2008
DOE Hydrogen Program
Merit Review Presentation

Advanced Materials for Proton Exchange Membranes

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Project ID # FC16

McGrath Group 2008

Front Row: Rachael VanHouten, Natalie Arnett, Jim McGrath
Back Row: Dr. Gwangsu Byun, Mou Paul, Ozma Lane, Hae Seung Lee, Yu Chen, Dr. Abhishek Roy, Dr. Daniel Brandell (*now at Upsala Univ., Sweden*); missing, Dr. Chang Hyun Lee

Outline

- *Overview*
- *Acknowledgements*
- *Objectives*
- *Results*
- *Conclusions*
- *Current and Future Research*

OVERVIEW

Timeline	Barriers
•Project State Date: May 2006 •Project End Date: May 2011 •Percent Complete: 40%	•Conductivity at 120ºC and low RH •Swelling Deswelling
Budget	**Partners**
Total Project Funding: $1.5MM Funding received in FY07: $300K Funding for FY08: $350K	•Los Alamos National Labs •Giner Electrochemical Systems •Hydrosize, Inc. •Nissan Motors Co •Arkema

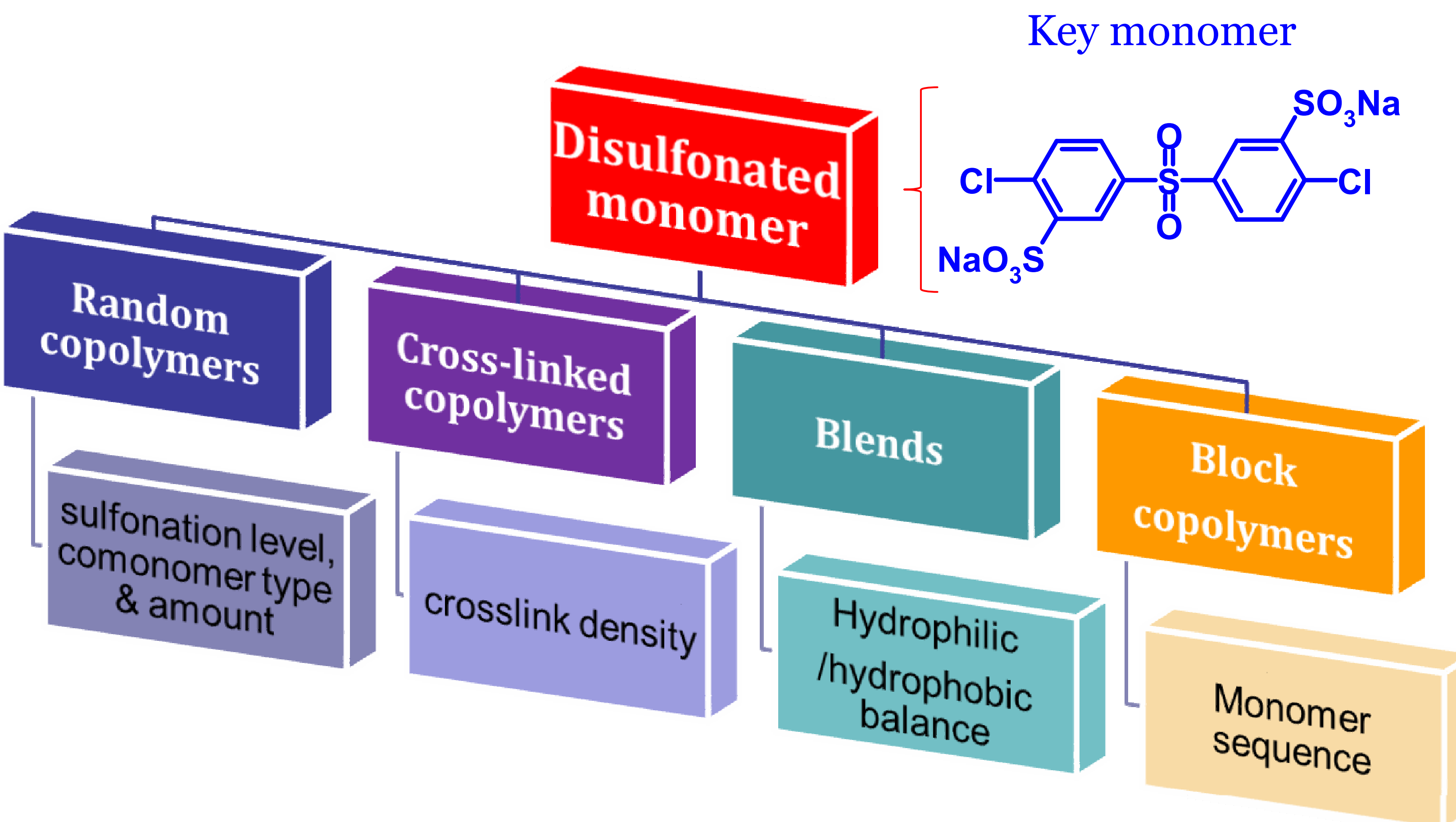
Acknowledgements

- McGrath Research Group: past and present
- May 2006" DOE Contract on "*High Temperature, Low Relative Humidity, Polymeric Membranes Based on Hydrophilic-Hydrophobic Disulfonated Poly(arylene ether) Block Copolymers*
- *Los Alamos National Laboratory (LANL)*
- *Nissan Motor Co*

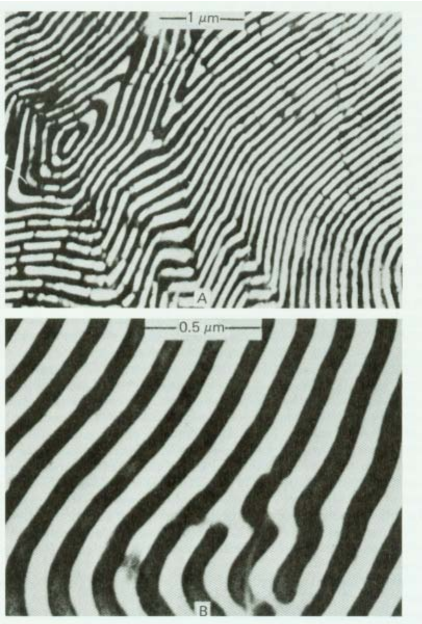
Objectives and Approach

- 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 H2/Air Systems at 100-120^{o}C/low RH
- Nano-phase Separated Hydrophilic-Hydrophobic Thermally Stable Multi-Block Copolymers
- Correlate Water Diffusion Coefficients with Proton Conductivity Under Partially Hydrated Conditions
- Relate Thermodynamics of Nano-phase Formation to Ordered Morphology and to Conductivity, Diffusivity and Novel Membrane Self Assembly

Material Design Options



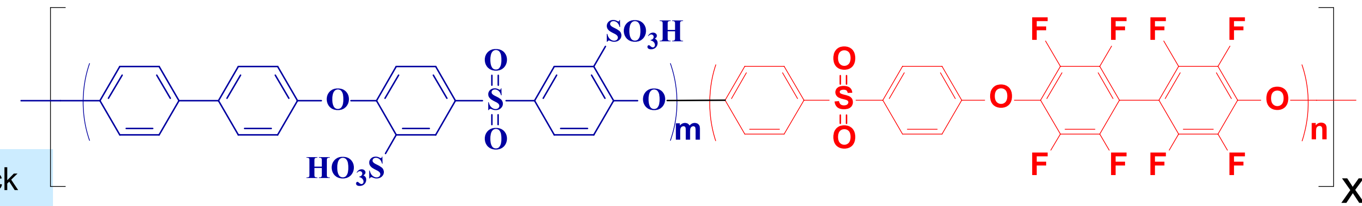
Highly Hydrophobic-Hydrophilic Multiblock Copolymers



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 Initial work:



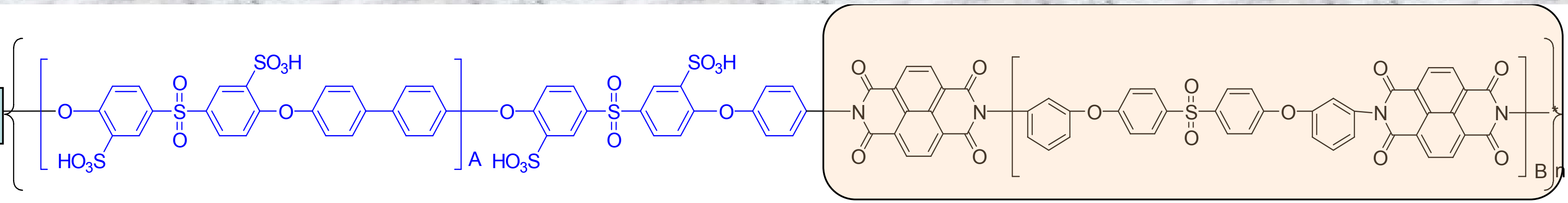
Hydrophilic segments, provides Proton conductance

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.

Hydrophilic-Hydrophobic Multi-Block and Random(control) Copolymers

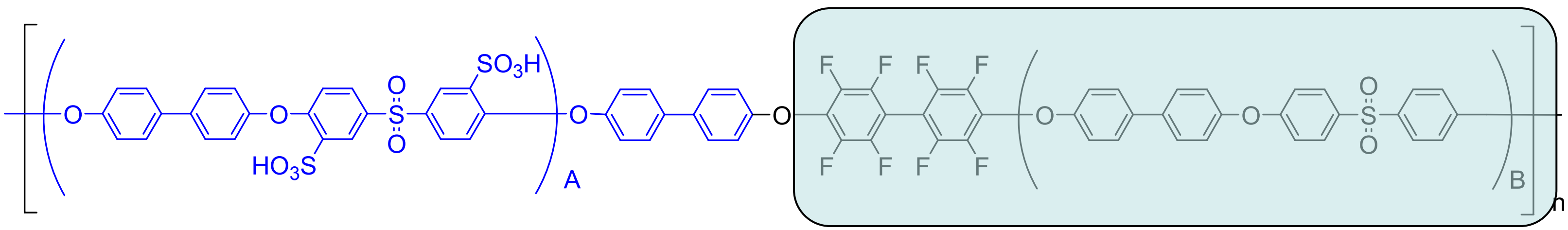
1



BPSH-PI (A:B)

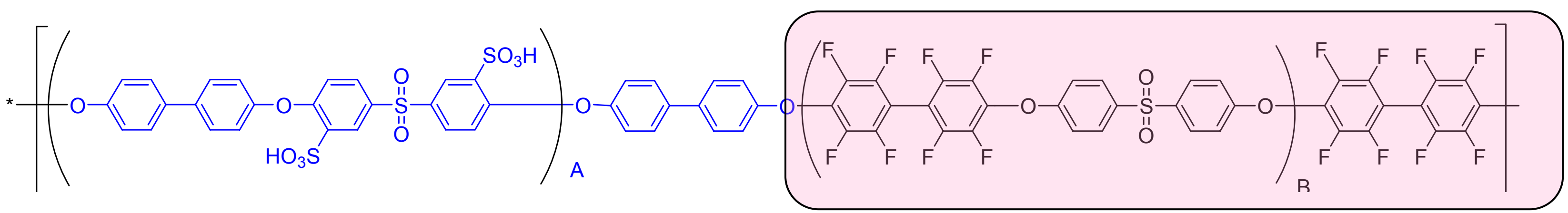
A~ Hydrophilic block length in kg/mole, B~ Hydrophobic block lengths in kg/mole

2



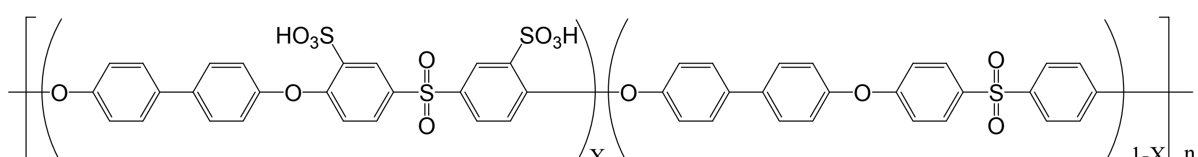
BPSH-BPS (A:B)

3



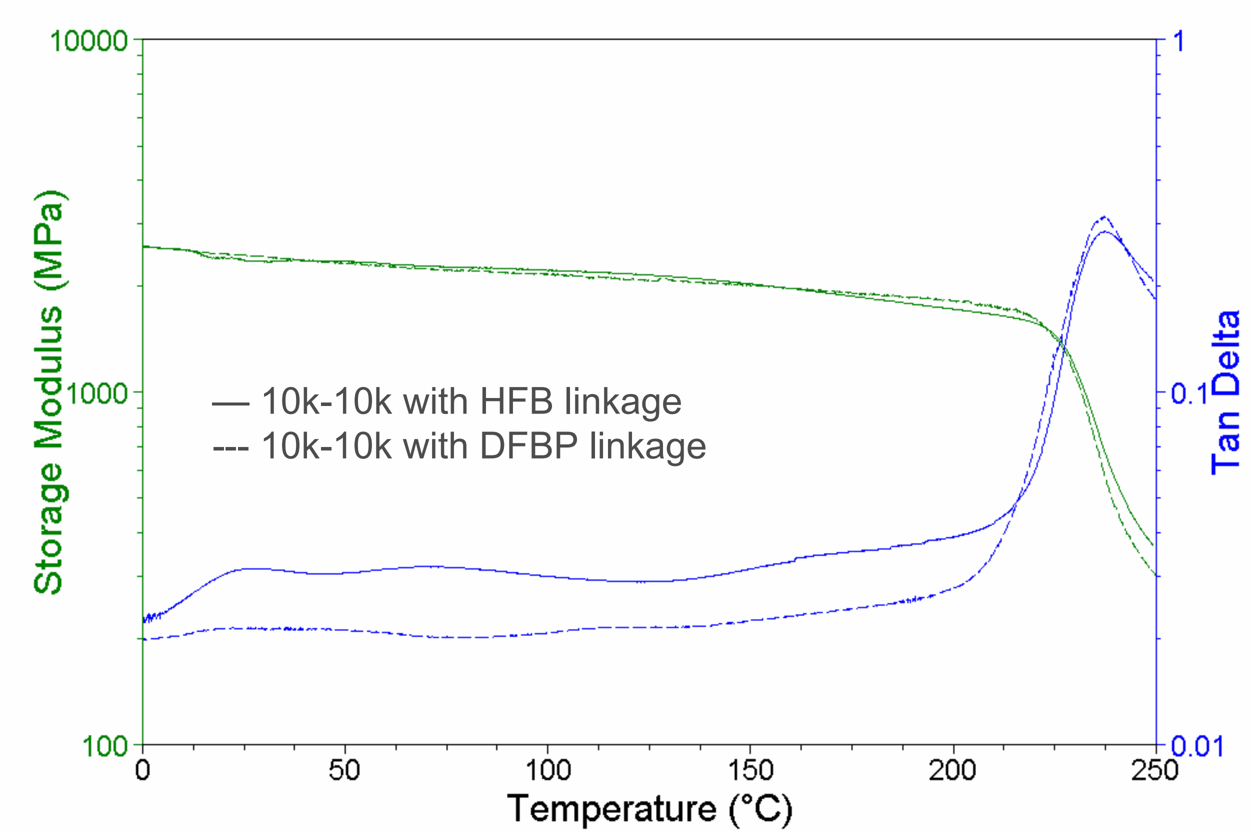
BPSH-BisSF (A: B)

4



BPSH-xx random

Modulus-Temperature Behavior of a 10K-10K BPSH100-BPS-0 Multi-Block Copolymer



- T_g virtually identical for both linkage types

Analysis performed with TA Instruments DMA 2980 at 1 Hz. An initial drying run to 200 °C for 10 min followed by cooling with liquid N_2 to 0 °C for 10 min preceded each temperature sweep. Samples heated at 5 °C/min to 250 °C. Displacement set at approx. 0.1% of sample length.

Toward Improved Conductivity of Sulfonated Aromatic Proton Exchange Membranes at Low Relative Humidity

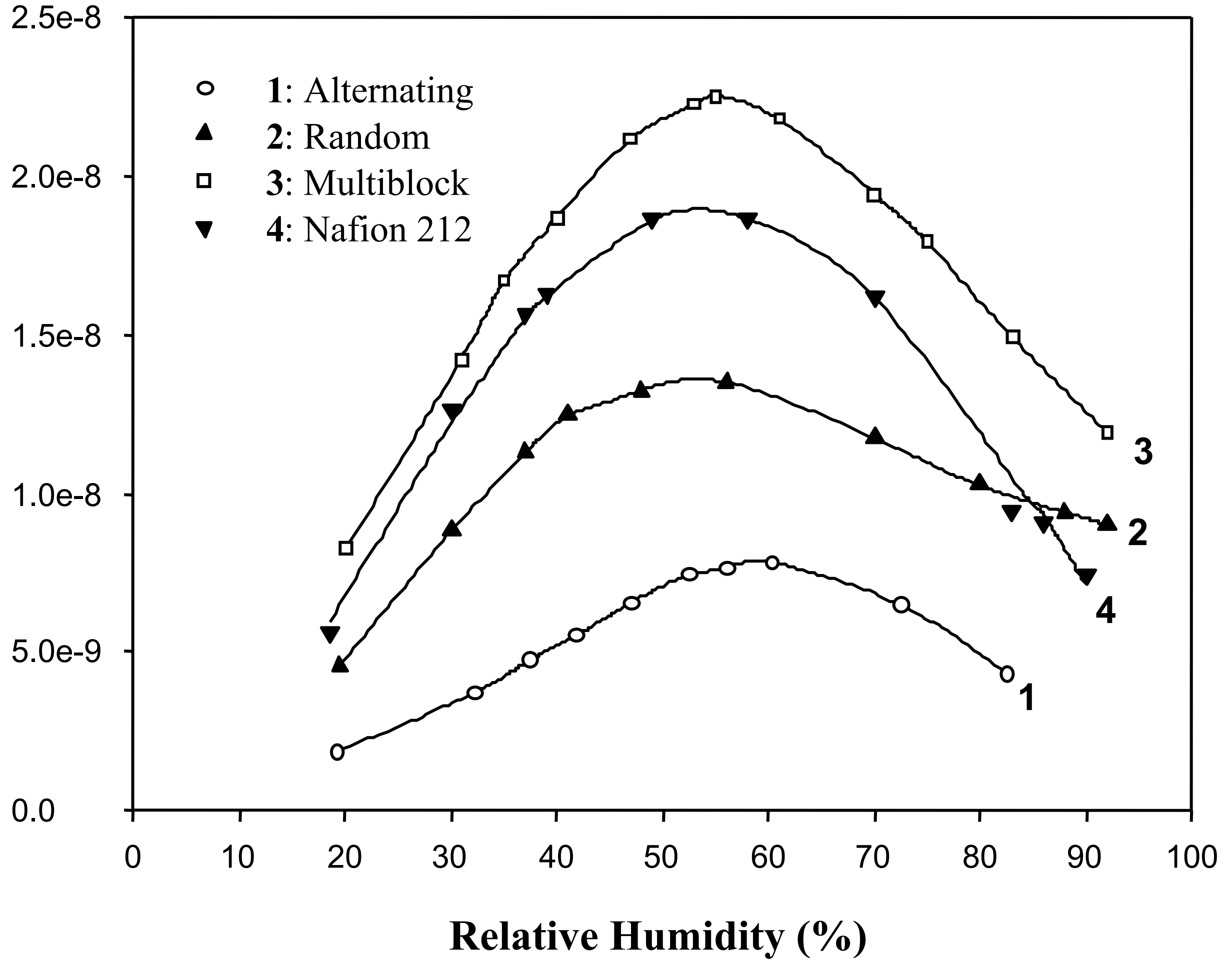
Melinda L. Einsla[1], Yu Seung Kim*[1], Marilyn Hawley[1], Hae Seung Lee[2], James E. McGrath[2], and Bryan S. Pivovar[1]

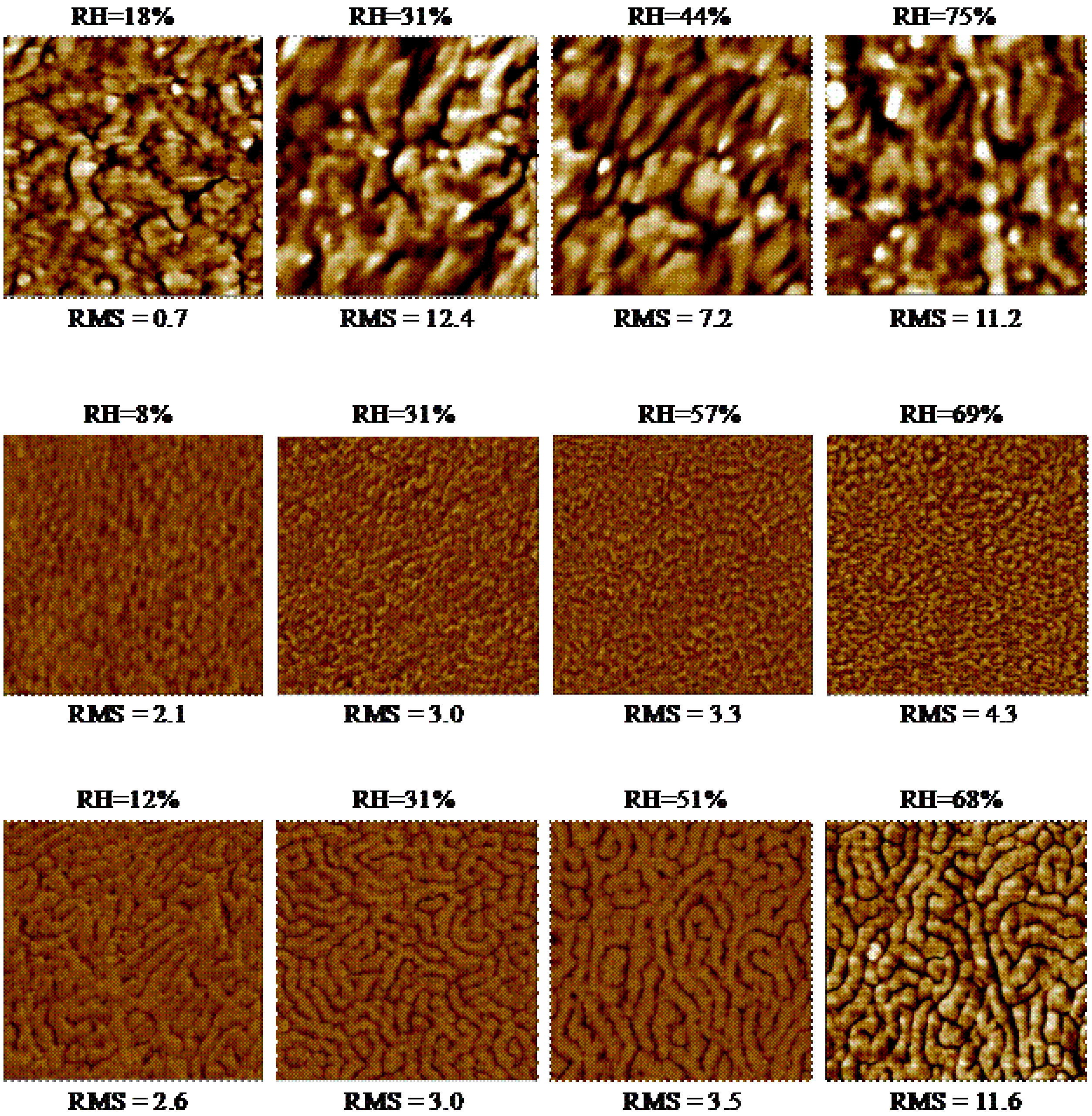
[1]Sensors and Electrochemical Devices Group, Los Alamos National Laboratory, Los Alamos, NM 87545

[2]Macromolecules and Interfaces Institute, Virginia Tech Blacksburg, VA 24061

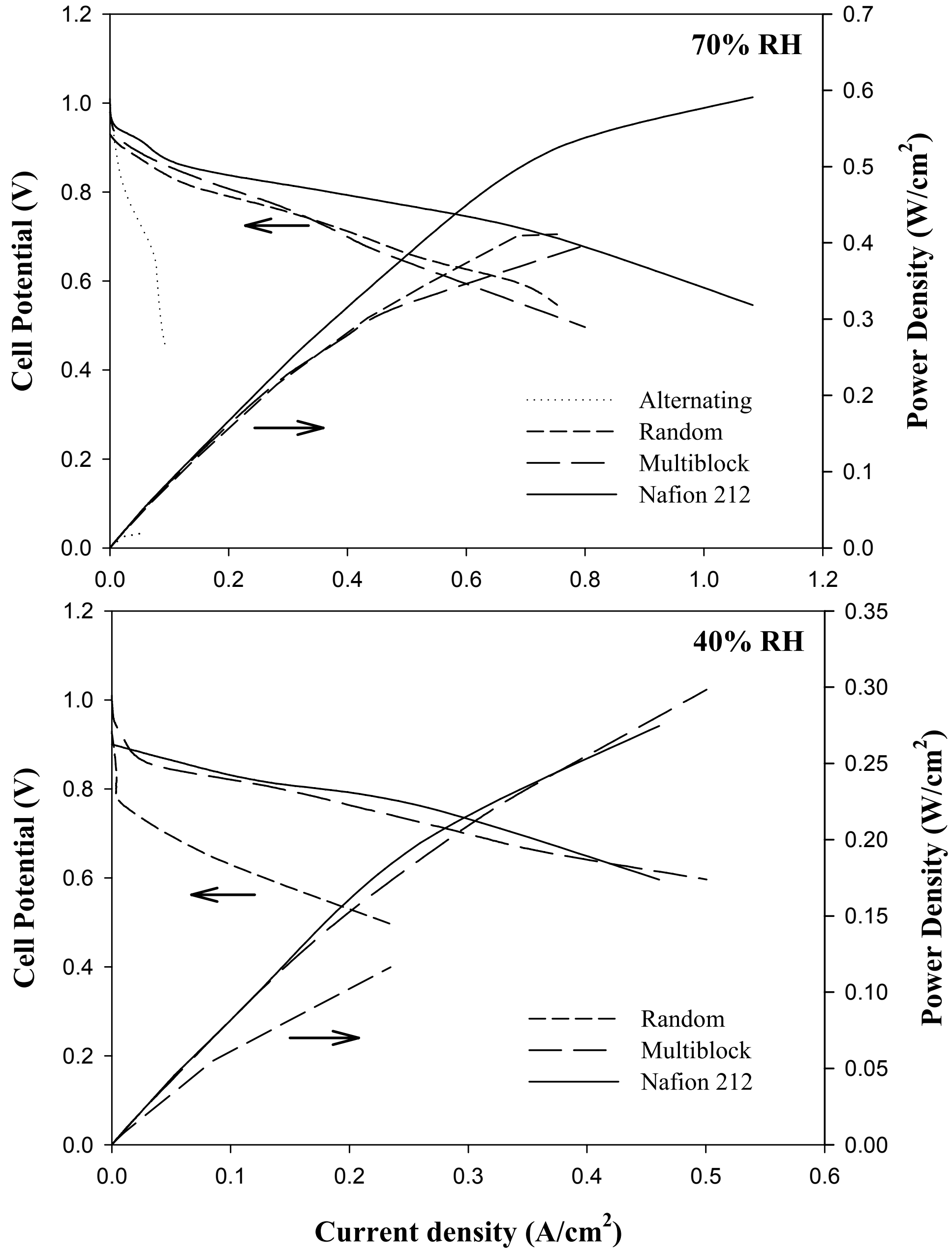
***Submitted to Chemistry of Materials*

Diffusion coefficients of hydrocarbon copolymers and Nafion as a function of relative humidity (Nafion is shown for comparison)



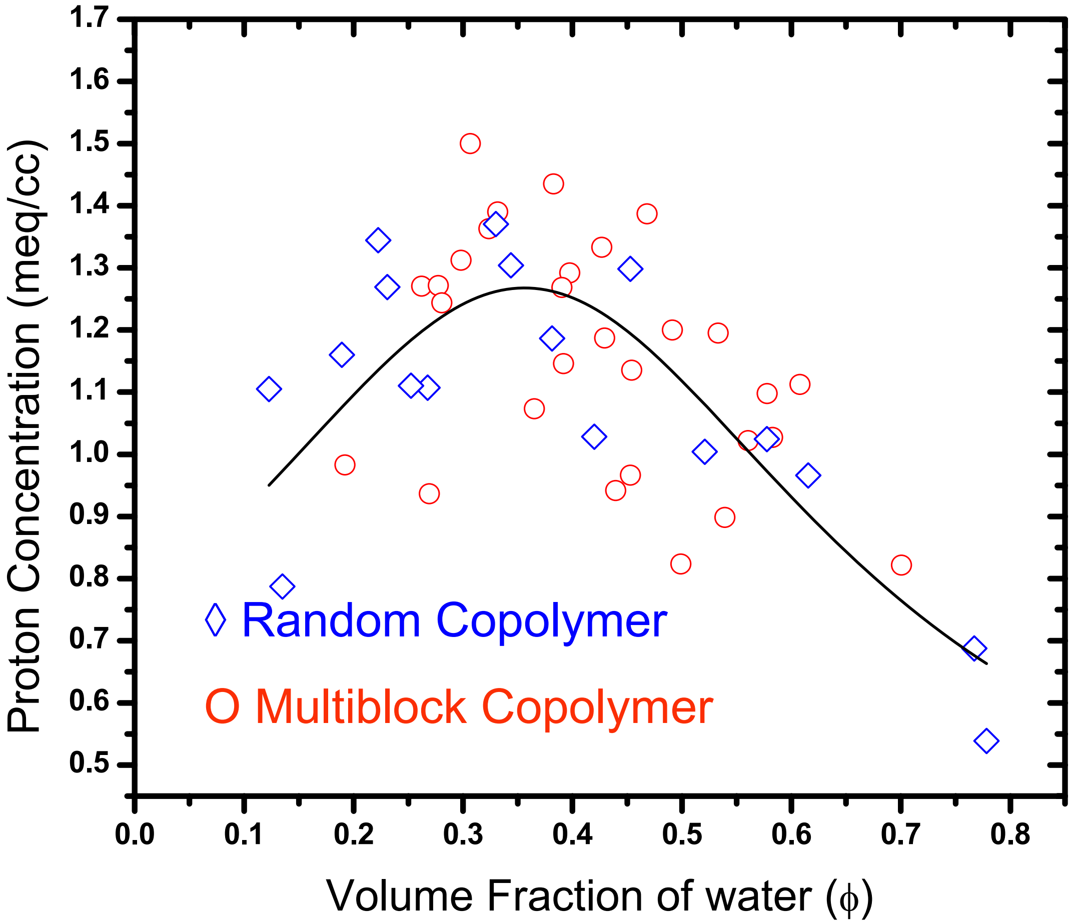


SFM images of alternating (top), random (center), and multi-block (bottom) copolymers at low and high humidity. Image size is 1 mm and phase range is 40° for all images.



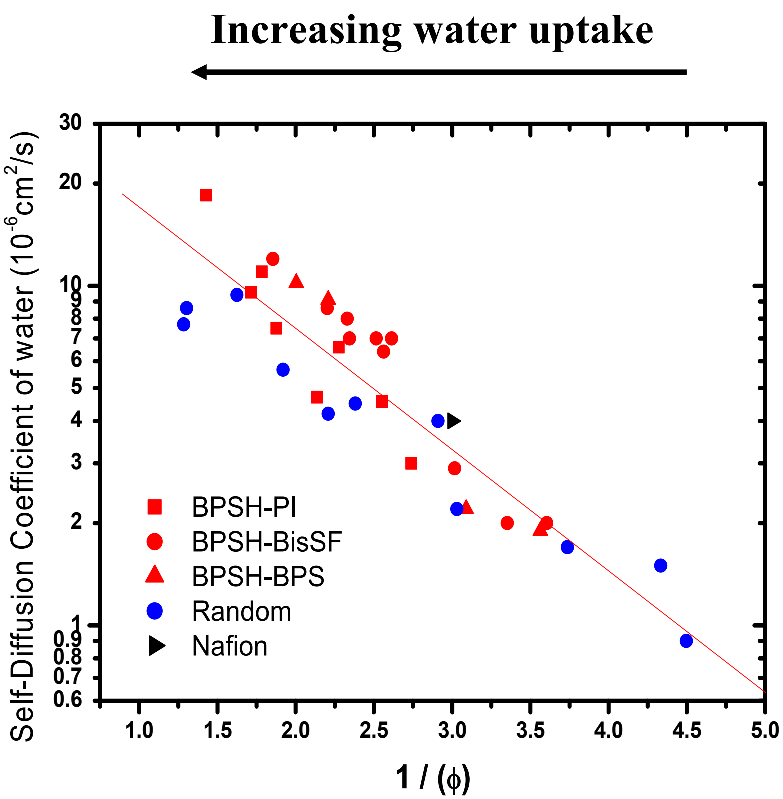
Hydrogen-air fuel cell performance of alternating, random and multiblock aromatic copolymers at 100 °C with Humidification at 70% (top) and 40% (bottom). Nafion 212 is shown for comparison.

Effect of water uptake on proton concentration

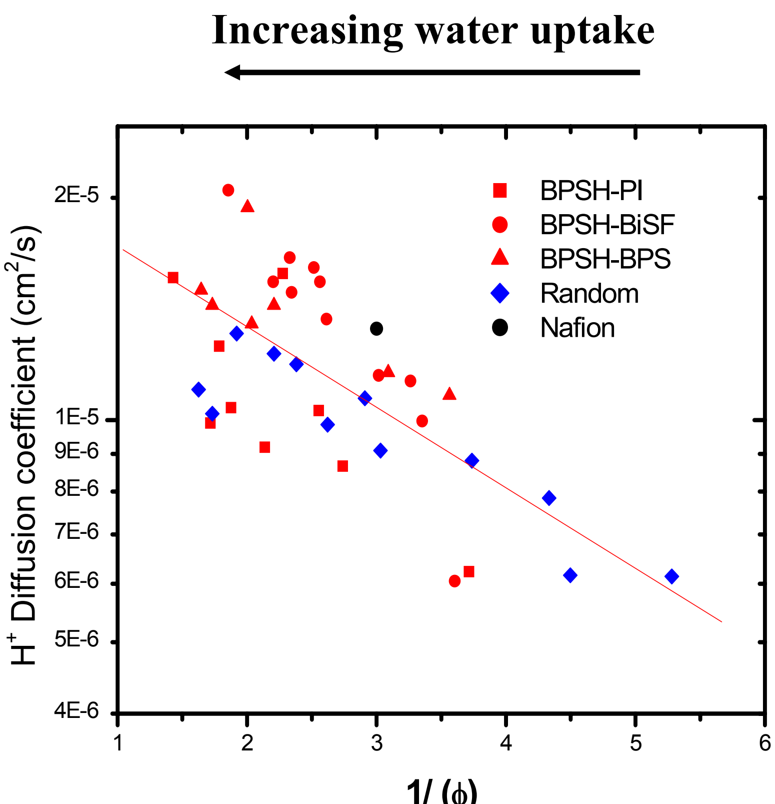


- Effective C_{H^+} theoretically increases with IEC. However water uptake also increases
- Increasing water uptake decreases effective proton concentration
- Hence, C_{H^+} goes through a maxima when plotted against water volume fraction .

Multiblock copolymers have higher water and proton diffusion coefficients than random copolymers



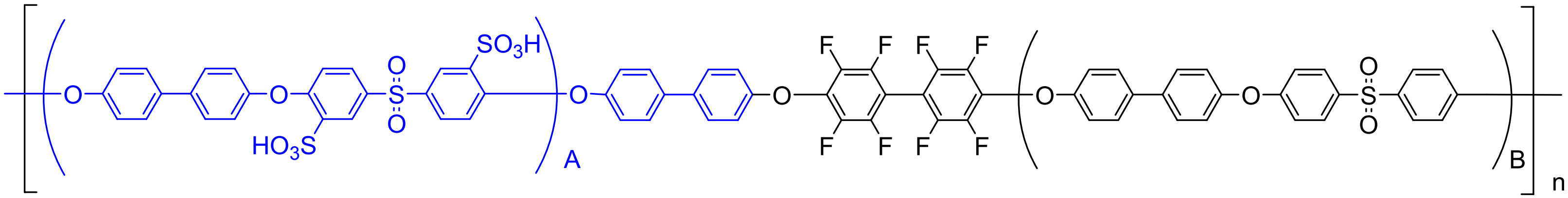
Measured from PGSE NMR, 25 º C



Measured form Impedance method, 30ºC

- Both water and proton diffusion coefficient increases with water volume fraction
- Well connected phase separated morphology of block copolymers results in higher diffusion coefficients than the random copolymers at a given water content

Characterization of the BPSH-BPS Multiblock Copolymers



Block Copolymer[a]	Ion Exchange Capacity (IEC) (meq/g)	Water Uptake (%)	Hydration Number (λ)	Proton Conductivity[b] (S/cm)	E_a Proton transport[c] (kJ/mole)
BPSH35	1.50	36	13.3	0.070	13.3
BPSH3-BPS3	1.33	30	12.5	0.065	14.4
BPSH5-BPS5	1.39	33	13.2	0.088	13.4
BPSH10-BPS10	1.28	60	25.6	0.095	8.12
BPSH-10-BPS-5	**1.83**	**100**	**30.3**	**0.160**	**9.8**
BPSH-15-BPS-10	1.71	90	29.2	0.140	8.9
BPSH-20-BPS-15	1.71	70	22.7	0.120	8.8

a. Acronym : BPSH-x-BPS-y x = Molecular Weight of Sulfonated Poly(arylene ether) in kg/mol
y = Molecular Weight of Poly(arylene ether) in kg/mol

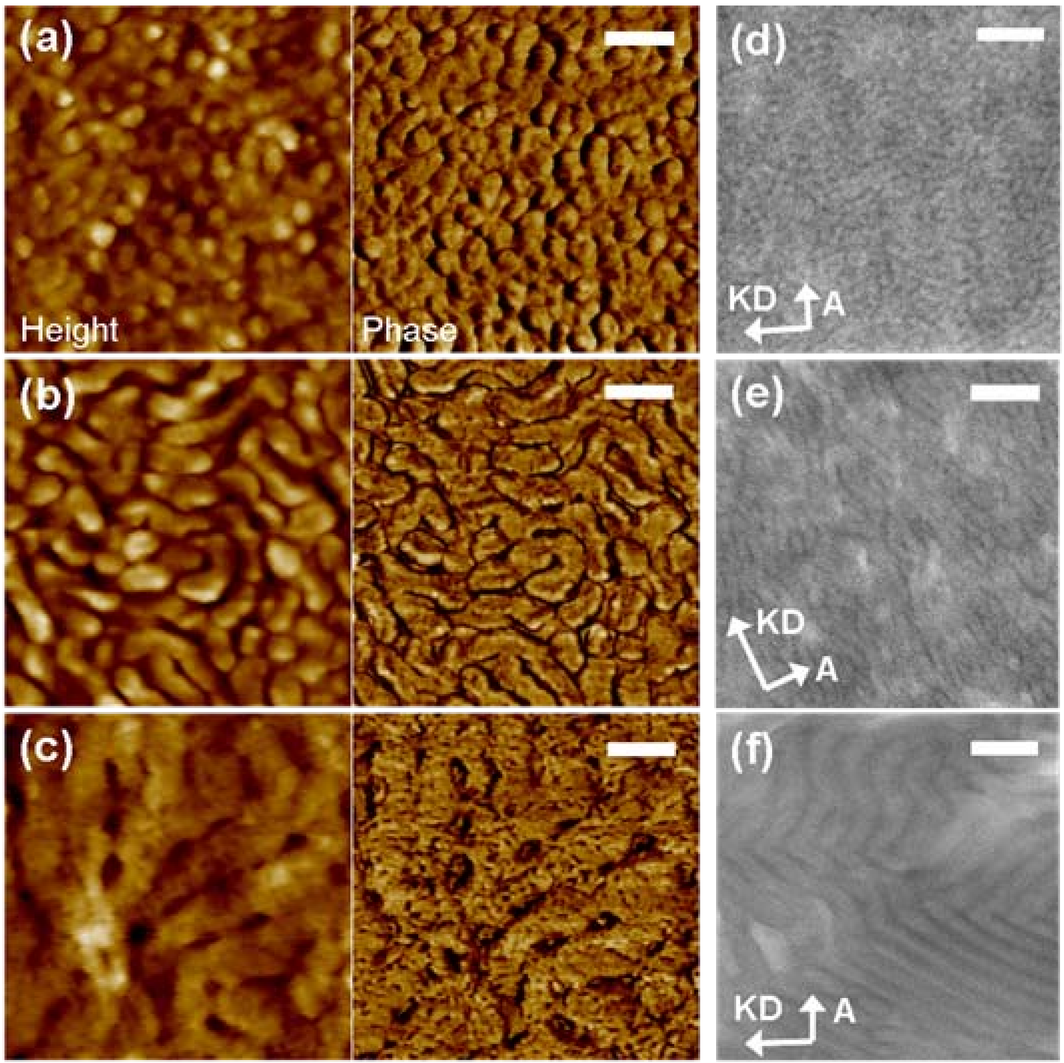
b. Measurements were conducted in water at 30ºC c. Measured in liq water over temp range of 30 to 80 degree C

DFBP series with unequal block lengths

10k-5k

15k-10k

20k-15k



	Proton Conductivity (S/cm)[a]	Water Uptake (%)	I.V. (dL/g)[b]	IEC (meq/g)[c]
10k-5k	0.160	100	0.94	1.83
15k-10k	0.140	90	0.97	1.71
20k-15k	0.120	70	1.12	1.71

[a]At 30 ºC in DI water
[b]In NMP at 25 ºC w/ 0.05 M LiBr
[c]Determined by titration

AFM setpoint ratios: 0.91, 0.95, 0.89; Z ranges: 12, 12, 25 nm and 30°. TEM micrographs: “A” denotes direction of air side. “KD” denotes the knife direction during microtoming. Scale bars = 100 nm.

Reverse Roll Film Casting

- **Ratio of speeds of coating and transporting rolls**

  α =1.5 to 2.0

- **Gap between coating and metering rolls**

  Gap = $(T_w/\alpha)/(\lambda/2) = (1+\rho/c)\ T_d/(\alpha\ \lambda/2)$ (Lubrication model)

  where

  T_w: Thickness of wet films

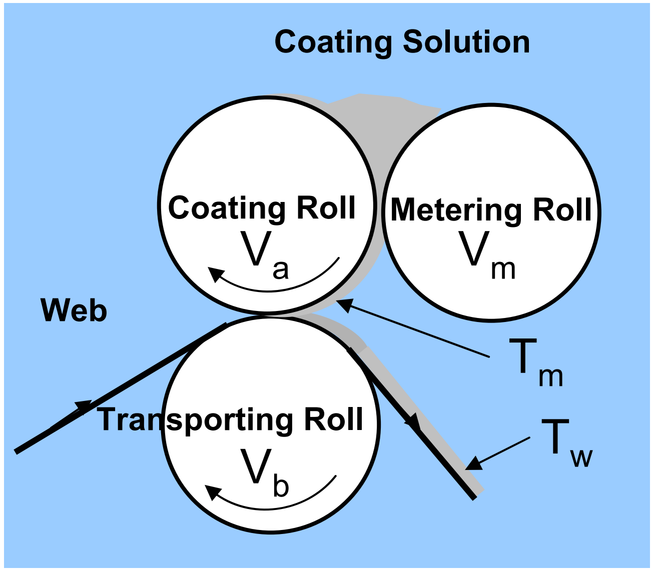
  T_d: Thickness of dry films

  α: Ratio of speeds of coating and transporting roll (wipe ratio)

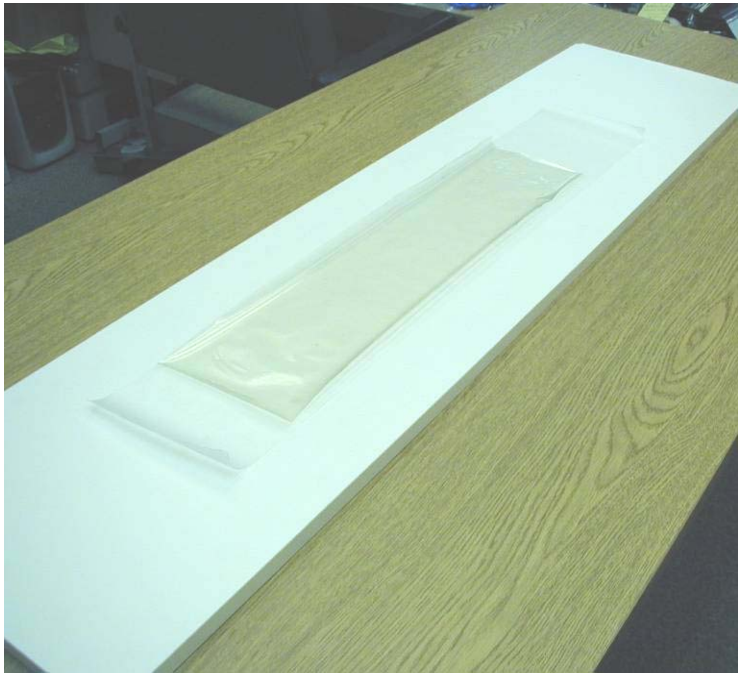
  λ: Dimensionless flow rate between 1.23~1.33

  ρ: Density of the polymer

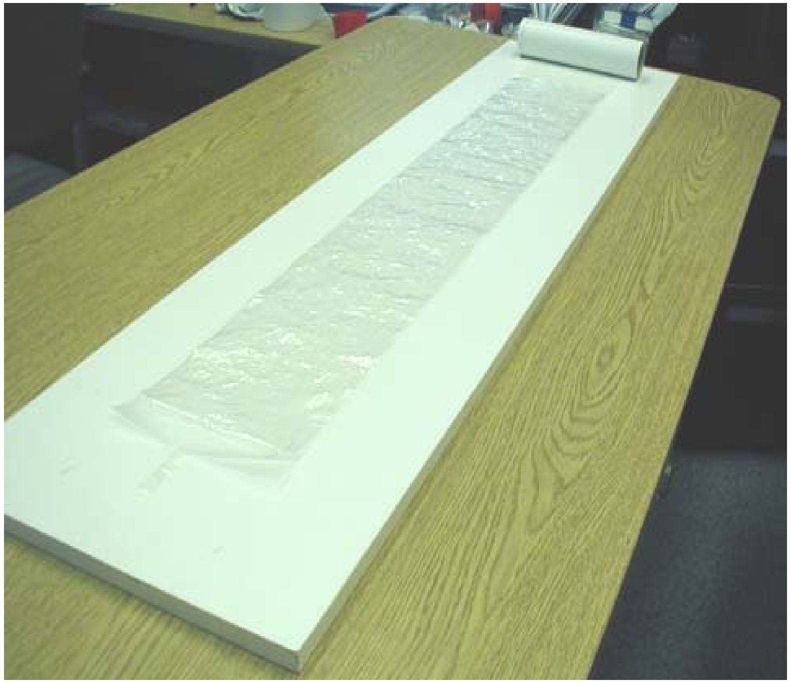
  c: Concentration of casting solution in w/v



Polymer Processing Influences Performance of Continuous Cast Films

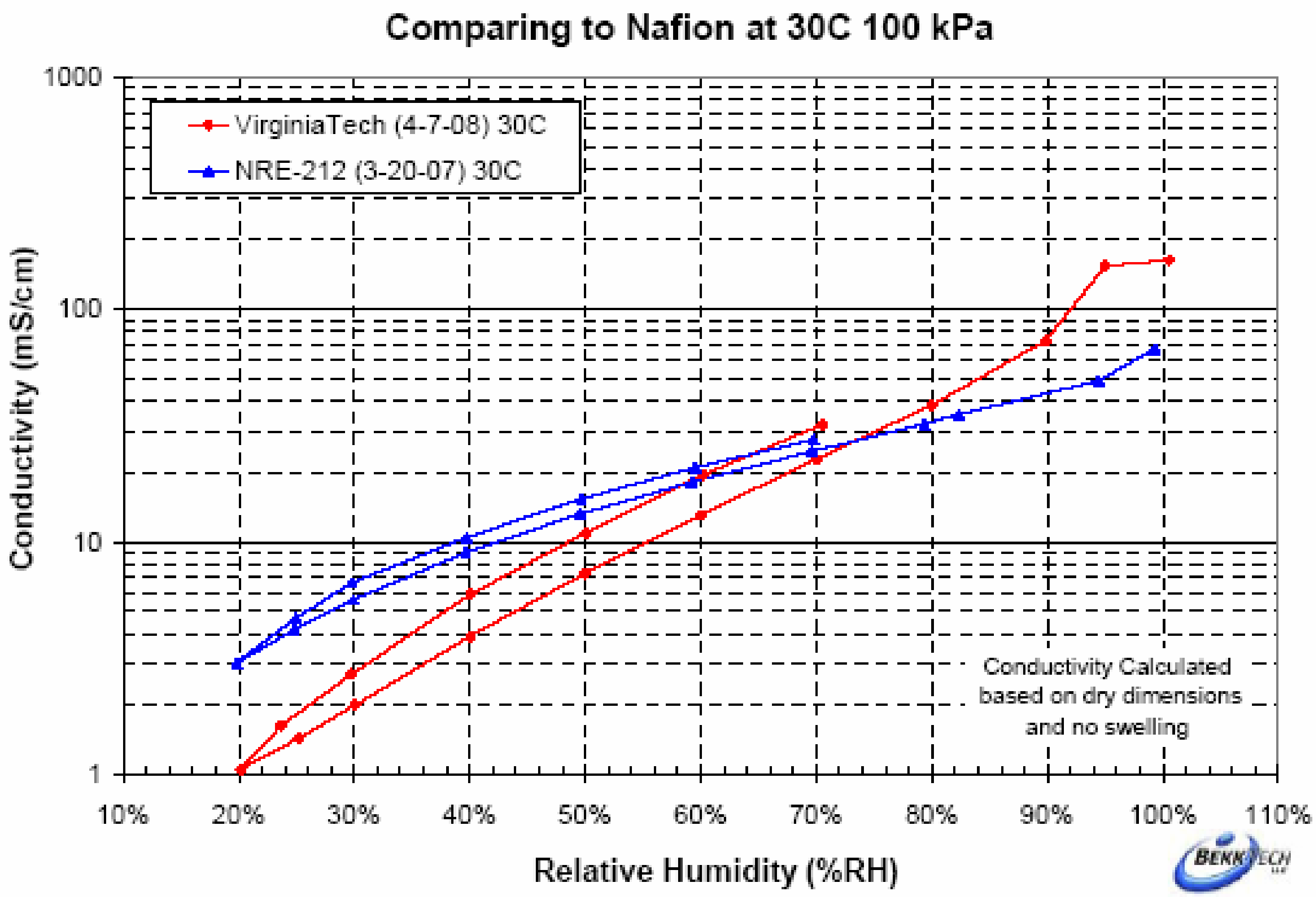


BisSF 17k/12k Block Copolymer Films

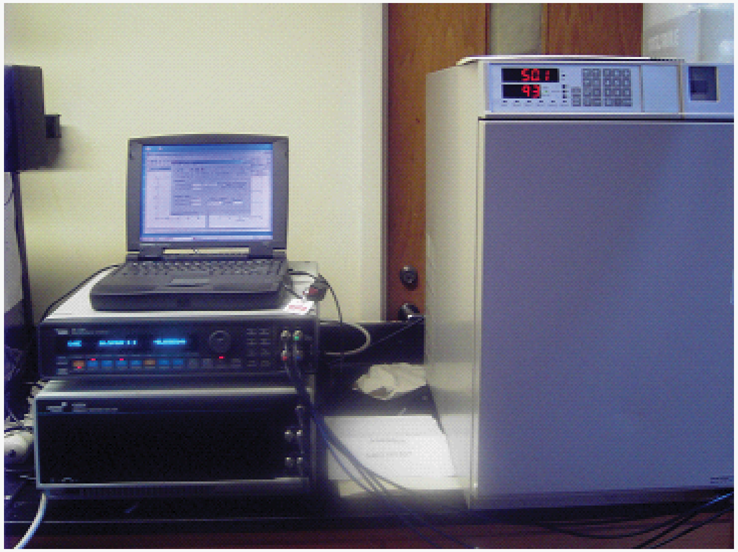


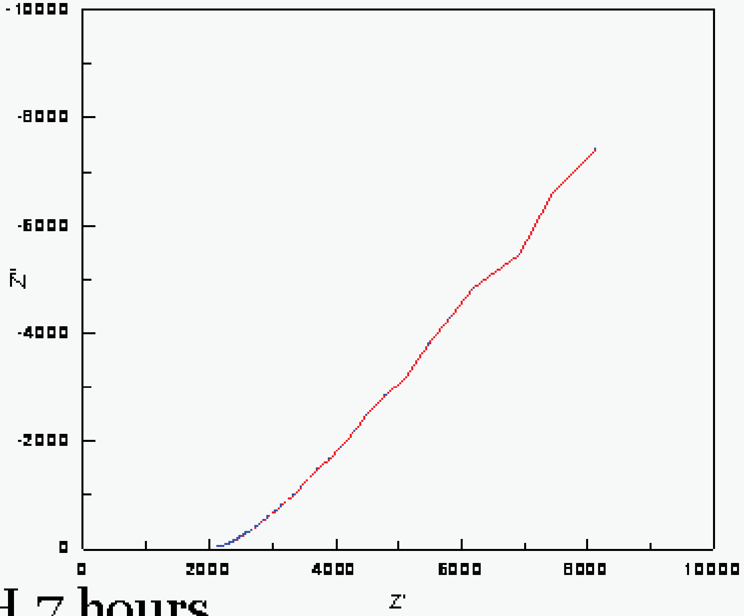
6F40 Random Copolymer Films

Proton conductivity as a function of RH @ 30^{o}C for VT(BPSH-BPS-10-5) sample and NRE212 measured by BekkTech



Proton conductivity at VT as a Function of RH using a ESPEC Humidity Oven and Solartron Impedance Analyzer

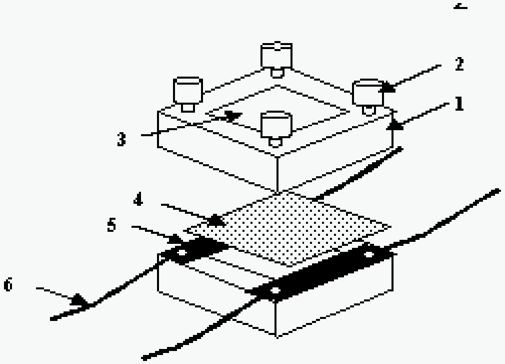




- Membrane conditioned at 30C,70%RH,7 hours

- Conventional RH oven (ESPEC SH240 was used)~ larger equilibration window

BPSH100-BPS-0, 10K-5K



- Step down, from either 95 or 80%RH to 30 % RH
- 4h for each RH(80mS/cm. 80%RH,RT

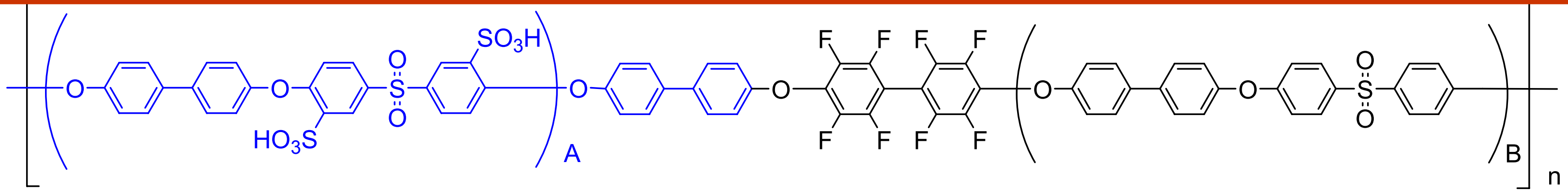
Resistance (ohms)

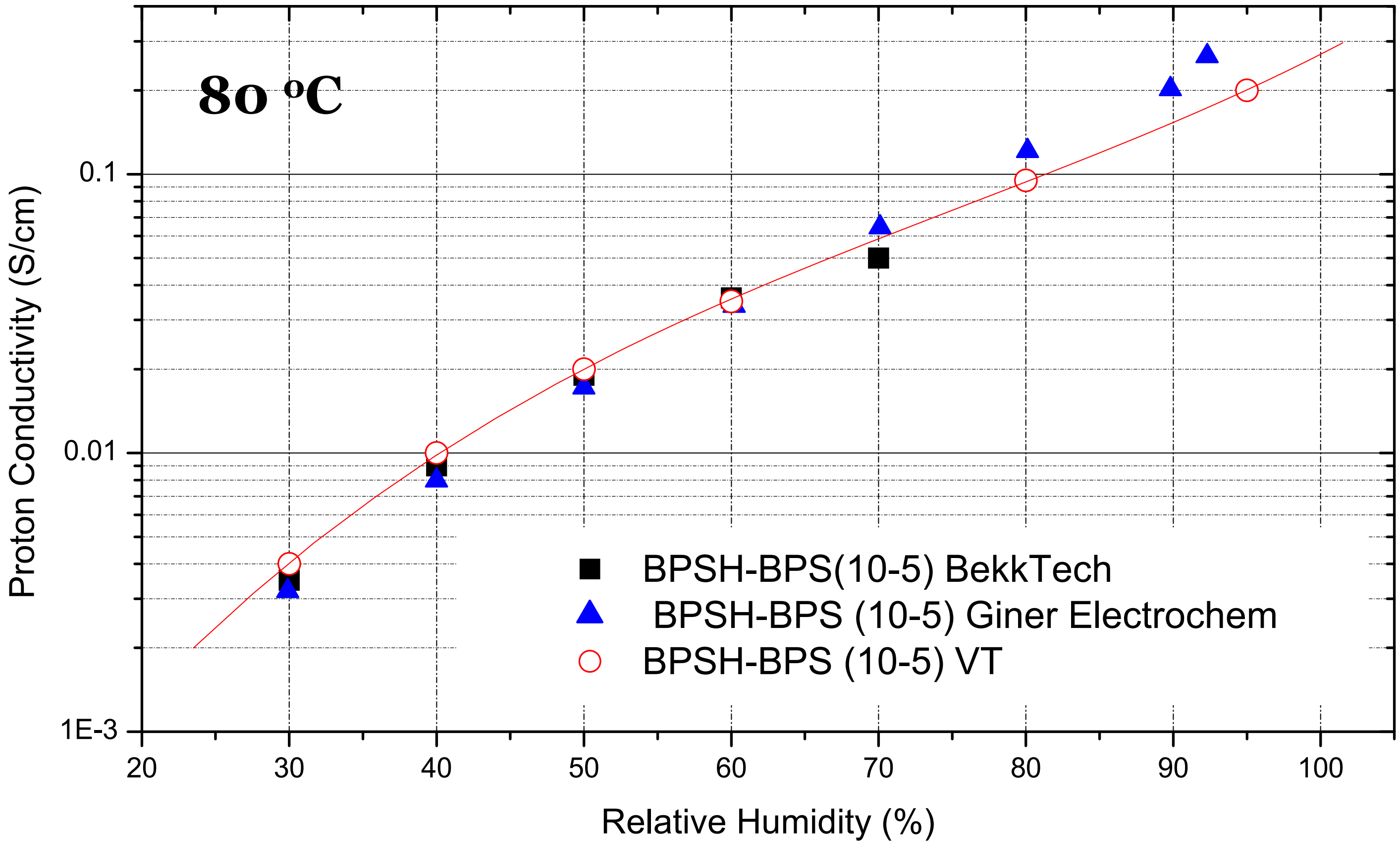
- Changes in thickness with RH considered

$$|Z| = \sqrt{R^2 + (X_L - X_C)^2}$$

Two Point, in-plane electrode method

Comparison of VT Sample (BPSH-BPS-10-5) performance at 80° C between BekkTech, VT and Giner





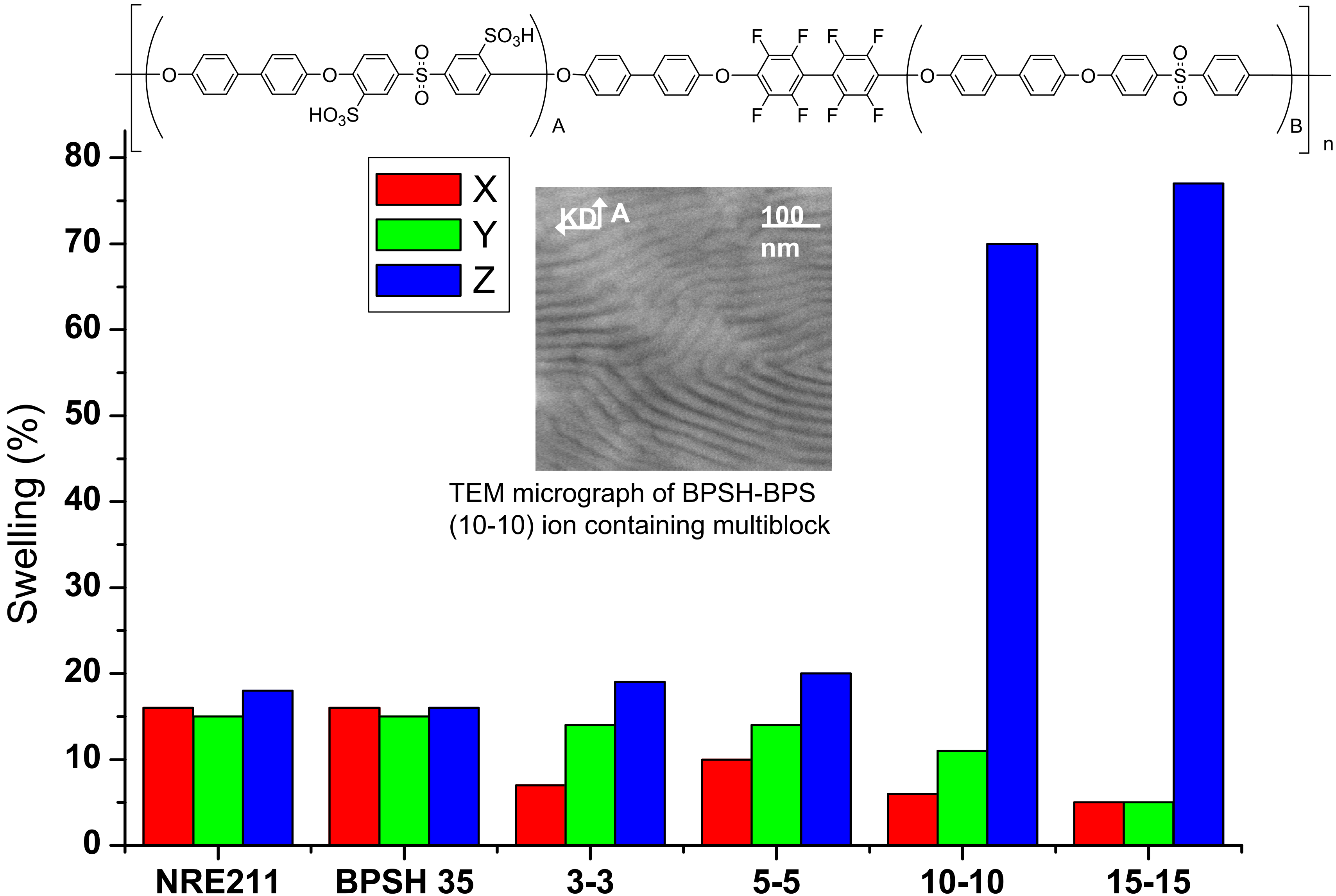
Only step down process is considered.

In case of BekkTech, step down was from 70 % RH , for VT, from 80 %RH

VT perspective on the sample performance

- BekkTech results ~ 38 mS/cm (VT Sample) @ 80 %RH, 30^{o}C, higher than NRE212(~30 mS/cm)
- The value for **VT sample** at 80% RH is expected to be **much higher**, if it was taken during **step-down process**
- "Step-down" gave higher proton conductivity than "step-Up" process for the VT sample ~ differences in vapor phase water absorption and desorption in the sample
- The conductivity value for the BPSH-BPS(10-5) sample is similar to NRE212 up-to 50% RH (considering the step down process) @ 30^{o} C and then drops
- Performance at low RH (~40-20%) may be due to the higher through plane swelling-deswelling nature of the sample.
- Can be definitely improved with longer block length materials and with reasonable swelling-deswelling characteristics

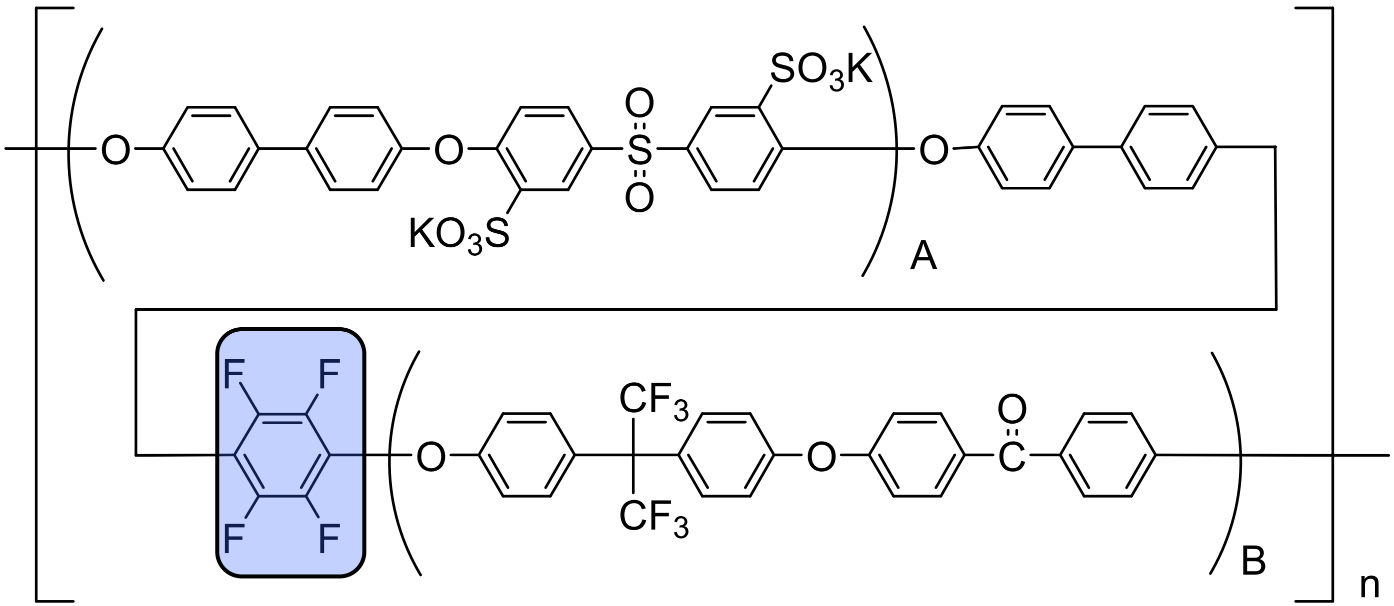
BPSH-BPS Multiblock Copolymers with Higher Block Lengths show Anisotropic Swelling



TEM micrograph of BPSH-BPS (10-10) ion containing multiblock

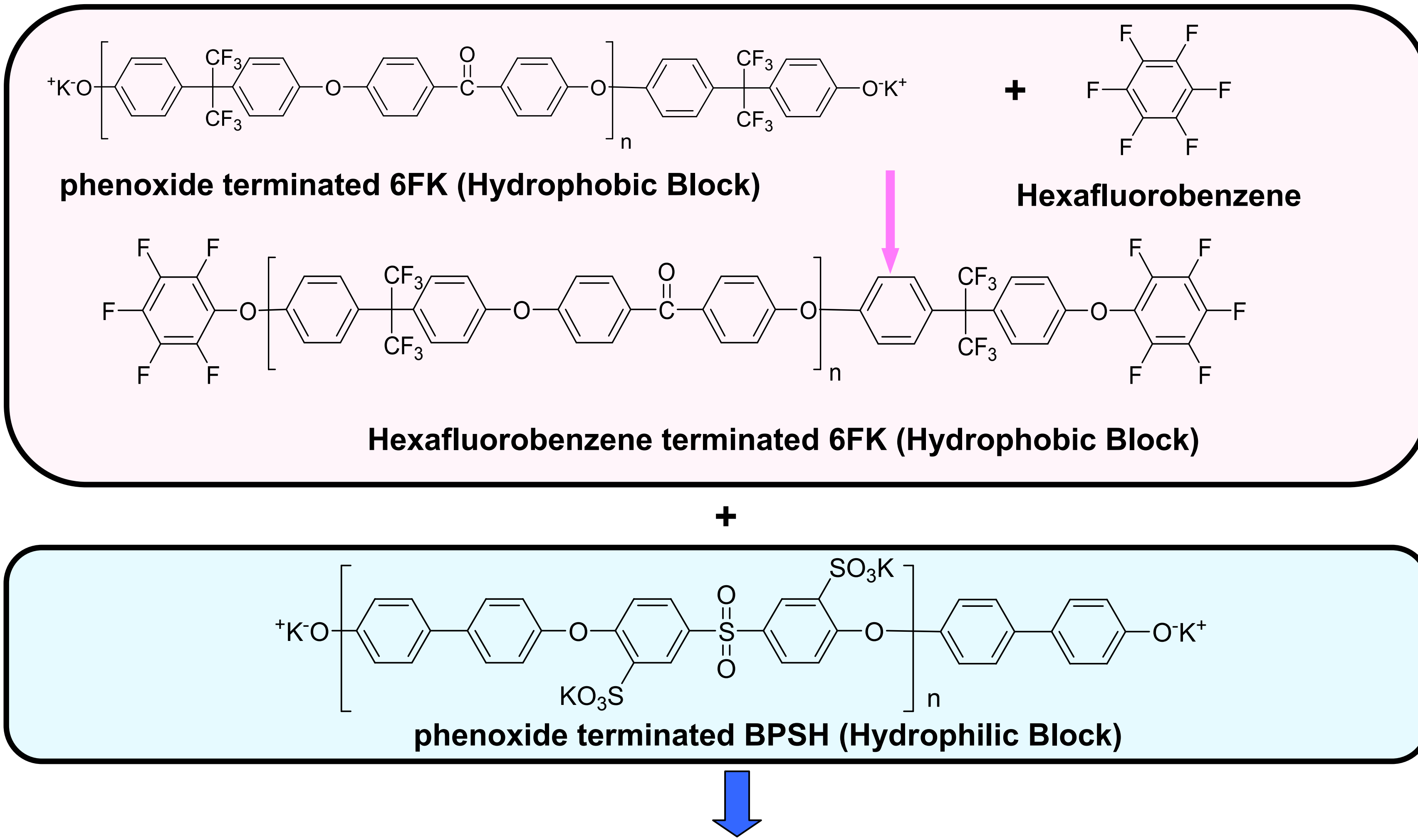
Multi-block Copolymers from BPSH-100 and Amorphous Poly(arylene ether ketone) (6FK)

(larger thermodynamic Xi parameter differential)



BPSH-6FK Multiblock Copolymer with Hexafluorobenzene Linkage Group

Synthesis of BPSH – 6FK Hydrophilic-Hydrophobic Multiblock Copolymers at 100C



~~(Sulfonated Poly(arylene ether sulfone)$_m$)~~ (Partially Fluorinated Poly (ether ketone)$_n$~~

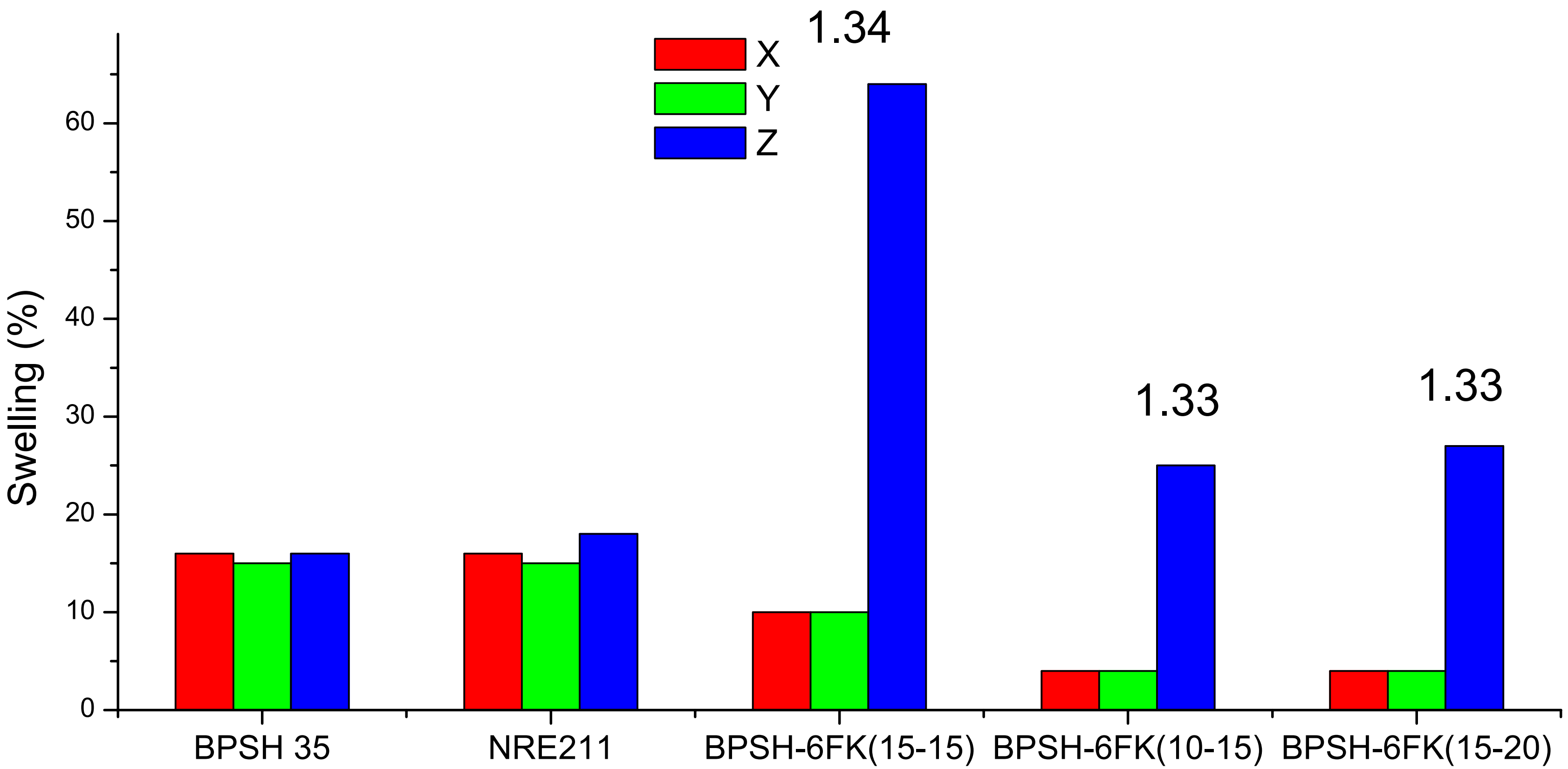
Influence of Unequal Block Lengths on Properties

Copolymer [a]	*Ion Exchange Capacity (IEC) (meq/g)*	*Water Uptake (%)*	*Hydration Number (λ)*	*Proton Conductivity* [b] *(S/cm)*
BPSH20-6FK15	1.70	178	58	0.09
BPSH10-6FK15	1.32	20	8.3	0.07
BPSH15-6FK20	1.33	45	19	0.10
Nafion112	0.9	25	15	0.09

a. Acronym : BPSH-x-6FK-y, x and y block lengths in kg/mole of hydrophilic and hydrophobic respectively

b. Measurements were conducted in water at 30ºC

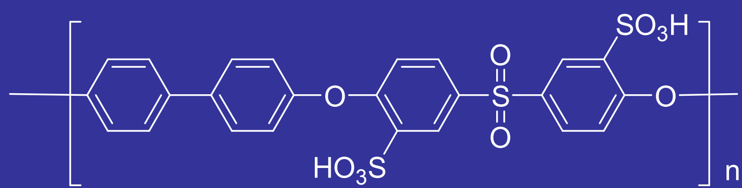
Significant Reduction in in-Plane Swelling can be Achieved by Increasing the Fraction of the Hydrophobic Block



The numbers represent IECs in meq/g

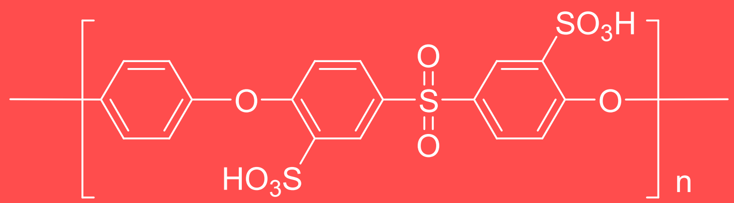
Current and Future Research: Hydroquinone-Based Hydrophilic Oligomers

BPSH 100



IEC = 3.31 meq/g

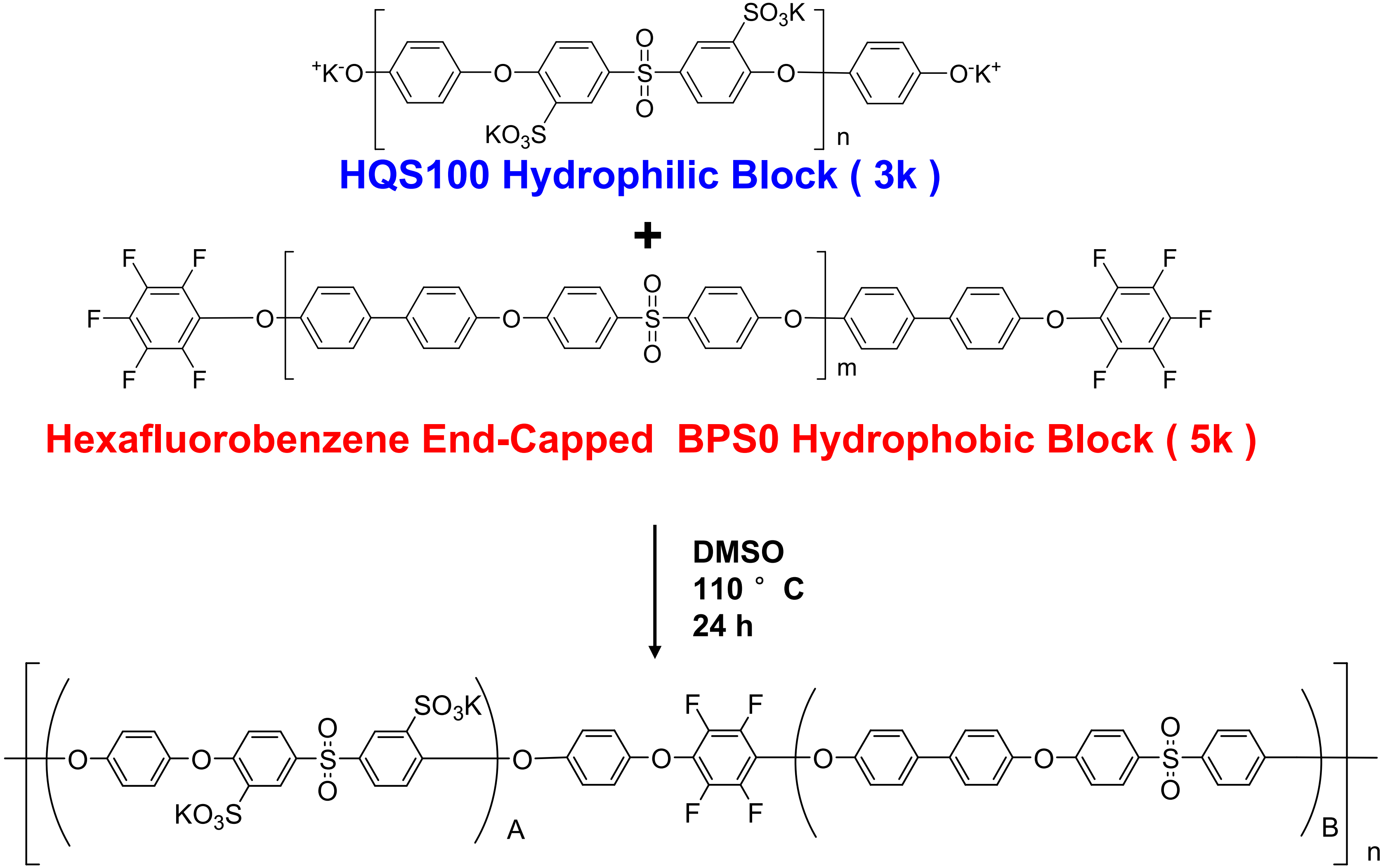
HQSH100



IEC = 3.78 meq/g

- **HQSH100 is more hydrophilic than BPSH100 (Higher χ parameter → Sharper Phase Separation)**
- **At the same IEC value, the HQSH100 system uses more hydrophobic segments →lower water uptake**
- **Hydroquinone is cheaper than biphenol**

Synthesis of Multiblock Copolymer HQSH-BPS Via Activated Hexafluorobenzene Coupling and Mild Reaction Conditions



HQSH-BPS multiblock copolymer (3k - 5k)

Conclusions

- Multiblock copolymers based on polyimides or hydrocarbon, partially or highly fluorinated hydrophobic blocks were prepared by coupling activated aryl fluoride ends with very hydrophilic BPSH-100 under mild reaction conditions to produce mechanically tough films and highly ordered morphologies by AFM and TEM.
- Proton conductivity and water self diffusion coefficients increased with block lengths and with the "sharpness: of the nanophase separation
- Cooperation with LANL produced MEA's with conductivity comparable to Nafion 212 at 100C and 40%RH
- Unequal block length materials with higher hydrophobic block lengths also show anisotropic swelling which correlates with the ease of self assembly, affording higher conductivity at lower RH values
- 80mS/cm on one block copolymer was demonstrated at 80%RH and 30C at VT; lower behavior at Becktech could be rationalized by comparing conditioning procedures and extending the data range using independent VT, Giner and Becktech Data

Future Research

- Continue ongoing efforts with LANL and others for understanding chemical structure-processing property relationships in PEM block copolymers and what controls conductivity at low RH
- Investigate new 6FK-0-HQ100 multiblock copolymers utilizing hexafluorobenzene mediated endlinking and mild reaction temperatures
- Swelling-deswelling features of the block copolymers and its possible connection to the most desirable modulus and water swelling values to maximize fuel cell durability
- Scale up Selected Block Copolymer PEM's, Continuously Cast into films via Reverse Roll Coating
- Further Develop Film Casting Expertise for the Multi-Block Copolymers (modeling, time, temperature, substrate, concentrations, dispersion casting, morphology development relationships with conductivity)