



DOE Hydrogen Program

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

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FC17

This presentation does not contain any proprietary, confidential, or otherwise restricted information



# 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

<ul style="list-style-type: none"><li>• Overall</li></ul>	<ul style="list-style-type: none"><li>• Fabricate a hybrid HPA polymer (polyPOM) from HPA functionalized monomers with:<ul style="list-style-type: none"><li>– <math>\sigma &gt; 0.1 \text{ S cm}^{-1}</math> at <math>120^\circ\text{C}</math> and <math>&lt; 1.5 \text{ kPa H}_2\text{O}</math></li></ul></li></ul>
<ul style="list-style-type: none"><li>• 2006</li></ul>	<ul style="list-style-type: none"><li>• Selection of most hydrolytically stable HPA to monomer linkage chemistry</li><li>• Synthesize free acids of HPA polymers</li></ul>
<ul style="list-style-type: none"><li>• 2007</li></ul>	<ul style="list-style-type: none"><li>• Synthesis and optimization of hybrid HPA polymers for conductivity from RT to <math>120^\circ\text{C}</math></li></ul>



# 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 -  $>100^\circ C$  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.

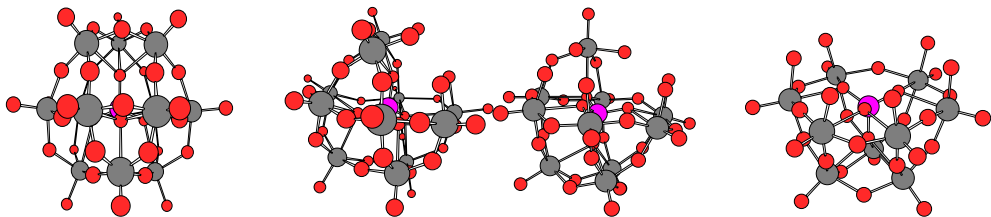


# Technical Accomplishments/ Progress/Results

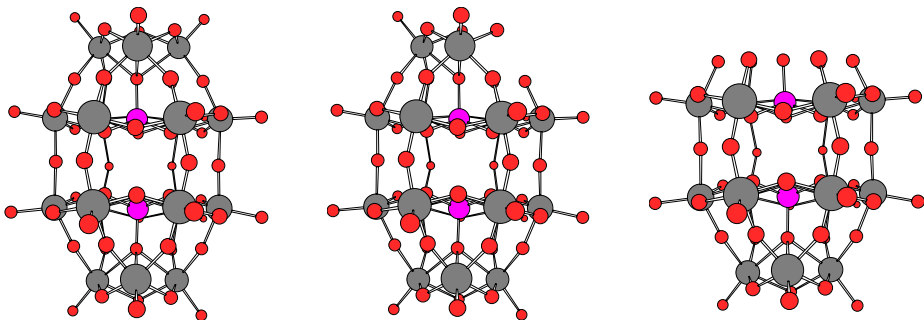
- Demonstration of superior stability of phosphonate linkage in boiling 6 mol HCl or 3% H<sub>2</sub>O<sub>2</sub>
- Generation of free acid PolyPOMs even with less stable linkages
- Achievement of acceptable films by smart formulation (polyPOM formulations are proprietary to 3M/CSM and so will not be discussed in this presentation)
- Preliminary conductivity data



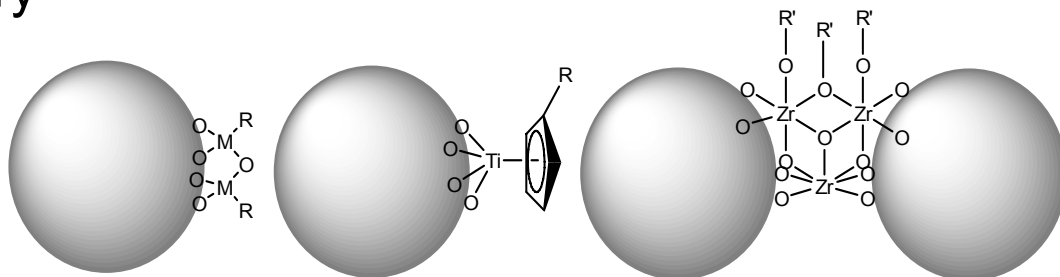
# Model Phenyl Derivatives Synthesized for Stability Testing



- 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<sub>2</sub>O<sub>2</sub> 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



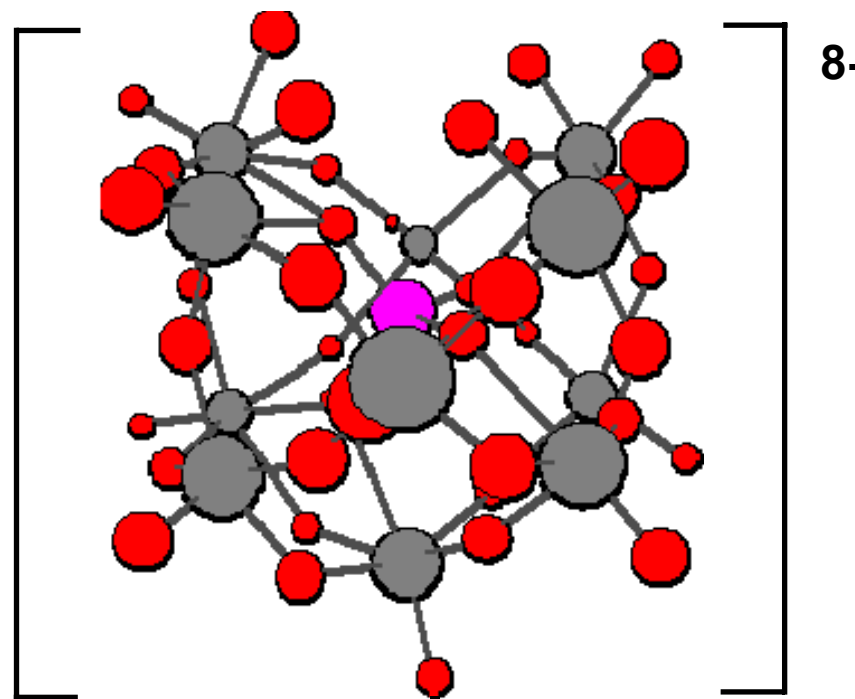


# Preparation of Lacunary HPA



## Methods of Preparation

1. Direct Synthesis
2. Basic Degradation of Saturated HPA

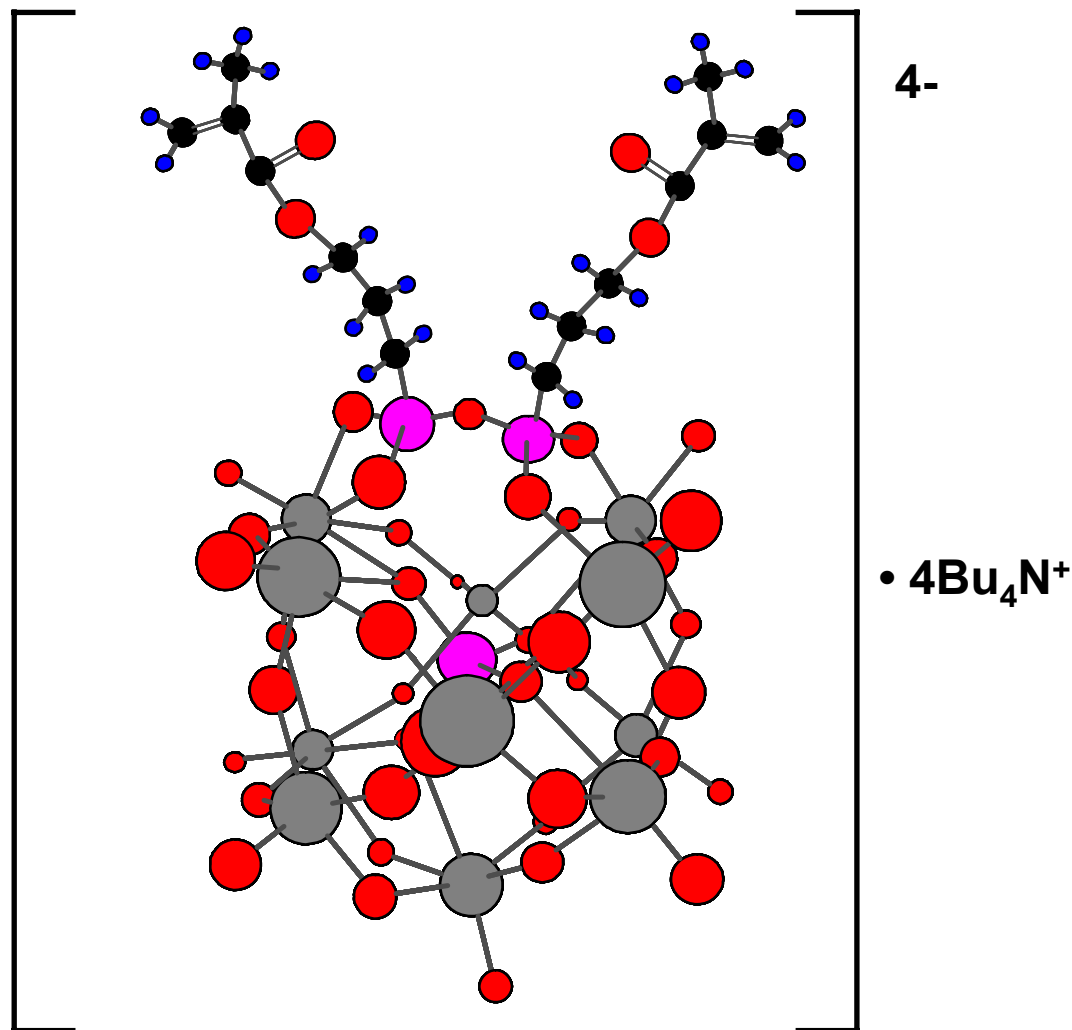


*$\alpha$ -*,  *$\beta$ -*, and  *$\gamma$ -Dodecatungstosilicic acids: isomers and related lacunary compounds*; Teze, A.; Herve, G., Eds. *Inorganic Syntheses*; John Wiley & Sons: New York, 1990; Vol. 27.



# Hybrid $\text{SiW}_{11}\text{O}_{39}(\text{Methacryl})$ Monomer

Reaction of  $\text{SiW}_{11}\text{O}_{39}^{4-}$   
with 3-Methacryloxy-  
propyltrimethoxy silane.



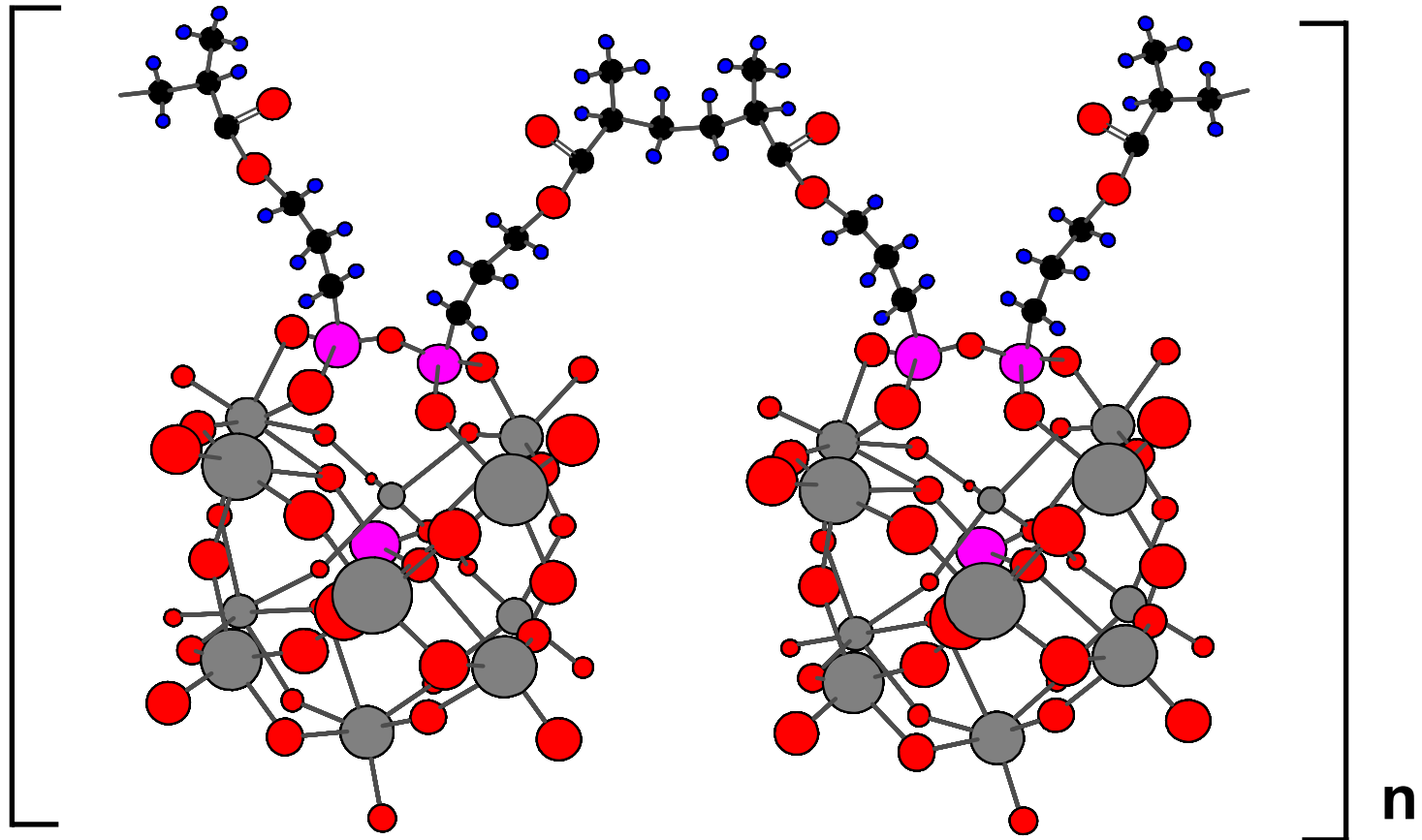
Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 759-760.

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



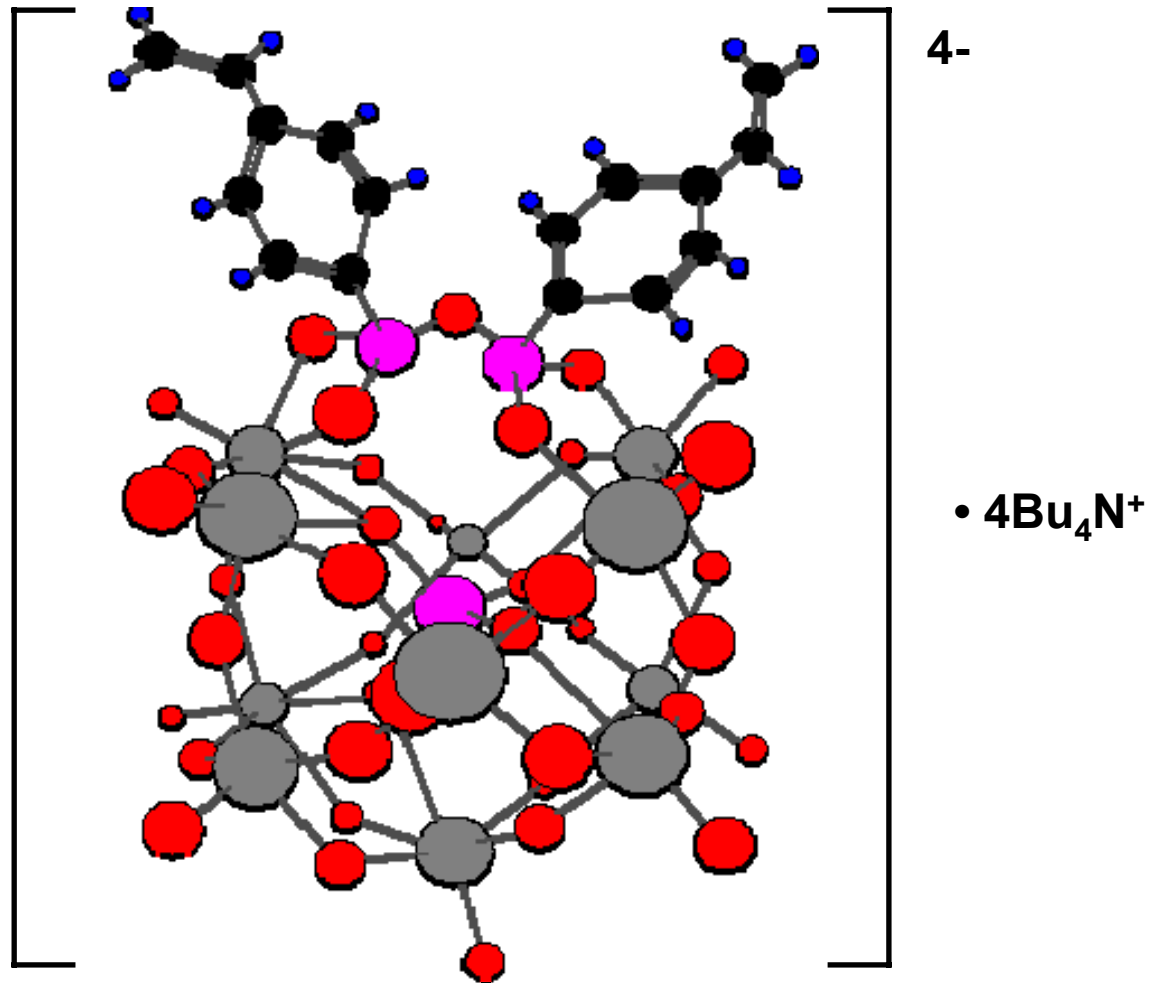
# PolyPOM100m

Radical polymerization of C=C functional group of organic component



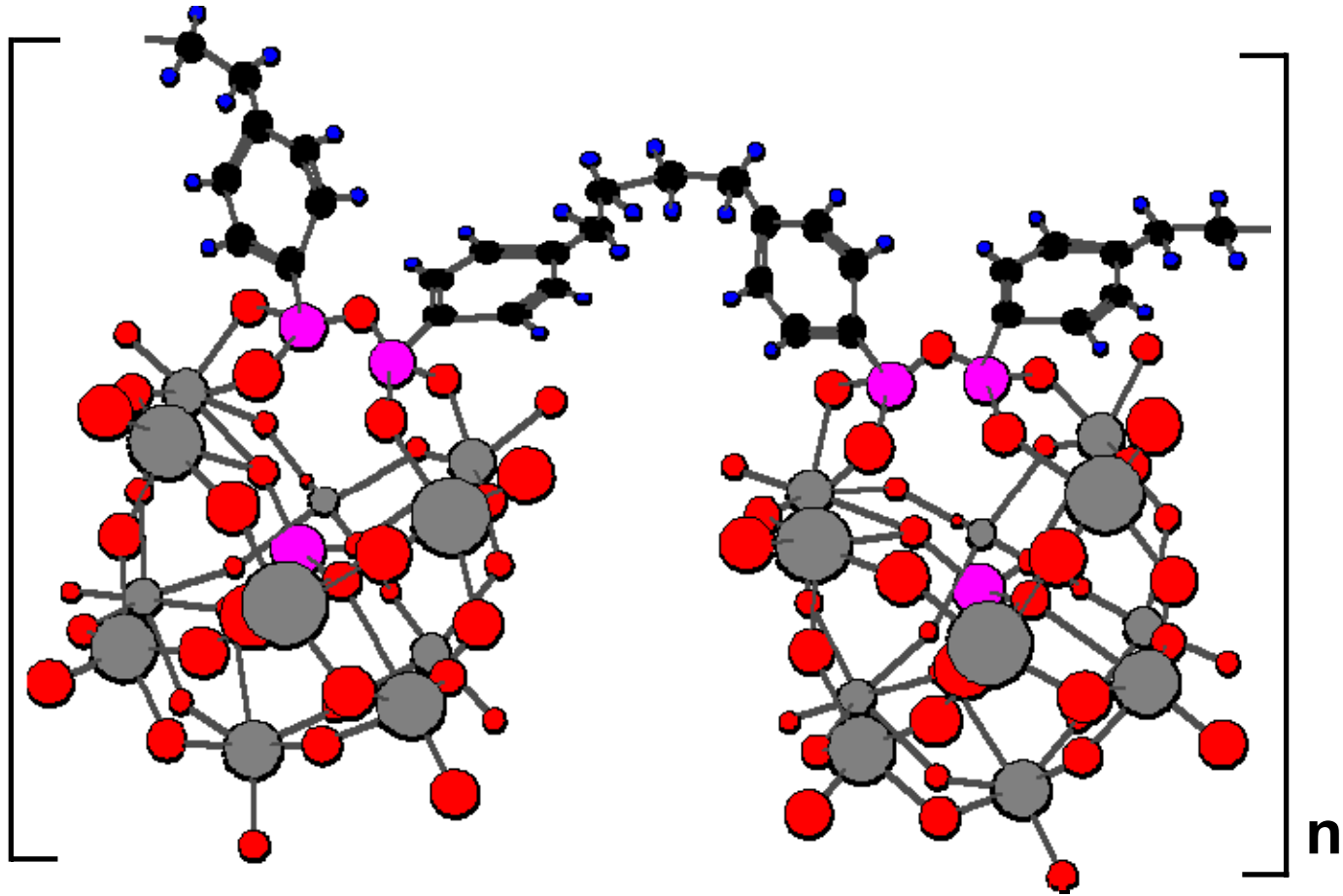
# Hybrid $\text{SiW}_{11}\text{O}_{39}(\text{Styryl})$ Monomer

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



# PolymerPOM100s

Radical polymerization of C=C functional group of organic component



# Formulation varies film properties



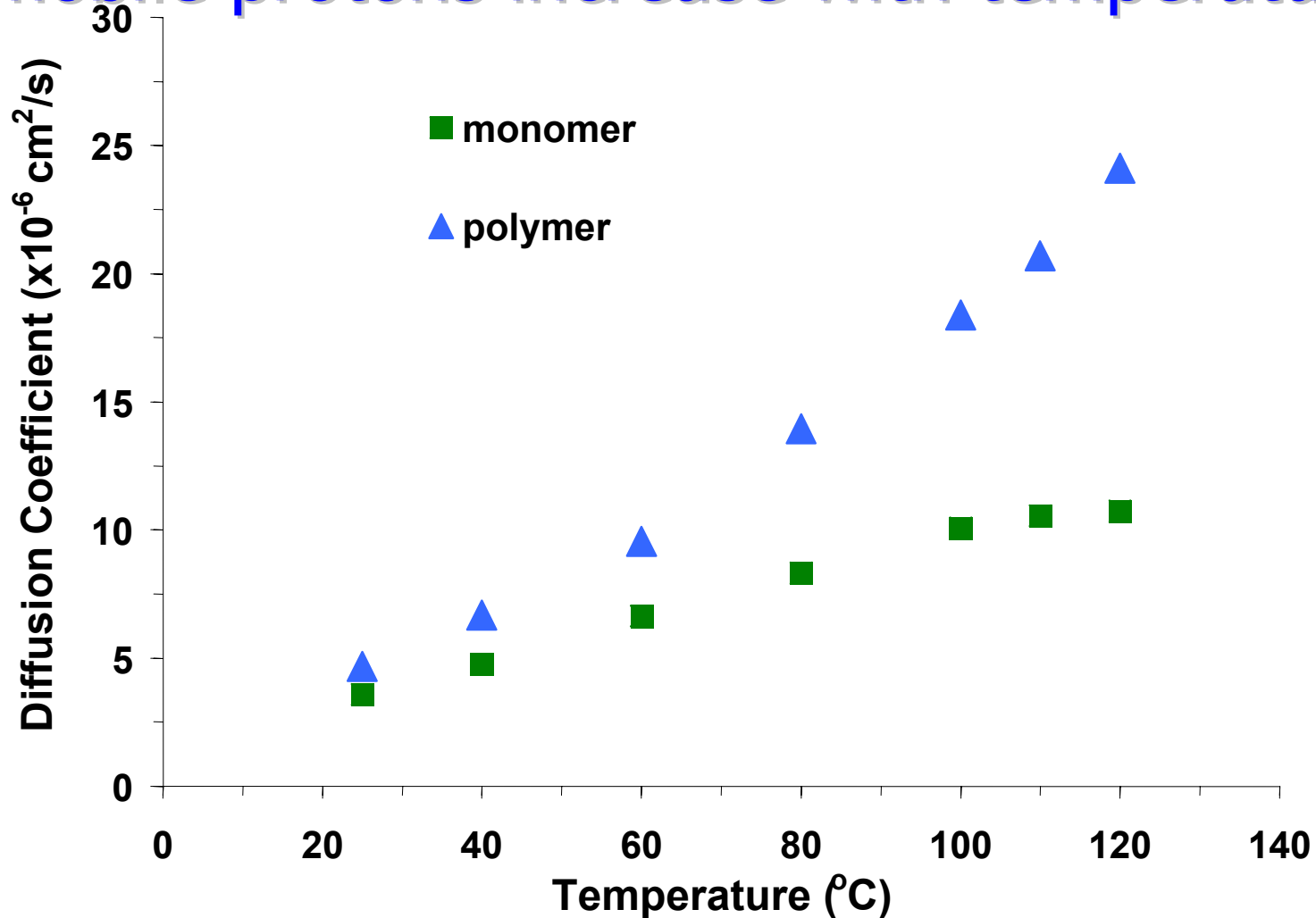
- PolyPOMXm

- 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**



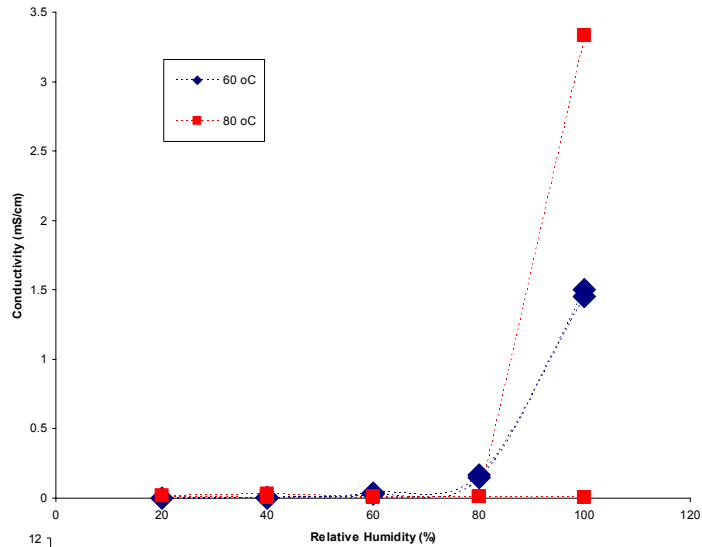
# Self diffusion coefficients (PFGSE NMR) of mobile protons increase with temperature



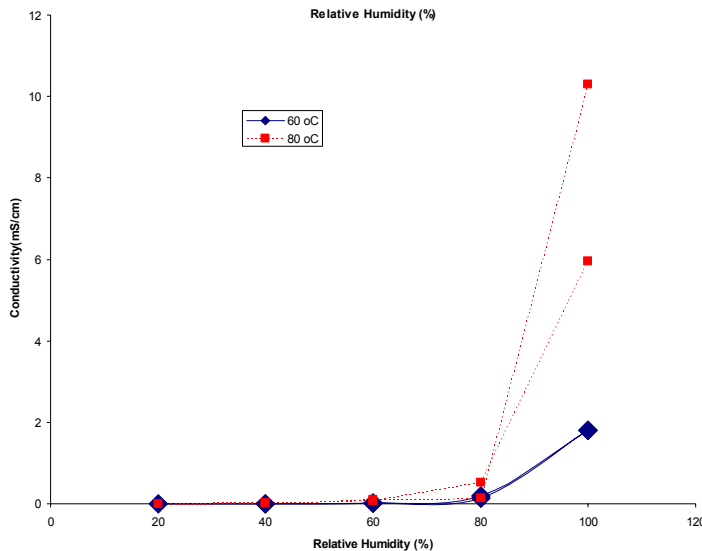
- Data for a hydrated polyPOM50s



# In-plane H<sup>+</sup> conductivity of low HPA PolyPOMx films



- PolyPOM8m

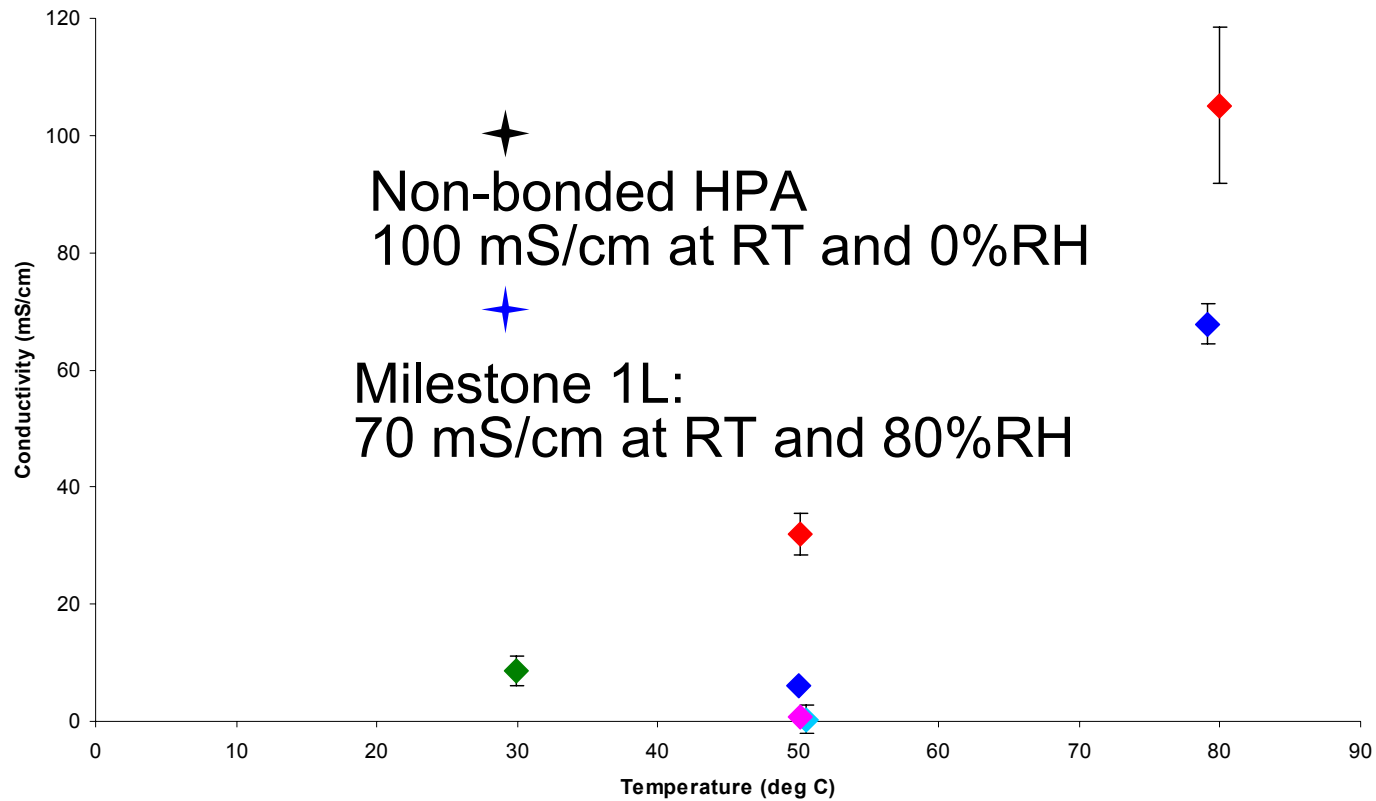


- PolyPOM11s





# In-plane H<sup>+</sup> conductivity of a PolyPOM50m



- Conductivity increases with POM content
  - **H<sup>+</sup> 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



# Future Work

- **Continue to explore methacrylate model system**
- **Develop P linked monomers and polymers**
  - The emphasis will be polyPOM50x systems
- **Achieve 1<sup>st</sup> 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 immobilized HPA (polyPOMs) are readily synthesized**
- **Proton conductivities comparable to PFSA ionomers were achieved before system optimization**

	April 2007	Project milestone	DOE 2010 target
H <sup>+</sup> conductivity	110 mS/cm 100%RH 80°C	70 mS/cm 80%RH, RT	100 mS/cm No inlet RH at 120°C

