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Nanoscale Ionic Aggregates in Ionomer Melts

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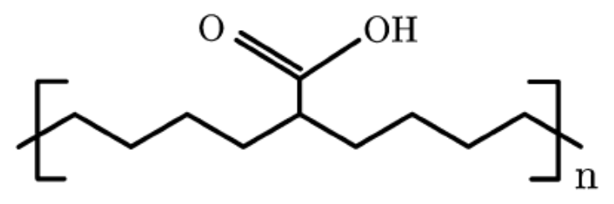
Abstract

Ionomers are polymers that contain both electrically neutral and charged chemical groups, and are being investigated as potential solid electrolytes in batteries. We report atomistic molecular dynamics (MD) simulations of model ionomers with precise spacing between charged groups (polyethylene-co-acrylic acid). We explore different counterion types, neutralization levels, and spacer lengths between acid groups and provide a thorough analysis of the resulting nanoscale ionic aggregate morphologies. Structure factors computed from the simulations are in good agreement with previous experimental X-ray scattering data, which provides strong validation of the simulation methods. Aggregate morphologies, which cannot be readily observed experimentally, are shown to range from small spherical aggregates to string-like shapes and large percolated networks. These unexpected morphologies suggest the need for a novel interpretation of scattering data, and may have important consequences for ion transport.

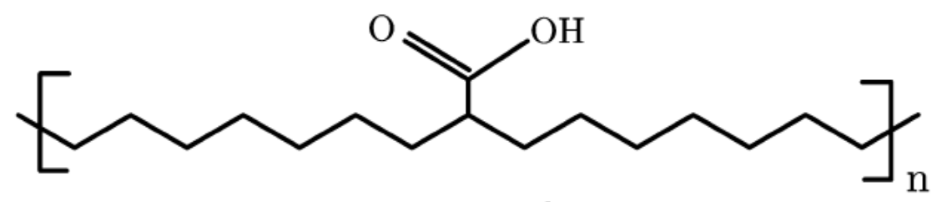
Introduction

- Nanoscale ion-rich aggregates form in ionomer melts
  → unique mechanical, thermal and electrical properties
- Relationship between chemical structure and aggregate morphology poorly understood → motivates **simulations of precise ionomer systems**
- PE backbone with precisely spaced COOH functional groups

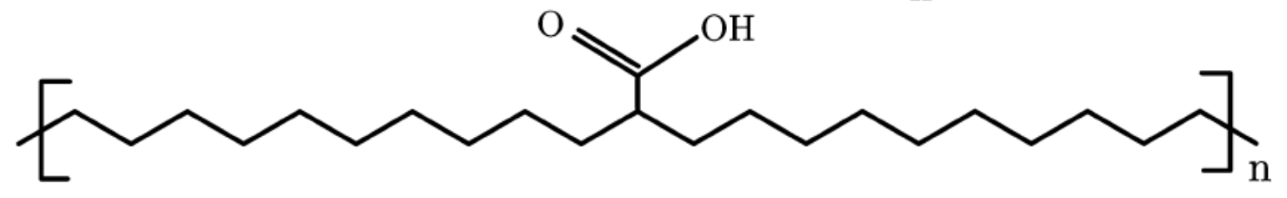
p9AA



p15AA



p21AA



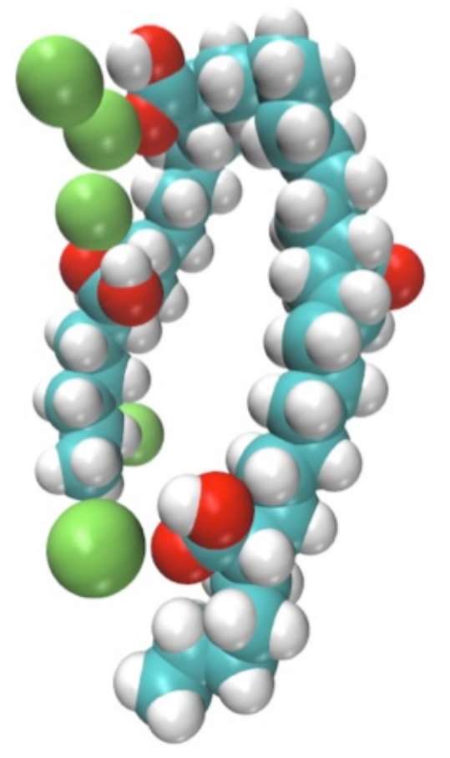
- Variations in spacer length, neutralization level and cation type
- Nomenclature:

Neutralization level

Precise spacer length
(9 carbons here) ← p9AA –43%Li → Cation type

Methods

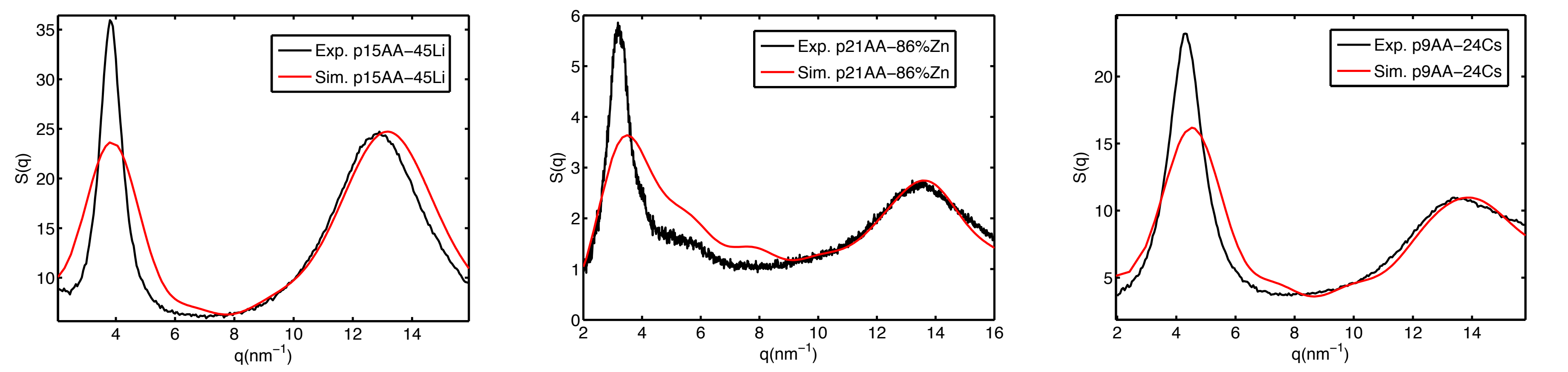
- 80-200 molecules, n = 4 repeat units
  → ~ 64 X 64 X 64 Å simulation box, total ~ 25,000 atoms
- PBCs, NVT ensemble, 150°C (well above T_g)
- LAMMPS used for MD production runs (~ 30 ns each), OPLS-AA fully atomistic force field



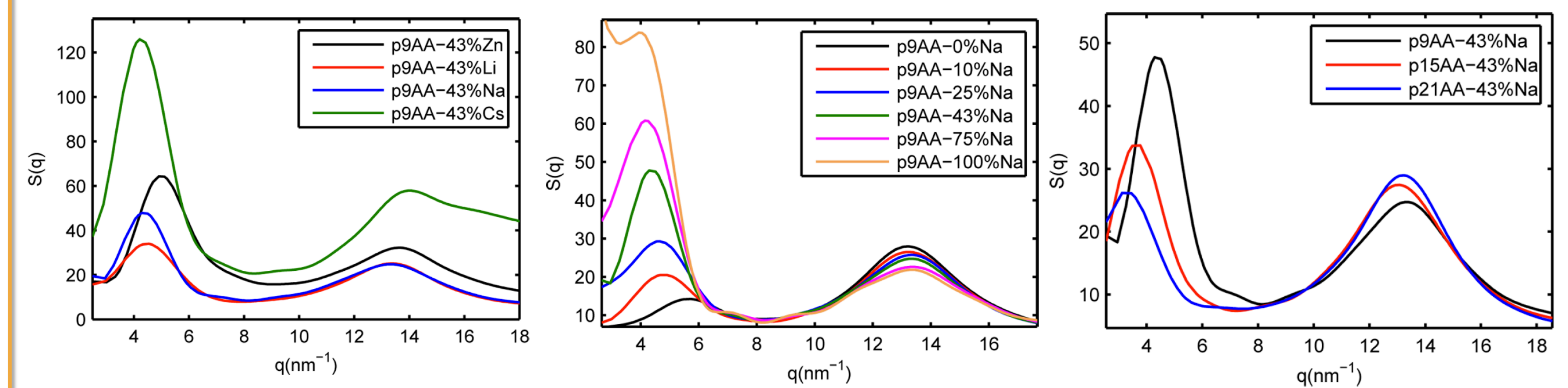
Fully atomistic representation of a single chain neutralized with Li^+

Results: Scattering data

Good agreement between computed S(q) and experimental scattering data[3]:



Simulation structure factor data:



Effects of cation type

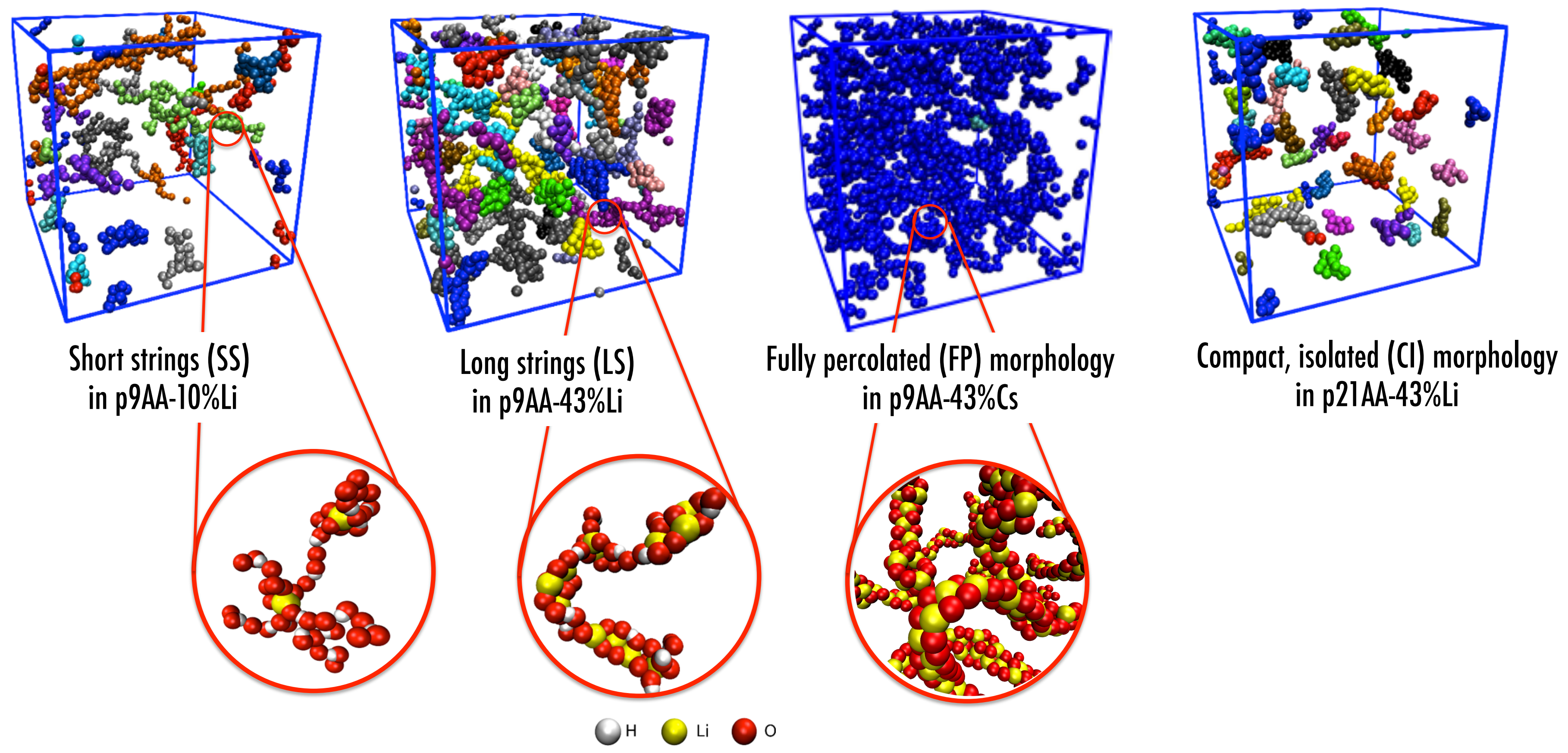
Effects of neutralization level

Effects of spacer length

- Major features: ionomer peak at low q and amorphous halo at high q
- Higher neutralization → higher ionomer peak → increased aggregate order
- Longer spacer → ionomer peak shifts to low q → increased inter-aggregate spacing
- S(q) insufficient to determine aggregate structure: see images below

Results: Aggregate morphologies

- Aggregate morphologies visualized directly in MD simulations
  - all atoms in same cluster have same color ?
  - color is by aggregate size ?
  - only display O and cation atoms ?
- Surprising diversity of morphologies as a function of cation type, neutralization and spacer length:



Short strings (SS) in p9AA-10%Li

Long strings (LS) in p9AA-43%Li

Fully percolated (FP) morphology in p9AA-43%Cs

Compact, isolated (CI) morphology in p21AA-43%Li

Two mechanisms of aggregate formation:

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

Results: Aggregate Types/Sizes

morphology summary

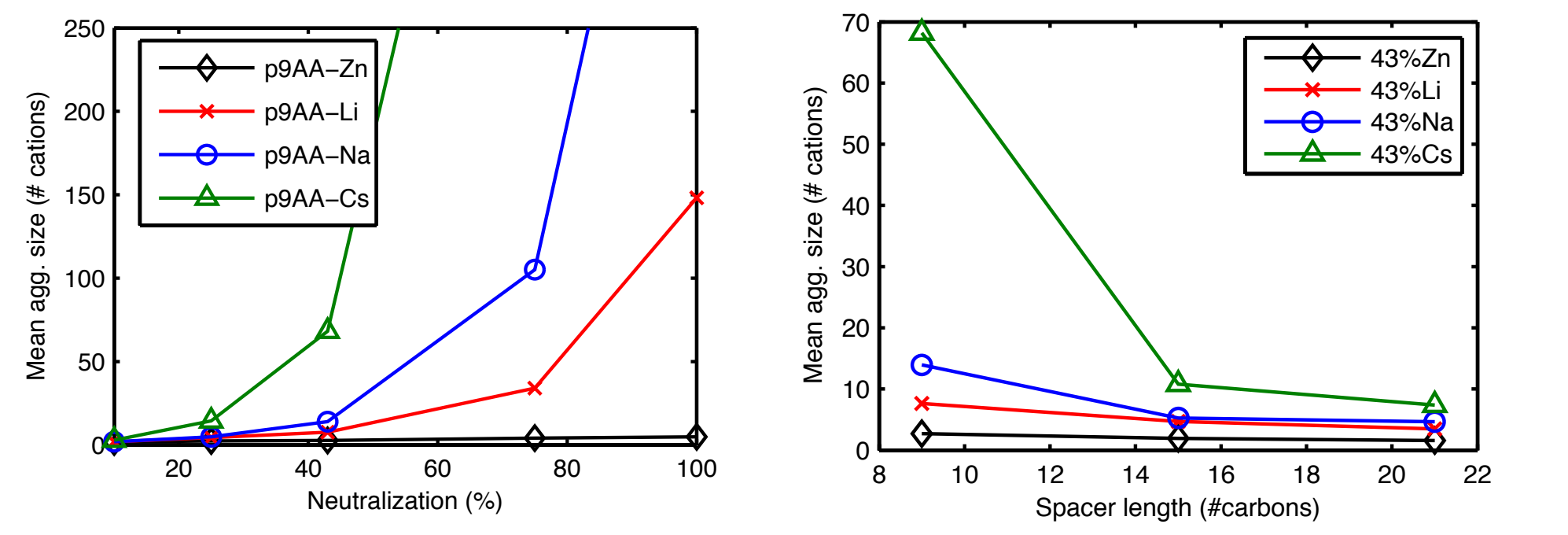
p9AA-y%M

	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

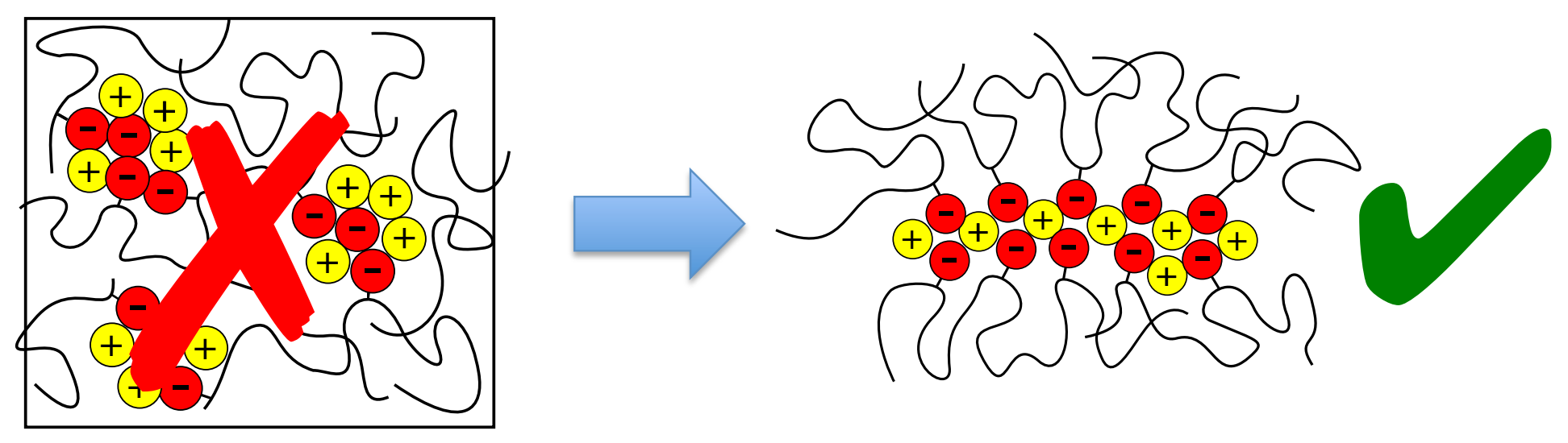
	p9	p15	p21
Zn	SS	SS/CS	CS
Li	LS	SS	SS/CS
Na	PP	SS	SS/CS
Cs	FP	LS/PP	LS/SS

mean aggregate sizes



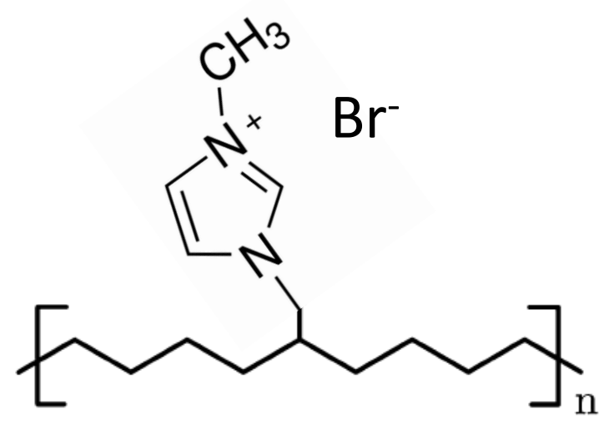
Conclusions and Future work

- A wide variety of morphologies exists as a function of cation type, neutralization and spacer length
- Aggregates are not typically spherical
- S(q) is insufficient to determine aggregate structure
  → simulations provide additional insight



Future Work

- Effect of applied electric field (see Ting et al for analogous coarse-grained model)
- Analysis of dynamics for much longer simulations (GPU-enabled)
- Ionomers with chemical structures closer to realistic battery materials, e.g. methylimidazolium bromide:



References and Acknowledgements

1. Bolintineanu et al, *ACS Macro Letters*, v. 2, pp 206-210, 2013
2. Bolintineanu et al, *Macromolecules*, v. 46, pp. 5381-5392, 2013
3. Buitrago, Bolintineanu et al, in prep.

CINT users: Karen Winey group (U. Penn.), Jim Runt (Penn. State)

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