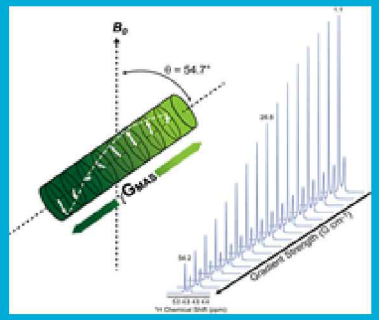
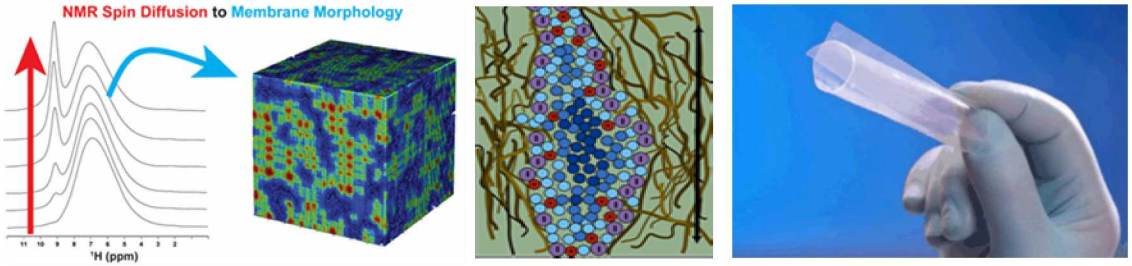
SAND2018-3005C

Probing the Hydrophilic Domain Structure and Water Transport in SDAPP Proton Exchange Membranes





American Chemical Society (ACS) National Meeting
Structure and Dynamiocs of Materials via NMR Methods
March 18th, 2018

PRESENTED BY

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Albuquerque, NM 87185

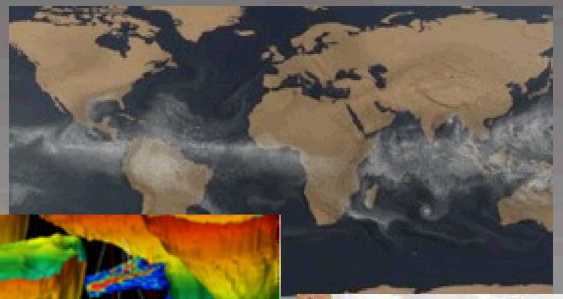
Energy at Sandia

Energy Research

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

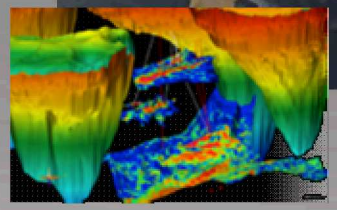
Climate & Environment

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

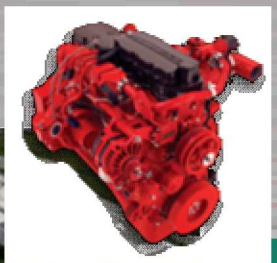


Renewable Systems & Energy Infrastructure

Renewable Energy, Energy Efficiency,
Grid and Storage Systems

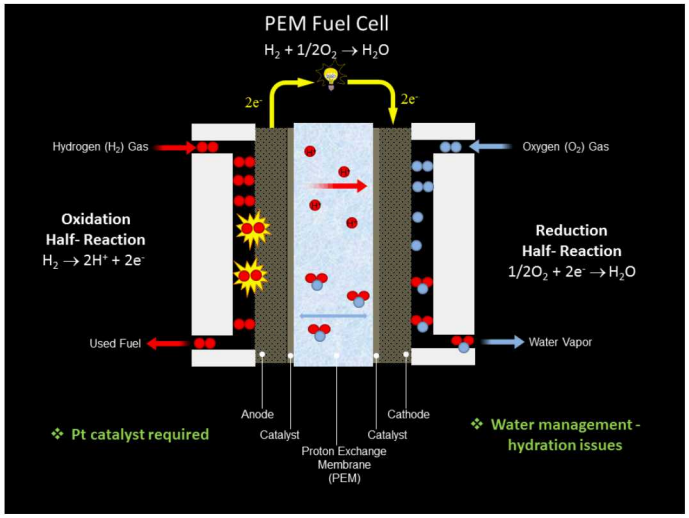
Transportation Energy & Systems

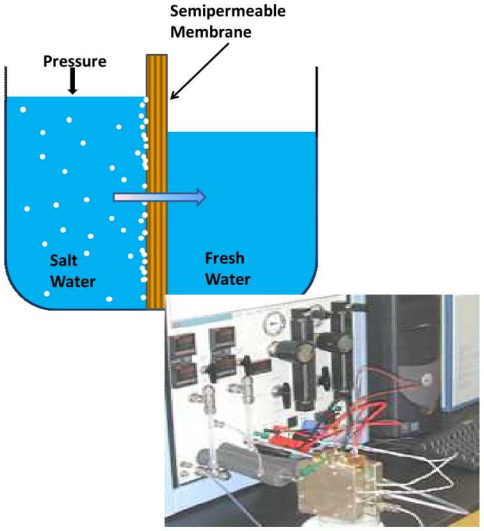
Vehicle Technologies, Biomass, Fuel Cells & Hydrogen Technology



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…"

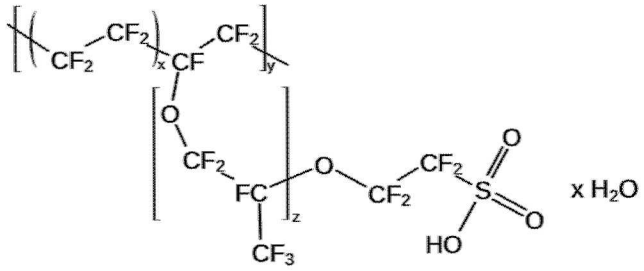
Outline

- Motivation for SDAPP
- MD Simulations of Nanomorphology
- ^{1}H MAS NMR Chemical shift – hydrogen bond stength
- NMR Diffusometry (PFG NMR)
- ^{1}H DQ-Filtered Spin Diffusion Experiments
- ^{1}H-^{19}F REDOR-Filtered Spin Diffusion Experiments

Sulfonated Diels Alder Polyphenylene (SDAPP) Membranes

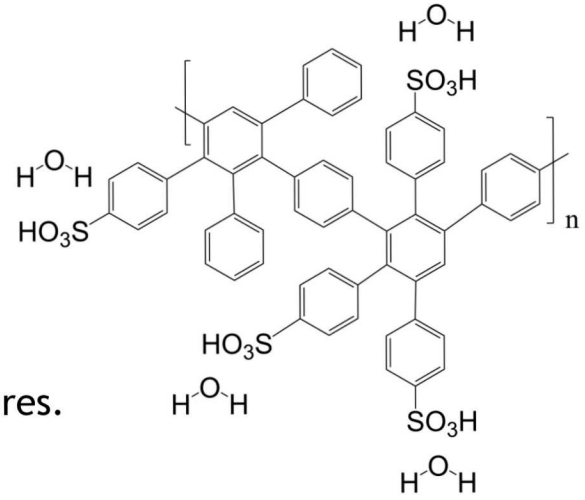
Nafion

(perfluoronated membranes)

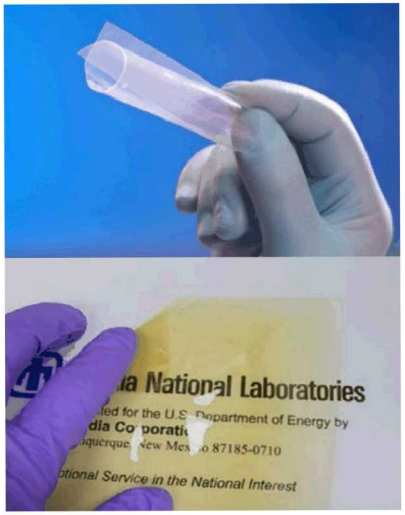


- Good conductivity at low temperatures.
- The present industry standard.

SDAPP

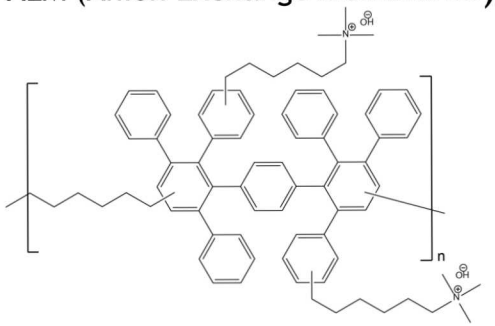


- Stable in alkaline environments.
- High T_g (~350 °C).
- Easily processed.
- Wide range of functionalities.
- Promising alternative to Nafion.
- No F (*i.e.* HF production).



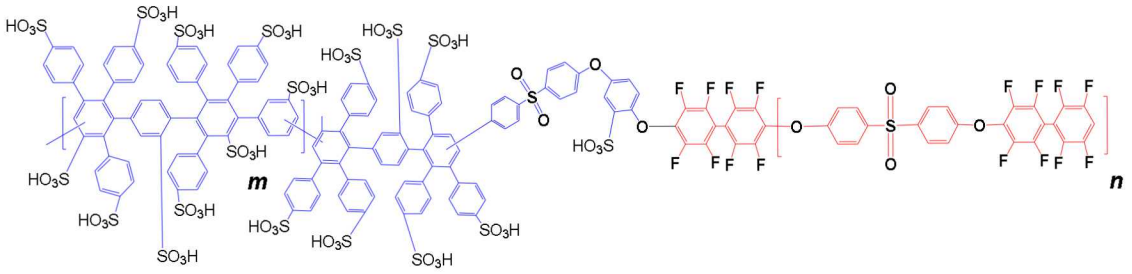
SDAPP Analogues

AEM (Anion Exchange Membranes)



MeOH fuel cell (Hibbs, SNL)

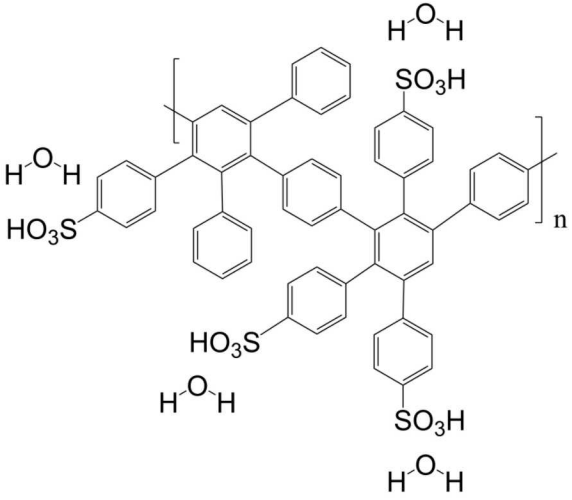
SDAPP-FDPS Copolymers

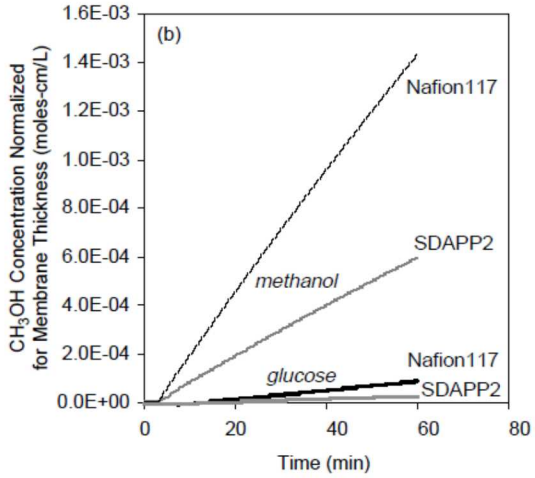


Fujimoto, C. H., Hickner, M. A., Cornelius, C. J., Loy, D. A., Macromolecules 2005, 38 (12), 5010-5016.

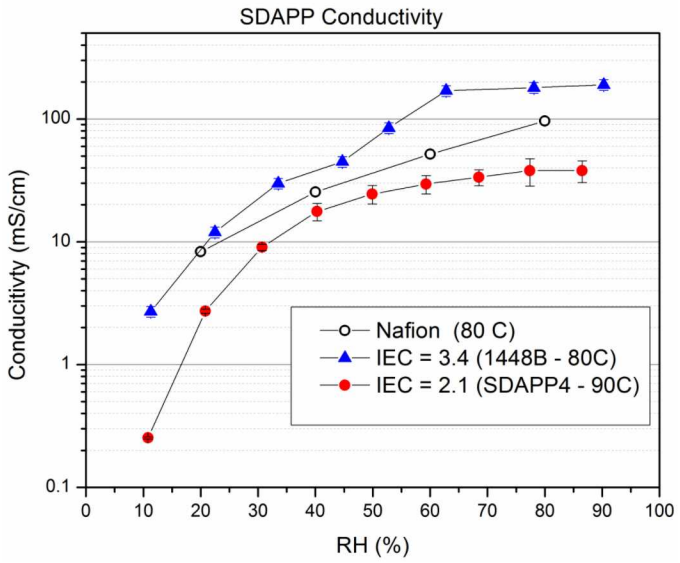
Sulfonated Diels Alder Polyphenylene (SDAPP) Membranes

SDAPP



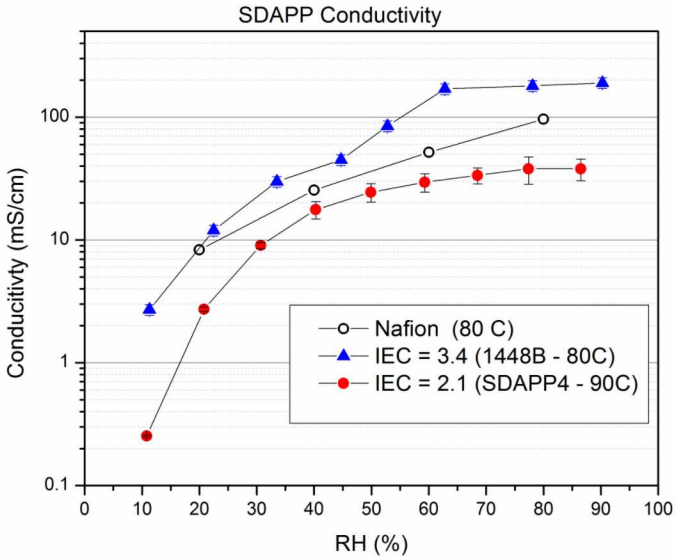


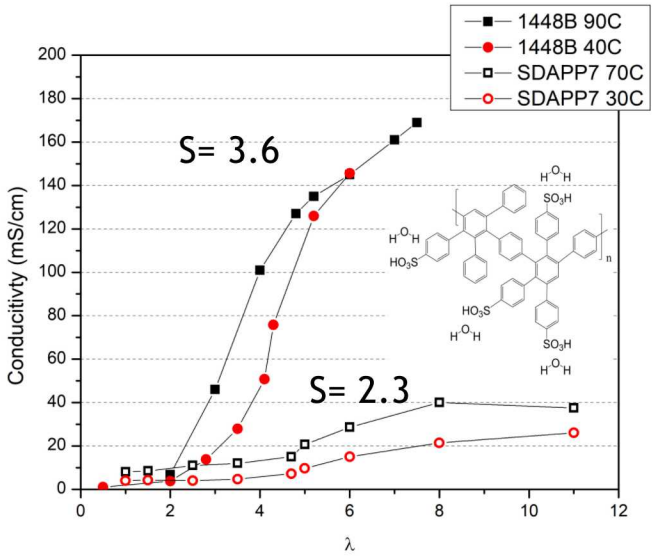
- Conductivity equal to Nafion.
- Improved fuel barrier.
- Can reach high ion exchange capacity (IEC) without solubility issues.
- Improved H conductivity over wide RH%.



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

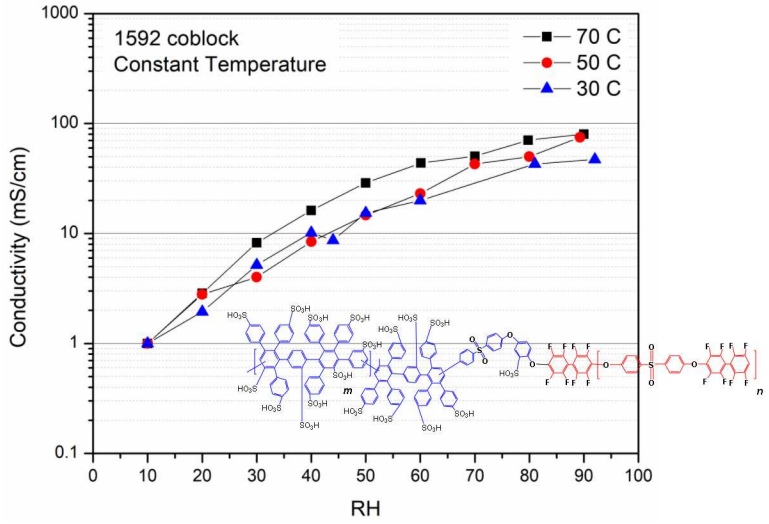
What is Controlling SDAPP Conductivity?



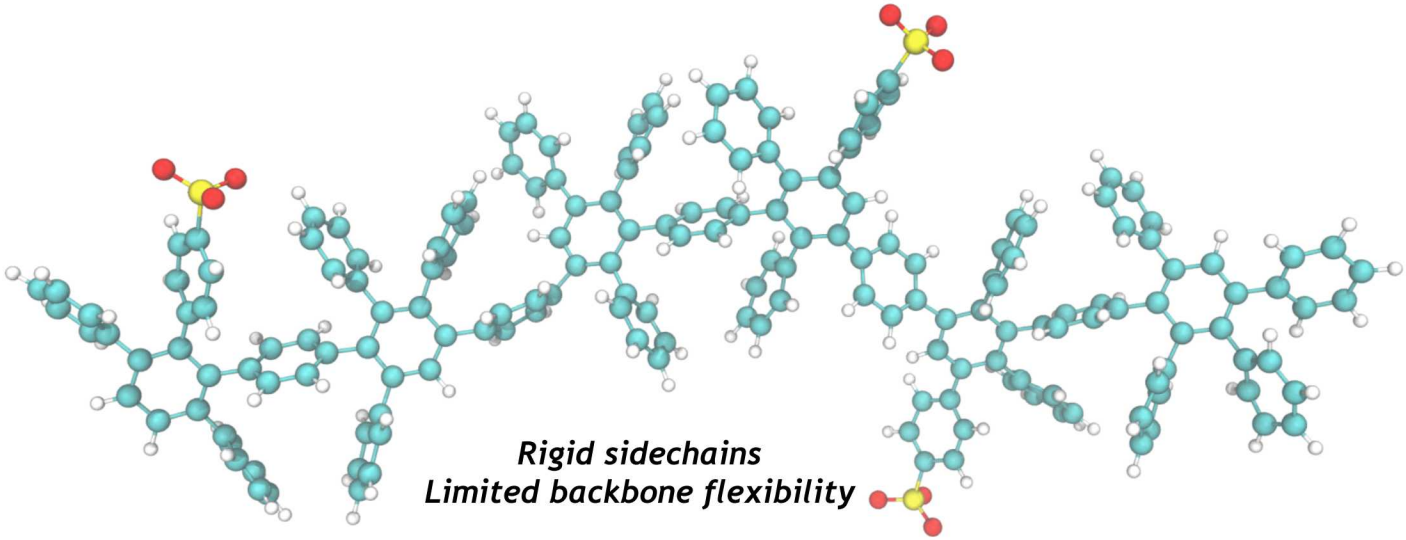


Questions we would like to answer

- Why the different conductivity versus hydration behavior with increasing sulfonation (S)?
- Why the low temperature variation in the fluorinated coblock polymer?
- Why the low conductivity temperature variations in the F coblock polymer?



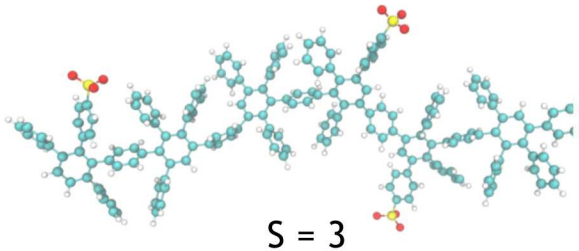
SDAPP Nanoscale Morphology Expected to be Different than Nafion



Combination of Efforts

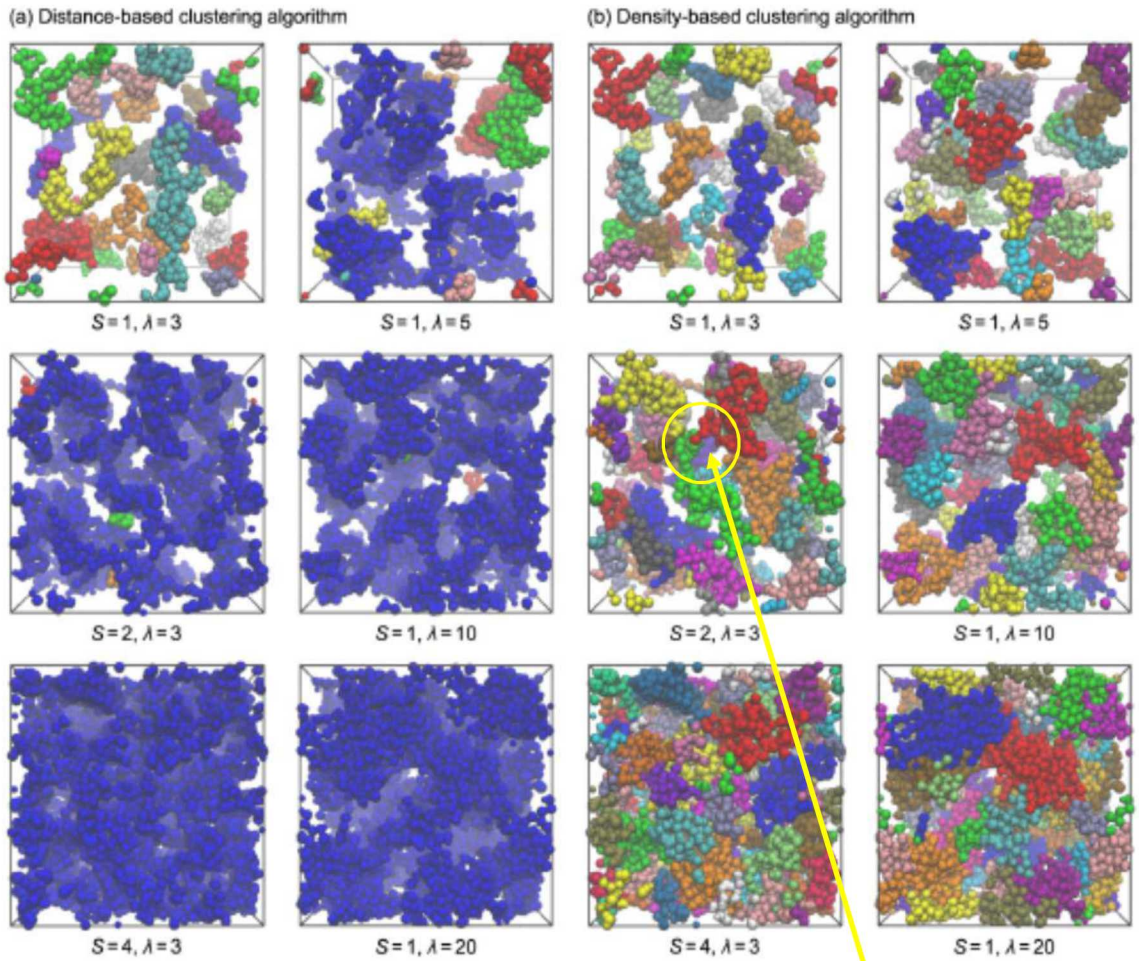
- Quantum calculation of water binding energetics.
- MD simulations of nanoscale morphology.
- X-ray Scattering of SDAPP Membranes
- NMR spin diffusion domain size measurements.
- Connecting MD and experimental NMR spin diffusion.
- NMR Diffusomtery

SDAPP Molecular (MD) Simulations



S = 3

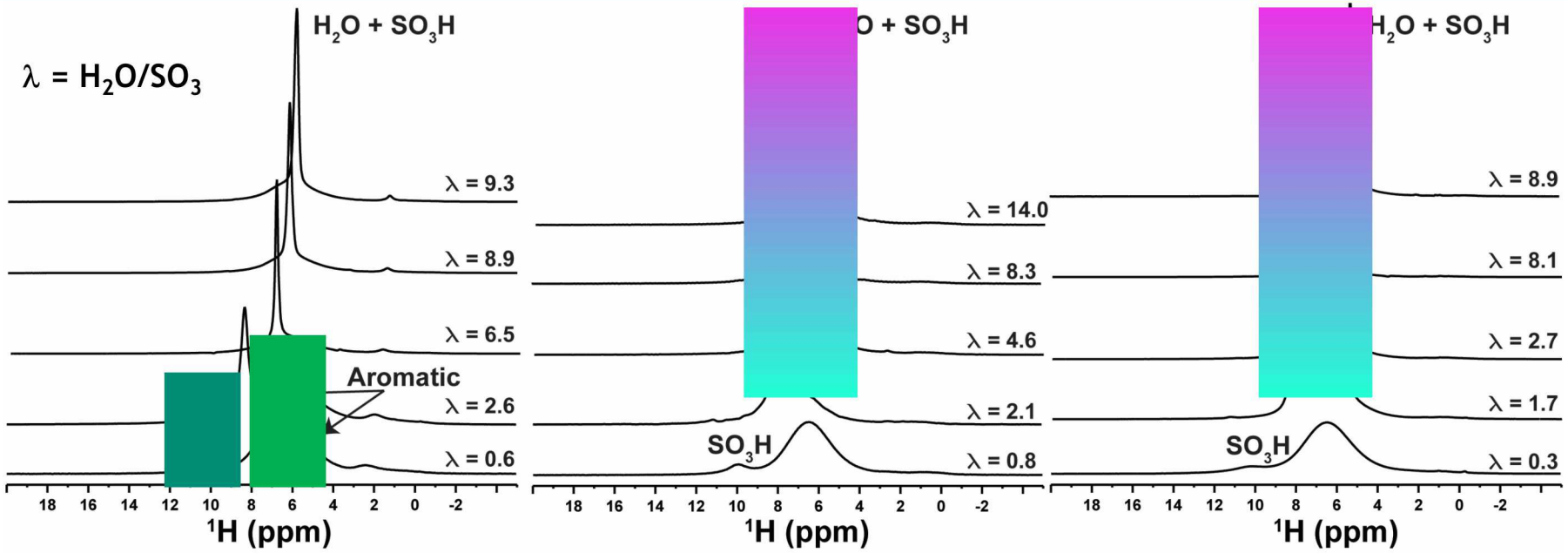
- Local structure depends on the degree of sulfonation (S) and the hydration (λ) levels.
- Cluster domain shape depends on how it is defined: distance based versus density based methods.
- Increasing S and λ resulted in larger and more spherical cluster sizes, with the formation of fully percolated ionic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

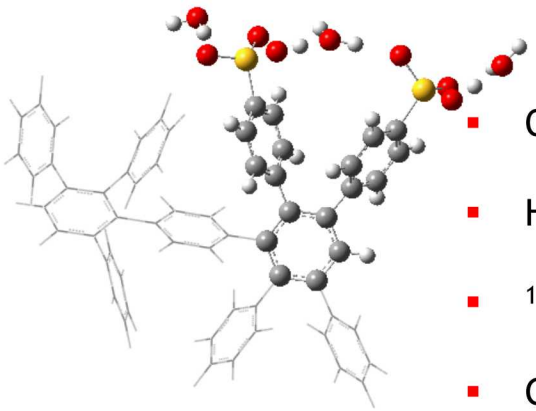


Thin connections are not considered a domain in density based algorithm.

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

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

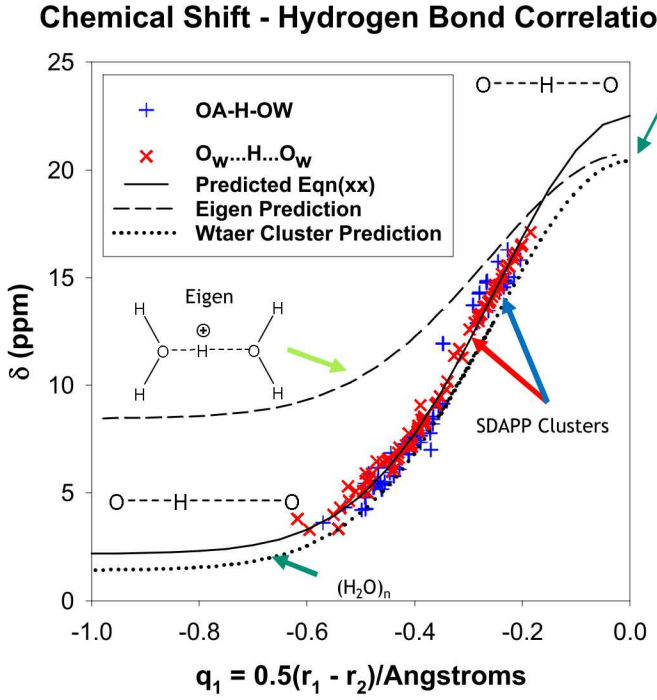


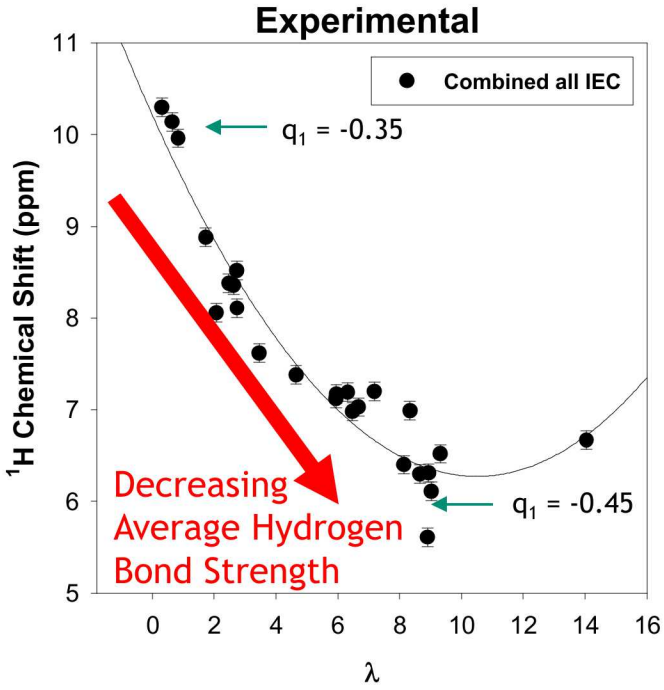


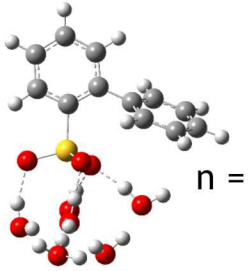
- Only 3 ^{1}H environments (aromatic, H_2O, SO_3H).
- H_2O+SO_3H in rapid exchange (single resonance)
- ^{1}H NMR chemical shift reflects relative concentration of SO_3^- coordination.
- Can chemical shift be related to “average” hydrogen bond strength?
- Similar information from IR?

Chemical Shift Hydrogen Bond Stength Correlations

$$\delta\left({}^{1}\mathrm{H}\right) = a + b\exp\left[-cq_1^2\right]$$







n = 6

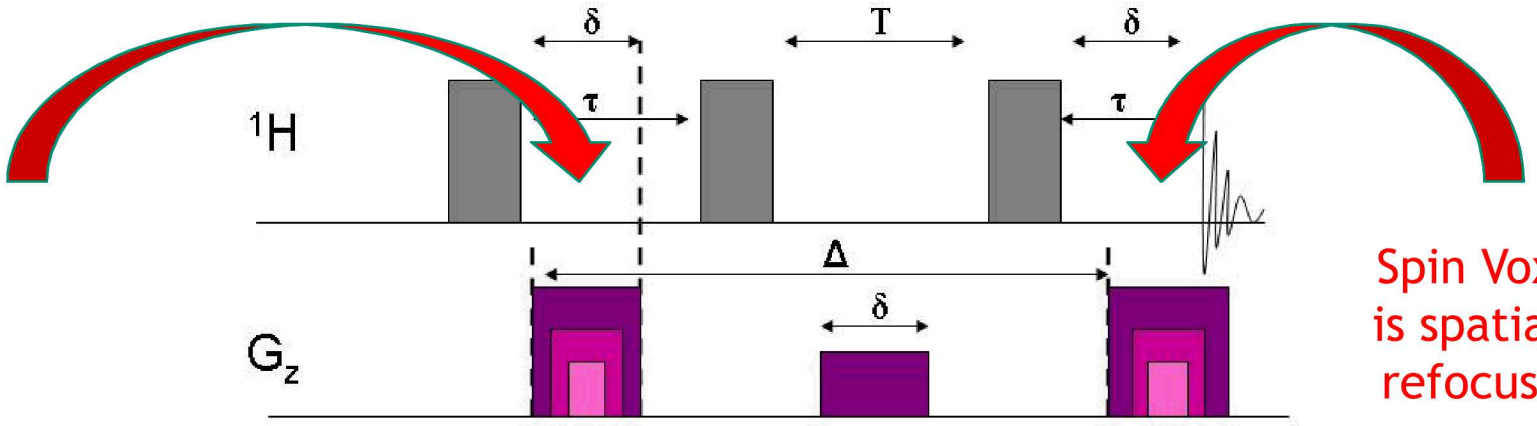
- *Ab initio* ^{1}H chemical shift calculations for all SDAPP $_n(H_2O)$ clusters (n = 1 to 6).
- Correlations follow definition of Limbach and company.
- Experimental is a dynamic average over all H environments, but provides a measure of the changing hydrogen bond strengths with hydration.
- Reduction in hydrogen bond strength → increase in Grotthuss mechanism (proton defect).

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).

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:

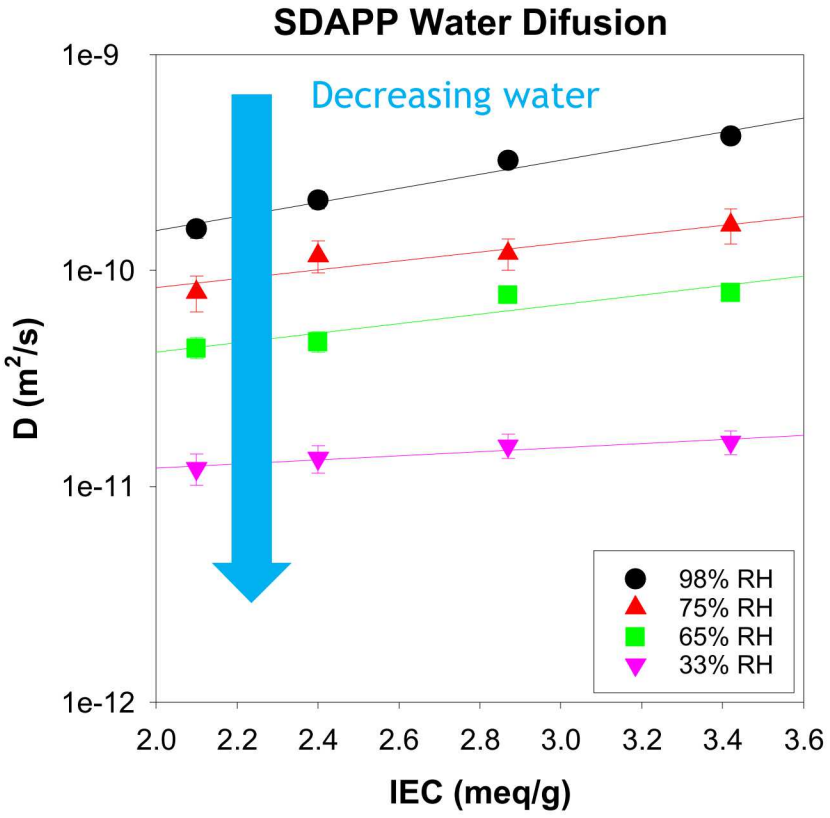
$$S(T+2\tau_1) = \frac{M_0}{2}\exp(-2\tau_1/T_2 - T/T_1)\exp\left[-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)\right]$$

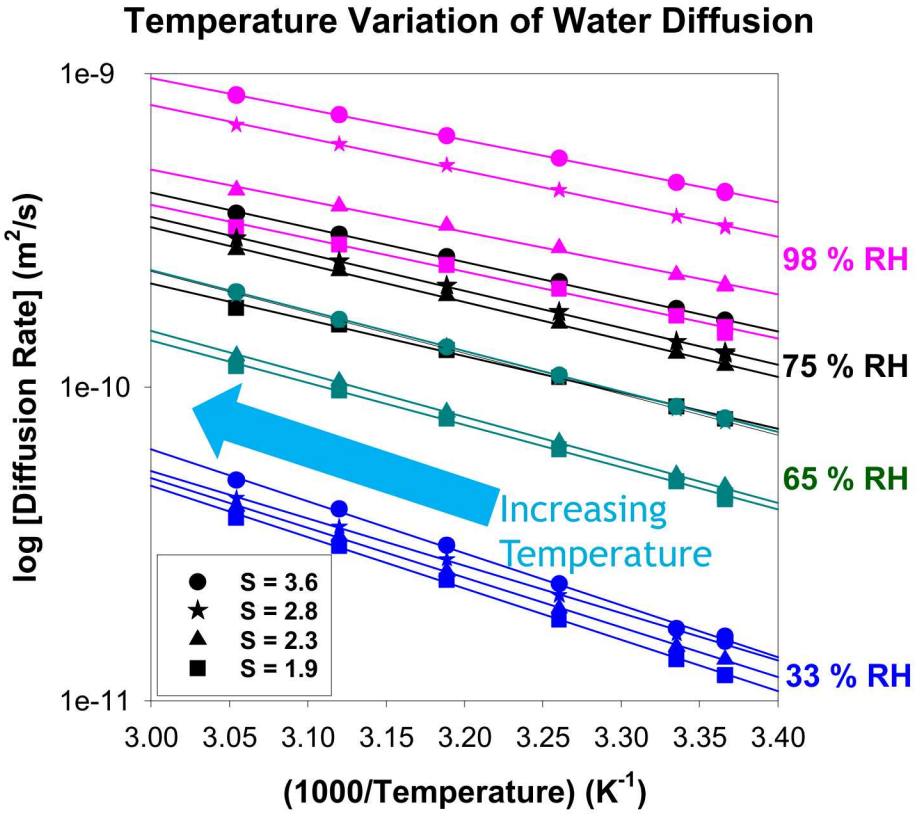
Where:

- 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.

NMR Diffusometry - SDAPP Membranes

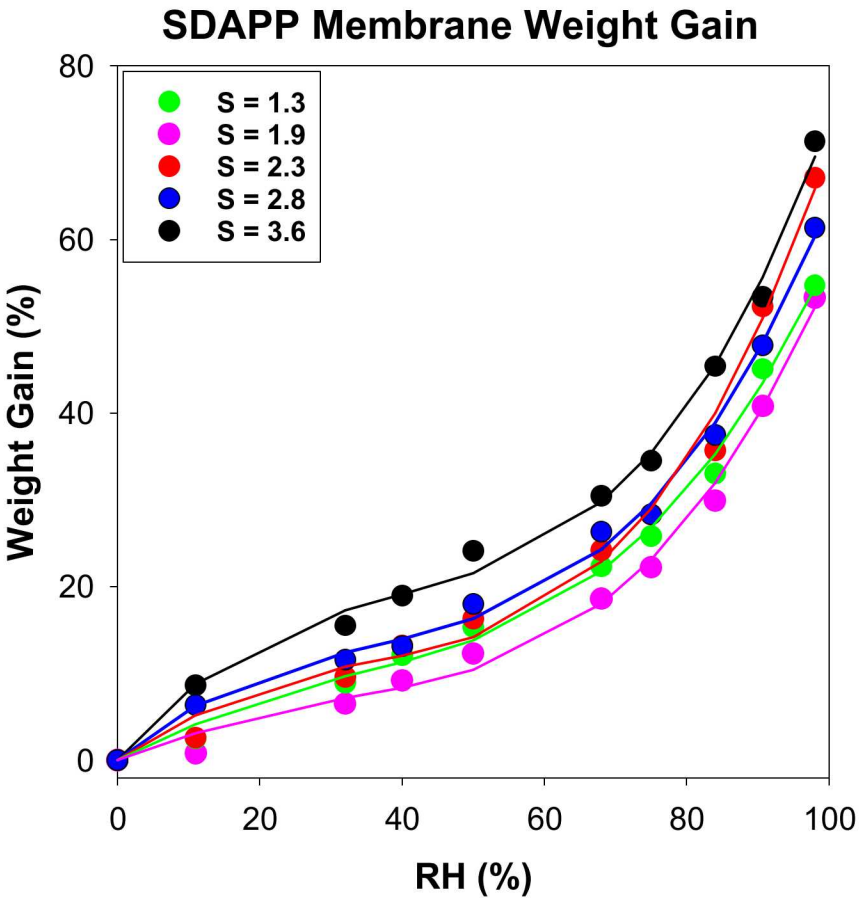


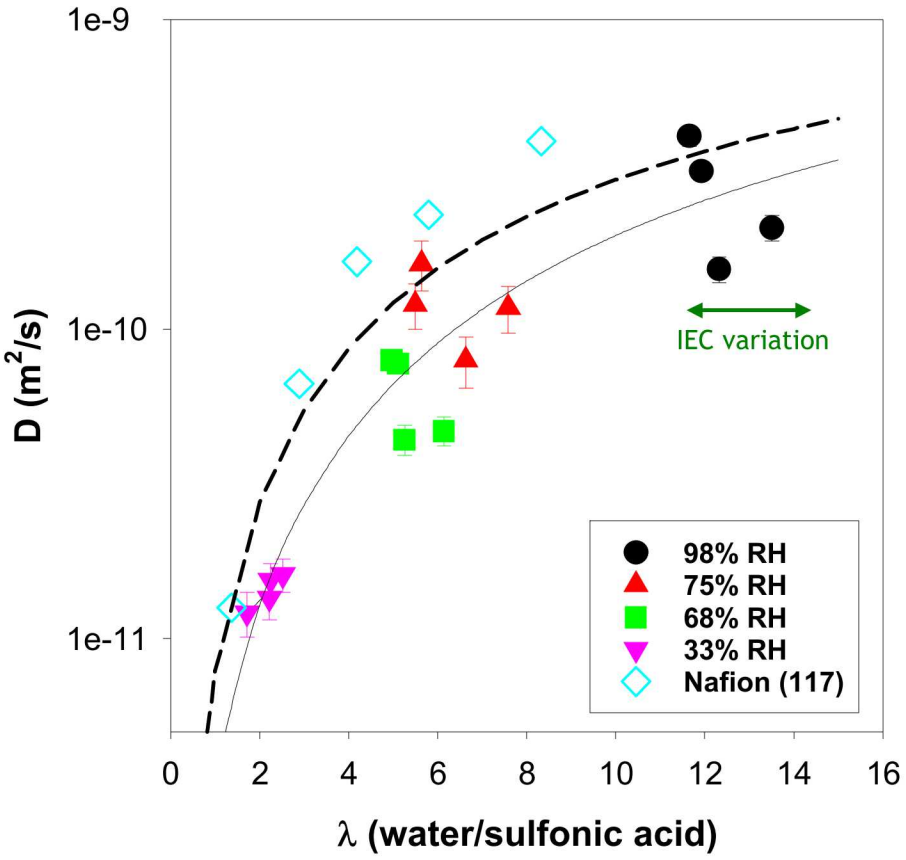


Sample	E_a (kJ/mol)			
	33%	65%	75%	98%
S = 1.9	31.3	25.8	22.2	20.4
S = 2.3	30.4	26.4	22.9	19.1
S = 2.8	29.0	24.7	22.6	20.1
S = 3.6	31.8	24.7	21.1	19.0

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

NMR Diffusometry - SDAPP Membranes





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

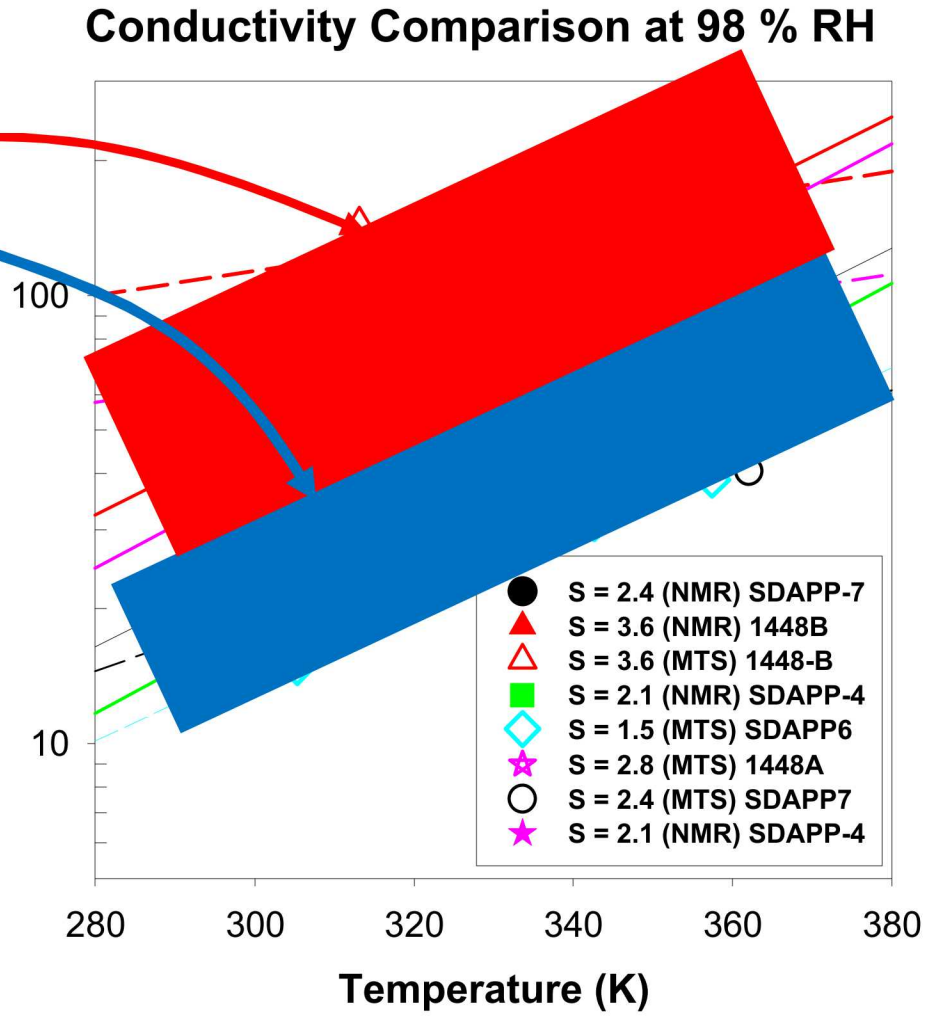
SDAPP Conductivity from Diffusivity

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

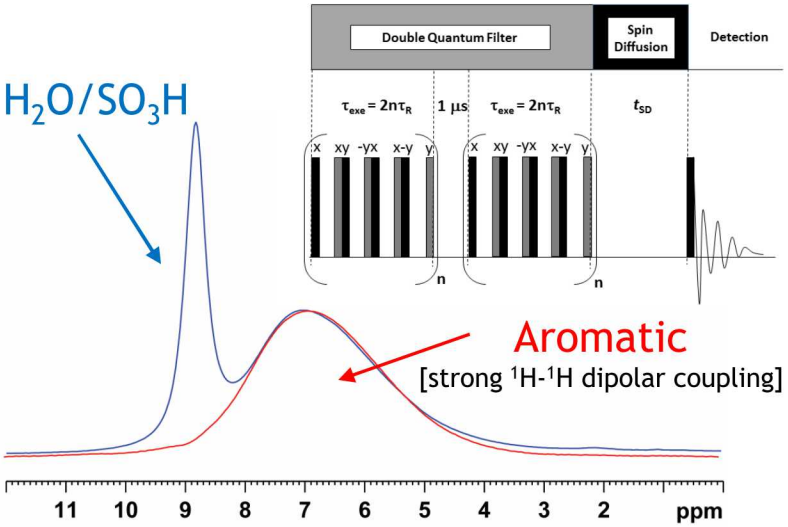
Surface Grotthuss Vehicular

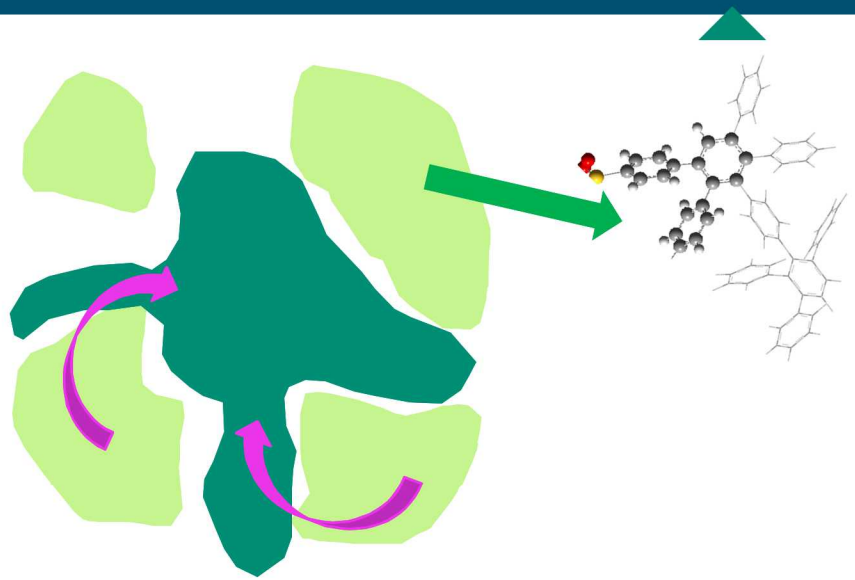
$$\sigma = \frac{F^2}{RT}\left(D_{H^+}^{Surf} C_{H^+}^{Surf} + D_{H^+}^{Grott} C_{H^+}^{Grott} + D_{H^+}^{Veh} C_{H^+}^{Veh}\right)$$

- At low-moderate S conductivity controlled by water vehicular transport .
- With increasing S, Grotthuss mechanism becomes significant and leads to increased conductivity beyond simple diffusion.
- Membrane design rule strive for the highest D^{veh}, but H^+ requires an environment (hydrogen bond strength) allowing Grotthuss hopping.

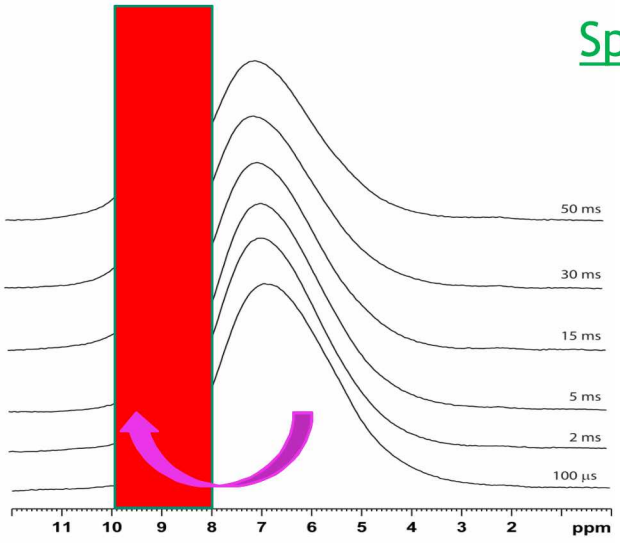


^{1}H NMR Spin Diffusion Experiments

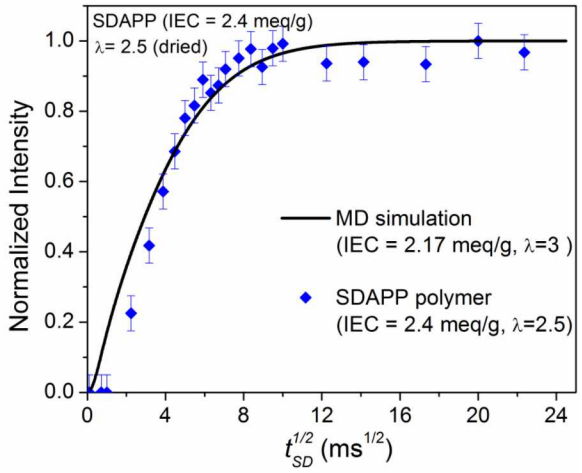




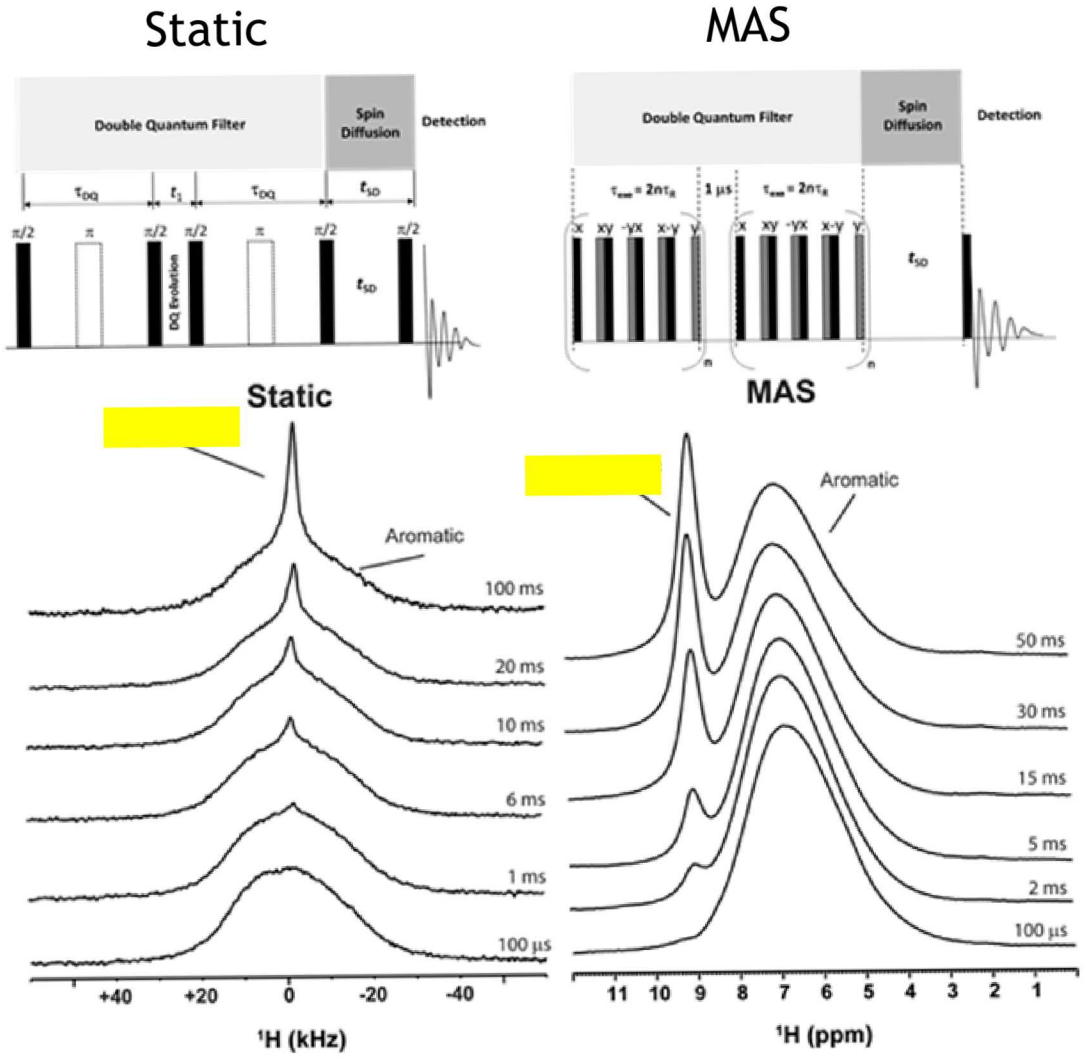
Spin Diffusion Experiment



"spin temperature" equilibration

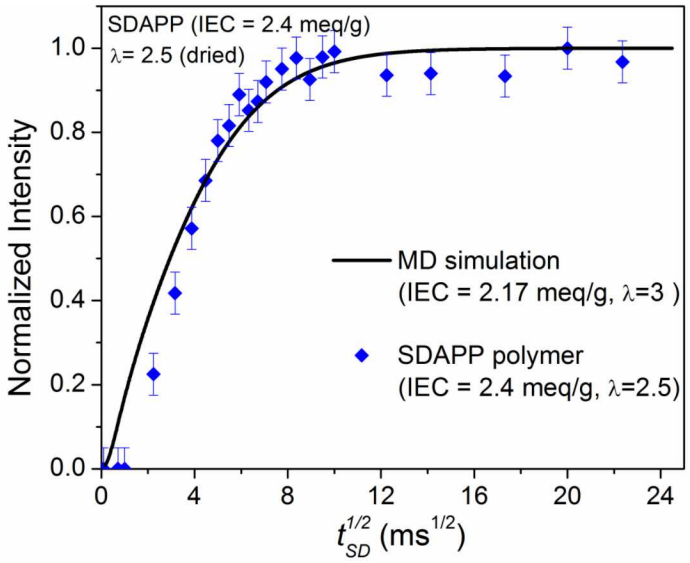


^{1}H DQ-Filtered Spin Diffusion Experiments



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

NMR Spin Diffusion Analysis



Proportion to Interface Surface

Very structure/model specific

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

Density & Volume Fraction

Spin Diffusion Constants

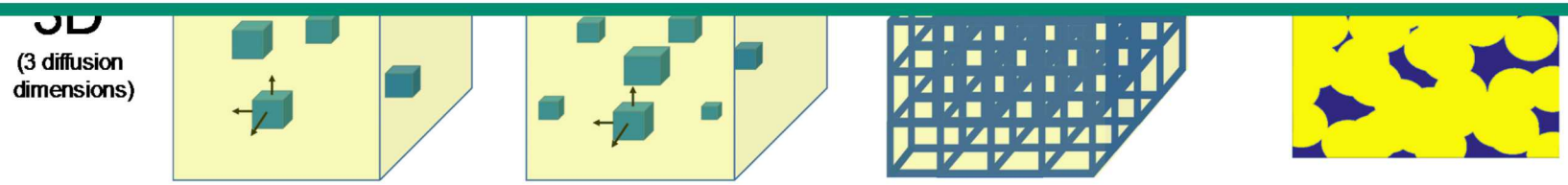
For Simple Models
Related to Domain Size

Connecting Models to NMR Spin Diffusion

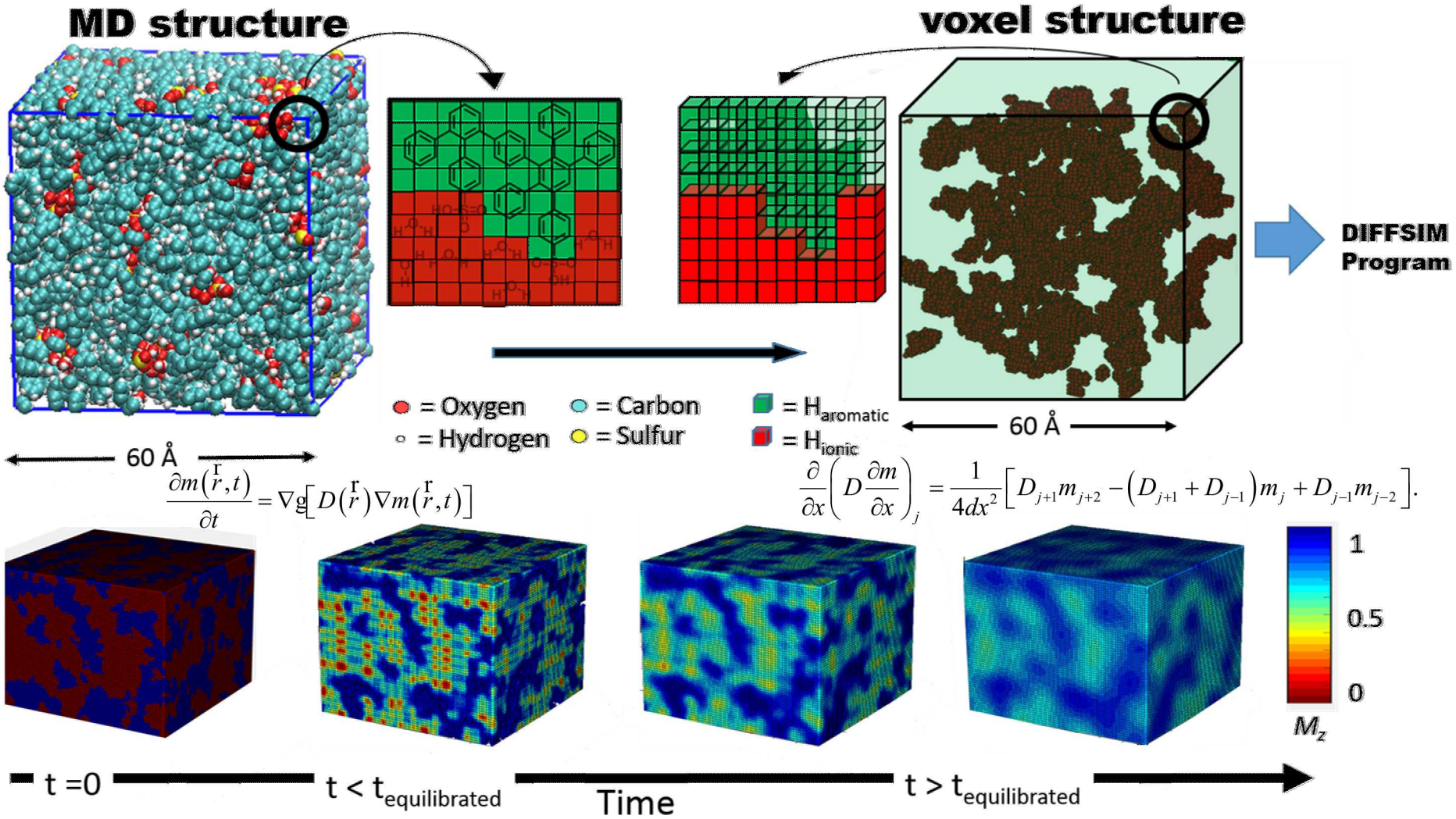
- Analytical solutions for the simplest cases.
- Solutions become unwieldy for distribution of more complex structures!!
- Would like to simulate structured from MD and Course Grain simulations.

- 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 → Spin Diffusion Experiments



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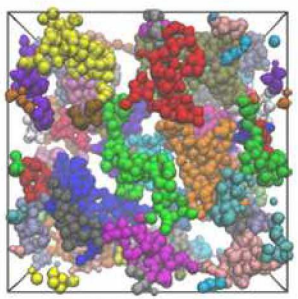
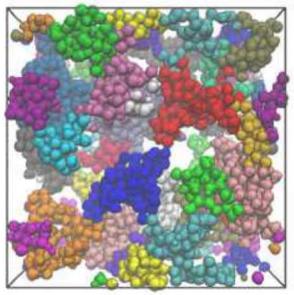
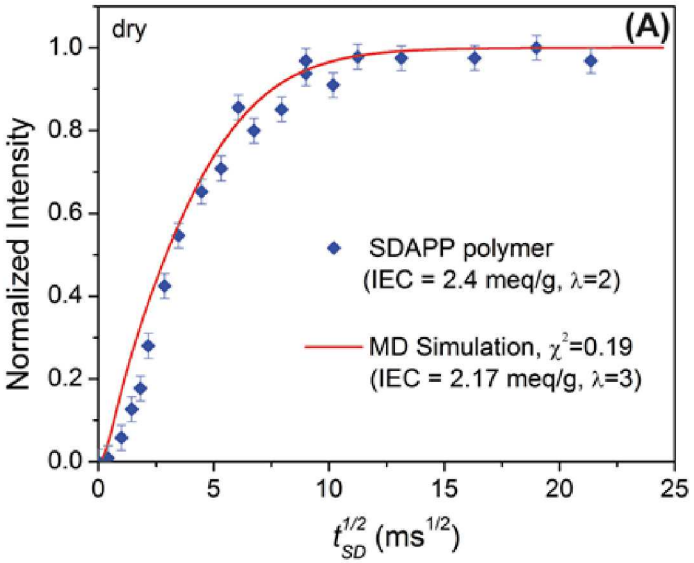
Connecting MD to Spin Diffusion Experiments

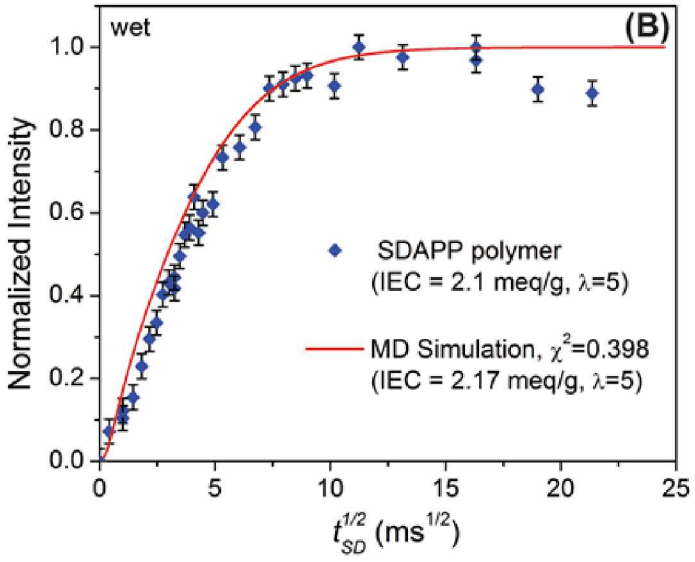


$S = 2, \lambda = 3$



$S = 2, \lambda = 5$



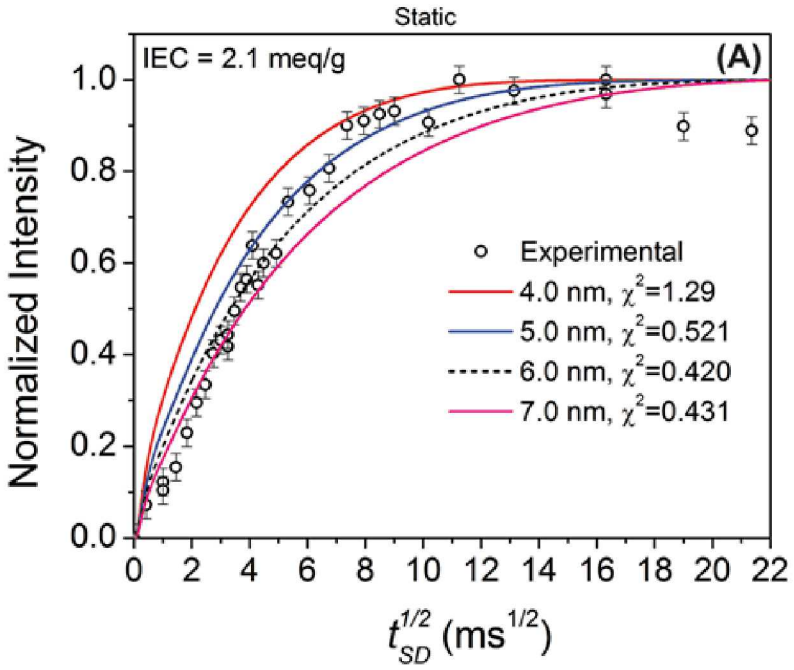


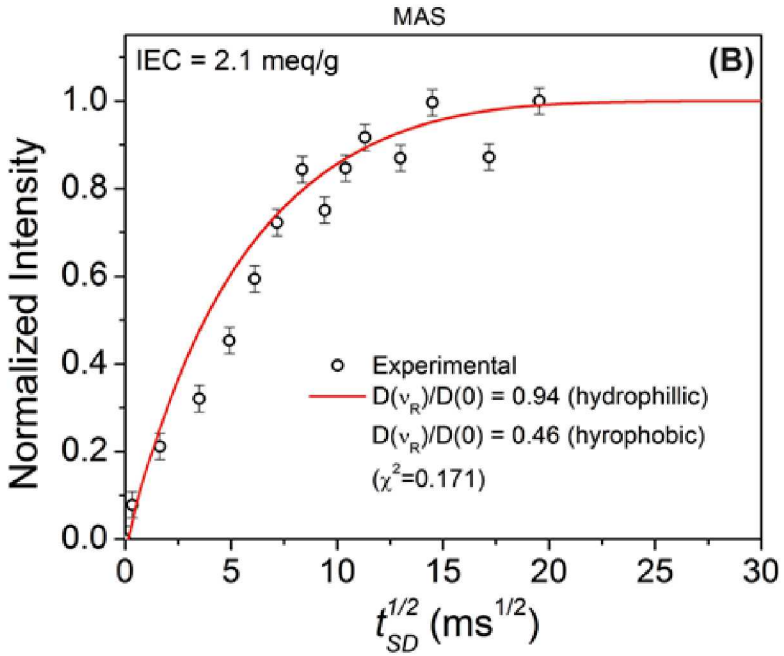
- MD structure (morphology from simulation)
- Diffusion constants (from line width), volume fractions, etc. are fixed.
- No adjustable parameters in these fits!!!!
- Deviations at higher hydration levels [finite simulation size]

Impact of MAS on Spin Diffusion Rates

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

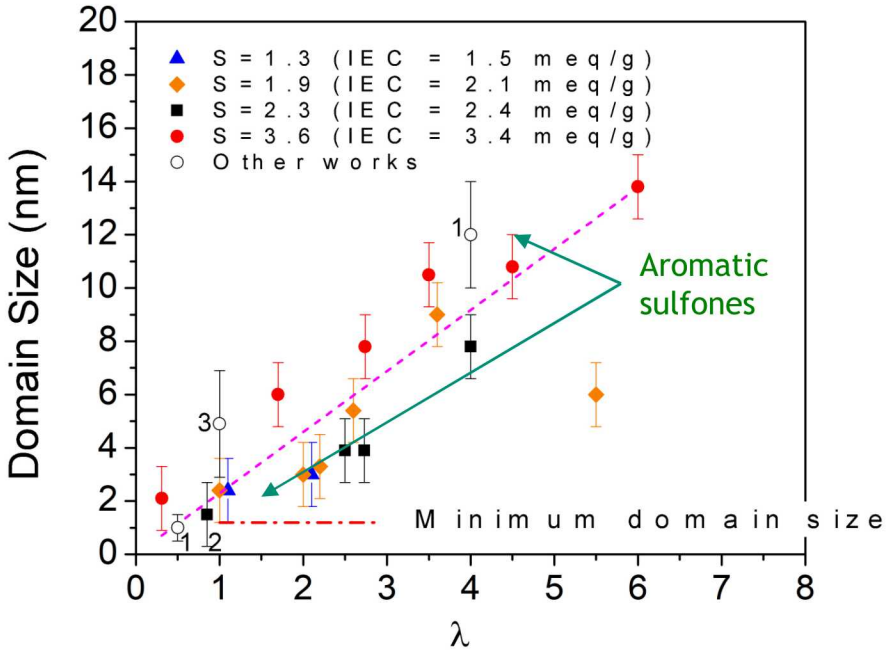
$$\frac{D(\nu_R)}{D(0)} = \tan\left[\frac{\pi}{2}\frac{D^2(\nu_R)}{D_0^2}\right]\left[\frac{1}{\tan\left[\frac{\pi}{2}\frac{D^2(0)}{D_0^2}\right]} + \frac{2\alpha\sqrt{2\ln 2}D_0\nu_R}{D(0)\Delta\nu_{1/2}^0}\right],$$

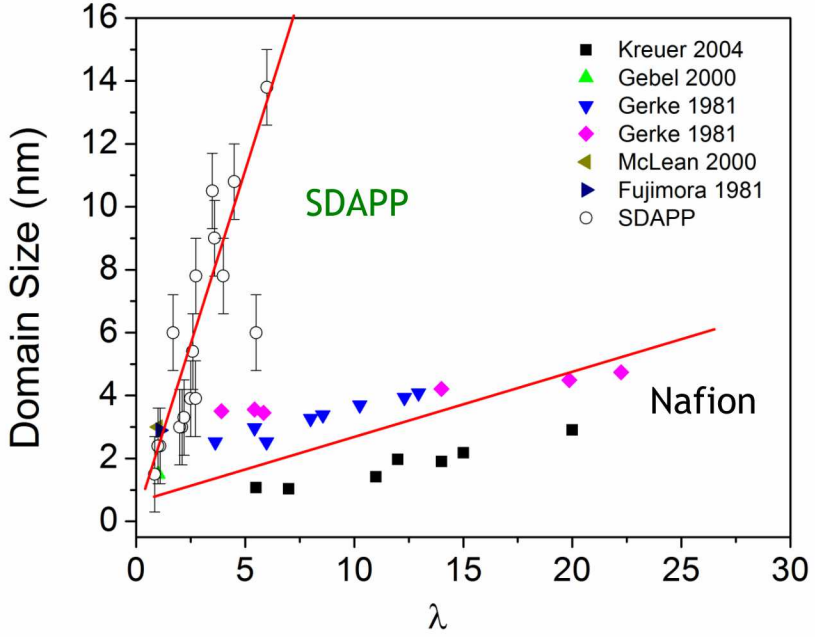




Z. Jia, L. Zhang, Q. Chen, E. Hansen, *J. Phys. Chem. A* **2008**, *112*, 1228-1233.

Estimation of Domain Size

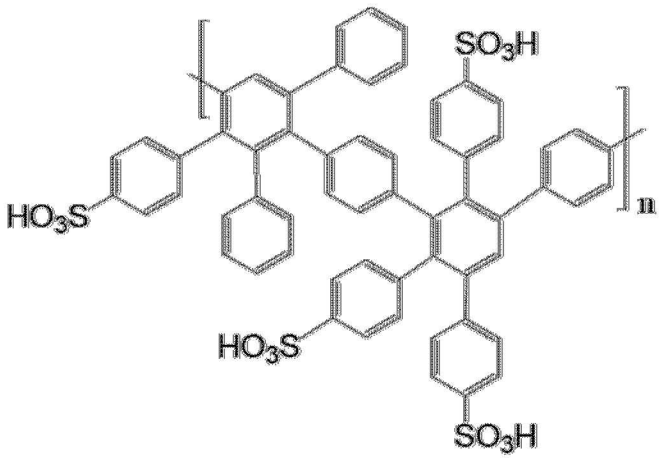




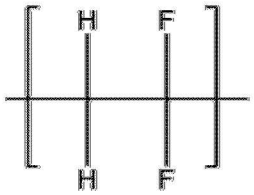
- Continous variation with hydration level (factor of ~7).
- Domain size larger than Nafion. Is this a function of method?
- NMR spin diffusion reflects distance based description of the hydrophylic domain in MD simulation.
- NMR spin diffusion does not give a clear indicator of shape or anisotropy!

Blends and Copolymers

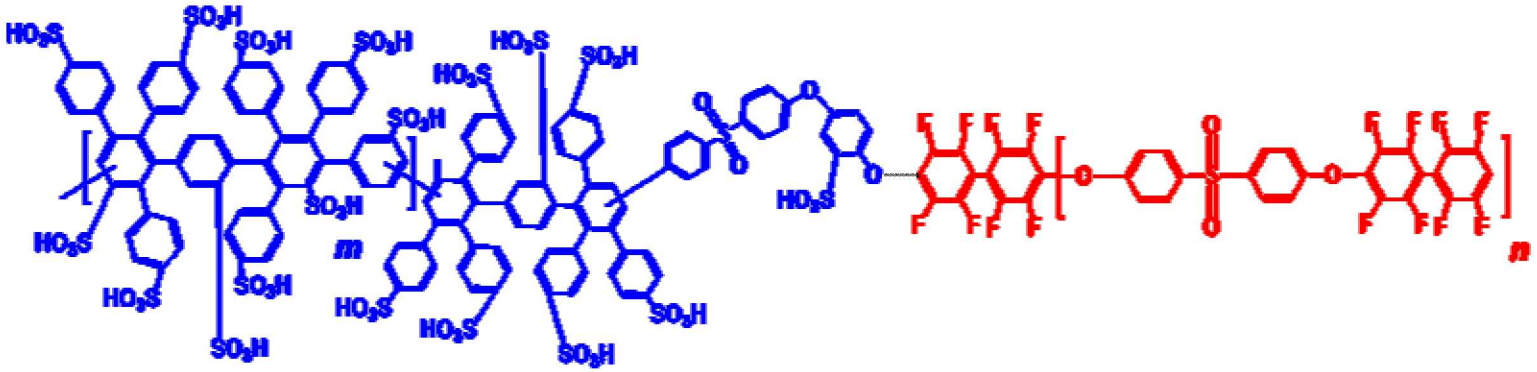
SDAPP



PVDF

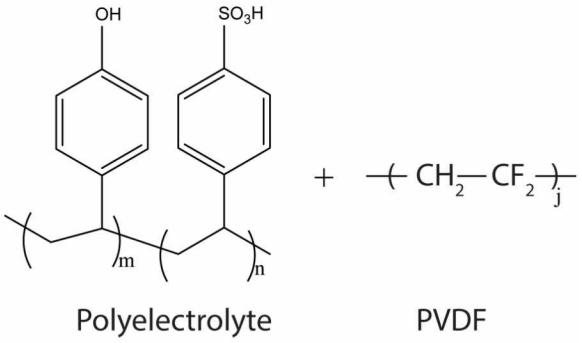


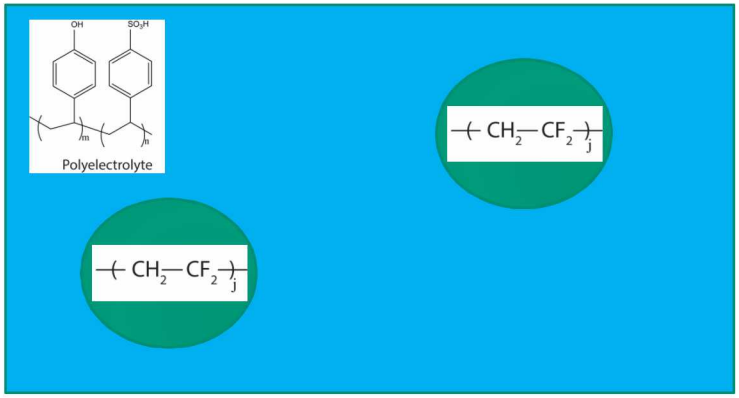
SDAPP-FDPS Copolymers

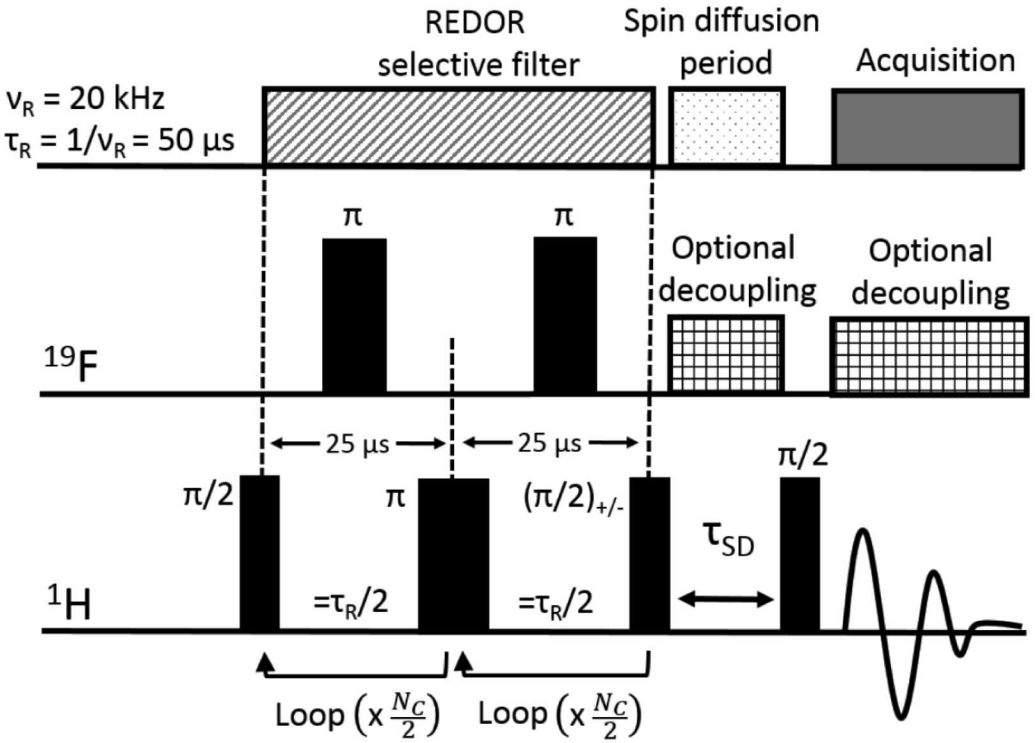


In original copolymers no domain resolution by relaxation-filters.

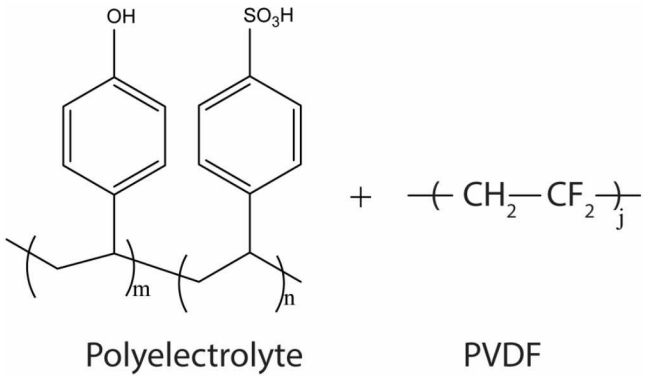
^{1}H detected - ^{19}F REDOR filter





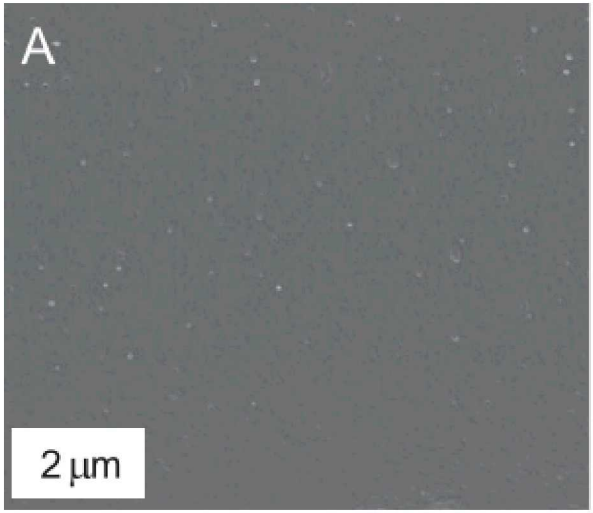


Arkema Inc. polymer
(vinylbenzyl alcohol/sulf. acid + PVDF)



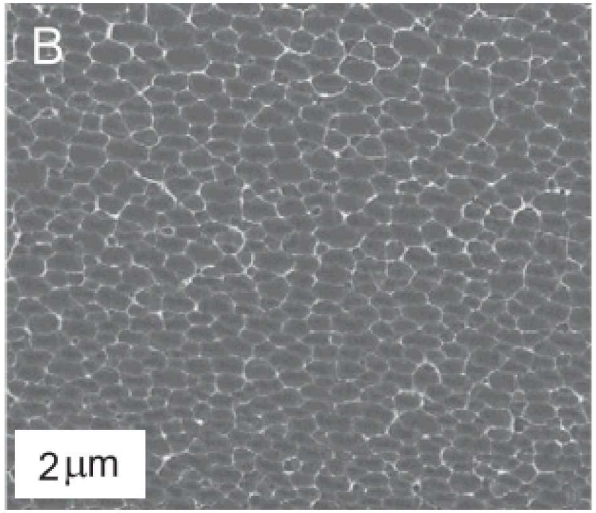
SEM Images

95% TBA-OH



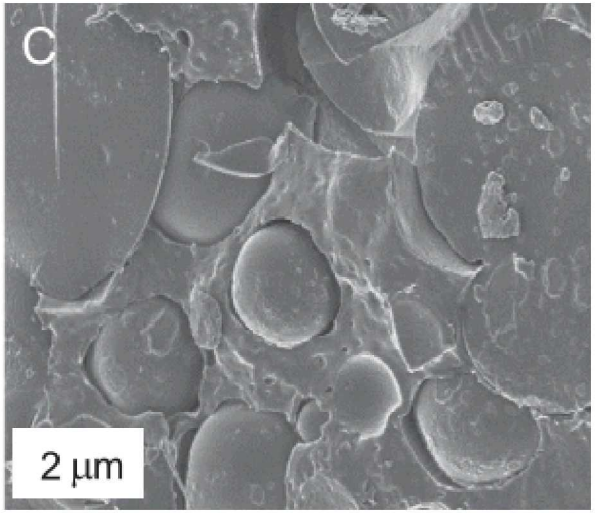
σ= 140 +/- 5 mS/cm

50% TBA-OH



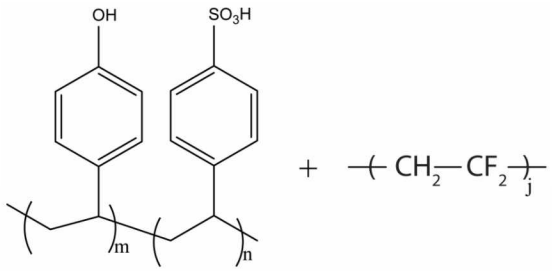
σ = 90 +/- 5 mS/cm

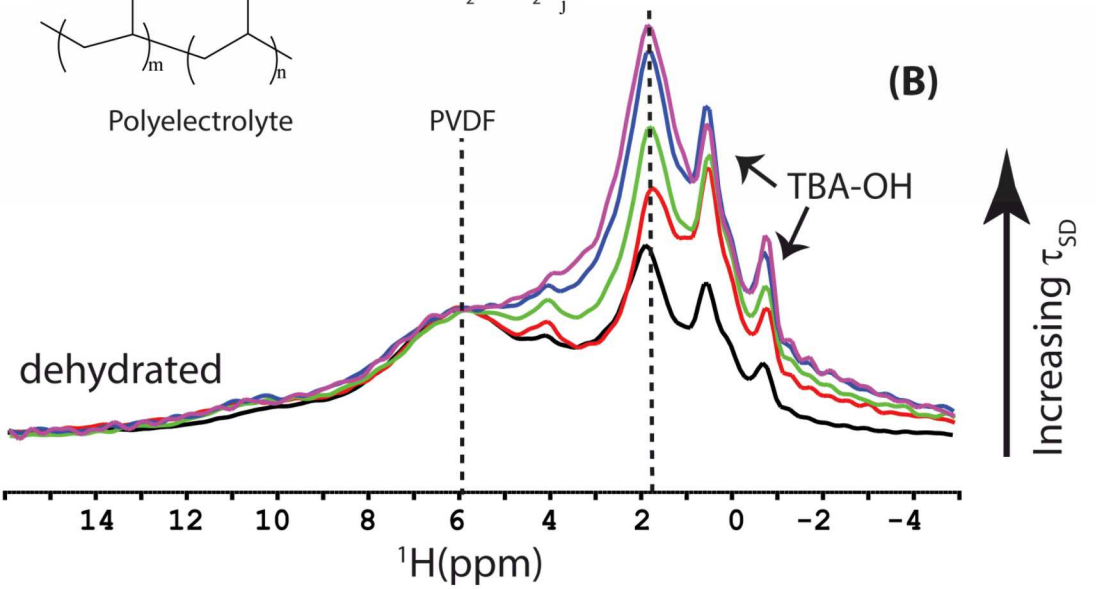
0% TBA-OH

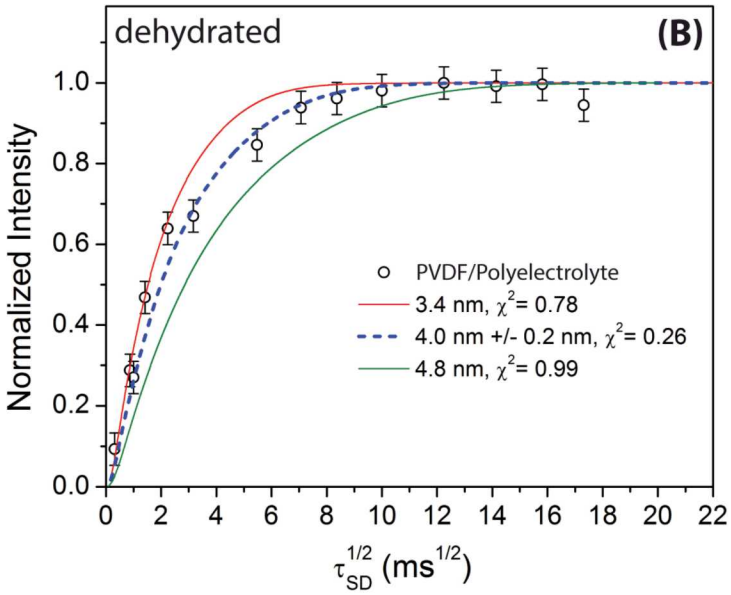


σ = 10 +/- 1 mS/cm

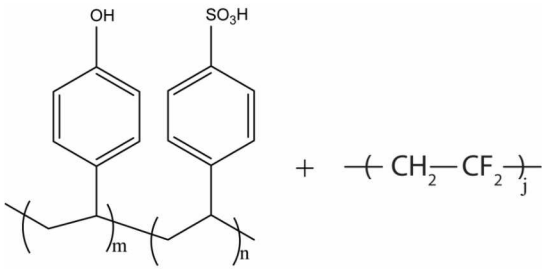
^{1}H Spin Diffusion Results

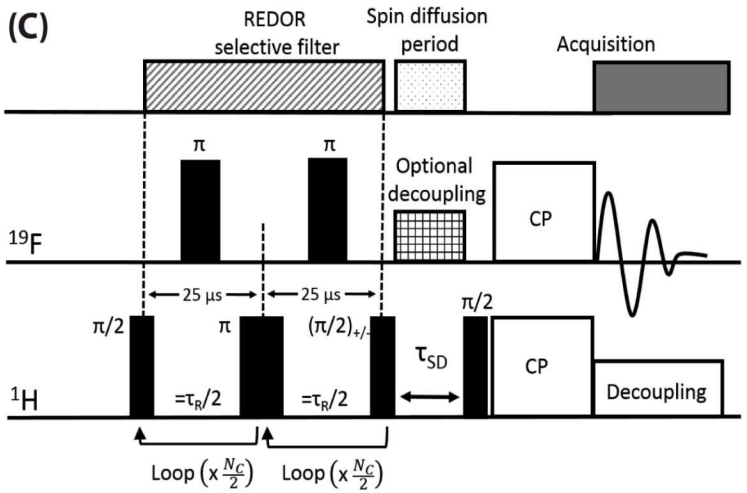


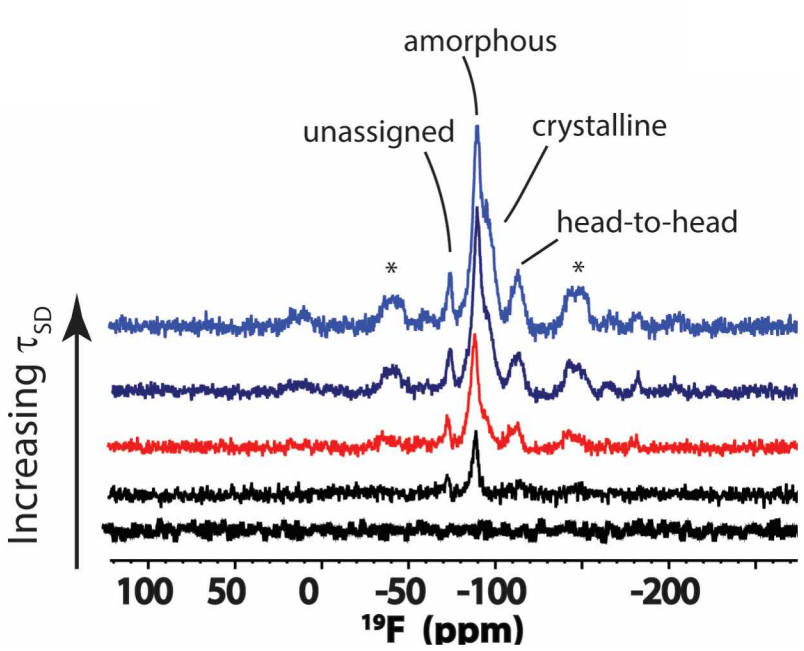


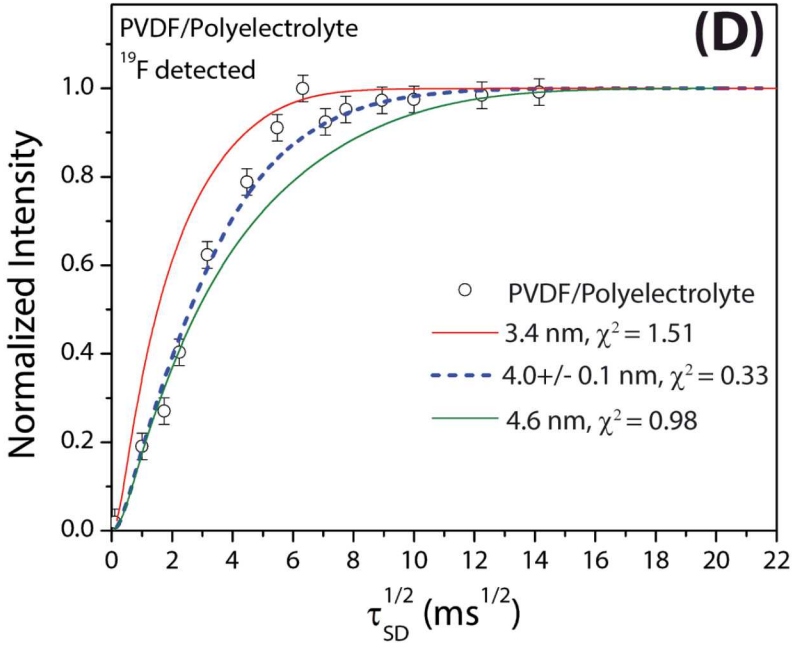


^{19}F detected- ^{19}F REDOR filter

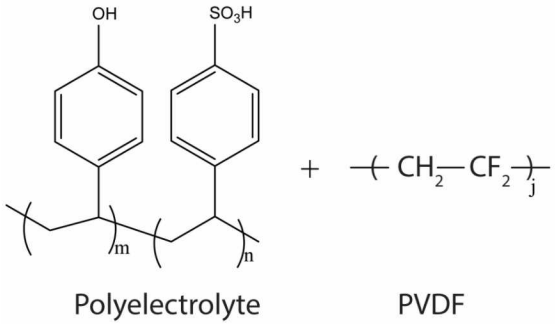


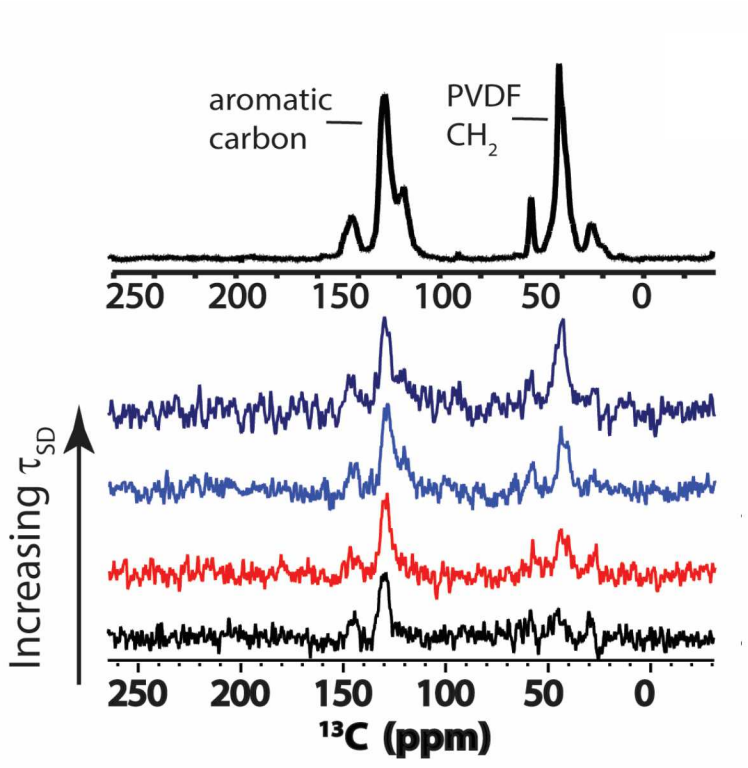


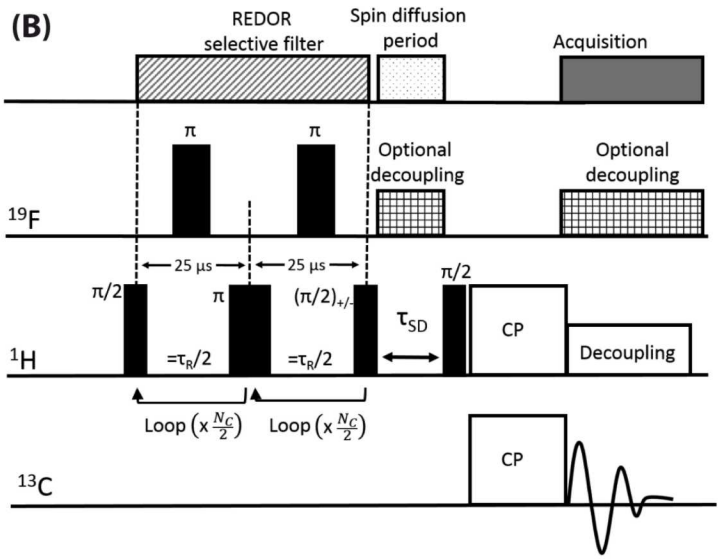


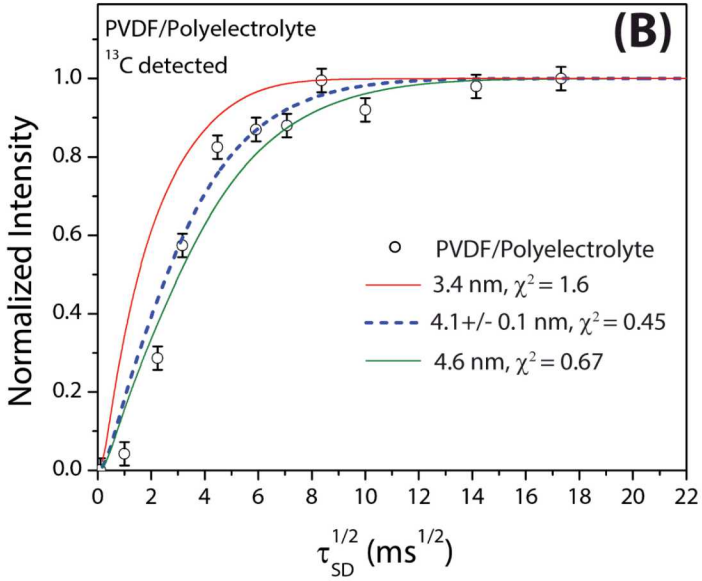


^{13}C detected- ^{19}F REDOR filter



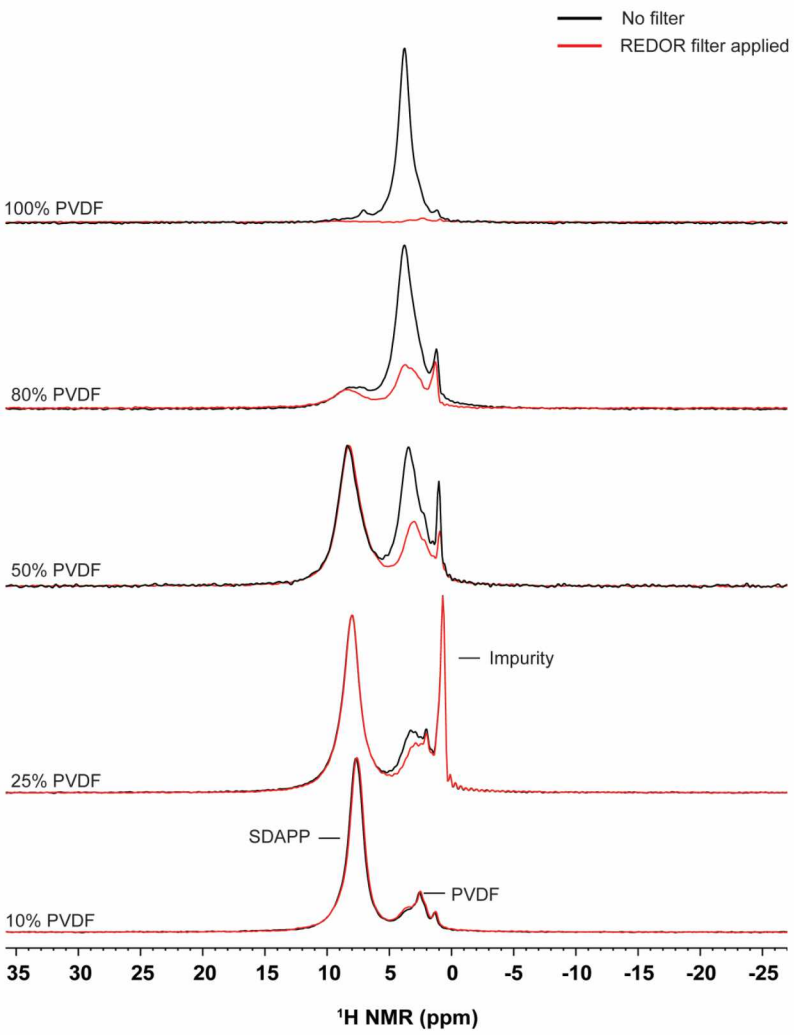






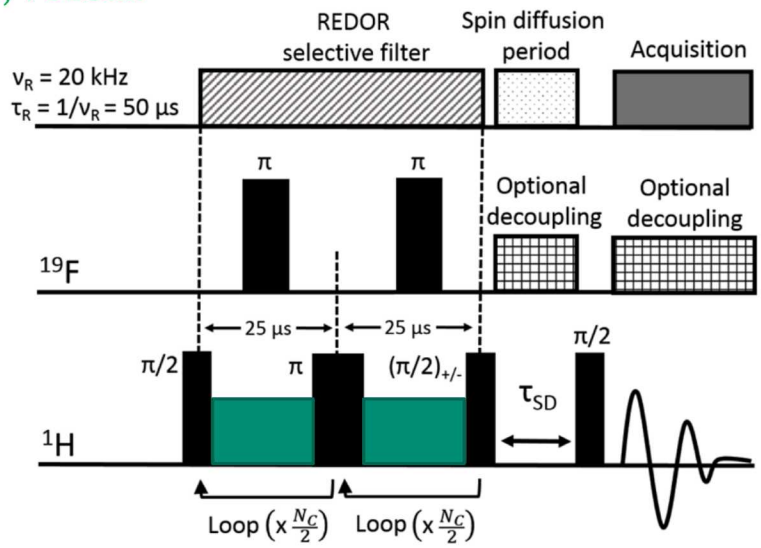
^{1}H-^{19}F REDOR Filtering - SDAPP Blend Issues!

Suppression by REDOR-filter in PVDF+SDAPP Random Copolymers



- REDOR suppression a function of polymer.
- Perfect in 100% PVDF
- Not entirely relaxation (S_0 signal)
- Strong spin diffusion processes during REDOR
- Implementing ^{1}H homonuclear decoupling

MREV, FSLG....



Acknowledgements

Dr. Amalie Frischknecht (SNL) - MD Simulations
Prof. Janelle Jenkins (Prof. at E. Washington Univ.)
Dr. Lauren J. Abbott (SNL…now NASA) - MD Simulations
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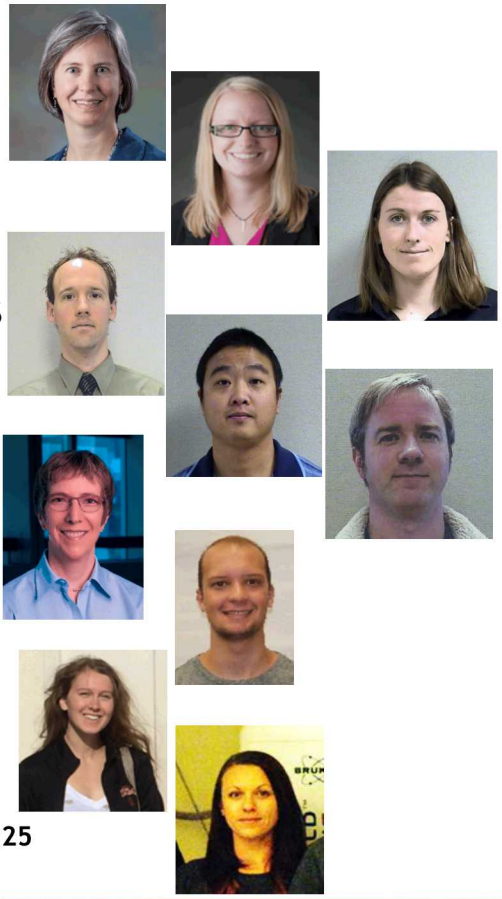
Dr. Cy Fujimoto (SNL) - SDAPP Synthesis
Dr. Michael Hibbs (SNL) - AEM Synthesis

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

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

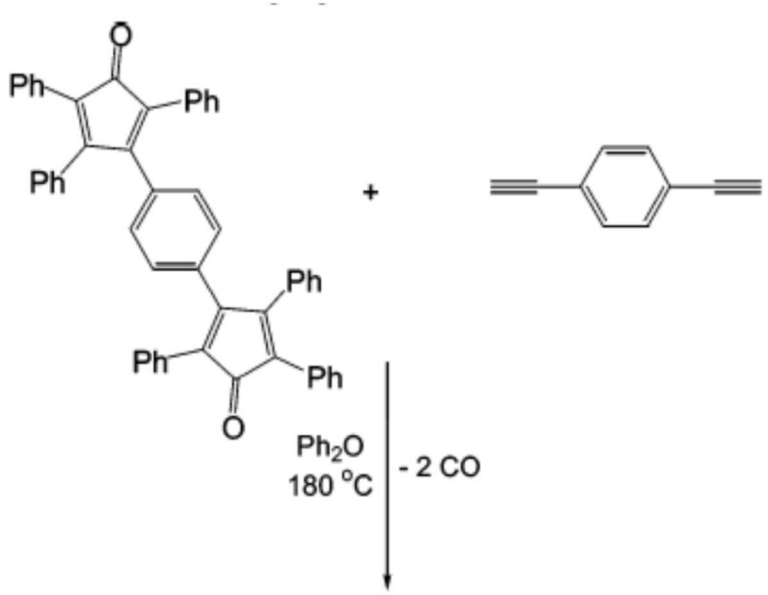


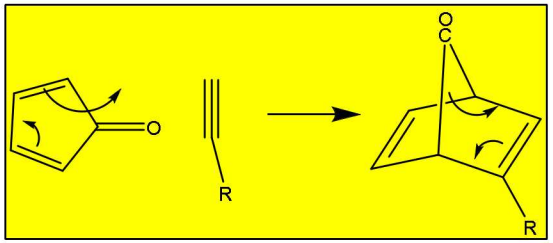
"Chemical Degradation of Model Sulfonated Polyphenylene Proton Exchange Membranes" POLY 525
Tuesday (Polymer session 6-8 PM) - Sci Mix (Monday 8-10 PM)

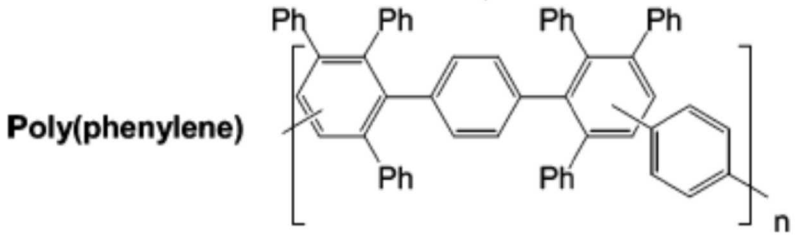
Project funding through the Sandia LDRD program

Backup Slides

Diels Alder Polymerization







DAPP

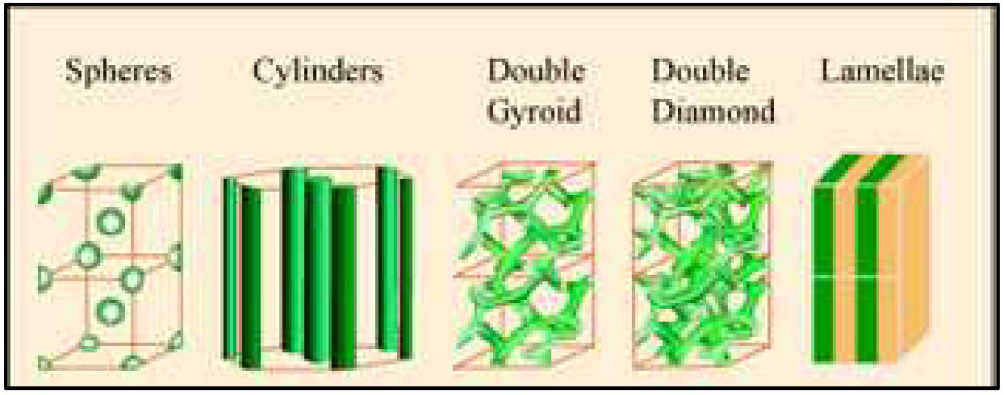
sulfonation

SDAPP

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

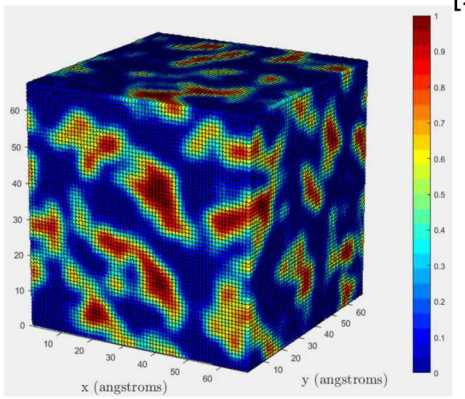
II. Morphology Control is Essential (Gross, 2009)

- 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.



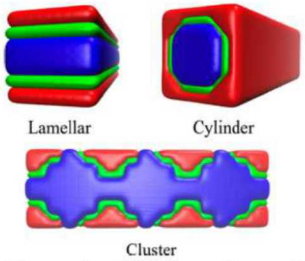
[1]

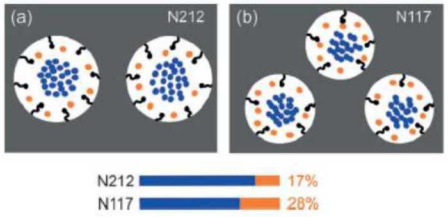
[2]



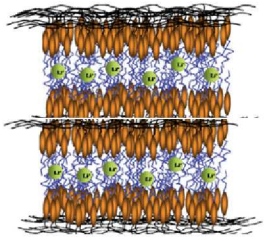
[3]

[5]



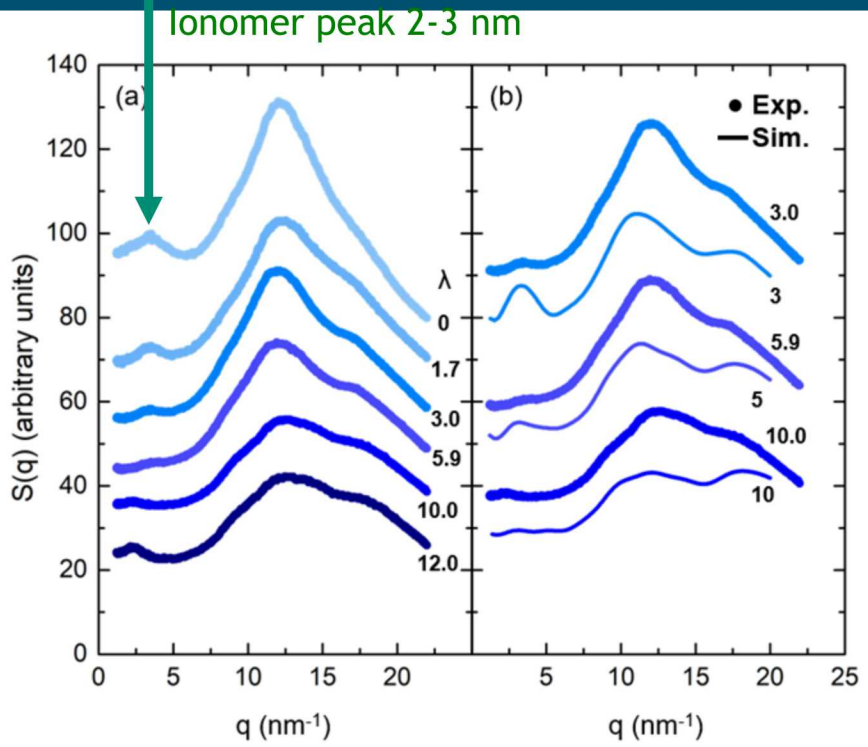


[4]

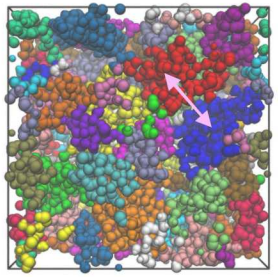


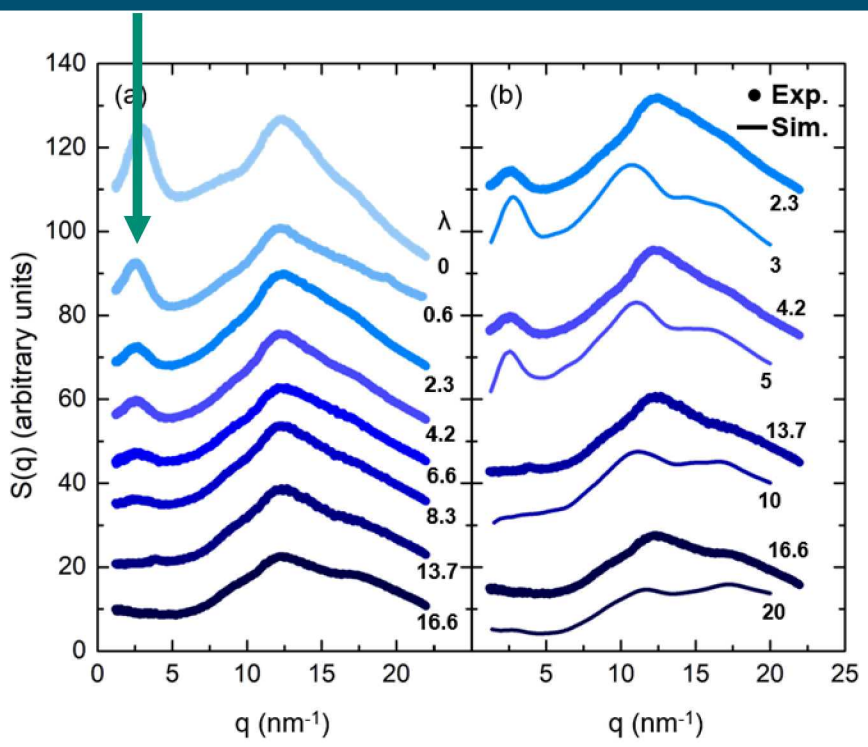
[1] Prof. Thomas, Figure by MIT OpenCourseWare. [2] Liu, S.; Savage, J.; Voth, G. A., Mesoscale Study of Proton Transport in Proton Exchange Membranes: Role of Morphology. The Journal of Physical Chemistry C 2015, 119 (4), 1753-1762. [3] Lauren J. Abbott and Amalie L. Frischknecht,"Nanoscale Structure 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 Scattrering

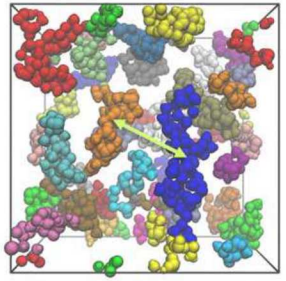


14-48B (S=3.6) versus S=4 (MD)



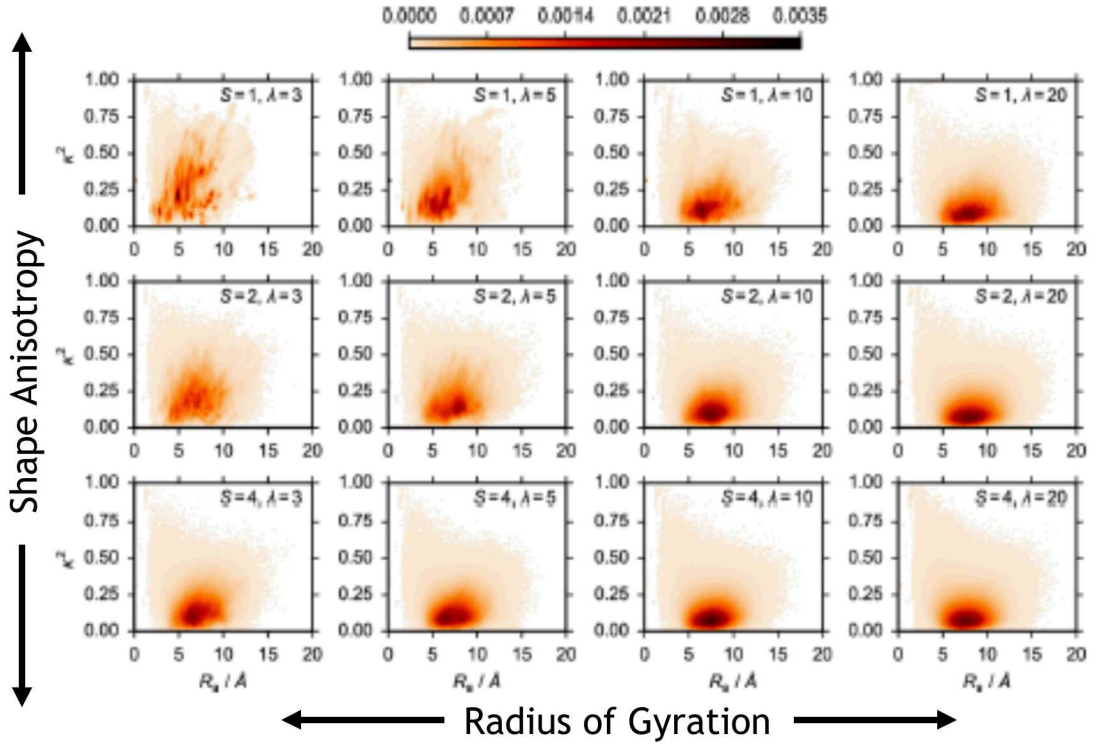


SDAPP7 (S=2.3) versus S=2 (MD)

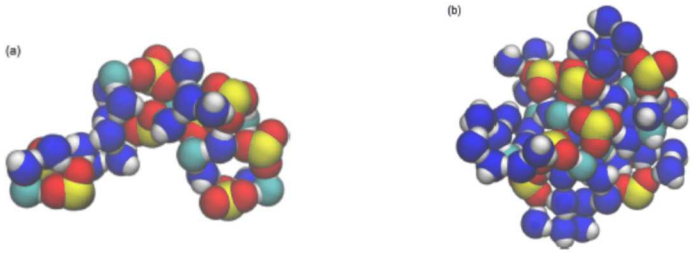


What additional information can be obtained about the hydrophilic domains?

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.



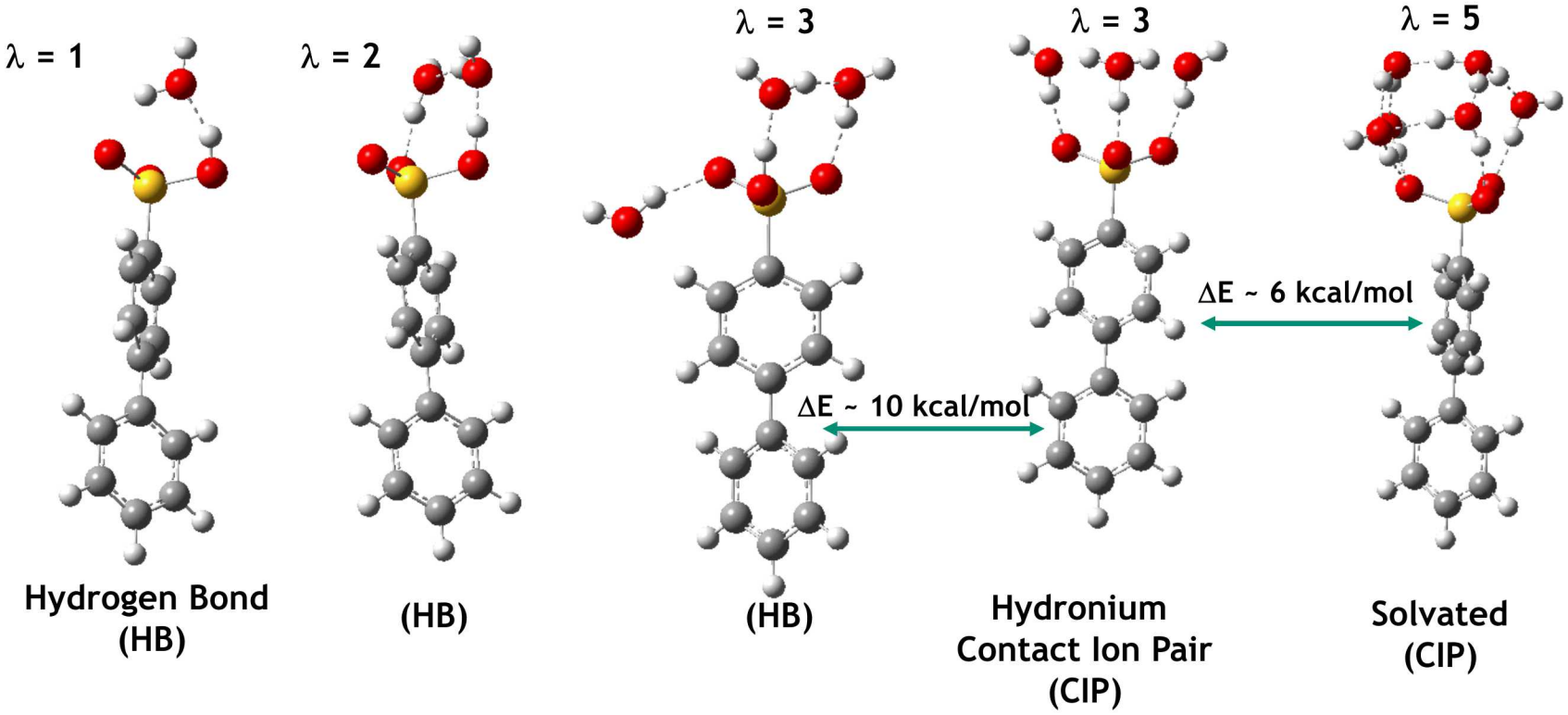
Can we obtain experimental verification of these proposed domain structures and changes in the structure with increasing hydration?

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

Ab Initio Calculations
Water Adsorption Energies & Hydrogen Bonding Types

$$\Delta E_{\text{Ads}}^{\text{Opt}} = E\left(\text{Clutser}+n\text{H}_2\text{O}\right) - E^{\text{Opt}}\left(\text{Cluster}\right) - \sum_{i=1}^{N} E^{\text{Opt}}\left(\text{H}_2\text{O}\right)$$

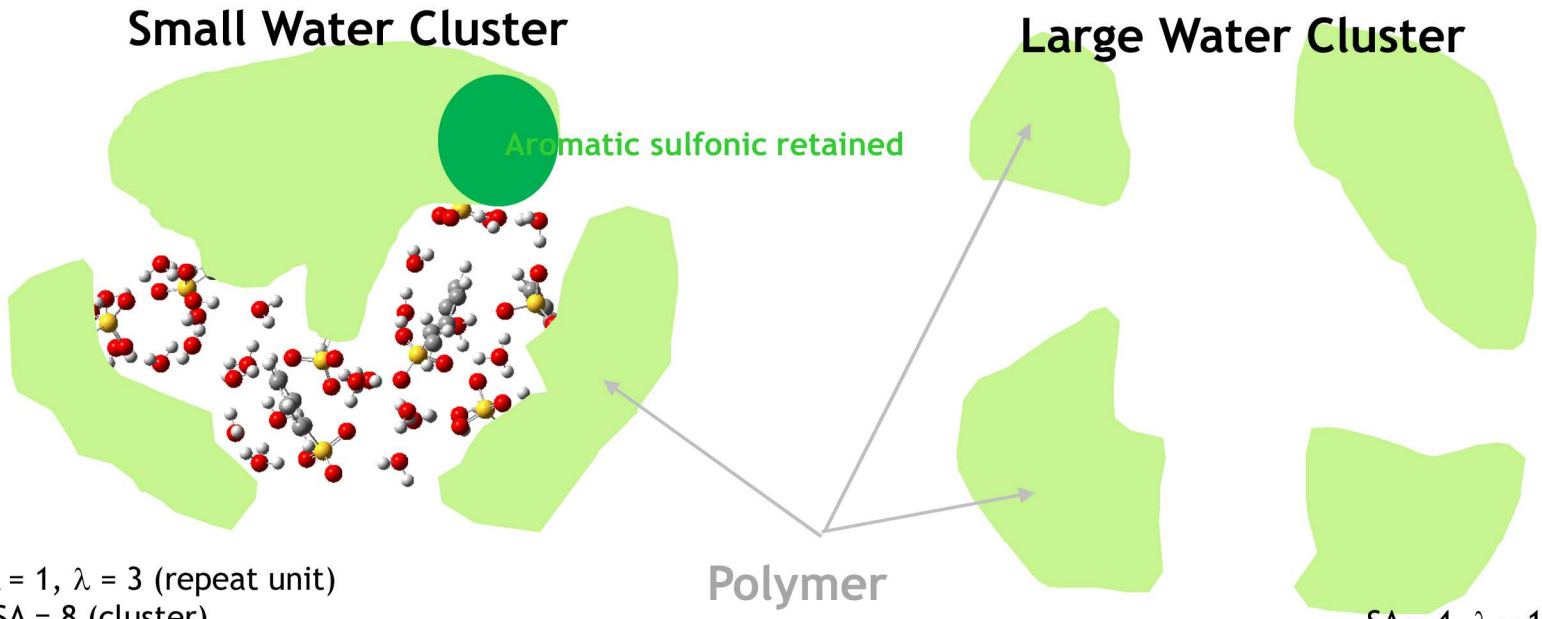
DFT 6-311**



For small clusters very limited structural impact!

T. M. Alam "Ab Initio Study of Sulfonic Acid Micro-Hydration in Sulfonated Diels Alder Poly(Phenylene) Polymers", J. Phys. Chem. C (2018) *Submitted*

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^+

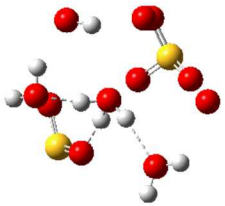
$$\Delta E_{\text{Ads}}^{Total} = \Delta E_{Ads}^{H_3O^+} + \Delta E_{Ads}^{H_2O} = \sum_{j=1}^{n} \Delta E_{Ads}^{H_3O^+}(j) + \sum_{i=1}^{m} \Delta E_{Ads}^{H_2O}(i)$$

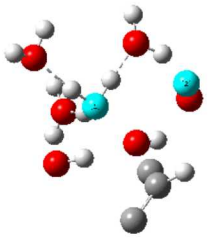
$$\Delta E_{\text{Ads}}^{H_2O}(i) = E\left(\text{Cluster}\left[m\text{H}_2\text{O}\right]\right) - E\left(\text{Cluster}\left[(m-1)\text{H}_2\text{O}(i)\right]\right) - E^{Opt}\left(\text{H}_2\text{O}\right)$$

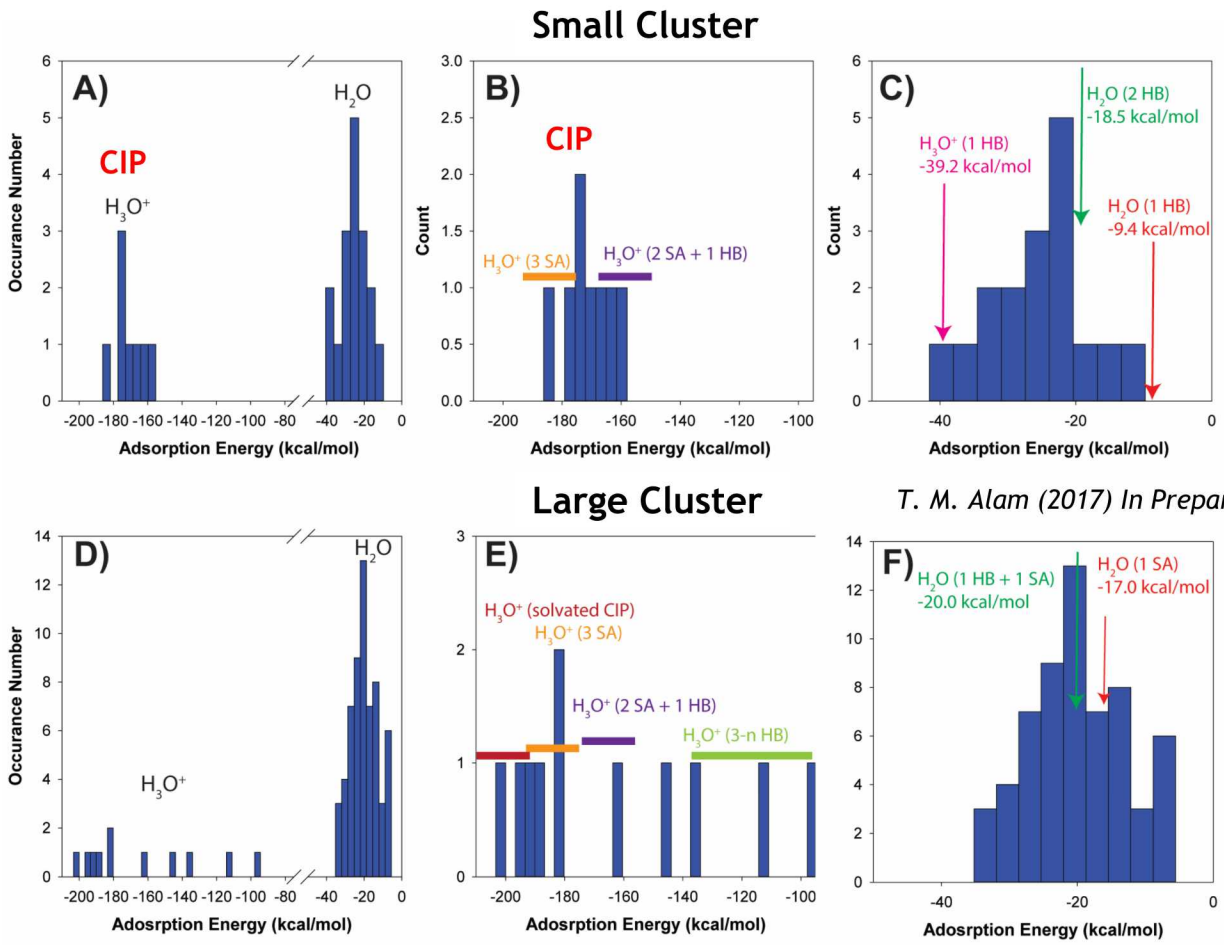
$$\Delta E_{\text{Ads}}^{H_3O^+}(j) = E\left(\text{Cluster}\left[n\text{H}_3\text{O}^+\right]\right) - E\left(\text{Cluster}\left[(n-1)\text{H}_3\text{O}^+(\text{j})\right]\right) - E^{Opt}\left(\text{H}_3\text{O}^+\right)$$

T. M. Alam "Ab Initio Study of Sulfonic Acid Micro-Hydration in Sulfonated Diels Alder Poly(Phenylene) Polymers", J. Phys. Chem. C (2018) *Submitted*

Adsorption Energies
Large Water/Acid Clusters from MD Simulations







T. M. Alam (2017) In Preparation

- 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 or maximize all HB interactions.

Conductivity and Diffusion

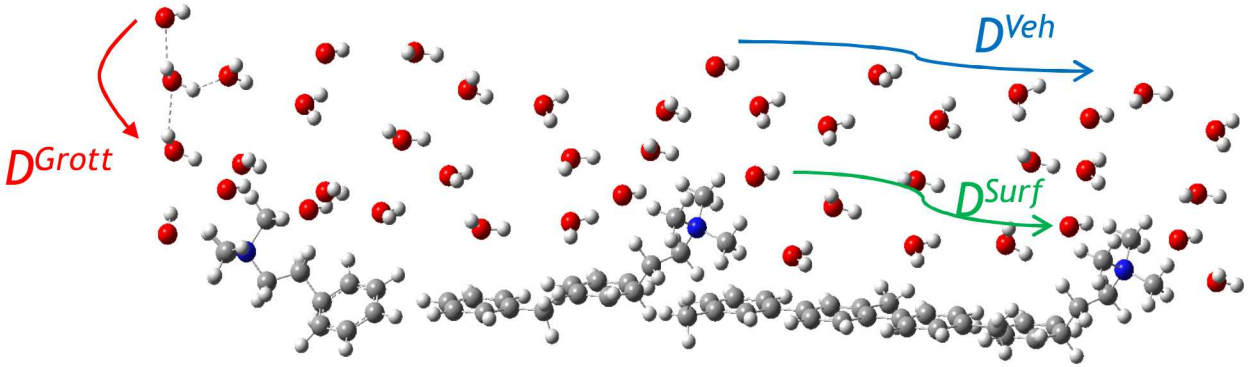
Nernst-Einstein Equation

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

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.