Higher Temperature PEM Composite Systems for Fuel Cells

DOE HT REVIEW

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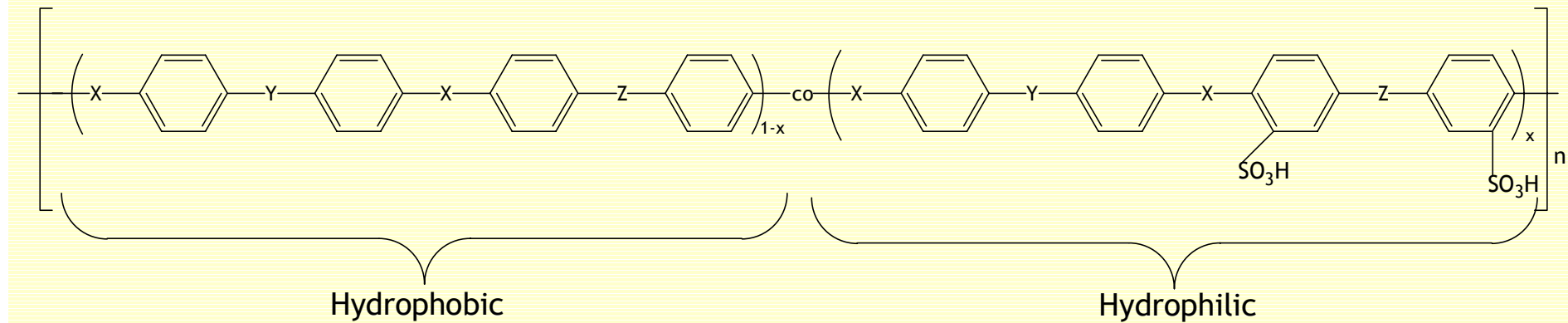Jmcgrath@vt.edu

October 7,2004

Objectives

- Explore the conductivity and mechanical behavior of sulfonated polyarylene ether sulfone(BPSH) or polyarylene ether nitrile(PAEN) random copolymer membranes thin films(1 mil) at (>100°C) under partially humidified conditions.

- Characterize Composite Organic -Inorganic membranes based on the PEM-zirconium phosphonate (and related systems with Prof C Alberti,U.Perugia) for PEM applications.

- Investigate sulfonic acid acidity and sequence length(block copolymers) and/or in Miscible PBI blends on conductivity/humidity relationships

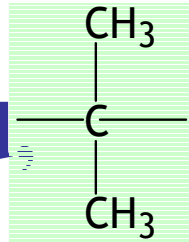# Common Themes Critical to All High-performance Proton Exchange Membranes

1. high protonic conductivity,even at low RH
2. low electronic conductivity
3. low permeability to fuel and oxidants
4. low water transport - diffusion and electro-osmosis
5. oxidative and hydrolytic stability under acidic conditions, for thousands of hours!
6. Good dry and wet mechanical properties at ambient and higher temperatures
7. Cost and capability for fabrication into robust membrane electrode assemblies (MEAs)

M. Hickner, H. Ghassemi, Y.Kim ,B. Einsla and J E McGrath,Chem Reviews,Accepted August 2004.
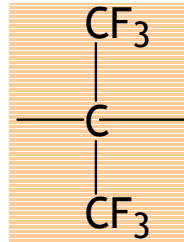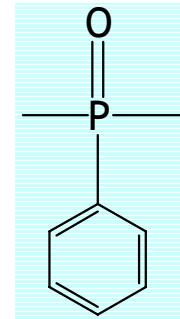
Proton Exchange Membranes (PEM) for Fuel Cells

$$\left[\left(X - \bigcirc - Y - \bigcirc - X - \bigcirc - Z - \bigcirc\right)_{1-x} co \left(X - \bigcirc - Y - \bigcirc - X - \bigcirc_{SO_3H} - Z - \bigcirc_{SO_3H}\right)_{x}\right]_n$$

Hydrophobic   Hydrophilic

$X = O, S$

$Y = a \ bond$

$$\begin{array}{c} CH_3 \\ | \\ -C- \\ | \\ CH_3 \end{array} \quad , \quad \begin{array}{c} CF_3 \\ | \\ -C- \\ | \\ CF_3 \end{array} \quad , \quad SO_2 \quad , \quad \begin{array}{c} O \\ \| \\ -P- \\ | \\ \bigcirc \end{array}$$

$Z = SO_2,$

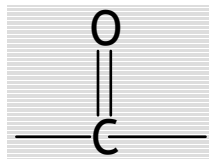$$\begin{array}{c} O \\ \| \\ -C- \end{array} \quad , \quad \begin{array}{c} O \\ \| \\ -P- \\ | \\ \bigcirc \end{array}$$
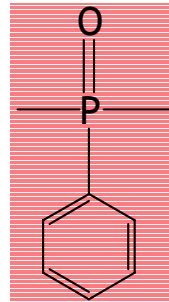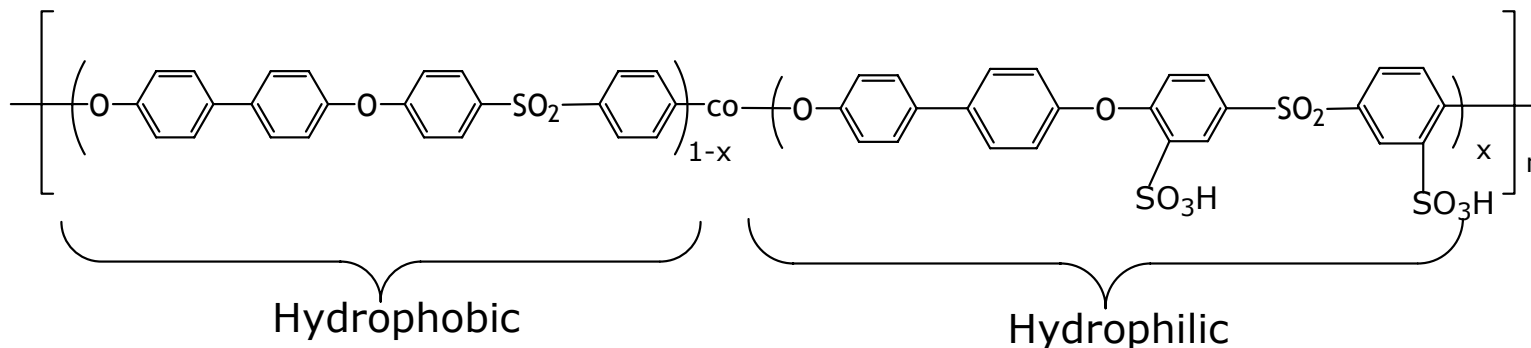
W. Harrison, F. Wang, J. Mecham, V. Bhanu, M. Hill, Y. Kim, and J. E. McGrath, Synthesis of Sulfonated Poly(arylene ether copolymers). J. Poly.Sci. 41, 2264-2276 (2003).

Poly(AryleneEther)Random copolymers (BPSH)

Hydrophobic   Hydrophilic

❖ **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.

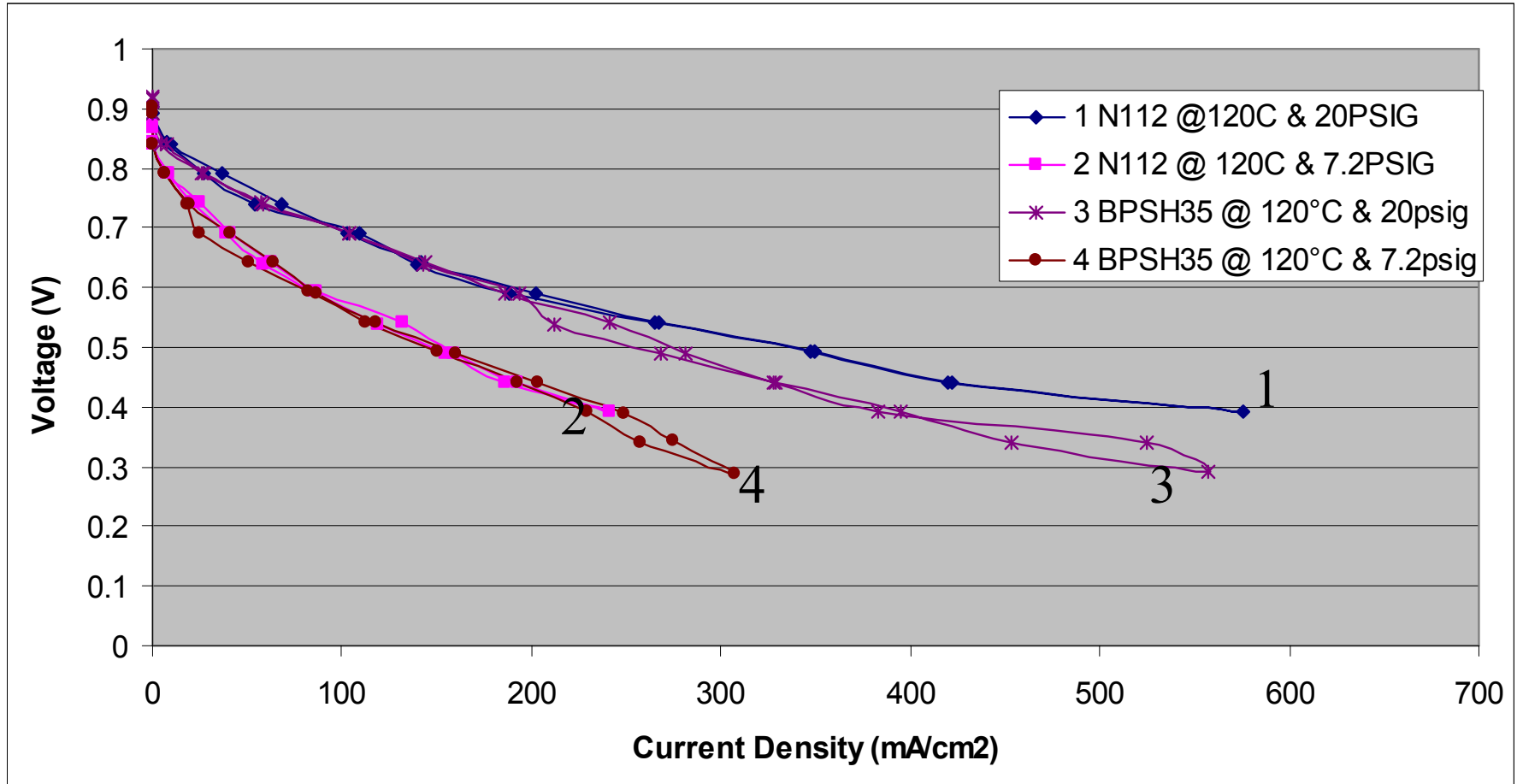# Comparing Four Electrode Conductivity of BPSH 35 120°C, 500 sccm H2, 230 kPa
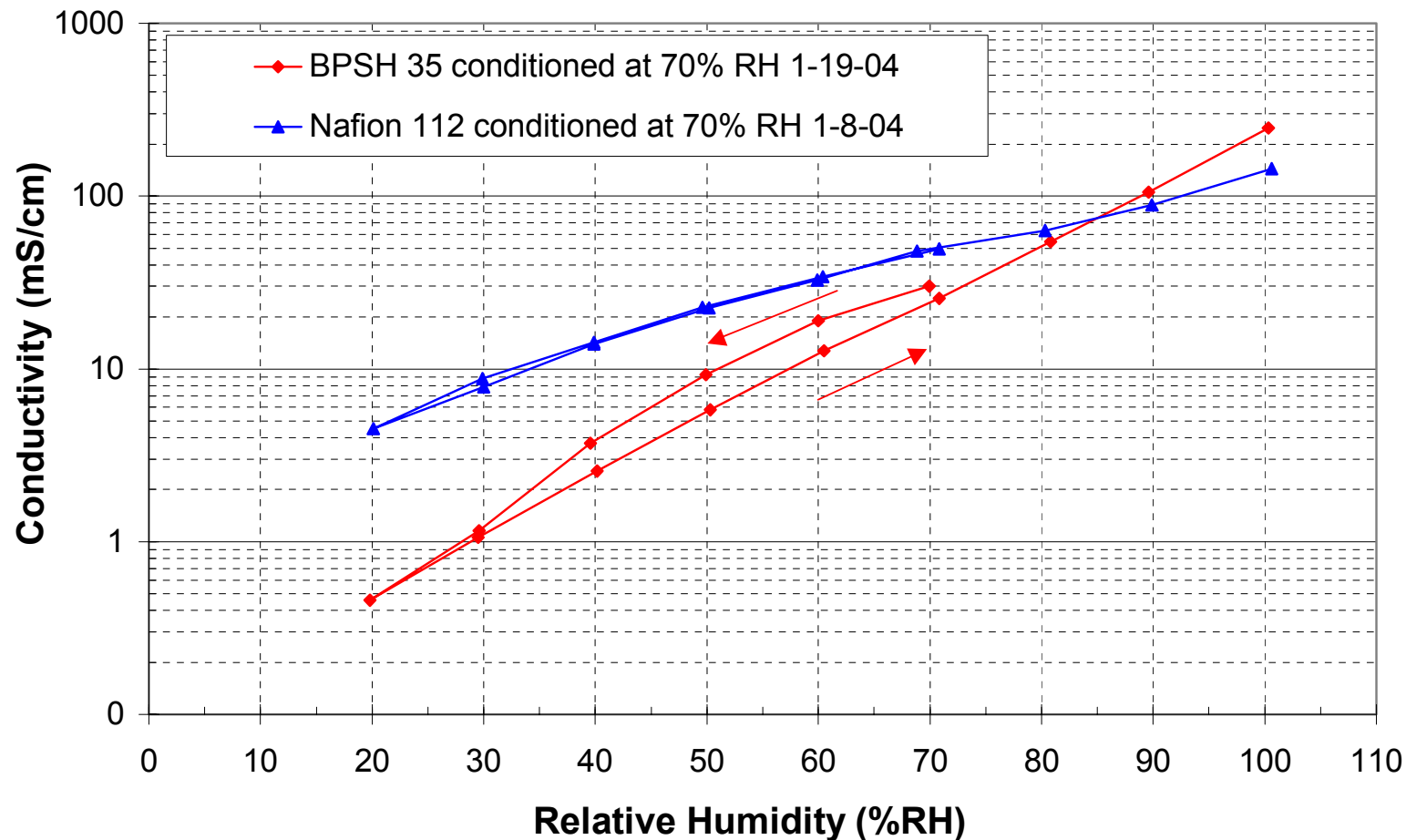
Comparison of Stress-Strain Behavior of BPSH-40 and Nafion 117*
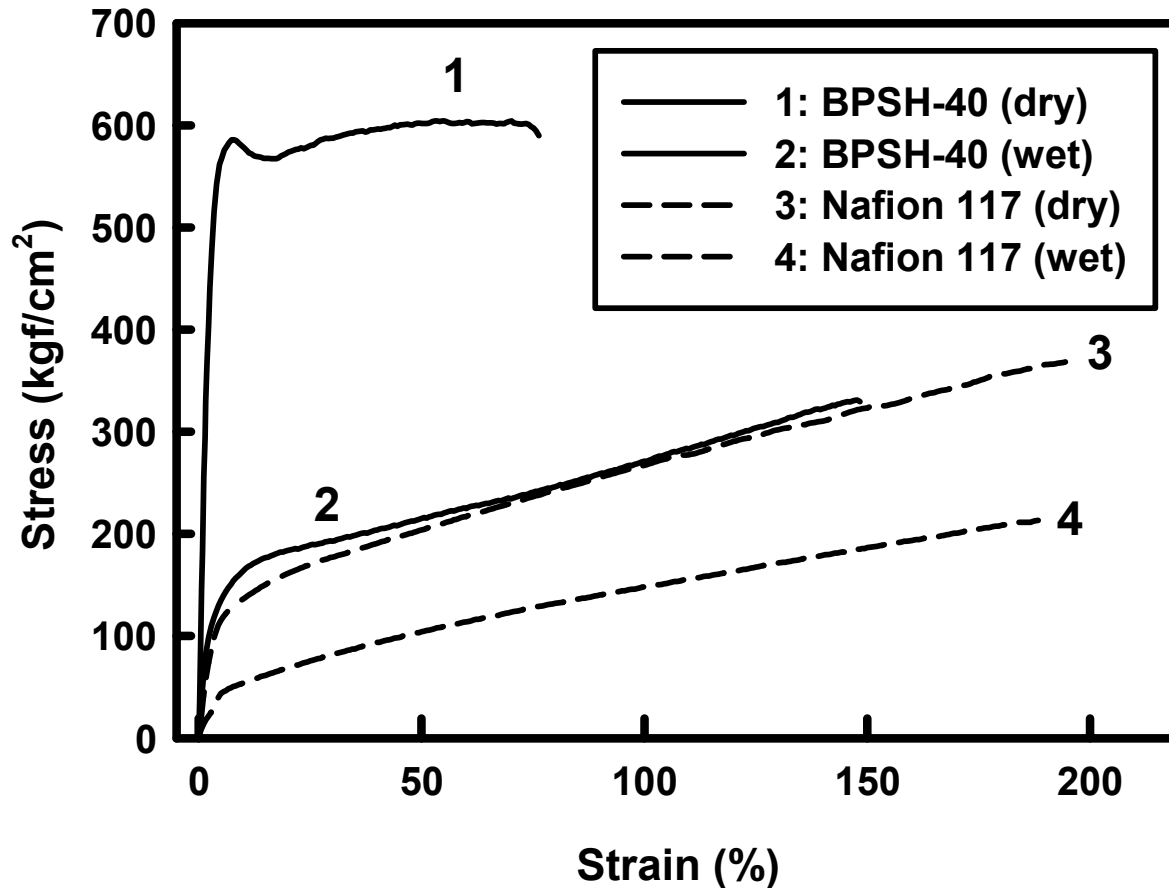
The wet state of BPSH-40 and Nafion 117 contains water of 22% and 16%, respectively.

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

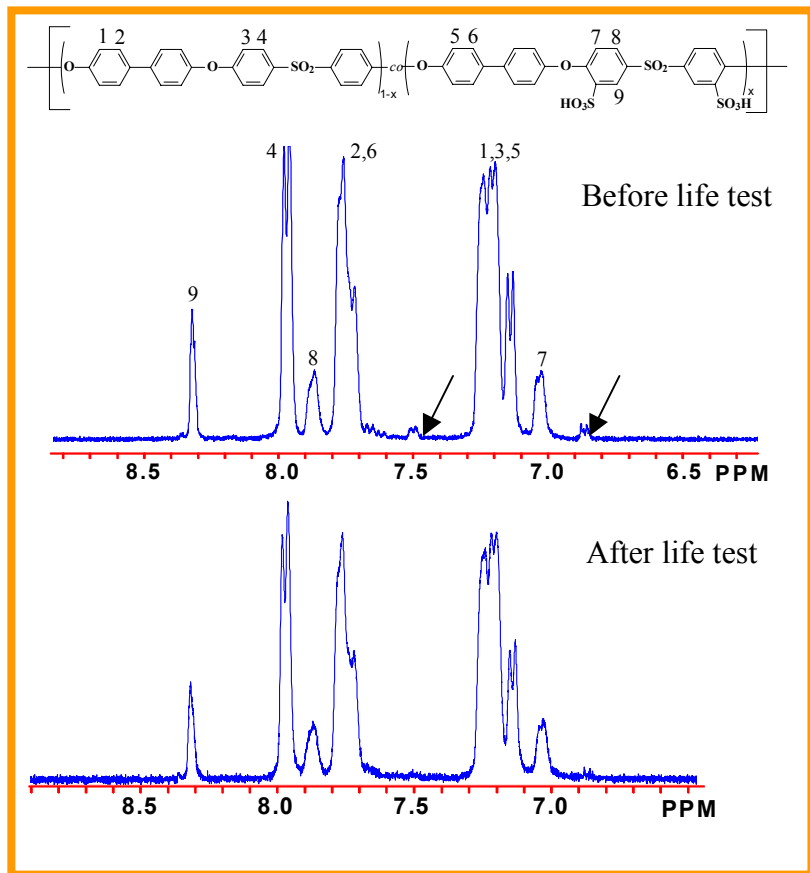At cell temperature of 80°C: Anode bottle=105°C
Cathode bottle=90°C
At cell temperatures of 100°C and 120°C: Anode bottle=100°
Cathode bottle=100°C

Characterization of BPSH-35 After a 700 Hr Life Test

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

Life test	Disulfonation by ¹H NMR (%)	IEC (meq/g)		IV (dL/g)	Water uptake (wt.%)
		calculated	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

Earlier Conclusions

- Hydrogen/air PEMFC's based on alternative membranes have good mechanical properties and the potential to provide satisfactory performance below 100°C.
  - Conductivity at 120°C and low RH is challenging and may require more acidic membranes, long sequenced block copolymers to generate a lamellae hydrophilic-hydrophobic morphology and/or organic-inorganic composite systems.
  - Membrane MW is a Critical parameter defining PEM durability.
  - Miscible polymer blends may be useful to control T_g, mechanical behavior and hydrophilic character

  Tailored membrane/electrode interfaces are important to control swelling and/or improve bonding to Nafion electrodes

- Wholly aromatic sulfonic PEM systems display suppressed species transport (e.g. water, methanol and protons) as compared to Nafion and are more dependent on %RH

s

Conclusions(continued)

- High molecular weight multiblock copolymers were successfully synthesized from perfluorinated poly(arylene ether) oligomers and highly sulfonated BPS

- Membrane properties of the copolymers shows high conductivity based on impedance spectroscopy.

- Making MEA's for fuel cell test.

- Synthesis of additional multiblock copolymers underway.

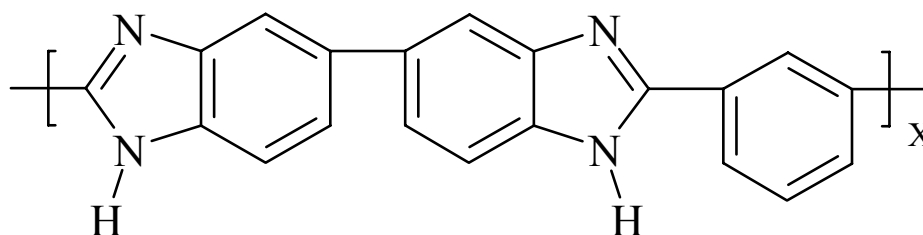# Multiblock Copolymers with Hydrophilic-Hydrophobic Blocks
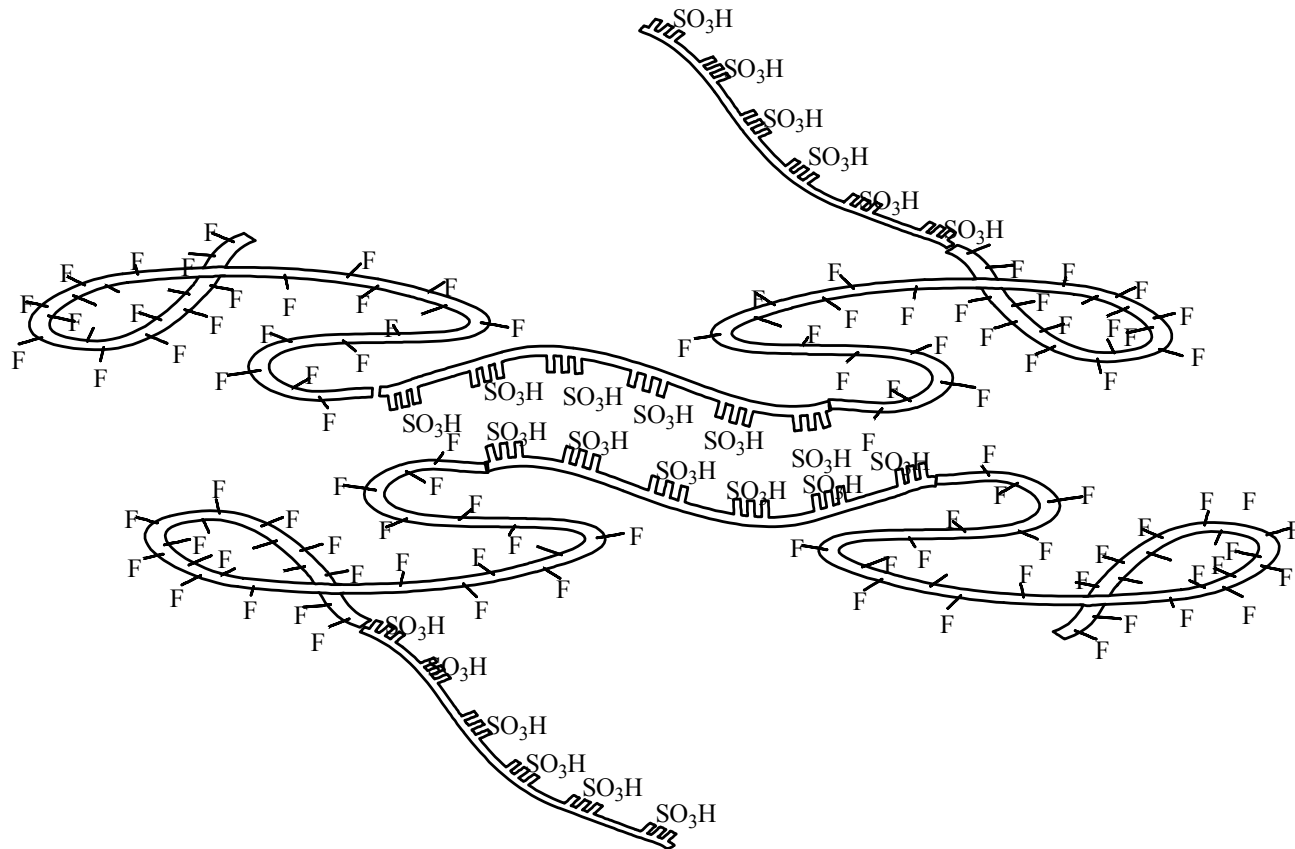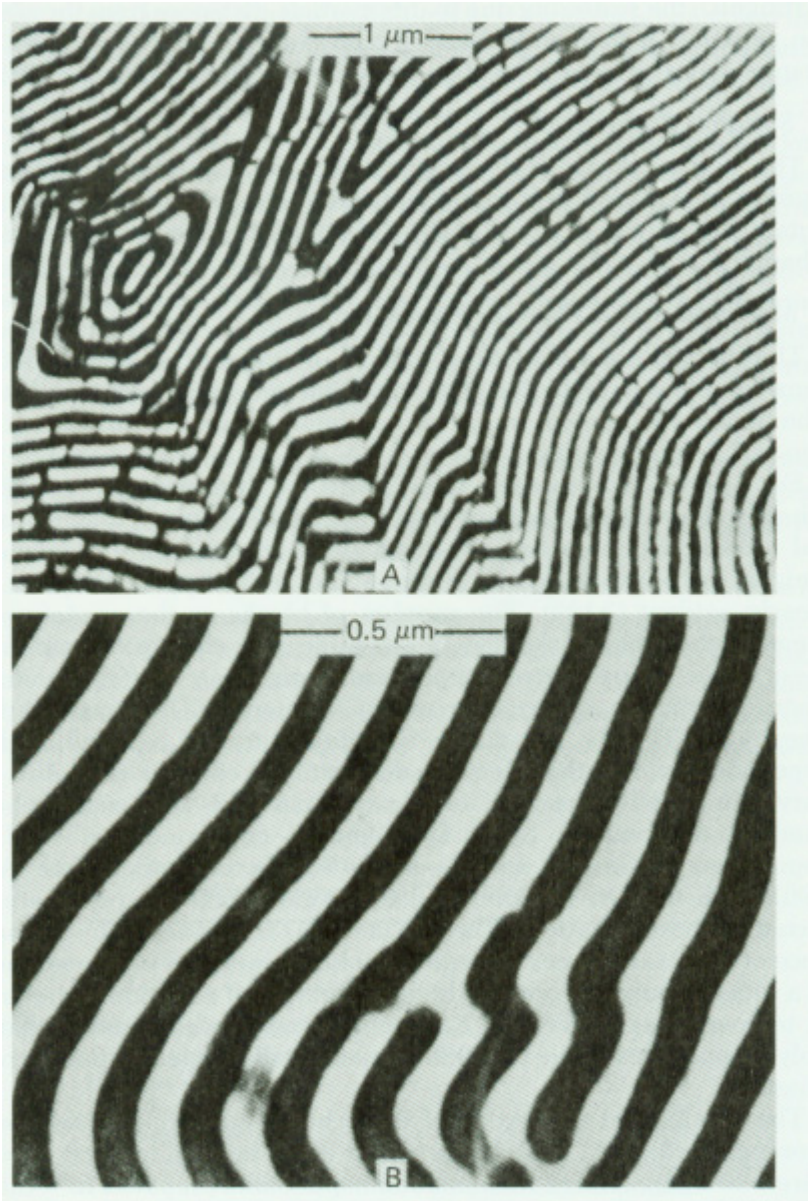
# An Example of an OsO4 stained TEM Cocontinuous Lamellae Film Morphology in Block Copolymers

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

Polybenzimidazoles (PBI)

- Excellent thermal & oxidative stability

- Good hydrolytic resistance

- Acid stable;protonic conductive with H3PO4 additives

- Now, miscibility(1 Tg) has been demonstrated Between PBI and Directly Copolymerized BPSH Systems!

- Conductivities of at least 35ms/cm at 80C

Synthesis of Multiblocks
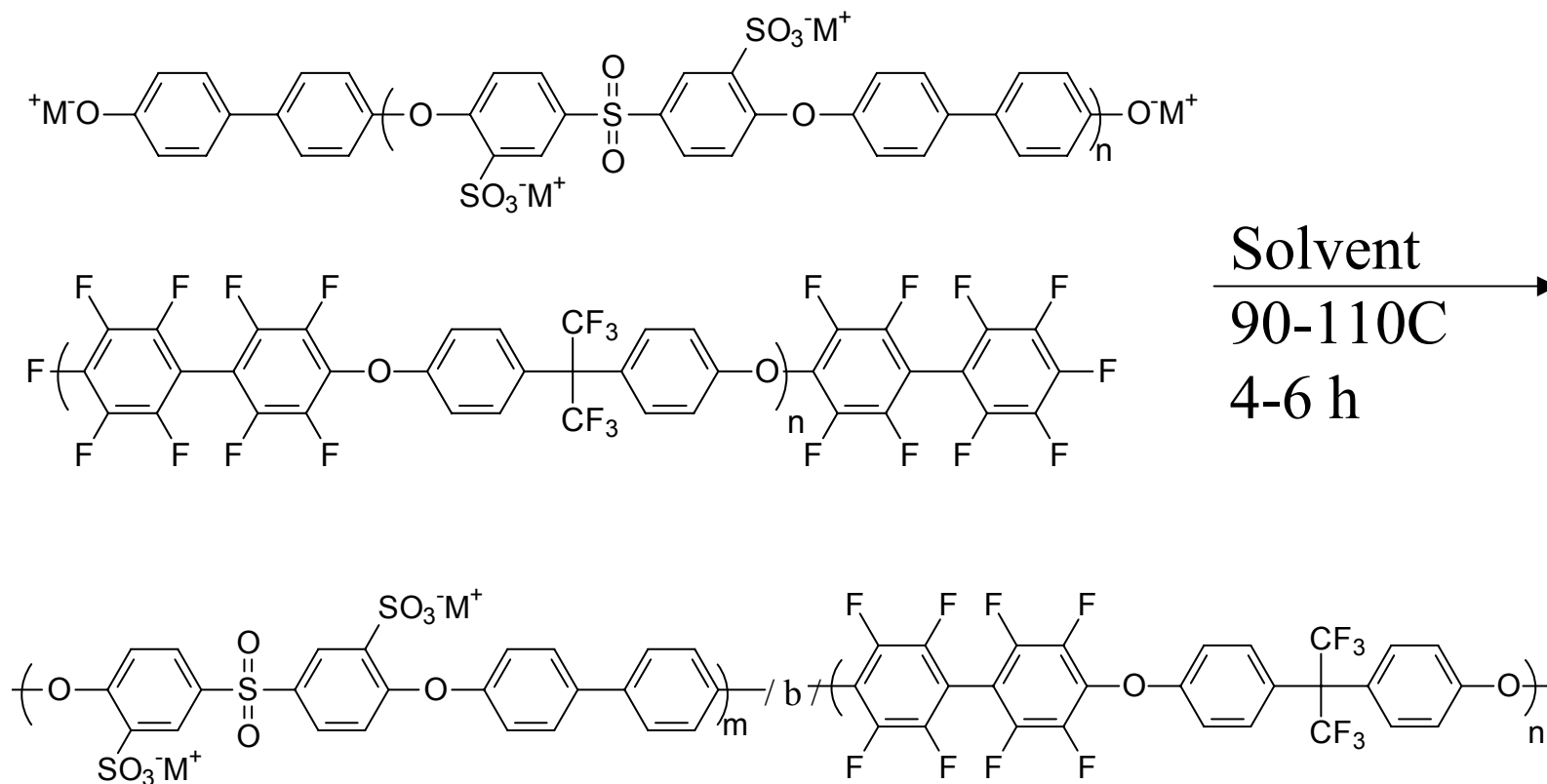
Hossein Ghassemi, William Harrison, Tom A. Zawodzinski, Jr., and James E. McGrath, "New Multiblock Copolymers Containing Hydrophilic-Hydrophobic Segments For Proton Exchange Membrane," *Polymer Preprints* (American Chemical Society, Division of Polymer Chemistry) (2004), 45(1),68-69.

Influence of relative humidity on proton conductivity
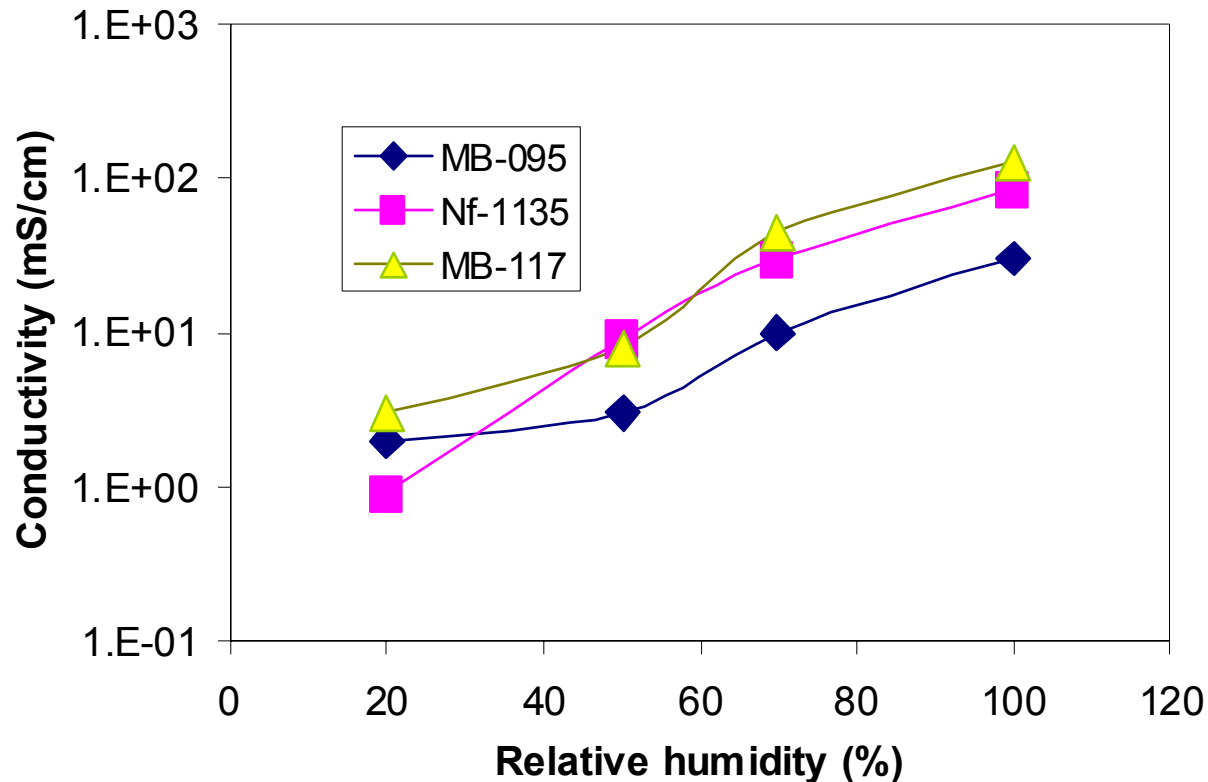
H. Ghassemi and T. Zawodzinski, ECS Abstracts, October 2004.

Characterization of multiblock copolymers

Sample	Block size (Kg/mol)[1]		IEC (meq/g)[2]		Water Uptake (%)
	S	F	Calc.	Exp.	
MB-229	5	2.8	2.05	2.29	470
MB-210	5	2.8	2.05	2.10	360
MB-150	5	5	1.55	1.50	130
MB-117	5	5	1.55	1.17	115
MB-095	3.2	5.3	1.17	0.95	41
Nf-1135	-	-	-	0.89	38

(1) Target value, (S) represents the sulfonated block and (F) represents the fluorinated block. (2) Samples were acidified in 0.5 M boiling sulfuric acid for 2 h and boiling deionized water for 2 h.

H. Ghassemi and T. Zawodzinski, ECS Abstracts, October 2004.

MOLECULAR WEIGHT CHARACTERIZATION OF SULFONATED POLY(ARYLENE ETHER SULFONE) COPOLYMERS

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Virginia Tech
1872

Motivation: Why Molecular Weight is Important

Most reports of new proton exchange membrane materials have included information on ion content (EW or IEC), protonic conductivity, and water uptake. Despite the large body of research on this topic, one of the most glaring omissions in new ion conducting polymer research is the characterization of molecular weight. Molecular weight is a critical parameter defining PEM durability and this has not been properly characterized for any PEM membranes including Nafion! The overall aim of our research is to establish molecular weight vs. mechanical and electrical property correlations for sulfonated poly(arylene ether sulfone) copolymers that could be used as proton exchange membranes in fuel cells.

The viscosity of a dilute polymer solution can be related to molecular weight…

Viscosities of dilute polymer solutions depend on:
• **Temperature**
• **Polymer-solvent interactions**
• **Polymer concentration**
• **Polymer size**
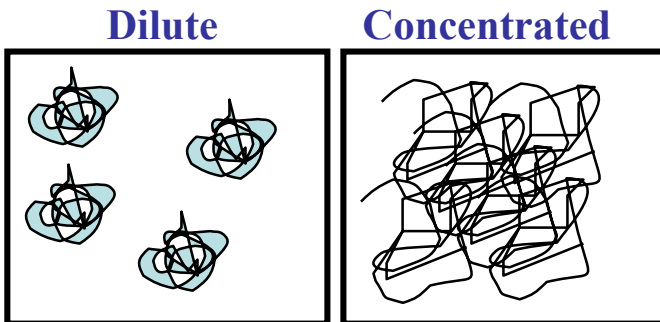
Mark-Houwink-Sakurada equation: $[\eta] = KM_v^{\,a}$
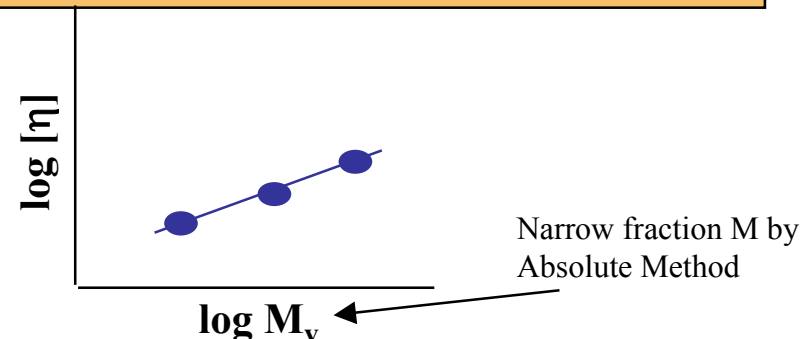
$\text{Log}\,[\eta] = \text{Log}\,K + a\,\text{Log}\,M_v$

M_v = Viscosity Average Molecular Weight

$$M_v = \left(\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right)^{1/a}$$

As "a" approaches 1, M_v approaches M_w

"a" is 0.5 - 0.8 and is dependent on polymer-solvent interactions

$\therefore\ M_n < M_v < M_w$

Dilute   **Concentrated**

log [η]

log M_v

Narrow fraction M by Absolute Method

Intrinsic Viscosity

(dilute solution viscosity)

$$\eta_{REL} = \frac{\eta}{\eta_s} \approx \frac{t}{t_s}$$

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} \approx \frac{t - t_s}{t_s} = \eta_{REL} - 1$$

$$\eta_{RED} = \frac{\eta_{sp}}{c} = \frac{\eta_{REL} - 1}{c}$$

$$\eta_{Inh} = \frac{\ln \eta_{REL}}{c}$$

η = solution

η_s = pure solvent

Mark

Mark

Capillary Tube
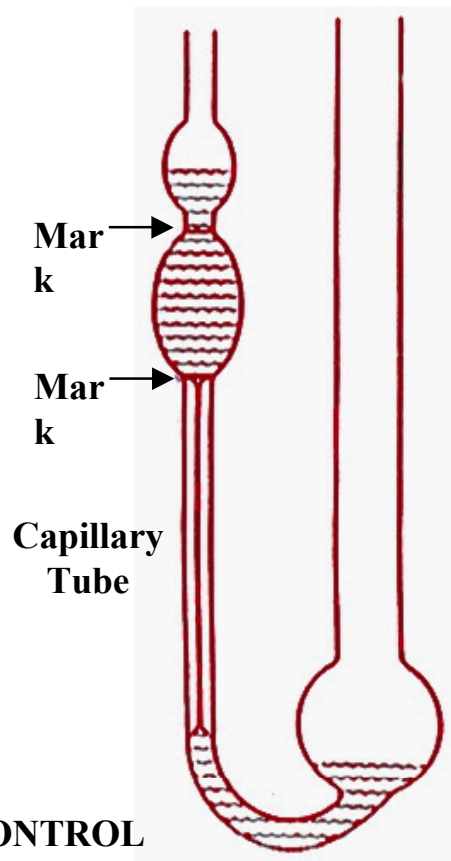
CONTROL TEMPERATURE

OSTWALD VISCOMETER. Time "*t*" is measured for fluid to flow out of upper bulb (between marks).

$$\lim_{c \to 0} \frac{\eta_{sp}}{c} = [\eta]$$

Endgroup Analysis As a Methodology for Measuring the Number Average Molecular Weight (M̄n)

How many endgroups per chain?

Limited to < ≈ 50,000 g/mole

C = O
  OH

C = O
  OH

OH

C = O
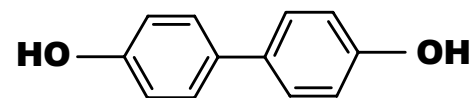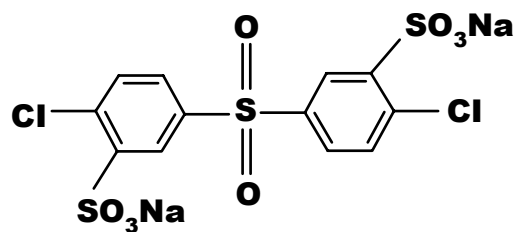 OH
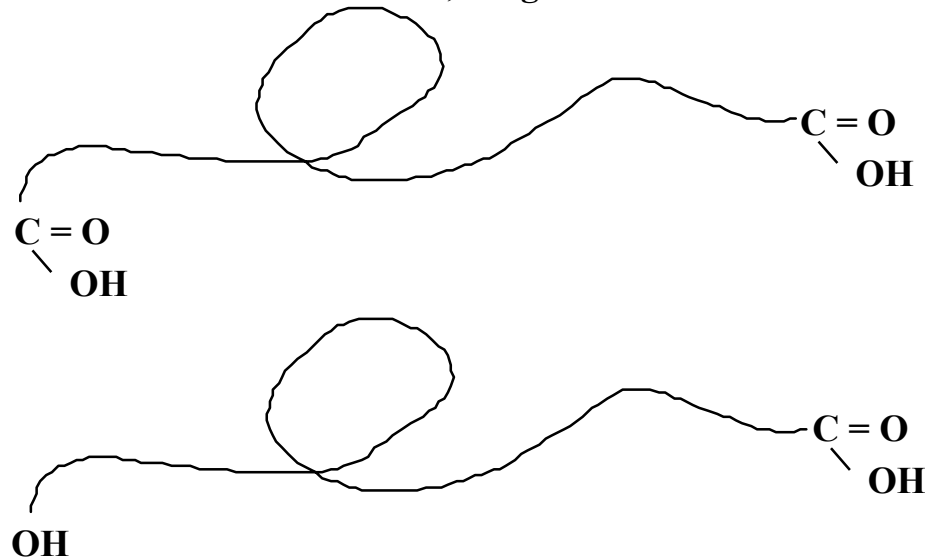
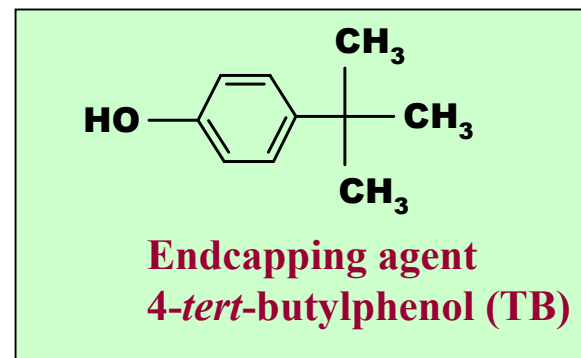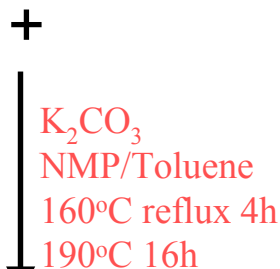# Synthesis of Tert-butylphenol Terminated Poly(arylene ether sulfone)s Containing Sulfonate Groups
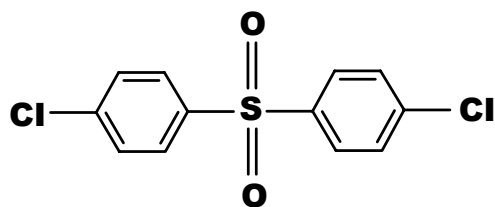
4,4'-dichlorodiphenylsulfone (DCDPS)

Biphenol (BP)
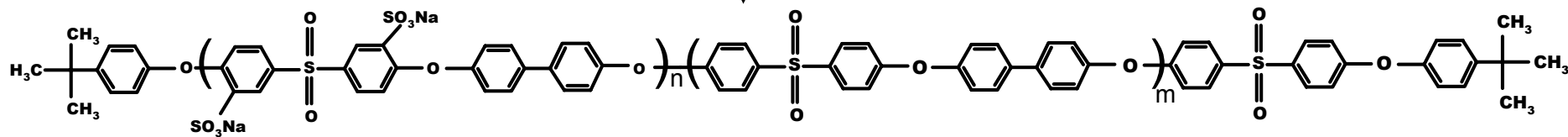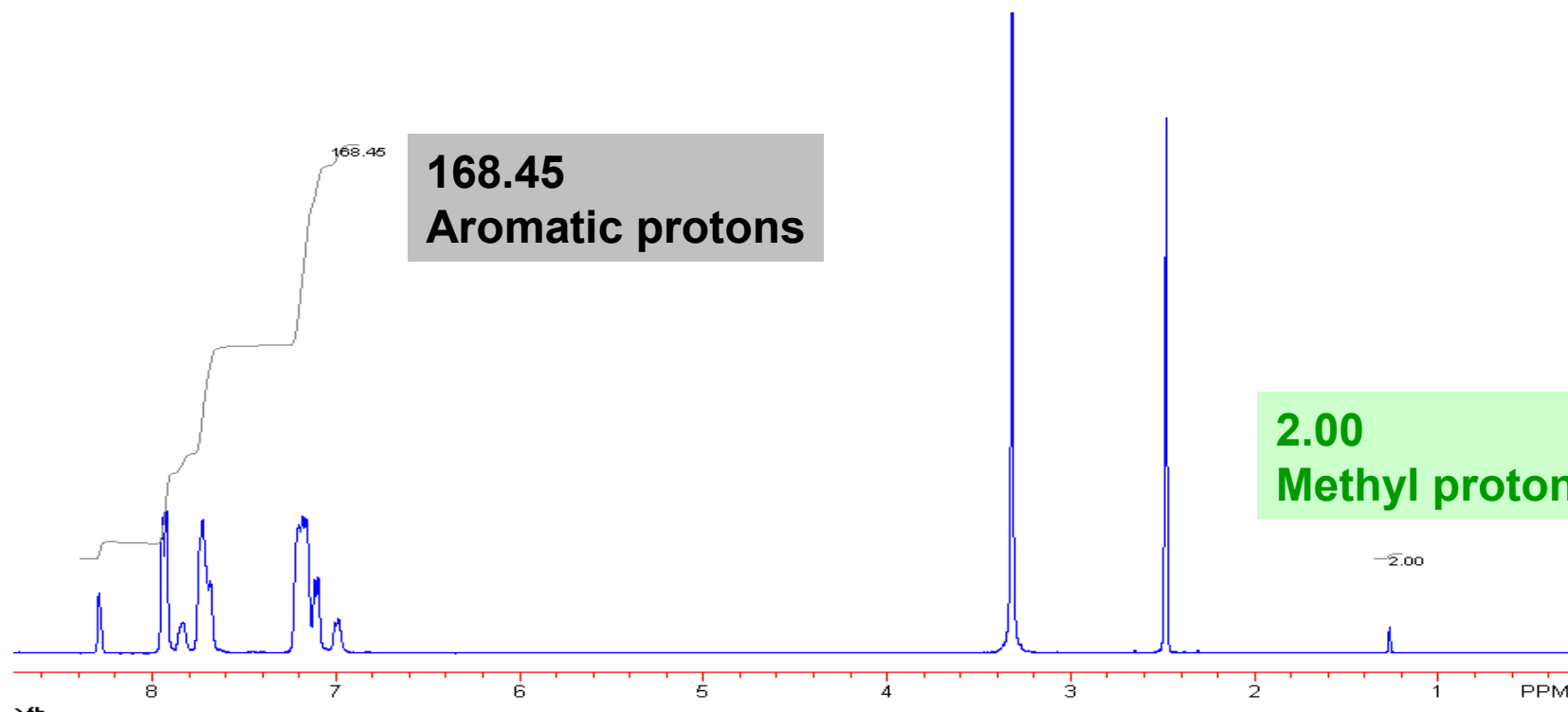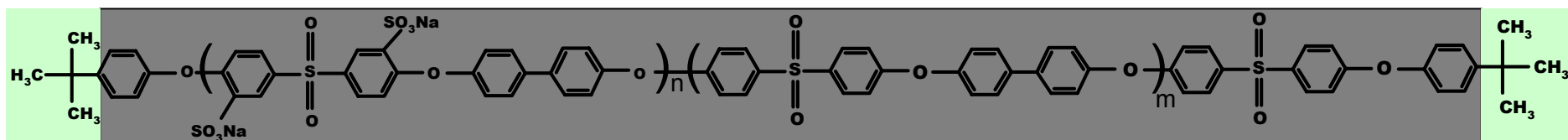
3,3'-disulfonated 4,4'-dichlorodiphenylsulfone (SDCDPS)

K_2CO_3
NMP/Toluene
160°C reflux 4h
190°C 16h

Endcapping agent
4-*tert*-butylphenol (TB)

m/n = 65/35

BPS35_20K, BPS35_40K, BPS35_50K

Ref. Wang, F; McGrath, J. E., *Polymer Preprints* 2002, 43(1), 492

# ¹H NMR Spectrum of BPS35_50K Polymer

168.45
Aromatic protons

2.00
Methyl protons

Molecular Weight Calculations of BPS35_50K Polymer
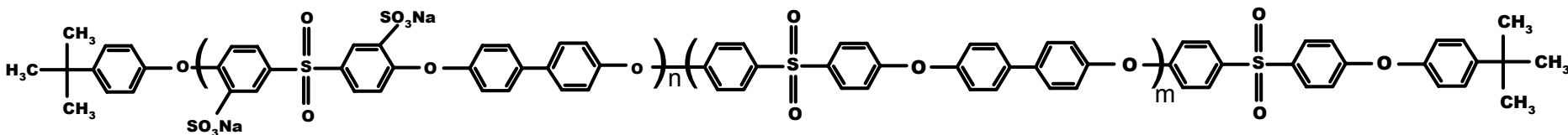
➢ **The average MW per repeating unit: 400*0.65+604*0.35=471.8**

➢ **18 methyl protons on the two end *tert*-butyl groups**

➢ **Average protons per repeating unit: 16*0.65+14*0.35=13.585**

➢ **# of protons attached on the terminal phenyl rings: 8+8*0.65+6*0.35=15.3**

➢ **Therefore,** $\dfrac{13.585 * k + 15.3}{18} = \dfrac{168.45}{2}$ ⟶ Aromatic protons

⟶ Methyl protons

   (k: number of repeating unit)

   # of repeat unit k was calculated to be 110.47

➢**Mn=471.8*110.47+ 2endgroups= 52119.6+601.4=52721**

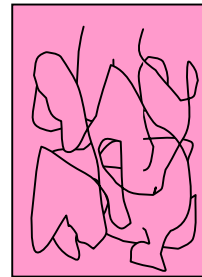# Comparison of Neutral and Charged Macromolecules
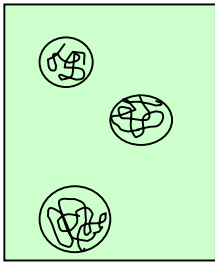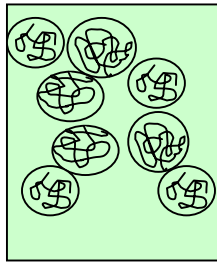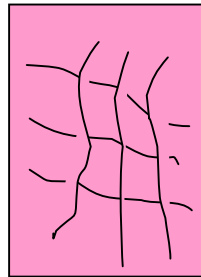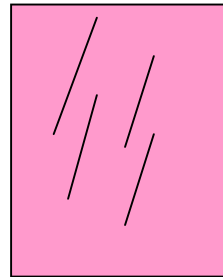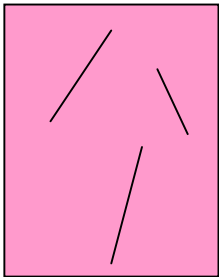
$c < c^*$ $c = c^*$ $c^* < c < c^{**}$ $c = c^{**}$

Neutral macromolecules keep the coil conformation, even below the overlap concentration.

Charged macromolecules strongly extend with dilution due to the mutual repulsion of the charges on the polymer backbone.

Ref. Schmidt, M., Polyelectrolytes with Defined Molecular Architecture, *Advances in Polymer Sciences*, 2004
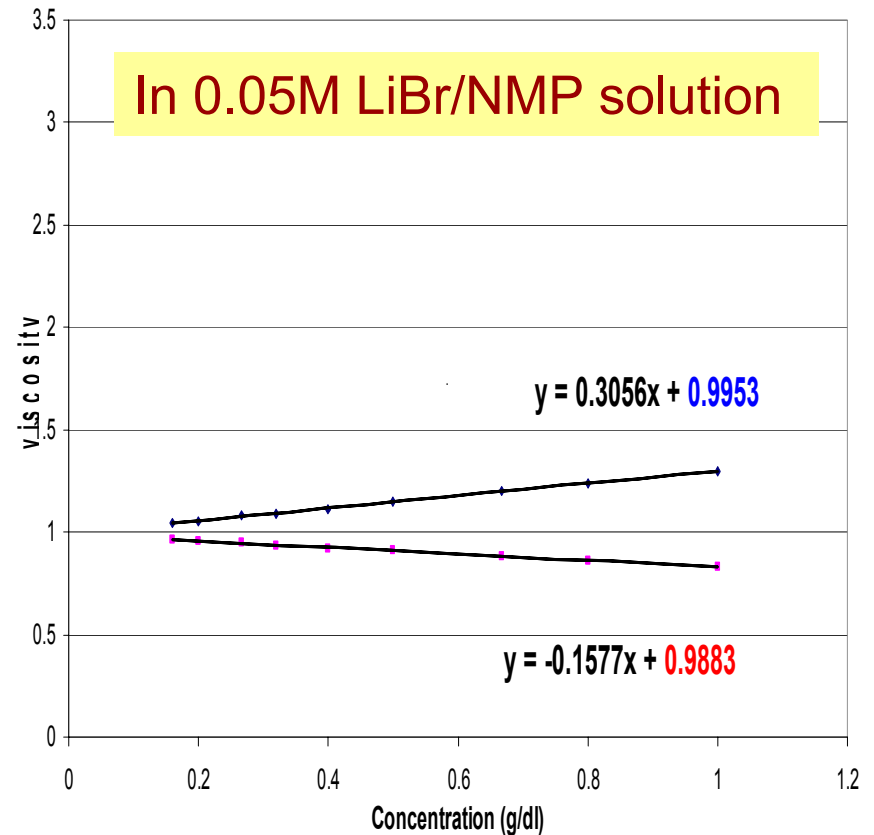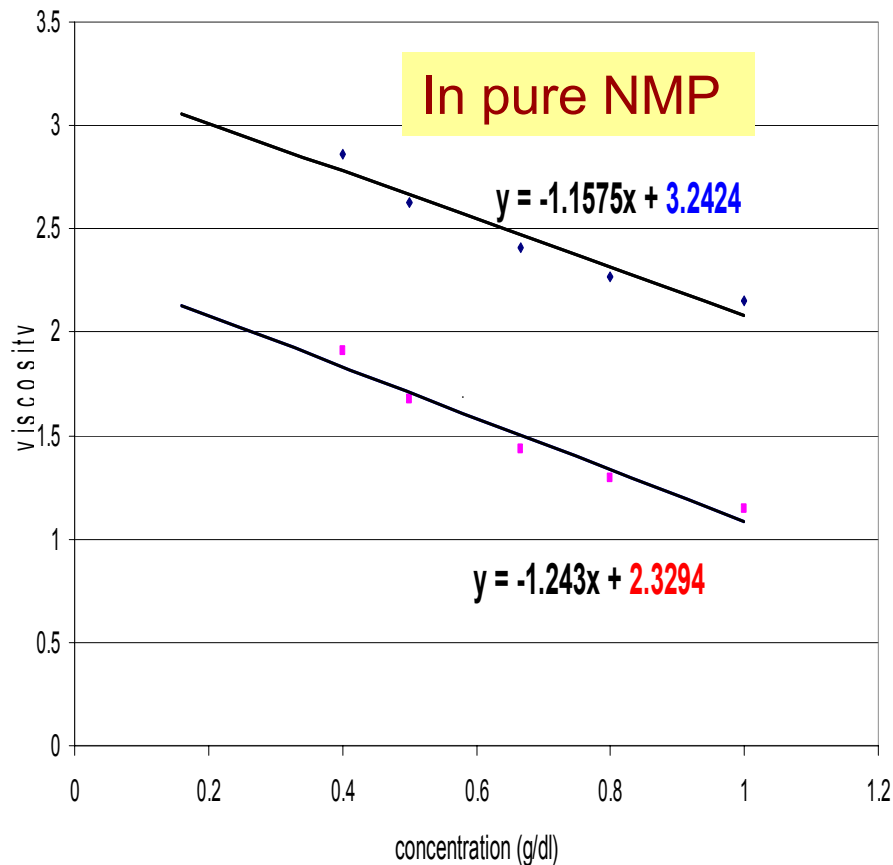
How to Perform Dilution Viscometry with Polyelectrolytes?

❖ **The measurements have to be performed in presence of low molar mass salt to screen the charges.**

❖ **The optimum salt concentration may depend on**
   the chemical structure
   the molar mass range
   the charge density

Measurement of Intrinsic Viscosity
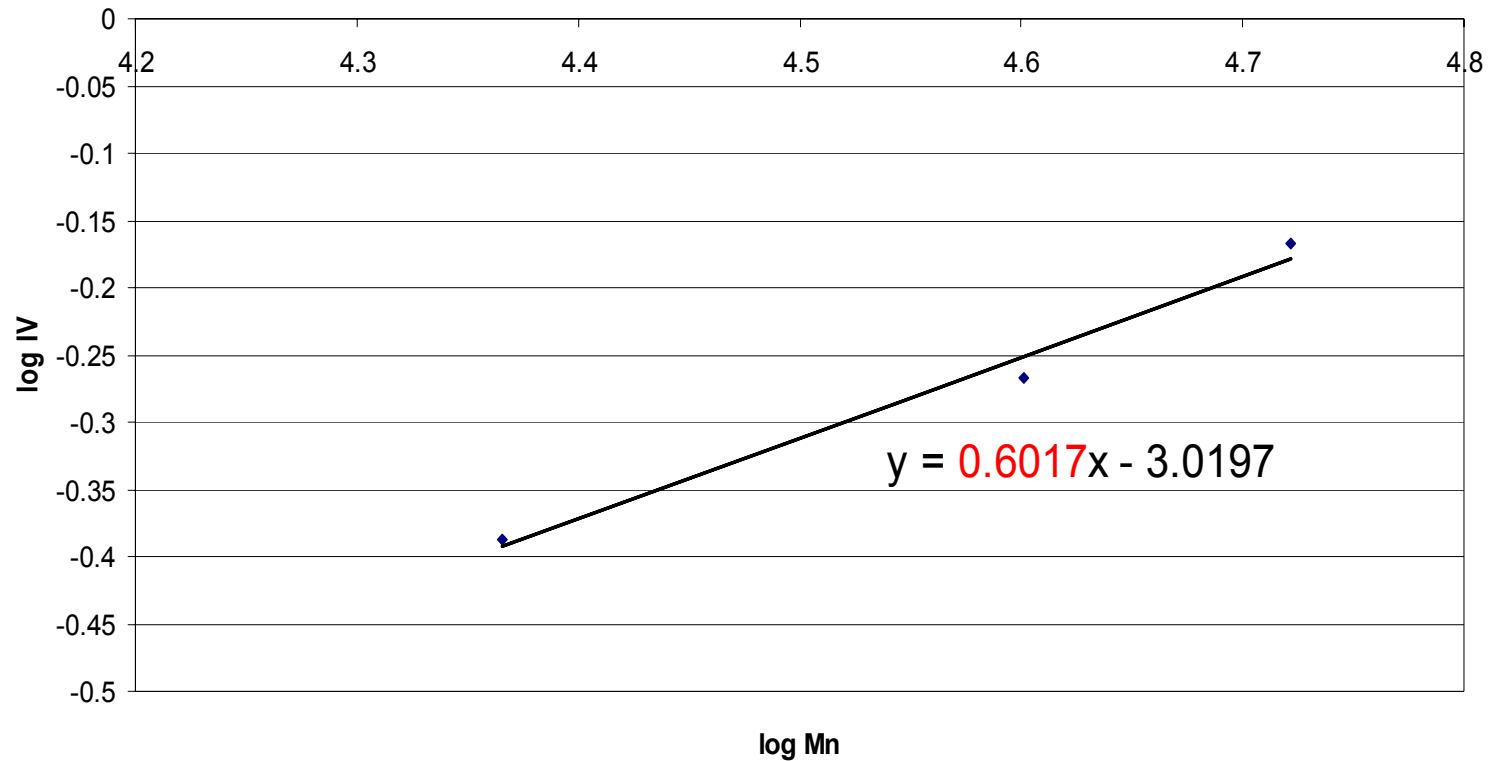
Sample: hydroxyl functional BPS35   Temp: 25°C

In pure NMP

$y = -1.1575x + 3.2424$

$y = -1.243x + 2.3294$

In 0.05M LiBr/NMP solution

$y = 0.3056x + 0.9953$

$y = -0.1577x + 0.9883$

viscosity

concentration (g/dl)

Concentration (g/dl)

How do Intrinsic Viscosity Results Compare with NMR Results

Polymer	$[\eta]$ (0.05M LiBr/NMP) at 25°C (dL/g)	Mn by NMR (kg/mol)
BPS35_20K	0.41	23.2
BPS35_40K	0.54	39.9
BPS35_50K	0.68	52.7

❖ The molecular weight of endcapped copolymers determined from ^{1}H NMR spectra was consistent with the theoretical values.

❖ The intrinsic viscosity result was also in agreement with the NMR results. These endcapped copolymers could serve as the broad standards for the future GPC measurements.

Log IV vs log Mn Plot

$y = 0.6017x - 3.0197$

Continue….

BPS35_hydrosize*
pure NMP

$y = -0.1416x + 0.6273$

$y = -0.1983x + 0.591$

BPS35_20K
pure NMP

$y = -0.2542x + 0.9425$

$y = -0.3371x + 0.8544$

BPS35_40K
pure NMP

$y = -0.3974x + 1.342$

$y = -0.5098x + 1.163$

BPS35_50K
pure NMP

$y = -0.6521x + 1.9008$

$y = -0.7561x + 1.5464$

BPS35_hydrosize*
0.05M LiBr/NMP

$y = 0.032x + 0.3265$

$y = -0.005x + 0.328$

BPS35_20K
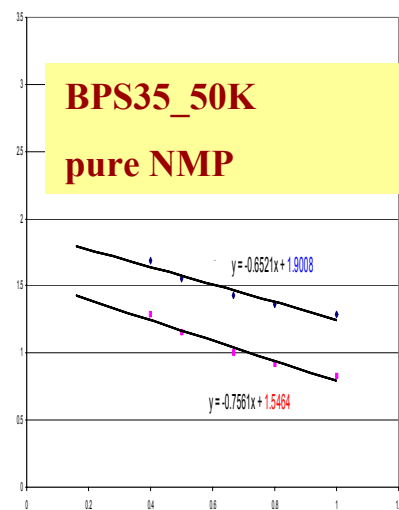0.05M LiBr/NMP

$y = 0.0588x + 0.425$

$y = -0.0299x + 0.4244$

BPS35_40K
0.05M LiBr/NMP

$y = 0.1191x + 0.537$

$y = -0.035x + 0.5396$

BPS35_50K
0.05M LiBr/NMP

$y = 0.1284x + 0.6833$

$y = -0.083x + 0.6766$
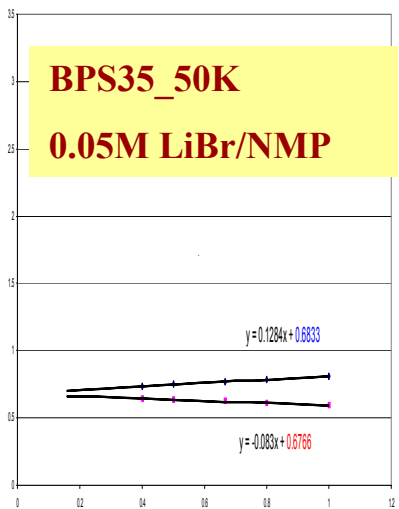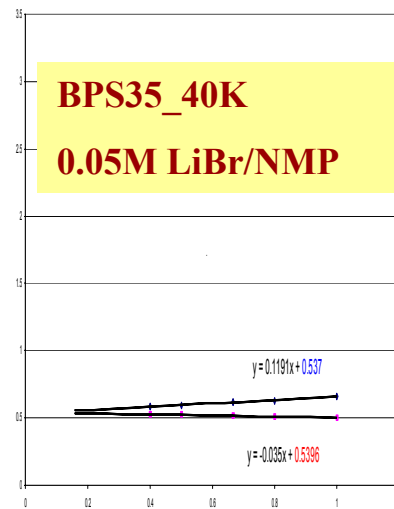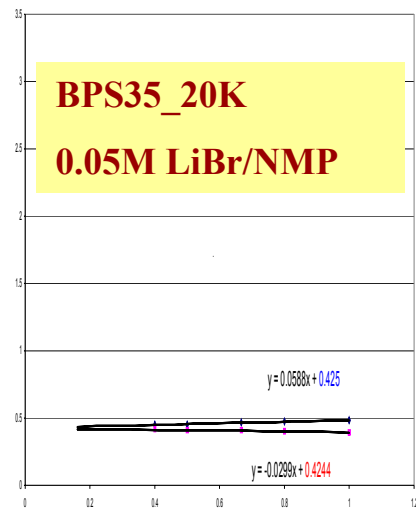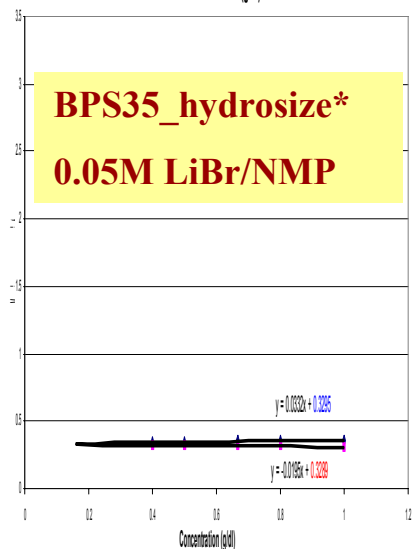
Summary of Intrinsic Viscosity Measurements

Polymer	$[\eta]$ (NMP) at 25°C (dL/g)	$[\eta]$ (0.05M LiBr/NMP) at 25°C (dL/g)	$[\ ]$ (NMP) / $[\eta]$ (0.05M LiBr/NMP)
BPS35_hydrosize	0.61	0.33	0.61/0.33=1.85
BPS35_20K	0.9	0.41	0.9/0.41=2.2
BPS35_40K	1.25	0.54	1.25/0.54=2.31
BPS35_50K	1.72	0.68	1.72/0.68=2.53
Non-endcapped	2.79	0.99	2.79/0.99=2.82

❖ Poly(arylene ether sulfone) copolymers tend to exhibit rigid chain structure due to the high content of charges on the polymer backbone. Addition of salt could alter the chain flexibility and conformation of the polymer and lead to the reduction in the viscosity.

❖ With the increase of the molecular weight, the contrast between intrinsic viscosity measurements in two different solvents increases.

Conclusions

❖ *Tert*-butylphenyl terminated sulfonated poly(arylene ether sulfone) copolymers with different molecular weight were successfully prepared by di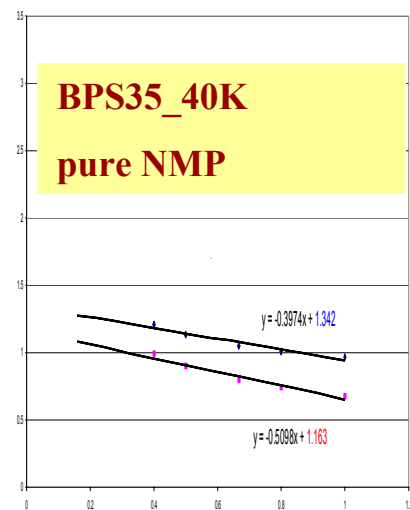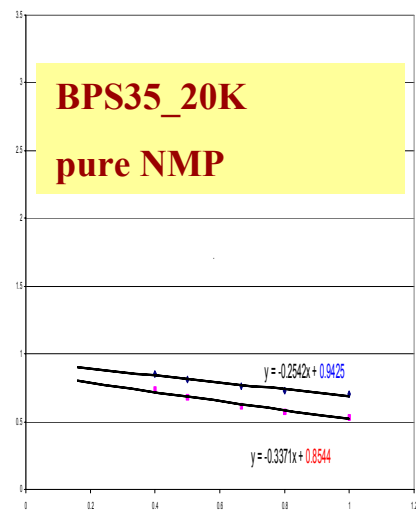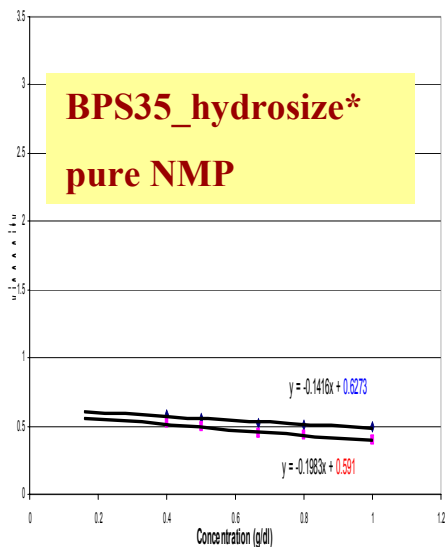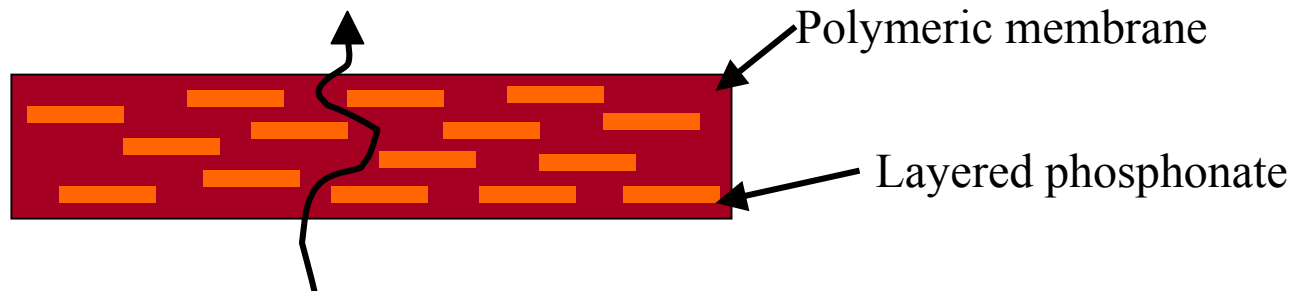rect polymerization of the activated halides, biphenol and the endcap, 4-tert-butylphenol. The molecular weight determined from ^{1}H NMR spectra was consistent with the theoretical values.

❖ Intrinsic viscosity measurements were conducted in 0.05M LiBr/NMP solution. The salt (LiBr) was used to shield the polyions from intramolecular expansion and afforded linear plots. The intrinsic viscosity increases with the molecular weight, as expected.

❖ Combining endcapping, proton NMR analysis and intrinsic viscosity measurement, we have demonstrated a powerful tool in characterizing molecular weight of sulfonated poly(arylene ether sulfone)s that could be used as proton exchange membranes in fuel cells.

❖ Future research will initiate studies on universal calibrated size exclusion chromotography (SEC).

❖Block copolymers containing hydrophilic and hydrophobic sequences may have promise in developing protonic conductivity at low humidity. Further work is in progress.

Motivation for Incorporating Inorganic Additives into PEMs

- Increased conductivity, especially at elevated temperatures

- Ease of fabrication (straightforward synthesis)

- Low extraction (not water soluble in most cases)

- Improved mechanical properties

- Lower water uptake/methanol permeability

- Possibility of layered structures

Polymeric membrane

Layered phosphonate

G. Alberti and M. Casciola, "Composite Membranes for Medium-Temperature PEM Fuel Cells," *Annu. Rev. Mater. Res.*, 33 (2003) 129.

Future Research

- Further characterization of ZrPP/BPSH composites (morphology, methanol permeability, high temperature/low humidity studies).

- Collaboration with Dr. G. Alberti (University of Perugia, Italy) on new, more conductive composites.

Use of precursor solutions of phosphonates in the preparation of hybrid ionomeric-membranes

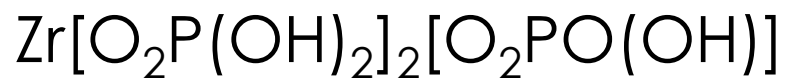Precursor solution of zirconium phosphate-phosphonate

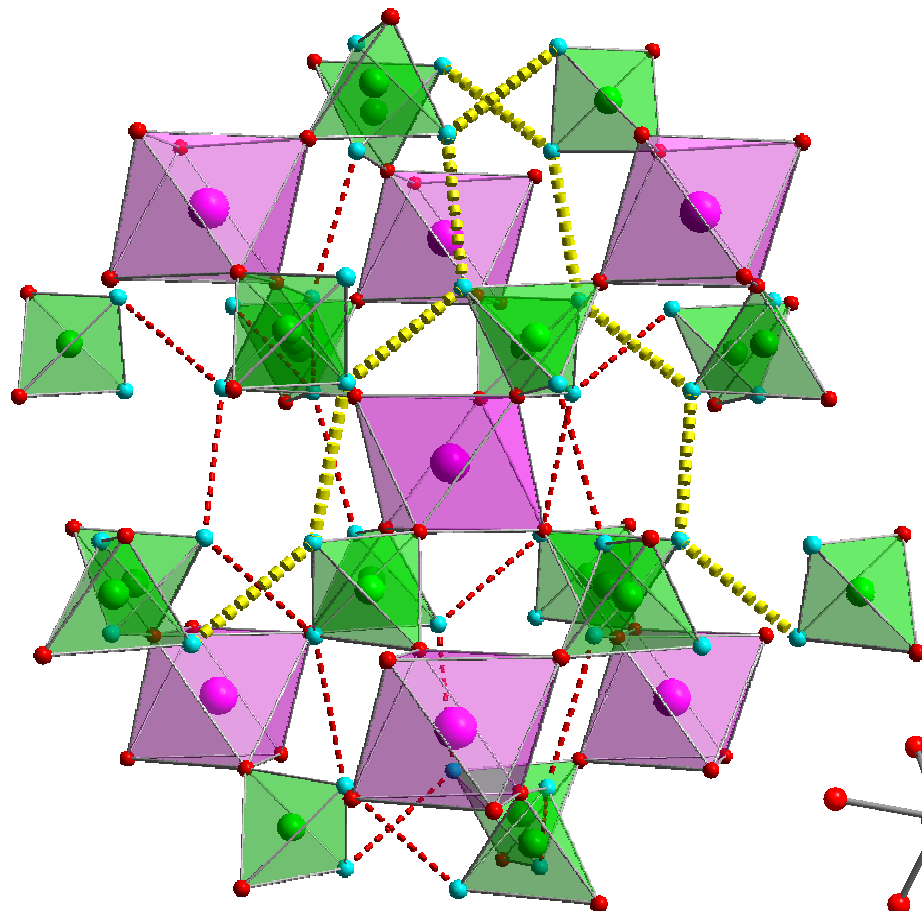Proton conductor ionomer in organic solvent

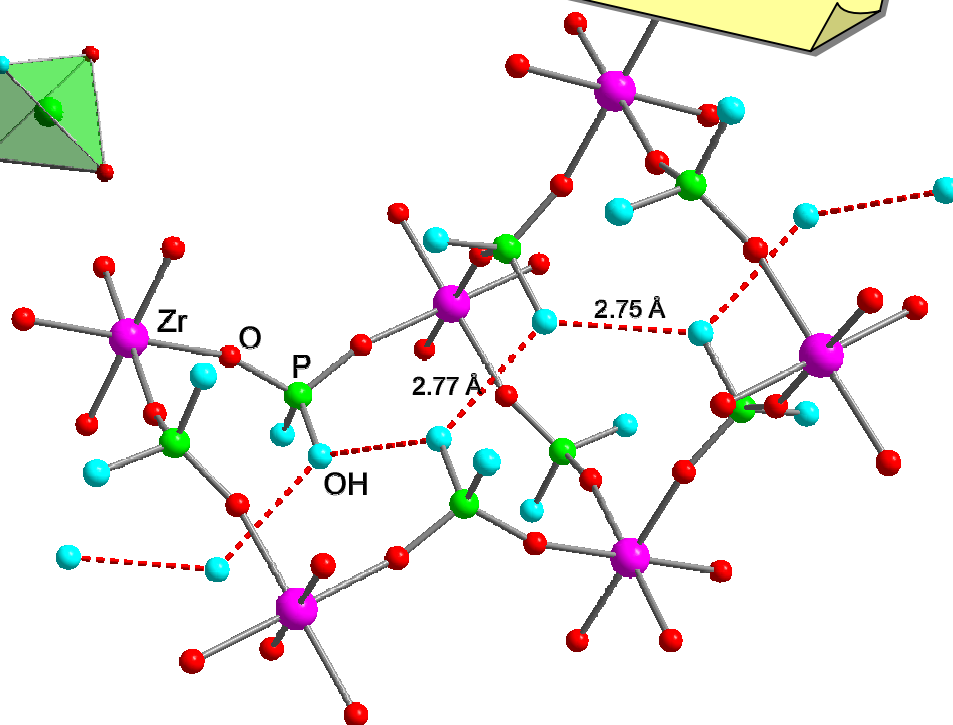Mixed solution

Casting and drying

Hybrid membrane

**Reference: Ongoing research by Dr. G. Alberti, University of Perugia, Italy

Zr[O₂P(OH)₂]₂[O₂PO(OH)]   (ZrP3)

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