

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

Morton Litt

Macromolecular Science

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Project ID # FC 19 - I

Overview

Timeline

- Start date 4/15/2006
- End date 4/15/2011
- Percent complete 40%

Budget

- Total Project Expenses
 - DOE \$1,492,572
 - Contractor \$530,569
- DOE Cost Share
- FY07 \$230,204 \$111,680
- FY08, Est. \$255,000 \$113,220

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

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
6/11	Go/No-Go PEM cost. Starting materials are relatively cheap in Kg. quantities. Synthetic details and upscaling costs need to be worked out to determine final price. If mechanical properties are good, membranes can be very thin.
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.

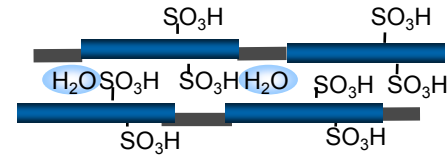
Structural Approach

Frozen in Free Volume: Basic concepts

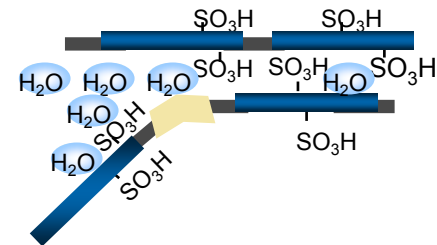
Use rigid-rod nematic liquid crystalline polymers.

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.

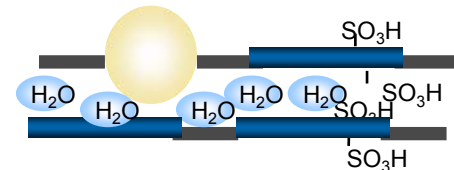
(a). Homopolymer .
Chains can pack closely



(b). Copolymers with angled comonomers



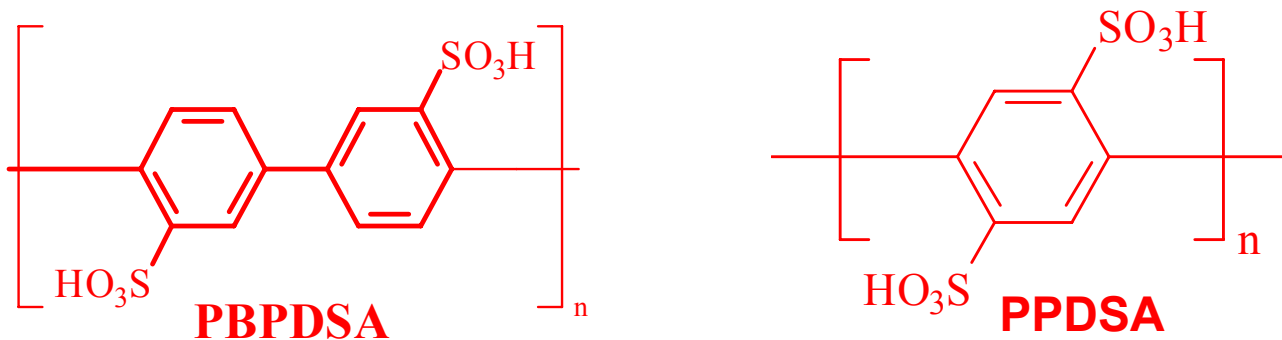
(c). Copolymers with linear, bulky comonomer



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.*

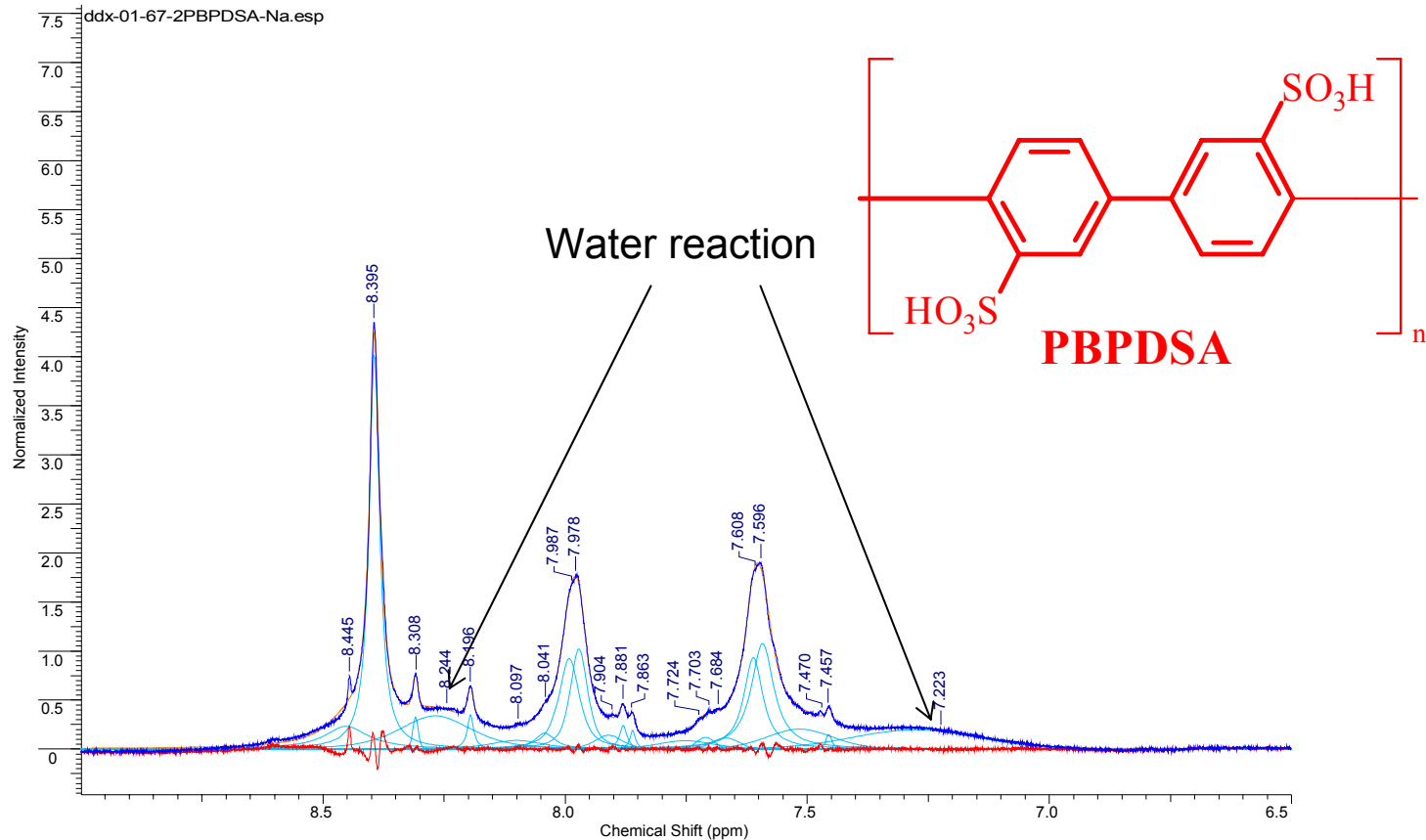
2. Decided to work with poly(p-phenylenes) with one and two sulfonic acids per ring. These have lower equivalent weights (higher IEC) and *cannot hydrolyze*.



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

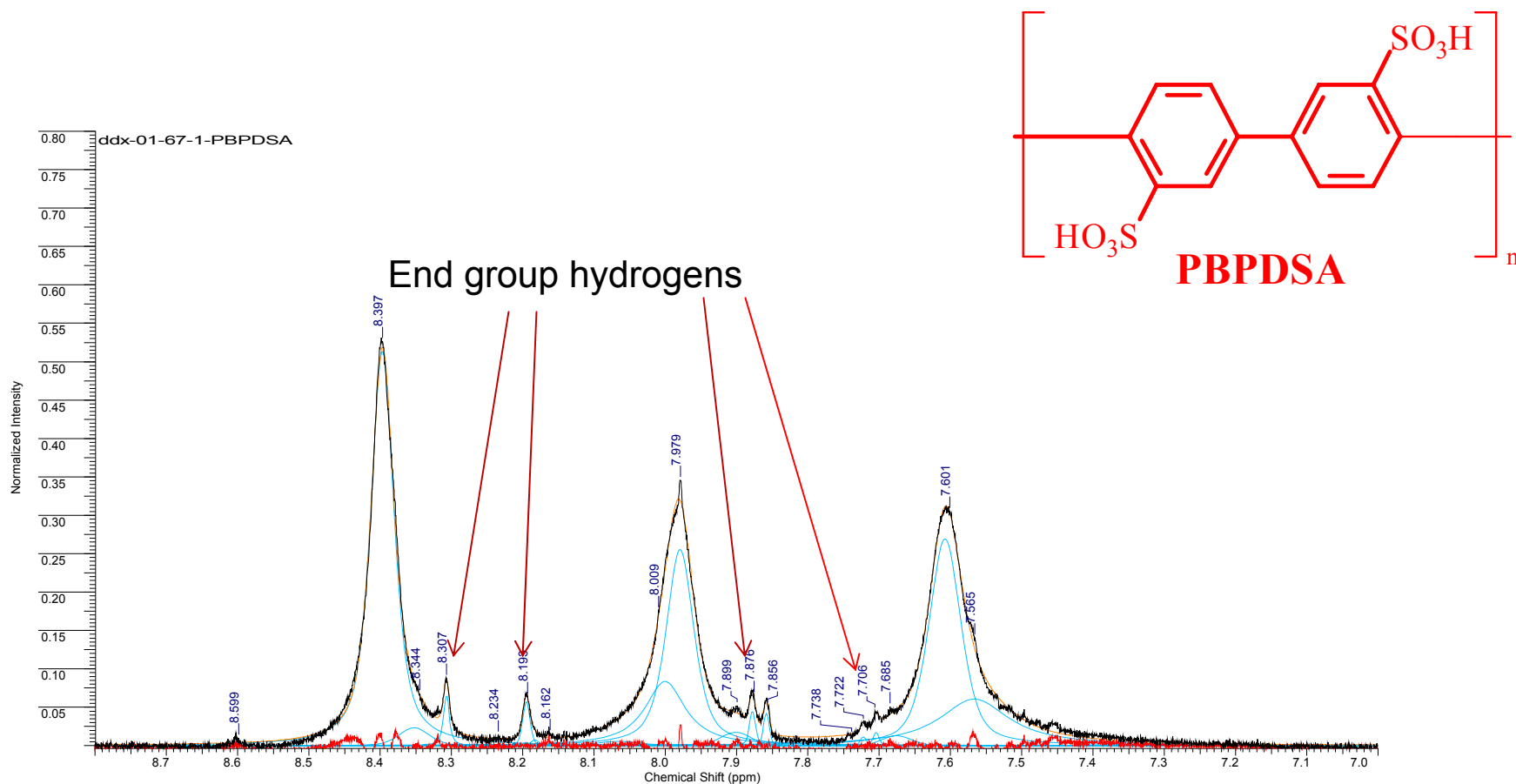
4. The free volume effect on conductivity is much greater with poly(phenylene disulfonic acid) PPDSA, discussed later. We are working on both systems at present.

Earlier PBPDSA homopolymers (^1H NMR)



- Typical NMR spectrum: Best polymer made before present, η_{sp}/c (0.5 gm/dL) = 0.95 dL/gm. Degree of polymerization ~ 25 (?).
- *Two problems*: 1. The polymer Li salt crystallizes from solution and cannot continue to grow. 2. Very difficult to dry. Residual water may hydrolyze bromo or sulfonate groups.

Present PBPDSA homopolymer (^1H NMR)

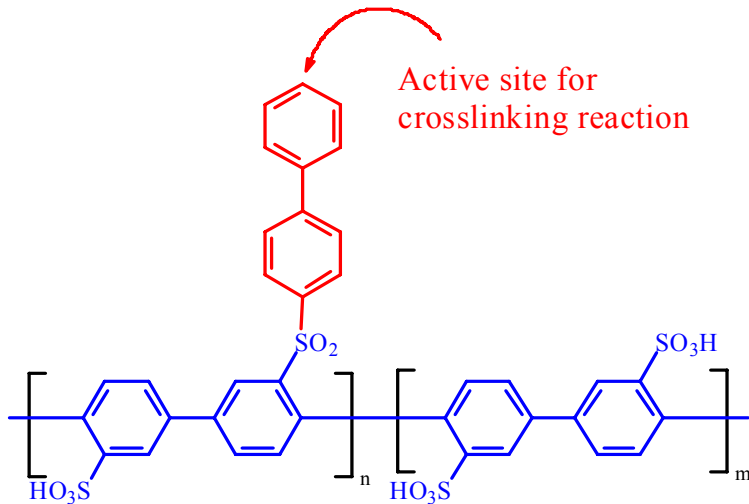


- Best material made (4/08). η_{sp}/c (0.5 gm/dL) = 1.05 dL/gm. Degree of polymerization ~ 33 (66 benzene rings), MWt. = 10,300.
- Completely dry starting materials. No by-product resonances!
- Reaction time reduced to 12 hrs at 145°C.

Membrane Stabilization

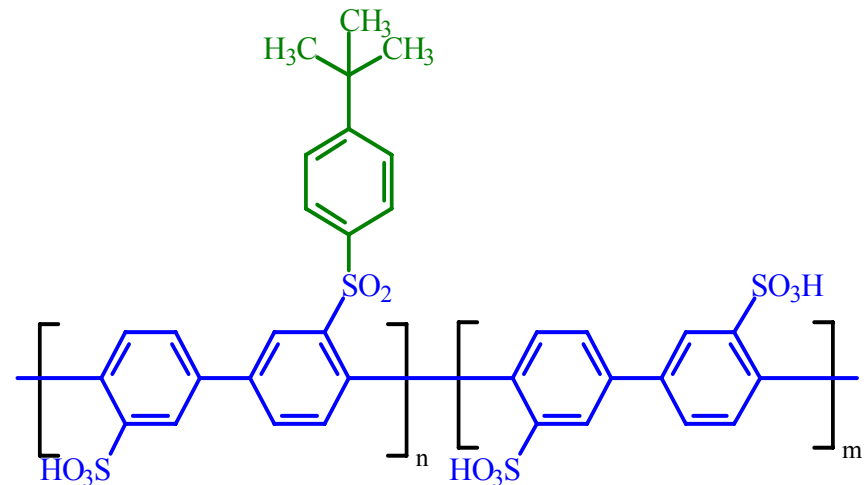
Grafting done using polyphosphoric acid

Incorporation of cross-linkable biphenyl groups.



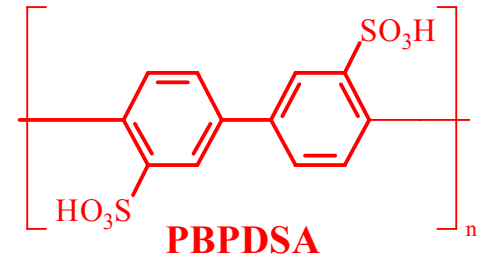
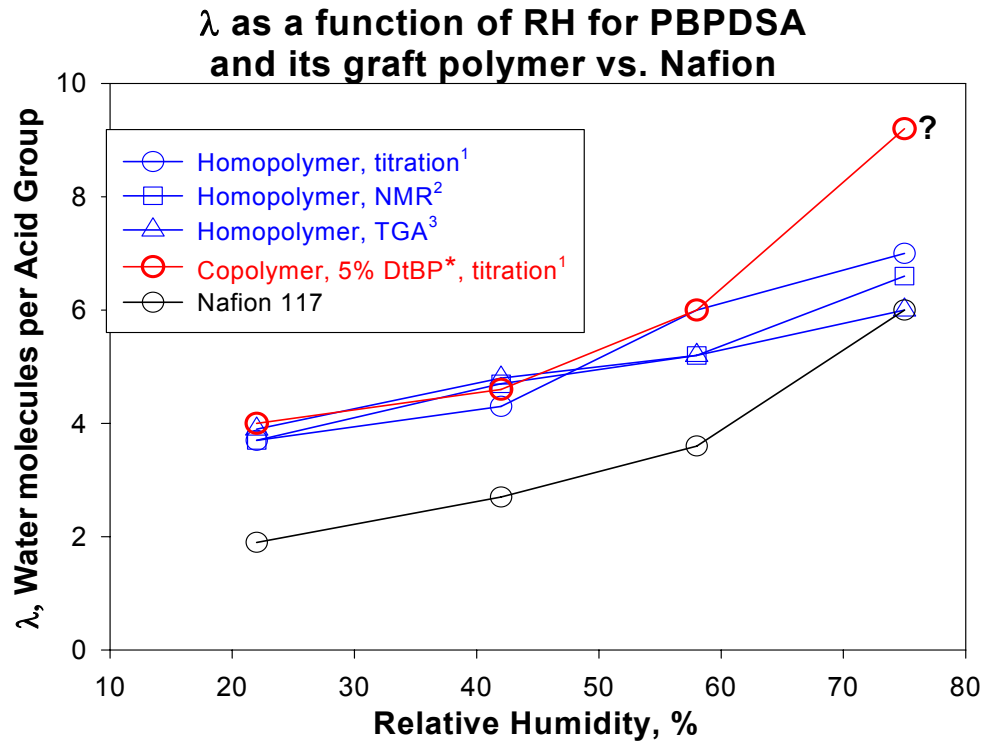
Graft copolymers containing from 5 to 25 mole% of biphenyl sulfone groups were water soluble. 10 minutes at 200°C cross-linked the polymer.

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.

Measurement of λ by different techniques



* Di-t-butyl phenol graft.

1 Sample equilibrated at given R. H., weighed, put into .1M NaCl solution and titrated with 0.01 M NaOH to phenolphthalein end point.

2 Sample equilibrated, weighed & dissolved in 0.50 cc. D₂O containing a calibrated amount of Na acetate. HDO content measured vs. acetate CH₃, also vs. aromatic hydrogen for soluble polymer.

3. Sample equilibrated at given RH in TGA apparatus, and then heated. Fraction of weight lost at ~200°C (plateau) was used to calculate the water content of the polymer.

PBPDSA λ ~1.5 waters higher than Nafion over lower RH range.

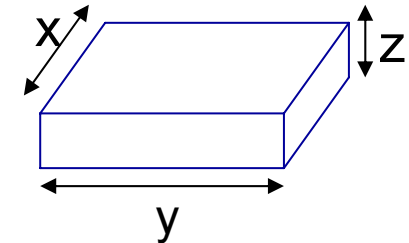
Polymer swelling as a function of relative humidity

Dimensional changes of copolymer films from 22% to 100% RH.

Grafting group	"Mole %" of grafted group (Equiv. Wt.)**	Δx (%)	Δy (%)	Δz (%)
Biphenyl*	10	2	2	45
Biphenyl*	20	1	1	35
Biphenyl*	55	~0	1	15
t-Butylbenzene	5	1	2	85
t-Butylbenzene	25	1	1	50
Di-t-butylphenol	5 (243)	~0	~0	50
Di-t-butylphenol (batch 1)	8 (260)	~0	~0	33
Di-t-butylphenol (batch 2)	10 (265)	~0	~0	17
Di-t-butylphenol (batch 3)	8.4 (235)	~0	~0	26
Di-t-butylphenol (batch 4)	8.4 (235)	~0	~0	28
Di-t-butylphenol	15 (270)	~0	~0	15

* After cross-linking, 10 min at 200°C

** Equivalent Wt. homopolymer = 156

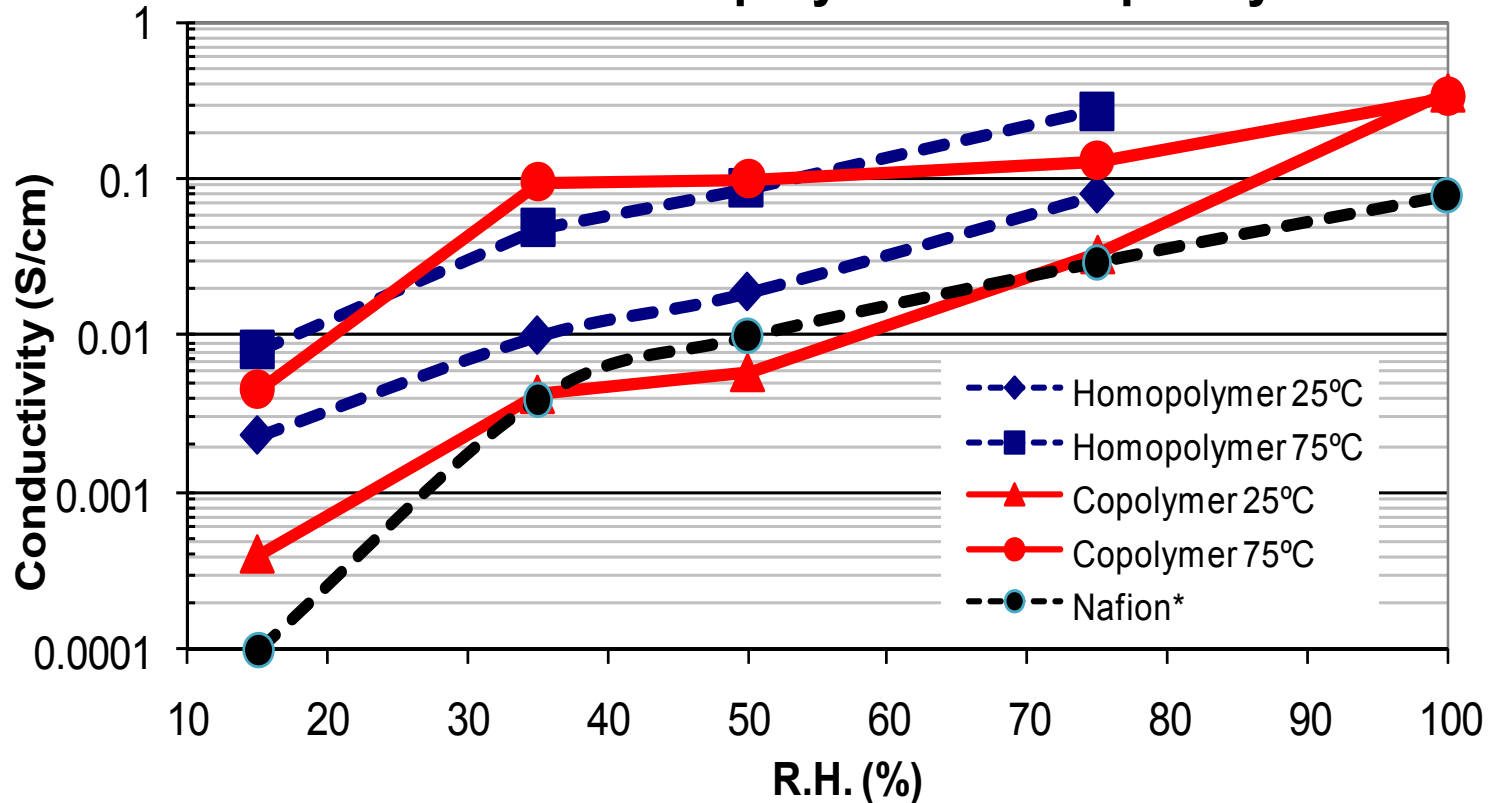


The **x** and **y** axes are parallel to the film plane. The **z** axis is perpendicular to the plane.

- Rigid rod polymer chains are parallel to the film surface. Swelling is only along the Z axis.
- The very hydrophobic t-butyl groups restrict swelling, probably by hydrophobic interactions.
- Two t-butyl groups per graft are much more effective than one.
- High conductivity despite low swelling

Conductivity of cross-linked graft polymer vs temperature and RH

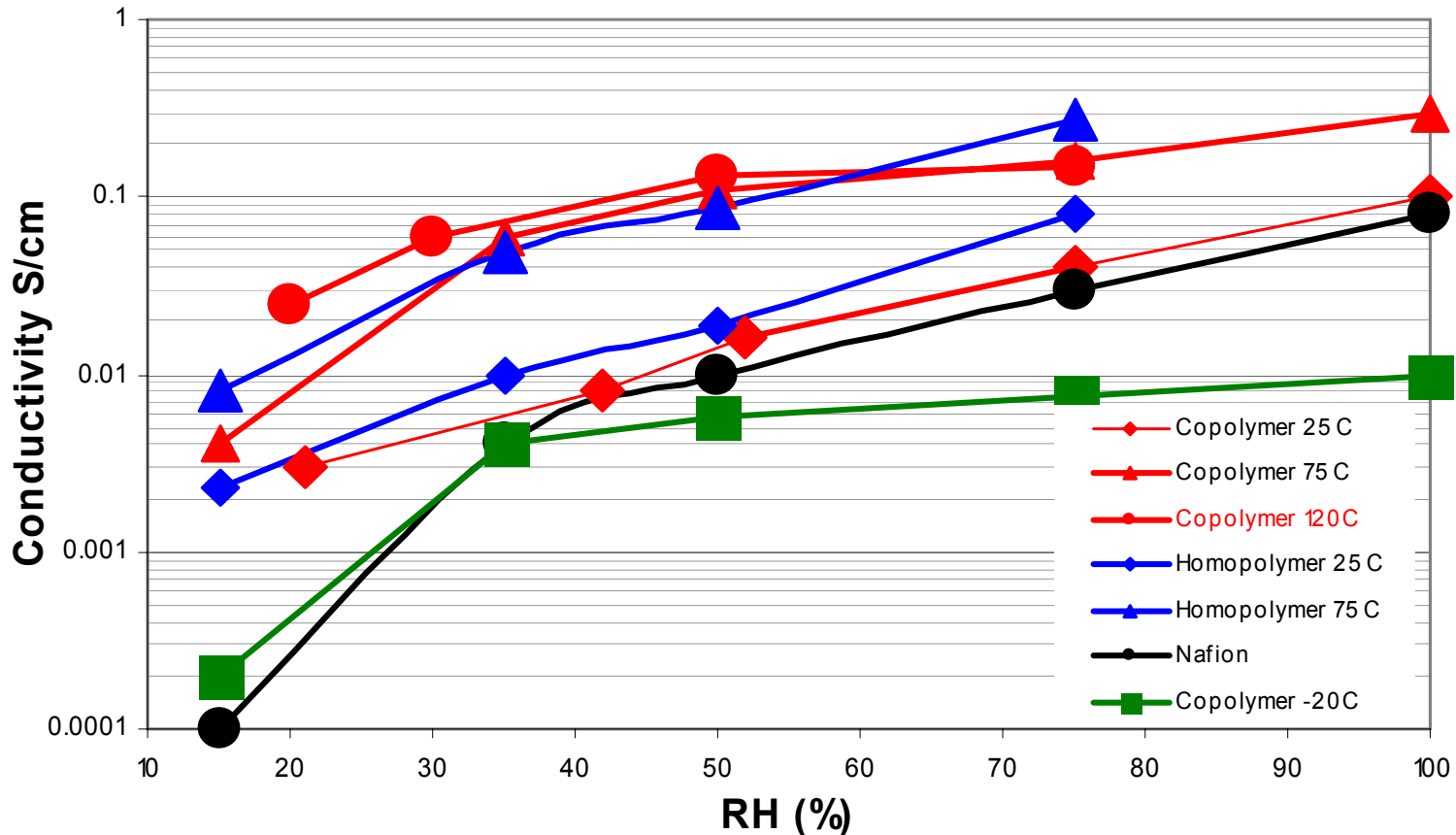
Crosslinked copolymer 10% biphenyl



- Excellent high temperature conductivity.
- Problems: Low elongation. Cross-linking procedures difficult to control. Each run different.

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



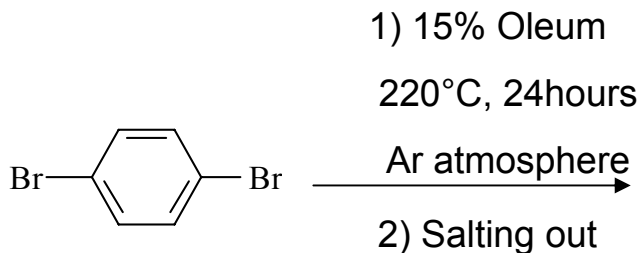
• These early graft polymers reach the DOE benchmarks for 2005.

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

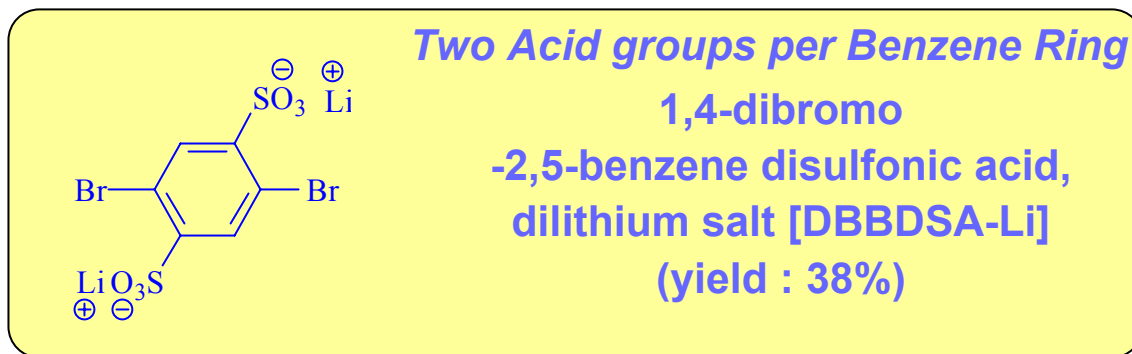
• Problem. Low elongation

PPDSA, a most unusual material

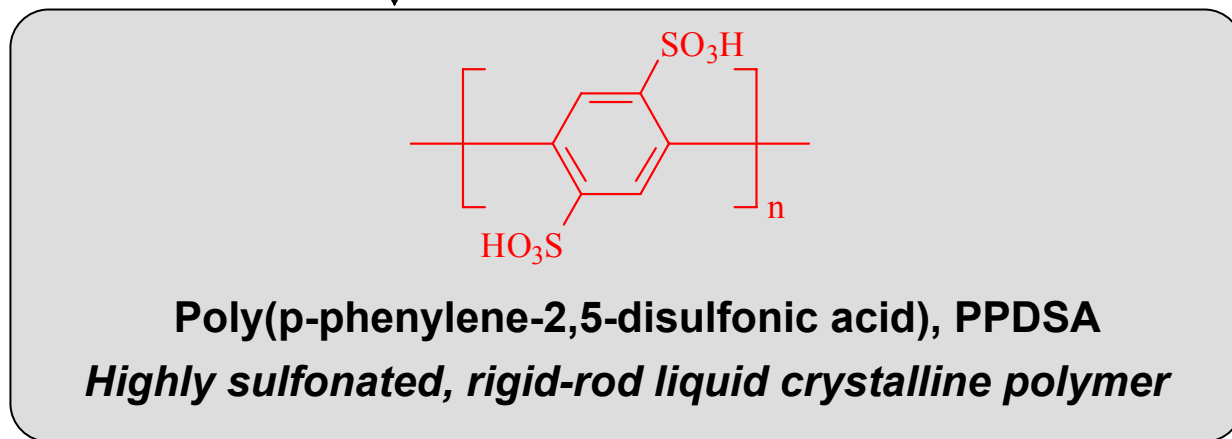
Homopolymerization : *Ullmann coupling*



With Junwon Kang



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

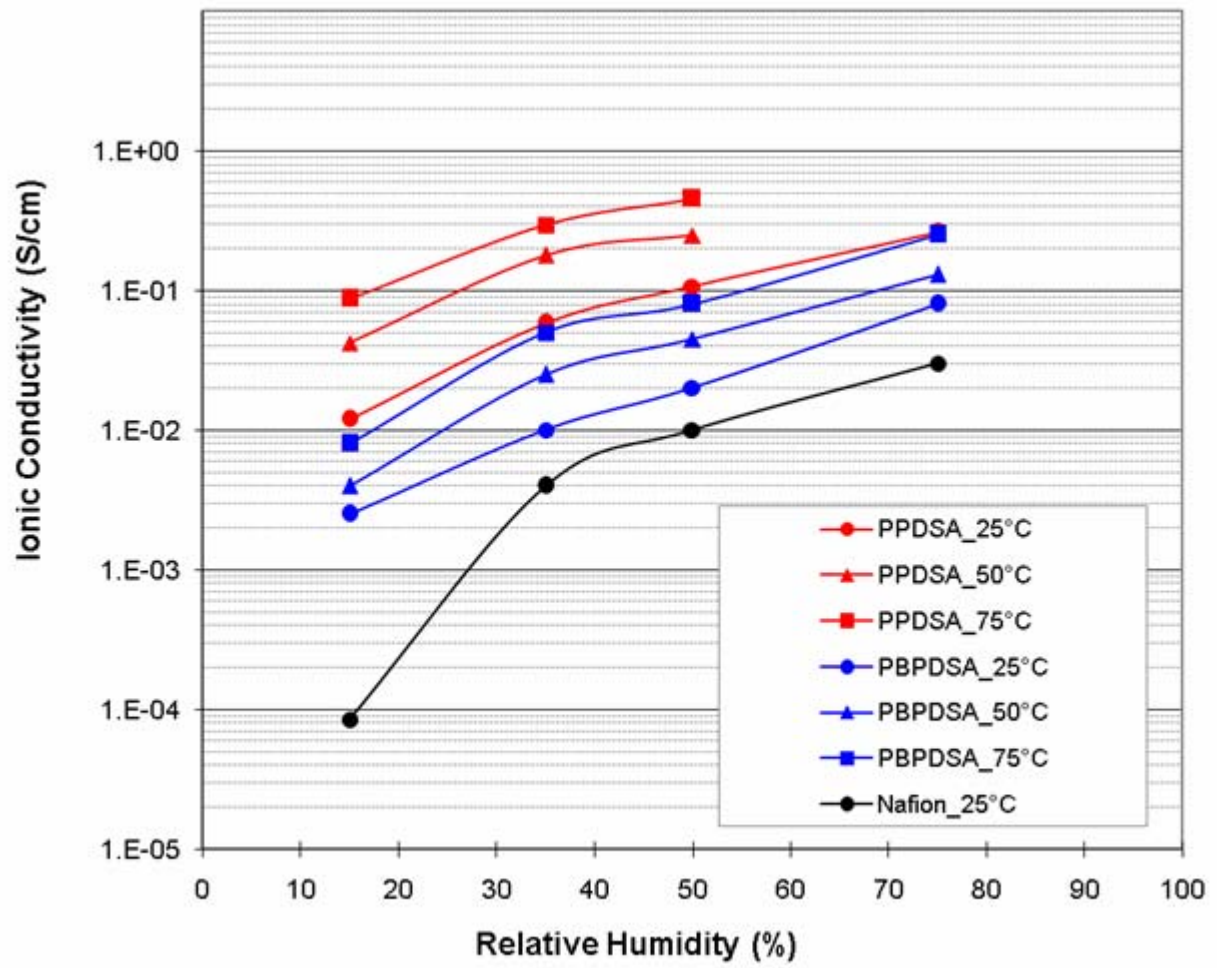
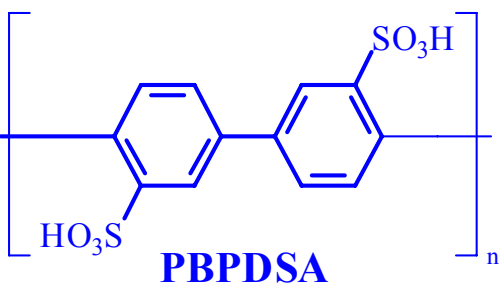
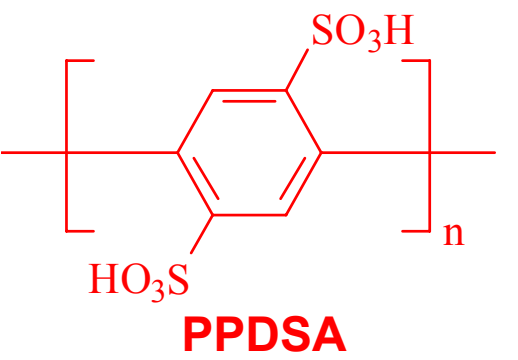


Earlier results: Best DP ~ 170

Present results, 4/30:

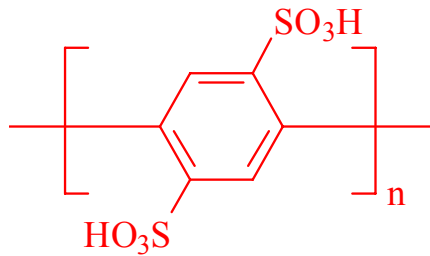
- Reaction of **dry** monomer in NMP takes < 1 day.
- Highest degree of polymerization reached ~350; MWT ~ 40,000

Comparison of PBPDSA and PBDSA: Conductivity vs Relative Humidity



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

PPDSA Ionic Conductivity, Effect of chain length

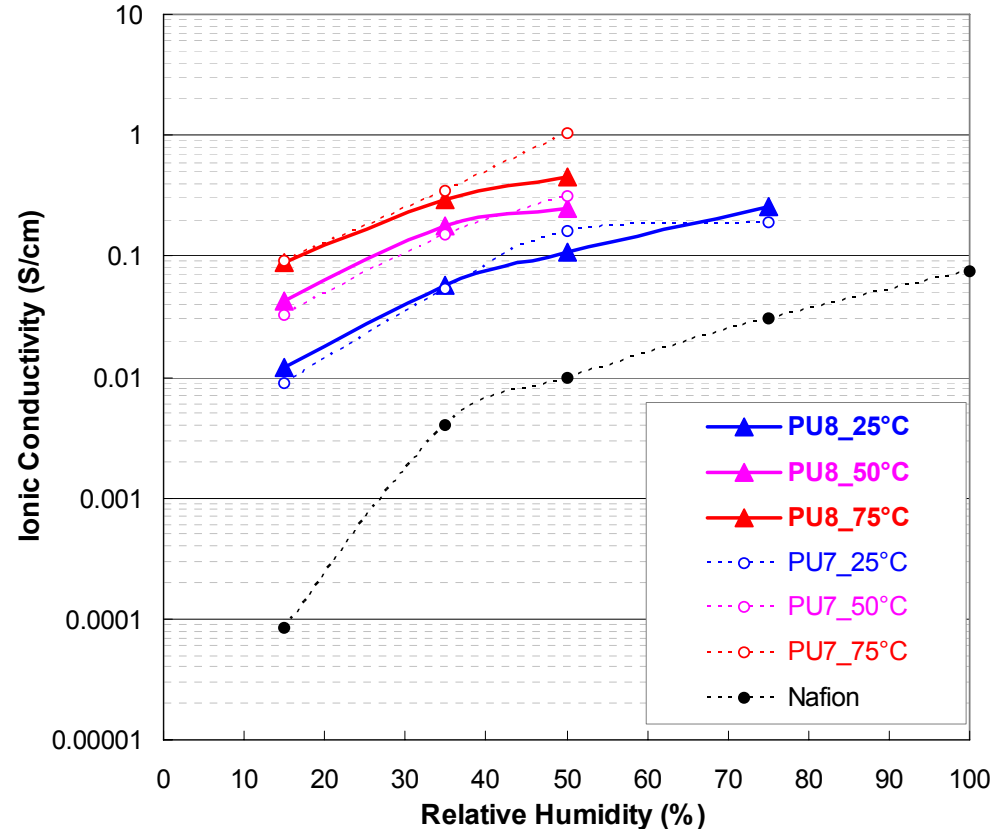


1. At low humidity, (15%RH) and 75°C, PPDSA has a conductivity of 0.1 S/cm, >1000 times higher than that of Nafion.

2. Ionic conductivity independent of x/y/z direction.

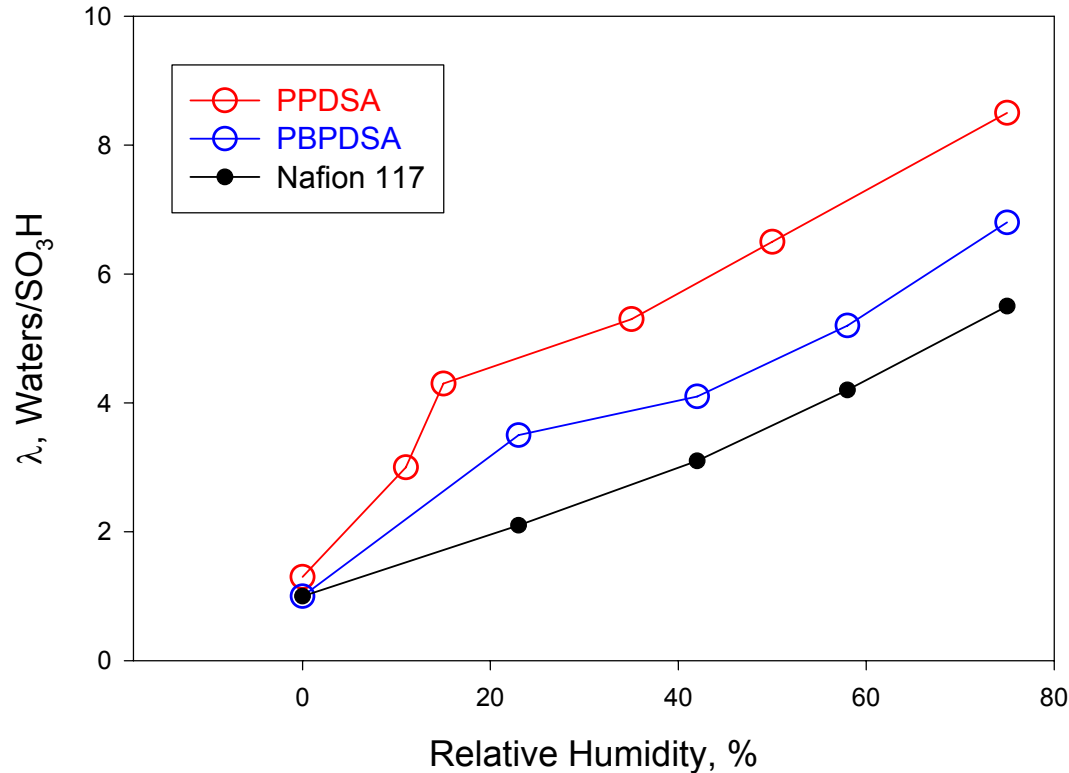
3. Higher molecular weight PPDSA (PU8) has about the same conductivity the earlier PU7. Measurements taken on two or three films for each polymer.

These are real numbers!



Water uptake for Polyelectrolytes

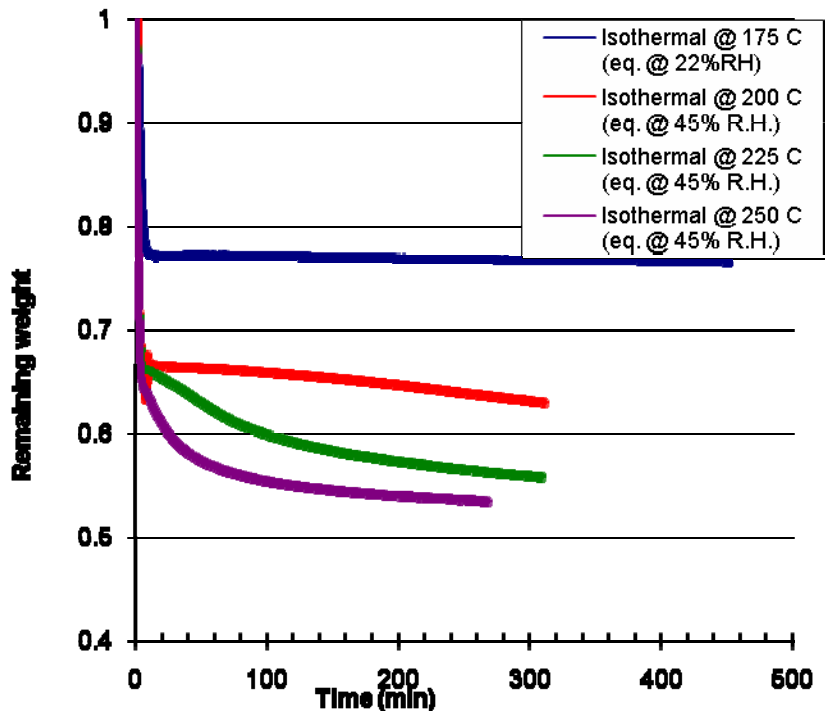
Comparison of λ vs. Relative Humidity for Nafion and Rigid-Rod Polyelectrolytes



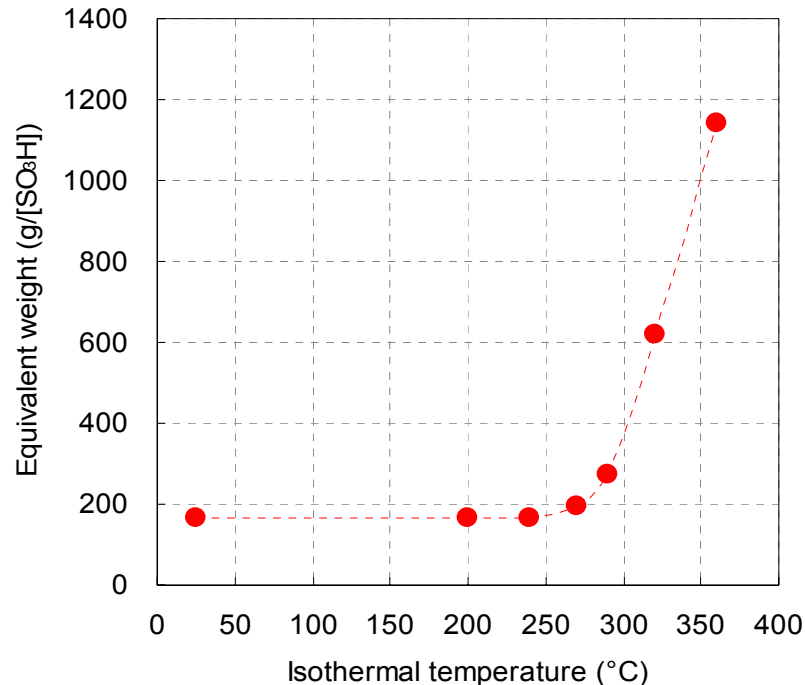
- PPDSA: λ is ~2.5 *higher* than that of Nafion 117 from 15 to 75%RH. **Highest σ .**
- PBPDSA: λ is ~1.2 to 1.5 higher than Nafion 117 from 22 to 75% RH; $\sigma \sim 2x$ Nafion σ at 35% RH and above. σ about 50x higher at 22% RH.
- High IEC might promote high λ . **However, rapid rise of λ at low humidity implies that frozen-in free volume is the major cause.** (Proved but not enough time to demonstrate in this talk.)

Thermal Stability of Polymers

Remaining weight vs. time



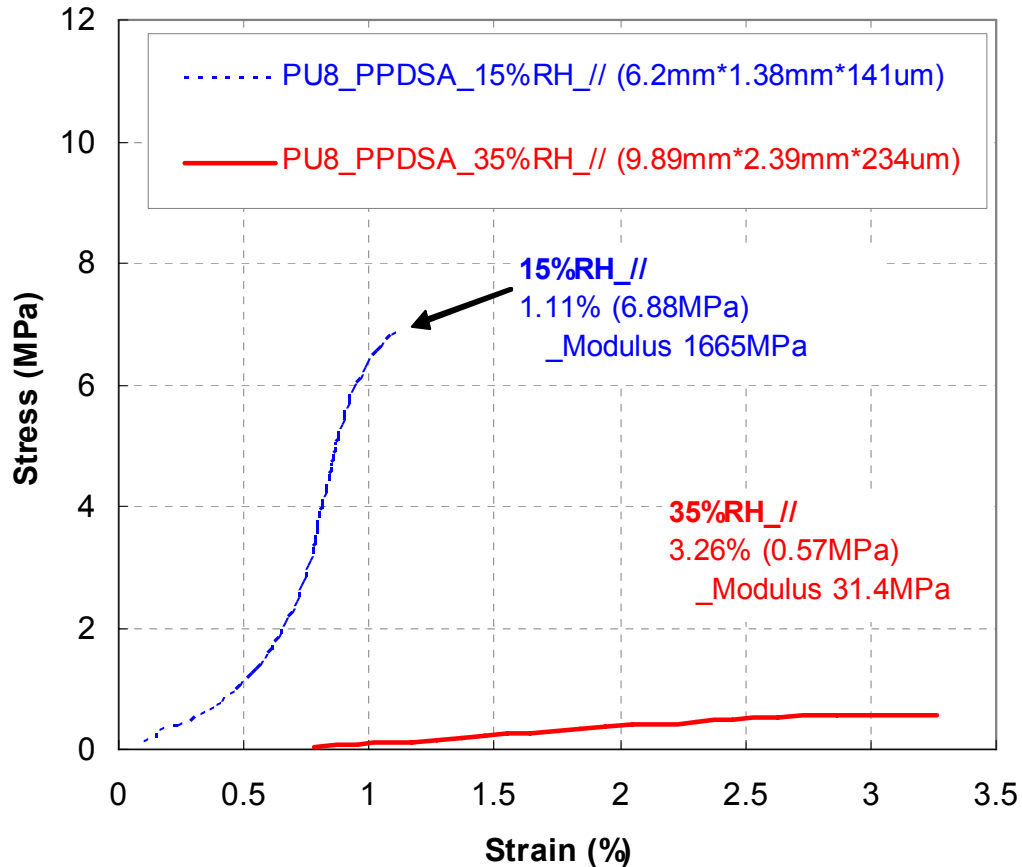
PBPDSA conditioned in TGA & heated to annealing temperature; λ and thermal stability measured in same operation.



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.**

Stress-strain results



Problems

1. Homopolymer is water soluble. It absorbs water easily and modulus drops drastically.
2. **Very** low elongation at break. Due to short chain length, $X_n \sim 170$, and nematic organization.

Present Problems

1. Molecular weight limited by polymer precipitation as reaction proceeds. Polymers are rigid rods and tend to have poor elongation.
2. Homopolymers are water soluble. Grafting of non-polar moieties to make water insoluble polymers is heterogeneous and not easily reproduced. t-Butyl groups are scrambled.
3. Several non-polar comonomers synthesized and copolymerizations run. All comonomers reacted *very* slowly. No good copolymer could be made.

Approaches to Solutions

Most of the problems can be remedied by chain extension of the polyelectrolyte molecules using non-polar linking groups.

1. For rigid rod materials, non-polar groups **must** interact *intermolecularly*. Hydrophobic bonding can be very effective at low molar ratios, generating water insolubility and dimensional stability while retaining high IEC. (e. g. grafted PBPDSA).
2. Increase in chain length by chain extension plus hydrophobic bonding of the non-polar linking groups should increase both elongation and modulus for polymers.
3. Chain extension can be done using many linking structures. This allows secondary modification of the polymer morphology, and thus its mechanical properties.
4. If necessary, the materials can be blended with reinforcing polymers to improve mechanical properties.

Future Work

FY 2008 & 2009

- Develop polymerization techniques to: 1. ensure dry conditions, 2. increase chain length (solvent and counterion variation) and **3. make relatively large runs (10 to 20 gm per run vs. 1-2 gm now).**
- All molecules have reactive bromophenyl end groups. **We will use these for chain extension** with non-polar biphenols, bi-thiols (They can be oxidized later to sulfones.), etc. to make water insoluble polymers.
- **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.
- 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 can have very high IEC (high conductivity) combined with water insolubility and dimensional stability.**
- **Frozen-in free volume can be built in, producing high λ at low RH, thus facilitating high conductivity, viz 0.1 S/cm at 15% RH and 75°C for PPDSA.**
- **Problems are: 1. Poor solubility during synthesis → low molecular weight (10,000 to 30,000), resulting in 2. Poor mechanical properties, and 3. Very poor copolymerization with non-polar comonomers.**
- **Possible solution to all problems at once is: Chain extension with non-polar linking groups, increasing molecular weight and mechanical properties, generating water insolubility, and perhaps increasing σ at low RHs.**