2009 DOE Hydrogen Program Merit Review Presentation

Advanced Materials for Proton Exchange Membranes

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FC_05_McGrath

OVERVIEW

Timeline	Barriers
•Project Start Date: May 2006 •Project End Date: March 31,2009 •Percent Complete: 100%(no cost extension through July)	•Conductivity at 120^{o}C and low RH
Budget	**Partners**
Total Project Funding: $950,949 Funding received in FY08: $350,000 Funding received in FY09: $150,949	•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 Arn

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?

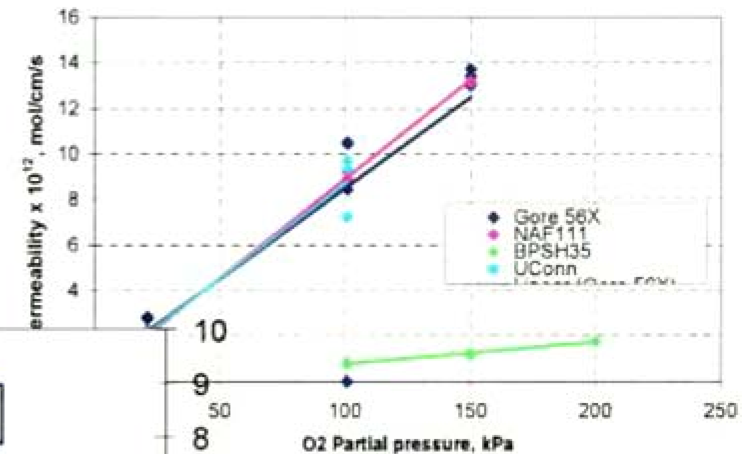
Low fuel and oxidant permeability

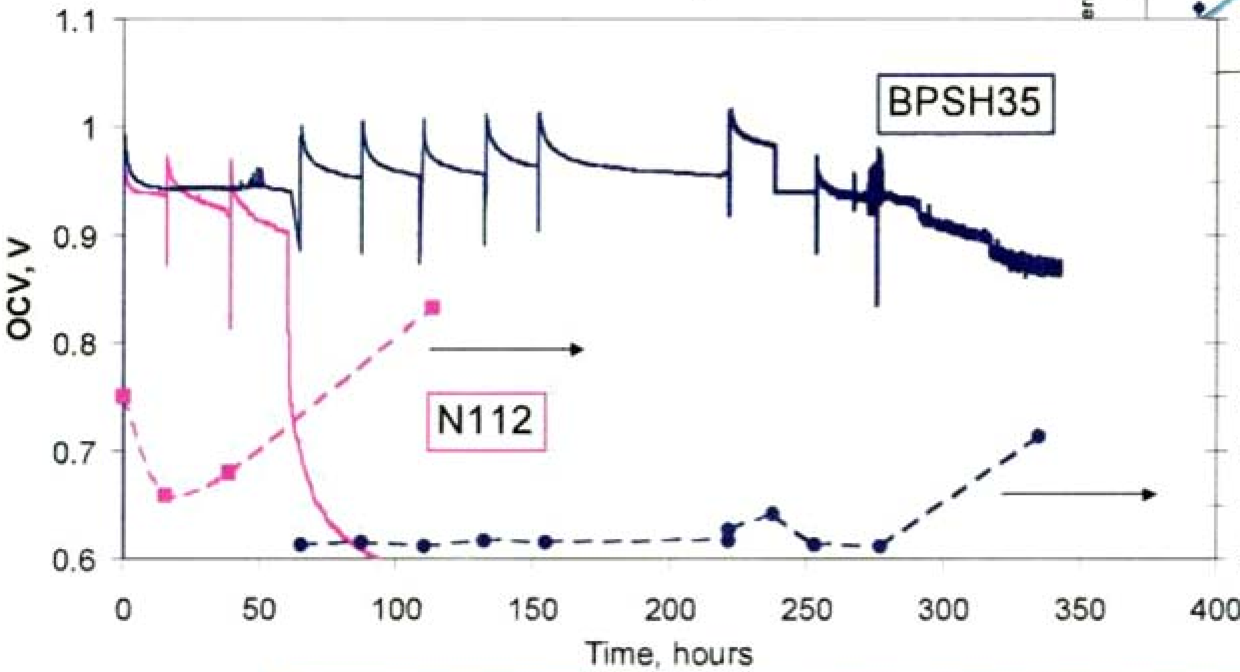
- ✓ Oxidative and hydrolytic stability
- ✓ Appropriate water uptake
- ✓ Good mechanical properties both in the dry and hydrated state
- ✓ Low x, y Dimensional Swelling
- ✓ Fabrication into Robust Membrane Electrode Assemblies (MEAs)
- ✓ Cost, Processiblity, Manufacture

✓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 that of PSFA-like membrane - significantly increases durability



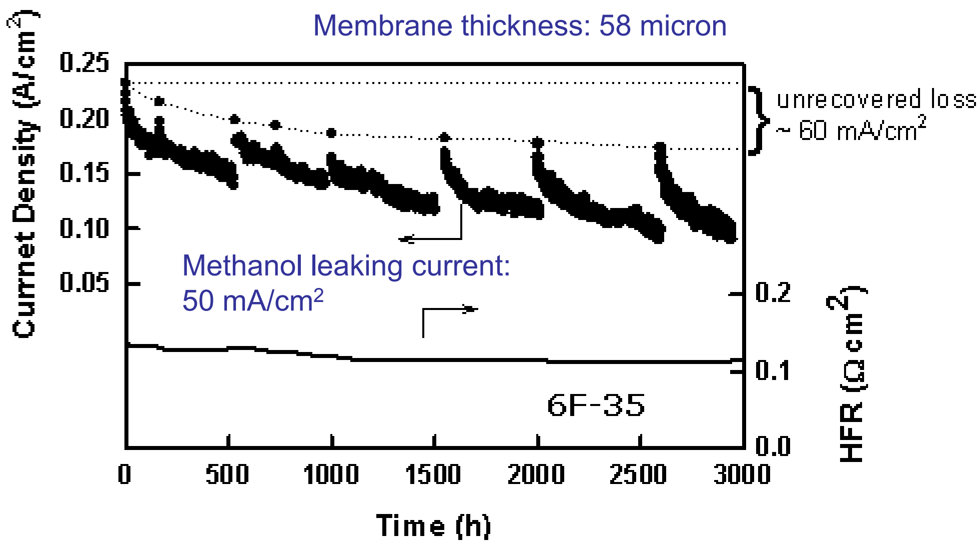


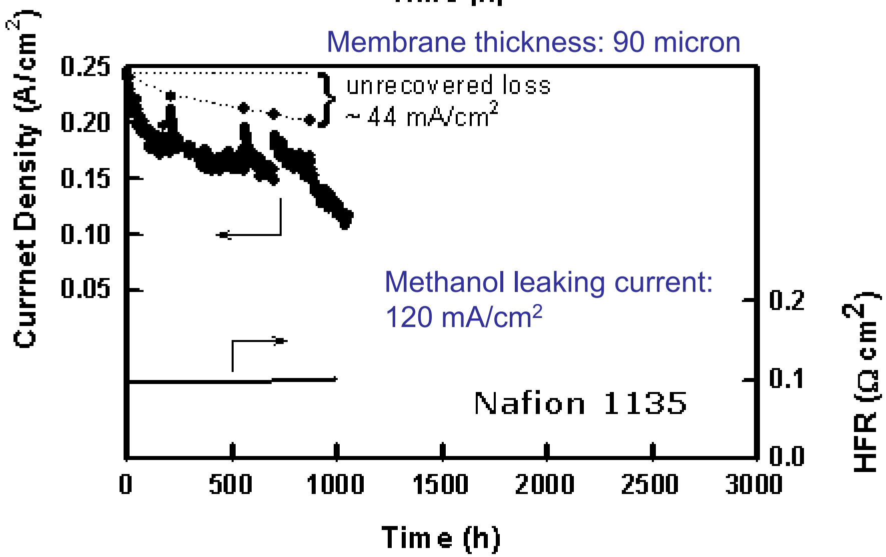
Accelerated Membrane Degradation Test Conditions:

100°C, 25%RH, 1.5atm

H2/O2

Long-Term Performance of Interface In Cooperation with LANL



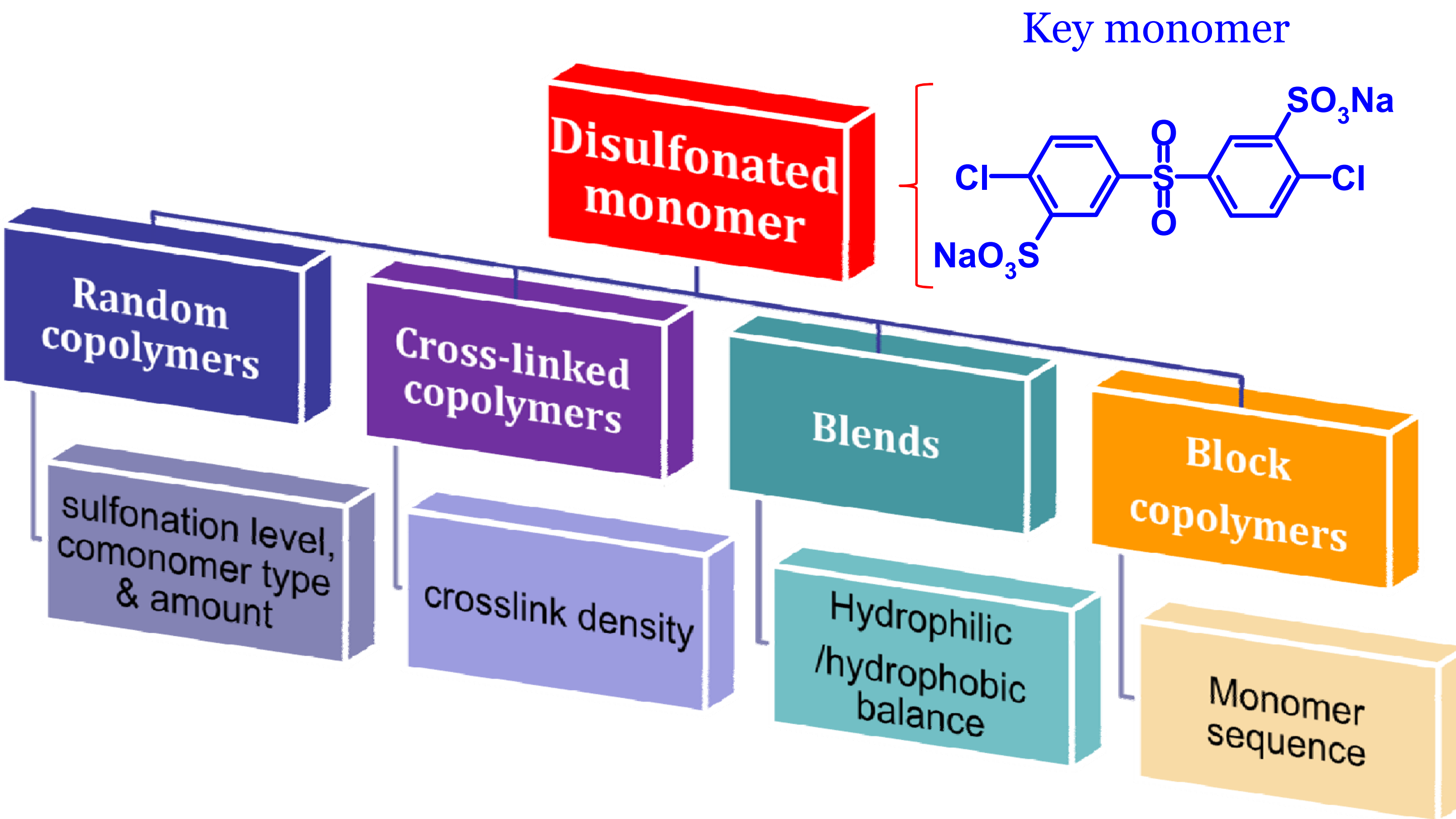


Interface optimized non- Nafion® membrane (6F-35) exhibited stable long-term performance* with decreasing cell resistance under DMFC conditions

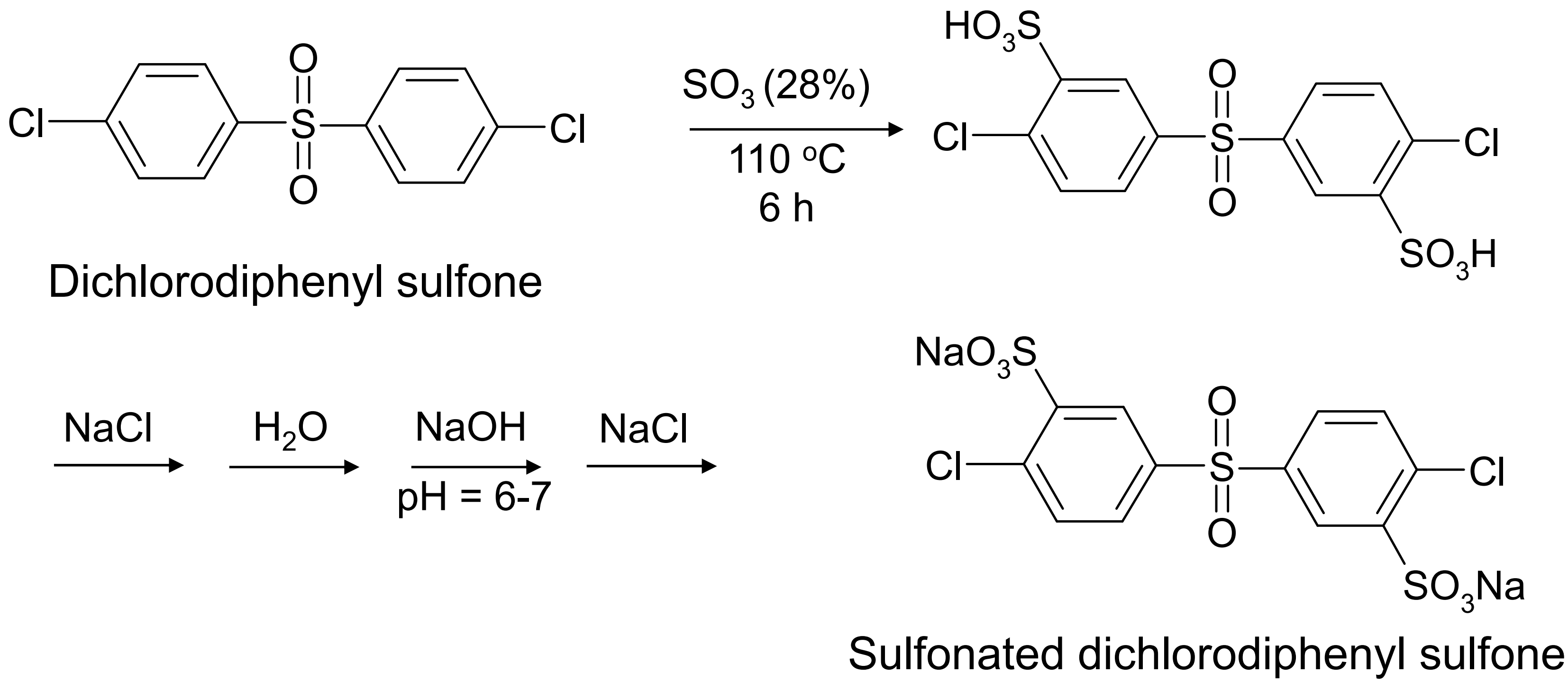
Performance loss after 3000 h life test for 6F-35 was 60 mA/cm², which was comparable to that of state of the art Nafion® MEA.

**2005 technical target for MEA durability 10% loss after 2000 h at < 80°C under H_2/air conditions*

Considerable Flexibility is Possible for Specific Membrane Applications

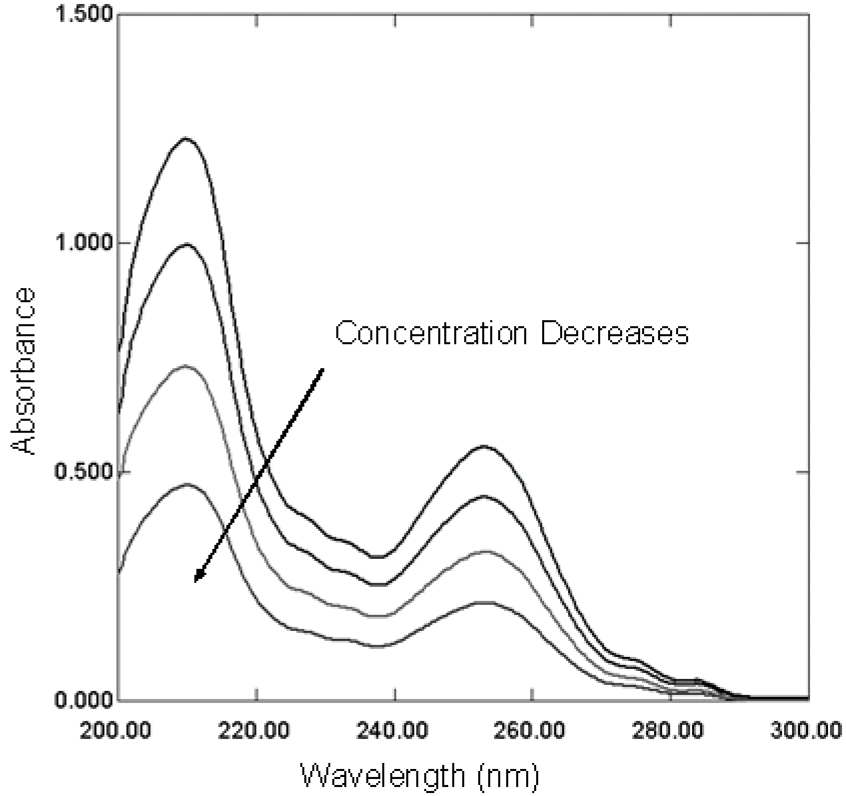


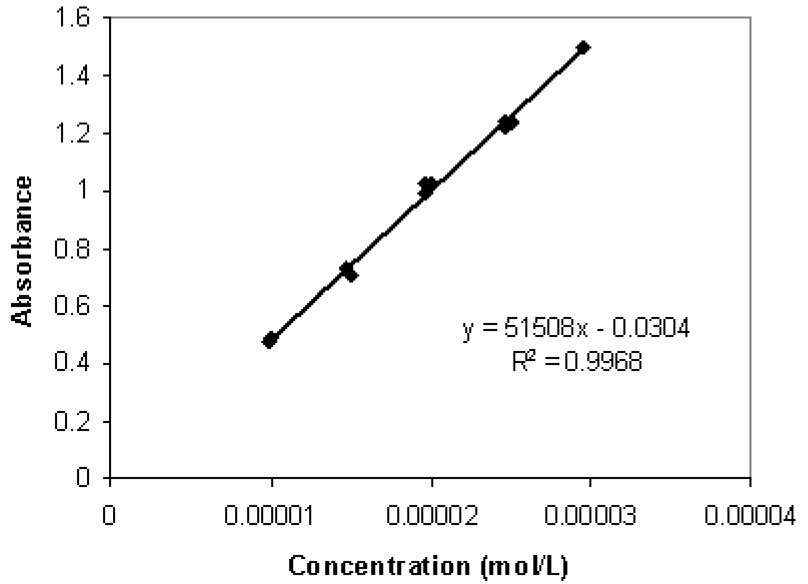
A Scalable (> 2 kg) One Step Synthesis of 3,3'-Disulfonated 4,4'-Dichlorodiphenylsulfone (SDCDPS) Comonomer has been Demonstrated



- 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



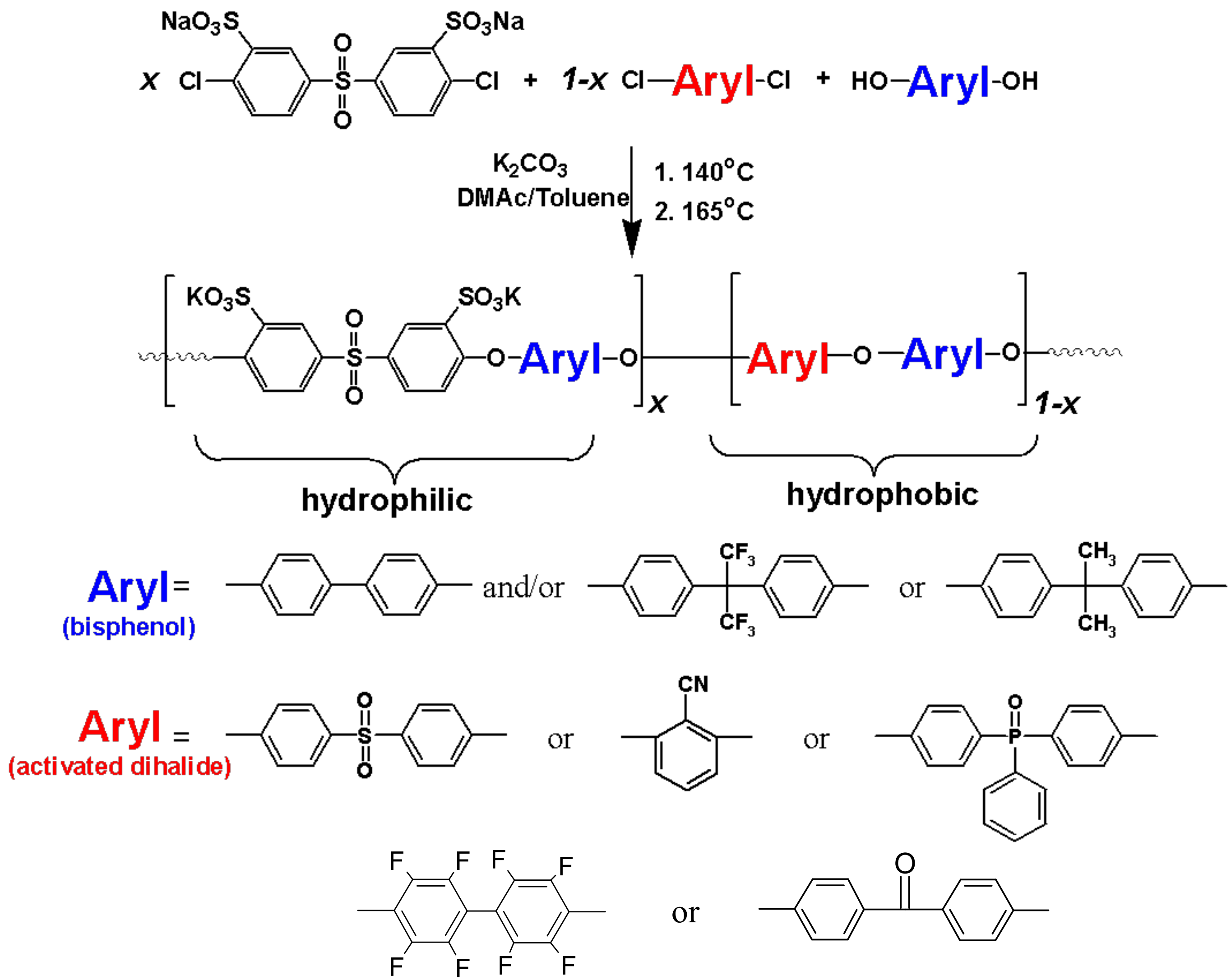


Beer's Law: A = εbc

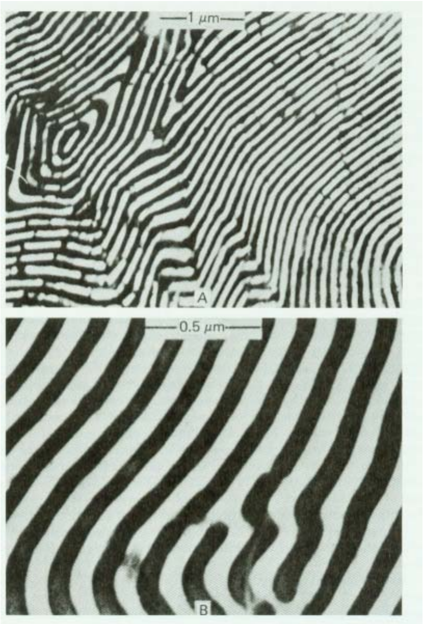
A calibration curve was developed using solutions of various known concentrations of highly purified SDCDPS in methanol

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. Poly*mer*, **2008**, *49*, 3014-3019.

Disulfonated Poly(arylene ether sulfone) Random (BPS) via Commercially Viable Direct Copolymerization



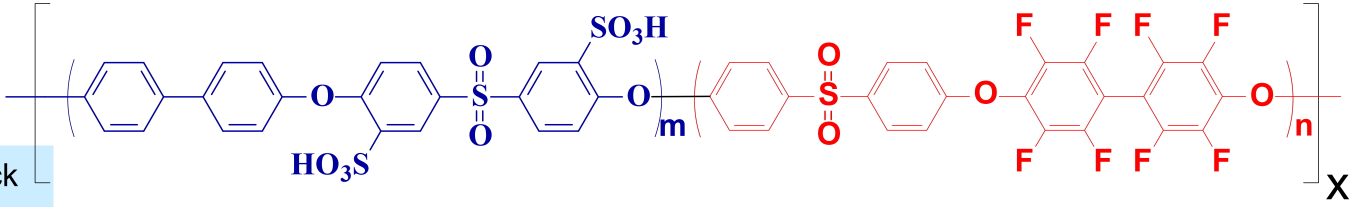
Highly Hydrophobic-Hydrophilic Multiblock Copolymers



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

Our Initial work:

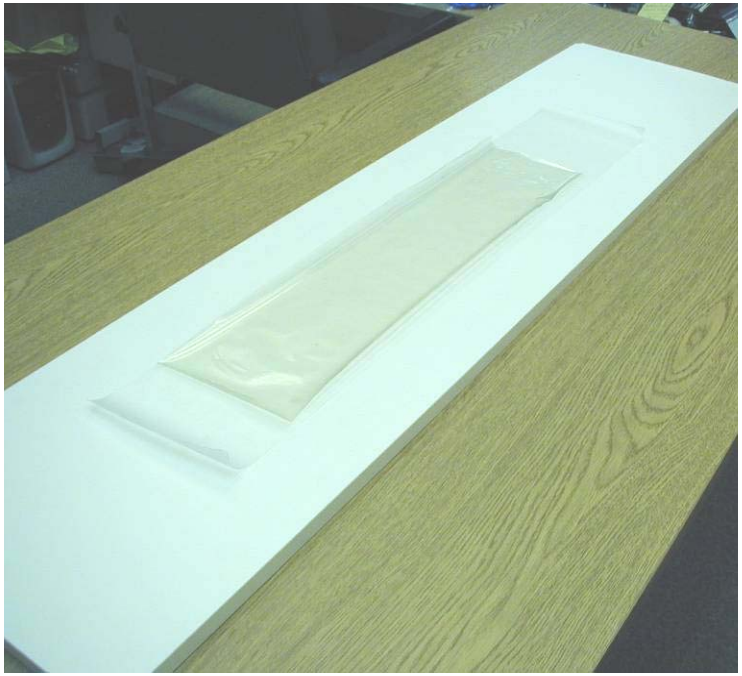


Hydrophilic segments, provides Flux

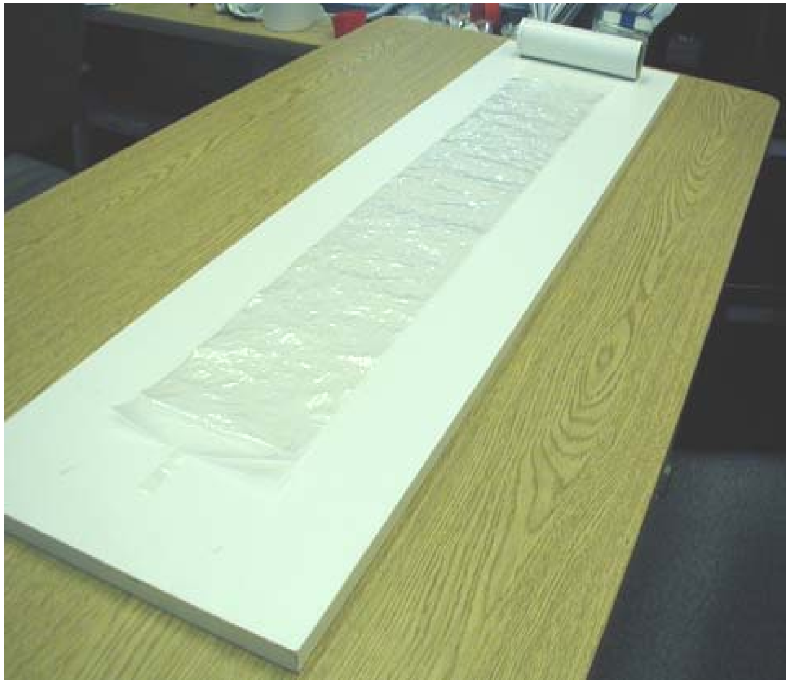
Hydrophobic segments, imparts mechanical integrity

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

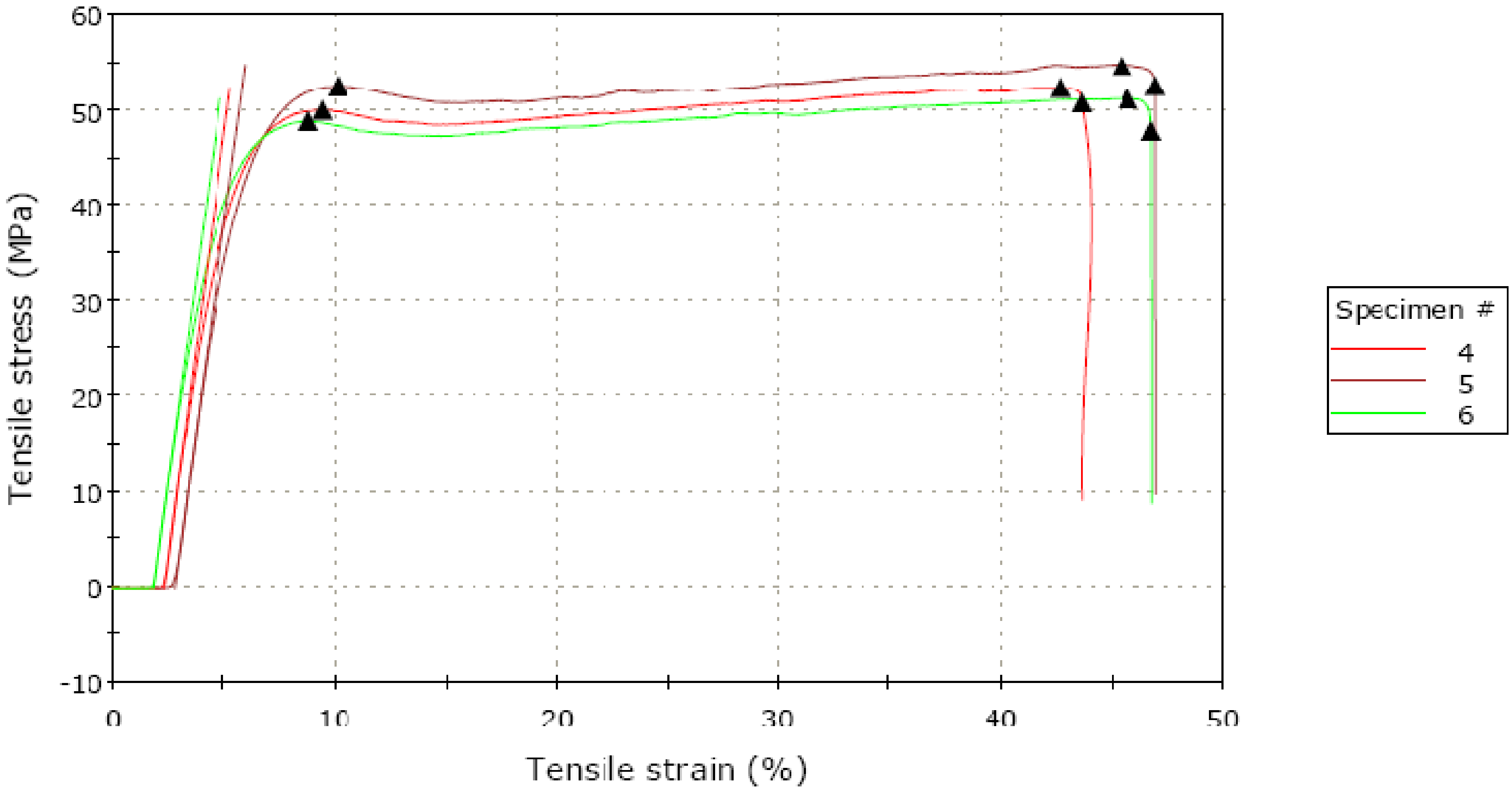


BisSF 17k/12k Block Copolymer Films

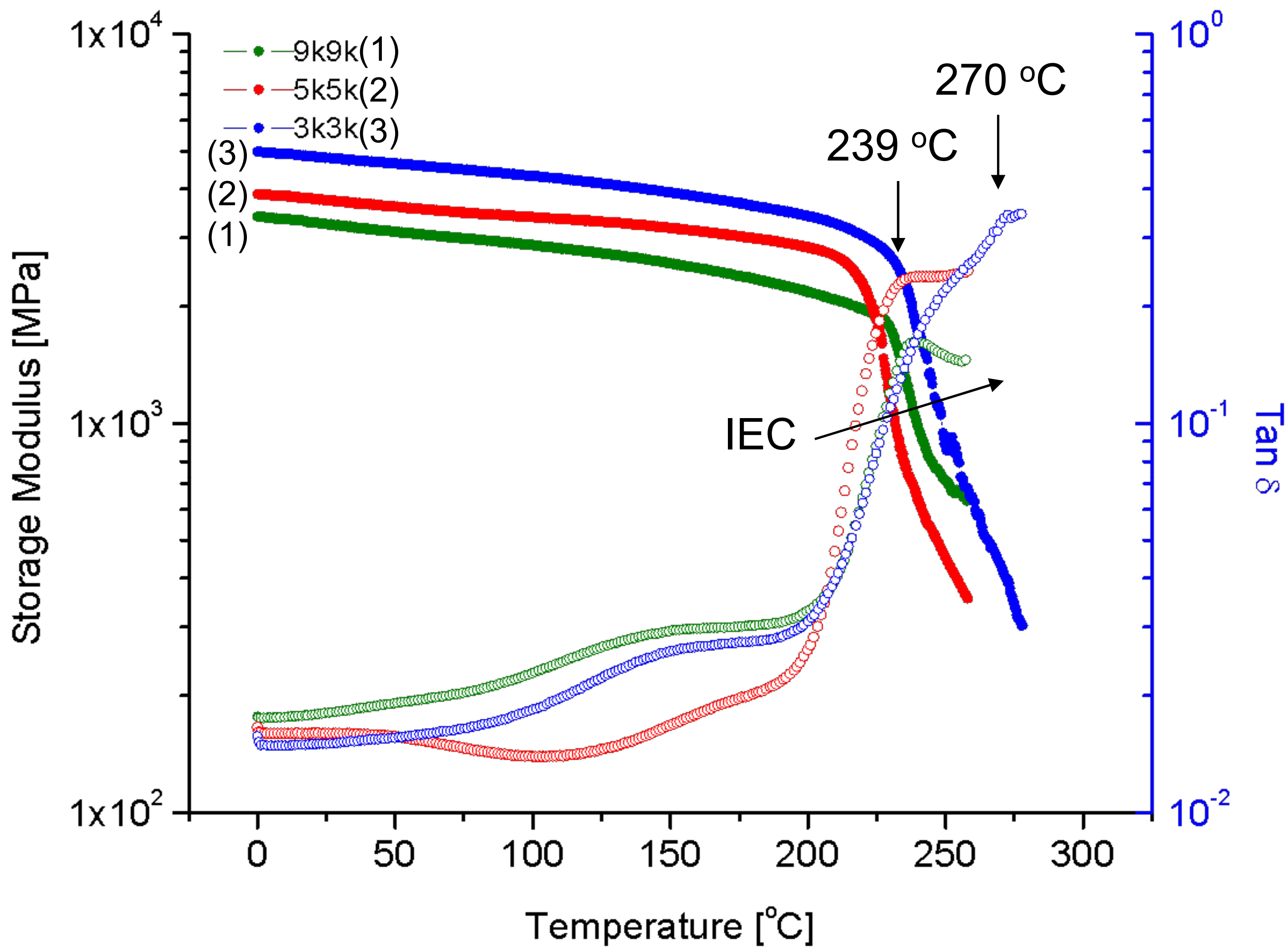


6F40 Random Copolymer Films

BisSF-BPSH100 Block Copolymer Yields Tough Films,

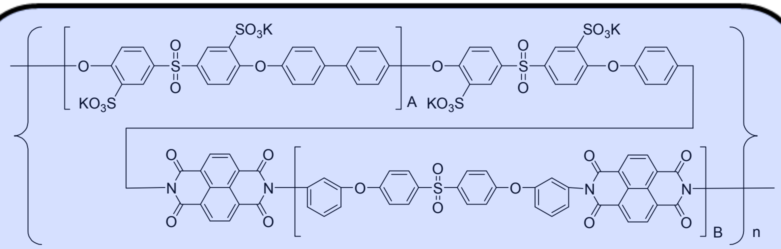


Segmented BisSF-BPSH100 Copolymers Show Good Modulus Temperature Behavior



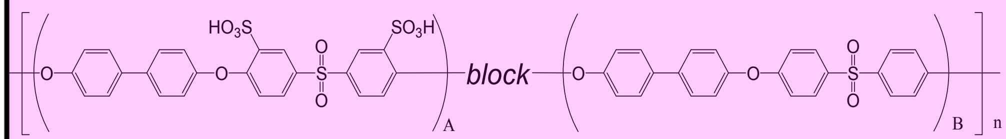
*Acid form; dried for 10 minutes at 180 °C prior to run; 5 °C/min

Self Assembling Nano-Phase Separated PEM Morphologies Improve Proton Conductivity



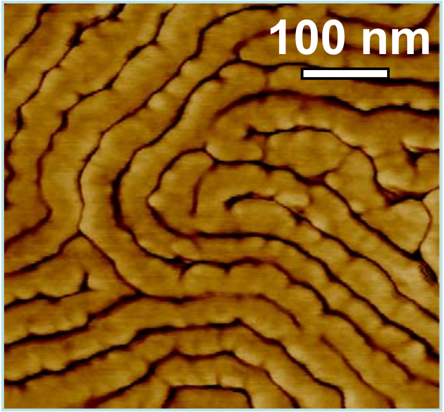
BPSH – PI Multiblock Copolymer

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

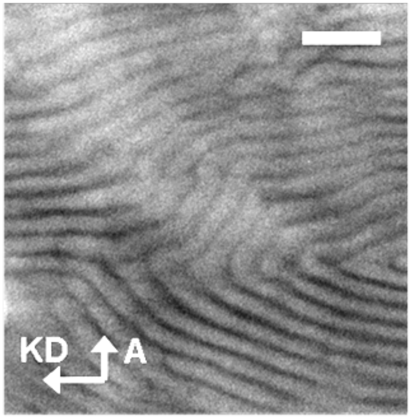


BPSH – BPS Multiblock Copolymer

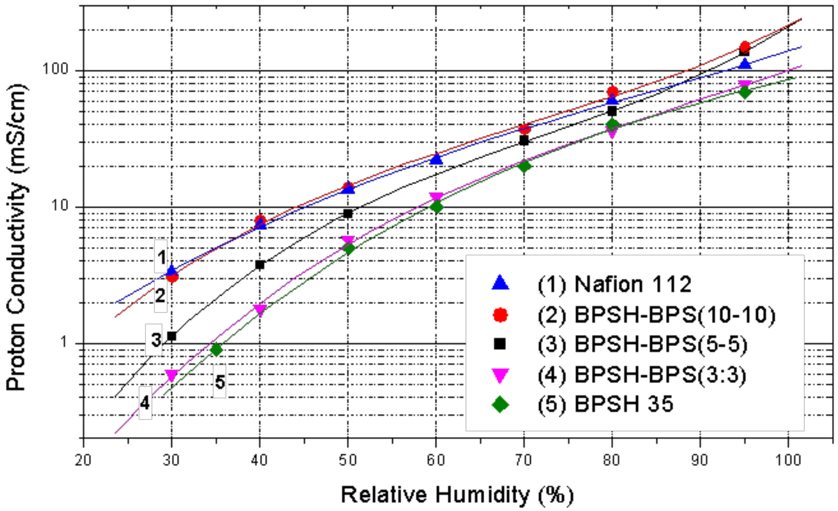
HS Lee, JE McGrath et al, Polymer, 49 (2008), 715-723



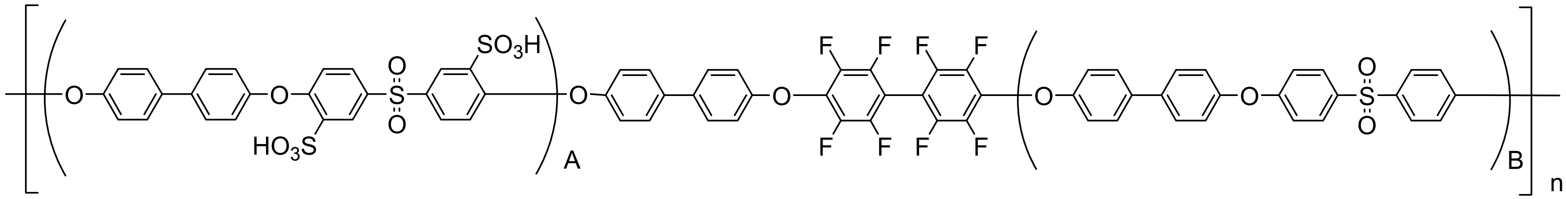
AFM Phase Image of BPSH-PI (15k-15k)

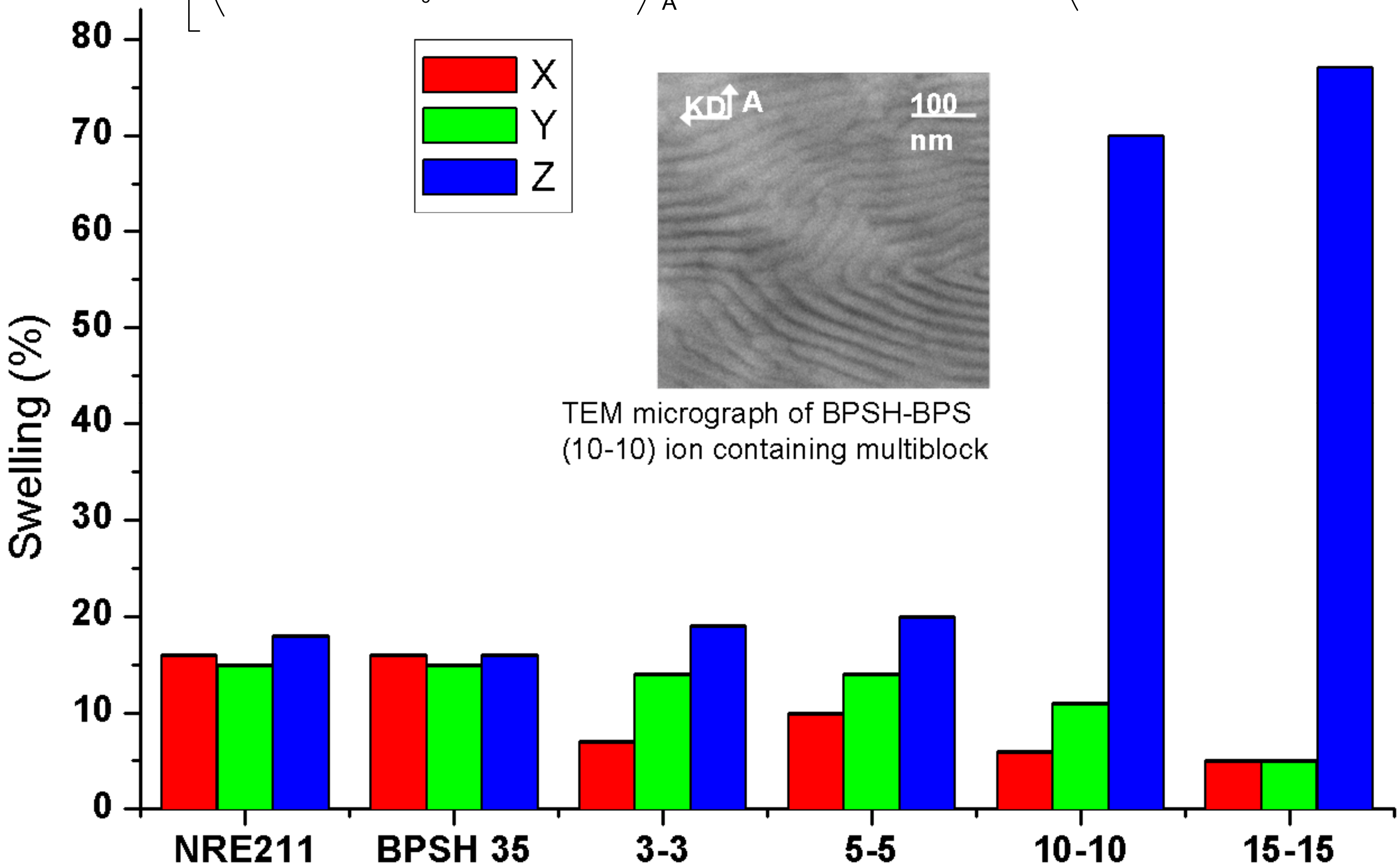


TEM Image of BPSH-BPS (10k-10k) Stained with Cesium

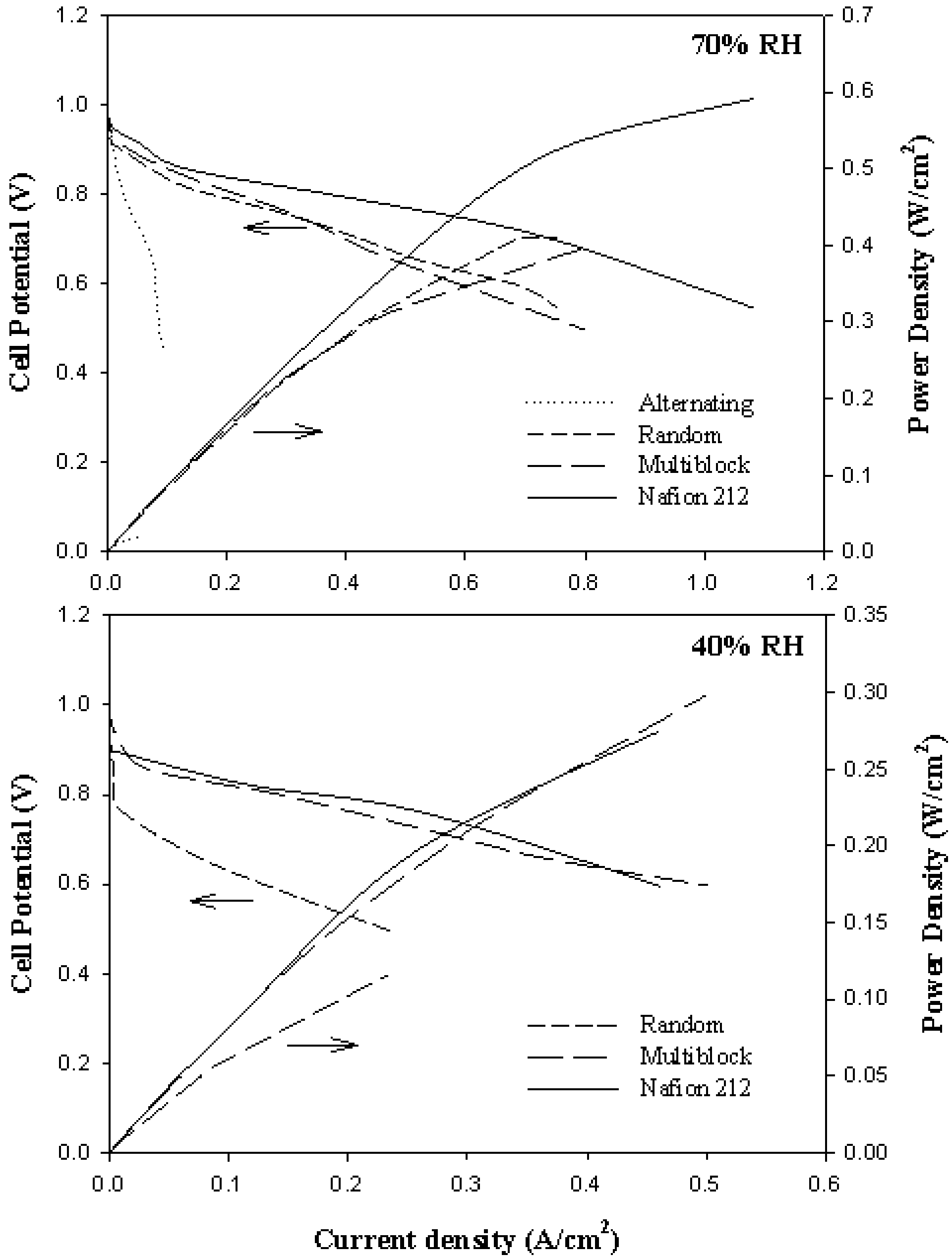


BPSH-BPS Multiblock Copolymers with Higher Block Lengths show Low X,Y Swelling



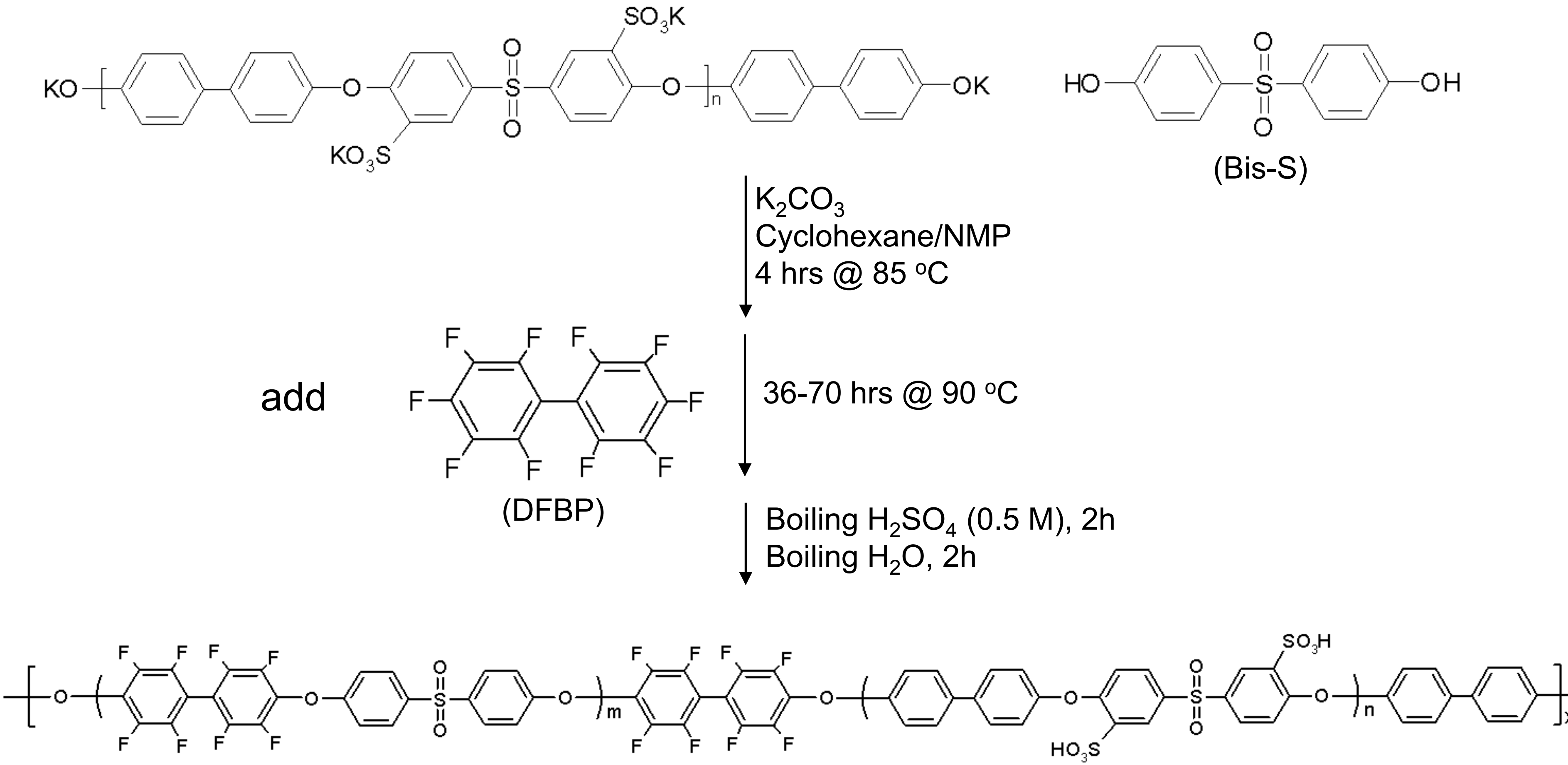


TEM micrograph of BPSH-BPS (10-10) ion containing multiblock



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

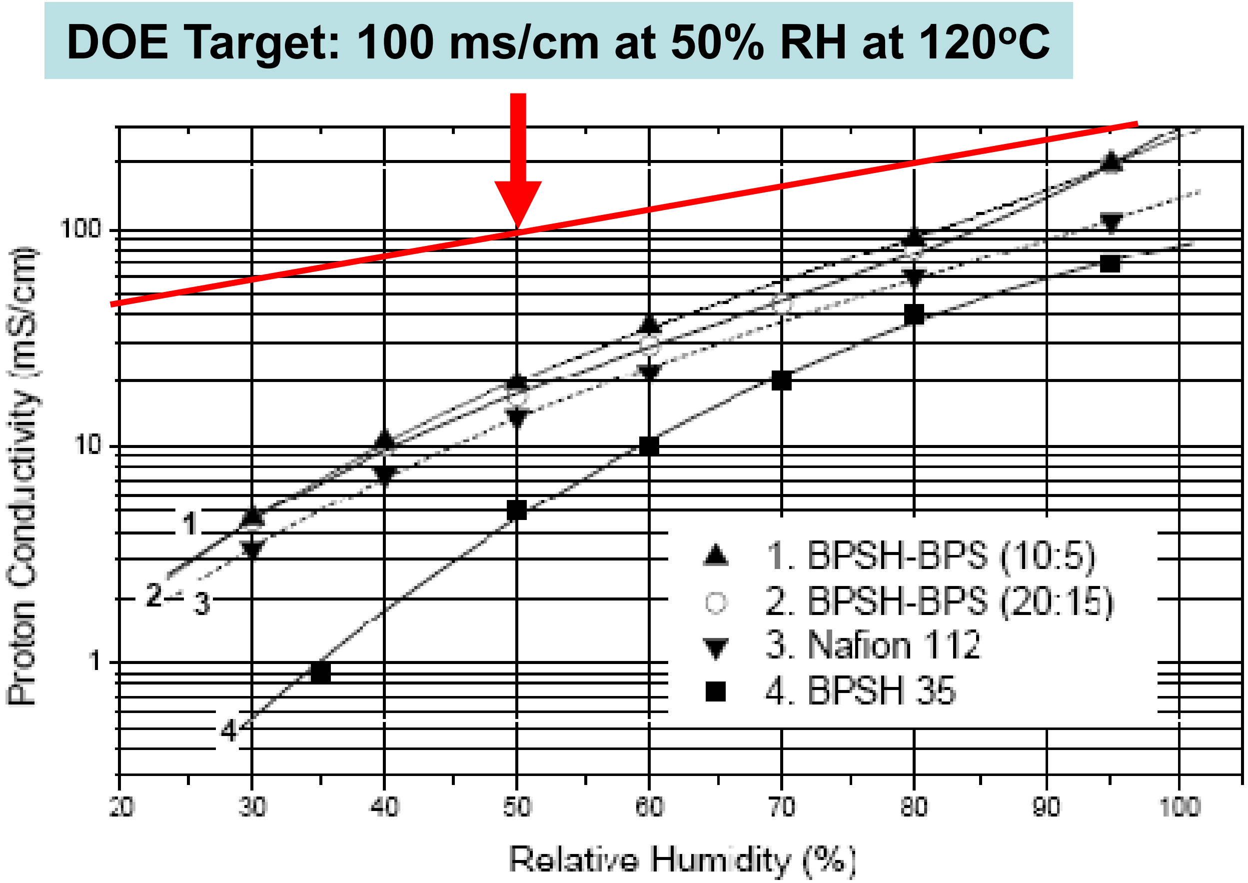
A simpler One Step Synthesis of Segmented Hydrophilic-Hydrophobic Copolymers has been Defined



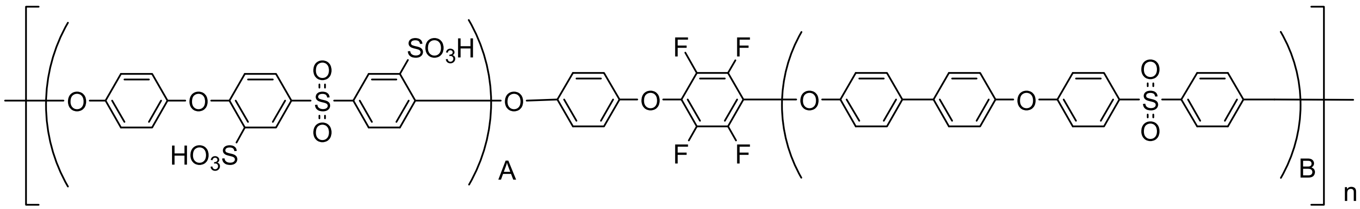
BisSF-BPSH100; (x:y)K,

where x is the theoretical hydrophobic block length and y is the hydrophilic block length (Kg/mole)

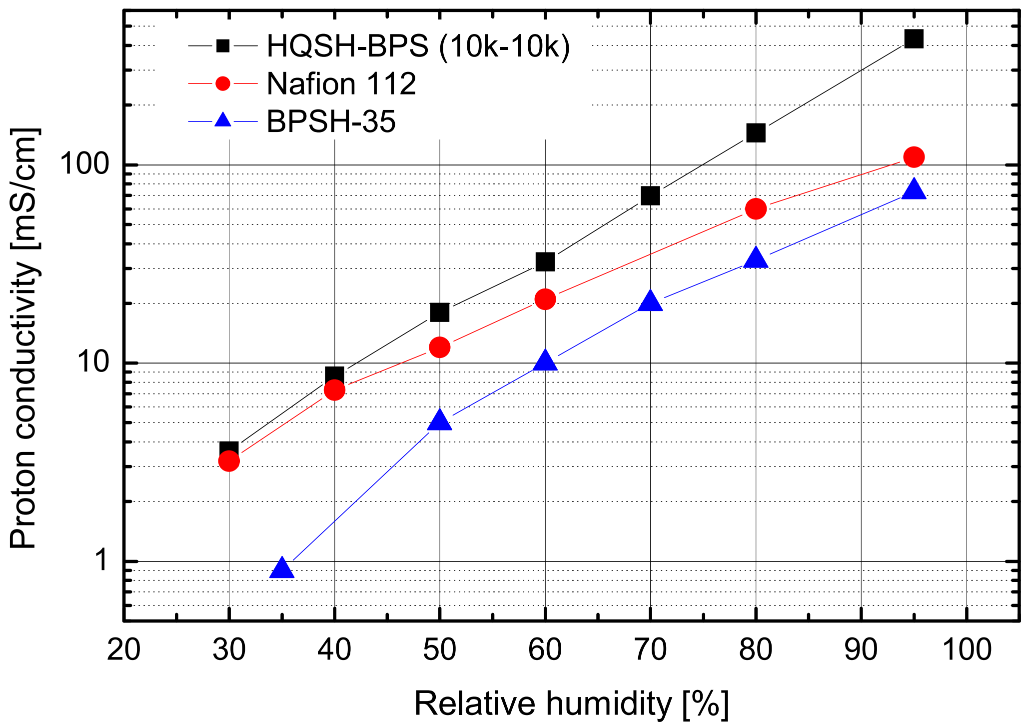
Proton Transport Behavior as a Function of RH

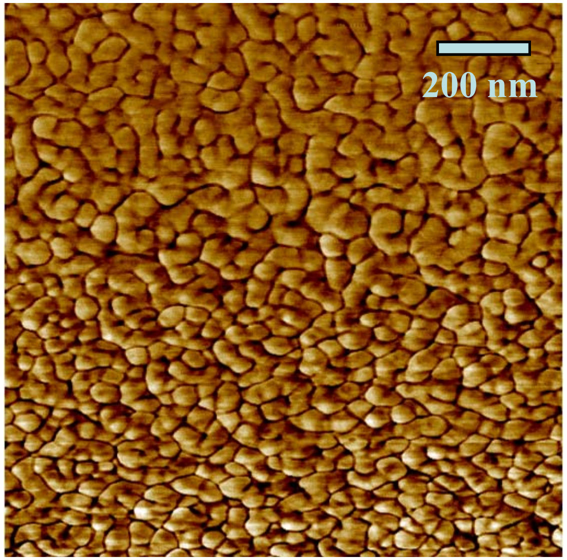


HQSH-Based Multiblock Copolymers; Proton Conductivity at 80oC



HQSH-BPS multiblock copolymer

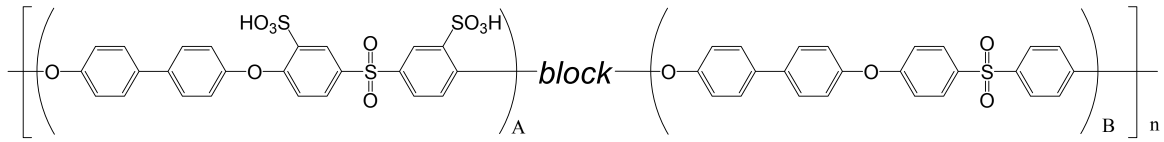




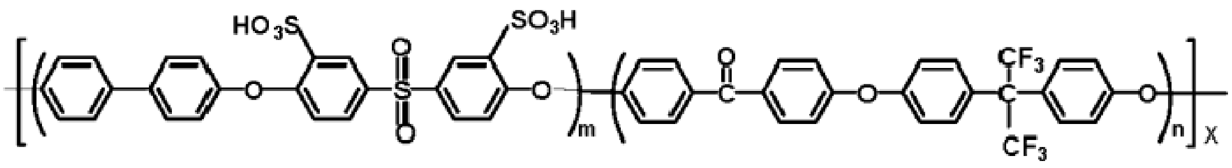
Tapping Mode AFM Image of the HQSH 10- BPS 10

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

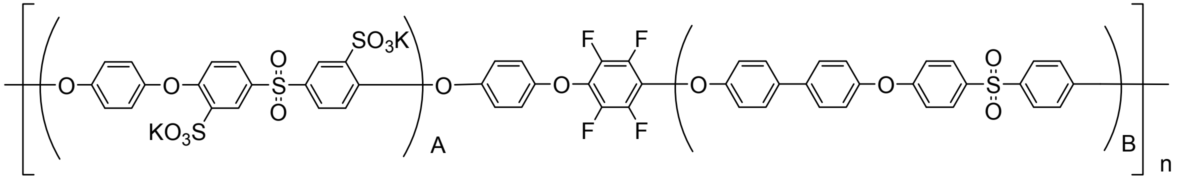
1. BPSH-BPS (20k-5k), Target IEC = 2.65 meq/g



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

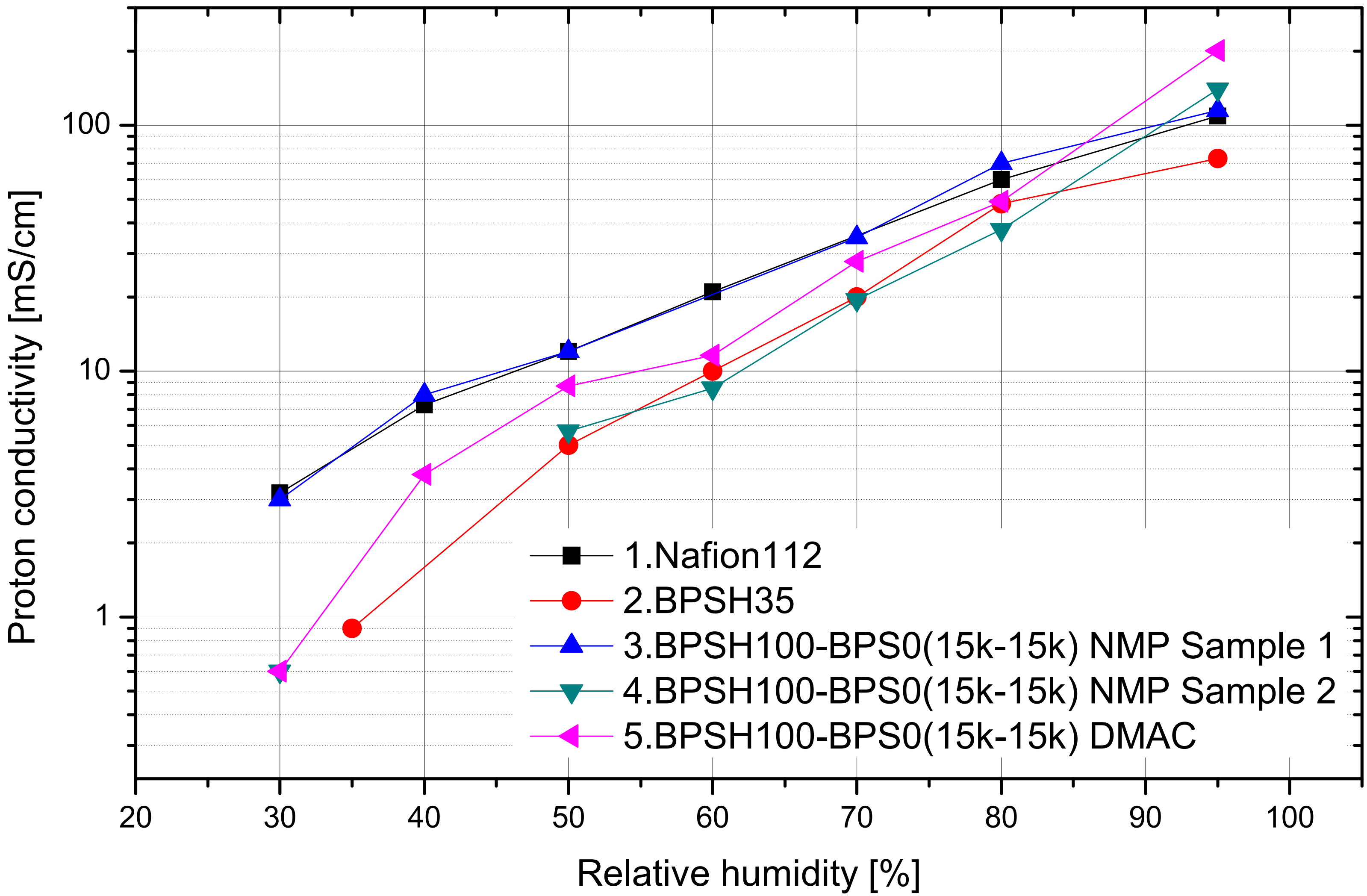


3. HQSH-BPS (15k-5k), Target IEC = 2.83 meq/g

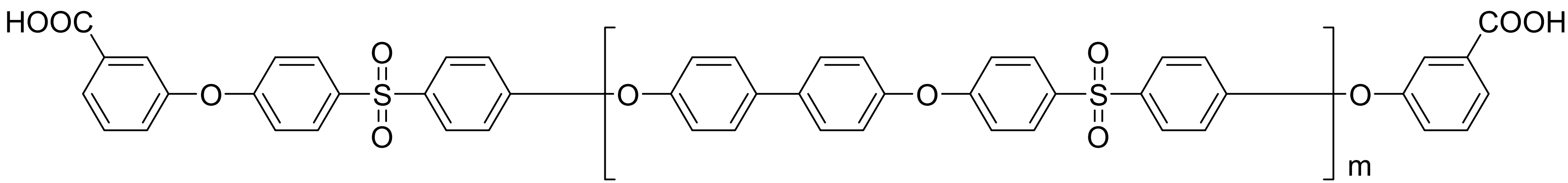


The copolymers were acidified and successfully cast on Mylar® (PET) substrates.

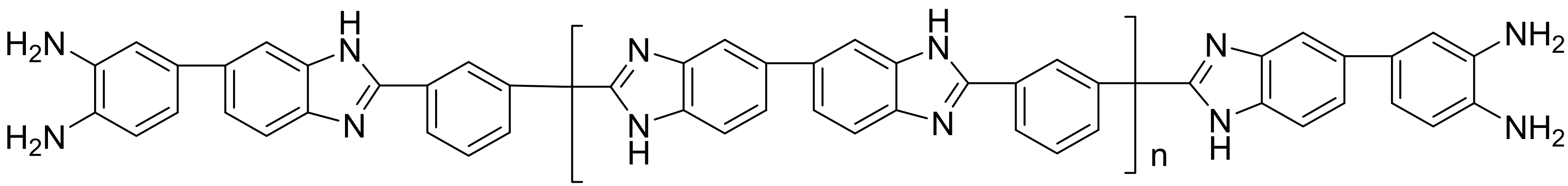
Film Casting Influences Conductivity and a Block Copolymer Affords the 2008 DOE Goal of 70mS/cm at 80% RH at 30C



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



Acid - terminated Biphenyl Sulfone (BPS)



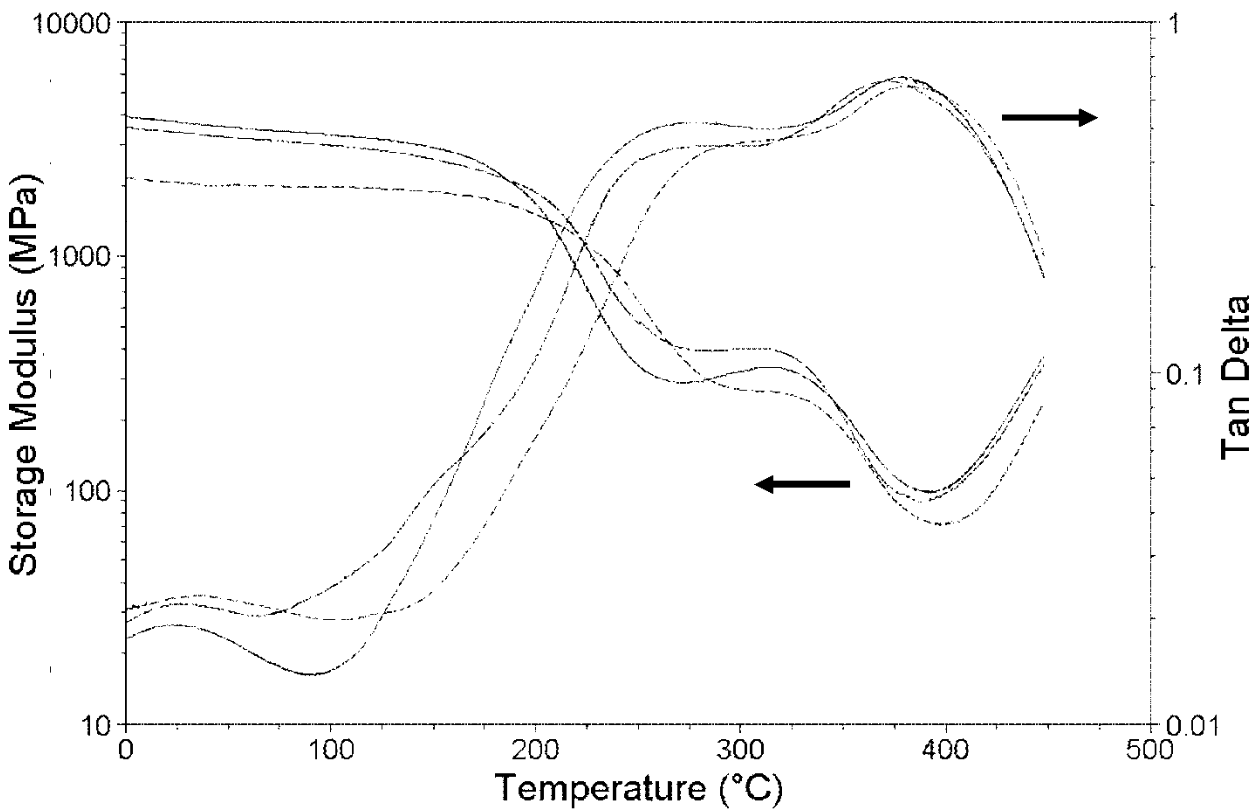
Diamine-terminated Polybenzimidazole (PBI)

NMP
200 °C 48hr

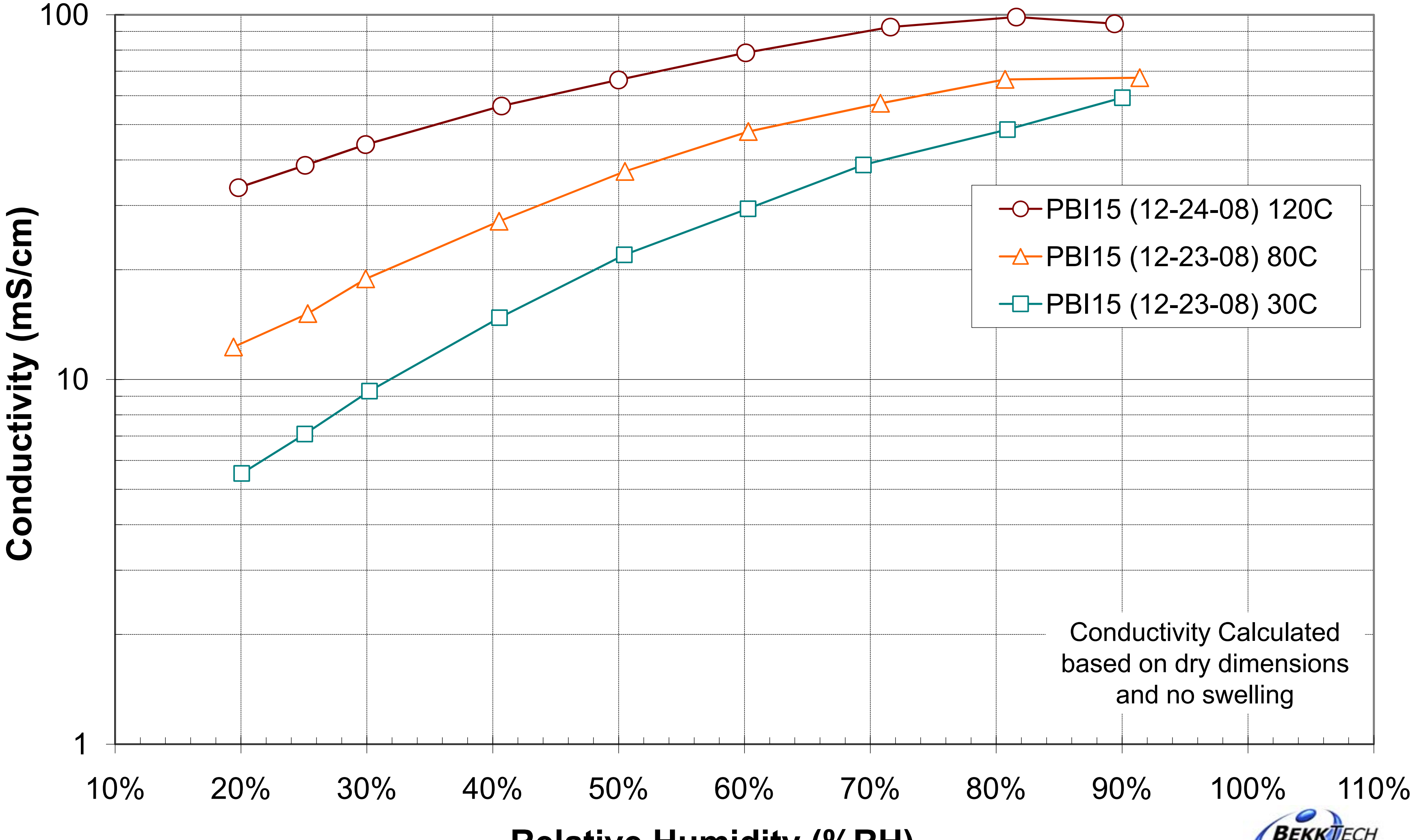
~~~~~~~~(Poly arylene ether sulfone)$_m$~(Polybenzimidazole)$_n$~~~~~~~~~~~~

(mechanical strength) **(proton conductivity)**

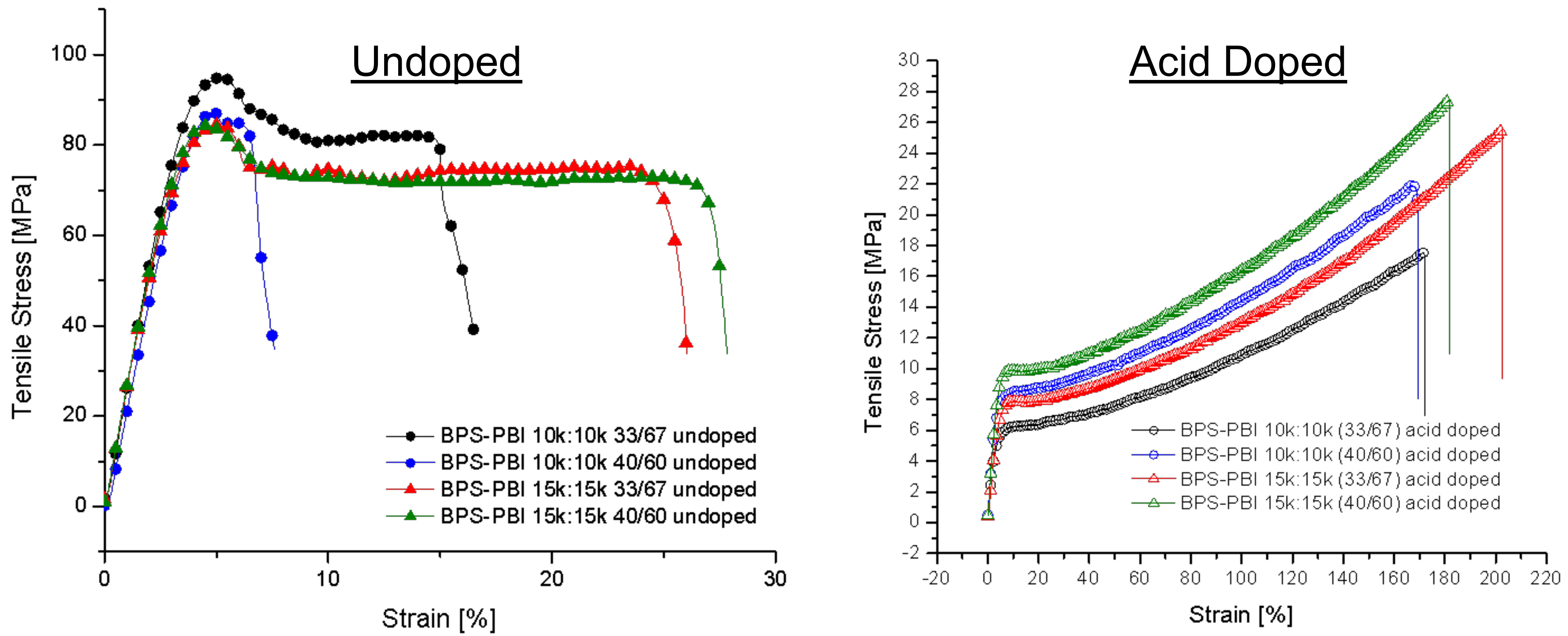
Storage Modulus and Tan Delta Shows 2 Nanophases for BPS-PBI Copolymers; the PBI Phase was selectively doped with H3PO4



Bekktech Conductivity - Increasing RH Only



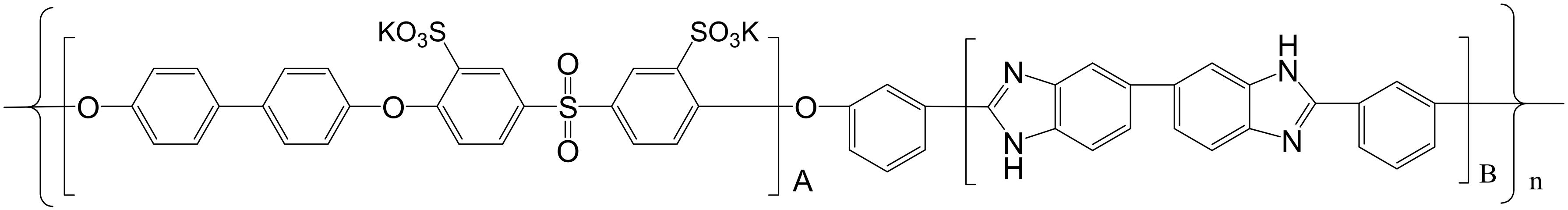
Acid Doped BPS-PBI Membranes Have Good Tensile Strength and Higher Elongations than the Control BPS-PBI Multiblock Copolymer Membranes-Strength is 2X Nafion® Control



*Membranes were equilibrated at 25 ^{o}C, 40% RH prior to testing. Testing conducted at 25 ^{o}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

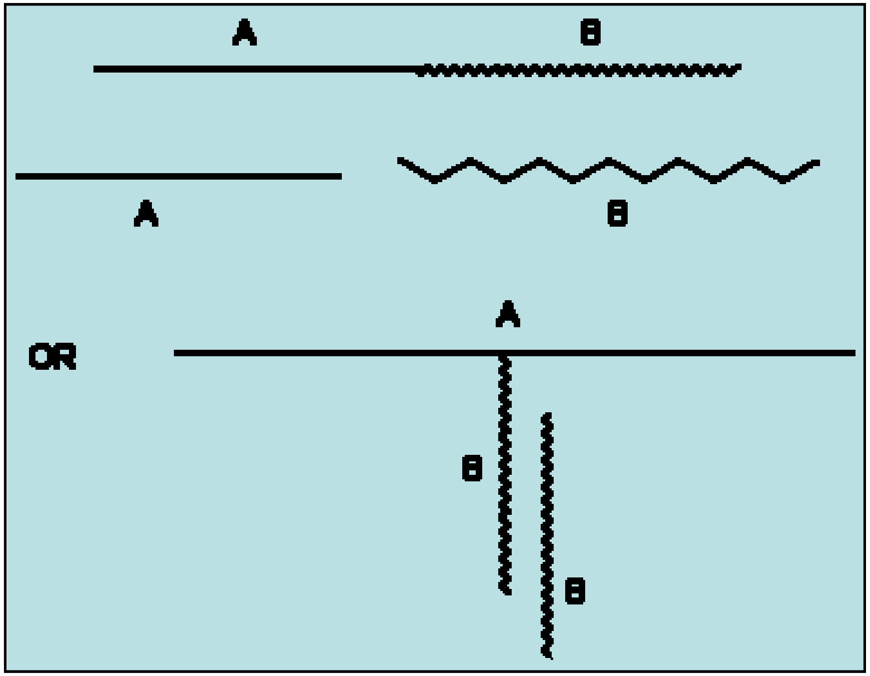
Salt Form : 14% Acid Form : 21%

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

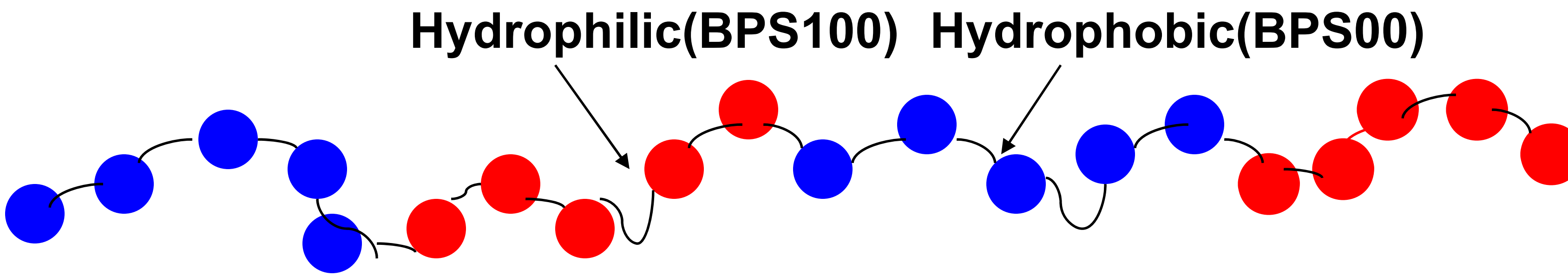
- Block and graft copolymers are usually "mechanically" compatible with their constituent homopolymers and the new compositions may enhance conductivity



"Emulsification" or Compatibilization is achieved, ≈1μ dimensions possible in the blends.

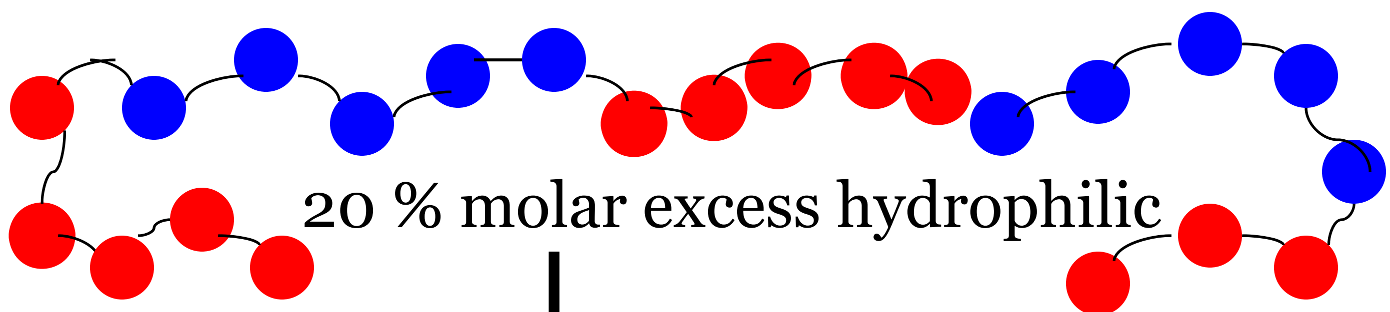
Crosslinking Ionic Multiblocks

1.



Hydrophilic : Hydrophobic = 1 : 1 mol ratio

2.

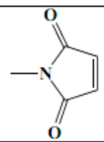
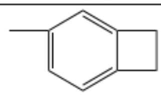
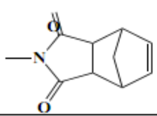
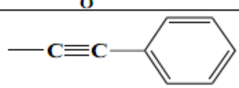
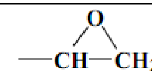
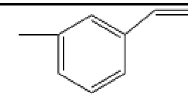
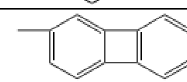
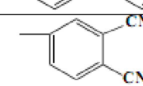
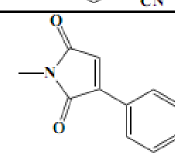


- The phenoxide groups can react with a suitable crosslinker
- Tetra epoxy or ethynyl

Crosslinked Block Copolymer

Reactive Groups for High-Performance Thermosets

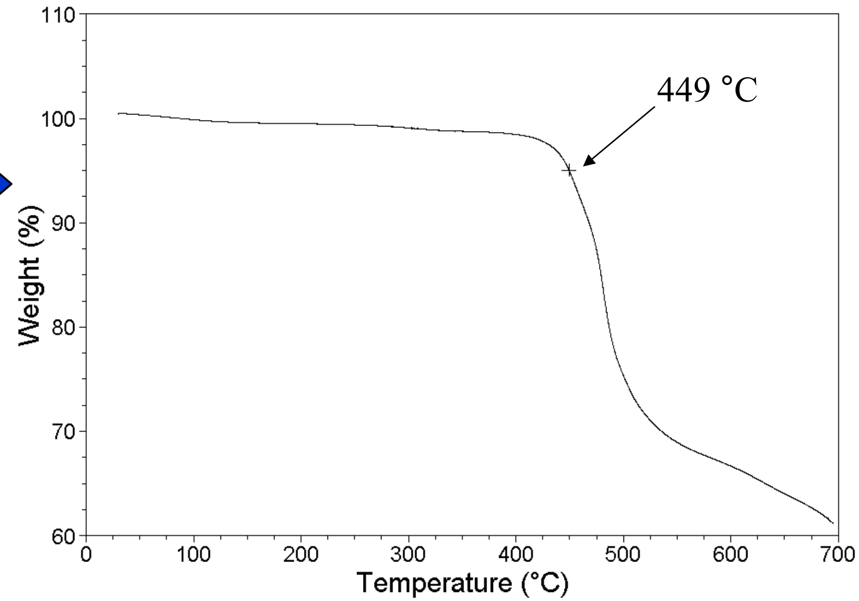
Table 2.1 Reactive Groups for High-Performance Thermosets[61]

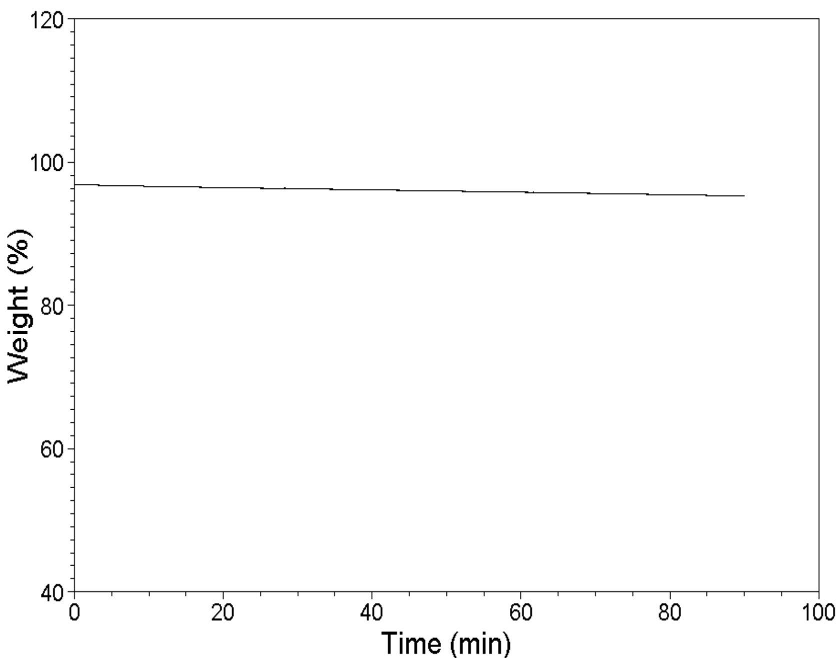
Functionality Structure	Functionality Name	Approximate Cure Temp. (°C)
	maleimide	200
—OCN	cyanate ester	170
	benzocyclobutene	200
—C≡CH	ethynyl	200
	nadimide	300
	phenylethynyl	350
	epoxide	variable with catalyst and co-reactant
	styrenyl	200
	biphenylene	300
	phthalonitrile	250
	phenylmaleimide[62]	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, N_2 atmosphere

Surface-Fluorination of BPSH PEM *Cooperation with Prof Y. M. Lee and Colleagues*

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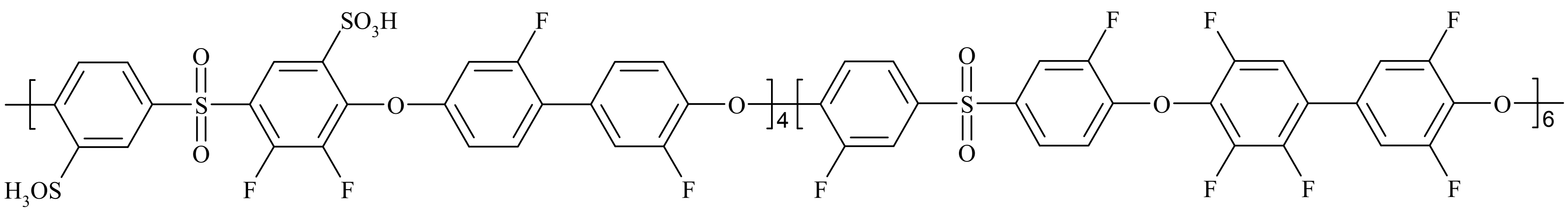
Objectives

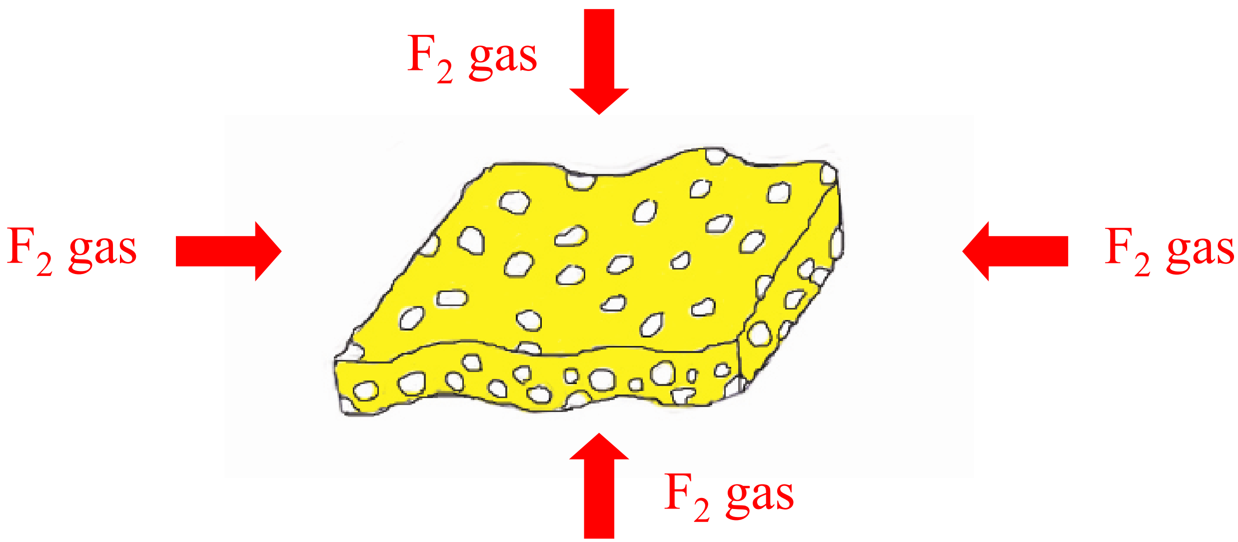
- Can surface fluorination effect disulfonated poly(arylene ether sulfone) (BPSH) copolymer structure, morphology and membrane properties

- What is the relationship between contact time and electrochemical properties including long-term fuel cell MEA performance?

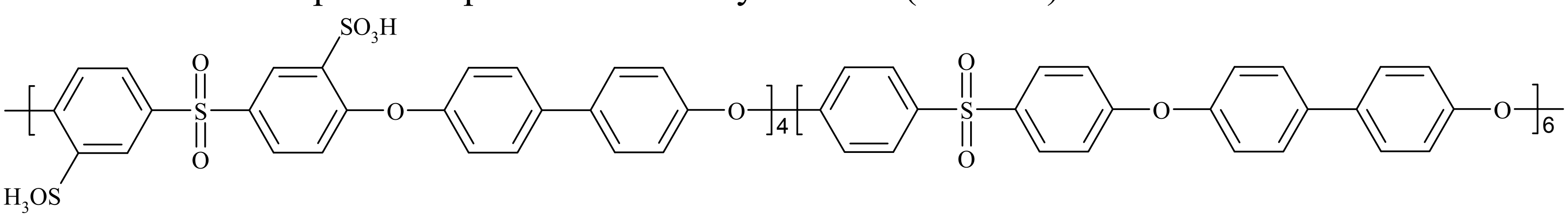
Basic Concepts of Membrane Post Fluorination

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

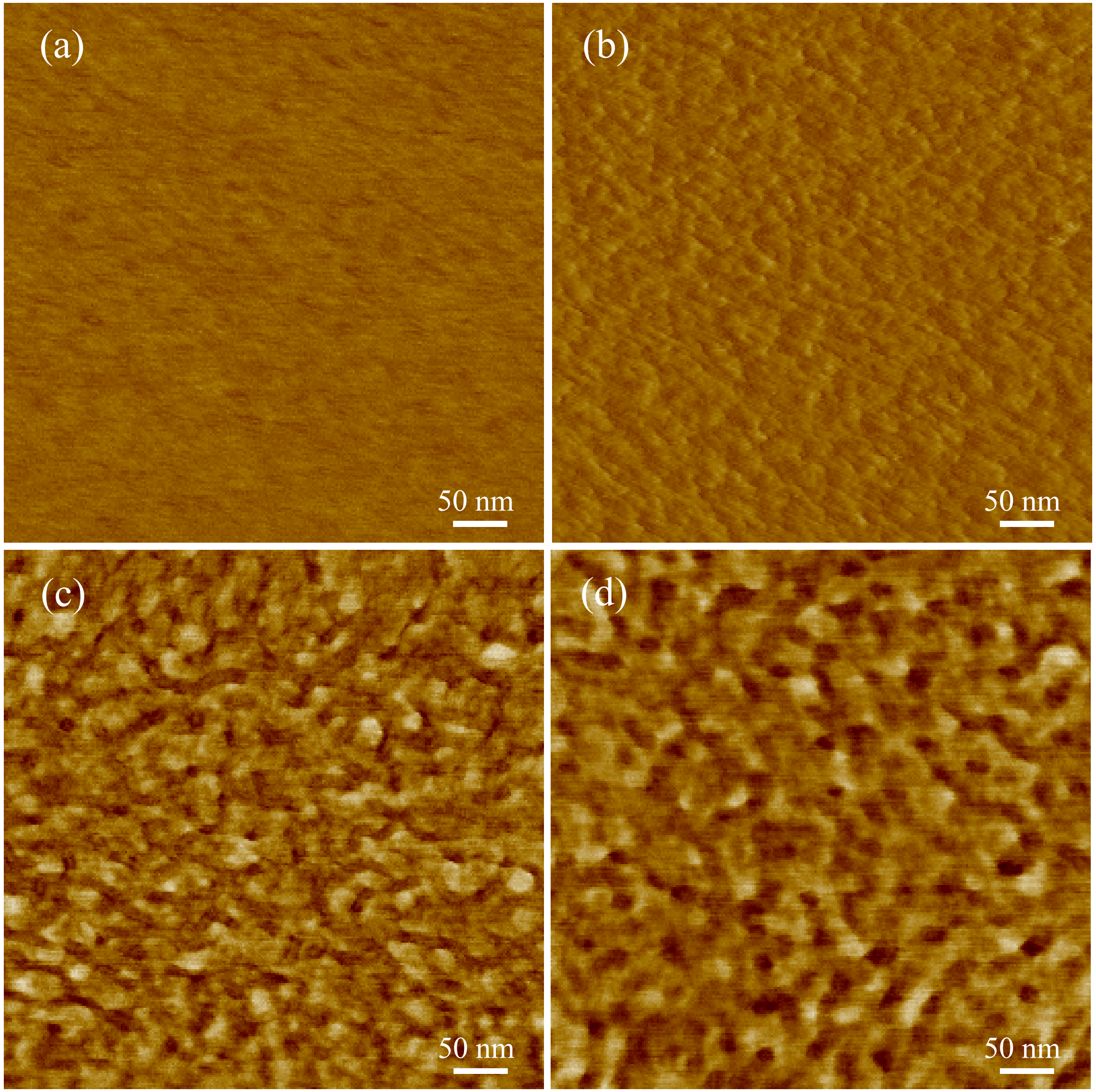




- No modification: poor compatible with catalyst binder (Nafion®) in electrodes



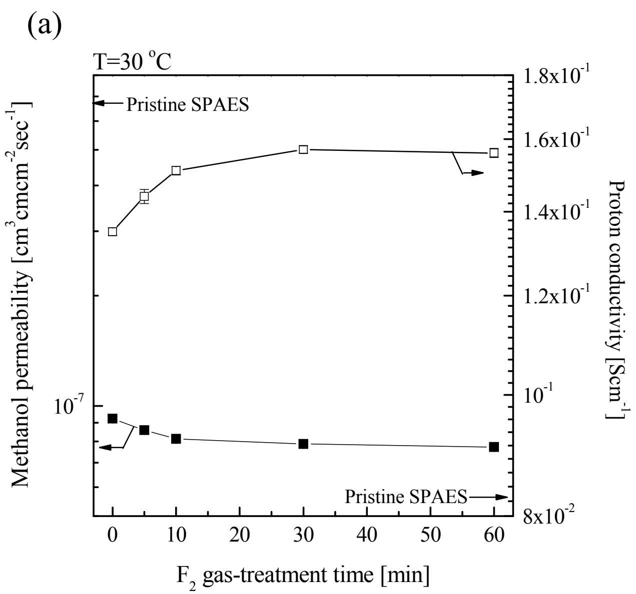
Fluorination Develops Morphological Order in BPSH-40



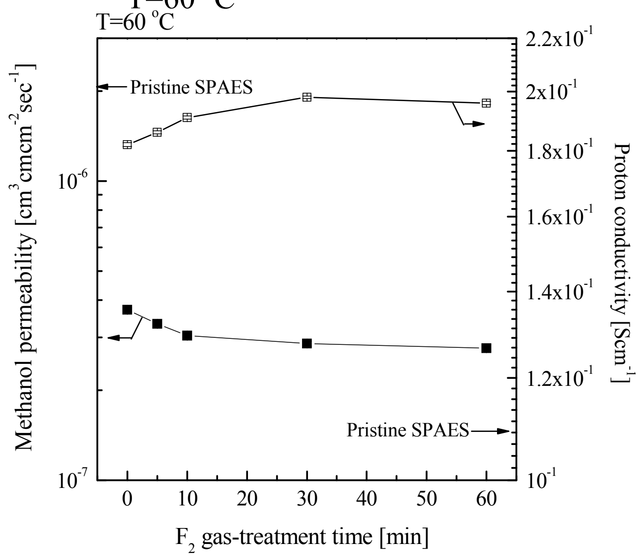
AFM tapping mode phase images of
(a) SPAES Control
(b) FSPAES 10 minutes
(c) FSPAES 30 minutes
(d)FSPAES-60 minutes

Relative humidity was about 35% RH.

Fluorination Increases Proton Conductivity and Decreases Methanol Permeability



T=60 °C



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

$P_{\text{MeOH\_pristine SPAES}} = 6.64 \times 10^{-7}$ cm^{3}cmcm^{-2}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

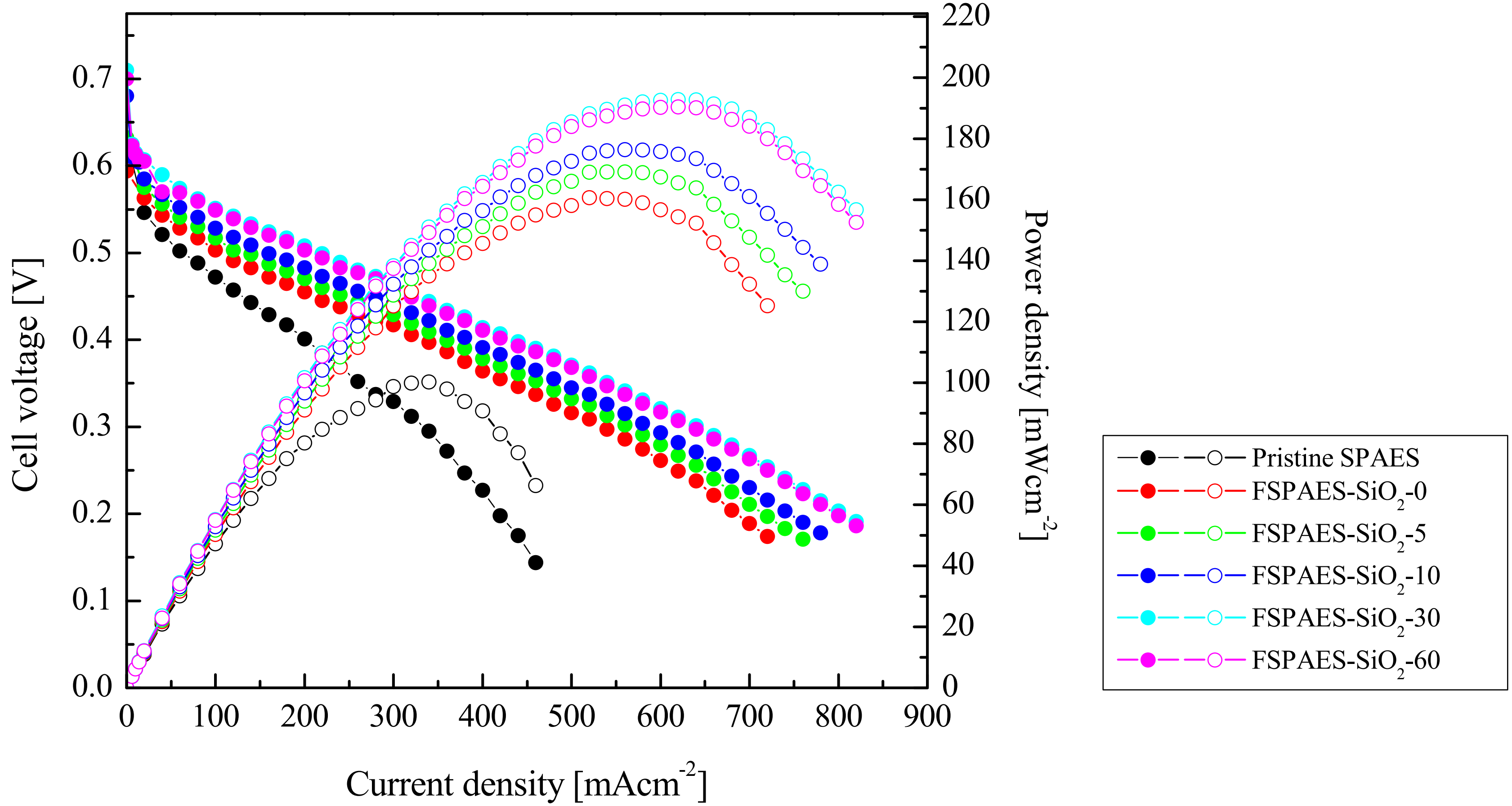


Figure 8. Electrochemical single cell performances of SPAES membranes under a flow rate of 1M MeOH/O_2=1 sccm/200 sccm at 90 ^oC

Long Term Durability is Greatly Improved:Enhanced Interfacial Behavior ?

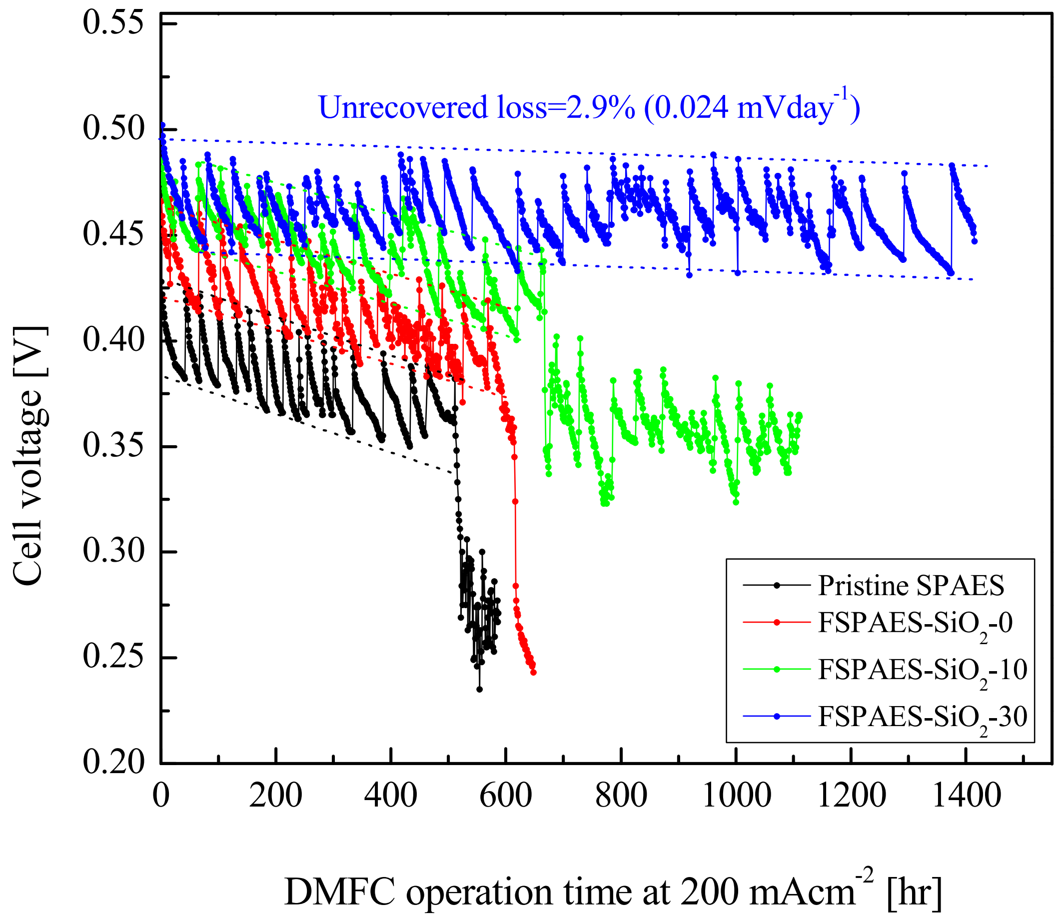


Figure 9. long-term electrochemical performances of SPAES membranes under a flow rate of 1 M MeOH/O_2= 3 sccm/ 1,000 sccm at 90 ^oC

Nanophase Separation in Hydrophilic-hydrophobic Nonionic Block Copolymers

- Obeys: ΔG = ΔH – TΔS
- Balance of enthalpic and entropic forces
  - Enthalpic: Dissimilar *A,B* phases want to repulse (positive Flory-Huggins χ parameter, χ_{AB})

$$\chi_{AB} = (z/kT)[\varepsilon_{AB} - ½(\varepsilon_{AA} + \varepsilon_{BB})]$$

  - Entropic: Linkages between phases prevent macroscopic separation (elastic restoring force), proportional to chain length (*R*), size (*a*) of *N* monomers

$$\Delta G_{elastic} = 3kTR^2 / (2Na^2)$$

  - 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

Noshay A, McGrath JE. *Block Copolymers: Overview and Critical Survey*. New York: Academic Press, 1977,
[1] Bates FS, Fredrickson GH. *Physics Today.* **1999**, *52*(2), 32.
[2] Leibler L. *Macromolecules.* **1980**, *13*(6), 1602.

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