

Rigid Rod Polyelectrolytes: Effect on Physical Properties Frozen-in Free Volume: High Conductivity at low RH

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Macromolecular Science

Case Western Reserve University

June 11, 2010

Project ID # FC037

Overview

Timeline

- Start date 4/15/2006
- End date 4/15/2011
- Percent complete 80%

Budget

- Total Project Expenses: \$2,023,140
 - DOE \$1,492,571
 - Contractor \$530,569
- DOE Funding
 - FY08 \$350,000
 - FY09 \$243,478
 - FY10 \$356,522

Barriers

- High conductivity at 80°C and <1.5KPa input water vapor pressure
- MEA mechanical and electrical stability in use at elevated temperatures.

Interactions

Robert Savinell
Jesse Wainright
Peter Pintauro
Interest from GM, 3M,
ATK Space Systems

Objectives

- **Synthesize polyelectrolytes that reach or exceed DOE low humidity conductivity requirements.**
- **Use materials and synthetic methods that could lead to cheap PEMs.**
- **Understand structure/property relationships in order to improve properties.**
- **Develop methods to make these materials water insoluble and dimensionally stable with good mechanical properties.**

Milestones

| Month/Year | Milestone or Go/No-Go Decision |
|------------|--|
| 9/07 | Milestone. Make PEMs that meet DOE 2011 conductivity objectives. Done |
| 12/09 | Milestone. Understanding structure is necessary to find right approaches to increase water retention and dimensional stability. |
| 12/09 | Go/No-Go Dimensional stability and improved mechanical properties. Very poor for homopolymers. Must make copolymers with non-polar components that reach requirements, or incorporate water insoluble polyelectrolytes in a reinforcing matrix. |
| 6/11 | Go/No-Go PEM cost. Starting materials and synthetic procedures can be relatively cheap. Synthetic details and upscaling costs need to be worked out. If mechanical properties are good, membranes can be very thin (probable very low gas permeability). |



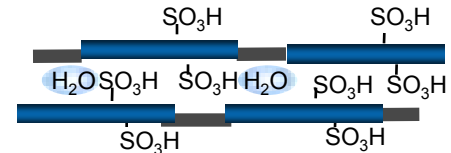
Structural Approach

Frozen in Free Volume: Basic concepts

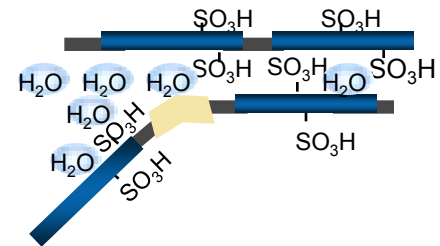
Use rigid-rod nematic liquid crystalline polymers.

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 very low relative humidities.

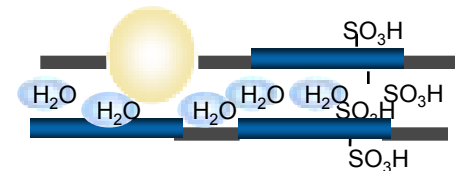
(a). Homopolymer .
Chains can pack closely



(b). Copolymers with angled comonomers



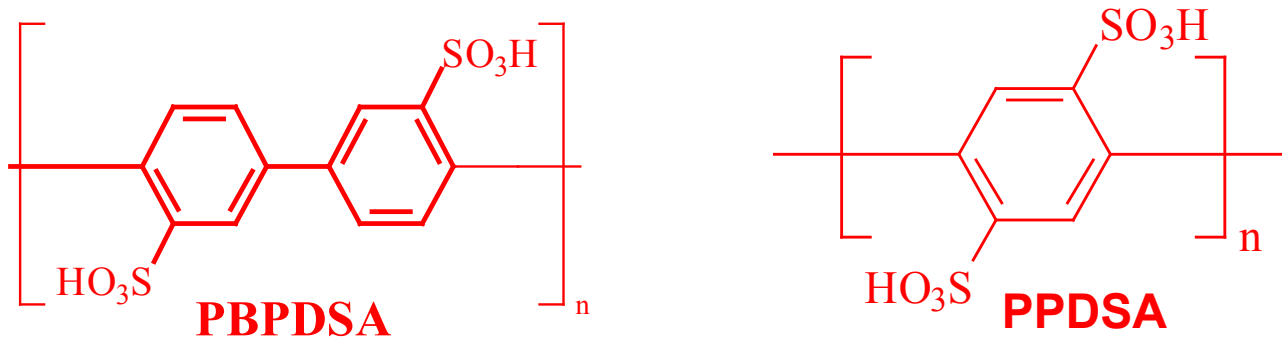
(c). Copolymers with linear, bulky comonomer



Present Approaches

1. Worked with polyimides (2001-2004). The acid form hydrolyzes slowly at room temperature and rapidly at 100°C in water. Best σ at 22% RH and RT was ~ 0.002 S/cm. *Need polyelectrolytes with higher conductivity and stable backbones.*

2. Shifted to poly(p-phenylenes) with one and two sulfonic acids per ring. These have lower equivalent weights (higher IEC) and *cannot* hydrolyze.



3. Initial work (2004 to present) was on poly(biphenyl disulfonic acid), PBPDSA, and its graft copolymers.

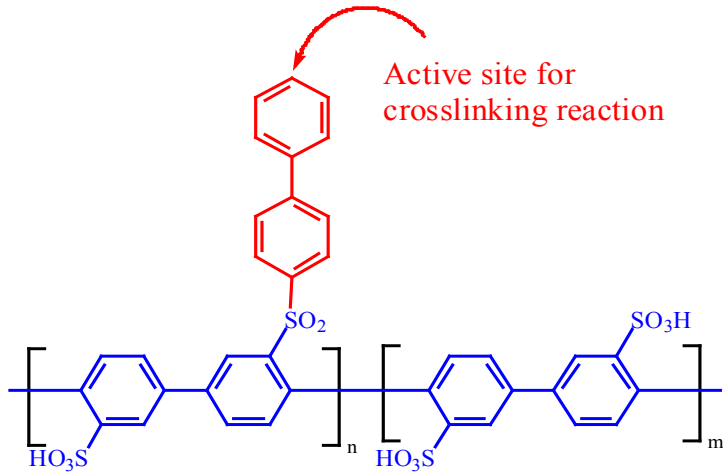
4. The free volume effect on conductivity is much greater with poly(phenylene disulfonic acid) PPDSA. We have shifted almost completely to PPDSA.

5. Reaction conditions were further optimized during the past year. High viscosity homo- and co-polymers of PBPDSA and PPDSA were made. Earlier maximum IV was 1.05 dL/gm; it is now 1.5 dL/gm for homo- and co-polymers. Procedures have been developed for larger scale reactions; 10 to 20 gm polymer batches have been made.

Membrane Stabilization

Grafting done using polyphosphoric acid (PPA)

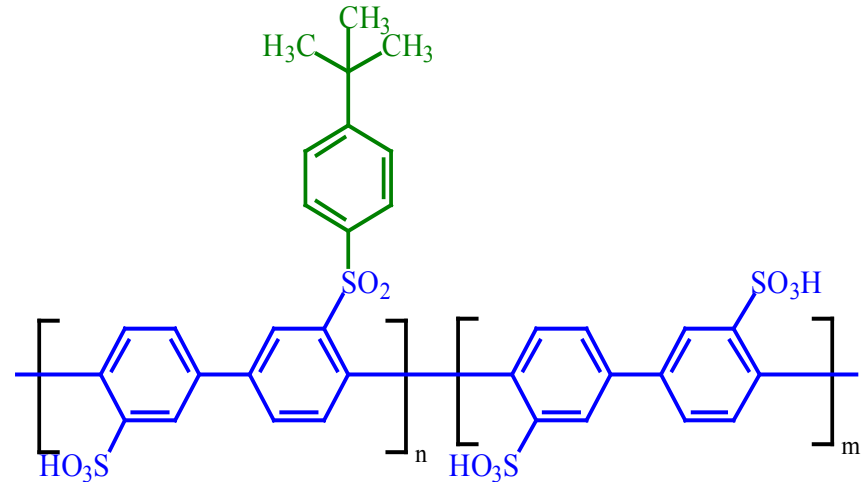
Incorporation of cross-linkable biphenyl groups.



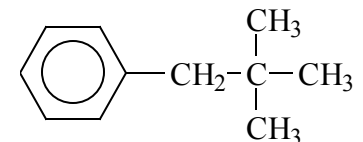
Graft copolymers containing from 5 to 25 mole% of biphenyl sulfone groups were water soluble. 10 minutes at 200°C cross-linked the polymer.

Recent work used neopentyl benzene (NPB), stable in PPA, for grafting. Graft polymers tend to be water soluble. We have shifted to C₈ and C₁₂ n-alkyl benzene grafts on PPDSA.

Incorporation of bulky non-polar t-butyl benzene groups.

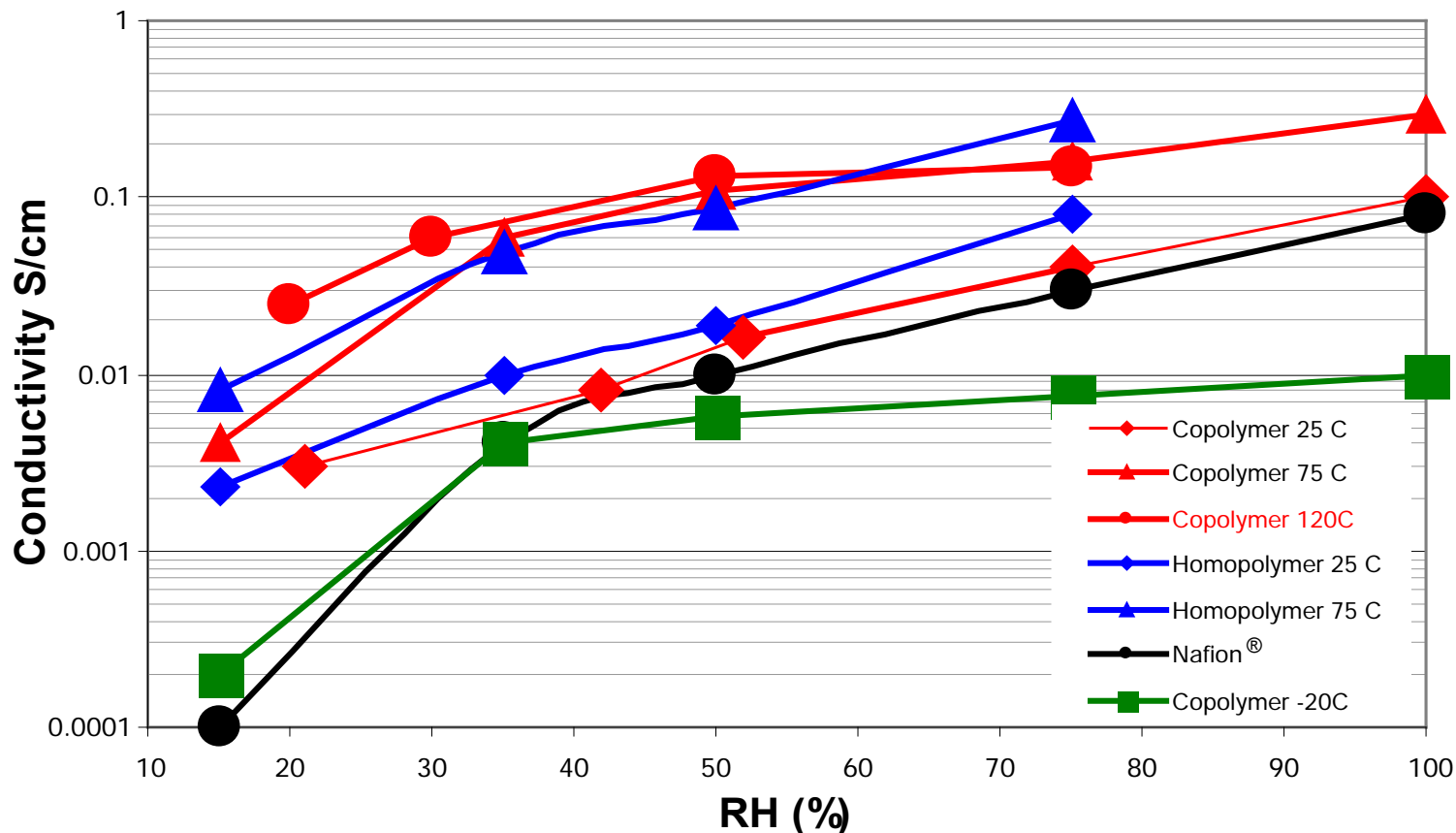


"5" mole% t-butyl benzene or 2,6-di-t-butyl phenol as sulfone graft renders the copolymer water insoluble. t-Butyl groups tend to scramble. Best PEMs showed 27% swelling in Z direction, 0% in X, Y (20 to 100% RH).



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

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



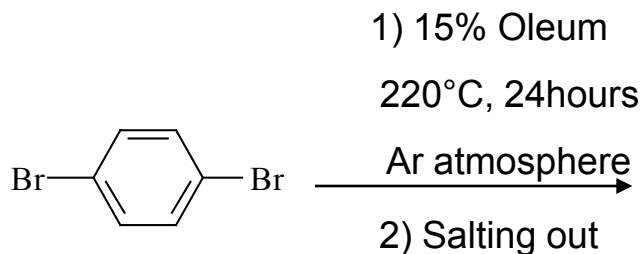
• These early graft polymers reach the DOE benchmarks for 2005.

• Advantage over biphenyl graft: Polymer is soluble in alcohol and can be cast easily.

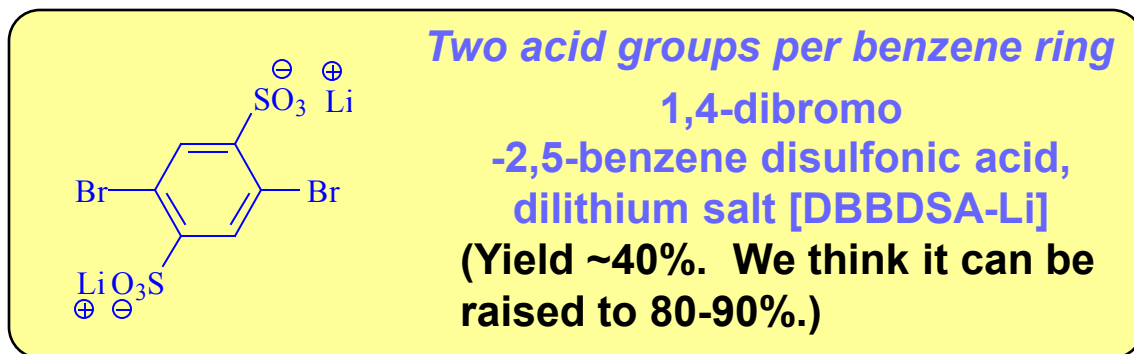
• Problem: Low elongation for both types of graft (low molecular weight?).

PPDSA, a most unusual material

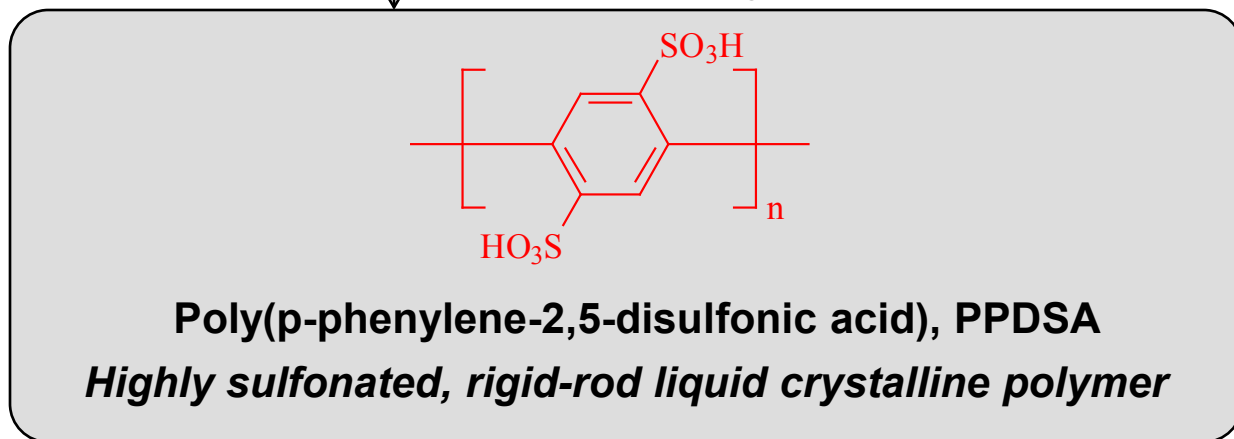
Homopolymerization : *Ullmann coupling*



With Junwon Kang



1. Monomer & copper powder in dry DMF at 135°C for 7 days under Ar
2. Ion exchange to Acid form

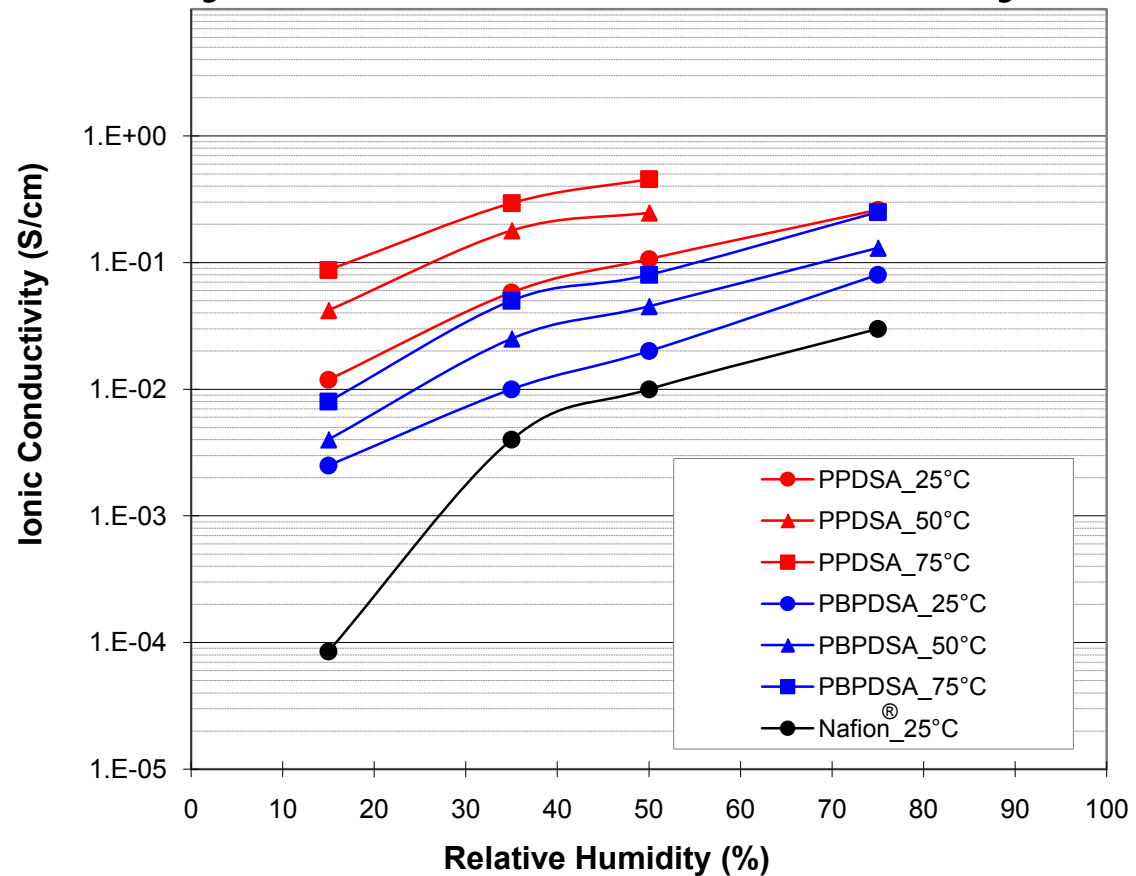
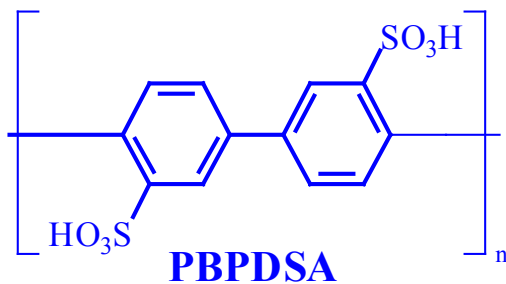
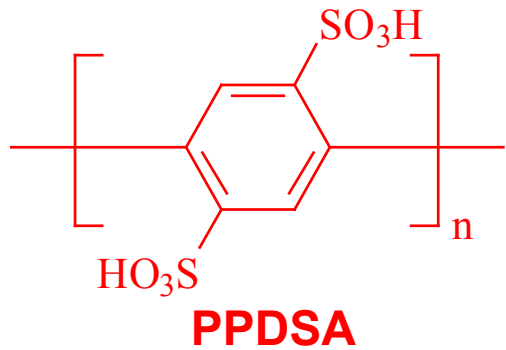


Earlier results: Best DP ~ 170

Present results, 12/30:

- Reaction of **dry** monomer in NMP takes 12 hrs.
- Highest DP reached ~400;
Mwt ~ 48,000, IV~1.5 (0.5%)

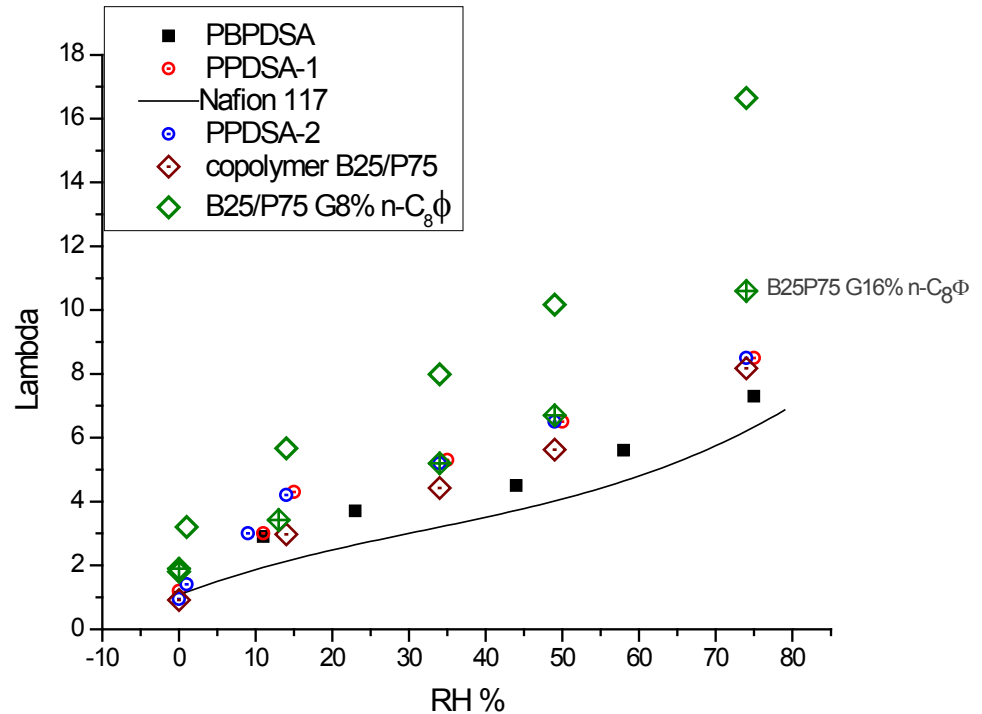
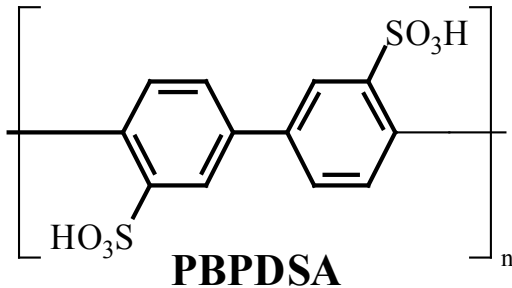
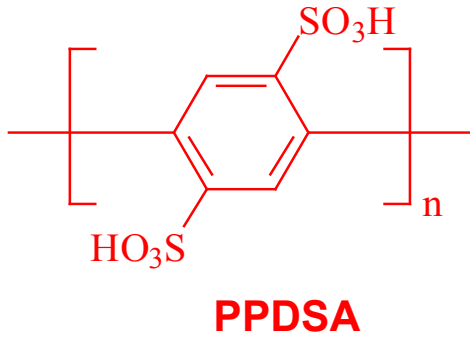
Comparison of PBPDSA and PBDSA: Conductivity vs Relative Humidity



PPDSA and its copolymers should meet the DOE conductivity goals for 2015. $\sigma = \sim 0.1$ S/cm at 75°C and 15% RH. The two monomers copolymerize easily; their copolymers are being studied.

Water uptake for Polyelectrolytes

Comparison of λ vs. RH for Nafion[®] 117 and a series of Rigid Rod polymers and copolymers



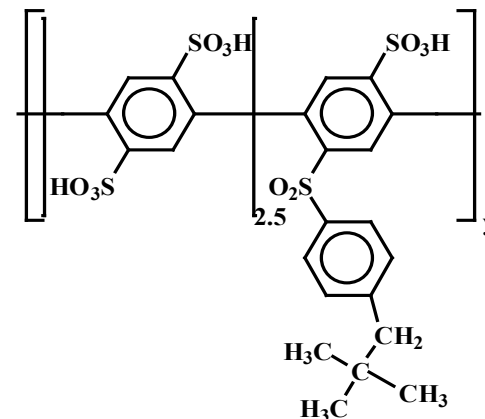
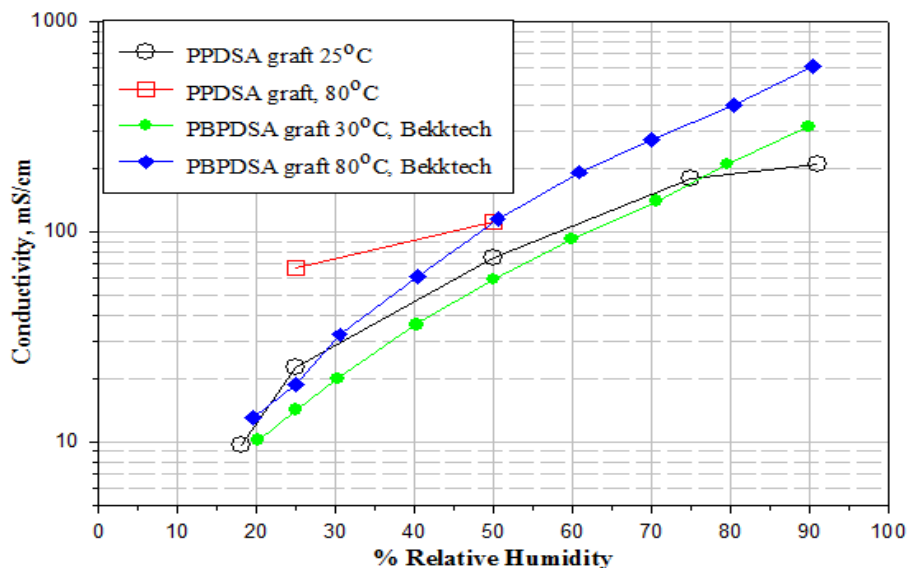
- λ for PPDSA is ~2.5 higher than that of Nafion[®] 117 from 15 to 75%RH. Repeat is same.
- λ for PBPDSA is ~1.2 to 1.5 higher than Nafion[®] 117 from 22 to 75% RH.
- B25P75 copolymer λ is between those of PPDSA and BPDSA.
- Copolymer grafts: -G8 λ very high at low RH. -G16 λ lower, near those of PPDSA.

Recent results with graft copolymers

1. Grafting on PPDSA with NPB.

- 17% of acid groups grafted. Calc. IEC = 6.1 mEq/gm.
- Slowly water dispersible. Very soft at room conditions.

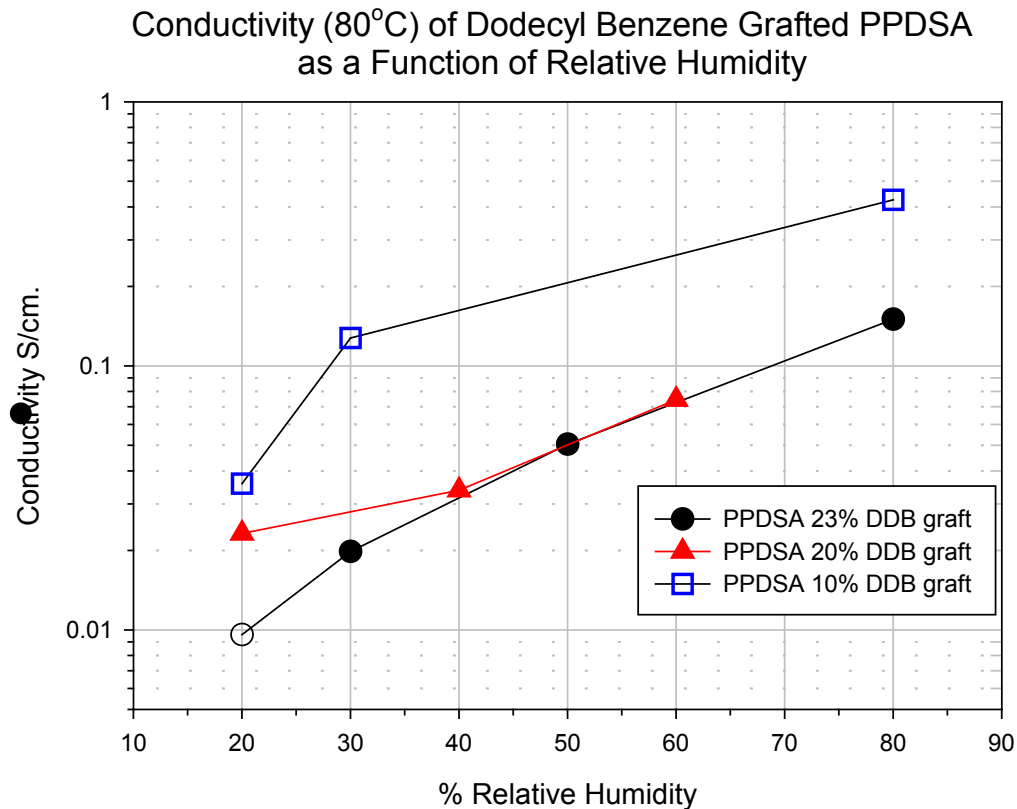
Conductivity of PPDSA 89 (NPB 17 mol% graft) at 25 and 80°C compared with PBPDSA (NPB ~4 mol% graft) (Bekktech RDM-03 data).



- Film not acid washed; may contain some DMF.
- σ at 25% RH and 25°C is 50% higher than that of RDM-03 at 30°C. Same σ at higher RHs.
- Conductivity at 80°C shows the effect of PPDSA high water retention at low RH.

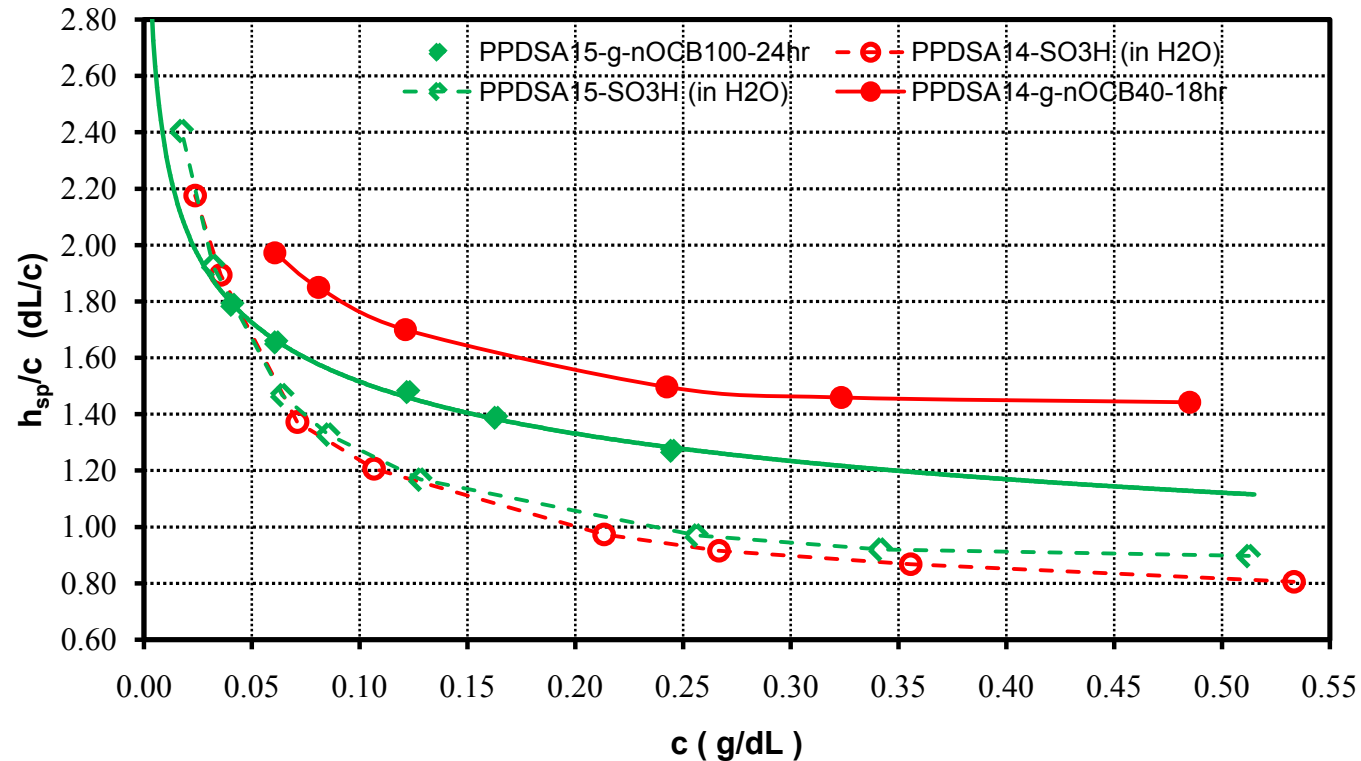
Recent results with graft copolymers 2: n-dodecyl benzene

- All polymers were very dark; phase separated during casting. n-Butanol gave best results.
- Films disintegrated in water; they were not washed with acid or water.



- Conductivity of 10% graft at 35% RH 30% lower than that of pure PPDSA.
- 20% Graft conductivity the same or lower than the BPDSA graft. Butanol could be left.

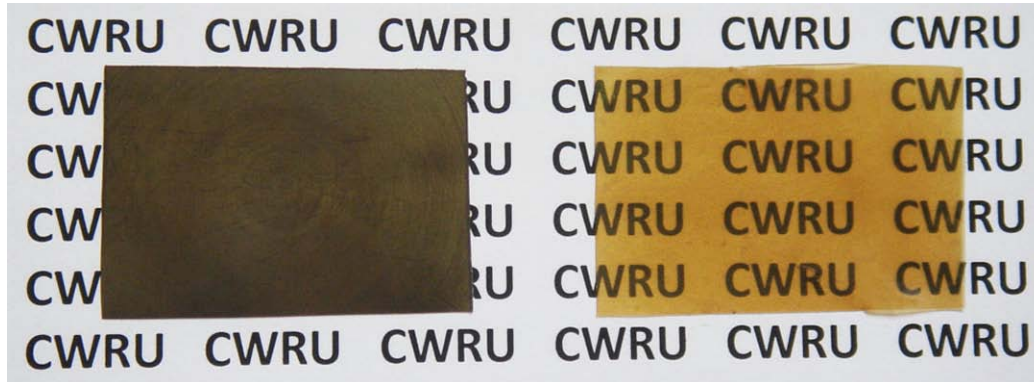
Comparison of reduced viscosity for starting and n-octyl benzene grafted polymers



- PPDSA14-G12% and PPDSA15-G17%
- Grafting raises reduced viscosity. True for almost all grafts.

Recent results with graft polymers 3

n-Octyl benzene grafts



PPDSA15-G 17% n-OB, IEC = 5.7 mEq./gm B25P75-G 8% n-OB, IEC = 6.5 mEq./gm

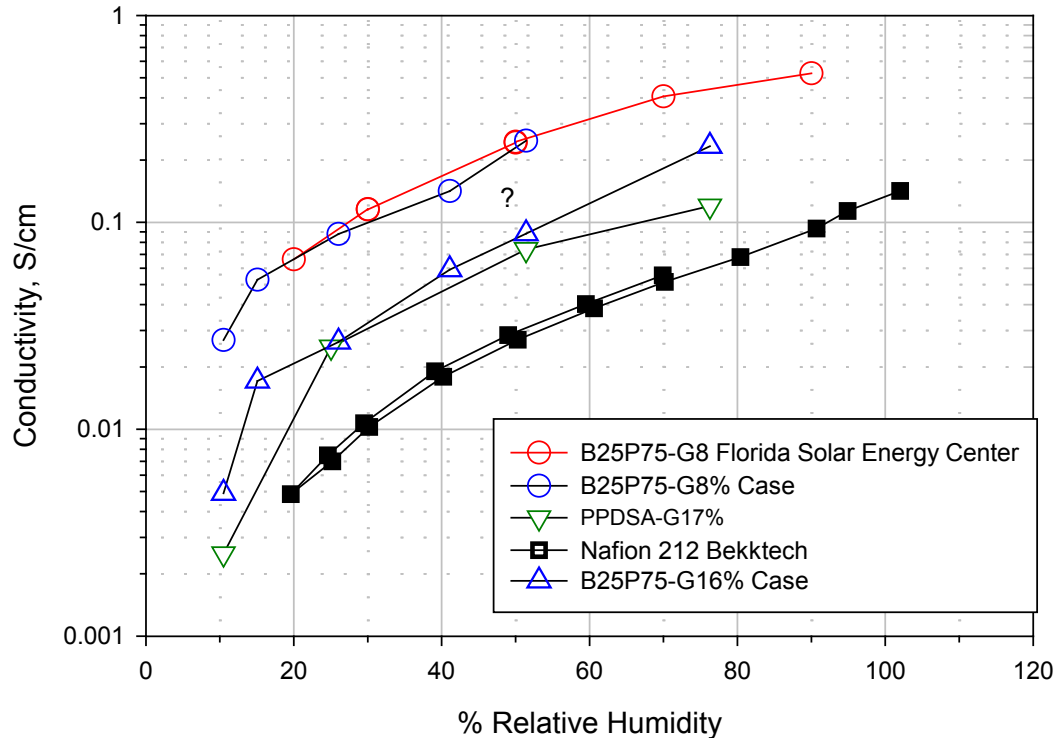
Old versus new grafting procedure (complete exclusion of oxygen)

- Films cast from methanol solution in a Teflon[®] dish.
- Neither film is stable in water. The dark one disintegrates. The light one (from grafted phenyl/biphenyl copolymer) slowly dissolves to give a clear solution.
- A 16% graft prepared using the new procedure swelled in water and disintegrated. We are looking at different casting solvents.
- Conductivity very high for B25P75-G8%. B25P75-G16 conductivity measured at Case.
- Both new grafts form liquid crystal films with chains parallel to surface. PPDSA grafts not liquid crystal.

Recent results with graft polymers 3

n-Octyl benzene

B25P75-G8% and G16% Conductivity at 80°C, compared with PPDSA-G17% and Nafion®212



- Our results, based on saturated solution vapor pressures, agree with Florida's results.
- B25P75-G8%: high conductivity, not as good as PPDSA. Reasonable mechanical properties. Easily handled but low elongation.
- B25P75-G16%: reasonable conductivity and mechanical properties. Water insoluble but swells.
- PPDSA-G17%: high humidity conductivity worse than PBPDOSA graft tested earlier, but higher <30% RH.
- All conductivities much better than that of Nafion® 212.

Discussion of grafting results

Problems

1. Polymer held at 125 to 140°C in very acidic environment, PPA. [Degradation?](#)
2. Hydrocarbon to be grafted not soluble in PPA. Grafting takes place at interface. Long alkyl tails can form hydrocarbon micelles. All polymers dispersible in water to form emulsions even at high grafting degree. [Inhomogeneous grafting?](#)
3. Until recently, oxygen not completely excluded during grafting. Films become very dark and have very bad mechanical properties. [Oxidative coupling of alkyl benzenes before grafting?](#)

Analysis

1. [Degradation?](#) Polymer viscosities increase after grafting and titration shows no loss of acid.
2. [Inhomogeneous grafting?](#) Probable; see point 3. Graft polymer yields were well below 100%. For older grafts, no solvent tried gave good films; there was phase separation during casting – very poor mechanical properties. Neopentyl benzene grafted well, but tail was too short to confer insolubility.
3. [Oxidative coupling of alkyl benzenes before grafting?](#) Older, dark grafts did not form liquid crystal films – very large molecules grafted? Neopentyl benzene grafts were light colored – too hindered to oxidize easily? Grafts made using oxygen exclusion give light colored, easily handled, liquid crystal films.

Possible routes to better materials

Grafting: 1. Cast from low polarity solvent or solvent combinations that include a small fraction of medium boiling non-polar liquid. As the solvent evaporates, the non-polar portion swells the alkyl tails while the acid part aggregates. The alkyl tails can overlap as the solvent evaporates, hopefully giving good hydrophobic bonding.

We have tested this with B25P75-G16% n-OB. The resulting film can be created without breaking. It swells in water but does not disintegrate.

2. Graft biphenyl groups on the backbone. These should graft homogeneously; the grafted moiety is too small and too polar to dissolve free biphenyl. Cast films can be cross-linked by heating to $\sim 200^{\circ}\text{C}$.

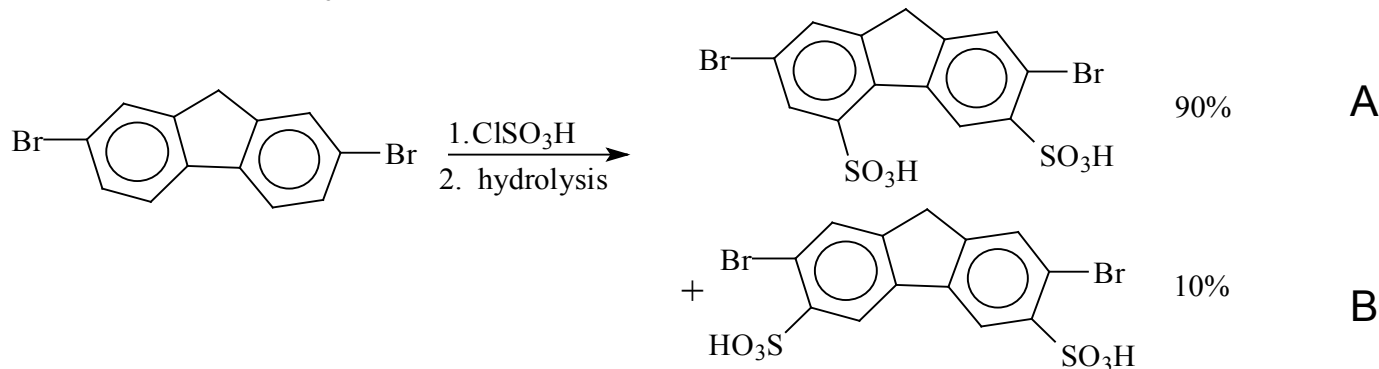
Copolymerization: If the monomer is copolymerized with a co-monomer that can be post-reacted with alkyl or fluoroalkyl groups, the copolymers can be made water insoluble. Good copolymerization implies relatively random placement.

We have developed a much simpler comonomer than those proposed last year. It has been reacted and gives reasonable copolymers. We have just shown that the comonomer can react with alkyl halides to add alkyl groups. This approach is expanded on the next slides.

Copolymer Syntheses

Model reactions: Approaches proposed and tried last year gave poor yields of intermediates. We decided to make and test 2, 7-dibromofluorene 3, 6-disulfonic acid as a comonomer. It is a direct analogue of the monomer reactive ends and has two replaceable hydrogens.

Synthesis of dibromofluorene disulfonic acid

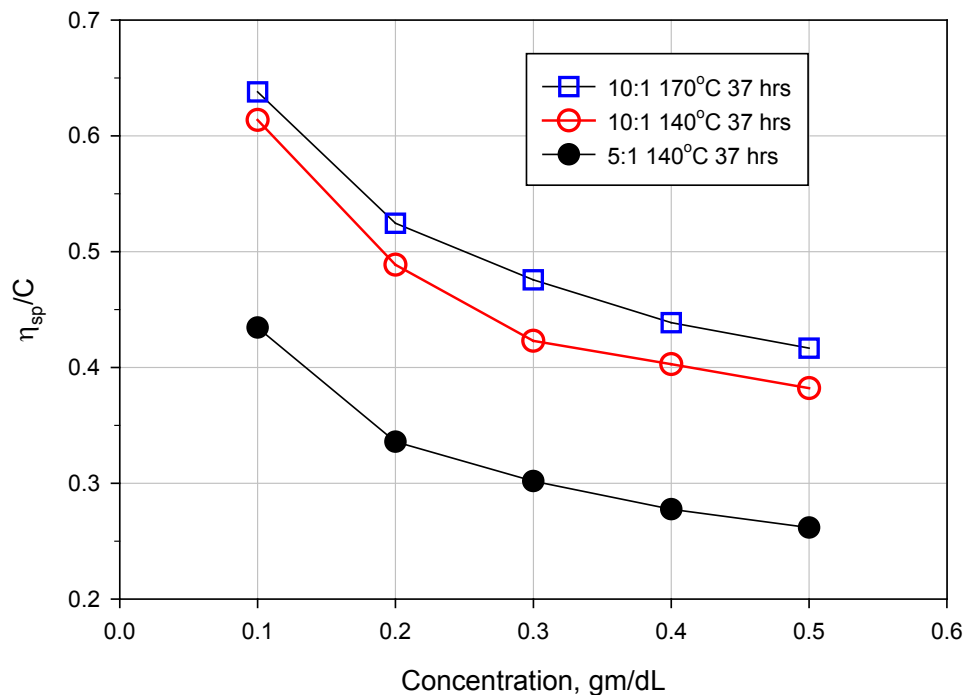


We hoped that 2, 7-dibromofluorene 3, 6-disulfonic acid, B, would be the major product. Reaction with chlorosulfonic acid gave 10% B and 90% A; fuming sulfuric acid gave pure A. We therefore copolymerized A with the monomers. Reasonably high molecular weight copolymers were obtained using either monomer! The copolymers precipitated after the reaction had run for ~10 hours.

Copolymer synthesis and properties

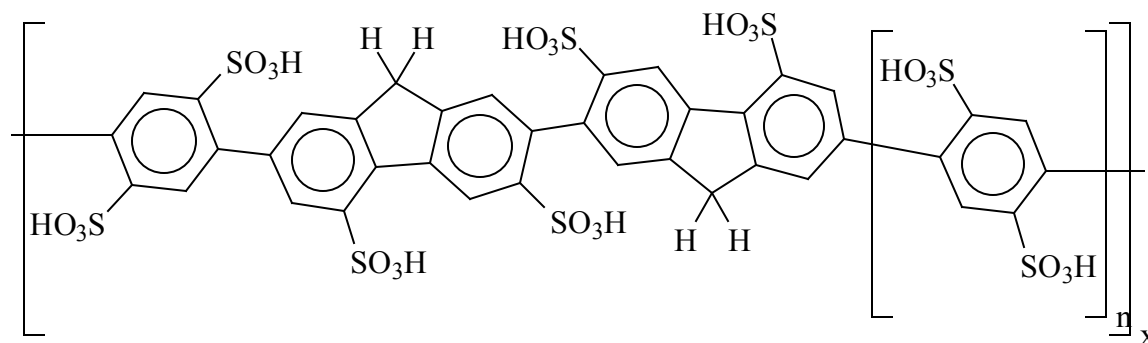
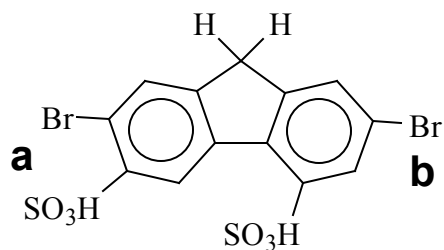
Comonomer was homopolymerized, and copolymerized with dibromo phenylene disulfonic acid in 5/1, 10/1 and 20/1 mole ratios, and also with dibromo biphenyl disulfonic acid.

Reduced viscosity plots of phenylene/fluorene copolymers:
Effect of mol ratio and polymerization conditions



- The lower the monomer/comonomer ratio, the lower the final viscosity.
- Reaction at 170°C raised the molecular weight slightly.
- Molecular weight limited by precipitation of polymer.
- Polymers purified by ultrafiltration.

Probable copolymer structure and reactions



2, 7-dibromo fluorene 3,5-disulfonic acid

NMR studies of the copolymers and the fluorene homopolymer imply that the structure above forms. The **a** side of the fluorene is the most reactive group in the system; the **b** side is least reactive. The fluorene dimerizes first; the dibromo phenyl monomer then reacts with itself and the fluorene dimer. Polymerization stops when the molecules precipitate. (We are studying procedures to keep the polymers soluble during polymerization.)

The aliphatic hydrogens shown are relatively acidic; many literature procedures have been developed to quantitatively replace them with alkyl groups. We found that the monomer reacts quantitatively with dodecyl bromide; we are working on reacting the polymer.

The great advantage of this system is that no sulfonic acid groups are lost when alkyl groups are added. If a 10/1 fluorene copolymer is substituted with two dodecyl groups ($n=19$, ~20 volume% non polar), its IEC would be 7.3 mEq./gm. At a 5:1 mole ratio, the IEC would be 6.5 meq/gm. A 20% n-octyl benzene graft on PPDSA has an IEC = 5.25 mEq./gm.

Present Problems

- Molecular weight limited by polymer precipitation as reaction proceeds. However, DP has risen as we gain experience. Polymers are rigid rods and tend to have poor elongation.
- Homopolymers are water soluble. Grafting with non-polar moieties has made water insoluble polymers with very high low RH conductivity. However, grafting is heterogeneous and not easily scaled up. Film water resistance is poor due to heterogeneity.
- Most co-monomers tried did not copolymerize. The only ones that reacted well had bromobenzene sulfonic acid moieties at each end.

Approaches to Solutions

- Increase in chain length should increase polymer elongation and break strength. We are studying ways to improve polymer solubility during polymerization.
- Non-polar tails in rigid rod materials must interact *intermolecularly*. Hydrophobic bonding should be effective even at high IEC, generating water insolubility and dimensional stability (e. g. grafted PBPDSA and PPDSA).
- Grafting of long chain moieties on sulfonate groups seems to be heterogeneous. Small molecule grafting, e.g. biphenyl, should be homogeneous. Cast films can be post crosslinked. We would have dimensional stability but very poor elongation.
- Copolymerization with a polar comonomer should be homogeneous. If it has reactive sites, long alkyl or fluoroalkyl chains can be post-reacted to generate water stability. We found one comonomer that fits the requirements, 2, 7-dibromofluorene 3, 5-disulfonic acid, made in ~100% yield from commercial material in one step.
- If necessary, the final polymers can be put into an expanded matrix of reinforcing polymer to improve mechanical properties.

Future Work

FY 2010 & 2011

- Optimize polymerization techniques to: 1. increase chain length (solvent and counterion variation) and 2. make larger polymerization and copolymerization runs to generate materials for extensive testing.
- Continue grafting studies to determine if it is possible to make dimensionally stable polymers with high conductivity. If not, make cross-linkable grafts.
- Refine copolymerization of fluorene comonomer and develop good procedures for substituting with alkyl and fluoroalkyl groups.
- Study electrospinning (Pintauro) of copolymers with binder to make dimensionally stable films.
- Make and characterize water insoluble PEMs for conductivity, dimensional stability and mechanical properties. Do initial characterization of the best as MEAs in single fuel cells.
- Send our better materials to Florida for extensive characterization.
- Continue studies to understand structure/property relationships in the materials. **Structure and organization determine properties.**
- Start study of polyelectrolyte stability under “working” conditions.

Summary

- Rigid rod, liquid crystalline polyelectrolytes are unique materials. We have made water insoluble PEMs with high IEC and high conductivity by grafting alkyl benzenes on the sulfonic acids. Some have dimensional stability.
- Frozen-in free volume can be built in, producing high λ at low RH, facilitating high conductivity, viz 0.1 S/cm at 15% RH and 75°C for PPDSA.
- Problems are: 1. Poor mechanical properties because they are rigid rod materials, and 2. Very poor copolymerization with non-polar comonomers.
- Present approaches to solutions are:
 1. Copolymerization with a new class of comonomer which can be post-reacted to make water insoluble, high IEC copolymers. These should hold water well, increasing λ and therefore conductivity at low RHs.
 2. Increasing molecular weight by finding better polymerizations conditions. Such polymers should have better mechanical properties.
 3. Grafting, cross-linking and use of a flexible matrix are fallback positions, but are being pursued concurrently.