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Atomistic simulations reveal a surprising variety of morphologies in precise ionomers

Dan S. Bolintineanu, Mark J. Stevens, Amalie L. Frischknecht

Center of Integrated Nanotechnologies and Sandia National Laboratories

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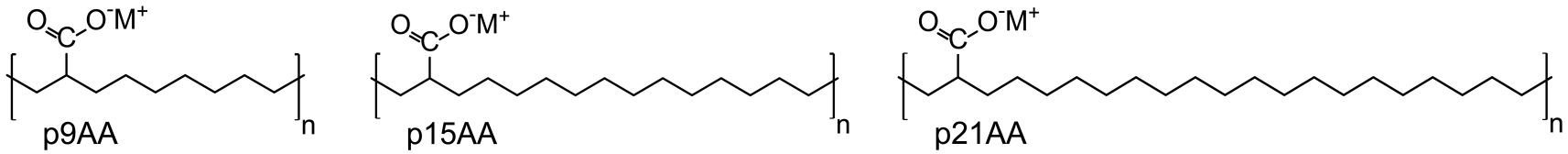
Motivation

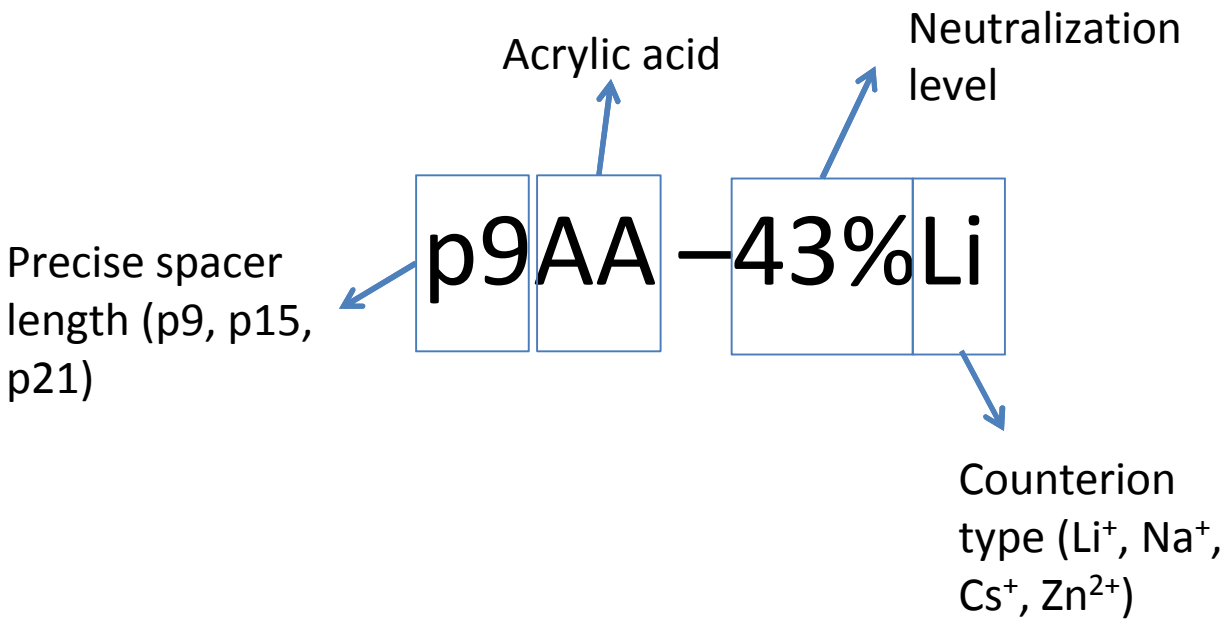
- Ionomers: polymers with a small fraction of covalently bound ionic groups
- Potential application as solid electrolytes in batteries
- Ionomer structure/morphology relationships poorly understood

Background

- Polyethylene backbone with **precisely** spaced acrylic acid functional groups (ADMET synthesis[1]):



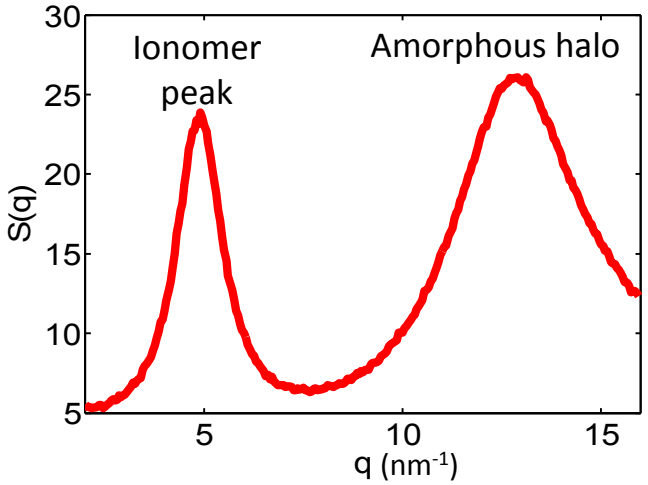
- Nomenclature:



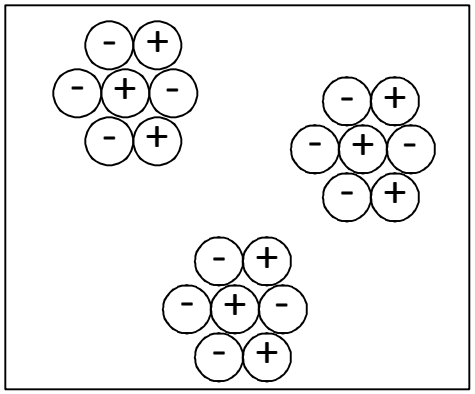
[1]Baughman et al, Macromolecules, 40, 6564

Background

- Experimental X-ray scattering data[1]



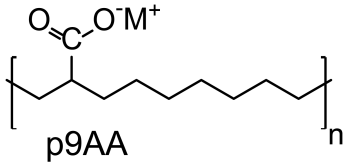
Spherical, liquid-like order



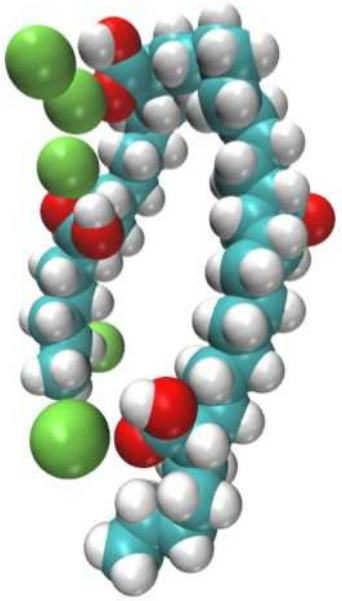
- Low wavevector peak associated with inter-aggregate scattering in all ionomers
- Shape and size of aggregates inaccessible to experiments → motivation for simulations

[1] Karen Winey group

MD methods

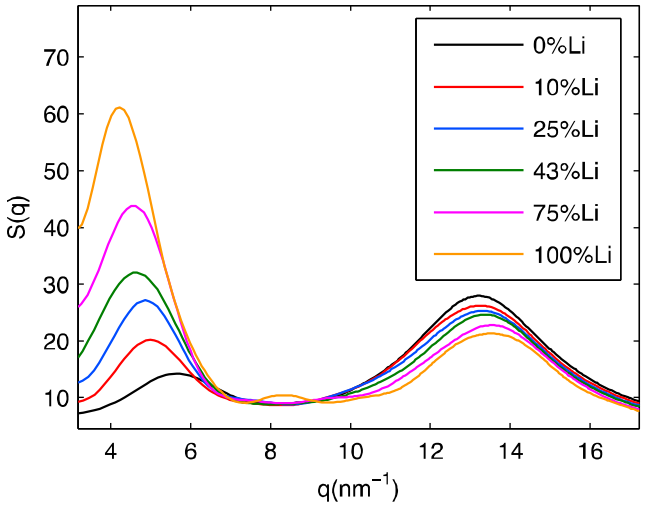


- Variations in:
  - Counterion type: M = Li^+, Na^+, Cs^+, Zn^{2+}
  - spacer length: p9, p15, p21
  - neutralization level: 0, 10%, 25%, 43%, 75%, 100%
- 80-200 molecules, n = 4 repeat units
  → ~64 X 64 X 64 Å box, total of ~25,000 atoms
- OPLS-AA fully atomistic force field
- PBCs, NVT ensemble, **150°C → well above T_g**
- LAMMPS used for MD production runs (~30 ns each)

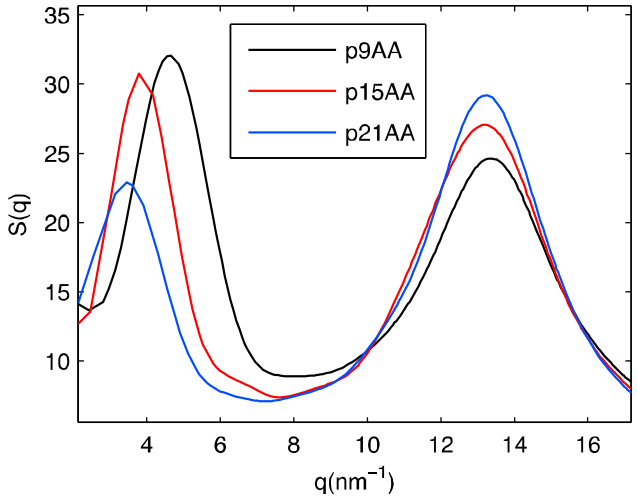


Results: lithium counterion

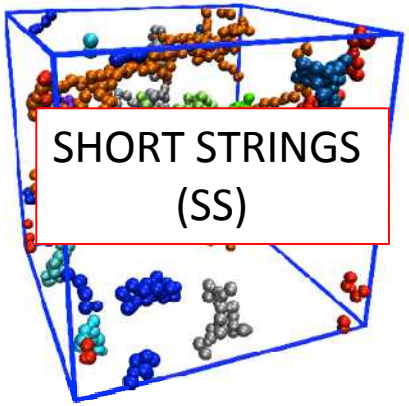
Variations in neutralization level



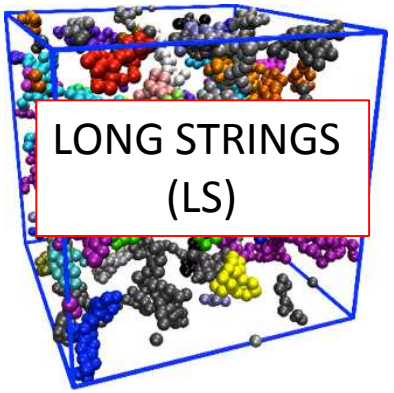
Variations in spacer length



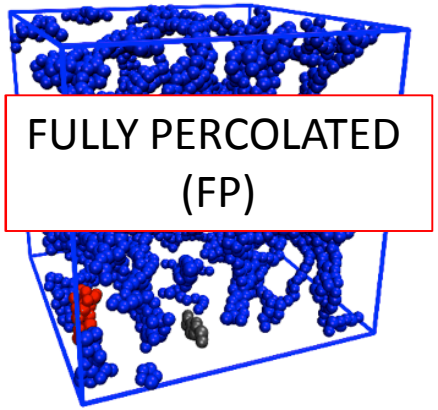
p9AA-10%Li



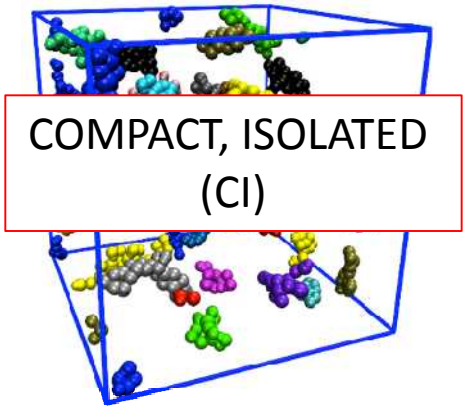
p9AA-43%Li



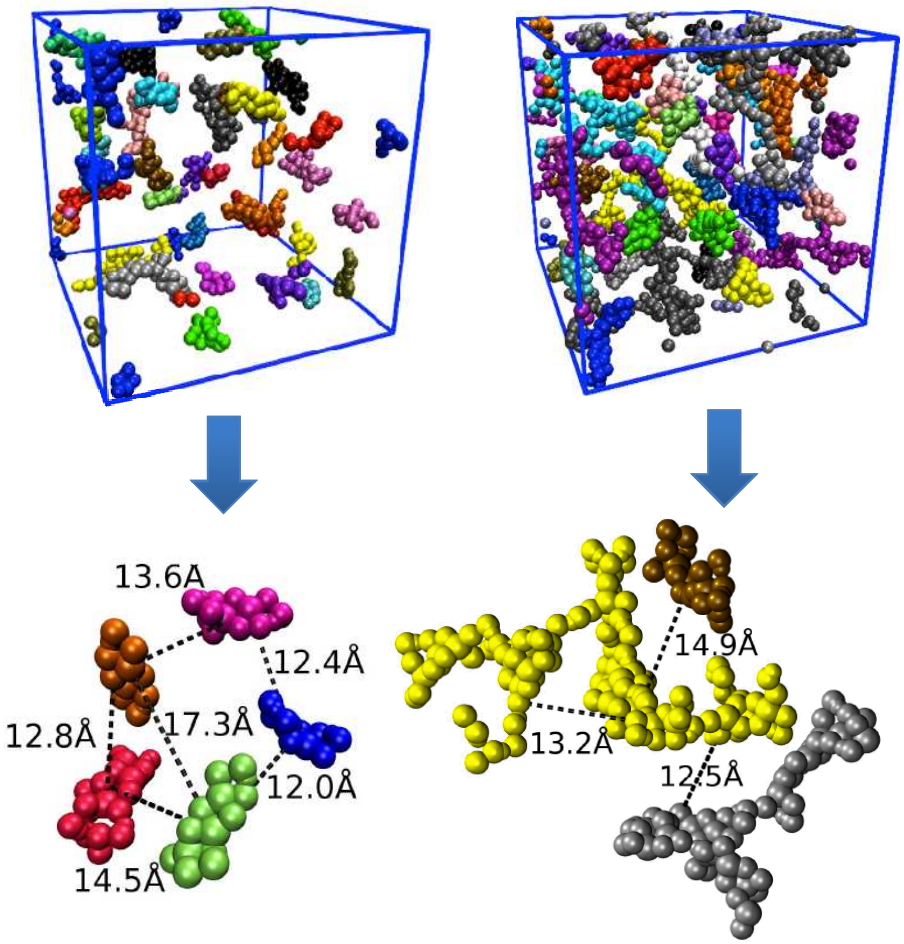
p9AA-100%Li



p21AA-43%Li

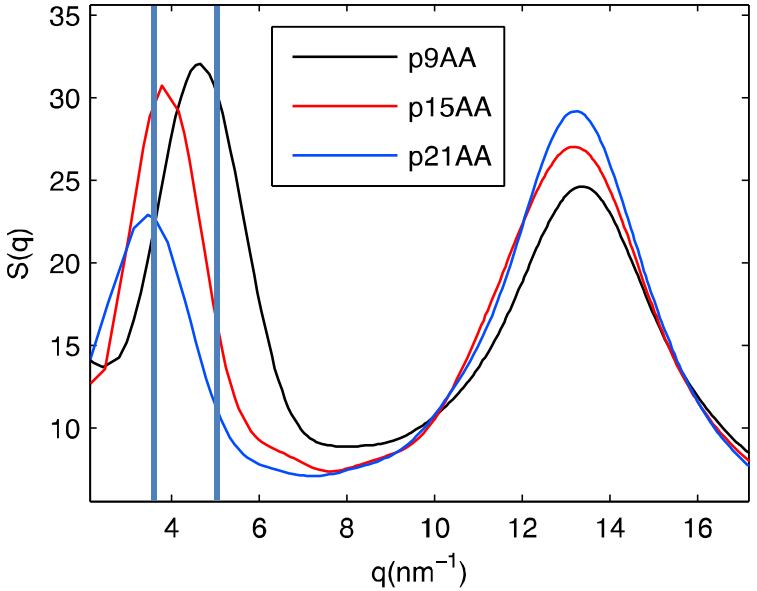


Relating aggregates to S(q)



$q = 2\pi/L \rightarrow 2\pi/1.7nm$ to $2\pi/1.2nm$

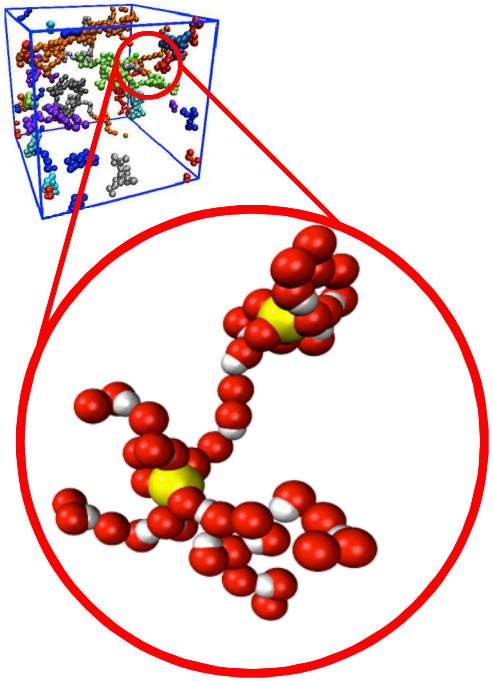
q range ~ 3.7 to 5.2 nm^{-1}



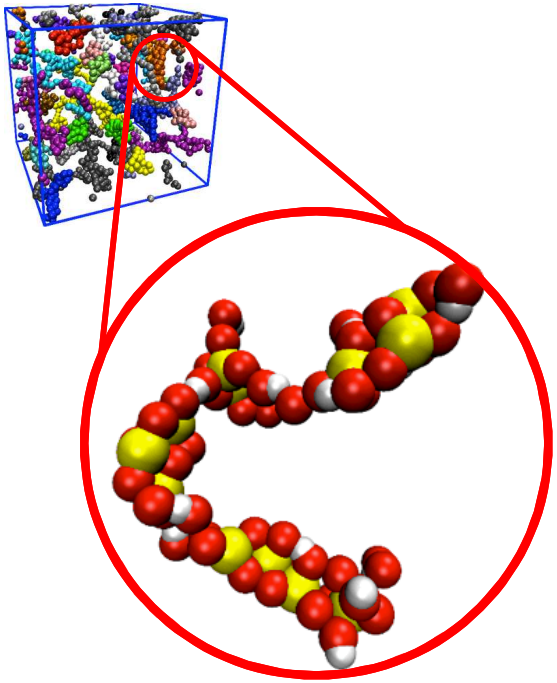
Ionomer peak is indeed due to interaggregate scattering!

Closer look at aggregates

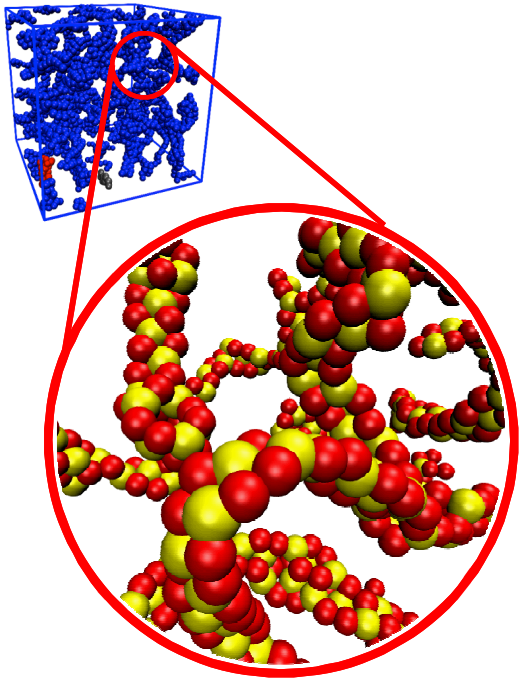
p9AA-10%Li



p9AA-43%Li



p9AA-100%Li

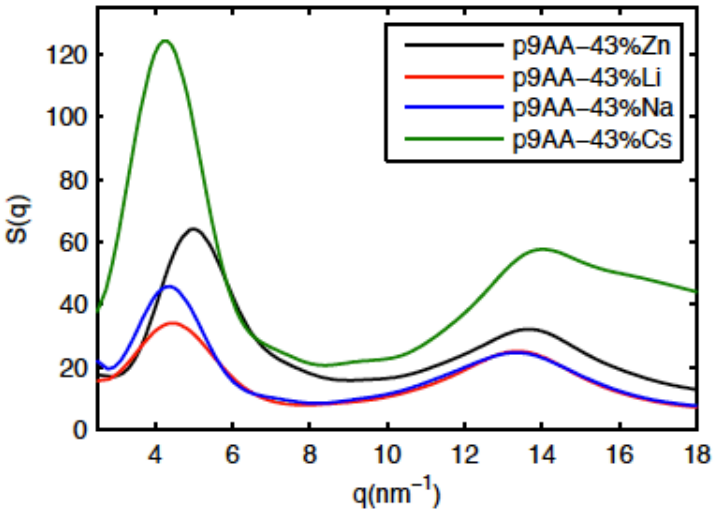


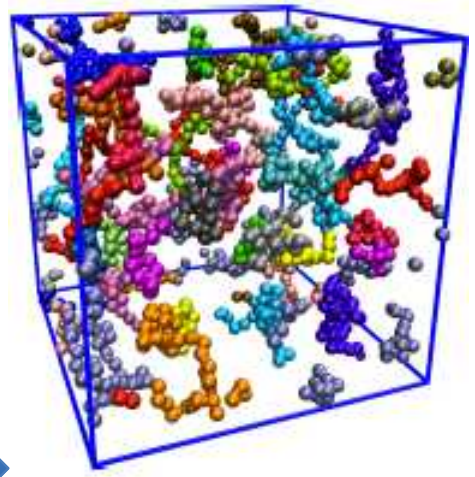
Two mechanisms of aggregate formation:

1. Counterion-oxygen association → dominant at **moderate to high** neutralization
2. Hydrogen-bonded networks → dominant at **low** neutralization

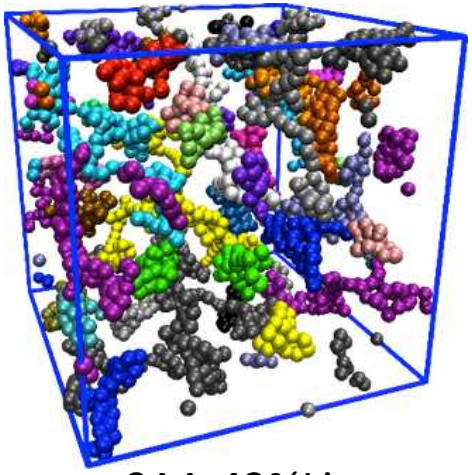
Variation in cation type

Cations: Zn^{2+}, Li^{+}, Na^{+}, Cs^{+}

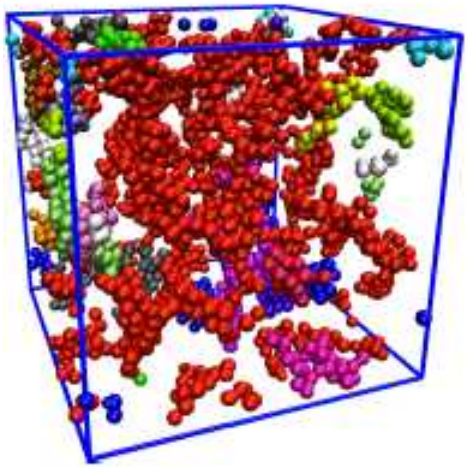




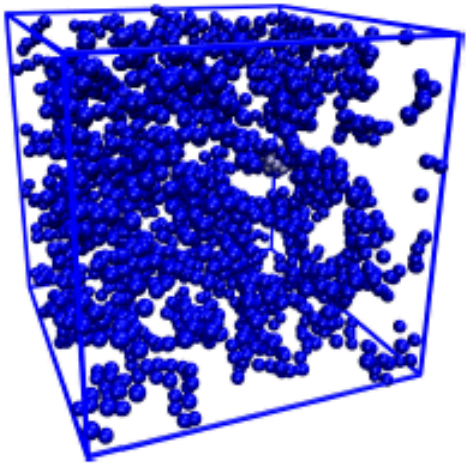
p9AA-43%Zn



p9AA-43%Li



p9AA-43%Na

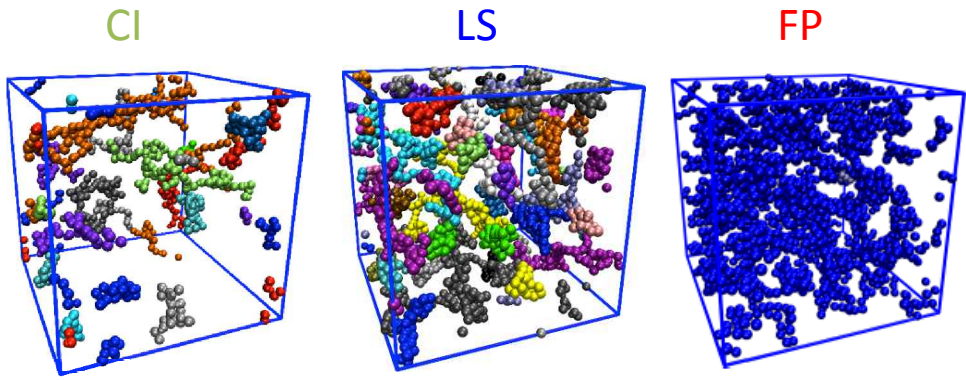


p9AA-43%Cs

Aggregate classification

Several morphologies distinguishable:

- Compact, roughly spherical (CI)
- Short, stringy (SS)
- Long, stringy (LS)
- Partially percolated (PP)
- Fully percolated (FP)

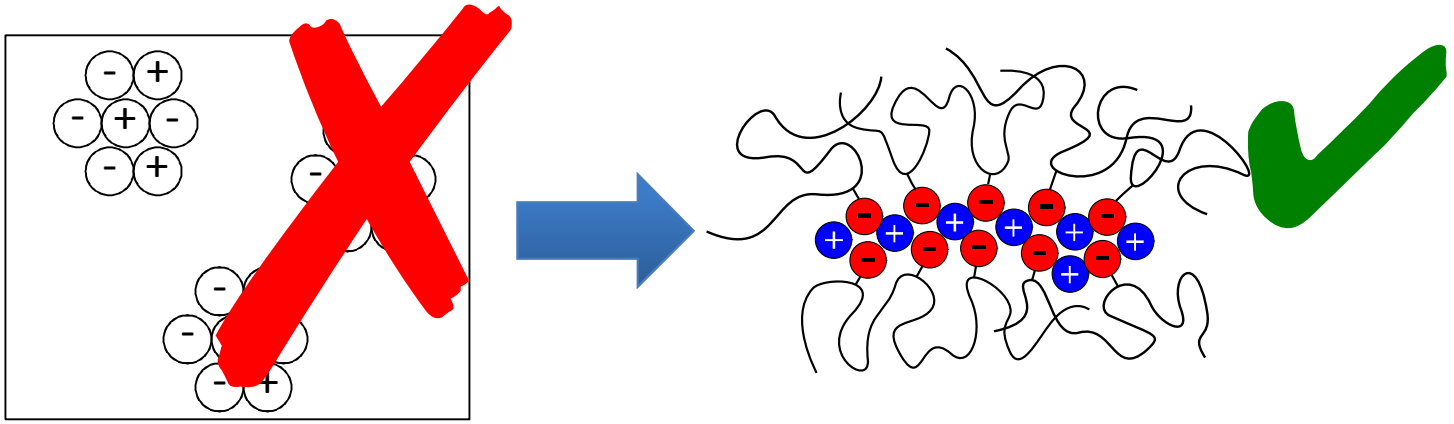


	10%	25%	43%	75%	100%
Zn	LS	LS	SS	SS	SS/CI
Li	SS/LS	LS	LS	LS/PP	PP/FP
Na	SS	SS/LS	PP	FP	FP
Cs	LS	PP	FP	FP	FP

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

Summary

- Unexpected aggregate morphologies suggest need for novel interpretation of scattering data



- Significant variation in morphology as a function of neutralization, spacer length and cation type
- Two mechanisms of aggregate structure formation: counterion-oxygen association and hydrogen bonding → also explains aggregation in acid forms (0% neut.)

Acknowledgements

- Prof. Karen Winey, Francisco Buitrago – University of Pennsylvania
- Ken Wagener Group – University of Florida
- Lisa Hall, Chris Lueth
- National Energy Research Scientific Computing (NERSC) center
- Sandia Laboratory Directed Research and Development (LDRD) grant

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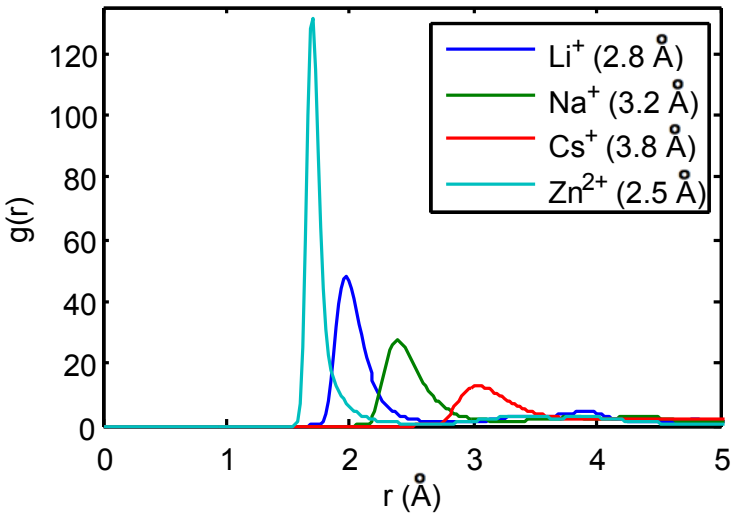
QUESTIONS?

Extra slides

Analysis of aggregates

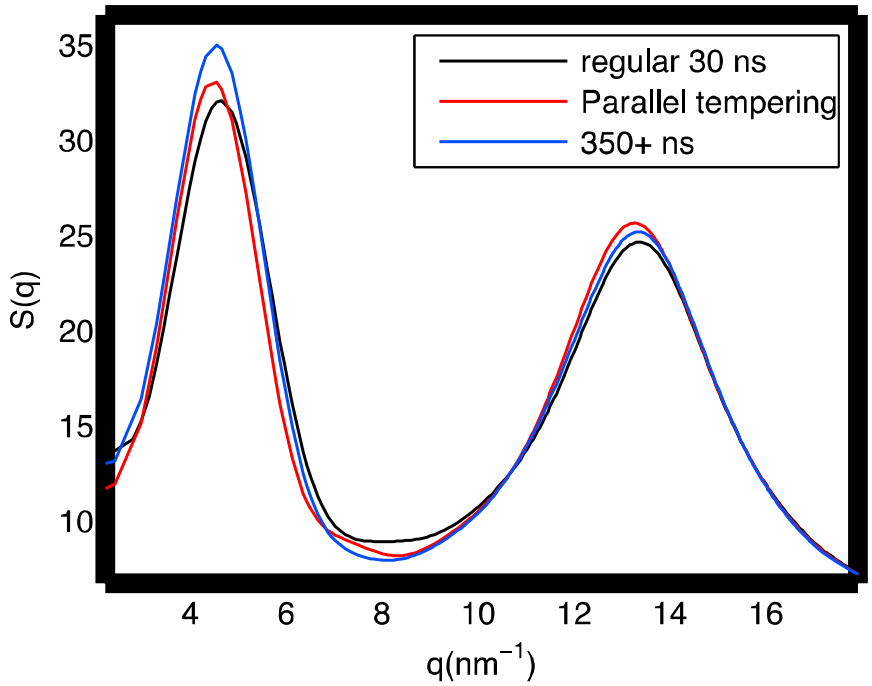
- Aggregates defined by pairwise cluster search over all ion-oxygen and oxygen-hydroxyl hydrogen pairs
- Oxygens and hydrogens on same carboxyl group always included in same aggregate
- Pairwise cutoff distance based on g(r):



- Aggregates with less than 2 ions not included in analysis

Results: structure factor convergence

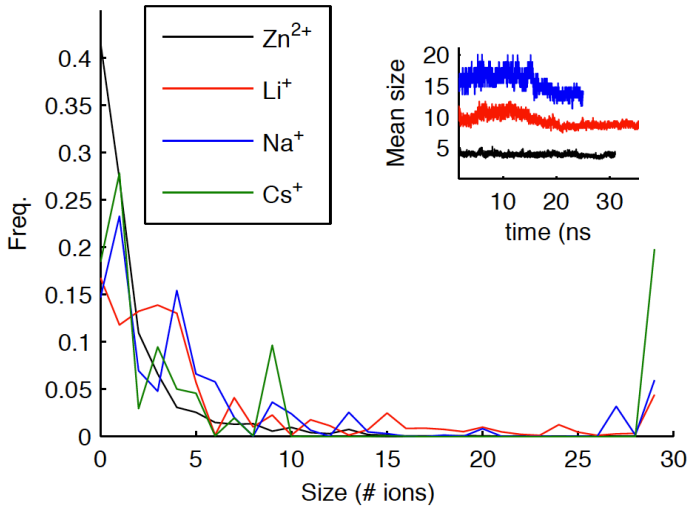
- Most simulations run for ~30 ns
- To check convergence: compare to longer simulation, parallel tempering



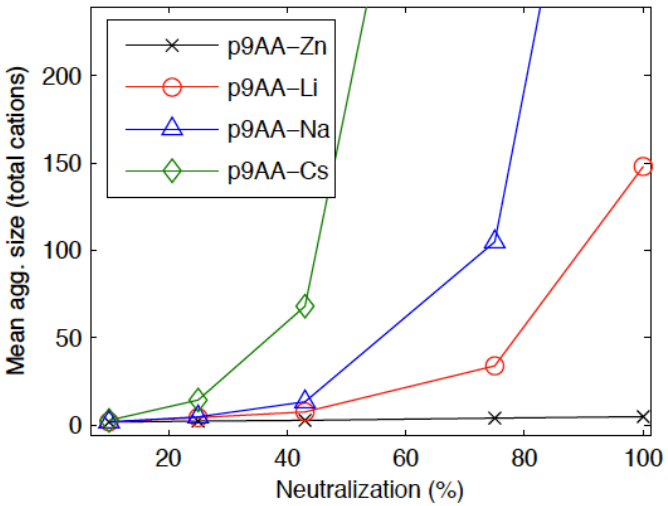
→ Simulations appear to be well-converged after 30 ns

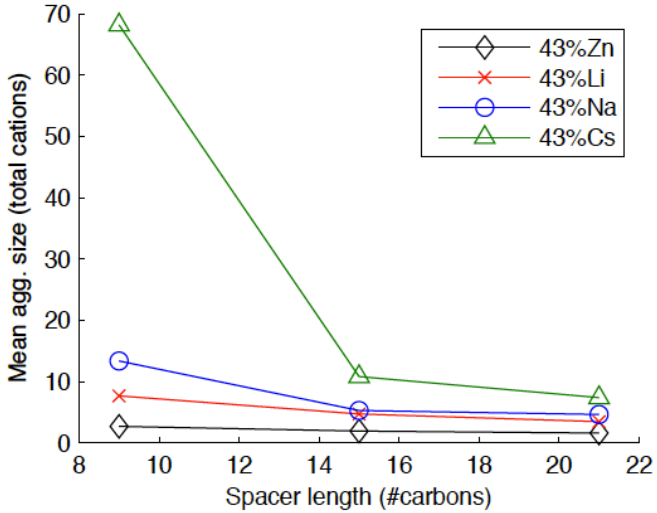
Quantifying aggregates

Aggregate size distribution for p9AA-43% cases



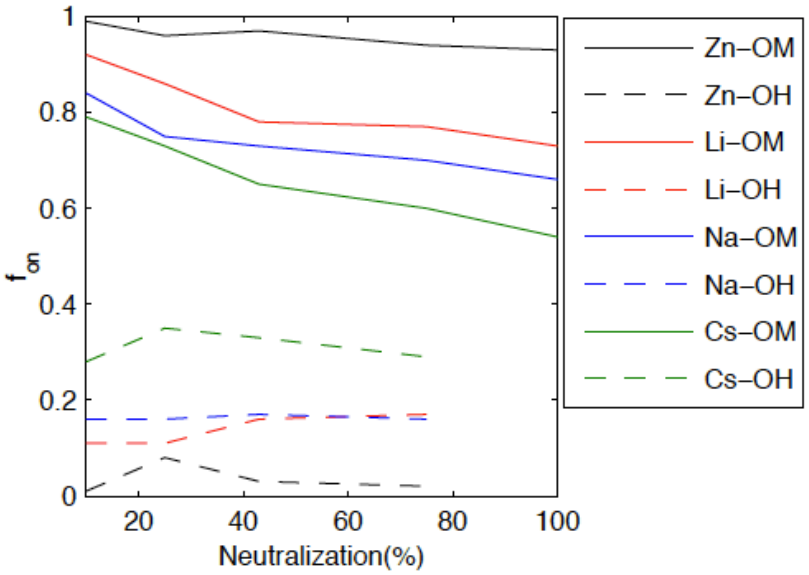
- Aggregate size ranking: Cs > Na > Li > Zn
- Increased neutralization, decreased spacer length leads to larger aggregates
- Percolated morphologies apparent in sharp size increase



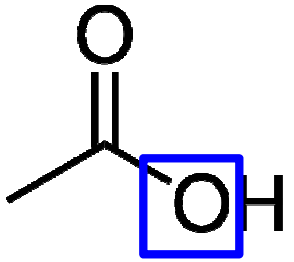


Quantifying ion-oxygen interactions

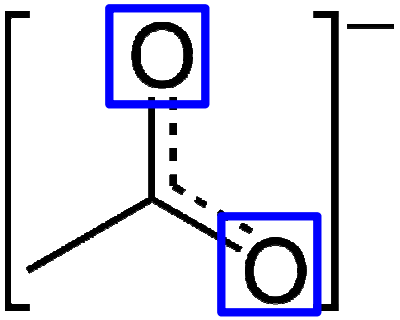
f_{on} : mean fraction of simulation time a particular cation-oxygen pair is associated



OH:



OM:

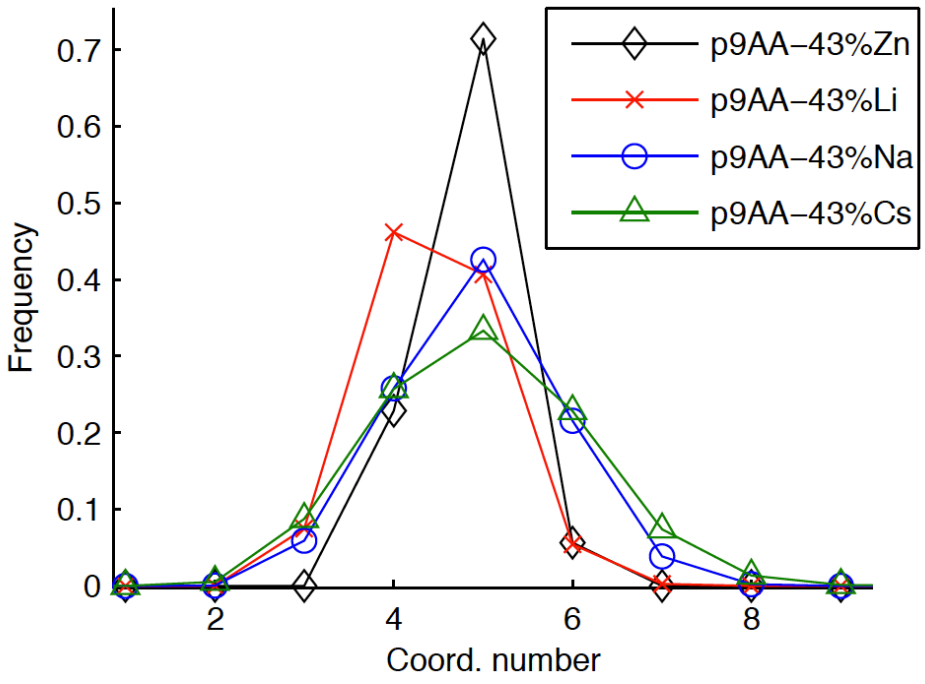


- Ion-OM association: Zn > Li > Na > Cs
- Follows expected Coulombic interaction strength, BUT exact reverse order of aggregate size rankings

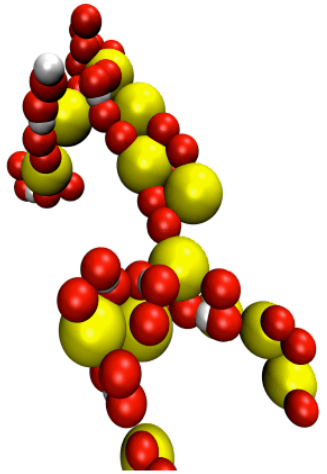
→ Weaker ionic association **promotes** aggregate growth

Quantifying ion-oxygen interactions

Distribution of coordination numbers
Oxygen around cations



- Higher Coulombic attraction leads to tighter coordination structures
- Tight coordination structures not favorable for aggregate growth!



ults: structure factors

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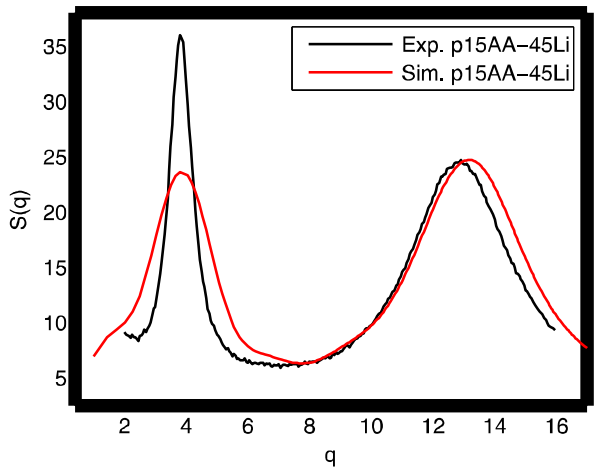
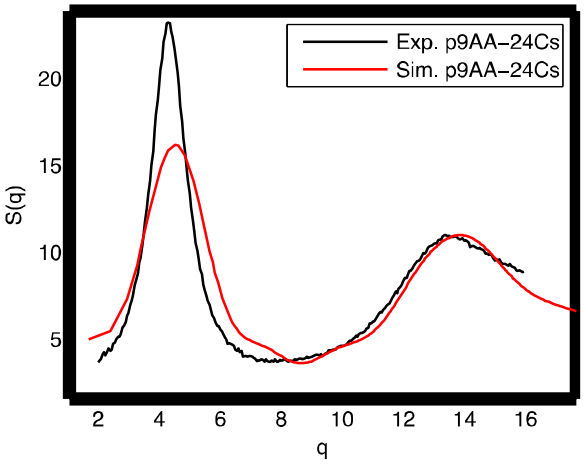


$$S(q) = \frac{1}{N}\sum_{i,j=1}^{N} f_i f_j \left\langle e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \right\rangle$$

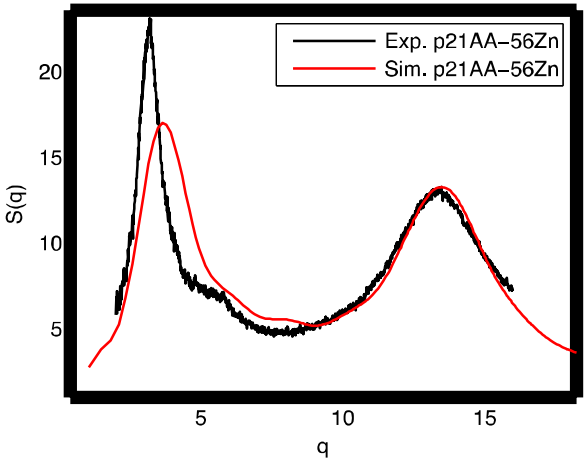
$$= \sum_k c_k f_k^2 + 4\pi\rho \int_0^\infty \frac{\sin(qr)}{qr} r^2 \sum_{k,l} c_k c_l f_k f_l \left(g_{kl}(r) - 1\right) dr$$

$$f_k = c_k + \sum_{i=1}^{5} a_{ik} \exp(-b_{ik} q_0^2)$$ #

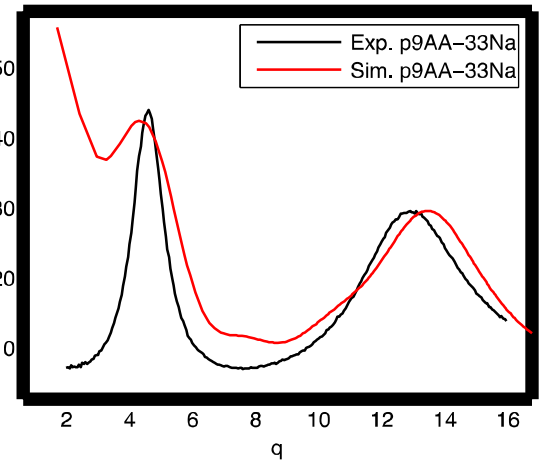
Cs^+



Zn^{2+}



Na^+



* Experimental data from Karen Winey group

Waasmaier and Kirfel, Acta Cryst. A51, 416-431 (1995)