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Ion Transport in Ion-Containing Polymers from MD Simulations

Amalie L. Frischknecht

Sandia National Labs

TSRC on Polymer Physics

June 28, 2017

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Dynamics in Precise Acid and Ion-Containing Polymers from MD Simulations

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Sandia National Labs

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Madhu Tyagi
Christopher Soles

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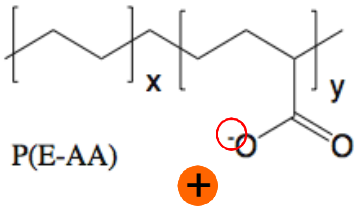
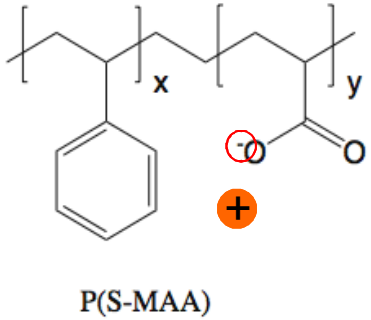
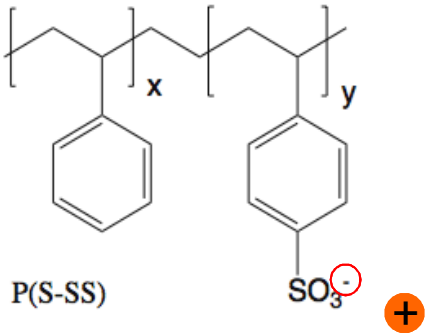
Ionomer Melts: Polymers + Ions

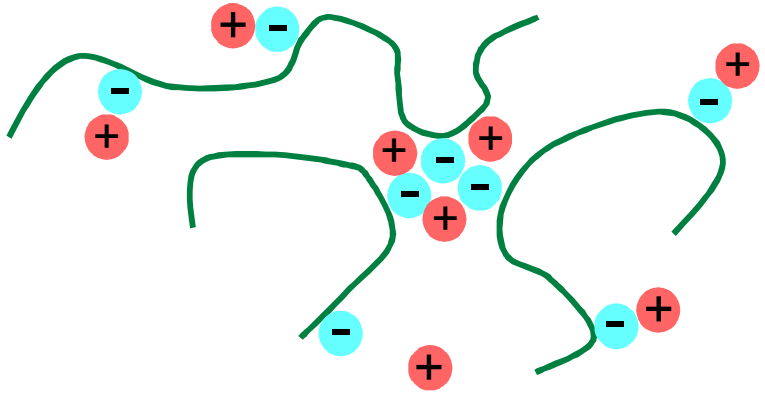
(no solvent)







Coulombic forces favor aggregates
polymer entropy limits size



nm-scale ionic aggregates

Effects of Ionic Aggregates

- improved toughness
- interesting rheology
- reduced crystallinity

- typically low ionic conductivity

DuPont™ Surlyn®

To control and improve ion conductivity

- Where are the ions?
- How do the ions move?
- What can we do to make ions move faster?

How do we improve conductivity?

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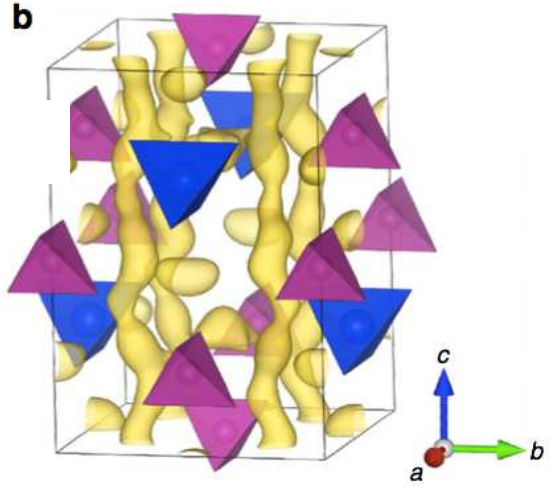
ceramics can be superionic conductors

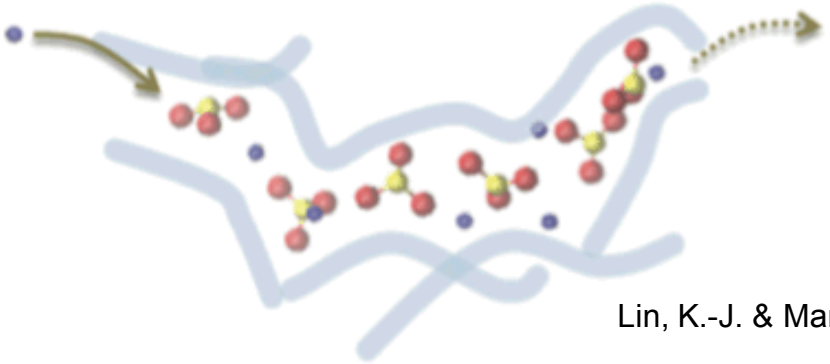
Li^+ in $Na_{10}SnP_2S_{12}$

0.4 mS/cm at room temperature



Richards, W. D. *et al. Nature Communications* **7,** 1–8 (2016).

melt: ionic aggregates can help ions move collectively

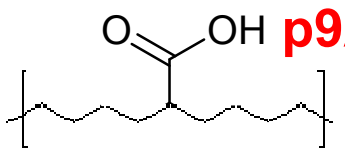


Lin, K.-J. & Maranas, J. K. *Phys Rev E* **88,** 052602 (2013).

design percolated morphologies?

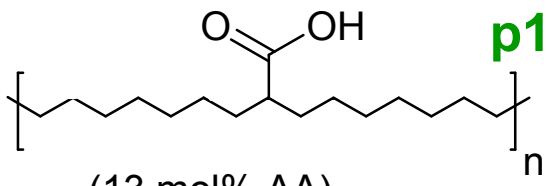
Precise poly(ethylene-co-acrylic) acid

PE backbone with **precisely** spaced carboxylic acid functional groups



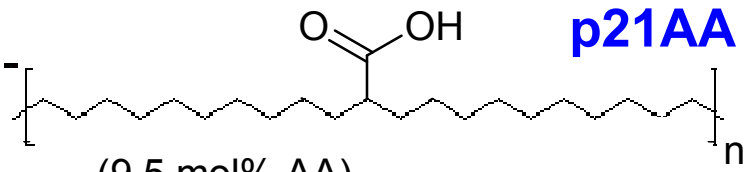
p9AA

(22 mol% AA)



p15AA

(13 mol% AA)



p21AA

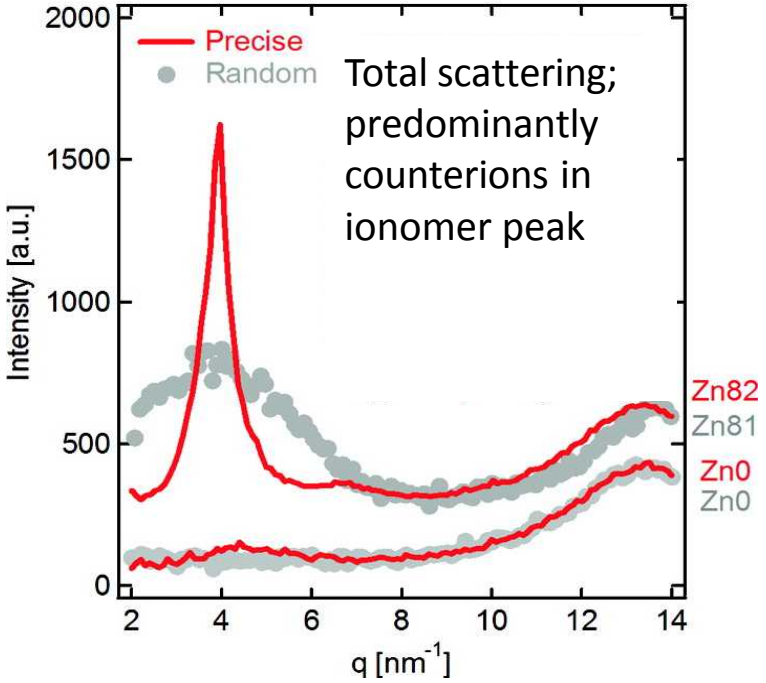
(9.5 mol% AA)

Neutralization level

p9AA – 43% Li

Precise spacer length (p9, p15, p21)

Counterion type (Li^+, Na^+, Cs^+, Zn^{2+})



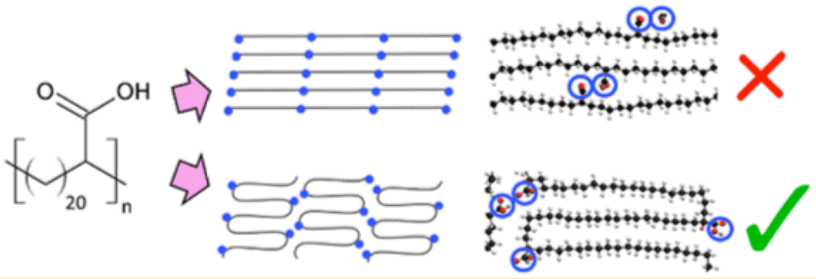
Wagener group, University of Florida

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

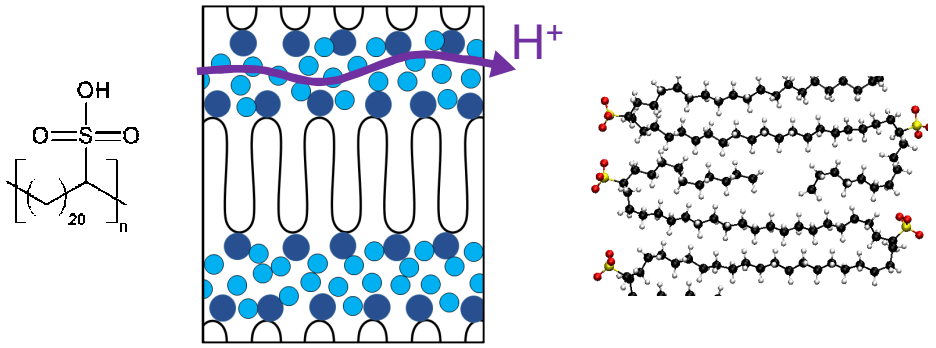
Why Precise Polymers?

- easier to understand mechanisms
- comparison between experiment and simulation
- might give a handle to building hierarchical order

p21AA forms acid layers in crystals

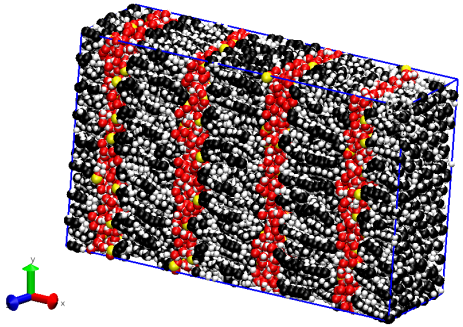


p21SA: Highly ordered, tunable

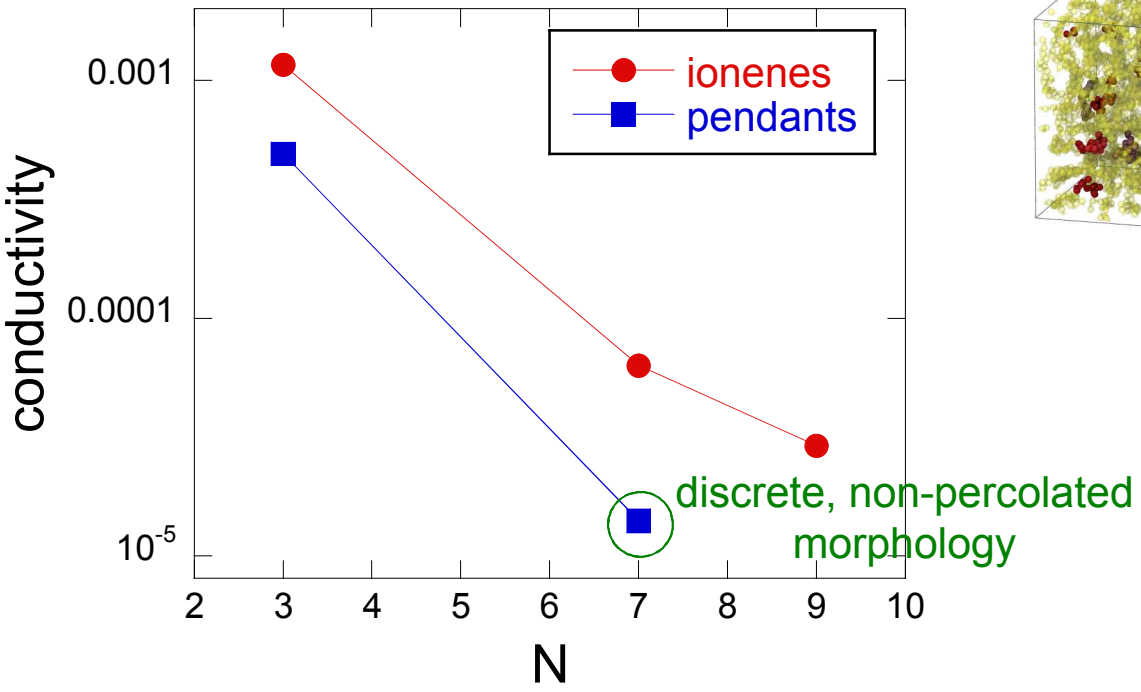


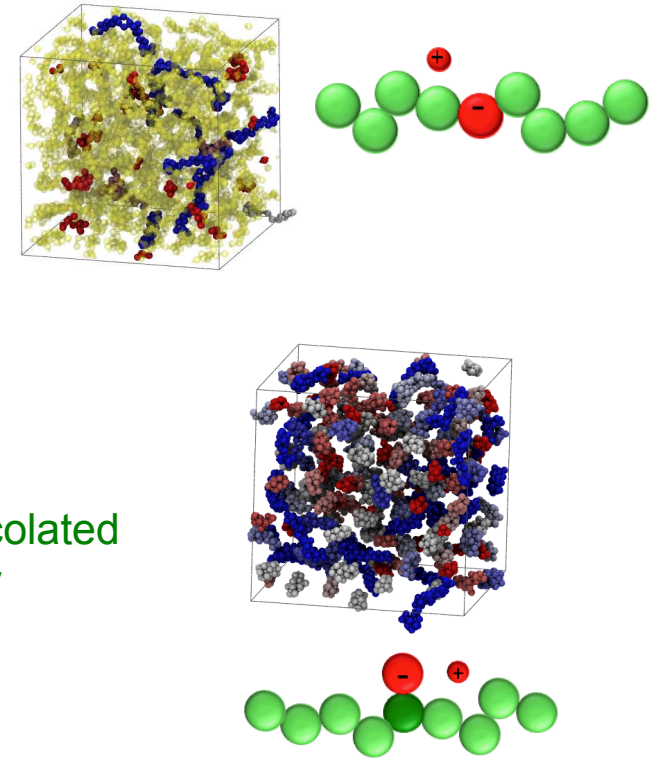
Trigg, E. B., Stevens, M. J., & Winey, K. I. (2017), *JACS*, *139*, 3747–3755

Trigg et al, in preparation



Coarse-grained model



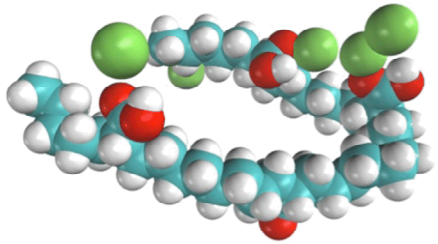


- conductivity decreases with decreasing ion concentration
- lowest for non-percolated aggregate morphology

Hall et al, *Macromolecules*, 2012; Ting et al., *Macromolecules*, 2015

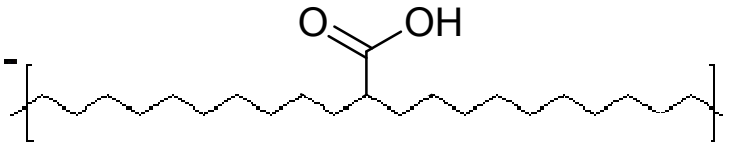
Rest of the talk

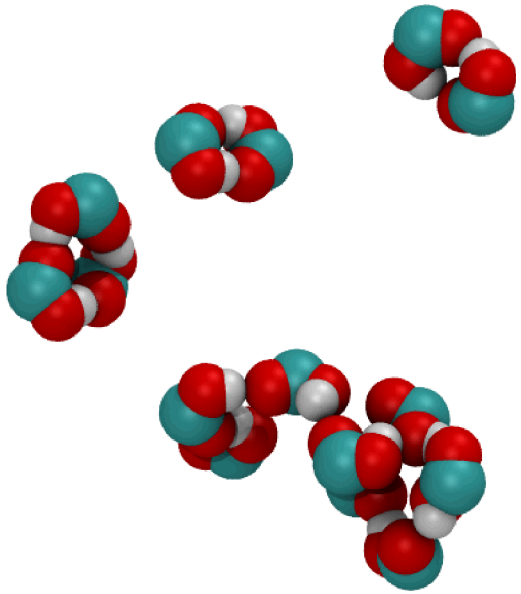
- dynamics in acid-containing precise polymers
  - QENS vs MD
  - analysis of MD
- dynamics in ion-containing precise polymers
  - preliminary results

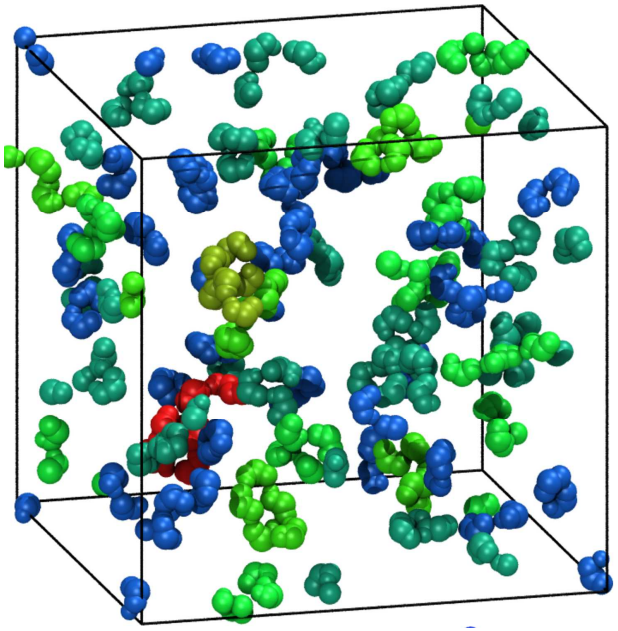


Precise Acid Copolymers

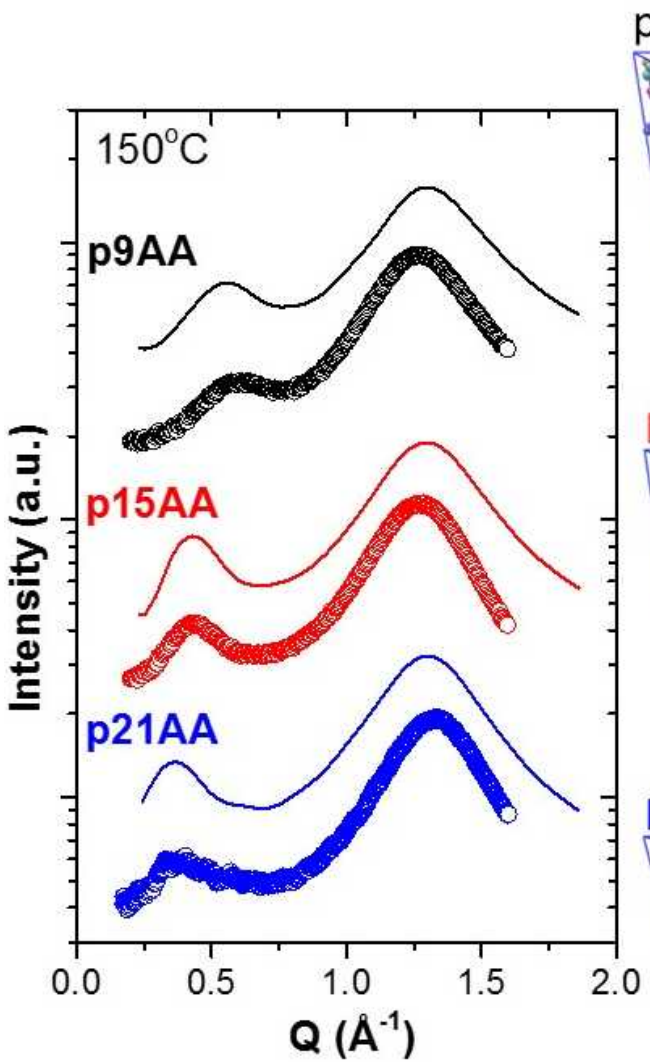
acid groups hydrogen bond to form aggregates

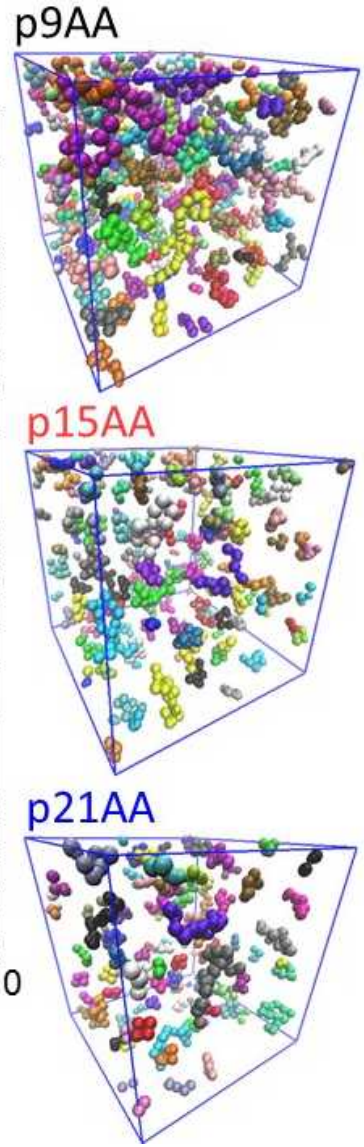


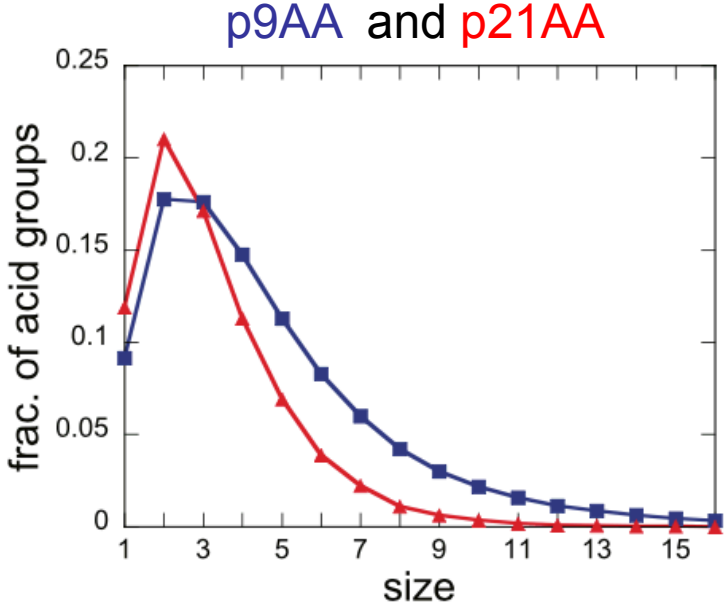




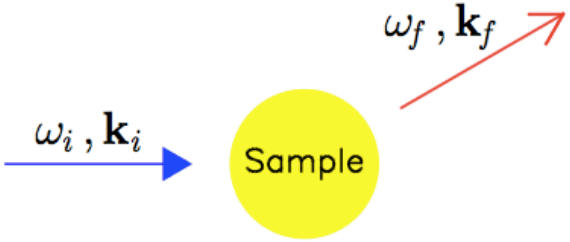
Precise Acid Copolymers Morphology







Quasi-Elastic Neutron Scattering



Energy transfer

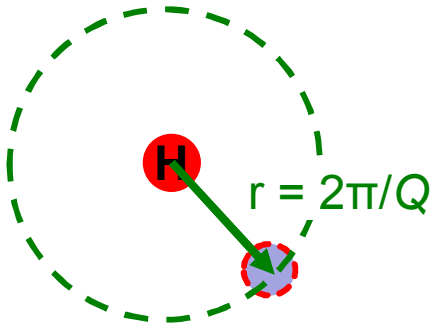
$$E = \hbar\omega = \hbar(\omega_f - \omega_i)$$

Momentum transfer

$$\mathbf{P} = \hbar\mathbf{Q} = \hbar(\mathbf{k}_f - \mathbf{k}_i)$$

incoherent, inelastic: sensitive to self-motion of hydrogens

$G_s(r,t)$: given an atom was at r=0 at time t=0, the probability that the atom is at r at time t



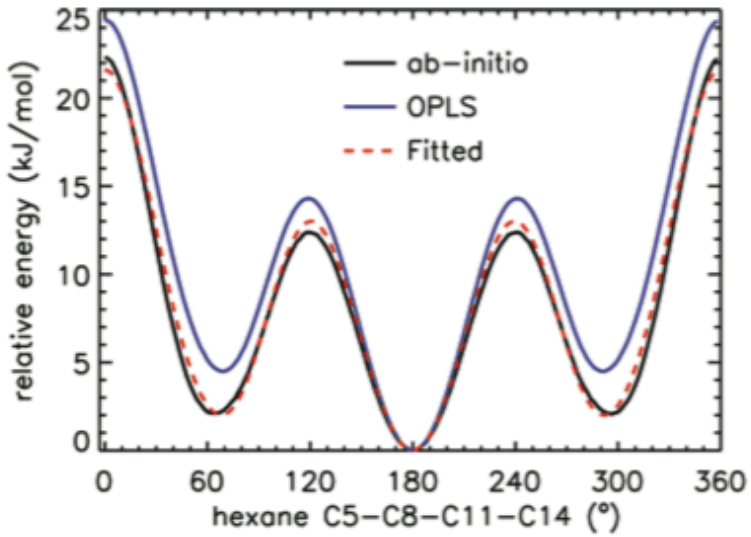
from MD: $$S(Q,t) = \int G_s(r,t)\frac{r\sin(Qr)}{Q}dr$$

from QENS: $$S(Q,t) = \frac{\int S_{exp}(Q,\omega)e^{i\omega t}d\omega}{\int R(Q,\omega)e^{i\omega t}d\omega}$$

Force Field

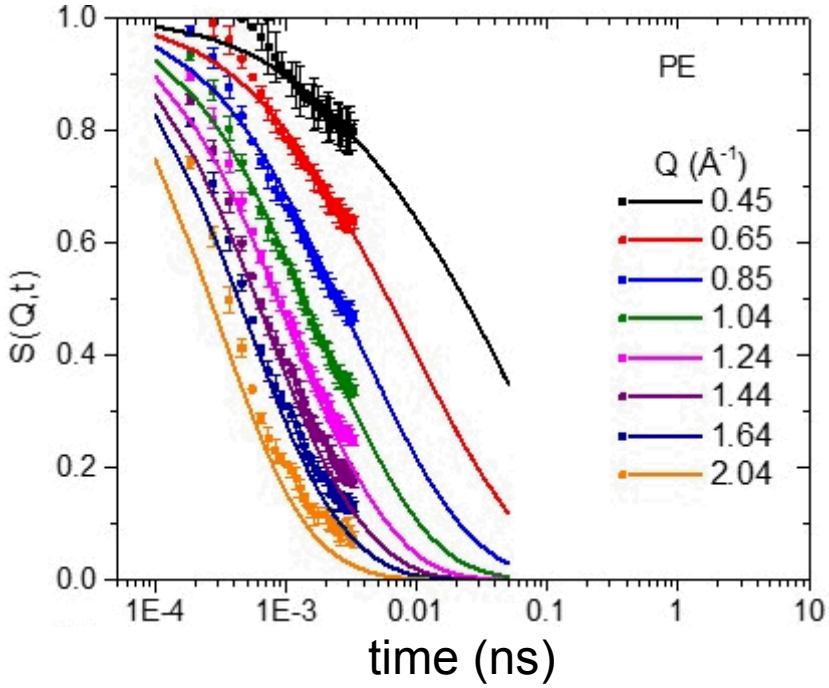
OPLS-AA: PE crystallizes at 150° C! (T_m ≈ 130 °C)

L-OPLS: newly parameterized for long hydrocarbons



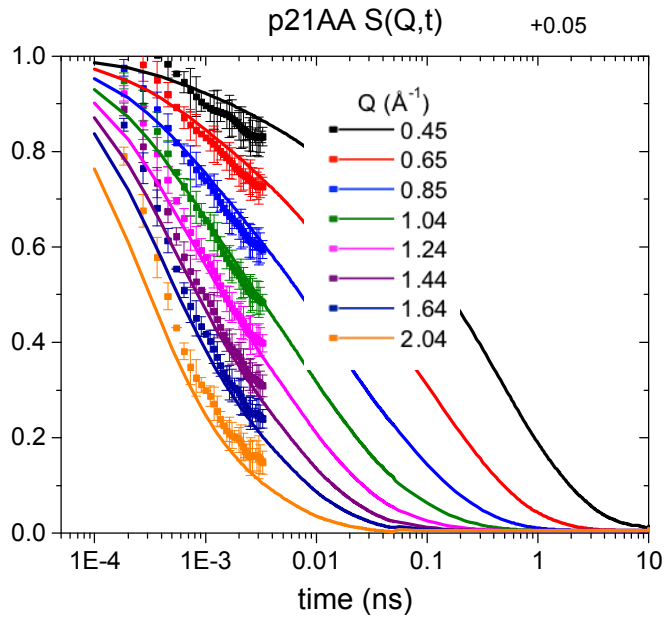
Siu, S. W. I., Pluhackova, K. & Böckmann, R. A. *J Chem Theory Comput* **8,** 1459–1470 (2012)

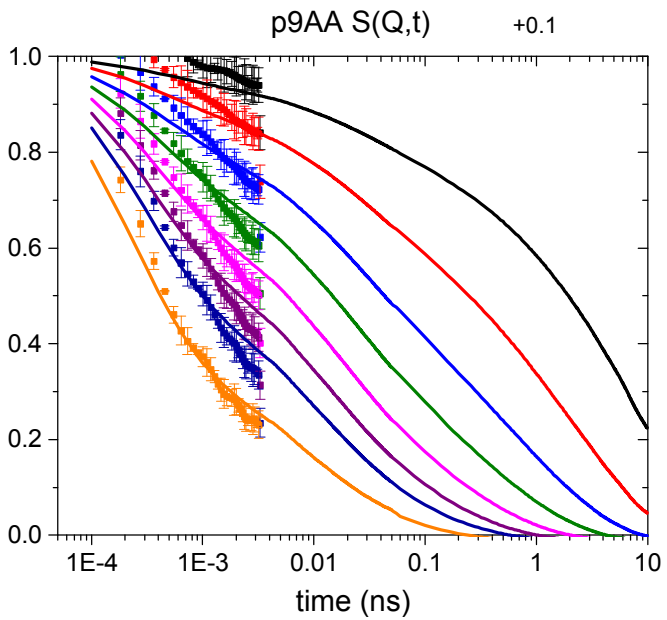
QENS vs MD for PE



- correct gel-to-liquid transition temp in pentadecane
- improved viscosity, diffusion coefficients

QENS vs MD





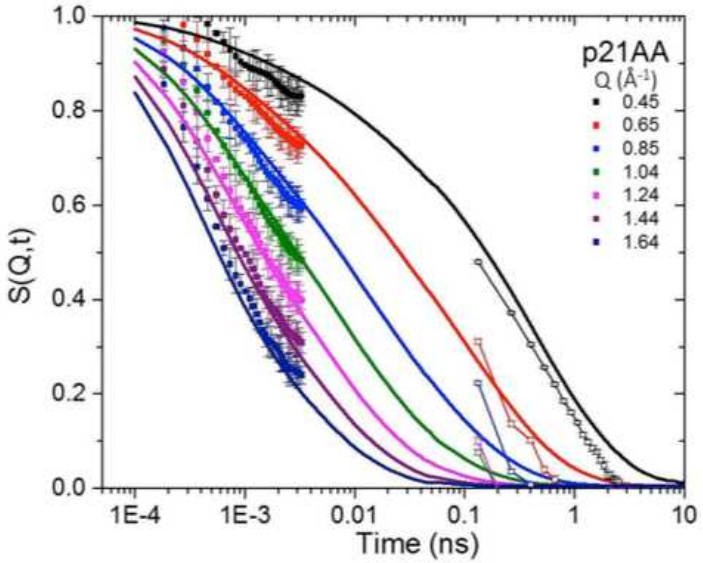
excellent agreement between QENS and MD

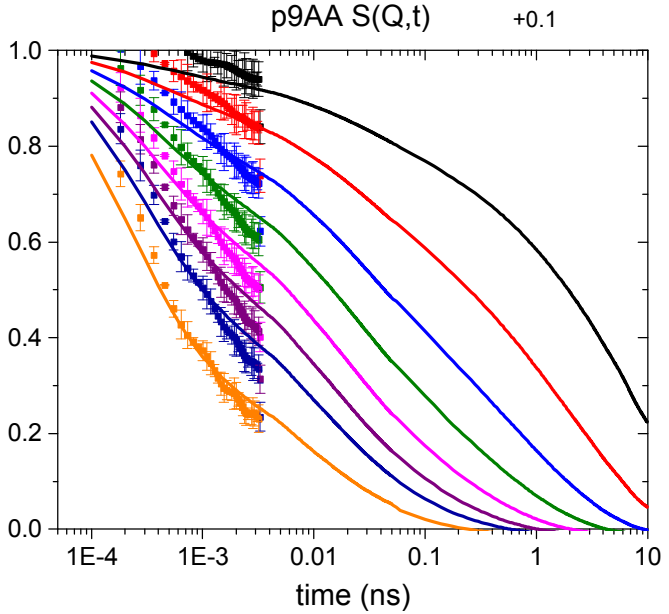
relevant length scales:

amorphous halo: Q ≈ 1.35 Å^{-1}

ionomer peak: Q ≈ 0.3 – 0.6 Å^{-1}

QENS vs MD





excellent agreement between QENS and MD

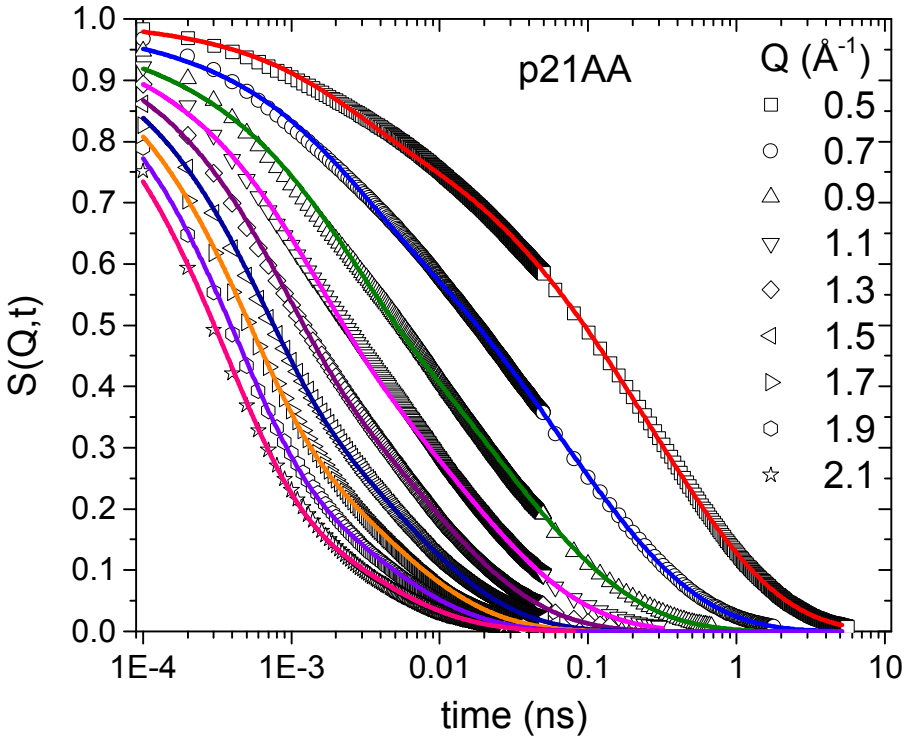
relevant length scales:

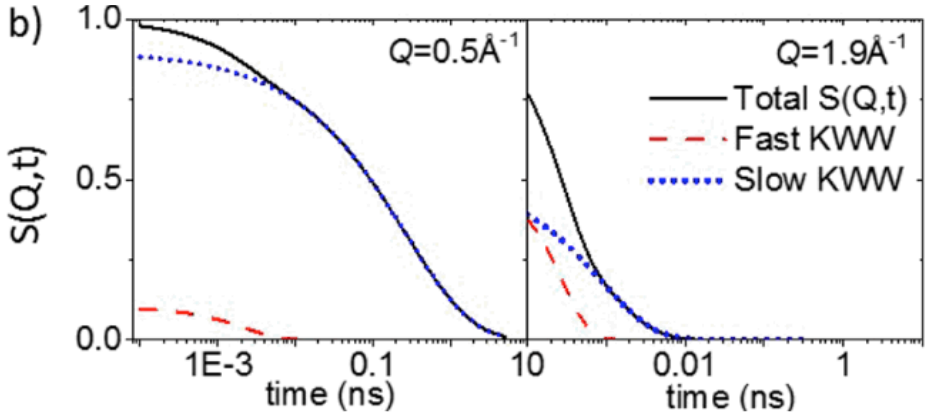
amorphous halo: Q ≈ 1.35 Å^{-1}

ionomer peak: Q ≈ 0.3 – 0.6 Å^{-1}

Fit S(Q,t) to Two KWW Functions

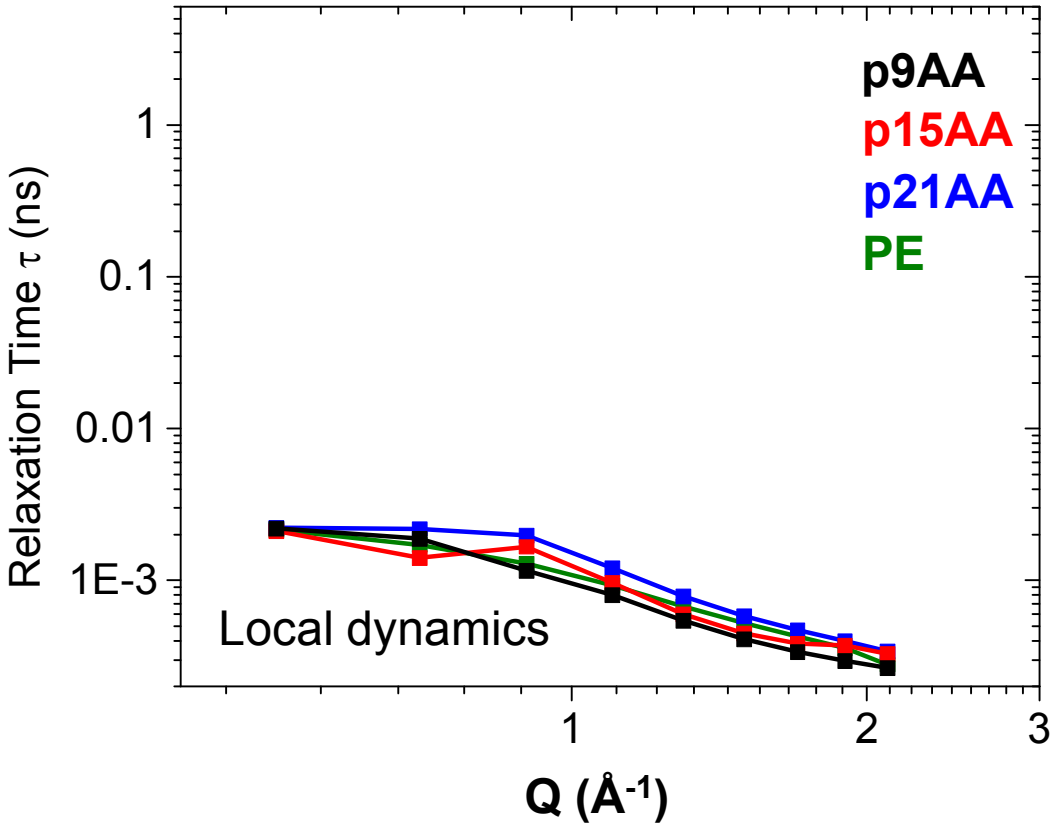
$$S(Q,t) = \phi_{slow} e^{-\left(\frac{t}{\tau_{slow}}\right)^{\beta_{slow}}} + (1-\phi_{slow}) e^{-\left(\frac{t}{\tau_{fast}}\right)^{\beta_{fast}}}$$





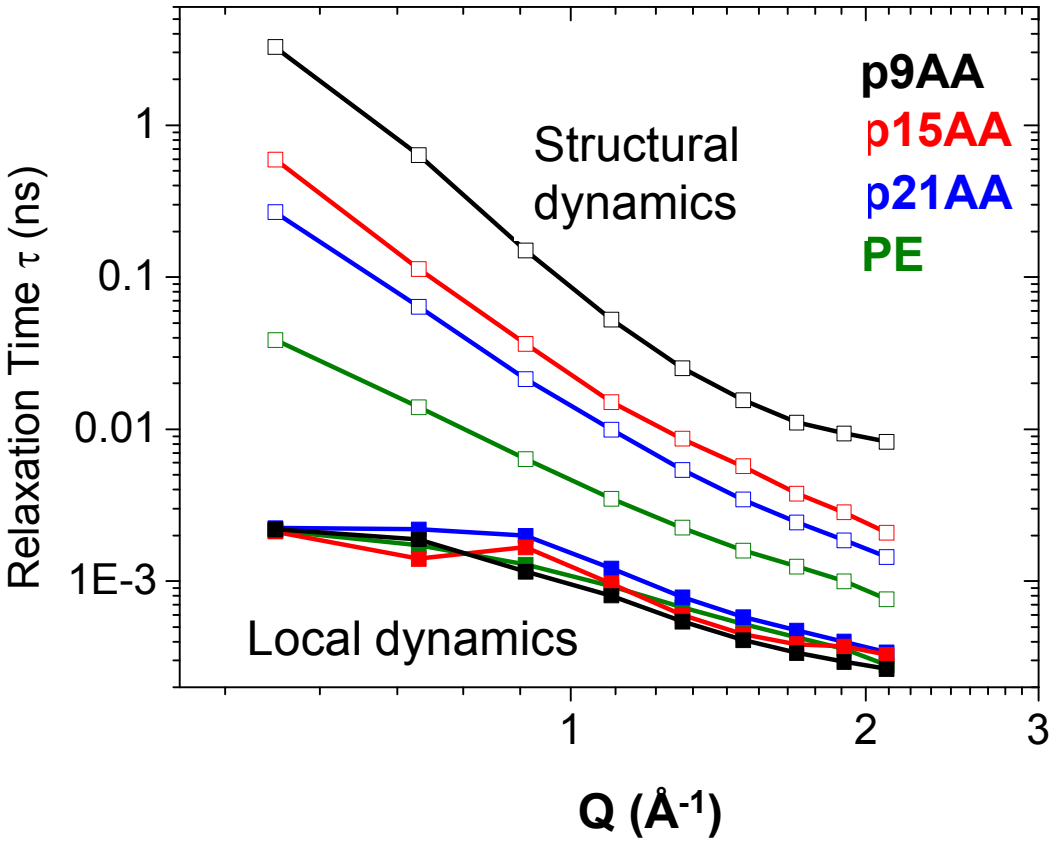
- One stretched exponential relaxation cannot fit data, two needed
- Extract time scales τ and stretching parameters β

Dynamics from KWW



Fast: local dynamics that are insensitive to composition (vibrations, librations, etc.)

Dynamics from KWW

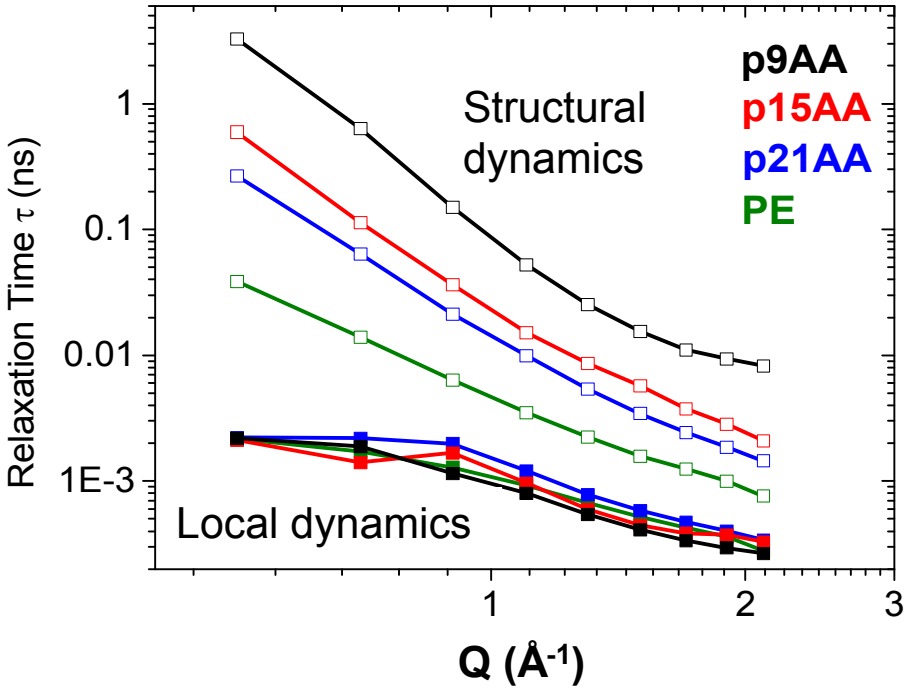


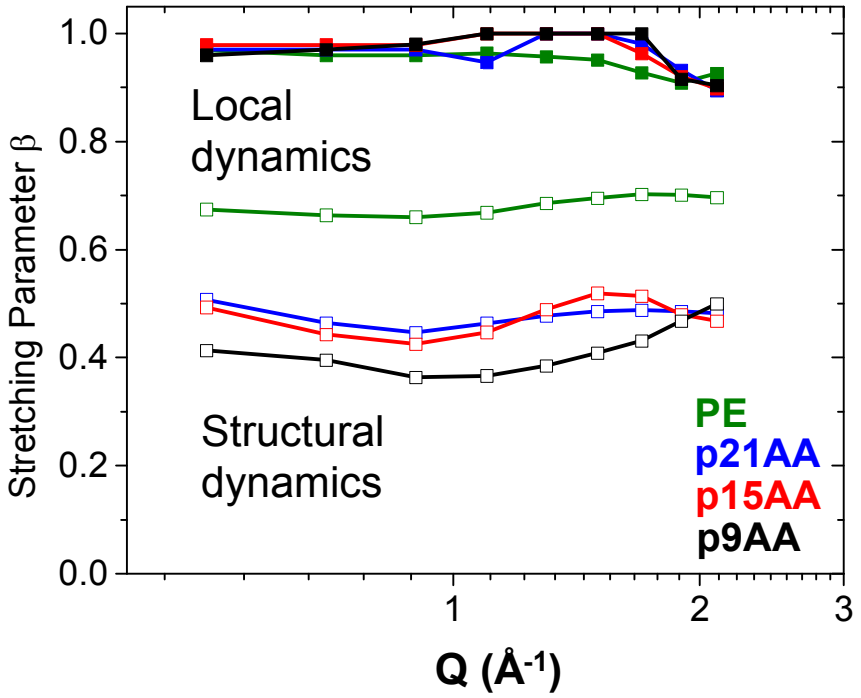
Slower: structural dynamics of the chain

- Highly composition sensitive
- Length scale dependent
- $\tau \sim Q^{-2/\beta}$

Fast: local dynamics that are insensitive to composition (vibrations, librations, etc.)

Acid content slows dynamics

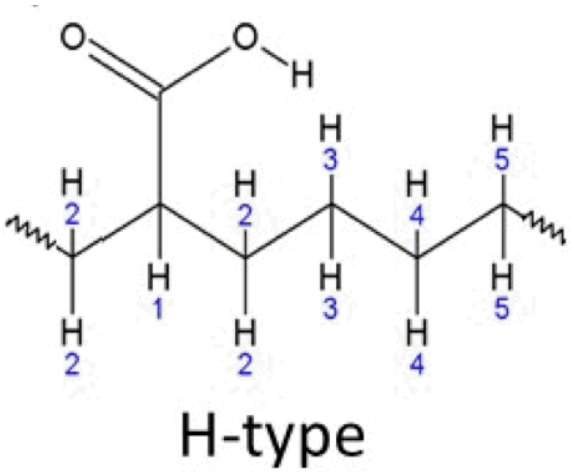


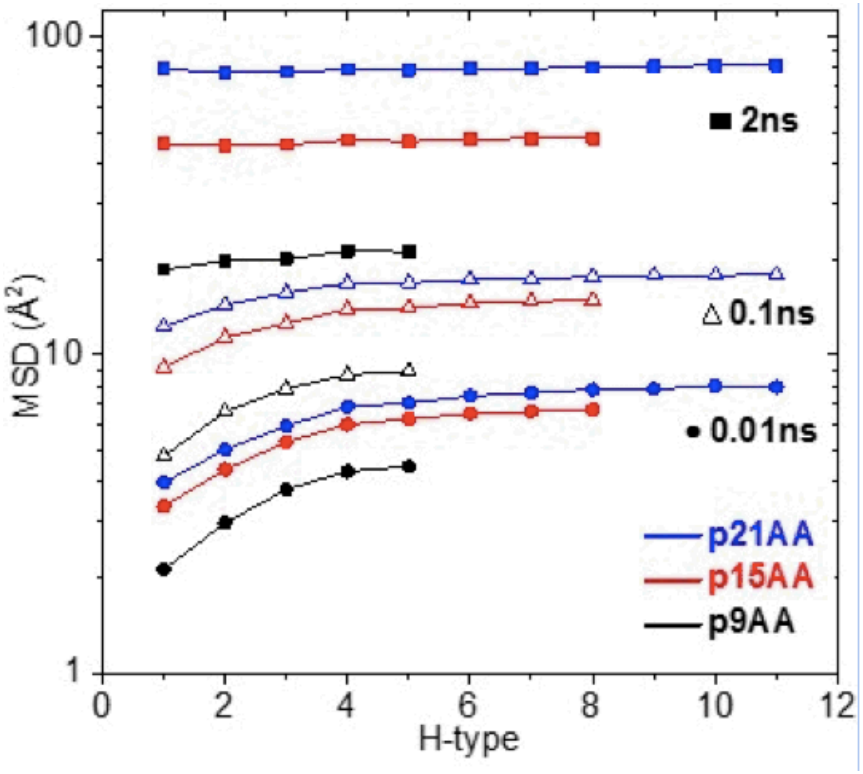


20% acid content causes 100x slowing in timescale of chain dynamics

Acid content increases the stretching of the relaxation time scales

Local Dynamics





short times: H1 motion much slower than middle of chain
long times: aggregates rearrange, all H motions similar

Middleton et al, Macromolecules (2016)

Acid aggregates rearrange

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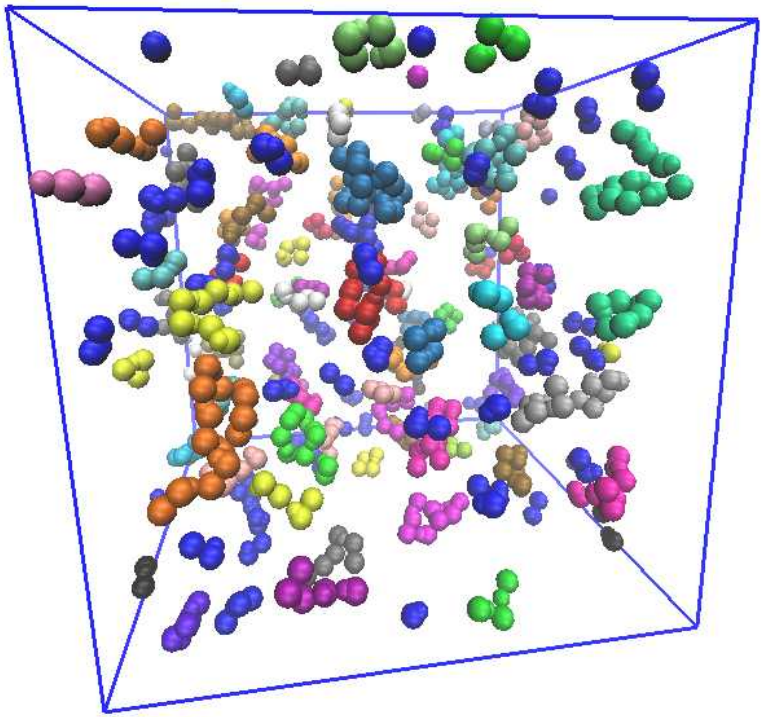
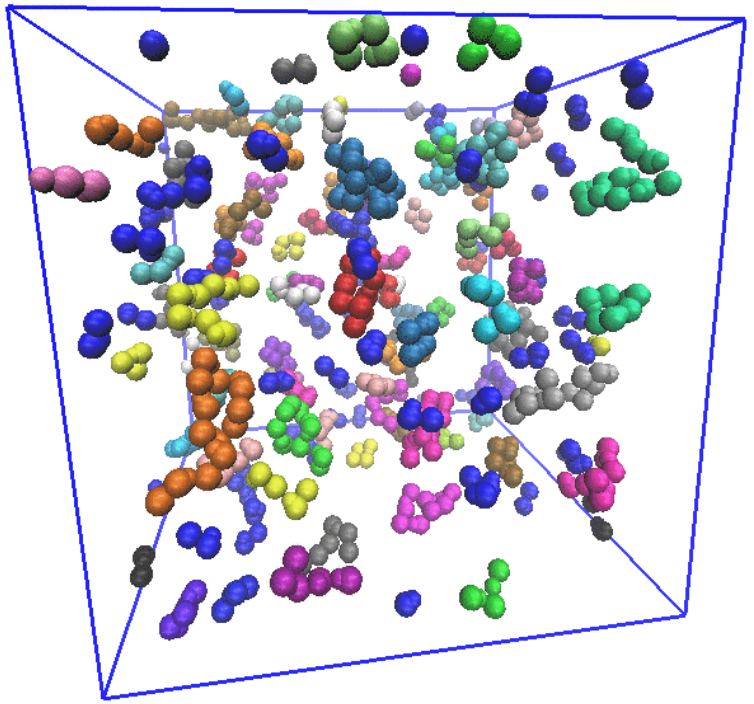
t = 0

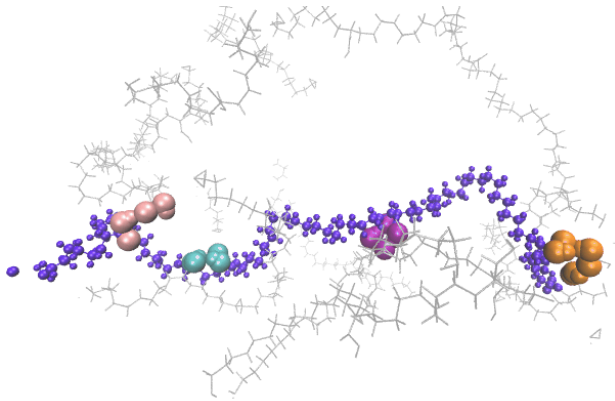




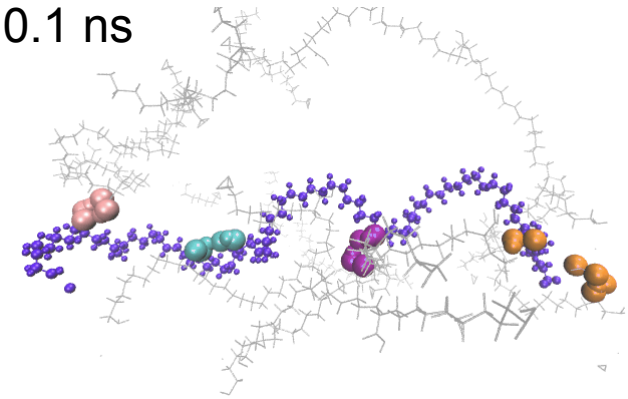
Acid aggregates rearrange

p21AA: one chain

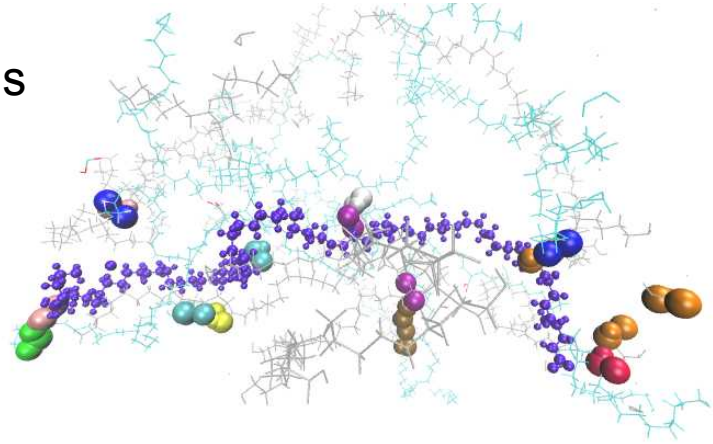
t = 0



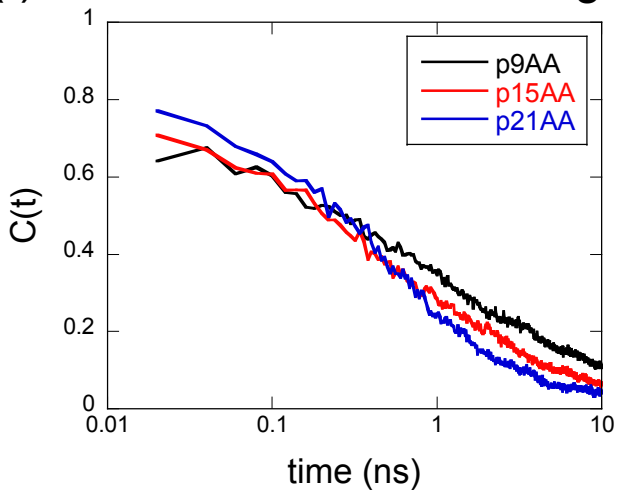
t = 0.1 ns



t = 1 ns



C(t) = autocorrelation of acid groups

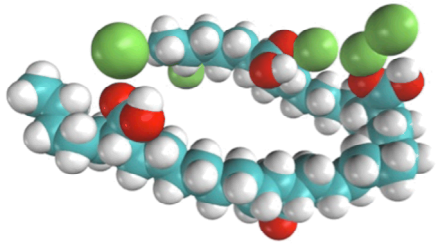


Middleton et al, *Macromolecules* **49**, 9176 (2016)

Rest of the talk

- dynamics in acid-containing precise polymers
  - QENS vs MD
  - analysis of MD

- dynamics in ion-containing precise polymers
  - preliminary results



Li ionomer morphology

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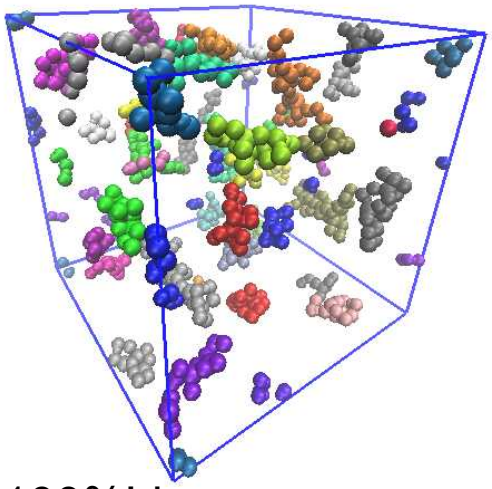
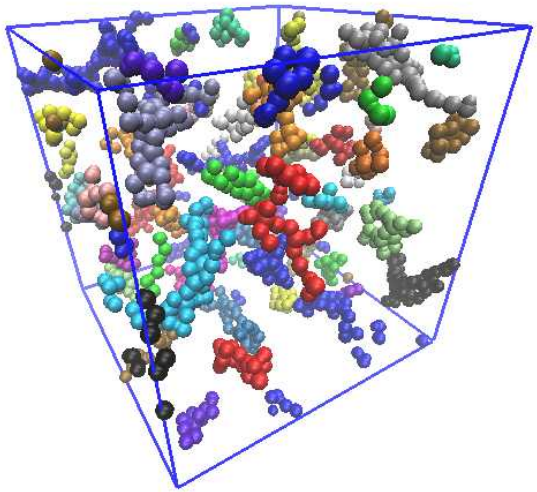
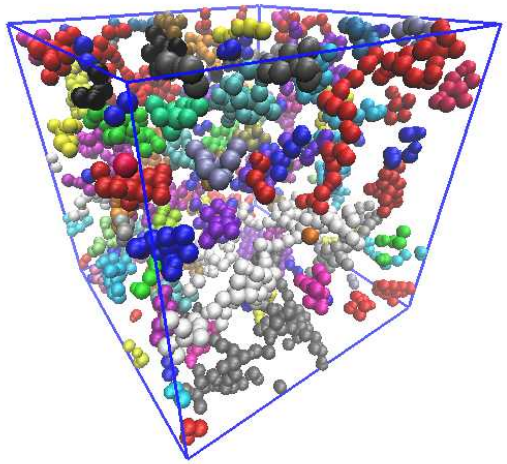
p21-37%Li



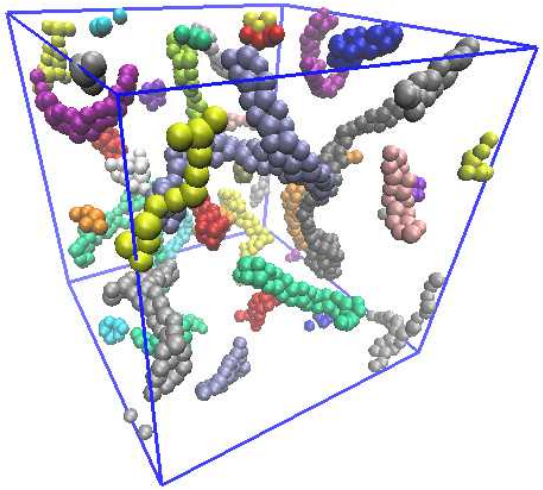
p15-38%Li



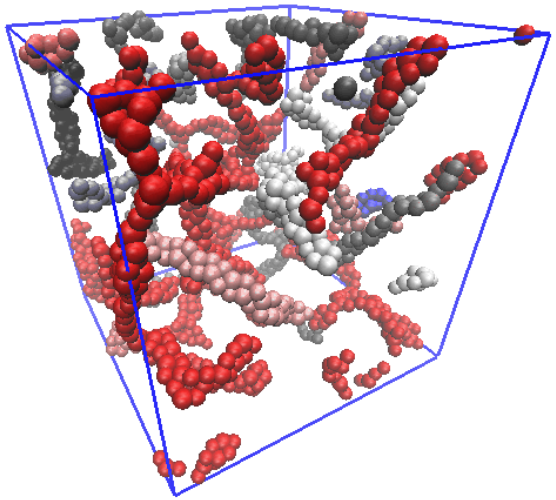
p9-20%Li



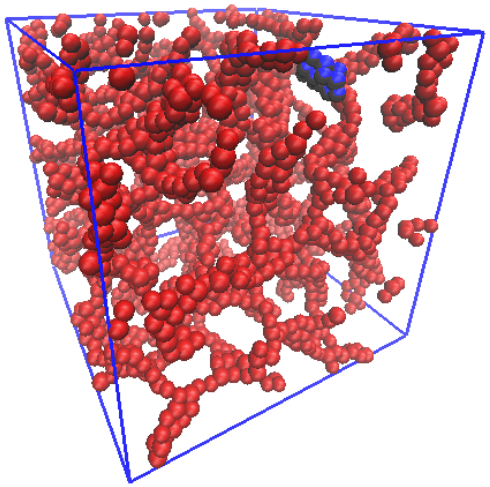
p21-100%Li



p15-100%Li

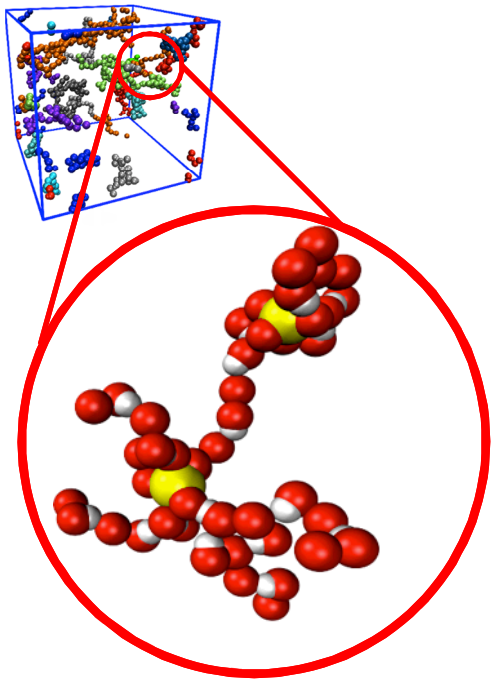


p9-100%Li

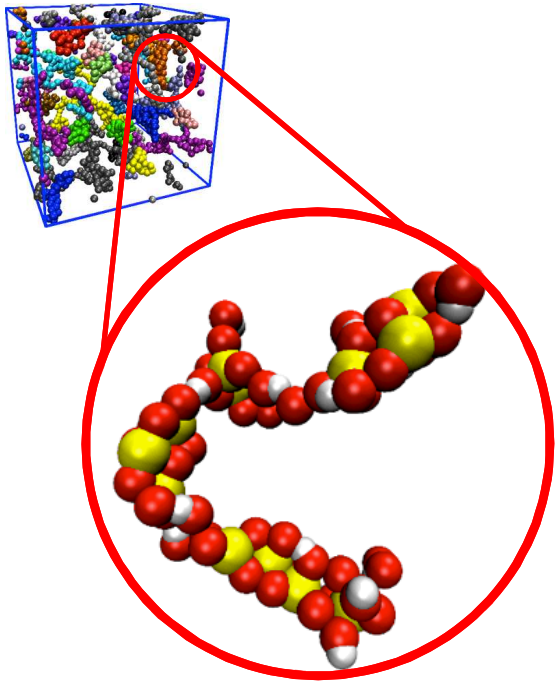


Closer look at aggregates

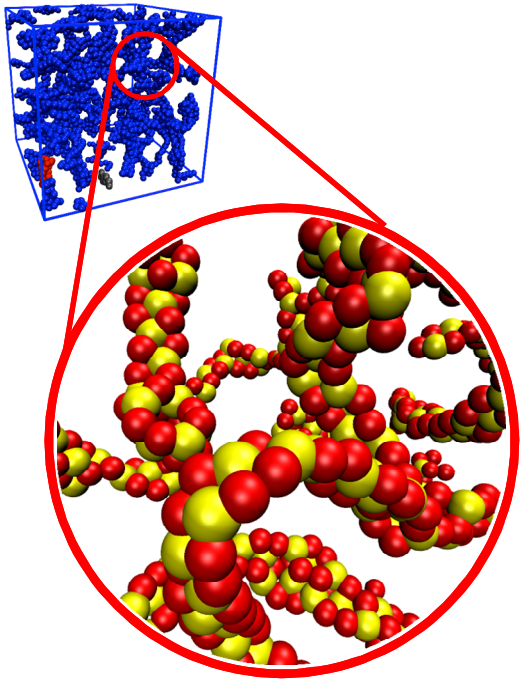
p9AA-10%Li



p9AA-43%Li



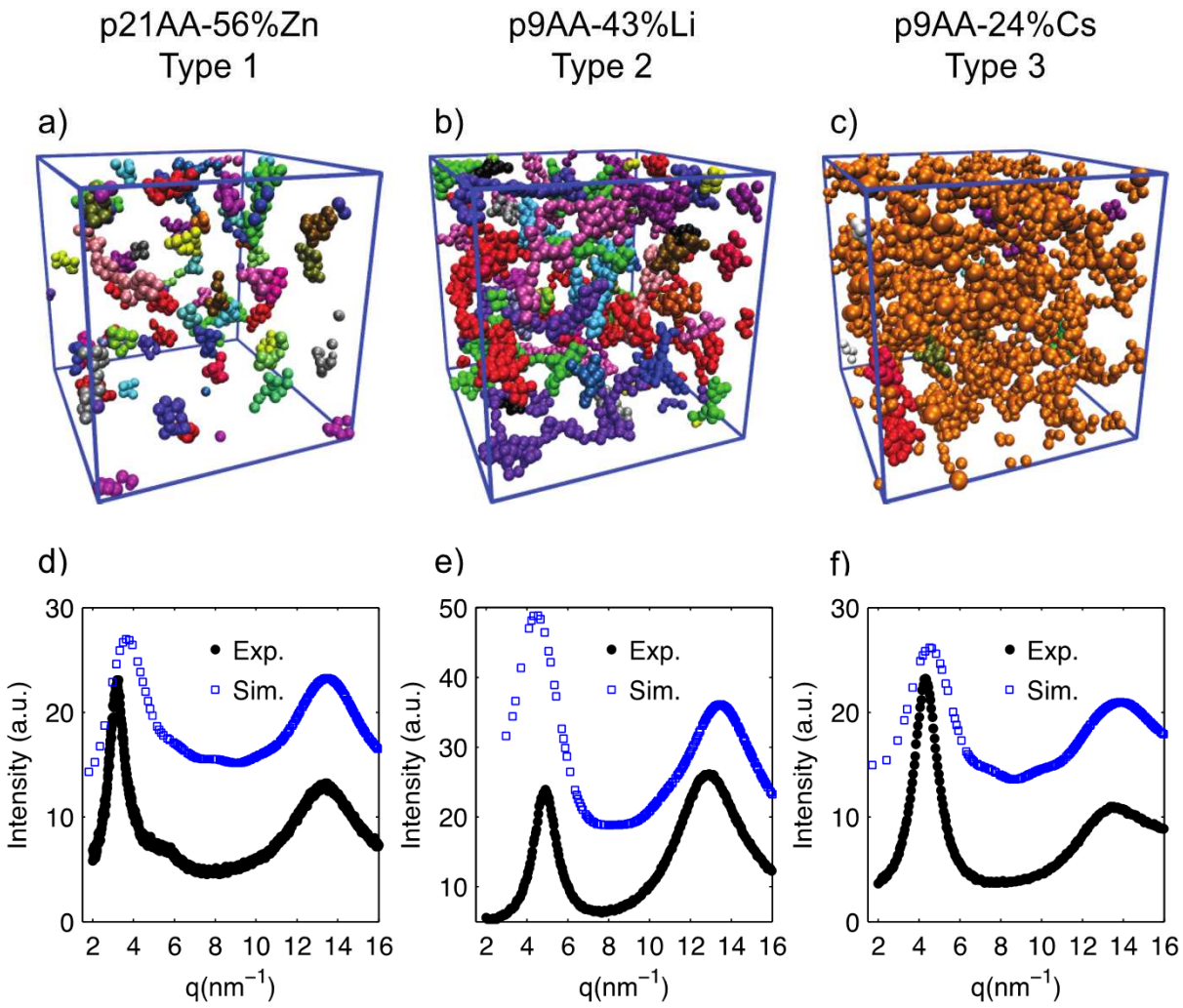
p9AA-100%Li



Two mechanisms of aggregate formation:

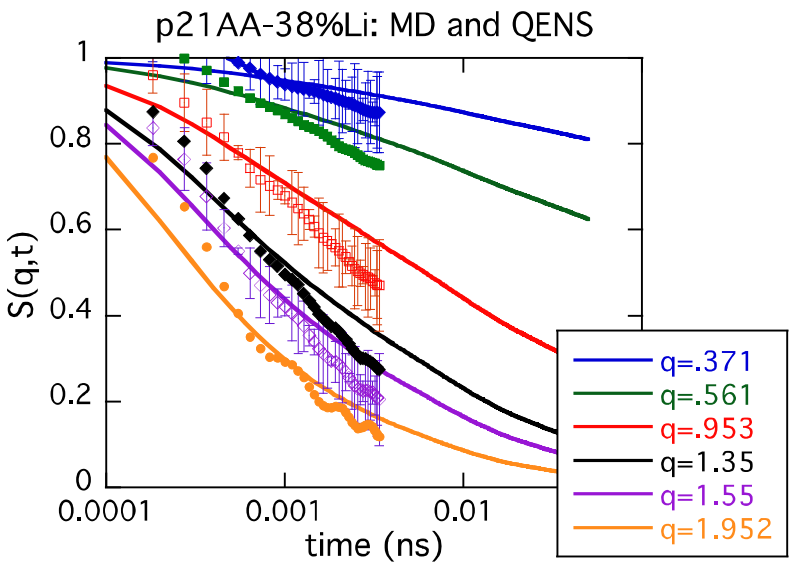
1. Counterion-oxygen association → dominant at **moderate to high** neutralization
2. Hydrogen-bonded networks → dominant at **low** neutralization

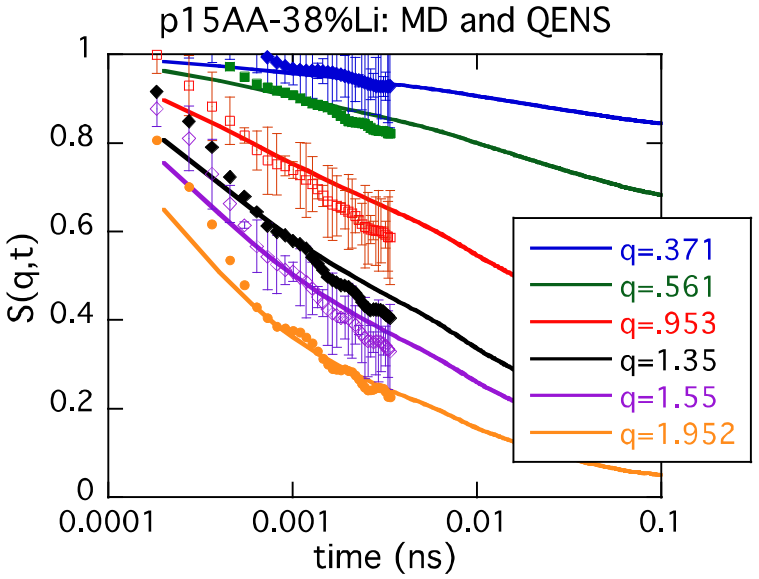
Comparison to X-ray Scattering



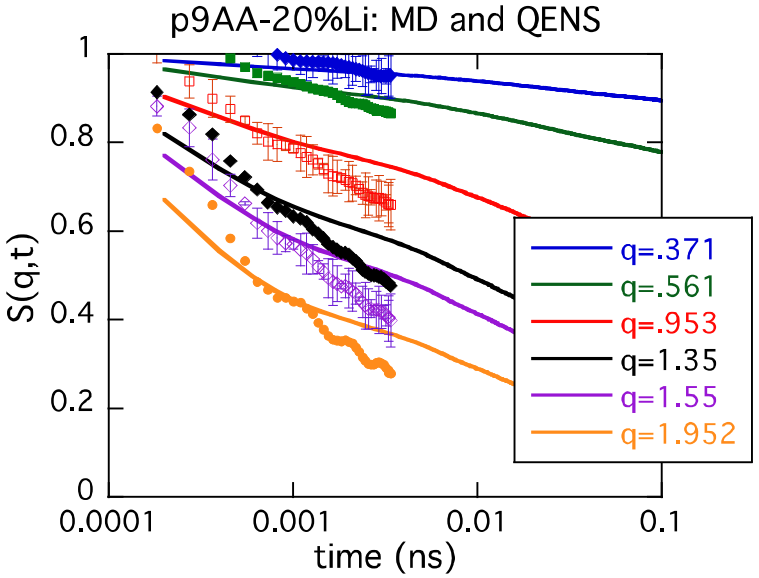
Buitrago, C. F. *et al. Macromolecules* **48,** 1210–1220 (2015).

QENS vs MD

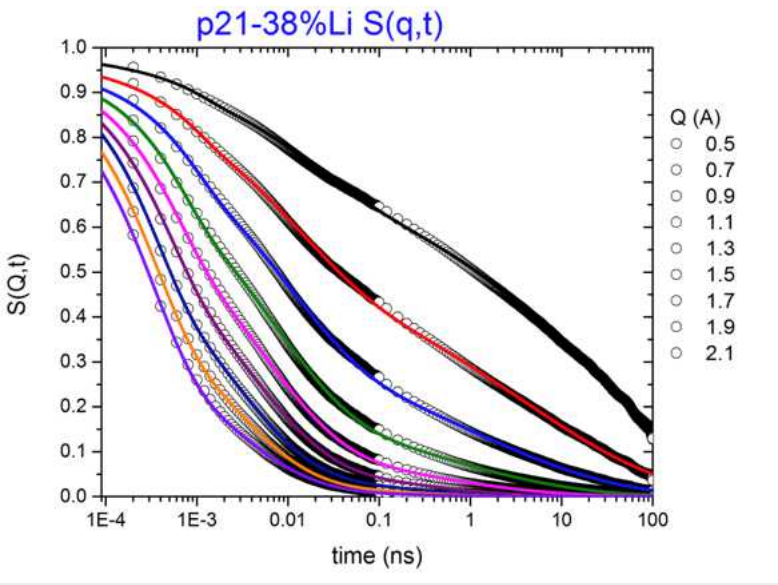


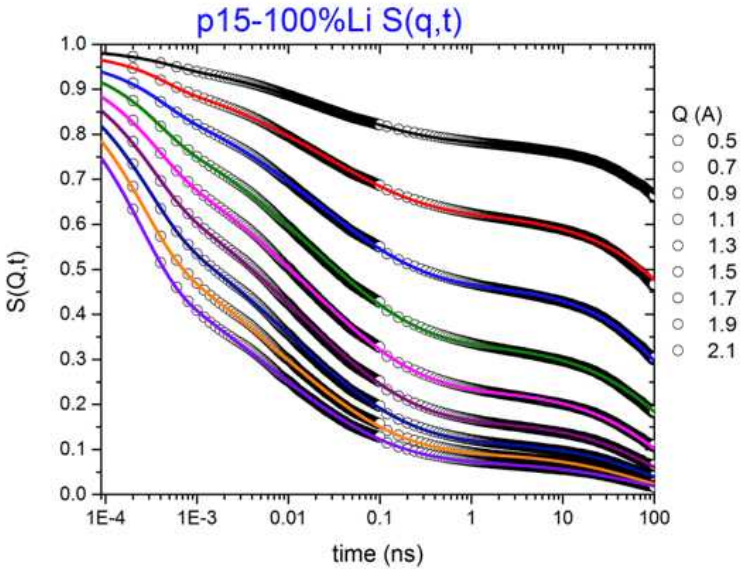


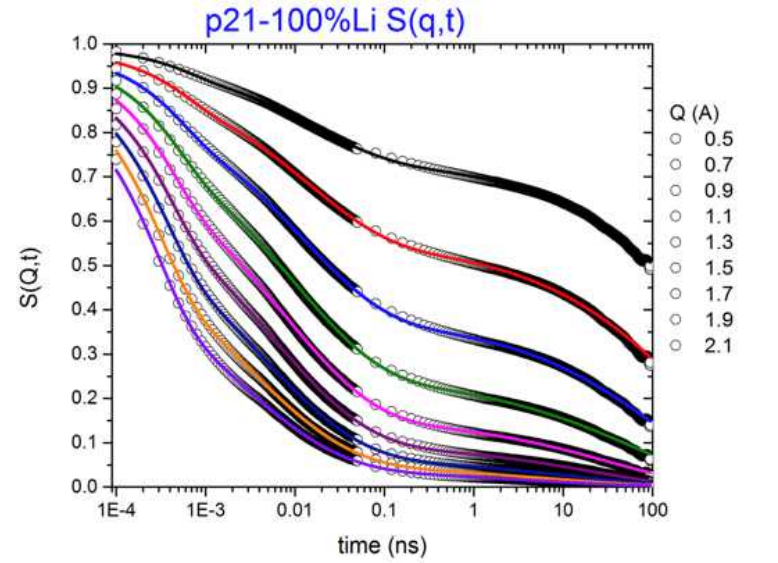
reasonable agreement



S(q,t) shows 3 relaxation processes



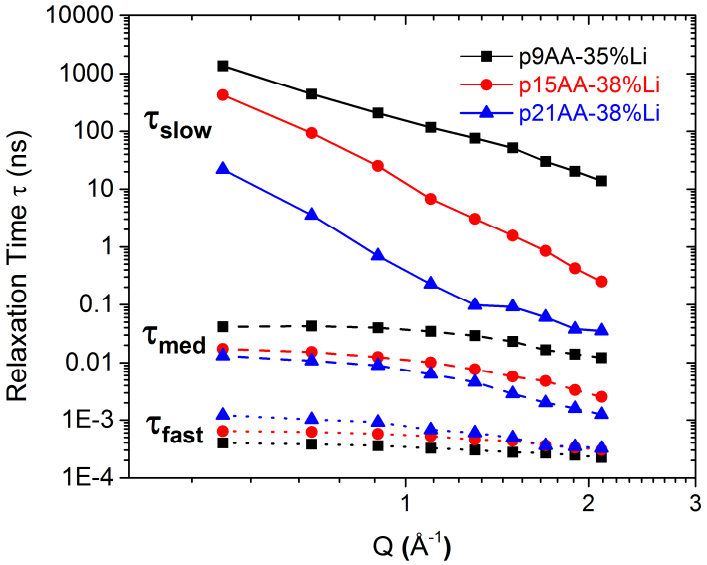


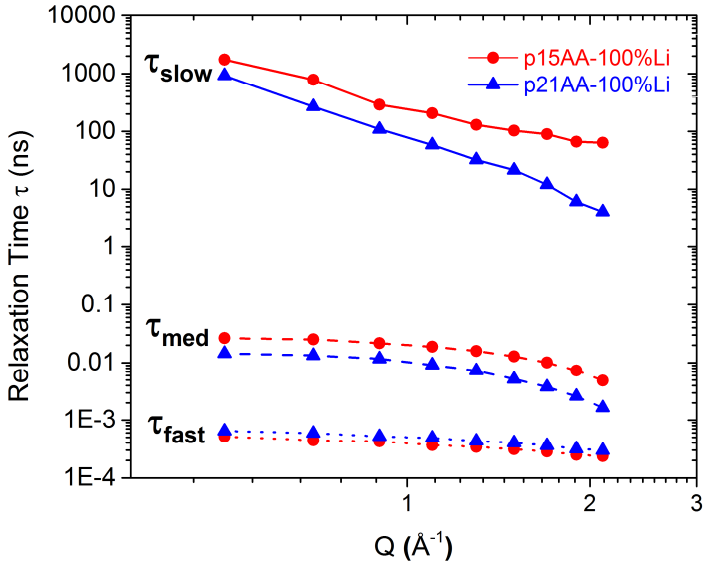


fit to 3 KWW functions

KWW relaxation times

$$S(Q,t) = \varphi_{slow} e^{-\left(\frac{t}{\tau_{slow}}\right)^{\beta_{slow}}} + \varphi_{med} e^{-\left(\frac{t}{\tau_{med}}\right)^{\beta_{med}}} + \varphi_{fast} e^{-\left(\frac{t}{\tau_{fast}}\right)^{\beta_{fast}}}$$



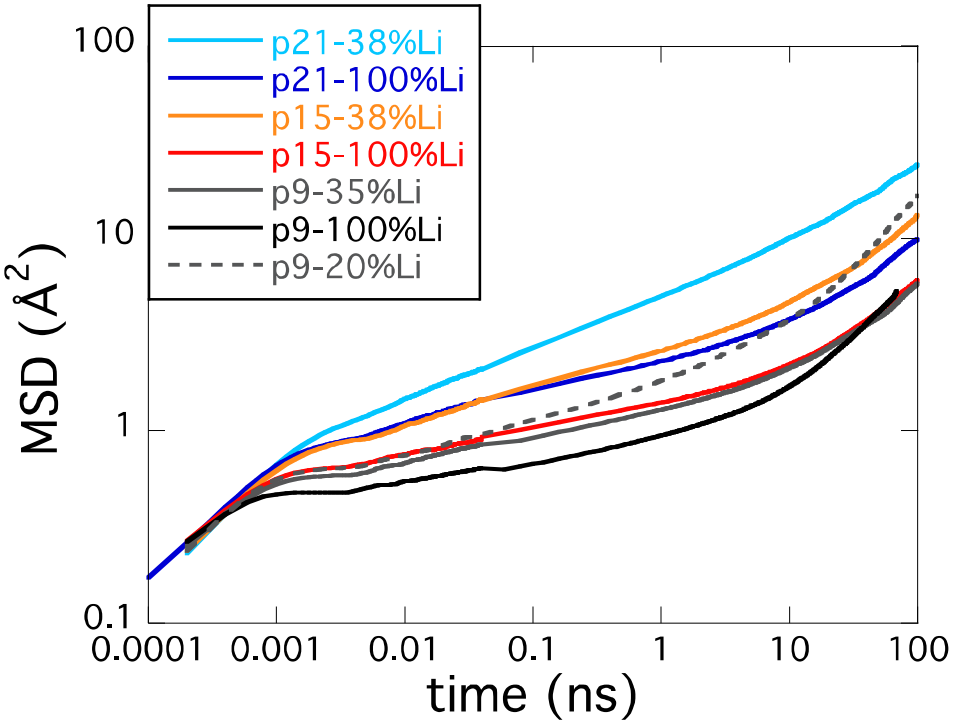


- fast motion: mostly independent of %Li and q, local motion
- medium motion: small q dependence, does depend on system
  - H relaxation while clusters still pinned
- slow motion: structural relaxation of chains
  - beginning of cluster rearrangement?

Mean-square displacements

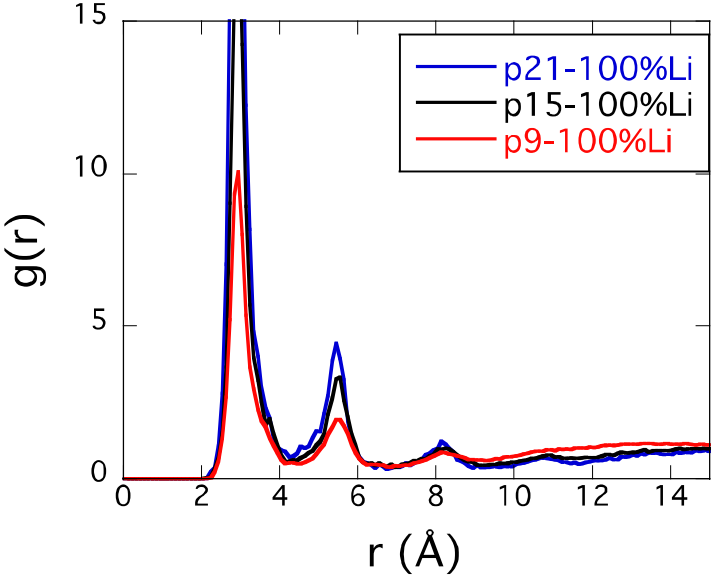
T = 150 ℃

Li$^+$ motion

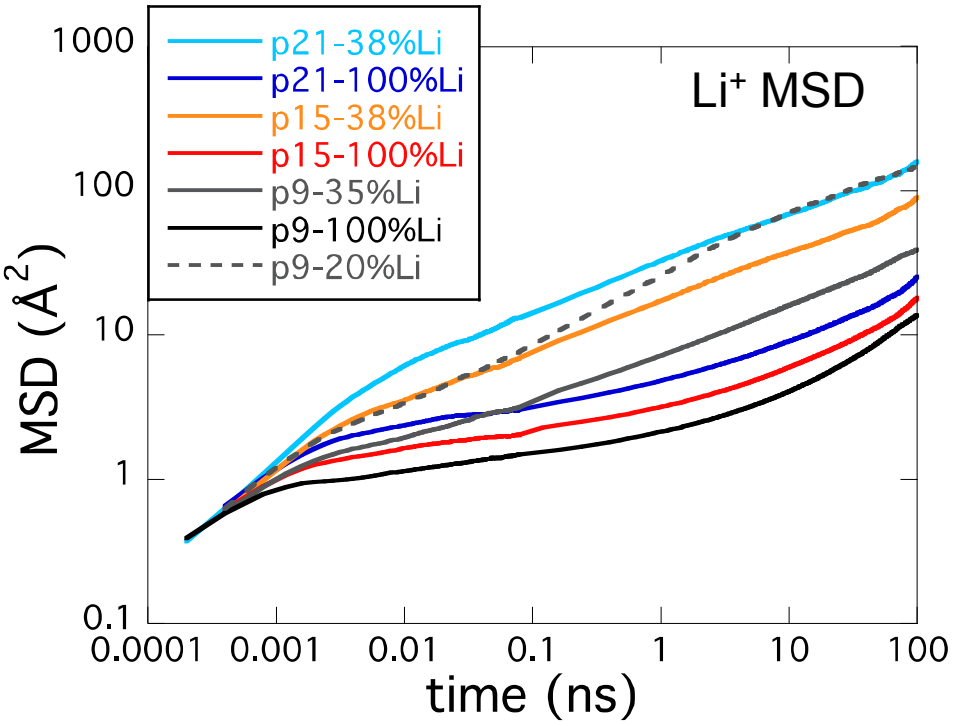


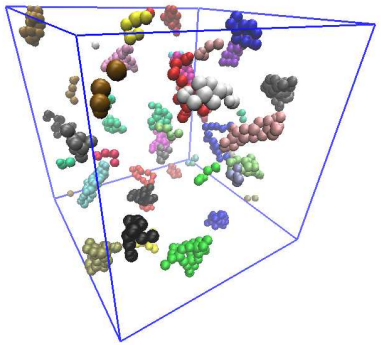
very slow!

Li+ needs to go 4 Å to trade with neighbor

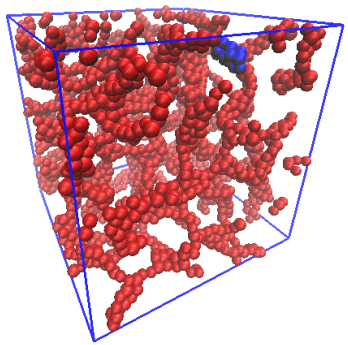


Higher temperature: T = 600K





p21-38%Li



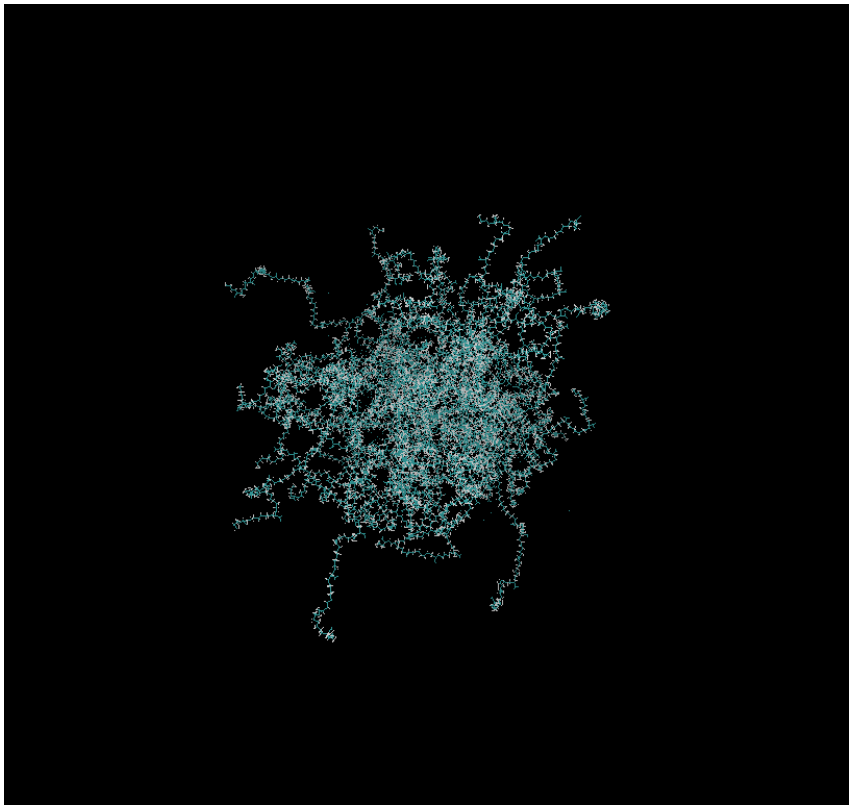
p9-100%Li

for t < 100 ns, Li^+ moves faster at lower concentration

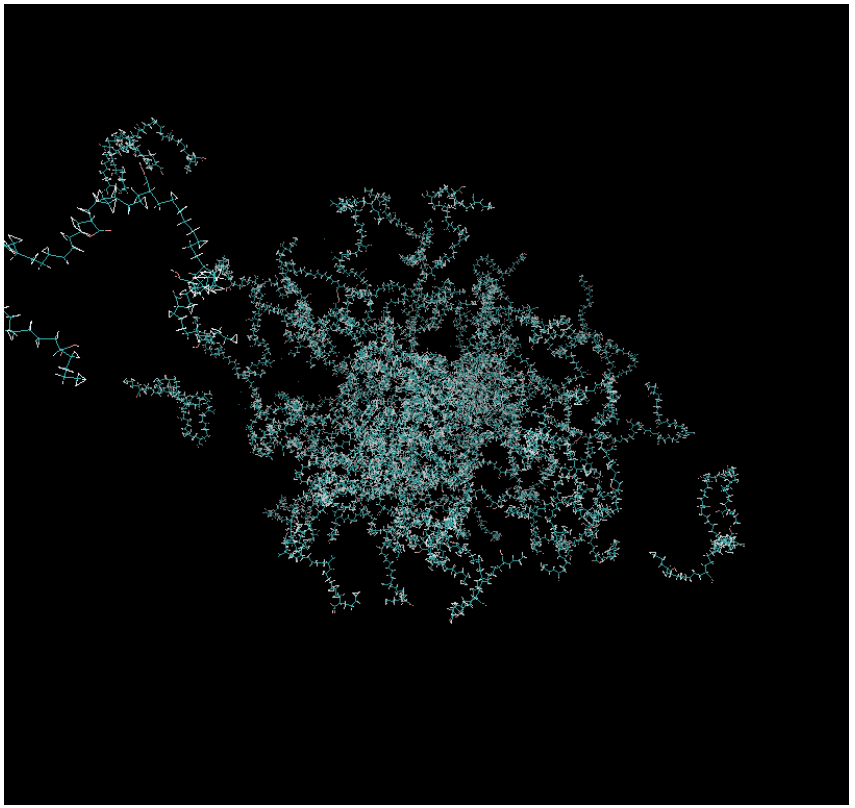
Chain dynamics

frames are every 0.5 ns, about 50 ns total

p9-100%Li



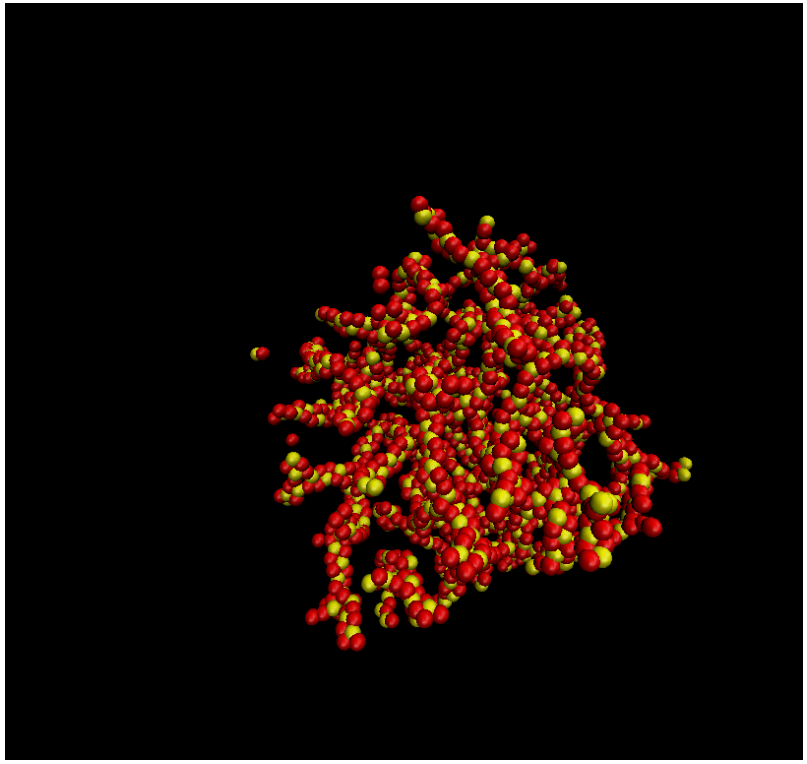
p9-20%Li



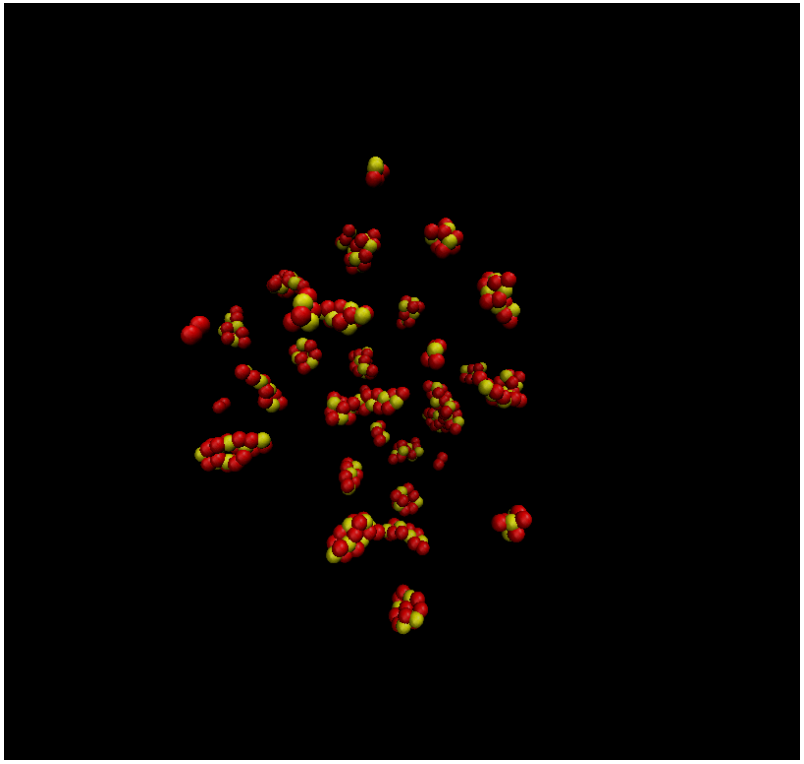
Cluster dynamics

frames are every 0.5 ns, about 50 ns total

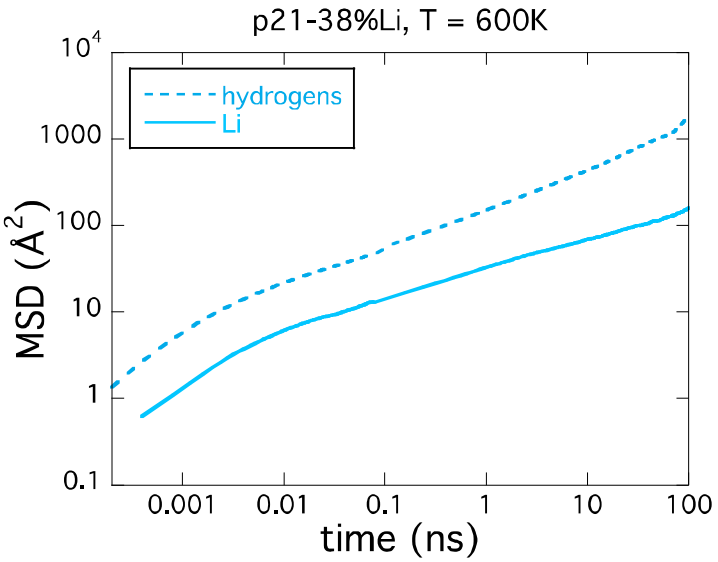
p9-100%Li

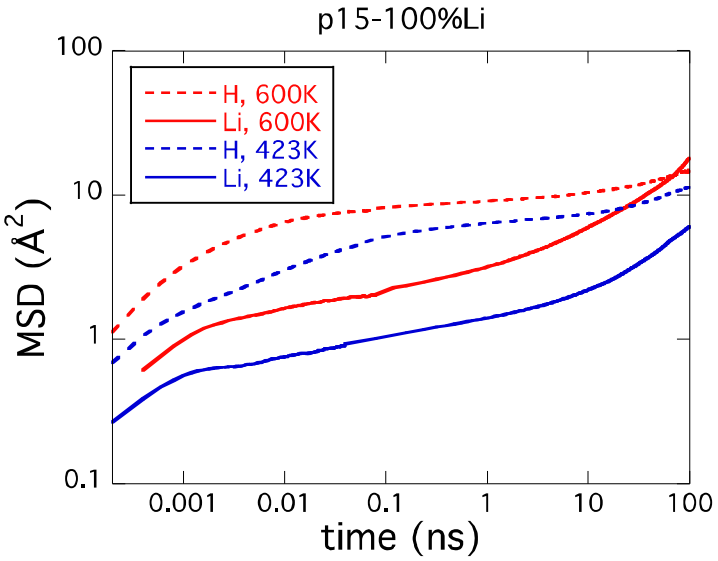


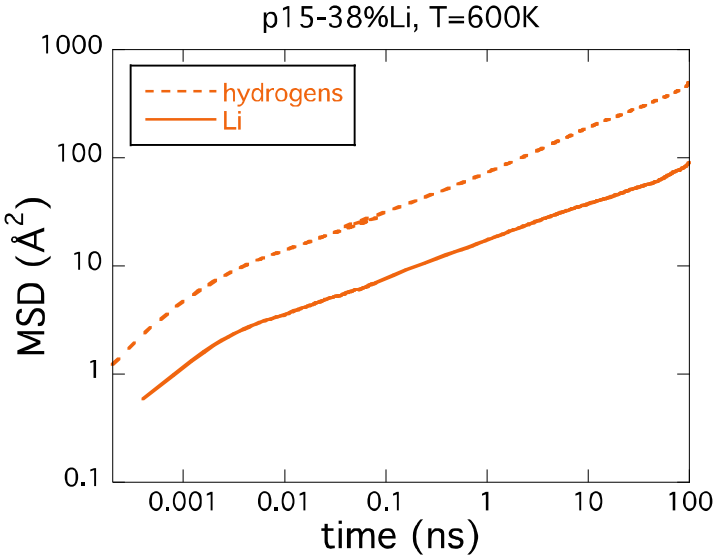
p9-20%Li

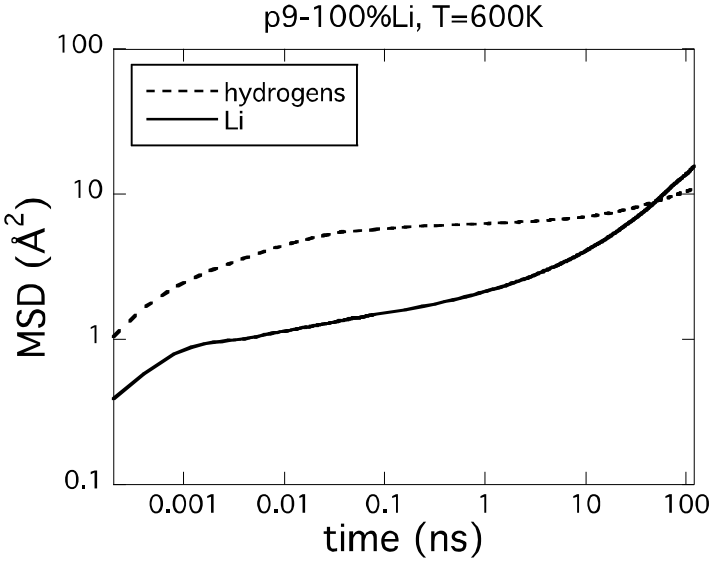


Li vs H motion



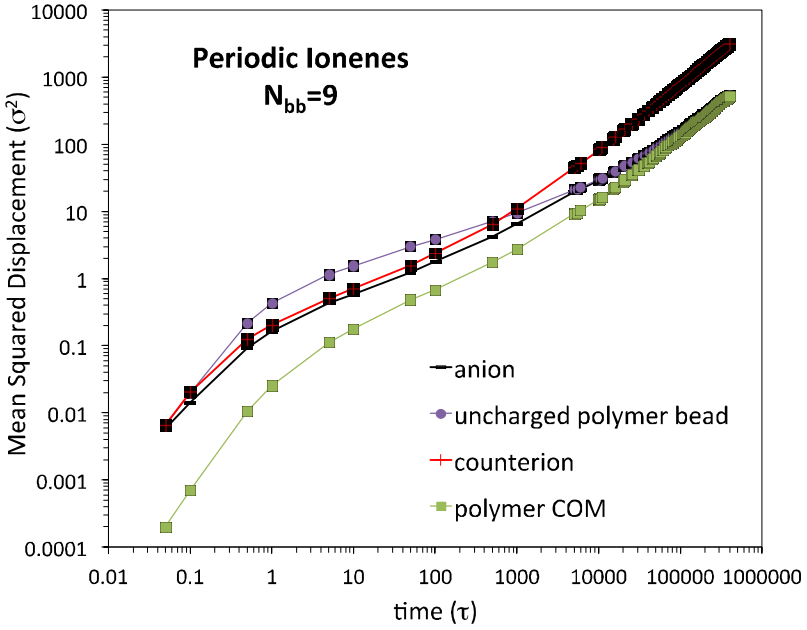


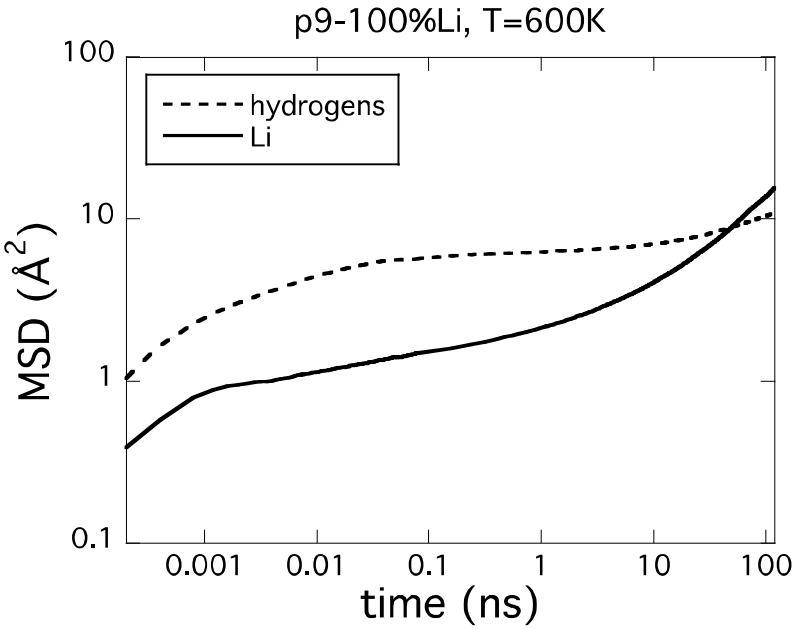




Li^+ moving faster than chains at longer times

Dynamics look similar to CG model





Li^+ MSD crosses H MSD first in most percolated system

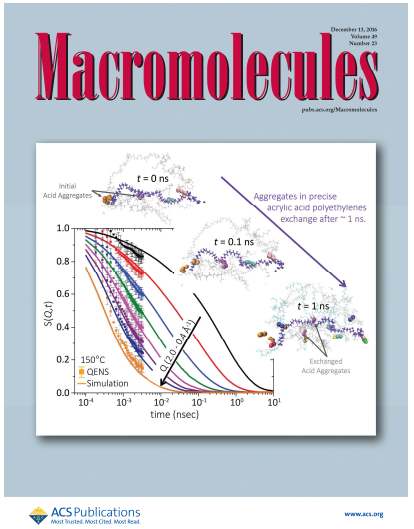
p9-100%Li: at about 47 ns

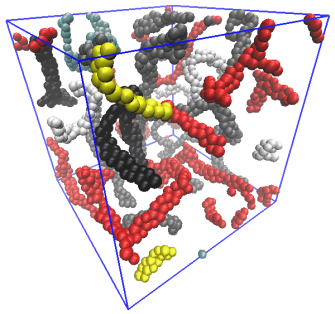
p15-100%Li: at about 70 ns

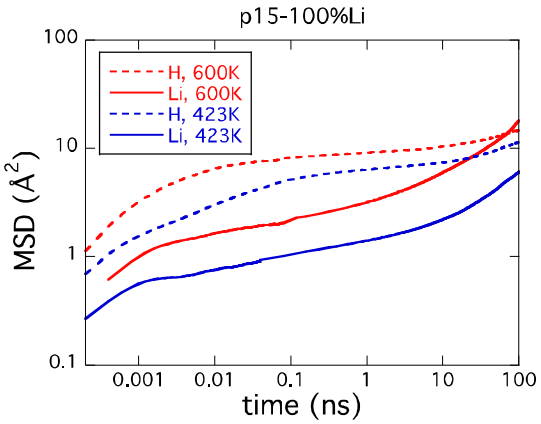
p21-100%Li: > 100 ns

Conclusions

- atomistic MD agrees with QENS at short times
- acid copolymer dynamics slowed by aggregates
  - heterogeneous chain dynamics at short times
  - aggregates rearrange around 1-2 ns
- Li ionomer dynamics further slowed
  - H dynamics show 3 relaxations
  - percolated morphology may eventually have fastest ion motion



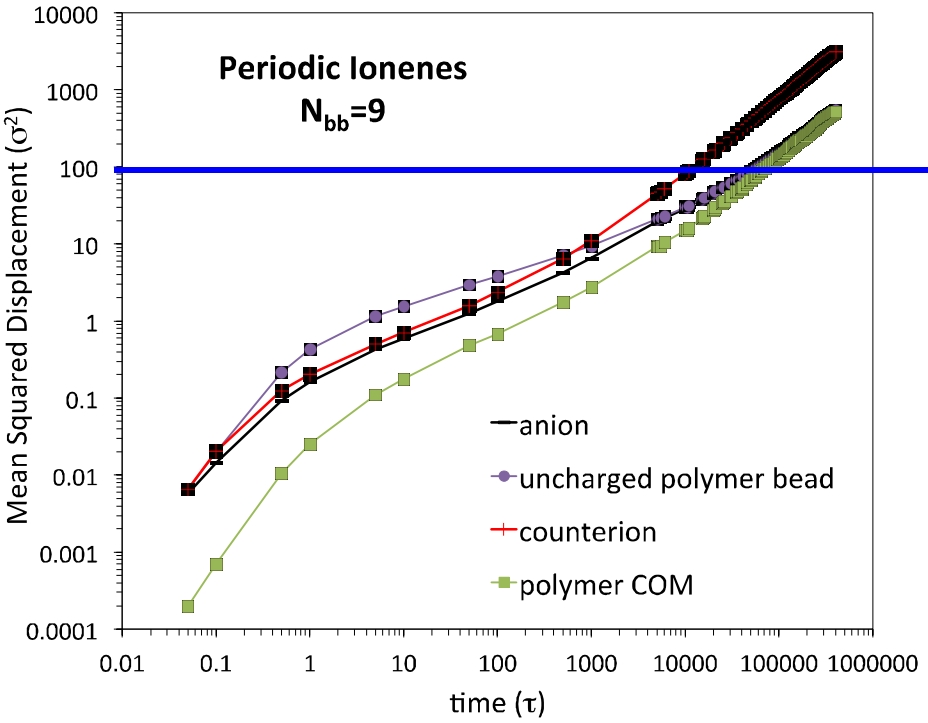


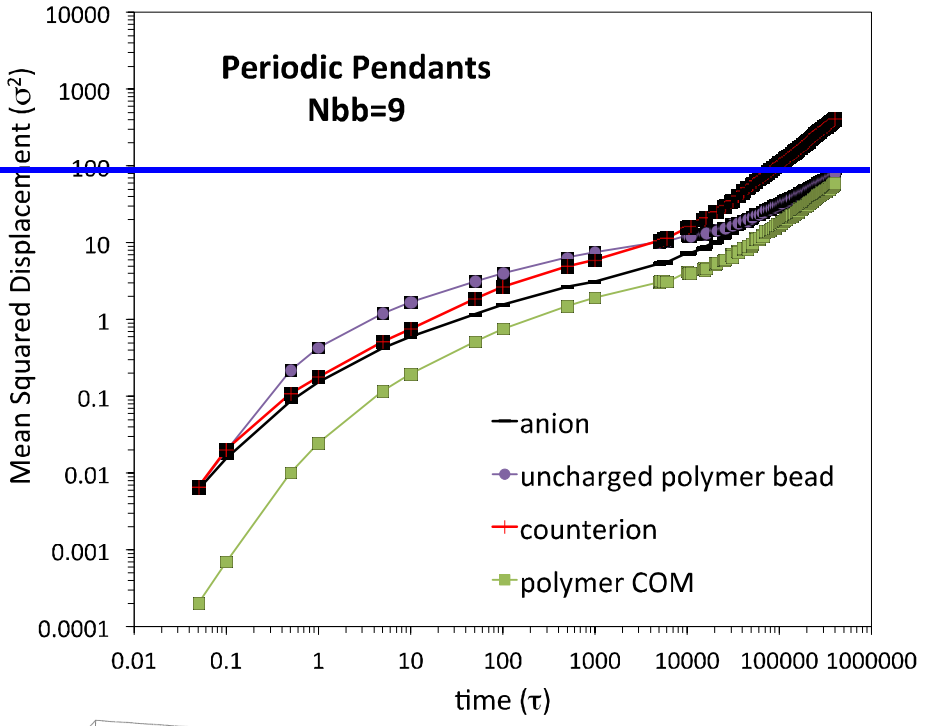


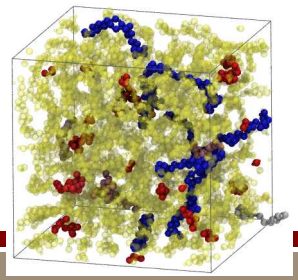
Middleton et al, Macromolecules (2016)
Paren et al, in preparation (2017)

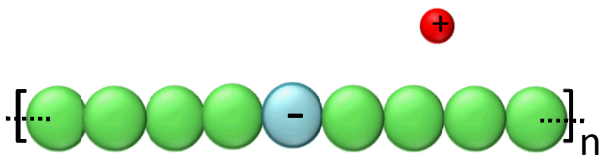
Mean Squared Displacements

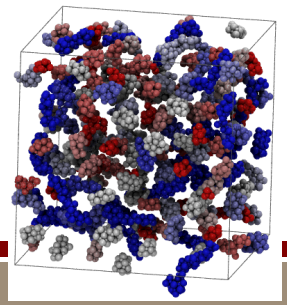
- Ionenes, pendants similar at short times
- Pendants slower but qualitatively similar at long times

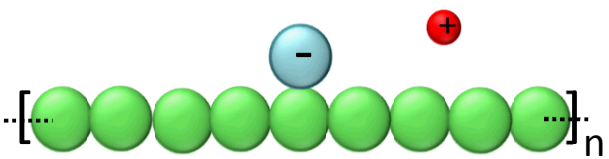




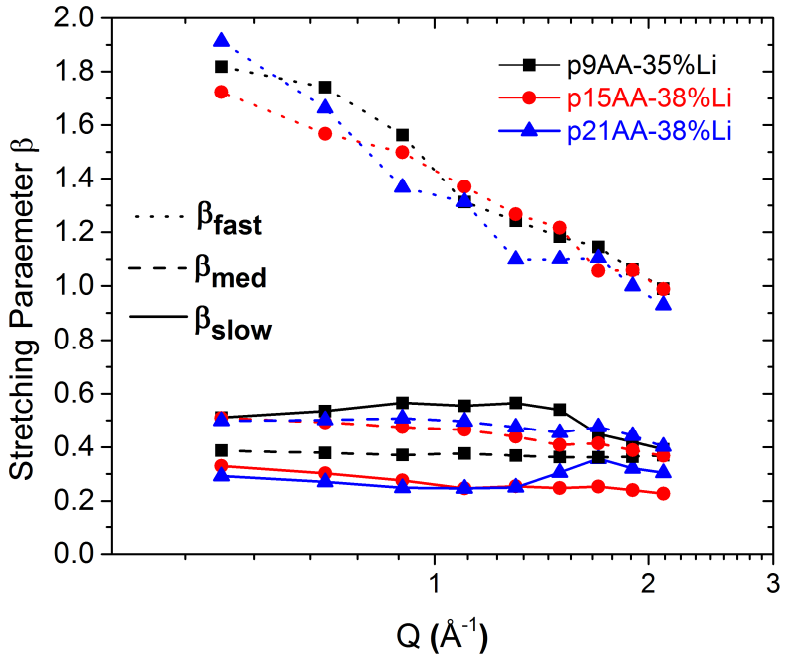


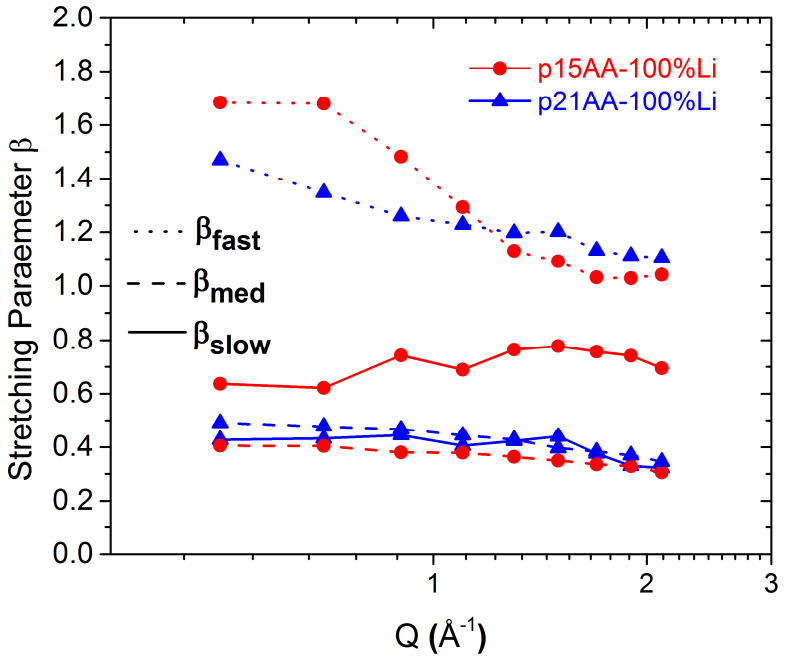




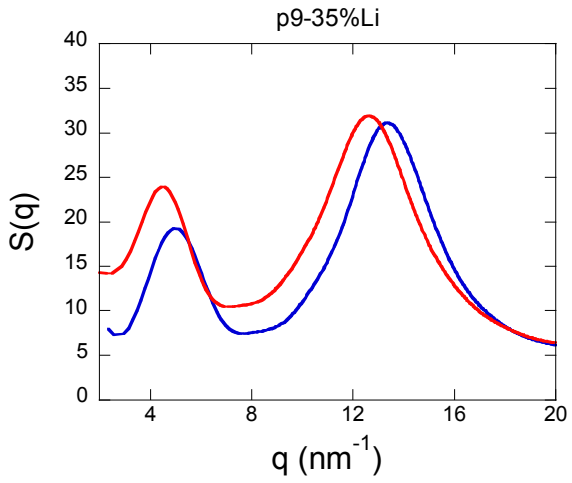


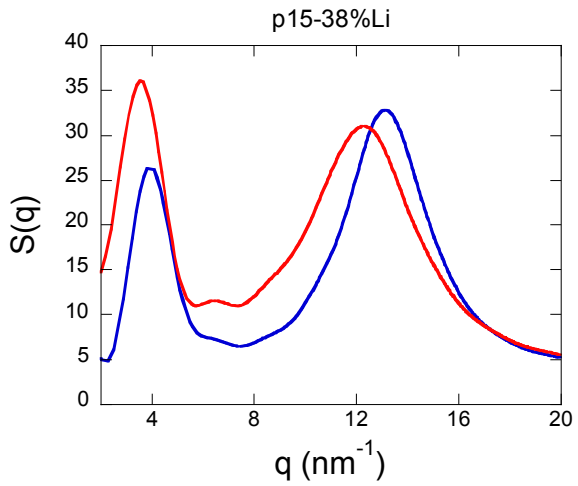
Stretching parameters

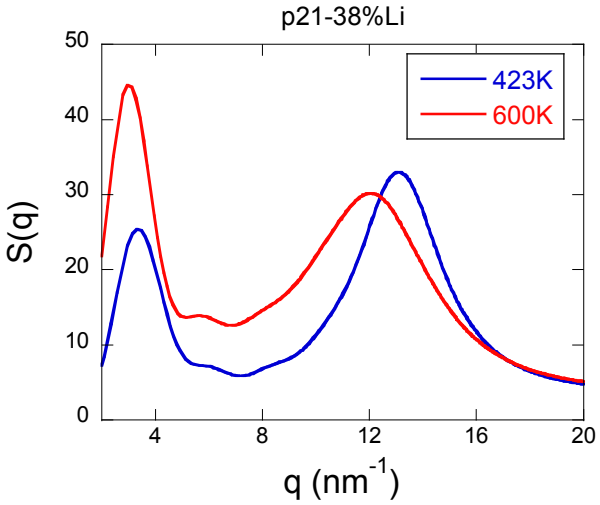


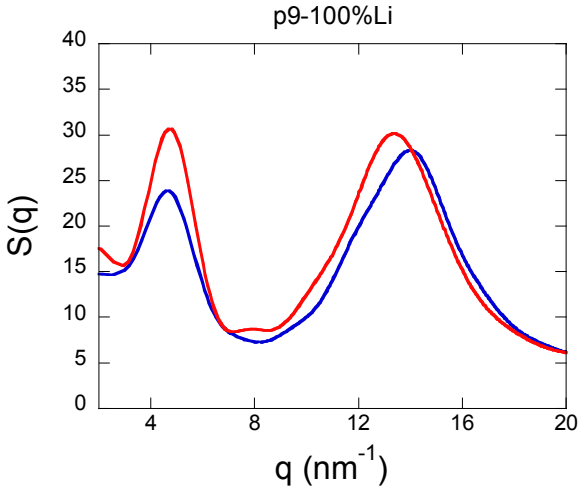


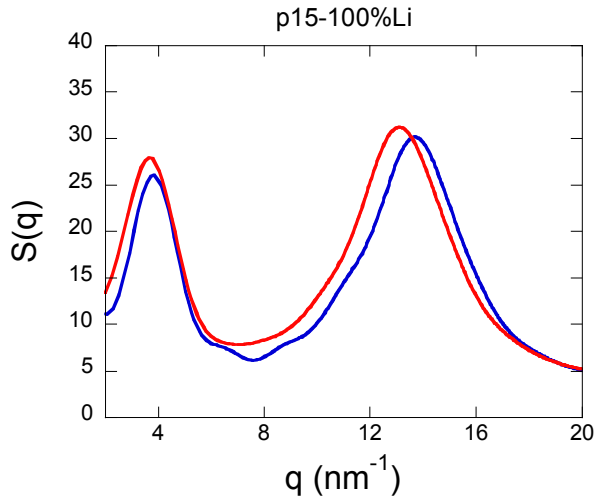
Morphology at higher temperature

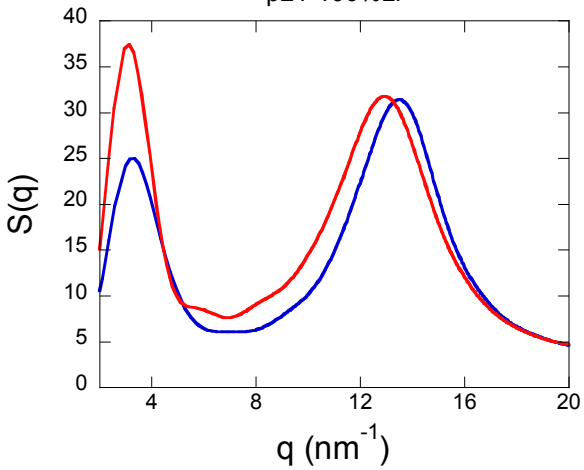






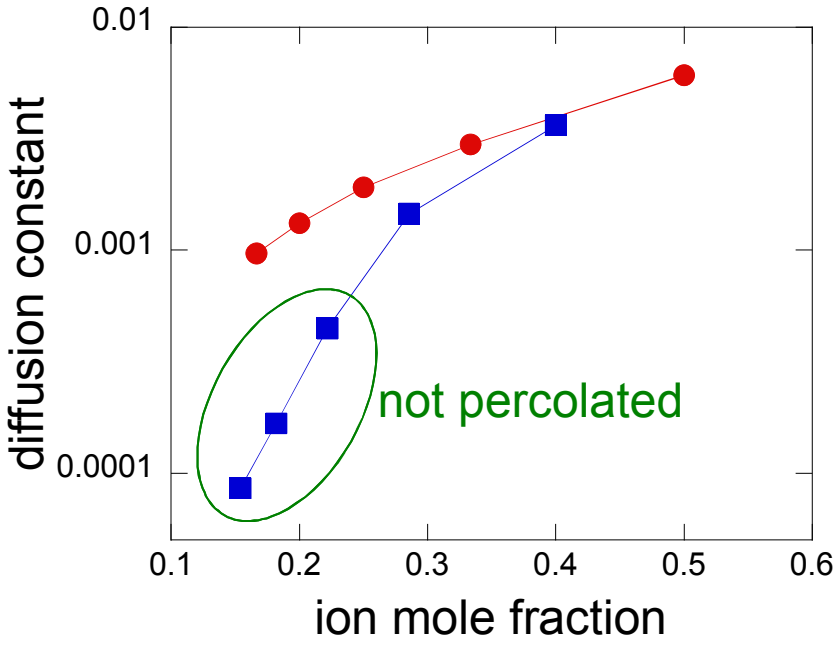


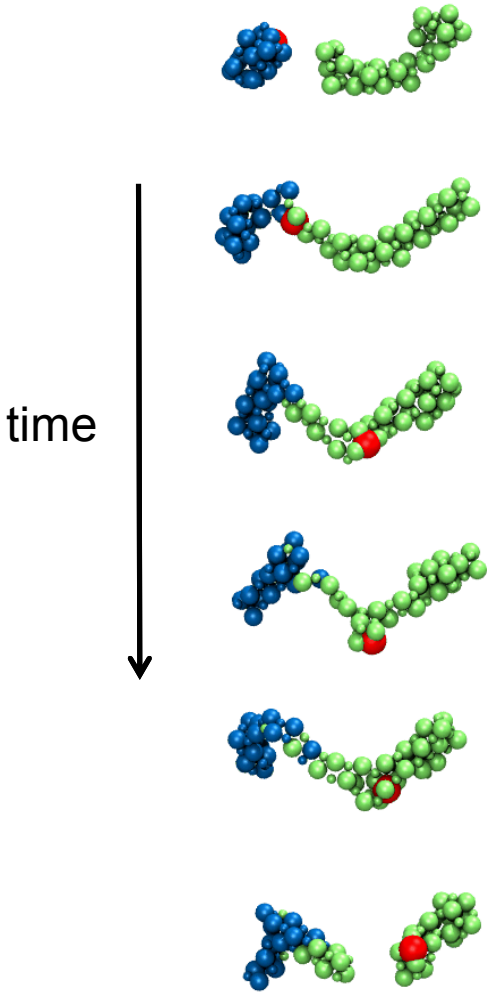




Counterion Diffusion Constants

$$\langle \mathbf{r}^2(t) \rangle = 6Dt$$





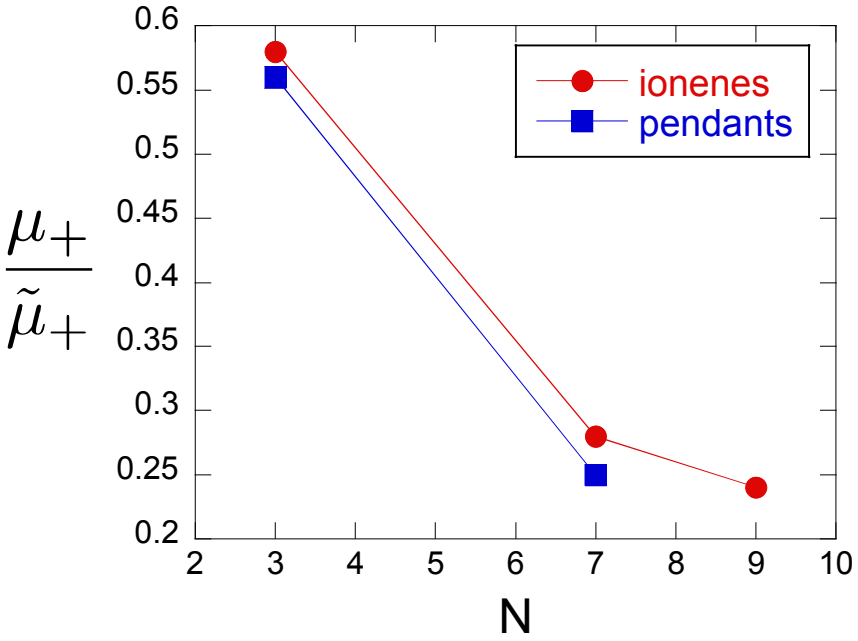
- Ionenes have faster diffusion than pendants
- Percolated systems have faster diffusion

Hall et al., *Macromolecules* (2012)

Ion motion is correlated

from non-equilibrium simulation in field: $\mu_i = \langle v_{x,i} \rangle / E$

from equilibrium Einstein relation $\tilde{\mu}_i = zeD_i / kT$

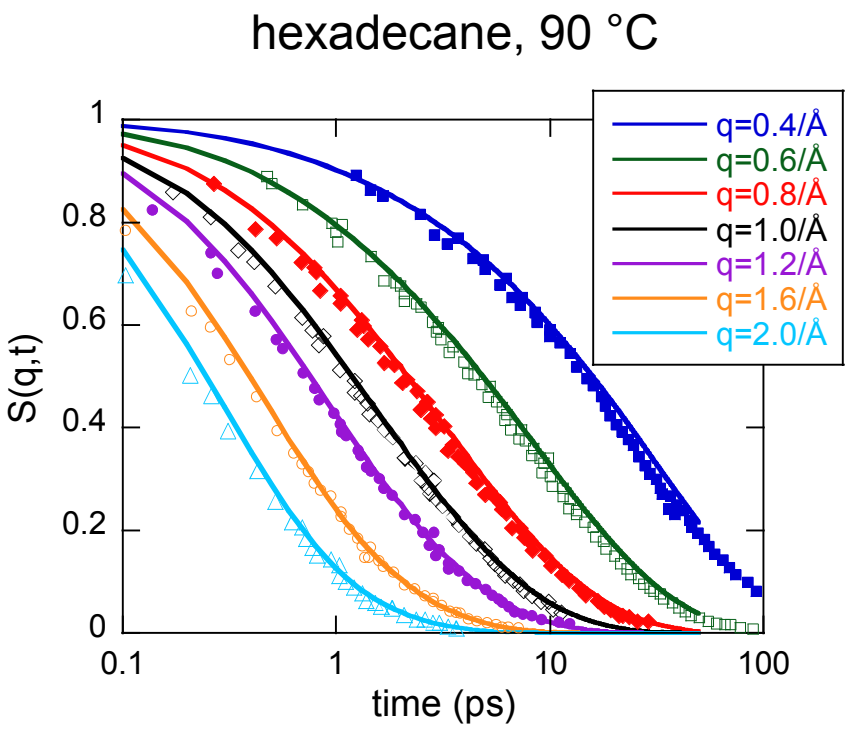


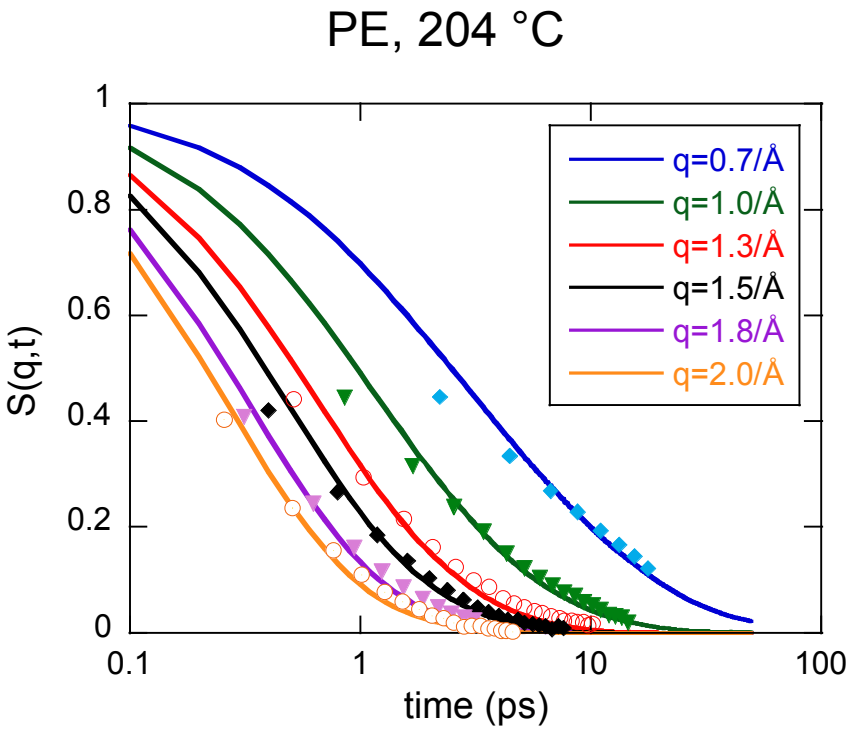
f factor < 1
Haven ratio $H_R > 1$

ionic aggregates slow conduction

Ting et al., *Macromolecules*, 2015

Test of L-OPLS Force Field





Morhenn, H., Busch, S. & Unruh, T. *J Phys-Condens Mat* **24,** 375108 (2012).

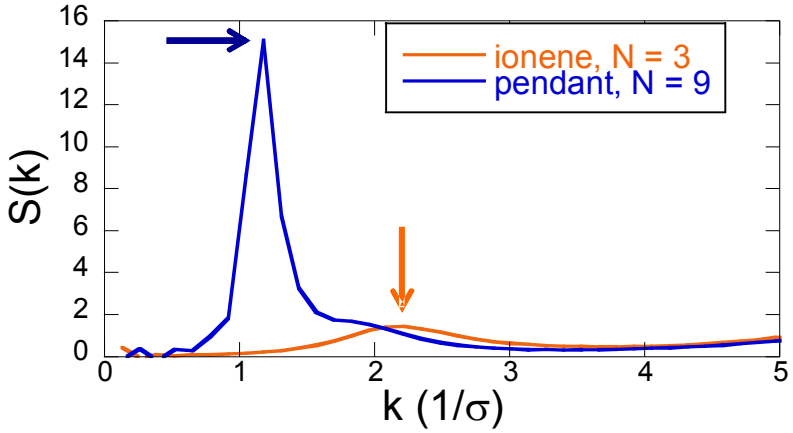
Arbe, A. & Colmenero, J. *Phys Rev E* **80,** (2009).

Time-dependent Structure Factors

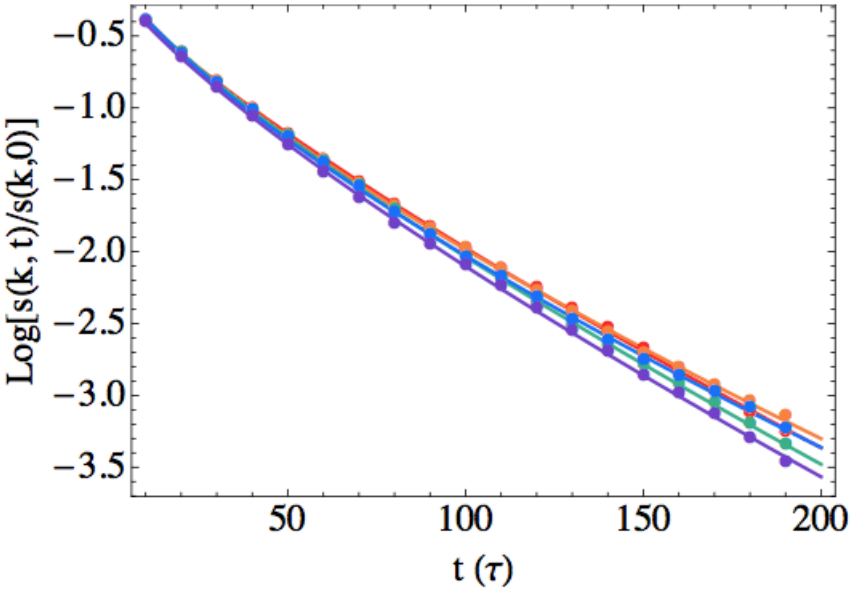
decay of counterion-counterion scattering peak

$$S(k,t)/S(k,0) = \exp[(-t/\tau)^{\beta}]$$

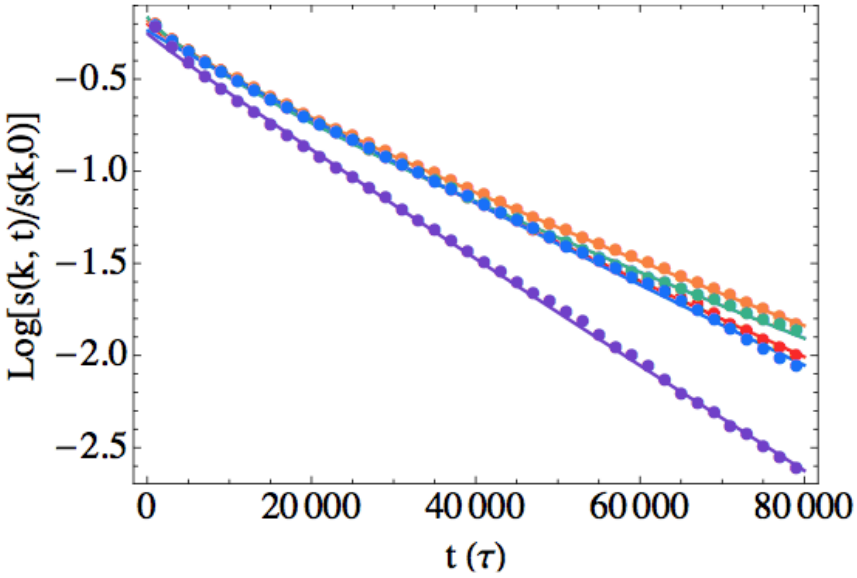
$0.66 < \beta < 0.96$



ionenes N = 3



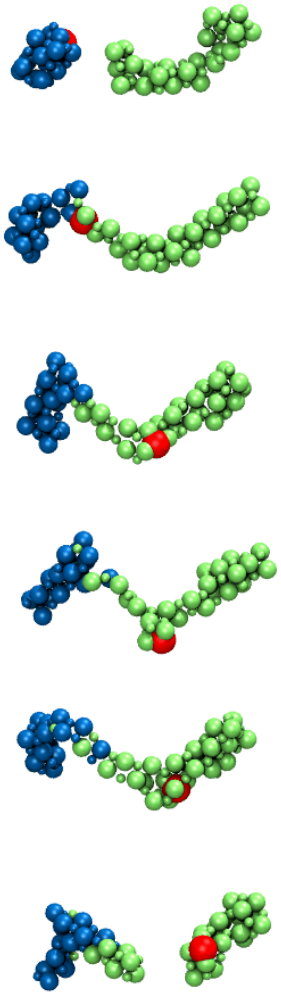
pendants N = 9



Ion Trajectories: CG MD

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

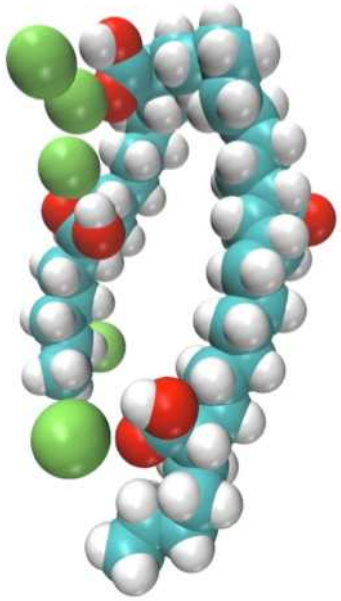
Clusters reform with ion moved

Hall et al., *Macromolecules* (2012)

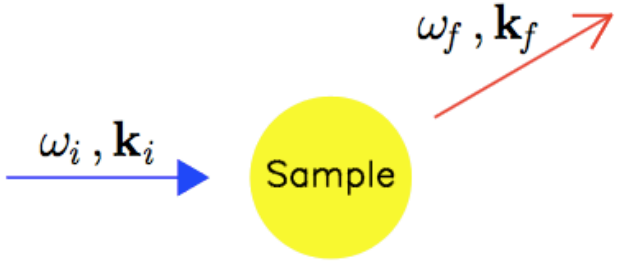
Atomistic MD Simulations

- Variations in:
  - cation type: M^+ = Li^+, Na^+, Cs^+, Zn^{2+}
  - neutralization level = % COO^-M^+ vs COOH
  - spacing length: p9, p15, p21

- All atom OPLS-AA force-field
- 80-200 polymers, n = 4 repeat units (4 acid groups)
  - ~ 64 Å box, total of ~25,000 atoms
- NVT ensemble, **150°C → well above T_g**
- 30 ns (400 ns in one case)
- LAMMPS



Quasi-Elastic Neutron Scattering



Energy transfer

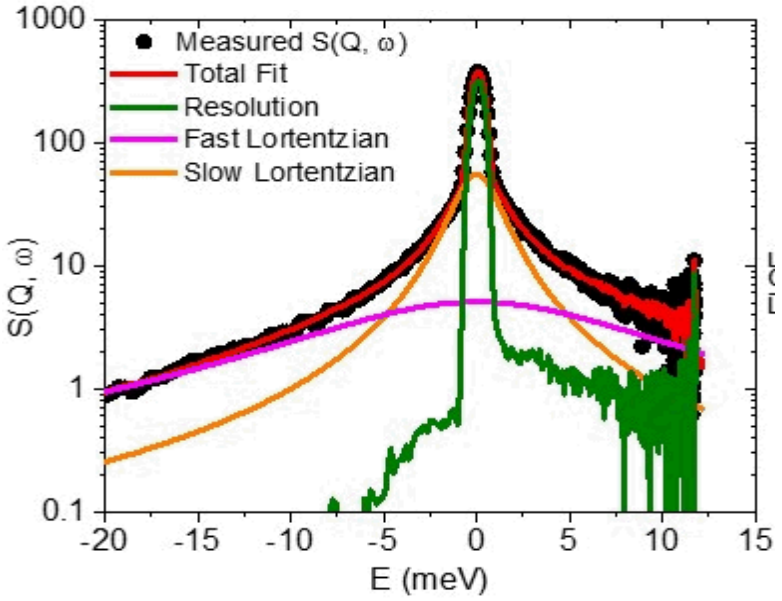
$$E = \hbar\omega = \hbar(\omega_f - \omega_i)$$

Momentum transfer

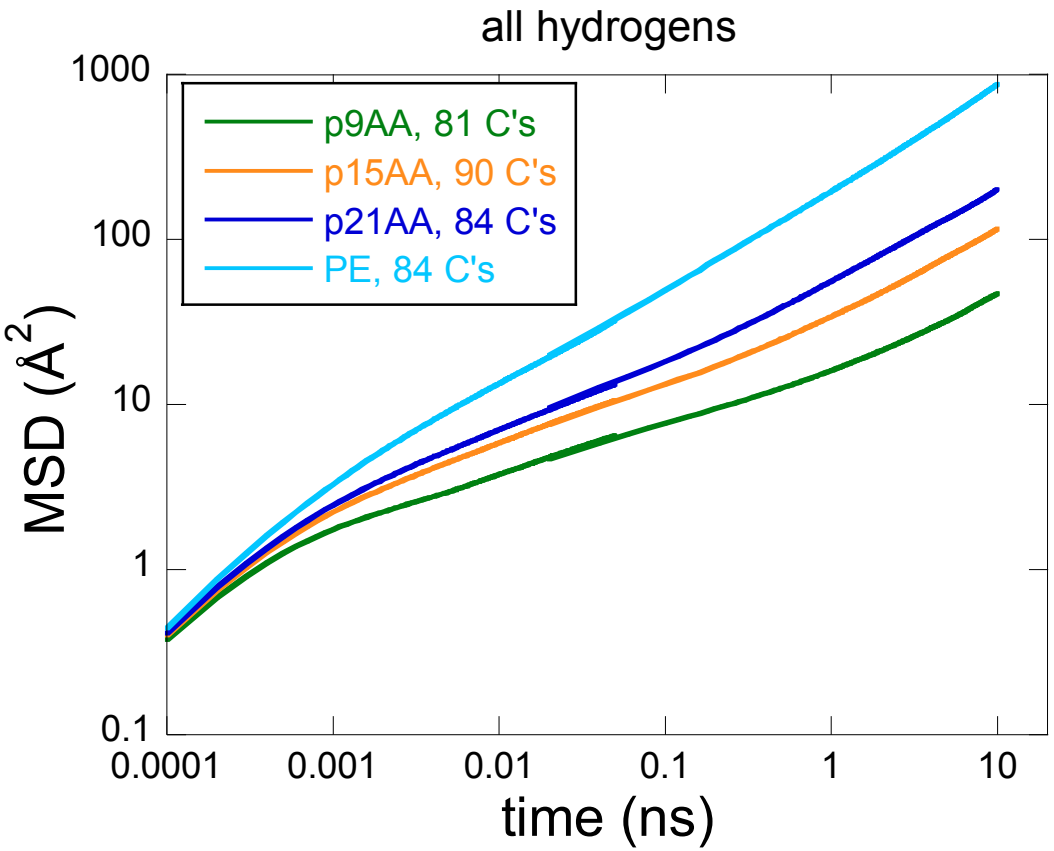
$$\mathbf{P} = \hbar\mathbf{Q} = \hbar(\mathbf{k}_f - \mathbf{k}_i)$$

incoherent, inelastic: sensitive to self-motion of hydrogens
scattering intensity proportional to I(Q,ω)

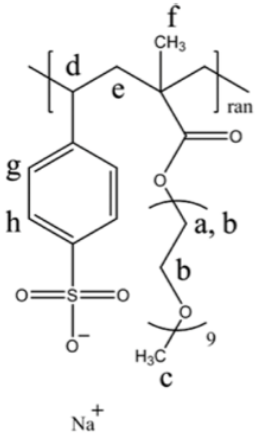
NIST
disk chopper spectrometer
T = 150 °C

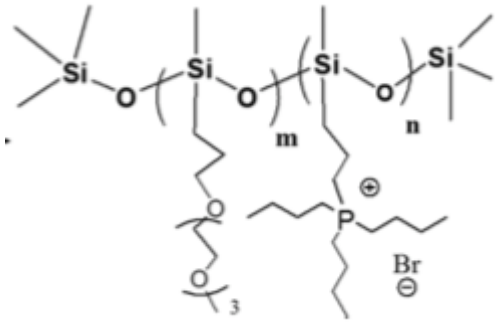


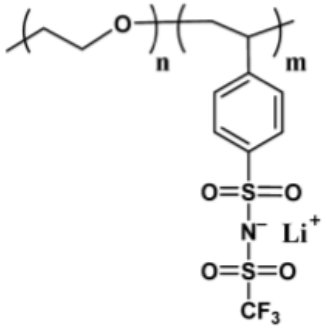
Hydrogen MSDs



Ionomer Melts as Single-Ion Conductors

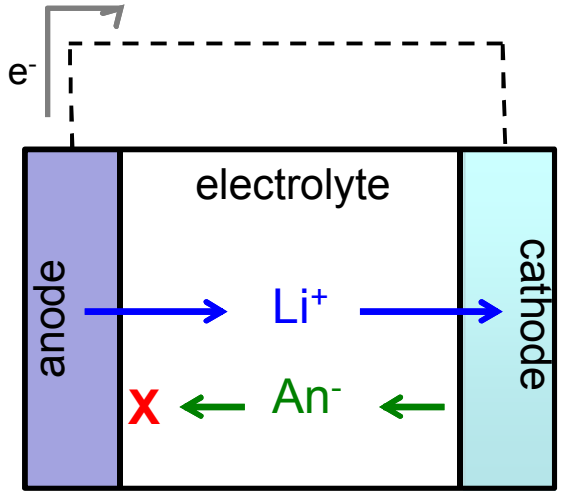






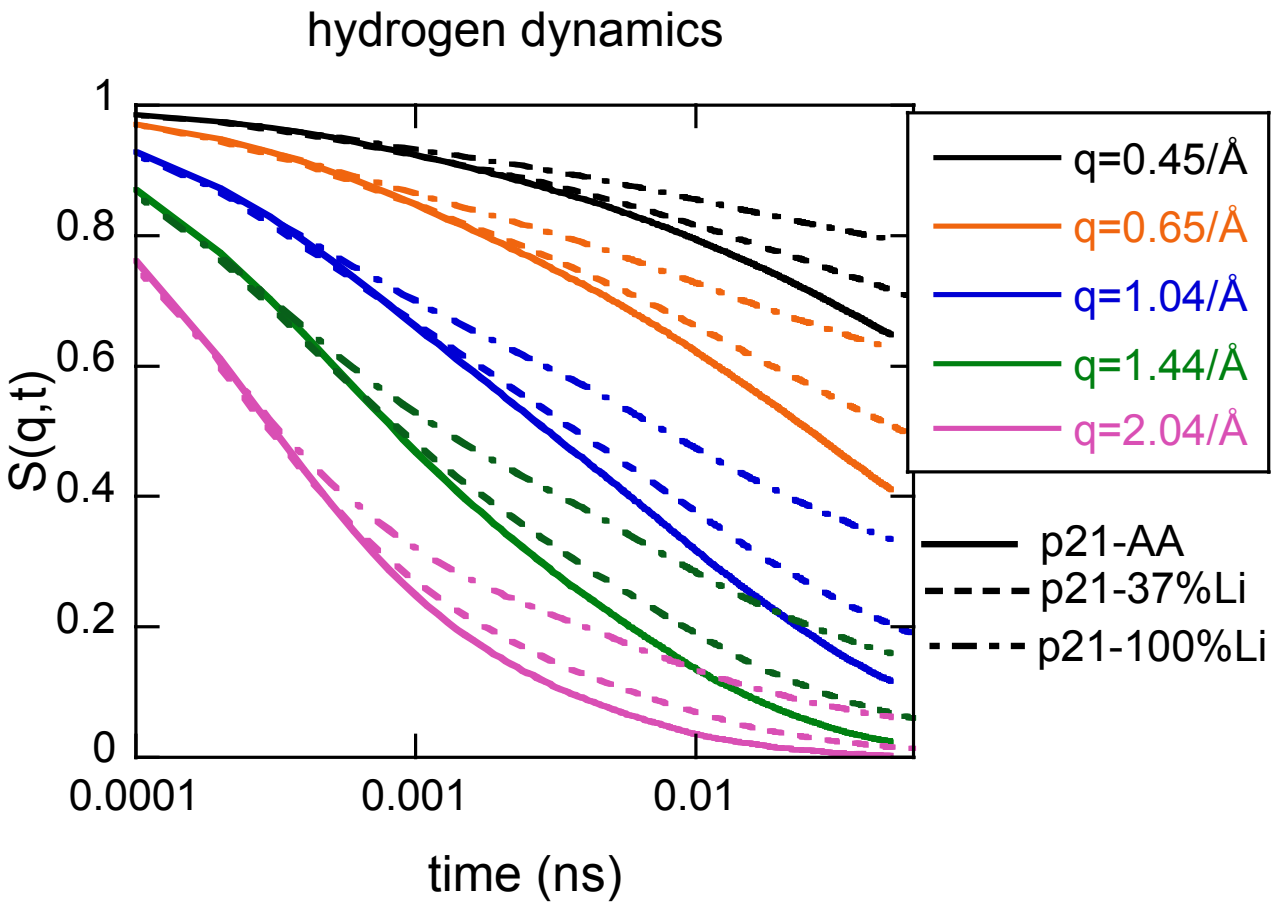
why single-ion?

- high transference number
- no concentration gradients



Wang, J.-H. H. *et al. Macromolecules* **48,** 7273–7285 (2015).
Liang, S. *et al. Macromolecules* **47,** 4428–4437 (2014).
Rojas, A. A. *et al. Macromolecules* **48,** 6589–6595 (2015).

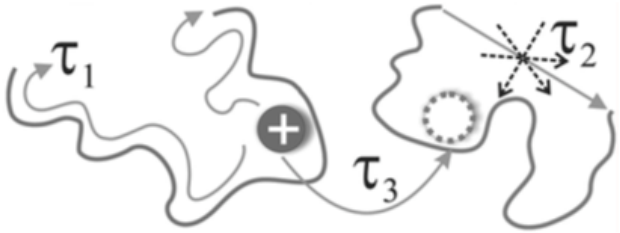
Early-time dynamics in p21-x%Li



ionic aggregates further slow polymer motion

Moving ions in polymers

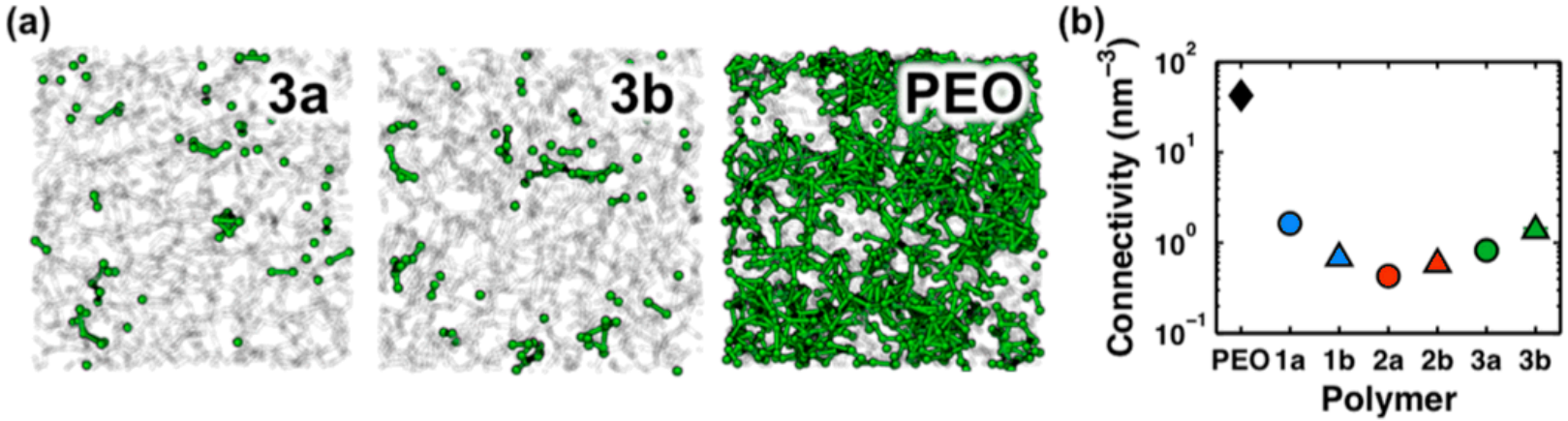
most studied polymer electrolyte: PEO + Li salts



inter- and intra-chain motion

Maitra, A., & Heuer, A. (2007) *Physical Review Letters*, *98*, 227802.

Li solvation sites in various polyesters:



Webb, M. A., et al. (2015). *ACS Central Science*, *1*(4), 198–205.