

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

Morton Litt

Department of Macromolecular Science and Engineering
Case Western Reserve University

FC037

Coworkers:

Ryszard Wycisk

Kun Si

Daxuan Dong

May 11, 2011



Overview

Timeline

- Start date 3/1/2006
- End date 5/31/2012
- Percent complete 80%

Budget

- Total Project Expenses:
 - DOE \$1,492,571
 - Contractor \$530,571

	<u>DOE</u>	<u>Cost Share</u>
FY10	\$300,000	\$ 78,000
FY11	\$ 92,571	\$ 70,000

Barriers

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

Interactions

- Robert Savinell, Jesse Wainright
- Florida Solar Energy Center, UCF (Darlene Slattery and Jim Fenton)
- GM interested; will test PEMs
- Possible joint project with Sunocs LLC

Objectives

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

Milestones

Month/Year	Milestone or Go/No-Go Decision	
09/06	Milestone: Make PEMs that meet DOE 2011 conductivity objectives.	Done
06/09	Milestone: Make PEMs that meet DOE 2015 conductivity objectives.	Done
12/09	Milestone: Understanding structures to find right approaches to increase water retention and dimensional stability.	Done
09/10	Milestone: Test PEMs in fuel cells. (Very good for first trials.)	Done
12/11	Go/No-Go: Dimensional stability and improved mechanical properties.	Ongoing
12/11	Go/No-Go: Cost. Starting materials should be chosen and approaches to synthetic procedures developed which show that such PEMs could reach target cost.	Starting

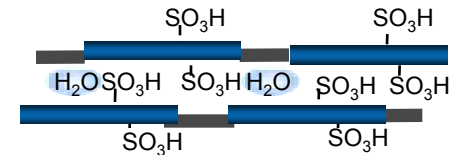
Structural Approach

Frozen in Free Volume: Basic Concepts

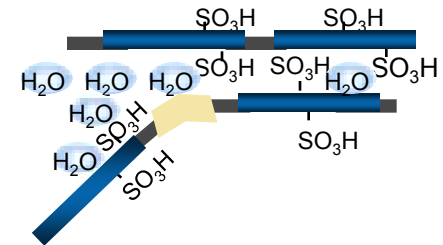
Use rigid-rod nematic liquid crystalline polymers.

A few bulky or angled comonomer units can force the chains apart over their whole length, creating permanent nanopores lined with SO_3H groups. The controlled architecture of these materials allows them to hold water strongly, generating high conductivity even at very low relative humidities. We have found that the SO_3H groups also do this.

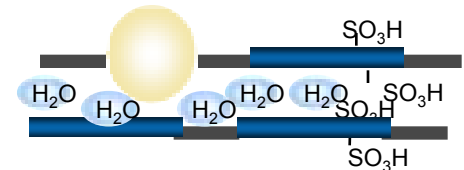
(a) Homopolymer . Chains can pack closely



(b) Copolymers with angled comonomers

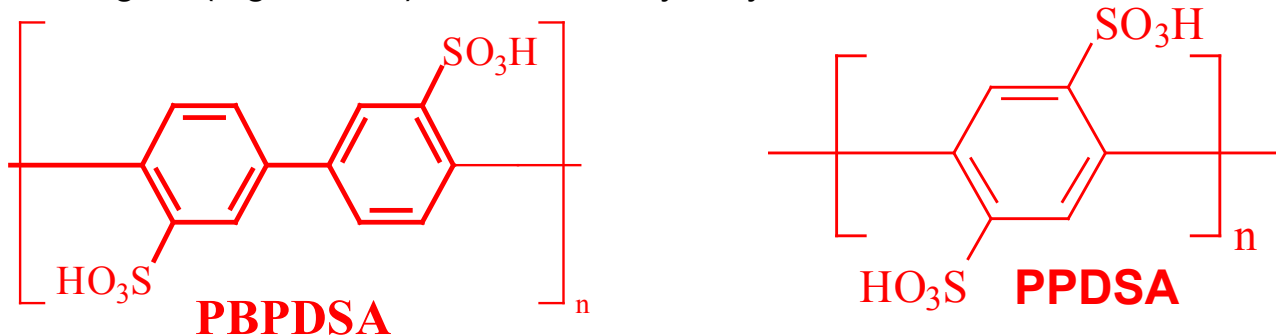


(c) Copolymers with linear, bulky comonomer



History

- Worked with polyimides (2001-2004). Could get high viscosity polymers with up to 25% elongation at break. The acid form hydrolyzed slowly at room temperature and rapidly at 100 C in water. Best σ at 22% RH and 25°C was ~ 0.002 S/cm. *Needed polyelectrolytes with higher conductivity and stable backbones.*
- Shifted to poly(p-phenylenes) with one and two sulfonic acids per ring. They have lower equivalent weights (higher IEC) and cannot hydrolyze.

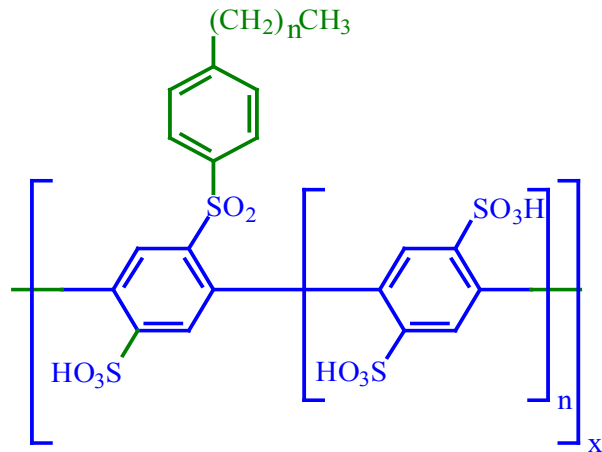


- Initial work (2004 to 2008) was on poly(biphenylene disulfonic acid), PBPDSA, and its graft copolymers.
- The free volume effect on conductivity is much greater with poly(phenylene disulfonic acid) PPDSA (higher λ and σ at low RH). We have shifted almost completely to PPDSA and its copolymers.
- Reaction conditions were further optimized. Higher viscosity homo- and co-polymers of PBPDSA and PPDSA were made (copolymers BmPn: B = Biphenylene, P = Phenylene, m/n = mole ratio).
- Larger scale reactions (10 to 20 gm polymer) had lower viscosity, worse mechanical properties.

Membrane Stabilization

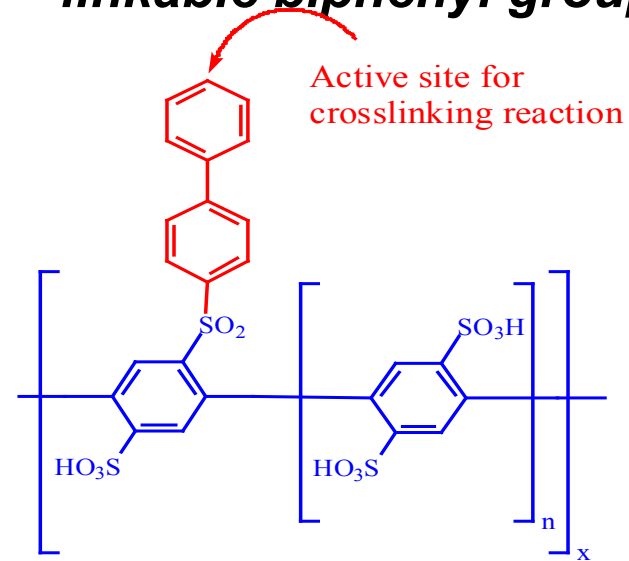
Grafting non-polar moieties using polyphosphoric acid (PPA)

Incorporation of bulky alkyl benzene groups.



Last Year's Approach: Neopentyl benzene grafts water soluble. N-octyl and -dodecyl benzene grafts insoluble above 10 mole% graft; high conductivity at low RH. Films flowed at high humidity and disintegrated in water. Approach abandoned.

Incorporation of cross-linkable biphenyl groups.



Present Approach: Graft copolymers made containing 3 to 15 mole% biphenyl sulfone groups. Grafting inhomogeneous. Heating at high temperature under vacuum crosslinked the material.

- Work centered on improving grafting conditions, studying crosslinking conditions to get best dimensional stability and mechanical properties.
- Conductivity, swelling, stress/strain properties, etc. were measured at Case. Films were sent to FSEC for extensive characterization.

Crosslinking

Equivalent weights and IECs for some vacuum dried, non-crosslinked and crosslinked films, plus λ (determined by titration and NMR*).

Sample	Weight (mg)	0.01N NaOH (ml)	Eq. Wt. (g/SO ₃ H)	IEC (mmol/g)	λ^{**} Titration (NMR)
B2P8***	18.9	12.17	159	6.3	1.8 (2.0)
B2P8-g-BP10%	8.1	4.41	184	5.4	1.6 (1.5)
B2P8-g-BP12%	9.8	5.38	186	5.4	1.4 (1.6)
B2P8-g-BP12%-210C-120min	13.1	6.72	199	5.0	
B2P8-g-BP12%-210C-180min	14.8	6.93	218	4.6	
PPDSA-g-BP12%	11.3	6.16	187	5.3	1.9 (2.0)
PPDSA-g-BP12%-170C-60min	34.2	18.95	184	5.4	
PPDSA-g-BP12%-210C-60min	18.8	9.45	203	4.9	

* Theoretical equivalent weights for PPDSA, B2P8, B2P8-g-BP10%, B2P8-g-BP12% and PPDSA-g-BP12% are 118, 125, 155, 161 and 153, respectively.

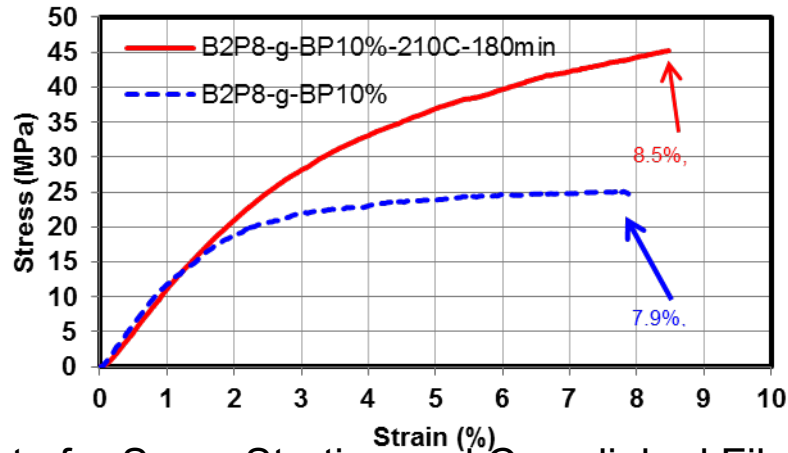
** Lambda was calculated as the difference between the experimental equivalent weight and the theoretical equivalent weight divided by 18. The values in parentheses were determined using NMR.

*** Copolymer: Biphenylene(20 mole%)/Phenylene(80 mole%) disulfonic acid

- Based on titrations (and swelling), only a small fraction of biphenyl is doubly reacted (crosslinks) after heating at 170°C. All heated PEMs were water insoluble.
- PPDSA-g-BP-12% about 60% doubly reacted after 1 hr at 210°C (assumes same λ as for uncrosslinked polymer).
- B2P8-g-BP12% about 70% reacted after 2 hrs at 210°C; about 100% reacted after 3 hrs.
- Heating at 225°C for 2 hr gave good crosslinking with little or no acid loss; see Slide 10.

Stress/Strain Properties

Stress/Strain Curves (0.2%/min.) for B2P8-g-BP10% Before and After Crosslinking



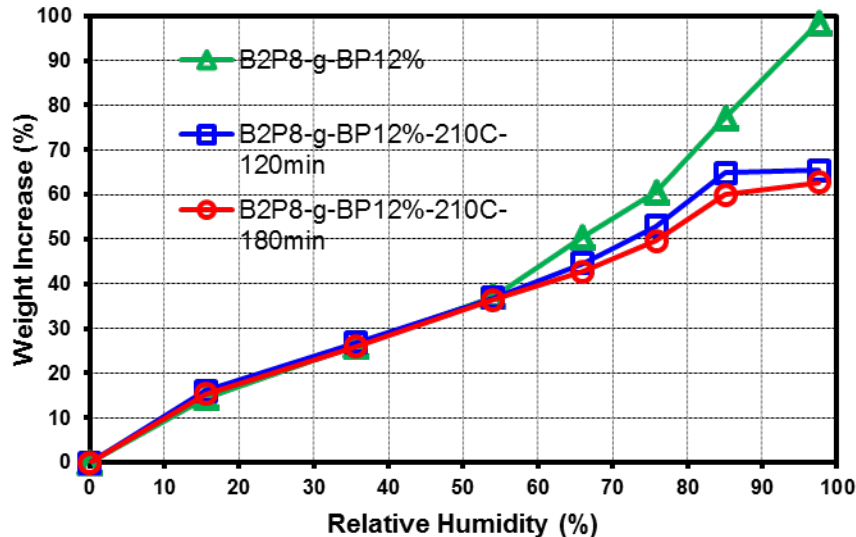
Stress/Strain Data for Some Starting and Crosslinked Films* (lab RH)

Film Sample	RH (%)	Elastic Modulus (GPa)	Breaking Stress (MPa)	Elongation at Break (%)
B2P8-g-BP10%	29	1.3	25	7.9
B2P8-g-BP12%	29	0.8	27	6.7
B2P8-g-BP12%	17	9.3	54	4.4
B2P8-g-BP10%-190C-300min	29	2.2	41	6.2
B2P8-g-BP10%-210C-180min	29	1.2	45	8.5
PPDSA-g-BP12%	22	0.9	23	7.1
PPDSA-g-BP12%-190C-120min	22	2.2	35	6.1

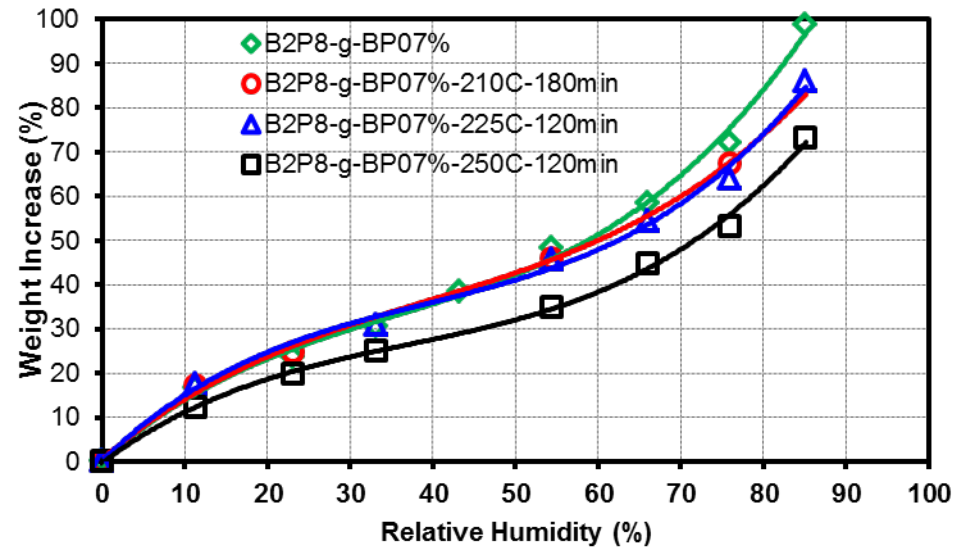
*Base B2P8 copolymer reduced viscosity (0.5 gm/dL) was 0.72 dL/gm.

- Modulus of 9.3 GPa at 17% RH demonstrates rigid rod liquid crystal organization. Ordinary crystalline or glassy polymers have moduli ≤ 3 GPa.
- Lower moduli at higher RH shows water lubrication of chains (e. g. Nafion117®: 1.5 GPa dry, 0.2 GPa wet). For most PEMs, elongation at break > 50%.

Water Absorption vs. RH: Effects of Crosslinking



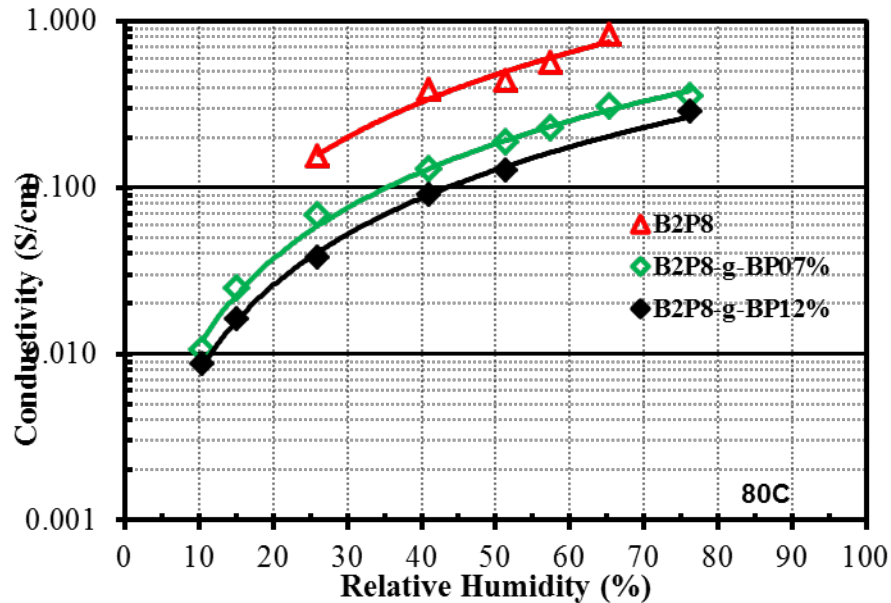
Water absorption at 25°C for B2P8 g-BP12% before and after crosslinking.



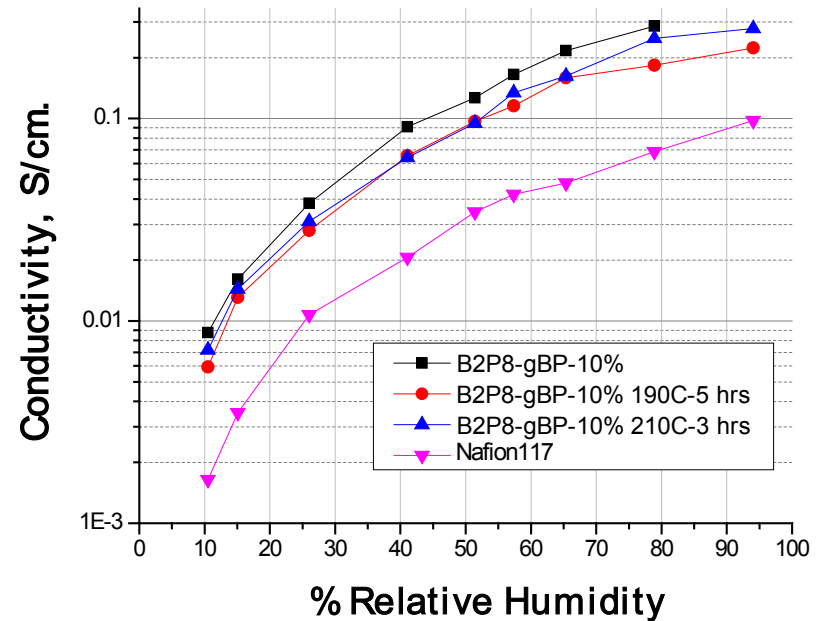
Effect of crosslinking temperature and time on water absorption

- Crosslinking at 225°C or below has no effect on water absorption.
- Essentially complete crosslinking after 3 hrs at 210°C.
- Swelling below 50% RH is independent of crosslinking ($\leq 225^\circ\text{C}$).
- λ almost independent of graft %; may increase slightly after crosslinking.
- ~25% acid loss after 2 hrs at 250°C, none at 225°C.

Conductivity



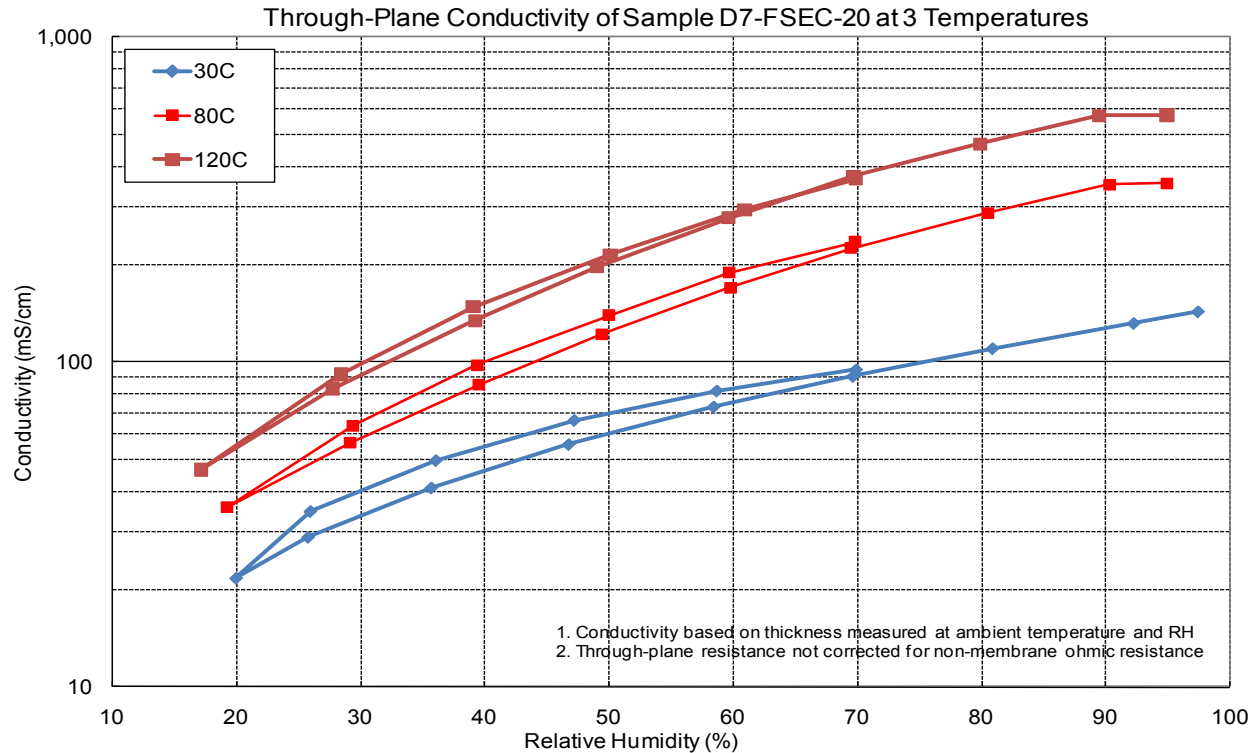
Conductivity of B2P8 copolymers (80°C) as a function of % BP grafted.



Effect of crosslinking on conductivity (80°C)

- Grafting lowers conductivity. IEC drops due to loss of acid groups and addition of non-ionic material.
- Crosslinking has very little effect on conductivity, even though IEC decreases. Possible major cause of conductivity drop is pathway obstruction by grafted groups.
- Conductivities of 10 and 12% BP grafts are identical within experimental error.

Through Conductivity Measurements (FSEC)

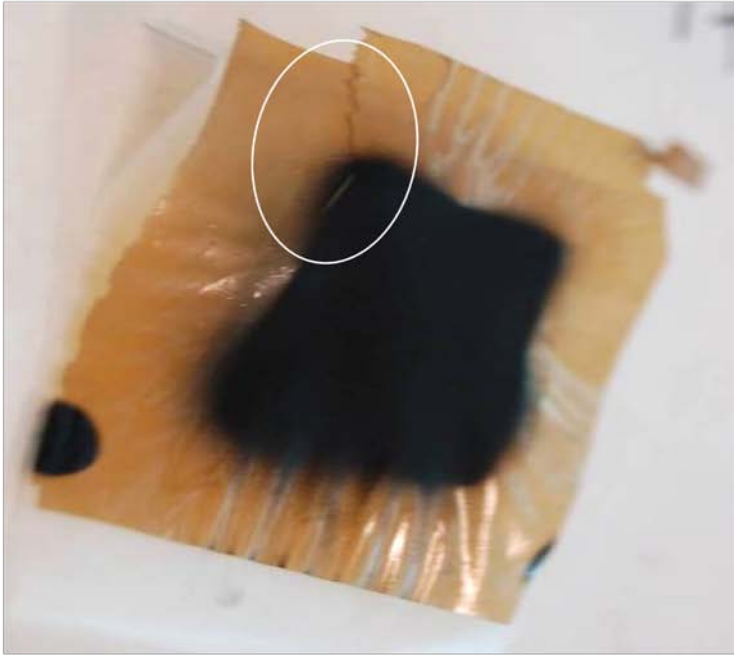


Two electrode through plane conductivity of B2P8-gBP12%-210°C-3hrs as a function of RH at 30, 80 and 120°C; includes electrode resistance.

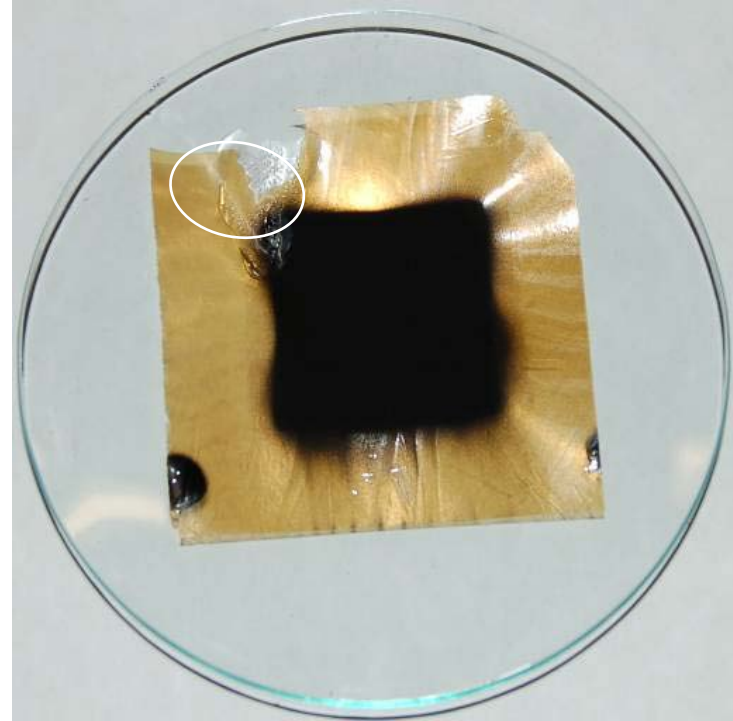
- Parallel conductivity at 80°C slightly lower than through conductivity, even with electrode resistance.
- Flattening of conductivity at high RH could show restriction of swelling, viz slide 10.
- Conductivity at 120°C meets DOE 2015 requirements. Lower % graft should be higher.

Fuel Cell Testing (FSEC)

- Several films were tested in a fuel cell configuration by the Florida Solar Energy Center (UCF).
- Small tears developed in D7 and D9 during electrode pressing; there was high hydrogen cross-over in most runs.
- One run, B2P8-gBP-12% 210°C-3hrs (D7), is shown in detail and summary data for all tests are presented.



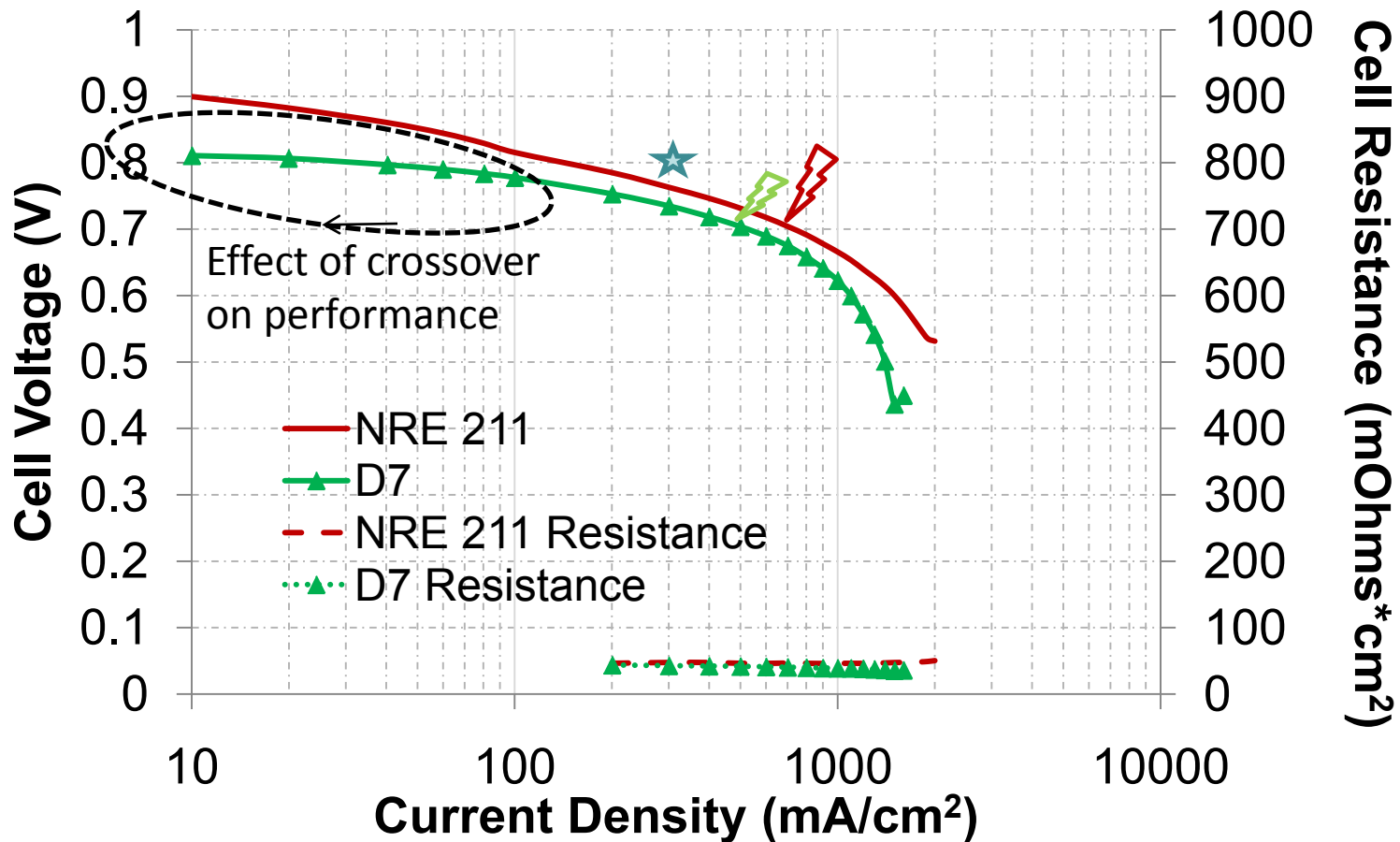
D7 CCM after spraying, with crack above.



D7 CCM showing patched region after patching with 3M ionomer dispersion and heating at 70°C for one hr.

FSEC D7 Performance: 1

80°C/100% RH, 7psig, H₂/air



★ DOE Target at 0.8 V (1/4 power) = 300 mA/cm²

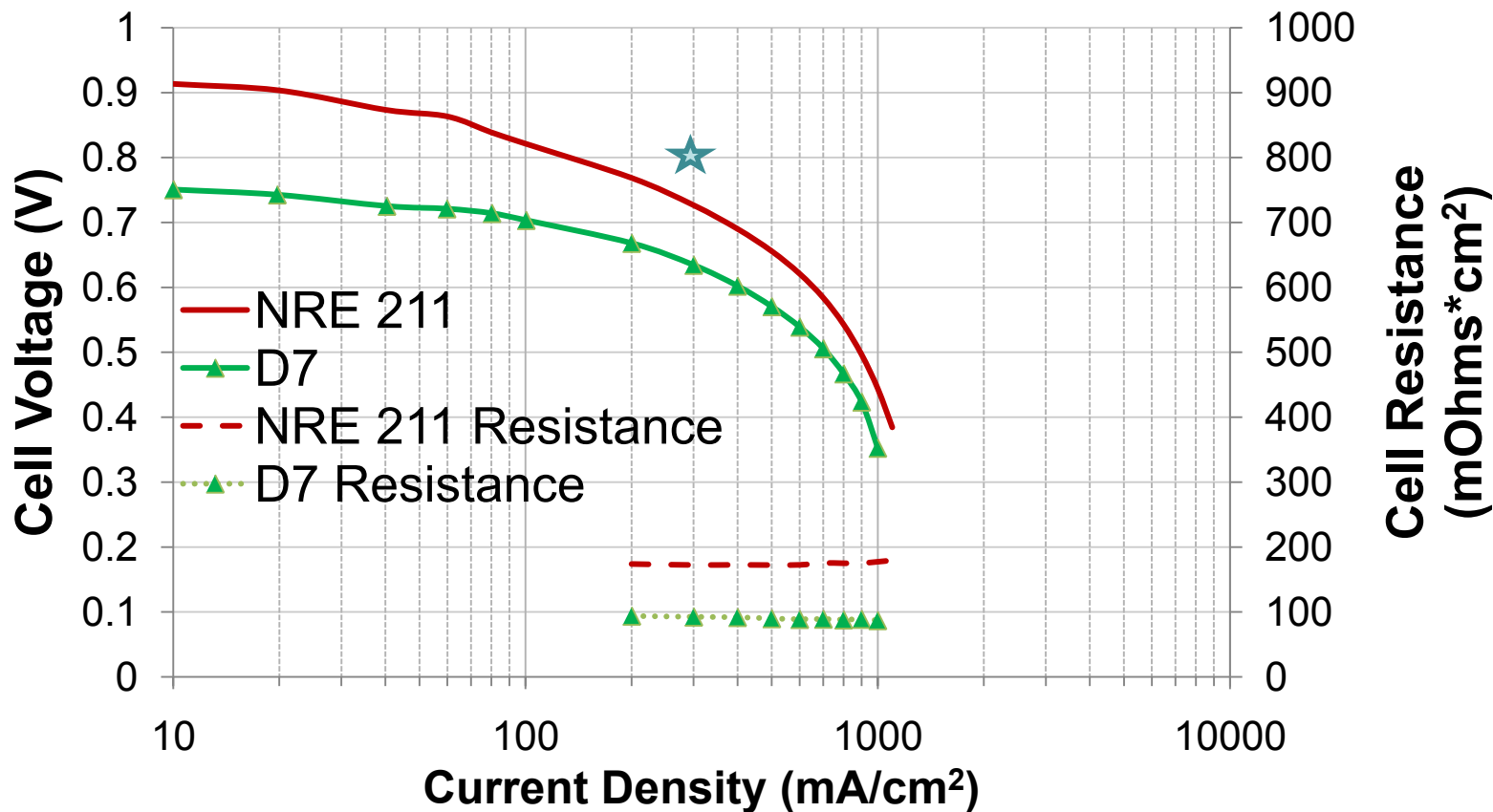
⚡ D7 (0.70 V) Power = 350 mW/cm²

⚡ NRE211 (0.70V) Power = 480 mW/cm²

- At a given amperage D7 Power is about 95% that of NRE211 Power over most of the range despite the hydrogen leak.

FSEC D7 – Performance 2

120°C/35% RH, 7psig, H₂/air



★ DOE Target at 0.8 V (1/4 power) = 300 mA/cm²

- Low OCV shows large hydrogen leakage at lower humidity: film shrinks, opening small tears?
- A 2005 fuel cell test of grafted PBPDSA at 80°C reached 0.9V at low current, but had high resistance.

CWRU Membranes**

Compared to DOE Targets (FSEC)

Characteristic	Units	Target 2015	D6	D7	D9	NRE211
Area specific proton resistance ^c at:						
120 ° C and 70 kPa water partial pressure	Ohm cm ²	≤ 0.02	N/D	0.05	0.097	0.15
80°C and 38 kPa water partial pressure	Ohm cm ²	≤ 0.02	0.055	0.02	0.018	0.02
Maximum Hydrogen cross-over ^a	mA / cm ²	2	10.8	1.9	136	0.76
Minimum electrical resistance ^b	Ohm cm ²	1000	8.4	31	14	2100
Performance @ 0.8 V (¼ power)	mA / cm ²	300	N/D	34	N/D	151
	mW / cm ²	250	N/D	27	N/D	120
Performance @ rated power	mW / cm ²	1000	N/D	108	N/D	480

* Values are at 80°C unless otherwise noted.

** D6 was an n-Octyl Benzene graft (uncrosslinked). D7, D9 were B2P8-gBP-12%. D7 was cast and crosslinked at Case, D9 at FSEC.

a. Measured in humidified (100% RH) H₂/N₂ at 25 C

b. Measured in humidified H₂/N₂ using LSV curve from 0.4 to 0.6 V at 80 C. (Other possible meanings?)

c. Determined by subtracting contact resistances from cell current interrupt values

CWRU membranes show promise to meet DOE ASR targets

Grafted Polymers: Summary & Conclusions

- We can routinely make polymers and copolymers with chains long enough to give reasonable though not excellent mechanical properties. The films can be handled.
- Grafting of biphenyl to PPDSA and B2P8 copolymer with subsequent crosslinking gives water stable polymers with high conductivity at low RH.
- Elongation at break at intermediate RHs is low, 6 to 8%. PEMs are brittle at very low or very high RH; it was difficult to fabricate high quality MEAs.
- D7 and D9 probably had cracks due to drying and shrinkage at the temperatures used for attaching the electrodes. (High hydrogen cross-over that fluctuated wildly as test conditions changed.)
- The low voltage at low current is due to hydrogen crossover. An earlier test on a biphenyl disulfonic acid graft reached 0.9V at low current. (Prepared and measured at Case.)
- Nevertheless, for first tests on a completely new material, the results are very encouraging.

Problems & Possible Solutions:

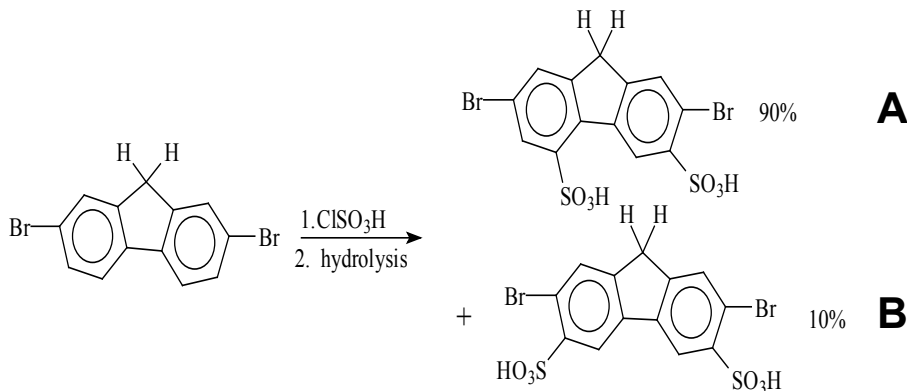
- Low elongation: The polymer precipitates during polymerization, limiting molecular weight. We are studying ways to increase polymer solubility: complexing the Li ions and/or raising reaction temperature. Rigid rod polyimides, with viscosities of ~2 dL/gm, had elongations at break as high as 20%.
- Grafting inhomogeneity: Biphenyl is insoluble in PPA during grafting, resulting in inhomogeneous crosslinking. We are searching for an inert solvent for all components, and a grafting moiety reactive enough to graft in such a solvent. If this succeeds, we should be able to go to 3 to 5% grafted polymer that will crosslink rapidly to give highly conductive MEAs with much better mechanical properties and low swelling.

Alternate Approach

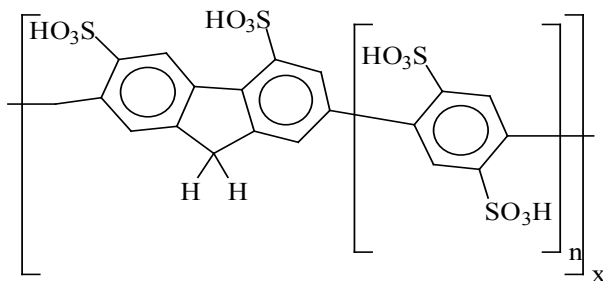
Comonomer Synthesis and Copolymerization

New comonomer with easy grafting sites:

- 2, 7-Dibromofluorene disulfonic acid, an analog of the biphenyl monomer (copolymerized well) was selected as a comonomer. Sulfonation yield was 100%.
- The aliphatic hydrogens are easily replaced by alkyl aromatic groups for crosslinking (many literature syntheses) *with no loss of sulfonic acid* (Higher IEC).



- **B** was expected. However, the product was 90% **A**. (100% A using fuming sulfuric acid).

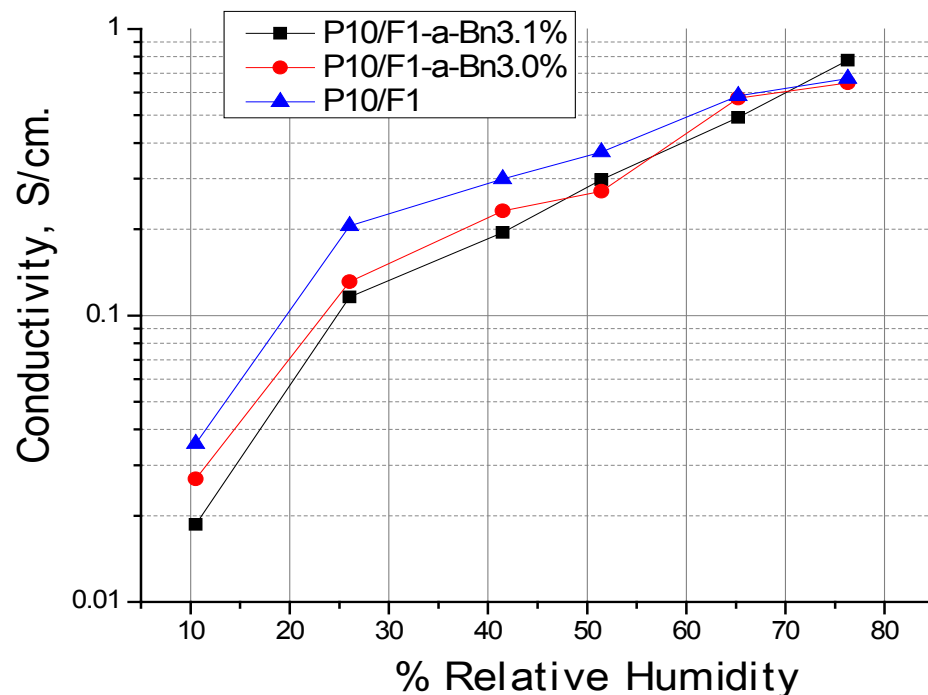


Expected copolymer, PnF1

- A copolymerized well with our base monomers. Early PnF1 copolymers (n Phenylenes/1 Fluorene composition) had low viscosities (~0.4 dL/gm for P10F1), low molecular weight.
- Copolymer viscosity inversely proportional to P/F ratio. P20F1 viscosity reached 0.9 dL/gm.
- Recent change in reaction temperature (200°C) raised P10F1 viscosity to 0.9 dL/gm.
- Chloromethyl benzene grafting on the CH₂ in DMSO gave ≤ 30% substitution.

Parallel Conductivity of P10F1 Polymer and its Benzyl Grafts

- P10F1 conductivity same as that of B2P8 and PPDSA.
- As usual, grafting lowers conductivity. Values close to those of other polymers with same % graft.
- Film brittleness increased with crosslinking. No good crosslinked film yet made. Molecular weight too low and wrong molecular orientation; chains perpendicular to film surface.



Conclusions and Recommendations:

- Early, short chain length PPDSA films had chains perpendicular to surface; new higher viscosity, longer chain length films have chains parallel. We expect similar behavior with these copolymers. Higher viscosity polymers could produce crosslinked films with reasonable mechanical properties.
- We have discovered how to graft in NMP; we should be able to reach 100% grafting. The F/P ratio can be lowered to 1/20 or less.

Polymer Cost

- p-Dibromo-benzene (starting compound) is relatively expensive, \$20/lb in 25 Kg lots (City Chemical). Can it be replaced with p-dichloro benzene, (\$3/lb from City Chemical in 50 Kg lots, and less weight loss when making polymer)?
- The present reaction conditions need a large excess of sulfuric acid and SO_3 and give monomer yields of only ~40 to 45%; the rest is the 2, 6-disulfonic acid isomer. Can this be re-isomerized to increase the yield?
- Can we find other reaction procedures that use much less P_2O_5 and SO_3 ? Based on supply house prices they cost much more than dibromo-benzene, using the present procedures.
- What will the grafting moieties cost? Dibromo fluorene is expensive but can be made easily. Moieties to be grafted, such as biphenyl, dibenzofuran, etc. are cheap.
- How much time does the reaction need? The effect of reaction conditions on molecular weight has not been studied. Long polymerization times can increase capital costs.

Plans for coming year:

- We will synthesize 1, 4-dichloro benzene 2, 5-disulfonic acid and run polymerizations using it.
- We will test potential solvents that could dissolve all components. They could use much less P_2O_5 and should generate homogeneous grafts, resulting in better polymer properties. The solvents could be recycled.

Electrochemical Testing

- All films with reasonable mechanical properties will be sent to FSEC for testing as MEAs. (This assumes they will have the money to continue testing. Our materials will then be part of a round robin of testing by many companies.)
- There are facilities at Case to make MEAs and test them in fuel cells. This will be done for selected crosslinked PEMs.
- Once we have films with “good” mechanical and electrochemical properties, some will be sent to GM for testing. If the results are interesting, they will probably want large quantities of grafted polymer to cast their own films.
- The above assumes that we can reproducibly make and graft large batches of high viscosity polymers. That task is part of our next year’s program.

Summary: Accomplishments

- We have made reasonably high viscosity PPDSA and its copolymers with the biphenyl comonomer.
- Biphenyl was grafted on our base polymers and the graft was thermally crosslinked with no loss in conductivity or mechanical properties. Even using a base polymer with relatively low degree of polymerization, the materials had elongations at break as high as 8%.
- Crosslinked PEMs submitted to FSEC were tested for conductivity and as MEAs in fuel cells. Conductivity at 120°C hit the DOE 2015 target.
- Initial fuel cell tests on this completely new material showed very encouraging results. Even with hydrogen leaks and possible poor electrode adhesion, the performance was almost as good as that of Nafion[®]212.
- New copolymers using dibromo fluorene disulfonic acid as a comonomer were made. These can be grafted in solution, avoiding inhomogeneous grafting problems. Conductivity is comparable to that of the other PEMs.

Summary: Present Problems

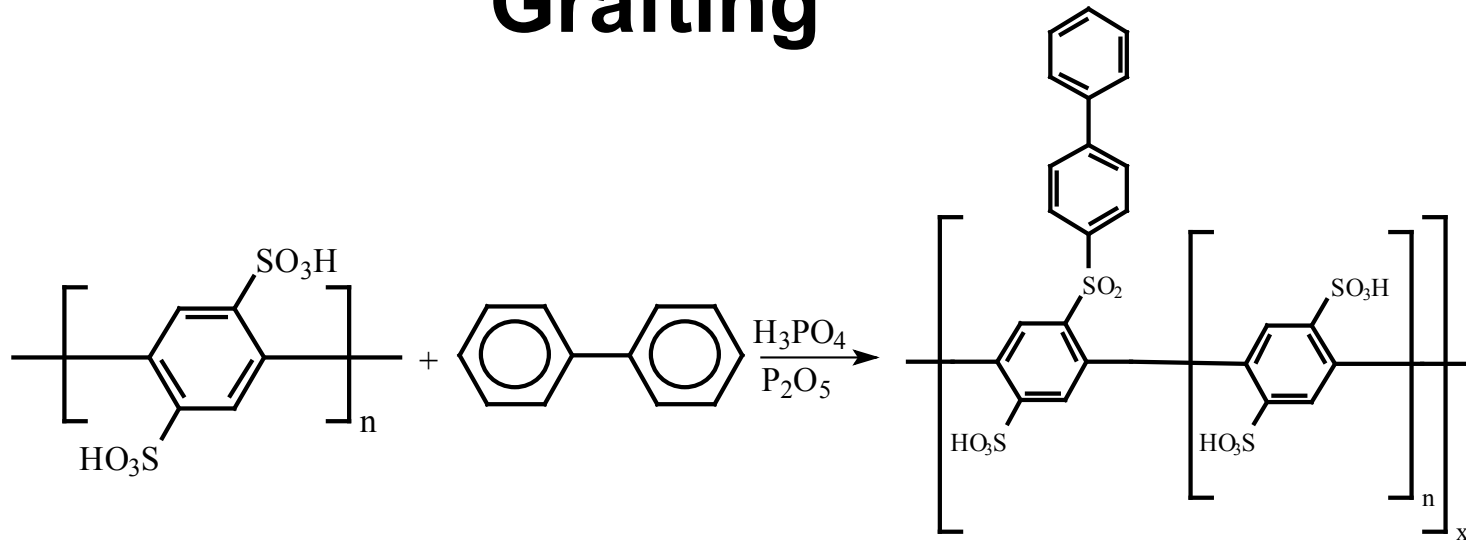
- Molecular weight is limited by polymer precipitation as reaction proceeds. However, the degree of polymerization (characterized by viscosity) has risen as we gain experience.
- Homopolymers are water soluble. Biphenyl grafting and post-crosslinking generates water insoluble polymers with very high low RH conductivity. However, present materials are brittle at very low or very high humidities and at best have elongation at break < 10%.
- We have found a good comonomer, dibromofluorene disulfonic acid. We have not yet been able to graft crosslinking groups on the copolymer in high yield.
- Comonomers containing crosslinking or non-polar moieties copolymerize very poorly. Only oligomers form.

Approaches to Solutions

- Increase chain length to increase polymer elongation and break strength. We think we have found a method to increase polymer solubility during polymerization and thus increase chain length. Polymerization at 200°C gives higher molecular weight polymers.
- PPA grafting of aromatic groups is heterogeneous. We are looking for very reactive moieties that can graft homogeneously on PPDSA using a common solvent inert enough to allow homogeneous grafting. This should improve mechanical properties and stability.
- One comonomer, 2, 7-dibromofluorene 3, 5-disulfonic acid, made in one step in ~100% yield from a commercial material, copolymerizes randomly and could be post-grafted with no loss of acid. Approaches were found that should enable 100% grafting on the fluorene methylene groups. Molecular weight is raised by reducing the comonomer mole fraction.
- If necessary, the final polymers can be put into an expanded matrix of, or co-cast with, a reinforcing polymer to improve mechanical properties.

Technical Back-up Slides

Grafting



Initial Procedure:

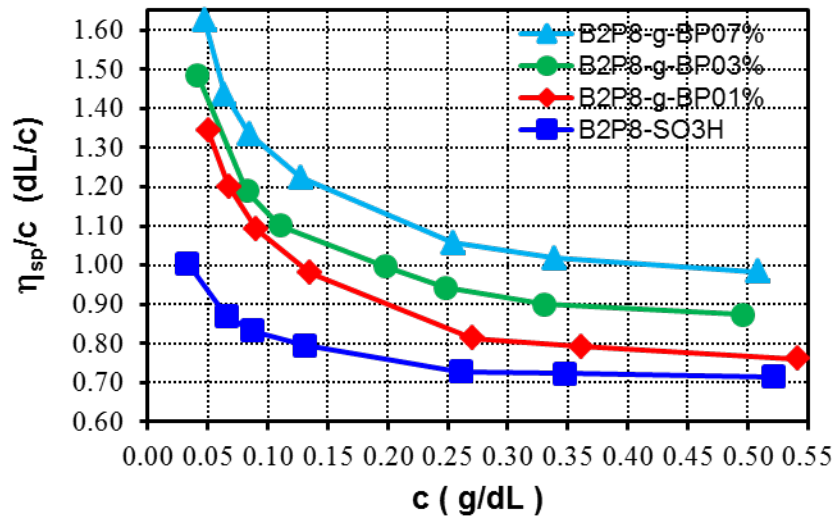
- 1 gm polymer dissolved in 9 cc phosphoric acid and equimolar amount of biphenyl added.
- 22 gm P₂O₅ added in 0.5 gm batches with cooling.
- System stirred at 125°C for predetermined times. ~10 Mol% graft present before heating.

Revised Procedure:

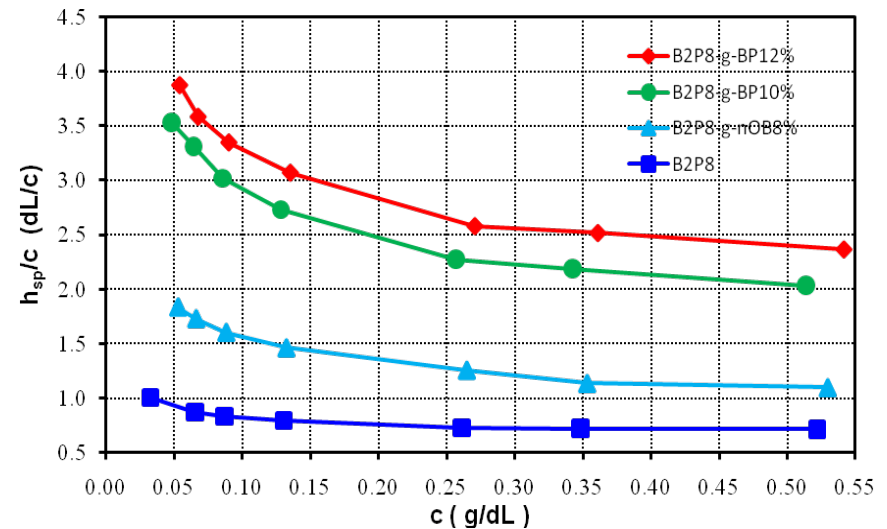
- 1 gm polymer dissolved in 9 cc phosphoric acid and equimolar amount of biphenyl added.
- 22 gm P₂O₅ added in 0.2 gm batches with **strong** cooling.
- System stirred at 70°C. Found: ~1% graft before heating. Slow further grafting of biphenyl.



Viscosities of Grafted Copolymers



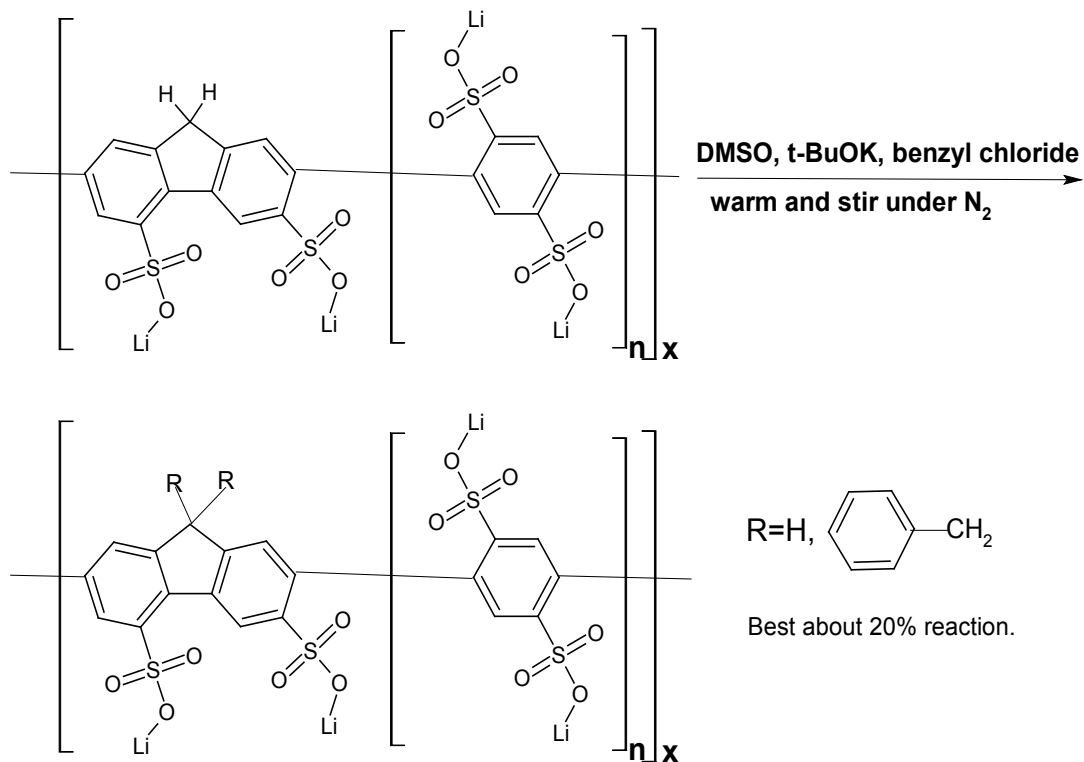
Reduced viscosity of B2P8 and its low % BP grafts



Reduced viscosity of B2P8 and its high % BP grafts, plus nOB graft

- Grafting raises viscosity, even for n-octyl benzene graft. (hydrophobic interactions ?)
- Viscosity of biphenyl grafts rises dramatically as % grafting rises.
- Probable cause: Even though once reacted biphenyl is deactivated, a small fraction may react twice, linking chains and raising viscosity.
- Viscosity of starting polymer key to mechanical properties. Higher viscosity (chain length) needed.

New Copolymer Grafting



- Reaction tested first on monomer using $\text{C}_{12}\text{H}_{25}\text{Br}$. Two dodecyl chains added.
- Only non-(active hydrogen) solvent found for polymer Li salt was DMSO.
- $\text{C}_{22}\text{H}_{45}\text{Br}$ was reacted with copolymer. One chain per fluorene was added. Polymer insoluble in water but became a swollen mush.

- Benzyl chloride was reacted; the phenyl group is a crosslinking site. For $n = 10$, a fully reacted and crosslinked copolymer should have an IEC ~ 7.0 mEq/gm. Grafted films ($\sim 30\%$ grafted), crosslinked at 220°C , were water insoluble but very brittle.
- WAXD showed that polymer chains were oriented perpendicular to film surface \rightarrow low elongation.