

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

Morton Litt Macromolecular Science
Case Western Reserve University

May 19, 2009

Project ID # FC_08_Litt

Overview

Timeline

- Start date 4/15/2006
- End date 4/15/2011
- Percent complete 60%

Budget

- Total Project Expenses
 - DOE \$1,492,572
 - Contractor \$530,569
 - DOE
 - FY07 \$230,204
 - FY08, \$241,000
 - FY09, Est. \$343,168
- | | Cost Share |
|------------------------|------------|
| • FY07 \$230,204 | \$111,680 |
| • FY08, \$241,000 | \$113,220 |
| • FY09, Est. \$343,168 | \$120,000 |

Barriers

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

Interactions

Tom Zawodzinski
Robert Savinell
Jesse Wainright
Peter Pintauro
Interest from GM, 3M

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).

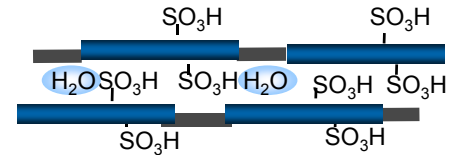
Structural Approach

Frozen in Free Volume: Basic concepts

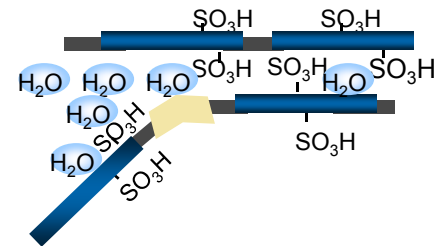
Use rigid-rod nematic liquid crystalline polymers.

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.

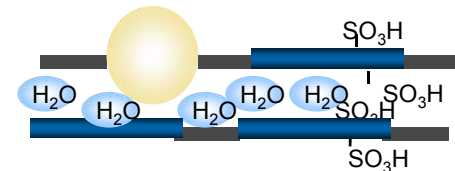
(a). Homopolymer .
Chains can pack closely



(b). Copolymers with angled comonomers



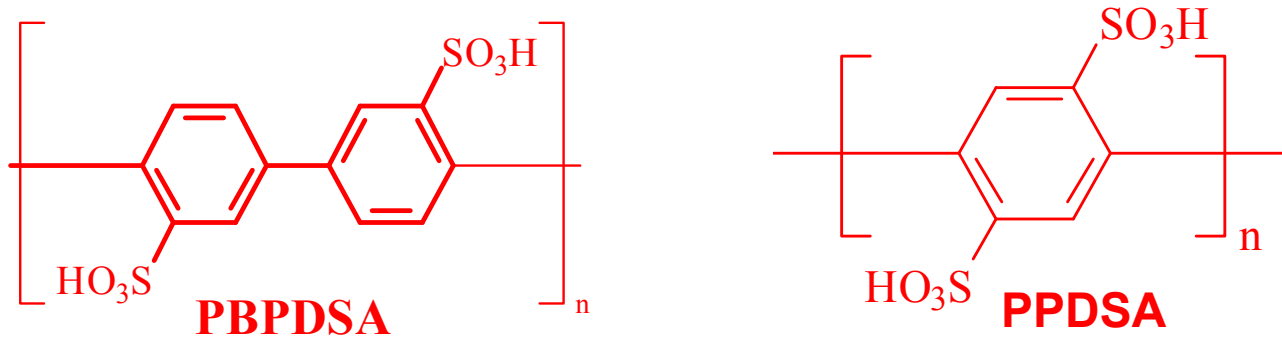
(c). Copolymers with linear, bulky comonomer



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.

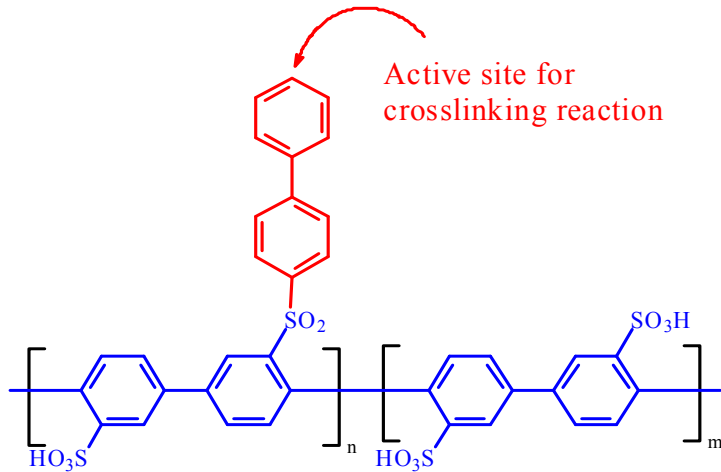
4. The free volume effect on conductivity is much greater with poly(phenylene disulfonic acid) PPDSA. We are working on both systems at present.

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

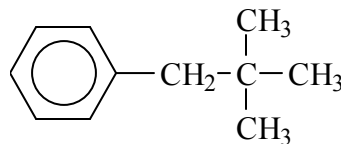
Grafting done using polyphosphoric acid (PPA)

Incorporation of cross-linkable biphenyl groups.

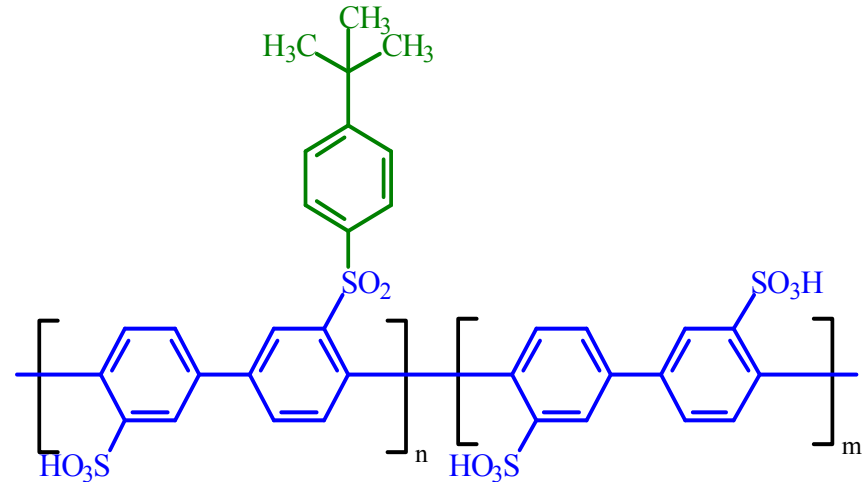


Graft copolymers containing from 5 to 25 mole% of biphenyl sulfone groups were water soluble. 10 minutes at 200°C cross-linked the polymer.

Recent work uses neopentyl benzene (NPB) for grafting. This is stable in PPA.



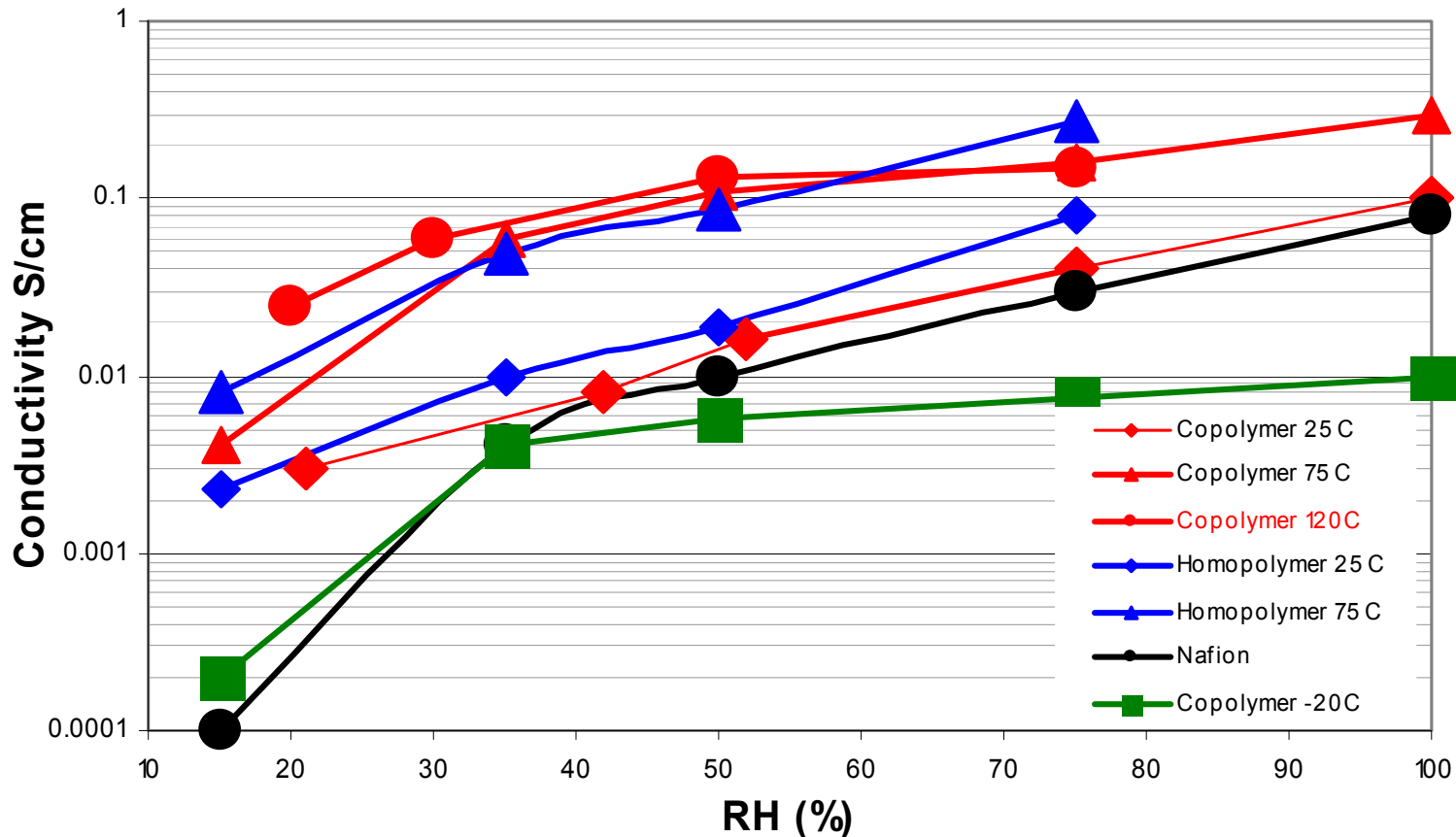
Incorporation of bulky non-polar t-butyl benzene groups.



"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



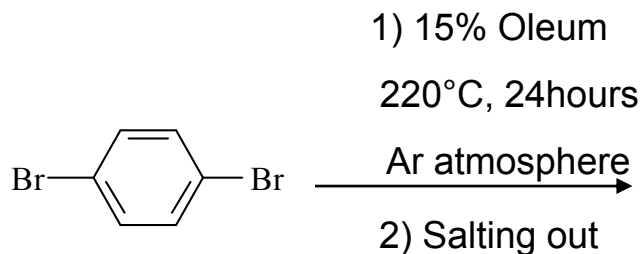
• These early graft polymers reach the DOE benchmarks for 2005.

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

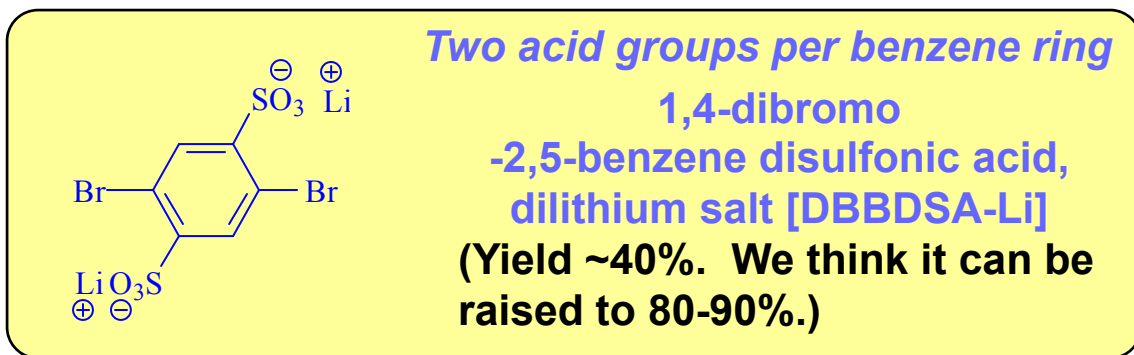
• Problem: Low elongation for both types of graft (low molecular weight?).

PPDSA, a most unusual material

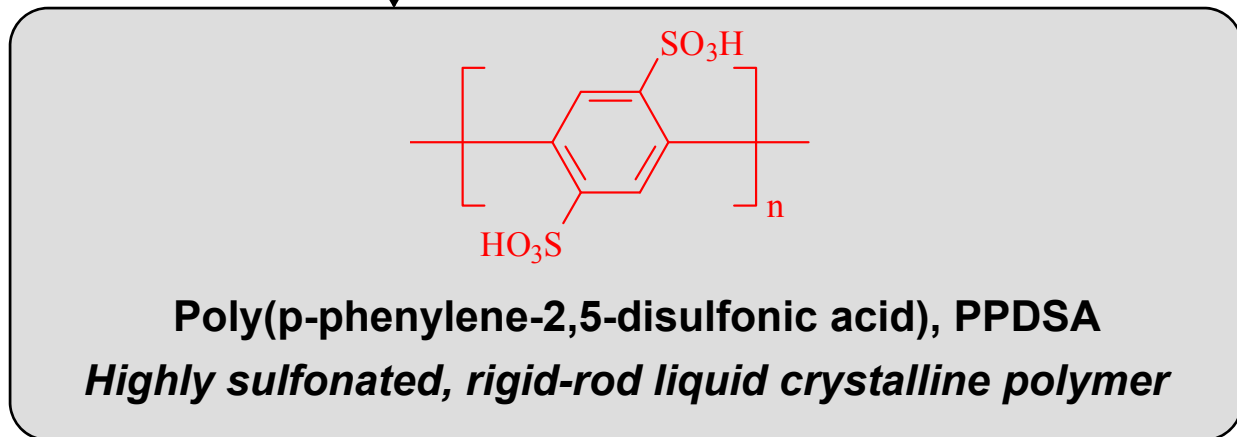
Homopolymerization : *Ullmann coupling*



With Junwon Kang



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

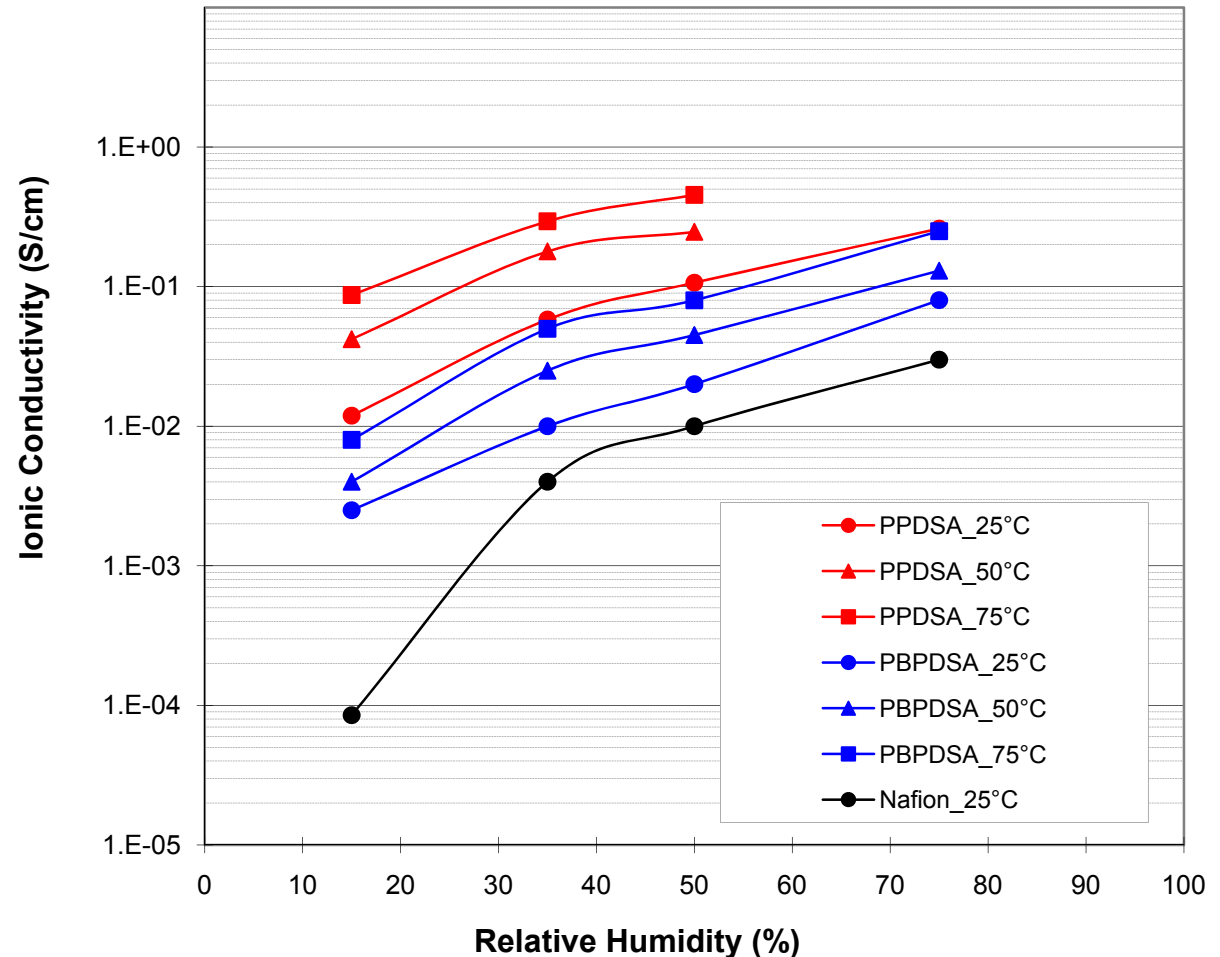
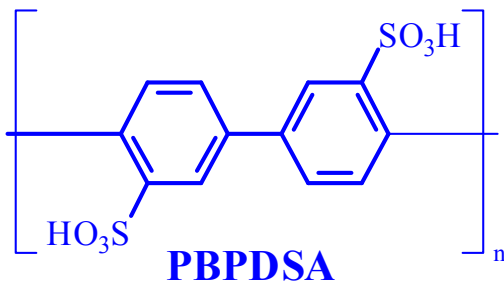
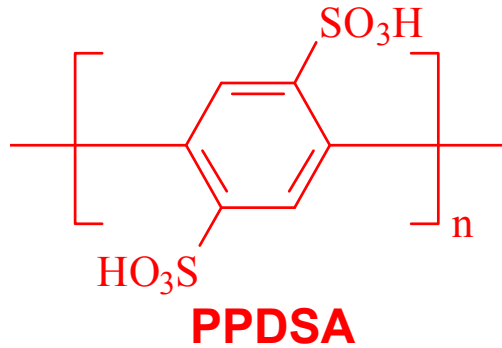


Earlier results: Best DP ~ 170

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%)

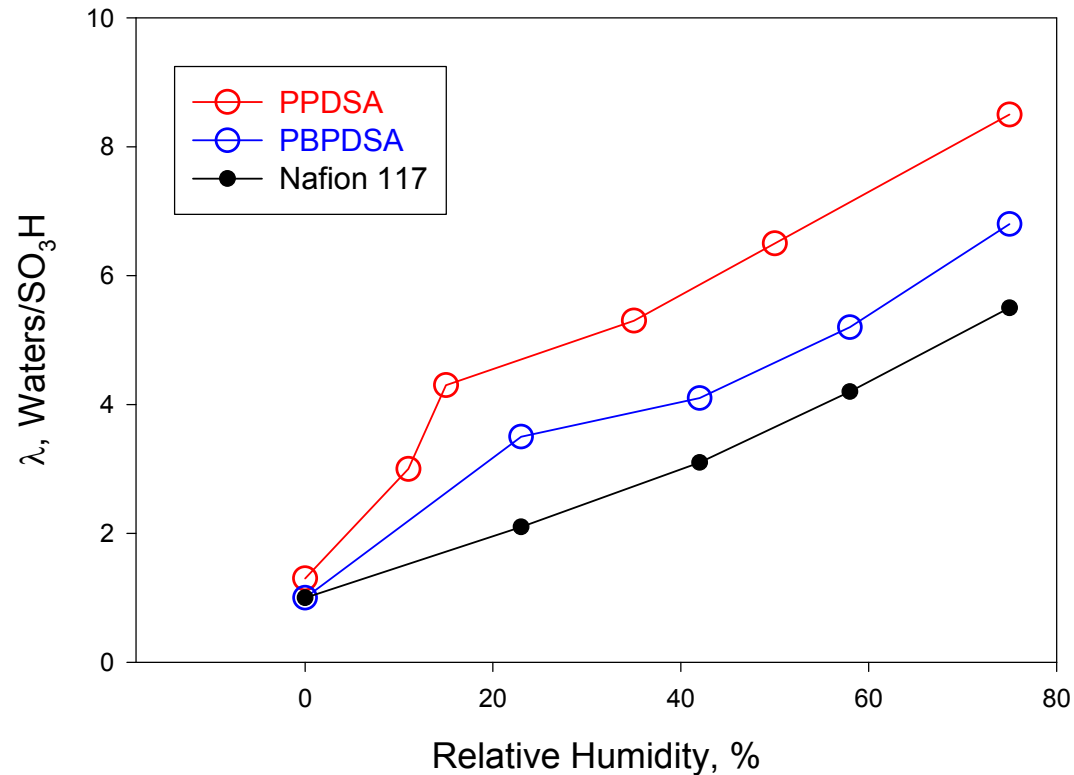
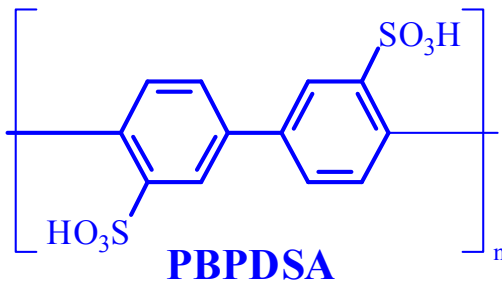
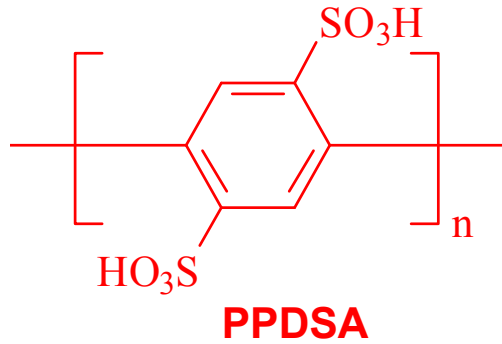
Comparison of PBPDSA and PBDSA: Conductivity vs Relative Humidity



PPDSA and its copolymers should meet the DOE conductivity goals for 2015. $\sigma = \sim 0.1$ S/cm at 75°C and 15% RH.

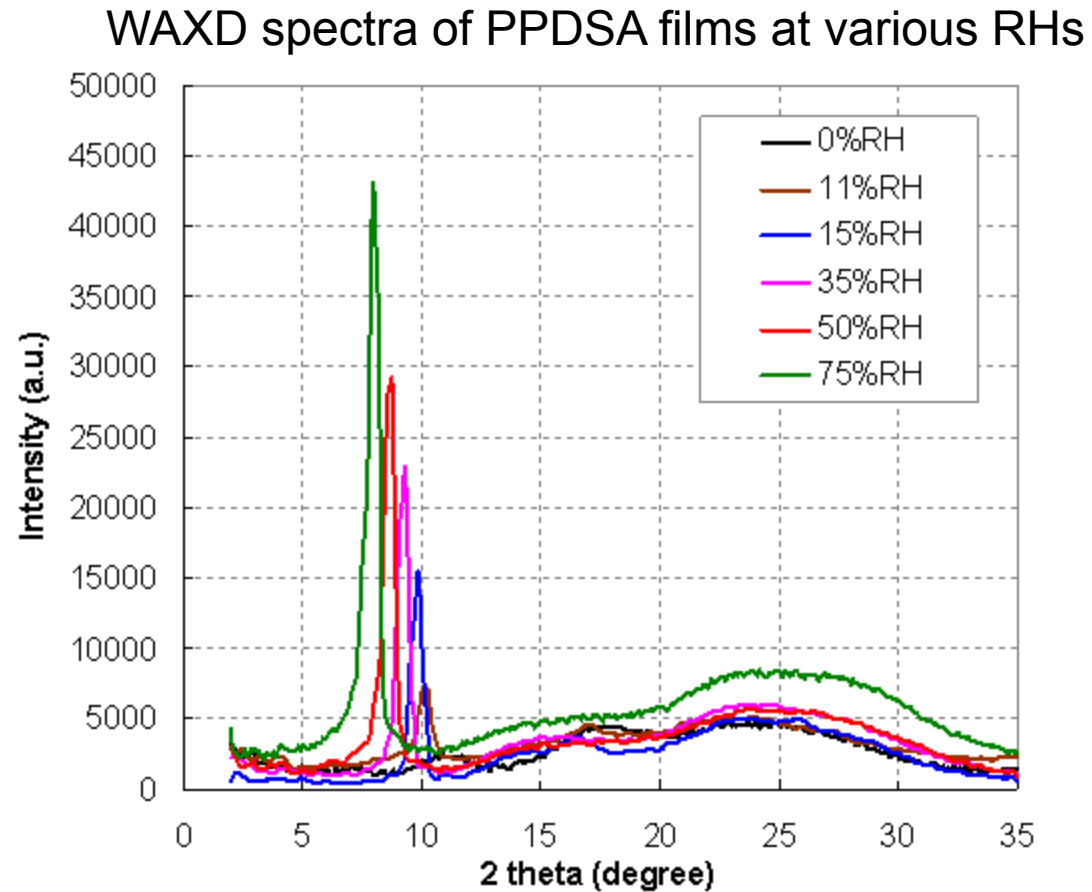
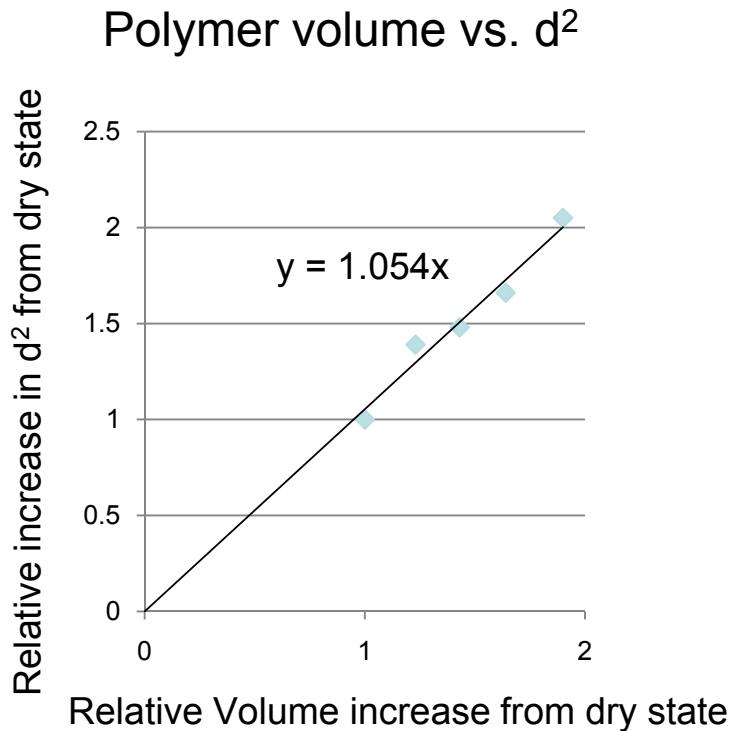
Water uptake for Polyelectrolytes

Comparison of λ vs. Relative Humidity for Nafion[®] and Rigid-Rod Polyelectrolytes



- PPDSA: λ is ~2.5 more than that of Nafion[®] 117 from 15 to 75%RH. σ ~10x higher than Nafion[®] from 35 to 75% RH, > 100x higher at 15% RH.
- PBPDSA: λ is ~1.2 to 1.5 more than Nafion[®] 117 from 22 to 75% RH; σ ~ 2x Nafion[®] σ at 35% RH and above, ~ 30x higher at 15% RH.
- High IEC might promote high λ . **However**, rapid rise of λ at low humidity implies that frozen-in free volume is the major cause.

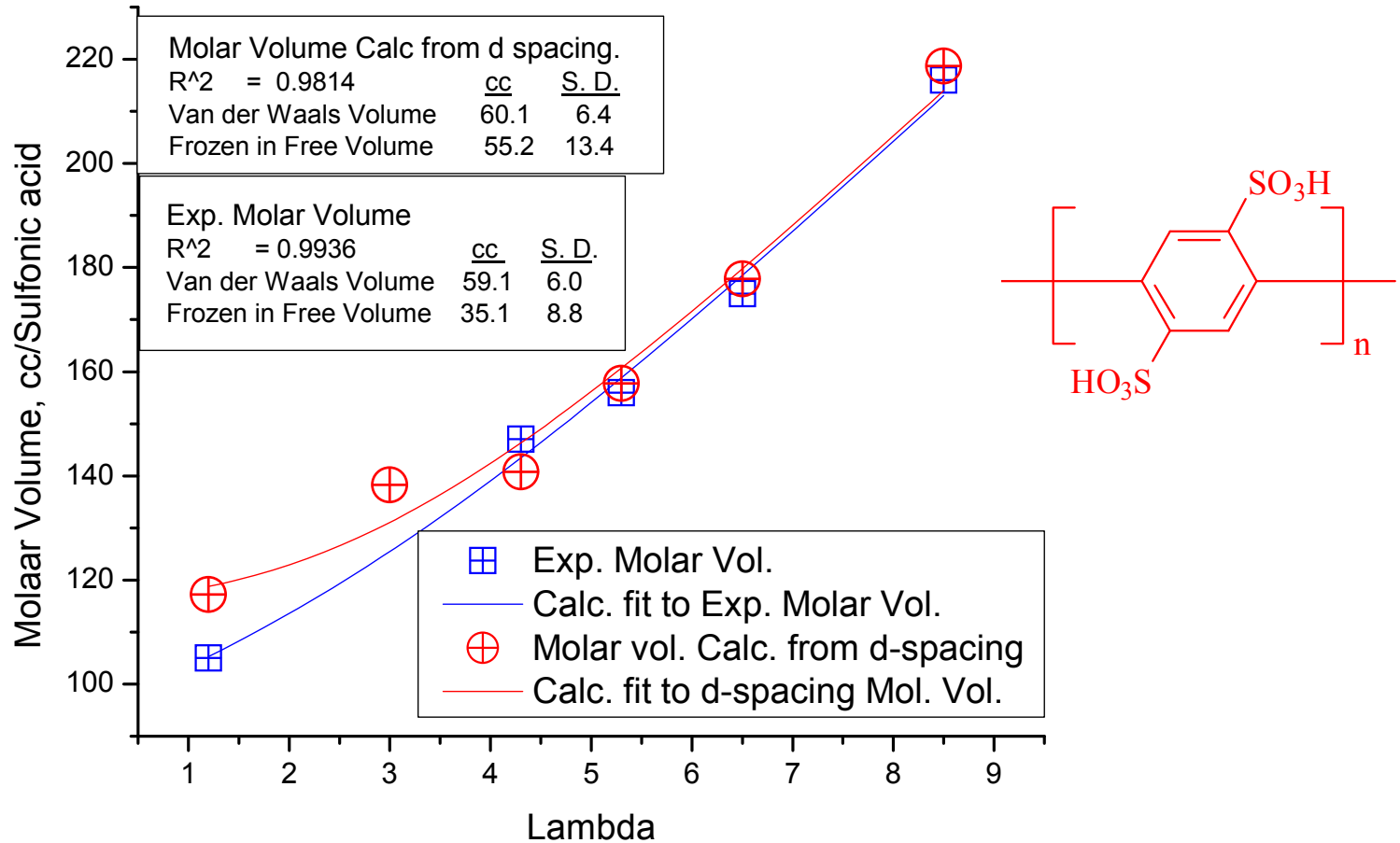
PPDSA: WAXD (transmission mode) spacings, and water absorption.



1. Slope of relative volume change vs. relative d^2 change is **1.0**. This shows that chains are parallel within a domain, generating 2D expansion.
2. Long spacings are large and sharp only in transmission mode, implying that molecules are mainly perpendicular to film surface.

Frozen in Free Volume in PPDSA due to crowding of acid groups

PPDSA: Determination of Van der Waals and Frozen-in Free Volume



Fitting Equation 1: *Experimental Molar volume* = $18 \cdot \lambda + I_1 + I_2 \cdot (1 - \tanh(K \cdot \lambda))$

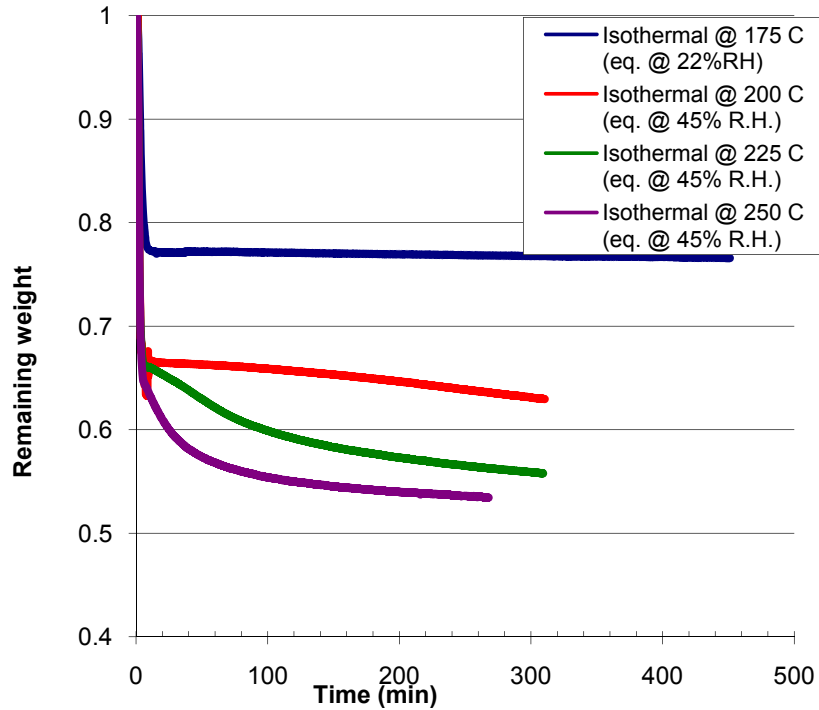
Fitting Equation 2: *Molar volume* = $1.782 \cdot d^2 = 18 \cdot \lambda + I_1 + I_2 \cdot (1 - \tanh(K \cdot \lambda))$

I_1 = Polymer Van der Waals Volume. I_2 = Frozen in Free Volume. $(1.782 = 0.602 \cdot 2.1^2 \cdot \text{cc}/\text{\AA}^2)$

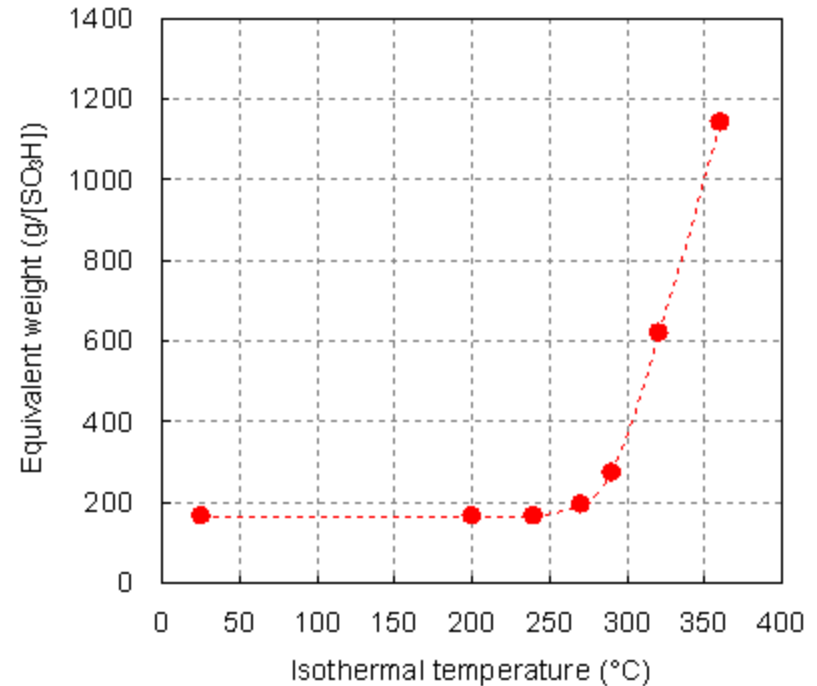
Free volume per acid group is 35 to 55 cc, 2 to 3 water molecules. Frozen in free volume almost equal to polymer Van der Waals volume.

Thermal Stability of Polymers

Remaining weight vs. time



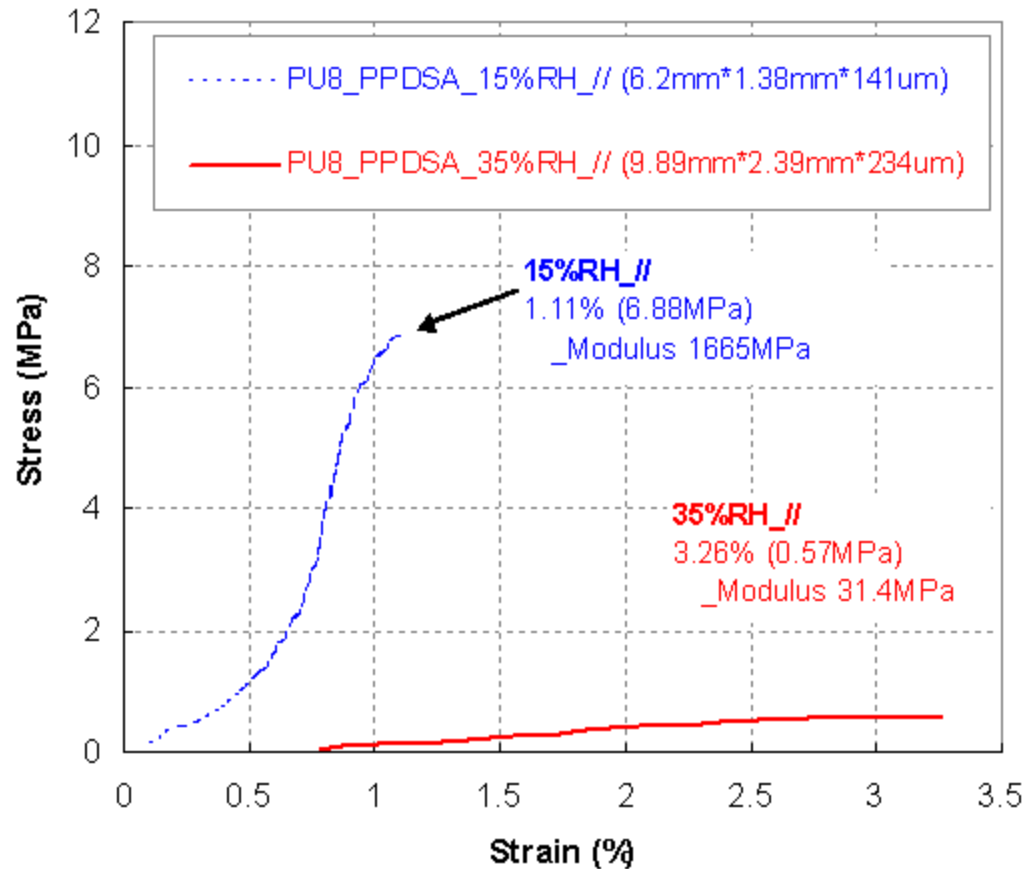
PBPDSA conditioned in TGA & heated to annealing temperature; λ and thermal stability measured in same operation.



PPDSA annealed for one hour at temperature shown and then titrated

PBPDSA stable at 175°C but degrades at 200°C. **PPDSA stable at 240°C for > 1 hour.**

Stress-strain results

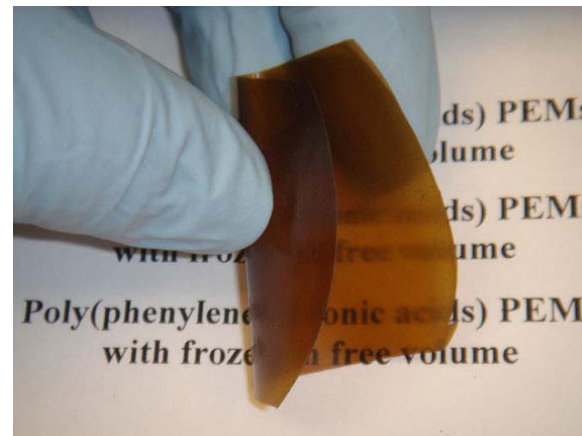
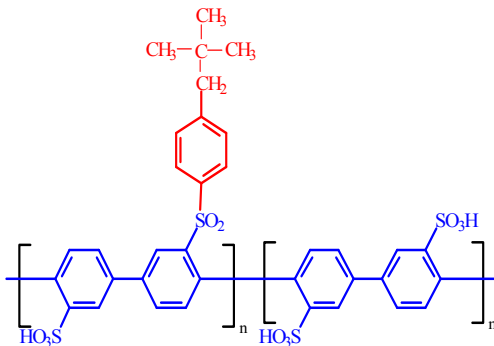


Problems

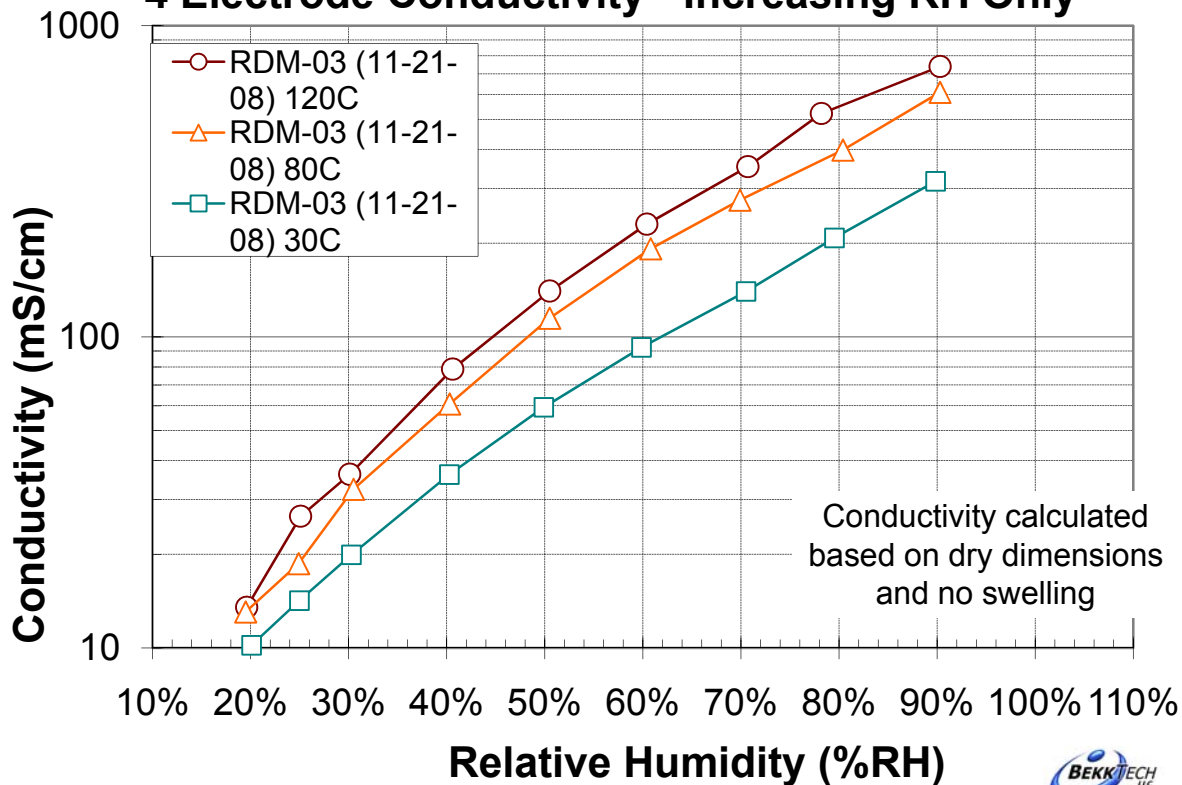
1. Homopolymer is water soluble. It absorbs absorbs water easily and modulus drops drastically.
2. Very low elongation at break. Possibly due to short chain length, $X_n \sim 170$, nematic organization and chain orientation.
3. Higher DP water insoluble graft polymers may also become very soft at high RH.

Recent results with graft copolymers

- Grafting PBPDSA with NPB. Graft (4% NPB) is water insoluble; film disintegrates in water. Reasonable mechanical properties. Sent to Bekktech for testing. Calc. IEC=5.9 mEq/gm. Tested 11/21/08. Reported 1/05/09.



4 Electrode Conductivity - Increasing RH Only

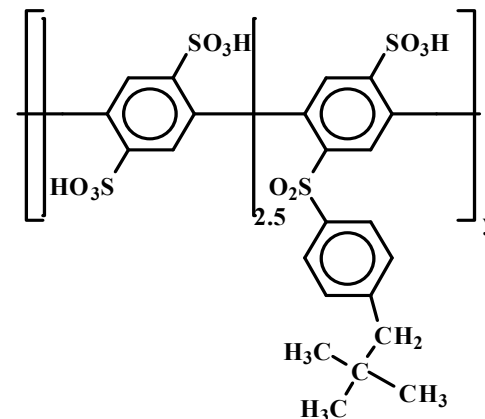


Meets DOE requirements;
 >100 mS/cm >75°C and
 50% RH

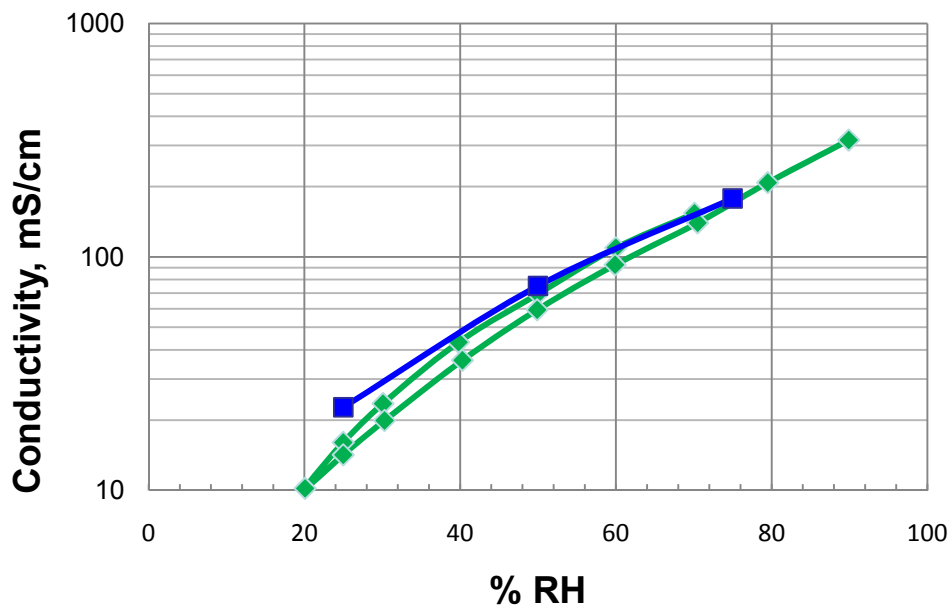
Recent results with graft copolymers

2. Grafting on PPDSA with NPB.

- 15% of acid groups grafted. Calc. IEC = 6.1 mEq/gm.
- Water insoluble but very soft at room conditions.
- 24% grafted PPDSA film had high modulus. Calc. IEC=5.1 mEq/gm. Characterization in progress.



Comparison of PPDSA 15% graft ■ (25°C) with Bekktech RDM-03 (30°C)



- Film not acid washed; may contain DMF.
- σ at 25% RH and 25°C is 50% higher than that of RDM-03 at 30°C. Same σ at 50, 75% RH, & at 80°C, 50%RH.
- Conductivity about 75% that of PPDSA at 50 & 75% RH, but ~90% at 25% RH.
- Holds water better than homopolymer!

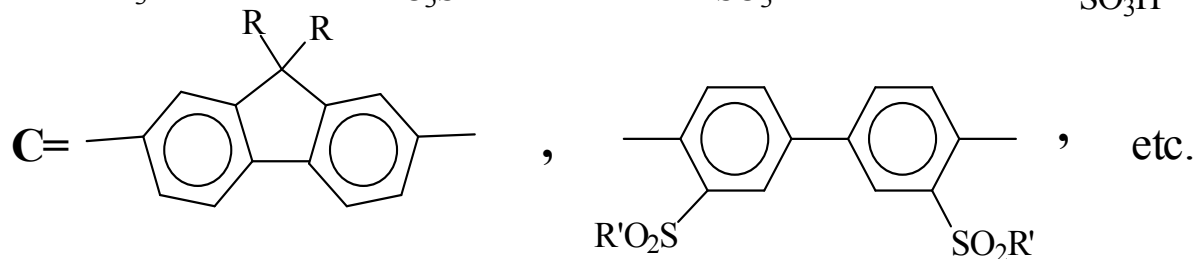
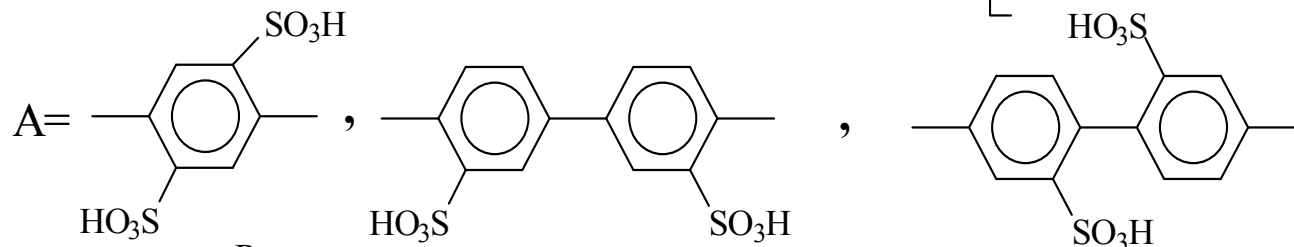
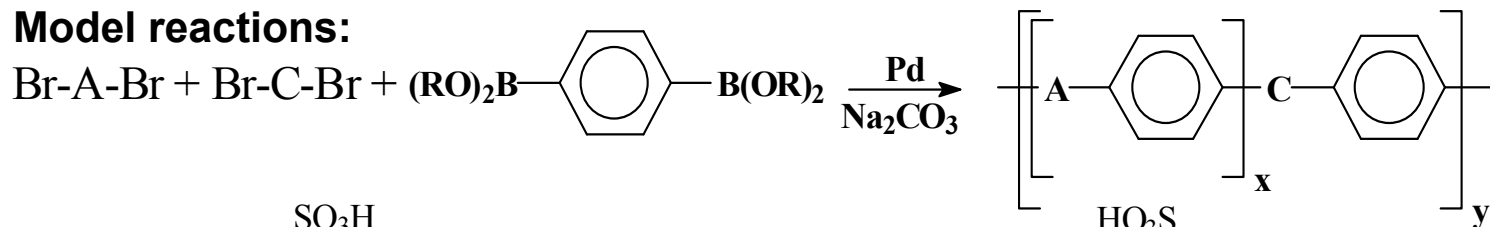
Twenty gm. of high viscosity PPDSA just synthesized. Will be used to optimize grafting conditions. Best polymers will be thoroughly characterized and films sent to Bekktech.

Copolymer Syntheses

Use of Suzuki reaction to make copolymers

Work in progress. Many copolymers are being made. Lower IEC than grafts.

Model reactions:



R = Alkyl or Alkyl-aryl groups

R' = Alkyl-aryl or Alkyl-aryloxy groups

Copolymers with 5 to 30 mole% non-polar groups are being synthesized.

Copolymers containing phenyl and biphenyl disulfonic acids are also being made.

Polymerization conditions are still being optimized.

2D Polymers

- Part of the proposed research was to make 2D polymers, a rigid honeycomb structure with edges of linked phenylene sulfonic acid groups. The nanopores in such a material should hold water as strongly as molecular sieves or silica gel.
- Preliminary calculations show that λ should be at least 4 for the simplest structure. Insertion of another phenylene sulfonic acid unit should increase λ to 6.
- Research up to now was concerned with defining reagents and reaction conditions needed to synthesize such materials.
- We have just finished the synthesis of the first of these materials, IEC = 5.5 mEq/gm. Initially it is water soluble, but after concentrating the solution it precipitates and is completely water insoluble. This is what is expected if the 2D honeycombs can stack into 3D aggregates with polar pores.
- [Stay tuned for further news.](#)

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 very interesting water insoluble polymers. However, grafting is heterogeneous and not easily reproduced or scaled up.
- Physical properties are still poor, but getting better as DP increases.
- Most co-monomers tried did not copolymerize. The only one that reacted well had bromobenzene sulfonic acid moieties at each end.

Approaches to Solutions

Most of the problems can be remedied by copolymerization with non-polar comonomers with appropriate end groups. We have developed a high yield synthetic approach for making non-polar comonomers with 4-bromophenyl 3-sulfonic acid end groups.

- For rigid rod materials, non-polar groups interact *intermolecularly*. Hydrophobic bonding should be effective even at high IEC, generating water insolubility and dimensional stability (e. g. grafted PBPDSA and PPDSA).
- Increase in chain length using better polymerization conditions should increase polymer elongation.
- The easiest comonomers to make would come from alkyl-aryl sulfones of our monomers or from 9, 9-disubstituted alkyl or alkyl-aryl dibromo fluorenes.
- If necessary, the materials can be blended with reinforcing polymers to improve mechanical properties. This will almost certainly be necessary for the 2D polymers.

Future Work

FY 2009 & 2010

- 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.
- Make non-polar comonomers with reactive 4-bromophenyl 3-sulfonic acid end groups and copolymerize them. Continue grafting studies until good copolymers are made.
- Study techniques for casting 2D polymers as PEMs (with binder?).
- Study electrospinning (Pintauro) of copolymers and 2D polymers 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 best materials 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. They have been made water insoluble (grafting) with very high IEC, high conductivity and 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.**
- **2D polymers have been made which hold water *very* strongly.**
- **Problems are: 1. Poor mechanical properties because they are rigid rod materials, and 2. Very poor copolymerization with non-polar comonomers.**
- **Possible solutions are: Copolymerization with new classes of comonomers under optimum conditions to make water insoluble copolymers which hold water well, increasing σ and therefore conductivity at low RHs. Increasing molecular weight will generate better mechanical properties. Grafting or use of a flexible matrix are fallback positions.**