Morphology of proton-exchange membranes based on functionalized syndiotactic polystyrene via small-angle neutron scattering (SANS)

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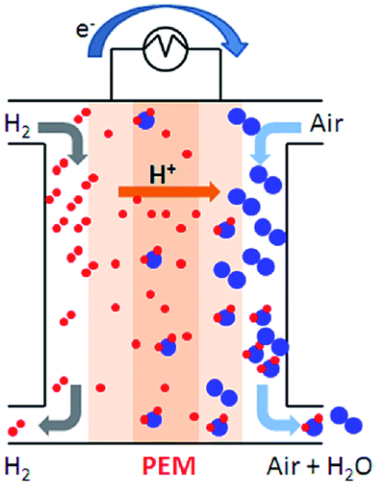
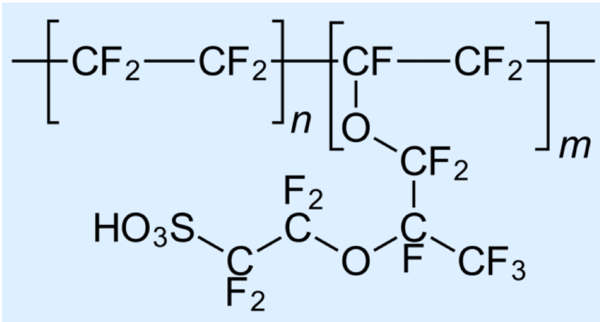
Proton Exchange Membrane Fuel Cells

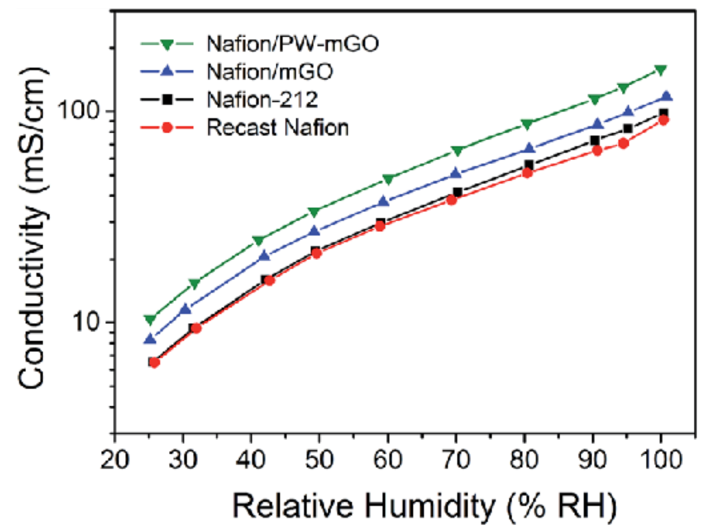


Perfluorosulfonate semicrystalline ionomers (PFSI's) – commercially successful



Crystallinity – 25% to 35%

T_g – 90–120 °C ; T_m – 230–250 °C

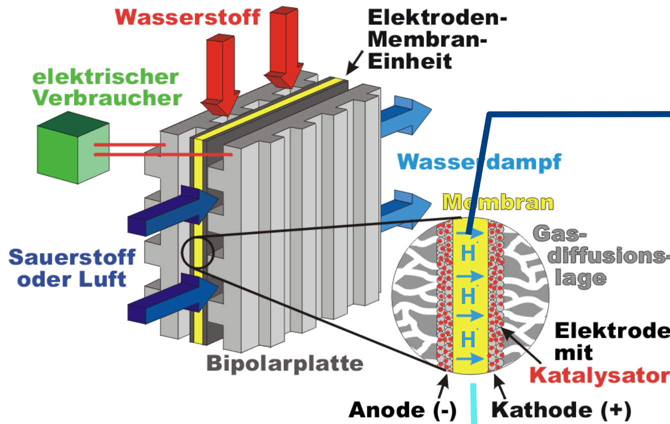


NAFION – benchmark in the FC industry (between 500 and 800 \$/m²); price, safety, T limitations → drawbacks!

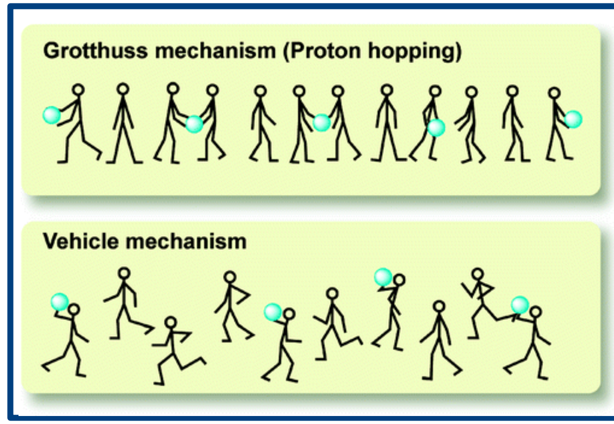
New materials –
microscale phase separation – hydrophilic domains and hydrophobic regions
→ high proton conductivity & good chemical and mechanical stability

NAFION – nanoscale structure

NAFION
nanoscale structure –
still disputed
(SAS investigations)



T. Ueki & M. Watanabe, Macromolecules 2008



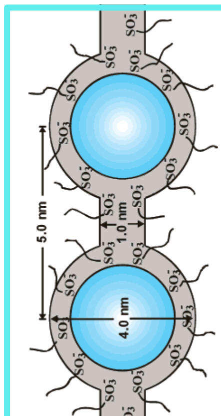
network of spherical water clusters (Gierke et al., J. Polym. Sci. Polym. Phys. 1981)

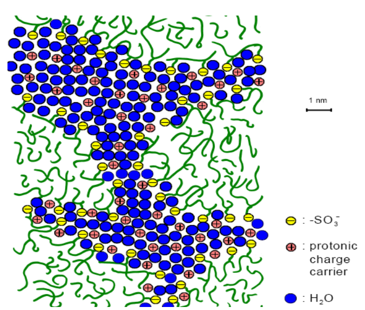
hydrophobic-hydrophilic domains (Kreuer, Journal of Membrane Science 2001)

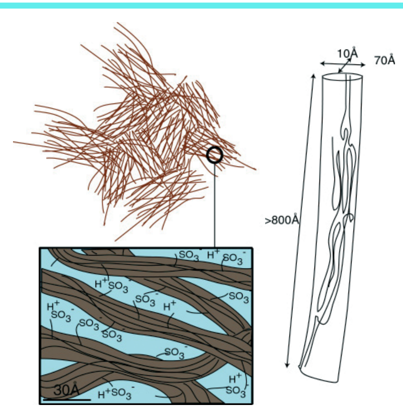
bundles of fibrils (Rubatat et al., Macromolecules 2004)

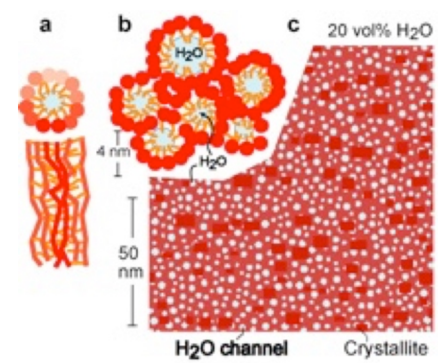
parallel cylindrical water nano-channels (Schmidt-Rohr et al., Nature Mater. 2008)

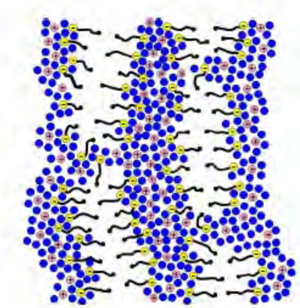
water sheets between polymer layers (Kreuer et al., Adv. Func. Mater. 2013)



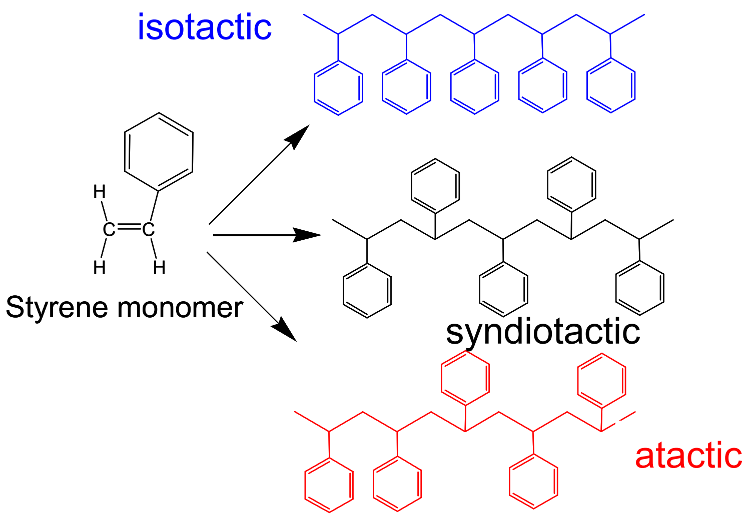




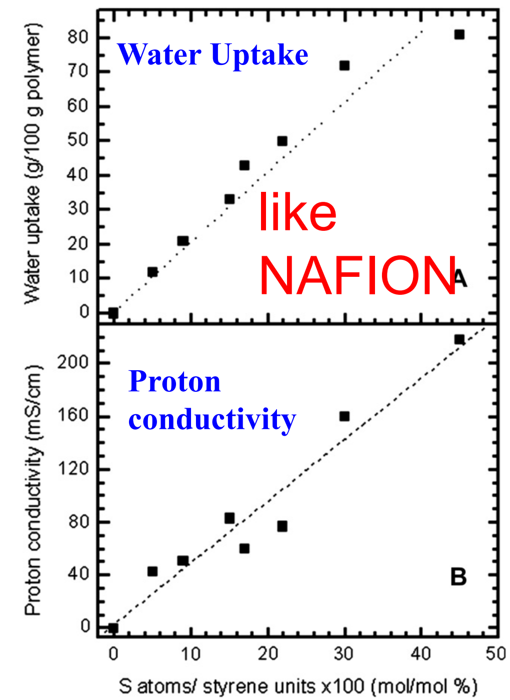




Sulfonated syndiotactic polystyrene



β-form films ⇒ functionalization (sulfonation) & doping with radical scavengers (fullerenes) ⇒ PEM



sulfonation of sPS β-form – very slow, not uniform

δ co-crystals ⇒ Reaction of sulfonation ⇒ **δ co-crystals sulfonated** ⇒ Annealing at high T ⇒ **β-form sulfonated**

Clathrates (δ co-crystals) ⇒ uniform functionalization of phenyl rings only in the amorphous phase, preservation of crystallinity

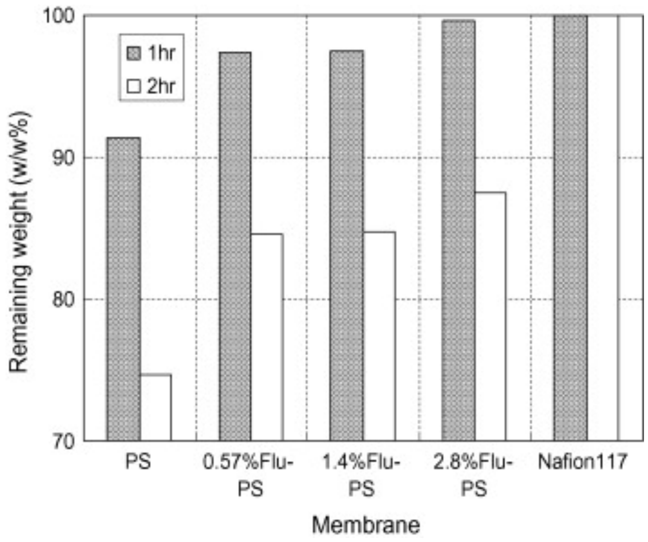
Fasano *et al.*, *Int. J. Hydrog. Energy* 2011

Boriello *et al.*, *Int. J. Hydrog. Energy* 2011

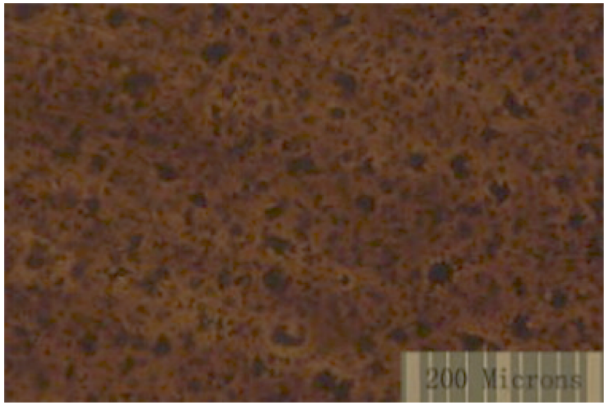
Sulfonated sPS (s-sPS) with fullerenes

s-sPS / fullerenes composite membranes

- Fenton's test – improved oxidation resistance
- solution-cast composite membrane holds the fullerene more tightly than doped membrane



0.5 w% C60 in composite membrane with Nafion – C60 aggregates



The proton conductivity (σ, mS cm^{-1}) of the fullerene–Nafion® composite membranes including Nafion® 117 under 25, 50, and 95% RH at 20 and 80 °C

	25%	50%	95%
20 °C			
C_{60}/Nafion® 117	3.1	13.1	80.3
PHF/Nafion® 117	1.9	8.6	40.2
Nafion® 117	1.1	7.4	70.1
80 °C			
C_{60}/Nafion® 117	3.4	14.1	86.5
PHF/Nafion® 117	2.1	9.3	43.4
Nafion® 117	1.2	8.0	76.2

composite membranes – improved conductivity

Saga et al., *J. Power Sources* 2008

Tasaki et al., *J. Membr. Sci.* 2006; *Polymer* 2007

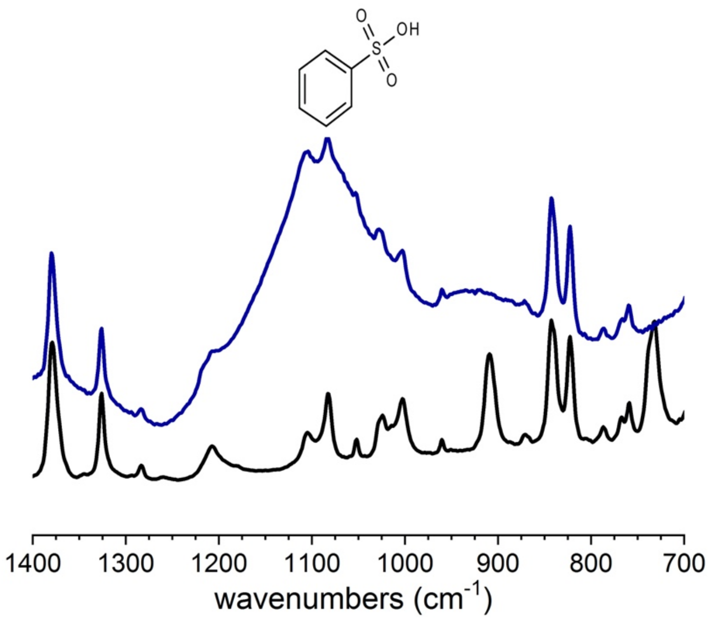
Uni-axially deformed films

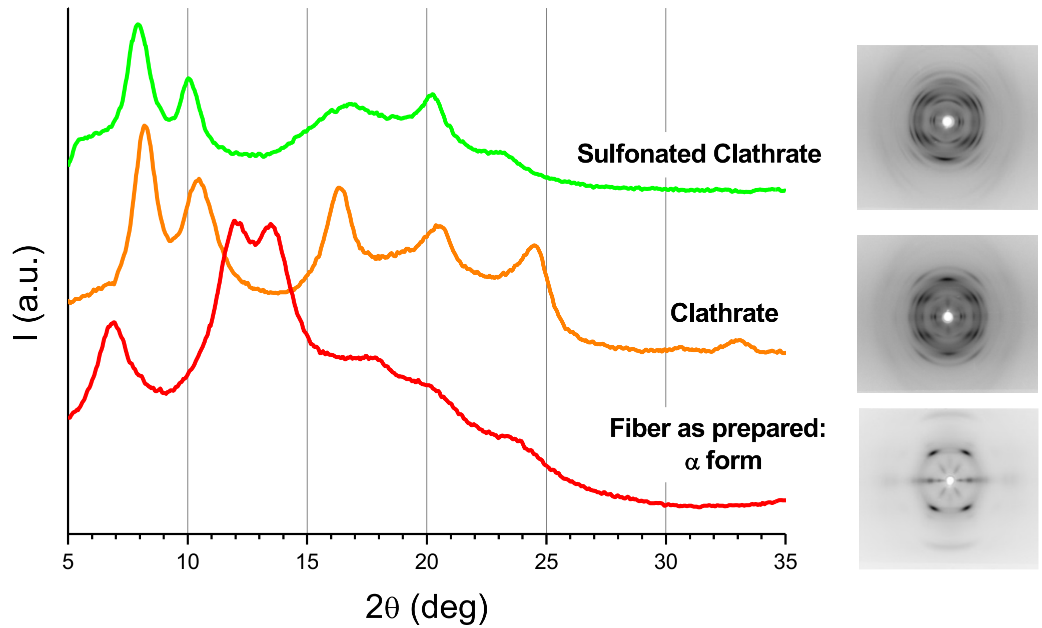
Deuterated films → casting → uniaxially stretching at 200% → sulfonation

Ionic Exchange Capacity (IEC) (25 °C)
~2.14 [meq/g]
comparable with commercial PEMs.

PGNAA (neutron activation) → degree of sulfonation (variable, 20 – 50%)

$*W_{up\text{-}take}$	~ 120 %
$**W_{content}$	~ 55 %
$***\lambda = [H_2O]/[SO_3^-]$	31





M.M. Schiavone, *Solid State Ionics* 2018

$*(W_{wet}-W_{dry})/W_{dry}\times 100\%$

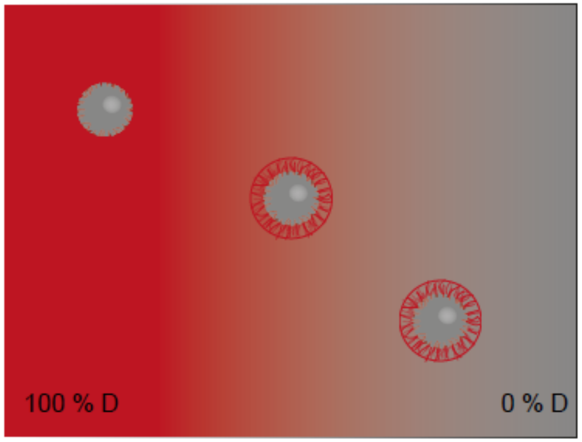
$**(W_{wet}-W_{dry})/W_{wet}\times 100\%$

$$*** \frac{\text{Water up-take (\%)} \times 10}{18 \times \text{IEC (meq/g)}}$$

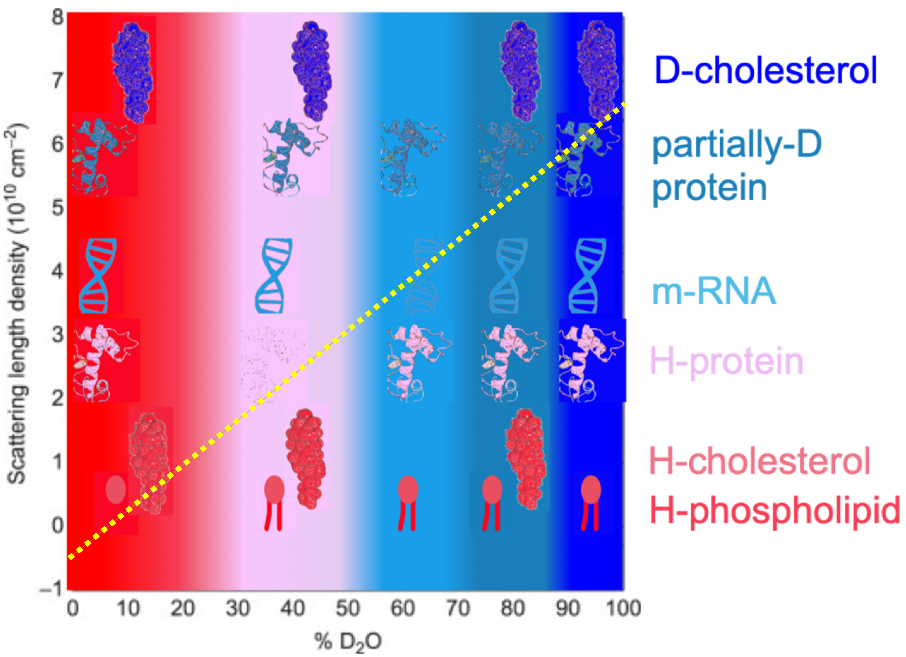
Small-angle neutron scattering

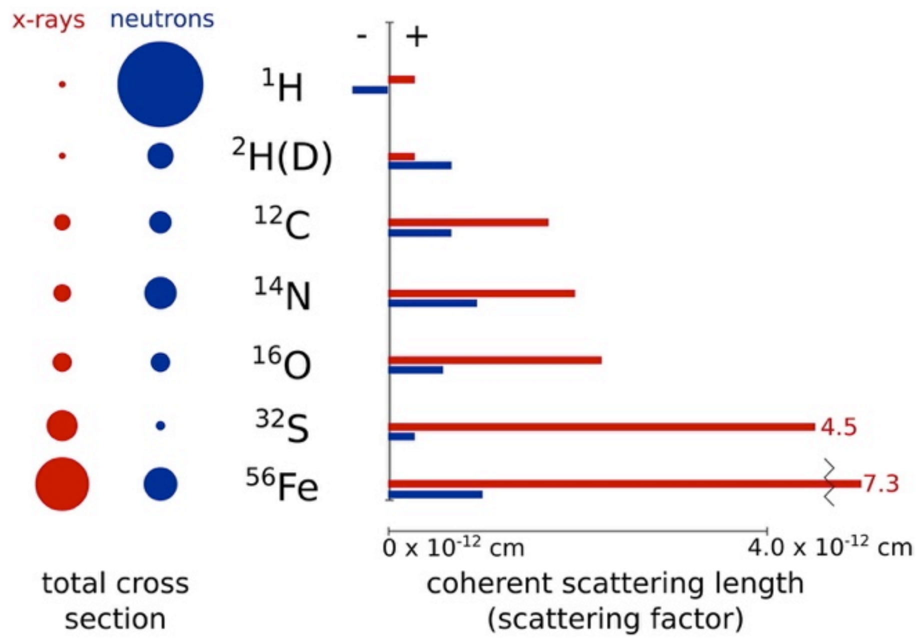
contrast variation & matching
in hydrocarbon system

soft matter



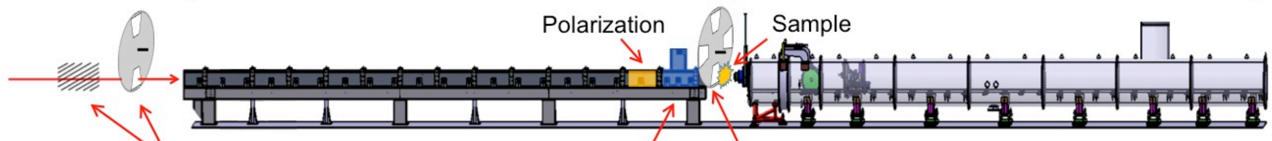
biophysics

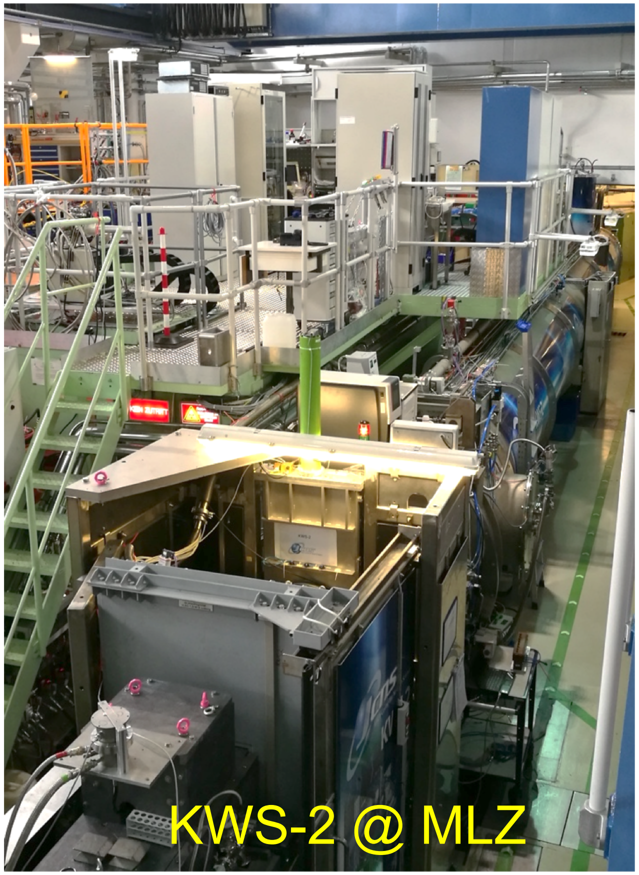


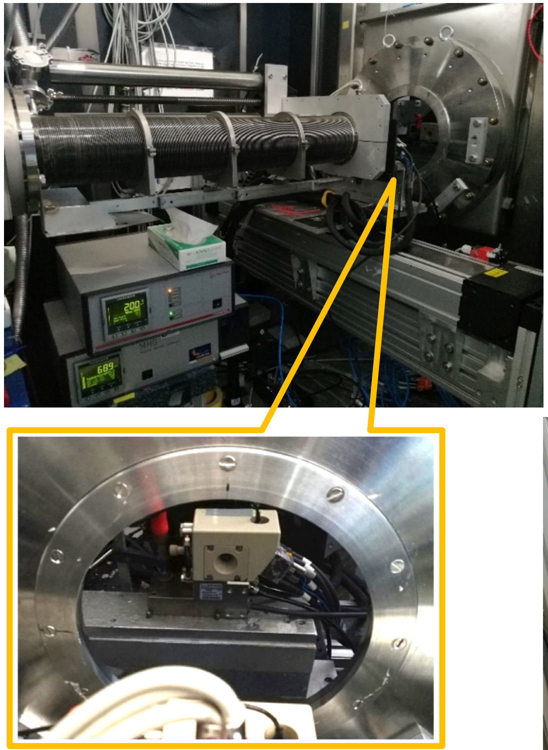


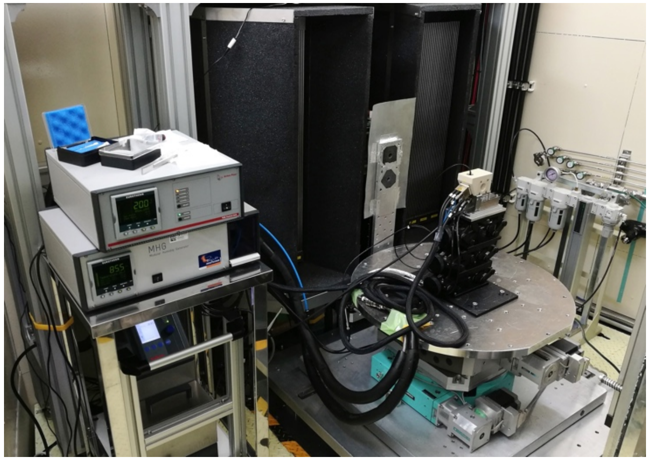
M. Castellanos et al., *Comput. Struct. Biotechnol. J.* 2017

SANS diffractometers







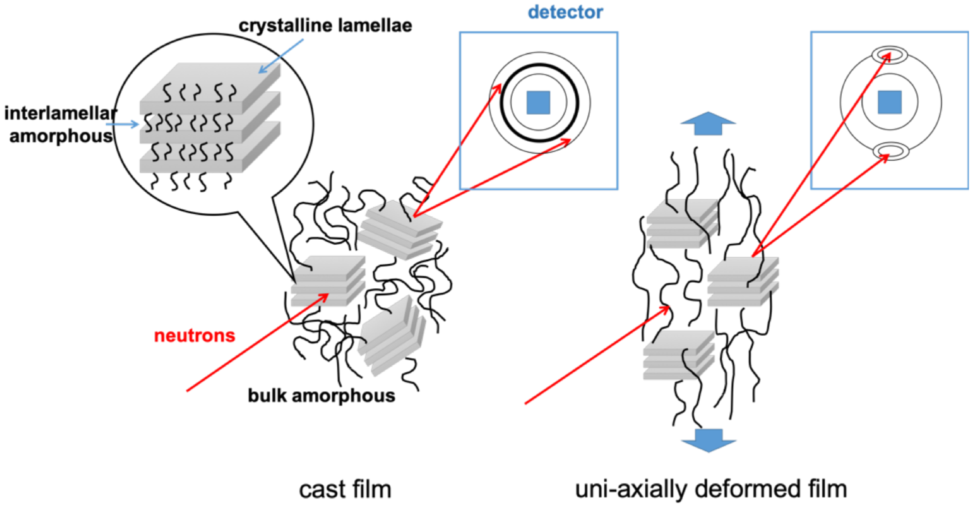


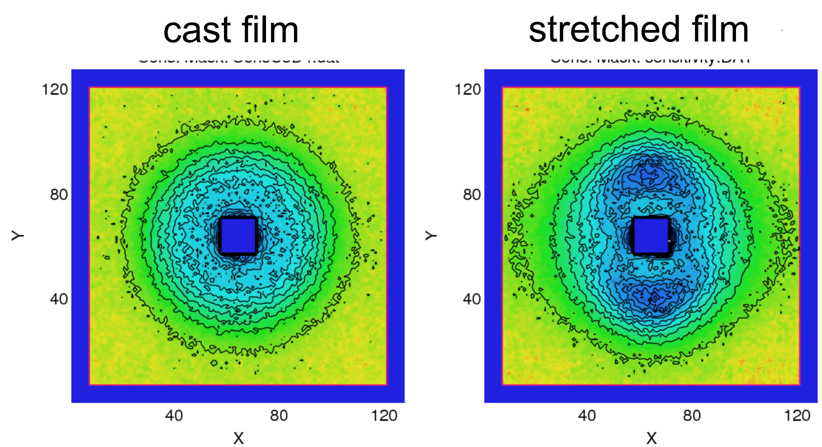
in-situ control of RH (5% to 95%) and T (RT to 80 ^{o}C)

A. Radulescu et al., *J. Vis. Exp*. 2016; *J. Appl. Cryst*. 2015

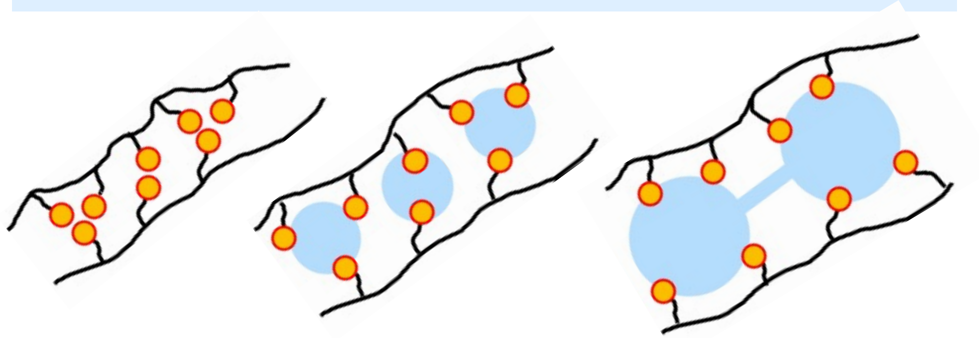
S. Takata et al. et al., *JPS Conf. Proc.* 2015

Uni-axially deformed sPS films

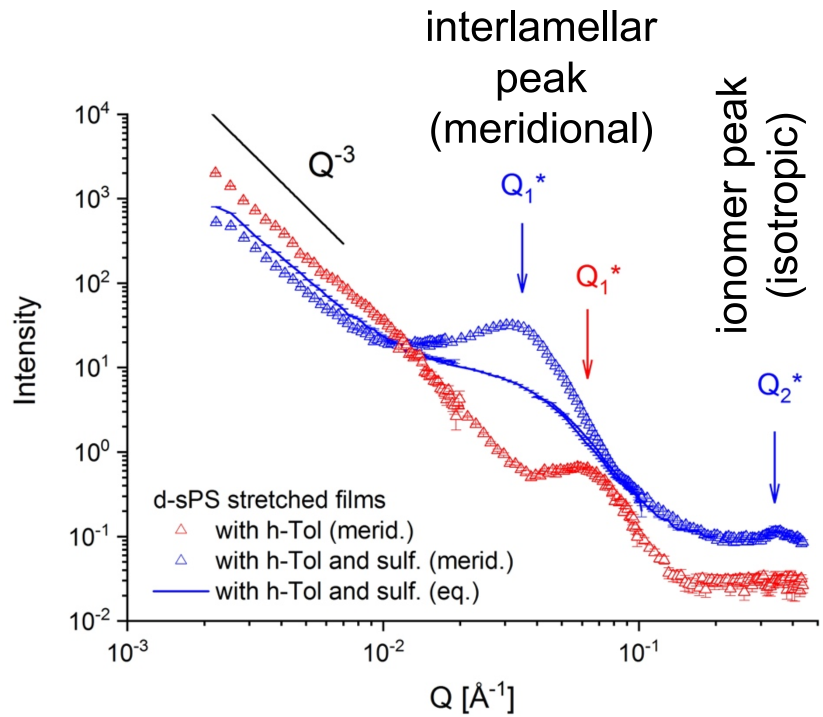




uni-axially deformed sulfonated & <u>deuterated</u> sPS films needed!

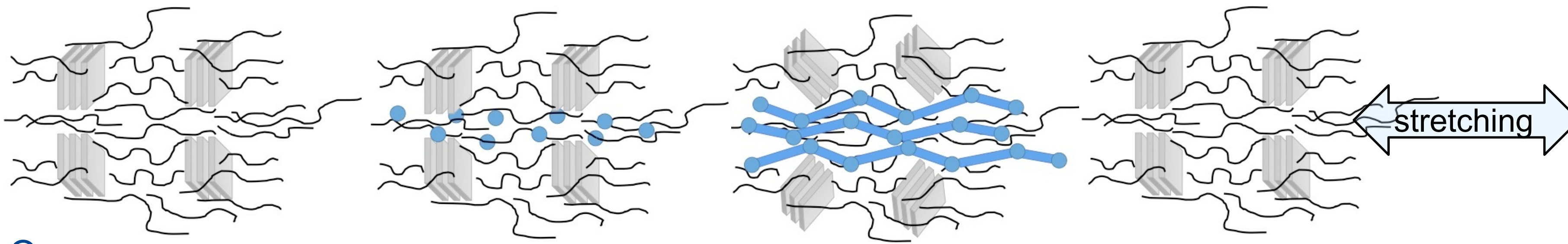


ionic clusters ⇒ ionomer peak, ↑ RH – ↓ Q



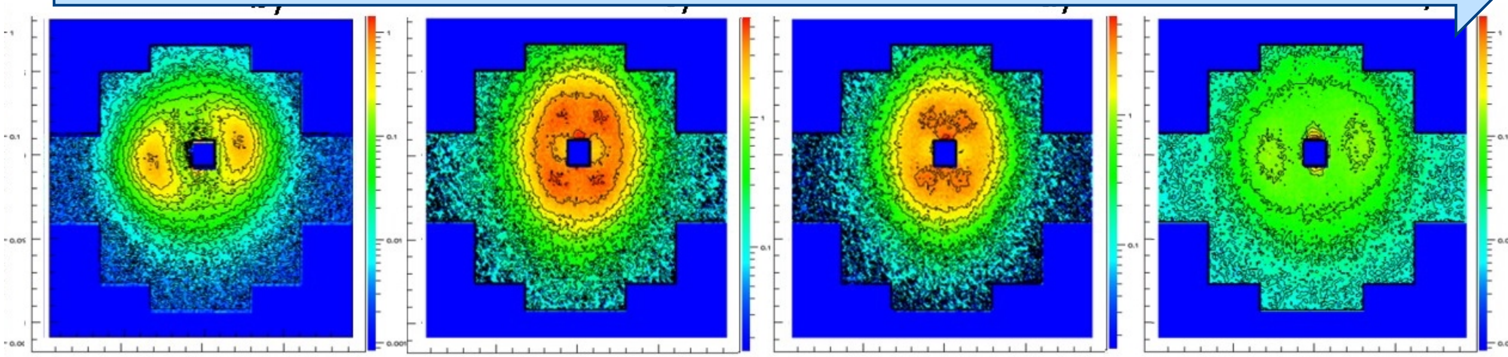
M.M. Schiavone, A. Radulescu et al., *Solid State Ionics* 2018
M.M. Schiavone, A.Radulescu et al., *Membranes* 2019

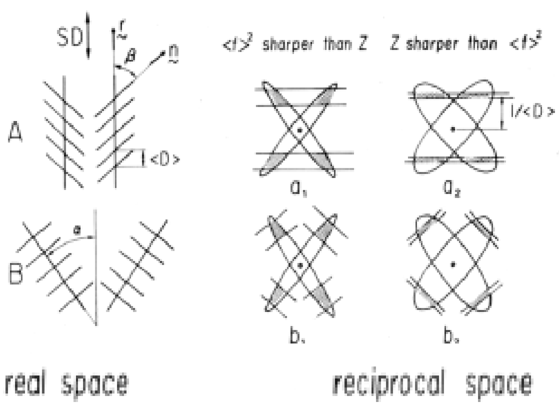
s-sPS: membrane robustness

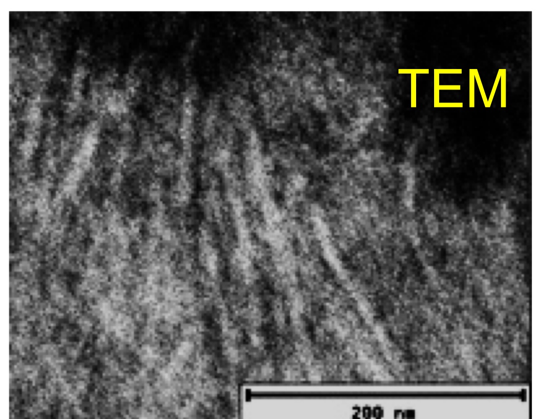


H_2O vapors

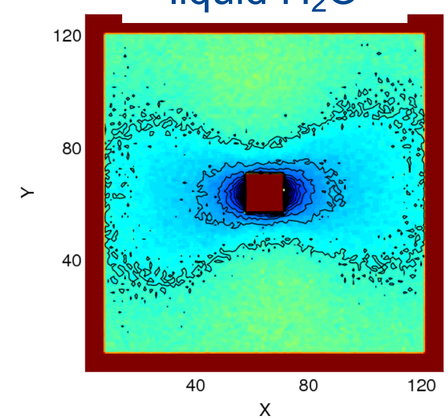
RH 50% - 80% 85% 95% 10%







liquid H_2O



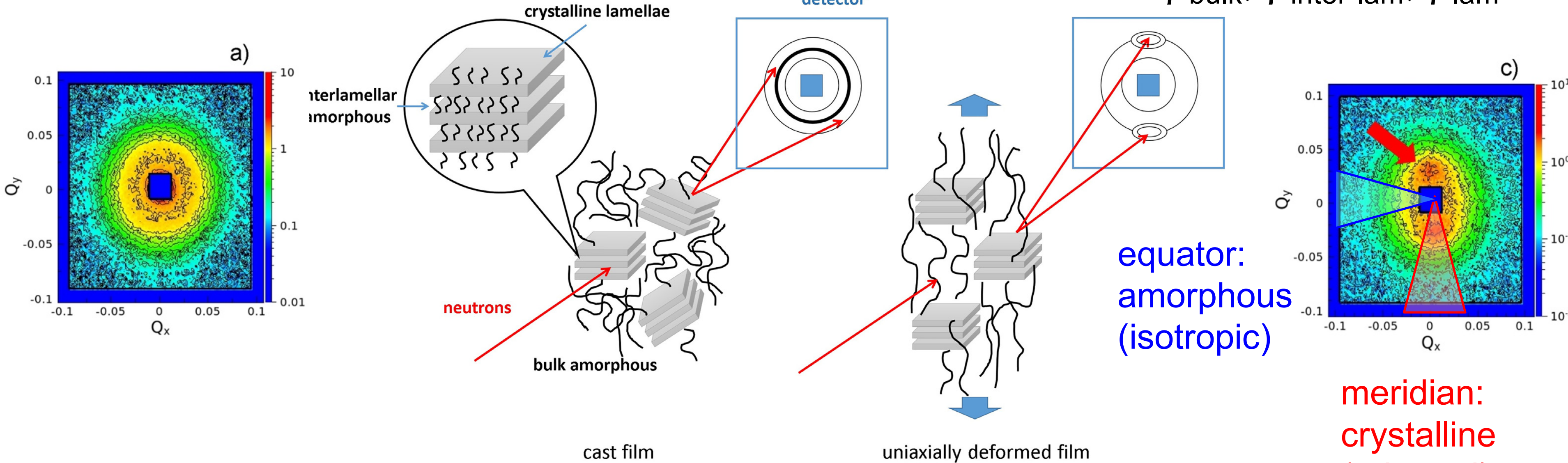
T. Hashimoto et al., *Macromolecules* 1985

M.M. Schiavone, A. Radulescu et al., *Solid State Ionics* 2018

Model: amorphous bulk & lamellar stacks

M.M. Schiavone, A. Radulescu et al., *Solid State Ionics* 2018

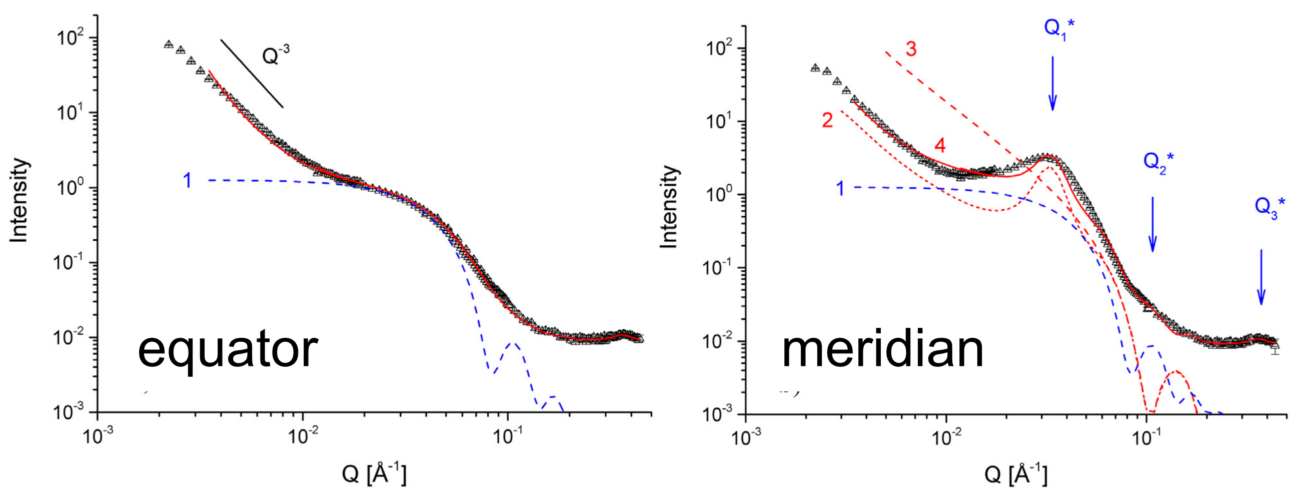
ρ_{bulk}, $\rho_{inter\text{-}lam}$, ρ_{lam}



equator: amorphous (isotropic)

meridian: crystalline (oriented)

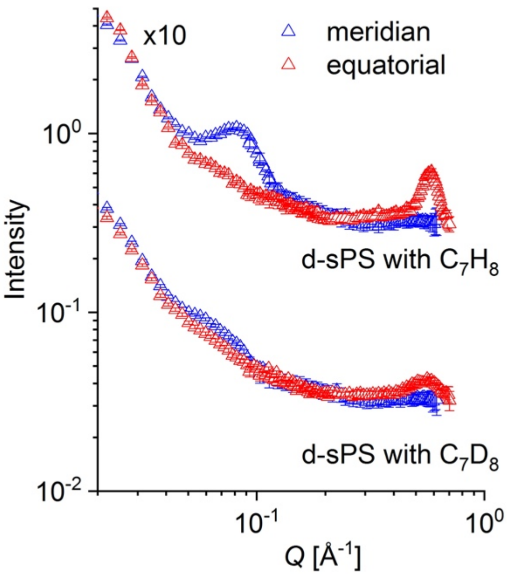
P(Q) spherical domains w/wo S(Q)
+ low-Q fractal
+ high-Q bckgd.
+ high-Q peak



equator + crystalline-amorphous lamellar stacks

A. Radulescu, L.J. Fetters, D. Richter, *Adv. Polym. Sci.* 2008

Extended Q-range – high-Q regime



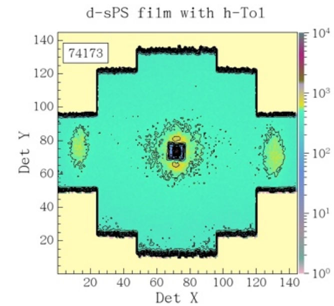
guest exchange in sPS

h-Tol in d-sPS

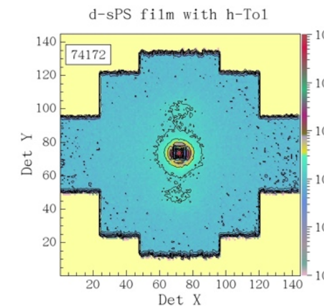
contrast variation – crystalline region

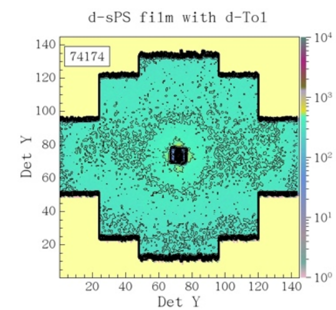
d-Tol in d-sPS

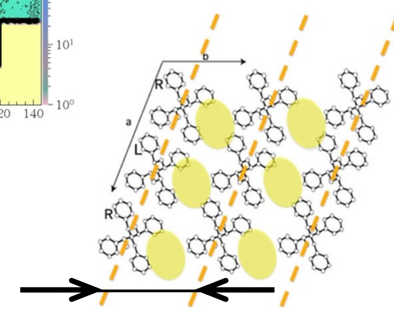
1m detection



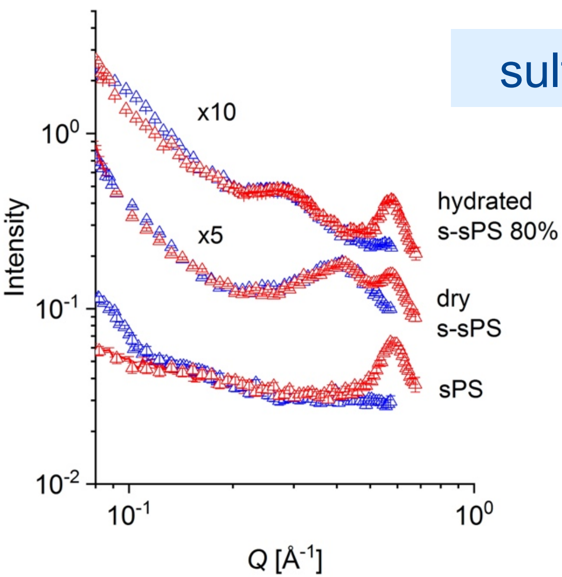
4m detection

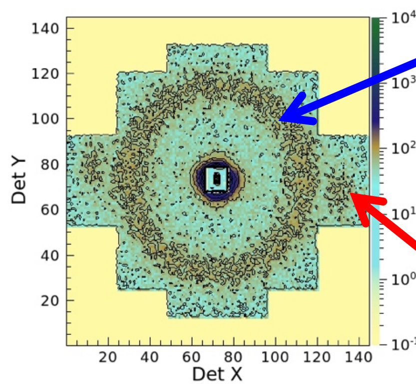






sulfonated & hydrated sPS





ionomer peak

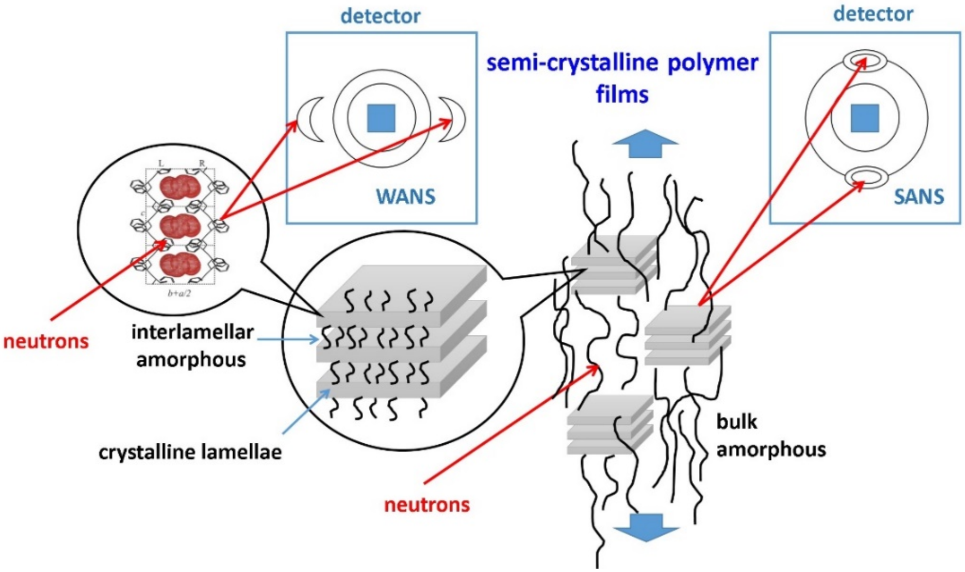
010 reflection

high-Q observations – preservation of crystalline regions during chemical treatment & hydration

M.M. Schiavone, A. Radulescu, et al., *Membranes* 2019

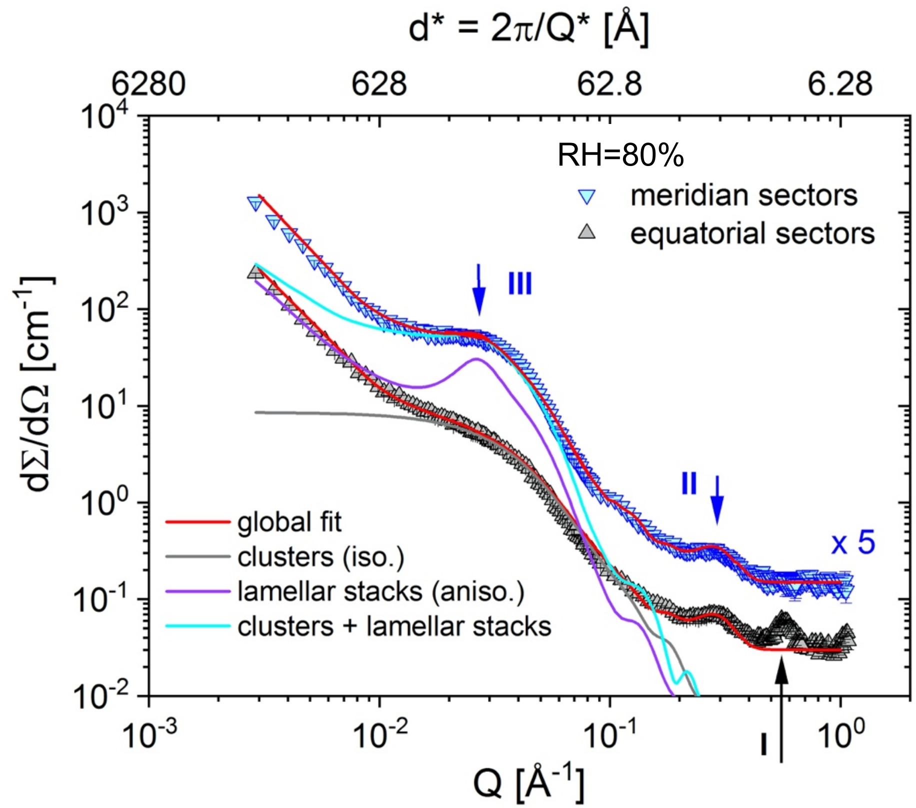
Extended Q-range SANS

KWS-2: lenses + pinhole ⇒ Q: 0.0001 – 1.0 $Å^{-1}$ at the same instrument



III – interlamellar peak (meridian)

II – ionomer peak (isotropic)



I – 010 crystalline peak (equator)

- adjustable neutron SLD of amorphous (hydration) & crystalline (guest exchange) regions
- overlap with XRD & ND range

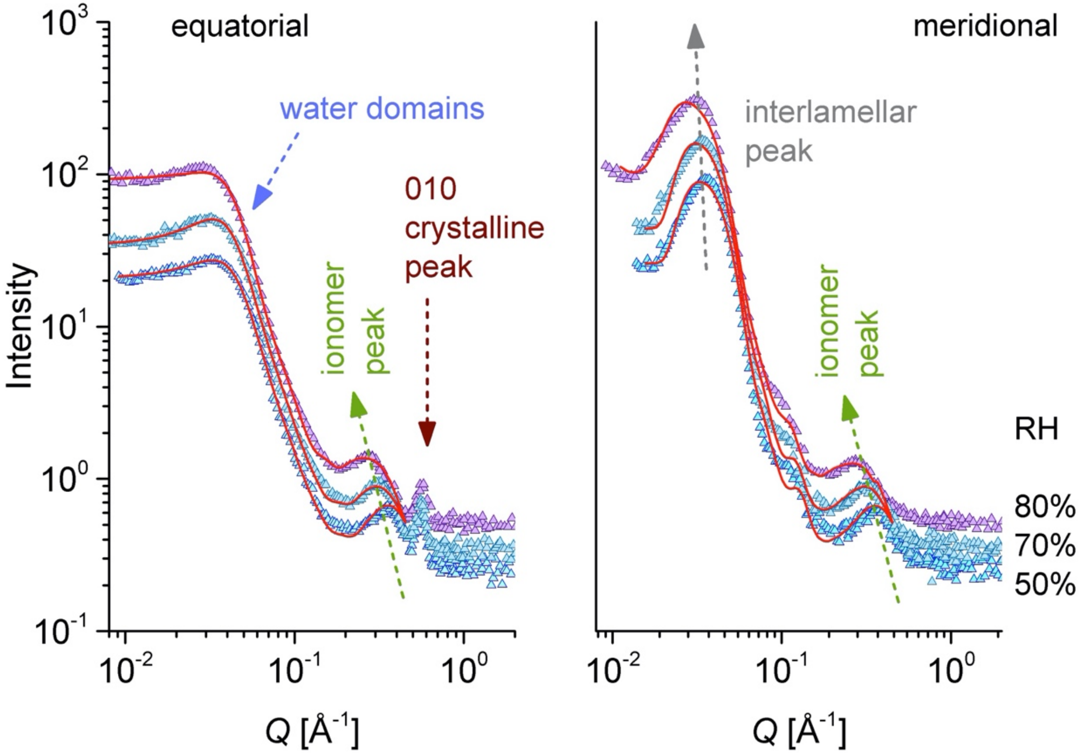
M.M. Schiavone, et al., *Solid State Ionics* 2018, *Membranes* 2019

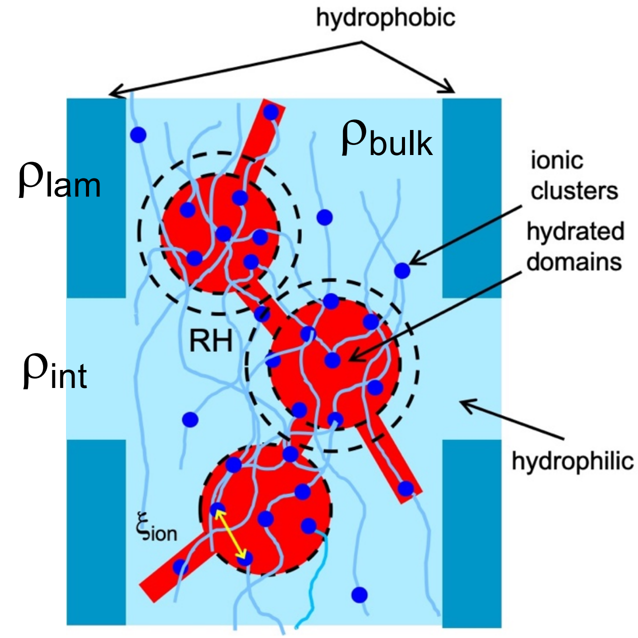
High sulfonation: RH variation

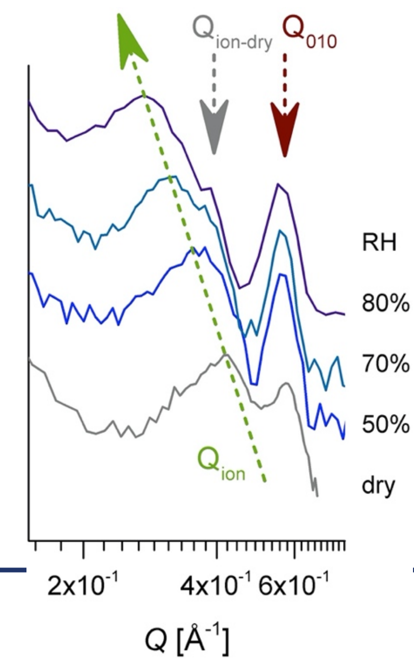
high sulfonation degree (40%) ⇒ correlated water domains (RH)

high crystallinity

$\xi_{ion} = 2\pi / Q_{ion}$



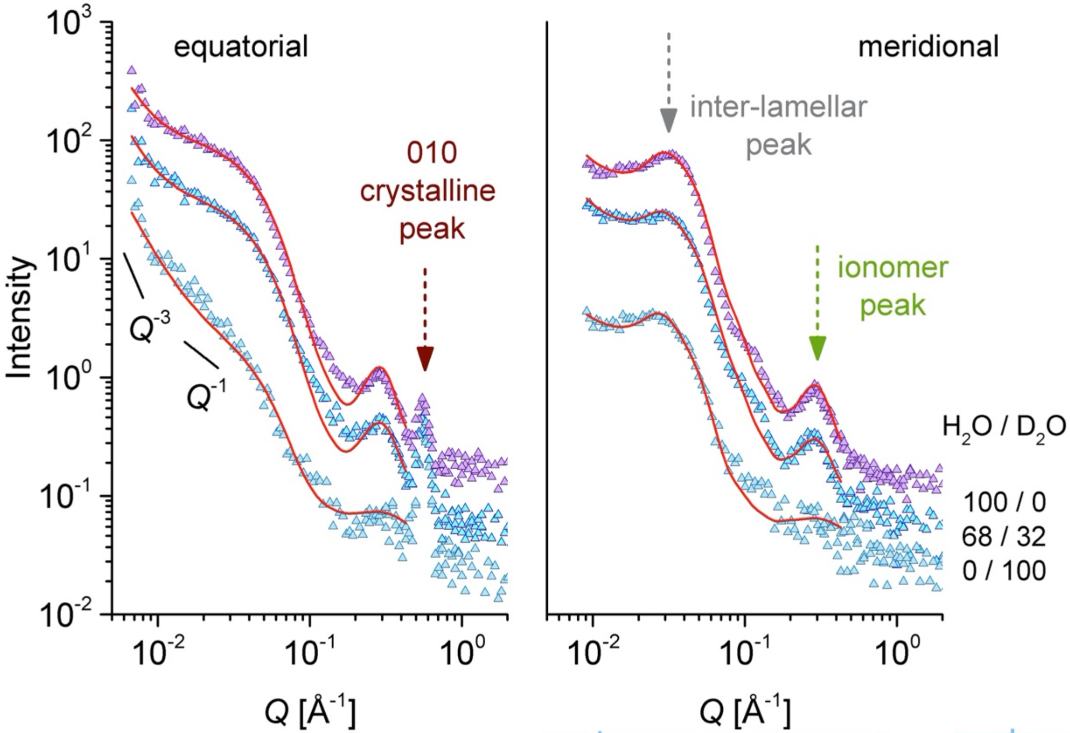




$(\phi_{water})^{inter\text{-}lam} < (\phi_{water})^{bulk}$

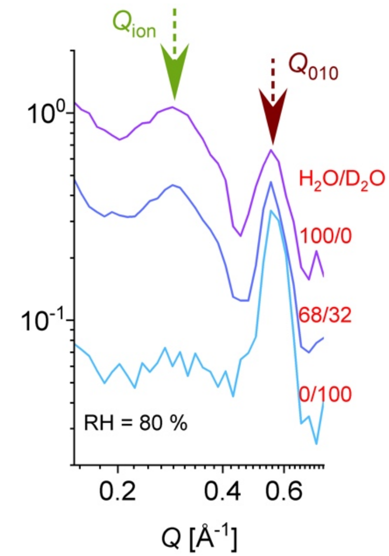
M.M. Schiavone, A. Radulescu et al., *Membranes* 2019

Low sulfonation: contrast variation



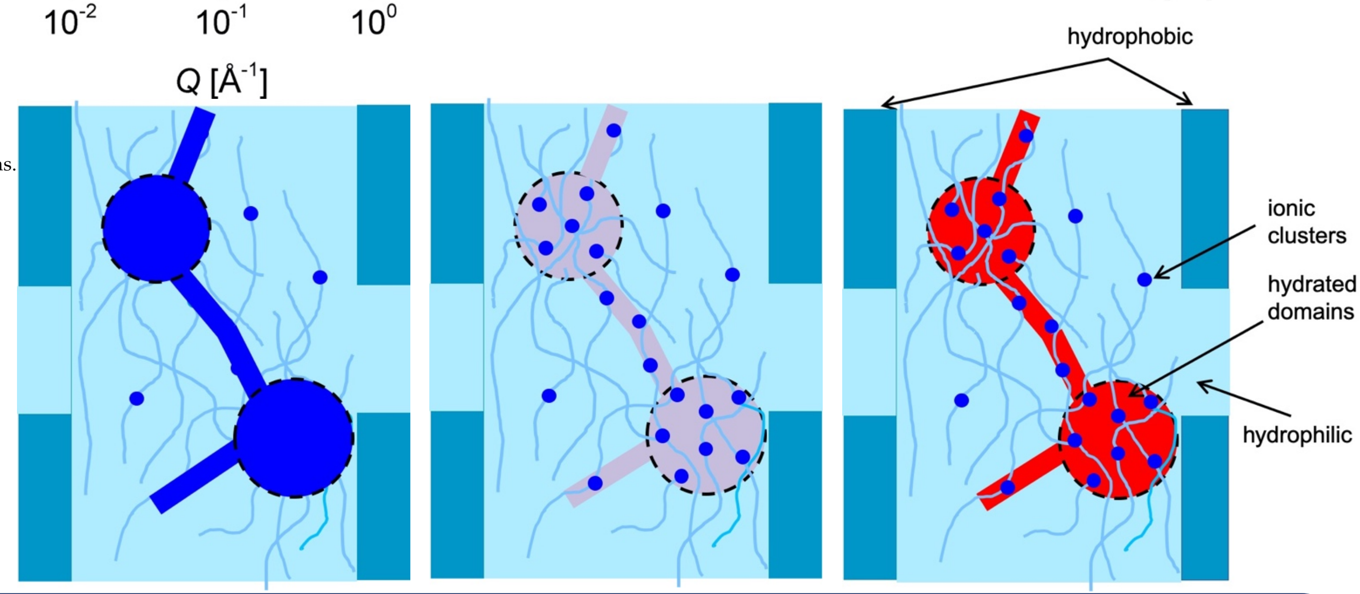
low crystallinity
RH=80%

low sulfonation degree (20%)
⇒ isolated water domains



The calculated SLD for different components of the s-sPS films.

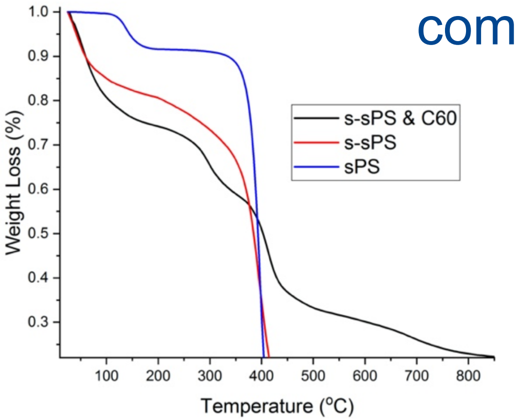
Compound	SLD, $x10^{10}$ cm^{-2}
sPS (crystalline)	6.47
sPS (amorphous)	6.00
s-sPS (amorphous)	6.34
$-SO_3H$	1.32 (1.1 [28])
D_2O	6.38
H_2O	-0.56
d-Tol	5.66
h-Tol	0.94
C60	5.50
C70	5.67

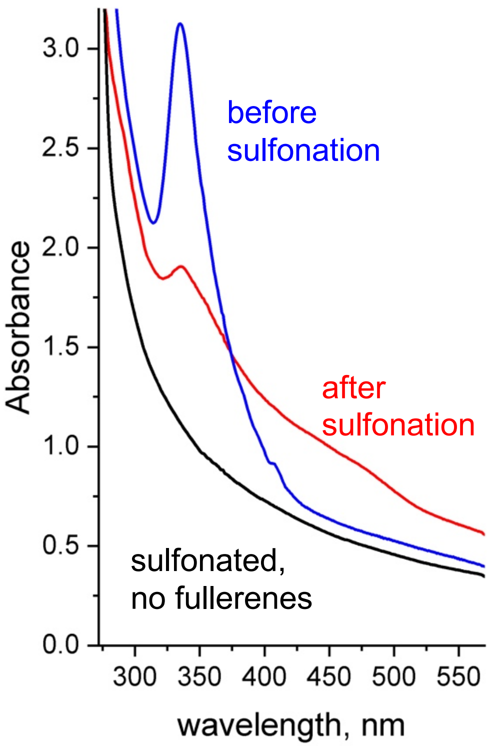


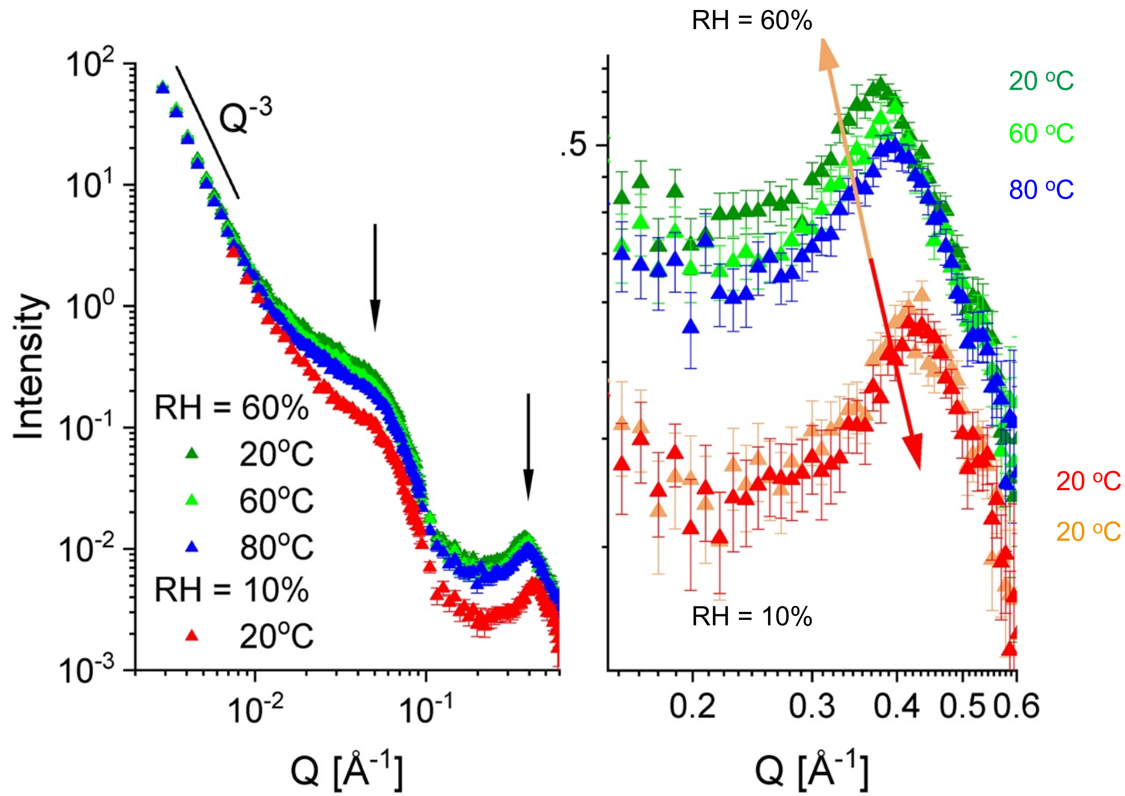
M.M. Schiavone, A. Radulescu et al., *Membranes* 2019

Temperature effect

composite membranes - C70 (0.5 wt%)





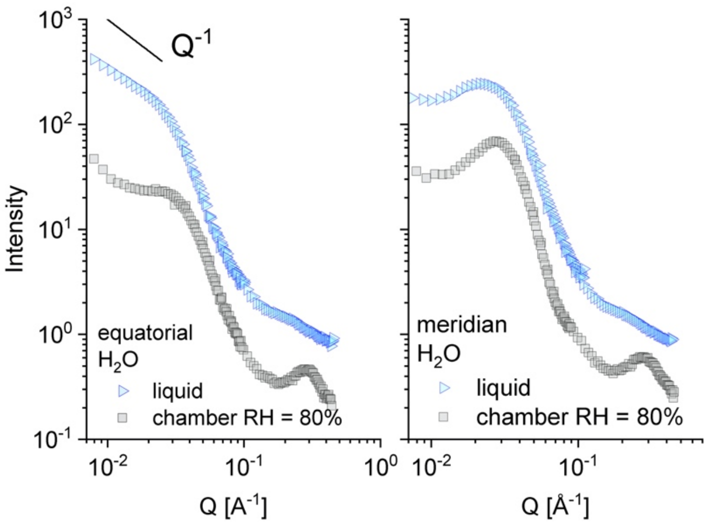


with increasing temperature:

- low water desorption
- small decrease in the ionic correlation length
- same effect observed on sPS uni-axially deformed films

M.M. Schiavone, A. Radulescu et al., *Membranes* 2020

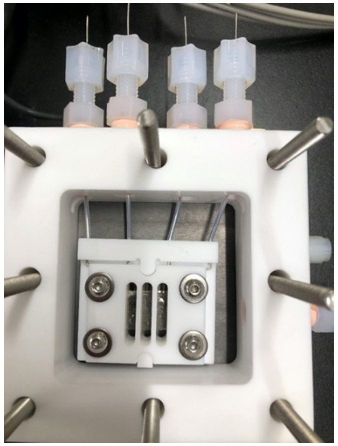
Conductivity vs. hydrated paths



RH increases:
clusters ⇒ channels (1D)

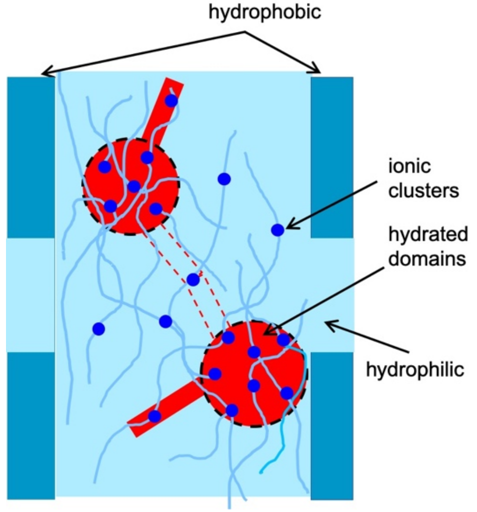
composite membranes

hydration / temperature	σ mS/cm	morphology hydrated domains
liq. phase, 30 °C	180	cylindrical, channels
liq. phase, 80 °C	450	cylindrical, channels
RH 50%, 30 °C	1.5	spherical, partially interconnected clusters
RH 70%, 30 °C	10	spherical, interconnected clusters
RH 80%, 30 °C	19	spherical, interconnected clusters
RH 80%, 60 °C	1.2	spherical, partially interconnected clusters



T increases:

- **in liquid phase**: large increase in conductivity – large continuous water paths (channels)
- **RH = 80%**: moderate water desorption (SANS) vs. large drop in conductivity – interrupted water paths (polymer chains?)

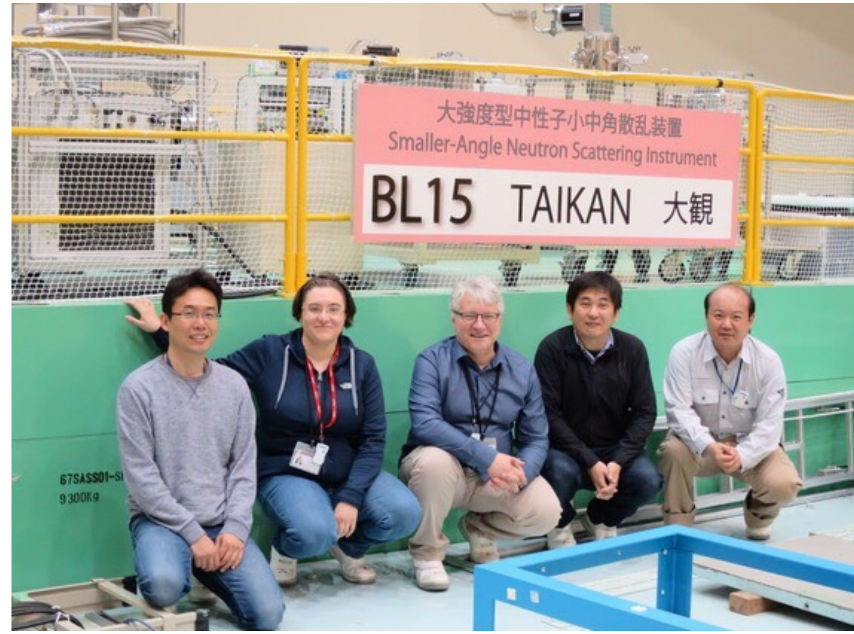


M.M. Schiavone, A. Radulescu et al., *in preparation*

ongoing study

Acknowledgements

Experiments at **KWS-2** @ MLZ (Germany) and **TAIKAN** @ J-PARC (Japan)



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