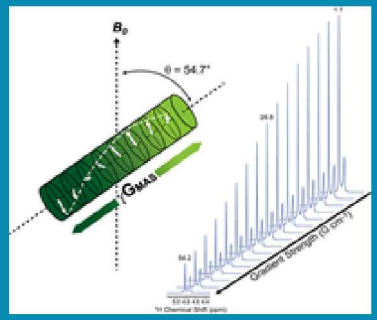
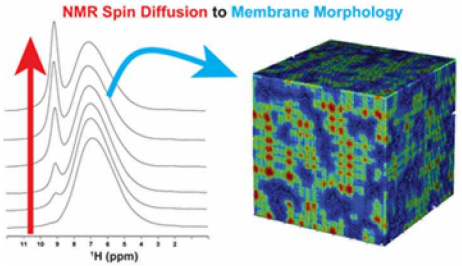
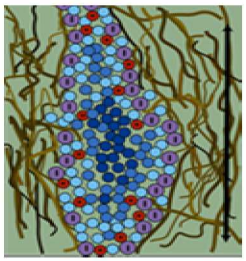
SAND2018-9175C

NMR Techniques to Measure Hydrophilic Domain Structure and Water Transport in Polymer Exchange Membranes







American Chemical Society (ACS) National Meeting

Ion Transport at the Nanoscale:
Research & Capabilities at the DOE's Nano Centers

Aug. 20th, 2018

PRESENTED BY

Todd M. Alam

Organic Materials Science Department
Sandia National Laboratories
Albuquerque, NM 87185

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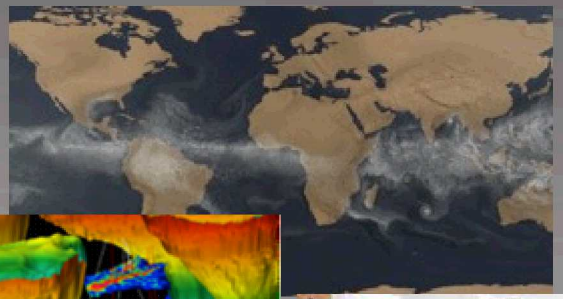
Energy Research at Sandia

Energy Research

ARPAe, BES Chem Sciences, ASCR, CINT, Geo Bio Science, BES Material Science

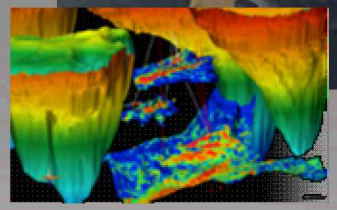
Climate & Environment

Measurement & Modeling, Carbon Management, Water & Environment, and Biofuels



Nuclear Energy & Fuel Cycle

Commercial Nuclear Power & Fuel, Nuclear Energy Safety & Security, DOE Managed Nuclear Waste Disposal

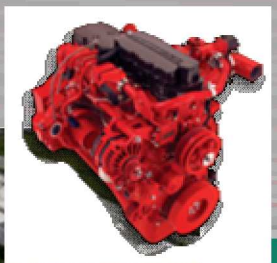


Renewable Systems & Energy Infrastructure

Renewable Energy, Energy Efficiency,
Grid and Storage Systems

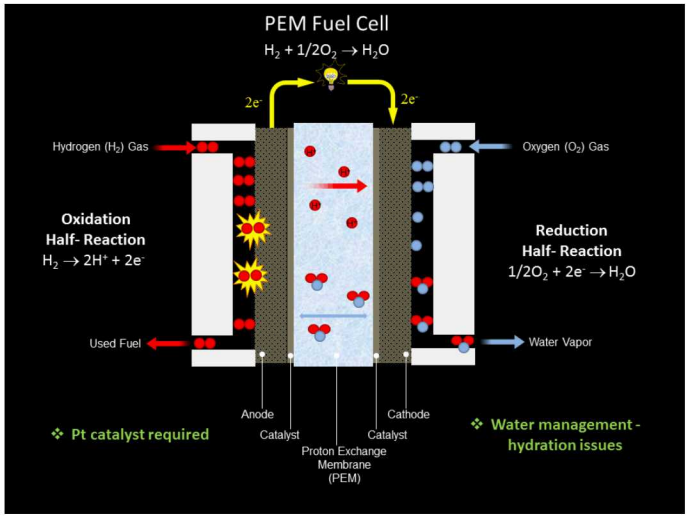
Transportation Energy & Systems

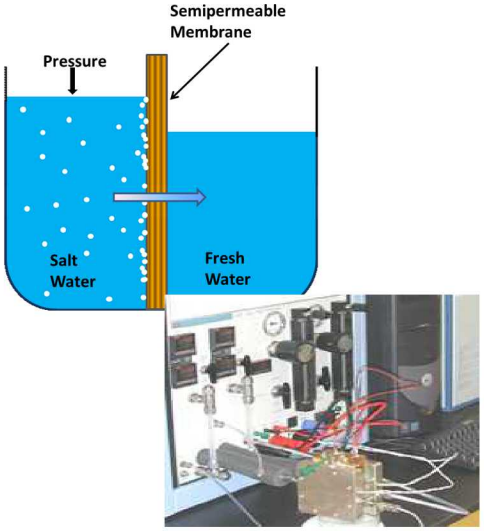
Vehicle Technologies, Biomass, Fuel Cells & Hydrogen Technology



Polymer Exchange Membranes (PEM) at Sandia

Proton Exchange Membranes





- Fuel Cells (PEMs and AEM)
- Battery Separators
- Flow Batteries (V, Na, Fe *etc.*)
- Catalyst Support Binder

- Desalination
- Reverse Osmosis
- Electrolysis
- Ion Selective Electrodes

"Development of new membranes materials for a wide range of technological applications ultimately based on fundamental understanding of transport…"

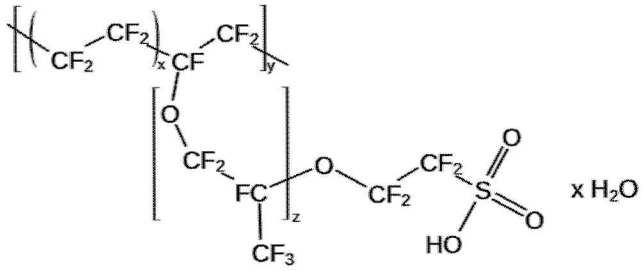
Outline

- Motivation for SDAPP PEMs
- DFT Simulations of Hydrogen Bond Strength → NMR
- MD Simulations of Nano Morphology → NMR
- ^{1}H DQ-Filtered Spin Diffusion Experiments of Domain Size
- ^{1}H-^{19}F REDOR-Filtered Spin Diffusion Experiments
- NMR Diffusometry via Pulsed Field Gradient (PFG) NMR

Sulfonated Diels Alder Polyphenylene (SDAPP) Membranes

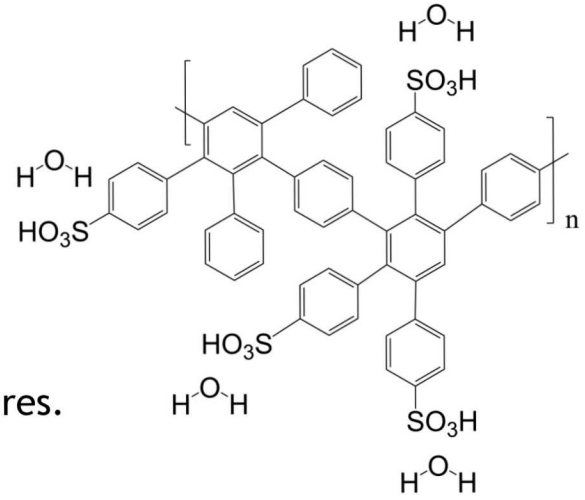
Nafion

(perfluoronated membranes)

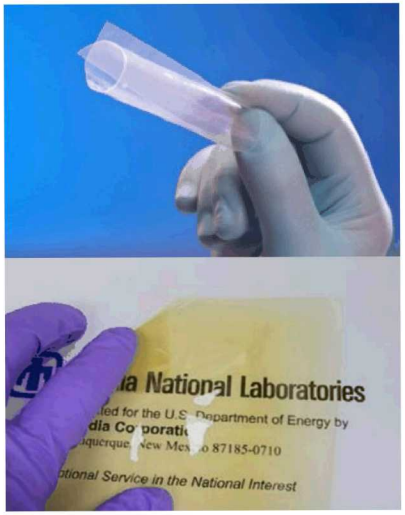


- Good conductivity at low temperatures.
- The present industry standard.

SDAPP

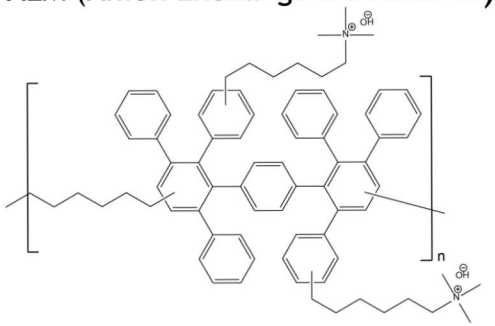


- Stable in alkaline environments.
- High T_g (~350 °C).
- Easily processed.
- Wide range of functionalities.
- Promising alternative to Nafion.
- No F (*i.e.* HF production).



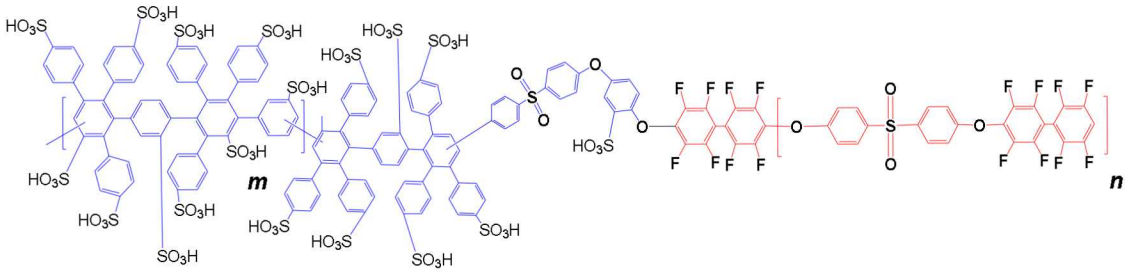
SDAPP Analogues

AEM (Anion Exchange Membranes)



MeOH fuel cell (Hibbs, SNL)

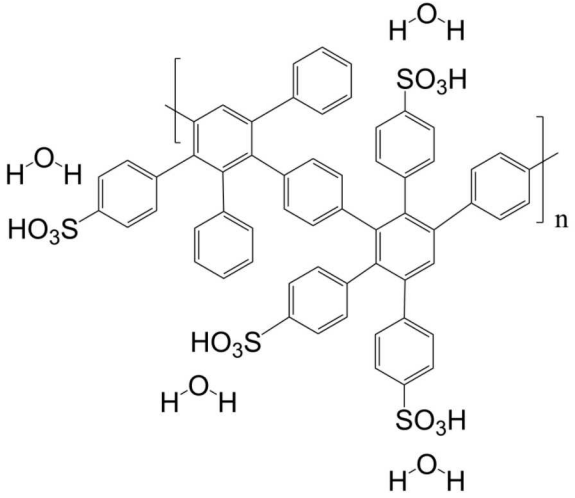
SDAPP-FDPS Copolymers

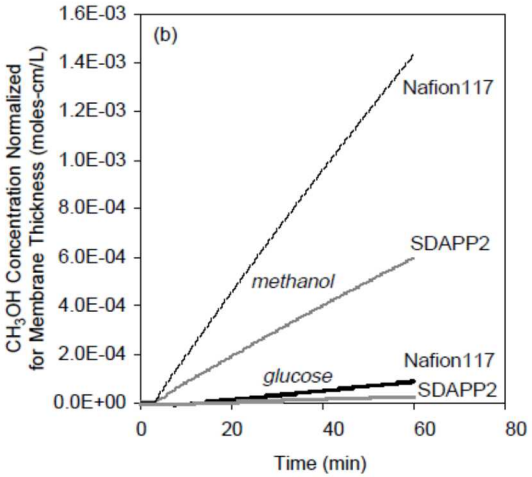


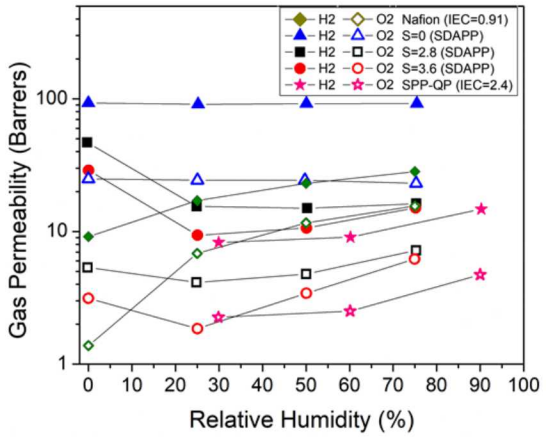
Fujimoto, C. H., Hickner, M. A., Cornelius, C. J., Loy, D. A., Macromolecules 2005, 38 (12), 5010-5016.

Sulfonated Diels Alder Polyphenylene (SDAPP) Membranes

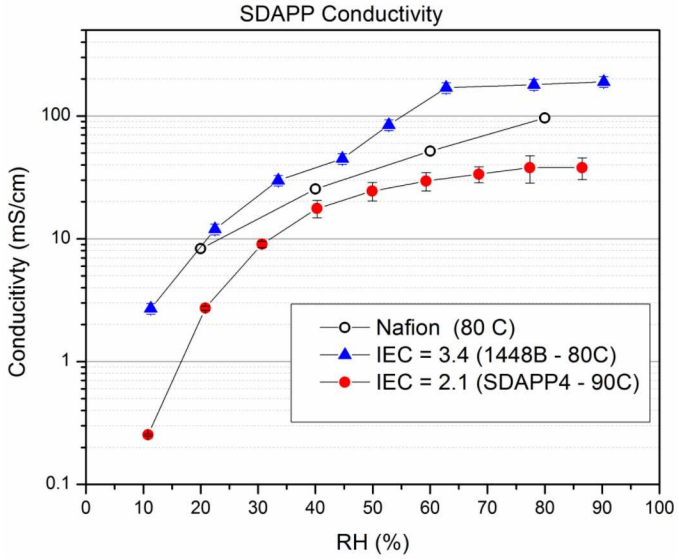
SDAPP





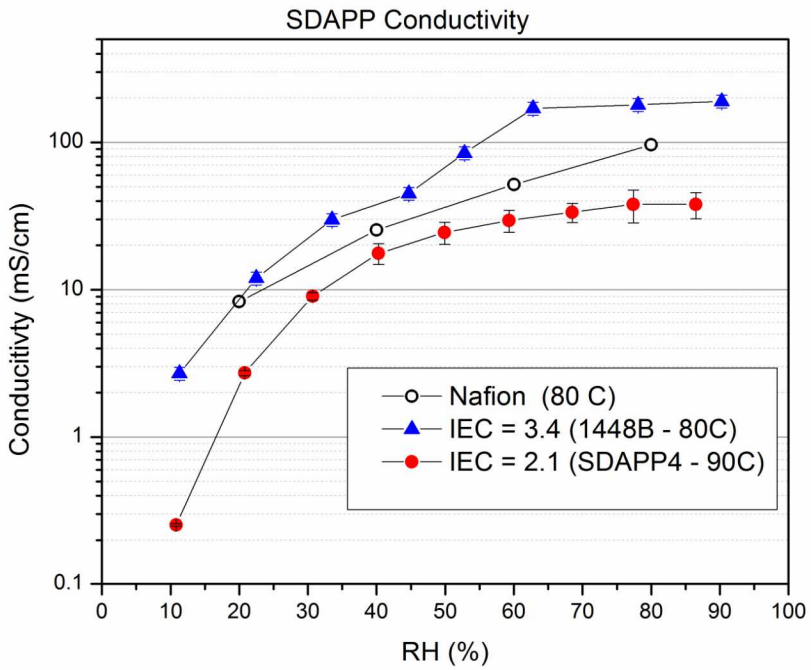


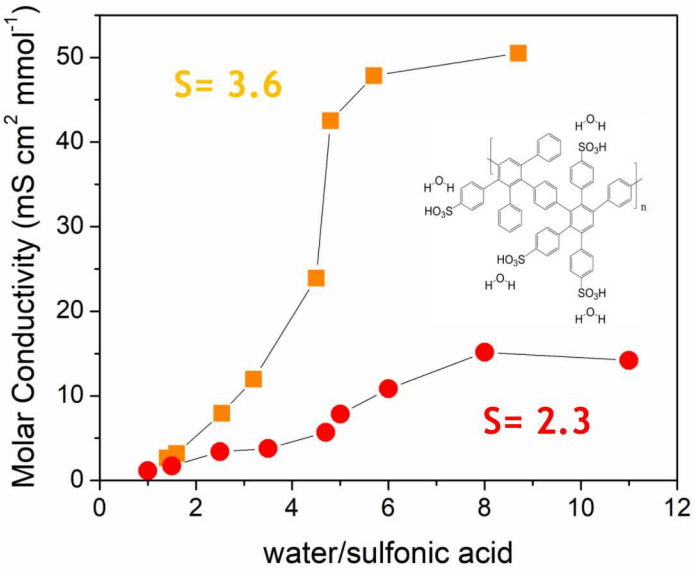
- Proton conductivity equal/surpasses to Nafion.
- Can operate at higher temperatures.
- Improved fuel barrier (O_2, H_2, MeOH).
- Can reach high ion exchange capacity (IEC) ~ 3.8 without solubility issues.
- Improved H conductivity over wide RH%.
- No heteronuclear atoms – aging impact.

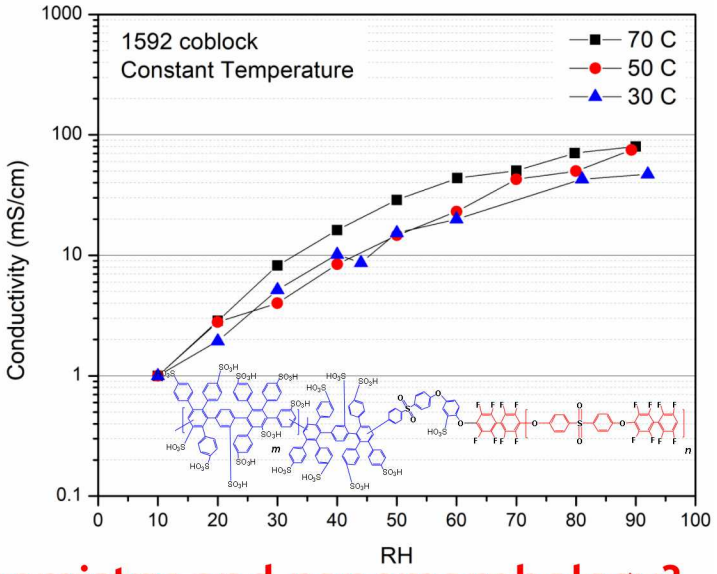


M. A. Hickner, C. H. Fujimoto, C. J. Cornelius, Polymer 47 (2006) 4238-4244

What is Controlling SDAPP Conductivity?





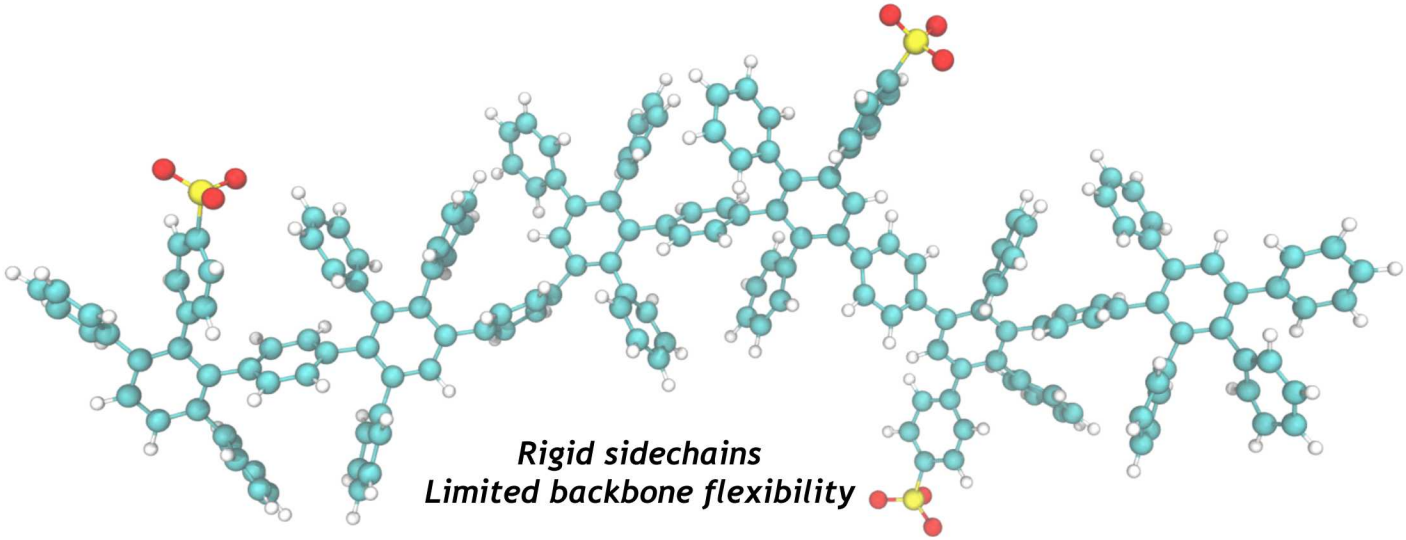


Questions we seek answers to:

- What chemistry/morphology driving improved conductivity with increasing hydration?
- Why the different conductivity versus hydration behavior with increasing sulfonation (S)?
- Why the low temperature variation in the fluorinated co-block polymer?

What can be said about the atomic level chemistry and nanomorphology?

SDAPP Nanoscale Morphology Expected to be Different than Nafion



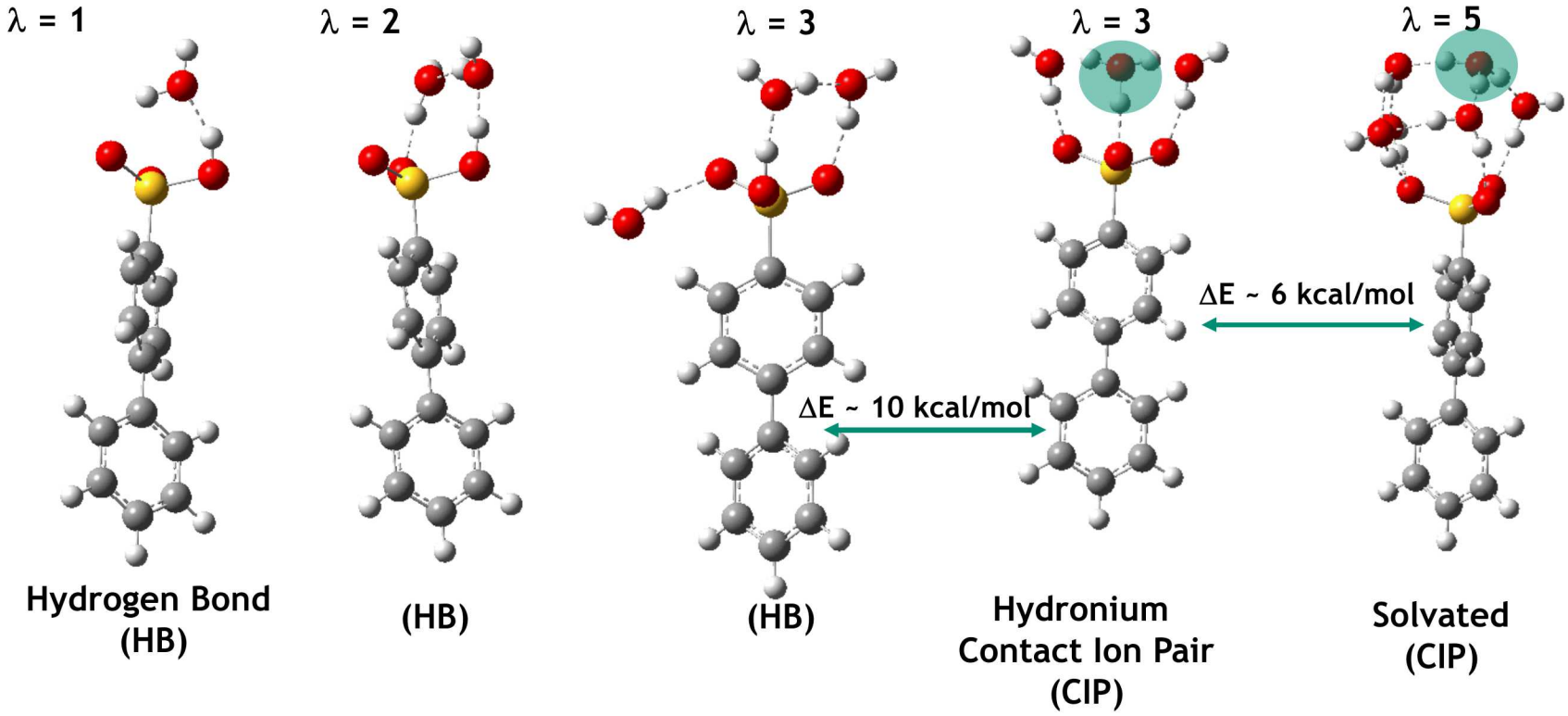
Combination of Efforts

- Quantum DFT calculation of water binding energetics and HB strength.
- MD simulations of nanoscale morphology.
- X-ray Scattering of SDAPP Membranes
- NMR spin diffusion domain size measurements.
- *Connecting DFT and MD simulations to experimental NMR.*
- NMR Diffusometry of water transport.

DFT Quantum Calculations
Water Adsorption Energies & Hydrogen Bonding Types

$$\Delta E_{\mathrm{Ads}}^{\mathrm{Opt}} = E\left(\mathrm{Clutser}{+}n\mathrm{H_2O}\right) - E^{\mathrm{Opt}}\left(\mathrm{Cluster}\right) - \sum_{i=1}^{N} E^{\mathrm{Opt}}\left(\mathrm{H_2O}\right)$$

DFT B3LYP 6-311**

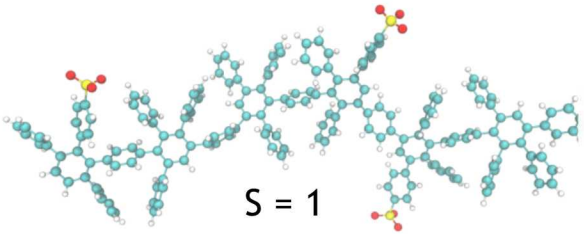


For small clusters very limited structural impact!

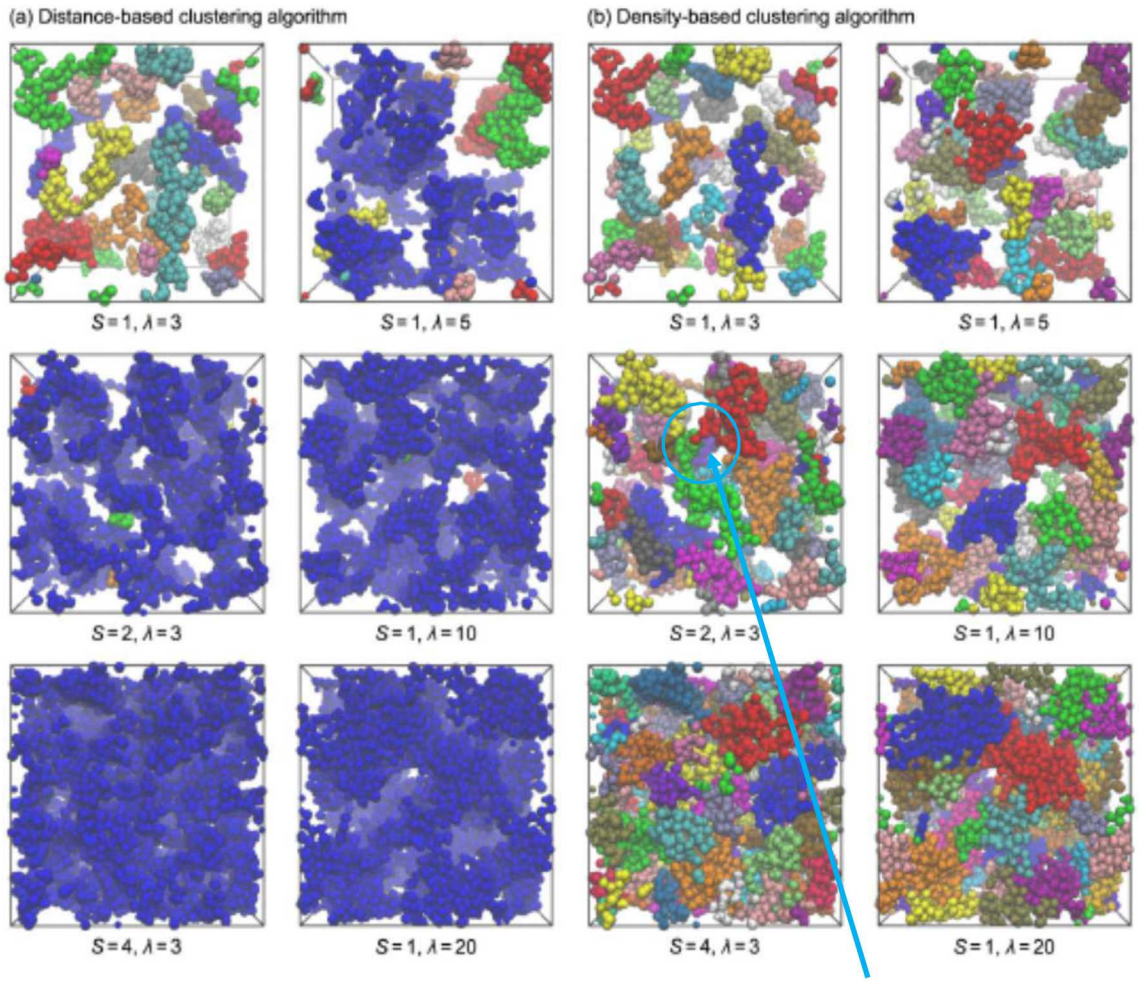
Todd M. Alam, "Computational Study of Microhydration in Sulfonated Diels-Alder Poly(phenylene) Polymers", J. Phys. Chem. A, 122, 3927-3938 (2018) DOI: 10.1021/acs.jpca.8b01354

SDAPP Molecular (MD) Simulations

Rigid backbone should be different than Nafion



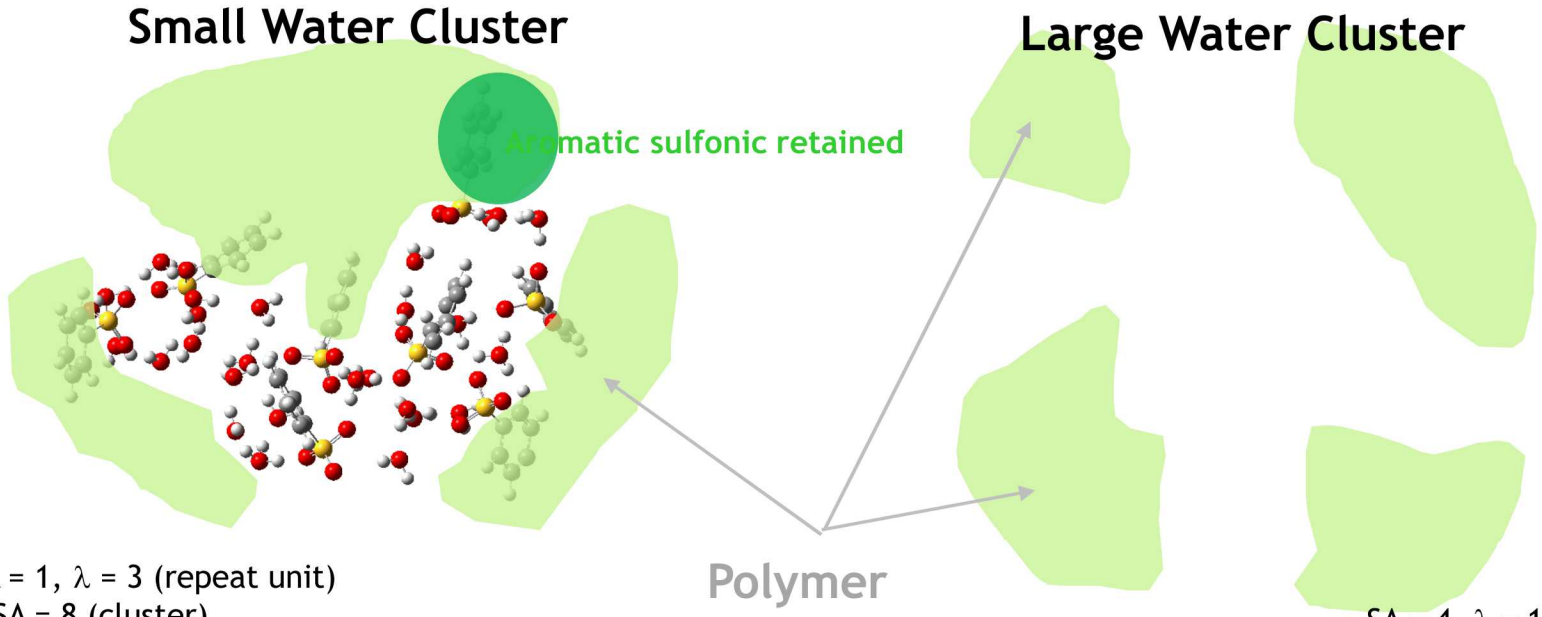
- Local structure depends on the degree of sulfonation (S) and the hydration (λ) levels.
- Cluster domain shape depends on how it is defined: distance based versus density based methods.
- Increasing S and λ resulted in larger and more spherical cluster sizes, with the formation of fully percolated ionic domains.
- Conductivity still occurs below percolation thresh hold.



Thin connections are not considered a domain in density based algorithm.

L. A. Abbott, A. Frischknecht, *Macromolecules*, 50(3), 1184-1192, **2017**.

Large Water/Acid Clusters (from MD Simulations)



SA = 1, λ = 3 (repeat unit)
# SA = 8 (cluster)
17 H_2O, 8 H_3O^+
Gyration = 7.6 Angstroms

SA = 4, λ = 10 (repeat unit)
# SA =11 (cluster)
42 H_2O, 11 H_3O^+
Gyration = 7.7 Angstroms

Adsorption energies determined for each individual H_2O/H_3O^+

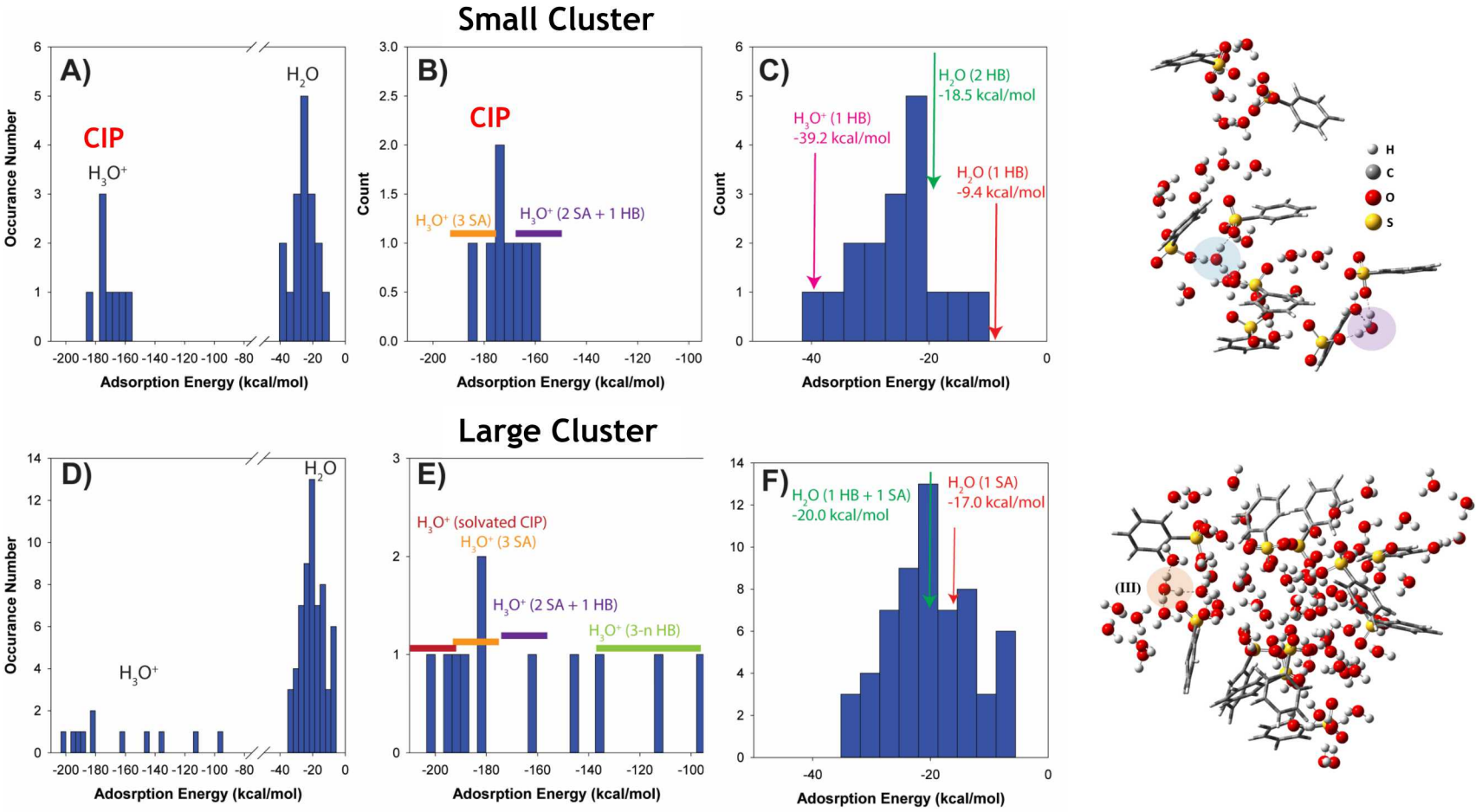
$$\Delta E_{\text{Ads}}^{Total} = \Delta E_{Ads}^{H_3O^+} + \Delta E_{Ads}^{H_2O} = \sum_{j=1}^{n} \Delta E_{Ads}^{H_3O^+}(j) + \sum_{i=1}^{m} \Delta E_{Ads}^{H_2O}(i)$$

$$\Delta E_{\text{Ads}}^{H_2O}(i) = E\left(\text{Cluster}\left[m\text{H}_2\text{O}\right]\right) - E\left(\text{Cluster}\left[(m-1)\text{H}_2\text{O}(i)\right]\right) - E^{Opt}\left(\text{H}_2\text{O}\right)$$

$$\Delta E_{\text{Ads}}^{H_3O^+}(j) = E\left(\text{Cluster}\left[n\text{H}_3\text{O}^+\right]\right) - E\left(\text{Cluster}\left[(n-1)\text{H}_3\text{O}^+(\text{j})\right]\right) - E^{Opt}\left(\text{H}_3\text{O}^+\right)$$

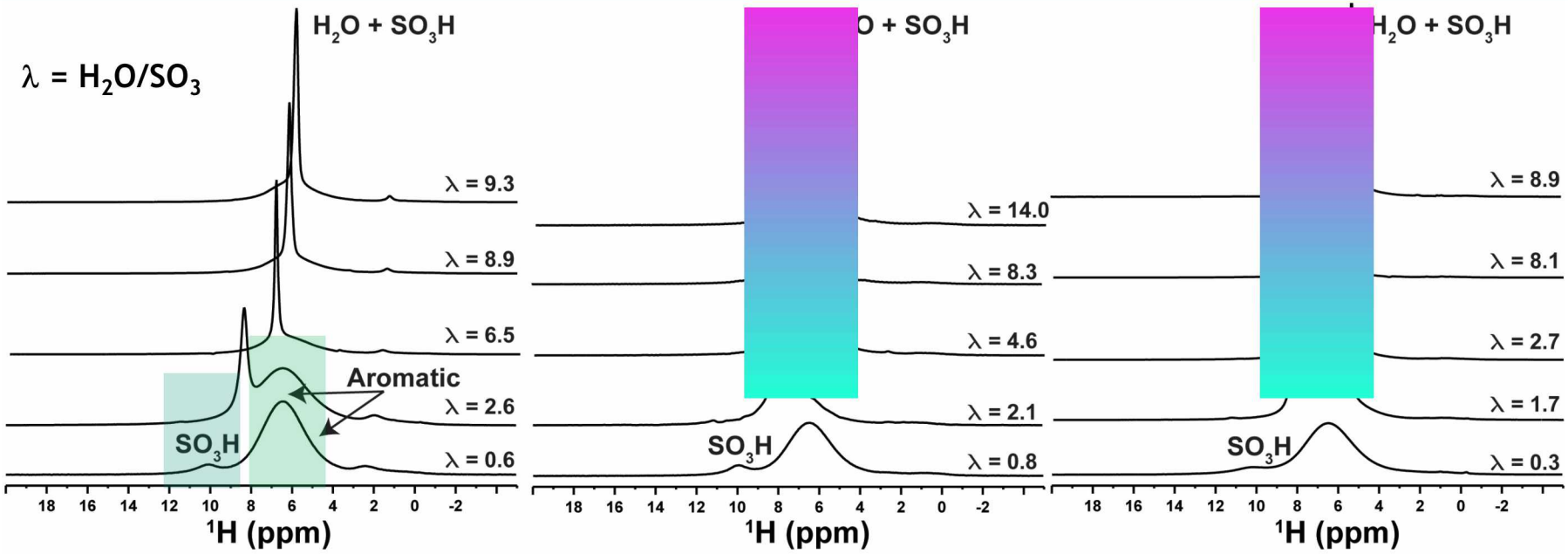
Todd M. Alam, "Computational Study of Microhydration in Sulfonated Diels-Alder Poly(phenylene) Polymers", J. Phys. Chem. A, 122, 3927-3938 (2018) DOI: 10.1021/acs.jpca.8b01354

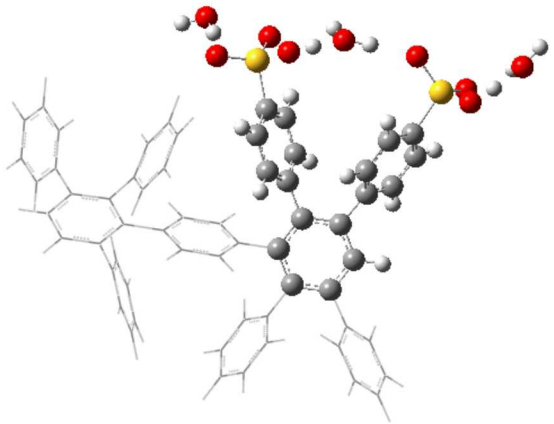
Adsorption Energies
Large Water/Acid Clusters from MD Simulations



- Increasing hydration allows formation of solvate CIP – large adsorption energy.
- Inter-chain coordination of H_2O/H_3O^+ important!
- This driving force counteracted by chain energetics and maximization all HB interactions.
- Larger domain structure gives a wider range of hydrogen bond strengths – improved H transport.

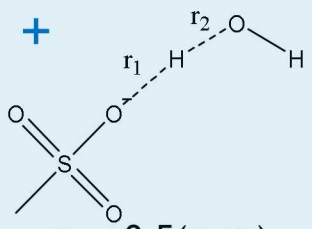
^{1}H Magic Angle Spinning (MAS) NMR

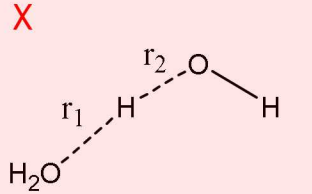


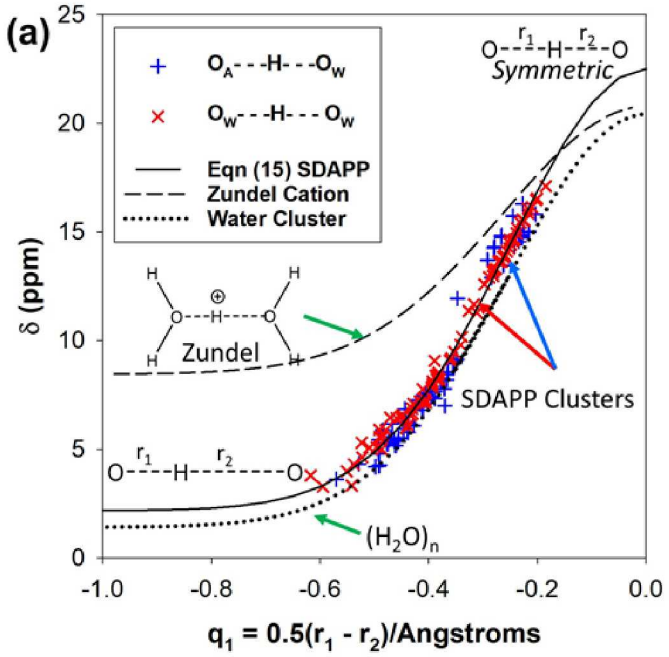


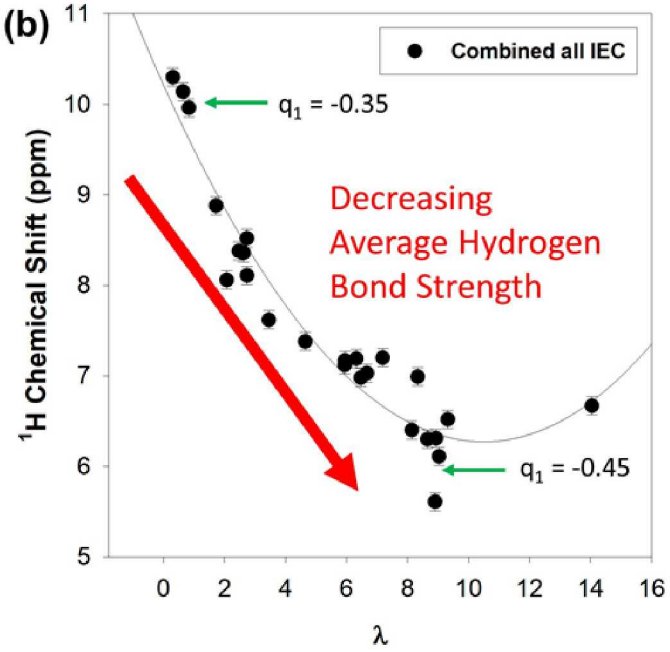
- Only 3 ^{1}H environments (aromatic, H_2O, SO_3H).
- H_2O+SO_3H in rapid exchange (single resonance).
- ^{1}H NMR chemical shift reflects relative concentration of SO_3^- coordination.
- Can chemical shift be related to “average” hydrogen bond strength?
- Similar information from IR?

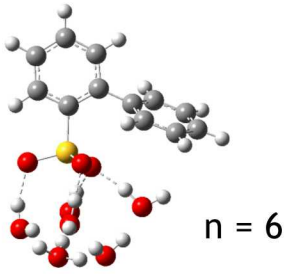
NMR Chemical Shift Hydrogen Bond Strength Correlations











- DFT ^{1}H NMR chemical shift calculations for all SDAPP$_n$(H_2O) clusters (n = 1 to 6).
- Correlations follow definition of Limbach and company. $\delta\left(^1\mathrm{H}\right) = \mathrm{a} + \mathrm{b}\exp\left[-\mathrm{c}q_1^2\right]$
- Experimental is a dynamic average over all H environments, but provides a measure of the changing *average* hydrogen bond strengths with hydration.
- Reduction in hydrogen bond strength → increase in Grotthuss mechanism (proton defect).

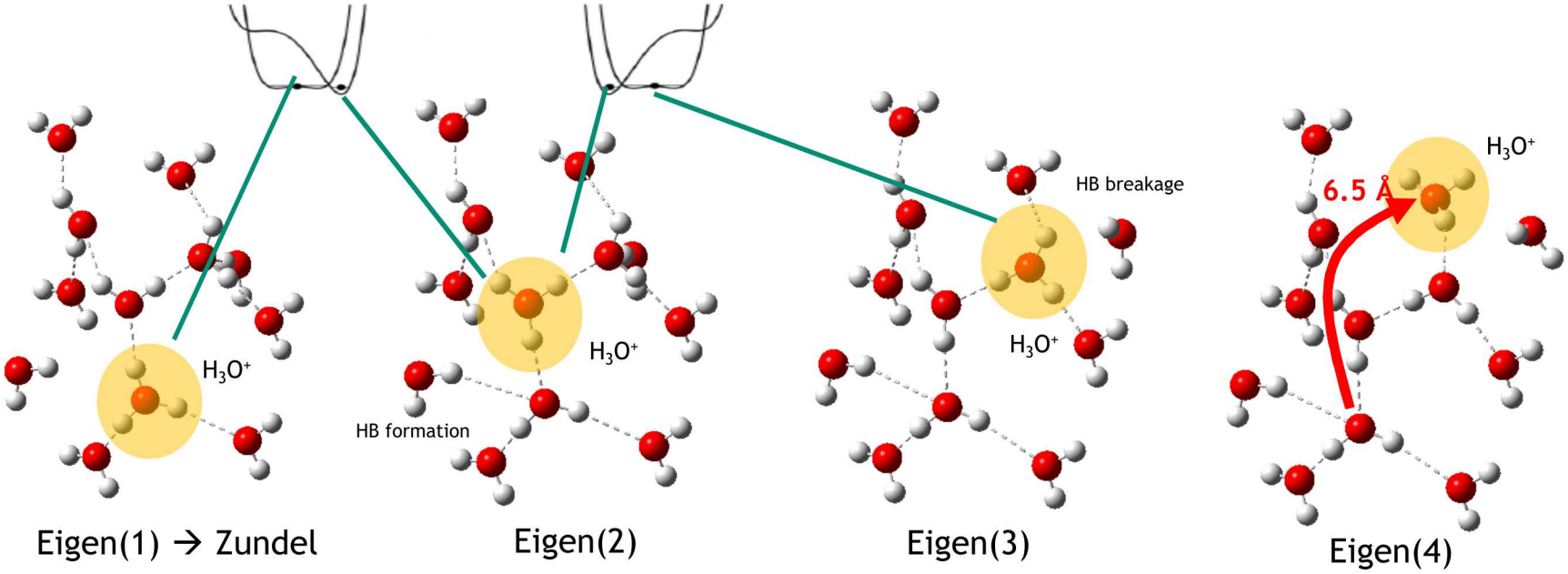
Todd M. Alam, "Computational Study of Microhydration in Sulfonated Diels-Alder Poly(phenylene) Polymers", J. Phys. Chem. A, 122, 3927-3938 (2018) DOI: 10.1021/acs.jpca.8b01354

Eric G. Sorte, Benjamin Paren, Christina G. Rodriquez, Cy Fujimoto, Cassandria Poirier, Lauren J. Abbotte, Nathaniel A. Lynd, Karen I. Winey, Amalie L. Frischknecht, and Todd M. Alam, "Impact of Hydration and Sulfonation on the Morphology and Ionic Conductivity of SDAPP Proton Exchange Membranes", *Submitted.*

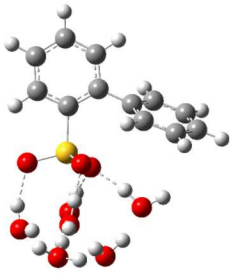
H.-H. Limbach, P. M. Tolstoy, N. Perez-Hernandez, J. Guo, I. G. Shenderovich, G. S. Denisov, "OHO Hydrogen Bond Geometries and NMR Chemical Shifts: From Equilibrium Structures to Geometric H/D Isotope Effects, with Application for Water, Protonated Water and Compressed Ice", *Israel J. Chem.*, **49**, 199-216 (2009).

Proton Conduction via Grotthuss: Hydrogen Bonding

Proton Conduction in Hydrophilic Phases



Eigen(1) → Zundel | Eigen(2) | Eigen(3) | Eigen(4)

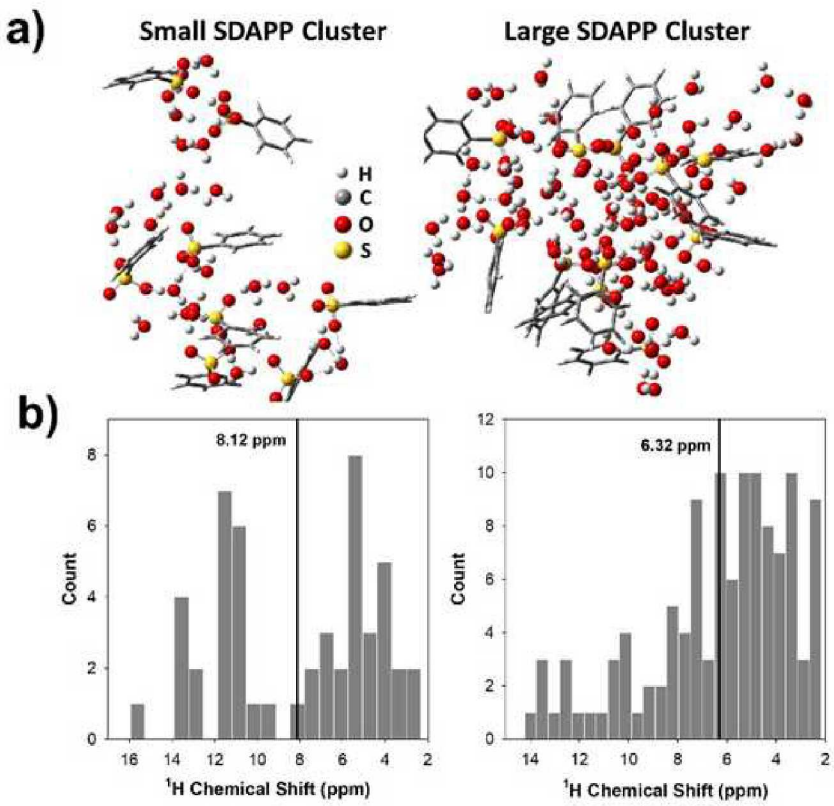


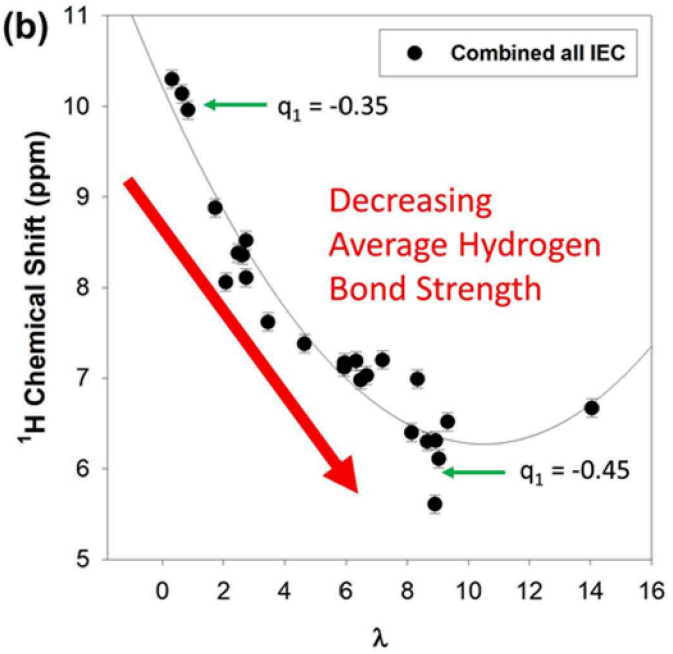
n = 6

- Activation energy for this process is dominated by the hydrogen bond breaking and forming.
- HB contracted in localized center of H^+ defect "barrierless proton translocation"
- Hydrogen bond breaking and formation is the weaker HB on the outer parts of the complex.
- NMR confirms this reduction in HB strength with increasing λ and S.

K.D. Kreuer, S. J. Paddison, E. Spohr, M. Schuster, "Transport in Proton Conductors for Fuel-Cell Applications: Simulations, Elementary Reactions, and Phenomenology", *Chemical Reviews*, (2004) 104, 4637-4678.

Extend Hydrogen Bond Correlations to MD structures

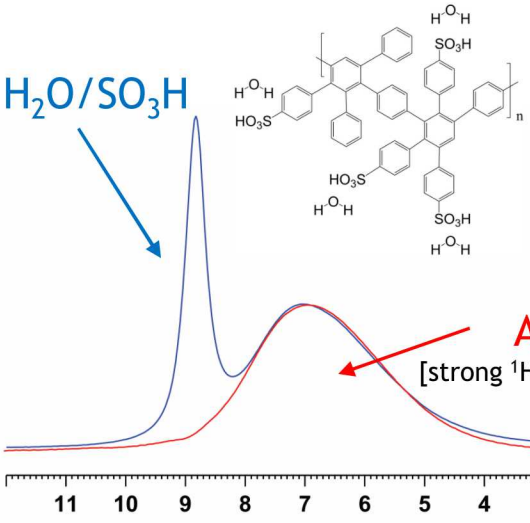


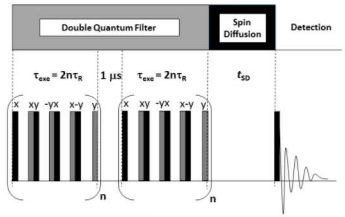


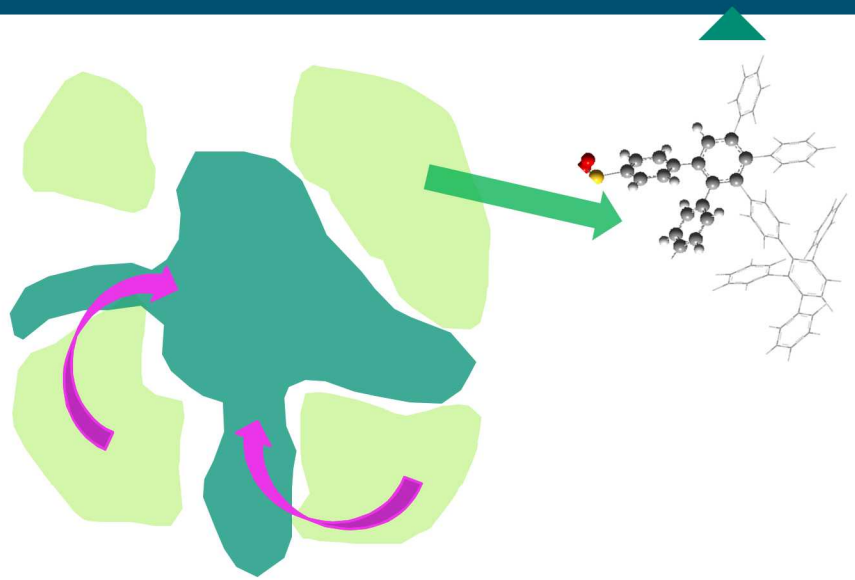
- Can use these empirical chemical shift/HB correlation on larger predicted structures.
- Hydrophilic domains from MD simulations also predict a reduction in the average HB strength.
- Lower RH increase HB strength tend to reduce Grotthuss mechanism – but higher S/V of SDAPP (vs. Nafion) increases cooperative effects in the energetics of CIP solvation.

Eric G. Sorte, Benjamin Paren, Christina G. Rodriquez, Cy Fujimoto, Cassandria Poirier, Lauren J. Abbotte, Nathaniel A. Lynd, Karen I. Winey, Amalie L. Frischknecht, and Todd M. Alam, "Impact of Hydration and Sulfonation on the Morphology and Ionic Conductivity of SDAPP Proton Exchange Membranes", *Submitted*.

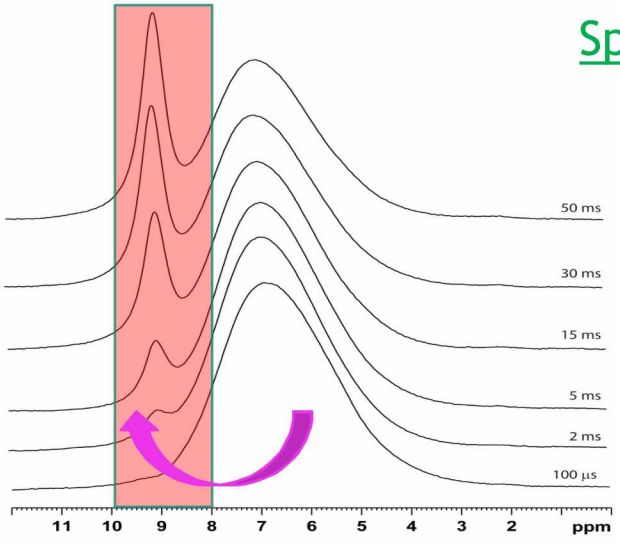
Domain Size via ^{1}H NMR Spin Diffusion Experiments



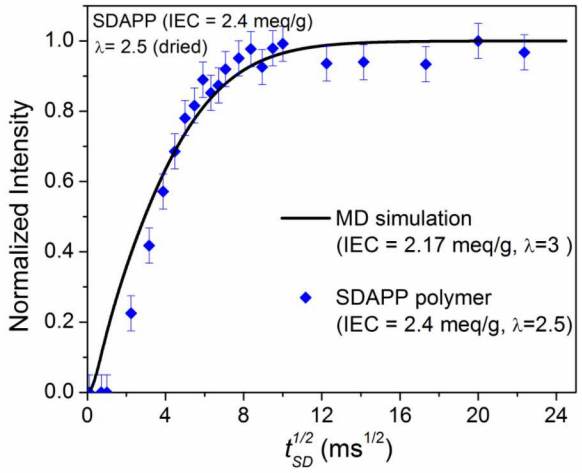




Spin Diffusion Experiment

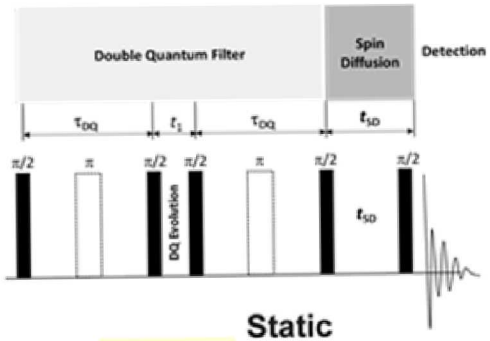


"spin temperature" Equilibration via ^{1}H-^{1}H dipolar mediated spin diffusion

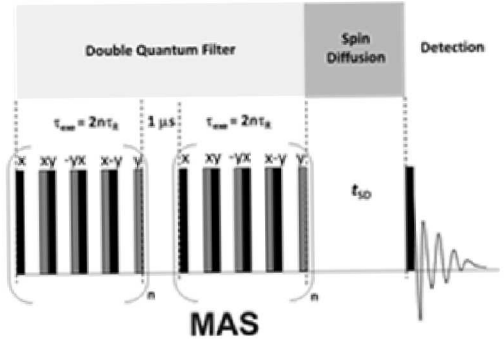


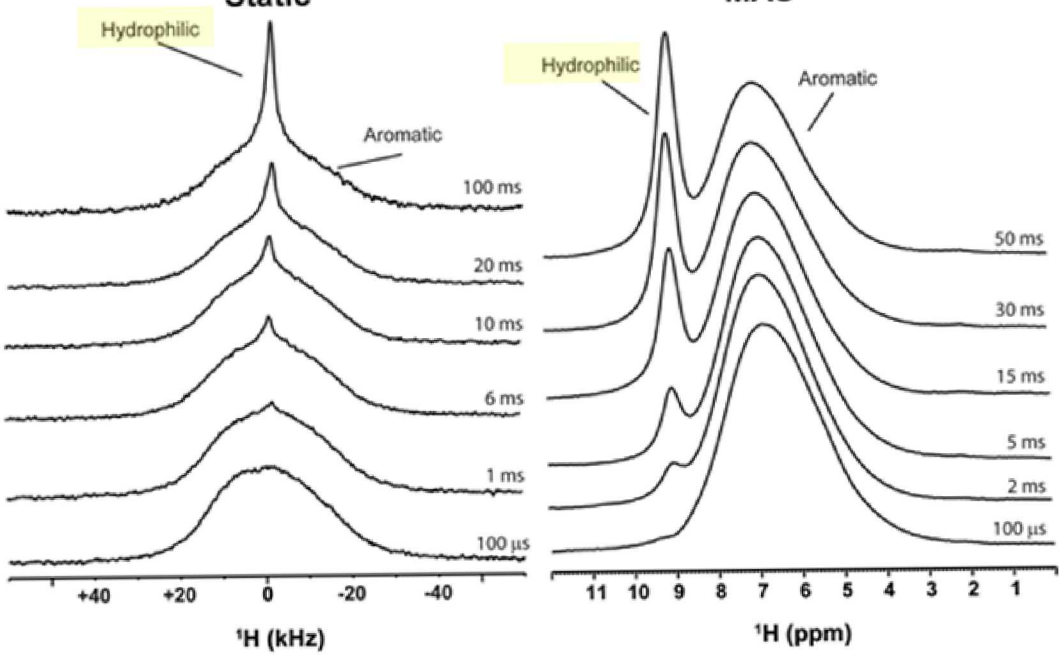
^{1}H DQ-Filtered Spin Diffusion Experiments

Static

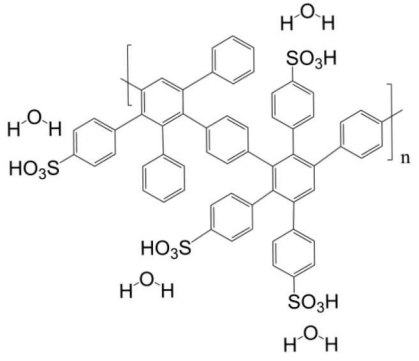


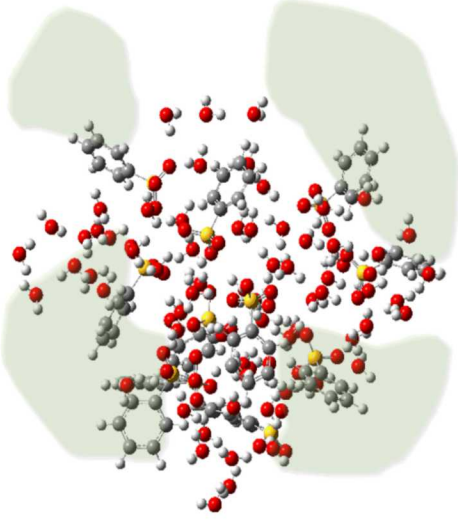
MAS



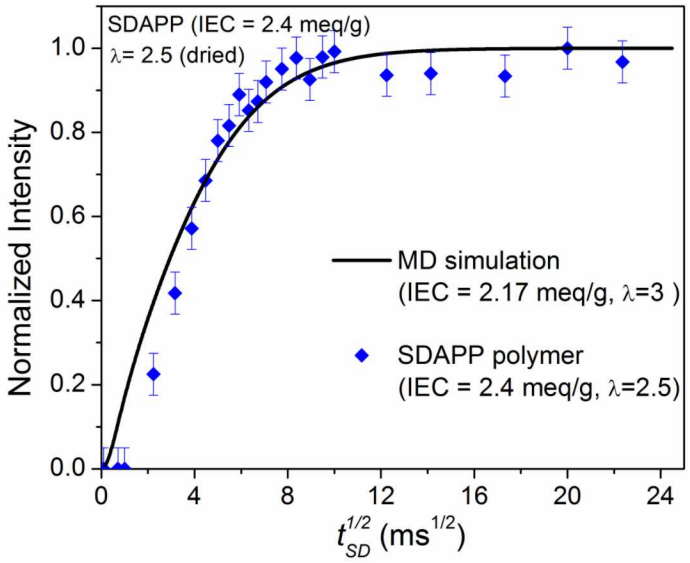


In both cases we want the hydrophilic domain (water and acid) to be the sink ("hole")





NMR Spin Diffusion Analysis



Proportion to Interface Surface Area

Density & Volume Fraction

Very structure/model specific

$$\frac{M_B(t_{SD})}{M_B(t_{SD}\to\infty)} \approx \frac{S}{V_{total}}\sqrt{t_{SD}}\,\frac{2}{\sqrt{\pi}}\left(\frac{\rho_{HA}\phi_A+\rho_{HB}\phi_B}{\phi_A\phi_B}\right)\left[\frac{\sqrt{D_A D_B}}{\rho_{HA}\sqrt{D_A}+\rho_{HB}\sqrt{D_B}}\right]-O\left(\sqrt{t_{SD}}^{2}\right)$$

Spin Diffusion Constants

$$d = 2\varepsilon\phi_B\frac{V_{total}}{S}$$

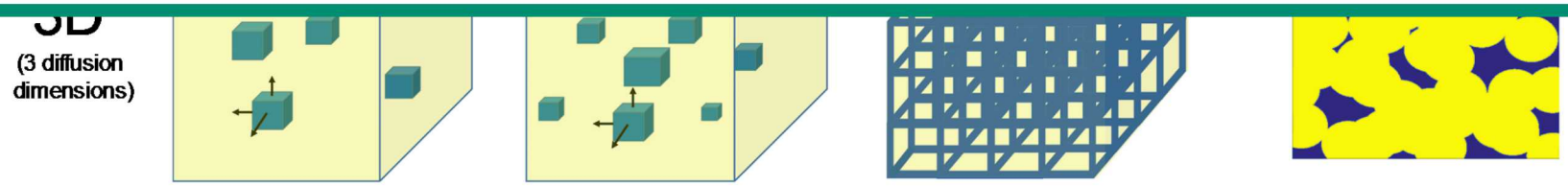
For Simple Models Related to Domain Size

Connecting Morphology Models to NMR Spin Diffusion

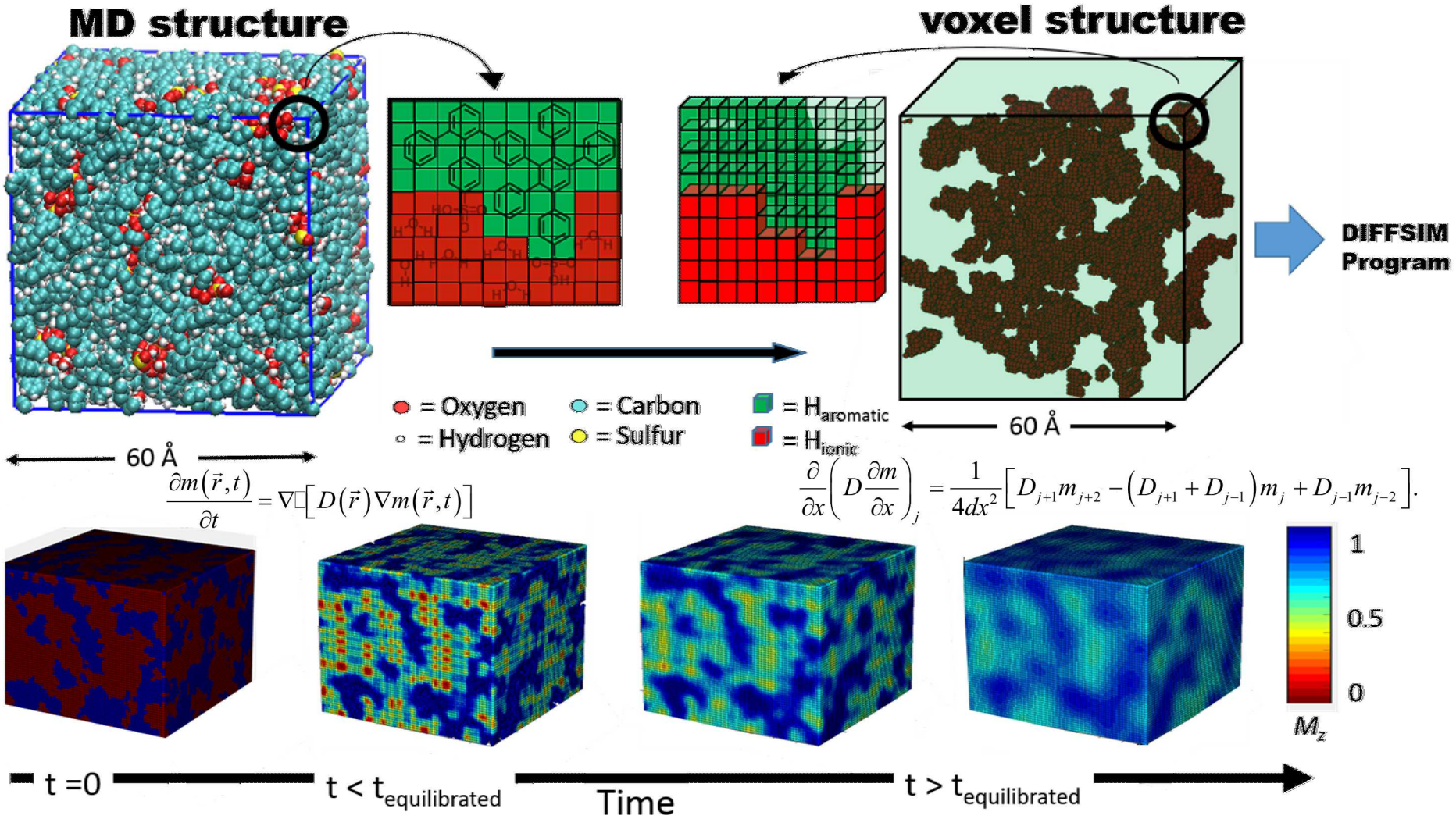
- Analytical solutions for the simplest cases.
- Solutions become unwieldy for distribution of more complex structures!!
- Would like to simulate structured from MD and Coarse Grain simulations.

- Developed the program (NMR_DIFFSIM) to simulate any proposed structure.
- Used to estimate domain size in SDAPP polymer membranes.

Sorte, E. G., Lauren J. Abbott, Mark Wilson, Amalie Frischknecht, and Todd M. Alam, "Hydrophilic Domain Structure in Polymer Exchange membranes: Simulation of NMR Spin Diffusion Experiments to Address Ability for Model Discrimination", J. Polym. Sci., Part B: Polym. Phys. 2018, **56**, 62-78.

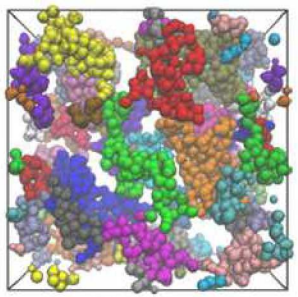


MD → NMR Spin Diffusion Experiments

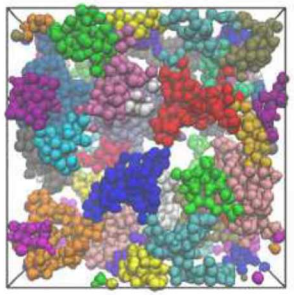


Sorte, E. G., Lauren J. Abbott, Mark Wilson, Amalie Frischknecht, and Todd M. Alam, "Hydrophilic Domain Structure in Polymer Exchange membranes: Simulation of NMR Spin Diffusion Experiments to Address Ability for Model Discrimination", J. Polym. Sci., Part B: Polym. Phys. 2018, **56**, 62-78.

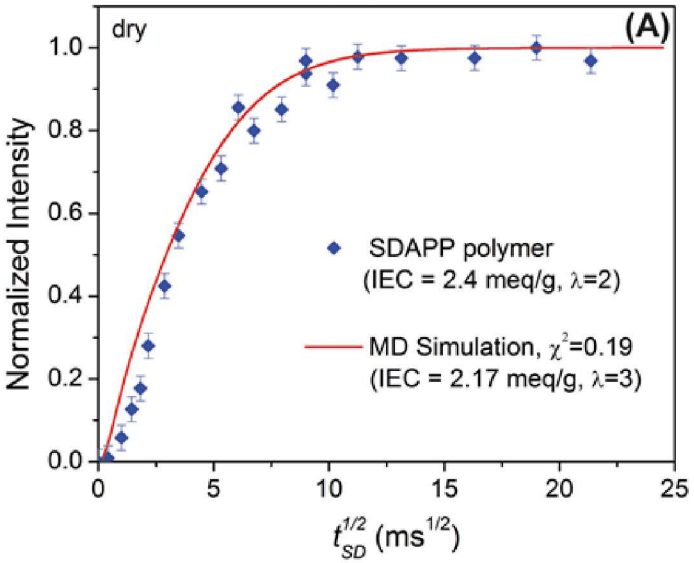
Connecting MD to Spin Diffusion Experiments

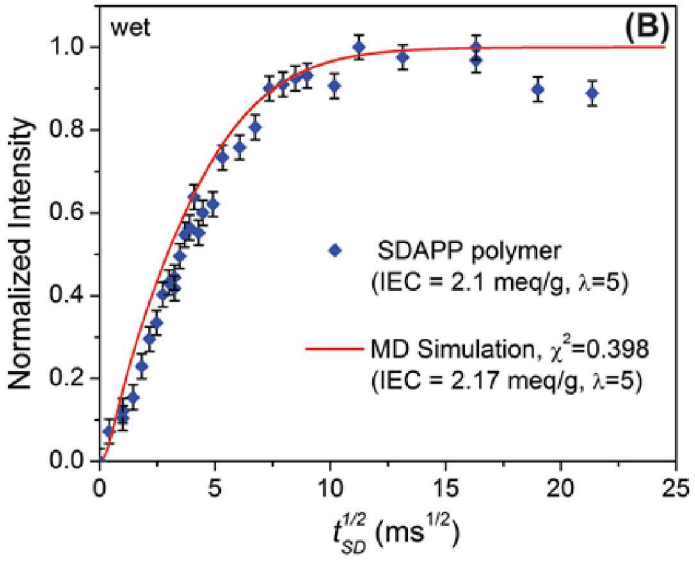


S = 2, λ = 3



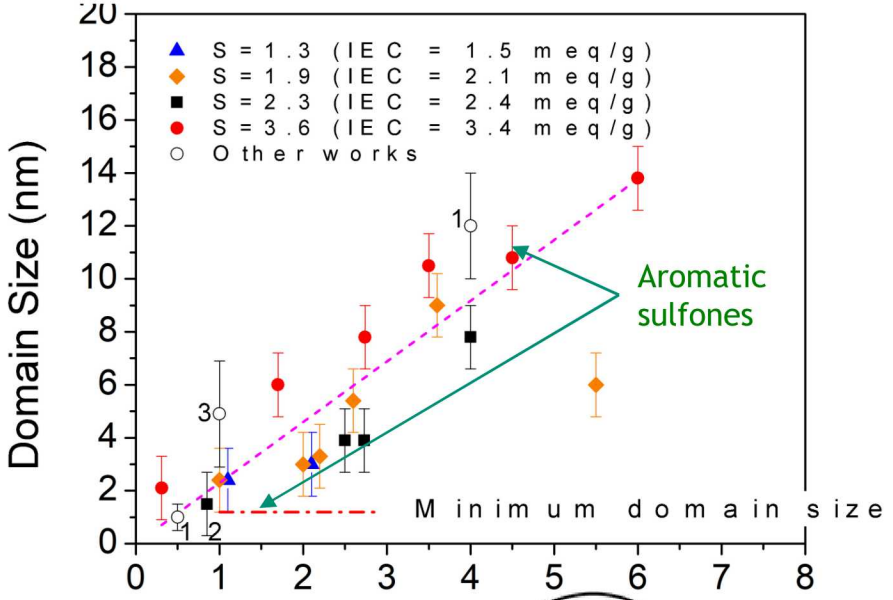
S = 2, λ = 5

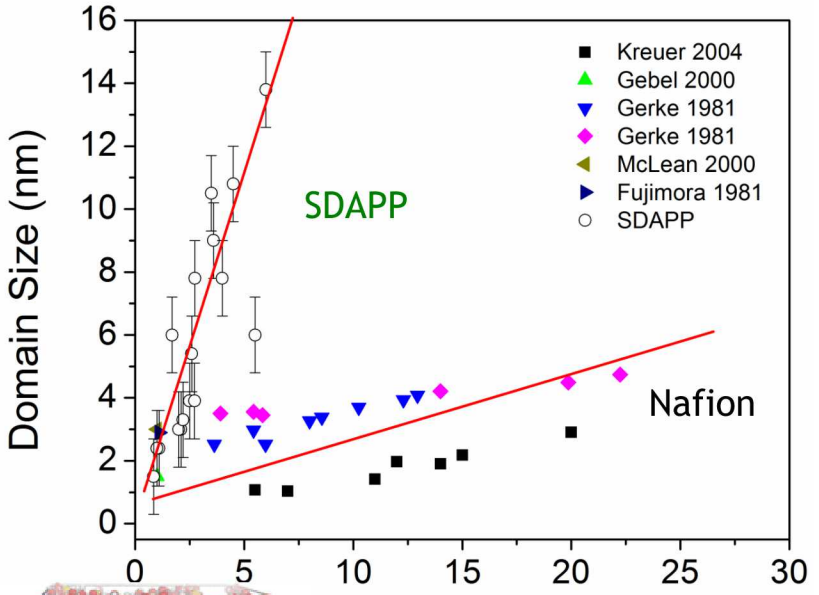


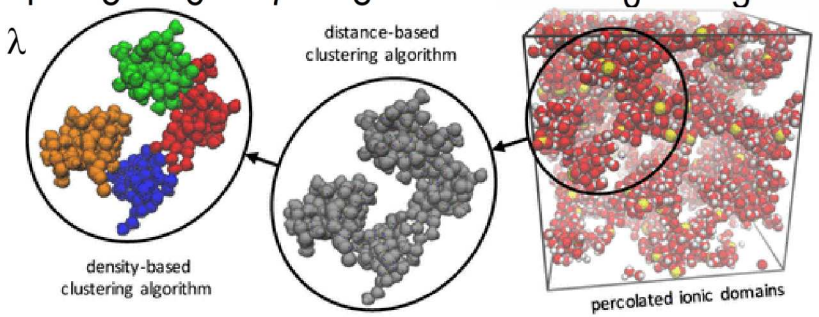


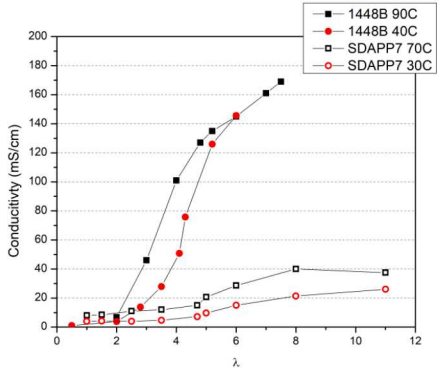
- MD structure (morphology from simulation)
- Spin diffusion constants (from line width), volume fractions, etc. are fixed.
- No adjustable parameters in these fits!!!!
- Deviations at higher hydration levels [finite simulation size? NMR relaxation?]

Estimation of Domain Size with Hydration





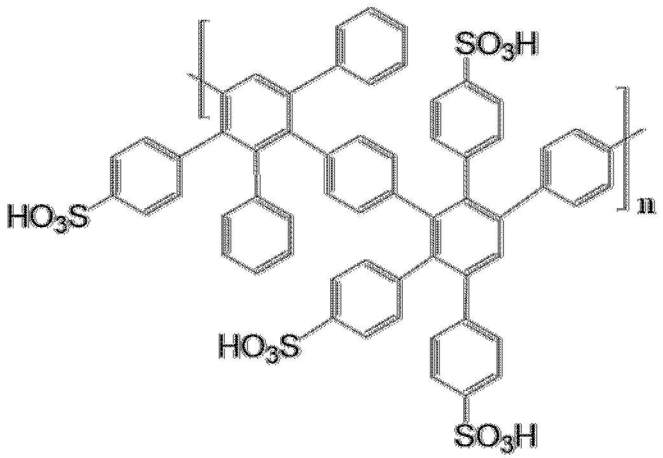




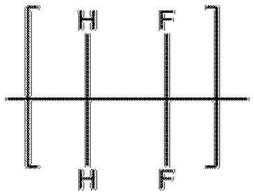
- Continuous variation with hydration level (factor of ~7).
- Domain size larger than Nafion. Is this a function of method?
- NMR spin diffusion reflects distance description of the MD hydrophilic domain.
- NMR spin diffusion does not provide details of shape or anisotropy!

Blends and Copolymers – Measuring Domain Size?

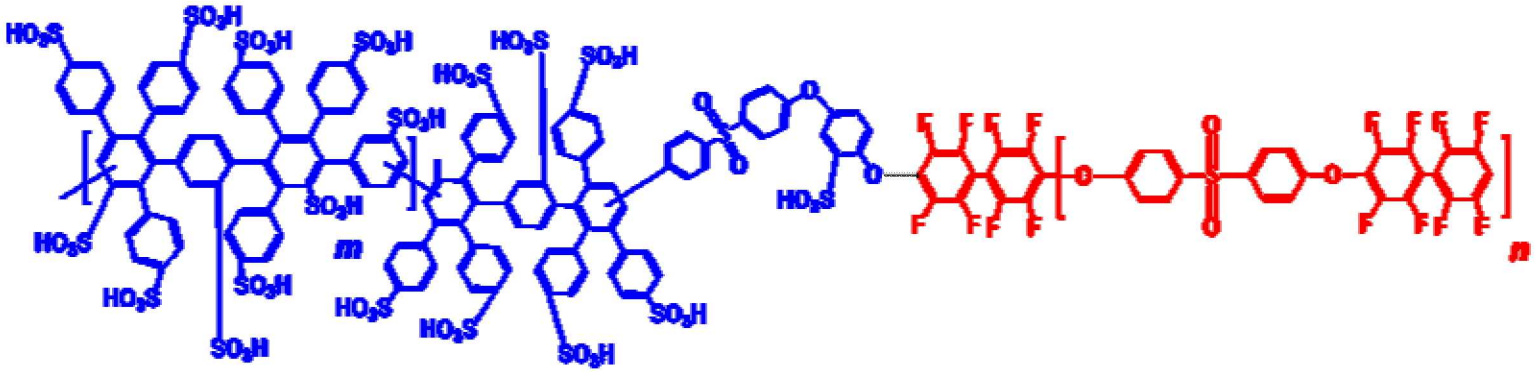
SDAPP



PVDF

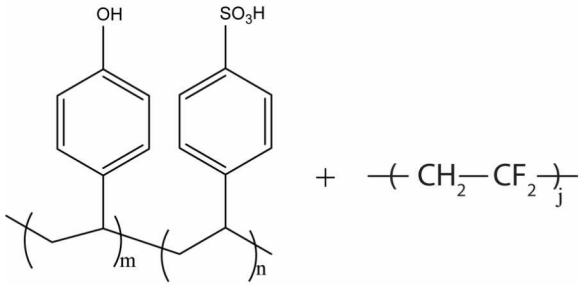


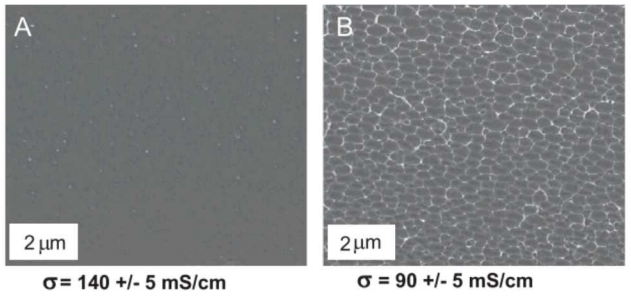
SDAPP-FDPS Copolymers

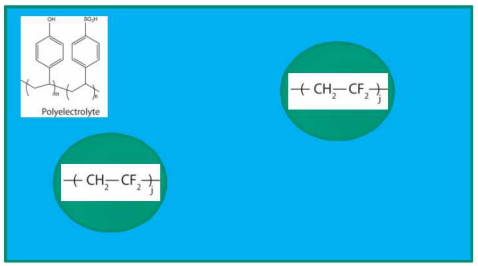


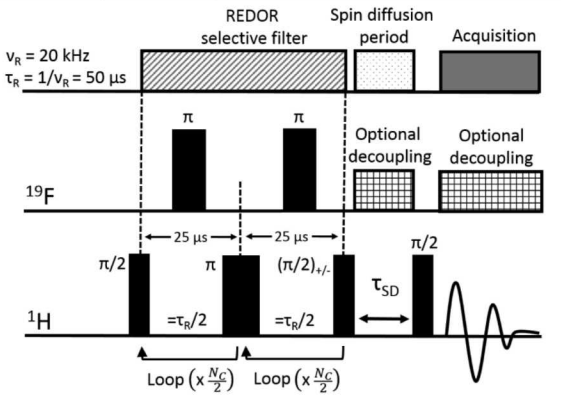
In original copolymers no domain resolution by relaxation-filters.

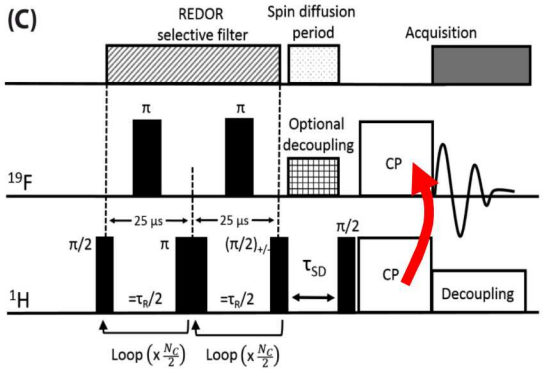
^{1}H detected - ^{19}F REDOR Filtered Spin Diffusion

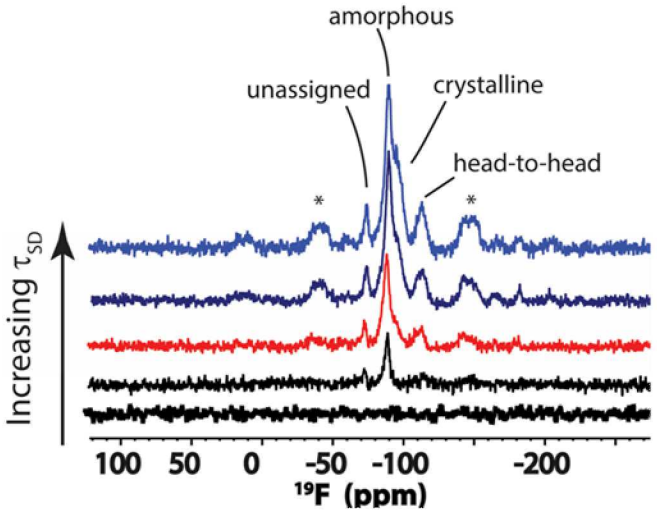


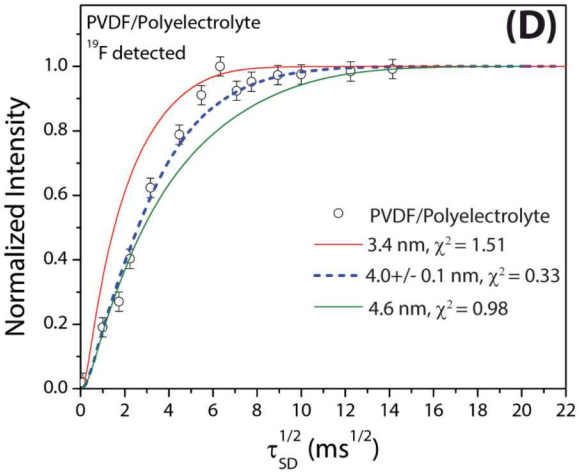










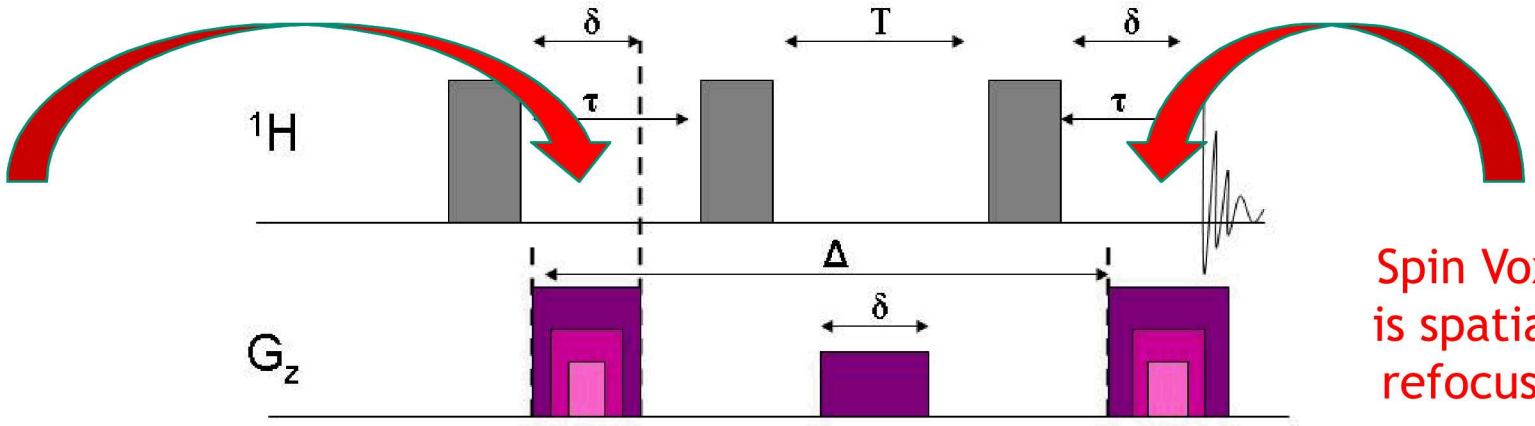


Eric G. Sorte and Todd M. Alam TM, "^{1}H-^{19}F REDOR-Filtered NMR Spin Diffusion Measurements of Domain Size in Heterogeneous Polymers" *Magn. Reson. Chem.*, 1-9 (2017). https://doi.org/10.1002/mrc.4623

NMR Diffusometry - Pulsed Field Gradient (PFG) NMR

Stimulated Echo (STE)

Spin Voxel is spatially "tagged"



Spin Voxel is spatially refocused

Signal decay is measured by:

$$S(T+2\tau_1) = \frac{M_0}{2}\exp(-2\tau_1/T_2 - T/T_1)\exp\left[-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)\right]$$

Where:

- T_1 = spin-lattice relaxation time
- δ = length of gradient pulse
- g = gradient strength
- γ = gyromagnetic ratio
- T_2= spin-spin relaxation time
- Δ= inter pulse delay
- D= diffusion constant
- τ, T: inter-pulse spacing

Pulse Field Gradient (PFG) NMR provides one method for characterizing the self-diffusion transport of species within the membrane.

Conductivity and Diffusion

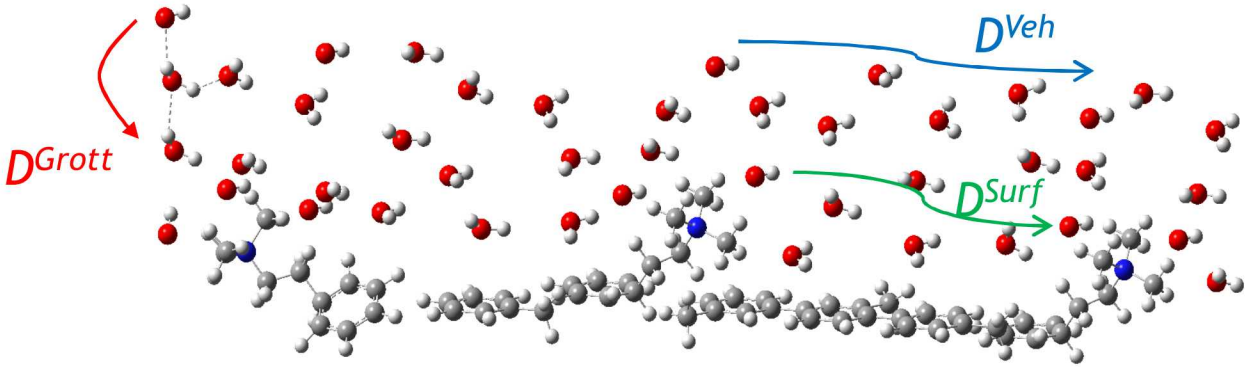
Nernst-Einstein Equation

$$\sigma = \frac{F^2 c\left(D_+ + D_-\right)}{RT} \xrightarrow{\text{Only involves } H^+ \text{ (or } OH^-\text{)}} \sigma = \frac{F^2 c\left(D_+\right)}{RT}$$

Surface Grotthuss Vehicular

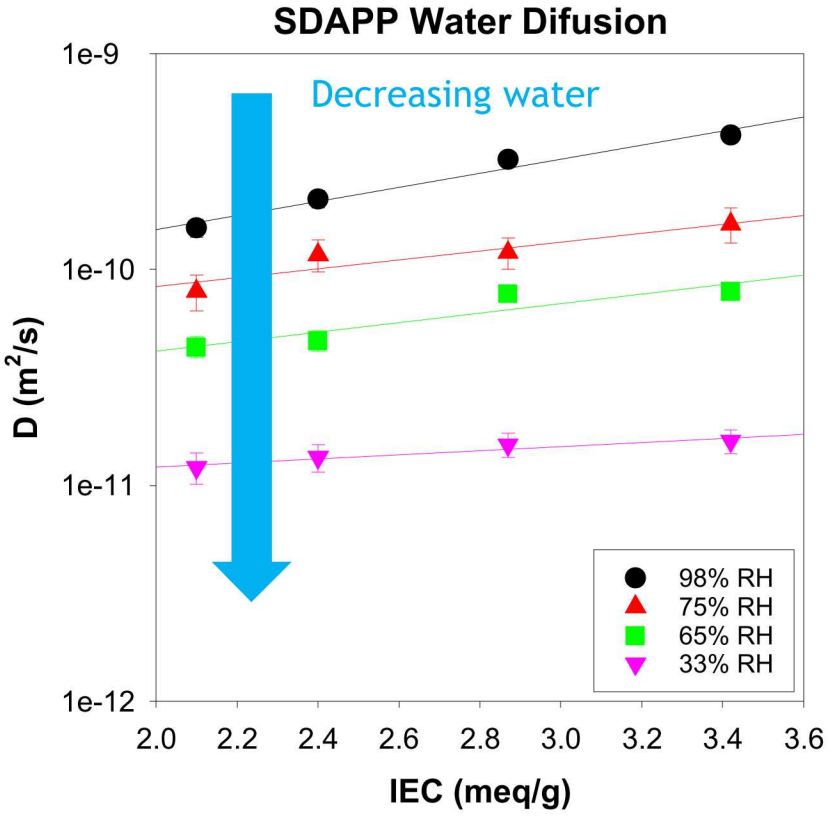
$$\sigma = \frac{F^2}{RT}\left(D_{H^+}^{Surf} C_{H^+}^{Surf} + D_{H^+}^{Grott} C_{H^+}^{Grott} + D_{H^+}^{Veh} C_{H^+}^{Veh}\right)$$

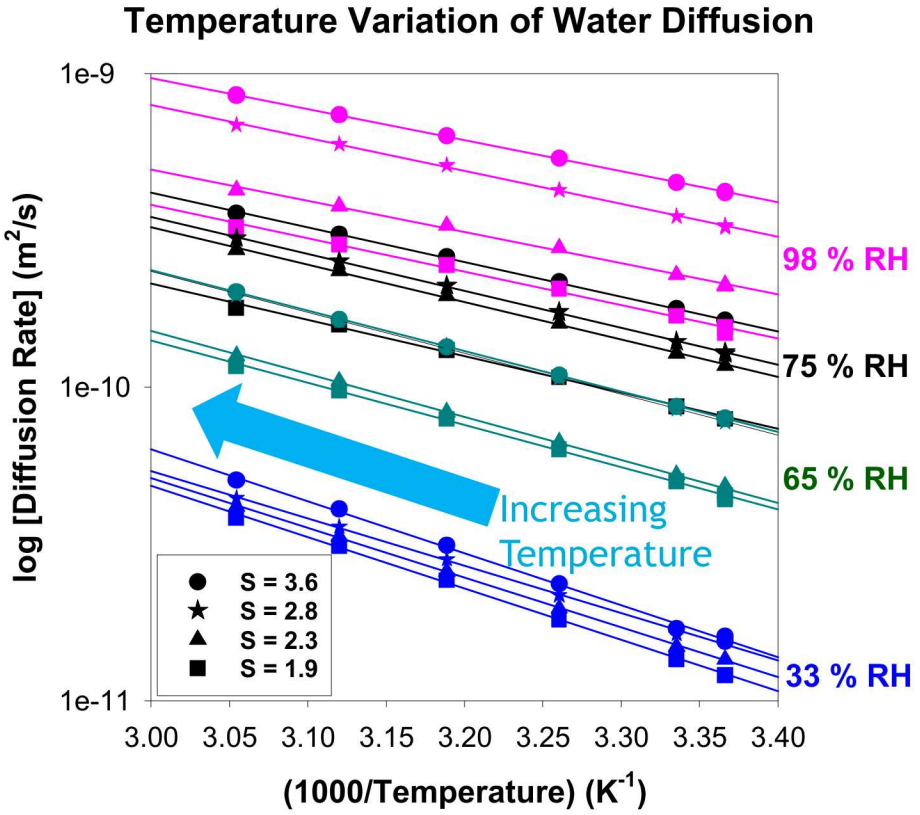
The transport of H^+ in PEMs can also be discussed in terms of different diffusion environments.



If we can measure diffusion individually, we can evaluate different contributions.

NMR Diffusometry - SDAPP Membranes





Sample	E_a (kJ/mol)			
	33%	65%	75%	98%
S = 1.9	31.3	25.8	22.2	20.4
S = 2.3	30.4	26.4	22.9	19.1
S = 2.8	29.0	24.7	22.6	20.1
S = 3.6	31.8	24.7	21.1	19.0

- E_a similar to other PEMs at higher hydration levels.
- At < 33% RH increasing E_a.
- PFG NMR not obtainable at very low RH%

SDAPP Conductivity from Diffusivity

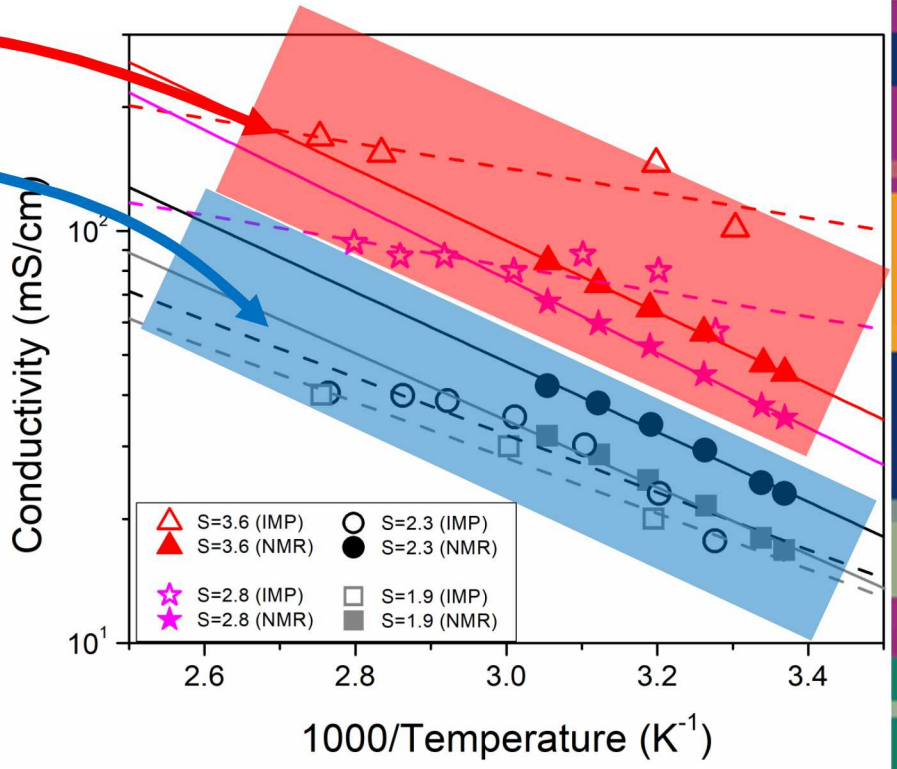
Nernst-Einstein Equation

$$\sigma = \frac{F^2 c\left(D_{H^+}\right)}{RT} \Leftrightarrow \sigma_{NMR} = \frac{F^2 c\left(D_{PFG}\right)}{RT}$$

Grotthuss Vehicular

$$\sigma = \frac{F^2}{RT}\left(D_{H^+}^{Grott} C_{H^+}^{Grott} + D_{H^+}^{Veh} C_{H^+}^{Veh}\right)$$

$$\sigma(T) = \frac{F^2 C_{H^+}}{RT}\left[D_0^{Grott} \exp\left(-E_a^{Grott} / RT\right) + D_0^{Veh} \exp\left(-E_a^{Veh} / RT\right)\right]$$



- At low-moderate Sulfonation (S) proton conductivity controlled by water vehicular transport.
- With increasing S, Grotthuss mechanism becomes significant and leads to increased conductivity beyond water simple diffusion.
- Activation energies diverge because these are different physical processes dominating.
- Membrane design rule strive for the highest D^{veh}, but H^+ requires an environment (reduced hydrogen bond strength) allowing Grotthuss hopping.

Acknowledgements

- ★ Dr. Amalie Frischknecht (SNL) - MD Simulations
  Prof. Janelle Jenkins (Prof. at E. Washington Univ.)
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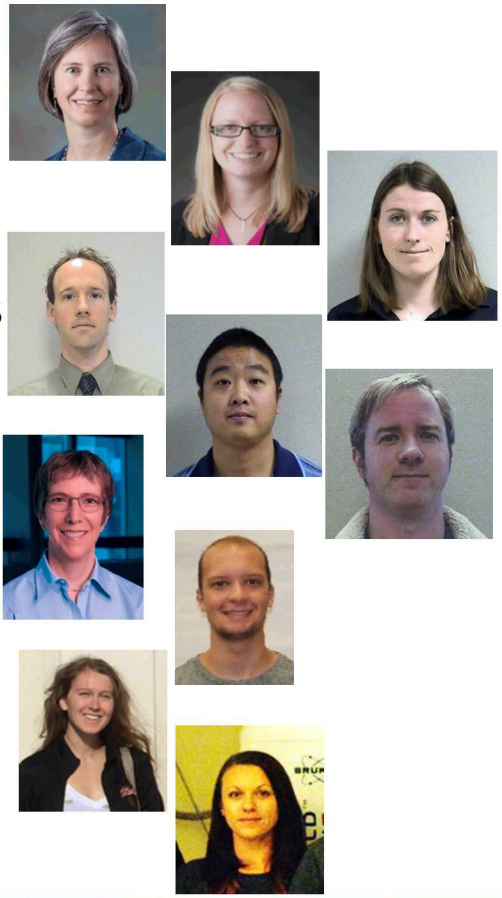
  Dr. Michael Hibbs (SNL) - AEM Synthesis

  Prof. Karen Whiney (Univ. of Penn)
  Ben Paren (Graduate Student, U. Penn)

  Kim Childress (Graduate Student, UC-Boulder)
  Randi Miller (NMR Technician)



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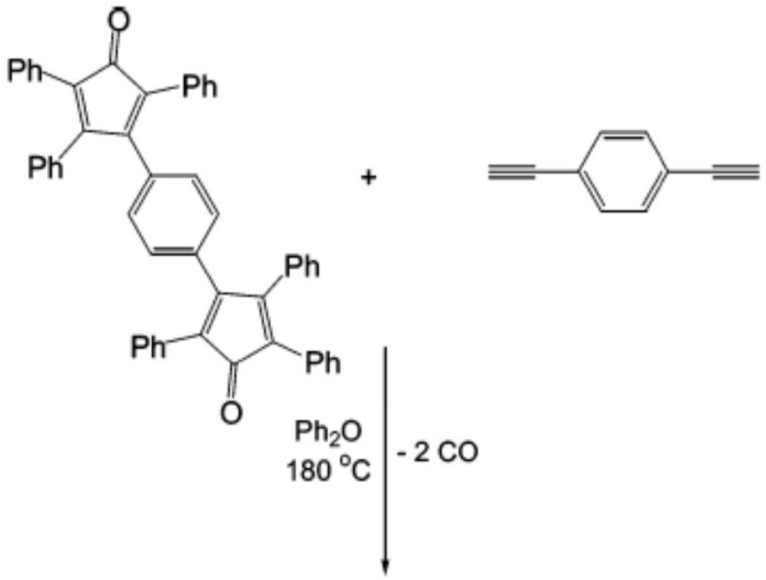
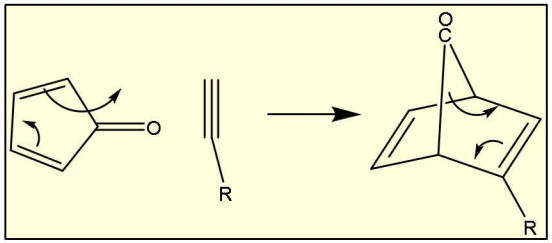
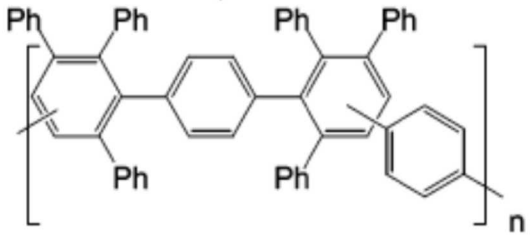
Backup Slides

Diels Alder Polymerization





Poly(phenylene)



DAPP

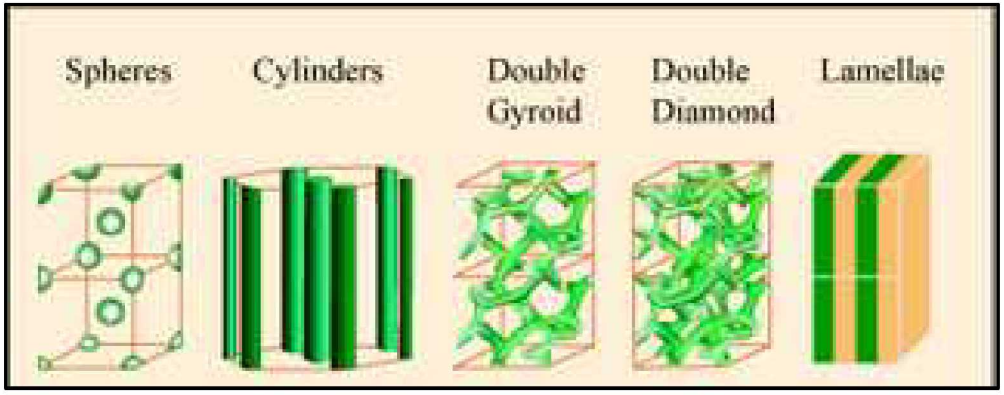
sulfonation

SDAPP

Nanoscale Morphology Impacts Design Principals for Improved Performance of Hydrocarbon Based PEMs

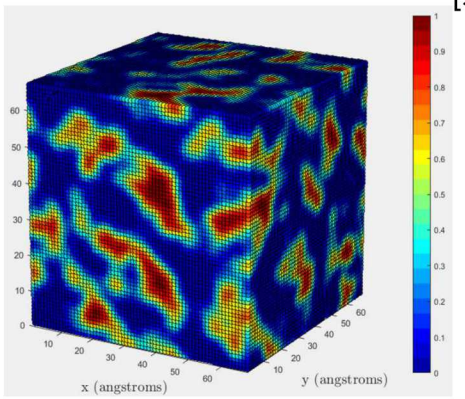
II. Morphology Control is Essential (Gross, 2009)

- Produce morphologies that provide percolation/transport pathways.
- Bicontinuous/random morphologies with numerous contacts between hydrophilic domains.
- Positional dependent diffusion constant (PDDC).
- Anisotropic directional alignment added benefit.



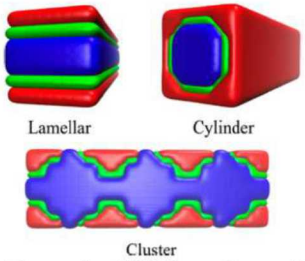
[1]

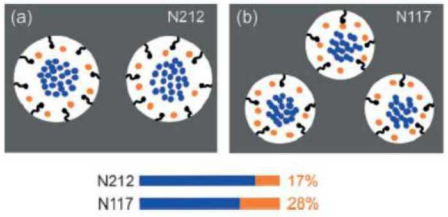
[2]



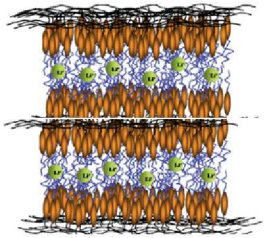
[3]

[5]



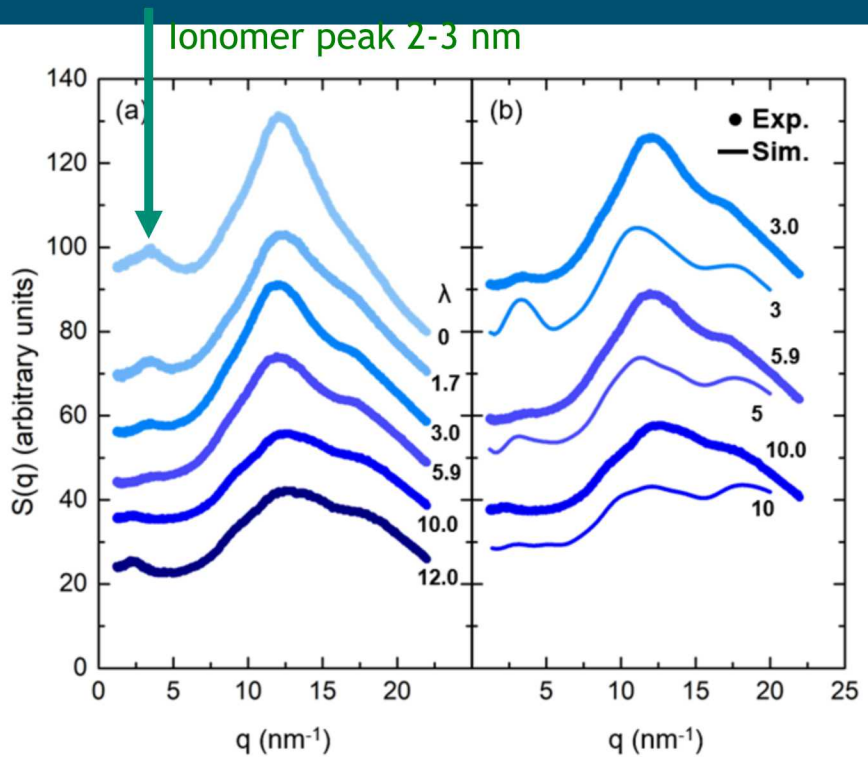


[4]

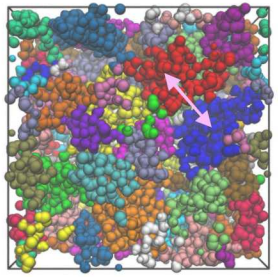


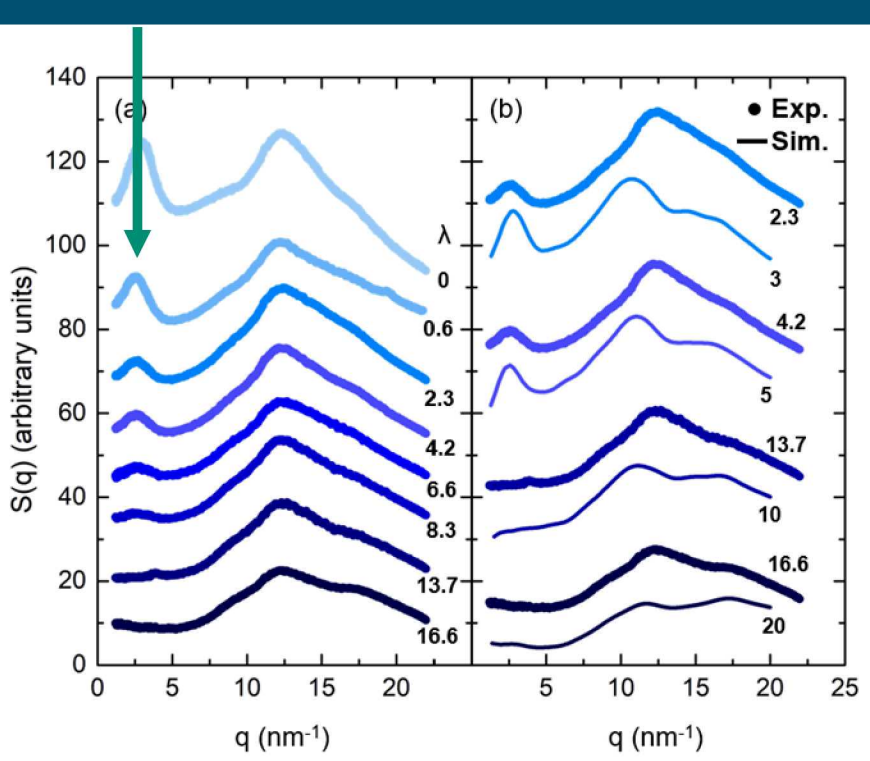
[1] Prof. Thomas, Figure by MIT OpenCourseWare. [2] Liu, S.; Savage, J.; Voth, G. A., Mesoscale Study of Proton Transport in Proton Exchange Membranes: Role of Morphology. The Journal of Physical Chemistry C 2015, 119 (4), 1753-1762. [3] Lauren J. Abbott and Amalie L. Frischknecht,"Nanoscale Structure and Morphology of Sulfonated Polyphenylenes via Atomistic Simulations" *Macromolecules 2017, 50(3), 1184-1192*. [4] Ling, X.; Bonn, M.; Parekh, S. H.; Domke, K. F., Nanoscale Distribution of Sulfonic Acid Groups Determines Structure and Binding of Water in Nafion Membranes. Angewandte Chemie International Edition 2016, 55 (12), 4011-4015. [5] P. W. Majewski *et al.*, "Anisotropic Ionic Conductivity in Block Copolymer Membranes by Magnetic Field Alignment" (2010), J. Am. Chem. Soc., 132, 17516-17522.

X-Ray Scattering

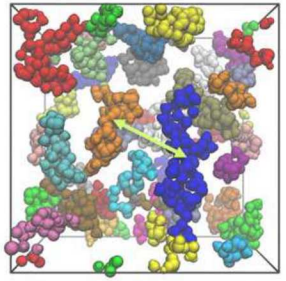


14-48B (S=3.6) versus S=4 (MD)



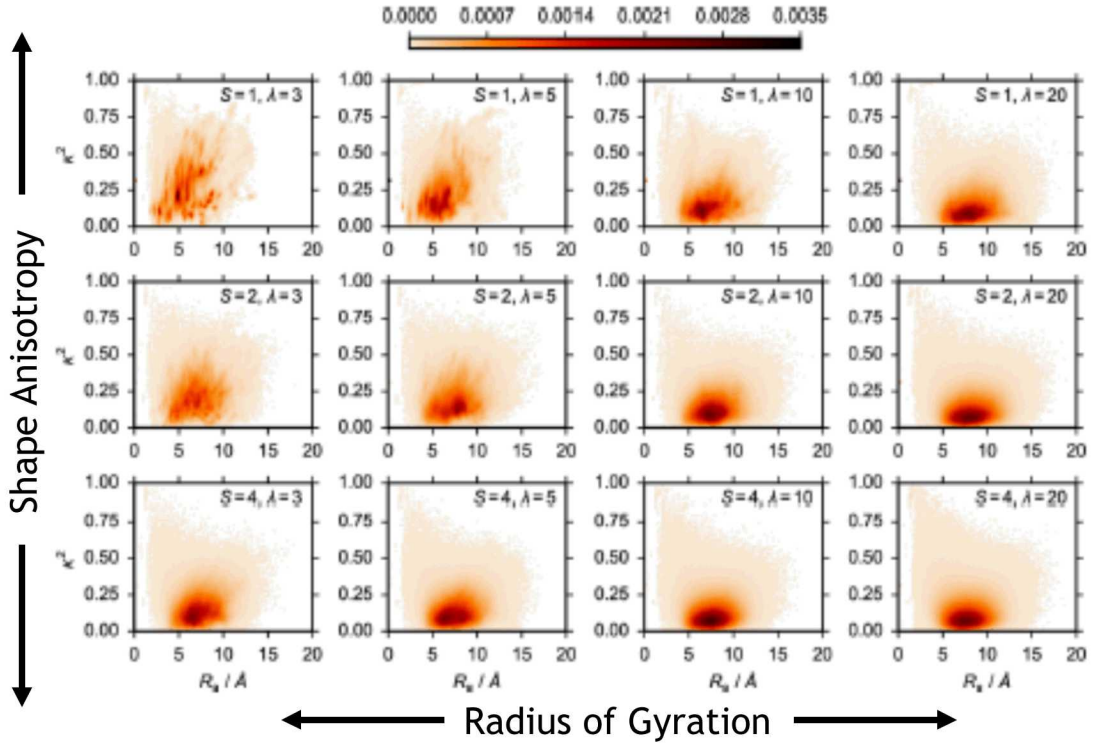


SDAPP7 (S=2.3) versus S=2 (MD)

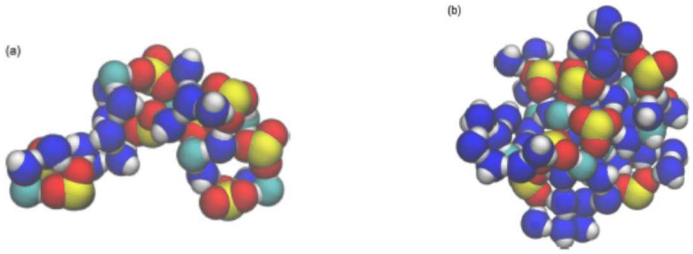


What additional information can be obtained about the hydrophilic domains?

SDAPP Molecular (MD) Simulations



- At low sulfonation (S) and hydration (λ) levels, the ionic clusters elongated in shape and poorly connected.
- The sulfonate groups became more hydrated at higher S and λ, producing more solvated contact ion pairs (CIPs).
- These changes are predicted to produce improved proton transport.



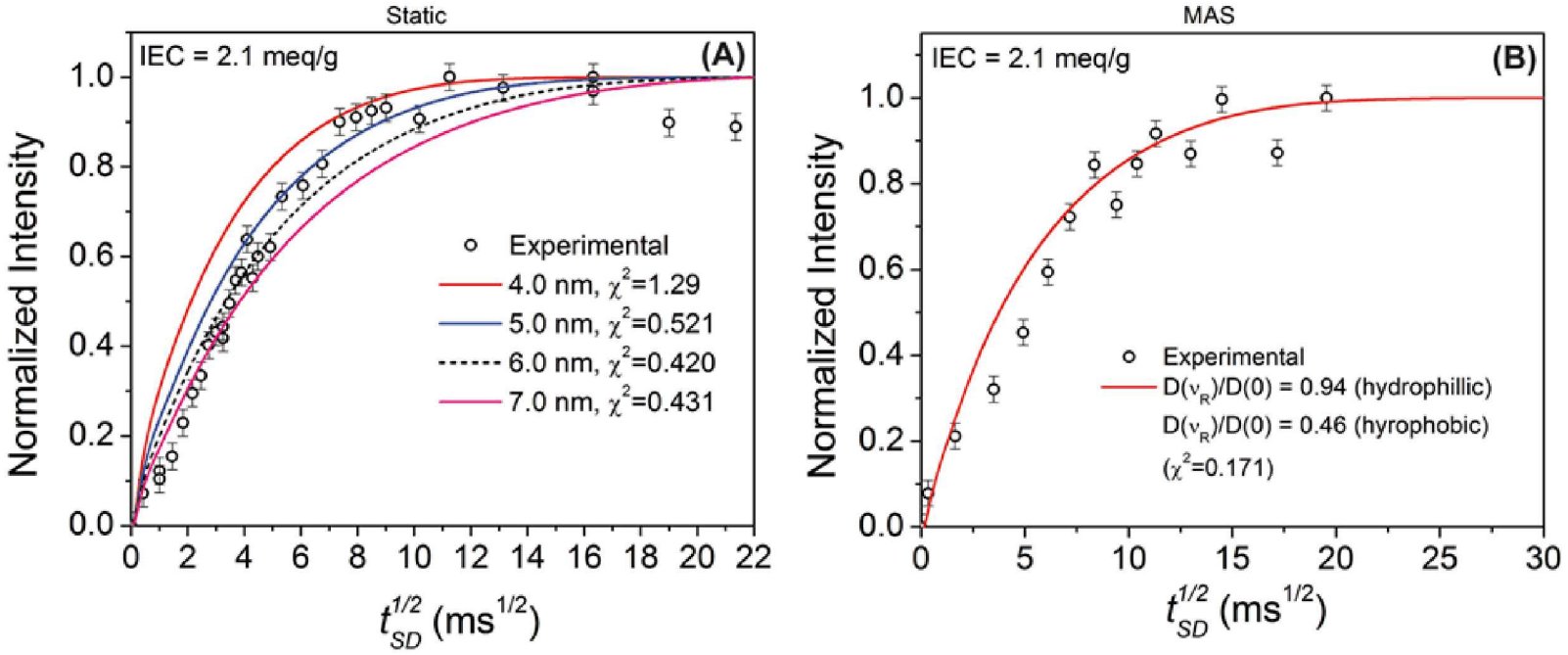
Can we obtain experimental verification of these proposed domain structures and changes in the structure with increasing hydration?

L. A. Abbott, A. Frischknecht, *Macromolecules*, 50(3), 1184-1192, **2017**.

Impact of MAS on Spin Diffusion Rates

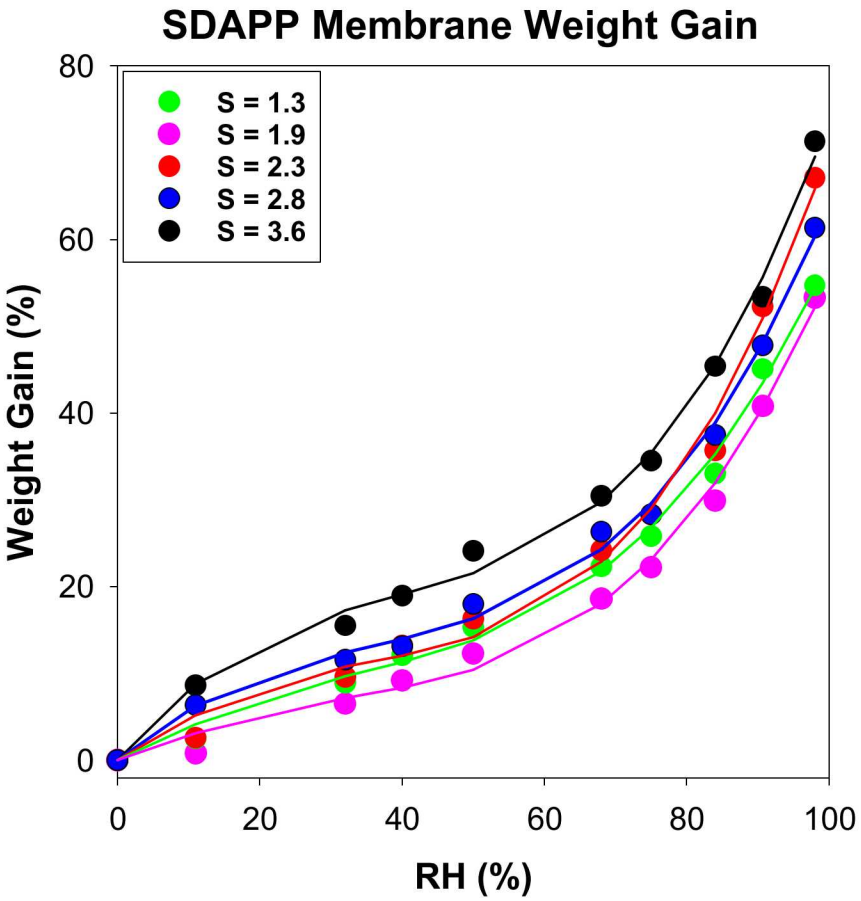
Estimate impact following the empirical argument of Jia and co-workers

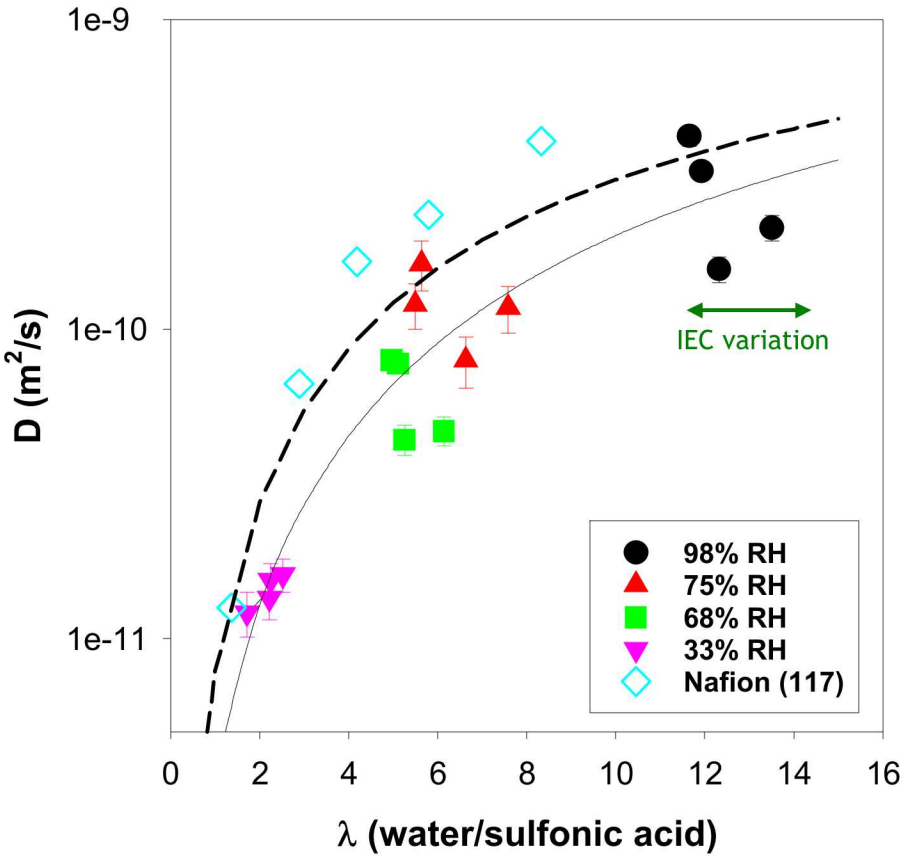
$$\frac{D(\nu_R)}{D(0)} = \tan\left[\frac{\pi}{2}\frac{D^2(\nu_R)}{D_0^2}\right]\left[\frac{1}{\tan\left[\frac{\pi}{2}\frac{D^2(0)}{D_0^2}\right]} + \frac{2\alpha\sqrt{2\ln 2}D_0\nu_R}{D(0)\Delta\nu_{1/2}^0}\right],$$



Z. Jia, L. Zhang, Q. Chen, E. Hansen, *J. Phys. Chem. A* **2008**, *112*, 1228-1233.

NMR Diffusometry - SDAPP Membranes





- Diffusion trends are same order of magnitude as Nafion.
- Small variations as a function of IEC.