

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

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5/19/09

FC_11_Herring

Overview

Timeline

- April 1st 2006
- March 31st 2011
- 60% Complete
Budget
- Total project funding
 - DOE - \$1,500K
 - Contractor - \$375K
- Funding for FY08
 - \$313K (\$46K)
- Funding for FY09 to date
 - \$300K (\$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">• 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 using model system
<ul style="list-style-type: none">• 2009	<ul style="list-style-type: none">• Optimize hybrid polymers in more practical systems for proton conductivity and mechanical properties

Go/No-Go 08/09

Month/Year	Milestone or Go/No-Go Decision
Jan 09	<p data-bbox="542 339 1802 482">Demonstrate conductivity of 100 mS cm^{-1} at 50% RH and 120°C –</p> <p data-bbox="542 501 1367 582">30°C 60% RH 120 mS cm^{-1}</p> <p data-bbox="542 582 1406 664">80°C 100% RH $>300 \text{ mS cm}^{-1}$</p> <p data-bbox="542 672 1590 786"><i>Comparable to PFSA membranes under FC operating conditions</i></p> <p data-bbox="542 786 1483 868">120°C 40-50%RH $>100 \text{ mS cm}^{-1}$</p>
Feb 09	<p data-bbox="542 901 1676 958">Deliver membrane to topic 2 awardee –</p> <p data-bbox="542 972 1734 1186">Lower conductivity, unfortunately hard to control model film quality and durability at high HPA loadings</p>

Relevance

Objective

- To fabricate PEMs with a proton conductivity $< 100 \text{ ms cm}^{-1}$ for operation in a vehicular system up to 120°C with no inlet RH
- Films were synthesized that meet this DOE performance target at temperatures $> \text{RT}$
- Future work will address both cost and durability targets

Collaborators

3M

- Corporate Materials Research laboratory
 - Matthew Frey (Sub)
- Fuel Cell Components Group
 - Steven Hamrock (Consultant)

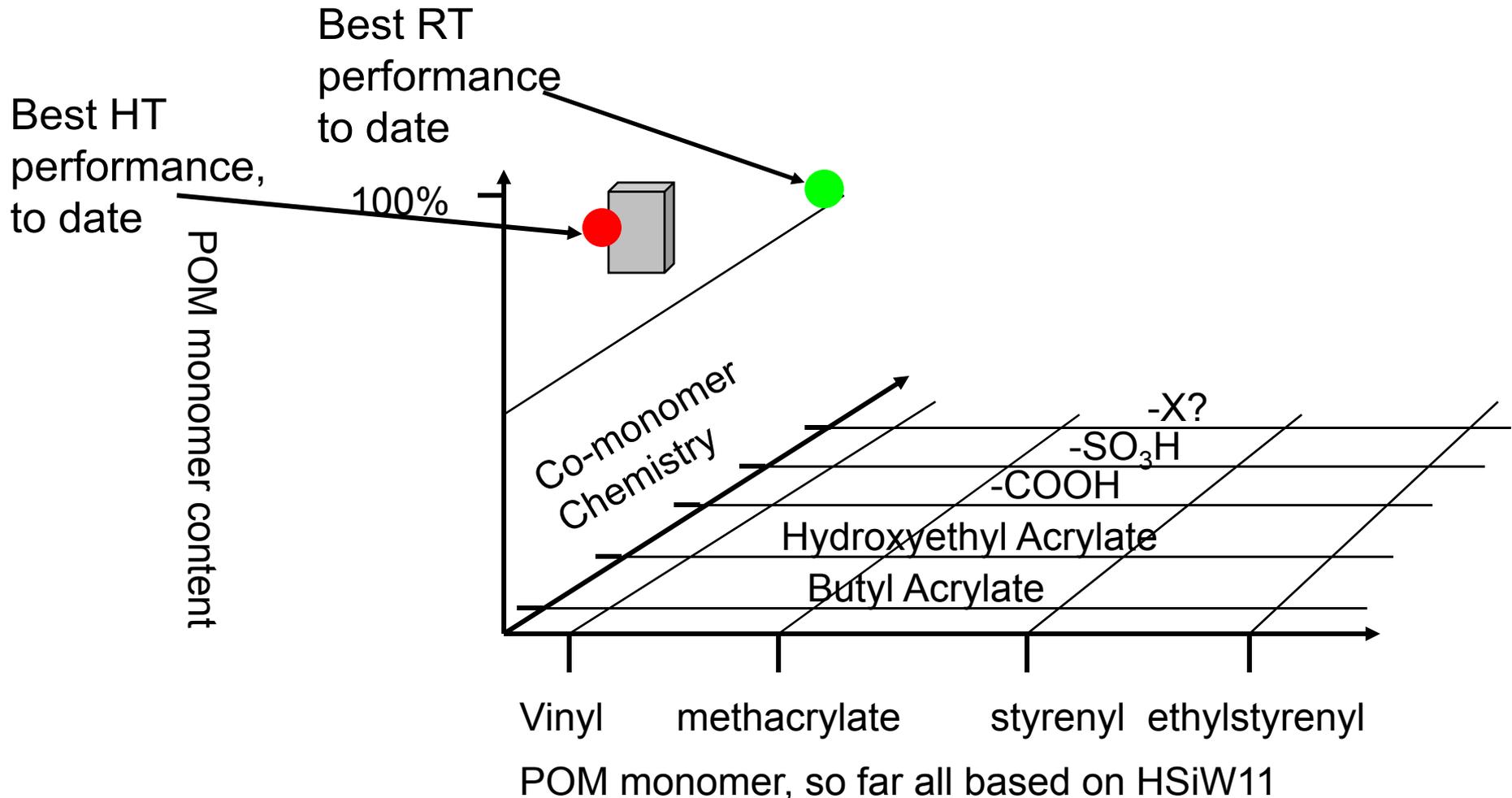
Unique Approach

- Materials Synthesis based on HPA Monomers, Novel “High and Dry” proton conduction pathways mediated by organized HPA moieties – **A NEW Ionomer System**
- Task 2.1: Synthesis and Optimization of hybrid HPA polymers for 120°C conductivity for Go/No Go Decision - Complete
- Task 2.2 – Synthesis and selection of protonic additive for hybrid HPA polymers for 120°C conductivity for Go/No Go Decision - Complete
- Task 3.1 – Down Selection of potential practical approaches – 10% complete

Generation I Model System: Acrylate Co-Monomers

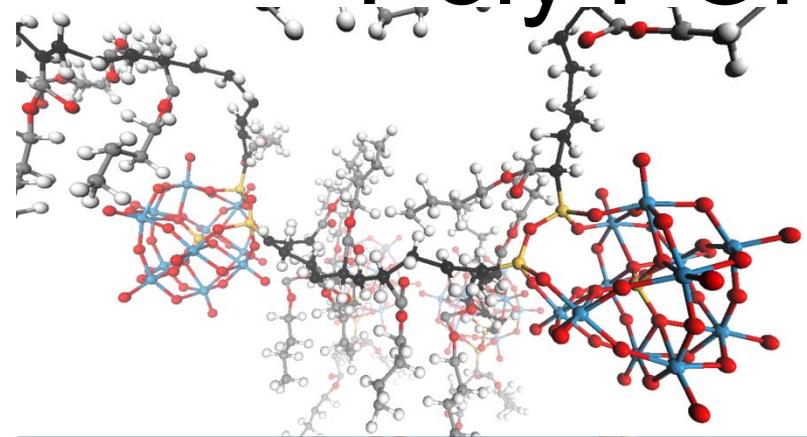
- Polymer system in a kit
- Allows Chemistry to be varied
- Effect of Morphology can be studied
- Full Disclosure
- But...
 - Ester linkage unstable to hydrolysis
 - Oxidizable CH₂ groups and an oxidizing super acid moiety
 - The formulation is not optimized and becomes brittle with time
 - *Residual unpolymerized volatile butyl acrylate acts as a plasticizer and is continually being lost from the film.*
 - *The morphology of these materials is hard to control and may indeed be changing during testing.*
 - For UV cured films, although solid films are obtained, the degree of polymerization may vary between the surface and the interior of the film
 - In previous work, we showed that under very dry conditions, approaching 0% RH, some of the protons became unsolvated and irreversibly bound to the HPA structure.

Design Space for Model System



- We can control chemistry
- Need to understand morphology

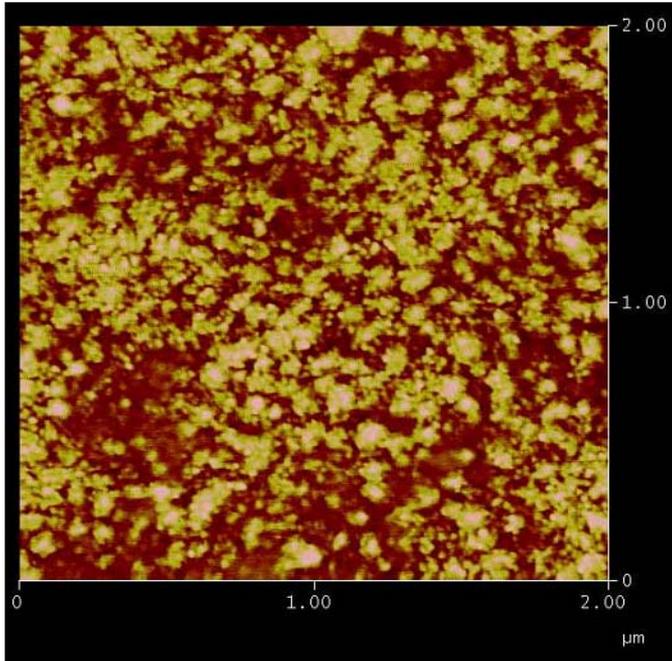
Technical Accomplishments: Poly POMs Cross-linked



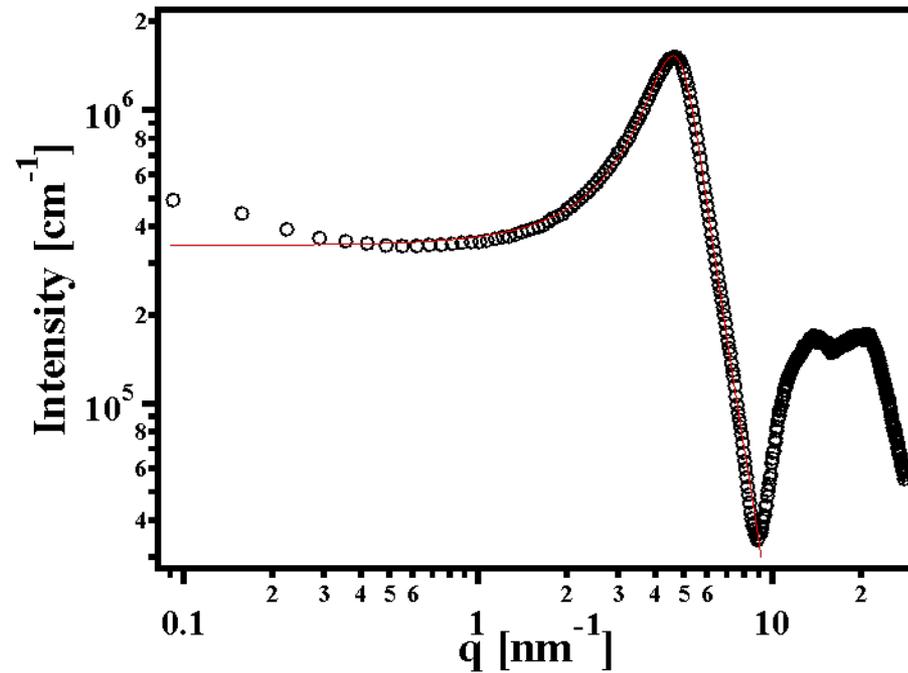
- PolyPOM75v/BA
- $\rho = 2.58 \text{ g cm}^{-3}$
- $\approx 100 \text{ }\mu\text{m}$

Poly POM 75v Morphology

(Phase Separation at loadings >50wt% HPA)

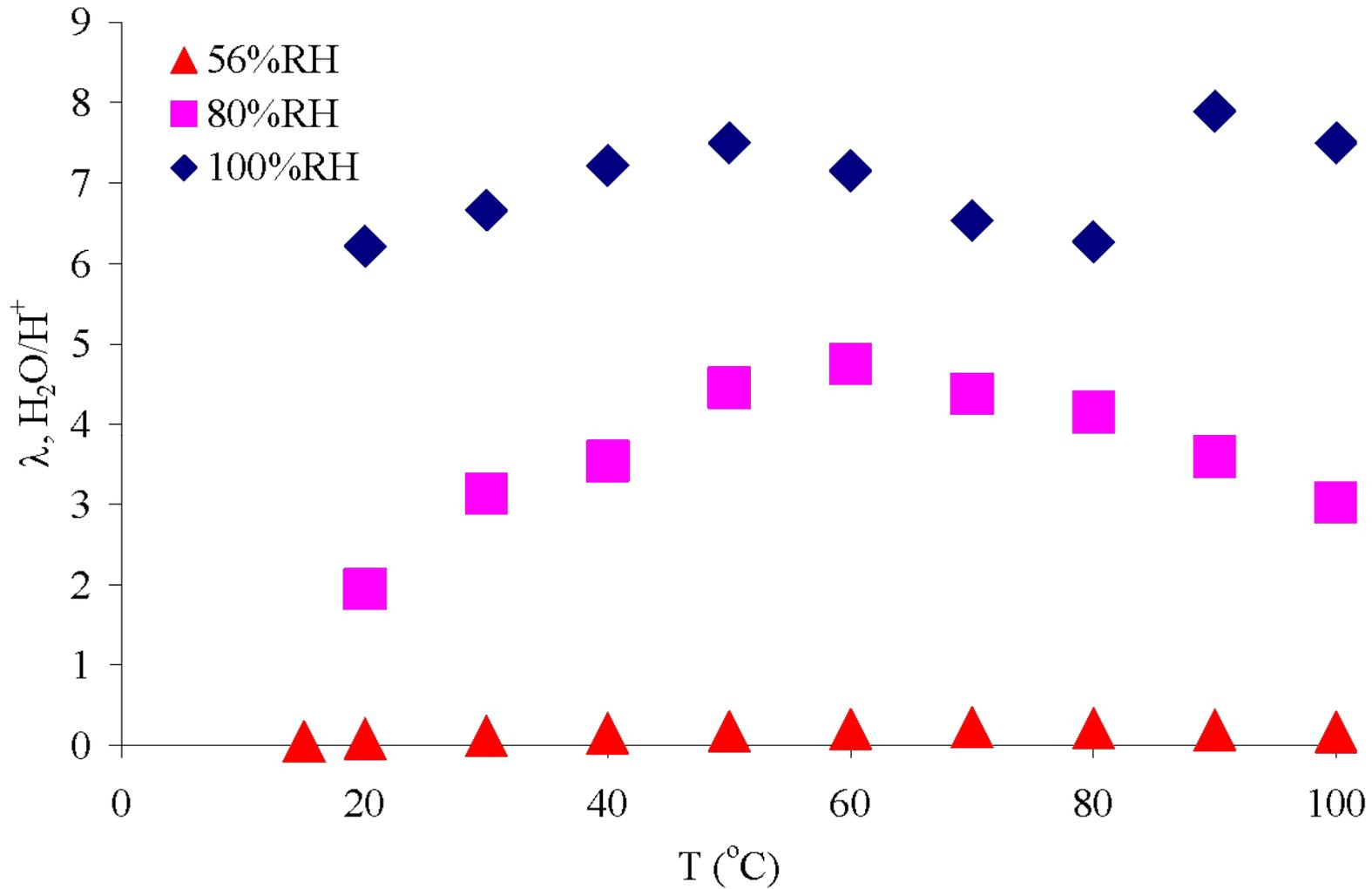


AFM

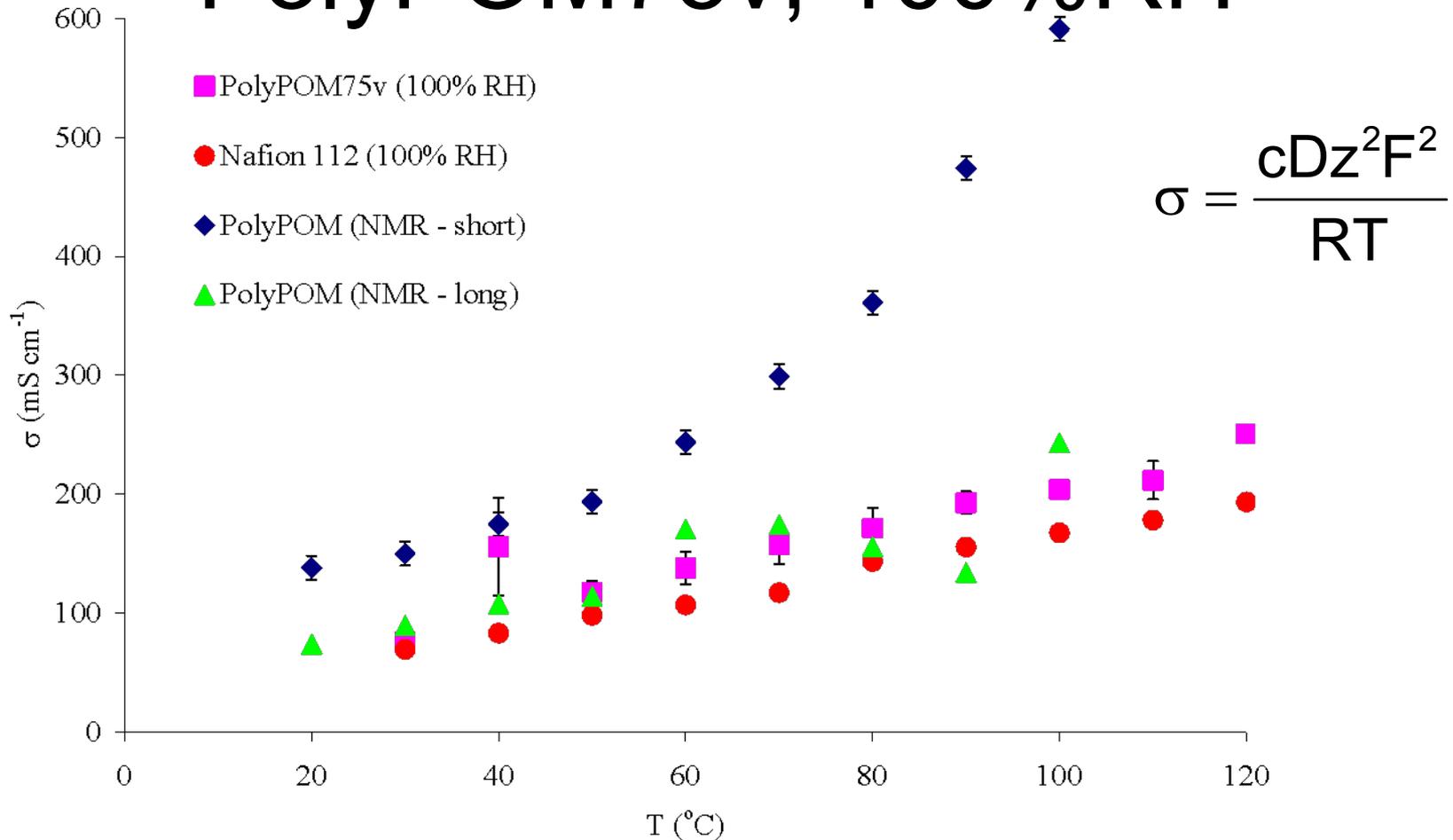


SAXS

Water content decreases for PolyPOM75v with RH

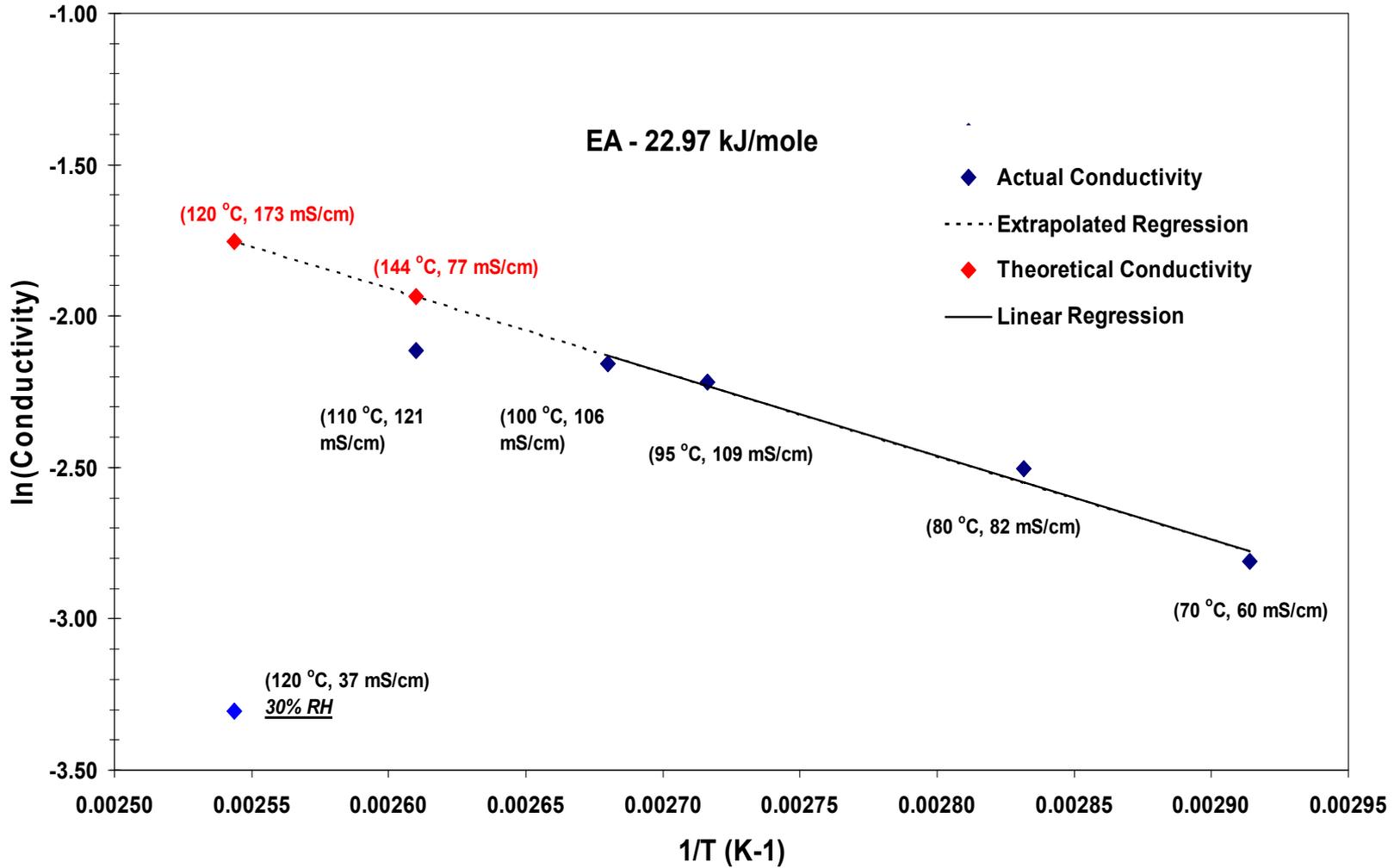


PolyPOM75v, 100%RH



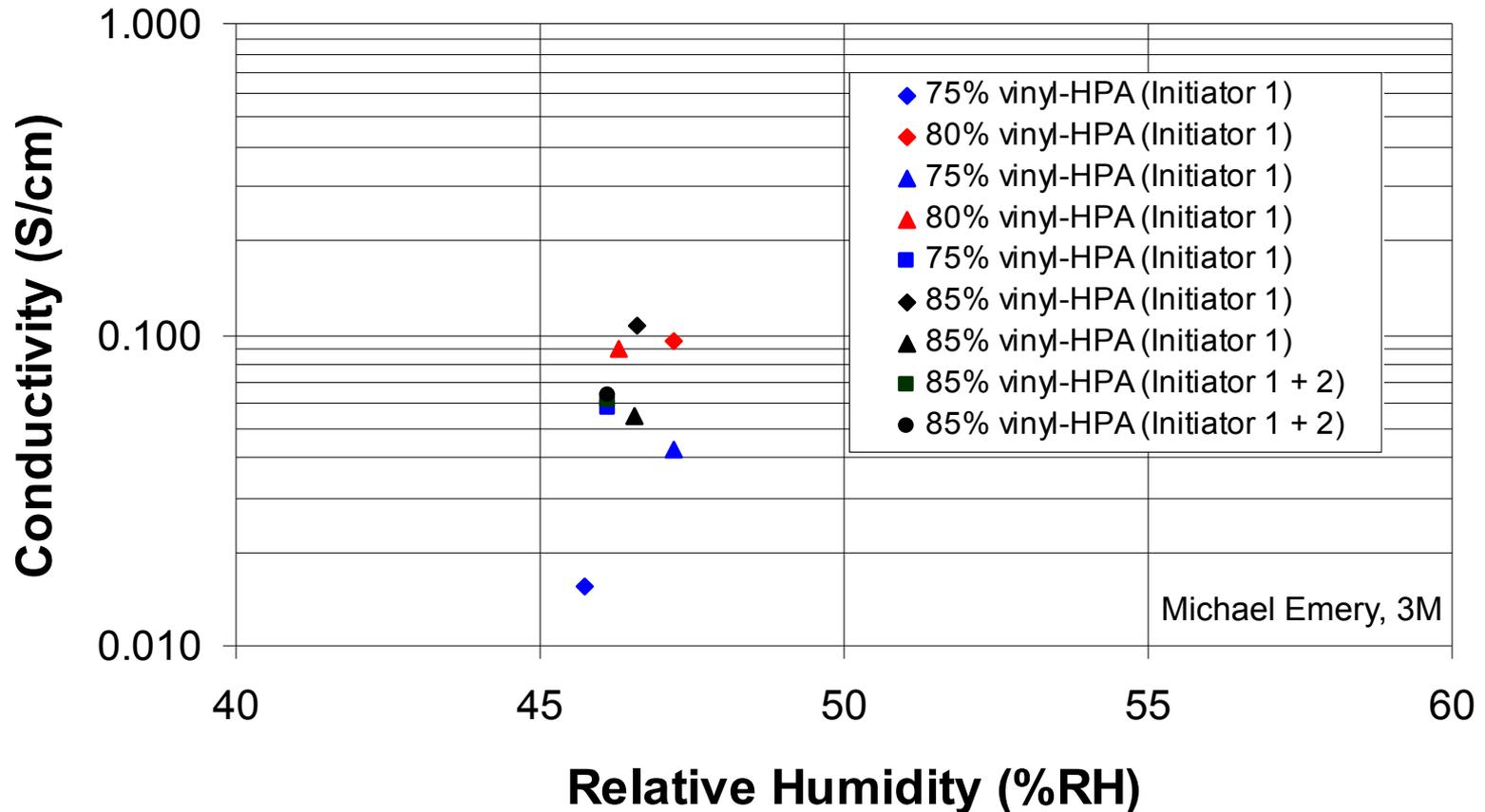
- Proton Conductivity higher than Nafion®
- Very High Proton Conductivity calculated from Nernst-Einstein Equation

P(SiW1180V-co-BA-co-HDDA), 50%RH



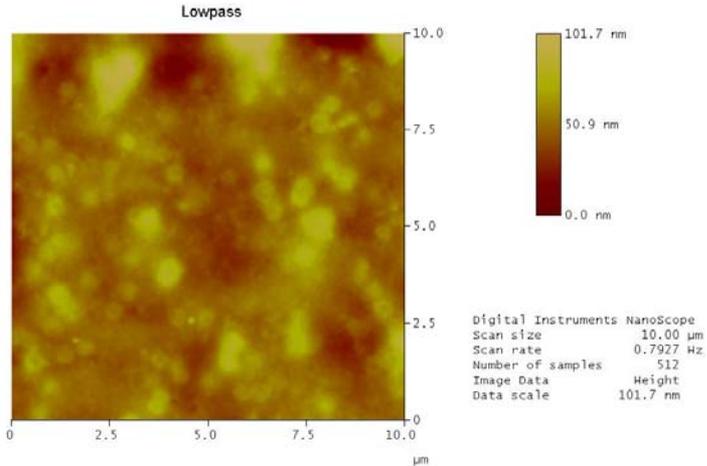
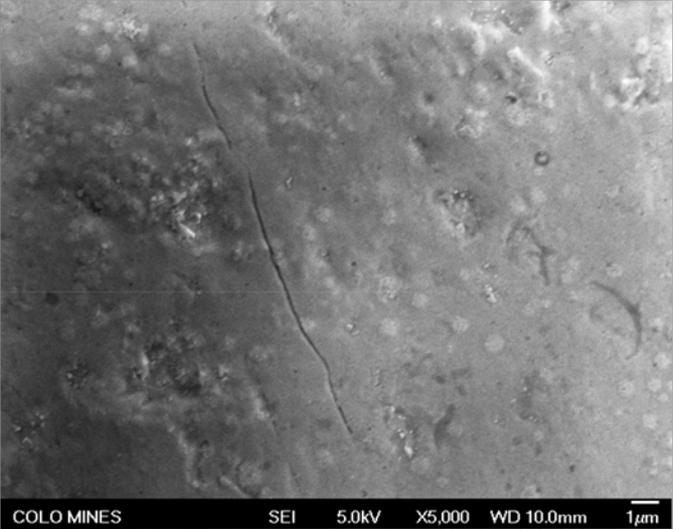
High Proton Conductivity can be Obtained at 120°C

Measurements made at 3M (single condition)
Data are averages of figures collected after 70 to 110 min. at condition
TestEquity oven, atmospheric pressure
Bekktech sample fixture

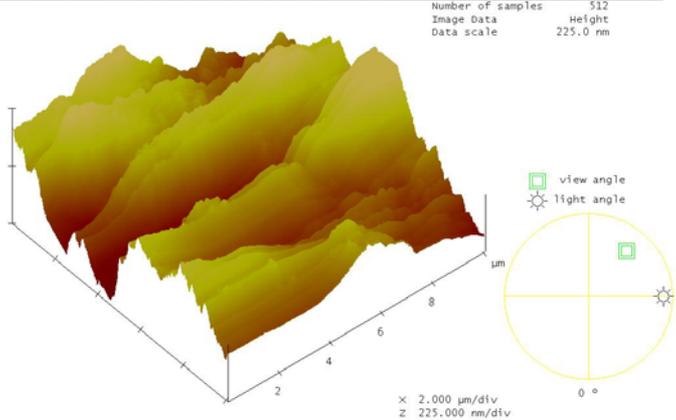
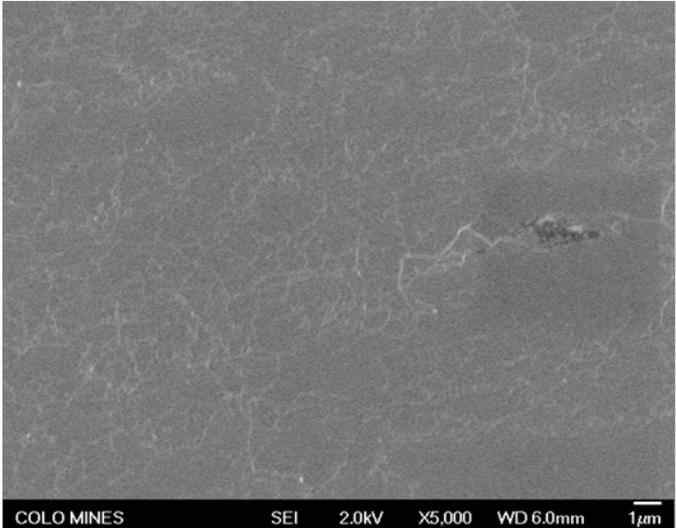


(Balance of compositions, in all cases, is 90:10 *n*-butylacrylate:hexanediol diacrylate)

Thermal vs UV changes Morphology



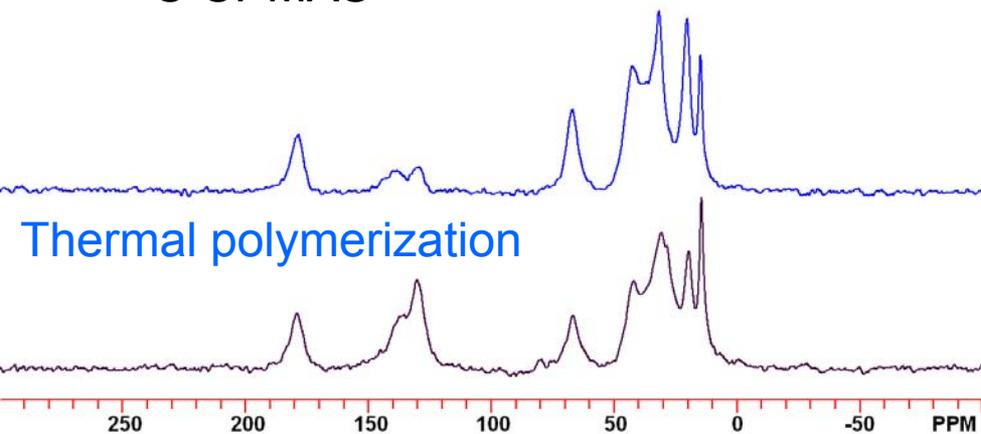
Thermal - clusters



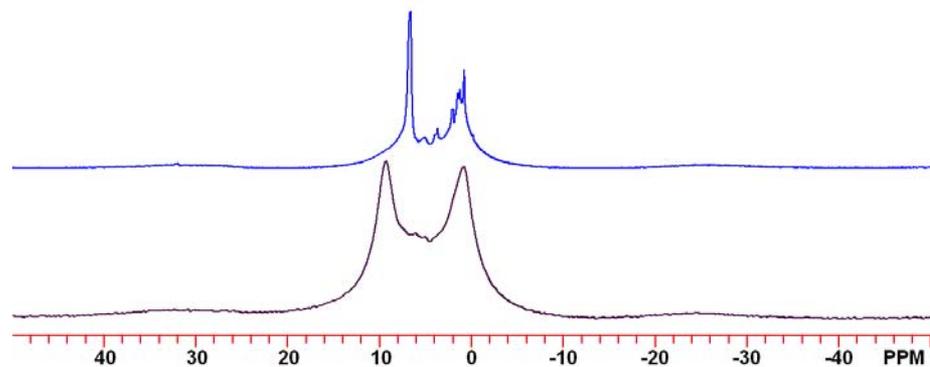
UV - networks

Dramatic Differences in Transport for Thermal vs UV cured PolyPOM80v

¹³C CPMAS



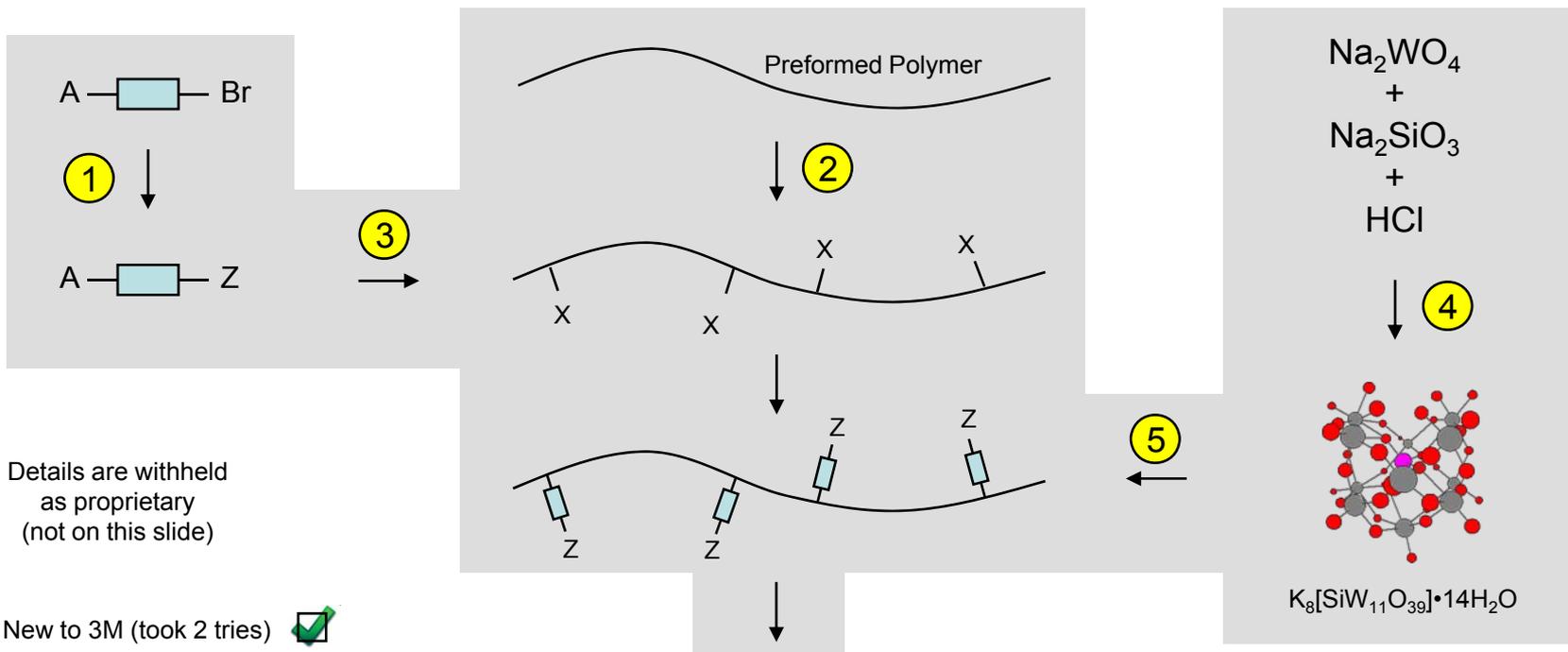
¹H



UV polymerization

Polymerization Method	$D(0) \times 10^5$ (cm ² s ⁻¹)	$D(\infty) \times 10^5$ (cm ² s ⁻¹)	$\sigma(0)$ (mS cm ⁻¹)	$\sigma(\infty)$ (mS cm ⁻¹)
Thermal	0.84	0.13	65	10
UV	2.48	0.95	191	73

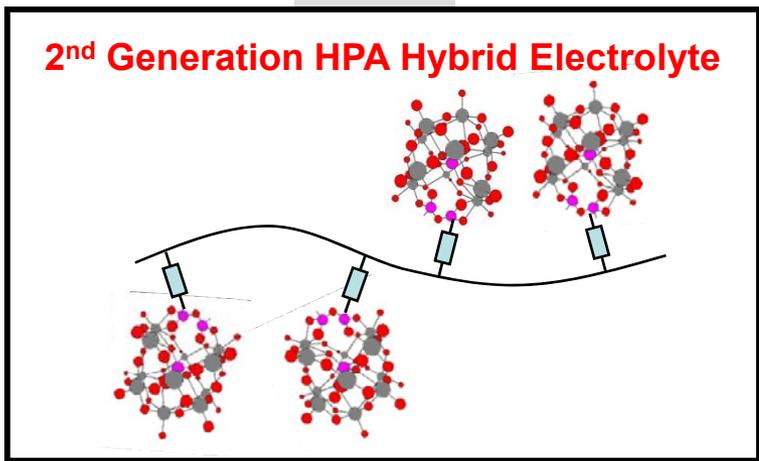
Future Work – 3M



Details are withheld as proprietary (not on this slide)

- 1 New to 3M (took 2 tries)
- 2 Core 3M chemistry
- 3 Extension of 3M chemistry
- 4 Core CSM chemistry
- 5 Extension of CSM chemistry

2nd polymer also on the drawing board.



Changes w.r.t. Phase I

- Different backbone
- New linkage
- Different film-forming process

Features

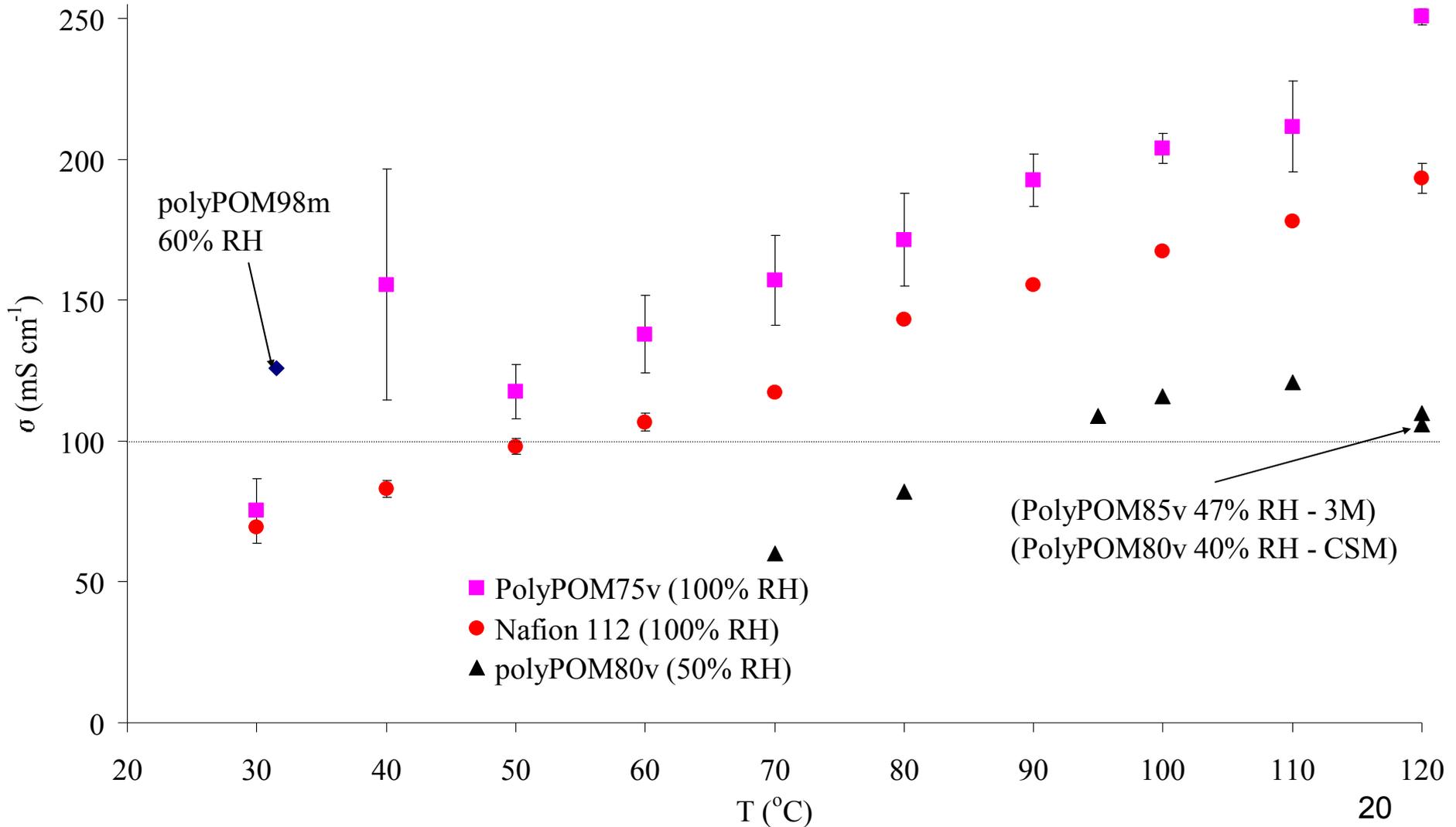
- More durable (chem & mech)
- Expected to be easier to mfr.
- Crosslinkable
- Expecting better reproducibility

Future Work - CSM

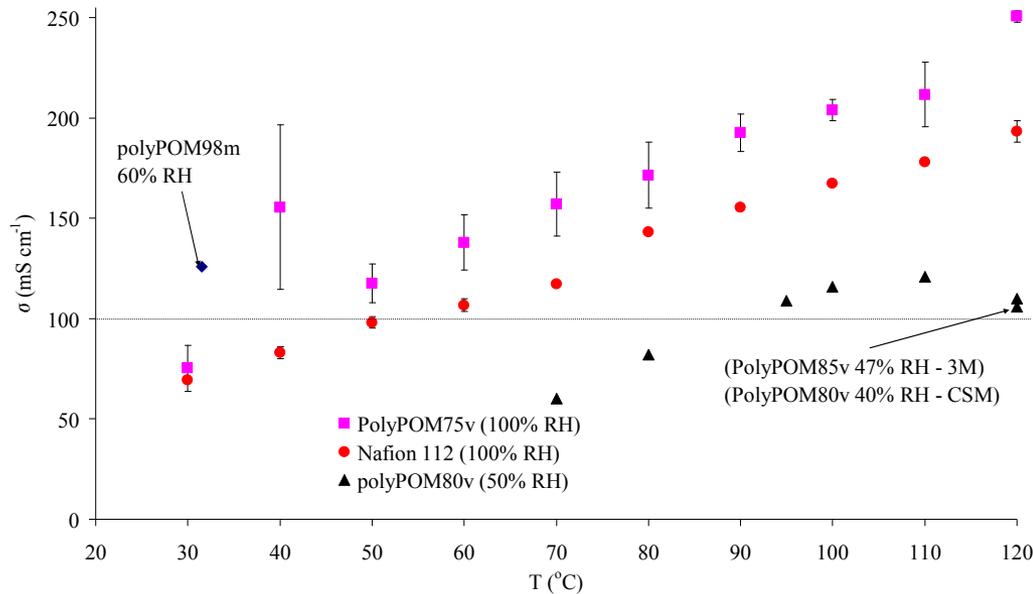
Continue to Fabricate Hybrid Polymers from monomeric building blocks

- Eliminate ester and CH_2 functionalities from Monomers
- Improve Morphology – Channels vs Clustering
 - Monomer System A
 - Monomer System B
 - Monomer System C
- Down select at end of Year 4
- Optimize for end of Year 5

Summary



Summary



	April 2008	RT milestone Exceeded August 2008	Met DOE 2010 target January 2009
H ⁺ conductivity	300 ms/cm 100%RH 80°C	126 ms/cm 60%RH, 31°C	100 ms/cm 47%RH at 120°C