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Molecular Dynamics Simulations of Percolated Ionic Aggregates in Precise Sulfophenylated Polyethylene Polymers

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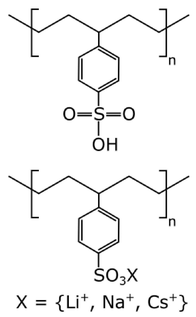
Introduction

Due to their capacity to function as single-ion conductors, ion-containing polymers present an attractive potential alternative to standard electrolytes in Li-ion batteries. To facilitate the design of ion-containing polymers for this purpose, a greater understanding of their microscopic structure and dynamic properties is needed. We present molecular dynamics simulations of a novel set of single ion-conducting polymers containing precisely-spaced sulfonated phenyl groups, which are fully neutralized with a counterion X^+ (Li^+, Na^+, or Cs^+). The focus is on the structure of self-assembled ionic aggregates and ion dynamics.

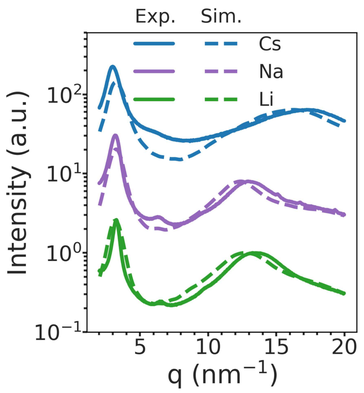


Molecular Dynamics Simulations

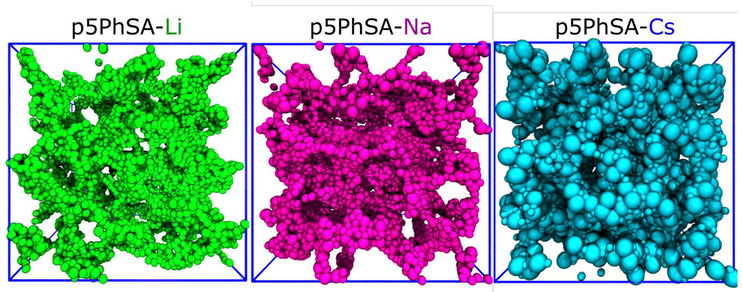
- OPLSAA force field
- n = 8, 95% sulfonation, 64 to 728 molecules, 15k to 400k atoms
- Production runs at 433 K for 100 ns to 9 μs

Aggregate Structure Factor and Percolation

- Structure factor computed from MD simulation (Fourier Transform of g(r) – 1) corresponds to intensity profiles obtained from X-ray scattering



- Ionomer peak intensity and amorphous halo shape influenced by cation species
- Simulation and experiment agree reasonably well in position and relative intensity of ionomer peak and amorphous halo
- Ionomer peak (q_1) occurs at about 3 nm^{-1} for each ion

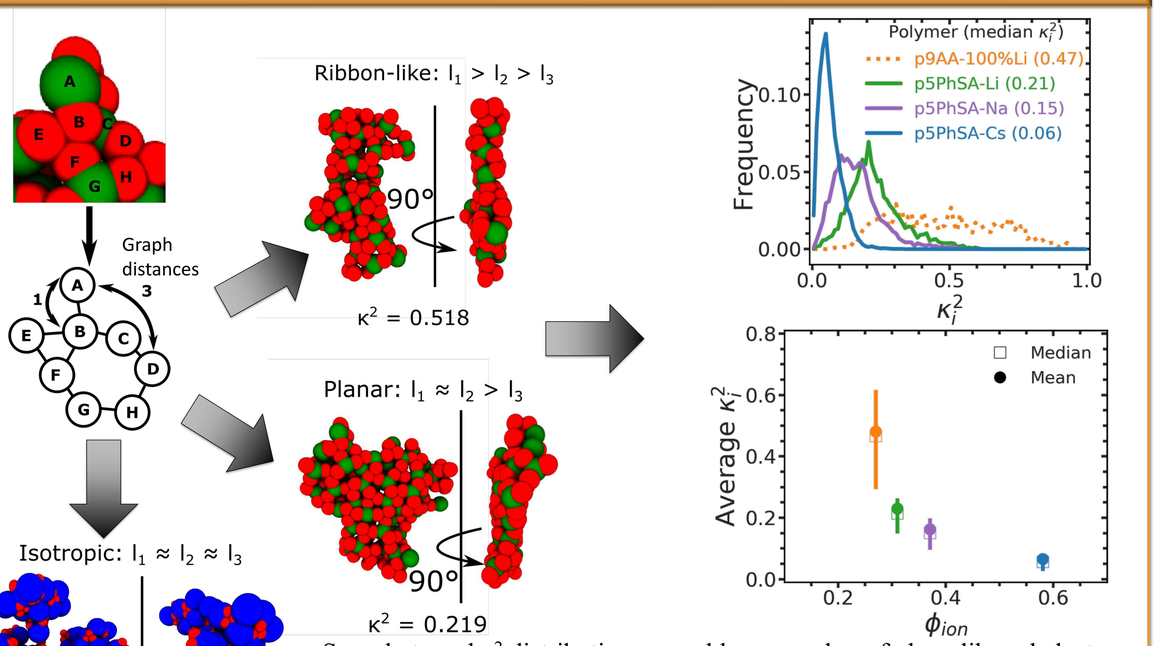


- First maximum of radial distribution functions used to define cutoff distances to determine if atoms are in the same cluster
- Cations and oxygen atoms form single percolating cluster
- Intraaggregate spacings correspond to q_1 peak in structure factor

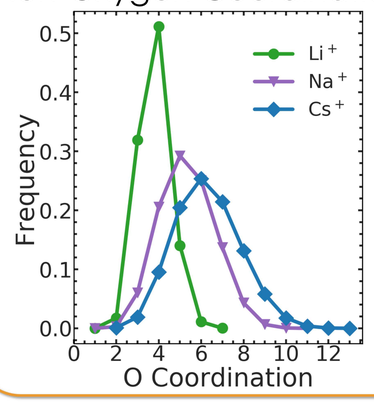
Aggregate Morphologies

Intermediate Subclusters

- Mapped aggregate structure to graph theory representation using cutoffs obtained from RDFs.
- Extracted subclusters using *graph-distance* cutoff
- Compute relative shape anisotropy (κ_i^2) of extracted subcluster
- Compare with previously studied p9AA-100 Li system



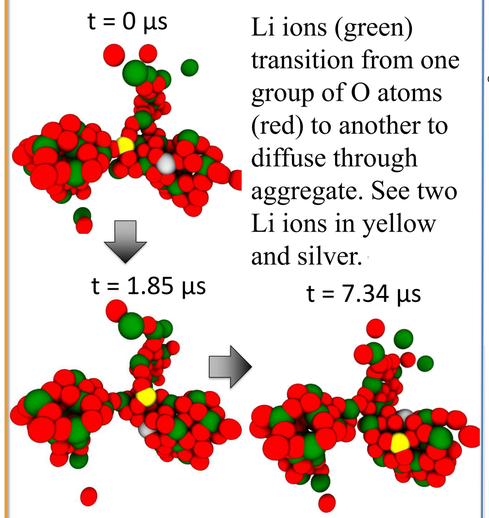
Ion-Oxygen Coordination



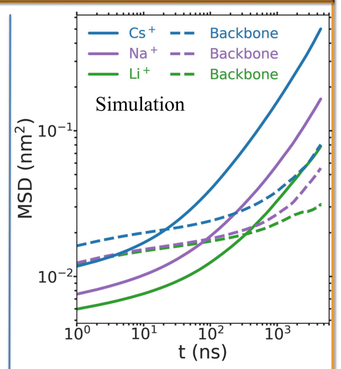
- Snapshots and κ^2 distributions reveal large number of plane-like subclusters in Li and Na polymers, but greater isotropy in Cs polymers
- Previously studied p9AA-100 Li polymers exhibit ribbon-like and string-like domains with higher values of κ^2
- Correlation between volume fraction of ionic groups in polymer and relative shape anisotropy of aggregate structures

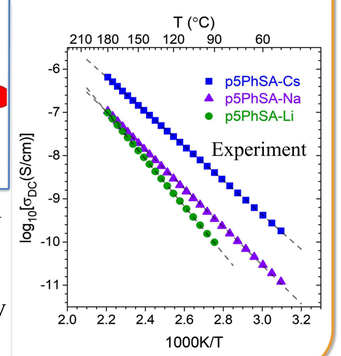
Dynamics

Li motion in aggregate



Li ions (green) transition from one group of O atoms (red) to another to diffuse through aggregate. See two Li ions in yellow and silver.





- Exponential dependence of measured conductivity on 1/T indicates Arrhenius behavior
- Qualitative agreement in conductivity between experiment and MSDs

Conclusions

- Reasonably good agreement between computed and experimentally measured structure factors.
- Ionic groups assemble to form percolating aggregates
- Cation species has significant impact on local and intermediate structure of aggregate; Li and Na aggregates contain several planar regions while Cs tends to yield more isotropic subclusters
- Qualitative agreement between MSD and conductivity
- Arrhenius temperature dependence of conductivity, larger cation diffusivities relative to polymer backbones, and observed intraaggregate diffusion indicate decoupled ion transport.

Future Work

- Probe impact of hydration on aggregates and conductivities
- Study impact of polarization on simulations

References

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