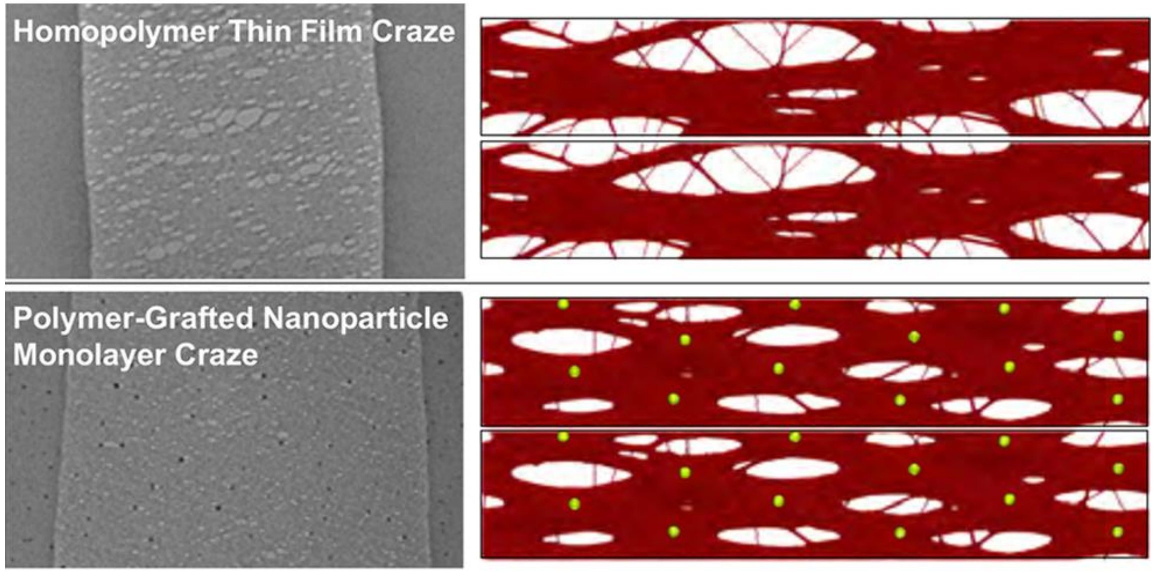
Collaboration with Drummy and Vaia at Air Force Research Lab: PGN monolayer films



- ❑ Qualitative comparison: no attempt to match chain length, particle size
- ❑ Homopolymer films have wide distribution of void sizes
- ❑ PGN films have more uniform voids
- ❑ PGN films are tougher

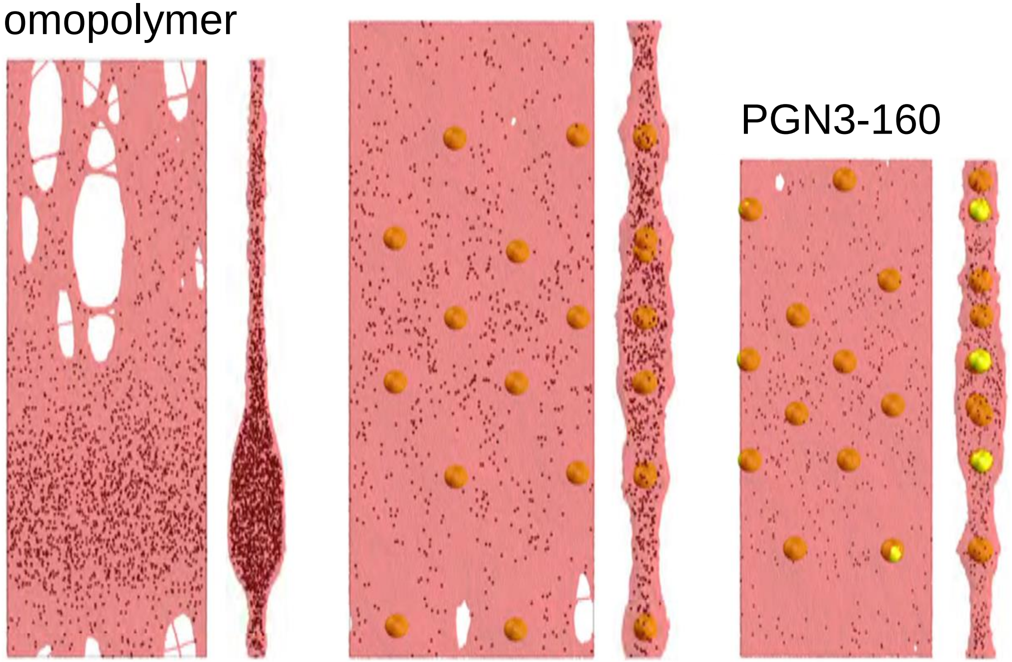
Conclusions

- Topological (Z1) and mean path entanglement analyses provide similar information; mean path method avoids fixing chain ends
- Grafting to nanoparticle adds a constraint on chain motion, as though there are additional entanglements vs. homopolymers of same length



Ongoing Work

- PGN phase behavior in solutions
- Bulk neat PGNs
- How does entanglement location change with strain?
- How can we relate entanglements to local and overall mechanical properties?



Double kink locations at L/Lo=3

Acknowledgements

- **Jeff Ethier**
- **Nicholas Liesen**
- **Anna Schuler**
- **Felipe Pacci Evaristo**
- Richard Vaia, AFRL (experimental)
- OSC HPC Resources
- DoD Modernization Program (additional HPC resources)

Funding

- AFRL/DAGSI Ohio Student-Faculty Research Fellowship and AFRL Minority Leaders Program
- AFOSR with Daniel Hallinan

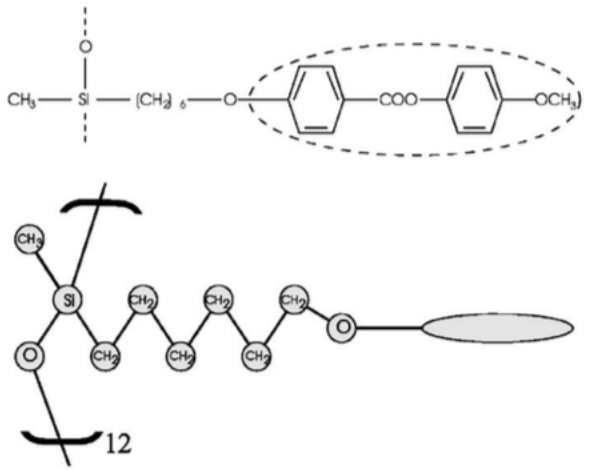
THE OHIO STATE UNIVERSITY

New Direction: LC Polymers

- Relatively flexible backbone with liquid crystal groups attached on side chains: either end-on or side-on

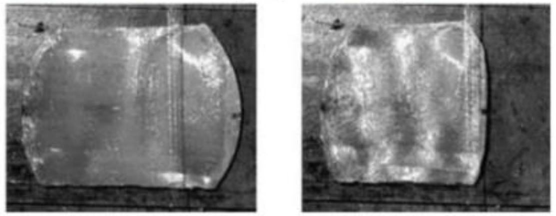
- Crosslink to make responsive materials

- Can we mix different LC attachment types to control response?



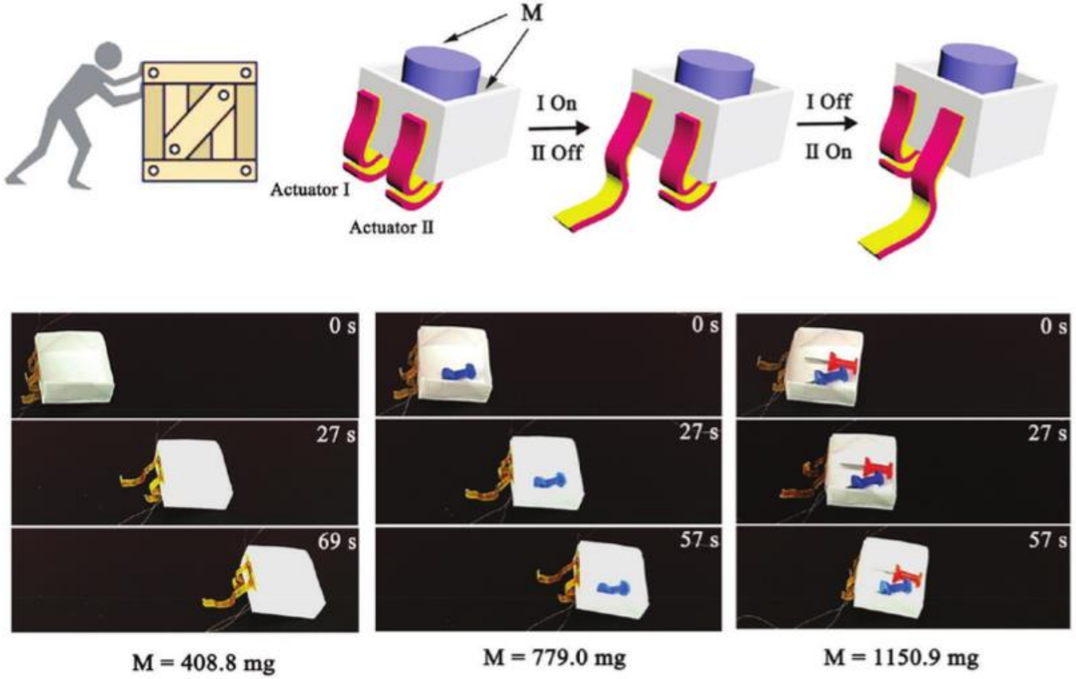
Stimson and Wilson, *J. Chem. Phys.*, **123**, 2005

Artificial muscles (first proposed by de Gennes, 1997)



M. Li and P. Keller, *Phil. Trans. R. Soc. A*, **364**, 2006

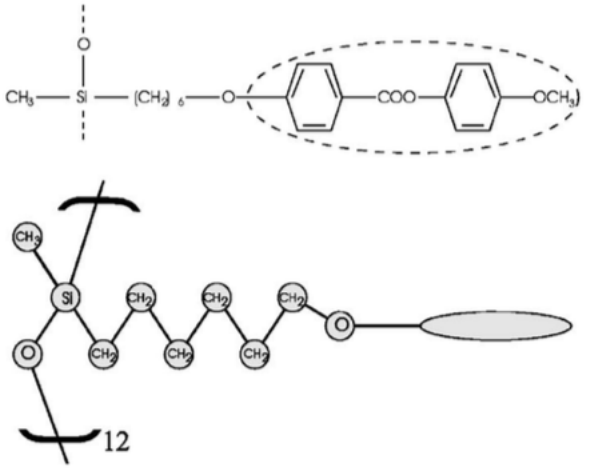
Biomimetic locomotion



Xiao, *et al.*, *Advanced Materials*, **31**, 2019

New Direction: LC Polymers

- Acknowledgements: PRF-ND award, experimental collaborator **William Wang**, OSU; postdoc **Diego Becerra**
- Relatively flexible backbone with liquid crystal groups attached on side chains: either end-on or side-on
- Can crosslink to make responsive materials



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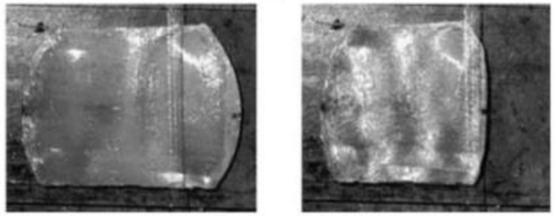

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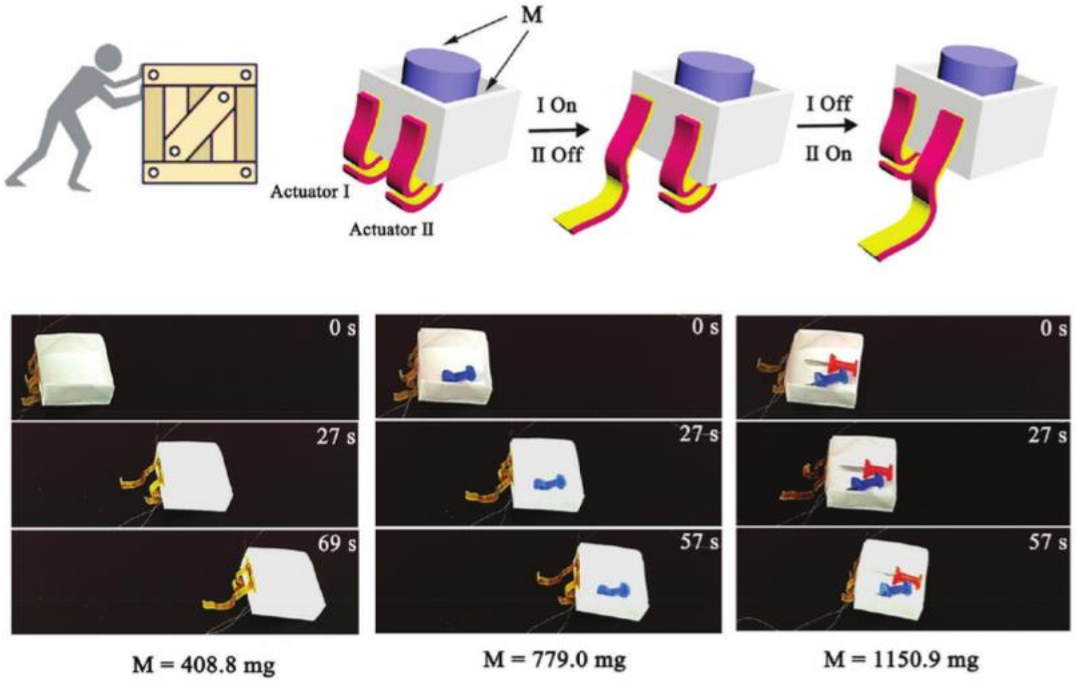
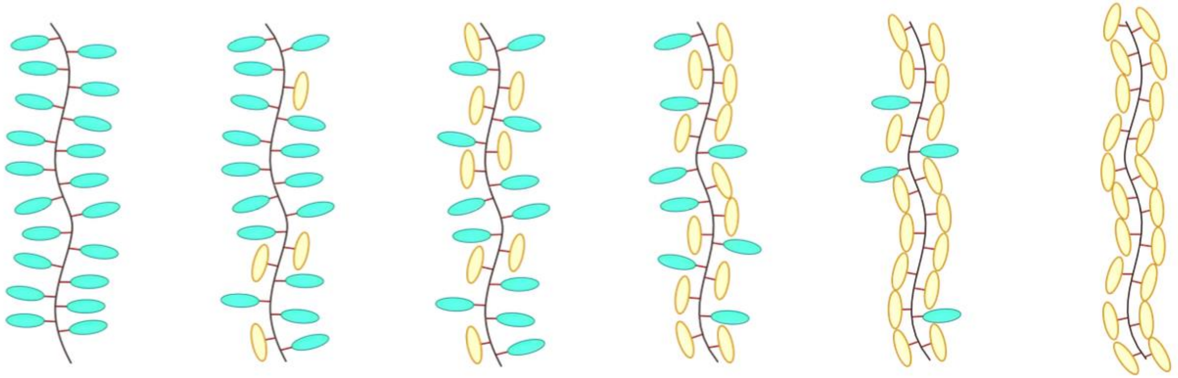


Xiao, *et al.*, *Advanced Materials*, **31**, 2019

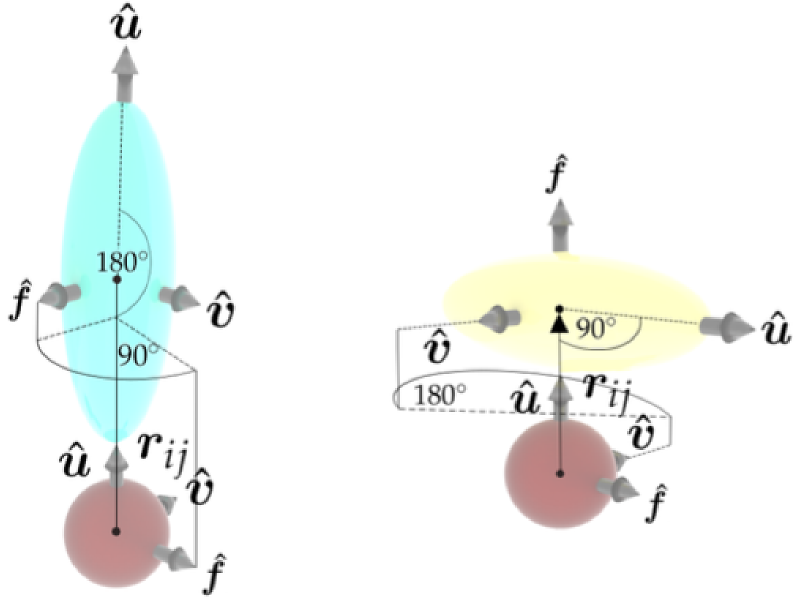
LC Polymer Model

- Include orientations/torsions on all beads
- LC groups: Gay-Berne ellipsoids
- Can we control response by mixing type of attachment?



Experimental systems: 4-(6-acryloxy-hex-1-yl-oxy) phenyl 4-(hexyloxy) benzoate end-on LC groups or 4”-acryloyloxybutyl 2,5-di(4’-butyloxybenzoyloxy) benzoate side-on groups on polydimethylsiloxane (PDMS) backbones.

Bonded interactions include torsional interactions that constrain both the relative position and orientation of bonded sites.



The nonbonded interactions between two sites depends on the site types i and j and distance between them, $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$.

$$\begin{array}{ll} U_{\mathrm{LJ}}(\boldsymbol{r}_{ij}) & \text{if } i \in \text{Polymer},\ j \in \text{Polymer} \\ U_{\mathrm{GB}}(\hat{\boldsymbol{u}}_i,\ \hat{\boldsymbol{u}}_j,\ \boldsymbol{r}_{ij}) & \text{if } i \in \text{LC group},\ j \in \text{LC group} \\ U_{\mathrm{GB/LJ}}(\hat{\boldsymbol{u}}_i,\ \boldsymbol{r}_{ij}) & \text{if } i \in \text{LC group},\ j \in \text{Polymer} \\ U_{\mathrm{GB/LJ}}(\hat{\boldsymbol{u}}_j,\ \boldsymbol{r}_{ij}) & \text{if } i \in \text{Polymer},\ j \in \text{LC group} \end{array}$$

LJ$\sim$ Lennard-Jones potential; GB$\sim$ Gay–Berne potential;
$\hat{\boldsymbol{u}}_i$ and $\hat{\boldsymbol{u}}_j$ $\sim$ orientations of the main axis of the mesogenic groups of sites i and j.

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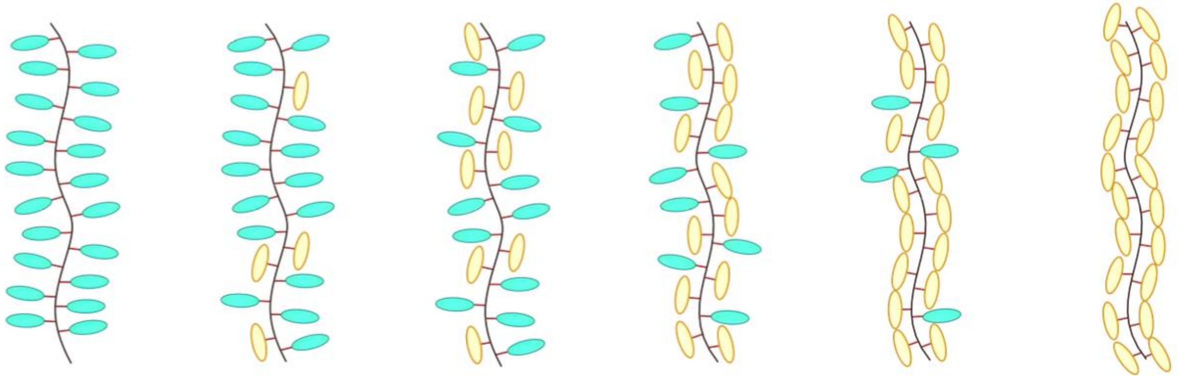

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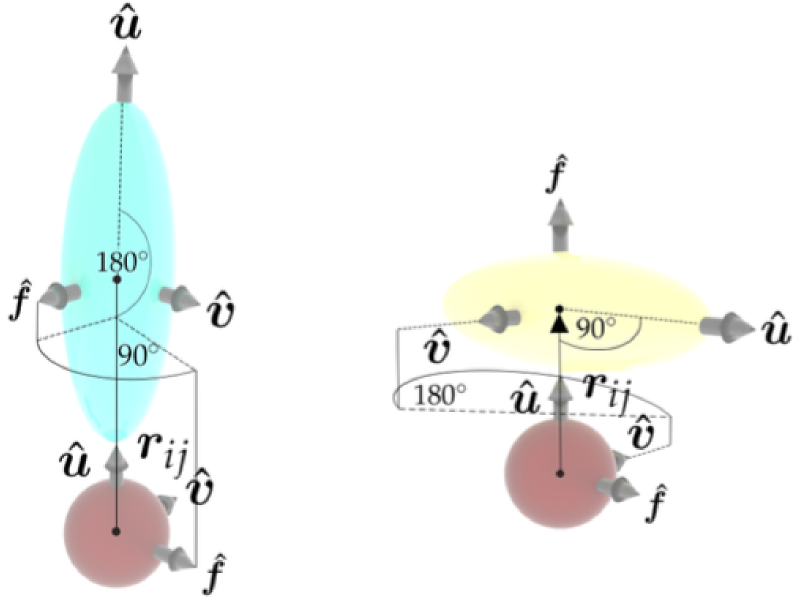

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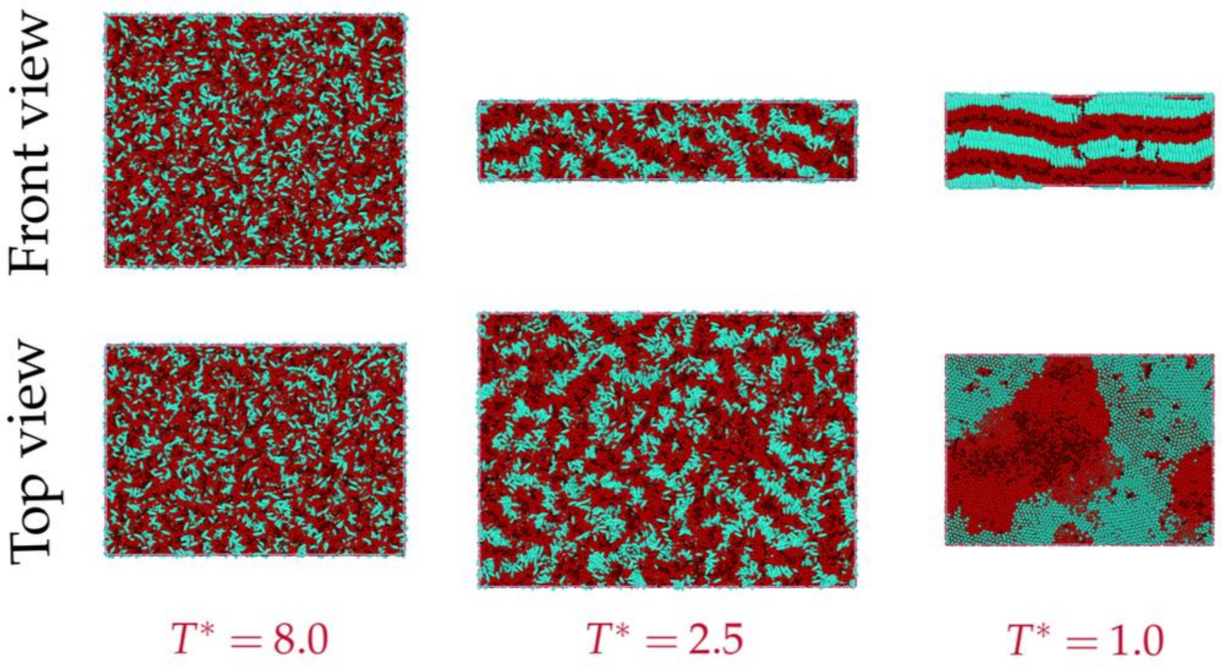
$U_{\text{LJ}}(\boldsymbol{r}_{ij})$	if i ∈ Polymer, j ∈ Polymer
$U_{\text{GB}}(\hat{\boldsymbol{u}}_i,\ \hat{\boldsymbol{u}}_j,\ \boldsymbol{r}_{ij})$	if i ∈ LC group, j ∈ LC group
$U_{\text{GB/LJ}}(\hat{\boldsymbol{u}}_i,\ \boldsymbol{r}_{ij})$	if i ∈ LC group, j ∈ Polymer
$U_{\text{GB/LJ}}(\hat{\boldsymbol{u}}_j,\ \boldsymbol{r}_{ij})$	if i ∈ Polymer, j ∈ LC group

LJ∼ Lennard-Jones potential; GB∼ Gay–Berne potential;
$\hat{\boldsymbol{u}}_i$ and $\hat{\boldsymbol{u}}_j$ ∼ orientations of the main axis of the mesogenic groups of sites i and j.

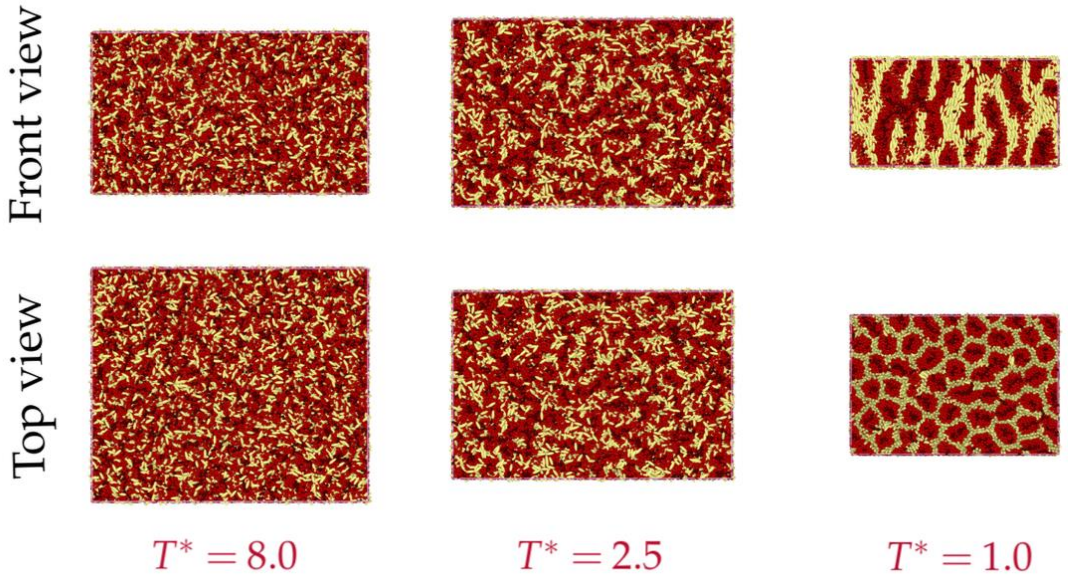
Mesoscale structure depends on attachment type

Equilibrate at high T, cool while intermittently imposing alignment field to avoid multiple grains

End-on



Side-on

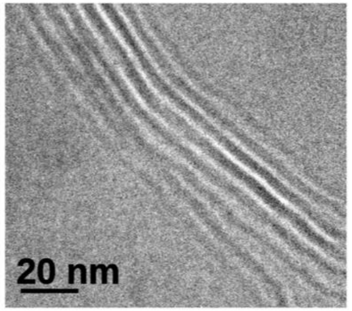


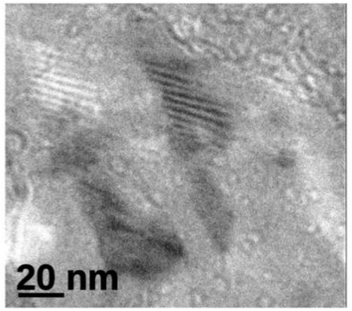
Mesoscale structure depends on attachment type

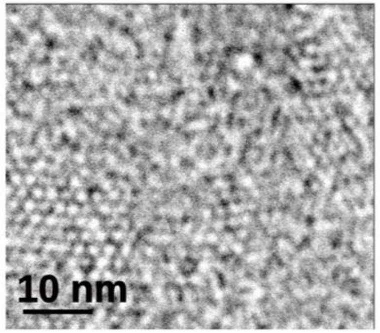
Qualitatively matches experiment

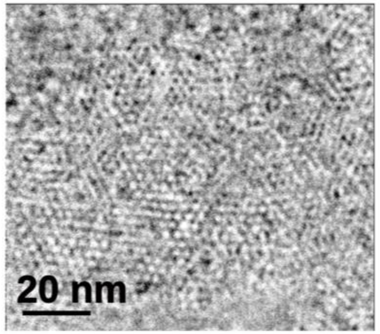
End-on

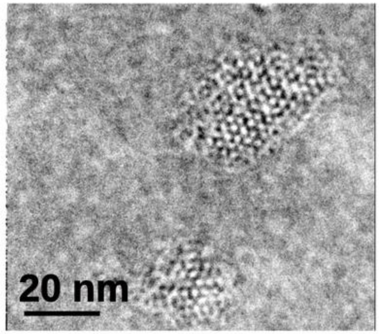
Side-on



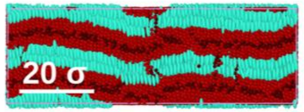


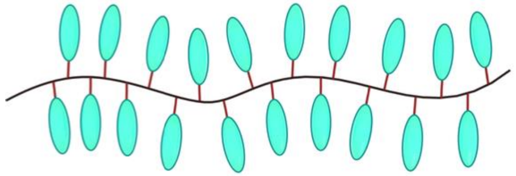




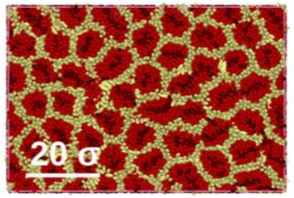


Front view



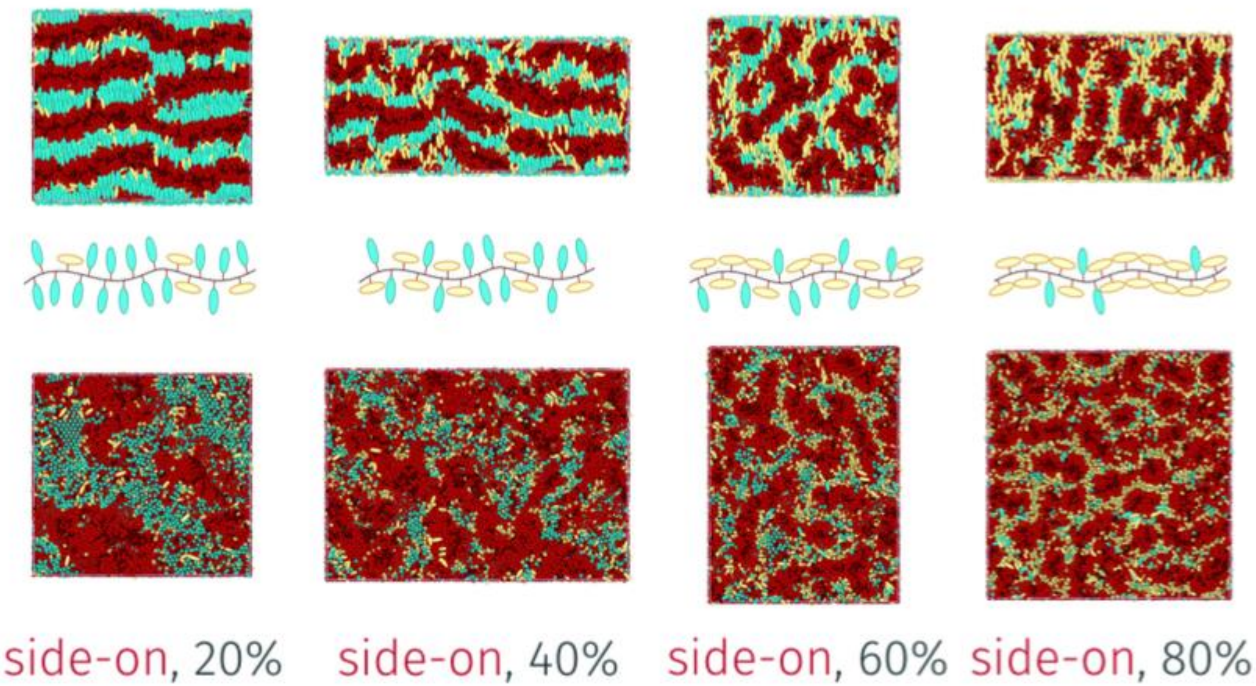


Top view

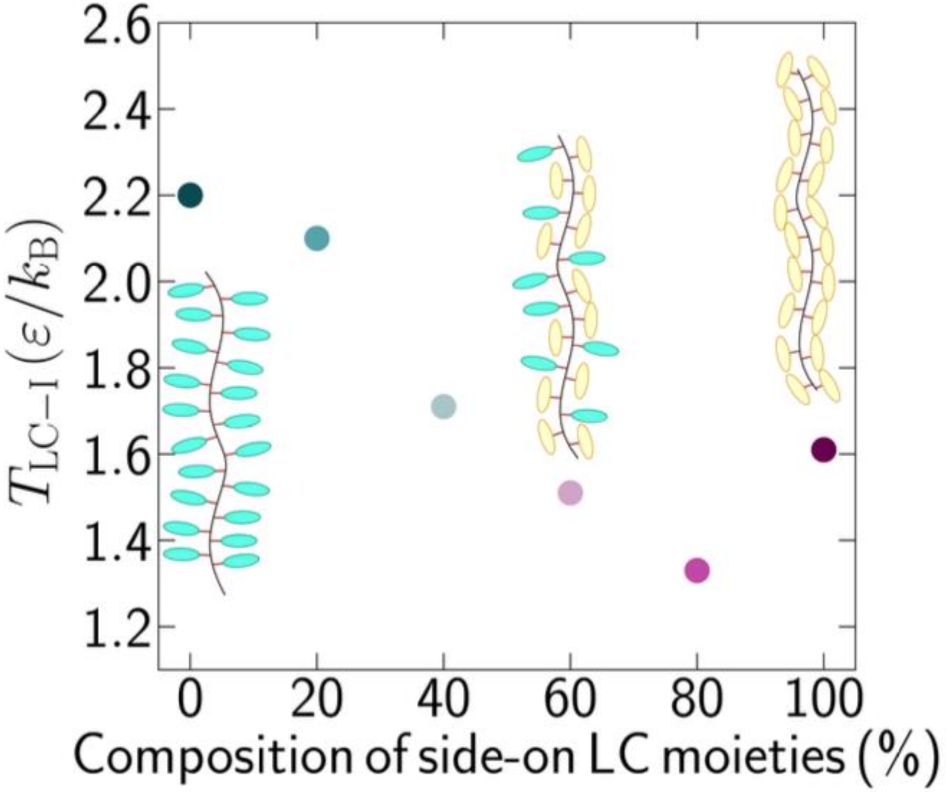


Experimental TEMs at room temperature courtesy of William Wang: 4-(6-acryloxy-hex-1-yl-oxy) phenyl 4-(hexyloxy) benzoate end-on LC groups or 4”-acryloyloxybutyl 2,5-di(4’-butyloxybenzoyloxy) benzoate side-on groups on polydimethylsiloxane (PDMS) backbones. Benzene-rich groups stained (LC groups dark in images).

Mixing attachment types disrupts ordering



Transition temperature matches experimental trend



Mixing attachment types changes conformations