Proton Conducting **Phase-Separated Multiblock Copolymers** with Sulfonated Poly(Phenylene Sulfone) Blocks for Electrochemical Applications

G. Titvinidze, **K.-D. Kreuer**, M. Schuster, C. C. de Araujo, J. Melchior, and W. H. Meyer

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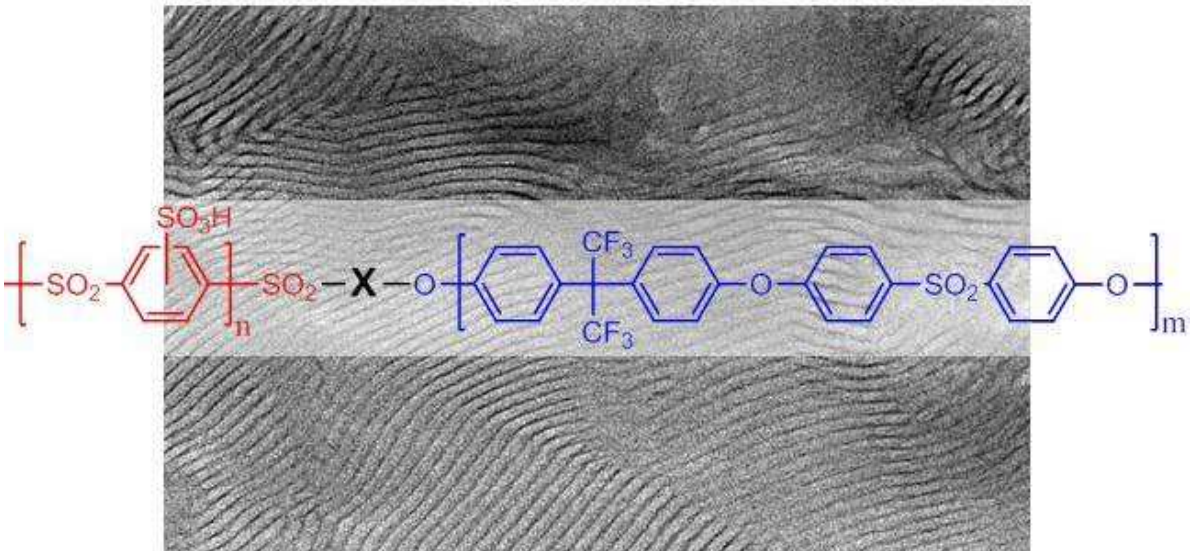
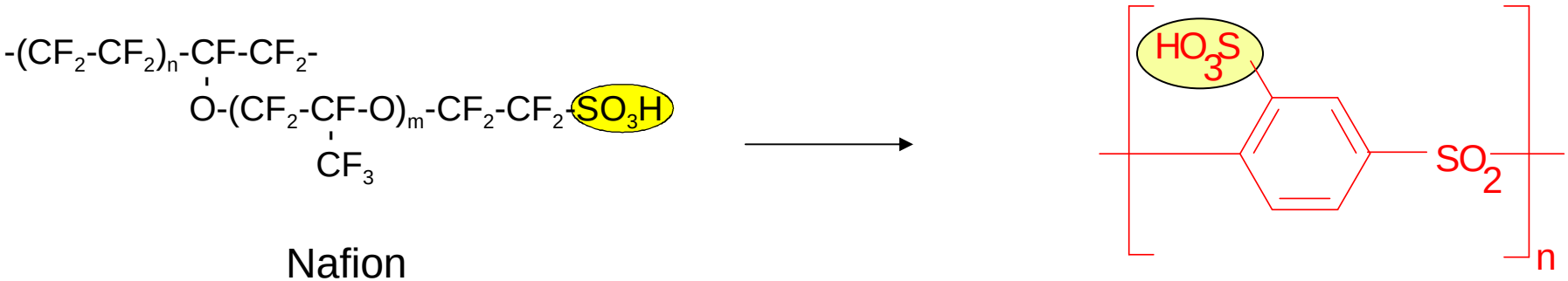
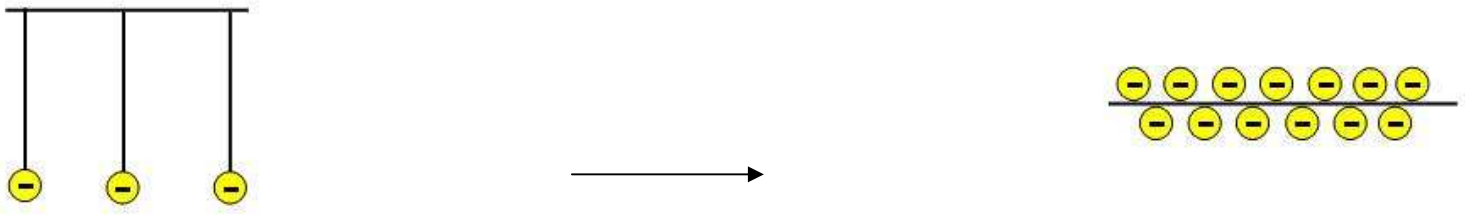




Nafion

C.C. de Araujo, K.D. Kreuer, M. Schuster, G. Portale, H. Mendil-Jakani, G. Gebel, J. Maier
PCCP **11** 3305-3312 (**2009**)



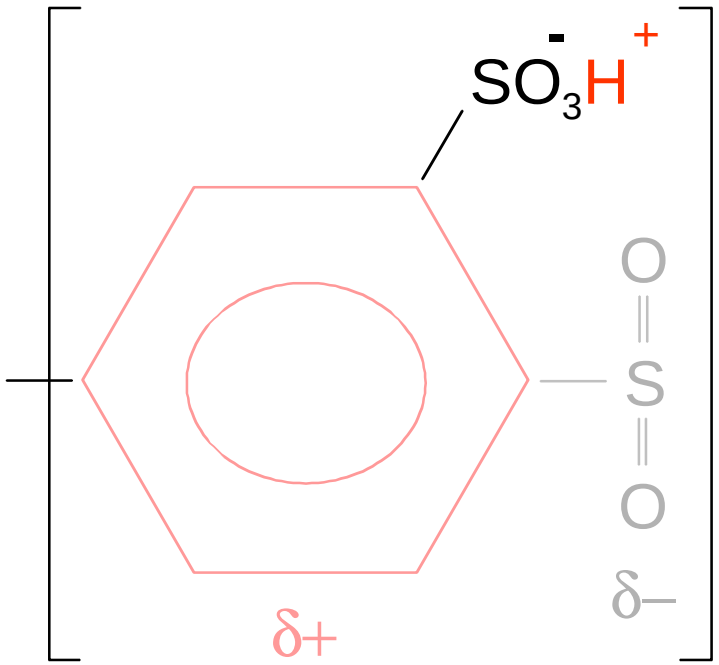
ionomer *polyelectrolyte*

C.C. de Araujo, K.D. Kreuer, M. Schuster, G. Portale, H. Mendil-Jakani, G. Gebel, J. Maier
PCCP **11** 3305-3312 (**2009**)

electron poor sulfonated poly (phenylene-sulfone)s

a base polyelectrolyte for new proton conducting membranes

S-220

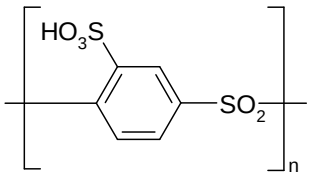


this polyelectrolyte combines in a unique way:

- *high* ***stability***
- ***methanol rejection***
- *very* ***low electroosmotic water drag***
- *very* ***high proton conductivity***
  at high T and low λ (RH)

M. Schuster, K.D. Kreuer, H.T. Andersen and J. Maier, *Macromolecules*, **40**, 598-607 (2007)

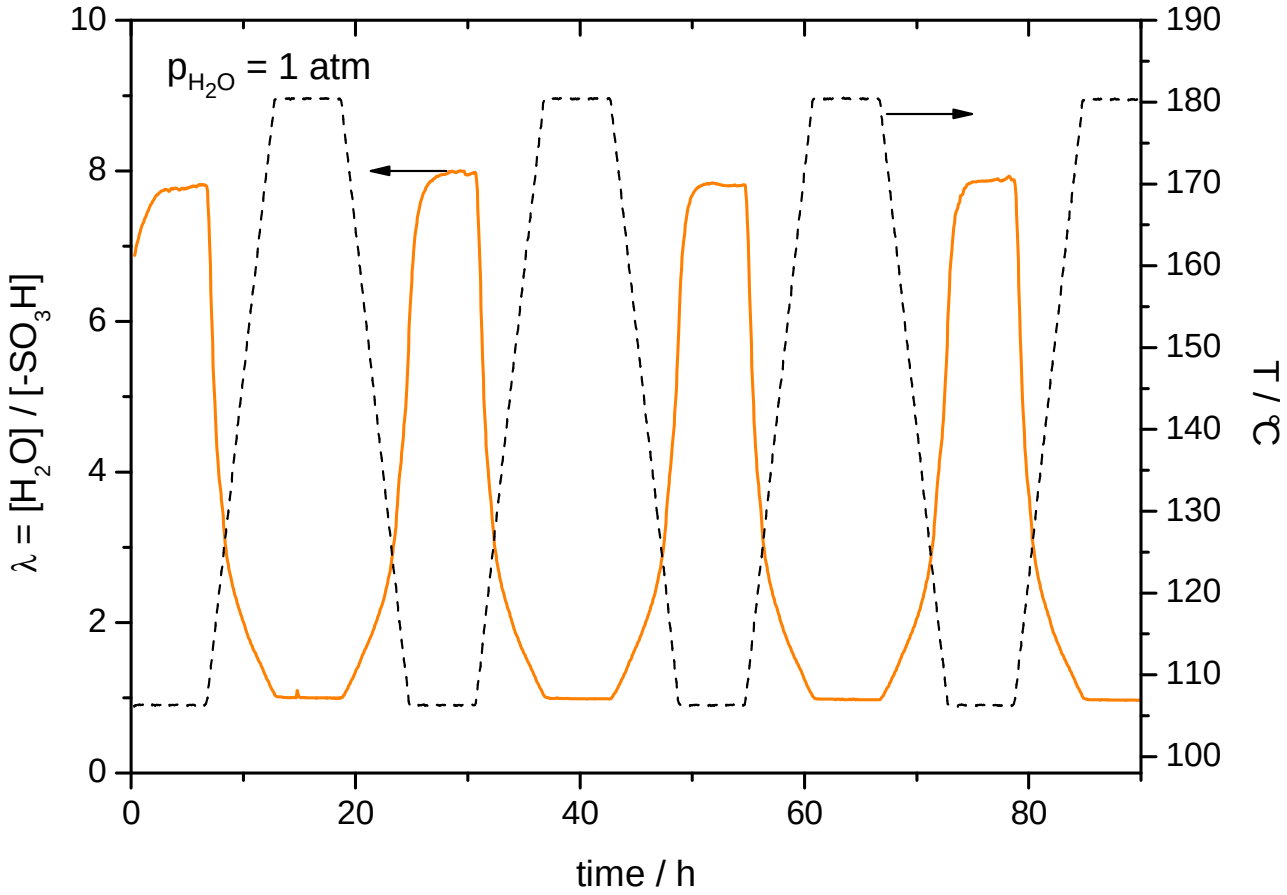
M. Schuster, C. C. de Araujo, V. Atanasov, H. T. Andersen, K.D. Kreuer, and J. Maier
Macromolecules **42**, 3129–3137 (2009)



S-220

thermo gravimetric analysis in steam

T-cycling 110 – 180 ℃



→ high hydrolytic stability

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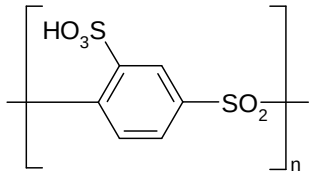
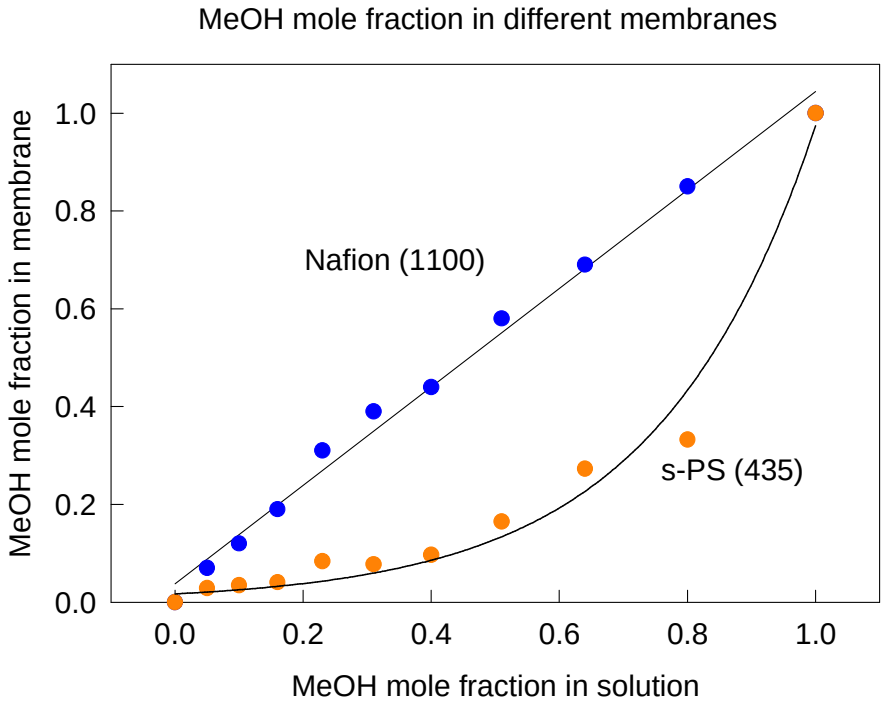
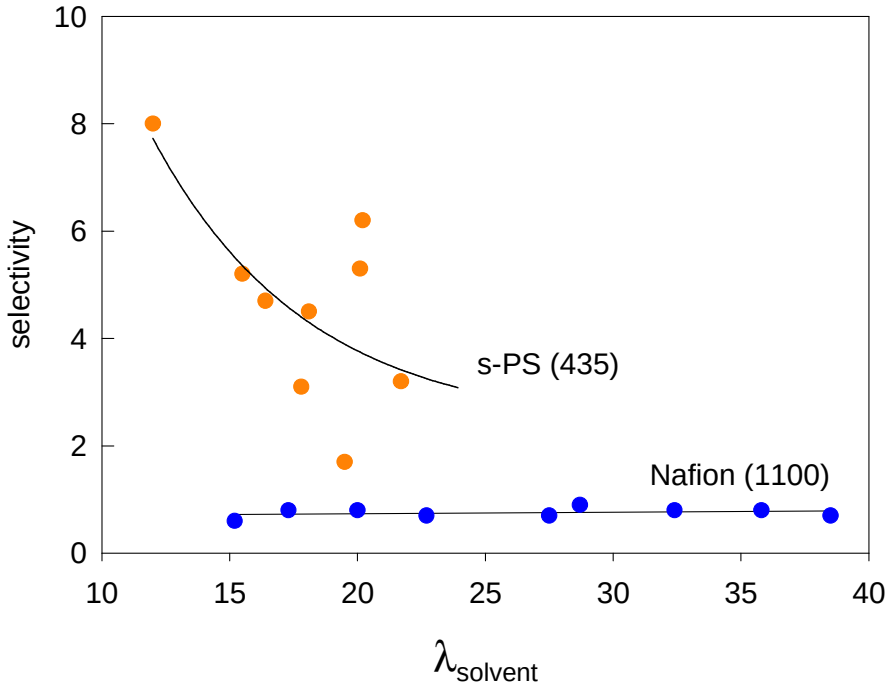


S-220

for those who are interested in DMFC applications:

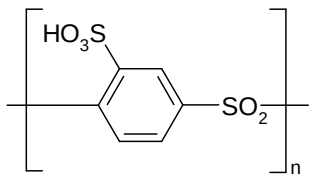
methanol rejection





→ reduction of methanol cross-over (~12 times)!

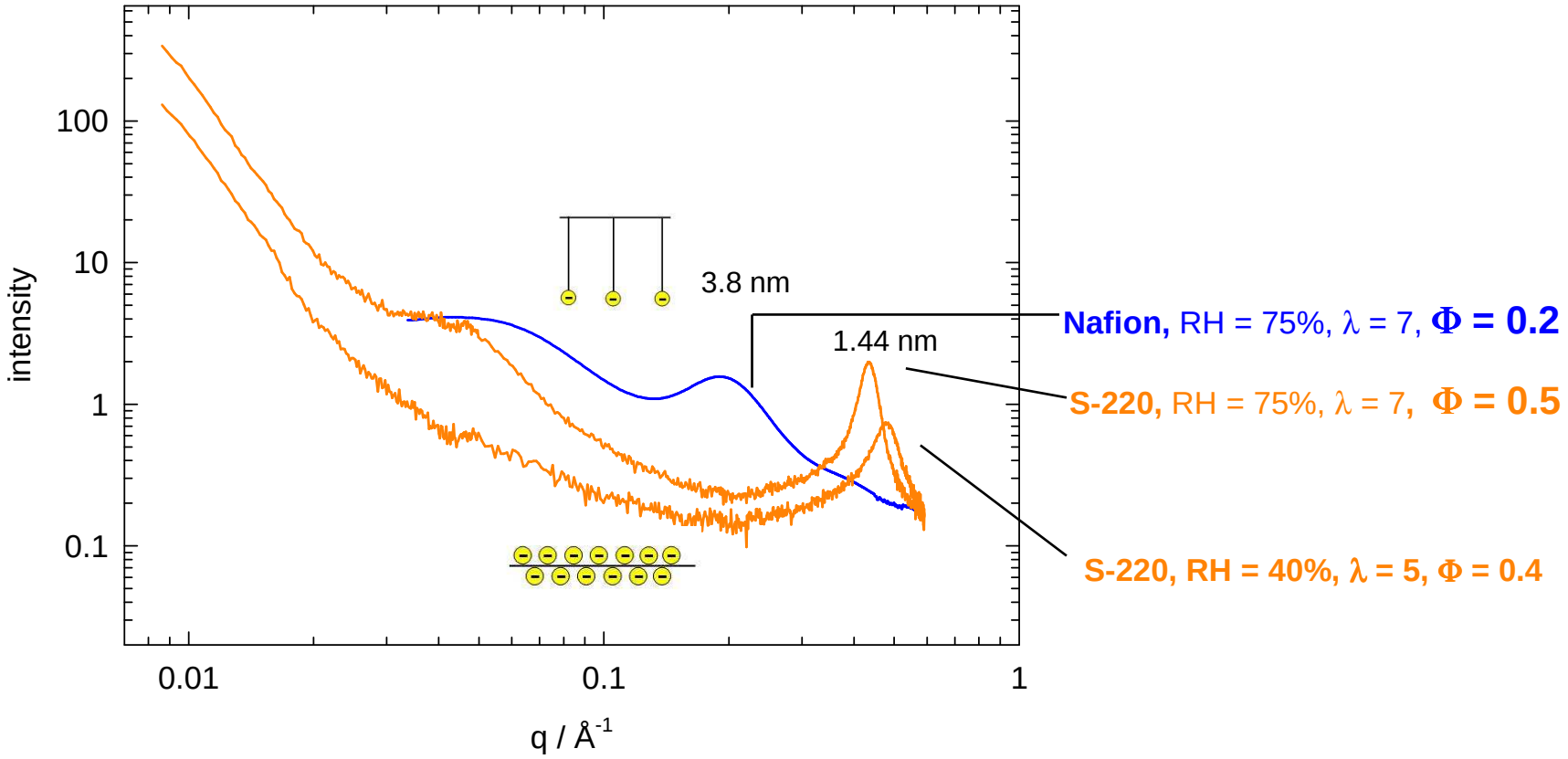
V. Saarinen, K.D. Kreuer, M. Schuster, R. Merkle, J. Maier, *Solid State Ionic* **178**, 533-537(2007)



S-220

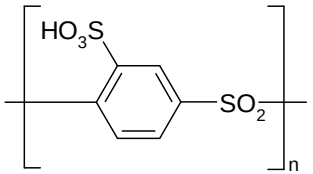
unique microstructure

controlled by electrostatic interaction



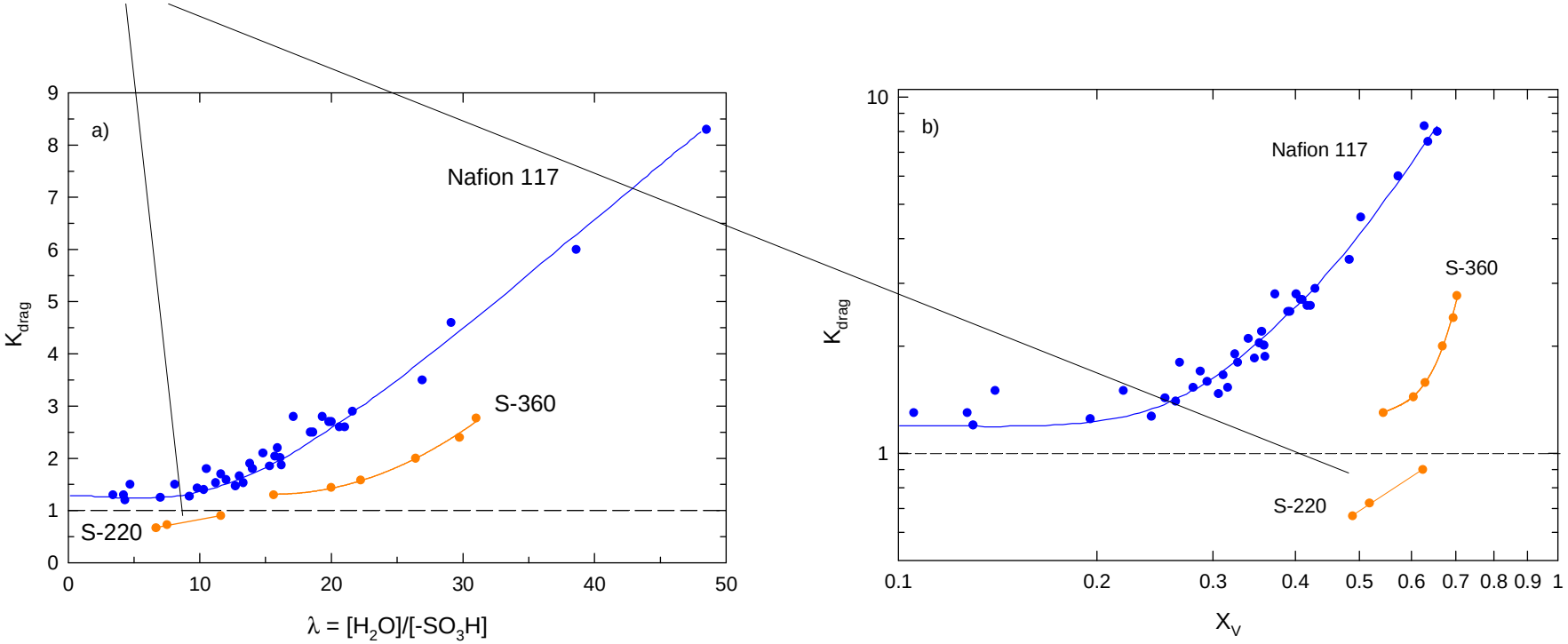
development of a high density of very narrow well ordered hydrated domaines (water films)

Kreuer 2012 C.C. de Araujo, K.D. Kreuer, M. Schuster, G. Portale, H. Mendil-Jakani, G. Gebel, J. Maier: *PCCP* **11** 3305-3312 (**2009**)



S-220

electrophoretic NMR

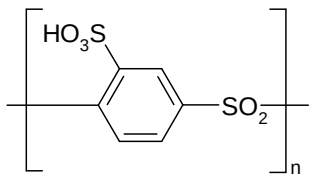


very low electroosmotic water drag

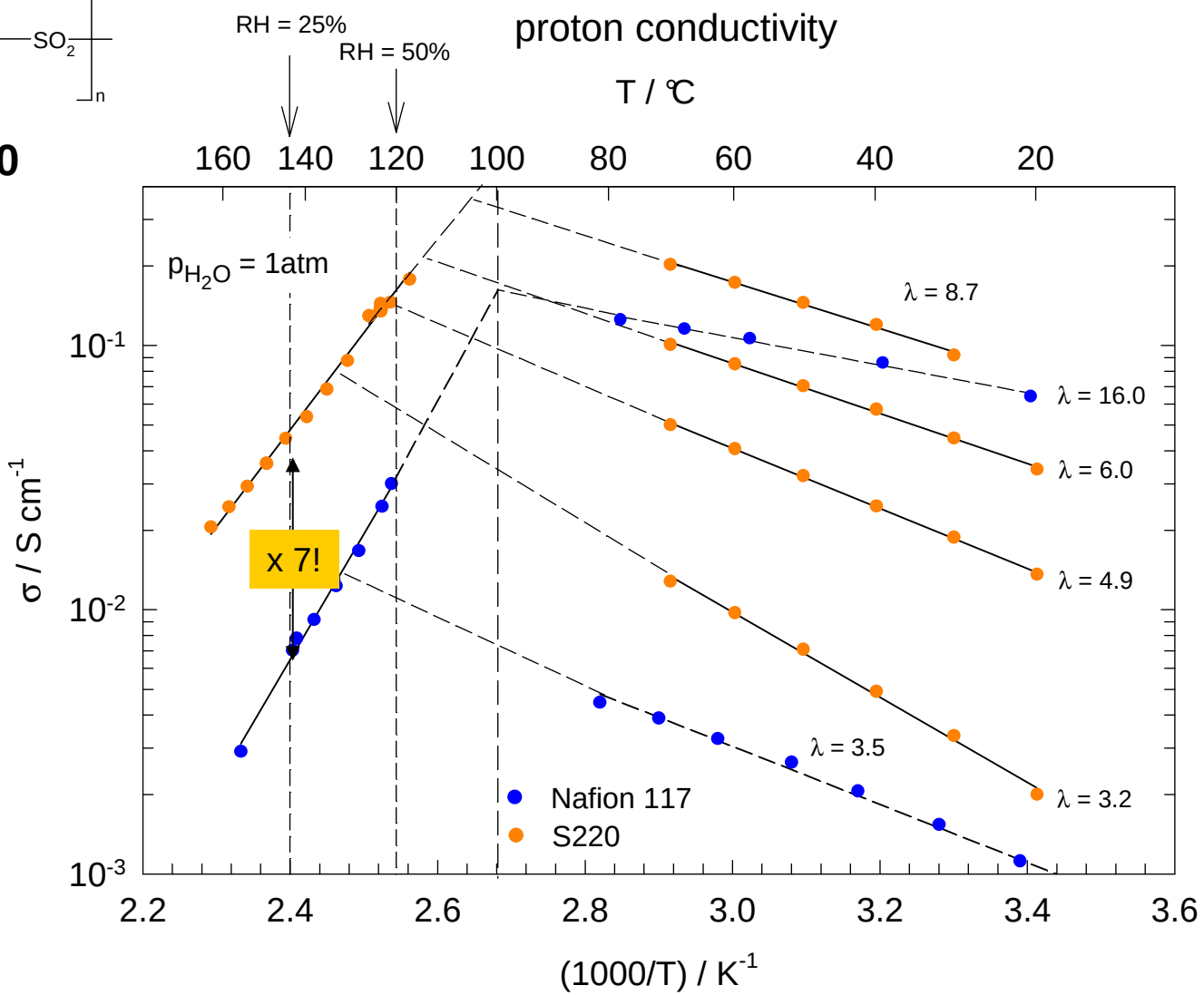
(hydrodynamic transport)

G. Titvinidze, K.- D. Kreuer, M. Schuster, C. C. de Araujo, J. Melchior, and W. H. Meyer

Kreuer 2012 *Advanced Functional Materials* **DOI: 10.1002/adfm.201200811**



S-220



higher conductivity at low RH mainly result of higher **charge carrier concentration** and higher water volume fraction (λ=const) leading to **better percolation**
(note: **local mobilities much smaller** !!!)

highly sulfonated poly (phenylene sulfone):

- *brittle in the dry state (salt like)*
- *water soluble*

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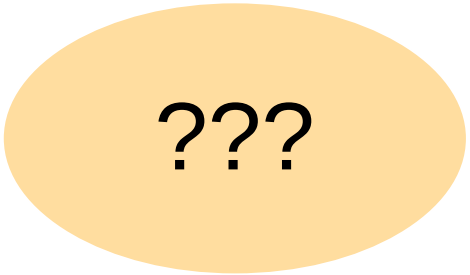

How to use sulfonated poly (phenylene sulfone)s as **constituent of separator membranes** without loosing its advantageous properties ?

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- reducing IEC

  polyelectrolyte → *ionomer*

Kreuer 2012

- reducing IEC

  polyelectrolyte → *ionomer*

non-linear decrease of conductivity !

Kreuer 2012

- reducing IEC

  polyelectrolyte → *ionomer*

- blends with compatible high Mw polymers

  e.g. ***S-220*** *– PBI*

Kreuer 2012

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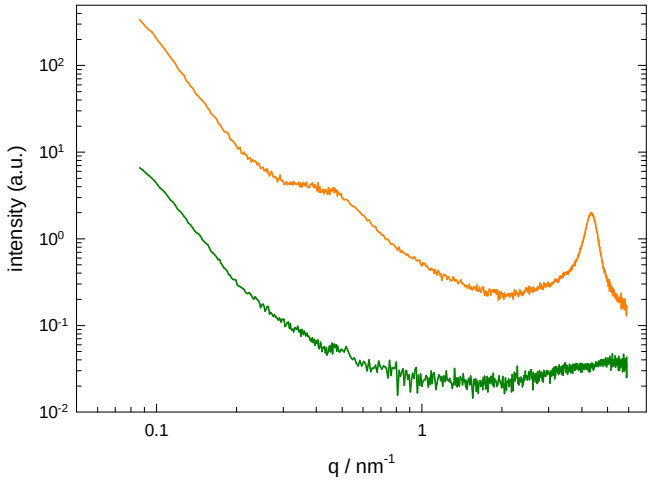
  e.g. ***S-220*** *– PBI*



Kreuer 2012

- reducing IEC

  polyelectrolyte → *ionomer*

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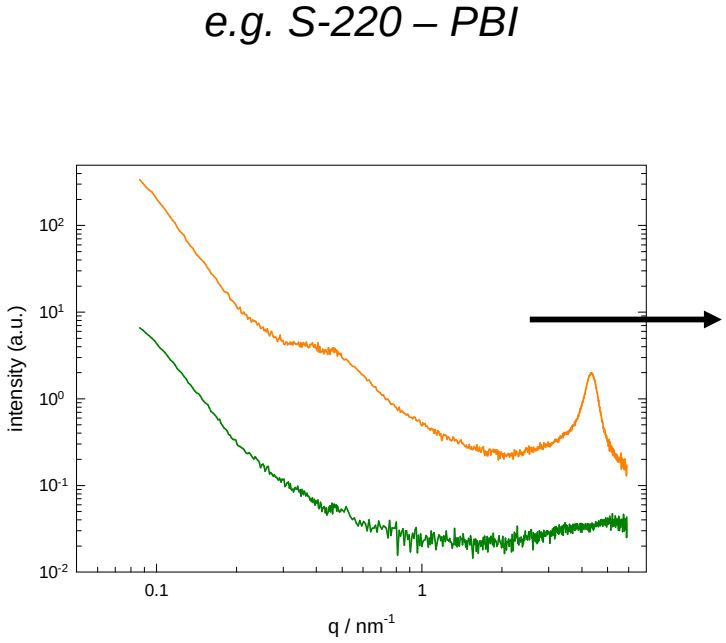
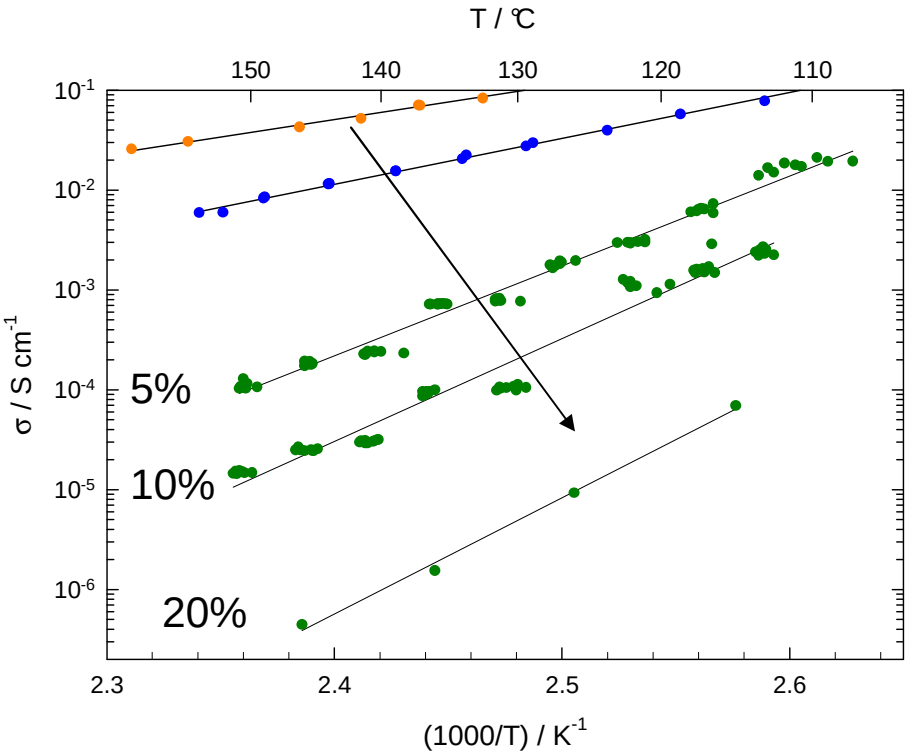
  e.g. S-220 – PBI





Kreuer 2012

- reducing IEC

  polyelectrolyte → *ionomer*

- blends with compatible high Mw polymers

  e.g. S-220 – PBI

- **multiblock copolymers**

Kreuer 2012

- reducing IEC

  polyelectrolyte → *ionomer*

- blends with compatible high Mw polymers

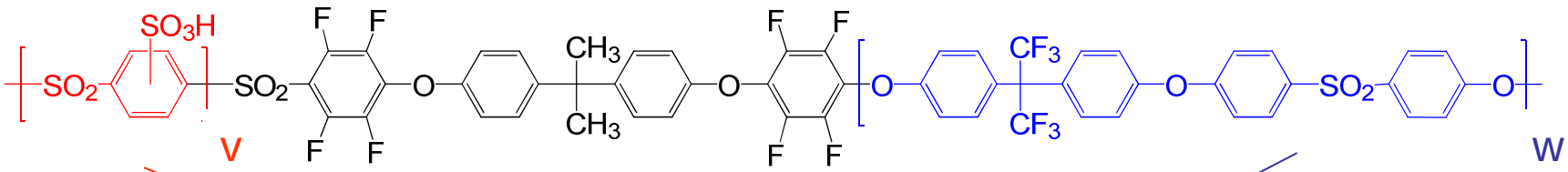
  e.g. S-220 – PBI

- **multiblock copolymers**

advantageous properties of
S-220 locally preserved !

Kreuer 2012

building multi-block-co-polymers *(colaboration with W.H.Meyer MPI-P)*



S-220

SU_vFS_w

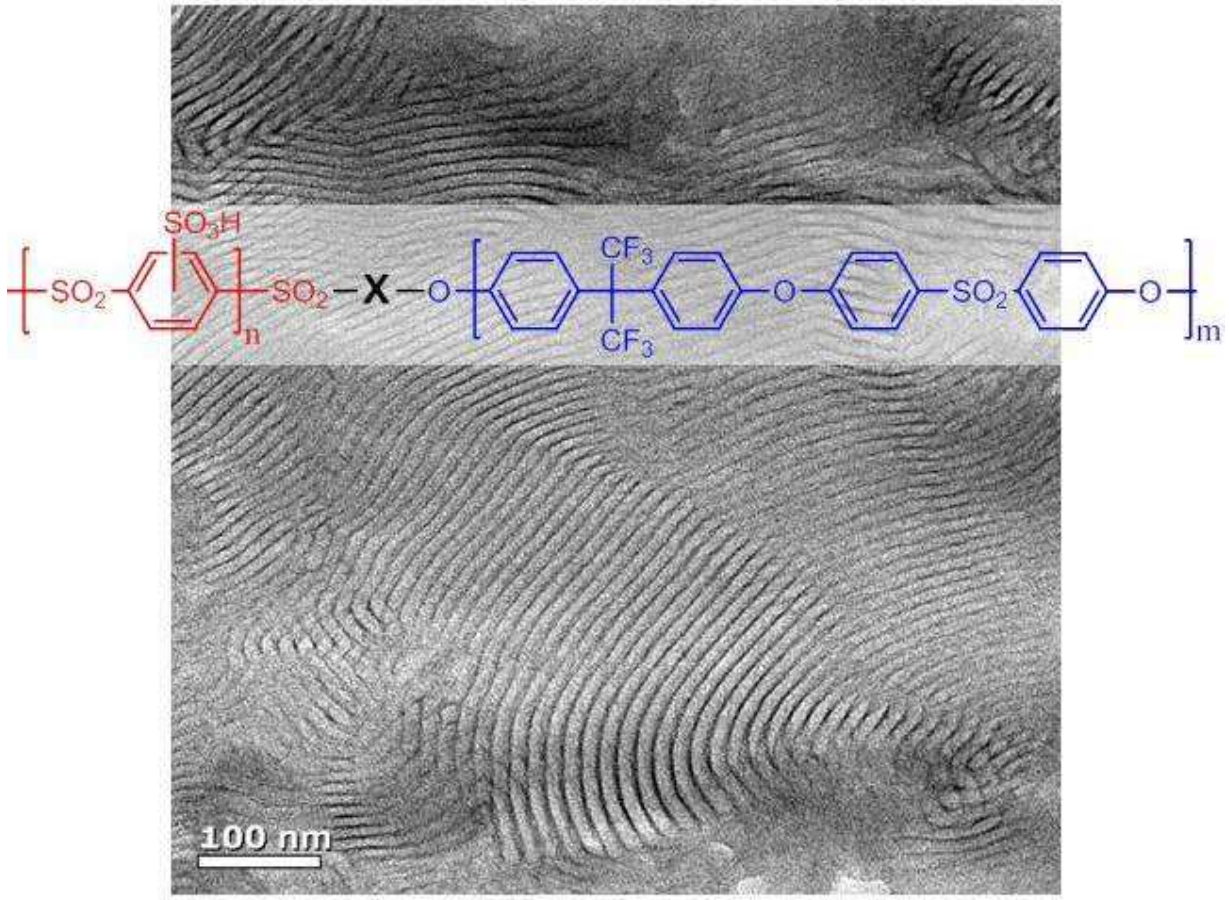
similar approaches by:

- K. Miyatake
- P. Jannasch
- J . McGrath

G. Titvinidze, K.- D. Kreuer, M. Schuster, C. C. de Araujo, J. Melchior, and W. H. Meyer
Advanced Functional Materials **DOI: 10.1002/adfm.201200811**

morphology

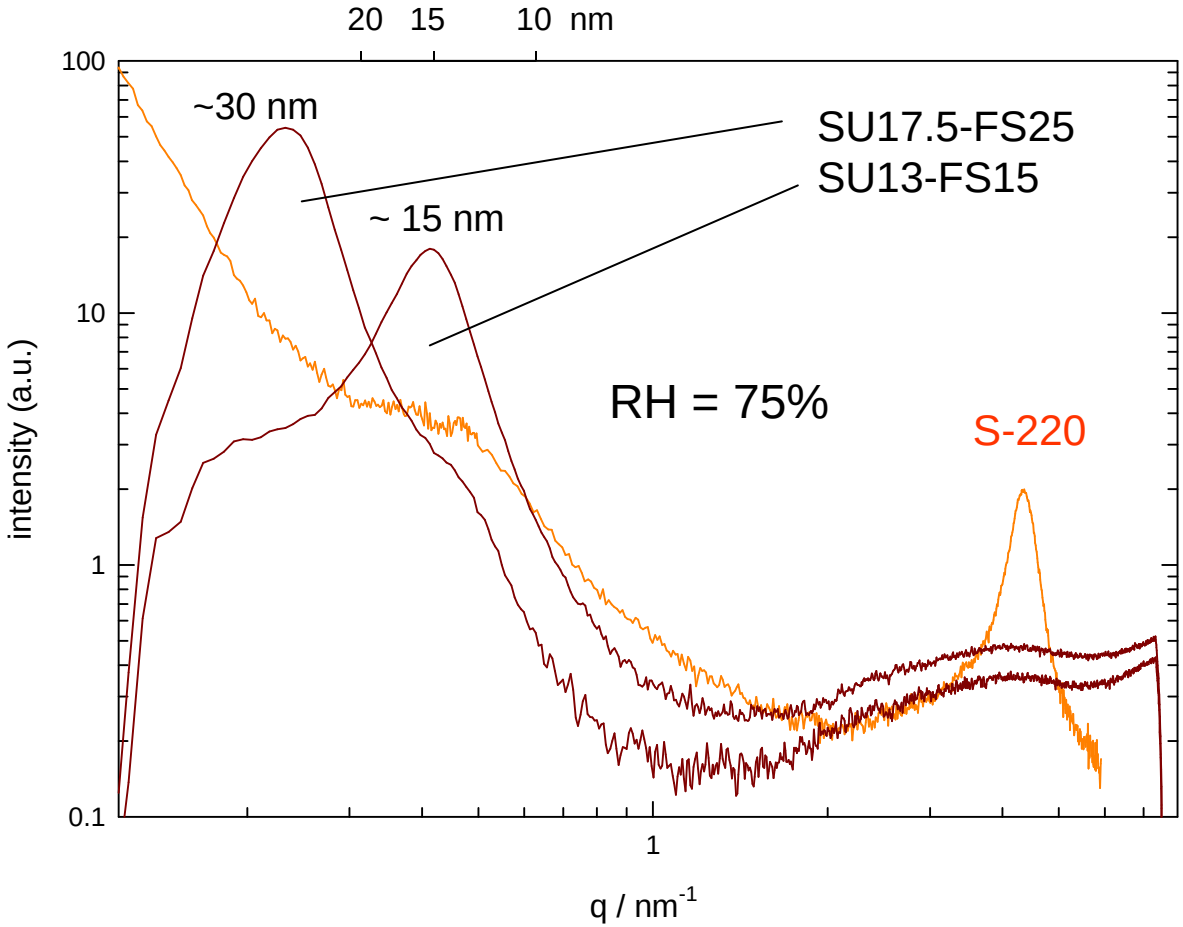
TEM of slice cut perpendicular to membrane surface



Kreuer 2012 → clear phase-separation

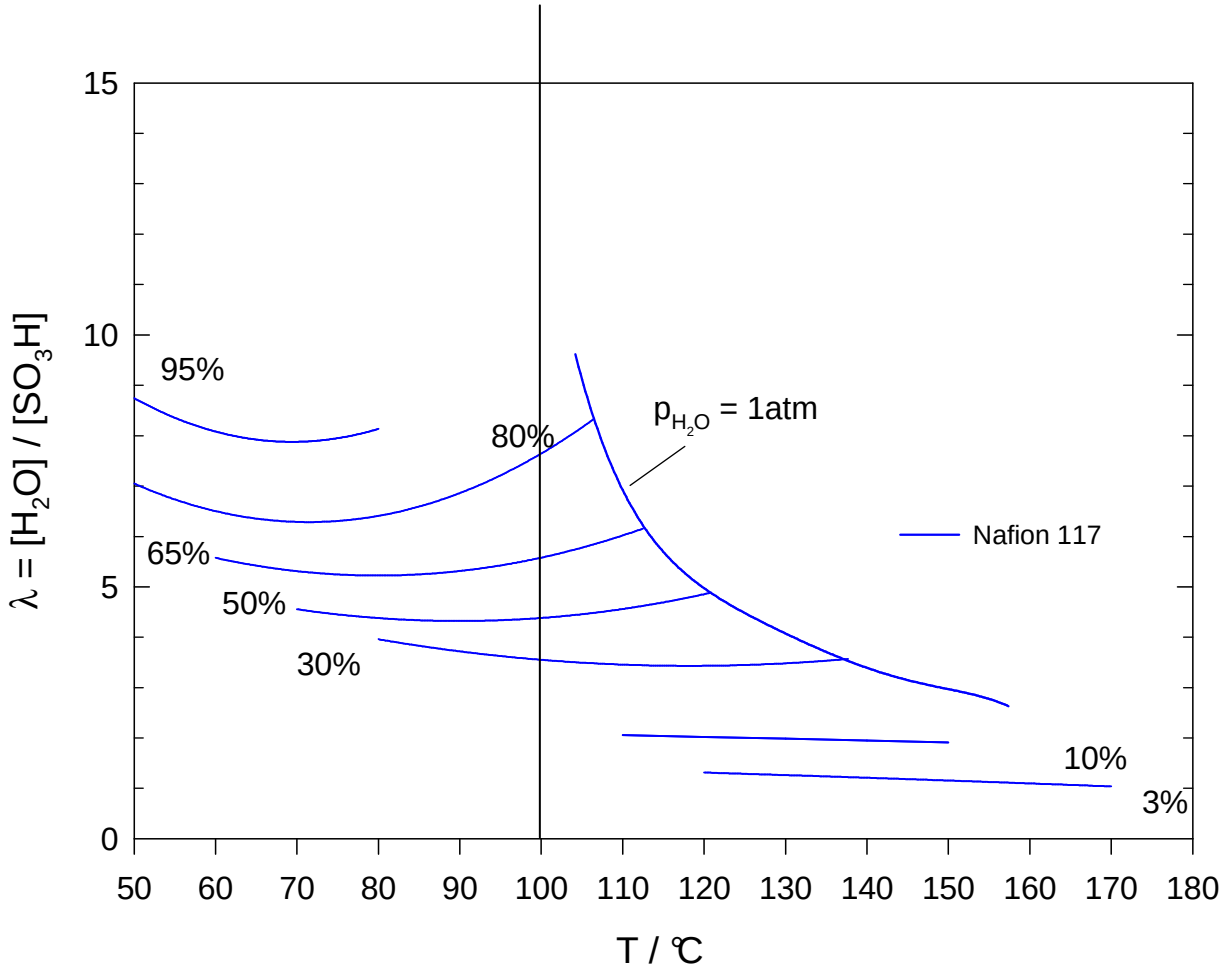
morphology

small angle x-ray scattering SAXS (ESRF)



- distict correlation lengths related to block lengths in a complex way
- residual local ordering within S-220 domain

hydration behavior



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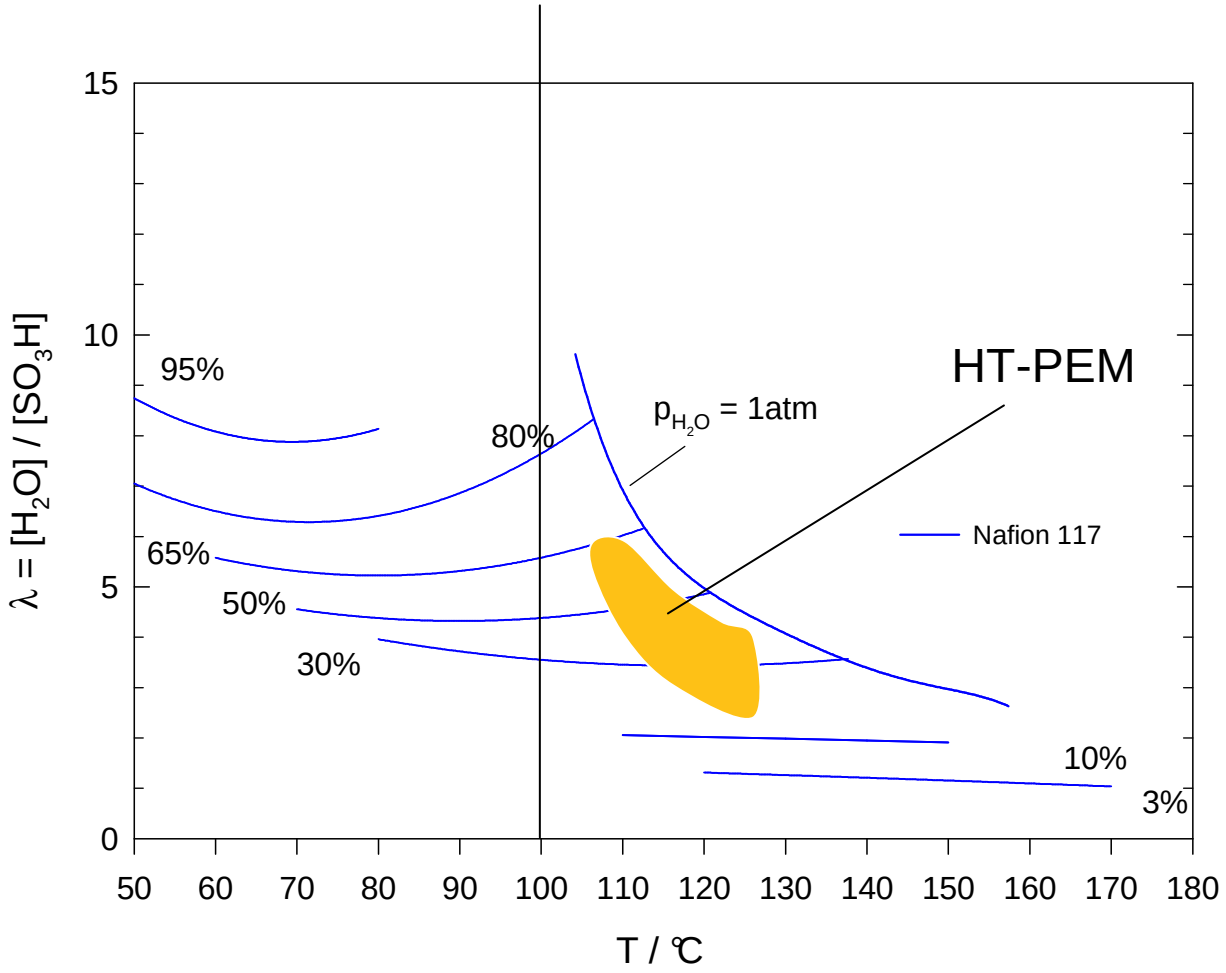
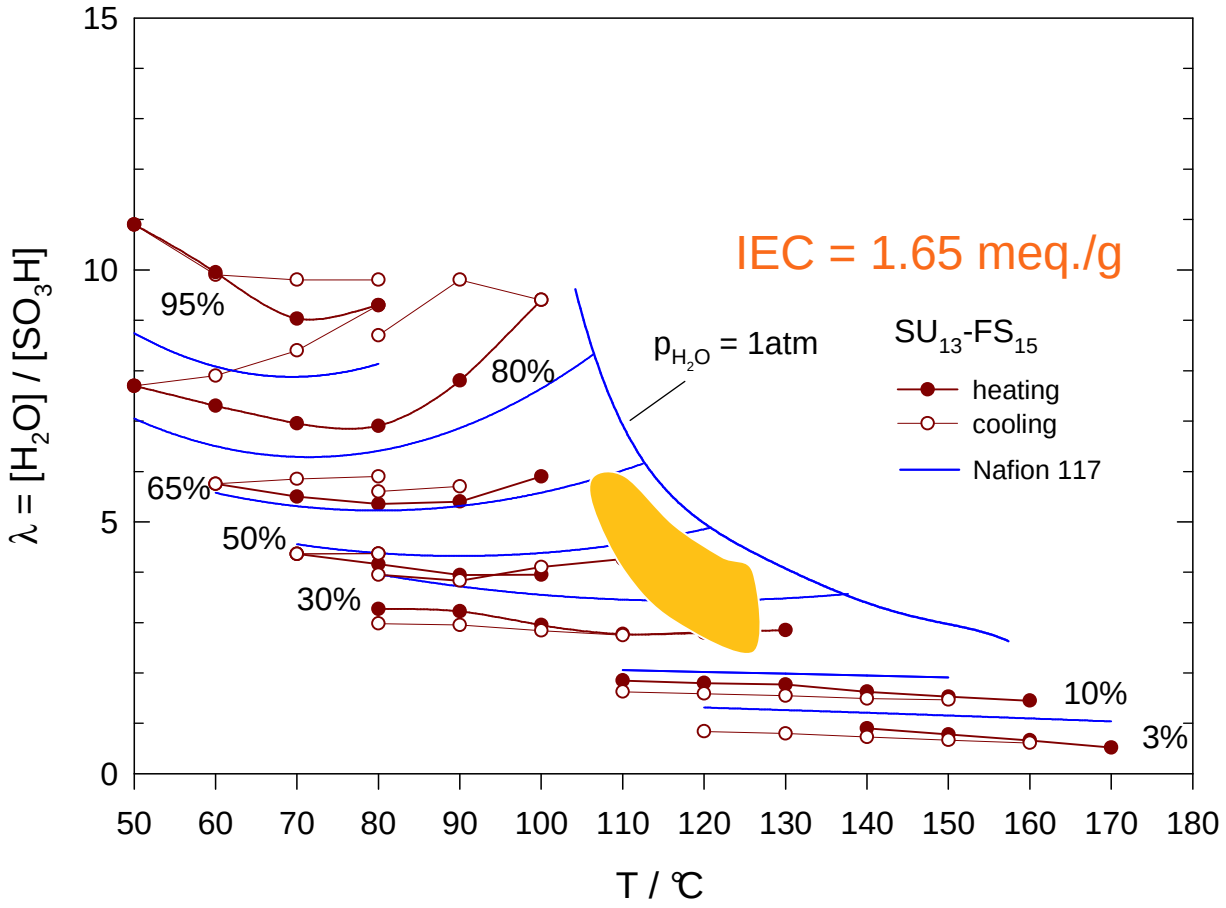
hydration behavior



Kreuer 2012

hydration behavior



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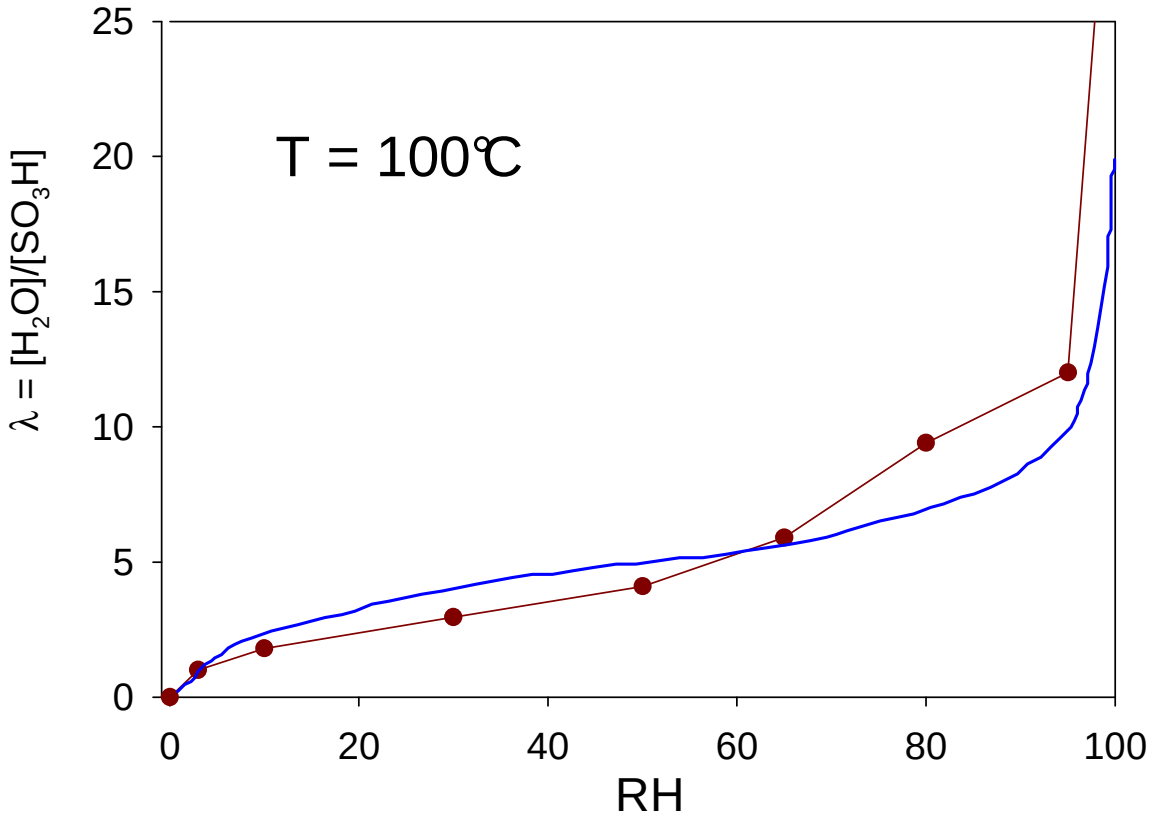
hydration behavior



slightly lower hydration at low RH

because of more negative hydration entropy

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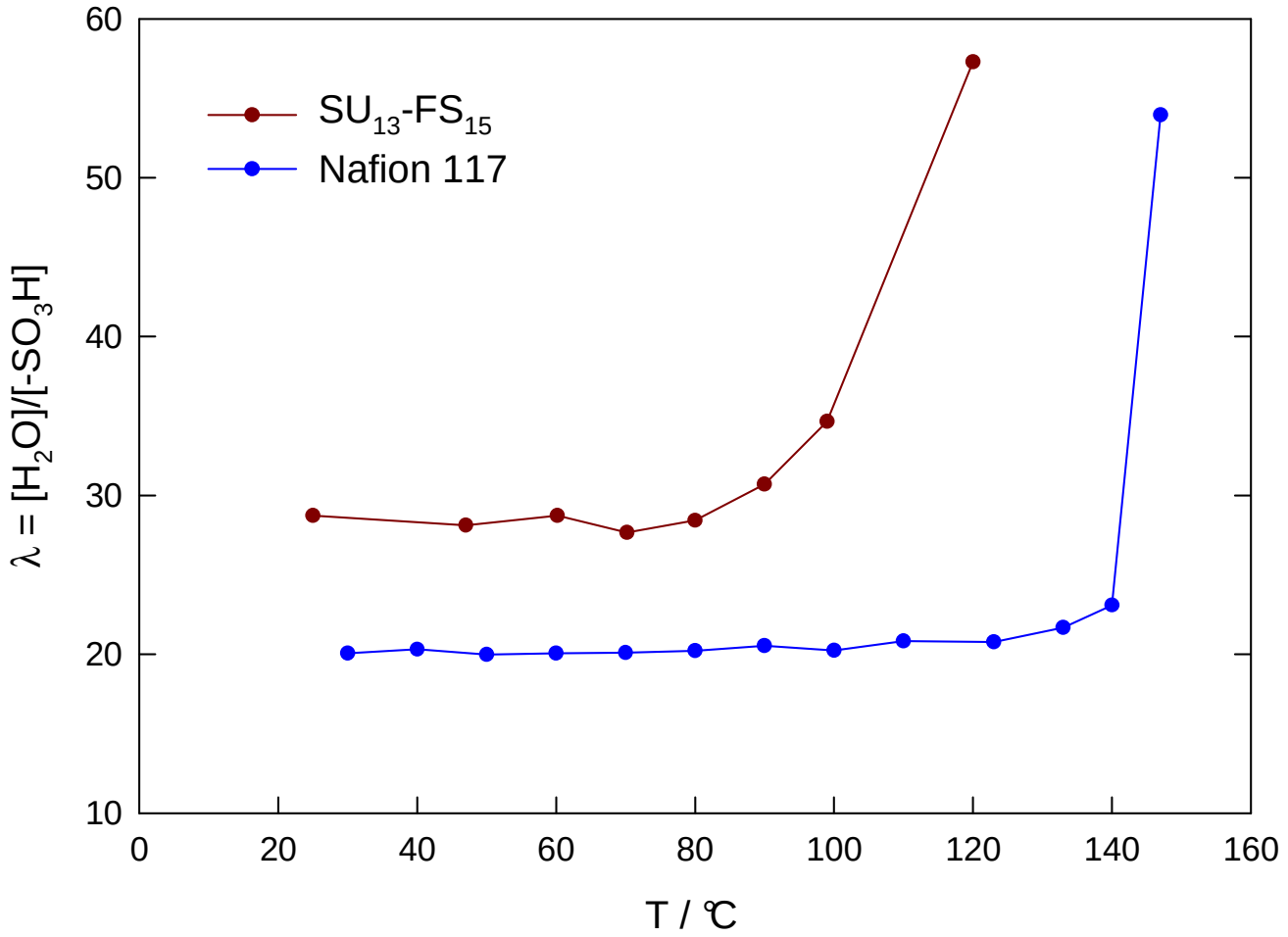
hydration behavior

swelling in water



swelling in water much higher but

irrelevant von HT-PEM application

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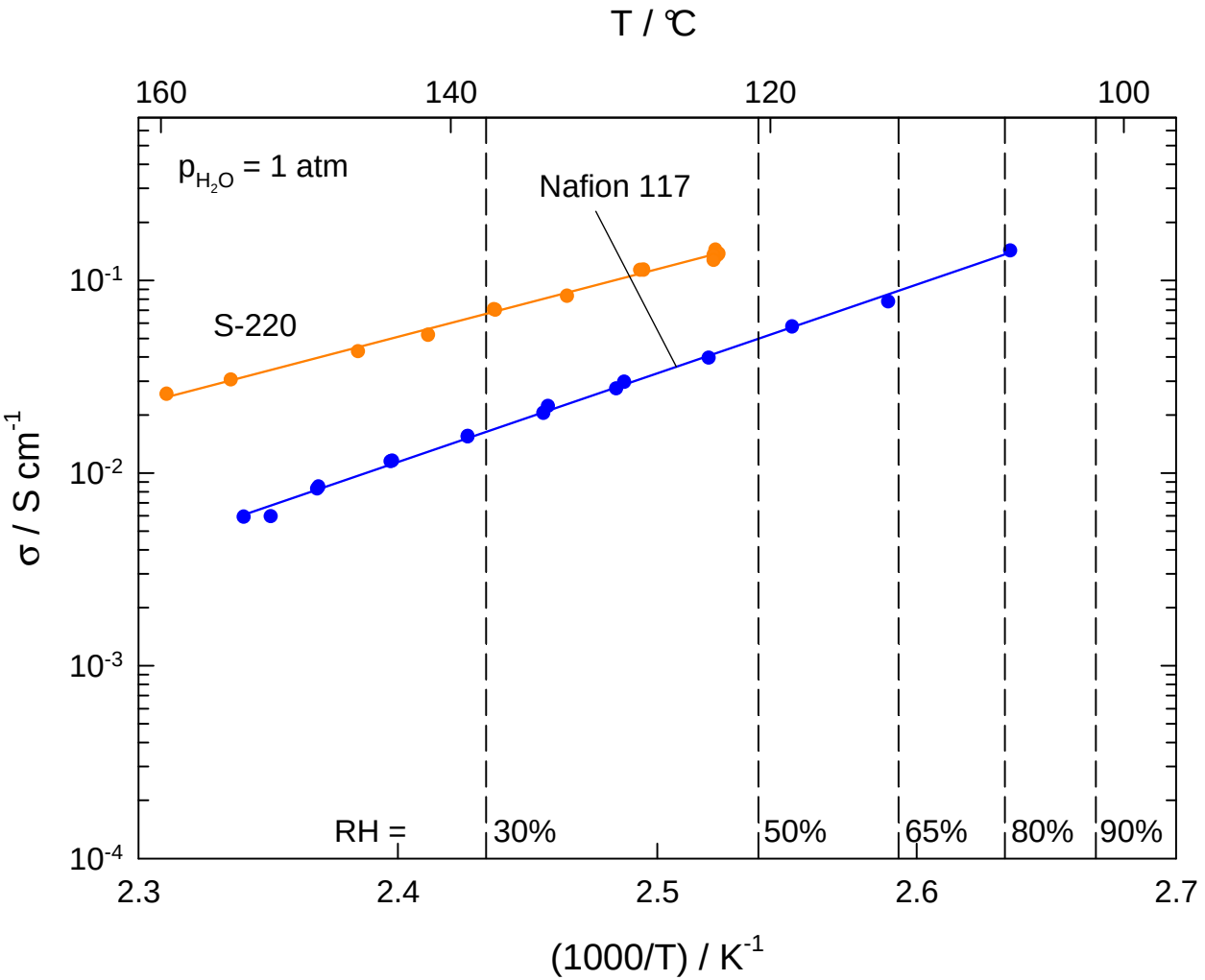
proton conductivity



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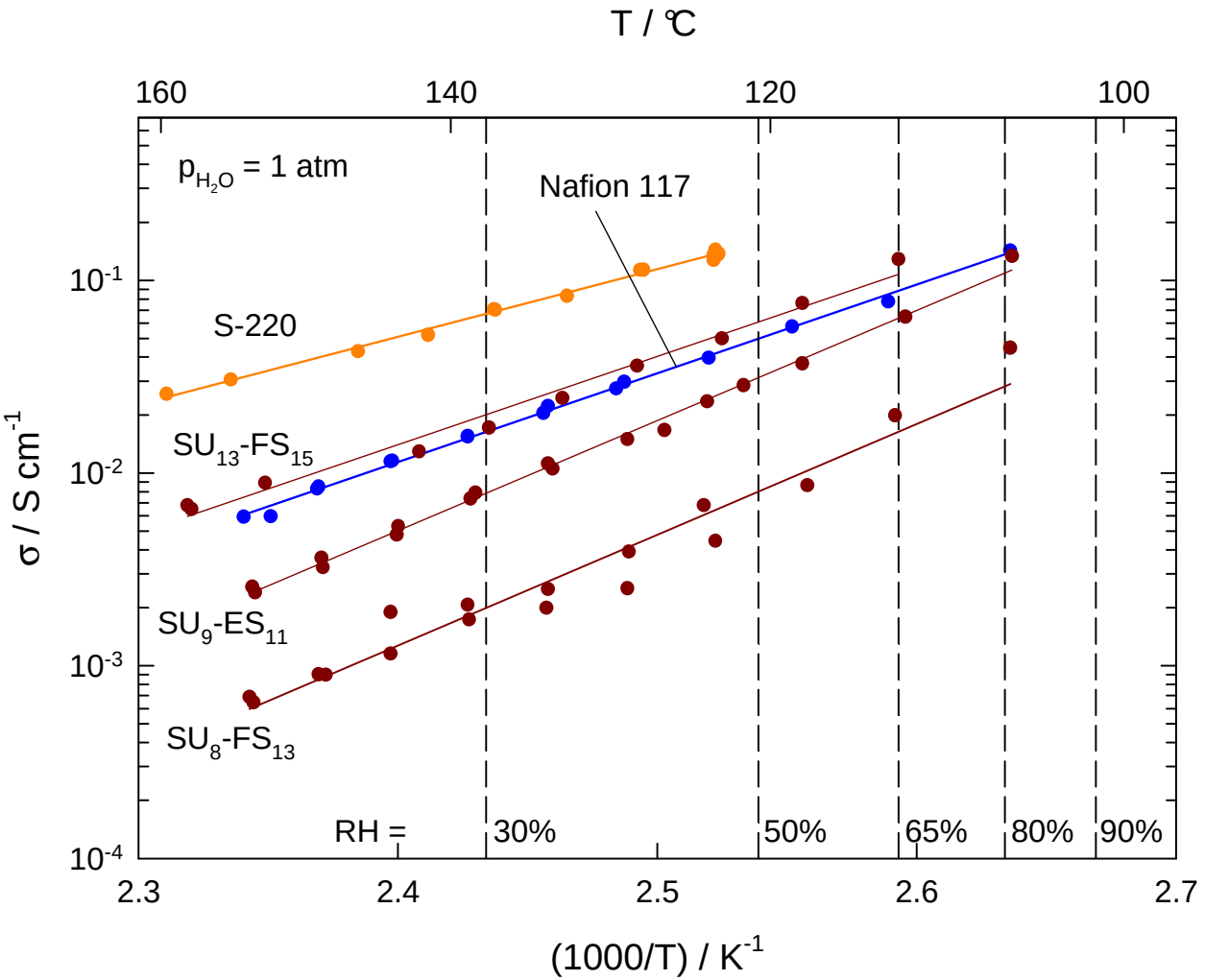
proton conductivity



1.65 meq./g

1.70 meq./g

1.30 meq./g

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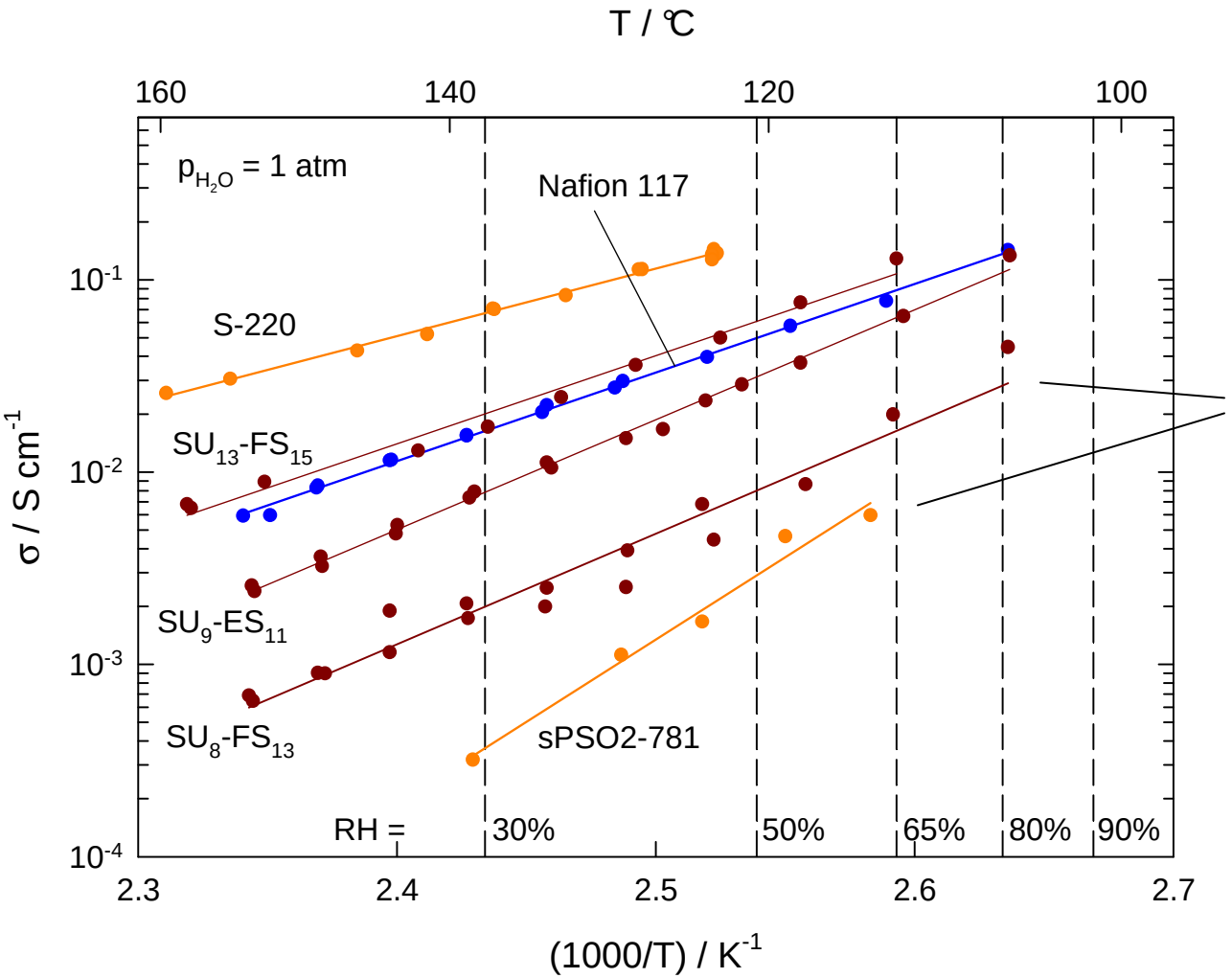
proton conductivity



positive effect of phase separation on conductivity

non-linear relation between IEC and conductivity

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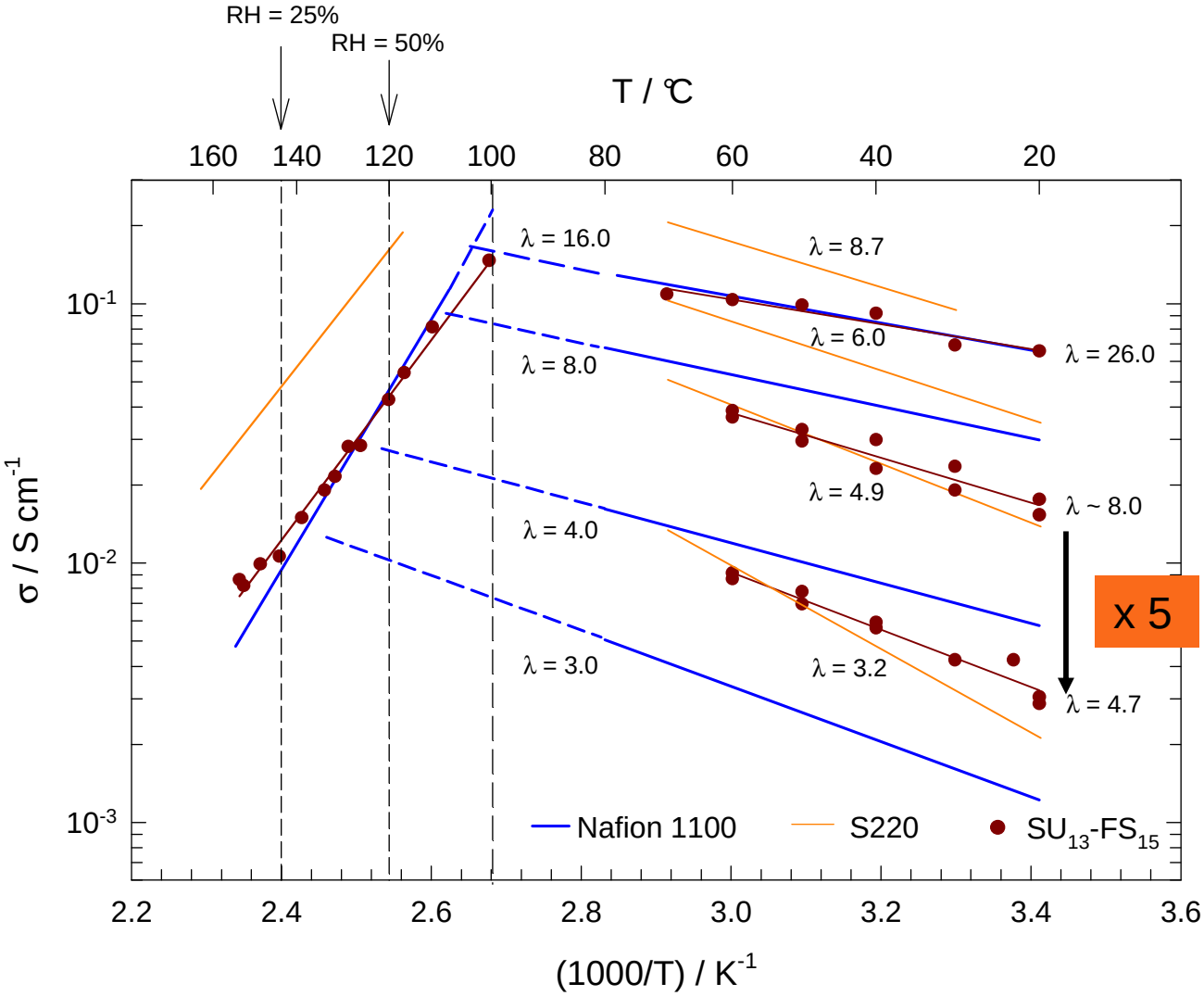
proton conductivity



proton conductivity locally preserved

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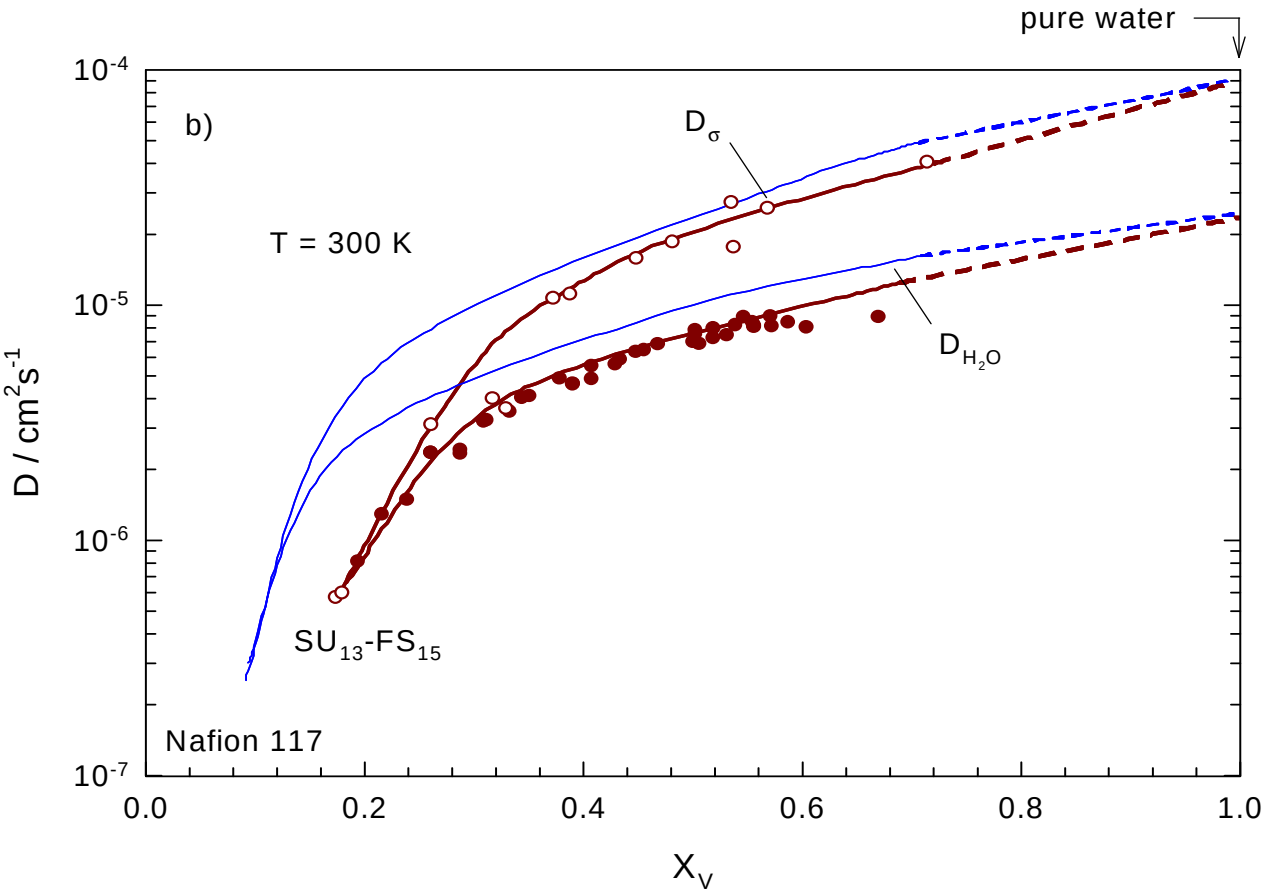
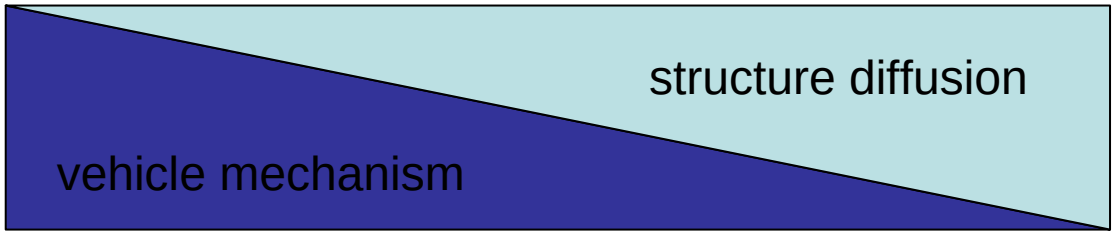
proton conductivity and water diffusion





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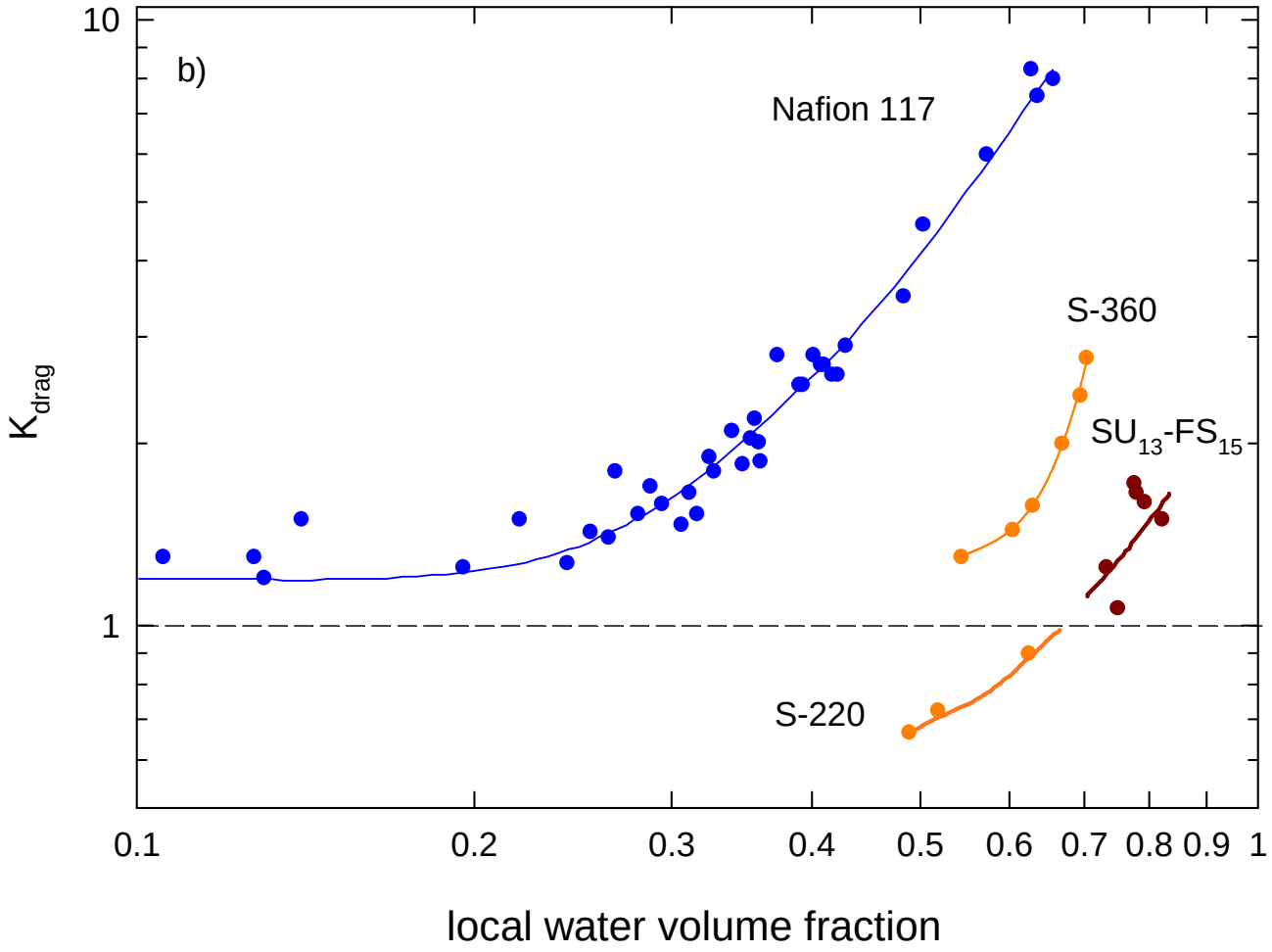
hydrodynamic water transport



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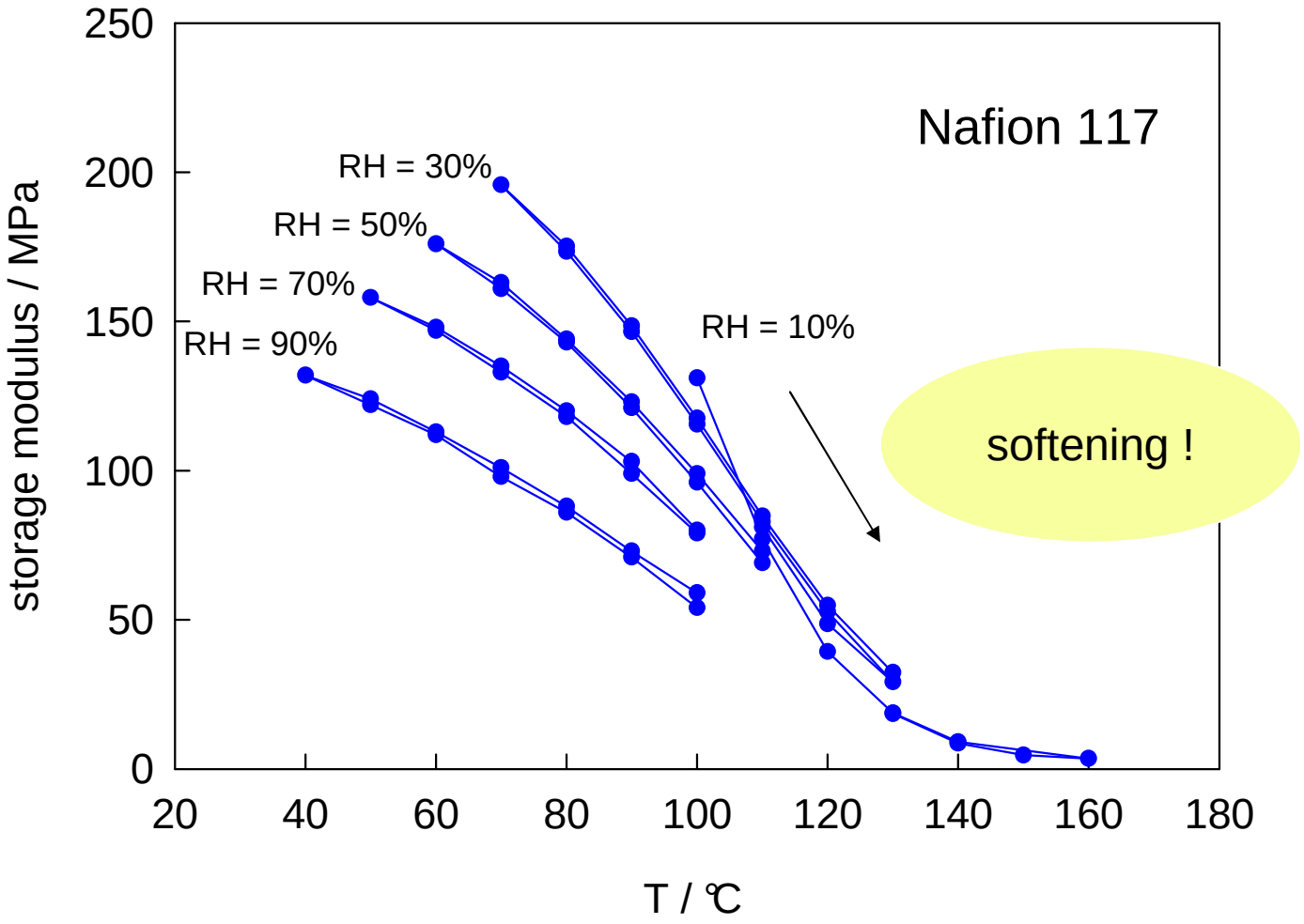
electoosmotic water drag in line with this of S-220

viscoelastic properties



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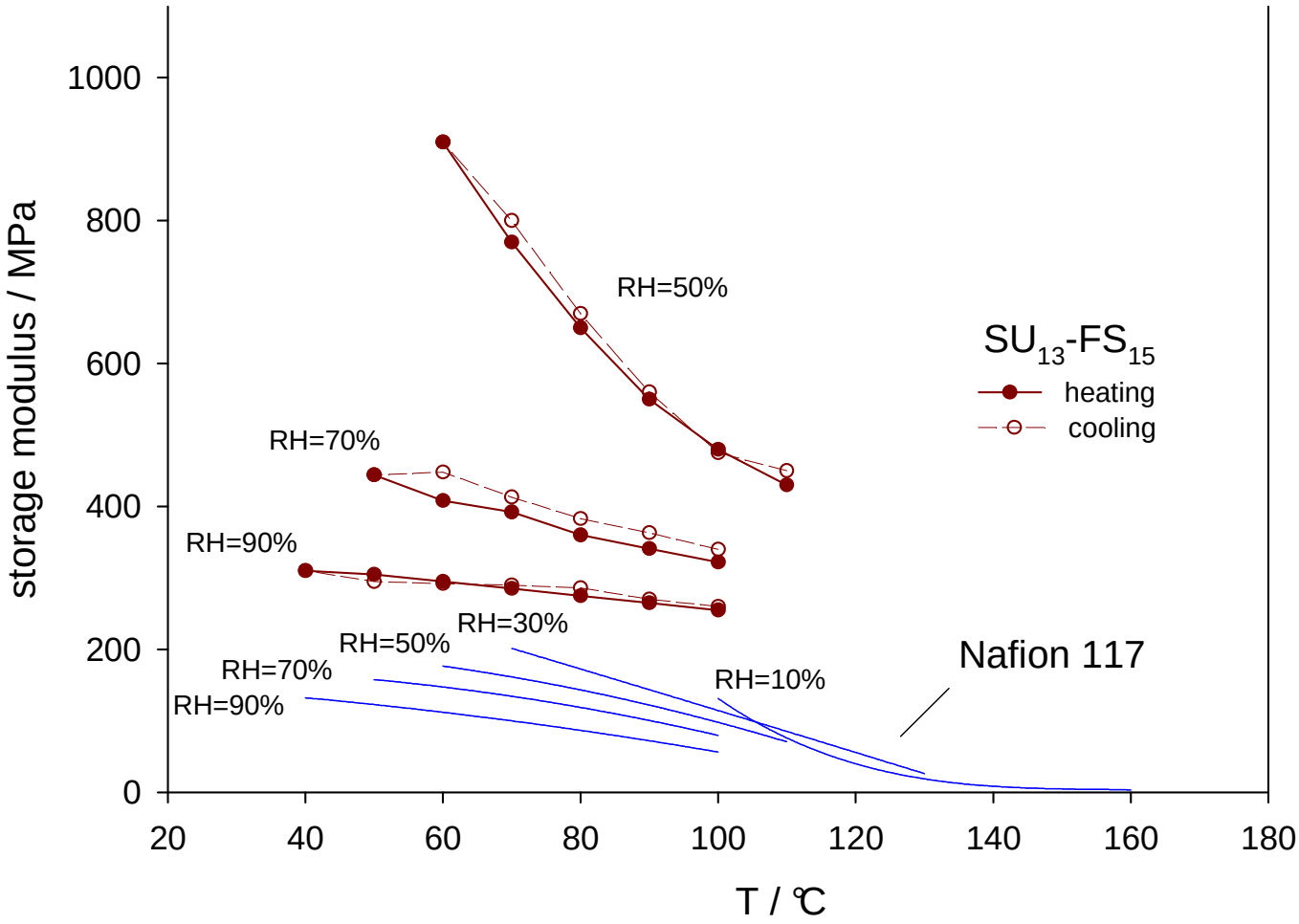
viscoelastic properties



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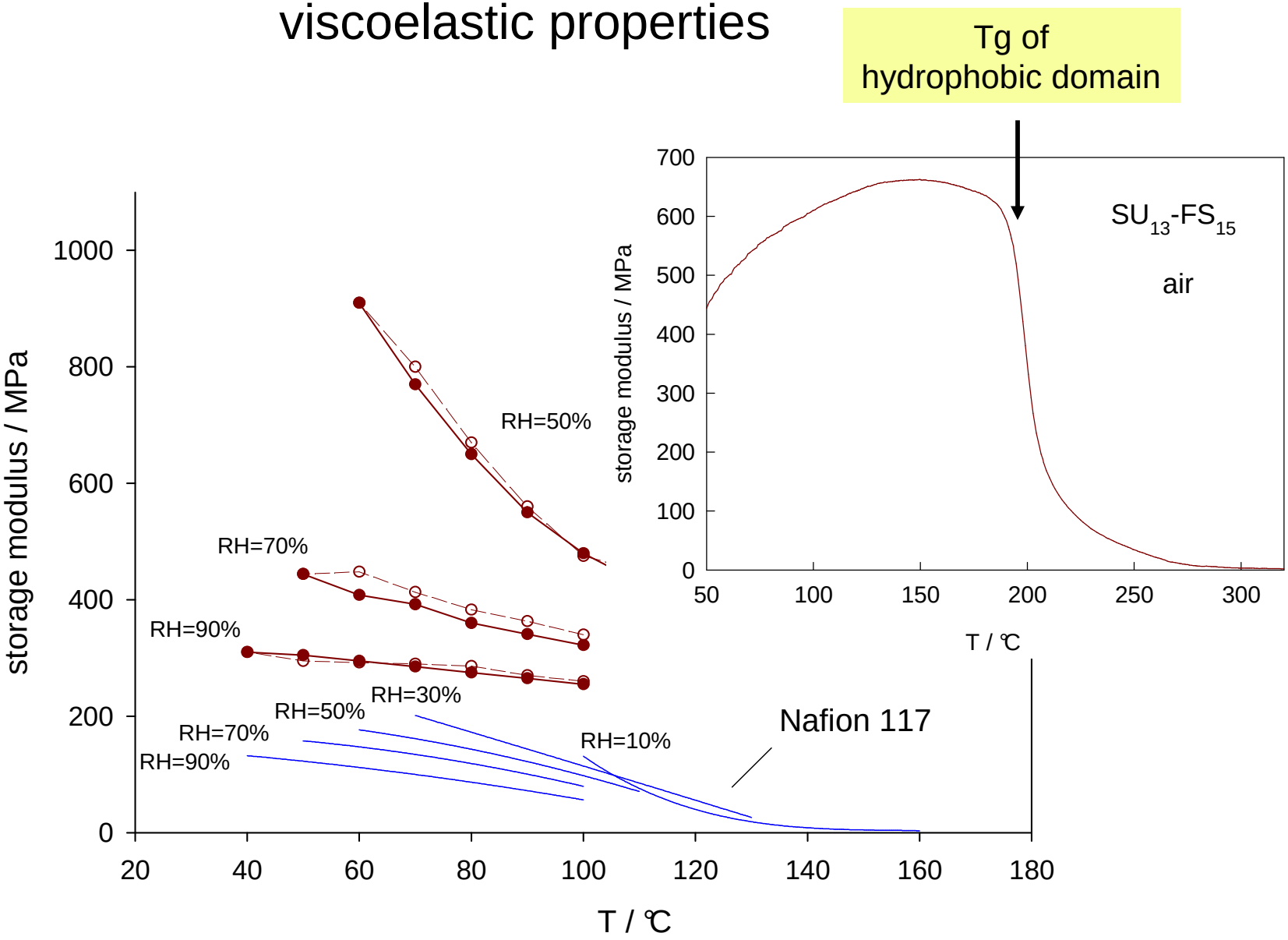
viscoelastic properties



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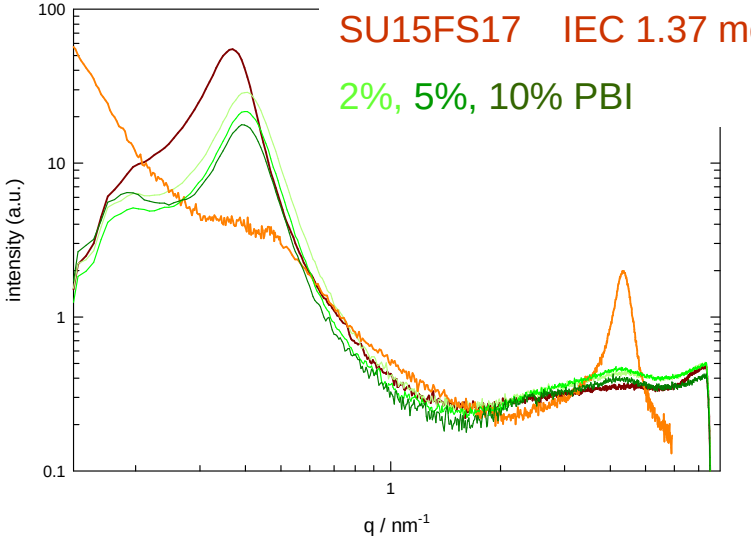
viscoelastic properties

increasing toughness by blending with small amounts of PBI



blending with high Mw PBI does not change nano-mophology !!!

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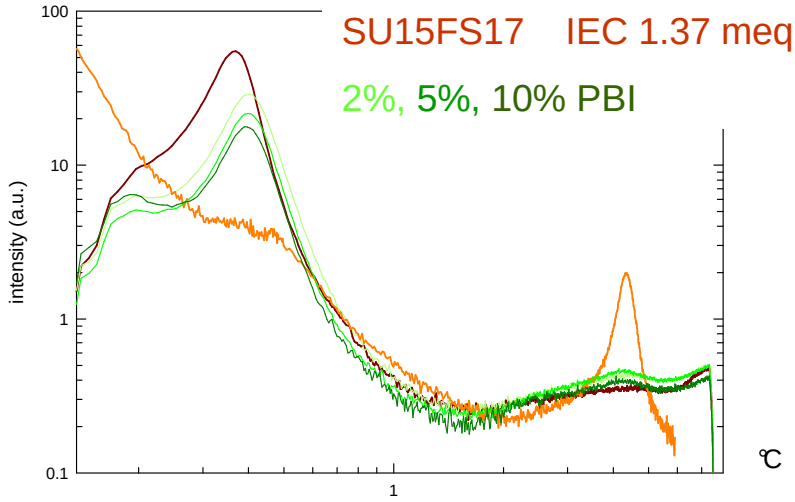
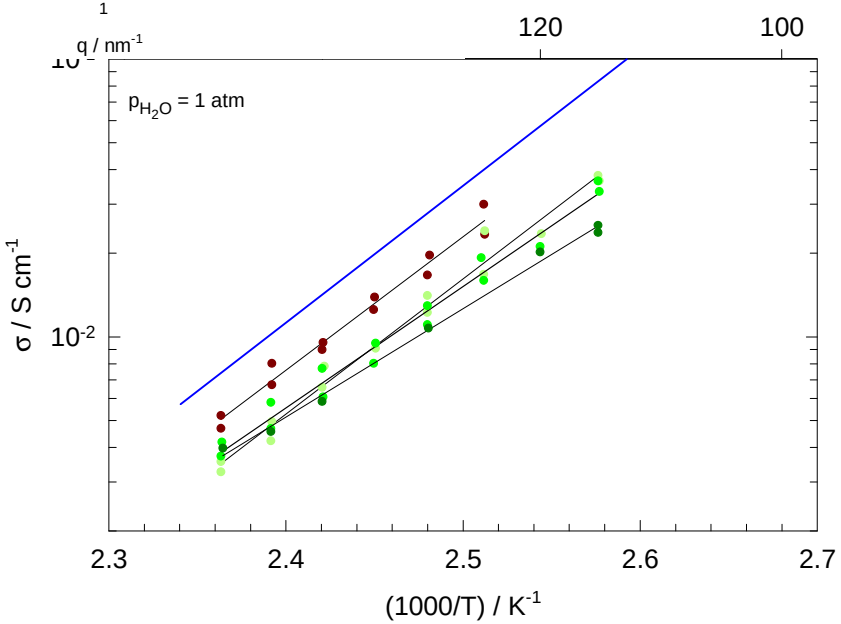
viscoelastic properties

increasing toughness by blending with small amounts of PBI





blending with high Mw PBI does not change nano-mophology !!!

with only small reduction of proton conductivity

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message

advantageous properties of the polyelectrolyte S-220 may be locally preserved within the hydrophilic domain of multi-block copolymers

tough thin membranes available with:

- proton conductivity similar to this of PFSA type membranes
- morphological and chemical stability at high T and low RH
- very low hydrodynamic water transport (e.g. electroosmotic drag)

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Advanced Functional Materials **DOI: 10.1002/adfm. 2012 00811**

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