V.G.12 Poly(p-Phenylene Sulfonic Acids): PEMs with Frozen-In Free Volume

Morton Litt (Primary Contact), Peter Pintauro, Ryszard Wycisk, Kun Si, Casey Check, Junwon Kang and Daxuan Dong
Case Western Reserve University
10900 Euclid Ave.
Cleveland, OH 44106-7202
Phone: (216) 368-4174; Fax: (216) 368-4202
E-mail: mhl2@case.edu

DOE Technology Development Manager:
Terry Payne
Phone: (202) 586-9585; Fax: (202) 586-9811
E-mail: Terry.Payne@hq.doe.gov

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

Technical Advisor: John Kopasz
Phone: (630) 252-7531; Fax: (630) 972-4405
E-mail: kopasz@anl.gov

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Objectives

The project objectives are to optimize routes to rigid rod poly (phenylene sulfonic acids), develop methods to make water-insoluble polymers and characterize the materials as proton exchange membranes (PEMs). This requires:

- Study the parameters in the Ullman polymerization reaction necessary to get high molecular weight polymers.
- Increase the polymer sulfonic acid density by using phenylene disulfonic acid monomers.
- Develop reliable methods for grafting non-polar groups on the backbone to make water-insoluble, dimensionally stable PEMs.
- Synthesize non-ionic comonomers and copolymerize them to generate water-insoluble copolymers.
- Perform basic characterization on copolymers to understand the relationship between molecular structure, supermolecular organization and PEM properties.
- Submit the most successful materials for intensive testing.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost
(C) Performance

Technical Targets

Technical Targets: Membranes for Transportation Applications

Characteristic	Units	2005 Status [a]	2010	2015
Inlet water vapor partial pressure	kPa	50	<1.5	<1.5
Oxygen cross-over [b]	mA/cm^2	5	2	2
Hydrogen cross-over [b]	mA/cm^2	5	2	2
Membrane conductivity at inlet water vapor partial pressure and: Operating temperature 20°C -20°C	Siemens/cm Siemens/cm Siemens/cm	0.10 0.07 0.01	0.10 0.07 0.01	0.10 0.07 0.01
Operating temperature	°C	<80	≤120	≤120
Area specific resistance	ohm - cm^2	0.03	0.02	0.02
Cost [c]	$/m^2	25 [d]	20	20
Durability with cycling At operating temperature of ≤80°C At operating temperature of >80°C	h h	~2,000 [e] N/A	5,000 [f] 2,000	5,000 [f] 5,000 [f]
Unassisted start from low temperature	°C	-20	-40	-40
Thermal cyclability in presence of condensed water		Yes	Yes	Yes

[a] First year for which status was available.
[b] Tested in MEA at 1 atm O$_2$ or H$_2$ at nominal stack operating temperature.
[c] Based on 2002 dollars and costs projected to high-volume production (500,000 stacks per year).
[d] Based on 2005 TIAX study and will be periodically updated.
[e] Steady-state durability is 25,000 hours.
[f] Includes typical driving cycles.

Accomplishments

- The factors needed to get the highest molecular weight polymer possible using Ullman coupling have determined. They are complete removal of oxygen and water. Polymerizations now take about

12 hours instead of ~150 hours. Molecular weight is limited by crystallization of the polymer from solution. Copolymers may be more soluble.

- Two new comonomers have been synthesized that should be completely stable in use. Others are being made. We are studying ways of incorporating them.

- Water uptake and conductivity as a function of relative humidity (RH) has been studied. The newest polymer, poly (phenylene disulfonic acid), has a λ of 4.3 at 15% RH; even the homopolymer has a large frozen-in free volume. It had high conductivity at very low RH, ~100 mS/cm at 50% RH (25°C), and at 15% RH (75°C). It may meet the DOE 2015 requirements.

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Introduction

There are many problems associated with the use of aromatic polysulfonic acids derived from benzophenone, or the corresponding sulfone, ethers as PEMs. High sulfonation produces water-soluble polymers with a maximum ion exchange capacity (IEC) of 2.6 meq/g. Water-insoluble material with good conductivity swells greatly at high RH and loses conductivity rapidly as humidity drops [1]. Dimensionally stable polymers have a relatively low IEC and are not highly conductive except when wet. Recent approaches to overcome some of these problems use block copolymers where the dimensional stability is generated by a non-polar block and the conducting block can have maximum sulfonation [2]. Block polymers still lose conductivity rapidly as RH decreases. Modeling suggests that the problem is due to the polyelectrolyte backbone structure. It is jointed and can collapse, losing volume easily by rotation around the ether links as humidity decreases. These structures would retain water at low humidities and therefore maintain conductivity even at elevated temperatures.

Approach

Our approach derives from a combination of polymer structure analysis and cost considerations. What type of polymer backbone can have high sulfonic acid content, hold water strongly, and yet have dimensional stability? The analysis suggested that poly (p-phenylene sulfonic acids), rigid rod liquid crystals that organize with all molecules locally parallel, should be suitable. These structures have small cross-section backbones with projecting sulfonic acid groups. Absorbed water separates the chains. At low humidity, the sulfonic acids hit other acid groups or a neighboring polymer backbone. The system cannot shrink further and still has voids which can hold water (frozen in free volume). As water is added, this structure can

only expand perpendicular to the rod axes. It can be dimensionally stabilized by addition of non-polar groups that promote hydrophobic bonding, or by cross-linking [3]. Non-polar groups can be incorporated that protrude further from the backbone than the acid groups; this increases the minimum chain (rigid rod) separation and thus increases the frozen-in free volume [4]. Such structures have non-collapsible nanopores lined with a high density of sulfonic acid groups. These hold water very strongly, both through H-bonding and capillary attraction.

Results

Early Results

- The first polyelectrolytes tested passed the 2005 goals for membrane conductivity.

- Measurements of gaseous MeOH permeability (<0.04 mA/cm^2 for a 20-µ thick film at 100°C with a 2/1 MeOH/H$_2$O input) imply that the very polar membrane environment should reduce oxygen and hydrogen crossover to values much lower than the target values.

- The graft copolymers had high dimensional stability, e. g. 27% expansion (z direction only) from 22 to 100% RH while retaining good conductivity.

Polymer Synthesis. Monomer synthesis is simple and straightforward – one step from cheap commercial materials, p-dibromo benzene or 4, 4'-dibromo biphenyl and fuming sulfuric acid, to the monomers, p-dibromo phenylene 2, 5-disulfonic acid, and 4, 4'-dibromo biphenyl 3, 3' disulfonic acid. The polymerization route chosen was the Ullman reaction, coupling of halogen substituted aromatic compounds using copper metal to remove the halogens. While the reaction is well known, this is the first time it was used to make polymers with completely aromatic backbones. It was found that water retards the polymerization very strongly, and may also act to remove terminal bromines. When the reactants were dried at 120°C under high vacuum for one to two days, polymerization time at 140°C decreased from nine days to twelve hours and polymer was obtained with higher molecular weight than any made earlier. The nuclear magnetic resonance (NMR) spectra are clean showing only the major peaks and peaks due to the terminal bromophenyl groups. Integration showed a degree of polymerization of 35 to 40 (MW ~10,000) for poly(biphenylene disulfonic acid) (PBPDSA), Figure 1, and about 300 for poly(phenylene disulfonic acid) (PPDSA, MW ~35,000), not shown. Polymerization stopped when the polymer precipitated (probably crystallized). Further heating at 170°C for one and two days did not increase the viscosity.

Copolymerization. Three comonomers, 4, 4'-dibromobiphenyl 3, 3'-di (4-t-butyl-phenyl sulfonate),

4, 4'-dibromobiphenyl 3, 3'-di (3, 5-di-t-butyl phenyl sulfonate) and 4, 4' dibromo biphenyl, 3, 3' di(biphenyl sulfone), were synthesized and tested in homopolymerization and copolymerization. In all cases, homopolymerization at 140°C for 150 hrs produced mainly dimer and trimer with traces of higher molecular weight material. Copolymerization with either monomer generated a water-soluble fraction that contained almost no comonomer, plus a very low molecular weight organic-soluble fraction with about 50 mole% comonomer. An attempt using delayed addition, dropping a solution of the Li salt of 1, 4-dibromo phenylene 2, 5-disulfonic acid (DBPDSA) in dimethyl formamide (DMF) over an 18-hr period into a reaction vessel containing comonomer and copper, and continuing the polymerization at 140 to 155°C for a total of 124 hrs, produced a low molecular weight copolymer with ~50/50 polar/non-polar composition, plus homopolymer.

These comonomers used above have potential deficiencies. Two are esters and could hydrolyze in use. The biphenyl sulfone crosslinks when heated. Two new comonomers, 4, 4'-dibromo biphenyl 3, 3'-di(4-neopentyl phenylsulfone) and 4, 4'-dibromo biphenyl 3, 3'-di(4-(3, 5-bis(trifluoromethyl) phenyl) phenyl sulfone) have been made. These should be stable in use. We have started to study other methods of copolymerizing them.

Water Absorption and Conductivity. Water uptake of PPDSA as a function of RH was measured and compared to that for PBPDSA and Nafion®, see Figure 2. Even after extensive drying at 80ºC under vacuum, the polymers retained one water molecule per acid group. (Dried Nafion® holds one water molecule per acid group strongly.) Both homopolymers absorb water strongly at low humidity, compared to Nafion®. PPDSA at 15% RH has a λ of 4.3. Nafion® reaches this value at ~75% RH.

The major driving force for water absorption in the polymer is its frozen-in free volume. At low humidity, water is absorbed with very little change in polymer volume; density initially rises with water content, and then falls as λ increases. The polymer volume as a function of water absorption was modeled assuming that water initially absorbs mainly in the frozen-in free volume. As this fills, water starts separating the chains, increasing the polymer volume. Two PPDSA data sets were used. Polymer molar volumes were measured. The wide-angle X-ray diffraction low angle peaks, the chain separation d spacings, were measured for each RH. Polymer molar volume could be calculated from the d-spacings. The frozen

in free volume was estimated to be about 45 ± 10 cc per mole of sulfonic acid, Figure 3. The PPDSA density if there were no free volume was calculated to be 2.0 gm/cc.

The strong water absorption was also demonstrated by differential scanning calorimetry measurements. PPDSA showed no low temperature endotherm up to $\lambda = 8.5$, the highest λ measured (75% RH). Water is strongly absorbed. The usual sulfonic acid polymers, both Nafion® and the aromatic phenylene ethers, show a low temperature endotherm (weakly bound water) at $\lambda > 7$ [5].

We do not yet have water-insoluble polymers with good mechanical strength, but it is worthwhile to compare conductivities of the homopolymers as a function of RH and temperature, Figure 4. High molecular weight PPDSA was measured; it is more dimensionally stable than the earlier lower molecular weight materials. Even so, it was too soft at 75% RH and higher temperatures for measurements to be taken. The effect of frozen in free volume is evident. Conductivity for PBPDSA at 75°C is about that of PPDSA at 25°C over the whole RH range. Conductivities for both are much higher than those of Nafion® over this RH range. From Figure 2 we see that λ is 4.3 for PPDSA at 15% RH, for PBPDSA at ~50% RH and for Nafion® at ~75% RH. The conductivities of the polymers at these RHs, Figure 4, are fairly close. The major factors governing conductivity seem to be λ and temperature. The low RH conductivity demonstrates this very well. PPDSA conductivity at 75°C and 15% RH was 80 to 100 mS/cm. Since water is held very
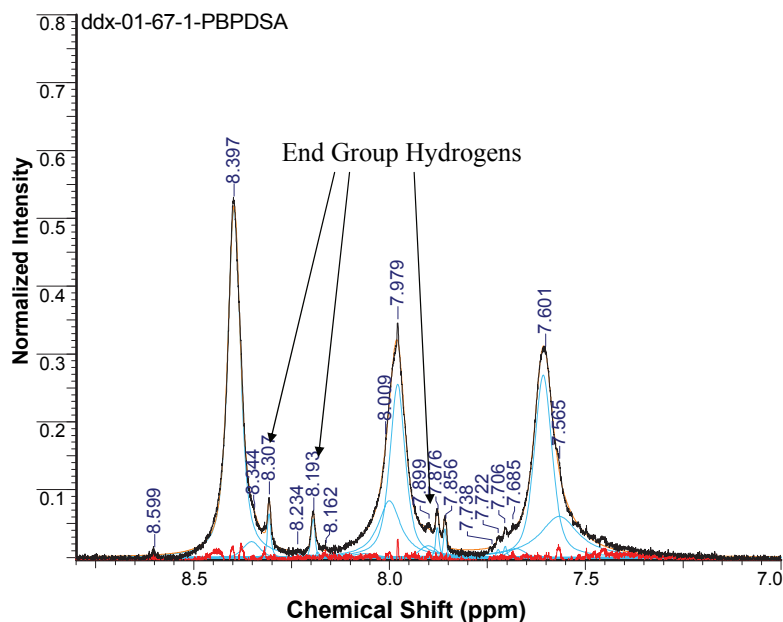

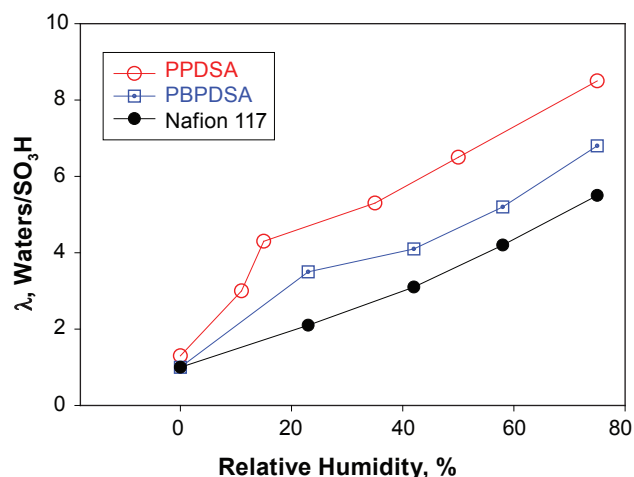**FIGURE 1.** ¹H NMR Spectrum (D₂O) of PBPDSA, Acid Form

FIGURE 2. Comparison of λ vs RH for Nafion® and Rigid Rod Electrolytes

FIGURE 4. Comparison of PPDSA, PBPDSA and Nafion® Conductivities as a Function of Temperature and RH
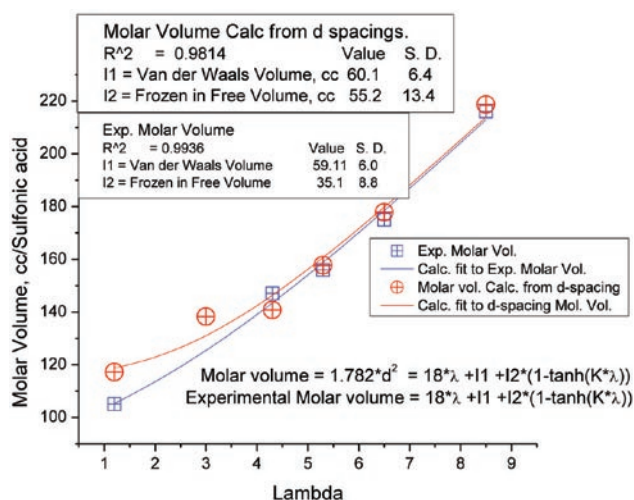

FIGURE 3. Modeling PPDSA Volume as a Function of λ, a Demonstration of Frozen-In Free Volume

strongly, that generated by the fuel cell operation could be enough to maintain high conductivity above 100°C.

Graft Copolymers. Di-t-butyl phenol was grafted on PBPDSA in order to make water-insoluble PEMs. Unfortunately, the polymer was an early batch with low molecular weight and did not form coherent films. Both graft and homopolymer were therefore blended with aromatic poly(sulfone ether sulfonic acids) from McGrath's laboratory. The homopolymer was blended with sPS2.1 and 2.6 while the copolymer was blended with sPS2.1. The blends were cast into films and conductivities were measured, Figure 5. The homopolymer blend improved the sPS2.6 conductivity at lower RH. However, at lower humidities all conductivities were much lower than those of the graft polymer (made in 2006) and homopolymer. Some of
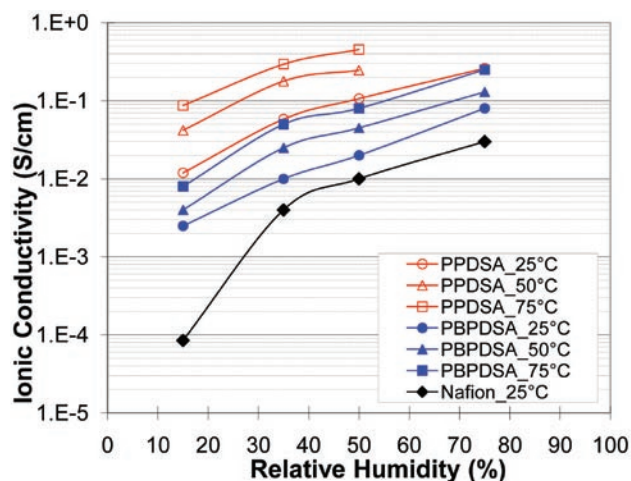
the homopolymer blends reached the DOE requirement of 70 mS/cm at 75% RH. Films were not sent for evaluation because we were not satisfied with the conductivity of the water-insoluble blend.

Recent grafting attempts using di-t-butyl phenol gave completely cross-linked polymers. The phenol reacts to form sulfonate esters, and some of the ester groups probably reacted again to cross-link through sulfone formation.

Conclusions and Future Directions

- Polymerization conditions for the Ullman reaction have been optimized. The limiting factor for getting high molecular weight polymer is polymer precipitation (crystallization) from solution.
- We have demonstrated the existence of frozen-in free volume and its importance for retaining high conductivity at low RH. Incorporating bulky non-polar substituents should increase the frozen-in free volume, maintaining low humidity conductivity while making the polymer dimensionally stable.
- The homopolymers are water-soluble. Grafting of non-polar groups on the backbone occurs under heterogeneous conditions. This makes the grafting difficult to control. We had made water-insoluble, dimensionally stable, highly conductive PEMs earlier using this method, but each run tended to give material with different properties.
- The major remaining synthetic challenge is to make high molecular weight water-insoluble copolymers. Work has started on some new approaches. First, the bromo-groups on a non-polar "comonomer" can be transformed to boronic acids and coupled with monomer using the Suzuki reaction to make a comonomer that has a central non-polar substituent
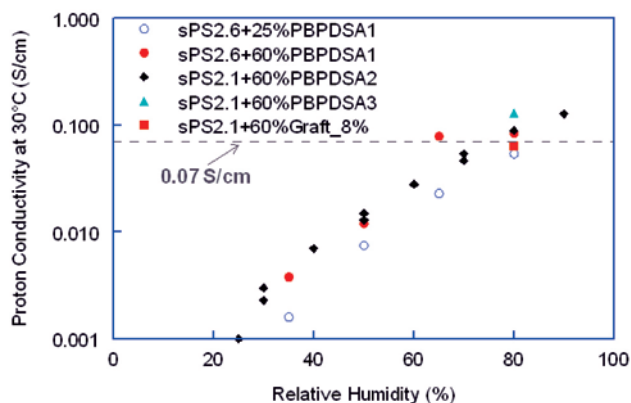
FIGURE 5. Conductivity of Blends of PBPDSA with sPS2.1 and 2.6 as a Function of RH

and end groups that are identical with those of the base monomer. This was done earlier and worked well, but the group chosen gave water-soluble homopolymer; it was not hydrophobic enough. Second, oligomers can be chain extended, but at the cost of introducing some ether groups into the polymer. Non-polar, bulky bis-phenols or bis-thiols can be used as chain extenders to generate water-insoluble, high molecular weight polymer. Early work has shown that linking groups can be used that maintain the rigid-rod organization necessary to generate the free volume.

- Once water-insoluble polymers are made, the next challenge is to develop reasonable mechanical properties. Chain extension or copolymerization should give polymers that do not crystallize because the bulky groups in the backbone keep the chains apart; they should reach higher molecular weight than we are now getting. That, plus the hydrophobic interactions of the non-polar groups should produce dimensionally stable polymers with reasonable elongation. Dimensionally stable PEMs, even with relatively poor mechanical properties, will be submitted for further evaluation.

- Work to understand the structure/property relationships in these systems will continue.

Special Recognitions & Awards/Patents Issued

1. The patent application, Litt, Morton H.; Granados-Focil, Sergio. **Liquid crystal poly(phenylene sulfonic acids).** U.S. Pat. Appl. Publ. (2005), was accepted by the patent office without revision. It is being divided into two patents.

2. A patent application on **Liquid crystal poly(phenylene disulfonic acids)** by Morton Litt and Junwon Kang was submitted to the U.S. Patent Office early in 2008.

FY 2008 Presentations

1. 1/31/08 Invited Speaker, Case Chemical Engineering Department.

2. 4/16/08 FCIT Review Greenfield, MI.

3. 4/25/08 H$_2$ Program, Purdue U., W. Lafayette, IN.

4. 5/19/08 ECS Meeting, Phoenix, AZ.

5. 8/20/08 ACS Meeting, Fuel Chemistry Div., Philadelphia PA.

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2. J. McGrath et al. DOE Program Review, 6/08 Washington, D.C.

3. S. Granados-Focil, Ph. D. thesis CWRU, 2006; Sergio Granados-Focil and Morton H. Litt, *ACS Polymeric Materials Science & Engineering Preprints*, **89**, 438 (2003); Sergio Granados-Focil, Thomas Young and Morton H. Litt, ACS *Fuel Chemistry Division Preprints,* , **49(2)** 528-529 (2004).

4. Y. Zhang, Ph. D. Thesis, CWRU, 2001; M.H. Litt, S. Granados-Focil; Y. Zhang and T. Young, Molecular design of rigid rod polyelectrolytes: Effect of structure on water retention and conductivity. *ACS Fuel Chemistry Division preprints* **49(2)** 594-595 (2004).

5. T.A. Zawodzinski Jr., T.E. Springer, F. Uribe, S. Gottesfield, *Solid state ionics.* **1993** *60*, 199-211.