

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

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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

<ul style="list-style-type: none">• Overall	<ul style="list-style-type: none">• Fabricate a hybrid HPA polymer (polyPOM) from HPA functionalized monomers with:<ul style="list-style-type: none">– $\sigma > 0.1 \text{ S cm}^{-1}$ at 120°C and 25%RH
<ul style="list-style-type: none">• 2007	<ul style="list-style-type: none">• Synthesis and optimization of hybrid HPA polymers for conductivity from RT to 120°C
<ul style="list-style-type: none">• 2008	<ul style="list-style-type: none">• Synthesis and optimization of hybrid HPA polymers for conductivity from RT to 120°C with an understanding of chemistry/morphology conductivity relationships

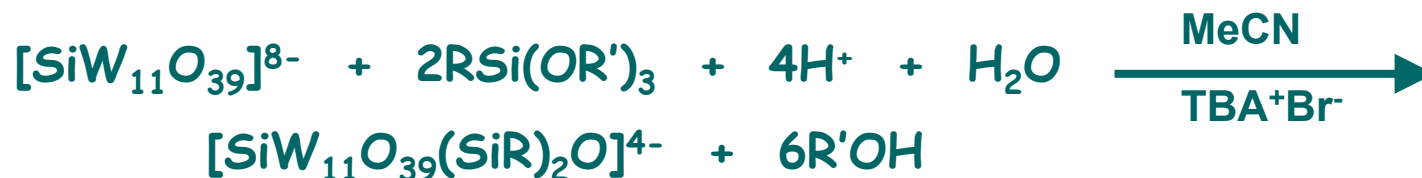
Milestones 07/08

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

Unique Approach

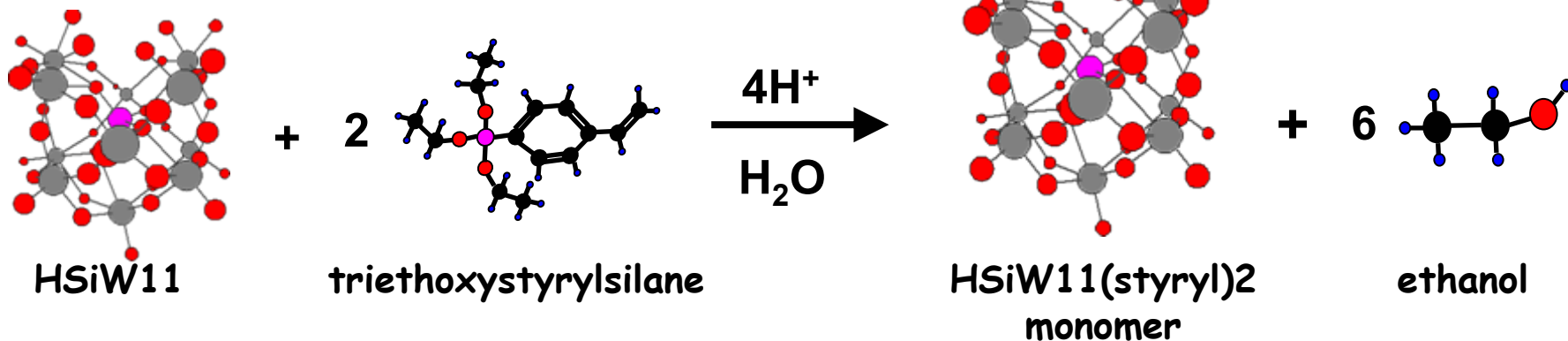
- Materials Synthesis based on HPA Monomers, Novel “High and Dry” proton conduction pathways mediated by organized HPA moieties – **A NEW Ionomer System**
- Task 1.1 – Phenyl link stability – complete
- Task 1.2 – Protonation approach – complete
- Task 2.1 – Development of HPA polymers – 50% complete
- Task 2.2 – Hybridization of polymer – 25% complete

Synthesis of Hybrid Monomer



R =

- styryl ($-\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$)
- Methacrylpropyryl ($-(\text{CH}_2)_3\text{OCOCCH}_3=\text{CH}_2$)
- Vinyl ($-\text{CH}=\text{CH}_2$)

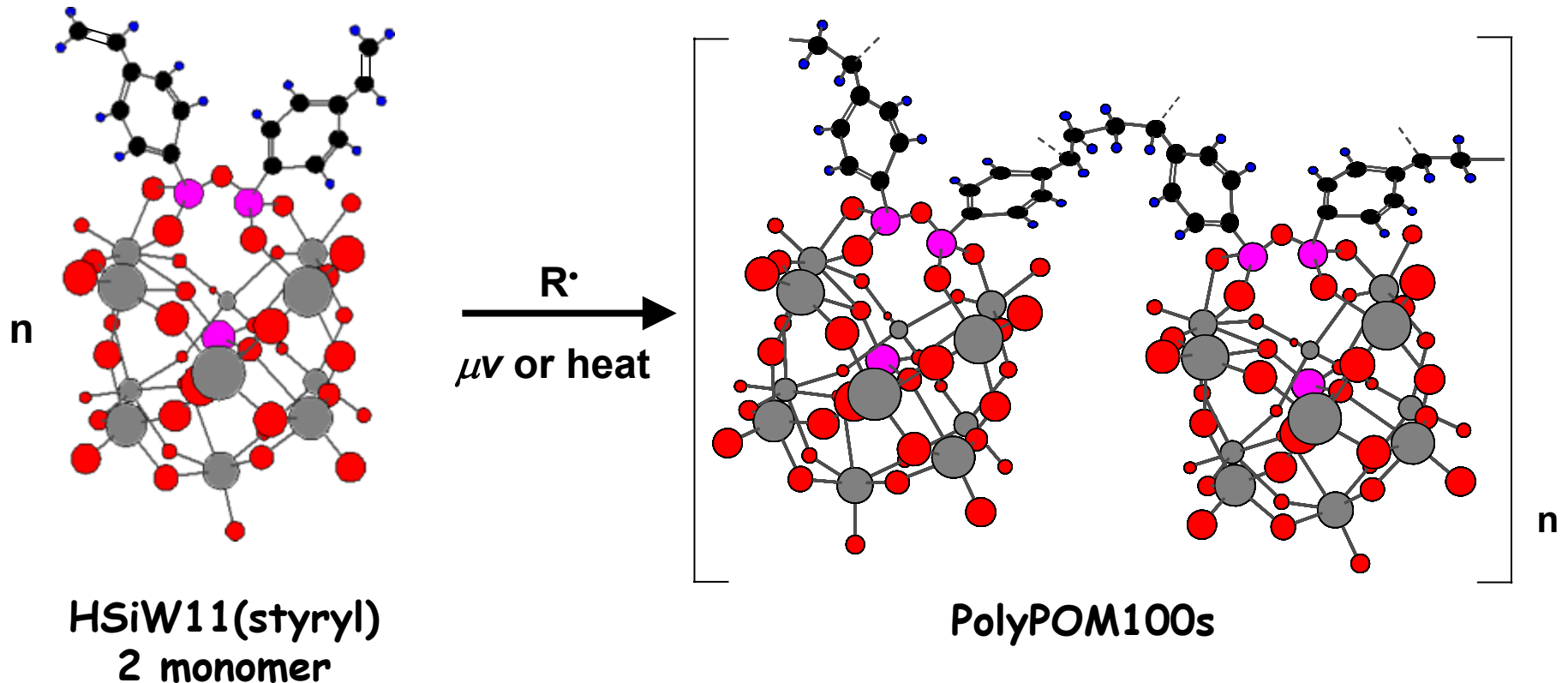


Judeinstein, P. *Chem. Mater.* **1992**, 4, 4-7

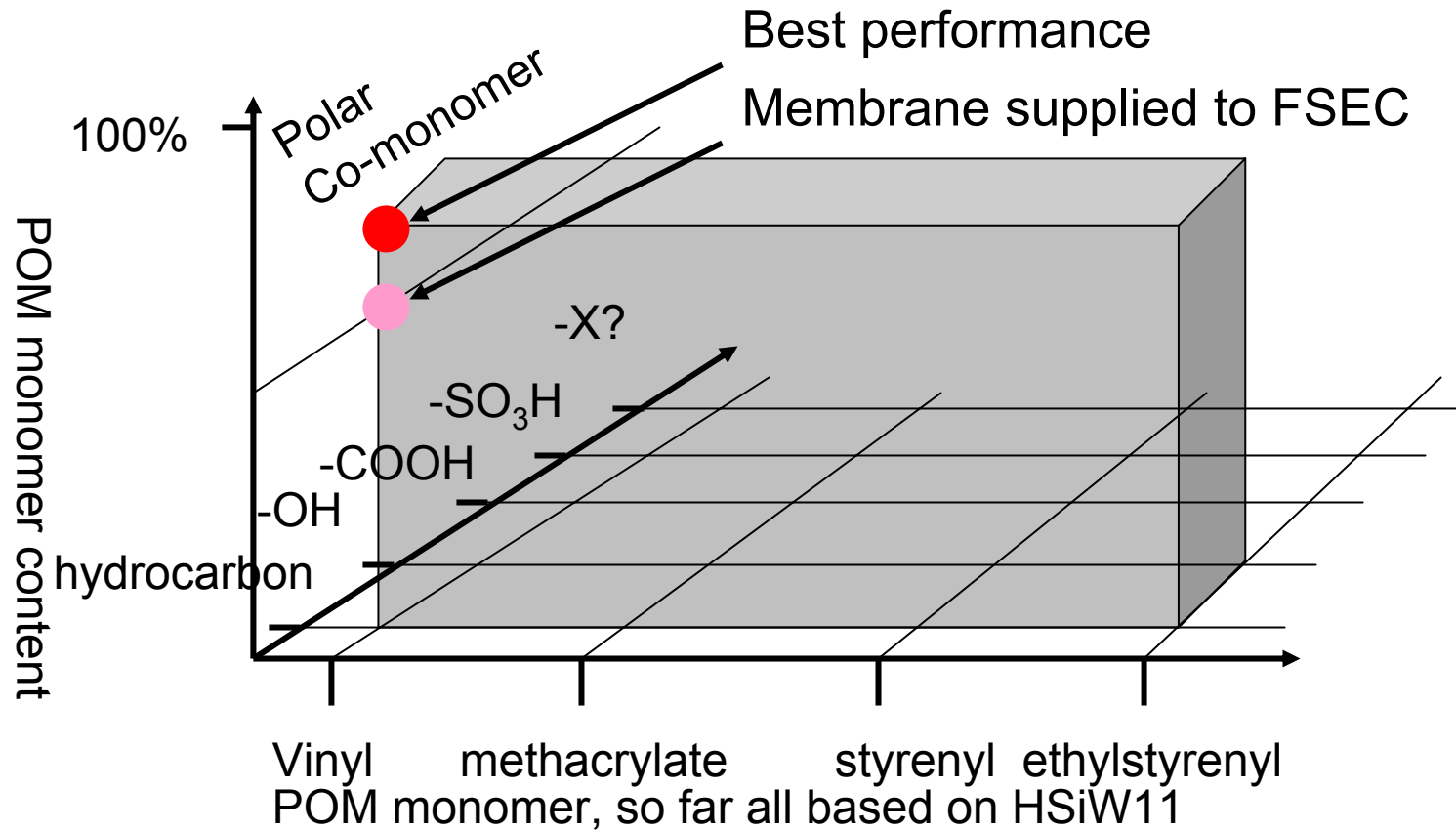
Mayer, C. R.; Thouvenot, R.; Lalot, T., *Chemistry of Materials* **2000**, 12, (2), 257-260

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

Synthesis of PolyPOM



Design Space

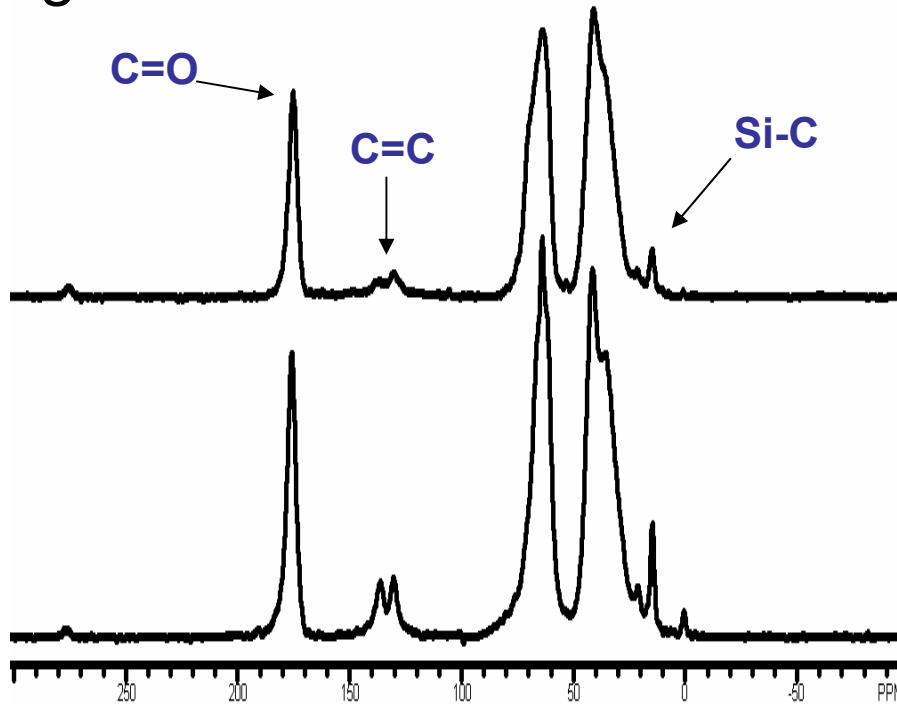


- Only PolyPOM with >50wt% HPA have adequate proton conductivity
- Monomer components systematically varied with advice from 3M to emphasize film forming properties
- We can control chemistry
- Need to understand morphology

Immobilization

100 MHz ^{13}C CPMAS NMR

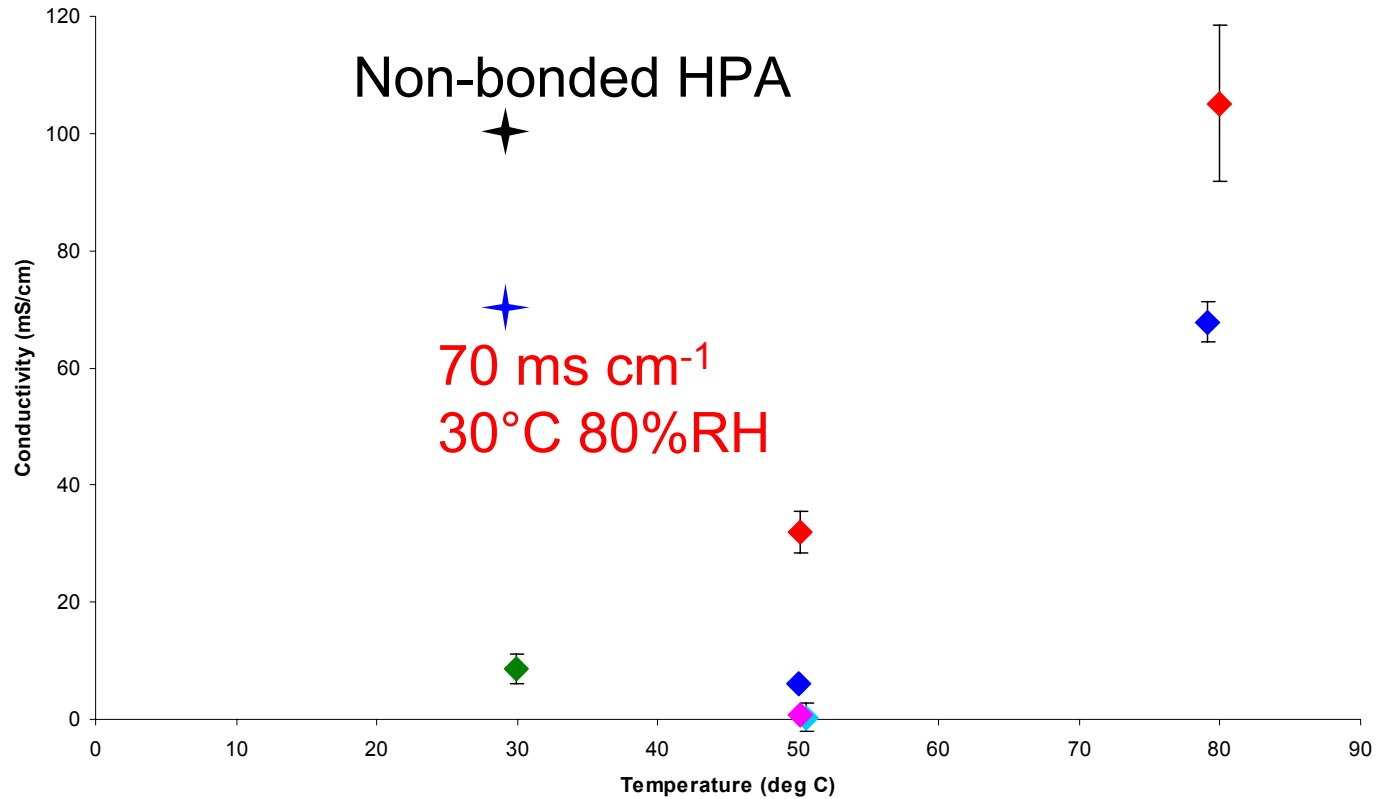
Aged membrane



As cast membrane

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

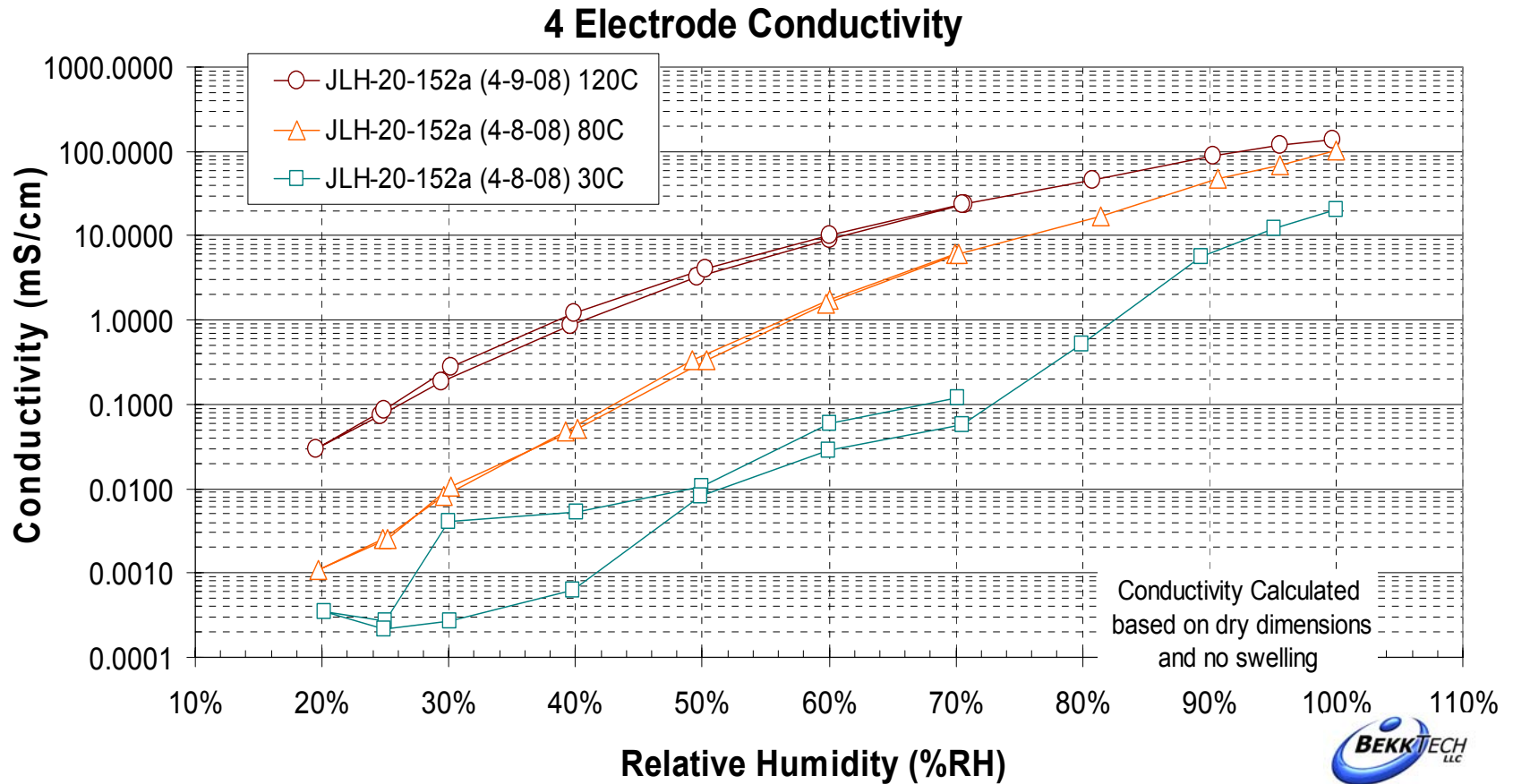
State of the art last year - PolyPOM50m



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

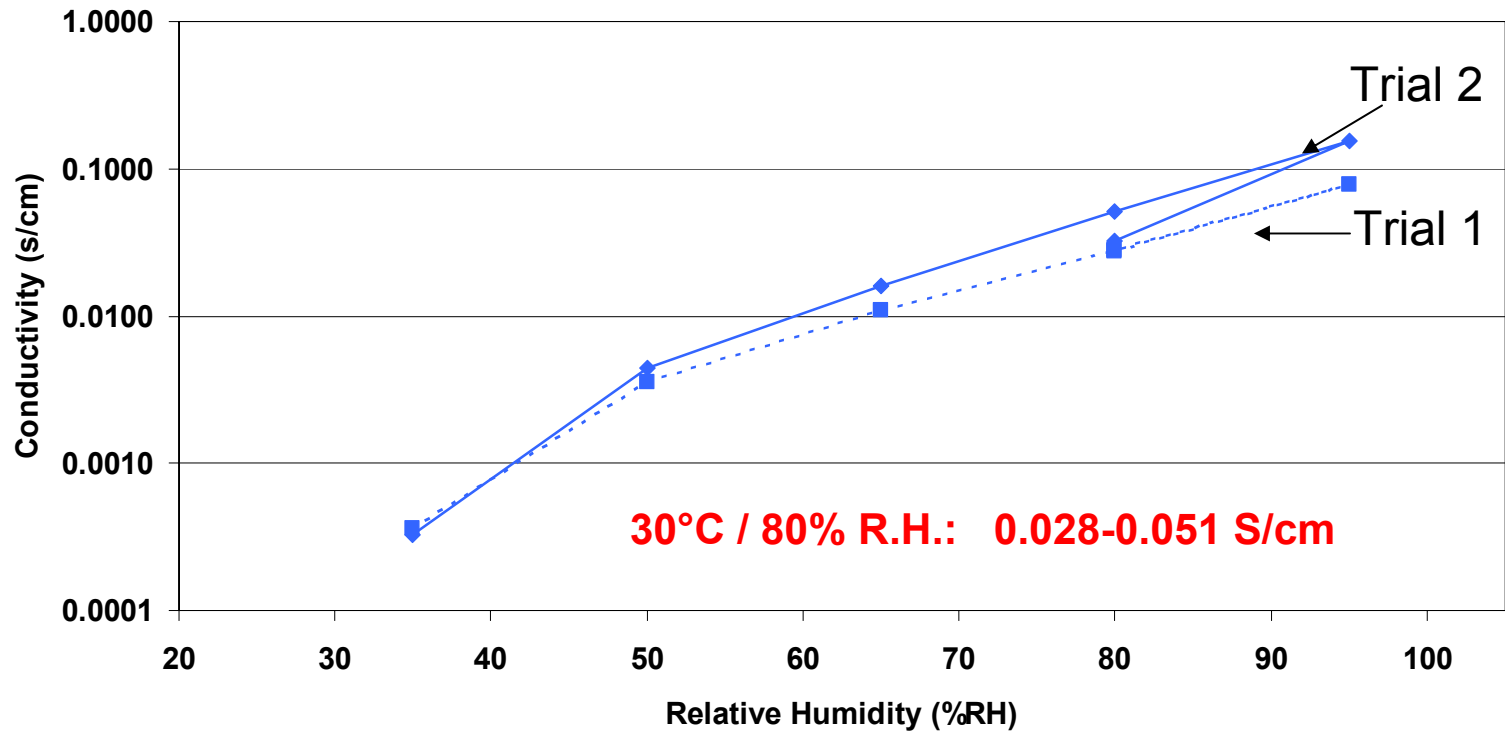
◆ 25%RH, ◆ 50% RH, ◆ 75% RH, ◆ 80% RH, ◆ 100% RH

FSEC Results PolyPOM50v

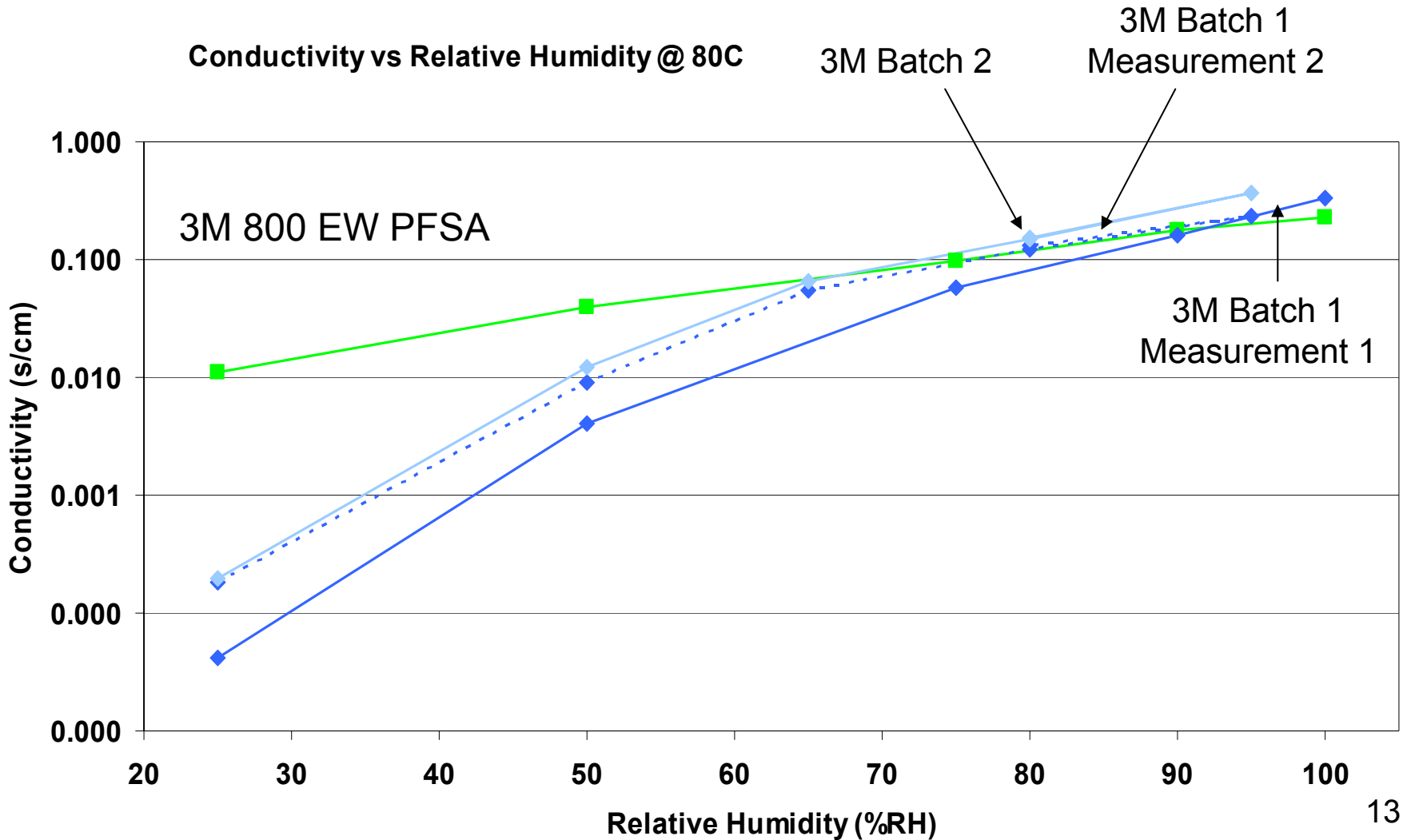


Conductivity at 30°C for PolyPOM75v

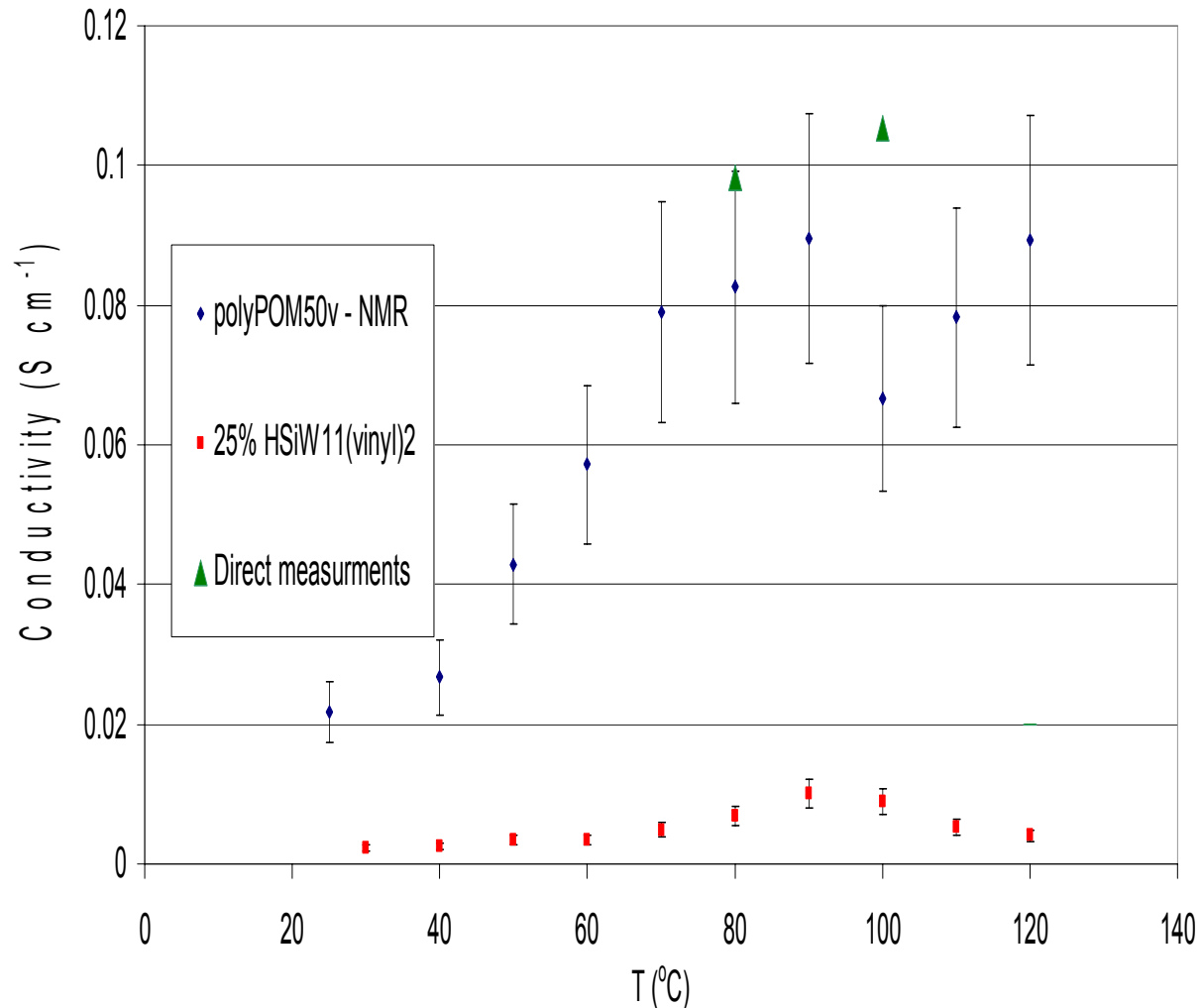
Conductivity vs Relative Humidity @ 30C



80°C PolyPOM75v – impressive conductivities >75%RH

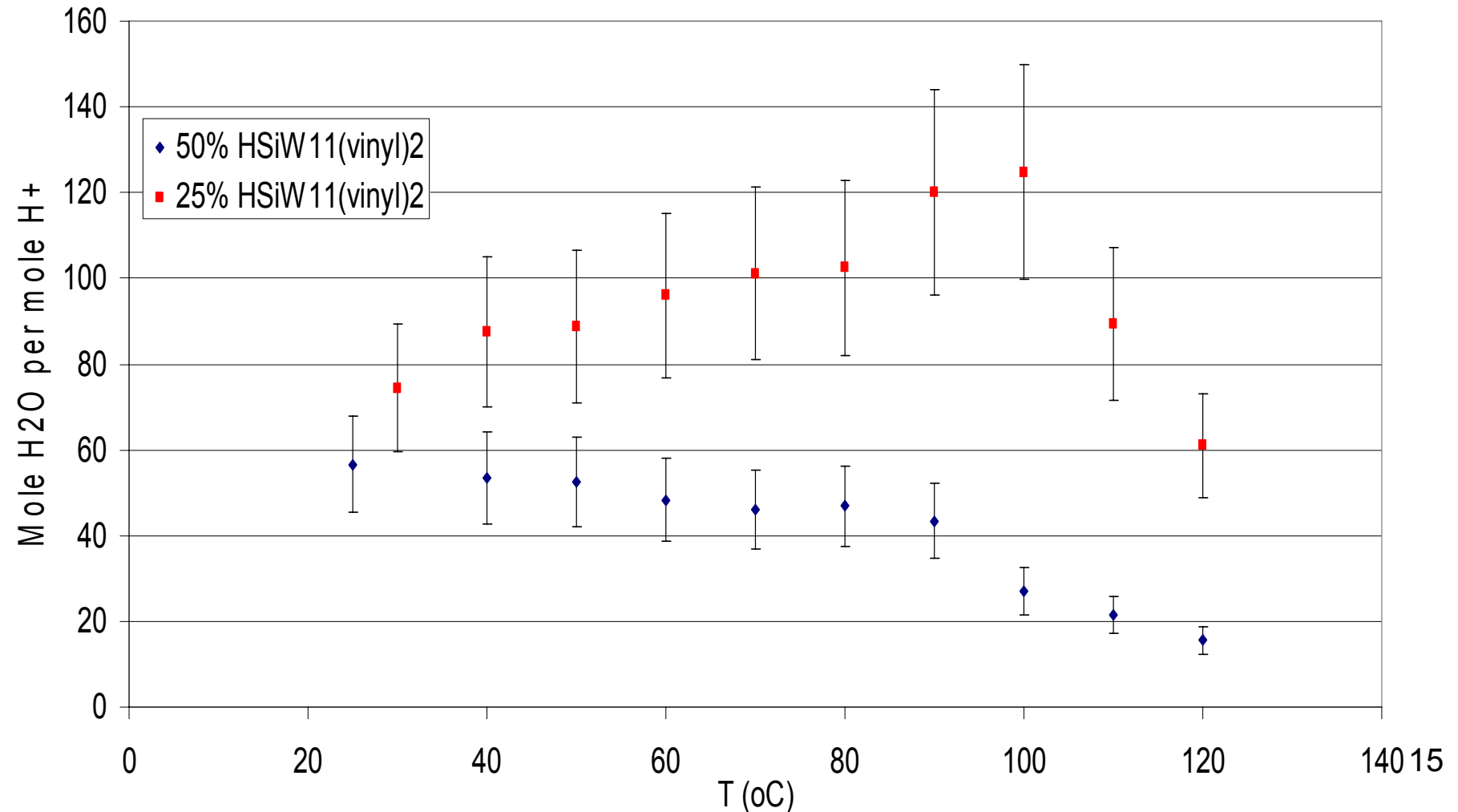


Conductivity Calculated from Nernst-Einstein equation and NMR measurements at 100%RH

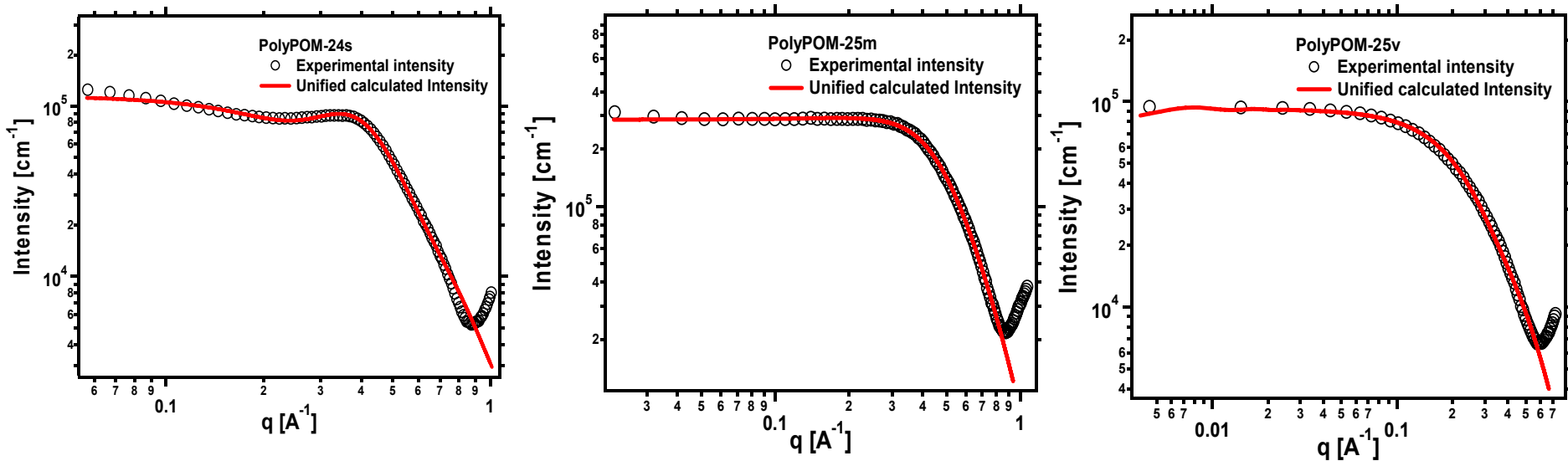


Challenge 1: Water uptake excessive

(similar to sulfonated hydrocarbon polymer)

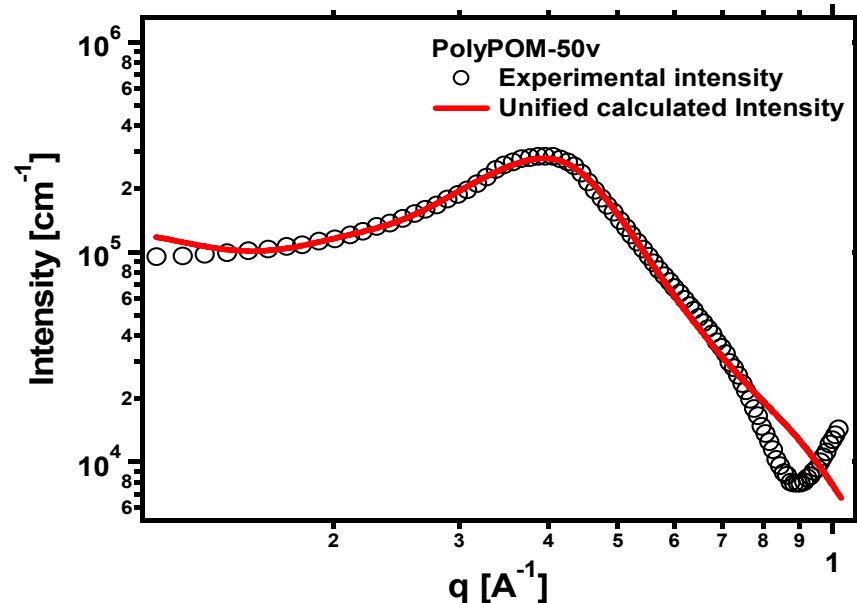
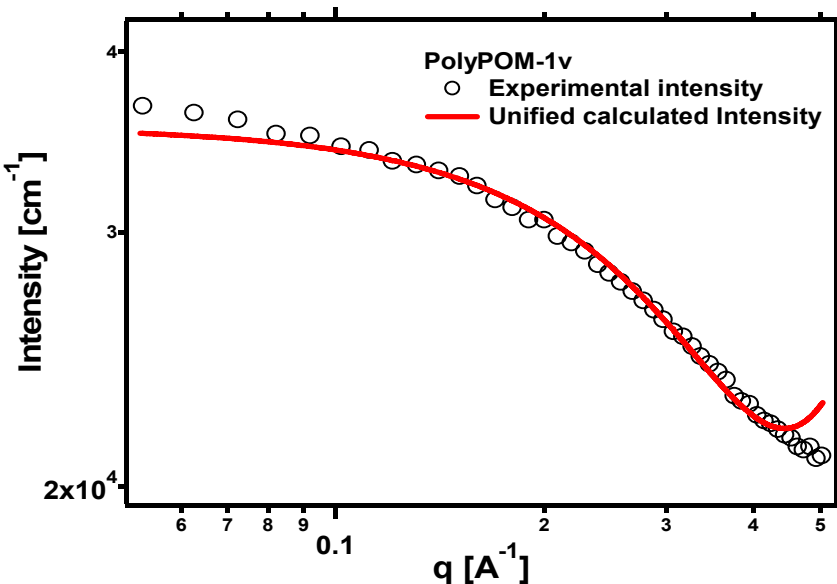


SAXS indicates that monomer influences packing of HPA



Concentration/ Level #	P	Rg [Å]	Eta [Å]	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

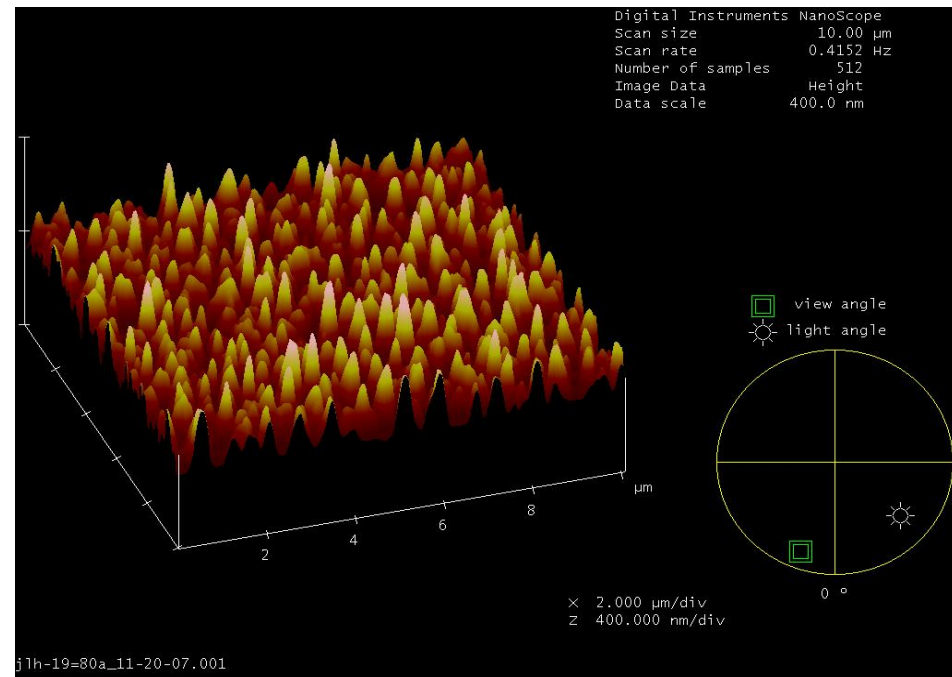
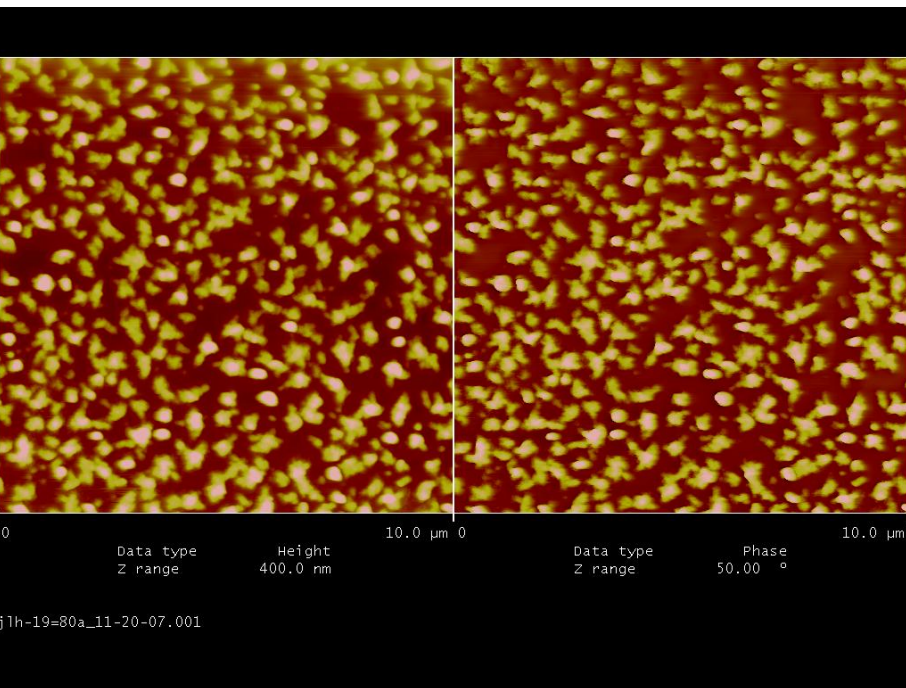
>50% HPA leads to significant clustering



Concentration/ Level #	P	Rg [Å]	Eta [Å]	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

Challenge 2: Morphology

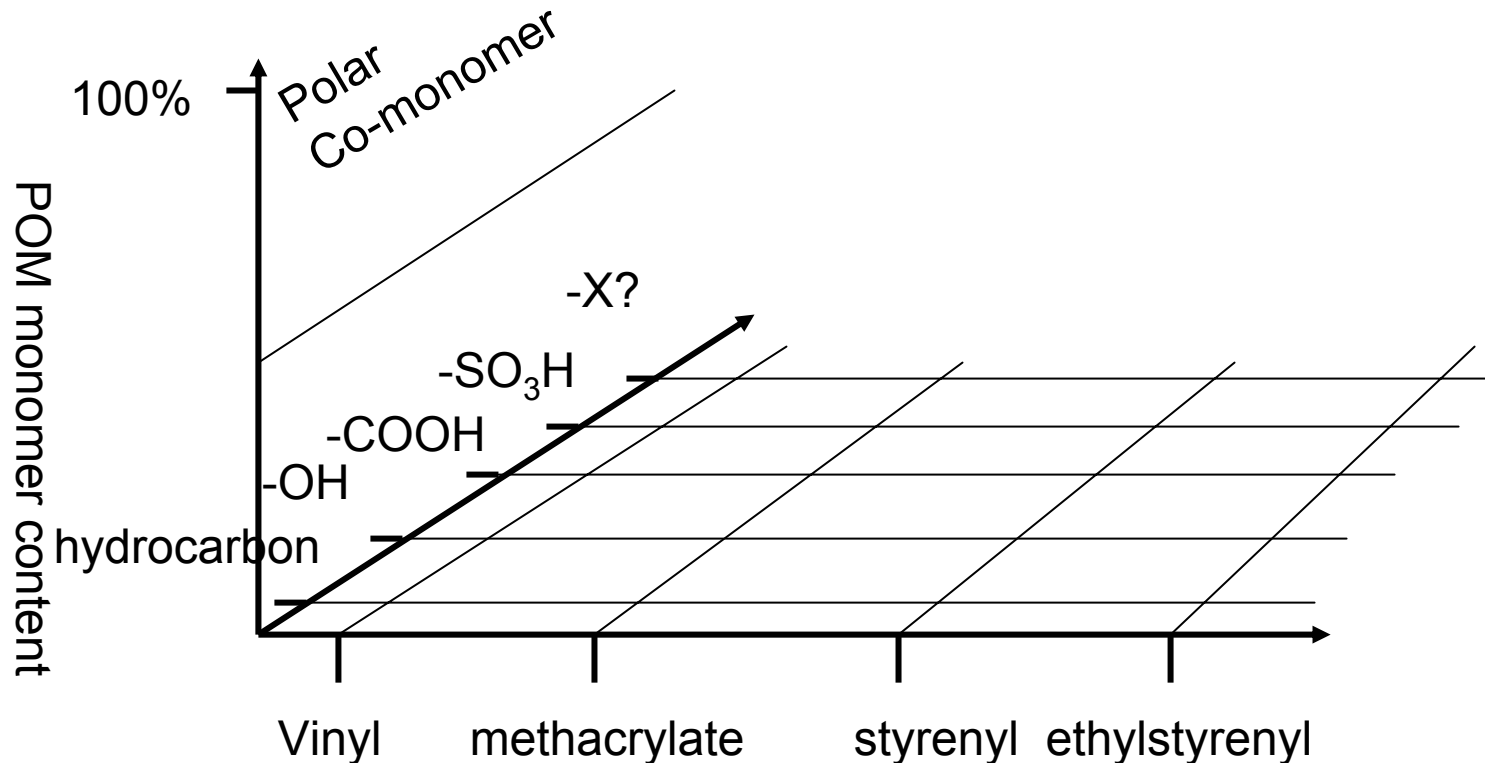
(AFM shows cluster on the order of 100s of nm)



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 80°C	70 ms/cm 80%RH, 30°C	100 ms/cm 25-40%RH at 120°C