

V.M.8 Poly(p-phenylene sulfonic acids): PEMs with Frozen-In Free Volume

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Objectives

- Optimize routes for polymerizing dibromo biphenyl disulfonic acid, and make graft copolymers.
- Synthesize novel dibromo biphenyl disulfone and dibromo phenyl disulfone comonomers.
- Synthesize water insoluble poly(phenylene sulfonic acid) (PPSA) random and block copolymers.
- Do basic characterization on copolymers to understand the relationship between molecular structure, supermolecular organization and polymer electrolyte membrane (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:

- (B) Cost
- (E) System Thermal and Water Management

Technical Targets

TABLE 1. Progress Towards Meeting Technical Targets

Characteristic	Units	2005 Status	2010	2015
Inlet water vapor partial pressure	kPa	50	<1.5	<1.5
Membrane conductivity at inlet water vapor partial pressure and:				
Operating temperature 20°C	Siemens/cm	0.10	0.10	0.10
-20°C	Siemens/cm	0.07	0.07	0.07
	Siemens/cm	0.01	0.01	0.01
Operating temperature	°C	<80	≤120	≤120
Area specific resistance	Ohm/cm ²	0.03	0.02	0.02
Cost	\$/m ²	25	20	20
Thermal cyclability in presence of condensed water		Yes	Yes	Yes

Polyelectrolyte Membranes

This project involves synthesis and characterization of rigid-rod aromatic sulfonic acid containing homo- and copolymers. Our ionomers have met or surpassed the 2005 goals for membrane properties. Since they have not yet been tested in a fuel cell configuration, we cannot be certain that they meet all the requirements but indicate they will do so.

- Graft copolymers made by the project's start met conductivity requirements and were dimensionally stable with swelling of 35% in the Z direction going from 22 to 100% relative humidity (RH) at room temperature.
- The cost should be low. Monomers are made in high yield by disulfonation of 4, 4'-dibromo biphenyl and are polymerized using Ullman coupling, a simple and cheap reaction.
- Comonomers are needed to make copolymers that are water insoluble. We have made the first comonomer recently, but have not yet studied copolymerization. We expect that satisfactory copolymers will have no more than 10 to 20 mole% comonomer, and may need less. Comonomers will cost more to make, but can be made in one step from the starting monomer.

Accomplishments

- Earlier homopolymer syntheses have been reproduced. One grafting reaction produced a water insoluble polymer, but the base polymer had

low molecular weight and could not be cast into mechanically stable films.

- We have spent much effort on comonomer synthesis. At present, we have made one comonomer in low yield: 4, 4'-dibromo biphenyl 3, 3'-di(4-biphenyl sulfone).
- We have synthesized a new class of polyelectrolytes derived from 1, 4-dibromo benzene 2, 5-disulfonic acid – poly (p-phenylene 2, 5-disufonic acid) (PPDSA) but have not yet made a water insoluble polymer. It shows even greater promise than the earlier polymers; conductivity at 75°C is 0.1 S/cm at 15% RH (6 kPa).



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 produced water soluble polymers with a maximum ion exchange capacity (IEC) of 2.6 meq/gm. Water insoluble material with good conductivity swelled highly at high relative humidity and lost conductivity rapidly as humidity dropped. Dimensionally stable polymers had a relatively low IEC and were not highly conductive except when wet. Present 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. They still lose conductivity rapidly as relative humidity decreases. Our analysis suggested that the problem was due to the polyelectrolyte backbone structure. It is jointed and can collapse and easily lose volume as humidity lowers by rotation around the ether links. Conductivity drops rapidly with water loss. The solution might lie in designing structures that cannot collapse.

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 PPSA rigid rods with a liquid crystal organization with all molecules locally parallel should be suitable. This type of structure has a small cross-section backbone with projecting sulfonic acid groups. At low humidity, the sulfonic acids hit either another acid group 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 expand only perpendicular to the rod axis. It can be dimensionally stabilized by the addition of non-polar

groups to promote hydrophobic bonding, or by cross-linking. Such non-polar groups protrude further from the backbone than the acid groups and can increase the frozen-in free volume. The first polymers made, before DOE support, with one sulfonic acid per benzene ring, have an equivalent weight of 156 gm/eq (IEC = 6.4 meq/gm) and reasonably high conductivity at low humidity. The synthesis is simple and straightforward – two steps from cheap commercial materials to polymer. More recently we have made polymers with two sulfonic acids per benzene ring (IEC = 8.5 meq/gm) using the same structural and synthetic approach.

Results

Our first objective was to synthesize a graft polymer that fit most of the DOE requirements, based on our previous work. This was to be made using the Friedel-Crafts reaction of di-t-butyl phenol with the base polymer to generate “di-t-butyl sulfone” grafts. The reaction was heterogeneous and difficult to control. However, after several attempts, we made a polymer that was dimensionally stable, with ~0% expansion in the X-Y directions and only 27% expansion in the Z direction as the relative humidity went from 22% to 100%. The conductivity from -20°C to 120°C met the DOE 2005 requirements. The elongation to break was ~8%; this is not high but is good enough that one could make simple fuel cells with it. The grafting reaction was run first on a low molecular weight PPSA. It was successful (see Figure 1) but the graft formed films that were too brittle to test. Our first attempt generated a polymer with about 85% graft compared to the earlier polymer. We are making more using a better starting polymer.

We have made our first co-monomer, 4, 4'-dibromo biphenyl 3, 3'-di(biphenyl sulfone) using a zinc chloride catalyzed reaction of biphenyl with 4, 4'-dibromo biphenyl 3, 3'-disulfonyl chloride. The yields are not high and purification is still time consuming. We will start copolymerization reactions soon.

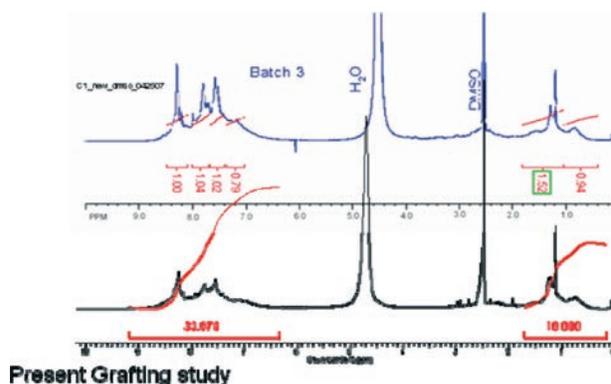


FIGURE 1. Reproduction of Grafting Process: Nuclear Magnetic Resonance Comparison of New Material to Earlier Synthesis

A parallel research involved the synthesis and polymerization of 1, 4-dibromo 2, 5-disulfonic acid. Monomer yields at present from dibromo benzene and fuming sulfuric acid are about 40%. Polymers are made using the Ullman reaction (copper aided coupling in a polar, aprotic solvent). We can cast good films, but the homopolymer (PPDSA) is water soluble and has poor elongation. We expect that its water insoluble copolymers will be tougher with little loss of conductivity. Its properties are remarkable. It holds about 4.3 waters per acid group at 15% RH (frozen in free volume) and retains conductivity at very low humidity due to its water retention and high IEC. Its conductivity is much higher than that of PPSA (see Figure 2). Wide-angle X-ray diffraction scans and other evidence indicate that the polymer chains orient approximately perpendicular to the film surface. This implies that through conductivity will be as high as or higher than in-plane conductivity. Thermogravimetric analysis studies on PPDSA show that decomposition is very slow at 240°C; there is no decomposition after one hour (Figure 3). This compares very favorably with PPSA, which shows some decomposition after one hour at 200°C.

Conclusions and Future Directions

- We have not yet made PEM copolymers suitable for testing.
- We will make one graft PPSA copolymer as promised and submit it for testing.
- We have made one comonomer and will be copolymerizing it to make water insoluble random or block poly(biphenyl disulfonic acid) copolymers for testing as PEMs.
- We have made the first of a new class of novel polyelectrolytes, PPDSA, with outstanding properties in most ways. The homopolymer is water soluble, but we expect we will be able to make suitable PEMs from copolymers.
- Work on PPSA and PPDSA has shown that the concept of using rigid rod poly (sulfonic acids) to generate frozen-in free volume is a fruitful approach that has produced PEMs with highly exceptional conductivity and thermal stability.
- Most of the future effort will be directed towards making and characterizing water insoluble, dimensionally stable poly(p-phenylene disulfonic acid) copolymers. They have the best properties in many ways, but we must find ways to make them less brittle.

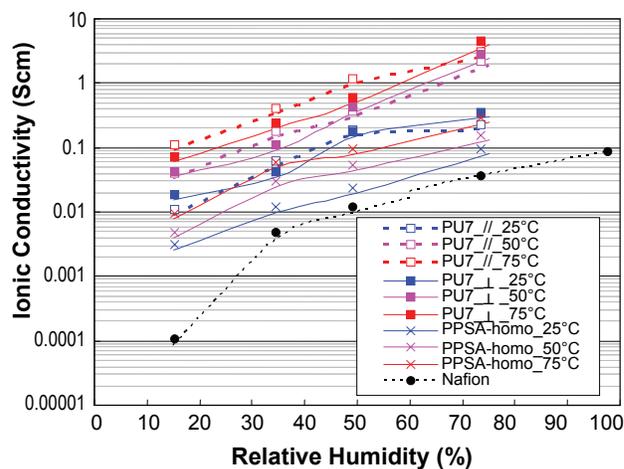


FIGURE 2. PPDSA PU7 Conductivity vs. RH and Temperature, Compared with PPSA

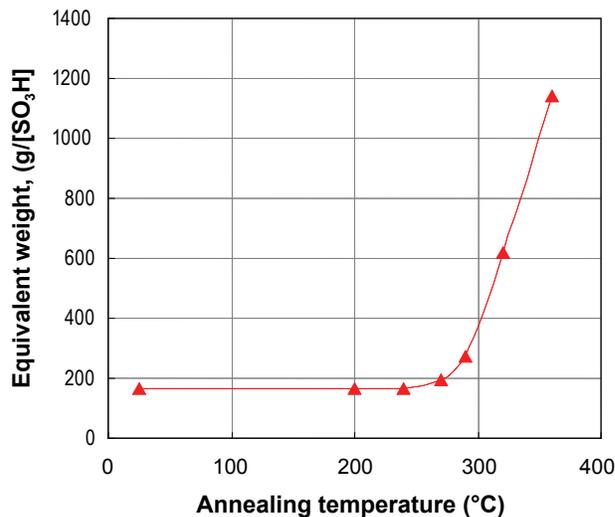


FIGURE 3. Equivalent Weight of PPDSA (Lot 1) after Annealing under Vacuum for One Hour at the Indicated Temperatures

Special Recognitions & Awards/Patents Issued

1. There is a patent pending on PPSA and its copolymers.
2. A patent application on PPDSA and its copolymers is being written and will be submitted soon.

FY 2007 Publications/Presentations

1. A paper on PPSA has been submitted to *Macromolecules*.