Critical Measurements to Enable the Use of Polymers in Membranes, Composites, & Impact Mitigation

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Functional Polymers Group

Polymer Transport Membranes

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- C Soles
- R Nieuwendaal
- *B Frieberg (nSOFT)*
- *V Oleshko*
- P Beaucage
- A Burns
- V Witherspoon
- W Mulhearn

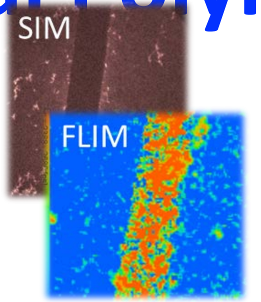
nSoft

2

"Transport Materials at the Energy – Water Nexus"

Polymer Matrix Composites

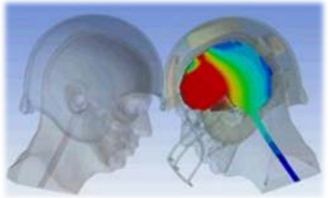
- J Gilman – Lead
- F Phelan
- J Obrzut
- *J Woodcock*
- K Khare
- B Natarajan
- W Xia
- S Seethramaju
- C Emiroglu
- I Patel



"Improved Composite Interfaces Enabled By Computational Materials Design"

Polymer Mechanics

- E Chan – 642 Lead
- G Holmes
- A Forste
- M Riley (
- K Ito
- M Reyes
- *R Sheridan*



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"Polymer Chemistry & Physics of Impact Mitigation"

Jeff Gilman

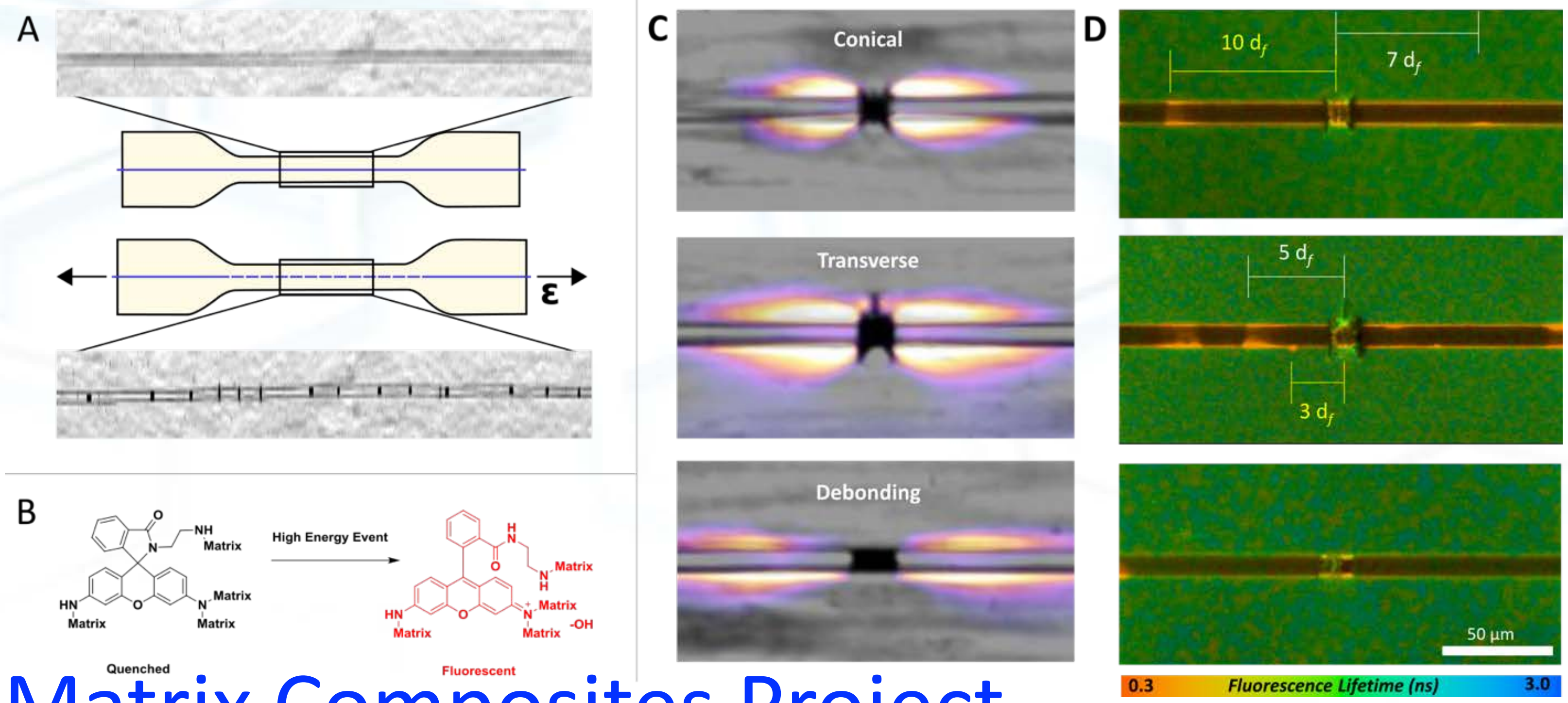
Polymer Matrix Composites Project – Overview

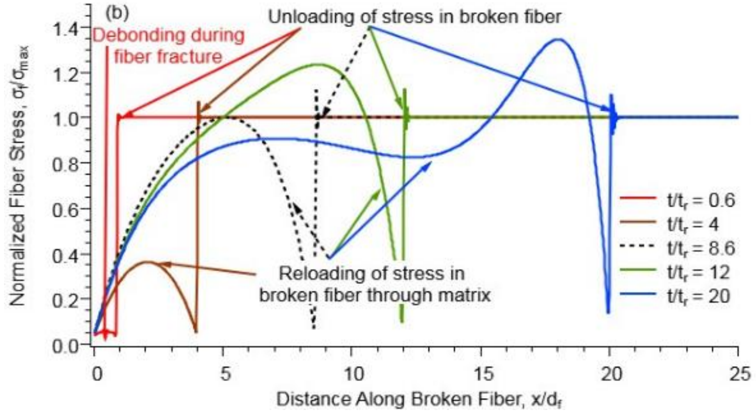
Motivation

- Create tools that create robust structure-property relations for structural composites under environmental conditions, enhance competitive performance, & facilitate manufacturing processes

Objectives

- Develop methods to quantify and image mechanical properties and damage at buried interfaces in polymer matrix composites, especially under hydrated conditions
- Develop non-contact RF/microwave dielectric measurements to quantify buried interfaces in polymer matrix composites, especially absorbed water.
- Integrate computational design and modeling tools with experimental validation to realize the design rules to develop and manufacture high performance structural composites.





Customers and Partners: CNST, MMSD, EL

THE INFLUENCE OF POLYMER DYNAMICS ON THE FUNCTIONAL PROPERTIES OF MATERIALS FOR IMPACT MITIGATION

Polymer Mechanics Project - Overview

Edwin Chan

Need

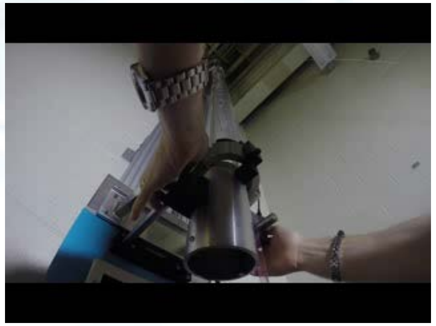
- Polymers are a found in many applications where impact mitigation, toughness, & durability are critical
- Polymers can harness a diverse range of toughening or energy absorption mechanisms
- Enhancing mechanical properties requires understanding of the interaction of strain, stress, & material deformation across a diverse range of length & time scales (ns to days)

Objectives

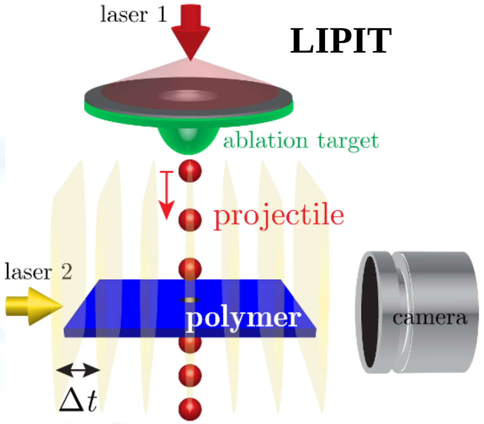
- Develop the quasi-static and high rate mechanical testing infrastructure of soft materials for impact mitigation & toughness
- Interface experiments with theory, simulation, and modeling to facilitate computational materials design

Achievements and Impact

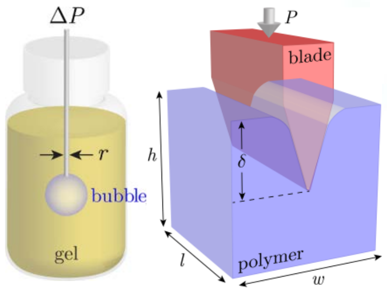
- Evaluate materials on impact performance provided to the NFL Head Health Challenge (643); NIST is the judge
- Developed a poromechanical approach to study the structure of polymer gels
- Measured effect of polymer concentration on the elasticity and fracture of gelatin networks
- Established ChiMAD partnership on materials for impact mitigation



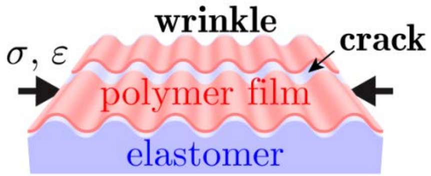
Low Rate Impact



Ballistic Impact



Gel Fracture



Thin Film Mechanics

Partners and Collaborators

CORNING nSoft UNDER ARMOUR Pfizer CHiMaD NFL

Contributors - Polymer Mechanics

NIST

- Bradley Frieberg
- Edwin Chan
- Madhusudan Tyagi
- Kanae Ito
- Adam Burns
- Adam Biacchi
- Angie Hight-Walker

UC Irvine

- Albert Yee
- Jianwei Liu (Seagate)

Army Research Lab

- Kevin Masser
- Joe Lenhart

U Mass Amherst

- Jae-Hwang Lee
- Wanting Xie

National Institute of Standards and Technology
U.S. Department of Commerce

Polymers for Impact Mitigation

Absorb the Applied Energy

- Molecular scale
- Microstructural scale
- Systems level

Distribute the Damage

- Blunter is better

Maintain Structural Integrity

- Don't fail me now!

Materials for High-Performance Impact Mitigation: Design, Synthesis, Characterization, & Validation

Christopher L. Soles (NIST)
Joseph L. Lenhart (ARL)
Ellen M. Arruda (Michigan)
Juan J. de Pablo (U Chicago)

257th ACS National Meeting & Exposition
Meeting Theme: *Chemistry for New Frontiers*
March 31 - April 4, 2019
Orlando, FL

Energy Dissipation (K_{IC}, G_{IC}, J-integral, work of fracture) vs Strength & Stiffness

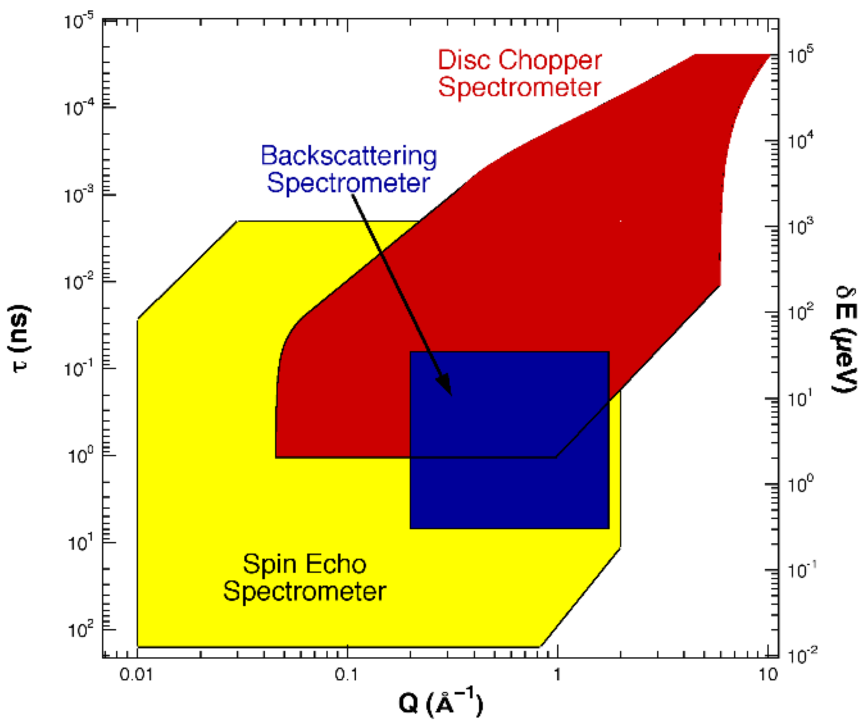
High Strain Rate Impact Testing

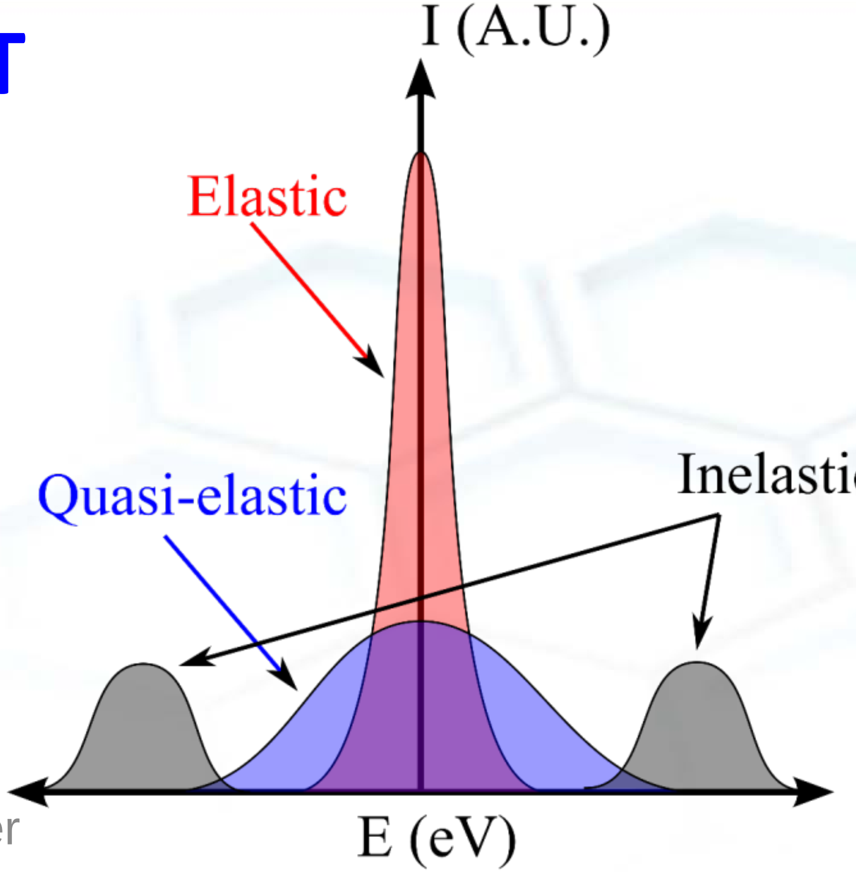
Projectile	Mass (g)	Velocity (m/s)	Kinetic Energy (J)	Strain Rate (1/s)
0.308 Sniper Rifle	11	823	3,217	8.23E+05
0.223 Assault Rifle	4	975	1,854	9.75E+05
357 Sig Handgun	8	410	672	4.10E+05
9 mm Handgun	7.5	353	467	3.53E+05
Hockey Puck	165	54	241	5.40E+04
Baseball off a Bat	145	53	204	5.30E+04
NFL Running Back	113,398	5	1,417	1.00 E+03
Instron Mechanical Test	100	0.001	5.0E-8	1.00E-02
LIPIT (3.7 μm silica particle)	2.80E-08	1000	1.4E-6	1.00E+08
Space Dust	1.00E-02	10000	500	1.00E+07
Atomistic MD (10 nm cube)	1.80E-18	0.01	9.0E-26	1.00E+08

Significant need to understand polymer mechanics at high strain rates!

Is LIPT is a good intermediate between modeling at real world ballistic response?

Quasielastic Neutron Scattering at NIST





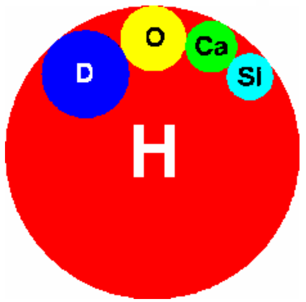
Chopper Spectrometer

– picosecond time scales

High Flux Backscattering Spectrometer

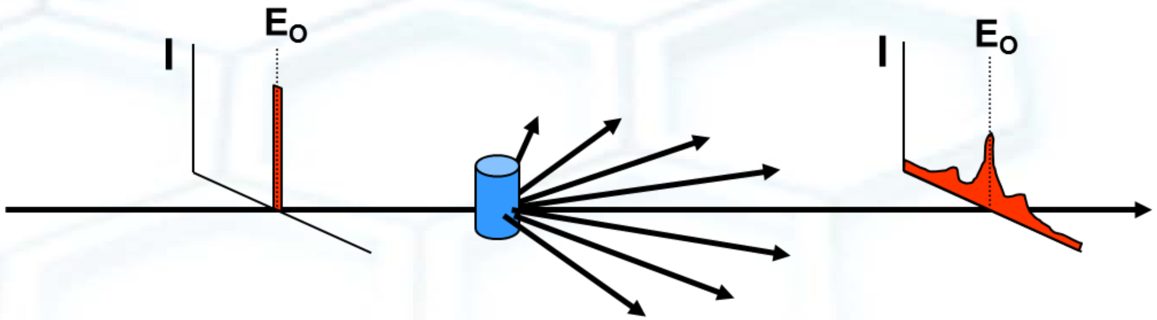
– nanosecond time scales

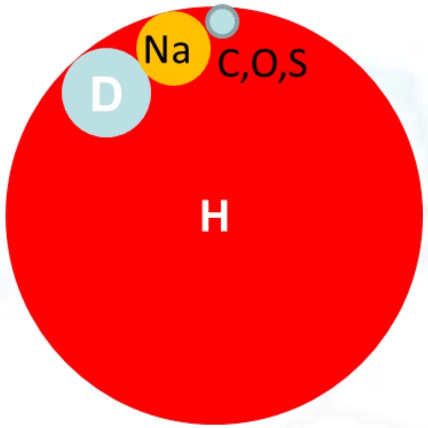
Quantify *self* correlations in the H dynamics



Incoherent Neutron Scattering Cross Section

Incoherent Neutron Scattering





Hydrogen weighted dynamics

$$S_{inc}(Q,\omega) = \frac{3N\hbar}{2M} e^{-2W} Q^2 \frac{n(\omega)+1}{\omega} g(\omega)$$

e^{-2W} is the Debye-Waller Factor with $W = \frac{1}{6} Q^2 \langle u^2 \rangle$

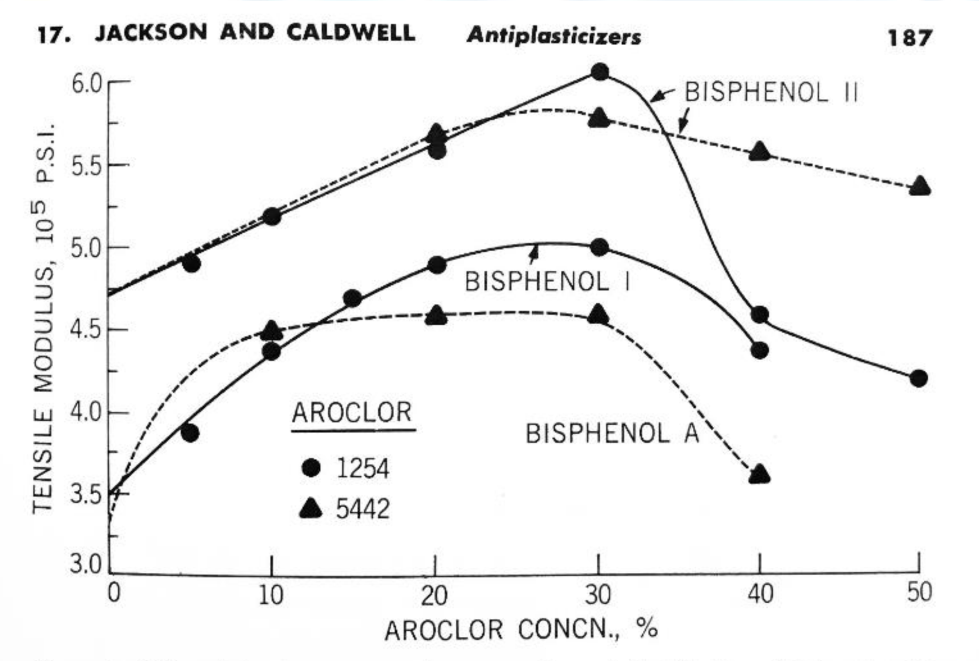
Simplify: (1) in high T limit $n(\omega) \approx k_B T / \omega$ (2) as $\omega \to 0$, $g_{debye}(\omega) \propto \omega^2$

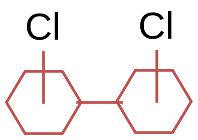
$$I_{inc,elastic}(Q) \propto \exp\left(-\frac{1}{3} Q^2 \langle u^2 \rangle \right)$$

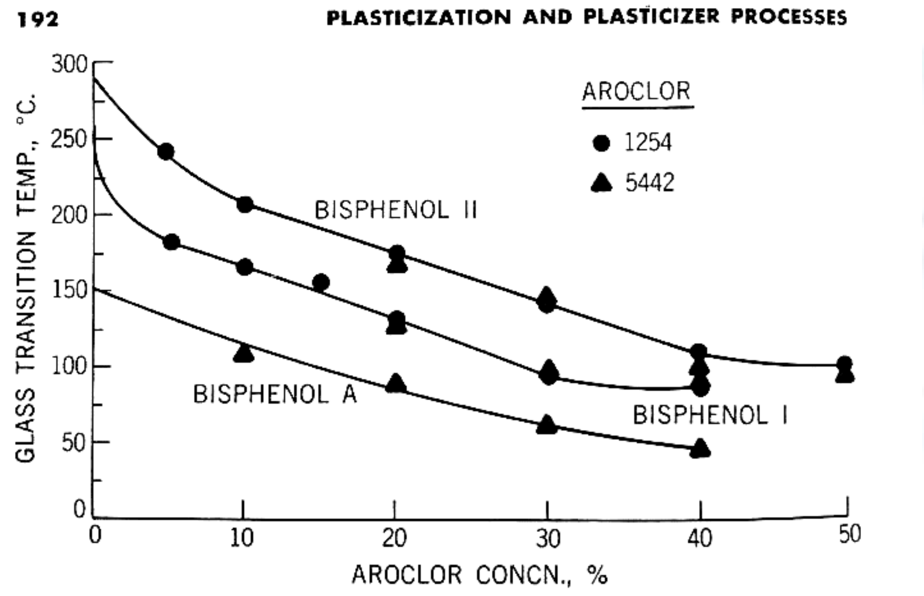
pico to nano second time scales
1 to 100 Å length scales

G. Zaccai, Science **288**, 1604 (2000)

Plasticized Polycarbonates



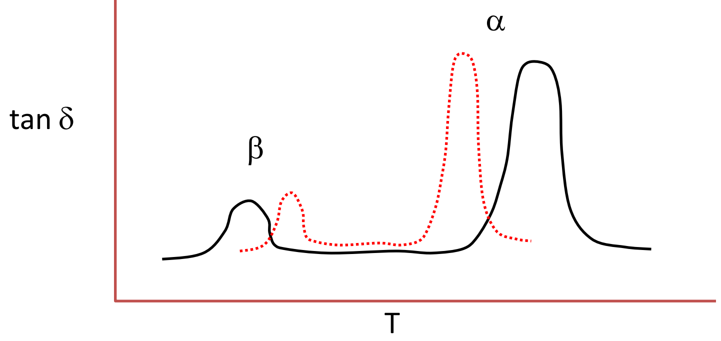




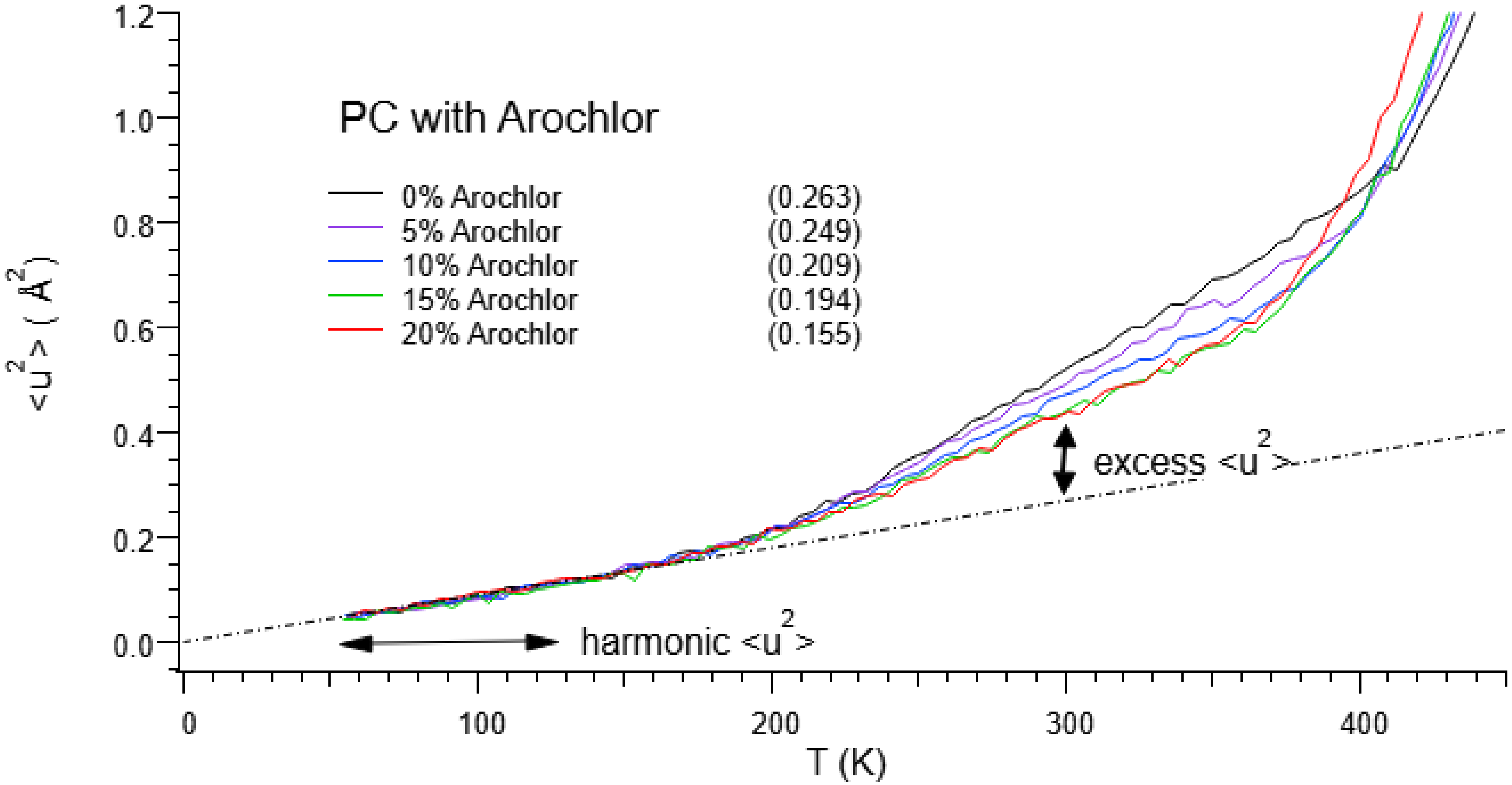
Classic Plasticization – Antiplasticization Response

Plasticizers typically reduce Tg

But also
- increase stiffness
- decrease elongation at break
- decrease impact strength



Polycarbonate with Arochlor



Dynamics above T_g are facilitated with Arochlor, but stiffened below T_g

Consistent with classic plasticization / antiplasticization phenomenon

Arochlor embrittles PC – reduced toughness

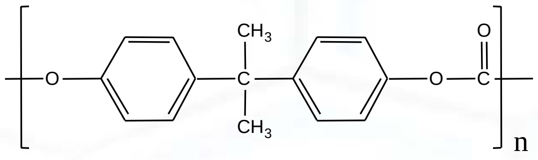
Modified Polycarbonates

Albert F. Yee, Jianwei Liu, Jingsheng Wu (Michigan – late 90’s)

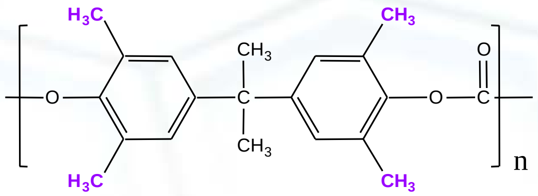
bisphenol-A polycarbonate based copolymers

tetramethyl bisphenol-A polycarbonate based copolymers

B or PC

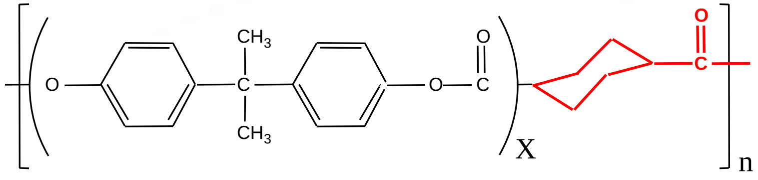


T

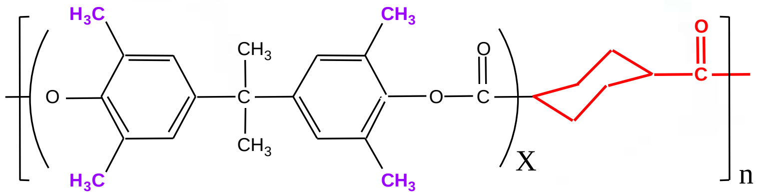


incorporate flexible 1,4-cyclohexylene linkages

B_xC

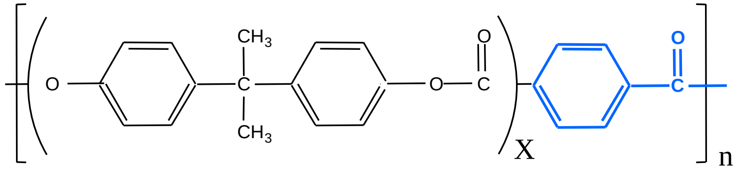


T_xC

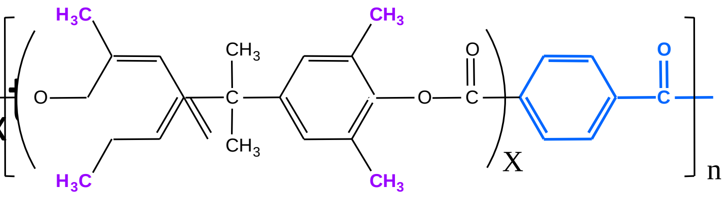


incorporate rigid, chain-extending terephthalate linkages

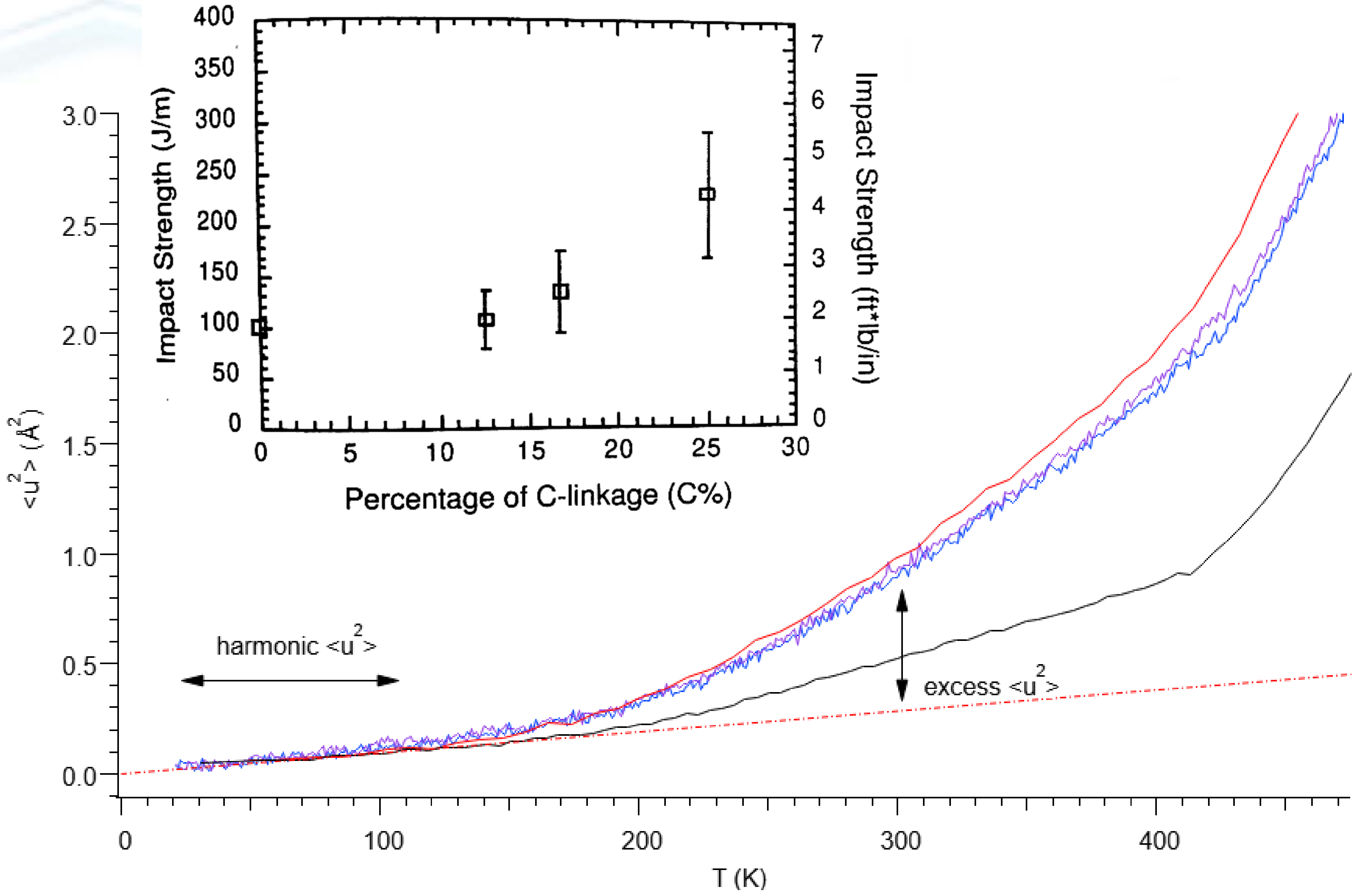
B_xt



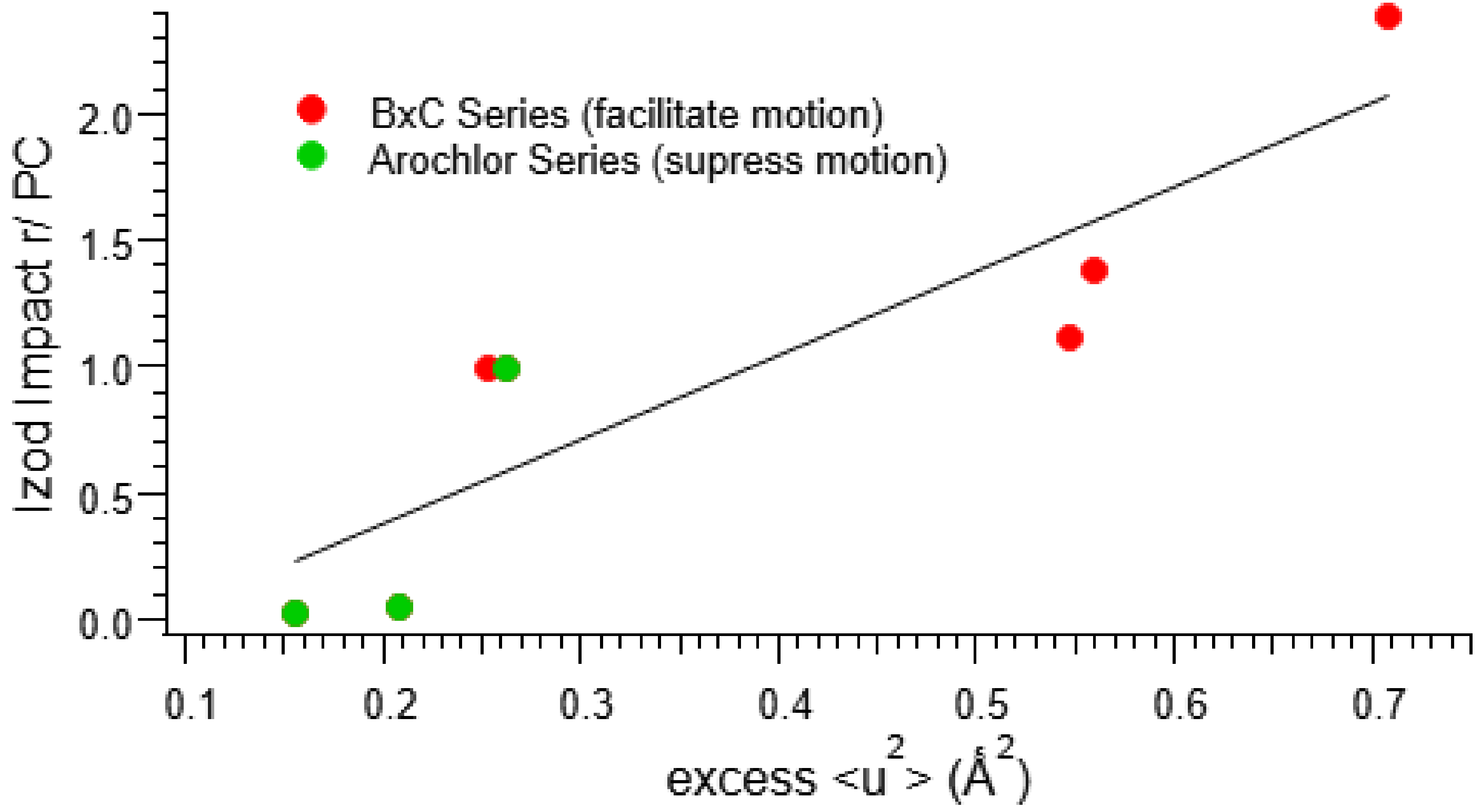
T_xt



Modified Polycarbonates



Fast Dynamics & Impact in Polycarbonates



Fast dynamics seem to facilitate impact mitigation in PCs!

Key Observations

The incorporation of cyclohexyl linkage into PC increases both toughness and molecular mobility at the ns time scale

The addition of Arochlor decrease both toughness and molecular mobility at the ns time scale

Appears to be a strong correlation between fast dynamics and toughness, both at low and high impact rates.

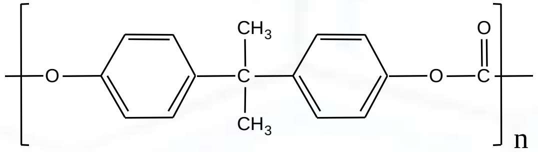
Modified Polycarbonates

Albert F. Yee, Jianwei Liu, Jingsheng Wu (Michigan – late 90’s)

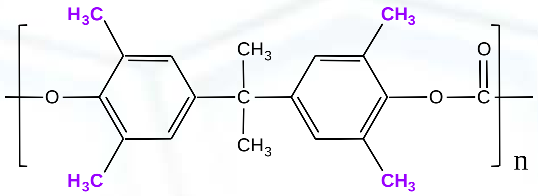
bisphenol-A polycarbonate
based copolymers

tetramethyl bisphenol-A polycarbonate
based copolymers

B or PC

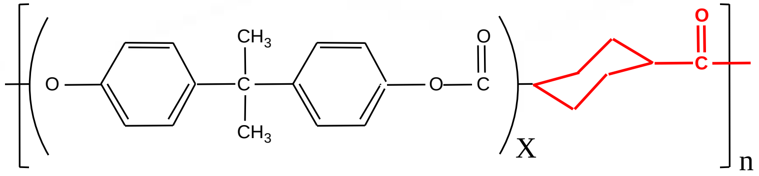


T

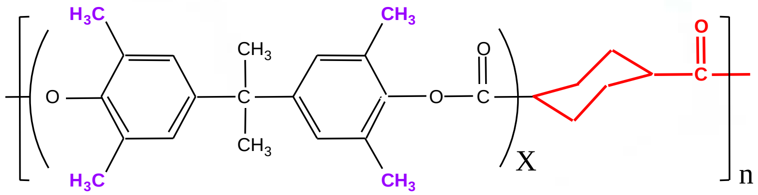


incorporate flexible 1,4-cyclohexylene linkages

B_xC



T_xC



incorporate rigid, chain-extending terephthalate linkages

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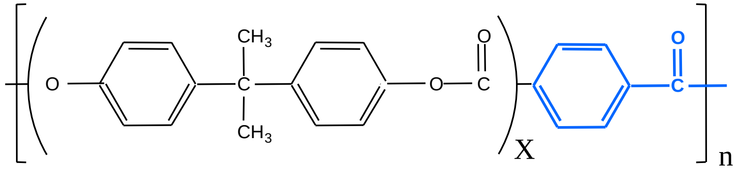

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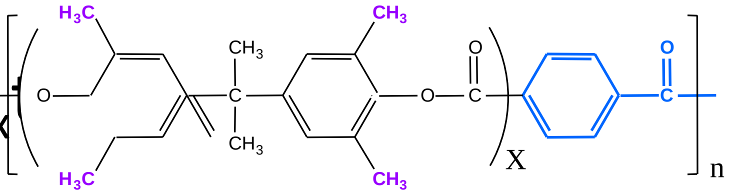

Modified Polycarbonates

Macromolecules **1995,** *28,* 7157–7164 **7157**

Effect of Limiting Chain Mobility on the Yielding and Crazing Behavior of Bisphenol-A Polycarbonate Derivatives

C. J. G. Plummer,[†] **C. L. Soles,**[‡] **C. Xiao,**[‡] **J. Wu,**[‡] **H.-H. Kausch,**[†] **and A. F. Yee***[,‡]

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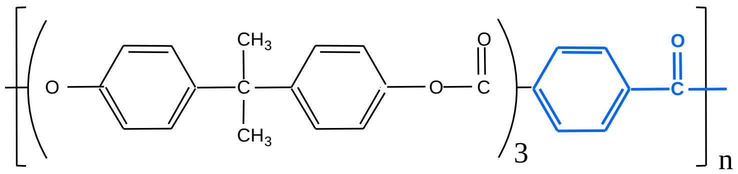
Received March 3, 1995; Revised Manuscript Received July 24, 1995[®]

ABSTRACT: The sub-T_g relaxations of Bisphenol-A polycarbonate (BPA-PC) can be selectively altered by appropriate chemical modification. It is established that these secondary relaxations are responsible for the in-chain cooperative motions of BPA-PC and have profound effects on the deformation behavior of the bulk material. Through investigations of the microdeformation behavior of BPA-PC and alternating block copolymers based on BPA-PC, it is found that the extent of cooperative motion is also influential in activating the disentanglement crazing mechanism at elevated temperatures.

B_3t



Modified Polycarbonates

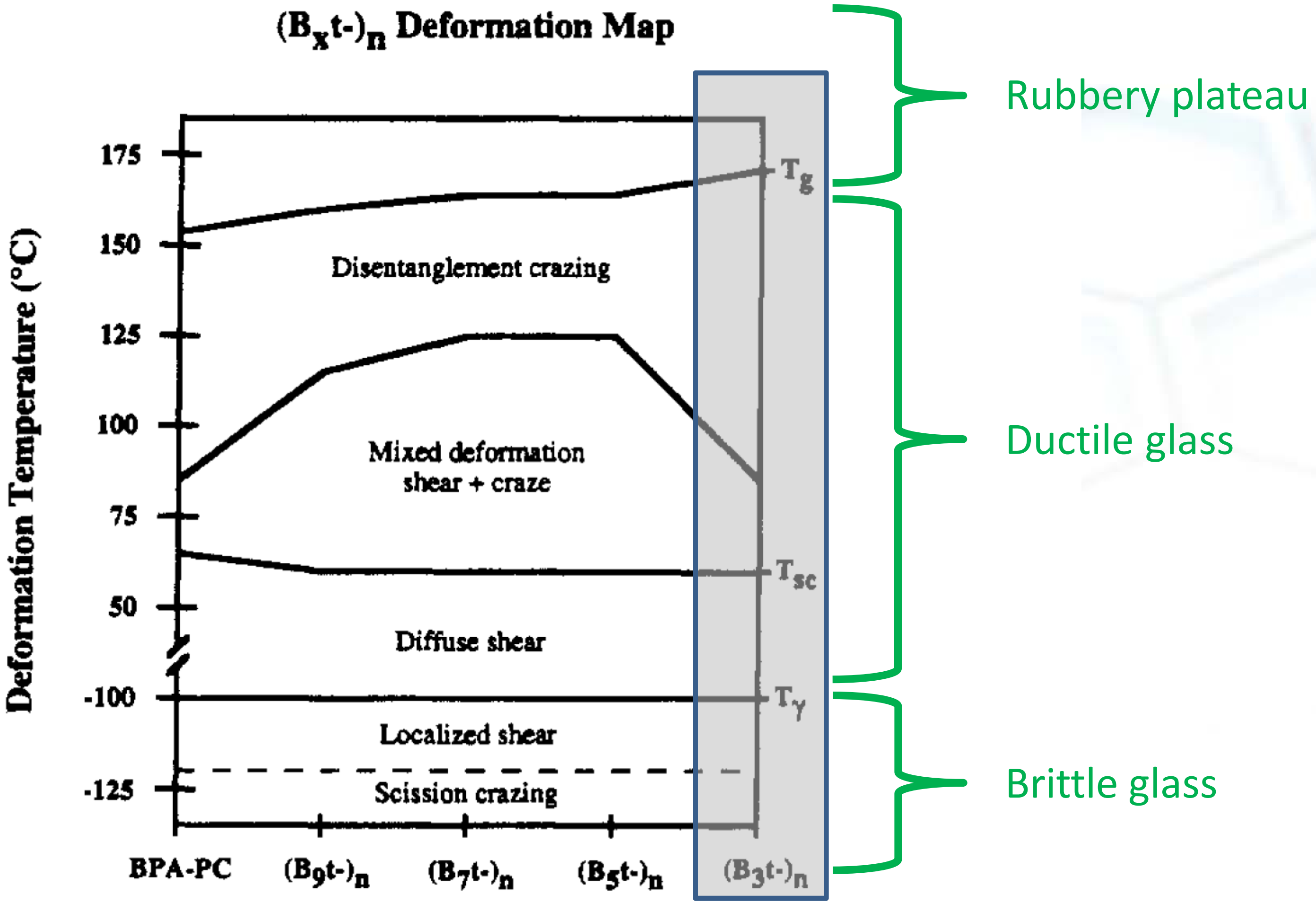
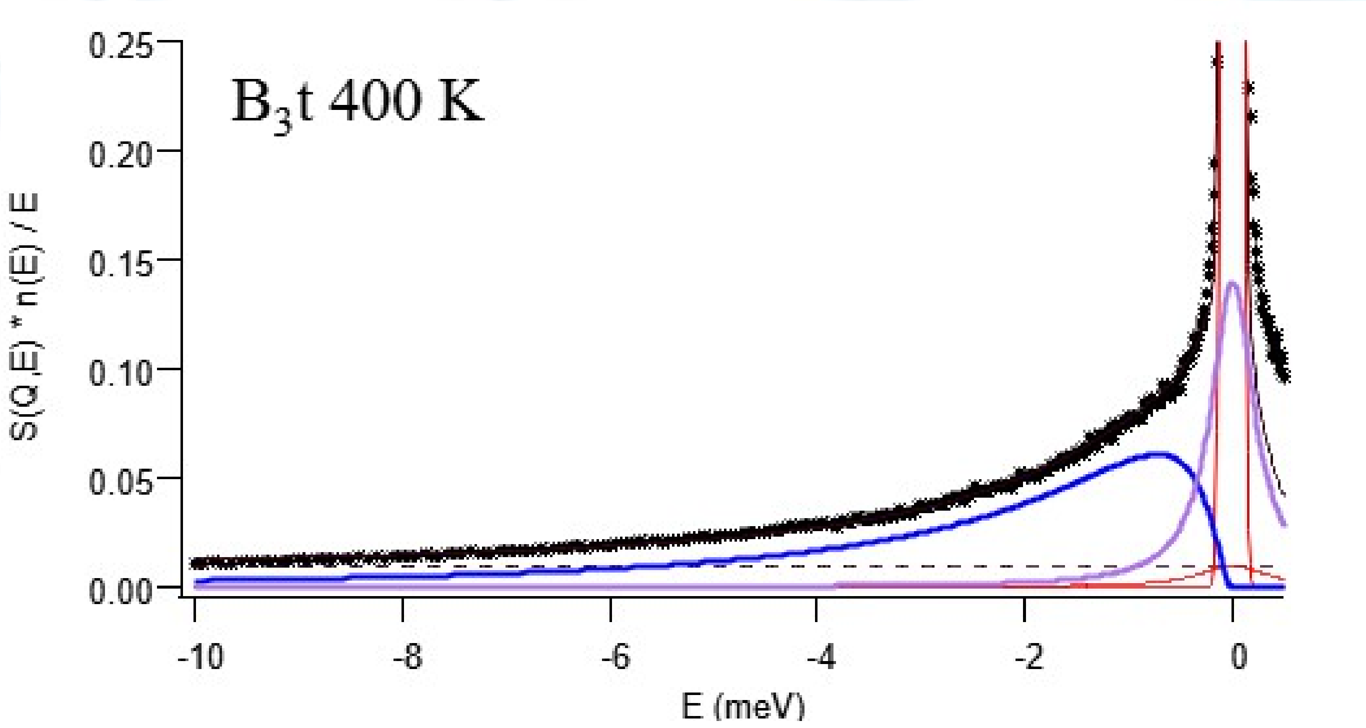


Figure 8. Deformation behavior of the $(B_x t)_n$ copolymers as compared to BPA-PC at various temperatures. All tests were performed at a strain rate of 2×10^{-4} s^{-1}.

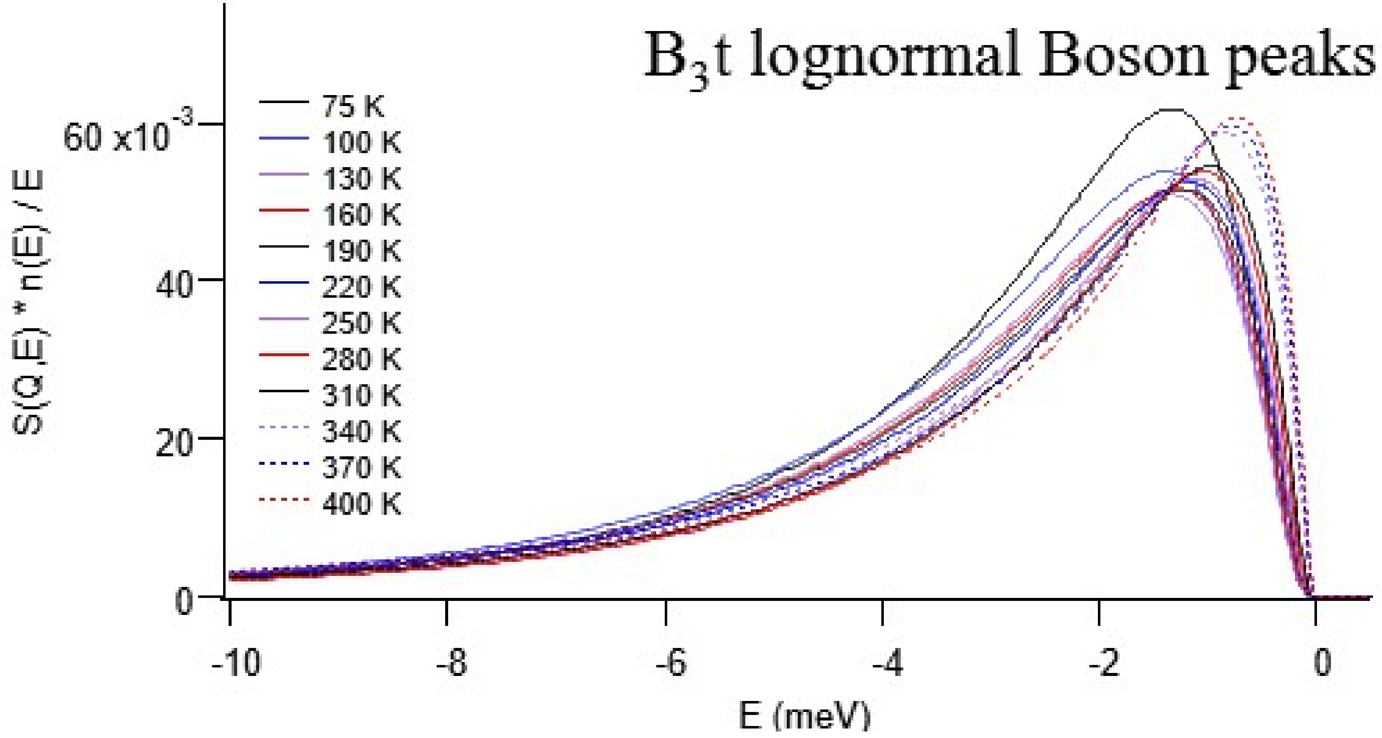
Modified Polycarbonates



Quasielastic / Inelastic neutron spectra fitting (play slide show mode)

(red is elastic resolution, blue is Boson Peak, purple is quasielastic)

Modified Polycarbonates

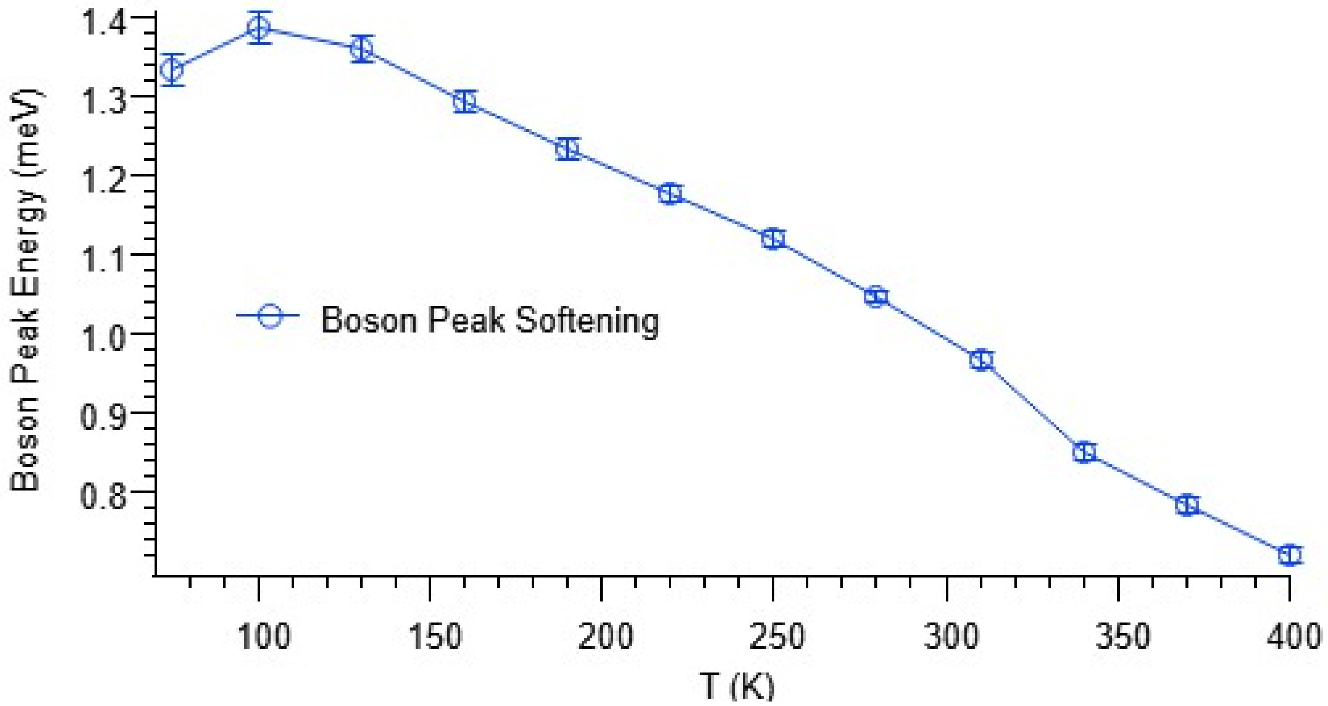


Boson Peak is collective vibration across 100's of atoms
(about 8 cm^{-1} in Raman scattering or 2.5×10^{11} Hz)

Boson Peak mode does not really propagate

Also does not grow in strength / intensity with T

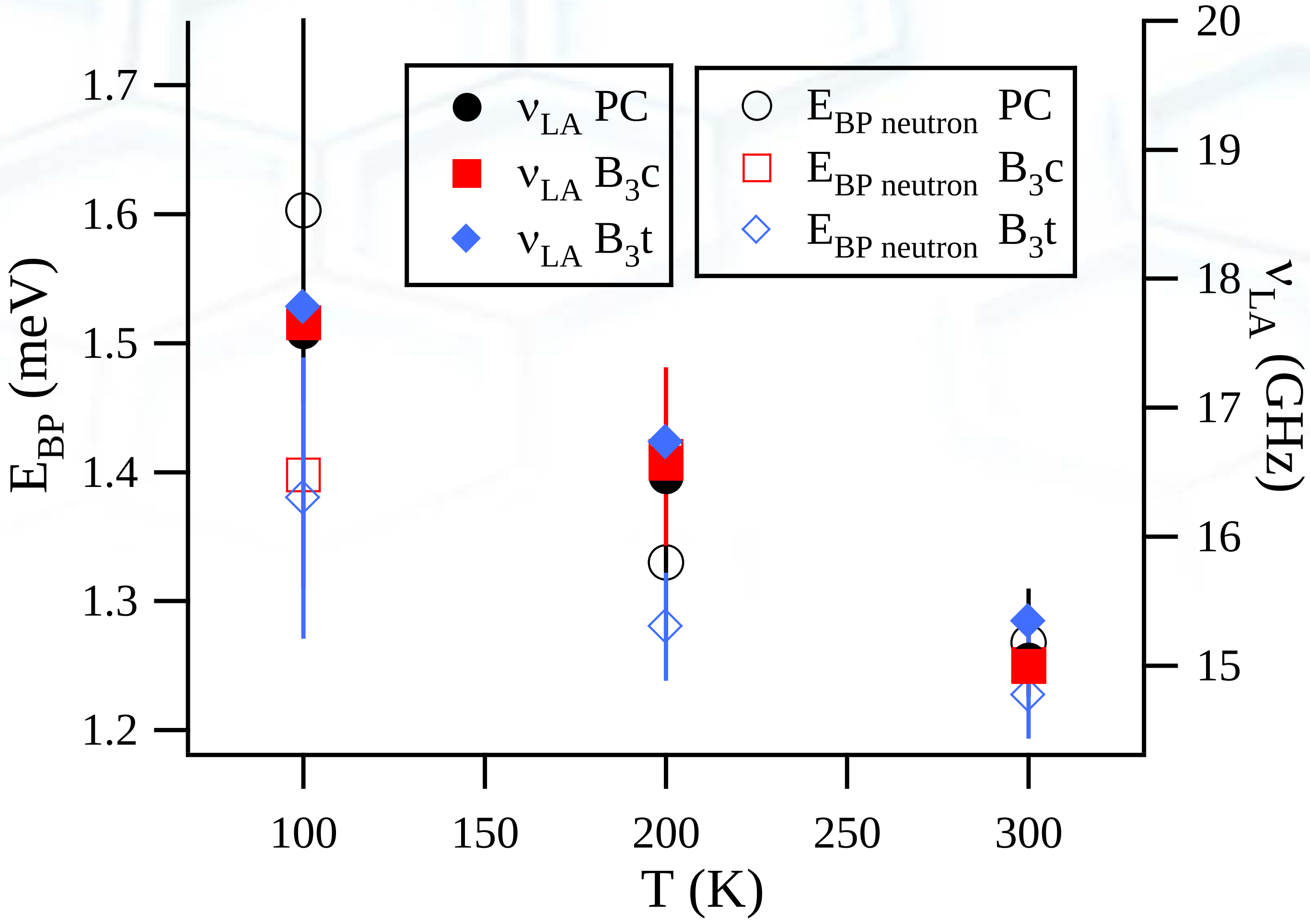
Modified Polycarbonates



Boson Peak frequency / energy does soften with T
(peak shifts to lower energy)

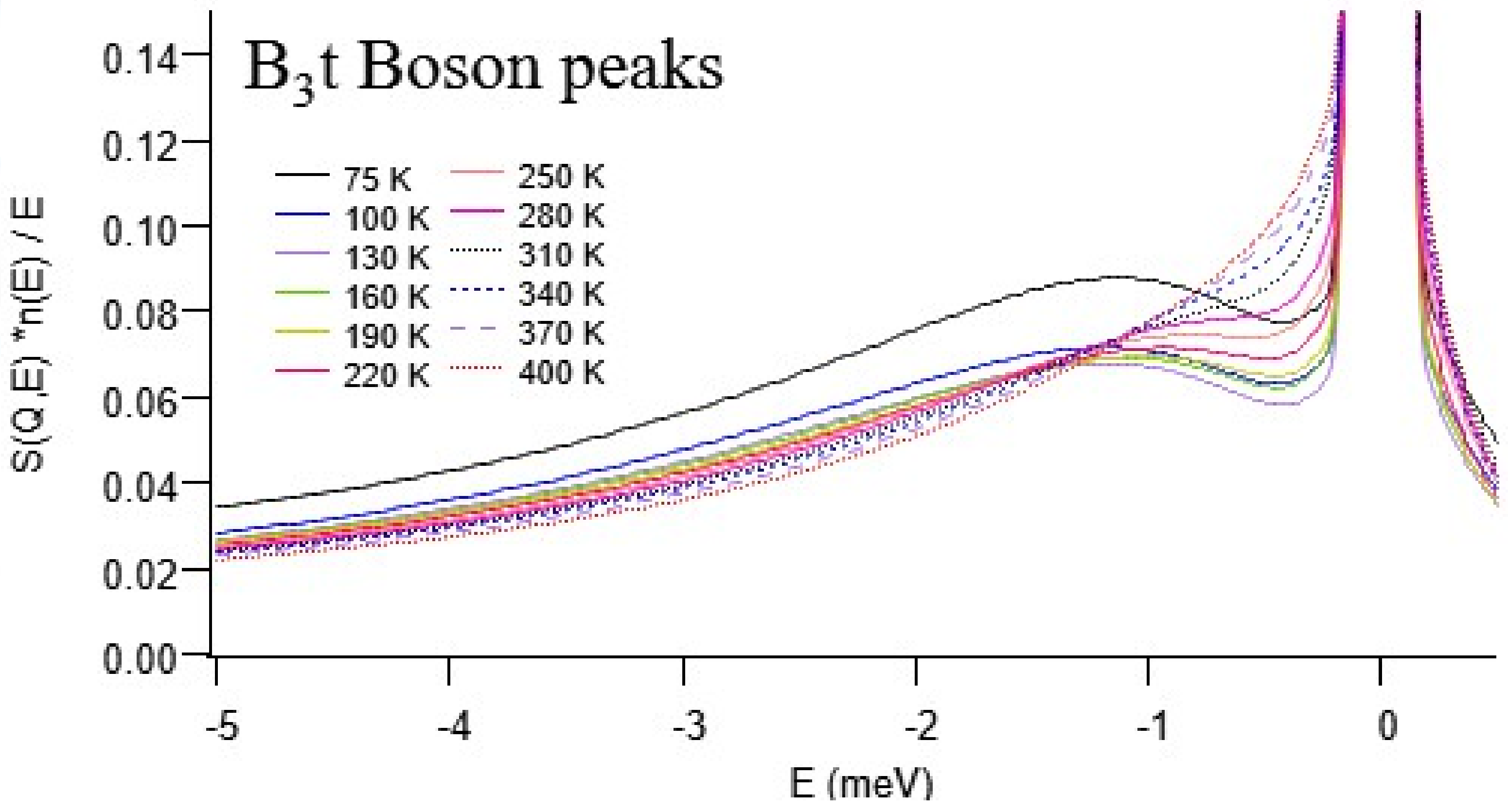
Generally follows acoustic phonon softening

Modified Polycarbonates



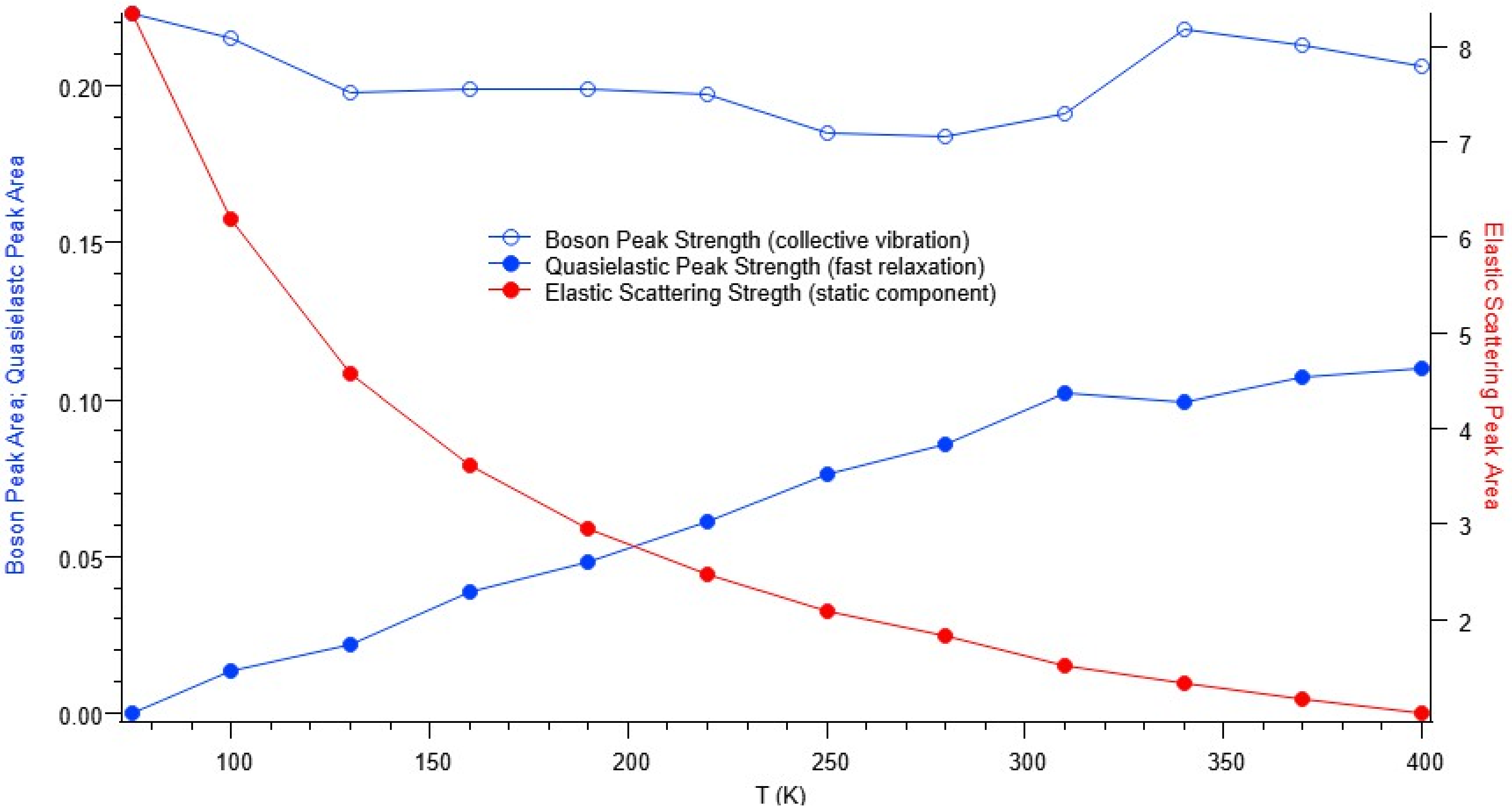
Generally follows acoustic phonon softening

Modified Polycarbonates



Softening of Boson Peak vibrations (attempt frequency) gives way to quasielastic broadening (successful relaxations) at higher T

Modified Polycarbonates



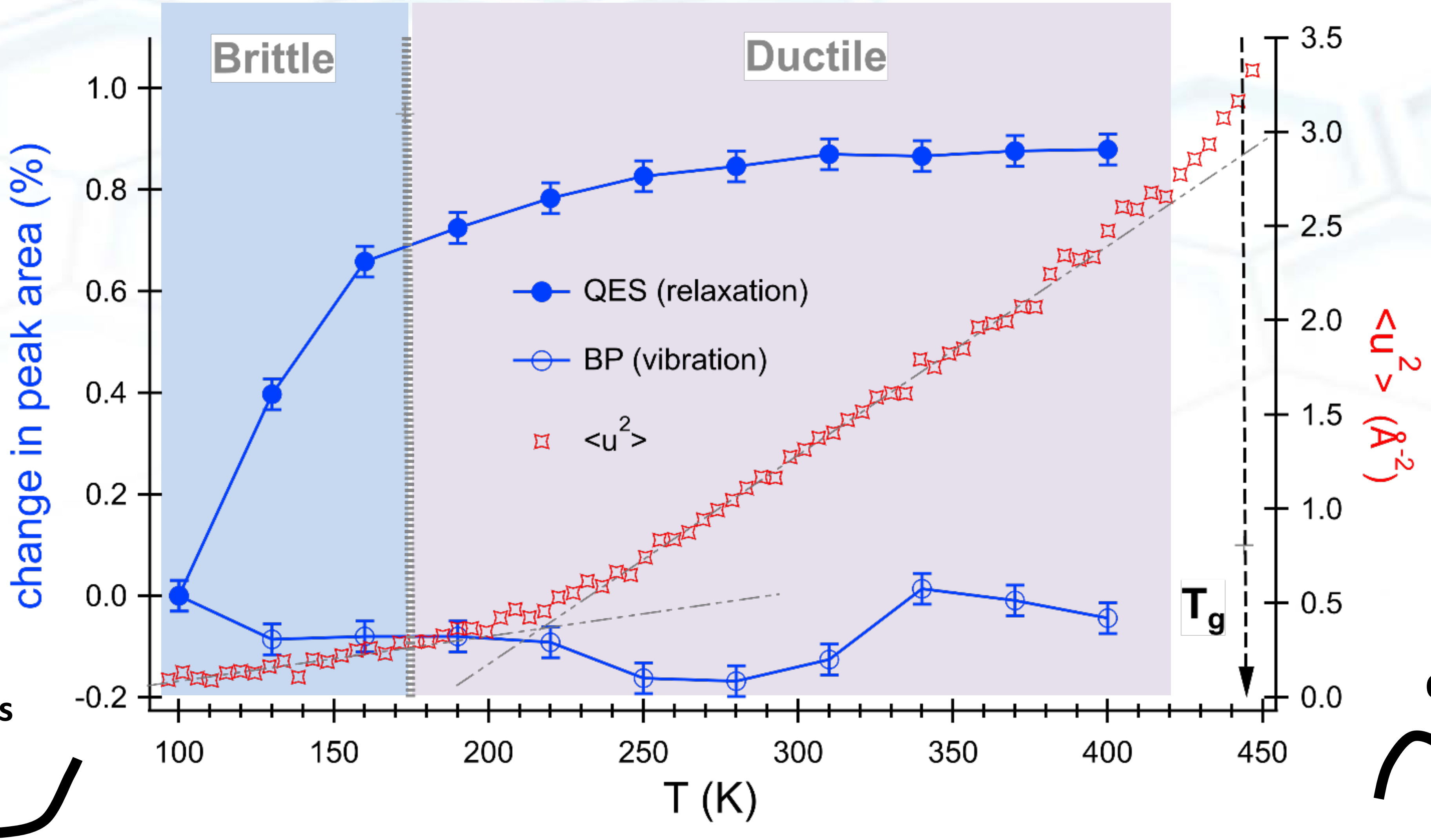
Decrease in elastic scattering leads to a softening of the BP, but not a change in intensity, concurrent with an increase in the population of QES scattering events.

Modified Polycarbonates – Ductile to Brittle Transition (DBT)

Brittle Deformation

Localized Shear Banding

Chain Scission Crazing



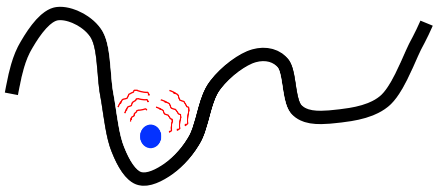
Ductile Deformation

Diffuse Shear Banding

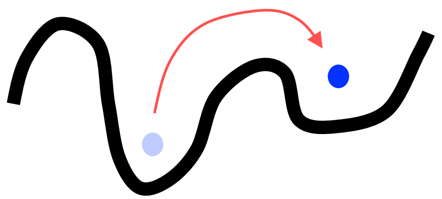
Extensive Disentanglement Crazing

Mixed Modes

BP Vibrations



QES Relaxations



Toughness facilitated by the activation of fast (ns to ps) relaxations

Modified Polycarbonates

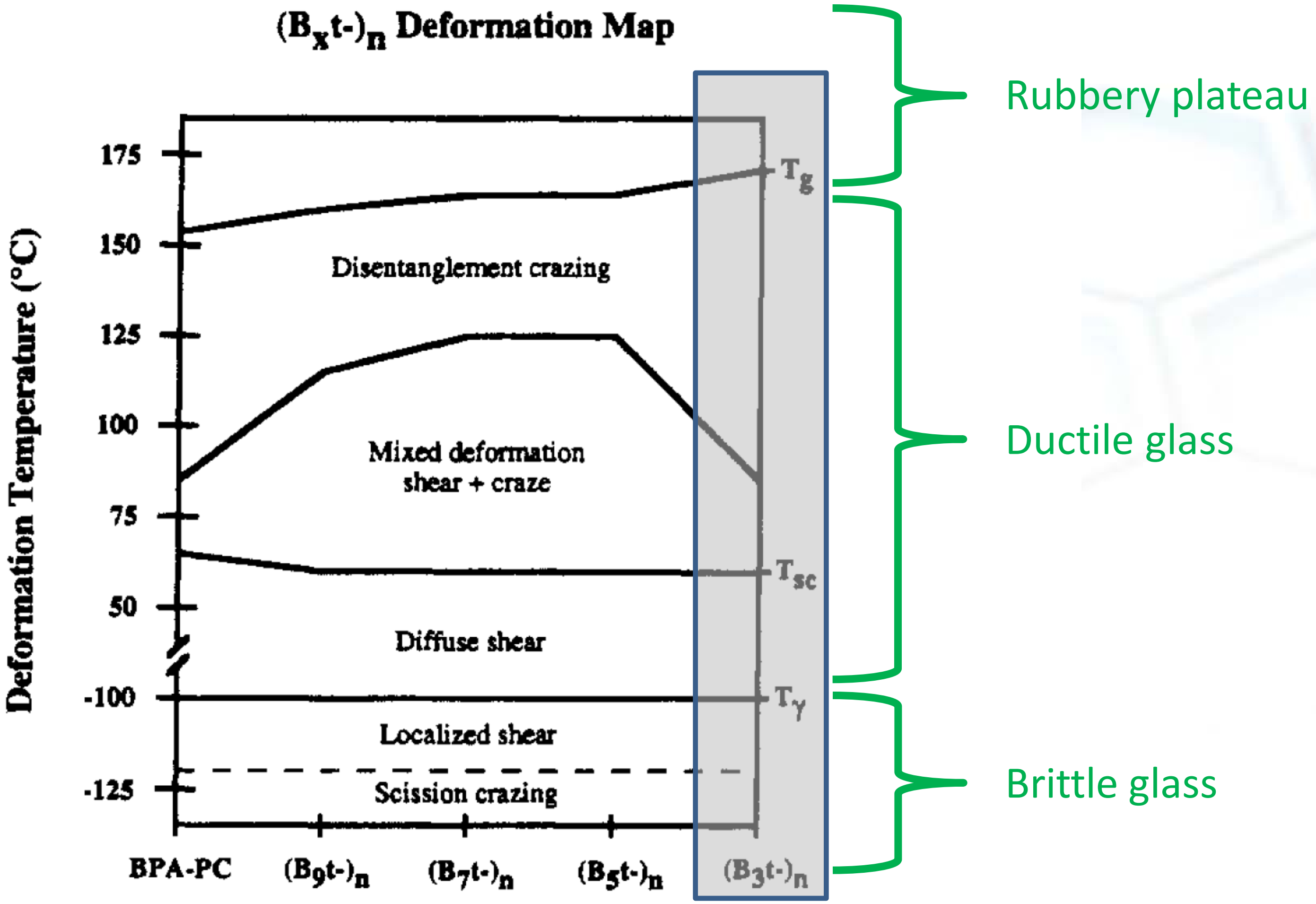
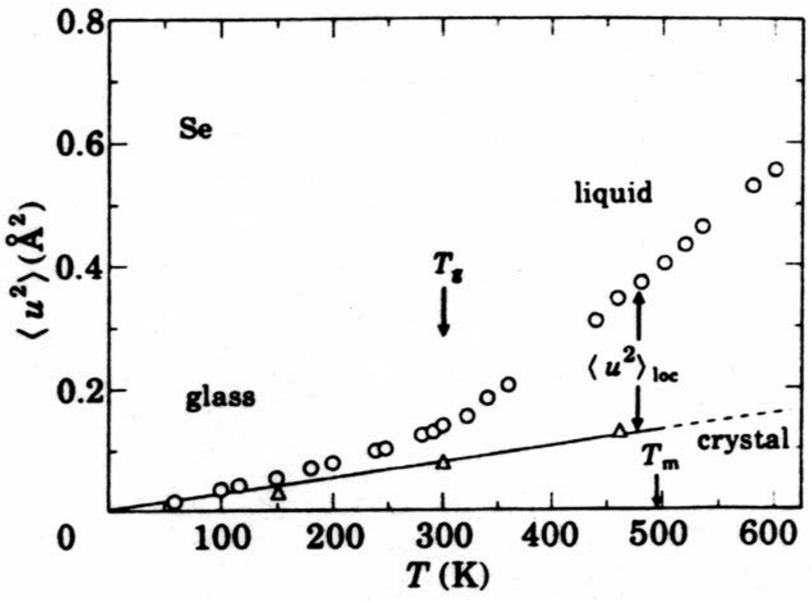


Figure 8. Deformation behavior of the $(B_xt)_n$ copolymers as compared to BPA-PC at various temperatures. All tests were performed at a strain rate of $2 \times 10^{-4}\ s^{-1}$.

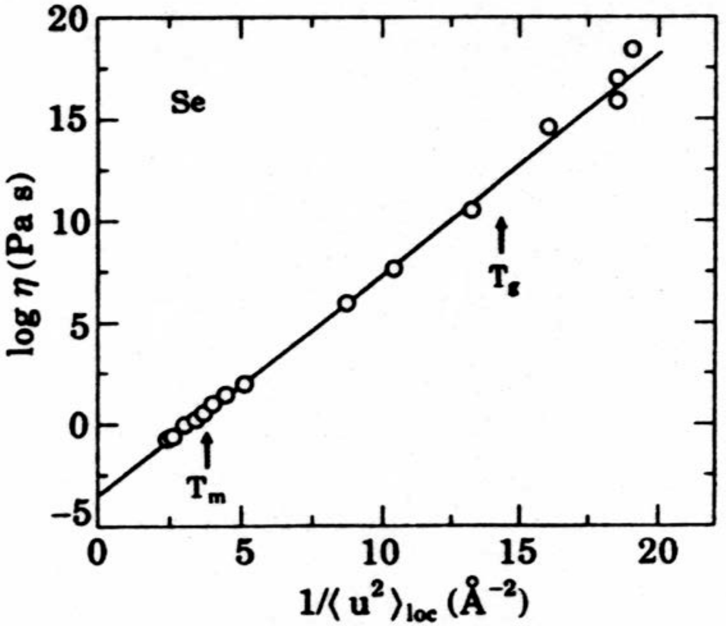
Does this make sense?



$<u^2>$ & Viscosity (η)

$$\eta = \eta_o \exp\left(\frac{<u^2>_o}{<u^2>_{loc}} \right)$$

Observed in metallic & polymeric glasses over a broad temperature range



<u>Experimental support</u>:

(Se) Buchenau & Zorn, *Euro. Phys. Lett*. **18**, 523 (1992)
(PB) Kanaya et al, *Phys. Rev. E* **60**, 1906 (1999)

<u>Theoretical support</u>:

Hall & Wolynes, *J. Chem. Phys*. **86**, 2943 (1987)
Dyre et al, *Phys. Rev. B* **53**, 2171 (1996)
Zurcher & Keyes, *Phys. Rev. E* **60**, 2065 (1999)

Viscosity decrease exponentially with the inverse of $<u^2>$

Viscosity is a mechanical dissipation (measured over seconds!)

Conclusions

Seems to a phenomenological correlation between the a materials ability to transition fast vibrations (ps) into fast relaxations (ps to ns) and mechanical ductility or toughness.

Analogous to old school correlations between dynamic mechanical data (tan δ) and toughness, but measurements are at the right time scale to see molecular scale processes

QENS and low frequency Raman seem to be important techniques to quantify the molecular processes that contribute to ballistic impact resistance in polymers

CHARACTERIZATION AND MEASUREMENT NEEDS IN POLYMERIC TRANSPORT MEMBRANES

Contributors – Transport Membranes

NIST
- Chris Stafford
- Edwin Chan
- Madhusudan Tyagi
- Jacob Tarver
- Bradley Frieberg
- Cheol Jeong
- Gery Stafford
- Velencia Witherspoon
- Devin Shaffer

National Institute of Standards and Technology
U.S. Department of Commerce

U Mass Amherst
- Bryan Coughlin
- Tsung-Han Tsai
- WenXu Zhang

Dow Chemical
- Abhis… y
- Stev… s

PMSE
2019 Cooperative Research Award in Polymer Science & Engineering

UC Boulder
- D Higgs
- Steven George

Penn State
- Mike Hickner
- TJ Zimudzi

Goals for this Section

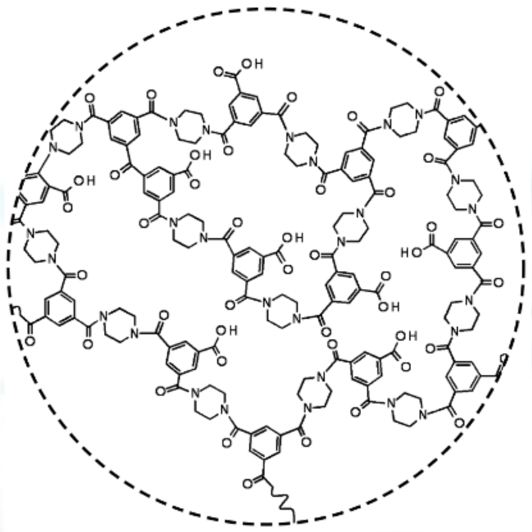
Discuss the diversity of models to describe transport in polymeric materials and membranes

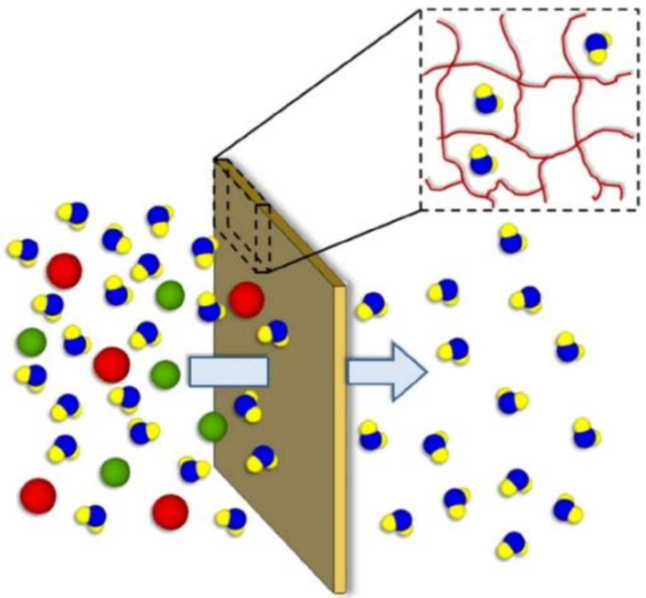
Emphasize the correlated nature of structure, dynamics and transport in polymer membranes

Highlight the metrology and measurements needs

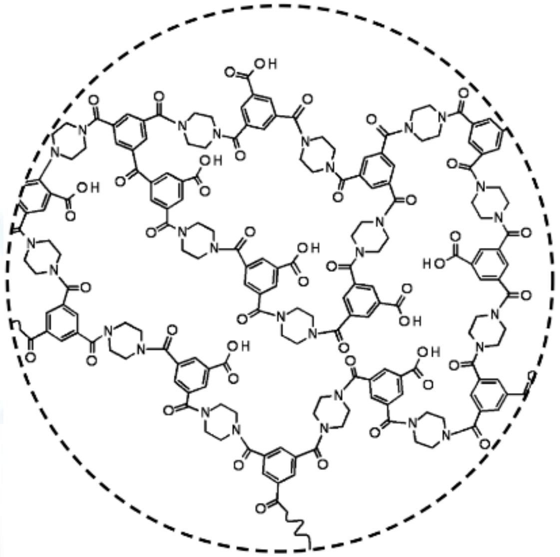
Provide examples on 3 model systems: epoxies, polyamides, & ion alkaline exchange membranes (water is our model penetrant)

Emphasize the need for physical experiments to validate theory, simulation, and modeling as the only path forward to fully understand transport in polymer membranes





Polymer Membranes with Controlled Transport Properties



Polymers with "tuned" transport a critical for a range of technologies

Absorbents to capture and sequester unwanted species

getters & super-absorbents – H_2O, O_2,CO_2, hydrocarbons, solvents

Selective transport water, gas, ions, hydrocarbons, solvents

water filtration (RO, FO, NF), chemical separations, battery electrolytes, fuel cell membranes; chemFET sensors, electrolytes and membranes; oxygenation membranes

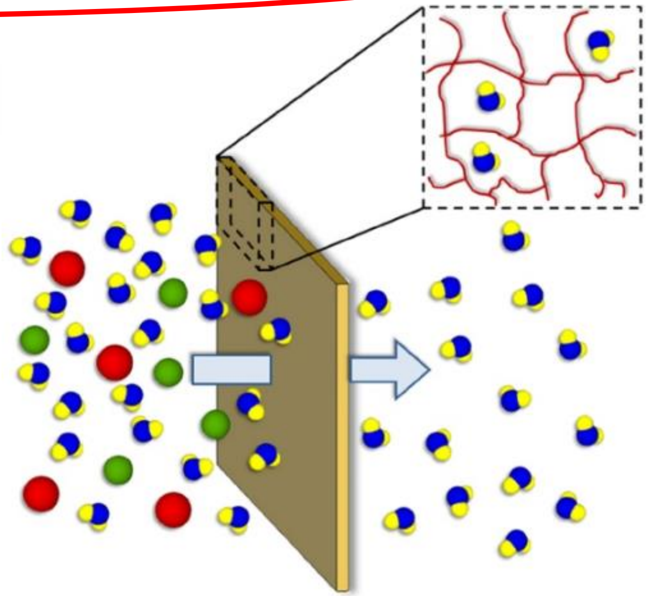
Hindered transport water and gas

barrier films, coatings, structural composites

Plethora of models to describe transport behavior

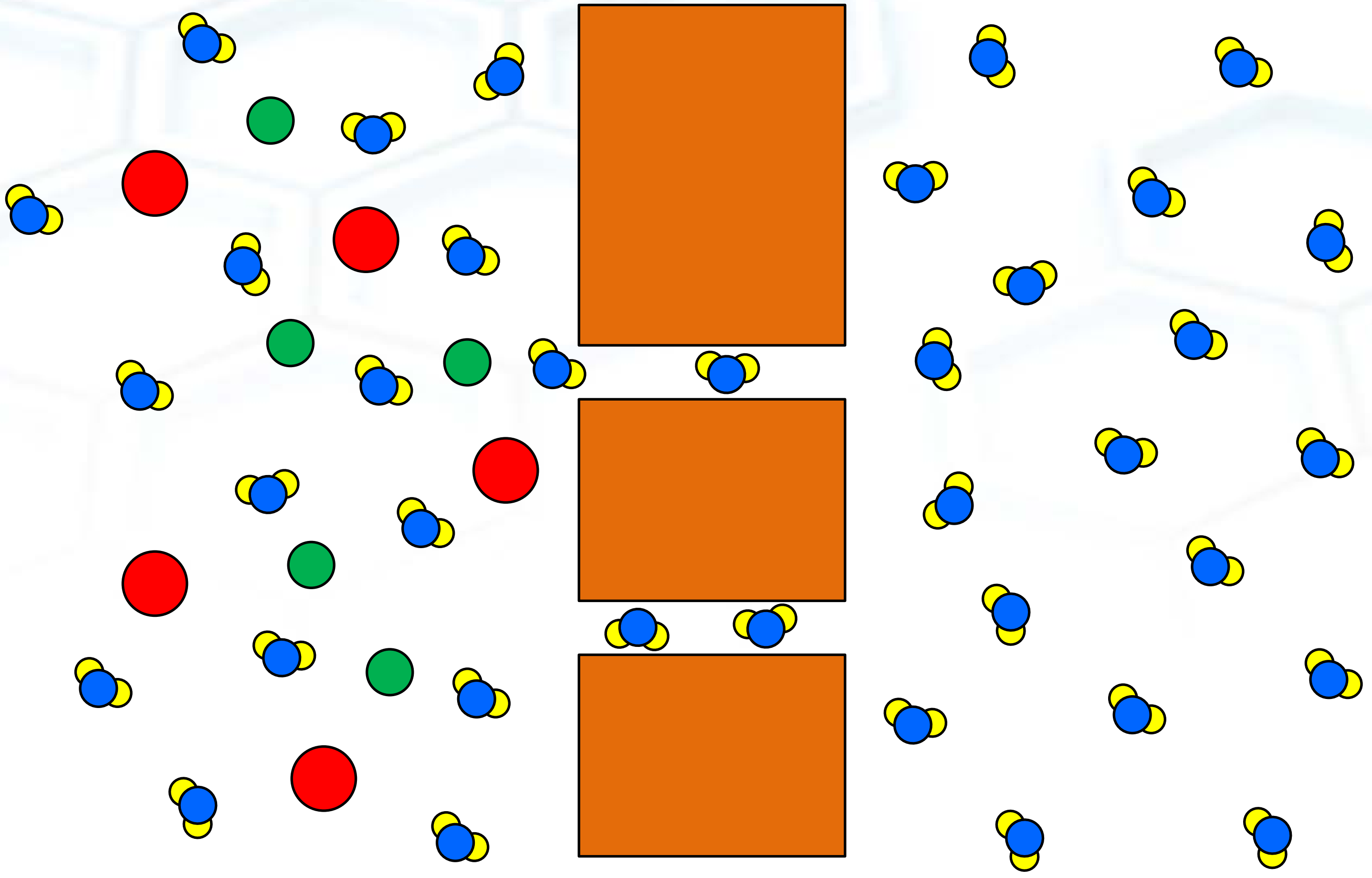
free volume, dual mode sorption, solution-diffusion, pore-flow, Fickean, non-Fickean, case II

Insight needed at molecular mechanism level to predict and tune transport



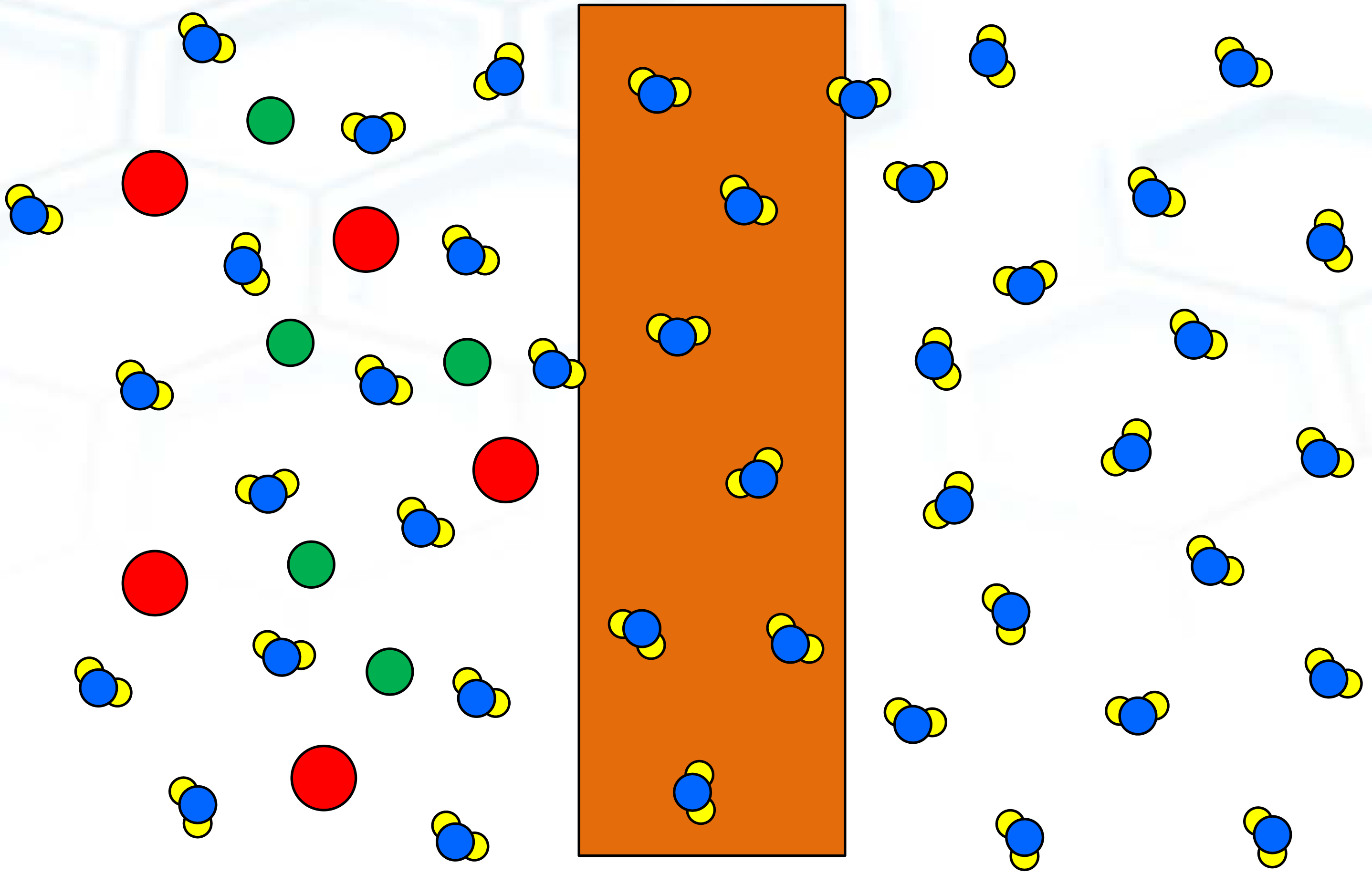
Direct Relevance to Printed & Flexible Electronics

Membrane Transport Mechanisms



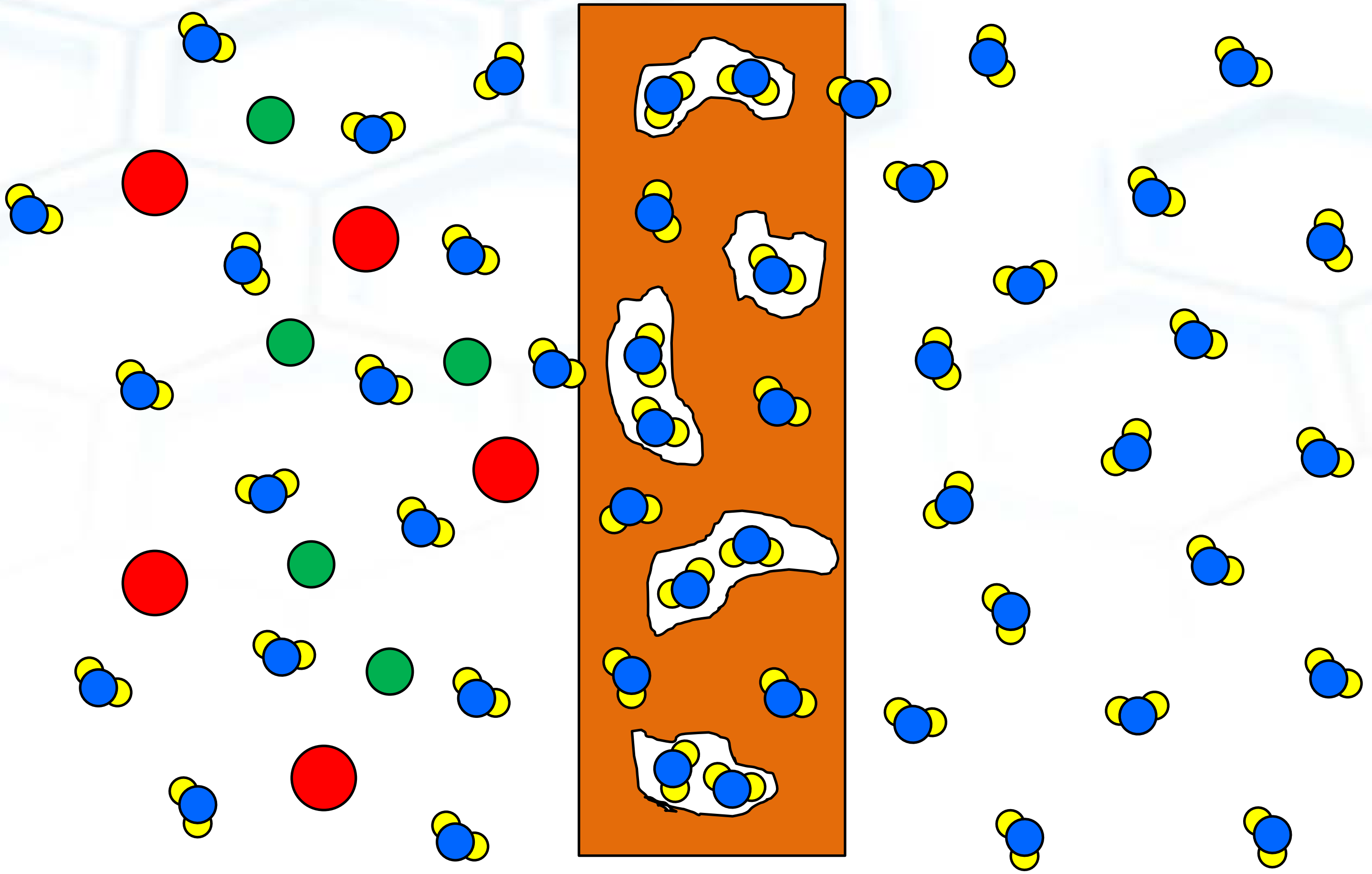
Pore-Flow

Membrane Transport Mechanisms



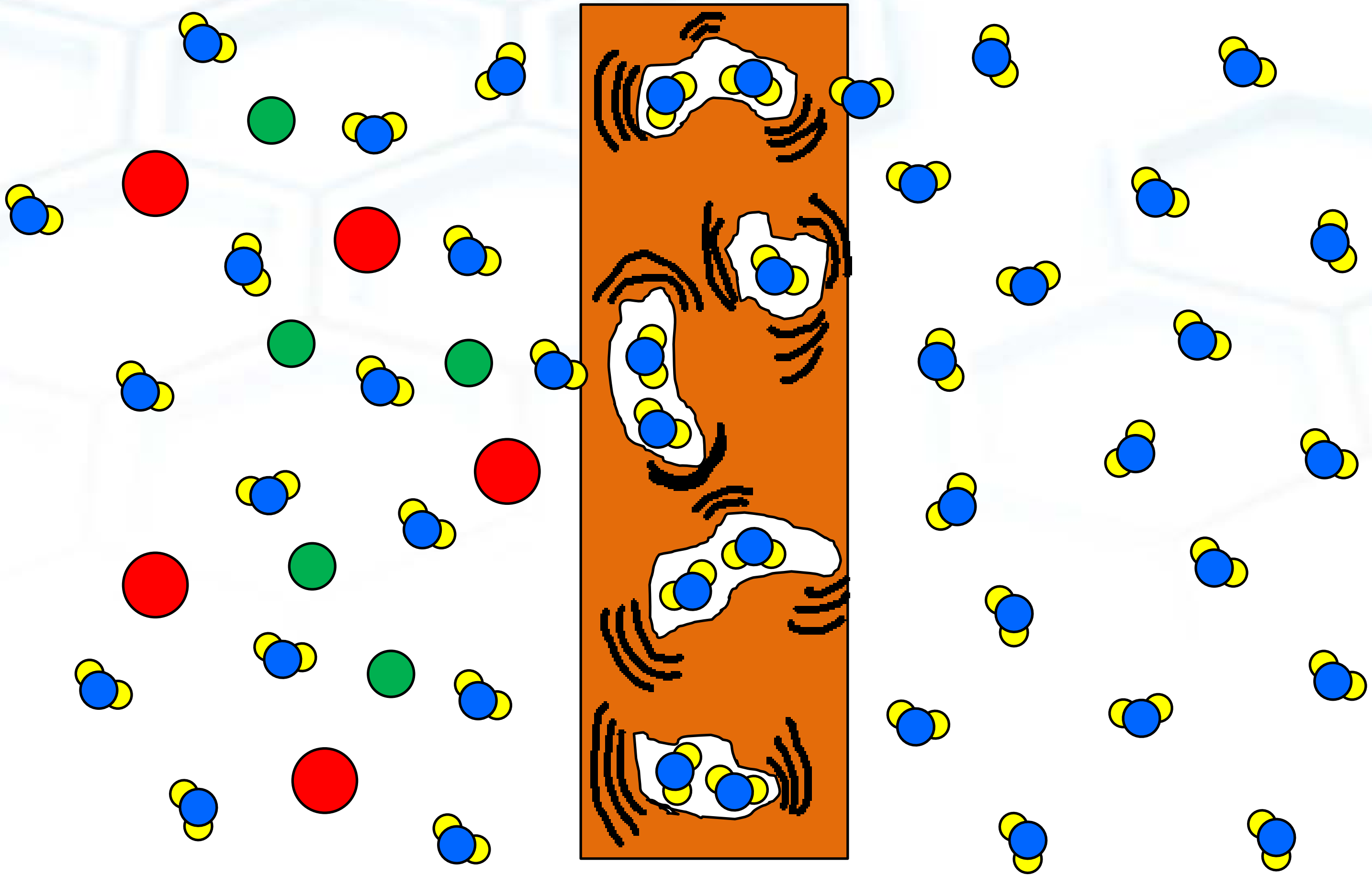
Perm-Selective

Membrane Transport Mechanisms



Dual-Mode Sorption

Membrane Transport Mechanisms



Free-Volume Transport

Issues when trying to understand transport

Complicated and inter-related effects

- Cross-linking affects structure, functionality, dynamics, modulus, swelling, and diffusivity………..
- Thin films and interfaces are different from bulk
- Penetrant affects membrane – plasticization / antiplasticizations, morphology, structure, prosity, diffusivity……

Non-equilibrium processes

- Concentration dependent transport; pathway dependent (up vs down jump)
- Physical ageing & rejuvenation
- Chemical ageing & degradation

Hierarchical processes

- Time scales of picoseconds to hours
- Length scales from nanometers to centimeters
- Local, fast process couple to long range transport; nature of coupling is complicated

Diversity of membrane materials

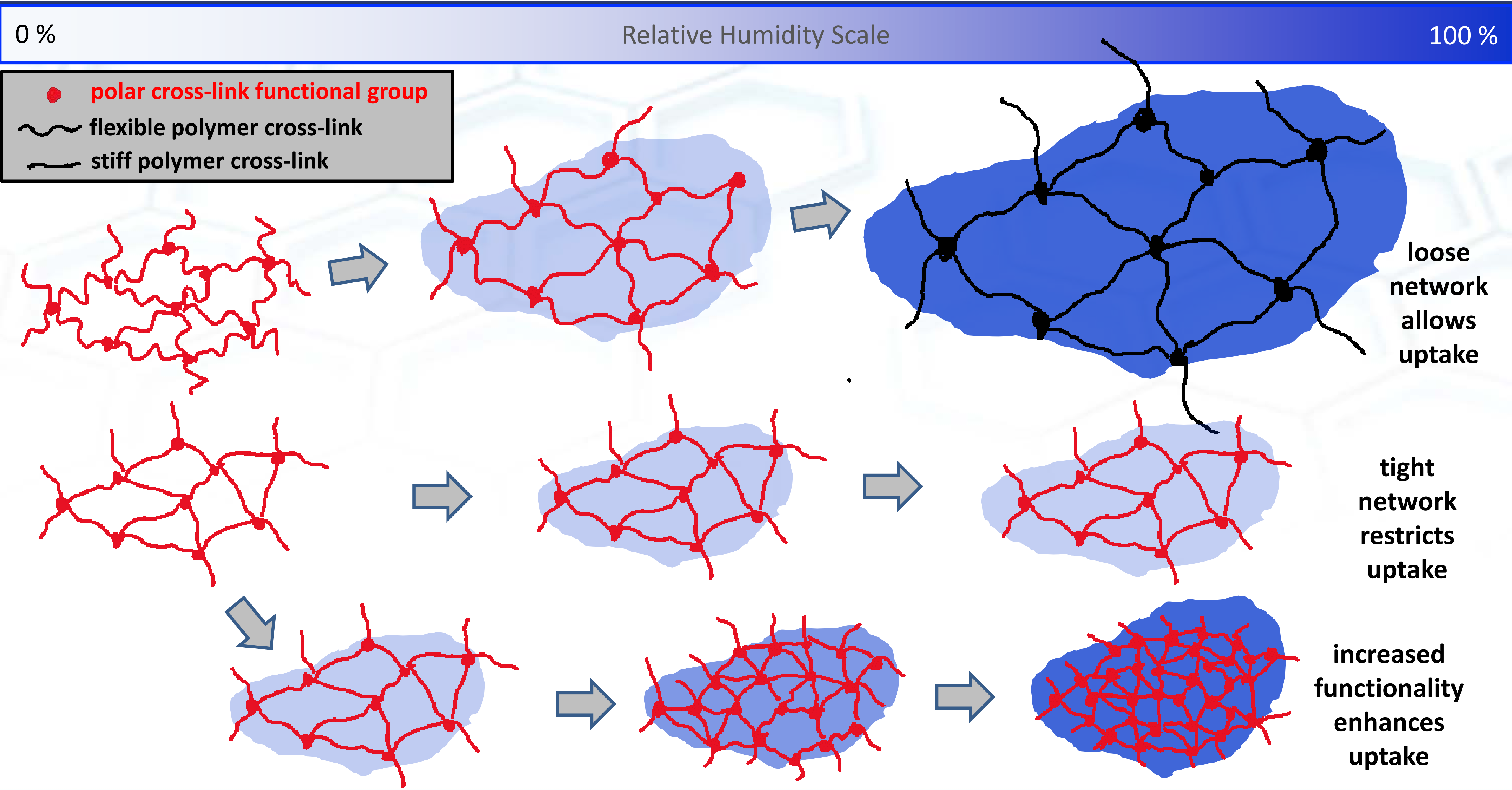
- Epoxies, polyamides, ionomers, electrolytes, glasses, gels, etc.

Connections between models and measurements is non-trivial

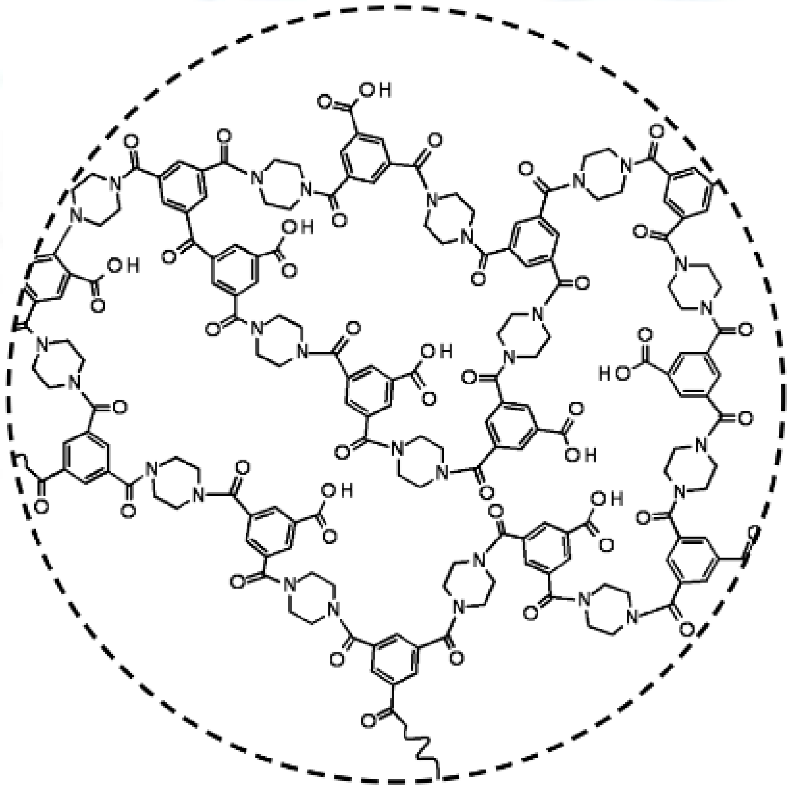
- How to measure free volume?
- How to handle broad range of time and length scales?

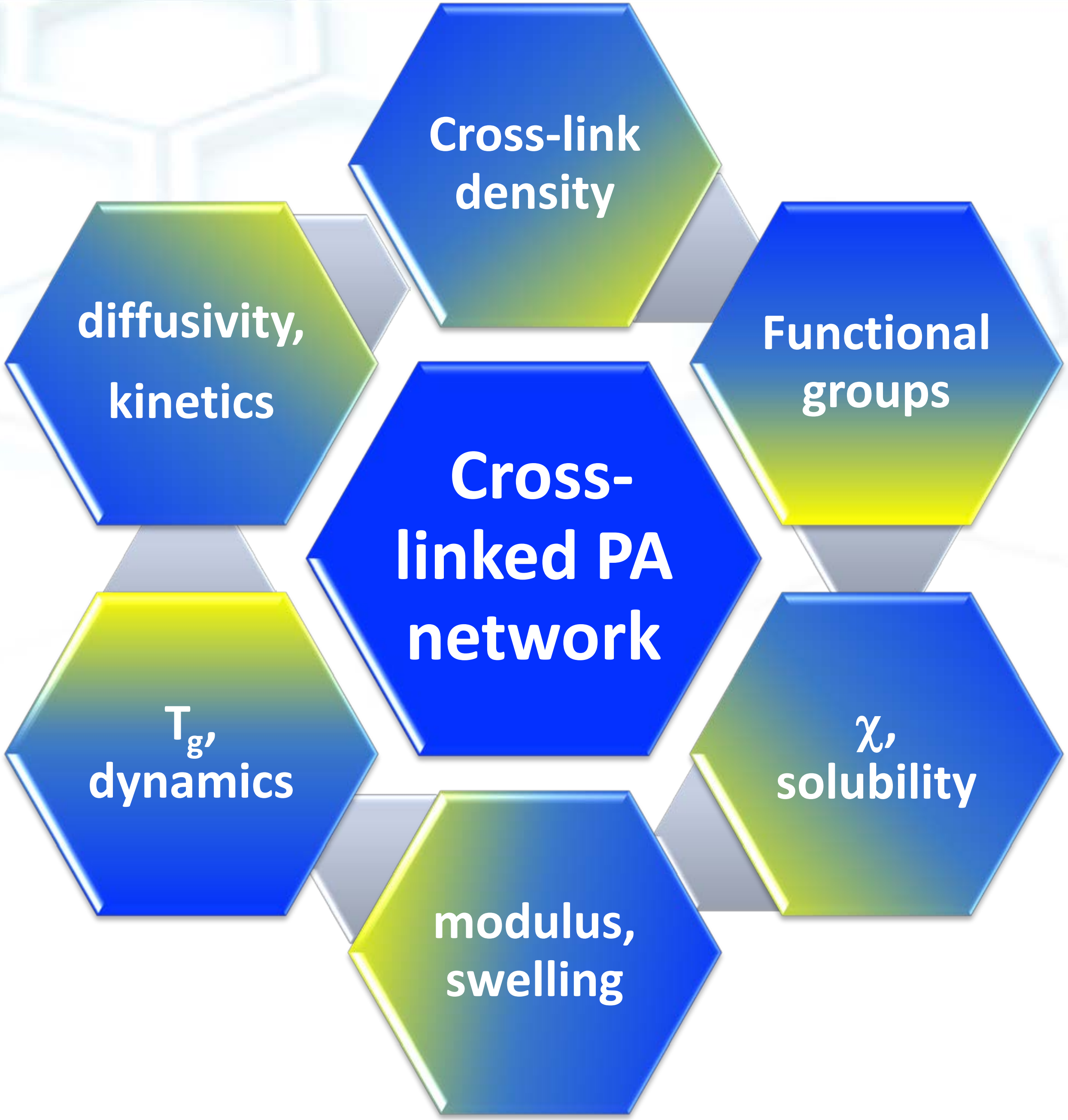
Poorly defined samples

- Thickness variations (transport is intensive), compositional heterogeneity, structural heterogeneity, multi-phase materials


0 %
Relative Humidity Scale
100 %
polar cross-link functional group
flexible polymer cross-link
stiff polymer cross-link
loose network allows uptake
tight network restricts uptake
increased functionality enhances uptake

It’s Complicated

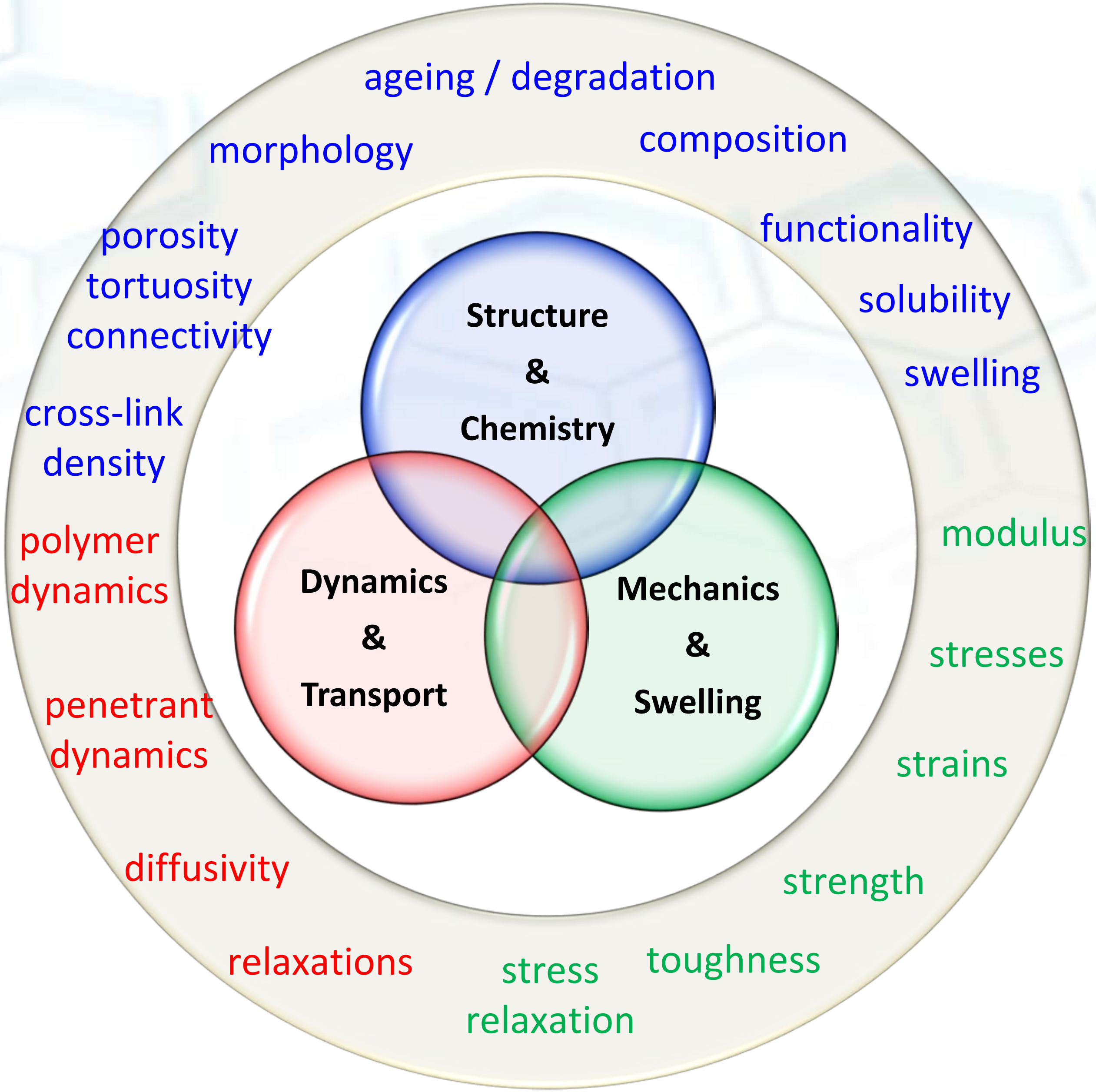




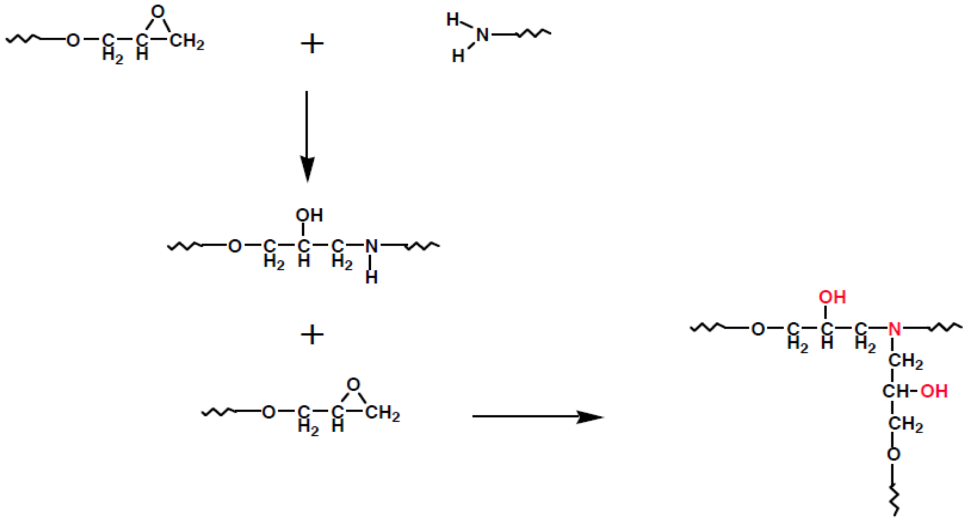
Structure & Chemistry (S, χ)
IR techniques (FTIR, ATR, PMIRAAS)
SAXS, WAXS, SANS
SXR, NR, VASE
PALS
NMR
calorimetry
TEM, SEM

Dynamics & Transport (D, η)
QENS, Raman
μwave dielectric, DRS
QCM, mass uptake
PRI
NMR
DMA, rheology

Mechanics & Swelling (σ, ε, E)
Cantilever bending
Buckling & Wrinkling
PRI
BLS

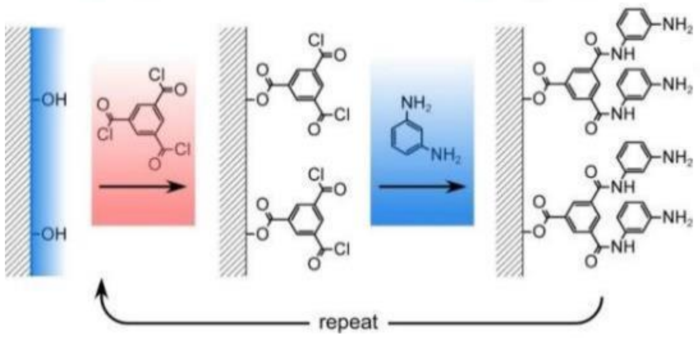


Materials Systems



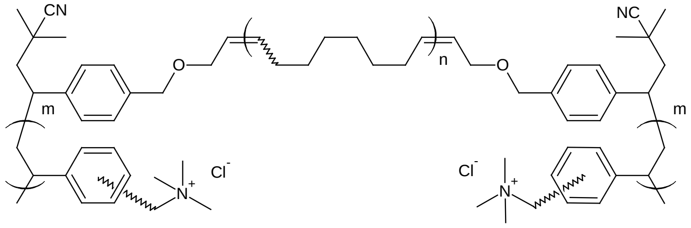
Epoxy Networks

- High T_g, glass networks
- Matrix for fiber reinforced composites
- Aerospace, transportation, infrastructure



Polyamide Networks

- High T_g, glass networks
- Active layer for water purification
- RO, FO, nanofiltration

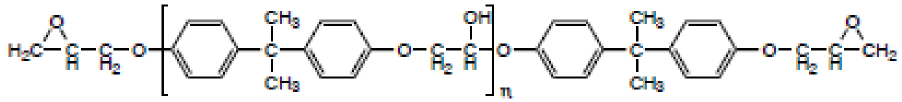


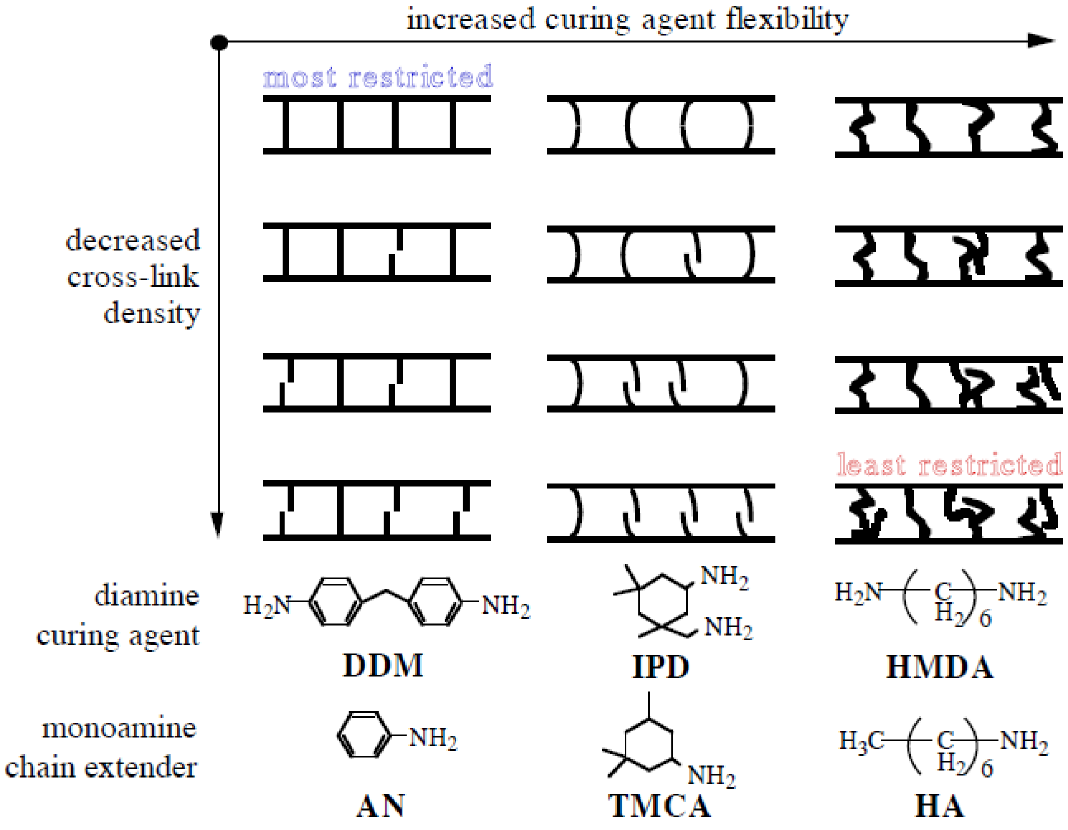
Hydrated Ion Containing Polymers

- Block copolymer based membranes
- Alkaline exchange membranes

Epoxy Network Variations

DER 332 - difunctional epoxy (with n=0):





"rigid" "semi-flexible" "flexible"

Positron Annihilation Lifetime Spectroscopy

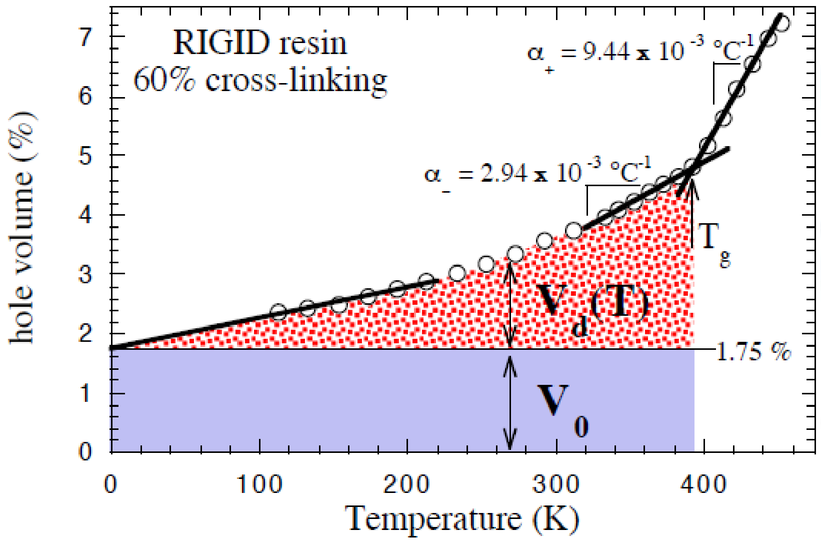
PALS can measure:

- $\tau_3 \Rightarrow$ avg. nano-pore radius or volume v(T)
- $I_3 \Rightarrow$ # of nano-pores
- $V_h(T) \Rightarrow$ volume fraction of nano-pores

$\Downarrow$

$$V_h(T) = Cv\,(T)\, I_3(T)$$

$$V_h(T) = V_0 + V_d(T)$$



typical epoxy studied here:

$r \approx 2.5$ to 3.1 Å

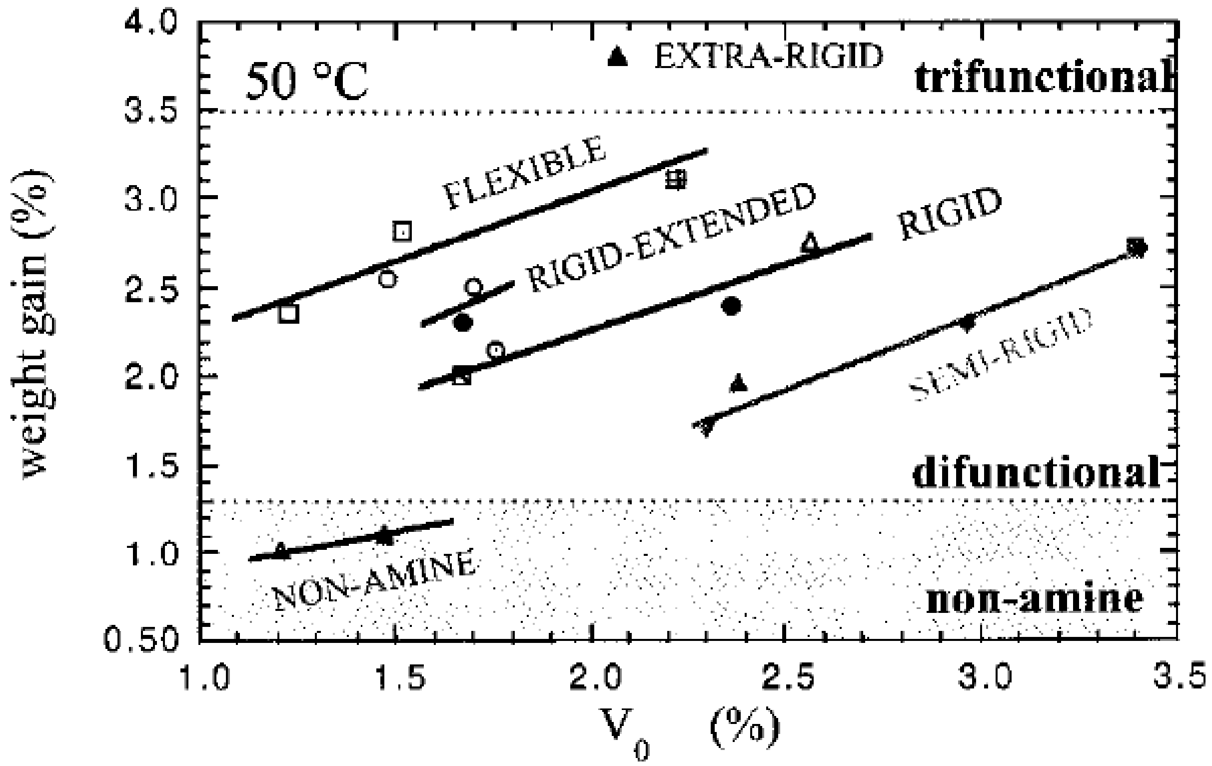
$V_h(T) \approx 3$ to 7 volume %

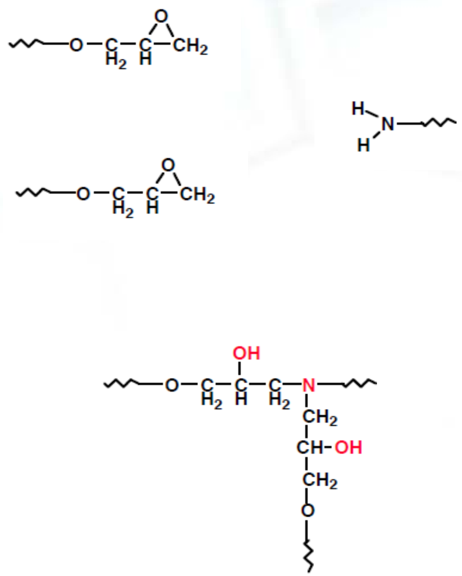
$V_d(T) \approx 2/5$ (RIGID $\uparrow$XL)

$V_d(T) \approx 4/5$ (FLEXIBLE $\downarrow$XL)

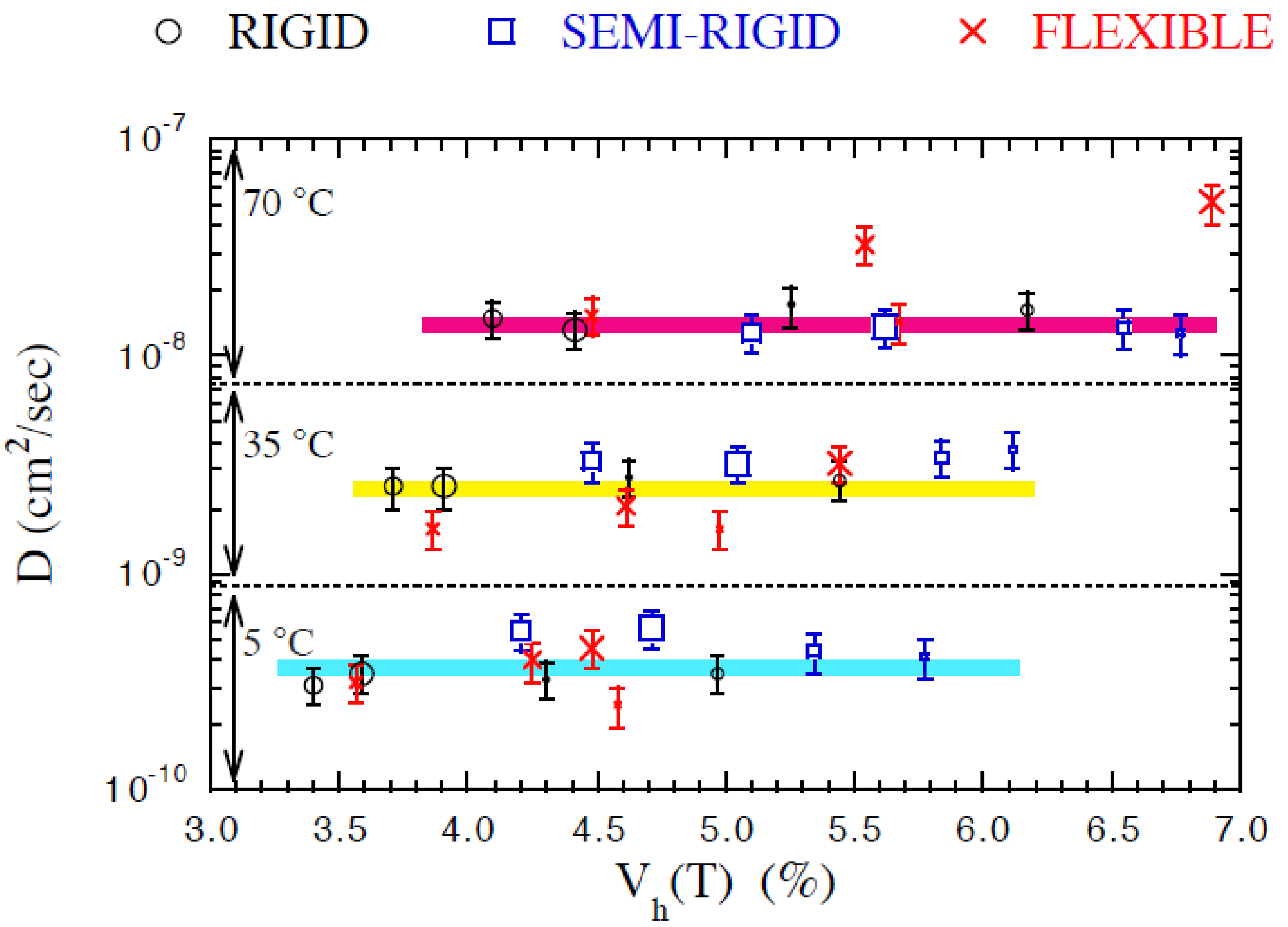
PALS and Equilibrium Moisture Uptake

Static volume is important, but polarity is more important!





PALS and Moisture Diffusivity

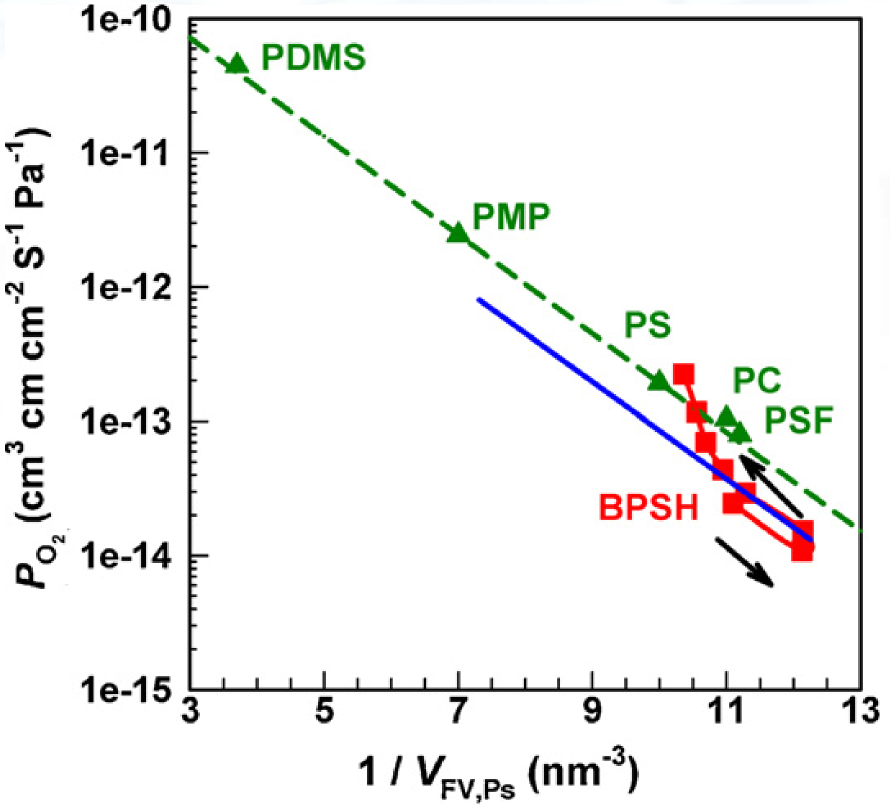


$$D = A\exp\left(\frac{-\gamma V^*}{V_f}\right)$$

Free volume notion of diffusion is not useful in glassy epoxies
(if you think that PALS measures free volume)

PALS & Gas Permeability in Amorphous Thermoplastics

There are robust correlations between PALS hole volumes and O_2 (and other gas) permeation rates published elsewhere



J. *Membrane Sci*. **360**, 84-89 (2010)

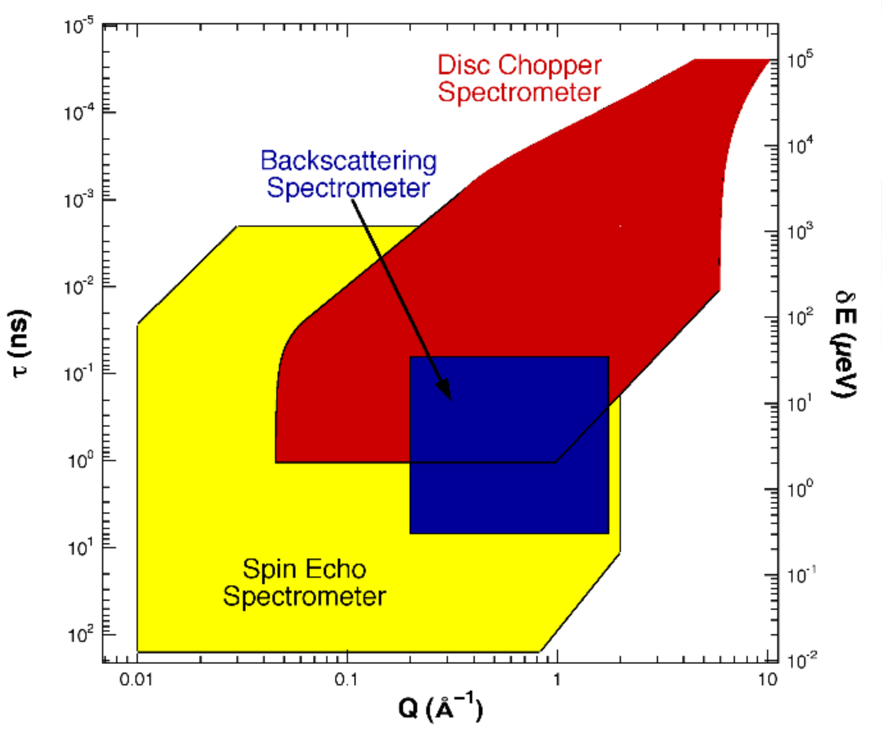
$$P = D \times S$$

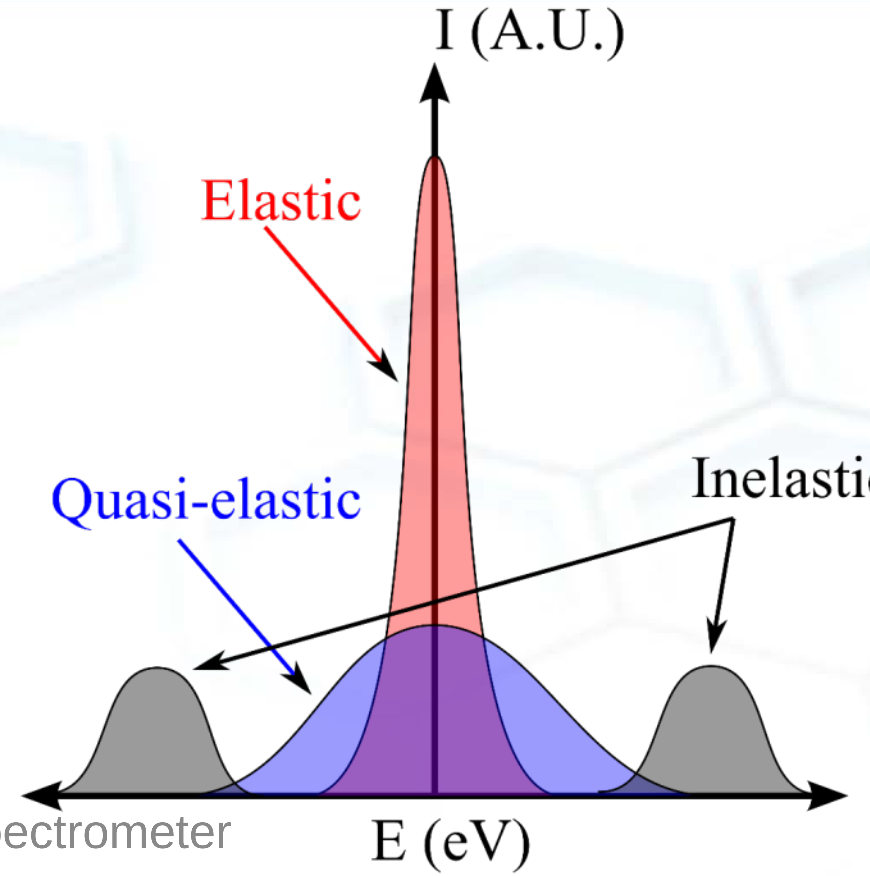
Might suggest that O_2 transport is more "pore-flow" than "solution diffusion?"

Need to isolate the effects of D and S

PALS appears useful for gas permeability in thermoplastics than water in epoxy

Quasielastic Neutron Scattering at NIST





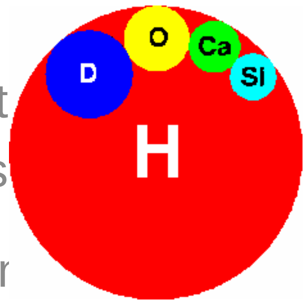
Spectrometer

– picosecond time scales

High Flux Backscattering Spectromet

– nanosecond time scales

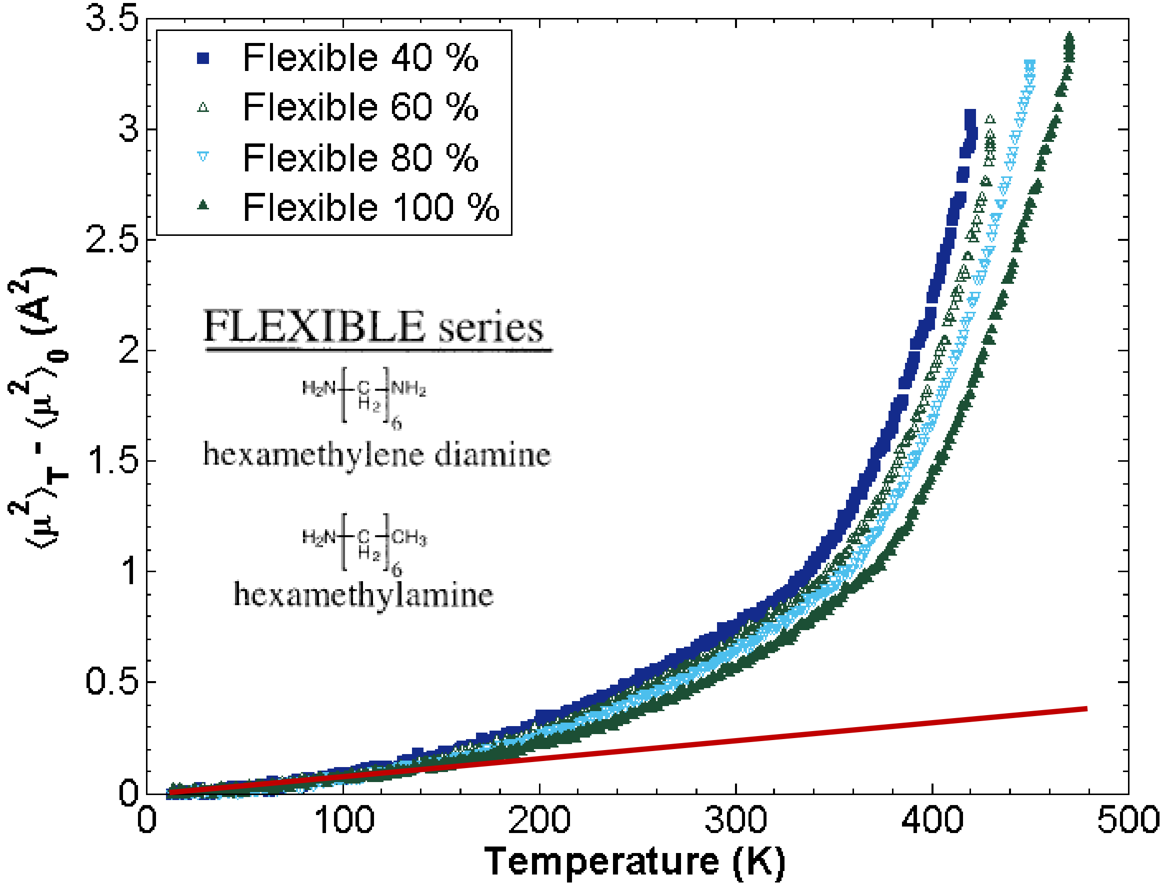
Quantify *self* correlations in the H dynar



Incoherent Neutron Scattering Cross Section

Dry Epoxy Mean Square Atomic Displacements

Measurements in the dry (neat) epoxy



$$\frac{I(q,T)}{I(q,T_{min})} = e^{-\langle\mu^2\rangle q^2/3}$$

Measured on NG2 HFBS at NIST

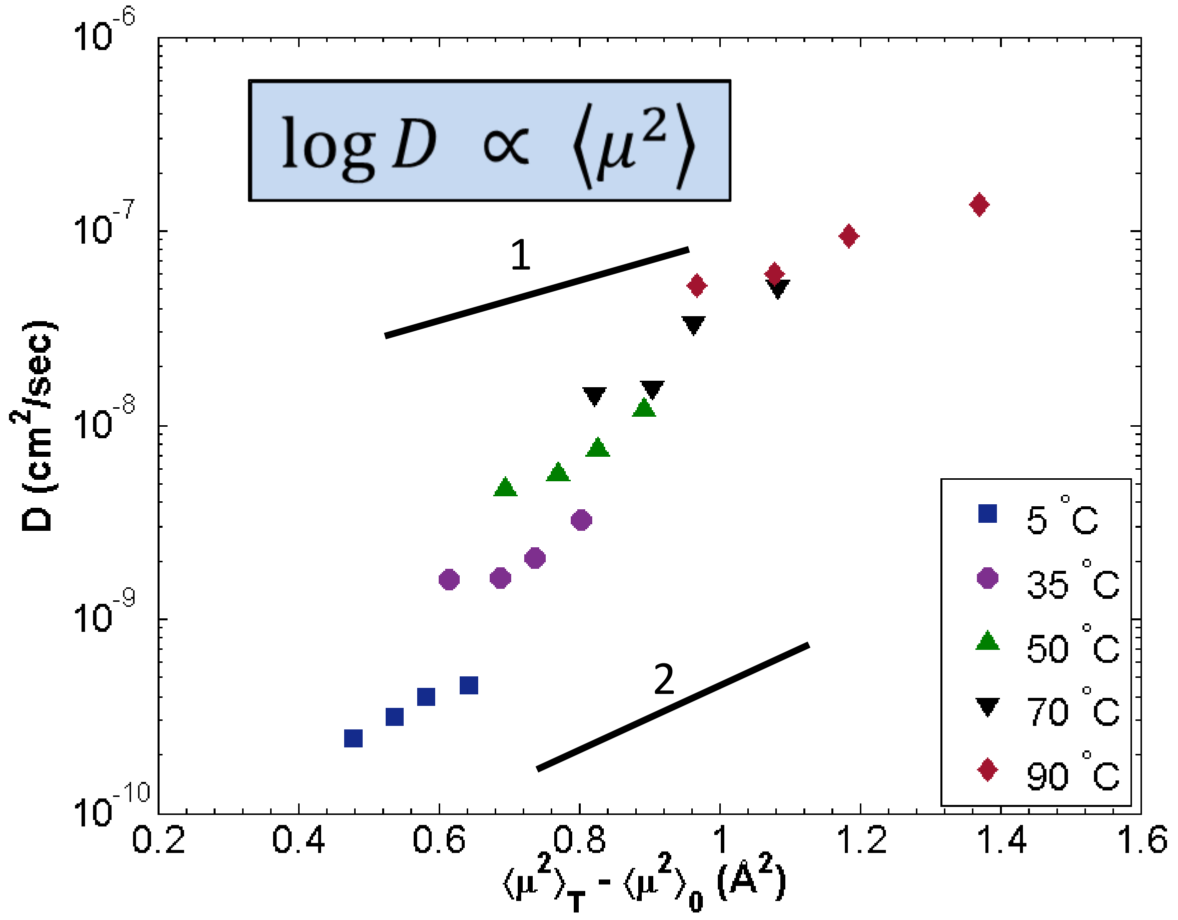
Measure of fast atomic fluctuations in the dry epoxy networks before exposing to water

<*u*²> represents fluctuations moving faster than approximately 1 ns (0.80 μev resolution)

Low T evolution defines harmonic spring constant

$$\kappa = 3\,k_B T/\langle\mu^2\rangle$$

Water Diffusivity & Dry Epoxy Mean Square Displacement



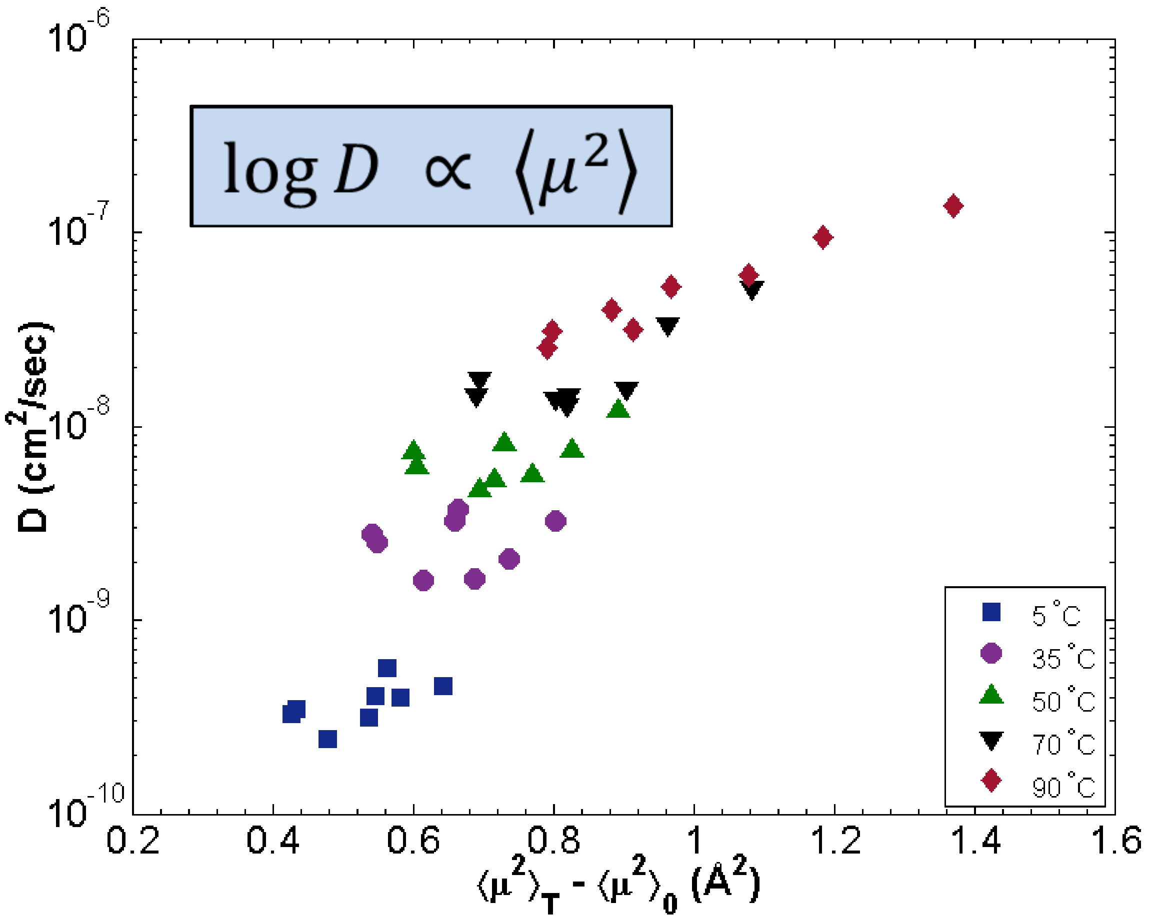
The correlation between the MSD and water diffusion coefficient.

Only the Flexible series of materials are shown in this plot.

The correlation is much more apparent, showing that the chemistry of the epoxy also influences the correlation.

Typical error is approximately ±20%.

Water Diffusivity & Dry Epoxy Mean Square Displacement

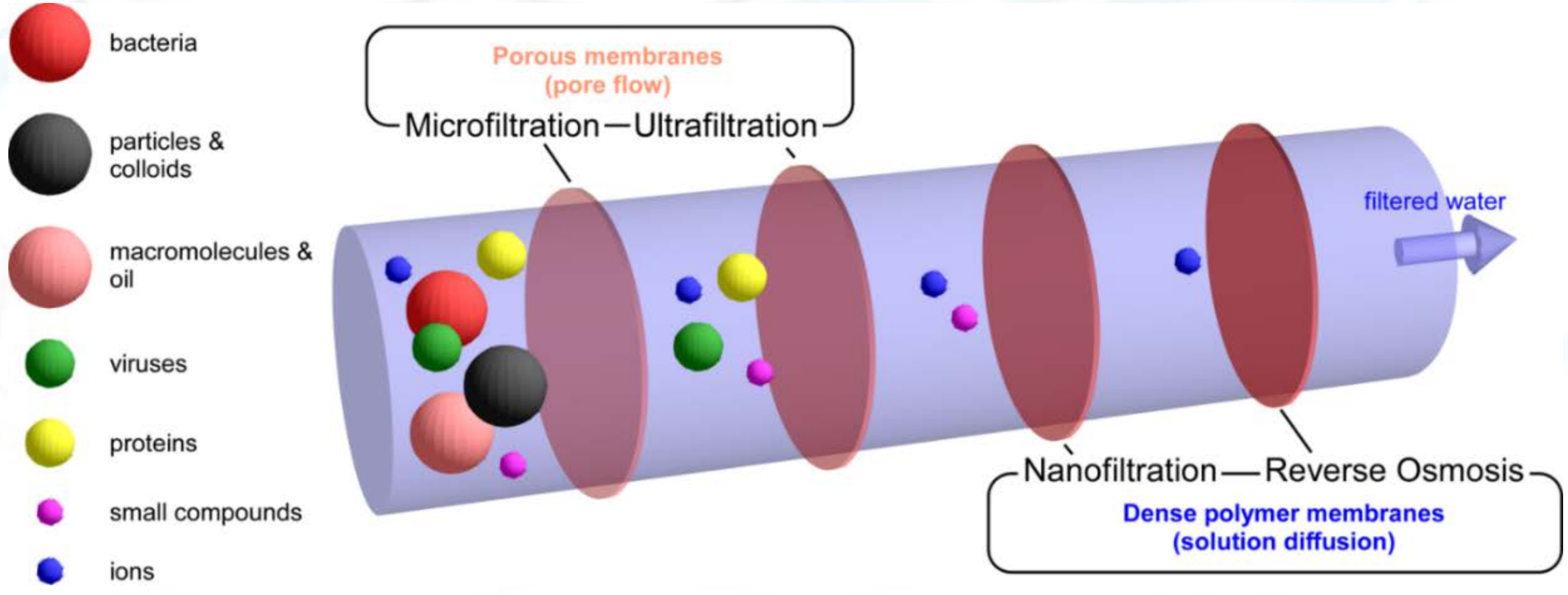


The scaling seems to hold for other epoxy chemistries, but there may be another factor such as polarity that is influencing the diffusion coefficient

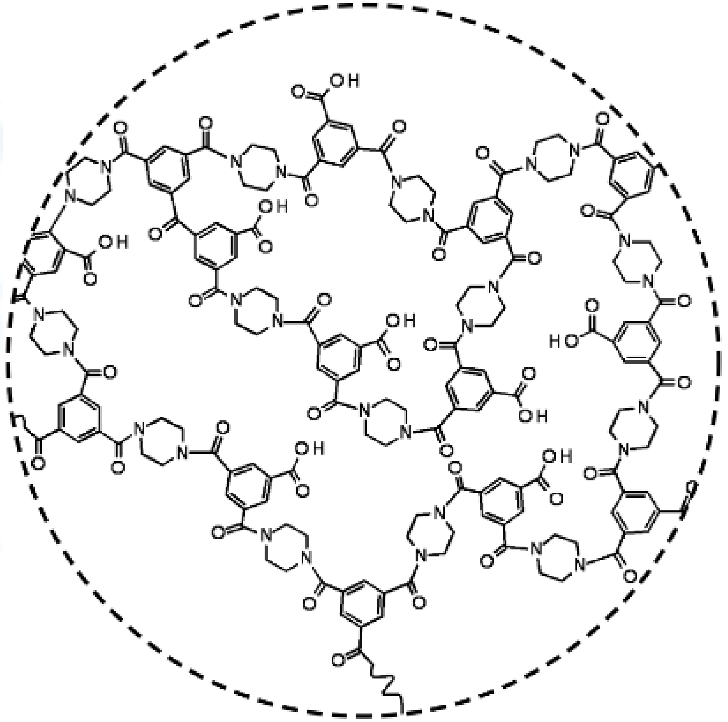
Bear in mind that <u^2> is measured in dry epoxies; D is measured from water soaked epoxies

Typical error is approximately ±20%.

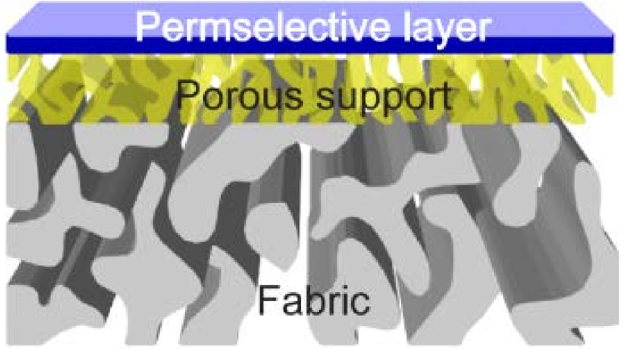
Membranes for Water Filtration

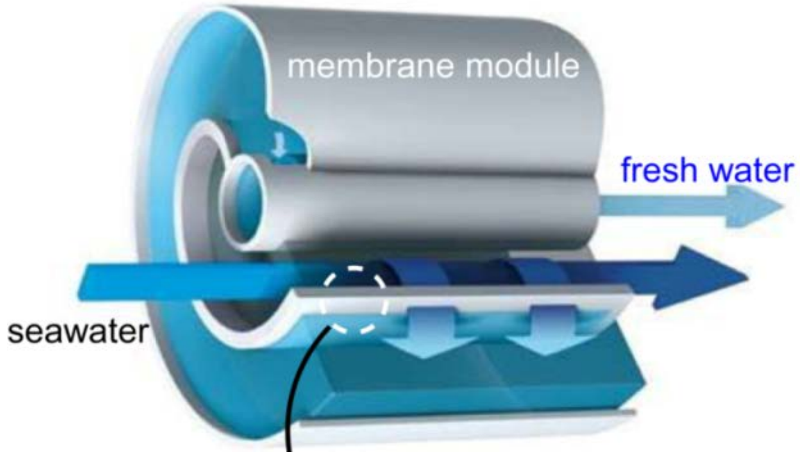


Polyamide (PA) Active Layer

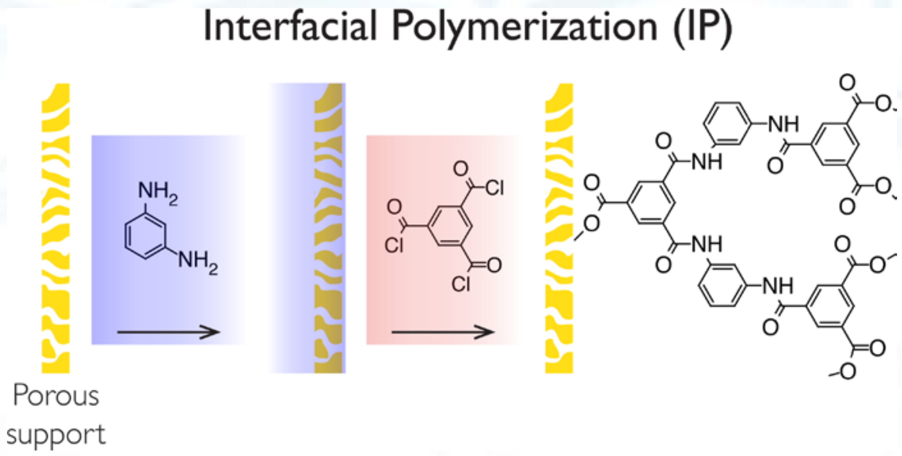


Thin Film Composite Membrane





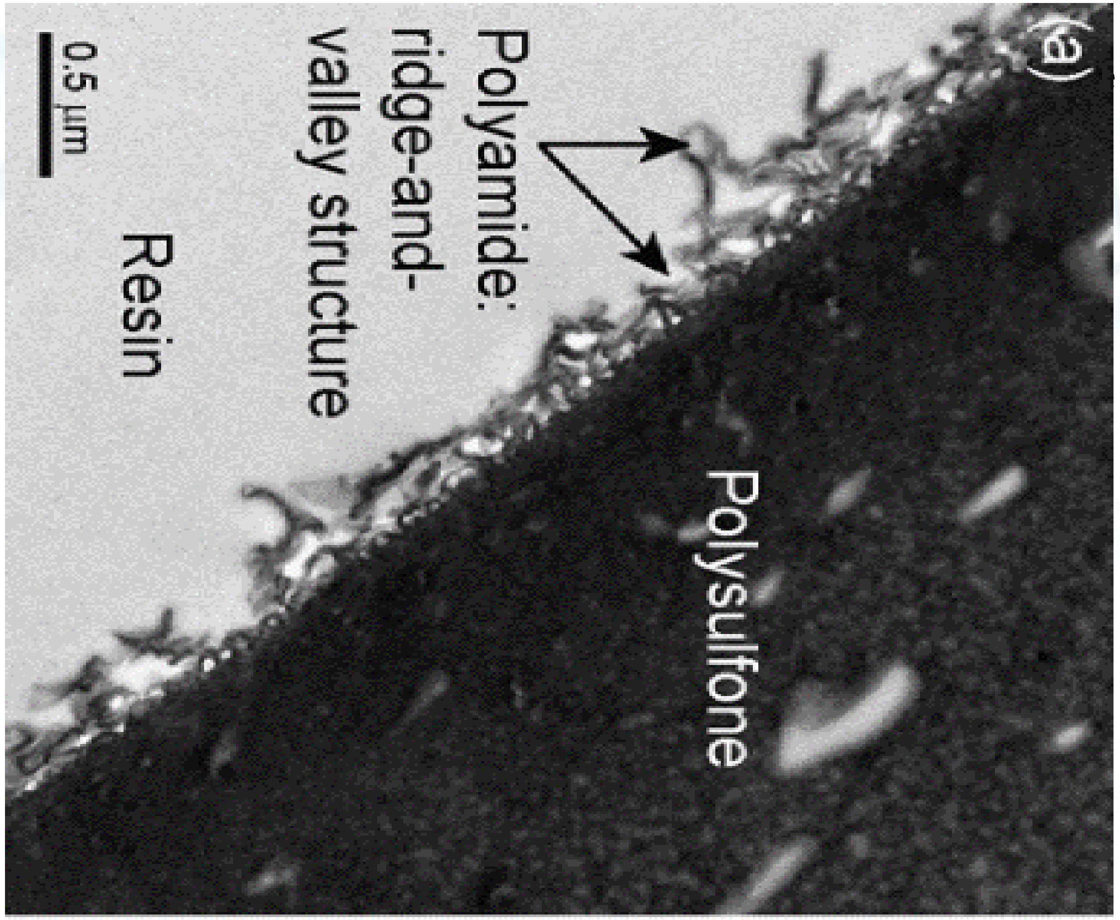
Commercial PA Membranes Fabrication



$$J_{water} \propto \frac{1}{h}$$

Membrane active layer has to be:

- incredibly thin (10s – 100s nm)
- defect free
- mechanically robust
- chlorine tolerant
- fouling resistant

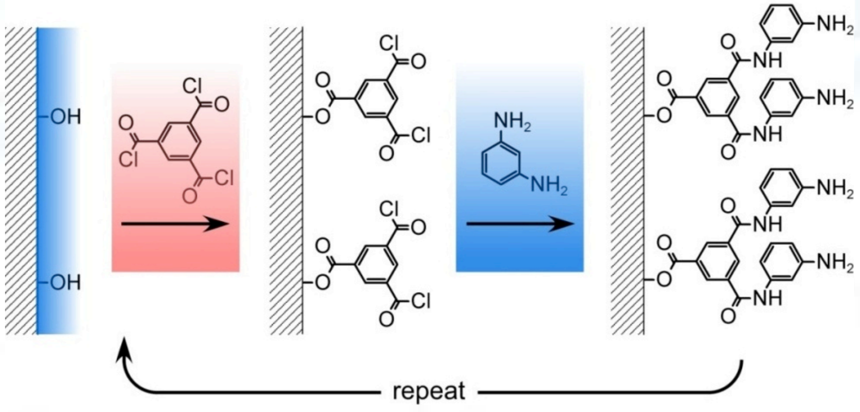


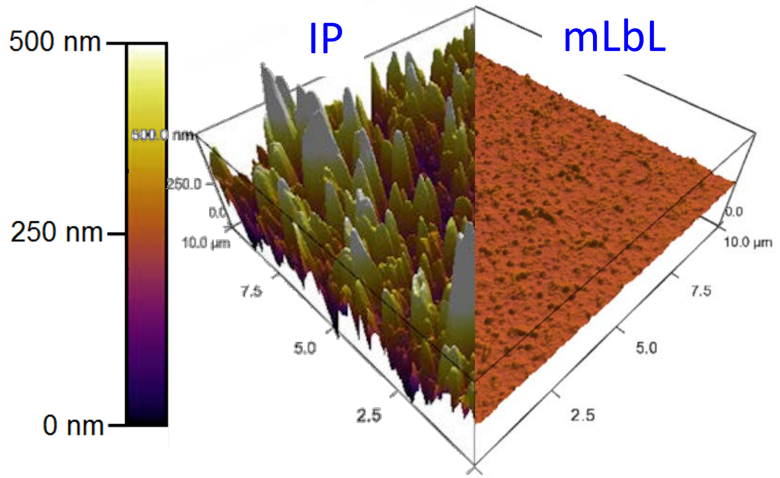
"The lack of correlation between film thickness and permeability suggests the entire film thickness may not contribute to separation"

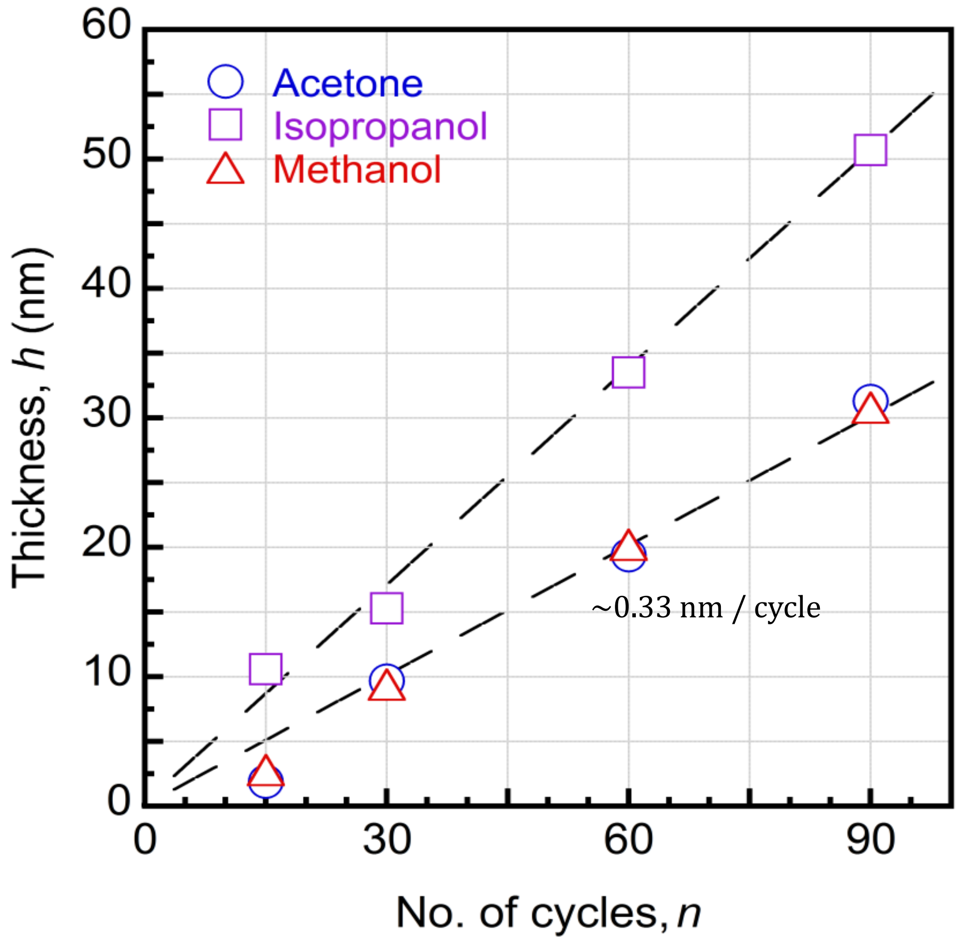
- *J. Membrane Sci.* **311**, 34-45 (2008)

Model PA Membranes for Quantitative Measurements

molecular Layer-by-Layer (mLbL)

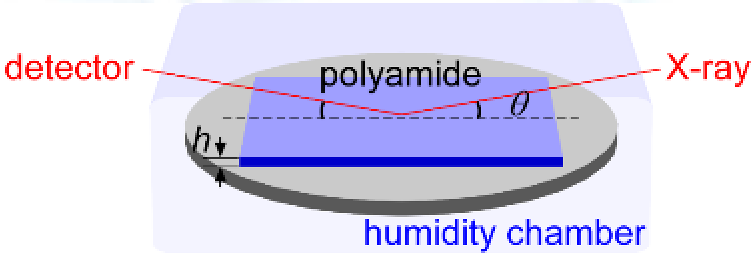






P. M. Johnson, et al.; *JPSB* **2011**, 50, 168.

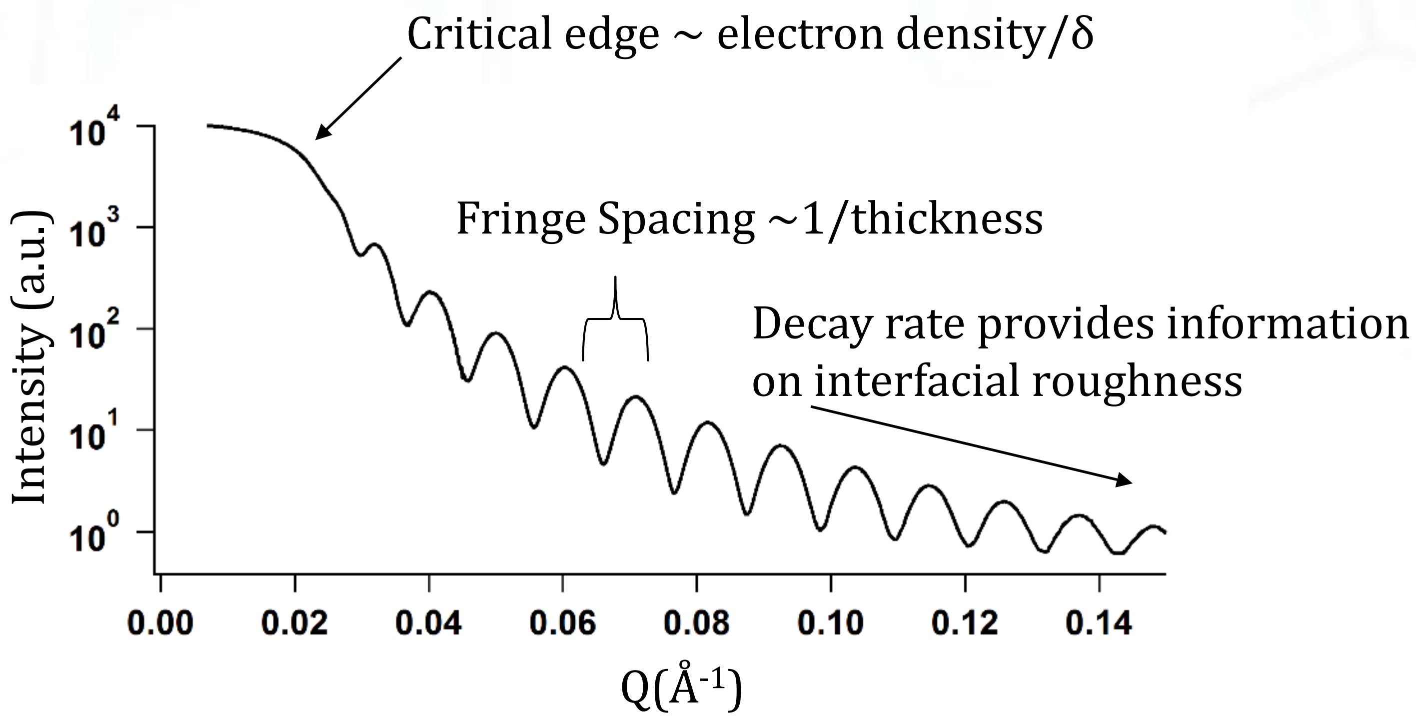
X-Ray Reflectivity



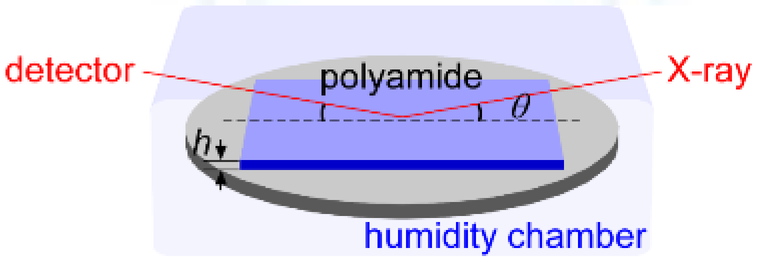
Reflectivity from "hard x-rays" can measure:

- Thickness
- Roughness
- Electron/mass density

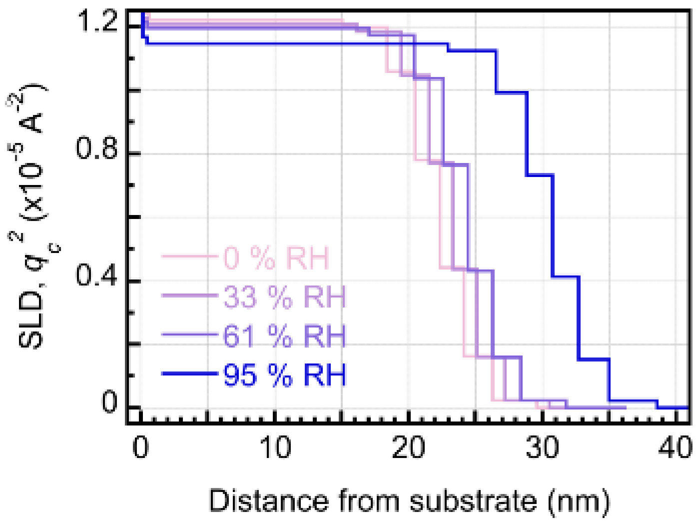
Contrast : differences in electron density

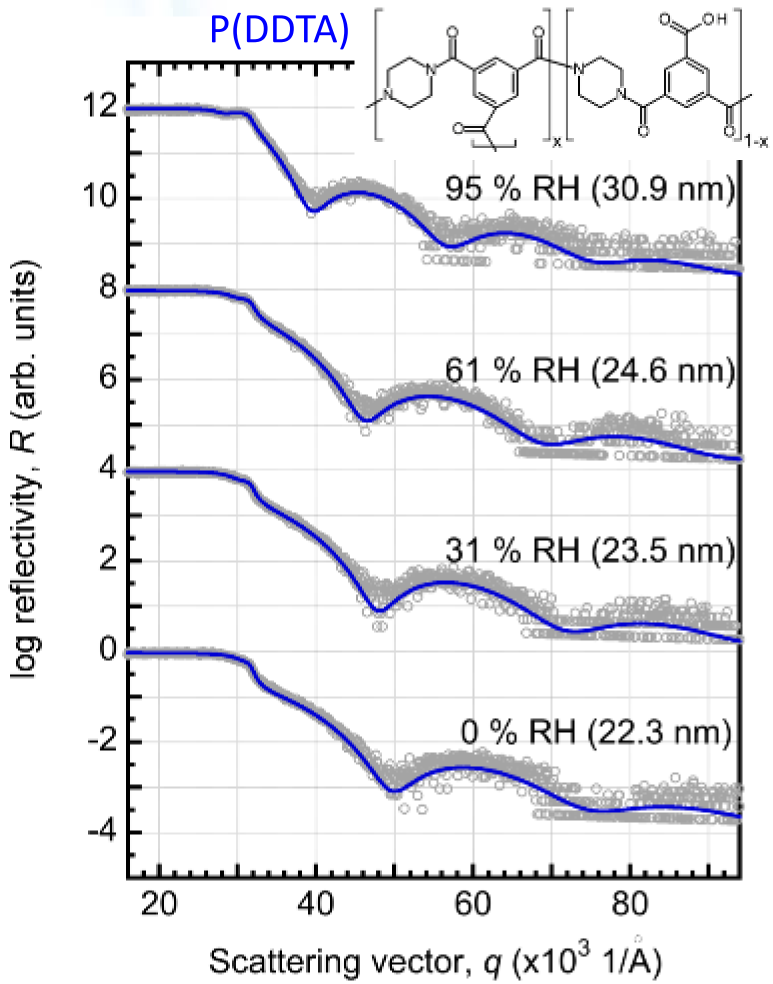


X-Ray Reflectivity for Swelling



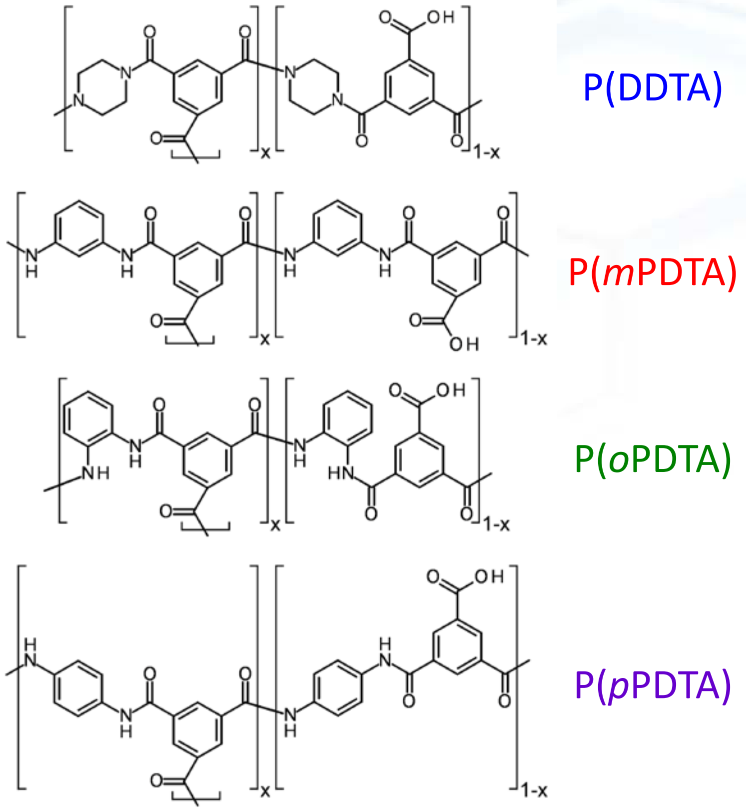
Scattering Length Density

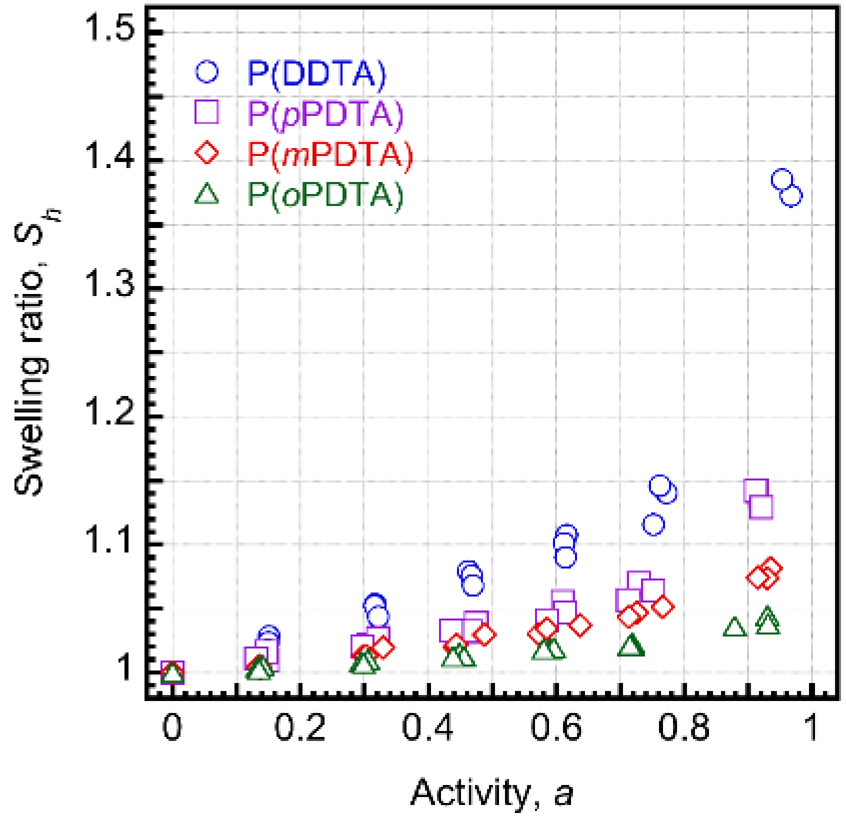




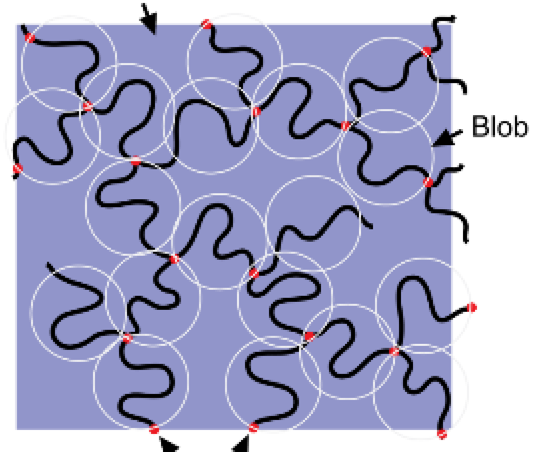
E. P. Chan, et al. *JPSB*, **2013**, 51, 385.
E. P. Chan, et al. *JPSB*, **2013**, 51, 1647.

X-Ray Reflectivity for Swelling





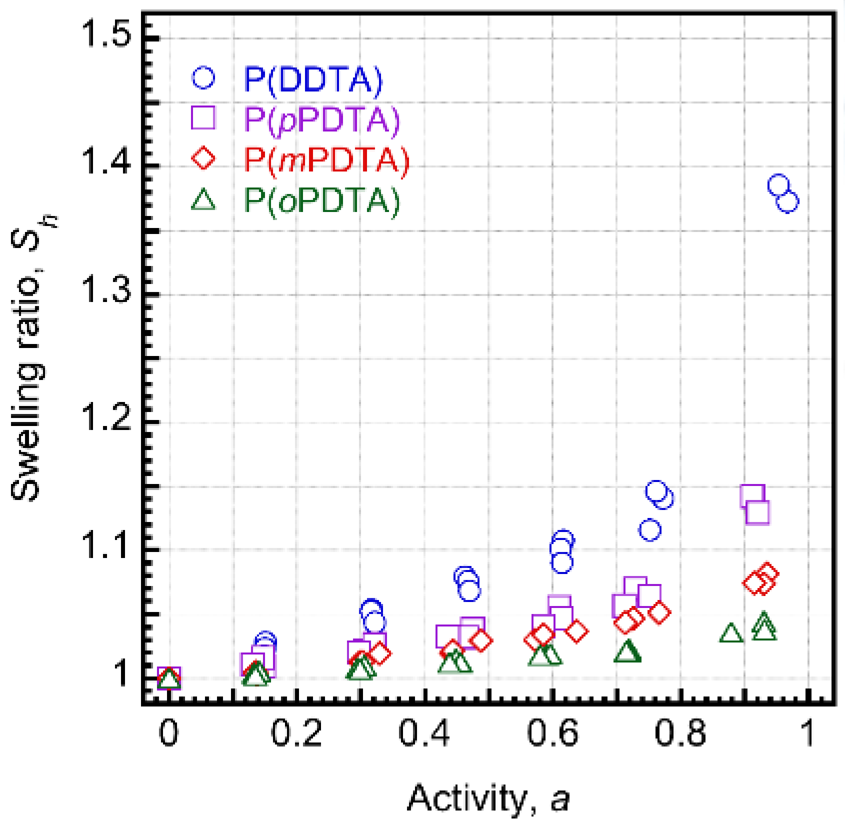
Blob Model of Network Swelling



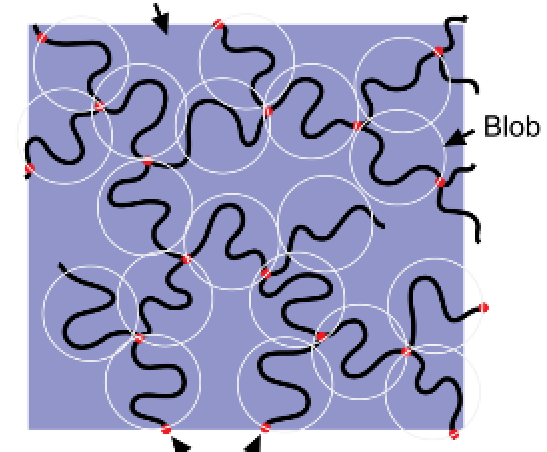
Painter-Shenoy model for 1D swelling,

$$\ln a = \ln\left(1-\frac{1}{S_h}\right)+\frac{1}{S_h}+\frac{\chi}{S_h^2}+\frac{1}{N_x}\left(\frac{S_h}{N_x}+\left(\frac{1}{2}-\frac{2}{f}\right)\frac{1}{S_h}\right)$$

Flory interaction parameter, $\chi = \chi_o + \frac{\chi_1}{S_h} + \frac{\chi_2}{S_h^2}$



Blob Model for Network Swelling



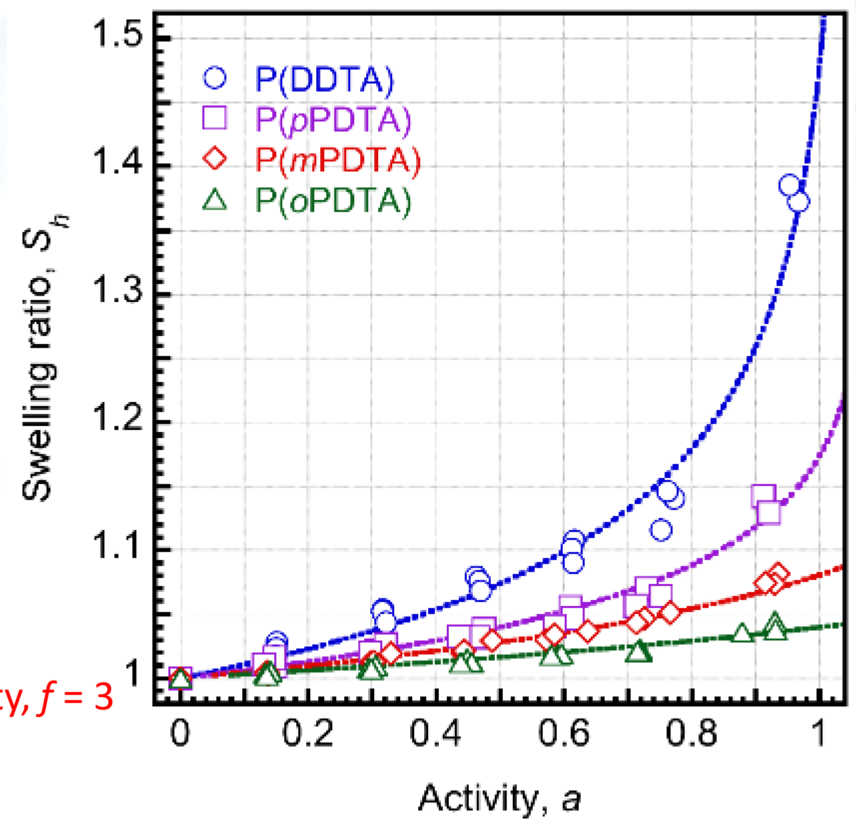
Painter-Shenoy model for 1D swelling,

$$\ln a = \ln\left(1 - \frac{1}{S_h}\right) + \frac{1}{S_h} + \frac{\chi}{S_h^2} + \frac{1}{N_x}\left(\frac{S_h}{N_x} + \left(\frac{1}{2} - \frac{2}{f}\right)\frac{1}{S_h}\right)$$

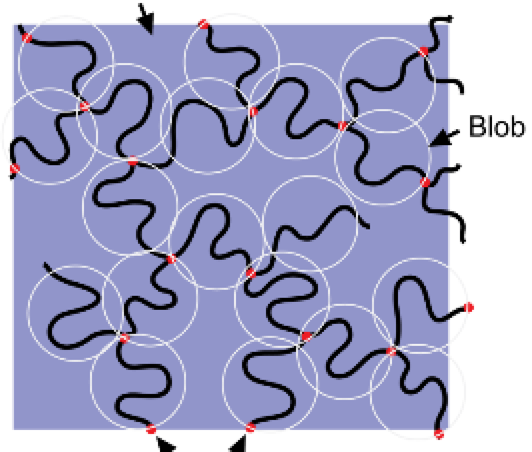
monomers betw. crosslinks

network functionality, f = 3

Flory interaction parameter, $\chi = \chi_o + \frac{\chi_1}{S_h} + \frac{\chi_2}{S_h^2}$



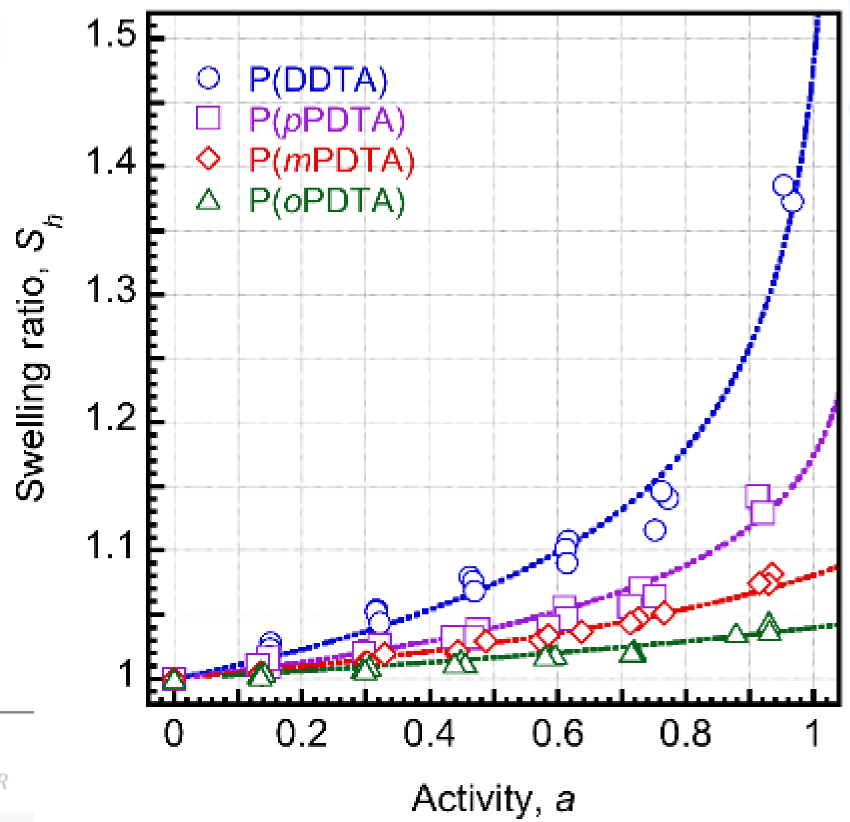
Blob Model for Network Swelling



Painter-Shenoy model for 1D swelling,

$$\ln a = \ln\left(1-\frac{1}{S_h}\right)+\frac{1}{S_h}+\frac{\chi}{S_h^2}+\frac{1}{N_x}\left(\frac{S_h}{N_x}+\left(\frac{1}{2}-\frac{2}{f}\right)\frac{1}{S_h}\right)$$

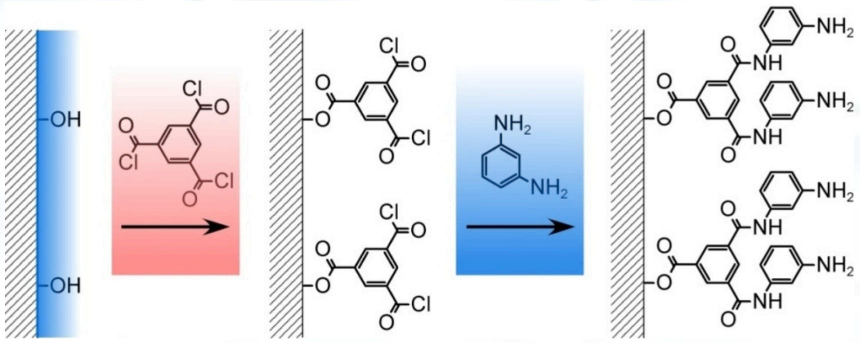
PA system	S_h	χ_{PS}	N_{PS}	χ_{FR}	N_{FR}
P(DDTA)	≈ 1.50	0.966	10.7	0.963	357.6
P(*p*PDTA)	≈ 1.16	1.498	7.6	1.496	247.0
P(*m*PDTA)	≈ 1.08	1.909	3.6	1.912	24.9
P(*o*PDTA)	≈ 1.04	2.294	2.0	2.293	5.0

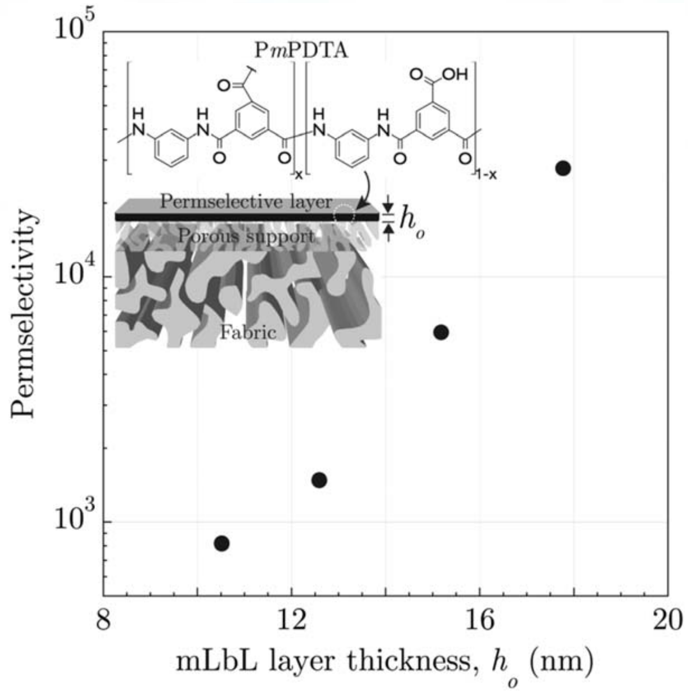


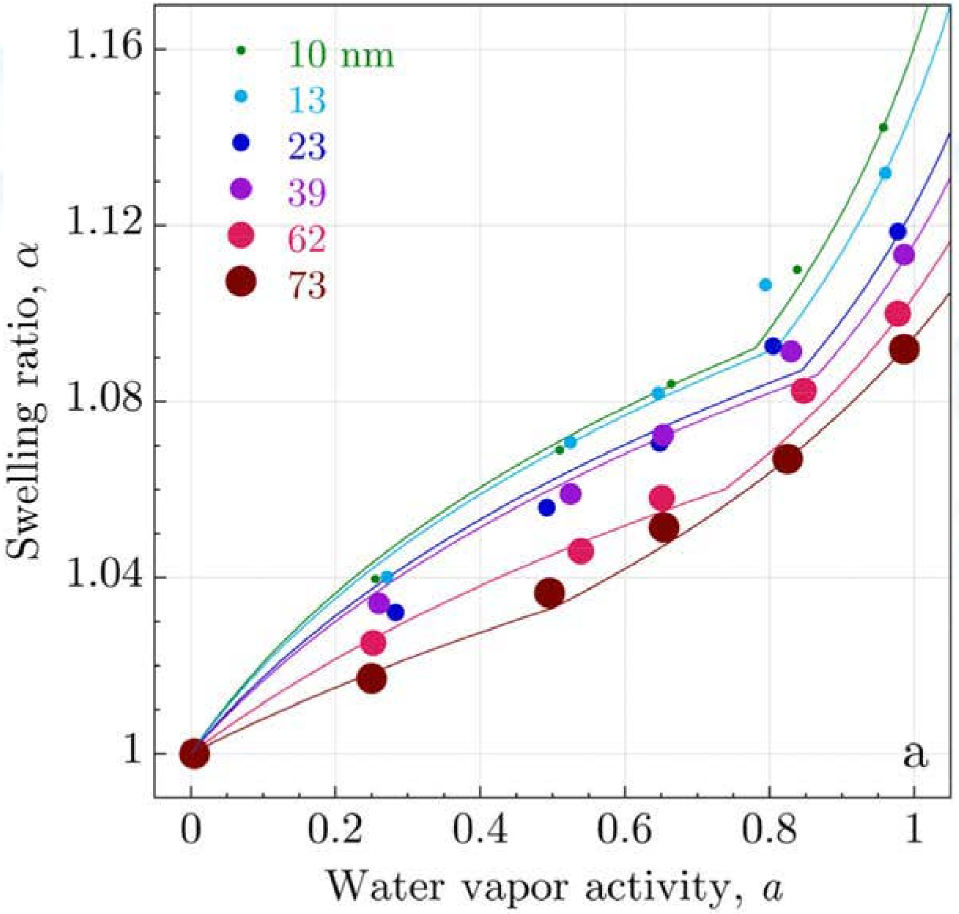
Consistent w/ elemental (C:N:O) analysis via X-ray Photoelectron Spectroscopy

Effects of Film Thickness on PA Swelling

molecular Layer-by-Layer (mLbL)







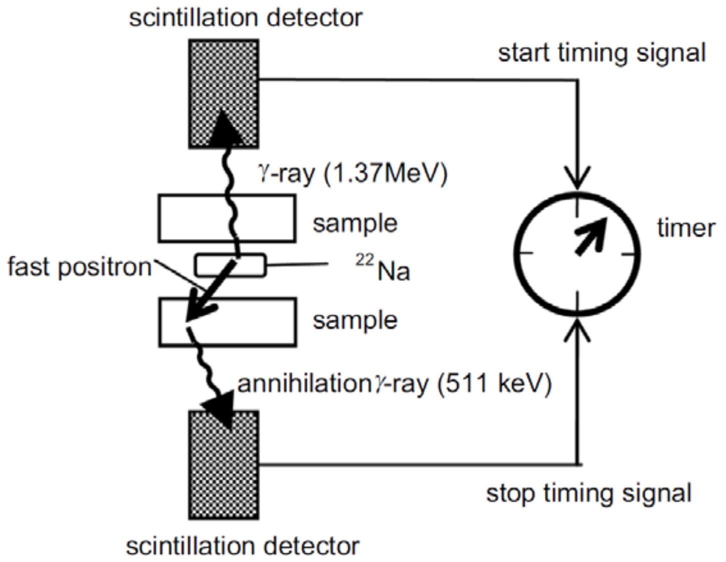
Enhanced swelling in thin films; membrane performance deteriorates

Indicative of incomplete network formation at low cycle numbers

W. Choi, et al. *ACS Nano* **2015**, 9, 345.

PALS for Nanoscale Porosity (network pore)

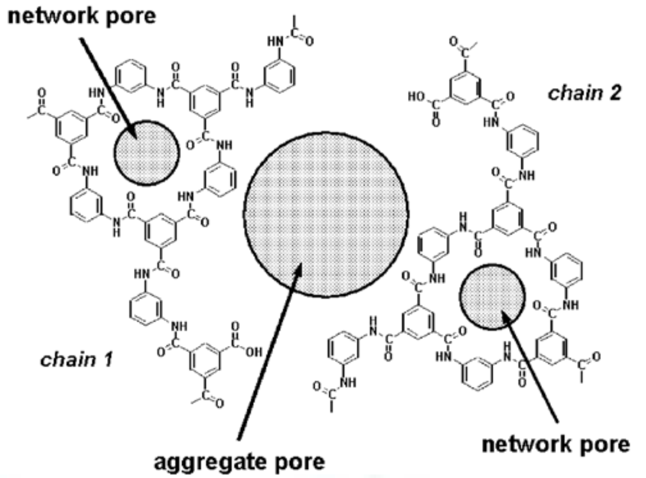
Positron Annihilation Lifetime Spectroscopy (PALS) to measure the unoccupied volume.

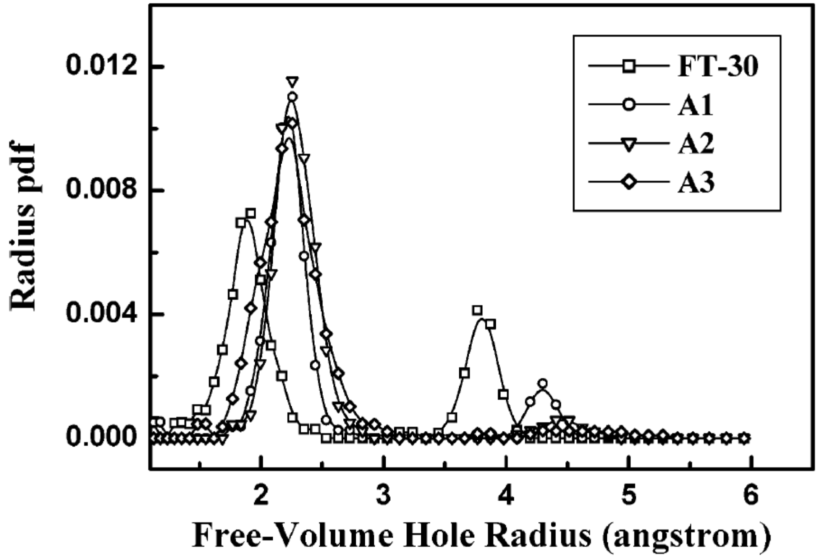


Total nanopore content
Derived from τ_3

$$V_h = C v_h I_3$$

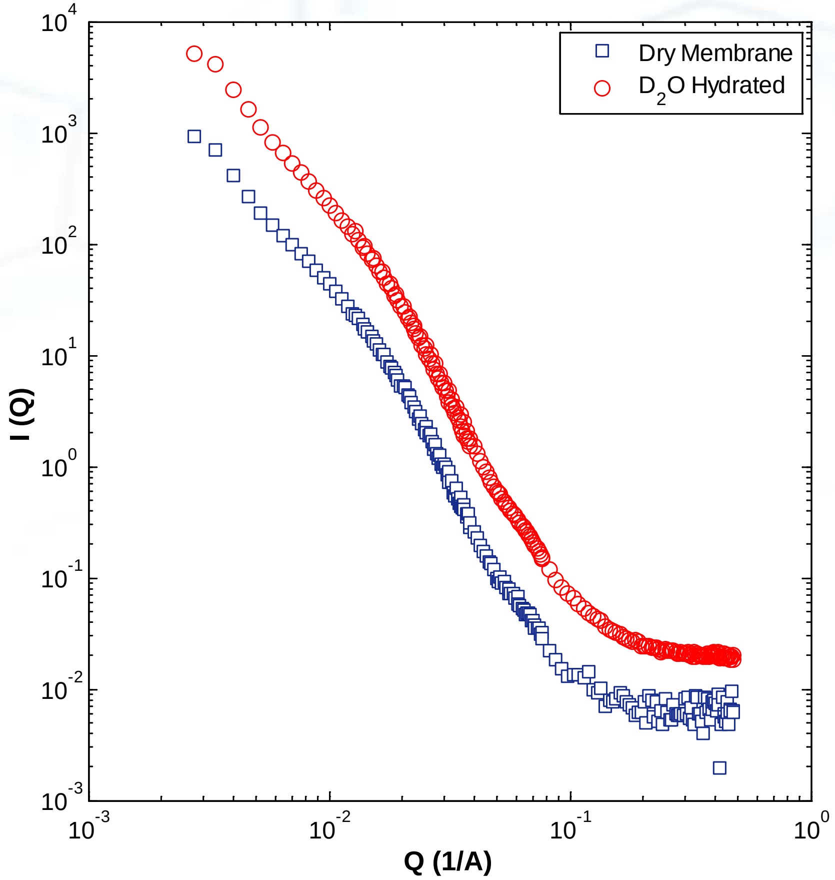
$$v_h = \frac{4}{3}\pi R^3$$

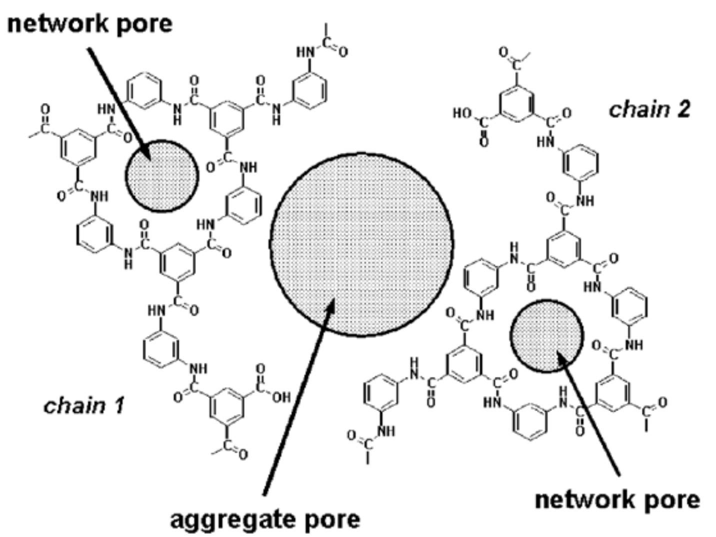




Fujioka, et al., *J Mem. Sci.* 486 (2015). Kim, et al., *Environ. Sci. Technol*. 39 (2005).
Hung, et al., *RSC Adv*. 6 (2016).

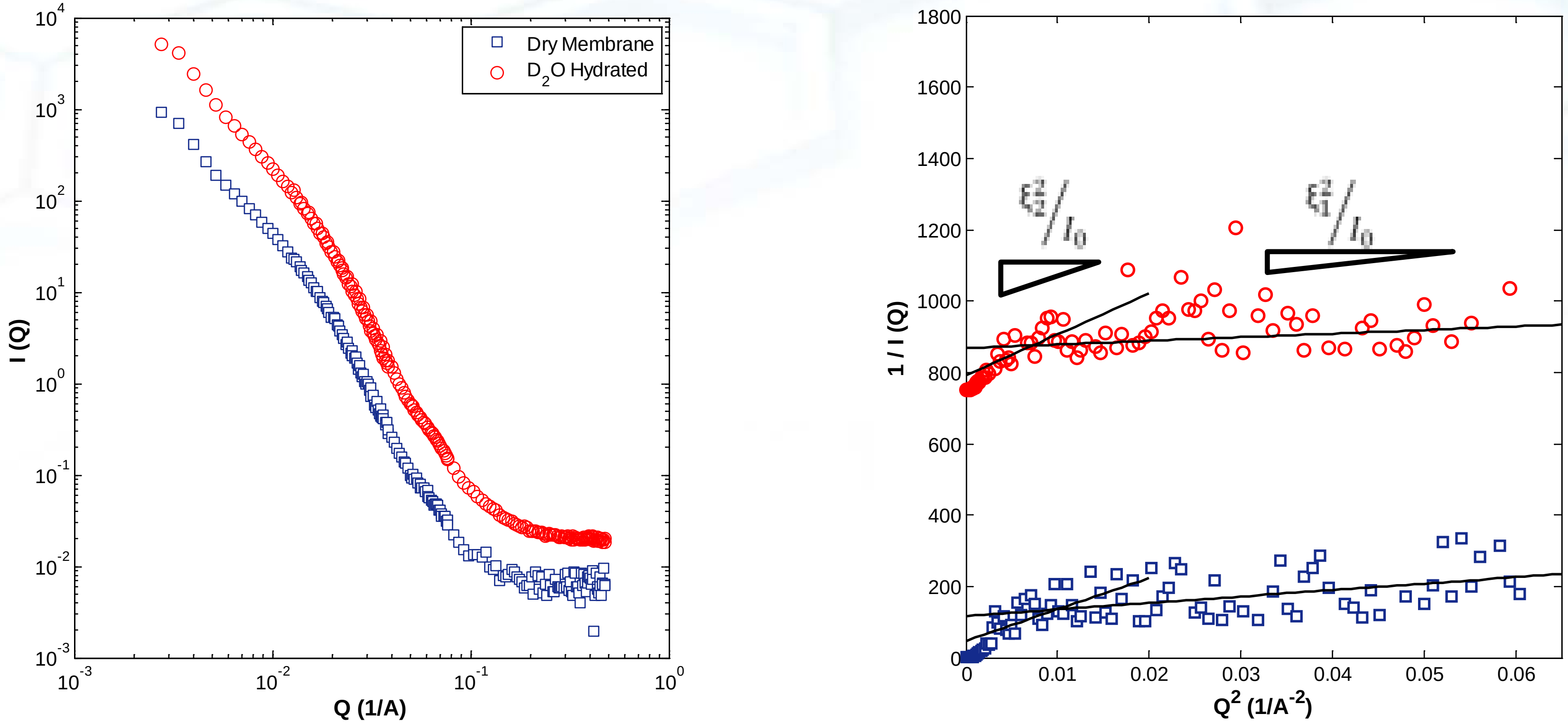
SANS for Nanoscale Porosity (aggregate pore)





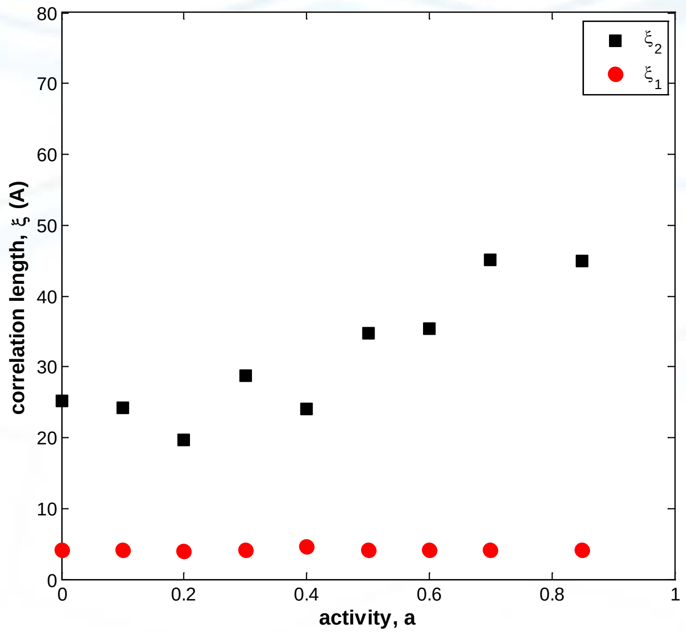
$$I(Q) = \frac{A}{Q^4} + \frac{C}{1+Q^2\xi_2{}^2} + \frac{D}{1+Q^2\xi_1{}^2} + B$$

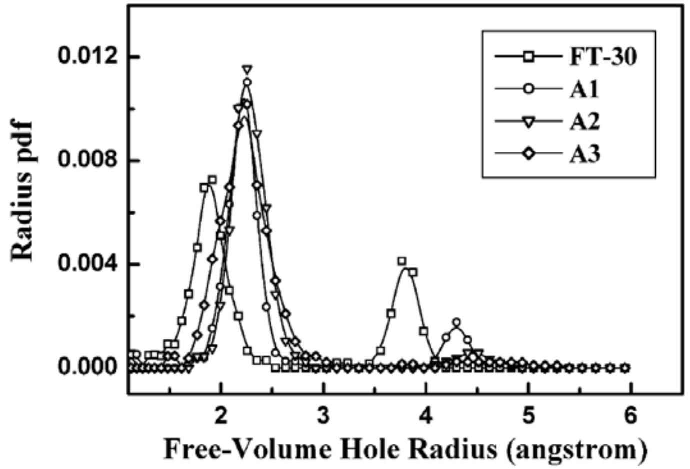
SANS for Nanoscale Porosity (aggregate pore)



$$I(Q) = \frac{A}{Q^4} + \frac{C}{1+Q^2\xi_2^{\ 2}} + \frac{D}{1+Q^2\xi_1^{\ 2}} + B$$

SANS for Nanoscale Porosity (aggregate pore)





ally system swells by 5 to 8 % with water

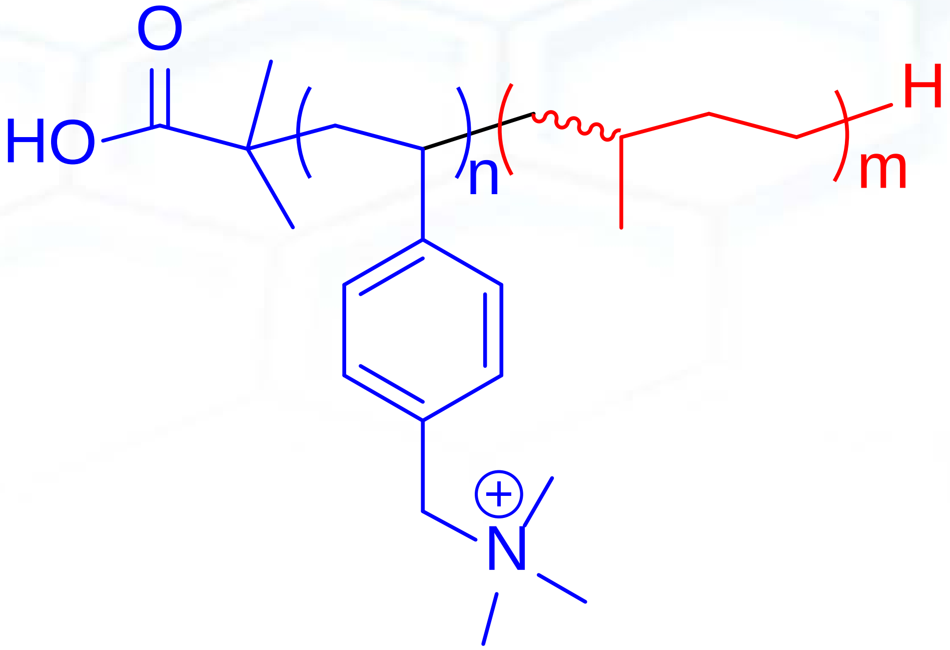
a 50% change in correlation length!

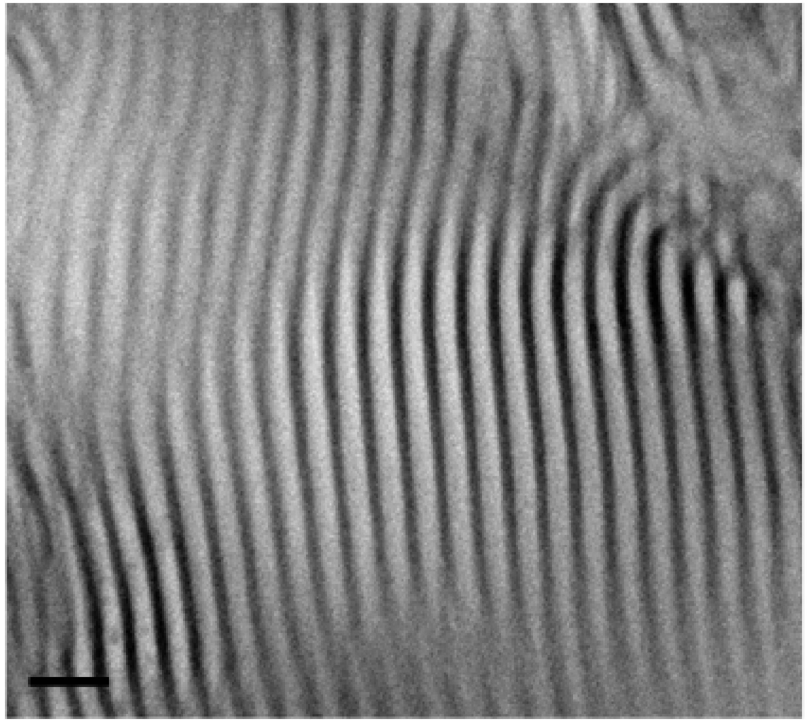
ıpports notion of heterogenous

swelling in regions of

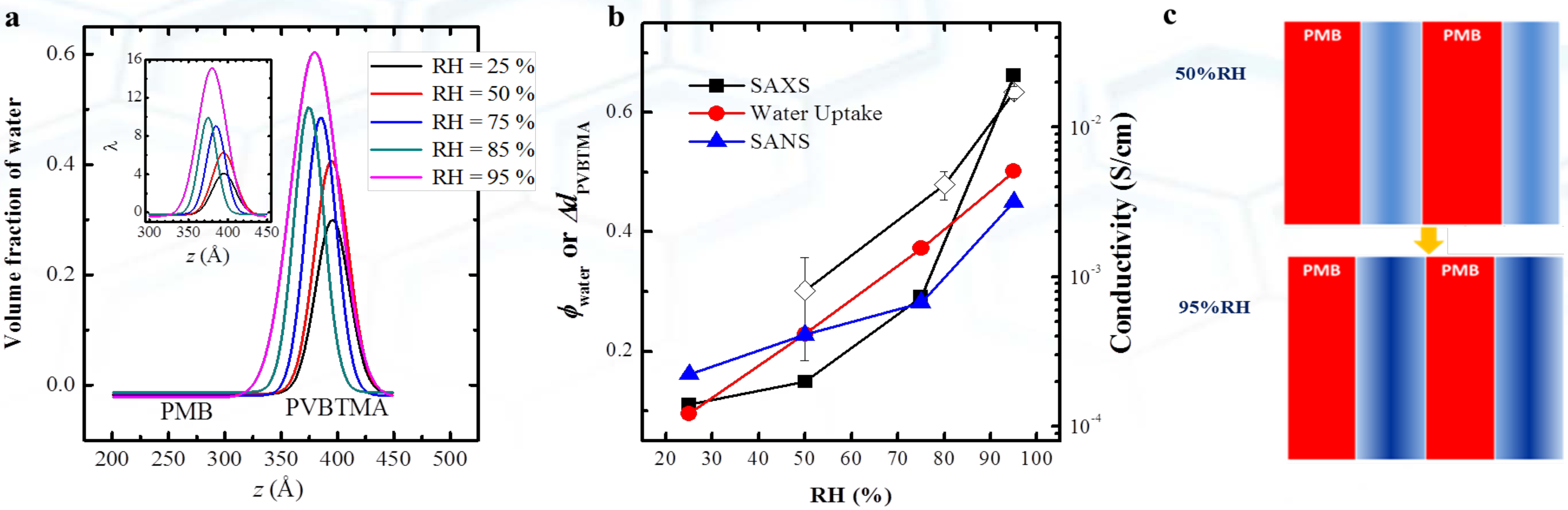
different cross-link density

(PVBTMA)(Br)-b-(PMB) Diblock Copolymer AEMs





Water Distributions in the PVTBMA Domains



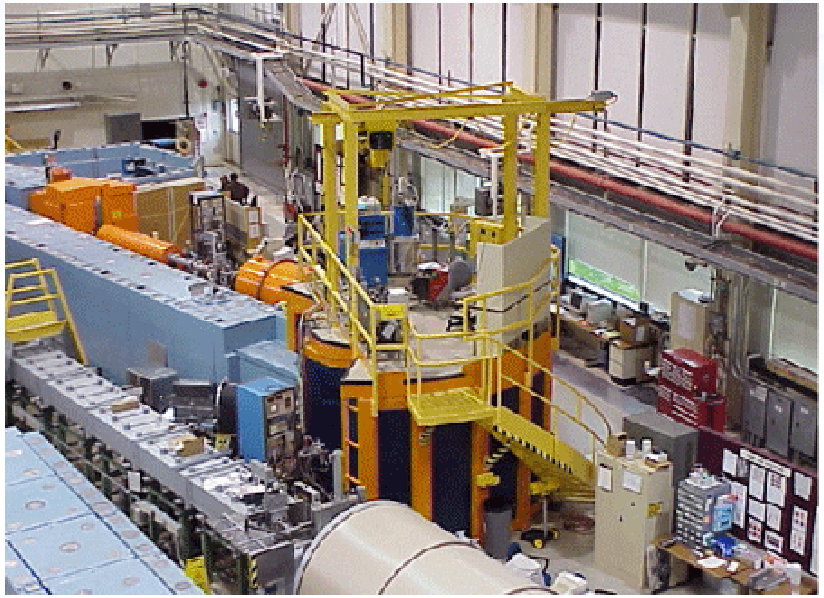
Water enrichment in the center of the hydrophilic domain

Water content consistent with gravimetric and SAXS measurements

What happens to the dynamics of water when this segregation occurs?

Inelastic Neutron Scattering

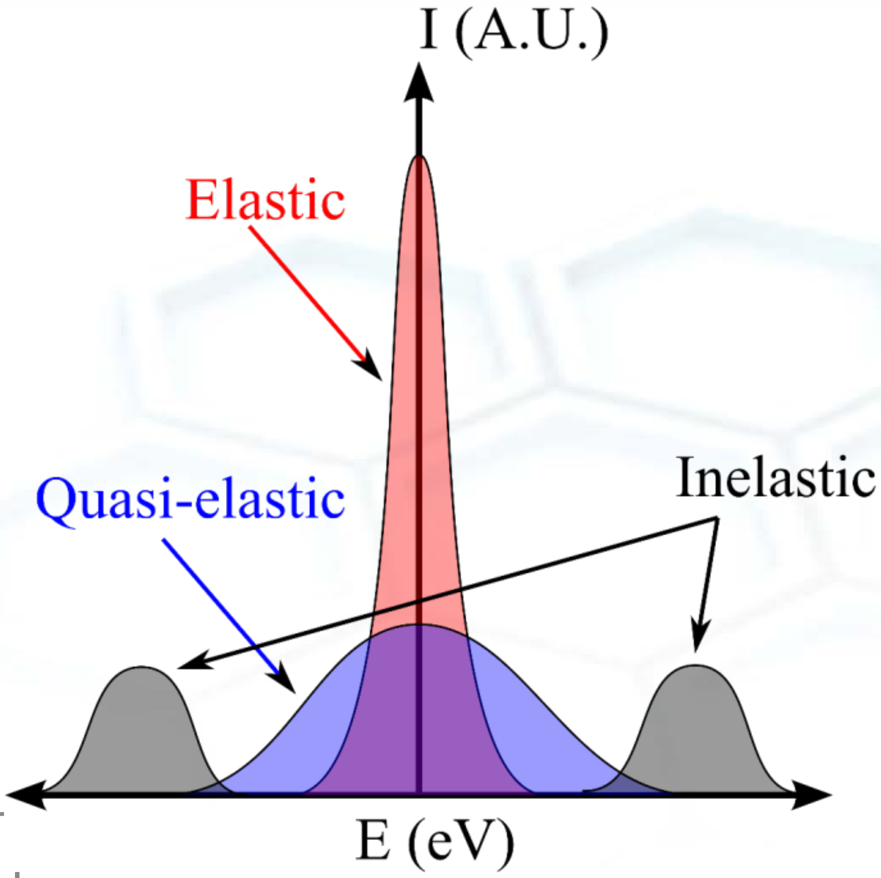
NIST Center for Neutron Research

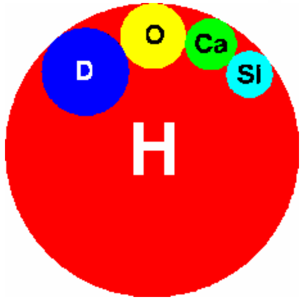


opper Spectrometer
– picosecond time scales

High Flux Backscattering Spectrometer
– nanosecond time scales

Quantify *self* correlations in the H dynamics

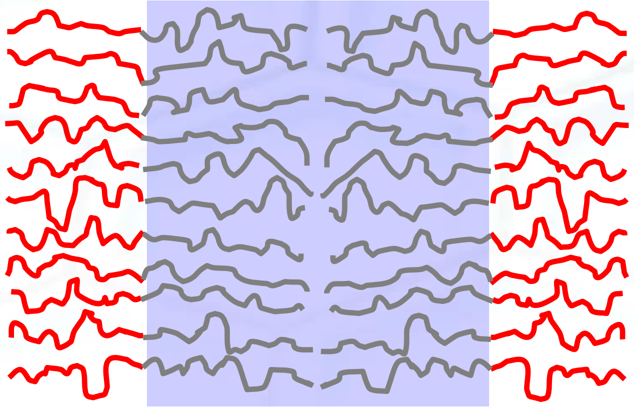


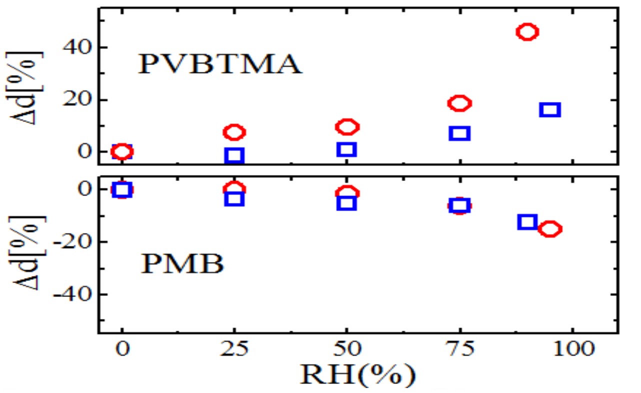


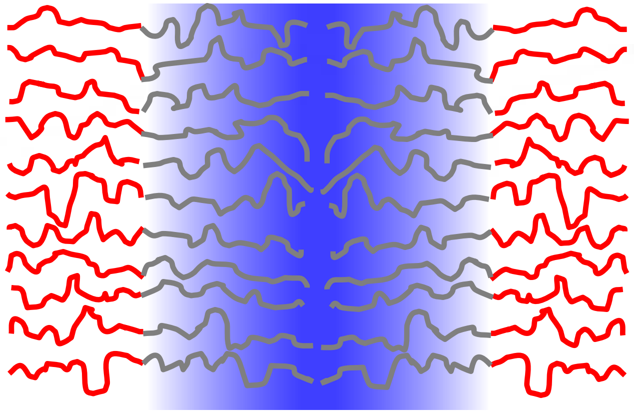
Incoherent Neutron Scattering Cross Section

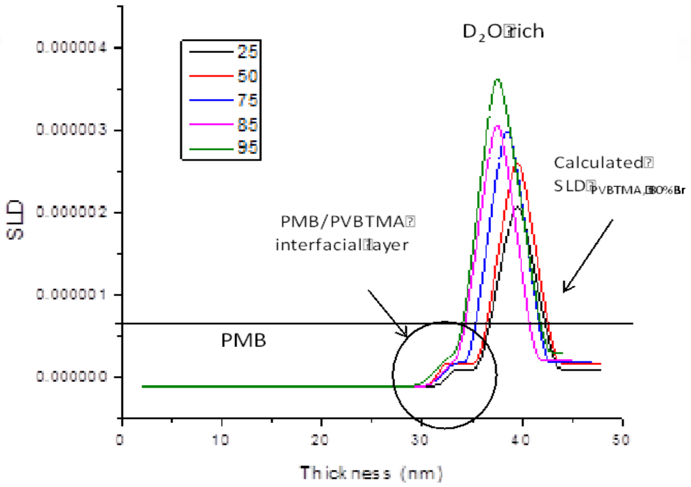
Isolating Water Dynamics from Polymer with QENS

BCP & H_2O Dynamics - BCP & D_2O Dynamics = H_2O Dynamics



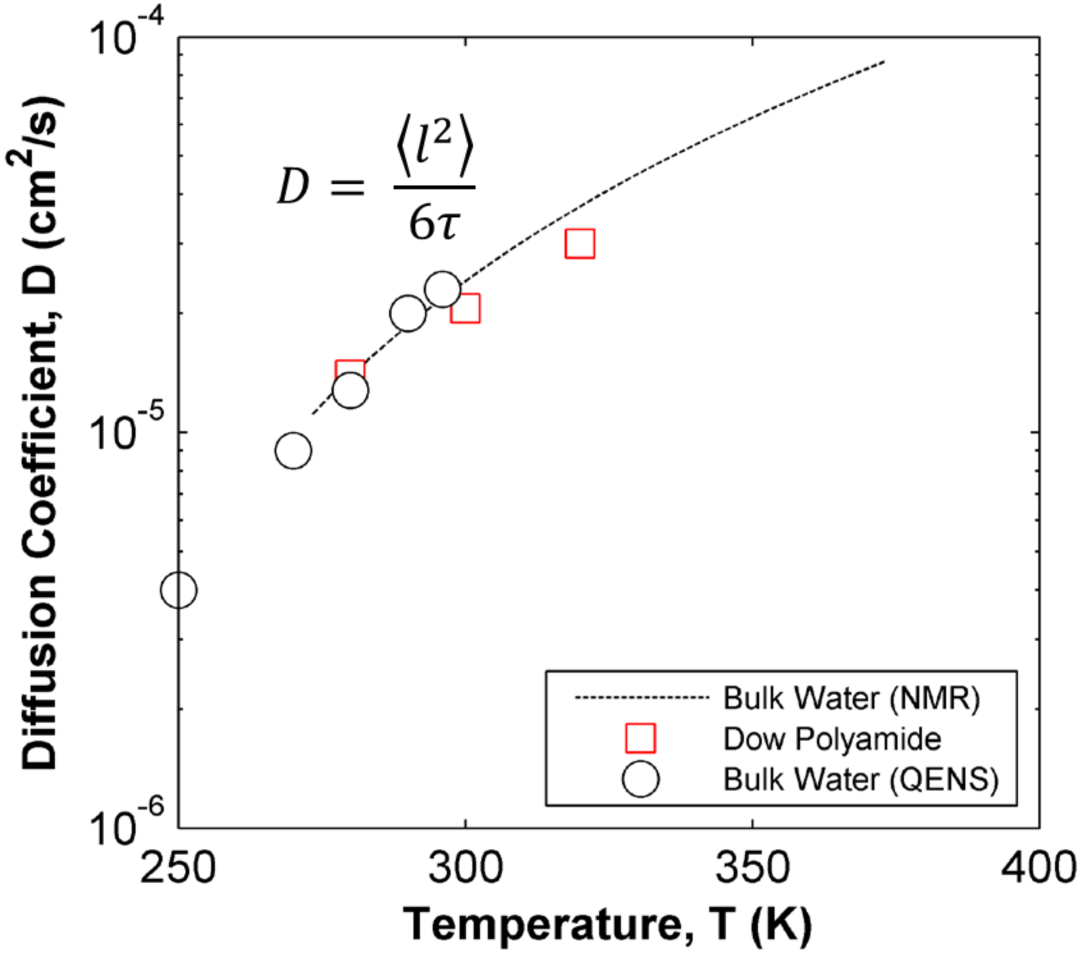




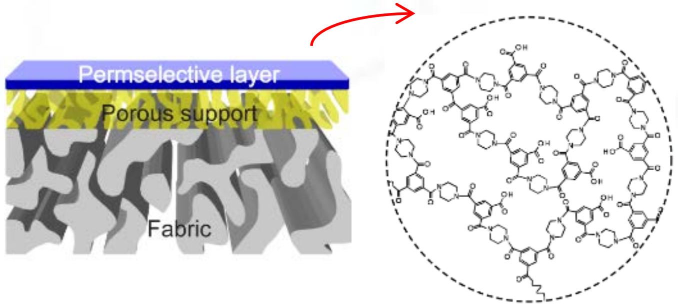


Key assumptions: (1) polymer dynamics are the same in H_2O / D_2O
(2) absorption effects are negligible

Water Dynamics in a Diverse Set Hydrated Membranes

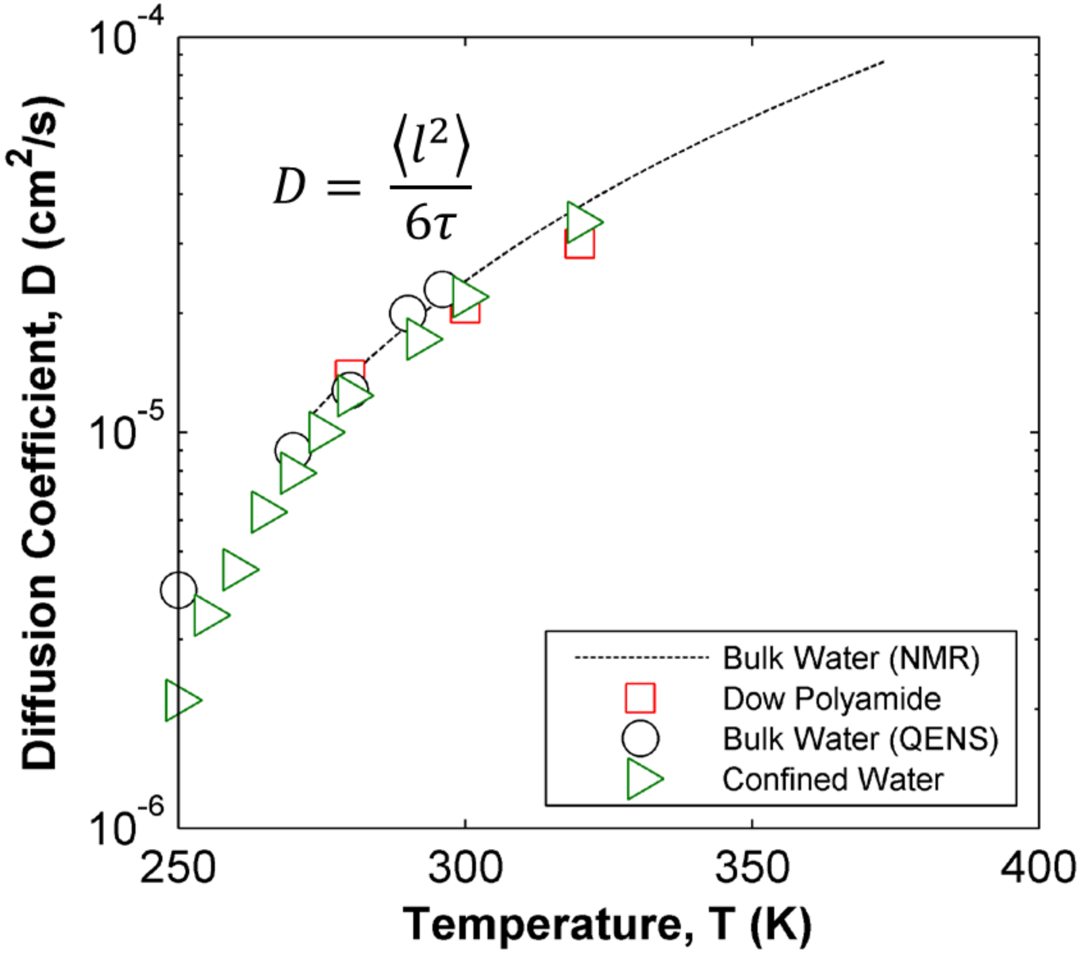


Swollen porous membrane

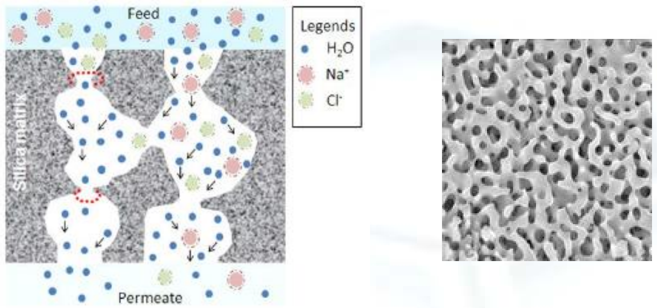


Hall, Ross, *Mol Phys* (1981) **42**, 673.
Holz, et al, *PCCP* (2000) **2,** 4740.
Fuchs, et al, *J Phys Chem B* (2015) **119**, 15892.
Mitra, et al, *J Phys Cond Mat* (2001) **13**, 8455.

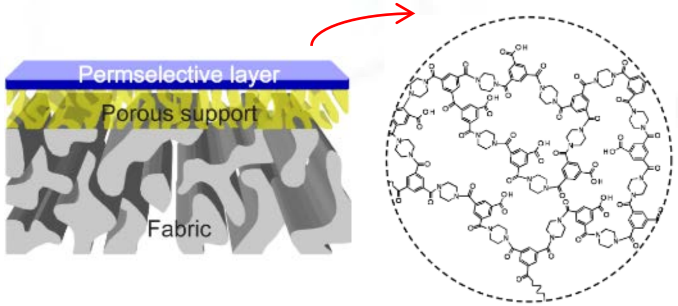
Water Dynamics in a Diverse Set Hydrated Membranes



Rigid porous membrane



Swollen porous membrane



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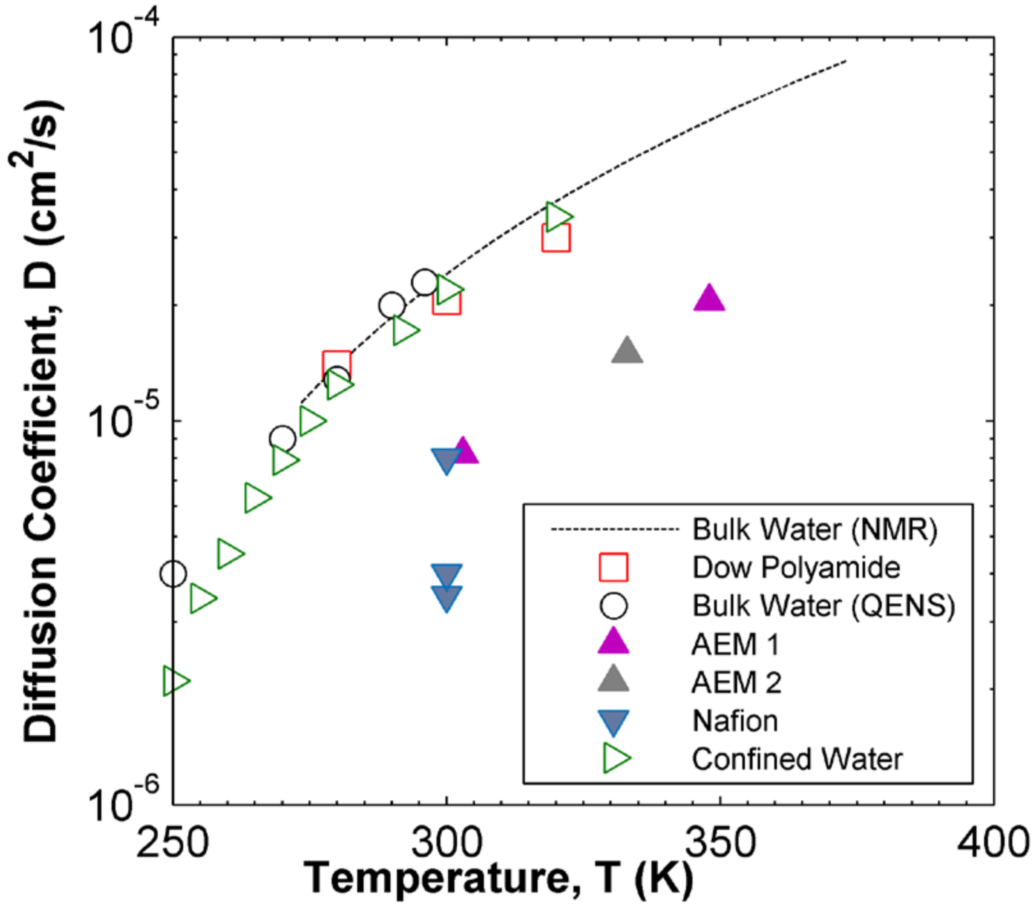
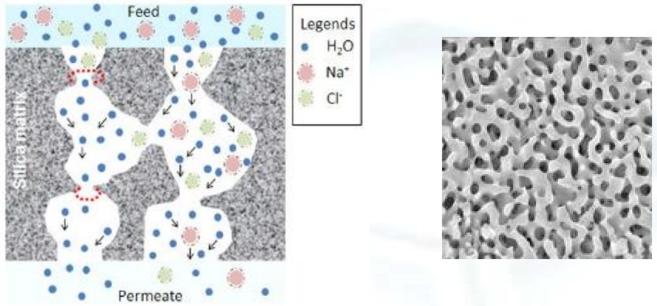
Chen, et al, *PNAS* (2006) **103,** 12974.

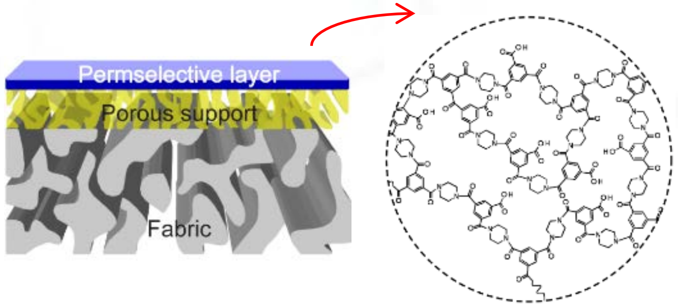
Water Dynamics in a Diverse Set Hydrated Membranes



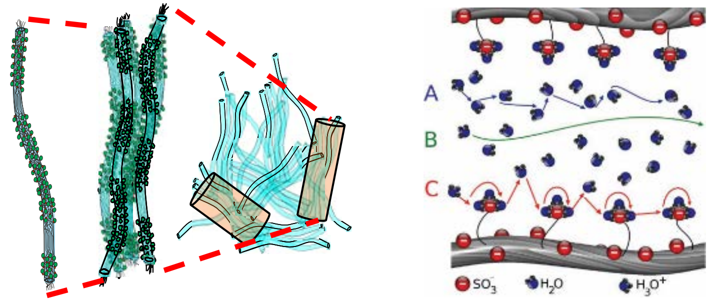
Rigid porous membrane



Swollen porous membrane



Solvated ionic membrane



Pivovar, et al, *J Phys Chem B* (2005) **109**, 785.

Key Takeaways from this talk

Epoxy Networks

- Swell minimally with water (less that 3% uptake by volume)
- Water is closely coupled to matrix, probably as isolated molecules
- Free volume concepts of diffusion are not useful for kinetics, but pore filling does appear to describe uptake
- Water diffusion strongly coupled to polymer dynamics

Polyamide Networks

- Swell moderately with water (between 5 to 10% by volume)
- Swelling opens up network pores or density heterogeneities on the order of 5 nm
- Water appears to move freely through the network; very little coupling between polymer and water dynamics
- Transport resembles pore-flow, but does not have strong evidence of pore filling

Hydrated Ion Containing Polymers

- Swell significantly with water (20 to 60 % by volume)
- There is a strong coupling of polymer/ion dynamics and water dynamics
- At high uptake levels water rich domains emerge, but water does not diffuse freely
- Transport resembles solution-diffusion

Structure & Chemistry (S, χ)

IR techniques (FTIR, ATR, PMIRAAS)
SAXS, WAXS, SANS
SXR, NR, VASE
PALS
NMR
calorimetry
TEM, SEM

Dynamics & Transport (D, η)

QENS, Raman
µwave dielectric, DRS
QCM, mass uptake
PRI
NMR
DMA, rheology

Mechanics & Swelling (σ, ε, E)

Cantilever bending
Buckling & Wrinkling
PRI
BLS