SAND2013-0429P

Simulation of Ionic Aggregation and Ion Dynamics in Ionomers

Amalie L. Frischknecht

January 24, 2013

Sandia National Laboratories

Exceptional service in the national interest

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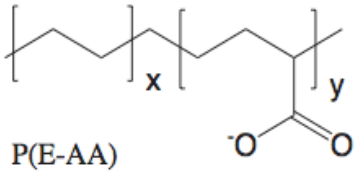
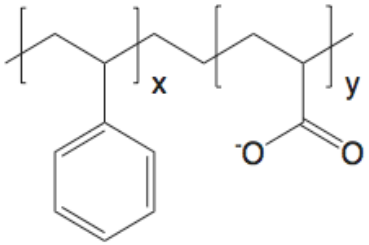
What is an ionomer?

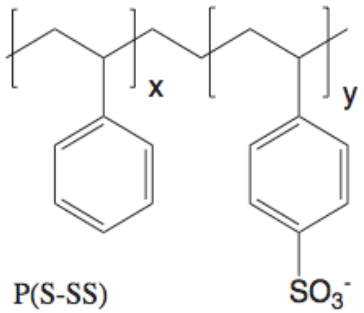
a copolymer
with a small fraction
of covalently-bonded ionic groups



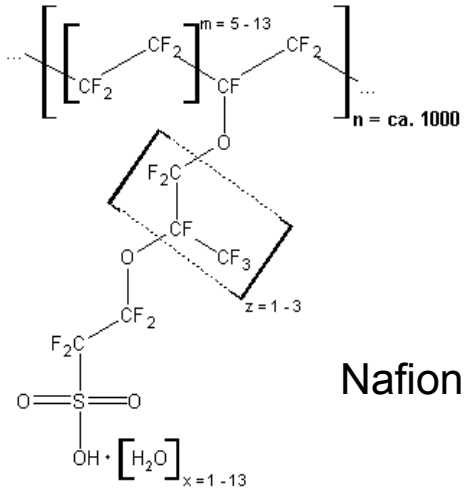
P(E-AA)



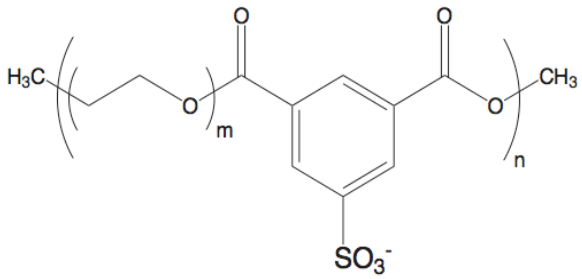
P(S-MAA)



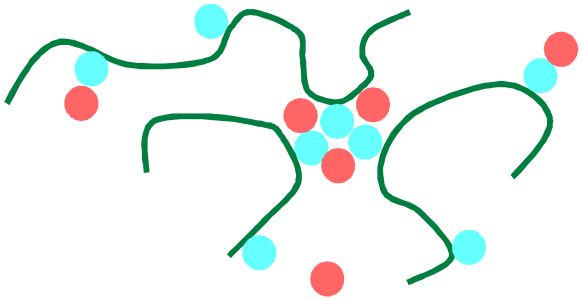
P(S-SS)



Nafion™

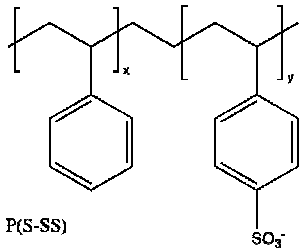


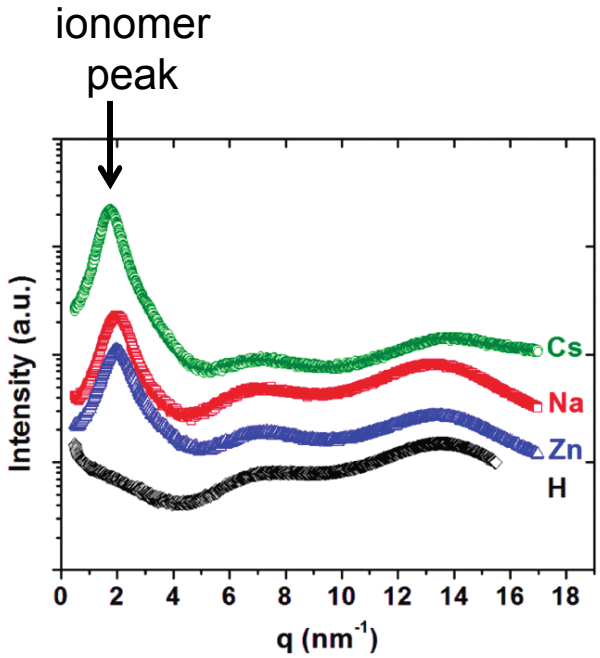
Aggregates in Ionomer Melts



"ionomer peak"
- ubiquitous
- low wavevector peak in scattering
- from inter-aggregate scattering

Coulombic forces favor aggregates
strong pair energy, ≈ 40 kT
polymer entropy limits size





A. M. Castagna, et al. *Macromolecules*, **2011,** 44, 5420

Applications of Ionomers

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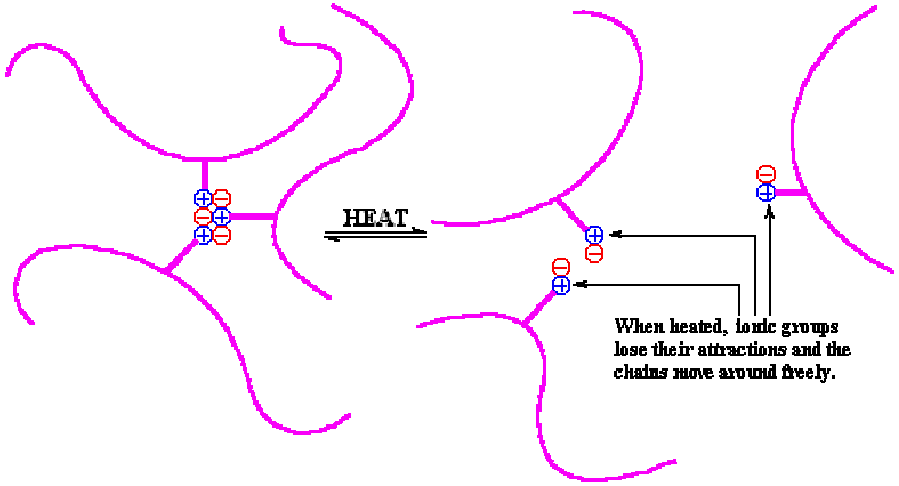
thermoplastic elastomers



- low T: ionic aggregates behave like crosslinks
  - material is elastic
  - high strength
- high T: ionic aggregates break up
  - material flows (is a liquid)

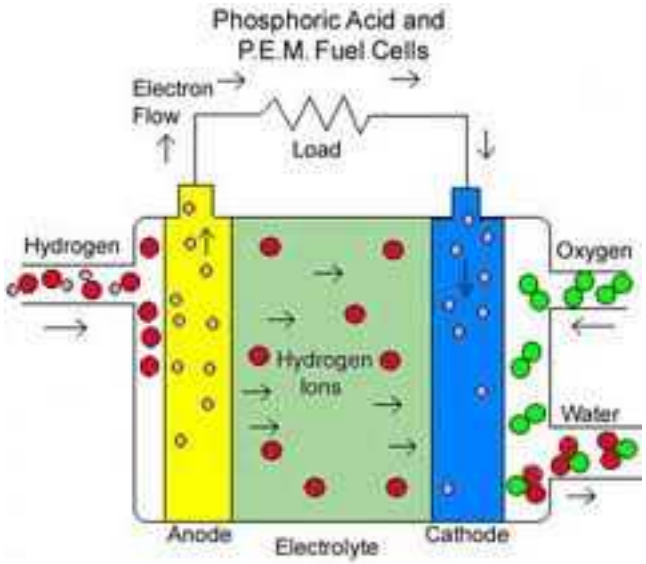
- golf balls: covers, mantles, intermediate layers, …
- coatings
- packaging (e.g. foods, cosmetics, …)
- clear plastic parts
- modifiers in other plastics

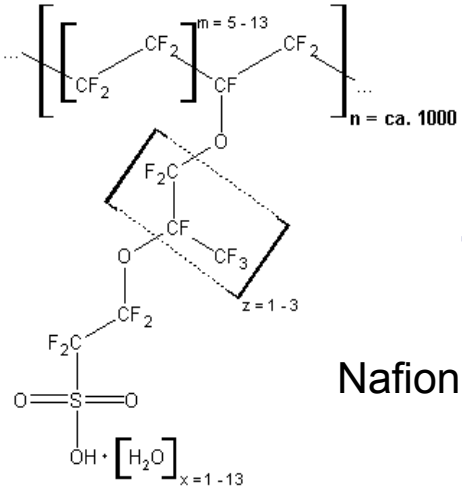
DuPont™ Surlyn®

Membranes

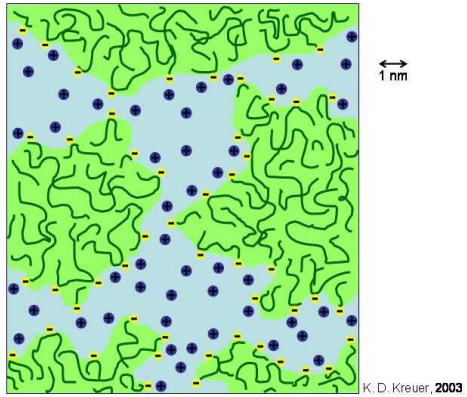
ion-selective membranes
typically in water

- water purification
- fuel cells





Nafion™



Possible Application: Batteries

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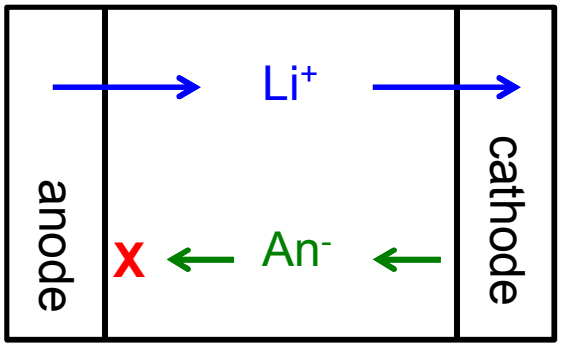
Issues with current electrolytes in Li-ion batteries:

- organic solvents
- PEO + lithium salts + solvent
  - need containment
  - flammable!

- solvent free PEO + salt
  - conductivity dominated by anions
  - salt concentration at electrodes
  - extra heating



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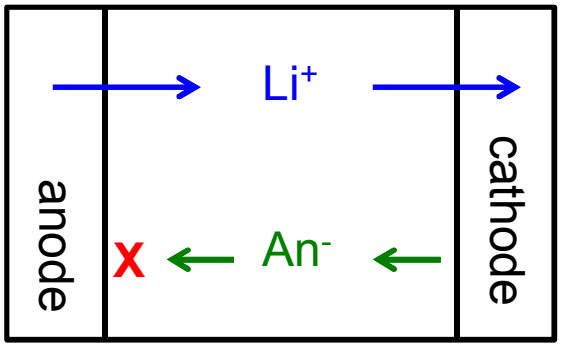
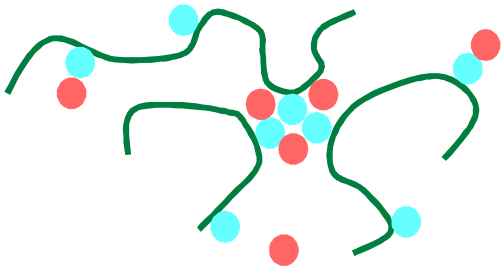


ionomers as next generation electrolytes?

- safer: no solvent
- serve as electrolyte & separator
- less packaging
- improved electrochemical stability
- higher efficiency: single ion conductors

Ionomer Conductivities



- conductivity too low
  - needed for Li-ion batteries: ≥ 10^{-3} S/cm
  - Li salt + solvent: ≈ 10^{-2} S/cm
  - gel polyelectrolytes: 1-3 10^{-3} S/cm
  - ionomers: generally < 10^{-5} S/cm

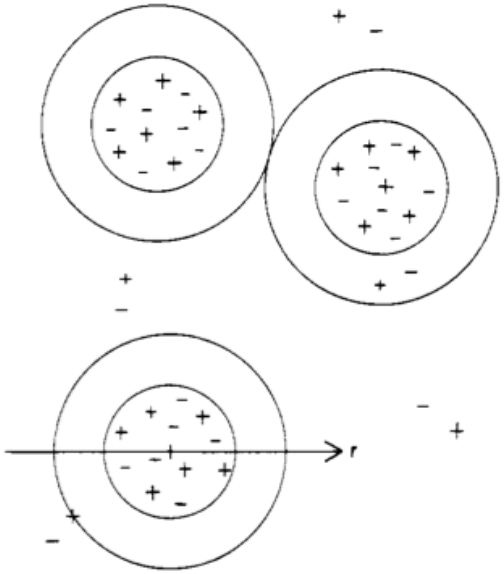
- why?
  - few mobile ions (ion pairs instead)
  - often get ionic aggregates

Need for electrochemical apps:

- relation between molecular architecture & morphology
- effects of morphology on ion transport
- understanding of ion transport mechanisms

Historical View of Ionomer Melts

- spherical ion-rich aggregates
- surrounded by ion-poor polymer
- arranged with liquid-like order



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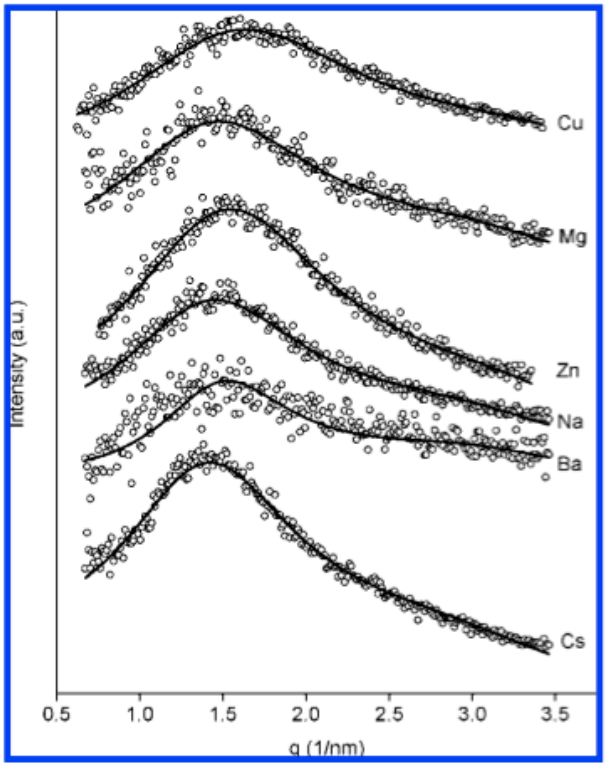


PSS ionomers

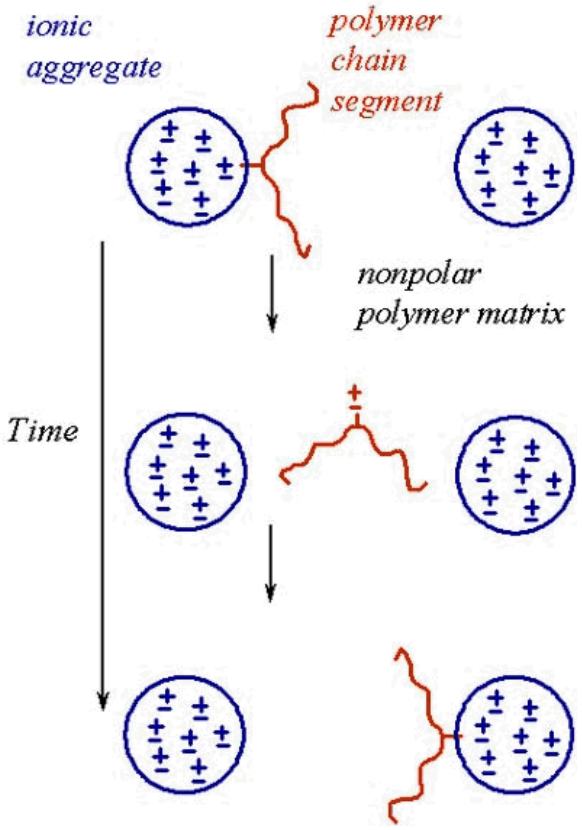
Zhou et al. Macromolecules (2008) vol. 41 (16) pp. 6134-6140

D. J. Yarusso; S. L. Cooper; *Polymer* **1985,** 26, 371-378.

Historical View of Dynamics

- requires traversing low dielectric polymer matrix
- large activation energy barrier
- ion **pairs** “hop” between aggregates

this is SLOW

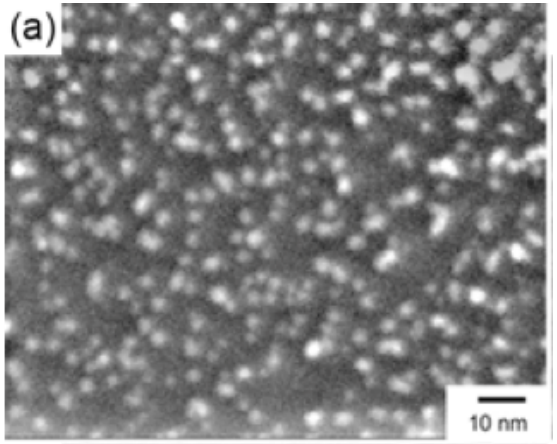


http://www.princeton.edu/cbe/people/faculty/register/group/research/ionomers/ionomer-melt-rheology-and/

Outstanding Questions

- What do the aggregates look like, exactly?
  - composition
  - size
  - shape
- What's the dependence on polymer architecture?
  - spacing between charged groups
  - cations
  - anions
- How does ion association affect dynamics?

spherical aggregates



Karen Winey
U Penn

Difficult to measure local structure experimentally.

Can simulations resolve issue?

New Materials

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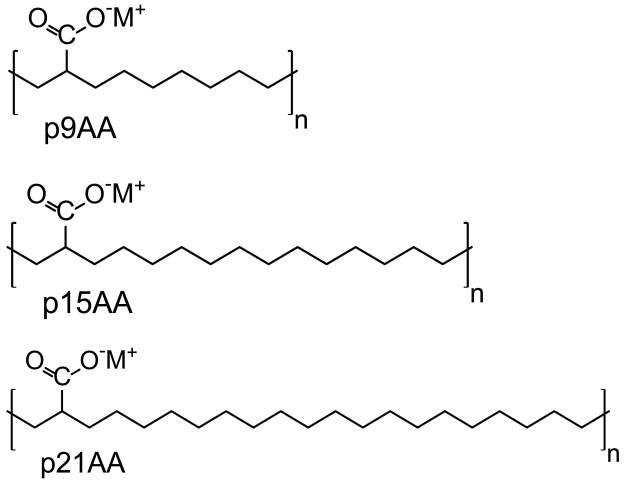
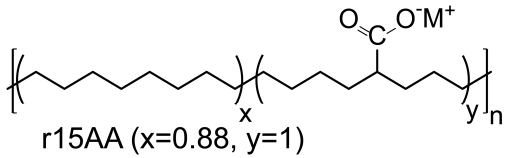
Acyclic Diene Metathesis (ADMET) Precise Copolymer



Ring-Opening Metathesis Polymerization (ROMP) Pseudo-Random Copolymer



r15AA (x=0.88, y=1)

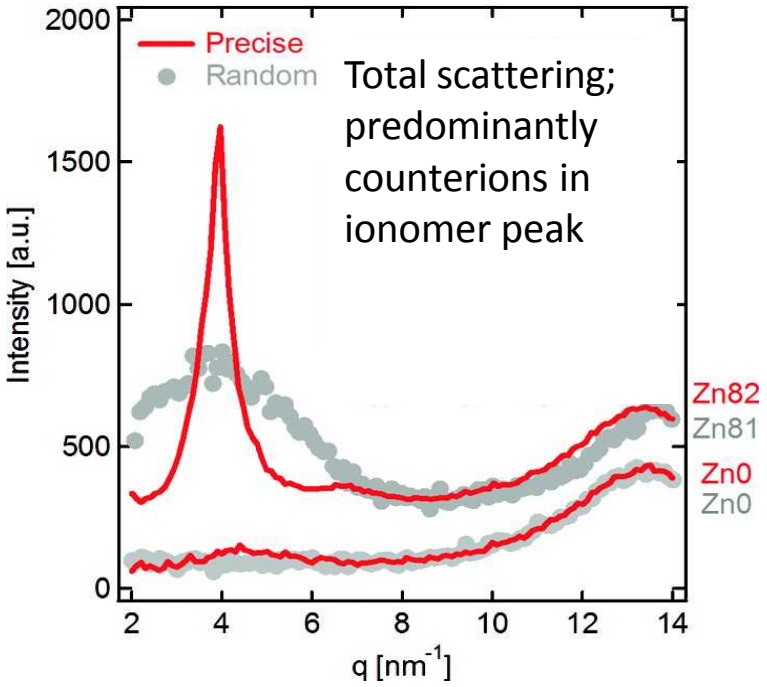
precise polymers:

- acid group every 9, 15, 21 carbons
- swap H for Zn^{2+}, Li^{+}, Na^{+}, Cs^{+}
- nomenclature: pxAA-y%M

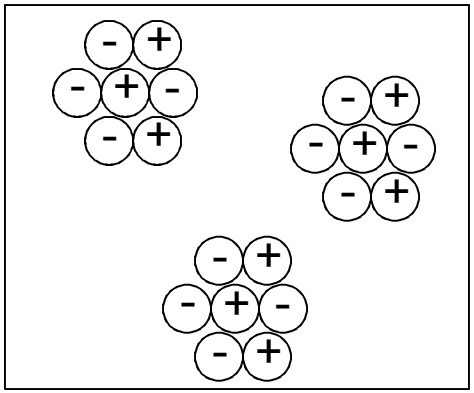
Ken Wagener,
University of Florida

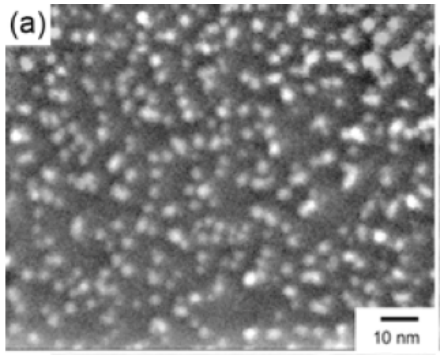
Zn-neutralized Precise Ionomers

much more defined peak from precise ionomers
ideal for comparison to simulation

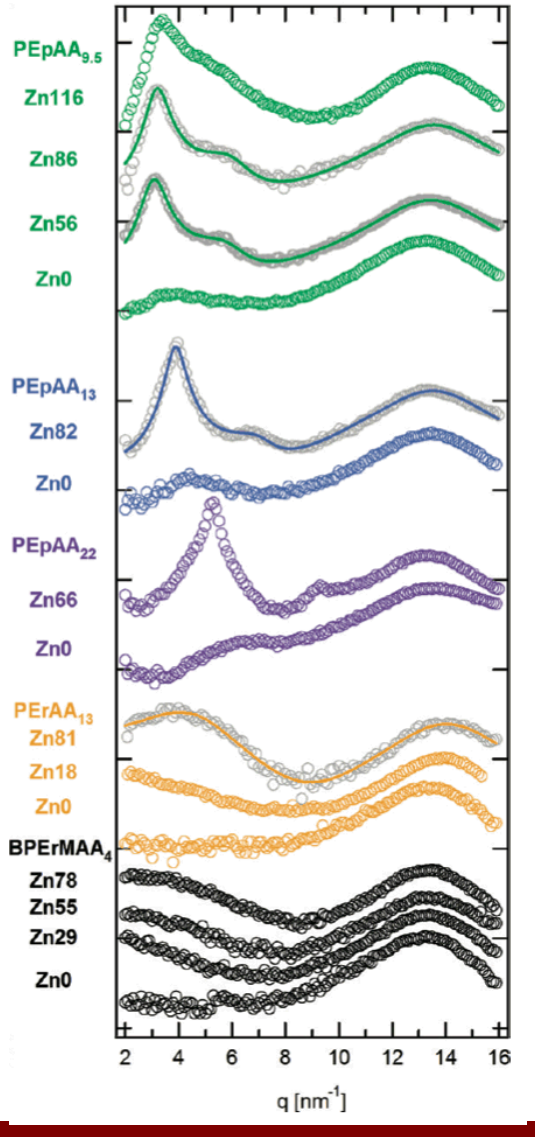


modified hard sphere model





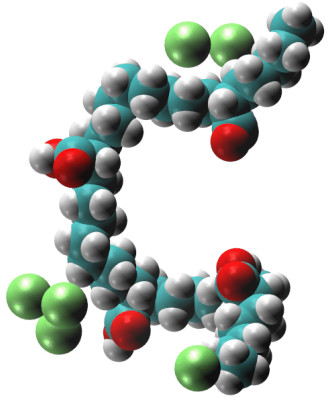
p21AA-56%Zn



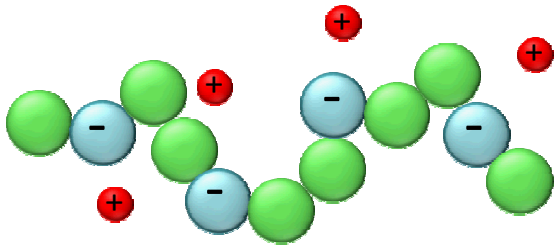
M. E. Seitz et al., *J. Am. Chem. Soc.* **2010,** 132, 8165-8174.

Outline

- atomistic simulations
  - varying cations: Li^+, Na^+, Cs^+, Zn^{2+}
  - varying neutralization
  - compare directly to experiment
  - limited dynamics

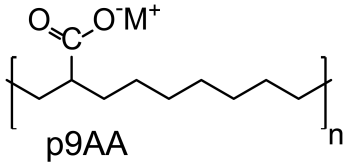


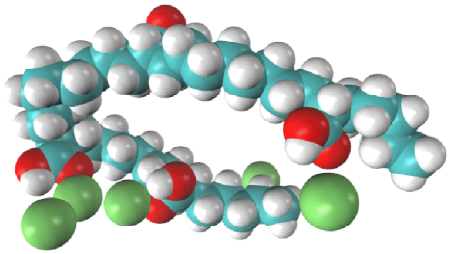
- coarse-grained simulations
  - morphology
  - dynamics



Atomistic Ionomer Simulations

- pAA materials:



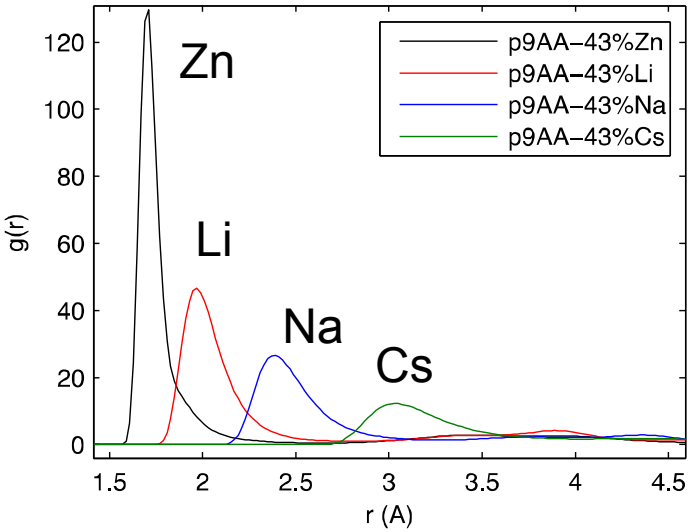


- Variations in:
  - cation type: M^+ = Li^+, Na^+, Cs^+, Zn^{2+}
  - neutralization level = % COO^-M^+ vs COOH
  - spacing between acid groups
- All atom OPLS force-field
- n = 4 repeat units (4 acid groups)
- ~ 64 Å box, total of ~25,000 atoms
- T = 150 C

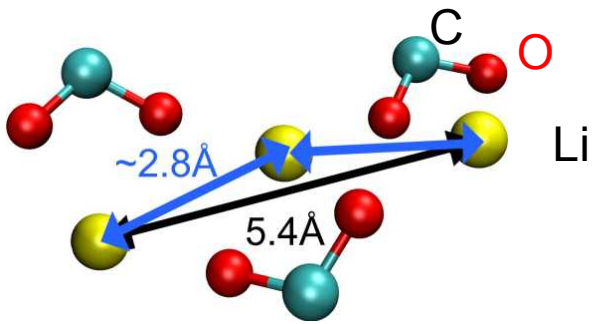
Correlation Functions

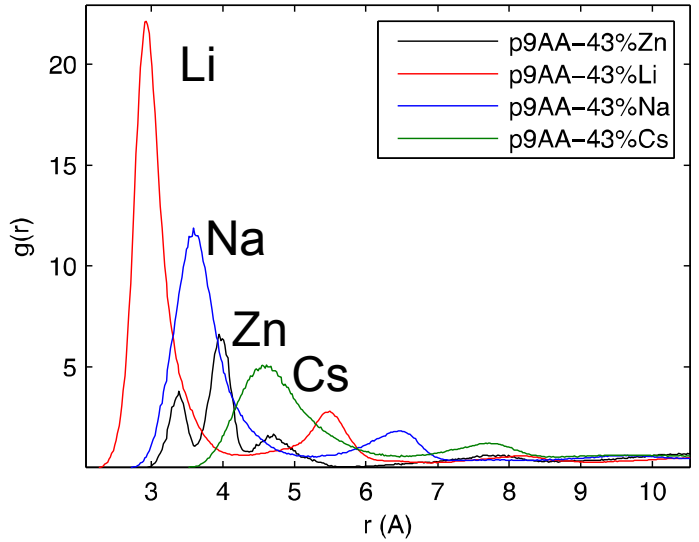
O-ion – +
- very large peaks
- peak ~ ion size
- height decreases for larger ions

cluster analysis:
O-ion in same cluster if separation within 1st peak
carbonyl O (OH) in same cluster



ion-ion ++ – –
- 1st peak at next-nearest neighbor distance
- secondary peaks visible





Morphology: Li-neutralized pAA

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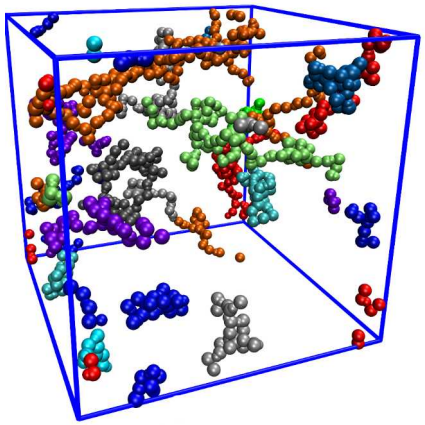
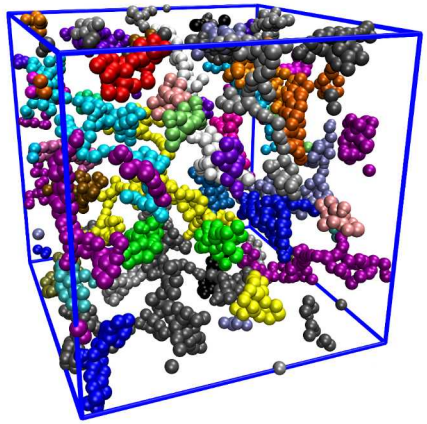
coloring by cluster

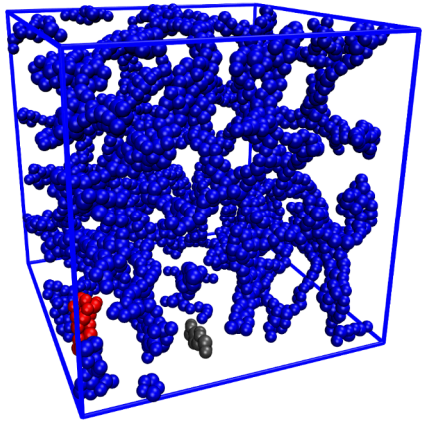
p9AA-10%Li

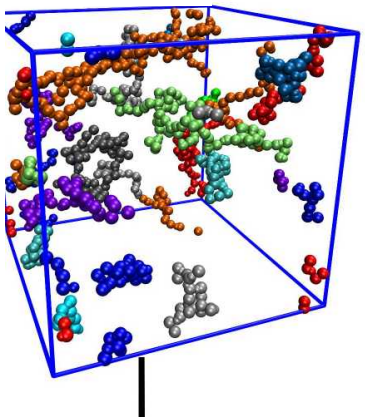


p9AA-43%Li

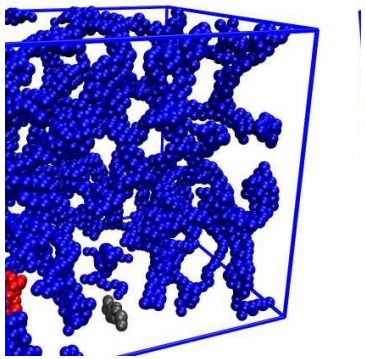


p9AA-100%Li

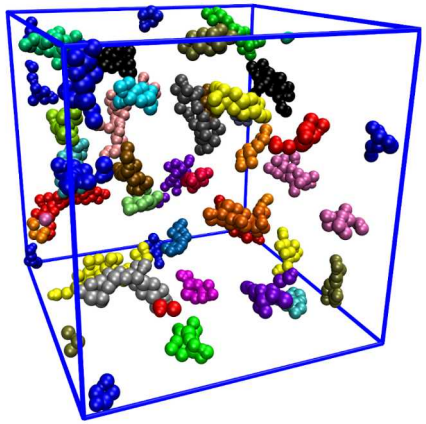




c. p9AA-100%Li
FP



p21AA-43%Li



Morphology for Different Cations

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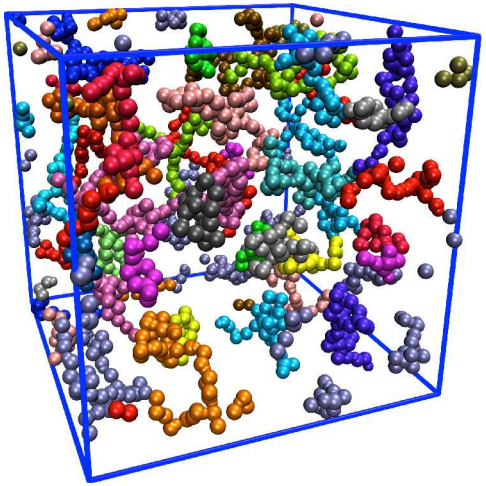
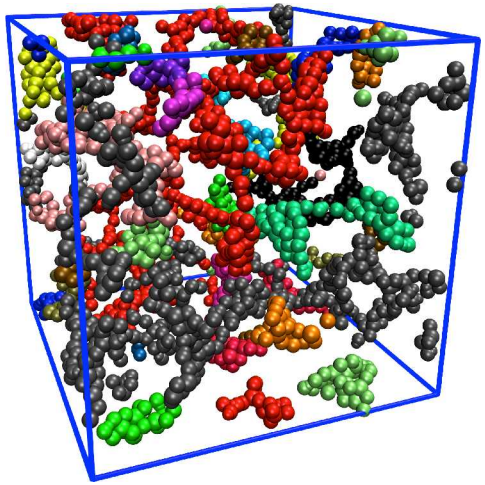
p9AA-43%M

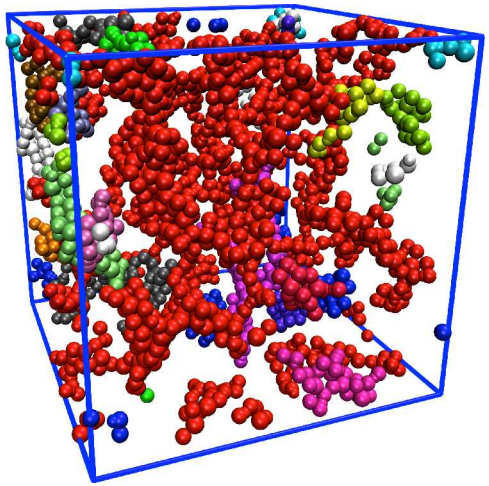
Zn^{2+}



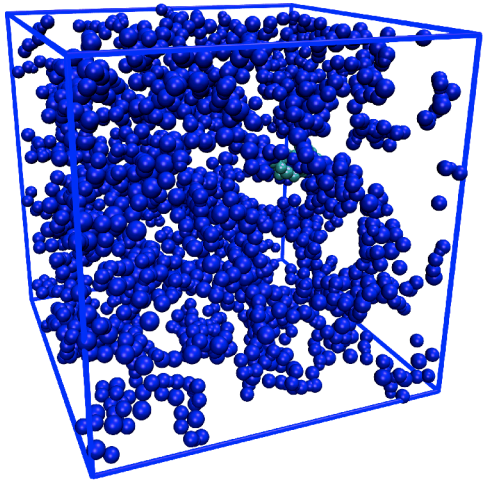
Li^{+}



Na^{+}



Cs^{+}



p9AA-y%M

	10%	25%	43%	75%	100%
Zn	LS	LS	SS	SS	SS/CS
Li	SS/LS	LS	LS	LS/PP	PP/FP
Na	SS	SS/LS	PP	FP	FP
Cs	LS	PP	FP	FP	FP

pxAA-43%M

	p9	p15	p21
Zn	SS	SS/CS	CS
Li	LS	SS	SS/CS
Na	PP	SS	SS/CS
Cs	FP	LS/PP	LS/SS

Stringy Aggregates

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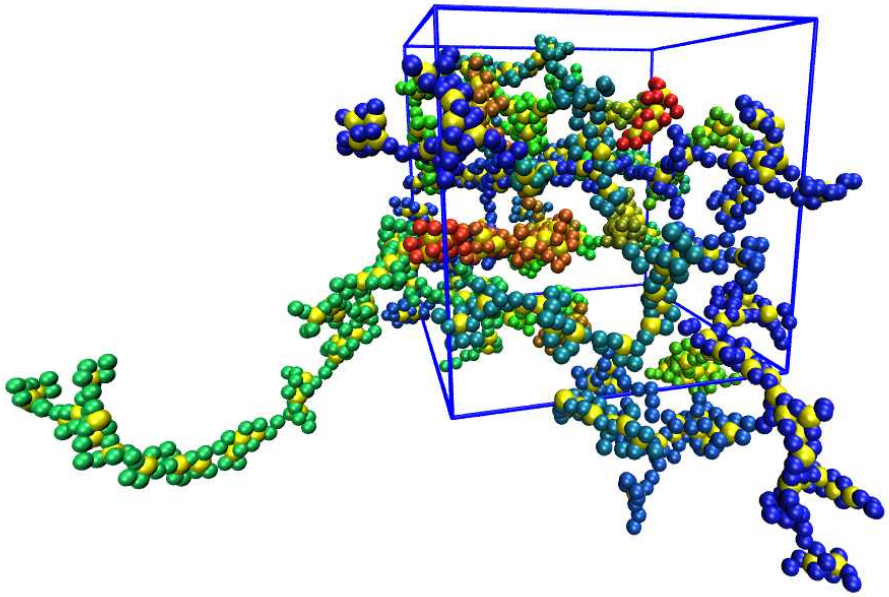
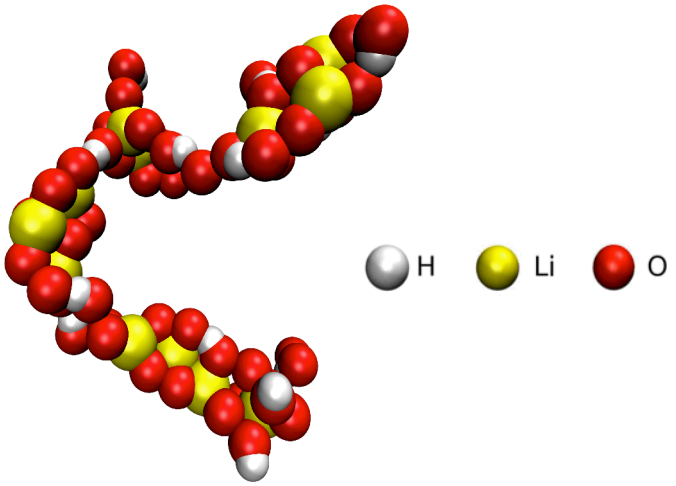
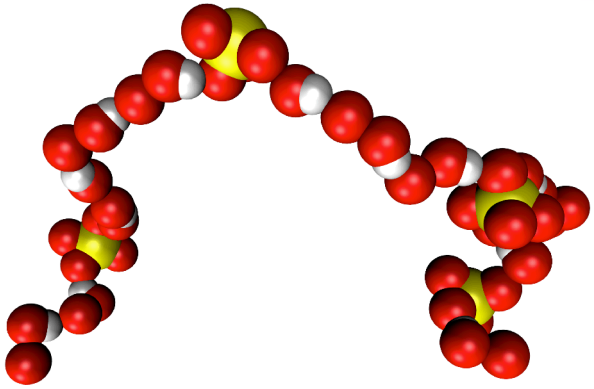
hydrogen bonding contributes to clusters

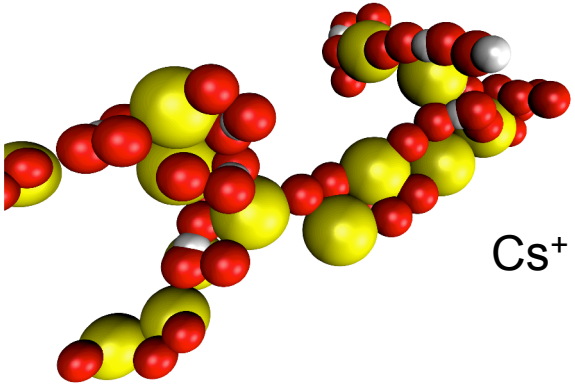


Li^+



Zn^{2+}

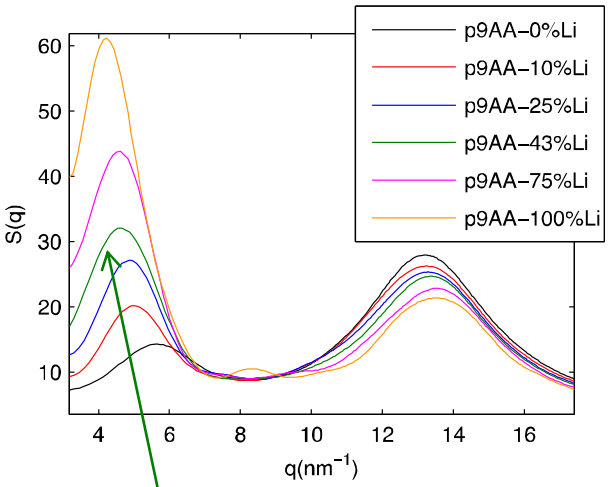


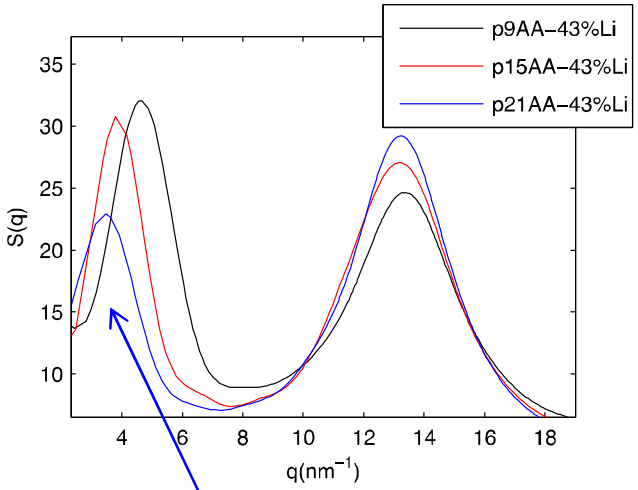


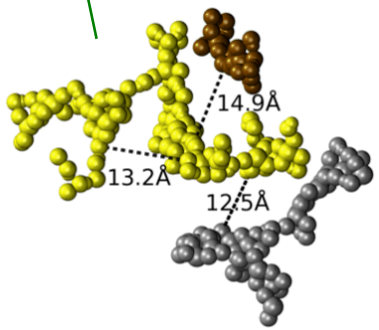
Cs^+

Total Structure Factors for Li-neutralized pAA

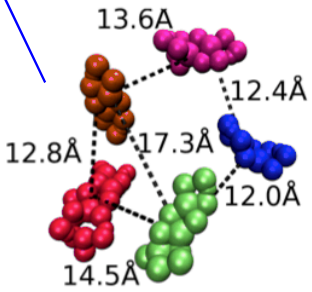
$$S(q) = \sum_i c_i f_i^2 + 4\pi\rho \int_0^\infty \frac{\sin(qr)}{qr} r^2 \sum_{i,j} c_i c_j f_i f_j \left(g_{ij}(r) - 1\right) dr$$







12-17Å
q ≈ 3.6-5.2/nm



ionomer peak from inter-aggregate scattering

Structure Factors vs Cation

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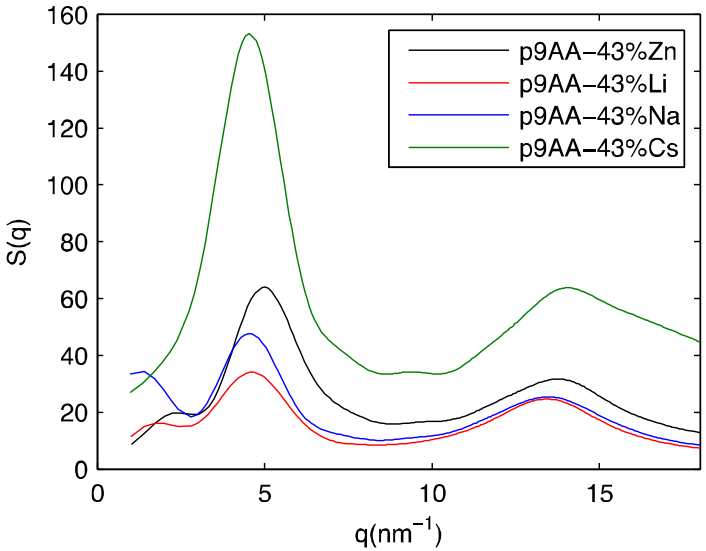
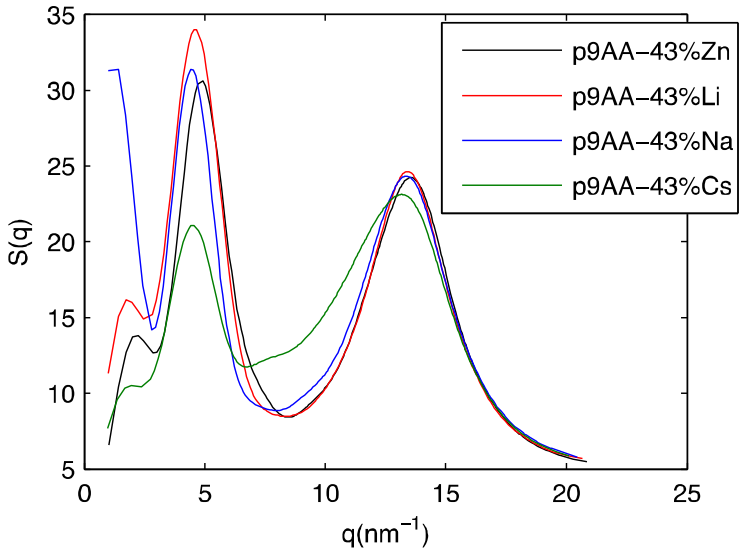
Alchemy

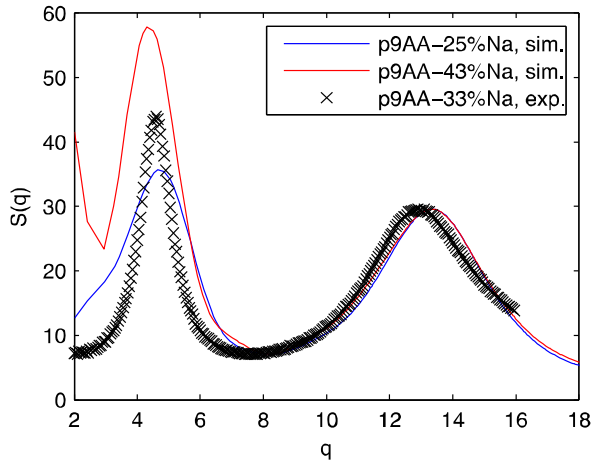


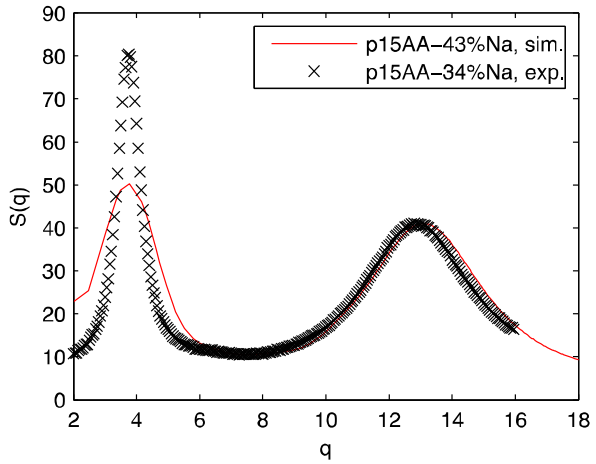
Li^+ form factor for all ions

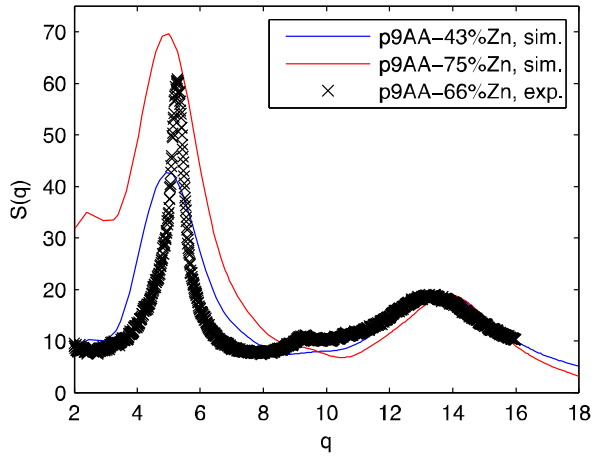
$f_M \rightarrow f_{Li}$



Comparison to X-ray Scattering







- peaks in correct locations
  - also true for Li, Cs
- x-ray intensity in arbitrary units
  - fit to height of amorphous halo

M. E. Seitz et al., *J. Am. Chem. Soc.* **2010,** 132, 8165
Hall et al., *J. Am. Chem. Soc.* **2012**, 134, 574

Local Li^+ Environment

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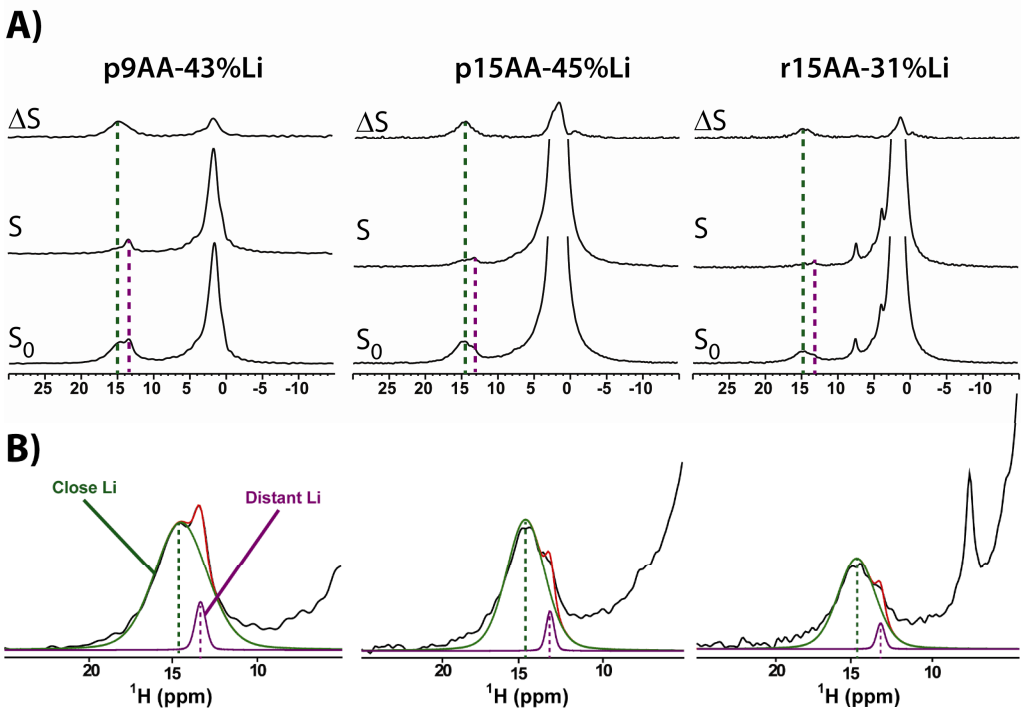
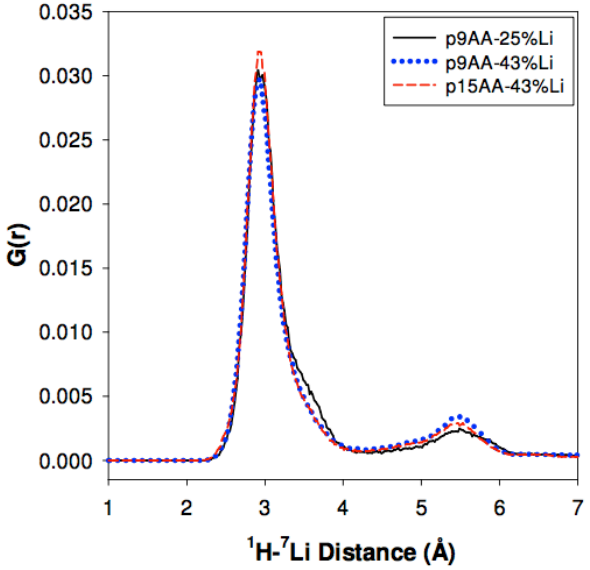
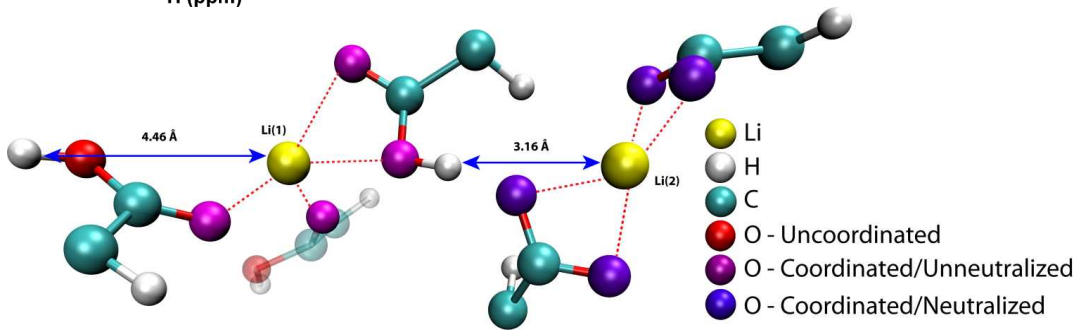
^1H-^7Li REDOR MAS NMR



atomistic MD



- 2 H-Li distances
- reflects variety of coordination in aggregates



Alam et al., Materials 5, 1508 (2012)

Summary of Atomistic Simulations

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- range of morphologies
  - stringy
  - can be percolated
  - not all spherical as previously assumed (except maybe Zn)
  - not well resolved in scattering
  - ionomer peak due to interaggregate scattering
- trends
  - longer aggregates as neutralization increases
  - shorter aggregates as spacer length increases
- hydrogen bonding important in partially neutralized systems
- simulations match experimental S(q) well

Coarse-grained Simulations

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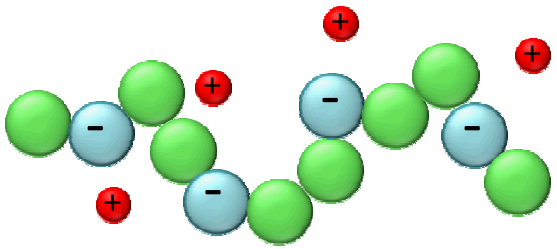
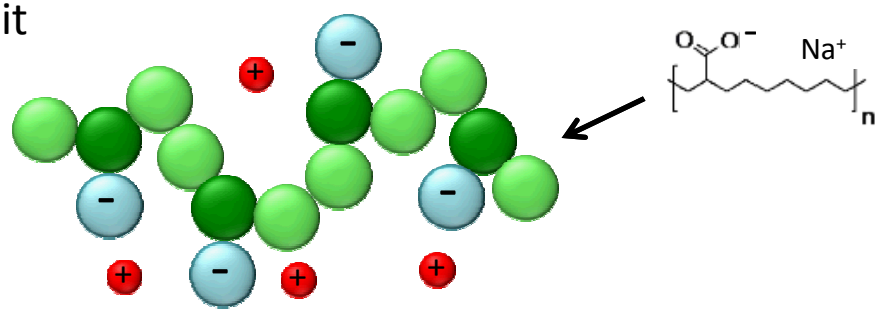
Ions in the polymer backbone:
"**ionenes**"



backbone beads per repeat unit

$N_{bb} = 3$

Ions pendant to the backbone:
"**pendants**"



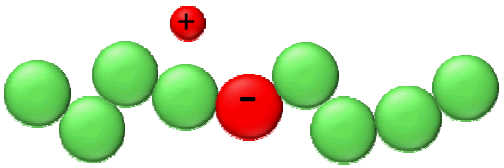
$N_{bb} = 3, 5, 7, 9\ (11)$
800 polymers
100% neutralization
bulk dielectric constant = 4
counterion size = ½σ
Bjerrum length = 35.7σ

10^8 time steps

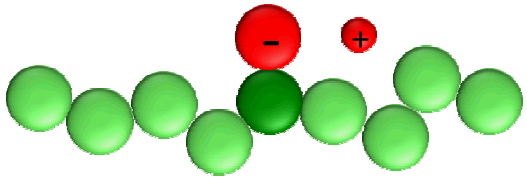
$$\ell_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT} = 35.7\sigma$$

$$R_g \approx 3.1 - 3.3\sigma$$

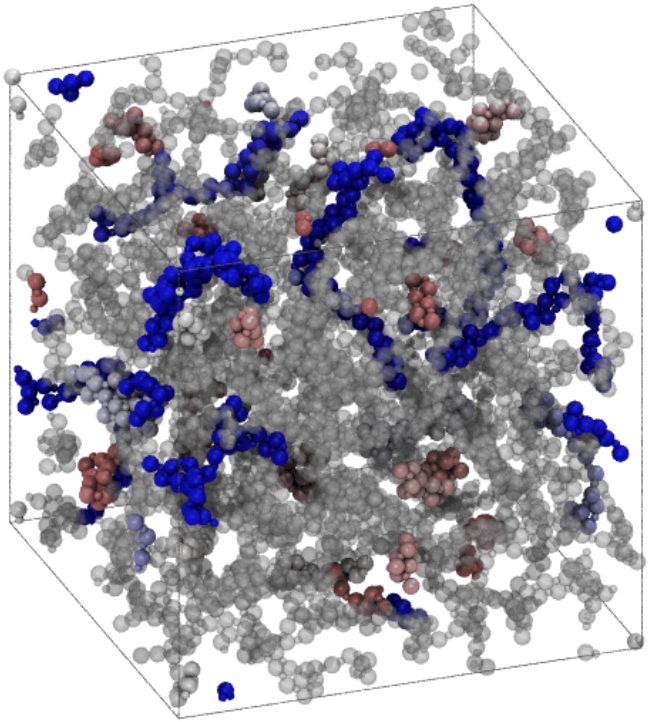
Aggregate Morphology: Architecture Matters



Ionenes: percolated

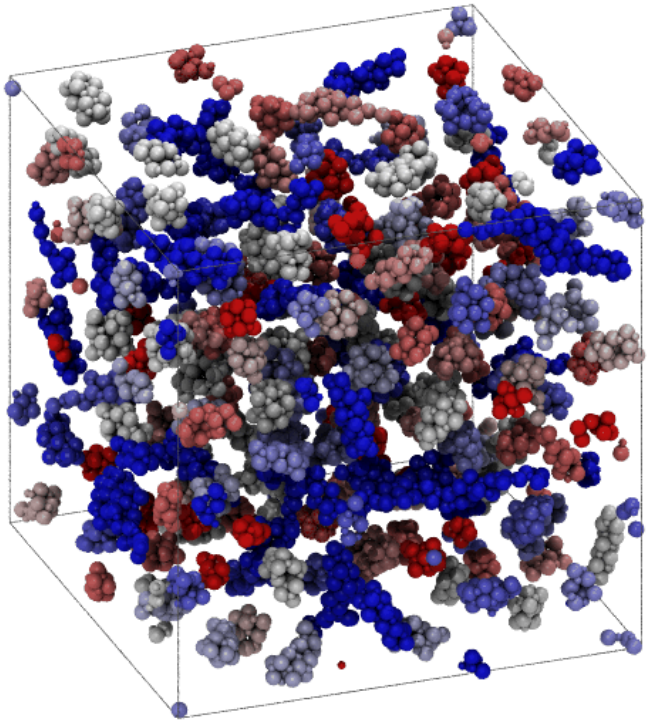


Pendants: not percolated



$N_{bb} = 9$

$\varepsilon_r = 4$



Small clusters → Large clusters

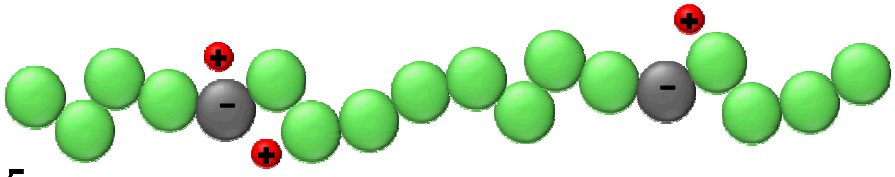
Only charged beads shown

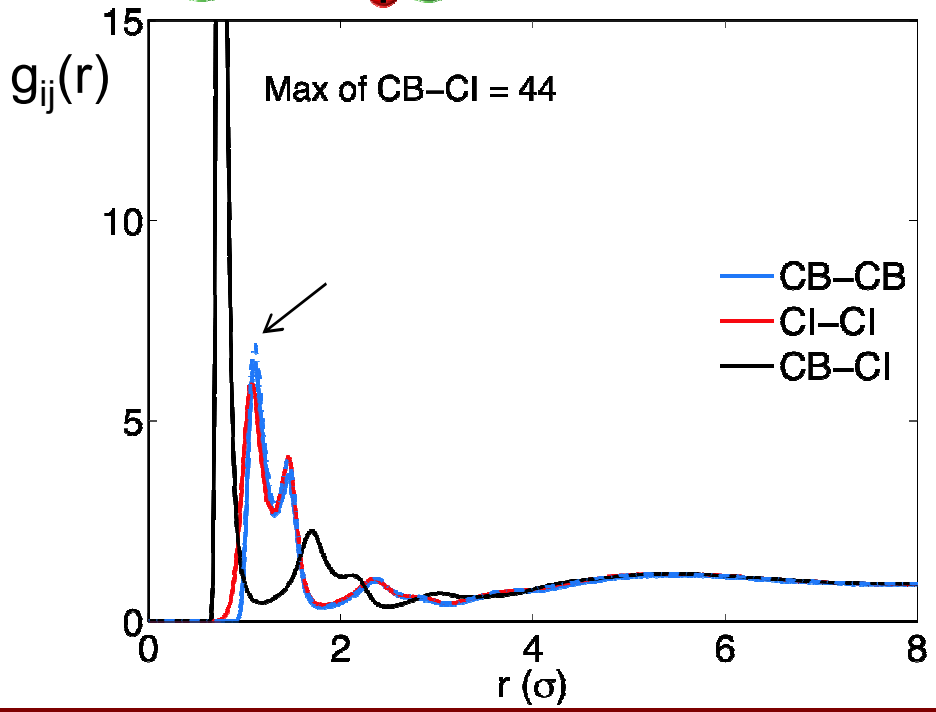
Hall et al., *Phys. Rev. Lett.* (2011)

Ion-Ion Pair Correlation Functions

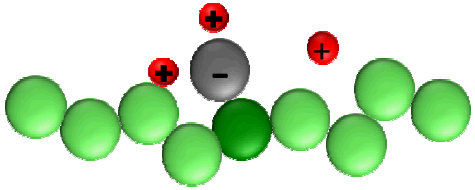
- A clue to difference between ionenes and pendants
- Pendants have larger peaks
- More counterions about pendant charge in polymer

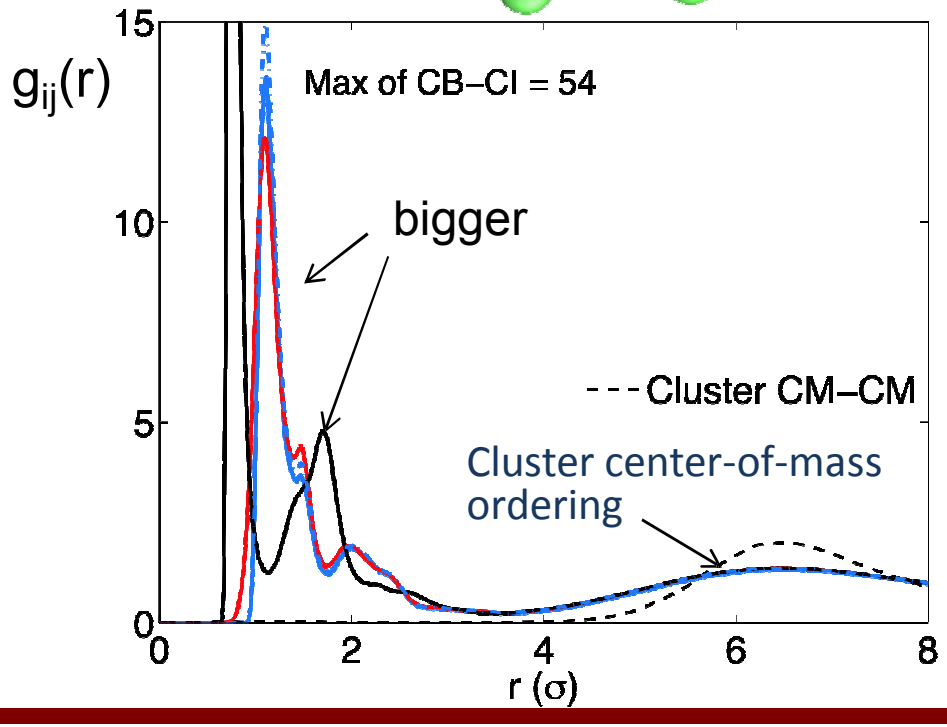
Ionenes





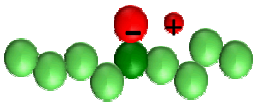
Pendants

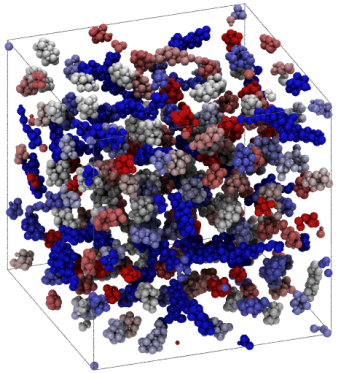


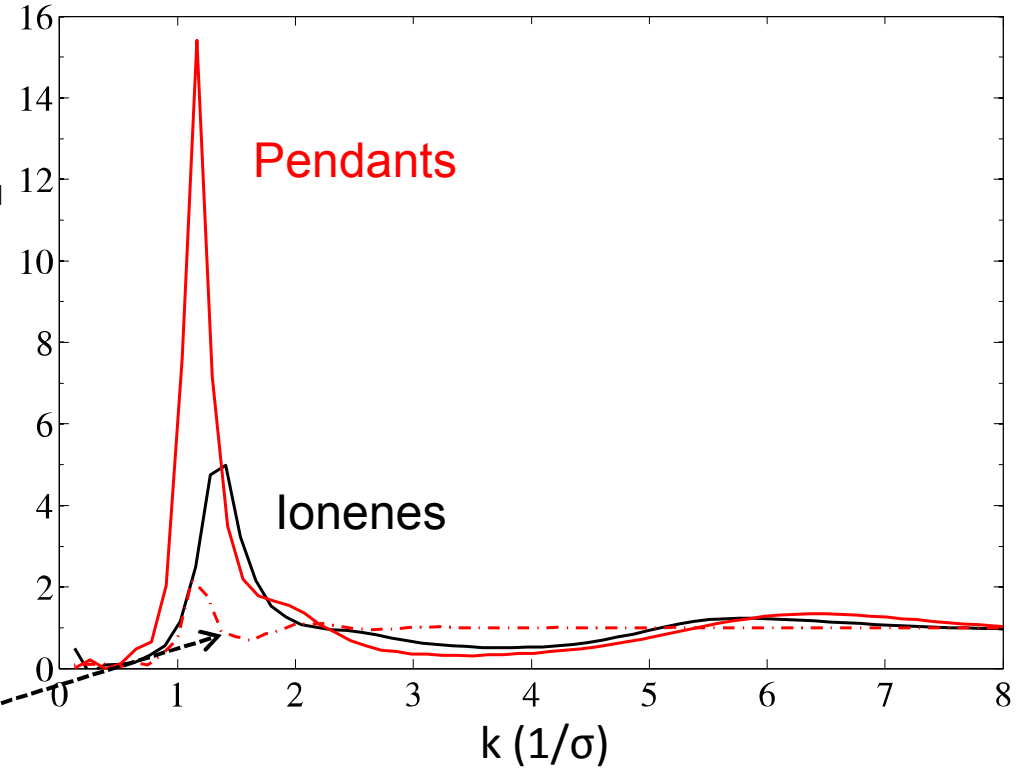


Structure Factor (Scattering)

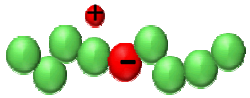
- Ionomer peak for *both* ionenes, pendants
  - Ionene peak: mesoscale order within percolated aggregate
  - Pendant peak: cluster center-of-mass to center-of-mass order
- Experimental peak ~4 nm^{-1}, MD peak 1.2-1.8 σ^{-1} → ~3-4 nm^{-1}





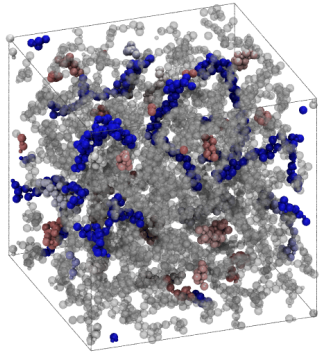


Pendants: cluster center-of-mass order



Ionenes:

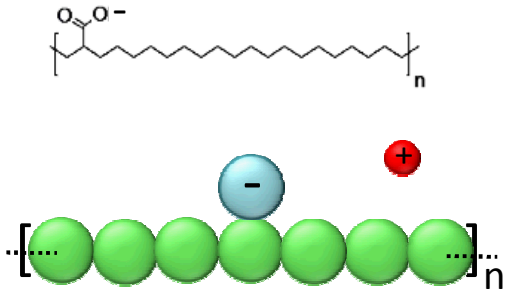
Mesoscale order within percolated structure



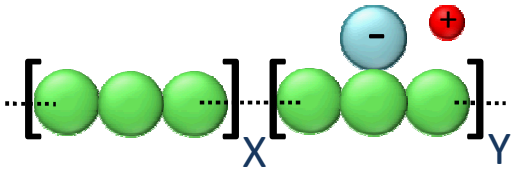
Randomly Spaced Ionomer Model

- random block
  - mimic ROMP
- fully random
  - mimics typical random polymerization

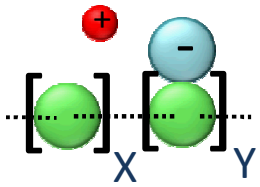
Periodic



Random Block Copolymer



Fully Random Copolymer



connect blocks randomly

vary X/Y

N_{bb} = Number of **b**ackbone **b**eads per charged bead

Aggregate Morphology: Random vs. Periodic

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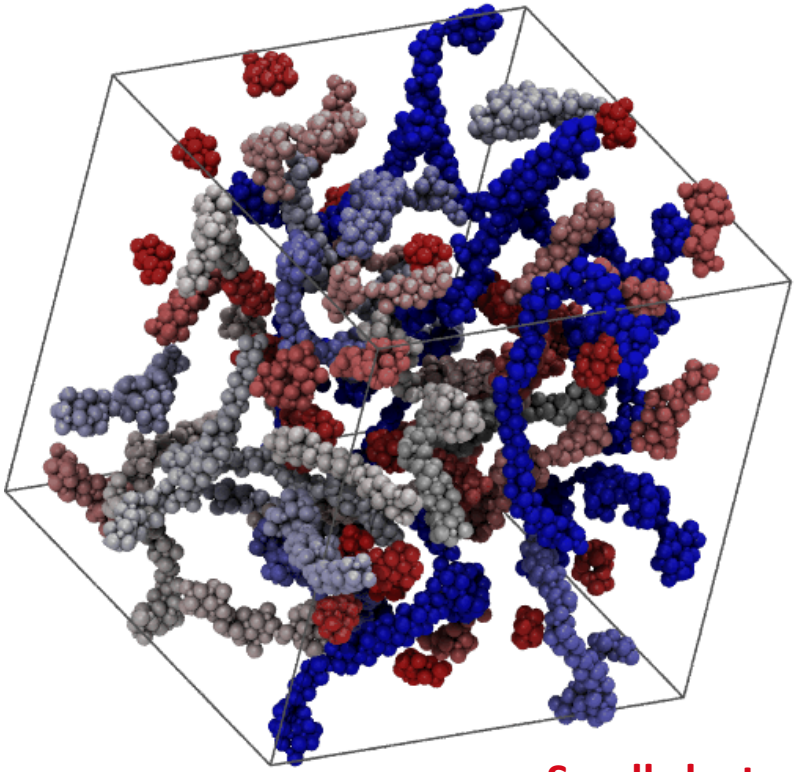
Random Block Copolymer
Pendants: stringy, large clusters

Mean cluster size 87

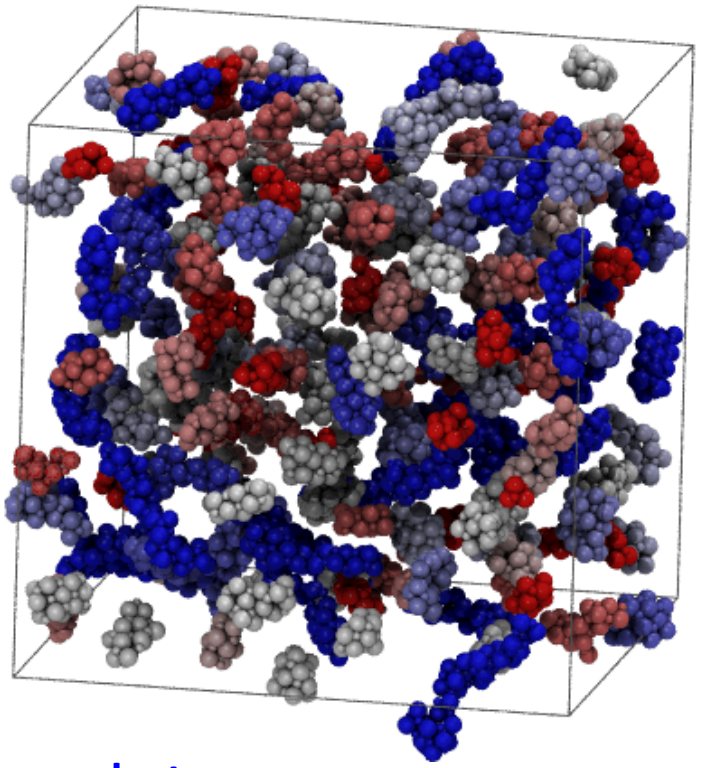


$\varepsilon_r = 4$

$N_{bb} = 9$

Periodic Pendants:
narrow cluster size distribution

Mean cluster size 31

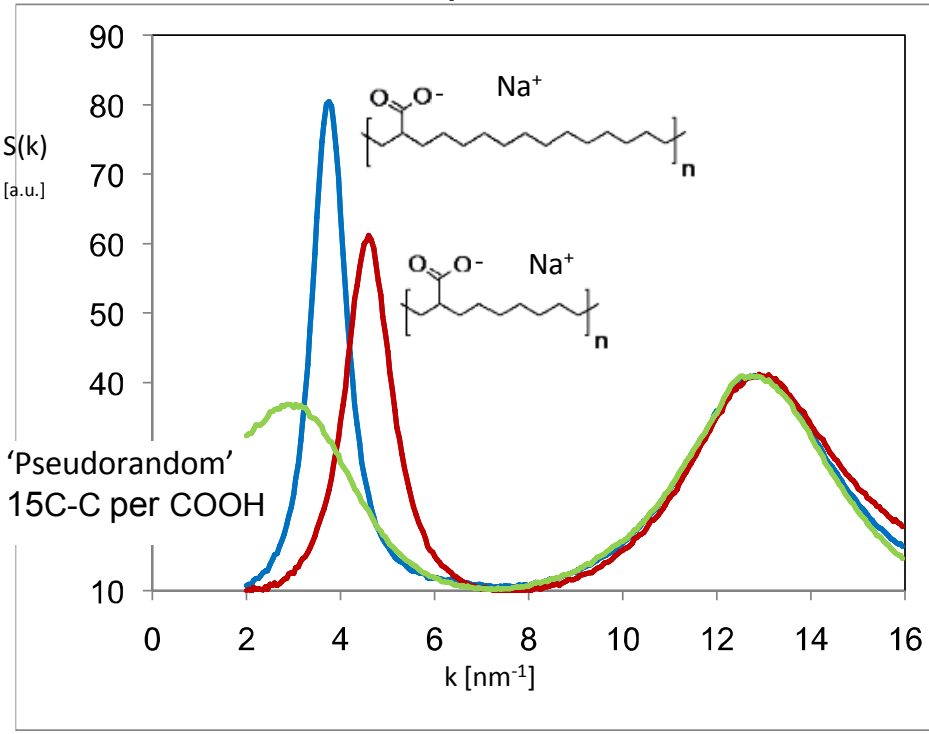


Small clusters → **Large clusters**

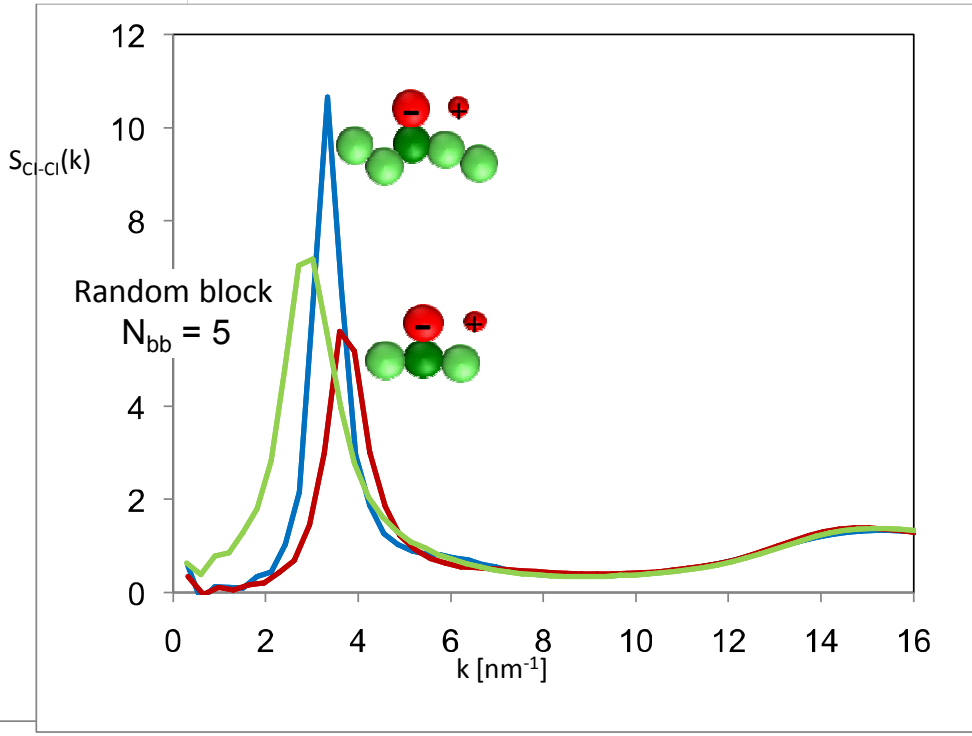
CG MD: Comparison to X-ray Scattering

- Experimental/Simulation Agreement
  - Peak location similar
  - Increasing spacing moves peak to left
  - Random spacing moves and broadens peak

Experiment



Simulation



Hall et al., *J. Am Chem. Soc.* (2012)

Cluster Dynamics

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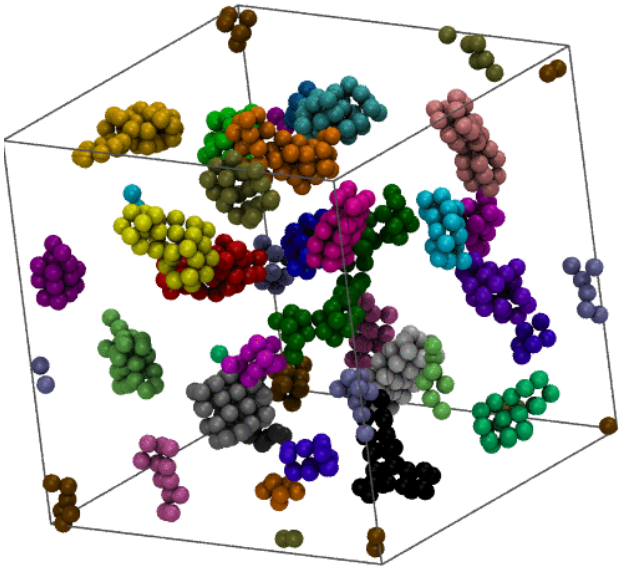
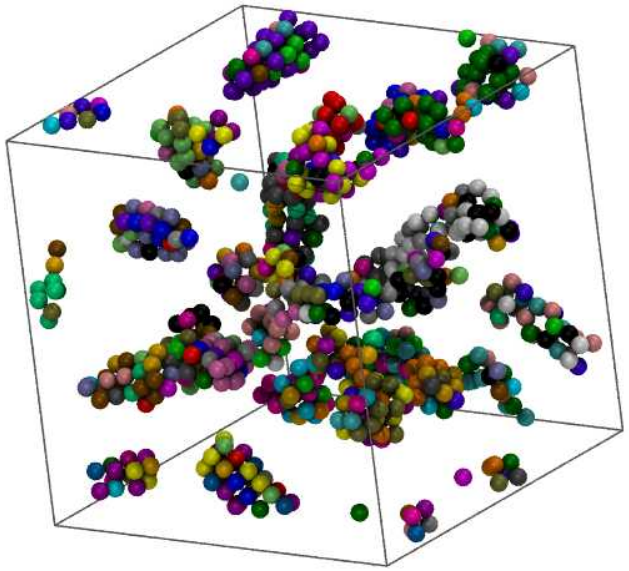
Is there any?

Color distinct clusters by different color

Start



Finish (10^7 steps later)



Ions move.

Ion Trajectories

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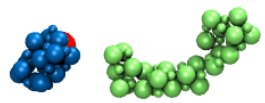
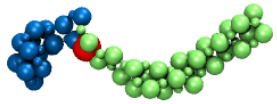
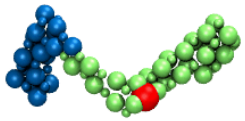
periodic pendants N_{bb}=9

2 separate clusters
Follow one counterion

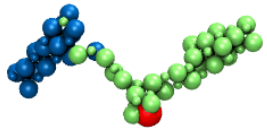


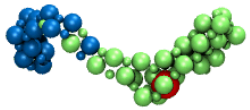


Clusters have collided

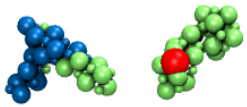


Ion has moved to other cluster.
NEVER separated from a cluster.





ions move by cluster rearrangment/collision



Clusters reform with ion moved

Energies and Cluster Dynamics

+ – pair energy (contact) is 48 kT.

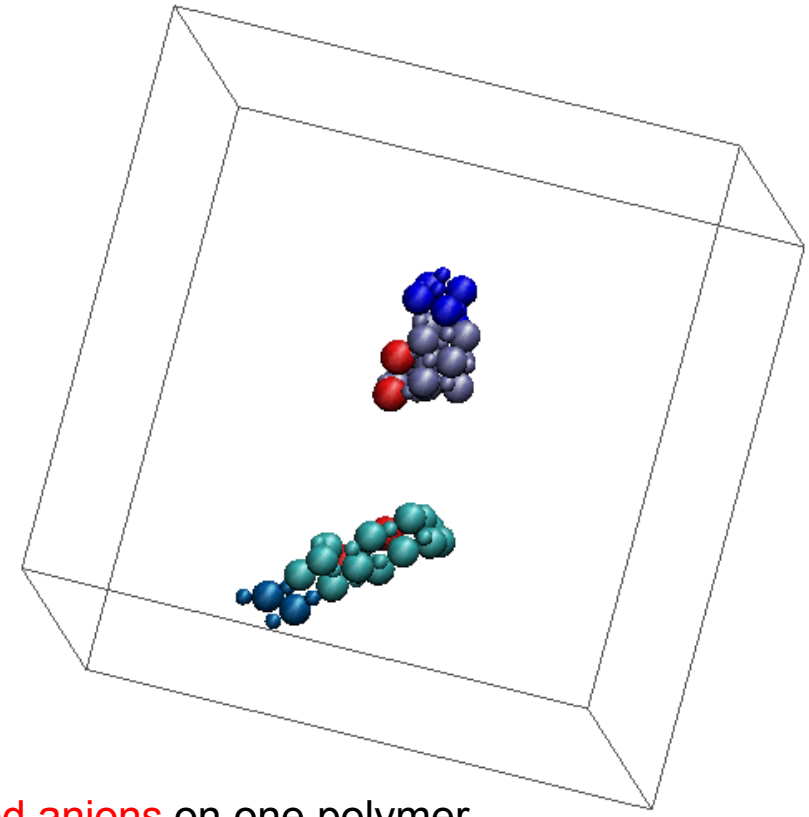
pairs are not likely to separate.

energy to split a cluster is much less
ideal, 2D crystallite has a separation energy of
only 20 kT:

simulations show clusters are flexible (they're liquids after all) and the energies will be less than these crystallite calculations.

ions move a lot within a cluster

Pendant (discrete clusters)



Red anions on one polymer.

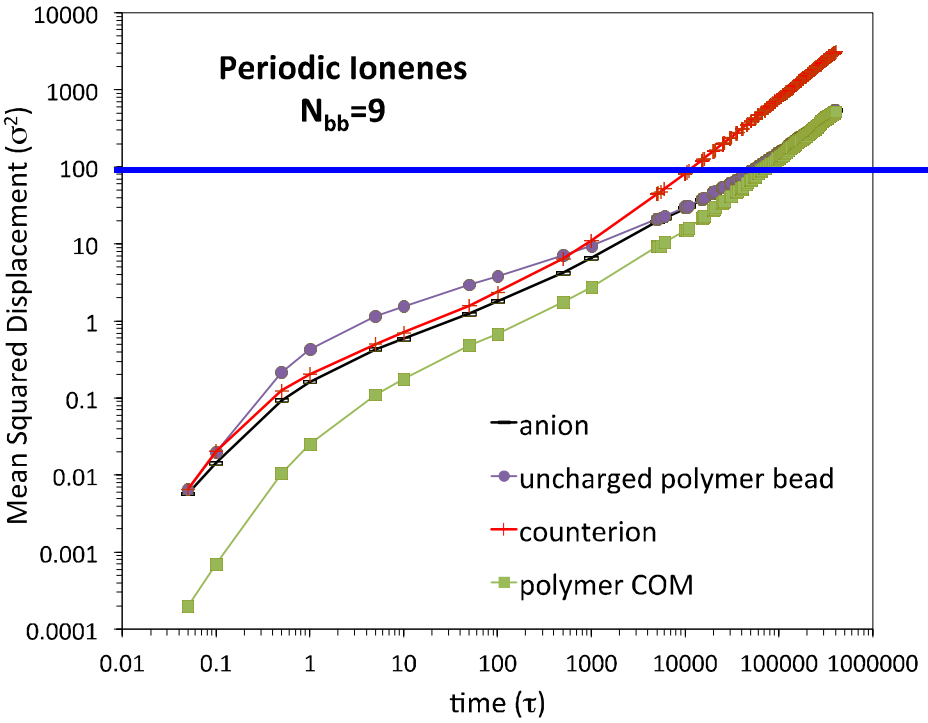
Blue ions initially within 3σ of red anions.

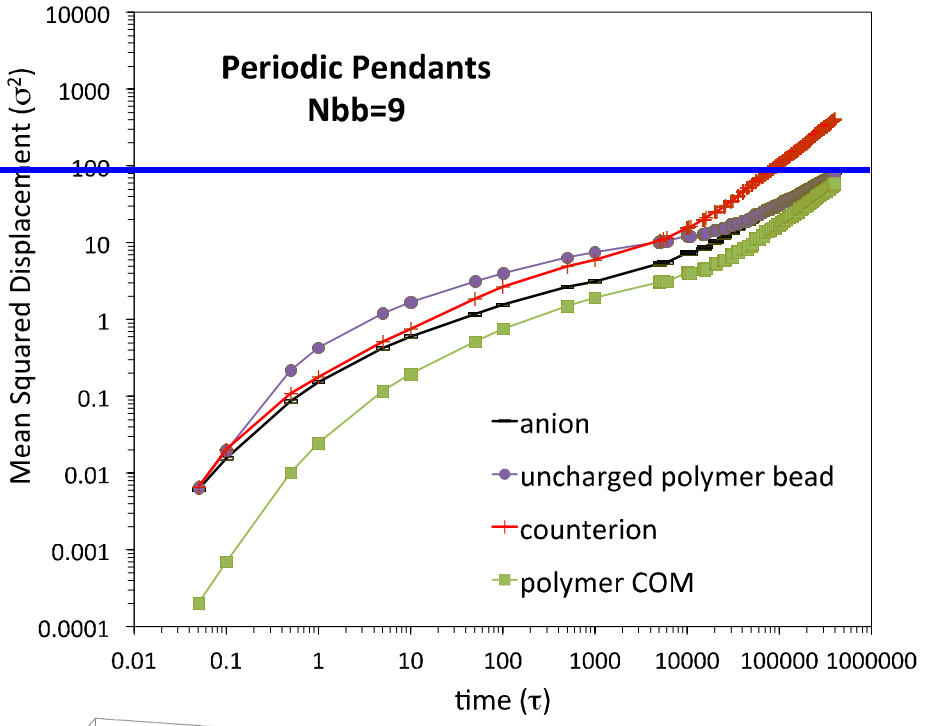
Other ions which temporarily come within 3 σ are transparent.

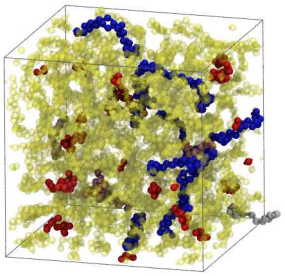
5000 τ X million time steps

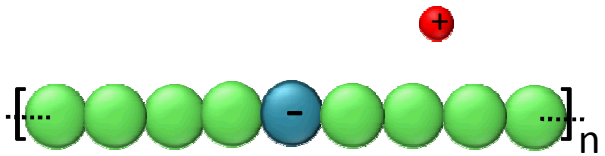
Mean Squared Displacements

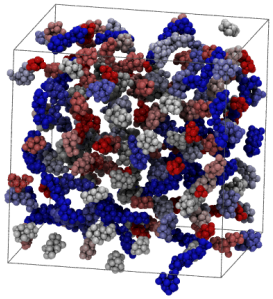
- Ionenes, pendants similar at short times
- Pendants slower but qualitatively similar at long times

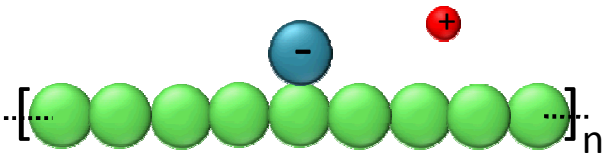












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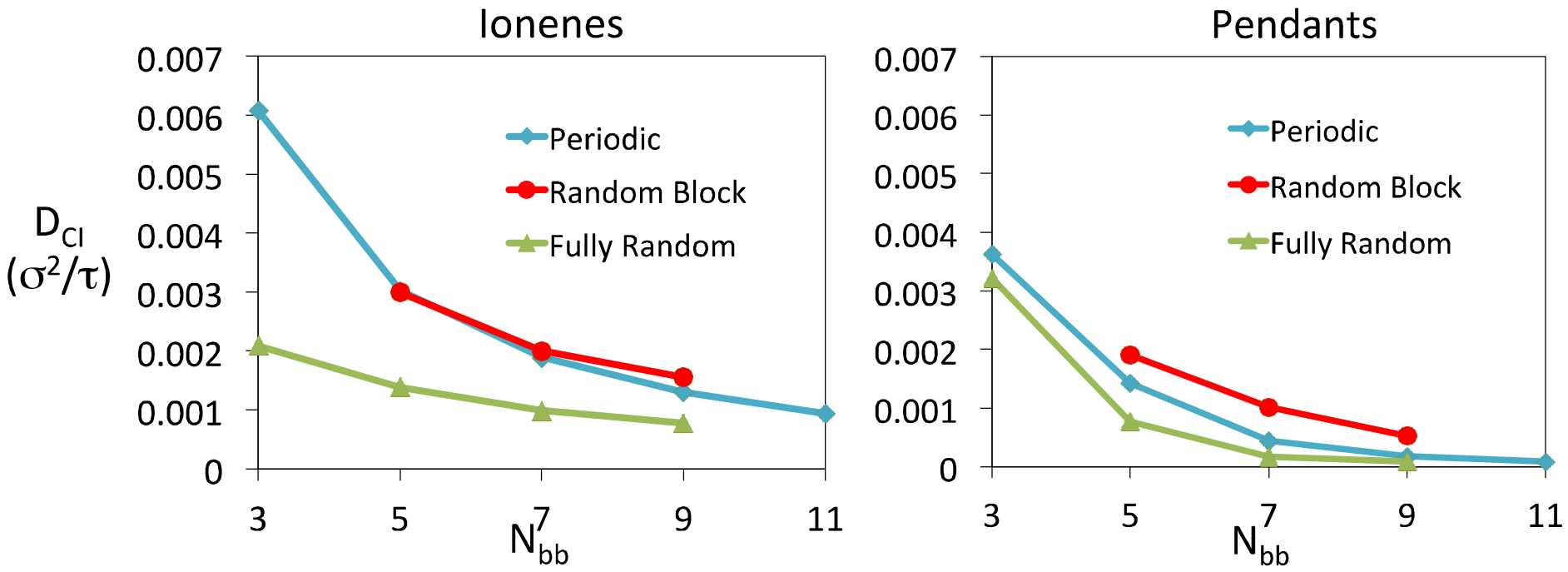
Counterion Diffusion Constants

- Ionenes conduct better than pendants
- Greater concentration of ions increases diffusion
- Blocky random copolymerization increases diffusion



$\varepsilon_r = 4$

Hall et al., *Macromolecules* (2012)

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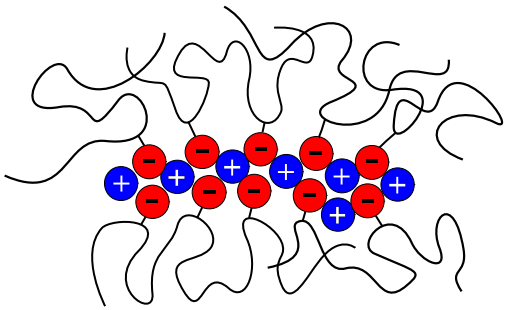
The New Picture



- Aggregates are stringy
  - + – + – ordering
  - polymer backbone constraints
- Counterion influences structure (partial neutralization)
  - Na^+, Li^+: medium-sized, stringy aggregates
  - Cs^+: Percolated network
  - Zn^{2+}: small, isolated clusters
  - Small ion-O^- clusters are bridged by -OH and =O groups

- molecular architecture important
  - pendant vs ionene
  - isolated aggregates for pendants or large spacing
  - percolation for ionenes or short spacing
- ion motion by cluster rearrangment
- ions diffuse faster in percolated morphologies

Hall, et al., *Phys Rev Lett* **106,** 127801 (2011); *J. Am Chem. Soc.* **134**, 574 (2012); *Macromolecules*, **45**, 8097 (2012)

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The “Ionomers” LDRD team
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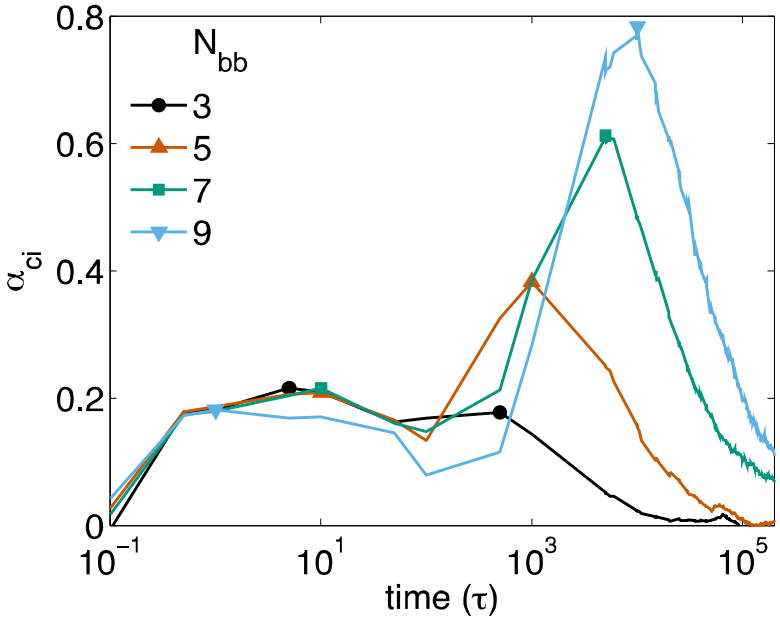
CINT
NERSC

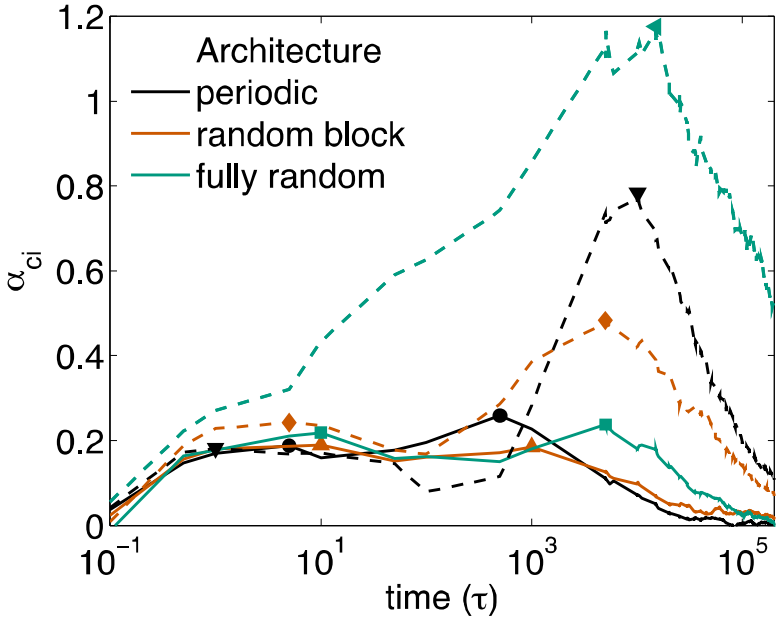
Ion Dynamics

non-Gaussian parameter $$\alpha(t) = \frac{3\left\langle (r(t))^4 \right\rangle}{5\left\langle (r(t))^2 \right\rangle^2} - 1$$

cations in periodic pendants



cations for N_{bb} = 9



indicative of 2 time scales:

- local motion in clusters
- slower rearrangment between clusters

Average Local Structure

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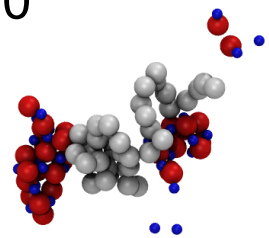
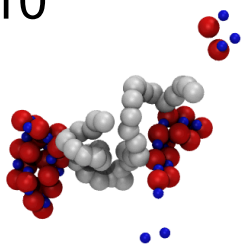
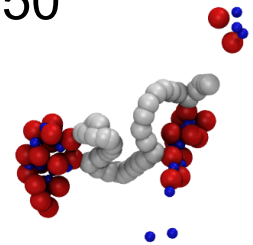
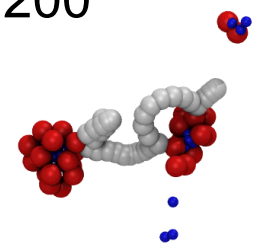
one polymer (white, red anions) and nearby ions (red anions, blue counterions)
N_{bb}=9, frames are 1000 steps apart

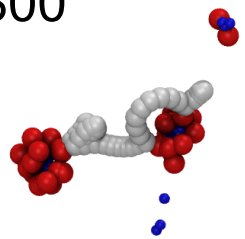
periodic pendant, frames averaged:

0 

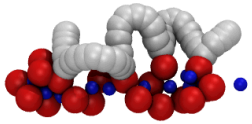
10 

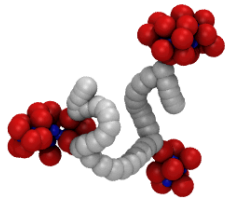
50 

200 

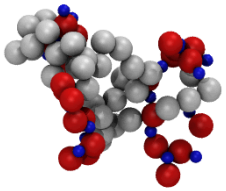
800 

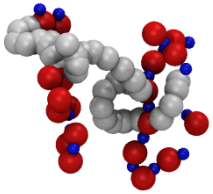
other periodic pendant examples

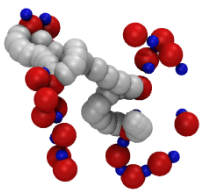
200 

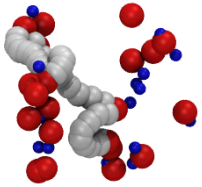


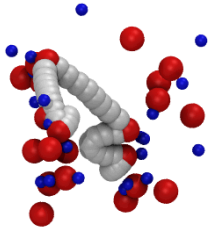
periodic ionene, frames averaged:

0 

10 

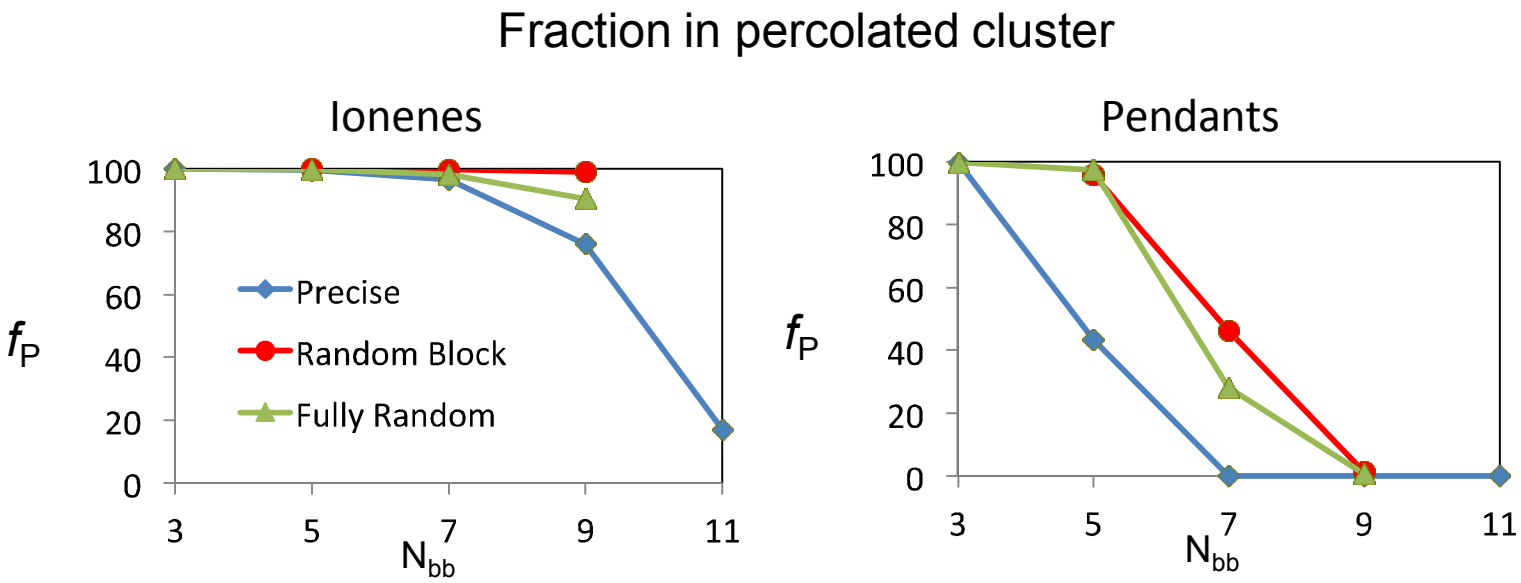
50 

200 

800 

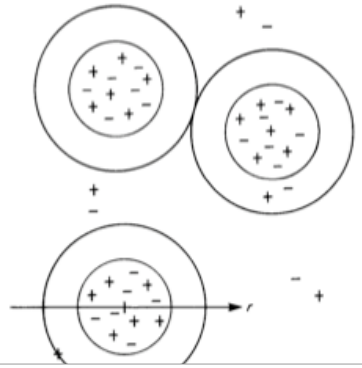
Effect of Architecture on Clustering

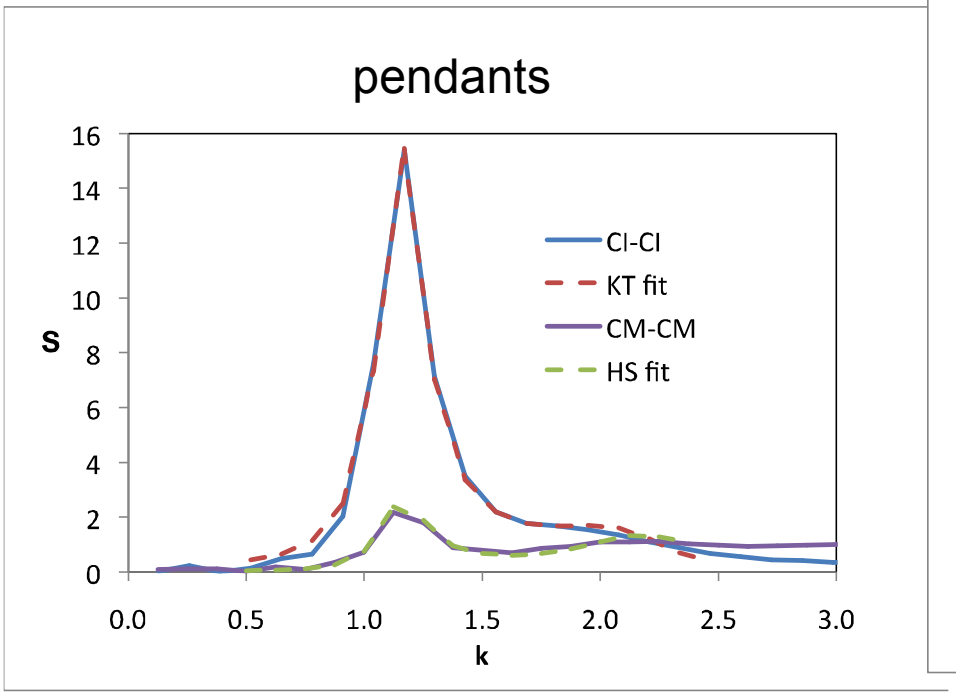
- Ionene architecture, randomness increases percolation
- Randomness usually increases non-percolated cluster size

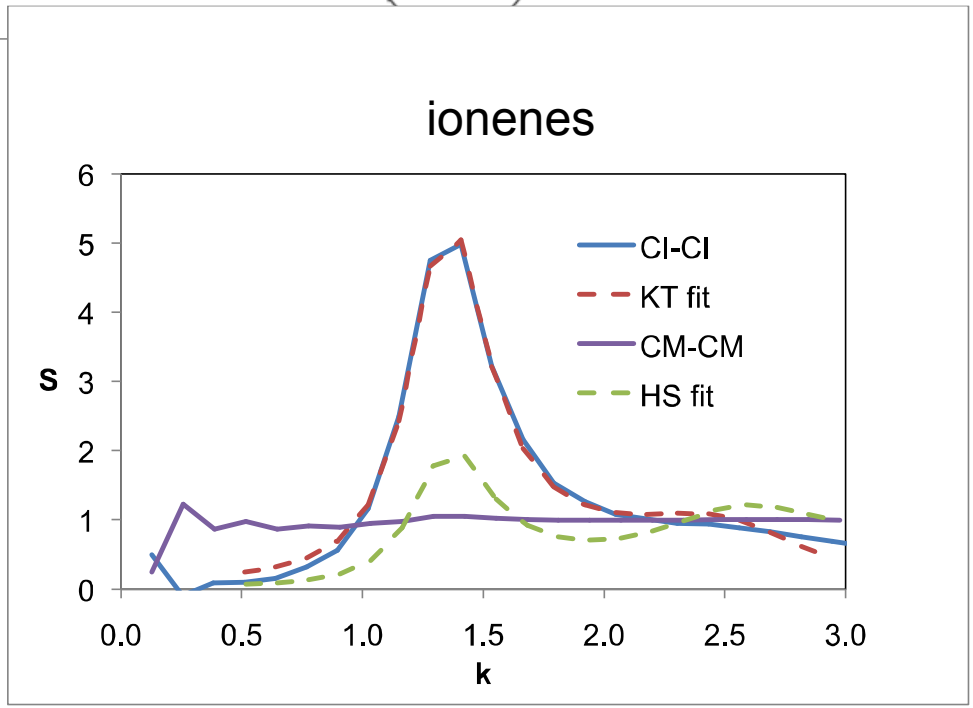


Fit to Scattering

- modified hard sphere model
  - fits pendants well
    - fit parameters match physical meaning
  - fits ionenes well
    - fit parameters don't match







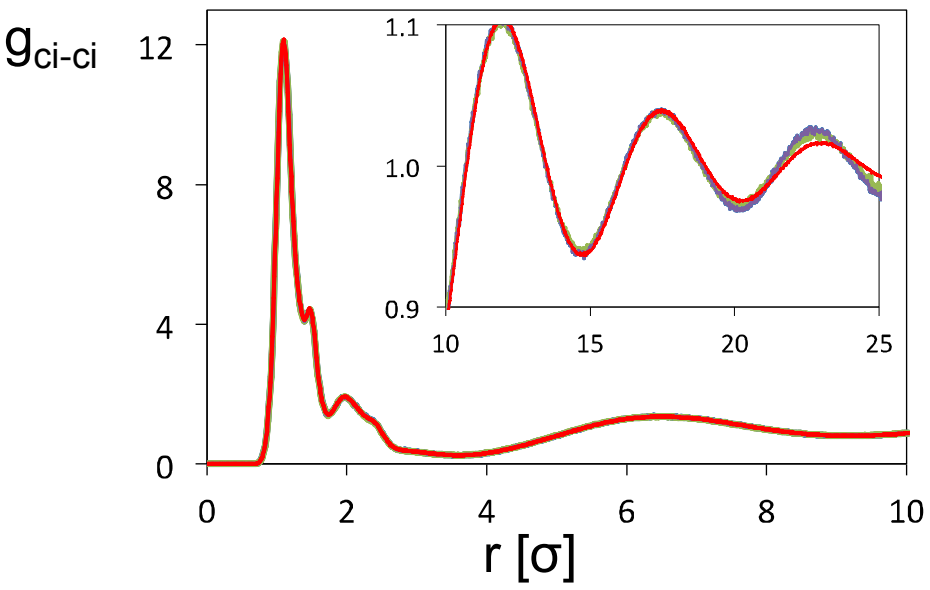
Equilibration of Simulations

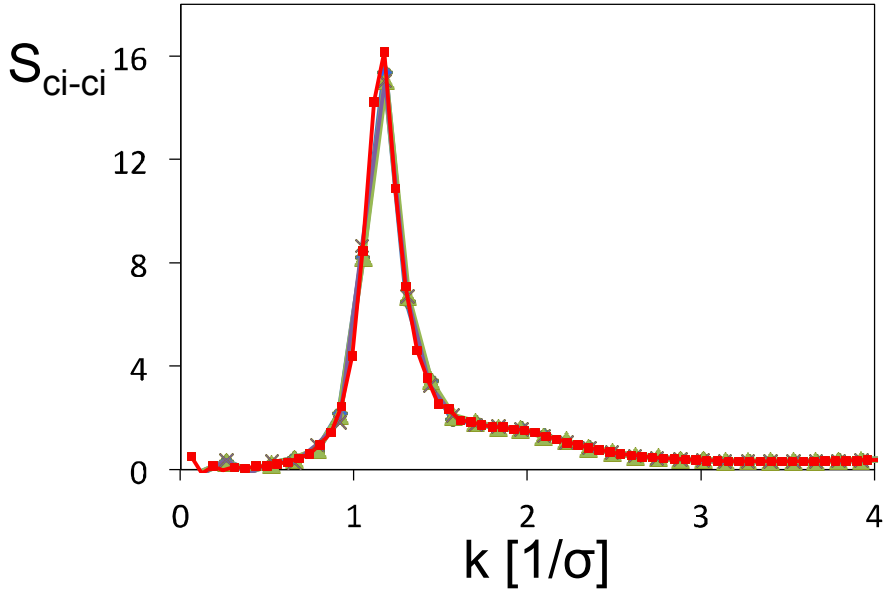
- From random initial configuration, equilibrate for 10^7 steps
- MSD of polymer centers of mass during equilibration > R_g^2
- Dynamics data collection start at 3×10^7 steps

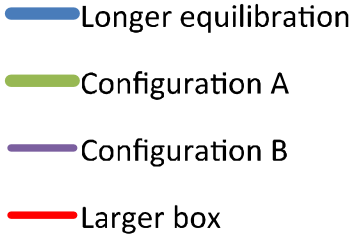
$\varepsilon_r = 4$, $N_{bb} = 9$ pendants: one of the slowest

no change in structure with:

- equilibrating 4 times longer
- using twice the box length
- starting from a different random initial configuration

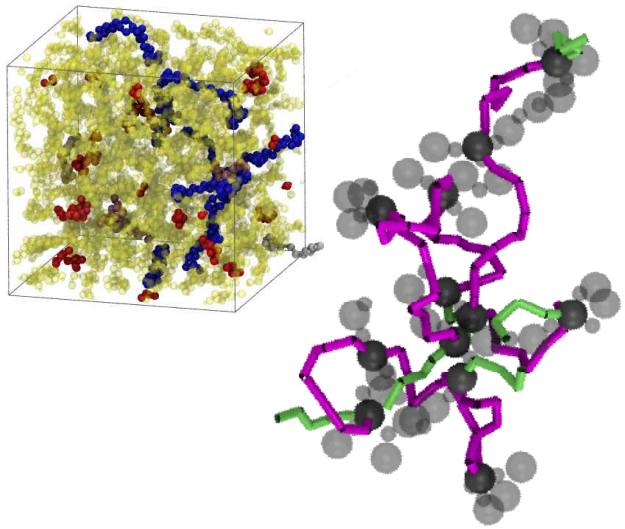






Polymer Morphology

Ionenes



3 nearby polymers

Charged beads

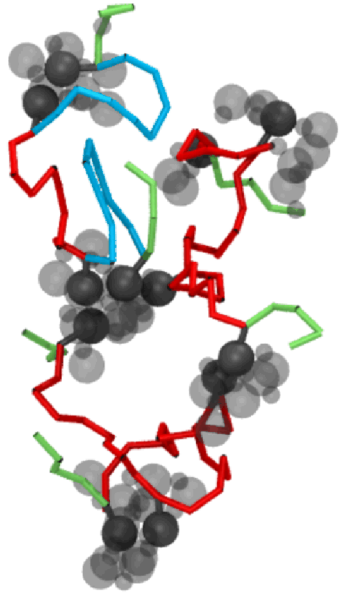
End segments

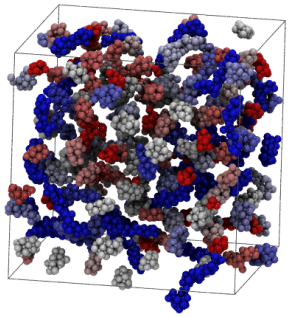
'Loops'

Close loops

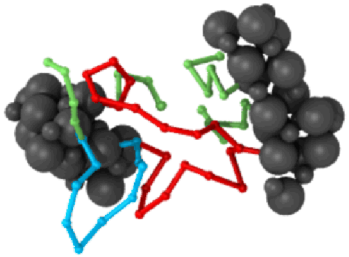
Bridges

Pendants





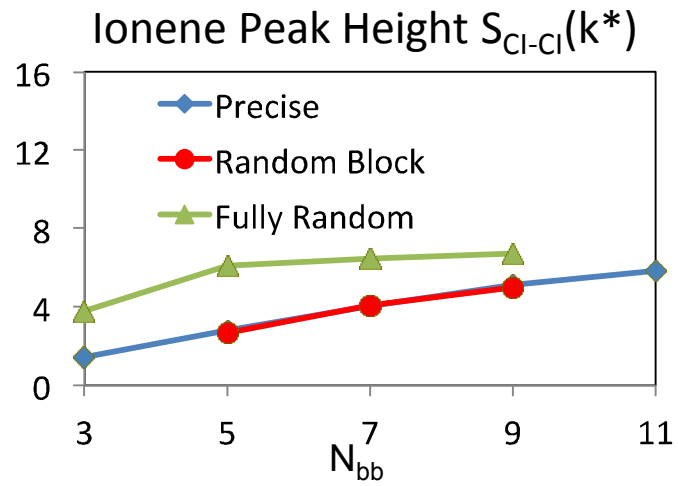
Polymer segments between 2 clusters

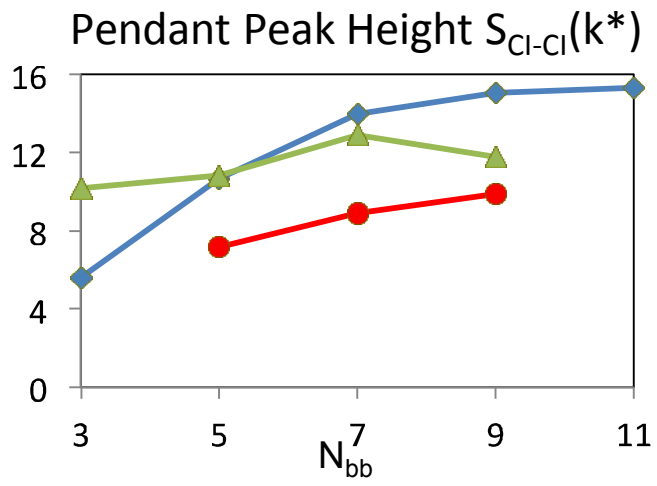


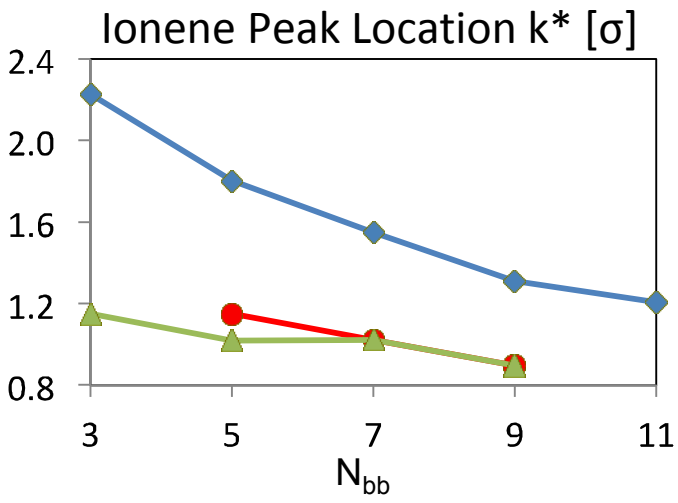
- Architecture determines aggregate morphology
  - Ionenes cannot easily form a compact cluster
  - Pendant backbone more separated from clusters
- Cluster-cluster length scale set by bridges?
  - Pairs of close loops or tails can set similar length scale
  - Decreasing backbone spacing leads to closer aggregates

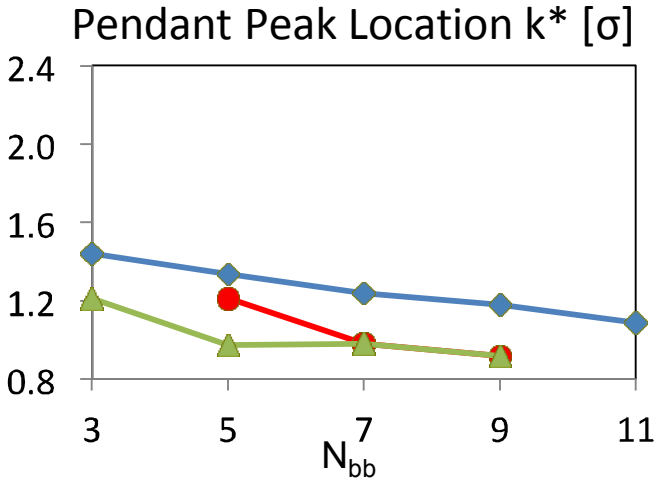
Effect of Architecture on Ionomer Peak

- Pendants have larger peak than ionenes
- Randomness moves peak to lower wavevector









$\varepsilon_r = 4$

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Molecular Dynamics Simulations

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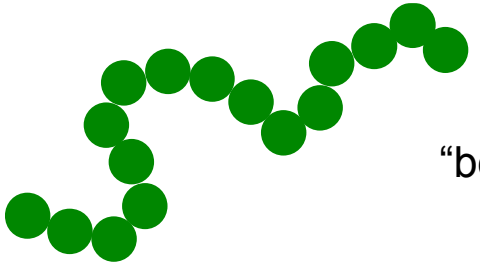
- put atoms in a box
- solve *F* = *ma* for each atom
- calculate statistical properties (averages) over trajectories

bead-spring polymer model
(Kremer & Grest, 1990)

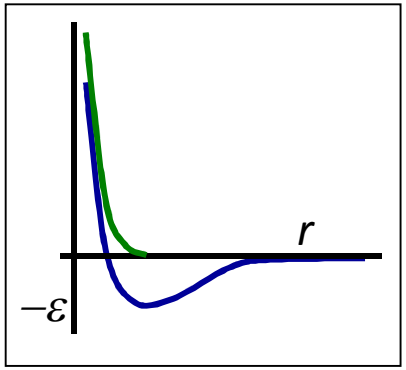


"bead" diameter σ

interactions between all "beads"

Lennard-Jones potential:

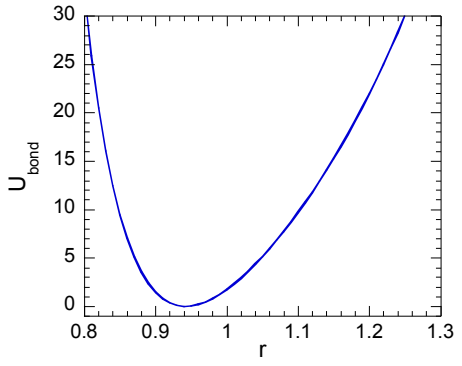
$$u_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



interactions between bonded beads

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

$U_{bond} = u_{LJ} + u$



Ionomer MD Simulations

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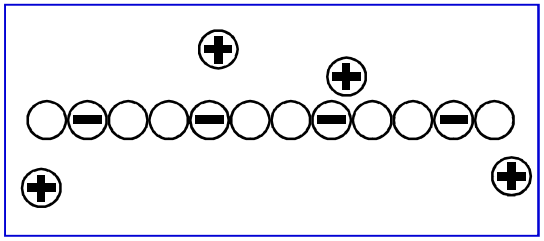
Coulomb interactions $$U(r) = \frac{q_1 q_2}{4\pi\epsilon_0\epsilon r}$$



counterions: single beads, size 0.5σ

NVT ensemble: Langevin thermostat

$$f_i = -m_i\Gamma\nu_i + W_i(t)$$ noise *W* sets temperature

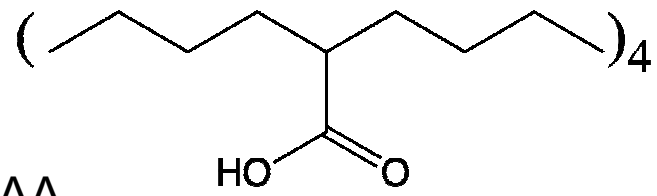
System

- 800 chains of 35-36 beads; 4-12 charges per chain
- 1 counterion per charged bead;
- density $\rho\sigma^3$ = 0.7 (polymer melt)

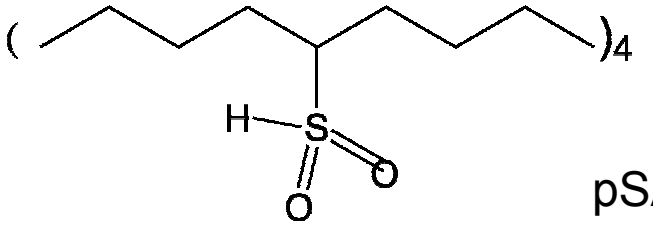
LAMMPS: open source MD code from Sandia

http://lammps.sandia.gov/

Acid Copolymer Simulations



pAA

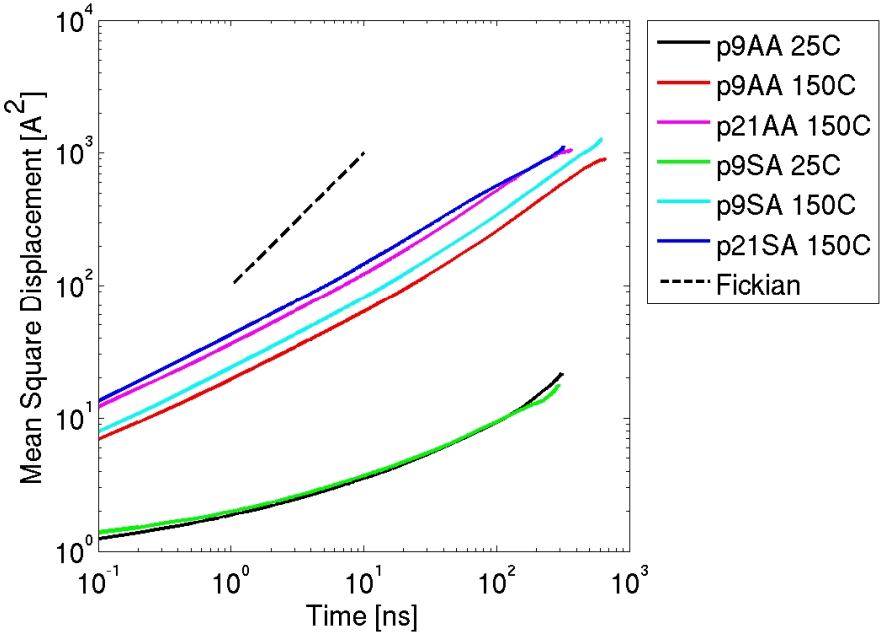


pSA

- all-atom OPLS force field
- p9AA, p9SA
  - 128 polymers
- p21AA, p21SA
  - 64 polymers
- box size 55 Å^3
- 150 °C

slow dynamics!

acid H diffusion



H-bonded Aggregates

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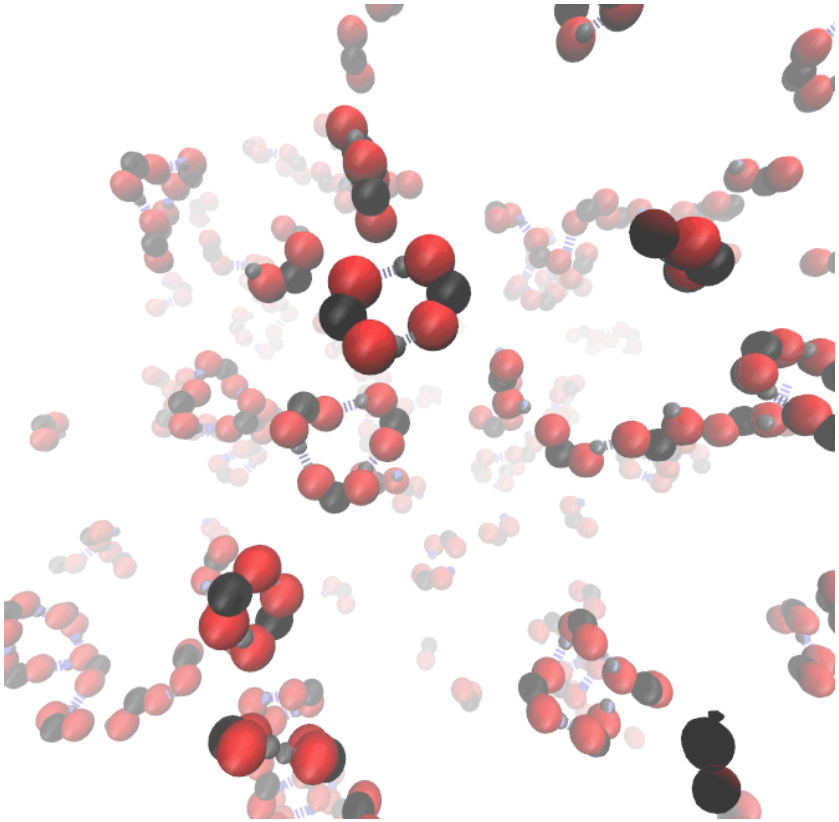
p21AA



p21SA