

DOE Hydrogen Program  
Poly(p-phenylene Sulfonic Acid)s with Frozen-in Free  
Volume for use in High Temperature Fuel Cells

Morton Litt and Peter Pintauro, P. I.s

Casey Check, Dahuan Dong (Grad Students), Ryszard Wycisk  
(Research Associate), Yuyan Shao and Kun Si (Post-Doctoral  
Fellows)

Case Western Reserve University  
Cleveland, Ohio

5/16/2007

This presentation does not contain any proprietary, confidential, or otherwise restricted information

# Overview

## Timeline

- Start date 4/15/2006
- End date 4/15/2011
- Percent complete 15%

## Budget

- Total project funding
  - DOE \$1,492,572
  - Contractor \$530,569
- Funding received in FY06, \$150,000
- Funding for FY07, \$250,000

## Barriers

- High conductivity at 80°C and <1.5KPa input water vapor pressure
- MEA mechanical and electrical stability in use at elevated temperatures.

## Interactions

Tom Zawodzinski,  
Robert Savinell  
Jesse Wainright

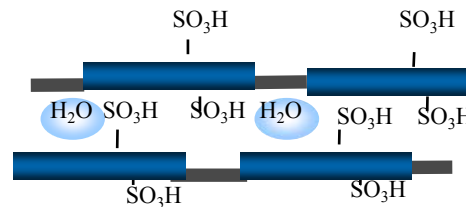
# Earlier Technical Accomplishments

- Frozen in Free Volume: Basic concept

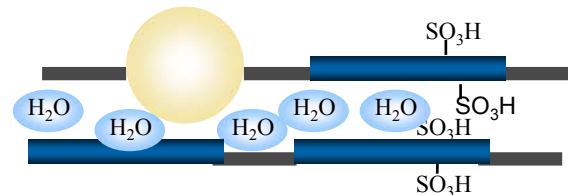
## Use rigid-rod liquid crystalline polymers.

A few bulky or angled comonomer units can force the chains apart over their whole length, creating permanent pores lined with  $\text{SO}_3\text{H}$  groups. The controlled architecture of these materials allows them to hold water very strongly, generating high conductivity even at low relative humidities.

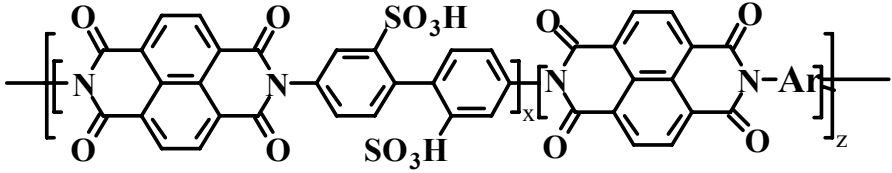
(a) Homopolymer. Complete collapse when dry.



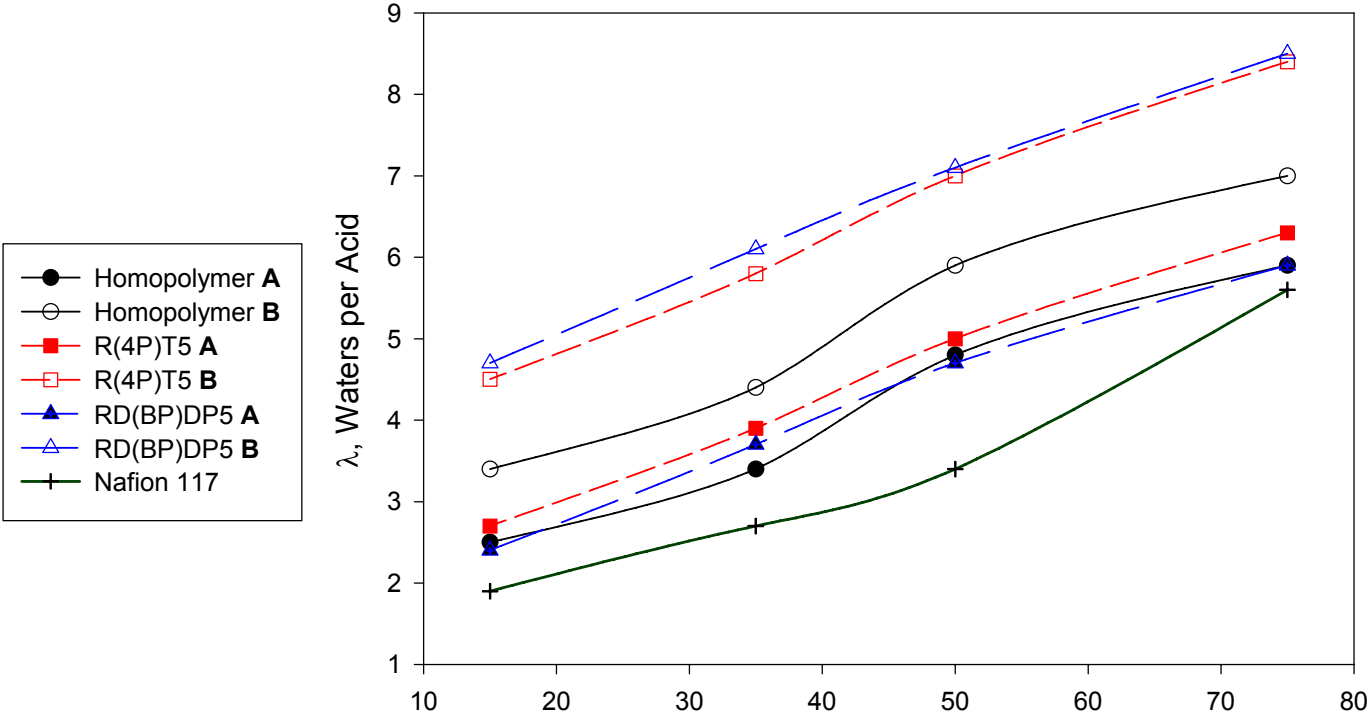
(b) Polymer with bulky comonomer. Chains kept apart.



# Polyimides: Water Retention as a Function of Drying Conditions



Effect of Drying Procedure on Retained Water



**A:** Polymer dried at **80°C** for **three days** under vacuum  
**B:** Polymer dried at **150°C** for **one hour** under vacuum.

- Homopolymer holds ~1 water after procedure **A** drying.
- Copolymers with only 5 mole% comonomer hold ~2 waters after procedure **A** drying.

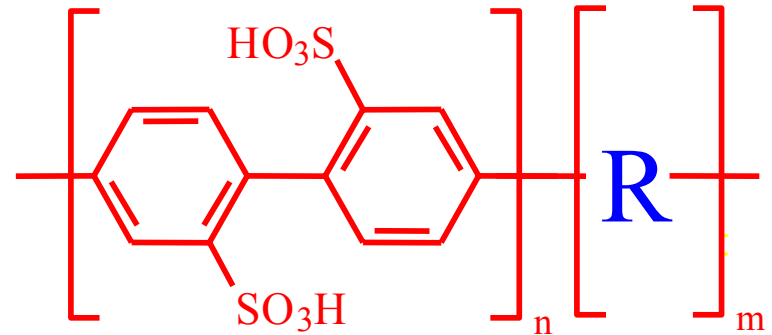
**• Problem: Polymers in acid form slowly hydrolyze. Cannot be used.**

# Poly (p-Phenylene Sulfonic acids\*)

## Objectives

**Obtain highly conductive, thermally and hydrolytically stable polymer electrolytes that retain conductivity over a wide range of relative humidities and temperatures.**

**Approach:** As before, use Rigid Rod, Liquid Crystalline polymers with the acid groups directly attached to the backbone. **Use poly(p-phenylene sulfonic acid); it cannot hydrolyze. Use bulky comonomers to generate free volume.**



R = bulky comonomer

Specific tasks:

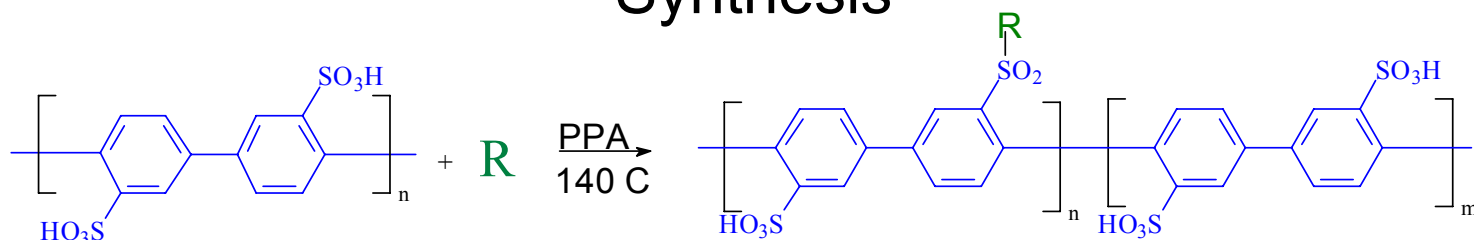
- 1.- Choice and optimization of an efficient, inexpensive polymerization approach.
- 2.-Comonomer synthesis and copolymerization.
- 3.- Structural characterization of the obtained materials.
- 4.- Evaluation of water absorption, proton conductivity, fuel permeability and thermal stability of the polymer membranes. Compare with existing PEMs.

\*Work from 2002 to 2005

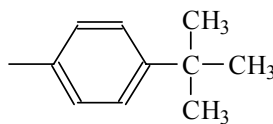
# Poly (p-Phenylene Sulfonic acids): Graft Copolymers

- Homopolymer water soluble.
- Comonomer synthesis difficult; only now accomplished.
- Most effort went into grafting groups on the sulfonic acids to make sulfones.
- Best results were achieved with grafted t-butyl substituted aromatics.

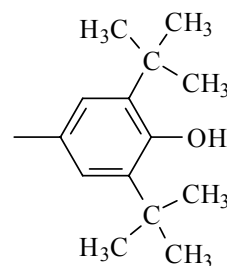
## Synthesis



Crosslinkable group

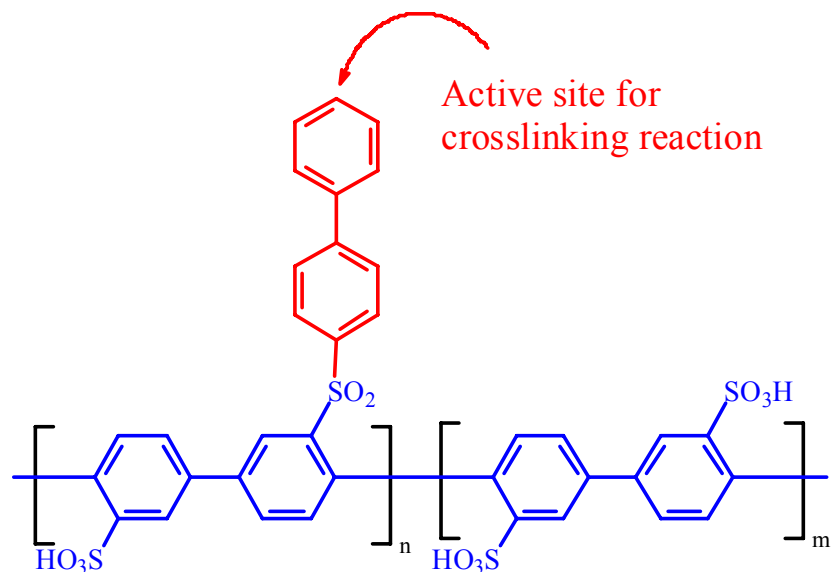


Bulky non-crosslinking, hydrophobic groups



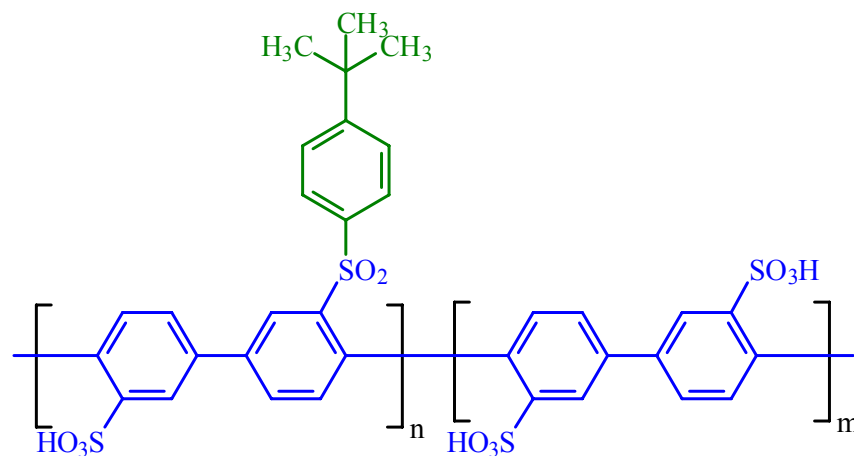
# Membrane Stabilization

Incorporation of cross-linkable biphenyl groups.



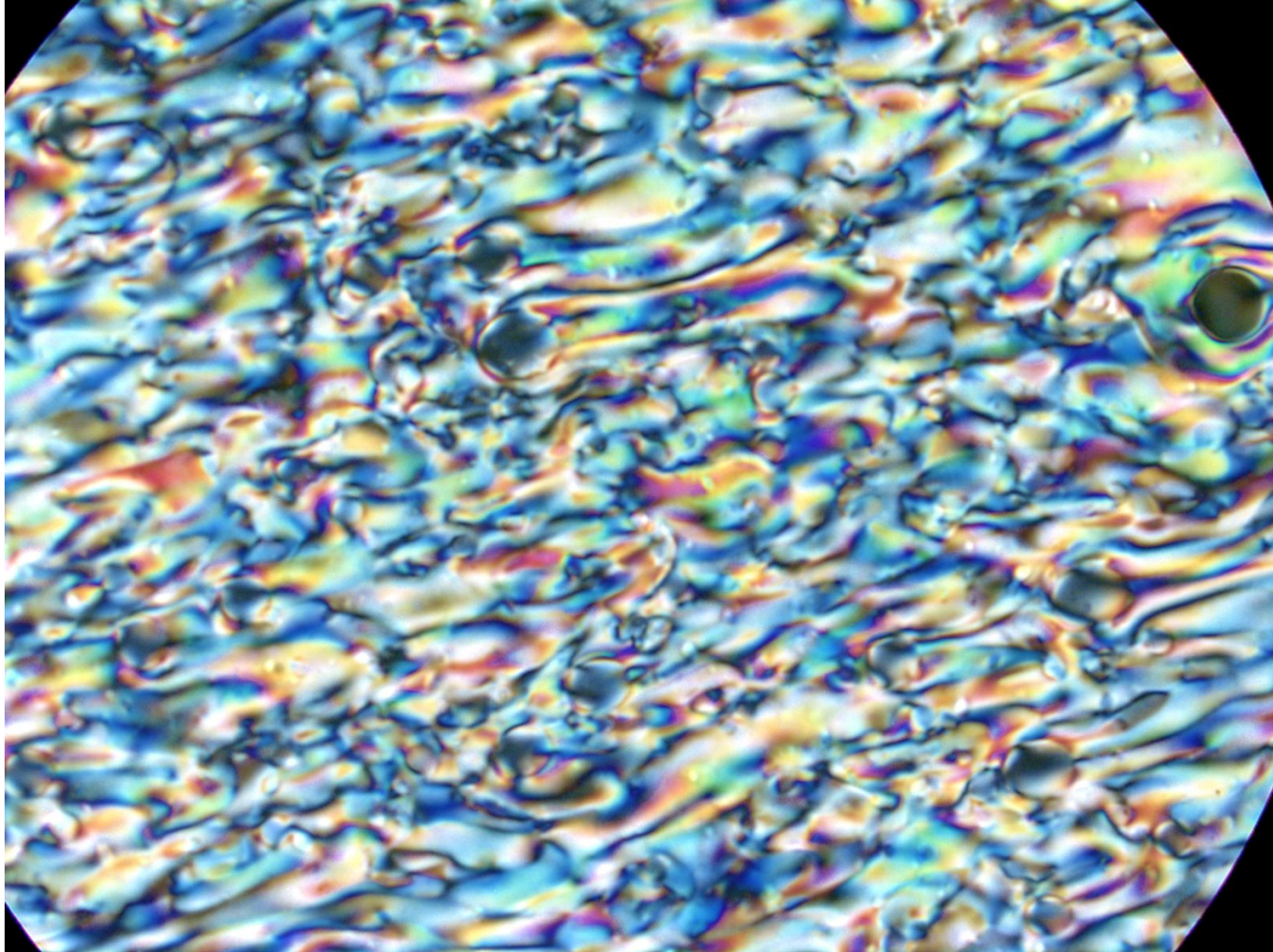
Copolymers containing from 5 to 20 mole% of biphenyl sulfone groups crosslink after 20 minutes at 200°C. Water soluble before crosslinking.

Incorporation of bulky tert-butyl benzene groups.



“5 mole%” of t-butyl benzene or 2,6-di-t-butyl phenol sulfone renders the copolymer water insoluble. t-Butyl groups scramble during grafting.

15% solution of PPSA in Water  
(0.3 M LiCl), after shearing (X500); typical nematic structure.





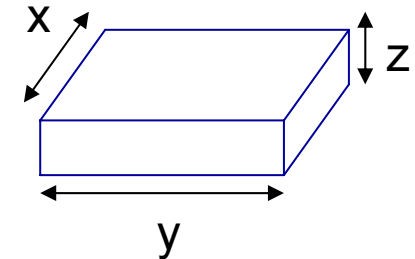
# Polymer swelling as a function of relative humidity

## Dimensional changes of copolymer films from 22% to 100% RH.

| Grafting group             | Mole % of t-butyl groups (Equiv. Wt.)** | $\Delta x$ (%) | $\Delta y$ (%) | $\Delta z$ (%) |
|----------------------------|---|----------------|----------------|----------------|
| Biphenyl*                  | 10                                      | 2              | 2              | 45             |
| Biphenyl*                  | 20                                      | 1              | 1              | 35             |
| Biphenyl*                  | 55                                      | ~0             | 1              | 15             |
| t-Butylbenzene             | 5                                       | 1              | 2              | 85             |
| t-Butylbenzene             | 25                                      | 1              | 1              | 50             |
| Di-t-butylphenol           | 5 (243 )                                | ~0             | ~0             | 50             |
| Di-t-butylphenol (batch 1) | 8 (260)                                 | ~0             | ~0             | 33             |
| Di-t-butylphenol (batch 2) | 10 (265)                                | ~0             | ~0             | 17             |
| Di-t-butylphenol (batch 3) | 8.4 (235)                               | ~0             | ~0             | 26             |
| Di-t-butylphenol (batch 4) | 8.4 (235)                               | ~0             | ~0             | 28             |
| Di-t-butylphenol           | 15 (270)                                | ~0             | ~0             | 15             |

\* After cross-linking, 10 min at 200°C

\*\* Equivalent Wt. homopolymer = 156

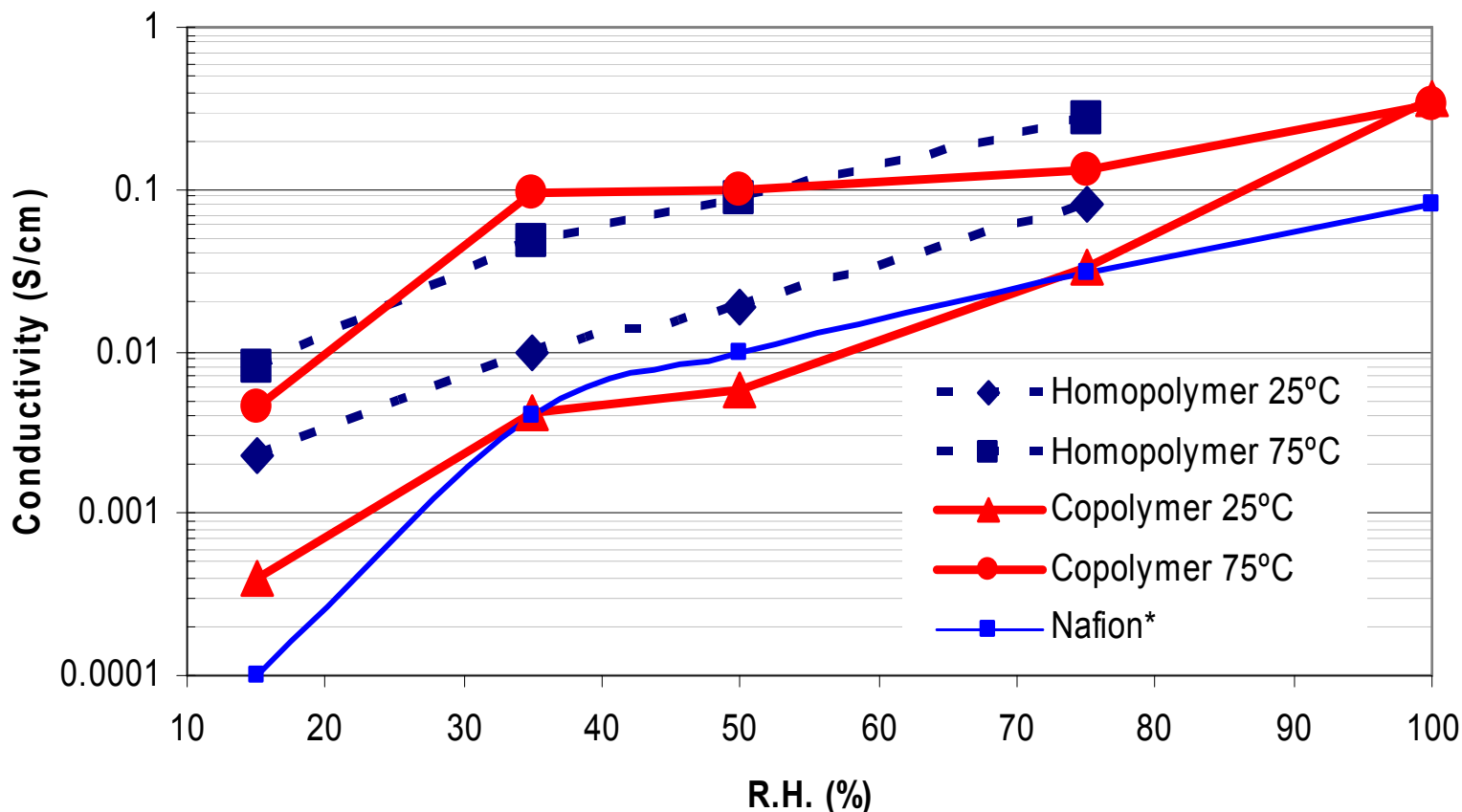


The **x** and **y** axes are parallel to the plane of the film. The **z** axis is perpendicular to the plane.

- Rigid rod polymer chains are parallel to the film surface. Swelling is only along the Z axis.
- The very hydrophobic t-butyl groups restrict swelling, probably by hydrophobic interactions.
- Two t-butyl groups per graft are much more effective than one.
- High conductivity despite low swelling

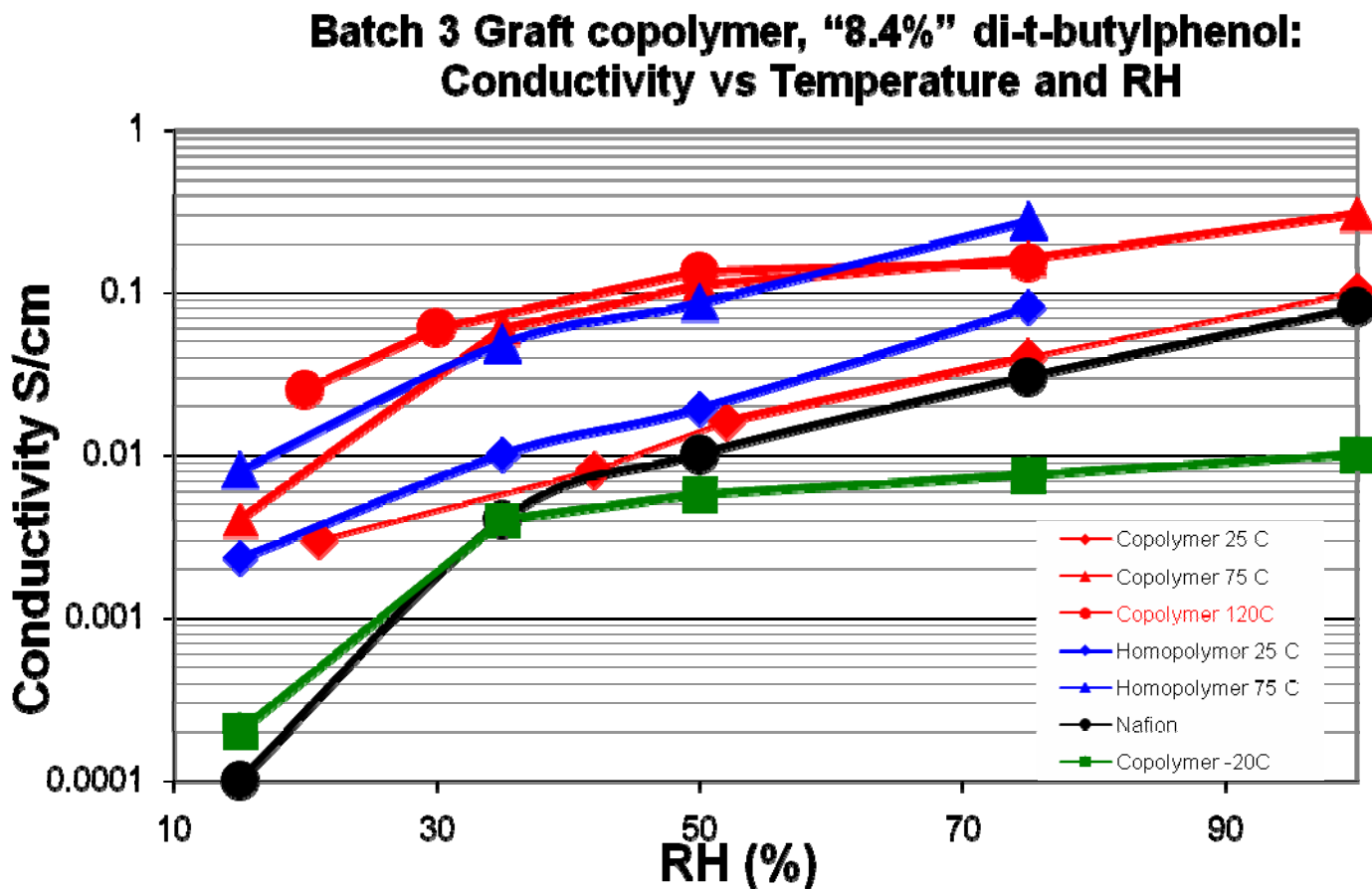
# Effect of temperature on conductivity of cross-linked graft polymer

## Crosslinked copolymer 10% biphenyl



Proton conductivity as a function of relative humidity and temperature for the cross-linked copolymer containing 10% biphenyl. PPSA and Nafion® are included for comparison. (Cross-linking conditions not properly controlled; film heterogeneity. Data from low swelling portion.)

# PPSA Graft Copolymers: Conductivity as a Function of Temperature and Relative Humidity



These early copolymers reach the DOE benchmarks for 2005. However, measurements were taken parallel to surface.

# Problems to be addressed

- Molecular Weight: Break elongation is poor. The best we have obtained is 8%.
- Graft Copolymer Synthesis: 1. The grafting reaction is heterogeneous; getting reproducible results is difficult. 2. The acid catalyzed grafting causes scrambling of the t-butyl groups. We do not have a simple material. Will shift to true random and block copolymers.
- Conductivity: This was measured parallel to the film surface. Since the film is anisotropic, through conductivity could be lower. The film morphology must be understood.
- Permeability: Liquid crystalline materials are highly impermeable to gasses. Will there be a cut-off at high current densities?
- Acid Loss: There is concern about sulfonic acid hydrolysis or decomposition at elevated temperatures. Will the membranes function for 5 years at 125 or 150°C?
- Oxidative Stability: Will non-fluorinated materials be oxidatively stable, or will they degrade at use temperatures?

# Work under present DOE Grant

## Polymer Synthesis:

With all new personnel, the work has gone relatively slowly. Homopolymer synthesis has reproduced earlier results but still with low molecular weight. We have recently found that Li salts of the polymer are soluble in NMP and DMF. See Table below. The polymer trimethyl benzyl ammonium salt made earlier is insoluble in NMP, the preferred polymerization solvent. We expect to make polymer with reasonable mechanical properties in the next few weeks.

## Grafting:

We have run one reaction on an early polymer batch, grafting di-*t* butyl phenol. The reaction was successful (next slide) – it reproduced the earlier structure - but the mechanical properties were too poor to cast films.

## Comonomer Synthesis:

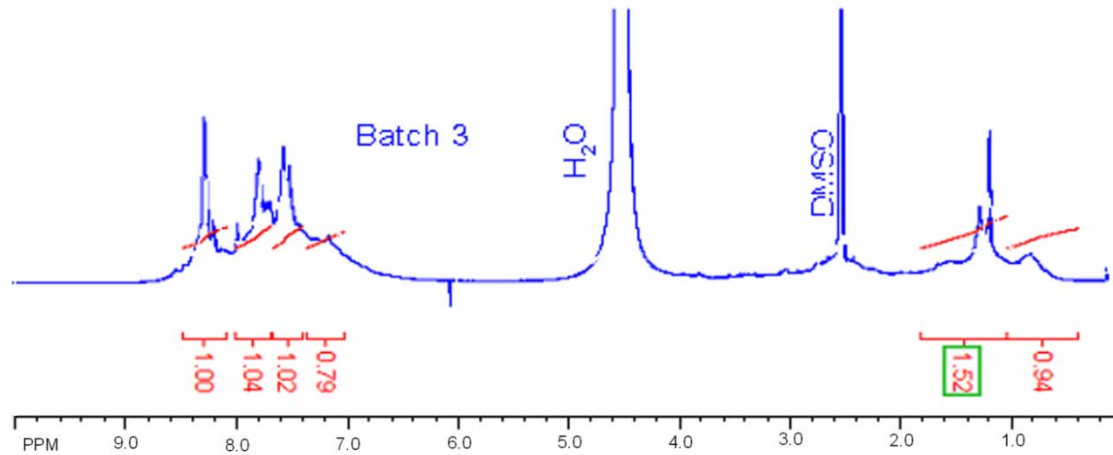
Many mild Friedel-Crafts catalysts have been tested using *p*-toluene sulfonyl chloride as a surrogate for the monomer acid chloride. Recent literature suggests that Zinc (or Zinc Oxide) is a possible candidate. We have grafted biphenyl in high yield using mild conditions, but have not yet grafted *t*-butyl or neopentyl substituted aromatic moieties without some scrambling. However, even a bis-biphenyl sulfone comonomer should produce water insoluble copolymers without crosslinking, and crosslinking is always an option.

# Effect of counterion on monomer and polymer solubility

Table 1. Solubility of three different ionic forms of the monomer (M) and the polymer (P) (BTMA, Li and Cs) in two solvents (NMP and DMF). The solubility was not visibly influenced by temperature in 25-90°C range. 1=insoluble and 5=perfectly soluble (no turbidity or sediment).

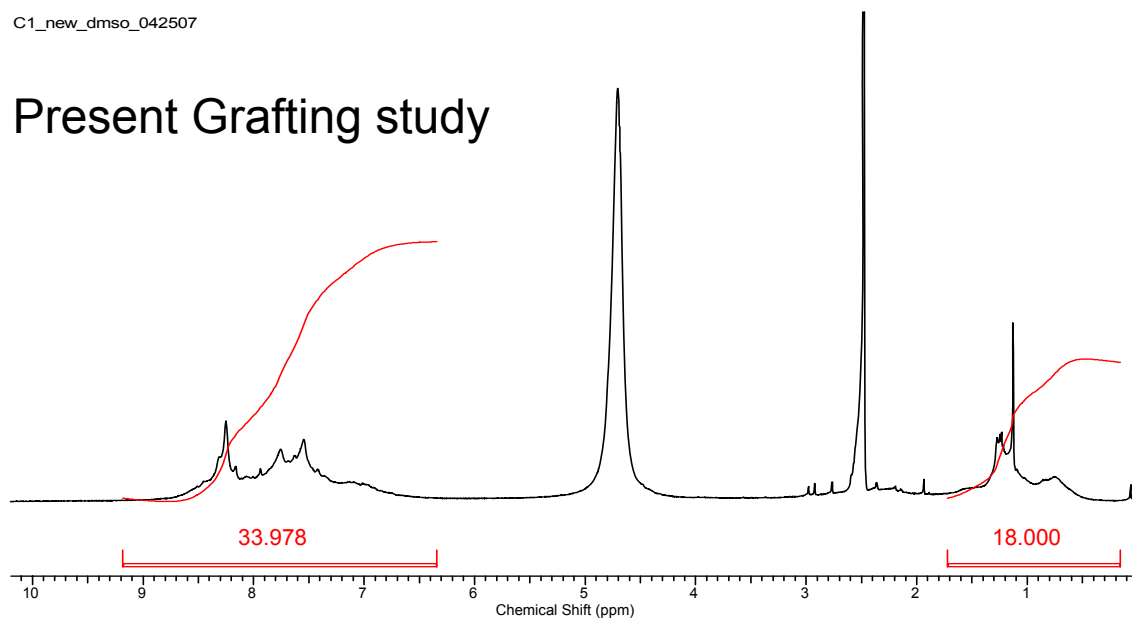
| Solute | Solvent    | 10 wt.%  | 5.0 wt.% | 2.5 wt.% | 1.25 wt.% | 0.62 wt.% |
|--------|------------|----------|----------|----------|-----------|-----------|
| M-BTMA | <i>NMP</i> | <b>2</b> | <b>3</b> | <b>4</b> | <b>5</b>  | <b>5</b>  |
| P-BTMA |            | 1        | 1        | 1        | 1         | 1         |
| M-Li   |            | <b>1</b> | <b>2</b> | <b>3</b> | <b>4</b>  | <b>4+</b> |
| P-Li   |            | <b>1</b> | <b>1</b> | <b>2</b> | <b>3</b>  | <b>4</b>  |
| M-Cs   |            | <b>1</b> | <b>1</b> | <b>1</b> | <b>1</b>  | <b>1</b>  |
| P-Cs   |            | <b>1</b> | <b>1</b> | <b>1</b> | <b>1</b>  | <b>1</b>  |
| M-BTMA | <i>DMF</i> | -        | <b>3</b> | <b>4</b> | <b>4</b>  | <b>5-</b> |
| P-BTMA |            |          | 1        | 1        | 1         | 1         |
| M-Li   |            | -        | <b>2</b> | <b>2</b> | <b>3</b>  | <b>4+</b> |
| P-Li   |            | -        | <b>2</b> | <b>2</b> | <b>3</b>  | <b>4+</b> |
| M-Cs   |            | -        | <b>1</b> | <b>1</b> | <b>1</b>  | <b>1</b>  |
| P-Cs   |            | -        | <b>1</b> | <b>1</b> | <b>1</b>  | <b>1</b>  |

# Replication of di-t-butyl phenol grafting : comparison of new material to earlier synthesis.



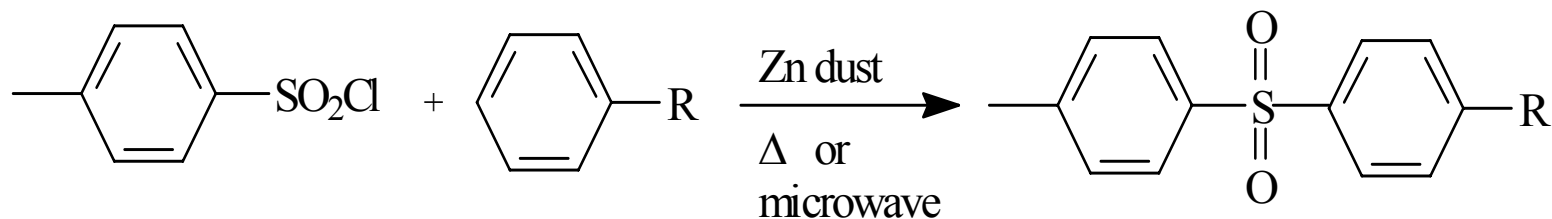
C1\_new\_dms0\_042507

## Present Grafting study



Spectra are very similar. T-butyl scrambling is minimized compared to other grafting procedures.

# Comonomer Synthesis



R=

-CH<sub>3</sub>

-C<sub>6</sub>H<sub>5</sub>

-CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>

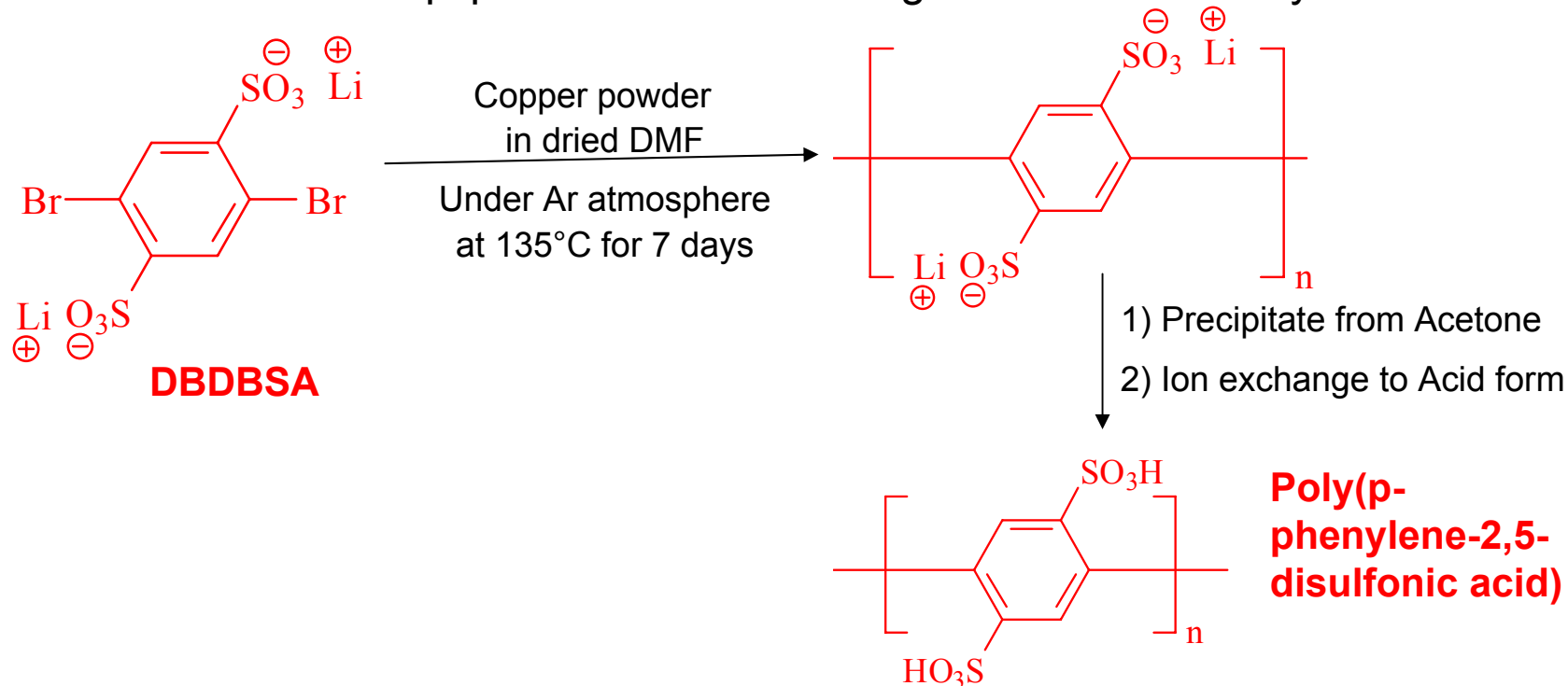
Reaction works well with toluene or biphenyl. There is some alkyl scrambling when neopentyl benzene is used, but the reaction seems to work. If zinc is a reagent, the reaction mechanism is unknown. I think this is a Friedel-Crafts reaction and the catalyst is zinc oxide; we are currently testing this.

Bandgar, B. P. and Kasture, S. P., *Synthetic Communications* 31(7), 1065-1068 (2001)



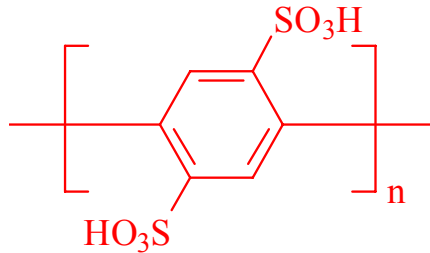
# Related work on poly(p-phenylene sulfonic acids); not DOE supported

We have been working on analogous materials as part of the general push. This work has progressed well but matured too late to be included in the DOE proposal. The student, Mr. J. W. Kong, is funded by his company, Samsung. The chemicals and equipment used were bought with DOE money.



**Very low equivalent weight rigid-rod sulfonic acid  
liquid crystalline polymer. Most recent run had  
reasonable mechanical properties.**

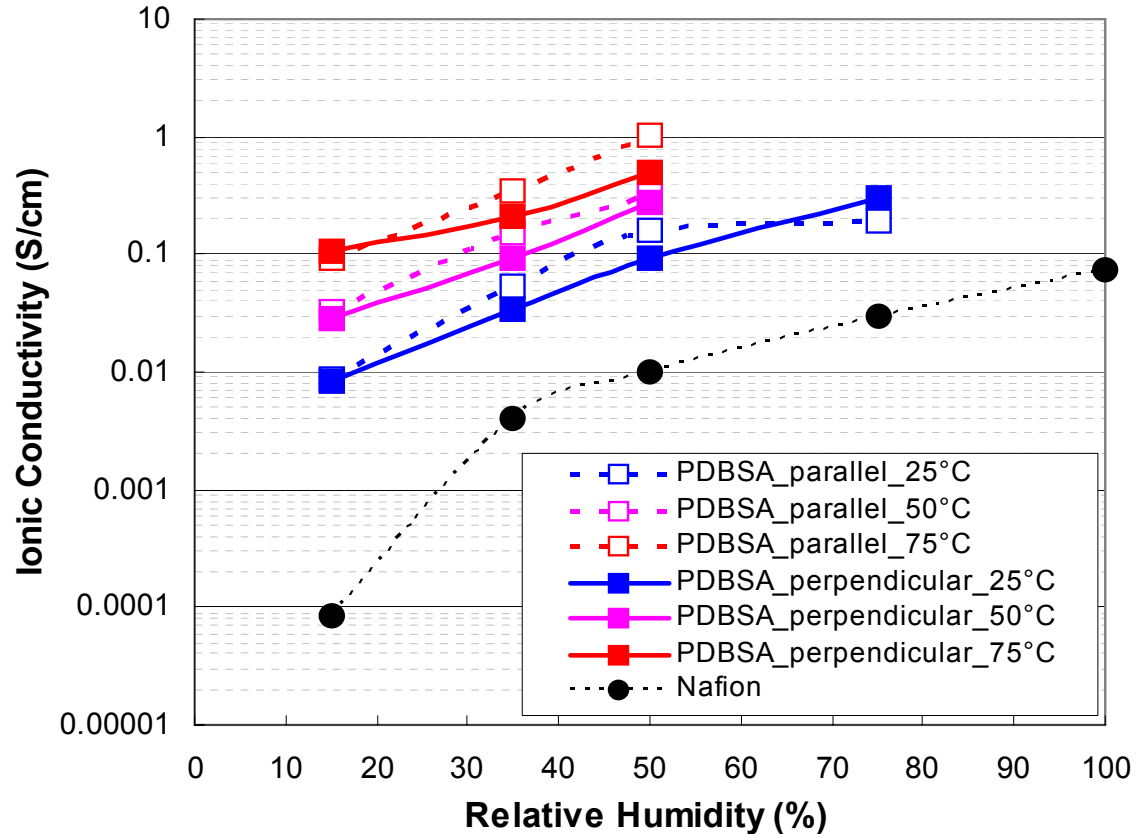
# Conductivity of PPDSA as a function of Temperature and RH.



1. At low humidity, (15%RH) and 75°C, PPDSA has a conductivity of **0.1 S/cm**, about 1000 times higher than that of Nafion.

2. Ionic conductivity is independent of x/y direction.

3. X-ray and swelling data imply that film is reasonably isotropic.



- at 15% RH and 25°C is ~4.3, vs. 1 for Nafion.
- Problem: homopolymer is water soluble. Will make copolymers.

# Conclusions

1. We have reproduced earlier work on grafting to the backbone.
2. Within the next few weeks, the project should be making materials for testing.
3. Synthesis conditions still need improvement to get higher molecular weight. A possible solution is to polymerize the monomer Li salt.
4. We have developed a synthesis route for some co-monomers. Copolymerization studies will start very soon.
5. Several requirements were not discussed in this report. The transverse conductivity, not measured, may be lower than the parallel conductivity. This is morphology and orientation dependent and we do not have full understanding of the polymer morphology. We must learn how to control morphology and orientation during casting.
6. Another, very promising, class of polyelectrolytes has been developed, PPDSA. As yet only the water soluble homopolymer has been made, but we expect to start making water insoluble copolymer soon. Conductivity could depend on morphology, but we have indirect evidence that there is no anisotropy in conductivity.

# Future Work

## **Near Term Work.**

1. Find best combination of solvent, counterion and temperature to produce high molecular weight polymer.
2. Make relatively large amount of graft copolymer for submission to Group 2 people.
3. Study the effect of casting procedures and solvents on morphology and conductivity of the grafted polymers. Submit preliminary casting procedures together with cast films to Group 2.
4. Start making random and block copolymers and study the relationship of block length and equivalent weight on morphology, conductivity, water retention and swelling.
5. Make larger quantities of the best materials for submission to the Phase 2 Group, both as powders and as cast films.

## **Longer term work.**

1. Make and study more comonomers.
2. Start work on film hydrolytic stability under fuel cell operating conditions.
3. Correlate copolymer film morphology quantitatively with water absorption and conductivity (measurement of frozen-in free volume). PPSA and PPDSA probably self-assemble differently.