

V.D.5 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), polymers that retain high conductivity at low humidity, develop methods to make water insoluble polymers and characterize the materials as proton exchange membranes (PEMs). The requirements are:

- Analyze the Ullman polymerization reaction in order to increase polymer molecular weights and decrease reaction time.
- Increase the polymer sulfonic acid density and water absorption: use phenylene disulfonic acid monomer to make homo- and co-polymers.
- Develop reliable methods for grafting non-polar groups on the backbone to make water insoluble, dimensionally stable PEMs.
- Synthesize comonomers that can be copolymerized to produce water insoluble copolymers either directly or in a subsequent step.
- Characterize polymers, copolymers and grafts 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 (3.4.5) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost

Technical Targets

This project involves the synthesis and characterization of homo- and co-polymer rigid-rod aromatic sulfonic acids.

- Our ionomers have passed the 2005 goals for membrane conductivity and probably reach the 2015 goals.
- Earlier tests of MeOH permeability ($<0.04 \text{ mA/cm}^2$ for a 20 μ thick film at 100°C with a 2/1 MeOH/H₂O gas input) imply that the very polar membrane environment should reduce oxygen and hydrogen cross-over to values much lower than the target values.
- The starting materials are relatively cheap; there are only two steps from commercial starting materials, fuming sulfuric acid and dibromo-biphenyl or dibromo-benzene, to the homopolymer sulfonic acids. Copolymers will raise the cost.
- Some of our early graft copolymers showed 27% expansion (z direction only) from 22 to 100% relative humidity (RH) while retaining high conductivity at 50% RH and 80°C.

Since the polymers have not yet been tested in a fuel cell configuration, we cannot be certain that they meet the requirements but the indications are that they will do so.

Remaining Barriers:

- The homo- and graft polymers tested so far have very low elongation; the best was 8% at 40% RH. They are brittle when very dry. However, these were low molecular weight polymers, molecular weight at 10,000.
- Homopolymer molecular weights are limited because they crystallize from solution and stop growing. The maximum molecular weight for poly(p-biphenylene disulfonic acid) is ~10,000. It is higher for poly (p-phenylene disulfonic acid),

Table 3.4.11 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	Siemens/cm	0.10	0.10	0.10
	20°C	0.07	0.07	0.07
	-20°C	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 ^c	\$/m ²	25 ^d	20	20
Durability with Cycling: At Operating Temperature of ≤80°C At Operating Temperature of >80°C	hours	~2,000 ^e	5,000 ^f	5,000 ^f
	hours	not applicable	2,000	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 is available.

^b Derived from performance data at rated power targets specified in Table 3.4.14.

^c Based on 2005 TIAX study and will be periodically updated.

^d Based on 2002 dollars, platinum cost of \$450/troy ounce = \$15/g, loading <0.2 g/kWe and costs projected to high volume production (500,000 stacks per year).

^e Steady-state single-cell durability is 25,000 hours.

^f Includes typical driving cycles.

PPDSA, up to 100,000, but the homo and graft polymers become very soft above 50% RH.

- We have not yet developed a reliable, scalable method for making water insoluble copolymers by direct grafting of a large non-polar moiety. Grafting is difficult to control since it is a heterogeneous reaction. Normal copolymerization approaches have failed. Other approaches are being studied.
- Long chain alkyl benzenes grafted on PPDSA-generated water insoluble materials that could form good films but swelled rapidly and disintegrated in water to a suspension of particles. We think that grafting is inhomogeneous, which is why they shear easily above 50% RH and are not water stable.

- We have finally developed a polar comonomer that copolymerizes well with the base monomers. It contains a weakly acidic CH₂ group. Once copolymerized, these hydrogens can be replaced by non-polar chains to generate water insoluble copolymers. This has been demonstrated but films have not yet been cast.
- We have made nano-pore containing two-dimensional (2-D) polymers (ion exchange capacity [IEC] = 5.5 mEq/gm) that have no non-polar groups but are water insoluble; they aggregate during preparation. We are still learning how to handle them to cast good films. We expect that the volume will be independent of humidity.

Accomplishments

- The two base monomers were found to copolymerize well. The copolymer precipitated from solution but at higher molecular weight.
- The grafting procedure has been improved; oxygen is now completely excluded. Recent grafts are light in color and cast films are easily handled. They hold water very well and have high conductivity at low humidity; the best conductivity found was 0.1 S/cm at 30% RH and 80°C. The copolymer and its grafts hold more water than the homopolymers and their grafts at a given RH, but they have comparable conductivities.



Introduction

There are many problems associated with the normal aromatic sulfonic acid PEMs. The better conducting materials swell very much in water. Even with these materials, conductivity drops rapidly as humidity is lowered [1]. Block polymers swell less at high humidity, but conductivity is still poor at low RH [2]. They can be used only at high humidity which limits the fuel cell operating temperature to <90°C. The materials described below were designed to hold water

very strongly at low humidity. They could be used effectively at higher temperatures, up to at least 120°C, with little or no added water in the fuel stream since the water generated in the reaction should be sufficient to maintain high conductivity. High temperature operation has the additional advantages that kinetics are faster, lower purity hydrogen can be used and heat can be removed easily.

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 PPDSA, 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 molecules still have voids which hold water (frozen in free volume): further water loss generates compression which distorts bond angles and requires high energy. The last few waters are removed with difficulty and are reabsorbed rapidly. 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]. This structural design generates

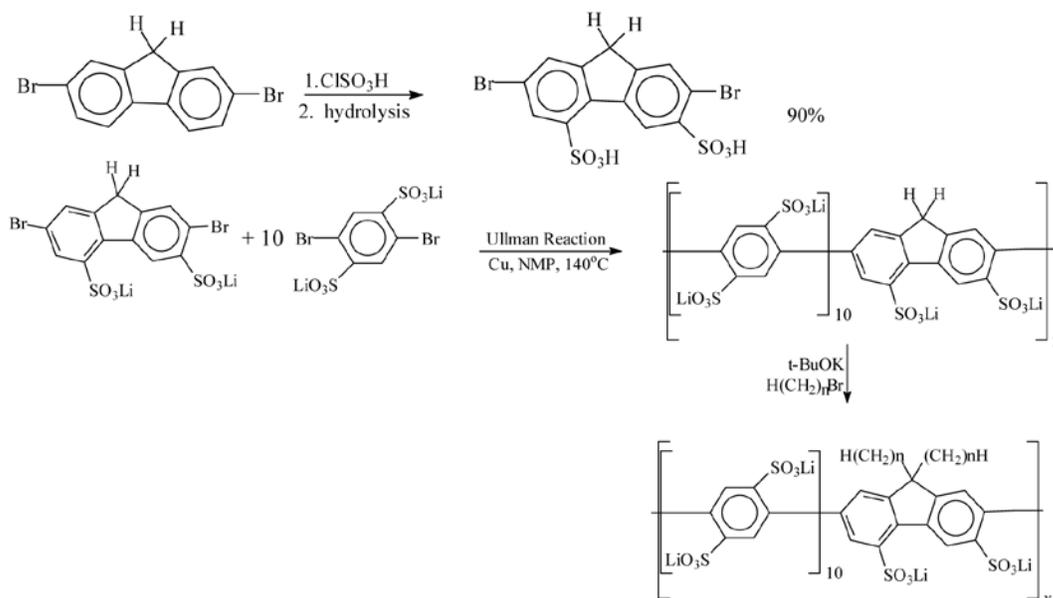
non-collapsible nanopores lined with a high density of sulfonic acid groups which hold water very strongly.

Attached non-polar groups interact by hydrophobic bonding which restricts swelling as humidity rises. Because the molecules are rigid rods, non-polar groups on a chain can interact only intermolecularly, with similar groups on neighboring chains. Thus, a relatively low mole fraction of non-polar groups should make such polymers water insoluble and dimensionally stable with little loss of conductivity. This was demonstrated earlier for poly(p-biphenylene disulfonic acid), PBPDSA, grafts but has not yet been achieved for PPDSA grafts [3].

Results

Copolymerization: Over the past year we have copolymerized several mole ratios of the two base monomers. They reacted well but we have not yet determined how random the copolymerization is. During the reaction the copolymer takes longer to precipitate and the solution (2 to 3% copolymer) becomes viscous, showing that high molecular weight copolymer is soluble. The copolymers hold water very strongly. The best PPDSA reduced viscosities (0.5% solution) were in the range of 0.7–0.9 dL/gm. A copolymer (80/20 ratio, P80B20) had a reduced viscosity of 1.1 dL/gm. An earlier copolymer (P55B45) had a reduced viscosity of 1.5 dL/gm.

We have made a new comonomer, 2, 7-dibromofluorene 3, 5-disulfonic acid, F. It copolymerized well with the two base monomers to give water soluble copolymers. The fluorene group has two active hydrogens which can be replaced easily with alkyl groups, see Scheme 1. We have demonstrated this



SCHEME 1. Approach to Synthesis of New Random Copolymer, P10F1, and Preparation of Water Insoluble Materials for PEMs

with one of its copolymers, P10F1, adding two $C_{22}H_{45}$ groups to each residue. (Calculated IEC = 6.7 mEq/gm.) Unfortunately, we have not been able to find a solvent for the reacted copolymer; it does not swell in water even with such a high IEC. Work is continuing in this area.

Grafting: PPDSA homopolymer and the P80B20 copolymer were grafted with n-octyl benzene (nOB) and/or n-dodecyl benzene (nDDB). Various mole ratios of alkyl benzene to sulfonic acid were used during grafting. At 100/40 and 100/100 (SO_3H /alkyl benzene), grafting went smoothly; grafts containing between 7 and 23 mole% alkyl benzene were obtained. The grafting procedure was improved during the year; oxygen was systematically excluded. Films cast early in the year were black and very brittle. It was difficult to get strips large enough to make conductivity measurements. After oxygen was excluded, cast films were pale yellow and could be easily handled. The new procedure was used for most of the nOB grafts. Figure 1 shows before and after cast films.

Grafted polymers with more than 10 mole% graft were water insoluble. However, all the films swelled rapidly in water and eventually disintegrated to a cloudy suspension. The films became very soft above 50% RH. We think this is because the grafting of non-polar groups was inhomogeneous, with regions of high graft density and long stretches of ungrafted polymer. The homopolymer loses modulus rapidly as humidity rises and becomes a gel above 75% RH.

Water Absorption: Homo and graft polymer water absorption was measured in several ways: weight gain, 1H nuclear magnetic resonance analysis and titration. Figure 2 shows the average λ s as a function of RH for the homopolymer, copolymer, and their grafts with n-octyl benzene. The copolymer holds more water at a given RH than the PPDSA homopolymer. The grafted copolymers hold more water than the starting material, possibly because the hydrocarbon groups force the chains apart. This is best seen at 0% RH (drying at 10 mm and 90°C for one day); the P80B20 grafts have lambdas of two versus one for the starting copolymer. Lambda decreased slightly for the PPDSA graft polymers compared to the starting polymer.

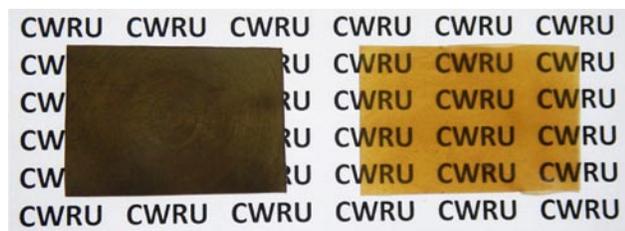


FIGURE 1. Cast Films Of Graft Copolymers: left, PPDSA GnOB 17% old; right P80B20 GnOB 7.3%

Water absorption was compared to that of Nafion117®. The copolymer and its grafts have lambdas about 1.5 to 2 higher over the whole RH range. New preparations of PPDSA have lower lambdas than those reported earlier [5], possibly due to higher molecular weight and better crystallinity, but are still higher than Nafion117®. Grafting lowered lambda but did not seem to affect conductivity.

Conductivity: Conductivity versus RH data for the nOB grafts on PPDSA and the P80B20 copolymer are shown in Figure 3. Conductivity of the PPDSA/nDDB grafts, not shown, was about the same at a given mole fraction of graft. Samples were sent to the Florida Solar Energy Center. The P80B20 GnOB 7.3% conductivity at 80°C was measured there and also at Case; the

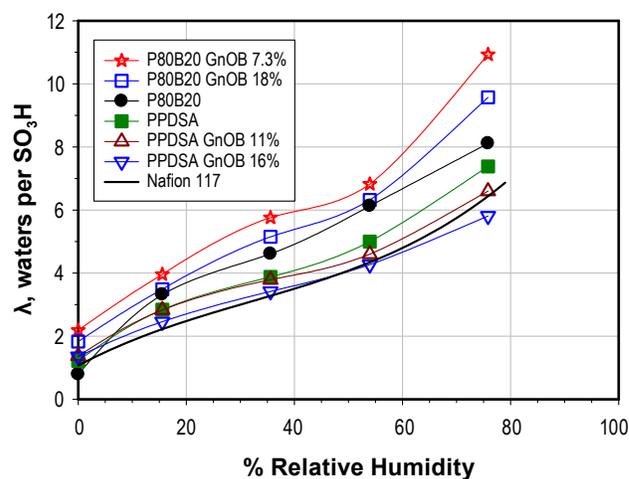


FIGURE 2. Lambda as a function of RH for PPDSA, P80/B20 copolymer and their grafts with nOB compared with Nafion117® [5].

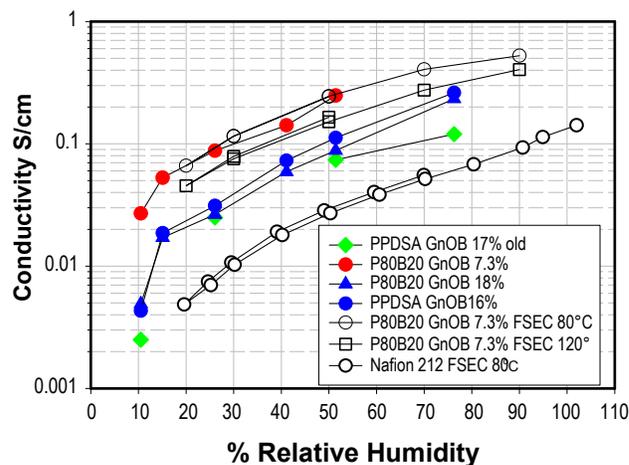


FIGURE 3. Conductivity of nOB-grafted materials, including results from Florida Solar Energy Center. Measurements were at 80°C unless otherwise indicated.

values agreed within experimental error. This gives us confidence in our measurement procedures. The data show that conductivity at lower RH remains high for these PEMs if there is less than 10% grafting. It parallels the PPDSA homopolymer at 80°C [5] but is slightly lower, dropping to 100 mS/cm at 30% RH. At 16 to 18% grafting, conductivity drops further by a factor of two, but is still very high.

When the new PEM conductivities are compared to that of Nafion212[®], it is obvious that the better retention of water generates much higher conductivity at low RH. The 20 to 50% RH conductivity of the best materials is an order of magnitude higher than that of Nafion212[®]. The conductivity drop at 120°C is unexpected and is possibly due to starting the testing at 50% RH. The sample would be so soft at that RH and temperature that the electrode pressure could thin it at the electrode edges, raising its resistance. Several attempts were made at the Florida Solar Energy Center to make a membrane electrode assembly (MEA) using a film of P80B20 GnoB 16%. Under their preparation conditions, the polymer was so soft that it was pressed into the gas diffusion layer; no testable MEA could be made. We expect this problem to vanish when we have dimensionally stable PEMs.

2-D Polymers: These were discussed fully in a special report sent in as a quarterly report, dated April 6, 2010. Unfortunately, Casey Check had to stop research in order to write up his his doctorate thesis. We expect to start research again in September.

We have succeeded in finding procedures and reagents that enabled us to make very large planar molecules in the form of a hexagonal lattice of p-biphenylene disulfonic acids interconnected through benzene rings at the 1, 3, 5 positions (Suzuki reaction using starvation polymerization conditions). The hexagons are calculated to be about 2.2 nm from side to side with a central hole about 1.5 nm in diameter. Wide angle X-ray diffraction scans do not show any sharp reflections; this implies that that there may be some pentagonal or heptagonal holes in the structure.

Because the molecules were very large, they coalesced towards the end of the polymerization into water insoluble aggregates. Since the IEC is ~5.5 mEq/gm and there are no large non-polar groups, this was unexpected. If crosslinking had occurred, the whole solution would have gelled early in the reaction rather than becoming cloudy towards the end. The aggregates could be dispersed by sonication into smaller particles. Films of the sonicated materials were cast from water; they were stable to water after drying and could be handled easily. However, they were brittle in water. Preliminary characterization of initial aggregates by scanning electron microscopy and atomic force microscopy (AFM) showed that the molecules had coalesced into large stacks, showing that



FIGURE 4. AFM Scan of CPPSA-3, Na Salt, after Preliminary Sonication

they were planar. Figure 4 shows an AFM scan of one of the better polymerizations, after sonication to break up secondary association. Such stacks should contain nano-pores parallel to the stack direction. Water was held very tightly; lambda for the best preparations was ~6 at 50% RH. For such systems, conduction would be one dimensional, along the pore axis. These must be perpendicular to the film surface to get high through conductivity. We have not found casting conditions that would do this properly; the work is suspended for the time being.

Conclusions and Future Directions

- Since grafting of long chain alkyl benzenes on PPDSA did not give water-stable materials, probably due to heterogeneous grafting, we are shifting to the production and study of cross-linked films. Biphenyl groups can be grafted homogeneously on the sulfonic acids; they are too small to promote inhomogeneous grafting. Because the biphenyl reactivity is reduced after one end is grafted, it is possible to get water-soluble polymer with as much as 15% grafting. Materials with 5 to 15% graft will be cast and the films will be crosslinked by heating under vacuum at 175°C or higher. (Preliminary studies show that these conditions can be used.) We are determining the reaction conditions needed to get complete crosslinking at a degree of substitution that gives dimensionally stable films, hopefully with high conductivity.

- The new copolymers made using dibromo fluorene disulfonic acid did not have as high viscosity as the homopolymers. We are studying reaction conditions and have made copolymers with higher viscosity. Molecular weight is very important in improving mechanical stability at high humidity. We will make a series of copolymers with various mole ratios of fluorene comonomer (5 to 20 mole%) and graft on alkyl chains, C₈ to C₂₂, to determine which combination gives the best final properties. If these cannot give satisfactory mechanical properties, fluoroalkyl groups can be grafted on the backbone.
- Work will continue on the 2-D polymers. The first task is to find counterions or additives that will keep the material soluble throughout the polymerization to enable us to cast good films. The additive and/or counterion should also be easily removable or replaceable by protons. We have some ideas that will be tested soon. The second task is to make sure that the final structure is completely regular, a purely hexagonal lattice. We will be working on that problem also. Cast films should have the molecules parallel to the film surface and very well stacked. Molecular overlap should be high between the primary stacks to give materials with reasonable strength, though low elongation. Such films should have good conductivity, high modulus and constant dimensions, independent of RH.

Special Recognitions & Awards/Patents Issued

1. 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. It is still pending.
2. An invention record for the 2-D polymers is being processed.

FY 2010 Publications/Presentations

1. Litt, Morton; Granados-Focil, Sergio and Kang, Junwon, Rigid Rod Polyelectrolytes with Frozen-In free volume: High Conductivity at Low RH. *ACS Symposium, Series, Fuel Cell Chemistry and Operation*, Ed. Herring, A. et al, pp. 49-63 Electronic publication 4/2010.
2. Talk at University of Genoa, Genoa, Italy 7/8/10.
3. Talk at IUPAC meeting, Glasgow, Scotland 7/13/10.

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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. Yue Zhang, Ph. D. Thesis, CWRU, 2001; Morton H. Litt, Sergio Granados-Focil; Yue Zhang and Thomas 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. Morton Litt; Sergio Granados-Focil and Junwon Kang, Rigid Rod Polyelectrolytes with Frozen-In free volume: High Conductivity at Low RH. *ACS Symposium, Series, Fuel Cell Chemistry and Operation*, Ed., A. Herring, et al, pp. 49-63 Electronic publication 4/2010.