Characterization of Structure-Property Relationships in Hydrophilic-Hydrophobic Multiblock Copolymers for Use in Proton Exchange Membrane Fuel Cells

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Thesis submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Master of Science

In

Macromolecular Science and Engineering

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November 18, 2011
Blacksburg, VA

Keywords: fuel cells, multiblock copolymers, proton exchange membranes, poly(arylene ether sulfone)s, morphology

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ABSTRACT

Proton exchange membrane fuels cells (PEMFCs) are one of the primary alternatives to internal combustion engines. The key component is the proton exchange membrane, or PEM, which should meet a number of requirements, including good proton conductivity under partially humidified conditions. A number of alternative PEMs have been synthesized by copolymerizing various aromatic comonomers, but the smaller ion channels prohibit rapid proton transport under partially hydrated conditions. One solution has been to synthesize multiblock copolymers from hydrophilic and hydrophobic oligomers to ensure sufficient ion channel size.

Four multiblock systems were synthesized from hydrophobic and hydrophilic oligomers and were characterized in this thesis. The first multiblock system incorporated a partially fluorinated monomer into the hydrophobic block, to improve phase separation and performance under partially humidified conditions. The second study was focused on phase separation and structure-property relationships as a function of casting conditions of a biphenol-based multiblock series.

The third study featured a novel hydroquinone-based hydrophilic oligomer in the multiblock copolymer, which showed the promise of a higher ionic density, degree of phase separation and proton conductivity values. The fourth study in this thesis entailed
the comparison of a block copolymer produced with two distinct synthetic routes: the multiblock synthesis from separate oligomers as previously published in the literature, and a segmented route seeking to achieve comparable structure-property relationships with the same monomers, but using a simpler synthetic route. The two block copolymer series were found to be comparable in their structure-property relationships.
Acknowledgements

I would like to thank my advisor, James E. McGrath, for his endless patience and guidance over the years. His understanding and advice was invaluable, and I cannot emphasize enough how I am grateful and proud to have spent my time at Virginia Tech in his research group. It has truly been a privilege to learn here under Dr. McGrath with my colleagues, and I feel very lucky to have had the chance. I would also like to thank Dr. Judy Riffle and Dr. John Dillard for their input and time as my committee members.

I would also like to acknowledge the support, advice and companionship from my colleagues in my research group, both past and present. Not only did you help in my development as a researcher, but our conversations were always entertaining and thoughtful. Particular thanks go to Dr. Hae-seung Lee for his friendship and help in my research during his time here. Additionally, I would like to thank Yu Chen, Dr. Anand Badami, Dr. Natalie Arnett, Dr. Abhishek Roy, Dr. Mou Paul, Dr. Xiang Yu, Dr. Yanxiang Li, Dr. Gwangsu Byun, Dr. Myoungbae Lee, Dr. Gwangyu Fan, Dr. Kwan Soo Lee, Dr. Chang Hyun Lee, and Drs. Melinda and Brian Einsla. I am also thankful for the assistance and teaching I received from Frank Cromer, Steve McCartney, and Niven Monsegue. I literally could not have done it without you.

I am very grateful to Laurie Good for her endless help and kindness while managing the administrative needs of Dr. McGrath and the McGrath group. Tammy Jo Hiner, Angie Flynn, and Mary Jane Smith all deserve recognition for their assistance in handling the many requirements of the MII and MACR programs at Virginia Tech.

I am thankful for the continuous love and support of my mother, Caroline Lane, and my brother and sister, Lex and Seana Lane. I am also thankful for the support of my aunts Rebecca
Simmons, Mary Jo Swift, Miriam Pierce, Shelly Pierce, Stacy Pierce, Mary Phillips, and my uncles David, Andy, and Joseph Pierce, Larry Swift, and Paul Simmons, as well as my many cousins. I would never have made it through my time at Virginia Tech without their encouragement, support and advice. Thank you so much.

To my nephew Lane Shaffer, and my niece Eleanor Kate Shaffer, you are amazing and an inspiration to me. This thesis is dedicated to you.
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1.0 Introduction to Fuel Cells

The rapidly increasing demand for finite quantities of fossil fuels—coupled with intensifying pressure to alleviate the environmental strain of fossil fuel consumption—heightens the need to develop feasible alternative energy sources. One of the more challenging applications has to do with the use of fuel cells for automotive applications. Currently, there are few viable energy alternatives that will provide a safe, clean source of automotive power with sufficient power density. When compared to batteries, fuel cells require only the time needed to refuel in comparison to the lengthy recharging time needed for batteries. Furthermore, while batteries scale poorly to larger sizes, fuel cells are easily scaled from Watt to megaWatt scale according to need.

Hydrogen fuel cells are one of the primary candidates for replacing traditional combustion engines due to their ability to produce an electrical current from the electrochemical reaction of hydrogen and oxygen with only water and some waste heat as byproducts. The fuel cell has clear advantages over a combustion engine, which creates a host of inorganic and organic pollutants from burning fossil fuels. Fossil fuels must also be obtained from mining or drilling, which creates the certainty of environmental damage, as well as the risk of environmental disaster in the event of an accident or mishap during fossil fuel extraction. These disadvantages are in addition to the political risks of being dependent on occasionally unstable nations for the fossil fuel needs of the nation.

In addition, combustion engines have a much lower efficiency since they must convert chemical energy into physical energy. Because this conversion relies on the pressure resulting
from an exothermic reaction, much of the potential energy of the fuel is lost as waste heat. Even though the fuel cell creates some waste heat during the reaction, this novel system will be more efficient at higher temperatures; therefore, a certain amount of waste heat is not necessarily undesirable.\[^6\]

There are a number of hurdles to be cleared before fuel cells can be successfully implemented at the commercial level, however. The primary fuel used in fuel cells is hydrogen, which lacks both a viable storage and transportation infrastructure, and possesses a low volumetric energy density.\[^5\] Furthermore, most fuel cells require platinum-based catalysts for the dissociation of hydrogen at the cathode; until efforts to produce an alternative catalyst are successful, this is cost-prohibitive at the commercial level.

### 1.1 Types of Fuel Cells

A fuel cell may appear to be very similar to a battery, as it generates power from an electrochemical reaction in the form of an electric current. The primary difference between a fuel cell and a battery is that a fuel cell is not consumed while producing electricity. Instead, it can continue to operate as long as there is a supply of available fuel. In some respects, therefore, it is similar to a combustion engine in that both are “chemical factories” contingent on fuel supply.\[^5\]

The fuel cell—or at least the notion that hydrogen and oxygen could be coupled and used to drive an electrochemical reaction to produce a current—was first developed by Sir William Grove in 1839, but remained largely unexplored for almost a century. No practical development occurred until Francis Bacon started investigating fuel cells in 1937, finally developing a 6kW fuel cell 20 years later.\[^6\] Research efforts increased significantly with the U.S. Space Program, and the first polymer electrolyte membrane fuel cells were developed by NASA for the Gemini Program in the 1960s, with a more comprehensive fuel cell system created for the Apollo
Fuel cells comprise a diverse range of assemblies, classified primarily by their conducting electrolyte, and secondarily by their potential fuels. The five main categories of fuel cells are (1) solid oxide fuel cells, (2) phosphoric acid fuel cells, (3) molten carbonate fuel cells, (4) alkaline fuel cells, and (5) proton exchange membrane fuel cells. Although some are more promising than others, all entail the breakdown of hydrogen, a hydrocarbon, or alcohol to produce a current. Another commonality they share is that the carrier species that moves across the electrolyte to complete the reaction may be hydrogen, hydroxide ion, or a carbonate ion. While most are not suitable for powering personal vehicles due to excessive operating temperatures, some still remain viable sources of energy for stationary power generators, power sources for portable electronic devices, and powering large public transportation vehicles such as buses. Higher operating temperatures may also allow these fuel cells to run on alcohols, acids or other hydrocarbon-based fuels, from fossil fuels or from agricultural waste, and to limit concerns of platinum catalyst poisoning by carbon monoxide or sulfur. Table 1-1 lists a summary of these types of fuel cells, their operating conditions, advantages, and disadvantages.

Table 1-1. A summary of different types of fuel cells and their key characteristics.

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Fuel Type</th>
<th>Efficiency (%)</th>
<th>Operating Temperature range (°C)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Oxide</td>
<td>Hydrogen, hydrocarbons</td>
<td>50-60</td>
<td>600-1000</td>
<td>Can run on many fuels</td>
<td>Expensive materials, high temperature causes design challenges</td>
</tr>
<tr>
<td>Phosphoric Acid</td>
<td>Hydrogen</td>
<td>40</td>
<td>180-210</td>
<td>Inexpensive electrolyte</td>
<td>Low efficiency, uses expensive Pt catalyst</td>
</tr>
<tr>
<td>Molten</td>
<td>Hydrogen,</td>
<td>45-55</td>
<td>550-650</td>
<td>Can run on many</td>
<td>CO2 management,</td>
</tr>
<tr>
<td>Carbonate hydrocarbons, alcohols</td>
<td>fuels</td>
<td>expensive materials</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>----------------------------------</td>
<td>------</td>
<td>---------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkaline Hydrogen 50 60-250</td>
<td>Inexpensive materials</td>
<td>Sensitive to poisoning, KOH needs monitoring</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEMFC Hydrogen 40-50 30-90</td>
<td>Highest power density</td>
<td>Expensive Electrolyte, low ceiling operating temperature</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Methanol (DMFC) 40-50 30-80</td>
<td>Good candidate for portable electronics</td>
<td>Electrolyte is permeable to methanol, high Pt loading</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 1.1.1 Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFCs) use a ceramic metal oxide, generally yttria-stabilized zirconia (YSZ) as a conducting electrolyte. The SOFC is unique among the main fuel cell types in that the conducted ion species is $O_2^-$ rather than protons or hydroxide ions. It also produces water at the anode, unlike the proton exchange membrane fuel cells. The cells can operate at up to $1000^\circ C$, where carbon monoxide is readily oxidized to carbon dioxide, but sulfide poisoning is still a problem. The fuel used in SOFCs is primarily hydrogen, with carbon monoxide present as an impurity. The high operating temperature and low power density excludes the SOFC from portable applications, but has expanding potential as a stationary generator. The electrochemical reactions occurring at the anode and cathode are as follows:

**Anode:** $H_2 + O_2^- \rightarrow H_2O + 2e^-$

**Cathode:** $\frac{1}{2} O_2 + 2e^- \rightarrow O_2^-$

$CO + \frac{1}{2} O_2 \rightarrow CO_2$

The primary advantages in using a SOFC include flexibility in fuel use, high efficiency, and the opportunity to use the waste heat for other applications in proximity to the fuel cell. The
most important of these is the fuel flexibility, as it exempts the SOFC from the significant hurdle of hydrogen production and infrastructure that affects the rest of the fuel cell devices under development.\textsuperscript{5, 7}

The SOFC also has several drawbacks, mainly caused by the high operating temperature. The materials used in the hardware needed in forming the fuel cell stacks, sealing them, and connecting them have concerns with matching thermal expansions, maintaining mechanical integrity under thermal and mechanical stress, and reliability over the lifetime of the fuel cell.\textsuperscript{5, 7}

\subsection*{1.1.2 Phosphoric Acid Fuel Cells}

Phosphoric acid fuel cells (PAFCs) use a thin layer of SiC matrix saturated with a concentrated liquid $\text{H}_3\text{PO}_4$ electrolyte, layered on either side with a porous graphite electrode and Pt catalyst.\textsuperscript{5} Hydrogen gas dissociates at the electrode, with protons migrating across the $\text{H}_3\text{PO}_4$ electrolyte and an electron current completing the circuit by being conducted to the cathode, where oxygen is reduced in the presence of the transported protons to produce water as shown in the equations below. To avoid solidification of the phosphoric acid, PAFCs must be operated above 42°C and below 210°C to avoid a phase transition of the $\text{H}_3\text{PO}_4$ which results in an unusable product. Typical operating conditions are at the higher end of that range, 180-210°C.

\begin{align*}
\text{H}_2 + \text{O}^2- & \rightarrow \text{H}_2\text{O} + 2\text{e}^- \\
\frac{1}{2}\text{O}_2 + 2\text{e}^- & \rightarrow \text{O}^{2-}
\end{align*}

Using a PAFC offers several advantages, namely a reliable and well-developed technology featuring a simple design and an inexpensive electrolyte. The higher operating temperatures afford an increased degree of tolerance to poisoning by the carbon monoxide, which is frequently present in hydrogen gas, with 0.5-1.5\% being acceptable without significant
The PAFC also has several inherent drawbacks. It has a lower efficiency than some of the other fuel cell types, about 40%, making them only practically applicable for a stationary power source, although some models have been evaluated for use in powering buses. They use an expensive platinum catalyst, and the phosphoric acid evaporates at operating temperatures, requiring constant replenishment in addition to providing fuel.\textsuperscript{5,7}

\subsection*{1.1.3 Molten Carbonate Fuel Cells}

Molten carbonate fuel cells (MCFCs) use molten lithium and/or a potassium carbonate salt as the electrolyte, with the carbonate anion specifically providing the conductivity. This requires very high temperatures, which excludes the molten carbonate from portable applications such as electronics or cars, but the high power density and efficiency leaves molten carbonate fuel cells as an excellent potential candidate for stationary power.

The carbonate acts as a charge carrier by reacting with the hydrogen at the anode to form CO\textsubscript{2}, water, and the release of two electrons. The CO\textsubscript{2} must be able to circulate and reach the cathode, where in the presence of oxygen and the return of the two electrons, CO\textsubscript{2} is regenerated as CO\textsubscript{3}\textsuperscript{2-}, as shown in the reactions below.

\begin{equation*}
H_2 + CO_3^{2-} \rightarrow CO_2 + H_2O +2e^- \\
\frac{1}{2} O_2 + CO_2 +2e^- \rightarrow CO_3^{2-}
\end{equation*}

An additional advantage is provided by the operating temperature of at least 650\degree C, which virtually eradicates any concerns of carbon monoxide poisoning, and thus eliminates the
need to purify the fuel source. This also enables the molten carbonate fuel cells to use fuels other than hydrogen, enabling hydrocarbons, alcohols, and some acids to be used as alternative fuels.\textsuperscript{5} While the fuel flexibility is a major advantage, it also results in additional waste products, typically CO\textsubscript{2}, which negates part of its environmental advantage.\textsuperscript{5} The high temperature also allows for a nickel/chromium or lithiated nickel catalyst for the anode and cathode respectively, both of which are much cheaper than the platinum catalyst required by most other classes of fuel cells. The high temperature also provides waste heat which may be used for cogeneration applications.\textsuperscript{5-7}

1.1.4 Alkaline Fuel Cells

Alkaline fuel cells (AFCs) are analogous to polymer electrolyte membrane fuel cells, except that they generally use a concentrated potassium hydroxide solution as their electrolyte, which conducts hydroxide ions in lieu of protons. Alkaline fuel cells were first used in the Apollo space program, but are unsuitable for automobiles due to their lower power density. They may have a niche as a stationary reserve generator due to their inexpensive construction.\textsuperscript{5}

The electrochemical reactions at the anode and cathode of the AFC present a greater than usual challenge for water management during the fuel cell operation, due to the production of water at the anode being twice as fast as at the cathode, as shown in the reactions below. Thus there is a simultaneous risk of anode flooding and dehydration at the cathode, with the greater disadvantage lying in the management of water at the anode because the KOH electrolyte may become diluted.\textsuperscript{5}

\[
\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-
\]
\[ \frac{1}{2} \text{O}_2 + 2e^- + \text{H}_2\text{O} \rightarrow 2\text{OH}^- \]

AFCs are very sensitive to carbon dioxide as well as carbon monoxide, and so must have both a pure fuel and pure oxygen supply, rather than using ambient air as an oxidant as other fuel cell types do. AFCs require periodic maintenance to replenish the supply of OH\(^-\) as it declines, as well as removing any precipitated K\(_2\)CO\(_3\) which forms from CO\(_2\) contamination in the fuel or oxidant supply, as shown below.\(^5,7\)

\[
2\text{OH}^- + \text{CO}_2 \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}
\]

\[
2\text{K}^+ + \text{CO}_3^{2-} \rightarrow \text{K}_2\text{CO}_3
\]

1.1.5 Proton Exchange Membrane Fuel Cells (PEMFCs)

Both direct methanol fuel cells (DMFCs) and proton exchange membrane fuel cells (PEMFCs) utilize a polymeric proton exchange membrane (PEM) as an electrolyte, and a slightly modified PEM in the electrode. They are separated according to their use of methanol or hydrogen as a fuel, but are otherwise similar, using oxygen or ambient air as an oxidant, producing water and waste heat, and in the case of DMFCs, carbon dioxide as byproducts. There are slight differences in the design and needs of each fuel cell system, and their respective advantages make them ideal for different applications.\(^5,6\)

1.1.5.1 Direct Methanol Fuel Cells

A subgroup of PEM fuel cells, intended for use in personal electronic devices due to a
power density insufficient for transportation vehicles, is the direct methanol fuel cell (DMFC). The basic membrane electrode assembly is the same as in PEMFCs. The electrodes in the DMFC require a higher level of platinum loading than in the hydrogen-based PEMFC.

The electrochemistry of the DMFC fuel cell is slightly more complicated than that of the hydrogen-based fuel cells. An overview of the reactions at the anode, cathode, and the overall balanced DMFC reaction are shown below, respectively. One of the inherent drawbacks to the DMFC compared with the H₂ PEMFC is that the kinetics of the methanol oxidation reaction are slower than the dissociation of the hydrogen molecule.¹⁰ The detailed chemistry of the reactions and intermediates involving the catalysts at the anode and cathode has been well studied.¹¹,¹²

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 6\text{H}^+ + \text{CO}_2 + 6\text{e}^-
\]

\[
\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}
\]

\[
\text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]

A primary challenge and area for development in DMFCs is that of methanol permeability, as the current commercial membrane Nafion™ has a high methanol permeability and may only operate with diluted methanol solutions. In the event that methanol permeates through the membrane, it will be oxidized causing a mixed potential, production of waste heat, and reaction inefficiency. This phenomenon is called methanol crossover and is a major challenge in DMFC development at this time.¹⁰ As Nafion™ is the predominant commercial PEM candidate available, the current solution is to use a thicker membrane and dilute the methanol feed to about 1 M, although tailoring cell design may allow for increased concentration. Increasing the methanol concentration to improve the power density, either by modifying the Nafion surface or replacing it entirely with a different material, has also become
one of the main challenges in DMFC research. Successfully resolving this challenge would make DMFCs much more competitive with the rechargeable batteries presently used in cellular phones and other mobile electronic devices.\textsuperscript{10,11}

1.1.5.2 Hydrogen PEMFCs

Proton exchange membrane fuel cells which rely on hydrogen as a fuel utilize a thin proton exchange membrane material as the electrolyte portion of the membrane. A proton exchange membrane material, typically the same as that used in the electrolyte, is also used in the electrode in conjunction with a Pt/C or Pt/Rh/C catalyst. In a single cell, a membrane electrode apparatus (MEA) is formed from layering the polymer-catalyst electrode and a porous gas diffusion layer (GDL) on either side of the PEM electrolyte layer. In a PEMFC, hydrogen is dissociated on a platinum catalyst at the anode, with the protons migrating across the thickness of the thin PEM film to the cathode, where they reduce the oxygen to form water, as in the following equations:

\[
\begin{align*}
H_2 & \rightarrow 2H^+ + 2e^- \\
\frac{1}{2} O_2 + 2H^+ + 2e^- & \rightarrow H_2O
\end{align*}
\]

The primary advantage of the hydrogen PEMFC over other types of fuel cells is its power density, which is the highest of these fuel cells listed here. Furthermore, it is operable at room temperature, although there are some challenges in operations below 0\degree C. When the good start-stop capabilities are considered, this makes PEMFCs an ideal candidate for replacing internal combustion engines in personal vehicles. The drawbacks of using PEMFCs are not insignificant, but may be surmountable with further research and development. One challenge is the expensive
platinum catalyst and its inefficient loading in the MEA, with much of the catalyst material wasted. Management of water within the membrane is also problematic, with flooding at the cathode from water production a challenge as much as dehydration at the anode layer. Furthermore, the sensitive catalyst and low operating temperatures render the PEMFC sensitive to carbon monoxide and sulfur poisoning.\textsuperscript{5,7} Improvements in performance and reduction in the use of expensive materials therefore are critical to the development of PEMFCs as a viable commercial alternative to the internal combustion engine.

1.2 Proton Exchange Membrane candidates and properties

Polymer PEM candidates are typically sulfonated copolymers, with one component being a hydrophobic, non-proton-conducting material that provides good mechanical properties, while its sulfonated analog imparts proton conductivity and ionomeric behavior.\textsuperscript{13-16} These two components may be two statistically copolymerized comonomers—which typically represents the simpler and more affordable route—but for reasons which will be discussed below, use of these comonomers may also result in undesirable properties. The two components may also be polymerized into distinct oligomers, which are then coupled to produce a nanophase-separated multiblock copolymer. This latter option involves more complex synthetic procedures, but the resulting PEM performance advantages more than justify the additional synthetic complexity.

If they are to be used commercially, proton exchange membrane materials need to meet rigorous performance standards. Thus, they must feature high proton conductivity, low electronic conductivity, low permeability to both fuels and oxidants, ease of fabrication into
MEAs, low swelling/deswelling ratios, good mechanical properties, good thermal, hydrolytic, and oxidative stability, and low cost. Since certain properties typically afforded by the hydrophilic portion of the copolymer (especially water uptake sufficient for high proton conductivity) are in conflict with properties afforded by the hydrophobic portion (e.g., mechanical stability), it is essential that each component be present in specific ratios for improved performance.

Proton conductivity in an ionic copolymer involves one of two primary modes of transport: the Grotthus mechanism and the vehicle mechanism. The Grotthus mechanism consists of transport via a passageway of hydrogen bonds, effectively forming and reforming hydronium (H$_3$O$^+$) ions as a method of transit. The Grotthus mechanism is thought to be the primary means of proton transport when high levels of hydration are present. Conversely, the vehicle mechanism consists of the bulk diffusion of the proton and one or more water molecules, which then serves as a comparatively constant ‘vehicle’ for moving the H$^+$ across the membrane. The vehicle mechanism predominates at low hydration levels in the membrane as shown by Zawodzinski et al., and the slower kinetics result in a performance drop for most PEMs as the hydration level decreases.

High proton conductivity is desirable to maximize fuel cell performance, and is generally obtained by creating a material with a high ion exchange capacity (IEC), which is a unit measuring the number of milliequivalents of ion conducting molecule per gram of dehydrated polymer (meq/g). A related term, equivalent weight (EW), is measured in terms of g/eq and found by dividing the IEC into 1000. While low electronic conductivity is generally not a concern in materials with high proton conductivity, a high IEC can conflict with the desire for low swelling/deswelling ratios. Most PEM candidates require adsorbed water to facilitate rapid
proton transport across the membrane, and a higher content of conducting material increases the potential amount of adsorbed water. This water uptake may be measured strictly in mass and dimensional terms, such as percent mass water uptake (w/w) or percent dimensional swelling, both of which are unitless and described by the following equations:

\[
\text{Mass Water uptake} = \frac{\text{mass}_{\text{wet}} - \text{mass}_{\text{dry}}}{\text{mass}_{\text{dry}}} \times 100\%
\]

\[
\text{Dimensional Water uptake} = \frac{\text{length}_{\text{wet}} - \text{length}_{\text{dry}}}{\text{length}_{\text{dry}}} \times 100\%
\]

While mass or dimensional water uptake values are useful for studying the impact of swelling and deswelling over the operating lifetime of a fuel cell MEA, water uptake may also be described in terms of the number of water molecules per ionic group site (□). This measurement method is especially useful when trying to understand the impact of changing levels of membrane hydration on proton transport mechanisms as discussed above, particularly in assessing transitions between the two under partially hydrated conditions. Studying changes in \( \lambda \) with hydration, temperature, and changes in copolymer structure is useful for determining copolymer architecture with optimized conductivity.

It has been proposed that in a fully hydrated proton exchange membrane, water molecules in the hydrophilic phase exist in three different states.\(^{22-24}\) The first is non-freezing bound water, which has a strong affinity for the hydrophilic component of the copolymer structure and has a plasticizing effect, but does not show a freezing/melting behavior in differential scanning calorimetry. The second state is freezable bound water, which is loosely associated with the hydrophilic portion of the copolymer, and has a broad melting transition around 0°C. The third state is free water, which exhibits no apparent physical interaction with the hydrophilic copolymer and has a clear, sharp melting transition at 0°C.\(^{23}\)
While the thermal, hydrolytic, and oxidative stability of the PEM is generally unaffected by the level of water uptake, the mechanical properties may vary widely based on the level of hydration, due to the plasticization of the ionic component of the membrane by the adsorbed water molecules dropping both the glass transition temperature and the modulus of the membrane. Fuel and oxidant permeability is a greater factor in DMFC development, but it is important that the PEM material be impermeable to both hydrogen and oxygen to avoid crossover and a loss of cell performance due to fuel reacting at the incorrect location.\(^5,6\)

While no membrane meets all of these requirements, several candidates have been successfully developed for limited applications, such as space flight and prototype hydrogen fuel cell vehicles. The primary commercial candidate is Nafion\(^\text{®}\), although due to considerations of economy and performance, others are undergoing intense evaluation and development. These candidates are typically divided into fluorinated and hydrocarbon-based materials.

### 1.2.1 Nafion

The current predominantly used commercial PEM is Nafion\(^\text{®}\), which is a poly(perfluorosulfonic acid) statistical copolymer that has been the main standard for PEMs in recent decades. Nafion was developed in the 1960s and provided a superior alternative to the oxidatively unstable sulfonated polystyrene-divinylbenzene copolymers used in the Gemini space program.\(^13\) Nafion is produced by the DuPont Company, and the balance of desired properties as discussed earlier is tailored by varying the relative fractions of the comonomers as illustrated in Figure 1. Although the precise details of the synthesis of Nafion are uncertain, it is generally believed that after free radical polymerization of the unsaturated perfluoroalkyl
sulfonyl fluoride and tetrafluoroethylene, the copolymer is extruded in sulfonyl form where it is melt processible. Hydrolysis and acidification produce the final structure in Figure 1-1.\textsuperscript{13,25}

\[
\left[ \left( \text{CF}_2-\text{CF}_2 \right)_x \left( \text{CF-CF}_2 \right)_y \right]^n \text{OCF}_2-\text{CF-O(CF}_2)_2-\text{SO}_3\text{H} \]

Figure 1-1. The chemical structure of Nafion (R), wherein x and y are the mole fractions of each comonomer and n represents the total number of repeat units.

Nafion is produced in a variety of forms, and has a unique nomenclature in order to describe its details. The trade name is followed by a three number code, with the first two numbers indicating the equivalent weight (EW) and the third the thickness in mils. Therefore, Nafion 117 is an 1100 equivalent weight material which has been extruded in a film seven mils thick. Extruded Nafion is available under the trade names of Nafion 1110, 117, 115, and was previously available as Nafion 112. The 1100 EW Nafion series is commonly used, as it shows good conductivity (~100mS/cm) and a tolerable level of water uptake. However, the thicker membranes are needed in methanol fuel cells to combat the high methanol permeability, resulting in higher membrane resistance and a loss of performance.\textsuperscript{13,25,26}

Nafion can also be recast from a dispersion (sometimes incorrectly called a solution), which is available as Nafion (NRE) 212 and 211. Produced by heating extruded Nafion in an alcohol-water mixture, recast Nafion displays somewhat altered properties if the membrane is used as received due to the altered morphology, decreased level of crystallinity and the lack of anisotropic properties typically associated with extruded Nafion. Recast Nafion may be annealed
to restore its qualities to those of extruded Nafion, although the anisotropy produced during extrusion is, of course, not induced by annealing.\textsuperscript{13, 25}

Nafion dispersions are used in the membrane electrode assemblies (MEA) used for proton exchange membrane fuel cells (PEMFCs). However, regardless of the conducting electrolyte, determining the optimal MEA composition and application parameters for a new material can be extremely challenging. The slightly higher permeability to oxygen and hydrogen of Nafion compared to some hydrocarbon-based membranes is a roadblock to replacing Nafion as an electrode material.\textsuperscript{27, 28} This is an ongoing challenge for those investigating the application of novel alternatives to Nafion as potential PEM candidates, due to poor adhesion between the Nafion-based electrode and non-Nafion PEMs.\textsuperscript{28-31}

Nafion displays good chemical and oxidative stability—as do most fluoropolymers—due to the greater strength of the carbon-fluorine bond compared to the carbon-hydrogen bond.\textsuperscript{32} Nafion is thermally stable up to approximately 90$^\circ$C when fully hydrated, due to the plasticization effect of water lowering the phase transition temperature. The mechanical properties of extruded Nafion are adequate for use in fuel cells, but not comparable to those of some alternative PEM candidates based on engineering thermoplastics.\textsuperscript{33-36} These mechanical properties become further reduced at high temperatures and high levels of hydration.\textsuperscript{13, 33, 37} As noted earlier, however, the use of Nafion can be prohibitive due to its cost.\textsuperscript{13}

As briefly discussed, even though Nafion has shown unparalleled performance in hydrogen PEMFCs, its high permeability to methanol makes it less ideal for DMFCs. The thinner sheets of Nafion 112, 211 and 212 are used in PEMFCs, while thicker membranes of Nafion are used in DMFCs for reducing methanol crossover. Unfortunately, the use of these
thicker membranes increases the resistive losses of the DMFC, which then couples with the reduced power density due to the dilute methanol feed, thereby resulting in a DMFC that operates well below its potential performance with a thinner, more resistant material. Modifying the Nafion surface for improved durability in DMFCs has become a significant area of research, but the inherent vulnerability of the material also makes the development of a replacement PEM with low methanol permeability a challenging goal. 

Due to the extensive and expansive application of Nafion, it is one of the most well-studied PEM ionomers available. In spite of this investigation, many details of its thermomechanical behavior and morphology have been a source of contention among researchers. As recently as 2004, Mauritz and Moore published a significant body of evidence indicating that the alpha transition occurring at 244 °C was indicative of an ionic transition of the copolymer, while the beta transition at 160 °C was confirmed to be the actual glass transition temperature.

1.2.1.1 Morphology

The morphology of Nafion has been characterized by multiple types of microscopy and spectroscopy over the years, and much like the study of the thermomechanical transitions, this has been an unclear course of study. The history of the study of Nafion’s morphology and structure-property relationships has involved a wide array of models and theories, which have evolved as a greater variety of experimental techniques became available and then refined in precision. This study has been complicated in part by the available technology at the given time,
but also the inability to precisely characterize the molecular weight, make a true solution, or have a more profound understanding of the synthesis of Nafion.\textsuperscript{25}

![Figure 1-2. Cluster-network model of hydrated Nafion ion channels.\textsuperscript{25}](image)

Geirke and coworkers proposed a schematic showing the cluster-network theory possibly responsible for the swelling behavior of Nafion, which shows several hydrophilic clusters with narrow interconnecting channels (Figure 1-2)\textsuperscript{44-46}. This theory was supported by a series of experimental techniques. First, small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD) data showed peaks that increased in intensity in unhydrolyzed Nafion samples with higher EW—and therefore higher ionic content—but which disappeared when the temperature approached the melting point of polytetrafluoroethylene (PTFE), implying they were associated with crystalline organization. After hydrolysis, an additional peak appeared indicating ionic clusters spaced at 3-5nm. \textsuperscript{45} However, these ionic peaks increased with a decrease in EW, and increased with added water, leading Geirke and coworkers to conclude that hydrated Nafion had a morphology of spheroid ionic clusters with an inverted micellar structure.

Gierke’s model remained the most popular and widely accepted for years, and most models which followed were adapted in some way from his work. Fujimora et al. used derivatized Nafion in scattering and diffraction groups and asserted that the morphology was
better described as an intraparticle core-shell model, wherein an ion-rich core is surrounded by an ion-poor shell phase, in a matrix which is largely hydrophobic copolymer. This is also referred to as the depleted-zone core-shell model. \(^{47}\) Cooper et al. argued that the morphology supported a structure of uniformly hydrophilic spheres distributed across a largely hydrophilic phase. \(^{25}\) The morphological model most commonly accepted among the research community is now the cluster-multiplet model as developed by Moore and Eisenberg. Eisenberg was the first researcher to propose a model incorporating both the microscopy and scattering data with the structure-property information available, based on a series of fundamental assumptions regarding the electrostatic interactions prompting the aggregations of ionic groups and the energetics of ionic aggregation and destabilization. In the cluster-multiplet or EHM (Eisenberg, Hird, and Moore) model, an ionic aggregate serves as an anchor, reducing mobility in the immediate area around it by binding the ionic portions of the polymer chains. This anchoring effectively
Figure 1-3. Impact of water volume fraction on Nafion morphology according to the cluster-multiplet model.¹
increases the molecular weight of the polymer chains, reducing free motion of the adjoining hydrophobic portions.  

As can be seen above in Figure 1-3, the impact of increasing water content has a very significant effect on Nafion’s molecular architecture, which is well described by the cluster-multiplet model. In the completely dry state, the membrane morphology consists of largely isolated aggregates 1.5 nm in diameter, approximately 2.7 nm apart. Once a small volume fraction of water is introduced, the aggregates swell (spherical geometry continues at this point to minimize surface energy), until a sufficient volume (dependent on EW) allows the percolation threshold to be reached, forming cylindrical pathways of water in between the increasingly swollen ionic clusters. If the volume fraction ($\phi_w$) of water exceeds 0.5, the phases will invert and the hydrophilic domain will form an interconnected network of rods, eventually producing a colloidal dispersion of rods as the volume fraction approaches 1.  

1.2.1.2 Related polyperfluorosulfonic acid copolymers

Other materials featuring structural variations of Nafion have also been developed for PEMFC applications. These materials include Aciplex, produced by the Asahi Chemical Company, and Flemion, produced by the Asahi Glass Company. Although their synthetic and performance details vary, both feature a number of Nafion-like drawbacks, such as expensive comonomer production and copolymer synthesis, poor mechanical properties, and a low glass transition temperature that reduces the ceiling operating temperature for fuel cell use.
Dow produced a membrane in the 1980s, which is now being synthesized by Solvay Solexis via a separate synthetic method, which is known as Hyflon Ion.\textsuperscript{49-51} Hyflon Ion has a structure very similar to that of Nafion, but with a shorter side chain as shown below in Figure 1-4.\textsuperscript{49} This shorter side chain affords a higher glass transition temperature than Nafion while still showing good oxidative stability. This feature also facilitates greater efficiency at higher operating temperatures, and thus a slightly improved ability to avoid catalyst poisoning. Research to characterize Hyflex Ion as a potential alternative to Nafion is ongoing.\textsuperscript{49, 51-56}

\[
\begin{align*}
-(\text{CF}_2\text{-CF})_n-(\text{CF}_2\text{-CF}_2)_m & - \\
\text{OCF}_2\text{CF}_2\text{SO}_3\text{H} & \\
\text{(a)}
\end{align*}
\]

\[
\begin{align*}
-(\text{CF}_2\text{-CF})_n-(\text{CF}_2\text{-CF}_2)_m & - \\
\text{OCF}_2\text{CFCF}_3\text{-OCF}_2\text{CF}_2\text{SO}_3\text{H} & \\
\text{(b)}
\end{align*}
\]

Figure 1-4. Comparison of Hyflex Ion (a) and Nafion (b) chemical structures.\textsuperscript{49}

1.2.2 Hydrocarbon Membranes

Hydrocarbon membranes have been explored during the search for an alternative to Nafion\textsuperscript{TM}, primarily due to their lower cost and methanol permeability, less hazardous synthetic procedures, greater monomer availability and superior mechanical properties.\textsuperscript{13, 14, 36} Due to issues of thermal and oxidative stability, as well as in the interest of improved mechanical properties, many hydrocarbon membranes under development currently are aromatic-based or
are made from a combination of aromatic and heterocyclic molecules such as polybenzimidazoles.\textsuperscript{57-59} The primary conducting ionic group in most hydrocarbon membranes has been sulfonic acid \textsuperscript{13, 36, 60-64}, although bound and absorbed phosphoric acid has been investigated as well, primarily in polybenzimidazoles.\textsuperscript{65-67, 57, 65, 68}

The earliest hydrocarbon membranes used in PEMFCs were the sulfonated polystyrene-divinylbenzene materials used in the Gemini program by NASA.\textsuperscript{13} However, their poor oxidative stability resulted in an insufficient operational lifetime, as the membranes degraded in the cell during use. One approach, taken by Ballard, to overcome this challenge was to produce a sulfonated polystyrene with fluorine substituted on the aliphatic carbons. This avoids the difficulty in aliphatic hydrogens, which are susceptible to oxidative degradation in the harsh fuel cell environment.\textsuperscript{6, 13, 25} The material introduced by Ballard Advanced Materials Corporation is synthesized from a combination of sulfonated $\alpha,\beta,\beta$-trifluorostyrene and substituted $\alpha,\beta,\beta$-trifluorostyrene. While successful at mitigating oxidative degradation to the main chain, only limited research has been reported on these materials, presumably due to the cost of production and lack of competitiveness with current membranes such as Nafion.\textsuperscript{13}

Dais Analytic has also produced a sulfonated styrene-ethylene-butylene-styrene (SEBS) block copolymer membrane. As the styrene is synthesized via the easily controlled free radical polymerization, control of the degree of sulfonation and oligomer molecular weight is relatively easy. While this membrane shows good conductivity and is more affordable, particularly due to the phase-separated morphology, it shares the oxidative susceptibility of the earlier polystyrene-divinylbenzene materials. However, Dais Analytic is developing these membranes for applications of 1 kW or less, with a ceiling operating temperature of 60°C, with the hopes of developing a functional system under a lower oxidative stress.\textsuperscript{13, 69, 70}
Other sulfonated polystyrene copolymers have been developed using various synthetic schemes such as grafted copolymers\textsuperscript{71, 72, 72}, multiblock copolymers with polyethylene\textsuperscript{70, 73} and polytetrafluoroethylene, block copolymers with poly(vinylidene fluoride)\textsuperscript{74}, and radiation grafting\textsuperscript{75}. While sulfonated polystyrene has been thoroughly investigated for applications in PEM fuel cells, there is increasing focus on copolymers with an aromatic-based backbone or even all-aromatic polymer chain structure, both for improved thermomechanical properties and increased thermal and oxidative stability.

1.2.3 **Sulfonated Poly(arylene ether)s**

The poly(arylene ether) family, typically with sulfonic acid derivatization, have been one of the most ideal hydrocarbon alternative PEM candidates explored in the literature, due to their excellent mechanical properties, high thermal and oxidative stability, and high glass transition temperature.\textsuperscript{36, 76-78} Poly(arylene ether) copolymers are a group which encompasses a range of related materials that have also been investigated for possible use in PEMFCs such as poly(arylene ether sulfones)\textsuperscript{79, 80}, poly(arylene ether ketone)s\textsuperscript{81, 82}, poly(arylene ether ether ketone)s\textsuperscript{82, 83}, poly(ether ketone)s\textsuperscript{84} and other copolymers. Nonsulfonated and sulfonated bisphenol-A based poly(arylene ether sulfone)s and closely related materials have been investigated in a variety of other membrane applications, such as reverse osmosis\textsuperscript{85-87}, forward osmosis\textsuperscript{88}, ultrafiltration\textsuperscript{89}, nanofiltration\textsuperscript{90-92}, and gas separation\textsuperscript{93}.

Kreuer\textsuperscript{84} has asserted that poly(arylene ether)-based PEMs would have smaller hydrophilic channels than perfluorosulfonic acid-based (PFSA) copolymers due to their more
rigid aromatic structure. These smaller channels lead to both greater distance between sulfonic acid groups (which migrating protons must cross during transport), as well as a higher degree of branching of the hydrophilic pathways for ions, which increases the number of dead-end pathways and thus decreases overall PEM efficiency.\textsuperscript{84} While this appears to be accurate for statistically copolymerized poly(arylene ether sulfone)s (PAES) materials, longer hydrophilic and hydrophobic channels may be seen in multiblock copolymers, which are more ordered than those in PFSA copolymers; this will be discussed in greater detail later.\textsuperscript{20, 84, 94}

Poly(arylene ether sulfone)s (PAES) have a notably lower permeability to methanol, and are being investigated along with a variety of similar copolymers as a replacement for Nafion in DMFCs. Of the materials available in the poly(arylene ether) material family, PAES materials show superior thermal stability due to the resonance structure afforded by the sulfone group and the high oxidative state of the sulfur atom, allowing for melt processing at up to 400\textdegree{}C for non-ion-containing copolymers.\textsuperscript{95, 96} The flexible ether linkages allow for reduced material rigidity, and the mechanical properties and glass transition temperature may be tailored by incorporating different functional groups into the polymer backbone.\textsuperscript{63, 96-99} However, their implementation is dependent on the development of a suitable electrode material or the optimization of their incorporation into an electrode formula, as Nafion-based electrodes are still used in evaluation and have poor compatibility at the electrode-electrolyte interface.\textsuperscript{100}

### 1.2.3.1 Post-sulfonated polymer

Post-sulfonation using concentrated sulfuric acid, fuming sulfuric acid, chlorosulfonic acid, or sulfur trioxide is a widely used procedure to sulfonate aromatic copolymers. It has been a
very common technique due to its flexibility and reliability as a means to produce a partially sulfonated polymer from the inexpensive commercial polymer, rather than taking the resources to develop a synthetic scheme from sulfonated comonomers.

Early work in sulfonation of poly(arylene ether sulfone)s typically entailed the reaction of the polymer in sulfuric acid, chlorosulfonic acid, fuming sulfuric acid, and related compounds. The initial investigations into the viability of partially disulfonated poly(arylene ether sulfone)s in the McGrath group\textsuperscript{101} were performed on Udel, which was sulfonated by means of a 2:1 ratio of SO\textsubscript{3} and triethyl phosphate as was described by Noshay and Robeson\textsuperscript{102}.

The disadvantage of this means of sulfonated poly(arylene ether sulfone) production is that the electrophilic aromatic substitution onto the activated ortho position of the aromatic ring produces a fairly unstable end product. The post-sulfonated poly(arylene ether sulfone) is also limited in the degree of sulfonation, due to the presence of only one sulfonic acid group per repeat unit. The resulting sulfonated PAES is difficult to control in both degree of sulfonation and molecular weight, and may also feature degradation of the polymer backbone which would reduce the previously exceptional hydrolytic stability.\textsuperscript{13}

\textbf{1.2.3.2 Directly copolymerized PAES based on biphenol and DCDPS}

To overcome the disadvantages of the post-sulfonated PAES, the McGrath group adapted a procedure from Ueda et al., developed for other purposes\textsuperscript{103}, which provided a means of sulfonating 4,4’-dichlorodiphenyl sulfone (DCDPS) by means of the reaction shown in Figure 1-5 to produce 3,3’-disulfonated, 4,4’dichlorodiphenyl sulfone (SDCDPS).\textsuperscript{15,104,105} This synthetic procedure meant that the SDCDPS could then be copolymerized with biphenol and DCDPS to
produce ‘directly copolymerized’ sulfonated poly(arylene ether sulfone), as shown in Figure 1-5. The synthesis has been further refined to improve the yield of the monomer in an improved one-step process by modifying the reactant mole ratio, and the purity of SCDPS is easily characterized with UV-VIS spectroscopy.

![Figure 1-5. Initial synthetic procedure for producing 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone.](image)

The development of these materials offers several practical advantages over post-sulfonated PAES, while the only arguable disadvantage is that associated synthetic procedures are somewhat more involved. The comparative structures of post-sulfonated and directly copolymerized poly(arylene ether sulfone)s are shown in Figure 1-6. It should be noted that even though the single sulfonic acid is attached to the activated biphenol ring in the post-sulfonated copolymer, it is more unstable and less acidic than the two sulfonic acid groups bound to the DCDPS portion of the directly copolymerized PAES. In addition to the added stability and acidic character, the directly copolymerized copolymer may be easily tailored to the desired degree of disulfonation and molecular weight.

The sulfonated poly(arylene ether sulfone) developed by the McGrath group is known as
BPS, which stands for BiPhenylSulfone. The degree of sulfonation is denoted by adding the percent disulfonated monomer on the end, i.e., BPS-35 describes a copolymer with 35% of the DCDPS comonomers being disulfonated. The copolymers are synthesized in salt form, but are converted to acid form by boiling the membrane in 0.5 M H$_2$SO$_4$ for 2 hours. The characterization steps may require membranes to be in one form or the other, which is also indicated in the copolymer nomenclature. For example, BPS-35 denotes a membrane in salt form, while BPSH-35 describes a membrane in acid form.

![Figure 1-6. Comparison of structures of post-sulfonated (top) and directly copolymerized (bottom) poly(arylene ether sulfone) chains.](image)

The directly copolymerized random PAES or BPS depicted in Figure 1-7 has been characterized over a range of molecular weights and degrees of disulfonation. While changes in the molecular weight do not significantly impact the proton conductivity, surface morphology, or water uptake at a 35% disulfonation level, the superior mechanical properties deteriorate
between 30 and 40 kg/mol number average molecular weight.\textsuperscript{98,107} At molecular weights above approximately 40 kg/mol, however, the copolymer produces a tough, ductile, flexible membrane with a modulus of at least 1.4 GPa.\textsuperscript{98}

Increasing the degree of sulfonation in the BPS copolymer causes an increase in the glass transition temperature, water uptake and proton conductivity values, to a point as shown below in Figure 1-7. Between 50 and 60% disulfonation the polymer becomes water soluble, and the hydrophilic phase becomes semicontinuous, causing the membrane to swell much more significantly and conductivity measurements to be impractical.

![Figure 1-7. Mass water uptake and proton conductivity properties of BPSH polymer as a function of disulfonation, illustrating the impact of the percolation threshold on the former.](image)

This limit is called the percolation threshold, and it is a concern with all linear partially-ionic systems. The percolation threshold can be bypassed by using multiblock copolymers which compartmentalize the advantages and disadvantages of each phase into a hydrophilic and hydrophobic oligomer; these oligomers are synthesized separately and then coupled.\textsuperscript{108-110} This approach will be discussed with respect to the PAES-based multiblocks developed in the
McGrath group in greater detail below.

Another means of improving conductivity by increasing the degree of disulfonation (without exceeding the percolation threshold) is to incorporate crosslinkable groups into the copolymer and forming a crosslinked gel. This process limits water swelling, ensuring that the network will remain water insoluble, while maintaining a high concentration of sulfonic acid groups.\textsuperscript{111,112}

\begin{center}
\includegraphics[width=\textwidth]{figure1-8.png}
\end{center}

\textbf{Figure 1-8.} Synthetic scheme of the statistically copolymerized BPSH-xx system, where XX represents the degree of disulfonation.\textsuperscript{13}

\subsection*{1.2.3.3 PAES comonomer variation and properties}

Having gained a fundamental understanding of the behavior of the BPS-based series, the McGrath group as well as other researchers sought to expand on this by substituting a bisphenol A comonomer for the biphenol into the general scheme discussed above and shown in Figure 1-8. This so-called BisA copolymer was done with the intent of increasing free volume in the
resulting copolymer and possibly providing a boost in conductivity, due to the ionic groups having a greater mobility and being able to form larger, more continuous ion-conducting channels than in the biphenol-based BPS. The same procedure was also investigated for a fluorine-substituted version of the aliphatic hydrogens of the BisA copolymer, with the intent of reducing water uptake and improving adhesion to the Nafion-based MEA electrodes.

A variety of hydrophobic comonomers have been investigated with the intent of improving membrane properties. A copolymer of SDCDPS, DCDPS, and naphthalene based dianhydride produced a statistical polyimide with the intent of application in DMFCs which demonstrated good mechanical properties and low methanol permeability, but less than competitive proton conductivities.

Another study investigated the impact of incorporating phosphine oxide into the copolymer backbone in order to further improve oxidative stability, but the conductivity results were not comparable to BPSH copolymers of a similar IEC. Other researchers have pursued the incorporation of phosphine oxides into novel PEM copolymers, with similar results.

There has also been some investigation into alternative hydrophilic comonomers for improved PEM performance. While the majority of the directly copolymerized, partially disulfonated poly(arylene ether sulfone)s and related materials investigated in the McGrath group contain 3,3’-disulfonated-4,4’-dichlorodiphenyl sulfone and biphenol, an alternative statistically copolymerized PEM was produced from the reaction of SDCDPS and hydroquinone, resulting in a material with a higher ionic density and improved proton conductivity.

1.2.3.4 PAES Multiblock copolymers and properties
While the research on the statistical copolymers detailed above resulted in a broad understanding of how to tailor proton conductivity, water uptake, mechanical strength and glass transition temperature by selecting both comonomer chemical groups and the degree of disulfonation, the proton conductivity performance under low partially humidified conditions remained uncompetitive with Nafion. In order to overcome this challenge, researchers in the McGrath group developed multiblock copolymers, with hydrophobic and hydrophilic comonomers respectively polymerized into separate oligomers, then coupled together.\textsuperscript{82, 121-123} Other research groups have taken a similar approach in the development of multiblock PAES and poly(arylene ether) systems.\textsuperscript{108, 124, 125} The multiblock approach has also been evaluated for less similar copolymer systems.\textsuperscript{60, 126}

The use of multiblock copolymers with nanophase-separated hydrophobic and hydrophilic regions has provided several advantages over using statistically copolymerized copolymers. A higher overall IEC may be obtained by using hydrophilic oligomers which are 100\% disulfonated, but are prevented from being water soluble by the adjoined hydrophobic oligomers. Also, the separation of the phases allows for easier water retention under partially humidified conditions, resulting in higher proton conductivity values even after partial dehydration. Finally, the water swelling which does occur is anisotropic, with little swelling in the x and y directions, or the in-plane, and most swelling in the z direction, or through-plane. As the block length increases, both the increase in proton conductivity performance under partially humidified conditions and the swelling anisotropy become more pronounced, along with the development of evidence from morphological images that long-range order develops as well.\textsuperscript{127-131, 122, 67, 132}

The McGrath group has investigated multiblock copolymers of varying composition and
sequence length. In this research, the synthetic goals have been targeted with the intention of improving nanophase separation, and thus performance under partially humidified conditions, improving water uptake behavior, and improving overall proton conductivity values by modifying the ratio of hydrophilic to hydrophobic block lengths or molar ratios, and by using a hydroquinone-based hydrophilic block with a higher ion exchange capacity.\textsuperscript{17, 79, 133, 134}

There have been several investigations in the synthesis and characterization of multiblocks with partially fluorinated hydrophobic blocks, with several objectives in mind.\textsuperscript{129, 132, 135, 136} First, the presence of the fluorine will ideally boost the phase separation of the hydrophilic and hydrophobic domains, facilitating the formation of co-continuous hydrophilic channels. Secondly, the highly hydrophobic character of these blocks is hoped to decrease overall water uptake of the multiblock copolymer, and finally in the stage of MEA fabrication, the fluorine content is hoped to boost adhesion with the Nafion-based electrode.\textsuperscript{132, 137} Other research groups have incorporated fluorenyl groups into their multiblock copolymers with many of these same goals in mind.\textsuperscript{138}

Other multiblock copolymers have been produced based on incorporating heterocyclic copolymers such as benzimidazole as the hydrophilic oligomer (after doping with phosphoric acid) with a nonsulfonated DCDPS-based hydrophobic oligomer, with the intent of producing stronger, more temperature-resistant materials for high-temperature, partially humidified operating conditions.\textsuperscript{67} A polyimide-BPSH100 copolymer was also synthesized, with the intent of producing improved mechanical properties and improved ceiling operating temperatures, as well as the general improvement of proton conductivity performance over that of statistically copolymerized polyimides with SDCDPS.\textsuperscript{115, 116, 122, 139}
1.2 Morphology of PEM Multiblock Ionomers

The arrangement and interactions of the ionic and non-ionic components of ionomers have a powerful impact on the resulting ionomer morphology. Analyzing the factors which impact ionomer morphology is a complex and subtle task, requiring an array of microscopic and spectroscopic techniques. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) may be used to indicate phase separation or crystallinity, where the former acquires images of the upper surface of a copolymer and the latter shows the morphology of the bulk phase. Small angle x-ray scattering and wide angle x-ray diffraction may confirm the presence and degree of crystallinity. In multiblock copolymers, $^{13}$C NMR can verify block formation and the lack of randomization due to ether-ether interchange, a frequent concern in coupling reactions occurring at high temperatures. Thorough characterization of a given ionomeric copolymer is also critical to understanding the performance as a function of synthetic and processing conditions, particularly in block and blended copolymers. While the hydrophilic and hydrophobic segments of random, or statistically copolymerized ionomers are typically too short to be able to separate into recognizable phases, blocks of increasing length have been shown to develop increasing domains of phase separation. As this phase separation is particularly critical for improvement of PEM performance, the ability to characterize both bulk and surface morphology is critical for the understanding of how these multiblock copolymers behave.

An additional variable which complicates the behavior of multiblock copolymers and the study of their morphology is the impact of various casting conditions and solvents. Even in statistically copolymerized materials, varying the time and temperature of acidification treatment in already cast membranes results in very different morphologies, water uptakes, and proton
conductivity performances. Studies performed on styrene-butadiene multiblock copolymers have shown that the kinetics of phase separation, and therefore the timing of the temperature ramp in solution casting, play a crucial role in the resulting morphology of solution-cast films. While the differences in the observed morphology are not always readily observable or easy to interpret, the impact of changing the times and temperatures of solution casting, or the nature of the solvent used, may still have a marked impact on the performance of the produced PEM.

The morphology of a multiblock copolymer is generally considered a function of the relative volume fraction of its component blocks. The generally accepted gradient of morphologies are as follows: below 20 wt%, the minority polymer forms a structure of spheres within the matrix of the majority polymer, at roughly 20-35 %, the minority polymer forms a structure of cylinders within the majority polymer, and at 40-60% both polymer phases form a lamellar structure. In the multiblock copolymers developed within the McGrath group, within many multiblock series there were both equal block length hydrophilic-hydrophobic multiblocks synthesized, as well as offset block lengths favoring a more hydrophobic or hydrophilic majority. While a lamellar structure was still observed at offset block lengths, the ideal compromise of hydrophobic and hydrophilic properties was generally found at equal block lengths, and out of a series of several equal oligomer block lengths, the multiblock synthesized from approximately 10kg/mol oligomers tended to display the best proton conductivity performance under partially humidified conditions. It may be that the very long-range order developed in multiblocks made from higher molecular weight oligomers actually decreases the number of available ion channels, as a portion of the protons must travel through lengthy dead-end pathways during proton transport.
1.4 Characterization methods

The nature of the structure and performance of PEMs is broad and complex. To obtain a comprehensive understanding of a novel membrane, studies must investigate its surface and bulk morphology as discussed in the previous section (the former under heated and hydrated conditions if possible), thermomechanical behavior, proton conductivity under fully and partially hydrated conditions, and mechanical properties. While Scanning Probe Microscopy (SPM) is very effective at describing the morphology of a material’s surface, a good understanding of a PEM ionomer’s through-plane conductivity and morphology cannot be acquired without thorough characterization of the copolymer’s bulk morphology, via Transmission Electron Microscopy (TEM).

The thermomechanical properties and thermal stability, as acquired via differential scanning calorimetry, dynamic mechanical analysis, and thermogravimetric analysis, are helpful for confirming the thermal transitions of the material or the separate phases of a material, as well as the possible limits of thermal exposure and the likely mechanism for thermal degradation.

The proton conductivity performance of a given material is fundamentally the most critical variable studied, and it is most often measured by impedance spectroscopy.

1.4.1 Scanning Probe Microscopy (SPM)/Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is the primary application of scanning probe microscopy (SPM), in which information about the height and surface hardness of a given material is obtained by scanning a nanomachined probe tip with a defined rigidity across a small
defined surface area. This information is compiled, line by line, to create a composite ‘image’ which illustrates the material morphology and topography. AFM is one of the few characterization techniques which features atomic resolution, although most imaging is performed on a much coarser level. The quality of imaging resolution and reproducibility is most dependent on the tip quality and compatibility with the sample surface in terms of spring constant, applied force, and tip composition, as well as a sample surface and working environment free of contamination.

While scanning, the probe tip is maintained at a constant height above the material surface by feedback to the piezoelectric actuator upon which it is mounted. This feedback is acquired from a laser beam which bounces off of the probe tip as it scans across the sample surface, and then lands upon a photodiode. The position of the beam on the photodiode is used to both calculate the surface topography and to determine the amount of correction necessary to return the probe tip to a constant height.

During each scan of the probe tip, there are several different types of energetic interactions between the tip and surface. At very low tip-surface distances favored by contact mode AFM, repulsive forces dominate. As the tip moves further away from the surface, the repulsive forces quickly drop off and are replaced by attractive forces such as Van der Waals, which is the region typically favored by noncontact mode.

There are three primary modes for collecting AFM images, non-contact mode, contact mode (in which the scanning probe or tip comes into actual contact with the material surface) and tapping mode (in which the probe or tip is repelled from the surface). There are also a number of specialized applications of AFM, such as electrostatic force microscopy, chemical
force microscopy, AFM coupled with thermomechanical analysis, and magnetic force microscopy.\textsuperscript{148, 150}

Non-contact mode is distinguished by the distance at which the tip oscillates, typically 5-15 nm from the surface, without physical contact with the surface at any point. At this distance, while long range Van der Waals forces are detected by the tip, the repulsive and much of the attractive forces which predominate tapping and contact mode are not influential. However, non-contact mode does leave the tip susceptible to errors caused by any solid or liquid components suspended in the air which have adsorbed onto the sample area.\textsuperscript{148}

Contact mode mode is distinguished by the tip maintained in near-actual physical contact with or effectively in contact with the sample surface, where repulsive atomic forces push the tip away. Constant deflection maintains the distance between the surface and the tip static.\textsuperscript{148}

Tapping mode is a hybrid of both contact and non-contact mode in which the tip is lowered while oscillating at resonance frequency until it comes into physical contact with the tip surface. The oscillations prevent destruction of the fragile tip as the tip is lifted from the surface before any features on the surface may damage it. This mode is ideal for the high-resolution topographical mapping of complex surfaces.\textsuperscript{149-151}

\textbf{1.4.2 Transmission Electron Microscopy (TEM)}

Transmission electron microscopy (TEM) uses an electron beam under high vacuum in order to image a sample. Unlike a scanning electron microscope (SEM), the TEM produces an image by passing the electron beam through a very thin sample, rather than acquiring an image
from a reflected beam. As described by Egerton, the somewhat complex system of the TEM may be broken down into three main components: the illumination system, consisting of the gun and condensing lenses, the specimen stage, which allows for the entry and withdrawal of the sample as well as its manipulation within the vacuum chamber, and the imaging system, which entails a minimum of three lenses which produce a diffraction pattern or image on a screen, film, or monitor.\textsuperscript{152}

The most critical part of acquiring a TEM image lies in the sample preparation. If the sample consists of two phases which differ significantly in electron density, such as polydimethylsiloxane and a polyethylene or polypropylene, staining may not be necessary. However, for most materials, a stain is applied which will selectively adhere to one of the material phases. The stain can be selected based on the chemical composition of the selected phase. After staining, the sample is typically embedded in an epoxy resin and microtomed, or cryomicrotomed with liquid nitrogen cooling in the case of a glass transition temperature below ambient temperature. The thin sections (~100 nm) are collected and stored on sample holding grids, prior to imaging.\textsuperscript{148, 152, 153}

Osmium tetraoxide is frequently used to stain materials which contain frequent alkene bonds, by cross-linking two of these carbon-carbon double bonds into four single bonds between the carbons and the four oxygens of the osmium tetraoxide molecule. Osmium is also used to stain polymers contain ether bonds, amide bonds, ethers, esters, alcohols, aldehydes, amines, and acids.\textsuperscript{148, 154}

Ruthenium tetraoxide is primarily used to stain aromatic-based copolymers, as well as saturated hydrocarbons in aliphatic copolymers. It is also used in polymers with ether, amine,
alcohol, aldehyde, ester, and acid groups in lieu of osmium tetraoxide.\textsuperscript{148, 154} Other stains commonly used include ebonite, hydrazine, and silver sulfide, but many chemicals including an atom with a high electron density which may preferentially bond with a given chemical group may be used.\textsuperscript{148, 153}

The disulfonated poly(arylene ether sulfone) copolymers developed in the McGrath group are typically stained via titration with a cesium hydroxide or lead (II) acetate stain in aqueous solution. In this case, the cation simply exchanges with the sodium or protons associated with the sulfonic acid groups.

### 1.4.4 Impedance Spectroscopy for proton conductivity measurement

Good proton conductivity, coupled with poor electron conductivity, is one of the most critical requirements of a proton exchange membrane. Proton conductivity can be measured either across the thickness of the membrane, termed through-plane, or along the plane of the membrane surface, termed in-plane. Although through-plane proton conductivity measurement is a more accurate approximation of PEM performance in a test fuel cell, it is a more sensitive and cumbersome procedure as the resistance across the thickness of a membrane which may be as little as 20 microns is difficult to measure accurately and precisely. Therefore, more measurements are performed in-plane, using AC impedance spectroscopy.

AC impedance spectroscopy is the most common method for quickly and precisely measuring proton conductivity prior to assembling a sample into a MEA for testing in a fuel cell.
testing apparatus. This method uses an Impedance/Gain-Phase Analyzer over the frequency range of 10 Hz – 1MHz, using a cell geometry indicated in Figure 1-11, chosen such that the membrane resistance dominated the response of the system. The resistance of the film was measured at the frequency where the minimum response is found, and the conductivity is then calculated according to the following equation:

\[
\sigma = \frac{l}{Z' A}
\]

In which \(s\) represents the proton conductivity, \(l\) is the distance between electrodes, \(A\) is the cross-sectional area of the sample membrane (3 in Figure 1-11), and \(Z'\) is the resistance value determined from the impedance response.\(^{155}\)

![Figure 1-9. Overview of a conductivity testing cell. (1) Ceramic or Teflon block, (2) Screws, (3) Open window to allow sample equilibration in ambient conditions, (4) Sample, (5) 0.1 mm Pt electrodes, (6) Conductive wire for carrying signal.](image)


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2.0 Characterization of multiblock copolymers based on hydrophilic disulfonated poly(arylene ether sulfone) and hydrophobic partially fluorinated poly(arylene ether ketone) for use in proton exchange membrane fuel cells

Abstract

Novel multiblock copolymers were synthesized with a partially fluorinated hydrophobic oligomer incorporating 4,4’-hexafluoroisopropylidenediphenol and biphenol, and a hydrophilic oligomer consisting of BPSH100. The fluorinated comonomer was incorporated with the intent of improving phase separation between the two components, decreasing overall water uptake, and possibly boosting adhesion to a Nafion-based electrode in MEA fabrication. The copolymer series was characterized by means of water uptake, surface morphology using atomic force microscopy (AFM), and proton conductivity under both fully and partially hydrated conditions. The multiblocks showed improvement over the performance of randomly copolymerized controls in proton conductivities at low relative humidities, particularly at higher oligomer block lengths. There was a similar block length effect shown with the anisotropy of dimensional swelling data, and long-range order was shown to develop at higher block lengths in AFM imaging.

2.1 Introduction

Due to the associated economic, environmental, and political costs of relying on the world’s limited supply of fossil fuels, a number of alternative energy candidates are being considered.¹ In the niche of fueling vehicles for personal transportation, one of the most viable
candidates is the proton exchange membrane fuel cell (PEMFC). Due to its relatively simple design and the inherently superior efficiency of electrochemical reactions over thermal combustion, hydrogen PEMFCs offer a significant improvement in efficiency while producing only water and heat as waste.

While PEMFCs have been under development since the first manned spaceflight, one of the most important parts of this development has been the proton exchange membrane (PEM) material. A number of critical parameters are needed to create a good membrane, including high proton conductivity, low electronic conductivity, low permeability to both fuel and oxidant, ease of fabrication into MEAs, low swelling/deswelling ratios, good mechanical properties, good thermal, hydrolytic, and oxidative stability, and low cost. There are presently no materials that sufficiently meet all of these requirements, and the focus of research to find a good candidate that presents a viable compromise.

The current standard is Nafion, which is a poly(perfluorosulfonic acid) ionomer exhibiting good proton conductivity across a range of partially humidified conditions. The downside of Nafion is that it is very expensive and has a low ceiling operating temperature of about 80°C due to the plasticization effect of water. Additionally, Nafion has a high permeability to methanol, which renders it a poor candidate for methanol-based PEMFCs (also known as direct methanol fuel cells or DMFCs), and its mechanical properties are inadequate for such use.

To remedy these deficiencies, a great deal of research has occurred in developing partially sulfonated poly(arylene ether)s and related materials, which display much lower methanol permeabilities, greater affordability, excellent mechanical properties and high glass transition temperature. The McGrath group at Virginia Tech has, in particular, developed a
series of statistically copolymerized partially sulfonated poly(arylene ether sulfone)s, which show comparable proton conductivity under fully hydrated conditions. On the down side, their performance is compromised under partially humidified conditions.\textsuperscript{4,11-13} One resolution to this problem has been to produce hydrophilic-hydrophobic multiblock copolymers, where nanophase separation of the proton-conducting domains and the hydrophobic domains (which provide mechanical strength) affords more competitive and sometimes superior performance under partially humidified conditions in comparison to Nafion controls.\textsuperscript{14-16} An unanticipated benefit of the phase separation was the appearance of anisotropic dimensional swelling behavior in the hydrated membranes, which show smaller in-plane swelling in favor of increased through-plane swelling.\textsuperscript{17,18} This feature is helpful in minimizing stress fractures in the MEA during the hydration/dehydration cycles associated with daily operation.

In this research, a multiblock copolymer series was synthesized by coupling a hydrophobic block containing partially fluorinated poly(arylene ether ketone) (6FK) and a hydrophilic block consisting of fully disulfonated poly(arylene ether sulfone) (BPSH100). The details of the synthesis have been published but will be summarized here.\textsuperscript{19} The partially fluorinated monomer was incorporated into the hydrophobic segment with the intent of improving nanophase separation from the hydrophilic phase, with an ultimate goal of improved proton conductivity. The multiblock copolymers were coupled under mild reaction conditions (<100°C), and by combining various oligomers molecular weights, ten different multiblock copolymers with varying block lengths and ion exchange capacities (IECs) were produced. This series will be described in terms of proton conductivity, water uptake, swelling behavior, and surface morphology, and these values will be discussed with respect to their influence on PEM fuel cell performance.
2.2 Experimental

2.2.1 Materials

4,4’-biphenol (BP) was provided by Eastman Chemical Company, and was dried in vacuo at 110°C for 24 h prior to use. 4,4’-dichlorodiphenyl sulfone (DCDPS) was provided by Solvay Advanced Polymers, and was dried in vacuo at 110°C for 24 h prior to use. Following previously reported procedures for synthesis and purification, 3,3’-disulfonated-4,4’-dichlorodiphenyl sulfone (SDCDPS) was synthesized. 4,4’-hexafluoroisopropylidenediphenol (6F-BPA) was received from Ciba and recrystallized in toluene and then vacuum dried prior to use. 4,4’-difluorobenzophenone was received from Aldrich, and recrystallized in ethanol and vacuum dried prior to use. N,N-dimethylacetamide (DMAc) was received from Aldrich and vacuum distilled before use. Potassium carbonate (K₂CO₃), hexafluorobenzene (HFB), 2-propanol (IPA), acetone, and toluene were obtained from Aldrich and used as received.

2.2.2 Synthesis and coupling of oligomers

The details of the copolymer synthesis have been reported elsewhere, but will be summarized here. Hydrophobic oligomers (6FK) were made targeted to five molecular weights: 3, 5, 10, 15, and 20 kg/mol. These oligomers were synthesized from the reaction of the 4,4’-difluorobenzophenone and the 4,4’-hexafluoroisopropylidenediphenol in DMAc with added K₂CO₃ at 180°C for 36 h. The oligomers were then endcapped with hexafluorobenzene (HFB) in DMAc, using cyclohexane as an azeotroping agent. The dissolved oligomer was initially allowed to reflux for 4 h at 100°C to remove water, after which time the cyclohexane was removed and the reaction was started with the addition of the HFB, proceeding for 12 h at 80°C. The solution...
was allowed to cool and then filtered, then precipitated into methanol and further washed and filtered. The resulting endcapped oligomer was dried under vacuum at 110°C for 24 h prior to use. Figure 2-1 contains a schematic of the oligomer synthesis.

Figure 2-1. Schematic of the hydrophobic block synthesis.

The hydrophilic oligomers (BPSH100) were targeted to five molecular weights: 3, 5, 10, 15, and 20 kg/mol. These oligomers were made by reacting biphenol and SDCDPS in DMAc with added K$_2$CO$_3$ and toluene as an azeotroping agent. After azeotroping for 4 h at 145°C, the toluene was removed and the reaction was continued for 96 h at 180 °C. Figure 2-2 shows a schematic of the BPSH100 hydrophilic oligomers synthesis.
Figure 2-2. Schematic of the hydrophilic oligomer synthesis.

The oligomers were coupled in DMAc, by first adding the hydrophilic oligomers with 
$K_2CO_3$ and cyclohexane and azeotroping for 4h at 100°C. After removing the cyclohexane, HFB-
endcapped hydrophobic oligomers were added and the coupling reaction was allowed to proceed 
for 24 h at 105-110 °C. After reacting, the solution was filtered and precipitated in IPA, and 
purified via Soxhlet extraction with methanol and chloroform for 24 h each to remove unreacted 
hydrophilic and hydrophobic oligomers, respectively. The resulting multiblock copolymer was 
dried under vacuum at 120°C for 24 h prior to use. The nomenclature used to indicate multiblock 
copolymer composition BPSHx-6FKy, where x denotes the molecular weight of the hydrophilic 
block and y denotes the molecular weight of the hydrophobic block in kg/mol. The multiblock 
copolymers were synthesized in ten different combinations of oligomer weights, in three 
different groups. The first group was with longer hydrophobic block lengths: BPSH5K-6FK10K, 
BPSH10K-6FK15K, and BPSH15K-6FK20K. The second group featured equal block lengths for 
both hydrophilic and hydrophobic oligomers: BPSH3K-6FK3K, BPSH5K-6FK5K, BPSH10K-
6FK10K, and BPSH15K-6FK15K. The third group was synthesized with longer hydrophilic 
blocks: BPSH10K-6FK5K, BPSH15K-6FK10K, and BPSH20K-6FK15K.
Figure 2-3. Schematic of the oligomer coupling reaction.

Oligomer structure and molecular weights were confirmed by $^1$H NMR analysis on a Varian INOVA 400 MHz spectrometer with DMSO-d6. Intrinsic viscosity data was collected in NMP containing 0.05 M LiBr at 25°C using a Ubbelohde viscometer. The ion exchange capacity values were determined via titration with 0.01 M NaOH.

2.2.3 Membrane casting and preparation

The copolymers were dissolved in dimethylacetamide (DMAc) at a 7% (w/w) concentration and cast onto a clean glass plate. The solvent was evaporated under an IR lamp at 60°C for 24 h. The remaining solvent was then removed by drying under vacuum at 110°C for 24h. Due to the synthetic procedure, the copolymers are synthesized in salt form. The films were converted to acid form by boiling in 0.5 H$_2$SO$_4$ for 2 hours, followed by 2 hours of boiling in deionized water as reported elsewhere. The films were then allowed to equilibrate for 48 hours in deionized water at room temperature, exchanging fresh deionized water every 24 h.
2.2.4 Measurement of water uptake

Water uptake measurements were gravimetrically performed by weighing fully hydrated samples of each copolymer after blotting, and then re-weighing the samples after 24 hours of heating under vacuum at 110°C. Each copolymer had an average of three samples measured and averaged. The water uptake was determined according to the following equation:

\[
\text{Water Uptake} = \frac{\text{mass}_{\text{wet}} - \text{mass}_{\text{dry}}}{\text{mass}_{\text{dry}}} \times 100\%
\]

The dimensional swelling of the copolymers was measured both in the in-plane (x and y directions) and the through-plane (z-direction) orientation. The sample films were initially measured with a micrometer after having been fully hydrated in deionized water for 24 h. They were then re-measured after again drying for 24 hours under vacuum in a convection oven at 110°C. Again, three samples were used for each copolymer, with an average sample size of approximately 2.5 x 2.5 cm.

The hydration number \( \lambda \), which describes the number of adsorbed water molecules per sulfonic acid unit, was determined using the water uptake data and IEC values as follows:

\[
\lambda = \frac{(W_{\text{wet}} - W_{\text{dry}})/MW_{\text{water}}}{IEC \times W_{\text{dry}}} \times 1000
\]

2.2.5 Measurement of proton conductivity

Proton conductivity measurements of acidified, equilibrated membranes were conducted using a Solartron 1252A + 1287 impedance analyzer over a range of 10 Hz to 1 MHz. The cell geometry was selected to ensure that the membrane resistance dominated the response of the system, and film resistance was measured at the frequency that produced the minimum imaginary response. Measurements were taken from 30 to 80 °C in liquid water, and from 30 to
95% relative humidity at 80 °C. An initial equilibration step at 80% relative humidity and 80 °C was used, with an equilibration time of 4 h in between relative humidity measurements.

2.2.6 Measurement of surface morphology

Tapping mode atomic force microscopy (AFM) was performed using a Digital Instruments MultiMode Scanning Probe microscope with a NanoScope IVa controller. A Veeco silicon probe with an end radius <10 nm and a force constant K of 42 N/m was used to image samples. Samples were in acid form and equilibrated at 40% relative humidity and 30 °C for at least 12 h prior to imaging.

2.3 Results and Discussion

Initial characterization data using intrinsic viscosity, \(^1\)H NMR, room temperature fully hydrated proton conductivity, and water uptake are listed below in Table 2-1. The comparison of theoretical vs. experimentally determined IECs showed a fairly close correlation, indicating that the coupling reaction occurred successfully with minimal oligomer loss. The intrinsic viscosity values obtained ranged from 0.6 to 0.94 dL/g, indicating that the multiblock molecular weight was sufficient to produce tough, ductile membranes. The mass water uptake results largely correlated with the IEC values, as expected from other multiblock systems produced in the McGrath group.\(^{23, 24}\)

In the predominantly hydrophobic group, water uptake increased significantly from BPSH10-6FK15 to BPSH15-6FK20 even though their IEC values were largely identical. This was likely due to the larger physical domains formed with the longer hydrophilic block lengths.
in the latter copolymer. In the equal oligomers block length series, the first three polymers produced likewise had nearly identical IECs of approximately 1.5 meq/g, but similarly showed an increase in mass water uptake with an increase in the size of the hydrophilic oligomers domains. The fourth polymer, BPSH15K-6FK15, showed still higher water uptake despite having an IEC of 1.34 meq/g, likely due to the same effect.

Curiously, the opposite trend was noted in the predominantly hydrophilic multiblock copolymers. However, due to the extremely high water uptake data, the hydrophilic phases may not have been able to maintain physical consistency and was diluted by the absorbed water beyond the ability of the hydrophobic phase to maintain physical integrity.

In an examination of the ambient fully hydrated proton conductivity data, a similar phenomenon was observed. In all three categories of copolymers, the proton conductivity increased from the shortest block length copolymer to the longest block length copolymer, even in the case of BPSH15K-6FK15K which had a markedly lower IEC than the other equal block length copolymers.

When studying the hydration number data, there is a looser but consistent trend which is most clear in the equal block length multiblock copolymer group. The $\square$ value increases smoothly from BPSH3K-6FK3K to BPSH15K-6FK15K. In the predominantly hydrophilic block, the highest hydration number is found in the shortest block length copolymer, which is likely due to the higher ratio of hydrophilic to hydrophobic oligomers (2:1), which is lower in the two following copolymers (3:2 and 4:3, respectively). The scale of the $l$ values relative to the other samples also indicates that the predominantly hydrophilic multiblocks are overly hydrated, possibly to the point of diluting the sulfonic acid groups. This would explain the otherwise
unexpectedly low conductivity values for the given IEC values.

Table 2-1. Properties of BPSH-6FK multiblock copolymers in acid form.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Theoretical IEC (meq/g)</th>
<th>Experimentally determined IEC (meq/g)</th>
<th>Intrinsic Viscosity (dL/g)</th>
<th>Water Uptake (%)</th>
<th>Conductivity (mS/cm)</th>
<th>Hydration Number (λ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 112</td>
<td>N/A</td>
<td>0.90</td>
<td>N/A</td>
<td>25</td>
<td>90</td>
<td>15.0</td>
</tr>
<tr>
<td>BPS35</td>
<td>1.53</td>
<td>1.50</td>
<td>0.70</td>
<td>36</td>
<td>70</td>
<td>13.3</td>
</tr>
<tr>
<td>BPS5K-6FK10K</td>
<td>1.05</td>
<td>1.01</td>
<td>0.62</td>
<td>23</td>
<td>40</td>
<td>13</td>
</tr>
<tr>
<td>BPS10K-6FK15K</td>
<td>1.21</td>
<td>1.32</td>
<td>0.80</td>
<td>20</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>BPS15K-6FK20K</td>
<td>1.47</td>
<td>1.33</td>
<td>0.65</td>
<td>45</td>
<td>100</td>
<td>19</td>
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<tr>
<td>BPS3K-6FK3K</td>
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<td>1.51</td>
<td>0.78</td>
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<tr>
<td>BPS5K-6FK5K</td>
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<td>1.53</td>
<td>0.62</td>
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<tr>
<td>BPS10K-6FK10K</td>
<td>1.54</td>
<td>1.48</td>
<td>0.88</td>
<td>81</td>
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<tr>
<td>BPS15K-6FK15K</td>
<td>1.62</td>
<td>1.34</td>
<td>0.70</td>
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<tr>
<td>BPS10K-6FK5K</td>
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<td>0.94</td>
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<tr>
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<td>1.70</td>
<td>0.72</td>
<td>178</td>
<td>90</td>
<td>58</td>
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</tbody>
</table>

* Determined by titration with 0.01 M NaOH

* In NMP with 0.05 M LiBr

* Measured in deionized water at 30°C.

Proton conductivity data recorded over a range of 30-80°C, shown below in Figure 2-4, indicate that the equal block length samples of the multiblock copolymer series were comparable to or superior to Nafion in their performance. The multiblocks shown here also all feature a
similar slope, indicating uniform behavior of the hydrophilic domain and no phase transitions in the featured temperature range. BPSH10K-6FK10K showed excellent performance data, with a conductivity of 185 mS/cm at 80°C. The multiblocks produced in this study showed a lower dependence on temperature for increases in proton conductivity, likely indicating a higher activation energy.

When comparing proton conductivity performance under partially humidified conditions at 80°C, as shown below in Figure 2-5, the ability of the multiblock copolymers to maintain good proton conductivity data at lower relative humidities increased with oligomer block length. This has been confirmed in related multiblock systems, and improved low humidity performance appears to correlate with the formation of larger, more well-ordered hydrophilic channels at higher oligomeric block lengths. It is interesting to note that the BPSH15K-6FK15K copolymer maintained slightly superior performance to the BPSH10K-6FK10K copolymer, despite the
superior IEC value of the latter polymer and superior performance during the fully hydrated temperature survey.

While the multiblocks showed superior performance at high relative humidities, they were not competitive with Nafion 112 at low relative humidities. It is notable to see the significant improvement over the performance of the statistically copolymerized BPSH35 used here as a standard. The change in slope between the multiblock and statistically copolymerized poly(arylene ether sulfone)s was significant, as seen in other studies on different copolymers produced in this group.  

![Graph](image)

**Figure 2-5.** Performance of selected multiblock copolymers, Nafion 112, and random BPSH35 standard during partially humidified conditions at 80°C.

The dimensional swelling data of the water uptake investigation of the equal block length copolymers is shown below in Figure 2-6. The swelling ratios of Nafion 112 and statistically copolymerized BPSH35 are shown as controls, as well as for comparison with the partially humidified conductivity data shown above in Figure 2-5. While both controls demonstrated
isotropic swelling data, all multiblock copolymers demonstrated a distinctive anisotropy as shown in other multiblock systems produced by this group. While the in-plane (X and Y direction) swelling showed a very slight decrease with higher block length, the through-plane or Z directional swelling showed a significant increase at longer oligomer block lengths, quadrupling from the shortest to the longest oligomer block lengths. This is consistent with expectations developed from other investigations, and will be supported by the morphological observations below.

![Figure 2-6. Anisotropy in dimensional water swelling data for a series of multiblock copolymers.](image)

Morphological data from AFM confirmed the development of long-range order with an increase in oligomer molecular weight. The phase images shown in Figure 2-6 show the increase in domain size and connectivity from the BPSH100-6FK 5K-5K to the BPSH100-6FK 15K-15K
In all AFM phase images shown here, the light and dark portions of the images represent hard hydrophobic and soft hydrophilic domains, respectively.

This development of nano-phase separated morphology supports the observations from the proton conductivity performance data under partially humidified conditions with regards to the molecular weight effect. Although there is very little connectivity between the dark-colored hydrophilic phases in the left-hand BPSH100-6FK 5K-5K sample, this quickly evolves into a network of fully interconnected hydrophilic channels in the BPSH100-6FK 10K-10K sample. Although there is no significant improvement in morphology between the BPSH100-6FK 10K-10K and BPSH100-6FK 15K-15K samples, the interconnected hydrophilic channels are still present. The lack of difference in these samples may be due to the slightly lower hydrophilic volume fraction implied by the lower IEC of the BPSH100-6FK 15K-15K sample.

Phase images were also collected for the predominantly hydrophobic offset block length copolymers, BPSH100-6FK 5K-10K, BPSH100-6FK 10K-15K, and BPSH100-6FK 15K-20K, shown below in Figure. While these materials did not have adequate fully hydrated proton conductivity data to merit partially humidified conductivity testing, their morphology was
characterized to improve the fundamental understanding of these copolymers. The higher proportion of hydrophilic block did not interfere with good long-range order in nanophase separation of the hydrophilic and hydrophobic domains. Although the ratio of hydrophobic to hydrophilic block length is 2:1 in the left hand image in Figure 2-8, the hydrophilic domain is still able to form continuous channels, albeit separated by long finger-like projections of hydrophobic phase.

![Figure 2-8. AFM phase images (1 μm x 1 μm) of BPSH100-6FK offset predominantly hydrophobic multiblocks. From left to right: BPSH100-6FK 5K-10K, BPSH100-6FK 10K-15K, BPSH100-6FK 15K-20K.](image)

### 2.4 Conclusions

A series of multiblock copolymers were successfully synthesized from partially fluorinated hydrophobic oligomers and fully disulfonated hydrophilic oligomers. These copolymers were made across a variety of oligomer weights, at varying hydrophilic-hydrophobic ratios. The highly reactive hexafluorobenzene was used as an endcapping and linkage group in order to successfully couple the oligomers at relatively low temperatures (~105°C) while avoiding the sequence randomization that may occur at higher reaction temperatures. The
multiblock copolymers produced tough, ductile films and were compared with BPSH35 and Nafion 112 using a variety of characterization techniques. Proton conductivity under both fully and partially humidified conditions, as well as water uptake and morphological characterizations indicated the development of a nanophase separated morphology which improved performance at low relative humidities. The development of nanophase separation between the hydrophilic and hydrophobic domains correlated with the increase in anisotropic swelling behavior in the multiblock copolymers, while the two statistically copolymerized controls maintained isotropic swelling behavior.

Acknowledgements

The authors thank the Department of Energy (DE-FG36-06G016038) for its support of this research.

References:

9. Kim, D. S.; Robertson, G. P.; Kim, Y. S.; Guiver, M. D., Copoly(arylene ether)s Containing Pendant Sulfonic Acid Groups as Proton Exchange Membranes. Macromolecules (Washington, DC, United States), ACS ASAP.


3.0 Impact of solvent selection and block length on morphology and proton conductivity of multiblock disulfonated poly(arylene ether sulfone) copolymers as proton exchange membranes

Abstract

The fundamental structure-property relationships of the BPSH100-BPS0 multiblock copolymers have already been investigated and reported in the literature. However, as previous research in related copolymers indicates a strong influence of processing conditions, i.e. solvents and drying temperatures as well as acidification treatments, on the final performance of the produced proton exchange membrane (PEM). In this study, BPSH100-BPS0 multiblock copolymers of equal block lengths were evaluated as a function of their casting solvent (NMP or DMAc) and casting temperature (20, 40, 60, and 80 °C). The copolymers were investigated by means of TEM, drying rate and proton conductivity under fully hydrated conditions. While drying temperature did not show any significant impact on proton conductivity, an increase in temperature did result in an increase in the degree of anisotropy in dimensional water uptake. In the comparison of solvents, films cast from DMAc showed a higher conductivity under fully hydrated conditions than films cast from NMP, regardless of block length or drying conditions.

3.1 Introduction

After a lengthy period of dominance, the dwindling stores of fossil fuels and the steadily increasing environmental, political, and economical costs of the world’s dependence on oil for energy have spurred development on all front of alternative energy. While some options are well-tailored to supporting the electrical grid or to supplement energy consumption within the
home, proton exchange membrane fuel cells (PEMFCs) running on hydrogen are one of the prime candidates for personal vehicles. The unmatched power density of hydrogen coupled with the simplicity of a PEMFC car, which requires no moving parts, is very efficient, and produces only water and waste heat, makes for a very appealing replacement of the noisy, pollution-producing, and complicated combustion engine. There are several remaining hurdles to introducing PEMFC hydrogen cars as a commercially competitive alternative.\textsuperscript{1, 2}

One of these hurdles is the current predominantly used membrane, Nafion\textsuperscript{TM}.\textsuperscript{3-6} The ideal proton exchange membrane (PEM) is inexpensive and easy to fabricate into a membrane electrode apparatus (MEA), has high proton conductivity under partially or fully humidified conditions, has low electronic conductivity, has low permeability to fuel and oxidant, is resistant to chemical degradation under the harsh fuel cell environment, and has a glass transition temperature sufficient to allow high-temperature fuel cell operations.\textsuperscript{3} While Nafion displays good proton conductivity, it is very expensive and its hydrated glass transition temperature results in a ceiling operating temperature of about 80°C.\textsuperscript{4}

While a number of alternative materials have been explored in the search for a replacement without the disadvantages of Nafion, one of the most thoroughly developed candidates is a partially disulfonated biphenol-based poly(arylene ether sulfone), largely investigated by the McGrath group at Virginia Tech.\textsuperscript{3, 7} This material is typically termed BPSHxx for BiPhenyl Sulfone, where the xx represents the percentage of disulfonated monomer. While BPSH materials are much more affordable than Nafion and the most commonly used BPS35 copolymer has a much higher glass transition temperature, allowing for a higher ceiling operating temperature, the statistically copolymerized material has difficulties remaining competitive with Nafion in performance in a partially humidified environment.\textsuperscript{3, 7} This is largely
due to the smaller ionic channels developed in a statistically copolymerized aromatic-based copolymer, which is less able to contain the loosely bound and free water needed for rapid proton transport.\textsuperscript{5, 6, 8} Regardless, there is still a great deal of research in the development of aromatic-based copolymers as alternative proton exchange membranes.\textsuperscript{9-12} This research includes statistically copolymerized materials, multiblock copolymers, blends, and cross-linked membranes.\textsuperscript{11-13, 12, 14, 15}

The McGrath group overcame this drawback with the synthesis of a multiblock copolymer, where the hydrophobic oligomer was synthesized as BPS0 and the hydrophilic oligomer was fully disulfonated BPSH100.\textsuperscript{16} This development, much like some other multiblock copolymers developed in the group, produced a multiblock which was either competitive with or superior to that of Nafion 112 when tested under partially humidified conditions.\textsuperscript{17-20} The McGrath group has since focused most research on the optimization and development of novel multiblock copolymers, typically varying the composition of the hydrophobic oligomer while maintaining a hydrophilic block of fully disulfonated BPSH100.\textsuperscript{21, 22} Some variation of the hydrophilic block has also been attempted to produce a more ion-dense phase, and segmented copolymers have also been produced.\textsuperscript{18, 23}

An important variable which complicates the behavior of multiblock copolymers and the study of their morphology is the impact of various casting conditions and solvents. Even in statistically copolymerized materials, varying the time and temperature of acidification treatment in already cast membranes results in very different morphologies, water uptakes, and proton conductivity performances.\textsuperscript{24} Studies performed on styrene-butadiene multiblock copolymers have shown that the kinetics of phase separation, and therefore the timing of the temperature ramp in solution casting, play a crucial role in the resulting morphology of solution-cast films.\textsuperscript{25}
While the differences in the observed morphology are not always readily observable or easy to interpret, the impact of changing the times and temperatures of solution casting, or the nature of the solvent used, may still have a marked impact on the performance of the produced PEM.\textsuperscript{26-28}

In this investigation, the impact of both solution casting conditions of time and temperature and the effect of different solvents on the morphology and performance of a series of BPSH100-BPS0 copolymers was characterized. The impact of these variables on the different sizes of oligomers in equal block length copolymers was also observed, and compared with water uptake and proton conductivity.

3.2 Experimental

3.2.1 Materials

Dimethylacetamide and N-methylpyrrolidone (NMP) were purchased from Sigma at (>99%) purity and used as received. The multiblock and random copolymers were produced according to the synthesis outlined below and used as received and described in the membrane casting and preparation section.

3.2.2 Synthesis and coupling of oligomers and copolymers

The synthesis of the multiblock copolymers used in this paper has been reported elsewhere, but will be briefly described here.\textsuperscript{16} The hydrophobic BPS0 oligomer was synthesized by reacting biphenol and 4,4’-dichlorodiphenylsulfone in a solution of DMAc, using toluene as an azeotroping agent and potassium carbonate to mediate the condensation reaction. The reaction was allowed to reflux at 145°C for four hours, then the toluene was removed via a Dean Stark
trap and the reaction was allowed to proceed at 180°C for 48 h. The resulting oligomer was precipitated in isopropanol and filtered, and then vacuum dried prior to the endcapping reaction. The endcapping procedure consisted of a reaction between the BPS0 oligomer and hexafluorobenzene (HFB) in DMAc with cyclohexane as an azeotroping reagent. The solution of BPS0, DMAc, and cyclohexane was heated to 100°C and refluxed for 4 h to remove water, and then allowed to continue at 80°C for 12 h after the addition of the HFB. After the reaction was stopped, the oligomer was once again precipitated in isopropanol and dried under vacuum prior to use.

The hydrophilic BPSH100 oligomer was synthesized by reacting biphenol and 3,3’-disulfonated, 4,4’-dichlorodiphenylsulfone in a solution of DMAc, using toluene as an azeotroping agent and potassium carbonate to mediate the condensation reaction. The reaction was allowed to reflux at 145°C for 4 h, then the toluene was removed via a Dean Stark trap and the reaction was allowed to proceed at 180°C for 96 h. The resulting oligomer was precipitated in isopropanol and filtered, then vacuum dried prior to use.

The multiblock coupling reaction consisted of an initial step where the hydrophilic oligomer was dissolved in a solution with DMAc, potassium carbonate, and cyclohexane and refluxed at 100°C for 4 h to remove any water. After the removal of the cyclohexane and water, the endcapped hydrophobic oligomer was added to the solution and the temperature was raised to 105°C for 24 h.

The random BPSH35 used as a control in this experiment was synthesized via direct aromatic nucleophilic substitution condensation of the sodium salt form of 3,3’-disulfonated, 4,4’-dichlorodiphenylsulfone, 4,4’-dichlorodiphenylsulfone, and biphenol in the appropriate ratios,
using potassium carbonate in a solution using dimethylacetamide (DMAc) as a solvent. This procedure has been published in greater detail elsewhere.\textsuperscript{29}

### 3.2.3 Membrane casting and preparation

Multiblock copolymers of BPSH100-BPS0 were acquired at three separate oligomer weight combinations: 5K-5K, 10K-10K, and 15K-15K. Solutions were made of each multiblock in both DMAc and NMP at 15\% (w/v) weight concentration. The solutions were then cast using a casting apparatus, with a controlled casting temperature of 20, 40, 60, or 80\(^\circ\)C. Samples of statistically copolymerized BPSH35 were also produced for comparison.

During film casting, a flowmeter and two air heaters were used to confirm the velocity (20 cm/sec) and temperature (variation \(<2\) °C), respectively, in the film casting apparatus. A balance in the apparatus was used to monitor the weight and determine when the drying procedure was complete. The resulting films were approximately 25 microns thick, and were acidified by immersion in boiling 0.5 M H\(_2\)SO\(_4\) for 2 hours, followed by 2 hours of boiling in deionized water and 48 hours in two changes of fresh deionized water.

### 3.2.4 Measurement of water uptake

Water uptake measurements were gravimetrically performed by weighing fully hydrated samples of each copolymer after blotting, and then re-weighing the samples after 24 hours of heating under vacuum at 110\(^\circ\)C. Each copolymer had an average of three samples measured and averaged. The water uptake was determined according to the following equation:
\[ \text{Water Uptake} = \frac{(m_{\text{wet}} - m_{\text{dry}})}{m_{\text{dry}}} \times 100\% \]

The dimensional swelling of the copolymers was measured both in the in-plane (x and y directions) and the through-plane (z-direction) orientation. The sample films were initially measured with a micrometer after having been fully hydrated in deionized water for 24 h. They were then re-measured after again drying for 24 hours under vacuum in a convection oven at 110°C. Again, three samples were used for each copolymer, with an average sample size of approximately 2.5 x 2.5 cm.

### 3.2.5 Measurement of proton conductivity

Proton conductivity measurements of acidified, equilibrated membranes were conducted using a Solartron 1252A + 1287 impedance analyzer over a range of 10 Hz to 1 MHz. The cell geometry was selected to ensure that the membrane resistance dominated the response of the system, and film resistance was measured at the frequency that produced the minimum imaginary response. Measurements were taken at 30°C in liquid water, with one hour allowed for the equilibration of the samples after assembly within the apparatus.

### 3.2.6 Measurement of bulk morphology

For transmission electron microscopy imaging, acidified membranes were stained with a CsOH aqueous solution to enhance the electron density of the hydrophilic block and provide contrast within the sample. Samples were embedded in epoxy and microtomed into approximately 70 nm thick sections with a diamond knife. Samples were then imaged on a Philips EM 420 Transmission Electron Microscope using an accelerating voltage of 100 kV.
3.3 Results and Discussion

In Figure 3-1, the typical film drying behavior is presented in terms of solvent removal vs. time. The much shorter drying time of the DMAc-cast copolymers is easily distinguished from the NMP-cast copolymers, due to its higher vapor pressure. It should be noted that for the samples dried at 60 and 80 °C, the NMP-cast films saw a loss of solvent rate comparable to the group of DMAc-cast copolymers. The difference between the 20 and 80 °C cast copolymers is
only about a scale of five-fold for the DMAc-cast copolymers, but in the NMP-cast copolymers it is over an order of magnitude. As expected, the drying rate decreases as the solvent evaporates, due to the increasing concentration of the polymer and decreasing relative concentration of the solvent impeding the rate at which the solvent can diffuse out of the polymer.

![Figure 3-2](image_url)

**Figure 3-2. The impact of solvent, oligomer block length and solution casting temperature on mass water uptake.**

The solvent effect in water uptake mass measurements was not as easily distinguished as shown in Figure 3-2. While the BPSH35 control had equal water uptake values for all solvent and casting condition combinations, the DMAc-cast multiblocks showed much higher water uptake values at lower casting temperatures, which was more pronounced at higher oligomer block lengths. The NMP-cast films showed a slight version of this phenomenon at the 15K-15K samples, but nothing significant was observed in the 5K-5K or 10K-10k samples tested. As
shown in Figure 3-3, the DMAc-cast 15K-15K samples showed a significant decrease in the degree of anisotropy in dimensional water uptake data, although even at high casting temperatures the anisotropy was clearly present. This phenomenon was noticed on a smaller scale for the other DMAc-cast multiblocks and the 15K-15K NMP-cast multiblocks, but was not observed at significant levels for the 5K-5K and 10K-10K samples.

![Swelling ratio vs temperature](image)

**Figure 3-3.** Higher drying temperatures in the DMAc-cast 15K-15K block copolymer result in a decrease in the anisotropy of dimensional water swelling data.

While there is normally a very close relationship observed between water uptake and conductivity in a given copolymer series, the temperature effect on water uptake within the same oligomer length and casting solvent (e.g. 15K-15K and DMAc) was not accompanied by any similar trends in proton conductivity under fully hydrated conditions as shown in Figure 3-4. However, there was a significant increase in proton conductivity from a given polymer sample cast from NMP and the sample multiblock cast from DMAc, regardless of temperature. Again, the increase in conductivity was more marked at higher oligomer molecular weights, which is expected based on performance in other high block-length multiblock copolymers.
The hydrated proton conductivity performance of BPSH100-BPS0 equal length multiblocks, cast from two solvents at varying temperatures.

A morphological study of the study used BPSH35 and BPSH100-BPS0 films of all three oligomer block lengths cast from NMP at 20 °C, which were stained with CsOH and prepared for TEM imaging. The acquired images are shown in Figure 3-5. As expected, the hydrophilic domains of the BPSH35 sample are small and isolated, showing no specific order. Consistent with other microscopic investigations of multiblock copolymers, the domain size becomes larger and more ordered from the 5K-5K to the 15K-15K sample. This is consistent with the observations made of trends in the mass water uptake, anisotropy in dimensional water uptake, and proton conductivity, as well as observations from investigations in other multiblock systems.
3.4 Conclusions

The impact of solution-casting temperature and solvent on the morphology and proton conductivity performance of a multiblock disulfonated poly(arylene ether sulfone), BPSH100-BPS0 copolymer series was investigated using an array of characterization techniques. While casting temperature appeared to have no significant impact on fully hydrated proton conductivity, the choice of casting solvent produced a significant change in performance. TEM imaging clearly indicated a long-range development of order in samples produced from longer oligomer block lengths, confirming the formation of long-range hydrophilic channels across the
membrane plane.

Although no significant relationship was observed between drying temperature and fully hydrated proton conductivity, the increase in drying temperature did decrease the observed anisotropy in the dimensional water uptake behavior. This relationship did not appear to be significant in the 5K-5K copolymers produced but became apparent in the 10K-10K copolymer and was most significant in the 15K-15K samples.

References:


4.0 Impact of solvent selection and block length on PEM properties of multiblock copolymers with a hydroquinone-based hydrophilic block

Abstract

The structure-property relationships of a series of hydrophilic-hydrophobic multiblock copolymers based upon hydroquinone and 3,3’disulfonated, 4,4’-dichlorodiphenylsulfone hydrophilic blocks as proton exchange membranes were determined using AC impedance spectroscopy, atomic force microscopy, transmission electron microscopy, differential scanning calorimetry, and dynamic mechanical analysis. Phase separation of the hydrophobic and hydrophilic blocks was confirmed using AFM, and improved performance under partially humidified conditions. Performance under partially humidified conditions and also improved with increasing oligomer block length. Free water, which has been shown to correlate with improved proton conductivity, was also shown to increase with block length.

4.1 Introduction

The growing demand for limited quantities of fossil fuels and an intensifying need to alleviate the environmental strain of their consumption produce a compelling pressure to develop feasible alternative energy sources. Proton exchange membrane (PEM) hydrogen fuel cells are one of the most viable candidates for alternatives to combustion engines in personal vehicles. An ideal PEM possesses the following qualities: excellent proton conductivity, poor electron conductivity, ease of fabrication into membrane electrode assemblies (MEAs), low cost, low permeability to fuels, good mechanical properties in both the dry and hydrated states, and a low
swelling/deswelling ratio.\textsuperscript{1-3} Control of water swelling is an issue of growing concern as the swelling and deswelling which occurs during fuel cell use has a strong impact on limiting MEA lifetime.

The predominant commercial membrane is Nafion®, a poly(perfluorosulfonic acid) polymer developed by Dupont. It possesses excellent electrochemical and mechanical properties, with exceptionally resilient conductivity performance under partially humidified conditions. However, it is also expensive and exhibits low permeability to methanol, as well as impaired proton conductivity and mechanical strength above 80 °C. Other commercial membranes include perfluorosulfonate-based polymers with a similar structure produced by Asahi Chemical and Asahi Glass Companies, and a PEM based on sulfonated polystyrene synthesized by Ballard.\textsuperscript{3, 4} Alternative membranes under development include partially sulfonated poly(ether ether ketones), some of which may potentially boost performance by forming composites with other polymers, as well as organic and inorganic compounds.\textsuperscript{5-7}

The McGrath group has been engaged in the development of polymers based on partially disulfonated poly(arylene ether sulfone)s (PAESs) as alternative PEMs. The initial work on statistical copolymers produced from disulfonated and nonsulfonated monomers showed promising conductivity values and excellent mechanical properties, as well as increased ceiling operation temperatures due to higher glass transitions.\textsuperscript{8-10} Varying monomer structure, predominantly the hydrophobic monomer, can provide tailored glass transition temperatures, conductivities, water uptake behaviors, and fuel permeabilities in the resulting copolymers.\textsuperscript{11-13} One major hurdle was the impaired performance under partially hydrated conditions, which was not comparable to Nafion®. By synthesizing hydrophobic and hydrophilic oligomers separately and coupling them to form nanophase-separated multiblock copolymers, we were able to
substantially improve performance at low relative humidities. Nanophase separation in these polymers has been observed using atomic force microscopy (AFM) and transmission electron microscopy (TEM). The development of long-range order in the separation of hydrophilic and hydrophobic phases was shown to correlate with increasing free water as measured by differential scanning calorimetry (DSC), pulsed gradient spin echo nuclear magnetic resonance (PGSE NMR) and the improvement of proton conductivity under partially hydrated conditions.

Previous research by the McGrath group has primarily entailed varying the chemical structure of the monomers in the hydrophobic block to improve phase separation and membrane performance. There has also been some investigation into the impact of using hydroquinone to replace biphenol in statistical copolymers, both due to the lower cost as well as to lower rigidity (by reducing two rings to one) and to increase the ionic density of the hydrophilic unit. This paper describes the structure-property relationships of two multiblock copolymer systems which incorporate hydroquinone in the hydrophilic block. One series of multiblock copolymers utilizes a longer hydrophobic block length to minimize the impact of high water uptake, and another utilizes hydrophilic and hydrophobic oligomers of equal block lengths. The synthesis of these polymer series is reported elsewhere. Hydrophilic hydroquinone-based oligomers result in an improvement in conductivity under partially and fully hydrated conditions. This correlates with an increase in long-range order and phase separation with increasing block length, which is consistent with previous multiblock systems described by the McGrath group at Virginia Tech. The purpose of this investigation is to determine the structure-property relationship of a hydrophilic-hydrophobic multiblock copolymer with a hydroquinone-based hydrophilic component.
4.2 Experimental

4.2.1 Materials

Hydrophilic oligomers of 100% disulfonated poly(arylene ether sulfone) were synthesized from hydroquinone and 3,3’-disulfonated, 4,4’-dichlorodiphenylsulfone at molecular weights of approximately 3, 5, 6, 9, 10, 12, and 15 kg/mol, as reported in the Journal of Power Sources. Hydrophobic oligomers were synthesized from biphenol and 4,4’-dichlorodiphenylsulfone at molecular weights of approximately 3, 5, 10, 15 and 20 kg/mol. The molecular weights of the hydrophilic and hydrophobic oligomers were confirmed with H\(^1\) NMR, and these results are summarized in Tables 4-1 and 4-2, respectively.

The oligomers were then coupled as shown in Figure 4-1 to produce two series of multiblock copolymers: one of approximately equal hydrophilic and hydrophobic block lengths.

![Figure 4-1. Synthesis of HQSH100-BPS0 copolymers.](image-url)

Table 4-1. Comparison of target and actual molecular weights for HQSH100 oligomers.

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<th>Target (M_n) (kg mol(^{-1}))</th>
<th>Determined (M_n) (kg mol(^{-1}))(^a)</th>
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<td>15.0</td>
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</table>

\(^a\) Determined by \(^1\)H NMR
\(^b\) In NMP with 0.05 M LiBr at 25°C.

Table 4-2. Comparison of target and actual molecular weights of BPS0 oligomers.

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<th>IV (dLg(^{-1}))(^b)</th>
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<td>0.51</td>
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</table>

\(^a\) Determined by \(^1\)H NMR
\(^b\) In NMP with 0.05 M LiBr at 25°C.

4.2.2 Membrane casting and preparation

The copolymers were dissolved in DMF (7% w/v) and filtered using a 0.45 mm Teflon ® filter, then cast from solution onto a clean glass substrate. Solvent was removed by drying under an IR lamp at 60 °C for 24 hours, and then under vacuum at 110 °C for 24 hours. The membranes were removed from the substrate by immersion in water, and then converted to acid form by boiling in 0.5 M H\(_2\)SO\(_4\) for two hours, and then deionized water for two hours, according to
standard procedure in the literature. 3

4.2.3 Measurement of water uptake

Water uptake data was determined by weighing and measuring membranes that had been
dried under vacuum at 100 °C for 24 h in the x, y (in-plane) and z (through-plane) directions, and
then repeating the measurement after immersing them in deionized water at room temperature
for 24 h. Mass uptake was calculated as the ratio of the increase in mass to that of the dry film,
and expressed as a percentage. Dimensional swelling was calculated as the ratio of the increase
in each measured length or thickness to that of the dry film, and expressed as a percentage.

4.2.5 Measurement of proton conductivity

Proton conductivity measurements of acidified, equilibrated membranes were conducted
using a Solartron 1252A + 1287 impedance analyzer over a range of 10 Hz to 1 MHz. The cell
geometry was selected to ensure that the membrane resistance dominated the response of the
system, and film resistance was measured at the frequency that produced the minimum
imaginary response. Measurements were taken from 30 to 80 °C in liquid water, and from 30 to
95% relative humidity at 80 °C. An initial equilibration step at 80% relative humidity and 80 °C
was used, with an equilibration time of 4 h in between relative humidity measurements.

4.2.6 Measurement of surface and bulk morphology

Tapping mode AFM was performed using a Digital Instruments MultiMode Scanning
Probe microscope with a NanoScope IVa controller. A Veeco silicon probe with an end radius
<10 nm and a force constant K of 60 N/m was used to image samples. Samples were in acid form
and equilibrated at 40% relative humidity and 30 °C for at least 12 h prior to imaging.
For transmission electron microscopy imaging, acidified membranes were stained with a cesium hydroxide aqueous solution to enhance the electron density of the hydrophilic block and provide contrast within the sample. Samples were embedded in epoxy and microtomed into approximately 70 nm thick sections with a diamond knife. Samples were then imaged on a Philips EM 420 Transmission Electron Microscope using an accelerating voltage of 100 kV.

### 4.3 Results and Discussion

The HQSH100 and BPS0 oligomers were coupled together into two series, with a representative multiblock copolymer referred to as 3K5K, where 3K refers to a HQSH100 oligomer of 3,000 g/mol and 5K refers to the 5,000 g/mol BPS0 oligomer. The first series maintained a 3:5 (wt/wt) ratio of hydrophilic HQSH100 and hydrophobic BPS0 as described in Table 4-3. The second series used a 1:1 (wt/wt) ratio of hydrophobic and hydrophilic oligomers, as summarized in Table 4-4. Each series was characterized in terms of water uptake, proton conductivity in liquid water at 30 °C and under partially humidified conditions at 80 °C, tapping mode atomic force microscopy (AFM), and transmission electron microscopy (TEM).

#### 4.3.1 Characterization of the copolymer series with unequal block lengths

Liquid water conductivity and mass water uptake results as summarized in Table 4-1, were significantly lower than expected based on the experimental IEC values. While the IEC of the unequal block length series ranged from 1.2-1.37 meq/g, which is markedly higher than Nafion 112 (0.9 meq/g) and slightly less than that of BPSH-35 (1.50 meq/g), the resulting fully hydrated conductivities were much lower than expected. This was explained by the AFM images shown in Figure 4-2, which illustrate an insufficient hydrophilic domain to form continuous
hydrophilic phases, instead producing isolated spherical domains. This ‘pinprick’ morphology was observed across the unequal block length series. It was determined that the greater density of the hydrophilic phase combined with the smaller volume fraction was responsible for the observed morphology and behavior. Due to the inadequate performance in liquid water and undesired morphology, partially humidified proton conductivity testing and transmission electron microscopy (TEM) characterization were not performed.

<table>
<thead>
<tr>
<th></th>
<th>IEC by Titration (meq/g)</th>
<th>Water uptake (%)</th>
<th>Intrinsic Viscosity (dL/g)</th>
<th>Proton conductivity (S/Cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HQSH3-BPS5</td>
<td>1.32</td>
<td>27</td>
<td>0.56</td>
<td>0.04</td>
</tr>
<tr>
<td>HQSH6-BPS10</td>
<td>1.21</td>
<td>18</td>
<td>0.60</td>
<td>0.03</td>
</tr>
<tr>
<td>HQSH9- BPS15</td>
<td>1.20</td>
<td>13</td>
<td>0.68</td>
<td>0.03</td>
</tr>
<tr>
<td>HQSH12-BPS20</td>
<td>1.37</td>
<td>17</td>
<td>0.68</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 4-3. Properties of a series of HQSH100-BPS0 copolymers with unequal block lengths.

a In NMP with 0.05 M LiBr at 25°C.
b In liquid water at 30°C.
Figure 4-2. AFM phase images of HQSH100-BPS0 multiblock copolymers, a) 3K-5K and b) 9K-15K.

4.3.2 Characterization of the series of copolymers with equal block lengths

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>IEC by Titration (meq/g)</th>
<th>Water uptake (%)</th>
<th>Intrinsic Viscosity (dL/g)</th>
<th>Proton Conductivity at 30°C (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HQSH 3-BPS 3</td>
<td>1.79</td>
<td>110</td>
<td>0.52</td>
<td>0.130</td>
</tr>
<tr>
<td>HQSH 5-BPS 5</td>
<td>1.88</td>
<td>180</td>
<td>0.51</td>
<td>0.170</td>
</tr>
<tr>
<td>HQSH 10-BPS 10</td>
<td>1.78</td>
<td>160</td>
<td>0.98</td>
<td>0.210</td>
</tr>
<tr>
<td>HQSH 15-BPS 15</td>
<td>1.67</td>
<td>150</td>
<td>0.99</td>
<td>0.160</td>
</tr>
</tbody>
</table>

Table 4-4. Basic properties of equal block length HQSH100-BPS0 multiblock copolymer series.

a In NMP with 0.05 M LiBr at 25°C.

b In liquid water at 30°C.
In the copolymer series with equal block lengths, there was a great increase over the results of the series with unequal block lengths in the conductivity in liquid water at 30 °C, as well as the mass water uptake, as shown in Table 4-2. In Figure 4-3, AFM images of the copolymer surfaces showed the evolution of increasing domain size and co-continuous morphology with an increase in oligomer block length.

![AFM images of HQSH100-BPS0 multiblock copolymers, a) 5K-5K, b) 10K-10K, and c) 15K-15K.](image)

Figure 4-3. AFM tapping mode images of HQSH100-BPS0 multiblock copolymers, a) 5K-5K, b) 10K-10K, and c) 15K-15K.

This phase separated morphology was confirmed by the TEM image (Figure 4-4) of cross-sections of the bulk phase of the 10K-10K copolymer. The development of phase separation with block length was supported by anisotropy in dimensional water uptake as shown in Figure 4-5. A disproportionate increase in z swelling (across the thickness of the membrane) has been correlated between co-continuous morphology and improved proton conductivity under partially humidified conditions in other multiblock systems.\textsuperscript{14, 15, 20} This correlation was shown again in the evaluation of the 10K-10K copolymer under partially humidified conditions at 80 °C (Figure 4-6), in which proton conductivity was greater than or comparable to Nafion 112 for the duration of the test.
Figure 4-4. TEM image of HQSH100-BPS0 10K-10K copolymer.

Figure 4-5. Water swelling data as a function of polymer block lengths.
4.4 Conclusions

Two series (one of unequal block length and one of equal block length) of multiblock copolymers incorporating hydroquinone into the hydrophilic block were synthesized. Both series were evaluated with regard to water uptake, fully hydrated proton conductivity, and surface morphology. The initial unequal block length series was determined to have an insufficient fraction of hydrophilic oligomer, but the equal block length series showed good phase separation and proton conductivity. TEM characterization confirmed good phase-separated morphology in the bulk phase and conductivity testing under partially hydrated conditions showed excellent performance.
hydroquinone

18.

5044.

poly(arylene ether sulfone)s as novel proton exchange membranes 2008, exchange membranes. (polyarylene ether nitrile)

copolymers. on proton exchange membrane properties of sulfonated 15.

copolymers based on poly(arylene ether sulfone) via low 14.

conditions.


Roy, A.; Lee, H.-S.; McGrath, J. E., Hydrophilic-hydrophobic multiblock copolymers based on poly(arylene ether sulfone)s as novel proton exchange membranes - Part B. Polymer 2008, 49 (23), 5037-5044.

Lee, H.-S.; Lane, O.; McGrath, J. E., Development of multiblock copolymers with novel hydroquinone-based hydrophilic blocks for proton exchange membrane (PEM) applications. J. Power
Sources 2010, 195 (Copyright (C) 2011 American Chemical Society (ACS). All Rights Reserved.), 1772-1778.


5.0 Characterization of a segmented hydrophobic-hydrophilic, fluorinated-sulfonated ‘one-pot’ block and multiblock copolymer systems for use as proton exchange membranes

Abstract
A series of segmented hydrophobic-hydrophilic block copolymers based on highly fluorinated and sulfonated monomers was synthesized and evaluated for use as proton exchange membranes in hydrogen fuel cells. This series was synthesized using a ‘one-pot’ approach whereby a highly fluorinated hydrophobic oligomer was initially produced, after which a hydrophilic oligomer was added to create a segmented copolymer. This copolymer series produced high molecular weight, transparent, ductile films with good mechanical properties. At a comparable ion exchange capacity, the water uptake increased with oligomer length, suggesting the development of phase separation and long-range order, which was confirmed by TEM and AFM imaging. These copolymers showed improved proton conductivity with increasing block length under partially-humidified conditions. A series of multiblock hydrophobic-hydrophilic copolymers using the same co-monomers and oligomer molecular weights was also synthesized and evaluated as a control for comparison.

5.1 Introduction

With the growing political, economic and environmental costs associated with fossil fuel extraction, there is an increasing need for viable alternatives to current combustion engine technology.¹ Hydrogen-powered proton exchange membrane fuel cells (PEMFCs) are viewed as one of the more promising candidates for powering 21st century vehicles.² ³ Fuel cells using other fuels—for example, methanol or ethanol—may also be adapted for stationary power
applications such as personal electronic devices (e.g., laptop computers and cell phones). PEMFCs have a number of advantages compared to other types of fuel cells. For example, they are able to generate more power for a given volume or weight of fuel cell. This high-power density characteristic makes them compact and lightweight. In addition, their operating temperature is less than 100ºC, which allows rapid start-up. Importantly, PEMFCs have a negligible environmental impact with only water and heat produced during operation. These traits make them superior candidates for automotive power applications.

There are, however, a number of technical hurdles to overcome before the large-scale commercial production of these vehicles can be realized. In addition to the difficulty of hydrogen storage, hydrogen distribution and delivery will require the construction of a costly distribution infrastructure (combining transport and storage of hydrogen) and the development of a dense network of refueling stations. But before those problems can be addressed, scientists must first address the challenges associated with materials development. Specifically, the predominant commercial membrane in use today is Nafion®, which is a poly(perfluorosulfonic acid) ionomer. While it displays good proton conductivity, it has several drawbacks which at present are prohibitive to practical commercial application. These include high permeability to fuels, excessive materials cost, the difficulty in processing the copolymer, and a low operating temperature of about 80ºC under hydrated conditions. To overcome these challenges, a number of alternate proton exchange membrane candidates, membrane treatment procedures, and membrane additives are under development.

The McGrath group at Virginia Tech has been developing statistically copolymerized partially disulfonated poly(arylene ether sulfone)s as alternative PEM candidates. While these materials offer improvement both in raw materials cost and ceiling operating temperature, the
statistical copolymers showed poor performance at low relative humidity. The recent
development of nanophase-separated multiblock copolymers has consistently shown improved
proton conductivity under partially humidified conditions, due to the formation of ion-rich
channels which are better able to retain water while the highly hydrophobic channels
surrounding them provide mechanical strength and help decrease water loss. The higher ion
exchange capacity (IEC) afforded by this division of labor also produces good proton
conductivity under fully hydrated conditions. The nanophase separation additionally results
in anisotropic behavior which could reduce membrane stresses due to reduced in-plane
swelling. During fuel cell operation, in-plane swelling and deswelling stresses, due to
hydration and dehydration of the membrane electrode apparatus (MEA), can cause failure
between the electrode and polymer electrolyte layers. As the decreased in-plane swelling
becomes more pronounced with higher oligomer block lengths, there is an interest in developing
nanophase-separated multiblock copolymers to optimize PEMFC performance both in terms of
proton conductivity and fuel cell durability.

Typically, these novel multiblock copolymers are produced from two separately
synthesized oligomers of controlled molecular weight. The hydrophilic oligomer is afforded by
incorporating 3,3’-disulfonated, 4,4’dichlorodiphenyl sulfone (SDCDPS) with another
conomomer. The structure of the hydrophobic oligomer is then varied to tailor mechanical
properties, phase separation, and other desired variables.

Previously in the McGrath group at Virginia Tech, highly sulfonated, highly fluorinated
multiblock copolymers were synthesized from decafluorobiphenyl, bis(4-hydroxyphenyl)
sulfone, 4,4’-biphenol and SDCDPS, which showed good proton conductivity and improved
mechanical properties. This copolymer was termed BisSF-BPSH100, where BisSF refers to the
hydrophobic block synthesized from Bis(4-hydroxyphenyl) Sulfone and decaFluorobiphenyl, and BPSH100 refers to the hydrophilic block synthesized from SDCDPS and 4,4’-biphenol. A highly fluorinated monomer was chosen to be incorporated into the hydrophobic oligomer to provide greater phase separation as well as ease of synthesis due to the activity of the fluorine end groups. Bis(4-hydroxyphenyl sulfone) was selected for its availability and affordability.

The focus of this research is to synthesize a nanophase-separated segmented copolymer which is morphologically similar to the multiblock copolymer, using a one-pot synthetic process. In addition to offering a simpler synthetic approach, this approach may avoid the problems encountered in coupling multiblock copolymers where the two oligomers do not share a common good solvent. The segmented and multiblock copolymers will be compared for congruency in morphology and proton conductivity performance.

5.2 Experimental

5.2.1 Materials

Decafluorobiphenyl (DFBP) was obtained from Matrix Scientific and dried overnight under vacuum at room temperature. Bis(4-hydroxyphenyl) sulfone (Bis-S) was obtained from Alfa Aesar and dried for 24h under vacuum at 60°C prior to use. Monomer grade 4, 4’-biphenol (BP) was obtained from ChrisKev Company and dried for 24h under vacuum at 60°C prior to use. 4,4’-dichlorodiphenyl sulfone was kindly provided by Solvay Advanced Polymers and used as received to synthesize 3,3’-disulfonated, 4,4’dichlorodiphenyl sulfone (SDCDPS) according to previously reported procedure25-27, which itself was an adaptation from the procedure published by Ueda et al.28

The SDCDPS was dried under vacuum at at 160°C for 48 h prior to use to remove any
adsorbed moisture. \(N,N'-\text{dimethylacetamide (DMAc)}\) and \(N\text{-methyl-2-pyrrolidone (NMP, Aldrich)}\) were vacuum distilled over calcium hydride onto molecular sieves and stored under nitrogen prior to use. Potassium carbonate (\(K_2\text{CO}_3,\) Aldrich) was dried under vacuum at 120°C prior to use. Toluene, cyclohexane, acetone, and isopropyl alcohol (IPA) were used as received from Aldrich. Concentrated sulfuric acid (\(\text{H}_2\text{SO}_4\)) was obtained from VWR and diluted to produce a 0.5 M aqueous solution.

### 5.2.2 Synthesis of segmented copolymer

A detailed sample copolymerization procedure has been reported\(^ {29}\), but an overview will be given here. The reaction proceeded in a three-neck, round-bottom flask using a mechanical stirrer, Dean-Stark trap, condenser, and \(\text{N}_2\) inlet to protect the reaction from ambient oxygen. The BPSH100 oligomer was first synthesized by reacting 4,4’-biphenol with SDCDPS in DMAc with a molar ratio calculated to both control molecular weight and ensure a hydroxyl-endcapped oligomer from an excess of biphenol, as shown in Figure 1. The reaction bath was set to 85°C, and the monomers were allowed to dissolve under a nitrogen purge while \(K_2\text{CO}_3\) and toluene were added. The reaction bath temperature was raised to 155°C for 4h in order to azeotrope water, and then the toluene was removed after the reaction bath temperature was raised to 180°C. The reaction was maintained at this temperature for 96h, after which it was cooled, filtered, and precipitated into acetone. The oligomer was dried under vacuum for at least 24h at 110°C and the structure was confirmed by NMR spectroscopy. The BPSH100 oligomers were synthesized with target weights ranging from 3000 to 9000 g/mol.
Using the same labware as in the BPSH100 oligomer synthesis, the segmented copolymer was synthesized by dissolving the desired BPSH100 oligomer and bis(4-hydroxyphenyl) sulfone into NMP under a nitrogen purge. Cyclohexane was then added as an azeotroping agent, and K₂CO₃ was added to provide a slightly alkaline environment to facilitate the reaction. After 4h of azeotroping at 110°C, the cyclohexane was removed and the bath temperature lowered to 85°C. After adding DFBP and additional NMP, the reaction bath temperature was raised to 90°C for 36h. The solution was then cooled and precipitated into IPA, followed by filtering and washing in deionized water at 60°C for 12 h and acetone for 12 h. It was dried at 110°C under vacuum for 24 hours prior to dissolving and casting into films. The reaction scheme is shown in Figure 5-2.

Figure 5-1. Synthesis of phenoxide-terminated BPSH100.

Figure 5-2. Synthesis of segmented BisSF-BPSH100 copolymer.
5.2.3 Synthesis of multiblock copolymer controls

The details of the synthesis of the multiblock controls has been reported elsewhere, but is summarized in Figure 5-3. There were some minor modifications detailed here, and the overall reaction is shown in Figure 3.

The fluorine-terminated hydrophobic oligomers were synthesized with target weights ranging from 3000 to 9000 g/mol. Using a three-neck, round-bottom flask equipped with mechanical stirrer, Dean Stark trap, N₂ inlet and condenser, Bis-S and DFBP were dissolved in DMAc at 50°C. Next, K₂CO₃ and cyclohexane were added and the temperature was increased to 110°C for 5h and allowed to cool. After cooling, the reaction was filtered to remove salts and precipitated into a 1L solution of 50% methanol, 50% water by volume. The oligomer was washed for 12 h in deionized water and dried under vacuum at 90°C prior to use.

The phenoxide-terminated hydrophilic BPSH100 oligomers were synthesize by reacting 4,4’-biphenol with SDCDPS in DMAc with a molar ratio calculated to both control molecular weight and ensure a hydroxyl-endcapped oligomer from an excess of biphenol. The reaction bath was set to 85°C, and the monomers were allowed to dissolve under a nitrogen purge while K₂CO₃ and toluene were added. The reaction bath temperature was raised to 155°C for 4h in order to azeotrope water, and then the toluene was removed, after which the reaction bath temperature was raised to 190°C. After 36 h the bath temperature was lowered to 85°C for the coupling reaction to proceed.

The coupling reaction was carried out by adding the desired hydrophobic oligomer to the resulting hydrophilic oligomer still in solution in order to produce a 14% (w/v) concentration.
The bath temperature was increased to 90°C for 36 h. The solution was then precipitated into IPA, filtered, and washed in deionized water at 60°C for 12h and acetone for 12h. The polymer strands were then dried under vacuum at 110°C for 24h prior to dissolution and casting into films.

![Diagram of synthetic coupling of BisSF-BPSH100 multiblock copolymer.]

**Figure 5-3. Synthetic coupling of BisSF-BPSH100 multiblock copolymer.**

### 5.2.4 Membrane casting and preparation

The copolymers were dissolved in dimethylacetamide (DMAc) at a 7% (w.w) concentration and cast onto a clean glass plate. The solvent was evaporated under an IR lamp, which was ramped after 24 h at 30-35°C to 35-40°C for an additional 24 h. The remaining solvent was then removed by drying under vacuum at 110°C for 24h. Due to the synthetic procedure, the copolymers are synthesized in salt form. The films were converted to acid form by boiling in 0.5 H₂SO₄ for 2 hours, followed by 2 hours of boiling in deionized water as reported elsewhere. The films were then allowed to equilibrate for 48 hours in two changes of deionized water at room temperature.
5.2.5 Measurement of water uptake

Water uptake measurements were gravimetrically performed by weighing fully hydrated samples of each copolymer after blotting, and then re-weighing the samples after 24 hours of heating under vacuum at 110°C. Each copolymer had an average of three samples measured and averaged. The water uptake was determined according to the following equation:

\[
Water \ Uptake = \frac{Mass_{\text{Wet}} - Mass_{\text{Dry}}}{Mass_{\text{Dry}}} \times 100\%
\]

The dimensional swelling of the copolymers was measured both in the in-plane (x and y directions) and the through-plane (z-direction) orientation. The sample films were initially measured with a micrometer after having been fully hydrated in deionized water for 24 h. They were then re-measured after again drying for 24 hours under vacuum in a convection oven at 110°C. Again, three samples were used for each copolymer, with an average sample size of approximately 2.5 x 2.5 cm.

5.2.6 Measurement of proton conductivity

Proton conductivity measurements of acidified, equilibrated membranes were conducted using a Solartron 1252A + 1287 impedance analyzer over a range of 10 Hz to 1 MHz. The cell geometry was selected to ensure that the membrane resistance dominated the response of the system, and film resistance was measured at the frequency that produced the minimum imaginary response. Measurements were taken from 30 to 80 °C in liquid water, and from 30 to 95% relative humidity at 80 °C. An initial equilibration step at 80% relative humidity and 80 °C was used, with an equilibration time of 4 h in between relative humidity measurements. The membrane thickness was measured at 95, 80, and 30% RH in order to provide accurate conductivity measurements across the scale.
5.2.7 Measurement of surface morphology

Tapping mode AFM was performed using a Digital Instruments MultiMode Scanning Probe microscope with a NanoScope IVa controller. A Veeco silicon probe with an end radius <10 nm and a force constant K of 42 N/m was used to image samples. Samples were in acid form and equilibrated at 40% relative humidity and 30 °C for at least 12 h prior to imaging.

5.2.8 Measurement of bulk morphology

For transmission electron microscopy imaging, acidified membranes were stained with a lead acetate aqueous solution to enhance the electron density of the hydrophilic block and provide contrast within the sample. Samples were embedded in epoxy and microtomed into approximately 70 nm thick sections with a diamond knife. Samples were then imaged on a Philips EM 420 Transmission Electron Microscope using an accelerating voltage of 100 kV.

5.3 Results and Discussion

5.3.1 Water uptake and dimensional swelling

In general, all the segmented and multiblock copolymers showed good control of oligomer target molecular weight and IEC. Both series of copolymers also displayed good mechanical strength and intrinsic viscosity (IV) values, as shown in Table 5-1.29 It should be noted, however, that the IV data for the multiblock copolymers were higher in comparison to the segmented copolymers. This difference was attributed to a small amount of branching from the decafluorobiphenyl group during synthesis, which did not impact the copolymer’s ability to be
solution cast into a film. As expected from previous multiblock copolymer research, water uptake increased with block length due to the development of long-range order in the nanophase-separated morphology. One unexpected observation was that the segmented copolymers showed a block length effect with liquid water conductivity values, whereas the multiblock copolymers did not—despite the fact that IEC values decreased as block length increased. Overall water uptake by mass was higher for the 5K:5K and 9K:9K multiblock copolymers, which could be expected from the slightly higher IEC values.

Table 5.1. Characterization Summary of Segmented and Multiblock BisSF-BPSH100 Copolymers

<table>
<thead>
<tr>
<th></th>
<th>IEC (meq/g)</th>
<th>Conductivity (S/cm)</th>
<th>Mass Water Uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Experimental</td>
<td>I.V.</td>
</tr>
<tr>
<td><strong>Segmented</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3K:3K</td>
<td>1.6</td>
<td>1.8</td>
<td>0.63</td>
</tr>
<tr>
<td>5K:5K</td>
<td>1.6</td>
<td>1.5</td>
<td>0.50</td>
</tr>
<tr>
<td>9K:9K</td>
<td>1.7</td>
<td>1.5</td>
<td>0.82</td>
</tr>
<tr>
<td><strong>Multiblock</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3K:3K</td>
<td>1.8</td>
<td>1.8</td>
<td>1.07</td>
</tr>
<tr>
<td>5K:5K</td>
<td>1.6</td>
<td>1.6</td>
<td>0.89</td>
</tr>
<tr>
<td>9K:9K</td>
<td>1.7</td>
<td>1.7</td>
<td>0.84</td>
</tr>
</tbody>
</table>

a. Calculated form experimental loading: IEC = (g of Hydrophilic * IEC of BPSH100)/(g of Hydrophobic + g of Hydrophilic)
b. Calculated from $^1$H NMR
c. Performed in liquid water at 30°C

When compared to BPSH-35 (a disulfonated poly(arylene ether sulfone)s random copolymer with 35 mole% disulfonated moiety), we noted dramatically different anisotropic values for the segmented and multiblock copolymers were evident, as shown in Figure 5-4. While the degree of anisotropy was slightly higher for the 5K:5K multiblocks, in general the two series were comparable in their behavior. Both 9K:9K copolymers showed the highest degrees of anisotropy, consistent with previous research on other multiblock systems. This reduced in-plane
swelling may help to reduce membrane electrode failure from changes in MEA water content during fuel cell operations.

Figure 5-4. Dimensional swelling data for segmented and multiblock BisSF-BPSH100 copolymers.

5.3.2 Conductivity under partially humidified conditions

Relative humidity testing showed similar performance between both copolymer series, as shown in Figure 6.5. As has been observed in other multiblock systems\textsuperscript{18, 20, 22}, longer copolymer block length tends to correlate with improved conductivity at lower relative humidities. Therefore, the performance of the BisSF-BPSH100 copolymers did not appear to have been impacted by the synthesis route, indicating that the simpler segmented synthetic method may be considered a satisfactory improvement over the previously used multi-step multiblock synthetic procedures. Both 9K:9K multiblock and segmented copolymers displayed conductivity values close to that of Nafion 112 across the entirety of testing conditions.
5.3.3 Morphological results

The TEM images shown in Figure 5-6 reflect both the development of long-range domain order with an increase in block length from 5K:5K to 9K:9K, but also show similar results for both the segmented and multiblock series. This is consistent with our observations of other multiblock copolymer systems. The AFM images similarly show the development of long-range order with an increase in block length, although phase separation appears to be slightly more distinct in the segmented block copolymer series. The surface morphology appears to show less co-continuous formation than the structures shown from the bulk TEM images.
Figure 5-6. TEM images of (A) 5K:5K Multiblock, (B) 9K:9K Multiblock, (C) 5K:5K Segmented, and (D) 9K:9K Segmented BisSF-BPSH100 copolymers. All images are taken at 96000 magnification.
5.4 Conclusions
A series of segmented copolymers was successfully synthesized using a one-pot, oligomer-two monomer approach. The copolymers were compared with a series of multiblock copolymers and the two were found to have similar conductivity under partially humidified conditions, bulk and surface morphology, water uptake behavior, and mechanical properties.

The water uptake increased with block length and the development of nanophase separation as expected. The development of longer-range order also correlated with improved performance under partially humidified conditions.

References:


