

2006 DOE Hydrogen Program Poly(p-phenylene Sulfonic Acid)s with Frozen-in Free Volume for use in High Temperature Fuel Cells

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Overview

Timeline

- Start date 4/15/2006
- End date 4/15/2011
- Percent complete 0%

Budget

- Total project funding
 - DOE \$1,492,572
 - Contractor \$530,569
- Funding received in FY05, \$150,000
- Funding for FY06, \$300,000

Barriers

- Low break elongation.
- Comonomer synthesis and copolymerization
- MEA stability in use at elevated temperatures

Interactions

Tom Zawodzinski,
Robert Savinell

Objectives

- Overall:

Synthesis and characterization of materials capable of operating “indefinitely” as MEAs at 125°C and < 50% relative humidity.

- **New project:** Progress in earlier work.

Demonstrated “frozen in free volume” for two PEM systems. Second system, PPSA, is basis of present research. Showed retention of conductivity at low RHs up to 125°C.

- 2005:

Study synthesis mechanism to increase molecular weights.

Remake successful PEMs, characterize them fully, and do preliminary studies of MEAs made with them under operating fuel cell conditions.

Start synthesis of comonomers and their copolymers with complete control over composition and morphology.

Plan and Approach

- **Increase Molecular Weight:**

Ensure monomer purity, catalyst activation and water-free solvent. Find solvent in which polymer remains soluble. Follow and understand polymerization and copolymerization kinetics. This necessary in order to generate high molecular weight polymer, and to define copolymer microstructure.

- **Graft copolymers:**

The best water-insoluble material made so far is a graft copolymer. The synthesis and characterizations will be repeated under completely controlled conditions so that we know its full response to temperature and RH, and its performance as an MEA.

- **Comonomers and Copolymers:**

Full structural control can only be achieved by making comonomers and studying the kinetics of their random and block polymerization. We favor comonomers that have very bulky, very hydrophobic substituents.

- **Applications:**

Copolymer PEMs will be characterized for conductivity and permeability. The best will be studied as MEAs for fuel cell use and submitted to the Topic 2 group for extended study.

- **Thermal and hydrolytic stability:**

The operational limits of these systems will be determined by the effect of water vapor and temperature on the PEM chemical stability. TGA studies at different temperatures and relative humidities will measure weight loss, and subsequent characterization will determine what changes have occurred.

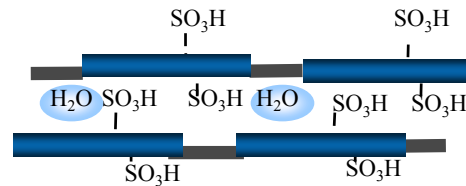
Earlier Technical Accomplishments

- Frozen in Free Volume: Basic concept

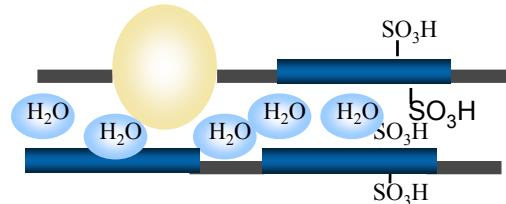
Use rigid-rod liquid crystalline polymers.

A few bulky or angled comonomer units can force the chains apart over their whole length, creating permanent pores lined with SO_3H 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.

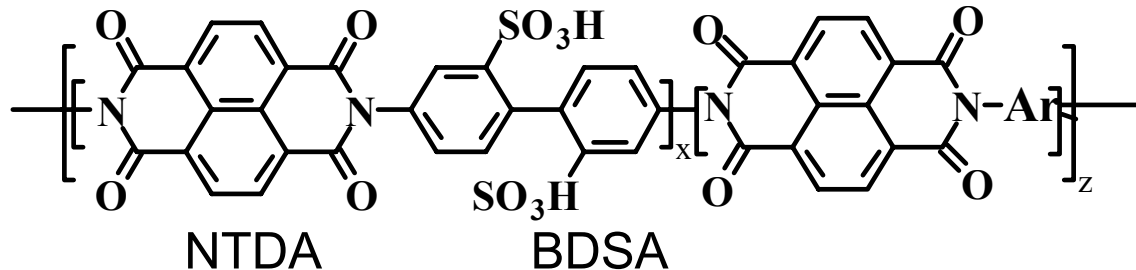


(b). Polymer with bulky comonomer. Chains kept apart.



Earlier Technical Accomplishments

Polyimides: Structures



Monomers used:

Naphthalene tetracarboxy dianhydride (NTDA)

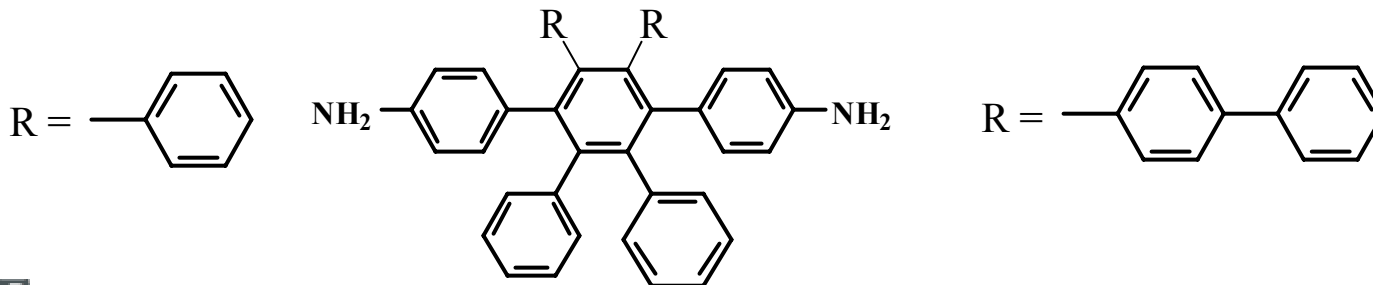
Benzidine 2,2'-disulfonic acid (BDSA)

Some of the Aromatic comonomers used:

2', 3' Di(Biphenyl) 5', 6'-DiPhenyl Triphenylene 4, 4'' diamine RD(BP)DPT5

R = random copolymer, 5 = five mole % in the copolymer

2', 3', 5', 6' – Tetra (4) Phenyl Triphenylene 4, 4'' diamine R(4P)T5



Earlier Technical Accomplishments

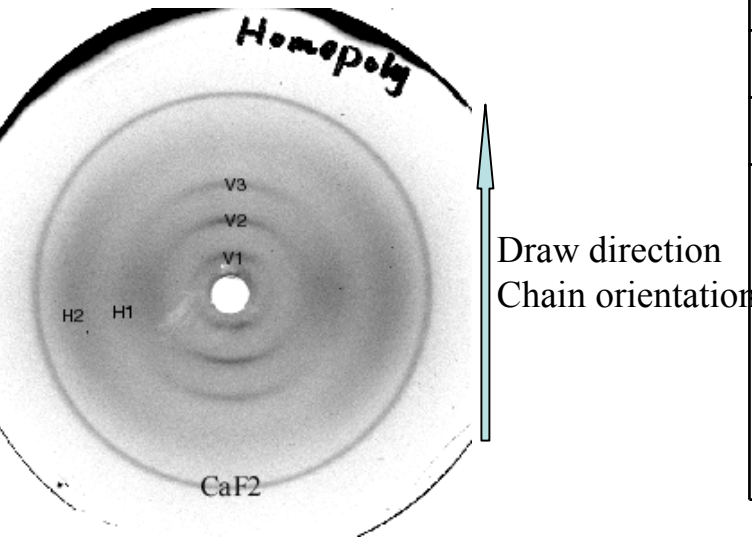
Polyimides: Dry polymer chain separation

- Interchain distance in dry polymer depends on bulk of comonomer.

d-spacings of selected polyimides.

Polyimide		Equatorial diffractions, Å (S.D.)		Meridional diffractions, Å (S.D.)	
		d_{H1}^*	d_{H2}	d_{V2}	d_{V3}
Homopolymer		6.03 (.06)	3.74 (.04)	8.02 (.06)	5.44 (.03)
a*	BP10(18/2)	5.88 (.05)	3.73 (.02)	8.10 (.01)	5.49 (.01)
b*	RF5	6.23	3.73	8.04 (.02)	5.46 (.03)
	RO5	6.32	3.74	8.08	5.52
c*	R(3P)T5	6.33 (.10)	3.75 (.01)	8.11 (.02)	5.48 (.01)
	R(4P)T5	6.14	3.78	8.11	5.49
	RD(BP)P2.5	6.36 (0.20)	3.77 (0.03)	8.02 (0.03)	5.45 (0.02)

X-ray diffraction photo of oriented homopolymer fiber.



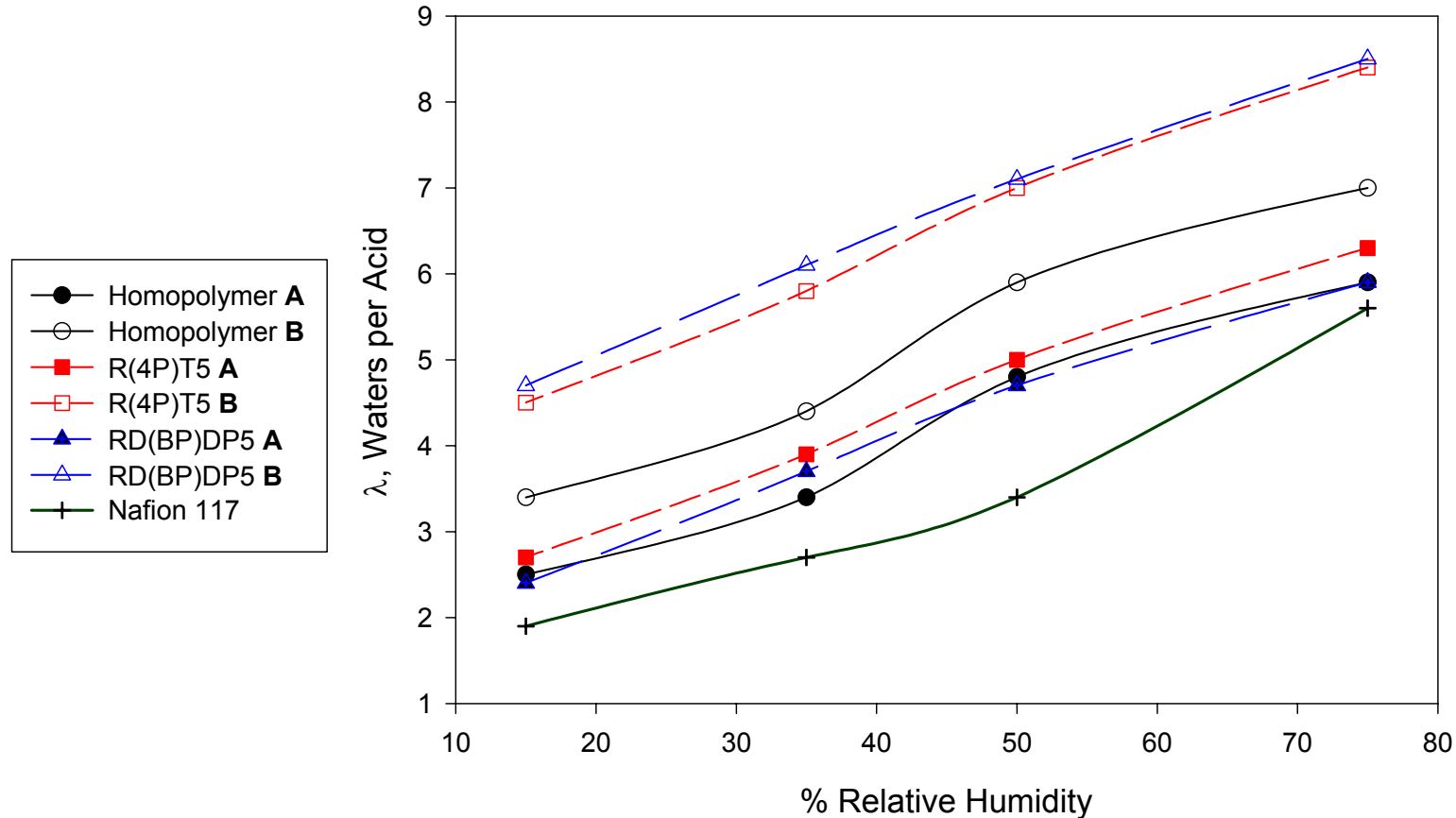
* d_{H1} is the intermolecular spacing. It varies with the comonomer cross-sectional area.

** Comonomer: **a.** linear, small cross-section; **b.** angled; **c.** linear, large cross-section

Interchain distance can increase 5% with 2.5 to 5 mole% comonomer. Total volume increases by 10%

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.

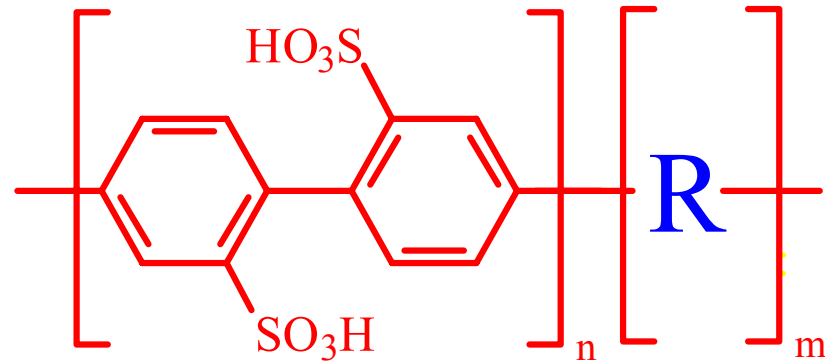
- Homopolymer holds ~1 water after procedure **A** drying.
- Copolymers with only 5 mole% comonomer hold ~2 waters after procedure **A** drying.
- **Problem: Polymers in acid form slowly hydrolyze. Cannot be used.**

Poly (p-Phenylene Sulfonic acids)

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.

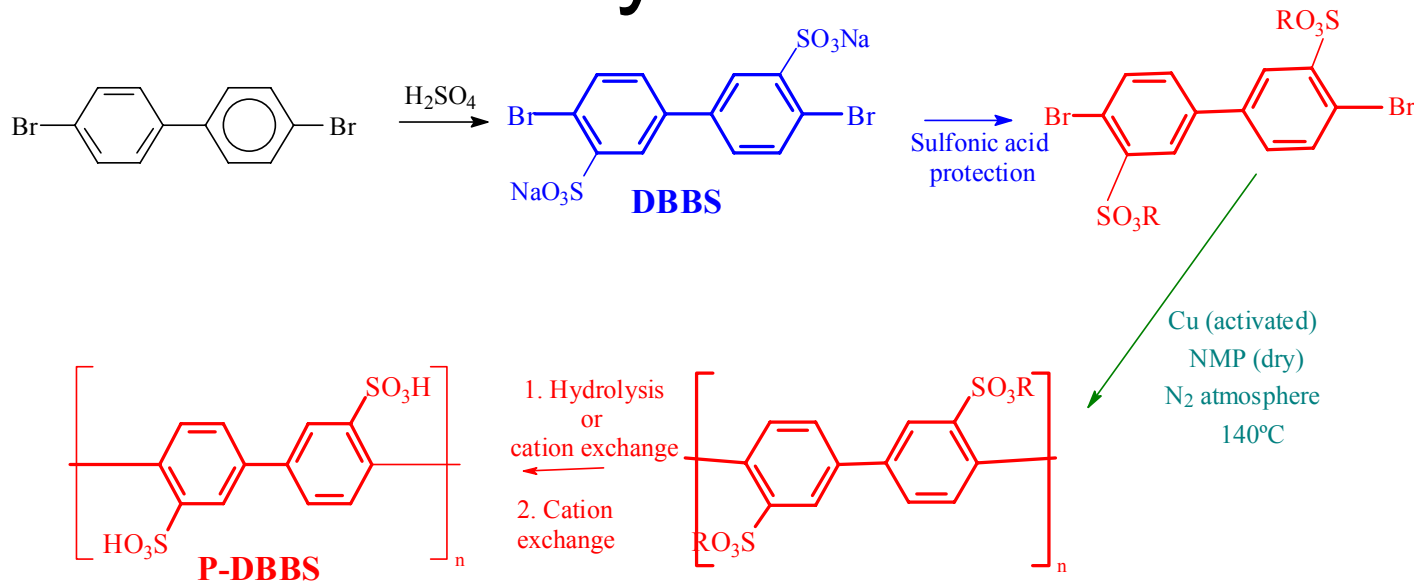


R = bulky comonomer

Specific tasks:

- 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



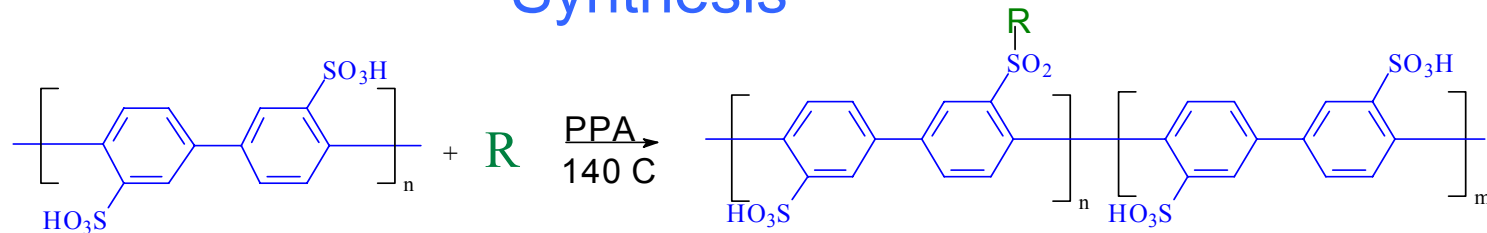
• Polymer with I.V. = 0.4 dL/gm. formed brittle films. New polymer batches have I.V.s of ~1.3 dL./gm. Film mechanical properties improve but elongation is still low.

• Homopolymer is water soluble!

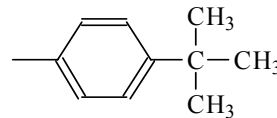
Poly (p-Phenylene Sulfonic acids): Graft Copolymers

- 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.

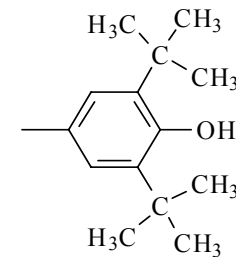
Synthesis



Crosslinkable group

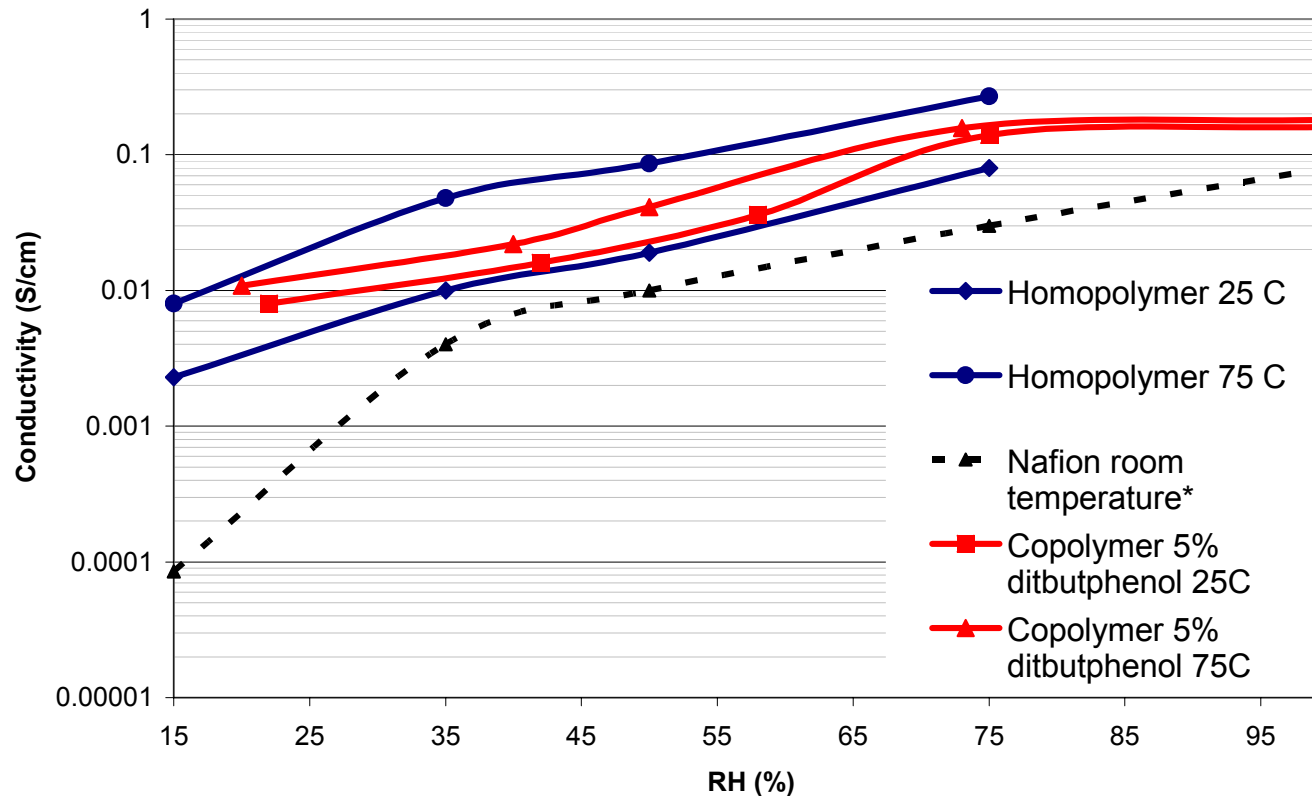


Bulky non-crosslinking, hydrophobic groups



Initial conductivity results

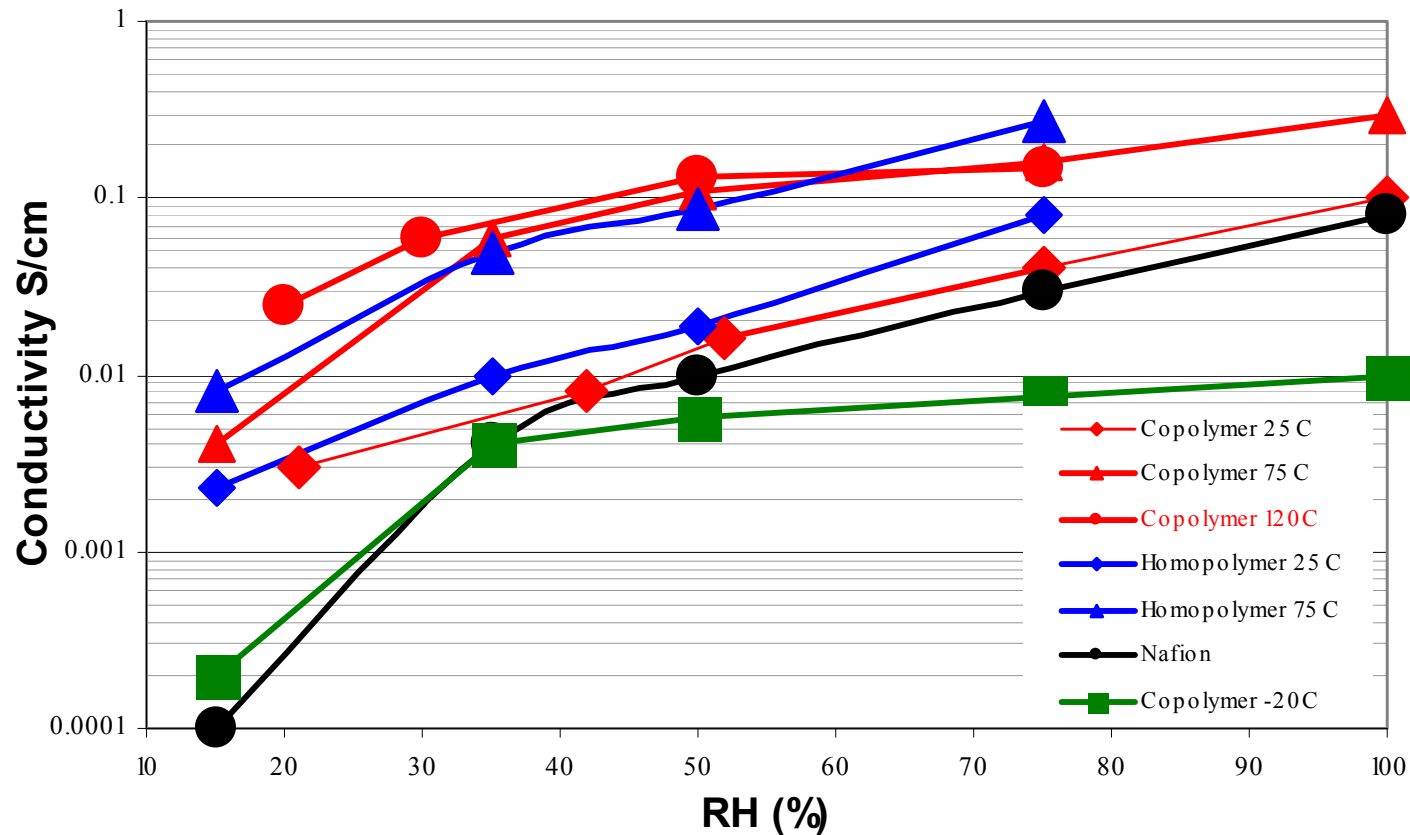
Copolymer 5% di'tertbutylphenol



• Conductivity is >100mS/cm at 75% RH, even at 25°C.

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

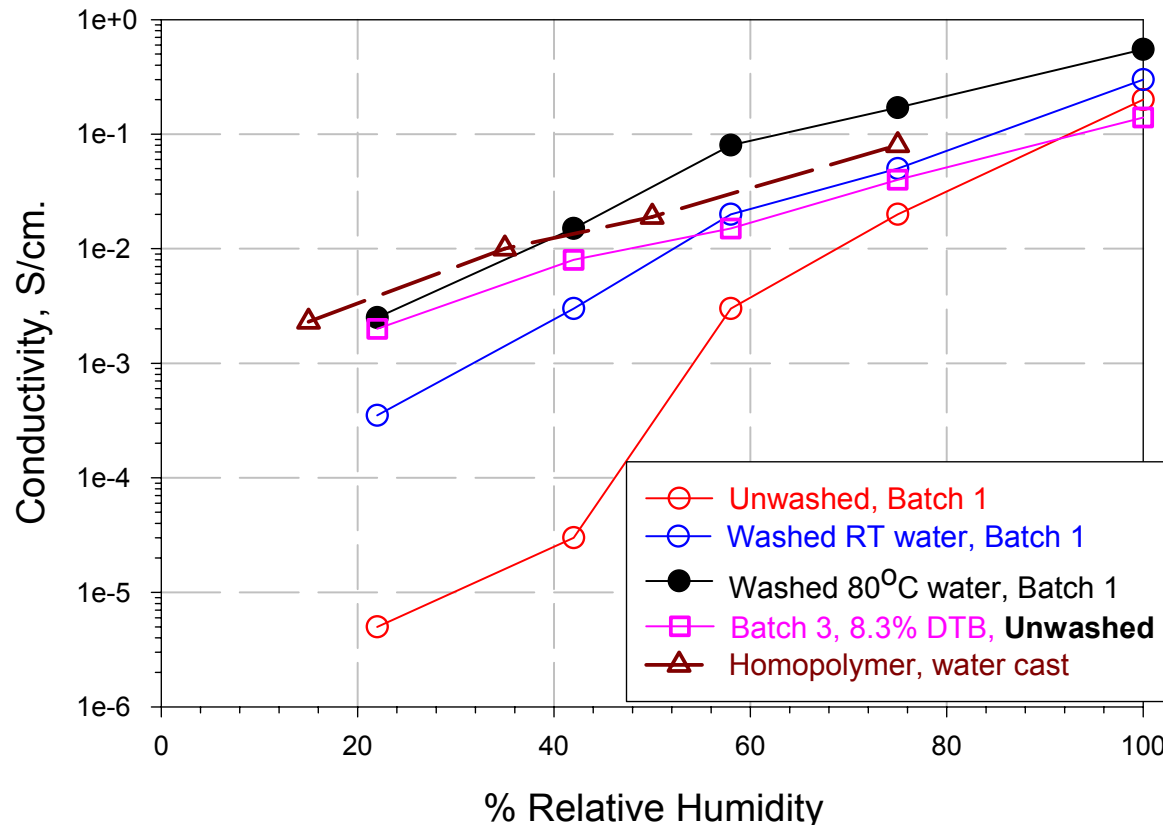
Batch 3 Graft copolymer, 8.4% di-t-butylphenol:
Conductivity vs Temperature and RH



• These early copolymers reach the DOE benchmarks for 2005.

PPSA t-butyl phenol Graft Copolymers: Conductivity as a Function of Post-casting Treatment

Effect of washing on 25°C conductivity, DTB copolymers
Copolymer films cast from DMF, dried at RT.

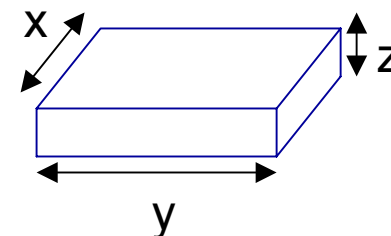


- Washing at 80°C raised Batch 1 film conductivity at 55% RH from 3 mS to 90 mS!
- Batch 3 has intrinsically higher conductivity than Batch 1; film was not washed.

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. The film swells 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: 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 in use at lower temperatures?

Future Work: 1

Fiscal year 05-06

- **Molecular weight:** – Better monomer and solvent purification. Change polymer solubility during polymerization – new solvents or new counter-ions. Increased molecular weight means better mechanical properties.
- **Resynthesize previous graft polymer:** – Measure properties under controlled conditions. Will be a benchmark for later results. Make MEAs and run preliminary fuel cell tests. If good, submit for further evaluation.
- **New comonomer and copolymer synthesis** – Procedures have been developed to synthesize highly non-polar phenyl sulphone comonomers; several candidates are being considered. Initial copolymerization and random copolymer properties will be studied.

Future work: 2

Fiscal year 06-07

- **Copolymerization kinetics and mechanism:** - Use GPC to measure monomer consumption and polymer molecular weight. Needed for next synthesis phase.
- **Block copolymers:** - We expect that block copolymers could have higher 3-D conductivity plus much better ductility than random copolymers. Polymerization is heterogeneous; kinetics and mechanism must be completely understood in order to make reproducible structures. The effects of copolymer mole ratio, block length and casting procedure on mechanical and electrical properties will be determined.
- **Structure:** Mechanical and electrical properties are highly structure dependent in anisotropic materials. Optimum property generation depends on understanding structure. Will use X-ray, STM, AFM, DMTA, viscosity and molecular weight determination as the major tools.
- **Polymer Stability:** Will run long term conductivity studies on our best materials at room and elevated temperatures at DOE specified relative humidities. Will also run accelerated degradation tests at 175 to 200°C, at several relative humidities.

Project summary

- **Relevance:** Synthesis of “inexpensive” PEMs that function at 125°C or higher at low relative humidity (~1 Atm. pressure of incoming gasses).
- **Approach:** Use rigid rod liquid crystalline poly (sulfonic acids) that have frozen in free volume. They hold water very strongly and remain conductive at low humidities.
- **Technical Accomplishments:** This is a new project. **Earlier work, funded by DARPA, demonstrated that our present membranes met or exceeded DOE 2006 conductivity milestones.** However, they fell short in other requirements.
- **Technology Transfer/ Collaborations:** Extensive collaboration with T/J Technologies and DuPont. Many presentations. Patents applications in works.
- **Proposed Future Research:** Generate polymers with better water retention and conductivity than present ones. Improve mechanical properties. Determine polymer supermolecular structure and morphology. Study polymer degradation and define operational window. Submit best materials for extensive evaluation in fuel cells.

Acknowledgements

- DARPA and DOE support for research

Students:

Yue Zhang (Ph. D.)

Hyoung-Jun Kim (Ph. D.)

Sergio Granados-Focil (Ph. D.)

Thomas Young (M. S.)

Casey Check

Collaborators:

Jesse Wainright

Robert Savinell

Jerome Vendramini

Devon Renrock

Jung-qing Ma

Mark Teasley

Mark Roelofs

Publications and Presentations

None from this work.

Past presentations:

- **Molecular Design Considerations in the Synthesis of High conductivity PEMs for Fuel Cells**, Yue Zhang, Morton Litt, Robert Savinell and Jesse Wainwright, *Polymer Preprints* 40(2), 480 (1999)
- **Molecular Design of polyimides toward high proton conducting materials**, Yue Zhang, Morton Litt, Robert Savinell, Jesse Wainwright and Jerome Vendramini; *Polymer Preprints* 41(2) 1561 (2000)
- Kim, Hyoung-Juhn; Litt, Morton H.; Shin, Eun-Mi; Nam, Sang Yong. **Hydrolytic stability of sulfonic acid-containing polyimides for fuel cell membranes.** *Macromolecular Research* (2004), 12(6), 545-552.
- Sergio Granados-Focil and Morton H. Litt, **Novel highly conductive poly(phenylene sulfonic acid)s and their evaluation as proton exchange membranes for fuel cells.** *Polymeric Materials Science & Engineering Preprints*, 89, 438 (2003)
- Granados-Focil, Sergio; Litt, Morton H.. **A new class of polyelectrolytes, polyphenylene sulfonic acid and its copolymers, as proton exchange membranes for PEMFC's.** *Preprints - American Chemical Society, Division of Fuel Chemistry* (2004), 49(2), 528-529.
- Litt, Morton H.; Granados-Focil, Sergio; Zhang, Yue; Young, Thomas. **Molecular design of rigid rod polyelectrolytes: Effect of structure on water retention and conductivity.** *Preprints - American Chemical Society, Division of Fuel Chemistry* (2004), 49(2), 594-595.
- Litt, Morton. **Modeling conductivity in polyelectrolytes.** *Preprints - American Chemical Society, Division of Fuel Chemistry* (2005), 50(2), 692-694.
- Renock, Devon; Zhang, Pu; Ma, Junqing; Lei, Hanwei; Peiter, Charlie; Litt, Morton; Granados-Focil, Sergio. **Improving the power density of PEM fuel cells.** *Society of Automotive Engineers, [Special Publication] SP* (2005), SP-1965(Applications of Fuel Cells in Vehicles), 69-71.

Critical Assumptions and Issues

- **Conductivity:** The 2005 goals are almost met by the early examples of our membranes. Frozen-in free volume allows water to be held strongly, with concomitant high conductivity. The problem will be to meet the 2010 target. We think this can be done, though not necessarily cheaply.
- **Electrolyte stability at elevated temperature:** Degradation testing has been done only under dry conditions (175 to 250°C). Results are poor. However, membranes function with water present. Initial results at Case show degradation rates at 200-250°C decrease even at < 0.1% RH. Wet membrane degradation at high temperatures will be studied. This can be extrapolated to define a use window and provide guidelines for operating temperatures of any aromatic sulfonic acid PEM.
- **Gas permeability:** This could be a problem for materials with a large non-polar volume fraction. Oxygen and hydrogen dissolve in the non-ionic domains. Not true for liquid crystalline materials. They always have excellent barrier properties. Our research includes measuring permeability, but this should not be an issue.
- **Oxidative Stability:** Almost everyone considers resistance to Fenton's reagent as the ultimate criterion. This is a self defeating assumption; any non fluorocarbon material will be attacked. The real question is: "Are hydroxyl radicals formed during operation, and if so, how far will they diffuse from the catalytic surface before reacting?". Any hydrogen peroxide formed rapidly decomposes to oxygen and water under strong acid conditions. If hydroxyl radicals are formed and desorb from the catalytic surface, they cannot diffuse far (low diffusion constant). Only the electrode adhesive and carbon backing can be attacked. Oxidative degradation of the adhesive under working conditions will be studied to decide this issue.
- **Cost:** No material meets the criterion when laboratory prices are used. The lab. starting materials are cheaper for our system than for most of the others, and the synthetic procedure is not expensive. Should meet the criterion if done on an industrial scale. Bromine can be recycled if necessary.