High Temperature/Low Humidity Polymer Electrolytes Derived from Ionic Liquids

James M. Boncella (Point of Contact)
Rob Gilbertson
Yu Seung Kim
Bryan Pivovar

Los Alamos National Laboratory
Institute for Hydrogen and Fuel Cell Research

May 18, 2006

FC25 Boncella

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start FY 03
- Ongoing project

Barriers

- D.) Thermal, Air and water management.
- B.) Cost

Budget

- FY05 funding $200K
- FY06 funding $200K
- Non-cost shared

Collaborators

- LBNL (John Kerr)
- U. Mass. (Bryan Coughlin)

Project Objectives

Overall Objective: Contribute to DOE effort in developing high temperature polymer electrolytes for transportation applications.

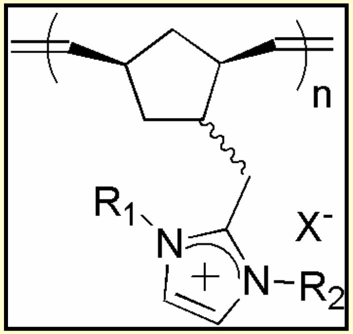
Specific goals:

- Improve fundamental understanding of conduction in 'free' proton containing ionic liquids
- Investigate how phase separation behavior affects conductivity in well defined phase separated ionomers
- Probe the dependence of properties on ion capacity, water content and temperature
- Increase conductivity at high temperature (~120˚C) and low relative humidity (<50% RH)

LANL Approach

- Investigate ionic liquids based on imidazole cations and dihydrogen phosphate ($H_2PO_4^-$) or bisulfate (HSO_4^-) anions capable of proton conduction in high temperature membranes

- Advantages of ionic liquids are
  – Thermally stable (up to 300 ˚C)
  – Stable to oxidation and reduction
  – Essentially no vapor pressure
  – High intrinsic ionic conductivity



- Investigate conduction limits of these materials, incorporate the most promising candidates into polymeric materials.

Project Timeline

Investigation of proton containing ionic liquids began in February of 2003.

FY ’06 Milestones and Progress:

Synthesize and test polymers/oligomers containing target materials.

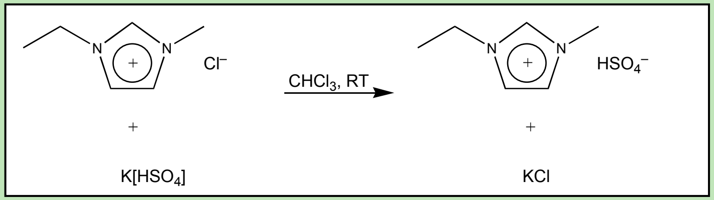
Status: First generation polymers already synthesized and tested, second generation block copolymers being synthesized.

Synthesize and test block copolymers with pendant imidazole groups.

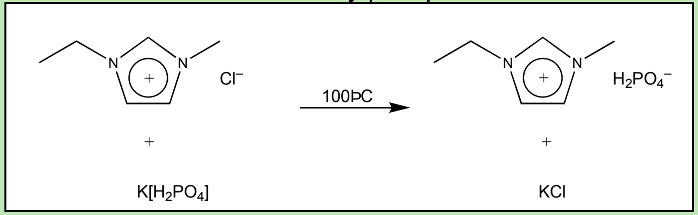
Status: First block copolymers synthesized, conductivity of materials measured and structure of films being characterized by AFM. Modifications of functional groups on monomers being explored to enhance phase separation characteristics.

Acid-Imidazole Pairs

Ionic Liquids



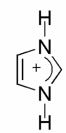
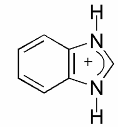
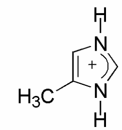
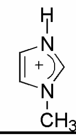
- Mixture is filtered to eliminate bulk of KCl
- Residual KCl removed by precipitation from chloroform



- Solid reaction product is extracted into methanol and filtered
- Methanol is removed under vacuum and residual KCl removed by precipitation from CHCl$_3$

Ethyl Methyl Imidazolium (EMI) Salts

- 'Free' proton containing acid-imidazole pairs synthesized
- Pairs characterized in terms of properties (melting point, conductivity, stability, etc.)

Imidazole Cation	Counterion	Melting Point (°C)
	$H_2PO_4^-$	124-126
	HSO_4^-	<100
	$B(OH)_3$ (1:1 mixture)	60 softening
	$H_2PO_4^-$	157-159
	$H_2PO_4^-$	134-136
	$H_2PO_4^-$	132-135

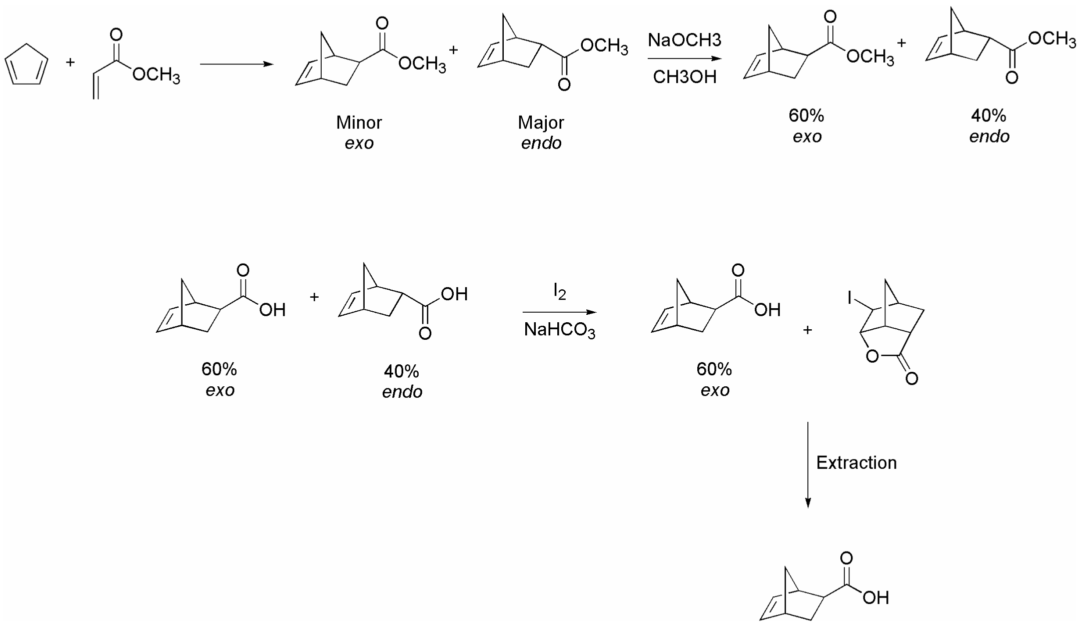
Los Alamos NATIONAL LABORATORY

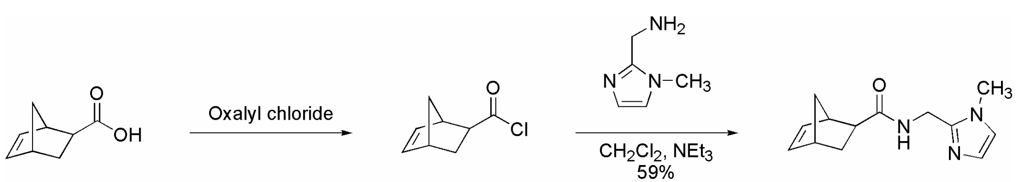
Why use Polynorobornenes (NBEs)?

- Well defined polymers – low polydispersity
- Easy to make block copolymers
- Readily available monomers and catalysts
- Can be functionalized with little difficulty

While chemical stability of backbone is doubtful, this architecture allows us to study performance in well controlled morphologies with target functionality.

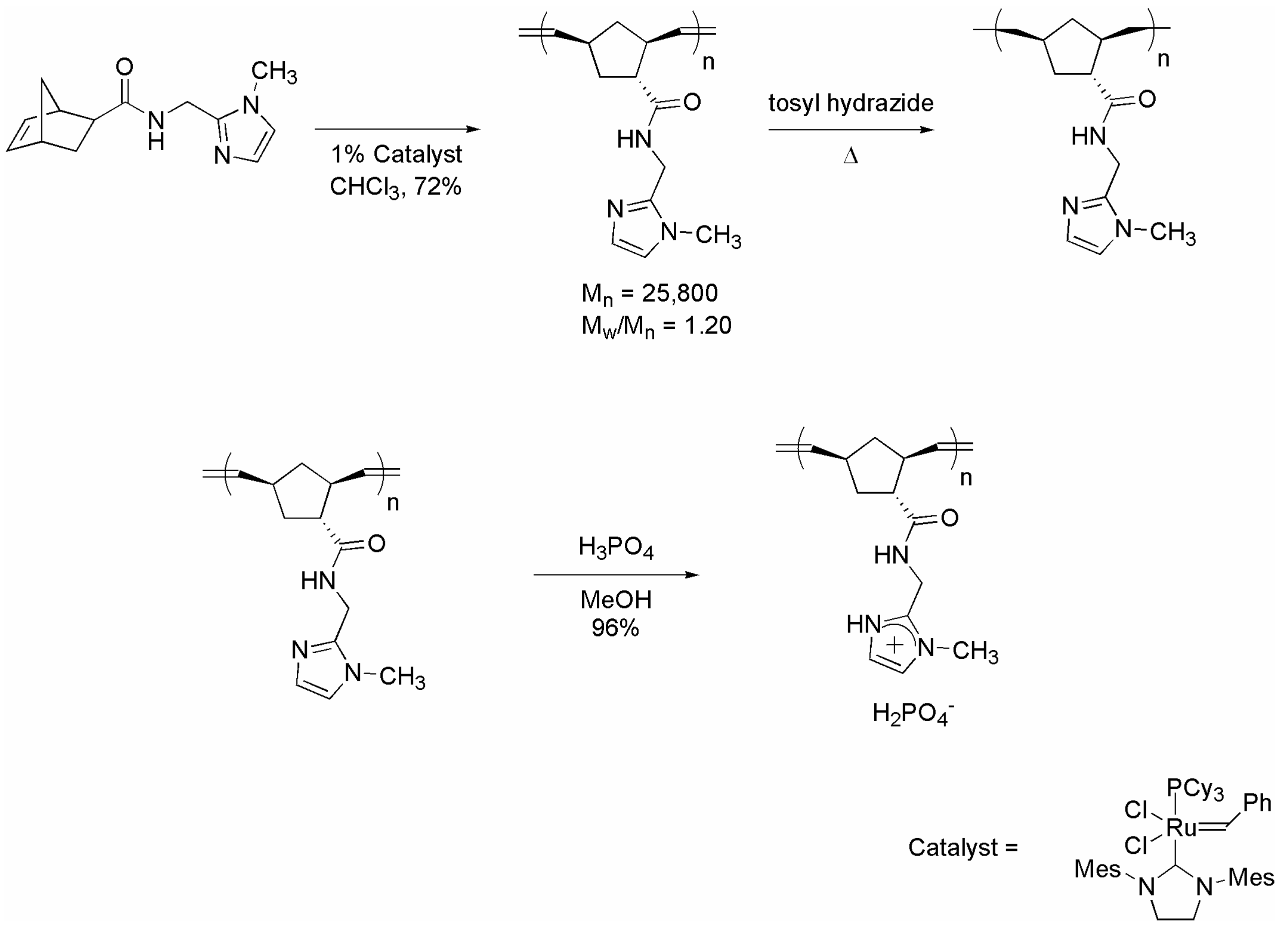
Synthesis of exo Monomers





- Synthesis of poly-norbornene was limited by the endo isomer
- The exo isomer was isolated
- The exo isomer can then be functionalized to give a monomer that yields reasonable molecular weight polymer
- Reaching this step took significant effort

Norbornene Polymerization

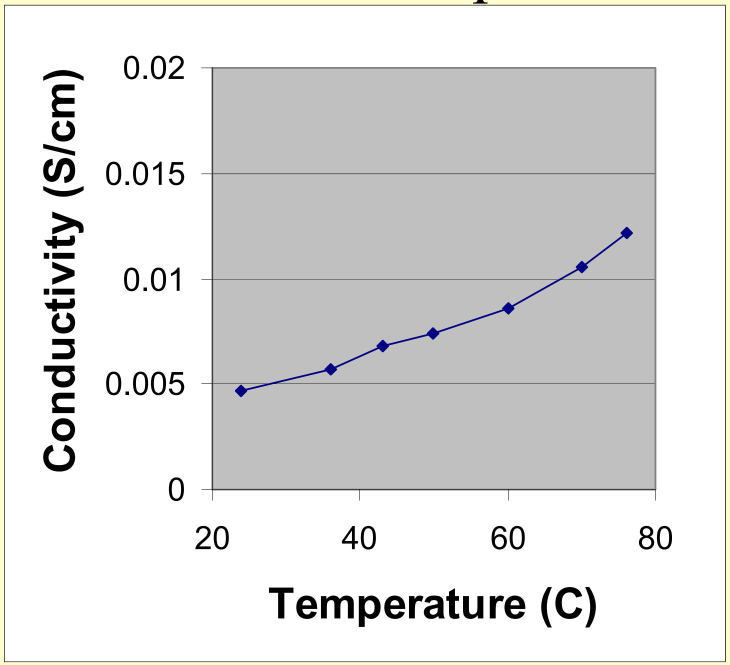


- We have synthesized polymers of reasonable molecular weight and film casting properties
- Very few polymer chemistries have been explored (copolymers, density or type of functional groups, etc.)

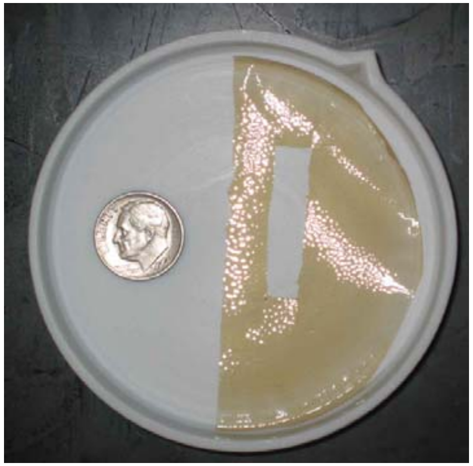
Hydrated Membrane Conductivity

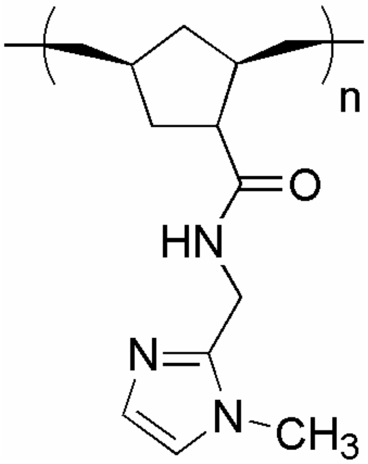
AC Impedance Spectroscopy

PNBA-2-MI in liquid water



- Initial tests showed surprisingly high conductivity, albeit far below Nafion.

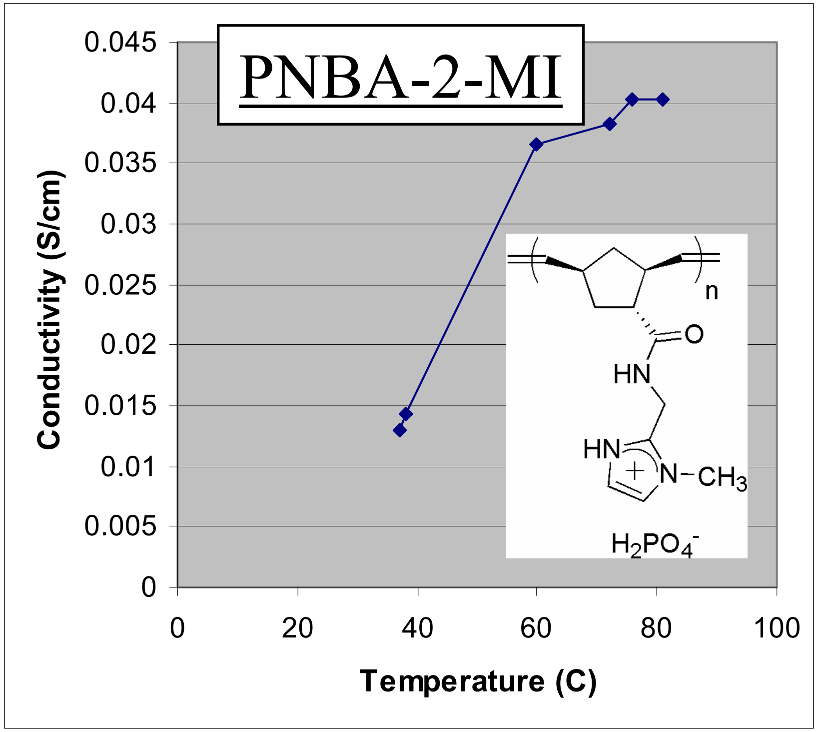




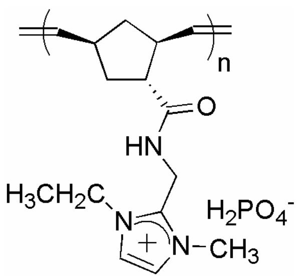
water uptake is high (45%) and this particular membrane is water soluble when doped with acid.

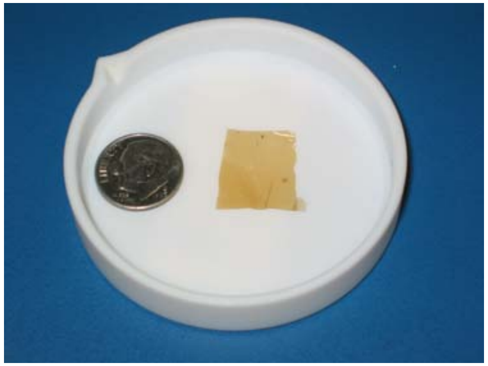
PNBA-2-MI poly-dihydro(norbornene-2-carboxy-N-(1-methyl-1H-imidazol-2-ylmethyl)-amide)

Membrane Conductivity Dependence on Water Content



- PNBA-2-MI phosphate is water soluble, but shows reasonable conductivity even in the dry state
- The role of the phosphate anion and proton in conduction needs to be clarified





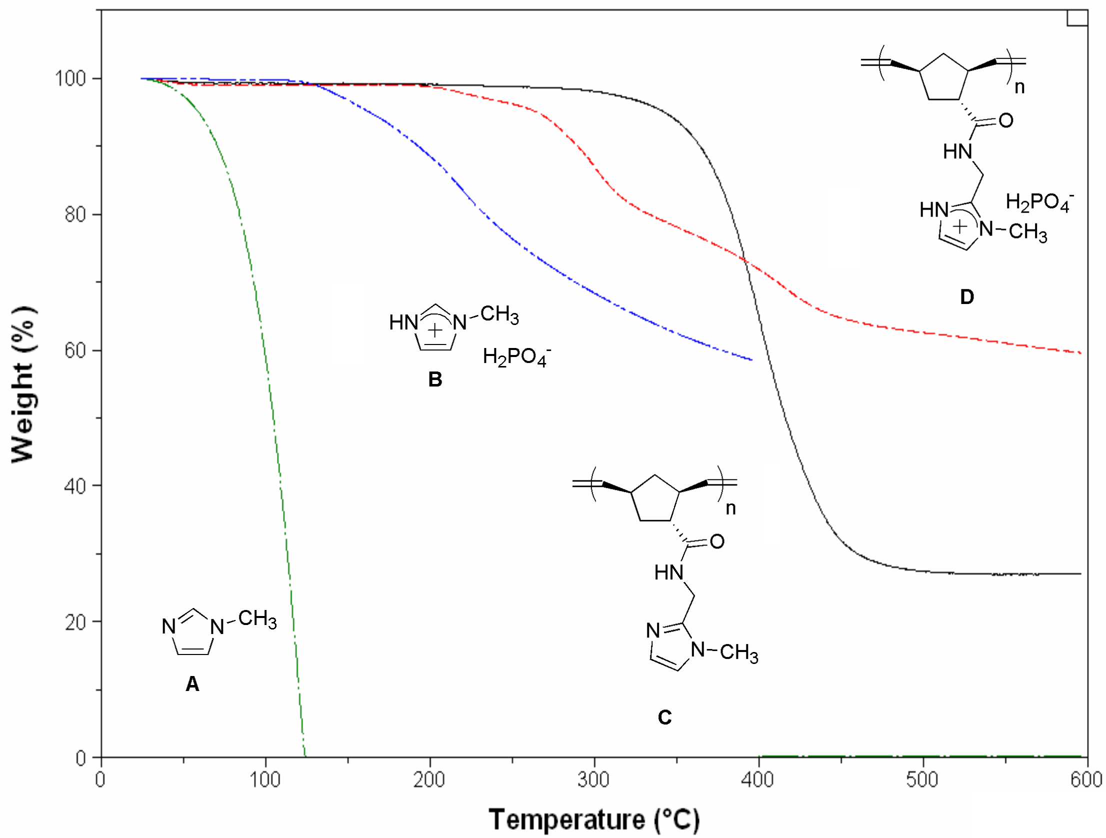
PNBA-2E5MI

Conductivity (90˚C)	Relative Humidity
0.035 S/cm	10%
0.047 S/cm	25%

- PNBA-2E5MI is the ethylated version of PNBA-2-MI and is also water soluble, but likewise shows reasonable conductivity at low RH

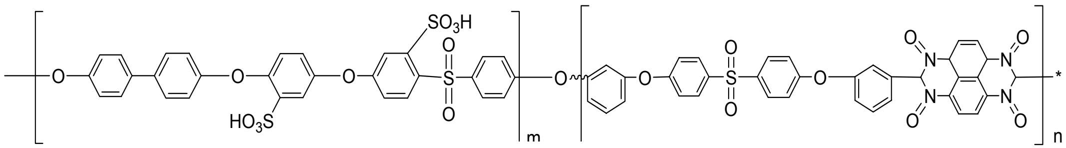
Los Alamos NATIONAL LABORATORY

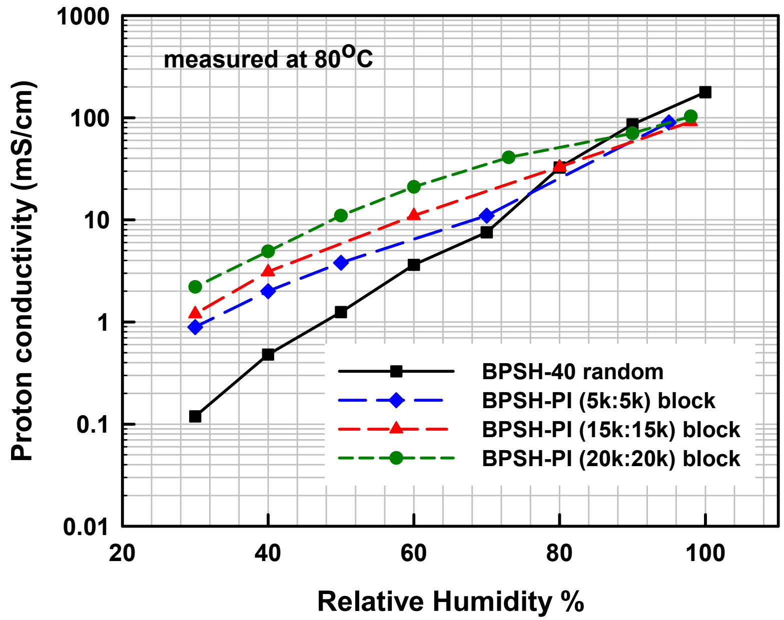
Thermal Analysis

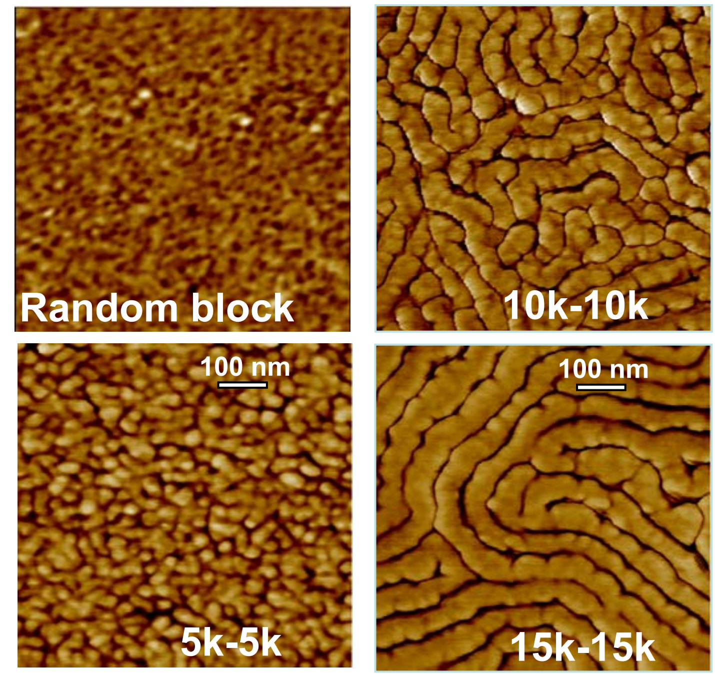


- Methyl imidazole evaporates at low T (30˚C)
- Methyl imidazole – dihydrogen phosphate shows mass loss at moderate T (150˚C)
- Polymer analogues show good temperature stability to at least 200˚C for the acid analogue, 300˚C for neutral polymer

Phase Separation





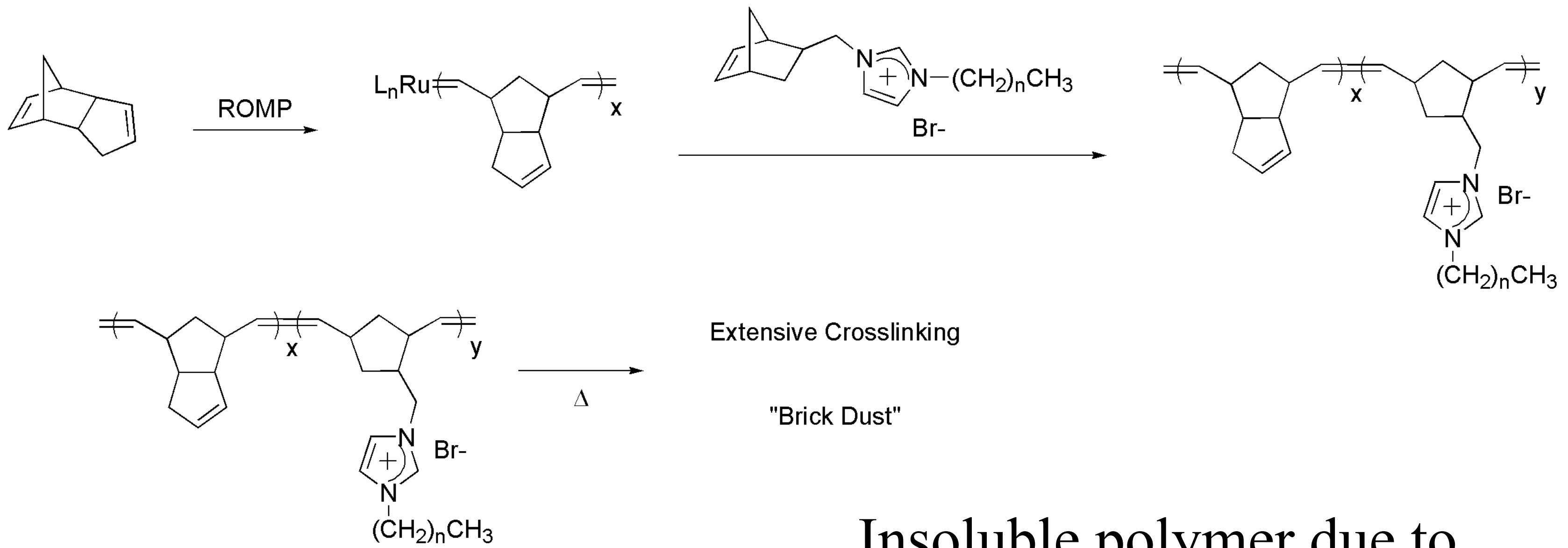


Effect of Block Length of BPSH-*b*-PI Copolymers on Morphology (by TM-AFM)

Phase separation results in segregation of the functional and structural blocks. Preliminary results show increased phase separation leads to better low RH conduction. The materials presented here have poor PDIs (~2) and therefore less well defined morphology than what is achievable with low PDI blocks.

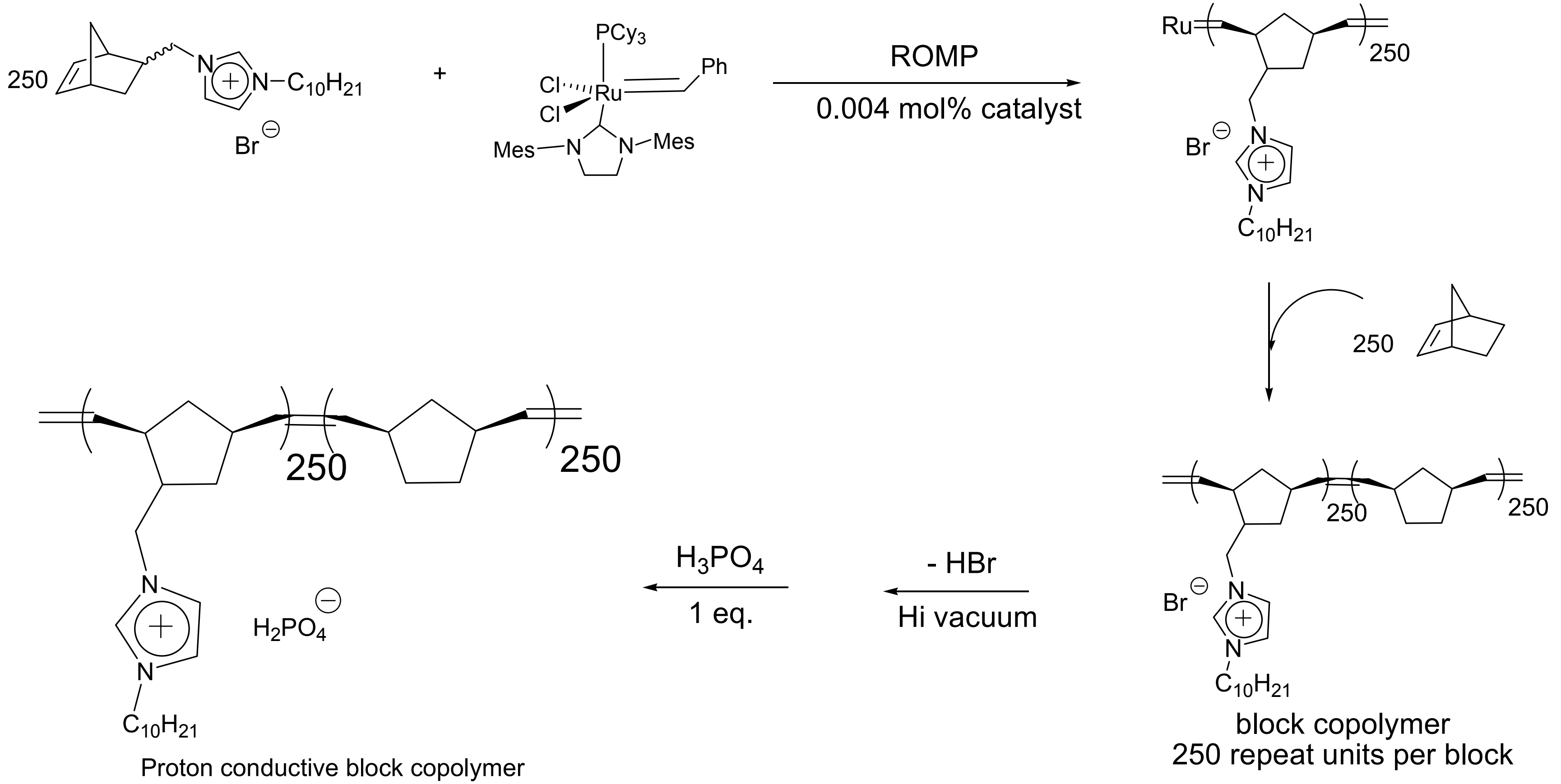
Collaboration with Prof. McGrath (VT)

Block Copolymers



Insolube polymer due to
Uncontrolled crosslinking.

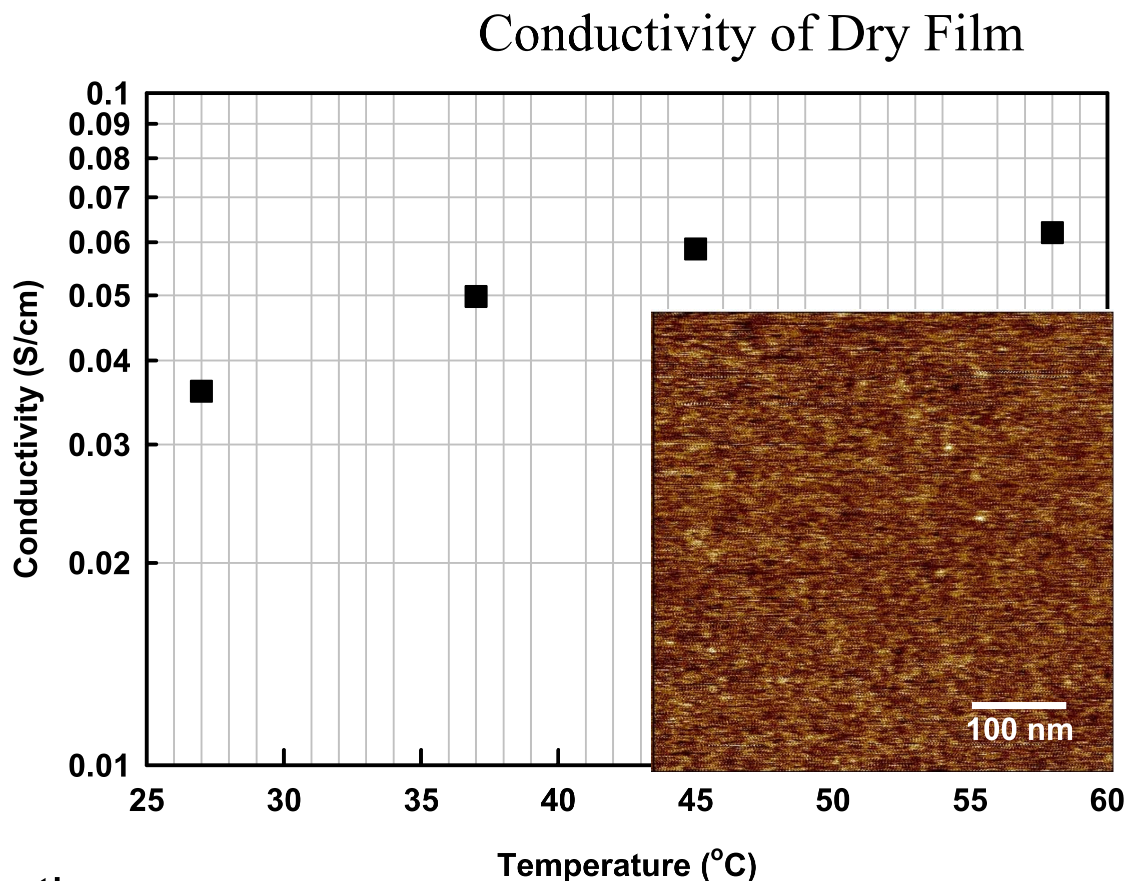
Norbornene-Imidazole Copolymer



Copolymer Conductivity

Liquid submerged samples (room T)

Nafion: 0.09 S/cm
Copolymer:
Up to 0.11 S/cm (but unstable)

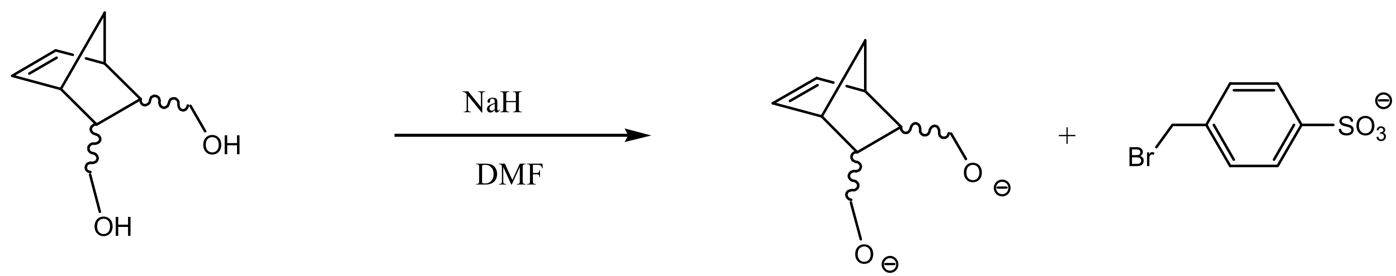


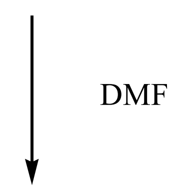
Poorly defined phase separation was observed in our initial films.

Dew point ~ -5^{o}F

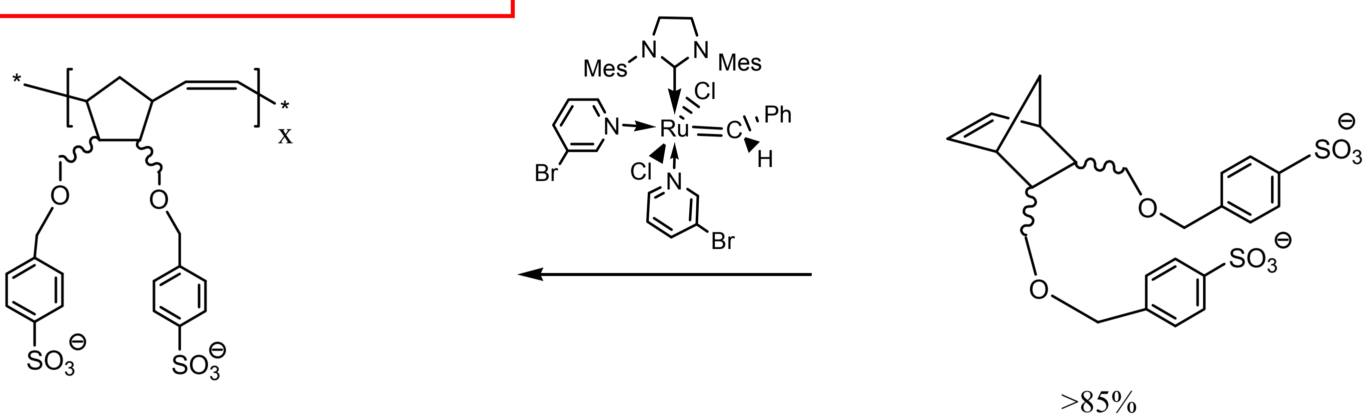
AFM supplied courtesy of Geoff Brown, LANL

Sulfonated Phenyl Substituted Norbornene

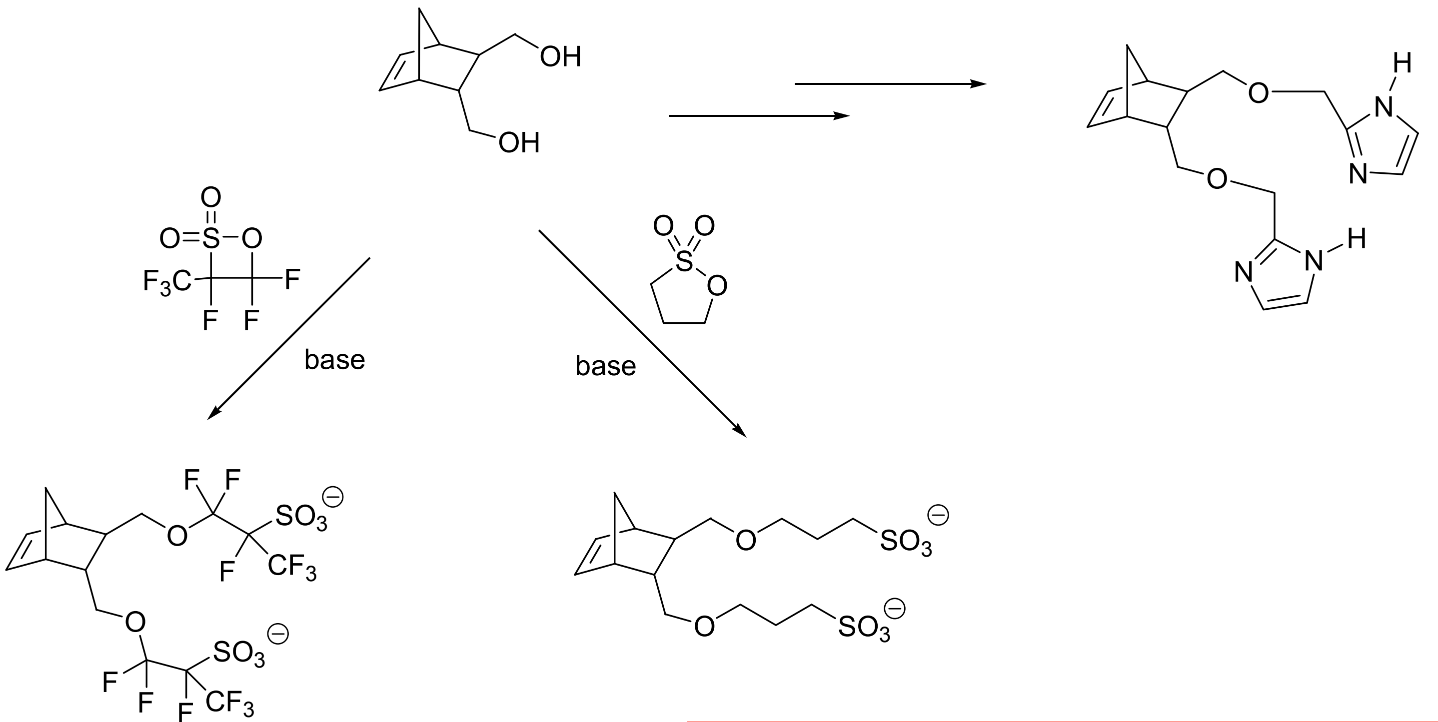




With two sulfonate groups per repeat unit, the polymer will have a very large concentration of proton conducting groups.

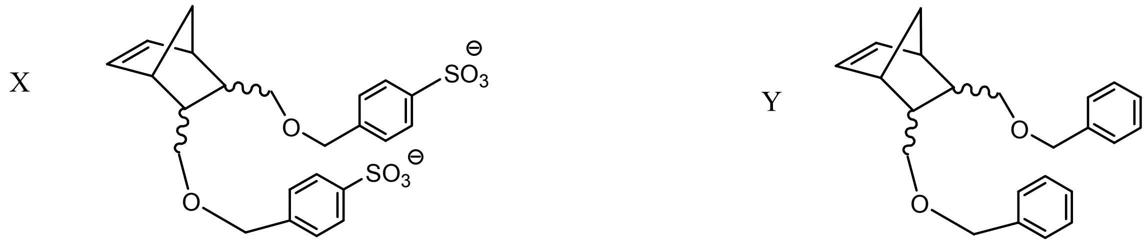


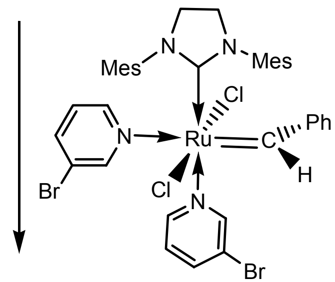
Future Work: Other Norbornene Monomers



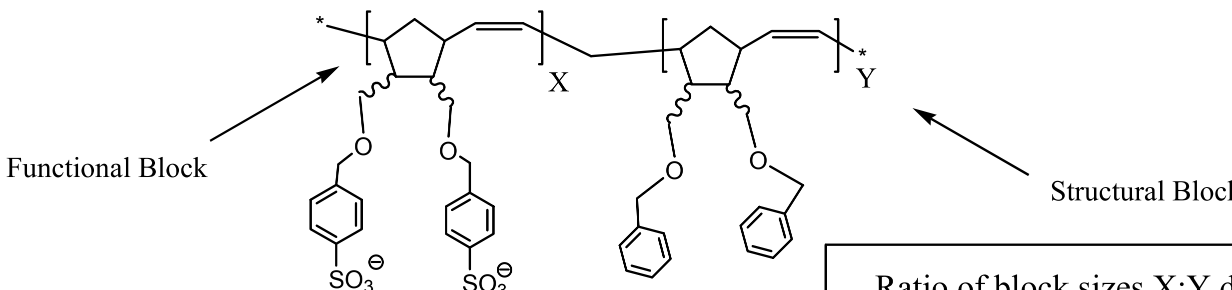
Facile functionalization leads to a variety of monomers that can be incorporated into phase separated structures.

Future Work: NBE Sulfonate Block Copolymers





Sequential addition of monomers leads to block co-polymer formation



Ratio of block sizes X:Y determines the nature of the phase separation.

Project Summary

- Imidazole-acid pairs show reasonable conductivity at high temperatures even at low humidity, while still exhibiting good thermal stability
- We have successfully synthesized and characterized norbornene tethered ionic liquids
- The resulting polymers can be thermally stable up to at least 200 ˚C
- While water solubility is a concern, conductivity data for the films is very promising
- Block copolymers show promising conductivity at 1:1 block ratio (molar).
- Relative monomer volumes need to be adjusted to achieve desired phase separation of the block copolymers, processing routes need to be explored.

Publications

M. Hickner and B. Pivovar, "The Chemical and Structural Nature of Proton Exchange Membrane Fuel Cell Properties," *Fuel Cells Fund. to Sys*., 2005, 5, 213.

Response to Reviewers Comments

Project not reviewed in FY 05.

Critical Assumptions and Issues

- We have yet to synthesize membranes with good phase separation.
  - We have demonstrated well defined block sizes and the ability to synthesize a wide array of monomers.

- The materials investigated are unlikely to be fuel cell stable and similar materials with adequate stability may be difficult to synthesize.
  - We are investigating fundamental properties and limits of materials, to determine whether or not conductivity goals can be met.