

2009
DOE Hydrogen Program
Merit Review Presentation



Advanced Materials for Proton Exchange Membranes

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OVERVIEW

Timeline

- Project Start Date: May 2006
- Project End Date: March 31,2009
- Percent Complete: 100%(no cost extension through July)

Barriers

- Conductivity at 120°C and low RH

Budget

Total Project Funding: \$950,949
Funding received in FY08: \$350,000
Funding received in FY09: \$150,949

Partners

- Los Alamos National Labs
- Giner Electrochemical Systems
- Arkema
- Akron Polymer systems

2009 McGrath Group



Back Row: Rachael VanHouten, Dr. Desmond VanHouten, Harry Lee, Ozma Lane, Dr. Gwangsu Byun
Front Row: Dr. Ruilan Guo, Yu Chen, Prof. James E. McGrath, Dr. Chang Hyun Lee (Missing: Natalie Arno)

Fuel Cell Research Strategies May 2009

Synthesis (VT), (Akron Polymer Systems (APS) can Scale Up to Multi-Kilogram Quantities)



Characterization
(McGrath/Moore/Madsen) (VT)



Processing
(VT, Baird)



Fuel Cell Testing
(LANL ,DOE/ Bekktech, Arkema, Giner, VT)



Sample Films

- DOE LANL and Contractors (Arkema. Giner)

Required Properties for a High Performance Polymeric Electrolyte Membrane(PEM); where do we stand after 3 years?

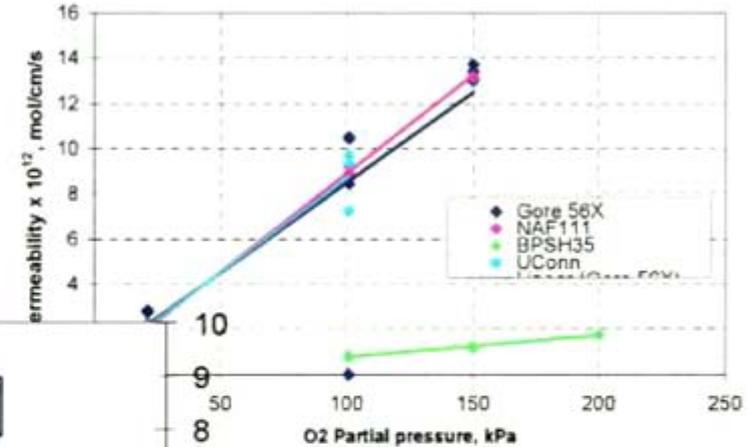
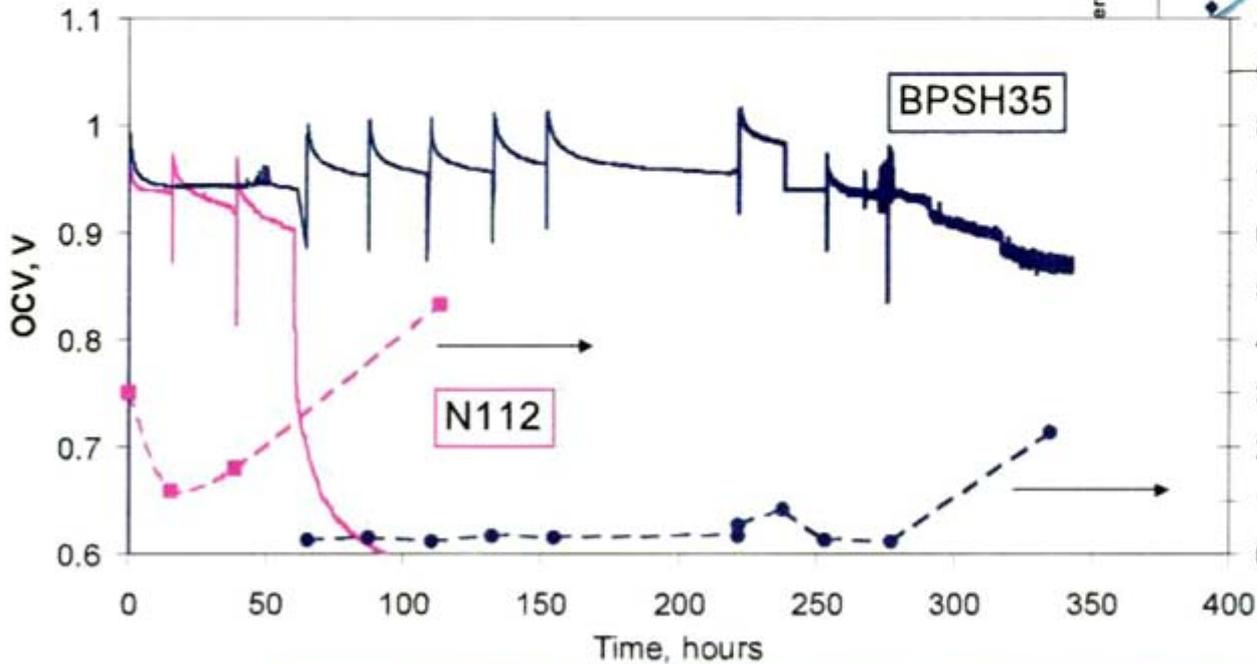
- Low fuel and oxidant permeability
- ✓ Oxidative and hydrolytic stability
- ✓ Appropriate water uptake
- ✓ Good mechanical properties both in the dry and hydrated state
- ✓ Low x, y Dimensional Swelling
- ✓ Fabrication into Robust Membrane Electrode Assemblies (MEAs)
- ✓ Cost, Processibility, Manufacture

- ✓ High protonic conductivity, even at low relative humidity

BPSH Hydrocarbon Membranes Outperform PSFA Membrane (Nafion®) in Open Circuit Voltage (OCV) H₂/O₂ Accelerated Tests at 100°C

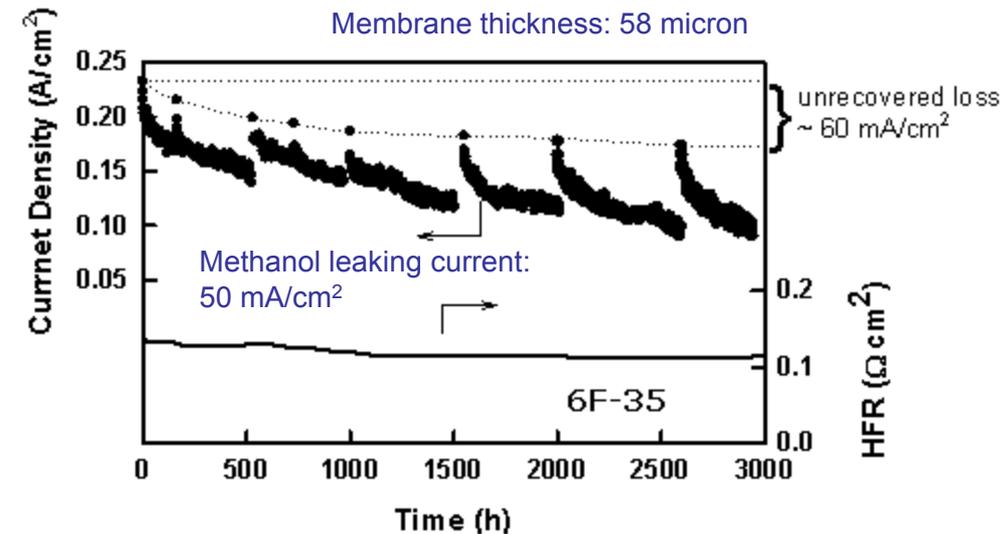
- BPSH O₂ permeability is 10x lower than that of PSFA-like membrane - significantly increases durability

Accelerated Membrane Degradation Test



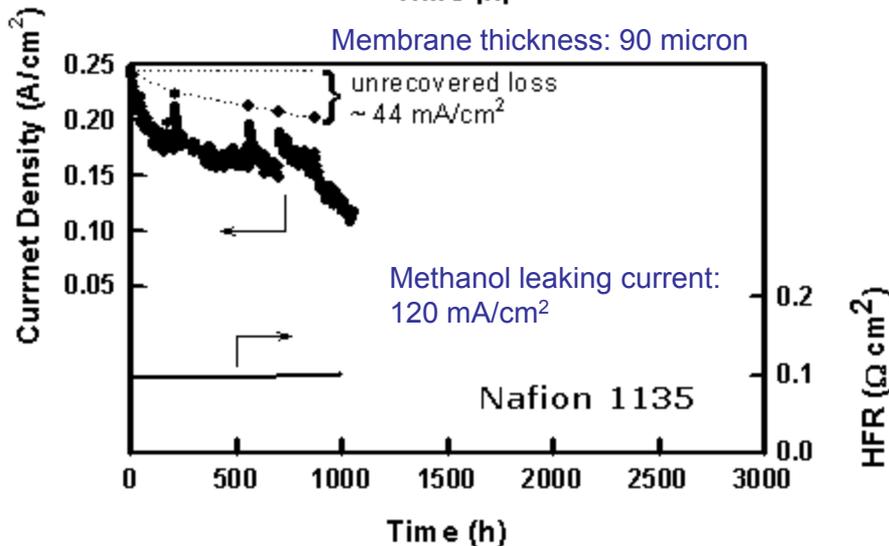
Accelerated Membrane Degradation Test Conditions:
 100°C, 25%RH,
 1.5atm
 H₂/O₂

Long-Term Performance of Interface In Cooperation with LANL



Interface optimized non- Nafion[®] membrane (6F-35) exhibited stable long-term performance* with decreasing cell resistance under DMFC conditions

Performance loss after 3000 h life test for 6F-35 was 60 mA/cm², which was comparable to that of state of the art Nafion[®] MEA.

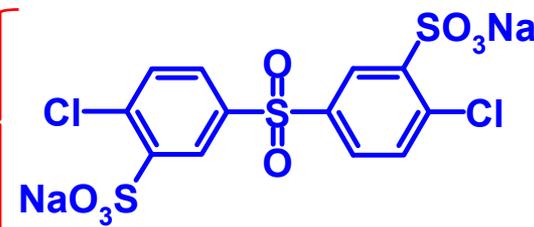


**2005 technical target for MEA durability
10% loss after 2000 h at < 80°C under
H₂/air conditions*

Considerable Flexibility is Possible for Specific Membrane Applications

Key monomer

Disulfonated monomer



Random copolymers

sulfonation level, comonomer type & amount

Cross-linked copolymers

crosslink density

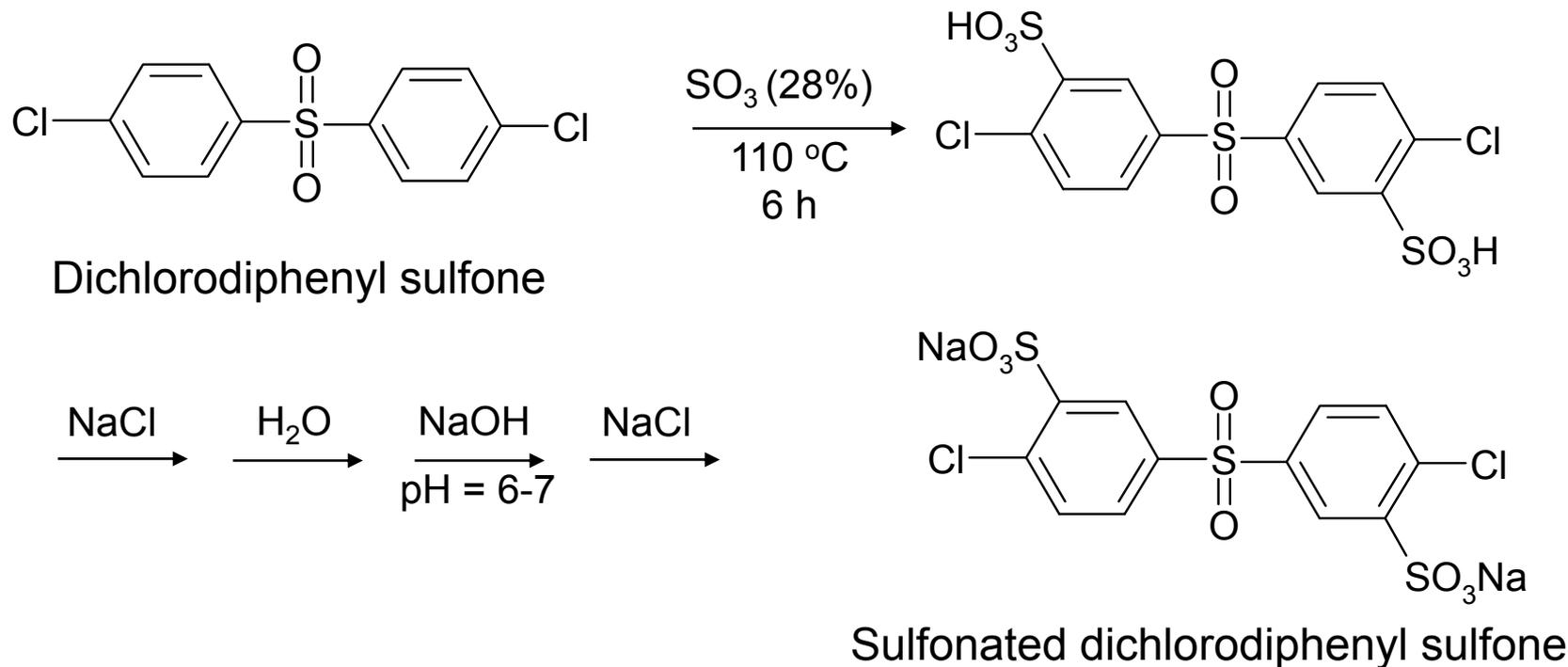
Blends

Hydrophilic /hydrophobic balance

Block copolymers

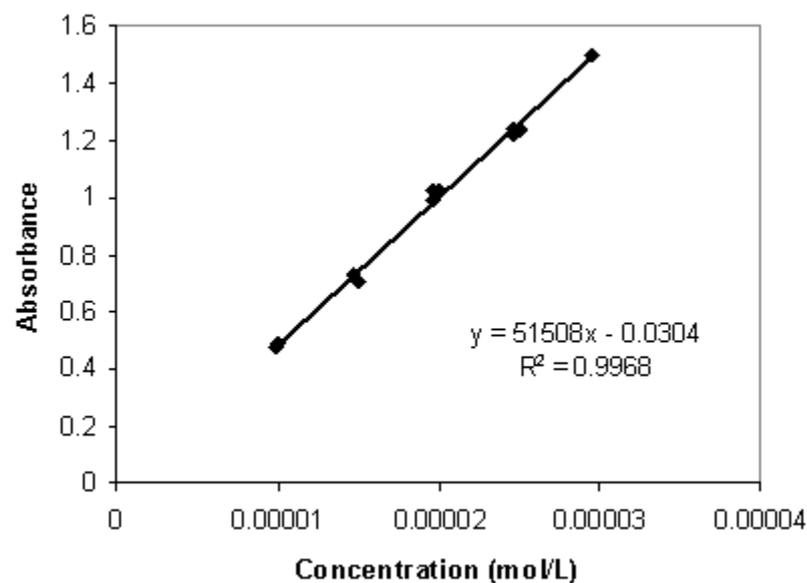
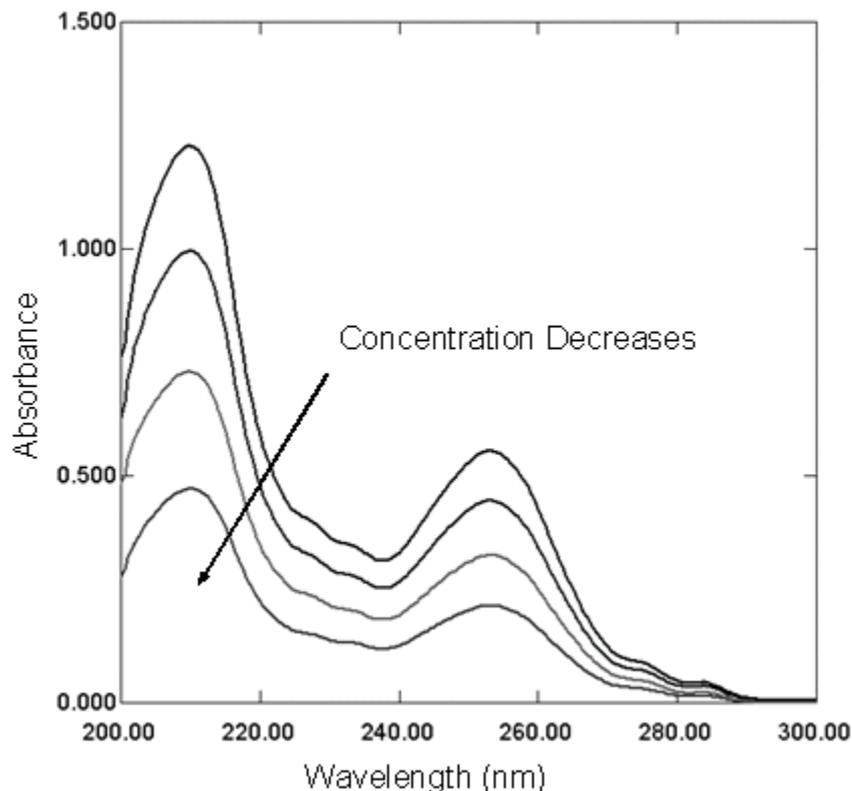
Monomer sequence

A Scalable (> 2 kg) One Step Synthesis of 3,3'-Disulfonated 4,4'-Dichlorodiphenylsulfone (SDCDPS) Comonomer has been Demonstrated



- The starting monomer is produced by Solvay Advanced Polymers
- The only impurity that remains in the comonomer is salt; yield ~100%

SDCDPS Purity using UV-Visible Spectroscopy Has Allowed Copolymer Synthesis using Pilot Plant Comonomer

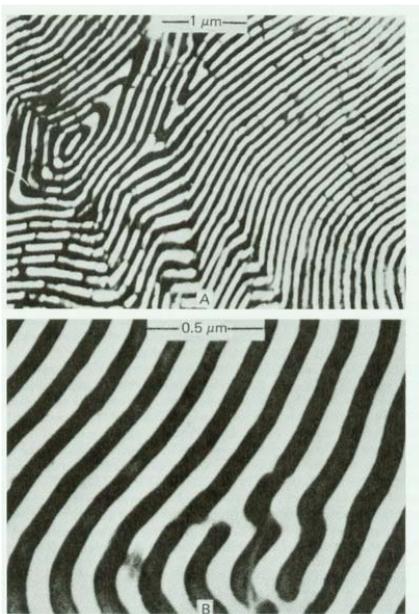


Beer's Law: $A = \epsilon bc$

A calibration curve was developed using solutions of various known concentrations of highly purified SDCDPS in methanol

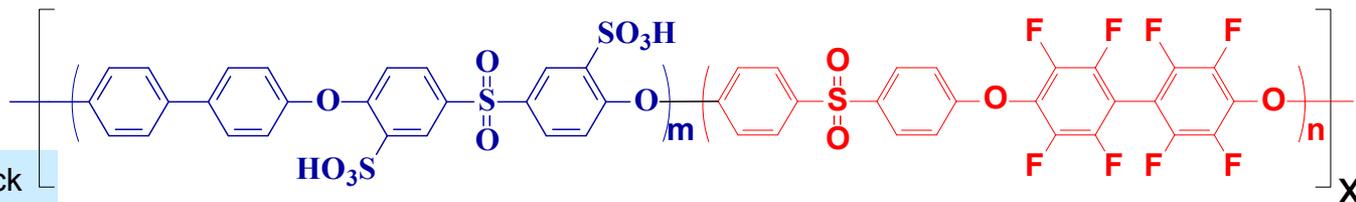
Li, Y.; VanHouten, R.; Brink, A.; McGrath, J.E. Purity Characterization of 3,3'-Disulfonated-4,4'-Dichlorodiphenyl Sulfone (SDCDPS) Monomer by UV-visible Spectroscopy. *Polymer*, **2008**, 49, 3014-3019.

Highly Hydrophobic-Hydrophilic Multiblock Copolymers



- Nanophase-separated morphology can be precisely controlled through synthesis.
- Enhanced water diffusion, conductivity and better mechanical strength with thinner films are possible.

Our Initial work:



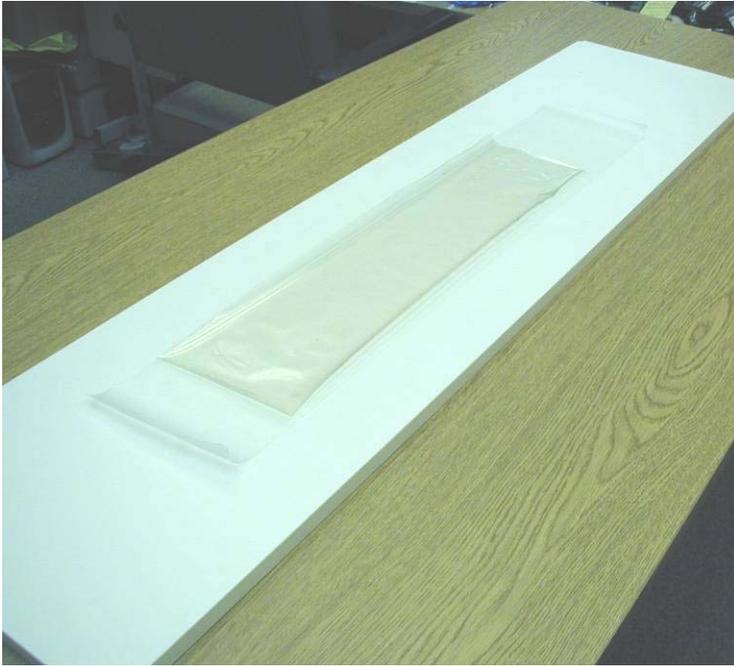
Hydrophilic segments, provides Flux

Hydrophobic segments, imparts mechanical integrity

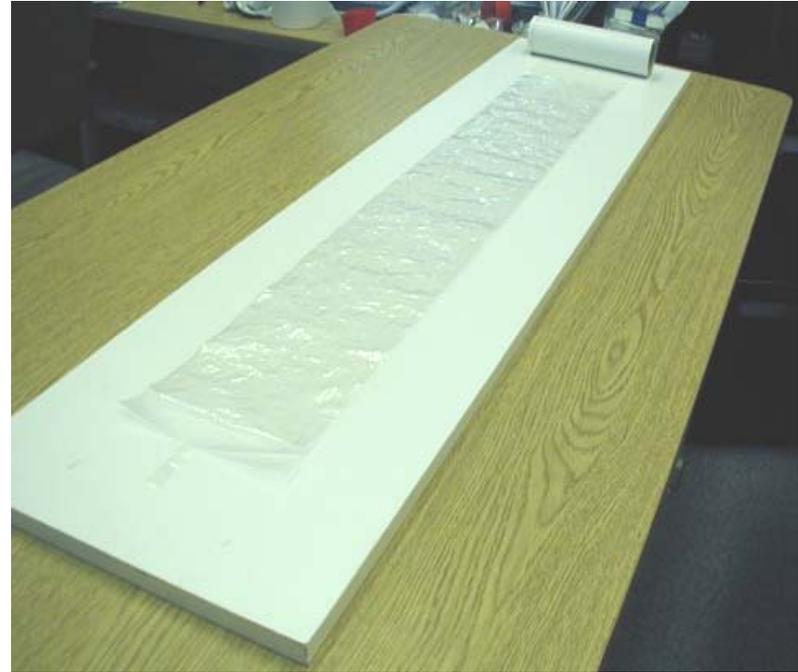
A. Noshay and J. E. McGrath, "Block Copolymers: Overview and Critical Survey," Academic Press, New York, January 1977, p.91. an S-B diblock copolymer

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.

Polymer Processing of Continuous 20 Micron Cast Films has been Demonstrated from both Solutions and Aqueous Dispersions

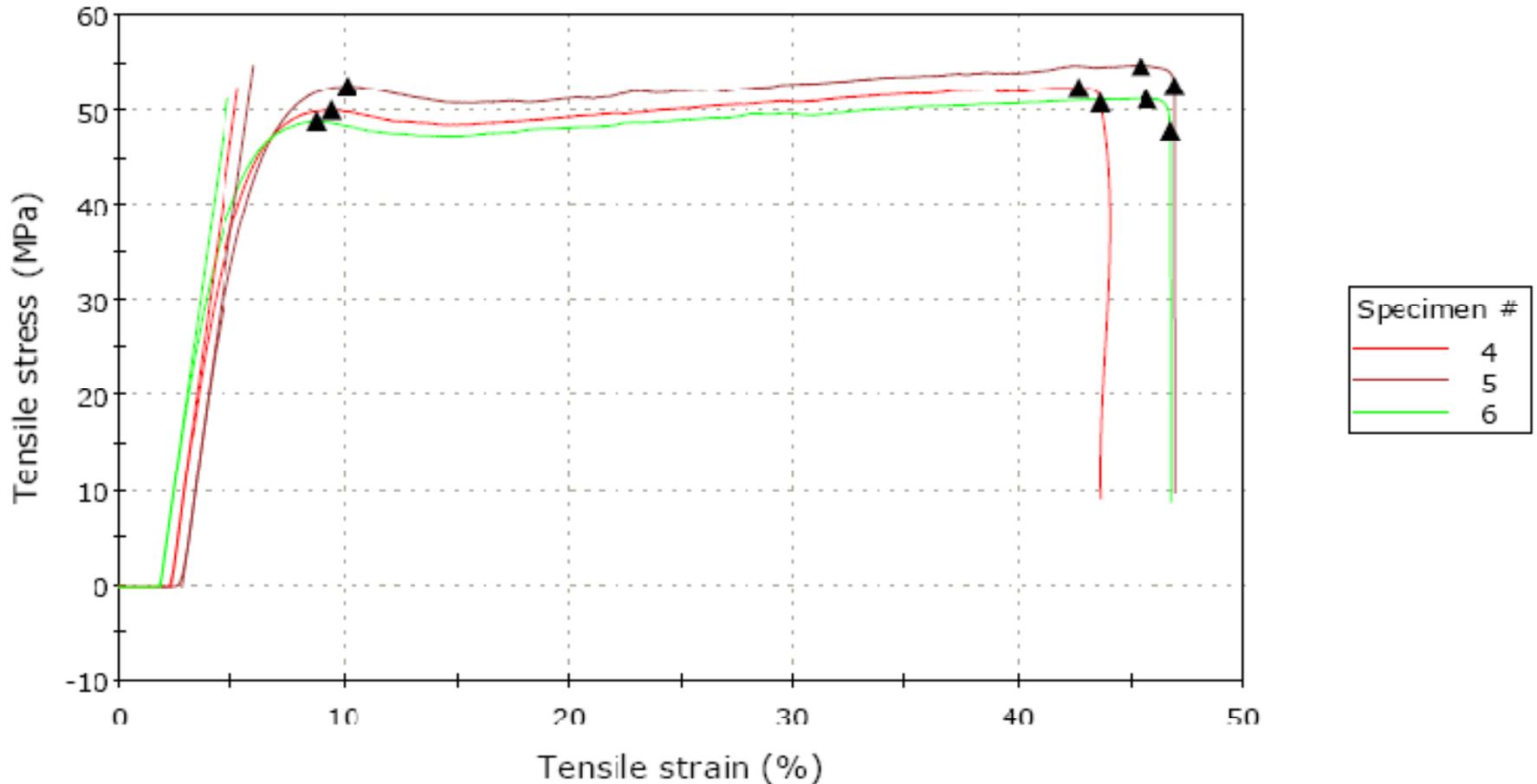


BisSF 17k/12k Block Copolymer Films

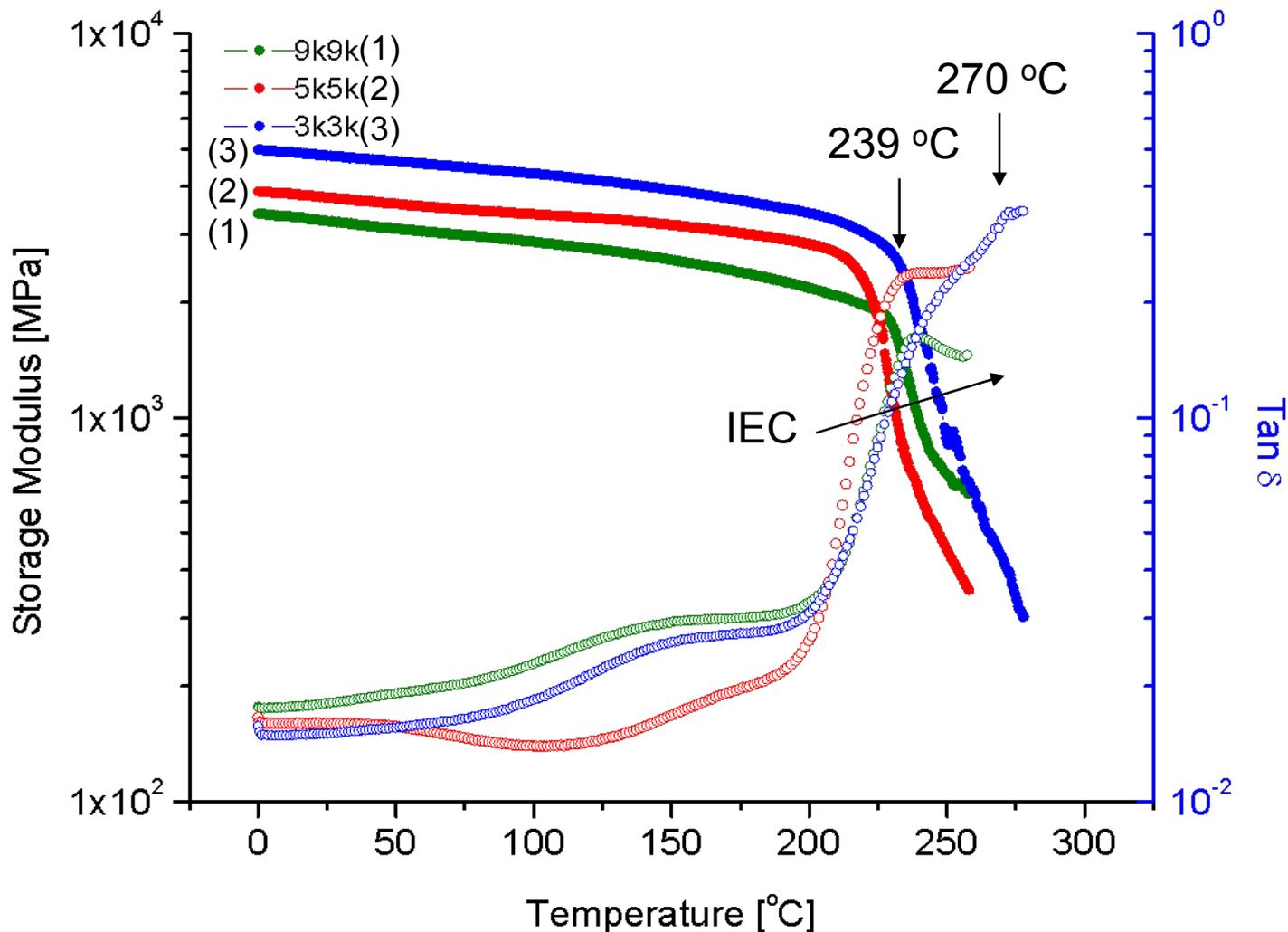


6F40 Random Copolymer Films

BisSF-BPSH100 Block Copolymer Yields Tough Films,

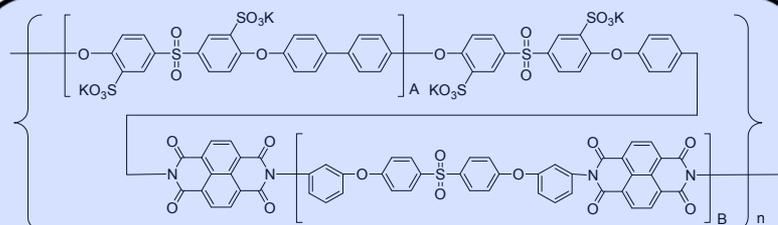


Segmented BisSF-BPSH100 Copolymers Show Good Modulus Temperature Behavior



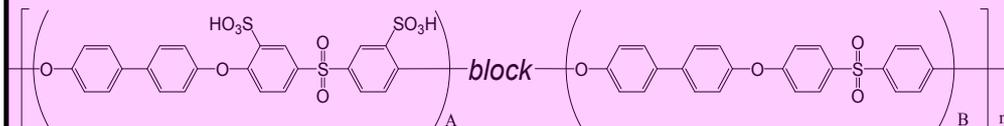
*Acid form; dried for 10 minutes at 180 °C prior to run; 5 °C/min

Self Assembling Nano-Phase Separated PEM Morphologies Improve Proton Conductivity



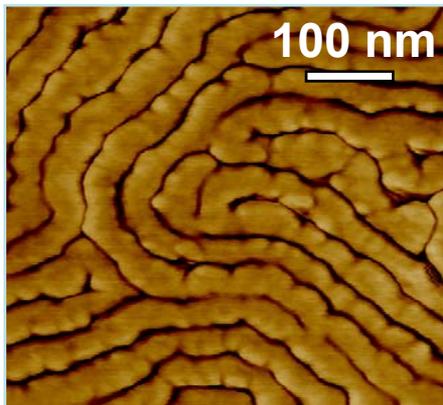
BPSH – PI Multiblock Copolymer

HS Lee, JE McGrath et al, *J. of Pol. Sci.:* 45, 4879 (2007)

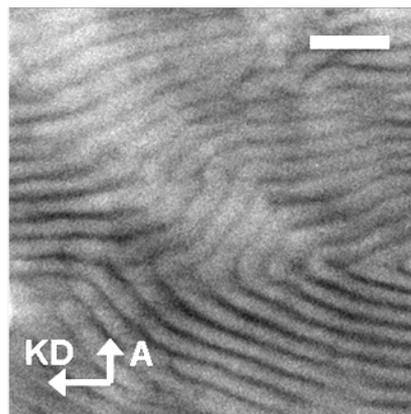


BPSH – BPS Multiblock Copolymer

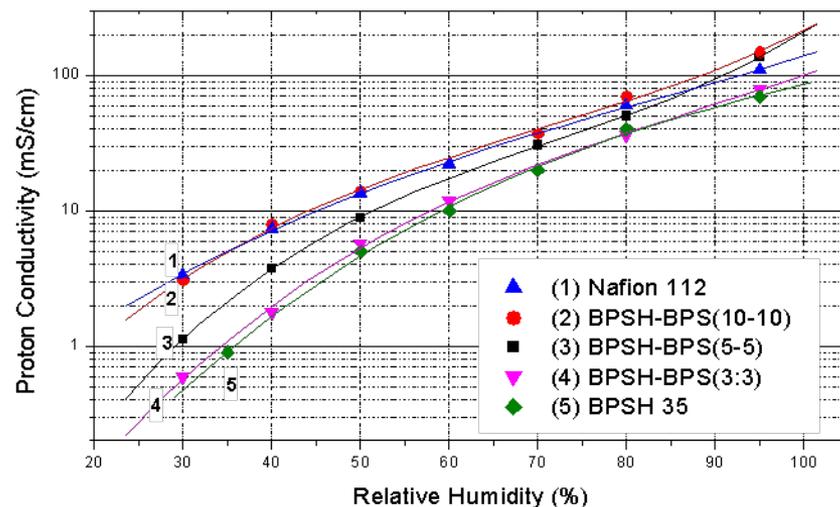
HS Lee, JE McGrath et al, *Polymer*, 49 (2008), 715-723



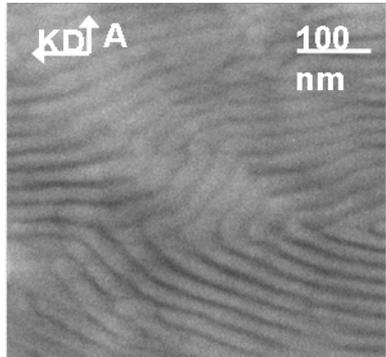
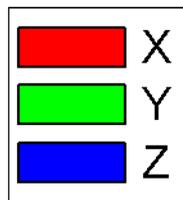
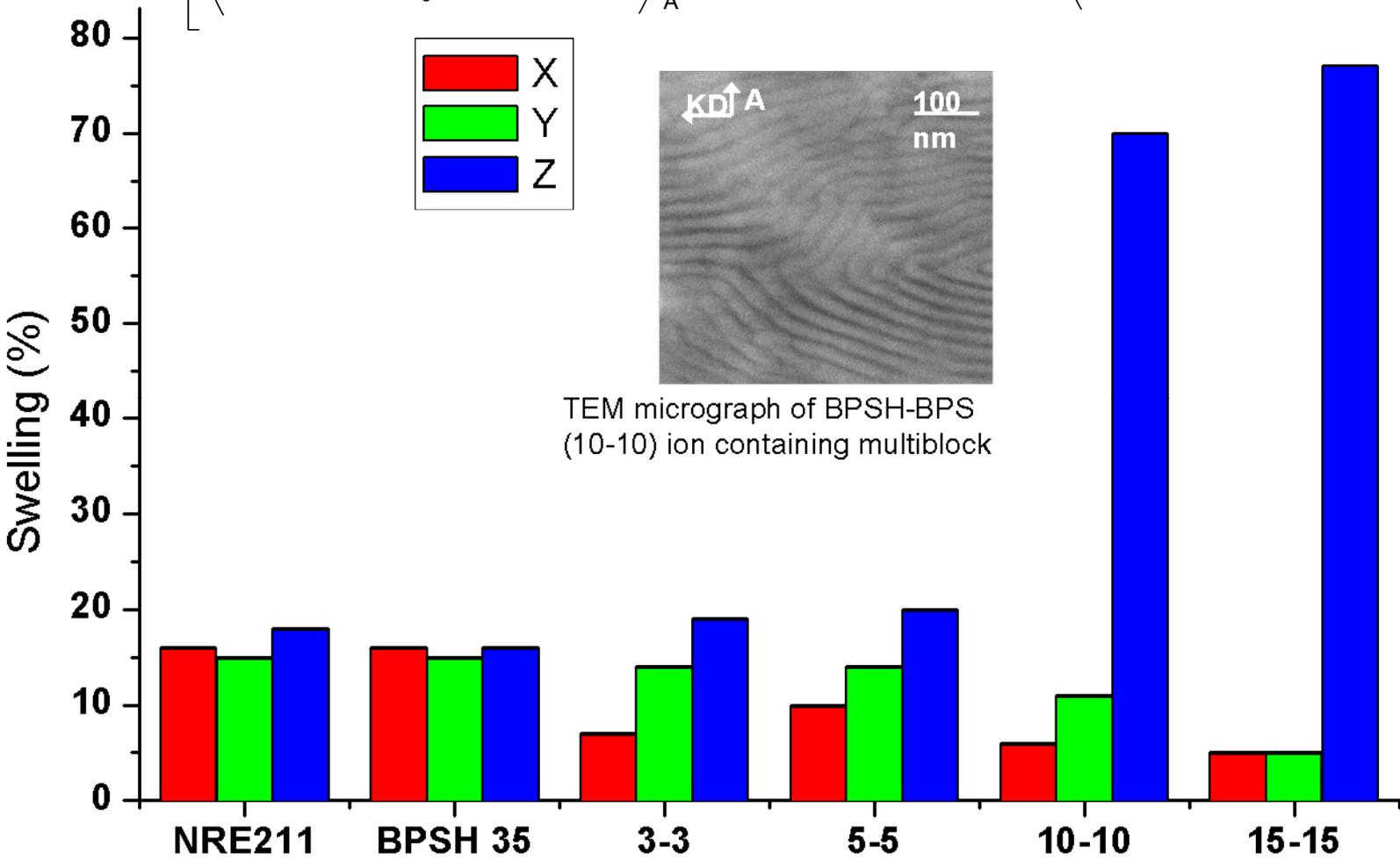
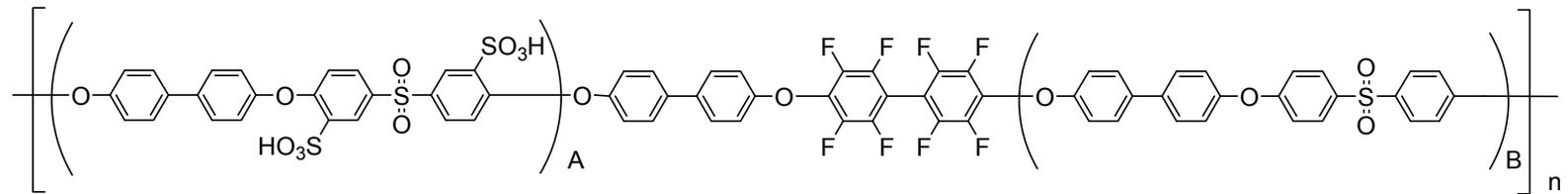
AFM Phase Image of
BPSH-PI (15k-15k)



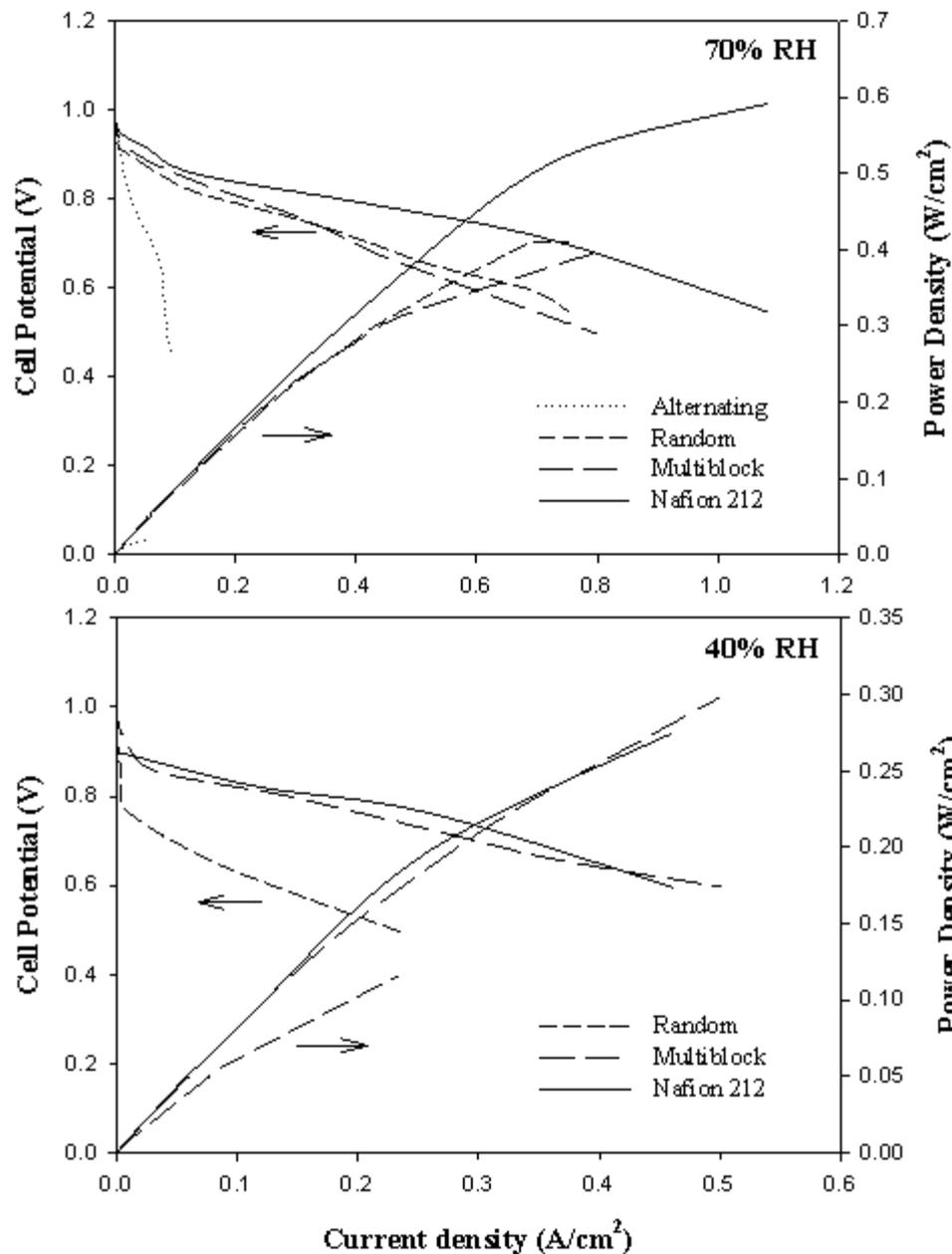
TEM Image of BPSH-BPS
(10k-10k) Stained with Cesium



BPSH-BPS Multiblock Copolymers with Higher Block Lengths show Low X,Y Swelling

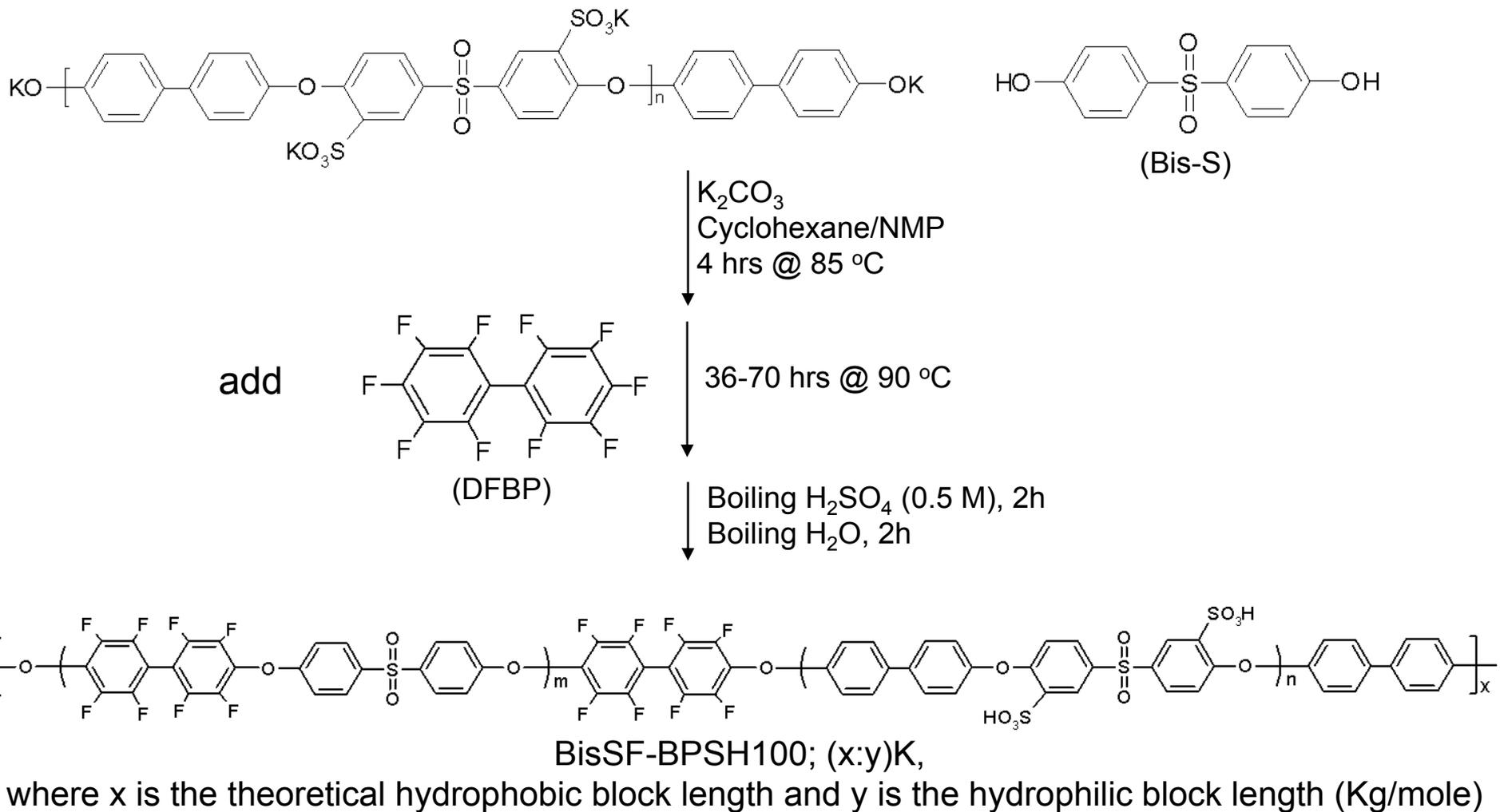


TEM micrograph of BPSH-BPS (10-10) ion containing multiblock



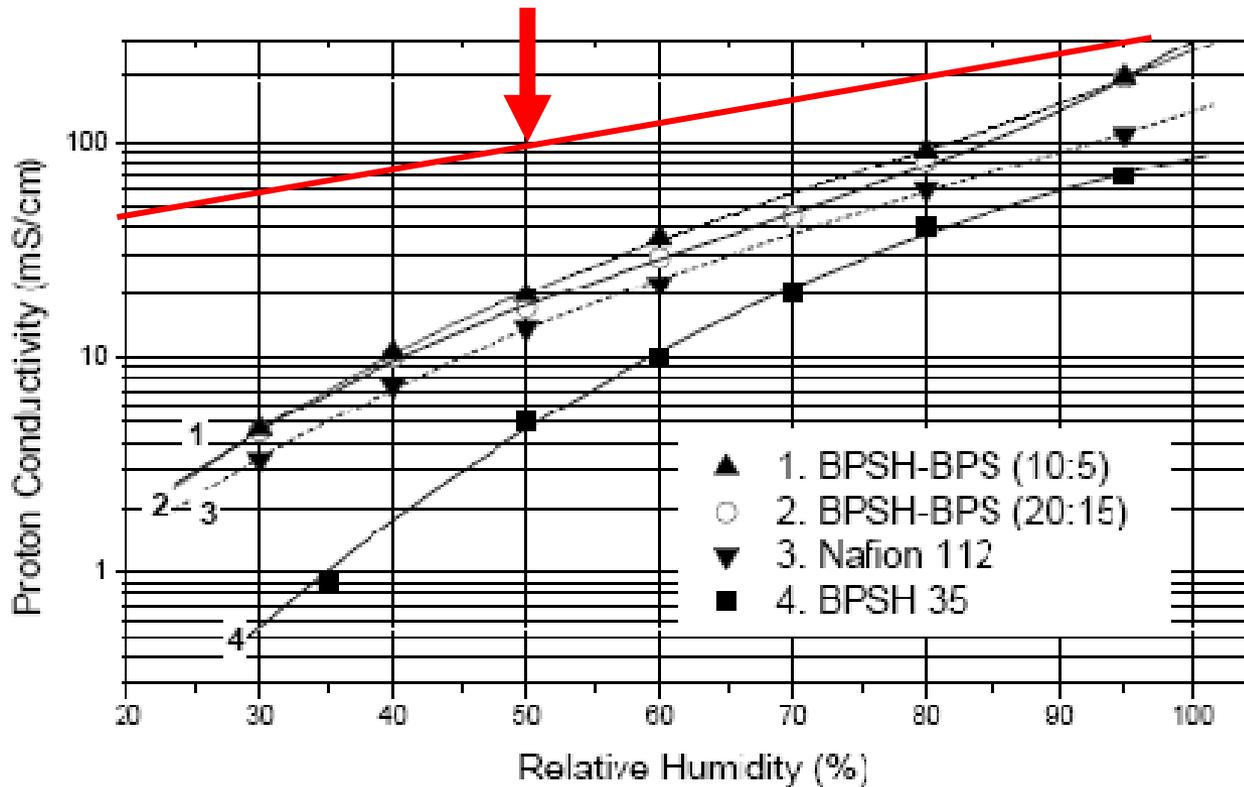
Membrane Electrode Assemblies (MEAs) were prepared at LANL, which showed good performance at 100C and 40%RH

A simpler One Step Synthesis of Segmented Hydrophilic-Hydrophobic Copolymers has been Defined

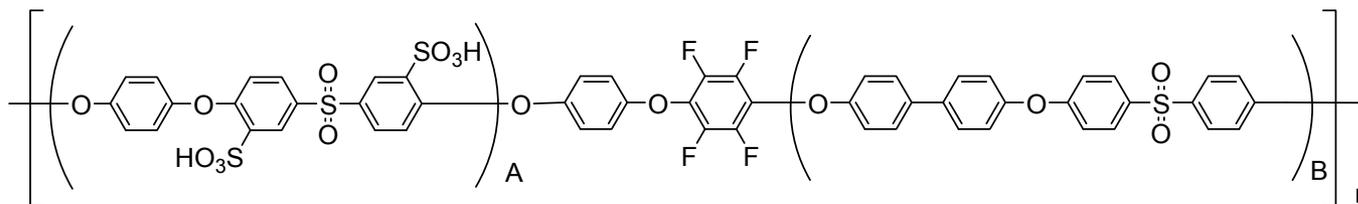


Proton Transport Behavior as a Function of RH

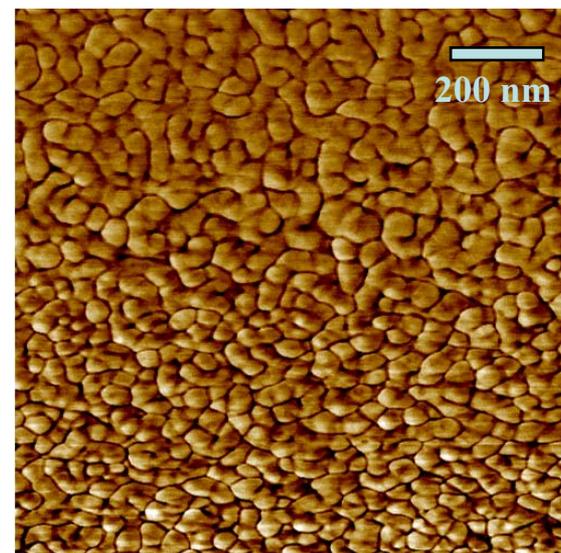
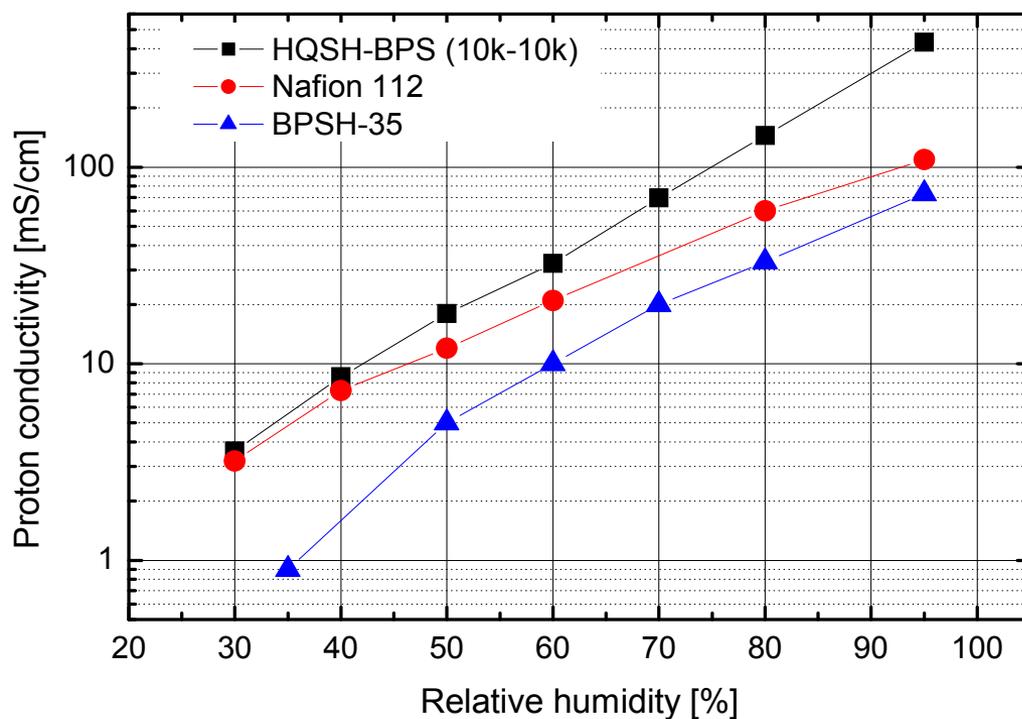
DOE Target: 100 mS/cm at 50% RH at 120°C



HQSH-Based Multiblock Copolymers; Proton Conductivity at 80C



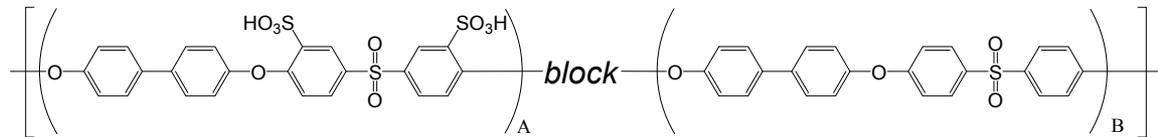
HQSH-BPS multiblock copolymer



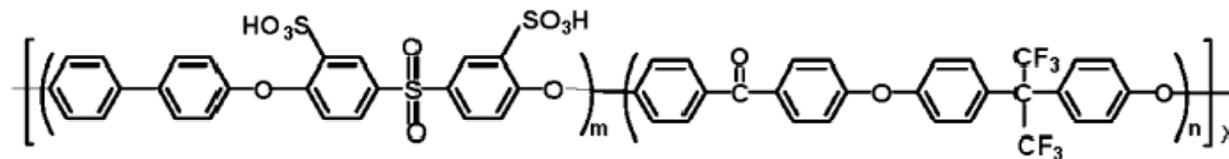
Tapping Mode AFM Image of the HQSH 10- BPS 10

Multiblock Copolymers with High IEC May Display Improved Conductivity at 50% RH

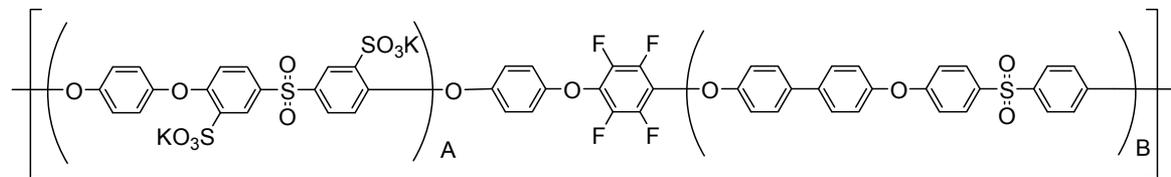
1. BPSH-BPS (20k-5k), Target IEC = 2.65 meq/g



2. BPSH-6FK (20k-5k), Target IEC = 2.65 meq/g

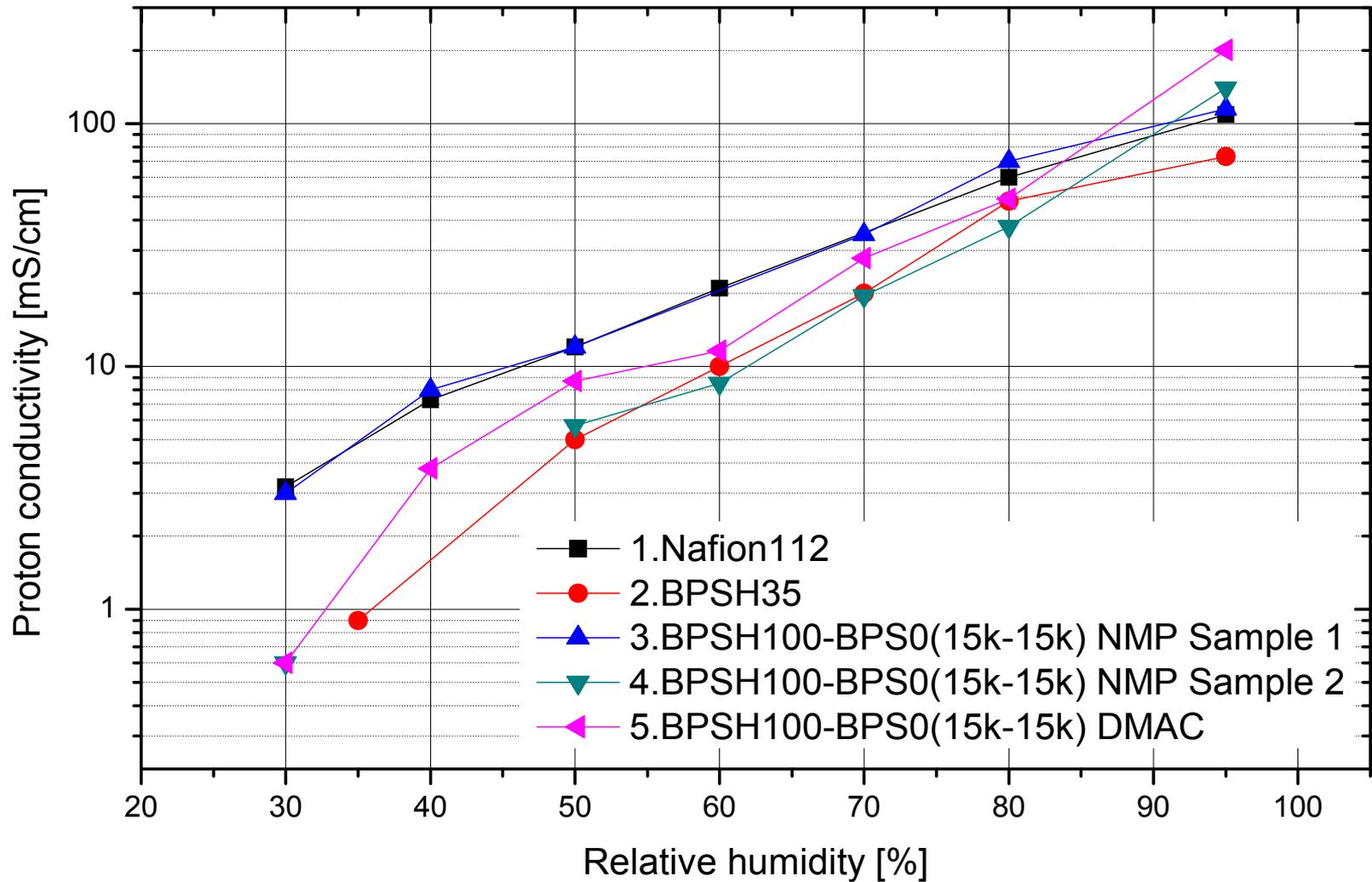


3. HQSH-BPS (15k-5k), Target IEC = 2.83 meq/g

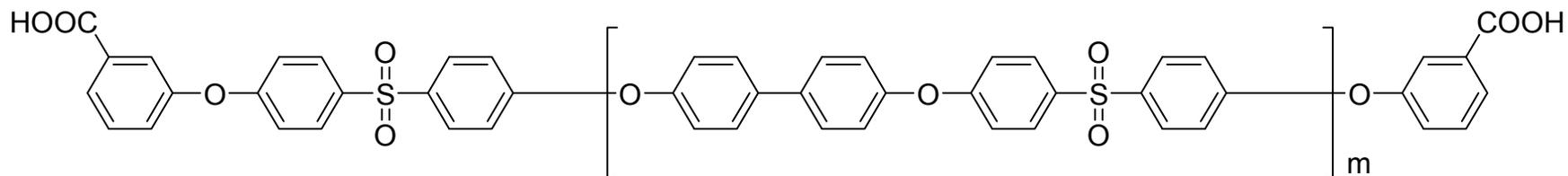


The copolymers were acidified and successfully cast on Mylar® (PET) substrates.

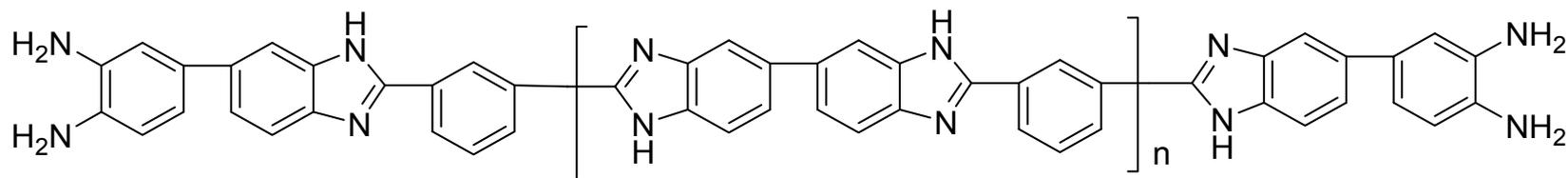
Film Casting Influences Conductivity and a Block Copolymer Affords the 2008 DOE Goal of 70mS/cm at 80% RH at 30C



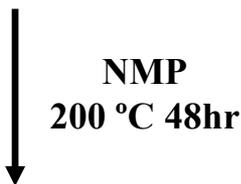
Exploratory Studies of Poly(arylene ether)-Polybenzimidazole Multiblock Copolymers



Acid - terminated Biphenyl Sulfone (BPS)



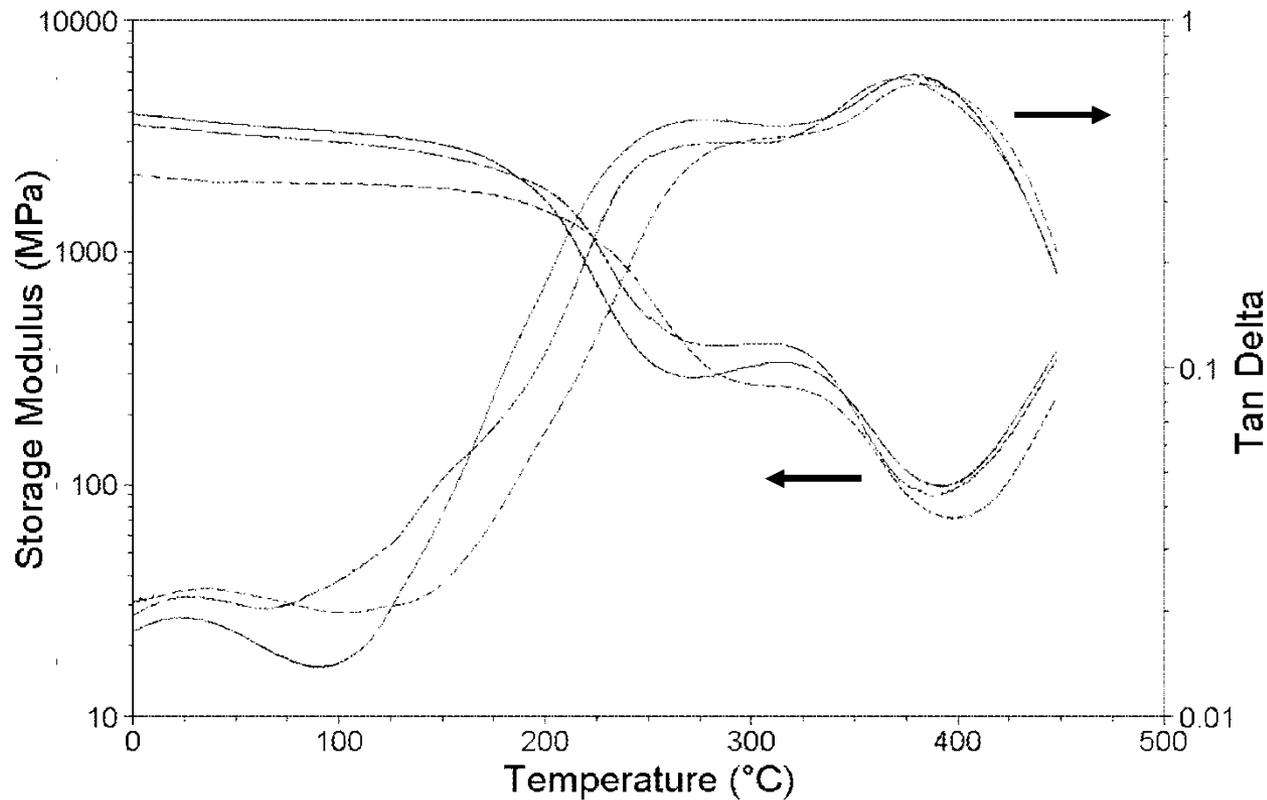
Diamine-terminated Polybenzimidazole (PBI)



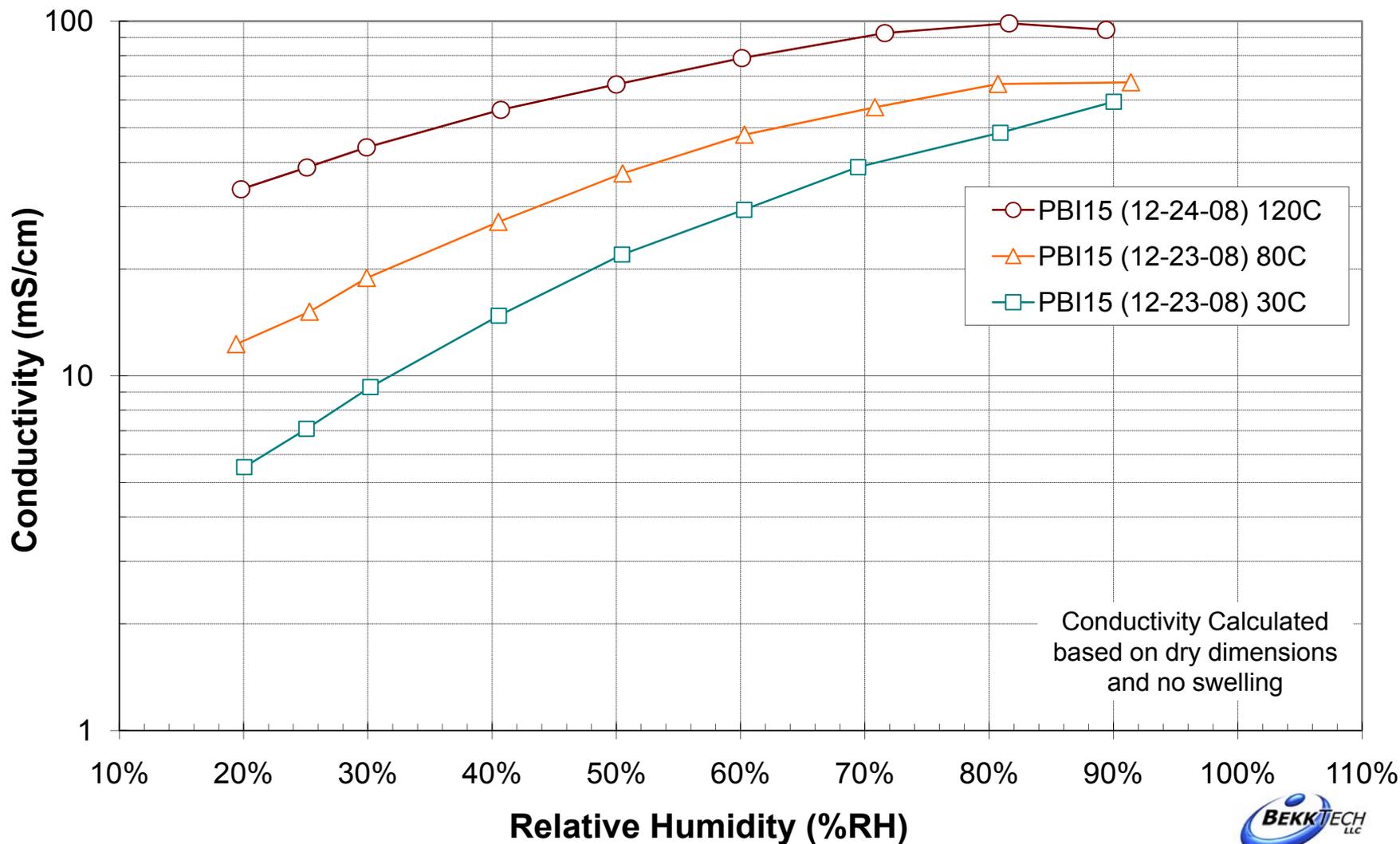
(mechanical strength)

(proton conductivity)

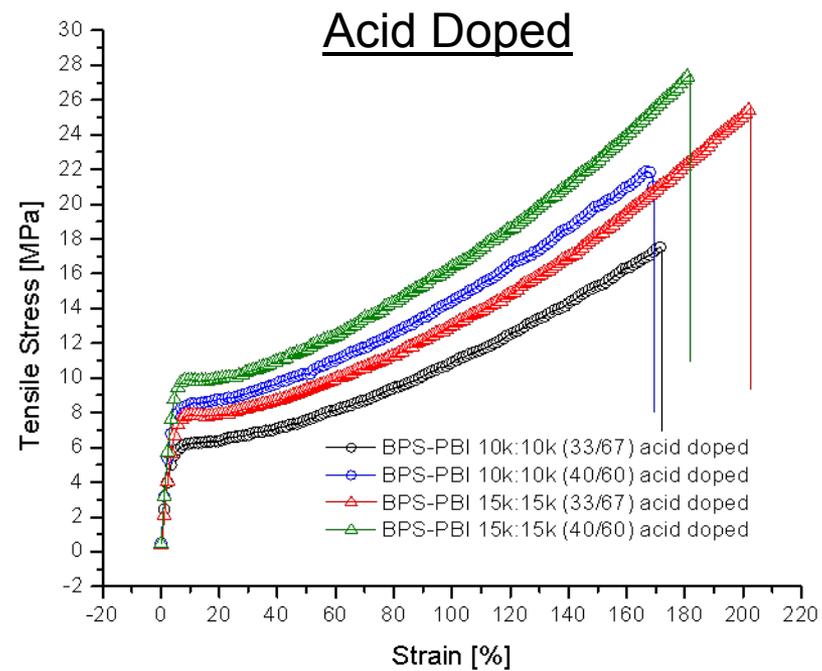
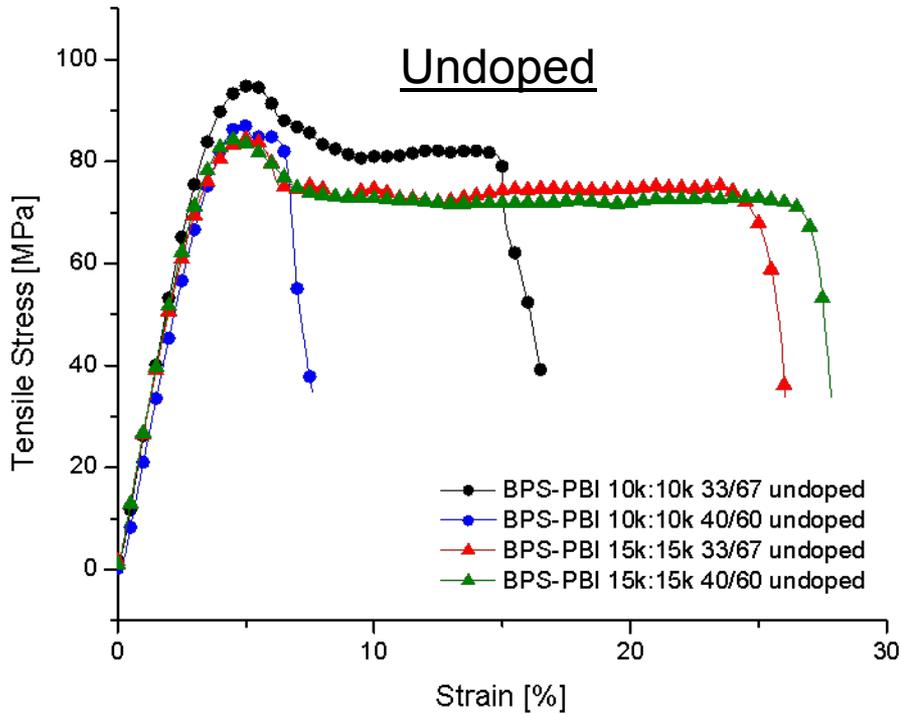
Storage Modulus and Tan Delta Shows 2 Nanophases for BPS-PBI Copolymers; the PBI Phase was selectively doped with H_3PO_4



Bekktech Conductivity - Increasing RH Only

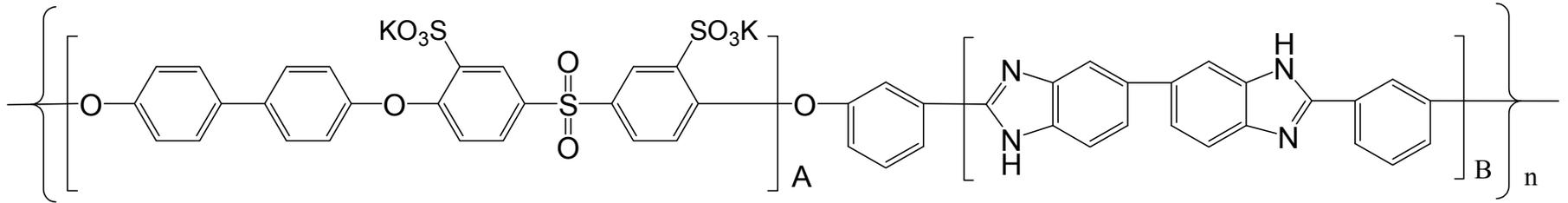


Acid Doped BPS-PBI Membranes Have Good Tensile Strength and Higher Elongations than the Control BPS-PBI Multiblock Copolymer Membranes-Strength is 2X Nafion[®] Control



*Membranes were equilibrated at 25 °C, 40% RH prior to testing. Testing conducted at 25 °C and a rate of 5 mm/min.

Multiblock Copolymer with Sulfonated Polysulfone (BPSH-100) and Polybenzimidazole (PBI) Have Been Made No Phosphoric Acid



[First Systems shows 80 mS/cm at 80C

- BPS100-PBI (20k-10k or 20k-5k) systems are in progress

- Water uptake measurements were conducted with the copolymer

Salt Form : 14%

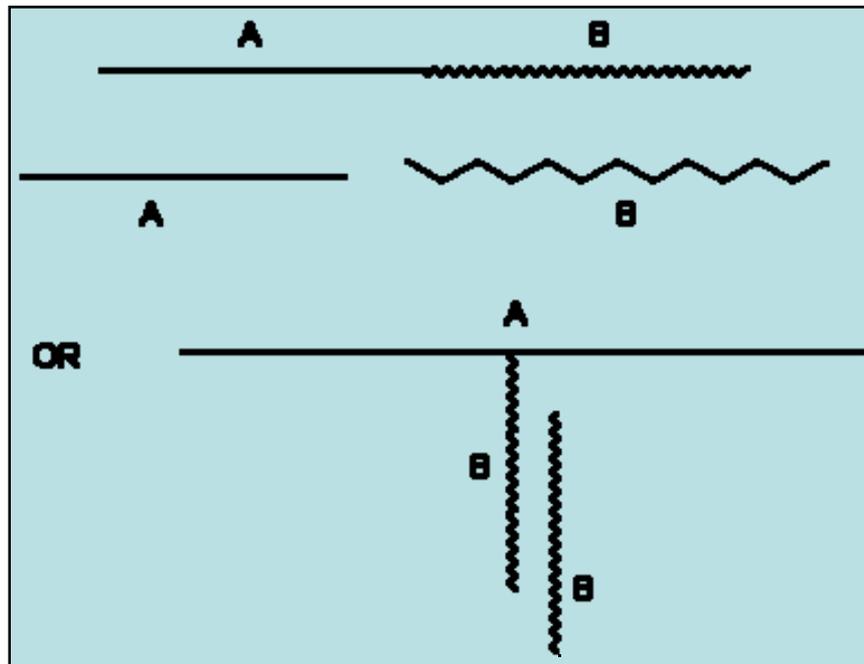
Acid Form : 21%

Blends of BPSH-100 with the Block Copolymer are being investigated as acid-base water replacement conducting systems

PolyBlends

Block and Graft Copolymer Blends are Stabilized at the Interface with Homopolymers

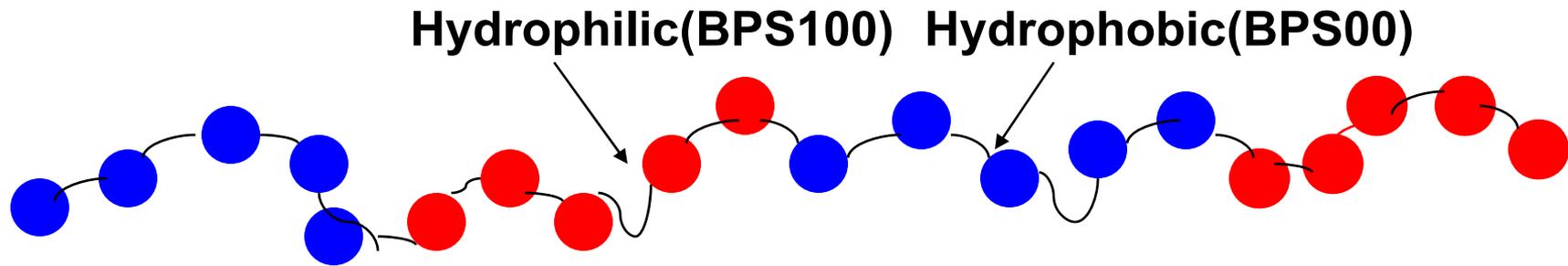
- Block and graft copolymers are usually “mechanically” compatible with their constituent homopolymers and the new compositions may enhance conductivity



**“Emulsification”
or
Compatibilization
is achieved, $\approx 1\mu$
dimensions
possible
in the blends.**

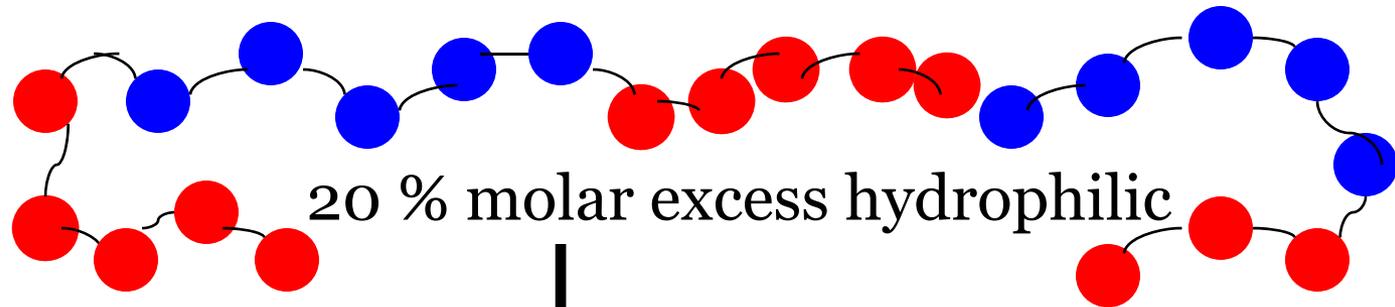
Crosslinking Ionic Multiblocks

1.



Hydrophilic : Hydrophobic = 1 : 1 mol ratio

2.

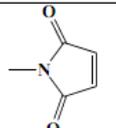
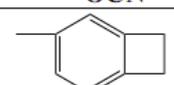
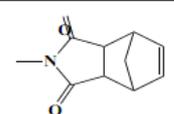


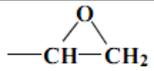
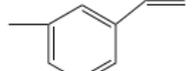
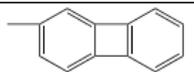
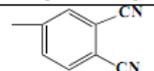
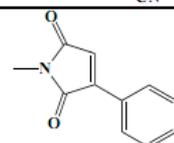
- The phenoxide groups can react with a suitable crosslinker
- Tetra epoxy or ethynyl

Crosslinked Block Copolymer

Reactive Groups for High-Performance Thermosets

Table 2.1 Reactive Groups for High-Performance Thermosets⁶¹

Functionality Structure	Functionality Name	Approximate Cure Temp. (°C)
	maleimide	200
—OCN	cyanate ester	170
	benzocyclobutene	200
$\text{—C}\equiv\text{CH}$	ethynyl	200
	nadimide	300
$\text{—C}\equiv\text{C—}$ 	phenylethynyl	350

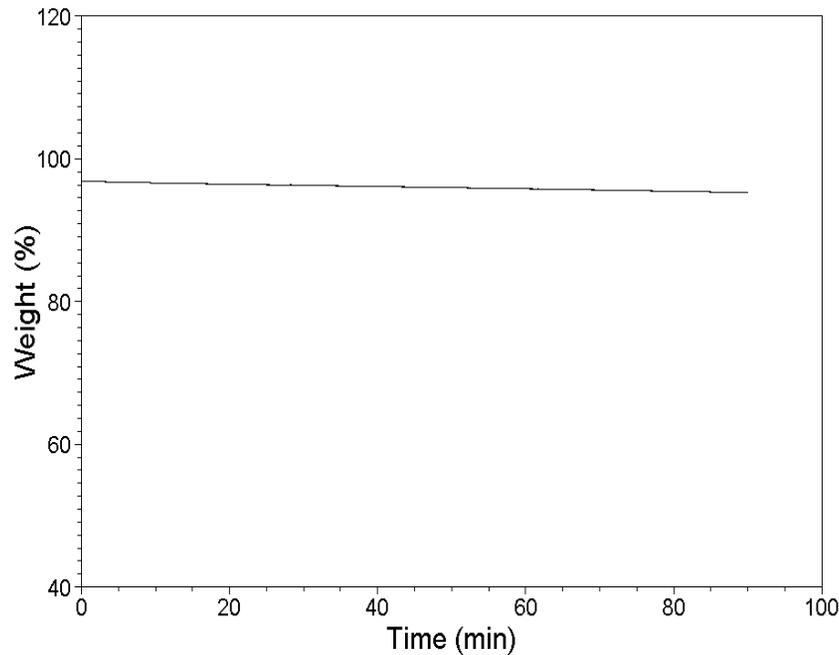
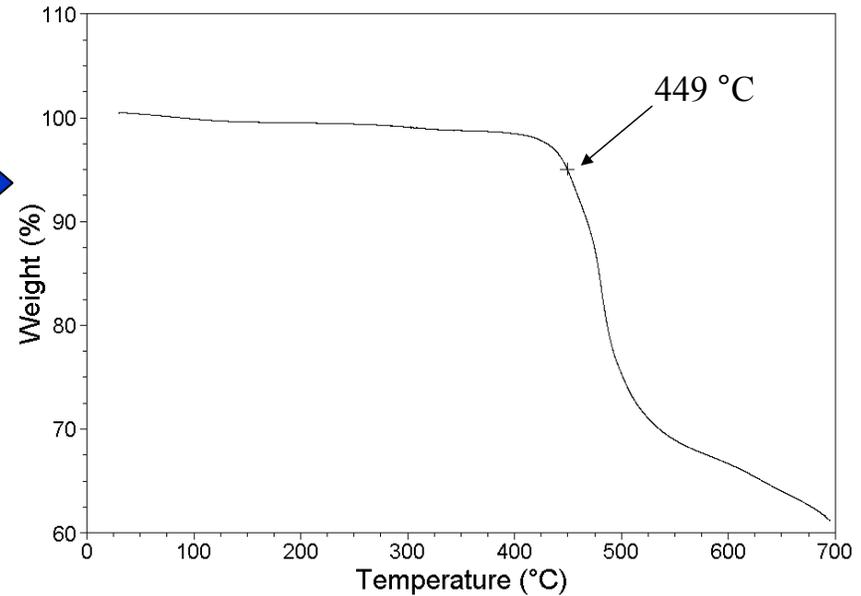
	epoxide	variable with catalyst and co-reactant
	styrenyl	200
	biphenylene	300
	phthalonitrile	250
	phenylmaleimide ⁶²	350

S. J. Mecham, Synthesis and Characterization of Phenylethynyl Terminated Poly(arylene ether sulfone)s as Thermosetting Structural Adhesives and Composite Matrices, Ph D thesis, Virginia Tech, Blacksburg, 1997.

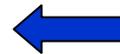
TGA of FPEB-BPS-50 Membranes (Salt Form)

Demonstrate Excellent Thermal Stability and Can Be Acidified After Cure

FPEB-BPS-50 blend membrane shows 5 % weight loss at ~ 449 °C



Isothermal heating at 360 °C for 90 min shows no significant weight change



10 °C/min, N₂ atmosphere

Surface-Fluorination of BPSH PEM

*Cooperation with Prof Y. M. Lee and
Colleagues*

Chang Hyun Lee¹, So Young Lee¹, Young Moo Lee¹, Ozma Lane², and James E. McGrath²

¹School of Chemical Engineering, College of Engineering,
Hanyang University, Seoul, Korea

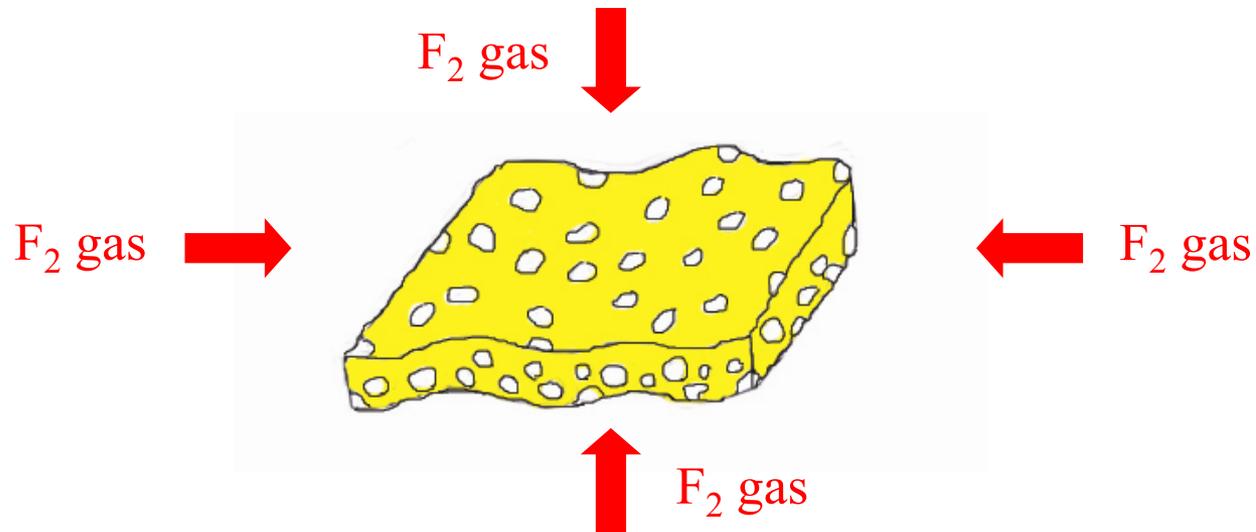
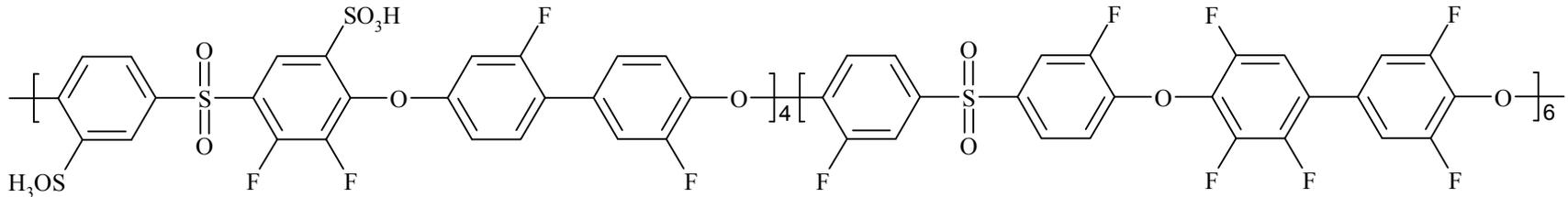
²Macromolecules and Interface Institute, Virginia
Polytechnic Institute and State University, Blacksburg, VA
24061, USA

Objectives

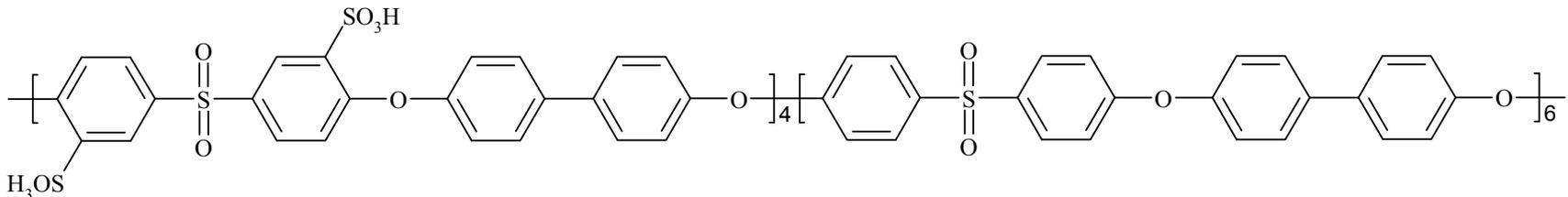
- Can surface fluorination effect disulfonated poly(arylene ether sulfone) (BPSH) copolymer structure, morphology and membrane properties
- What is the relationship between contact time and electrochemical properties including long-term fuel cell MEA performance?

Basic Concepts of Membrane Post Fluorination

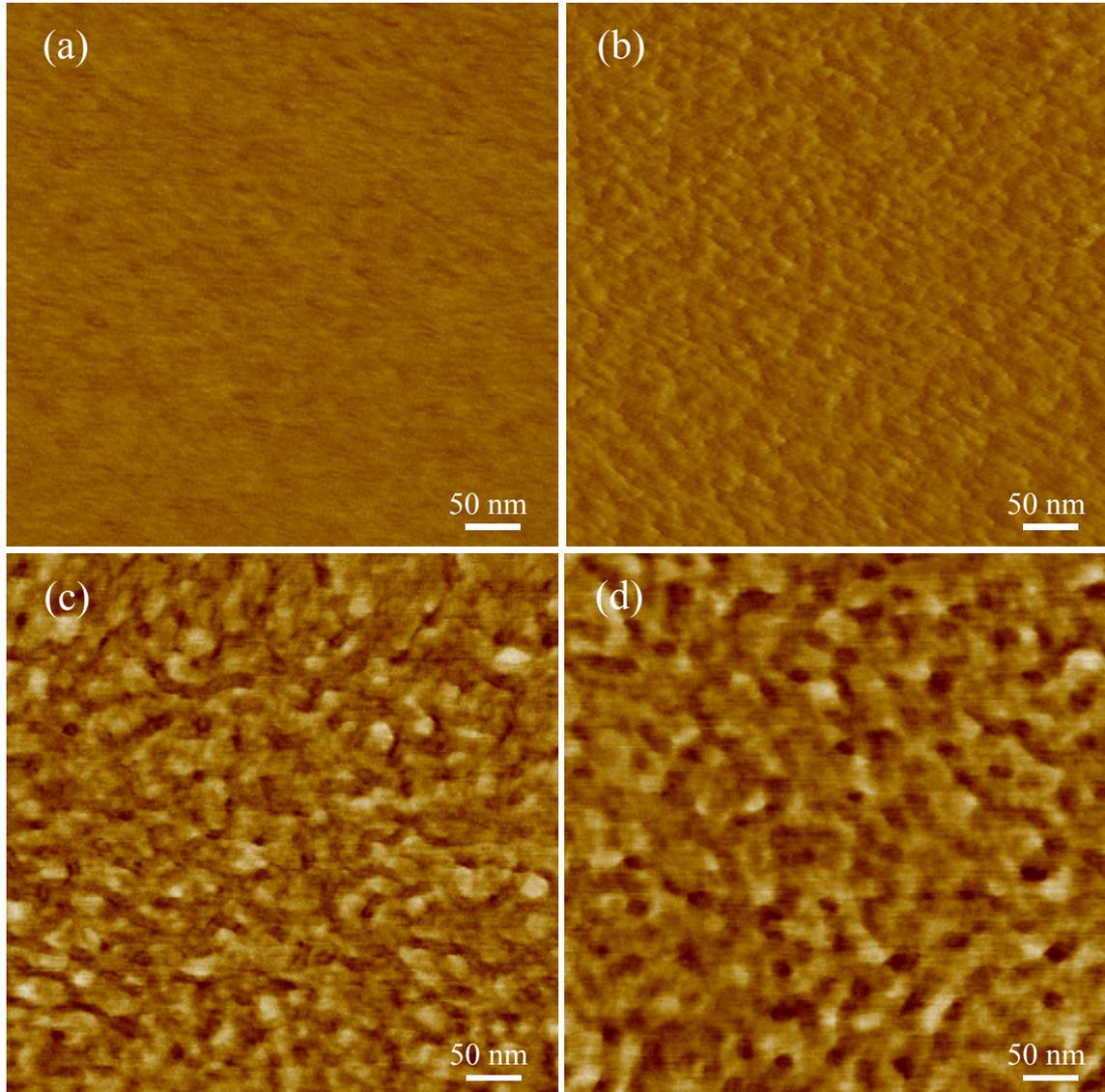
- **Fluorination:** May enhance Morphology and Improve Interfacial behavior with (Nafion®) in the Electrodes



- **No modification:** poor compatible with catalyst binder (Nafion®) in electrodes



Fluorination Develops Morphological Order in BPSH-40



AFM tapping mode phase images of

(a) SPAES Control

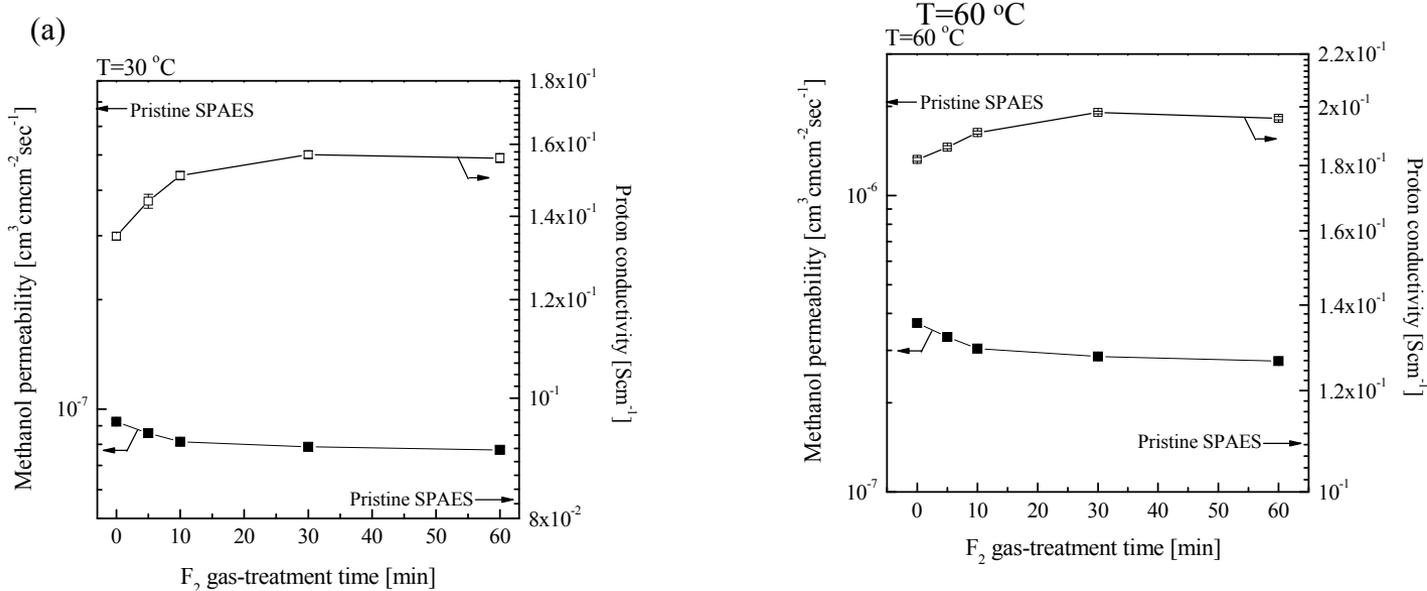
(b) FSPAES 10 minutes

(c) FSPAES 30 minutes

(d) FSPAES-60 minutes

Relative humidity was about 35% RH.

Fluorination Increases Proton Conductivity and Decreases Methanol Permeability



$$\sigma_{\text{pristine SPAES}} = 8.36 \times 10^{-2} \text{ Scm}^{-2}$$

$$P_{\text{MeOH_pristine SPAES}} = 6.64 \times 10^{-7} \text{ cm}^3\text{cmcm}^{-2}\text{s}^{-1}$$

Transport behavior of Fluorinated SPAES as a function of fluorination time measured at (a) 30 °C, and (b) 60 °C

Fluorination improves MEA Performance

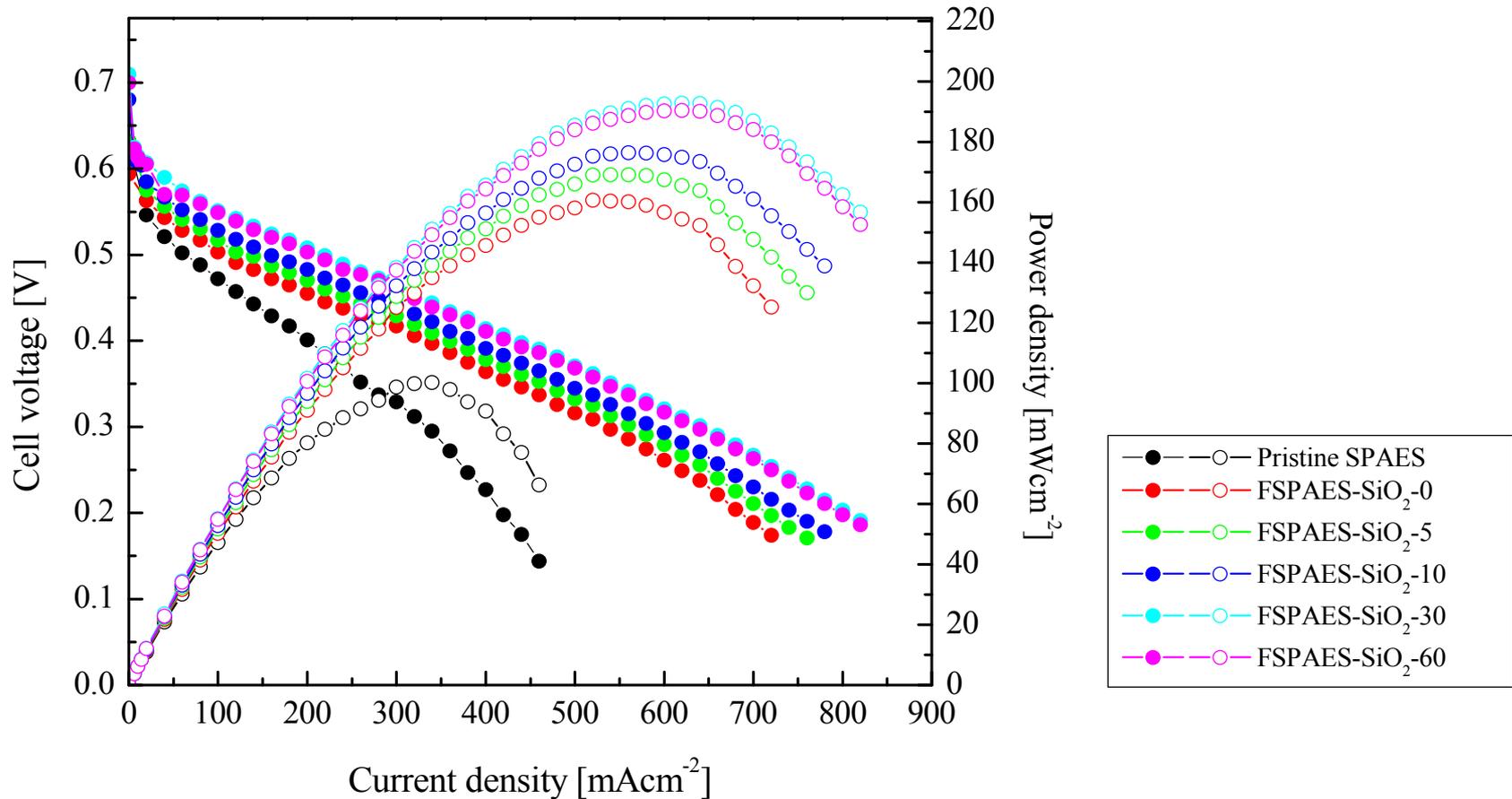


Figure 8. Electrochemical single cell performances of SPAES membranes under a flow rate of 1M MeOH/O₂=1 sccm/200 sccm at 90 °C

Long Term Durability is Greatly Improved: Enhanced Interfacial Behavior ?

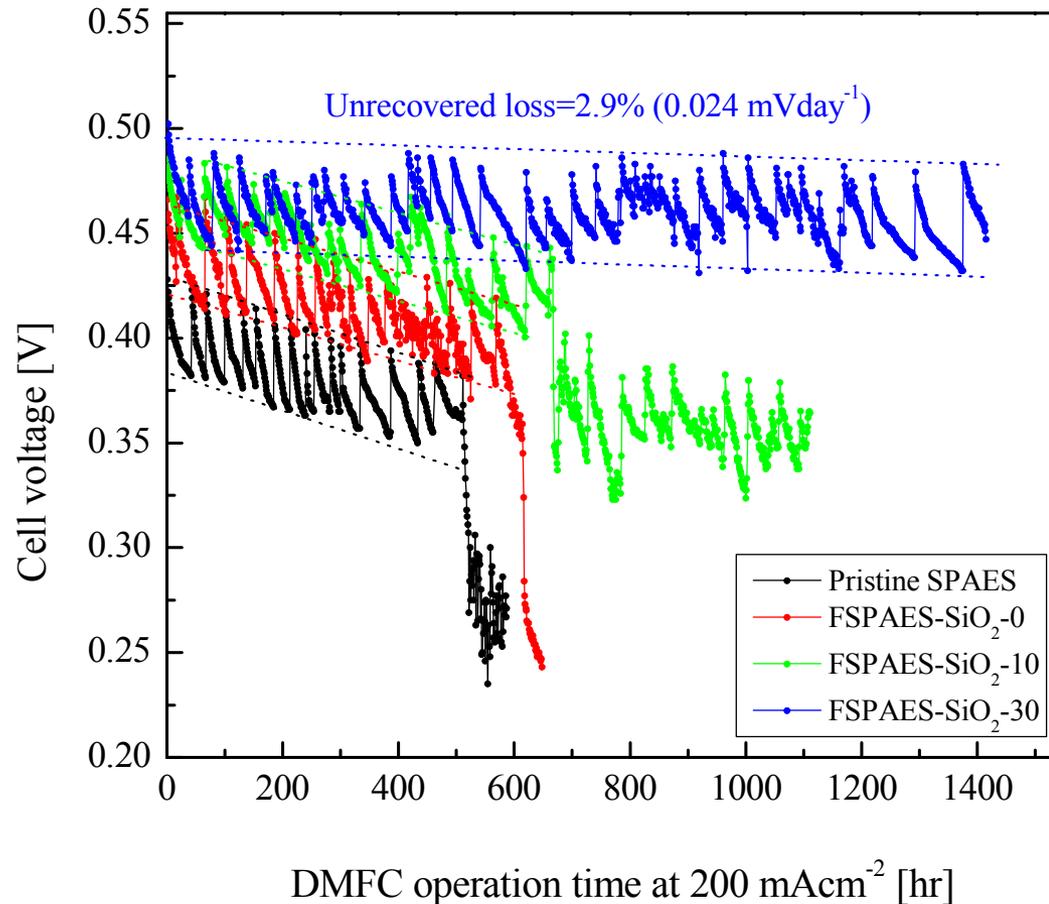


Figure 9. long-term electrochemical performances of SPAES membranes under a flow rate of 1 M MeOH/O₂= 3 sccm/1,000 sccm at 90 °C

Nanophase Separation in Hydrophilic-hydrophobic Nonionic Block Copolymers

- Obeys: $\Delta G = \Delta H - T\Delta S$
- Balance of **enthalpic** and **entropic** forces
 - **Enthalpic**: Dissimilar A,B phases want to repulse (positive Flory-Huggins χ parameter, χ_{AB})
$$\chi_{AB} = (z/kT)[\epsilon_{AB} - 1/2(\epsilon_{AA} + \epsilon_{BB})]$$
 - **Entropic**: Linkages between phases prevent macroscopic separation (elastic restoring force), proportional to chain length (R), size (a) of N monomers
$$\Delta G_{\text{elastic}} = 3kTR^2 / (2Na^2)$$
 - Phase separation when $\chi_{AB}N > 10.5^2$
highly hydrophobic linkage groups may alter this balance
- For ion-containing copolymers, χ_{AB} is largely unknown

Conclusions: Post Fluorination

- Enhanced single cell performance for BPSH-40
- Probably will work for block copolymers also

- ✓ Improved proton conductivity
- ✓ Reduced methanol permeability

➤ Extended life-time

- ✓ Increase of membrane water-swelling in *Z-axis direction*
- ✓ Decrease of membrane water-swelling in *XY-axis direction*
- ✓ Reduced methanol permeation through a membrane
- ✓ Improved compatibility between a membrane and catalyst layers
- ✓ containing Nafion[®]
(EW=1,100) binder and, , reduced interfacial resistance

Summary

.BPSH Block copolymers were developed

- ❑ Many good PEM Characteristics have been demonstrated
- ❑ Oxidative and Hydrolytic Stability, Mechanical Behavior, low H₂ and O₂ Permeability, Scalability, Robust MEA's, Performance at 100C/ 40% RH
- ❑ 100mS/120C/50%RH not yet achieved; An approach using high IEC Crosslinked Systems in Progress
- ❑ BPSH-PBI blocks/blends can be doped with H₃PO₄ or may function per se
- ❑ Post Fluorination shows Promise to enhance Conductivity and to Stabilize the Membrane-Electrode Interface

Current & Future(April to August, 2009) Research

- Continue ongoing efforts with LANL and others for understanding chemical structure-processing property relationships in PEM block and segmented copolymers and what controls conductivity at low RH
- High IEC (low equivalent weight) crosslinked homo- and multiblock copolymers
- Post Fluorination of Random and Block Hydrophilic-Hydrophobic Copolymers