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

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Project ID
FC039

Overview

Timeline

- Project Start: April 1st 2006
- Project end: September 30th 2011 (6 month NCE)
- 100% Complete

Barriers

– C **Performance**
– B **Cost**
– A **Durability**

Budget

- Total project funding
  – DOE - $1,500K
  – Cost Share - $376K
  – FY11 Funding - $100K
  – Planned FY12 Funding - $0

Partners

- 3M - Industrial
- Project lead - CSM

Objectives/Relevance

•Overall	•Demonstrated a hybrid HPA polymer (polyPOM) from HPA functionalized monomers with: – σ >0.1 S cm^{-1} at 120°C and <50% RH (Barrier C)
• 2010	•Optimize hybrid polymers in practical systems for proton conductivity and mechanical properties - achieved (Barrier C and A)
• 2011	•Optimize hybrid polymers for proton conductivity, mechanical properties, and oxidative stability/durability (Barrier A, B, and C)

Unique Approach

- Materials Synthesis based on HPA Monomers and attachment to commercially viable polymers, Novel “High and Dry” proton conduction pathways mediated by organized HPA moieties – A NEW Ionomer System

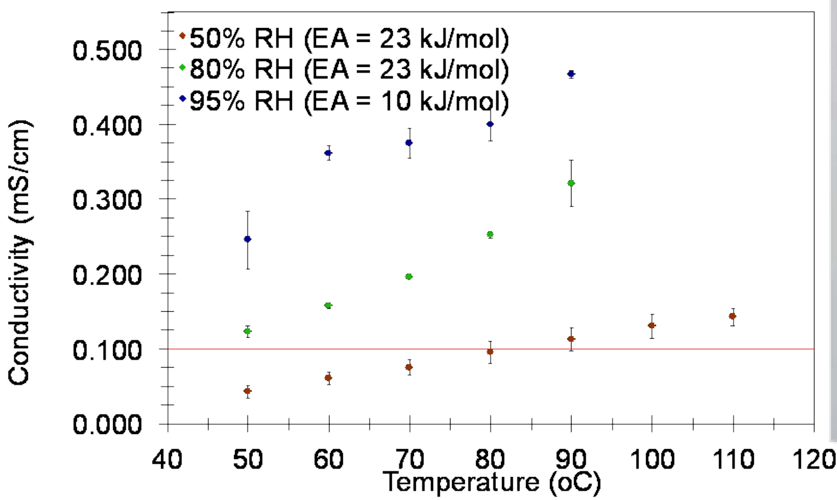
- *Generation I films* – Acrylate co-monomers, polymer system in a kit,
- *Generation II films* – TFVE co-monomers
- *Generation III films* – Attachment to 3M Dyneon™ Fluoroelastomers

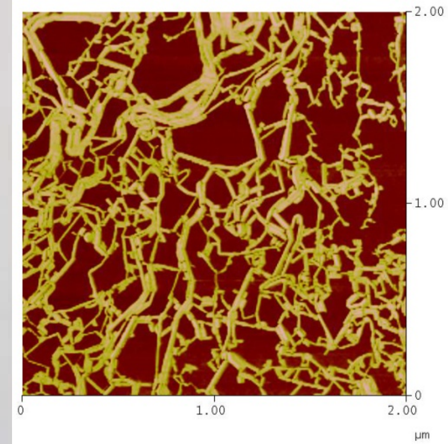
Approach - use Functional Inorganic Super Acids: Heteropoly acids

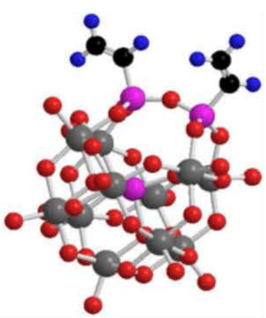
- +
  - High proton conduction, *e.g.* 0.2 S cm^{-1} at RT for 12-HPW
  - Thermally stable at the temperatures of interest, <200 °C
  - Synthetically Versatile - even simple salts are interesting
- +/-
  - Water soluble – but easily immobilized by functionalization in polymers
  - Reduced form – electrically conductive, but fuel cell membrane environment generally oxidizing, however can be used to advantage on anode
  - Proton conductivity dependency on water content/interaction with polar/protonic components
  - Known to decompose peroxides

Previous Accomplishments

Generation I Films – PolyPOM85v/BA



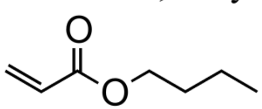




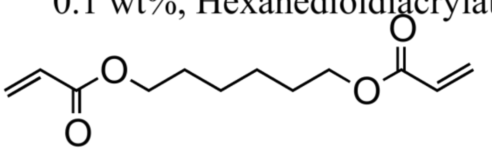
3wt%, $H_4[SiW_{11}O_{40}(Si(CH{=}CH_2))_2]$

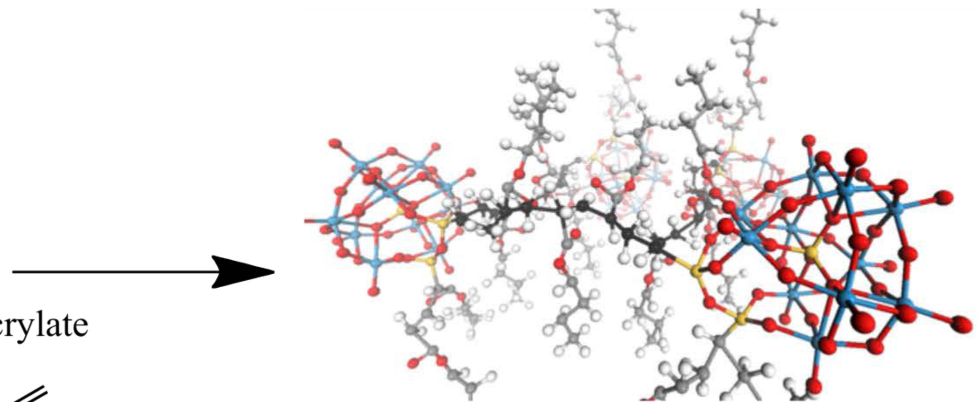
\+

0.9 wt%, Butylacrylate



0.1 wt%, Hexanedioldiacrylate

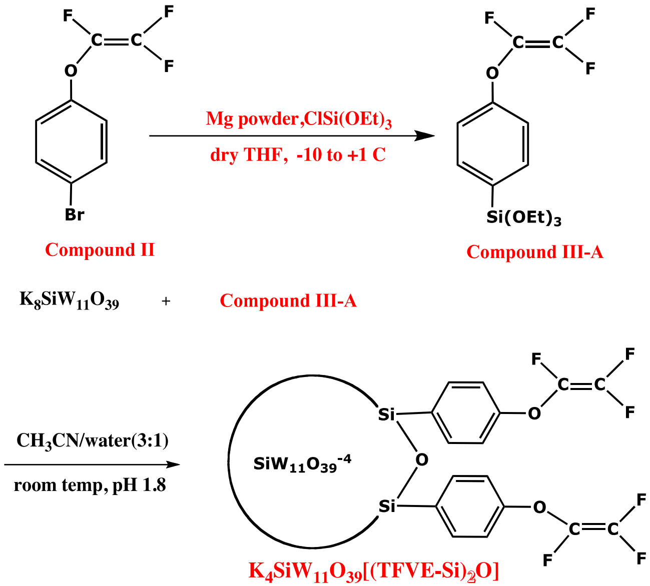




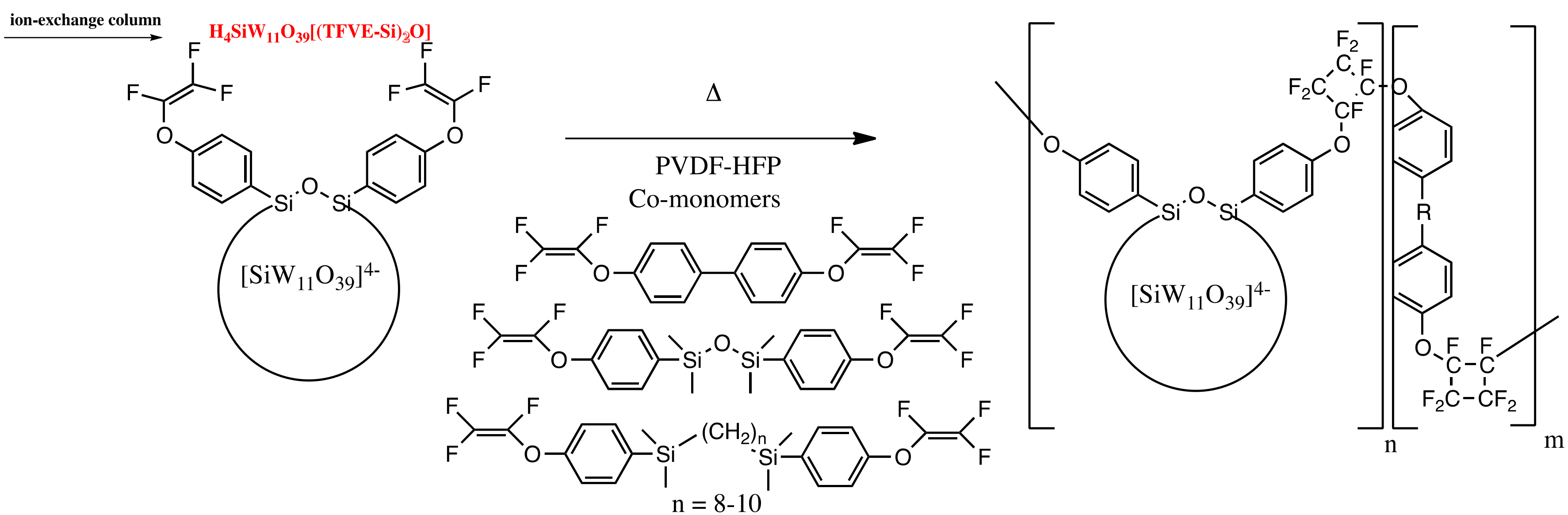
[P(SiW1175v-co-BA-co-HDDA)]
(PolySiW11(75)BA)

Films Generally thick but ASR <0.02 Ω cm^2

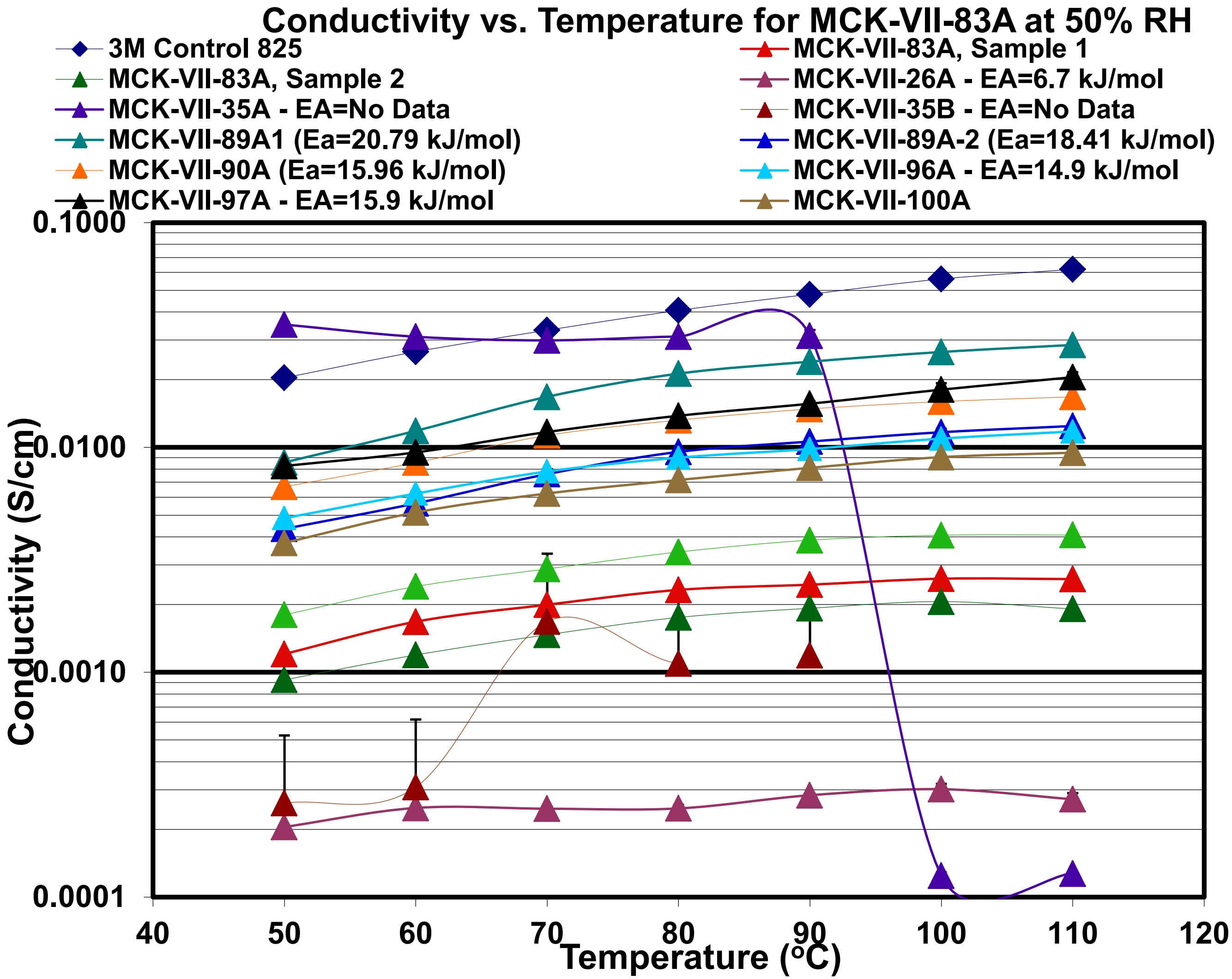
Progress - Generation II Films TFVE-HPA copolymers



- Trifluorovinyl ethers (TFVE) functionalized HPA monomers synthesized on <100g scale
- Trifluorovinyl ethers polymerize thermally
- Large number of co-monomers available

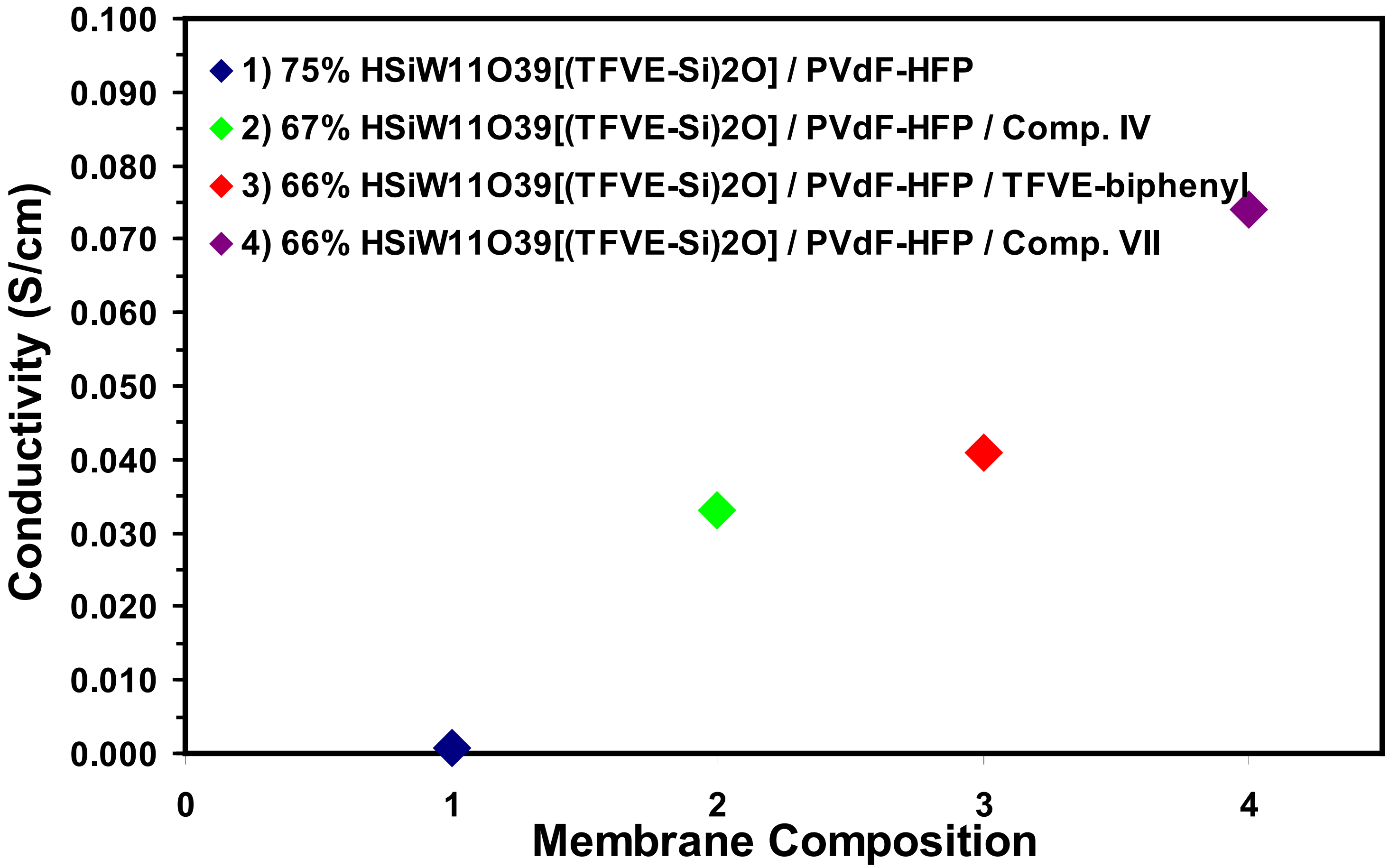


Proton Conductivity - Variable



- Appears to synergistically vary based on film forming, chemistry, and morphology – complex design space

Conductivity Dependence on Morphology at 80 °C, RH 80%

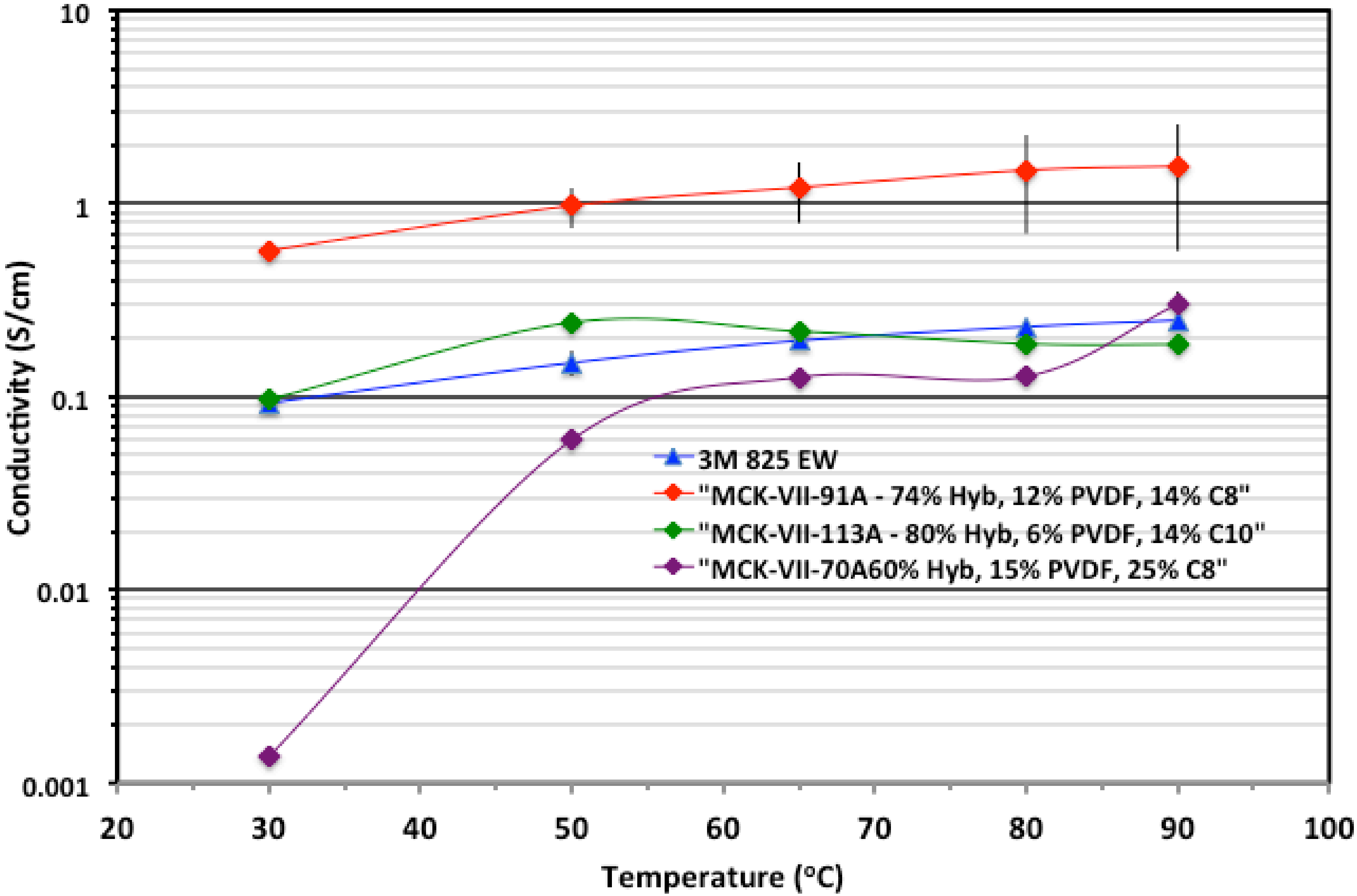


For hybrid TFVE membranes

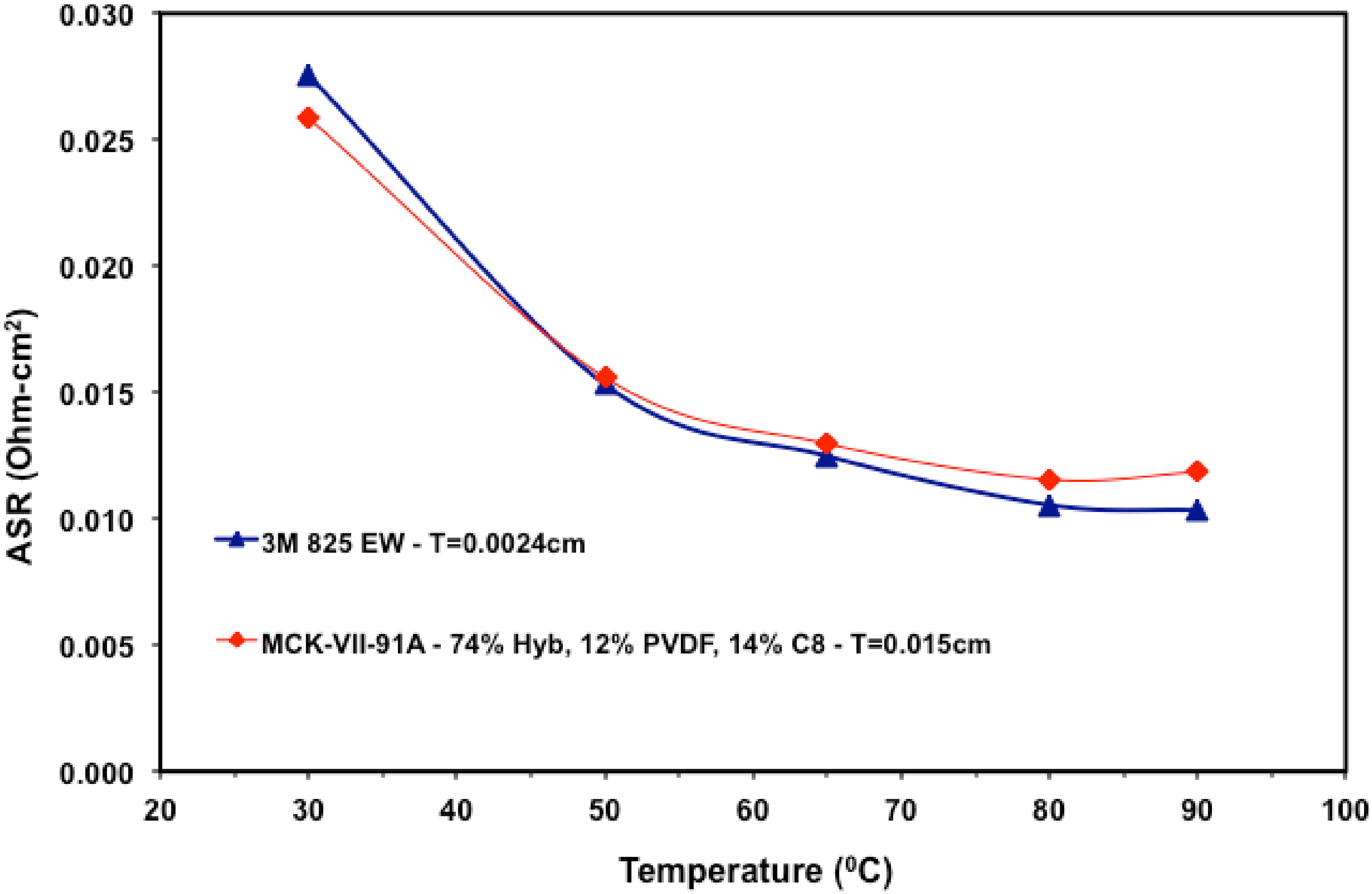
Wt% based on $HSiW_{11}O_{39}[(TFVE\text{-}Si)_2O]$ monomer present

- 1st Approximation co-monomer chemistry important

95% RH Script Conductivity Results

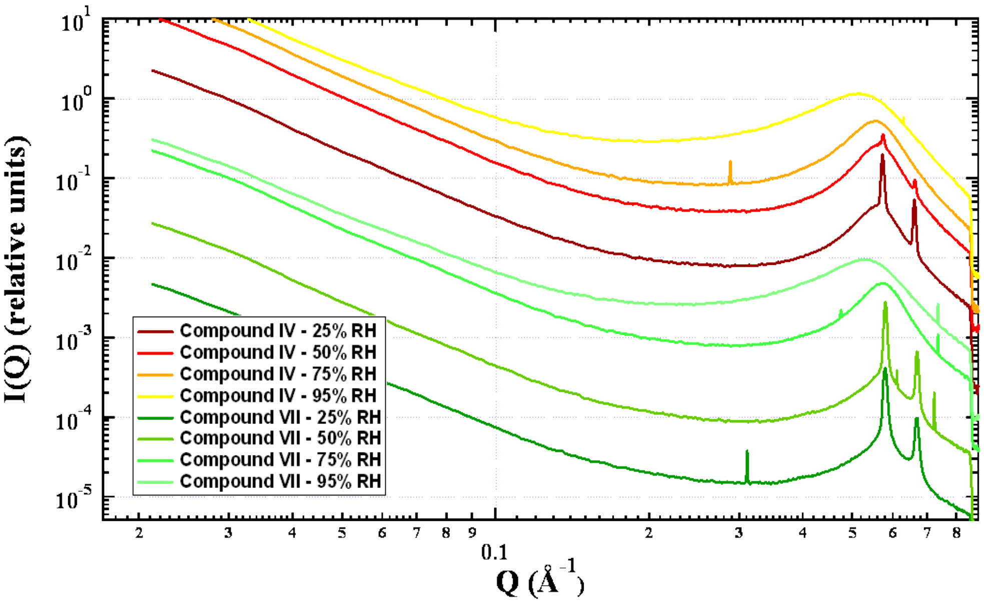


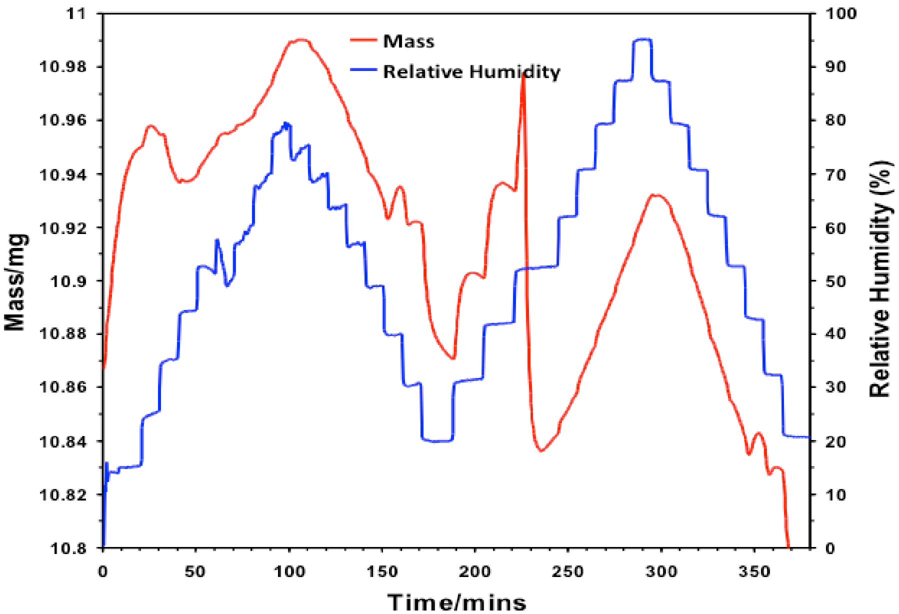
State of the art film same ASR as 3M 825EW but 7 x as thick



Crystalline Phases observed at low RH

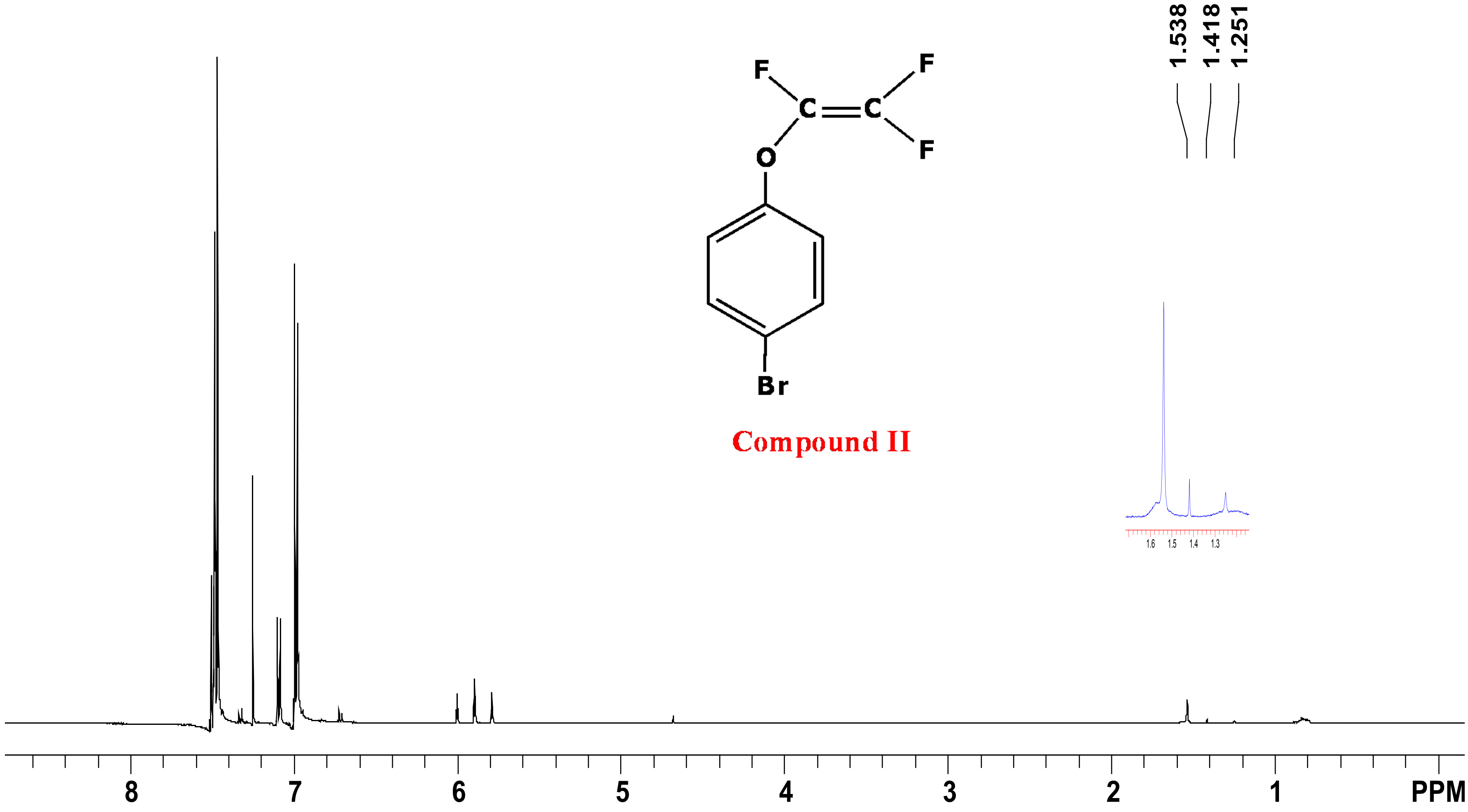
SAXS, 25%, 50%, 75% and 95% RH and 80 °C **DVS, 60 °C**



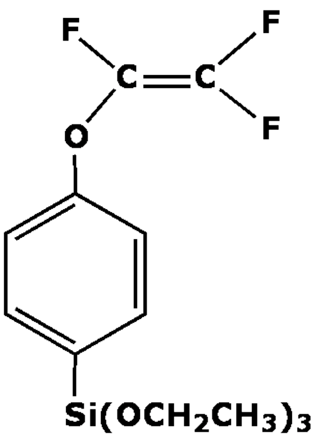


- Bragg peaks observed at low RH in SAXS, Phase changes observed at low RH in DVS
- Amorphous phase is the highly conducting phase
- Water content decreases on RH cycling (implies hard to measure equilibrium properties and increasing brittleness on cycling)

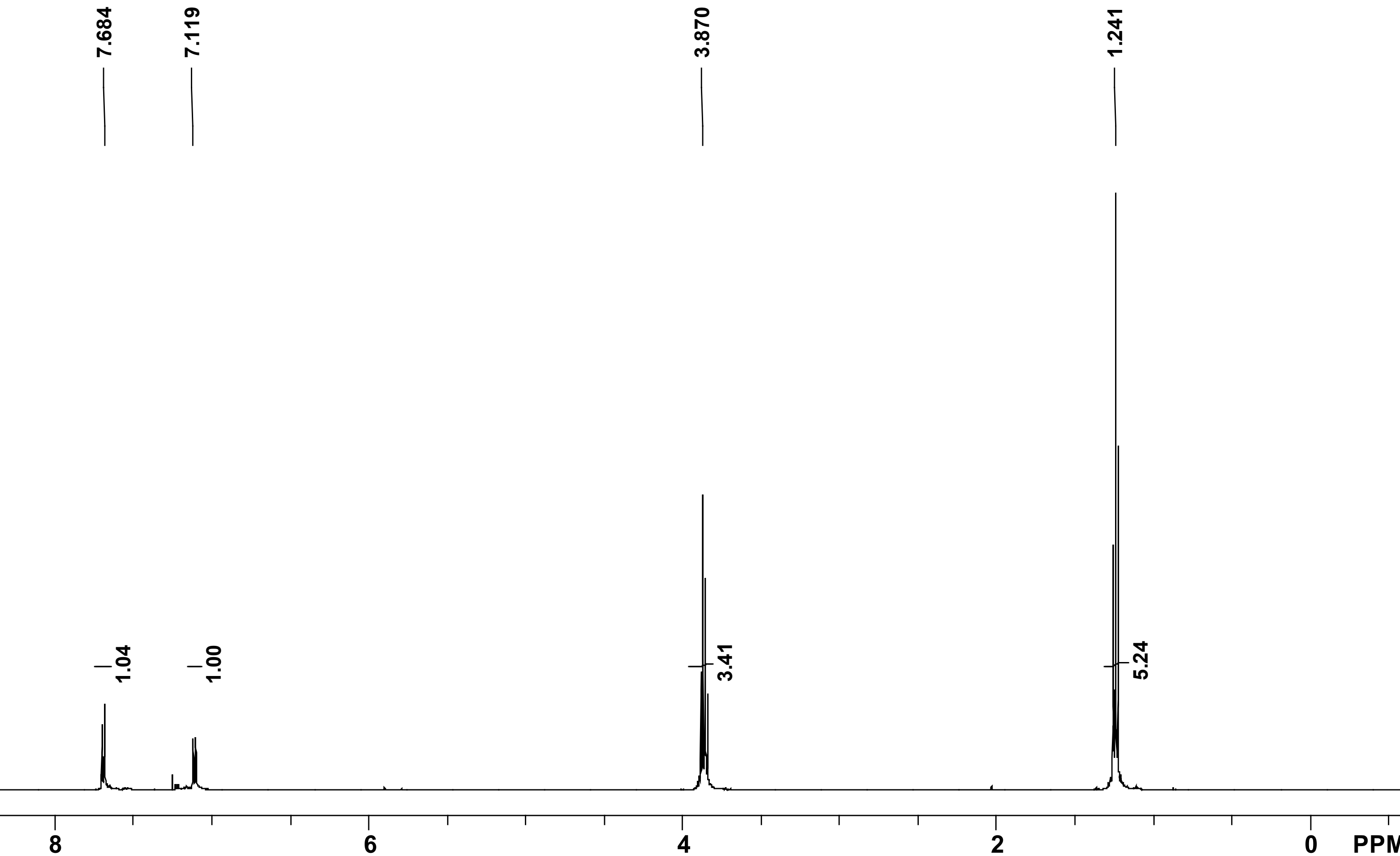
[1]H NMR spectrum for 4-[(Trifluorovinyl)oxy]bromobenzene



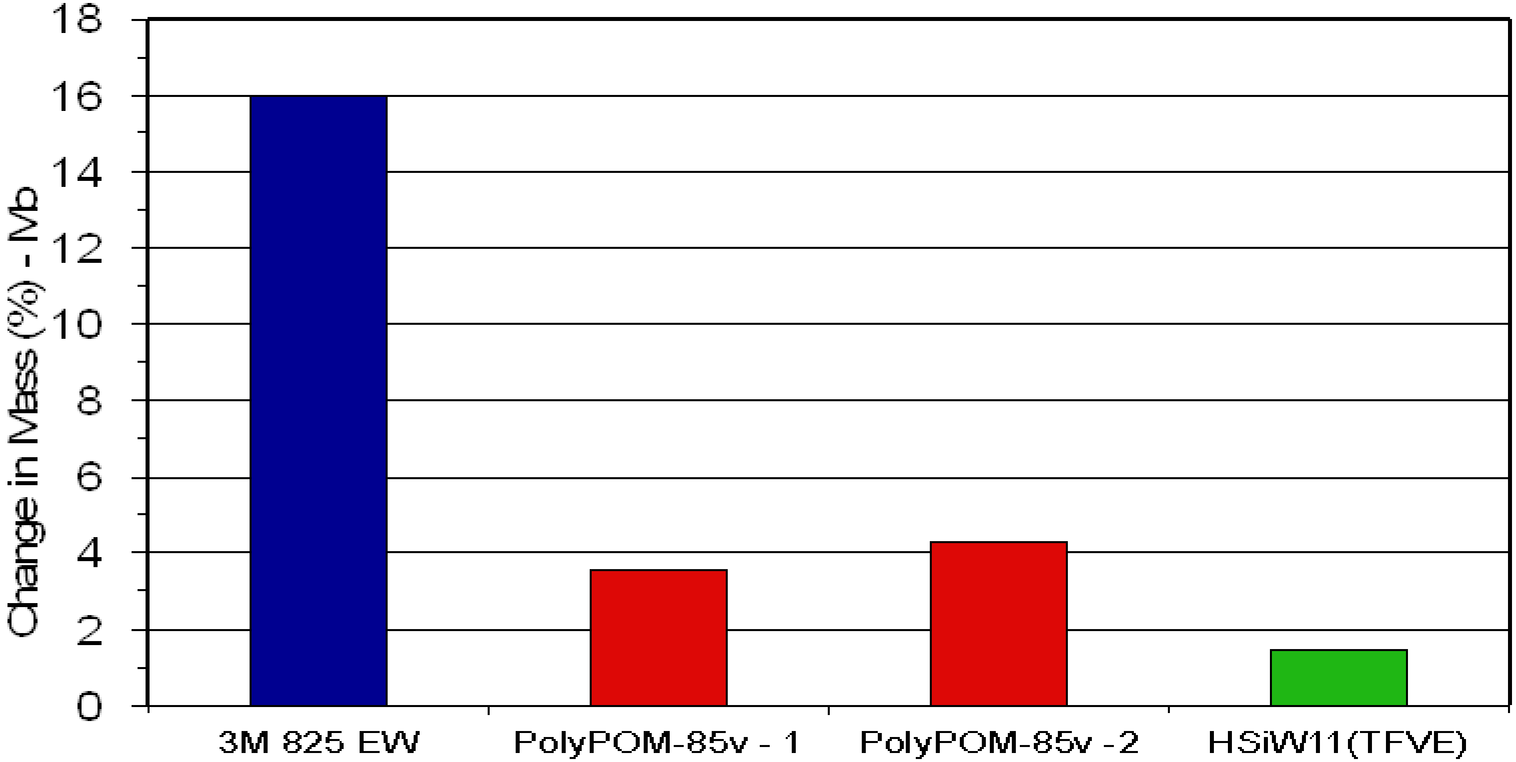
^{1}H NMR spectrum for pure 4-[(Trifluorovinyl)oxy]phenyltriethoxysilane



TFVE-Si(OEt)$_3$



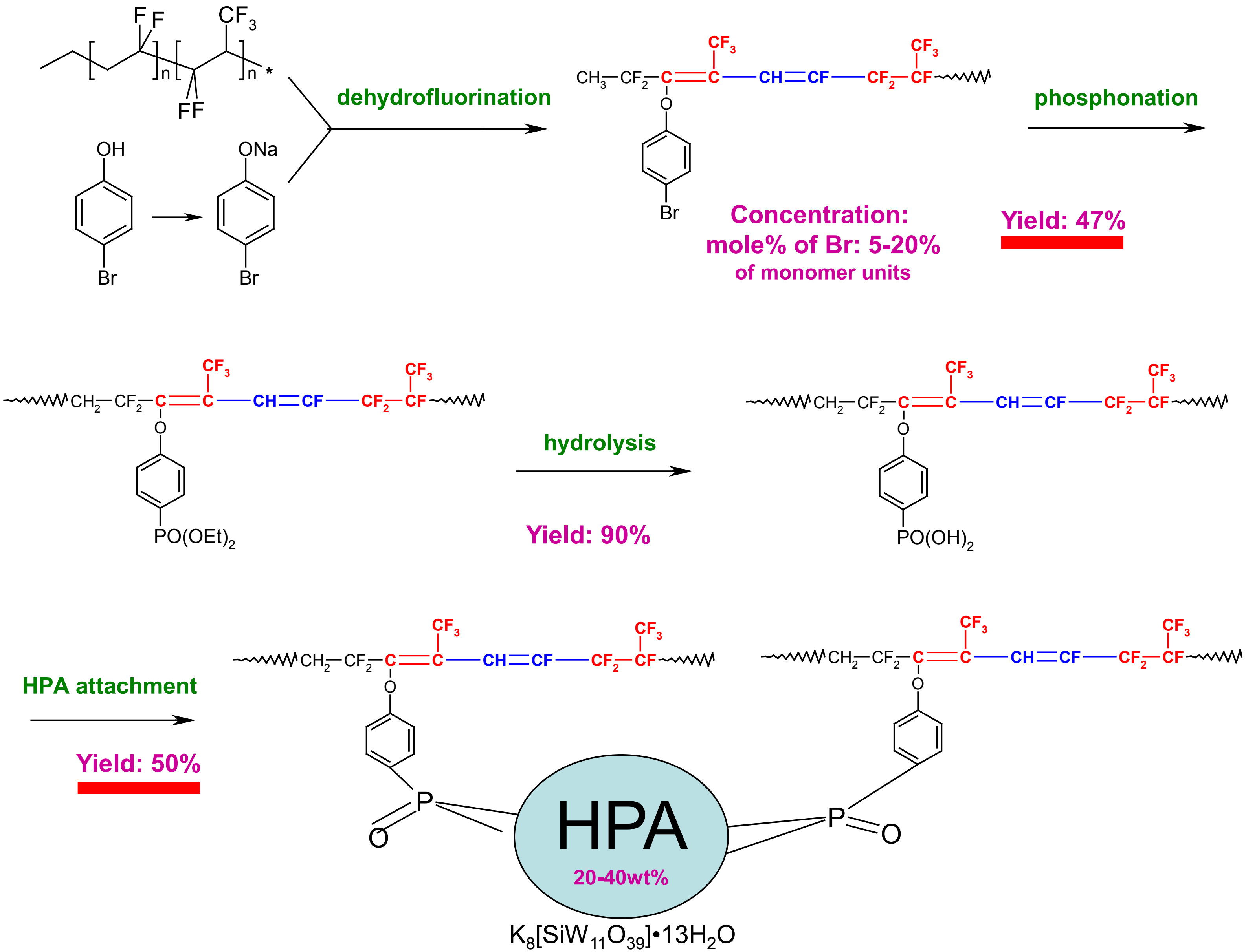
Mass % Water Uptake of Three Different Membranes



Digital vapor sorption – total over 2 relative humidity cycles, based on initial mass (M_o)

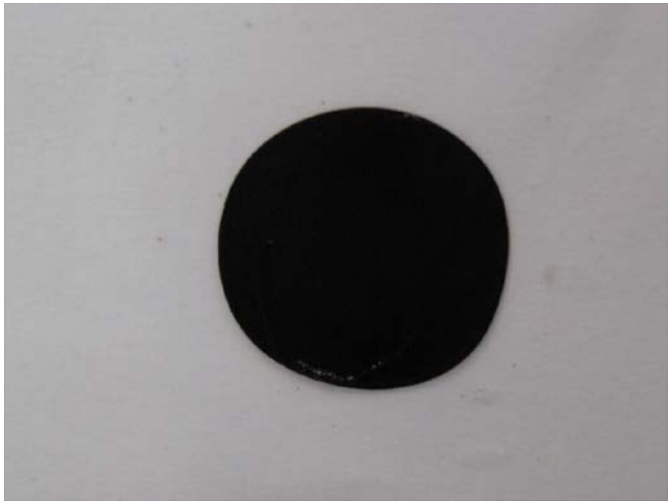
- HPA containing membranes have considerably less water uptake than PFSAs

Progress, Generation III Polymer – Synthesis



Membrane Processing

HPA attached, acidified hybrid fluoropolymer (crumb) was dissolved in DMSO at 4% concentration. Solution was then cast on ClearSIL®T10 silicone coated liner (or Kapton® polyimide (PI) liner in some cases). The resulting membrane below was first heated at 120ºC for 10min; Temp was then increased to 180ºC, membrane was heated at 180ºC for 10min.

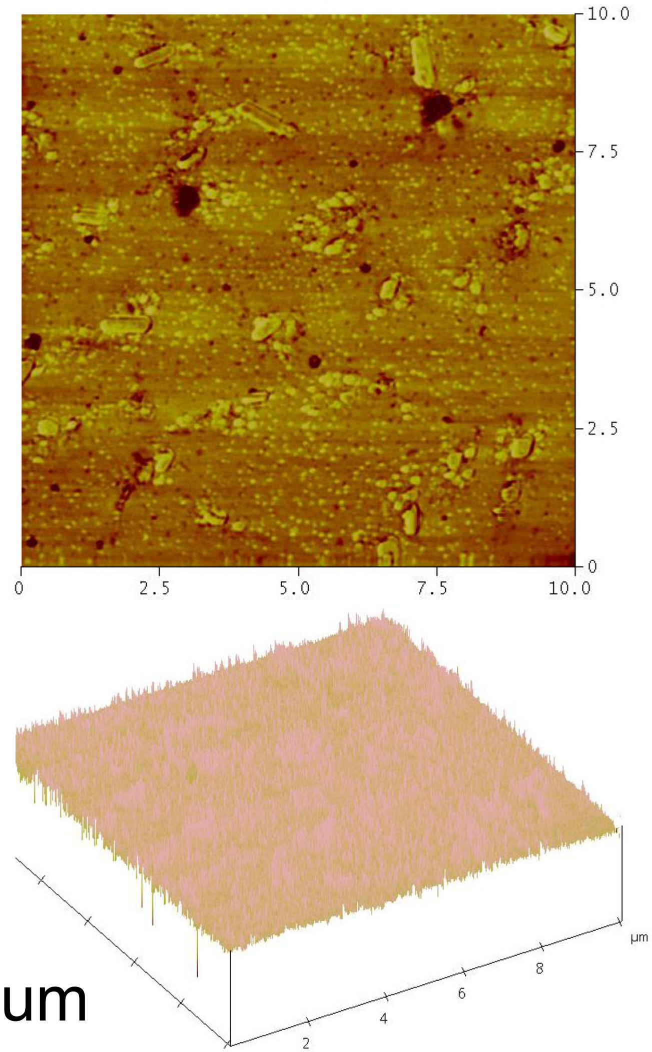


HPA attached hybrid fluoropolymer membrane cast on T10.

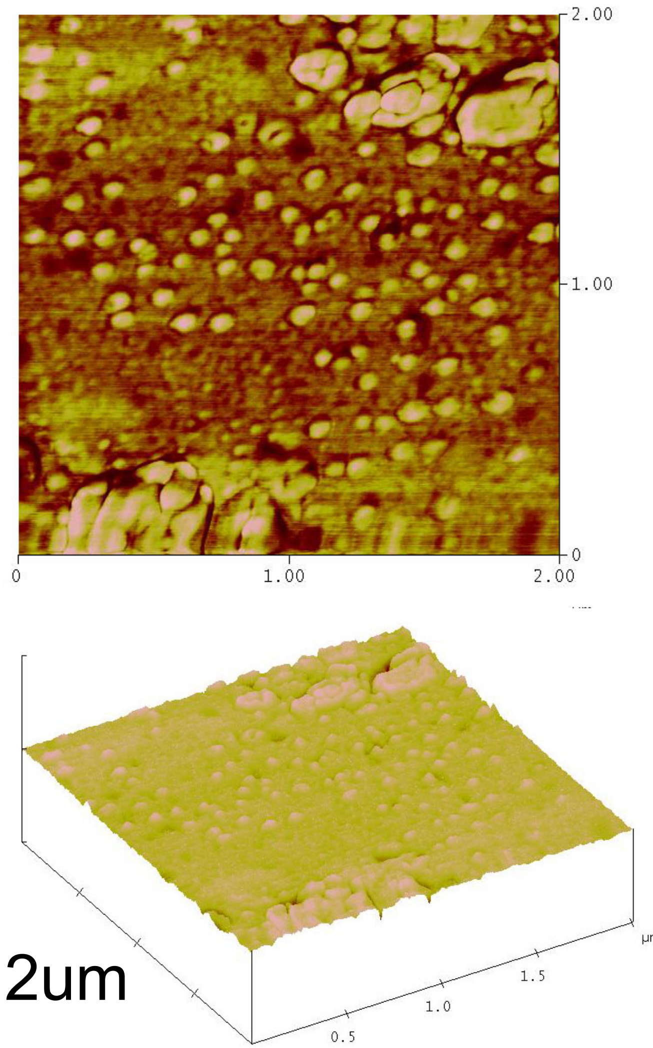
- Film processing critical to high performance

Morphology

AFM imaging --- Phase Image (recorded at CSM)

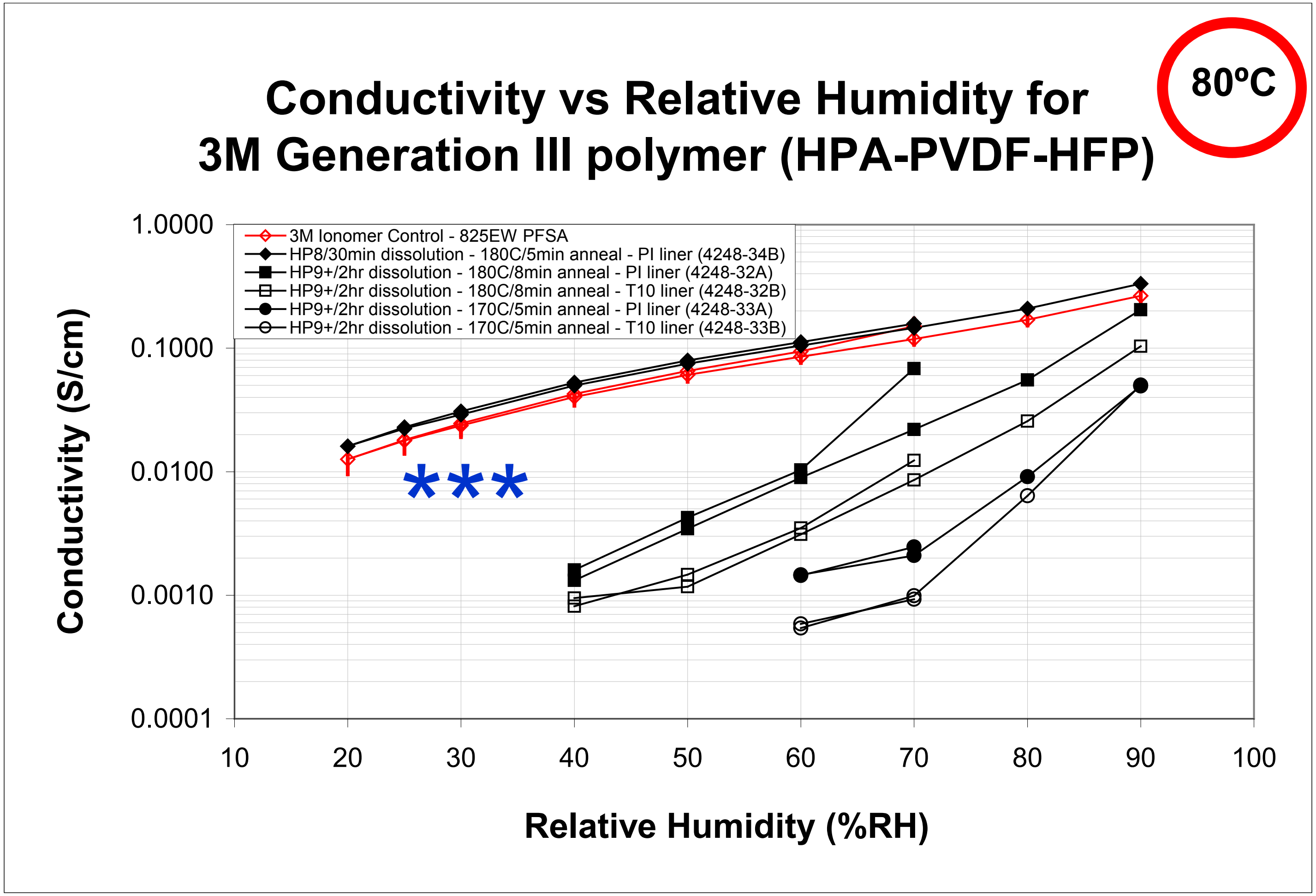


10um



2um

Proton Conductivity, 80°C



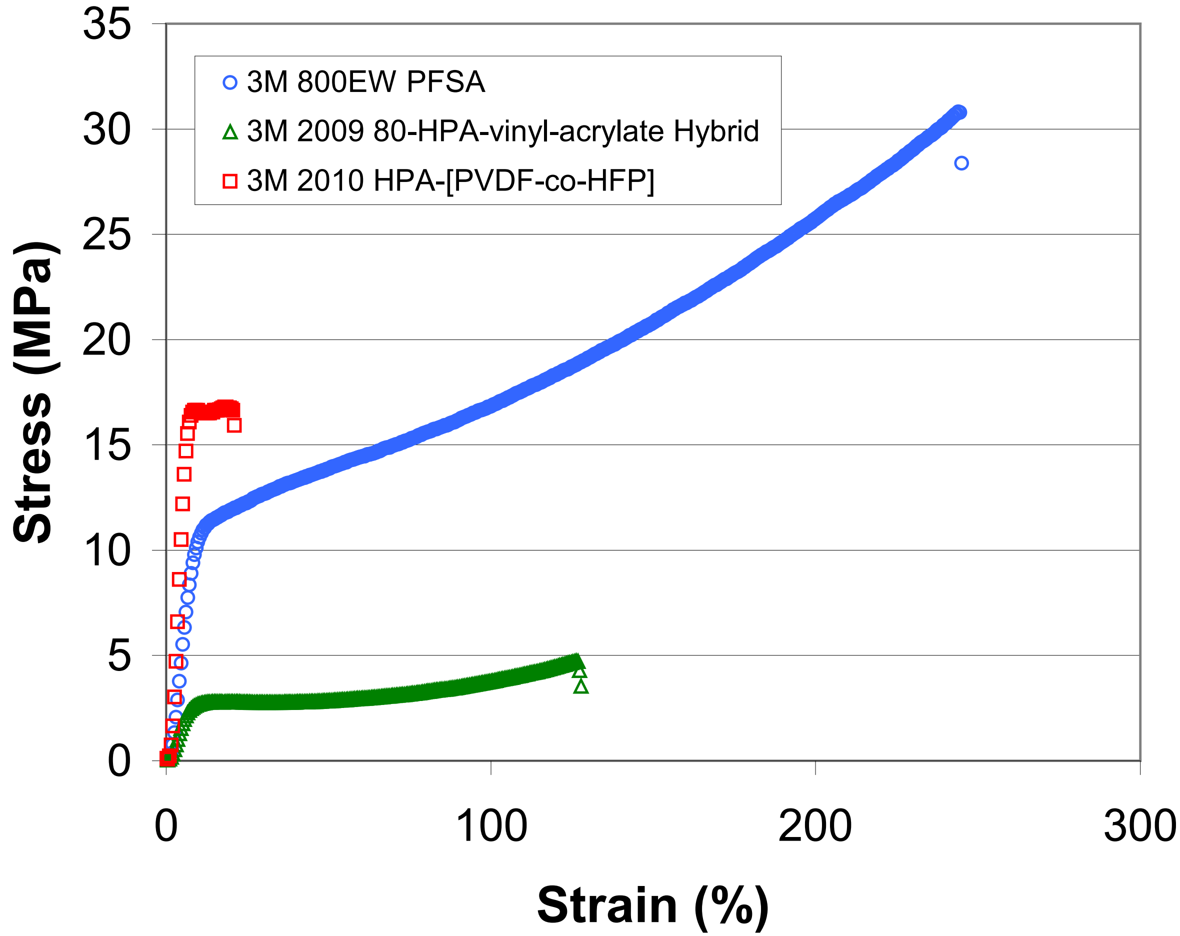
Measured by Michael Emery, 3M
TestEquity oven, atmospheric pressure
Bekktech sample fixture

HP: Hot plate setting
PI: Kapton® polyimide
T10: ClearSIL®T10 silicone coated

*** Incompletely dissolved in DMSO (casting solvent); tested in November 2010; 37% HPA

- Film forming critical to high performance

Tensile Testing



- Functionalized Polymer gives stronger film could be tailored by Dyneon chemistry

Manufacturing Feasibility Assessment

Selected high-level comments:
- “This is a complex fine chemical synthesis.”… “Fine chemical processing is a lot like this.”
- “Chemically, there are no showstoppers.”…“No chemistry here that scares me.”
- “I wouldn‘t be too discouraged.”
- “There are no exotic conditions…normal glassware.”

Selected detailed comments:
- “Process optimization is needed to improve volume utilization.”
- “% solids of each of these process steps will have a big impact on your reactor volume efficiency.”
- “A lot of dissolving and drying” … “Can you avoid drying to a solid every time?”…“Can you do any steps neat?”
- “Can you do solvent exchanges?”…”keep it soluble?”
- “Can you use a different PVDF-HFP?…some may be easier than others…different molecular weight?”
- “To use less solvent, could you carry some impurities along, and then clean up just once, at the end?”

If one were to pursue this material commercially at 3M, next steps:
- Initiate “New Materials Introduction” program within MRD.
- Review for entry into MRD lab.
- Carry out focused work against detailed comments above.

Overall Conclusions:
- The HPA-modified PVDF-HFP preparation appears likely to be feasible in manufacturing.
- Any additional development work on this type of material should include objectives related to solvent usage and process simplicity, as suggested above.

Collaborations

- Prime: Colorado School of Mines – STEM University
- Sub: 3M Corporate Material Research Laboratory
- Other Collaborators: the following have agreed to test membranes ex-situ or as MEAs from promising films.
  - 3M Fuel Cell Components Group
  - ProtonOnsite
  - GM (has offered to test promising materials)
  - Nissan Technical Center, North America (has offered to test promising materials)

Proposed Future Work (unfunded)

- New series of films with pure TFVE monomer, structured diblocks
- Improve Dyneon attachment chemistry with polymer designed for HPA attachment
- Incorporate work on Zr phosphonate hybrid films.

Summary

- Consistently High Proton Conductivity in Robust films
- 2 New Film Chemistries optimized
  - High Oxidative stability
  - Excellent Mechanical properties

	DOE target 2017/ Ω cm^2	CSM TFVE-HPA 2011/ Ω cm^2	Thickness /μm	CSM TFVE-HPA if 10 μm
120/40% RH	0.02	0.43 50%RH	180	0.02
80/85% RH	0.02	0.13	130	0.01
30/90%RH	0.03	0.026 95%RH	150	0.002

The data presented is for the best performing film at each condition. Further work is required to fully optimize one material for all conditions