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Morphology and Ion Transport in Hydrated Ion-Containing Polymers

Amalie L. Frischknecht

Sandia National Labs

Fall ACS Meeting, August 25, 2021

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Congratulations Karen!!

Thanks for many years of great collaborations! (and hikes!)

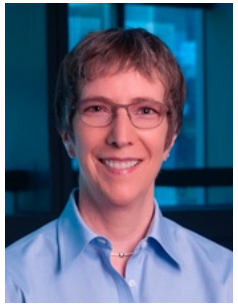
Polymer Physics
Gordon Research Conference

June 29 - July 4, 2008

Chair	Vice Chair
Jane E. Lipson	Karen I. Winey

Salve Regina University
100 Ochre Point Avenue
Newport, RI, US

Venue and Travel Information



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Mark Stevens


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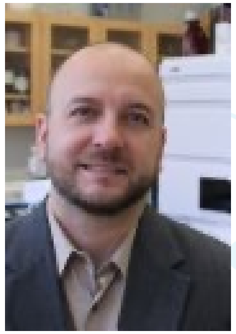
Ben Paren


Karen Winey

Florida State


Justin Kennemur

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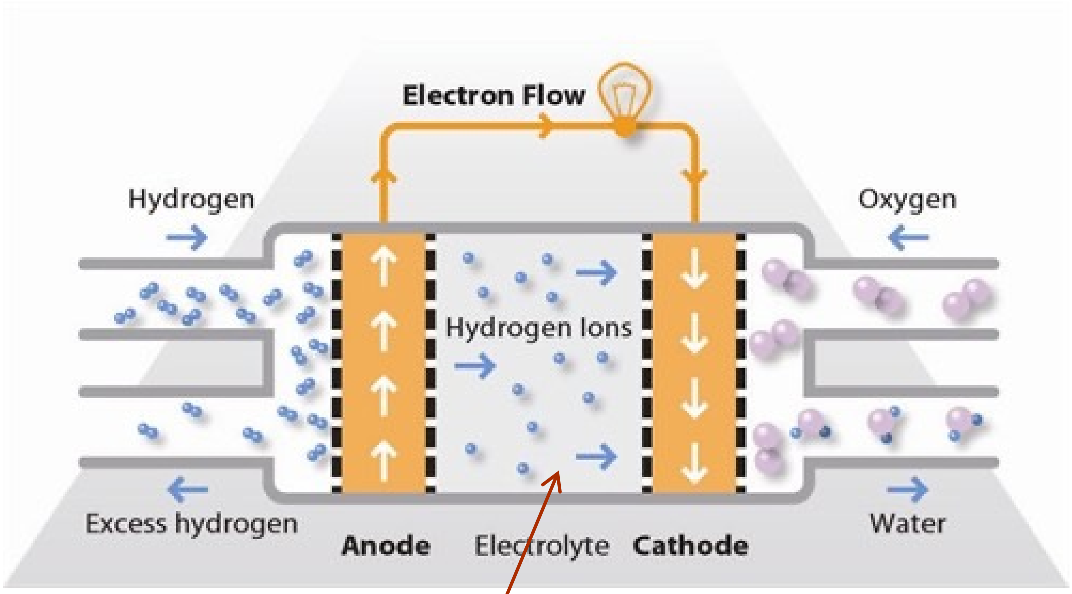
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

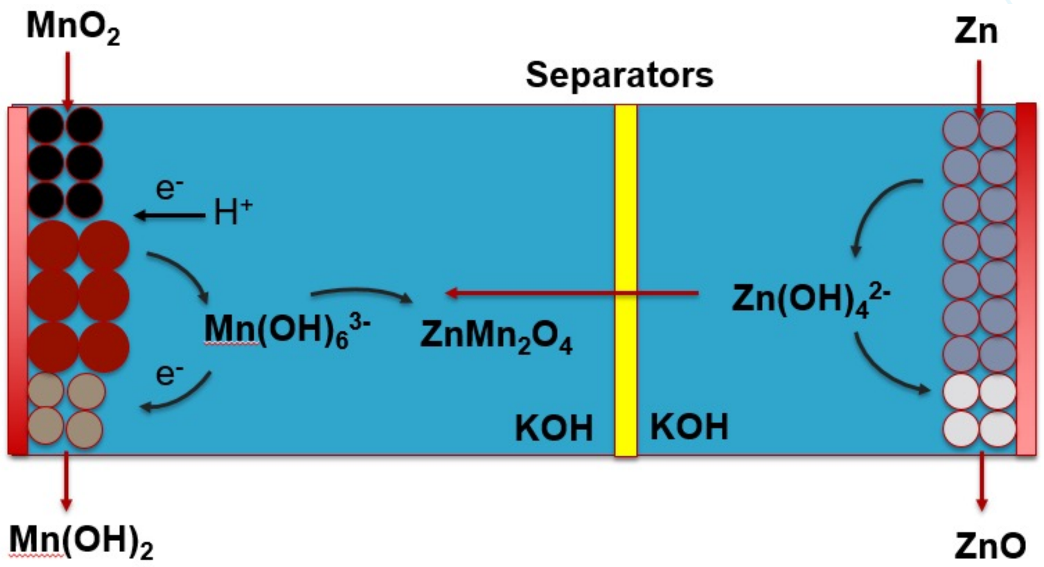
Polymer Membranes in Energy Storage

fuel cells



polymer membrane

Zn-based batteries

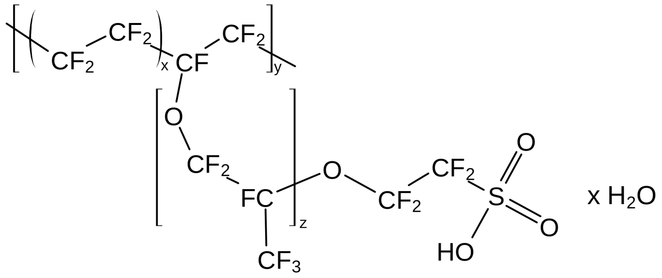


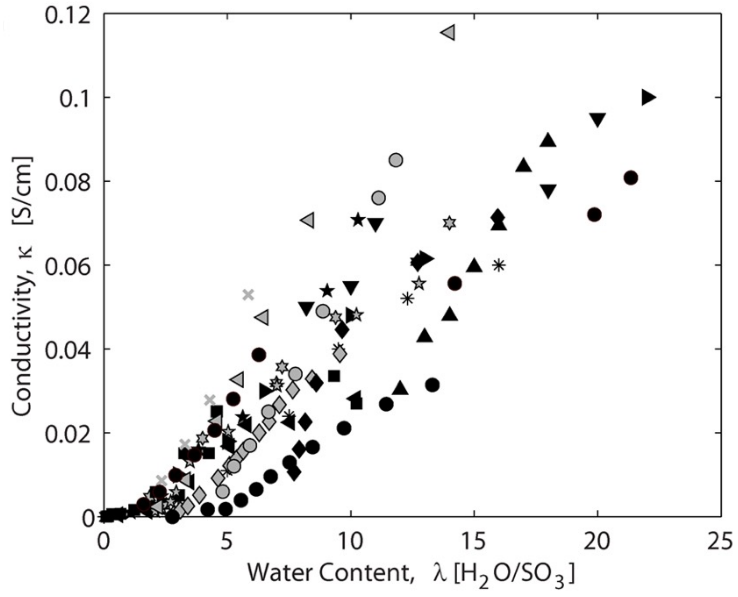
polymer membranes need to

- conduct ions efficiently (protons or OH-)
- be mechanically/chemically robust
- prevent crossover of undesirable species

Conductivity is Related to Morphology

State-of-the-art PEM membrane: Nafion

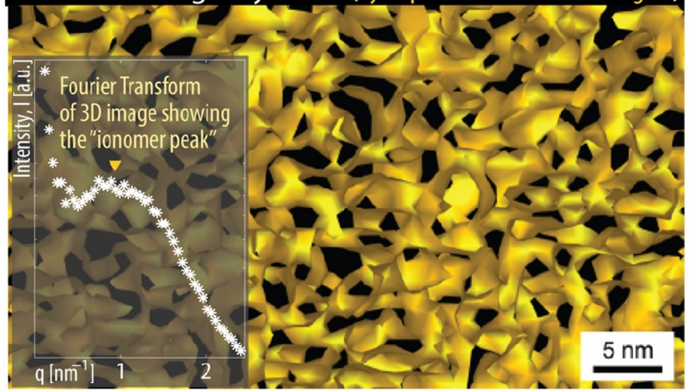


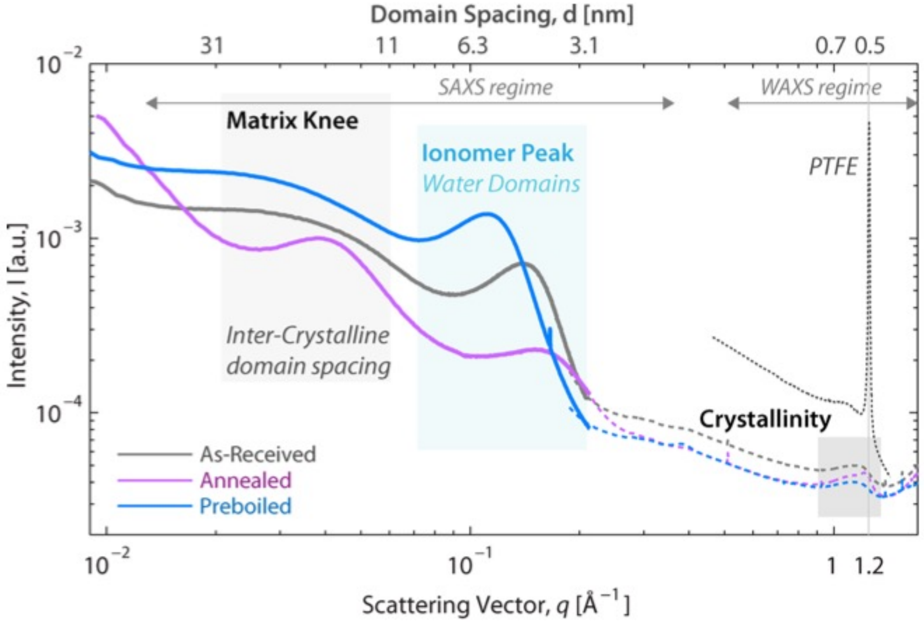


Allen, F. I. et al. *ACS Macro Lett* **2015**, 4, 1-5.

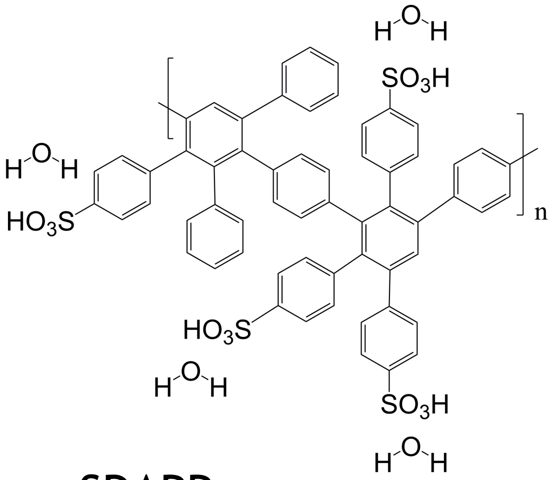
Kusoglu, A. & Weber, A. Z. *Chem Rev* **117,** 987–1104 (2017).

3D nanoscale morphology of as-cast hydrated Nafion obtained through cryo-TEM (hydrophilic domains shown in gold)

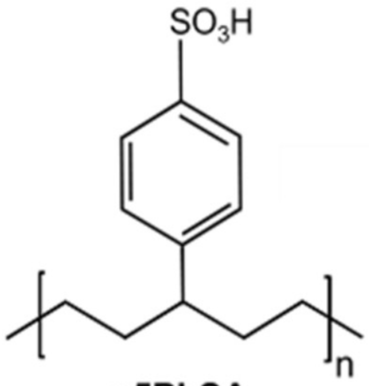




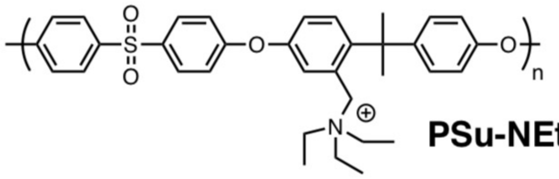
Hydrocarbon-based Polymers



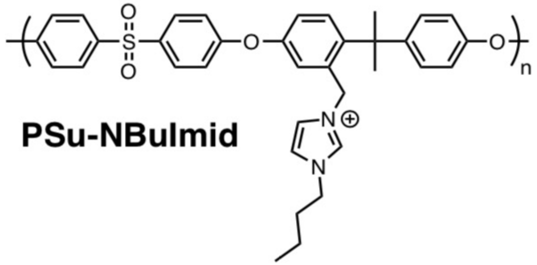
SDAPP



p5PhSA



PSu-NEt$_3$

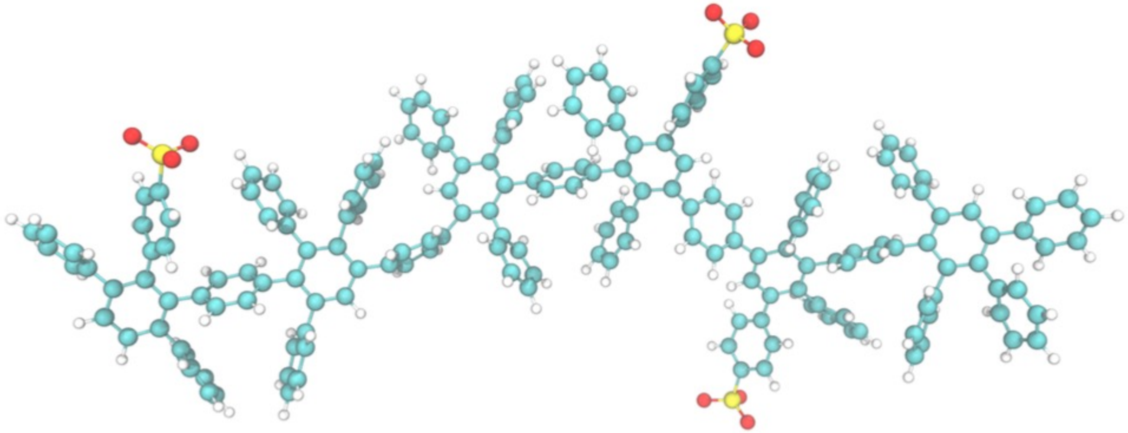


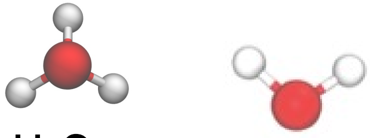
PSu-NBuImid

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

SDAPP Simulations

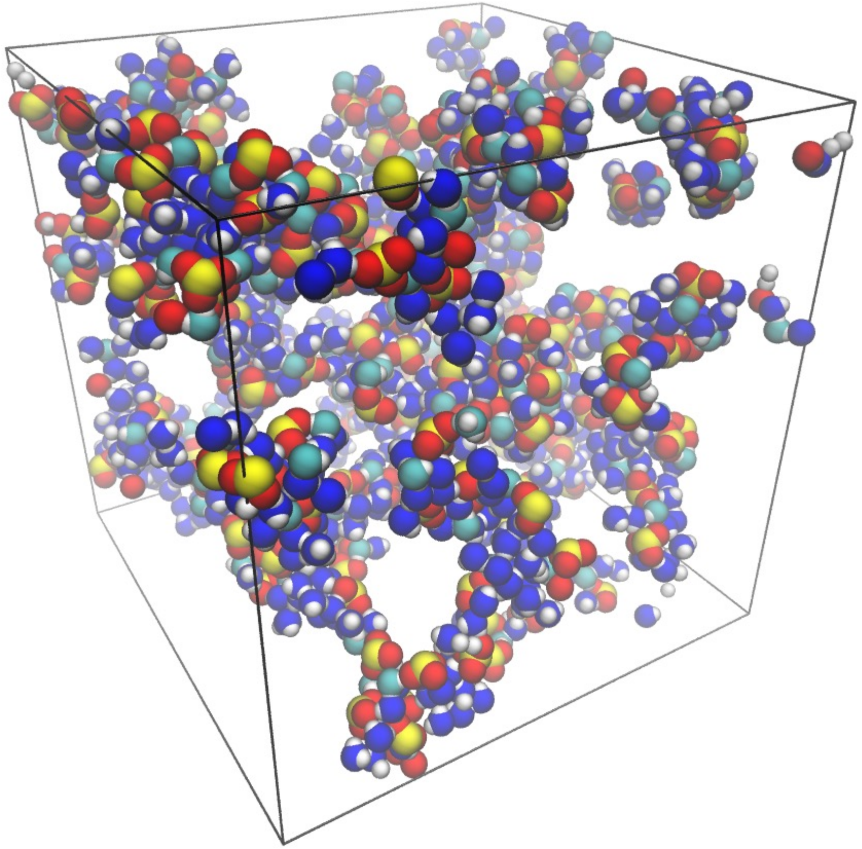
short SDAPP chain





H_3O^+ H_2O

70 chains
3 monomers/chain
box size about 60Å



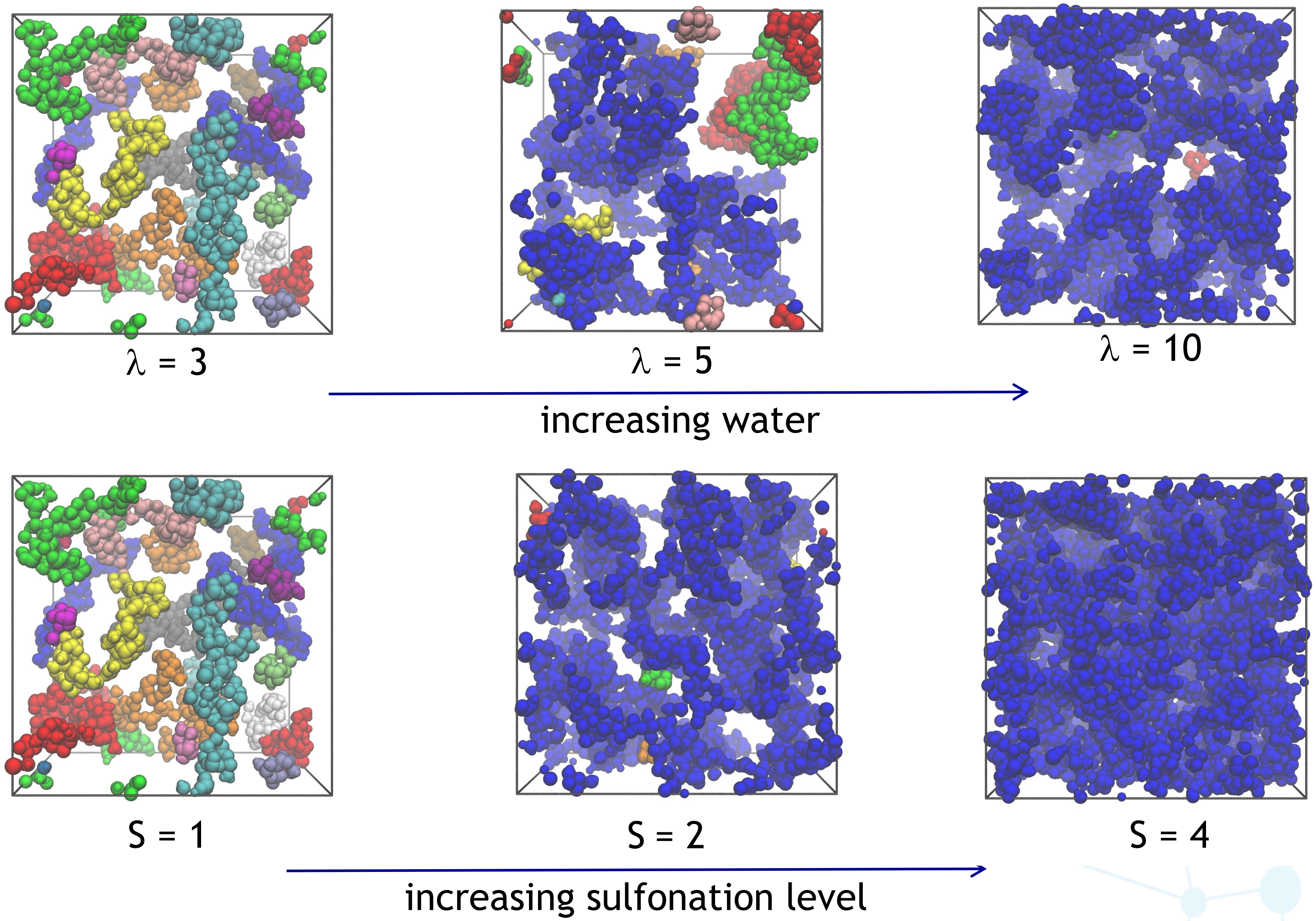
sulfonic acids/monomer: S = 1, 2, 4
(IEC = 1.2, 2.2, 3.7)

waters/sulfonic acid λ = 3, 5,10, 20

Nanoscale Morphology from MD Simulations

S = 1 sulfonic acid/monomer

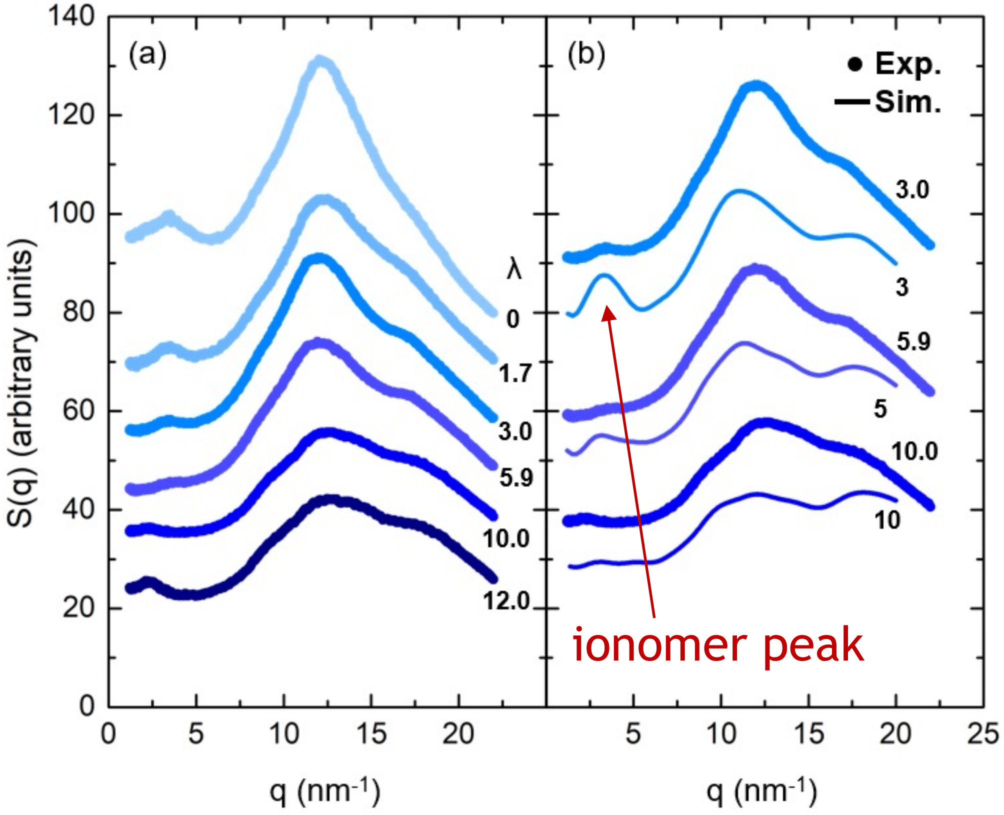
λ = 3



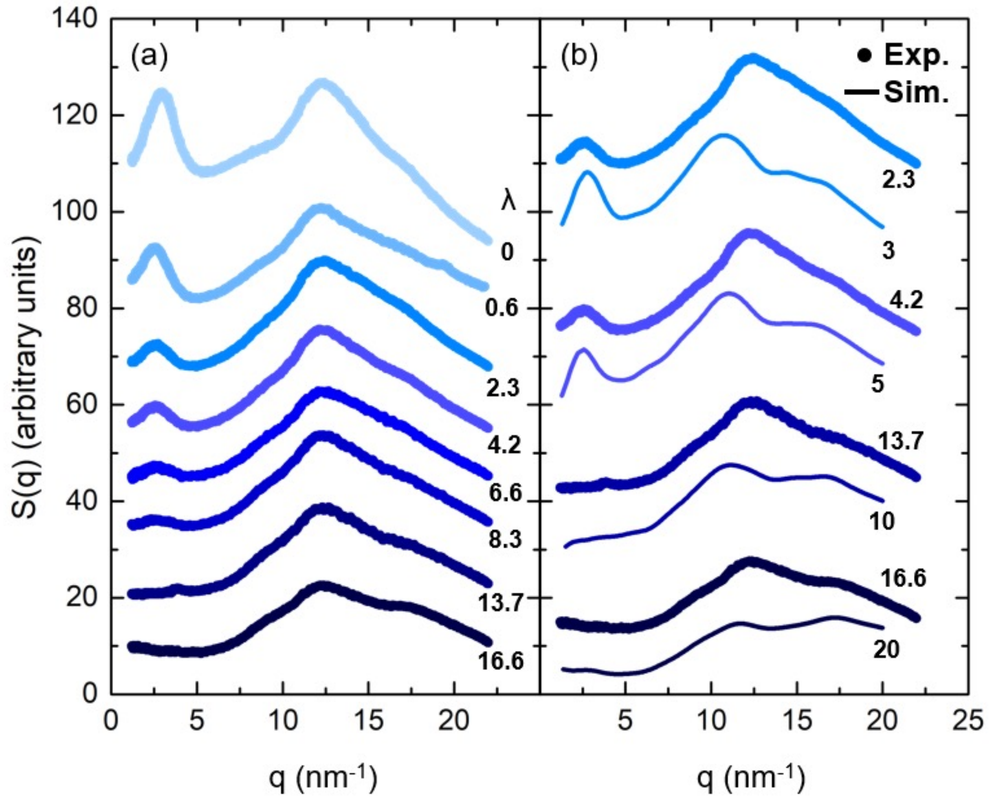
Abbott, L. J. & Frischknecht, A. L. *Macromolecules* **2017**, 50, 1184-1192.

X-Ray Scattering and MD

experiments S=3.6 MD, S=4



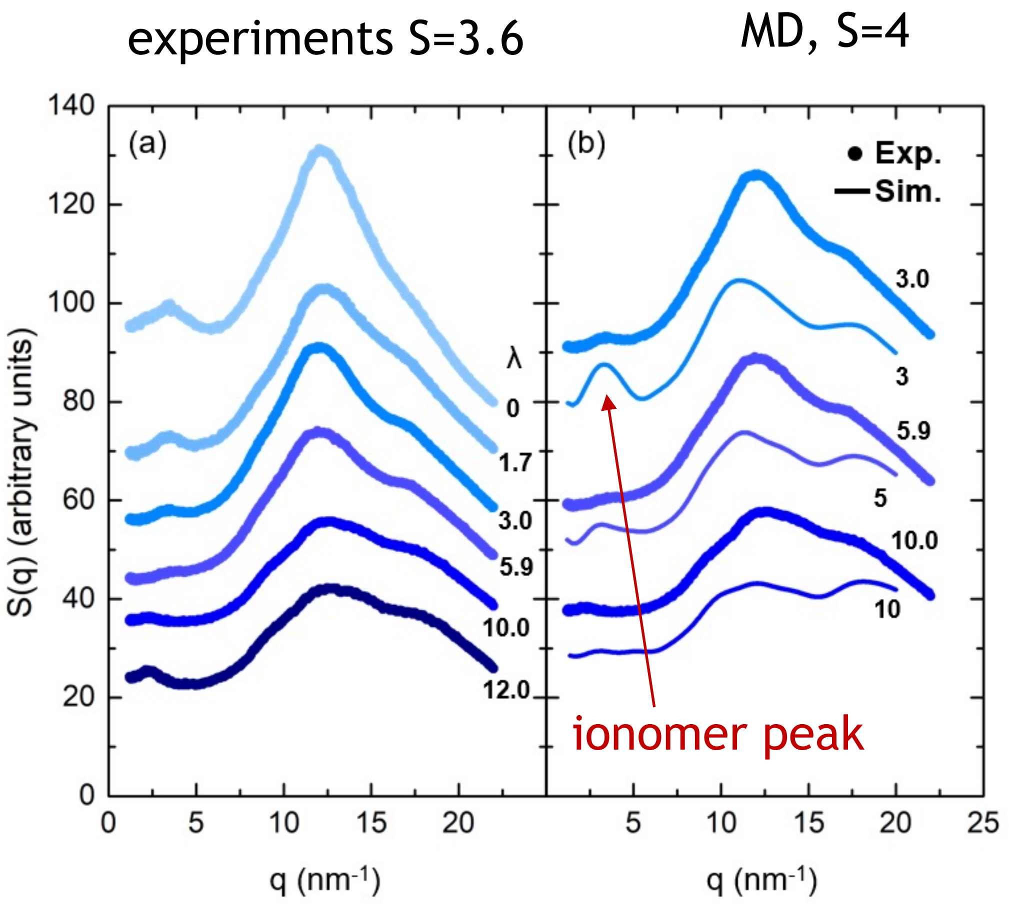
experiments, S=2.3 MD, S=2

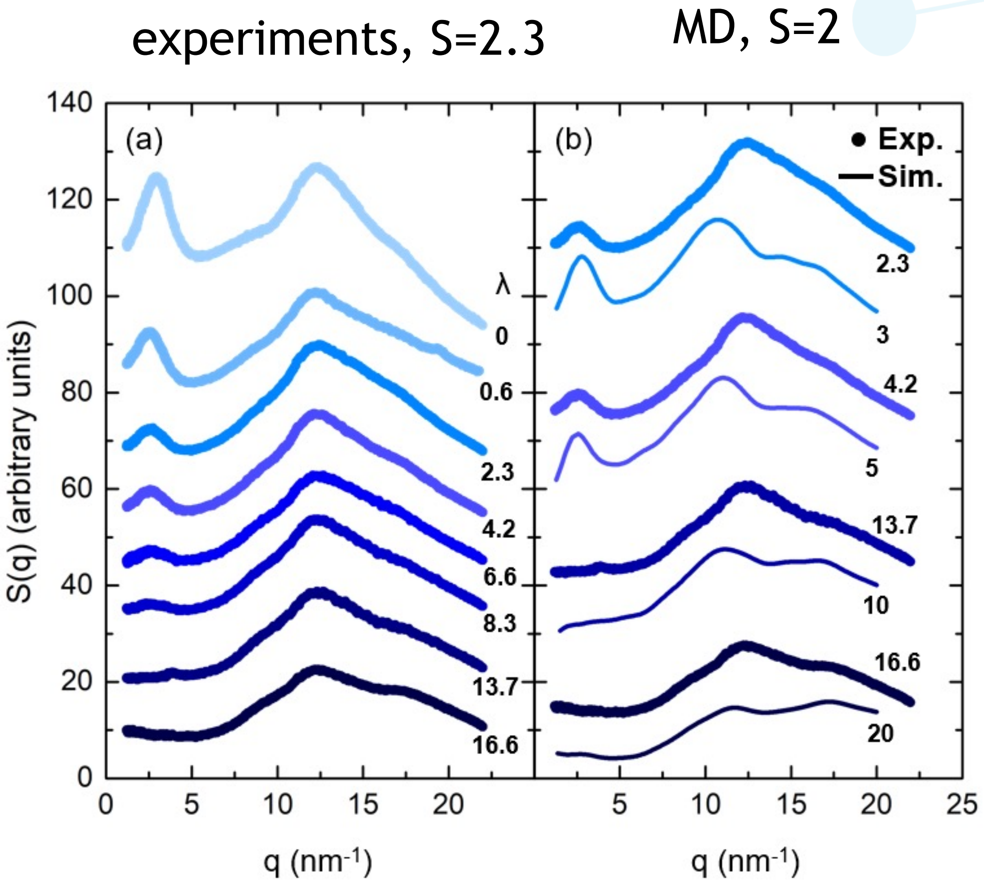


$$S(q) = \sum_i c_i f_i^2 + 4\pi\rho \int_0^\infty \frac{\sin(qr)}{qr} r^2 \sum_{i,j} c_i c_j f_i f_j \big(g_{ij}(r) - 1\big) dr$$

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

X-Ray Scattering and MD



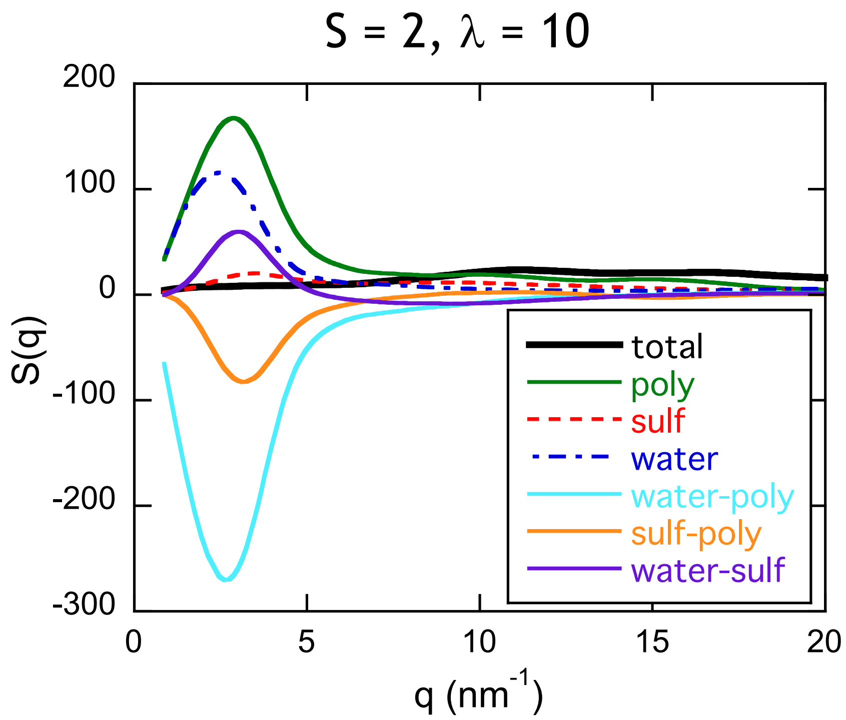


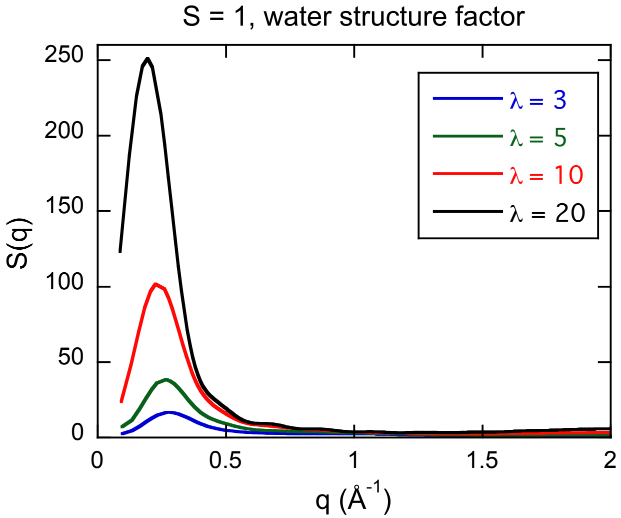
why does the ionomer peak disappear??

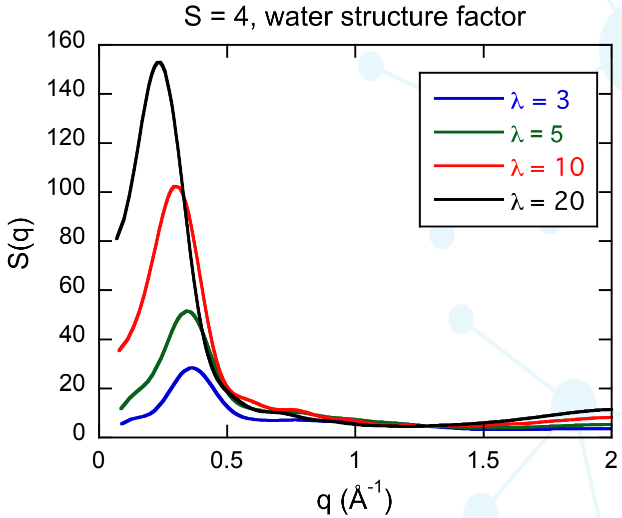
Sorte, E. G. et al. *Macromolecules* **2019**, 52, 857-876.

Partial Structure Factors from MD

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





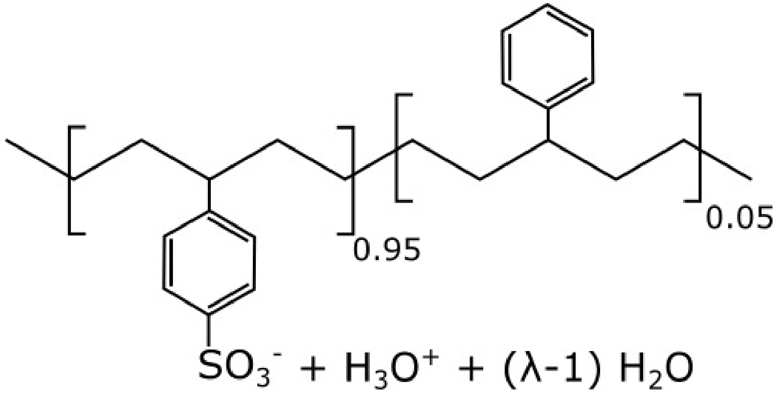


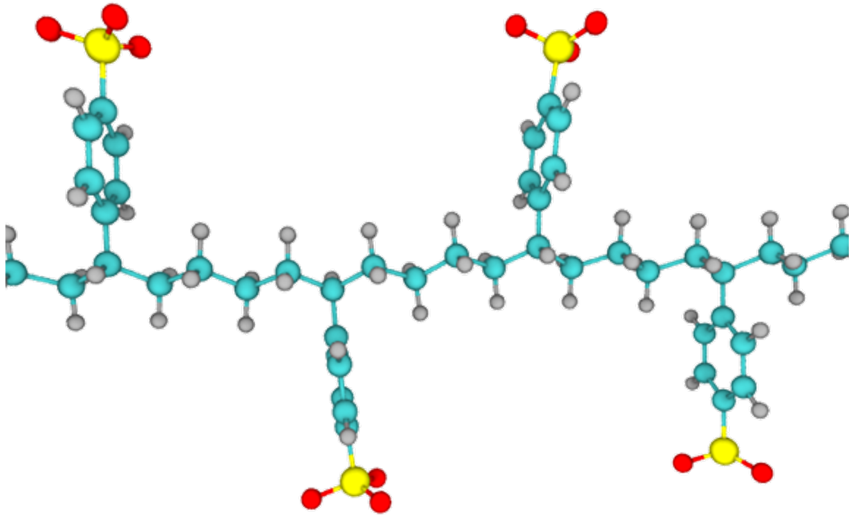
water-polymer cross-correlations cancel other peaks

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 filed
- Ion and hydronium partial charges scaled to account for polarization effects to first order
- Simulations at $\lambda = 3, 4, 6, 9,$ and 12
- IEC = 4.2 mmol/g

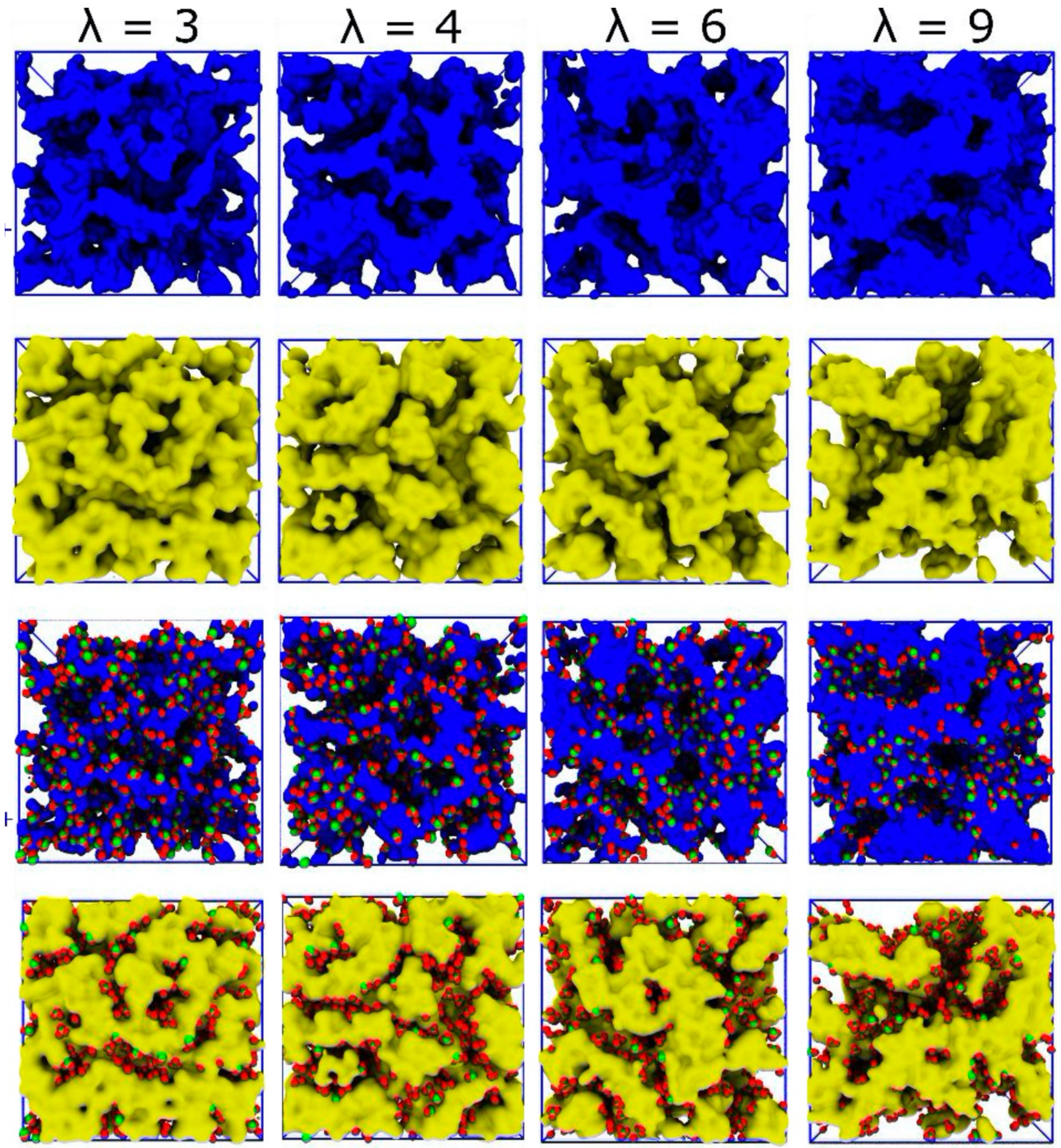
MD Snapshots

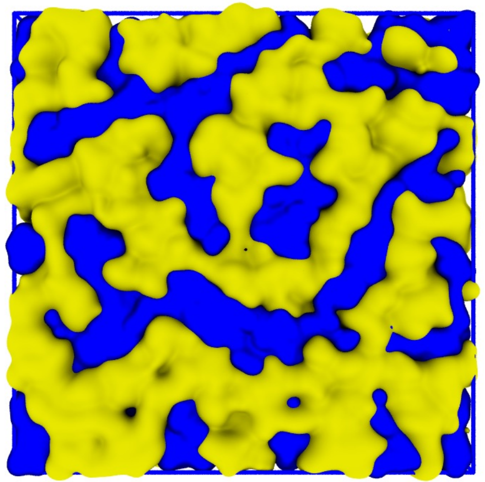
water + H_3O^+

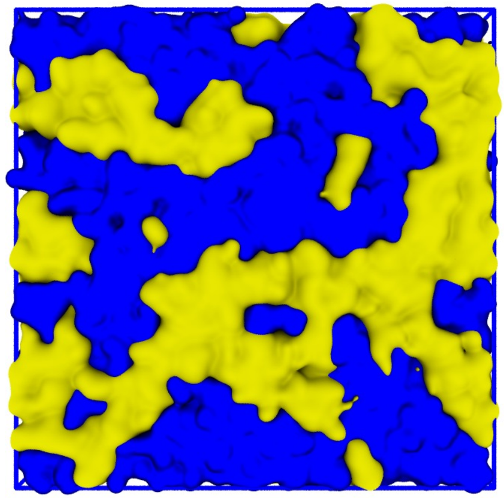
polymer

green = S

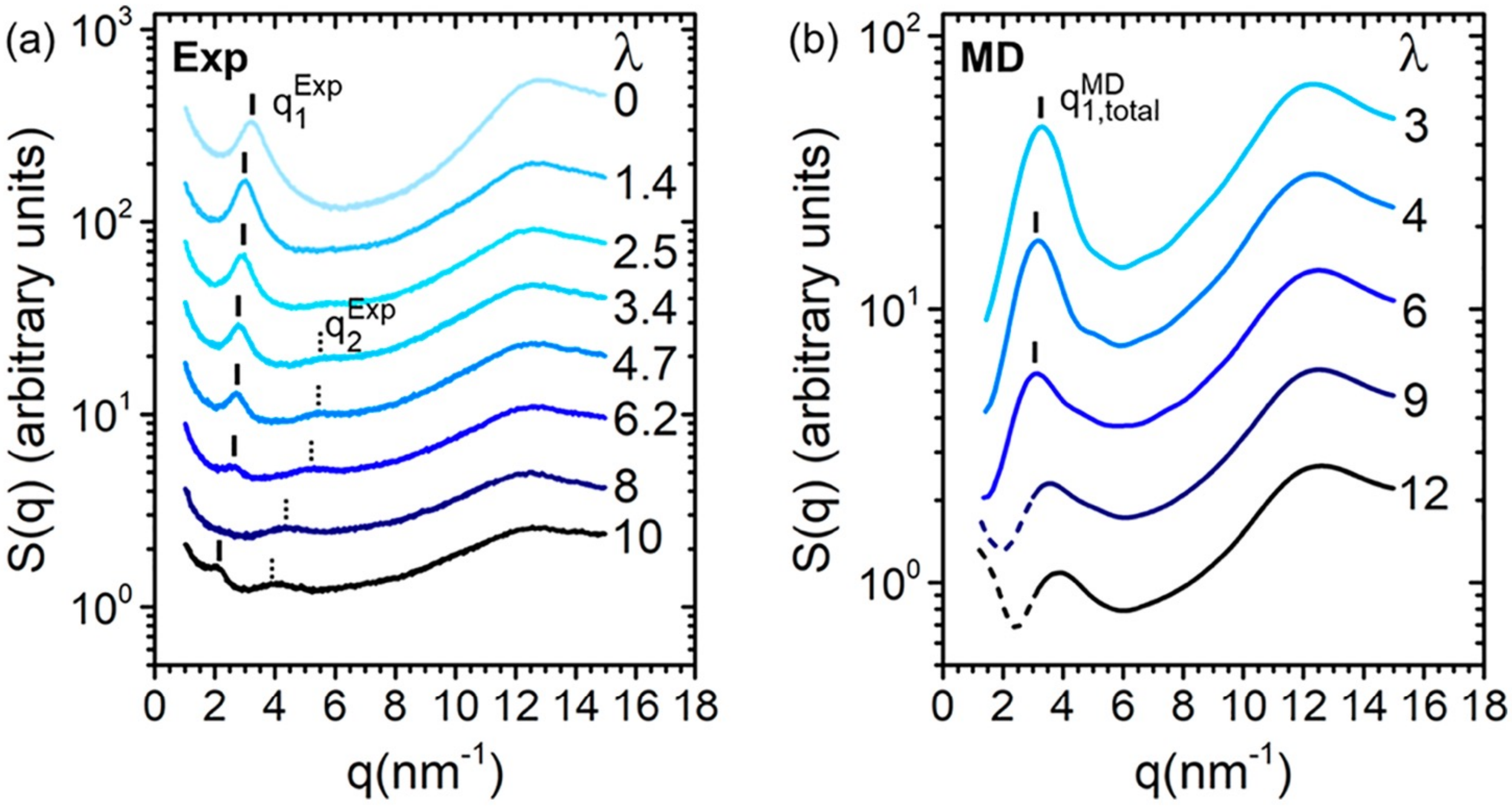
red = O in SO_3







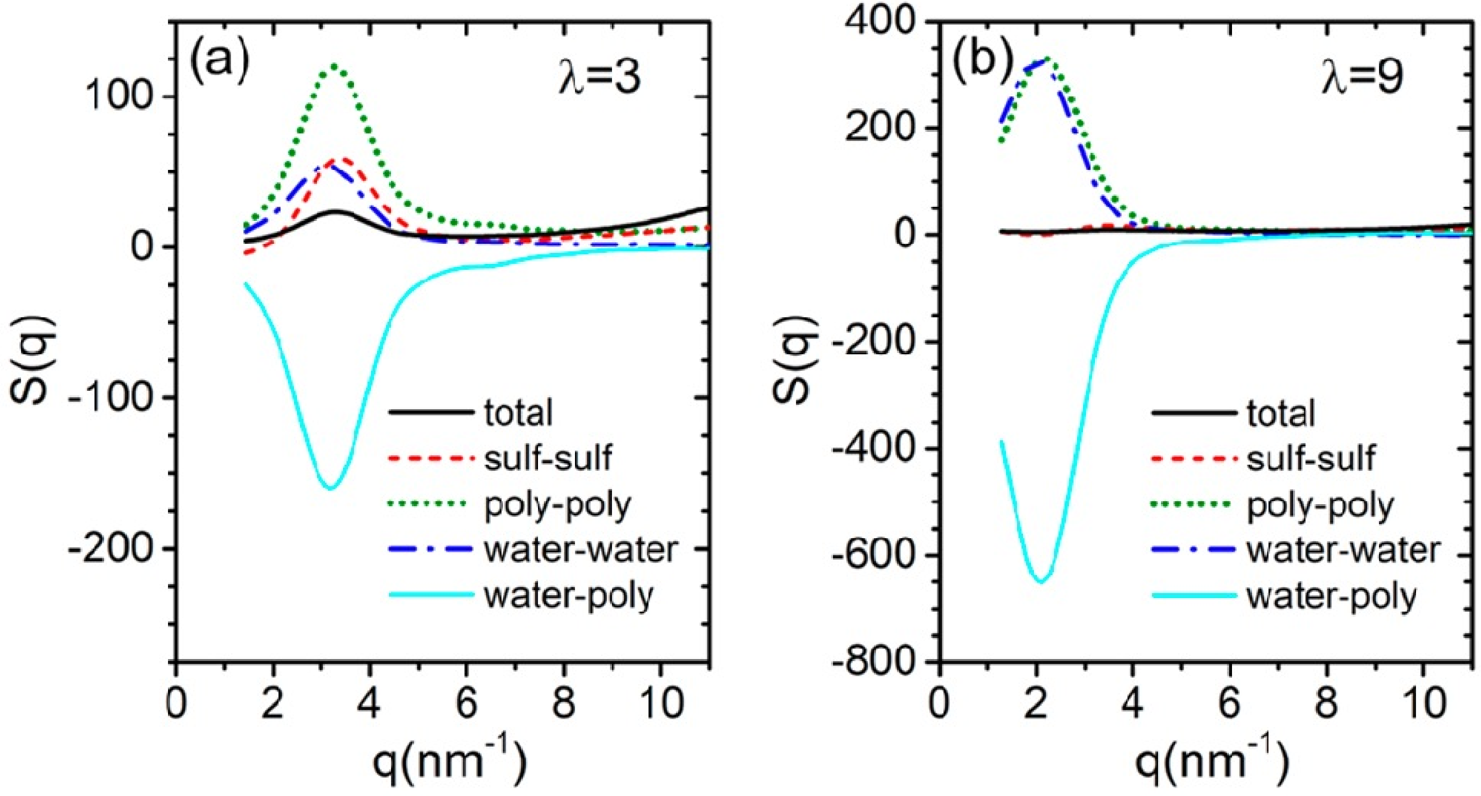
X-Ray Scattering and MD

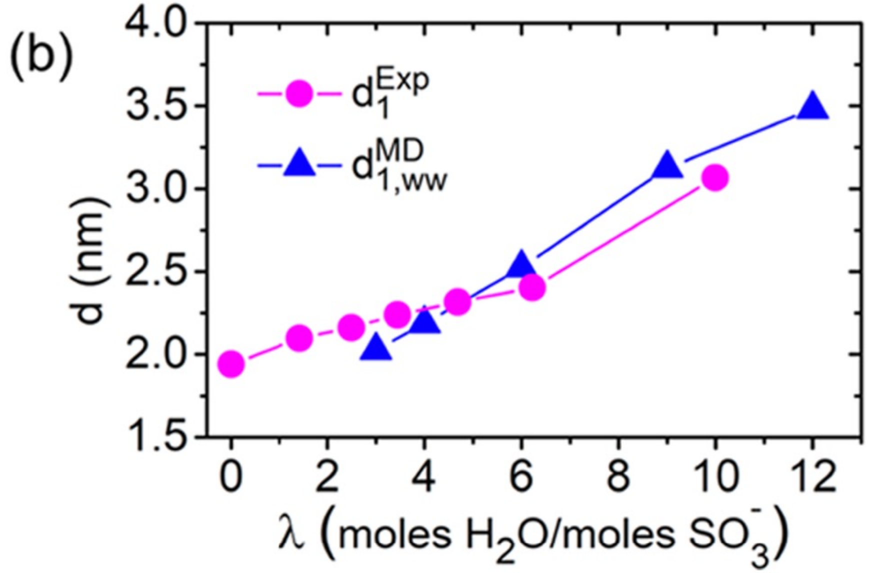


again: loss of ionomer peak at high water contents

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

Partial Structure Factors



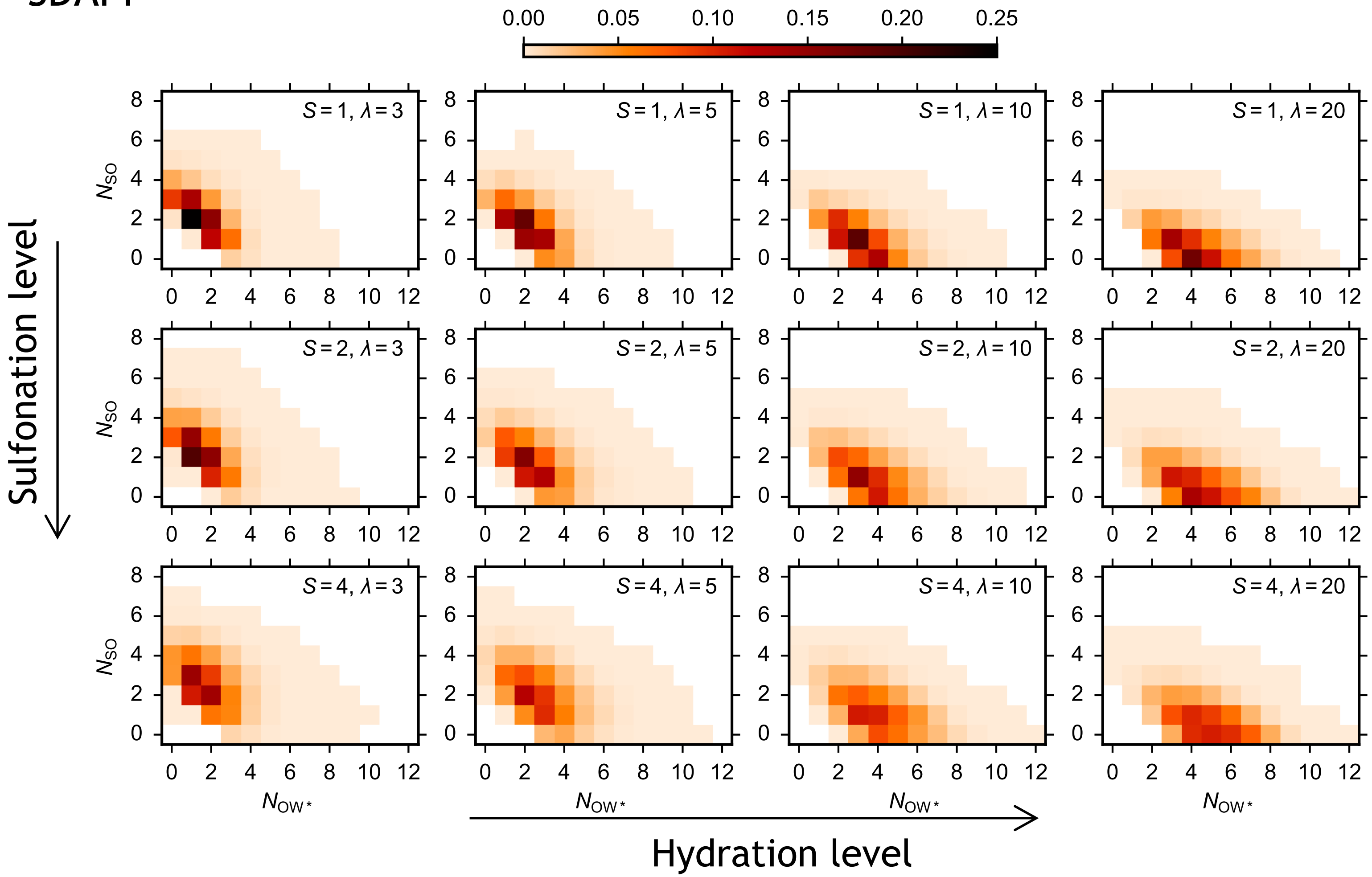


spacing between water channels in MD consistent with peak in X-ray

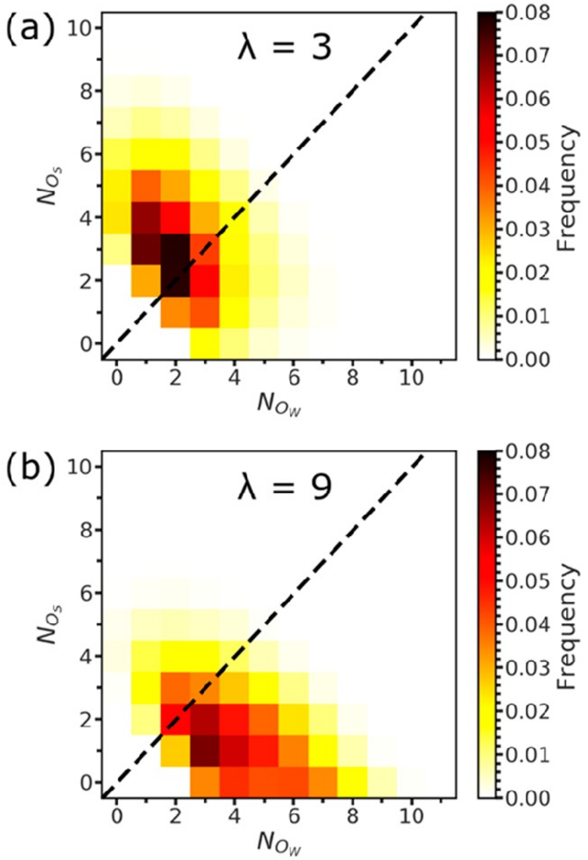
Paren, B. A. et al. *Chem. Mater.* **2021**, 33, 6041-6051.

Coordination Environments

SDAPP



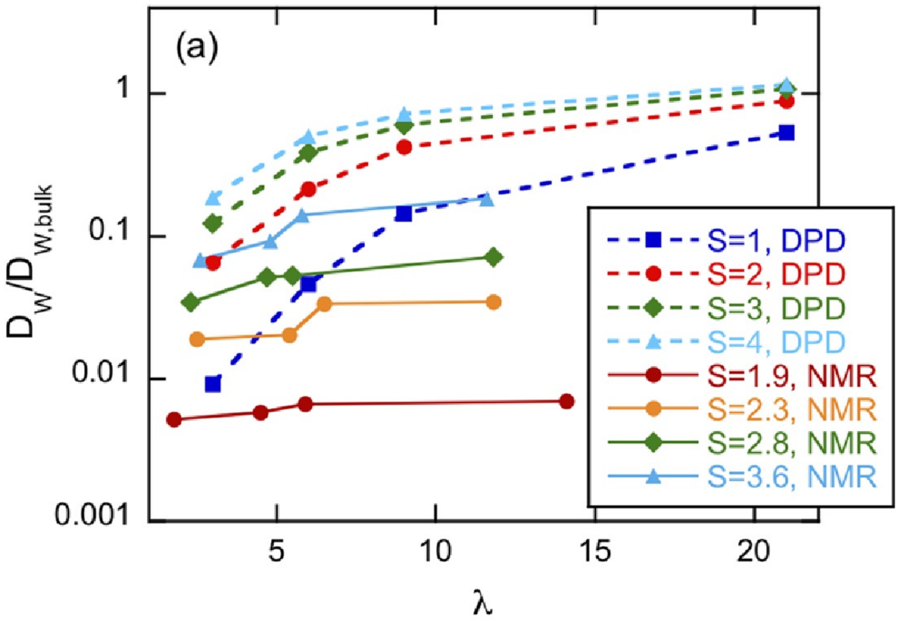
p5PhSA



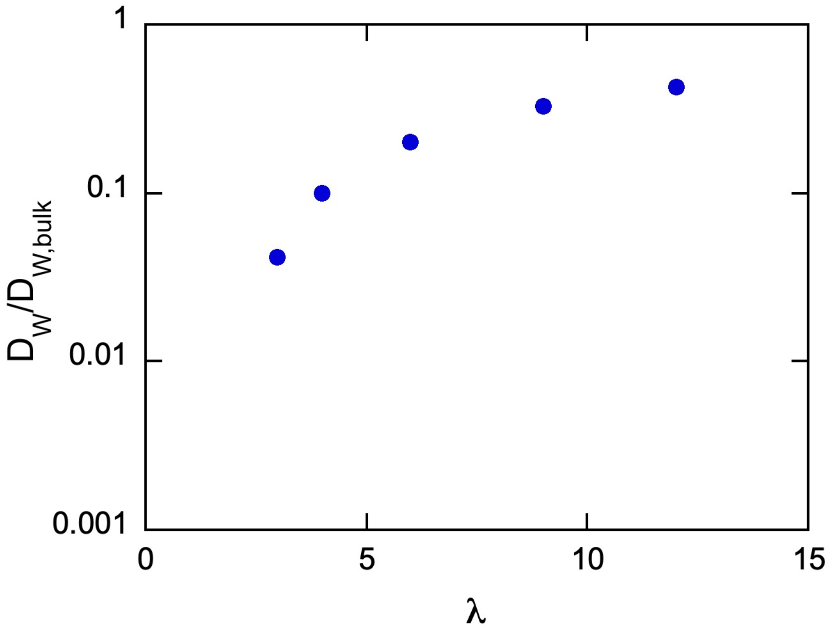
at higher λ: H_3O^+ less associated with SO_3^-, more associated with water

Water Diffusion Constants

SDAPP: DPD and NMR



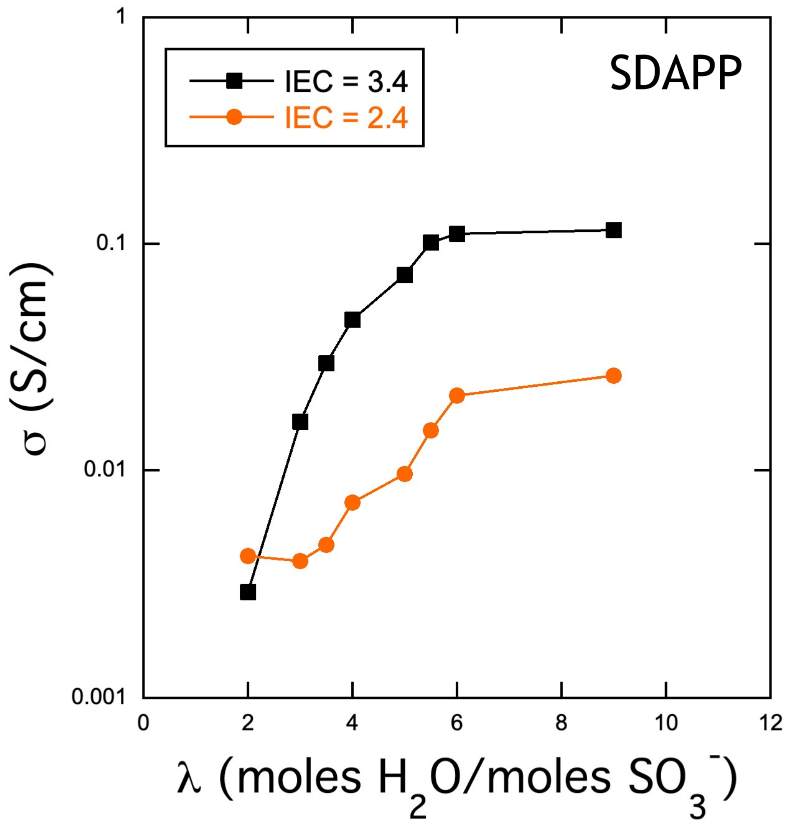
p5PhSA: MD

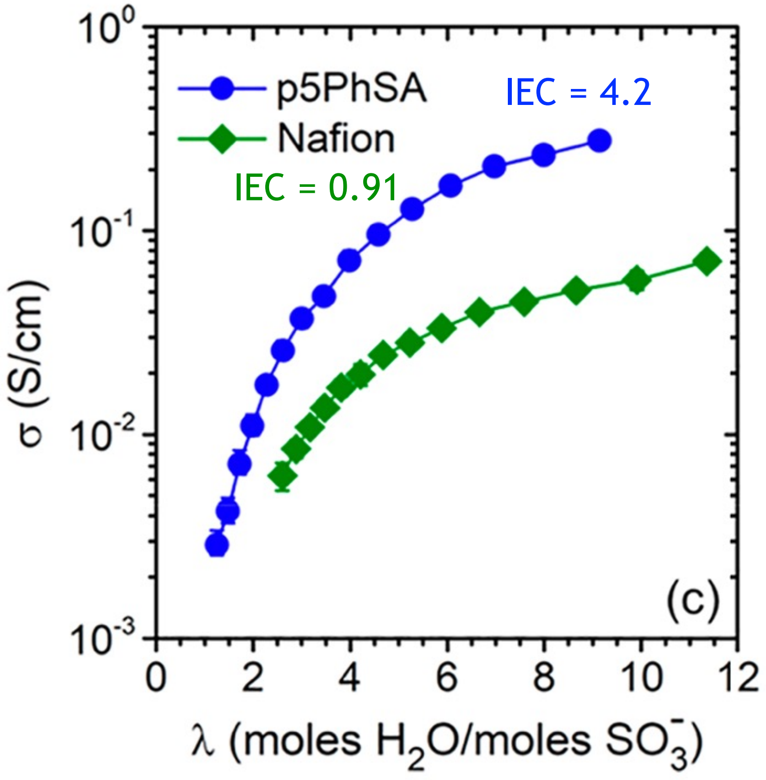


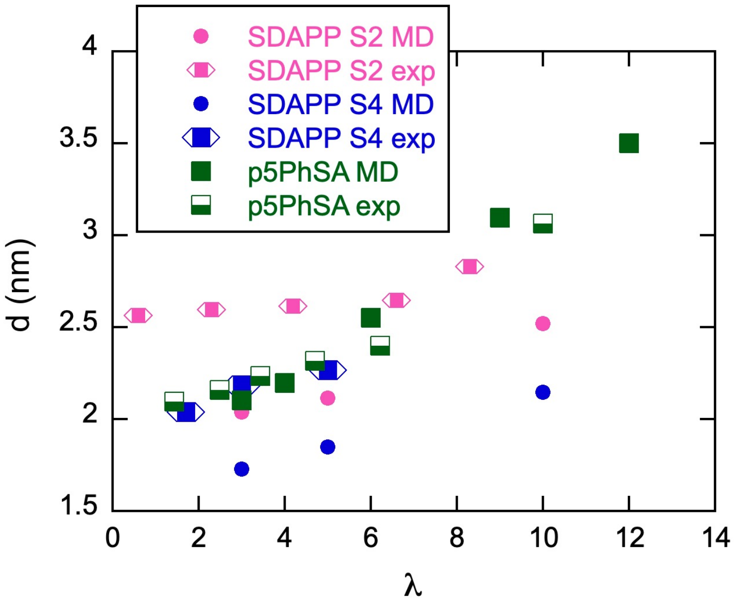
water diffusion suppressed by confinement in membranes

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

Experimental Proton Conductivity



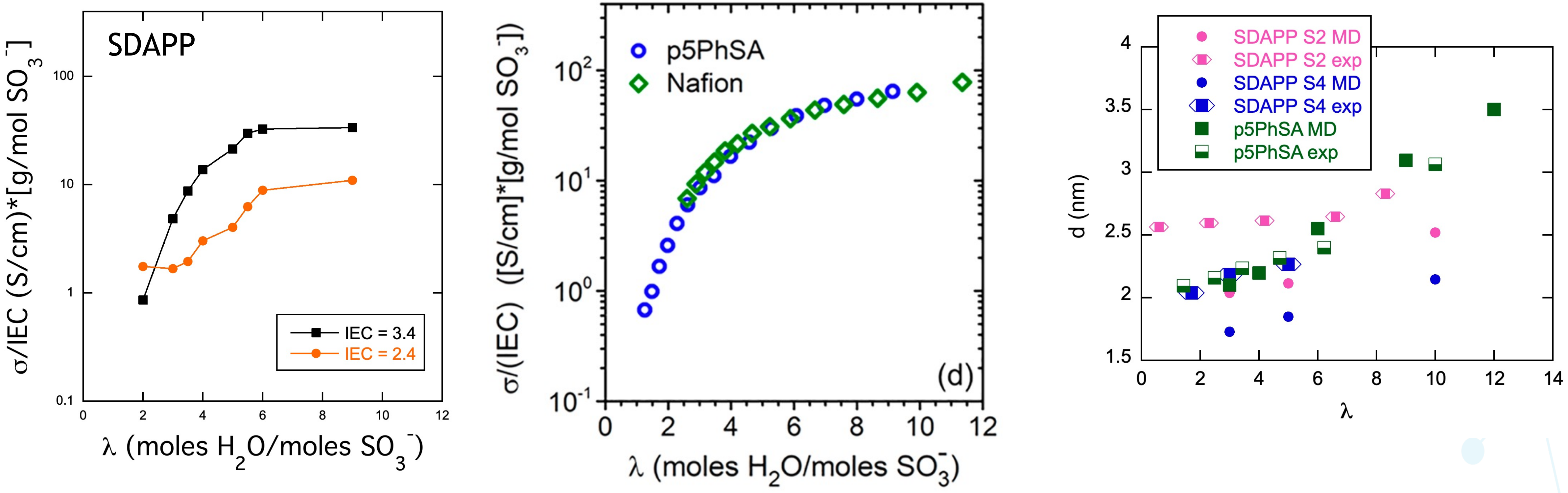




very good for both polymers
higher at higher IEC, λ
promoted by strong phase separation

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

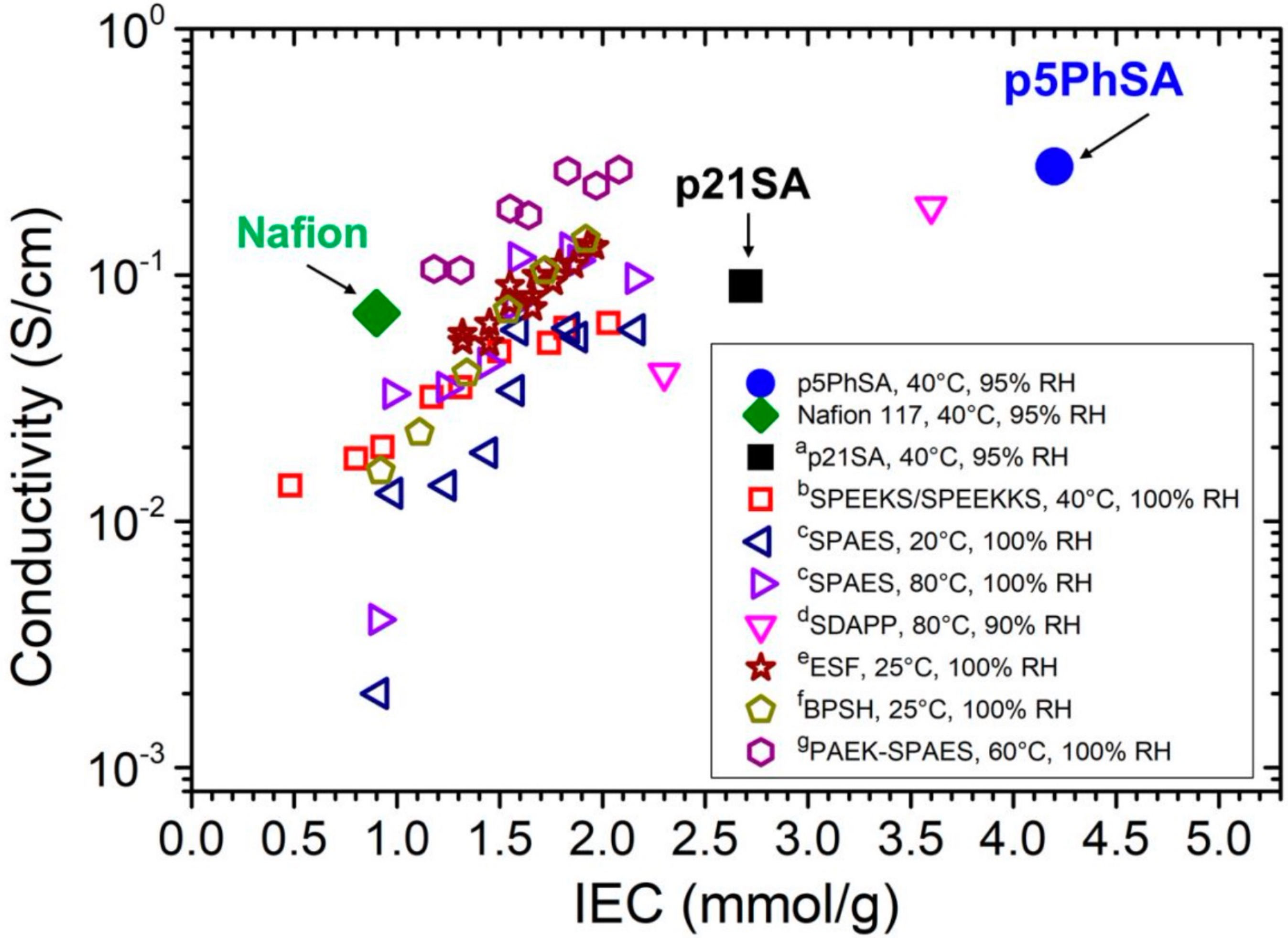
Experimental Proton Conductivity



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

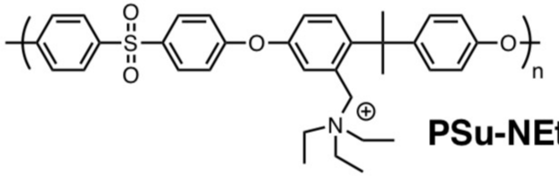
Comparisons of Proton Conductivity



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

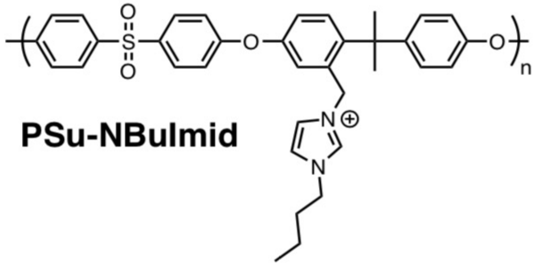
Functionalized Polysulfones: OH^- Conductors

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



PSu-NEt_3

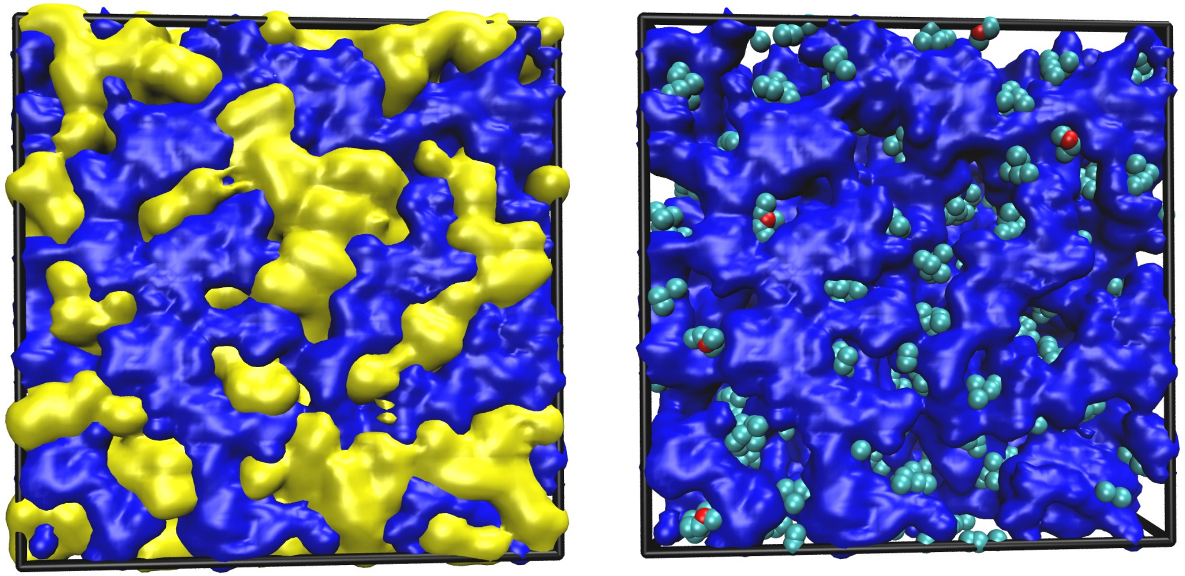
IEC = 1.7



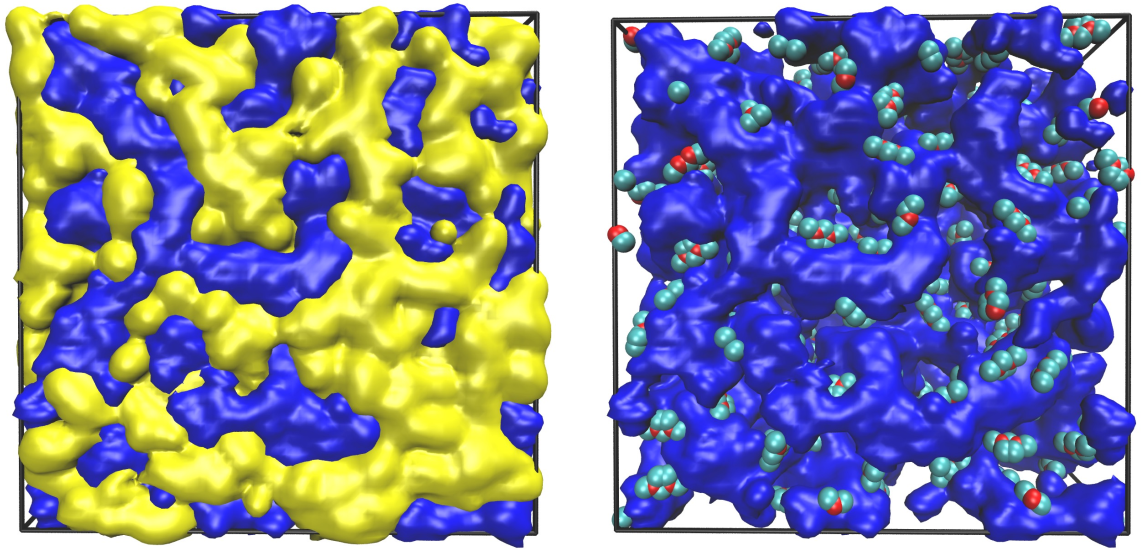
PSu-NBuImid

IEC = 1.8

λ = 23



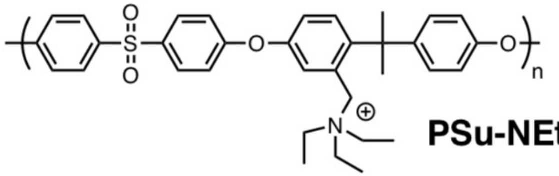
λ = 15

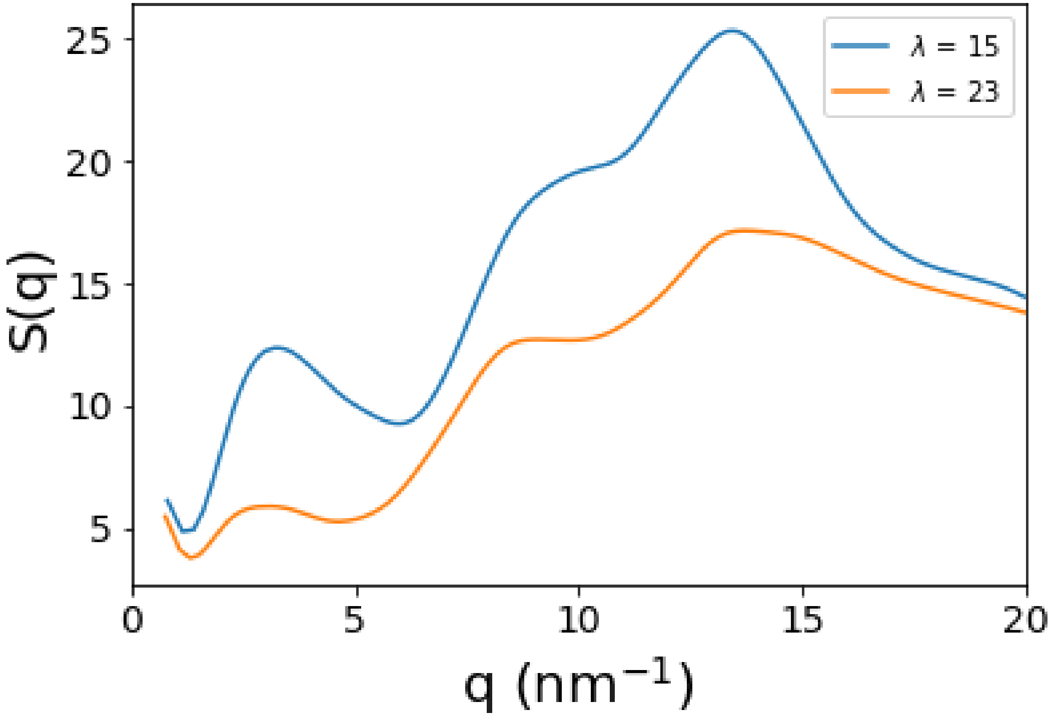


Weak Ionomer Peaks

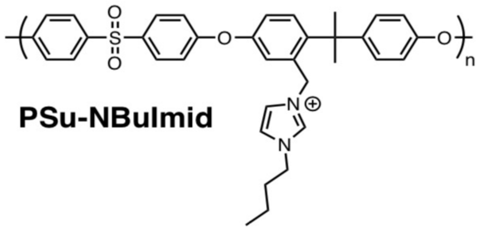
total scattering intensity

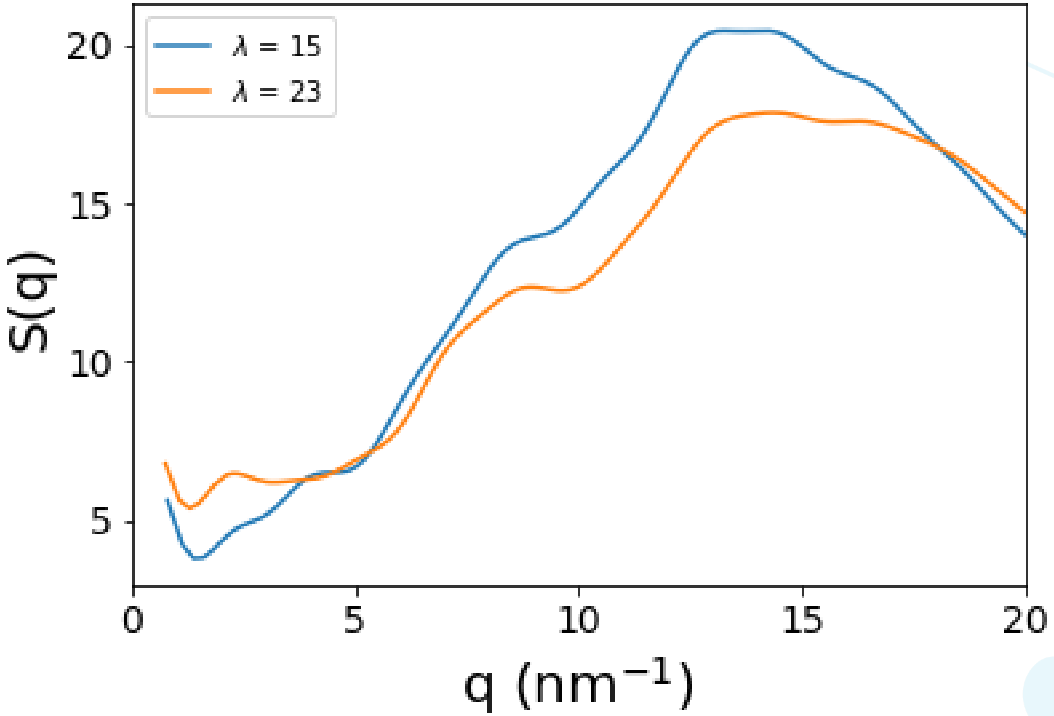
NEt3



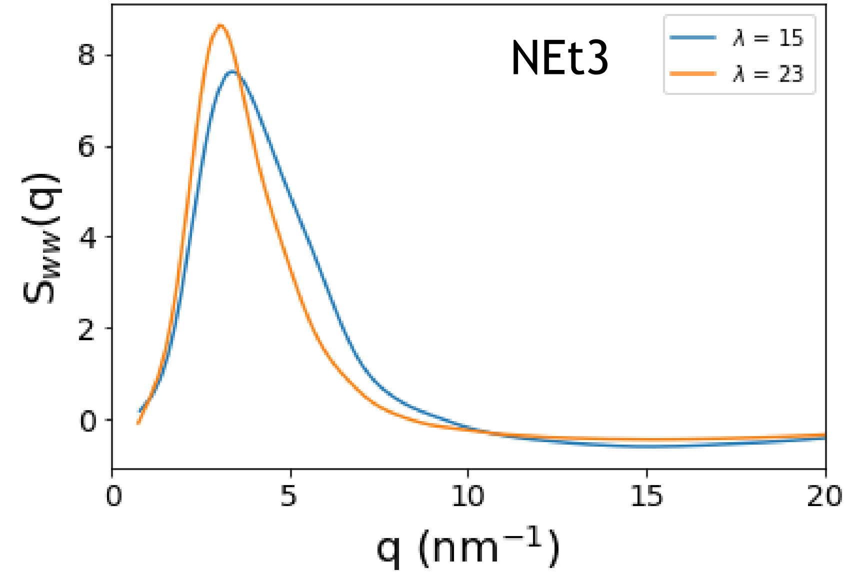


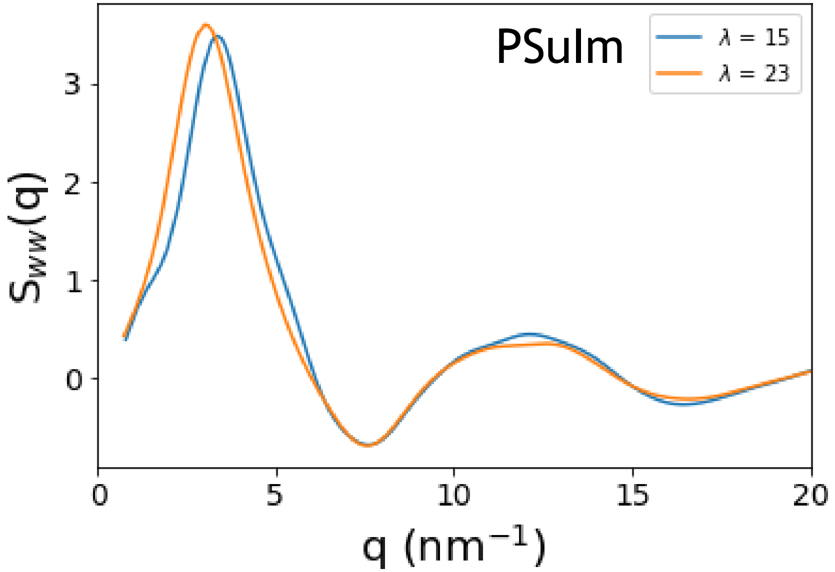
PSuIm



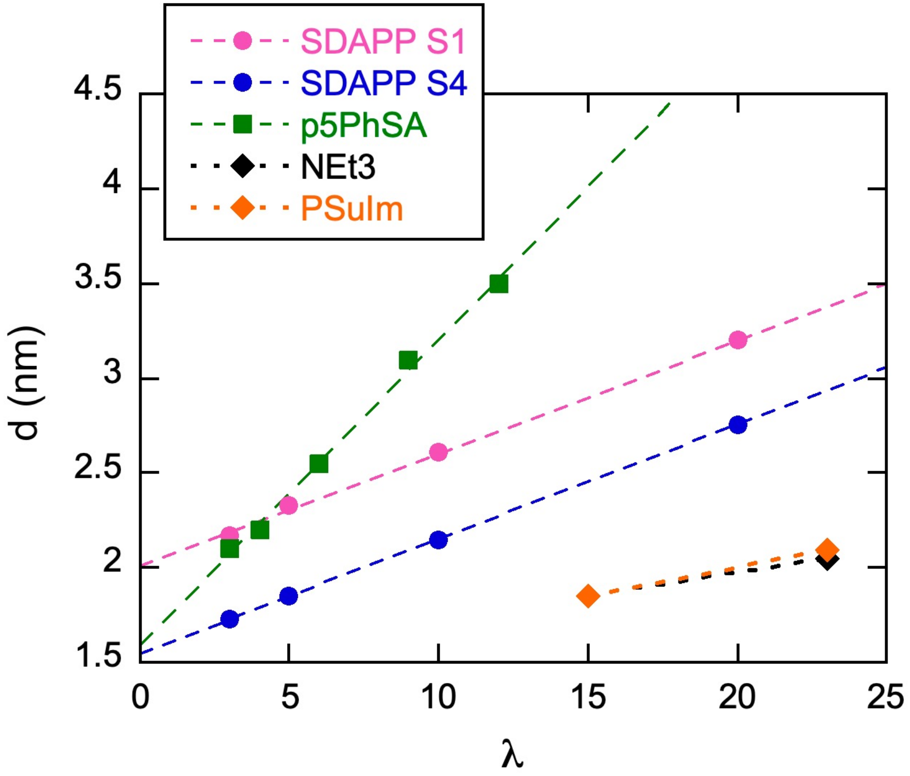


Water Partial Structure Factors



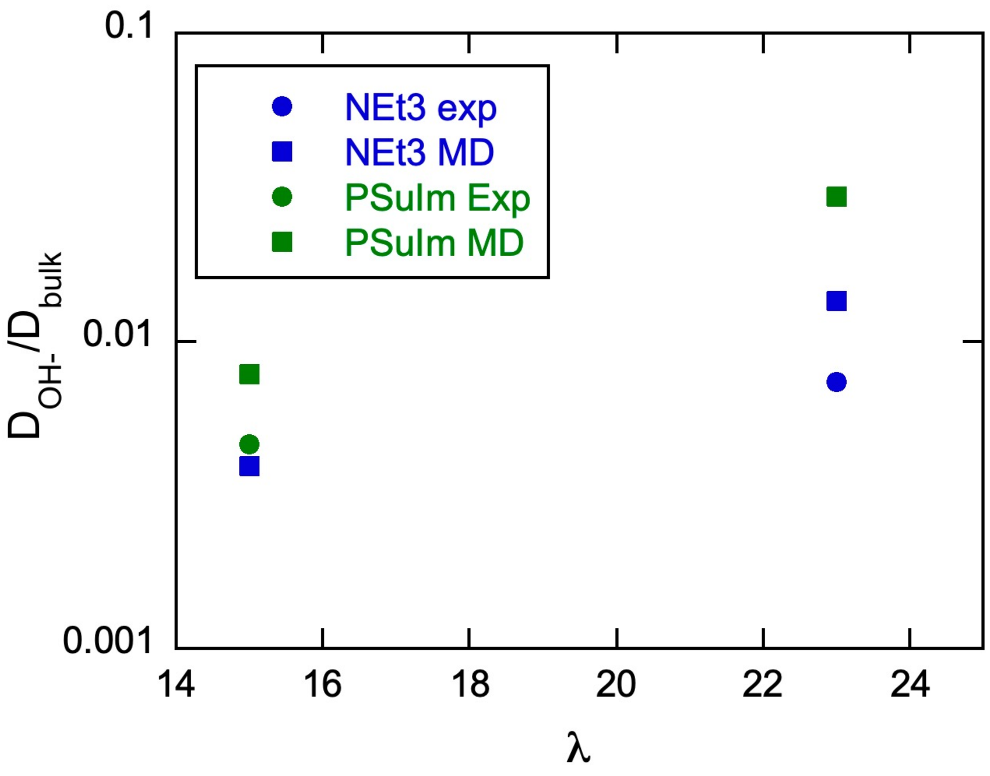


all water spacings from $S_{ww}(q)$ from MD



Hydroxide Diffusion/Conductivity

OH- diffusion constants

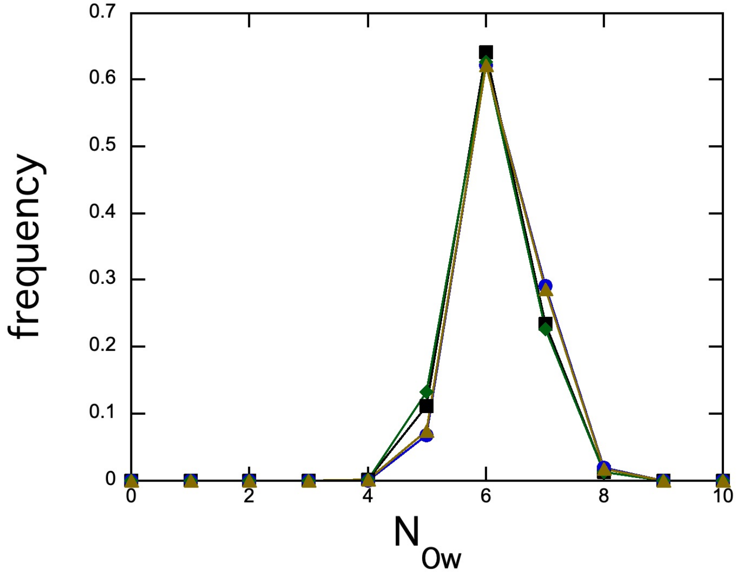


OH- conductivity (experiment)

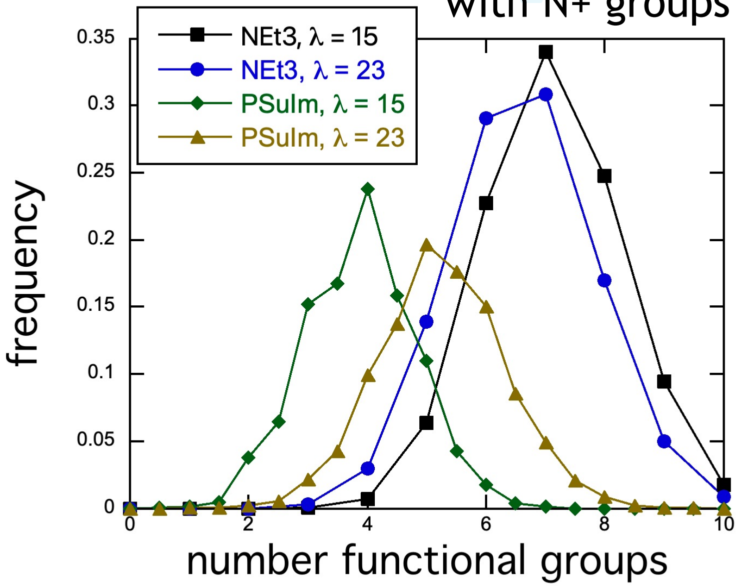
NEt3: 7.4 ± 0.5 mS/cm
PSulm: 9.0 ± 1.4 mS/cm

not just due to “bulk” water
NEt3: 74% water (λ = 23)
PSulm: 55% water (λ = 15)

OH- coordination with water



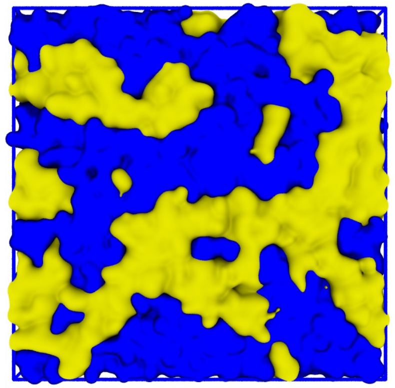
with N+ groups



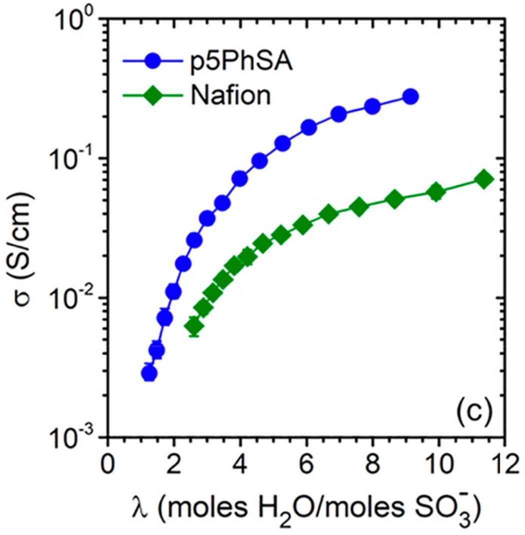
Kolesnichenko, I. V. et al. *ACS Appl Mater Interfaces* **2020**, 12, 50406-50417
Frischknecht et al, in preparation

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
  - local interactions also important!



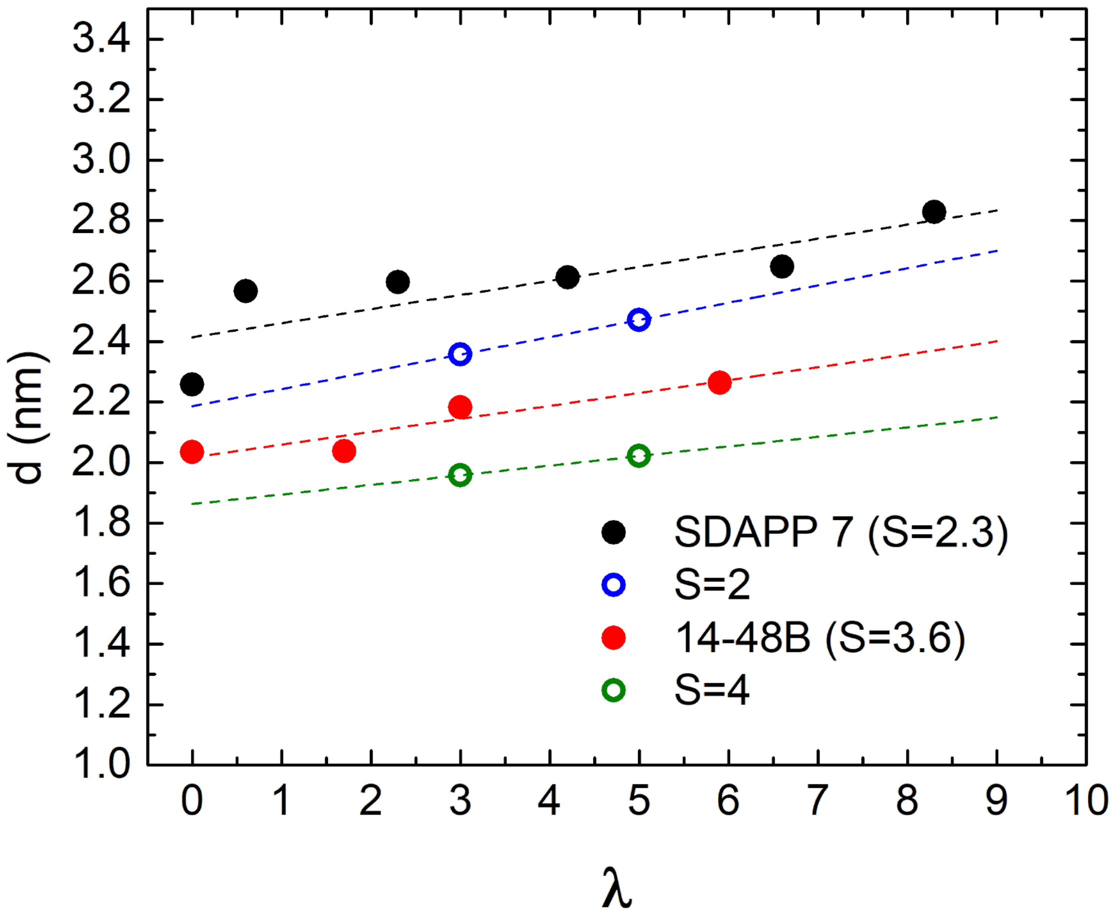
Abbott, L. J. & Frischknecht, A. L. *Macromolecules* **2017**, 50, 1184-1192.
Clark, J. A., Santiso, E. E. & Frischknecht, A. L. *J. Chem. Phys.* **2019**, 151, 104901.
Sorte, E. G. et al. *Macromolecules* **2019**, 52, 857-876.

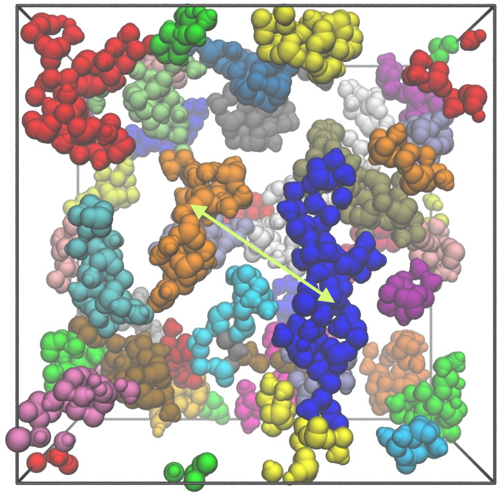
Paren, B. A. et al. *Chem. Mater.* **2021**, 33, 6041-6051.

Backup

Correlation Distance between Aggregates

$d = 2\pi/q^*$, q^* = ionomer peak location





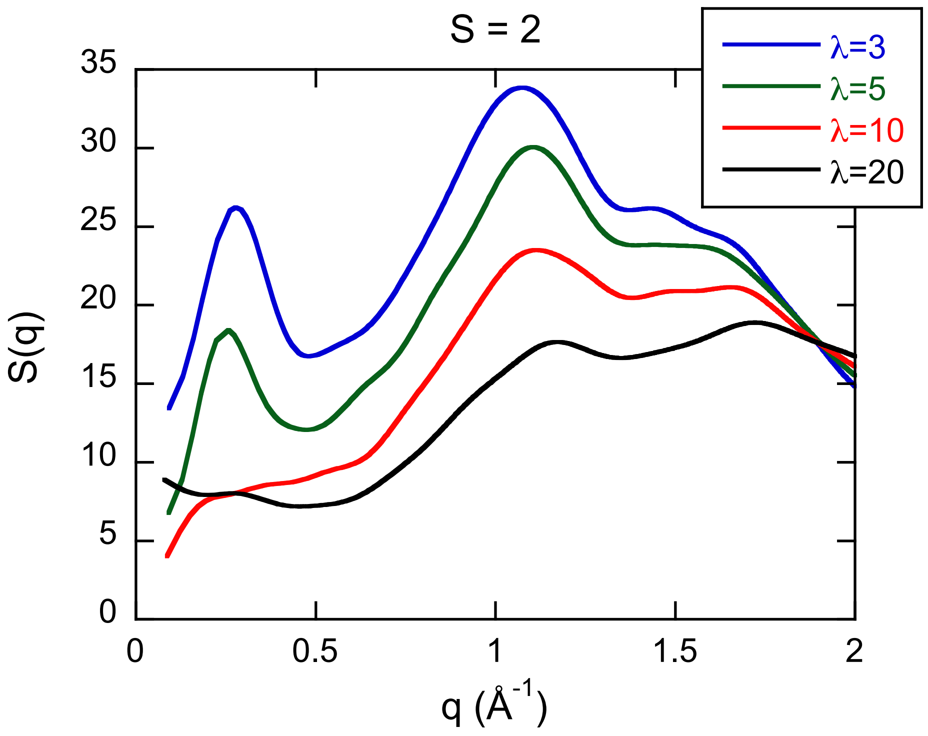
S=1, λ =3

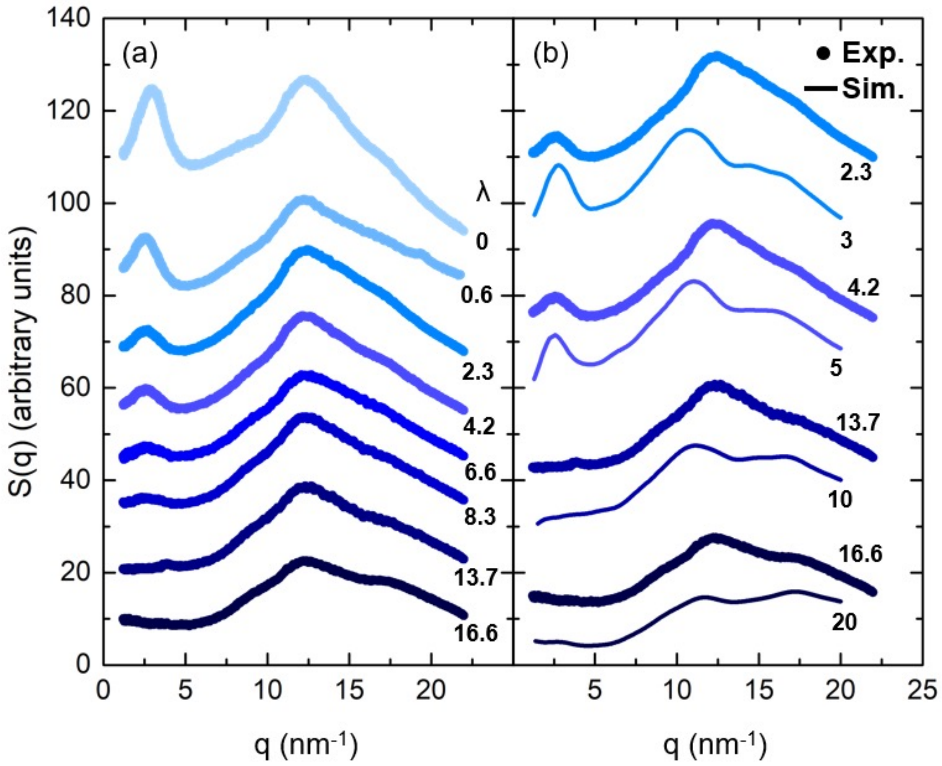
from real space snapshots, low λ:
S = 2, d = 23 Å
S = 4, d = 19 Å

MD consistent with X-ray

Why Does the Ionomer Peak Disappear?

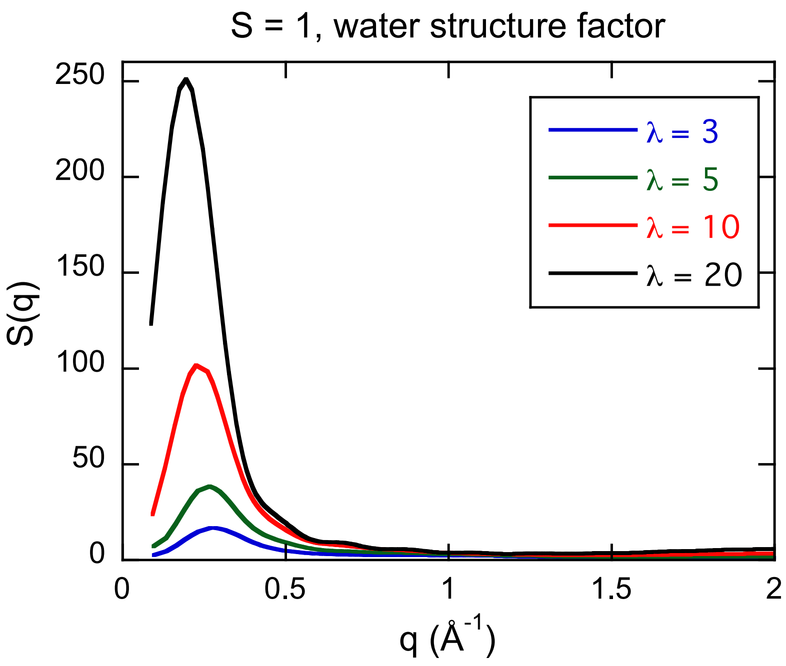
total S(q)

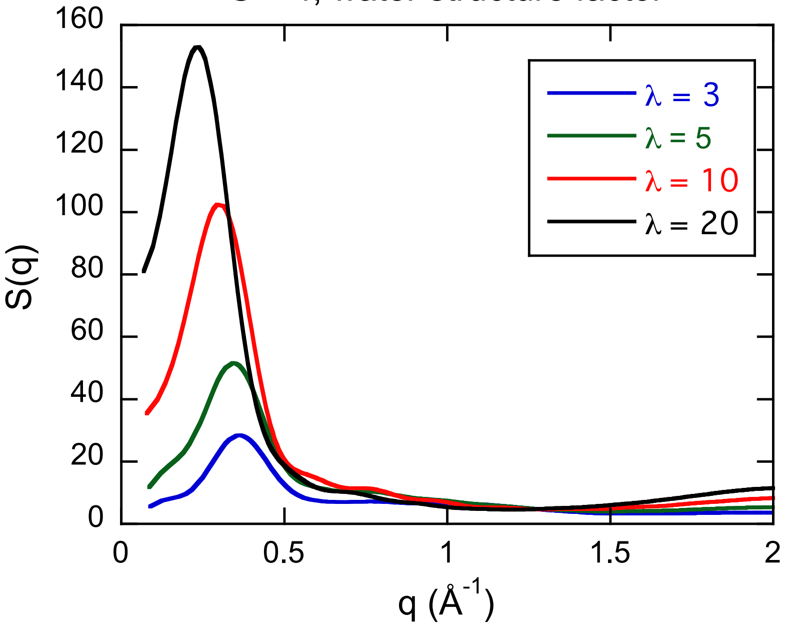


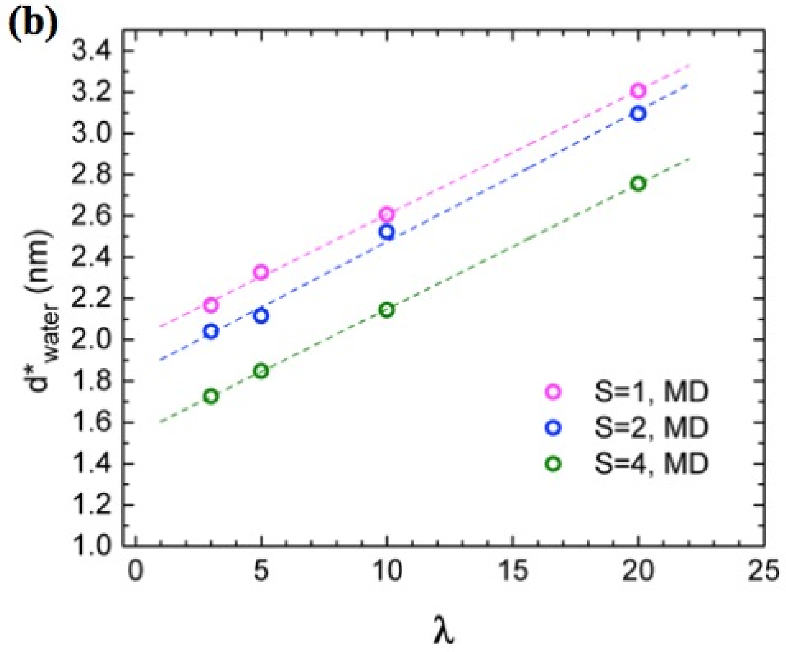


does this mean the water and sulfonic acids are no longer phase segregated?

Water Structure Factors







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