Polyphenylene Sulfonic Acid: a new PEM

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Outline of Talk

- Introduction and rationale
- Materials syntheses
- Polymer charcterization
- Effect of comonomers
- Conclusions and future work

PEM desired properties

- High proton conductivity with low sensitivity to relative humidity. Conductivity should be a minimum of 0.05 S/cm at operating conditions.

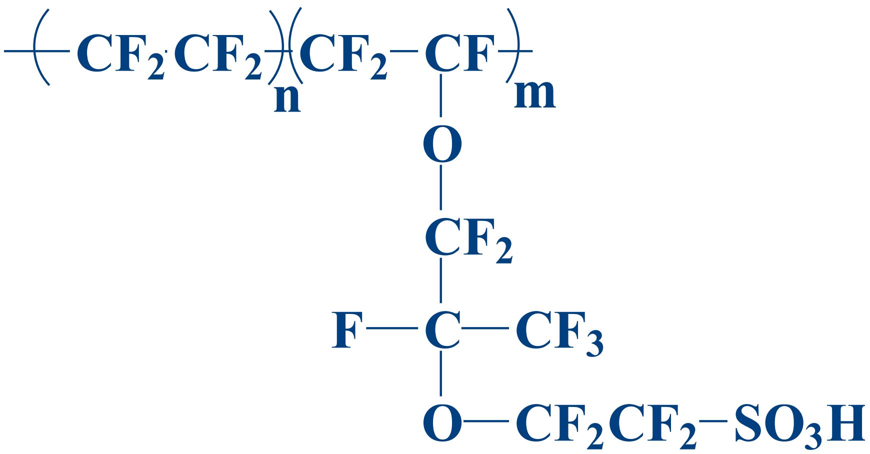
- Fuels should have essentially no permeation through the PEMs.

- High chemical, dimensional, and mechanical stability during the preparation and under the working conditions of the fuel cell. Membrane must be water insoluble in its final form and show little or no swelling.

- Can be directly cast on electrode as PEM in MEA processing for low power micro-fuel cells.

<u>*Nafion ®*</u>

The most widely used polymer electrolyte for the manufacturing of fuel cells.



Main limitations:

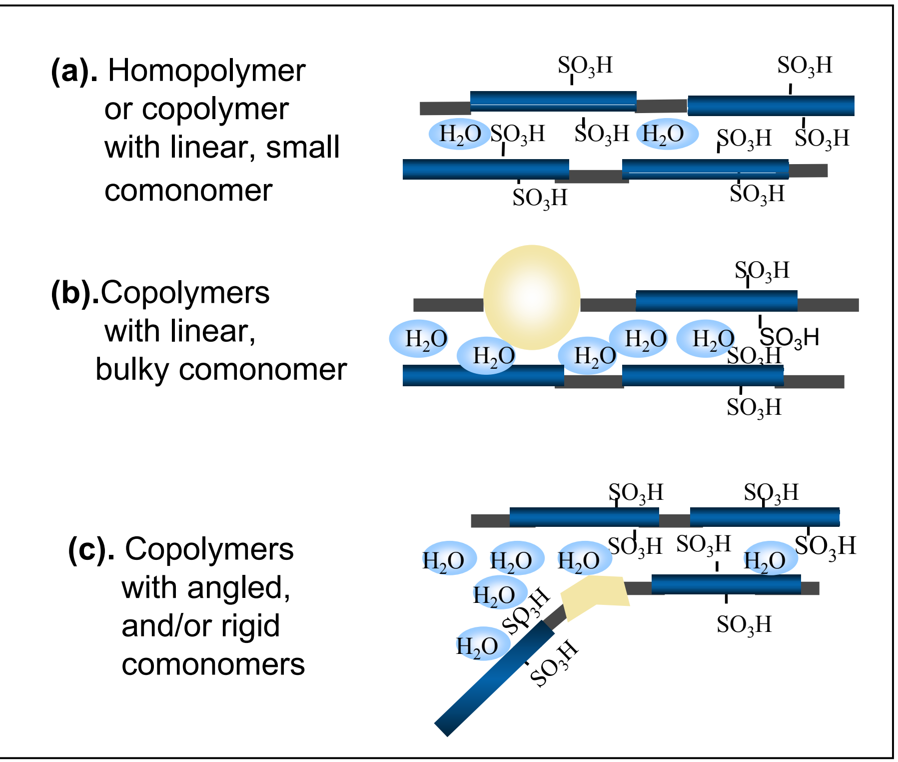
•Structural instability at temperatures above 100ºC

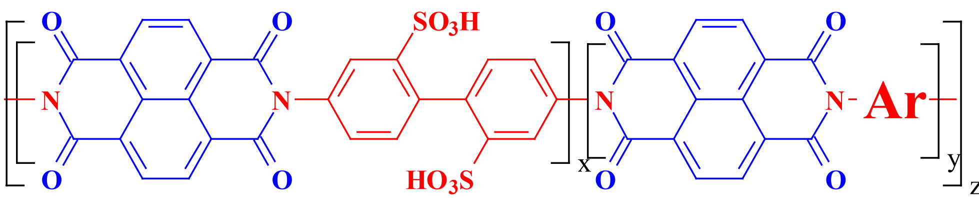
•Low conductivity at low relative humidity: if high temperatures are needed, must work at elevated pressure.

•High methanol permeability, limiting its use in Direct Methanol Fuel Cells

Materials alternative to Nafion®, molecular design

Use rigid-rod liquid crystalline polymers in which a few bulky or angled comonomer units can separate chains 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.





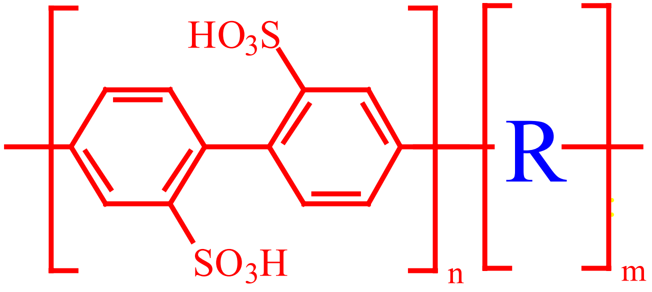
Ar= Bulky or angled comonomer

- Thermally stable up to 300ºC
- Maximum conductivity ~ 0.8 S/cm (100% RH, 100ºC)
- Conductivity remains above 10^{-3}S/cm even at 15% R.H.
- Imide groups slowly hydrolyze in acidic environments

Y. Zhang, M.H. Litt, ACS Polymer preprints Aug. 1999, 40(2), 480

Main Goal

Use the same molecular design approach that worked for the polyimides to obtain hydrolytically stable polymer electrolytes able to absorb and retain water over a wide range of relative humidity and temperature.



R: Bulky or angled comonomer

Specific tasks:

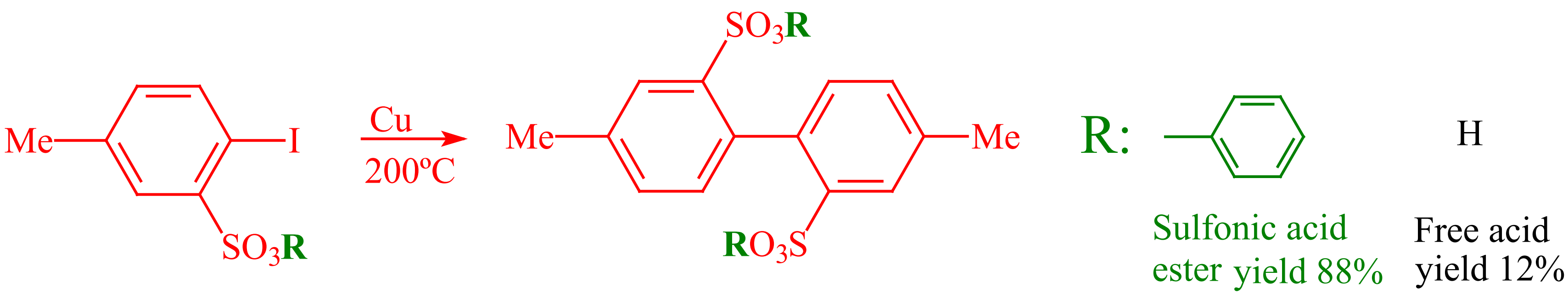
1.- Design and optimization of an efficient polymerization approach.

2.- Structural characterization of the obtained materials.

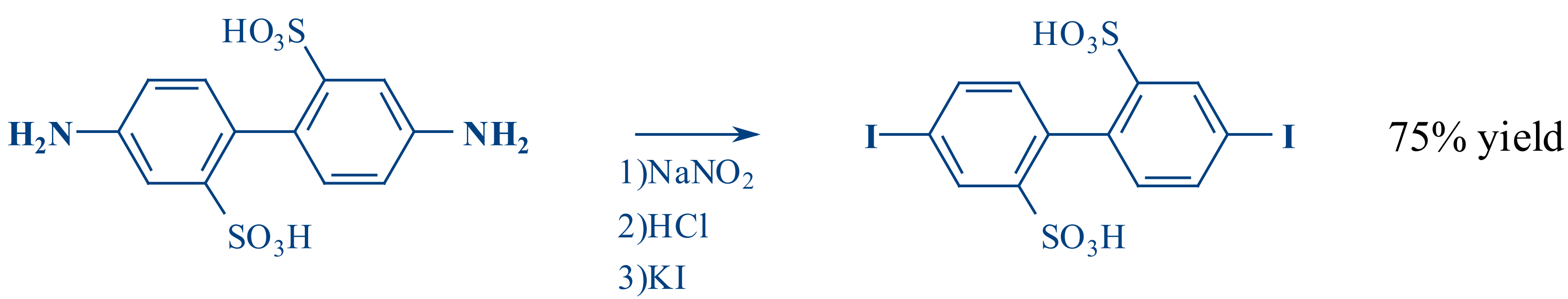
3.- Evaluation of water absorption, proton conductivity and thermal stability of the polymer membranes, and comparison with existing PEMs.

Design and optimization of the polymerization approach

Ullman coupling (P.E. Fanta, Chem. Rev. 64, 613 (1964))



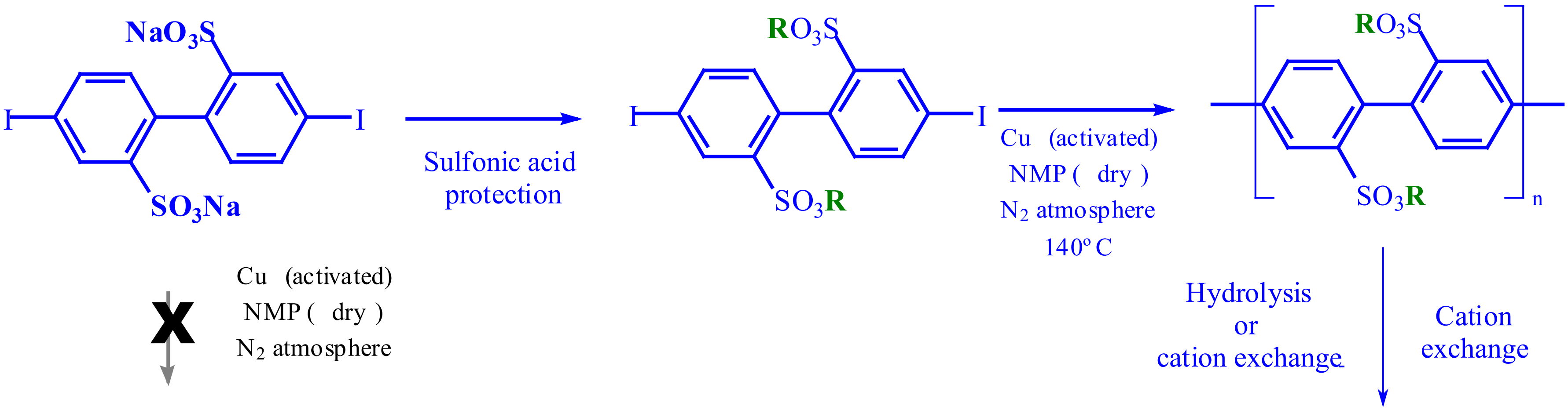
Diazotization (Courtot Ch., Lin C.C. *Bull. Soc. Chim. Fr.* 1931, [4] **49,** 1047)

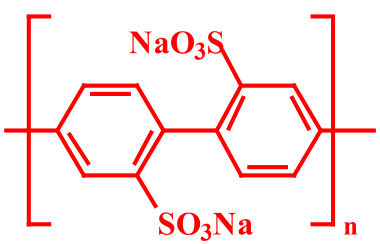


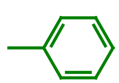
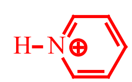
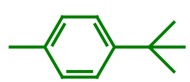
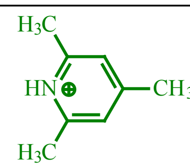
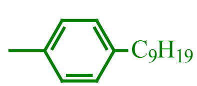
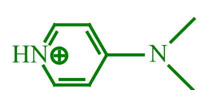
4,4'-diamino-2,2'-biphenyldisulfonic acid

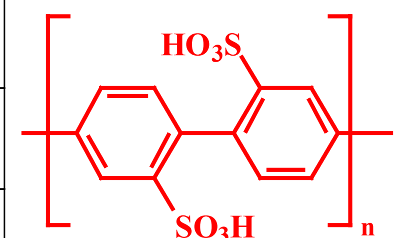
4,4'-diiodo-2,2'-biphenyl disulfonic acid

Design and optimization of the polymerization approach



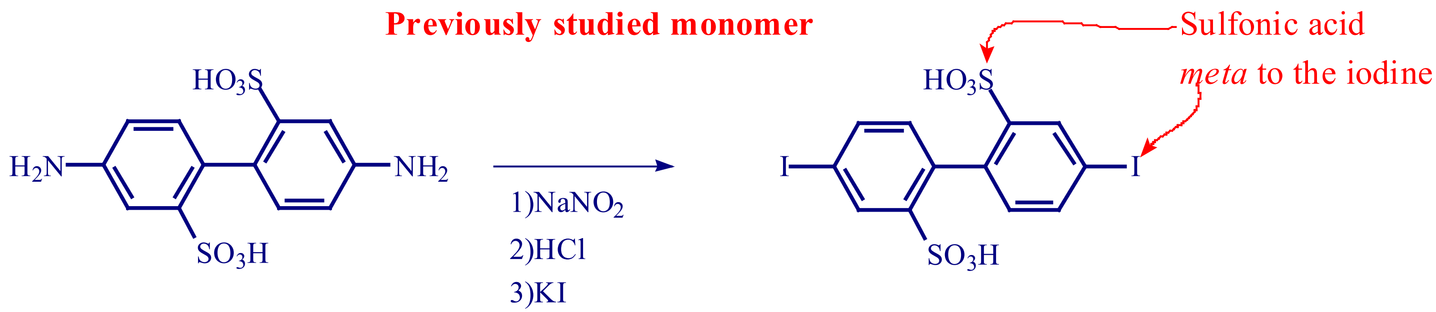


R	Intrinsic Visc. (dl/g) Synthesis at 150ºC	R	Intrinsic Visc. (dl/g) Synthesis at 150ºC
	0.09		0.24
	0.12		0.12
	0.07		0.07



Design and optimization of the polymerization approach

Previously studied monomer

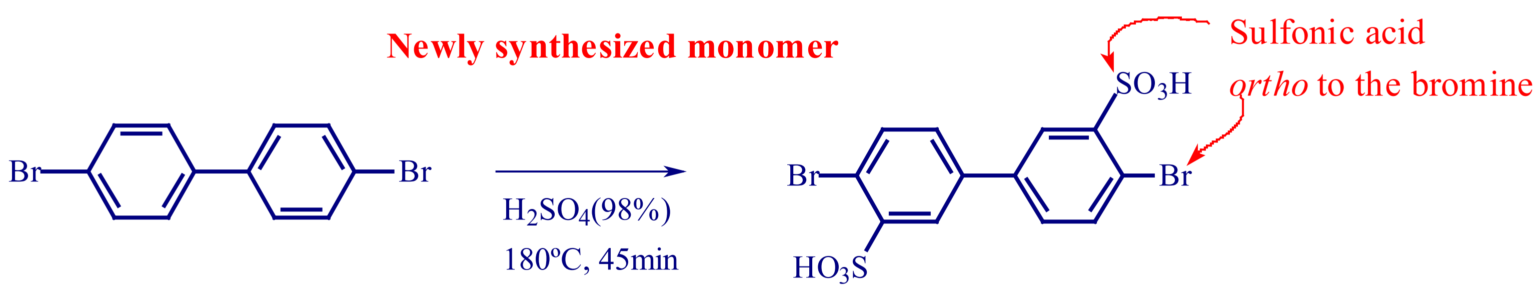


4,4´diamino-2,2´biphenyldisulfonic acid

4,4´diiodo-2,2´biphenyldisulfonic acid

A new monomer in which the halogen atom, as well as its position relative to the sulfonic acid, has been changed, couples more efficiently to yield higher molecular weight polymers than the previous monomer did.

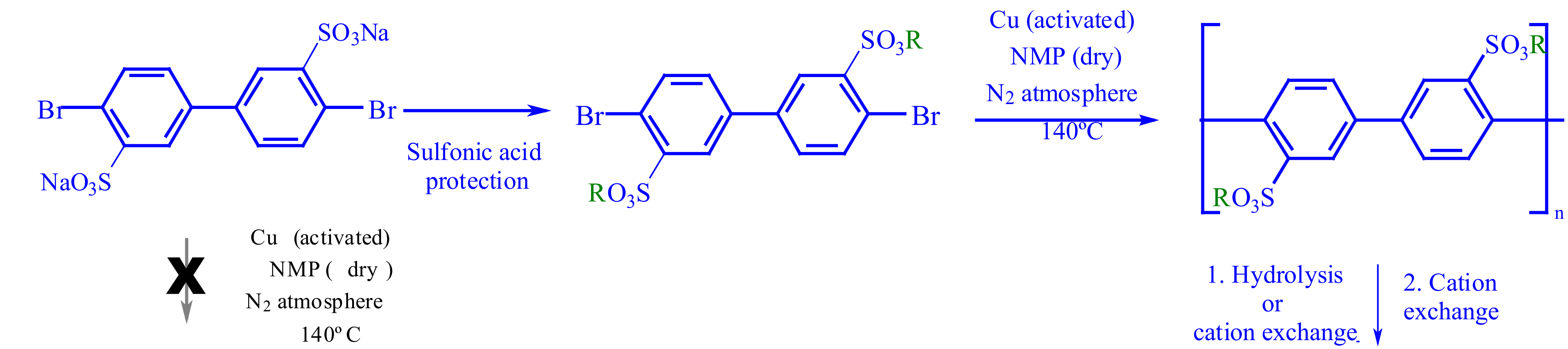
Newly synthesized monomer

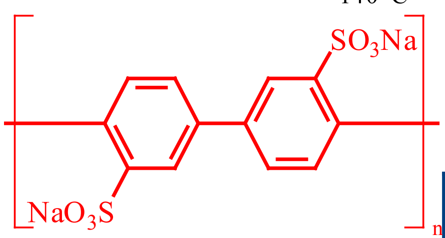


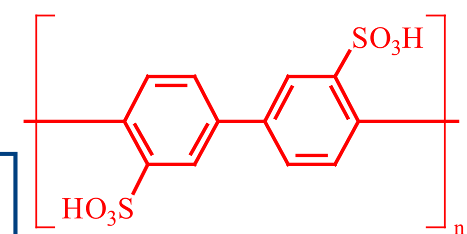
4,4´dibromobiphenyl

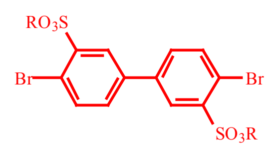
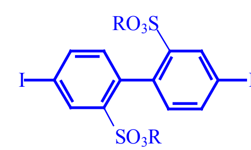
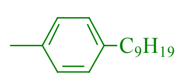
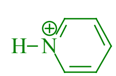
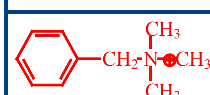
4,4´dibromo-3,3´biphenyldisulfonic acid

Design and optimization of the polymerization approach

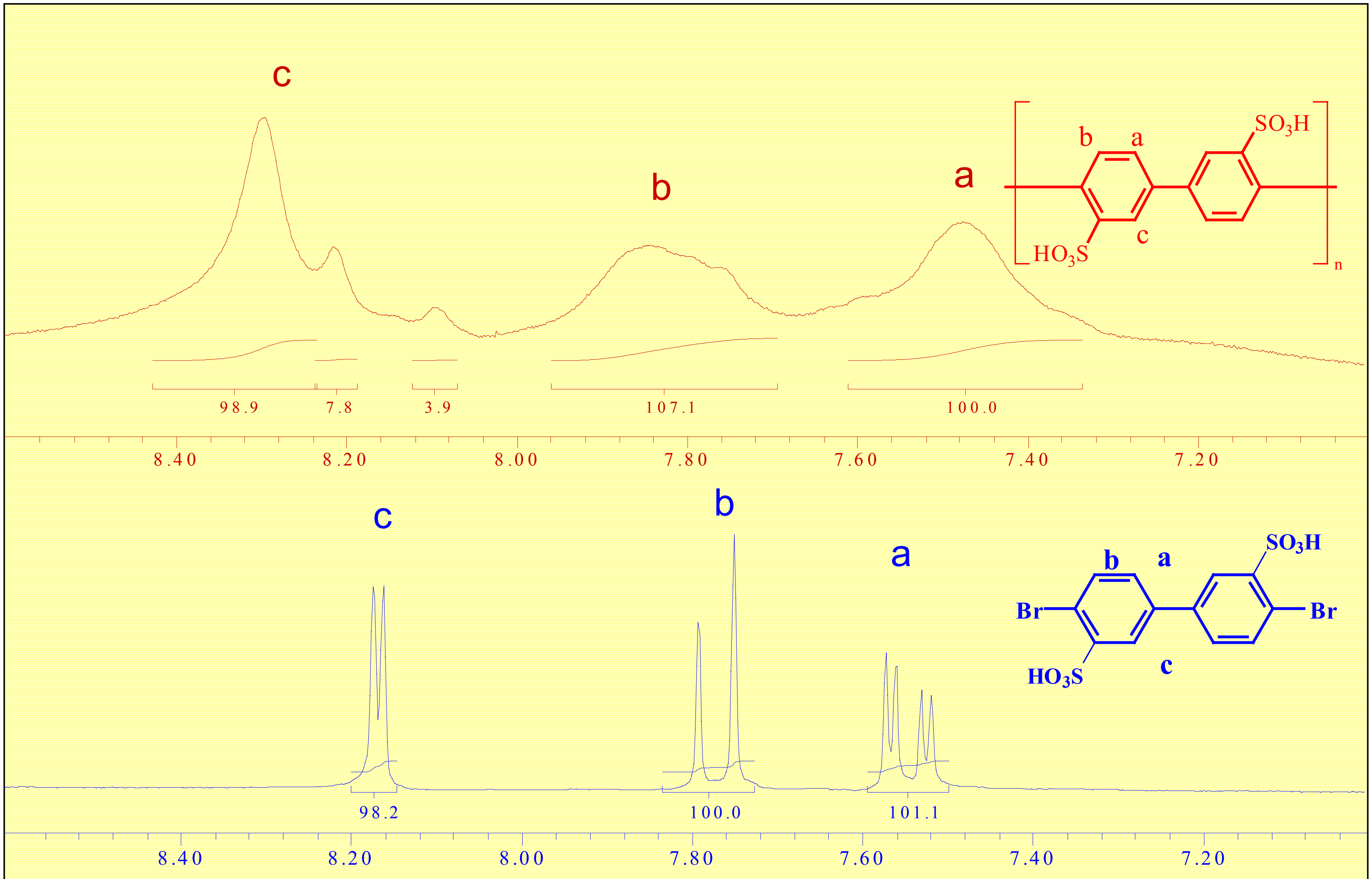




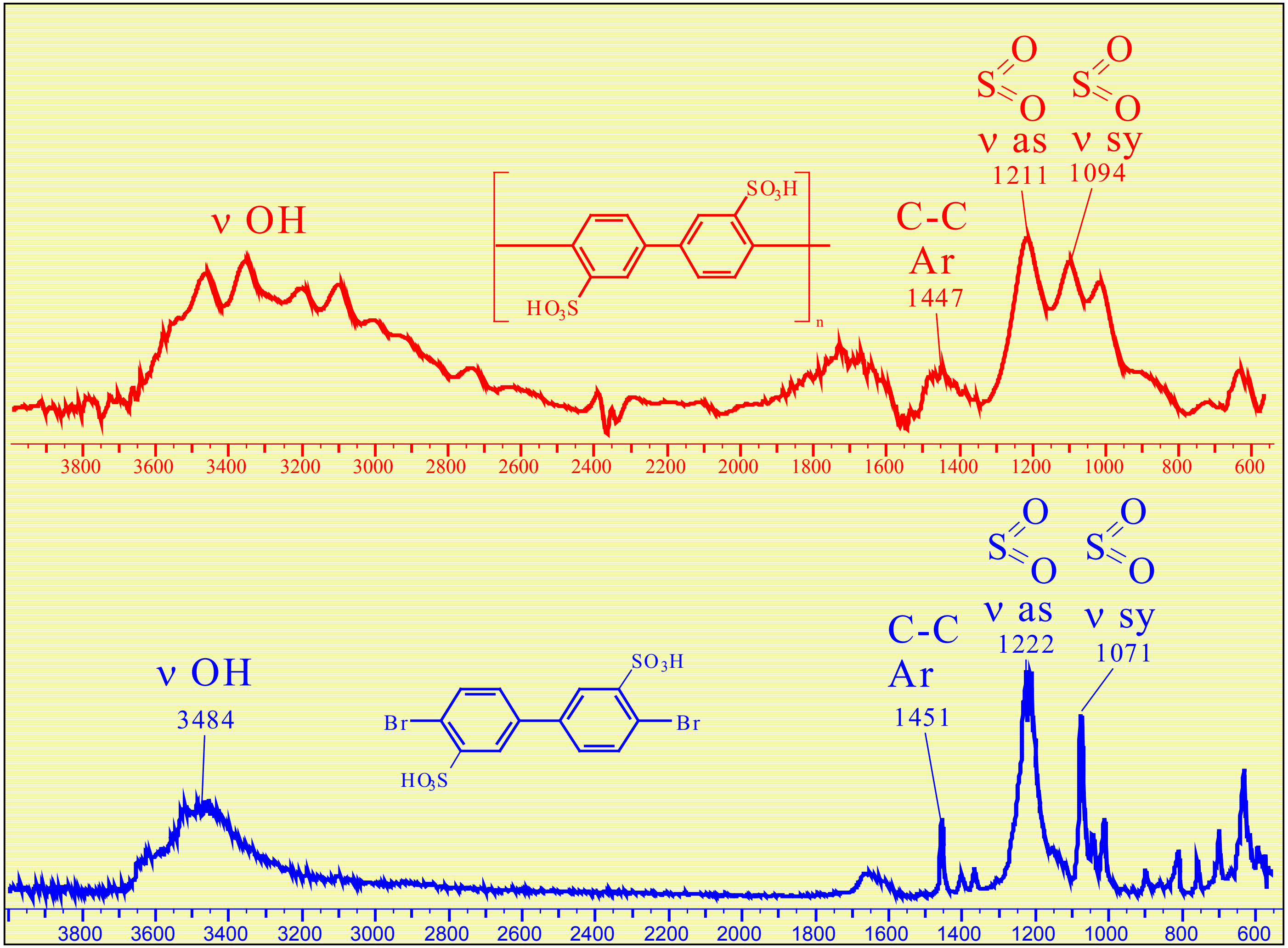


R	Intrinsic Visc. (dl/g) DiBrBS 	Intrinsic Visc. (dl/g) DiIPS 
	0.07	0.08
	0.31	0.2
	**0.61**	0.16

Structural characterization
NMR analysis

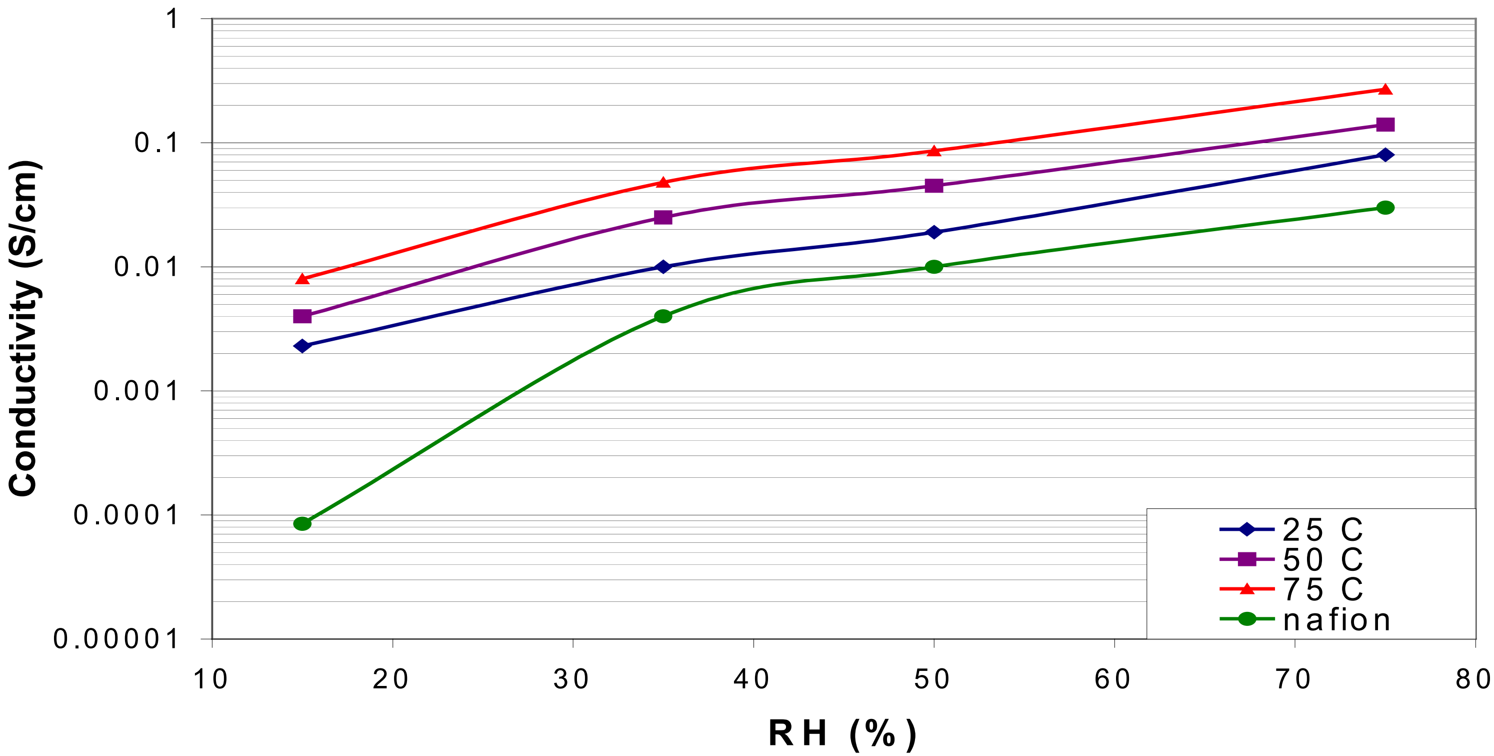


Structural characterization
FTIR analysis



Evaluation of conductivity and water absorption of polymer membranes

Conductivity as a function of Relative Humidity and Temperature



Temp (ºC)	Conductivity DBBS-Pol (S/cm) 15%R.H	Conductivity Nafion ®* (S/cm) 15%RH	Conductivity DBBS-Pol (S/cm) 35%R.H.	Conductivity Nafion ®* (S/cm) 35%RH	Conductivity DBBS-Pol (S/cm) 50%R.H.	Conductivity Nafion ®* (S/cm) 50%RH	Conductivity DBBS-Pol (S/cm) 75%R.H.	Conductivity Nafion ®* (S/cm)
25	0.0023	0.00008	0.010	0.004	0.019	0.01	0.080	0.03
50	0.0040	0.00008	0.025	0.004	0.045	0.01	0.140	0.03
75	0.0081	0.00008	0.048	0.004	0.086	0.01	0.270	0.03

*Sone Y., Ekdunge P. and Simonson D., *J. Electrochem. Soc.* **1996**, 143 (4) 1254.

Determination of Methanol Permeability in Polymer Electrolytes

RESULTS FOR DBBS POLYMER at 125 C

Methanol Pressure (torr)	Sorption g methanol per g polymer	Sorption Coefficient moles of methanol per (cm^3 film x torr)	Diffusion Coefficient cm^2/s
248	0.0020	2.5×10^{-7}	ca. 1×10^{-7}
392	0.0035	2.8×10^{-7}	ca. 1×10^{-7}

Estimated Crossover current for a 50 micron thick film:
= 1.1 mA/cm^2 (1:1 Methanol:Water Feed)

Water Sorption Results suggest water will be preferentially sorbed over methanol

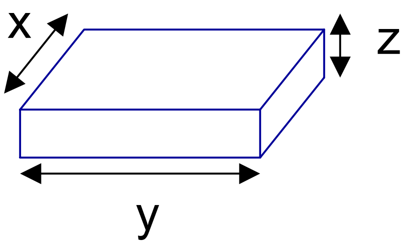
Evaluation of conductivity and water absorption of polymer membranes

Water absorption at room temperature

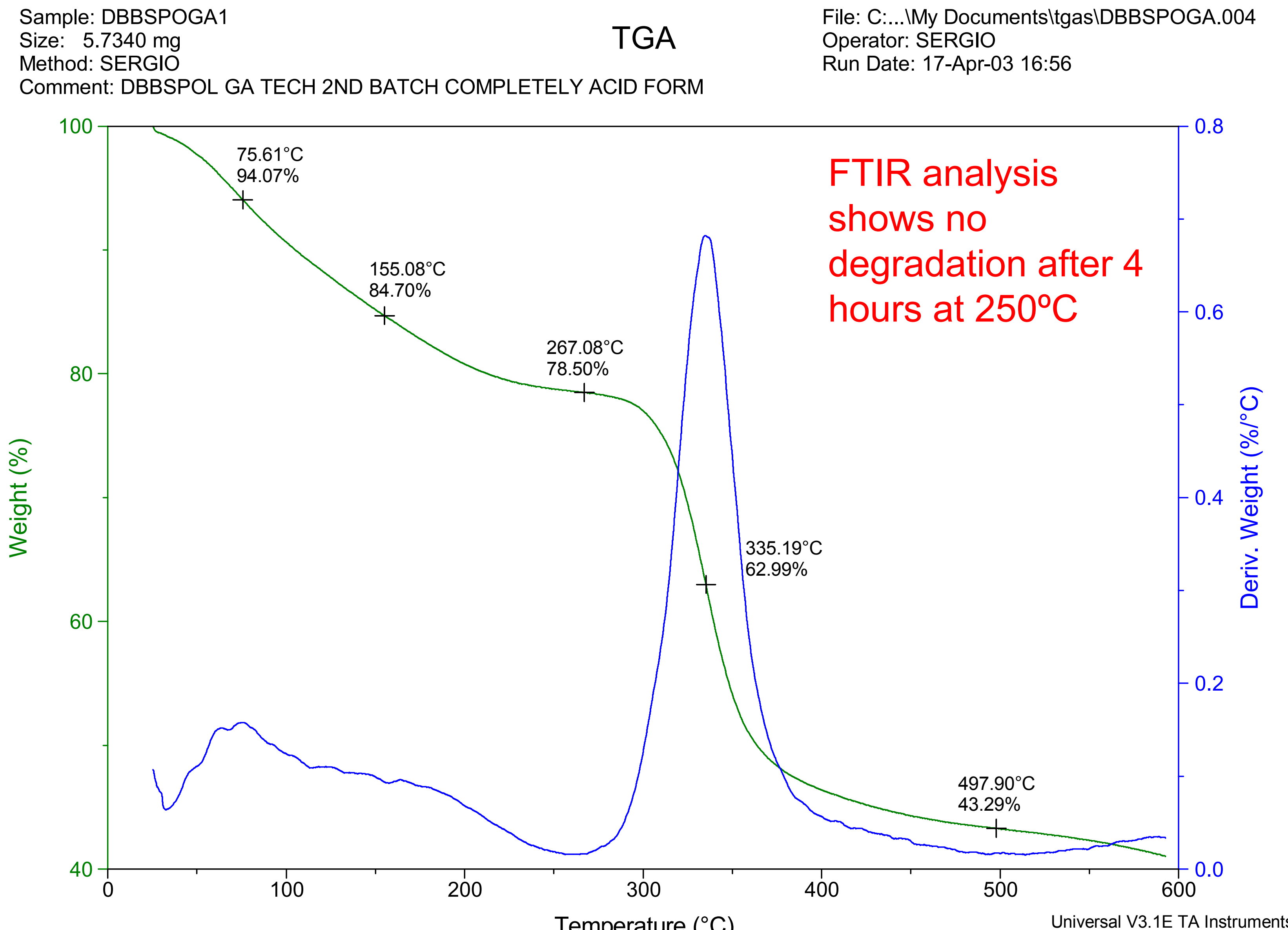
R.H. (%)	Molecules of water absorbed per sulfonic acid (λ)	
	DBBS-Pol	Nafion ®#
35	4.8	2.7
50	5.8	3.4
75	7.6	5.6

Dimensional change from 20% R.H.

Change in dimensions (%)	Relative Humidity		
	35%	50%	75%
Δx	2	3	5
Δy	3	4	5.5
Δz	32.5	45.83	79.82



Thermal stability



FTIR analysis shows no degradation after 4 hours at 250ºC

PEM special requirements

- High proton conductivity with low sensitivity to relative humidity. Conductivity should be a minimum of 0.05 S/cm at operating conditions.

Conductivity of the homopolymer is 0.27S/cm at 75% RH and 75ºC

- Fuels should have essentially no permeation through the PEMs.

Preliminary measurements show essentially no permeation of Methanol

- High chemical, dimensional, and mechanical stability during the preparation and under the working conditions of the fuel cell. Membrane must be water insoluble in its final form and show little or no swelling.

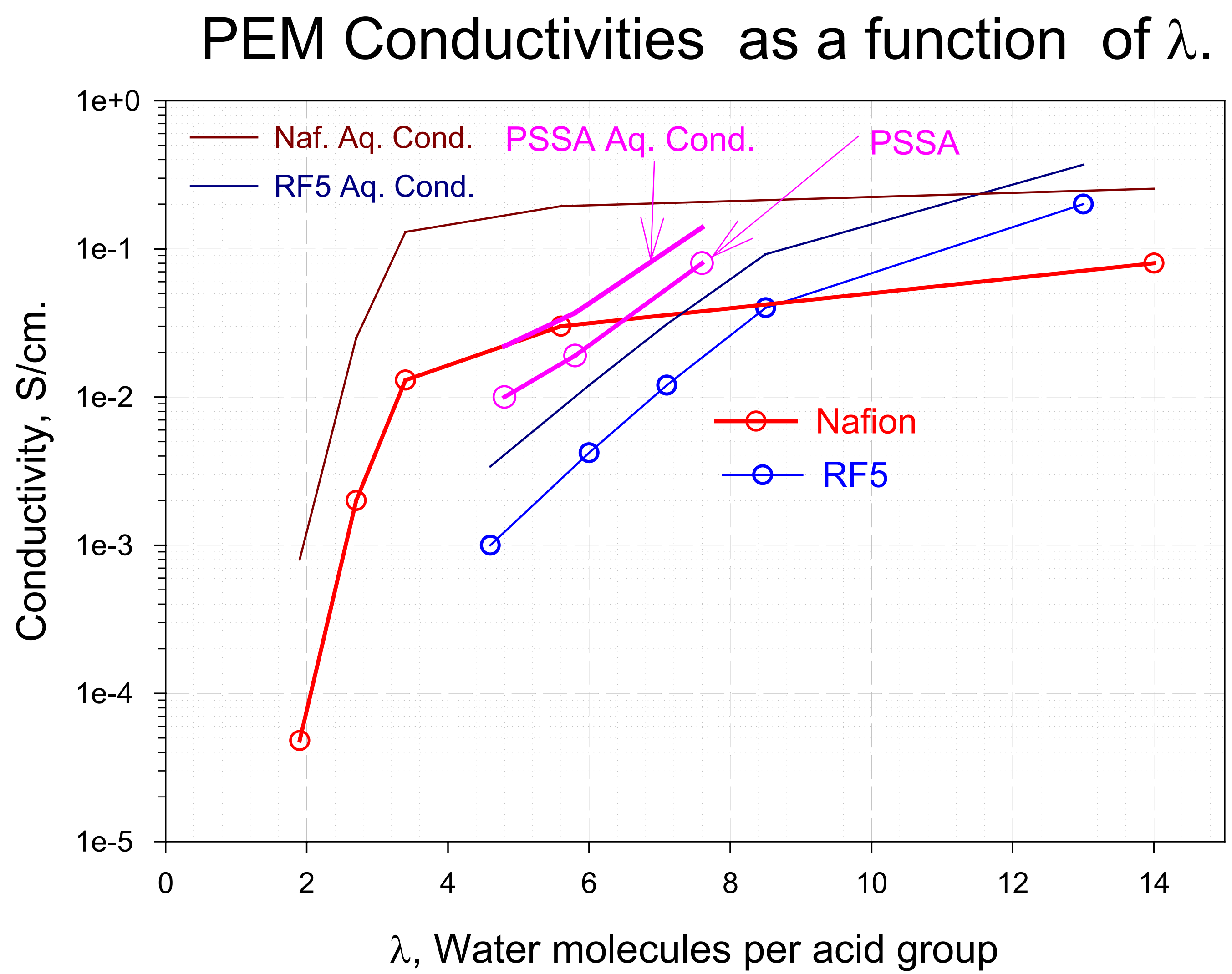
The newly synthesized polymers are stable up to 250 C.

Membranes are soluble in water and swell significantly.

- Can be directly cast on electrode as PEM in MEA processing for low power micro-fuel cells.

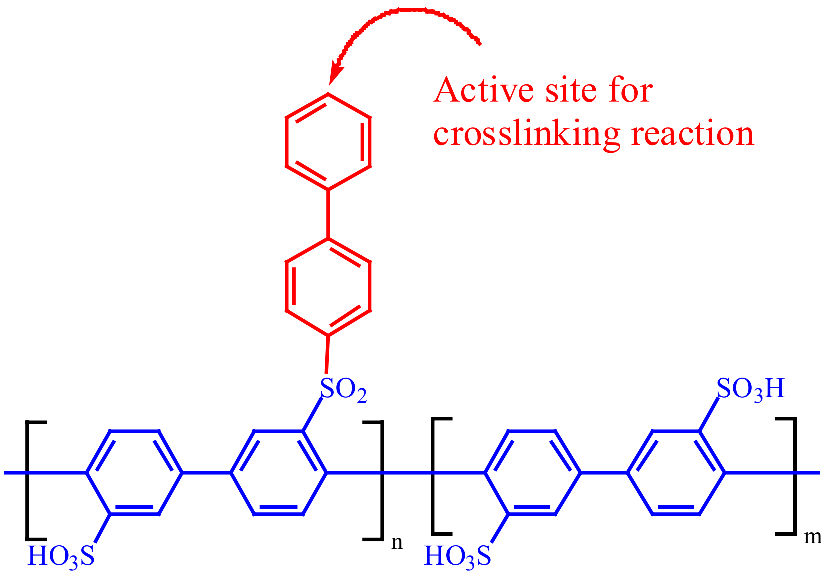
Films can be cast from water and a variety of polar organic solvents

Intrinsic Conductivity Comparison



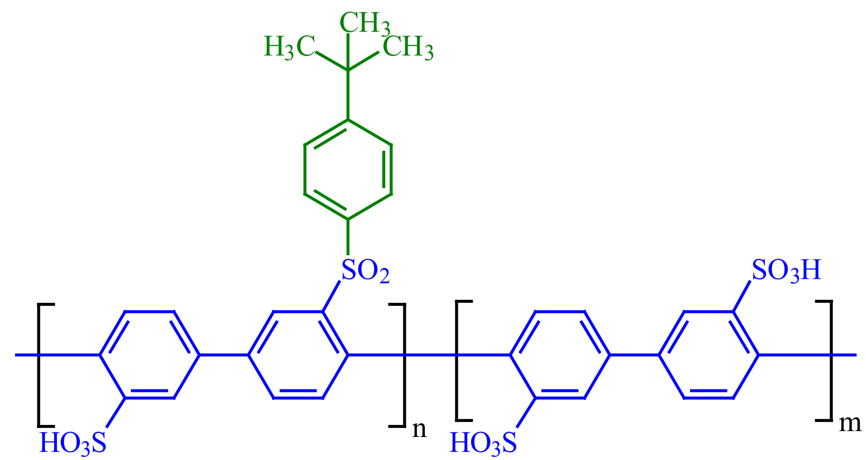
Membrane stabilization

Incorporation of cross-linkable biphenyl groups.



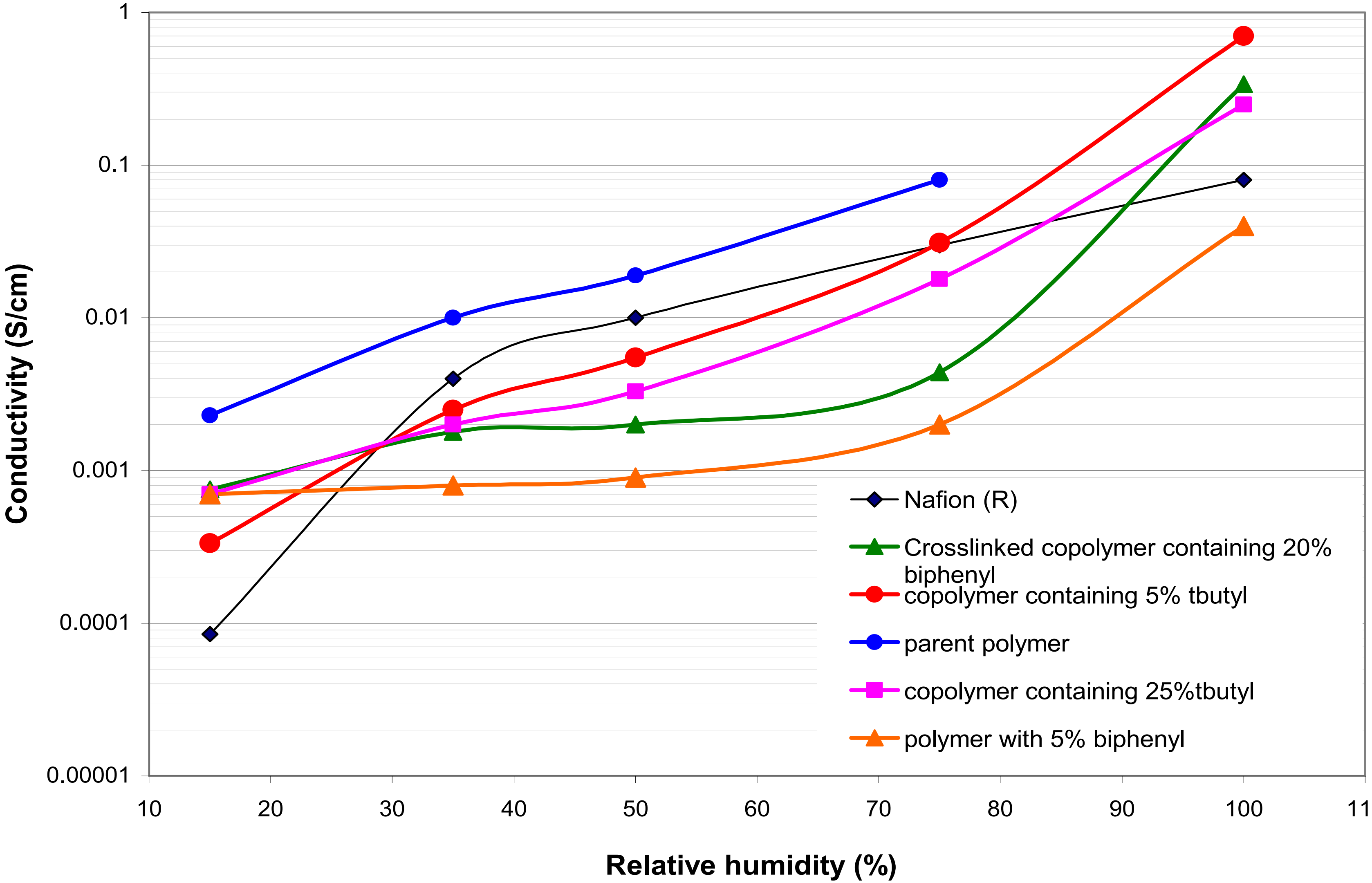
Copolymers containing from 5 to 20% of biphenyl sulfone groups crosslink after 20 minutes at 200ºC.

Incorporation of bulky tert-butyl benzene groups.



5% of t-butyl benzene sulfone renders the copolymer water insoluble

Proton conductivity of water insoluble polymer membranes



What we have learned from the bulky and crosslinked copolymers

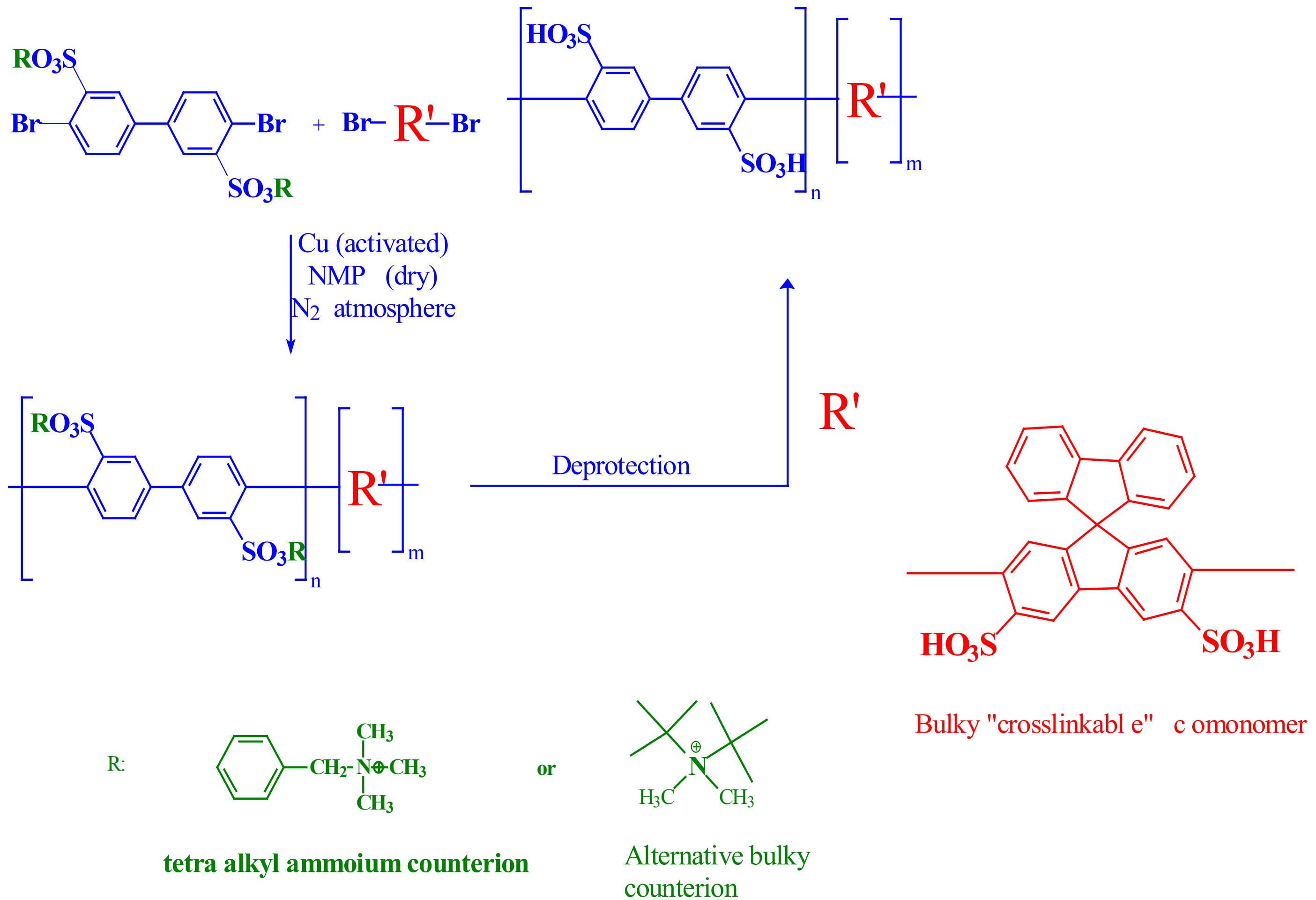
- Both the bulky and crosslinked copolymers have much lower conductivity than the homopolymer. The dependence of conductivity on relative humidity suggests that the membrane structure de-swells rapidly as humidity drops until it approaches its built-in free volume. It then holds the remaining water tightly.
- The use of larger bulky and/or crosslinkable comonomers should increase the built-in free volume, improving water retention and thus the low humidity membrane conductivity.

Conclusions

- A new poly (phenylene sulfonic acid) has been obtained using the copper catalyzed coupling of dibromo aromatic sulfonates in high molecular weight to cast free standing films.
- The polyphenylene sulfonic acids have conductivities at 25^{o}C and 15% relative humidity that range from 0.8 to 2.3 mS/cm. Conductivity rises rapidly with temperature.
- The newly synthesized materials are chemically stable up to 250^{o}C.
- Copolymers containing bulky or crosslinkable groups have much lower conductivity than the homopolymer, but the data imply that bulkier comonomers could generate materials with high conductivities at low humidities.
- Further work needs to be done to increase the molecular weight and improve the dimensional stability of the materials without sacrificing proton conductivity.

Future work

- Further increase the polymer molecular weight by optimizing the Ullman coupling conditions and/or using alternative coupling methods
- Optimize the reaction conditions to obtain copolymers containing bulky, crosslinkable groups.



Future work

Characterization:

a. Analysis: X-Ray to confirm structure

b. Optimization of crosslinking conditions.

c. Mechanical properties of new polymers as a function of composition and environment (water/MeOH in liquid and gaseous state).

d. Water content and conductivity as a function of RH and temperature for all new copolymers.

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Acknowledgments

- DARPA for the support of the project
- Drs. Jesse Wainright and Robert Savinell for their advice and help in learning to measure conductivity.