

V.L.2 Alternate Fuel Cell Membranes for Energy Independence*

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*Congressionally directed project

- Utilize synthesized proton-conducting block copolymers to produce films that exhibit nanophase-separated morphologies based on block composition; determine the relationship between proton conductivity and membrane morphology.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Cost
- (C) Performance

Technical Targets

- Synthesize bisphenolic comonomers for poly(arylene-ether-sulfone) (PAES) that contain an ion-exchange moiety on a perfluoroalkyl chain tether. Polymerize new comonomers and study membrane conductivity, accelerated degradation, and fuel cell in situ properties. Reproduce known sulfonated poly(arylene-ether-sulfone) (sPAES) benchmark polymers and subject to identical testing. Compare our materials to performance standards established by the DOE.
- Investigate influence of annealing on macromolecular structure, chain dynamics and morphology.
- Knowledge of chemical and mechanical degradation mechanisms and their inter-relationship in membranes.

Fiscal Year (FY) 2011 Objectives

Molecular-morphological tailoring and evaluation of novel, low-cost hydrocarbon fuel cell membranes with high-temperature performance and long-term chemical/mechanical durability. This effort supports the Hydrogen Program stated in the Multi-Year Program Plan by developing high-temperature, low relative humidity (RH), high proton conductive membranes for use in polymer electrolyte membrane (PEM) fuel cells – focus is on alternative materials with performance up to 120°C at low RH.

- Synthesis of aromatic hydrocarbon polymers. Organic structure tailoring includes variation of linking moieties between aromatic groups, ion exchange density/distribution, molecular weight and block vs. random copolymers (Storey, Patton, Savin).
- Fundamental information regarding microstructure and physical properties and correlation using advanced characterization tools (Mauritz, Savin).
- Having identified superior materials and optimized membrane electrode assembly (MEA) processing, the nature/mechanisms of coupled chemical and mechanical degradation and morphological alteration investigated during accelerated ex situ degradation and PEM fuel cell testing (Mauritz).
- Mechanical/chemical/thermal stability of the membranes will be increased over a broad temperature-humidity range. MEAs fabricated from synthesized ionomers and tested for fuel cell performance and durability.

FY 2011 Accomplishments

- Verified polymer coupling via solution self-assembly (dynamic light scattering, DLS) and have begun to observe nanophase-separated morphologies in polymer films via atomic force microscopy (AFM) and transmission electron microscopy (TEM).
- Explored new coupling chemistries for reactions between perfluorinated polymers and other proton-conducting polymers, utilizing different functionalities to improve coupling efficiency and stability of linkage.



Introduction

The basic theme of the synthetic effort is the synthesis of aromatic hydrocarbon polymers of the poly(arylene ether sulfone) (PSf) or poly(arylene ether ketone) type, containing ion exchange groups tethered to the backbone via perfluorinated alkylene linkages. The implementation

of the 1-H-1,2,3-triazole into a PSf is an approach to create a proton exchange membrane that can operate at high temperatures and low humidity. Triazoles are amphiprotic charge carriers, e.g., moieties capable of serving both as proton donors and proton acceptors, so water is no longer necessary as a proton transport medium. Also, the fuel cell can operate at higher temperatures increasing the efficiency of the electrodes.

Traditionally, polymers have been blended for many years to create hybrid properties in a bulk material. Mixing polymers that are chemically/physically incompatible usually results in large, inconsistent phase segregation of each polymer within the bulk material. However, covalent linking of these incompatible polymers to create “diblock copolymers” results in materials with uniform microphase behavior (morphology) and the associated morphologies as a function of block composition ϕ_A and segregation strength χN for bulk coil-coil block copolymers. In our work, our intention was produce block copolymers containing a proton-conducting block and a perfluorinated propylene oxide (PFPO) polymer; the PFPO block is highly incompatible (strongly segregating) with the proton-conducting block leading to well-defined morphologies based on established criteria. By varying the composition of each respective block in the copolymer, we seek to produce a myriad of well-defined morphologies with long-range order (creating proton-conducting channels) and develop a relationship between membrane morphology and proton conductivity. Phase behavior of block copolymers will be mapped vs. block composition using TEM, AFM and small angle X-ray scattering (SAXS). Synthesized materials will be characterized for proton conductivity and mechanical/chemical/thermal stability over broad temperature and RH ranges using a variety of spectroscopic, dielectric, microscopic and viscoelastic methods and evaluated for fuel cell performance.

Approach

In the past year, new structural variations were examined with the aim of providing improved morphological connectivity of ion exchange groups within the bulk membrane material. These approaches included synthesis of hydrophilic/hydrophobic multi-block copolymers, new

ion-containing comonomers with a longer tether length, and new hydrophobic comonomers.

A 1-H-1,2,3-triazole tethered PSf has the potential to eliminate a lot of issues associated with the current PEM material. The 1-H-1,2,3-triazole can be achieved through a copper-catalyzed 1,3-dipolar cycloaddition of an alkyne with azidomethyl pivalate to give the terminal N-protected triazole. Further synthesis can afford a 4-bromophenol functionalized triazole followed by a C-H activation and Suzuki-Miyaura reaction onto the PSf backbone.

For block copolymer synthesis, our interests lie in determining factors that affect bulk morphology, water content, and ion exchange capacity in block copolymers composed of PFPO and a proton-conducting block. We synthesize a variety of polymers with varying composition to map the phase behavior of PFPO-based/proton-conducting block copolymers. Successful synthesis of block copolymers will be confirmed by NMR and DLS. Solutions of the synthesized block copolymers will then be cast and annealed to make films, whereby the films will be characterized in terms of morphology by AFM, TEM, and SAXS. Lastly, we will determine ion exchange capacity and water uptake.

Results

PAES multi-block copolymers were prepared from hydrophilic and hydrophobic prepolymers. Prepolymers were synthesized by reaction of the new ion-containing comonomer, N,N-diisopropylethylammonium 2,2-bis(p-hydroxyphenyl)pentafluoropropanesulfonate (HPPS) (see Figure 1), with bis-(4-fluorophenyl) sulfone (FPS), and biphenol (BP) with FPS, respectively. Prepolymers and multi-block copolymers were prepared at 180°C in N,N-dimethylacetamide in the presence of K_2CO_3 . The prepolymers were reacted overnight; the multi-block copolymers were reacted only 80 min to minimize transesterification. ^{19}F NMR provided molecular weight of hydrophilic prepolymers bearing aryl fluoride end groups. Gel permeation chromatography was used to characterize the multi-block copolymers. Copolymer block lengths were determined by quantifying ^{13}C NMR peak areas of quaternary carbon atoms adjacent to sulfur in FPS moieties. Hydrophilic and hydrophobic block lengths were in the range 9.4-23.4 and 4.4-11.8 repeating units, respectively. AFM

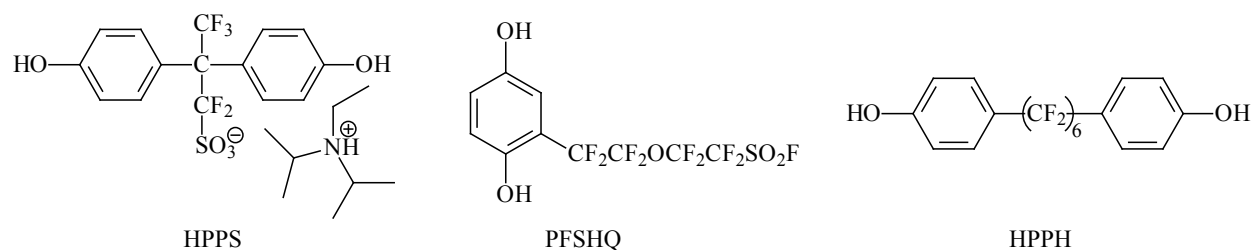


FIGURE 1. Three New Monomers for Ion-Containing PAES

showed phase separation for all block lengths. Conductivity at 80°C and 100% RH ranged from 6.2–34.3 mS/cm, with the best value obtained for hydrophilic/hydrophobic block lengths of 13.3/6.0.

Performance of HPPS-containing PAES were disappointing, and it was hypothesized that the tether element was too short. Thus, a new ion-containing bisphenolic monomer incorporating a longer tether, 2-(5-fluorosulfonyl-3-oxaoctafluoropentyl)-1,4-dihydroxybenzene (PFSHQ) (see Figure 1), was synthesized in two steps from 1,4-dimethoxybenzene and the tether element, 5-iodooctafluoro-3-oxapentanesulfonyl fluoride. Purified yield for the first step was low (12%); purified yield of the second step was 64%. The structure of the monomer (potassium sulfonate form) was proven by NMR and mass spectrometries. Gram quantities of the new monomer were produced, and used in an attempted synthesis of a new poly(arylene ether sulfone) polymer; however, a crosslinked product resulted.

Synthesis of a new hydrophobic monomer, 1,6-di(4-hydroxyl)phenylperfluorohexane (HPPH) (see Figure 1), was accomplished using a copper coupling reaction between 2 eq of 4-iodophenol and 1 eq of 1,6-diiodoperfluorohexane. The yield was 56%, the structure was confirmed by NMR spectroscopy. Copolymerization of HPPH with 3,3'-disulfonate-4,4'-difluorodiphenylsulfone in the presence of K_2CO_3 , however, resulting only in homopolymerization of HPPH to yield an insoluble polymer (assumed to be crosslinked). The failure of both PFSHQ and HPPH in nucleophilic aromatic substitution polymerization is apparently due to attachment of a CF_2 moiety directly to the aromatic ring. In contrast, HPPS polymerizes in a very predictable fashion.

The synthesis of triazole-functionalized polymers followed Figure 2. The rigidity of the PSf backbone limits the mobility of the triazoles and decreases its charge transfer capabilities even at a concentration of triazoles of one per repeat unit. The stiffness of the

backbone also limits the ability of the material to undergo phase separation to create channels for the protons to travel through.

Initially, our work establishing efficient coupling strategies of acid chloride-functional PFPO with hydroxyl-functional poly(styrene) was centered around direct coupling of the two blocks. The challenges here were to determine proper solvent/solvent mixtures, reaction temperatures, concentrations, etc., to effectively produce block copolymers. The DLS results confirm (1) successful polystyrene (PS)-b-PFPO (SF) copolymer formation and (2) aggregate size in methanol after sulfonation of the PS blocks thereby forming sulfonated-PS-b-PFPO (sSF) block copolymers. Figure 3 presents an AFM phase image for SF 5-4 (~55 wt% polystyrene). This image suggests cylindrical formation with domain sizes of approximately 10 nm. The aggregate size in tetrahydrofuran illustrates efficient synthesis of SF block copolymers; however, after sulfonation, the aggregate sizes are extremely small. This suggests that scission is possibly occurring between PS and PFPO which seems to be a likely occurrence since the two blocks are connected by an ester linkage (susceptible to hydrolysis).

Further work has persisted on (1) modifying the functionality of PFPO-COOH to facilitate efficient coupling with proton-conducting blocks (i.e. PAES) and (2) attempted coupling reactions of modified PFPO with hydroxyl-terminated PAES to yield stable, robust linkages. PFPO chain end modification was performed by reacting PFPO-COOH with diamino halide compounds to form benzimidazole groups. We attempted nucleophilic aromatic substitution coupling with hydroxyl-terminated PAES. Encouragingly, we were able to make a homogenous solution in hexafluoroisopropanol, and the reaction was allowed to react for 1 day at 120°C. We are currently performing light scattering and NMR experiments to confirm to product of the reaction, and we note that the reaction yielded a product with a color (reddish) different from the two reactants.

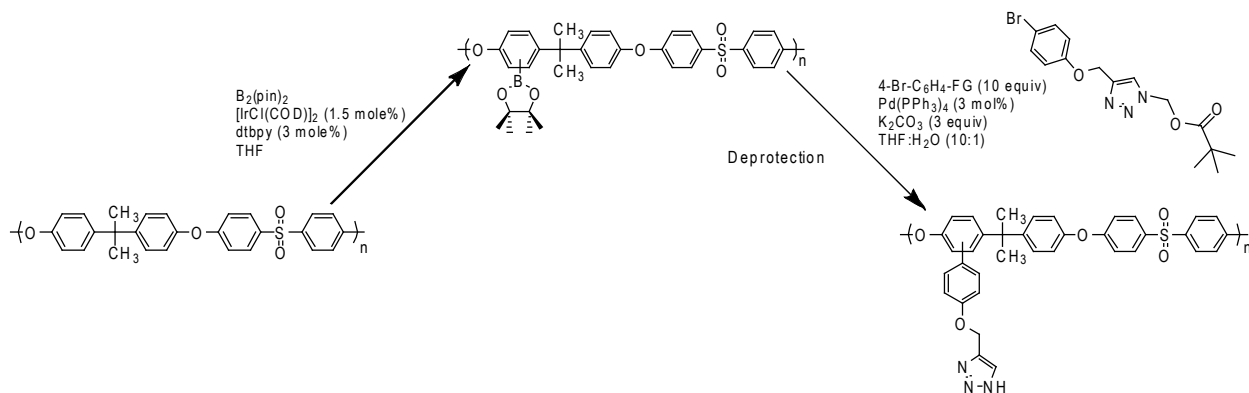


FIGURE 2. Functionalization of Aromatic Rings of Polysulfone through C-H Activation and Suzuki-Miyaura Reaction followed by Deprotection under Basic Conditions

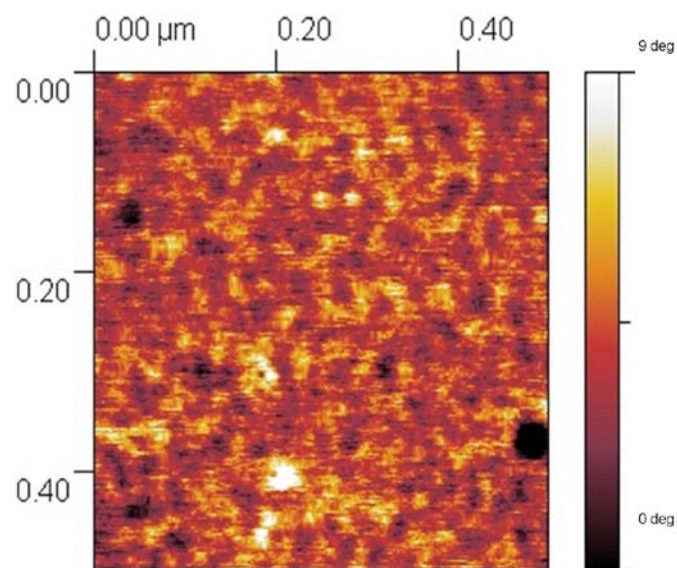


FIGURE 3. AFM Phase Image of a 50 mg/mL PFPO_{4K}-PS_{5K} Spin-Cast from a solution of 80% Trifluorotoluene and 20% Methoxy-nonafluorobutane

Mechanically robust membranes were prepared by blending the triazole-PSf and phosphonic acid PSf. However, preliminary conductivity measurements show the films exhibit low conductivity at 120°C. Triazole-PSf membrane films were also doped with phosphoric acid to improve their conductivity at high temperatures. However, conductivities at 120°C for the films were very low at over the range of RH. The reason for low conductivity is thought to be the -NH groups of the triazole tether is not accessible to H₃PO₄ or phosphonic acid groups. Efforts are now in progress to prepare and test PSf backbone with higher concentrations of tethered triazole (Figure 4).

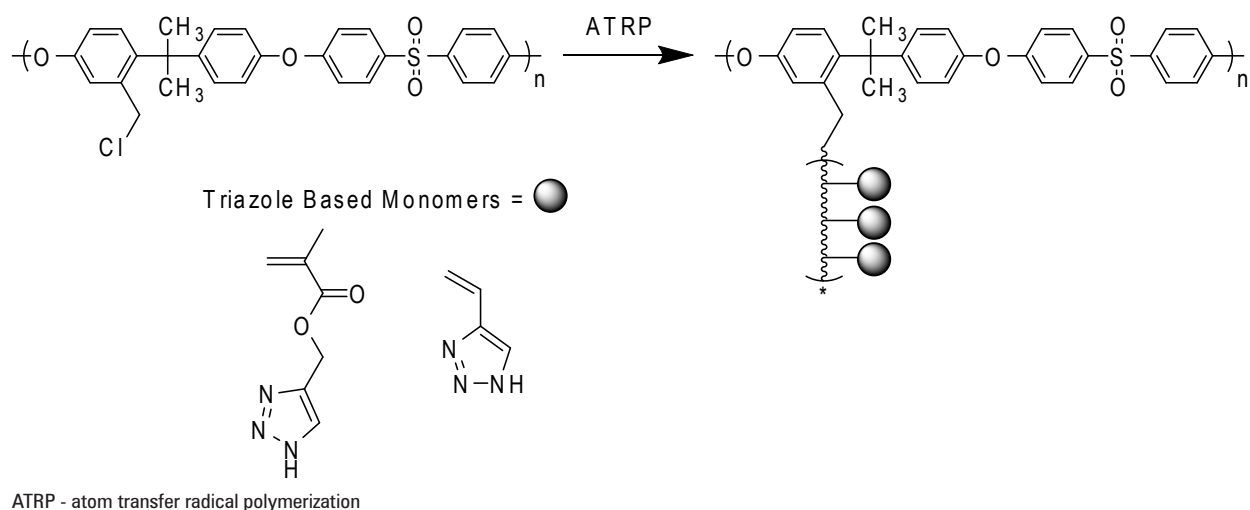


FIGURE 4. Polymerization of Triazole-Based Vinyl Monomers off of a Chloromethylated PSf Backbone via Atom Transfer Radical Polymerization

Conclusions and Future Directions

- The single tethered triazoles are limited due to the rigidity of the PSf backbone.
- A higher concentration of triazoles will allow for better phase separation to occur and can be achieved by growing triazole based monomers from a chloromethylated PSf backbone via atom transfer radical polymerization.
- Produce films of synthesized block copolymers and study the nanophase-separated behavior (due to the coupling producing triblock copolymers, we can exploit the block composition to produce even more morphologies than we see with diblock copolymers).
- Coupling of PFPO-bzimF with hydroxyl-functional PAES that has a higher degree of sulfonation (higher hydrophilicity and introduction of proton conductivity).

FY 2011 Publications/Presentations

Publications

1. Li, H.; Jackson, A.B.; Kirk, N.J.; Mauritz, K.A.; Storey, R.F. "Poly(arylene ether sulfone) Statistical Copolymers Bearing Perfluoroalkylsulfonic Acid Moieties" *Macromolecules* **2011**, 44(4), 694–702.
2. Li, H.; Kirk, N.J.; Mauritz, K.A.; Storey, R.F. "Poly(arylene ether sulfone) Multi-Block Copolymers Bearing Perfluoroalkylsulfonic Acid Groups" *Polymer*, **2011**, DOI: 10.1016/j.polymer.2011.05.057.
3. Nalawade, A.; Hassan, M.K.; Mauritz, K.A.; Litt, M.H. *ACS Preprints, Div. Fuel Chem.* **2010**, 55 (2), 243. "Broadband Dielectric Spectroscopy Studies of Instrument - in situ Annealed Poly (2,5- benzimidazole) Membrane Materials."

4. Nalawade, A.; Hassan, M.K.; Jarrett, W.A.; Mauritz, K.A.; Litt, M.H. “Broadband Dielectric Spectroscopy Studies of Glassy State Relaxations in Annealed Poly (2,5-benzimidazole)”, **Accepted**, *Polymer International*.
5. Analysis of Macromolecular and Proton Motions in Fuel Cell Membranes using Dielectric Spectroscopy. Mohammad K. Hassan, Amol Nalawade, and Kenneth A. Mauritz, *Polymer Preprints* **2011**, ACS Preprint Website.
6. Mauritz, K.A.; Nalawade, A.; Hassan, M.K. “Proton Exchange Membranes for H₂ Fuel Cells Applications”; Submitted to the book “Sol-Gel Processing for Conventional and Alternative Energy”; Klein, L.C. et al., Editor, Springer, 2011.

Presentations

1. Amol Nalawade, “Broadband Dielectric Spectroscopy Studies of Instrument - in situ Annealed Poly (2,5- benzimidazole) Membrane Materials”, Oral talk, 240th ACS National Meeting: Fuel Chem. Division, August 22–26, 2010, Boston, Massachusetts.
2. Amol Nalawade, “Analysis of Macromolecular and Proton Motions in Fuel Cell Membranes using Dielectric Spectroscopy”, Poster, 241th ACS National Meeting: Polymer Chemistry Division, March 27–31, 2011, Anaheim, California.