

2006 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
Case Western Reserve University
Cleveland, Ohio

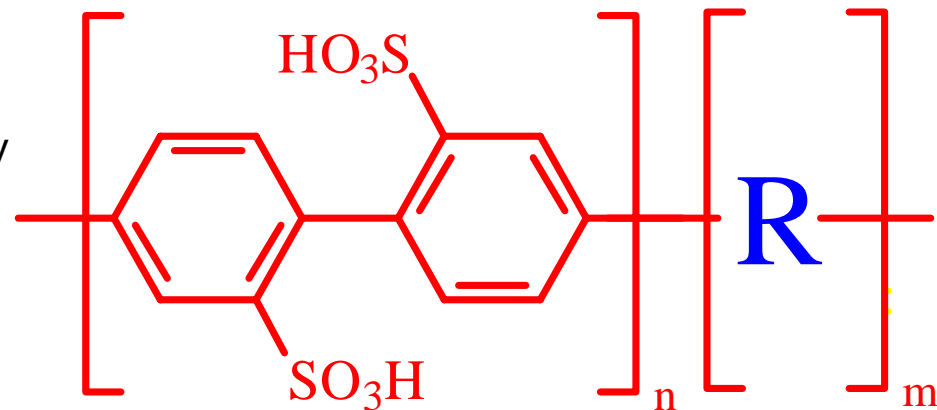
5/16/2006

Poly (p-Phenylene Sulfonic acids)

Main Goals

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 can't hydrolyze. Find inexpensive routes to the final materials.

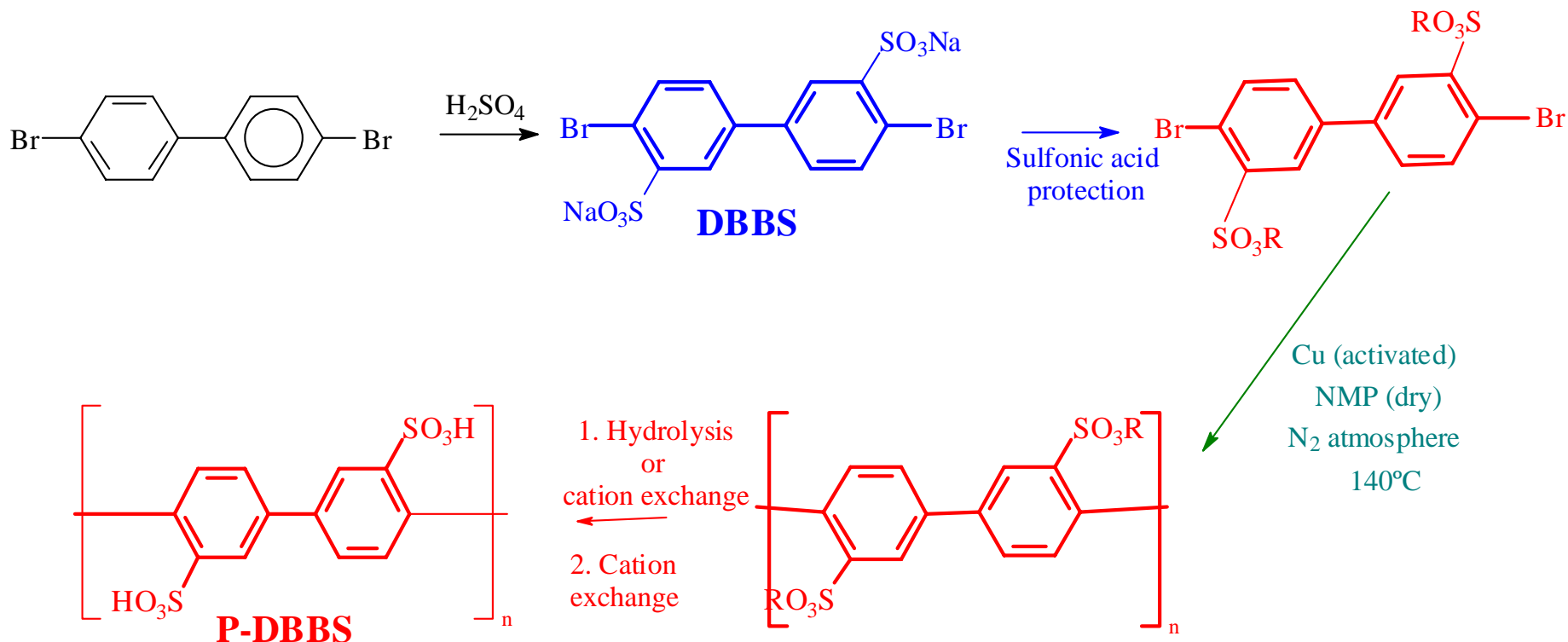


Specific tasks:

R = bulky comonomer

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

Poly (p-Phenylene Sulfonic acids): Synthesis



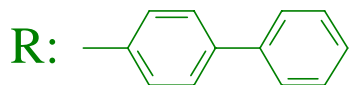
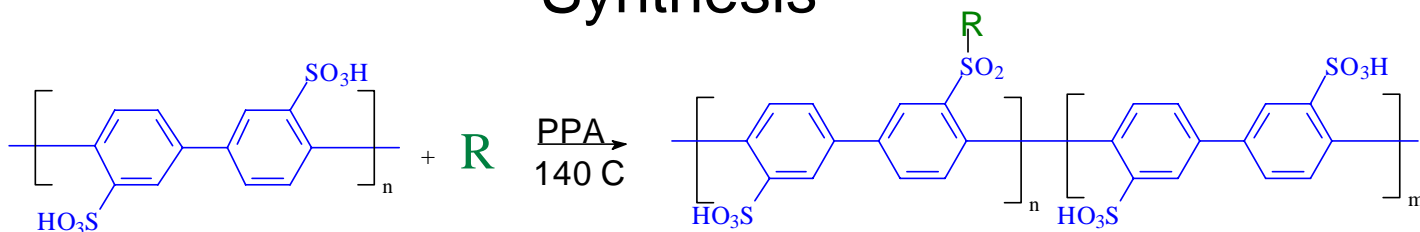
• Polymer with I.V. = 0.4 dL/gm. formed brittle films. New polymer batches have I.V.s of ~1.3 dL./gm. Film mechanical properties improve but elongation is still low.

• **Homopolymer is water soluble!**

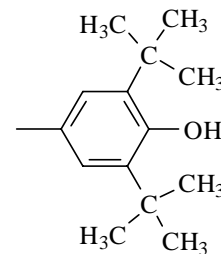
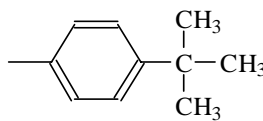
Poly (p-Phenylene Sulfonic acids): Graft Copolymers

- Comonomer synthesis difficult; only recently accomplished.
- Most effort went into grafting groups on the sulfonic acids to make sulfones.
- Best results were achieved with grafted t-butyl substituted aromatics.
- The remaining discussion will focus on di-t-butyl phenol grafts.

Synthesis



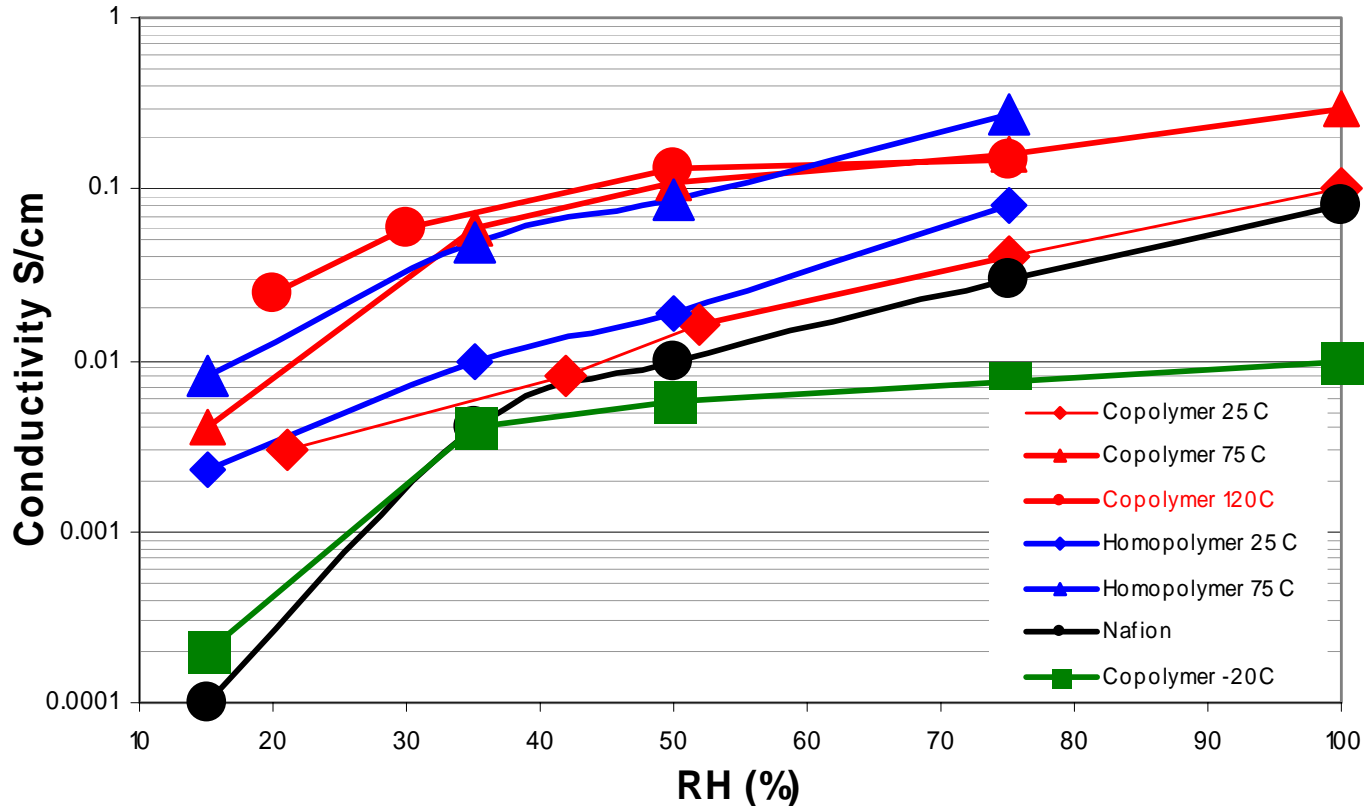
Crosslinkable group



Bulky non-crosslinking, hydrophobic groups

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

**Batch 3 Graft copolymer, 8.4% di-t-butylphenol:
Conductivity vs Temperature and RH**

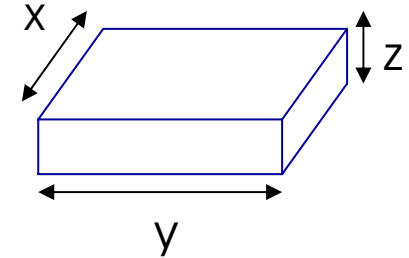


•These early copolymers reach the DOE benchmarks for 2005.

Polymer swelling as a function of relative humidity

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

Grafting group	Amount grafted (mole % of total acid)	Δx (%)	Δy (%)	Δz (%)
Biphenyl*	10	2	2	45
Biphenyl*	20	1	1	35
Biphenyl*	55	~0	1	15
t-Butyl-benzene	5	1	2	85
t-Butyl-benzene	25	1	1	50
Di-t-butyl-phenol	5	~0	~0	50



* After cross-linking, 10 min at 200°C; uncross-linked film is water soluble.

- 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

Problems to be addressed

- Molecular Weight: Polymer gels during polymerization. Break elongation is poor; the best we have obtained is 8%. Will change counterion or solvent, or both to prevent gelation.
- 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 usually measured parallel to the film surface. The film is anisotropic, through conductivity is lower. The film morphology must be understood. Block copolymers should have better through conductivity.
- 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? Test for acid loss at elevated temperatures under wet conditions.
- Oxidative Stability: Will non-fluorinated materials be oxidatively stable, or will they degrade in use at lower temperatures? Will analyze electrode adhesive for evidence of degradation.