Alternative Fuel Membranes for Energy Independence

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Project ID #FC071

Overview

Timeline

- Project start date
  - 8/01/2008
- Project end date
  - 1/31/2011
- Percent complete 40%

Budget

- Total funding share
  - DOE share $1,935,500
- Funding received in FY09
  - $951,500
- Funding for YR10/11
  - $ 0

Barriers

- Synthetic challenge: identification of successful routes/conditions for generation of (1) aromatic polymers having tethered acid sites, (2) pendant N-heterocycle aromatic main chain polymers, (3) poly(fluoropropylene oxide) - based block copolymers with desirable morphologies and membrane properties.
- Performance challenge: 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.
- Challenge in achieving economy of cost through 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		94%	Near Completion
2.0	Synthesis of Polymers	1/31/10	1/31/11		25%	On-Going
2.1	Synthesis of Aromatic Polymers w/Tethered Acidic Ion Exchange	1/31/10	1/31/11		60%	On-Going
2.2	Synthesis of Pendant N-heterocycle Aromatic Main-chain Polymers	1/31/10	1/31/11		10%	Started
2.3	Synthesis of Phase Behavior of PFPO-based Block Copolymers	1/31/10	1/31/11		5%	Started
3.0	Establishment of Standard Membrane Benchmark Data	3/31/09	1/31/10		N^1 100% H^2 20%	On-Going
Y1Q4	**Benchmark Nafion®**		**1/31/10**		**100%**	**Complete**
4.0	Membrane Characterization and MEA Fabrication	1/31/10	1/31/11		N^1 100% H^2 15%	On-Going
4.1	Membrane *ex situ* Durability Characterization	1/31/10	1/31/11		N^1 100% H^2 0%	Started
4.2	MEA Fabrication Development	1/31/10	1/31/11		N^1 100% H^2 0%	Started
Y2Q2	**Baseline Data Hydrocarbon Membranes**		**1/31/11**		**H^2 0%**	**Started**
5.0	Inorganic Sol-Gel Modification and Characterization of Nanocomposite Membranes	1/31/10	1/31/11		N^1 100% H^2 0%	On-Going
6.0	Fuel Cell Performance and Membrane Durability Studies	1/31/10	1/31/11		N^1 100% H^2 0%	On-Going
Y3Q2	**Demonstrate synthesis approach improved relative to baseline materials**				**H^2 0%**	**Not Started**
7.0	Project Management and Reporting	1/31/10	1/31/11		60%	On-Going

Synthesis of Aromatic Polymers with Tethered, Acidic Ion Exchange Sites

Subtask 2.1 - Approach
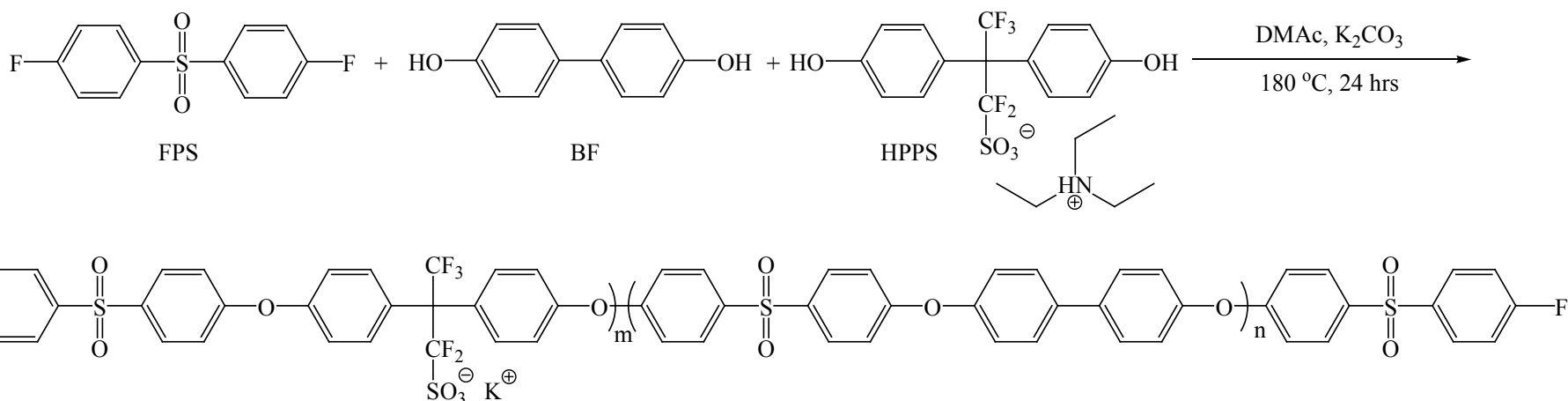
Our approach is toward new membrane polymers combining the desirable features of sulfonated poly(arylene ether sulfone)s and perfluorosulfonic acid polymers. A key accomplishment has been development of the ion-containing bisphenolic monomer, *N,N*-diisopropylethylammonium 2,2-bis(p-hydroxyphenyl)pentafluoropropanesulfonate (HPPS).

Synthesis of New Ion-Containing Bisphenolic Monomer, HPPS

Subtask 2.1 - Technical Accomplishments and Progress
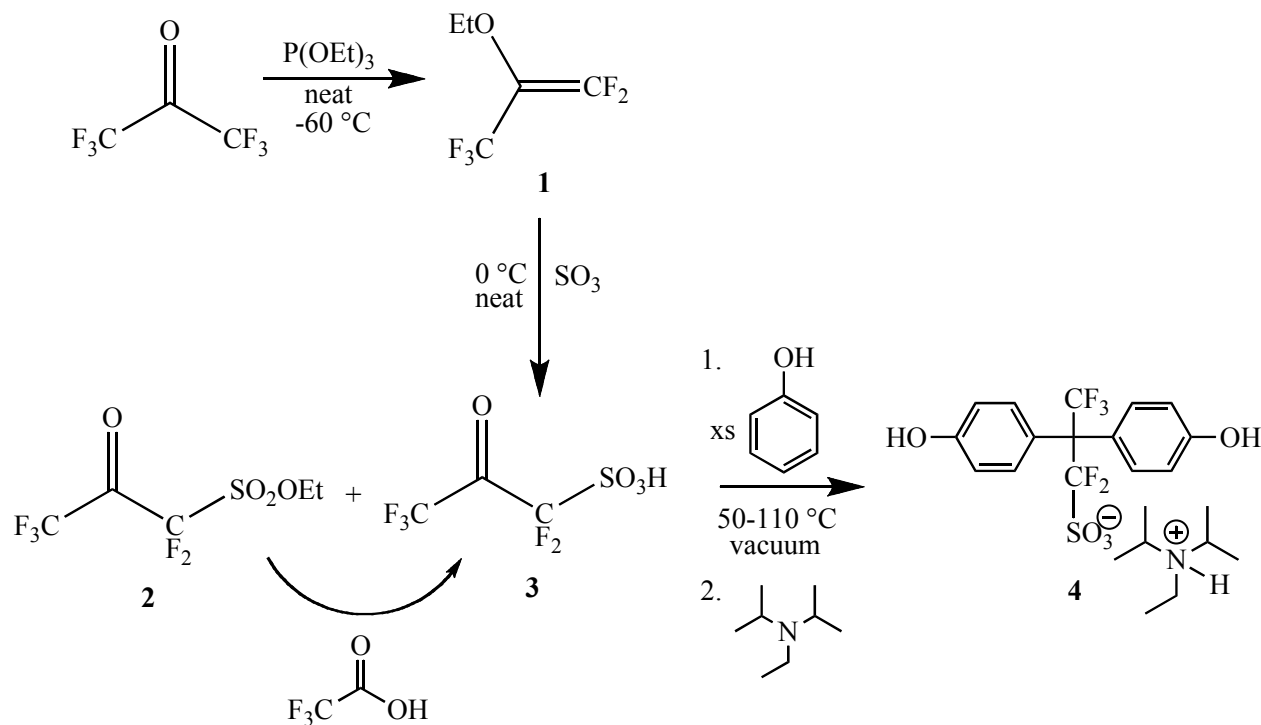
HPPS was successfully synthesized in three steps as follows:

Step 1: Ethyl pentafluoroisopropenyl ether (1) from hexafluoroacetone

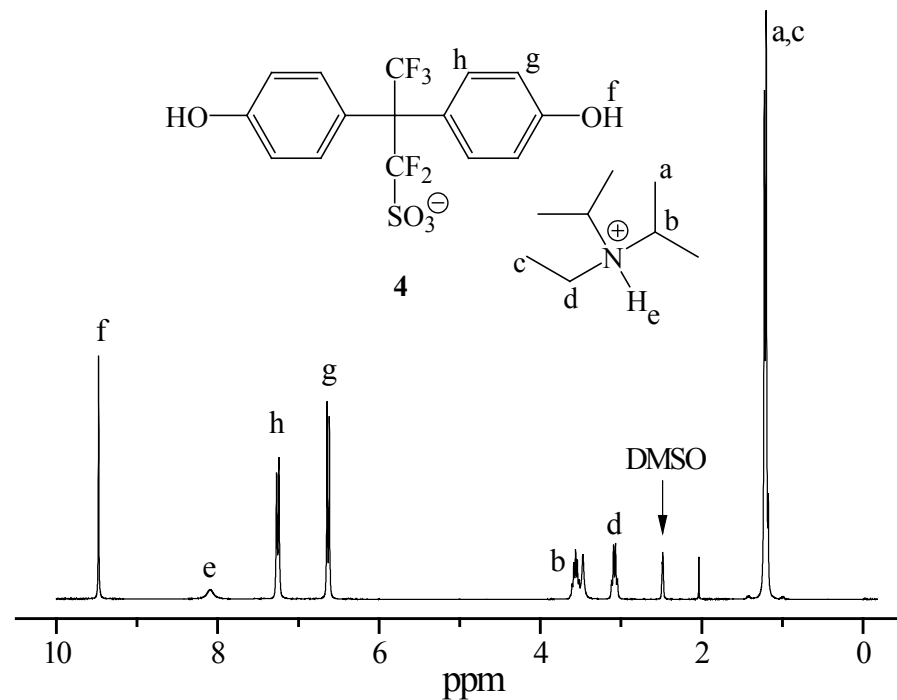**Step 2:** 2-Ketopentafluoropropanesulfonic acid (3) from sulfonation of 1

Step 3: HPPS (4) from condensation of 3 with two equivalents of phenol

Characterization of HPPS
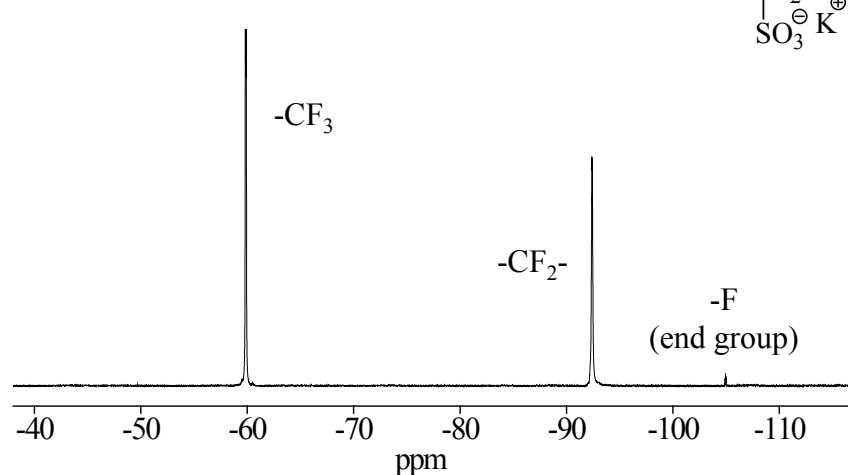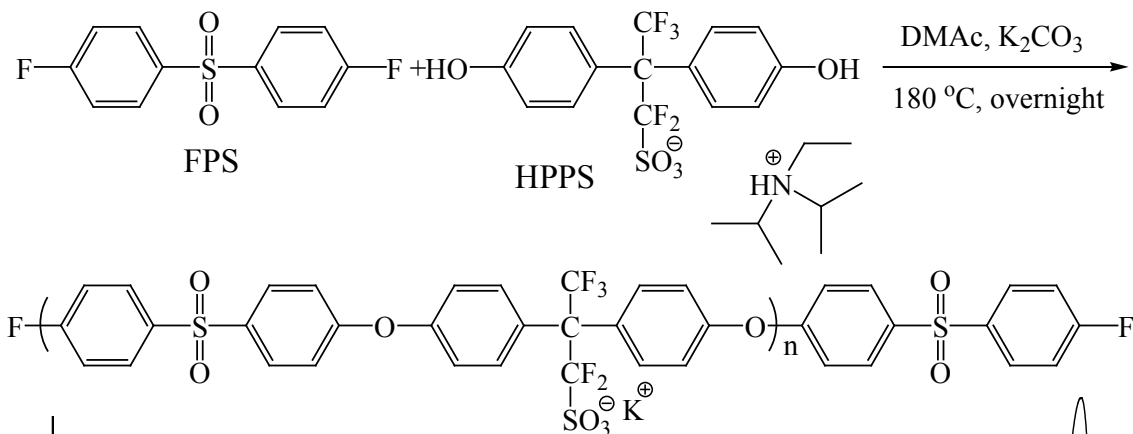## Subtask 2.1 - Technical Accomplishments and Progress
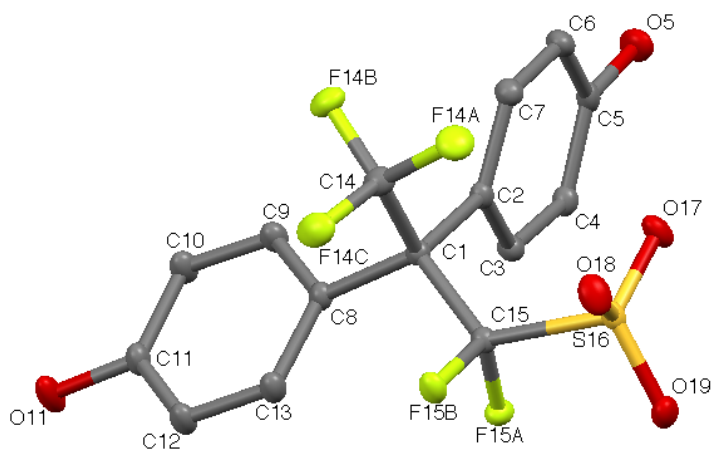
Thermal ellipsoid diagram of HPPS

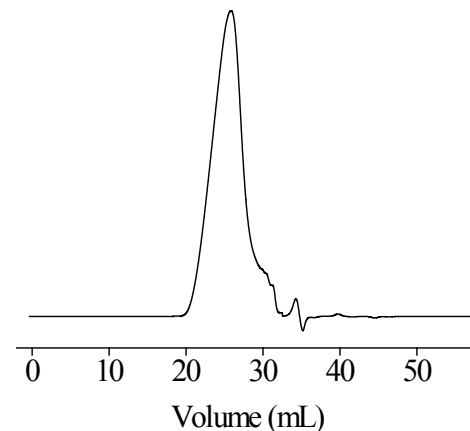

^{1}H NMR spectrum of HPPS

Synthesis of Homo-Poly(arylene ether sulfone) from HPPS and FPS

Subtask 2.1 - Technical Accomplishments and Progress

^{1}H NMR spectrum of homo-PAES

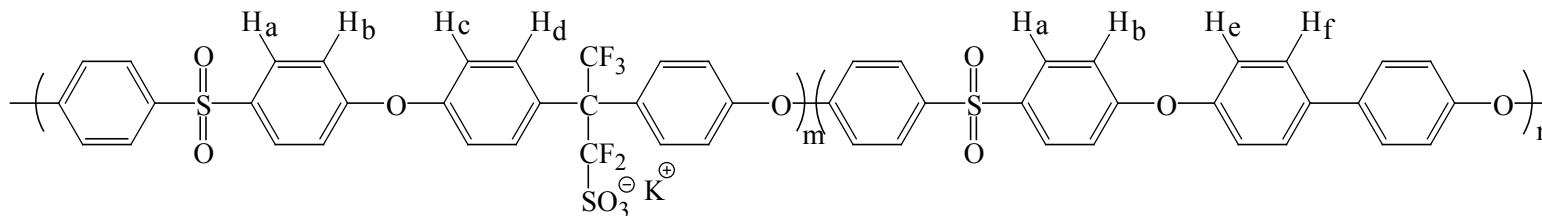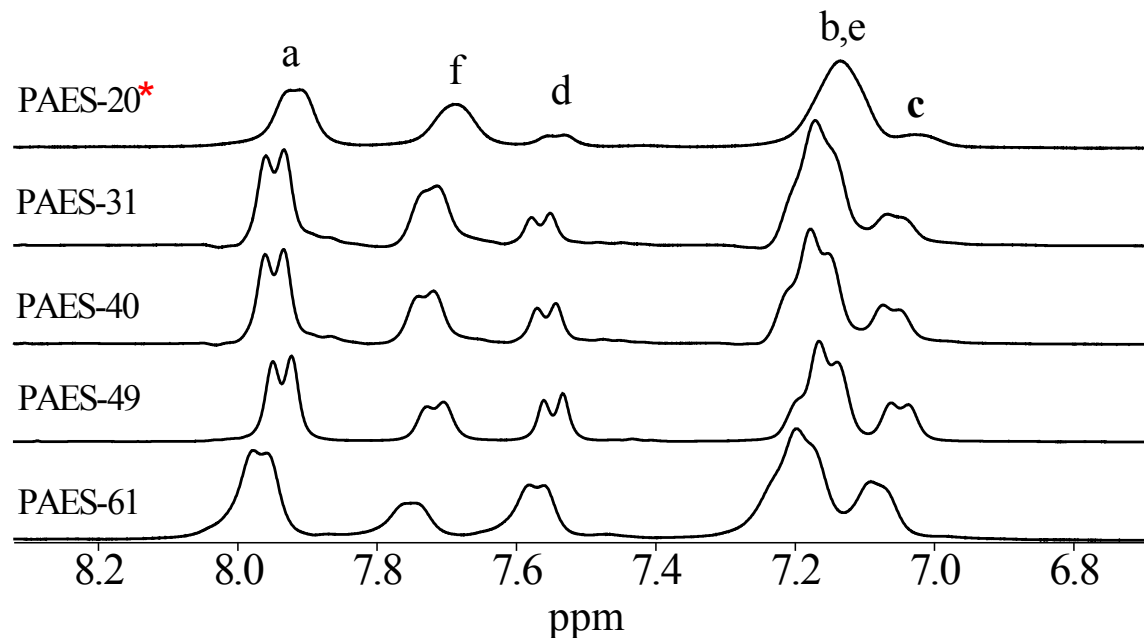M_n = 25,100 g/mol from relative peak intensity

GPC trace of homo-PAES

Mobile phase: DMF/0.02 M LiBr

M_n = 19,300 g/mol, PDI = 1.74 (MALLS)

Copolymerization of HPPS, BP, and FPS
Subtask 2.1 - Technical Accomplishments and Progress

Table
Composition and Molecular Weights of Copolymers from BP, HPPS, and FPS

Copolymer	Composition (theo)[a]	Composition (NMR)[b]	$M_{n,theo}$ (g/mol)	$M_{n,NMR}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
PAES-20	20/80	20/80	25,000	27,100	28,400	1.63
PAES-31	30/70	31/69	33,700	31,900	27,500	1.76
PAES-40	40/60	40/60	29,100	27,800	38,700	1.63
PAES-49	50/50	49/51	32,200	31,400	33,700	1.88
PAES-61	60/40	61/39	35,900	28,500	29,900	2.11

[a] From comonomer feed ratios
[b] m/n (see polymer structure above) determined by ^{1}H NMR

Copolymer Composition from ^{1}H NMR
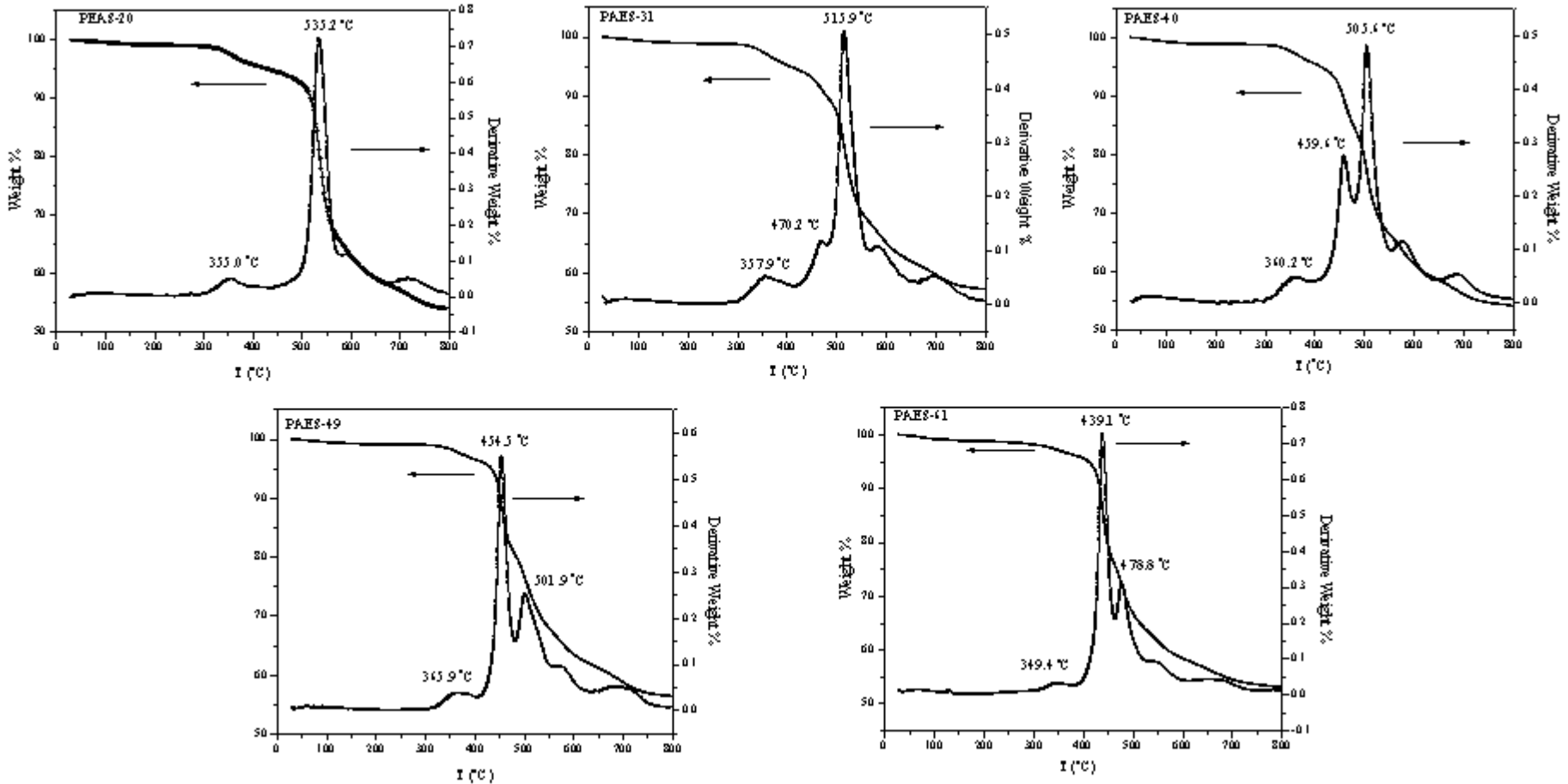## Subtask 2.1 - Technical Accomplishments and Progress

*20, 31, 40, etc. indicate the value of m/(m+n) x 100%
m/(m+n) was calculated as, $Area_d/(Area_f + Area_d)$

TGA of Copolymers (K Salt)

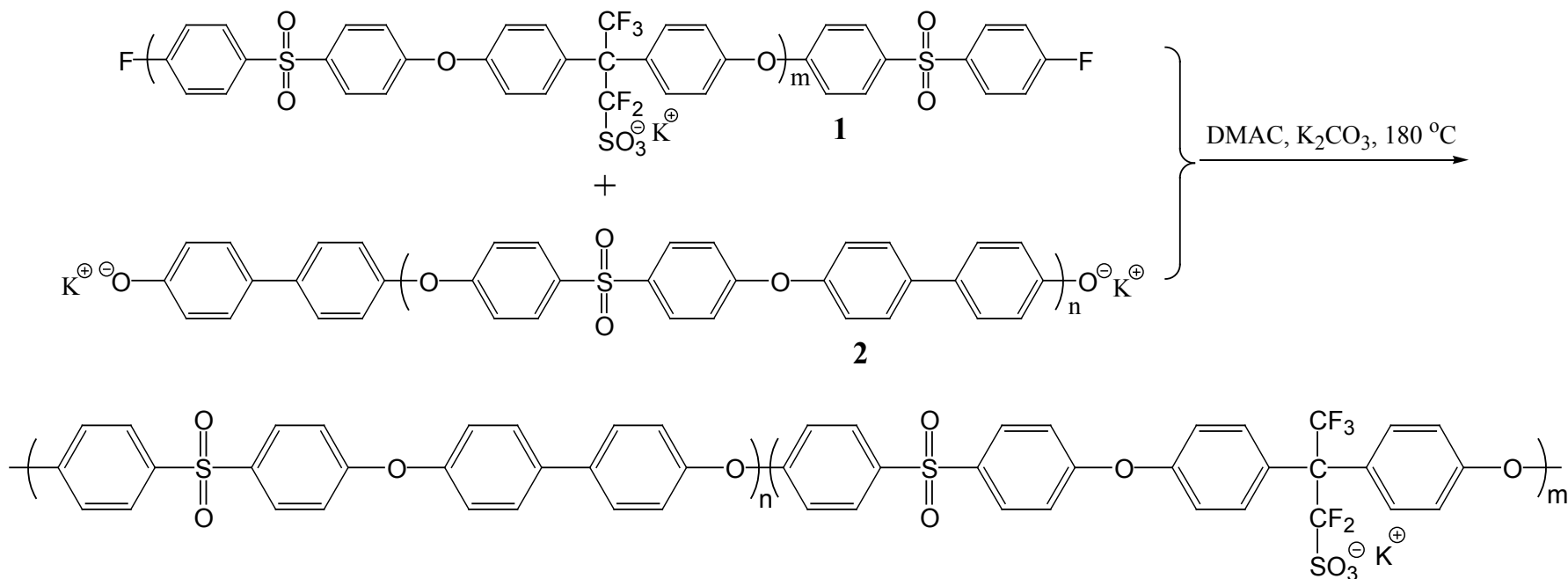## Subtask 2.1 - Technical Accomplishments and Progress

Under nitrogen, with 10 ^{o}C/min ramp. All five copolymers showed multi-step decomposition patterns, and all are stable below 300 ^{o}C.

HPPS/FPS-*b*-BP/FPS Block Copolymers via Prepolymer Approach
Subtask 2.1 - Technical Accomplishments and Progress

Block copolymers were prepared from HPPS/FPS (1) and BP/FPS (2) prepolymers as shown in the scheme above.

# Theoretical vs. Measured (^{1}H NMR) Block Length

Subtask 2.1 - Technical Accomplishments and Progress

Sample	HPPS-BP (7-2)	HPPS-BP (9-2)	HPPS-BP (14-4)	HPPS-BP (17-4)
Theoretical Block Length (m/n)	10.1/4.3	13.9/6.0	21.8/9.4	25.4/10.9
Calculated Block Length (m/n)	9.4/4.4	13.3/6.0	16.1/8.2	23.4/11.8

Synthesis of Pendant N-Heterocycle Aromatic Polymers
Subtask 2.2 - Technical Progress

**Post-Polymerization Modification**
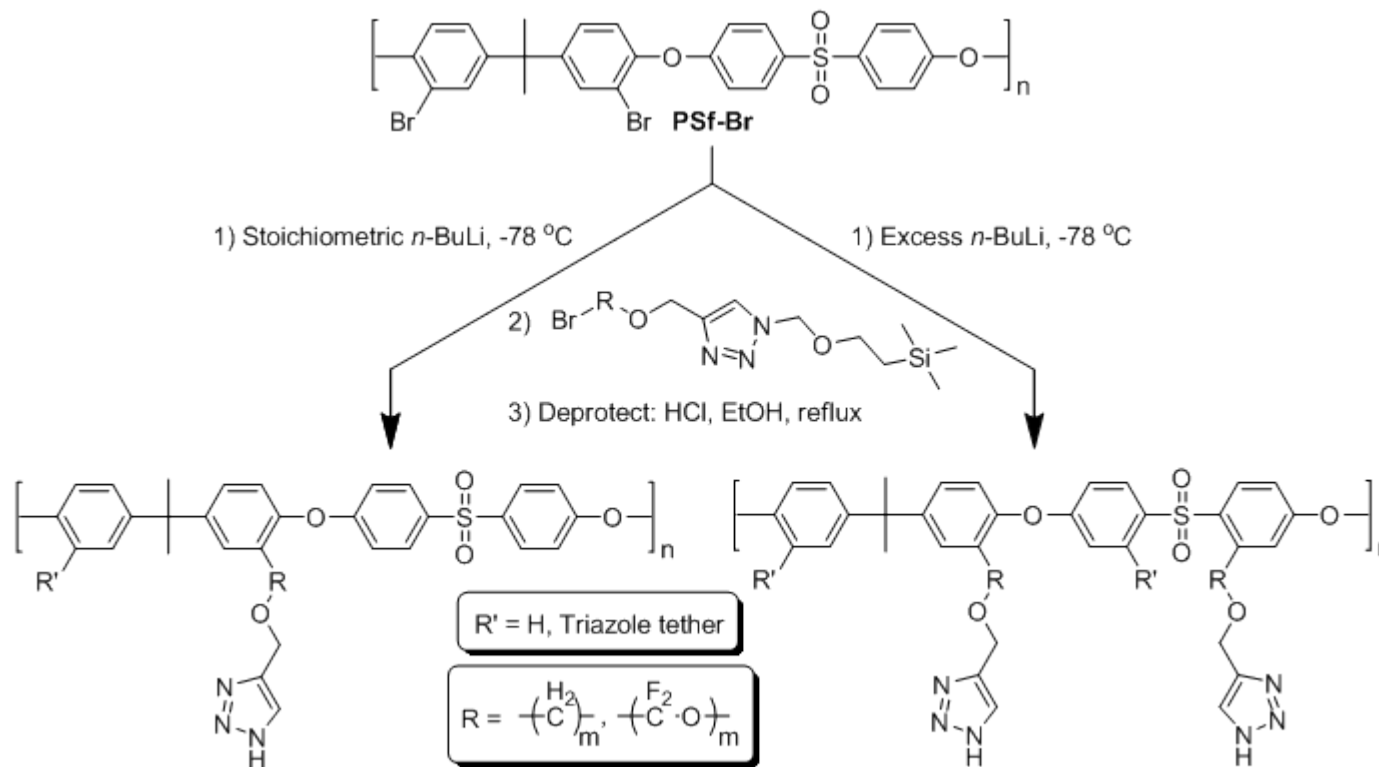
PSf based on commercially available Radel/Udel derivatives. MW ≈ 38K, 43K, 48K   PDI ≈ 1.25, 1.25, 1.29

Synthetic Design Parameters

- Charge carrier concentration, i.e. tether density
- Tether length
- N-heterocycle identity, i.e. 1,2,3- vs. 1,2,4-triazole

Phase Behavior in Bulk BCPs
Subtask 2.3 - Approach

Spheres (BCC) Cylinders (HEX) Gyroid (GYR) Lamellar (LAM)
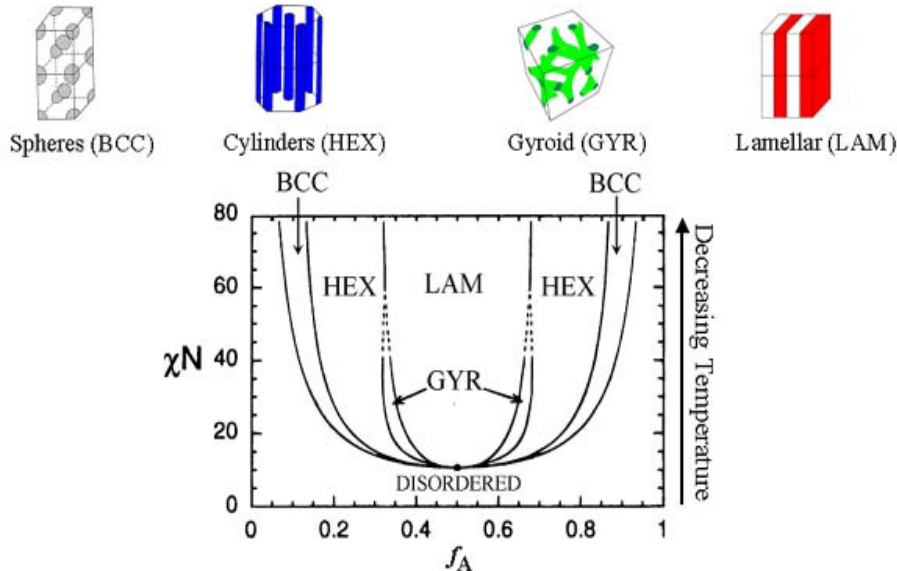
| PFPO	PS	w_F	Morph
6	5	0.55	L
6	10	0.38	C/L/G
6	13	0.32	C
4	5	0.44	L
4	10	0.29	C
4	13	0.24	S/C
2.5	5	0.33	C
2.5	10	0.20	S/C
2.5	13	0.16	S
6	100	0.06	S of PFPO

- **Exploit phase-separated domains to produce ion-conducting channel.**
- **Block copolymer variant of Nafion®**

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

- Drives χ to SSSL
- Used as a compatibilizer for Nafion®/MMT composite membranes

Synthetic Scheme
Subtask 2.3 – Technical Progress
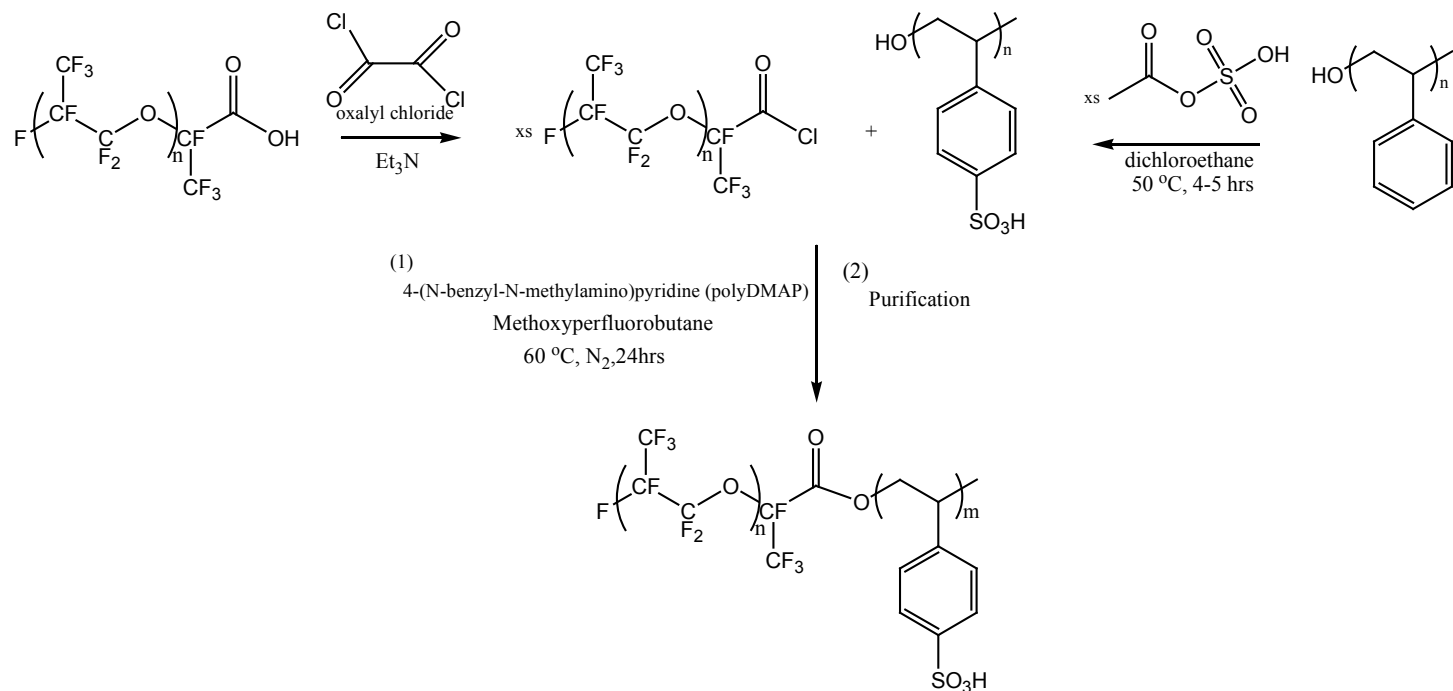
- Challenges lie in the solubility of both homopolymers in the coupling reaction
  - ✓ Other possible solvents include: methoxynonafluorobutane
  - ✓ Other possible coupling agents include
    - WSC = 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide HCl

- Purification of the coupled copolymer is a rigorous process

Synthetic Scheme
Subtask 2.3 – Technical Accomplishments

- DuPont Krytox™ is used as the perfluorinated block and poly(styrene sulfonate) as the conducting block
- Obtained samples of PFPO-COOH and PS-OH for the modular synthesis of block copolymers using standard coupling chemistry
- Developed potential synthetic schemes
  - One of the key issues is determining if sulfonation has to be done prior to coupling (i.e.: if the ester linkage is stable to mild sulfonation conditions) or after
  - This impacts solubility of the component blocks in the coupling reaction that we are currently studying
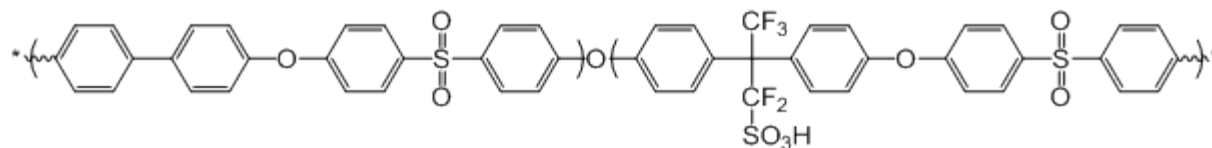
Copolymer Composition and Conductivity
Subtask 4.0 – Technical Accomplishment and Progress

sPAES
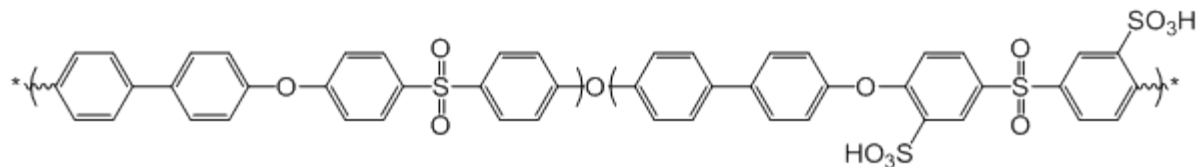
HPPS

Sample	M_n	M_n (hydrophilic block)	M_n (hydrophobic block)	EW (g/mol)	Conductivity (mS/cm)
HPPS Random	27,000	-	-	954	.014
sPAES Random	15,000	-	-	1323	129.49
HPPS-BP (7-2)	-	6,600	1,700	1019	11.2
HPPS-BP (14-4)	-	14,200	3,764	670	13.6
HPPS-BP (9-2)	-	9,044	2,384	877	35.9
HPPS-BP (17-4)	-	16,530	4,352	656	5.4
Nafion® 112	-	-		1100	141.92

The conductivity of each sample was measured using a Bekktech proton conductivity analyzer at 80 °C and various humidities to provide preliminary data about the performance of these materials as a PEM. Optimization of these materials is in progress however, these results show that the multi-block copolymers greatly outperform random copolymers of similar composition.
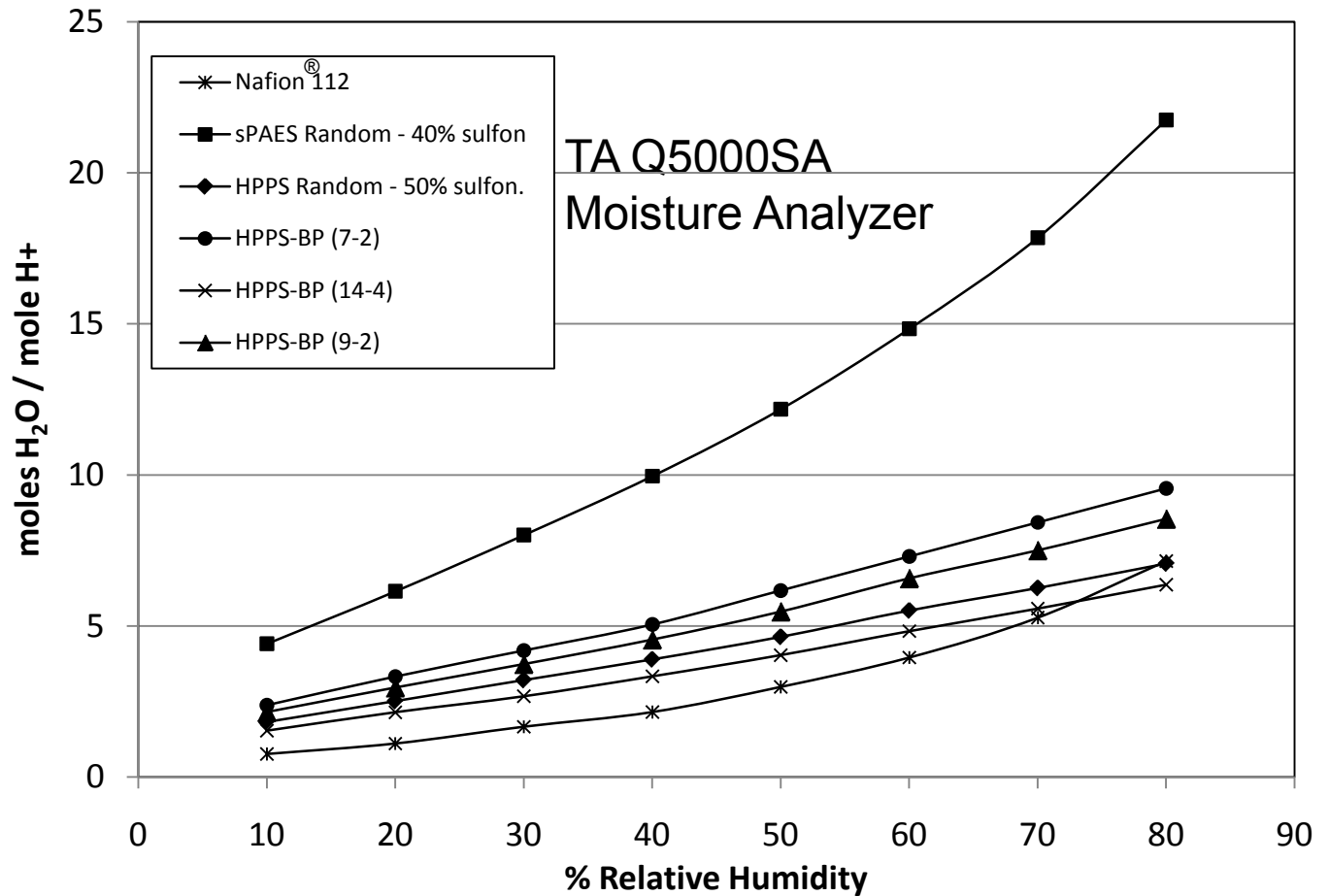
Water Uptake- Vapor Pressure Isotherms at 80 C
Subtask 4.0 – Technical Accomplishment and Progress

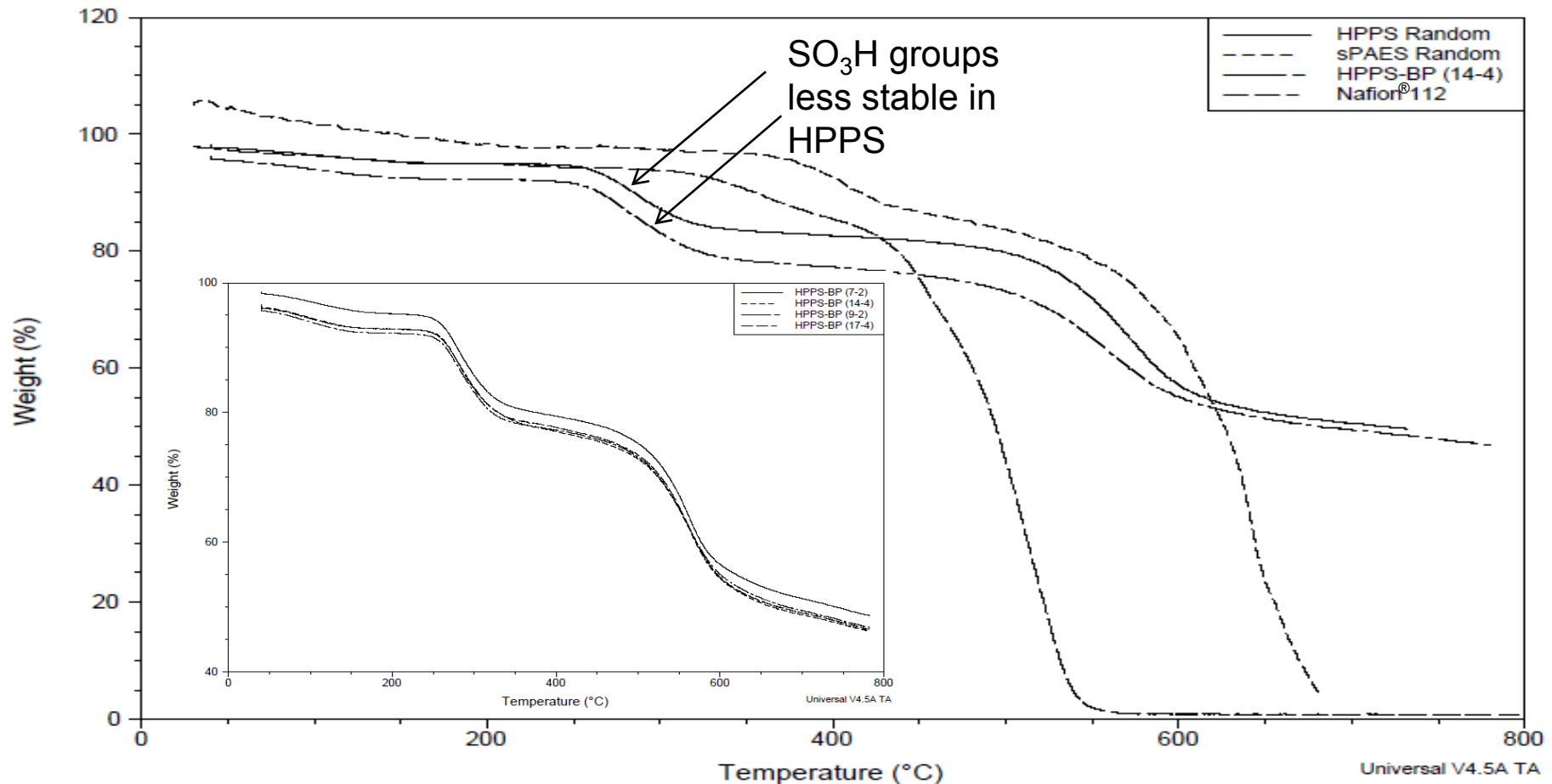HPPS block copolymers have higher water uptake than random copolymers of similar composition.

Likely due to increased phase separation.

Need to increase degree of hydration.

TA Q5000SA
Moisture Analyzer

Legend:
- Nafion® 112
- sPAES Random - 40% sulfon
- HPPS Random - 50% sulfon.
- HPPS-BP (7-2)
- HPPS-BP (14-4)
- HPPS-BP (9-2)

X-axis: % Relative Humidity
Y-axis: moles H_2O / mole H+

TGA-Thermal Degradative Stability
Subtask 4.0 – Technical Accomplishment and Progress

Thermogravimetric analysis of the membranes was performed to compare their thermal stability. The sulfonic acid groups of random and block HPPS exhibited reduced thermal stability, however such high temperatures are not encountered during fuel cell operation.

DMA: Tan δ vs. Temperature
Subtask 4.0 – Technical Accomplishment and Progress
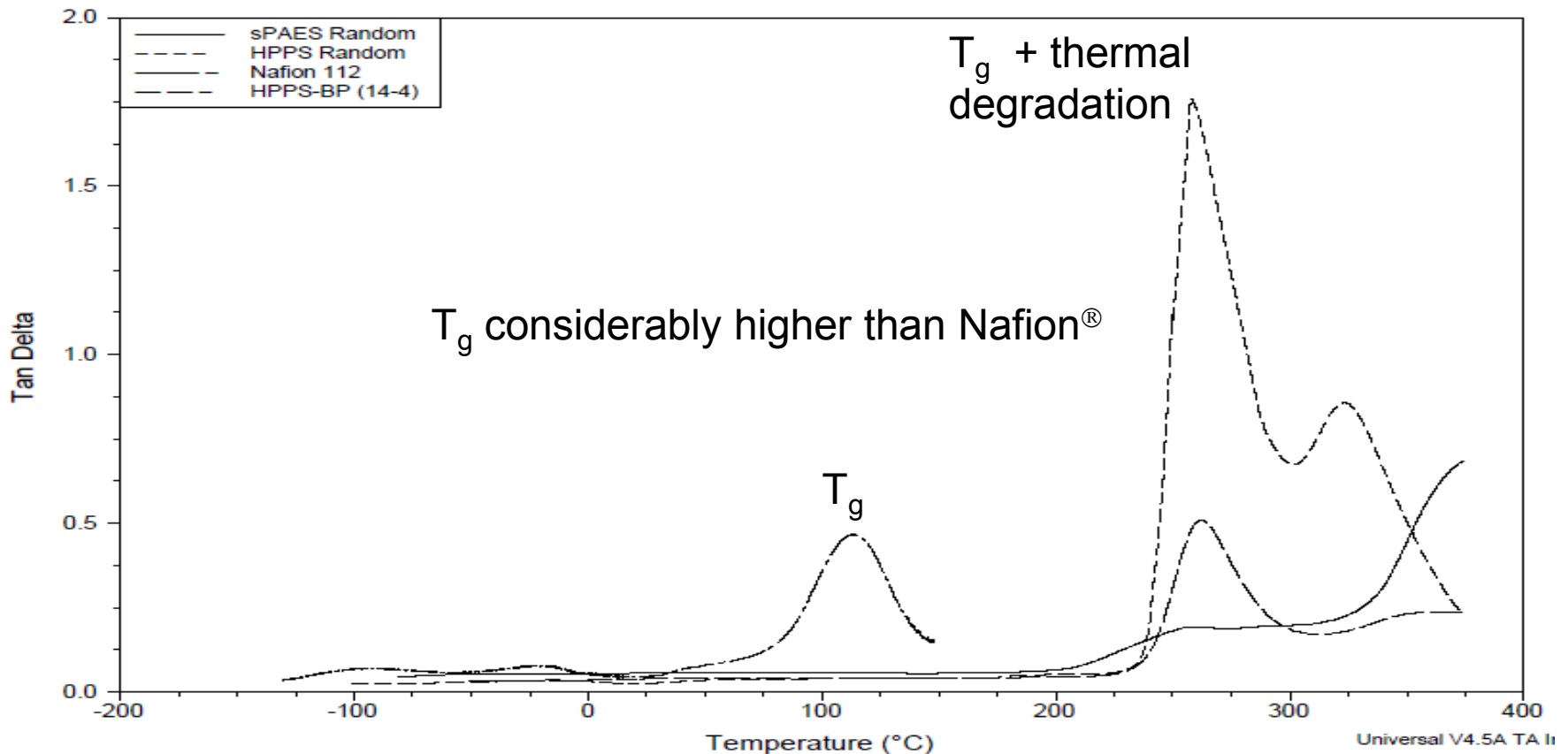
Dynamic mechanical analysis of the materials shows that the aromatic copolymers have a much higher T_g than Nafion®. It was observed that the T_g occurs in the same temperature range as the thermal degradation of sulfonic acid groups.
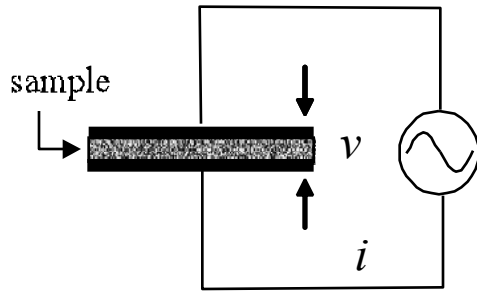
DMA: Tan δ vs. Temperature
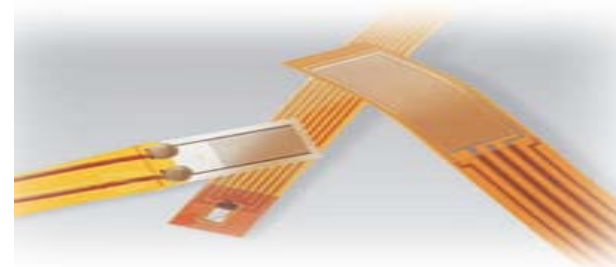## Subtask 4.0 – Technical Accomplishment and Progress
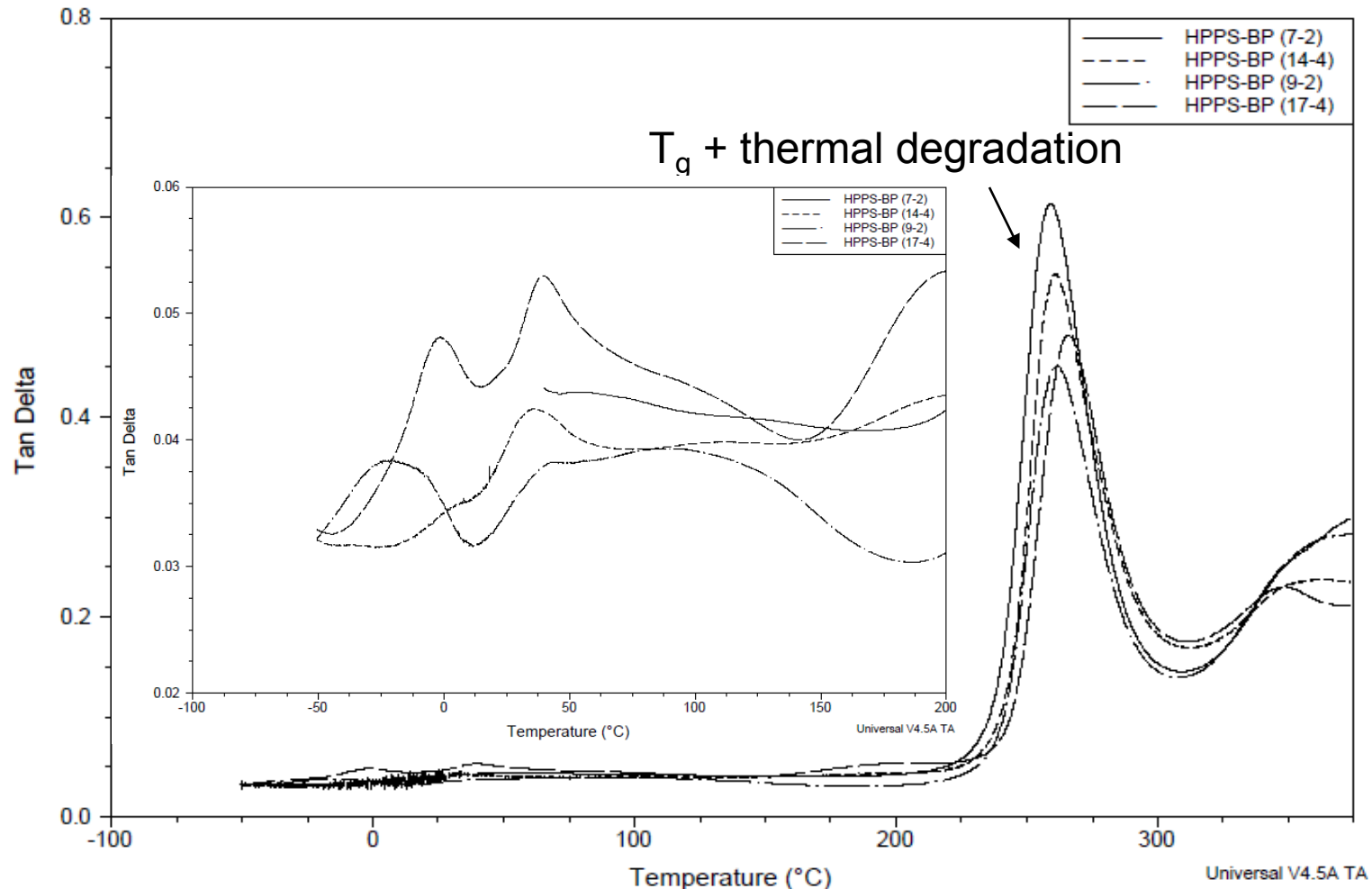
Due to their similar compositions, block copolymers exhibited similar transitions.
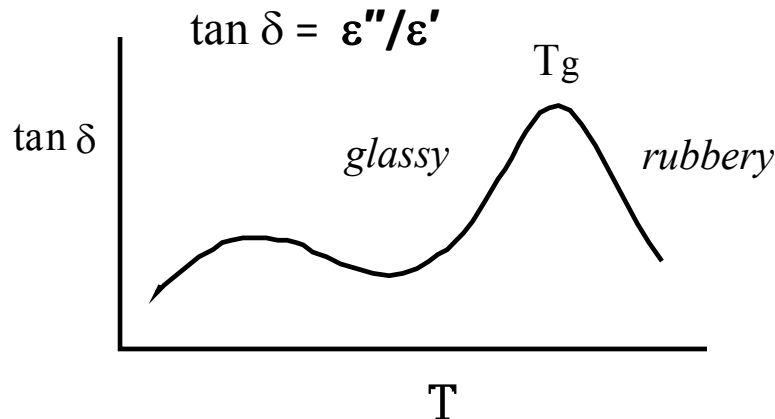
Dielectric Spectroscopy
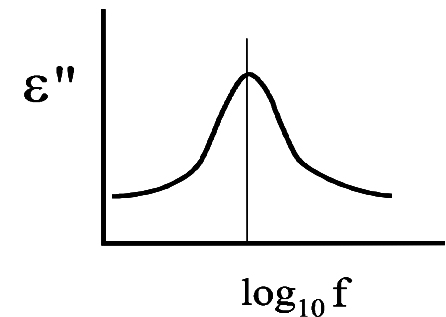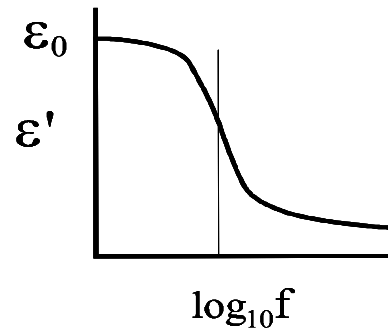
Subtask 4.0 – Technical Accomplishment and Progress

sample

phase angle
between i and v

v

i

Inter-digitated electrode sensor

$\tan \delta = \varepsilon''/\varepsilon'$

Tg

$\tan \delta$

glassy

rubbery

ε_0

ε'

$\log_{10} f$

ε''

$\log_{10} f$

T

Observe polymer transitions

Single Relaxation Time $= \tau = 1/(2\pi f_{max})$

ε', ε'' = storage, loss components of complex dielectric permittivity: $\varepsilon^* = \varepsilon' - i\,\varepsilon''$

f = frequency $(10^{-3} - 10^9$ Hz)

Fast, accurate, vast range of characteristic time scales
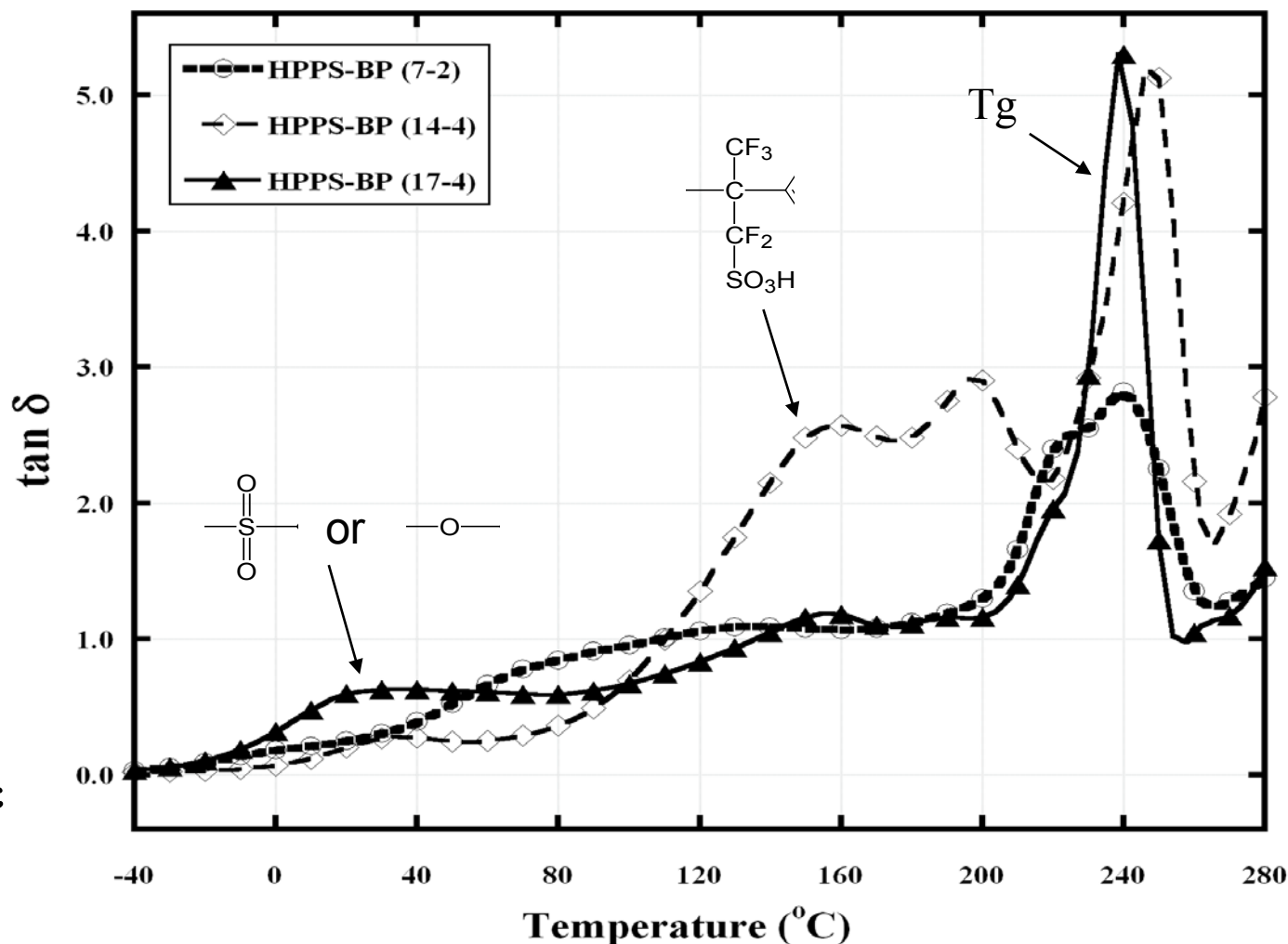
Broadband Dielectric Spectroscopy (BDS)
Tan δ vs. Temperature at f = 1Hz
Subtask 4.0 – Technical Accomplishment and Progress

- Samples stored in humidity chamber before start of experiment.
- Temperature sweep from -80 to 300° C w/ no *in situ* BDS annealing.

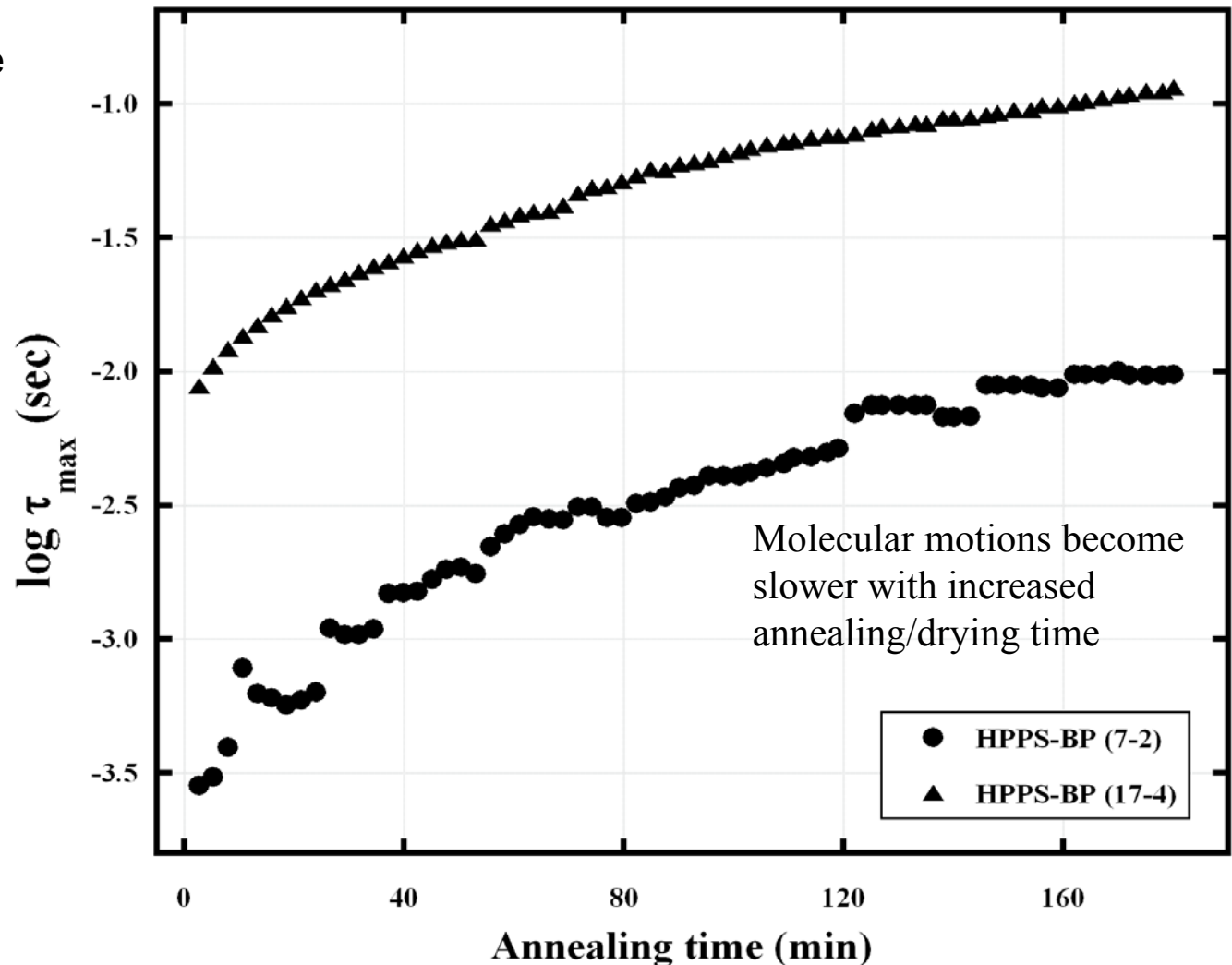- T$_g$ associated with aromatic backbone motion.

$$\tan \delta = \varepsilon'' / \varepsilon'$$

BDS *in-situ* Annealing @ 80° C
Subtask 4.0 – Technical Accomplishment and Progress

- Samples stored in humidity chamber before experiment
- BDS -*in situ* annealing @ 80° C for 3h.

- Track changes in time scale of relaxation active at 80° C thought to be for fluorinated moieties; info about –SO$_3$H aggregates.

- Info about nature of water desorption process during high temperature FC operation.

Molecular motions become slower with increased annealing/drying time

Legend:
- HPPS-BP (7-2)
- HPPS-BP (17-4)

Axes: log τ_{max} (sec) vs Annealing time (min)

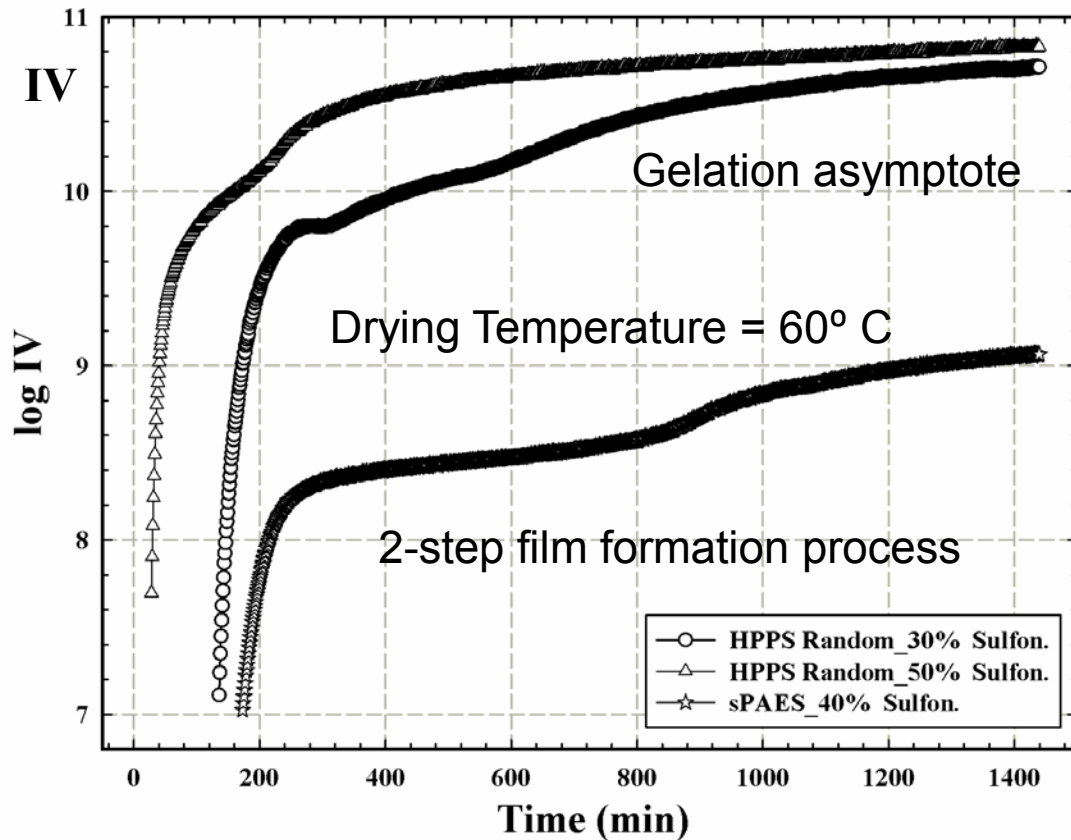# Significance of Fuel Cell Membrane Relaxations
Subtask 4.0 – Technical Accomplishment and Progress

- T_g is related to high temperature membrane stability and water retention

- sub-T_g molecular motions are implicated in molecular transport processes (water, protons, fuel gases),

- sub-T_g molecular motions are implicated in polymer aging, and chemical-mechanical degradation as relating to long term durability in fuel cells

- Low frequency region on loss permittivity curves yields proton conductivity as coupled to relaxations observed at high frequencies
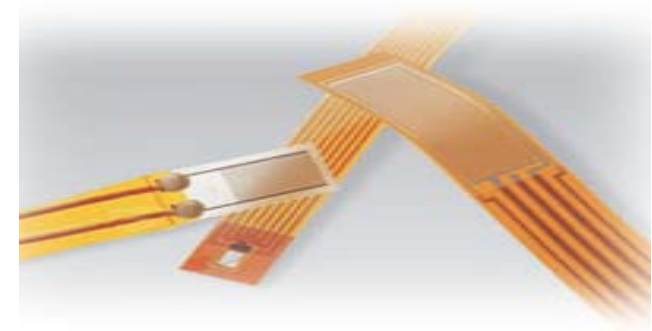
Kinetics of Sulfonated Poly(arylene ether sulfone) Membrane Film Formation via Sensor-based, Real Time Dielectric Spectroscopy

5 wt% solution in dimethyl acetamide (DMAc)

Subtask 4.0 – Technical Accomplishment and Progress

Solution coated directly on remote interdigitated electrode sensor surface:

Gelation asymptote

Drying Temperature = 60º C

2-step film formation process

- HPPS Random_30% Sulfon.
- HPPS Random_50% Sulfon.
- sPAES_40% Sulfon.

Ion viscosity = IV = $1/\sigma$ derived from ε'' at low frequency f using equation $\sigma = 2\pi f\, \varepsilon''\, \varepsilon_o$

σ = electrical conductivity
ε_o = vacuum permittivity

- Differences in spectra w/ MW and degree of sulfonation tracked w/sensor based dielectric spectroscopy.
- Correlate to chemical variations at the molecular level

Proposed Future Work

- Synthesis of blocky PAES copolymers from *N,N*-diisopropylethylammonium 2,2-bis(p-hydroxyphenyl)pentafluoro-propanesulfonate (HPPS), bisphenol (BP), and bis(4-fluorophenyl)sulfone (FPS).
- Synthesis of new ion-containing bisphenol monomers possessing two tethered sulfonate moieties per bisphenol monomer unit and longer perfluorinated tethers for enhanced proton conduction.
- N-Heterocycle Aromatic Polymer
  - Evaluate thermal properties and conductivity of 1,2,3-triazole tethered PSf as a function of composition
- Synthesis of model PFPO-PSS block copolymers
- Morphology Characterization:
  - TEM, AFM
  - (SAXS)
- Shear alignment of phase separated domains
- Testing:
  - Water content
  - Ion transport
- Incorporation of other proton-conducting blocks with PFPO using our modular approach: PBI, poly(arylene ester sulfones)
- Test novel hydrocarbon membranes synthesized by Storey, Patton and Savin with BDS over temperature range -80 to 300° C; determine T_g and sub-T_g molecular motions as relating to high temperature stability and chemical and mechanical degradation as relating to long term durability in fuel cells.
- Samples will be tested with 100% of either hydrophobic or hydrophilic blocks to correctly assign the BDS transition peaks in block copolymers.
- *In-situ* annealing experiments will be conducted at fixed temperatures from 80 to 140° C to get more info about changes in molecular motions and the nature of water desorption during high temperature FC operation.
- Generate water vapor pressure isotherms to correlate BDS results with water content.
- Perform complementary DMA-RH studies (viscoelastic spectra vs. relative humidity)

Summary Slide

- Synthesized /characterized new ion-containing bisphenolic monomer, *N*,*N*-diisopropylethylammonium 2,2-bis(p-hydroxyphenyl)pentafluoropropanesulfonate (HPPS).

- Synthesized poly(arylene ether sulfone) copolymers w/ various ion contents from HPPS, bisphenol, and bis(4-fluorophenyl)sulfone (FPS). MW, PDI, copolymer composition characterized w/ NMR, GPC. Thermal properties characterized w/ TGA, DSC.

- Developed chemistry for synthesis of triazole tethers and postmodification of PSf backbones .

- Developed chemistry for modular synthesis of block copolymer variants of Nafion®. Initial studies involve PFPO-PSS model copolymers and extended to use novel proton conducting blocks.

- Determined equivalent weights, proton conductivities of sPAES membranes.

- Generated water vapor pressure isotherms for sPAES membranes.

- Established thermal degradative stabilities and T_gs of sPAES membranes using dynamic mechanical analysis.

- Uncovered molecular motions in, and monitored kinetics of formation of sPAES membranes using broadband dielectric spectroscopy.