

# **Alternative Fuel Cell Membranes for Energy Independence**

K. A. Mauritz , R. F. Storey, D. Patton, and D. Savin  
School of Polymer Science and High Performance Materials  
The University of Southern Mississippi  
Hattiesburg, MS 39406

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Project ID #FC071

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# Overview

## Timeline

- Project start date 8/01/2008
- Project end date 8/31/2011
- Percent complete 80%

## Budget

- Total funding share
  - DOE share \$1,935,500
  - Cost share \$483,875
- Project is fully funded

## Barriers

Durability: Achieve good chemical and mechanical durability through synthetic design of membranes

Performance: Overcome obstacles to affect (1) good mechanical and thermal stability, (2) good chemical and physical durability, (3) good proton conductivity at high temperature and low humidity, good fuel cell performance.

Cost: Utilizing inexpensive monomers and processing ease.

## Partner

- University of Southern Mississippi, Kenneth A. Mauritz, Project Lead

# Project Objectives - Relevance

- The objective is to engage in the fine molecular and morphological tailoring and evaluation of novel, low cost hydrocarbon fuel cell membranes that possess high temperature performance and long term chemical/mechanical durability in PEM fuel cells.
- This effort will support the EERE Hydrogen Program, as stated in the Multi-Year Program Plan by developing high temperature, low relative humidity, high proton conductive membranes for use in PEM fuel cells – the focus is on alternative materials with performance up to 120°C at low relative humidity.

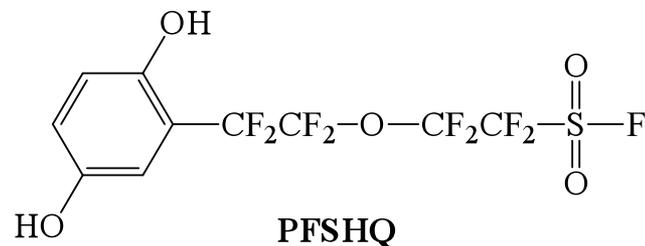
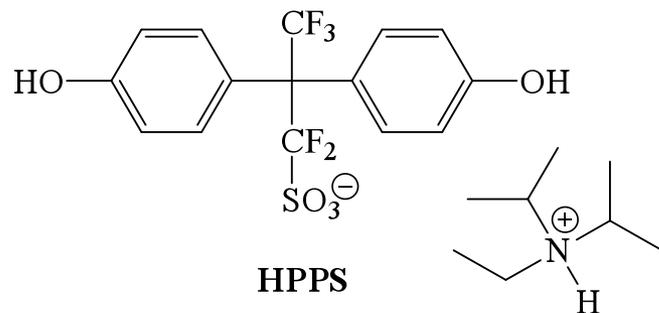
# Project Objectives - Approach

- Synthesis of aromatic hydrocarbon polymers will be conducted. Fine tailoring of organic structures includes variation of linking moieties between aromatic groups, ion exchange site density and distribution, molecular weight and block vs. random copolymers. There are three synthetic directions in the program (Storey, Patton and Savin).
- Fundamental information will be gathered regarding the microstructure and basic physical properties of these materials, and how they are correlated using advanced characterization tools (Mauritz and Savin).
- Having identified superior membrane materials and optimized membrane electrode assembly (MEA) processing, the nature and mechanisms of coupled chemical and mechanical degradation, as well as morphological alteration, will be investigated during accelerated *ex situ* chemical degradation and *in situ* PEMFC testing (Mauritz).
- Mechanical/chemical/thermal stability of the membranes will be increased over a broad temperature and humidity range. MEAs will be fabricated from synthesized ionomers and tested for fuel cell performance and durability.

# Milestones

Task Number	Project Milestones	Task Completion Date				Progress notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1.0	Acquisition of Equipment	6/30/09	6/30/10		100%	Near Completion
2.0	Synthesis of Polymers	1/31/10	8/31/11		45%	On-Going
2.1	Synthesis of Aromatic Polymers w/Tethered Acidic Ion Exchange	1/31/10	8/31/11		80%	On-Going
2.2	Synthesis of Pendant N-heterocycle Aromatic Main-chain Polymers	1/31/10	8/31/11		35%	Started
2.3	Synthesis of Phase Behavior of PFPO-based Block Copolymers	1/31/10	8/31/11		20%	Started
3.0	Establishment of Standard Membrane Benchmark Data	3/31/09	8/31/10		N <sup>1</sup> 100% H <sup>2</sup> 20%	On-Going
<b>Y1Q4</b>	<b>Benchmark Nafion</b>		<b>1/31/10</b>		<b>100%</b>	<b>Complete</b>
4.0	Membrane Characterization and MEA Fabrication	1/31/10	8/31/11		N <sup>1</sup> 100% H <sup>2</sup> 25%	On-Going
4.1	Membrane <i>ex situ</i> Durability Characterization	1/31/10	8/31/11		N <sup>1</sup> 100% H <sup>2</sup> 0%	On-Going
4.2	MEA Fabrication Development	1/31/10	8/31/11		N <sup>1</sup> 100% H <sup>2</sup> 0%	On-Going
<b>Y2Q2</b>	<b>Baseline Data Hydrocarbon Membranes</b>		<b>8/31/11</b>		<b>H<sup>2</sup> 20%</b>	<b>Started</b>
5.0	Inorganic Sol-Gel Modification and Characterization of Nanocomposite Membranes	1/31/10	8/31/11		N <sup>1</sup> 100% H <sup>2</sup> 0%	On-Going
6.0	Fuel Cell Performance and Membrane Durability Studies	1/31/10	8/31/11		N <sup>1</sup> 100% H <sup>2</sup> 0%	On-Going
<b>Y3Q2</b>	<b>Demonstrate synthesis approach improved relative to baseline materials</b>				<b>H<sup>2</sup> 0%</b>	<b>Not Started</b>
7.0	Project Management and Reporting	1/31/10	8/31/11		75%	On-Going

# Synthesis of Aromatic Polymers with Tethered, Acidic Ion Exchange Sites (Subtask 2.1) Approach

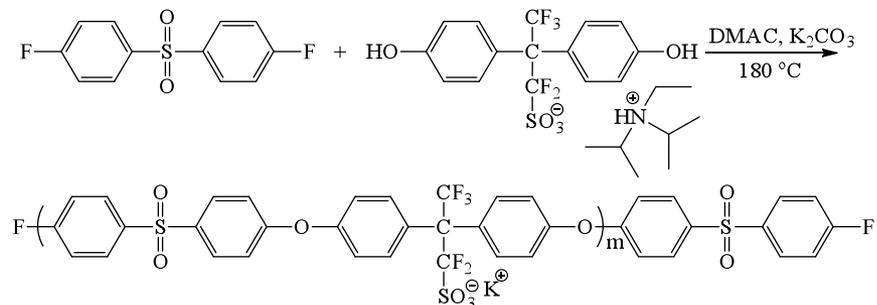


Our overall approach is toward new membrane polymers combining the desirable features of sulfonated poly(arylene ether sulfone)s and perfluorosulfonic acid polymers. We earlier reported the monomer, *N,N*-diisopropylethylammonium 2,2-bis(*p*-hydroxyphenyl)pentafluoropropanesulfonate (HPPS). Random poly(arylene ether sulfone) copolymers of HPPS, bis(4-fluorophenyl) sulfone, and biphenol showed disappointing conductivities. To improve conductivity our approach has been to:

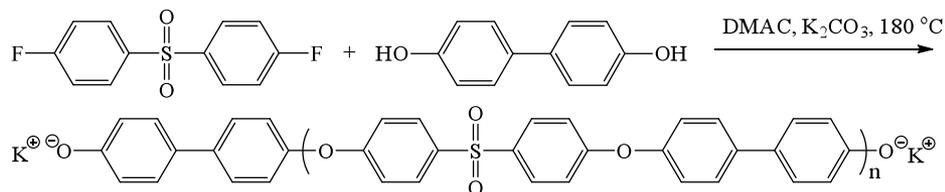
- 1) Enhance phase separation by synthesizing hydrophilic/hydrophobic multi-block copolymers from HPPS
- 2) synthesize a new monomer 1,1,2,2-tetrafluoro-2-[1,1,2,2-tetrafluoro-2-(2,5-dihydroxyphenyl)ethoxy] ethanesulfonyl fluoride (perfluorosulfonate hydroquinone) (PFSHQ).

# Synthesis of Hydrophilic/hydrophobic Multi-block Copolymers from HPPS

## (Subtask 2.1) Technical Accomplishments and Progress



Prepolymer 1



Prepolymer 2

- Multi-block copolymers were produced from HPPS by synthesizing hydrophilic Prepolymer 1 with aryl fluoride end groups and hydrophobic Prepolymer 2 with potassium phenolate end groups. The two prepolymers were then reacted together using nucleophilic aromatic substitution.
- Concentration of ion exchange groups in this manner was expected to increase conductivity.

# Properties of Hydrophilic/hydrophobic Multi-block Copolymers from HPPS

## (Subtask 2.1) Technical Accomplishments and Progress

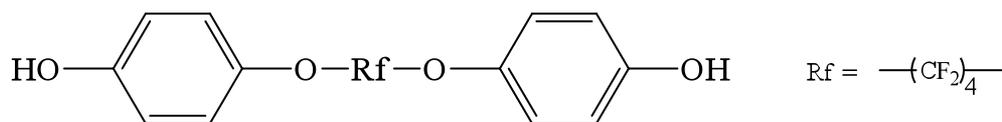
Copolymer	$M_{n,GPC}$ (PDI) (g/mol)	Block Lengths (exp.) (n/m)	IEC (theor.) (meq/g)	IEC (exp.) (meq/g)	Conductivity <sup>a</sup> (mS/cm)
MB-1	47,700 (2.61)	9.4/4.4	1.18	0.98	11
MB-2	84,300 (3.83)	13.3/6.0	1.20	1.14	36
MB-3	81,300 (2.81)	16.1/8.2	1.19	1.52	14
MB-4	55,100 (2.53)	23.4/11.8	1.21	1.18	5.4

<sup>a</sup>80°C, 100% RH

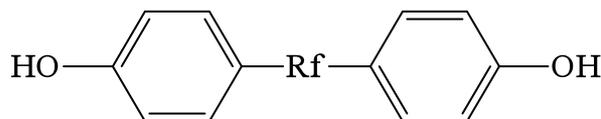
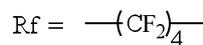
Best conductivity was achieved with medium block lengths and high polydispersity index.

# Synthesis of New Comonomers for Hydrophobic Blocks

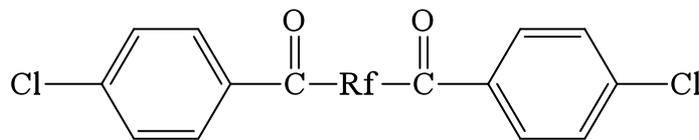
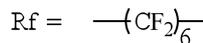
## (Subtask 2.1) Technical Accomplishments and Progress



1



2



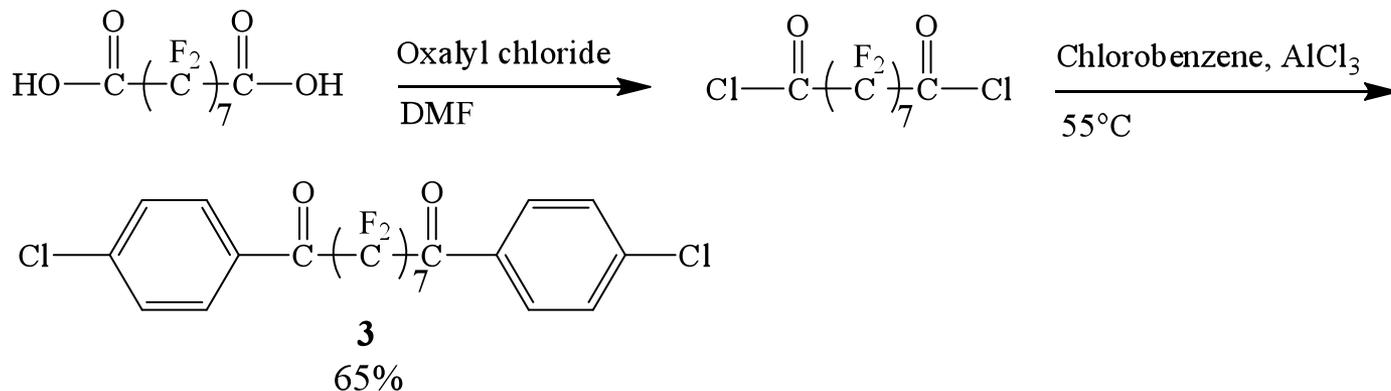
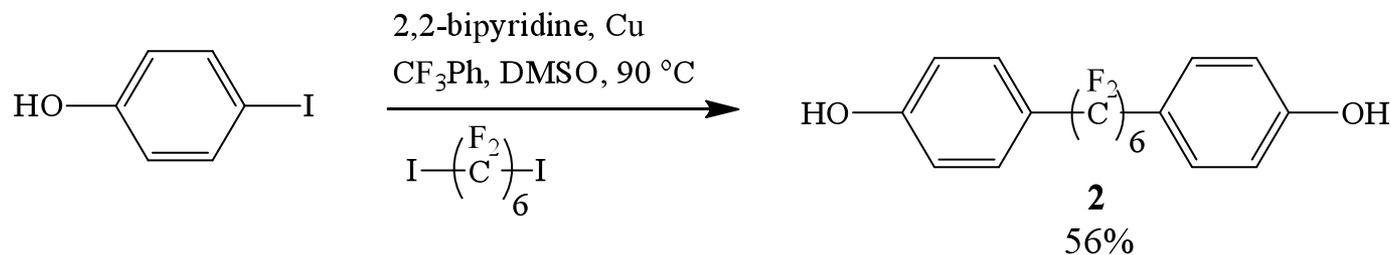
3

To improve conductivity of multi-block copolymers, new monomers for hydrophobic blocks have been synthesized:

- 1 Bisphenolic monomer with electron-rich phenyl rings (synthesis abandoned)
- 2 Bisphenolic monomer (synthesis successful, see next slide)
- 3 Bis aryl halide monomer (synthesis successful, see next slide)

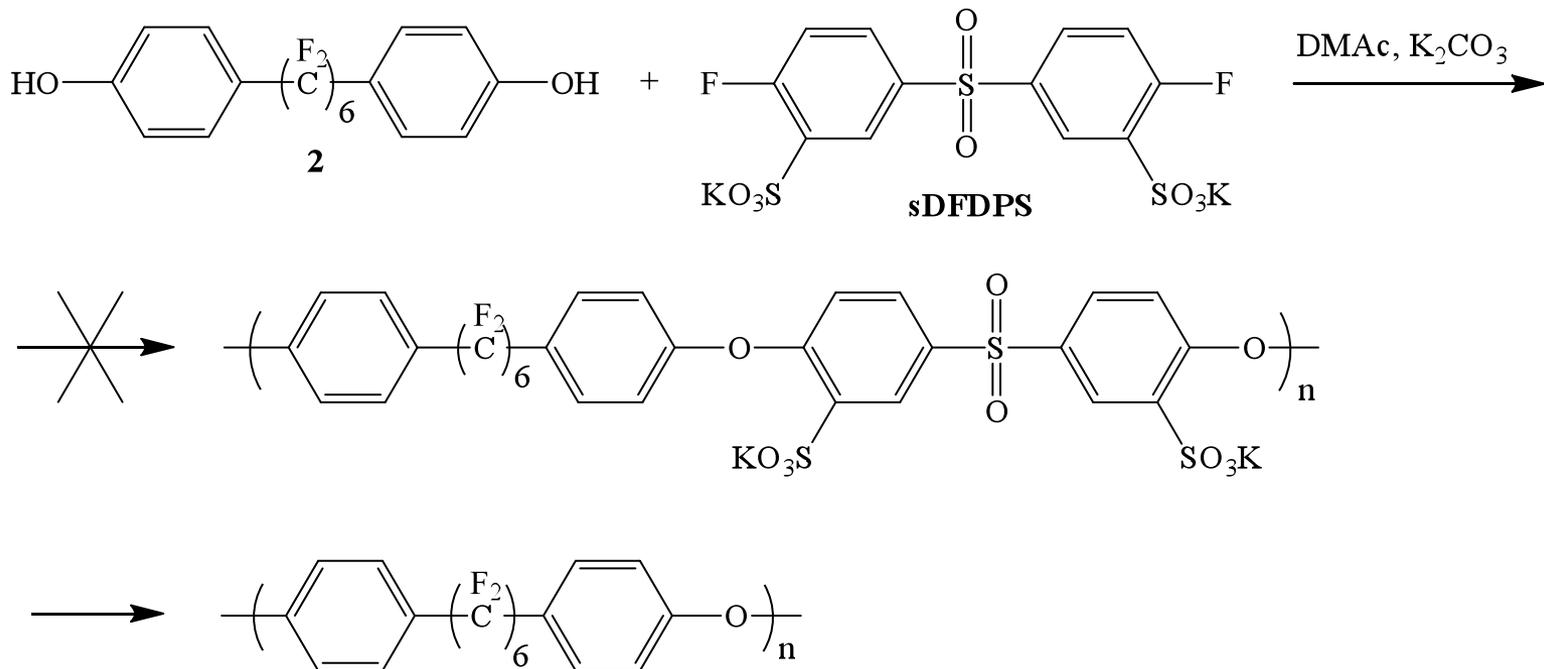
# Synthesis of New Hydrophobic-Block Comonomers 2 and 3

(Subtask 2.1) Technical Accomplishments and Progress



# Polymerization of New Hydrophobic-Block Comonomer 2

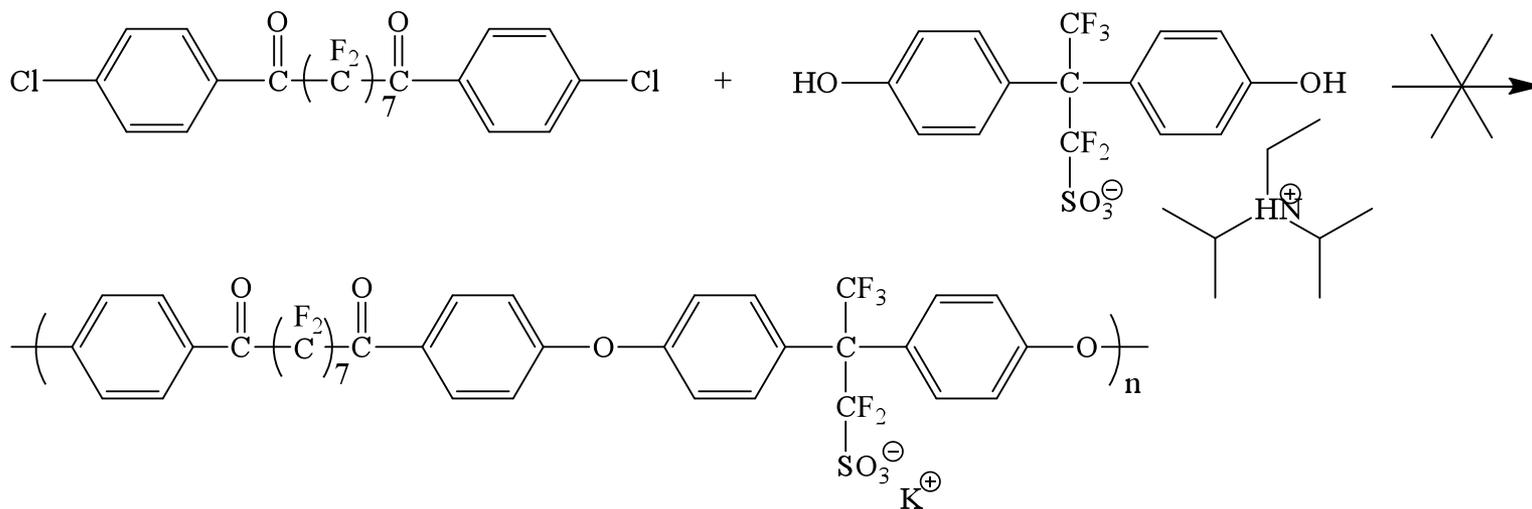
(Subtask 2.1) Technical Accomplishments and Progress



Instead of the expected polymerization with **sDFDPS**, homopolymerization of **2** was observed, with possible branching/crosslinking (the product is insoluble). The strong electron-withdrawing nature of  $-(CF_2)_6$  – apparently activates the phenyl ring to such an extent that -OH can serve as both nucleophile and leaving group.

# Polymerization of New Hydrophobic-Block Comonomer 3

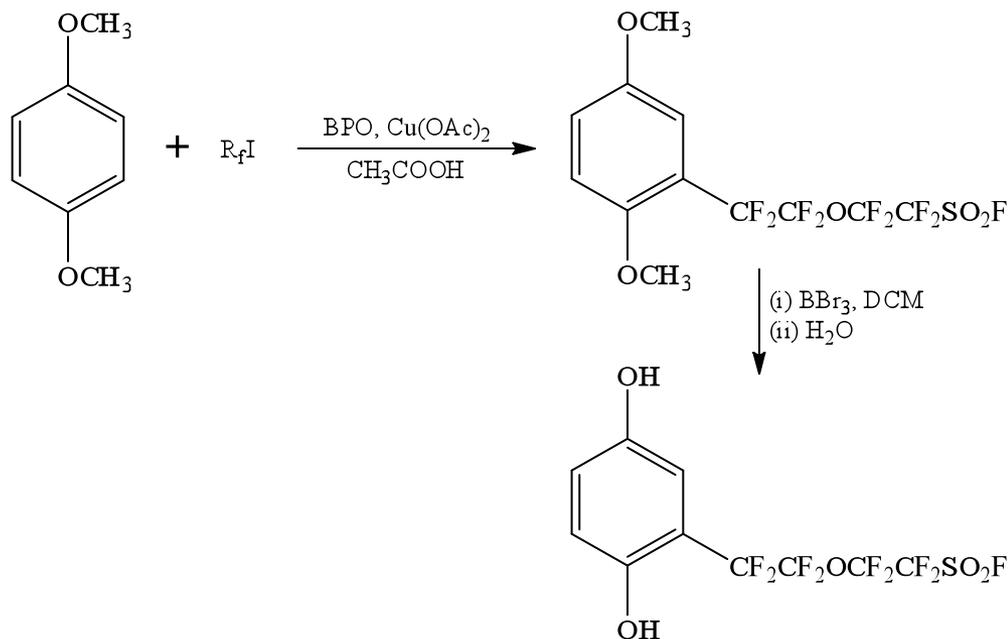
(Subtask 2.1) Technical Accomplishments and Progress



- Attempts to polymerize comonomer **3** with **HPPS** have so far been unsuccessful.
- We believe that phenolate attacks carbonyl instead of aryl chloride.

# Synthesis of Bisphenolic Monomer with Tethered Perfluorosulfonate Moiety

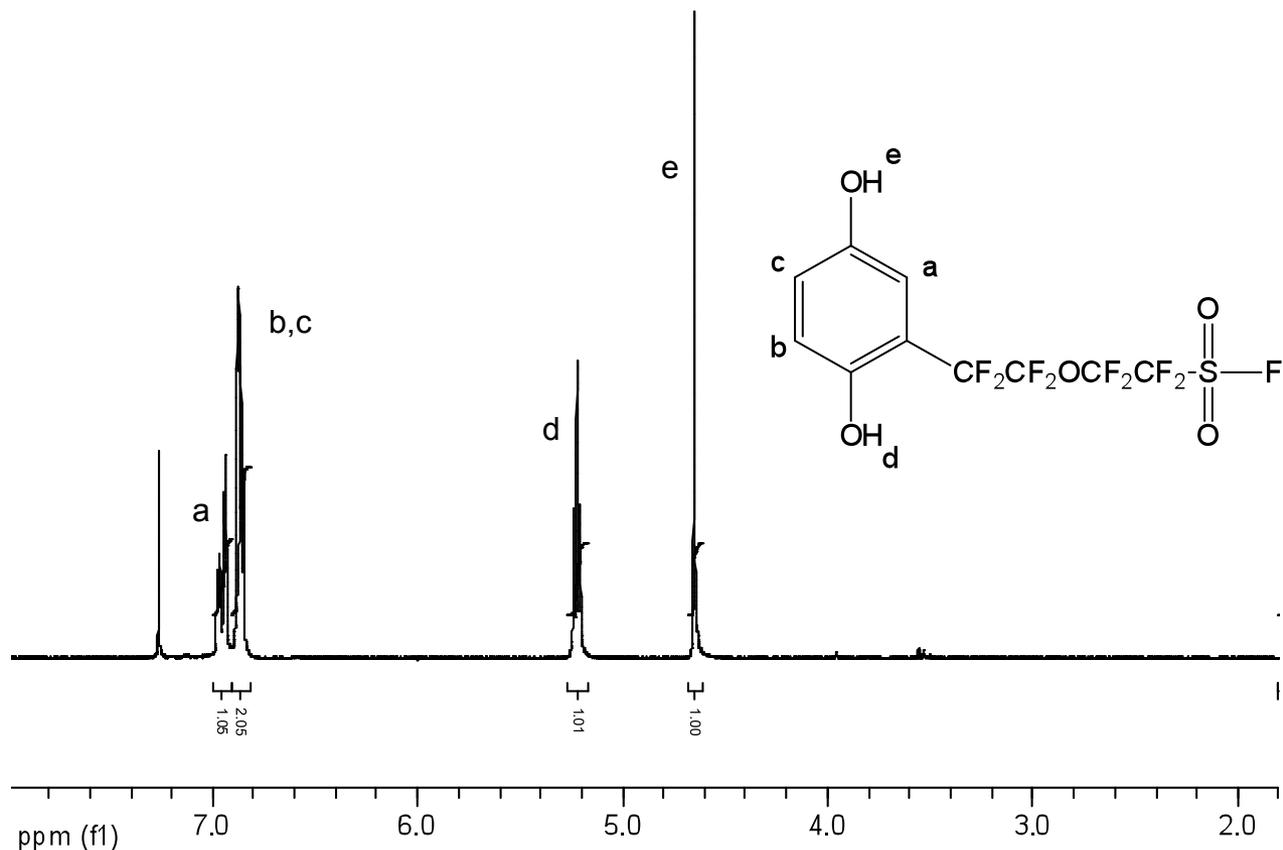
## (Subtask 2.1) Technical Accomplishments and Progress



- The synthesis scheme for 1,1,2,2-tetrafluoro-2-[1,1,2,2-tetrafluoro-2-(2,5-dihydroxyphenyl)ethoxy] ethanesulfonyl fluoride (PFSHQ) is shown.
- The ion exchange comonomer PFSHQ places the ion exchange group at the terminus of a long perfluoroalkyl ether tether. This is expected to yield better clustering of exchange groups and better conductivity.

# $^1\text{H}$ NMR Spectrum of PFSHQ

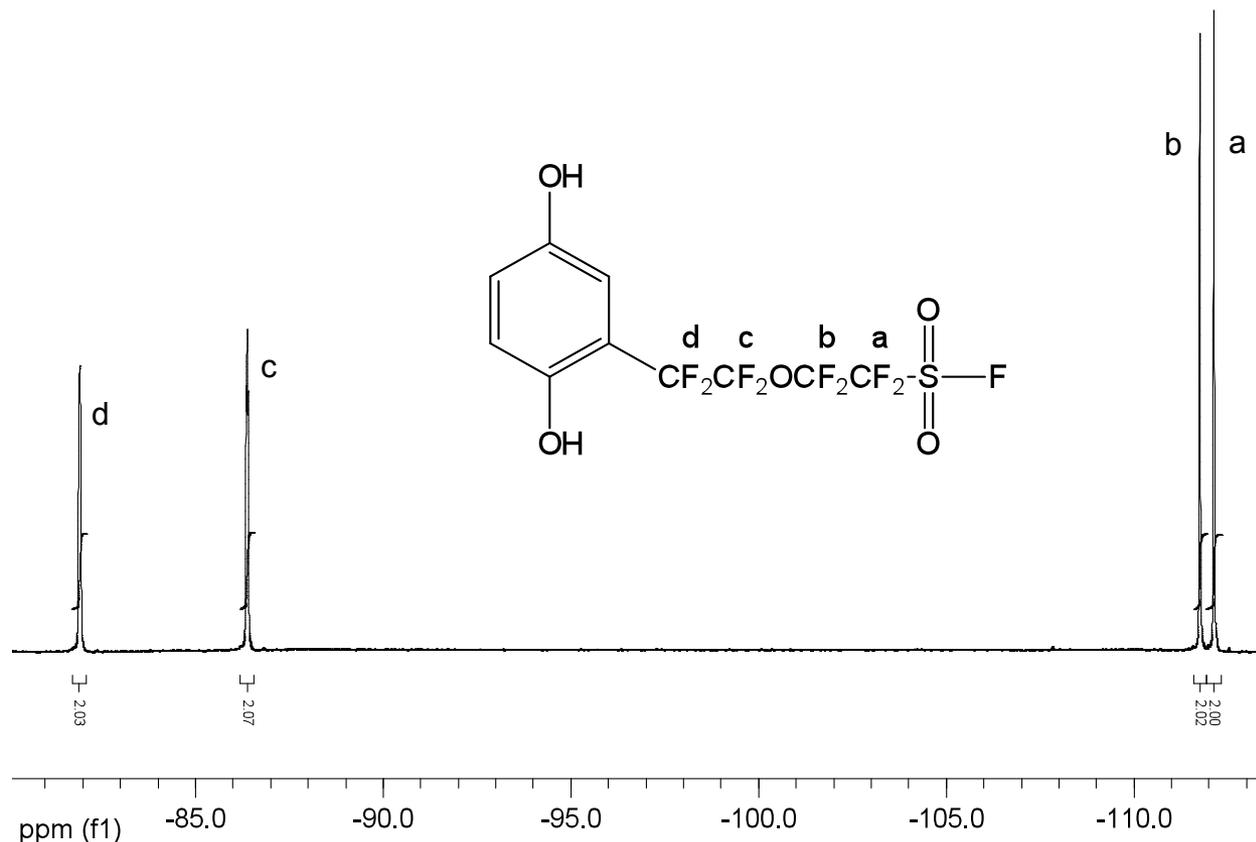
## (Subtask 2.1) Technical Accomplishments and Progress



PFSHQ was successfully synthesized, but the yield is low with current purification by column chromatography. The phenolic proton adjacent to the perfluorosulfonate tether appears as a triplet due to coupling with the  $-\text{CF}_2-$  group.

# Partial $^{19}\text{F}$ NMR Spectrum of PFSHQ

(Subtask 2.1) Technical Accomplishments and Progress

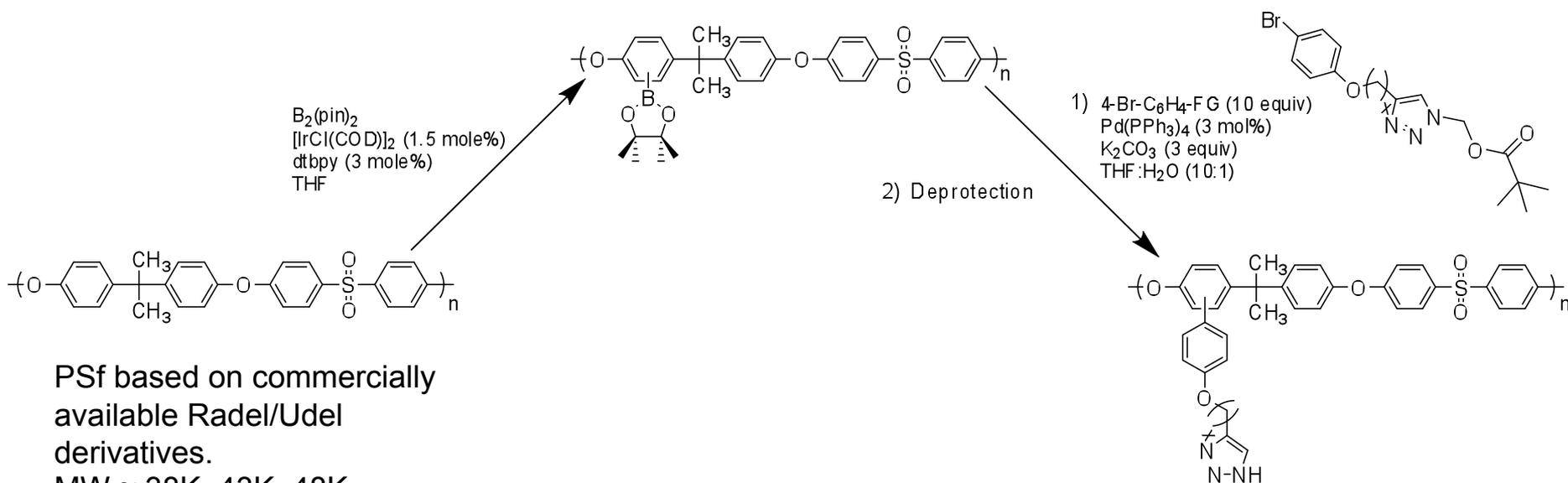


$^{19}\text{F}$  NMR spectrum clearly shows attachment of the perfluoroalkyl ether tether.

# Synthesis of Pendant N-Heterocycle Aromatic Polymers

## Subtask 2.2 - Technical Accomplishments

### Post-Polymerization Modification



PSf based on commercially available Radel/Udel derivatives.

MW  $\approx$  38K, 43K, 48K

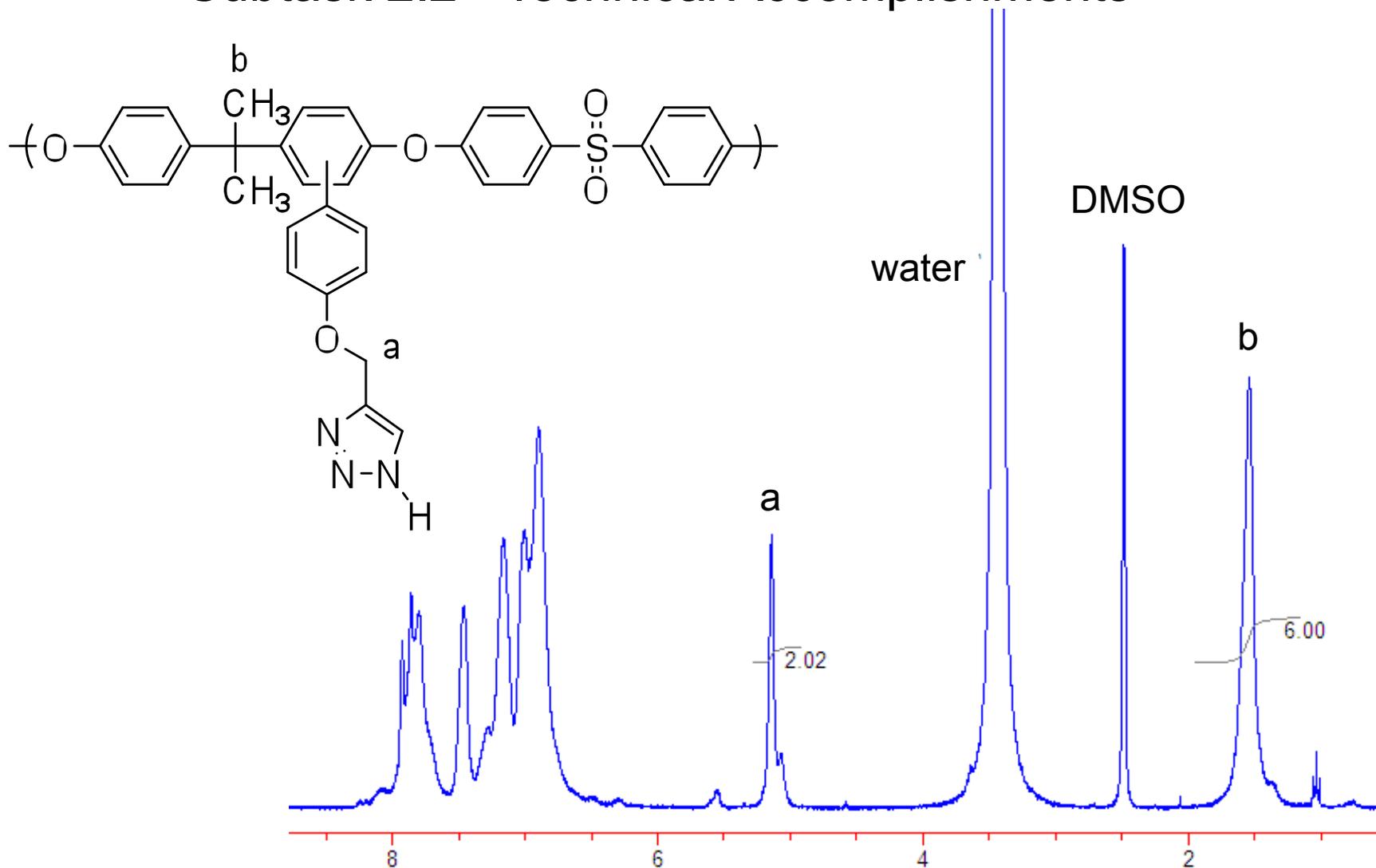
PDI  $\approx$  1.25, 1.25, 1.29

### Synthetic Design Parameters

- Charge carrier concentration, i.e. tether density ( $\rho_{\text{tether}} = 0.2\text{-}1.75$ )
- Tether length ( $x = 1, 2, 3, 4, \dots$ )
- N-heterocycle identity, i.e. 1,2,3- vs. 1,2,4-triazole

# Deprotecting Triazole

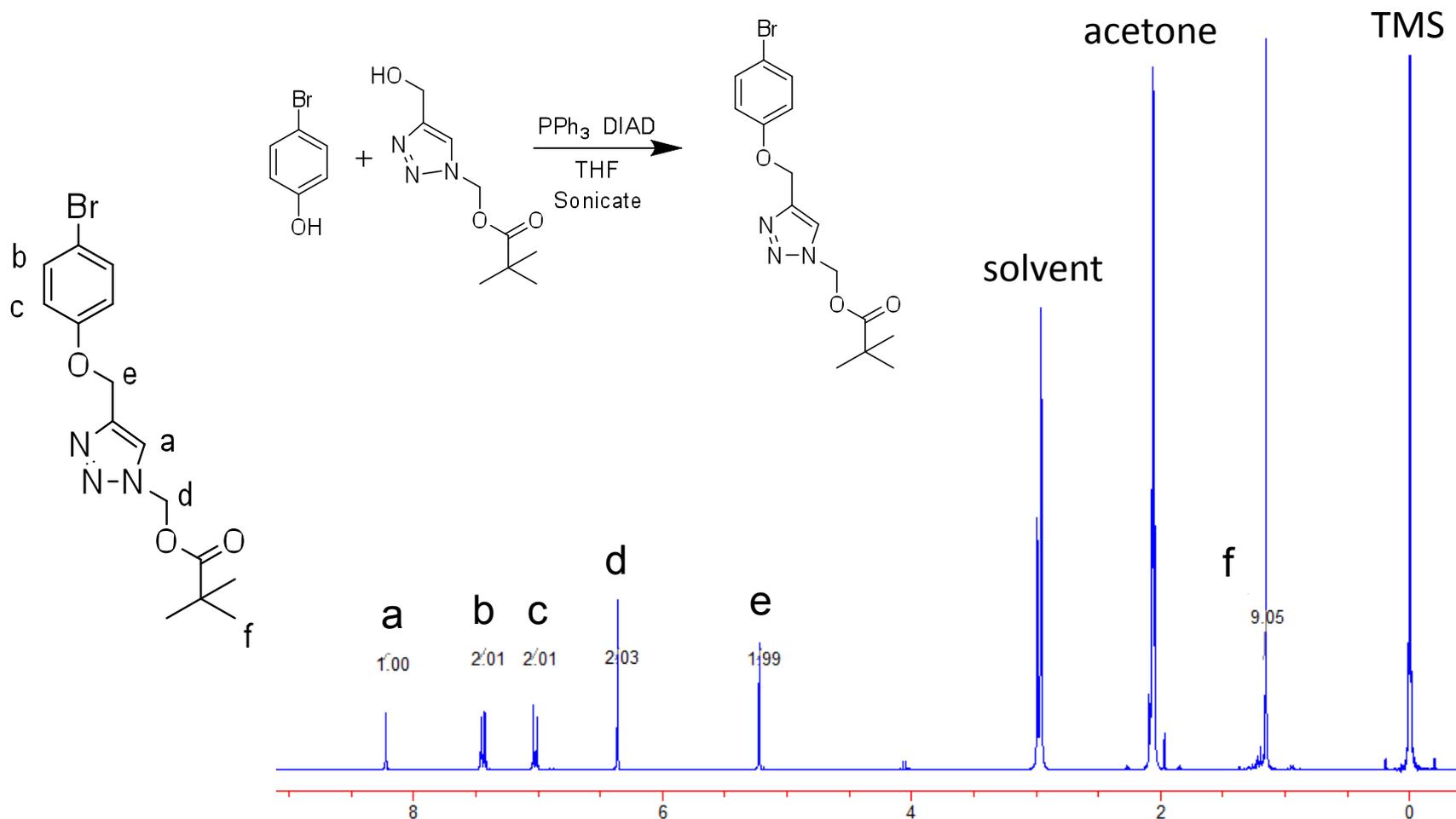
## Subtask 2.2 - Technical Accomplishments



- Successful deprotection of the triazole was confirmed by  $^1\text{H}$  NMR.

# Short Tether (x = 1)

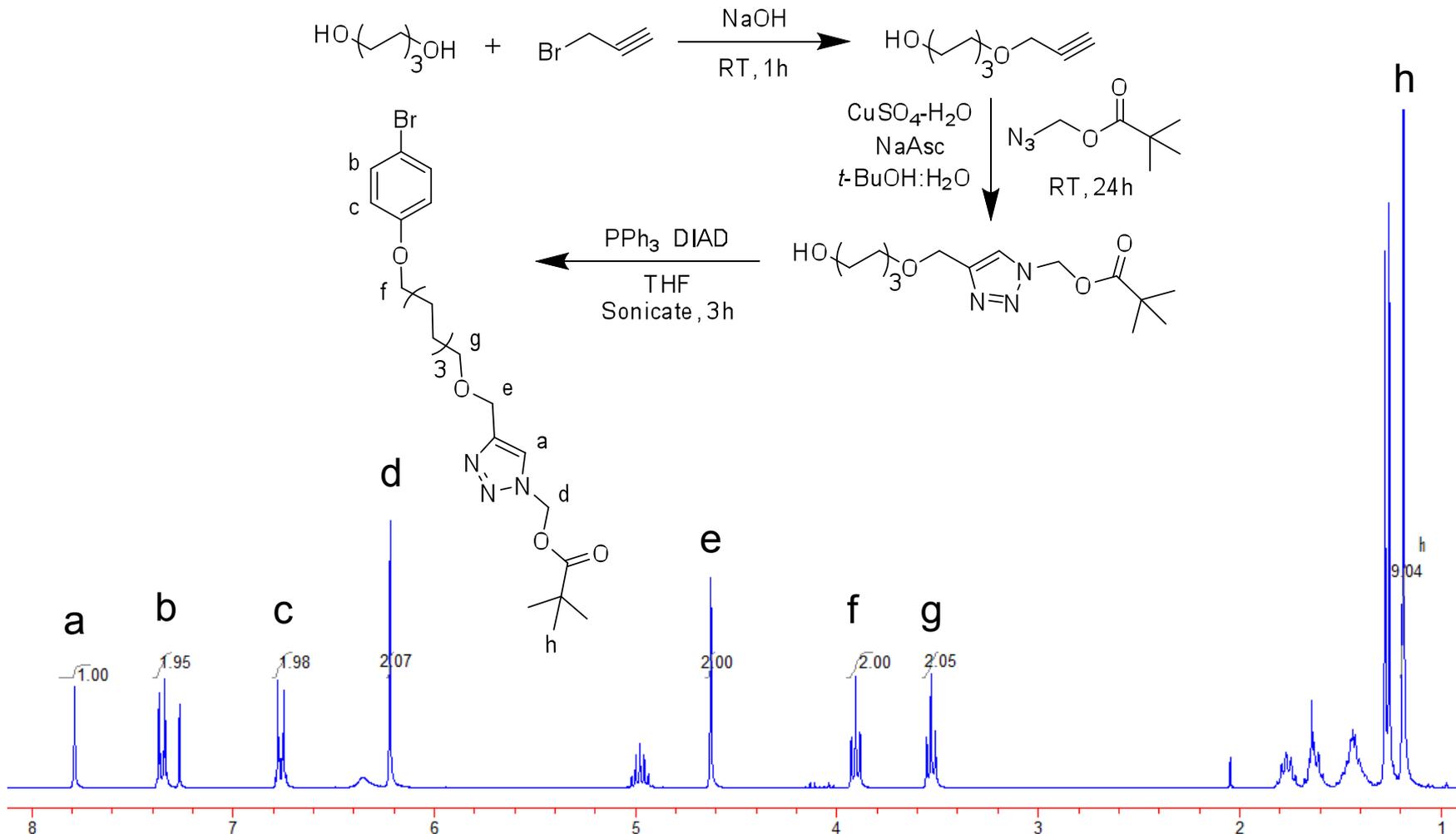
## Subtask 2.2 - Technical Accomplishments



- Tether length is expected to play an important role in anhydrous conductivity within the glassy PSf matrix. Synthesis of a short tether is demonstrated here.

# Long Tether (x = 6)

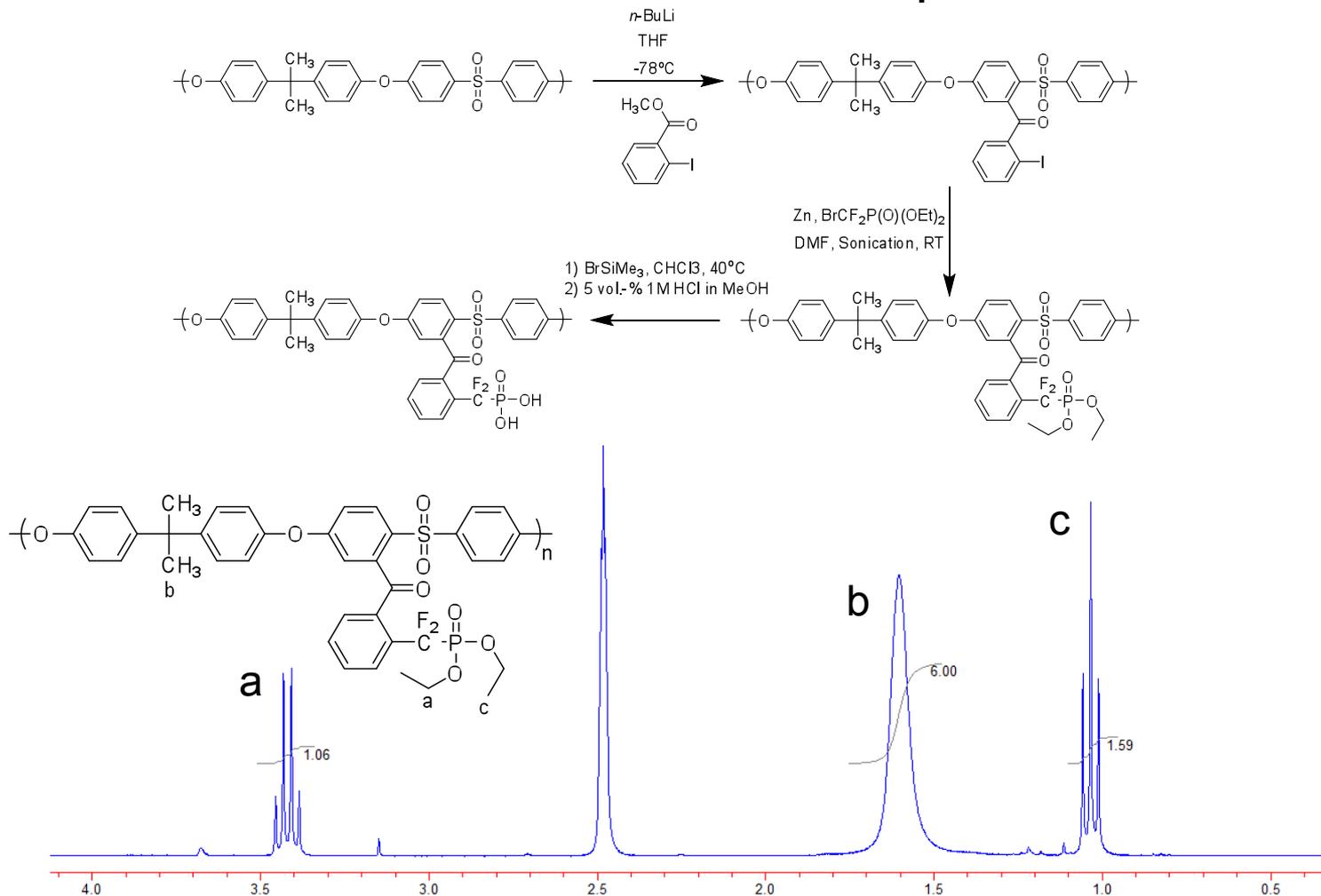
## Subtask 2.2 - Technical Accomplishments



- Long tether length introduces higher mobility of the triazole, but may be offset by increase in nonconductive constituents within the tether.

# Phosphonic acid functionalized PSf

## Subtask 2.2 - Technical Accomplishments

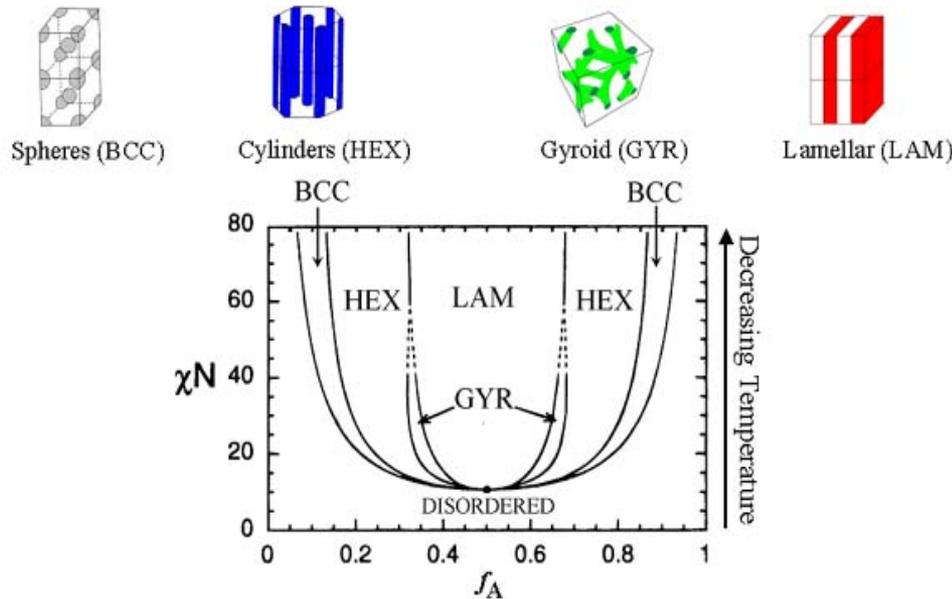


- PSU phosphonic acid donor synthesized with permanently immobilized acid moiety to improve conductivity and reduce acid leaching.

# Enhanced Proton Conduction via Block Copolymer Self-Assembly

## (Subtask 2.3) Approach

Phase Diagram for BCPs



Our general approach is to incorporate perfluorinated polymer blocks into preformed proton-conducting polymers to yield block copolymers that microphase separate into specific bulk morphologies to enhance proton conduction across the fuel cell membrane.

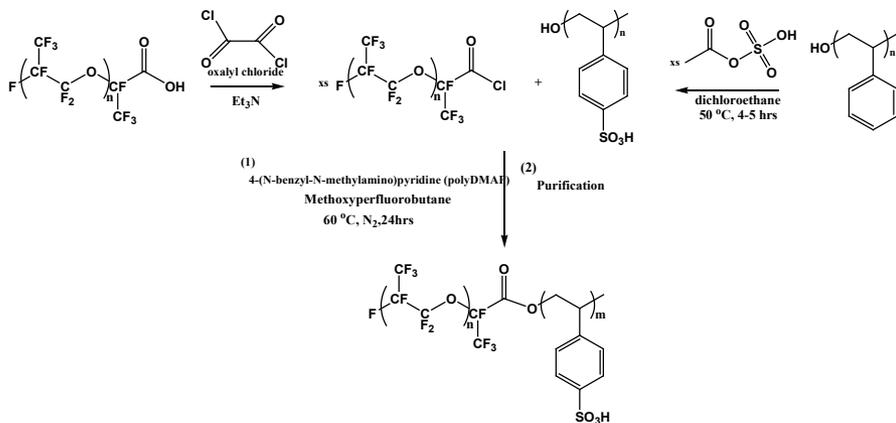
### Use of perfluorinated poly(propylene oxide) (PFPO) polymers:

- Drives  $c$  to SSSL
- Used as a compatibilizer for Nafion/MMT composite membranes

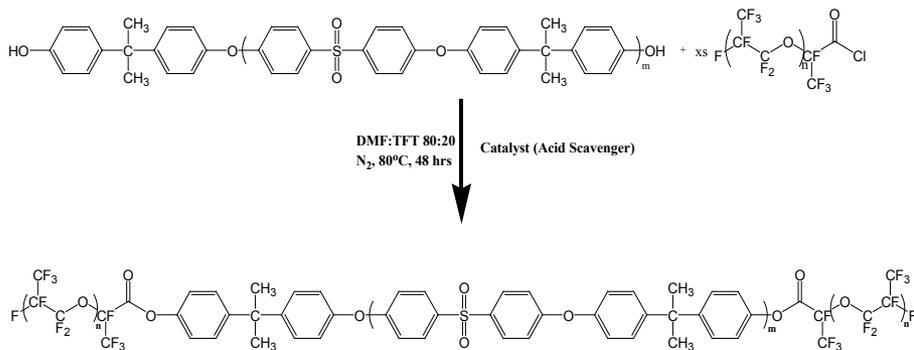
# Modular Coupling of Polymers: Synthetic Schemes

## (Subtask 2.3) Technical Accomplishments and Progress

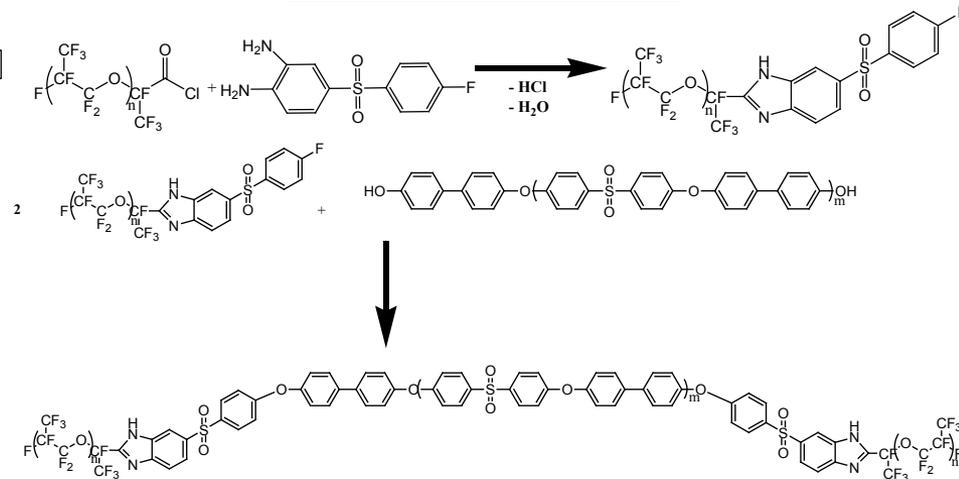
### Model Coupling of PFPO with PS



### Coupling PFPO with PES



### Changing Functionalities of PFPO for NAS with PES



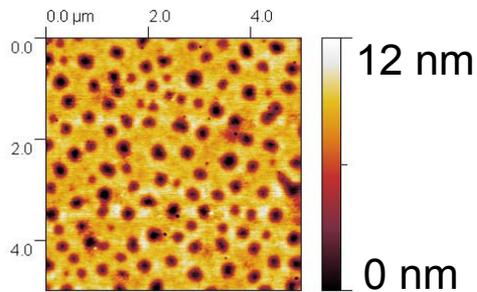
- Various coupling strategies have been attempted for block coupling

- 1) *J. Am. Chem. Soc.*, Vol. 123, No. 16, **2001**
- 2) *Macromolecules*, Vol. 37., No. 24, **2004**
- 3) *J. Mater. Res.*, **1995**, 10, 530

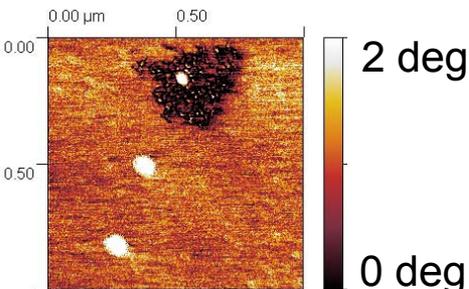
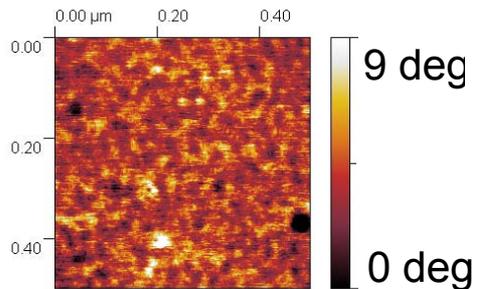
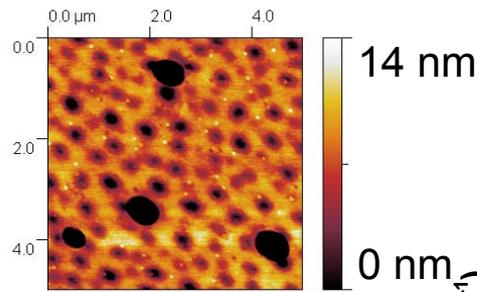
# Block Copolymer Phase Behavior and Dilute Solution Assembly

## (Subtask 2.3) Technical Accomplishments and Progress

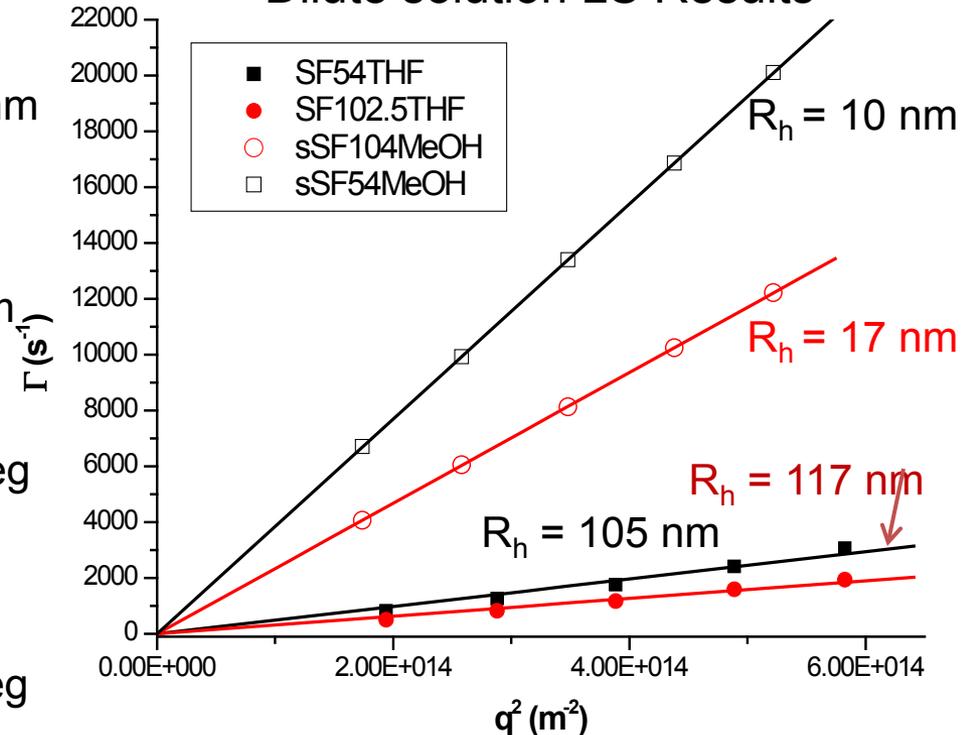
(SF 5-4)



(SF 10-4)



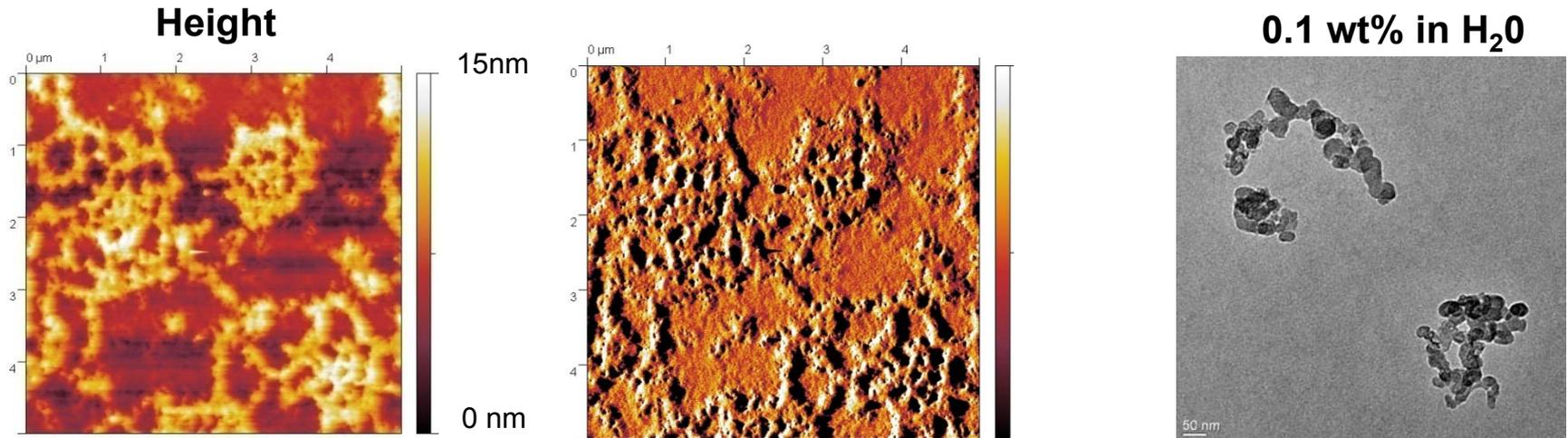
Dilute solution LS Results



- ✓ SF 5-4 phase image suggests expected lamellar morphology
- ✓ SF 10-4 image is inconclusive (theory suggests cylinders of PFPO)

# sSF 5-4 BCP (AFM/TEM)

## (Subtask 2.3) Technical Accomplishments and Progress

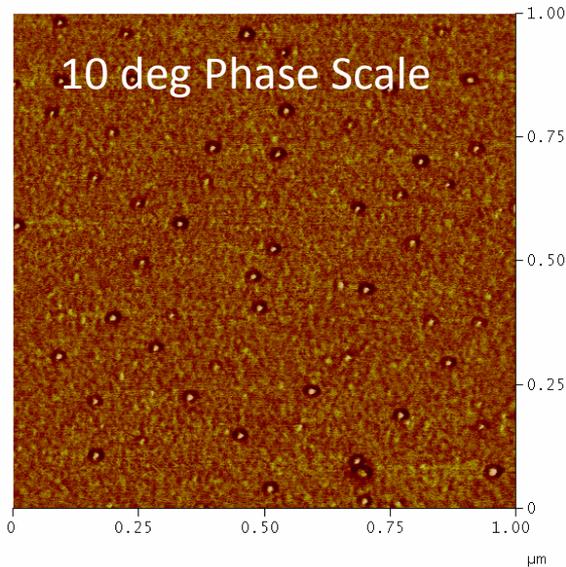


- ✓ AFM – spin-casted from THF (AFM and TEM indicates pearl necklace morphology)
- ✓ Indicates issues with solubility of both blocks; both blocks must be soluble to achieve equilibrated solid-state structures

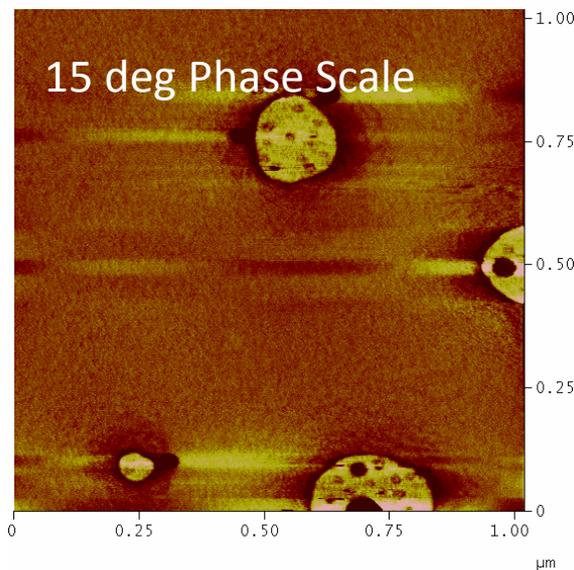
# AFM (Film Dependence on PS Content)

## (Subtask 2.3) Technical Accomplishments and Progress

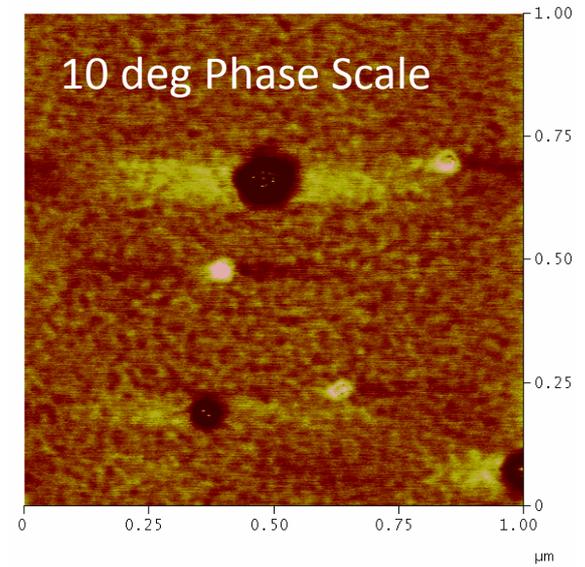
SF 5-2.5



SF 10-2.5



SF 5-6

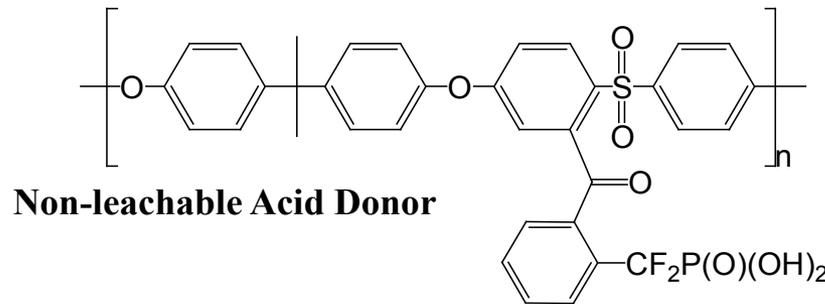


- SF 5-6 showed sufficient film formation with nanophase domains of  $\sim 10$  nm
- SF 10-2.5 showed sufficient thickness but large holes were evident
- Insufficient film thickness was noted for SF 5-2.5

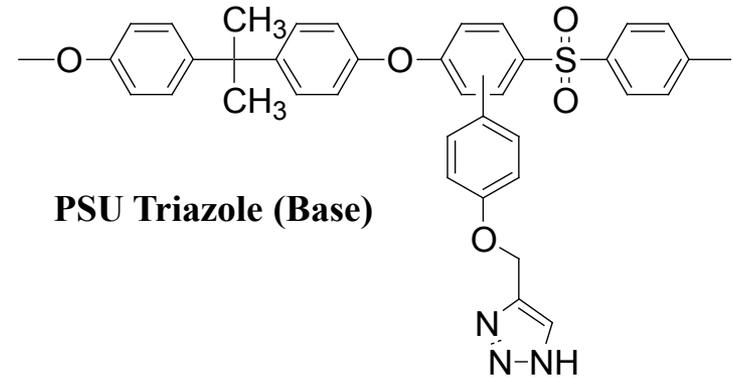
# Polysulfone-Triazole Membranes With Non-leachable Acid Donor

(Subtask 4.1) Technical Accomplishments and Progress

Phosphonic acid functionalized PSU



Non-leachable Acid Donor



PSU Triazole (Base)

## Non-leachable Acid Donor to address the following Issues and Targets:

- Achieve high conductivity @ hot and dry conditions.
- PSU phosphonic acid donor will be permanently immobilized along structured pathways so as to optimize proton conductivity.
- Free phosphoric acid can leach out of a membrane in contact with water causing conductivity reduction and wrinkles leading to gas and liquid leakage during operation.

## Membrane Film Formation:

A (60/40)% by wt. phosphonic acid PSU/triazole PSU mixture in DMAc was cast on glass plate @ 60° C for 12h. Then dried under vacuum @ 80° C for 15h.

Conductivity @ 120° C: Very Low – Triazole N-H groups not accessible to acid?

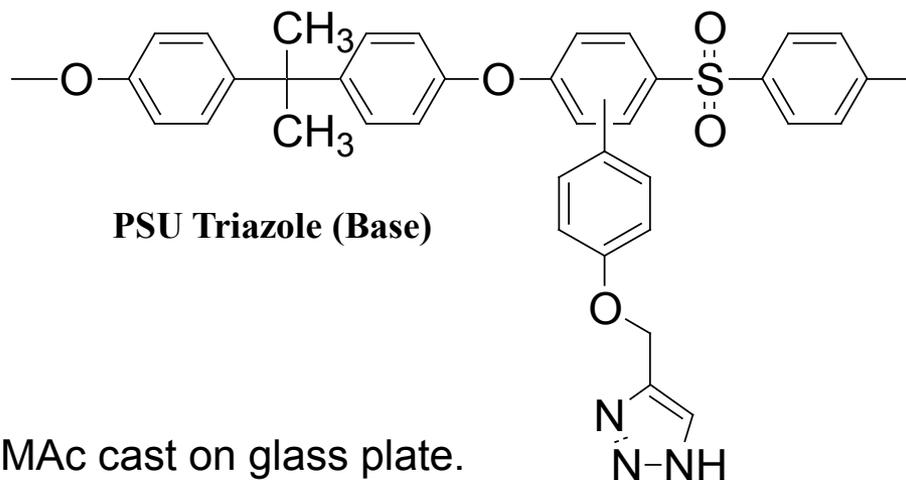
# Preparation of Doped Polysulfone-Triazole Membranes

## (Subtask 4.1) Technical Accomplishments and Progress

Simple model study to test accessibility of acid molecules to -NH groups:



Acid Donor



PSU Triazole (Base)

### Membrane Film Formation:

- 10% (wt/v) soln of PSU triazole in DMAc cast on glass plate.
- Soln dried under continuous air stream @ 60° C for 12h.
- Then, dried under vacuum @ 80° C for 15h.

### Doping w/H<sub>3</sub>PO<sub>4</sub>:

- Film immersed in 5M H<sub>3</sub>PO<sub>4</sub> for 4 d @ room temperature. Result: No acid uptake.
- Film immersed in 11M H<sub>3</sub>PO<sub>4</sub> for 4 d: Result: No acid uptake.

**Triazole N-H groups do not seem to be accessible to acid molecules.**

# Dynamic Mechanical Analysis of Polysulfone-Triazole Membranes

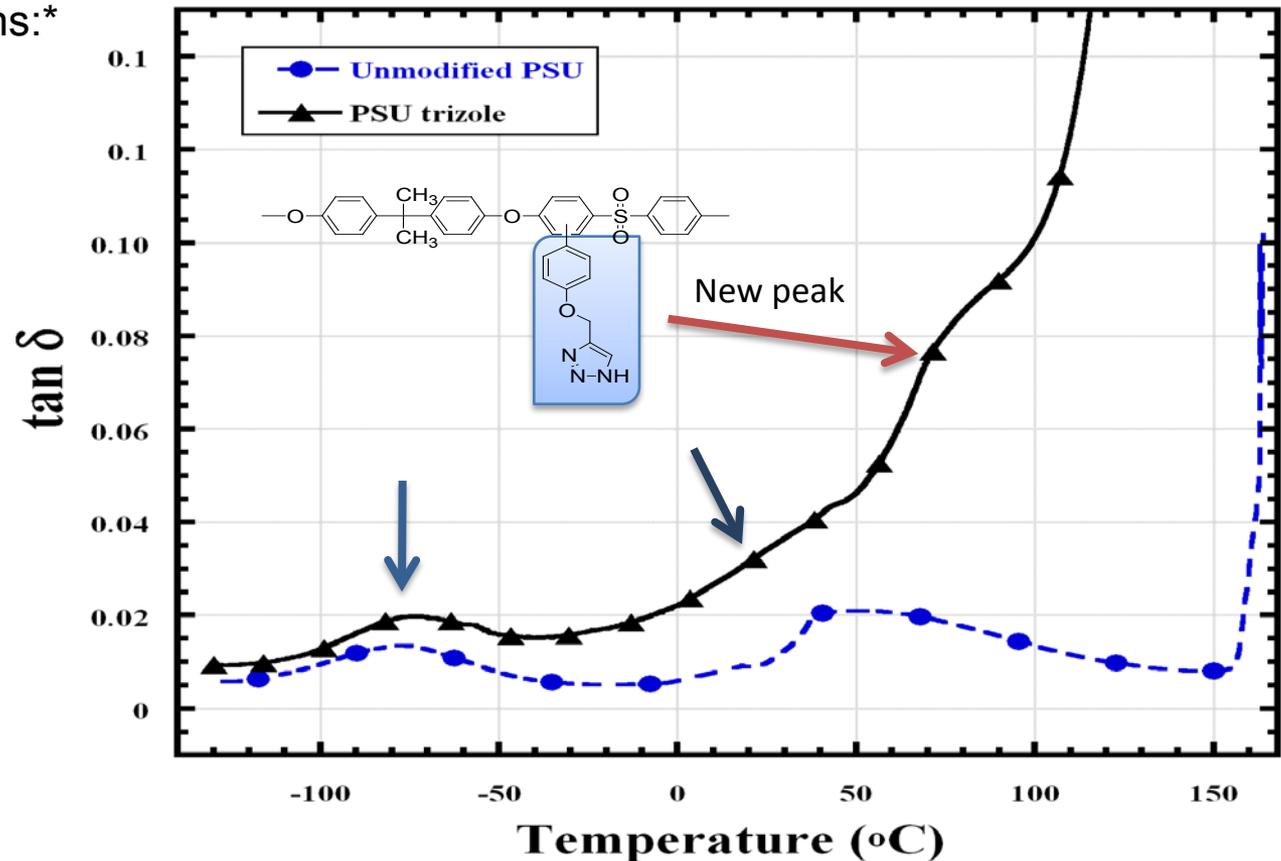
## (Subtask 4.1) Technical Accomplishments and Progress

Three sub-T<sub>g</sub> relaxations:\*

- fluctuations of triazole pendant side chain
- dipole moments (OSO and -O-) of main chain.
- packing defects in material.

New peak:

@ ≈ 75° C for pendant triazole linkage



# Collaborations

- Dr. Vijay Ramani, *Associate Professor of Chemical Engineering*,  
Illinois Institute of Technology
  - Unfunded Collaborator
  - University
  - Outside the DOE Hydrogen and Fuel Cells Program
  - Characterization testing and joint publications

# Proposed Future Work

- Synthesize hydrophobic block comonomer **2** with aryl halide rather than phenolic functional groups. Our approach will be coupling of 1,6-diiodoperfluorohexane with excess 1,4-diiodobenzene. This will place –(CF<sub>2</sub>)<sub>6</sub>– units into hydrophobic blocks of multi-block copolymers, which is predicted to produce better ion clustering and improved conductivity. **(Subtask 2.1)**
- Synthesize PFSHQ using an Ullmann Coupling Reaction approach rather than the current free radical approach. This will allow the synthesis of hydrophilic blocks with more mobile ion exchange groups, which is predicted to yield higher conductivity. **(Subtask 2.1)**
- Produce PSf backbone with higher concentrations of tethered triazole via a “grafting from” approach using RAFT polymerization to improve anhydrous proton transport. **(Subtask 2.2)**
- Establish film formation procedures with SF block copolymers that will yield thermodynamically equilibrated surface morphologies and establish appropriate solvent mixtures for reactions between PFPO and other proton-conducting polymers. **(Subtask 2.3)**
- Characterization of new modified membranes. **(Task 3.0)**
- Selected membrane with best high temperature conductivities will be tested in fuel cells and analyzed for molecular dynamics and BDS in-situ annealing studies using broadband dielectric spectroscopy (BDS). **(Task 3.0)**
- Fuel Cell Performance and Membrane Durability Studies to be performed in order to optimize the best materials for fuel cell operation. **(Task 6.0)**

# Summary Slide

## Subtask 2.1:

Progress toward the synthesis of perfluoroalkyl sulfonate PAES membranes with high proton conductivity has been made. Principle strategies pursued have been:

- Produce multi-block PAES copolymer membranes based on *N,N*-diisopropylethylammonium 2,2-bis(*p*-hydroxyphenyl)pentafluoropropanesulfonate (HPPS). Highest conductivity was obtained at moderate block lengths and high overall polydispersity.
- Synthesize new hydrophobic comonomers and new bisphenolic monomer with perfluorosulfonate moiety at the terminus of a long tether. Sulfonyl fluoride derivative of the latter monomer has been obtained in high purity, but yields are still low.

## Subtask 2.2:

- Triazole and phosphonic acid-pendant PSf were successfully synthesized and evaluated to explore anhydrous proton transport in glassy matrices

## Subtask 2.3:

- Established reaction conditions for a variety of polymer coupling strategies for modular synthesis of strongly-segregated block copolymer variants of Nafion<sup>®</sup>.
- Best conductivity at 80° C and 100% RH for hydrophilic/hydrophobic multi-block copolymers from HPPS was achieved with medium block lengths and high polydispersity index.
- Verified polymer coupling via solution self-assembly and have observed microphase-separated morphologies in polymer films via AFM and TEM.
- Conductivities at 120° C for films of PSf triazole and phosphonic acid-pendant PSf blends were very low at over the range of relative humidity.
- Secondary relaxations which are active within fuel cell operating temperatures were identified using dynamic mechanical analysis.