

**Synthesis and Characterization of Linear and Crosslinked Sulfonated Poly(arylene ether sulfone)s: Hydrocarbon-based Copolymers as Ion Conductive Membranes for Electrochemical Systems**

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## **ABSTRACT**

### **Synthesis and Characterization of Linear and Crosslinked Sulfonated Poly(arylene ether sulfone)s: Hydrocarbon-based Copolymers as Ion Conductive Membranes for Electrochemical Systems**

Amin Daryaei

Sulfonated poly(arylene ether sulfone)s as ion conductive copolymers have numerous potential applications. Membranes cast from these copolymers are desirable due to their good chemical and thermal stability, excellent mechanical strength, satisfactory conductivity, and excellent transport properties of water and ions. These copolymers can be used in a variety of topologies. Structure-property-performance relationships of these membranes as candidates for electrolysis of water for hydrogen production and for purification of water from dissolved ions have been studied.

Linear and multiblock sulfonated poly(arylene ether sulfone)s are potential alternative candidates to Nafion membranes for hydrogen gas production via electrolysis of water. In this investigation, these copolymers were prepared from the direct polymerization of di-sulfonated and non-sulfonated comonomers with bisphenol monomers. In systematic investigations, a series of copolymers with modified properties were synthesized and characterized by changing the ratio of the sulfonated/non-sulfonated comonomers in each reaction. These copolymers were investigated in terms of mechanical stability, proton conductivity and H<sub>2</sub> gas permeability at a range of temperatures and under fully hydrated conditions.

A multiblock copolymer was synthesized and evaluated for its potential as membranes for electrolysis of water and for fuel cell applications. The multiblock copolymer contained some

fluorinated repeat units in the hydrophobic blocks, and these were coupled with a fully disulfonated hydrophilic block prepared from 3,3'-disulfonate-4,4'-dichlorodiphenyl sulfone and biphenol. After annealing, the multiblock copolymer showed enhanced proton conductivity and a more ordered morphology in comparison to the random copolymer counterparts. At 90 °C and under fully hydrated conditions, improved proton conductivity and controlled H<sub>2</sub> gas permeability was observed. Finally, the performance of the multiblock copolymer, which was measured as the ratio of proton conductivity to H<sub>2</sub> gas permeability, was improved when compared to the state-of-the-art membrane, Nafion 212, by a factor of 3.

In another systematic study, two series of random copolymers were synthesized and characterized, and then cast into membranes to evaluate for electrolysis of water. One series contained solely hydroquinone as the phenolic monomer, while the second series contained a mixture of resorcinol and hydroquinone as phenolic comonomers. The polymers that contained only the hydroquinone monomer showed exceptionally good mechanical properties due to the *para*-substituted comonomer in the composition of the polymer. In the resorcinol-hydroquinone series, gas permeability was constrained due to the presence of 25% of the *meta*-substituted comonomer incorporated into its structure. Low gas permeability and high proton conductivity at elevated temperatures were obtained for both the linear random and multiblock copolymers. Performance of these copolymers was superior to Nafion at elevated temperatures (80-95°C). In order to enhance the durability of these materials in their hydrated states at elevated temperatures, the surfaces of these copolymer films were treated with fluorine gas. In comparison with pristine non-fluorinated membranes, the modified membranes showed decreased water uptake and longer durability in Fenton's reagent.

A series of linear and crosslinked copolymers were investigated with respect to their potential for use as membranes for desalination of water by electrodialysis and reverse osmosis. The crosslinked membranes were prepared by reacting controlled molecular weight, disulfonated oligomers that were terminated with *meta*-aminophenol with an epoxy reagent. The oligomers had systematically varied degrees of disulfonation and either 5000 or 10,000 Da controlled molecular weights. Membrane casting conditions were established to fabricate highly crosslinked systems with greater than 90% gel fractions. At such a high gel fraction, the water uptake of the crosslinked membranes was lower than that of the linear biphenol-based, disulfonated random copolymer with a similar IEC. Among these series of copolymers, it was shown that the crosslinked membranes cast from the oligomers with 50% degree of disulfonation and a molecular weight of 10,000 Da had the lowest salt permeability of  $10^{-8}$  cm<sup>2</sup>/sec.

For desalination applications, a comonomer was synthesized with one sulfonate substituent on 4,4'-dichlorodiphenyl sulfone. This new monosulfonated comonomer allows for even distribution of the ions on the linear copolymer backbone, and this may be important for controlling ion transport. Mechanical tests were conducted on the membranes while they were submerged in a water bath. The ultimate strength of a fully hydrated copolymer with an IEC of 1.36 meq/g was approximately 60 MPa with an elongation at break of 160%. Moreover, in a monovalent/divalent mixed salt solution, the monosulfonated linear copolymer exhibited a constant Na<sup>+</sup> passage of less than 1.0%.

## GENERAL ABSTRACT

Purification systems have become an increasingly important scientific and technological need for millions around who face water shortages and/or impure sources of potable water. In response, water purification and hydrogen gas production have been widely used to produce pure products from a variety of water sources. In general, current state-of-the-art methods in separation technologies feature two major drawbacks: they are energy intensive and costly processes. In response to the growing need for purified water or pure hydrogen gas for energy generation, polymeric materials are increasingly used in the form of membranes to produce a purer product and overcome the hindrances associated with current energy intensive and inefficient methods. These membranes serve as a barrier for unwanted species, while at the same time allowing the desired species to pass through. Under proper conditions, these purification or chemical processes would generate pure materials that can be used on demand.

The chemistry of candidate polymeric materials is extremely important to design a membrane with desired properties. Therefore, the principal goals of this investigation were to synthesize polymers for use as membranes in three areas: 1) Electrolysis of water for ultra-pure hydrogen gas generation 2) Fuel cells applications for electricity generation, and 3) Desalination of water to provide drinking water. For each technology, a series of sulfonated poly(arylene ether sulfone) copolymers were synthesized and characterized. By applying different monomers or chemistries, a range of appropriate copolymers were synthesized whose characteristics varied in topology and architecture, depending on the desired application. Once these copolymers were synthesized, they were cast into membranes under proper established conditions. In addition, the structure-property-performance relationship of these sulfonated polysulfone membranes were further investigated to provide a direction for future studies.

*Dedicated to my beloved parents Eisa Daryaei and Sharareh Shams for their endless support, love, and encouragement.*

*In memory of Professor James E. McGrath, a wonderful educator, advisor, friend and a great scientist*

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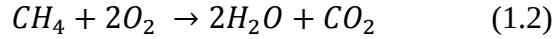
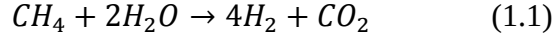
## **CHAPTER 1. Literature Review**

### **1.1 Introduction**

#### **1.1.1 Water Electrolysis and Hydrogen Production**

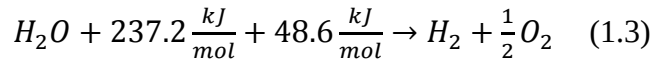
Global warming and climate change represent major environmental problems that demand immediate action.<sup>1-2</sup> Fossil fuels, for decades as the main source for energy production, are known to be a major contributor to global warming. In 2015, almost 67% of electricity produced in the U.S. was generated from fossil fuels.<sup>3</sup> Another issue of concern is that the cost of energy has increased over time due to the depletion of fossil fuel sources and increased energy consumption.<sup>4</sup> Using renewable energy sources such as wind power and solar cells as alternatives to conventional fossil fuel sources for energy production could potentially reduce current levels of pollution and hopefully reverse increased environmental damage.<sup>5-6</sup> The downside of alternative renewable energies, however, is that they are less efficient in generating electricity continuously due to fluctuations of resources, as well as low electricity generation during peak consumption times.

To overcome these drawbacks, hydrogen production technologies are being scrutinized for their viability as alternative sources of energy. Specifically, hydrogen represents a potentially attractive candidate for producing electricity due to some inherent advantages, which include high energy content per mass,  $3.54 \text{ kW/Nm}^3$ , scalability for large applications such as grid electricity generation, and high energy efficiency in conversion between its gaseous form and electricity.<sup>5, 7</sup> Because hydrogen is not found as a pure element, however, it must be produced via chemical reactions prior to use. Currently, hydrogen is commercially produced through a method called steam-reforming of methane (SRM), as shown in Equations 1.1 and 1.2.<sup>1</sup>



To its detriment, however, this method is highly dependent on fossil fuels, and also generates CO<sub>2</sub> as an environmentally unfriendly gas. Moreover, the SRM methodology is associated with the unwanted production of impure hydrogen.<sup>1, 6</sup>

In contrast, an environmentally friendly approach of producing high-purity hydrogen via water electrolysis was first introduced by Troostwijk and Diemann in 1789.<sup>6, 8</sup> As detailed more than two centuries ago, when a direct current is passed through an electrolyte, a non-spontaneous reaction occurs.<sup>9</sup> The electrolysis of water splits water molecules into two molecules, H<sub>2</sub> and O<sub>2</sub>.<sup>1, 6</sup> Normally, water electrolysis technologies are coupled with renewable energy sources, thereby producing hydrogen as the candidate source of fuel for electricity generation. The generated hydrogen is then stored for consumption when needed.<sup>5-6</sup> Water electrolysis can take place using electricity and heat, as detailed in equation 1.3.<sup>6</sup>



The first energy term can be provided by coupling a water electrolysis apparatus with a renewable energy source, while the second energy term is produced by the heat in a water electrolysis cell. Among a variety of water electrolysis methods, membrane water electrolysis (MWE) has attracted considerable attention over the past several decades. In MWE, an electrolyte layer is preferred for three principal reasons. First, it can function as an insulator for reactants and produced gases. Second, it allows for specific ions to pass the membrane from one electrode to the other in the cell. Third, it can serve as an electronic insulator for preventing electrons to pass through the membrane.<sup>10</sup> The electrolyte layer is sandwiched between multiple layers that typically include catalysts, gas barriers, current collectors, and other components. The end result is a membrane

electrode assembly (MEA), which represents a small compartment of a water electrolysis stack. A water electrolyser MEA is shown in Figure 1.1.

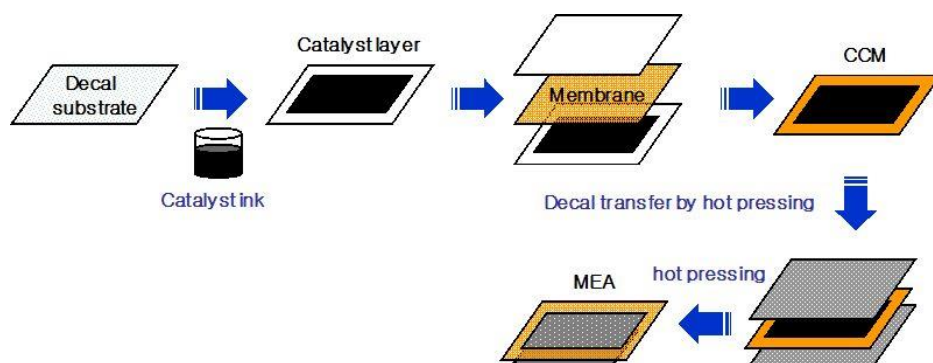


**Figure 1.1** Sandwiched membrane between the catalyst and other layers generating a membrane electrode assembly (MEA)<sup>11</sup>

### 1.1.2 Types of Electrolytes in Water Electrolysis

Although the process of electrolysis has been known for many decades, its many potential applications continue to expand. In water electrolysis, for example, there are many reports investigating different aspects of electrolyzer cells, such as the effects of various catalysts on the kinetics of electrolysis.<sup>4</sup> Additionally, many studies have detailed the electrolysis process under various conditions (e.g., high pressure and high temperature) in order to enhance the rate of electrolysis and increase hydrogen purity.<sup>12-13</sup> Polymer exchange membranes (PEMs) have been investigated for their incorporation as electrolytes in a water electrolyzer cell. Indeed, a PEM-based water electrolyzer represents a viable alternative to alkaline water exchange membranes, the current state-of-the-art technology for hydrogen generation. The major types of water electrolyzers will be briefly introduced in this review, as well as the various synthesis and fabrication aspects of polymer electrolyte membranes.

### 1.1.2.1 Alkaline Membrane Water Electrolysis

Alkaline electrolyzers are the most studied and commercially available types of water electrolysis systems.<sup>5-6</sup> For these electrolyzers, two types of aqueous electrolytes, sodium hydroxide or potassium hydroxide, are typically utilized. A gas separation membrane known as a diaphragm is used to separate the produced gases. The diaphragm enables hydroxide anions to pass through from the anode to the cathode electrode, which is commonly made of nickel-coated steel.<sup>5-6, 9</sup> A common alkaline membrane water electrolysis system is shown in Figure 1.2.

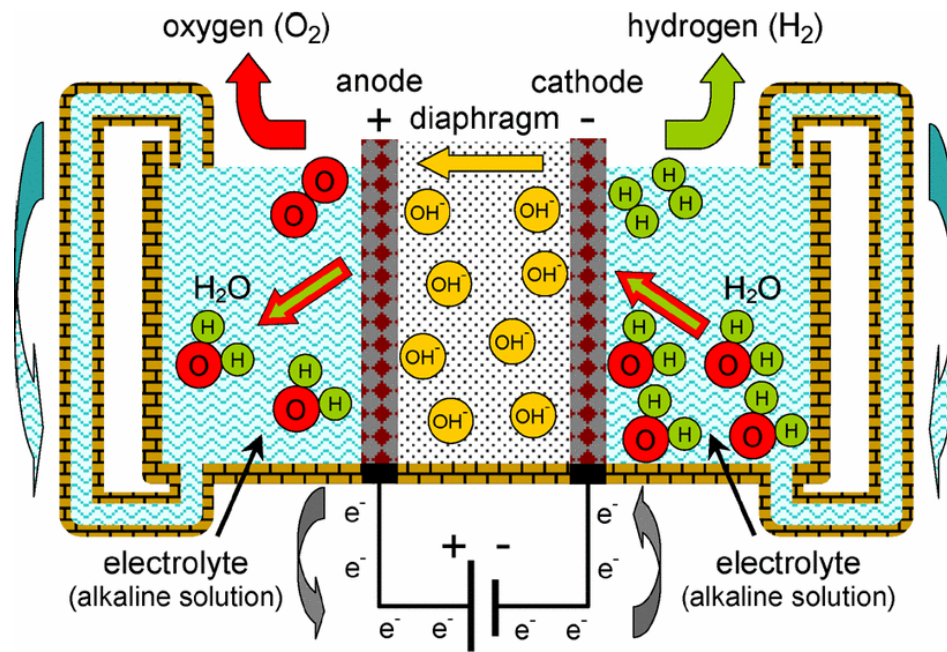


**Figure 1.2** Operating scheme of an alkaline water electrolysis cell with permission from Elsevier, 2012<sup>5</sup>

Despite its utility for producing a robust type of electrolyzer with enhanced durability, this method for hydrogen production does not yield high-purity hydrogen (e.g., >99.99%), with studies confirming that low hydrogen quality is due to the crossover of the gaseous products through the diaphragm.<sup>5-6</sup> Another drawback of alkaline electrolyzers is that they operate at low current

density, which can compromise the high efficiency of the cell. Furthermore, the use of liquid electrolytes precludes the possibility of operating under high pressure; as a result, bulky stacks of electrolyzers are required for these systems that need large spaces.<sup>5-6</sup> A major drawback of anion exchange membrane water electrolysis (AEMWE) is the precipitation of insoluble species such as  $K_2CO_3$  in highly concentrated solutions, which tends to clog the pores of the membrane and degrade its performance.<sup>5-6</sup> To overcome these issues, a variety of novel AEMs have been recently investigated that have the potential to enhance the reaction kinetics and properties of the diaphragm.<sup>7, 14-15</sup>

#### **1.1.2.2 Solid Oxide Water Electrolysis**

Although alkaline water electrolyzers currently represent the bulk of the commercial market, alternative cost-effective electrolyzers are being investigated for their ability to produce high purity hydrogen.<sup>16</sup> As a new generation of electrolyzers, solid oxide electrolyzers have been targeted by researchers.<sup>17</sup> High efficiency electrolyzers using solid oxide electrolytes were first introduced by Donitz and Erdle in the 1980s.<sup>16</sup> This type of electrolyte operates at high temperatures (i.e., at 800 °C and above<sup>18</sup>), such that water is introduced to the electrolyzer stacks as steam. As a result of the high temperature, water is split faster in comparison to water electrolysis through anion exchange. An operation scheme of this type of electrolyzer is shown in Figure 1.3, where steam is electrolyzed at the cathode producing  $H_2$ , and the ceramic electrolytes allow for  $O_2^{2-}$  anions to pass through the anode electrodes to generate oxygen gas.<sup>5-6</sup>

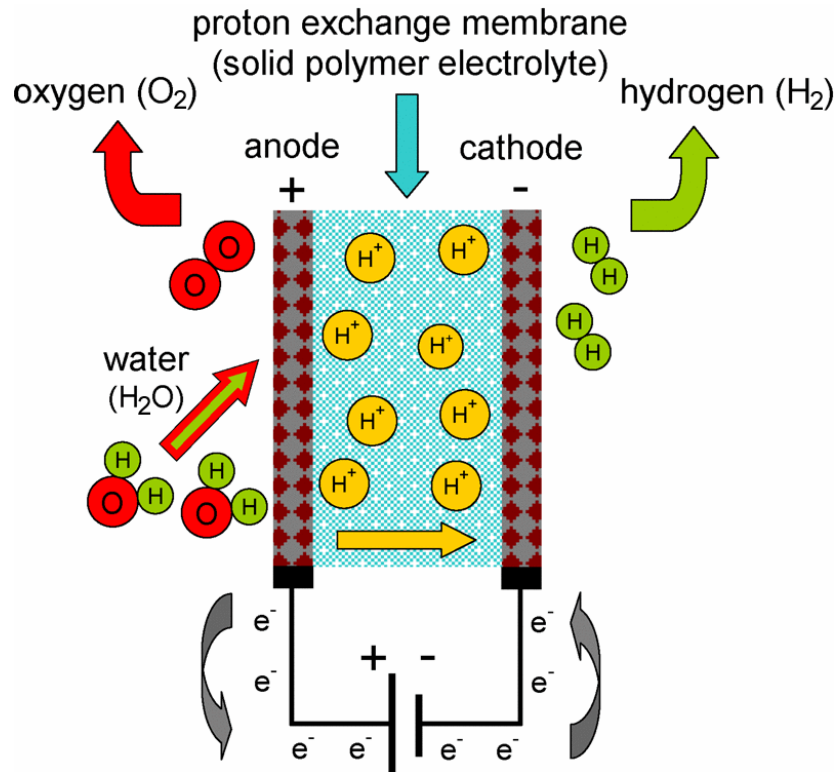


**Figure 1.3** Operating scheme of a solid oxide water electrolysis cell with permission from Elsevier, 2012<sup>5</sup>

Some advantages of solid oxide water electrolysis include lower overall cost, operation at high currents of about  $0.3 \text{ A/cm}^2$ , and low cell voltage of about  $1.07 \text{ V}$ .<sup>5</sup> In contrast, a drawback associated with this electrolysis method is that it is challenging to achieve the required high temperature with necessary efficiency. Despite the fact that such technology has yet to be fully developed, it does show great potential in becoming a commercially viable alternative in the near future.<sup>5-6</sup>

### 1.1.2.3 Proton Exchange Membrane (PEM)

A proton exchange membrane or polymer electrolyte membrane (PEM) is a solid polymer electrolyte placed in between two electrodes (an anode and a cathode). The first water electrolyser

PEM was a sulfonated polystyrene developed by General Electric in the late 1950s.<sup>5-6, 19</sup> In fact, a PEM was utilized electrochemical processes in the U.S. aerospace industry in the 1950s.<sup>5</sup> As illustrated in Figure 1.4, the acid groups incorporated into the polymer backbone allow for proton ions to pass through the membrane.

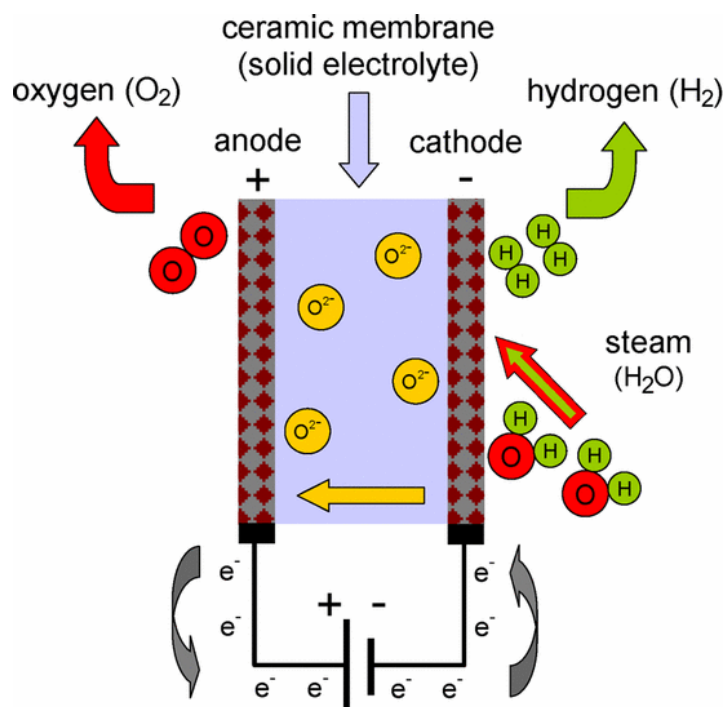


**Figure 1.4** Operating scheme of a solid oxide water electrolysis cell with permission from Elsevier, 2012<sup>5</sup>

However, sulfonated polystyrene PEMs feature a number of disadvantages—most notably poor chemical stability. In contrast, proton exchange membranes are superior to other electrolyzers, including alkaline and solid oxide electrolyzers, due to their rapid kinetics and high hydrogen purity product, which enables them to be used without further purification.<sup>5-6</sup> In addition, the ability of PEMs to operate at high current density, up to 2 A/cm<sup>2</sup>, as well as at differential pressure, results in higher efficiency that lower operation costs.<sup>5-6</sup> During this process, however, oxygen and hydrogen gases must be prohibited from passing through the solid electrolyte to prevent potential

explosions. One way to mitigate this explosion hazard is by utilizing a PEM in a water electrolyser cell.

### **1.1.3 Water Desalination via Membrane Technology**

The ready availability of potable water is a global issue that has the potential to impact countless numbers of human lives around the world in the near future.<sup>20-21</sup> Indeed, it is estimated that some 1.1 billion people around the globe lack access to water, and more than twice that number face water shortages for at least one month a year. Inadequate sanitation is also a problem for billions around the world, which results in a number of water-borne diseases such as typhoid fever and cholera. By 2025, two-thirds of the world's population may face water shortages, and ecosystems around the world will suffer even more.

One way of producing pure water is via the desalination of sea water—a process whereby salt and/or minerals are removed from water to make it potable. In most cases desalination is used in arid coastal regions to turn sea water into drinking water, but it is also used inland where local ground or surface water is brackish. The process, however, features a number of distinct disadvantages, including high energy consumption and the elimination of waste products.

Currently, multistage flash distillation (MSF) and multi-effect distillation (MED) of water are the most widely used methods for water purification. However, due to high energy consumption—namely, 7.5-12 kWh.m<sup>-3</sup> for MSF and 4-7 kWh.m<sup>-3</sup> for MED<sup>22</sup>—researchers are examining alternative methods for pure water production.<sup>23</sup> Membrane technologies represent attractive alternative methods for traditional water purification methods due to low energy consumption, high water recovery, and small setup systems.<sup>22</sup> As illustrated in Figure 1.5, the most

prevalent commercial membranes currently available are pore-flow membranes and dense membranes.

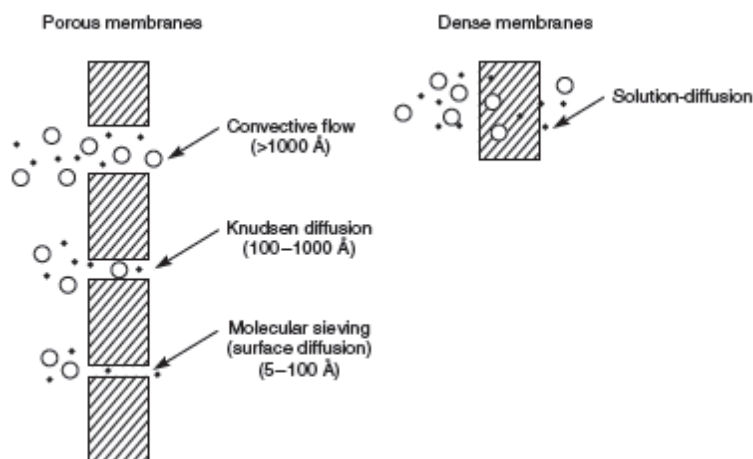


**Figure 1.5** Pore-flow membranes (left) and dense membranes (right) in separation technologies. Used with permission of John Wiley & Sons, Ltd, 2012<sup>24</sup>

Pore-flow membranes, which are typically used in ultrafiltration, nano-filtration and microfiltration, have smaller size, nano-scale pores that allows small species to pass through, while at the same time blocking the larger species from passing through membrane. Thus, clean water is collected once unwanted species or contaminants have been captured. The main drawback of this type of membrane is clogging and fouling of the membrane. The other type of membrane typically used in water filtration is known as a dense membrane, which is a polymeric membrane that is pore-free. This type of membrane is a dense film whereby permeate materials diffuse through by pressure, concentration, or electrical potential gradient. The polymeric material affects the permeability and selectivity of the membrane, and purification results are based on solubility differences in the membranes. Because some species are highly soluble in the polymer matrix they are able to dissolve in the polymer and diffuse to the other side of the film; in contrast, other

species' solubility in the polymer is very low. Typically, water is highly soluble in the ionic polymers while ions are not as soluble.<sup>25</sup> Dense membranes are used in reverse osmosis, forward osmosis, electrodialysis, and reverse electrodialysis. Here reverse osmosis and electrodialysis as two widely used solution-diffusion based membranes will be briefly introduced.

#### **1.1.3.1 Reverse Osmosis (RO)**

RO water purification is a rapidly-growing technology that relies on dense membranes as filtration materials—in part due to improvements in processing efficiencies. Although energy consumption will vary based upon the salinity of water and design of the RO system. Power consumption levels associated with this method have dramatically decreased since 1970 (Figure 1.6). In fact, the power consumption in RO purification has dropped to a mere 1.5-2.5 kWh.m<sup>-3</sup> for brackish water purification.<sup>23</sup>

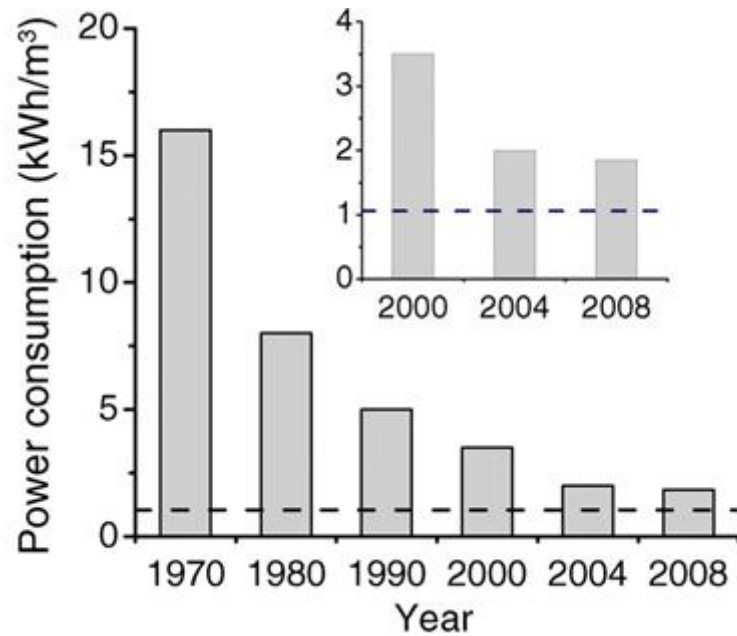


**Figure 1.6** RO energy consumption from the 1970s until 2008. Used with permission from American Association for the Advancement of Science, 2011<sup>21</sup>

During the osmosis process, the transport of ions occurs when there is concentration gradient on two sides of a membranes. Solvents can permeate through these membranes, even as the membranes remain impermeable to the solute. As a result of concentration differences, solvent is transported from the diluate side to the concentrated side, while the solute is rejected from the membrane. In contrast, RO uses an opposite transport direction. During the RO process, water moves from the high concentrate side to the diluate side with the aid of applied pressure on the high concentrate side of the membrane.<sup>26</sup> A simple schematic of the RO process is shown in Figure 1.7.

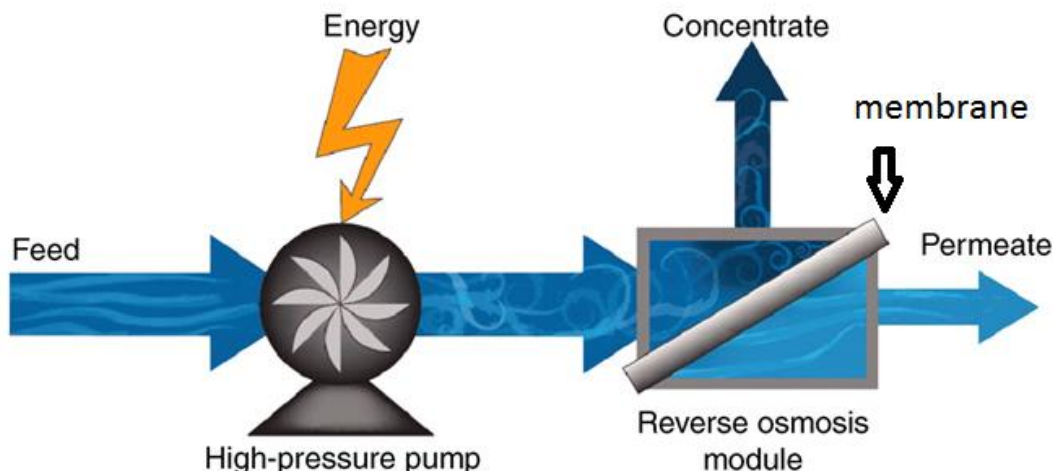
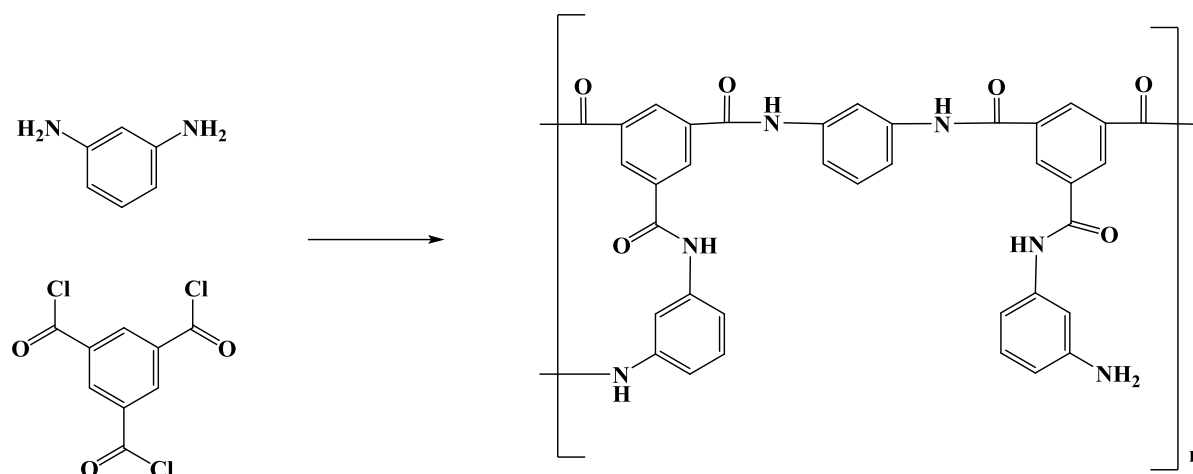


**Figure 1.7** Simple schematic of the RO process. Used with permission from the American Association for the Advancement of Science, 2011<sup>21</sup>

Currently, the benchmark membrane for RO is a fully aromatic crosslinked polyamide.<sup>27</sup> For mechanical stability, a thin film of the crosslinked membrane, about 0.1-3  $\mu\text{m}$ , is supported by a commercially available polysulfone film with a thickness of approximately 40  $\mu\text{m}$ .<sup>28</sup> The crosslinked polymer is synthesized via the interfacial polymerization of a diamine and an acid chloride on the support layer. In order to conduct the polymerization, the diamine monomer is dissolved in the aqueous solvent in which the support layer is immersed. The acid chloride, which is insoluble in the aqueous phase, is dissolved in an organic solvent. When the organic solution is mixed with the aqueous solution, the polymerization occurs at the interfacial layer via the diffusion of the diamine monomer into the organic layer to form a thin film—the so-called “skin.” This reaction procedure is shown in Scheme 1.1.



**Scheme 1.1** Reaction of the diamine and the acid chloride that generates the crosslinked membrane for RO<sup>27</sup>

Although these crosslinked membranes are desirably very thin and feature excellent salt rejection properties and good water flux, they tend to exhibit poor chlorine resistance.<sup>27</sup> Thus, extensive work is ongoing to overcome the chemical instability of currently available commercial membranes.<sup>27</sup> In addition, RO water purification requires a water pretreatment step to separate water from impurities other than salt.

### 1.1.3.2 Electrodialysis (ED)

ED is an attractive water purification method—principally due to its low energy requirement, high water recovery, and the fact that no water pretreatment step is required. Energy consumption in ED can be as little as 1.0 kWh.m<sup>-3</sup> for brackish water desalination.<sup>29</sup> ED cells purify water from ions using dense membranes with the aid of electrical potential as the driving force for ion transport. In ED, multiple membranes are used in a cell as illustrated in Figure 1.8. These ion-conducting membranes, which include anion exchange membrane (AEM) and cation exchange membrane (CEM), are placed in between two electrodes. When an electrical potential is

applied on the electrodes, the ions move toward the counter electrode. These ions are blocked from the membranes with the same charge as the ions, while they pass through the membranes with an opposite charge. Pure water and high concentrated salt are collected from the channels as shown in Figure 1.8.<sup>26, 30</sup>

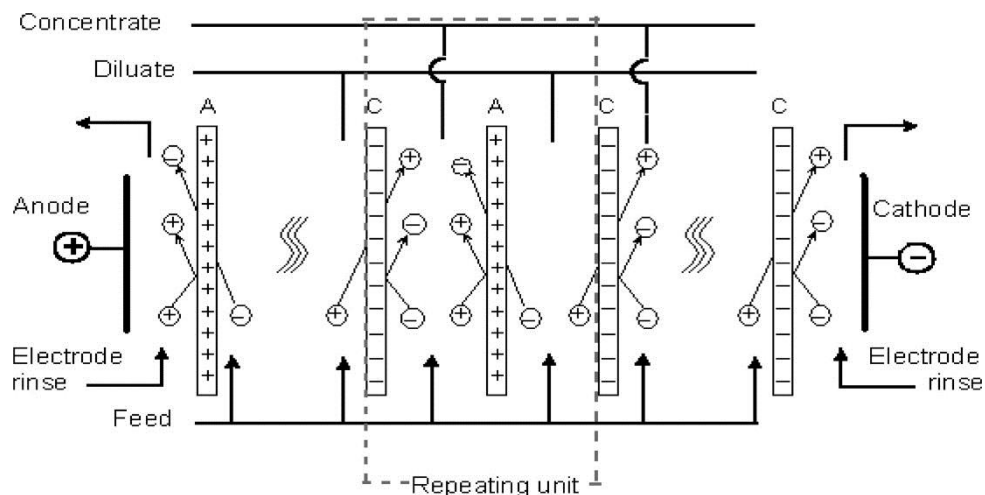
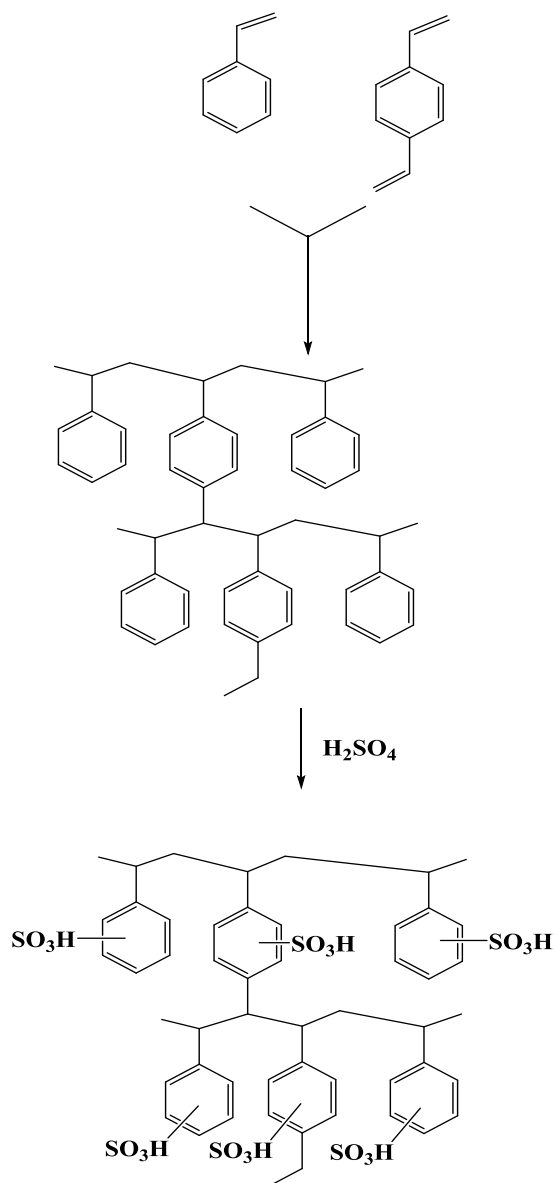


**Figure 1.8** An ED cell containing anion exchange membrane (AEM) and cation exchange membrane (CEM). Used with permission from American Chemical Society, 2013<sup>30</sup>

Currently the state-of-the-art membranes in ED are crosslinked sulfonated polystyrene-divinylbenzene, such as CEM. The reaction and structure of this crosslinked polymer is shown in Scheme 1.2.



**Scheme 1.2** Preparation of crosslinked sulfonated styrene-divinyl benzene membranes for ED<sup>26</sup>

Due to the relatively poor mechanical properties of these membranes, they become more efficient when they are embedded in a non-ionic support frame. When a support frame is utilized, the thickness of the membrane increases to about 600  $\mu\text{m}$ . Such an approach results in a supported membrane that evidences high electrical resistance, low ion conductivity, reduced ion selectivity, and eventually low energy efficiency.<sup>31-32</sup> Thus, research is ongoing to identify an alternative

membrane with high ion conductivity, the ability to form thin films without the need for a support frame, and good ion selectivity to improve the efficiency of the ED process.

## 1.2 Important Terms and Equations for Ion Conducting Polymers

Equivalent Weight (EW) a term applied to an ion exchange membrane, refers to the degree of sulfonic acid groups in the membrane. The EW is equal to the number of grams of the dry PFSA copolymer per moles of sulfonic acid groups in the material, as shown in Equation 1.4.

$$EW = \frac{1000 \text{ g}}{\text{mole of sulfonic acid groups}} \quad (1.4)$$

Ion Exchange Capacity (IEC), which is the inverse of EW, is used to define the amount of acid groups on the polymer backbone. IEC has a unit of (meq/g) and can be represented as shown in Equation 1.5.

$$IEC = \frac{1}{EW} = \frac{\text{Number of acid groups}}{\text{Dry weight of polymer}} \times 1000 \quad (1.5)$$

Water Uptake (WU) represents the amount of water that ionic polymers absorb. Generally, as IEC increases in a polymer, the water uptake also increases. WU is defined in Equation 1.6.

$$WU = \frac{Mass_{wet} - Mass_{dry}}{Mass_{dry}} \times 100 \quad (1.6)$$

### 1.3 Polymer Electrolyte Membranes

Due to a range of significant disadvantages associated with current state-of-the-art membranes (e.g., Nafion<sup>TM</sup>), the need for alternative polymeric-based systems for PEM applications is increasing. An ideal polymer electrolyte membrane, also known as proton exchange membrane (PEM), should exhibit the following criteria: good proton conductivity under fully hydrated conditions, good mechanical properties, controlled gas permeability, and cost effectiveness; PEM should also demonstrate good chemical and oxidative stability, feature controlled water uptake and ease of fabrication into a membrane electrode assembly.

It should also be noted that a membrane's performance characteristics will vary depending on its use. For example, a PEM intended for water electrolysis at high temperature and high pressure should exhibit certain critical parameters, including good proton conductivity, desirable mechanical properties, and low hydrogen permeability. If the intent is the effective desalination of water via reverse osmosis, a membrane with high ion rejection and high water flux is required. For the electrodialysis of water, certain other membrane parameters are essential, such as high ion content at controlled water uptake, high ion conductivity and low electrical resistance. However, in a PEM, there is frequently a tradeoff between sufficient ion conductivity and good mechanical properties due to the contributions of the hydrophilic and hydrophobic polymer components.<sup>33</sup> In this context, these polymeric membranes can be divided into two main categories: perfluorosulfonic acid membranes and hydrocarbon-based membranes. The synthesis, characterization, and properties of important polymers in each category will be discussed in detail.

### 1.3.1 Morphology of Ion Conductive Membranes

Morphology plays an important role in determining the final properties of the membrane. Specifically, ion conductivity and mechanical properties are highly dependent on the morphology of the copolymers. Smith et al.<sup>1</sup> confirmed that a microphase-separated microblock copolymer would have adequate mechanical properties, low swelling in water, and a  $T_g$  much higher than the operating temperature of a water electrolyzer. Their microphase-separated ionomer reached electrolysis cell efficiency of 88% at 80 °C, while the H<sub>2</sub> gas crossover was below 0.6% in O<sub>2</sub>, which is a considerably lower gas crossover level compared to many other systems.

Badami et al.<sup>34</sup> showed that under suitable conditions, a multiblock copolymer is able to phase separate into the hydrophobic-hydrophilic lamellar structure shown in Figure 1.9. The degree of phase separation changes depending on the block length and the linkage groups between the hydrophilic-hydrophobic blocks. In addition, the researchers documented that by enhancing phase separation, one can increase proton conductivity from 0.065 S/cm to 0.95 S/cm for hydrophilic-hydrophobic block length of 3k-3k and 10k-10k in each copolymer, respectively.

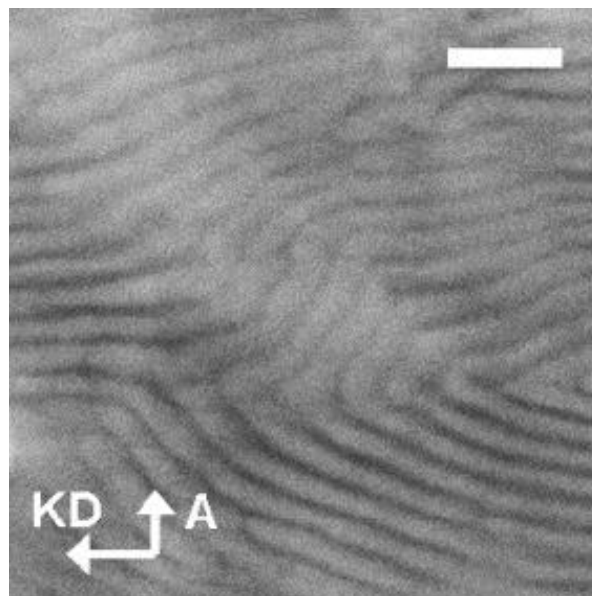


**Figure 1.9** TEM micrograph of a phase separated hydrophilic-hydrophobic multiblock copolymer after annealing at  $^{\circ}\text{C}$ , with permission from Elsevier, 2009<sup>34</sup>

Phase separation, however, is not observed in random copolymers. Instead, transmission electron microscopy (TEM) results for random copolymers have indicated the presence of aggregates of ionic hydrophilic domains and non-ionic hydrophobic segments that are not connected in either the dry or partially-hydrated state of the fuel cells.<sup>35</sup> Therefore, the conductivity of random copolymers is somehow lower than that of multiblock copolymers.<sup>36</sup> A schematic of these domains for Nafion<sup>TM</sup> is shown in Figure 1.10.<sup>37</sup>

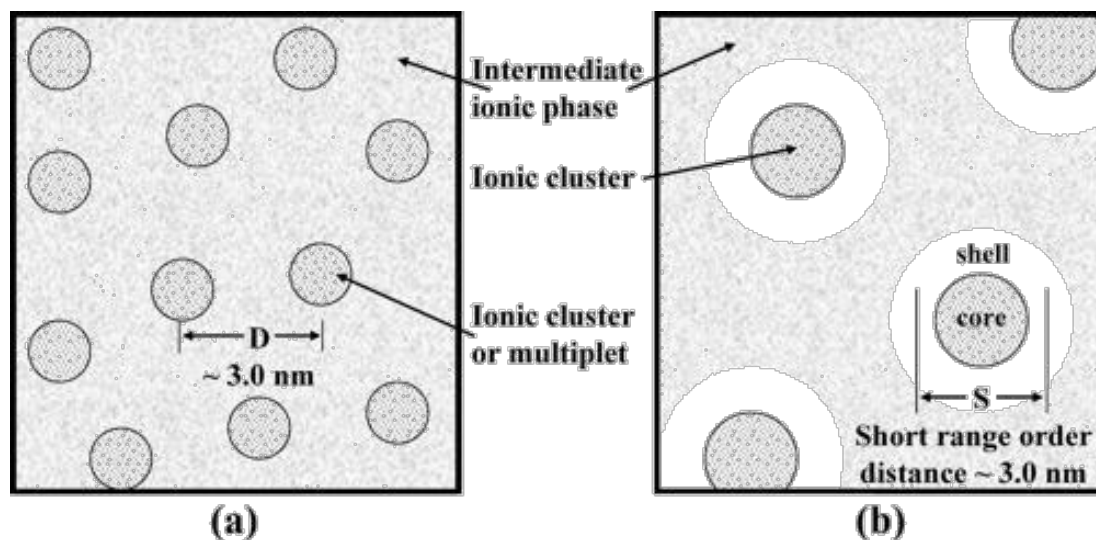


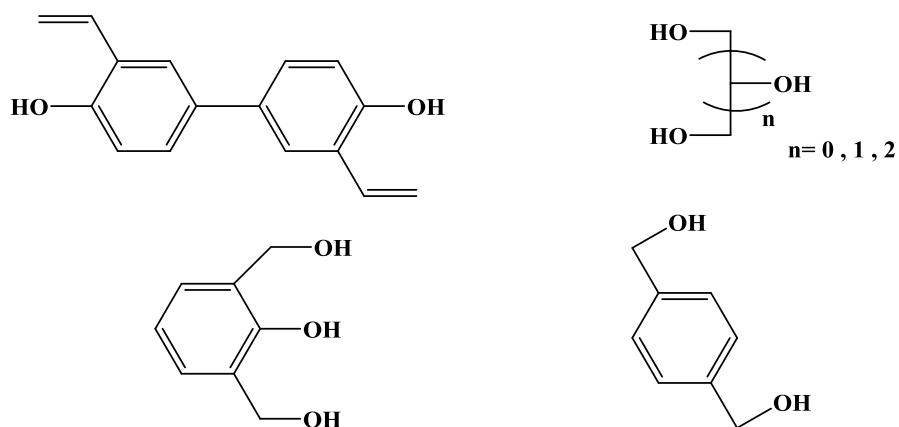
**Figure 1.10** Morphological models of Nafion™ domains with their relative sizes. Used with permission from the American Chemical Society, 2004<sup>37</sup>

### 1.3.2 Polymer Topologies for Ion Conductive Membranes

In addition to polymer composition, the topology of the polymer is a critical factor that must be considered for property-performance control of polymer systems. A combination of factors, including choice of monomers, monomers ratio, nature of functional groups and their location on the polymer chains, will lead to polymers with different architectures.<sup>38</sup> In other words, how polymer chains are connected to each other results in a variety of polymer topologies that subsequently impacts morphology. The difference in microstructure morphologies between linear, comb-shape, star-shape, and crosslinked copolymers results in major performance property variations. The synthesis, characterization, and performance of copolymers with various architectures have been widely studied for PEMs.<sup>33, 39-47</sup> However, one of the most formidable challenges in the successful commercialization of a PEM is reducing processing costs. Accordingly, some common polymer topologies for application in proton exchange membranes will be reviewed in the following sections.

### 1.3.2.1 Crosslinked Copolymers

In most PEM systems, there is typically a tradeoff between polymer swelling/hydrolytic stability and mechanical properties. Drastic water absorption or swelling leads to membrane electrode assembly (MEA) failure. Generally, increasing the ion exchange capacity in a copolymer results in excessive membrane swelling.<sup>48</sup> At elevated IECs, polymers turn into hydrogels; moreover, at excessively high IECs, they become water-soluble polymers. In contrast, crosslinking PEMs is an easy approach for preventing such unwanted outcomes. A polymer can be covalently or physically crosslinked depending on the application and operating conditions.<sup>49</sup> Crosslinking can be tuned by adjusting the desired level of the crosslinking agent in a polymer. Covalent crosslinking requires monomers with reactive functional groups such as vinyl sites, hydroxyl groups or those shown in Scheme 1.3.



**Scheme 1.3** Examples of crosslinked monomers for PEM<sup>50-51</sup>

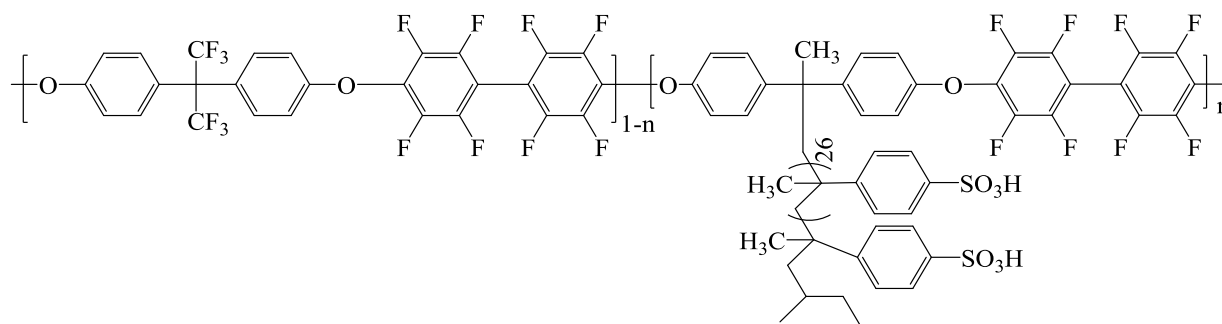
Crosslinking results in decreased proton conductivity by either using sulfonic acid groups as the crosslinking sites, or trapped sulfonic acid groups that are not available to contribute to the proton transfer process.<sup>52</sup> Mikhailenko et al.<sup>53</sup> prepared a series of highly sulfonated copolymers

and crosslinked them via polyatomic alcohols. Due to the extremely high degree of sulfonation in the pristine copolymers at room temperature, they demonstrated proton conductivity as high as 0.02 S/cm even after crosslinking.

### **1.3.2.2 Comb-shaped Copolymers**

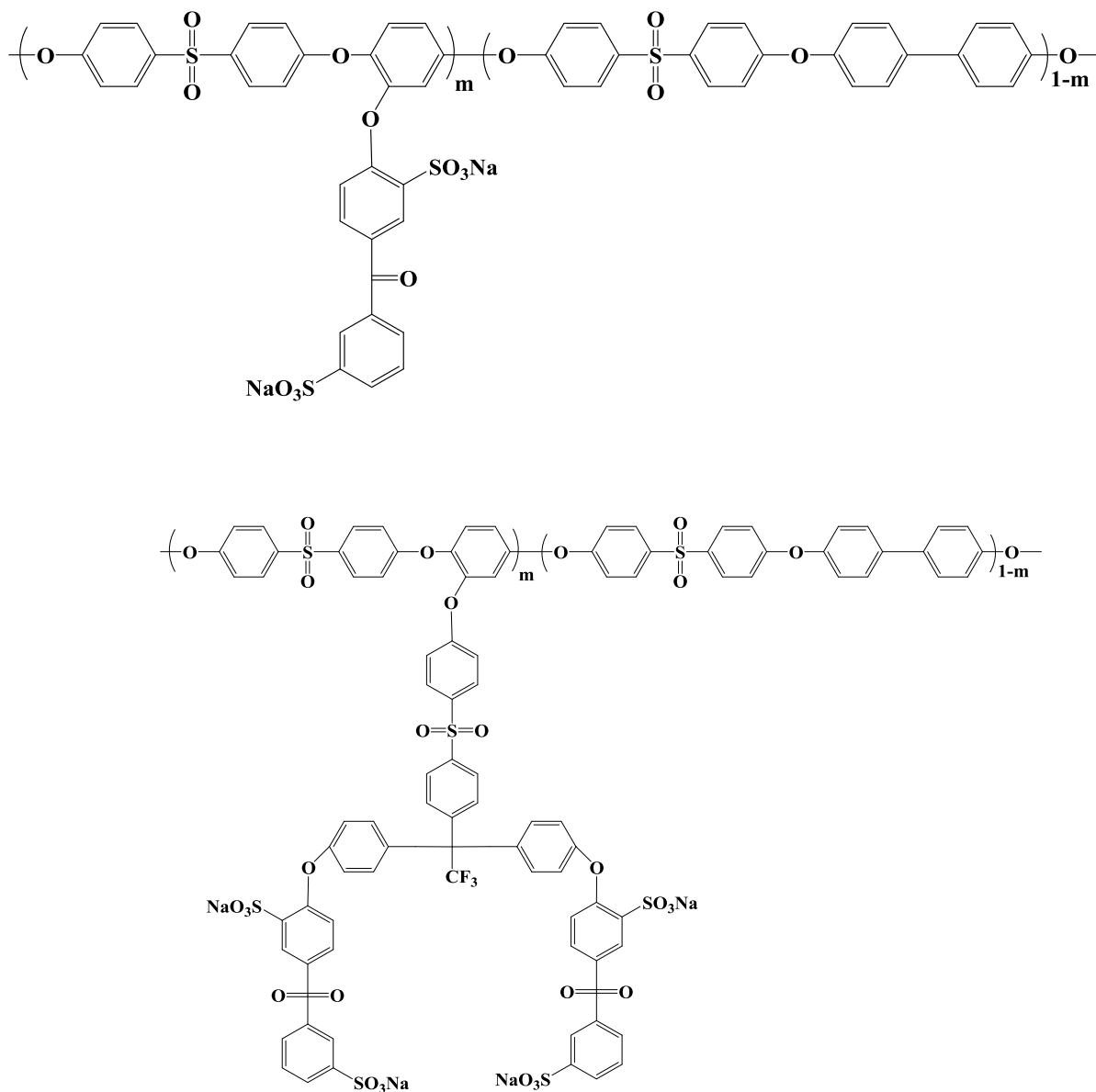
Comb-shaped copolymers are attractive architectures for use as PEM and anion exchange membranes (AEM).<sup>54-55</sup> These copolymers consist of a neutral long polymer backbone bearing side chains with ionic groups. The length of the side chains can be tuned to modify the properties of the final product.<sup>55</sup> Perfluorosulfonic acid polymers can be categorized as comb-shaped copolymers, and there are various methods of synthesizing hydrocarbon-based comb-shaped copolymers.

Nieh et al.<sup>56</sup> synthesized a series of comb-shaped proton exchange membranes via a three-step synthesis approach to yield the polymer shown in Scheme 1.4. These copolymers exhibited the properties of both fluoropolymers on the backbone and hydrocarbon polymers on the side chain.<sup>55</sup> Similarly, comb-shaped copolymers were prepared, which ranged from 19 wt% to 32 wt% in side chain content.<sup>56</sup> The researchers confirmed that as the ratio of the side chains and ion exchange capacity (IEC) increased, the proton conductivity improved as a result of more highly developed interconnected hydrophilic channels.<sup>56</sup>



**Scheme 1.4** A hydrocarbon-based comb-shaped copolymer<sup>56</sup>

Kim et al.<sup>46</sup> prepared two series of comb-shaped PEMs with short side chains, as shown in Scheme 1.5. These copolymers showed comparable proton conductivity to that of the state-of-the-art membrane; in contrast, the methanol permeability was drastically lower than the control polymer. Despite their relatively good mechanical properties, the fact that these copolymers were prepared using a multi-step synthesis procedure will hinder their widespread commercial applications as proton exchange membranes.



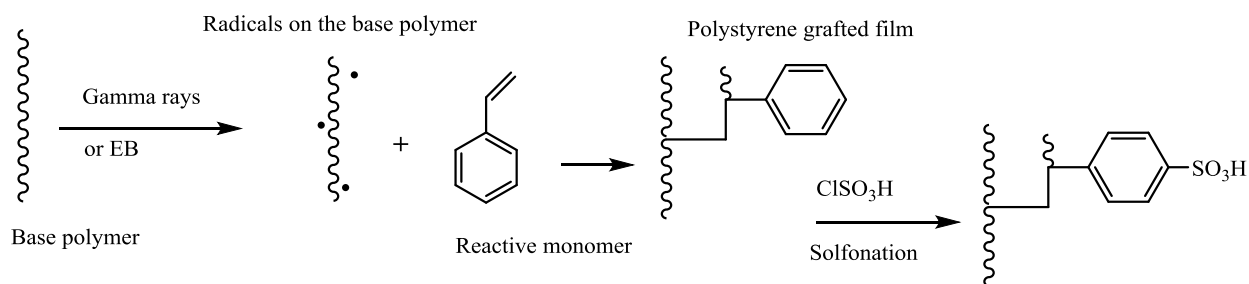
**Scheme 1.5** Two comb-shaped structures prepared by Kim et al.<sup>46</sup>

### 1.3.2.3 Graft Copolymers

Graft copolymers are similar to the comb-shaped variety, but with very long side chains. One approach for preparing graft copolymers for use in PEMs is via radiation-induced grafting (RIG), which has recently attracted attention in electrochemical systems—e.g., in water electrolyzers and fuel cells.<sup>57-59</sup> The advantage of this method includes ease of grafting functional

groups on both fluorinated polymers and non-fluorinated polymers, as well as altering the base polymer properties without any major modifications to the polymer.<sup>58</sup> Choosing the proper irradiation method and tuning of the polymers are important factors in RIG. Products prepared from RIG can be used in pre-shaped membranes for both low temperature and high temperature electrochemical reactions.<sup>58</sup> An overview of the RIG mechanism is shown in Scheme 1.6, which consists of three steps:

- Exposing the polymer to a high-energy beam to generate reactive radical sites
- Introducing a reactive monomer
- Introducing functional groups such as sulfonic acid groups on the grafts



**Scheme 1.6** Radiation-Induced Grafting (RIG) mechanism<sup>58</sup>

It must be noted, however, that in spite of the tremendous advances associated with RIG-generated PEMs, there are still problems associated with this approach.<sup>57</sup> In particular, the long term durability of the final hydrocarbon-based PEMs is not as high as expected. Other problematic issues associated with this method include the inability to homogeneously sulfonate the membrane, as well as maintain desired control over the membrane's thickness and sulfonation depth.

### 1.3.2.4 Linear Copolymers

Copolymers with linear architecture are of great importance for use as PEMs. Synthesis, characterization, and structure-property-performance of linear copolymers have widely been investigated for ion exchange membranes.<sup>60-63</sup> These copolymers can be post-modified homopolymers,<sup>64</sup> but they can also be copolymers synthesized from direct copolymerization of pre-sulfonated and non-sulfonated comonomers combined.<sup>65-68</sup> Linear copolymers can be statistical (random), block, and multiblock copolymers, as shown in Figure 1.11.

A random ion-conducting copolymer consists of randomly distributed hydrophilic and hydrophobic repeat units on the polymer backbone. Block copolymers are made from the covalent attachment of two different long chains; while multiblock copolymers are derived by attaching polymer blocks with different compositions.

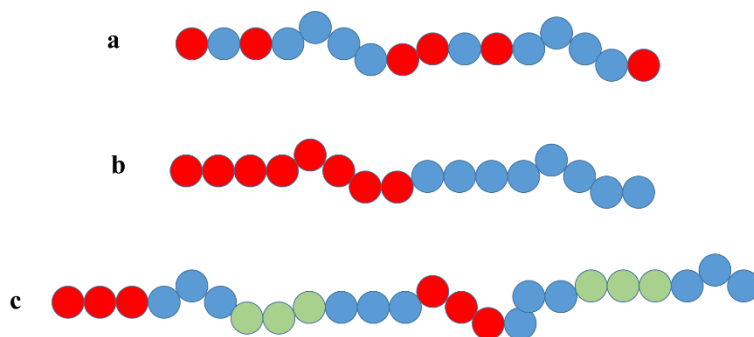


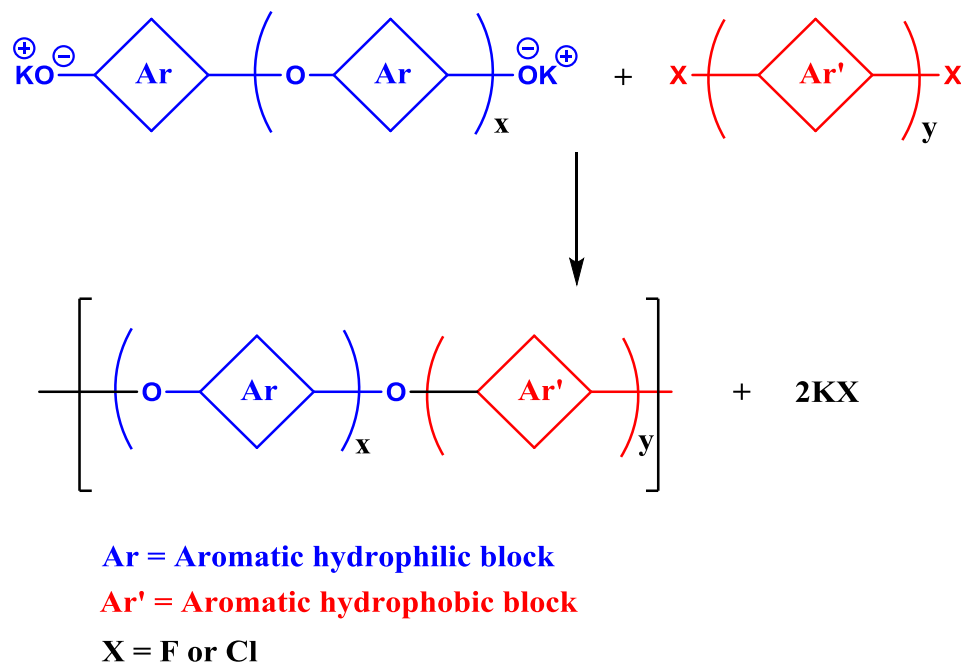
**Figure 1.11** Three different architecture of a linear copolymers. a) random copolymer b) block copolymer c) multiblock copolymer

High performance copolymers such as polysulfones, polyimides, and polybenzimidazoles are good candidates for use in hydrocarbon-based copolymers for desalination of water, fuel cells and electrolysis of water.<sup>69-73</sup> The synthesis of these copolymers can tuned to form random or block copolymers. In addition, they are preferred over aliphatic copolymers due to their higher chemical,

thermal, and mechanical stabilities—making them suitable candidates for use as ion-conducting polymers. Aromatic multiblock copolymers have improved performance in electrochemical applications due to developed phase separation.<sup>39, 74</sup> The downside, however, is that the synthesis of block and multiblock copolymers tends to be more sophisticated than synthesizing random copolymers.

Linear hydrocarbon-based PEMs generally feature good mechanical, chemical, and thermal stabilities—principally due to the presence of arylene rings in their backbone and their hydrophilic-hydrophobic domains.<sup>75</sup> When a sulfonated hydrocarbon-based copolymer is prepared from the direct copolymerization of sulfonated and non-sulfonated comonomers, the final random copolymer have hydrophilic and hydrophobic domains with sizes in the range of 10-25 nm.<sup>75-77</sup> These domain sizes differ depending on the amount of sulfonated monomers used in polymerization.

Block copolymers feature an attractive polymer architecture that has shown enhanced transport properties in fuel cell applications.<sup>78</sup> Generally, diblock copolymers phase separate to make cylindrical, spherical, and lamellar morphologies, while copolymers fabricated from higher number of blocks can shape complex morphologies.<sup>38</sup> These structures are made from coupling reactions between reactive sites on telechelic oligomers. A general hydrophilic-hydrophobic block copolymer synthesis is illustrated in Scheme 1.7. Hydrophilic and hydrophobic oligomers in multiblock copolymers contain incompatible segments that under certain conditions will phase separate to form lamellar microstructures.<sup>79</sup>



**Scheme 1.7** Synthesis general synthesis route of a multiblock copolymer via phenoxide-halogen end group coupling

The literature describes a number of polymerization methods for synthesizing block copolymers, including radiation grafting,<sup>57</sup> stable free radical polymerization (SFRP),<sup>80</sup> metal catalyzed polymerization,<sup>81</sup> and step-growth polymerization. However, the latter approach has been most intensively studied in our group.<sup>74, 82-84</sup> The enhanced properties obtained from step-growth polymerization are typically associated with polymer composition, block length, and the phase separation of the hydrophilic and hydrophobic blocks.<sup>85</sup> Figure 1.12 shows three phase-separated sulfonated poly(arylene ether sulfone) multiblock copolymers with different block lengths and compositions.

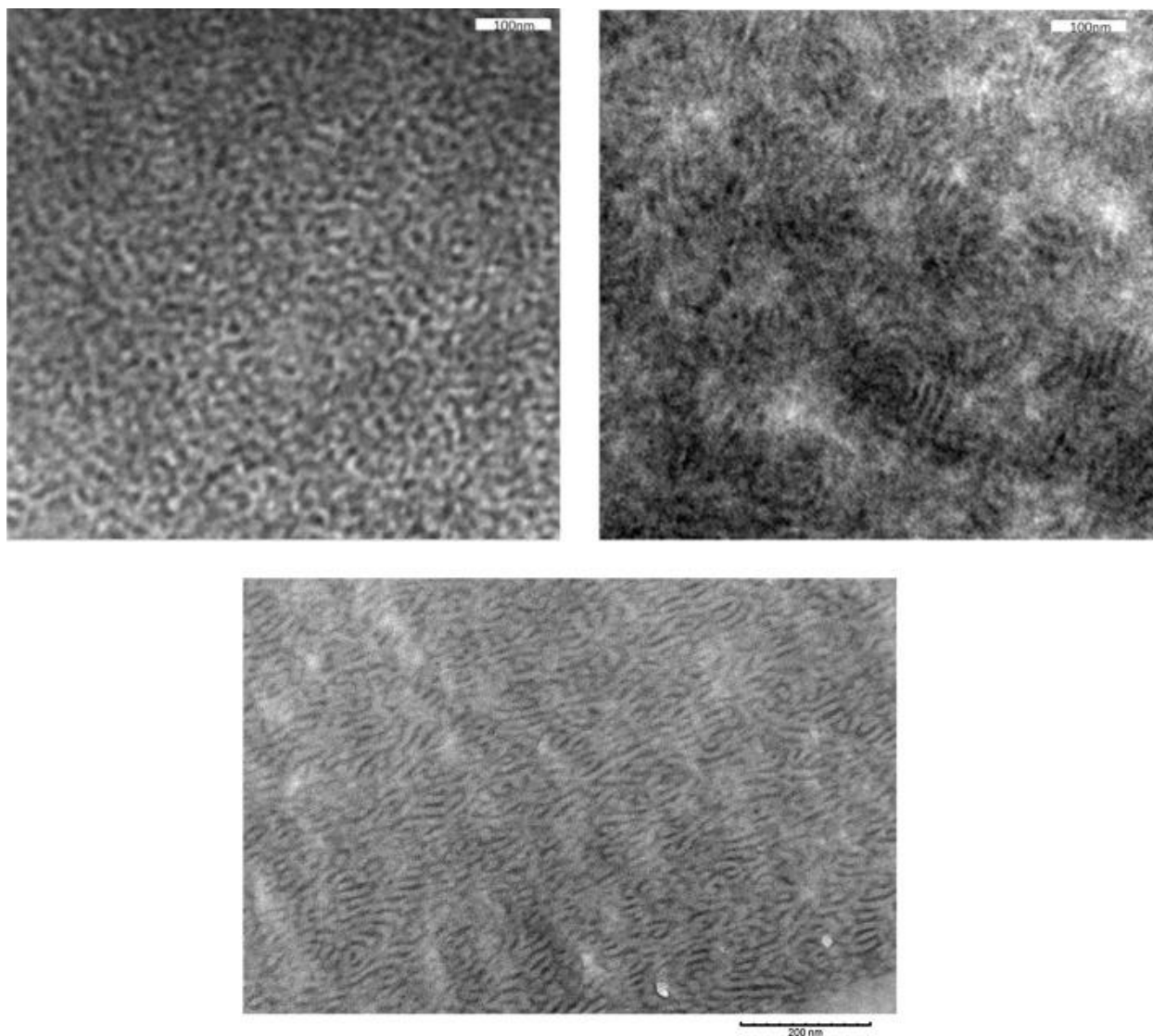


**Figure 1.12** TEM micrographs of some phase separated multiblock copolymers. Used with permission from Elsevier, 2013<sup>86</sup>

#### 1.4 Perfluorosulfonic Acid (PFSA) Membranes

Perfluorosulfonic acid membranes are fully fluorinated copolymers composed of C-F bonds on the backbone and side chains. They are generally comb-shaped polymers with a profound microphase-separated morphology due to presence of highly polar C-F bonds in their structure. The C-F bonds of PFSA polymers make them extremely resistant to common organic solvents,

acids, and bases. In addition, the high polarity of the C-F bonds on the side chains results in the higher acidity of the sulfonic acid groups in comparison to hydrocarbon copolymers. In other words, the transport properties of PFSA are superior to hydrocarbon copolymers as a result of the high electron-withdrawing properties of fluorines.<sup>87</sup> These polymers are widely used as PEMs due to exceptional chemical stability, good proton conductivity, and good mechanical properties at room temperature.

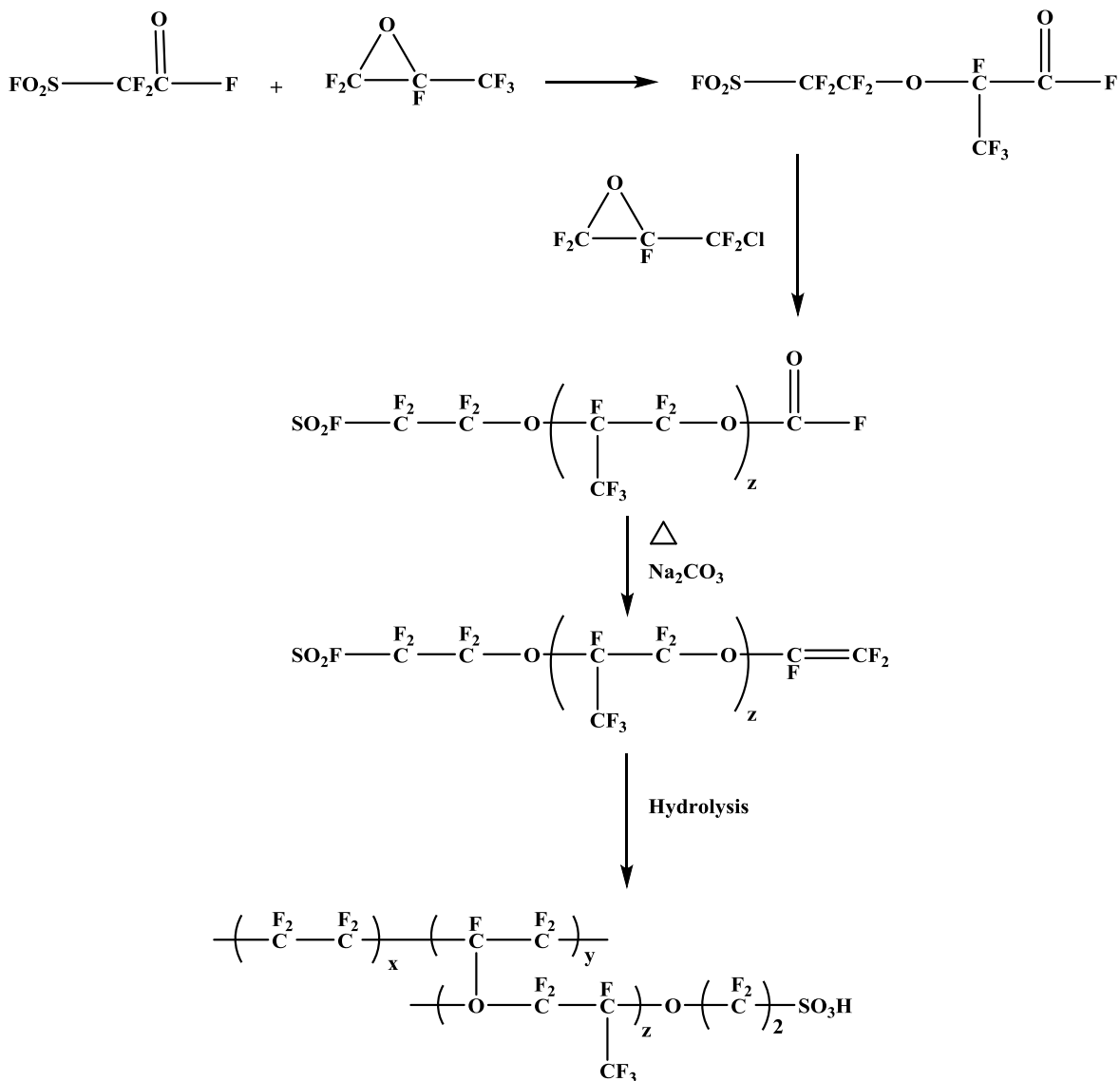
In particular, the desirable mechanical properties of these polymers are due the semi-crystalline backbone; in contrast, the sulfonic acid groups on the side chains are responsible for high proton conductivity. Although different types of PFSA copolymers have been used in a variety of commercial applications, Nafion<sup>™</sup> is the most well-known copolymer and remains the industrial standard proton conductor for PEM fuel cells because of its excellent thermal and mechanical stability. Other examples of perfluorosulfonic acid membranes include Aquivion<sup>®</sup> by Solvay Chemical Company, Aciplex<sup>®</sup> and Flemion<sup>®</sup> by Asahi Glass—all of which will be briefly mentioned herein.

#### **1.4.1 Nafion**

Nafion was the first PFSA synthesized by DuPont in 1960s<sup>33, 37</sup>. Early application of Nafion was in electrochemical cells for NaOH, Cl<sub>2</sub>, and KOH production.<sup>37</sup> Nafion's backbone consists of tetrafluoroethylene (TFE), while its side chains are made up of sulfonic acid-containing fluorinated vinyl ether that can reorganize into complex ionic and crystalline domains.<sup>37</sup> Currently, several types of Nafion are in use that differ in degree of sulfonation, membrane thickness, and terminal groups.<sup>88-89</sup> However, Nafion is not soluble in any solvent due to the high crystallinity of the backbone. Thus, membrane casting is conducted in a water:alcohol solution that results in a

suspension solution, after which the Nafion membranes are able to form once the water and alcohol are evaporated. Accordingly, Nafion membranes will differ in thickness based on the concentration of the casting solutions, and differences in membrane thickness produces membranes with varying equivalent weight (EW).

In general, Nafion used in PEM applications features an equivalent weight of 1000-1100 Da. Common types of Nafion available on the market include the 112, 115, 117 varieties with an EW of 1100, where the difference between each membrane is the thickness.<sup>37</sup> However, it is common to show the ionic conductivity of ion exchange membranes by their IEC. The commercial synthesis route for Nafion is shown in Scheme 1.8. Due to the insolubility issues associated with this type of PFSA, it is not possible to accurately measure molecular weight of this ionomer via light scattering (LS), size exclusion chromatography (SEC), or other commonly used molecular measurement methods such as NMR analysis.<sup>37</sup>



**Scheme 1.8** Preparation and structure of the monomer and Nafion copolymer<sup>90-91</sup>

For better insights into the performance of Nafion in different environments, one must fully understand the morphology of this copolymer. For example, the copolymer's highly hydrophobic backbone, coupled with the intense hydrophilicity of the side chain, afford outstanding properties to Nafion.<sup>92-93</sup> Despite Nafion's many advantages, however, it does feature a number of drawbacks—mostly notably its diminished performance at elevated temperatures and high pressure. Recall that the electrolysis of water at higher temperatures is desired due to faster reaction

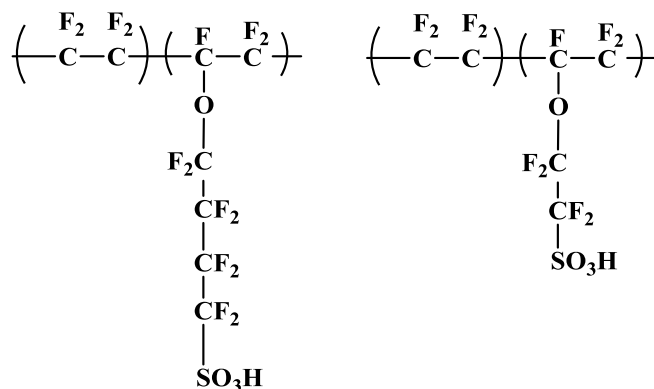
kinetics.<sup>94</sup> However, Nafion is not a good candidate for applications at temperatures higher than 80 °C because of its low glass transition temperature and changes in morphology at such temperatures.<sup>75, 94</sup> Additionally, Nafion is an expensive PFSA (i.e., approximately \$700/m<sup>2</sup>), and also shows high gas crossover.<sup>10</sup>

#### **1.4.2 Alternative PFSA Copolymers**

There are a range of other perfluorosulfonic acid membranes featuring a similar chemical structure to that of Nafion. The main difference between these copolymers is the length of the side chains. For example, Aquivion<sup>®</sup> is a poly(perfluorosulfonic acid) membrane made by Solvay. This PFSA features a shorter side chain and only two CF<sub>2</sub> groups. These short-chain PFSA feature increased glass transition temperature, as well as one of the two following possible relationships:<sup>90</sup>

1. Improved mechanical properties at comparable IEC
2. Increased IECs at comparable mechanical properties

As examples of short side chain PFSA, structures of Aquivion<sup>®</sup> and 3M ionomer are shown in Scheme 1.9.



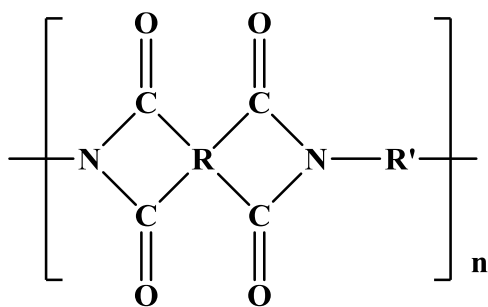
**Scheme 1.9** Short side chain PFSA structures: 3M ionomer (left) and Aquivion<sup>®</sup> (right)

### 1.5 Hydrocarbon PEMs

For the efficient electrolysis of water, identifying alternative PEMs is essential due to the drawbacks of perfluorosulfonic acid membranes, including (a) high gas crossover, (b) high cost, and (c) reduced mechanical properties at elevated temperatures. Similarly, for improved water desalination applications, alternative copolymers must be developed to overcome the drawbacks of current state-of-the-art membranes both in ED and RO. Using high performance hydrocarbon ionomers instead of perfluorosulfonic acid membranes represents one possible avenue for improving electrolysis systems. Moreover, these copolymers—which include polyimides, polybenzimidazoles, and poly(arylene ethers)—are likely to be good candidates for the desalination of water due to their good mechanical properties, ease of film formability, high chemical stability, and good transport properties.<sup>95</sup> In these PEMs, water uptake, proton conductivity, morphology, durability, gas crossover, salt rejection, and electrochemical performance are drastically influenced by composition, topology, synthesis method, degree of sulfonation (IEC), membranes casting conditions and membrane treatment.

### 1.5.1 Polyimides (PI)

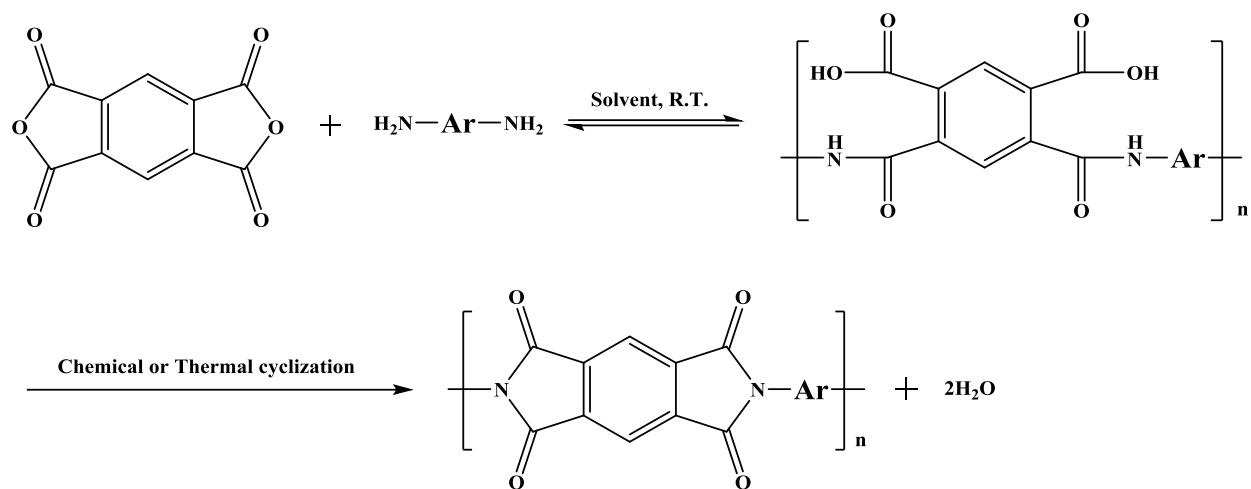
Polyimides are polymers with heterocyclic imide groups in their repeat units; the general structure for a polyimide is shown in Figure 1.13. Aromatic polyimides consist of five- or six-membered heterocyclic imide units. They are widely used commercially due to their high thermal and mechanical stability.<sup>96</sup> Although Renshaw et al.<sup>97</sup> first reported the first synthesis of a polyimide well over 100 years ago, the first commercially available PI was Kapton<sup>®</sup> produced by DuPont.<sup>96</sup>



R= Cycloaliphatic, Aromatic  
R'= Aliphatic, aromatic

**Figure 1.13** General structure of polyimides

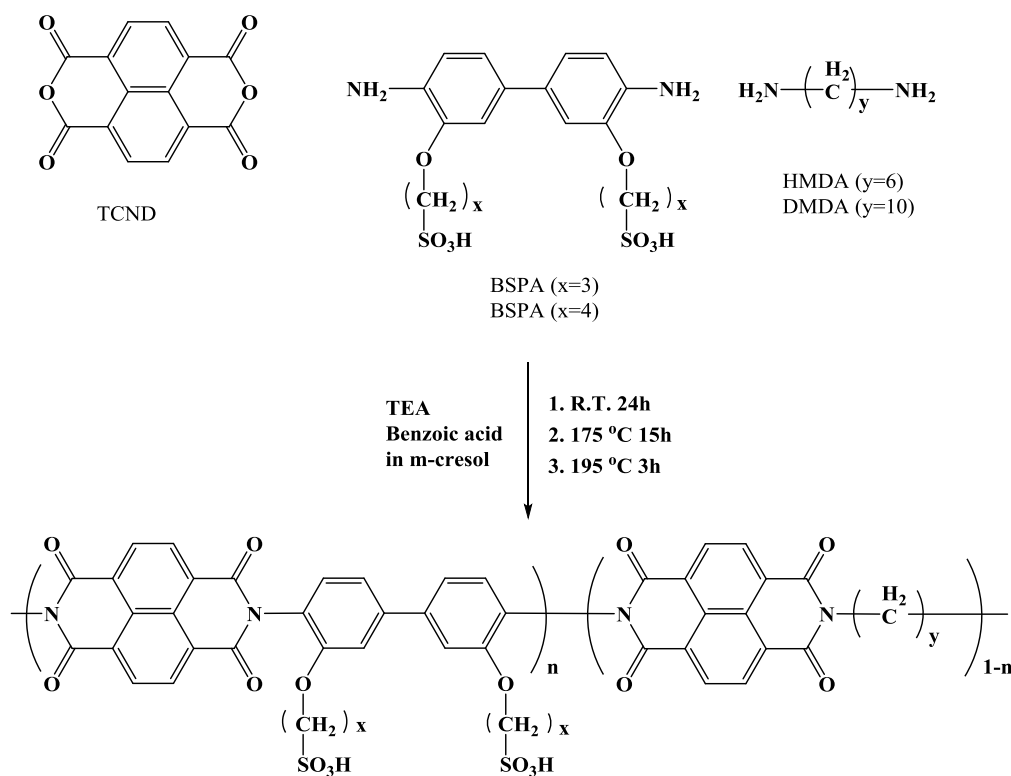
PIs are generally synthesized via step-growth polymerization of diamines and organic tetracarboxylic acids or dianhydrides. Among the various synthesis routes for producing polyimides,<sup>96</sup> the ester-acid route is widely used to make copolymers for fuel cell and gas separation applications. Specifically, the ester-acid route is a two-step process in which a poly(amic acid) is formed first, after which the PI is produced following a cyclization step at elevated temperature. Scheme 1.10 shows both steps of an ester-acid polymerization.



**Scheme 1.10** Ester-acid polymerization of Polyimides<sup>96</sup>

The presence of water molecules can exert a significant impact on both the polymerization parameters and the subsequent performance of PIs.<sup>96, 98</sup> During polymerization, water hydrolyzes the poly(amic acid) chains and prevent further polymerization by precipitating low molecular weight copolymer chains.<sup>96</sup> Therefore, it is imperative to remove any water molecules from the reaction via an azeotrope agent. After generating the poly(amic acid), cyclization can occur from either elevating the temperature under reduced pressure, or via chemical imidization.<sup>96</sup>

Asano et al.<sup>99</sup> prepared aromatic/aliphatic polyimide as shown in Scheme 1.11. These ionomers were synthesized with variable IECs by changing the side chain length to controlled water uptake and gas permeability. These SPIs showed extended durability up to 5000h under fuel cell conditions.<sup>99</sup>



**Scheme 1.11** Aromatic/aliphatic SPIs with different side chain length

Incorporating aliphatic chains in the copolymer improved the hydrolytic stability of the membrane. Under the harsh conditions of Fenton's reagent test (a common oxidative stability test for ion exchange membranes), these SPI membranes showed high stability. For example, membranes with IEC=1.85 meq.g<sup>-1</sup> retained up to 98% of their original weight. Although these SPIs demonstrated poor proton conductivity at low temperature, they showed considerably improved conductivity up to 1.8 S.cm<sup>-1</sup> under humidity and at temperatures of 140 °C. The high proton conductivity of SPIs was attributed to the presence of small ion clusters, which results in well distribution of the water molecules in the membrane. In addition, H<sub>2</sub> and O<sub>2</sub> gas permeability in these membranes was an order of magnitude lower than that of Nafion under both dry and humidified conditions.

### 1.5.2 Polybenzimidazoles (PBI)

The general structure of PBIs is shown in Figure 1.14. Polybenzimidazoles, which are aromatic heterocyclic copolymers with a benzimidazole repeat units, are amorphous, thermoplastic, and proton conductive polymers with acid-base complexation.

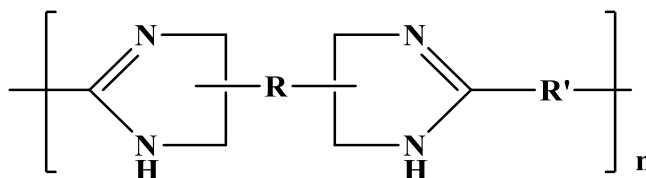
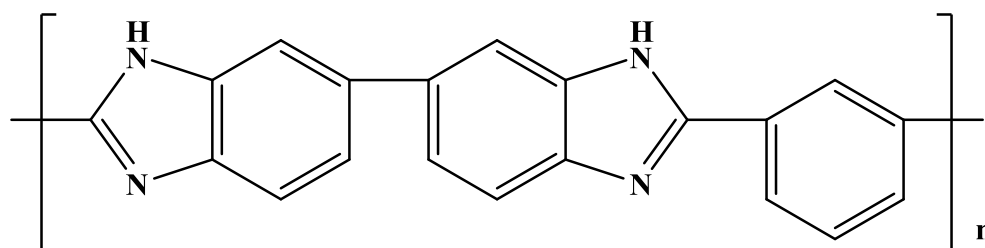


**Figure 1.14** General structure of PBI

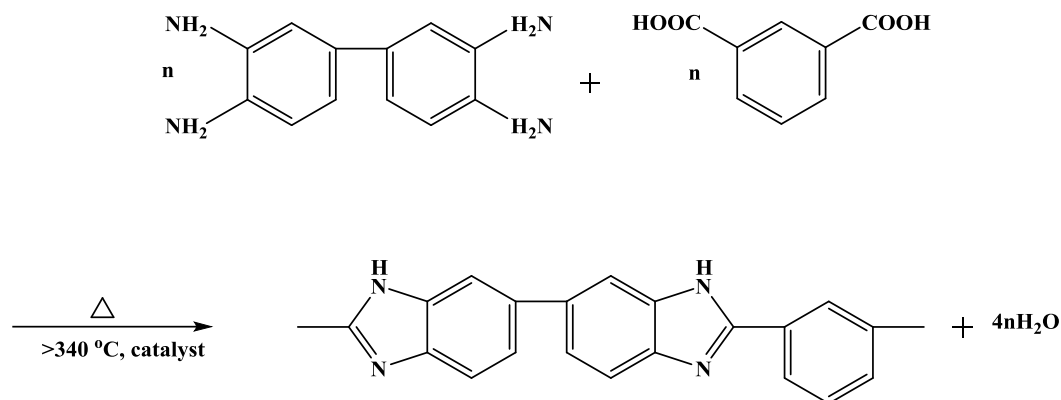
A commercial PBI produced by Celanese (Celazole<sup>®</sup>) is shown in Scheme 1.12. This polymer is highly stable under ambient pressure and temperatures suitable for variety of

applications—namely, in fibers, gas separation membranes, fuel cell PEM, ultrafiltration, and reverse osmosis.<sup>100</sup> In contrast, the solubility and processing parameters of PBIs are more limited. In addition, pristine PBIs have lower proton conductivity. However, using proton donor/acceptor acids such as phosphoric acid (PPA) results in improved proton conductivity, thereby enhancing their suitability for fuel cell and water electrolysis applications.



**Scheme 1.12** Celazole®; poly 2,2'-m-(phenylene)-5,5'-bibenzimidazole<sup>100</sup>

The first PBI synthesis was reported by Vogel and Marvel who used a somewhat tedious two-step synthesis process.<sup>101</sup> The first step involved the formation and isolation of the prepolymer. During the second step the polymer was subsequently dehydrated to cyclize at elevated temperatures.<sup>102</sup> However, since that time a more convenient method was developed by Choe et al., whereby PBI can be synthesized via one-step melt processed reaction.<sup>103</sup> As shown in Scheme 1.13, isophthalic acid (IPA) and teraaminobiphenyl (TBA) react at elevated temperature in the presence of a catalyst such as organo phosphorus and silicon compounds.<sup>100</sup>

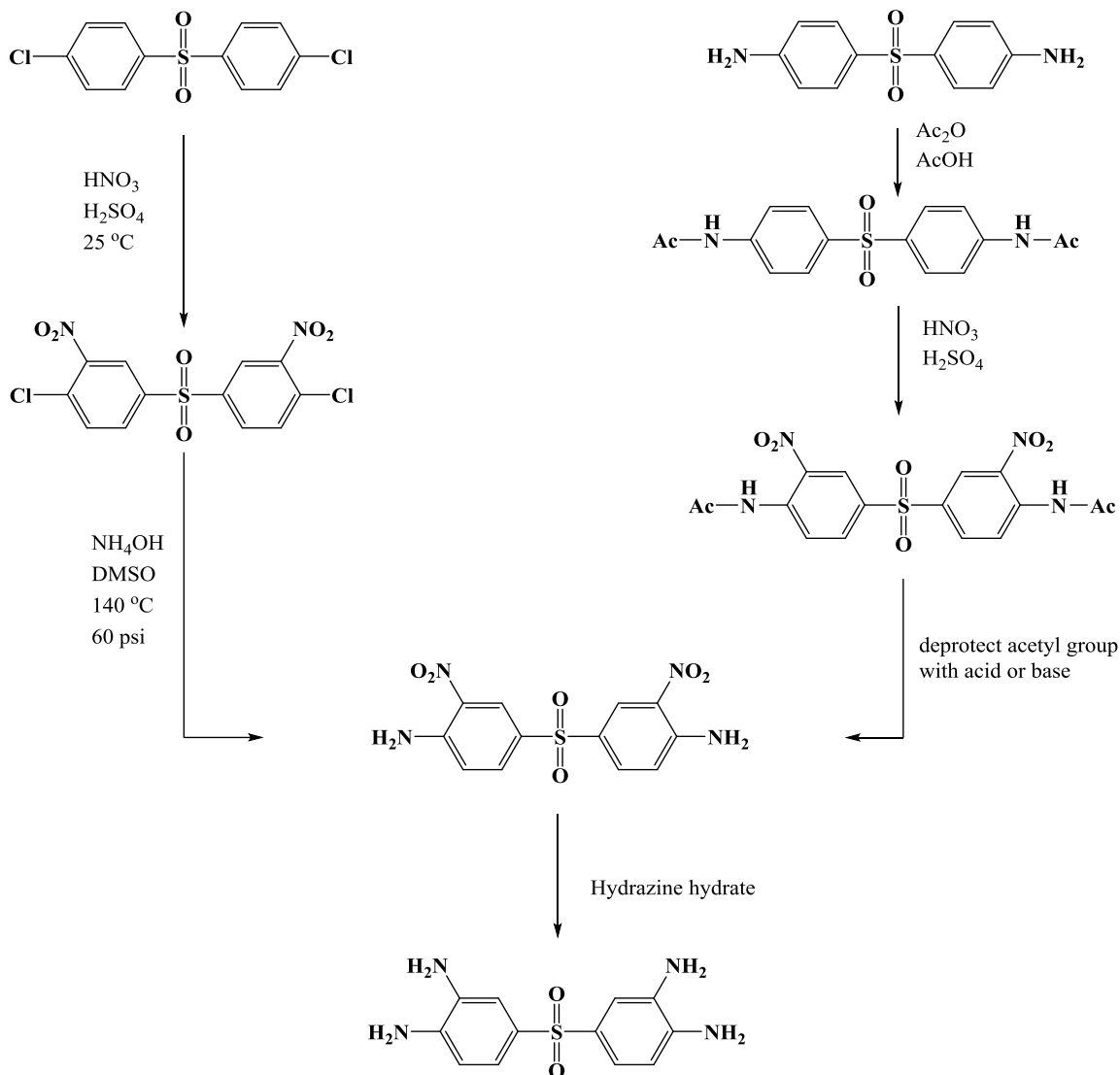


**Scheme 1.13** Choe's approach for one-step PBI one-step synthesis<sup>100</sup>

The two main approaches for synthesizing high molecular weight PBIs are as follow:

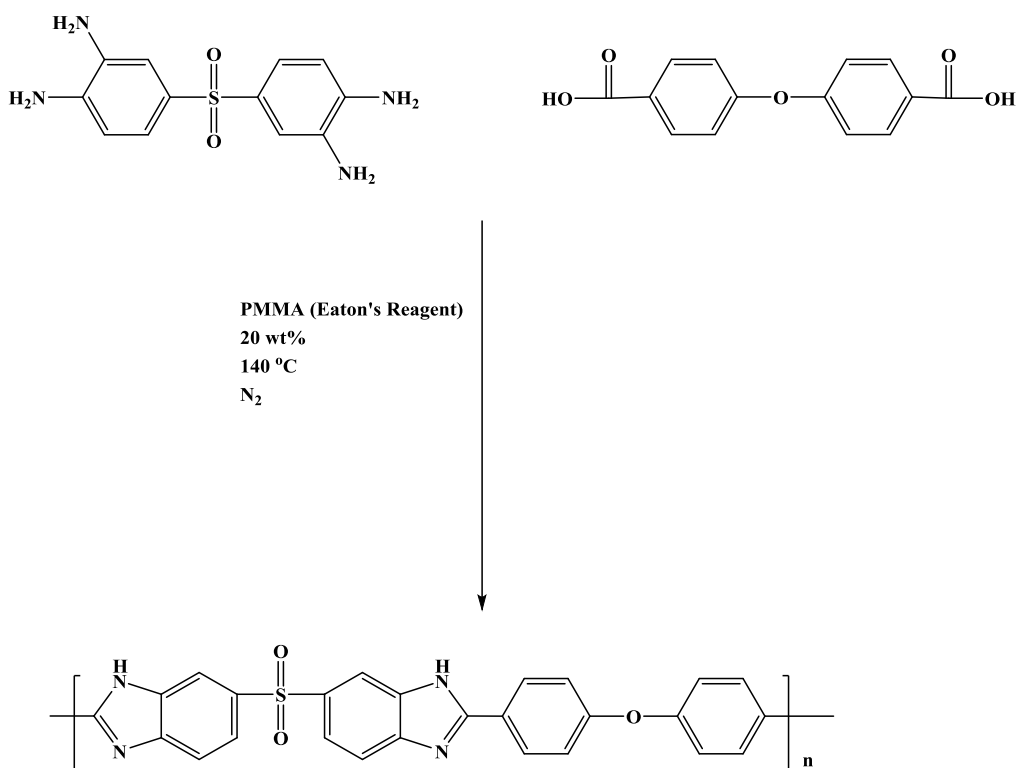
- a) Fabricating PBIs using monomers containing flexible linkages or functional groups<sup>104</sup>
- b) Post-polymer modifications via incorporation of monomers containing acidic groups

Borjigin et al. used the first approach to synthesize high molecular weight PBIs for gas separation applications.<sup>105</sup> In order to produce a cost-effective monomer, a 4,4'-dichlorodiphenyl sulfone (DCDPS) was used in a three step-reaction, instead of the more common four-step monomer synthesis procedure. This procedure is shown in Scheme 1.14.



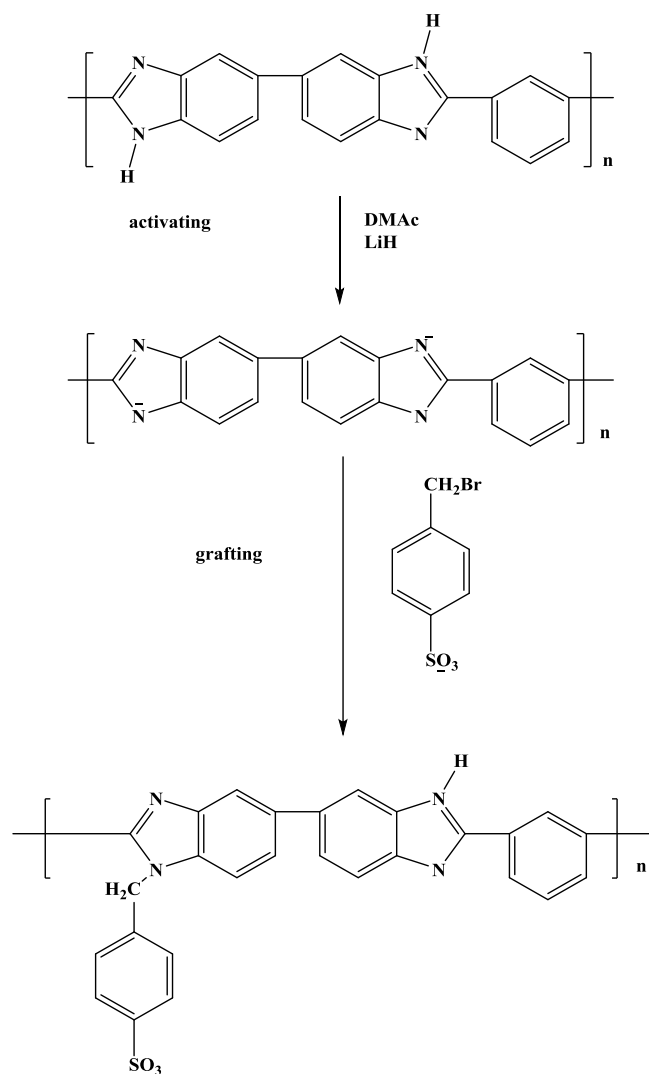
**Scheme 1.14** Borjigin's monomer synthesis vs. common method<sup>105</sup>

In addition, using Eton's reagent in PBI synthesis (Scheme 1.15) results in a high molecular weight copolymer with improved properties for gas separation applications.<sup>103</sup> In contrast, PBI synthesis in PPA tends to be more suitable for PEM-based applications.<sup>106</sup>



**Scheme 1.15** Synthesis of high molecular weight PBIs with flexible monomer <sup>105</sup>

Post-polymer modifications include incorporating substituent groups on the N-H reactive sites, as shown in Scheme 1.16, which produces a PEM with improved proton conductivity for water electrolysis and fuel cells.<sup>100</sup> In this synthesis, an alkali metal hydride is used to deprotonate the active nitrogen of the benzimidazole ring followed by reaction with sulfonated reagents such as arylsulfonates.<sup>107-108</sup> An example of a post-polymerization PBI modification is shown in Scheme 1.16.



**Scheme 1.16** Sulfonic acid group incorporation on the reactive N-H site of PBI<sup>107</sup>

### 1.5.3 Poly(arylene ether)s (PAEs)

Poly(arylene ether)s (PAEs) and sulfonated poly(arylene ether)s (SPAEs) are high-performance thermoplastic copolymers comprised of aromatic rings with ether, sulfone, and ketone linkage groups. Their synthesis was first described by 3M and Union Carbide in the U.S., and ICI Ltd. in the UK.<sup>109</sup> These copolymers have demonstrated high impact resistance, as well as improved thermal and chemical stability due to aromatic ether bonds along the backbone.<sup>110</sup> In

addition, these copolymers are easy to fabricate into thin film membranes. As such, they have been intensively investigated as alternative membranes with optimized chemical structures and composition for fuel cells, water electrolysis, and water purification applications.<sup>74, 87, 89, 111-116</sup>

The general structures for PAE and P(arylene sulfone)s (PAS) are shown in Figure 1.15. PAEs can be prepared via a variety of polymerization methods: oxidative coupling polymerization, electrophilic aromatic substitution reaction using Friedel–Crafts catalysts, and nucleophilic aromatic substitution reaction.

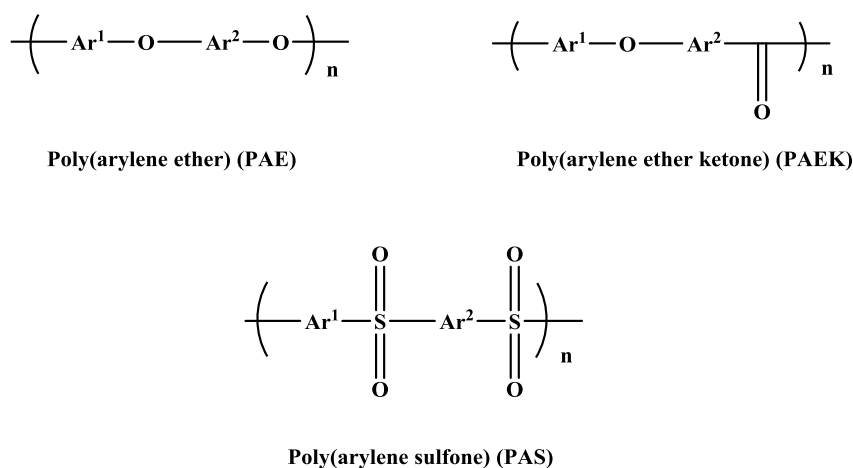
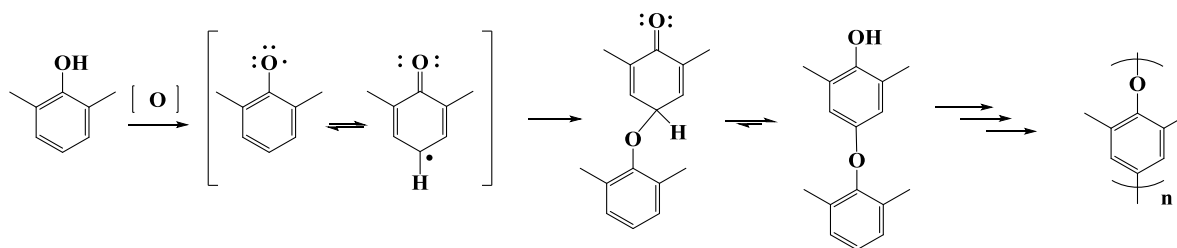


**Figure 1.15** General structures of polyarylene copolymers. Ar, Ar<sup>1</sup>, Ar<sup>2</sup> are the aromatic rings on the backbone<sup>110</sup>

The synthesis and properties of important categories of PAEs, including polyphenylene oxides (PPO), poly(arylene ether ketone)s (PAEK), and poly(arylene ether sulfone)s (PAES), will be described herein, along with examples of the aforementioned synthetic approaches.

### 1.5.3.1 Poly(2,6-dimethyl-1,4-phenylene oxide), PPO

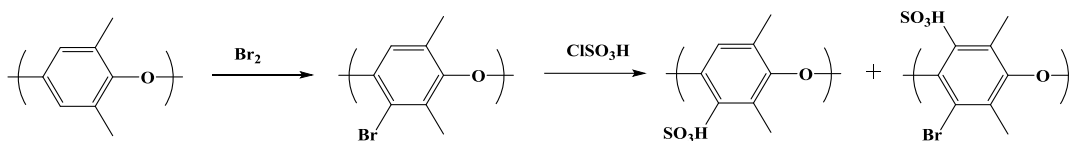
Poly(2,6-dimethyl-1,4-phenylene oxide), PPO, is a wholly aromatic poly(arylene ether) copolymer. The most common procedure synthesizing high molecular weight PPOs is oxidative coupling polymerization, which is depicted in Scheme 1.17. In general, this method is used for generating high molecular weight PPO and modified PPOs due to lack of reactive halogens on the monomer and its moderate reaction temperatures.<sup>110</sup> Oxidative coupling polymerization is a free radical polymerization; however, the polymerization of phenolic rings represents a step-growth polymerization, rather than a radical polymerization. This mechanism is such that the phenolic ring undergoes an oxidation from a copper-amine complex, which generates an aryloxy radical that subsequently undergoes enolization. A major drawback of this polymerization approach is the dimerization of the molecules, which inhibits the formation of a high molecular weight copolymer. Thus, further improvements of the reaction conditions for PPOs are needed.



**Scheme 1.17** Polymerization of poly(2,6-dimethyl-1,4-phenylene oxide), PPO<sup>110</sup>

When a hydrophobic comonomer such as fluorine or bromine is introduced into a PPO's structure, its mechanical properties (i.e., water uptake, IEC, and fixed charge concentration) will be altered.<sup>74, 115, 117</sup> These changes directly affect the transport properties of the membranes. Yu et

al.<sup>117</sup> incorporated controlled amount of bromine and sulfonic acid groups into PPO as shown in Scheme 1.18.



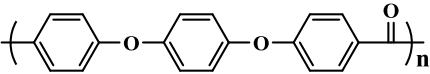
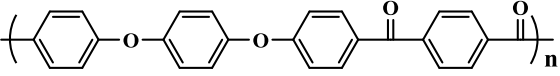
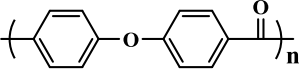
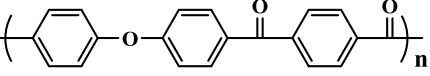
**Scheme 1.18** Modified PPO via bromine and acidic group<sup>117</sup>

The resulting series of copolymers displayed a wide range of IEC values, depending on the amount of incorporated bromide and acidic groups. Due to reduced IEC as a result of incorporated bromine into the polymer, the fixed charge concentration decreased, which resulted in depressed salt transport properties. It is noteworthy to mention that decreasing water uptake in an ion-conducting polymer is not always advantageous. In fact, an optimum amount of water is required in a membrane to assist salt transport in an electrodialysis system.

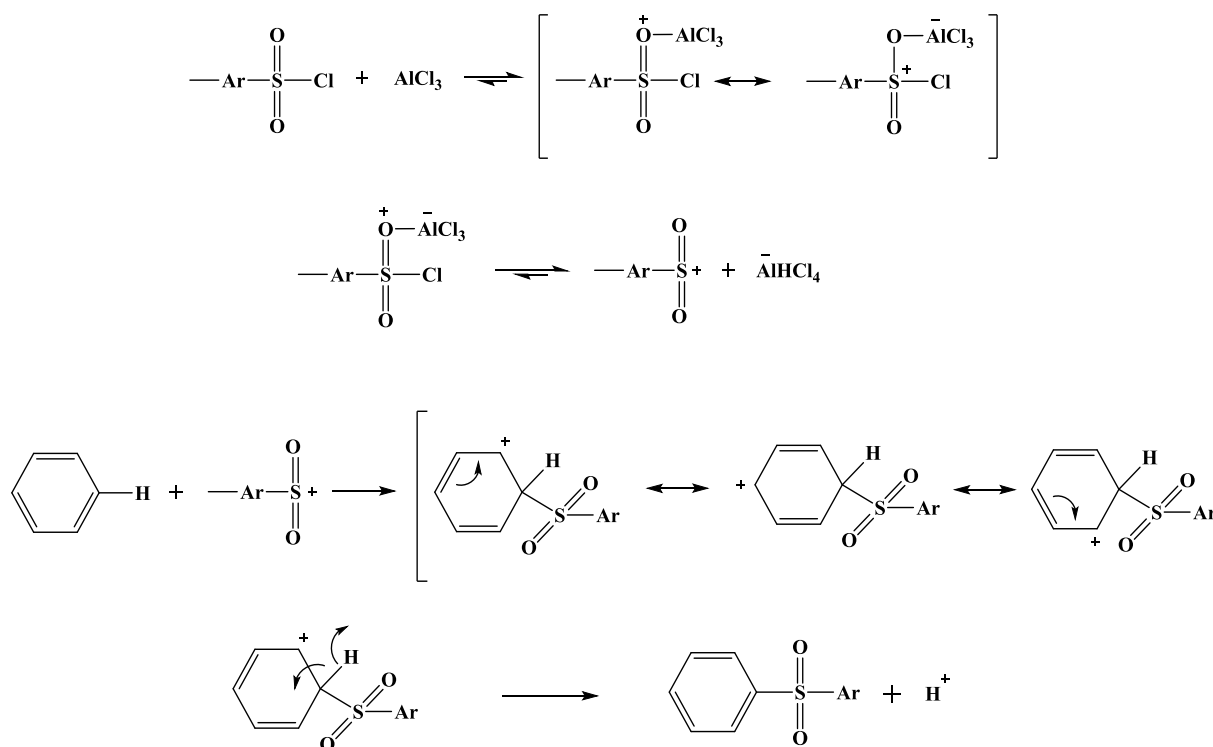
### 1.5.3.2 Poly(arylene ether ketone), PAEK

PEK, PEEK and PEEKK are members of the poly(arylene ether ketone) family; these copolymers all feature phenyl rings that are joined via ether (E) and ketone (K) bonds. These copolymers are semicrystalline in nature, with a wide range of glass transition,  $T_g$ , and melting temperatures,  $T_m$ .<sup>118</sup> The semicrystallinity of these copolymers results in low solubility in common solvents. Table 1.1 shows the properties of common and commercially available copolymers in this family of materials. The main difference between PEKs' structure is the number and position of the ether and ketone linkages, which produce the characteristic variations in  $T_g$  and  $T_m$ .<sup>110</sup>

**Table 1.1.** Structures of some common PEEKs and their thermal properties reproduced from reference 80<sup>110</sup>

|                                                                                   | Name | T <sub>g</sub> (°C) | T <sub>m</sub> (°C) |
|-----------------------------------------------------------------------------------|------|---------------------|---------------------|
|  | PEEK | 143                 | 335                 |
|  | PEKK | 154                 | 358-365             |
|  | PEK  | 154                 | 365                 |
|  | PEKK | 165-175             | 384                 |

Electrophilic aromatic substitution reaction using Friedel–Crafts catalysts can be used to synthesize PAEKs. This polymerization method has the advantage of being cost-effective and can be conducted at low temperatures. However, PAEK production via electrophilic aromatic substitution reaction is limited to electron-rich monomers such as naphthalene, sulfides and amines. Conversely, some drawbacks associated with the electrophilic aromatic substitution using Friedel–Crafts catalysts include (a) the limited choice of solvents, (b) issues with disposal of the reaction residue, and (c) precipitation of low molecular weight oligomers/catalyst complexes.<sup>110, 119-120</sup> Mechanism of this polymerization is shown in Scheme 1.19.

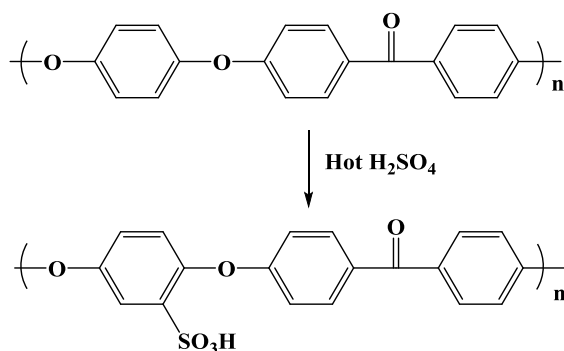


**Scheme 1.19** Mechanism of electrophilic aromatic substitution using Friedel–Crafts catalysts<sup>110</sup>

A significant and growing body of literature is addressing strategies for improving the reaction conditions of PAEK synthesis via Friedel–Craft polymerization to obtain copolymers with improved solubility, increased  $T_g$ , and enhanced processability.<sup>120–122</sup> Cai et al.<sup>118</sup> successfully used this polymerization approach to improve both the thermal and mechanical properties of PAEK, thereby enhancing processing parameters. Moreover, the synthesis of PAEK using a variety of novel monomers has resulted in products with remarkably improved solubility in common solvents such as NMP, DMAc, and DMSO.

Sulfonated random PEK (SPEK) copolymers have been prepared via the post sulfonation route. In this method, non-sulfonated polymers are dissolved in a concentrated acid such as sulfuric acid, chlorosulfonic acid, pure or complexed sulfur trioxide, acetyl sulfate, or methane sulfonic

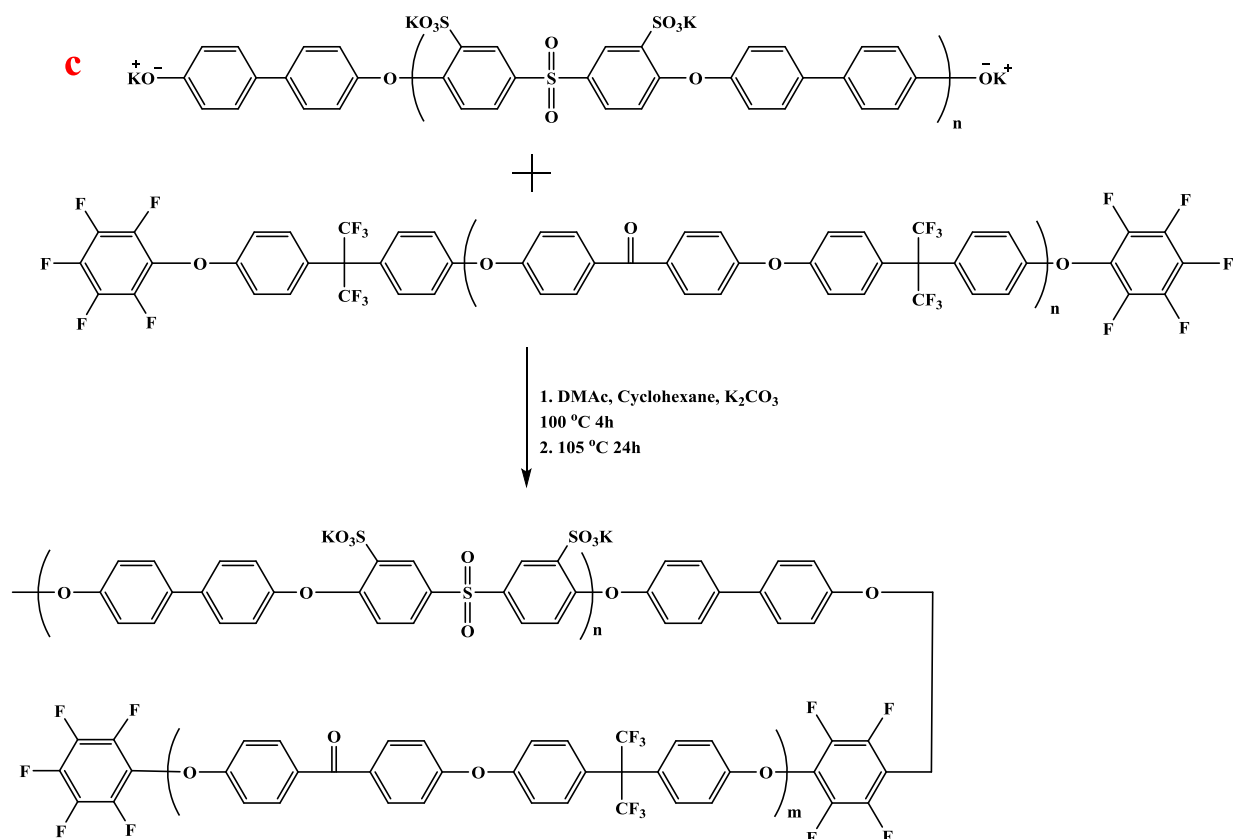
acid. Once the sulfonation is complete, the copolymer is precipitated in a non-solvent such as isopropanol. An example of post sulfonation of a PEK copolymer is shown in Scheme 1.20.



**Scheme 1.20** Post sulfonation of a PEK<sup>123</sup>

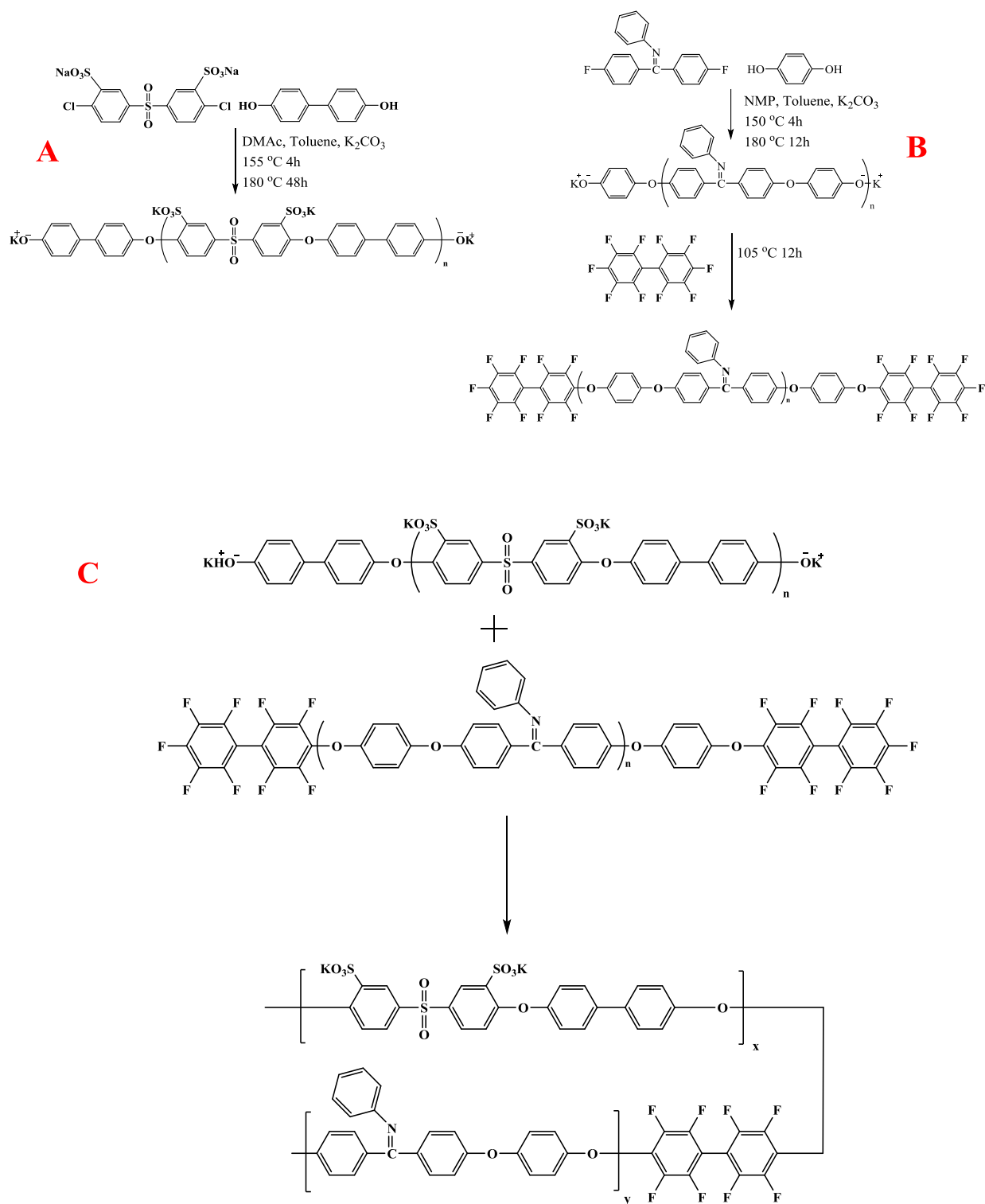
Although a number of desirable polymer properties can be achieved at high molecular weights, SPEEKs have demonstrated several drawbacks at high conversion levels.<sup>124</sup> In particular, morphological investigations of high molecular weight SPEEKs indicate a significant amount of dead-end hydrophilic channels that reduce proton conductivity.<sup>124-125</sup> In order to overcome low proton conductivity of the random SPEEKs, they can be copolymerized with different polymers to afford block copolymers. Lee et al. coupled a sulfonated polysulfone hydrophilic block with hydrophobic PEK segment to produce a PEK-SPAES block copolymer.<sup>83</sup> As illustrated in Scheme 1.21. a-c, the coupling reaction was achieved by reacting two phenoxide end groups of hydrophobic segment with highly fluorinated hexafluorobenzene linkage group. Due to the high reactivity of hexafluorobenzene, the coupling reaction must be conducted at low temperatures. In addition, using fluorinated monomers such as 6F-bisphenols breaks the crystallinity of the PEK and improves the stability of the final product under harsh fuel cell conditions.





**Scheme 1.21** Lee's low temperature reaction approach: a) synthesis of hydrophobic block and incorporation of the hexafluorobenzene b) hydrophilic block synthesis c) coupling reaction of hydrophilic and hydrophobic blocks<sup>39</sup>

In their study, Chen et al.<sup>114</sup> introduced ketamine groups into the polymer backbone in order to reduce crystallinity levels in PAEK, which is shown in Scheme 1.22. In this multiblock copolymer synthesis, difluorobenzophenone (DFK) was modified into ketimine to afford bulky group on the hydrophobic oligomer. Decafluorobiphenyl as the terminal group was incorporated into the hydrophobic segment to enhance the reactivity of this segment with the hydrophilic blocks. This synthesis procedure is shown in Scheme 1.22.

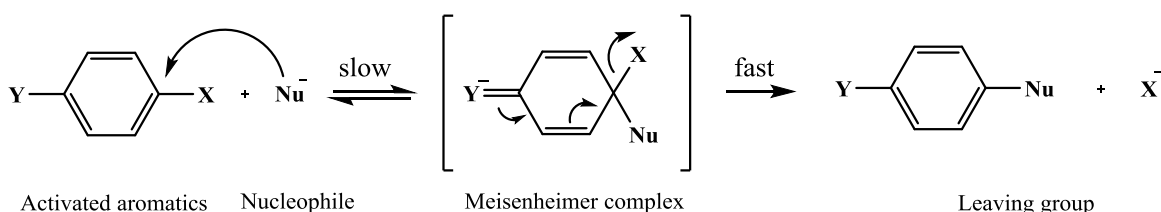


**Scheme 1.22** Incorporation of the bulky group for reducing the semicrystallinity of the PAEK.  
 A) hydrophilic block synthesis B) hydrophobic block synthesis C) block copolymer synthesis<sup>114</sup>

The resulting block copolymers have demonstrated notably improved proton conductivity, mechanical properties, thermal stability, and reduced water uptake. Moreover, TEM micrographs and AFM findings for these copolymers have confirmed that as the block length increases in the copolymers, interconnected hydrophilic channels that enhance proton conductivity can be improved.<sup>83, 114</sup>

### 1.5.3.3 Poly(arylene ether sulfone), PAES

PAES and sulfonated PAES are hydrocarbon copolymers containing aromatic rings covalently attached with a sulfone and ether linkage groups or any other moieties.<sup>126</sup> Due to high mechanical, thermal, and chemical stability, these copolymers can be utilized in a wide range of applications such as fire retardant fibers, membranes for water desalination, and in fuel cells.<sup>127</sup> The most common route for making PAEs is the nucleophilic aromatic substitution reaction, in which a variety of halogenated monomers can be polymerized. The mechanism of nucleophilic aromatic substitution reaction for PAE is shown in Scheme 1.23, which consist of a Meisenheimer complex.



**Scheme 1.23** Meisenheimer complex in nucleophilic aromatic substitution reaction<sup>110</sup>

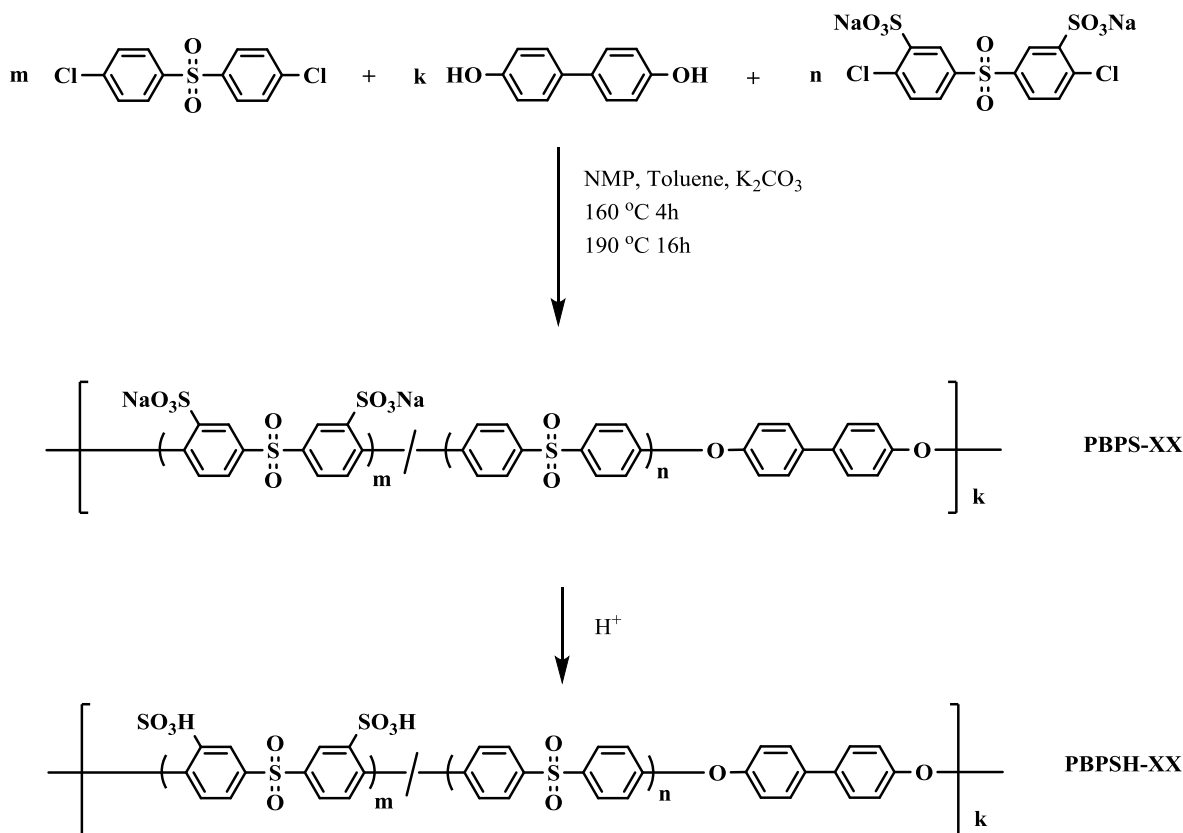
It is believed that the halide groups are reactive when they are in the para or ortho position of the linking groups; however, the para position is preferred due to faster reaction rate.<sup>109</sup> In addition to

the position of the leaving groups, their type and size can also influence the reactivity rate of the aromatic ring. Considering the Meisenheimer complex, fluorine-containing monomers are preferred because of the high polarity of the F-C bond and fluorine's ability to activate the aromatic carbon. Therefore, fluorinated monomers react faster than other halide-containing monomers.<sup>109</sup>

If the primary copolymer is a non-sulfonated copolymer, post sulfonation is used to synthesize sulfonated PAES.<sup>128</sup> Direct copolymerization of sulfonated monomers is commonly used to overcome the drawbacks of the post sulfonation. Moreover, research indicates that using pre-sulfonated monomers in the synthesis is preferred due to enhanced control of the degree of sulfonation (DS). Additionally, this approach enables one to position the acid groups on the deactivated position of the phenyl ring, while post-sulfonation of the polymers results in sulfonation of the activated phenyl rings.<sup>113, 123</sup>

PAES based on commercially available monomers have shown promising results under a range of fuel cell conditions.<sup>94</sup> However, the performance properties of these materials in fuel cells are highly dependent on membrane composition and membrane processing conditions.<sup>87, 94</sup> In particular, an important parameter for these copolymers involves the number of sulfonic acid groups on the backbone—with typical sulfonation levels for these copolymers ranging between 20-50%.<sup>87</sup> Below this range, however, the copolymers tend to be highly hydrophobic with very low water uptake and proton conductivity. Above the aforementioned range, the copolymers become excessively hydrophilic, resulting in poor mechanical properties under operating conditions. Other parameters are also impacted by the degree of sulfonation, including  $T_g$  and water uptake, water flux, and gas permeability. However, salt rejection and fixed charge density decrease dramatically due to decreased ion concentration by absorbing tremendous amount of water.<sup>87</sup> In addition to water uptake and  $T_g$ , the morphology of PAES is highly dependent on IEC

levels. As shown in Scheme 1.24, Wang and coworkers<sup>77</sup> used sulfonated dichlorodiphenyl sulfone (SDCDPS) and dichloro diphenyl sulfone (DCDPS) to directly synthesize a series of SPAES copolymers, and then studied morphology changes in relation to the degree of disulfonation.



**Scheme 1.24** Synthesis of random copolymer via direct copolymerization of disulfonated and non-sulfonated comonomers<sup>77</sup>

In their synthesis studies, the researchers controlled the hydrophilicity of the random copolymers by controlling the degree of sulfonation (DS). A noticeable impact of increasing DS was on  $T_g$ , such that at DS levels in excess of 50% two glass transition temperatures were observed. This outcome is associated with morphological changes in the copolymer from a hydrophobic dominant structure to an interconnected hydrophilic dominant structure. These morphological changes, as evidenced by AFM results, are shown in Figure 1.16.

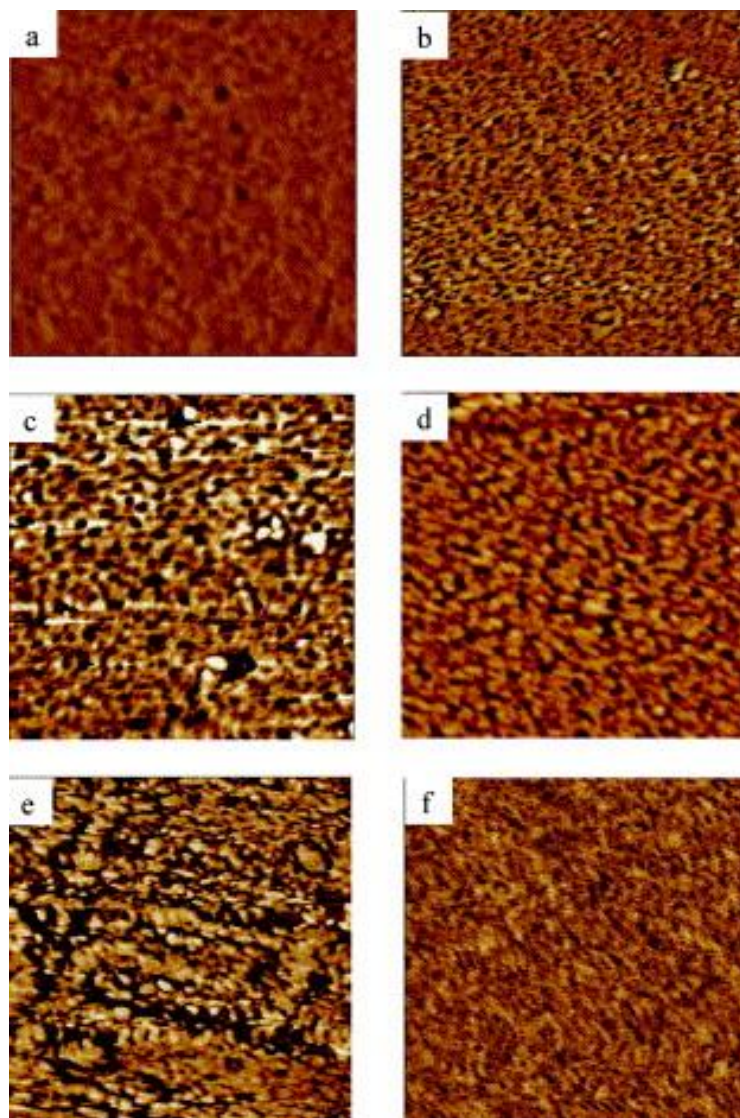


**Figure 1.16** Morphological changes in SPAES after increasing the degree of disulfonation. Used with permission from Elsevier, 2002<sup>77</sup>

Membrane casting and processing conditions will also dramatically impact the morphology and transport properties of the final product. For example, in their study of BPSH copolymers, Kim et al.<sup>129</sup> investigated the effects of an acidification treatment on water uptake and proton conductivity. One copolymers series was treated in 1.5 M sulfuric acid at 30 °C for 24h and then in DI water for 24h. A second series of copolymers was acidified in boiling 0.5 M sulfuric acid for 2h and then in boiling DI water for extra 2h. A strong dependence on the nature of the

acidification treatment was observed in both series, such that the first group of copolymers not only showed lower water uptake but also much lower proton conductivity at elevated temperature. The difference in proton conductivity between the two groups of copolymers increased up to 0.15 S/cm for copolymers with a high degree of disulfonation. AFM studies subsequently confirmed that irreversible morphology changes in the copolymers treated in boiling sulfuric acid was responsible for the drastic difference in proton conductivity. Figure 1.17 shows the AFM phase image of a BPSH-40 with two different morphologies of the membranes treated in various conditions.

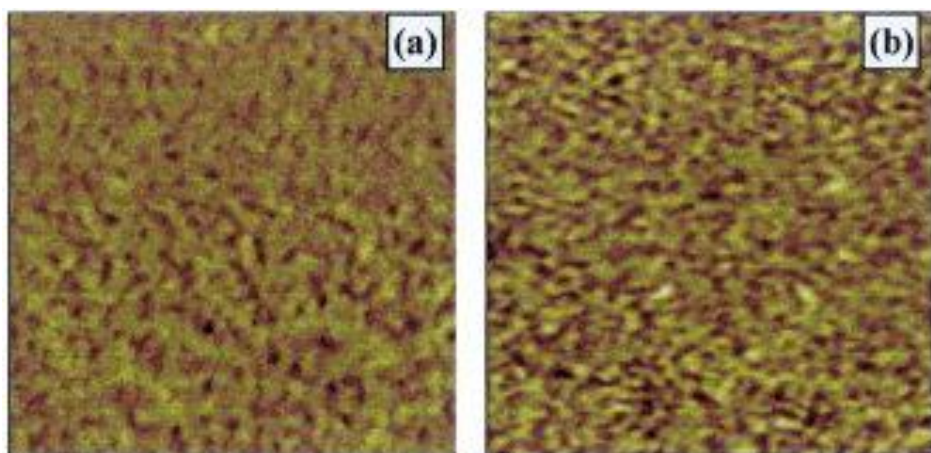
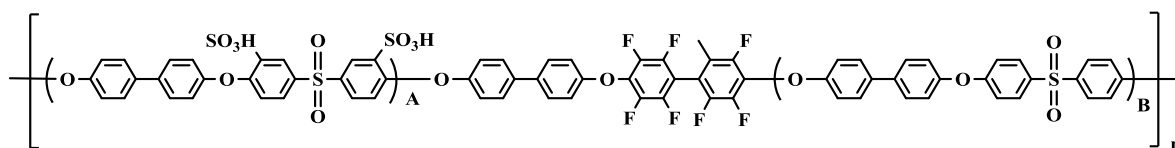


**Figure 1.17** BPSH-40 phase images: (a) after method 1, (b) after method 2. Used with permission from Wiley, 2003<sup>129</sup>

Similarly, Lee and coworkers showed that in a PAES block copolymer with a given structure (see Scheme 1.25.), solvent type, casting temperature, and solvent removal rate can significantly impact water uptake and membrane transport properties.<sup>130</sup>



**Scheme 1.25** Structure of a multiblock copolymer

As a result of the high selectivity of dimethylacetamide (DMAc) for hydrophilic segments in this copolymer, the proton conductivity of the PEM was higher than those cast in N-methyl 2-Pyrrolidone (NMP), which is selective for both hydrophilic and hydrophobic segments of the block copolymer.<sup>130</sup> This result was confirmed by comparing the degree of phase separation. TEM and SAXS investigations of the block copolymers cast in different solvents showed that the degree of phase separation is responsible for the difference in proton conductivity of copolymers. Generally, multiblock copolymers display higher proton conductivity in comparison to random copolymers at similar IECs. Indeed, comparing TEM micrographs for both random and multiblock copolymers confirmed the wider and co-continuous ionic domains in the block copolymers. However, Figure 1.18. shows that a random copolymer has a featureless micrograph, which is due to homogeneous distribution of the sulfonic acid groups along the polymer backbone; in contrast, a multiblock copolymer exhibits a clear phase separated micrograph. As the block length increases, the degree of phase separation and proton conductivity also increases in these copolymers.

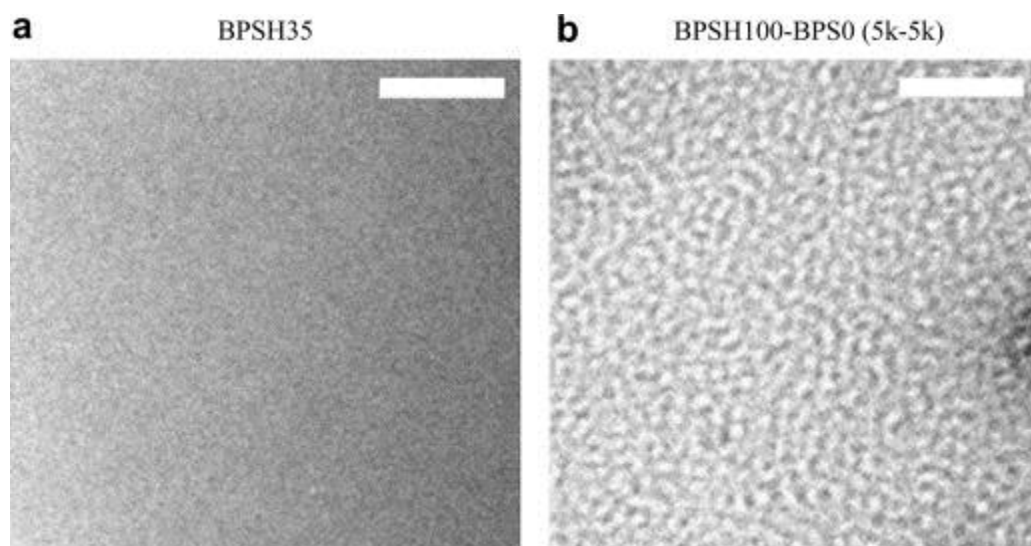


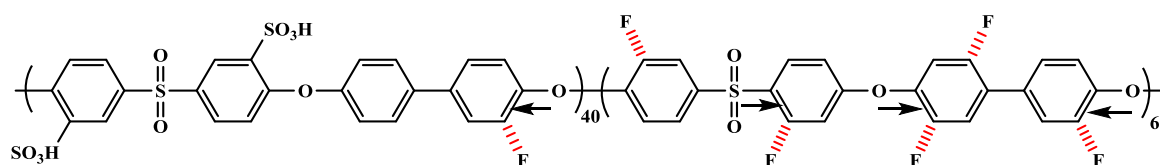
**Figure 1.18** TEM micrograph of a) BPS35 and b) BPSH100-BPS0 in which hydrophilic domains are in black and hydrophobic domains are in white color. Used with permission from Elsevier, 2009<sup>130</sup>

Excessive water uptake and swelling of a membrane can cause membrane failure.<sup>130</sup> In order to control water uptake in these copolymers without sacrificing proton conductivity, one can cast a membrane at elevated temperatures, as evidenced by the fact that water uptake of the copolymers cast at lower temperature was shown to be higher than those cast at elevated temperature. In fact, more ordered structure and longer domains were observed in copolymers cast at low temperature. These findings are associated with two factors:

- a) Higher hydrophilic-hydrophobic compatibility at elevated temperatures
- b) Kinetically trapped morphology at high temperature due to rapid solvent evaporation

It should also be stressed that the chemical and dimensional stability and proton conductivity of membranes will inevitably impact the overall performance of a PEM fuel cell. Fluorinated copolymers such as perfluorosulfonic acids have shown high chemical and dimensional stability, as well as high proton conductivity due to presence of strong C-F bonds.

However, these aforementioned polymers are not only expensive, but also demonstrate relatively poor performance at higher temperatures. One way of preparing fluorinated copolymers in a more cost-effective way is by treating the membranes with fluorine gas. Specifically, fluorine gas is a very reactive gas towards different organic and inorganic material and can modify these compounds via chain radical reactions. This modification is thermodynamically favored due to the replacement of weak C-H bonds with strong C-F bonds. Lee and colleagues used surface fluorination method to enhance the chemical and dimensional stability and proton conductivity of hydrocarbon-based random copolymers such as poly(arylene ether sulfone).<sup>92</sup> In this modification, a PEAS was randomly fluorinated via F<sub>2</sub> gas to prepare a PAES copolymer, as shown is Scheme 1.26. In addition, the degree of fluorination increased as the exposure time to fluorine gas was extended. The increased degree of fluorination not only enhanced the membrane binding to the electrode surface, but also resulted in low methanol permeability. As a result of improved membrane-electrode binding and low methanol permeability, the membrane lifespan under methanol fuel cell conditions increased from 600 hr to over 1400 hr.



**Scheme 1.26** Post fluorinated hydrocarbon copolymer<sup>115</sup>

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## **CHAPTER 2. Synthesis and Membrane Properties of Sulfonated Poly(arylene ether sulfone) Statistical Copolymers for Electrolysis of Water: Influence of meta and para-Substituted Comonomers**

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### **2.1 Abstract**

Two series of high molecular weight disulfonated poly(arylene ether sulfone) random copolymers were synthesized as proton exchange membranes for high temperature water electrolyzers. These copolymers differ based on the position of the ether bonds on the aromatic rings. One series is comprised of fully *para*-substituted hydroquinone comonomer and the other series incorporated 25 mol % of a *meta*-substituted comonomer, resorcinol, and 75 mol % hydroquinone. The influence of the substitution position on water uptake and electrochemical properties of the membranes were investigated and compared to that of the state-of-the-art

membrane, Nafion™. Mechanical properties of the membranes were measured for the first time in fully hydrated conditions at ambient and elevated temperatures. Submerged in water, these hydrocarbon-based copolymers had moduli an order of magnitude higher than Nafion™. Selected copolymers of each series showed dramatically increased proton conductivities at elevated temperature in fully hydrated conditions while their H<sub>2</sub> gas permeabilities were well controlled over a wide range of temperatures. These improved properties were attributed to the high glass transition temperatures of the disulfonated poly(arylene ether sulfone)s.

## 2.2 Introduction

Hydrogen gas as a green fuel is a high energy molecule that can be used in fuel cells to generate electricity for the grid and automobiles.<sup>1</sup> Among different commercial pathways for hydrogen gas production,<sup>2-3</sup> electrolysis of water using proton exchange membranes has attracted much attention as a result of positive aspects such as producing high purity product,<sup>4</sup> high current density,<sup>5-6</sup> and fast kinetics at elevated temperatures.<sup>7</sup> The electrolyzers can also be coupled to renewable energy sources such as wind turbines or solar cells as environmentally friendly electricity producers. Hydrogen produced by electrolysis can be directly used in a fuel cell to provide a potential alternative to fossil fuels for generating electricity.

The state-of-the-art PEM for electrolysis of water is DuPont's perfluorosulfonic acid membrane, Nafion™. Nafion™ is a good proton conductor and it is highly chemically resistant and mechanically robust at temperatures below its T<sub>g</sub>. However, it has drawbacks including high gas permeability and poor mechanical stability above the  $\alpha$  relaxation temperature of ~80 °C and at the high operating pressure of the electrolyzer. Such operating conditions eventually result in loss of mechanical strength and reduced proton conductivity.<sup>8-10</sup> Sulfonated random and block

copolymers such as polyimides,<sup>11-12</sup> poly(arylene ether ketones),<sup>13</sup> poly(arylene ether sulfones)<sup>14-17</sup> and polybenzimidazoles<sup>18</sup> have been intensively investigated as PEMs in fuel cells. Fuel cells and electrolyzers have similar requirements regarding membrane properties. Both systems operate under highly acidic conditions and this places special durability requirements on the membranes for extended use. High temperature water electrolyzers are operated at temperatures exceeding 100 °C and pressures above 350 bar in a fully hydrated environment and this requires a robust membrane to withstand mechanical pressure as well as hydrolysis reactions.<sup>6, 19-20</sup> However, in the literature, there are not as many studies on potential alternatives for Nafion™ for electrolysis of water. Creating a PEM that has decreased gas permeability to minimize gas crossover and superior conductive properties relative to perfluorosulfonic acid membranes is a challenge that needs to be addressed.

Smith et al.<sup>21</sup> prepared a poly(ether ketone) via step growth polymerization and post sulfonated this polymer in concentrated sulfuric acid at elevated temperatures. In comparison with Nafion™, this copolymer had comparable proton conductivity, lower gas permeability and better mechanical stability for use in electrolysis of water with higher efficiencies, most likely as a result of its microphase separated structure. Albert et al.<sup>22</sup> grafted styrene and acrylonitrile and a crosslinker onto an ethylene tetrafluoroethylene film using radiation, then post-sulfonated the styrenic rings. This synthesis method resulted in a cost effective membrane with better mechanical properties than Nafion™, but using aliphatic chains in PEMs can lead to lower chemical resistance under harsh electrochemical conditions.<sup>23</sup> Moreover, inhomogeneous sulfonic acid distribution across the membranes resulted in high membrane area resistance.

High membrane resistance could also be at least partially attributed to the presence of non-conductive hydrophobic polymer on the membrane surface that acts as a water (mass) transfer

inhibitor as suggested by Takimoto et al.<sup>24</sup> It is known that a direct synthesis route to disulfonated polysulfones using pre-disulfonated comonomers allows control over factors including random distribution of the sulfonic acid groups, ion exchange capacity (IEC) of the membrane, morphology and proton conductivity and it can also avoid crosslinking of the membrane.<sup>14, 25-27</sup>

In this work, gas permeability and proton conductivity in PEMs were investigated in two series of sulfonated poly(arylene ether sulfone) statistical copolymers. These series were synthesized based on the difference between phenolic monomers and their ratio in the polymer backbone. One series contains solely hydroquinone (HQ) as a *para*-substituted comonomer. The second series contains 25 mole % of resorcinol (RSC) as a *meta*-substituted phenolic comonomer, co-reacted into a hydroquinone-based linear copolymer. Both series of copolymers were synthesized by direct synthesis of disulfonated dichlorodiphenyl sulfone via step-growth polymerization. Fundamental properties of these PEMs for high temperature water electrolysis systems such as water uptake of the membranes in liquid water at room and elevated temperatures, H<sub>2</sub> gas permeability, mechanical stability, and the ratio of  $\frac{\text{Proton conductivity}}{\text{Gas Permeability}}$  from room temperature to 100 °C were established and compared with Nafion™.

## 2.3 Experimental

### Materials

1,4-Benzenediol (hydroquinone, HQ) was provided by Eastman Chemical Company. 4,4'-Dichlorodiphenylsulfone (DCDPS) was provided by Solvay Advanced Polymers. 1,3-Benzenediol, resorcinol (RSC, >99%), was purchased from Sigma-Aldrich. Toluene was purchased from Sigma-Aldrich and was used as received. DCDPS, hydroquinone, and resorcinol were recrystallized from toluene and dried under vacuum at 120 °C prior to use. *N,N*-

Dimethylacetamide (DMAc) was purchased from Sigma-Aldrich and distilled from calcium hydride before use. Calcium hydride (90–95%) was purchased from Alfa Aesar. 2-Propanol was obtained from Fisher Scientific and used as received. Sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%) was purchased from Spectrum Chemical and used as received. Potassium carbonate ( $\text{K}_2\text{CO}_3$ ) was purchased from Aldrich and dried under vacuum at 180 °C prior to use. 3,3'-Disulfonated-4,4'-dichlorodiphenylsulfone (SDCDPS, >99%) was purchased from Akron Polymer Systems and was dried at 180 °C prior to use. DuPont's Nafion™ 212 was provided by Giner Electrochemical Systems.

### Synthesis of statistical copolymers

Aromatic nucleophilic substitution step copolymerization was used to synthesize both series of disulfonated poly(arylene ether sulfone) copolymers. Synthesis of HQ-XX: A typical HQ 20 with 20% of the repeat units disulfonated was synthesized as follows. HQ (36.33 mmol, 4.00 g), DCDPS (29.06 mmol, 8.3451 g), SDCDPS (7.265 mmol, 3.57 g), and DMAc (55 mL) were charged into a 250-mL three neck round bottom flask equipped with a mechanical stirrer, condenser, nitrogen inlet, and Dean-Stark trap filled with toluene. The mixture was stirred in an oil bath at 150 °C until all the monomers completely dissolved.  $\text{K}_2\text{CO}_3$  (47.22 mmol, 6.52 g), and toluene (25 mL) were added into the flask. The reaction was refluxed for 4 h to azeotropically remove water from the system. Toluene was drained from the Dean-Stark trap, and the oil bath temperature was raised to 180 °C to remove residual toluene from the reaction. The reaction solution was stirred for 48 h to complete polymerization, then allowed to cool to room temperature. After dilution of the resulting solution with DMAc (150 mL), it was filtered to remove the salt. The transparent solution was precipitated by addition into isopropanol with vigorous stirring. The

white fibers were filtered and then stirred in boiling DI water for 4 h to remove any residual DMAc. The copolymer was filtered and dried at 120 °C under reduced pressure in a vacuum oven. Yield of this copolymer synthesis was 94%.

Synthesis of HQ<sub>0.75</sub>RSC<sub>0.25</sub>-XX copolymers: A typical HQ<sub>0.75</sub>RSC<sub>0.25</sub> 19 with 19 of the repeat units disulfonated was synthesized as follows. HQ (27.24 mmol, 3.00 g), RSC (9.08 mmol, 1.00 g), DCDPS (28.33 mmol, 8.137 g), SDCDPS (8.0 mmol, 3.93 g), and DMAc (55 mL) were charged into a 250-mL three neck round bottom flask equipped with a mechanical stirrer, condenser, nitrogen inlet, and Dean-Stark apparatus filled with toluene. The mixture was stirred in an oil bath at 150 °C until the monomers completely dissolved. K<sub>2</sub>CO<sub>3</sub> (47.22 mmol, 6.52 g), and toluene (25 mL) were added into the flask. The reaction was refluxed for 4 h, the toluene was drained from the Dean-Stark apparatus, then the oil bath temperature was raised to 180 °C to remove residual toluene from the reaction. The solution was stirred for 48 h at 180 °C, then cooled to room temperature. The solution was diluted with DMAc (150 mL), then filtered to remove the salt. The transparent solution was precipitated into isopropanol. The white fibers were filtered and stirred in boiling DI water for 4 h. The copolymer was then filtered and dried at 120 °C under reduced pressure in a vacuum oven. Yield of this copolymer synthesis was 95%.

#### Nuclear Magnetic Resonance Spectroscopy (NMR)

<sup>1</sup>H NMR analysis of the statistical copolymers was conducted on a Varian Unity Plus spectrometer operating at 400 MHz. The spectra of the copolymers were obtained from a 10% (w/v) solution in DMSO-d<sub>6</sub>.

## Size Exclusion Chromatography (SEC)

Molecular weights and polydispersities of the polymers were measured using SEC. The mobile phase was DMAc distilled from  $\text{CaH}_2$  containing dry LiCl (0.1 M). The column set consisted of 3 Agilent PLgel 10-mm Mixed B-LS columns 300 \* 7.5 mm (polystyrene/divinylbenzene) connected in series with a guard column having the same stationary phase. The columns and detectors were maintained at 50 °C. An isocratic pump (Agilent 1260 infinity, Agilent Technologies) with an online degasser (Agilent 1260), autosampler and column oven were used for mobile phase delivery and sample injection. A system of multiple detectors connected in series was used for the analyses. A multi-angle laser light scattering detector (DAWN-HELEOS II, Wyatt Technology Corp.), operating at a wavelength of 658 nm, a viscometer detector (Viscostar, Wyatt Technology Corp.), and a refractive index detector operating at a wavelength of 658 nm (Optilab T-rEX, Wyatt Technology Corp.) provided online results. The system was corrected for interdetector delay and band broadening using a 21,000 Da polystyrene standard. Data acquisition and analysis were conducted using Astra 6 software from Wyatt Technology Corp. Validation of the system was performed by monitoring the molar mass of a known molecular weight polystyrene sample by light scattering. The accepted variance of the 21,000 Da polystyrene standard was defined as 2 standard deviations (11.5% for  $M_n$  and 9% for  $M_w$ ) derived from a set of 34 runs. Specific refractive index values were calculated based on the assumption of 100% mass recovery.

## Membrane casting and characterization

The copolymers in their salt form were dissolved in DMAc (~6% w/v), and then filtered through a 0.45  $\mu\text{m}$  Teflon syringe filter. The solutions were cast onto clean glass substrates and dried under an infrared lamp at 50-60  $^{\circ}\text{C}$  for 8 h. Afterwards, the membranes were placed in a vacuum oven under reduced pressure at 120-140  $^{\circ}\text{C}$  for 4 h. The membranes were soaked in water for an additional 24 h to remove residual solvent and to delaminate them from the glass plates. The membranes were converted to their acid form by boiling in 0.1 M  $\text{H}_2\text{SO}_4$  for 2 h and they were then boiled in DI water for 2 h to remove residual acid.

## Ion Exchange Capacity (IEC)

Dry membranes in their acid form were weighed, then soaked in 1 M NaCl solution for 48 h to convert them to their salt form and eliminate HCl. Each membrane solution was titrated with 0.1 N NaOH solution. The IEC of each membrane in units of meq/g of dry membrane was calculated from Equation 2.1

$$IEC = \frac{V N}{M} \times 1000 \quad (2.1)$$

where V is volume of NaOH, N is NaOH normality, and M is the mass of the dry membrane.

## Water uptake at ambient and elevated temperatures

The water uptakes of the membranes were determined gravimetrically on samples weighing 0.1-0.2 g and 3 samples were measured for each film. First, the membranes in their acid form were dried at 120  $^{\circ}\text{C}$  under vacuum for 24 h and weighed. These membranes were soaked in water at room temperature for 48 h. Wet membranes were removed from the liquid water, blotted dry to remove surface droplets, and quickly weighed. For high temperature water uptake, the

previously wet membranes were placed in boiling water for at least 4 h. Then the hot, wet membranes were removed from the boiling water, immediately blotted dry to remove surface droplets, and quickly weighed. The water uptake of the membranes was calculated according to Equation 2.2, where mass dry and mass wet refer to the masses of the dry and the wet membranes, respectively.

$$\text{Water Uptake} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} * 100 \quad (2.2)$$

### Differential Scanning Calorimetry (DSC)

The glass transition temperatures ( $T_g$ s) of the copolymers were investigated using a TA Instruments DSC Q200. For dry samples, standard aluminum hermetic pans were used, and for hydrated samples, high volume DSC pans were used. The samples were hydrated by immersion in deionized water for 24 h prior to loading into the DSC pans. The polymers were heated under nitrogen at a rate of 10 °C min<sup>-1</sup> to 200 °C, cooled at a rate of 10 °C min<sup>-1</sup> to 0 °C, and heated again at a rate of 10 °C min<sup>-1</sup> to 240 °C. The  $T_g$ s of the samples were determined from the second heat by finding the inflection point of the W/g vs. temperature curve with the aid of TA Universal Analysis software.

### Tensile tests

Tensile samples were cut from hydrated solvent cast films using a Cricut Explore One™ computer controlled cutting machine. Nafion™ samples were prepared in the same manner from Nafion™ 212. The resulting dogbone shaped samples were consistent with sample Type V described in ASTM D638-14 (minimum 63.5 mm overall length, gage length 7.62 mm, width of narrow section 3.18 mm). The sample films were inspected for any visible flaws, defects, or

inclusions that may have arisen during the casting process. The seven highest quality samples were selected for testing. The sample thickness was measured at five points along the narrow section using a Mitutoyo digimatic micrometer model MDC-1" SXF.

Uniaxial load tests were performed using an Instron ElectroPuls E1000 testing machine equipped with a 250 N Dynacell load cell. The instrument was fitted with a water bath and the samples were completely immersed in deionized water for 24 h. The wet samples were loaded into the Instron situated in a tank, and the tank was filled with water. For elevated temperature tests, the water was heated to 80 °C, then the sample was allowed to equilibrate in the water for at least 3 min before testing to obtain fully hydrated mechanical data. For high temperature hydrated tests, the tank was fitted with an immersion heater and was well insulated to maintain the water at the target temperature of 80 °C. For all mechanical tests, the crosshead displacement rate was 10 mm/min and the initial grip separation was 25 mm.

Young's moduli were calculated from the slope of the initial linear region of the loading curve. The yield point was considered to be the intersection of the load curve with a 1% offset of this modulus line. This offset was chosen because it correlated with the yield point for lower IEC samples, some of which showed a distinct yield point in the load-displacement curve. Nominal strain at yield was calculated by dividing the change in grip separation by the initial grip separation. Tensile strength at yield was calculated by dividing the load by the average cross-sectional area of the narrow section, which was based on a sample width of 3.18 mm and the average of the five sample thickness measurements. Since the instrument's stroke was limited to around 5 cm (200% strain for this sample geometry) and some of the samples did not fail within this range, the ultimate properties of the polymers are not presented here.

### H<sub>2</sub> gas permeability (P)

A membrane was loaded into a Fuel Cell Technologies standard fuel cell hardware set. This set-up was installed inside a TestEquity environmental chamber with both heating and cooling capabilities. All flows were controlled or measured with Alicat mass flow controllers and meters. A flow of carrier gas was established on one side of the cell and the humidified permeant gas to the other. For these tests, over-humidified (condensing) permeant gas was used to simulate the flooded membrane of the electrolyzer. The permeant diffuses through the membrane, and a slipstream of the carrier gas is sent to an Agilent microGC for analysis of the permeant. The amount of permeant in the carrier gas was used to calculate the permeation rate of that gas through the membrane at that specific temperature. Then the temperature was changed and the process repeated. For a specific temperature, Equation 2.3 is used

$$P = \frac{DT}{tA\Pi} \quad (2.3)$$

where P is the H<sub>2</sub> gas permeability, D is the amount of permeant gas, T is the membrane thickness, t is the permeation time, A is the cell's effective area, and  $\Pi$  is the dry gas pressure.

### Proton conductivity ( $\sigma$ )

The conductivity test stand consisted of a house-made four-point probe assembly with platinum electrodes and a Wayne-Kerr LCR meter. The membrane was clamped between the probe assemblies and placed in the water bath at room temperature. The water bath was heated steadily to 100 °C and AC impedance measurements were taken at temperatures of 30, 60, 90, and 100 °C. Using the dimensions of the membrane, the conductivity of the ionomer in S/cm was calculated based on Equation 2.4

$$\sigma = \frac{l}{RA} \quad (2.4)$$

where  $\sigma$  is the conductivity,  $l$  is the length between electrodes,  $R$  is membrane's resistance, and  $A$  is the cross sectional area available for proton transport.

## Performance

The ratio of  $\sigma/P$  was calculated for selected membranes at temperatures of 30, 60, 90 and 100 °C. The performance of each copolymer was calculated by normalizing the  $\sigma/P$  to that of Nafion™ at each temperature based on Equation 2.5

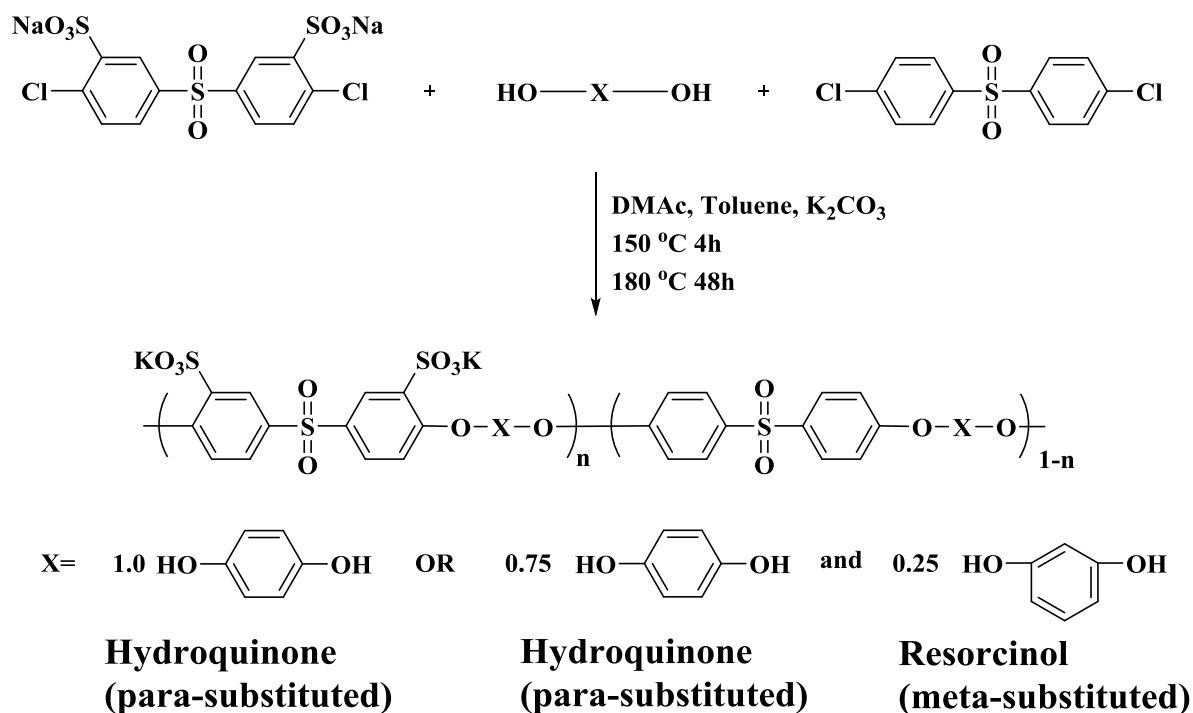
$$Performance = \frac{\frac{\sigma_{polymer}}{P_{polymer}}}{\frac{\sigma_{Nafion}}{P_{Nafion}}} \quad (2.5)$$

where  $\sigma_{polymer}/P_{polymer}$  is the ratio of proton conductivity to H<sub>2</sub> gas permeability for each copolymer and  $\sigma_{Nafion}/P_{Nafion}$  is the ratio of proton conductivity to H<sub>2</sub> gas permeability through Nafion™ respectively.

## 2.4 Results and Discussion

### Synthesis and characterization of statistical copolymers

Synthesis of sulfonated poly(arylene ether sulfone) random and block copolymers have been intensively studied by many research groups.<sup>25, 27-30</sup> In this study, two series of random copolymers were synthesized via step-growth polymerization based on the reaction shown in Scheme 2.1. It is noteworthy that as more resorcinol (the *meta*-substituted monomer) was incorporated into such copolymers, this detracted from the mechanical properties. Thus, only copolymers with 25 mole % of resorcinol together with 75 mole % of hydroquinone, where the mechanical properties were considered to be good, were pursued.



**Scheme 2.1** Random copolymer synthesis of a 100% para-substituted phenolic HQ-based copolymer or a 75% para- and 25% meta-substituted phenolic HQRSC copolymer

Reactions were designed so that the IEC of a copolymer in the hydroquinone-based series would match with one in the HQ<sub>0.75</sub>RSC<sub>0.25</sub> series. SEC confirmed that the molecular weight of each copolymer was well above the threshold entanglement point which is ~10,000 Da,<sup>31-32</sup> and therefore was suitable for these investigations. The molecular weights and IECs of the membranes are shown in Table 2.1. Representative <sup>1</sup>H NMR spectra of HQ 16 and HQRSC 17 in Figure 2.1 confirm the structures of these random copolymers.

**Table 2.1** Degree of disulfonation, IEC per gram of dry copolymer, and molecular weights of the copolymers

| Copolymer-Degree of disulfonation | IEC<br>(meq/g) | M <sub>w</sub><br>(kDa) |
|-----------------------------------|----------------|-------------------------|
| HQRSC 17                          | 0.95           | 107                     |
| HQRSC 19                          | 1.08           | 108                     |
| HQRSC 24                          | 1.33           | 70                      |
| HQRSC 25                          | 1.36           | 92                      |
| HQRSC 32                          | 1.63           | 104                     |
| HQ 16                             | 0.93           | 153                     |
| HQ 20                             | 1.12           | 199                     |
| HQ 23                             | 1.29           | 80                      |
| HQ 25                             | 1.39           | 101                     |
| HQ 30                             | 1.59           | 91                      |

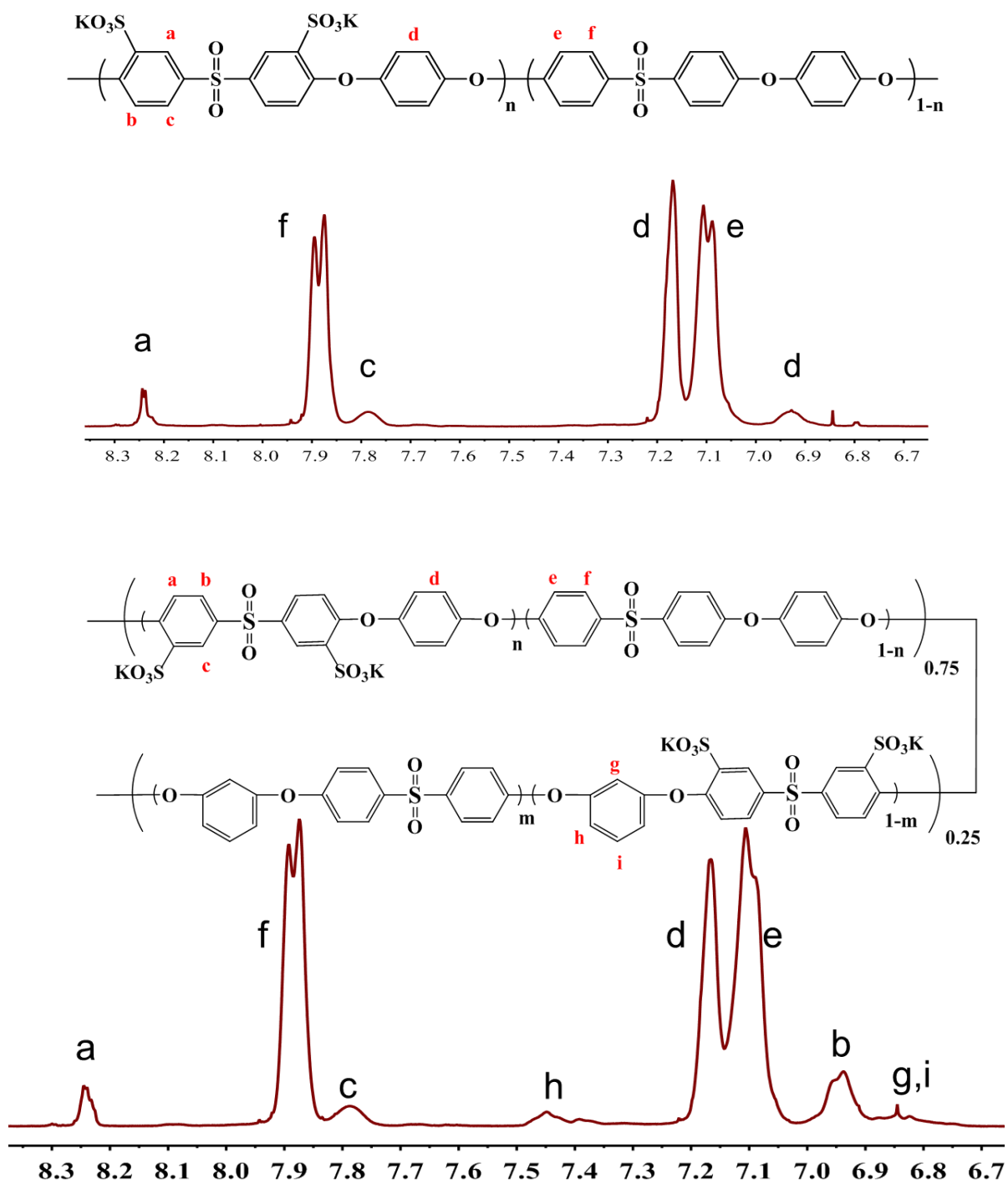


**Figure 2.1** <sup>1</sup>H NMR spectra of HQ 16 (top) and HQRSC 17 (bottom)

## Membrane water uptake

In general, an increase in water uptake correlates with a large increase in the proton conductivity of PEMs. This has been attributed to water molecules weakening the electrostatic interaction between  $H^+$  ions and the polymer backbone fixed  $SO_3^-$  groups, thus resulting in faster  $H^+$  ion transfer.<sup>33</sup> However, high water uptake directly correlates to a decrease in mechanical properties of the membrane in an electrochemical device.<sup>19, 34-35</sup> Figure 2.2 shows the weight percent of water uptake at ambient temperature and  $\sim 80^\circ C$  for both series of copolymers.

As expected, water uptake increases with IEC and the degree of disulfonation in both series. For cases of polysulfones without sulfonate groups and with varying *meta* versus *para* orientation of the backbone rings, it has been shown that polymers with *meta*-substituted rings in the dry state pack more tightly, have lower free volume, and generally have lower gas permeabilities.<sup>36</sup> The anticipated decrease in gas permeability with incorporation of the resorcinol was indeed one of our prime motivations for undertaking this study. The present case, however, is much more complicated than studying polymers in their dry state since the fixed sulfonate groups lead to significant water uptake. Figure 2 clearly shows a large increase in water uptake in the disulfonated copolymers that contain some resorcinol relative to those containing only the *para*-substituted hydroquinone. However, this is only prominent above the IECs that are of most interest for electrolysis (IEC  $\sim 0.9$  and  $\sim 1.1$  in meq/g of dry polymer). Figure 2 also shows increased water uptake at elevated temperatures relative to ambient temperature, but there is little difference in water uptake at the two temperatures at the lower IEC points of most interest.

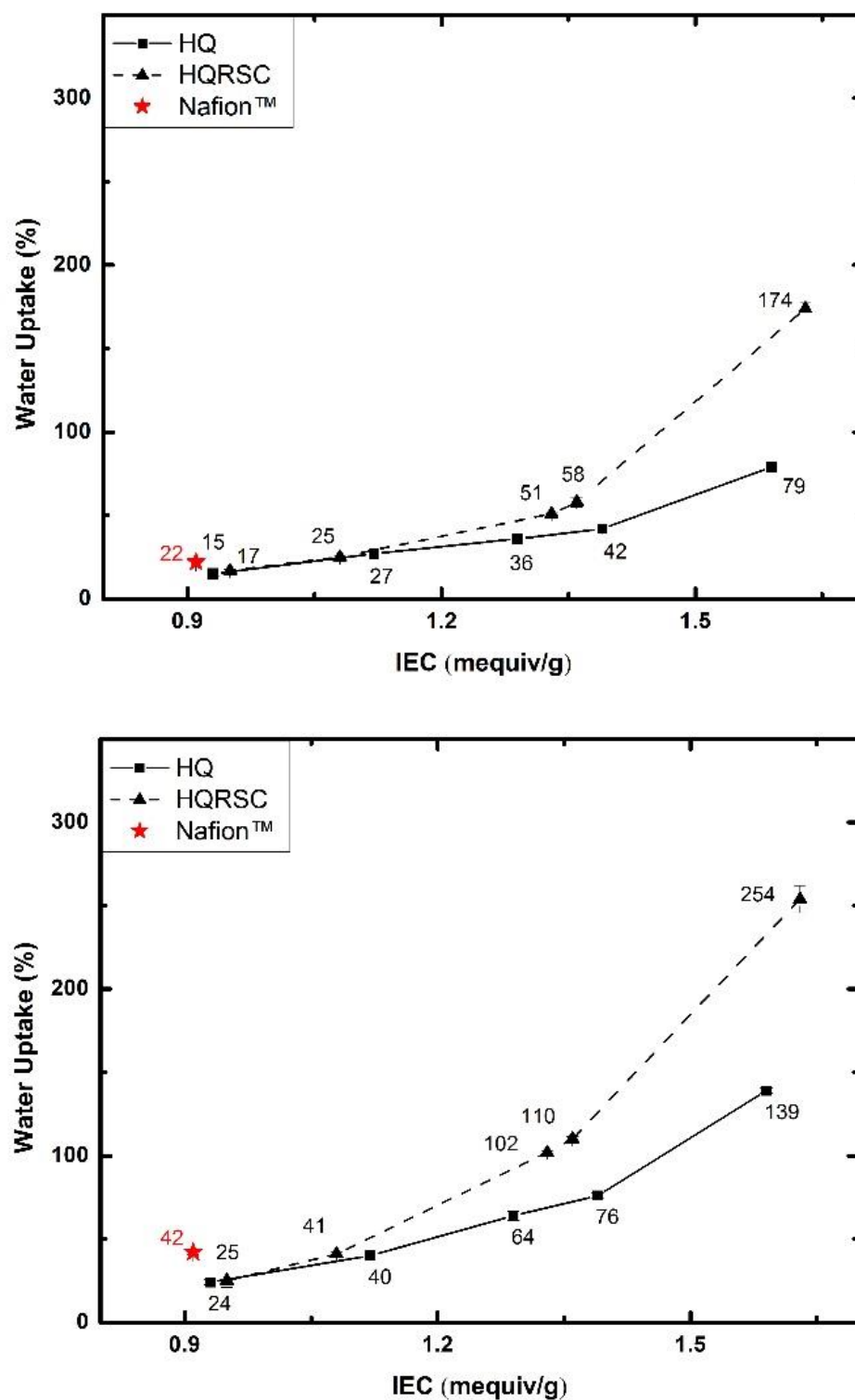


**Figure 2.2** Water uptake of the membranes at room temperature (top) and ~80 °C (bottom). Numbers on the graphs refer to % water uptake

## Membrane thermal properties

As shown in Figure 2.3, the glass transition temperatures of these copolymers in the dry state are high and they increase with increasing IEC for both the HQ and HQRSC copolymers. As the number of sulfonate groups are increased in the backbone, the chains stiffen and therefore are less mobile and unable to explore various conformations at low temperatures. Furthermore, the 100% HQ copolymers have higher  $T_g$ s at each comparable IEC than their HQRSC analogues in the dry state. This can also be explained by the chain stiffness. As confirmed by the modulus data that is discussed in this paper, the *para*-substituted hydroquinone moiety leads to a more rigid chain than the *meta*-substituted resorcinol. This also follows the trend noted with *para* versus *meta*-substituted rings without the added sulfonate groups.<sup>36</sup>

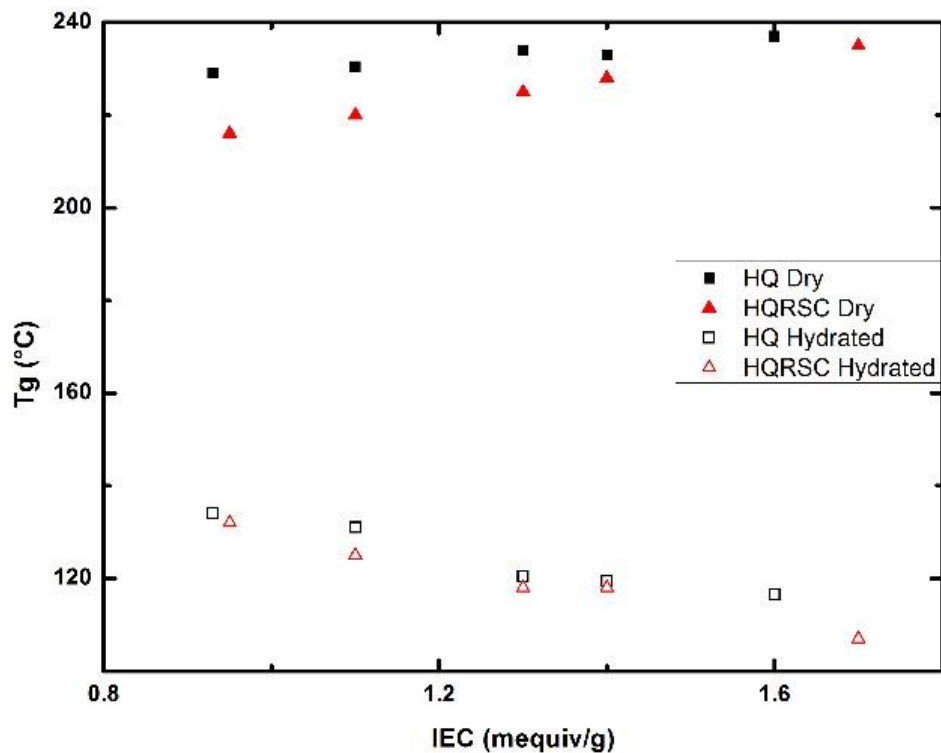


**Figure 2.3**  $T_g$ s of the random copolymers in their dry and hydrated states

In the hydrated state, HQ and HQRSC copolymers both show decreasing  $T_g$ s with increasing IEC. This is expected because as the number of sulfonic acids increases, the water uptake increases, leading to increased plasticization of the polymers. It is known that hydration of the membranes causes plasticization, resulting in decreased glass transition temperatures.<sup>37-38</sup> Interestingly, the HQ and HQRSC copolymers show a slight difference in  $T_g$  from one another at comparable IECs in the hydrated state. Figure 2.4 shows  $T_g$  vs water uptake for the HQ and HQRSC copolymers. Two morphological regimes are suggested with the transition between regimes occurring at water uptakes of 40-60%, where the slope of the curve appears to change. This transition is consistent with a transition from localized hydrophilic clusters to a percolating network of hydrated polymer, as presented elsewhere.<sup>39</sup>

The distinction between the two morphological regimes may be explained by the way in which the copolymers interact with water. As described by Roy et al.<sup>40</sup> ~9 moles of water per sulfonic acid group are non-freezable, while additional water was characterized as “loosely bound” to the sulfonic acid groups or “free water”.<sup>40</sup> A morphological transition was suggested with the rise in “free water” that occurred at an IEC of 1.2-1.4 meq/g and that corresponded to ~40-50% by weight of water uptake. The present paper expands such correlations for both hydroquinone and resorcinol-containing random copolymers. HQ 20 and HQ 23 have IECs and water uptakes of 1.12 meq/g and 27 % uptake and 1.29 meq/g and 36 % water uptake, respectively. By correlating these materials with those described earlier,<sup>40</sup> this correlates with 9 moles of non-freezable water and 5 and 7 moles of freezable water, respectively. In agreement with earlier suggestions, Figure 4 shows an abrupt change in the slope of  $T_g$  with water uptake at ~40-50% water. We believe this also signifies a change in morphology at these compositions. Above approximately 50% water uptake, the hydrated regimes reach a percolation threshold, and a dominant amount of the water is

considered to be free or unbound to the hydrophilic segments, and therefore does not lead to a strong plasticization effect.<sup>40-41</sup> At this point and above, the non-freezing water remains constant at 9 moles and freezing water content starts to rise from approximately 5 moles in HQ 20 to 19 moles of water in HQ 30.

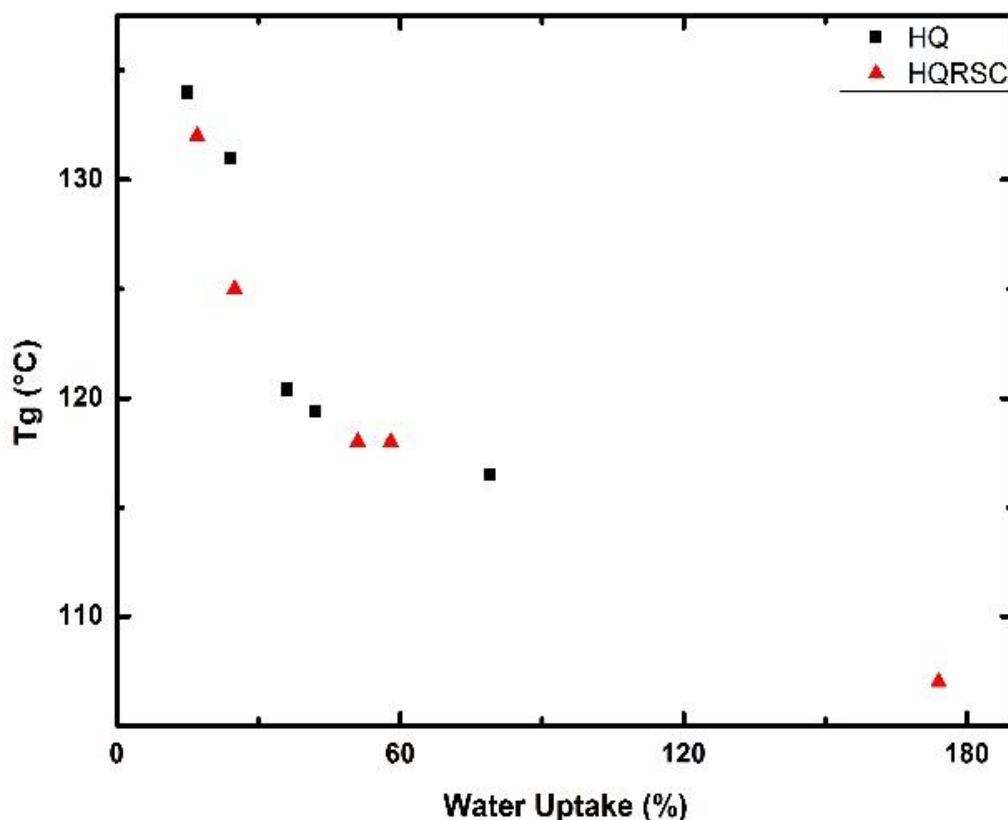


**Figure 2.4** T<sub>g</sub> vs room temperature water uptake for HQ and HQRSC copolymers

#### Mechanical properties

As shown in Figure 2.4, all of these hydrated copolymers are in the glassy state at both ambient temperature and 80 °C, but the copolymers with IEC's greater than 1.1 meq/g are fairly close to T<sub>g</sub> at 80 °C. The moduli displayed in Figure 2.5 are typical for glassy polymers (~10<sup>9</sup> Pa) at ambient temperature for those of most interest with IEC's of 0.9 and 1.1 meq/g, even in their fully hydrated state. Consistent with the decrease in T<sub>g</sub> as IEC is increased to ~1.2 and higher, with

the concomitant large increase in water uptake, the hydrated moduli drop drastically. Figure 2.6 shows the large drops in moduli at low water uptake (and low IECs), with a leveling out of moduli at high water uptakes. This also correlates well with the suggestion that there is a change in hydrated morphology at approximately 40-60% water uptake. While such a change in morphology has been suggested earlier, we believe this is the first time that the hydrated mechanical properties have been correlated with such changes. For copolymers with high water uptakes, we expect to have high free water content and a percolating network morphology,<sup>40</sup> and this is accompanied by a decrease in mechanical properties.

Since fully hydrated mechanical properties of candidate electrolysis membrane materials are rarely reported, it is instructive to provide such comparisons between Nafion and the materials investigated in this work. Albert et al.<sup>22</sup> reported fully hydrated properties of Nafion NR212 at ambient temperature to be 7-8 MPa ultimate stress with an ultimate elongation of ~60%. In close agreement, Shi et al.<sup>42</sup> reported hydrated properties of Nafion 212 as having an ultimate stress of 6 MPa and ultimate elongation of 35% at ambient temperature under immersion conditions, and these properties fell to an ultimate stress of 2 MPa and approximately 45% ultimate elongation at 70°C. The data on Nafion 212 collected in the present study showed the film extending out to the extension limit of our instrument (200% elongation) without failure so we could not discern ultimate properties but the stress at that extension limit was ~25 MPa (immersed in water at room temperature). All of the four poly(arylene ether sulfone)s of most interest in this study yielded, then strain hardened. The ultimate stresses at room temperature under immersion conditions were HQ 16 ( $54 \pm 8.2$  MPa), HQ 20 ( $40 \pm 2$  MPa), HQRSC 17 ( $42 \pm 3$  MPa) and HQRSC 19 ( $48 \pm 1$  MPa) with ultimate elongations of HQ 16 ( $113 \pm 8\%$ ), HQ 20 ( $105 \pm 8\%$ ), HQRSC 17 ( $82 \pm 5\%$ ) and HQRSC 19 ( $162 \pm 8\%$ ). At 80°C, these copolymers also yielded, then strain hardened, but

they also extended out to the extension limit of the instrument. Even so, the stresses at that 200% limit at 80°C were HQ 16 (~42 MPa), HQ 20 (~33 MPa), HQRSC 17 (~47 MPa) and HQRSC 19 (~31 MPa), all of which were greater than the stress at 200% elongation for Nafion 212 at room temperature. Even for the high IEC disulfonated polysulfone copolymers, both the strengths at yield and the elastic moduli are notably higher than for Nafion™ under similar hydration conditions. For lower IEC disulfonated random copolymers at ambient temperature and in the hydrated condition, the strength at yield is between 20 and 30 MPa and the modulus is between 800 and 1200 MPa. This result indicates that these copolymers are significantly more mechanically robust in the hydrated state than the current state of the art material, Nafion™, due to the stiffness of the aromatic backbone.

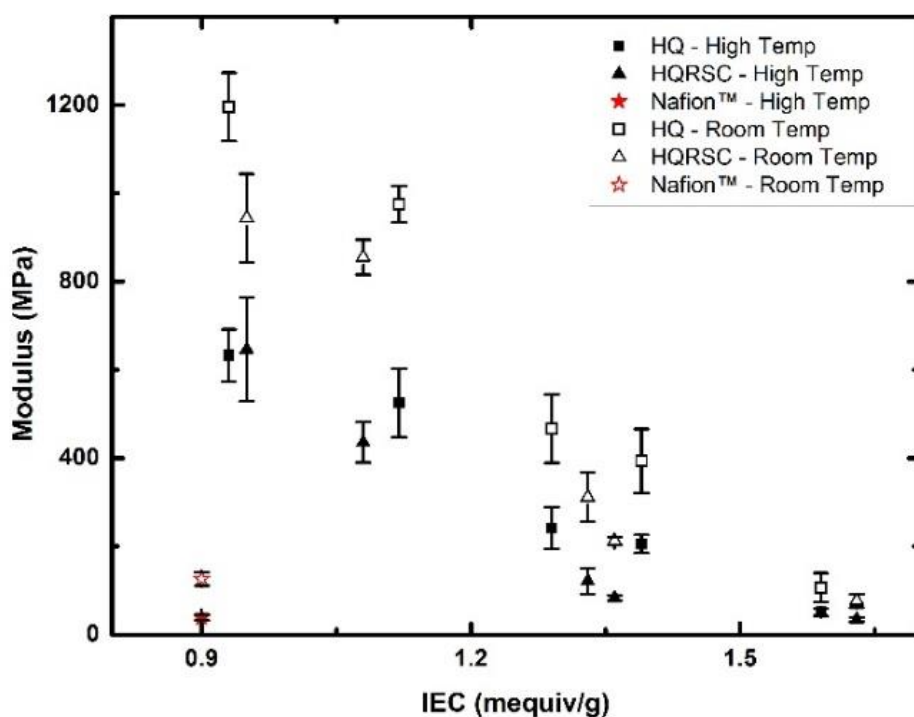


**Figure 2.5** Young's moduli vs. IEC for polymer films in the fully hydrated state at room and high temperatures

The aromatic copolymer membranes with fully *para*-substituted comonomers (HQ series) have consistently higher moduli at a given IEC than partially *meta*-substituted copolymers (HQRSC series), even in the fully hydrated state (Figure 2.5). The trend in the modulus vs. water uptake plot shown in Figure 2.6 is remarkably similar to the  $T_g$  data presented in Figure 2.4. It similarly shows two distinct regimes, with the transition between regimes occurring near 50% water uptake. The consistency of the trend in mechanical properties and thermal properties supports the occurrence of a morphological transition in these random copolymer systems as the degree of disulfonation is increased.

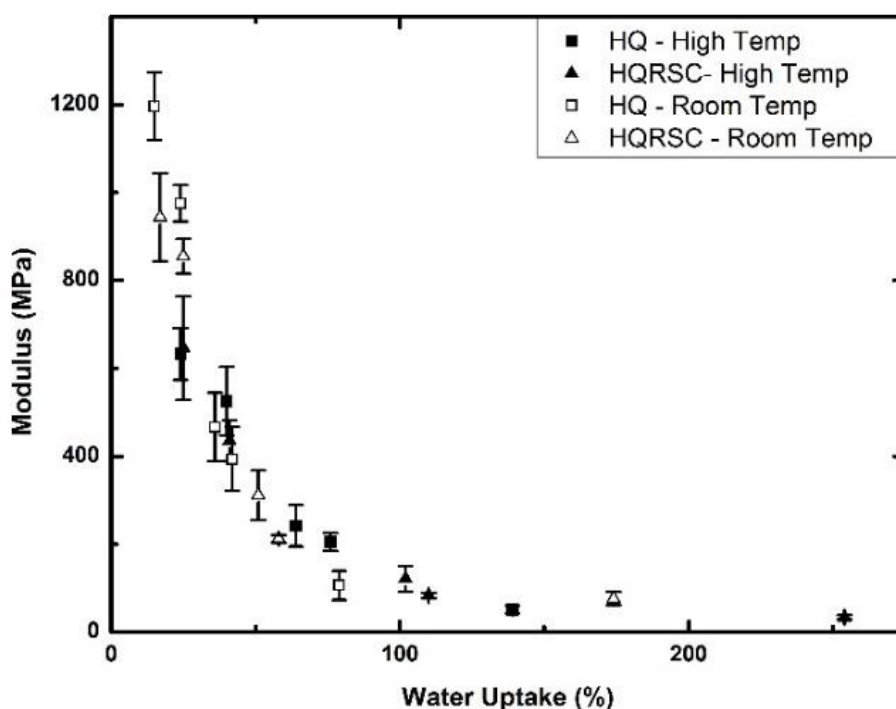


**Figure 2.6** Transition between morphological regimes shown by Young's moduli vs. water uptake for hydrated membranes

#### Proton conductivity

In this study, the proton conductivities of the copolymer membranes and Nafion™ were measured in liquid water at four temperatures: 30, 60, 90, and 100 °C. In each hydrocarbon-based

copolymer series, two polymers with IEC=0.9 and 1.1 meq/g were emphasized due to their reasonable water uptakes and superior mechanical properties. Copolymers with the lower IECs (HQ 16 and HQRSC 17) have similar IECs to Nafion™. Copolymers with IEC=1.1 meq/g (HQ 20 and HQRSC 19) showed comparable water uptakes at elevated temperatures to that of Nafion™ (40-42%). Table 2.2 shows the copolymers of interest and their relative proton conductivity at four temperatures.

**Table 2.2** Relative proton conductivity of the selected copolymers compared with Nafion™ in liquid water

| Temperature<br>e (°C) | $\sigma$ (S/cm) |          |       |          |         |
|-----------------------|-----------------|----------|-------|----------|---------|
|                       | HQ 16           | HQRSC 17 | HQ 20 | HQRSC 19 | Nafion™ |
| 30                    | 0.03            | 0.06     | 0.06  | 0.08     | 0.08    |
| 60                    | 0.06            | 0.08     | 0.09  | 0.12     | 0.13    |
| 90                    | 0.07            | 0.11     | 0.12  | 0.16     | 0.21    |
| 100                   | 0.08            | 0.12     | 0.13  | 0.18     | 0.23    |

Increasing temperature from 30 to 100 °C results in improved proton conductivity in all of these membranes including Nafion™.<sup>43</sup> This can be attributed to increased water uptake at higher temperatures.<sup>44</sup> Comparison of proton conductivities in two hydrocarbon-based copolymers at a given IEC revealed that copolymers containing the RSC comonomer have slightly higher proton conductivity than those of the solely HQ containing copolymers. The difference in proton conductivity becomes more pronounced when temperature is increased from 30 to 100 °C. This remarkable difference is correlated with increased chain flexibility in the RSC containing copolymers that have lower T<sub>g</sub>s in liquid water. In addition, it is hypothesized that the RSC comonomers decrease the rigidity relative to the HQ-based copolymers and allow for more mobility in the presence of water.

When IEC is increased in a series of copolymers, proton conductivity increases as expected.<sup>44</sup> Increasing the number of sulfonic acid groups on the backbone brings more water molecules into the membrane and improves proton transfer. Similar results are obtained when the *meta*-substituted phenolic comonomer is incorporated into the polymer backbone. This may allow for increased chain movement and water uptake by increasing the volume and chain spacing. The higher proton conductivity of Nafion™ at any given temperature may be due to its lower pKa than hydrocarbon-based copolymers.<sup>45</sup>

#### H<sub>2</sub> gas permeability in saturated water vapor

Decreasing gas permeability (i.e., crossover) in PEMs is an important factor for increasing efficiency of an electrolysis cell and safety.<sup>46</sup> Like proton conductivity and mechanical properties, H<sub>2</sub> gas permeability is highly dependent on water content in the PEM which acts as a plasticizer in the membrane by reducing the T<sub>g</sub>.<sup>47</sup> Figure 2.7 shows H<sub>2</sub> gas permeability through these PEMs in saturated water vapor at various temperatures.

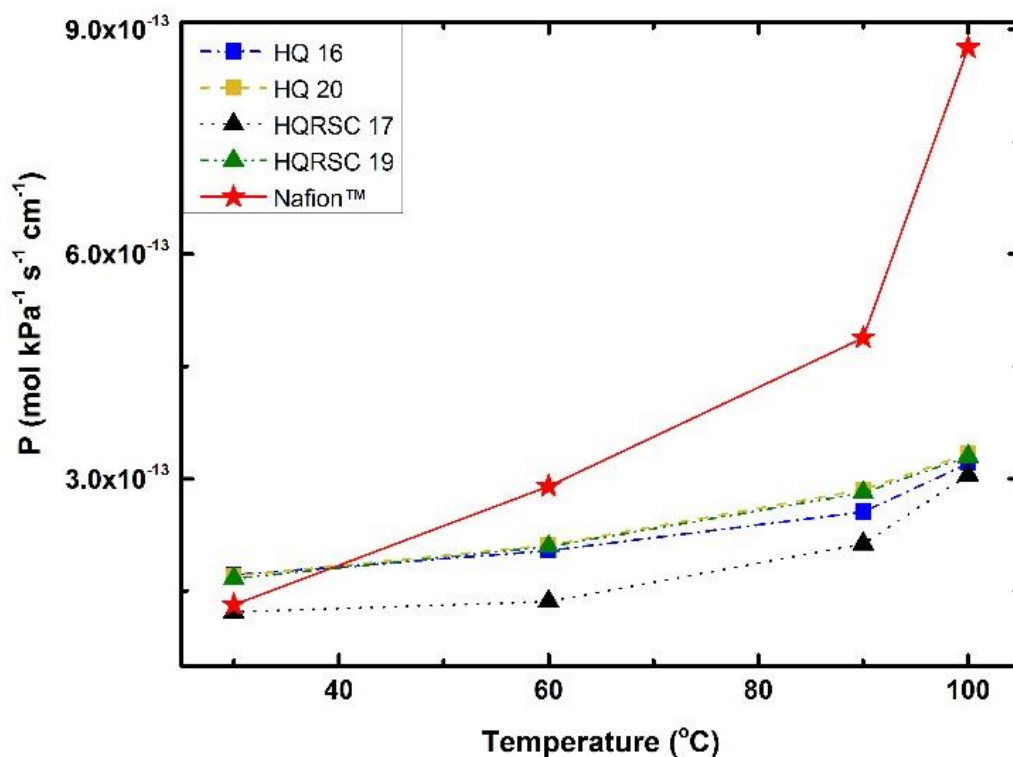


**Figure 2.7** H<sub>2</sub> gas permeability, P, through selected membranes in saturated water vapor at various temperatures

Comparison of gas permeability in hydrocarbon-based copolymers and Nafion™ shows two main regions and trends. At low temperature below ~40 °C, H<sub>2</sub> gas permeability of the Nafion membrane is slightly lower than that of most of the poly(arylene ether) copolymers (HQ 16, HQ 20, and HQRSC 19) and that of the HQRSC 17 is very close to Nafion™, while with increasing temperature, the opposite is observed for each of these hydrocarbon copolymers. Increasing temperature results in undesirable increased gas permeability in the Nafion™ membrane, such that above 60 °C a sharp increment is observed. However, gas permeability in the disulfonated copolymers only increases slowly and steadily. This behavior in PEMs is related to their T<sub>g</sub>s. As shown in the bottom of Figure 3, the T<sub>g</sub>s of all of these copolymers where the gas permeabilities were measured are above the measurement temperatures, so they are all in the glassy state.

Nafion™ has a significantly lower  $T_g$  relative to those of the aromatic copolymers.<sup>41, 48-49</sup> When Nafion™ is plasticized by water, its  $T_g$  decreases further to lower temperatures.<sup>44</sup> The drastic increase in gas permeability in the water at 60 °C and above is due to the low polymer  $T_g$ .

Unlike Nafion™ that has a low  $T_g$ , these disulfonated copolymers with higher wet  $T_g$ s show low gas permeabilities due to their aromatic rings and increased chain rigidity. Investigation of the effect of symmetric and asymmetric aromatic comonomers on gas permeability of glassy copolymers confirms that *meta*-substituted comonomers act as a good gas barrier in the copolymer, even in the hydrated state.<sup>36</sup> As expected, Figure 7 shows that incorporation of the *meta*-substituted RSC comonomer into these HQ-based copolymers resulted in lower gas permeabilities in this temperature range.

## Performance

The ratio of proton conductivity ( $\sigma$ ) and gas permeability ( $P$ ), defined as  $\sigma/P$  gives better insight regarding the performance of a membrane in the water electrolysis cell. As the high proton conductivity is critical for a PEM, gas crossover is of similar importance by improving the efficiency, safety, and purity of gaseous product.<sup>4, 50-51</sup> As an example, consider using Nafion™ as a reference point as we have done in this manuscript. Suppose one has a material that has  $\frac{1}{2}$  the conductivity of Nafion™, yet  $\frac{1}{4}$  of the gas permeability. If that membrane has  $\frac{1}{2}$  the thickness, the membrane resistance of the two become equal, while the thinner membrane will have  $\frac{1}{2}$  the gas crossover of Nafion™. Performance of each selected copolymer, normalized to that of Nafion™, (Equation 5) over the range of 30-100 °C are shown in Figure 2.8.

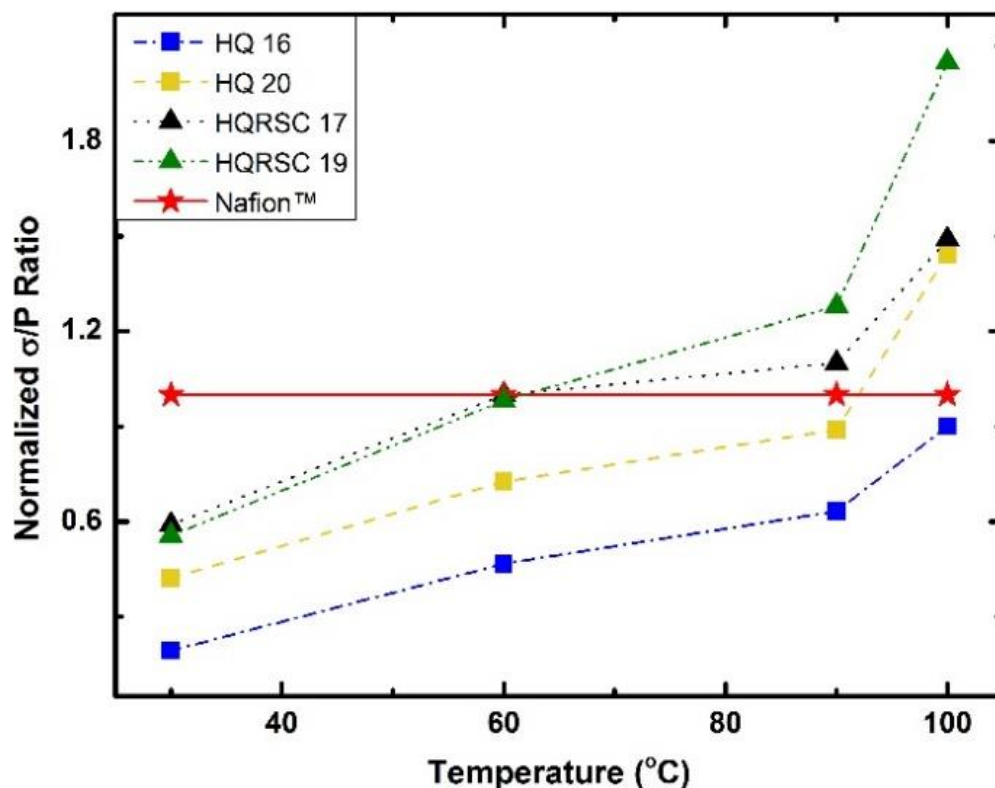


**Figure 2.8.** Performance of the selected copolymers at various temperatures

At low temperature where the proton conductivity of Nafion™ is higher than for the disulfonated copolymers and gas permeability is comparable, Nafion™ shows better performance. However, at the mid-temperature of 60 °C, due to increased conductivity for the disulfonated copolymers, and slow gas permeabilities, their performance is comparable to that of the Nafion™. The  $\sigma/P$  parameter at high temperature such as at 100 °C, where Nafion™ shows the highest conductivity, shows an opposite trend. Under these conditions, the disulfonated copolymers show significantly better results. This is due to improved conductivity at the higher temperature, but with controlled gas permeability in the disulfonated copolymers while Nafion™ shows much higher undesirable gas permeability.

## 2.5 Conclusions

Two series of hydrocarbon copolymers, based on completely *para*-substituted and partially *meta*-substituted compositions, were synthesized for high temperature water electrolysis. Addition of resorcinol, the *meta*-substituted comonomer, to the *para*-substituted copolymer structure results in decreased chain stiffness (decreased hydrated moduli with *meta*-substitution) and increased water absorption. These factors are reflected in the increased proton conductivities of the *meta*-substituted copolymers in the hydrated state.

Despite the slightly lower proton conductivities of the selected hydrocarbon-based copolymers in comparison to Nafion™, they showed remarkably lower H<sub>2</sub> gas permeabilities, particularly at elevated temperatures. This is attributed to their much higher T<sub>g</sub>s in their hydrated form relative to the perfluorinated polymer. In fact, Nafion™ has such a high gas permeability that having exceptional proton conductivity at elevated temperature was not sufficient to elicit reasonable performance. In addition to gas permeability, mechanical properties of Nafion™ near 100 °C is unsatisfactory for long term performance as a high temperature electrolysis membrane. In contrast, the aromatic HQ 17 and HQRSC 19 copolymers showed good proton conductivity, excellent mechanical properties, and good  $\sigma/P$ , performance ratios at elevated temperatures in their hydrated state.

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## **CHAPTER 3. Surface Fluorination of Sulfonated Poly(Arylene Ether Sulfone) Random Copolymers for Proton Exchange Membranes in Electrolysis of Water**

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### **3.1 Abstract**

Two high molecular weight sulfonated poly(arylene ether sulfone) random copolymers with an ion exchange capacity (IEC) of approximately 1.1 meq/g were synthesized for high temperature water electrolysis. These copolymers were cast into membranes via solution casting, acidified, and subsequently treated with fluorine gas at room temperature. Successful fluorination was confirmed via X-ray photoelectron spectroscopy (XPS). Investigation of membrane properties before and after surface treatment revealed that proton conductivity in the membrane improved after fluorination, while IEC remained constant with slightly decreased water uptake. Comparing membrane solubility before and after modification showed no difference in the ability of solvents such as DMAc, NMP, and DMSO to dissolve these random copolymers. In addition, oxidative stability testing in Fenton's reagent at 80 °C confirmed improved surface fluorinated membrane durability in harsh chemical environment.

### 3.2 Introduction

Electrochemical systems have been widely used as alternative sources of energy-generation.<sup>1-2</sup> In particular, the electrolysis of water is a highly efficient method for generating ultra-pure hydrogen gas.<sup>3</sup> The high purity product obtained from a proton exchange membrane (PEM) water electrolysis cell is then directly pumped to a hydrogen gas fuel cell for electricity generation. PEM water electrolysis has attracted increasing interest due to its ease of application, high current density, and high efficiency.<sup>4</sup> Water electrolysis cells that can perform at high temperature and high pressure are desired due to their rapid reaction kinetics and direct hydrogen gas storage in pressurized tanks.<sup>3</sup> Nafion, the state-of-the-art ionomer membrane, has been intensively studied for different applications including water electrolysis. However, we have previously shown that Nafion is not a good candidate for higher temperature and higher pressure applications due to its low glass transition temperature.<sup>5</sup> Nafion's low  $T_g$  results in excessive gas crossover and poor mechanical properties under wet conditions. Thus, hydrocarbon-based copolymers were investigated in this work as potential candidates for use in harsh electrolysis cell conditions.<sup>6</sup>

Smith and coworkers<sup>7</sup> synthesized high molecular weight block copolymers that were post sulfonated in concentrated sulfuric acid. The proton conductivity of these copolymers was very low at room temperature; at elevated temperatures the proton conductivity peaked at 0.63 mS/cm—a level that is still comparatively low compared to Nafion. However, these sulfonated copolymers demonstrated satisfactory properties in a water electrolysis cell due to their microphase separated morphologies, which resulted in improved proton conductivity at elevated temperatures. In addition, the block copolymers showed high efficiency and good mechanical integrity.

Surface fluorination has been used to modify hydrocarbon copolymer membranes to enhance their properties and lifespan in fuel cells and in gas separation applications due to the extreme reactivity of  $F_2$  gas with organic compounds.<sup>8-10</sup> Hu and coworkers<sup>11</sup> employed this approach with block copolymers in two forms, powders and membranes. The researchers confirmed that surface modification resulted in decreased water uptake, enhanced proton conductivity, and increased oxidative stability of the fluorinated membranes. Enhanced properties were attributed to the highly polar and hydrophobic nature of the C-F groups. A comparison of the two modified forms of hydrocarbon copolymers (powder and membrane) indicated that the powder form demonstrated superior properties due to higher powder surface area that resulted in higher degrees of fluorination in the polymer.

In the present study, we investigated the post fluorination of random copolymers of two different compositions and assessed their IECs. First, a hydroquinone-based copolymer was synthesized due to its exceptional mechanical properties, high proton conductivity, and low  $H_2$  gas permeability. Second, we synthesized a resorcinol-containing copolymer that demonstrated good mechanical properties, high proton conductivity and extremely low  $H_2$  gas permeability under wet conditions. These membranes were treated at room temperature with a  $F_2/N_2$  gas mixture at 10,000 ppm fluorine concentration. The surface-fluorinated copolymer films were characterized via X-ray photoelectron spectroscopy (XPS). Subsequently, important fundamental properties for water electrolysis including proton conductivity, water uptake, IEC, and oxidative stability of each modified copolymer were compared to that of the pristine copolymer.

### 3.3 Experimental

#### Materials

1,4- Benzenediol (hydroquinone, HQ) was provided by Eastman Chemical Company. 4,4'-Dichlorodiphenylsulfone (DCDPS) was provided by Solvay Advanced Polymers. 1,3-Benzenediol, resorcinol (RSC, >99%), was purchased from Sigma-Aldrich. Toluene was purchased from Sigma-Aldrich and was used as received. DCDPS, hydroquinone, and resorcinol were recrystallized from toluene and dried under vacuum at 120 °C prior to use. *N,N*-Dimethylacetamide (DMAc) was purchased from Sigma-Aldrich and distilled from calcium hydride before use. Calcium hydride (90–95%) was purchased from Alfa Aesar. 2-Propanol was obtained from Fisher Scientific and used as received. Sulfuric acid (98%) was purchased from Spectrum Chemical and used as received. Potassium carbonate was purchased from Aldrich and dried under vacuum at 180 °C prior to use. 3,3'-Disulfonated-4,4'-dichlorodiphenylsulfone (SDCDPS, >99%) was purchased from Akron Polymer Systems and was dried at 180 °C prior to use. DuPont's Nafion™ 212 was provided by Giner Electrochemical Systems. H<sub>2</sub>O<sub>2</sub> (30 wt%) and FeSO<sub>4</sub>·7H<sub>2</sub>O (>99%) were purchased from Sigma-Aldrich and used as received.

#### Synthesis of statistical copolymers

The synthesis and characterization of both random copolymers were carried out based on previously established methods.<sup>5</sup> Aromatic nucleophilic substitution step copolymerization was used to synthesize both series of disulfonated poly(arylene ether sulfone) copolymers. The synthesis of HQ-20 (where 20 represents 20% of the repeat units being disulfonated) was conducted as follows. HQ (36.33 mmol, 4.00 g), DCDPS (29.06 mmol, 8.3451 g), SDCDPS (7.265 mmol, 3.57 g), and DMAc (55 mL) were charged into a 250-mL three-neck round-bottom flask

equipped with a mechanical stirrer, condenser, nitrogen inlet, and Dean-Stark trap filled with toluene. The mixture was stirred in an oil bath at 150 °C until all the monomers completely dissolved.  $\text{K}_2\text{CO}_3$  (47.22 mmol, 6.52 g), and toluene (25 mL) were added to the flask. The reaction was refluxed for 4 h to azeotropically remove water from the system. Toluene was drained from the Dean-Stark trap, and the oil bath temperature was raised to 180 °C to remove residual toluene from the reaction. The reaction solution was stirred for 48 h to complete the polymerization, then allowed to cool to room temperature. After dilution of the resulting solution with DMAc (150 mL), it was filtered to remove the salt. The transparent solution was precipitated by combining with isopropanol under vigorous stirring. The white fibers were filtered and then stirred in boiling DI water for 4 h to remove any residual DMAc. The copolymer was filtered and dried at 120 °C under reduced pressure in a vacuum oven. Yield of this copolymer synthesis was 94%.

Synthesis of  $\text{HQ}_{0.75}\text{RSC}_{0.25}$ -19 copolymers: Synthesis of  $\text{HQ}_{0.75}\text{RSC}_{0.25}$  19 in which 19 represents 19% the repeat units being disulfonated was carried out as follows. HQ (27.24 mmol, 3.00 g), RSC (9.08 mmol, 1.00 g), DCDPS (28.33 mmol, 8.137 g), SDCDPS (8.0 mmol, 3.93 g), and DMAc (55 mL) were charged into a 250-mL three-neck round-bottom flask equipped with a mechanical stirrer, condenser, nitrogen inlet, and Dean-Stark apparatus filled with toluene. The mixture was stirred in an oil bath at 150 °C until the monomers completely dissolved.  $\text{K}_2\text{CO}_3$  (47.22 mmol, 6.52 g), and toluene (25 mL) were added to the flask. The reaction was refluxed for 4 h, the toluene was drained from the Dean-Stark apparatus, then the oil bath temperature was raised to 180 °C to remove residual toluene from the reaction. The solution was stirred for 48 h at 180 °C, then cooled to room temperature. The solution was diluted with DMAc (150 mL), then filtered to remove the salt. The transparent solution was precipitated into isopropanol. The white

fibers were filtered and stirred in boiling DI water for 4 h. The copolymer was then filtered and dried at 120 °C under reduced pressure in a vacuum. Yield of this copolymer synthesis was 95%.

#### Nuclear Magnetic Resonance Spectroscopy (NMR)

<sup>1</sup>H NMR analysis of the statistical copolymers was conducted on a Varian Unity Plus spectrometer operating at 400 MHz. The spectra of the copolymers were obtained from a 10% (w/v) solution in DMSO-d<sub>6</sub>.

#### Size Exclusion Chromatography (SEC)

The molecular weight and polydispersity of the copolymers were obtained using SEC. The mobile phase was DMAc distilled from CaH<sub>2</sub> containing dry LiCl (0.1 M). The column set consisted of 3 Agilent PLgel 10-mm Mixed B-LS columns 300 \* 7.5 mm (polystyrene/divinylbenzene) connected in series with a guard column having the same stationary phase. The columns and detectors were maintained at 50 °C. An isocratic pump (Agilent 1260 infinity, Agilent Technologies) with an online degasser (Agilent 1260), autosampler and column oven were used for mobile phase delivery and sample injection. A system of multiple detectors connected in series was used for the analyses. A multi-angle laser light scattering detector (DAWN-HELEOS II, Wyatt Technology Corp.), operating at a wavelength of 658 nm, a viscometer detector (Viscostar, Wyatt Technology Corp.), and a refractive index detector operating at a wavelength of 658 nm (Optilab T-rEX, Wyatt Technology Corp.) provided online results. The system was corrected for interdetector delay and band broadening using a 21,000 Da polystyrene standard. Data acquisition and analysis were conducted using Astra 6 software from Wyatt Technology Corp. The system was validated by monitoring the molar mass of a known

molecular weight polystyrene sample via light scattering. The accepted variance of the 21,000 Da polystyrene standard was defined as 2 standard deviations (11.5% for  $M_n$  and 9% for  $M_w$ ) derived from a set of 34 runs. Specific refractive index values were calculated based on the assumption of 100% recovery.

#### Membrane casting and characterization

The copolymers in their salt form (0.6 g) were dissolved in DMAc (12 mL), and then filtered through a 0.45  $\mu\text{m}$  Teflon syringe filter. After sonication for ~15 min, the solutions were cast onto 4"×4" clean glass substrates and dried under an infrared lamp at 50-60 °C for 8 h. Afterwards, the membranes were placed in a vacuum oven under reduced pressure at 120-140 °C for 4 h. The membranes were soaked in water for an additional 24 h to remove residual solvent and to delaminate them from the glass plates. The membranes were converted to their acid form by boiling in 0.1 M  $\text{H}_2\text{SO}_4$  for 2 h. They were then boiled in DI water for 2 h to remove residual acid.

#### Ion Exchange Capacity (IEC)

Dry membranes in their acid form were weighed, then soaked in 1 M NaCl solution for 48 h to convert them to their salt form and eliminate HCl. Each membrane solution was titrated with 0.1 N NaOH solution. The IEC of each membrane in units of meq/g of dry membrane was calculated from Equation 3.1

$$IEC = \frac{V \cdot N}{M} \times 1000 \quad (3.1)$$

### Water uptake at room and elevated temperatures

Water uptake of the membranes were determined gravimetrically. First, the membranes in their acid form were dried at 120 °C under vacuum for 24 h and weighed. The membranes were then soaked in water at room temperature for 48 h. The wet membranes were removed from the liquid water, blotted dry to remove surface droplets, and quickly weighed. For high temperature water uptake, the previously wet membranes were placed in boiling water for at least 4 h. The hot, wet membranes were then removed from the boiling water, immediately blotted dry to remove surface droplets, and quickly weighed. The water uptake of the membranes was calculated according to Equation 3.2, where mass dry and mass wet refer to the masses of the dry and the wet membranes, respectively.

$$Water\ Uptake = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100 \quad (3.2)$$

### Surface fluorination

Membranes in this study were surface fluorinated in their acid form in an aluminum chamber at room temperature. Each 4" × 4" membrane with a thickness of approximately 40-50 μm was treated in diluted fluorine gas with a concentration of 10,000 ppm (1%) for 30 min.

### X-ray photoelectron spectroscopy (XPS) analysis

X-ray photoelectron spectroscopy analysis was performed via an established approach.<sup>11</sup> Specifically, the analyses were carried out with an ESCALAB 250 (Thermo Fisher Scientific). The radiation was from an Al monochromatized source (280 eV) under atmosphere pressure. A 0.1

$\mu\text{m}^2$  area was observed on the samples. For these samples, high resolution spectra were recorded. The survey measurement was accomplished with five sweep cycles.

#### Oxidative stability

The chemical stability of each hydrocarbon-based copolymer was compared in a Fenton's reagent test.<sup>11-12</sup> Fenton reagent was prepared from  $\text{H}_2\text{O}_2$  (10 mL) in DI water (100 mL) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (0.1 g). A vial was filled with the Fenton reagent and heated to 80 °C. Then a sample of a 1 cm  $\times$  3 cm membrane was completely submerged into the preheated Fenton solution. The onset of degradation was recorded as the point at which each membrane began to change color from pale brown to dark brown.

#### Proton conductivity ( $\sigma$ )

The conductivity test stand consisted of a house-made four-point probe assembly with platinum electrodes and a Wayne-Kerr LCR meter. The membrane was clamped between the probe assemblies and placed in the water bath at room temperature. The water bath was heated steadily to 100 °C and AC impedance measurements were taken at temperatures of 30, 60, 90, and 100 °C. Using the dimensions of the membrane, the conductivity of the ionomer in S/cm was calculated based on Equation 3.4

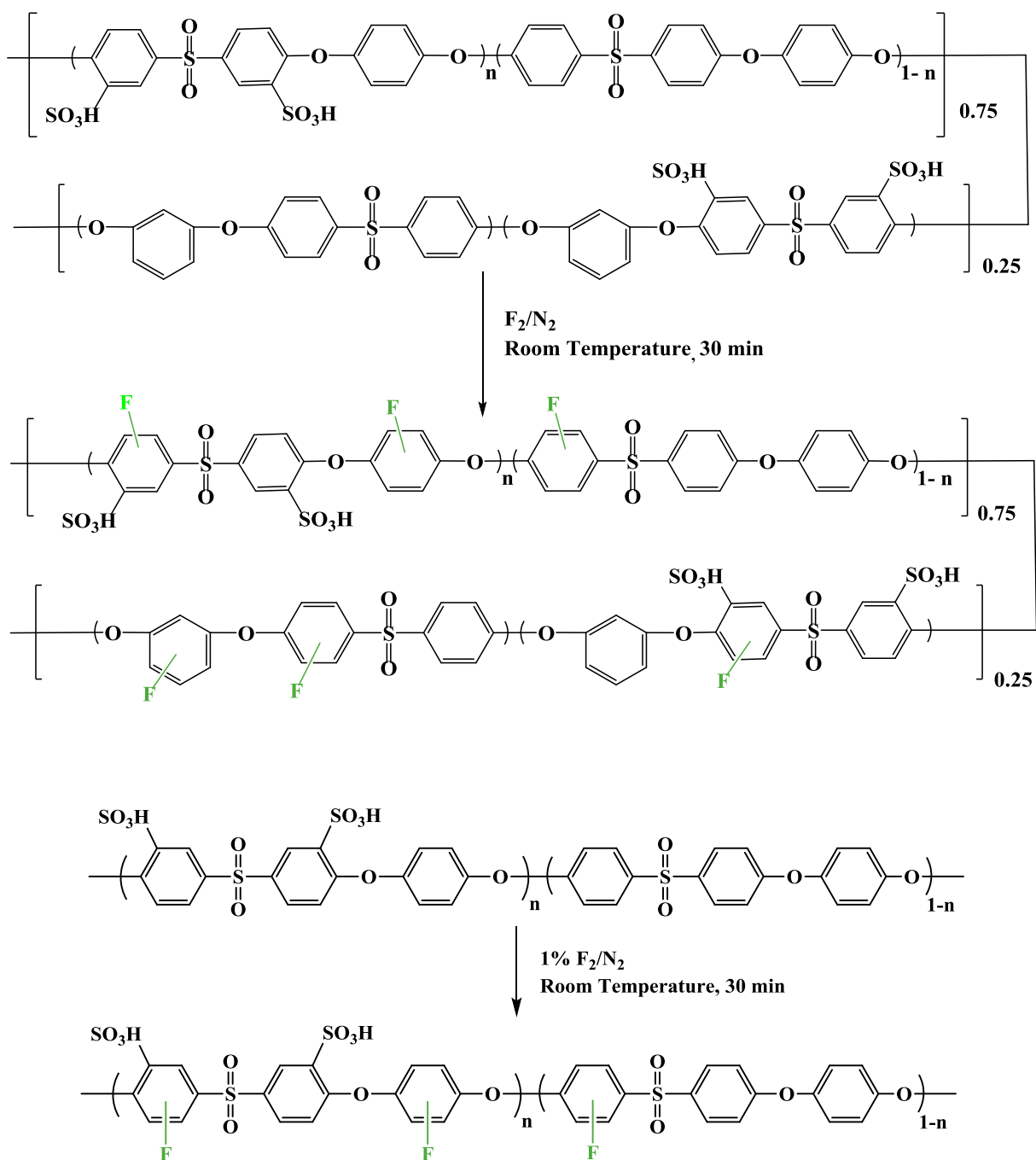
$$\sigma = \frac{L}{R \cdot A} \quad (3.4)$$

where  $\sigma$  is the conductivity, L is the length between electrodes, R is the membrane resistance, and A is the cross-sectional area available for proton transport.

### 3.4 Results and Discussion

#### Pristine copolymer synthesis and their surface fluorination

The synthesis and characterization of the pristine copolymers were reported previously in our group.<sup>13-15</sup> The HQ 20 and HQRSC 19 copolymers assessed in this investigation had IECs of 1.12 and 1.08 meq/g, respectively. When the membranes were treated with fluorine gas, weak C-H bonds of the copolymers on the surface were substituted with highly stable and strong C-F bonds due to the extremely high reactivity of the fluorine gas.<sup>16-17</sup> The polymer modification procedure and structures of the final products are shown in Scheme 3.1 for HQ 20 and HQRSC 19.



**Scheme 3.1** Pristine copolymers and surface fluorination process in HQRSC 19 (top) and HQ 20 (bottom)

$^1\text{H}$  NMR findings associated with the pristine copolymer did not change after fluorination, which indicates that the fluorination occurs heterogeneously and only on the surface of the copolymer—and thus was not detectible via NMR.<sup>17-18</sup> However, the presence of fluorine atoms on the surface of the membranes was confirmed via the characteristic peak at 689 eV in XPS spectra. XPS spectra of both modified copolymers are shown in Figure 3.1.

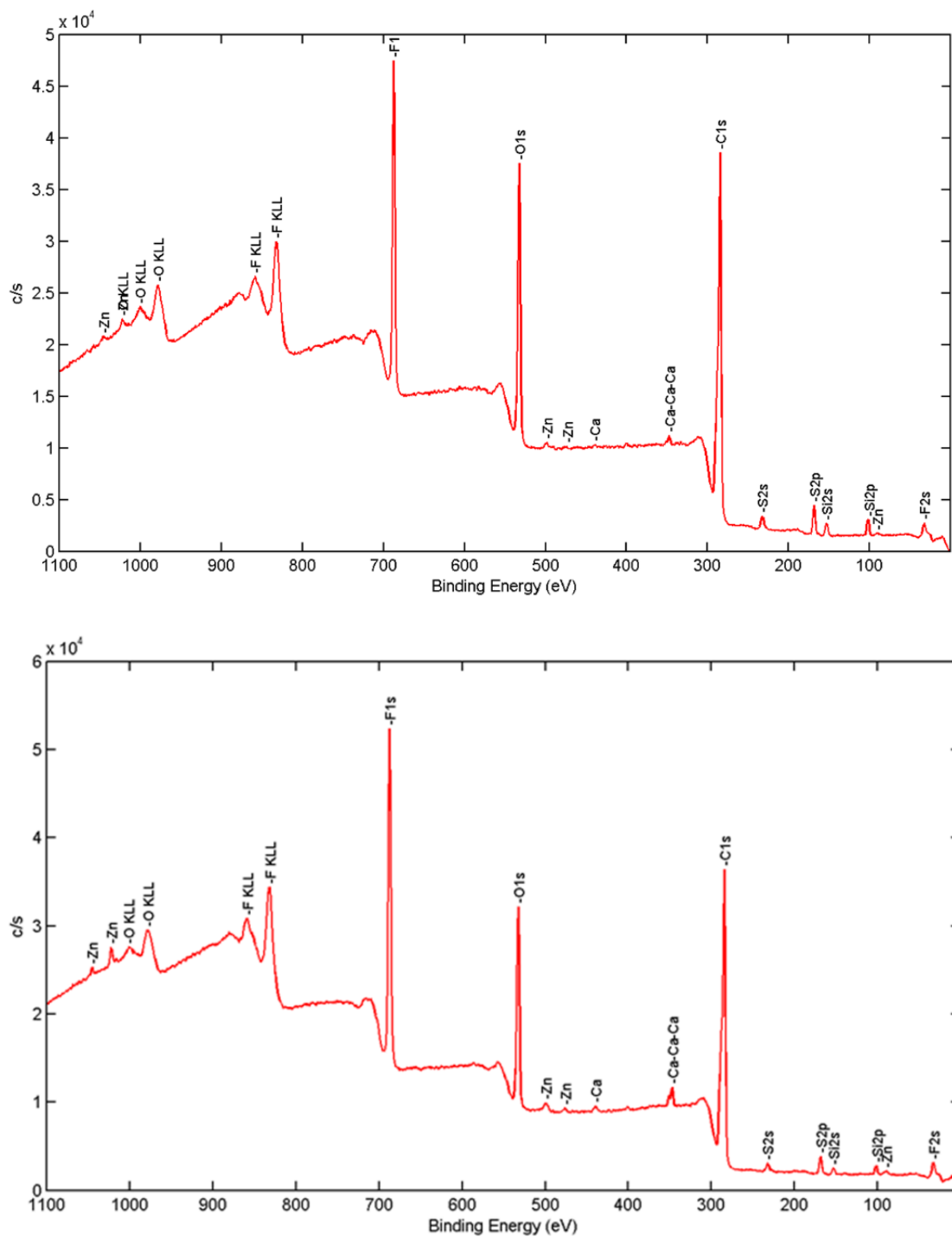


**Figure 3.1** XPS spectra for HQ 20 (top) and HQRSC 19 (bottom) confirm the occurrence of the modification on the membrane surface

Based on XPS analysis it was possible to measure levels of surface modification and fluorine content. Table 3.1 presents the surface atomic percentages in each fluorinated copolymer.<sup>8</sup>

**Table 3.1** Atomic percentage in each fluorinated copolymer

| Fluorinated polymer | Atom (%)        |                 |                 |                 |
|---------------------|-----------------|-----------------|-----------------|-----------------|
|                     | C <sub>1s</sub> | O <sub>1s</sub> | S <sub>2p</sub> | F <sub>1s</sub> |
| <b>F-HQ 20</b>      | <b>64.1</b>     | <b>18.4</b>     | <b>1.5</b>      | <b>14.1</b>     |
| <b>F-HQRSC 19</b>   | <b>63.6</b>     | <b>16.2</b>     | <b>1.2</b>      | <b>17.2</b>     |

As illustrated in Table 3.1 the fluorine content in each sample varied. The ratio of F/C was assessed at 22% and 27% in the HQ 20 and HQRSC 19 copolymers, respectively. It must be noted, however, that the difference in the fluorine content on the membrane surface was insignificant.

#### IEC and water uptake properties

The degree of disulfonation represents an important factor defining the hydrophilicity of the copolymers and their morphology. It is known that as the ion exchange capacity increases in a polymer, its water uptake also increases. For these copolymers, this leads to a morphological transition to co-continuous hydrophilic domains as the level of disulfonation is increased.<sup>19</sup> IEC assessments for the modified copolymers did not show any difference between the pristine polymer and the modified copolymers, confirming that room temperature fluorination at 1% concentration of F<sub>2</sub> in N<sub>2</sub> had no effect on the sulfonic acid groups in the membranes. However, the water uptake levels in these copolymers did change before and after fluorination, as shown in Table 3.2.

**Table 3.2** Water uptake of the copolymers before and after fluorination

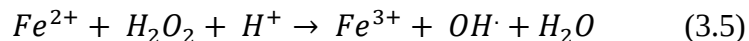
| Polymer samples | Water uptake at room and elevated temperature |         |
|-----------------|-----------------------------------------------|---------|
|                 | 30 °C                                         | 80 °C   |
| HQ 20           | 27 ±0.0                                       | 40 ±0.0 |
| HQRSC 19        | 25 ±1.1                                       | 41 ±1.0 |
| F-HQ 20         | 25.3 ±0.9                                     | 38 ±1.7 |
| F-HQRSC 19      | 20.7 ±0.6                                     | 32 ±0.6 |

Specifically, when water uptake levels of the copolymers were assessed prior to fluorination, it was revealed that the HQ 20 copolymer was more hydrophilic and had a higher tendency to absorb water in comparison to the HQRSC 19. We attribute this difference to the slightly higher IEC of HQ 20 when compared to HQRSC 19. At elevated temperatures, however, we observed an opposite trend due to the presence of the *m*-substituted resorcinol comonomer in the polymer composition. Despite the lower IEC for HQRSC 19, the incorporation of a *m*-substituted comonomer disrupts chain stiffness and allows more water molecules to fit in between the polymer chains. In addition, when the  $T_g$  levels of the wet membranes were assessed, it was revealed that the HQRSC 19 membrane had a lower  $T_g$ , which correlates to higher chain flexibility at elevated temperatures.

After fluorination, however, we confirmed that water uptake levels were influenced principally by the degree of fluorination in the copolymers—rather than by their ion exchange capacity. As the fluorine content of the copolymers increased, the corresponding membranes become more hydrophobic due to the hydrophobicity of the fluorinated structures. Thus, HQRSC 19 showed suppressed water uptake.

### Oxidative stability of the copolymers

A proton exchange membrane requires high mechanical, thermal and chemical stability at high pressure and high temperature. At such extreme conditions, there are corrosive species such as radicals that are able to degrade the polymer chains. Thus, high chemical stability is of great importance for these systems. One method for simulating the oxidative stability of a copolymer against harsh radicals is by treating the copolymer at high temperature with Fenton's reagent, which is a mixture of hydrogen peroxide and ferrous ion in aqueous medium. According to Equation 3.5, a Fenton reagent produces hydroxyl radicals that can react with the polymer backbone.<sup>20</sup>



When membranes were immersed in Fenton's reagent at 80 °C, the onset of degradation for non-treated copolymers was surprisingly early. For example, HQRSC 19 began to degrade after only 33 min, and HQ 20 degraded after 34 min. However, the degradation of surface-fluorinated membranes was delayed, which points to an extended lifespan in Fenton's reagent. Specifically, F-HQ 20 began to degrade after 56 min, while HQRSC 19 started to fail after 67 min. This extended stability of the modified membranes supports the premise that the fluorination reaction occurred primarily on the membrane surface.

### Proton conductivity of copolymers

Our investigation of the proton conductivity of these copolymers confirmed the expected trend for proton transport through surface-fluorinated membranes. In the surface-fluorinated

copolymers, parameters of interest such as the degree of surface fluorination and water uptake affect proton conductivity. This investigation confirmed that the proton conductivity of the fluorinated membranes was influenced by the hydrophobic and highly electron withdrawing characteristics of the fluorinated species, such that the improved acidity of the  $\text{--SO}_3\text{H}$  groups leads to high proton conductivity in surface-modified membranes.<sup>8, 11</sup> At elevated temperatures, however, the proton conductivity of the modified polymers increased due to increased water in the membrane and morphological rearrangement on the membrane surface.<sup>8</sup> Proton conductivity results for both copolymers were compared to that of the pristine polymers, as documented in Table 3.3.

**Table 3.3** Proton conductivity comparison of pristine copolymer vs. surface modified membranes in liquid water

| Temperature<br>(°C) | $\sigma$ (S/cm) |            |       |         |
|---------------------|-----------------|------------|-------|---------|
|                     | HQRSC 19        | F-HQRSC 19 | HQ 20 | F-HQ 20 |
| 30                  | 0.08            | 0.07       | 0.06  | 0.07    |
| 60                  | 0.12            | 0.12       | 0.09  | 0.14    |
| 90                  | 0.16            | 0.18       | 0.12  | 0.21    |

Comparing pristine HQRSC 19 and F-HQRSC 19 shows that at room temperature, the proton conductivity of the fluorinated polymer was slightly lower in comparison to the pristine copolymer. This slightly reduced conductivity is attributed to the hydrophobicity of the fluorinated species, which repels water molecules and decreases the membrane water uptake. However, at elevated temperatures and when water uptake was increased, proton conductivity increased. Conductivity improvements for the F-HQRSC 19 copolymer is more conspicuous in comparison

to the pristine copolymer due to both improved morphology and enhanced water uptake.<sup>8</sup> HQ 20 and F-HQ20 membranes followed the same water uptake trend as the HQRSC copolymers.

A comparison study of the F-HQ 20 and F-HQRSC 19 copolymers revealed that the rate of increased proton conductivity occurred more rapidly in the F-HQ 20 compound in comparison to the F-HQRSC 19 copolymer. We attribute this difference to the level of fluorine content, which was lower in the F-HQ 20 copolymer. Thus, the amount of fluorine on the surface of the F-HQ 20 membrane was large enough to alter the surface morphology, thereby enabling the membrane to absorb sufficient amounts of water for proton transfer. By contrast, the surface fluorination of the F-HQRSC 19 membrane was sufficiently dominant to impede the excessive water uptake by the membrane.

### 3.5 Conclusions

Modifying a copolymer by surface fluorination represents a useful strategy for improving the stability of the material against chemical degradation. For this investigation, two hydrocarbon linear copolymer membranes were surface fluorinated with low concentrations of fluorine in an F<sub>2</sub>/N<sub>2</sub> gas mixture at room temperature. Even at low modification levels, the water transport properties of the ion-conducting membranes improved after surface fluorination due to the hydrophobic nature of fluorinated species. The incorporation of strong C-F bonds into hydrocarbon copolymers was shown to promote the chemical stability of the modified membrane in harsh Fenton reagent solutions. The proton conductivity of the surface-modified membranes increased as a result of increased water uptake. Moreover, improved proton conductivity and chemical stability—coupled with possible decreased gas permeability—resulted in performance enhancements of the surface fluorinated copolymers in high temperature water electrolysis cells.<sup>8-</sup>

<sup>10</sup> Further investigations of H<sub>2</sub> gas permeability through surface-modified membranes under fully-hydrated conditions will be reported to evaluate the applicability of surface-modified polymers for hydrogen gas production via water electrolysis.

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## CHAPTER 4. Multiblock Poly(arylene ether nitrile) Disulfonated Poly(arylene ether sulfone) Copolymers for Proton Exchange Membranes: Part 2 Electrochemical and H<sub>2</sub>/Air Fuel Cell Analysis

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### 4.1 Abstract

This manuscript represents a second part to the investigation of multiblock disulfonated poly(arylene ether sulfone) and poly(arylene ether nitrile) copolymers. In Part 1 it was shown that the multiblock copolymers had high ion exchange capacities (IECs), phase separation, strong membrane integrity and moderate water uptake. In this second part, the electrochemical properties of the membranes are presented and compared against those of the perfluorosulfonated Nafion 212 membrane. The disulfonated poly(arylene ether sulfone) and poly(arylene ether

nitrile) multiblock copolymer membranes were fabricated into membrane electrode assemblies (MEAs), and tested in four different humidity environments at the electrodes (95/95%, 100%/50%, 50%/50%, and 75%/25%). The membranes vastly outperformed Nafion<sup>®</sup> at high levels of relative humidity, and at lower humidities had comparable properties to the perfluorosulfonated membrane. The cell testing of the MEAs agreed well with the relative humidity conductivity results obtained for the membranes.

## 4.2 Introduction

In part one of this project, a series of multiblock copolymers based upon a partially fluorinated poly(arylene ether nitrile) hydrophobic segment was presented and characterized.<sup>1</sup> The hydrophilic phase consisted of two different disulfonated segments, utilizing the strong success and results that had been observed previously with these types of hydrophilic-hydrophobic multiblock copolymers.<sup>1-9</sup> Most of these systems incorporated the hydrophilic “SDCDPS” (sulfonated dichloro diphenyl sulfone) monomer which is a pre-disulfonated sulfone moiety that can be used to directly synthesize random copolymers or used in two steps to form multiblock copolymers.<sup>10-12</sup> Research has shown the stability of the disulfonated random copolymers in accelerated studies.<sup>13-14</sup> However, very little data has been reported about assembly of the multiblock copolymer membranes in electrode assemblies (MEAs) and subsequent fuel cell testing for these systems.<sup>15-18</sup>

In a study by Takimoto *et al.*, it was shown that the conductivities were greatly improved when the multiblock copolymers were used over the random copolymers with the same composition and charge density.<sup>17</sup> While the difference in current densities with voltage between the random and multiblock copolymers were small at high humidities, the performance of the

multiblock copolymer membranes were vastly superior at low relative humidities. This effect was found to be partially associated with the phase separated structure, which allowed for higher conductivity and reduced water uptake for multiblock copolymers over the analogous random copolymers. The lamellar structure allows for well-connected aqueous channels for proton transport at low levels of humidity. In addition, the surrounding hydrophobic phase limits the swelling of the hydrophilic phase, producing membranes with less swelling and higher conductivity than analogous random copolymers with the same charge density. Therefore, robust and mechanically sound membranes with high levels of charge density can be produced.

However, for multiblock copolymers with longer block lengths, the large amount of surface area occupied by the hydrophobic phase can lead to poor connectivity at the electrode interface.<sup>17</sup> Thus, the partially fluorinated hydrophobic phase in this work incorporated polar benzonitrile groups to improve connectivity with the electrodes, while simultaneously maintaining phase separation by introducing the fluorinated component.<sup>19-20</sup> In fact, we previously reported good direct methanol fuel cell (DMFC) performance utilizing a similar system.<sup>15</sup> Thus, we aim to improve conductivity at low relative humidity for high temperature/low RH, H<sub>2</sub>/Air fuel cells. This manuscript reports the electrochemical properties of the poly(arylene ether nitrile) containing multiblock copolymers. The multiblock copolymers were tested over a range of different pressures and relative humidities and compared against the industrial standard Nafion<sup>®</sup> 212 membrane.

### 4.3 Experimental

#### Membrane preparation and acidification

The potassium sulfonate salts of the multiblock copolymers were dried at 150 °C under vacuum for 24 h, then they were dissolved in DMAc (~5% w/v), and the solutions were filtered

through a 0.45  $\mu\text{m}$  Teflon syringe filter. Each solution was cast onto a dry, clean glass substrate and the film was dried for 24 h under an infrared lamp at  $\sim 80^\circ\text{C}$ . The membranes were then annealed under vacuum at  $220^\circ\text{C}$  for 8 h, (about  $30^\circ\text{C}$  higher than the  $T_g$  of the 6FPAEB blocks and below the  $T_g$  of the hydrophilic block).<sup>1</sup> The membranes were acidified in boiling 0.5 M sulfuric acid for 2 h, followed by boiling in DI water for 2 h. Membranes were dried by heating lightly ( $< 50^\circ\text{C}$ ) between two glass plates to obtain a flat and wrinkle free membrane.

#### Water uptake

The water uptake of all membranes was determined gravimetrically. The membranes were equilibrated in DI water at room temperature for 2 days after acidification. Wet membranes were removed from DI water, blotted dry to remove surface droplets, and quickly weighed. The membranes were dried at  $120^\circ\text{C}$  under vacuum for 24 h and re-weighed. The water uptake of the membranes by weight was calculated according to Equation 4.1, where  $W_{\text{dry}}$  and  $W_{\text{wet}}$  refer to the mass of the dry and wet membrane, respectively.

$$\text{Water Uptake} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} * 100 \quad (4.1)$$

The water uptake by volume was calculated by assuming that the absorbed water had a density of one and multiplying the wt % of water uptake by the density of the multiblock copolymers,  $1.3 \text{ g/cm}^3$ , and 2.0 for the Nafion membrane (Equation 4.2).<sup>15</sup>

$$\text{Water Uptake (vol \%)} = \text{Water Uptake (wt\%)} \times \text{membrane density} \quad (4.2)$$

## Ion Exchange Capacity (IEC)

$^1\text{H}$  NMR analyses were conducted on a Varian Unity Plus spectrometer operating at 400 MHz to measure the IEC by weight ( $\text{IEC}_w$ ) in units of meq/g of the multiblock copolymers. These were obtained from a 10% (w/v) 1 mL solution in  $\text{DMSO-d}_6$ . The IEC by volume ( $\text{IEC}_v$ ) in units of meq/cm<sup>3</sup> of the dry state was calculated by using Equation 4.3

$$\text{IEC}_v(\text{dry}) = \text{density} \times \text{IEC}_w \quad (4.3)$$

The IEC by volume of the wet state was then calculated by Equation 4.4

$$\text{IEC}_v(\text{wet}) = \text{IEC}_v(\text{dry}) / (1 + 0.01 \text{water uptake (vol \%)}) \quad (4.4)$$

## Proton conductivity

A controlled humidity-temperature oven (ESPEC, SH240) was used to measure proton conductivity as a function of relative humidity of the membranes. Samples were cut and thickness of the membranes were measured in the wet state with a micrometer. Membranes were equilibrated at 95% relative humidity overnight prior to testing. Samples were equilibrated at each new humidity level for 30 min prior to measuring the proton conductivity. The range was from 95 to 30% relative humidity. To account for changes in sample thickness at different humidities the wet thickness and dry thickness were measured and these were extrapolated as a function of relative humidity. The conductivities of the samples were first measured starting from 95% relative humidity, then systematically decreased to 30% relative humidity. The oven temperature was held constant at 80 °C. Conductivities were measured in-plane with a four electrode configuration. A

Solartron (1252 + 1287) impedance/gain-phase analyzer over the frequency range of 10 Hz to 1 MHz was used for the measurements following a previously reported method.<sup>21</sup> The conductivity was calculated by using Equation 4.5

$$\sigma = \frac{L}{R.S} \quad (4.5)$$

where  $\sigma$  (S/cm) is proton conductivity,  $L$  (cm) is the distance between the two electrodes,  $R$  ( $\Omega$ ) is the resistance of the membrane and  $S$  (cm<sup>2</sup>) is the surface area available for proton transport through the membrane.

#### Fuel cell testing

Tanaka Pt/C (Pt: 46.7 wt%) was used as the catalyst for both the anode and cathode. Tanaka Pt/C (0.5 g) was mixed with 3.4 g of a 5 wt % commercial Nafion<sup>®</sup> dispersion (dispersion is isopropanol/water mixture from Ion Power) and 2 g of propanol. The ink mixture was subjected to ultrasonic treatment for 1 h, then it was sprayed onto both sides of the membranes. Both the anode and cathode had a platinum loading of 0.3 mg/cm<sup>2</sup> with 25 wt% Nafion<sup>®</sup> and 75 wt% Pt/C. The resultant MEA was assembled into a single 25 cm<sup>2</sup> cell from Fuel Cell Technology. The cell hardware consisted of triple serpentine flow-field plates for both anode and cathode under co-current flow. In the experiments the AvCarb<sup>®</sup> series EP40T material was employed as a gas diffusion layer (GDL). Silicone rubber-coated fiberglass fabric (SCF1007), with a thickness of 178  $\mu$ m (7 mil) from Saint Gobain was used as a gasket for assembly of the cell. All of the bolts were equally tightened at 50 in-lb to provide suitable compression force and to prevent leaks. The experiments were conducted using a fuel cell test station model 850e from Scribner and Associates

Inc. High purity hydrogen (99.997%) and compressed air were supplied to the anode and cathode, respectively. The fuel cell was conditioned for 12 h prior to experiments. For the conditioning or breaking process, the anode and cathode humidity was set at 95 and 80% relative humidity at 80 °C with the cell potential set at 0.6 V. The current was significantly increased during the first 10 h with stability achieved after 11-12 h.

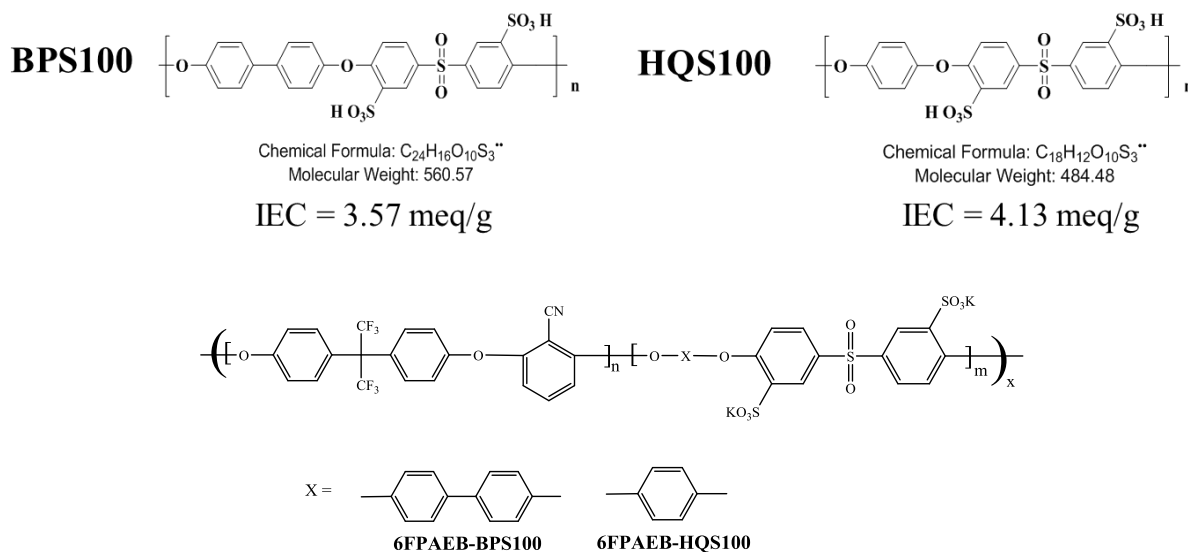
Polarization curves were performed under four different relative humidity conditions (i.e., 95/95%, 100/50%, 50/50%, and 75/25%) at a cell temperature of 80 °C with 101 kPa system pressure. The stoichiometry number was set to 1.5 at the anode and 2.0 at the cathode. After finishing the polarization curve, the cell was set to the next humidity condition and held for 1 h to stabilize the fuel cell. The cell potential and current were collected during the polarization curve, and high frequency resistance was collected during the experiment at 1000 Hz.

#### **4.4 Results and Discussion**

##### **Preparation and characterization of multiblock copolymer membranes**

The synthesis and membrane preparation of the multiblock copolymers were detailed in part one of this manuscript.<sup>1</sup> The structures are shown in Scheme 4.1, which includes two different disulfonated hydrophilic phases. The hydrophilic phases differed in the bisphenol species used in combination with the disulfonated monomer (SDCDPS). The nomenclature for the hydrophilic block that contained biphenol was “BPS100” and the second species which used hydroquinone was named “HQS100”. By using hydroquinone instead of biphenol, the charge density was increased, as there was one less aromatic ring but still two sulfonic acid groups present. Each of these hydrophilic species were combined with a partially fluorinated poly(arylene ether benzonitrile) hydrophobic block to form multiblock copolymers. The hydrophobic species was

given the name hexafluoropropane poly(arylene ether benzonitrile) (6FPAEB), thus making the name of the multiblock copolymers as 6FPAEB-BPS100 and 6FPAEB-HQS100. It has been previously shown that high conductivity and charge density could be achieved with the 6FPAEB systems, while maintaining moderate water uptakes and good mechanical properties.<sup>1, 20, 22</sup> The hexafluoropropane poly(arylene ether benzonitrile) multiblock copolymers were shown to have higher densities and conductivities, along with lower water uptakes than poly(arylene ether ketone) and poly(arylene ether sulfone) hydrophobic phases.<sup>15</sup> The proposed reason for the differences in conductivities was attributed to better phase separation between the hydrophilic and hydrophobic phases when utilizing the 6FPAEB segment in the multiblock copolymers.



**Scheme 4.1** Structures of multiblock hexafluoropropane poly(arylene ether benzonitrile) disulfonated poly(arylene ether sulfone) copolymers

Membrane properties of the multiblock 6FPAEB copolymer membranes are shown in Table 4.1 with volume and water absorption taken into consideration to give the IEC<sub>V</sub> (wet) and IEC<sub>V</sub> (dry) of the membranes. Despite fairly high IECs of the multiblock copolymers (1.53 -1.80 meq/g), the 6FPAEB based multiblock copolymers still only retained moderate water uptake (44-

84 wt%). This is essential to avoid excessive swelling that compromises the mechanical durability of the membrane and that decreases conductivity due to charge dilution. The block length seemed to have little effect on the  $IEC_v$  (wet) for the biphenol based 6FPAEB multiblock copolymers, with all of the membranes having similar values. This mirrors the results for water uptake of the hydrophilic-hydrophobic multiblock copolymers, with no dependence on block length being observed.

**Table 4.1** Properties of 6FPAEB-BPSH and 6FPAEB-HQSH multiblock copolymers that were tested for electrochemical properties

| <b>6FPAEB-BPSH</b><br>(Block Length) | $IEC_w$<br>(meq/g) <sup>a</sup> | $IEC_v$ (dry)<br>(meq/cm <sup>3</sup> ) <sup>b</sup> | $IEC_v$ (wet)<br>(meq/cm <sup>3</sup> ) <sup>b</sup> | Water Uptake<br>(wt %) <sup>c</sup> | Water Uptake<br>(vol %) <sup>b,c</sup> |
|--------------------------------------|---------------------------------|------------------------------------------------------|------------------------------------------------------|-------------------------------------|----------------------------------------|
| 7K-7K                                | 1.57                            | 2.04                                                 | 1.28                                                 | 46                                  | 60                                     |
| 9K-9K                                | 1.53                            | 1.99                                                 | 1.27                                                 | 44                                  | 57                                     |
| 13K-13K                              | 1.63                            | 2.12                                                 | 1.28                                                 | 51                                  | 66                                     |
| 15K-15K                              | 1.57                            | 2.04                                                 | 1.28                                                 | 46                                  | 60                                     |
| <b>6FPAEB-HQSH</b>                   |                                 |                                                      |                                                      |                                     |                                        |
| 5K-5K                                | 1.69                            | 2.20                                                 | 1.38                                                 | 46                                  | 60                                     |
| 7K-7K                                | 1.80                            | 2.34                                                 | 1.28                                                 | 64                                  | 83                                     |
| 9K-9K                                | 1.65                            | 2.15                                                 | 1.03                                                 | 84                                  | 109                                    |
| 15K-15K                              | 1.67                            | 2.17                                                 | 1.10                                                 | 75                                  | 98                                     |
| <b>Nafion® 212</b>                   | 0.91                            | 1.82                                                 | 1.26                                                 | 22                                  | 44                                     |

a. Measured from <sup>1</sup>H NMR in the acid form

b. Values were obtained for membranes in the acid form and a density of 1.3 g/cm<sup>3</sup> was used for the multiblock copolymers and 2.0 g/cm<sup>3</sup> for Nafion

c. Obtained for the acid form of the membrane

However, there was a significant change in the  $IEC_v$  (wet) and  $IEC_v$  (dry) for copolymers that contained hydroquinone in the hydrophilic phase. Part one described membranes with the

more polar hydroquinone-containing hydrophilic phase (HQS100) as having better phase separation relative to those that contained biphenol.<sup>1</sup> This morphology likely also contributes to some of the differences observed in the membrane properties between the biphenol and hydroquinone species that are shown in Table 4.1. Unfortunately, at longer block lengths the hydroquinone membranes swelled significantly more than with the lower block lengths or the biphenol-based membranes. Thus, the IEC<sub>v</sub> (wet) significantly dropped for the 9K-9K and 15K-15K 6FPAEB-HQSH multiblock copolymers.

#### Proton Conductivity Testing of the Membranes as a Function of Relative Humidity

Due to the excessive swelling observed with the longer block lengths of the HQSH multiblock copolymers, these membranes were not tested further and were not considered suitable as proton exchange membranes. However, the lower block length hydroquinone and all of the biphenol multiblock copolymers offered very promising systems and warranted further investigation. Therefore, the proton conductivities and the fuel cell performance of these membranes as a function of relative humidity were investigated.

For testing in different relative humidity environments, the method used for these measurements differed slightly from the method used in the past by our group to measure relative humidity performance. Previously, the membrane was removed from the controlled-humidity oven and the thickness was measured at each humidity level. However, this method was controversial due to the fact that opening the oven most likely perturbed the equilibrium present in the oven. Thus, in the method presented herein, the membranes were not removed from the oven during the entire experiment. However, the thickness of the membrane still needed to be accounted for because at lower humidities the membrane swelled less than at higher humidity levels. To account

for the thickness variation, thickness in the wet and dry states were used to simulate the thickness at 30% and 95% relative humidity. The values were then extrapolated to estimate the thickness at the other relative humidity levels. The results of these tests are shown in Figure 4.1.

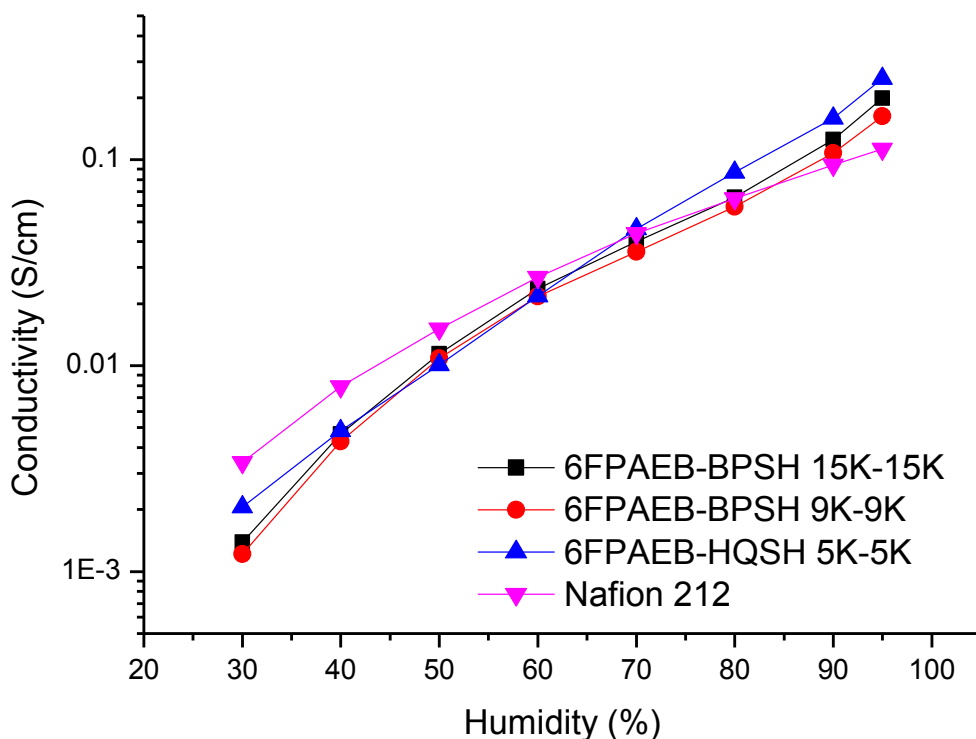


**Figure 4.1** Proton conductivity as a function of relative humidity from high to low humidity for the multiblock copolymer membranes compared against Nafion<sup>®</sup> 212 at 80 °C

All of the multiblock copolymers showed similar performance in the conductivity tests conducted at different relative humidities. The hydroquinone membrane had slightly better performance than the biphenol based membranes, which was more pronounced at the very high and very low humidity ranges. There was essentially no difference in performance among the biphenol based membranes with different block lengths. The increased conductivity in the hydroquinone species was likely a result of better phase separation brought on by the increased

charge density of the hydrophilic phase in the multiblock copolymer membrane. However, as all of these 6FPAEB membranes had conductivities at 30% RH relatively close to that of Nafion<sup>®</sup> 212, (while most disulfonated polysulfone membranes do not have conductivities within an order of magnitude relative to the Nafion<sup>®</sup> 212 membranes),<sup>10-12</sup> the results were considered good. Thus, the highly phase separated nature of the 6FPAEB multiblock copolymers leads to substructures that allow good proton transport even at very low RH.

Fuel cell testing of the membranes as a function of relative humidity

The 13K-13K 6FPAEB-BPSH biphenol-based multiblock copolymer was chosen for fuel cell testing because it had a high conductivity and charge density, thereby offering a good combined choice of IEC and block length. It has been shown previously that very long block lengths can lead to a poor membrane/electrode interface, due to a large portion of the membrane surface being hydrophobic.<sup>15, 17</sup> This is attributed to the thermodynamic driving force for a hydrophobic phase to segregate on the air surface of films. On the other hand, long block lengths are needed to obtain the phase separation that leads to high conductivities.<sup>15, 17-18</sup> In the future, fuel cell testing can be extended to a wide range of block lengths and to the hydroquinone based membranes to elicit a better understanding of structure-property relationships including ion concentration, block length, and membrane performance.

The membranes were tested over a range of conditions that included both high and low humidities. The high humidity tests were conducted at 95%/95% and 100%/50% RH, (the numbers refer to the inlet humidity of the anode and cathode respectively), and low humidity tests were done at 50%/50% and 75%/25% RH. Figure 4.2 shows the results from electrochemical testing, where Nafion<sup>®</sup> 212 was used as a standard to compare to the 6FPAEB-BPSH 13K-13K membrane.

Under high humidity conditions in the fuel cell, the MEAs containing the 6FPAEB multiblock copolymer greatly outperformed (higher potential at a given current density) the Nafion<sup>®</sup> 212 membrane, with almost no difference in HFRs (high frequency resistances). However, at the lower RHs, the Nafion<sup>®</sup> 212 MEAs showed only slightly better (to comparable) performance with lower HFRs than the multiblock 6FPAEB copolymer membranes. While the fuel cell performance results followed the same trend that was observed in the proton conductivity with relative humidity (Figure 4.2) tests, the differences in conductivity cannot solely account for the fuel cell performance differences.

Correcting for the resistance in the membranes allowed for a better understanding of how the membranes perform compared to each other. The HFR of the membranes found in testing of the MEAs is a combination of the resistance from the membrane plus other non-membrane factors in the cell. These non-membrane factors are thought to be caused from a combination of the electronic resistance, and the interfacial resistance resulting from the membrane interface with the catalyst layer.<sup>17</sup> This is a key point as the 13K-13K 6FPAEB-BPSH membrane based MEAs contained the Nafion ionomer in the catalyst layer. As the humidity was decreased, the compatibility between the 13K-13K 6FPAEB-BPSH membrane and the Nafion ionomer-based electrode likely further deteriorated. The MEAs with the Nafion<sup>®</sup> 212 based MEAs did not suffer from the same problem since the Nafion membrane was very similar to the Nafion ionomer contained in the electrodes. The iR corrected voltage polarization curves attempted to correct for the loss in voltage due to inefficiencies in the MEAs, where the difference between the MEAs at low humidities is primarily attributed to the interfacial resistance. The iR corrected polarization curves are shown in Figure 4.3.

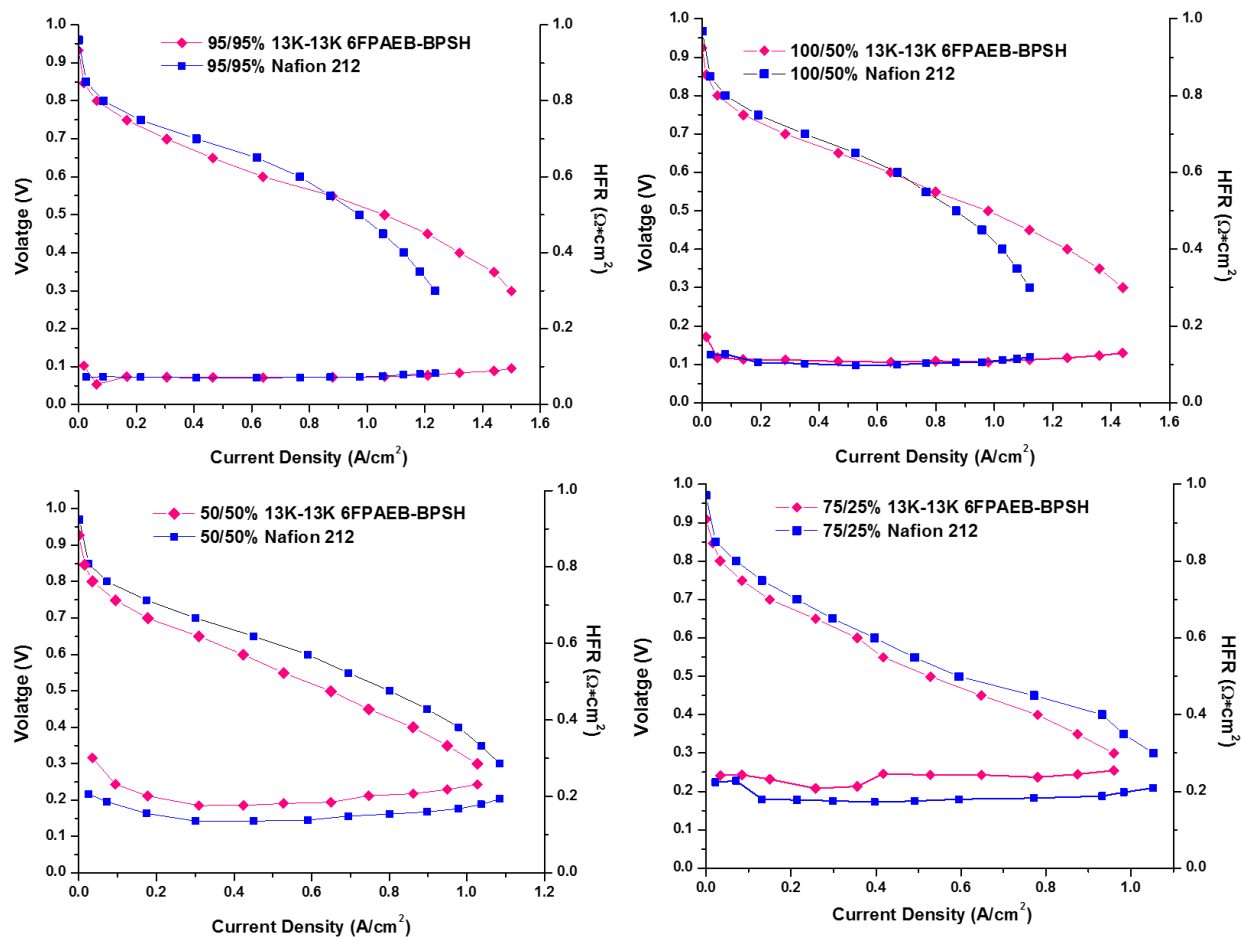


**Figure 4.2** Polarization curves of the multiblock copolymer and Nafion® 212 MEAs at four different RH conditions: 95%/95%, 100%/50%, 50%/50%, and 75%/25%. Testing was conducted in air at 80 °C with 101 kPa and 25 cm<sup>2</sup> MEAs. The bottom curves on the graphs are HFR as a function of current density, and the top curves are voltage as a function of current density

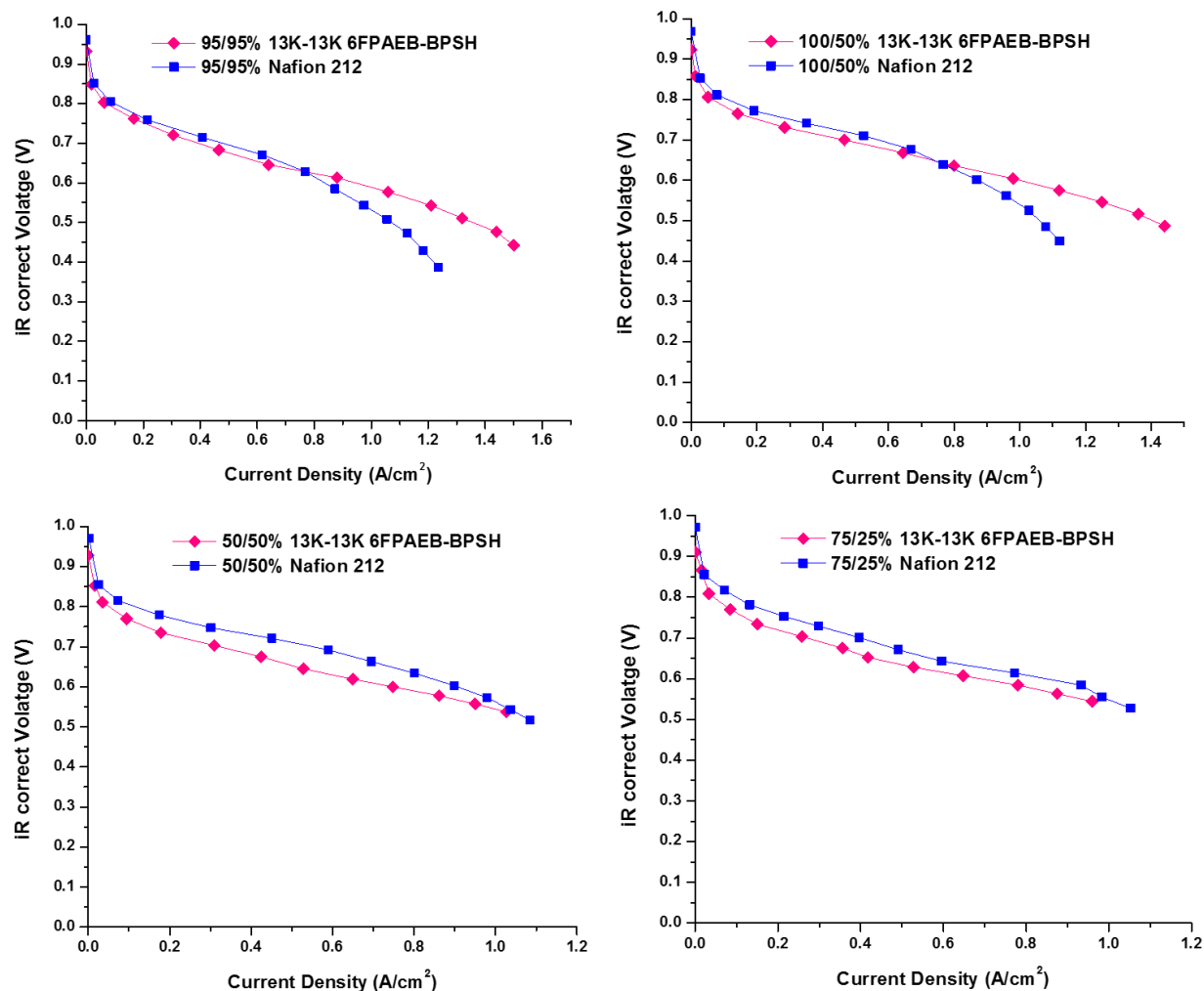


**Figure 4.3** Polarization curves of iR corrected voltage for the multiblock copolymer and Nafion<sup>®</sup> 212 MEAs at four different conditions: 95%/95%, 100%/50%, 50%/50%, and 75%/25%. Testing was conducted in air at 80 °C with 101 kPa air and 25 cm<sup>2</sup> MEAs

For the high humidities, the iR corrected curve showed very little change between performances of the membranes, as the 6FPAEB MEAs still greatly outperformed the Nafion<sup>®</sup> 212 MEAs. However, at low humidities the performance became almost identical between the MEAs. This was interesting as this shows much better results than what was observed with proton conductivity as a function of relative humidity. At low humidities, although the conductivity was less, the performance was identical. Furthermore, although the conductivities of the 6FPAEB membranes are higher at higher humidities, the increased performance over the Nafion membrane

is higher than one would expect from the conductivity difference alone. This added increase in performance was speculated to be from possible better water management of the multiblock copolymer based MEAs. Specifically regarding water management, the hydrocarbon based membrane is suggested to be better at preventing water flooding of the catalyst layer and the gas diffusion layer.

With the 6FPAEB based multiblock copolymers, reduced HFR and greatly increased performance was observed over that of other previously tested multiblock copolymers, especially at low RH levels.<sup>17</sup> Previously there were problems with high surface hydrophobicity of the membranes, which caused performance issues for membranes with long block lengths. This seems to be greatly mitigated with the partial fluorination and inclusion of the benzonitrile group in the hydrophobic segment of the multiblock copolymer. However, the interfacial resistance at low RH still needs further improvement for these membranes. Further structure or composition changes are needed, however it is likely that changes in the catalyst layer are needed as well to optimize the fuel cell system with the multiblock copolymers. This highlights the issues with replacing the Nafion membrane in PEM systems. As the catalyst layer is optimized towards the Nafion membrane there is added difficulty in finding replacement/alternative systems. It is possible that the incompatibility could be mitigated, and better performance of the multiblock copolymer membranes can be achieved by introducing a hydrocarbon ionomer in the electrode instead of the standard Nafion composition. With a hydrocarbon membrane in the catalyst layer, performance closer to that observed in the iR corrected curves, which showed superior membrane performance, than in the uncorrected polarization curves might be possible. Nonetheless with strong performance at high levels of humidity and comparable performance at low humidity levels

(uncorrected), even with the current setup these results further demonstrate that 6FPAEB based sulfonated multiblock copolymers are viable candidates for H<sub>2</sub>/Air fuel cell systems.

## 4.5 Conclusions

The electrochemical properties of the 6FPAEB based multiblock copolymers were investigated to elicit their feasibility H<sub>2</sub>/Air fuel cells operated at low humidities. These membranes had high IECs, but only moderate levels of water uptake due to strong phase separation between the disulfonated hydrophilic phase and the 6FPAEB hydrophobic phase. The membranes showed exceptional properties and fuel cell performance. The multiblock copolymers vastly outperformed the Nafion<sup>®</sup> 212 membrane at high humidity and they exhibited comparable performance under low humidity conditions. In addition, the multiblock copolymer structure and the 6FPAEB hydrophobic phase allowed for low HFR of the membranes, with values only slightly higher than Nafion at 50% RH. The good performance of the multiblock copolymer membranes suggest that they could be viable candidates for PEM fuel cells. Further structure and electrode modifications of these membranes may lead to even better electrochemical performance. The ability to surpass the performance of the Nafion membranes even at low humidities seems possible for H<sub>2</sub>/air fuel cell applications.

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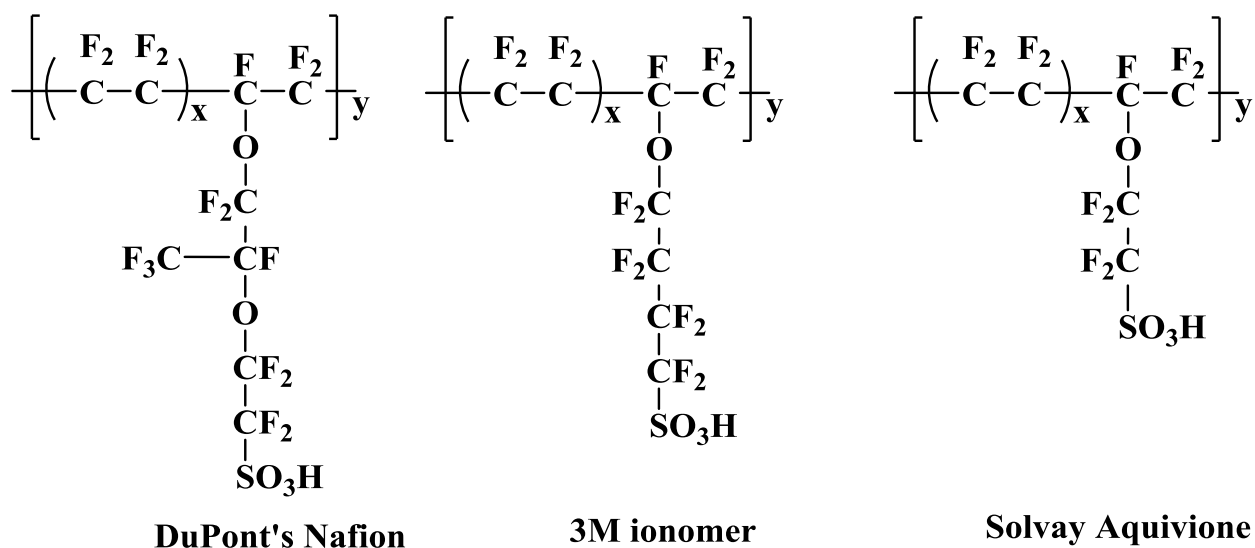
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## **CHAPTER 5. Synthesis and Characterization of a Partially Fluorinated Disulfonated Multiblock Copolymer for Electrolysis of Water**

### **5.1 Introduction**

Hydrogen gas, as an environmentally friendly and high energy gas, is used in fuel cells and many other devices.<sup>1-2</sup> In order to make an efficient hydrogen fuel cell, the feed gas should be extremely pure to prevent cell poisoning.<sup>3</sup> There are numerous ways of generating hydrogen gas, and electrolysis of water provides ultra-pure gas.<sup>4</sup> In this method, a polymer electrolyte membrane serving both gas barrier and ion conductor roles, is compressed between two electrodes. Water molecules are introduced to the catalyst layer of the anode electrode and current is applied, which splits the water molecules into oxygen, protons, and electrons.<sup>5</sup> In this process oxygen molecules are directly stored in tanks while the generated protons pass through the membrane from the anode to the cathode side of the cell. Electrons pass through an outer circuit to the cathodic layer to react with the protons coming from the anode catalyst layer. The reaction of electrons and protons results in hydrogen gas that can be stored in storage tanks. Electrolysis of water conducted at high pressures and high temperatures has shown improved reaction kinetics.<sup>6</sup>

Current state-of-the-art membranes for electrolysis of water are poly(perfluorosulfonic acid) membranes. These copolymers consist of highly fluorinated backbones bearing different side chain lengths as shown in Scheme 5.1.



**Scheme 5.1** Poly(perfluorosulfonic acid) structures with different side chain lengths<sup>7</sup>

Perfluorosulfonic acid systems owe their good chemical stability to a highly fluorinated backbone with fluorinated side chains that enhance the acidity of the sulfonic acid groups.<sup>8</sup> Siracusano et al.<sup>9</sup> have investigated the properties of Aquivion, a short side chain poly(perfluorosulfonic acid) membrane. Aquivion has a similar IEC to Nafion, has good proton conductivity and chemical stability. From an economical point of view, it is desirable to use a thin membrane in electrochemical systems. However, Aquivion shows slightly lower gas crossover to that of the Nafion's despite having a higher thickness. A desirable electrolysis membrane is a thin membrane with low gas crossover while maintaining high mechanical properties, chemical stability and ion conductivity.<sup>10</sup> However, at high temperatures and high pressures in the presence of water, poly(perfluorosulfonic acid) membranes such including Nafion and Aquivion show very poor mechanical properties due to a low glass transition temperature.<sup>11</sup> In addition, at extreme conditions of high temperature and high pressure, Nafion and other poly(perfluorosulfonic acid) membranes show high gas crossover.

Block copolymers have been intensively studied for fuel cell and gas separation applications.<sup>12-14</sup> These copolymers have interesting properties including high proton conductivity, good separation properties, and good mechanical stability. These properties have been attributed to the phase separation and long range order of the block copolymers.<sup>12, 15-16</sup> Rowlett et al.<sup>17</sup> have synthesized a series of multiblock copolymers with hydrophobicity in their hydrophobic block by incorporating methyl moieties on bisphenol A comonomers. These copolymers showed decreased water uptake as the hydrophobicity was increased. In addition, as the hydrophobicity was increased, improved phase separation was obtained due to the presence of tetramethyl bisphenol A (TMBPA), the most hydrophobic monomer in this series.

Surface fluorination of hydrocarbon-based copolymers is an approach employed to enhance properties of the copolymers for fuel cell applications. Improved proton conductivity, enhanced gas barrier properties, decreased methanol permeability, and increased membrane lifetime are properties that have been shown to be developed by post-fluorination.<sup>18-21</sup> However, due to the complexity of fluorination and the hazardous fluorination process, other approaches were considered. Using fully or partially fluorinated comonomers in the composition of the sulfonated copolymers is an attractive method of improving the PEM properties.<sup>22-23</sup>

This chapter describes a partially fluorinated comonomer in a multiblock copolymer to enhance properties of the PEM for electrolysis of water. A partially fluorinated bisphenol comonomer was synthesized and incorporated into the hydrophobic oligomer. A multiblock copolymer was synthesized by a coupling reaction between preformed hydrophobic and hydrophilic oligomers. Size exclusion chromatography (SEC) confirmed high molecular weight of the multiblock copolymer. A thin film membrane of the multiblock copolymer was cast and annealed into a phase separated lamellar structure. Transmission electron microscopy (TEM) of

these copolymers suggested that the long range order of the lamellae was responsible for the high proton conductivity and the controlled water uptake. Mechanical properties, IEC and water uptake of these copolymers were also measured. H<sub>2</sub> gas permeability of the multiblock copolymer in saturated water vapor conditions at a wide range of temperatures was compared to that of Nafion™.

## 5.2 Experimental

### Materials

2,6-Xylenol, 2,6-difluorobenzonitrile (DFBN), *N,N*-dimethylacetamide (DMAc), cyclohexane, and toluene were purchased from Sigma-Aldrich. DFBN and toluene were reagent grade and used as received, DMAc was distilled from calcium hydride before use. Monomer grade 4,4'-biphenol (BP) was provided by Eastman Chemical Company, and dried under vacuum at 80 °C prior to use. Monomer grade 3,3'-disulfonated-4,4'-dichlorodiphenylsulfone (SDCDPS) was purchased from Akron Polymer Systems and dried under vacuum at 170 °C for 3 days prior to use. 2,2-Bis(4-hydroxy-3,5-dimethylphenyl)propane (tetramethyl bisphenol A, TMBPA) was synthesized according to a previously established method.<sup>24</sup> Reagent grade potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), acetone, and isopropanol were purchased from Fisher Scientific. K<sub>2</sub>CO<sub>3</sub> was dried under vacuum at 170 °C prior to use, while acetone and isopropanol (IPA) were used without further purification. Triflic acid was purchased from Oakwood Chemical and used as received. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and Acetic acid were purchased from Fisher Scientific and used as received. Trifluoroacetophenone (99%) was purchased from Matrix Scientific and used as received. Dichloromethane (DCM) was purchased from Spectrum Chemicals. Magnesium sulfate

(anhydrous) was purchased from Sigma Aldrich. Methanol and ethanol were purchased from Decon Lab Inc. and used as received.

### Synthesis of TMBPA

This monomer was prepared based on a previously established method.<sup>24</sup> TMBPA was prepared by an acid-catalyzed condensation between 2,6-xyleneol and acetone. A 250-mL three-necked flask equipped with a mechanical stirrer was charged with 2,6-xyleneol (5 g, 41 mmol) and acetone (3.3 g, 57 mmol). The mixture was stirred at 15 °C until complete dissolution. Afterwards, the reaction vessel was placed in an ice bath. Using an addition funnel, sulfuric acid (10.0 g, 98 mmol) was added dropwise to the reaction. After complete addition of sulfuric acid, acetic acid (5 g, 83.4 mmol) was added dropwise to the solution. The reaction was continued for 24 h at room temperature. The reaction was diluted with water (70 mL) and DCM (100 mL) and then transferred to a separatory funnel. The organic layer was washed with water three times before collection. The DCM layer was dried over magnesium sulfate overnight to yield a dry organic layer. DCM was then evaporated and a slightly yellow product was obtained. The product was recrystallized from a 60:40 ethanol:water solution to obtain white crystals. The yield of this product was 76%. The melting point of the recrystallized product was 167-168 °C.

### Synthesis of 4,4'-(2,2,2-trifluoro-1-phenylethane-1,1-diyl)diphenol, (3F)

Synthesis of 3F monomer was adapted from previously established methods.<sup>25</sup> Phenol (4.28 g, 43.6 mmol) and 2,2,2-trifluoroacetophenone (2.7 mL, 15.5 mmol) were added to a 250-mL 4 necked flask equipped with a condenser, mechanical stirrer, nitrogen inlet and addition funnel. The oil bath temperature was set to 55 °C for the duration of the reaction. After 2 h,

trifluoromethanesulfonic acid (0.9 mL, 10 mmol) was added via the addition funnel slowly into the solution over 30 min. The solution quickly turned dark pink upon addition of the trifluoromethanesulfonic acid. The reaction was stirred for 2 h. Hot water (30 mL) was added to the reaction. The product solution was filtered and the filtrate was added to hot DI water (100 mL) and stirred for 30 min. The solution was filtered and the solid was washed with DCM and water 3 times until a white powder was obtained. The product was dried *in vacuo* at 80 °C to yield 80% product. The melting point of the dried product was 229-230 °C, which agreed well with previous literature values.<sup>26</sup>

#### Synthesis of hydrophobic oligomers

A nucleophilic aromatic substitution reaction was used for synthesis of the oligomers. A typical hydrophobic oligomer synthesis with a 12,000 Da targeted molecular weight ( $M_n$ ) is described. 3F (2.2 g, 6.4 mmol), TMBPA (1.8167 g, 6.4 mmol) and DMAc (30 mL) were added to a 150-mL three neck round bottom flask equipped with a nitrogen inlet, mechanical stirrer, dean-stark trap, and condenser. The mixture was heated to 150 °C and stirred under nitrogen. Once a transparent solution was obtained,  $K_2CO_3$  (2.1 g, 15.2 mmol) and cyclohexane (15 mL) were added into the flask. The reaction was allowed to reflux in an oil bath with the temperature set at 150 °C for 4 h to azeotropically remove water from the system, and then drained the toluene. Finally, the oil bath temperature was slowly raised to 180 °C to allow the monomers to react. The reaction temperature was decreased to 80 °C and DFBN (1.8719 g, 13.45 mmol) was added to the flask. The reaction was allowed to proceed for 8 h at 135 °C, then cooled to room temperature and filtered to remove  $K_2CO_3$ . The oligomer was precipitated into methanol (500 mL), stirred overnight, filtered and then dried *in vacuo* at 110 °C for 48 h. This oligomer was abbreviated as 3FTMBPA.

### Synthesis of a hydrophilic oligomer

Synthesis of hydrophilic blocks have been intensively investigated previously.<sup>13, 17, 27-28</sup> The synthesis of a BPS100 oligomer with a target molecular weight of 12,000 Da is described. BP (5.2463 g, 28.2 mmol), SDCDPS (13.5307 g, 26.7 mmol), and DMAc (94 mL) were added into a 150-mL, three neck round bottom flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean-Stark trap, and a condenser and stirred until dissolved. The oil bath temperature was raised to 150 °C and then K<sub>2</sub>CO<sub>3</sub> (2.4 g, 17.37 mmol) and toluene (45 mL) were added. The reaction was allowed to proceed to azeotropically remove water. After draining toluene from the Dean-Stark trap, the bath temperature was slowly raised to 180 °C and allowed to proceed for 72 h. The yellow solution was cooled to room temperature, filtered to remove the salt and then coagulated into IPA (1000 mL). The precipitated product was stirred overnight in IPA and then dried *in vacuo* at 120 °C for 48 h. The yield of the BPS100 oligomer was 91%.

### Synthesis of multiblock copolymers

A typical synthesis of a 12k–12k 3FTMBPA-BPS100 multiblock copolymer with targeted block lengths of 12k-12k was conducted. BPS100 12k (4.00 g, 0.33 mmol), K<sub>2</sub>CO<sub>3</sub> (0.150 g, 1.087 mmol), DMAc (40 mL), and cyclohexane (20 mL) were added to a 150-mL, three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean-Stark trap, and a condenser. The reaction bath was heated to 145 °C for 4 h to remove water from the system. After draining the cyclohexane, the reaction bath was cooled to 90 °C, and the 3FTMBPA 12k oligomer (4.000 g, 0.33 mmol) was added. The bath temperature was raised to 145 °C and held at this temperature for 48 h. The viscous reaction mixture was precipitated into IPA (1000 mL), resulting in a fibrous

copolymer. The product was stirred in IPA for 12 h, then in boiling deionized (DI) water at for 12 h, and dried *in vacuo* at 120 °C for 24 h. The yield of 3FTMBPA-BPS100 multiblock copolymer was 83%.

#### Membrane casting and membrane annealing

The salt form of the 3FTMBPA-BPS100 copolymer was dissolved in DMAc (~6%, w/v) and filtered through a 0.45 µm Teflon syringe filter. The filtered solution was cast onto a dry, clean 4" x 4" glass substrate and dried under an IR lamp at 50-60 °C for 12 h. The membranes were annealed under vacuum at 230 °C, which is well above the  $T_g$  of the disulfonated polysulfone multiblock copolymers.<sup>27</sup> All of the membranes were in the salt form and were converted to the acid form by boiling in 1 M sulfuric acid solution for 2 h, followed by boiling in deionized water for 2 h.<sup>29</sup>

#### Polymer composition and molecular weight characterization

Compositional characterization of the copolymers was conducted via  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR spectroscopy on a Varian INOVA spectrometer operating at 400 MHz. The spectra of the BPS100 oligomers and the multiblock copolymers were obtained in 10 wt/v% concentration in DMSO- $d_6$  solution at room temperature with 256 scans. The spectra of the hydrophobic oligomers was obtained from  $\text{CDCl}_3$  solution in 10 wt/v% concentration with 256 scans.

Molecular weights and polydispersities of the polymers were measured using SEC. The mobile phase was DMAc distilled from  $\text{CaH}_2$  containing dry LiCl (0.1 M). The column set consisted of 3 Agilent PLgel 10-mm Mixed B-LS columns 300 \* 7.5 mm (polystyrene/divinylbenzene) connected in series with a guard column having the same stationary

phase. The columns and detectors were maintained at 50 °C. An isocratic pump (Agilent 1260 infinity, Agilent Technologies) with an online degasser (Agilent 1260), autosampler and column oven were used for mobile phase delivery and sample injection. A system of multiple detectors connected in series was used for the analyses. A multi-angle laser light scattering detector (DAWN-HELEOS II, Wyatt Technology Corp.), operating at a wavelength of 658 nm, a viscometer detector (Viscostar, Wyatt Technology Corp.), and a refractive index detector operating at a wavelength of 658 nm (Optilab T-rEX, Wyatt Technology Corp.) provided online results. The system was corrected for interdetector delay and band broadening using a 21,000 Da polystyrene standard. Data acquisition and analysis were conducted using Astra 6 software from Wyatt Technology Corp. Validation of the system was performed by monitoring the molar mass of a known molecular weight polystyrene sample by light scattering. The accepted variance of the 21,000 Da polystyrene standard was defined as 2 standard deviations (11.5% for  $M_n$  and 9% for  $M_w$ ) derived from a set of 34 runs. Specific refractive index values were calculated based on the assumption of 100% mass recovery.

#### IEC measurements

The IEC of the multiblock copolymer was determined by  $^1\text{H}$  NMR and titration of the membrane. Dry membranes in their acid form were weighed, then soaked in 1 M NaCl solution for 48 h to convert them to their salt form and eliminate HCl. Each membrane solution was titrated with 0.1 N NaOH solution. The IEC of each membrane in units of meq/g of dry membrane was calculated from Equation 5.1

$$IEC = \frac{V \cdot N}{M} \times 1000 \quad (5.1)$$

where V is the volume of NaOH, N is the NaOH normality, and M is the mass of the dry membrane.

### Membrane water uptake

The water uptakes of the membranes were determined gravimetrically on samples weighing 0.1-0.2 g and 3 samples were measured for each film. First, the membranes in their acid form were dried at 120 °C *in vacuo* for 24 h and weighed. These membranes were soaked in water at room temperature for 48 h. Wet membranes were removed from the liquid water, blotted dry to remove surface droplets, and quickly weighed. The water uptake of the membranes was calculated according to Equation 5.2:

$$Water\ Uptake = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100 \quad (5.2)$$

where  $M_{wet}$  is the mass of the wet membranes and  $M_{dry}$  is mass of the dry membranes, respectively.

### Membrane mechanical properties

Uniaxial load tests were performed using an Instron 5500R universal testing machine equipped with a 200-lb load cell. The crosshead displacement rate was 5 mm/min and the gauge length was 26.5 mm. The tensile test specimens were prepared with dimensions of 50 mm length and a minimum width of 4 mm per ASTM D638-03. Prior to testing, the membrane samples in their acid form were dried *in vacuo* at 100 °C. All of the specimens were mounted in pressure locking pneumatic grips and tested at room temperature.

### Membrane morphology investigation via TEM

The bulk morphologies of the membranes were characterized by transmission electron microscopy (TEM). Electron density contrast between hydrophilic and hydrophobic segments

within the membrane samples was enhanced by quantitatively exchanging the acidic protons on the sulfonic acid moieties with cesium ions from a CsOH solution. The Cs stained membranes were then embedded in epoxy and ultramicrotomed into 50–70 nm thin sections with a diamond knife. Transmission electron micrographs were obtained using a Philips EM 420 transmission electron microscope (TEM) operating at an accelerating voltage of 96 kV.

#### Proton conductivity

The ohmic resistance (R) of the PEM membrane was measured using a custom made test cell via four-point probe alternating current (a.c.) impedance spectroscopy in the frequency range from 3 MHz to 10 Hz in liquid water at 30 °C. The resistance of each membrane was obtained by averaging at least five measurements. The wiring system for measuring the ohmic resistance was shielded from the platinum electrodes to the potentiometer (a combined system of an electrochemical interface, Solartron 1287, and an impedance/gain-phase analyzer, Solartron 1252A) to avoid electromagnetic noise. For measurements of proton conductivity in liquid water, each membrane was fully hydrated by soaking in DI water at room temperature for 24 h. The proton conductivity ( $\sigma$ , S/cm) was obtained from Equation 5.3

$$\sigma = \frac{L}{R \cdot S} \quad (5.3)$$

where  $\sigma$  (S/cm) is proton conductivity, L (cm) is the distance between the two electrodes, R ( $\Omega$ ) is the resistance of the membrane, and S (cm<sup>2</sup>) is the proton transport surface area that was tested.

## H<sub>2</sub> gas permeability

A membrane was loaded into a Fuel Cell Technologies standard fuel cell hardware set. This set-up was installed inside a TestEquity environmental chamber with both heating and cooling capabilities. All flows were controlled or measured with Alicat mass flow controllers and meters. A flow of carrier gas was established on one side of the cell and the humidified permeant gas to the other. For these tests, over-humidified (condensing) permeant gas was used to simulate the flooded membrane of the electrolyzer. The permeant diffuses through the membrane, and a slipstream of the carrier gas was sent to an Agilent microGC for analysis of the permeant. The amount of permeant in the carrier gas was used to calculate the permeation rate of that gas through the membrane at that specific temperature. Then the temperature was changed and the process repeated. For a specific temperature, Equation 5.4 is used

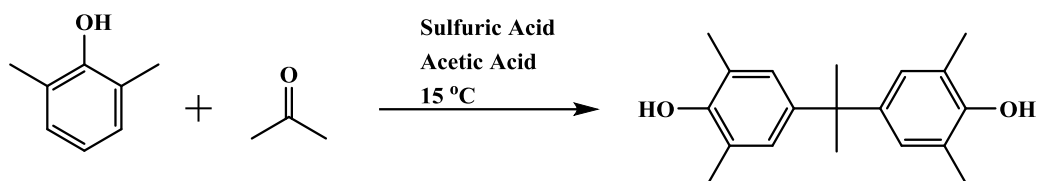
$$P = \frac{D \cdot T}{t \cdot A \cdot \Pi} \quad (5.4)$$

where P is the H<sub>2</sub> gas permeability, D is the amount of permeant gas, T is the membrane thickness, t is the permeation time, A is the effective area of the cell, and  $\Pi$  is the dry gas pressure.

## 5.3 Results and Discussion

### Synthesis and characterization of TMBPA

TMBPA is a highly hydrophobic comonomer. It has been shown that incorporation of this comonomer into multiblock copolymers can drastically reduce the water uptake of the multiblock copolymer.<sup>17</sup> It is a commercial monomer that can be easily synthesized in high yield from reaction of 2,6-xyleneol with acetone in an acid catalyzed medium as shown in Scheme 5.2.



**Scheme 5.2** Reaction procedure of TMBPA

In order to reach high yields in this reaction it was necessary to maintain the temperature constantly low to prevent evaporation of acetone. Moreover, it is important to add the sulfuric acid slowly to avoid the reaction temperature exceeding 15 °C. After recrystallization and isolation of the final product, its purity was confirmed via a narrow melting point range and the  $^1\text{H}$  NMR spectrum shown in Figure 5.1.

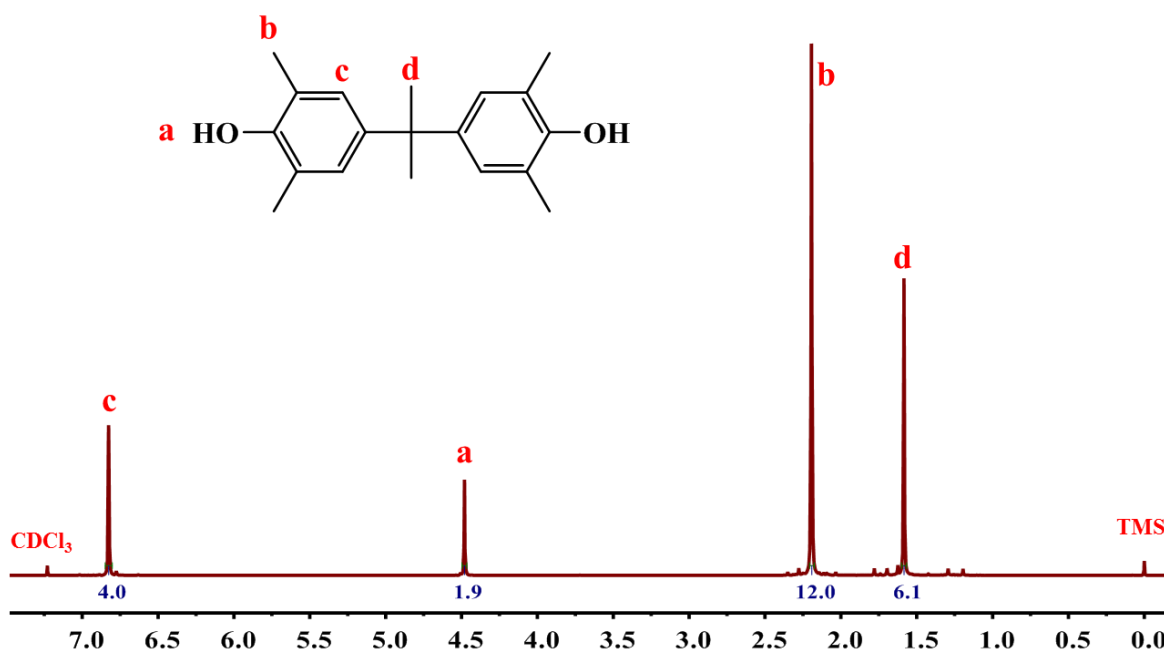
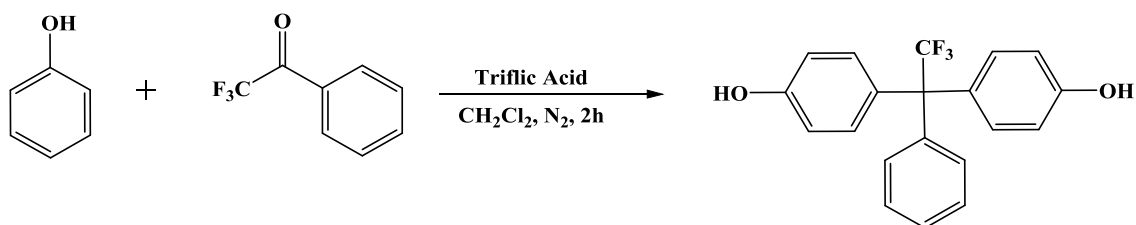


**Figure 5.1**  $^1\text{H}$  NMR spectrum of TMBPA in  $\text{CDCl}_3$

### Synthesis and characterization of 3F comonomers

Synthesis of the 3F comonomer was conducted under highly acidic conditions to activate the carbonyl oxygen of 2,2,2-trifluoroacetophenone. The reaction scheme is shown in Scheme 5.3.



**Scheme 5.3** Preparation of 3F comonomer

Once the monomer was purified by washing with hot water and CH<sub>2</sub>Cl<sub>2</sub>, the purity of the monomer was confirmed via its narrow melting point, 167-168 °C, and <sup>1</sup>H NMR spectrum as illustrated in Figure 5.2.

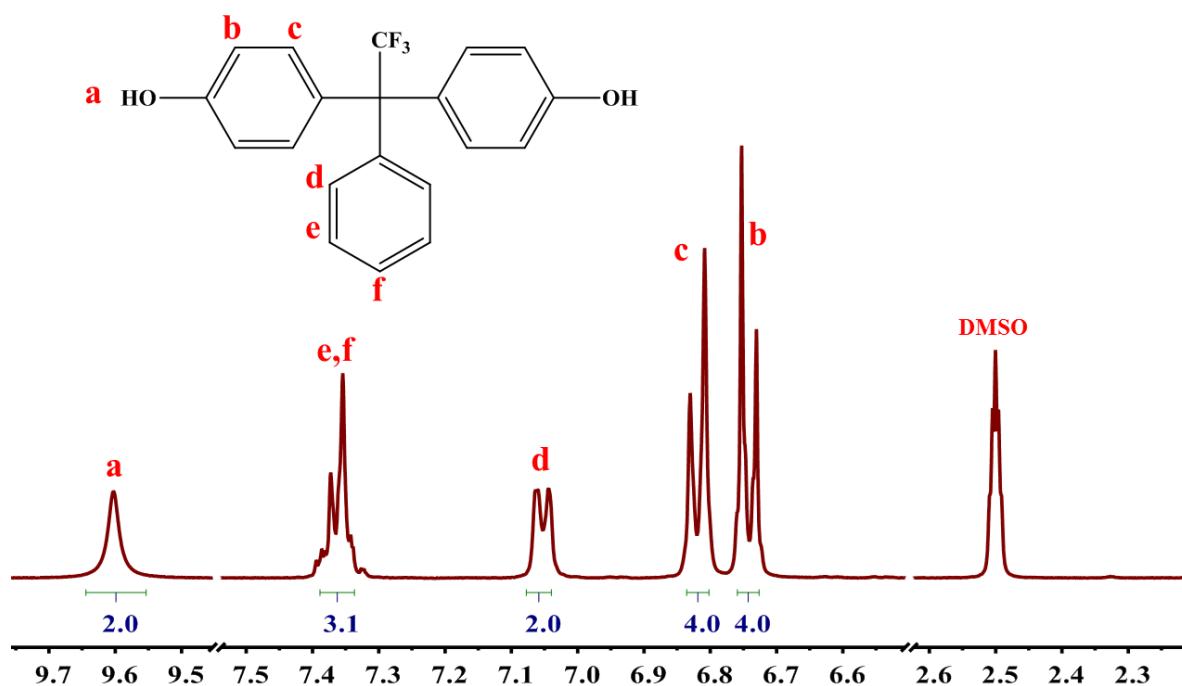


**Figure 5.2**  $^1\text{H}$  NMR spectrum of the 3F comonomer

#### Synthesis of BPS100 hydrophilic and 3F hydrophobic oligomers

Synthesis of the phenol terminated disulfonated biphenol-based hydrophilic oligomer (BPS100) was conducted according to previously established methods.<sup>13, 30</sup> Targeted molecular weight phenol terminated oligomers of 12 kDa were synthesized via a nucleophilic aromatic substitution reaction step growth polymerization. In order to control the molecular weight and place the phenoxide groups at the end of oligomers, biphenol was used in excess and reacted with SDCDPS. The structure of this oligomer and its  $^1\text{H}$  NMR spectrum are illustrated in Figure 5.3.

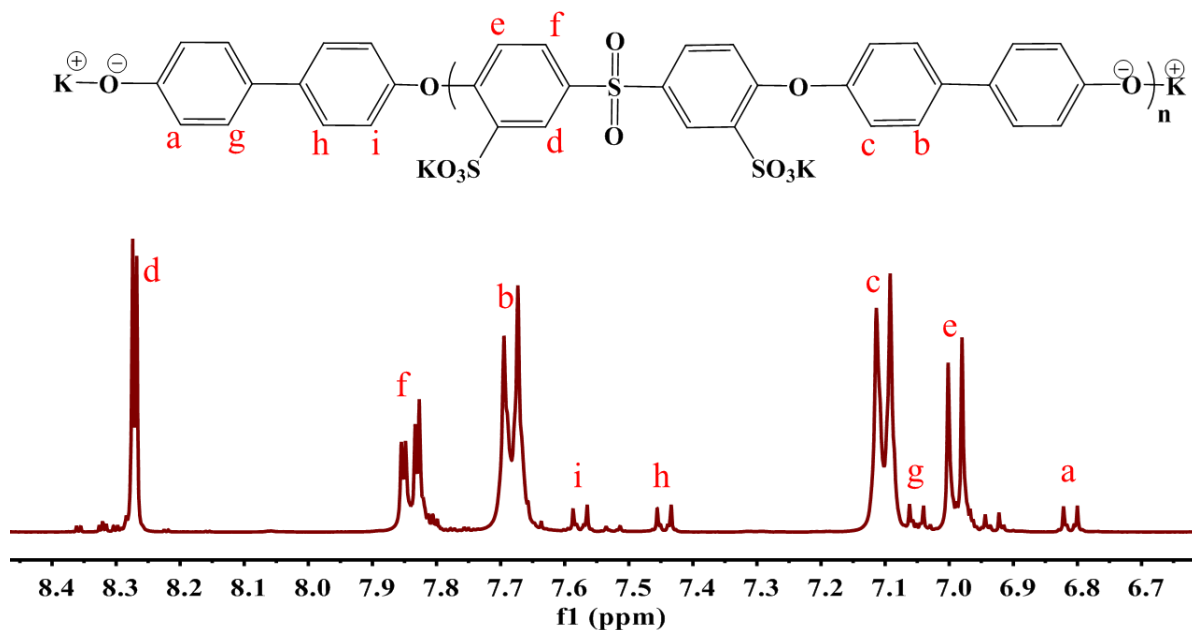
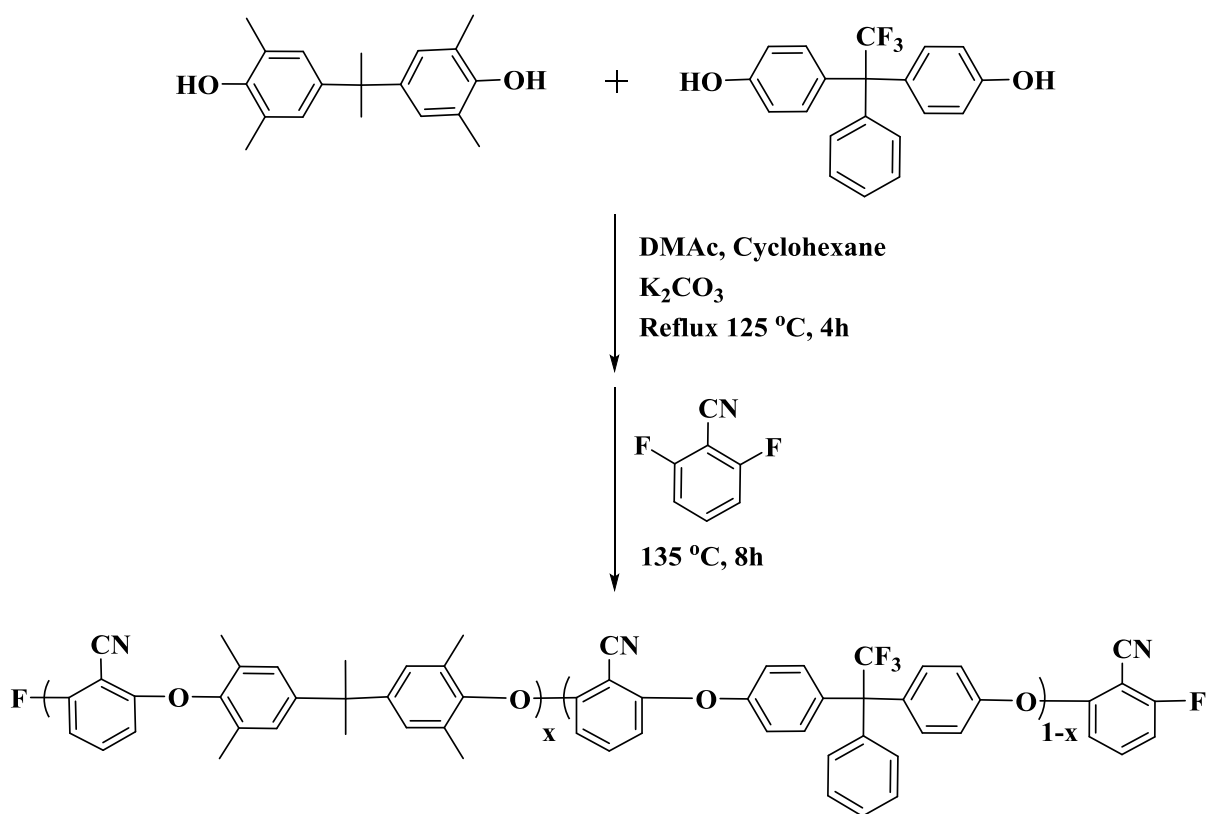


**Figure 5.3** Structure and  $^1\text{H}$  NMR spectrum of BPS100

Syntheses of hydrophobic oligomers were also conducted via a nucleophilic aromatic substitution reaction to prepare fluorine terminated oligomers. DFBN was used in excess and the reaction temperature was kept at 135 °C to prevent evaporation of this comonomer from the reaction medium. Scheme 5.4 shows the synthesis of the fluorine terminated hydrophobic oligomers.



**Scheme 5.4** Synthesis of fluorine terminated oligomers

An  $M_n$  of 12 kDa was targeted for the hydrophobic oligomer by adjusting the molar ratio of the bisphenols to the 2,6-difluorobenzonitrile. An equimolar ratio of TMBPA and 3F comonomers were charged to the reaction flask. Completion of the reaction was followed by  $^1H$  NMR spectroscopy in which the phenyl protons next to the phenoxide end groups disappeared.  $^{19}F$  NMR spectroscopy was used to measure the molecular weight of the hydrophobic oligomer by comparing the ratio of the fluorine on the benzonitrile terminated chain to the fluorine on the backbone of the main chain. Figure 5.4 illustrates the  $^{19}F$  NMR spectrum of 3FTMBPA oligomer.

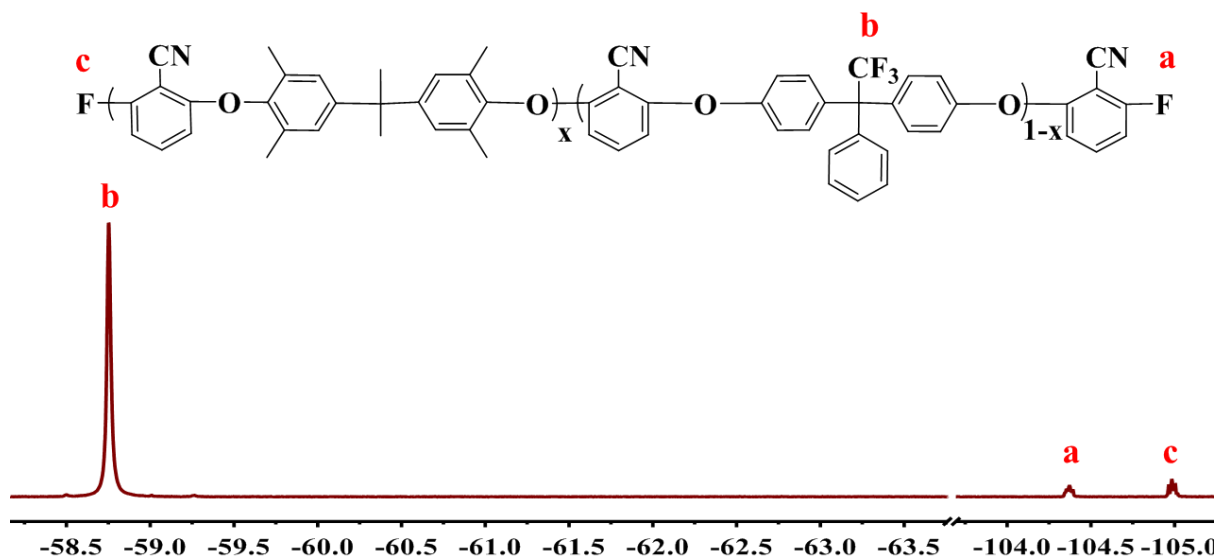


**Figure 5.4**  $^{19}\text{F}$  NMR of the 3FTMBPABP oligomer in  $\text{CDCl}_3$

Peak b in the  $^{19}\text{F}$  NMR at -58.75 ppm represents the fluorines of the  $\text{CF}_3$  in the 3F comonomer, while the other two peaks, a and c, represent the end group fluorine peaks attached to DFBN. DFBN attached to the 3F at the end of the chain is located downfield at approximately -104.5 ppm relative to the endgroup that is adjacent to the TMBPA, due to the electron withdrawing nature of the  $\text{CF}_3$  group in the 3F comonomer. The electron donating nature of TMBPA results in an upfield chemical shift of peak “c” at -105 ppm. The  $M_n$  of the hydrophobic oligomer was measured from the ratio of the end group integrals relative to those of the repeat unit integration (Table 5.1). Molecular weights of both oligomers were also measured by SEC. Molecular weights of both hydrophilic and hydrophobic oligomers were calculated from the  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR spectra. The molecular weights are shown in Table 5.1.

**Table 5.1** Multiblock copolymer hydrophilic and hydrophobic oligomers' molecular weights

| Oligomers      | M <sub>n</sub> from NMR analysis(kDa) | M <sub>n</sub> from SEC (kDa) <sup>a</sup> |
|----------------|---------------------------------------|--------------------------------------------|
| <b>BPS100</b>  | 12.5                                  | 10.3                                       |
| <b>3FTMBPA</b> | 12.8                                  | 11.5                                       |

<sup>a</sup> Measured with light scattering detector in 0.1M LiCl solution in DMAc

### Synthesis of multiblock copolymers

Synthesis of the multiblock copolymer was accomplished by reacting oligomers with similar molecular weights, both of which had M<sub>n</sub>s above the entanglement point of polysulfones reported as about 10000 Da elsewhere in the literature.<sup>31</sup> In addition, it has been shown that multiblock copolymers containing such high molecular weight oligomers can self-assemble to form long range ordered morphologies with improved PEM properties in compared to random copolymers.<sup>12</sup> The BPS100 hydrophilic oligomers were reacted with the fluorine terminated hydrophobic oligomers of similar molecular weight, approximately 12 kDa, to yield multiblock copolymers with partially fluorinated content. Previously, it had been observed that incorporation of the TMBPA in the hydrophobic blocks results in improved fuel cell performance.<sup>17</sup> In this work, TMBPA was used as one of the comonomers in the hydrophobic block and it was reacted with DFBN and the 3F comonomer. Synthesis of the multiblock copolymers is illustrated in Figure 5.5.

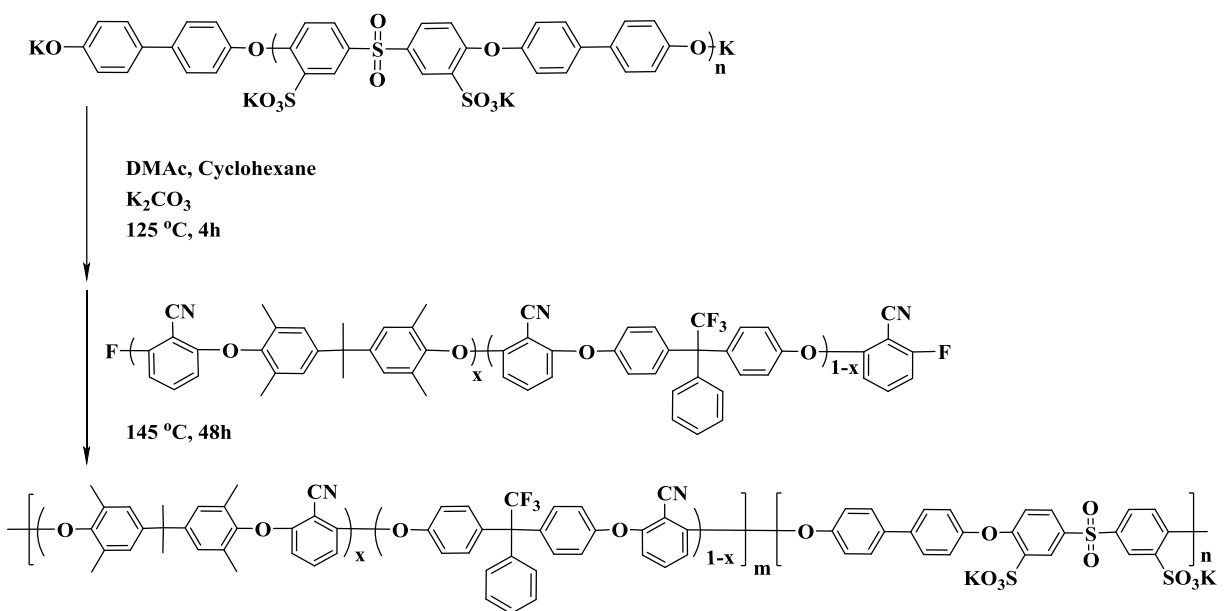


**Figure 5.5** Multiblock copolymer synthesis

In multiblock copolymer synthesis a possible undesired reaction at elevated temperature is the ether-ether exchange reaction that can result in randomization of the copolymers.<sup>32-33</sup> In order to prevent such a reaction it was necessary to conduct the reaction at mild temperatures. Completion of the reaction was followed by monitoring the increasing viscosity of the reaction mixture and its consistency after 48 hours. In addition, no phenoxide end group peak was observed in the  $^1\text{H}$  NMR spectrum, so this was considered an additional indication of reaction completion. The  $^1\text{H}$  NMR spectrum in Figure 5.6 was used to confirm the composition of the final product as well as the IEC of the copolymer.

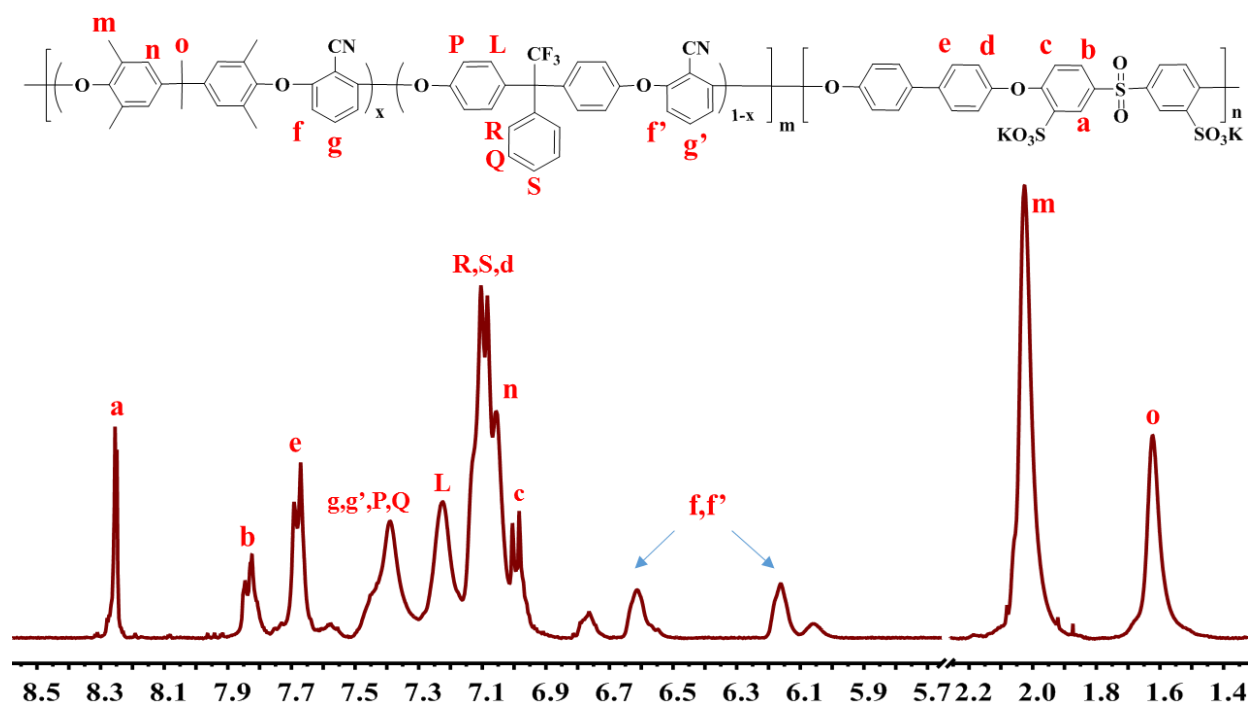


**Figure 5.6**  $^1\text{H}$  NMR of multiblock copolymers in  $\text{d}_6$ -DMSO

Molecular weight measurements via SEC confirmed the high molecular weight of this multiblock copolymer. Mechanical properties of the multiblock copolymer were conducted at room temperature and a rate of  $1 \text{ mm} \cdot \text{min}^{-1}$ . Good mechanical properties of this multiblock copolymer was confirmed by a stress at yield well above 55 MPa and an ultimate strain of approximately 27% elongation.<sup>14</sup> The stress-strain plot of the 3FTMBPA-BPS100 is illustrated in Figure 5.7.

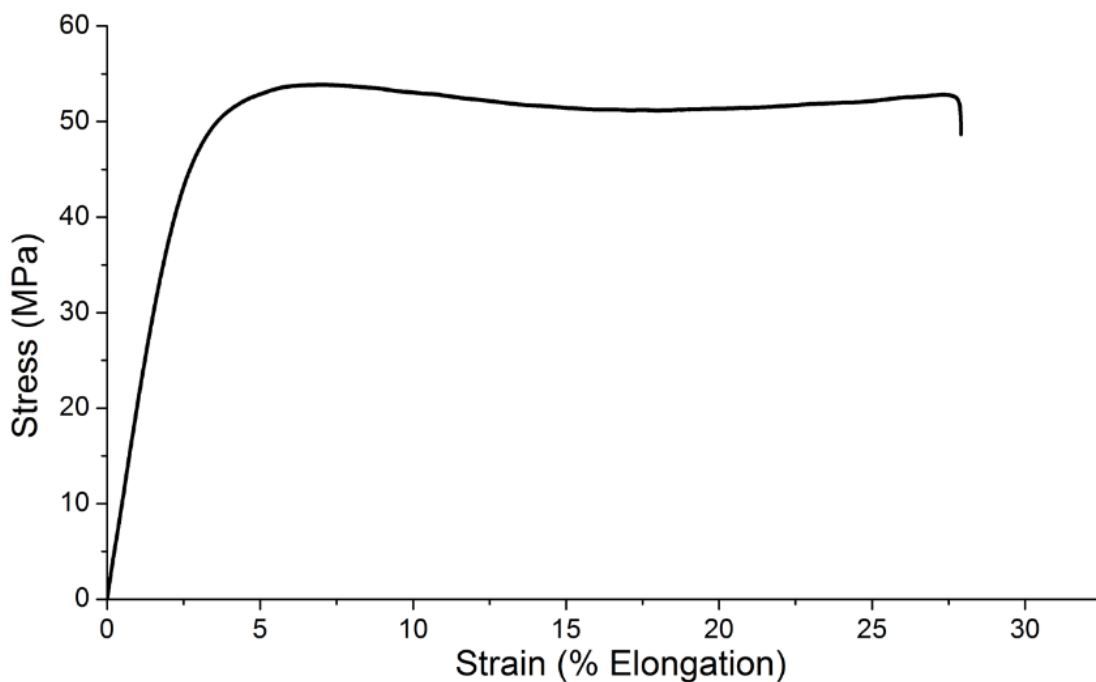


**Figure 5.7** Mechanical properties of the multiblock copolymer

The IEC of the copolymer was measured from  $^1\text{H}$  NMR by using the ratio of hydrophilic and hydrophobic peaks. This IEC was measured by using the ratio of peak “a” that corresponds to the hydrophilic block and the bridging methyl group peak “o” on TMBPA in the hydrophobic blocks. Theoretical IEC and measured IEC from titration are compared in Table 5.2.

#### Casting membranes and their properties

The procedure for casting membranes that was used in this work for these multiblock copolymers resulted in relatively thin films in the range of 35-40  $\mu\text{m}$ , and this is thinner than many poly(perfluorosulfonic acid) membranes.<sup>4, 34-35</sup> In order to improve the proton conductivity, thin membranes were annealed to develop a lamellar structure.<sup>36</sup> The TEM micrographs shown in Figure 5.8 confirm the phase separated morphology of these multiblock copolymers. Rearrangement in multiblock copolymers occurs when membranes are heated well above the glass

transition temperature of the hydrophobic blocks so that the polymer chains have sufficient energy for long range movement.<sup>37</sup>

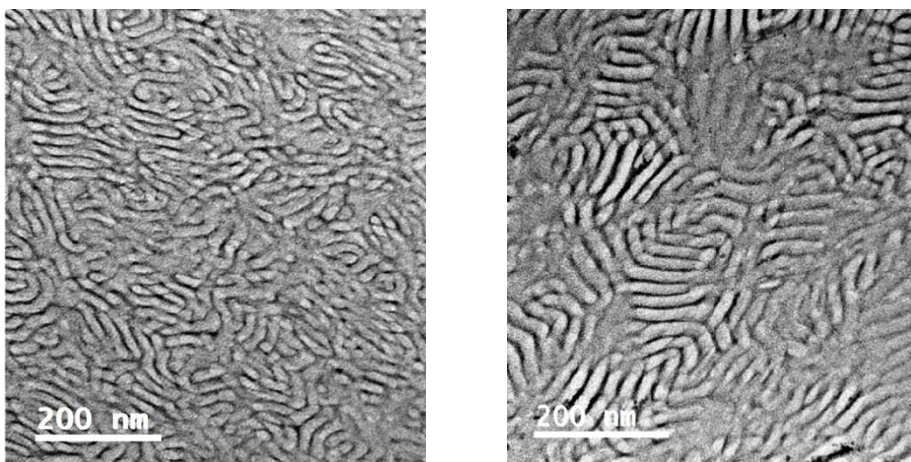


**Figure 5.8** Morphology of the 3FTMBPA-BPS100, 12k-12k, before annealing (left) and after annealing (right)

The fluorine atoms present in the hydrophobic block that contains 3F and the highly hydrophobic TMBPA comonomer are responsible for long lamellar domain size in the multiblock copolymer due to hydrophobicity of both monomers. In addition, the hydrophobic nature of these  $\text{CF}_3$  groups leads to lower water uptake which avoid excessive swelling of the multiblock copolymer.<sup>38</sup> The aforementioned reasons lead to lower water uptake in multiblock copolymers compared to linear copolymers with comparable IECs.<sup>39</sup> Water uptake and other relevant properties of the multiblock copolymer are shown in Table 5.2.

**Table 5.2** Properties of the multiblock 3FTMBPA-BPS100 copolymer

| Multiblock Copolymer  | M <sub>w</sub> (kDa) | $\sigma^a$ (S/cm) | $\sigma^b$ (S/cm) | IEC <sup>c</sup> (meq/g) | IEC <sup>d</sup> (meq/g) |
|-----------------------|----------------------|-------------------|-------------------|--------------------------|--------------------------|
| <b>3FTMBPA-BPS100</b> | 53                   | 0.06              | 0.08              | 1.25                     | 1.22                     |

<sup>a</sup> proton conductivity before annealing; <sup>b</sup> Proton conductivity after annealing; <sup>c</sup> Measured IEC via <sup>1</sup>H NMR; <sup>d</sup> Measured IEC via titration

IEC values measured from both <sup>1</sup>H-NMR and titration are very close. Despite the low water uptake of the multiblock copolymer, its proton conductivity is comparable to that of Nafion<sup>TM</sup>. Proton conductivities of the 3FTMBPA-BPS100 multiblock copolymer and Nafion<sup>TM</sup> at various temperatures are compared in Table 5.3. As expected, conductivities of both copolymers increase as temperature is increased due to increased water uptake at elevated temperatures.<sup>40-41</sup> However, Nafion<sup>TM</sup> is not a good candidate for high temperature applications due to its low glass transition temperature and high gas crossover.<sup>42</sup>

**Table 5.3** Proton conductivity of Nafion and 3FTMBPA-BPS100 multiblock copolymer at various temperatures

| Polymer               | Water Uptake at 30 °C (%) | Water Uptake at 90 °C (%) | $\sigma$ at 30 °C (S/cm) | $\sigma$ at 60 °C (S/cm) | $\sigma$ at 90 °C (S/cm) |
|-----------------------|---------------------------|---------------------------|--------------------------|--------------------------|--------------------------|
| <b>3FTMBPA-BPS100</b> | 16±1.5                    | 28±1.0                    | 0.08                     | 0.14                     | 0.18                     |
| <b>Nafion</b>         | 22±0.6                    | 42±1.7                    | 0.08                     | 0.135                    | 0.21                     |

#### 4.6. H<sub>2</sub> gas permeability (P)

Gas crossover is an important parameter in electrolysis of water for safety of the process, increased efficiency, and improved purity of the gaseous products.<sup>43</sup> H<sub>2</sub> gas permeability through

the multiblock copolymer membrane was compared to that of Nafion<sup>TM</sup> in saturated water vapor at different temperatures. Table 5.4 represents the gas permeabilities in the multiblock copolymer and Nafion<sup>TM</sup>.

**Table 5.4** H<sub>2</sub> gas permeability in 3FTMBPA-BPS100 multiblock copolymer and Nafion<sup>TM</sup>

| Polymer                    | P at 30 °C<br>(mol kPa <sup>-1</sup> s <sup>-1</sup> cm <sup>-1</sup> ) | P at 60 °C<br>(mol kPa <sup>-1</sup> s <sup>-1</sup> cm <sup>-1</sup> ) | P at 90 °C<br>(mol kPa <sup>-1</sup> s <sup>-1</sup> cm <sup>-1</sup> ) |
|----------------------------|-------------------------------------------------------------------------|-------------------------------------------------------------------------|-------------------------------------------------------------------------|
| <b>3FTMBPA-BPS100</b>      | 8.35E-14                                                                | 1.51E-13                                                                | 2.41E-13                                                                |
| <b>Nafion<sup>TM</sup></b> | 1.32E-13                                                                | 2.9E-13                                                                 | 8.6E-13                                                                 |

Water uptake remarkably affects the fundamental properties of a copolymer.<sup>44</sup> As the water content of a copolymer increases, the proton conductivity increases, but also the gas permeability in polymeric membranes is promoted due to the plasticization effect of water and more chain movement.<sup>45</sup> In general, sulfonated poly(arylene ether sulfone) copolymers have very high T<sub>g</sub>s and the plasticization effect from water is not as pronounced as in perfluorinated vinyl polymers. Plasticization of poly(arylene ether sulfone)s from water does not lead to a decrease in the T<sub>g</sub> below the water electrolysis performance temperature, which is close to the boiling temperature of water.<sup>33, 46</sup> In contrast, Nafion<sup>TM</sup> has higher gas permeability than 3FTMBPA-BPS100 at any temperature tested due to Nafion's lower T<sub>g</sub>.<sup>42</sup> In addition, when Nafion<sup>TM</sup> is in hydrated conditions, its T<sub>g</sub> is lowered leading to excessive gas permeability.

#### Performance ( $\sigma/P$ )

Proton conductivity,  $\sigma$ , and H<sub>2</sub> gas permeability, P, are considered the major transport parameters of membranes for the electrolysis of water, and performance is defined as the ratio of

( $\frac{\sigma}{p}$ ). Comparison of the performance of the multiblock copolymer and Nafion<sup>TM</sup> at three different temperatures reveals the overall properties of the multiblock copolymer. Overall performance of the multiblock copolymer and Nafion<sup>TM</sup> are shown in Figure 5.9.

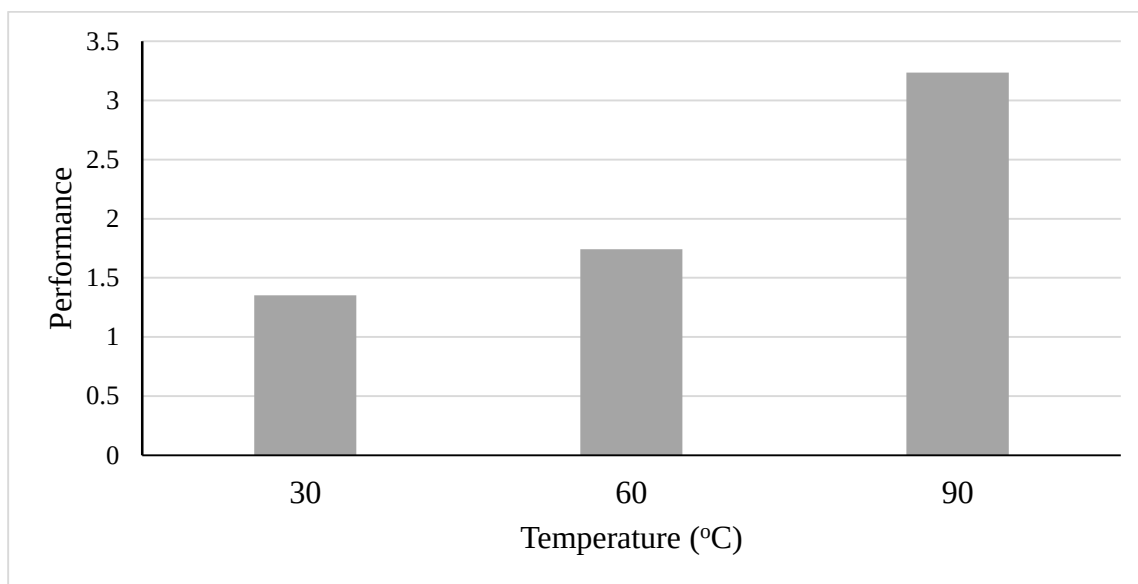


**Figure 5.9** Normalized performance of the 3FTMBPA-BPS100 to that of the Nafion<sup>TM</sup> at three different temperatures

As expected, the performance of Nafion<sup>TM</sup> drastically decreases as the water temperature is increased. This is likely a major cause of the poor performance of perfluorosulfonic acid membranes at temperatures above their  $T_g$ , due to high gas crossover. Despite decreased performance of the hydrocarbon-based copolymer possessing a higher  $T_g$  than Nafion<sup>TM</sup>, the declined performance is not as drastic as Nafion<sup>TM</sup> due to higher thermal stability. In addition, enhanced proton conductivity through the 3FTMBPA-BPS100 multiblock copolymer results in approximately three times better performance than Nafion<sup>TM</sup>.

## 5.4 Conclusions

The 3FTMBPA-BPS100 multiblock copolymer with low fluorine content showed well controlled water uptake at both room and elevated temperatures. As temperature was increased, slightly increased water uptake was observed in the hydrocarbon-based copolymer resulting in enhanced proton conductivity. The presence of fluorine in the hydrophobic block in addition to the highly hydrophobic TMBPA comonomer enhanced the water repulsion and phase separation of this copolymer after annealing. The phase separation and morphology in the copolymer is responsible for its good mechanical properties. Due to high proton conductivity and good gas barrier properties of the multiblock copolymer, its performance was remarkably better than Nafion™.

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## CHAPTER 6. Synthesis and Characterization of Crosslinked Disulfonated Poly(arylene ether sulfone) Membranes for Desalination of Water by Electrodialysis

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### 6.1 Abstract

Controlled molecular weight poly(arylene ether sulfone) oligomers with aromatic amine end groups and systematically varied degrees of disulfonation were synthesized by direct polymerization of disulfonated and non-sulfonated 4,4'-dichlorodiphenyl sulfone. <sup>1</sup>H NMR and size exclusion chromatography (SEC) confirmed the targeted molecular weights of the *m*-aminophenol (*m*-AP) terminated oligomers. The oligomers were crosslinked with a tetrafunctional epoxy curing agent in the membrane casting process. Fundamental properties of these copolymers were investigated for use as cation exchange membranes for water desalination by electrodialysis. At similar IECs, membranes with the shorter ~5000 Da oligomers absorbed less water than those

with 10,000 Da blocks, likely due to higher amounts of the hydrophobic curing agents in those network. The salt permeabilities correlate with water uptake, IEC, and fixed charge density in the networks. Among the series of crosslinked membranes, the one prepared with the 10,000 Da oligomer and 50% disulfonation (*mB5-10*) has an excellent combination of water uptake, mechanical properties, fixed charge density, and salt permeability.

## 6.2 Introduction

Pure water scarcity is a global challenge that needs to be addressed immediately.<sup>1-2</sup> Technologies such as reverse osmosis (RO)<sup>3</sup> and electrodialysis (ED)<sup>4-5</sup> use dense, non-porous membranes for water purification.<sup>6</sup> ED is typically limited to purifying low salinity water. It can be advantageous over RO due to possibilities for higher water recovery and lower cost.<sup>7-10</sup> The main components of ED are anion exchange membranes (AEM) and cation exchange membranes (CEM). These membranes are placed alternately in stacks between cathodic and anodic electrodes. Brine is pumped into the system between each AEM and CEM and a current is applied to drive the ions in opposite directions toward the respective electrodes. The role of the AEM and CEM is to promote counterion permeation through the membrane while preventing co-ion transport. The ED process leaves purified water in the diluate compartments.<sup>11</sup> The ability of the membrane to transport counterions of the fixed membrane charges and to block co-ion transport depends highly on the polymer structure, charge concentration in the membrane and water uptake.<sup>8, 12</sup> Desirable ED membranes have low electrical resistance, high chemical and mechanical stability, high counterion transport, low co-ion transport, high ion exchange capacity (IEC), and relatively low water uptake. Commercial CEMs for ED are highly crosslinked polymers such as sulfonated poly(styrene-co-divinylbenzene) with inherently poor mechanical properties. To improve the

mechanical properties, these crosslinked polymers are prepared in a non-ionic porous support membrane. Having the non-ionic support membrane results in lower ion permeability and ion conductivity, and higher electrical resistance.<sup>13-14</sup>

Many approaches including polymer modification, blending, and composite membrane preparation have been investigated to prepare membranes for ED.<sup>15-17</sup> Reig et al.<sup>18</sup> used a polymer modification approach to make highly ion selective polymer composites. Blends of poly(vinylidene fluoride) and sulfonated poly(vinylidene fluoride) were surface modified with polyaniline and subsequently doped with small molecules to make a composite with smooth surface. These polymers have shown high selectivity for sodium ions. However, the low ion exchange capacity (IEC) of these membranes led to poor overall performance of the polymer, especially as the amount of dopant was increased.

When linear ionic copolymers sorb water, they swell significantly, while crosslinked membranes with similar IECs sorb less water.<sup>19</sup> Previously, our group studied the properties of two series of crosslinked disulfonated poly(arylene ether sulfone)s for reverse osmosis.<sup>20</sup> These crosslinked copolymers were prepared from *m*-aminophenol terminated oligomers reacted with a tetra-functional epoxy reagent. At reverse osmosis conditions, these copolymers with low ion content showed good water flux and high NaCl rejection. However, only copolymers with low degrees of disulfonation and a maximum IEC of 1.84 meq/g were investigated. For ED applications, the properties of such copolymers with high IECs that are comparable to commercial crosslinked ion exchange membranes are not well understood.

This paper describes the properties and performance of related copolymers at IECs close to those of commercial ion exchange membranes. One approach was to increase the degree of disulfonation on short-chain, terminally-functionalized oligomers and to crosslink them at their

termini to minimize swelling. The second approach was to constrain the water absorption by synthesizing higher molecular weight oligomers with lower degrees of disulfonation, then to crosslink them. These methods resulted in copolymers with a range of IEC values from approximately 1.74 to 2.27 meq/g in the polymer networks. Effects of the degree of disulfonation and molecular weight of the oligomers were investigated with respect to water uptake, hydrated membrane mechanical properties and other important transport properties.

### 6.3 Experimental

#### Materials

Toluene was purchased from Sigma-Aldrich and used as received. 4,4'-Biphenol (BP) was provided by Eastman Chemical Company. 4,4'-Dichlorodiphenylsulfone (DCDPS) was provided by Solvay Advanced Polymers and was recrystallized from toluene and dried under vacuum at 120 °C prior to use. 3-Aminophenol (*m*-AP, 99%) was purchased from Acros Organics and used as received. 3,3'-Disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS, >99%) was purchased from Akron Polymer Systems and dried under vacuum at 180 °C for 72 h before use. Potassium carbonate was purchased from Sigma-Aldrich and dried under vacuum at 180 °C for 72 h before use. Calcium hydride (90–95%) was purchased from Alfa Aesar. Triphenylphosphine (TPP, 99%), and tetraglycidyl bis(*p*-aminophenyl)methane (TGBAM, 92%) were purchased from Sigma-Aldrich. Toluene and 2-propanol (IPA) were purchased from Fisher Scientific. *N,N*-Dimethylacetamide (DMAc) was purchased from Sigma-Aldrich, distilled from calcium hydride and stored over molecular sieves before use.

### Synthesis of *m*-AP terminated oligomers

Aromatic nucleophilic substitution step copolymerization was used to synthesize the terminally-reactive oligomers with *m*-aminophenol end groups. The nomenclature used in this manuscript is BiPhenyl Sulfone (*m*Bx-y) in which x-y represent 10% of the actual degree of disulfonation value and 0.1% of the oligomer molecular weight, respectively. A typical disulfonated *m*-Aminophenol terminated BiPhenyl Sulfone 60 with a molecular weight of 10000 Da expressed in the abbreviated form of *m*B6-10 was synthesized as follows. BP (0.47 mmol, 8.752 g), DCDPS (20 mmol, 5.743 g), SDCDPS (30.0 mmol, 14.767 g), *m*-AP (6 mmol, 0.639 g) and DMAc (100 mL) were charged into a 250-mL three neck round bottom flask equipped with a mechanical stirrer, condenser, nitrogen inlet, and Dean-Stark trap filled with toluene. The mixture was stirred in an oil bath at 150 °C until all the monomers completely dissolved. K<sub>2</sub>CO<sub>3</sub> (51 mmol, 8.44 g), and toluene (50 mL) were added into the flask. The reaction was refluxed for 4 h to azeotropically remove water from the system. Toluene was drained from the Dean-Stark trap, and the oil bath temperature was raised to 180 °C to remove residual toluene from the reaction. The reaction solution was stirred for 48 h to complete polymerization, then allowed to cool to room temperature. After dilution of the resulting solution with DMAc (100 mL), it was filtered to remove the salt. The transparent solution was precipitated by addition into isopropanol with stirring. The polymer was filtered and dried at 120 °C under reduced pressure in a vacuum oven. Yield 96% copolymer.

## Nuclear Magnetic Resonance Spectroscopy (NMR)

$^1\text{H}$  NMR analysis of the statistical copolymers was conducted on a Varian Unity Plus spectrometer operating at 400 MHz. The spectra of the copolymers were obtained from a 10% (w/v) solution in  $\text{DMSO-d}_6$  with 256 scans.

## Size Exclusion Chromatography (SEC)

Molecular weights and polydispersities of the polymers were measured using SEC. The mobile phase was DMAc distilled from  $\text{CaH}_2$  containing dry LiCl (0.1 M). The column set consisted of 3 Agilent PLgel 10-mm Mixed B-LS columns 300 \* 7.5 mm (polystyrene/divinylbenzene) connected in series with a guard column having the same stationary phase. The columns and detectors were maintained at 50 °C. An isocratic pump (Agilent 1260 infinity, Agilent Technologies) with an online degasser (Agilent 1260), autosampler and column oven were used for mobile phase delivery and sample injection. A system of multiple detectors connected in series was used for the analyses. A multi-angle laser light scattering detector (DAWN-HELEOS II, Wyatt Technology Corp.), operating at a wavelength of 658 nm, a viscometer detector (Viscostar, Wyatt Technology Corp.), and a refractive index detector operating at a wavelength of 658 nm (Optilab T-rEX, Wyatt Technology Corp.) provided online results. The system was corrected for interdetector delay and band broadening using a 21,000 Da polystyrene standard. Data acquisition and analysis were conducted using Astra 6 software from Wyatt Technology Corp. Validation of the system was performed by monitoring the molar mass of a known molecular weight polystyrene sample by light scattering. The accepted variance of the 21,000 Da polystyrene standard was defined as 2 standard deviations (11.5% for  $M_n$  and 9% for

$M_w$ ) derived from a set of 34 runs. Specific refractive index values were calculated based on the assumption of 100% recovery.

### Membrane casting and characterization

Dense crosslinked films were prepared by adding the oligomers to TGBAM in a 1:2.5 molar ratio. TPP was used in a 2.5% by weight ratio relative to the weight of TGBAM. The following steps were completed to prepare a crosslinked film containing *mB6-10*. A mixture of *mB6-10* (0.294 mmol, 3.0 g), TGBAM (0.735 mmol, 0.3105 g) and TPP (0.03 mmol, 7.7 mg) were dissolved in DMAc (45 mL) and stirred until a homogeneous solution was obtained. The solution was syringe filtered through a 0.45  $\mu\text{m}$  PTFE filter into a new vial. The solution was cast on a glass mold and a watch glass was placed on top of the mold. The mold was placed on a leveled surface inside a convection oven at 140  $^{\circ}\text{C}$  for 1 h. The oven temperature was raised to 155  $^{\circ}\text{C}$  for 2 h and finally to 175  $^{\circ}\text{C}$  for 1 h. The oven was turned off, and the film was allowed to cool slowly to room temperature for 6 h. The film was transferred to a boiling 0.02 M NaOH bath to aid in detaching the epoxy-cured network from the glass substrate. Once separated, the film was stored in dilute NaOH solution. Film thicknesses were approximately 200  $\mu\text{m}$ .

### Gel Fraction Measurements

Crosslinked films were dried at 120  $^{\circ}\text{C}$  under vacuum overnight. After drying, 0.1–0.2 g of the sample was placed in a 20-mL scintillation vial filled with DMAc and stirred at 100  $^{\circ}\text{C}$  for  $\sim 12$  h. The remaining solid was filtered, transferred to a weighed vial, dried at 160  $^{\circ}\text{C}$  under vacuum for  $\sim 12$  h, and then weighed. Three measurements were taken for each film, and gel fractions were calculated by Equation 6.1.

$$Gel\ Fraction\ (\%) = \frac{Final\ mass\ of\ extracted\ film}{initial\ mass\ of\ dried\ film} \times 100 \quad (6.1)$$

#### Water uptake

The water uptakes of the crosslinked membranes were determined gravimetrically. First, the membranes in their sodium salt form were dried at 120 °C under vacuum for 24 h and weighed. These membranes were soaked in water at room temperature for 24 h. Wet membranes were removed from the liquid water, blotted dry to remove surface droplets, and quickly weighed. The water uptake of the membranes was calculated according to Equation 6.2, where  $mass_{dry}$  and  $mass_{wet}$  refer to the masses of the dry and the wet membranes, respectively.

$$Water\ Uptake\ (\%) = \frac{Mass_{wet} - Mass_{dry}}{Mass_{dry}} \times 100 \quad (6.2)$$

#### Tensile tests

Highly crosslinked membranes were cut into dogbone samples, Type V according to ASTM D638-14, using a Cricut Explore One™ cutting machine. Seven samples with uniform thickness from each membrane were tested. The thickness of the dogbones were measured at five points along the narrow section using a Mitutoyo digimatic micrometer model MDC-1”SXF. The Instron was placed in a tank to allow for mechanical testing under fully hydrated conditions. The wet samples were loaded into the Instron in the tank, and the tank was filled with DI water. The samples were immersed in DI water for at least 24 h, removed just prior to testing, then equilibrated in the Instron in the water bath for 3 min. Uniaxial load tests were performed using an Instron ElectroPuls E1000 testing machine equipped with a 250-N Dynacell load cell. The crosshead displacement rate was 10 mm/min and the initial grip separation was 25 mm.

## Salt Permeability

Salt permeability was measured using direct permeation cells (Side-by-Side Cells, PermeGear, Hellertown, PA, USA). A polymer film was clamped between two cells equipped with a water jacket circulating water from an isothermal bath to maintain constant temperature at 25 °C. The driving force for salt transport through the polymer membrane in this experiment is the concentration difference between donor and receiver cells. Thus, the donor cell was filled with 0.1 M NaCl solution and the receiver cell was filled with DI water. The increase in salt concentration in the receiver cell was monitored and recorded with a conductivity meter (WTW LR 325/01 conductivity probe, Weilheim, Germany) as a function of time. A calibration curve for NaCl was established before salt permeability measurements and used for converting conductivity to salt concentration. The steady-state salt permeability,  $P_s$ , was calculated using Equation 6.3

$$\ln \left[ 1 - \frac{2C_{sl}^s[t]}{C_{s0}^s[0]} \right] = - \left( \frac{2AP_s}{VL} \right) t \quad (6.3)$$

where  $C_{sl}^s[t]$  is the receptor salt concentration at time  $t$ ,  $C_{s0}^s[0]$  is the initial donor concentration of salt (0.1 M NaCl in this study),  $V$  is the donor or receptor volume (35 mL),  $A$  is the effective film area (1.77 cm<sup>2</sup>), and  $L$  is the membrane thickness.

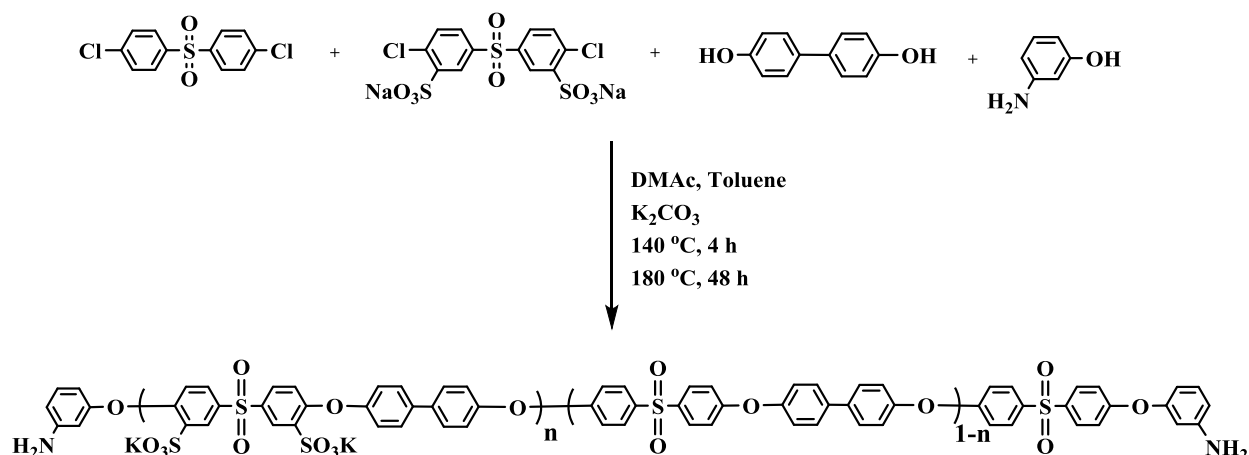
## 6.4 Results and Discussion

### Synthesis and Characterization of Disulfonated Poly(arylene ether sulfone) Oligomers with Terminal Functionality

Synthetic methods for preparing crosslinked disulfonated poly(arylene ether sulfone) oligomers with reactive phenoxide or aromatic amine terminal end groups have been previously

reported by our group for potential applications as desalination membranes by reverse osmosis or for use as proton exchange membranes for fuel cells.<sup>20-22</sup> The phenoxide terminated oligomers were difunctional while the oligomers bearing *meta*-aminophenol (*m*-AP) amine end groups were tetra-functional. Thus, in comparison with phenoxide terminated oligomers, more functional groups were available for crosslinking using the *m*-AP terminated oligomers.

Scheme 6.1 shows the nucleophilic aromatic substitution reaction that was used to synthesize controlled molecular weight *m*-AP terminated disulfonated poly(arylene ether sulfone) oligomers in the present work. Three copolymers in each series with targeted molecular weights of 5 and 10 kDa, calculated from the Carothers' equation, were synthesized so that the properties of the resultant thermoset networks could be investigated.



**Scheme 6.1** Nucleophilic aromatic substitution reaction for direct polymerization of controlled molecular weight disulfonated oligomers with a random arrangement of repeat units

SEC and <sup>1</sup>H NMR were used to measure the compositions and the degrees of disulfonation of the oligomers and the molecular weights. Figure 6.1 illustrates a <sup>1</sup>H NMR spectrum of *m*B6-10 that confirms the composition of this oligomer. Molecular weights calculated from the NMR

spectra of all of the oligomers were within the range of  $\pm 2$  repeat units of the targeted molecular weights. The NMR and SEC data agreed reasonably well in all cases (Table 6.1). The light scattering data was used to calculate the molecular weights by SEC.

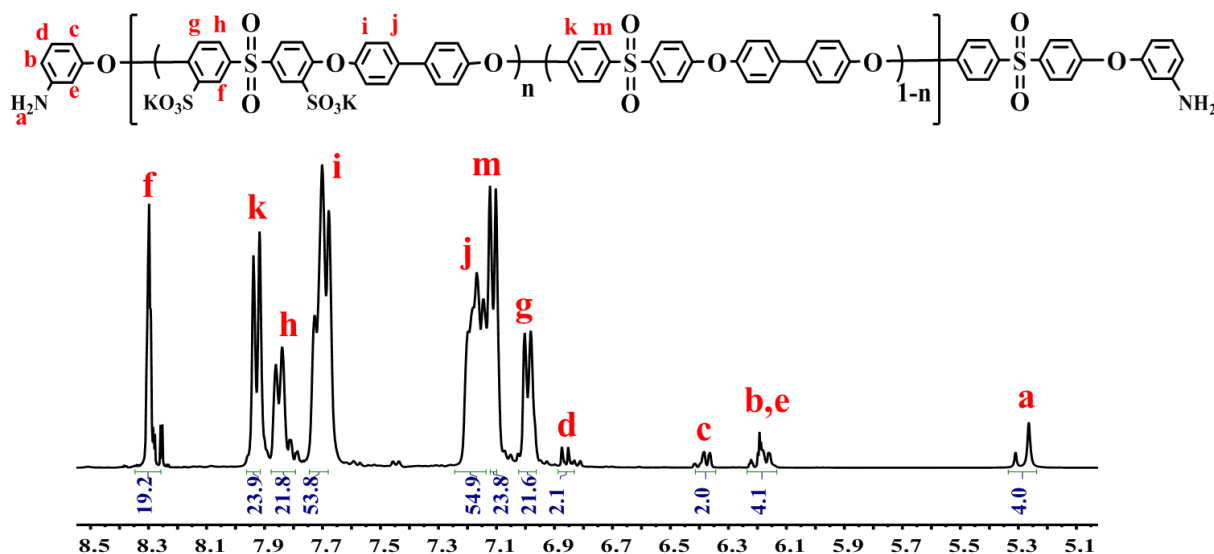


**Figure 6.1**  $^1\text{H}$  NMR spectrum of mB6-10 as a representative example of *m*-AP functional oligomers

As shown in Figure 6.1, peak (a) consists of two separate peaks which is due to structures with the two different monomers, SDCDPS and DCDPS, adjacent to the *m*-AP endgroup. In addition to the molecular weights of the oligomers, the degrees of disulfonation were calculated from  $^1\text{H}$  NMR. Resonance integrals of the *m*-AP functional group, DCDPS, and SDCDPS were used to evaluate the degrees of disulfonation according to Equation 6.4

$$\text{Degree of Disulfonation (DS)} = \frac{\left(\frac{H_f + H_g + H_h}{6}\right)}{\left(\frac{H_k + H_m}{8}\right) + \left(\frac{H_f + H_g + H_h}{6}\right)} \times 100 \quad (6.4)$$

All of the degrees of disulfonation fell within 2% of the targeted values. The corresponding oligomer IECs were also calculated (Table 6.1) from the degrees of disulfonation of each oligomer.

**Table 6.1** Structures and molecular weights of the *mBx-5* and *mBx-10* oligomers

| Oligomer      | Degree of Disulfonation (%) | Oligomer IEC (meq/g) | M <sub>n</sub> <sup>a</sup> (Da) | M <sub>n</sub> <sup>b</sup> (Da) |
|---------------|-----------------------------|----------------------|----------------------------------|----------------------------------|
| <i>mB6-5</i>  | 61                          | 2.24                 | 5400                             | 5900                             |
| <i>mB7-5</i>  | 69                          | 2.46                 | 5100                             | 6300                             |
| <i>mB8-5</i>  | 81                          | 2.74                 | 4800                             | 4200                             |
| <i>mB5-10</i> | 49                          | 1.90                 | 9800                             | 11200                            |
| <i>mB6-10</i> | 59                          | 2.20                 | 10200                            | 9800                             |
| <i>mB7-10</i> | 69                          | 2.46                 | 9900                             | 10300                            |

<sup>a</sup> Calculated via <sup>1</sup>H NMR    <sup>b</sup> Calculated via SEC

### Crosslinking of Oligomers and Membrane Casting

The film casting process wherein the crosslinking reaction takes place has a remarkable effect on the properties of the membranes.<sup>23</sup> In an ED membrane, high IECs with constrained water uptake leading to high fixed charge concentration are desirable to maximize co-ion rejection and improve counterion passage while mechanical integrity is retained.<sup>24</sup> In this work, membranes with a thickness of approximately 200 μm were prepared with a slow solvent evaporation rate. In the curing process, the solvent acts as a plasticizer that suppresses the T<sub>g</sub> of the copolymer during cure. The curing reaction temperature was begun at 140 °C, and the temperature was gradually raised to 190 °C during the reaction to control the DMAc solvent evaporation rate. For comparison, membranes of biphenol based linear copolymers were processed under the same conditions as the crosslinked membranes. Results of water uptake in membranes prepared from polymers of different architectures revealed that highly crosslinked membranes absorb less water than the

corresponding linear copolymers. The water uptake values are tabulated in Table 6.2. The lower water uptake of the crosslinked membranes in comparison with their linear high molecular weight counterparts is due to the presence of the hydrophobic curing agent TGBAM which reduces the affinity of the membrane for water. In addition, at similar IECs, membranes with a 5000 Da oligomeric length show relatively lower water uptake than those with 10000 Da blocks as a result of having more TGBAM in the networks. Highly crosslinked membranes were obtained when the *m*-AP end groups were reacted with the epoxy groups of the TGBAM. All of the crosslinked membranes reached a high gel fraction of >90% and this inhibited excessive water uptake and swelling (Table 6.2).<sup>20,25</sup> The fixed charge concentrations of these copolymers along with similar linear random copolymers with similar IECs are shown in Table 6.2.

**Table 6.2** Properties of biphenol-based crosslinked copolymers made via 5kDa and 10kDa oligomers

| Crosslinked Membrane | Gel Fraction (%) | Theoretical IEC of the Network (meq/g) | Water Uptake <sup>a</sup> (wt %) | Fixed Charge Concentration (mol of fixed charged groups / L sorbed water) |
|----------------------|------------------|----------------------------------------|----------------------------------|---------------------------------------------------------------------------|
| <i>m</i> B6-5        | 95.4±1.3         | 1.84                                   | 56±1.2                           | 3.28                                                                      |
| <i>m</i> B7-5        | 96.6±0.5         | 2.06                                   | 67±1.0                           | 3.07                                                                      |
| <i>m</i> B8-5        | 92.3±2.2         | 2.28                                   | 80±2.5                           | 2.85                                                                      |
| <i>m</i> B5-10       | 94.7±1.8         | 1.74                                   | 39±0.5                           | 4.46                                                                      |
| <i>m</i> B6-10       | 97.8±2.0         | 2.03                                   | 63±1.0                           | 3.22                                                                      |
| <i>m</i> B7-10       | 98.0±1.0         | 2.27                                   | 78±2.1                           | 2.91                                                                      |
| BPS-40 <sup>b</sup>  | -                | 1.65                                   | 55±2.8                           | 3.10                                                                      |
| BPS-50 <sup>b</sup>  | -                | 1.93                                   | 105±3.0                          | 1.84                                                                      |

<sup>a</sup> Sodium salt form <sup>b</sup> BPS represents the high molecular weight linear random copolymers synthesized from Biphenol, DCDPS, and SDCDPS

#### Fundamental Properties of the Crosslinked Membranes

The theoretical IECs of the membranes are the values calculated from the known IECs of the oligomers and considering the addition of the non-ionic curing agent. For example, the *m*B6-5

oligomer has an IEC of 2.24 meq/g and the *mB6-10* oligomer IEC is 2.20 meq/g. The IECs of the final crosslinked membranes are 1.84 and 2.03 meq/g for *mB6-5* and *mB6-10* respectively. This difference is due to incorporation of lower amounts of curing agents in the thermosetting reactions with longer oligomeric chains.

Mechanical properties of the fully hydrated ionic copolymers depend highly on the degree of disulfonation and water uptake.<sup>26-27</sup> In linear copolymers, as the degree of disulfonation increases, the ratio of free to bound water increases, and this results in a morphological transition in the copolymer.<sup>22, 28</sup> We have previously shown that linear copolymers with similar structures undergo this morphological transition at water uptakes of above approximately 50%.<sup>29</sup> This transition was confirmed with a reduced modulus of the linear statistical copolymers. Paul *et al.*<sup>22</sup> showed that crosslinked copolymers had decreased ratios of free to bound water as the degree of crosslinking was increased in the polymer networks. Thus, in the crosslinked membranes, the morphological transition likely occurs at higher IECs than in the linear copolymers. Sundell *et al.*<sup>20</sup> reported the synthesis of crosslinked membranes with water uptakes of less than 40% but no hydrated mechanical properties of those membranes were reported. In the present work copolymers similar to Sundell's work but with higher IECs and different oligomeric block lengths were investigated. Morphologies of the copolymers with near 50% water uptake tend to represent this morphology change and that is supported by the hydrated mechanical properties. As shown in Figure 6.2, the decreased moduli in the crosslinked membranes occur at a degree of disulfonation of above almost 60% in both series of *mBx-5* and *mBx-10* networks. At such degrees of disulfonation, the water absorption in the crosslinked networks is more than 50 wt%. However, the *mB5-10* membrane that absorbs less than 50% of water has higher modulus than all of the other copolymers.

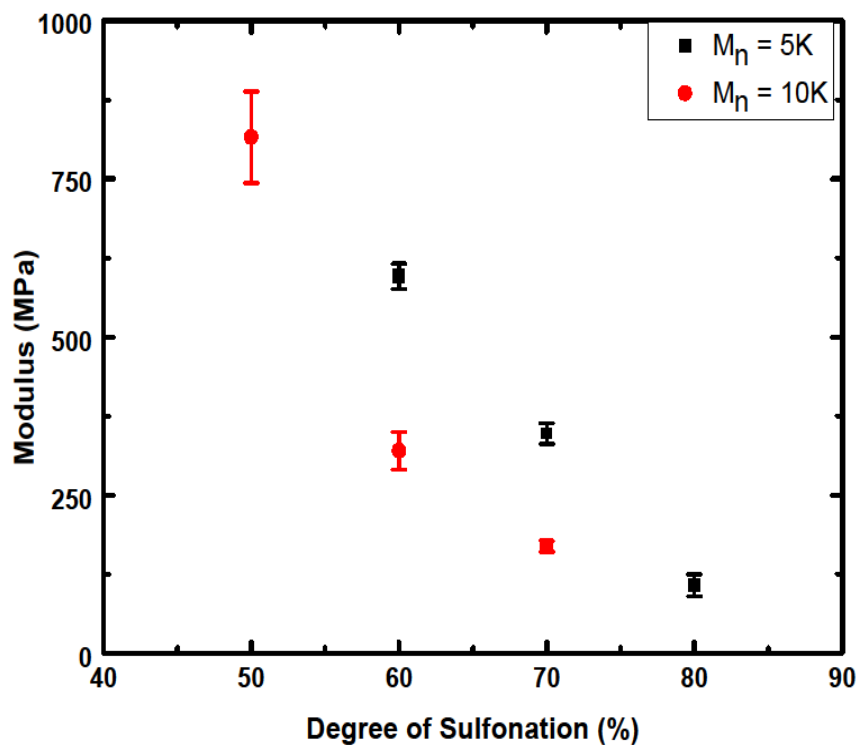


**Figure 6.2** Modulus vs. degree of disulfonation in two series of crosslinked membranes

The mechanical properties show that the highest stress at yield for these hydrated crosslinked membranes is obtained for the *mB5-10* membrane (Figure 6.3). This is due to the water uptake of this membrane constrained to 39%, well below the change in morphological regime.

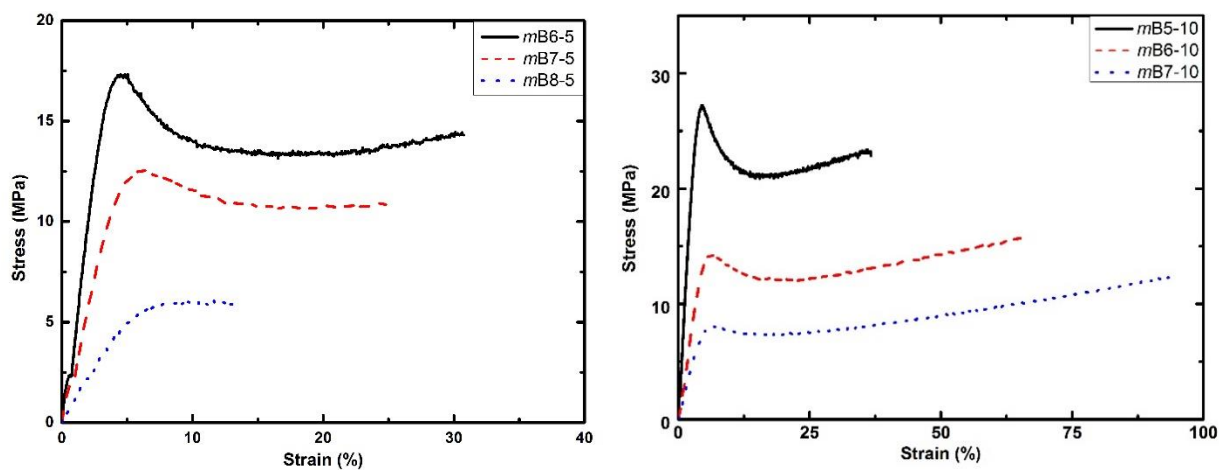


**Figure 6.3** Stress-strain plots of fully hydrated crosslinked membranes

### Salt Permeability

Salt permeability of the  $mBx-y$  membranes was measured using a direct permeation cell as described in the experimental section. Salt permeability,  $\langle P_s \rangle$ , for  $mBx-y$  membranes are presented as a function of water uptake in Figure 6.4. Upstream NaCl concentration was fixed at 0.1 M to facilitate comparison among different membranes. As shown in Figure 6.4, the salt permeability increases as water uptake increases.

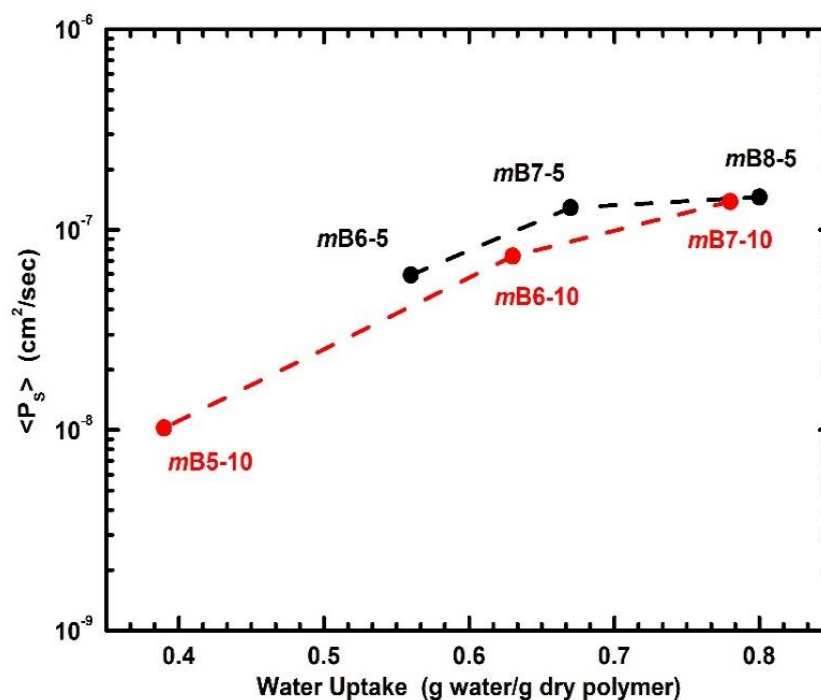


**Figure 6.4** Salt permeability,  $\langle P_s \rangle$ , measured with 0.1 M NaCl upstream solution for mBx-y membranes as a function of water uptake. Each data point represents the average of measurements made on at least three samples

Interestingly, salt permeability of these crosslinked membranes shows a strong correlation with water uptake regardless of the block length of the copolymer. For example, the salt permeabilities of *mB6-10* and *mB7-10* fall between the values for *mB6-5* and *mB8-5*. Previous studies suggested that ion transport in ion exchange membranes is mainly governed by water uptake and electrostatic interactions between fixed charge groups on the polymer backbone and mobile ions.<sup>30-31</sup> However, the hydrated mechanical properties may very well be strongly affected by the block length of the oligomers. In this work it is likely that the only membrane with sufficient hydrated strength is the *mB5-10* and this membrane is also the only example with low water uptake and salt permeability. Thus, further investigations to correlate the hydrated mechanical properties with the block lengths (crosslink density) will be necessary.

To illustrate the influence of electrostatic interaction between fixed charge and mobile ions on salt transport, salt permeability in crosslinked  $mBx-y$  membranes is presented as a function of fixed charge concentration in Figure 6.5. Fixed charge concentration,  $C_A^m$ , can be calculated by theoretical IEC value and water uptake of the membrane using the relationship in Equation 6.5.<sup>31</sup>

$$C_A^m = \frac{IEC}{water\ uptake} \quad (6.5)$$

where  $C_A^m$  is expressed as mols of fixed charge groups per L of sorbed water and the  $C_A^m$  values for  $mBx-y$  membranes are reported in Table 6.2. As shown in Figure 6.5, the salt permeability of the crosslinked membranes decreases as fixed charge concentration increases. This behavior is generally explained by Donnan exclusion. Ion transport in dense polymer membranes such as crosslinked polymers considered in this study follow the solution-diffusion mechanism, where ion sorption (i.e., partitioning) is a crucial factor.<sup>32</sup>

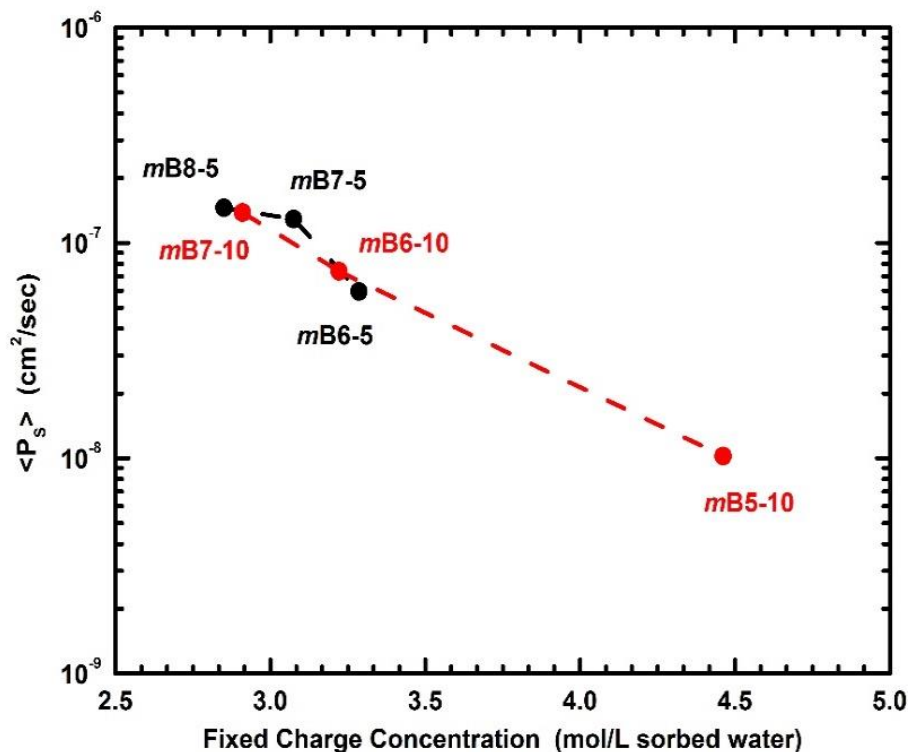


**Figure 6.5** Effect of fixed charge concentration on salt permeability,  $\langle P_s \rangle$ , measured with 0.1 M NaCl upstream solution for crosslinked mBx-y membranes. Each data point represents the average of measurements made on at least three samples

For a given upstream NaCl concentration (i.e., 0.1 M in this case), membranes with higher fixed charge concentration have stronger co-ion (i.e., ions with the same charge as that of the fixed charge groups) exclusion than membranes with lower fixed charge concentration owing to a greater Donnan potential at the membrane/solution interface.<sup>31</sup> Thus, reduced co-ion (i.e, Cl<sup>-</sup> ions) sorption in membranes with higher fixed charge concentration exhibit lower salt permeability compared to those with lower fixed charge concentration. Fundamental studies of salt solubility (i.e., sorption) and diffusivity in these materials will further elucidate the influence of fixed charge concentration and they will be the subject of a future investigation. Controlling fixed charge concentration and water uptake in cross-linked ion exchange membranes (IEMs) is crucial for practical applications. In membrane processes driven by a concentration gradient such as reverse

osmosis, forward osmosis, and pressure-retarded osmosis, low salt permeability and high water permeability are required to obtain high salt rejection and water recovery.<sup>6, 33</sup> Previously, we reported salt rejection and water permeability results for a series of cross-linked *mBx-5* membranes,<sup>20</sup> where increasing fixed charge concentration did not result in an increase in salt rejection. Salt rejection is related to water/salt selectivity (i.e., the ratio of water permeability to salt permeability).<sup>33</sup> Low water uptake results in low water permeability, which, in turn, leads to increased water/salt selectivity and salt rejection. Thus, water uptake of IEMs needs to be balanced with fixed charge concentration to obtain desirable transport properties. For membrane processes driven by an electric-field such as ED and capacitive deionization (CDI), selective transport of counter-ions (i.e., ions with opposite charge to that of the fixed charge groups) over co-ions is required, which can be better achieved by strong co-ion exclusion.<sup>34-35</sup> For IEMs made from linear polymers, increasing IEC does not necessarily lead to increased fixed charge concentration. As shown in Equation 6.5, the amount of increased water uptake is greater than that of IEC in linear polymers, which, in turn, decreases the effective fixed charge concentration. For IEMs made from cross-linked polymers, however, the amount of increased water uptake with increasing IEC is suppressed so that the fixed charge concentration stays relatively high. Therefore, crosslinked IEMs such as those investigated in this work may be designed to have desired water permeability and simultaneously to have salt permeability necessary for a given application.<sup>20-21</sup> It is promising that the *mB5-10* membrane from this work has a combination of high fixed charge concentration and low salt permeability with good hydrated mechanical properties. Further investigations will confirm whether the water flux in such a membrane is desirable for practical applications such ED or CDI.

## 6.5 Conclusions

In this paper a series of controlled molecular weight disulfonated *m*-aminophenol terminated oligomers were synthesized and cured with a tetrafunctional epoxy reagent under controlled heating conditions to result in highly crosslinked membranes. Structure-property relationships with regard to membranes for water purification were investigated. These included correlations among polymer network structure and water uptake, hydrated mechanical properties, and salt transport properties. From mechanical property investigations, it was shown that water uptake of above 50% in the networks resulted in a morphology that was dominated by a hydrophilic phase, and the mechanical stability of those copolymers was greatly reduced. However, the mechanical properties of the network containing the higher block length oligomer (10 kDa) that was 50% disulfonated (*m*B5-10) and that contained only 39% water uptake showed a greatly improved yield strength of ~27 MPa with a good ultimate elongation under immersion conditions. Moreover, salt permeabilities correlated with water uptake and fixed charge concentration, where salt permeability increased with increasing water uptake and decreased with increasing fixed charge concentration. The *m*B5-10 network with the better hydrated mechanical properties and with the highest fixed charge concentration also showed the lowest salt permeability, thus suggesting that this composition regime is quite promising. However, further investigation of the higher block length materials with intermediate degrees of disulfonation will be required to understand and deconvolute the influence of structure and water uptake on water and salt transport properties in such copolymers.

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## **CHAPTER 7. Synthesis of Mono Sulfonated Poly(Arylene Ether Sulfone) Copolymers for Desalination of Water: Direct Copolymerization of Mono Sulfonated Diphenyl Sulfone Monomer**

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### **7.1 Abstract**

A monosulfonated dichlorodiphenylsulfone monomer (MSDCDPS) was synthesized in one step. The structure and purity of MSDCDPS were confirmed via <sup>1</sup>H NMR, liquid chromatography mass spectroscopy (LC-MS), and time of flight mass spectroscopy (TOF-MS). A series of statistical copolymers with a controlled degree of monosulfonation were synthesized by direct copolymerization of biphenol (BP), 4,4'-dichlorodiphenyl sulfone (DCDPS), and MSDCDPS. The composition of the copolymers was confirmed via <sup>1</sup>H NMR. Membranes of each copolymer were cast from DMAc. To confirm the targeted degree of monosulfonation, ion exchange capacity (IEC) of these copolymers were measured via titration. The measured water

uptake of the linear monosulfonated copolymers in their  $\text{Na}^+$  counter ion form was significantly lower than analogous disulfonated copolymers. Tensile testing was conducted on these membranes while fully hydrated to evaluate their robustness in conditions similar to what they would be subjected to during water desalination. An optimized copolymer with an IEC of 1.38 meq/g had an ultimate strength of 60 MPa and an elongation of greater than 150%. Additionally, salt rejection measurements were conducted on a membrane with IEC of 1.16 meq/g, which showed salt rejection of 99.3% and this excellent salt rejection was not comprised by addition of up to 200ppm divalent  $\text{Ca}^{2+}$  salt.

## 7.2 Introduction

Based on the current world population and its growth rate, there is an urgent need for pure water production.<sup>1</sup> Many technologies have been used to overcome the lack of fresh water. In terms of cost, sustainability, required energy, and water production rate, water purification via membrane technologies have shown promising results for pure water production.<sup>2-3</sup> High performance polymers are widely used as membranes in fuel cell,<sup>4</sup> gas separation,<sup>5-6</sup> electrolyzers,<sup>7</sup> and water desalination.<sup>8</sup> These membranes are used as ion-conductive membranes as well as a gas barrier layer for separation applications.<sup>9-10</sup> The ion conductivity in membranes is provided either through positive charges like alkyl ammonium groups, allowing anions to pass through, or acidic groups, that transfer cationic species.<sup>11-12</sup> In both forms, membranes should meet the basic criteria such as mechanical robustness, high ion conductivity, and controlled water uptake.<sup>9</sup>

Cation exchange membranes (CEM) have anionic groups placed along the polymer backbone (e.g., sulfonate). Sulfonate containing copolymers can be synthesized in at least two ways. The sulfonate groups can be placed on the activated position of an aromatic ring or the

sulfonic acid groups can be placed on the deactivated position of the aromatic rings.<sup>13-14</sup> Copolymers synthesized from monomers with more than one sulfonate group have shown satisfactory performance in electrochemical systems.<sup>15-18</sup> These multi-sulfonated comonomers have also been investigated in membranes for water desalination.<sup>19</sup> However, separation of ions in desalination processes is complicated when saline water contains multivalent ions.<sup>20</sup> Making a robust and monovalent ion selective membrane is necessary to prevent chelation of multivalent ion with the acidic groups of the polymer.<sup>21-25</sup>

Several polymeric systems were investigated for separating monovalent and multivalent ions via electrodialysis and reverse osmosis water purification.<sup>22, 26</sup> To increase monovalent/divalent ion separation, Hou et al.<sup>23</sup> used functionalized polyphenylene oxide based copolymers in nanofibrous composite membranes containing negatively and positively charged groups. In this approach, application of electrospinning for membrane preparation resulted in a uniform composite film with good divalent ion rejection. However, applying quaternary ions in the composite had an adverse effect, specifically as the amount of positive charges increased in the matrix. While good ion selectivity was obtained, the co-ion passage increased as the amount of ammonium groups increased in the matrix.

In the past decade, graphene has attracted tremendous attention for a variety of applications due to its exceptional nanoscopic properties.<sup>27-29</sup> Recently, Surwade et al. reported preparation of a single layer graphene membrane via an oxygen plasma etching method. This approach resulted in a membrane with nano-sized pores having outstanding mechanical stability and desalination properties. In addition to a controlled pore size, an increased water transport and nearly 100% salt reject was observed with this material. However, due to the cost of graphene and scaling issues, commercialization of this material is not feasible at this time.

In this work, the synthesis of a mono-sulfonated 4,4'-dichlorodiphenylsulfone (MSDCDPS) monomer was investigated. The monomer structure was characterized via  $^1\text{H}$  NMR and mass spectroscopy. A series of linear poly(arylene ether sulfone) random copolymers was synthesized. In addition, fundamental properties of this copolymer were compared to other copolymers such as disulfonated linear poly(arylene ether sulfone) random copolymers and a monosulfonated hydroquinone-based random copolymer. Important fundamental properties of these copolymers for water desalination applications were measured including water uptake and mechanical properties in fully hydrated conditions. Finally, transport properties including monovalent and divalent mixed salt transport, water permeability, and NaCl rejection were evaluated.

### 7.3 Experimental

#### Materials

Fuming sulfuric acid (30%  $\text{SO}_3$ ) was purchased from Macron Fine Chemicals. Calcium hydride (90–95%) and sodium chloride (>99%) were purchased from Alfa Aesar and used as received. Sodium hydroxide was purchased from Spectrum Chemicals and used as received. 1-Butanol (>99%) and anhydrous magnesium sulfate were purchased from Sigma-Aldrich and used as received. 4,4'-Dichlorodiphenylsulfone (DCDPS) was provided by Solvay Advanced Polymers and it was recrystallized from toluene and dried under vacuum at 120 °C prior to use. 4,4'-Biphenol (BP) was provided by Eastman Chemical Company and was dried at 80 °C under vacuum before use. Potassium carbonate, purchased from Sigma-Aldrich, was dried under vacuum at 180 °C for 72 h before use. Chloroform, toluene, and 2-propanol (IPA) were purchased from Fisher Scientific

and used as received. *N,N*-Dimethylacetamide (DMAc) was purchased from Sigma-Aldrich, distilled from calcium hydride and stored over molecular sieves before use.

#### Synthesis of MSDCDPS monomer

DCDPS (17.4 mmol, 5 g) was introduced into a 250-mL, round bottom flask equipped with a mechanical stirrer and a condenser, and purged with nitrogen for 5 min. The nitrogen flow was stopped and fuming sulfuric acid (19.1 mmol, 4.8 mL) was introduced to the reaction flask. DCDPS was dissolved in the fuming sulfuric acid at room temperature. When dissolution was complete, the oil bath temperature was raised to 100 °C. The reaction was allowed to proceed under an air atmosphere for 6-7 h. The reaction mixture was allowed to cool to room temperature, then the reaction flask was placed in an ice bath. Over a period of 10 min, a mixture of DI water (40 mL) and crushed ice (40 g) was slowly added to the reaction flask while stirring. After complete addition of the ice water, the reaction was heated to 65 °C and NaCl (~30 g) was slowly added to precipitate the mixture. The mixture was filtered and the solids were returned to the reaction flask. DI water (~100 mL) was added to the flask to form a suspension that contained both insoluble and soluble products. It is likely that the insoluble material was predominantly DCDPS and the monosulfonated and disulfonated monomers were in solution. The suspension was neutralized by slowly adding 10 M aqueous NaOH solution. The neutralization was constantly checked with litmus paper. The suspension was re-precipitated by adding NaCl (~30 g) at 65 °C. The precipitate was filtered and the solids were collected. The solids were dissolved by adding DI water (~70 mL) and then CHCl<sub>3</sub> (30 mL) and the aqueous layer was collected. 1-Butanol (150 mL) was added to the aqueous layer and the mixture was shaken vigorously. Once 1-butanol and water separated into two layers, the top 1-butanol layer was collected, dried over MgSO<sub>4</sub>, and filtered. After solvent

evaporation via rotary evaporator, the product was collected and dried under vacuum at 160 °C for 48 h with a yield of 59%. The MSDCDPS did not melt up to the limit, 300 °C, of the melting point apparatus.

### Synthesis of sulfonated random copolymers

Aromatic nucleophilic substitution step copolymerization was used to synthesize a series of monosulfonated biphenol-based poly(arylene ether sulfone) (mBPS-X) and disulfonated biphenol-based poly(arylene ether sulfone) (BPS-Y) copolymers. In this series “X and Y” represent the degree of monosulfonation and disulfonation in MBPS and BPS, respectively.

A mBPS-80 with 80% of the repeat units monosulfonated was synthesized as follows. BP (14.96 mmol, 2.7863 g), DCDPS (2.2445 mmol, 0.6445 g), MDCDPS (12.85 mmol, 5.00 g), and DMAc (45 mL) were charged into a 250-mL three neck round bottom flask equipped with a mechanical stirrer, condenser, nitrogen inlet, and Dean-Stark trap filled with toluene. The mixture was stirred in an oil bath at 150 °C until the monomers completely dissolved. K<sub>2</sub>CO<sub>3</sub> (18.08 mmol, 2.5 g) and toluene (20 mL) were added into the flask. The reaction was refluxed for 4 h to azeotropically remove water from the system. Toluene was drained from the Dean-Stark trap, and the oil bath temperature was raised to 180 °C to remove residual toluene from the reaction. The reaction solution was stirred for 48 h, then allowed to cool to room temperature. After dilution of the solution with DMAc (100 mL), it was filtered to remove the salt. The transparent solution was precipitated by addition into isopropanol (1000 mL) with vigorous stirring. The white fibers were filtered and then stirred in boiling DI water for 4 h to remove any residual DMAc. The copolymer was filtered and dried at 120 °C under reduced pressure in a vacuum oven. Yield 90% copolymer.

## Nuclear Magnetic Resonance Spectroscopy (NMR)

$^1\text{H}$  NMR analysis of the monomer and statistical copolymers were conducted on a Varian Unity Plus spectrometer operating at 400 MHz. The spectra of the monomer and copolymers were obtained from a 10% (w/v) solution in DMSO- $\text{d}_6$  in 256 scans.

## Mass spectroscopy

Monomer purity was confirmed using an LC/MS model TS Quantum from Agilent Technologies with Phenomenex C<sub>18</sub> Luna 150 \*2.1 mm, 5 $\mu\text{m}$  column in acetonitrile +1.0 % formic acid as the mobile phase. The mass of the monomer was measured via Time of Flight Mass Spectrometry (TOF-MS) using an Agilent-6220 Accurate Mass instrument in negative ion mode.

## Size Exclusion Chromatography (SEC)

Molecular weights and polydispersities of the polymers were measured using SEC. The mobile phase was DMAc distilled from CaH<sub>2</sub> containing dry LiCl (0.1 M). The column set consisted of 3 Agilent PLgel 10-mm Mixed B-LS columns 300 \* 7.5 mm (polystyrene/divinylbenzene) connected in series with a guard column having the same stationary phase. The columns and detectors were maintained at 50 °C. An isocratic pump (Agilent 1260 infinity, Agilent Technologies) with an online degasser (Agilent 1260), autosampler and column oven were used for mobile phase delivery and sample injection. A system of multiple detectors connected in series was used for the analyses. A multi-angle laser light scattering detector (DAWN-HELEOS II, Wyatt Technology Corp.), operating at a wavelength of 658 nm, a viscometer detector (Viscostar, Wyatt Technology Corp.), and a refractive index detector operating at a wavelength of 658 nm (Optilab T-rEX, Wyatt Technology Corp.) provided online

results. The system was corrected for interdetector delay and band broadening using a 21,000 Da polystyrene standard. Data acquisition and analysis were conducted using Astra 6 software from Wyatt Technology Corp. Validation of the system was performed by monitoring the molar mass of a known molecular weight polystyrene sample by light scattering. The accepted variance of the 21,000 Da polystyrene standard was defined as 2 standard deviations (11.5% for  $M_n$  and 9% for  $M_w$ ) derived from a set of 34 runs. Specific refractive index values were calculated based on the assumption of 100% recovery.

#### Membrane casting and characterization

The copolymers in their salt form (0.7) were dissolved in DMAc (12 mL), and then filtered through a 0.45  $\mu$ m Teflon syringe filter. The solutions were cast onto 4"  $\times$  4" clean glass substrates and dried under an infrared lamp at 50-60  $^{\circ}$ C for 8 h. Afterwards, membranes were placed in a vacuum oven under vacuum at  $\sim$ 150  $^{\circ}$ C for 6 h. The membranes were extracted in room temperature water for 12 h to remove the residual solvent and to aid in delamination from the glass plates.

#### Water uptake

The water uptakes of the membranes in their salt form were determined gravimetrically. These membranes in the  $K^+$  salt forms were soaked in water at room temperature for 24 h. Wet membranes were removed from the liquid water, blotted dry to remove surface droplets, and quickly weighed. For water uptake measurements of the membranes in the sodium salt form, membranes in the  $K^+$  salt form were soaked in 2M NaCl solution for 2 days. These membranes were soaked in DI water to remove free NaCl from the membrane and then weighed. The water

uptake of the membranes was calculated according to Equation 7.1, where mass dry and mass wet refer to the masses of the dry and the wet membranes, respectively.

$$\text{Water Uptake (\%)} = \frac{Mass_{wet} - Mass_{dry}}{Mass_{dry}} \times 100 \quad (7.1)$$

### Tensile tests

Linear random copolymer membranes were cut into dogbone samples, Type V according to ASTM D638-14, using a Cricut Explore One™ cutting machine. Seven samples with uniform thickness from each membrane were tested. The thickness of the dogbones were measured at five points along the narrow section using a Mitutoyo digimatic micrometer model MDC-1”SXF. The Instron was placed in a tank to allow for mechanical testing under fully hydrated conditions. The wet samples were loaded into the Instron in the tank and the tank was filled with DI water. The samples were immersed in DI water for at least 24 h, removed just prior to testing, then equilibrated in the Instron in the water bath for 3 min. Uniaxial load tests were performed using an Instron ElectroPuls E1000 testing machine equipped with a 250-N Dynacell load cell. The crosshead displacement rate was 10 mm/min and the initial grip separation was 25 mm.

### Ion exchange capacity (IEC)

IECs were measured in the acid form of the membranes by soaking them (in their salt form) in boiling 1M H<sub>2</sub>SO<sub>4</sub> for 2 h, followed by immersion in boiling DI water for an additional 2 h. The membranes were dried under vacuum at 110 °C for 8 h. These dry membranes in their acid form were weighed, then soaked in 1 M NaCl solution for 48 h to convert them to their salt form. Each

membrane in solution was titrated with 0.1 N NaOH solution. The IEC of each membrane in units of meq/g of dry membrane was calculated from Equation 7.2

$$IEC = \frac{V*N}{M} \times 1000 \quad (7.2)$$

where V is volume of NaOH, N is NaOH normality, and M is the mass of the dry membrane.

#### Transport property measurements

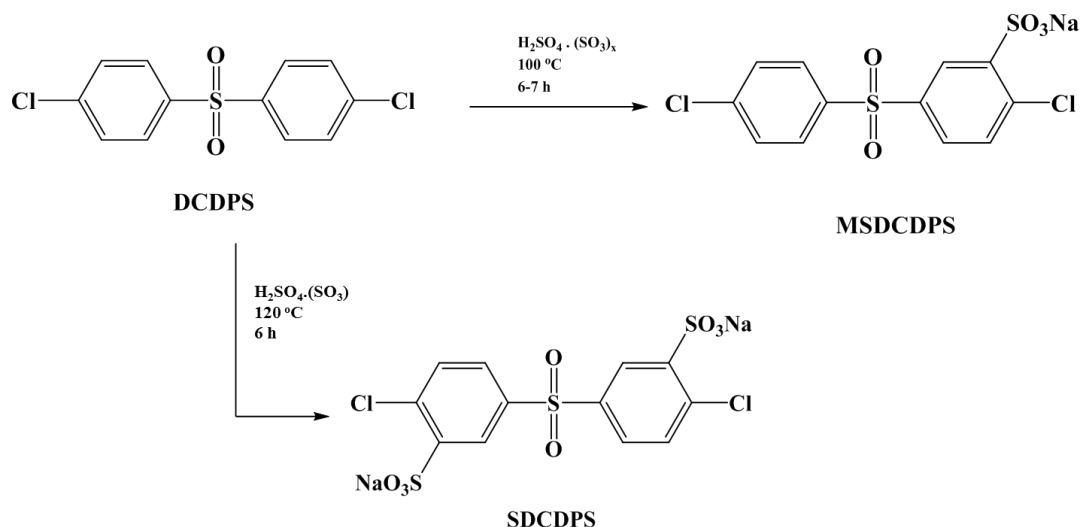
The water permeability ( $L \mu m m^{-2} h^{-1} bar^{-1}$  or  $cm^2 s^{-1}$ ), salt permeability ( $cm^2 s^{-1}$ ), salt rejection (%) and water/NaCl selectivity were determined at 25 °C using stainless steel crossflow cells. The pressure difference across the membrane ( $15.1 cm^2$ ) was 400 psi. The aqueous feed contained 2000 ppm NaCl, and the feed solution was circulated past the samples at a continuous flow rate of  $3.8 L min^{-1}$ . The feed pH was adjusted to a range between 6.5 and 7.5 using a 10 g/L sodium bicarbonate solution. NaCl concentrations in the feed water and permeate were measured with an Oakton 100 digital conductivity meter.

## 7.4 Results and Discussion

### Synthesis and characterization of a monosulfonated monomer (MSDCDPS)

DCDPS was monosulfonated to produce a new monomer for the synthesis of new polysulfones with different spacing of the sulfonate groups along the chain as compared to polymers produced from 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone.<sup>15</sup> Critical parameters in the synthesis of MSDCDPS were temperature, time, and reaction stoichiometry.<sup>17</sup> The starting materials,  $SO_3$  and DCDPS, were reacted at a 1.15:1 stoichiometric ratio at 100 °C for 6-7 hours.

Scheme 7.1 shows the synthesis of two possible products, SDCDPS and the targeted monomer, MSDCDPS.



**Scheme 7.1** Synthesis of monosulfonated dichlorodiphenylsulfone monomer (MSDCDPS) and disulfonated dichlorodiphenylsulfone (SDCDPS) from DCDPS

After neutralization of the suspension containing the crude mixture of products with the basic NaOH solution, they were salted out and the solids were isolated by filtration. The composition of the crude mixture was determined from  $^1\text{H}$  NMR that showed some unreacted DCDPS and a small amount of SDCDPS along with the desired MSDCDPS. Isolation of MSDCDPS was conducted using a two-step solvent-solvent extraction method. The solvents in each step were chosen based on their polarity and the solubility differences of each product. Thus, a chloroform:water mixture was first used to separate the non-polar DCDPS into the chloroform and the sulfonated products into the water. Then a 1-butanol:water mixture was used to separate the highly polar SDCDPS into the water and the less polar MSDCDPS into the butanol. This method allowed for all of the MSDCDPS to be isolated from the SDCDPS and the complete removal of NaCl from the mixture due to its low solubility in 1-butanol.<sup>30</sup> After each separation

step, the corresponding solvent was evaporated and the solid compound was analyzed via  $^1\text{H}$  NMR.

Mass-spectrometry and  $^1\text{H}$  NMR were used to confirm the chemical composition of the purified product (Figure 7.1). The  $^1\text{H}$  NMR spectra of three different monomers in this reaction, DCDPS, SDCDPS, and the desired product, MSDCDPS are shown below.

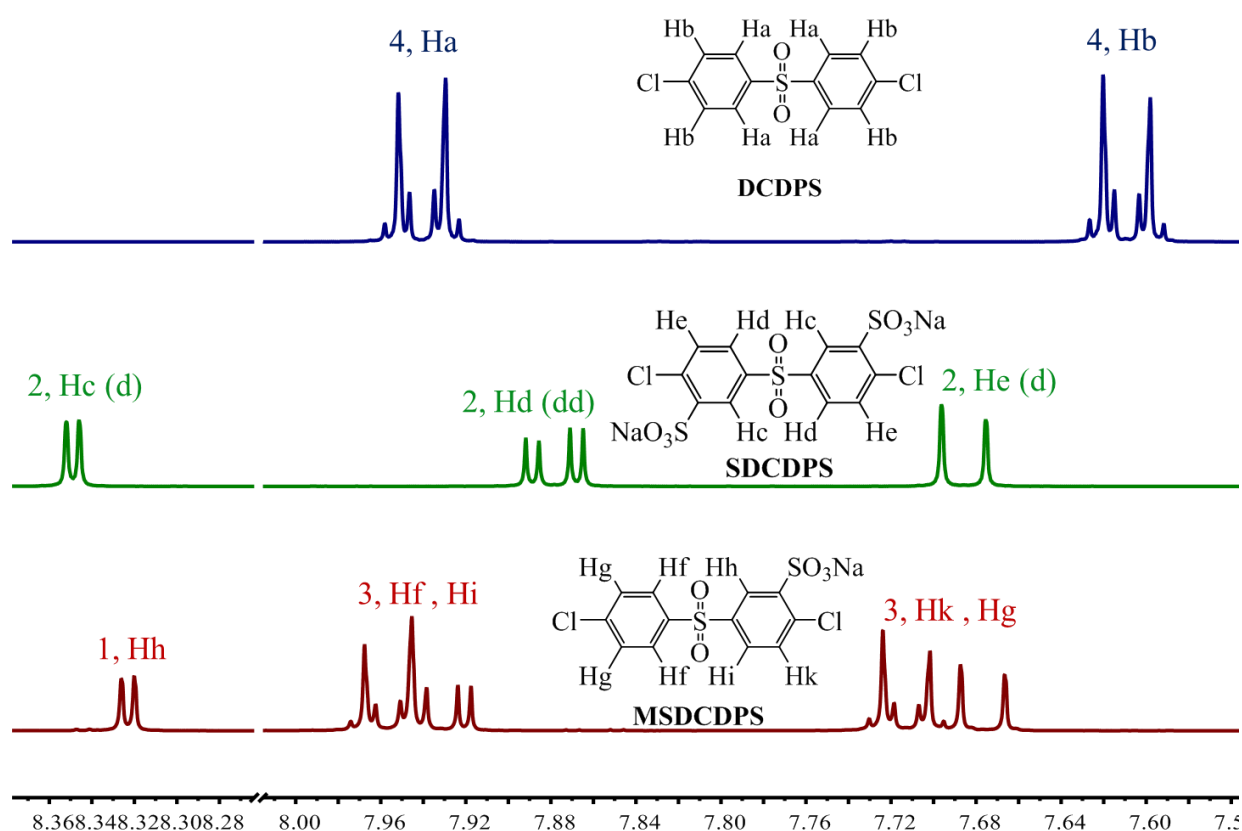


**Figure 7.1**  $^1\text{H}$  NMR of DCDPS, SDCDPS, and MSDCDPS in DMSO- $\text{d}_6$

Comparing the NMR spectra of DCDPS with SDCDPS, it is evident that the new peak (Ha) at 8.34 ppm in the SDCDPS spectra correlates to the proton next to the strong electron withdrawing SO<sub>3</sub>Na group and the integration of 2Hs confirms the disulfonation. As reported by Sankir et al.<sup>17</sup>

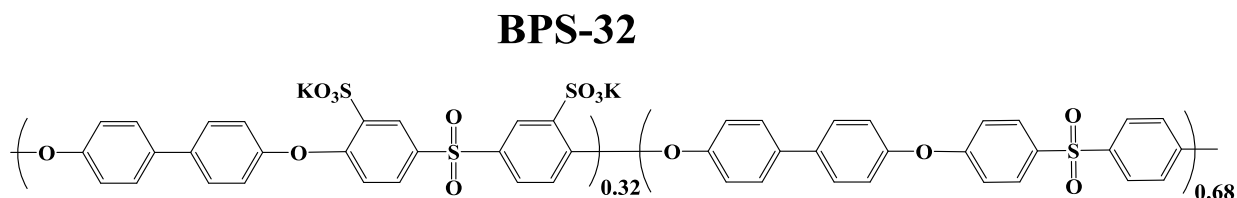
in SDCDPS, Hd corresponds to the proton *meta* to the chlorine and *para* to the sulfonate group while He is the proton *ortho* to chlorine group. These peak assignments are supported by the splitting pattern and the coupling constants observed for Ha, Hb and Hc. Ha ( $\delta$  8.35) has a long range coupling to Hd ( $\delta$  7.88) with a J value of  $\sim 2.3$  Hz and is split to a doublet. However, Hd is seen as a doublet of doublets (dd) which is a result of first splitting by He to a doublet with a J value of 8.25 Hz and subsequently by Ha with a J value of 2.3. He is just affected by Hd which results into a doublet with a J value of 8.25 Hz.

The NMR spectrum of MSDCDPS shows a peak at 8.32 ppm (Hh) that corresponds to the proton between the sulfone and sulfonates on the sulfonated ring. It resonates slightly upfield from the corresponding position of the Hc in SDCDPPS. The integration of 1 is an indication of a monosulfonated compound rather than a disulfonated species. Furthermore, the other two protons on the sulfonated ring, (Hi and Hk) shifted downfield (Hi, *para* to the sulfonate) and upfield (Hk, *meta* to the sulfonate and *ortho* to the chlorine). The chemical shifts of Hf (2H) and Hg (2H) on the non-sulfonated ring of the MSDCDPS also shifted downfield relative to the analogous resonances from the non-sulfonated rings on DCDPS. The chemical shifts of all of the protons on the MSDCDPS relative to the DCDPS and SDCDPS confirm that a new compound has been produced.

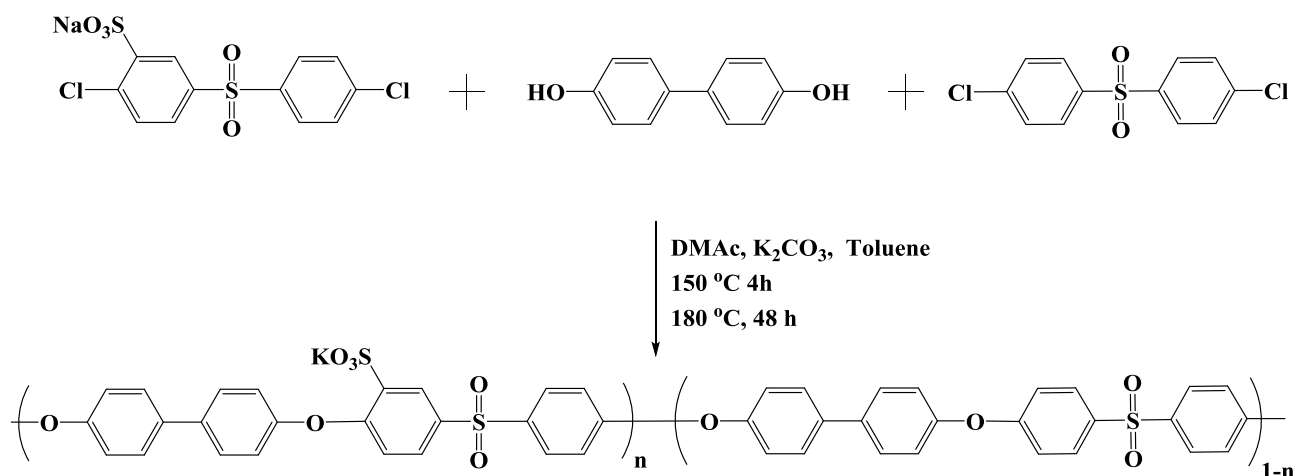
All the data for MSDCDPS is further supported by high resolution mass spectrometry (HRMS). The one fragmentation pattern was observed at 364.9107 which corresponds to molecular ion without the sodium counter ion. This is in agreement with the calculated mass of the MSDCDPS (364.9117).

## Synthesis and characterization of sulfonated random copolymers with the new MSDCDPS

The synthesis and characterization of disulfonated BPS copolymers have been intensively studied as membranes for fuel cell applications.<sup>31-33</sup> However, direct copolymerization and the properties of the linear mBPS copolymers bearing the sulfonic acid groups on the deactivated position of the aromatic ring of the monosulfonated monomers have not been investigated. To our knowledge, all of the linear random mono-sulfonated copolymers have previously been prepared via post sulfonation.<sup>34-35</sup> Thus, in this study we explored the properties of the mBPS-X copolymers and compared their properties with BPS-32, a biphenol-based disulfonated random copolymer synthesized via direct copolymerization of the SDCDPS comonomer. The structure of BPS-32 is shown in Scheme 7.2. The direct copolymerization route of the sulfonated monomers with non-sulfonated comonomers is shown in scheme 7.3.



**Scheme 7.2** Structure of the disulfonated BPS-32 prepared from direct copolymerization of SDCDPS, DCDPS and biphenol



**Scheme 7.3** Synthesis of the mBPS-X from direct copolymerization of the sulfonated monomers

In comparison to most polymers that are modified via post sulfonation, which results in crosslinking of the final product and uncontrolled degrees of sulfonation,<sup>36-37</sup> using a direct copolymerization with a sulfonated monomer eliminates these problems. As shown in Table 7.1, copolymers in the mBPS-X series were synthesized with a wide range of IECs. However, there is an important structural difference between mBPS-X and BPS-32 that is the number of the aromatic rings between two sulfonated rings. As shown in Schemes 7.2 and 7.3, there are no phenyl rings between the two sulfonated rings in the BPS copolymers. This distance is longer in mBPS-X copolymers with at least two phenyl rings in between sulfonated rings. It has been shown previously that disulfonated BPS copolymers have compromised NaCl passage when mixtures of salts containing divalent cations such as calcium are in the feedstream.<sup>38</sup> As suggested herein, we now recognize that the distribution of sulfonate ions along the chains are critical to mediating this negative aspect. The present work clearly shows that the difference in salt rejection properties depend significantly on the small difference in lengths between ionic groups. The small difference of having sulfonated adjacent rings versus having a minimum of two non-sulfonated rings between

sulfonated rings leads to critically improved salt rejection properties that are necessary for desalination of water.

SEC analysis confirmed the molecular weight of the mBPS-51 copolymer to be above the entanglement molecular weight of a polysulfone.<sup>39-40</sup> The structure of mBPS-X was confirmed via <sup>1</sup>H NMR (Figure 7.2).

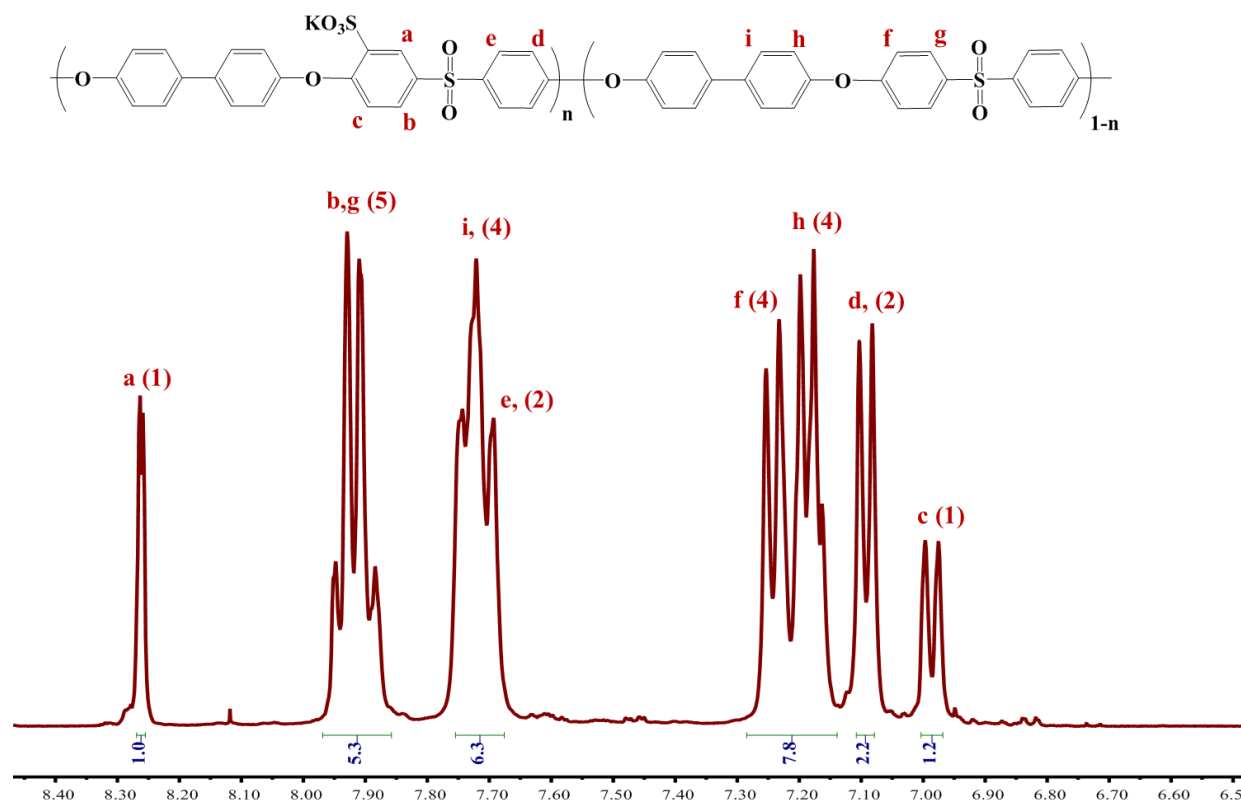


**Figure 7.2** <sup>1</sup>H NMR of monosulfonated copolymer confirms its composition

### Membrane casting and properties

The mBPS-X membranes were cast based on previously established membrane casting conditions for linear random copolymers.<sup>41</sup> However, these membranes were not treated with hot water at any stage. It has been established that as the degree of disulfonation is increased in BPS

membranes, they take up more water. Also, as the degree of disulfonation and water uptake are increased, a morphological transition occurs at approximately 50% water uptake to a structure with poor hydrated mechanical properties.<sup>42</sup> mBPS-X and BPS-Y membranes were characterized in their salt form for water desalination applications. These copolymers had different amounts of water uptake depending on their IEC and counter ion salts.<sup>43</sup>

**Table 7.1** Properties of mBPS-X and BPS-Y copolymers in various salt forms

| Copolymer      | Mw (kDa)    | IEC (meq/g) | Water Uptake in Na <sup>+</sup> form (%) |
|----------------|-------------|-------------|------------------------------------------|
| <b>mBPS-51</b> | 21.2        | 1.16        | 16 ± 1.0                                 |
| <b>mBPS-61</b> | In progress | 1.36        | 22 ± 1.5                                 |
| <b>mBPS-79</b> | In progress | 1.70        | 35 ± 1.1                                 |
| <b>BPS-32</b>  | -           | 1.32        | 48 <sup>a</sup>                          |
| <b>BPS-25</b>  | -           | 1.09        | 17 ± 0.8                                 |
| <b>BPS-33</b>  | -           | 1.38        | 40 ± 2.5                                 |
| <b>BPS-41</b>  | -           | 1.65        | 55 ± 0.6                                 |

<sup>a</sup> BPS-32 membrane was processed in a different way by boiling in DI water

As expected, water uptake of the membranes increased with increasing IECs. It was previously shown that the ionic polymer electrolyte membranes absorb more water when they are in their sulfonic acid form.<sup>44</sup> However, our monosulfonated mBPS-61 copolymer and the corresponding disulfonated BPS-32 showed that the monosulfonated copolymer absorbed less water than the disulfonated polymer. Since the only differences between the mBPS-X and BPS-Y polymer is the spacing between fixed ions, the differences in water uptake are hypothesized to reflect the different sequences of the repeat units.

The mechanical properties of the linear mBPS-X copolymers in fully hydrated conditions showed a dependency on the amount of water absorbed.<sup>41</sup> As depicted in Figure 7.3, two copolymers of mBPS-51 and mBPS-61 with water uptakes of 16% and 22%, respectively, showed reasonable strengths at yield (~25 MPa). The elongation at break of the mBPS-61 had a yield strength of ~25 MPa with a long elongation that exhibited some strain hardening. This area of research represents some of the first data on ionic engineering polymers in their fully hydrated conditions.

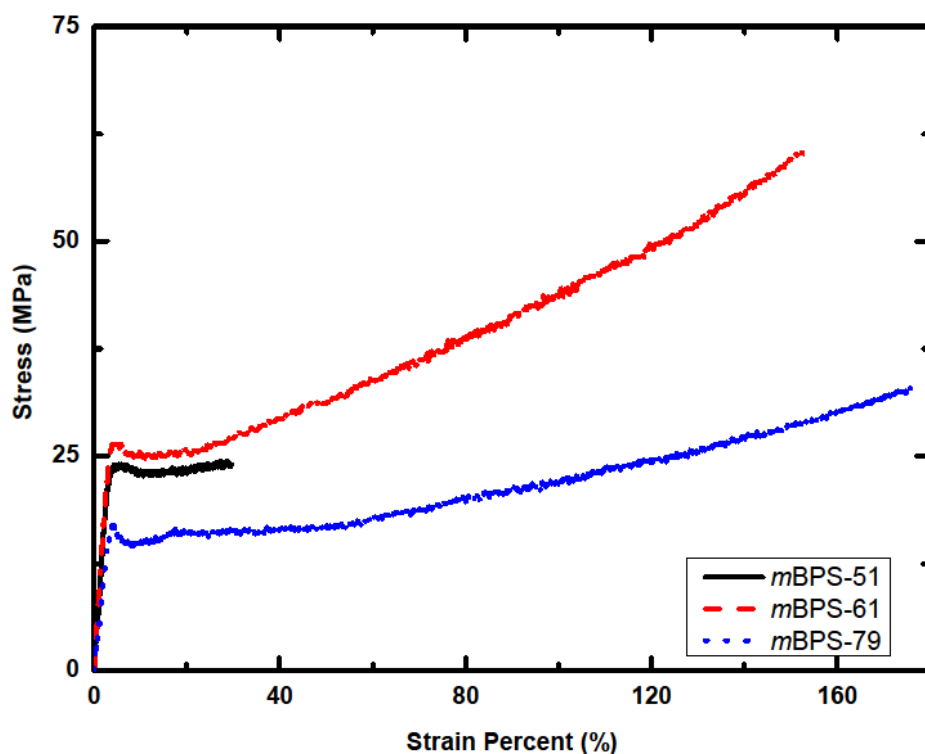


**Figure 7.3** Stress-Strain curves of the monosulfonated mBPS-X series in fully hydrated conditions

## Transport properties of the mBPS-51 membrane

The transport properties of mBPS-51 were compared to the BPS-32 copolymer (Table 7.2). In desalination processes there is a tradeoff relationship such that, as the salt rejection increases the water permeability decreases.<sup>45</sup> The tradeoff correlation was observed for mBPS-51 like other copolymers in Table 7.2. In this comparison, mBPS-51 showed significantly high salt rejection properties. However, as expected, the water permeability for mBPS-51 was lower than BPS-32 due to a lower IEC.

**Table 7.2** Transport properties mBPS-51 compared to BPS-32

| Copolymer | IEC (meq. g <sup>-1</sup> ) | Water permeability<br>(L . m <sup>-2</sup> . h <sup>-1</sup> . bar <sup>-1</sup> ) | NaCl rejection<br>(%) |
|-----------|-----------------------------|------------------------------------------------------------------------------------|-----------------------|
| mBPS-51   | 1.16                        | 0.18                                                                               | 99.3                  |
| BPS-32    | 1.32                        | 0.68                                                                               | 97.5                  |

The salt transport properties of the copolymers in a mixed monovalent/divalent salt solution showed that the monosulfonated copolymers outperformed the disulfonated copolymer over a wide range of divalent Ca<sup>2+</sup> ion concentrations. In the absence of Ca<sup>2+</sup>, the disulfonated BPS-32 copolymer showed similar Na<sup>+</sup> passage to mBPS-51 (Figure 7.4). However, as Ca<sup>2+</sup> was added to the solution, monovalent selectivity of BPS-32 decreased significantly resulting in an extremely high Na<sup>+</sup> passage.<sup>38</sup> However, mBPS-51 showed steady Na<sup>+</sup> passage, which was lower than the corresponding BPS-32 counterpart, even at elevated concentrations of Ca<sup>2+</sup> (up to 200 ppm). A constant Na<sup>+</sup> ion passage may suggest that divalent ions such as Ca<sup>2+</sup> can associate with multiple anions on the adjacent rings. In contrast, the presence of at least two phenyl rings between sulfonated rings leads to better distribution of the ions in monosulfonated mBPS-51.

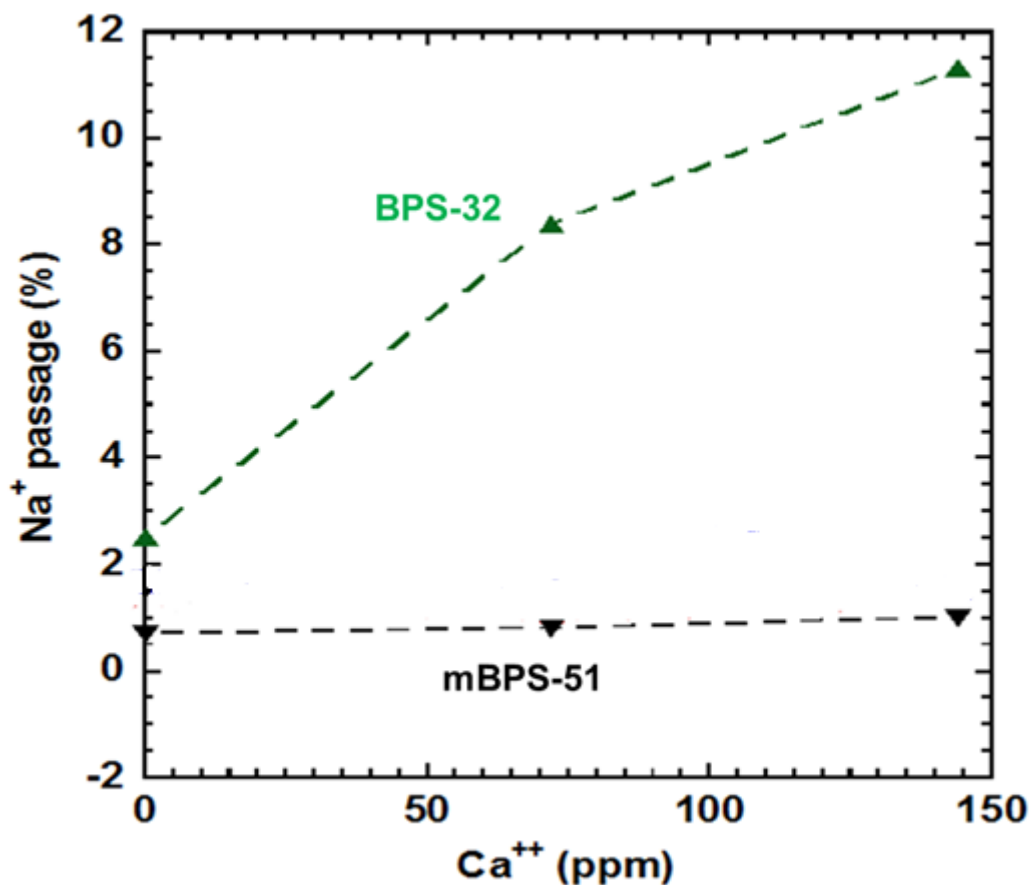


**Figure 7.4** Monovalent Na<sup>+</sup> passage through mBPS-51 and BPS-32 at different concentrations of divalent Ca<sup>2+</sup> ion

## 7.5 Conclusions

A one-step synthesis of MSDCDPS under controlled reaction conditions resulted in a monomer grade monosulfonated product. Controlling the ratio of the MSDCDPS and DCDPS in the direct copolymerization with a bisphenol comonomer yielded a series of linear random copolymers with a wide range of degrees of monosulfonation along the backbone. Among the copolymers, mBPS-61 showed good mechanical properties immersed in water. mBPS-51 had 98.1% NaCl rejection and extraordinary low Na<sup>+</sup> passage in mixed salt solutions that contained

Ca<sup>2+</sup>. Salt transport investigations on the mBPS-61 and mBPS-79 are in progress and will soon be reported to reveal more details of the effects of the inherent sequencing of ions in such copolymers on their salt and water transport properties. This work suggests that the direct copolymerization process combined with the spacing and distribution of ion along these chains is likely critical for advanced desalination of water via membrane separations.

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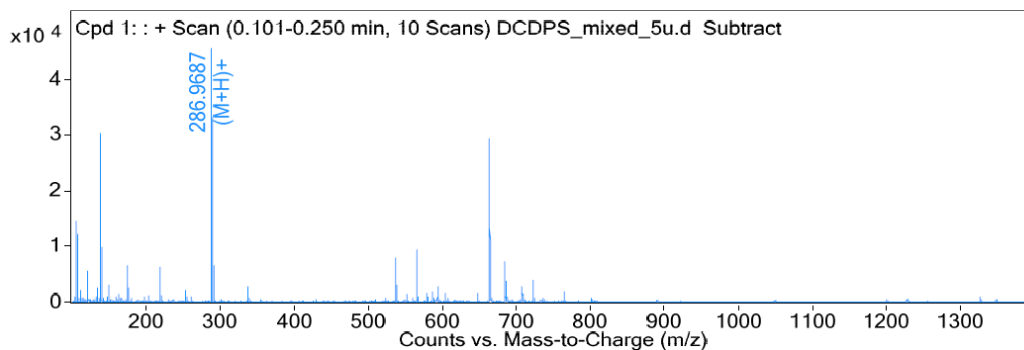
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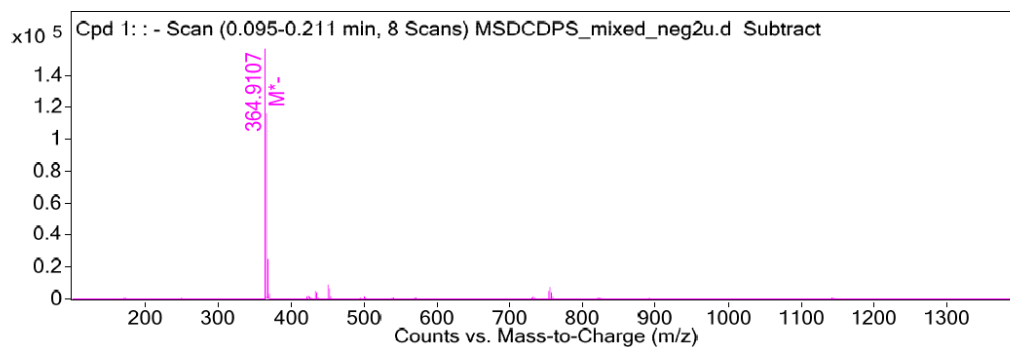
## 7.7 Supporting Information

HSRM for three comonomers (DCDPS, MSDCDPS, SDCDPS) in this chapter are shown in Figure 7.5.

a)



b)



c)

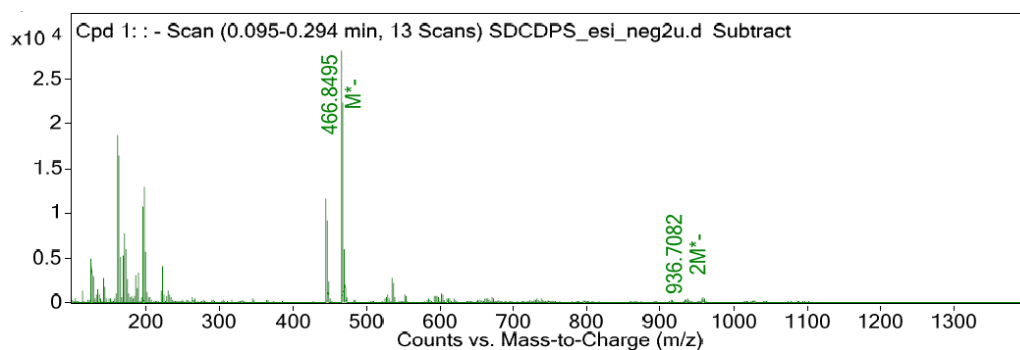


**Figure 7.5** HRMS of a) DCDPS b) MSDCDPS c) SDCDPS

## CHAPTER 8. Conclusions and Future Work

### 8.1 Conclusions

Results from this investigation augment our understanding of the structure-property-performance of sulfonated poly(arylene ether sulfone) membranes for use as ion conductive membranes in electrochemical systems and in water desalination applications. These applications include potential utilization in fuel cells, water electrolysis, electrodialysis, reverse osmosis, and others. The findings described in this dissertation confirm that poly(arylene ether sulfone)s with various topologies can be synthesized from the direct copolymerization of phenolic monomers and sulfonated comonomers. Additionally, we have shown that water absorption depends highly on polymer composition and morphology, and that membrane casting conditions represent an essential parameter influencing the morphology of the membranes.

Incorporation of monomers with substituents along varying positions of the aromatic rings drastically affects the fundamental properties of the copolymers—mainly, water uptake, mechanical properties, and gas transport properties. For example, the gas barrier properties of a membrane can be controlled by utilizing copolymers containing *m*-substituted resorcinol. In contrast, incorporating *p*-substituted hydroquinone comonomers into the polymer results in materials with a rigid backbone and constrained water uptake. Based on the resulting mechanical properties of the random hydrocarbon copolymers, we were able to confirm that the disulfonated copolymers undergo a morphological transition from materials having isolated hydrophilic domains at low IECs to co-continuous hydrophilic domains at elevated IECs. However, this transition occurs at remarkably higher IECs in crosslinked membranes versus linear copolymers.

In order to enhance the chemical and dimensional stability of hydrocarbon copolymers, we investigated the incorporation of hydrophobic and fluorinated comonomers in the polymer

composition. Moreover, post modification of the membranes with fluorine gas was investigated as a strategy for improving the gas barrier properties and proton conductivity of the membranes.<sup>1-2</sup> In summary, these methods were used to synthesize partially fluorinated random and multiblock copolymers. These surface fluorinated membranes showed reduced water uptake and improved durability in Fenton reagents. Preliminary proton conductivity tests on the modified membranes revealed increased conductivity, which we associated with the presence of strong, polar, and hydrophobic C-F bonds.

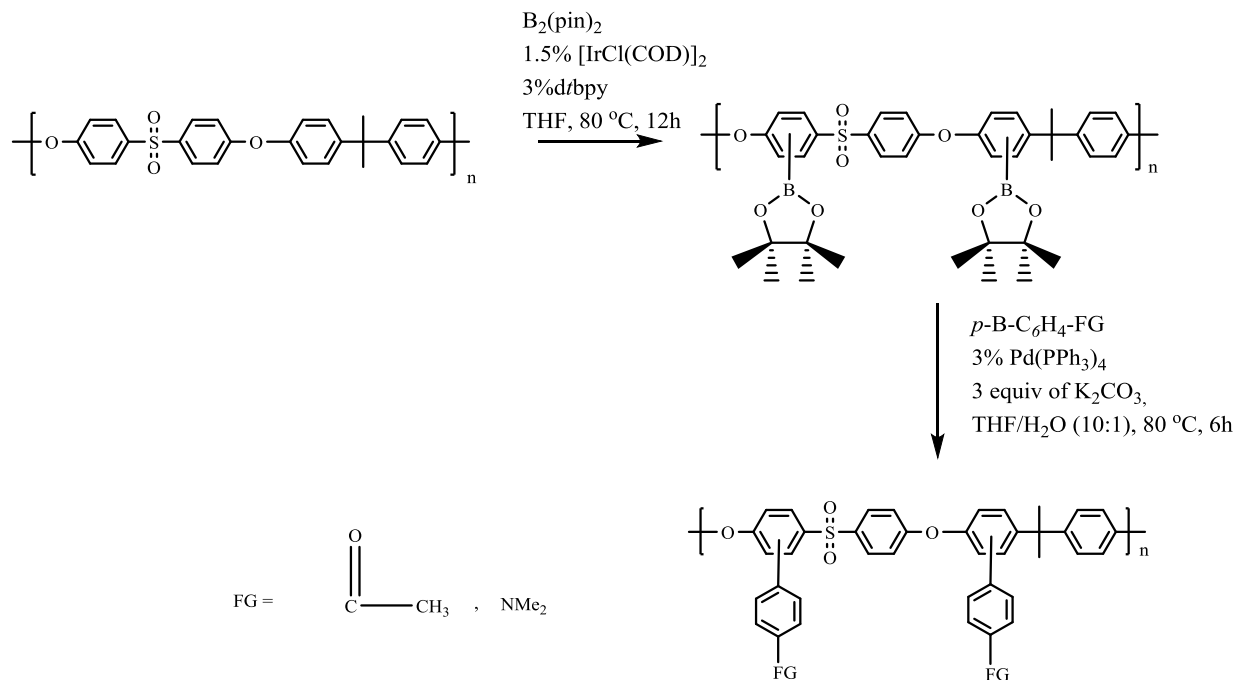
The findings described herein confirmed that controlled molecular weight oligomers containing *m*-aminophenol as the terminal group, SDCDPS and DCDPS as the sulfone monomers, and biphenol can form highly crosslinked membranes in the presence of a curing agent under heat and slow solvent-evaporation conditions. These crosslinked membranes show promising characteristics for desalination of water via electrodialysis. As expected, increasing the IEC resulted in increased water uptake. However, the morphological transition of these crosslinked membranes occurs at drastically higher IECs in comparison to linear copolymers of the same composition. Membranes with constrained water uptake and high IEC feature low salt transport properties due to increased fixed charge concentrations.

This study also confirmed that the incorporation of novel mono-sulfonated dichlorodiphenylsulfone (MSDCDPS) monomers into poly(arylene ether sulfone) copolymers results in systems with enhanced properties for desirable applications. Specifically, a new generation of linear copolymers was investigated via the direct copolymerization of MSDCDPS with bisphenol comonomers to yield random copolymers with controlled degrees of monosulfonation. Unlike disulfonated copolymers, the monosulfonated polymers show drastically lower water uptake at elevated IECs, resulting in high fixed charge concentrations. It is expected

that the high fixed charge concentration at a reasonable water uptake will improve Donnan exclusion and increase the co-ion rejection from the membrane surface.

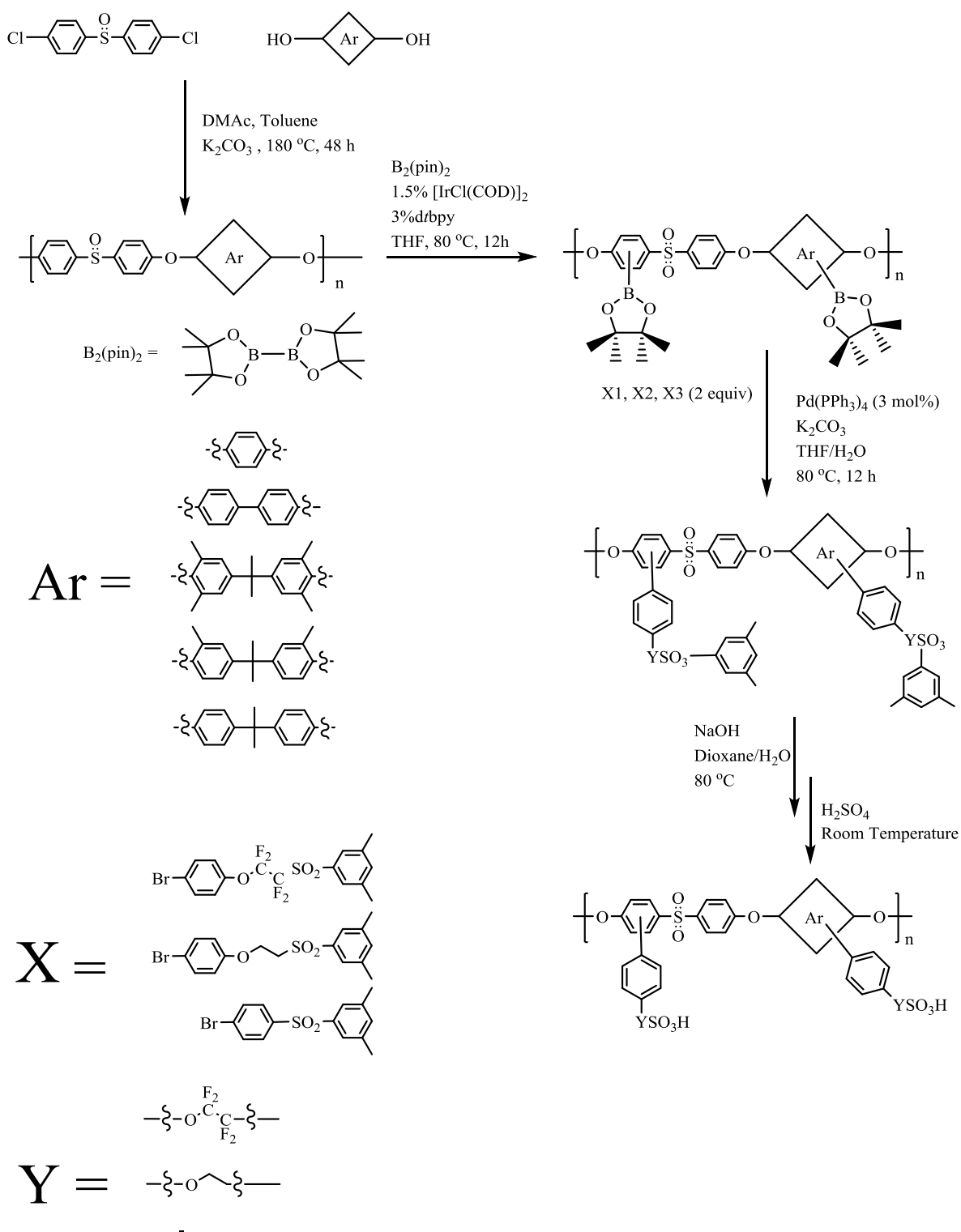
## **8.2 Suggestions for Electrodialysis and Fuel Cell Membranes**

Sulfonated linear hydrocarbon copolymers have shown good proton conductivity properties at high water uptake. However, it would be advantageous to enhance the degree of proton conductivity at a low degree of disulfonation where water uptake is not too high. This goal was achieved by fluorinating the surface of the membrane. However, other approaches have been utilized to enhance proton transport via modifications in molecular design.<sup>3</sup> For example, it is suggested to conduct a systematic study of the structure-property-performance of a variety of polymers featuring different chemistries—with the goal of producing copolymers with novel architectures and morphologies. For example, in an alternative approach, Jo et al.<sup>4</sup> synthesized short-side chain linear copolymers, wherein the sulfonic acid groups were positioned at the end of the side chains with relatively controlled length (see Scheme 8.1). These chains were attached to the linear copolymer by Iridium-Catalyzed C–H activation and Suzuki–Miyaura reactions. Chen et al.<sup>5</sup> reported that such copolymers have new morphological features that improve the proton conductivity, coupled with suppressed water uptake, at excessively high IECs.



**Scheme 8.1** Functionalization of the linear copolymer via Iridium-Catalyzed C–H activation and Suzuki–Miyaura reactions. Adapted by permission from American Chemical Society, 2009<sup>4</sup>

Using this approach, multiple functional groups of various compositions can be added to the linear polymers described in this dissertation. Toward that end, some of the possible structures that can be synthesized via C–H bond activation are shown in Scheme 8.2. Specifically, non-sulfonated copolymers can be modified such that they possess sulfonic acid groups as the terminal group of side chains with different lengths and compositions. For example, incorporating fluorinated side chains enhances the acidity of the sulfonic acid groups, which results in increased proton conductivity at lower degrees of disulfonation. The latter subsequently leads to lower water uptake and improved mechanical properties.

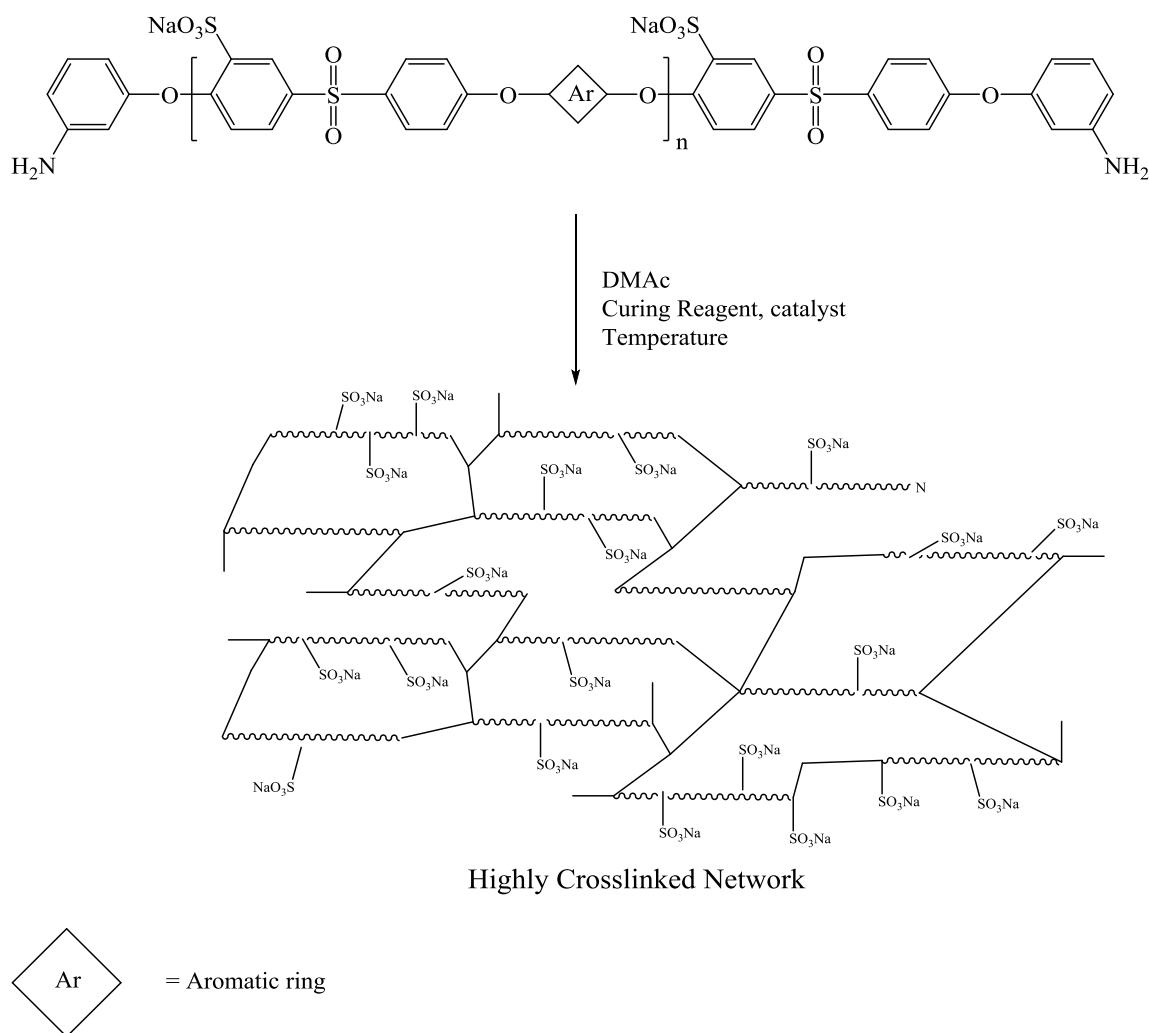


**Scheme 8.2** Synthesis of short side-chain hydrocarbon copolymers with sulfonic acid groups as the pendant groups on the chain ends

The results described herein also indicate that the incorporation of two types of moieties in these structures is of great importance. The first strategy pertains to the application of a variety of phenolic monomers with the potential to play an important role in controlling the IECs. For example, in a systematic study one can identify the optimum water uptake by incorporating tetramethyl bisphenol A (TMBPA), dimethyl bisphenol A, and bisphenol A comonomers. The second strategy of interest involves incorporating fluorinated or non-fluorinated side chains with a variety of chain lengths. These side chains not only alter the morphology of the comb-shaped copolymers, but by applying fluorinated side chains one can significantly enhance the acidity of sulfonic acid groups.

### **8.3 Suggestions for Electrodialysis (ED) and Reverse Osmosis (RO) Membranes**

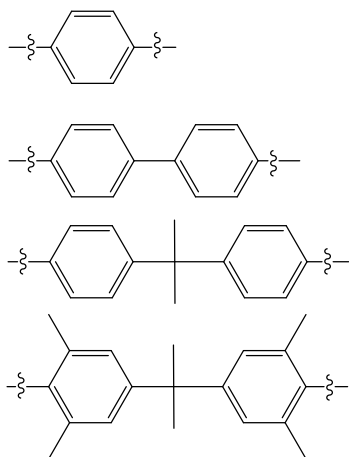
Ion conductive membranes for water purifications require high fixed charge concentration to exclude co-ions from the membranes. Thus, a desirable membrane needs to feature the following criteria: high IEC, constrained and tailored water uptake, and good chemical and mechanical properties under fully hydrated conditions. In this investigation we confirmed that linear disulfonated copolymers with high IECs possess poor mechanical properties due to increased water uptake and co-continuous morphologies. In contrast, monosulfonated poly(arylene ether sulfone)s have more controlled water uptake at elevated IECs of up to 1.7 meq/g. According to these results, it would be desirable to synthesize copolymers via the direct copolymerization of MSDCDPS. According to Scheme 8.3, reactive oligomers with terminal groups such as *m*-AP or phenoxide can be utilized to prepare crosslinked membranes in the presence of a curing agent.



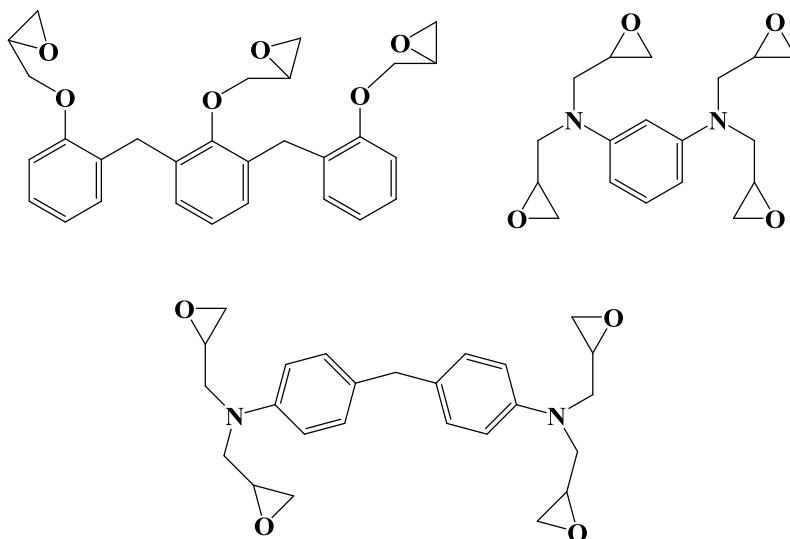
**Scheme 8.3** Crosslinking the m-AP terminated oligomers with MSDCDPS

Note that in Scheme 8.3, the “Ar” represents the aromatic rings that include phenolic monomers, as shown in Scheme 8.4. In addition, a variety of crosslinking reagents can be utilized to control the IEC and reactivity of the oligomers. Suggested curing reagents are illustrated in Scheme 8.4. Moreover, these copolymers can be tailored such that they contain short blocks of non-sulfonated and long blocks of 100% degrees of monosulfonation in the crosslinked systems. Thus, controlling the hydrophilic and hydrophobic chain lengths should result in a variety of desirable properties in the new crosslinked copolymers.

Ar =



Epoxy curing reagent =



**Scheme 8.4** Suggested phenolic and epoxy curing agents structures for preparing crosslinked membranes

## 8.4 References

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