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

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Overview

Timeline

- Start: April 1, 2006
- End: March 31, 2011
- 20% Complete

Budget

- Total project funding
  - DOE - $1,500K
  - Contractor - $375K
- Funding received in FY06
  - $150K
- Funding for FY07
  - $300K

Barriers

- B **Cost**
- D **Water Transport within the Stack.**
- E **System Thermal and Water Management.**

Partners

- Industrial - 3M
- Management - CSM

Objectives

• Overall	•Fabricate a hybrid HPA polymer (polyPOM) from HPA functionalized monomers with: – σ >0.1 S cm^{-1} at 120°C and <1.5 kPa H_2O
• 2006	•Selection of most hydrolytically stable HPA to monomer linkage chemistry •Synthesize free acids of HPA polymers
• 2007	•Synthesis and optimization of hybrid HPA polymers for conductivity from RT to 120ºC

Plan and Approach

- Task 1.1 Phenyl link stability
  Phenyl HPA derivatives subjected to low pH/high temperatures to determine optimum chemistry for fuel cell stability – A vast synthetic chemistry of hybrid organic/inorganic HPAs exists but none of it has been applied to fuel cell ready environments. (90% complete)
- Task 1.2 Ion exchange studies
  Determination of most facile conversion of HPA polymers to proton conducting systems – Most published HPA chemistry is concerned with HPA salts. In order to conduct H^+ we must learn how to convert these materials in to free acids. (50% complete)
- Task 1.3 Optimization of hybrid HPA polymers for RT
  Morphology and structure of polymers controlled to optimize proton conductivity, HPA clustering or order(20% complete)
- Task 2.1 Optimization of hybrid HPA polymers for 120°C
  Maximize H^+ availability, exploit HPA dissociable H^+ donor groups - >100°C HPA have fast H^+ diffusion but not all H^+ are available (10% complete)
- Task 3.2 Optimize oxidative stability
  Use oxidatively stable organic chemistry, exploit HPA peroxide catalysis

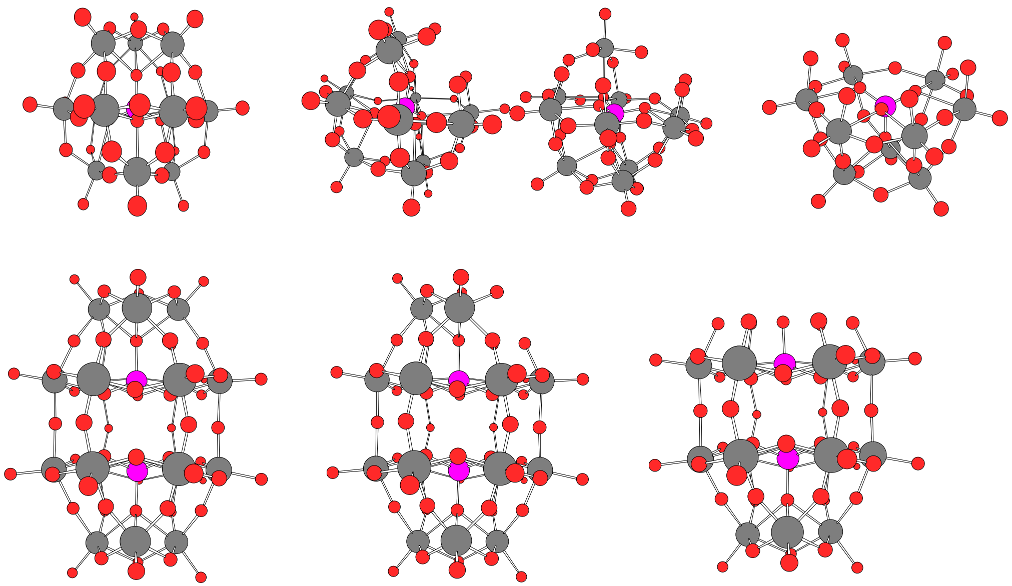
Unique Approach

- Materials Synthesis based on HPA Monomers
- Novel “High and Dry” proton conduction pathways mediated by organized HPA moieties
- 3M brings additional synthetic expertise and direct later stages of project towards manufacturability.

Technical Accomplishments/ Progress/Results

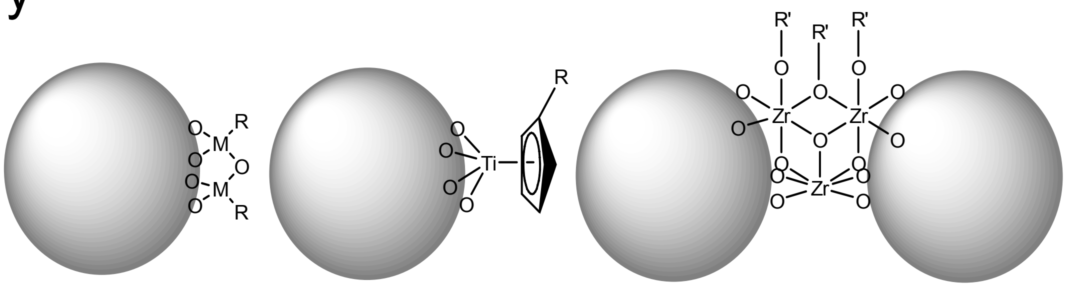
- Demonstration of superior stability of phosphonate linkage in boiling 6 mol HCl or 3% H_2O_2
- Generation of free acid PolyPOMs even with less stable linkages
- Achievement of acceptable films by smart formulation (polyPOM formulations are proprietary to 3M/CSM and so will not be discussed in this presentation)
- Preliminary conductivity data

Model Phenyl Derivatives Synthesized for Stability Testing



- Lacunary HPA allow easy attachment points

- Extensive linkage chemistry available
- M = P, Si, Ge, Sn
- R, R’ = Phenyl
- Zr – 3M



Testing of Model compounds

- Boiled in 6M HCl for 4h
- Boiled in 3% H_2O_2 for 4h
- Compound degradation probed by NMR and IR

- **PhPO-HPA linkage survived both tests**
- CpTi-HPA linkages showed some stability

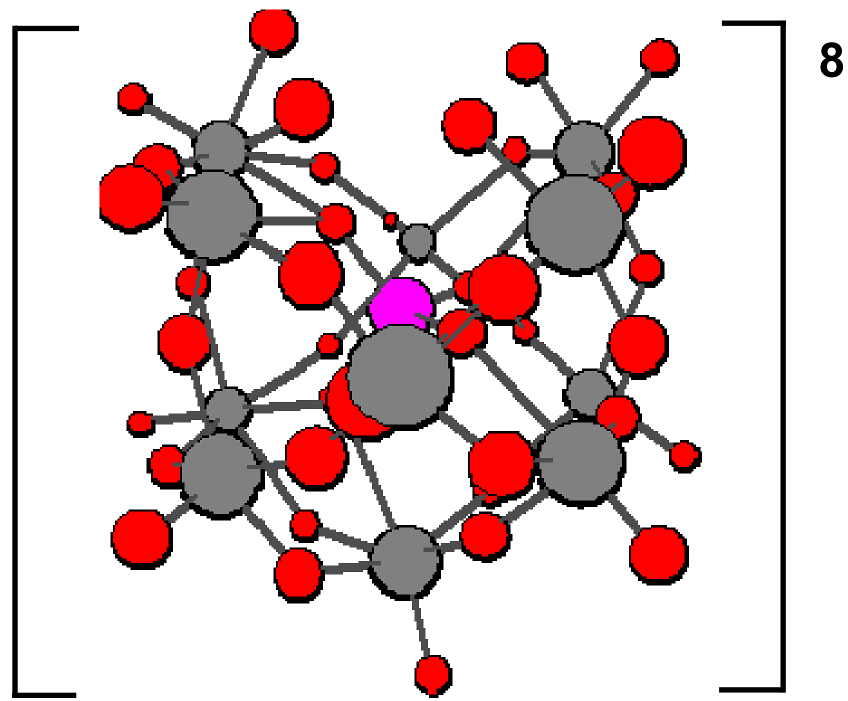
- Even though PhSiO-HPA did not survive, polyPOM containing SiO-HPA linkages could be ion exchanged in boiling acid, implying that **polymer provides additional stability**

- Additional MO-HPA model compounds are being synthesized at 3M

Preparation of Lacunary HPA

$SiO_3^{2-} + WO_4^{2-}$

↓



Methods of Preparation

1. Direct Synthesis

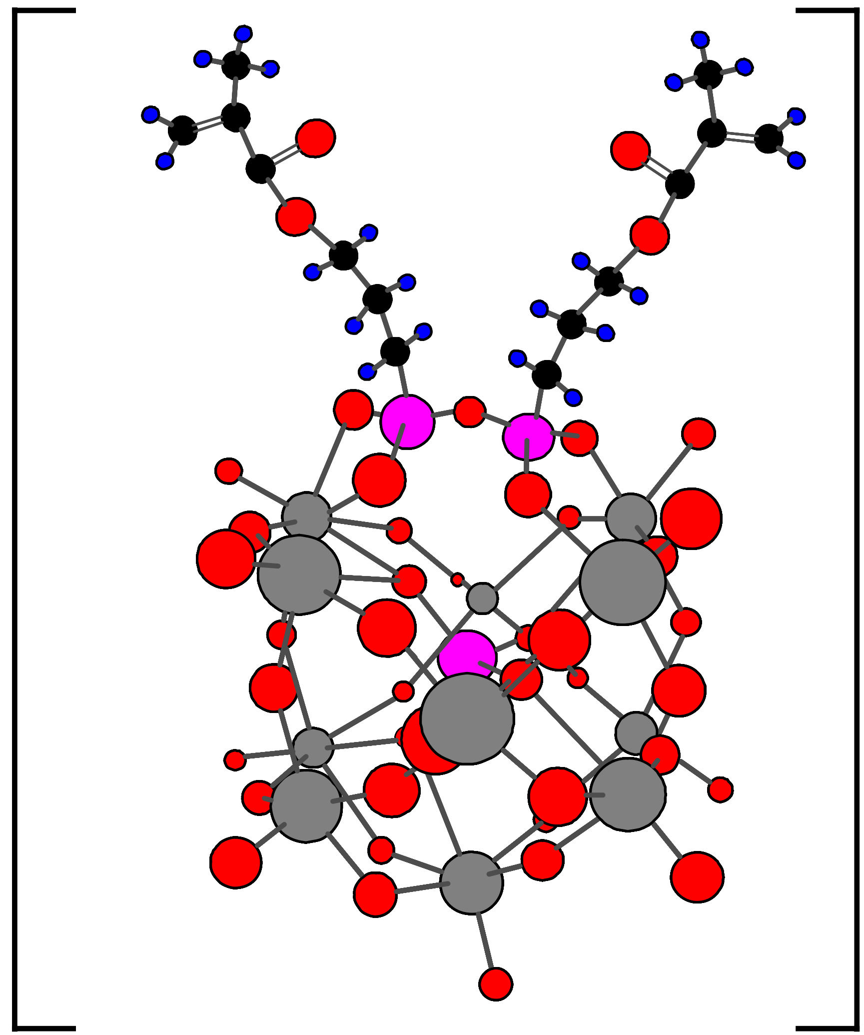
2. Basic Degradation of Saturated HPA

Lacunary$[SiW_{11}O_{39}]^{8-}$

α-,β-, and γ-Dodecatungstosilicic acids: isomers and related lacunary compounds; Teze, A.; Herve, G., Eds. *Inorganic Syntheses*; John Wiley & Sons: New York, 1990; Vol. 27.

Hybrid $SiW_{11}O_{39}$(Methacryl) Monomer

Reaction of $SiW_{11}O_{39}^{4-}$ with 3-Methacryloxy-propyltrimethoxy silane.



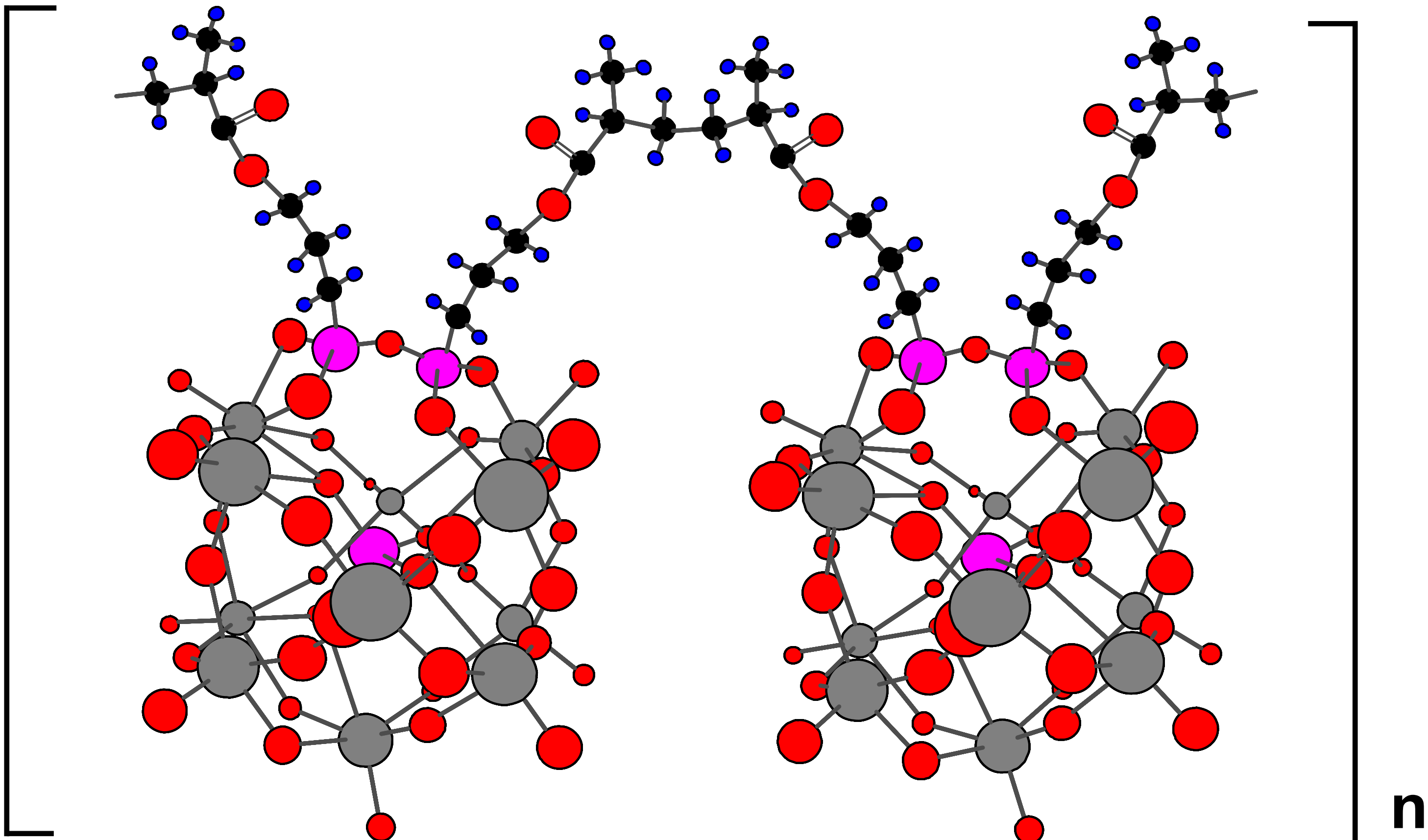
4-

• $4Bu_4N^+$

Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 759-760.
Weeks, M. S.; Hill, C. L.; Schinazi, R. F. *J. Med. Chem.* **1992**, *35*, 1216-1221.

PolyPOM100m

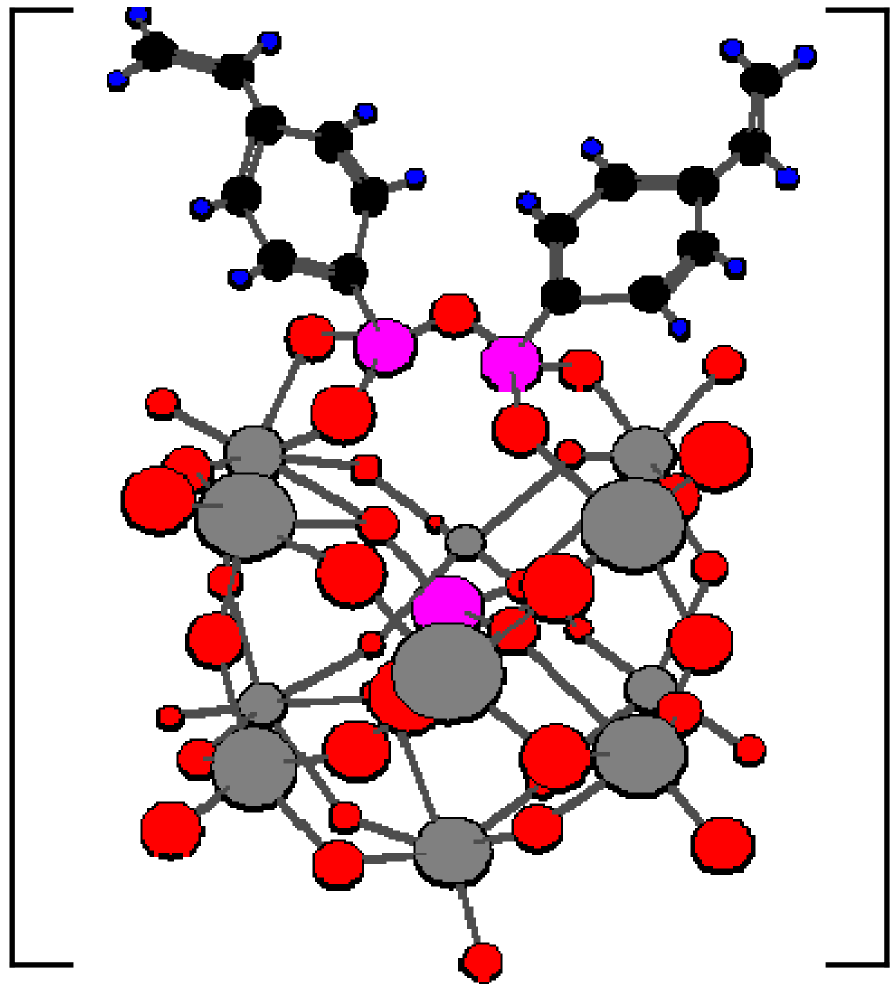
Radical polymerization of C=C functional group of organic component



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

Hybrid $SiW_{11}O_{39}$(Styryl) Monomer

Reaction of Lacunary HPA with Trichloro- (or Trialkoxy-) silanes to produce organic-inorganic hydrid monomer.



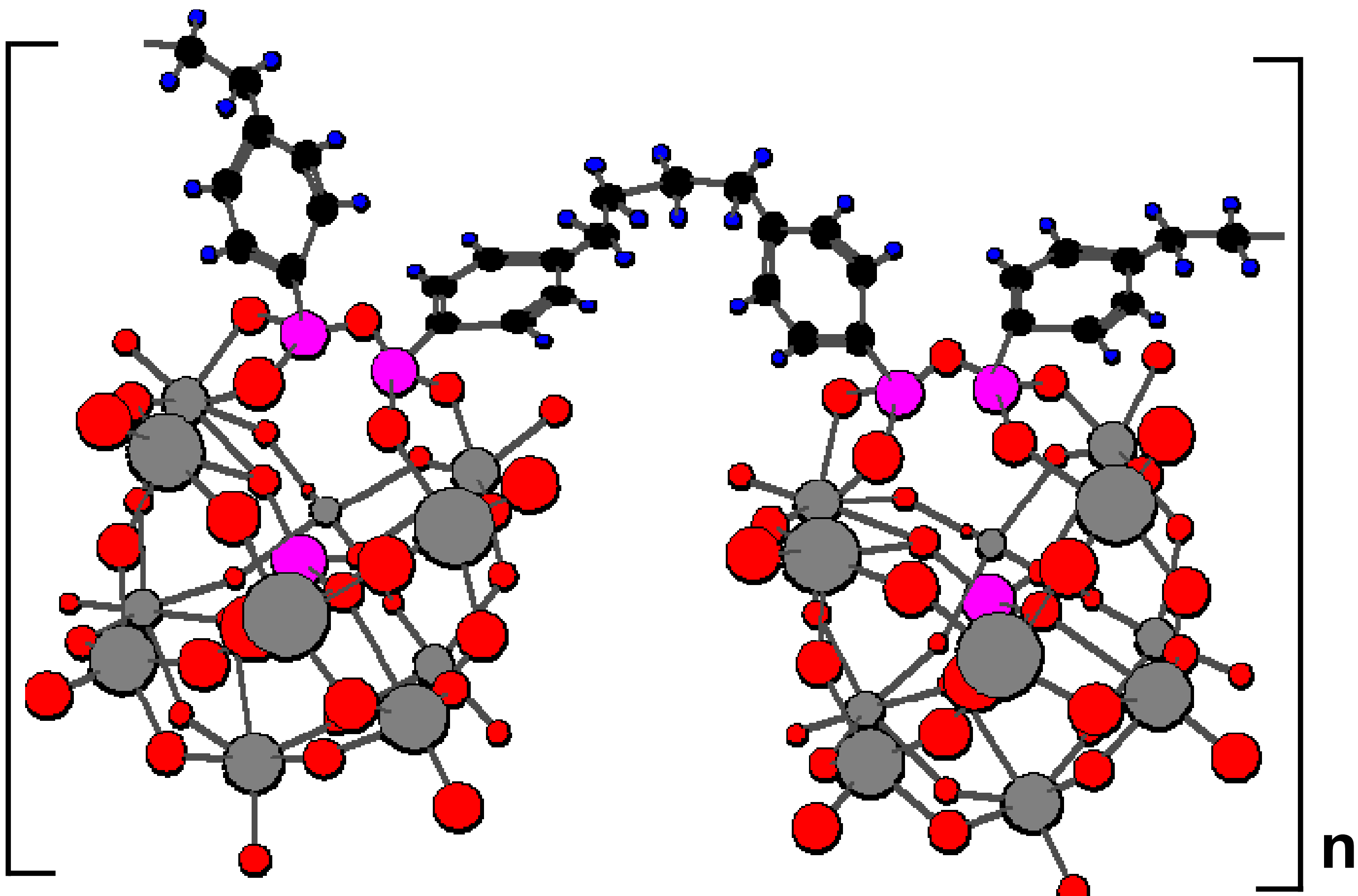
4-

• $4Bu_4N^+$

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

PolymerPOM100s

Radical polymerization of C=C functional group of organic component



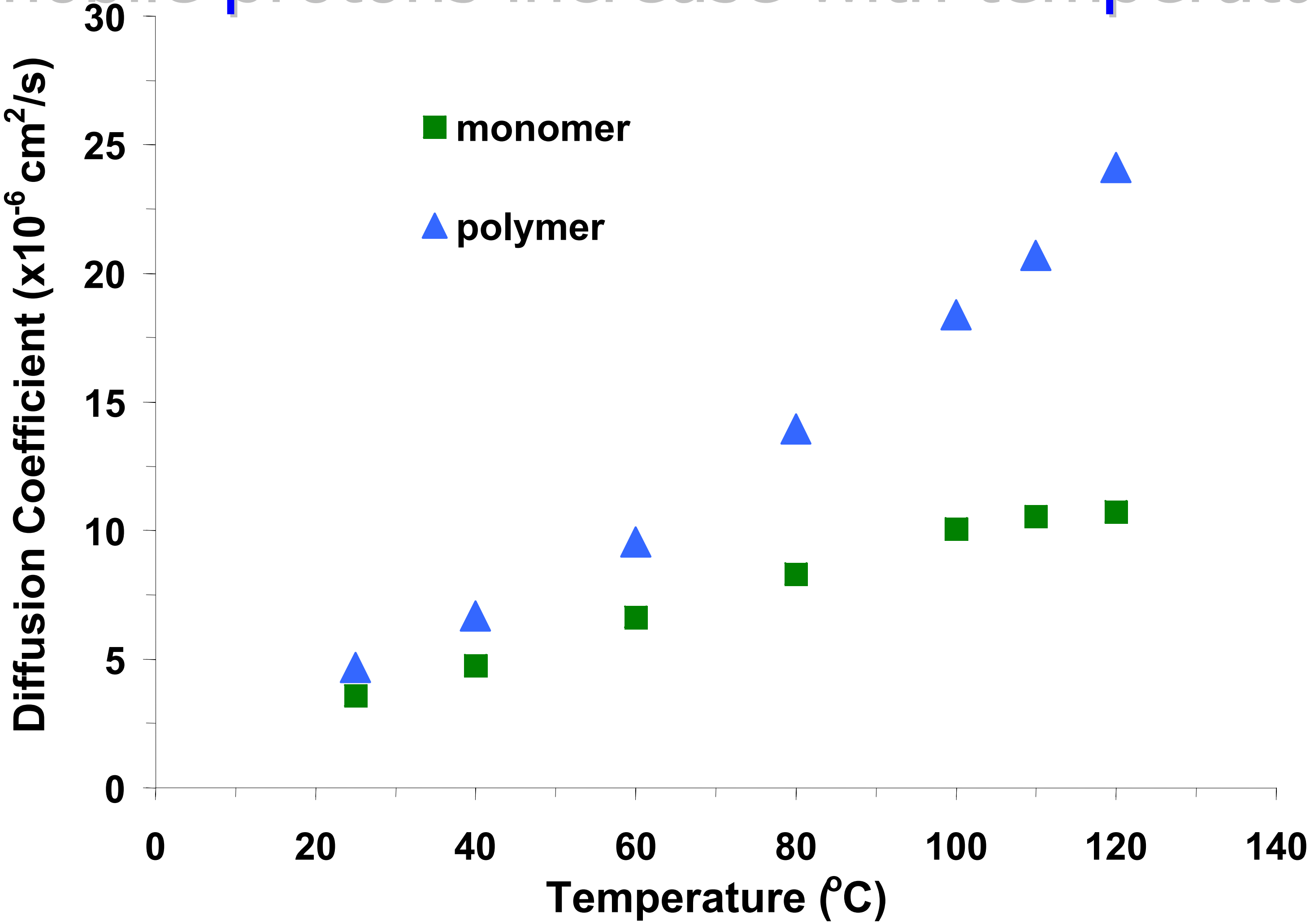
Judeinstein, P. *Journal of Sol-Gel Science and Technology* **1994**, *2*, 147-151

Formulation varies film properties

- PolyPOMXm
- PolyPOMXs

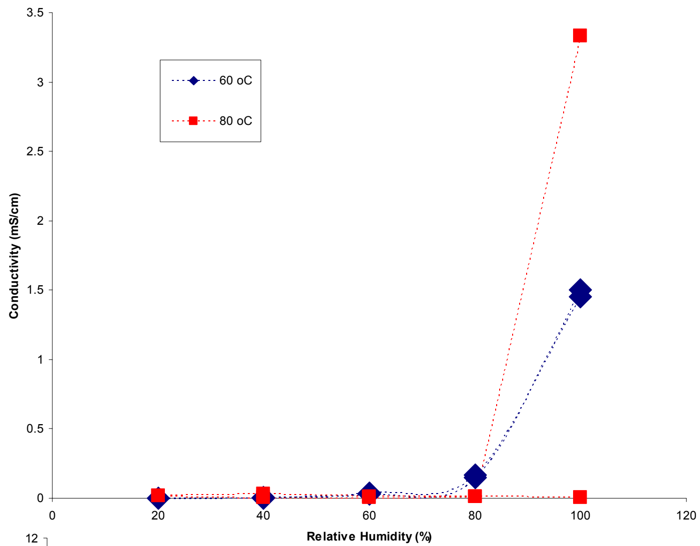
- 100+ films synthesized to date
- Free acid immobilized HPA films readily formed by simple acid exchange
- **3M expertise used to optimize formulation for films of acceptable quality**

Self diffusion coefficients (PFGSE NMR) of mobile protons increase with temperature

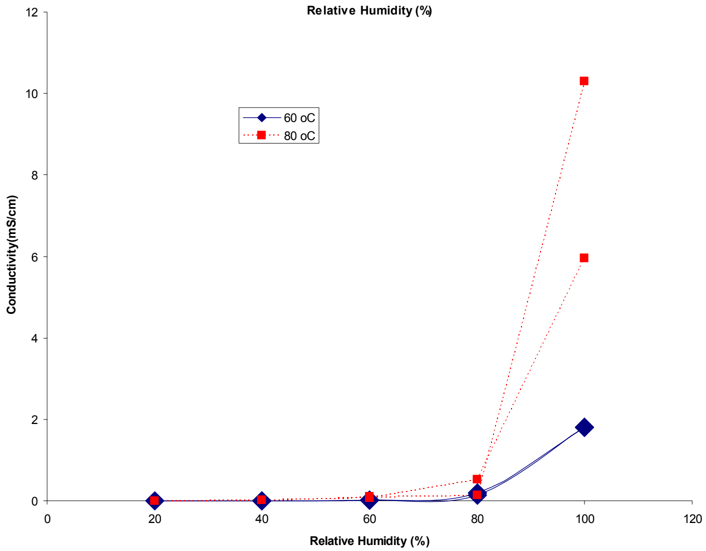


- Data for a hydrated polyPOM50s

In-plane H^+ conductivity of low HPA PolyPOMx films

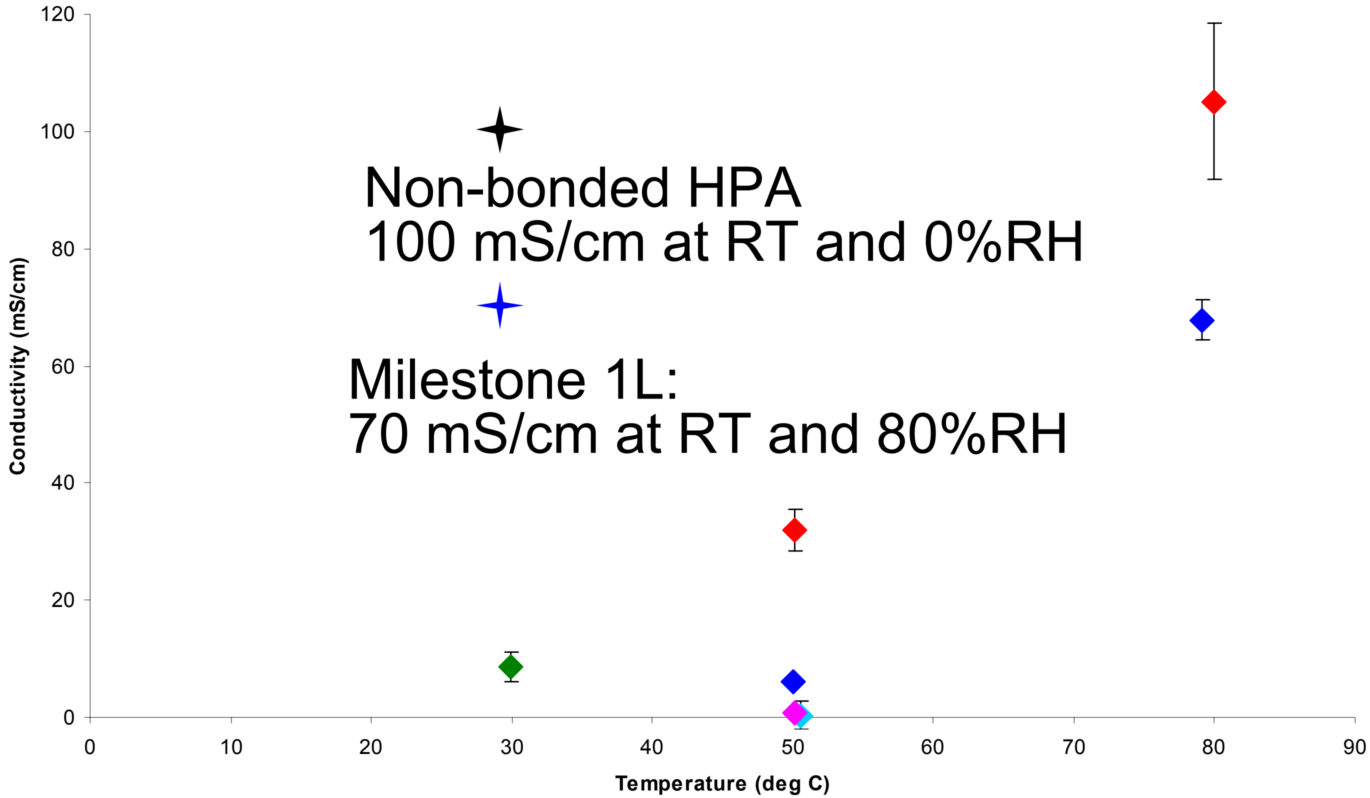


- PolyPOM8m



- PolyPOM11s

In-plane H^+ conductivity of a 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

Future Work

- Continue to explore methacrylate model system
- Develop P linked monomers and polymers
  - The emphasis will be polyPOM50x systems

- Achieve 1st milestone 70 mS/cm at RT and 80%RH -12/31/07

- Optimize conductivity and down select polymer system with consultation with 3M

Summary

- **Stable immobalized HPA (polyPOMs) are readily synthesized**
- **Proton conductivities comparable to PFSA ionomers were achieved before system optimization**

	April 2007	Project milestone	DOE 2010 target
H^+ conductivity	110 mS/cm 100%RH 80ºC	70 mS/cm 80%RH, RT	100 mS/cm No inlet RH at 120ºC