2006 DOE Hydrogen Program Review Presentation

Advanced Materials for Proton Exchange Membranes

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McGrath Group 2006

Front Row (L to R): Dr. W. Harrison (Ph.D. 2004), Prof. Y.J. Kim (Sung KyunKwan Univ, Korea), J.E. McGrath, A. Badami, H. Wang.

Back Rows (L to R): M. Paul, X. Yu, A. Roy, E. Morazzani (undergrad), A. Cleaton (undergrad) N. Arnett, M. Hill, Dr. Z. Zhang, R. Hopp, O. Lane, Y. Chen, H.S. Lee, Y. Li, Dr. G. Fan, Dr. M. Sankir, J. Yang, S. Takamuku (visiting scientist)

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*”

OUTLINE

- **Research Progress Objectives**
  - Approach and Strategy
  - Partially fluorinated systems
  - Multiblocks
  - Crosslinking
  - Blends
  - Film Casting

Objectives

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

Research Approach/Hypothesis

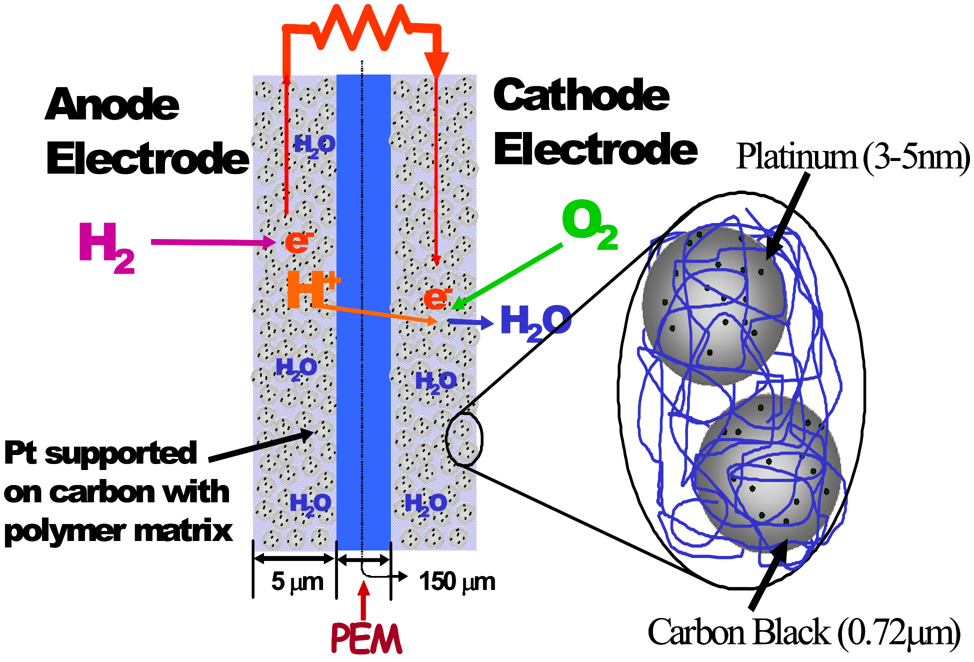
- Thermally, hydrolytically, and oxidatively stable aromatic ionomers with high T_g, ductility, and controlled hydrophilicity are required
- Synthesis
  - Linear and crosslinked statistical hydrophobic/hydrophilic copolymers
  - Linear multiblock hydrophobic/hydrophilic copolymers (current & future)

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)

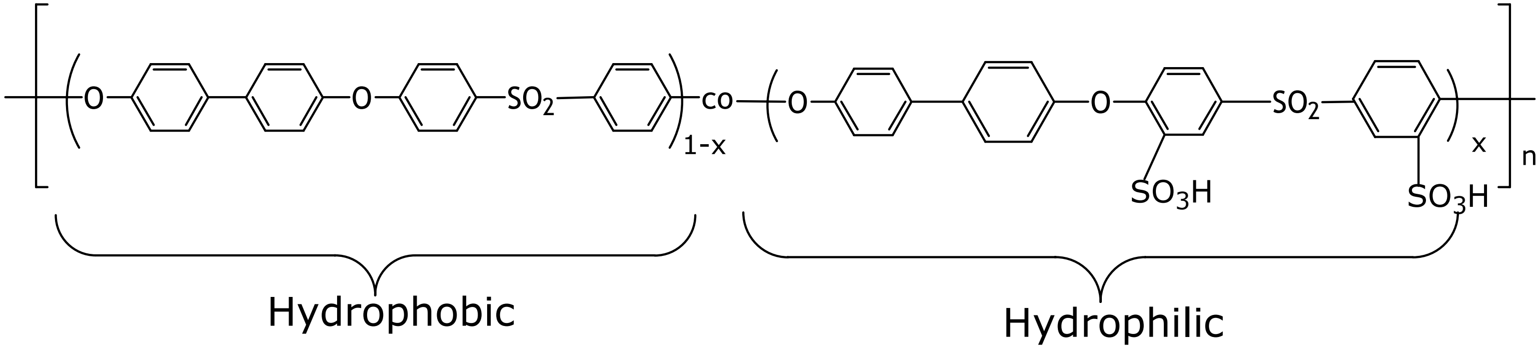
Membrane Electrode Assembly (MEA)



The benchmark is Nafion™ for the membrane and electrodes

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

Sulfonated Poly(arylene ether sulfone)s (BPSH)



- **Acronym: BPSH-xx-*Mx***

  Bi Phenyl Sulfone: H Form (BPSH)

  xx= molar fraction of disulfonic acid unit, e.g., 30, 40, etc.

  Mx: Acidification method, e.g., *M1*, etc.

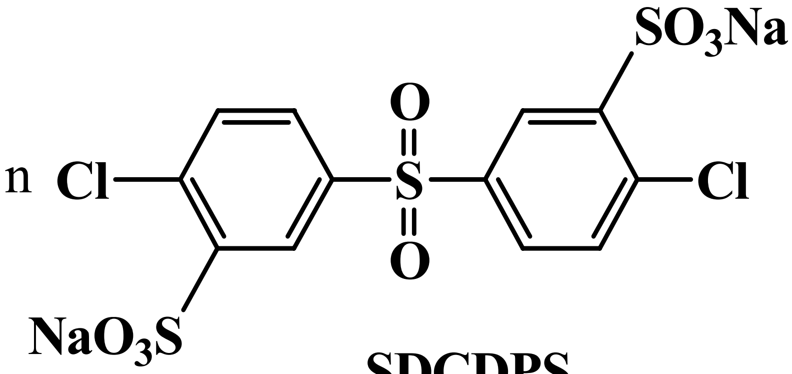
- **Acidification Treatment**

  Method 1: 1.5M H_2SO_4, 30°C, 24hrs, then deionized H_2O, 30°C, 24hrs.

  Method 2: 0.5M H_2SO_4, boil, 2hrs, then boiled deionized H_2O, 2hrs.

F. Wang, M. Hickner, Y.S. Kim, T. Zawodzinski and J.E. McGrath, "Synthesis and Characterization of Sulfonated Poly(arylene ether sulfone) Random (Statistical) Copolymers Via Direct Polymerization: Candidates for New Proton Exchange Membranes," *Journal of Membrane Science,* 197 (2002), 231-242.

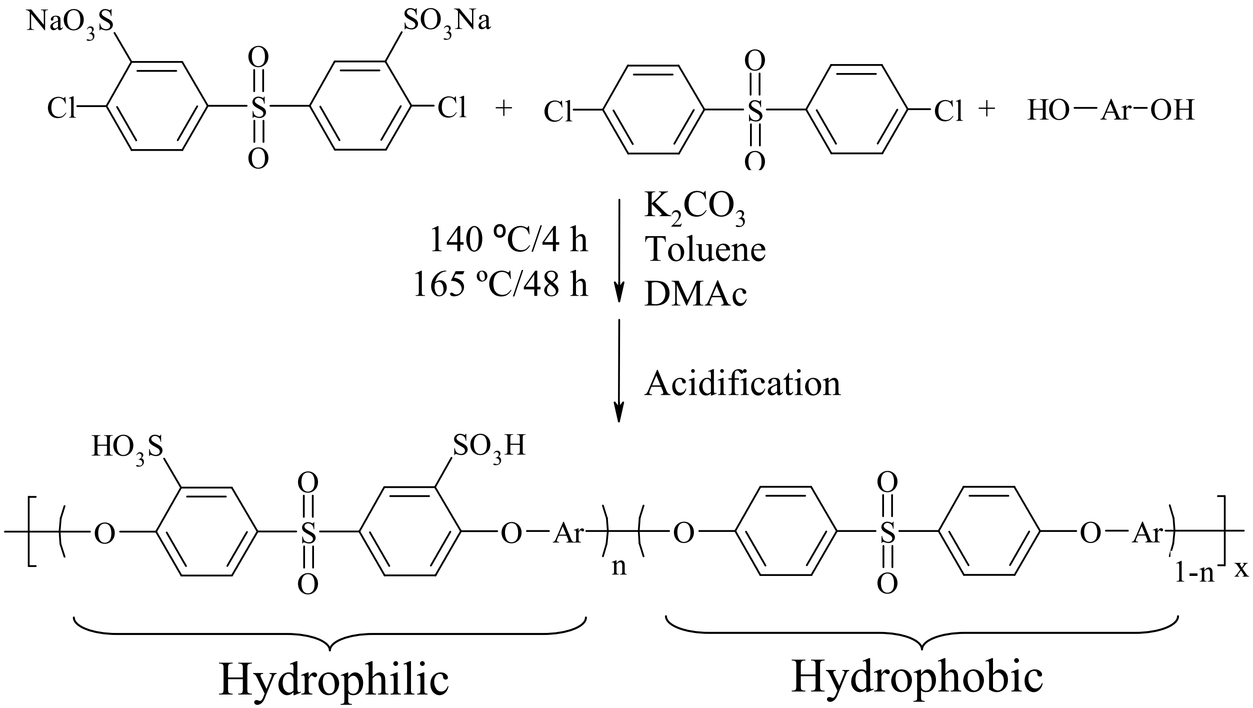
Advantages of Direct Polymerization

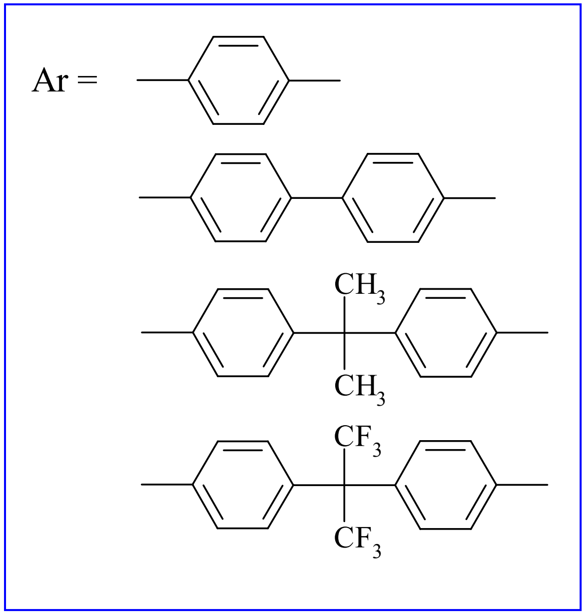


SDCDPS

- ✓ High yields from 40MM lb/year precursors
- ✓ Precise control of ionic concentration during synthesis
- ✓ Well-defined ion conductor location; morphology control
- ✓ High H^+ conductivity
- ✓ Enhanced stability due to deactivated position of $-SO_3H$
- ✓ Compatible with additives for >100°C studies
- ✓ Very high molecular weight copolymers possible

Copolymer Synthesis by Nucleophilic Aromatic Substitution

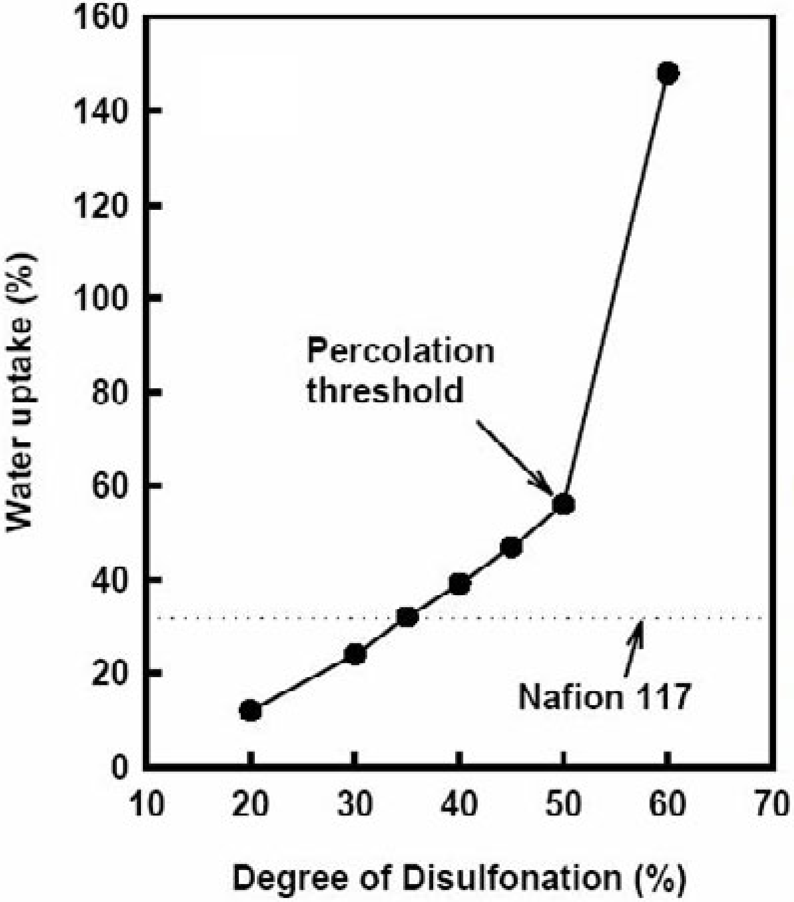


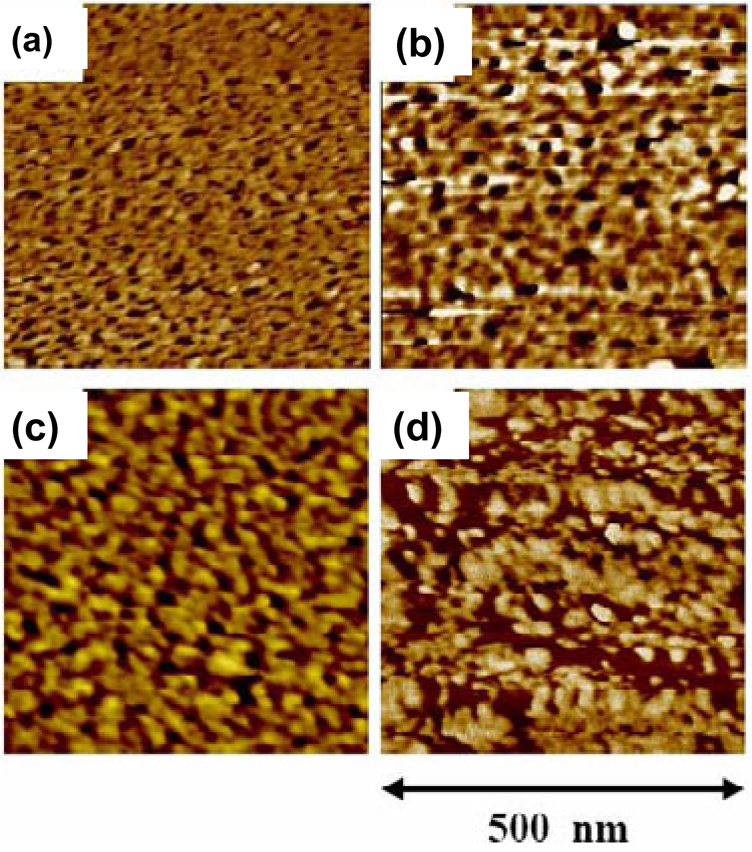


- Monomer and copolymers are scaleable to multi-kilogram quantities

Harrison, W.L.; Wang, F.; Mecham, J.B.; Bhanu, V.A.; Hill, M.; Kim, Y.S.; McGrath, J.E. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2264-2276.

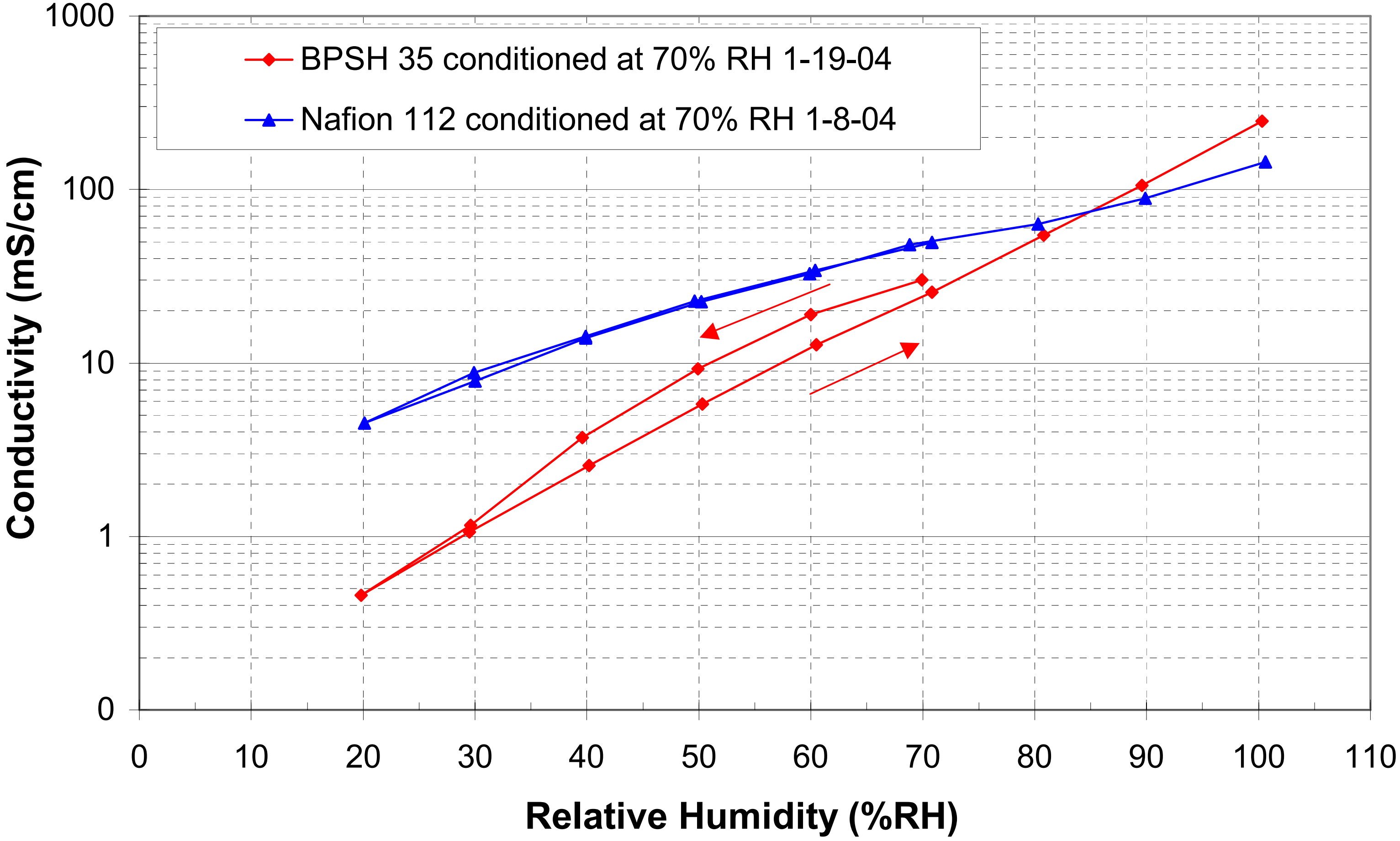
Water Uptake of BPSH Random Copolymers is Dependent on Morphology



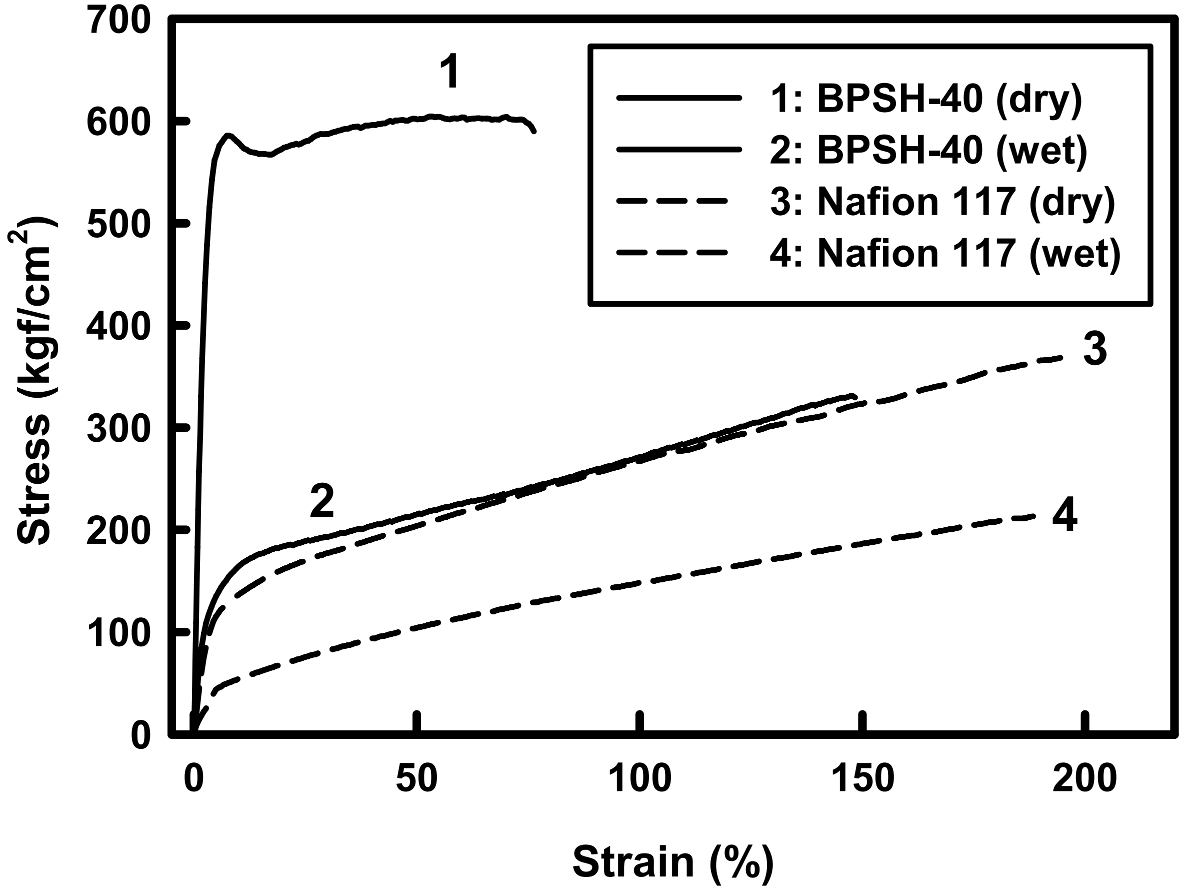


(a) Control; (b) 40% ionic content; (c) 50% ionic content; (d) 60% ionic content

Comparing Four Electrode Conductivity of BPSH 35 120°C, 500 sccm H_2, 230 kPa



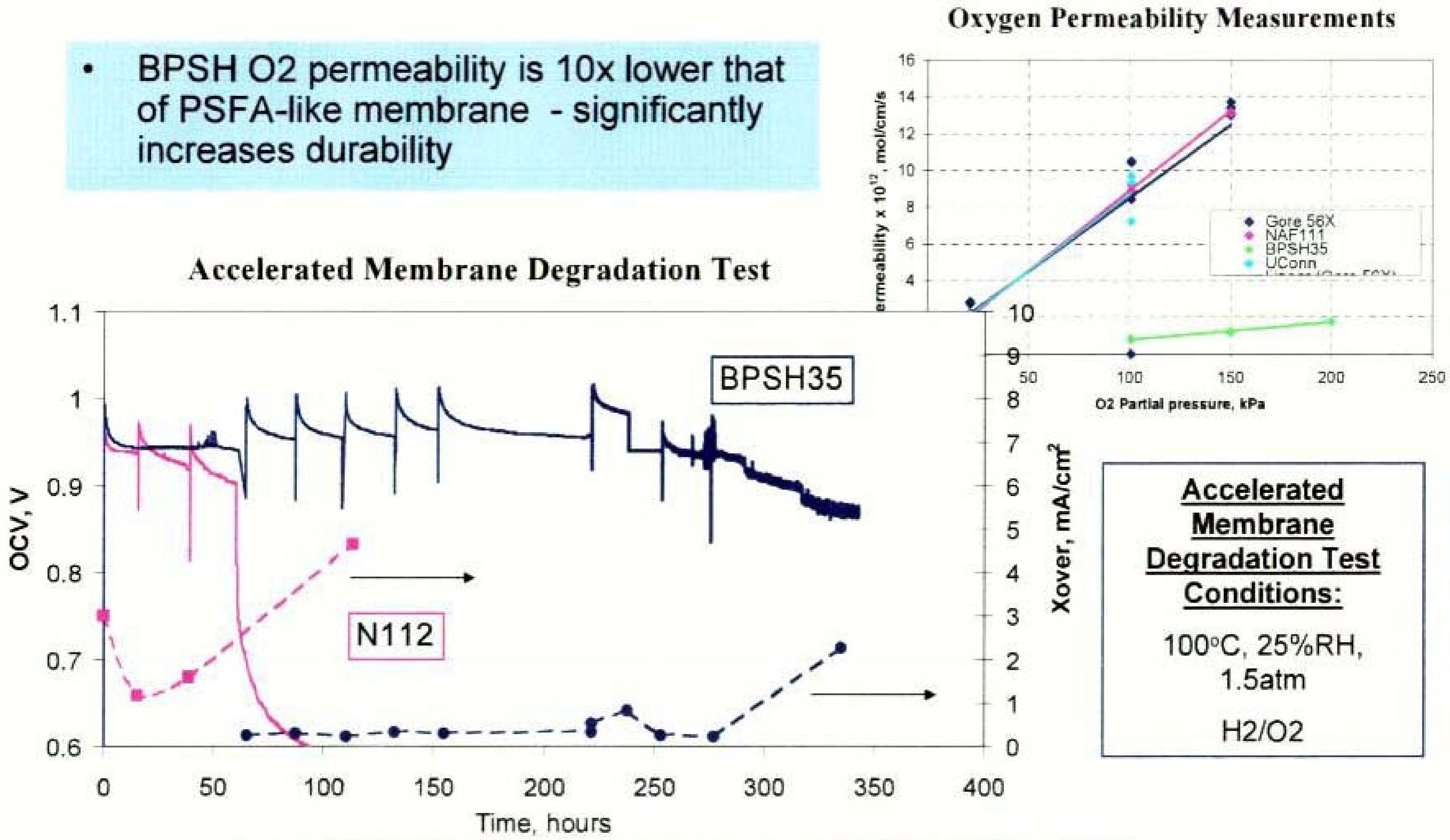
Comparison of Stress-Strain Behavior of BPSH-40 and Nafion 117*



The wet state of BPSH-40 and Nafion 117 had 22% and 16%, total water, respectively.

Colleagues at UTC (Dr. Protsailo/Dr. Haug) have shown BPSH outperforms the benchmark membrane as judged by open circuit voltage (OCV) in H2/O2 accelerated tests

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

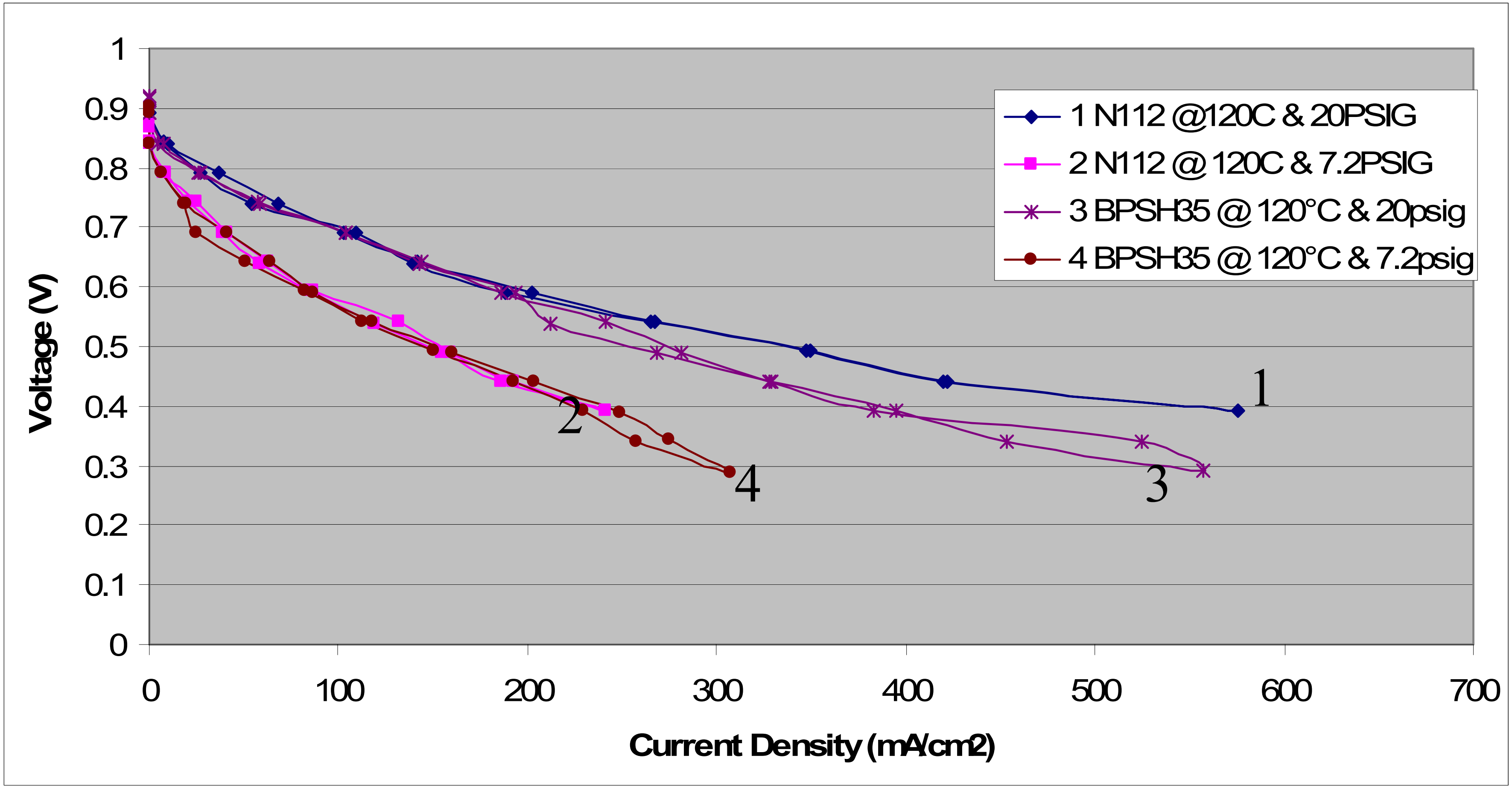


Accelerated Membrane Degradation Test Conditions:

100°C, 25%RH, 1.5atm

H2/O2

N112 and BPSH35-1mil at 120°C and 50%RH



At cell temperature of 80°C: Anode bottle=105°C

Cathode bottle=90°C

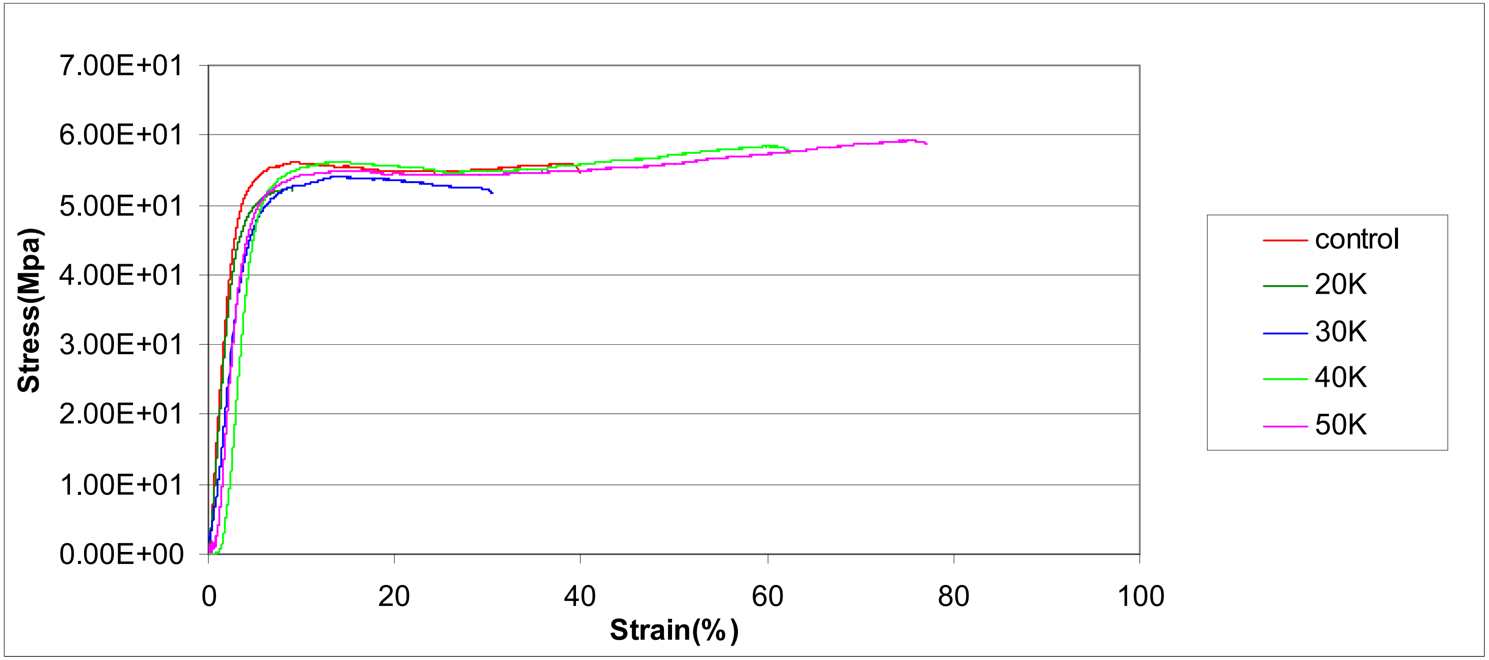
At cell temperatures of 100°C and 120°C: Anode bottle=100°

Cathode bottle=100°C

AGING STUDIES (no failures)

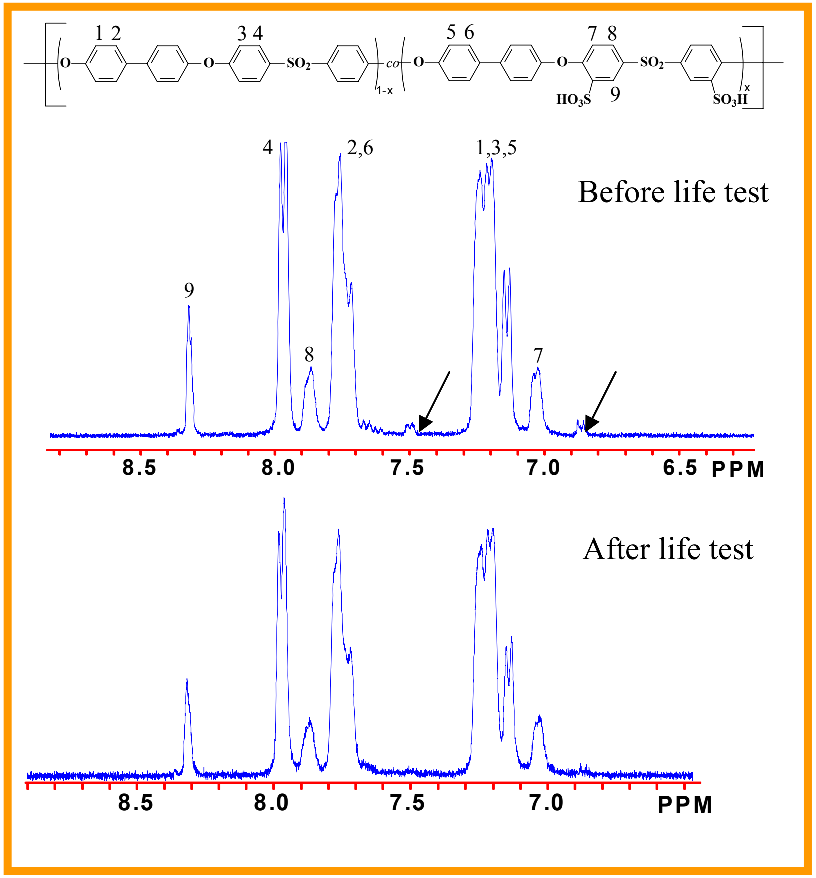
- Boiling water for 10,000 hours
- High pressure (2 atm) steam at 120^{o}C for 1000 hours
- MEA H2/air fuel cell, 80^{o}C, 1500 hours
- MEA, DMFC, 80^{o}c, 3000 hours

Comparisons of Stress-Strain Curves of BPSH35 Samples with Different Molecular Weights



The tensile testing was performed using a universal Instron machine at room temperature (23°C) and 40% R.H, with a crosshead displacement speed of 5mm/min.

Chemical Composition, IEC, Molecular Weight, and Water Uptake are Not Changed After a 700 hr Fuel Cell Test at 80°C



^{1}H NMR spectroscopy of BPSH-35 before and after life test

Life test	Disulfonation by ^{1}H NMR (%)	IEC (meq/g)		IV (dL/g)	Water uptake (wt.%)
		Calc.	Experimental		
Before	36	1.5	1.4	0.7	34
after	34		1.4	0.8	37 (33)[a]

[a] after life test and recast

No major chemical degradation of BPSH membrane was found

In cooperation with Dr. Y.S. Kim from LANL

States of Absorbed Water in a Hydrophilic Polymer

At Least Three States of Water

1. ***Non-freezable, tightly-bound water***

   plasticises polymer – lowers T_g

   water that is strongly bound to sulfonic acid groups

2. ***Freezable, loosely-bound water***

   broad melting behavior from -20 to 20°C

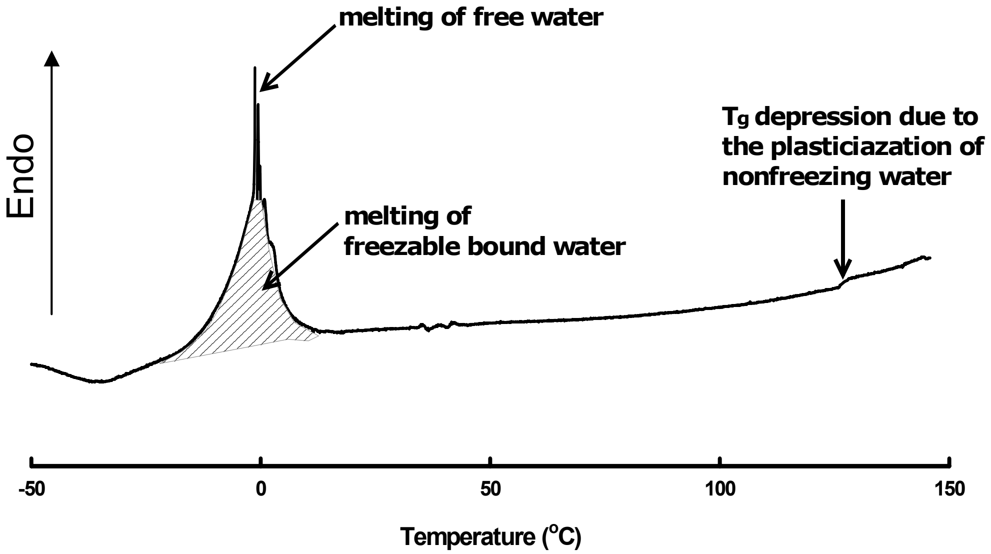
   water that weakly bound to the polymer chain

3. ***Free water***

   sharp melting point at 0°C

   water that has the same phase transitions as bulk water

DSC Thermogram



Nakamura, K.; Hatakeyama, T.; Hatakeyama, H. *Polymer* **1983**, 24, 871.
Kim, Y. S.; Dong, L.; Hickner, M. A.; Glass, T. E.; Webb, V.; McGrath, J. E. *Macromolecules* **2003**, 36(17), 6281

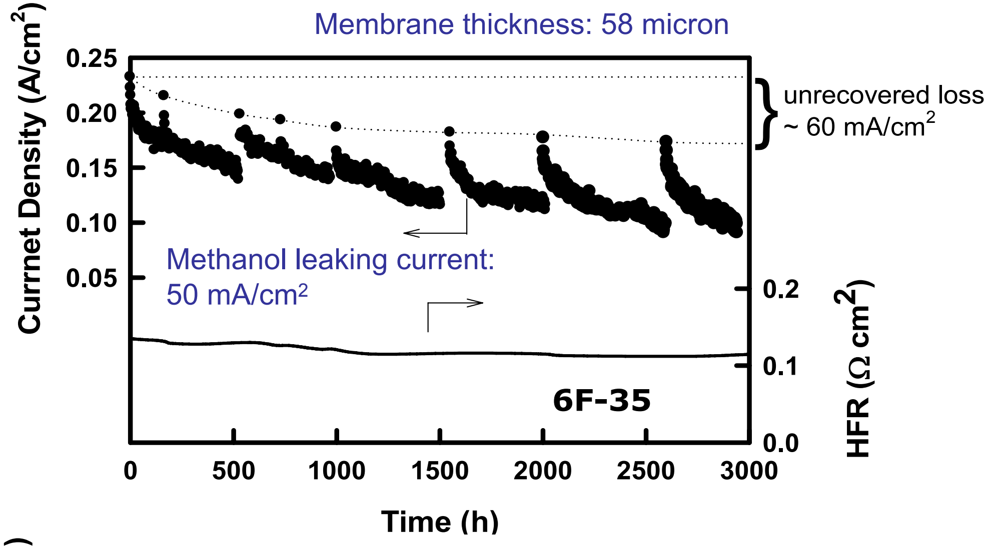
Why We Are Interested in States of Water in PEM?

Previous studies and current research show

- Only the bound non freezing water causes the depression in glass transition temperature .
- Presence of free water facilitates the transport process .
- Methanol permeability and conductivity tends to depend on free water and loosely bound water.
- Electro-osmotic drag increases with increase in free water.
- Activation energy for proton transport and methanol transport decreases with increasing amounts of free water.
- Operation of fuel cells under freezing conditions is likely a function of the states of water in the membrane

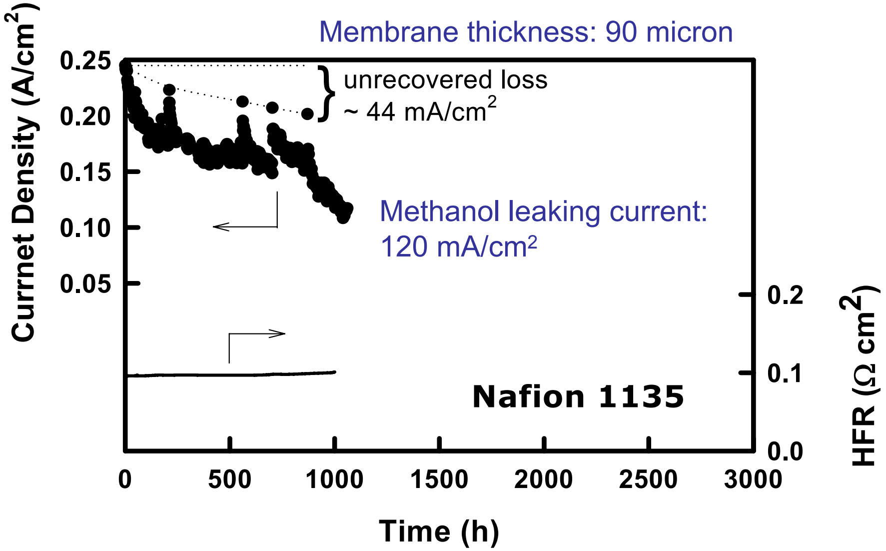
Kim, Y. S.; Dong, L.; Hickner, M. A.; Glass, T. E.; Webb, V.; McGrath, J. E. *Macromolecules* **2003**, 36(17), 6281

Long-Term DMFC Performance Studies at LANL (Y.S. Kim) on Partially Fluorinated BPSH(6FSH-35) showed Excellent Stability for 3000 Hours @ 80°C for Portable Power


Membrane thickness: 58 micron

unrecovered loss ~ 60 mA/cm²

Methanol leaking current: 50 mA/cm²


Membrane thickness: 90 micron

unrecovered loss ~ 44 mA/cm²

Methanol leaking current: 120 mA/cm²

Optimization of the membrane-electrode interface utilizing a partially fluorinated poly (arylene ether) membrane (6F-35) afforded stable long-term performance (3000 hours) with cell resistance that actually decreased under DMFC conditions.

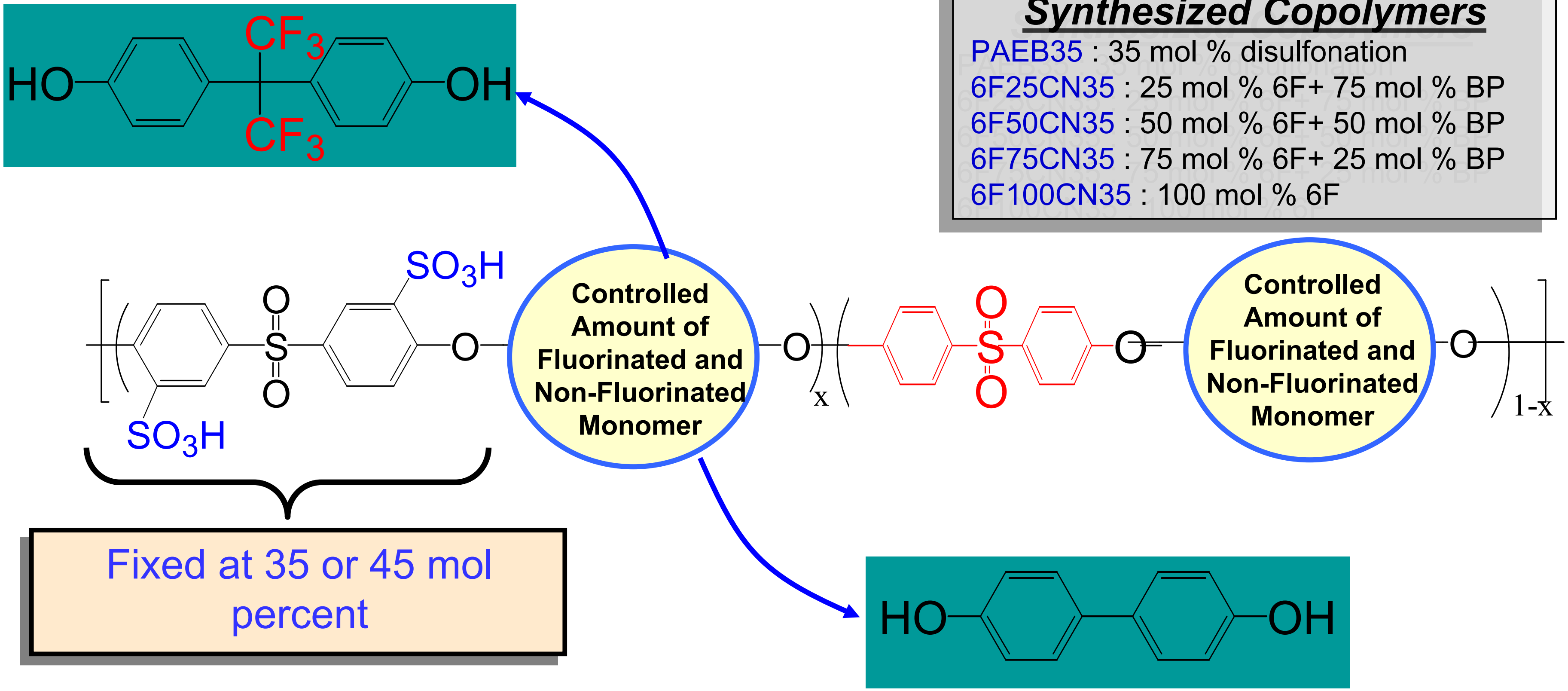
Performance loss after 3000 h of the life test for 6F-35 was only 60 mA/cm² and the methanol leaking current was reduced more than 50%.

In situ Determination of Proton conductivity as a Function of RH and Temperature Using ESPEC Humidity Oven and Solartron Impedance Analyzer

Membrane conditioning

80°C, 20%RH for 16 hr

Strategy to Achieve the Goal



Synthesized Copolymers

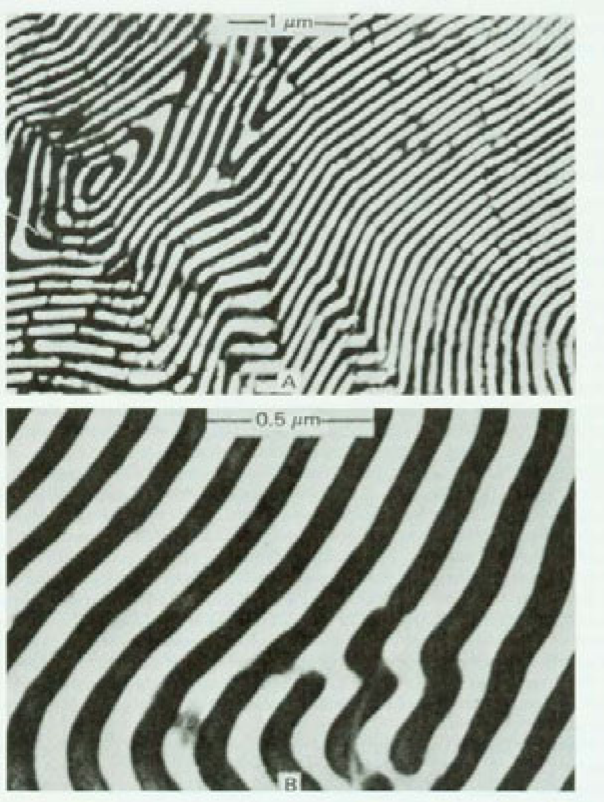
PAEB35 : 35 mol % disulfonation
6F25CN35 : 25 mol % 6F+ 75 mol % BP
6F50CN35 : 50 mol % 6F+ 50 mol % BP
6F75CN35 : 75 mol % 6F+ 25 mol % BP
6F100CN35 : 100 mol % 6F

Fixed at 35 or 45 mol percent

Copolymer PAEB-XX*	IV** (dL/g)
PAEB35	1.2
6F25CN35	1.1
6F50CN35	1.2
6F75CN35	1.5
6F100CN35	1.4

*XX: Target Degree of Disulfonation
**IV measurements were done using 0.05 M LiBr

Multiblock Copolymers with Hydrophilic-Hydrophobic Blocks



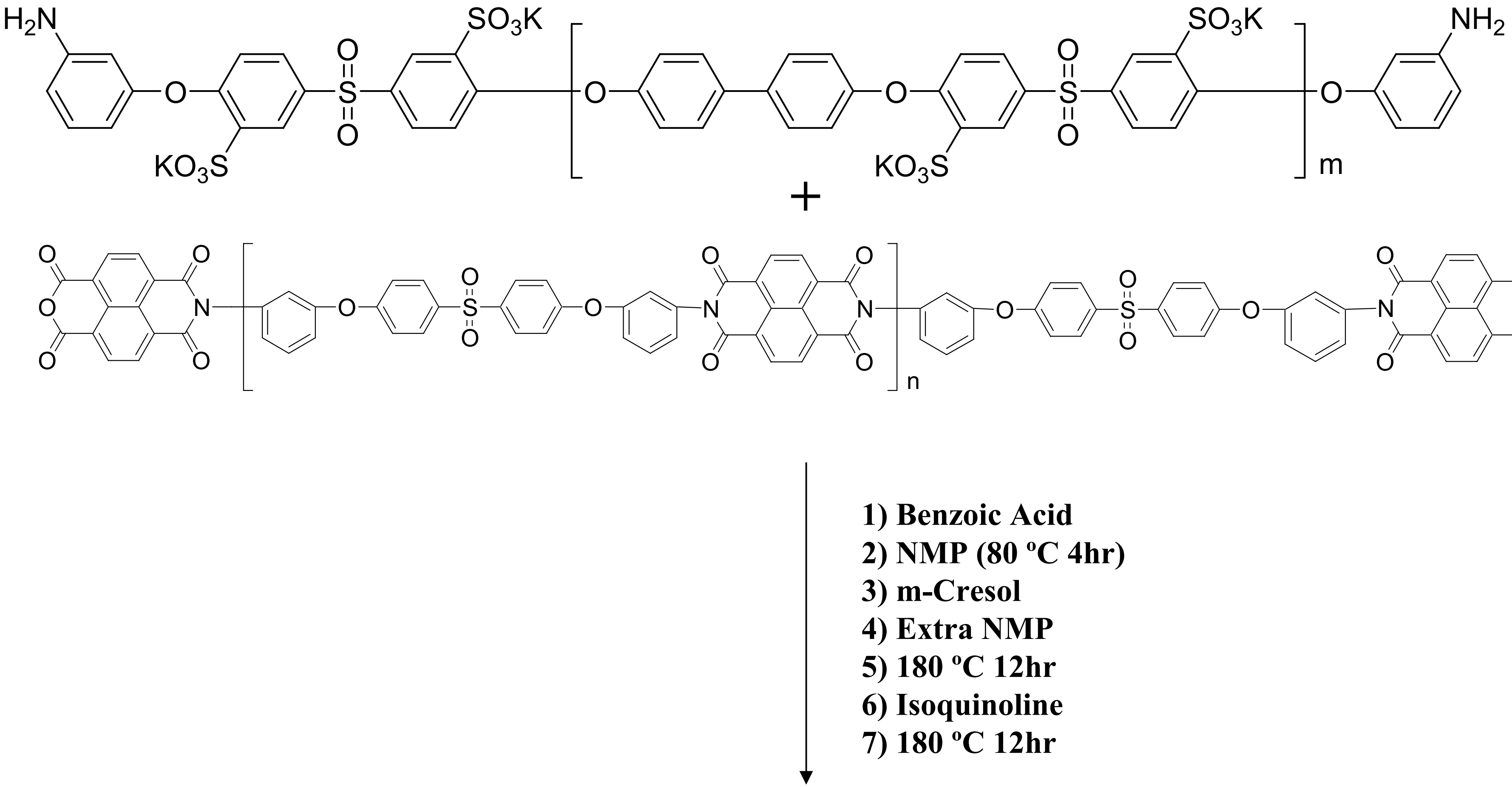
- Micro phase-separated morphology can be precisely controlled by synthesis

- Enhanced mechanical strength, water uptake, and proton conductivity are expected

An Example of an Ideal Cocontinuous Film Morphology in Block Copolymers

A. Noshay and J.E. McGrath, "Block Copolymers: Overview and Critical Survey," 520 pages, Academic Press, New York, January 1977, p.91.

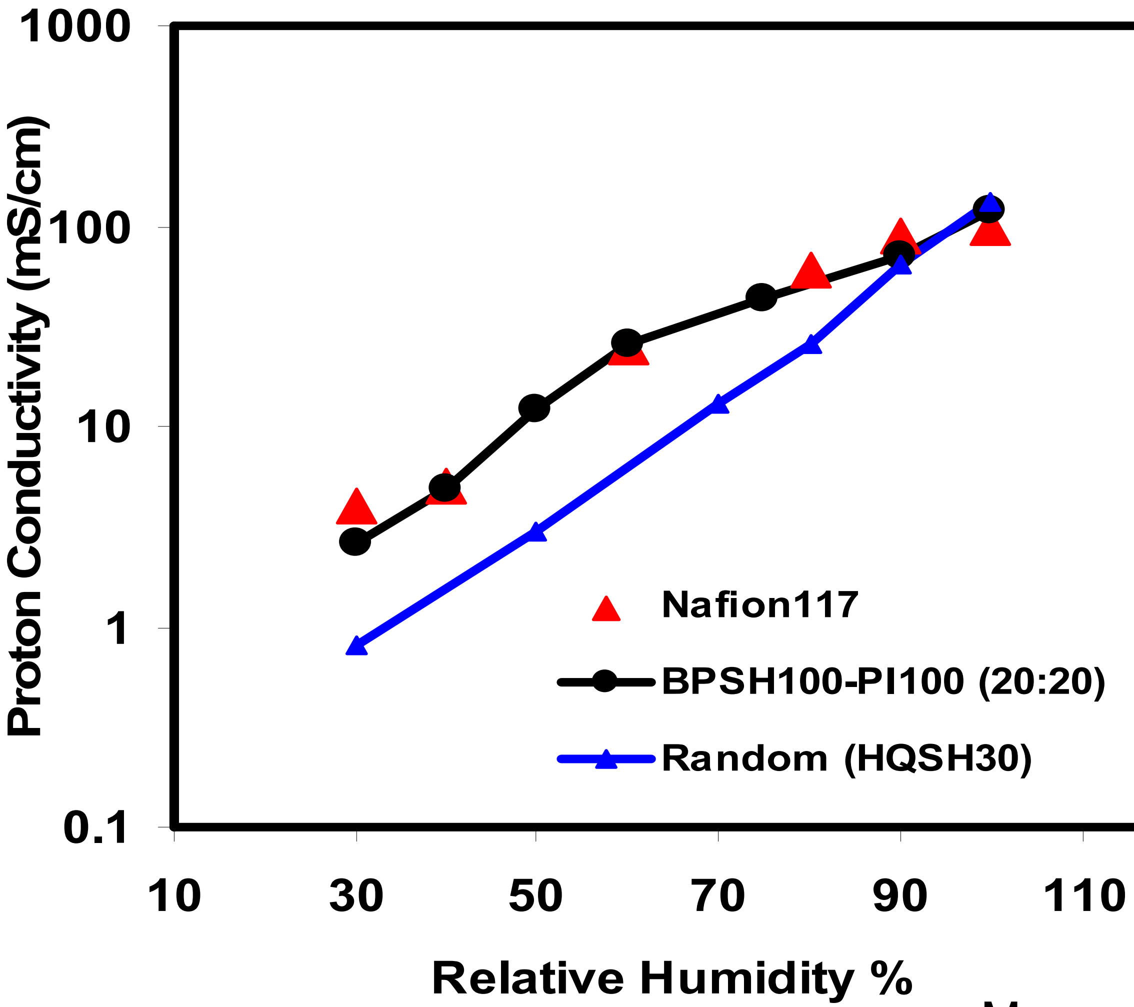
Synthesis of High MW Multiblock Copolymers Employing Mixed Solvent Systems



1) Benzoic Acid
2) NMP (80 ºC 4hr)
3) m-Cresol
4) Extra NMP
5) 180 ºC 12hr
6) Isoquinoline
7) 180 ºC 12hr

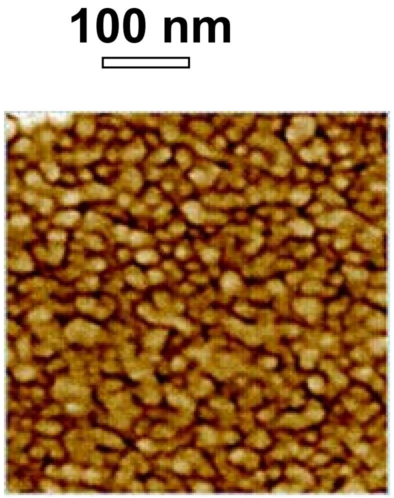
~~~~~~~~(Poly arylene ether sulfone)$_m$~~~~~(Polyimide)$_n$~~~~~~~~~~~

Why We Are Interested in Block Copolymers as PEMs?

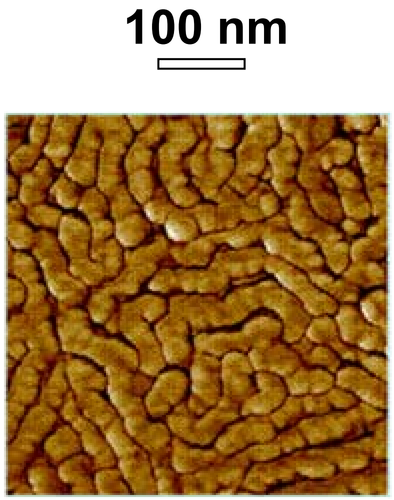


Measured at 80°C

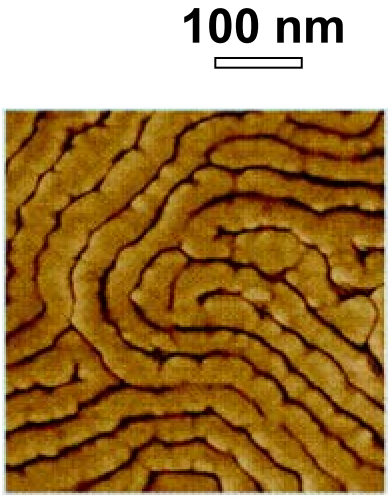
AFM Images of Multiblock Copolymers



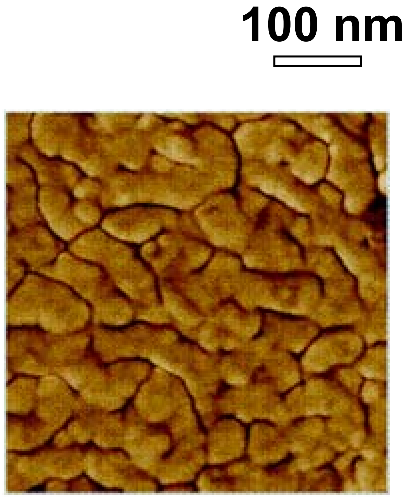
BPSH 5 – PI 5



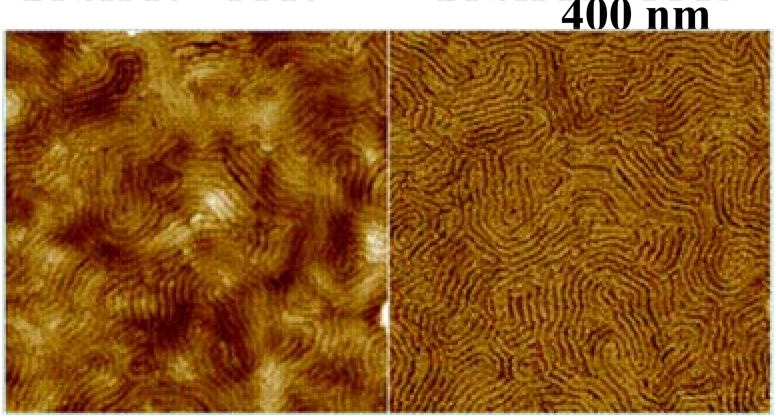
BPSH 10 – PI 10



BPSH 15 – PI 15

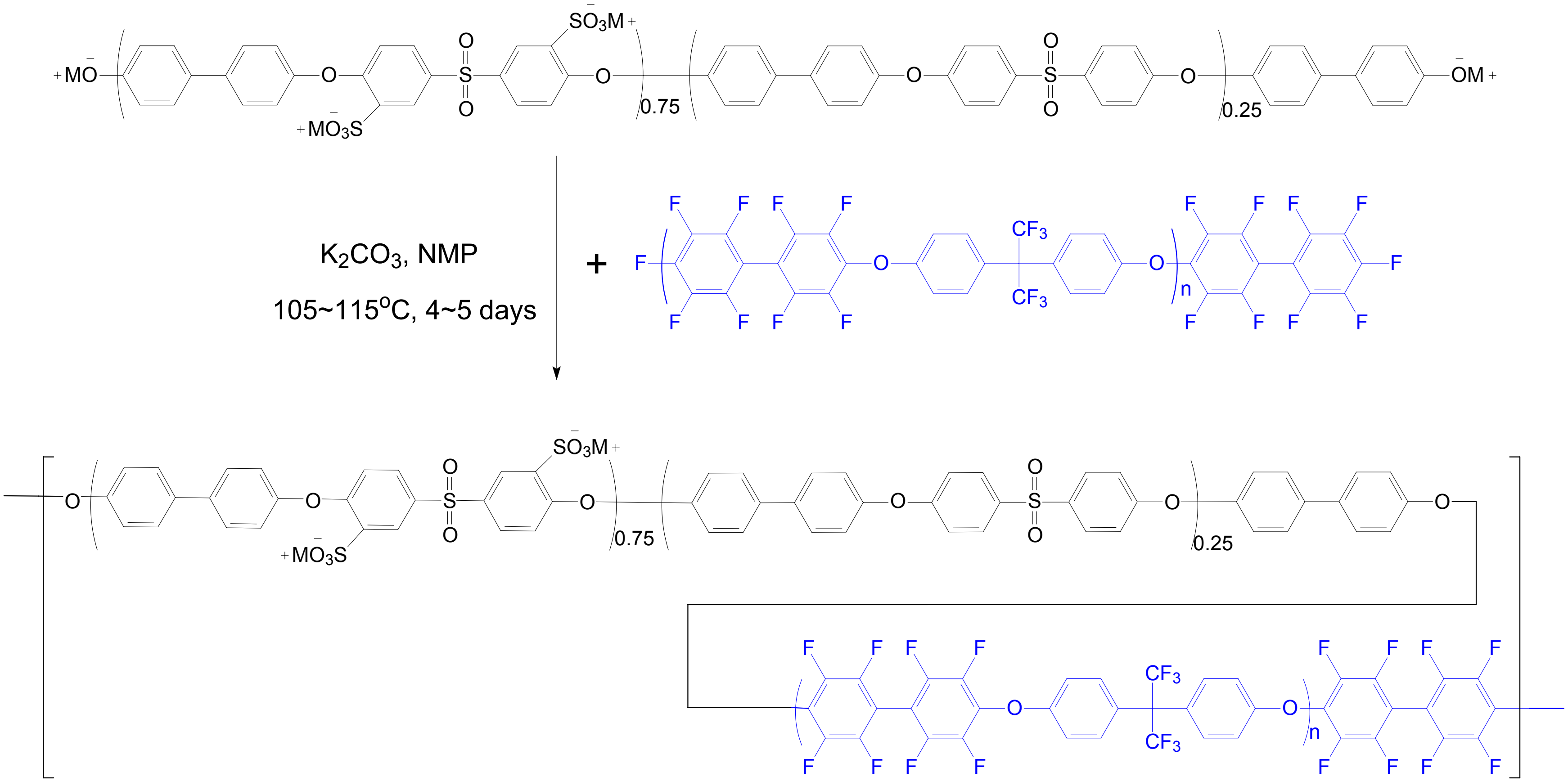


BPSH 20 – PI 20

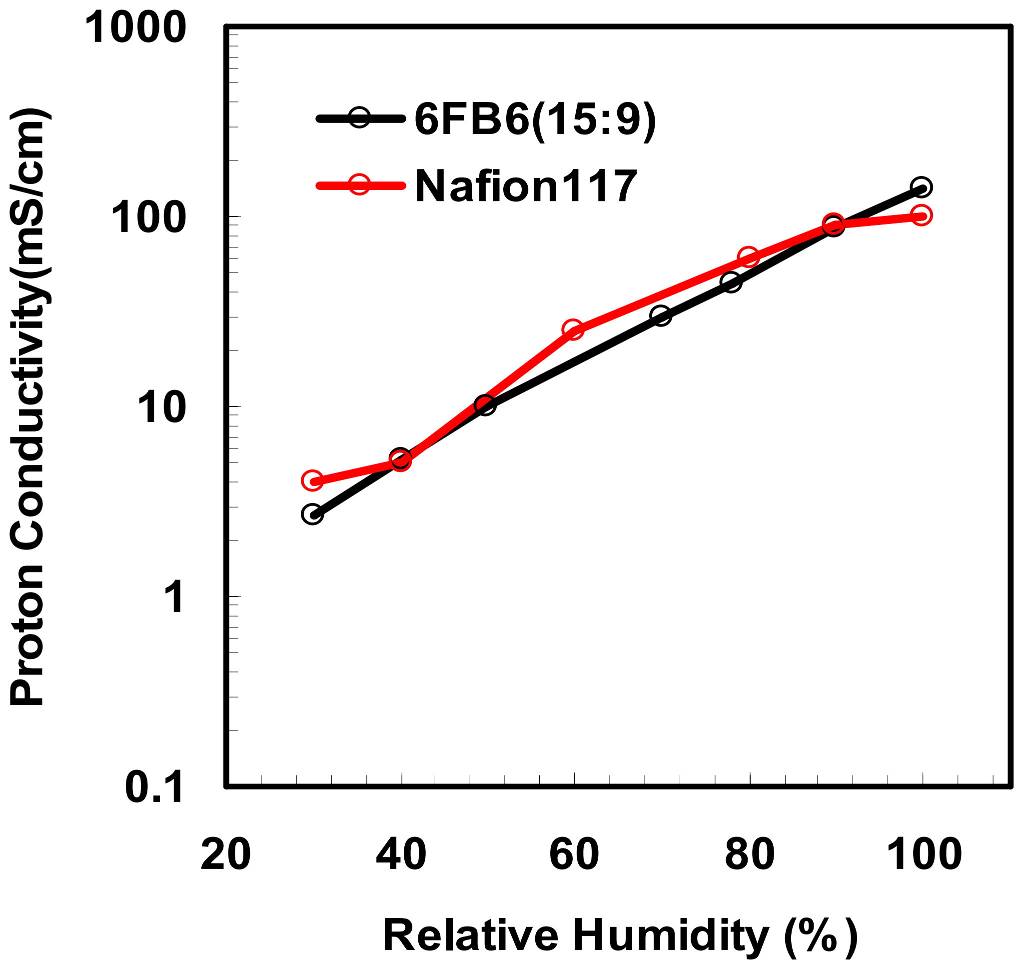


BPSH 15 – PI 15

Multiblock Perfluorinated Hydrophobic-Hydrophilic Copolymer Synthesis



Proton Conductivity vs. RH for 6FB6, a 15,000-9,000 gm/mole Multiblock Copolymer

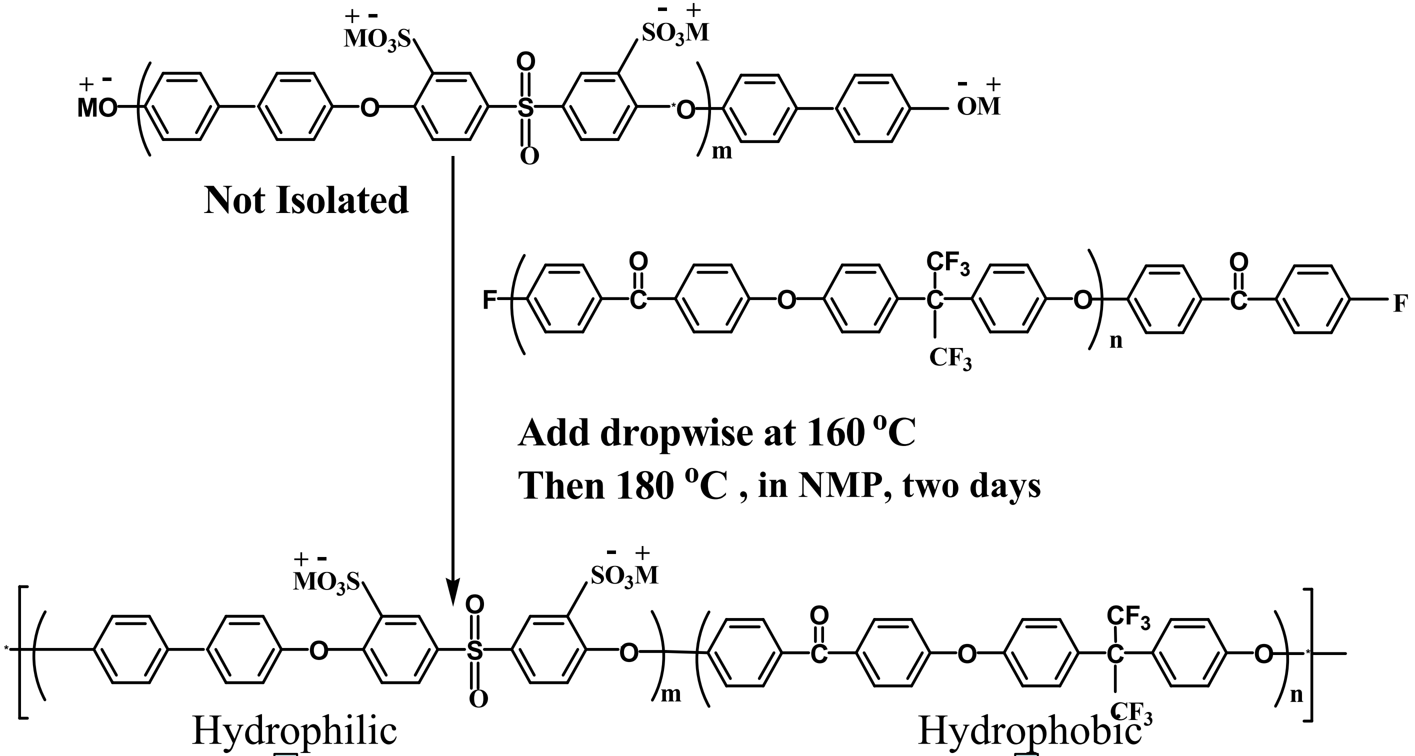


Target IEC: 1.25

Water uptake: 42%

Proton conductivity in liquid water: 0.09 S/cm

Synthesis of 6FK-BPSH Multiblock Copolymers



Not Isolated

Add dropwise at 160 °C
Then 180 °C , in NMP, two days

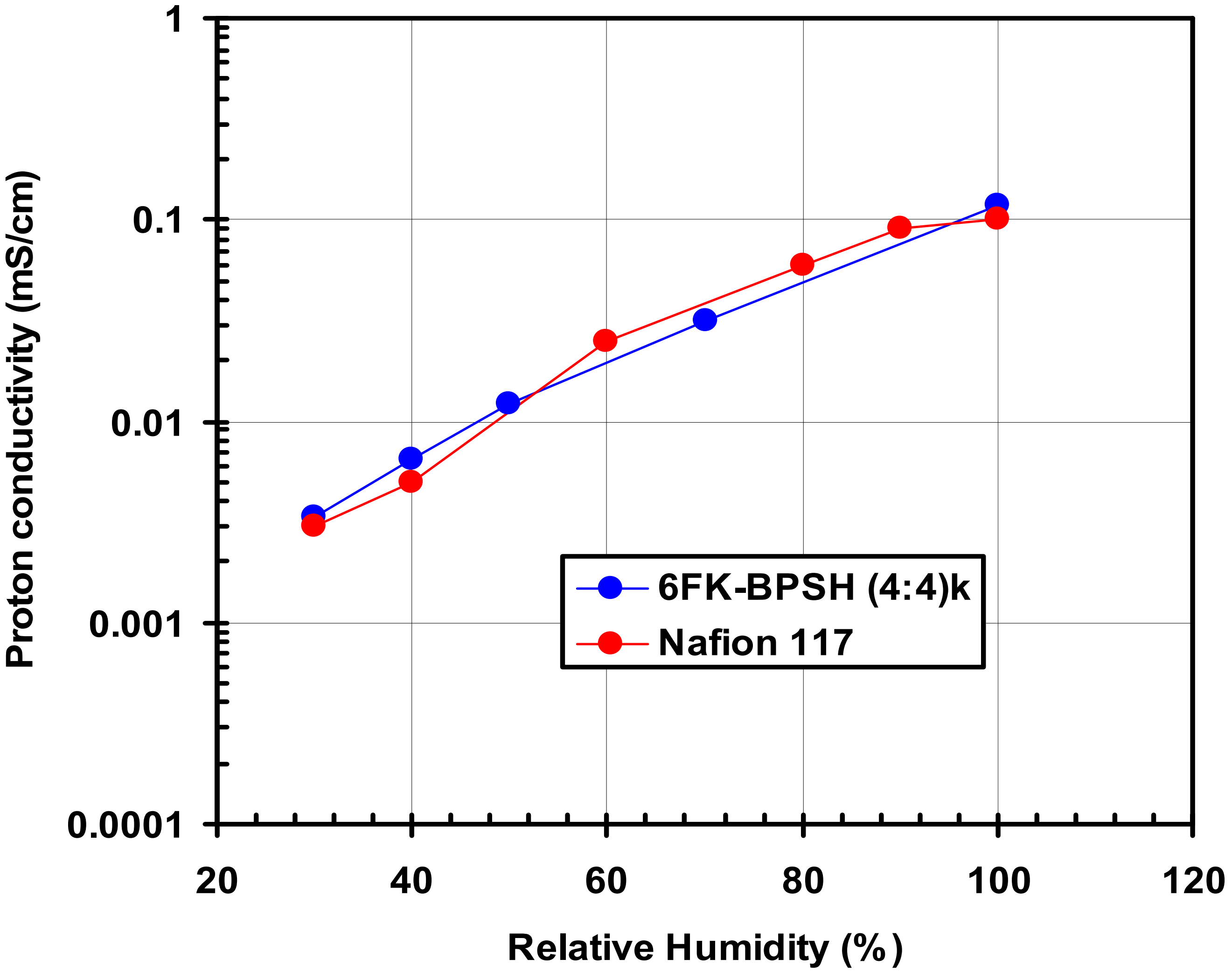
Hydrophilic

provides good proton conductivity and low permeability

Hydrophobic

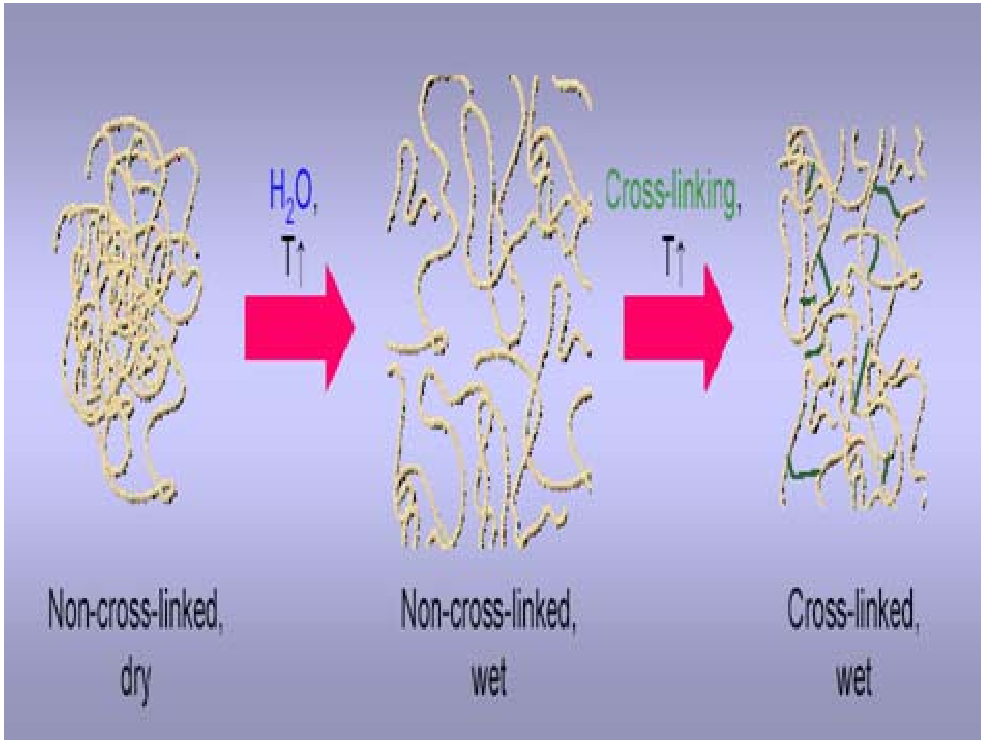
offers excellent thermal and mechanical properties

Comparison of Conductivity vs. RH for 6FK-BPSH Multiblock(4:4)K and Nafion 117



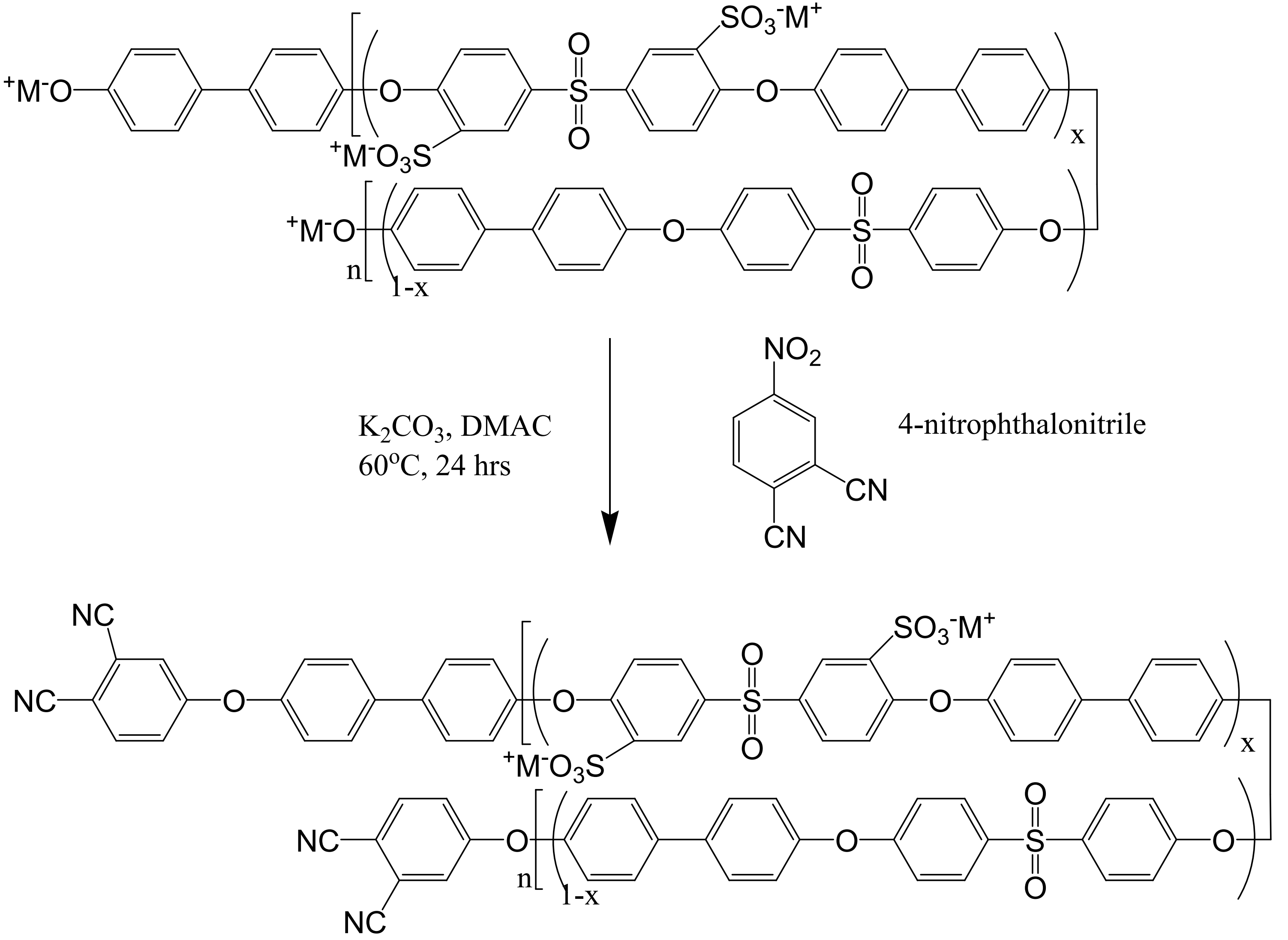
80 °C

Why We Are Interested in Crosslinked PEMs ?

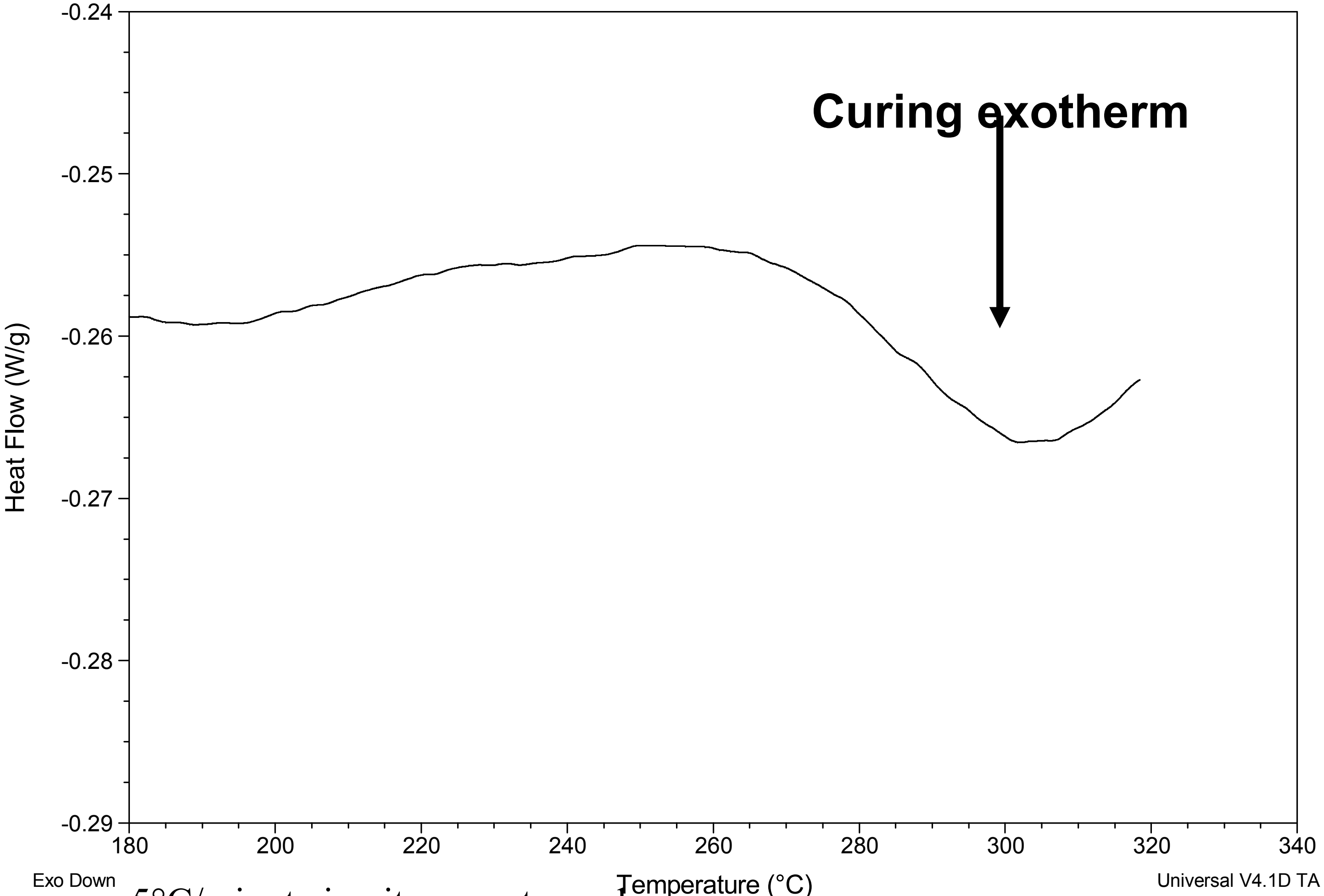


- Proton conductivity increases with increase in IEC or degree of disulfonation .
- But water uptake also increases at the same time causing the membrane to lose its dimensional stability .
- Introduction of crosslink within the membrane may reduce water uptake without losing conductivity .

Synthesis Route of 4-Phthalonitrile Containing BPS60-15k Copolymer



DSC Thermogram of a Phth-BPS-60 Film Shows Curing Exotherm Starting from 300°C



5°C/minute in nitrogen atmosphere

Film Casting of BPSH Polymers

BPSH-35 Films

CONCLUSIONS

- Hydrogen/air PEMFC's based on alternative membranes have good mechanical properties and the potential to provide satisfactory fuel cell performance below 100°C.
  - Conductivity at 120°C and low RH is challenging and may require long sequenced block copolymers to generate co-continuous hydrophilic-hydrophobic morphologies and/or organic-inorganic composite systems.
  - Membrane MW is a critical parameter defining PEM durability.
- Tailored membrane/electrode interfaces are important with Nafion electrodes.