

V.D.8 Poly(p-Phenylene Sulfonic Acids): PEMs with Frozen-In Free Volume

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Objectives

The project objectives are to optimize routes to rigid rod poly (phenylene sulfonic acids), develop methods to make them water insoluble, cast dimensionally stable films and characterize them as polymer electrolyte membranes (PEMs). This requires:

- Studying 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 making water-insoluble, dimensionally-stable PEMs by: 1) grafting non polar groups on the backbone, or 2), synthesizing water-insoluble comonomers that copolymerize well with the base monomers.
- Perform basic characterization of 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

See Table 1.

Accomplishments

- The factors needed to get the highest molecular weight polymer possible using Ullman coupling have been 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 of the two base sulfonic acid monomers are more soluble and reach higher molecular weight than either homopolymer.
- Water uptake and conductivity as a function of relative humidity (RH) has been studied. The newest polymer, poly (phenylene disulfonic acid) (PPDSA), has a λ of 4.3 at 15% RH. The homopolymer has a large frozen-in free volume. It had high conductivity at very low relative humidity, ~100 mS/cm at 50% RH (25°C), and at 15% RH (75°C). It may meet the DOE 2015 requirements.
- One way of making water-insoluble, dimensionally-stable PEMs is to graft non-polar moieties on some of the sulfonic acid groups. Neopentyl benzene was grafted on poly(biphenylene disulfonic acid) (PBPDSA). A 4 mole% graft was water insoluble: a cast film was sent to Bekktech for testing. Conductivity at 50% RH was 115 mS/cm (80°C) and 150 mS/cm (120°C). Conductivity dropped drastically at lower humidities but was always above that of Nafion® 212. A neopentyl benzene graft (15 mole%) on PPDSA was tested in house. Conductivity at 30 and 80°C was equal to or greater than that of the earlier grafted polymer, especially at lower humidities, though lower than that of the homopolymer.
- Water absorption and “frozen-in free volume” was studied quantitatively. PBPDSA λ is greater by about 1.2 and PPDSA λ is greater by about 2.5 water

TABLE 1. 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 | hours hours | ~2,000 ^e not applicable | 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 membrane electrode assembly (MEA) at 1 atm O₂ or H₂ 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 TIA study and will be periodically updated.^e Steady-state durability is 25,000 hours.^f Includes typical driving cycles.

molecules per sulfonic acid than Nafion® 117 from 15 to 75% RH. The “frozen-in free volume” for PPDSA was analyzed by comparing the volumes and inter-chain distance spacings (from X-ray scans) as a function of λ . The analysis showed a “frozen-in free volume” of 63 cc per sulfonic acid, a λ of 3.5, and a polymer van der Waals volume of 59 cc (the volume occupied by one half of a phenylene disulfonic acid in dilute solution). This was written up as a paper and is being published in an American Chemical Society (ACS) symposium volume (Andrew Herring, editor) of the 2008 Fuel Chemistry presentations.



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 (ion exchange capacity [IEC] > 2.6 meq/gm) produces water soluble polymers. 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. Conductivity drops rapidly with water loss. A possible solution is to design structures that cannot collapse as humidity is lowered. These could 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. As water is lost at low humidity, the sulfonic acids hit other acid groups or a neighboring polymer backbone. The system still has voids which can hold water (frozen in free volume): further compression distorts bond angles and requires high energy. As water is added, this structure can only expand perpendicular to the parallel polymer axes. It can be dimensionally stabilized by addition of non-polar groups that promote

hydrophobic bonding, or by cross-linking [3]. Non-polar groups that protrude further from the backbone than the acid groups can be incorporated; 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 (PBPDSA) passed the 2005 goals for membrane conductivity.
- Measurements of gaseous MeOH permeability ($<0.04 \text{ mA/cm}^2$ for a 20- μ thick film at 100°C with a 2/1 MeOH/H₂O input) imply that the very polar membrane environment should reduce oxygen and hydrogen cross-over 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. Yields are ~ 80% for the biphenyl monomer and ~ 40% for the phenyl monomer. (We think that this can be ultimately raised to ~80% and are working on this now.) 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. 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 12 hours and polymer was obtained with higher molecular weight than any made earlier. The ¹H nuclear magnetic resonance 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 (molecular weight [MWt] ~ 10,000 Daltons) for PBPDSA and 250 to 400 for PPDSA (MWt ~ 30,000 to 50,000 Daltons). Polymerization stopped when the polymer precipitated (probably crystallized). Further heating at 170°C for one and two days did not increase the viscosity.

The phenyl and biphenyl monomers copolymerized easily. There was some precipitation after 18 hours but the polymerization solution remained viscous.

The copolymer held water very strongly. The specific viscosity at 0.5% concentration was 1.5 dL/gm, much higher than the best of the homopolymers.

Recent studies on scaling up PPDSA homopolymerization showed that the present drying technique is difficult to use for larger batches. Viscosity of 0.5% solutions dropped as batch size increased, from 0.8 dL/gm (2 gm scale) to 0.6 to 0.7 (17 gm scale) to 0.25 (30 gm scale).

Copolymerization. Many potential comonomers were made by reacting the base monomer sulfonic acid groups to generate sulfones or sulfonates. None copolymerized effectively. Bis phenol sodium salts were also used in attempts to place non-polar groups on the backbone. Again, there was no effective reaction.

We have shifted the approach towards the synthesis of co-monomers that have long non-polar groups attached and have end groups that are direct analogues of the base monomers. This has worked, but the copolymer made was water soluble even at 33% substitution [3]. It had biphenyl substituents. We have since learned that long alkyl chains are necessary to get water insolubility at low degrees of substitution.

Graft Copolymers. Recent work has used neopentyl benzene (NPB) as the non-polar grafting moiety. We use polyphosphoric acid (PPA) as both solvent and condensing agent; the neopentyl group is not affected under the polymerization conditions. When NPB was grafted on to PBPDSA (4 mole%), a lightly crosslinked non water swelling polymer was obtained. This could be cast to make stable films with reasonable mechanical properties. They were stable at 100% RH, but disintegrated slowly when placed in water. A sample was sent to Bekktech for evaluation, which passed the DOE Go/No-Go requirements. The results are shown in Figure 1.

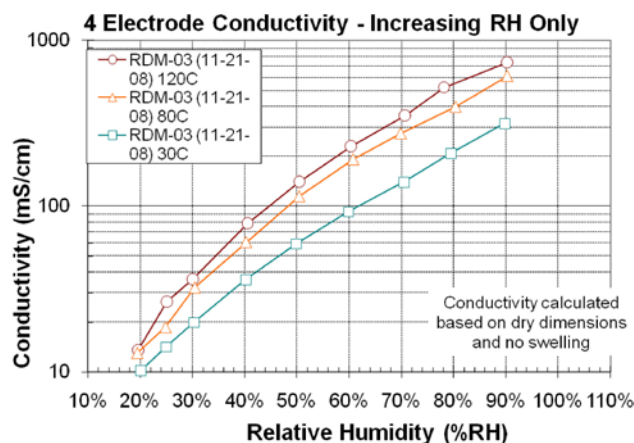


FIGURE 1. Conductivity of PBPDSA graft polymer (4 mole% NPB), Bekktech RDM-03, as a function of temperature and RH.

NPB was also grafted on PPDSA. A sample with 15 mole% substitution was cast and the film was tested in house; it had poor mechanical properties and was just water soluble. However, at low RHs its conductivity was better than that of the PBPDSA graft, Figure 2. PPDSA as the backbone polymer has advantages over PBPDSA; it has a higher IEC, holds water much better at low humidity and can have a higher molecular weight.

Water Absorption and “Frozen-In Free Volume”.

The water uptake of the two homopolymers has been reevaluated and correlated with their structures. Water uptake of PPDSA as a function of RH was compared to that for PBPDSA and Nafion® 117, Figure 3. (See

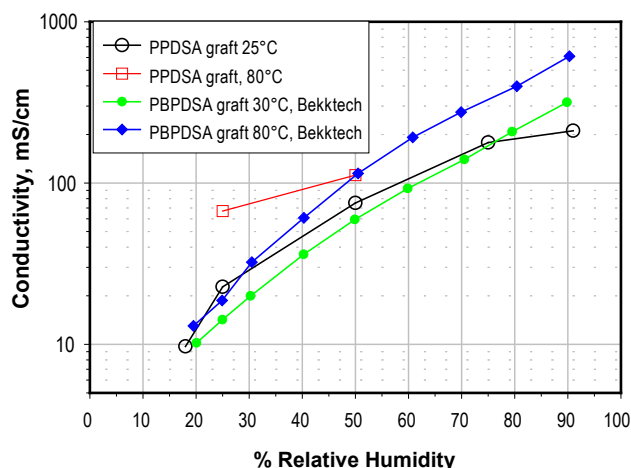


FIGURE 2. Comparison of PPDSA 15% NPB graft (25 and 80°C) and Bekktech RDM-03 (30 and 80°C): conductivities as a function of temperature and RH.

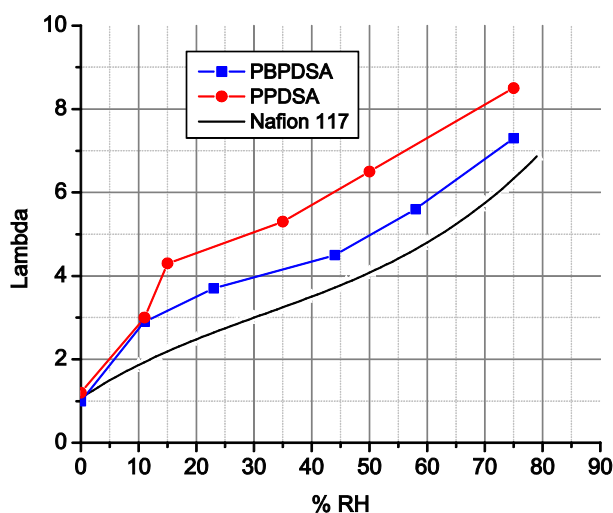


FIGURE 3. Comparison of lambda as a function of RH (25°C) for PPDSA, PBPDSA and Nafion® 117. Nafion® 117 λ is from least squares minimization of most literature values [6]. ($\lambda = 1.358 \times 10^{-5} (\%RH)^3 - 1.297 \times 10^{-3} (\%RH)^2 + 0.09105 (\%RH) + 1.067$)

reference 6 for the papers used to generate a least squares equation for Nafion® λ as a function of RH.) Even after extensive drying at 80°C under vacuum, the polymers retained one water molecule per acid group. (Nafion® holds one water molecule per acid group very 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. The molar volume of PPDSA as a function of water absorption was modeled, see Equations 1 and 2 in the Figure 4 caption. The assumption is that water is initially absorbed in the frozen-in free volume. As this fills, water starts separating the chains, increasing the polymer volume. Two PPDSA data sets were used: 1) polymer molar volumes were measured, and 2) the wide-angle X-ray diffraction (WAXD) low angle peaks, the chain separation d spacings, were measured for two film orientations at each RH. The measured volumes correlated linearly with d², showing that water absorption caused the chain separation to increase isotropically. The equations developed correlated both the measured molar volume and that calculated from the d spacings, Figure 4. The calculated “frozen-in free volume” was 63 cc/sulfonic acid, equivalent to a λ of 3.5 [5].

The important factors governing conductivity of sulfonic acid polymers seem to be λ and temperature; RH affects λ, but the polymer structure determines its value. The high conductivity of our materials at low

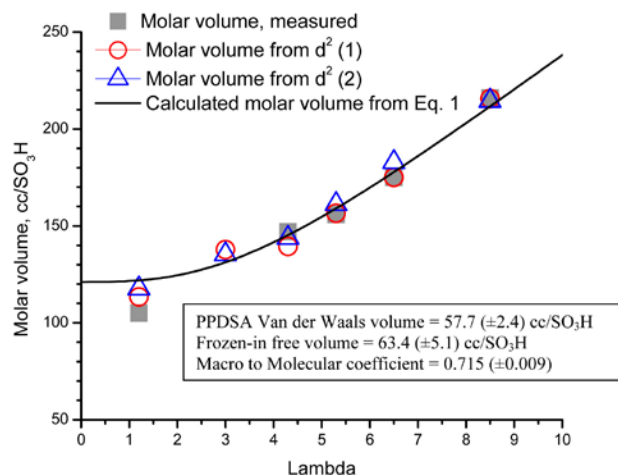


FIGURE 4. Determination of “frozen-in free volume” using Equation 1. Data for λ = 1.2 not used. WAXD scans taken through films. d(1) perpendicular to casting direction; d(2) parallel to casting direction.

1. $MV = VdWV + 18\lambda + FV * (1 - \tanh(18\lambda / FV))$
2. $1.27d^2 = K * MV$

MV = Molar Volume measured, per SO₃H group

VdWV = Polymer Van der Waals Molar Volume

FV = “Frozen-In Free Volume” per SO₃H group

K = Macro to molecular volume conversion coefficient

RH demonstrates this very well. PPDSA conductivity at 75°C and 15% RH was almost 100 mS/cm. Since water is held very strongly, that generated by the fuel cell operation could be enough to maintain high conductivity above 100°C.

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. Copolymerization of the two base monomers avoids this; higher viscosity polymer was obtained.
- The existence of frozen-in free volume and its importance for retaining high conductivity at low relative humidity has been demonstrated. Incorporating non-polar alkyl substituents should make the polymer water insoluble, imparting dimensional stability while maintaining low humidity conductivity.
- The homopolymers are water soluble. Grafting of non-polar groups on the backbone occurs under heterogeneous conditions and is difficult to control. Water-insoluble, dimensionally-stable, highly-conductive PEMs were made earlier using this method, but control of grafting and scaling up is very difficult. A new graft copolymer film from PBPDSA (4 mole% NPB) was made and sent to Bechtel for evaluation. Conductivity at 50% RH was above 100 mS/cm at both 80 and 120°C. PPDSA was grafted (15 mole% NPB) and conductivity was measured in house. Values at lower humidities were much higher than those measured for the PBPDSA graft.
- The major remaining synthetic challenge is to make high molecular weight water insoluble copolymer. Work has started on some new approaches. First, the Suzuki reaction can be used to make a comonomer that has a central non-polar substituent and end groups that are identical with those of the base monomer. This was done earlier and good copolymers were obtained, but the group chosen, biphenylene, gave water-soluble polymer even at 33 mole% substitution; it was not hydrophobic enough [3]. All work so far demonstrates that comonomers with long alkyl chains are necessary to confer dimensional stability.
- Once water insoluble polymers are made, the next challenge is to develop reasonable mechanical properties. Copolymerization of a non-polar comonomer with both base monomers might do this. The irregular arrangement of the groups in the backbone should keep the chains from crystallizing and we should be able to reach higher molecular weights 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 August 2008 Fuel Chemistry Division symposium on fuel cells has generated a Symposium volume (editor, Andrew Herring) that includes a paper based on my presentation. It will be published soon.

FY 2009 Presentations

1. 1/14/09 USCAR presentation, Greenfield, MI.
2. 5/19/09 DoE annual review, Washington, D.C.
3. 8/15/09 ACS Fuel Chemistry Division Symposium.

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