2007 DOE Hydrogen Program Merit Review Presentation

Advanced Materials for Proton Exchange Membranes

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McGrath Group 2007

Front Row (L to R): Natalie Arnett, Rachael VanHouten, James E. McGrath, Daniel Brandell, Hae Seung (Harry) Lee
Back Rows (L to R): Xiang Yu, Anand Badami, Juan Yang, Yu Chen, Yanxiang Li, Abhishek Roy, Ozma Lane, Shogo Takamuku,
Stuart Dunn, Mou Paul, Zhongbiao Zhang

Objectives

- Design, identify, and develop the knowledge base to enable proton exchange membrane films and related materials to be utilized in fuel cell applications, particularly for H_2/Air systems at 120°C/low RH

Acknowledgements

- McGrath Research Group: past and present
- May 2006" DOE Contract on "*High Temperature, Low Relative Humidity, Polymer-type Membranes Based on Disulfonated Poly(arylene ether) Block and Random Copolymers Optionally Incorporating Protonic Conducting Layered Water Insoluble Zirconium Fillers*"

Research Approach/Hypothesis

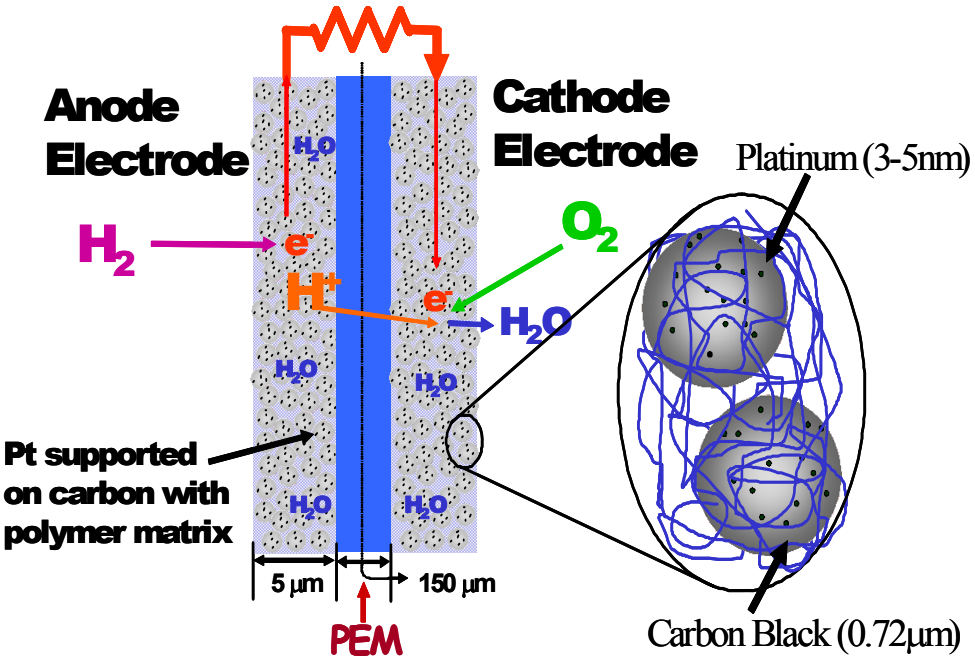
- Thermally, hydrolytically, and oxidatively stable aromatic ionomers with high T_g, ductility, and controlled hydrophilicity are required
- Synthesis
  - Linear and crosslinked statistical hydrophobic/hydrophilic copolymers (initially)
  - Linear multiblock hydrophobic/hydrophilic copolymers (this project)

M.A. Hickner, H. Ghassemi, Y.S. Kim and J.E. McGrath, Alternate Polymer Systems for Proton Exchange Membranes, *Chemical Reviews* (2004), 104(10), 4587-4611.

Proton Exchange Membrane (PEM) Requirements

- **CRITICAL PEM PROPERTIES**
  - high protonic conductivity, even at low RH
  - low electronic conductivity
  - low permeability to fuel and oxidants
  - low water transport - diffusion and electro-osmotic drag
  - oxidative and hydrolytic stability under acidic conditions, for thousands of hours!
  - Good dry and wet mechanical properties at ambient and higher temperatures
  - Cost effective and able to be fabricated into robust membrane electrode assemblies (MEAs)
  - Swelling-deswelling as a function of relative humidity.

Membrane Electrode Assembly (MEA)



The benchmark is Nafion™ for the membrane and electrodes

M. Hickner, H. Ghassemi, Y. Kim ,B. Einsla and J E McGrath, Chem Rev. 2004,104,4587-4611

OVERVIEW

Timeline

- Project State Date: May 2006
- Project End Date: May 2011
- Percent Complete: 20%

Barriers

- Conductivity at 120°C and low RH

Budget

Total Project Funding: $1.5MM

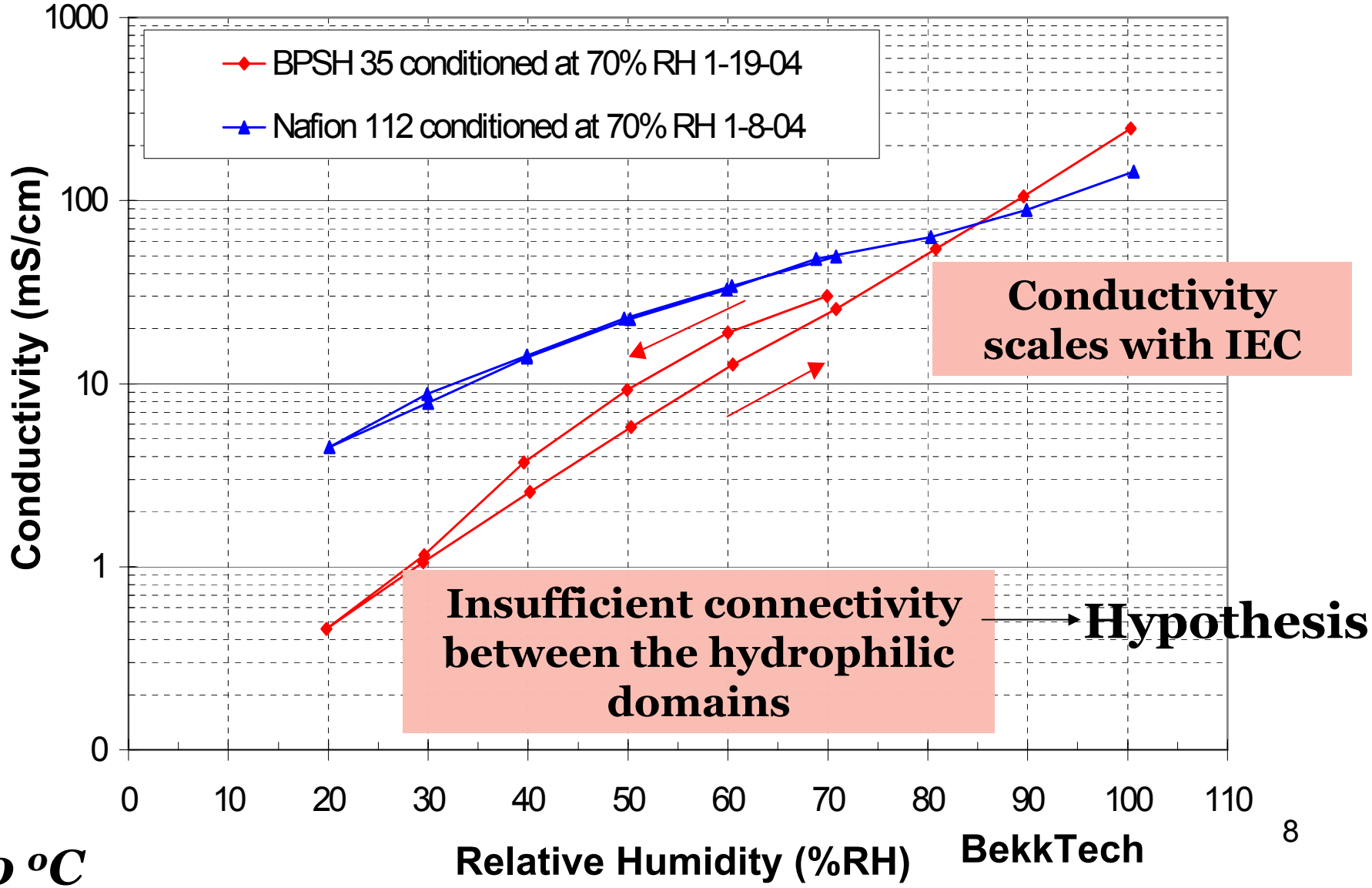
Funding received in FY06: $150K

Funding for FY07: $300K

Partners

- Los Alamos National Labs
- Giner Electrochemical Systems
- Hydrosize, Inc.

Proton Conductivity for random BPSH 35 copolymer is lower than Nafion™ at low RH



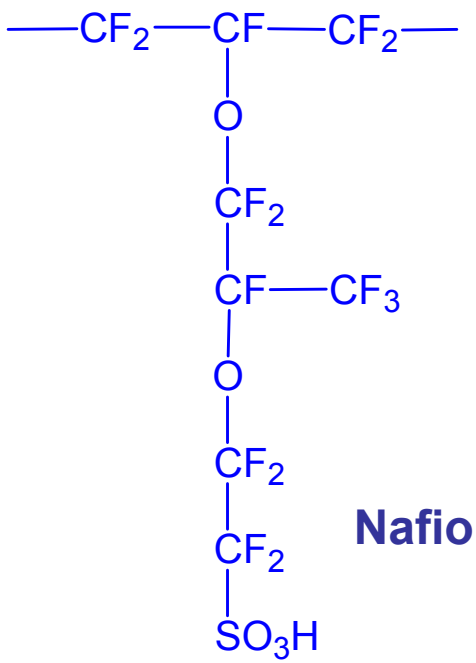
120 °C

BekkTech

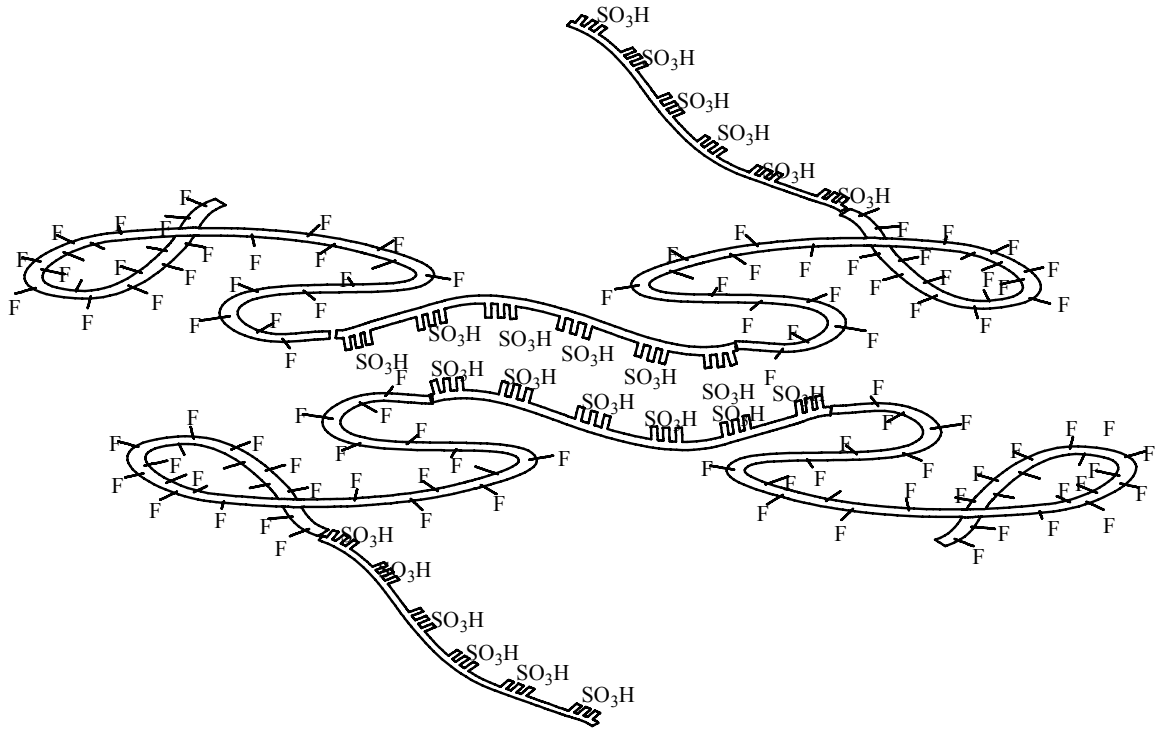
How Can One Maintain Proton Conductivity Under Partially Hydrated Conditions?

Side chain structure allows for flexibility (low T relaxation), promoting mobility in the sulfonic acid domains.

Nanophase Block copolymers permit transport via hydrophilic sequences



Nafion™



Roy, A.; Hickner, M.; Yu, X; Li, Y; Glass, T.; Li, Y.; McGrath, J.E. Journal of Polymer Science-Part B,44,2226-2239,(2006)

Why Multiblock Copolymers?

- Random copolymers have much lower conductivities at low RH than Nafion™.
- The morphology of the copolymer membranes can be controlled by varying the two sequence lengths
- Generation of a co-continuous hydrophilic phase may allow improved conductivity at low humidity because of higher water diffusion coefficients
- Multiblock systems allow use of high performance materials

*A. Noshay and J. E. McGrath, "Block Copolymers: Overview and Critical Survey," Academic Press, New York, January 1977, p.91., A stained S-B block copolymer

Microphase Separation Happens When:

☞ $\chi N > (\chi N)_{ODT}$ **(for volume fraction f = 0.5, $(\chi N)_{ODT}$ =10.5)**

- **χ_{AB} is the Flory-Huggins interaction parameter**
- **It reflects the interaction energy between different blocks and provides the driving force for the phase separation**
- **χ_{AB} usually varies inversely with temperature**
- **χ_{AB} ---*enthalpic* contribution to free energy**

- **N is the total degree of polymerization**
- **Large N leads to translational and configurational entropy loss**
- **N --- *entropic* contribution to free energy**

☞ **$\Delta G = \Delta H - T\Delta S$**

☞ **A competition between interfacial tension and the entropic penalty for stretching of polymer chains**

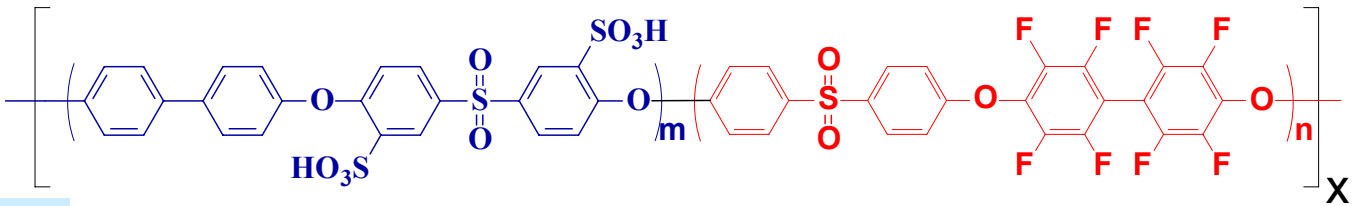
☞ **The product of χ_{AB} N is of interest but the parameter is unknown for ionic systems**

Highly Hydrophobic-Hydrophilic Multiblock Copolymers

A. Noshay and J. E. McGrath, "Block Copolymers: Overview and Critical Survey," Academic Press, New York, January 1977, p.91.an S-B diblock copolymer

- Nanophase-separated morphology may be precisely controlled through synthesis.
- Enhanced proton conductivity, water diffusion coefficient and mechanical strength are expected.

Our work:

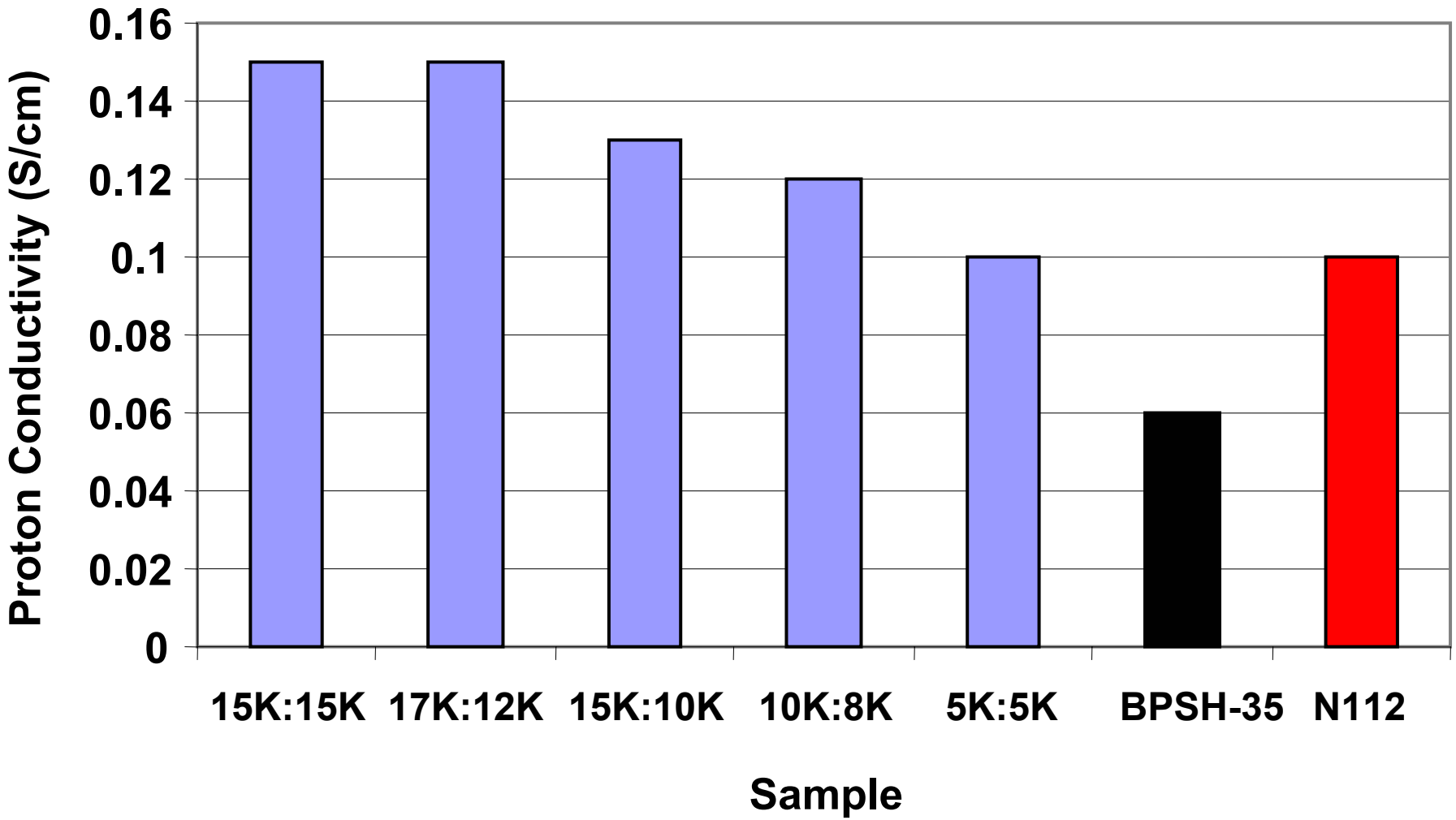


Hydrophilic segments, provides Proton conductance

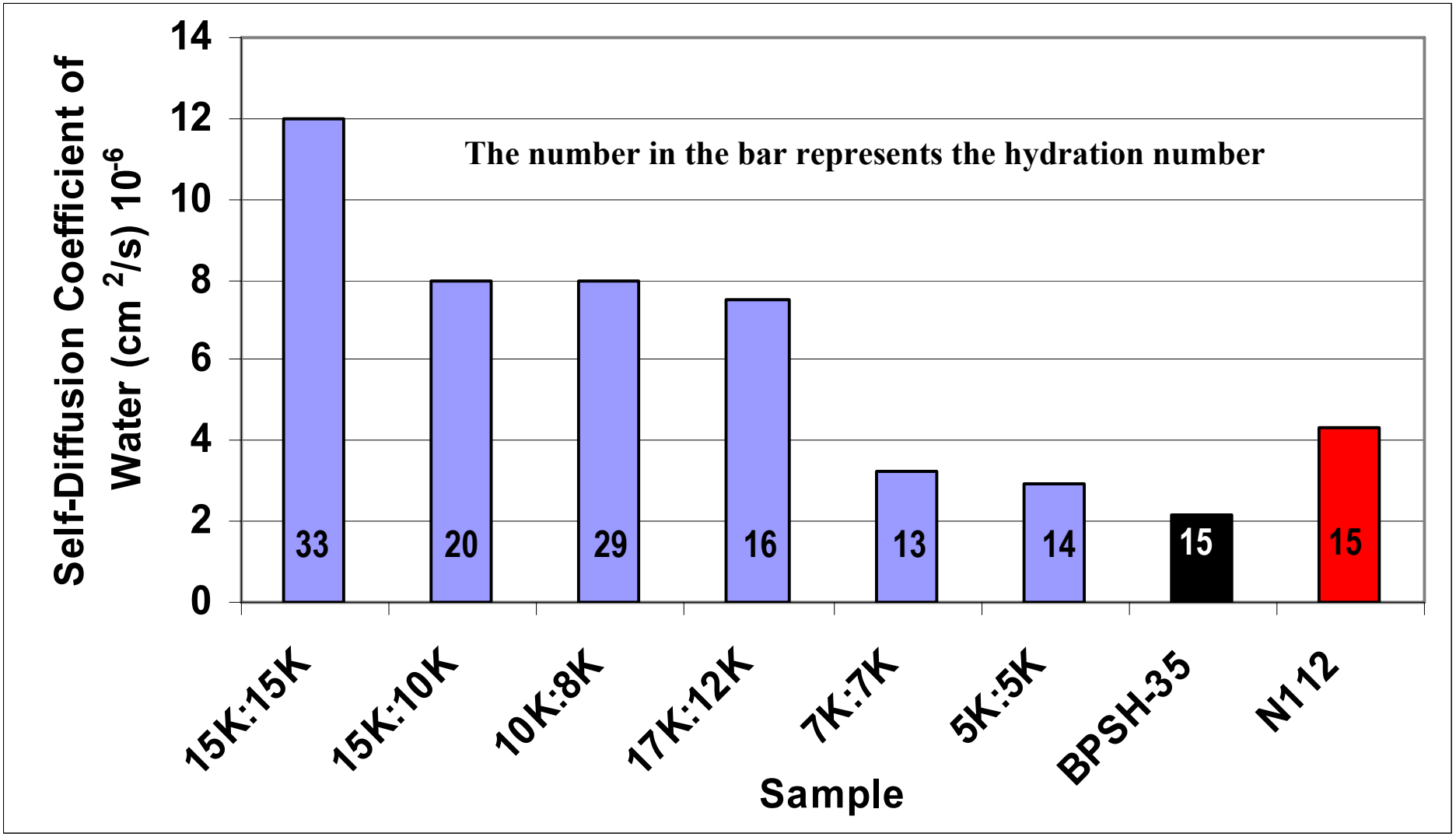
Hydrophobic segments, imparts mechanical integrity

Yu, Xiang; Roy, Abhishek; Dunn, Stuart; Yang, Juan; McGrath, James E. Synthesis and characterization of sulfonated-fluorinated, hydrophilic-hydrophobic multiblock copolymers for proton exchange membranes. Macromolecular Symposia (2006), 245/246(World Polymer Congress--MACRO 2006), 439-449.

Proton Conductivity in Liquid Water at 30ºC Increases with Increasing Block Length

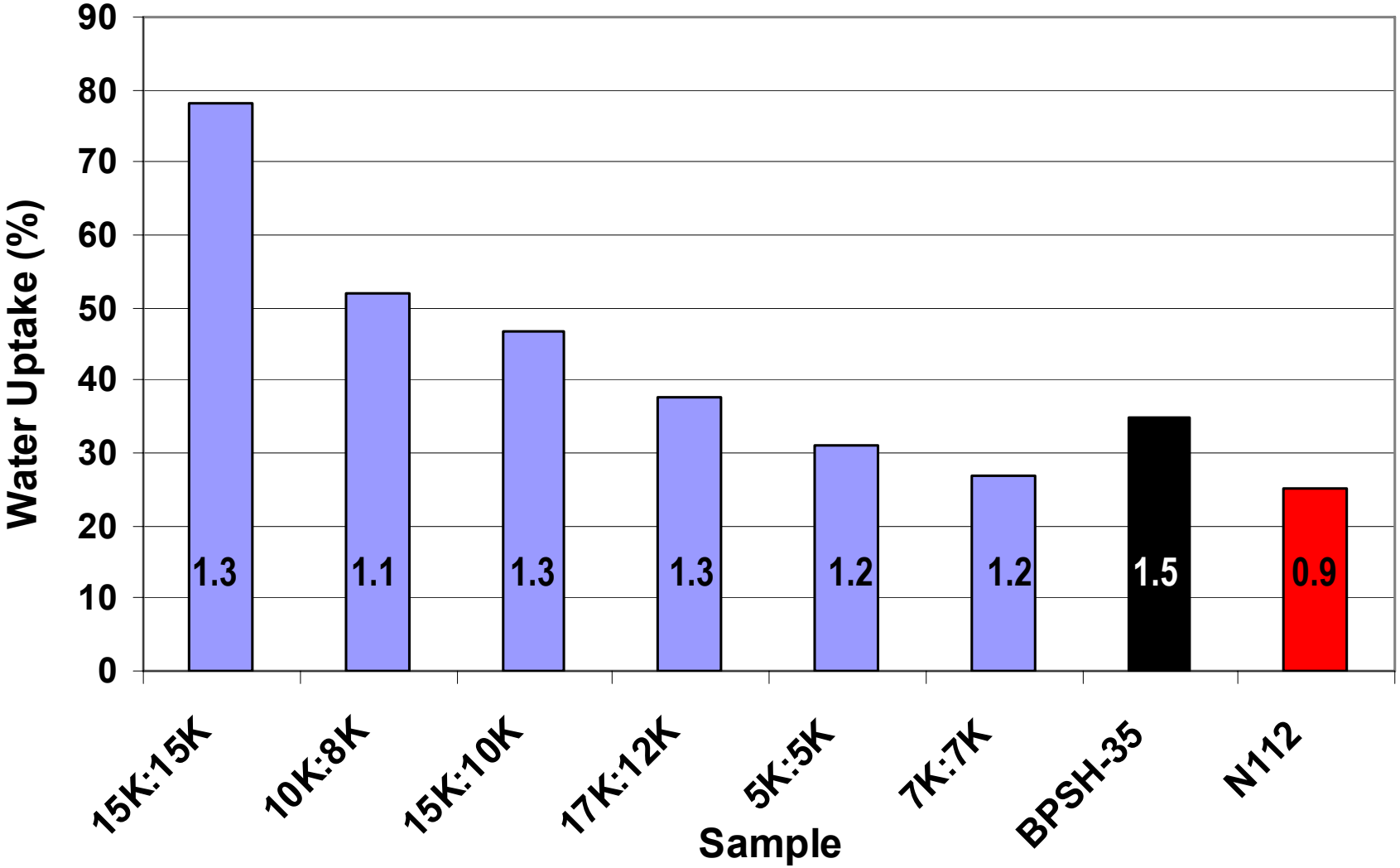


Self-Diffusion Coefficient Values Support the Proton Conductivity Trends



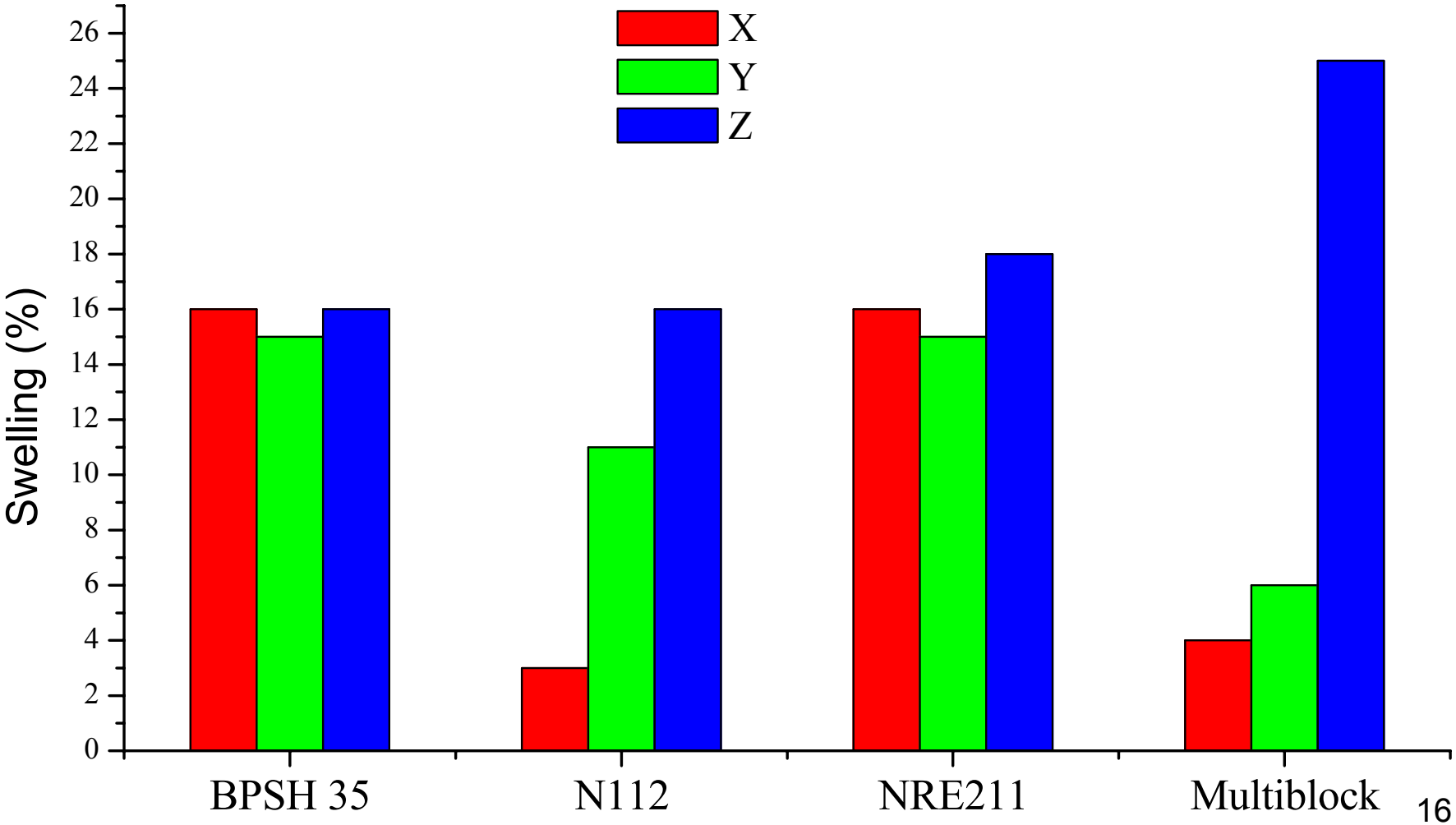
Roy, A.; Hickner, M.; Yu, X; Li, Y; Glass, T.; Li, Y.; McGrath, J.E. Journal of Polymer Science-Part B,44,2226-2239,(2006)

Water Uptake can be Controlled in the Block Copolymer By Increasing The Hydrophobic Block Length at Essentially the Same IEC

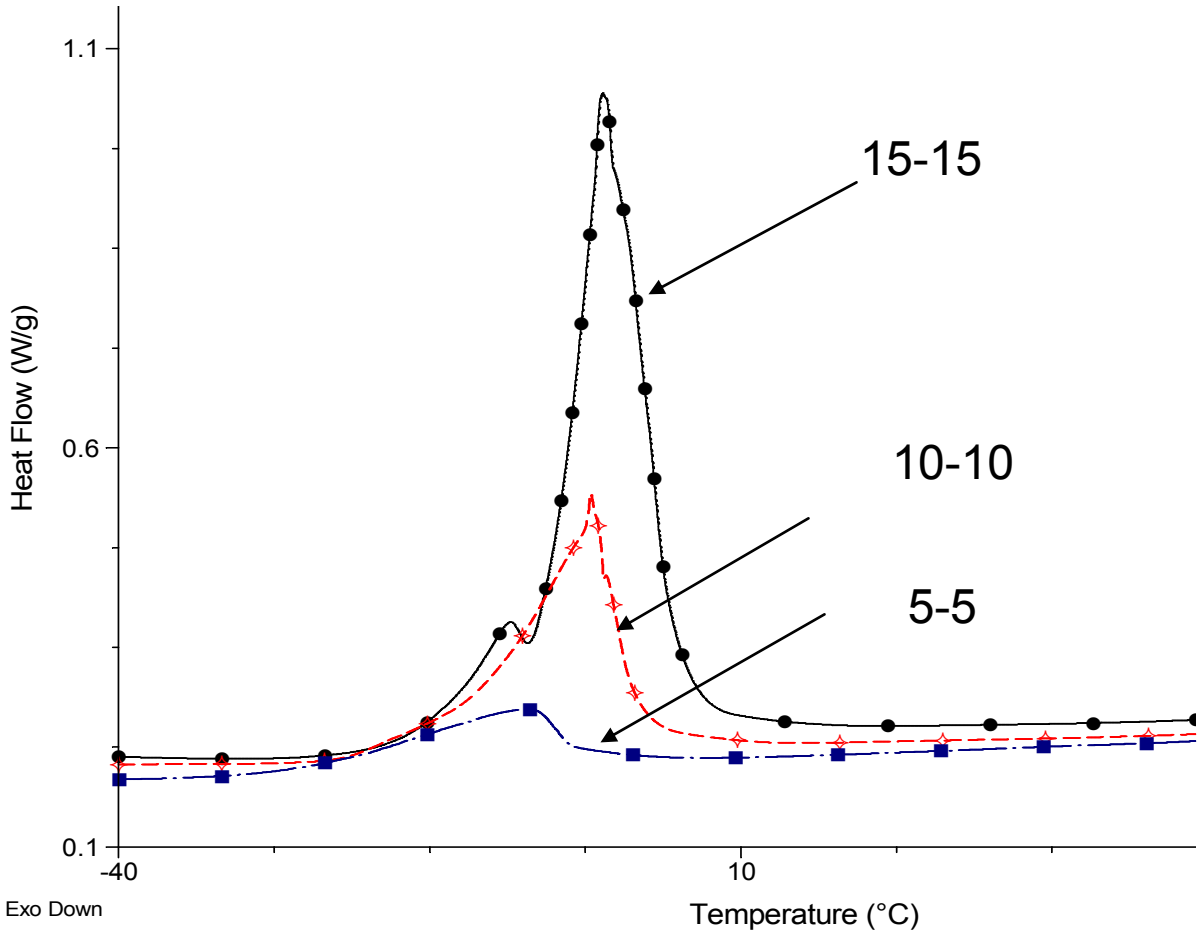


Note: the numbers in the bars represent the ion exchange capacity.

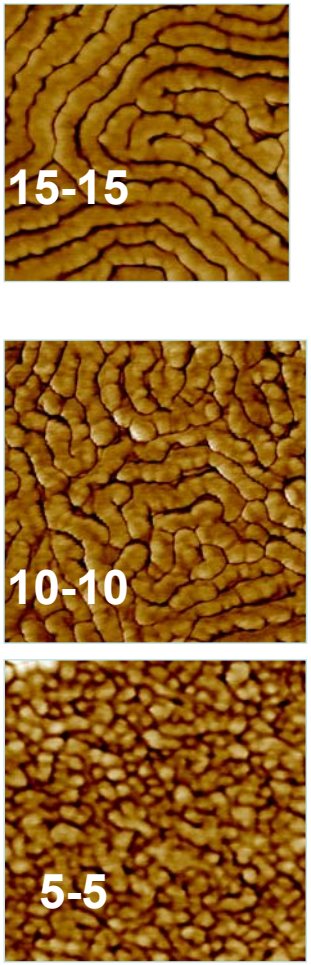
Multiblock Copolymers All Show Low x,y Swelling



Multiblock Copolymers (BPSH-PI) Develop Order and More "Free" Water as Block Length Increases



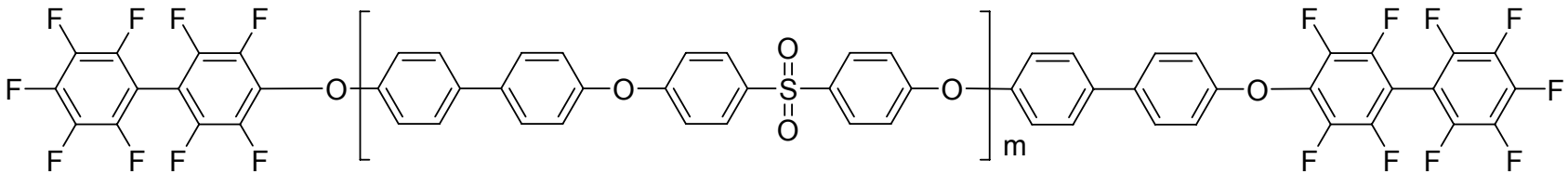
5°C/min,N_2



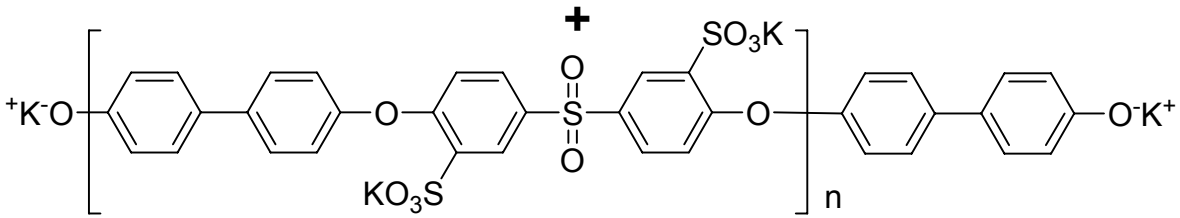
Melting endotherm of freezing water is a function of block length under similar IEC (1.6 meq/g)

500 nm

Synthesis of BPSH – BPS Multiblock Copolymers



Decafluorobiphenyl terminated BPS (Hydrophobic Block)

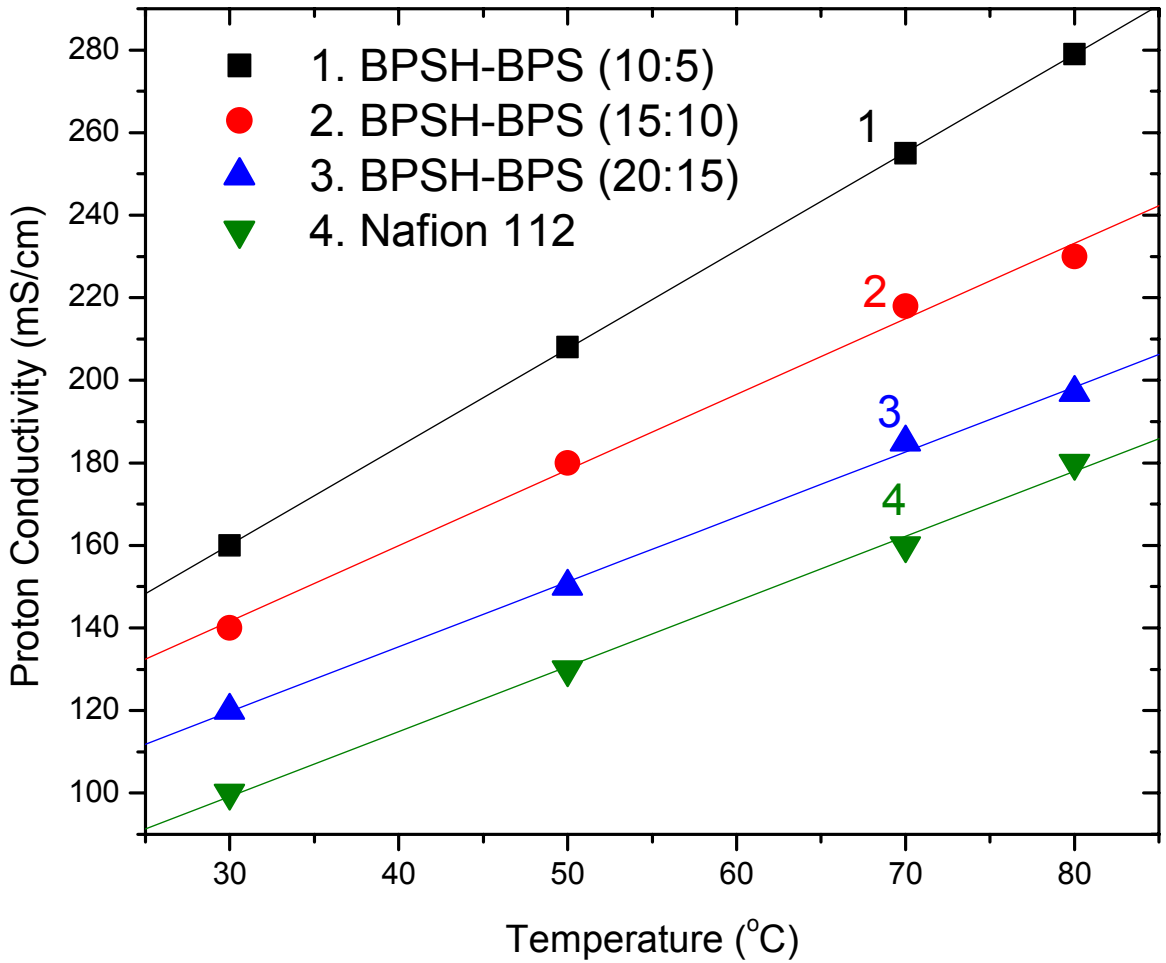


phenoxide terminated BPSH (Hydrophilic Block)

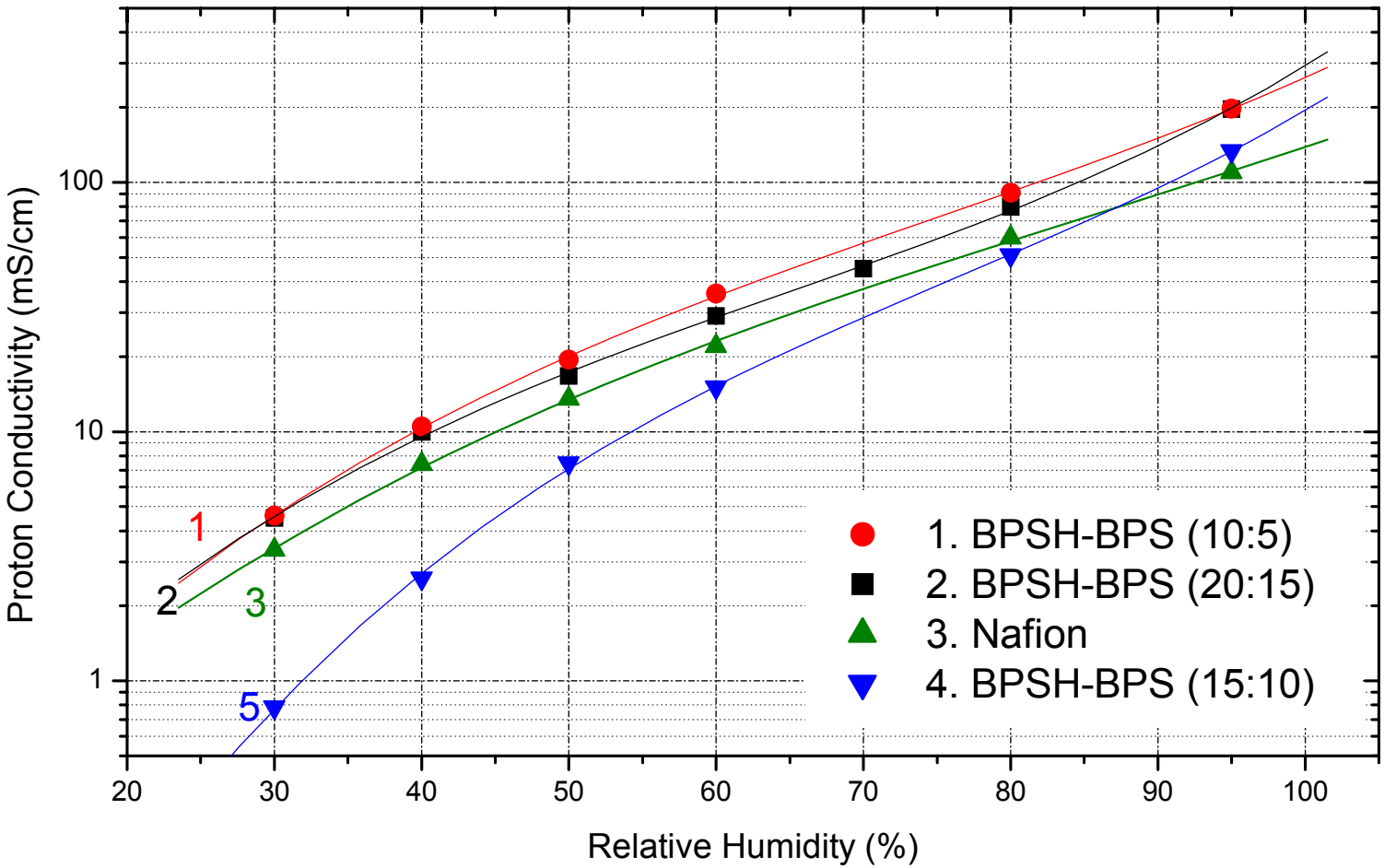
1. DMAc, Cyclohexane, K_2CO_3, 90 ºC, 4hr
2. DMAc, K_2CO_3, 110 ºC, 48hr

~~~~(Sulfonated Poly arylene ether sulfone)$_m$~~(Poly arylene ether sulfone)$_n$~~~~~

Effect of Temperature on Proton Conductivity for Unequal Block Lengths Copolymers (liquid water)

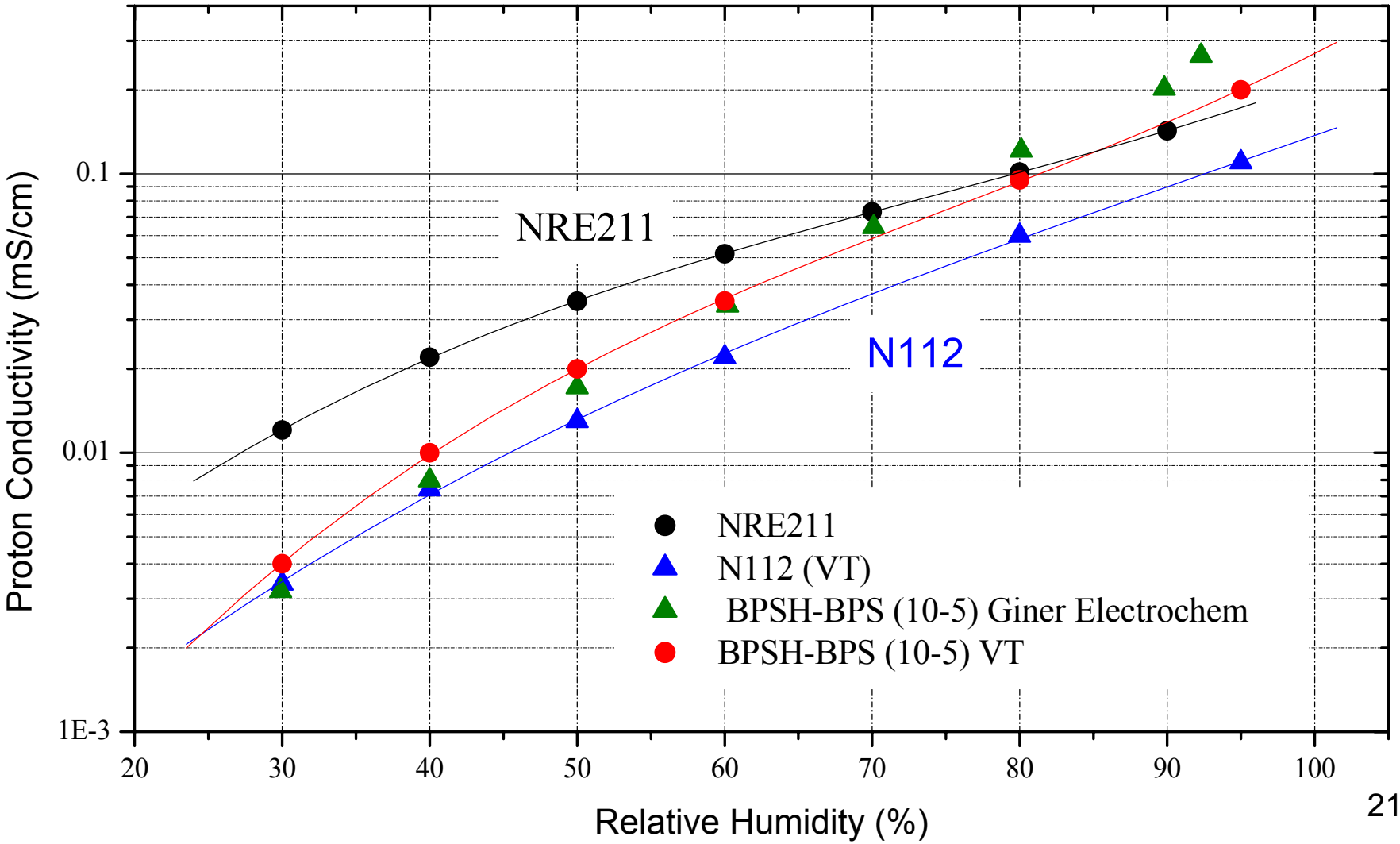


Effect of RH on Proton Conductivity for Unequal Block Lengths Copolymers

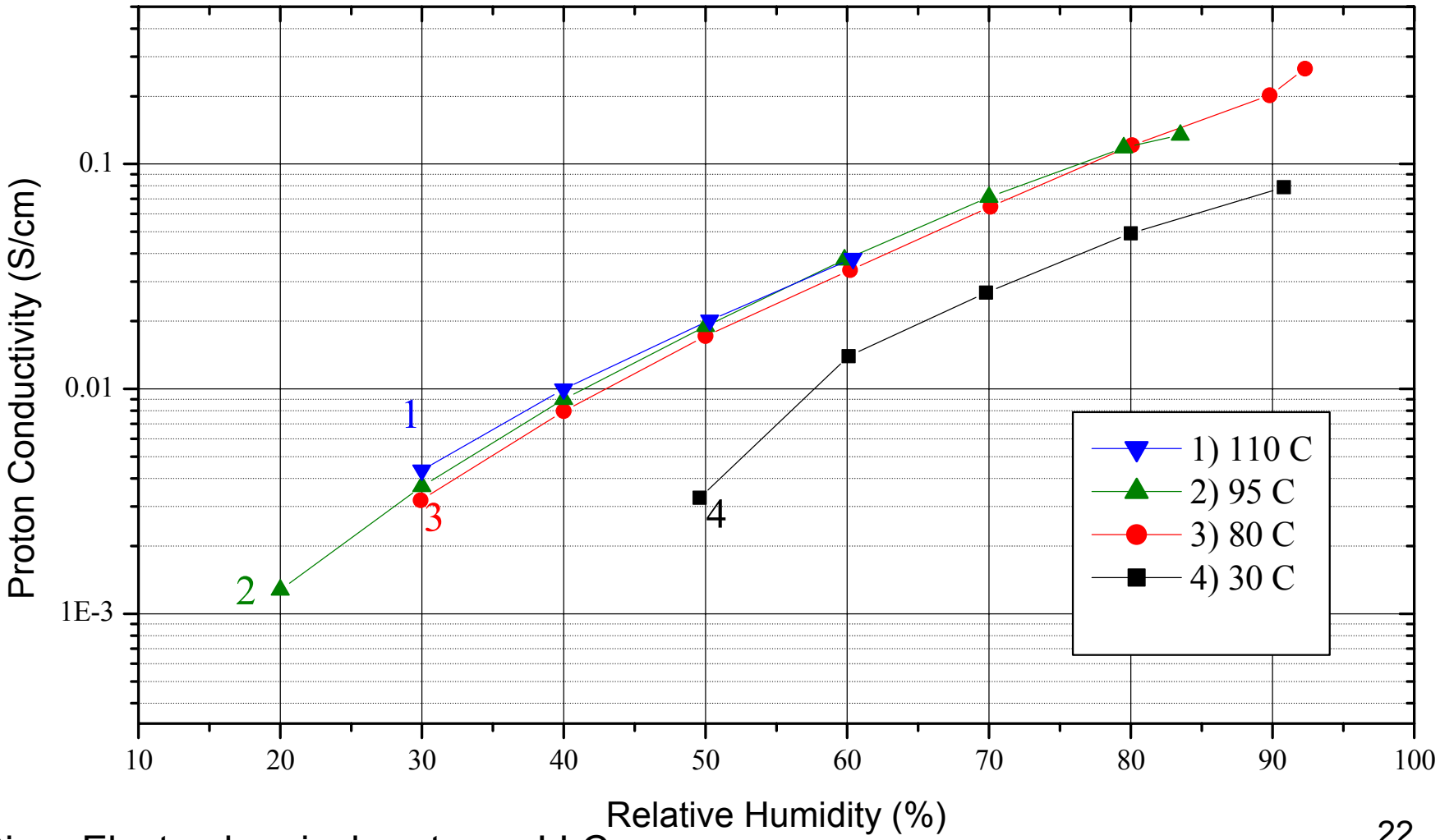


80 °C

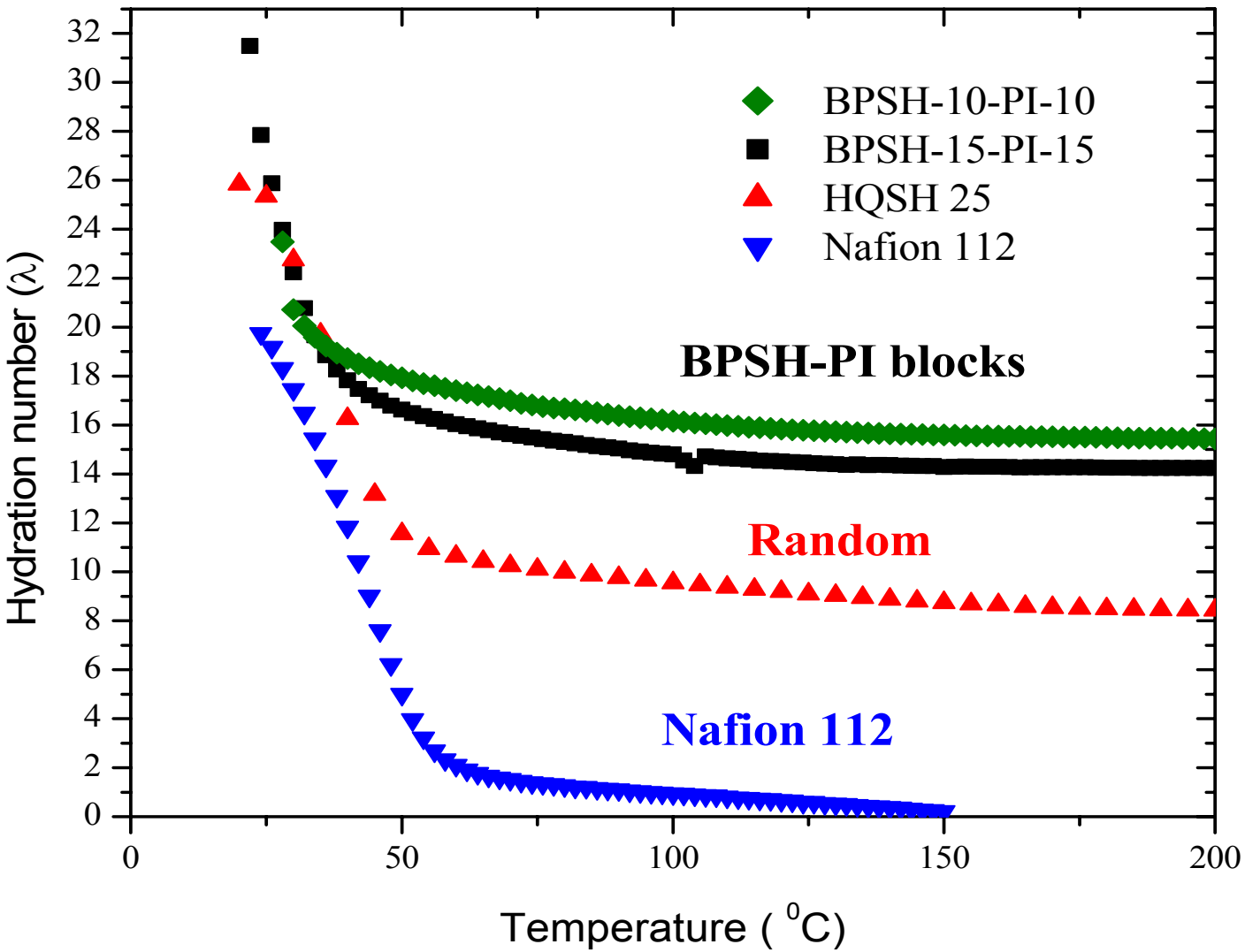
Proton Conductivity under partially hydrated conditions for BPSH multiblock at 80°C



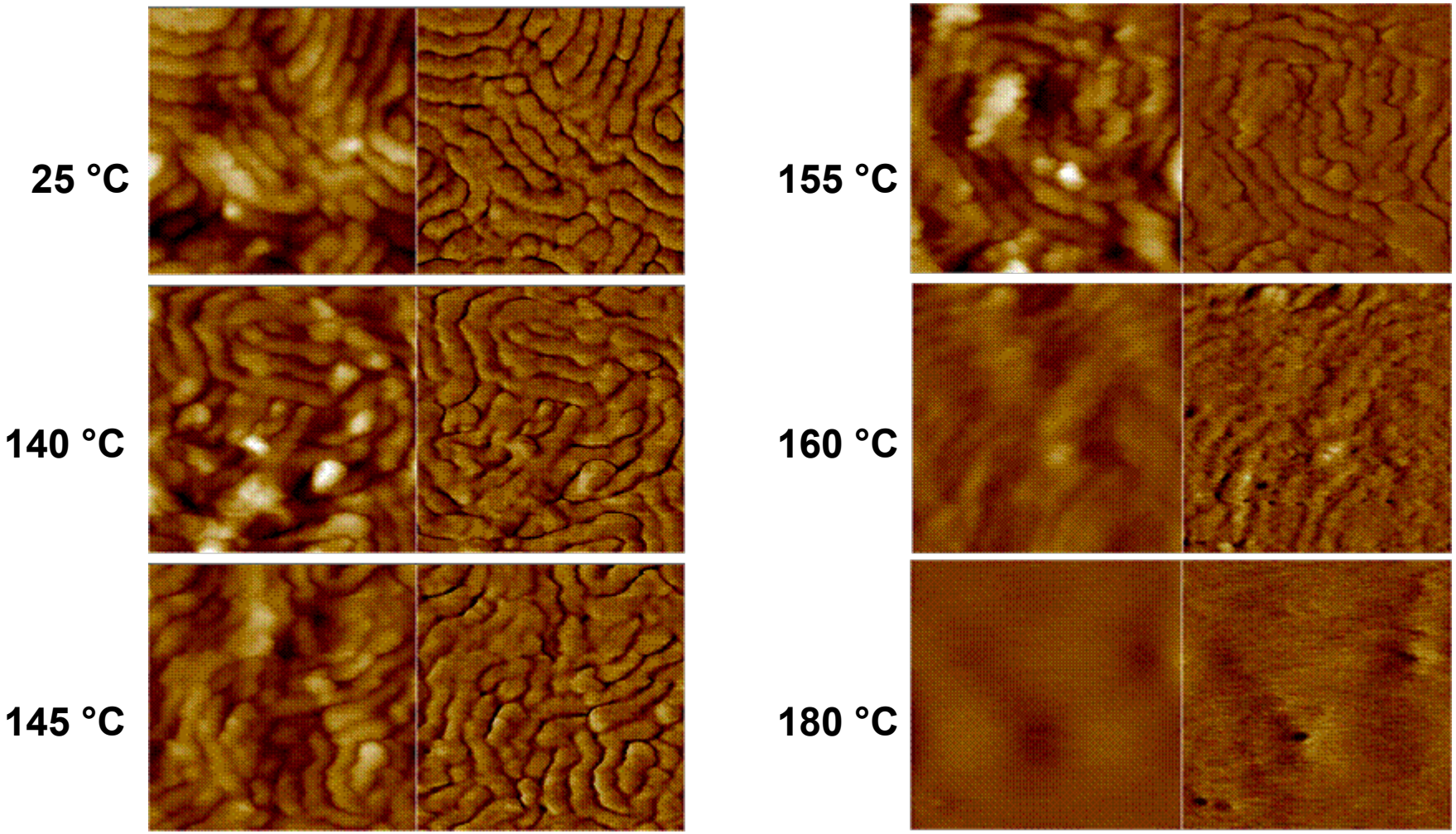
Proton transport at high temperatures for BPSH-BPS (10:5) multiblock



Multiblock Copolymers Retain Much Higher Amount of Water at High Temperatures

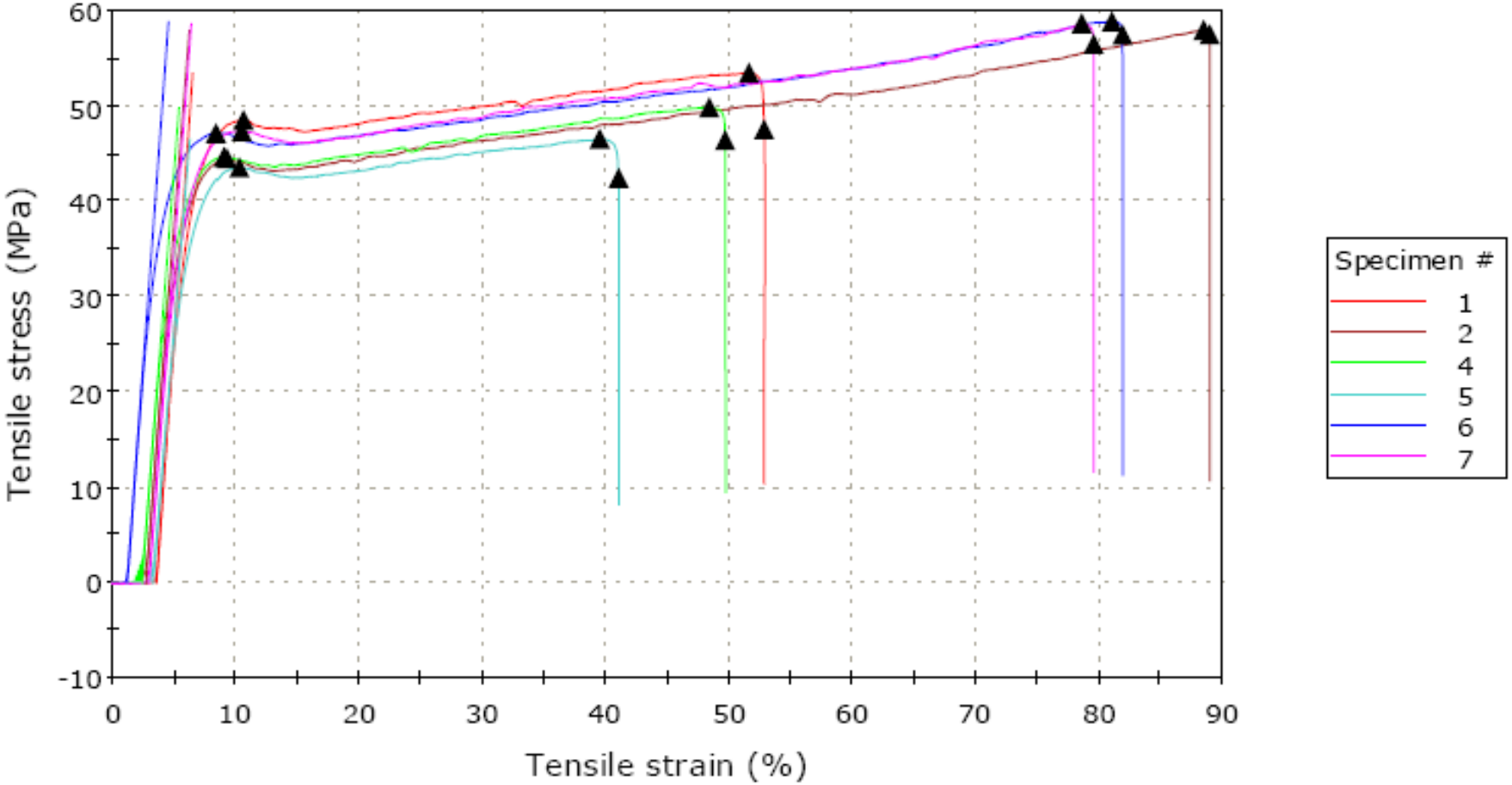


BPSH100-PI 15k-15k Morphology Appears Stable until 155°C

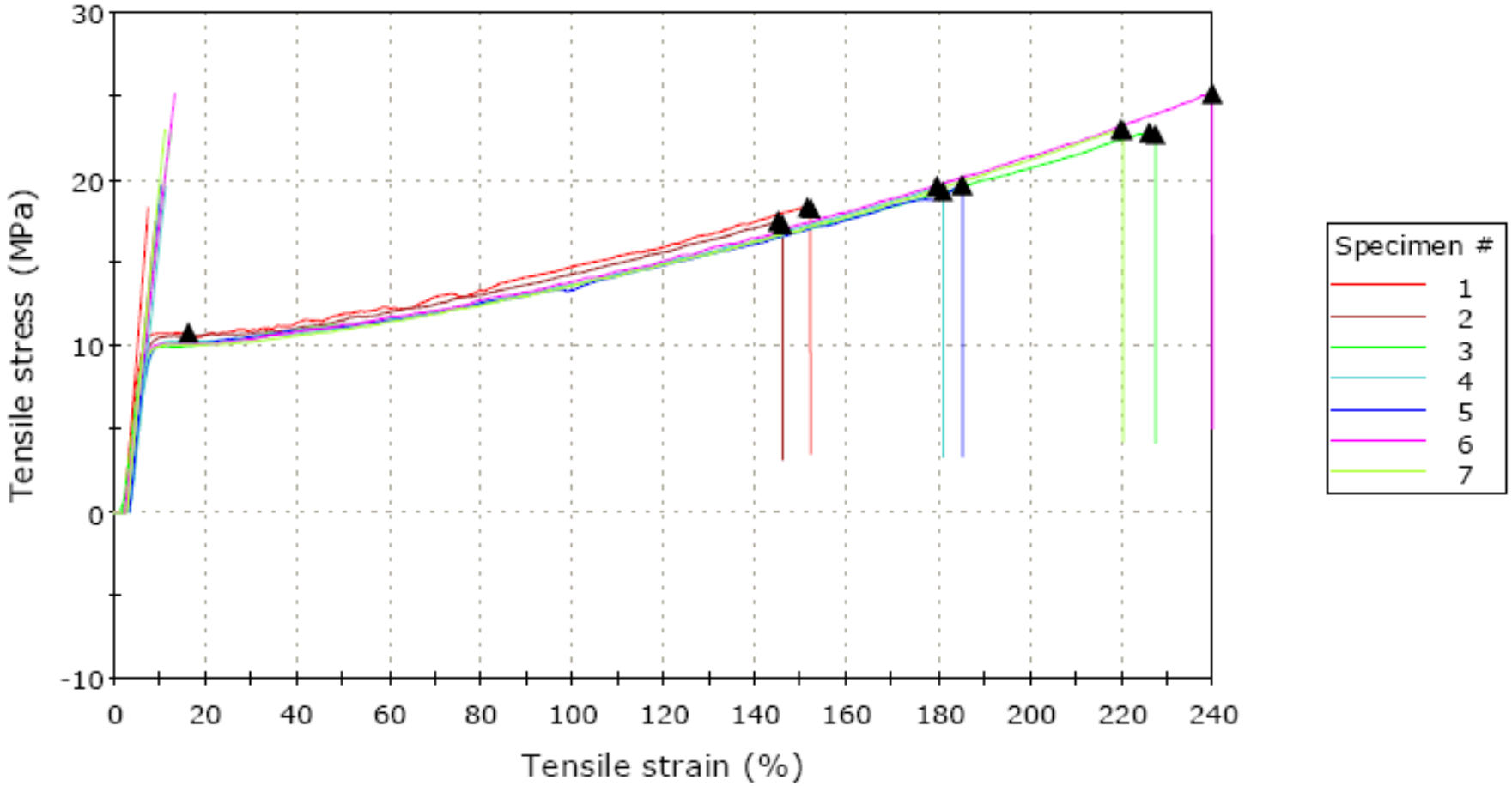


Membranes equilibrated 30 min before imaging; Setpoint Ratios: 0.86, 0.81, 0.86, 0.87, 0.84, 0.73;
Height images: z = 25 nm; Phase images: z = 40°

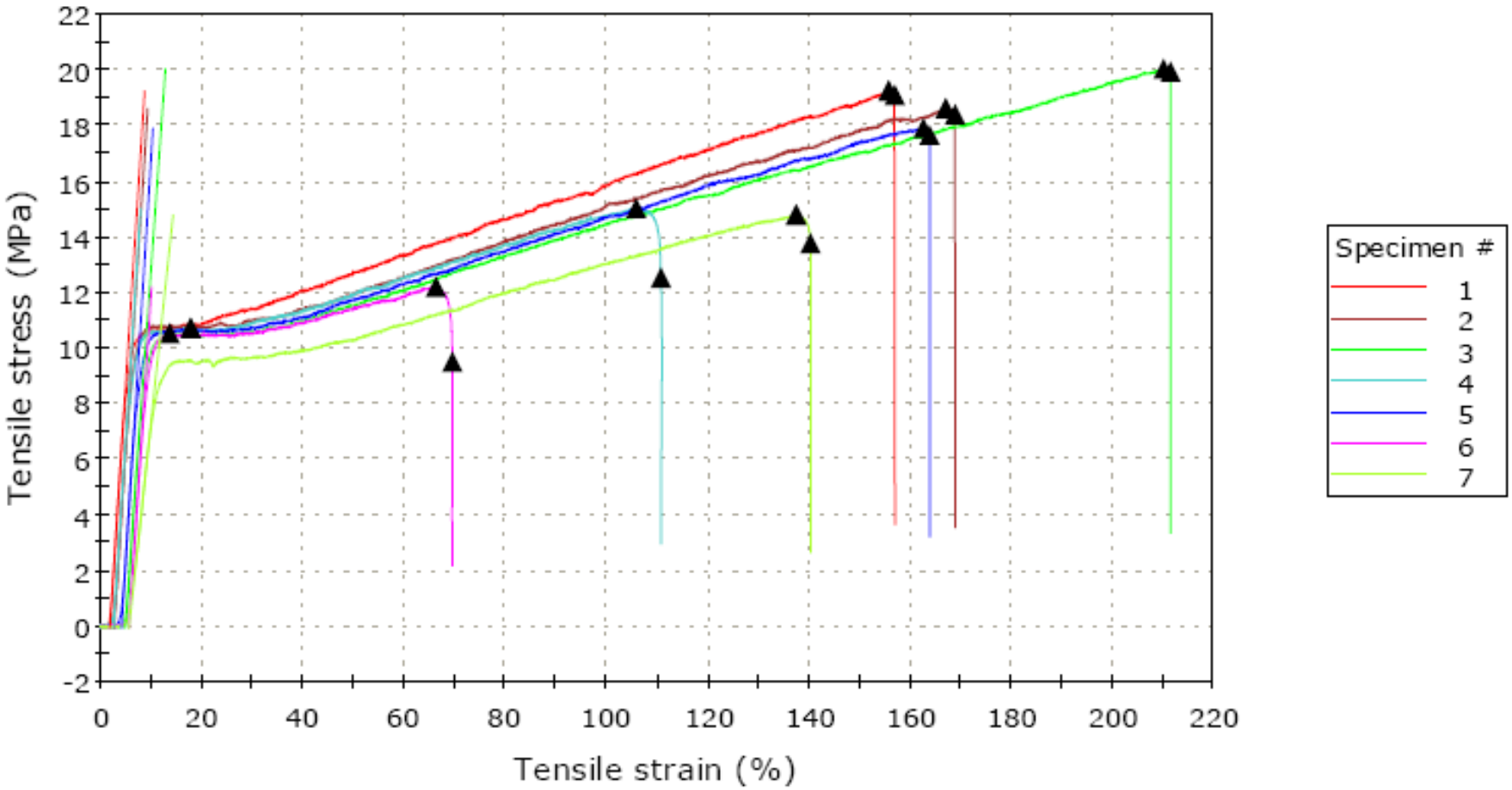
BPS-BPSH100 5k-5k



Nafion™ 112


Tensile stress (MPa)
30
20
10
0
-10
0
20
40
60
80
100
120
140
160
180
200
220
240
Tensile strain (%)
Specimen #
1
2
3
4
5
6
7

Recast Nafion™ NRE211



Conclusions

- Multiblock copolymers containing BPS hydrophilic blocks and highly fluorinated hydrophobic blocks were synthesized by coupling reactions of the telechelic oligomers.

- The BisSF-BPSH(*x*:*y*) multiblock copolymer series exhibits higher conductivity than Nafion™ 112 and the BPSH random copolymers at all temperatures in liquid water.

- Both in liquid water and under partially hydrated conditions, the proton conductivity increases with increasing block lengths.

- The self-diffusion coefficient of water dominates proton transport and is proportional to proton conductivity under partially hydrated conditions.

Future Research

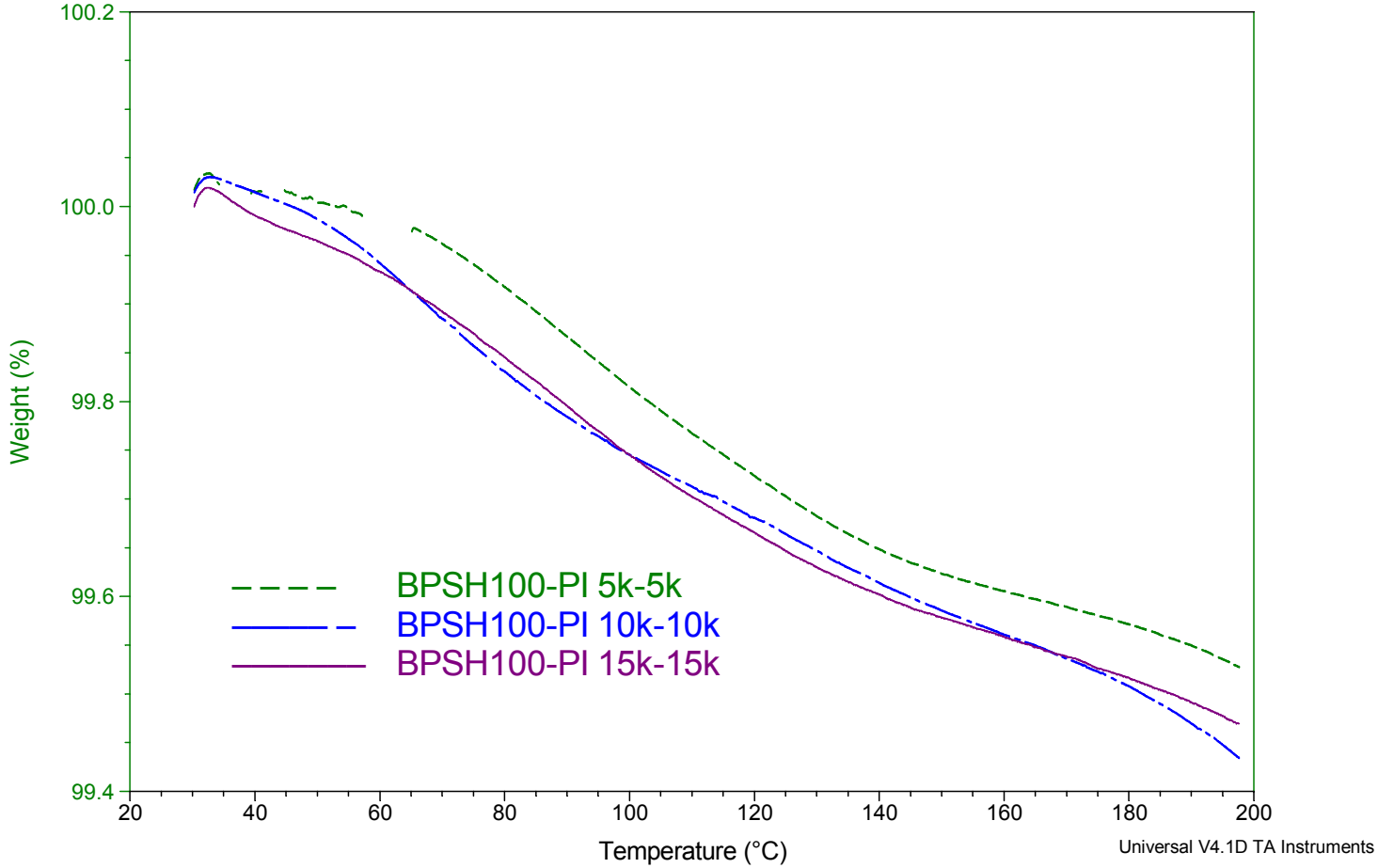
- Continue ongoing efforts understanding structure-property relationships in PEM block copolymers and what controls conductivity at low RH
- Further Investigate BPSH-0-100 multiblock copolymers utilizing hexafluorobenzene and decafluorobiphenyl-linking groups.
- Swelling-deswelling features in the block copolymers and its connection to fuel cell durability
- Scale up (20-50gm) selected block copolymer PEMs, Cast into films
- Screen compatibility with PVF2(Kynar); determine if lower modulus improves fatigue

Appendix-Explanatory slides

How to Determine Swelling Ratio ? (protocol)

- Sample equilibrated in water for 2 h
- Dimensions in x, y and z directions are measured by placing the membrane between two hydrophobic films.
- Dried in convection oven at 80°C for 2 h
- Change in dimensions are measured.
- Average of 9 measurements involving 3 different samples are taken

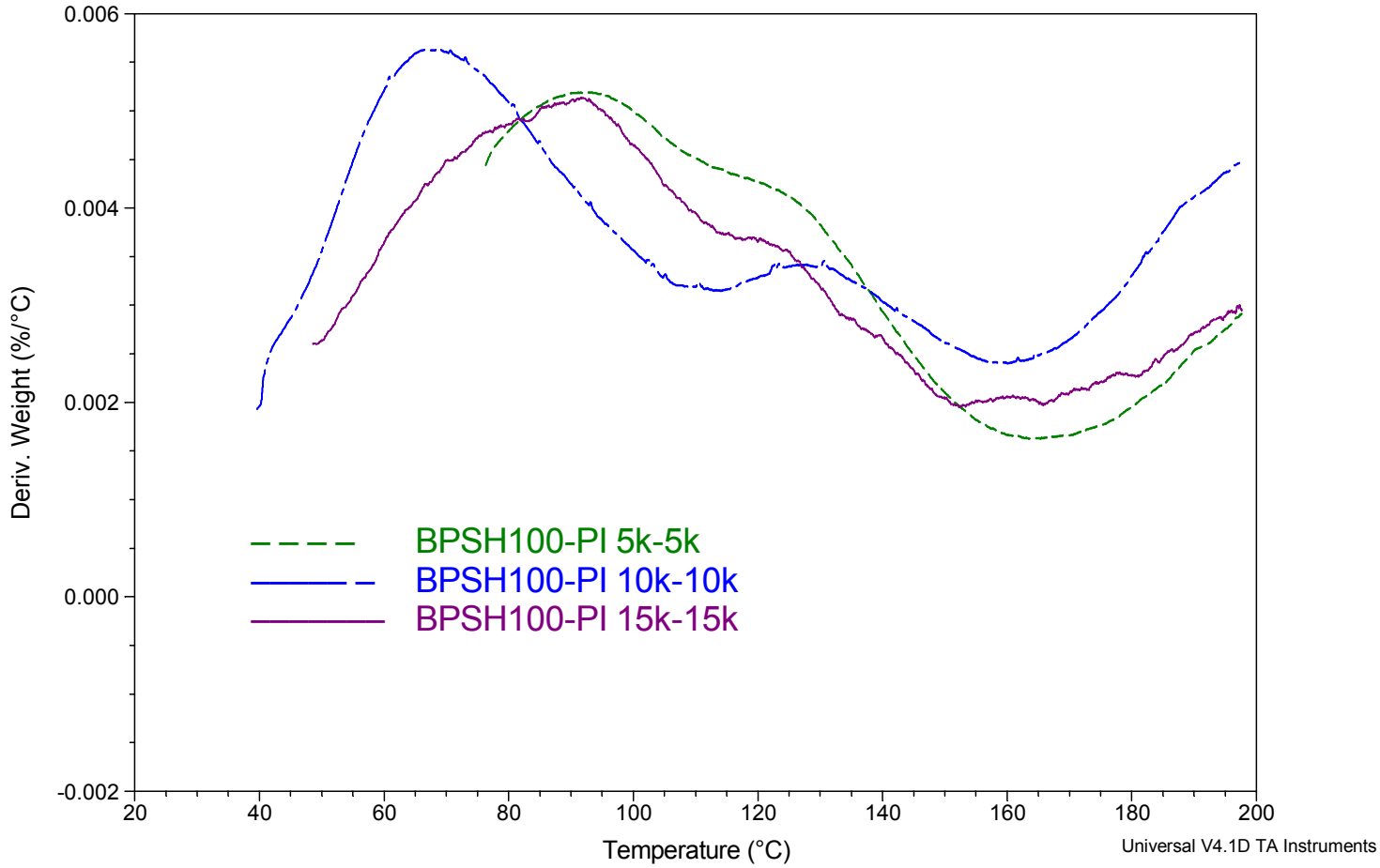
% Weight Loss vs Temperature for BPSH100-PI Series



- Weight loss continuously increases with temperature

Samples dried at 100 °C for 30 min before heating. Heating runs performed at 5 °C/min in air

Derivative of % Weight Loss vs Temperature for BPSH100-PI Series



- Minima may correspond to transitions in phase separation at elevated temperature
- Slower heating rate might reveal trend more clearly for smaller block lengths

Samples dried at 100 °C for 30 min before heating. Heating runs performed at 5 °C/min in air

Conclusions

- Increasing block length appears to help retain morphology at elevated temperature
- Temperatures at which morphologies change appear to correspond to transitions in TGA curves; more study required
- Isothermal heating of BPSH100-PI series shows that while water loss increases with temperature, it does not change with time at 120°C
- Block copolymer structures appear to retain water over time at 120°C