DOE Hydrogen Program

Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

Andrew M. Herring
Colorado School of Mines
Mathew H Frey
3M Corporate Research Materials Laboratory

6/11/08

FC21

Overview

Timeline

- April 1st 2006
- March 31st 2011
- 40% Complete

Budget

- Total project funding
  - DOE - $1,500K
  - Contractor - $375K
- Funding for FY07
  - $313K ($46K)
- Funding for FY08 to date
  - $125K ($45 K)

Barriers

- C **Performance**
- B **Cost**
- A **Durability**

Partners

- 3M - Industrial
- Project lead - CSM

Objectives

• Overall	•Fabricate a hybrid HPA polymer (polyPOM) from HPA functionalized monomers with: – σ >0.1 S cm^{-1} at 120°C and 25%RH
• 2007	•Synthesis and optimization of hybrid HPA polymers for conductivity from RT to 120ºC
• 2008	•Synthesis and optimization of hybrid HPA polymers for conductivity from RT to 120ºC with an understanding of chemistry/morphology conductivity relationships

Milestones 07/08

Month/Year	Milestone or Go/No-Go Decision
Dec-07	Demonstrate conductivity of 70 mS cm^{-1} at 80% RH and room temperature – **30ºC 80% RH 50 mS cm^{-1}** **80ºC 100% RH >300 mS cm^{-1}** *Comparable to PFSA membranes under FC operating conditions* **120ºC 90%RH >70 mS cm^{-1}** *Few measurements at this temperature to date*
June 08	Deliver membrane to topic 2 awardee – Lower conductivity but more durable membrane selected for more consistent validation of results, delivered in April 08

Unique Approach

- Materials Synthesis based on HPA Monomers, Novel "High and Dry" proton conduction pathways mediated by organized HPA moieties – A NEW Ionomer System

- Task 1.1 – Phenyl link stability – complete
- Task 1.2 – Protonation approach – complete
- Task 2.1 – Development of HPA polymers – 50% complete
- Task 2.2 – Hybridaization of polymer – 25% complete

Synthesis of Hybrid Monomer

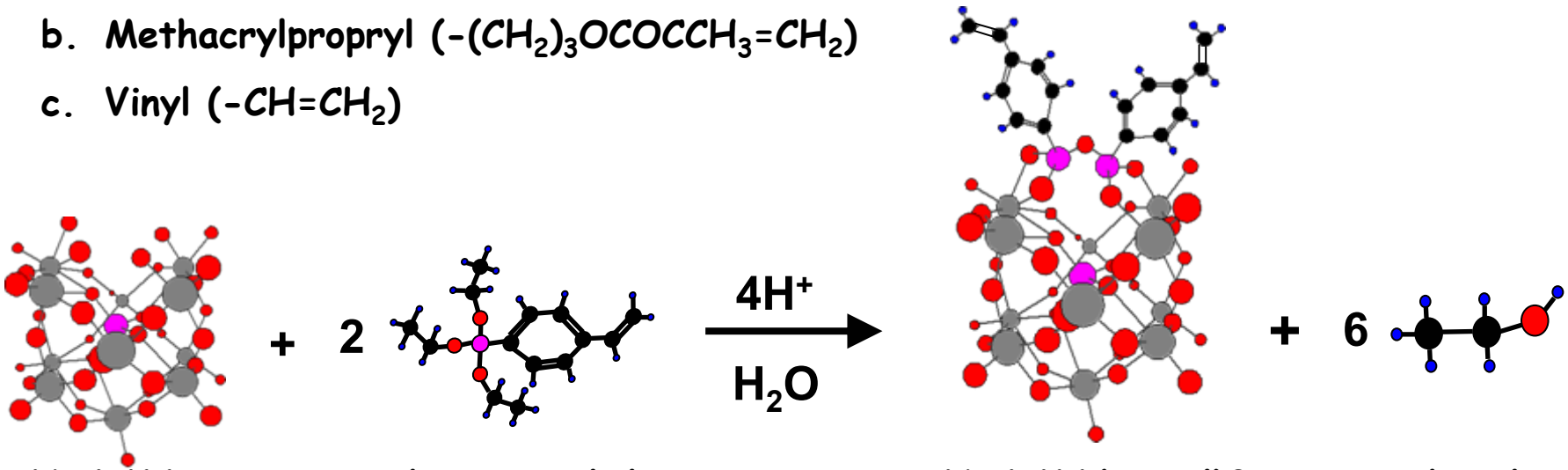
$$[SiW_{11}O_{39}]^{8-} + 2RSi(OR')_3 + 4H^+ + H_2O \xrightarrow[TBA^+Br^-]{MeCN} [SiW_{11}O_{39}(SiR)_2O]^{4-} + 6R'OH$$

R =

a. styryl ($-C_6H_5CH{=}CH_2$)

b. Methacrylpropryl ($-(CH_2)_3OCOCCH_3{=}CH_2$)

c. Vinyl ($-CH{=}CH_2$)



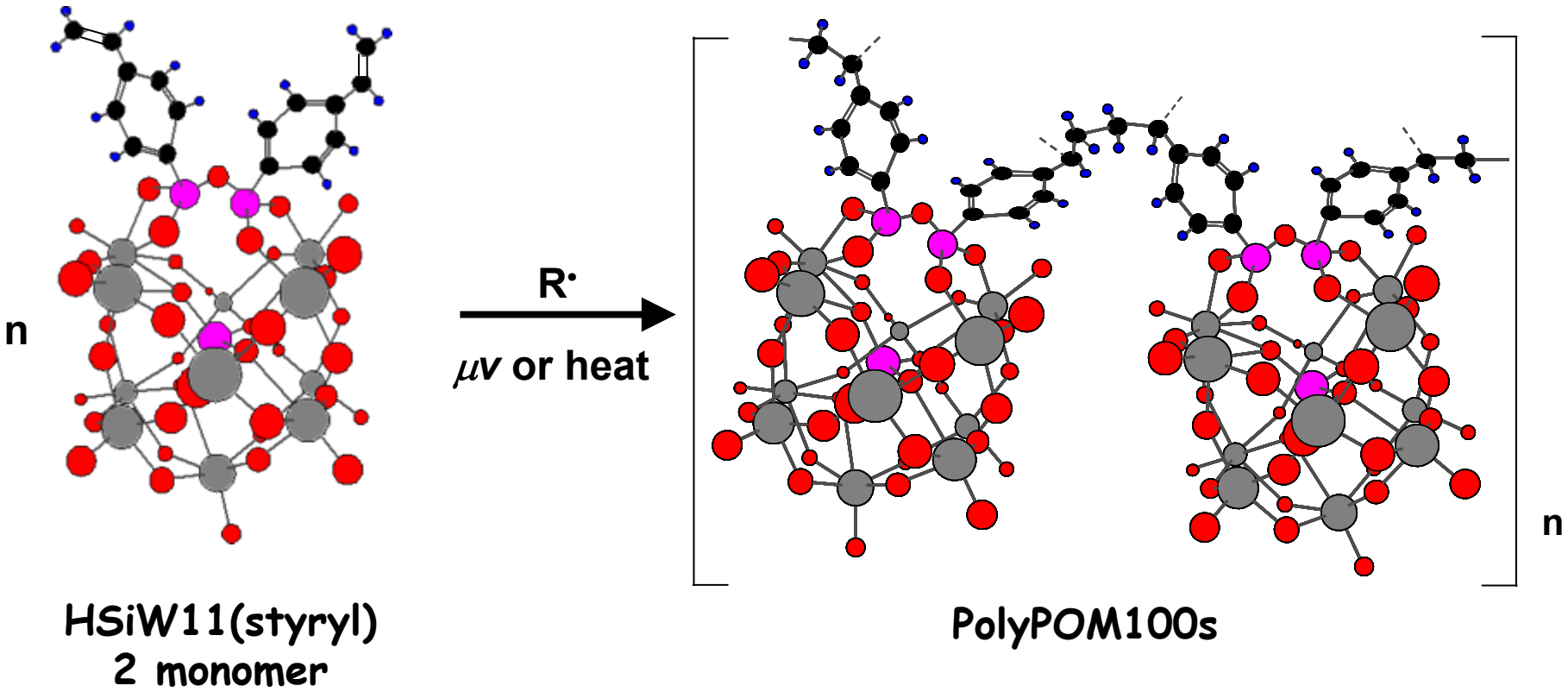
HSiW11 | triethoxystyrylsilane | HSiW11(styryl)2 monomer | ethanol

Judeinstein, P. *Chem. Mater.* **1992**, *4*, 4-7

Mayer, C. R.; Thouvenot, R.; Lalot, T., *Chemistry of Materials* **2000,** 12, (2), 257-260

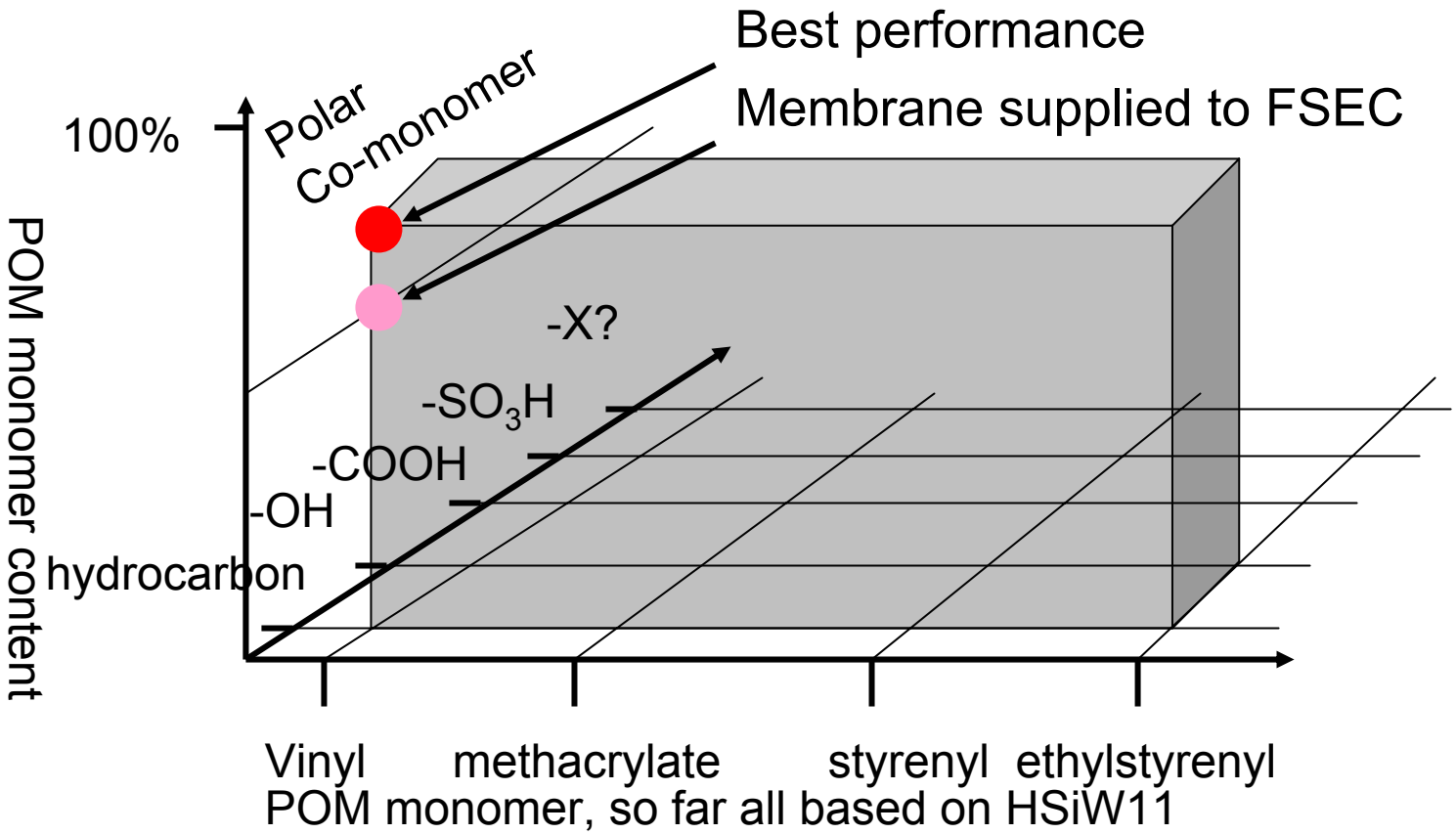
Weeks, M. S.; Hill, C. L.; Schinazi, R. F. *J. Med. Chem.* **1992**, *35*, 1216-1221

Synthesis of PolyPOM



Judeinstein, P. *Chem. Mater.* **1992**, *4*, 4-7

Design Space

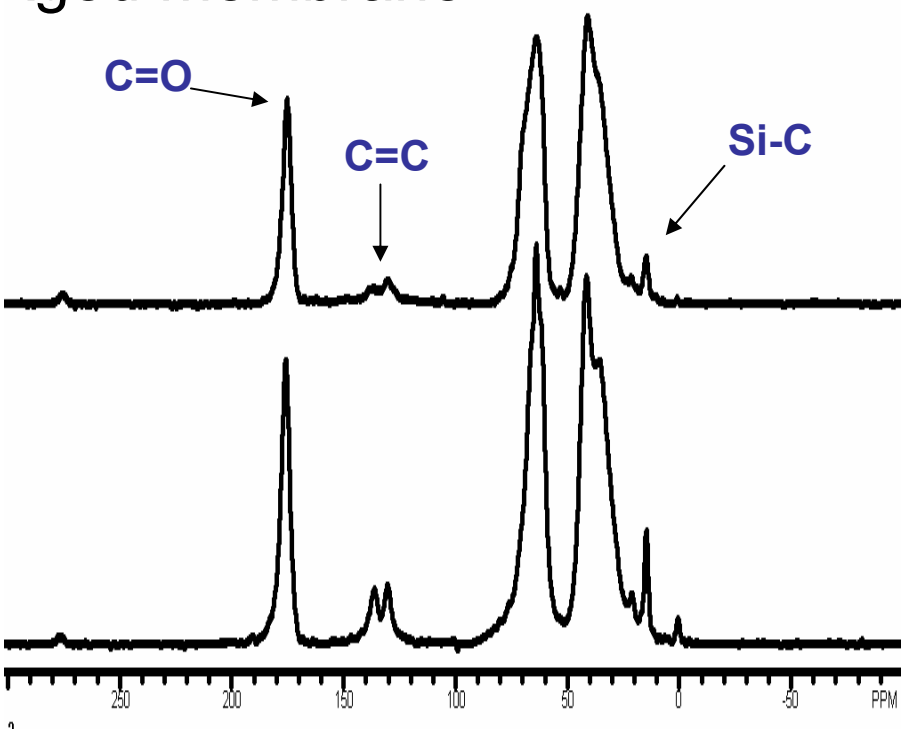


- Only PolyPOM with >50wt% HPA have adequate proton conductivity
- Monomer components systematically varied with advice from 3M to emphasize film forming properties
- We can control chemistry
- Need to understand morphology

Immobilization

100 MHz ^{13}C CPMAS NMR

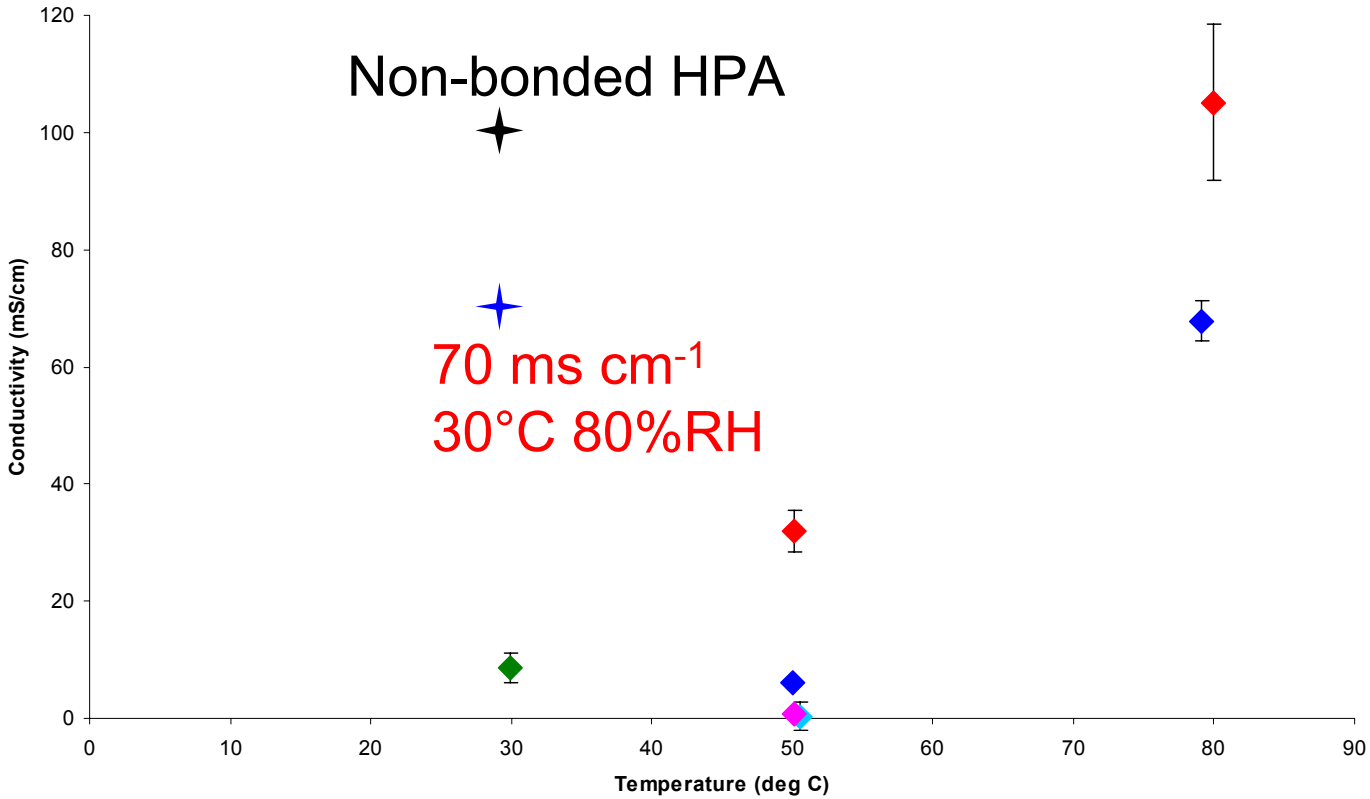
Aged membrane



As cast membrane

- Residual organic vinyl protons slow to polymerize
- Leaching studies suggest small hydrocarbon oligomers leach out – not HPA polymer

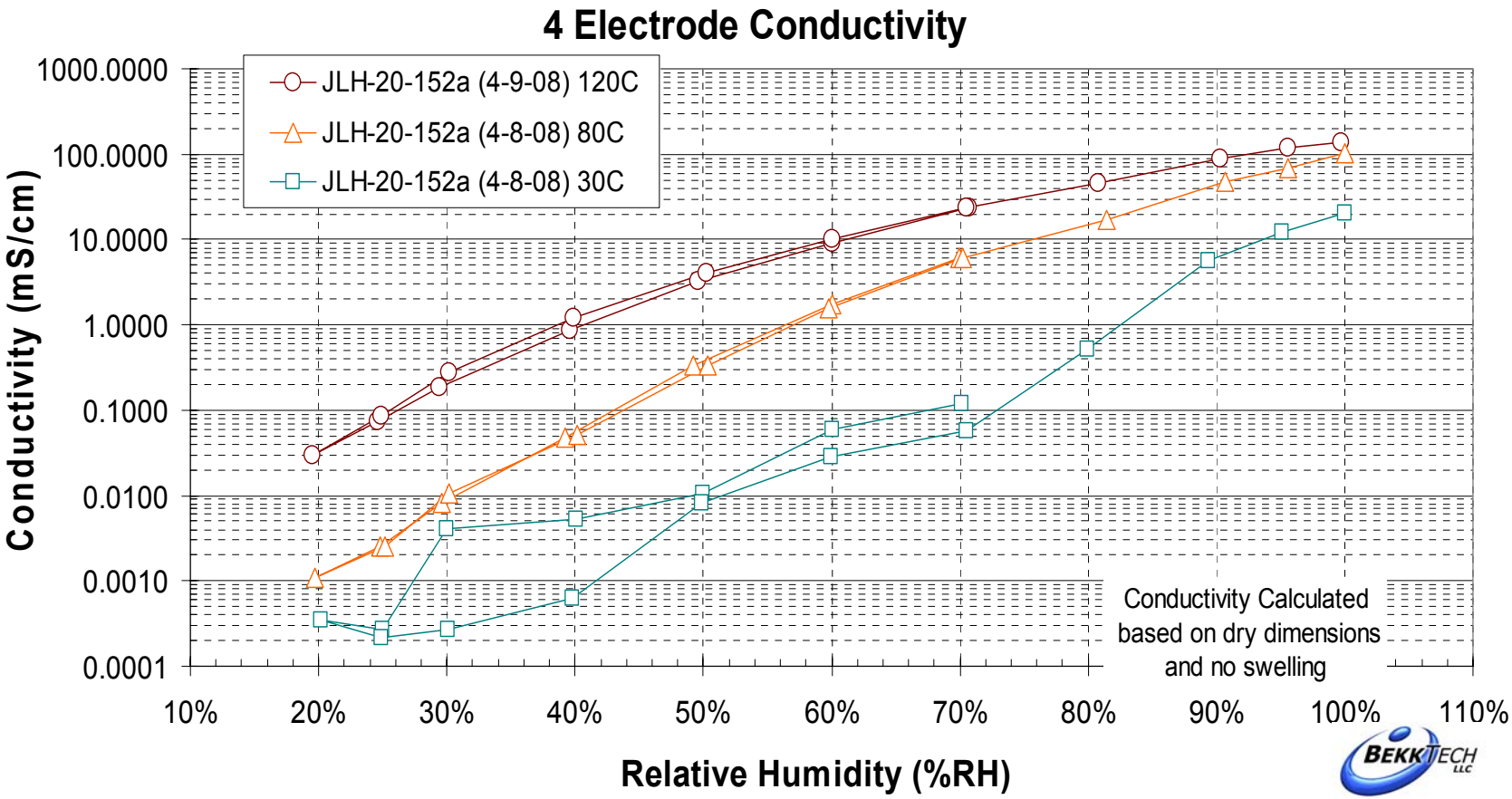
State of the art last year - PolyPOM50m



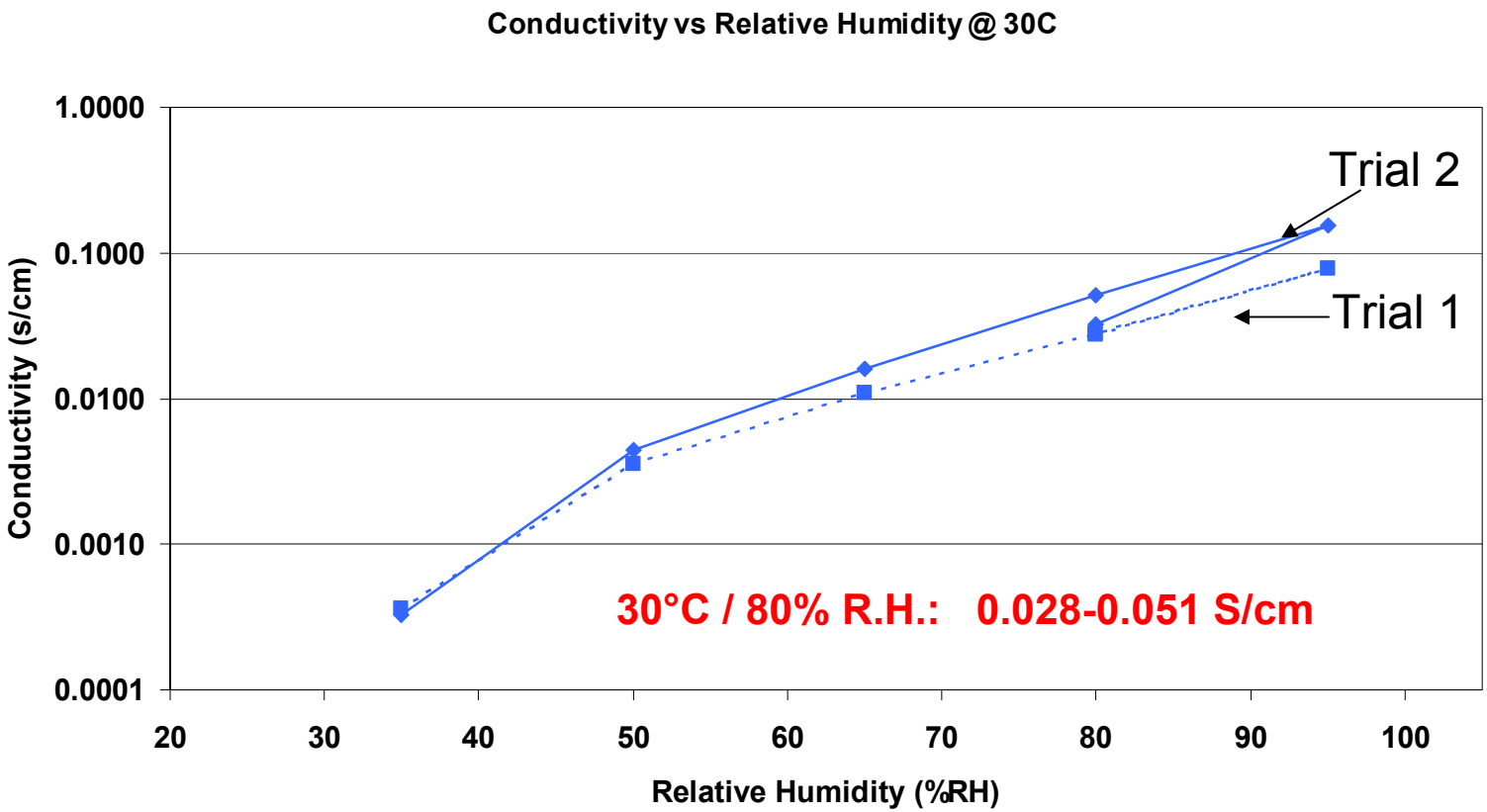
- Conductivity increases with POM content
- **H^+ conductivity Comparable to PFSA ionomers at 100%RH and 80ºC**
- Conductivity depends on correct molecular engineering of film

◆ 25%RH, ◆ 50% RH, ◆ 75% RH, ◆ 80% RH, ◆ 100% RH

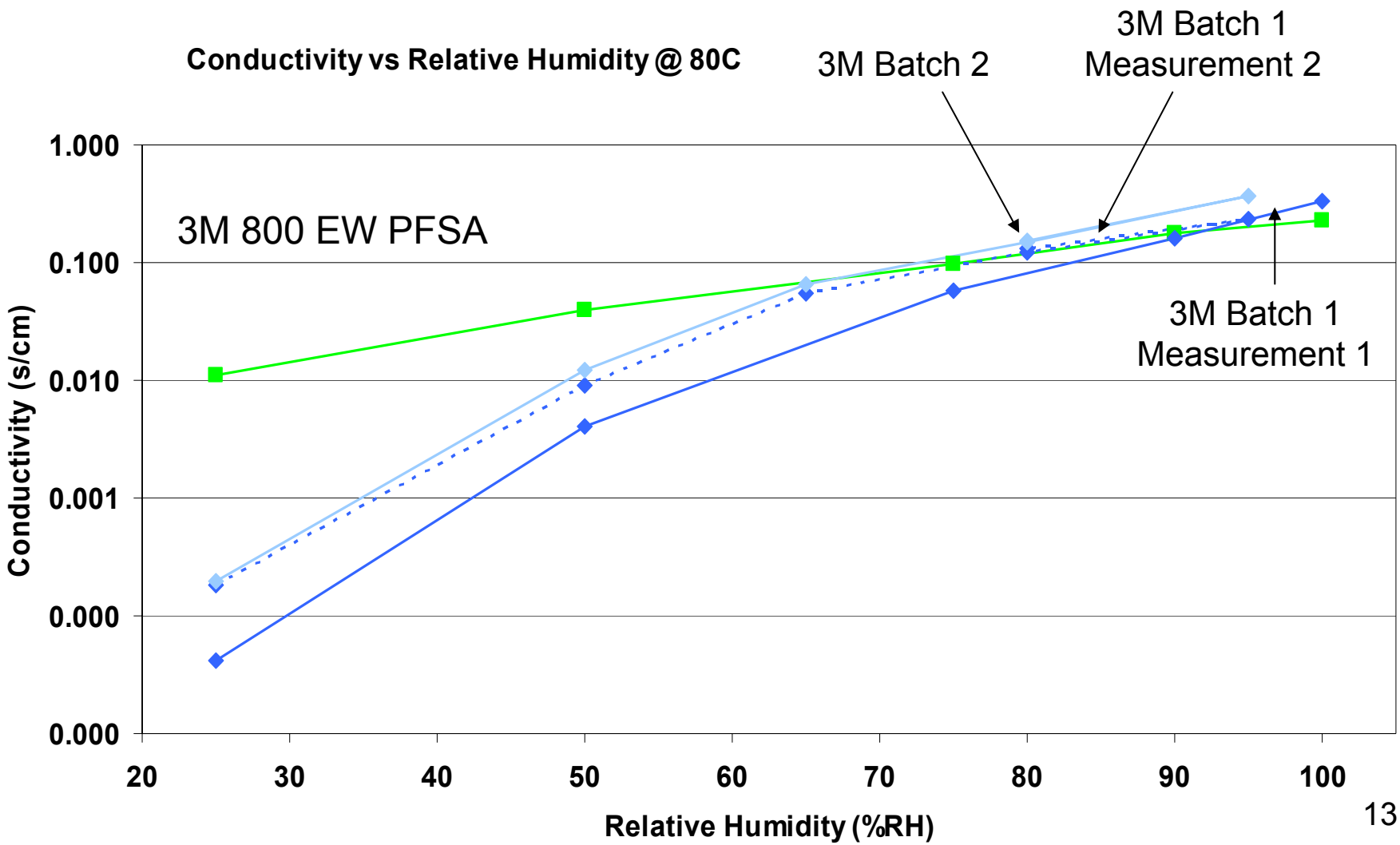
FSEC Results PolyPOM50v



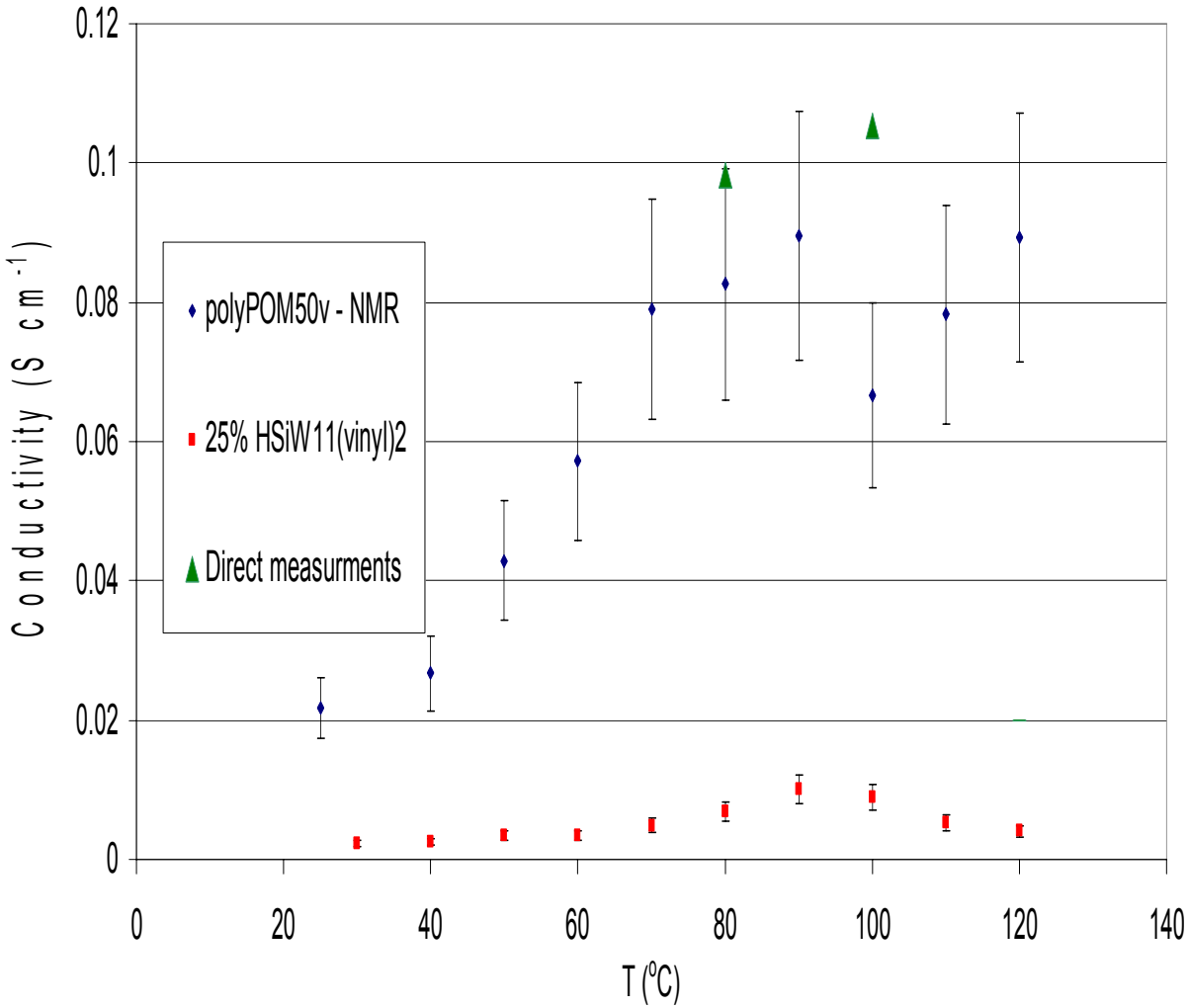
Conductivity at 30ºC for PolyPOM75v



80ºC PolyPOM75v – impressive conductivities >75%RH

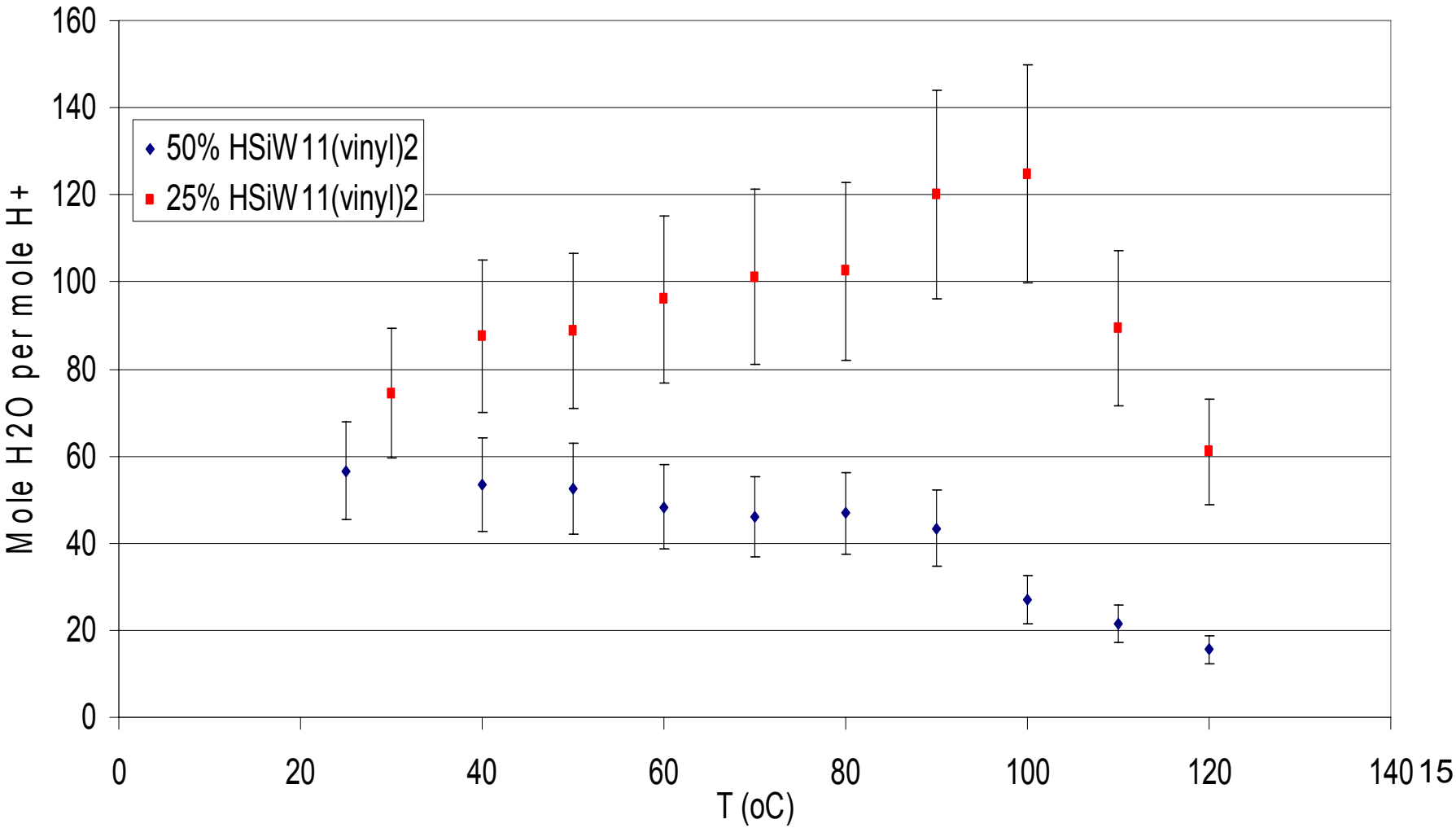


Conductivity Calculated from Nernst-Einstein equation and NMR measurements at 100%RH

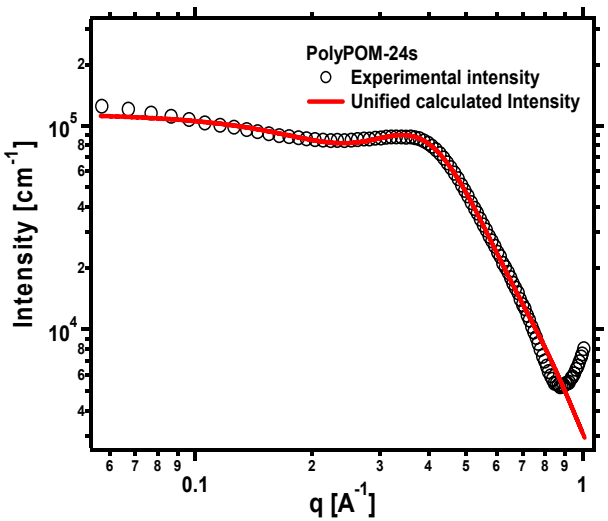


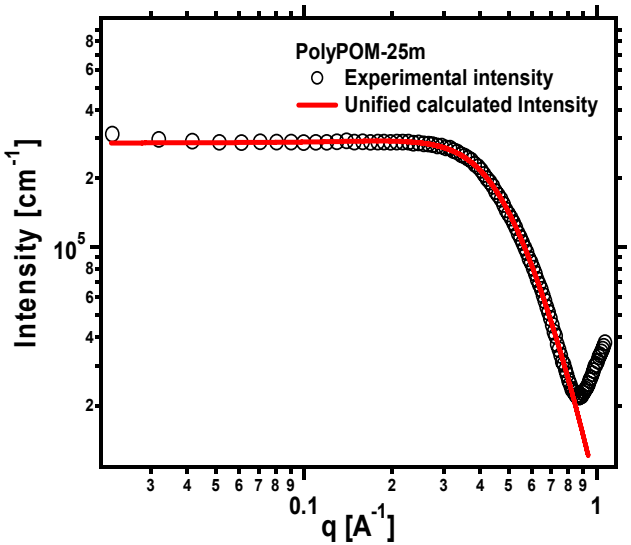
Challenge 1: Water uptake excessive

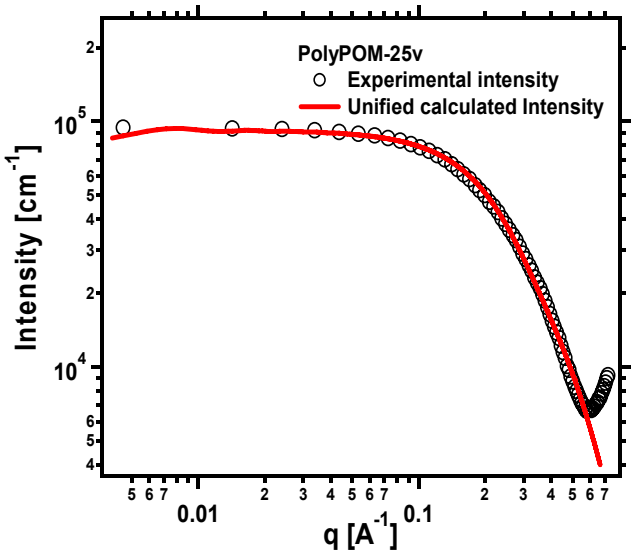
(similar to sulfonated hydrocarbon polymer)



SAXS indicates that monomer influences packing of HPA

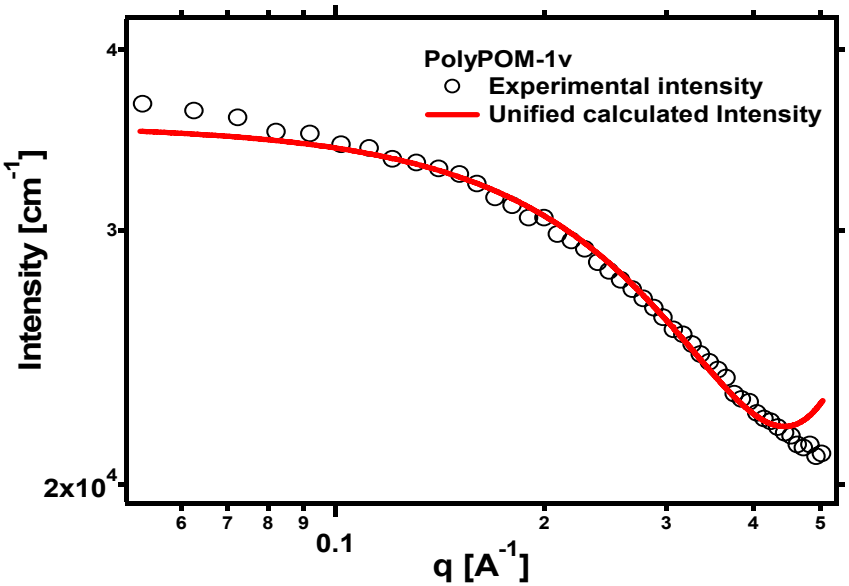


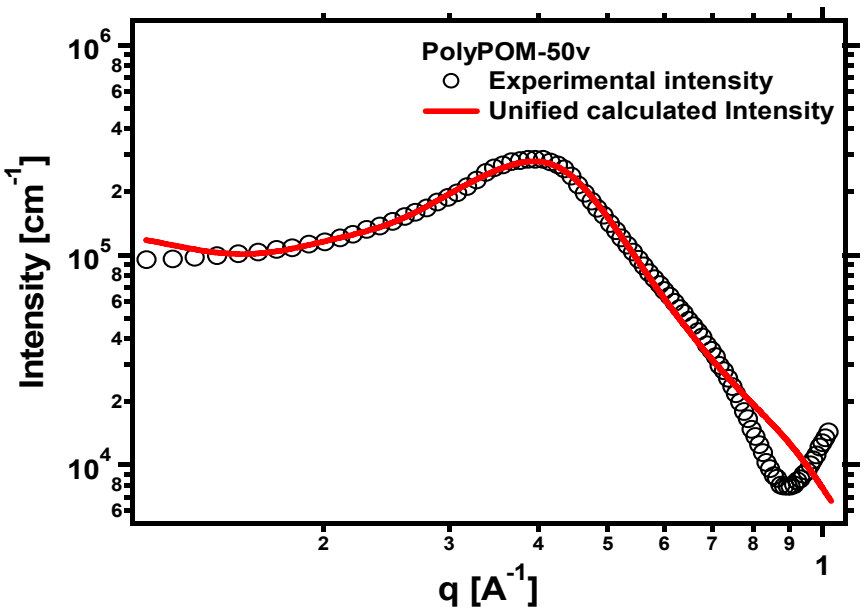




Concentration/ Level #	P	Rg [A]	Eta [A]	Packing Factor
PolyPOM-24s L1	4	3.4	34000	0.1
PolyPOM-25m L1	4	3.6	24000	0.001
PolyPOM-25v L1	4	4.7	1200	0.28

>50% HPA leads to significant clustering

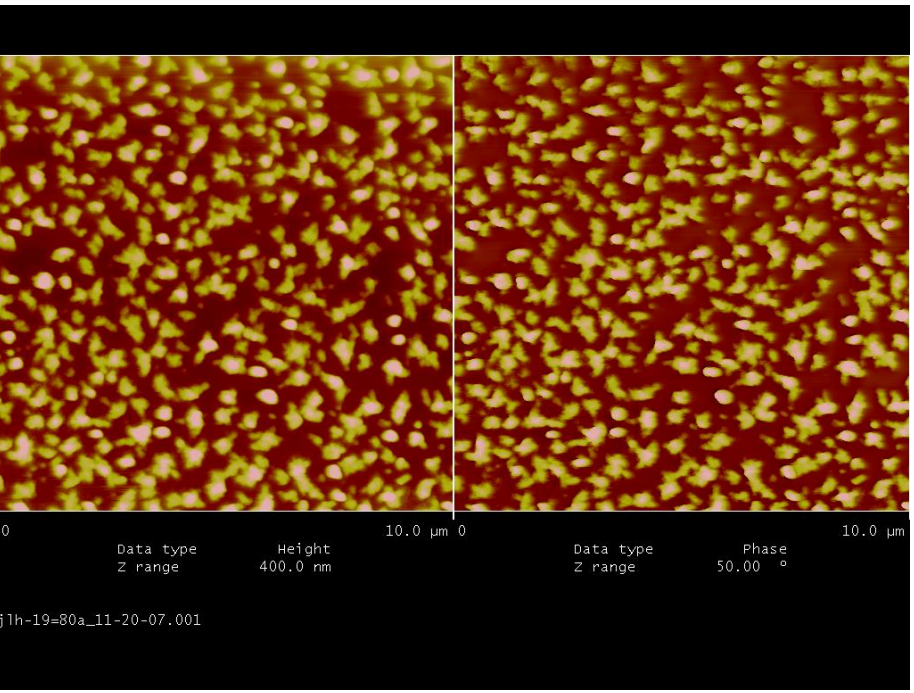


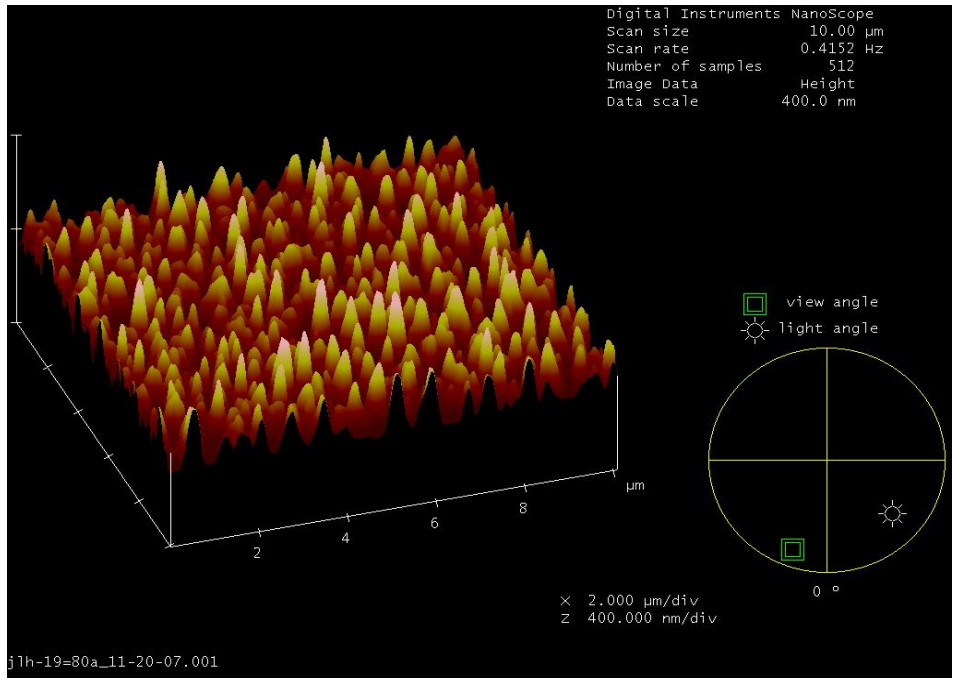


Concentration/ Level #	P	Rg [A]	Eta [A]	Packing Factor
PolyPOM-1v L1	4	3.4	34000	0.1
PolyPOM-5v L1	4	3.6	24000	0.001
PolyPOM-10v L1	4	4.7	1200	0.28
PolyPOM-25v L1	4	6.7	670	0.21
PolyPOM-50v L1	4	3.8	68	1.4
PolyPOM-50v L2	4	9.2	13	4.6

Beaucage, G., *J. Appl. Cryst.*, 1996; Vol. 29, pp 134-146

Challenge 2: Morphology
(AFM shows cluster on the order of 100s of nm)

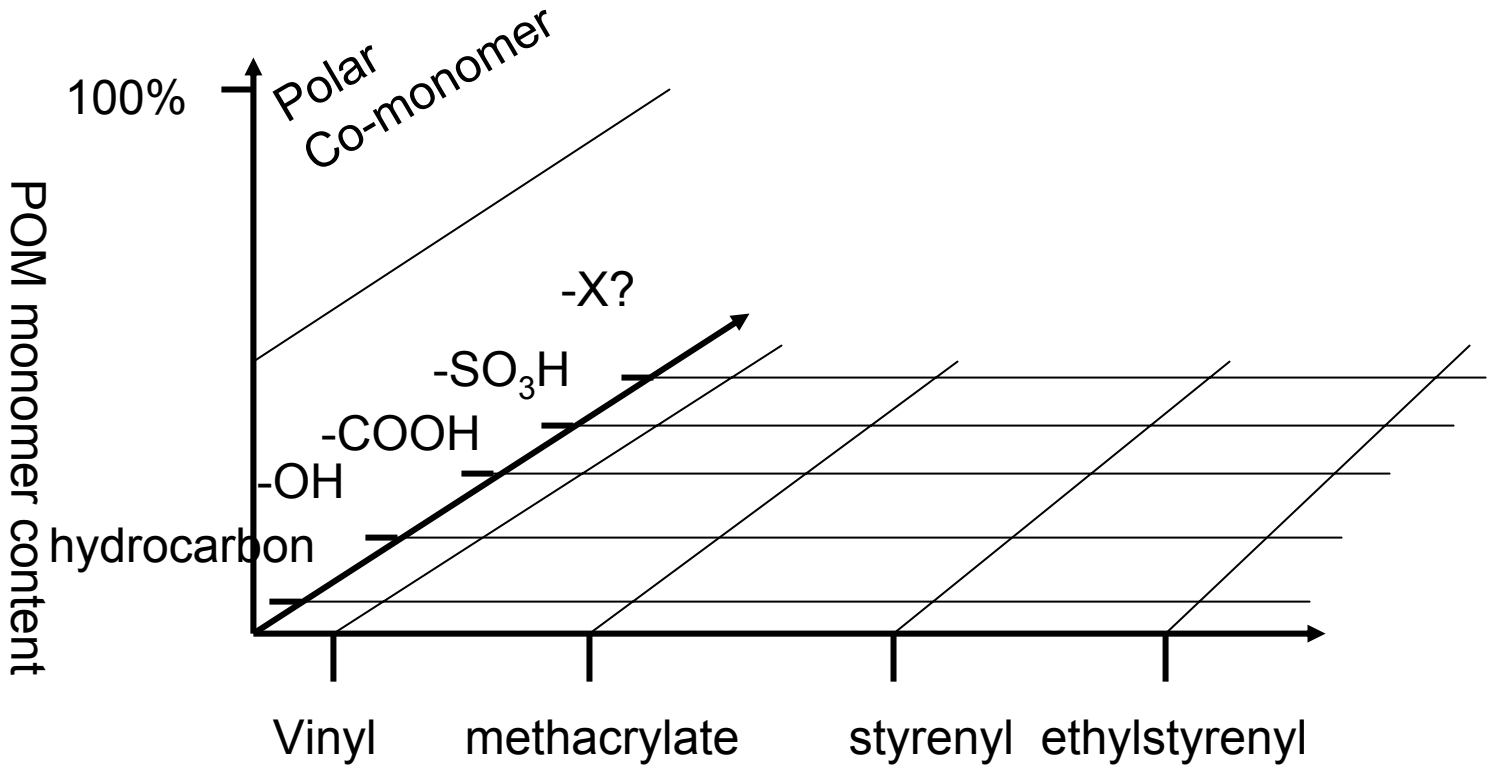




PolyPOM50v

Future Work

- Finish exploring design space for Si linked polyPOM – addition of dissociable proton functionalities should lead to high conductivity
- Develop more stable P linked polyPOM – move beyond model systems
- Fabricate polyPOM with significantly different polymer properties – 3M proprietary expertise



Summary

- Stable immobilized HPA (polyPOMs) are readily synthesized
- Si linked model compounds allow chemistry/morphology to be explored
- Proton conductivities comparable to PFSA ionomers were achieved before system optimization
- P linked and new polymer architectures readily available

	April 2008	Project milestone	DOE 2010 target
H^+ conductivity	300 ms/cm 100%RH 80ºC	70 ms/cm 80%RH, 30ºC	100 ms/cm 25-40%RH at 120ºC