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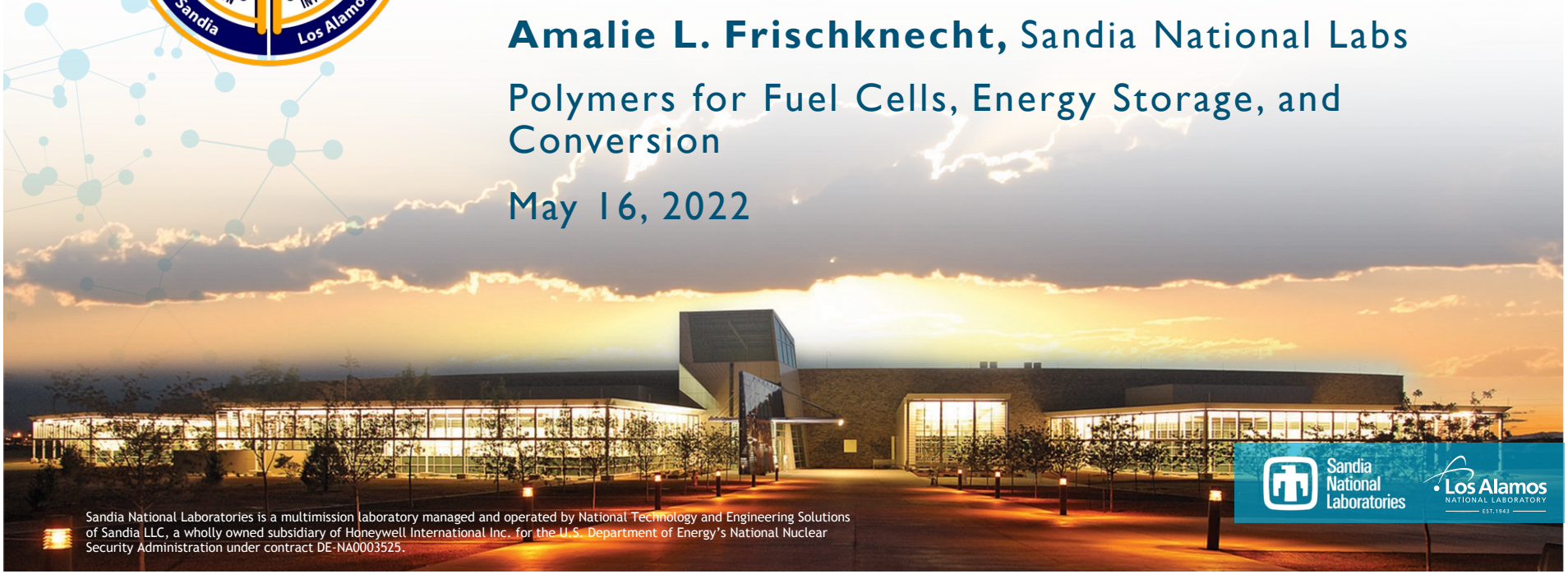
Insights into Hydrated Ion-Conducting Polymers from MD Simulations

Amalie L. Frischknecht, Sandia National Labs

Polymers for Fuel Cells, Energy Storage, and Conversion

May 16, 2022



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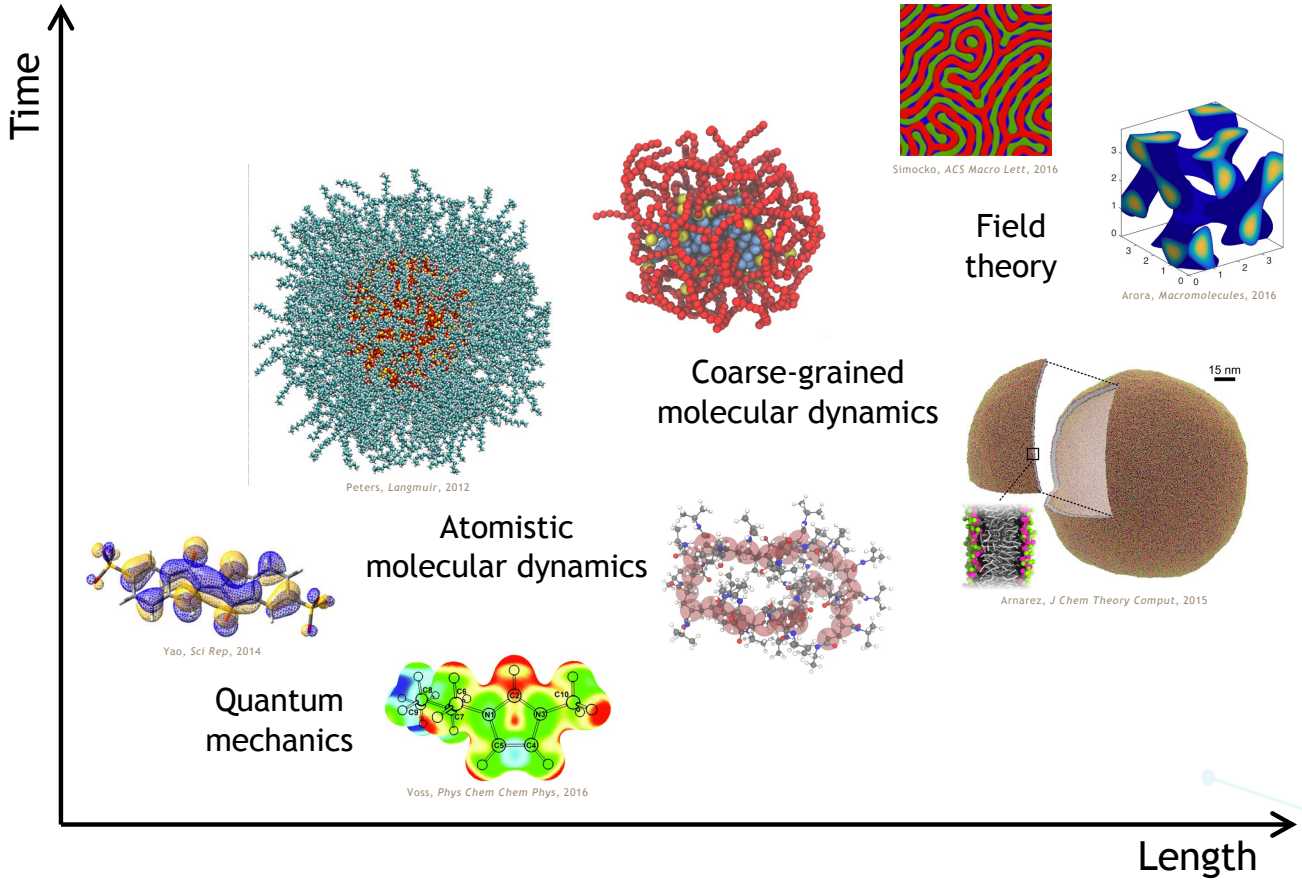
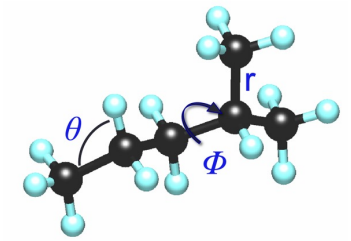
Computational Methods in Polymers

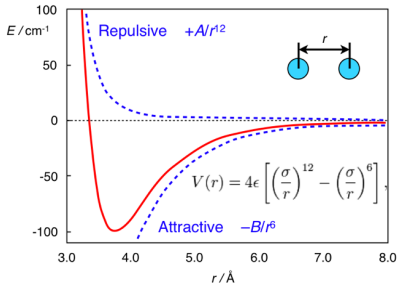


Atomistic MD Simulations

Needed ingredients:

- force fields (interaction parameters)
  - bonded: bonds, angles, dihedrals
  - nonbond: van der Waals, electrostatics
- equilibration method
  - easy in melts, harder in glasses

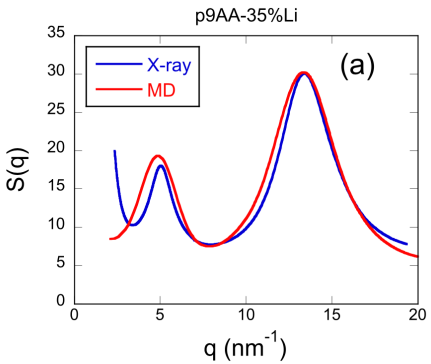


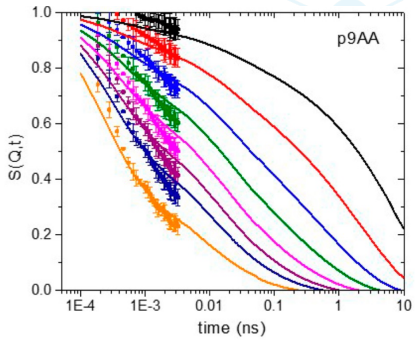


Scope:

- from < ps to 1 μs simulation time
- box sizes: 5-10 nm

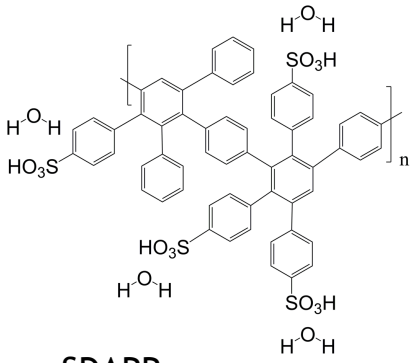
ideal for comparison to scattering!

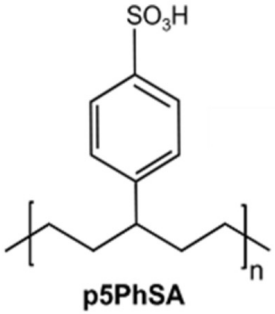


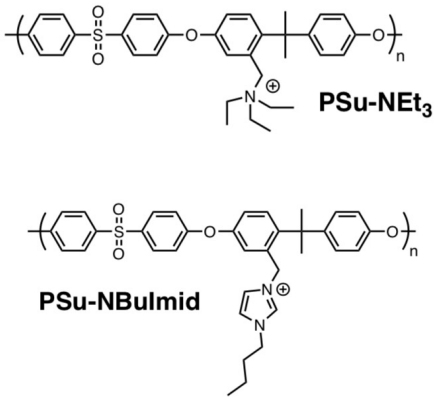


- good results only if force field is good
- fixed charges not always sufficient
- does not include Grotthuss mechanism for protons, OH^- transport

Hydrocarbon-based Polymers



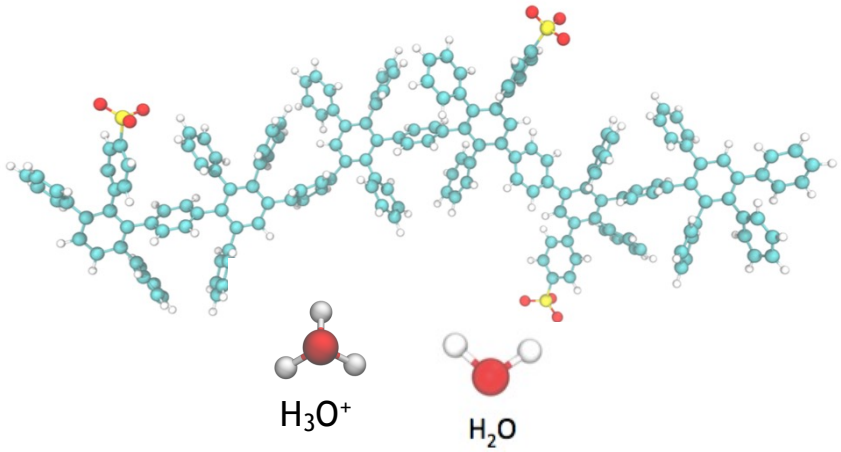




- what is the nanoscale morphology when hydrated?
- how does this affect H^+ or OH^- transport?

SDAPP Simulations

short SDAPP chain

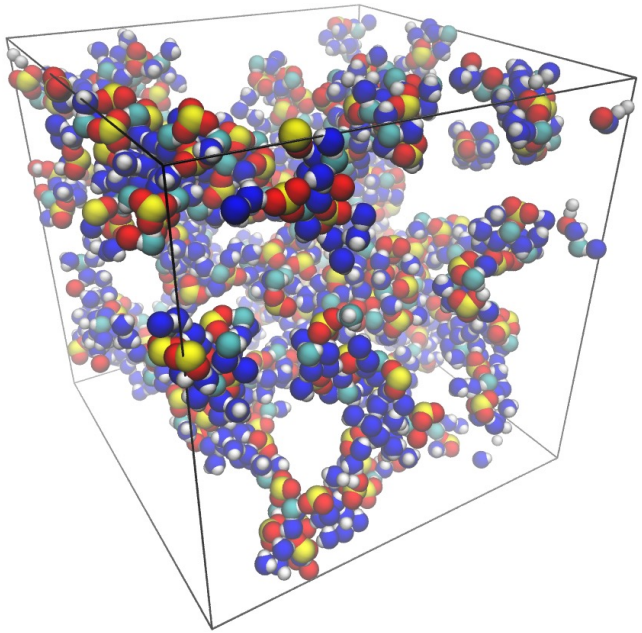


hydronium: treated as fixed ion

sulfonic acids/monomer: S = 1, 2, 4
(IEC = 1.2, 2.2, 3.7)

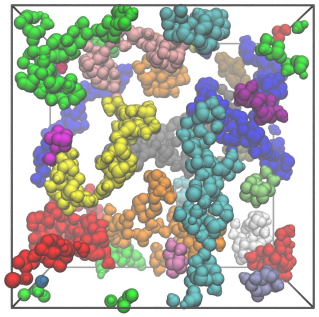
waters/sulfonic acid λ = 3, 5,10, 20

70 chains, 3 monomers/chain
box size about 60Å
OPLS-AA force field, TIP4P/2005 water model

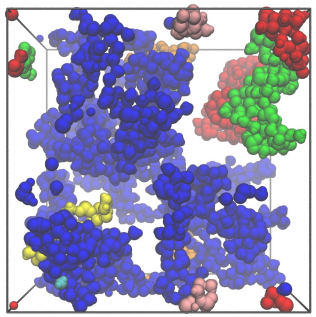


Nanoscale Morphology from MD Simulations

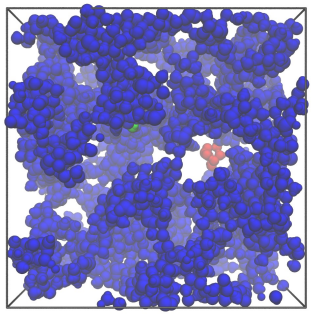
S = 1 sulfonic acid/monomer



λ = 3



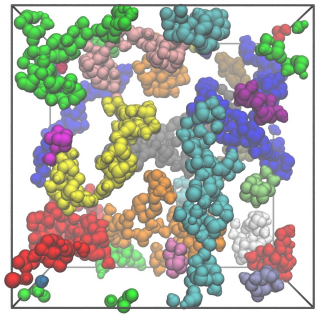
λ = 5



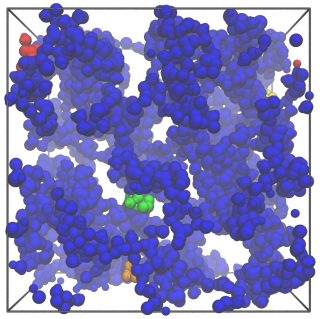
λ = 10

increasing water

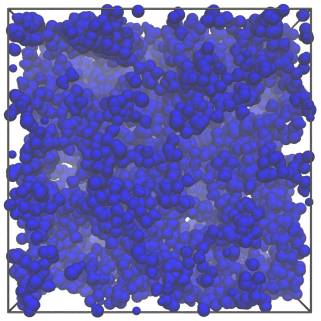
λ = 3



S = 1



S = 2



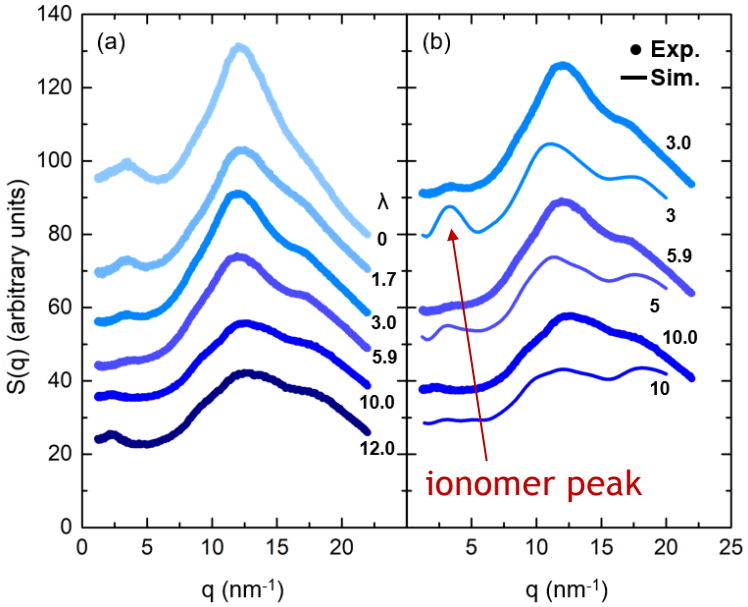
S = 4

increasing sulfonation level

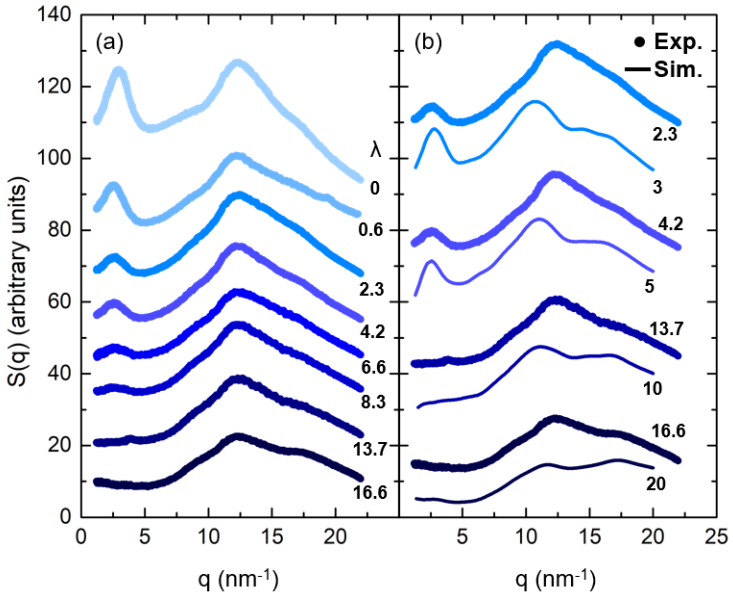
Abbott, L. J. & Frischknecht, A. L. *Macromolecules* **2017**, 50, 1184-1192.

X-Ray Scattering and MD

experiments S=3.6 MD, S=4



experiments, S=2.3 MD, S=2

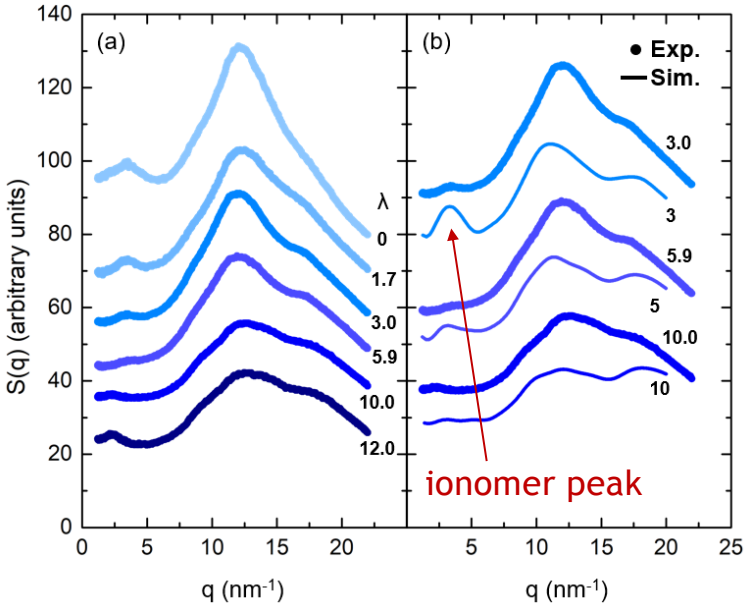


$$S(q) = \sum_i c_i f_i^2 + 4\pi\rho \int_0^\infty \frac{\sin(qr)}{qr} r^2 \sum_{i,j} c_i c_j f_i f_j \left(g_{ij}(r) - 1\right) dr$$

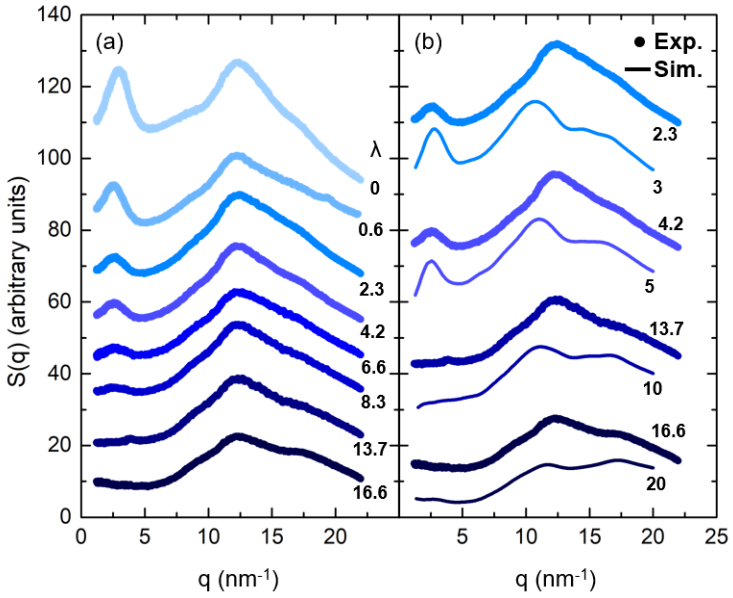
f_i = known x-ray atomic scattering function for each atom

X-Ray Scattering and MD

experiments S=3.6 MD, S=4



experiments, S=2.3 MD, S=2

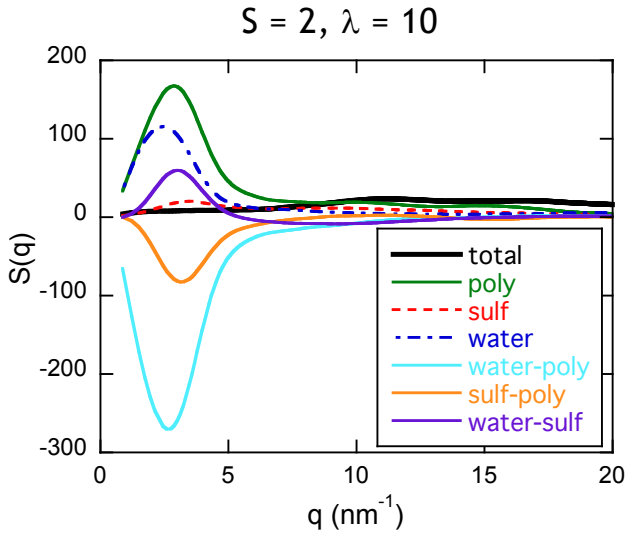


why does the ionomer peak disappear??

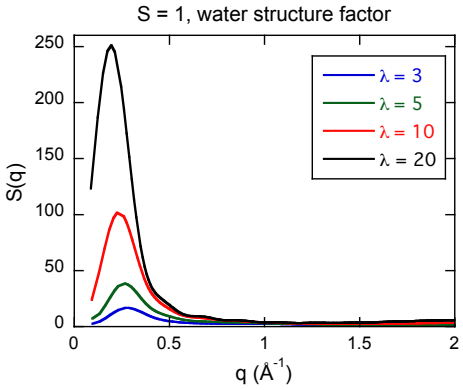
Sorte, E. G. et al. *Macromolecules* **2019**, 52, 857-876.

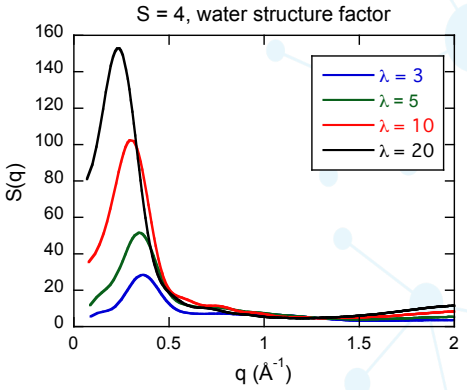
Partial Structure Factors from MD

$$S_{total} = S_{polymer} + S_{sulfonic} + S_{water} + S_{water\text{-}poly} + S_{sulf\text{-}poly} + S_{water\text{-}sulf}$$



water-polymer cross-correlations cancel other peaks

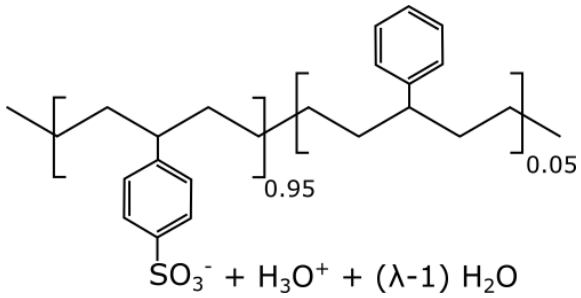


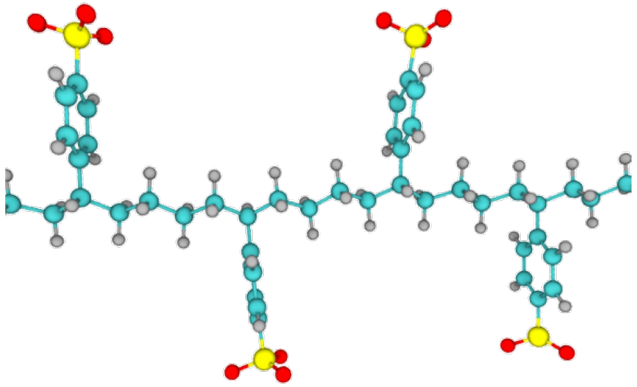


water peak increases in intensity with increasing λ
shifts slightly to the left (lower q, larger domains)

in hydrocarbon PEMs, loss of scattering contrast leads to loss of ionomer peak
still have nanoscale phase separation!

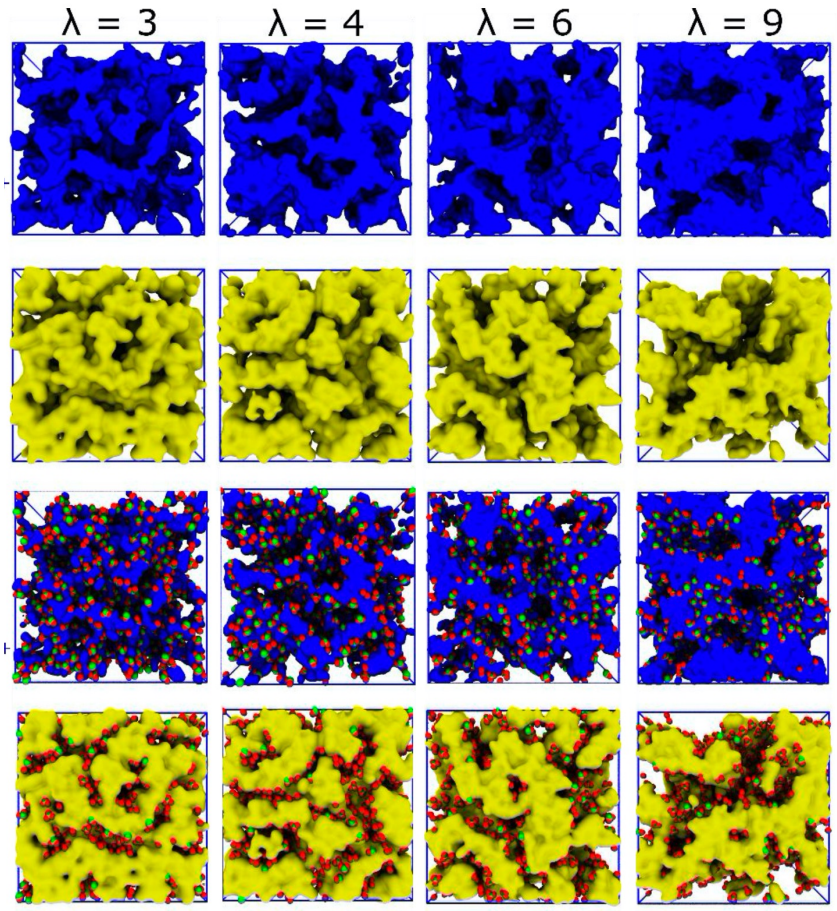
MD Simulations of p5PhSA

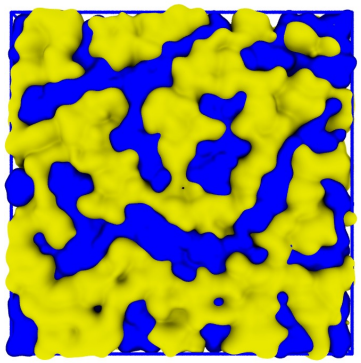


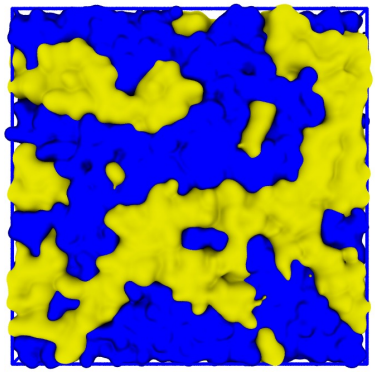


- Gromacs 2019
- OPLS-AA force field, TIP4P/2005 water
- Ion and hydronium partial charges scaled to account for polarization effects to first order
- Simulations at λ = 3, 4, 6, 9, and 12
- IEC = 4.2 mmol/g

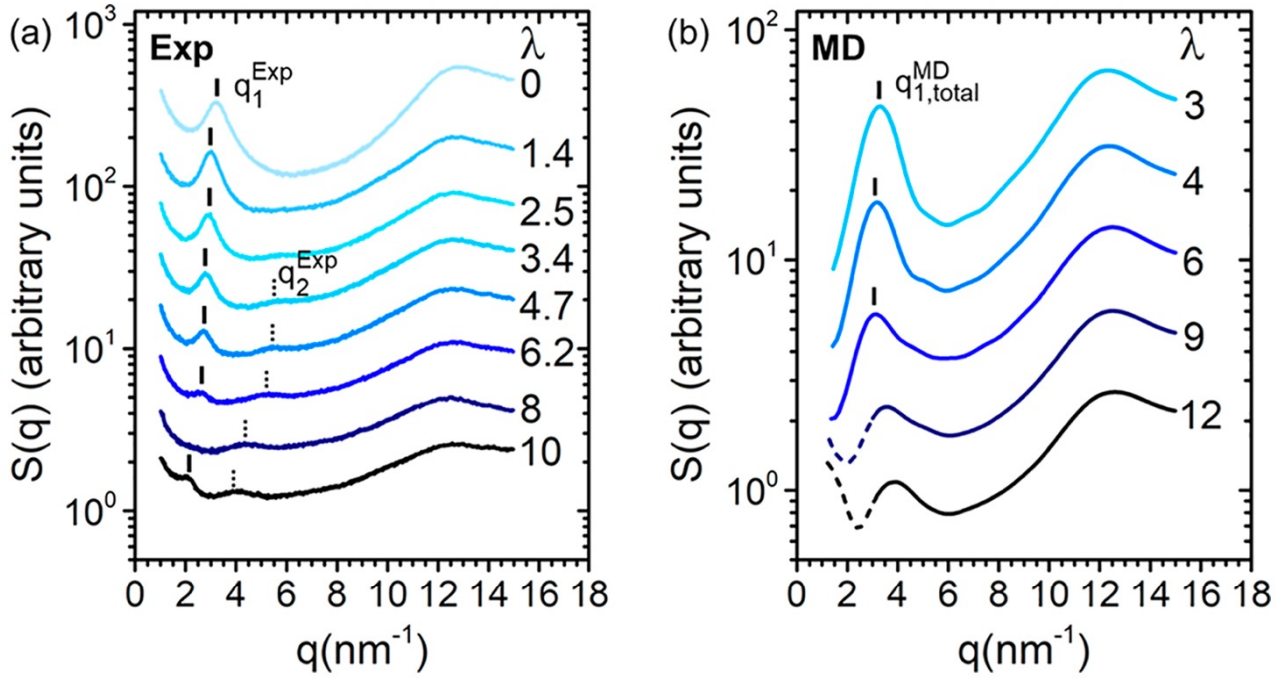
MD Snapshots







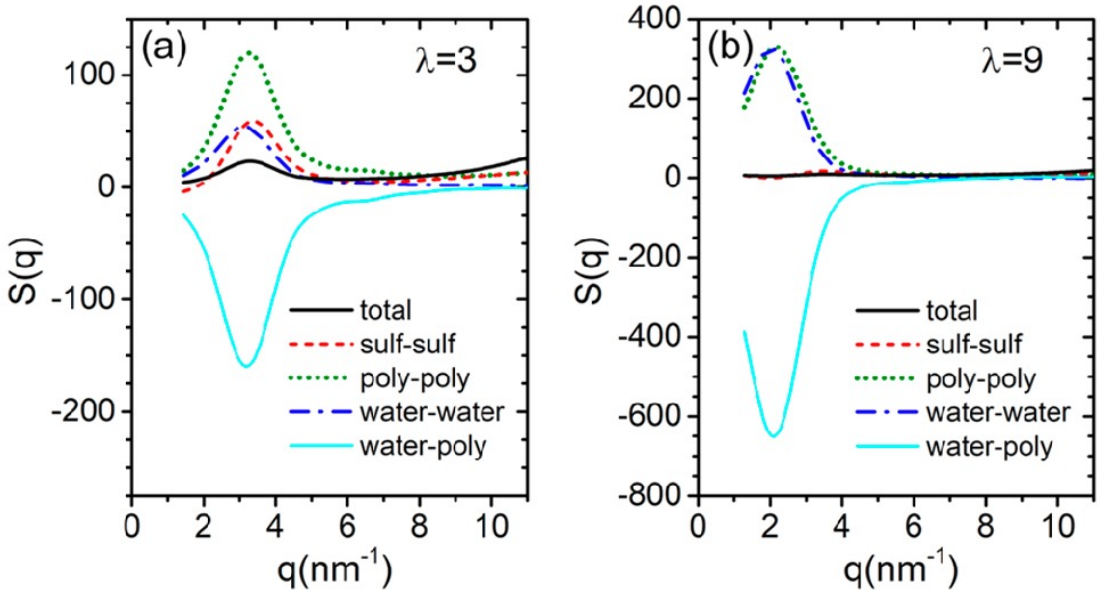
X-Ray Scattering and MD



again: loss of ionomer peak at high water contents

Paren, B. A. et al. *Chem. Mater.* **2021**, 33, 6041-6051.

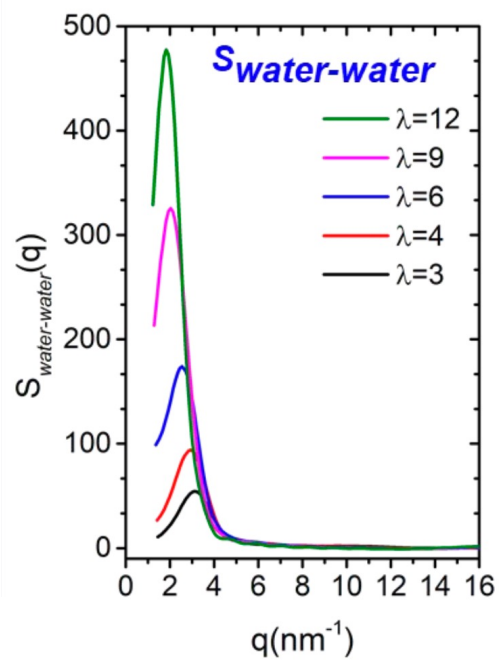
Partial Structure Factors



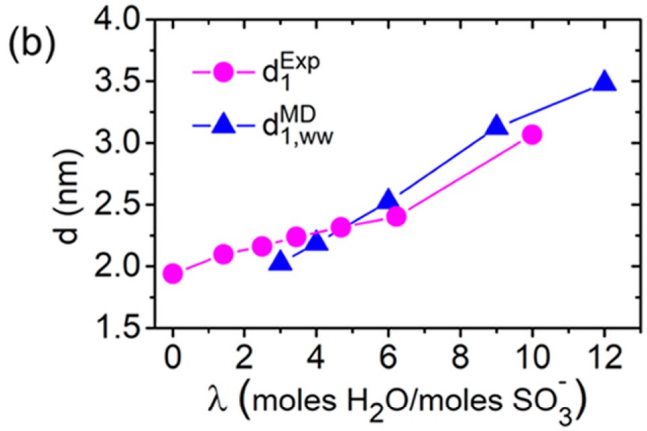
loss of contrast in scattering leads to loss of ionomer peak

Paren, B. A. et al. *Chem. Mater.* **2021**, 33, 6041-6051.

Scattering from Water Domains



d = 2π/q

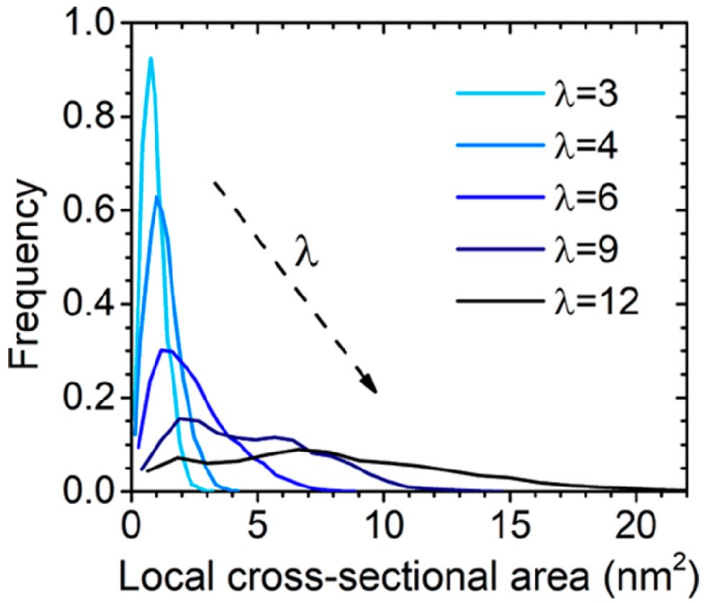


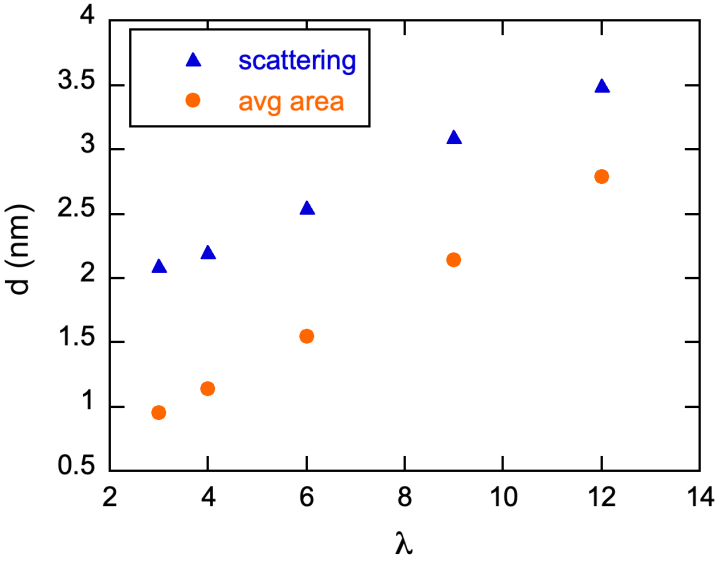
spacing between water channels in MD consistent with peak in X-ray

Water Domain Sizes

d in scattering: gives avg center-to-center distance between water domains
how large are the water channels?

minimal cross-sectional area distribution



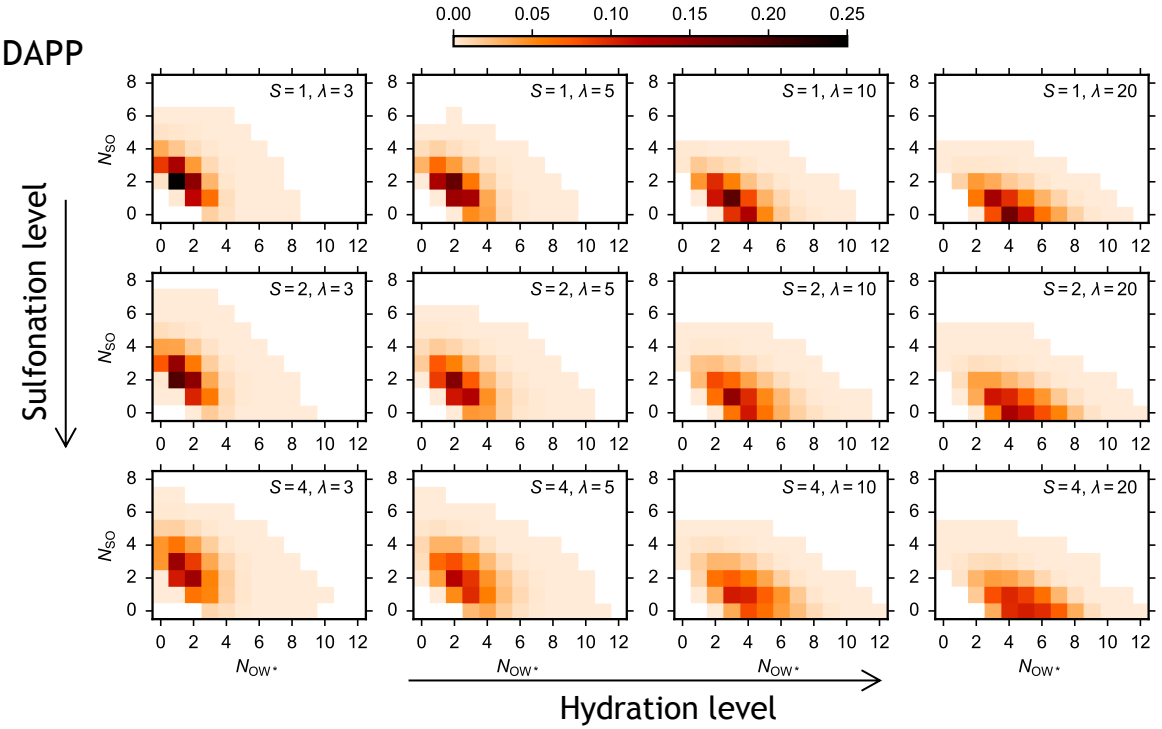


water channels from 1-2.8 nm

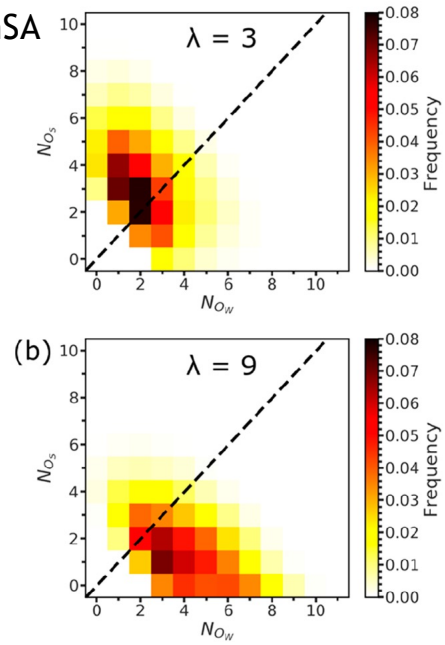
Coordination Environments

H_3O^+ is coordinated to N_{OS} sulfonate oxygens, N_{Ow} water oxygens

SDAPP

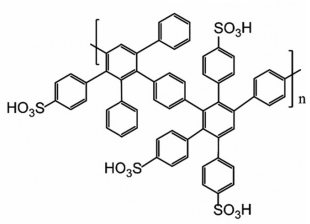


p5PhSA

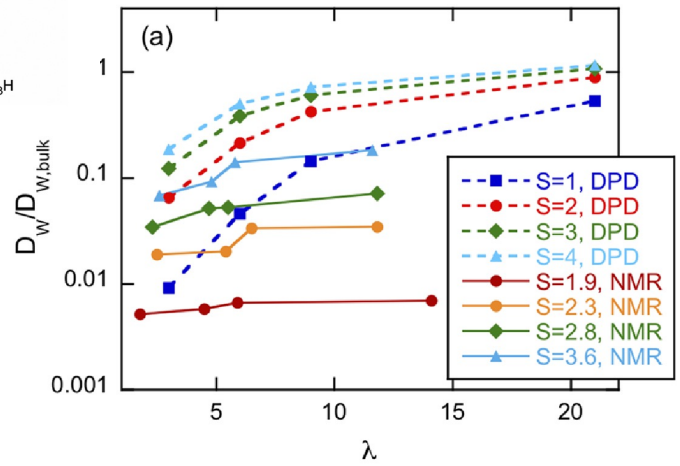


at higher λ: H_3O^+ less associated with SO_3^-, more associated with water

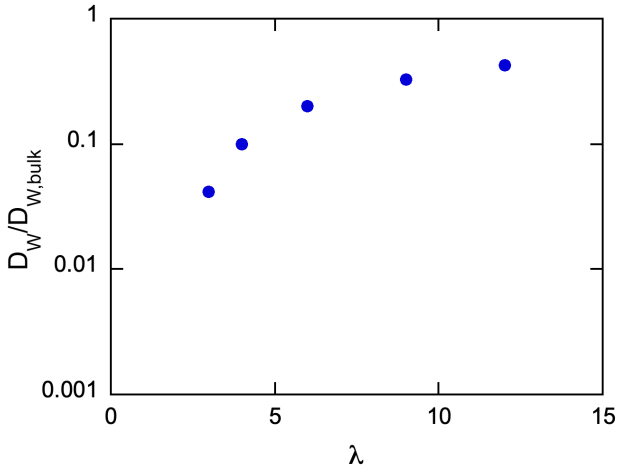
Water Diffusion Constants

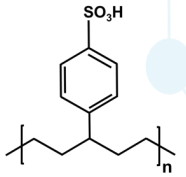


SDAPP: DPD and NMR



p5PhSA: MD

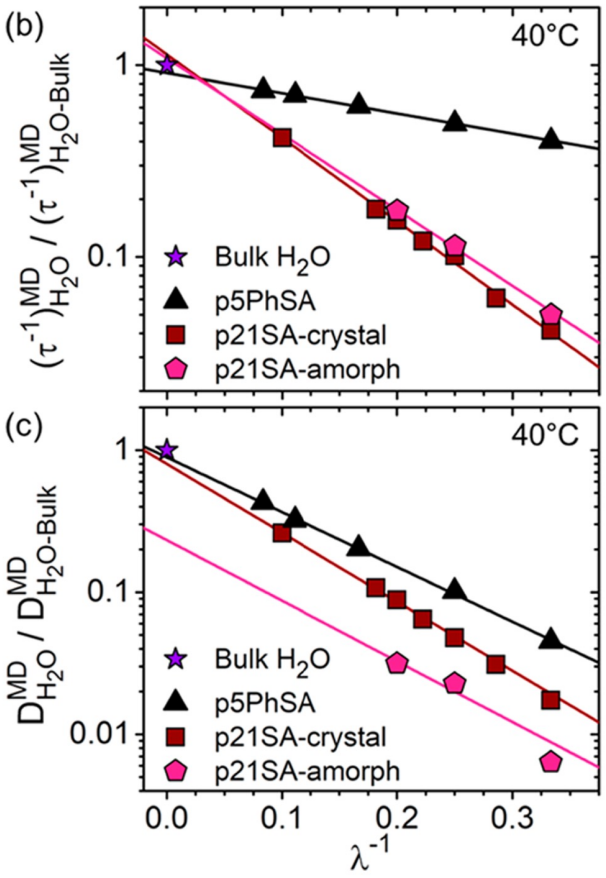




water diffusion suppressed by confinement in membranes

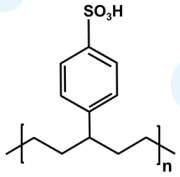
Clark, J. A., Santiso, E. E. & Frischknecht, A. L. *J. Chem. Phys.* **2019**, 151, 104901.

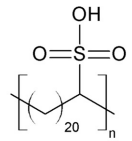
Water Dynamics



τ = water rotational diffusion time

D = water diffusion constant

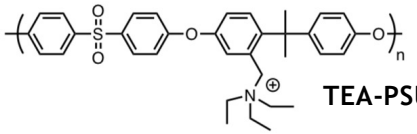




- τ, D approach bulk values at large λ
- faster water dynamics in p5PhSA than in p21SA
  - more water in p5PhSA for given λ
  - larger water channels in p5PhSA

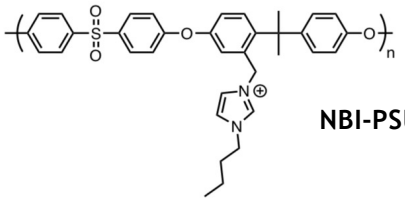
Functionalized Polysulfones: OH^- Conductors

MD simulations for λ = 15, 23
OPLS-AA force field



TEA-PSU

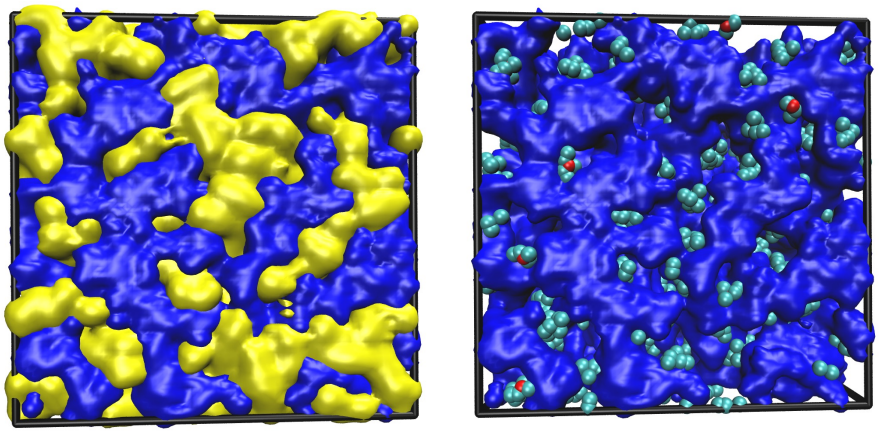
IEC = 1.7



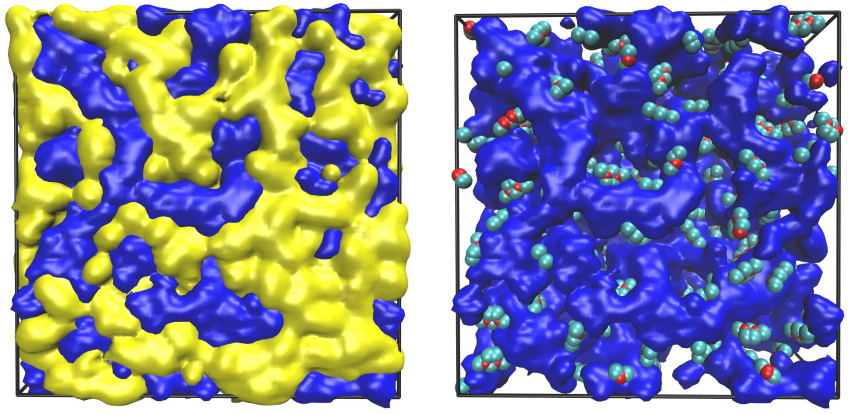
NBI-PSU

IEC = 1.8

λ = 23



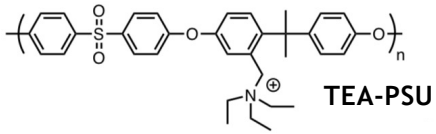
λ = 15



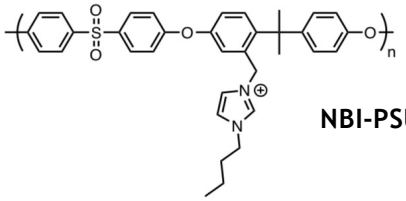
Frischknecht et al, *ACS Appl Polym Mater*, **2022**

Weak Ionomer Peaks

total scattering intensity

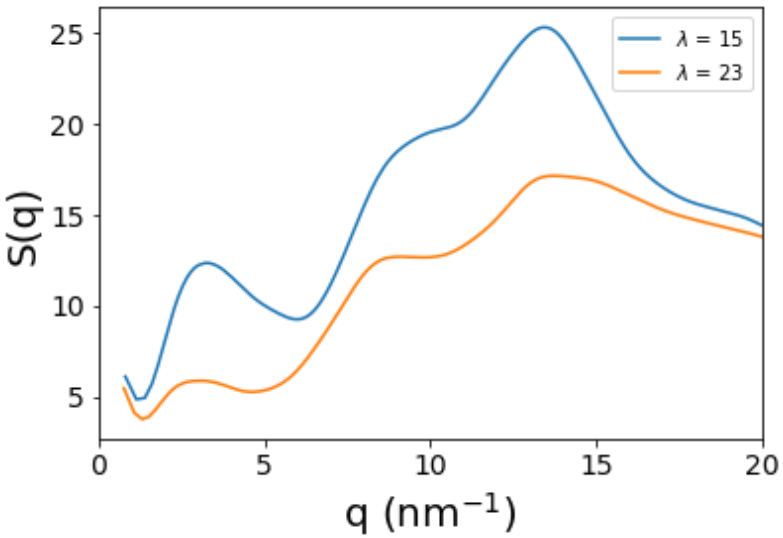


TEA-PSU

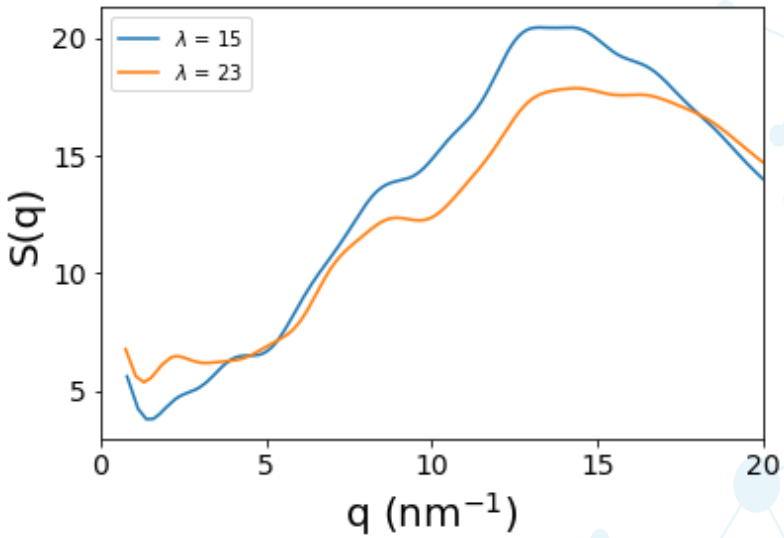


NBI-PSU

TEA



NBI



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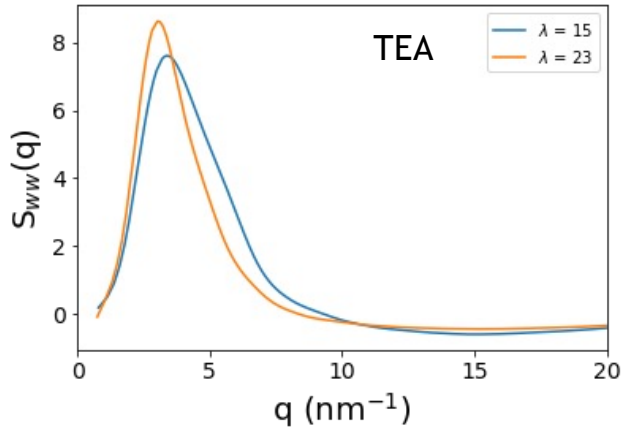
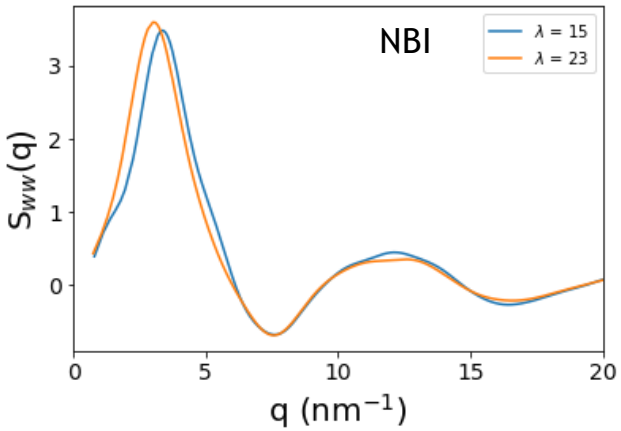
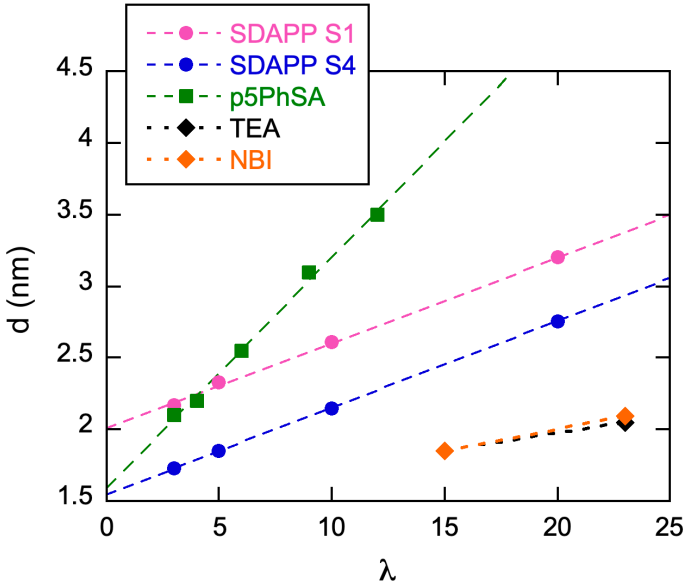
Water Partial Structure Factors





all water spacings from $S_{ww}(q)$ from MD



polysulfones have small water domains

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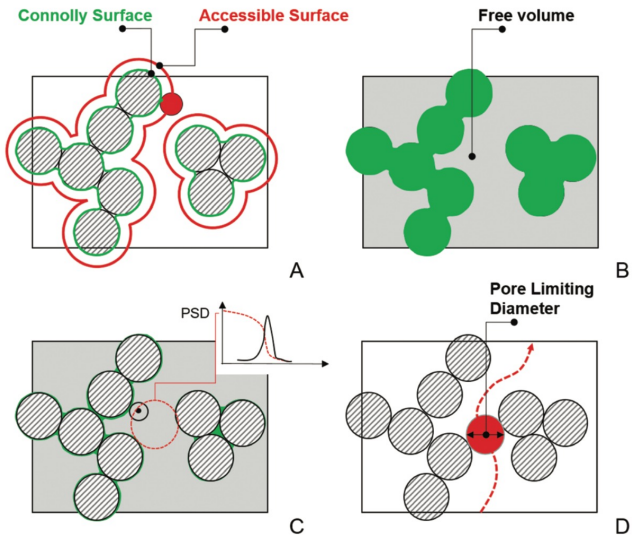
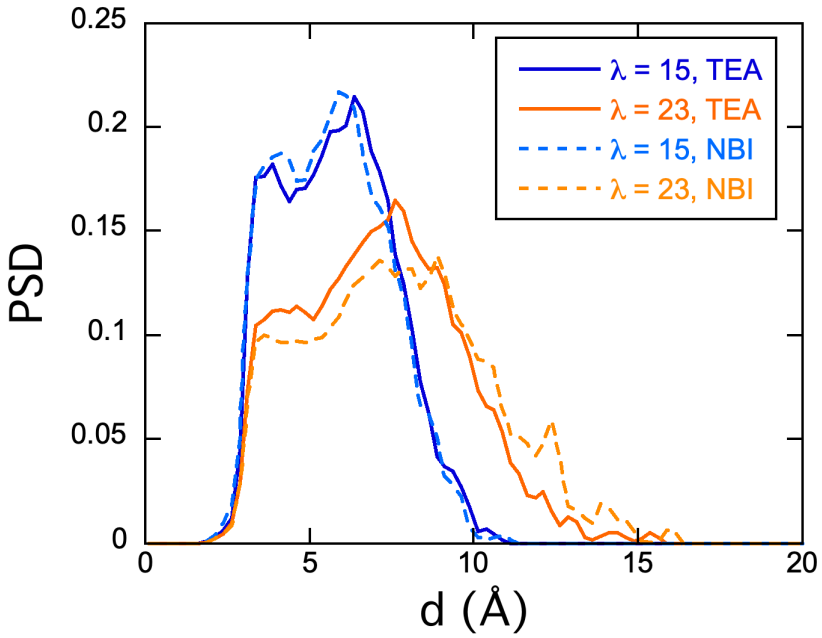
Water Domain Sizes

calculate pore size distribution (PSD) from PoreBlazer

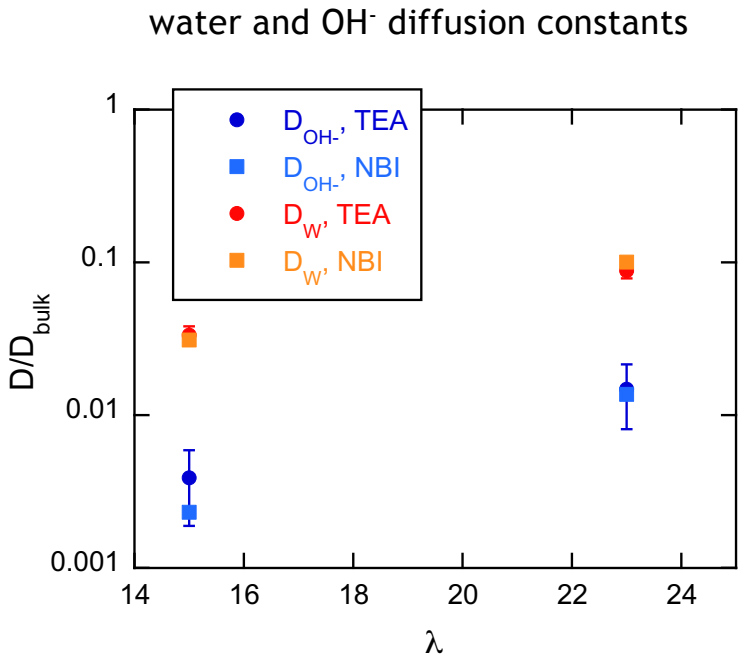




using water diameter for probe
small water domains, about 0.57 and 0.7 nm

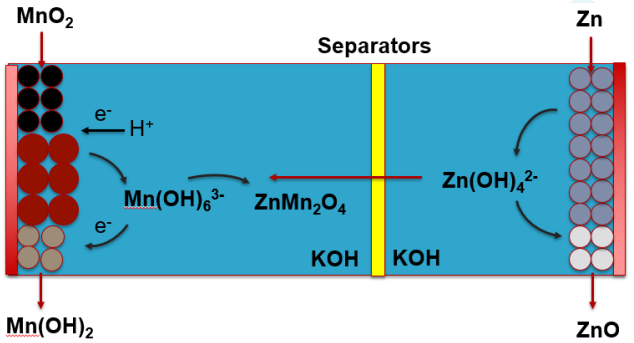
Fayon, P. & Sarkisov, L. *Phys Chem Chem Phys* 2019, 21, 26453-26465
Sarkisov, L., Bueno-Perez, R., Sutharson, M. & Fairen-Jimenez, D. *Materials Chem. Mater.* 2020, 32, 9849-9867

Water and Hydroxide Diffusion



Kolesnichenko, I. V. et al. *ACS Appl Mater Interfaces* **2020**, 12, 50406-50417
Frischknecht et al, *ACS Appl Polym Mater*, **2022**

Implications for Alkaline Batteries



Need to prevent crossover of zincate: $(ZnOH_4)^{2-}$

zincate "size": about 5-5.5 Å

selectivity: $R_s = D_{OH}/D_{Zn}$

experimental selectivity	minimal pore size from MD
NBI, λ = 15: R_s = 36 ± 2	NBI: PLD = 4.6 Å
TEA, λ = 23: R_s = 17 ± 8	TEA: PLD = 6.1 Å

smaller pores ⟶ prevent diffusion of zincate ⟶ higher selectivity

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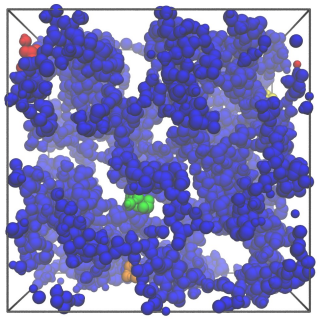
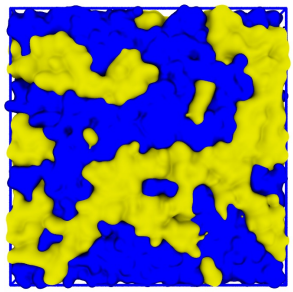
Conclusions

- nanoscale phase separation
  - loss of contrast in X-ray scattering with increasing water
  - modeling can give extra insight: not a loss of phase separation!



- interconnected, bulk-like water regions increase conductivity
  - confinement reduces water, ion diffusion
  - confinement can help with desired ion selectivity
  - local interactions also important!



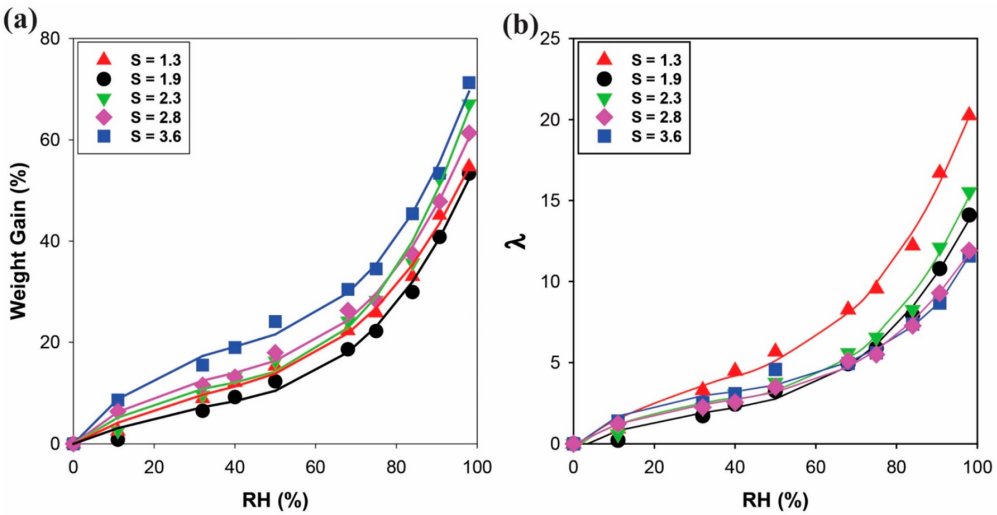
Abbott, L. J. & Frischknecht, A. L. *Macromolecules* **2017**, 50, 1184-1192.
Clark, J. A., Santiso, E. E. & Frischknecht, A. L. *J. Chem. Phys.* **2019**, 151, 104901.
Sorte, E. G. et al. *Macromolecules* **2019**, 52, 857-876.
Paren, B. A. et al. *Chem. Mater.* **2021**, 33, 6041-6051.
Frischknecht et al, *ACS Appl Polym Mater*, **2022,** 4, 2470-2480.

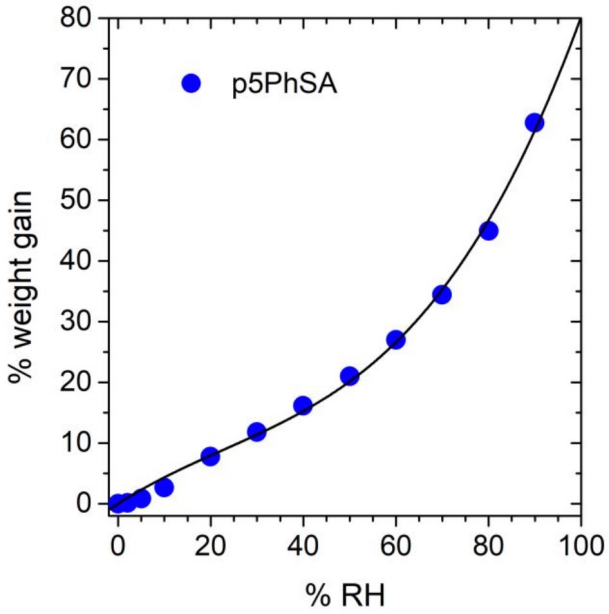
Backup


Sandia
National
Laboratories
Los Alamos
NATIONAL LABORATORY

Water Uptake

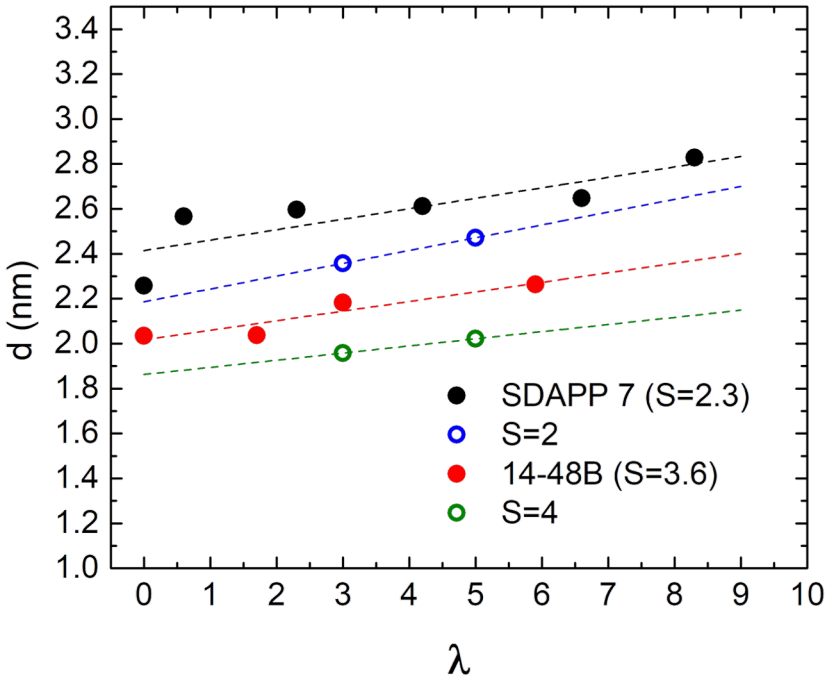
SDAPP

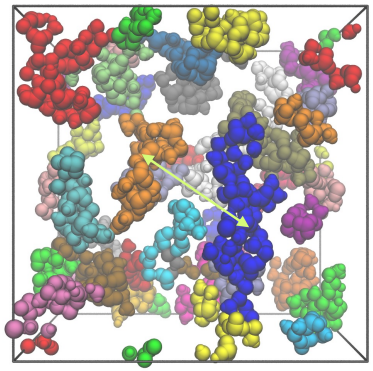




Correlation Distance between Aggregates

d = 2π/q*, q* = ionomer peak location





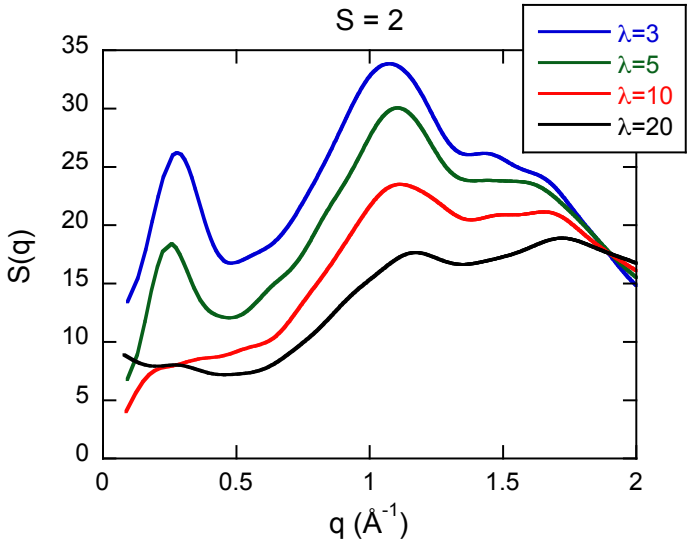
S=1, λ =3

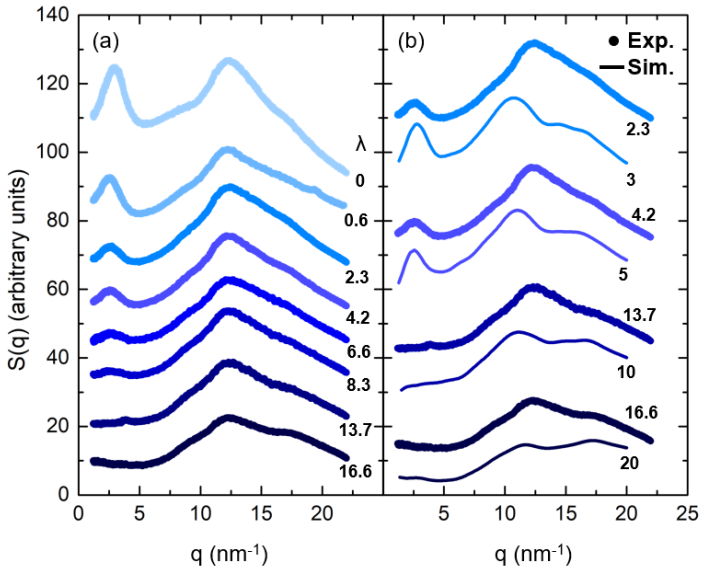
from real space snapshots, low λ:
S = 2, d = 23 Å
S = 4, d = 19 Å

MD consistent with X-ray

Why Does the Ionomer Peak Disappear?

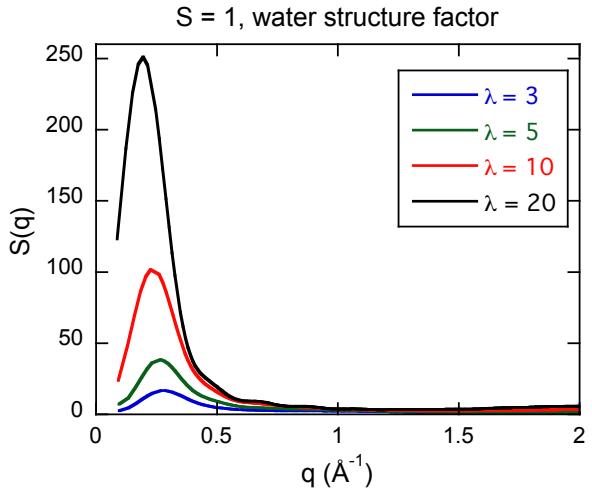
total S(q)

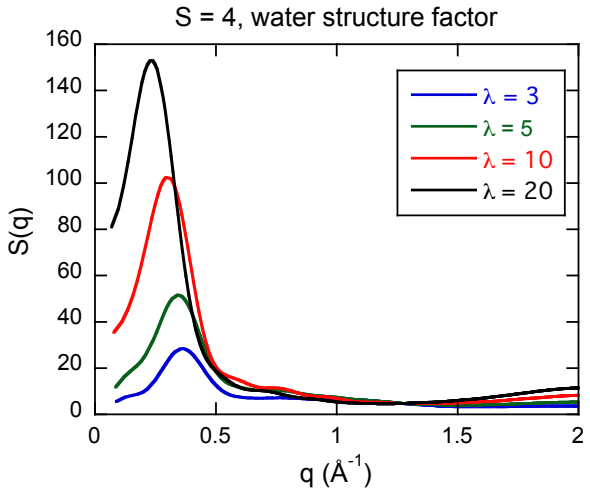


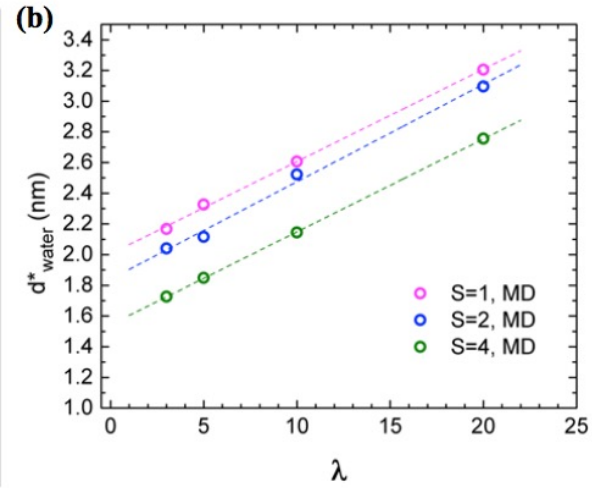


does this mean the water and sulfonic acids are no longer phase segregated?

Water Structure Factors



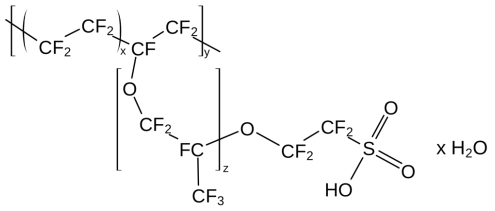


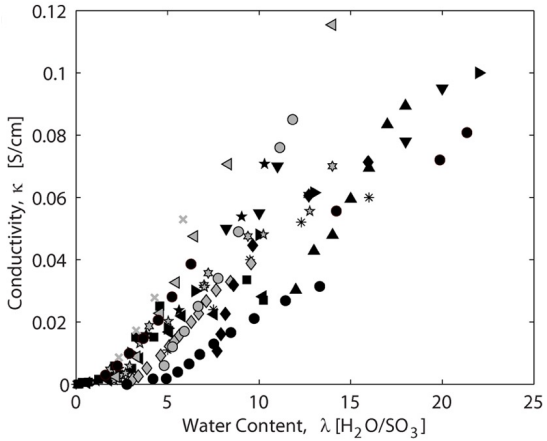


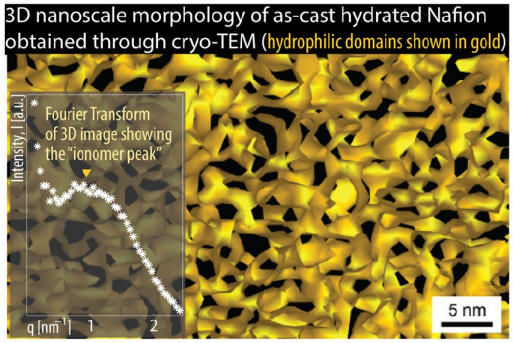
- water peak increases in intensity with increasing λ
- shifts slightly to the left (lower q, larger domains)

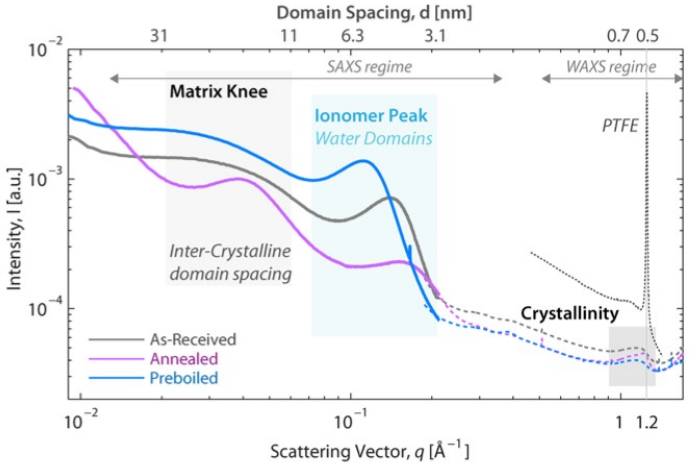
Conductivity is Related to Morphology

State-of-the-art PEM membrane: Nafion





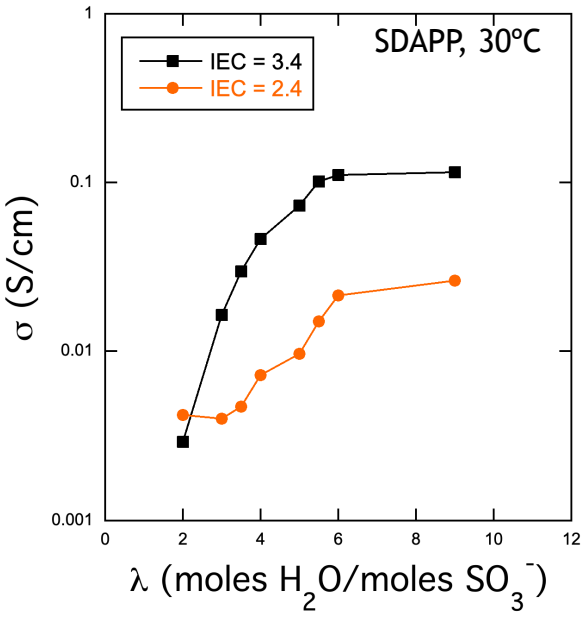


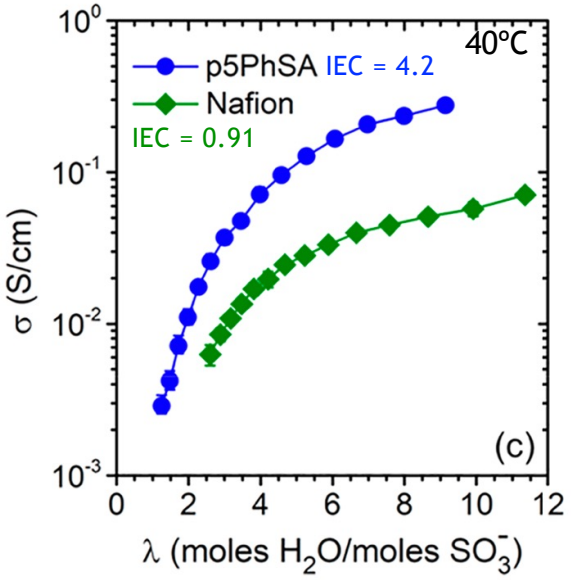


Allen, F. I. et al. *ACS Macro Lett* **2015**, 4, 1-5.

Kusoglu, A. & Weber, A. Z. *Chem Rev* **117,** 987–1104 (2017).

Experimental Proton Conductivity

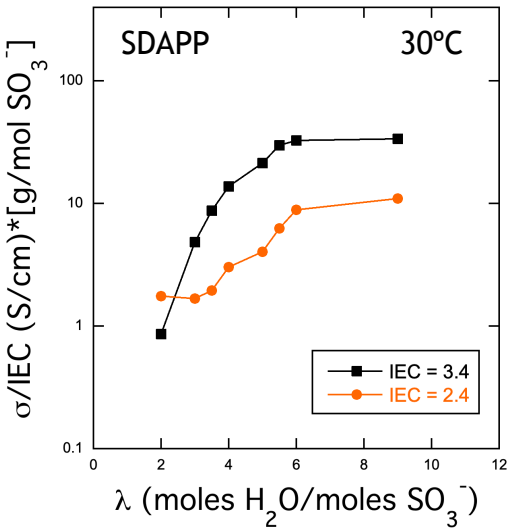


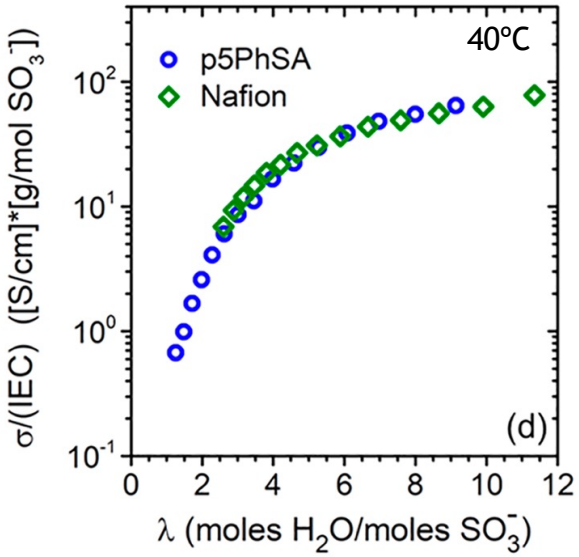


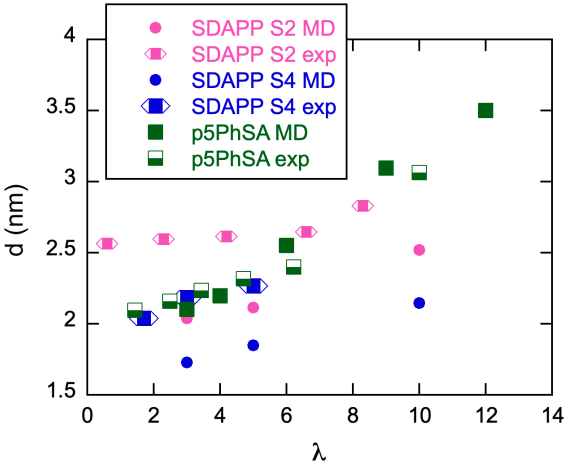
very good for both polymers
higher at higher IEC, λ
promoted by strong phase separation

Sorte, E. G. et al. *Macromolecules* **2019**, 52, 857-876.
Paren, B. A. et al. *Chem. Mater.* **2021**, 33, 6041-6051.

Experimental Proton Conductivity



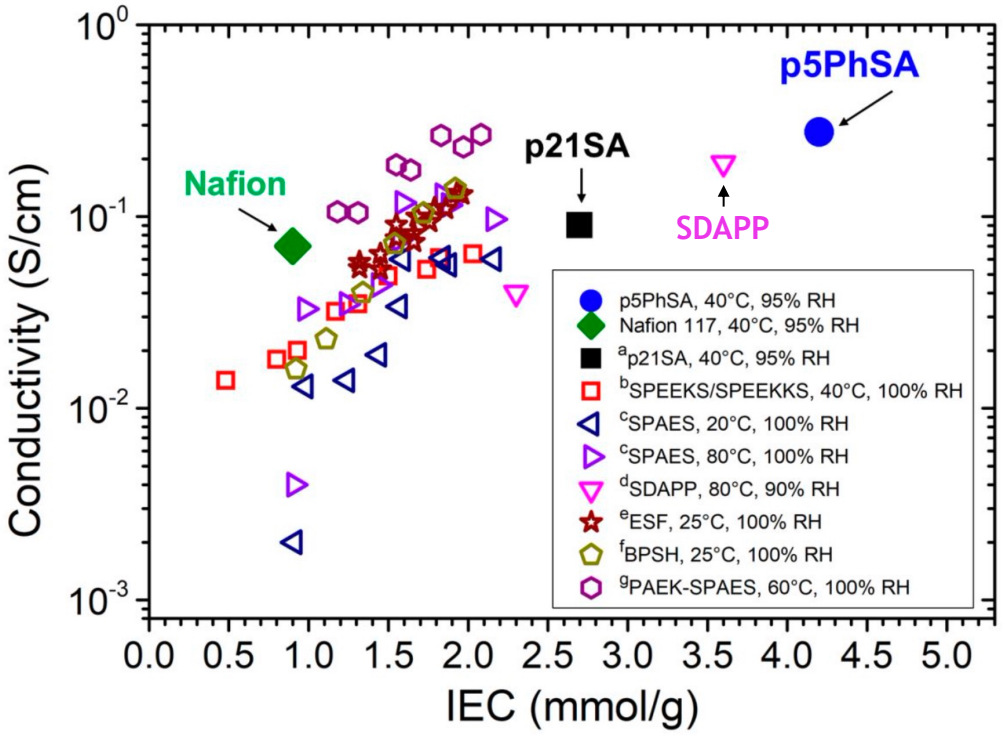




conductivity not only dependent on water channels, IEC

- when normalized by IEC, SDAPP conductivity still depends on IEC
- Nafion, p5PhSA very similar
- water channel spacing similar between SDAPP, p5PhSA
- water diffusion constant higher in p5PhSA than in SDAPP

Comparisons of Proton Conductivity



Paren, B. A. et al. *Chem. Mater.* **2021**, 33, 6041-6051.