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Poly(arylene ether sulfone)s Carrying Pendant(3-sulfonated) phenyl sulfonyl Groups for use as Proton Exchange Membranes

Kimberly E. Kern
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POLY(ARYLENE ETHER SULFONE)S CARRYING PENDANT (3-SULFONATED) PHENYL SULFONYL GROUPS FOR USE AS PROTON EXCHANGE MEMBRANES

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

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ABSTRACT

Kern, Kimberly E. M.S., Department of Chemistry, Wright State University, 2011.
Poly(arylene ether sulfone)s Carrying Pendant (3-sulfonated) Phenyl Sulfonyl Groups for Use as Proton Exchange Membranes

A series of poly(arylene ether)s, containing a pendant mono sulfonic acid group, was synthesized using 3-sulfonated-3’, 5’-difluorodiphenyl sulfone and a variety of bisphenols for use in proton exchange membranes (PEM). Nucleophilic aromatic substitution was utilized for homo and copolymerizations. In addition, the relationship between perfectly alternating and random copolymers and their effects on overall properties was studied. Polymerization reactions yielded linear sulfonated poly(arylene ether)s, sPAEs, with molecular weights ranging from 15,400 to 212,000 g/mol. All of the polymers were characterized by gel permeation chromatography (GPC), $^{13}$C NMR spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). All polymers exhibited excellent thermal stability in excess of 300 °C. The proton conductivity of several samples rival that of Nafion® under similar conditions while the water uptake values, in the acid form, were 26, 23 and 32%, respectively. A relationship exists between order and thermal properties of sPAES as the more closely alternating structures exhibited higher $T_g$’s as well as higher $T_{d5%}$ than their more random analogues. Pendant sulfonated systems do offer relatively low WU values and high conductivity, coupled with excellent thermal stability, making them attractive candidates for new PEMs.
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DEDICATION

I would like to dedicate this to my mom and dad. You are the best and most supportive parents anyone could ever ask for. You have been there when this project was both stressful and successful. You have taught me to never give up and that perseverance will ultimately result in a greater appreciation and understanding for my future career in science. I can’t thank you enough for your continual support.
1 INTRODUCTION

1.1 Background

In the past ten years, the national average gasoline prices have increased nearly 250% in price per gallon at the pump.¹ As fossil fuel supplies are quickly declining and world populations are increasing, the need for alternative fuel sources has become ever more critical.² Nonpolluting renewable energy sources are desirable as an alternative for devices currently powered by fossil fuels. In 2001, in the United States, alternative fuels only accounted for 0.2% of total transportation fuel consumption, thus, advancing the need for alternative fuel sources which can be readily available, nonpolluting, and that are fairly inexpensive.³ Hydrogen is the ultimate nonpolluting renewable, sustainable fuel for the future due to its abundance and availability. During president George W. Bush’s State of the Union Address in 2003 he announced the Hydrogen Fuel Initiative, which aims to develop hydrogen fuel cell technology that is both practical and cost effective by 2020.² With the push away from the dependence on fossil fuels, toward clean alternative energy, fuel cells are emerging as a key leader in the future for fuel technology.

Fuel cells are electrochemical devices that act similarly to batteries, but rely on a continuous fuel supply, rather than one that depletes over time. Rechargeable batteries require regeneration via charging to shift equilibrium in order to regenerate the energy supply whereas fuel cells do not. Fuel cells provide advantages such as a continuous supply of energy output as long as the chemical fuel is readily available, an advantage which is heavily sought after.
Academic and industrial institutions have been researching alternative power sources to fossil fuels for over a century and the demand for alternative sources is increasing rapidly. In the 1960’s, GE developed the first workable polymer electrolyte membrane fuel cell (PEMFC) for use on both the Apollo and Gemini space missions. Fuel cells may be the solution many have been searching for as a source of energy in a wide variety of applications from automobiles to cellular phones and beyond.

1.2 Types of Fuel Cells

Fuel cells are classified by the type of electrolyte they employ, the operating temperature range, the cathode and anode catalysts, and the type of fuel consumed. As the types of fuel cells vary, so do their properties including limitations as well as advantages and potential applications. There are currently several types of fuel cells being researched including: Polymer Electrolyte Membrane Fuel Cells (PEMFCs), Direct Methanol Fuel Cells (DMFCs), Alkaline Fuel Cells (AFCs), Phosphoric Acid Fuel Cells (PAFCs), Molten Carbonate Fuel Cells (MCFCs), Solid Oxide Fuel Cells (SOFCs), and Regenerative Fuel Cells (RFCs).

PEMFCs were deemed the most likely alternative fuel candidate by the Department of Energy due to the estimated 50-60% output efficiency of the fuel cell compared to internal combustion engines, which are only 30% output efficient. PEMFC’s are an ideal candidate for alternative energy uses in portable electronics, automobiles, and stationary power devices because they provide a constant supply of energy, have a small size, are light weight, and the fuel is portable.
1.3 How Proton Exchange Membranes Operate

In PEMFC’s, such as hydrogen fuel cells (HFC), the polymer electrolyte membrane acts as a proton conductor, separating the anode from the cathode as depicted below in Figure 1.

![Diagram of proton exchange](image)

**Figure 1.** Representation of how a PEM in a HFC conducts protons.

PEM’s transfer protons from the anode to the cathode, which are both typically platinum while the electrons are conducted in a circuit external to the membrane. The membrane itself also acts as a barrier to prevent fuel crossover, however, it may be permeated by CO that is an impurity in produced hydrogen gas from reforming hydrocarbons and water at high temperatures that may poison the catalysts. At the anode, the platinum catalyst causes diatomic hydrogen to oxidize into 2 protons, which can be
conducted through the PEM to the cathode, and 2 electrons, which are conducted, in an external circuit creating an electrical current. At the cathode oxygen from the atmosphere is reduced and combined with the protons to emit water as the byproduct that flows out of the cell. The half and net reactions are shown below:

**Anode**  
\[ 2 \text{H}_2 \rightarrow 4 \text{H}^+ + 4 \text{e}^- \]

**Cathode**  
\[ \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O} \]

**Net Reaction**  
\[ 2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} \]

Hydrogen, when combined with oxygen from air in a fuel cell, creates the byproducts of heat and water, making it an ideal “green” form of energy for the future.

### 1.4 Hydrogen Fuel Cells vs. Direct Methanol Fuel Cells

Long studied, hydrogen fuel cells (HFCs) have been around since 1839 when William Robert Grove developed the first HFC used to generate electricity by splitting water into hydrogen and oxygen gases then conducting protons in an electrolyte, using a dilute sulfuric acid solution, producing water and heat byproducts.\(^4\) Since the first HFC, technology has come a long way, yet the principle remains the same. Protons must be conducted through an electrolyte and electrons through an external circuit to generate usable energy.

Pure hydrogen gas is not the only useable fuel for PEMFCs. Methanol can also be used in a fuel cell as a source of hydrogen to create an electrical current producing CO\(_2\), water, and heat as byproducts; this is a Direct Methanol Fuel Cell (DMFC). Methanol is more easily produced, transported, and stored compared to hydrogen. Even though methanol has a higher energy density than hydrogen, a major drawback is the emissions
produced by DMFCs. DMFCs emit greenhouse gases, however the quantities are significantly lower than with gasoline. Also, chronic exposure to methanol has been shown to cause optic nerve damage. The reliance on consumable fuels, which produce greenhouse gases, is a challenge that must be overcome in the near future.

1.5 Ion Exchange Capacity versus Water Uptake: The Trade Off

Water management is an important concern for PEMFCs. Too much water, via low ionic resistance, in the cell will cause flooding, resulting in liquid condensate forming in the cell and a significant drop in energy output. Conversely, too little water via high ionic resistance results in drying of the membrane and energy output also decreases. Therefore, Water Uptake (WU) is a significant consideration for PEMs because it influences both proton conductivity as well as mechanical properties. As the percentage WU increases in membranes the conductivity also increases, however, the mechanical properties decrease due to dimensional swelling. \(^9\) \(^11\) WU is directly related to the amount of acid that is incorporated into the polymer. Equivalent Weight (EW) is the relationship between the masses of a polymer required to incorporate one mole of acid groups, Equation 1.

\[
EW\left(\frac{g}{equiv.}\right) = \frac{MW_{\text{repeat unit}}\left(\frac{g}{mol}\right)}{\text{moles}_{\text{acid}}\left(\frac{mol}{equiv.}\right)} \quad \text{Equation 1}
\]

EW is useful for the determination of another critical property in PEM’s, the Ion Exchange Capacity (IEC). As defined in Equation 2 a polymer’s IEC is the amount of acid, in milliequivalents, that is present in each gram of dried polymer.
\[ IEC \left( \frac{\text{mequiv.}}{g} \right) = \frac{1}{EW \left( \frac{g}{\text{equiv.}} \right)} \times 1000 \]  

Equation 2

IEC is critical in PEMs because higher amounts of acid often correlate to both the ability to conduct protons as well as the amount of water that the polymer will absorb, i.e. WU, thus contributing to the membrane’s overall integrity. Sulfonated polymers with high IEC values and high hydrophobicity are ideal for conducting membranes due to sulfonic acid groups behaving as proton transport carriers, however, too high of an IEC causes the membranes to swell excessively or become soluble in water. A key manner in which swelling may be reduced is through hydrogen bonding that effectively reduces swelling in membranes.\(^{12}\) There must be a balance between the IEC and WU to achieve an optimal polymer that is both an excellent conductor as well as mechanically robust.

1.6 PEMFC Background

For fuel cell purposes perfluorosulfonic acid (PFSA) membranes are most often used; they consist of a hydrophobic Teflon\(^{\circledR}\) backbone to which hydrophilic sulfonic acid containing side chains are attached. They are chemically inert in both oxidizing and reducing atmospheres.\(^{8,13}\) Commercially available PFSA PEM’s include Nafion\(^{\circledR}\), Gore-Select, Aciplex, Xus, and Flemion. These materials are widely used due to their exceptional properties such as high proton conductivity and chemical stability.\(^{8,9}\) Nafion\(^{\circledR}\) is by far the most common and well-known polymer electrolyte for fuel cells today. Nafion\(^{\circledR}\) membranes are highly acidic due to the presence of the pendant
perfluorosulfonic acid groups, with a pKₐ of -3.09, resulting in excellent proton conductivity (90-120 mS/cm at a range of 34-100% RH)\(^8,14\)

![Chemical structure of Nafion®](image)

**Figure 2:** The general chemical structure of Nafion\(^®\).

While the PFSA membranes possess many desirable properties for use as PEM materials, there are several commercial and technical issues, such as osmotic drag, high cost (~$800/m\(^2\)), low conductivity at low relative humidity, and a low T\(_g\), which restricts their application above 100 °C\(^8,10,12,13,15\). Another challenge set forth is achieving a proton conductivity above 150 mS/cm, which is needed for high-performance fuel cell proton exchange membranes. Unfortunately, Nafion® cannot meet this need at 100 °C and 100 % RH\(^{15,16}\). With the need to reduce costs from over $1,000/kW to $30/kW ($800/m\(^2\) to $20/m\(^2\)), increase energy output, increase the operating temperatures, and decrease the RH used in fuel cells, alternatives to Nafion® as PEMs are heavily sought after\(^{16}\).
1.7 Water Channels and Morphology

Nafion® is well recognized to have moderately low water uptake (WU) and high conductivity; much of this trend is attributed to the triflic acid derivate in the structure, which is strongly acidic and thus an excellent conductor of protons. The Teflon® backbone of Nafion® is highly hydrophobic and the acid groups are quite hydrophilic. Due to the different affinities for water between the backbone and the pendant acid group, Nafion® undergoes microphase separation. Microphase separation occurs when components of polymers are dissimilar and are essentially immiscible in one another. In the case of Nafion® hydrophilic domains, similar to a reverse micelle, form in a matrix of crystallites as represented in Figure 3.17

![Water Channel Model](image)

**Figure 3**: Water Channel Model adapted from Schmidt-Rohr & Chen.17

The super acid character of Nafion®’s hydrophilic sites allow protons to move through the water channels that are formed in the hydrophilic domains resulting in
relatively high conductivity while maintaining a relatively low incorporation of sulfonic acid moiety, thus limiting swelling caused by WU.\textsuperscript{13}

1.8 Alternatives to Nafion\textsuperscript{®}

The development of new acid-functionalized aromatic hydrocarbon polymers, as alternatives to PFSA, for PEMs has been investigated intensely over the past two decades.\textsuperscript{9} The need for high performance and low cost membranes capable of operating in fuel cells has focused research groups onto sulfonated aromatic backbone alternatives such as poly(ether ether ketone) (sPEEK), poly(benzimidazole) (sPBI), poly(arylene ether sulfone) (sPAES), poly(ether ether sulfone) (sPEES), poly(aryl ether ketone) (sPAEK), polyphenylene oxides (sPPO), poly(arylene ether sulfone amide) sPAESA, and many more.\textsuperscript{10, 13, 18, 19} With seemingly endless combinations of monomers that can react to form polymers with arylene backbones, this class of polymers exudes significant promise as highly thermally stable, cost efficient alternatives to PFSA membranes for the future.

1.9 Types of Conducting Groups

Protons may be conducted through a PEM by incorporating various types of acids as the conducting groups. Acids are ideal because they have a low affinity for protons, therefore, as the \( pK_a \) of the acid decreases, proton mobility increases allowing for protons to hop from one acid group to the next through a network of hydrogen bonds. There are 3 main types of acids that are used to conduct protons for PEMFC applications including: sulfonic acid, phosphonic acid, and carboxylic acid. The type of acid chosen depends upon the mobility of the protons at the operating temperature and RH needed in fuel cell
conditions. **Table 1** lists the \( pK_a \)'s of the 3 most common acids, when attached pendant to polystyrene, **Figure 4**. Sulfuric acid exhibits the lowest \( pK_a \) value, corresponding to the strongest acid and the highest mobility of protons.

**Table 1**: \( pK_a \) values of acid groups attached to polystyrene.\(^{20}\)

<table>
<thead>
<tr>
<th>acid</th>
<th>( pK_{a1} )</th>
<th>( pK_{a2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-SO(_3)H</td>
<td>&lt;1</td>
<td>---</td>
</tr>
<tr>
<td>-PO(_3)H(_2)</td>
<td>2-3</td>
<td>7-8</td>
</tr>
<tr>
<td>-CO(_2)H</td>
<td>5-7</td>
<td>---</td>
</tr>
</tbody>
</table>

**Figure 4**: Polystyrene repeat unit with sulfonic, phosphonic, and carboxyl groups attached pendant to the backbone.

1.10 s-PAES

PAES are high performance engineering thermoplastics that display excellent thermal, mechanical, and film forming properties. PAES also offer resistance to oxidation
and stability to acidic conditions. One objective is to create PEMs for fuel cells by sulfonating poly(arylene ether sulfone)s without sacrificing their excellent properties.

Sulfonation of polymers is achieved via two routes, synthesis of a monomer which is first sulfonated then used to polymerize, or post-sulfonation of polymers. Sulfonation reactions have been investigated since 1976, when Noshay & Robeson sulfonated commercially available polysulfone with SO$_3$ to post-modify on the activated electron donating ring, ortho to the aromatic ether bond.

![Figure 5: Pre and Post sulfonation location on PAES adapted from Wang et al.](image-url)
One problem with use of post-sulfonated polymers is that the exact structures are not clear, they tend to be less repeatable, and thermal desulfonation is likely to occur.\textsuperscript{9,10} Since the development of post-sulfonated PAES, pre-sulfonated monomers have been developed by numerous groups to control the location and degree of sulfonation in PAES.\textsuperscript{6,8,15} Sulfonation on electron poor rings, such as those attached to sulfones, enhances both the stability and acidity.\textsuperscript{15}

The effects of post and pre-sulfonation of PAES, \textbf{Figure 6}, with similar IECs have been previously reported by Lufrano \textit{et al.} and Zhang \textit{et al.}, respectively and are displayed in \textbf{Table 2}.\textsuperscript{22,23}

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|c|c|}
\hline
Polymer Sample & \% SO\textsubscript{3}H & IEC * (meq/g) & \(T_{d5}\%\) \# (\(^\circ\text{C}\)) & WU (wt. \% at 23 \(^\circ\text{C}\)) & Conductivity (mS/cm) \\
\hline
BiA-SPAES-3 & 60 & 1.15 & 431 & 24 & 57 \\
SPSU3 & 48.7 & 1.1 & \approx310 & 21.8 & 10 \\
\hline
\end{tabular}
\caption{A comparative analysis of structurally similar bisphenol A based sPAES: BiA-SPAES\textsuperscript{22} (Pre-sulfonated) and SPSU3\textsuperscript{23} (Post-sulfonated).}
\end{table}

\* based on elemental analysis
\# air

\textbf{Figure 6:} Structures of pre vs. post sulfonated sPAES from \textbf{Table 2}.

While the percentage of acid groups, IEC, and WU are similar, there is a notable difference in the observed conductivity between the two systems. The pre-sulfonated system has over 5.5 times higher conductivity when compared to the post-sulfonated
system. The difference in conductivity may be attributed to the spatial separation between the acid groups. Also, post-sulfonated polymers are more prone to crosslinking through the sulfonic acid groups. In order to achieve a similar conductivity to that of Nafion® polymers higher IECs are required with sulfonated poly(arylene ethers). The requirement is attributed to the lower acid strength, as well as backbone stiffness, present in the sPAE systems.

1.11 Pendant vs. Backbone

Since Nafion® is the standard for proton conducting polymers, when searching for an inexpensive and thermally stable alternative, it follows that a similar structure may be useful as a suitable replacement. For polymers with equal IEC, those that contain acid groups on longer side chains exhibit better conductivity as a result of the formation of distinct water channels. Figure 7 displays a copolymer system with both backbone and pendant functionalization, as reported by Harrison and Li et al., respectively.

![Figure 7](image)

**Figure 7:** Comparison of Bisphenol AF random copolymer systems that are either backbone or pendant functionalized.
The pendant and backbone systems can be sufficiently compared by use of the degree of sulfonation (% DS) in relation to other critical properties such as conductivity and WU as displayed in Table 3.

**Table 3:** Comparison of Bisphenol AF copolymer systems that are either backbone (6F-) or pendant functionalized (S2-PAES-).²⁴

<table>
<thead>
<tr>
<th>Polymer- % DS</th>
<th>IEC (meq/g)</th>
<th>Conductivity* (mS/cm)</th>
<th>T₄₅% °C</th>
<th>WU* (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6F-10</td>
<td>0.32</td>
<td>5</td>
<td>310</td>
<td>5</td>
</tr>
<tr>
<td>6F-20</td>
<td>0.59</td>
<td>8</td>
<td>300</td>
<td>9</td>
</tr>
<tr>
<td>6F-30</td>
<td>0.87</td>
<td>20</td>
<td>295</td>
<td>13</td>
</tr>
<tr>
<td>6F-40</td>
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S2-PAES systems @ 20 °C, 6F systems @ 30 °C

Similar IECs yield higher conductivity for the backbone system, however, the pendant systems offer a distinct advantage, the ability to incorporate a higher percentage of sulfonic acid groups while still remaining insoluble in water, a desirable feature for PEM candidates.

In addition, according to Ma et al., poly(arylene ether)s with the sulfonic acid groups attached on a pendant phenyl ring, rather than directly on the backbone, experience better chemical resistance due to the stability of the intermediate.¹²

Another potential way to enhance PEM performance is to distinctly separate the ionic hydrophilic regions from the hydrophobic polymer backbone.²⁶ Attaching the sulfonic acid groups away from the backbone in a pendant manner may achieve this separation.
1.12 Random, Alternating, Block Copolymers

In order to understand the different types of polymers they must first be defined by the type of repeat unit they employ. Homopolymers only have one kind of repeat unit; copolymers have more than one kind of repeat unit. For the purpose of this paper, alternating polymers involve two different kinds of B \textsubscript{2} monomers, B \textsubscript{2} & B \textsubscript{2}', which alternate with an A\textsubscript{2} monomer yielding a 4 monomer repeat unit. Block copolymers are two or more uninterrupted different polymer chains covalently bound to one another. Each type of polymer mentioned previously is defined below, Figure 8.

- Homopolymers
- Random Copolymers
- Alternating Copolymers
- Block Copolymers

Figure 8: Types of polymer repeat units.

It should be noted that the classifications of polymers mentioned previously are the average character of the polymer type and minimal deviations from the definitions may exist. The majority of copolymers are random because the distribution and reactivity of monomers differ, therefore, a random order and distribution occurs.
To achieve high number average molecular weights, $M_n$, in condensation polymers, the feed ratios of monomers must be equal; in this case the $M_n$ is infinity. A small imbalance of monomer feed ratios effectively limits how many repeat units may be formed in the polymerization. The number of repeat units formed in a polymerization is the *Degree of Polymerization* (DP). By the use of the Carothers Equation, **Equation 3**, specific theoretical molecular weights may be achieved through an intentional imbalance in feed ratio of the two monomers, where $r$ is the ratio of the stoichiometric limiting to the excess reagent and $r < 1$.

$$DP = \frac{1 + r}{1 - r}$$  \hspace{1cm} **Equation 3**

When two polymers are mixed together, they undergo *macrophase separation* in solution, separating into their pure components. Block copolymers allow for two or more polymers to be covalently linked together, therefore allowing properties of each block to be exhibited in a single chain, although *microphase separation* still occurs. Below the temperature in which the *order-disorder transition* occurs, microphase separation occurs resulting in various morphologies, which is especially useful when trying to tune properties.\textsuperscript{27} One of the approaches to improve performance in sulfonated copolymers is through the use of multi-block systems, consisting of hydrophilic and hydrophobic segments, and a lot of research on using them for PEMs has been reported.\textsuperscript{6, 7, 9, 13, 28-30} Multi-block copolymers are an excellent tool for controlling domain size after microphase separation occurs. The resulting water channels are expected to provide low WU and enable high proton conductivity, even at low RH.\textsuperscript{7, 9} Still, the formation of water channels is difficult to achieve in aromatic multi-block copolymers because of the
minimal differences in polarity between the hydrophilic and hydrophobic domains, when compared to PFSA membranes.\textsuperscript{9,31} However, despite extensive efforts, the performance of aromatic PEMs, especially conductivity under low relative humidity, do not yet rival PFSA membranes. In part, these observations may be due to weak microphase separation and imprecise water channels.\textsuperscript{9,13}

1.13 Current Project

The current project seeks to provide answers to several fundamental questions regarding pendant sulfonated systems. First, how can the properties be tuned by changing the amount of acid incorporated into the polymer? How does the order of assembly of monomers affect overall polymer properties? Are pendant sulfonated systems truly more advantageous for use in PEMs than their backbone counterparts?

A number of reports have indicated that incorporating the sulfonic acid group on a pendant group rather than directly on the backbone in PAE systems might provide additional benefits in terms of accessibility and the ability to adopt various morphologies.\textsuperscript{15,39,45,46}
Figure 9: A direct comparison of pendant vs. backbone sulfonation.

By placing the sulfonic acid group pendant on a polymer prepared from a 3,5-difluoro aromatic system, Figure 9, it is anticipated that the conductivity will be enhanced moderately by increasing accessibility. These 3,5-pendant systems are more hydrolytically stable compared to their 4,4’-backbone counterparts due to the stability of the intermediate if water were to act as the nucleophile in this system. The aryl ether bonds are slightly polar and readily hydrogen bond with water, as do the acid groups. In addition, 4,4’-backbone systems contain more localized water molecules between the ether bonds and acid groups. Even though ether bonds resist hydrolysis, at high temperatures, such as polymerization conditions, undesired side reactions may occur.

The effect of monomer assembly and order may also have vast effects on the polymer properties. Studies have previously reported that the use of multi-block
copolymers may be more advantageous than random copolymers. Taking the concept of random polymers, a study was performed to determine how random is “random” by comparing multi-block copolymers, perfectly alternating copolymers, and statistically random copolymers.

The preparation of PAES systems carrying a sulfonic moiety on a pendant phenylsulfonfyl group follows a straightforward approach, requiring minimal synthetic steps. The molecular weights, chemical structures, thermal stability, water uptake (WU), ion exchange capacity (IEC), and proton conductivity of the synthesized polymers were characterized via GPC, NMR, TGA, and DSC.
Experimental

2.1 Materials

*N*-methyl pyrrolidinone (NMP) and *N*,*N*-dimethylacetamide (DMAc) were purchased from Sigma Aldrich Chemical Co. and dried over CaH₂ and distilled under nitrogen prior to use. ACS grade Toluene was purchased from VWR and used as received. Anhydrous potassium carbonate powder (K₂CO₃) was purchased from Sigma Aldrich Chemical Co. and dried at 130 °C in an oven prior to use. 3,5-Difluorodiphenylsulfone, 1a, was prepared according to a previously reported procedure.³² Bisphenol AF, 2a, bisphenol A, 2b, 4,4’-oxydiphenol, 2c, and 4,4’-biphenol, 2d, were purchased from Sigma Aldrich Chemical Co., recrystallized from toluene, and dried in vacuo prior to use. 4,4-Difluorodiphenylsulfone, 4, *p*-methoxy phenol, 5, hydroquinone, 10, were purchased from Sigma Aldrich Chemical Co. and recrystallized from ethanol, vacuum distilled, and sublimed, respectively. 3,3’-Disodiumsulfonate-4,4’-Difluorodiphenylsulfone, 11, was obtained and prepared according to the procedure outlined by Wang et al.³³ Deuterated dimethylsulfoxide (DMSO-*d₆*), Deuterated water (D₂O), and deuterated chloroform (CDCl₃) were used as received from Sigma Aldrich. Hydrochloric Acid (HCl) was used as received from Pharmco-Aaper. Sodium hydroxide (NaOH) was used as received from Fischer Scientific. Non-iodized Morton salt (NaCl) was purchased from a local retailer and used as received.
2.2 Synthesis of 3-sulfonated-3',5'-difluorophenyl Sulfone, 1c

In a 50-mL RB flask equipped with nitrogen inlet and a condenser, were placed 15.0 mL (40.5 mmol) of fuming sulfuric acid and 10.0 g (39.3 mmol) of 3,5-difluorodiphenylsulfone, 1a. The reaction flask was then immersed in an oil bath and heated to 70 °C for 6 hours. The resulting dark brown solution was slowly poured into vigorously stirred DI water to afford a slightly cloudy mixture that was brown to tan in color. The mixture was vacuum filtered and the supernatant liquid containing 1b was then “salted out” by slowly adding NaCl to the solution until the organic material precipitated from the solution, at which point it was isolated by filtration. The solid was re-dissolved in DI water and brought to a pH of ~6.5 using 5 M NaOH. The solution was then “salted out” again using NaCl. Vacuum filtration was then utilized to isolate the crystals and brine solution was used to wash the residual crystals that remained in the beaker where the monomer was “salted out.” The crystals were allowed to dry under vacuum overnight. Monomer 1c was purified by recrystallization from a 9:1 solution of isopropanol/DI water. The crystals were separated via vacuum filtration and dried under vacuum in an Abderhalden drying pistol for 6 hours, using toluene as the solvent. An isolated yield of 87% was achieved upon recrystallization. A proton NMR spectrum was obtained on monomer 1c, in D₂O, which was in agreement with previous work.  

2.3 Synthesis of 4,4'-(((sulfonylbis(4,1-phenylene))bis(oxy))bis(4,1-phenylene))bis(propane-2,2-diyl))diphenol, 4

A slightly modified literature procedure by Ganguly et al. was used as guidance. In a 50 mL RBF equipped with a condenser, Dean-Stark Trap, nitrogen inlet, and magnetic stir bar, were placed 8.0 g (0.04 mol) of bisphenol A, 2a, 10 mL of DMAc, 10 mL of
toluene, and 4.8 g (0.04 mol) of potassium carbonate. The resulting mixture was heated to 150 °C for 3 hours at which point the temperature was increased to 160 °C and 1.0 g (4 mmol) of 4,4'-difluorodiphenyl sulfone, 3, dissolved in 20 mL DMAC, was added dropwise over a period of 4 hours. The solution was kept at 160 °C for an additional 6 hours with vigorous stirring. The resultant mixture was cooled, filtered, and was poured into a cold 10 % H₂SO₄ solution and additional 10 % H₂SO₄ was added until a pH of 3 was obtained, which created a separate layer. The organic layer was decanted off and the product was extracted into chloroform, washed with water, and evaporated to dryness.

The product was dissolved in ether and treated with a large excess of 5 % NaOH. A white precipitate formed and was separated via vacuum filtration. The solid was re-dissolved in chloroform and then washed 3 times with 5% H₂SO₄ and 3 times with DI water. The layers were separated and the organic layer was dried over MgSO₄, followed by evaporating to dryness. The product was recrystallized from methylene chloride to afford 2.4 g (92%) of a white crystalline solid, mp 147 °C (lit. 145 °C). The proton NMR spectrum was comparable to that previously reported. ¹H NMR (300 MHz, CDCl₃) δ: 7.8 (d), 7.2 (d), 7.1 (d), 7.0 (d), 6.9 (d), 6.8 (d), 4.9 (s, phenol H), 1.7 (s, CH₃) ppm.

2.4 Synthesis of bis-[4(p-methoxyphenoxy)phenyl] sulfone, 6

The literature procedure by Brunel et al. was used for guidance. To a 100 mL RBF, equipped with a magnetic stir bar, Dean-Stark trap, condenser, and nitrogen inlet, were added 30 mL of dry NMP, 30 mL of toluene, 5.5 g (44.1 mmol, 2.3 eq.) of p-methoxyphenol, 5, 5.0 g (19.6 mmol, 1.0 eq.) of 4,4'-difluorodiphenyl sulfone, 3, and 6.0 g (43.5 mmol, 2.2 eq.) of K₂CO₃. The flask was then heated to 150 °C for 4 hours, the Dean-Stark trap was then emptied and the reaction temperature was slowly raised to 180
°C for 3 hours. After cooling to room temperature, the resulting mixture was diluted with 200 mL of chloroform and washed with 10% HCl, saturated NaHCO₃, and then with DI H₂O three times. The organic layer was dried over MgSO₄ and then concentrated by evaporation. The resulting solid was recrystallized from 1:1 ethanol/H₂O yielding 7.8 g (86%). The product was characterized by melting point (mp 118.3 – 118.9 °C) and the proton NMR data were in excellent agreement with that reported previously.⁴⁶

2.5 Synthesis of bis-[4(p-hydroxyphenoxy)phenyl] sulfone, 7

In a 100-mL RBF, equipped with a magnetic stir bar, condenser and nitrogen inlet, were placed 7.8 g (15.1 mmol) of 6, 23 mL (203.3 mmol) of 48% HBr, and 40 mL of AcOH. The flask was heated to 120 °C for 3 days at which point DI H₂O was slowly added until the solution became slightly turbid. The turbid solution was allowed to cool to room temperature, crystals began to precipitate, and they were isolated by vacuum filtration. The product was recrystallized from petroleum ether to afford 5.3 g (81%) of 7 as a colorless crystalline solid. The product was characterized by melting point (191.0 – 191.5 °C) and ¹H NMR spectral data, which were in excellent agreement with those reported previously.⁴⁶

2.6 Representative Homopolymer Synthesis Procedure, 8a-d

Homopolymers containing various bisphenols (2a-d) were synthesized via step growth polymerization. A sample homopolymer synthesis, 8e, is as follows: 0.1540 g (1.0 mmol) of 2, and 0.1406 g (1.0 mmol) of 1c were added to a 25 mL RBF equipped with a condenser, stir bar, nitrogen inlet, and a Dean-Stark trap. Next, 2.5 molar
equivalents of potassium carbonate were added, followed by the addition of 1.5 mL of NMP to afford a 0.64 M solution. In addition, 1.5 mL of toluene was also added as an azeotropic drying agent. The reaction mixture was heated under reflux at 150 °C for 4 hours to dehydrate the system, followed by 16 hours at 180 °C to ensure controlled removal of all toluene and allow the polymerization to take place via nucleophilic aromatic substitution, NAS. After 16 hours, an additional 9 mole percent of 1c was added and the mixture was heated for four hours further at 180 °C to afford a highly viscous solution. The solution was cooled to room temperature and diluted with NMP to decrease the viscosity. The polymer was isolated as swollen strings by dropwise addition into vigorously stirred isopropyl alcohol, IPA. Finally, the filtered polymer was dried in an Abderhalden drying pistol, using toluene at 111 °C, to afford 0.25 g of 8c (84%). 13C NMR (75.5 MHz, DMSO-d6) δ: 110.4, 112.5, 120.1, 121.8, 124.2, 127.7, 127.9, 128.6, 129.9, 131.0, 135.9, 140.0, 143.7, 149.7, 154.3, 159.2.

All subsequent polymerizations were performed under similar conditions that included an azeotropic drying period of 3-4 hours, followed by removal of toluene and heating to 180 °C for 16 hours followed by additional 9 weight percent 1c and heating for 4 additional hours. The following yields were obtained: 8a (84%), 8b (84%), 8d (82%). All 13C NMR peaks were in excellent agreement with those reported previously by Abdellatif.
2.7 Representative Random Biphenol Copolymerization Synthesis Procedure, 9a-e

BP based copolymers of different IECs were synthesized via step growth polymerization. A sample copolymer synthesis, 9a, with an IEC of 0.91 is as follows: 0.1862 g (1.0 mmol) of 4,4’-biphenol, 2c, 0.1540 g (0.6 mmol) of 3, and 0.1406 g (0.4 mmol) of 1c were added to a round bottom flask equipped with a condenser, stir bar, nitrogen inlet, and a Dean-Stark trap. Next, 2.5 molar equivalents of potassium carbonate were added, followed by the addition of 1.5 mL NMP to afford a 0.64 M solution, also, 1.5 mL of toluene was added as an azeotropic drying agent. The reaction mixture was heated under reflux at 150 °C for 4 hours to dehydrate the system, followed by 16 hours at 180 °C to ensure controlled removal of all toluene and allow the polymerization to take place via NAS. After 16 hours, an additional 9 mole percent of 1c was added and the mixture was heated for four hours further at 180 °C to afford a highly viscous solution. The solution was cooled to room temperature and diluted with NMP to decrease the viscosity. The polymer was isolated as swollen strings by dropwise addition into vigorously stirred IPA. Finally, the filtered polymer was dried with toluene at 111 °C in an Abderhalden drying pistol to afford 0.34 g of 9a (78%). $^{13}$C NMR (75.5 MHz, DMSO-d$_6$) δ: 110.4, 112.5, 118.0, 120.1, 120.7, 121.9, 124.2, 127.6, 127.9, 128.6, 129.9, 131.0, 135.3, 135.9, 139.8, 140.0, 143.7, 144.0, 149.7, 153.0, 154.0, 154.3, 159.2, 160.1, 161.3, 173.8.

All subsequent polymerizations were performed under similar conditions that included an azeotropic drying period of 3-4 hours, followed by removal of toluene and heating to 180 °C for 16 hours followed by an additional 9 weight percent of 1c and heating for 4 additional hours. The following yields were obtained: 9b (83%), 9c (86%),
9d (79%), and 9e (81%). All $^{13}$C NMR peaks were found at the same chemical shifts as listed above, at varying intensities depending upon the initial monomer concentrations.

2.8 Representative Procedure for Making Multi-Block s-PAES

2.8.1 Hydrophobic Oligomer Synthesis, 10a

The oligomers were designed to be terminated with fluorine end groups by stoichiometrically offsetting the feed-ratio of monomers using Equation 3. An oligomer synthesis of 12,000 g/mol is as follows: 1.40 g (6.14 mmol) of 2a and 1.69 g (6.65 mmol) of 3 were added to a 50 mL RBF equipped with a condenser, Dean-Stark trap, nitrogen inlet, and magnetic stir bar. Next, 2.5 molar equivalents of potassium carbonate were added, followed by the addition of 10 mL DMAc as well as 10 mL of toluene as an azeotropic drying agent. The reaction mixture was heated under reflux at 150 ºC for 4 hours to dehydrate the system, followed by 16 hours at 180 ºC to ensure controlled removal of all toluene and allow the polymerization to take place via NAS. The solution was cooled to room temperature and diluted with DMAc to decrease the viscosity. The polymer was filtered and precipitated as swollen strings by dropwise addition into vigorously stirred IPA. Finally, the filtered polymer was dried in an Abderhalden drying pistol, using toluene at 111 ºC, to afford 3.02 g of 10a (98%).

2.8.2 Hydrophilic Block Synthesis, 10b

The oligomers were designed to be terminated with phenoxide end groups by stoichiometrically offsetting the feed-ratio of monomers using Equation 3. An oligomer synthesis of 12,000 g/mol is as follows: 1.40 g (6.14 mmol) of 2a and 1.69 g (6.65 mmol)
of 1c were added to a 50 mL RBF equipped with a condenser, Dean-Stark trap, nitrogen inlet, and magnetic stir bar. Next, 2.5 mole equivalent of potassium carbonate was added, followed by the addition of 10 mL NMP along with 10 mL of toluene as an azeotropic drying agent. The reaction mixture was heated under reflux at 150 ºC for 4 hours to dehydrate the system, followed by 16 hours at 180 ºC to ensure controlled removal of all toluene and allow the polymerization to take place via NAS. The solution was cooled to room temperature and diluted with NMP to decrease the viscosity. The polymer was filtered and then precipitated as swollen strings by dropwise addition into vigorously stirred IPA. The polymer was reprecipitated from DMSO into 9:1 ethanol/acidic water and filtered. Finally, the filtered polymer was dried in an Abderhalden drying pistol, using toluene at 111 ºC, to afford 2.60 g of 10b (84%).

2.8.3 Synthesis of Multi-Block s-PAES, 10c

The multi-block copolymer was synthesized by coupling the 10a & 10b oligomers. A typical coupling reaction was as follows: 50 mL of NMP and 50 mL of toluene were added to 1.47 g (0.1 mmol) of 10a, 1.52 g (0.1 mmol) of 10b, and 2.5 mole equivalents of K$_2$CO$_3$ in a 100 mL RBF equipped with a condenser, Dean-Stark trap, nitrogen inlet, and magnetic stir bar. The mixture was heated under reflux at 150 ºC for 4 hours to dehydrate the system, followed by 16 hours at 180 ºC to ensure controlled removal of all toluene and allow the polymerization to take place via NAS. The solution was isolated as swollen strands in a large excess of IPA. Finally, the filtered polymer was dried in an Abderhalden drying pistol, with toluene at 111 ºC, to afford 2.87 g of 10c (96%). $^{13}$C NMR (75.5 MHz, DMSO-$d_6$) δ: 30.5, 41.9, 110.1, 111.3, 114.7, 117.8, 119.2,
2.9 Representative Procedure for Making Random s-PAES, 12a-b & 14a-b

Random copolymers consisting of bisphenol A, 2a, or hydroquinone, 10, and 1c or 11, and 4 were synthesized via step growth polymerization. A sample copolymer synthesis, 12a is as follows: 0.4566 g (2.0 mmol) of 2a, 0.2543 g (1.0 mmol) of 3, and 0.3563 g (1.0 mmol) of 1c were added to a 25 mL RB flask, equipped with a condenser, stir bar, nitrogen inlet, and a Dean-Stark trap. Next, 2.5 molar equivalents of potassium carbonate were added, followed by the addition of 1.5 mL NMP, to afford a 0.64 M solution, as well as 1.5 mL of toluene as an azeotropic drying agent. The reaction mixture was heated under reflux at 150 ºC (125 ºC when using 10) for 4 hours to dehydrate the system, followed by 16 hours at 180 ºC (140 ºC when using 10) to ensure controlled removal of all toluene and allow the polymerization to take place via NAS. After 16 hours, an additional 9 mole percent of 1c was added and the mixture was heated for four hours further at 180 ºC to afford a highly viscous solution. The solution was cooled to room temperature and diluted with NMP to decrease the viscosity. The polymer was isolated as swollen strings by dropwise addition into vigorously stirred IPA. Finally, the filtered polymer was dried in an Abderhalden drying pistol, with toluene at 111 ºC, to afford 0.96 g of 12a (85%). $^{13}$C NMR (75.5 MHz, DMSO-$d_6$) δ: 30.5, 41.9, 110.1, 111.1, 114.8, 117.8, 119.2, 119.7, 124.2, 127.3, 127.7, 128.4, 128.9, 129.8, 131.0, 135.1, 139.9, 143.7, 146.7, 146.8, 147.7, 147.8, 149.7, 151.7, 152.1, 152.3, 152.5, 155.3, 161.4, 173.8.
All subsequent polymerizations were performed under similar conditions that included an azeotropic drying period of 3-4 hours, followed by removal of toluene and heating for 16 hours followed by additional 9 weight percent 1c, or 12 weight percent for 11, and heating for 4 additional hours. The following yields and chemical shifts were obtained:

**12b** (86%) $^{13}$C NMR (75.5 MHz, DMSO-$d_6$) δ: 30.5, 41.9, 116.9, 117.0, 117.8, 118.9, 119.7, 128.1, 128.4, 129.8, 130.2, 130.4, 134.0, 134.4, 135.1, 138.5, 146.0, 146.3, 146.8, 147.0, 152.2, 153.4, 158.5, 161.4, 166.3.

**14a** (71%) $^{13}$C NMR (75.5 MHz, DMSO-$d_6$) δ: 109.8, 112.0, 117.7, 121.8, 122.2, 124.2, 127.7, 129.8, 131.0, 135.2, 139.9, 143.3, 149.7, 151.3, 159.4, 161.5, 169.6.

**14b** (74%) $^{13}$C NMR (75.5 MHz, DMSO-$d_6$) δ: 117.6, 117.7, 122.0, 122.2, 128.1, 129.8, 134.1, 134.2, 134.9, 135.4, 138.7, 139.1, 150.5, 151.3, 151.9, 152.6, 158.4, 158.5, 161.5, 161.8.

### 2.10 Representative Procedure for Making Perfectly Alternating s-PAES, 15a-b & 16a-b

Alternating copolymers containing various sulfonated sulfones (1c, 11) were synthesized via step growth polymerization. A sample copolymer synthesis, **15a**, is as follows: in a 25-mL RB flask, equipped with a condenser, a Dean-Stark Trap, and nitrogen inlet, were placed 2 mL of toluene, 2 mL of NMP, 2.5 molar equivalents of potassium carbonate, 0.25 g (0.38 mmol) of 4 and 0.13 g (0.38 mmol) of 1c. The resulting mixture was stirred vigorously at 150 °C for 3 hours. The Dean-Stark Trap was emptied and the solution was heated for an additional 16 hours at 180 °C to ensure
complete removal of the toluene from the reaction mixture. The solution was left to cool
to room temperature, an additional 0.01 g (9 mole percent equivalent) of 1c was added to
the RBF, and the flask was heated again to 180 °C for 5 hours. The solution was cooled
to room temperature and the alt-sPAES was isolated as swollen fibers via drop wise
addition of the reaction mixture into a large excess of vigorously stirred IPA. The
polymer was isolated using a Buchner Funnel, equipped with a vacuum hose and allowed
to dry over night. The polymer was reprecipitated from DMSO into 9:1 ethanol/acidic
water and filtered. Finally, the filtered polymer was dried in an Abderhalden drying
pistol, with toluene at 111 °C, to afford 0.35 g of 15a (92%). 13C NMR (75.5 MHz,
DMSO-d6) δ: 30.5, 41.9, 110.1, 111.1, 117.8, 119.2, 119.7, 124.2, 127.7, 128.4, 129.8,
131.0, 135.1, 139.9, 143.7, 146.8, 149.7, 161.4, 173.8.

All subsequent polymerizations were performed under similar conditions that
included an azeotropic drying period of 3-4 hours, followed by removal of toluene and
heating at 180 °C for 16 hours followed by additional 9 weight percent 1c, or 12 weight
percent for 11, and heating for 4 additional hours. The following yields and chemical
shifts were obtained:

15b (94%) 13C NMR (75.5 MHz, DMSO-d6) δ: 30.5, 41.9, 117.8, 118.9, 119.7, 128.4,
128.4, 129.8, 133.9, 135.0, 138.7, 146.0, 146.8, 152.2, 153.4, 158.3, 161.4, 173.7.

16a (88%) 13C NMR (75.5 MHz, DMSO-d6) δ: 110.1, 111.1, 117.7, 121.8, 122.3, 124.2,
129.9, 131.0, 139.9, 143.8, 149.7, 151.2, 151.4, 159.5, 161.4.

16b (91%) 13C NMR (75.5 MHZ, DMSO-d6) δ: 117.5, 119.0, 122.0, 128.1, 129.8, 134.2,
135.0, 138.9, 150.5, 152.6, 158.3, 161.6.
2.11 Representative Membrane Preparation Procedure

Acid forms of the polymers were prepared by dissolving the precipitated polymer in DMSO to afford a 5-10% (w/w) transparent polymer solution, which was filtered with a 0.45 µm Teflon® syringe filter and then cast onto a clean glass substrate, followed by drying in a vacuum oven by slowly increasing the temperature from 40 - 100°C over 48 h. The membranes were removed from the substrate by immersion for 36 hours in 2 N sulfuric acid. The membranes were then soaked in deionized water for 48 h to remove residual acid.

2.12 Characterization

2.12.1 General Ion Exchange Capacity Titration Procedure

For determination of the experimental IEC, the membranes, in the acid form, were dried under vacuum at 100°C overnight in order to get their dry weight. The IEC was determined in a typical experiment, a known weight of dried membrane was placed in a solution of 1 M sodium sulfate (35 mL) and stirred for 24 h. Three 10 mL aliquots were taken and titrated with 0.01 M NaOH to a phenolphthalein endpoint. The IEC was then taken as the average of the three samples calculated using Equation 4:

\[
IEC \text{ (mequiv./g)} = \frac{mmol \ NaOH}{\frac{10ml}{35ml} \times polymer \ mass}
\]

Equation 4

2.12.2 General Procedure for Determining Percent Water Uptake

Water Uptake, WU, measurements were conducted for all polymers which formed resilient films in both the salt and acid forms. WU was determined by the difference in weight of the fully hydrated membrane, which was immersed in DI water at 22 °C for 24
h (\text{w}_{\text{wet}}) \text{ and the dried membrane prepared by drying} \text{ in vacuo} (\text{w}_{\text{dry}}) \text{ at } 140 \degree C \text{ to constant mass. The calculation for percent WU by mass is as follows:}

\[ WU\% = \frac{\text{w}_{\text{wet}} - \text{w}_{\text{dry}}}{\text{w}_{\text{dry}}} \times 100\% \quad \text{Equation 5} \]

Excess water was removed from the hydrated membranes surface by blotting with a Kim Wipe prior to obtaining the \text{w}_{\text{wet}}.

2.12.3 Thermal Gravimetric Analysis (TGA)

The thermal stability of the sPAE’s was investigated by using TGA to assess the thermal and thermo-oxidative stability using a TA Instruments Q500 Thermogravimetric Analyzer. A typical method included heating a 5 mg sample at a rate of 10 \degree C/min from 40 \degree C to 850 \degree C under a nitrogen atmosphere for salt forms and compressed air for acid forms. The weight loss was recorded as a function of time; thermal stability was reported at 5 \% weight loss, \text{T}_{d5\%}.

2.12.4 Differential Scanning Calorimetry (DSC)

DSC was utilized to determine the thermal transition temperatures of the sPAES’s. A typical sample size of 5 mg of synthesized polymer, in Tzero aluminum pans, was analyzed by the use of a TA Instruments Q200 Differential Scanning Calorimeter. The typical cycle included heating at 10 \degree C/min, cooling at 20 \degree C/min, and heating a second time at 10 \degree C/min, under a nitrogen atmosphere for the salt and acid forms. The glass transition temperature, \text{T}_g, was determined at the midpoint of the tangent
of the second heating cycle. The first heating cycle was utilized to erase the polymers thermal history.

2.12.5 Proton Conductivity

The conductivity of the PEMs was determined via a Four-Point conductivity measurement. The PEM was cut into 3 mm wide and 5 cm long strips. The PEM was placed onto the 4 platinum probes support, which was mounted on the Teflon® middle frame of the fuel cell. The distance between voltage probes is 42 mm. The cell was sealed and purged with water vapor saturated hydrogen gas. The relative humidity of the cell was controlled by the temperature of hydrogen humidifier tank and cell temperature.

2.12.6 Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton, $^1$H, and Carbon, $^{13}$C NMR, spectroscopy was used to determine the molecular structures of all monomers and polymers. NMR spectra were acquired using a Bruker AVANCE 300 MHz system, operating at 300 & 75.5 MHz, respectively. Samples were dissolved in appropriate deuterated solvents (DMSO-$d_6$, CDCl$_3$, or D$_2$O), at a concentration of 40 mg / 0.7 mL.

2.12.7 Gel Permeation Chromatography (GPC)

GPC was used to determine the molecular weights and molecular weight distributions of all polymer samples. The analysis was performed using a Viscotek Model 300 TDA system equipped with refractive index, viscosity, and light scattering detectors operating at 40 °C and a Perkin Elmer Series 200 pump operating at 0.8 mL/ minute.
Two polymer laboratories 5 µm PL gel Mixed C columns were used with NMP (with 0.2% LiBr) as the eluent with a 100 µl sample injection at a concentration of 2 mg/mL. A series of narrow polydispersity polystyrene standards (Polymer Laboratories) were used to generate a conventional calibration curve. Number average molecular weight ($M_n$) was determined by using the conventional calibration mentioned above. The weight average molecular weight ($M_w$) was determined using the light scattering detector. The polydispersity index (PDI) was calculated using Equation 6.

\[
PDI = \frac{M_w}{M_n} \tag{Equation 6}
\]

A second GPC was also used for analysis, a Viscotek Model 270 Duel Detector equipped with polymer laboratories 5 µm PL gel Mixed C column and a Polypore column used with DMF (with 0.2% LiBr) as the eluent. The same pump, flow rate, and calibration were used as described above.
3 RESULTS & DISCUSSION

3.1 Monomer Synthesis

Several monomers were synthesized for use in polymerizations. Each will be discussed briefly to understand the synthesis involved as well as the specific uses in polymerizations.

3.1.1 3-Sulfonated-3’,5’-difluorodiphenylsulfone, 1c

The synthesis of 1a via the reaction of 3,5-difluorophenylmagnesium bromide and benzene sulfonyl chloride was reported previously by Kaiti et al. The synthesis of 3-sulfonated-3’, 5’-difluorodiphenyl sulfone, 1c, was achieved via the two-step synthetic route outlined in Scheme 1.

![Scheme 1](attachment:image.png)

**Scheme 1**: Synthesis of 1c via EAS.

Sulfonation of 1a occurs *meta* to the sulfone, typical of EAS on electron withdrawing rings, after 6 hours at 40 °C. Isolation of 1b is difficult, therefore it was “salted out” to separate 1a and 1c. An ice bath was utilized upon the exothermic neutralization to prevent typical side reactions of a nucleophilic attack by hydroxide ions on the carbon *ipso* to the fluorines. An isolated yield of 87% was achieved upon recrystallization. A proton NMR spectrum was obtained on monomer 1c, in D2O, which was in agreement with previous work. The carbon spectrum of 1c appears in Figure
as 10 distinct signals, however, some individual peak assignments differ slightly from those previously reported. Carbons a-d all experience some degree of splitting due to coupling of the two C-F bonds and vary due to the position relative to the C-F bonds. Carbon a is a triplet at 110 ppm, carbon b is a doublet of doublets at 161-164.5 ppm, carbon c at 112 ppm is a doublet of doublets, and carbon d at 142 ppm is a triplet. Carbons e, f, g, h, i, and j were all identified as singlets and were found at 139.5, 124.5, 144, 131.3, 130.5, 131.0 ppm, respectively.

![Diagram](image)

**Figure 10**: 75.5 MHz $^{13}$C NMR spectrum of 1c in D$_2$O.

### 3.1.2 4,4'-(((sulfonylbis(4,1-phenylene))bis(oxy))bis(4,1 phenylene))bis(propane-2,2-diyl))diphenol, 4

The literature procedure provided by Ganguly et al. was modified and used for guidance. The synthesis of 4 was achieved via NAS of 2a on 3 in a controlled 1-step synthesis as illustrated in **Scheme 2**.
Scheme 2: Synthesis of 4 via highly controlled NAS using a slow addition method.

An excess (9:1) of 2a and K₂CO₃ was azeotropically dried with toluene at 111 °C for 3-4 hours prior to reacting with 3. After 3 hours the toluene was removed and the Dean-Stark trap was emptied. Then, a dilute solution of 3 was dissolved in DMAc was slowly added dropwise via syringe pump to the reaction mixture to prevent polymerization from occurring. Upon completion of the reaction, the mixture was filtered to remove excess 2a and K₂CO₃. The organic supernatant was then poured into acidic water, which formed 2 separate layers. In this condition most excess 2a remained in the organic DMAc layer, while 4 remained in the acidic aqueous layer. The two layers were separated and the product, 4, was extracted from the aqueous layer into chloroform. The chloroform layer was washed with water to remove residual acid and then concentrated via evaporation. The yellow product was dissolved in ether and washed with 5% NaOH to remove any Meisenheimer complex and 2a that remained. The ether layer was washed with 5% H₂SO₄ then with water to remove residual acid and evaporated once again. The resulting solid was recrystallized from methylene chloride.
3.1.3 bis-[4(\(p\)-hydroxyphenoxy)phenyl] sulfone, 7

The synthesis of 6 provided a precursor for subsequent reactions, 7 & 16a-b.

\[
\begin{align*}
\text{F} & \text{O} \\
\text{S} & \text{O} \\
\text{O} & \text{F} \\
\text{NMP/Toluene} & \text{K}_2\text{CO}_3 \\
\text{heat} & \text{2. H}_2\text{SO}_4 \\
\rightarrow \\
\text{H}_3\text{CO} & \text{O} \\
\text{S} & \text{O} \\
\text{O} & \text{O} \\
\text{O} & \text{O} \\
\text{OCH}_3 & \\
\end{align*}
\]


\(p\)-Methoxyphenol, 5, was used as a mono-protected phenol monomer, which is incapable of polymerization when reacted with 3, 4,4\(^\prime\)-difluorodiphenyl sulfone. Upon isolation of 6, a subsequent reaction to convert the methoxy end groups to phenols was carried out using hydrobromic acid. The resulting bisphenol represents an A-B-A unit, which can be utilized in achieving perfectly alternating copolymers such as 16a-b.

\[
\begin{align*}
\text{H}_3\text{CO} & \text{O} \\
\text{S} & \text{O} \\
\text{O} & \\
\text{O} & \\
\text{OCH}_3 & \\
\rightarrow \\
\text{HO} & \text{O} \\
\text{S} & \text{O} \\
\text{O} & \\
\text{O} & \\
\text{OH} & \\
\end{align*}
\]

Scheme 4: Deprotection synthesis of bis-[4(\(p\)-hydroxyphenoxy)phenyl] sulfone, 7
3.2 Polymer Synthesis

3.2.1 Homopolymer Series, 8a-d

The first part of this research was to look at structure/property influences of potential PEMs using 1c as the proton conductor when incorporated into homopolymers. A variety of bisphenols, 2a-d, were used to understand the influence of structure on the properties, such as hydrophobicity and conductivity (Scheme 5).

![Scheme 5](image)

**Scheme 5**: Synthesis of homopolymers 8a-d.

The polymerization proceeded via a NAS polycondensation reaction between a nucleophilic bisphenoxide monomer and a difluoro aromatic electrophile, reacting on the carbons *ipso* to the fluorine atoms. Typically, NAS reactions utilized to synthesize PAES occur *para* to an EWG, however, a very strong inductively withdrawing group provides sufficient activation to allow NAS to occur in the *meta* position. Additional 1c monomer
was added to the reaction mixture after 16 hours due to the highly hygroscopic nature of
the monomer that disrupts the stoichiometric feed ratio of monomers. The appropriate
amount of 1c to add was determined by heating the monomer up to 110 °C in the TGA
and determining the percent weight loss due to residual moisture. Upon completion of the
reaction, the polymers were precipitated from ethanol, isolated and dried. The acid forms
of 8a-d were prepared by immersion in 2 N H₂SO₄ for 24 hours, followed by soaking in
DI water for 24 hours to remove residual acid. Confirmation of sufficient reactivity of the
meta activated fluorine atoms is provided by noting the high molecular weights obtained
from GPC analysis as listed in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>% Yield</th>
<th>Form</th>
<th>Mₙ (g/mol)</th>
<th>Mₘ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>84</td>
<td>Acid</td>
<td>40,400</td>
<td>98,400</td>
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</tr>
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<td></td>
<td></td>
<td>Salt</td>
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<td>101,400</td>
<td>2.41</td>
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<tr>
<td>8b</td>
<td>84</td>
<td>Acid</td>
<td>22,800</td>
<td>134,800</td>
<td>5.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Salt</td>
<td>23,000</td>
<td>121,800</td>
<td>5.30</td>
</tr>
<tr>
<td>8c</td>
<td>84</td>
<td>Acid</td>
<td>15,400</td>
<td>28,300</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Salt</td>
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<td>28,600</td>
<td>1.78</td>
</tr>
<tr>
<td>8d</td>
<td>82</td>
<td>Acid</td>
<td>38,400</td>
<td>90,900</td>
<td>2.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Salt</td>
<td>39,100</td>
<td>91,100</td>
<td>2.33</td>
</tr>
</tbody>
</table>

All molecular weights, with the exception of 8c, were sufficiently high to allow
the preparation of resilient films. The small differences in molecular weights, when
comparing the salt to acid forms of the polymers, may be attributed to the difference in
the masses of the sodium ion and the hydrogen, respectively.

Characterization of the homopolymers allowed for identification of important
properties related to fuel cell conditions. The composition, molecular weight, and thermal
stabilities are among the most important parameters for fuel cell performance. In addition to these properties, PEMs require relatively low WU and high conductivity ( >100 mS/cm) to be considered as viable alternatives to Nafion®. The thermo-oxidative stability, $T_g$, IEC, water uptake, and conductivities for polymers 8a-8d are listed in Table 5.

Table 5: Characterization of Homopolymers

<table>
<thead>
<tr>
<th>Form</th>
<th>$T_g$ (°C)</th>
<th>$T_{d5%}$ (°C)</th>
<th>IEC calc. (meq./g)</th>
<th>IEC exp. a (meq./g)</th>
<th>% WU</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>acid 164</td>
<td>329</td>
<td>1.91</td>
<td>1.89</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>salt 240</td>
<td>351</td>
<td></td>
<td></td>
<td>62</td>
</tr>
<tr>
<td>8b</td>
<td>acid 165</td>
<td>346</td>
<td>1.59</td>
<td>1.56</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>salt 238</td>
<td>403</td>
<td></td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>8c</td>
<td>acid 196</td>
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<td>2.09</td>
<td>2.05</td>
<td>soluble</td>
</tr>
<tr>
<td></td>
<td>salt 261</td>
<td>397</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8d</td>
<td>acid 158</td>
<td>347</td>
<td>2.01</td>
<td>1.99</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>salt 257</td>
<td>416</td>
<td></td>
<td></td>
<td>57</td>
</tr>
</tbody>
</table>

a determined by titration with 0.01 M NaOH

The experimental IECs are in good agreement with the theoretical IECs indicating that the sulfonated monomer reacted sufficiently to form the polymers without excessive side reactions, such as thermal desulfonation. As expected, the water uptake increased along with the IEC, unfortunately, 8c, with an IEC of 2.09 was soluble in water. The sulfonic acid groups on pendant systems are evidently more accessible than the backbone counterparts. When approaching an IEC of ~2 meq./g in pendant systems 8c-d, solubility in water increases and 8c becomes completely soluble in water at room temperature. Wang et al. reported the backbone disulfonated isomer of 8c with a similar IEC of 2.2 is still insoluble in water, though the swelling of the membrane is exceedingly high (148%).
indicating that it is approaching solubility in water.\textsuperscript{15} Due to the differences in IEC and solubility between backbone sulfonated and pendant sulfonated systems, it may be reasonably concluded that pendant acid groups are more accessible than backbone ones. Since homopolymer 8c was soluble in water at 30 °C, 3c was then used in biphenol based random copolymers 9a-e.

With homopolymers having IECs approaching water solubility, conductivity measurements were carried out over a range of 40 – 80 °C to determine temperature effects on conductivity of polymers with high IECs at 100% RH, Table 6.

<table>
<thead>
<tr>
<th>IEC exp. \textsuperscript{a} (meq/g)</th>
<th>Temp. (°C)</th>
<th>(\sigma) \textsuperscript{b} (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>1.89</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>8b</td>
<td>1.56</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>8d</td>
<td>1.99</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
</tr>
</tbody>
</table>

\textsuperscript{a} determined by titration with 0.01 M NaOH
\textsuperscript{b} at 100% RH

At lower temperatures 8a&d exhibit high conductivity, however, as the temperature increases, the conductivities quickly diminish. The low conductivities at 80 °C may be attributed to excessive WU as well as increasing solubility of the membranes. After the conductivity tests were completed, there was visual evidence of deterioration of membranes 8a&d, while 8b was still intact and mechanically robust.
The thermal properties of all homopolymers were evaluated via TGA and DSC. The TGA traces exhibited two thermal degradation steps, the first is attributed to desulfonation around 300 °C and the second is degradation of the backbone around 450 °C. All homopolymers are highly thermally stable in the dry state up to 300 °C. The 5% weight loss of the homopolymers was higher in nitrogen than in air. The differences in stability were at least 60 °C. The salt form of each sulfonated copolymer was considerably more thermally stable than the comparable sulfonated polymer in its acid form.

Figure 11: TGA curves of 8a-d, this figure compares the stability of the acid form membranes using the same sulfonated monomer, 1c, and different bisphenols, 2a-d.
The DSC overlay, Figure 12, allows for a quantitative comparison of $T_g$ on 8a-d in the acid form. The $T_g$ is highly dependent on the stiffness and rigidity of the backbone, the more flexible (tetrahedral) monomers decrease in $T_g$ while more stiff (planar) monomers increase the $T_g$. Structurally similar, 8a-b, have mildly flexible backbones and display similar $T_g$’s. The most rigid backbone is found in 8c due to the planar biphenyl linkages and had the highest $T_g$. As expected, 8d exhibits the lowest $T_g$ arising from diphenyl ether, 2d, being the most flexible of the bisphenols studied. Differences were seen in $T_g$’s with these exact systems reported previously likely arising from only partial acidification of previously synthesized polymers. The acidification method previously reported involves dissolving the polymer in water and precipitating it out by addition of concentrated sulfuric acid. Only the 4,4’-biphenol based polymer is soluble in water at room temperature and no concentration of sulfuric acid solution was ever reported to determine if enough acid was present to convert the salt to acid form. Acidification should be performed on polymer films immersed in 2 N H$_2$SO$_4$ for at least 24 hours followed by at least 24 hours of immersion in DI water to remove residual acid. In addition, experimental determination of IEC was not performed to determine the actual level of sulfonic acid groups incorporated into the polymers.
**Figure 12**: DSC traces of 8a-d, the influence of incorporated bisphenols, 2a-d, on the $T_g$ of the acid form membranes.

The bisphenol AF based homopolymer, 8b, exhibited excellent conductivities over a range of temperatures at 100% RH. To determine if 8b will meet the demands for a PEM, it can be directly compared to the current state-of-the-art PEM, Nafion®, Table 7.

**Table 7**: Comparison of the Properties of 8b and Nafion®

<table>
<thead>
<tr>
<th>Property</th>
<th>8b</th>
<th>Nafion® 117</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ °C</td>
<td>165</td>
<td>124 (45)</td>
</tr>
<tr>
<td>$T_{d5%}$ °C</td>
<td>346</td>
<td>342 (45)</td>
</tr>
<tr>
<td>IEC (meq/g)</td>
<td>1.56</td>
<td>0.91</td>
</tr>
<tr>
<td>% WU</td>
<td>~26</td>
<td>~22 (39)</td>
</tr>
<tr>
<td>Conductivity (mS/cm) at 80 °C</td>
<td>266</td>
<td>120 (39)</td>
</tr>
<tr>
<td>$pK_a$</td>
<td>~0.7</td>
<td>-3.09 (46)</td>
</tr>
</tbody>
</table>
At a similar IEC of 1.77, the backbone disulfonated bisphenol AF copolymer produced by Harrison had a conductivity of only 100 mS/cm at 30 °C, proving once again that a more pendant side group and hydrophobic backbone are more advantageous to achieve high conductivity and low WU measurements. Both systems have the sulfonic acid groups incorporated on an electron poor ring. By doing so, thermal desulfonation is not as likely to occur as when the sulfonic acid is placed on an electron rich ring. Acidity is enhanced when on an electron poor ring because the EWG pulls electron density away from the acid group resulting in a less tightly bound proton and a more stable conjugate base.

3.2.2 Biphenol Based Copolymers, 9a-e

A 4,4’-biphenol copolymer series was carried out to reduce the solubility issues associated with the homopolymer, 8c, and to tune the IEC without significantly changing the overall structure. A typical copolymerization was utilized for the synthesis of the copolymers, which consisted of various ratios of 1c and 3, as illustrated in Scheme 6. Polymers 9a-e were prepared under the same conditions as the homopolymer, 8c, and the molecular weight characterization data are listed in Table 8.
Scheme 6: Synthesis of random biphenol based sulfonated PAES, 9a-e.

Table 8. Molecular weight and polydispersity data for the copolymers prepared from 1c, 3, and 2c.

<table>
<thead>
<tr>
<th></th>
<th>% Yield</th>
<th>Form</th>
<th>Mₙ (g/mol)</th>
<th>Mₘ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a</td>
<td>78</td>
<td>Acid</td>
<td>24,100</td>
<td>47,300</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Salt</td>
<td>25,400</td>
<td>44,600</td>
<td>1.76</td>
</tr>
<tr>
<td>9b</td>
<td>83</td>
<td>Acid</td>
<td>79,200</td>
<td>394,500</td>
<td>4.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Salt</td>
<td>81,900</td>
<td>367,100</td>
<td>4.48</td>
</tr>
<tr>
<td>9c</td>
<td>86</td>
<td>Acid</td>
<td>50,700</td>
<td>103,200</td>
<td>2.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Salt</td>
<td>53,200</td>
<td>96,400</td>
<td>1.81</td>
</tr>
<tr>
<td>9d</td>
<td>79</td>
<td>Acid</td>
<td>33,700</td>
<td>103,900</td>
<td>3.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Salt</td>
<td>35,600</td>
<td>106,800</td>
<td>3.00</td>
</tr>
<tr>
<td>9e</td>
<td>81</td>
<td>Acid</td>
<td>43,200</td>
<td>75,400</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Salt</td>
<td>45,200</td>
<td>73,800</td>
<td>1.63</td>
</tr>
</tbody>
</table>

All of the copolymers possessed sufficiently high molecular weight to afford resilient films and resolved the solubility problem associated with the homopolymer, 8c. It must be noted that 1c, 2c, and 3 were all added in a single reaction to form a randomly
ordered copolymer. The reactivities, toward NAS, of 1c and 3 are significantly different, as determined from the difference in Hammet σ constants. Thus, 3 (σ = 0.73) is expected to react much more quickly than 1c (σ = 0.64). Confirmation of the incorporation of both monomers was provided by 13C NMR spectroscopy (Figure 11). As expected the peaks $o-r$ increase and $a-j$ decrease due to the decrease in concentration of 1c as 3 is incorporated in increasing molar ratios.

Figure 13: Overlay of 75.5 MHz 13C Inverse Gated Decoupled NMR spectra (DMSO-$d_6$) of the bisphenol copolymers.

By tuning the IEC it follows that the WU and conductivity can also be tuned easily. The following techniques were utilized to characterize the series: conductivity, WU, 13C NMR, TGA, and DSC.
Table 9: Characterization of Bisphenol Copolymers 9a-e.

<table>
<thead>
<tr>
<th>Form</th>
<th>T_g (°C)</th>
<th>T_d5% (°C)</th>
<th>IEC calc. (meq./g)</th>
<th>IEC exp. a (meq./g)</th>
<th>WU (wt %)</th>
<th>σ b (mS/cm)</th>
</tr>
</thead>
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<tr>
<td>9a</td>
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<td></td>
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<tr>
<td>acid</td>
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<td>302</td>
<td>464</td>
<td></td>
<td></td>
<td>44</td>
<td></td>
</tr>
</tbody>
</table>

a determined by titration with 0.01 M NaOH
b determined at 80 °C & 100% relative humidity

There are trends with respect to the increase in 1c incorporation. As the IEC increases, so do the T_g, WU, and conductivity. An increase in WU, as the IEC is increased, is most likely due to the hydrophilicity of the sulfonic acid groups. WU is directly proportional to IECs below 1.63, however, as the IEC approaches the solubility point of an IEC ~2 the WU increases significantly. The proton conductivity values of 9d & 9e exceed that of Nafion® under similar conditions while the water uptake values of 23 & 32 % in the acid form, respectively, are rather modest.

A clear trend also exists in the DSC traces. With the addition of more sulfonated pendant groups into the copolymers, the T_g increases by increasing the rigidity of the chain and decreasing the free rotation of the pendant groups. Many factors can contribute to the T_g of a polymer such as bulky side groups, structure, symmetry, molecular weight, and rigidity of the backbone. The random dispersion of ionic groups affects the size and location of ionic domains, influencing the T_g. When considering sulfonated polystyrene,
Wallace found a linear relationship between the \( T_g \) and the degree of sulfonation accounted for by increasing intermolecular forces as more sulfonic acid groups were incorporated.\(^\text{38} \) The polarity of the sulfonic acid groups causes ionic aggregates to form, increasing the \( T_g \) as more ionic groups are incorporated into the copolymer. Hydrogen bonding is the primary force that causes an increase in \( T_g \) in these systems.

**Figure 14:** The influence of IEC on \( T_g \) of bisphenol based copolymers 9a-e in acid form.

The thermal stabilities of 9a-e are all similar. The first weight loss on the TGA, typically around 350 °C, is indicative of the loss of sulfonic acid groups. The second step indicates the degradation of the s-PAES backbone. s-PAES’s are thermally stable to the
temperature in which the second step occurs, yielding thermal stability greater than 400 °C for all polymers developed.

![Thermal Stability Graph](image)

**Figure 15:** Thermal stability of acid forms of the biphenol based copolymers 9a-e.

It is useful to determine if pendant sPAES are better candidates for PEMs, than their disulfonated backbone counterparts based on sulfonated dichlorodiphenyl sulfone, SDCDPS. One of the drawbacks to sulfonating directly on the backbone is high WU. By comparing the WU vs. IEC (**Figure 16**) it is easy to see that locating the sulfonic acid groups on truly pendant moieties is indeed advantageous. For the SDCDPS series, there is a clear trend in a significantly higher WU at the same IEC, 5-10% on average higher than the pendant systems. As the IEC increases, so does the WU, likely due to hydrogen bonding among the networks of hydrophilic regions.
Figure 16: Comparison of IEC vs. WU for all polymers and literature comparison.
SDCDPS series from Wang, et al.\textsuperscript{15}
Nafion 112 from Zawodzinski, et al.\textsuperscript{39}

Figure 17: Comparison of WU vs. Conductivity for polymers and literature comparison.
SDCDPS series from Wang, et al.\textsuperscript{15}
Nafion\textsuperscript{®} 112 from Zawodzinski, et al.\textsuperscript{39}
Pendant s-PAES, when compared to their backbone counterparts, have lower WU and higher conductivities as displayed in Figure 17. At similar WUs, 9d displays higher conductivity than Nafion®. WU can facilitate proton mobility in PEMs, however, minimal swelling is desired in potential materials for PEMs because excessive dimensional swelling can destroy the assembly of the PEM and decrease fuel efficiency. Copolymers 9d-e are highly thermally stable and display low WU as well as high conductivity, showing promise as potential candidates for PEMFC.

3.2.3 Bisphenol A Based Multi-Block, Perfectly Alternating, and Random s-PAES, 10c, 12a-b, 15a-b

The second part of this research was to look at structure-property relationships of a highly ordered (alternating/multi-block copolymers) polymeric system when compared to their more randomized counterparts. There is limited literature on the physical and thermal properties of perfectly alternating polymer sequences. The thermal and mechanical properties of a polymer depend upon the manner in which the monomer units are covalently bonded to one another. Malanga et al. found that the way in which monomers were assembled to form polymers had a vast impact on the resulting thermal properties; over a 150 °C range in $T_g$ for polyisobutylene samples. Due to the difference in their monomer assemblies, it was expected that random copolymers should have different thermal and mechanical properties than a perfectly alternating one.

To prepare perfectly alternating copolymers requires additional synthetic steps. First, a large bisphenolic species, 4, was prepared by stoichiometrically reacting two $A_2$ monomers with one $B_2$ monomer to yield a larger monomer (A-B-A) containing phenol end groups (Scheme 2). This oligomeric $A_2$ species was subsequently copolymerized
with a B₂ monomer. By doing so, highly ordered systems, 15a-b, were achieved and were compared quantitatively to their random counterparts, 12a-b, that were synthesized in a single step reaction sequence, Schemes 7 & 8. A similar series was conducted using hydroquinone, 10, instead of bisphenol A, 2a, and will be discussed later.

Scheme 7: Random (12a) and perfectly alternating (15a) pendant mono sulfonated PAES copolymer syntheses.

Scheme 8: Random backbone (12b) and perfectly alternating (15b) disulfonated PAES copolymer syntheses.
Due to the different reactivity of 1a and 3, demonstrated by $^{19}$F NMR, the random copolymers (12a-b) may form more microblock-like polymers, rather than a completely randomized polymer. To determine if 12a-b are assembled more block-like or closer to an alternating structure, a multi-block copolymer, 10c, was synthesized for comparison, Scheme 9.

**Scheme 9:** Synthesis of the hydrophobic block (10a), hydrophilic block (10b), and multi-block copolymer (10c).

The feed ratios of 10a & 10b were offset using the Carothers equation (Equation 3) to attain 12,000 g/mol segments. Upon isolation 10a was determined to have an $M_n$ of 11,400 g/mol and 10b possessed an $M_n$ of 13,800 g/mol. After the initial precipitation
10b had shown a significant presence of cyclic species on the GPC trace. Reprecipitation was utilized to achieve a pure high molecular weight block copolymer. Using the average molecular weights of each segment, a block copolymer was synthesized with the aim to control domain size and determine the influence of block species on $^{13}$C NMR spectra.

All copolymers were synthesized via NAS of the A$_2$ monomers on the B$_2$ and B$_2'$ monomers. Perfectly alternating polymers may offer advantages as a result of a more highly ordered system when compared to a random copolymer. The characterization data for polymers 10c, 12a-b, & 15a-b are listed in Table 10. The molecular weights are consistently higher for a perfectly alternating system (15a-b) when compared to the random system (12a-b).

**Table 10: Characterization of Bisphenol A based Copolymers.**

<table>
<thead>
<tr>
<th></th>
<th>Yield</th>
<th>Form</th>
<th>M$_n$ (g/mol)</th>
<th>M$_w$ (g/mol)</th>
<th>PDI</th>
<th>IEC calc. (meq./g)</th>
<th>T$_g$ (°C)</th>
<th>T$_{d5%}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10c</td>
<td>96</td>
<td>acid</td>
<td>86,900</td>
<td>145,600</td>
<td>1.68</td>
<td>1.23</td>
<td>112</td>
<td>330</td>
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<tr>
<td></td>
<td></td>
<td>salt</td>
<td>88,000</td>
<td>148,000</td>
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<td>197</td>
<td>459</td>
</tr>
<tr>
<td>12a</td>
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<td>acid</td>
<td>19,900</td>
<td>44,600</td>
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<td>1.01</td>
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<td>44,500</td>
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<td>220</td>
<td>396</td>
</tr>
<tr>
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<td>1.90</td>
<td>1.01</td>
<td>166</td>
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<tr>
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<td></td>
<td>salt</td>
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<td>59,900</td>
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<td></td>
<td>251</td>
<td>444</td>
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<tr>
<td>12b</td>
<td>86</td>
<td>acid</td>
<td>17,100</td>
<td>32,900</td>
<td>1.93</td>
<td>2.03</td>
<td>154</td>
<td>281</td>
</tr>
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<td>34,800</td>
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<tr>
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<td>acid</td>
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<td>50,500</td>
<td>1.53</td>
<td>2.03</td>
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<td>417</td>
</tr>
<tr>
<td></td>
<td></td>
<td>salt</td>
<td>33,900</td>
<td>50,400</td>
<td>1.53</td>
<td></td>
<td>326</td>
<td>460</td>
</tr>
</tbody>
</table>

All molecular weights should have been sufficient to form mechanically robust films, however, the random copolymers, 12a-b, were brittle when removed from the casting substrate.

As seen in Figure 18, a $^{13}$C NMR spectral overlay was utilized to compare the structural differences among 12a, 15a, and 10c. The positions of the peaks, as well as
their intensities, are of key importance when comparing 12a & 15a. Only the positions of peaks in 10c are of importance because not many blocks were incorporated, therefore peaks arising from the hydrophilic region vastly dominate the spectrum, while the positions of the hydrophobic peaks are of importance as well in understanding monomer assembly.

**Figure 18**: Inverse Gated Decoupled $^{13}$C NMR spectral overlay in DMSO-$d_6$ of bisphenol A based pendant mono sulfonated copolymer systems: a) random (12a), b) perfectly alternating (15a), and c) multiblock (10c).

**Figure 18** indicates that all three monomers were incorporated in each polymerization to achieve high molecular weight polymers. Unlabeled signals may arise from the presence of cyclic species that were seen in GPC traces, even after reprecipitation of the polymers. There are notable differences in all 3 spectra that arise
from the order of reaction among the monomers. The aromatic ether peaks, \( b \) & \( o \), have nearly identical integration values in 15a, indicating that the order in which they are dispersed is even; they always have the same nearest neighbor monomers. Interestingly, in 10c uneven distribution of the peaks ipso to the ether occurred between \( b \) & \( o \). The slightly more downfield signal, \( o \), corresponds to 3 having a lower degree of incorporation when compared to 1c, resulting in a higher incorporation of the hydrophilic block, 10b. The presence of minimal, low intensity secondary peaks indicates the linkages between blocks and the primary peaks arise from the separate blocks, 12a&b.

For 12a, there is a slightly uneven distribution of peaks \( b \) & \( o \), although the difference is marginal and additional secondary peaks arose. Secondary peaks are attributed to disorder in which monomeric units are attached to one another due to differences in reactivity of monomers. The weak intensities of secondary peaks may indicate that there is a higher degree of order than disorder in the completely randomized polymer 12a.

Carter studied monomer reactivity via \(^{19}\text{F} \) NMR and concluded that the more downfield a \(^{19}\text{F} \) signal is, the more reactive the electron deficient ipso carbon is toward nucleophilic attack.\(^{42}\) Although no \(^{19}\text{F} \) data on 1c exists, when 3 is compared to 1a, it is significantly more reactive with shifts of -104.1 & -106.3 ppm, respectively.\(^{43}\) Bisphenol A is likely to react first with 3, then 1c; this principle is not absolute, however. The apparent reactivity is not only based upon the strengths of the nucleophile and electrophile, but also on the concentrations of molecules present in solution. Since 3 is reacted with 2a first, the concentration of 3 in solution decreases and the relative concentration of 1c increases. There are more free 1c monomers in solution, resulting in
**1c** reacting more readily, not due to reactivity of the species, but due to abundance in solution and the nucleophilic phenoxides might react with their nearest neighbor, which may not always be the most reactive monomer. This trend is likely to occur several times, shifting concentrations between **1c** and **3** until all of the monomer has reacted and polymerization can no longer proceed.

A similar experiment was performed using **11** instead of **1c** because **3** and **11** should be of much more similar reactivity, compared to that aforementioned.

![Figure 19](image-url)

**Figure 19**: Inverse Gated Decoupled $^{13}$C NMR spectra overlay in DMSO-$d_6$ of bisphenol A based backbone disulfonated systems comparing random, **12b**, and alternating, **15b**, copolymers.

**Figure 19** indicates all three monomers were incorporated sufficiently in each polymerization. The reactivities of **3** and **11** are similar and no $^{19}$F data exists to support
differences among the two. Instead, kinetic studies using both monomers in competition have been previously reported. The results had shown that over a variety of temperatures, 3 is consistently more reactive toward nucleophilic attack than 11. Since monomers exhibit different reactivity, secondary peaks that persist in 12b are expected. Peaks e & j correspond to the carbon atoms in 2a ipso to the ether bonds, connected to 3 and 11, respectively. When the primary and secondary peaks are integrated together, e has a higher value than j in 12b displaying a preferential reactivity toward 3 over 11. Much like previously mentioned, micro-block like segments may be formed in 12b, though to a lesser extent than displayed in Figure 17 with 12a.

Another indication of the influence of structure on overall copolymer properties is through the T_g. Displayed in Figures 20 & 21, polymers with more regularly dispersed monomers would be expected to have a higher T_g as well as being more thermally stable.

Figure 20: DSC overlay of bisphenol A based copolymers comparing block (10c), random (12a), and alternating (15a) pendant sulfonated systems to random (12b) and alternating (15b) backbone sulfonated systems.
The alternating copolymers exhibit higher $T_g$’s than their random counterparts. The pendant block copolymer, 10c, exhibits the lowest $T_g$ of all polymers synthesized in this series; this is most likely due to a large free volume in the matrix and highly phase-separated domains. The backbone sulfonated polymers, 12b & 15b, are expected to have higher $T_g$’s than the pendant polymers. The similar $T_g$’s may be attributed to formation of more co-continuous domains and weak phase separation.

Figure 21: TGA overlay of bisphenol A based copolymers synthesized by adding monomers in different orders. Block (10c), random (12a), and alternating (15a) pendant sulfonated systems to random are compared as well as random (12b) and alternating (15b) backbone sulfonated systems.

The thermal stabilities in Figure 21 are all similar up to 250 °C; polymer 15b is the most thermally stable. The thermal stabilities are comparable to the membranes currently employed for PEMFCs.
3.2.4 Hydroquinone Based Random and Alternating Copolymers

A similar series to that discussed previously, Section 3.2.3, was conducted using hydroquinone, 10, instead of bisphenol A, 2a. The purpose was to determine if the observations hold true only for systems synthesized with 2a, or if generalizations can be made about bisphenols with different nucleophilic strengths.

Scheme 10: Random (14a) vs. perfectly alternating (16a) hydroquinone based pendant mono sulfonated PAES.

Scheme 11: Random (14b) vs. perfectly alternating (16b) hydroquinone based backbone disulfonated PAES.
Hydroquinone is expected to be a stronger nucleophile than 2a as determined by the $^{13}$C NMR spectra of both monomers. A stronger nucleophile has a further upfield shift on the phenolic carbon, therefore, 10 (149 ppm) is expected to be a stronger nucleophile than 2a (155ppm).

It is necessary to determine the behavior of using a stronger nucleophile, 10, to react with 3 and 1c or 11, to make a randomly ordered copolymer and compare it to a polymer that is perfectly alternating in structure. NMR spectroscopy is useful to determine whether a single reaction with 3 monomers at 140 °C will react in a random order or if they will react to form a nearly alternating polymer.

Figure 22: $^{13}$C NMR spectral comparison of hydroquinone based pendant mono sulfonated copolymer systems that are random, 14a, and alternating, 16a.
From Figures 22 & 23, it is evident that regardless of the comonomer used (1c or 11), at 140 °C the polymerization occurs in a random sequence giving only a marginal preference of hydroquinone to react with 3 over 11. From Figure 22, it appears that hydroquinone reacts much more favorably with 3 over 1c as seen from integration of peaks k & b.

![Diagram of polymer structure]

**Figure 23:** $^{13}$C NMR spectral comparison of bisphenol A based backbone disulfonated copolymer systems, which are random, 14b, and alternating, 16b.

The general properties of hydroquinone-based copolymers are summarized in Table 11. The molecular weights of the random copolymers, 14a-b, were consistently lower than those of the alternating copolymers, 16a-b.
Table 11: Characterization of hydroquinone based Copolymers.

<table>
<thead>
<tr>
<th></th>
<th>Yield (%)</th>
<th>Form</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>PDI</th>
<th>IEC calc. (meq./g)</th>
<th>$T_g$ (°C)</th>
<th>$T_{d5%}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14a</td>
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<td>acid</td>
<td>26,300</td>
<td>37,900</td>
<td>1.44</td>
<td>1.33</td>
<td>147</td>
<td>361</td>
</tr>
<tr>
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<td></td>
<td>salt</td>
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<td>43,100</td>
<td>1.49</td>
<td></td>
<td>238</td>
<td>432</td>
</tr>
<tr>
<td>16a</td>
<td>88</td>
<td>acid</td>
<td>38,300</td>
<td>75,100</td>
<td>1.96</td>
<td>1.33</td>
<td>245</td>
<td>372</td>
</tr>
<tr>
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<td></td>
<td>salt</td>
<td>41,600</td>
<td>83,400</td>
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<td></td>
<td>281</td>
<td>441</td>
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<tr>
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<td>2.10</td>
<td>2.66</td>
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<td>---</td>
</tr>
<tr>
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<td></td>
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<td>201,100</td>
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<td>2.24</td>
<td></td>
<td>---</td>
<td>437</td>
</tr>
</tbody>
</table>

--- No $T_g$ detected

The glass transition temperatures follow the same trend as observed for the bisphenol A based systems, more ordered systems exhibit higher $T_g$’s when compared to more randomized systems. The $T_g$ of a polymer typically increases as the molecular weight increases, which may be an additional contributor to the observed results. A higher degree of ionic channels also results in differences in $T_g$. Formation of ionic channels can cause a decrease in $T_g$ due to an increase in free volume and less restriction of chain movement. Polymer 14a is likely to contain more free volume than 16a, which is attributed to differences in monomeric assemblies. Copolymer 16a is forced to maintain an alternating structure while 14a is randomized and may allow for ionic clusters to form.

The alternating backbone system, 16b, exhibited a higher $T_g$ than its random counterpart, 14b. In part this may be due to significantly different molecular weights between the samples. As mentioned previously, 3 and 11 experience similar reactivities, likely resulting in the formation of minimal ionic domains. In systems that are less ordered, ionic domains may form more easily, as a result the spacing and free volume increases in these areas allowing the chains to move past one another at lower
temperatures thus yielding lower $T_g$’s. This holds true below where pendant systems are expected to form well-defined ionic domains than the backbone systems. The significant differences in $T_g$ of the random and alternating pendant copolymers are attributed to these domains. Backbone sulfonated copolymers do not form as well defined ionic domains, so the alternating and random systems (14b & 16b) are expected to have similar $T_g$’s. Also, the differences in reactivity of 1c and 11, relative to 3, can be used to explain the formation of ionic domains as well.

**Figure 24:** DSC overlay of hydroquinone based copolymers with $T_g$ indicated.

The thermal stabilities of the random copolymers are only slightly lower than those of the alternating copolymers. All of the copolymers in the series exhibited a typical 2 step thermal degradation seen for most sulfonated PAES. The first weight loss
on the TGA, around 375 °C, is indicative of the loss of the sulfonic acid groups. The second step around 525 °C indicates the degradation of the s-PAES backbone. All s-PAES’s are thermally stable at high temperatures making them excellent candidates for PEMFC applications.

**Figure 25:** TGA overlay of hydroquinone based copolymers with T\textsubscript{d5%} indicated.
4 CONCLUSIONS

A series of homo and co s-PAES materials bearing the acid group on a pendant phenyl sulfonyl moiety has been developed. The synthetic route to these materials required a minimal number of steps. The thermal stability of this novel class of s-PAES’s is excellent and the ability to cast stable, flexible films makes them prime candidates for PEM applications. The $T_g$ was dependent upon IEC, $M_n$, and the composition of the polymer. As expected, WU (% Wt.) was directly related to IEC. Conductivity, WU, and $T_g$ can all be tuned by varying the concentration of acid groups introduced into the pendant PEM systems.

For 8b & 9d-e, a higher ion exchange capacity was necessary to achieve similar conductivities to that of Nafion®, however, the ion exchange capacities of both are significantly lower than those of the backbone s-PAES’s, with similar conductivities reported.24 This may be due to the fact that with pendant sulfonic acid groups, a lower level of acid groups needed to be incorporated to achieve similar conductivity results. Under similar conditions the proton conductivity of 8b & 9d-e rivaled that of Nafion® while the water uptake values were 26, 23 and 32%, respectively.

Several of the limitations Nafion® is currently facing include cost and operating temperature over 80 °C. Due to the highly fluorinated, thus highly expensive, structure of Nafion®, it is currently rather expensive. Higher conductivities and glass transition temperatures were obtained with 8b, while incorporating a smaller percentage of fluorine per repeat unit than Nafion®. Incorporation of fewer fluorine atoms reduces the cost of
8b, while maintaining high conductivity and thermal stability, overcoming many of the drawbacks that Nafion® currently faces.

There was a direct relationship between order and thermal properties of all the sPAES studied. The more closely alternating structures exhibit higher T_g’s as well as higher T_d5% regardless of the A_2 monomer used. Pendant sulfonated systems do offer significantly low WU and high conductivity, coupled with excellent thermal stability, making them competitive candidates for new PEMs.
5 PROPOSED FUTURE WORK

Several studies are proposed for future work on these sulfonated pendant systems. First, films of 14a-b, 15a-b, and 16a-b copolymers should be formed to see how monomer order in a polymer affects WU, conductivity, and morphology. A series of random copolymers analogous to 9a-e using, bisphenol AF (2b), instead of biphenol (2c), should be synthesized to tune conductivity and WU. Conductivities of all polymers synthesized should be measured over a range of RH and temperatures.
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