DOE Hydrogen Program

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

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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

• Overall	•Fabricate a hybrid HPA polymer (polyPOM) from HPA functionalized monomers with: – σ >0.1 S cm^{-1} at 120°C and 25%RH
• 2008	•Synthesis and optimization of hybrid HPA polymers for conductivity from RT to 120ºC with an understanding of chemistry/morphology conductivity relationships using model system
• 2009	•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	Demonstrate conductivity of 100 mS cm^{-1} at 50% RH and 120ºC – **30ºC 60% RH 120 mS cm^{-1}** **80ºC 100% RH >300 mS cm^{-1}** *Comparable to PFSA membranes under FC operating conditions* **120ºC 40-50%RH >100 mS cm^{-1}**
Feb 09	Deliver membrane to topic 2 awardee – Lower conductivity, unfortunately hard to control model film quality and durability at high HPA loadings

Relevance

Objective

- To fabricate PEMs with a proton conductivity <100 ms cm^{-1} for operation in a vehicular system up to 120ºC with no inlet RH
- Films were synthesized that meet this DOE performance target at temperatures > 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

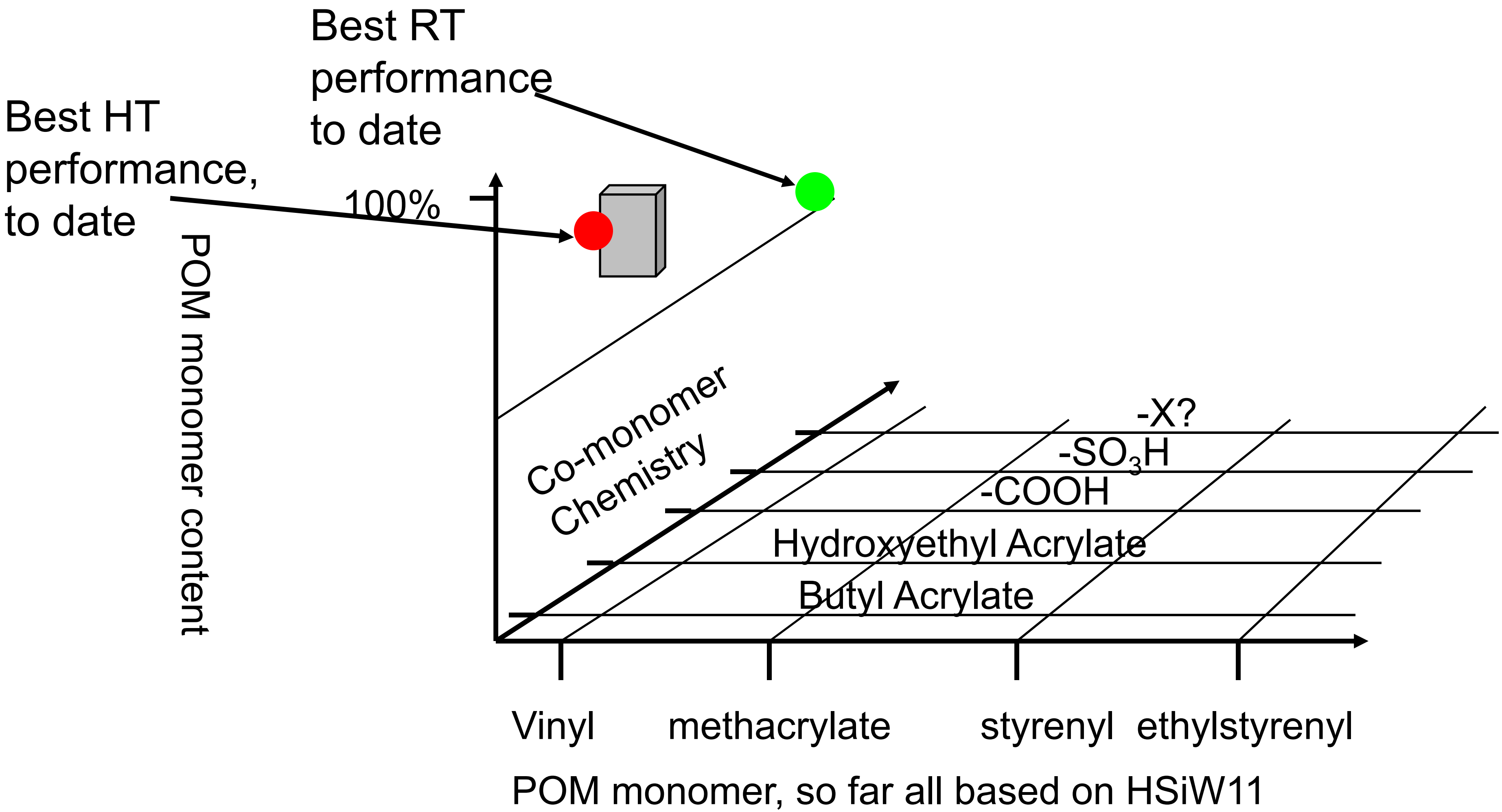
- Materials Synthesis based on HPA Monomers, Novel "High and Dry" proton conduction pathways mediated by organized HPA moieties – A NEW Ionomer System

- Task 2.1: Synthesis and Optimization of hybrid HPA polymers for 120ºC conductivity for Go/No Go Decision - Complete
- Task 2.2 – Synthesis and selection of protonic additive for hybrid HPA polymers for 120ºC 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

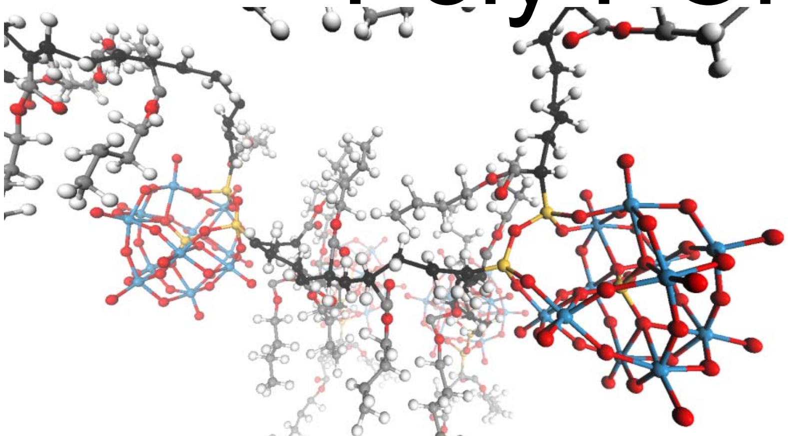
- Polymer system in a kit
- Allows Chemistry to be varied
- Effect of Morphology can be studied
- Full Disclosure
- But…
  - Ester linkage unstable to hydrolysis
  - Oxidizable CH_2 groups and an oxidizing super acid moiety
  - The formulation is not optimized and becomes brittle eith time
    - *Residual unpolymerized volatile butyl acrylate acts 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.

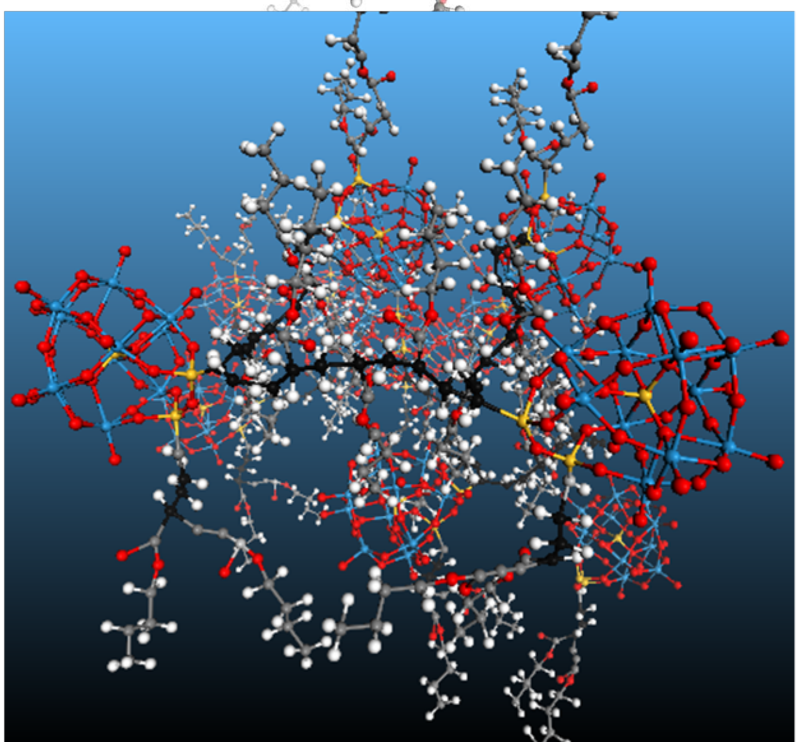
Design Space for Model System



- We can control chemistry
- Need to understand morphology

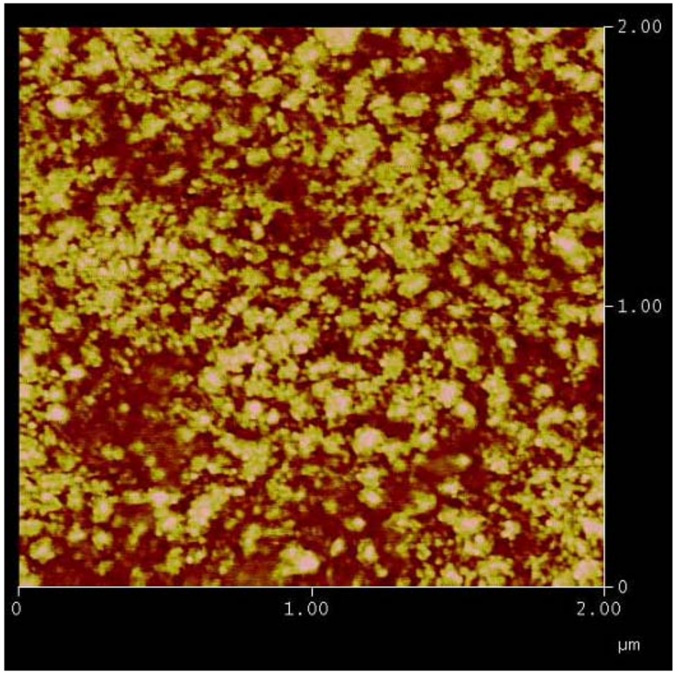
Technical Accomplishments: Poly POMs Cross-linked

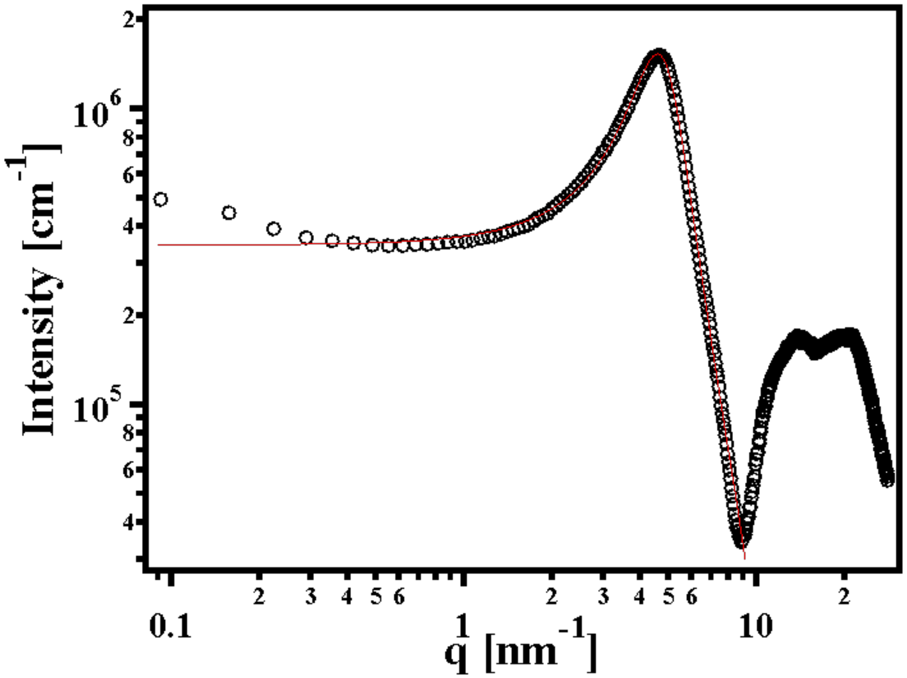




- PolyPOM75v/BA
- ρ= 2.58 g cm^{-3}
- ≈100 μm

Poly POM 75v Morphology
(Phase Separation at loadings >50wt% HPA)

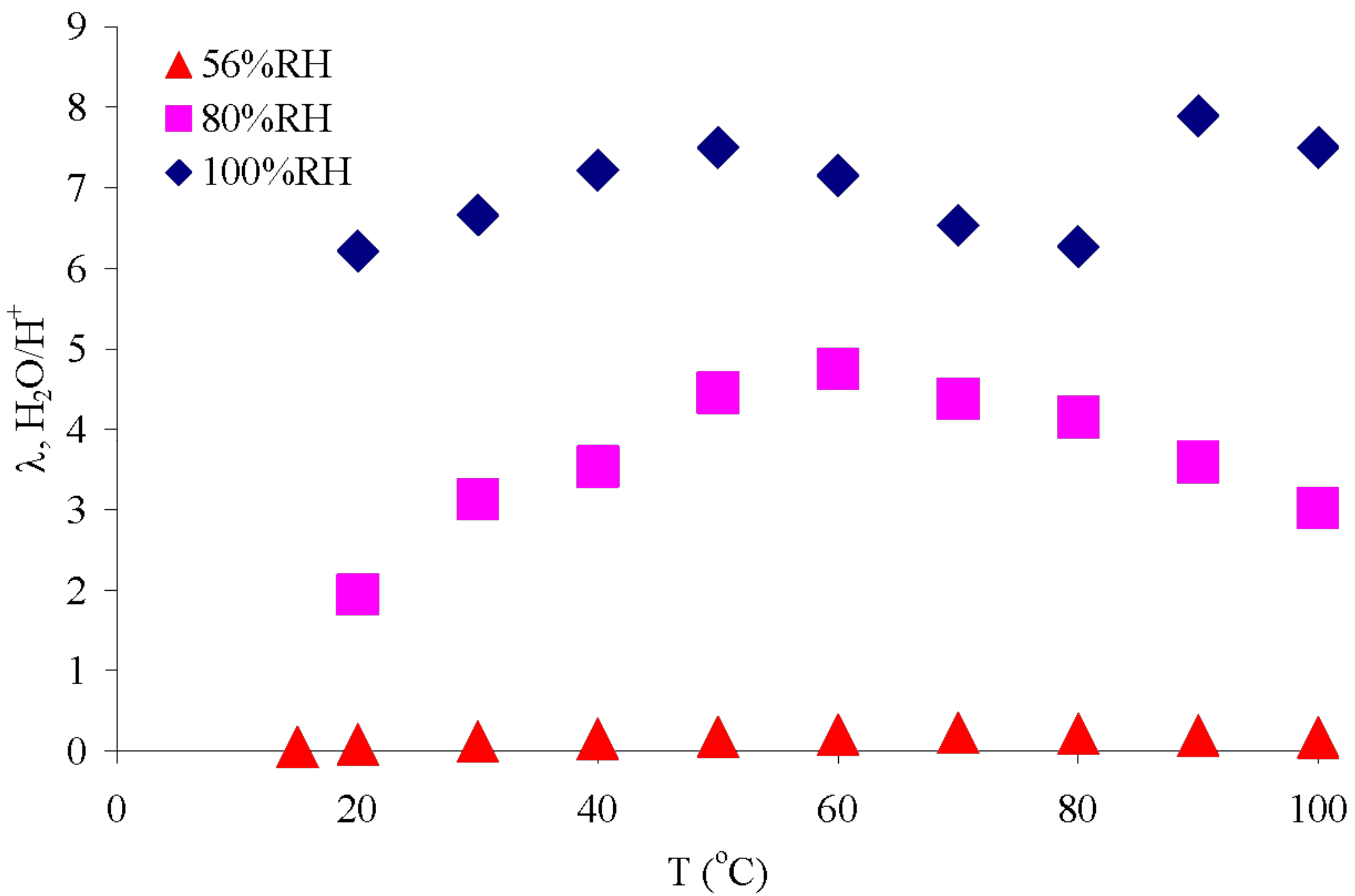




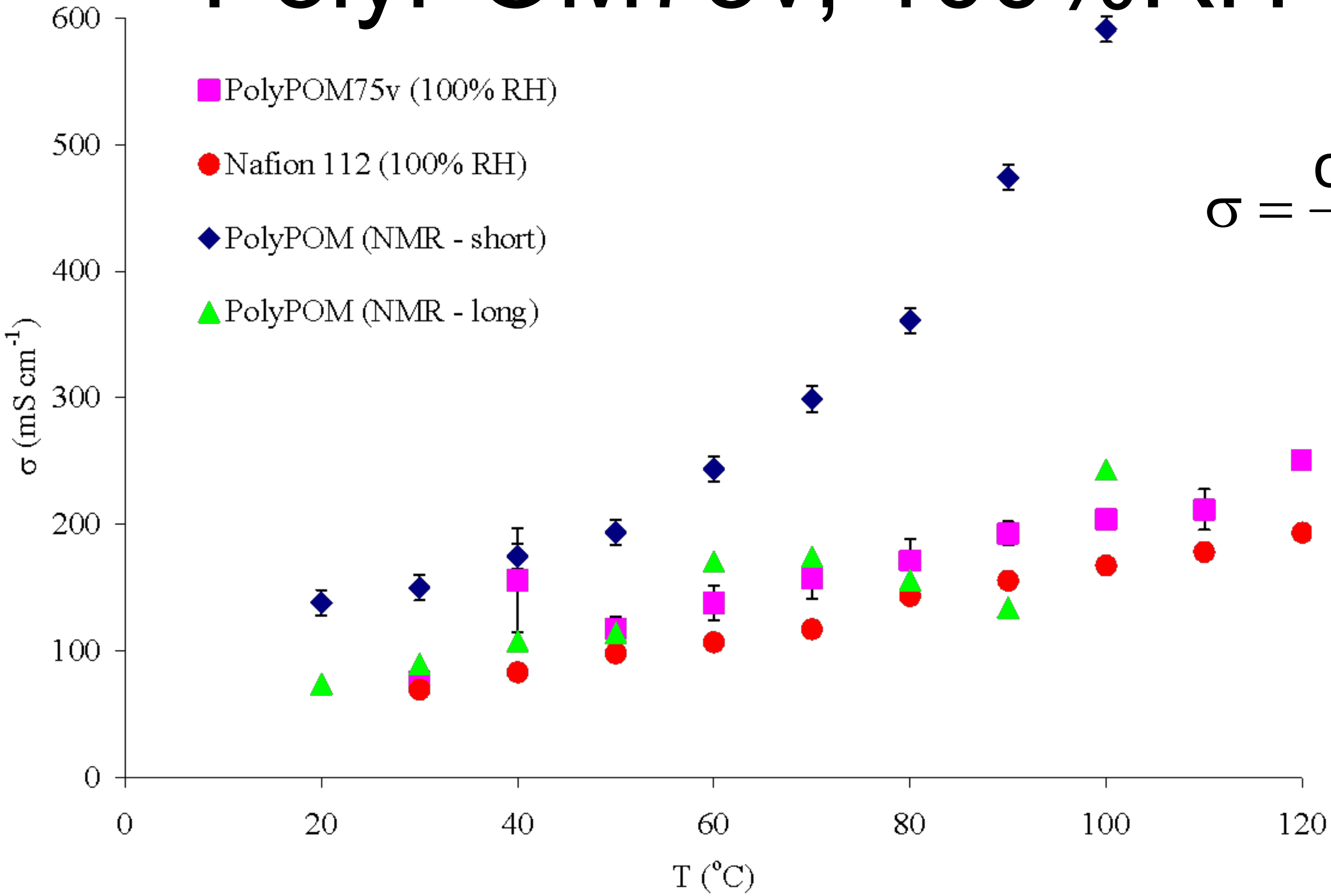
AFM

SAXS

Water content decreases for PolyPOM75v with RH



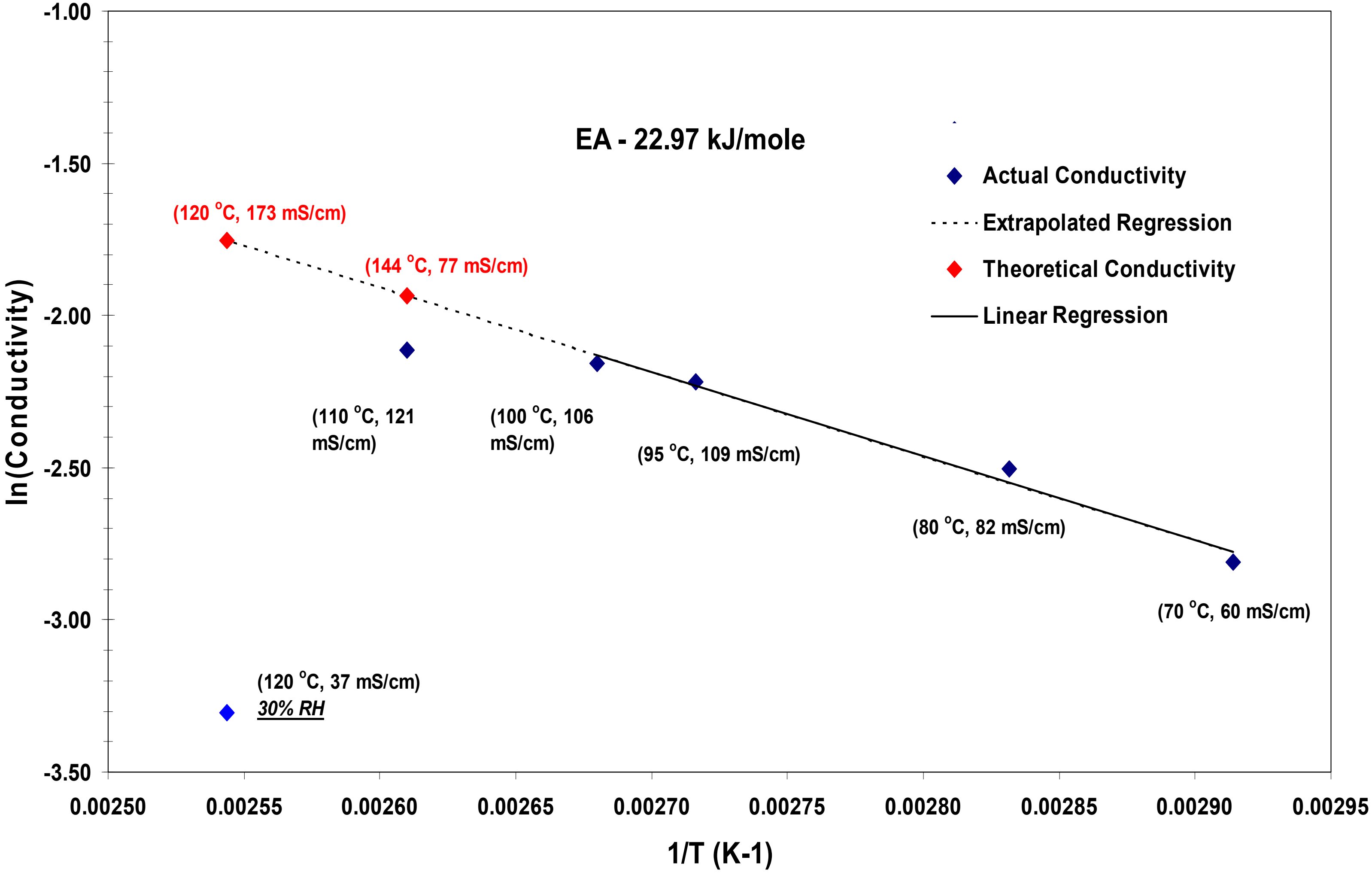
PolyPOM75v, 100%RH



$$\sigma = \frac{cDz^2F^2}{RT}$$

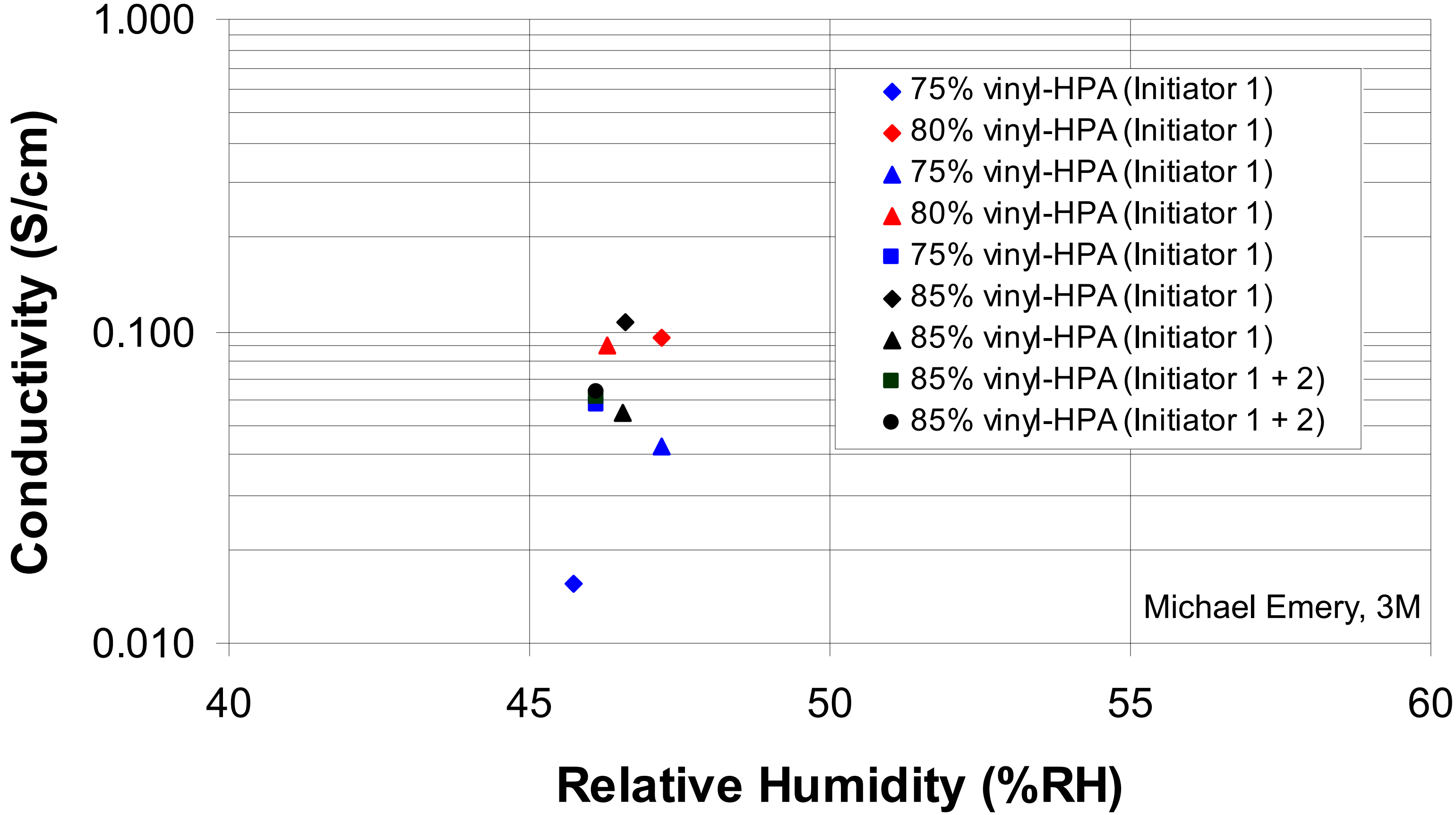
- Proton Conductivity higher than Nafion®
- Very High Proton Conductivity calculated from Nernst-Einstein Equation

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



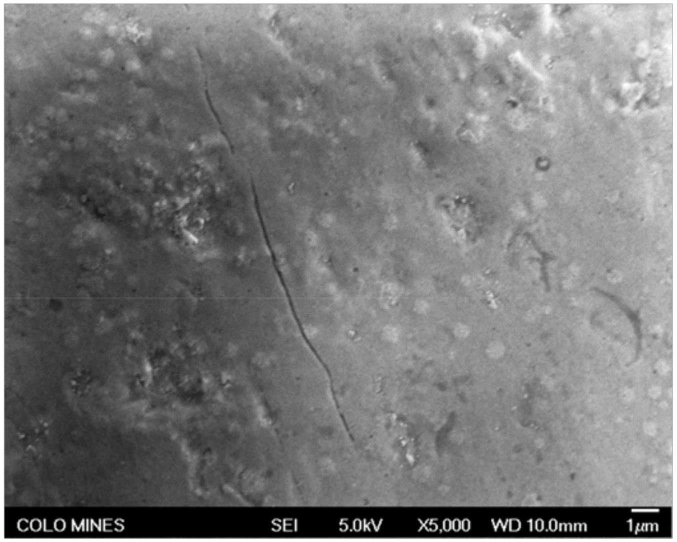
High Proton Conductivity can be Obtained at 120ºC

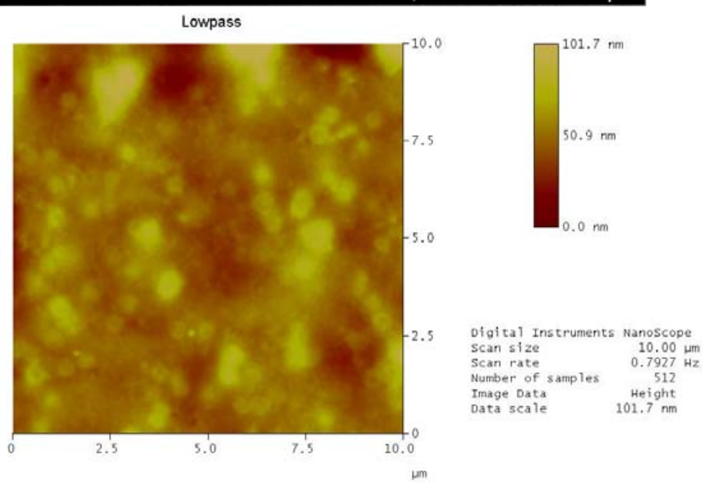
Measurements made at 3M (single condition)
Data are averages of figures collected after 70 to 110 min. at condition
TestEquity oven, atmospheric pressure
Bekktech sample fixture



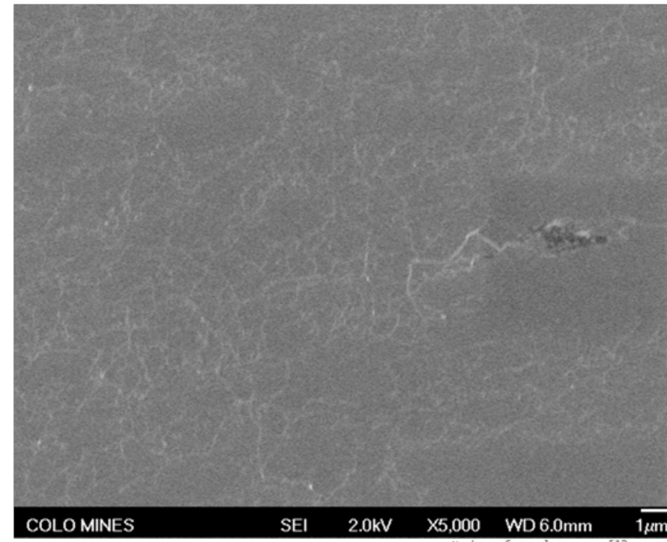
(Balance of compositions, in all cases, is 90:10 n-butylacrylate:hexanediol diacrylate)

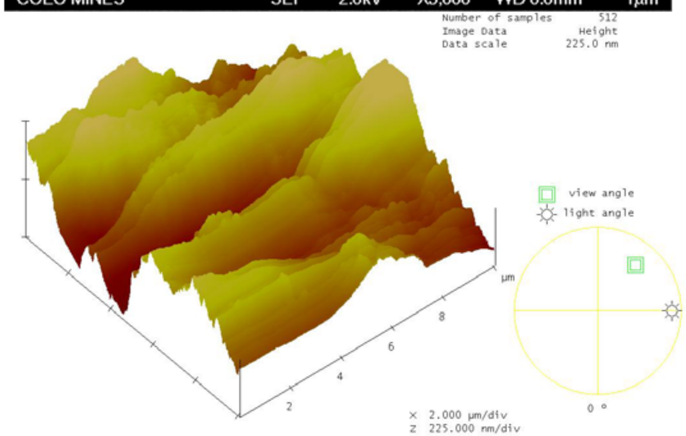
Thermal vs UV changes Morphology





Thermal - clusters

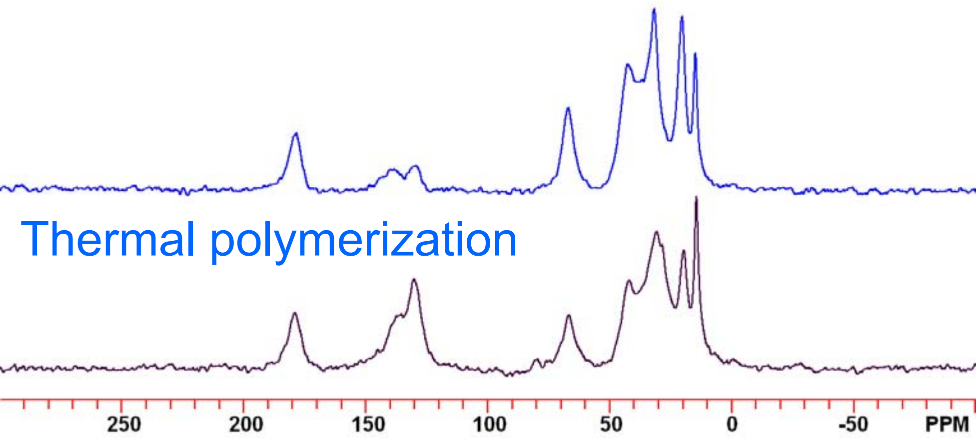




UV - networks

Dramatic Differences in Transport for Thermal vs UV cured PolyPOM80v

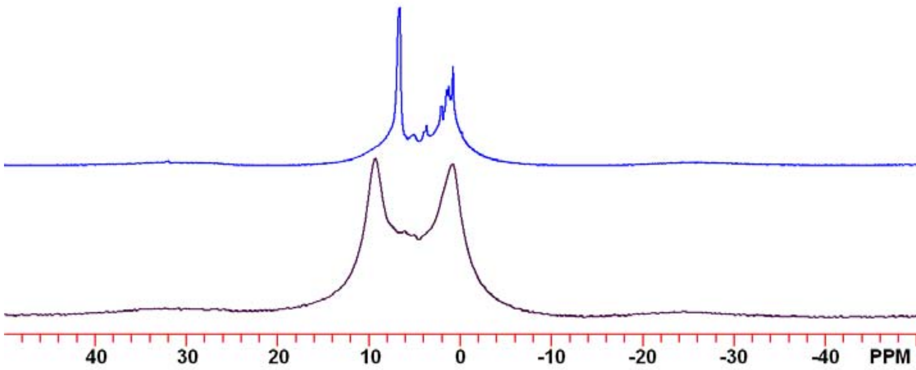
^{13}C CPMAS



Thermal polymerization

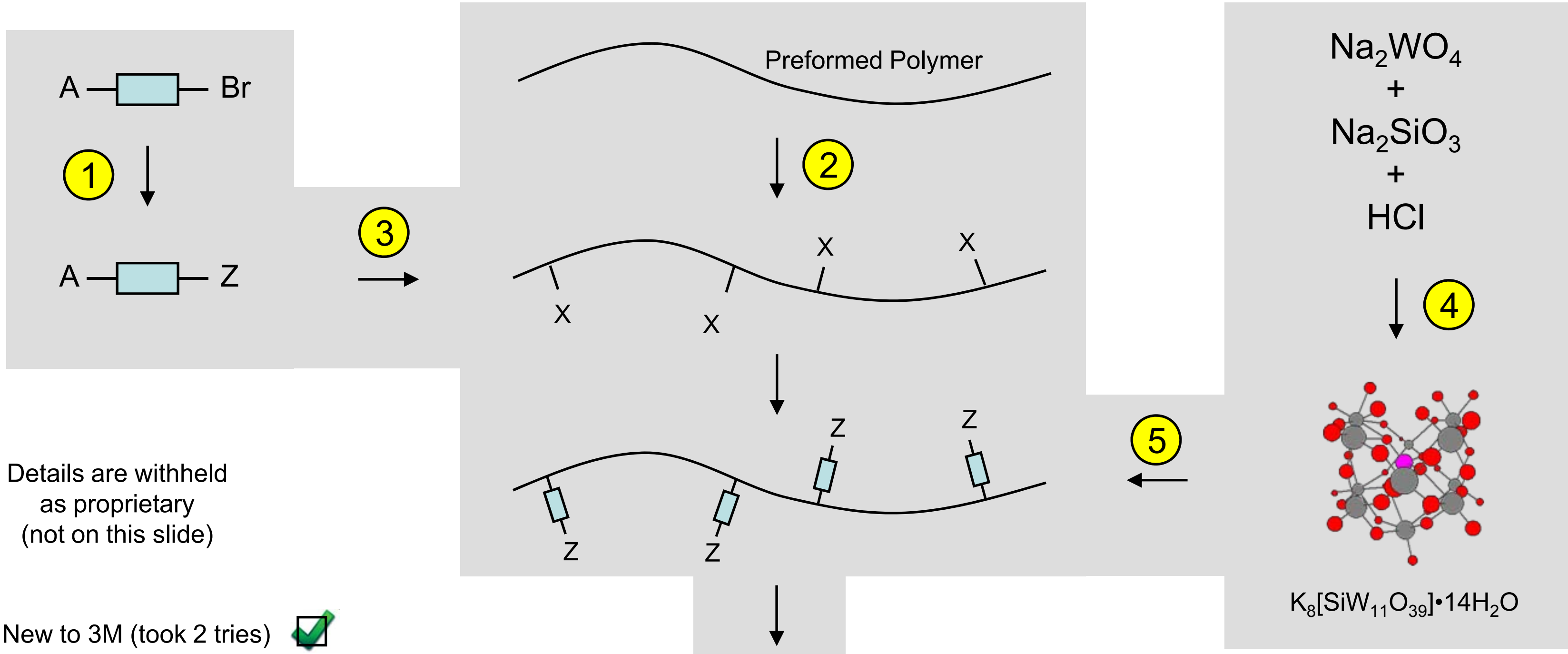
UV polymerization

^{1}H

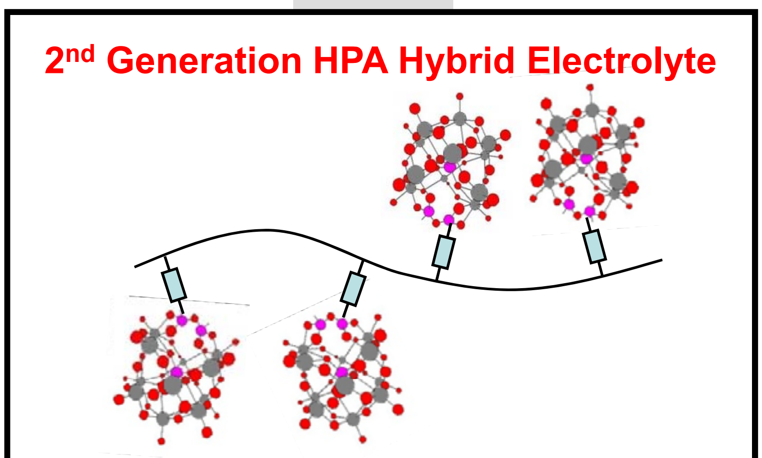


Polymerization Method	D(0) x 10^5 (cm^2 s^{-1})	D(∞) x 10^5 (cm^2 s^{-1})	σ(0) (mS cm^{-1})	σ(∞) (mS cm^{-1})
Thermal	0.84	0.13	65	10
UV	2.48	0.95	191	73

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

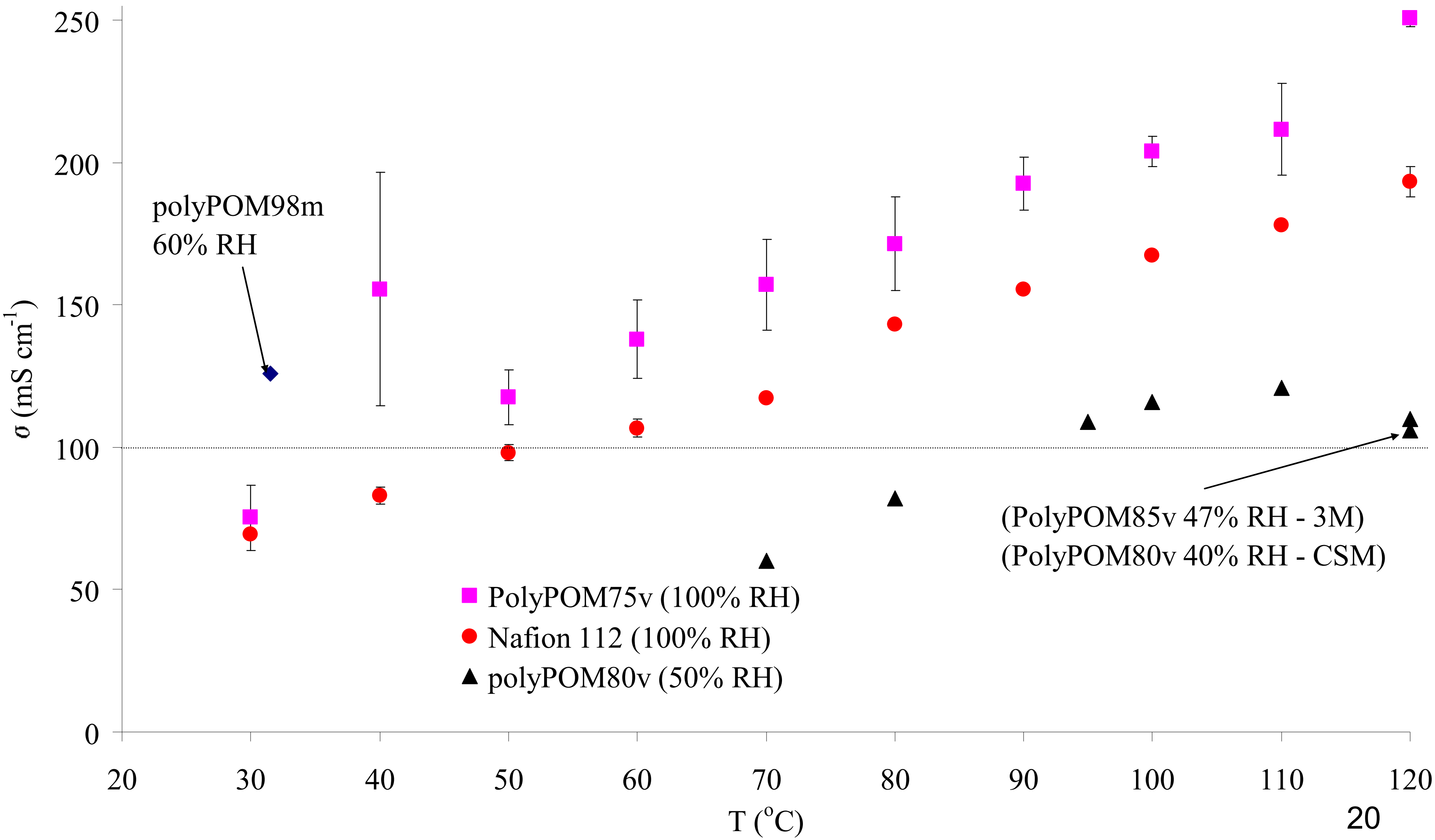
- More durable (chem & mech)
- Expected to be easier to mfr.
- Crosslinkable
- Expecting better reproducibility

Future Work - CSM

Continue to Fabricate Hybrid Polymers from monomeric building blocks

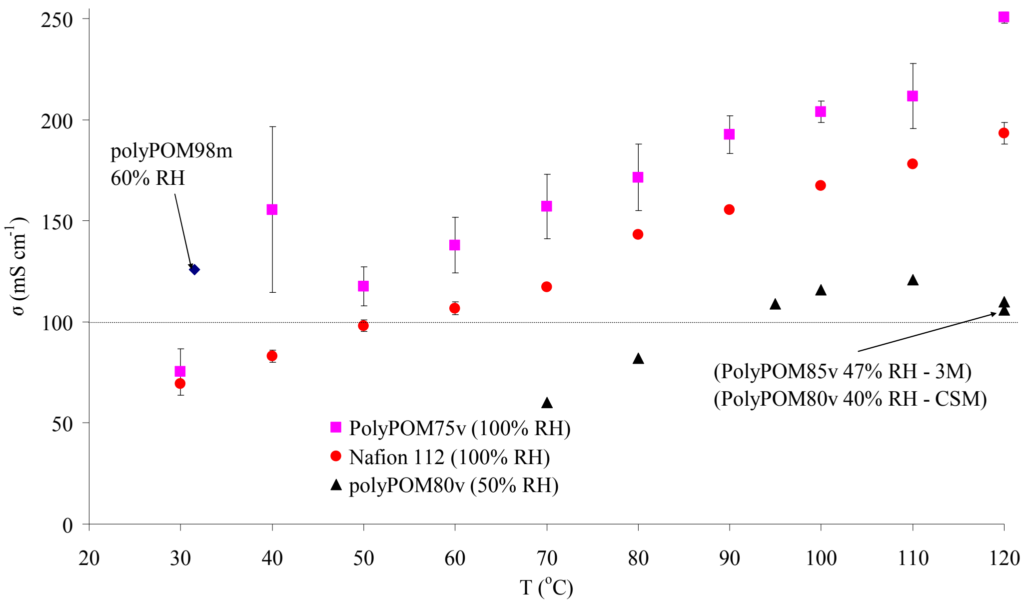
- Eliminate ester and CH_2 functionalities from Monomers
- Improve Morphology – Channels vs Clustering
  - Monomer System A
  - Monomer System B
  - Monomer System C
- Down select at end of Year 4
- Optimize for end of Year 5

Summary



polyPOM98m
60% RH
(PolyPOM85v 47% RH - 3M)
(PolyPOM80v 40% RH - CSM)
PolyPOM75v (100% RH)
Nafion 112 (100% RH)
polyPOM80v (50% RH)
σ (mS cm-1)
T (oC)
0
50
100
150
200
250
20
30
40
50
60
70
80
90
100
110
120

Summary



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