SAND2017-9018C

Polymer Science at the Center for Integrated Nanotechnologies (CINT)

Amalie L. Frischknecht

ACS Fall Meeting

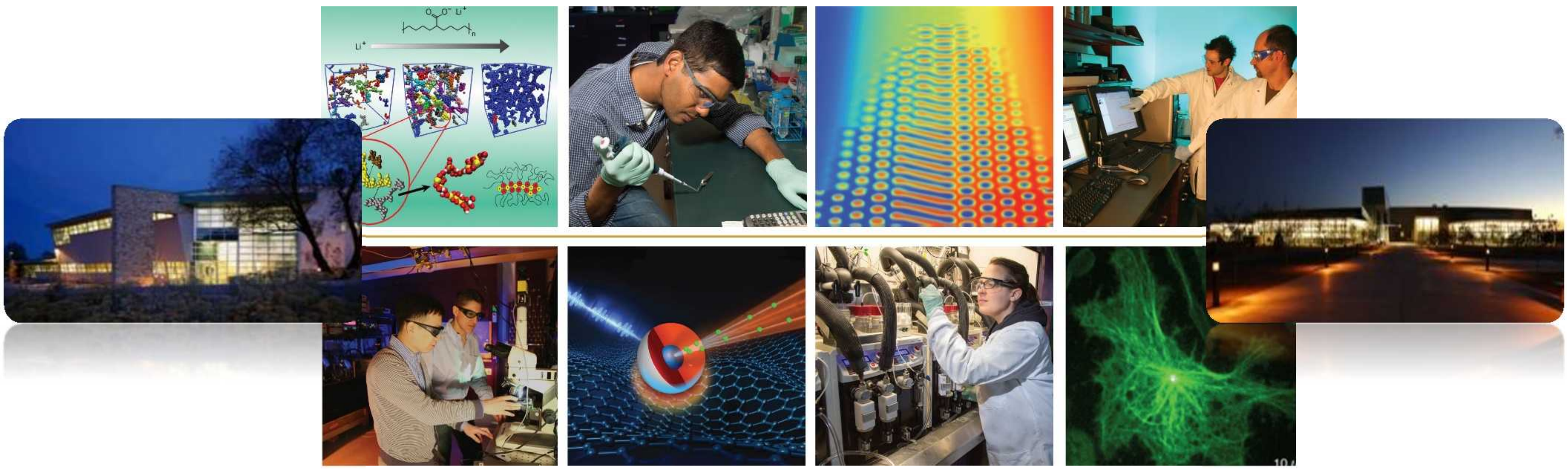
August 20, 2017

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

A Nanoscale Science Research Center (NSRC) focused on advancing the understanding of *nanostructure integration*

The User Community:

- Access to capabilities from two world-renowned National laboratories, Los Alamos and Sandia
- **<u>Free</u>** access for the research community via a proposal process!

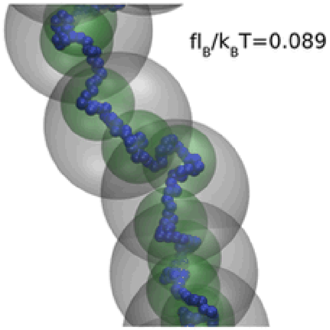


http://cint.lanl.gov | @CenterIntegratedNanotechnologies | #CINT

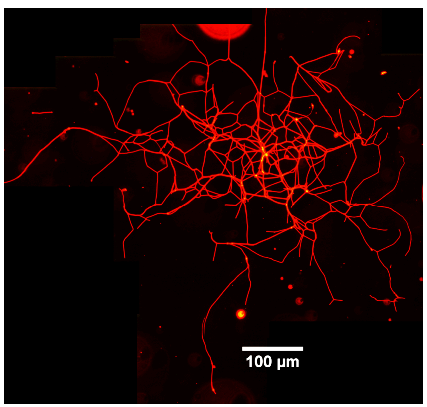
Los Alamos NATIONAL LABORATORY EST. 1943 | Sandia National Laboratories | U.S. DEPARTMENT OF ENERGY | Office of Science

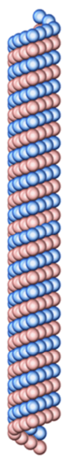
Polymer Science at CINT

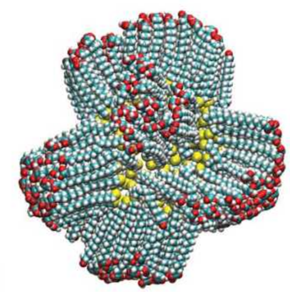
we develop strategies to enable hierarchical assembly of nanoconstituents to harness their collective/emergent behaviors

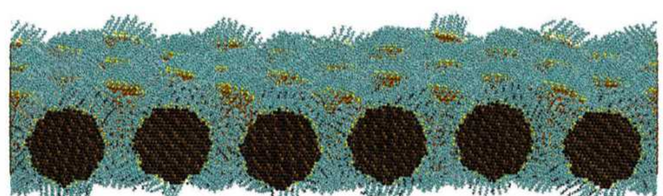


- Polymer Melts and Networks
- Responsive Polymer Interfaces
- Polymer Nanocomposites
- Coated Nanoparticle Assembly
- Polymer Brushes
- Ionic and Charged Polymers
- Polymersomes
- Biopolymers



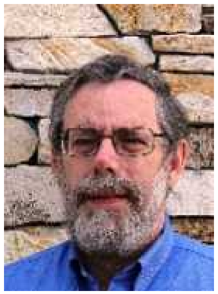






CINT Scientists with Polymer Research

theory/modeling



Gary Grest

Mark Stevens

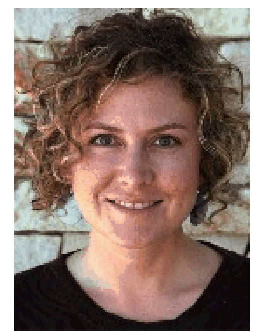
Amalie Frischknecht

experiment

George Bachand

Millie Firestone

Dale Huber

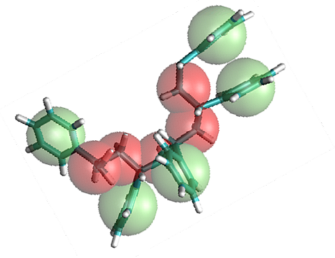


Jen Martinez

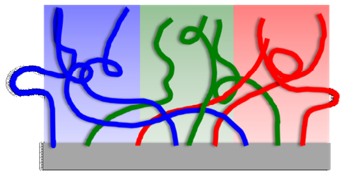
Wally Paxton

Highlights

- coarse-graining polymer simulations

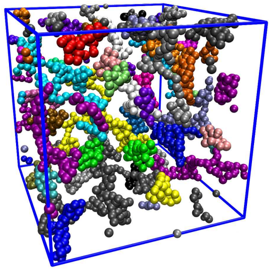


- mixed polymer brushes



- robust polymersomes

- acid and ion-containing polymers

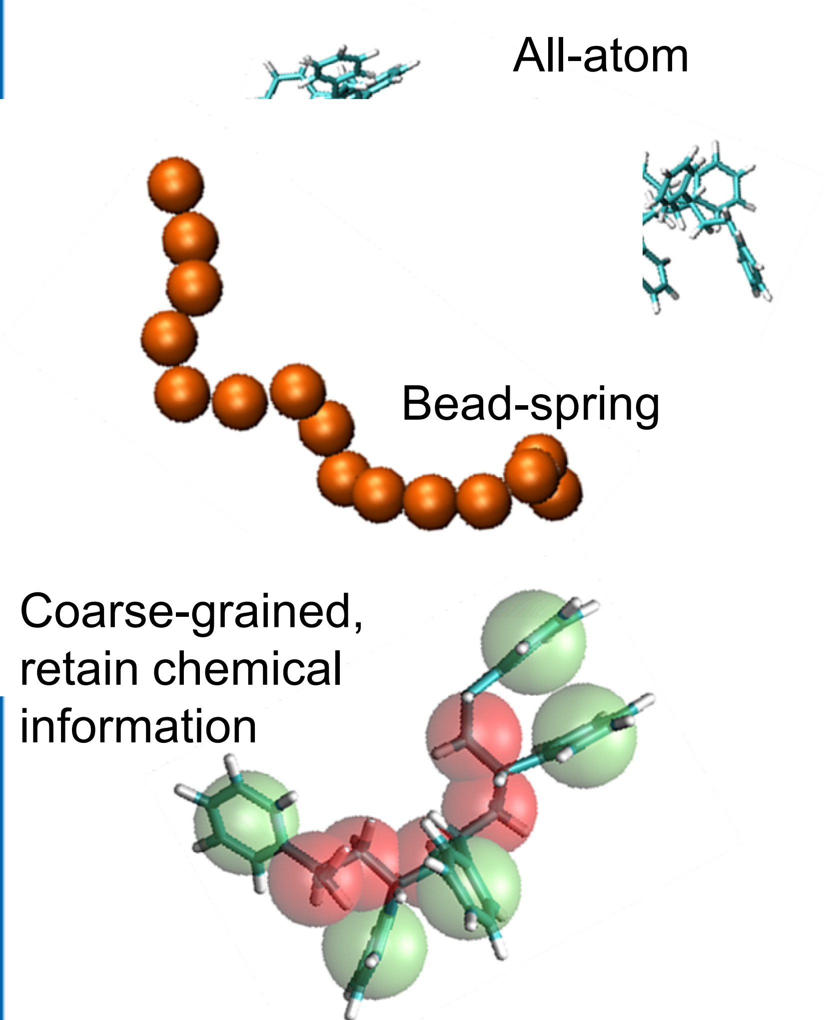


Computational Challenges in Polymers

- Longest relaxation time $\tau \sim N^3$
- Chains are Gaussian coils – $R \sim N^{1/2}$
  - Number of chains must increase as $R^3 \sim N^{3/2}$ so polymer chains do not to see themselves through periodic boundary conditions
- Double chain length – cpu required increases by at least a factor of $2^{4.5} \sim 23$
  - 1 month simulation becomes 2 years

Coarse-Graining of Polymers

- To reach larger length/time scales, new coarse graining methods are an active area of research



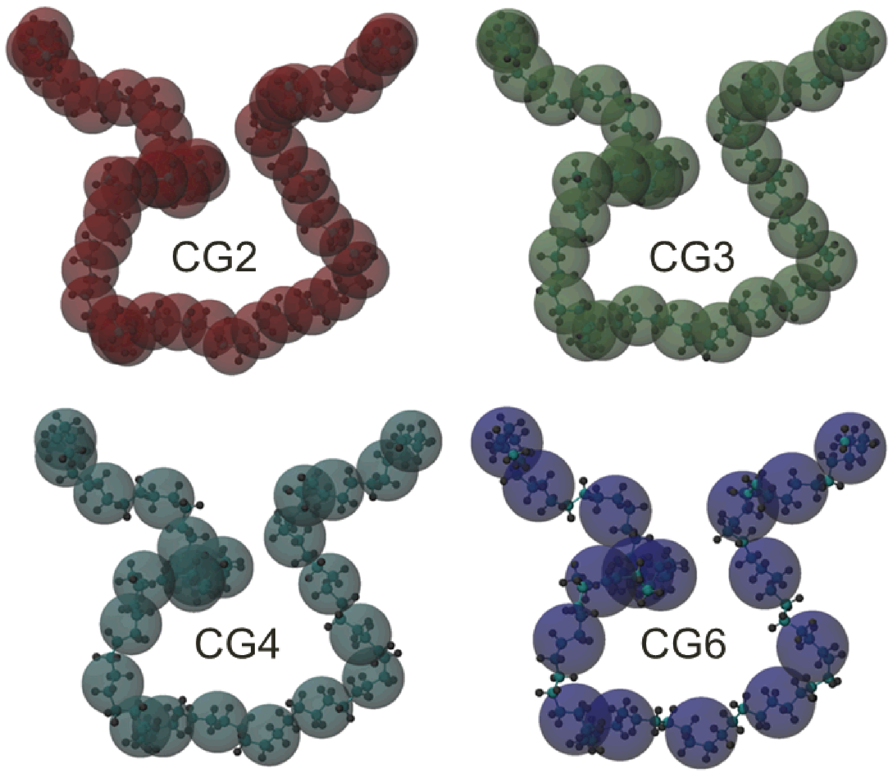
- Reduced number of degrees of freedom, simpler interaction potentials, reducing the overall computational effort

- Larger time steps (10-20x)

- Reduced effective bead friction due to lower energy barriers and/or a smoother energy landscape

- Back-mapping to fully atomistic model

Degree of Coarse Graining Polyethylene



$C_{96}H_{194}$ chain with increasing degree of coarse graining

- Largest lengths scales of polymer dynamics are controlled by entanglements
- Shortest time and length scales required to resolve dynamic properties not obvious

- Probe the degree of coarse graining (CGing) required to simultaneously retain significant atomistic detail and access large length and time scales

K M Salerno et al, Phys Rev Lett 116, 058303 (2016);
B. Peters et al, J. Chem Theory Comp 13, 2890 (2017)

Coarse-Graining Methodology

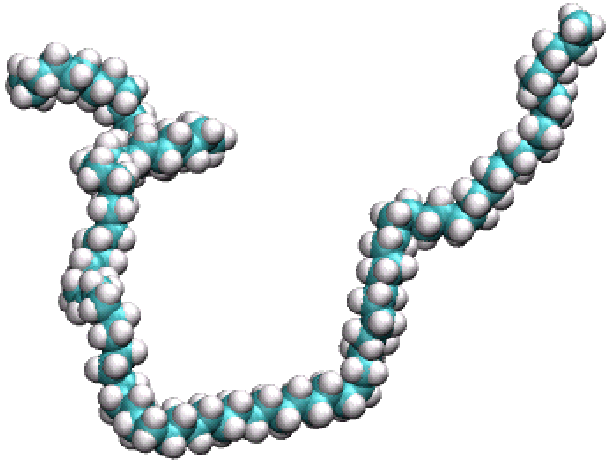
All-atom Melt MD simulation – LAMMPS*

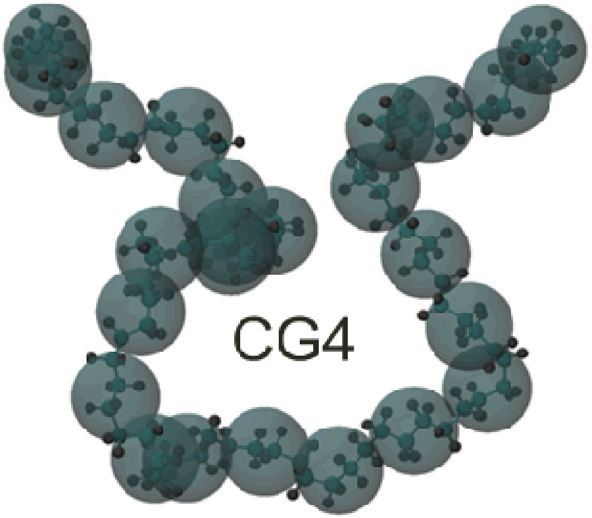
Define Beads

Bonded Interactions by Boltzmann Inversion

Nonbonded Interactions by Iterative Boltzmann Inversion (IBI)

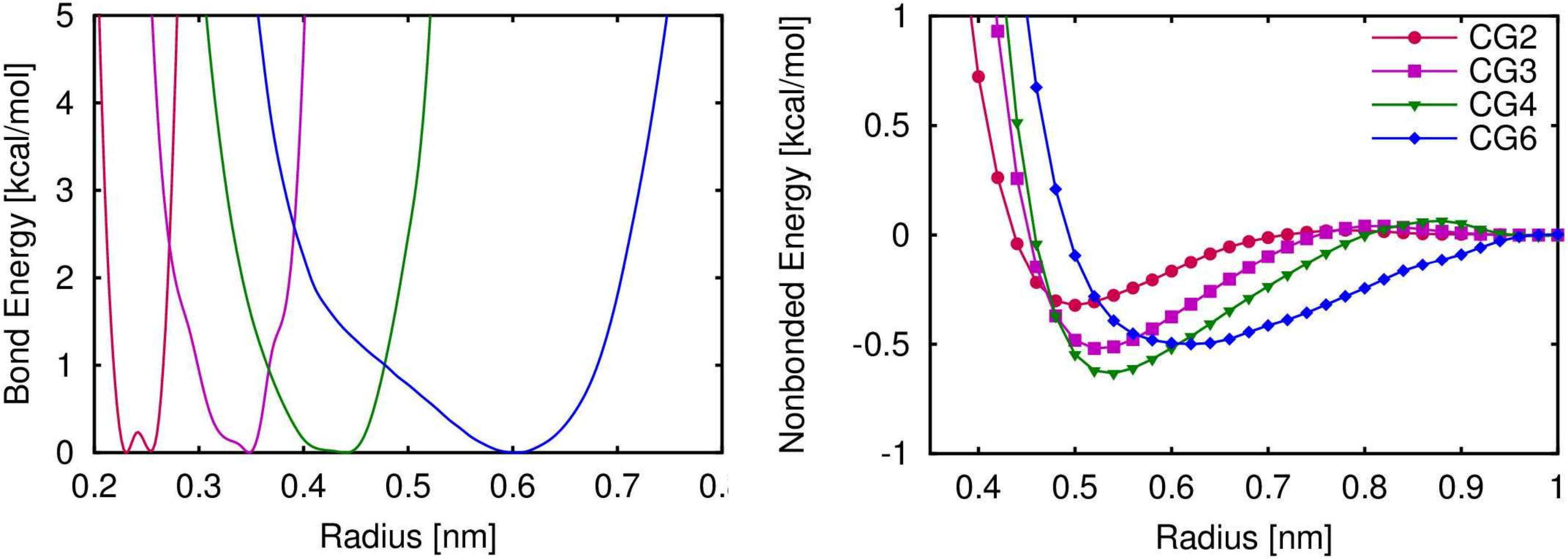
Validation





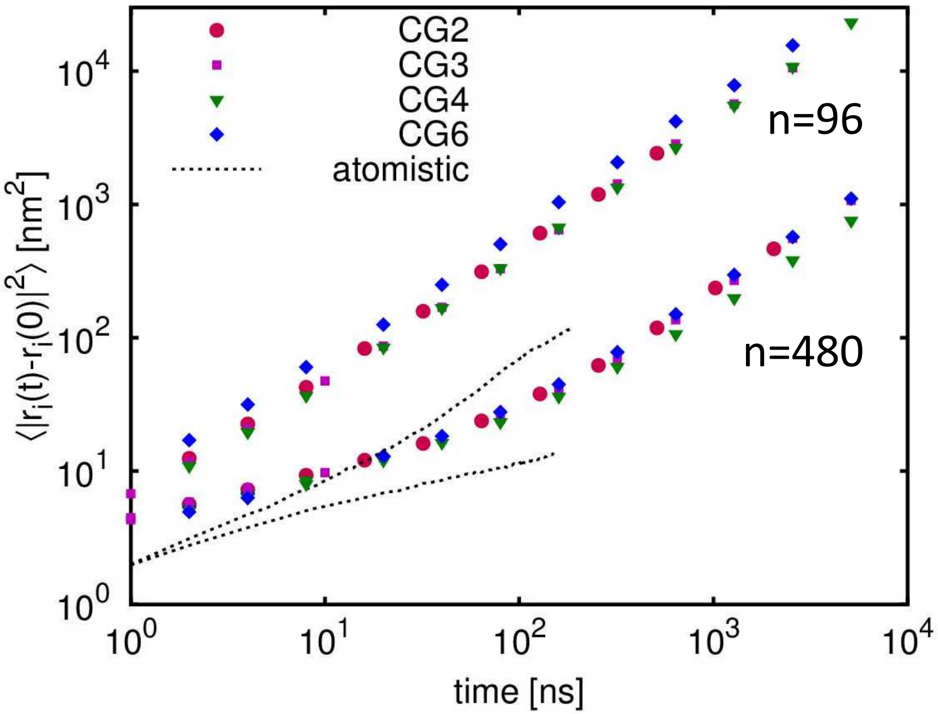
*http://lammps.sandia.gov/

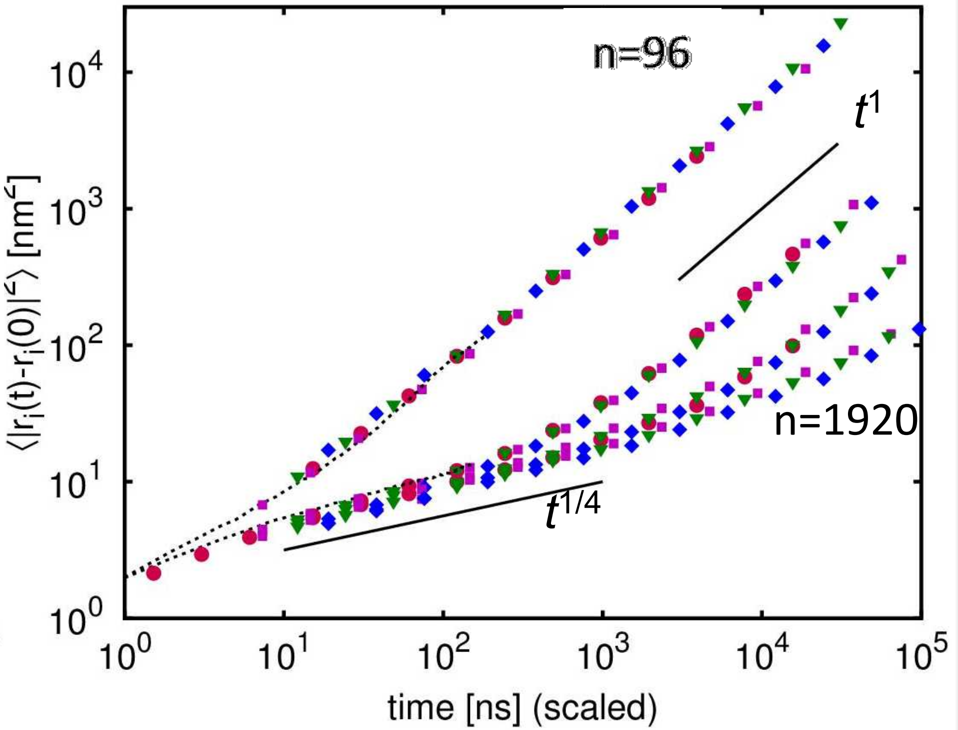
Coarse-Grained Potentials



- Average bond length increases, bond distribution broadens as level of CGing increases
- Non-bonded potential softens as level of CGing increases
- Time step increases from 1 fs to 10 -20 fs for $\lambda \geq 3$
- Surprisingly for $\lambda = 6$, chain can cut through each other
  - extra non-crossing constraint

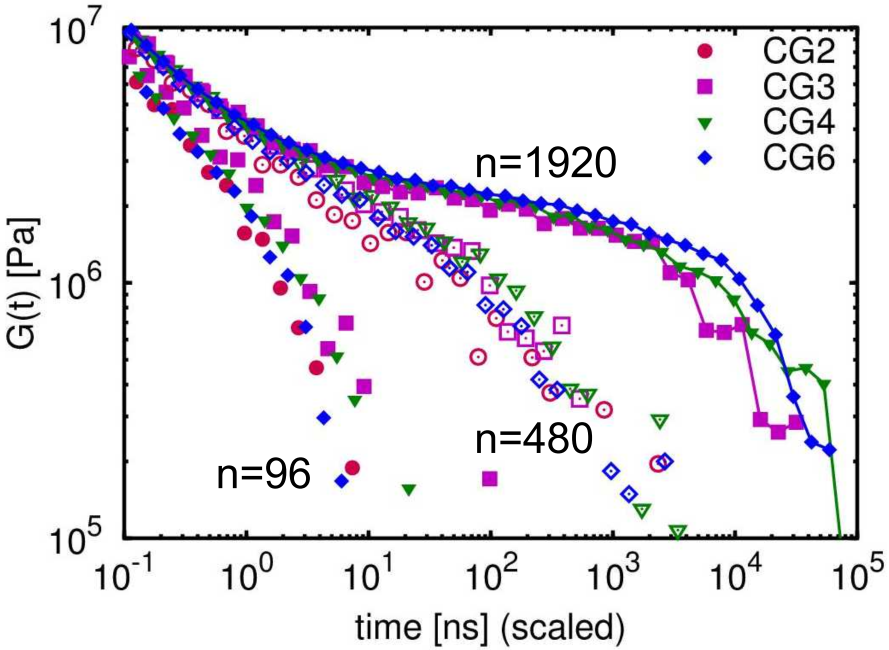
Chain Mobility





- Dynamics of Coarse Grained models 6-12 times faster
- Consistent scaling factor for n = 96 – 1920

Stress Relaxation



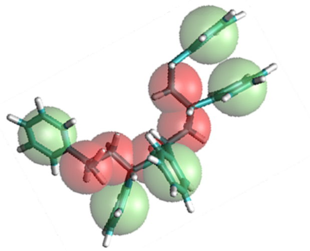
- Longer, more entangled chains form progressively more distinct plateau region
- Plateau modulus in good agreement with experiment

- Time and length scales not accessible by atomistic models

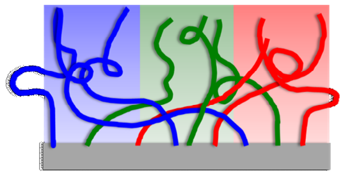
B. Peters et al, J. Chem Theory Comp 13, 2890 (2017)

Highlights

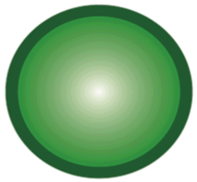
- coarse-graining polymer simulations



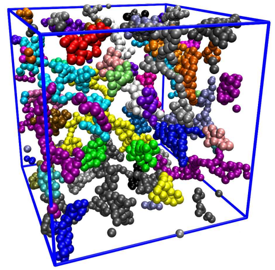
- mixed polymer brushes



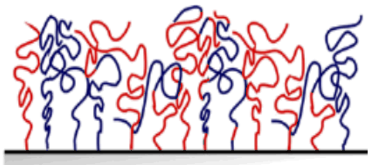
- robust polymersomes

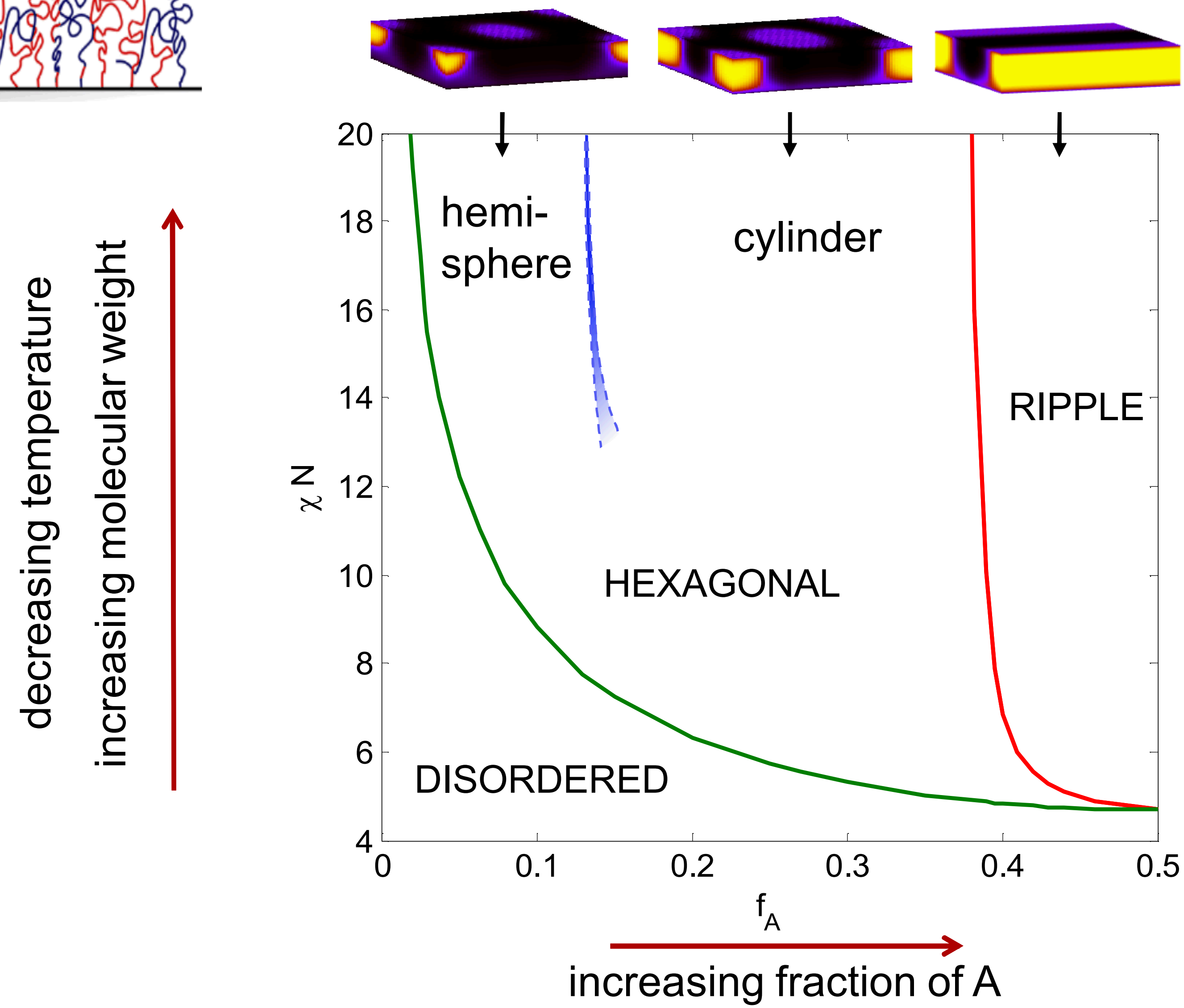


- acid and ion-containing polymers

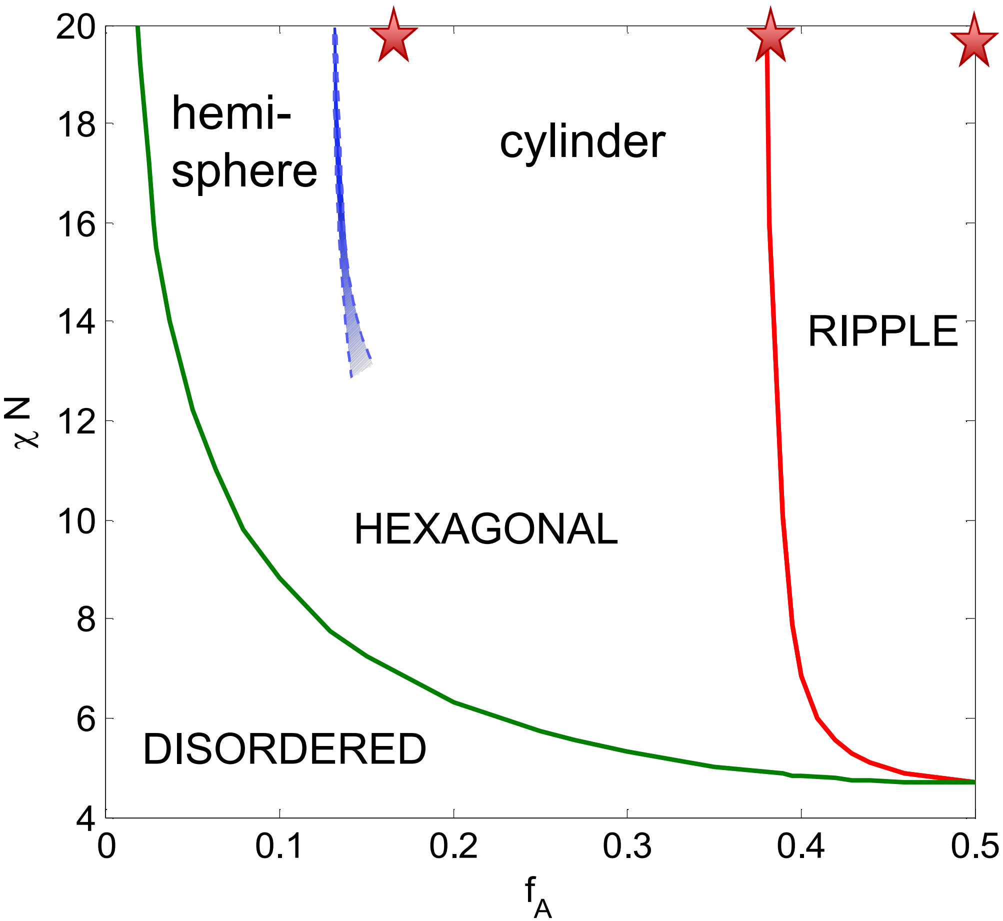


Mixed Polymer Brushes



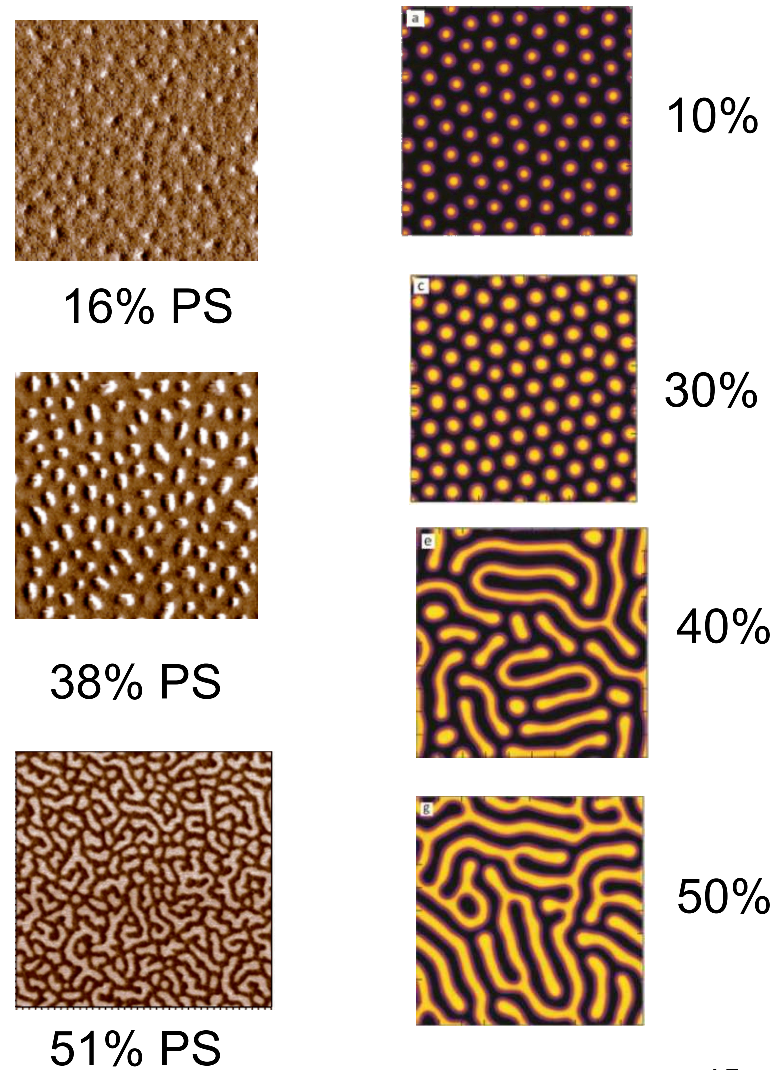


Mixed Polymer Brushes



AFM

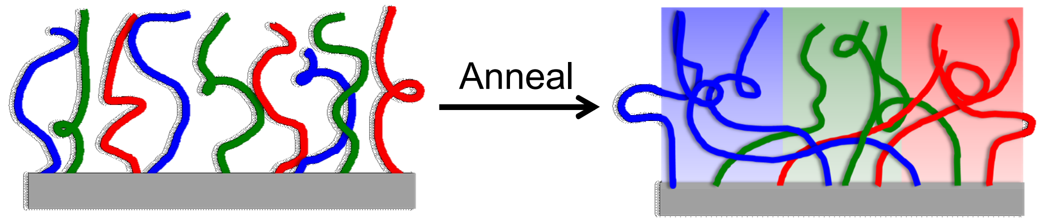
SCFT



Price et al., *Macromolecules* **45**, 510 (2012)

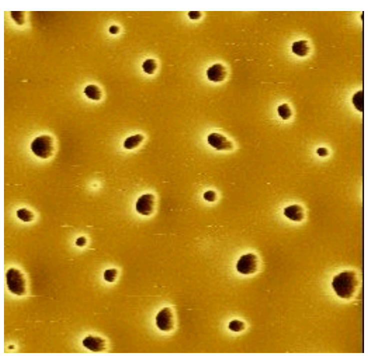
Ternary Polymer Brushes

- ternary polymer brush
- PMMA, PS, and P4VP
- Strongly segregating system
  - $\chi N_{PS\text{-}PMMA} \approx 18$
  - $\chi N_{PMMA\text{-}P4VP} \approx 65$
  - $\chi N_{PS\text{-}P4VP} \approx 320$

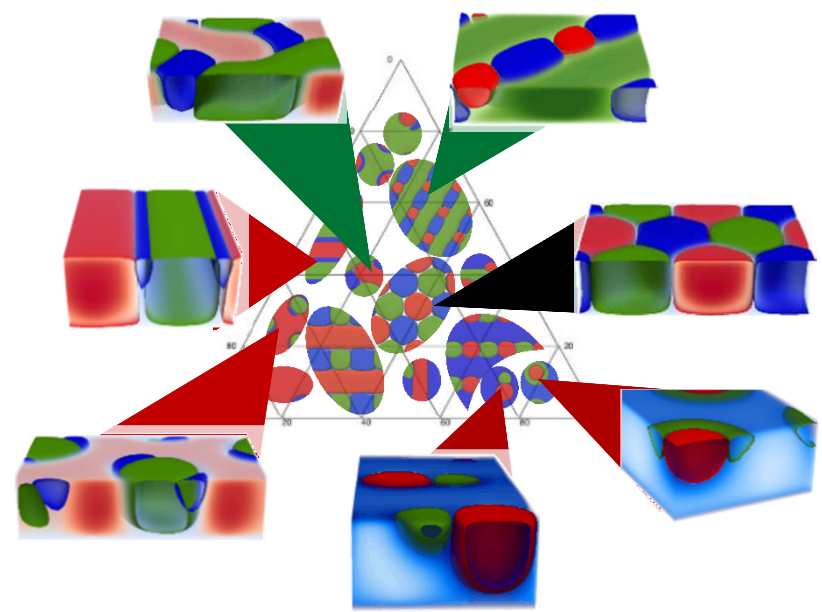


M_n: 56 – 130 kDa
brush thicknesses: 2.6 – 6 R_g
grafting density: 0.14 – 0.44 chains/nm^2

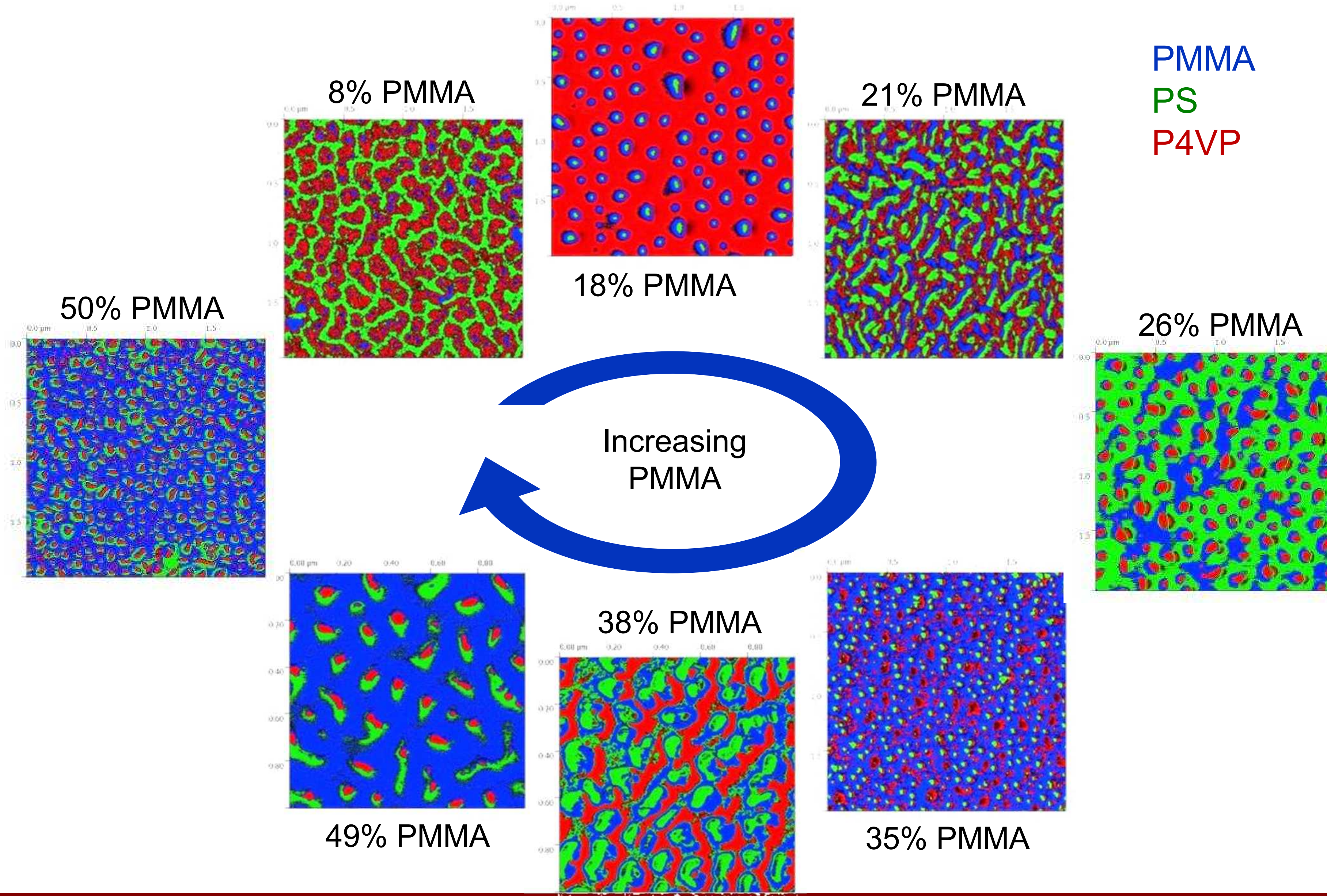
AFM phase contrast



phases predicted by SCFT

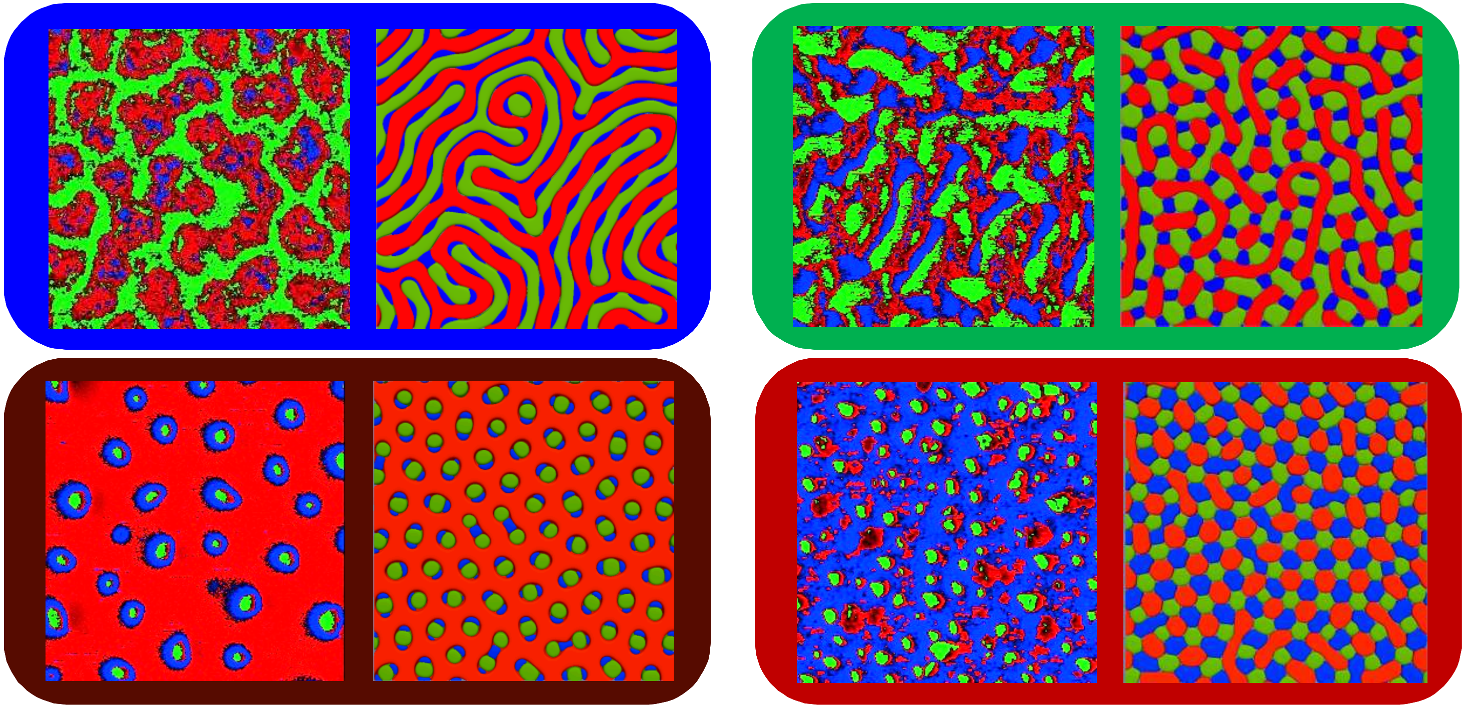


Experimental Phase Behavior



Self-Assembly: Mixed Polymer Brushes

experimental images 1x1 μm
simulation images 50x50 R_g

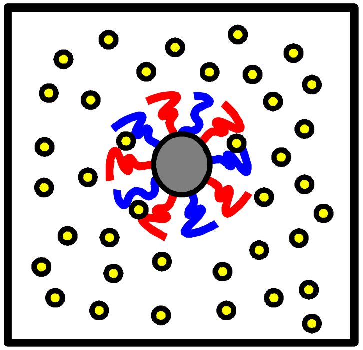


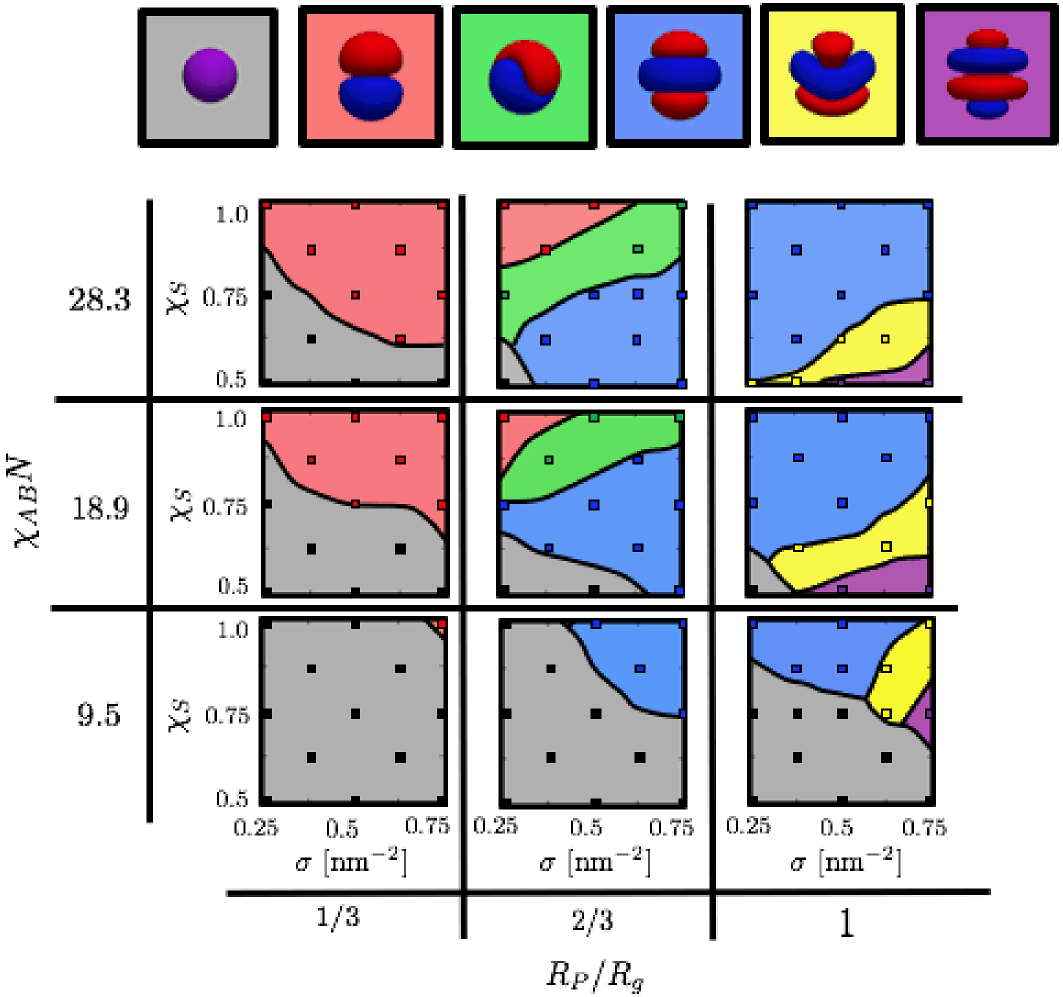
- strong lateral phase separation in mixed brushes
- qualitative agreement between theory and experiments

Simocko, Frischknecht, and Huber, *ACS Macro Lett.*, 5, 149 (2016)

Mixed brushes on nanoparticles

- A, B homopolymers on nanoparticle in solvent
- mean field theory (SCFT): phase diagram





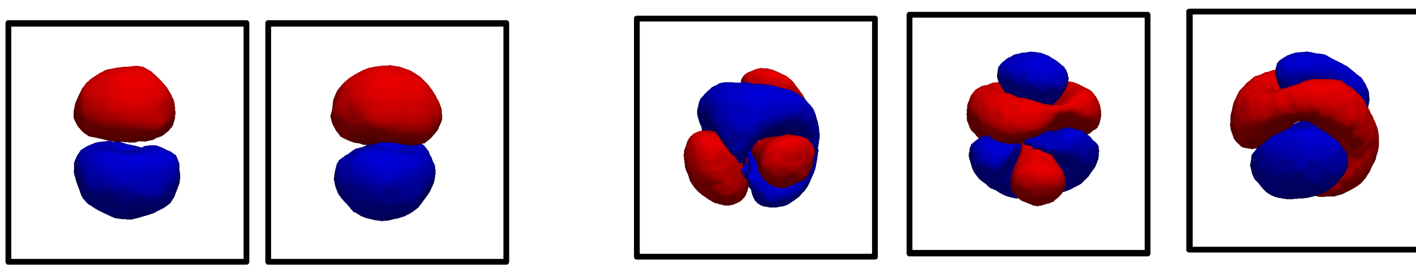
Fluctuations de-stabilize complex phases

$R_P = (1/3)R_g$

$R_P = R_g$

mean field theory (SCFT)

fluctuating field theory

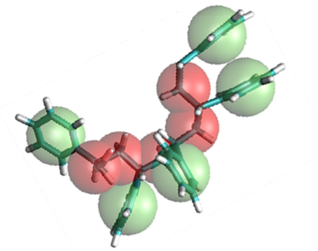


Thermal fluctuations de-stabilize the formation of complex phases

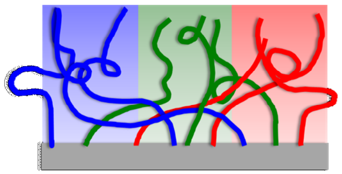
Koski and Frischknecht, in preparation

Highlights

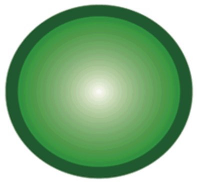
- coarse-graining polymer simulations



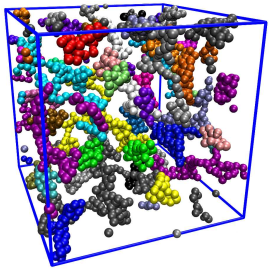
- mixed polymer brushes



- robust polymersomes

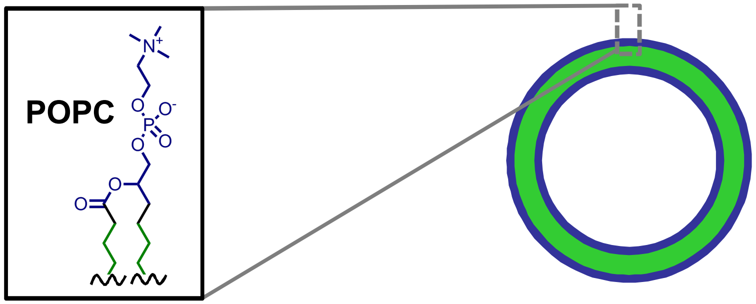


- acid and ion-containing polymers



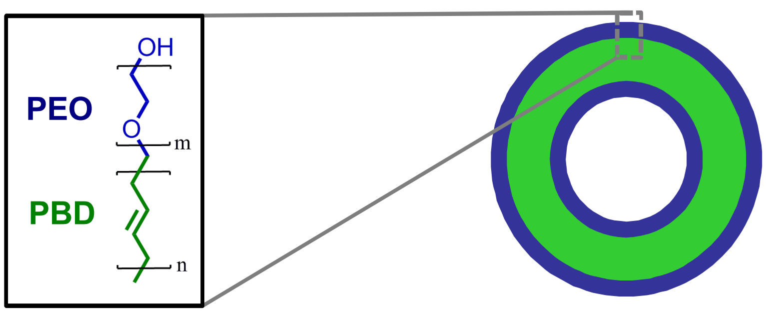
Mimicking Biological Membranes

Liposomes



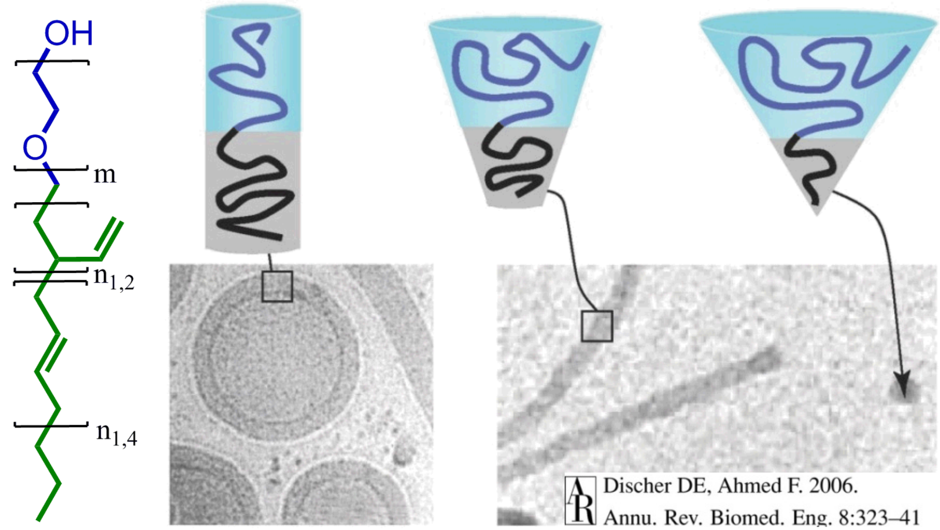
2 Major Challenges:
Limited Chemical and Mechanical Stability
Limited Modification Chemistries

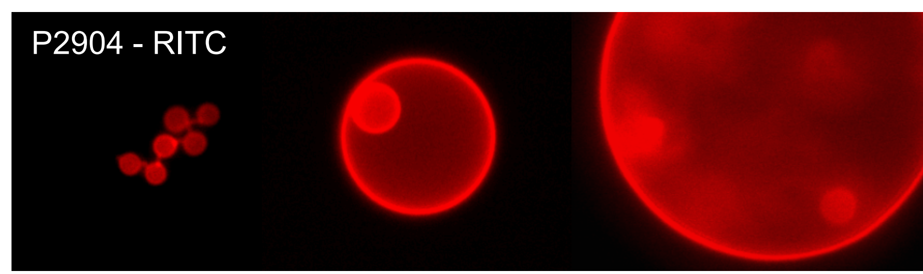
Polymersomes



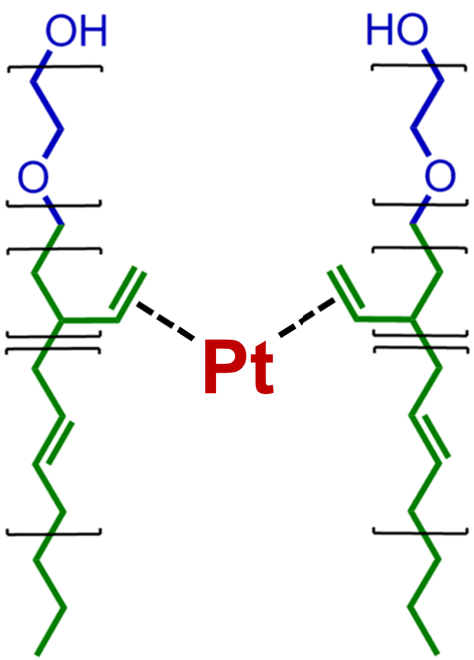
Polymersomes Can Help
Enhanced Chemical and Mechanical Stability
Unlimited Modification Chemistries

Can we incorporate or mimic **properties** and **functions** of biological cells to create robust **advanced materials**?

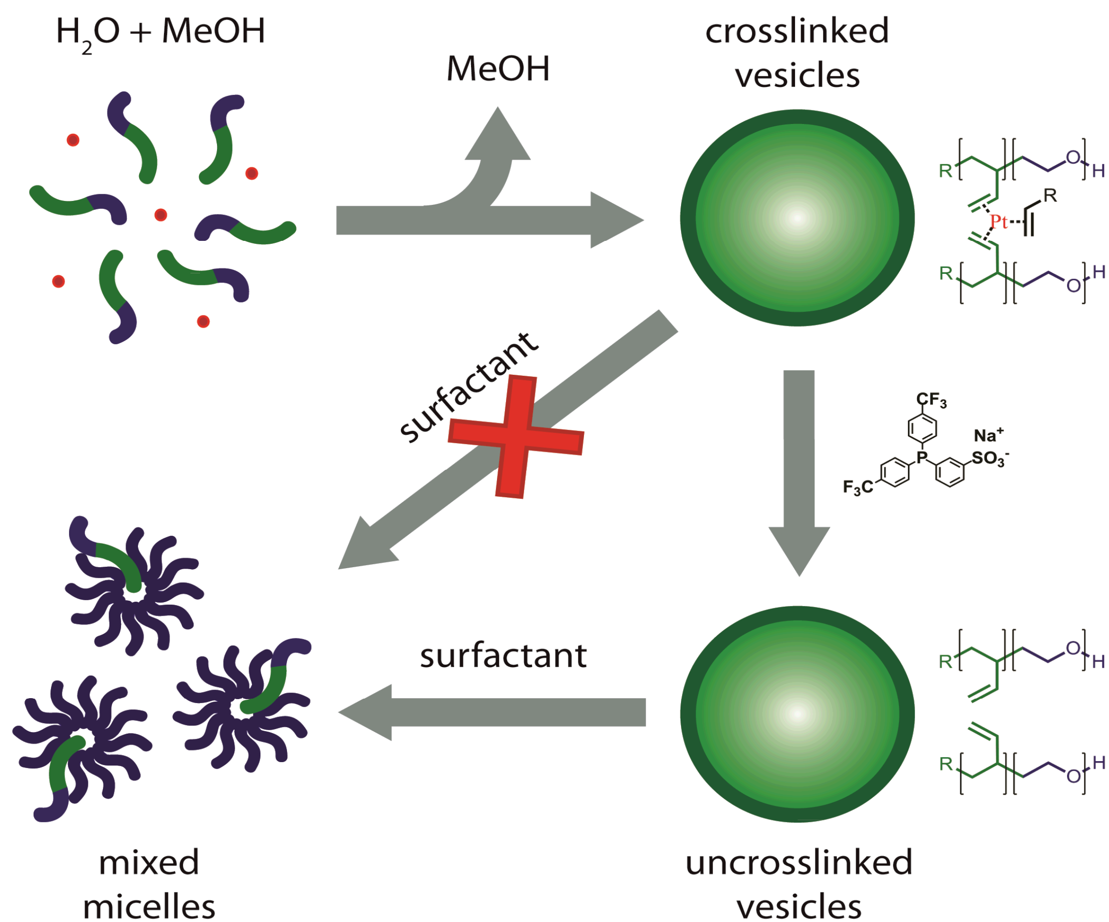




Capable Crosslinks: Polymersomes Reinforced with Catalytically Active Metal-Ligand Bonds

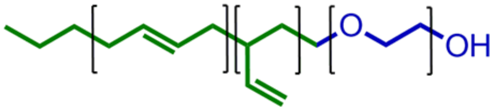


Exploit organometallic interactions to create membranes that are both ***robust*** and ***dynamic***.

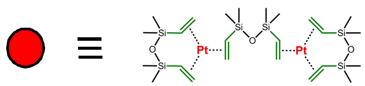


Henderson, I. M., Quintana, H. A., Martinez, J. A., & Paxton, W. F. (2015). *Chemistry of Materials*, *27*(13), 4808–4813.

Forming Cross-linked Vesicles with Pt and PEO-PBd



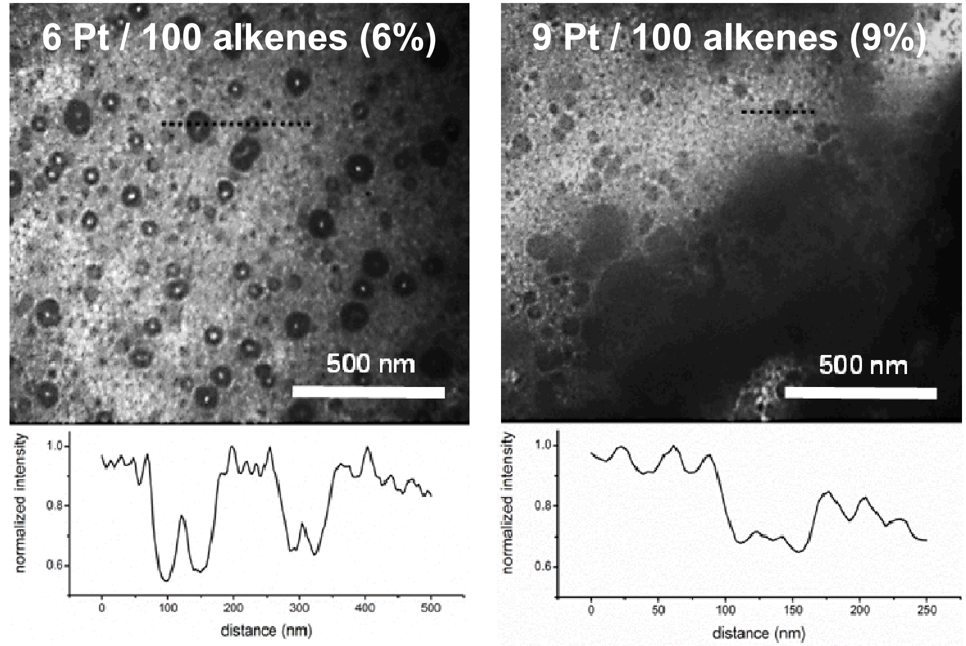
EO_{21} – Bd_{32} (1,2 addition)

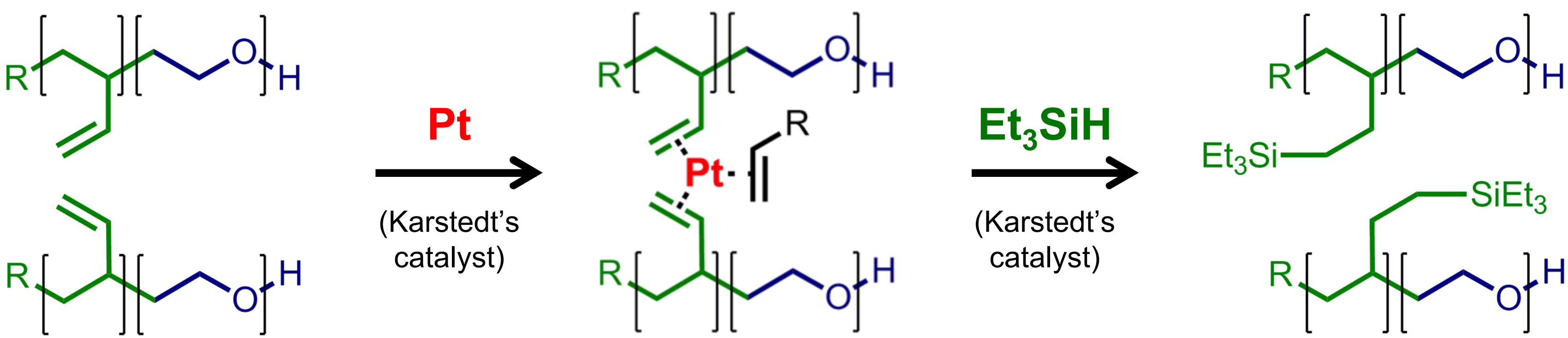


Karstedt's catalyst

60-100 nm vesicles

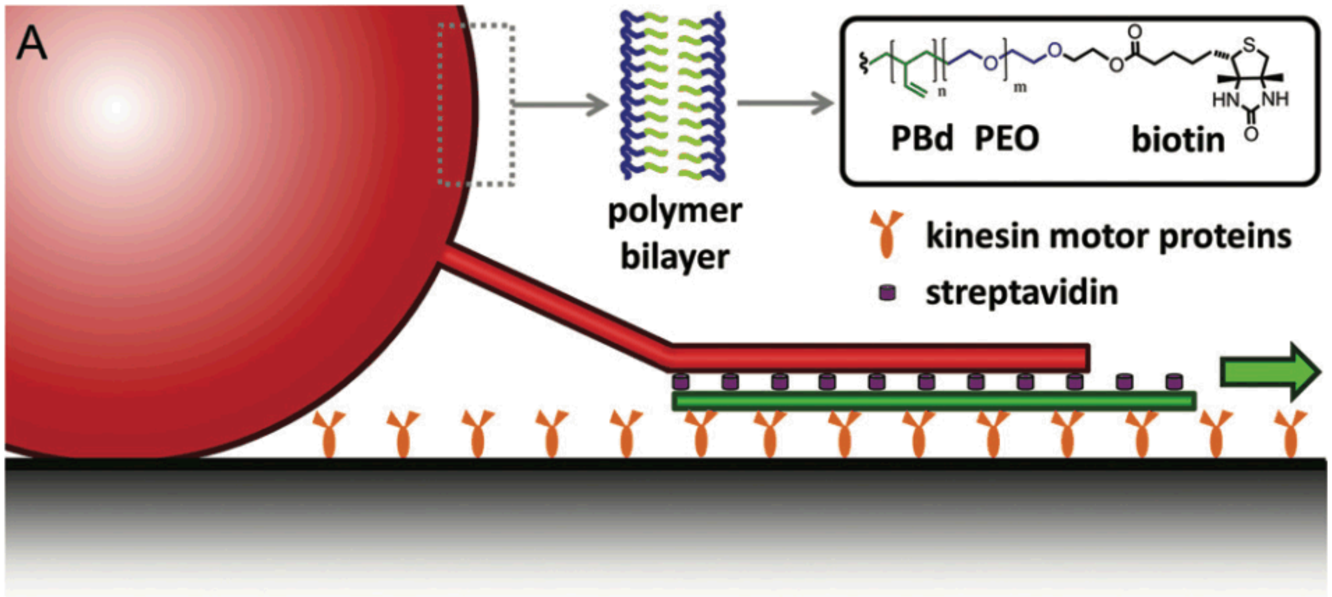
catalytically active





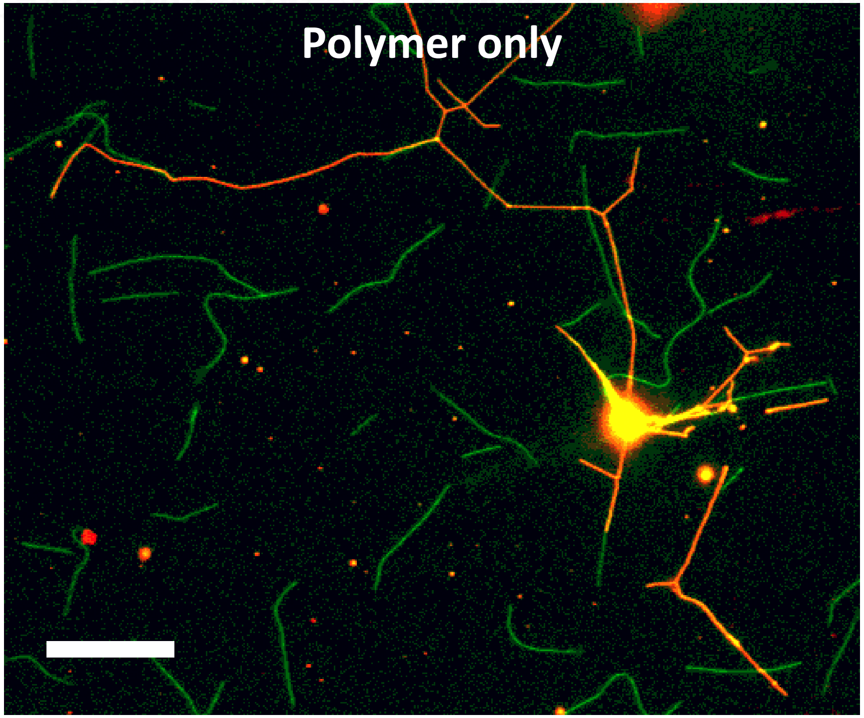
Pulling Nanotubes from Polymersomes

Can the collective force from kinesin motors extract nanotubes from polymersomes?

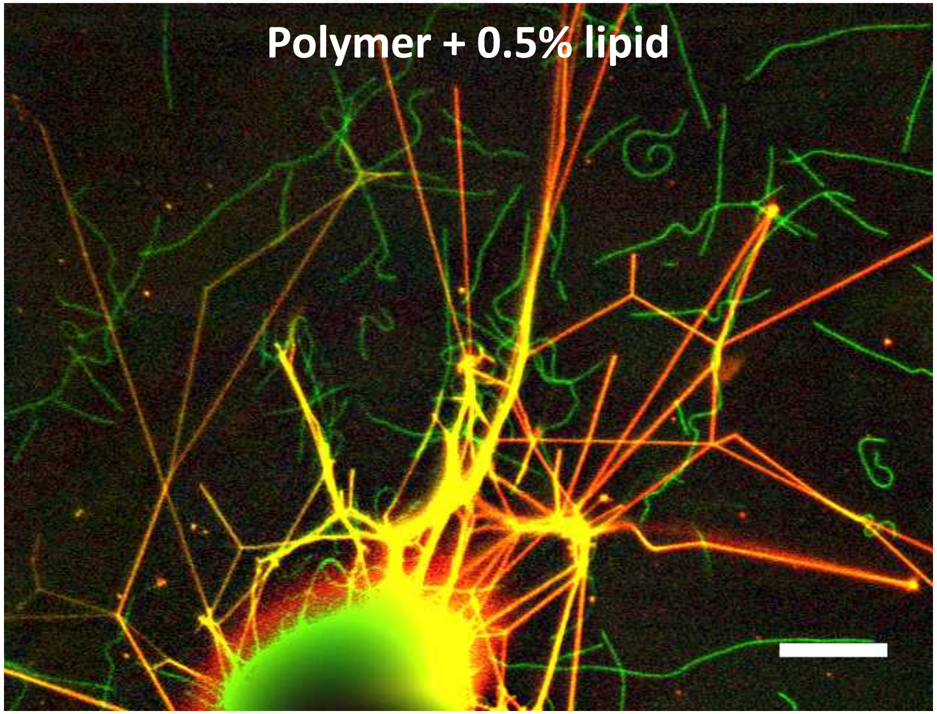


Assembly of Polymer Nanotube Networks

Yes: Addition of lipid enhances the formation of large extended networks from polymersomes.



PBD-PEO diblock copolymer



PBD-PEO + Texas Red-DHPE

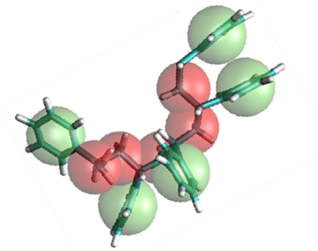
MTs, even as large as ~90 µm, extracting polymer nanotubes display decreased velocity (large opposing force)

Bousxein, et al (2015). *Nanoscale*, *7*(25), 10998–11004.

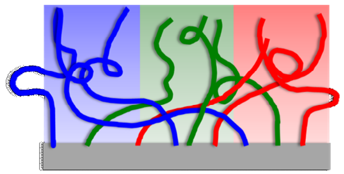
Sandia National Laboratories

Highlights

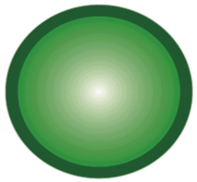
- coarse-graining polymer simulations



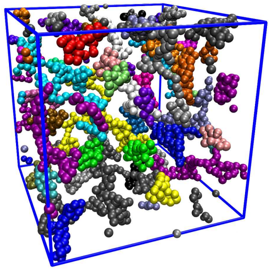
- mixed polymer brushes



- robust polymersomes



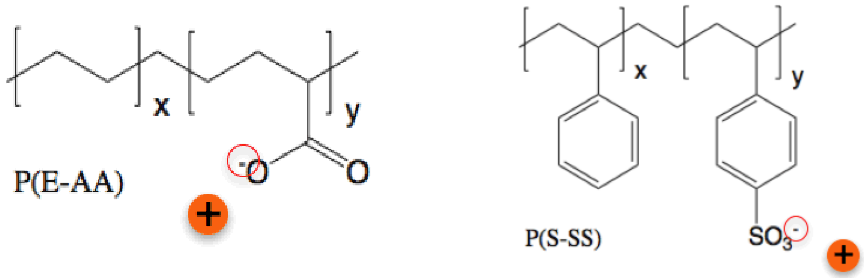
- acid and ion-containing polymers



Ion-Containing Polymers

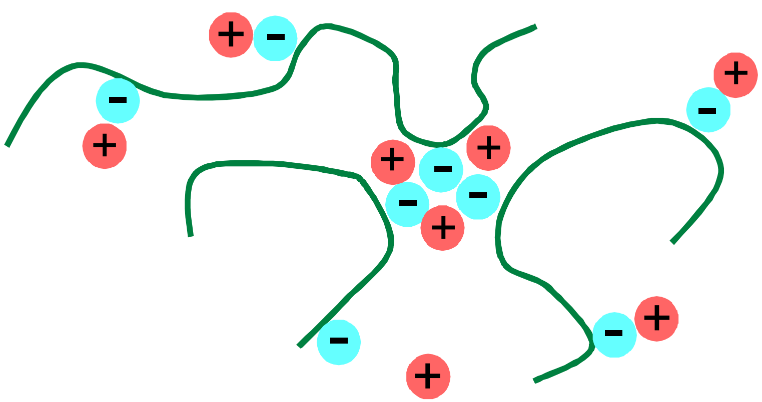
polymers with covalently-bonded ionic groups

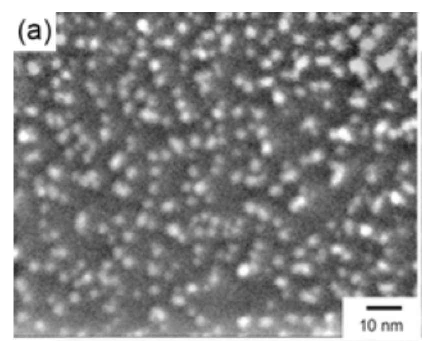
ionomers



melts! (no solvent)

nanoscale phase separation





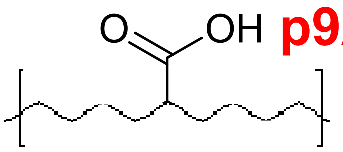
STEM showing aggregates

$PEpAA_{9.5}$-Zn56

Seitz et al., *J Am Chem Soc* 132, 8165 (2010)

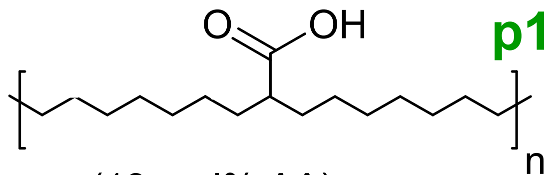
Model Materials: Precise Ionomers

p9AA



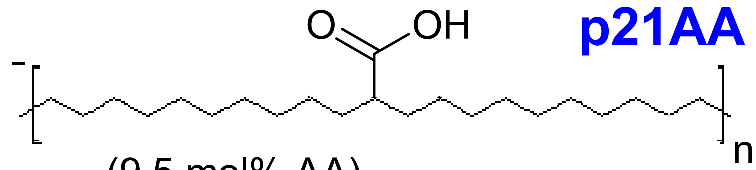
(22 mol% AA)

p15AA



(13 mol% AA)

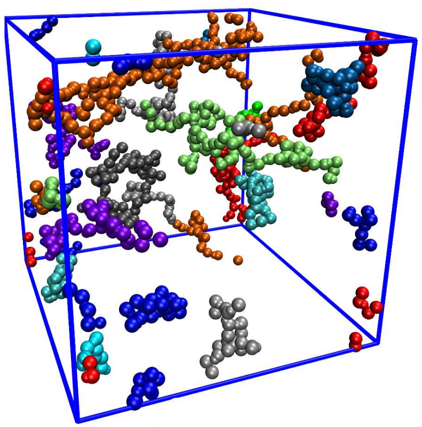
p21AA



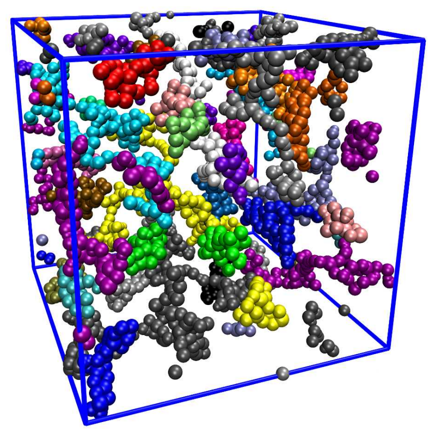
(9.5 mol% AA)

MD simulations show ionic aggregates

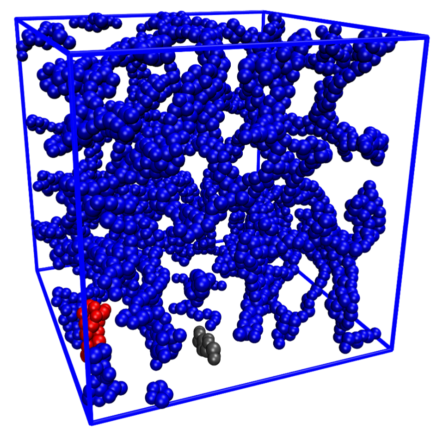
p9AA-10%Li



p9AA-43%Li



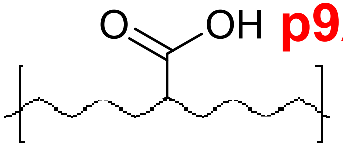
p9AA-100%Li



coloring by cluster

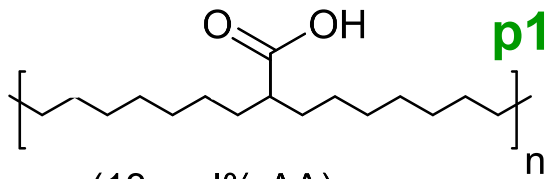
Bolintineanu, D. S., Stevens, M. J., & Frischknecht, A. L. (2013). *Macromolecules*, *46*(13), 5381–5392.

Model Materials: Precise Ionomers



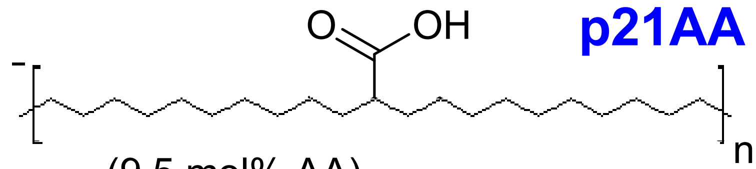
p9AA

(22 mol% AA)



p15AA

(13 mol% AA)

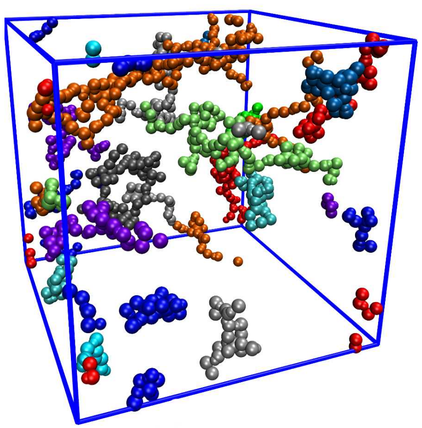


p21AA

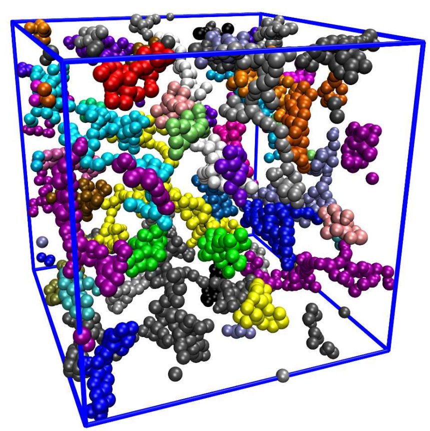
(9.5 mol% AA)

MD simulations show ionic aggregates

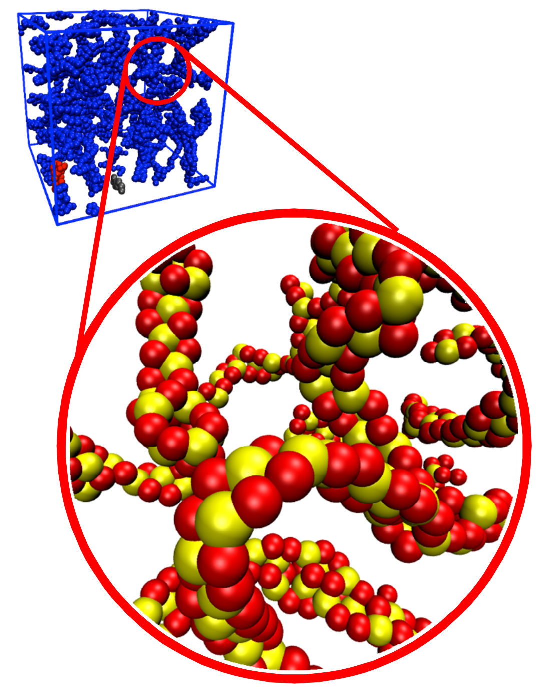
p9AA-10%Li



p9AA-43%Li



p9AA-100%Li

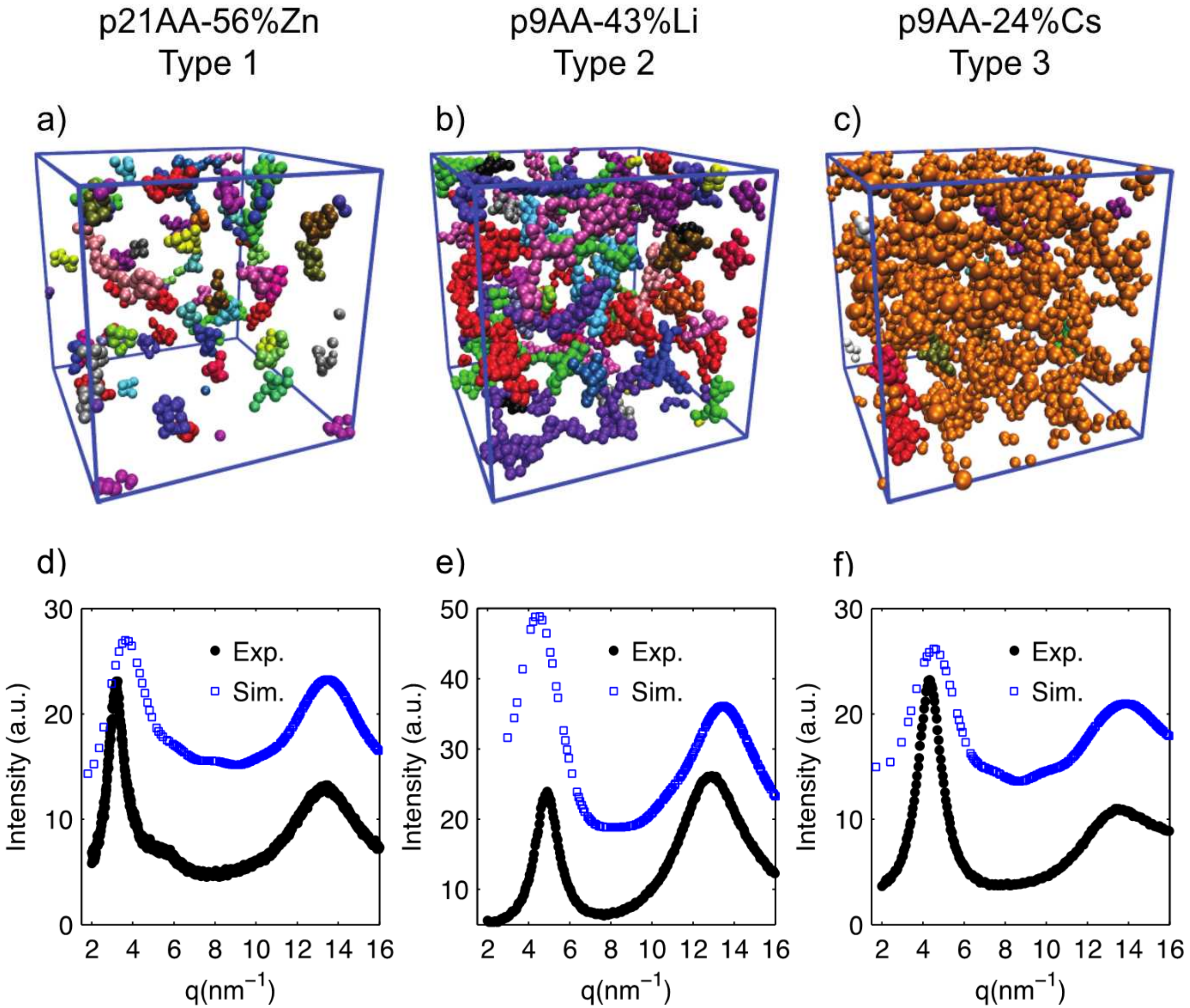


coloring by cluster

Bolintineanu, D. S., Stevens, M. J., & Frischknecht, A. L. (2013). *Macromolecules*, *46*(13), 5381–5392.

X-ray scattering compared to MD simulations

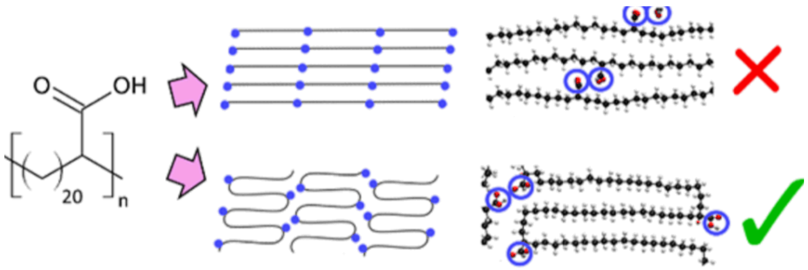
need simulations or imaging!

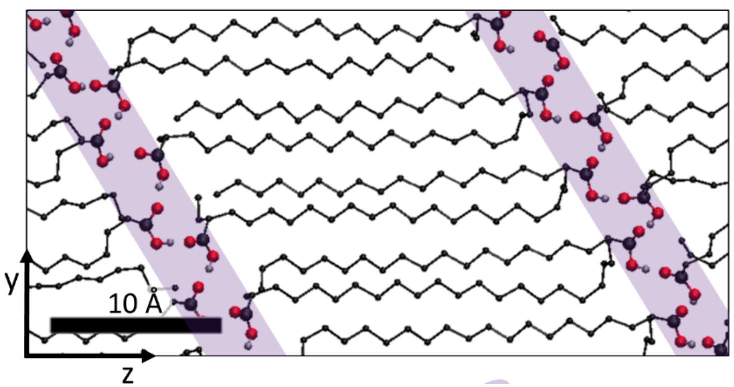


Buitrago, C. F. *et al. Macromolecules* **48,** 1210–1220 (2015).

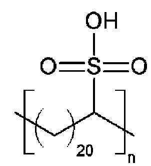
Semi-crystalline precise polymers

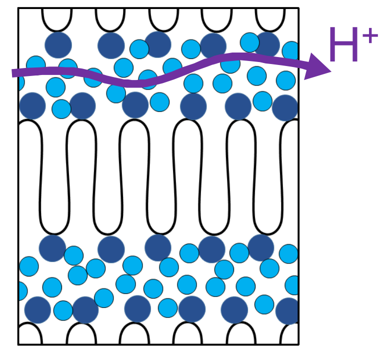
p21AA forms acid layers in crystals

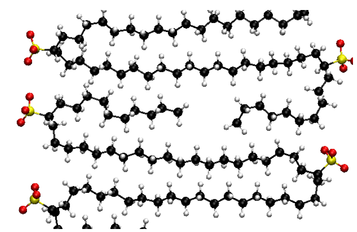


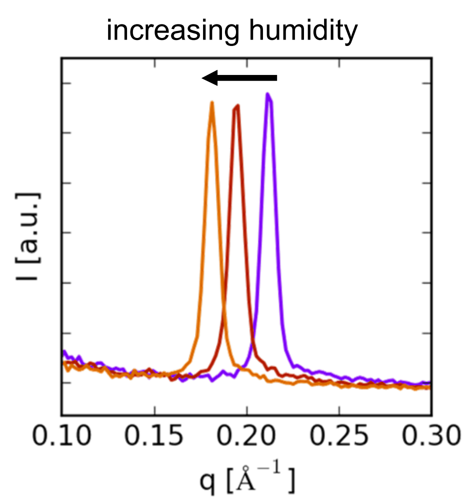


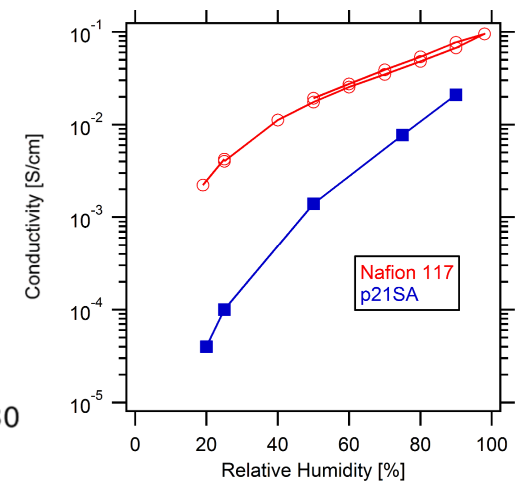
p21SA: Highly ordered, tunable, conductive









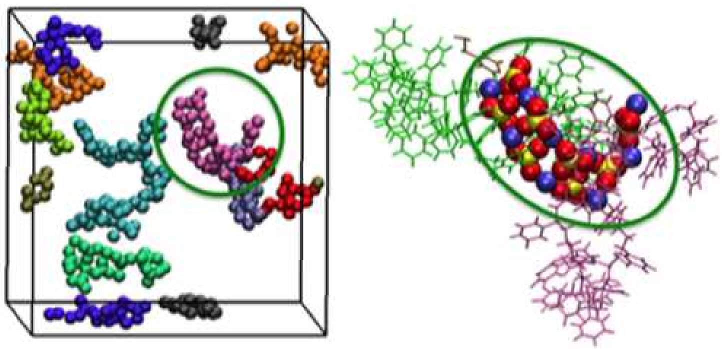


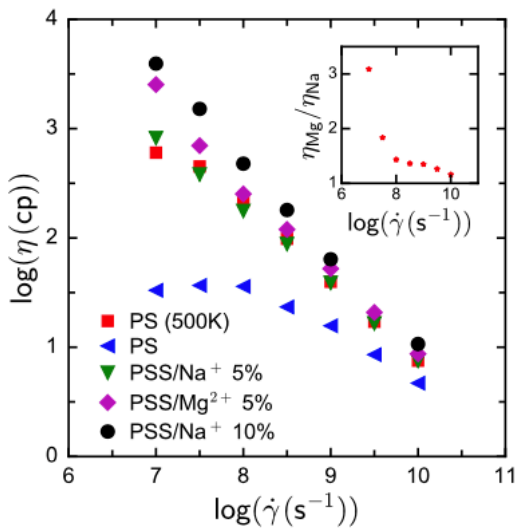
E. B. Trigg, M. J. Stevens, and K. I. Winey, *J. Am. Chem. Soc.*, **2017**

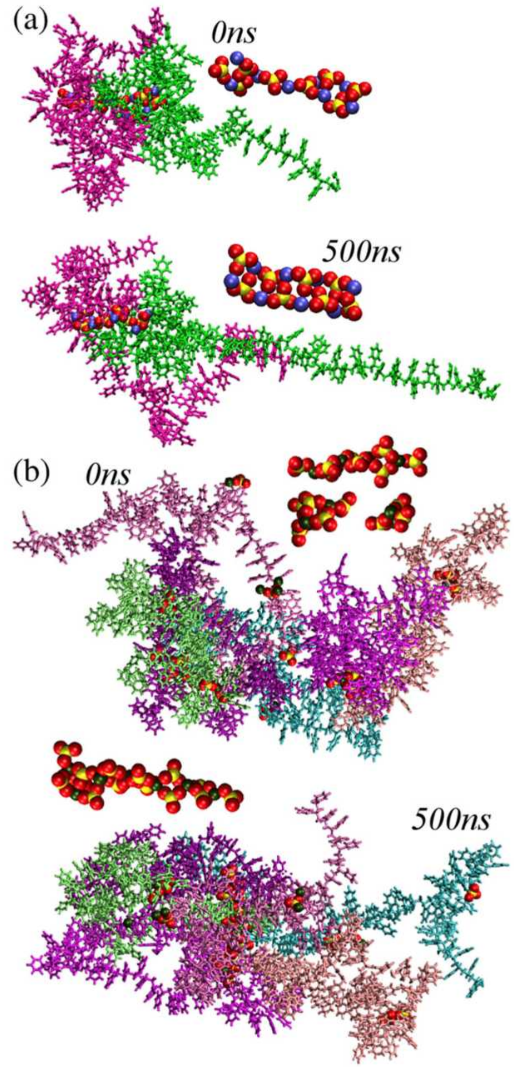
Trigg et al, in preparation

Morphology and dynamics in PSS

polystyrene sulfonate (PSS) with Na^{+} or Mg^{2+}



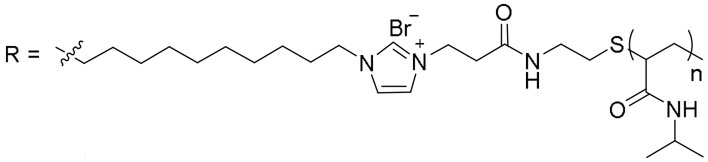


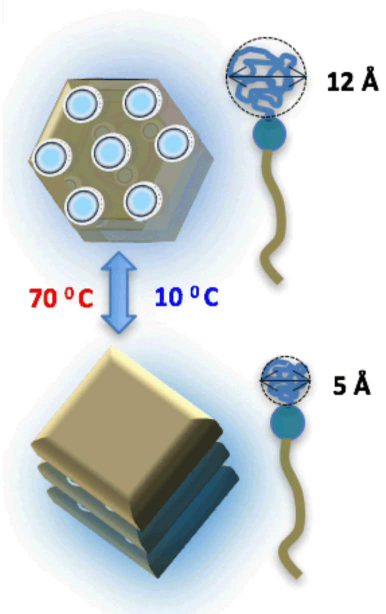


Agrawal, A., Perahia, D., & Grest, G. S. (2016), *Physical Review Letters*, *116*(15), 158001.
Agrawal, A., Perahia, D., & Grest, G. S. (2015), *Physical Review E*, *92*(2), 022601.

Novel polymers and assemblies

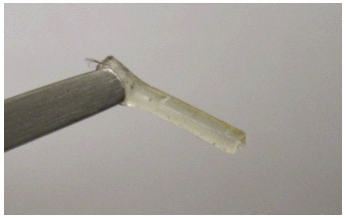
ionic liquid-PNIPAM conjugate

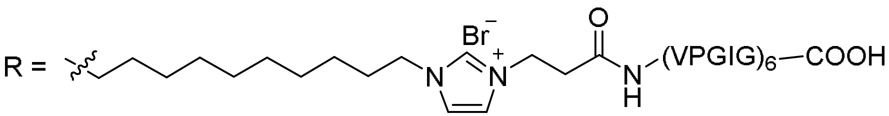




Network polymer reversibly converts from 2D hexagonal to 1D lamellar in response to modest temperature modulation

ionic liquid-elastin-like peptide conjugates



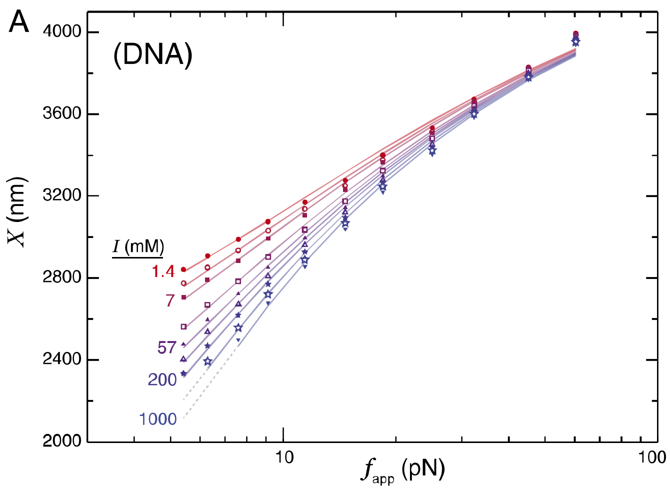


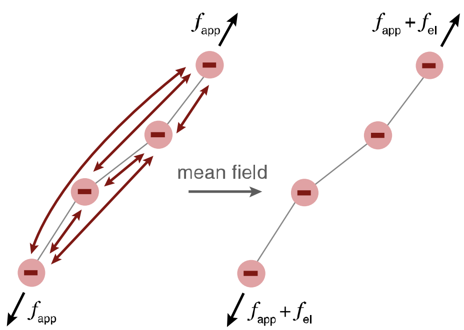
- Elastin-like polymers (VPGIG) prepared via genetically-encoded synthesis
  - precise control over sequence, chain length, architectures, dispersity
- Conjugated onto an IL for self-assembly and network polymer fabrication

PAPER ID: 2750438
Development of a new class of hybrid, hierarchical polymers that exhibit stimuli responsive properties (final paper number: PMSE 368)
DIVISION: Division of Polymeric Materials Science and Engineering
SESSION: Joint PMSE/POLY Poster Session
SESSION TIME: 6:00 PM - 8:00 PM

Biopolymers

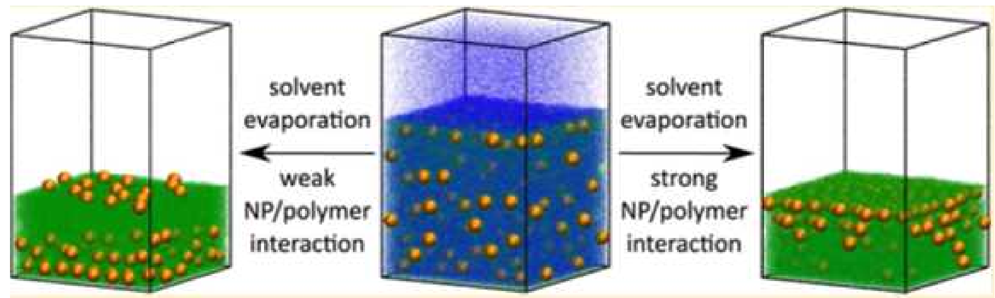
force extension of DNA





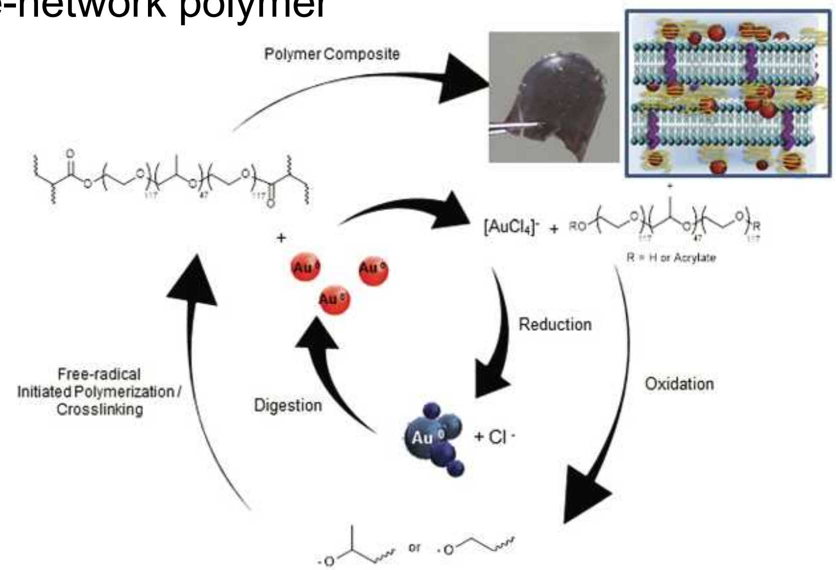
D.R. Jacobson, D.B. McIntosh, M.J. Stevens, M. Rubinstein and O.A. Saleh, *Proc. Nat. Acad. Sci.*, **2017**, *114,* 5095.

Nanocomposites



Cheng, S., & Grest, G. S. (2016). ACS *Macro Letters*, *5*(6), 694–698.

cascade synthesis of gold nanoparticle-network polymer composite



Ringstrand, B. S. et al, (2016). *Nanoscale*, *8*, 2601–2612

Acknowledgments

CINT

George Bachand
Millie Firestone
Gary Grest
Dale Huber
Jennifer Martinez
Wally Paxton
Mark Stevens

Dan Bolintineanu
Nathan Bousxein
Ian Henderson
Jason Koski
Harsha Magurudeniya
Julio Martinez
Brandon Peters
Andrew Price
Hope Quintana
Michael Salerno
Chet Simocko

CINT users mentioned

Glenn Fredrickson, UCSB
Dvora Perahia, Clemson
Omar Saleh, UCSB
Karen Winey, U Penn

BES Core program

Center for Integrated Nanotechnologies

Los Alamos NATIONAL LABORATORY

U.S. DEPARTMENT OF ENERGY | Office of Science

Sandia National Laboratories

Capabilities/Expertise at CINT

theory and modeling

- MD simulation (LAMMPS)
- classical density functional theory (Tramonto)
- polymer field theory

experiment

- synthesis
    - surface-initiated polymerization
    - microfluidics for controlled NP synthesis
- polymer characterization
- TEM