A discussion on improved HTMs

NREL

Bryan Pivovar

HTMWG Meeting
Honolulu, HI 2008

Co-authors: Yu Seung Kim: **Los Alamos National Lab**; Cortney Mittelsteadt: **Giner**

Strategies – Membrane R&D

Three Strategies for High-Temperature Membrane Research:

Strategy 1 – Phase segregation control (polymer & membrane)

a) Polymer - Separate blocks of hydrophobic and hydrophilic functionality incorporated within the same polymer molecule.

b) Membrane – Two-polymer composites. One polymer provides mechanical strength while the other polymer enables proton conduction.

Strategy 2 – Non-aqueous proton conductors

– Membranes that use inorganic oxides, heteropolyacids (HPA), or ionic liquids, rather than water, for proton conductivity.

Strategy 3 – Hydrophilic additives

– Membranes with additives that maintain water content and conductivity at higher temperature.

Kathi Epping Martin, Nancy L. Garland, John P. Kopasz "The U.S. DOE's High Temperature Membrane Effort" CARISMA International Conference on Progress MEA 2008, La Grande Motte, France, 21 September, 2008.

Tunable Parameters
What we control

Table 1 Transport properties and primary influencing factors (broken into tunable parameters and structural feature) for polymer electrolytes.

Transport Properties	Tunable Parameters	Structural Features
Proton conductivity	Backbone characteristics	Water domain size,
Water transport	Acid group	shape and interface
properties (D_{H2O}, E_D)	characteristics	Interanionic distances
Reactant permeability	Ion exchange capacity	Water uptake
	Processing/History	Tortuosity

M. Hickner, B. S. Pivovar, *Fuel Cells* **5, 213 (2005).**

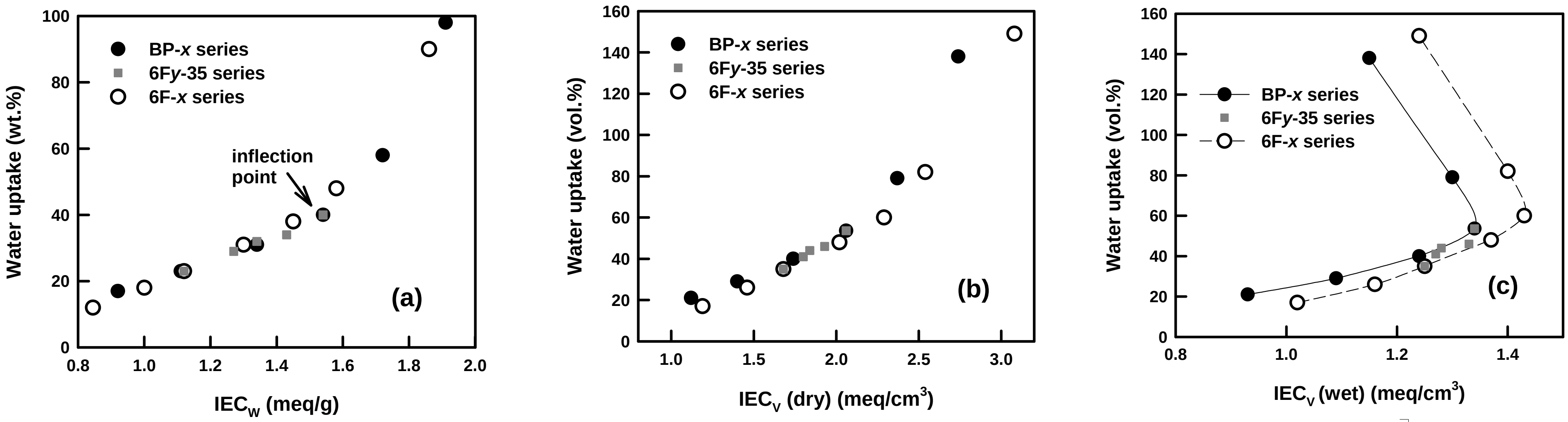
Tunable Parameters
What we control

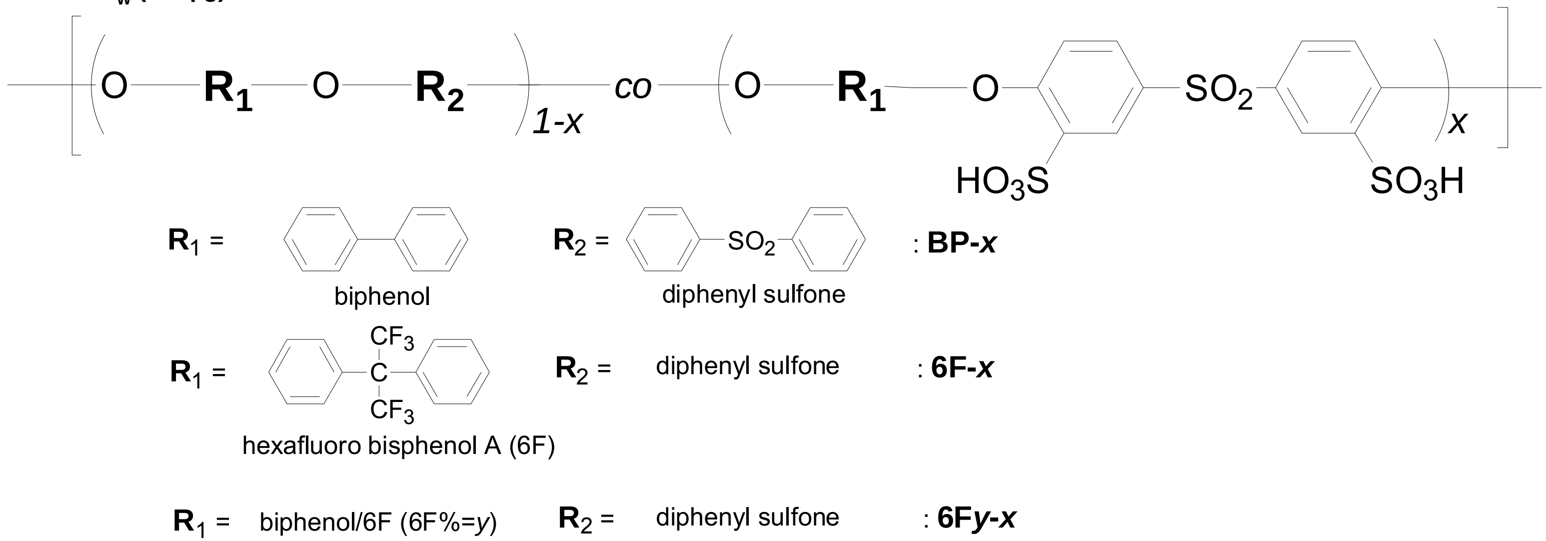
Table 1 Transport properties and primary influencing factors (broken into tunable parameters and structural feature) for polymer electrolytes.

Transport Properties	Tunable Parameters	Structural Features
Proton conductivity	Backbone characteristics	Water domain size, shape and interface
Water transport properties (D_{H2O}, E_D)	Acid group characteristics	Interanionic distances
Reactant permeability	Ion exchange capacity	Water uptake
	Processing/History	Tortuosity

M. Hickner, B. S. Pivovar, *Fuel Cells* **5, 213 (2005).**

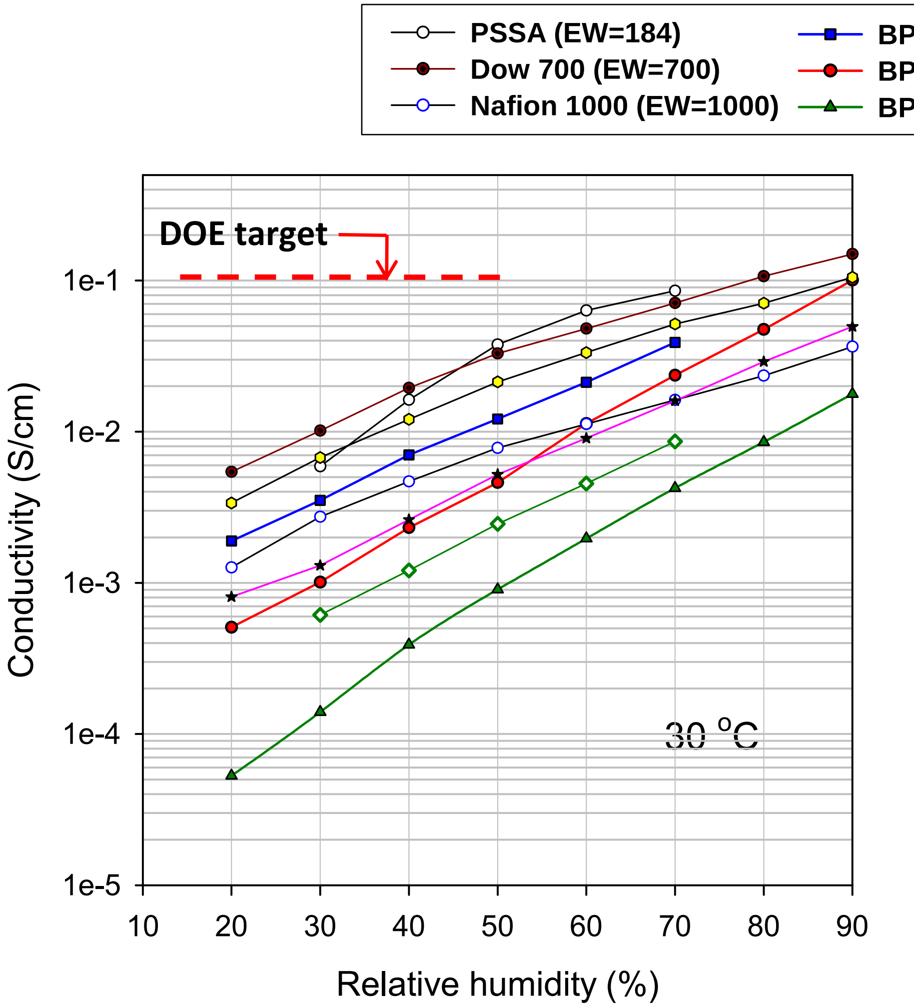
Water uptake vs. IEC

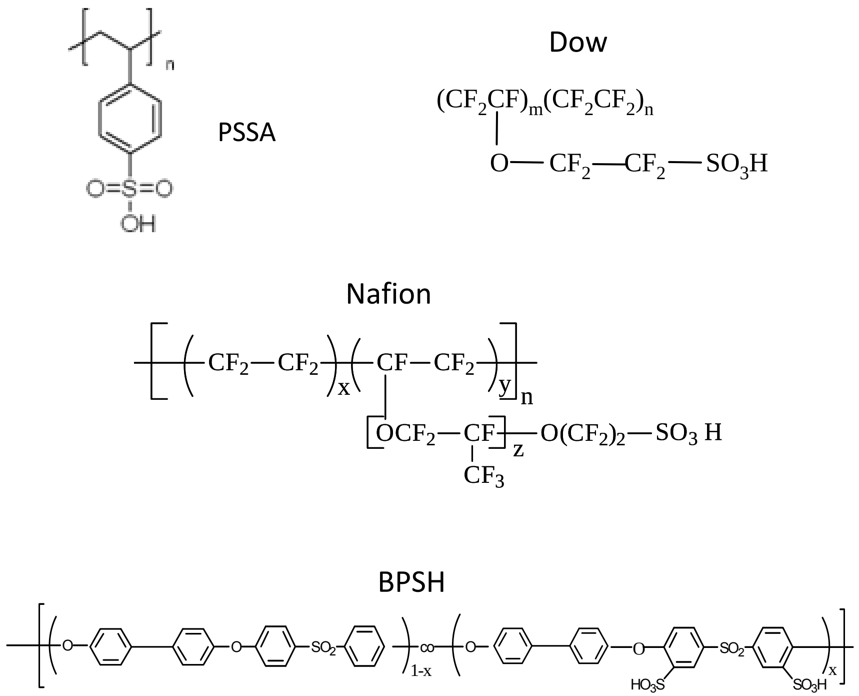




Y.S. Kim, B. Einsla, M. Sankir, W. Harrison, B. Pivovar, *Polymer*, 2006; 47, 4026.

Effect of Relative Humidity on Proton Conductivity of Various Sulfonated PEMs



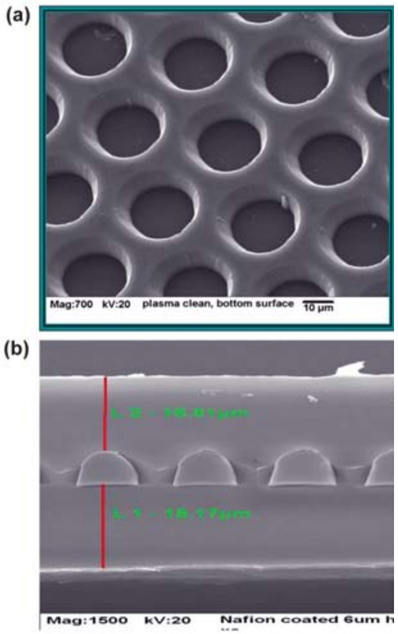


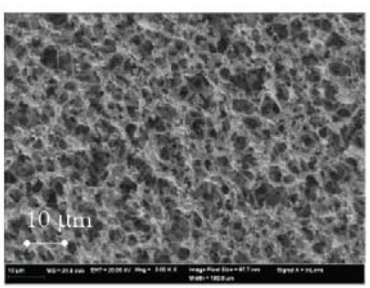
Strategy 1b, Phase segregation control using two-polymer composites

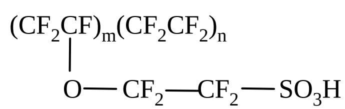
Composite membranes show promise for better conductivity at high temperature and low RH.

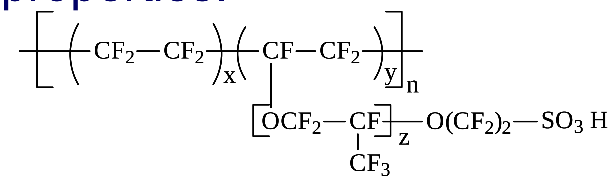
- Support structure allows use of lower equivalent weight ionomer to achieve higher conductivity while retaining mechanical properties.

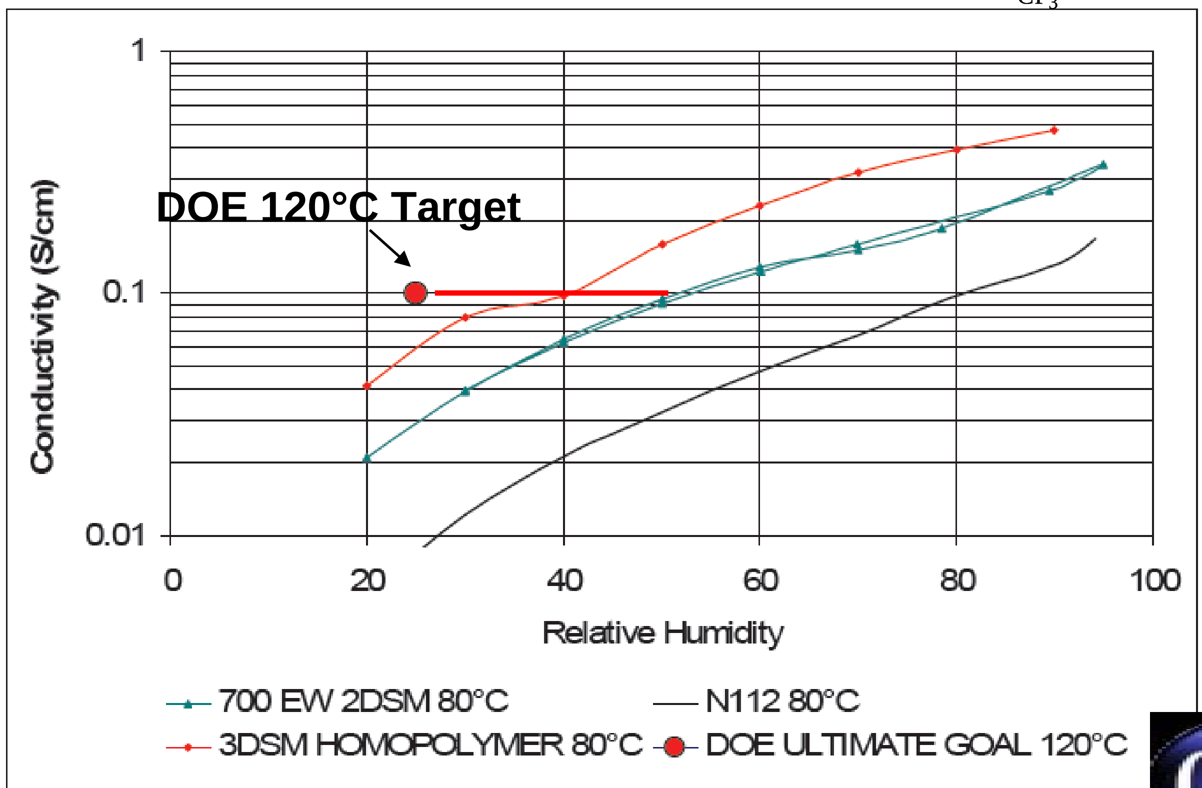
Strategy 1b







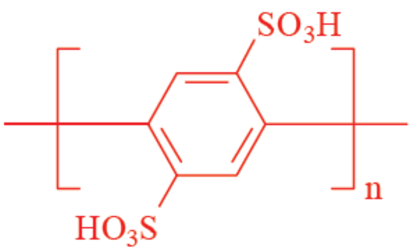




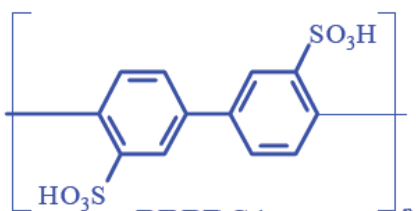
*Cortney Mittelsteadt, DOE AMR, 2008.

CWRU – High acid density

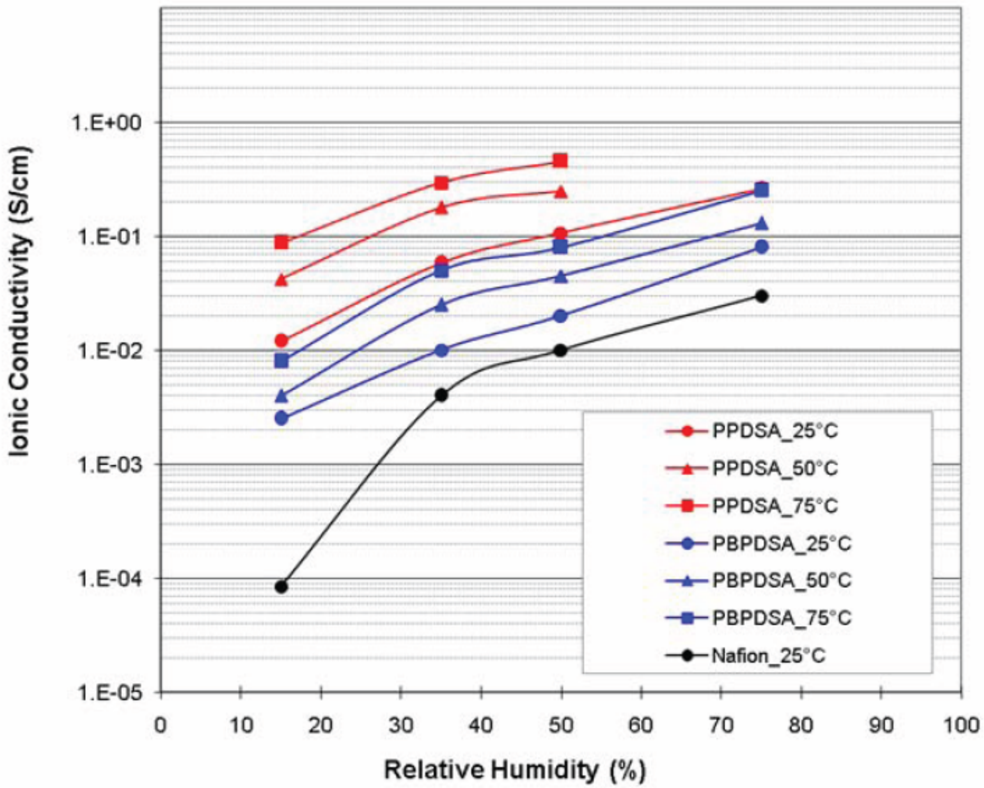
Comparison of PBPDSA and PBDSA: Conductivity vs Relative Humidity



PPDSA



PBPDSA

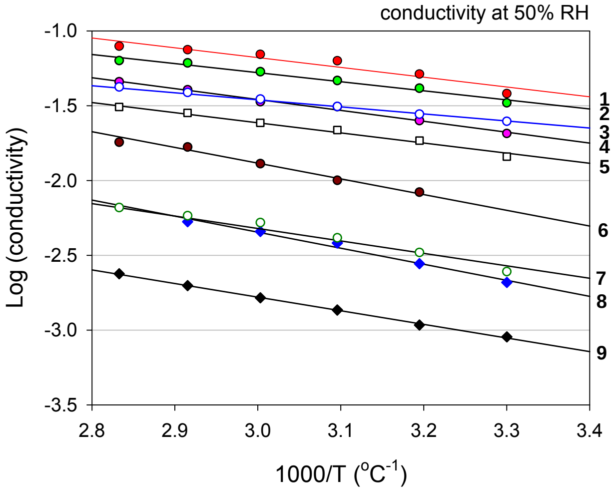


PPDSA should meet the DOE conductivity goals for 2015. σ = 0.1 S/cm at 75°C and 15% RH.

15

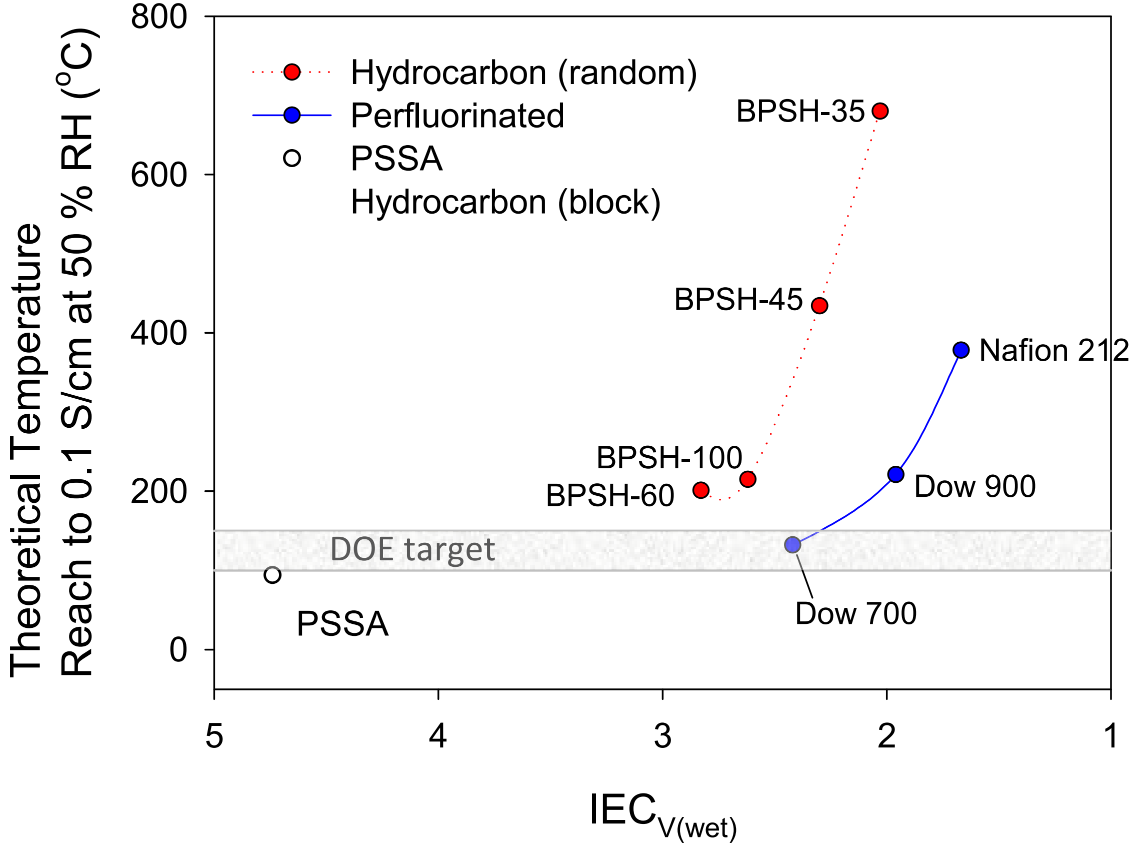
***Morton Litt, DOE AMR, 2008.**

Effect of Temperature on Proton Conductivity of Various PEMs



No.	PEM	E_a (kJ/mol)
1	PSSA	5.5
2	DOW 700	4.5
3	Dow-900	3.9
4	BPSH-100	6.0
5	Nafion 212	5.3
6	BPSH-60	8.2
7	BPSH-45	6.9
8	BPSH-Block	8.9
9	BPSH-35	7.6

Temperature Reach to 0.1 S/cm at 50% RH for Various PEMs



Atomic Radii

While IEC on a wet volume basis would be best relative gauge, #s of atoms/charge is likely a better “easy” gauge than IEC on a mass basis

van der Waals radii

Element	radius (Å)
Hydrogen	1.20
Carbon	1.70
Nitrogen	1.55
Oxygen	1.52
Fluorine	1.47
Sulfur	1.80

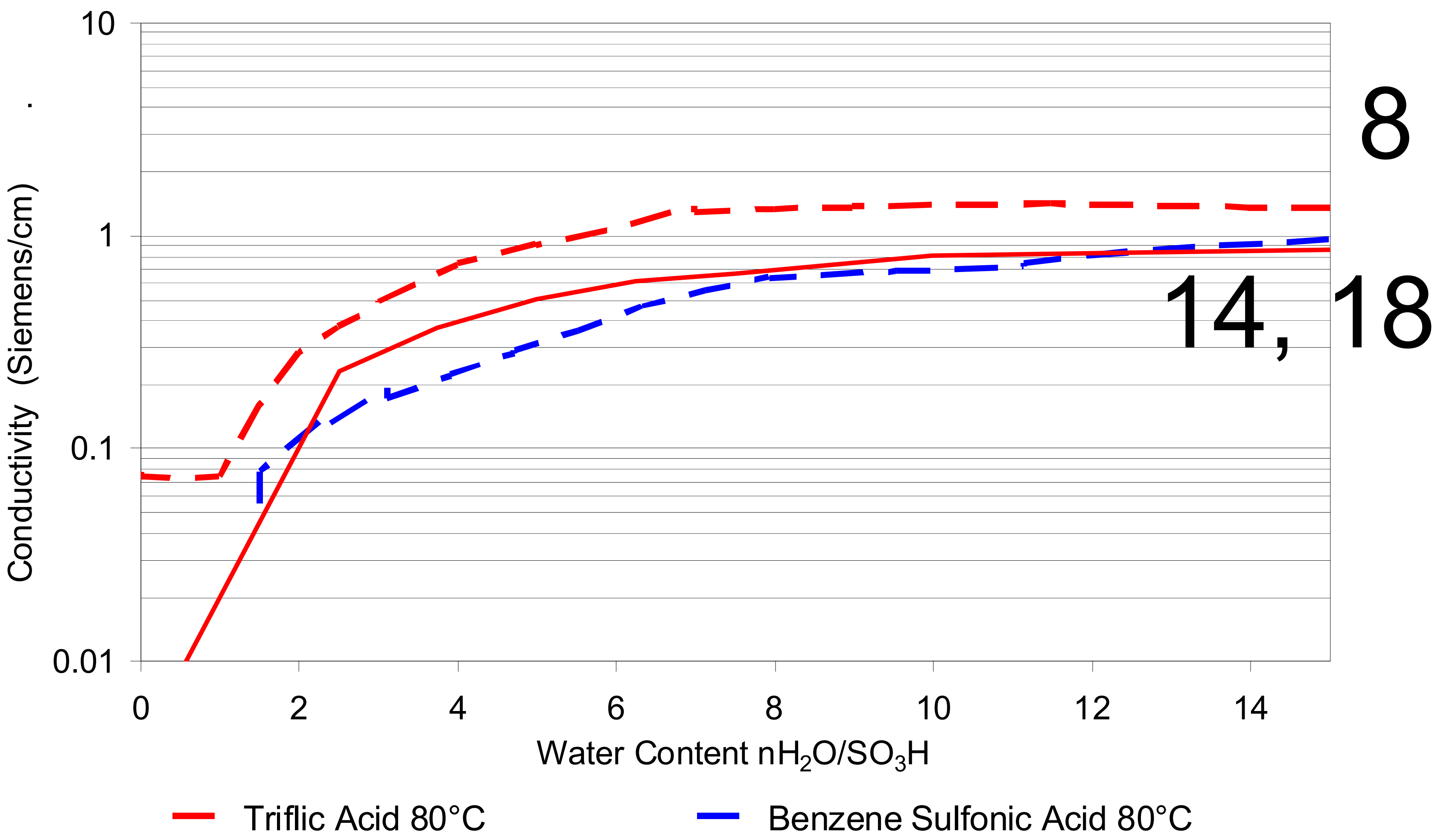
Van der Waals radii taken from Bondi's compilation (1964).[1] Values from other sources may differ significantly (*see text*)

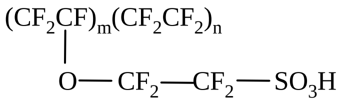
Covalent Radii

Z	Symbol	r (Å)
1	H	0.31(5)
6	C (sp^3)	0.76(1)
	C (sp^2)	0.73(2)
	C (sp)	0.69(1)
7	N	0.71(1)
8	O	0.66(2)
9	F	0.57(3)
16	S	1.05(3)

***www.wikipedia.com**

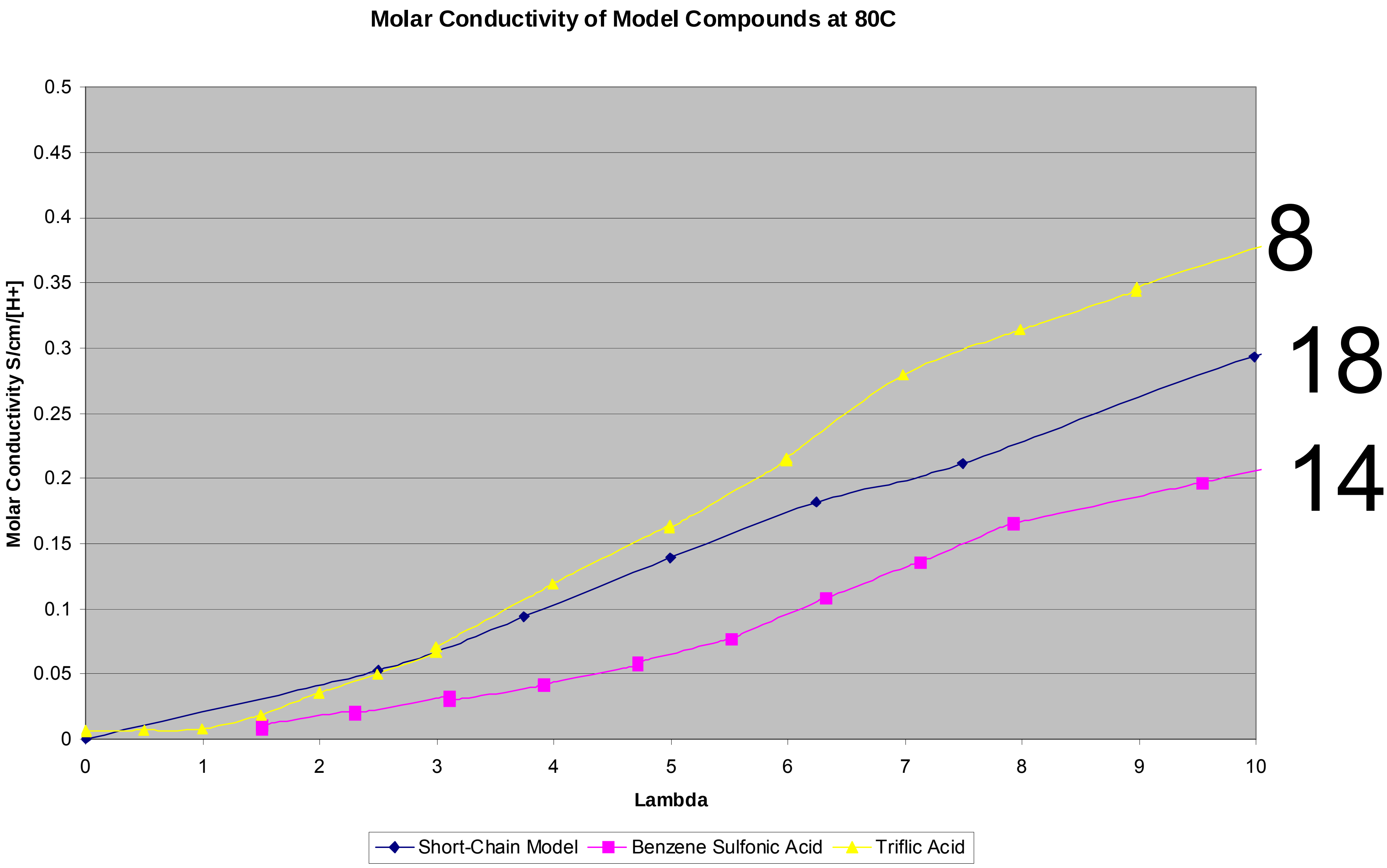
Acid Strength vs. Interanionic Distance





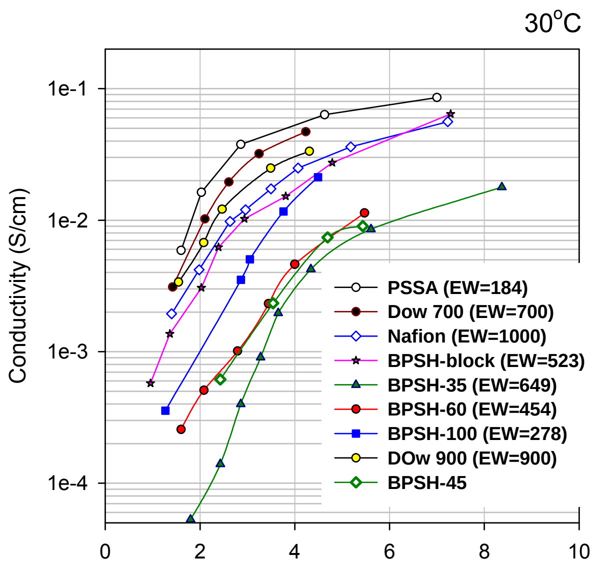
***Cortney Mittelsteadt.**

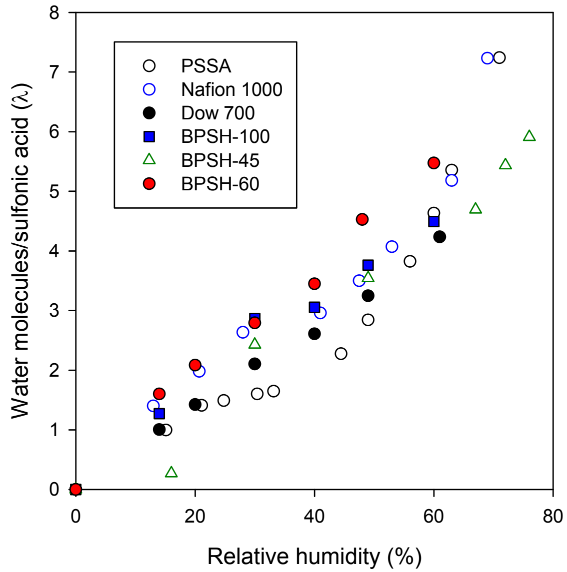
Acid Strength vs. Interanionic Distance



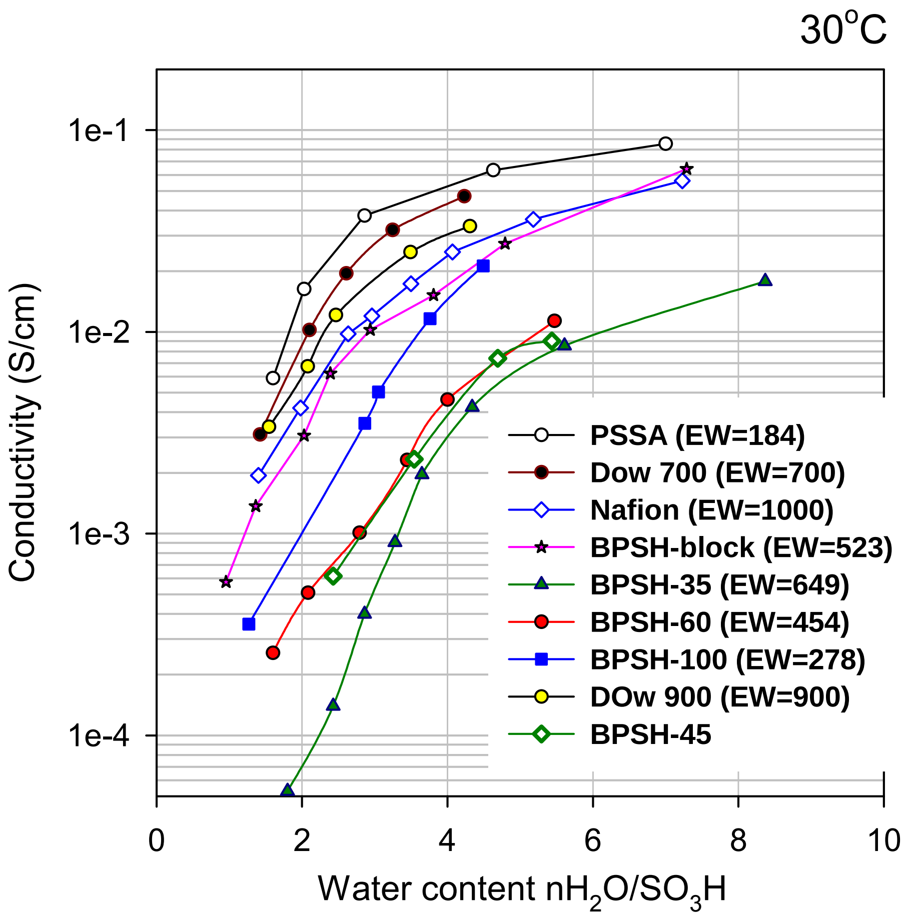
Required λ and RH to reach 0.1 S/cm at 120ºC

E_a (kJ/mol)	Conductivity at 30ºC (required for 0.1S/cm at 120ºC)	PEM having corresponding E_a	Required water /sulfonic acid	Required RH (%)
5.5	0.032	PSSA	2.7	48
4.5	0.039	DOW 700	3.6	54
5.3	0.032	Nafion 212	4.8	60
6.0	0.028	BPSH-100	4.9	64
8.2	0.018	BPSH-60	6.6	70
7.6	0.020	BPSH-35	9.1	93





Anionic Group Concentration Effect



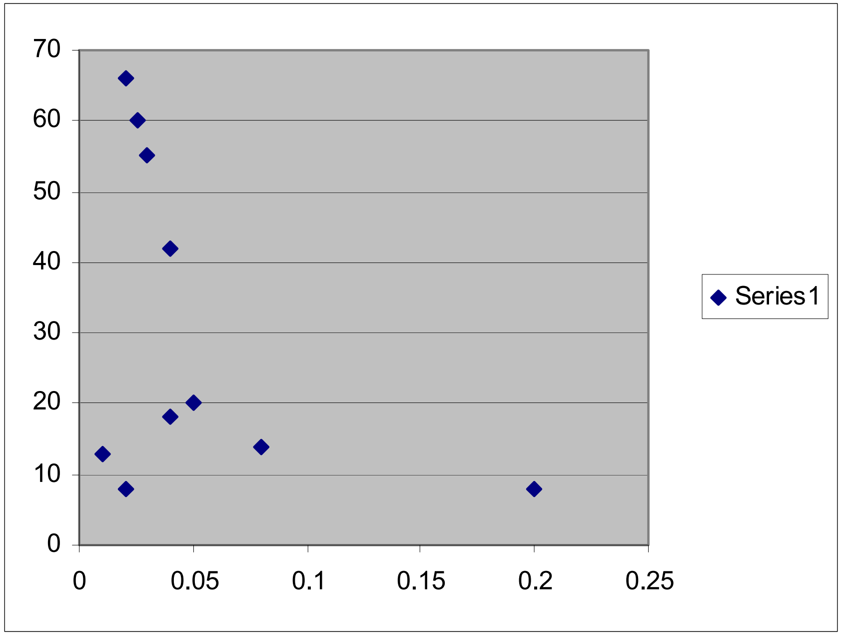
IECv(wet) vs. σ

Polymer	EW	IECv (wet)	σ (mS/cm)
PSSA	184	4.0	66
PFSA	700	2.3	49
PFSA	900	1.9	39
Nafion	1000	1.7	34
BPSH-35	649	1.8	6
BPSH-block (1)	523	2.0	29

Relatively low conductivity of BPSH-35 is due to morphology effect

Atoms vs. low water conductivity

Ionomer	EW	atoms/+	cond (50%RH)	cond (4)
Triflic acid	150	8		0.2
benzene sulfonic acid	158	14		0.08
Short sidechain		18		0.04
PPDSA	118	8	0.1	0.02
PBPDSA	156	13	0.02	0.01
PSSA	184	20	0.04	0.05
Dow	700	42	0.03	0.04
Dow	900	55	0.02	0.03
Nafion	1000	60	0.08	0.026
Nafion	1100	66	0.06	0.02
BPSH-100	278	27	0.01	0.015
BPSH-60	454	42	0.005	0.005
BPSH-45	520	54	0.003	0.004
BPSH-35	649	68	0.001	0.003
BPSH-BPS block	550	49	0.005	0.02
BPSH-PI block	662	61	0.002	0.03
Hydrocarbon PEM	560			0.01



Mechanical/Swelling Problems of High T Materials

Division of mechanical and transport domains.

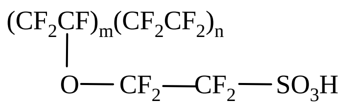
Limit swelling maintain mechanical properties at high RH.

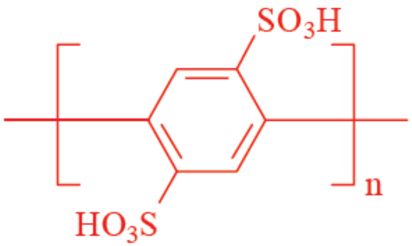
Crosslinking, additivies, self-assembling structures, forced assembly structures

Target Materials

Will have extremely high acid density and limit swelling.

Target structures?





PPDSA

Moving beyond demonstrated structures.