SYNTHESIS AND CHARACTERIZATION OF SULFONATED POLY (ARYLENE ETHER SULFONE) COPOLYMERS via DIRECT COPOLYMERIZATION: CANDIDATES for PROTON EXCHANGE MEMBRANE FUEL CELLS

by

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ABSTRACT

A designed series of directly copolymerized homo- and disulfonated copolymers containing controlled degrees of pendant sulfonic acid groups have been synthesized via nucleophilic step polymerization. Novel sulfonated poly (arylene ether sulfone) copolymers using 4,4'-bisphenol A, 4,4'-biphenol, hexafluorinated (6F) bisphenol AF, and hydroquinone, respectively, with dichlorodiphenyl sulfone (DCDPS) and 3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone (SDCDPS) were investigated. Molar ratios of DCDPS and SDCDPS were systematically varied to produce copolymers of controlled compositions, which contained up to 70 mol% of disulfonic acid moiety. The goal is to identify thermally, hydrolytically, and oxidatively stable high molecular weight, film-forming, ductile ion conducting copolymers, which had properties desirable for proton exchange membranes (PEM) in fuel cells.

Commercially available bisphenols were selected to produce cost effective alternative PEMs. Partially aliphatic bisphenol A and hexafluorinated (6F) bisphenol AF produced amorphous copolymers with different thermal oxidative and surface properties. Biphenol and hydroquinone was utilized to produce wholly aromatic copolymers.

The sulfonated copolymers were prepared in the sodium-salt form and converted to the acid moiety via two different methodologies and subsequently investigated as proton exchange membranes for fuel cells. Hydrophilicity increased with the level of disulfonation, as expected. Moreover, water sorption increased with increasing mole percent incorporation of SDCDPS. The copolymers' water uptake was a function of both bisphenol structure and degree of disulfonation. Furthermore, the acidification procedures were shown to influence the Tg values, water uptake, and conductivity of the copolymers. Atomic force microscopy (AFM) in the tapping mode confirmed that the morphology of the copolymers could be designed to display nanophase separation in the hydrophobic and hydrophilic (sulfonated) regions. Morphology with either co-continuous hydrophobic or hydrophilic domains could be attained for all the sulfonated copolymers. The degree of disulfonation required for continuity of the hydrophilic phase varied with biphenol structure.

Proton conductivity values for the sulfonated copolymers, under fully hydrated conditions, were a function of bisphenol and degree of sulfonation. However, at equivalent ion exchange capacities the proton conductivities were comparable. A careful balance of copolymer composition and acidification method was necessary to afford a morphology that produced ductile films, which were also sufficiently proton conductive. The copolymers of optimum design produced values of 0.1 S/cm or higher, which were comparable to the commercial polyperfluorosulfonic acid material Nafion™ control.

Dedicated to my loving wife, Dionne, and our children, Lamonte’ and Leah,
for
their support, understanding, and encouragement

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Finally I am grateful to my Lord Jesus Christ, who continues to be my refuge and my guiding light.

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CHAPTER 1

I. LITERATURE REVIEW: INTRODUCTION TO FUEL CELLS

The challenge of continually meeting the increasing world energy needs of its inhabitants will be one of the most important tasks that our world will face in the twenty-first century. Current energy sources are being depleted at high rates due to the growth of the world's population and its desire(s) to live at a high level of comfort. Petroleum is the world's most prevalent fuel. However, fossil fuels are becoming scarcer and their burning produces emissions that pollute the air. Furthermore, fossil fuels are not a renewable energy source.

Renewable and environmentally friendly energy sources will be essential for an ever-changing and populous planet. Solar power, hydropower, and wind power systems have been employed to complement current electric power sources. Arguably, the most attractive alternative energy sources are fuel cells. Hydrogen is used to produce energy by combining with oxygen in a fuel cell. Hydrogen is the cleanest, most sustainable and renewable energy carrier[1]. Fuel cells are viable, renewable, and environmentally friendly energy sources that do not require any special environmental conditions as do the aforementioned renewal energy devices.

1.1 Fuel Cells

Fuel cells are electrochemical devices that convert the chemical energy of reaction from a fuel directly into electrical energy[2,3]. Fuel cells are environmentally

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[1] Cheng, H.M.; Yang, Q.H.; Liu, C., *Carbon* 2001, 39 (10), 1447.

[2] Appleby, A. J., Ed. *Fuel Cells: Trends in Research and Applications*; Hemisphere Publishing Corp.: New York, 1987; p.281

[3] Zalbowitz, M.; Thomas, S. "Fuel Cells: Green Power," Department of Energy, 1999 LA-UR-99-3231.

friendly sources of energy since, in general, water and heat are the only byproducts[4]. A fuel cell, in theory, will be able to continually generate energy as long as the fuel and the

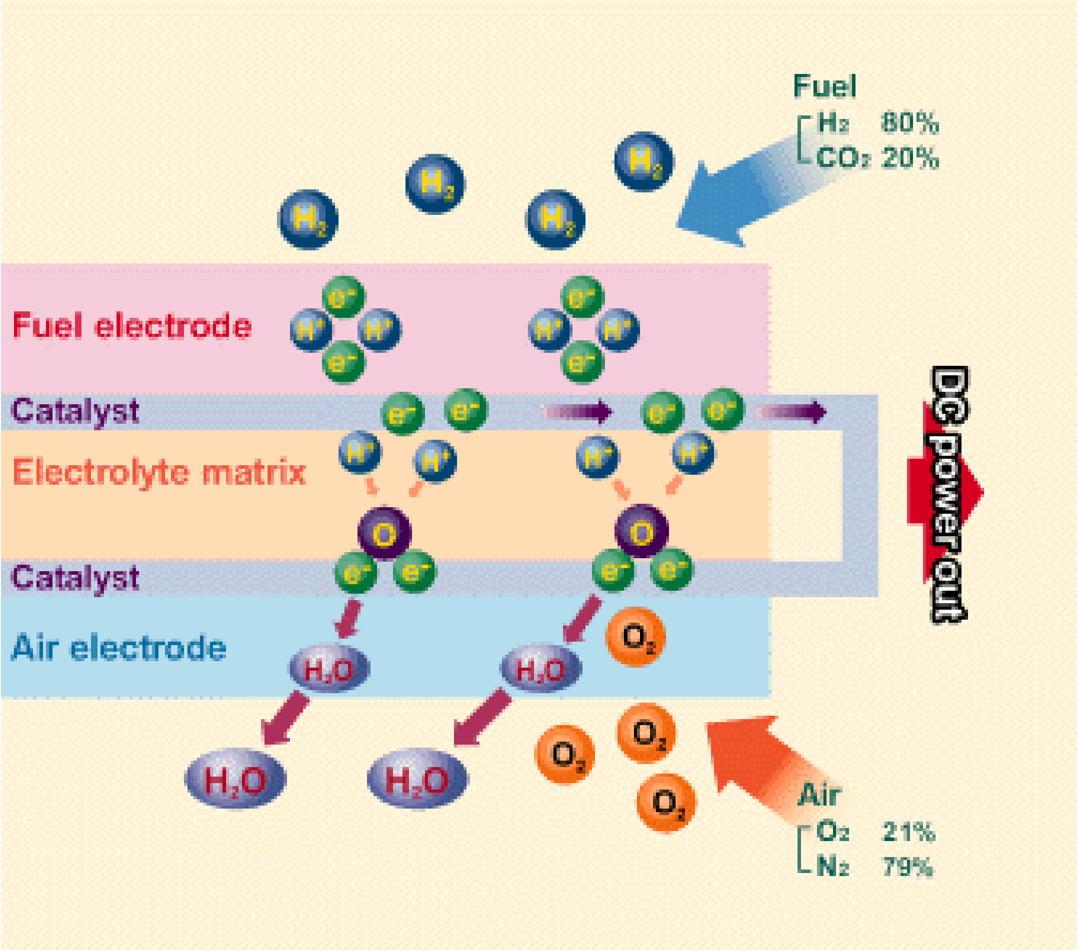

FIGURE 1. Schematic of a fuel cell and related electrochemical reactions to produce electricity.

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[4] Barbir, F.; Gomez, T., *Int. J. Hydrogen Energy* 1997, 22, 1027.

oxidant are provided to the cell. This is distinctly different from typical batteries, which are merely energy storage devices[5]. Since it is a storage appliance, the battery is dead (or discharged) when the stored reactants are exhausted[6]. The fuel for fuel cells is stored externally to the actual device, and therefore, will not become internally depleted.

Fuel cells operate without combustion, so they are virtually pollution free. Since the fuel is converted directly to electricity, a fuel cell has the potential to operate at much higher efficiencies than internal combustion engines, extracting more electricity from the same amount of fuel. Fuel cells are *mechanically ideal* because these devices have no moving parts - making them quiet and reliable sources of power.

There are essentially five fuel cell systems, each with its distinct electrochemical reaction and operation requirements. The different fuel cells are generally classified by the electrolyte used. They are: phosphoric acid fuel cells (PAFC), molten carbonate fuel cells (MCFC), solid oxide fuel cells (SOFC), alkaline fuel cells (AFC), and proton exchange membrane fuel cells (PEMFC). A brief general overview of each of these systems will be presented here, with most emphasis on the PEMFC systems.

1.1.1 **Phosphoric Acid Fuel Cells (PAFC)**

Phosphoric acid fuel cells use concentrated (100%) phosphoric acid (H_3PO_4) contained in a silicon carbide matrix as its electrolyte[7]. The typical operating temperatures for phosphoric acid fuel cells are 150 ^oC to 220 ^oC. At temperatures below this range phosphoric acid is a poor proton conductor and carbon monoxide poisoning of the platinum electrocatalyst reduces the performance of the cell[5,8]. Platinum alloys have also been investigated as electrochemical catalysts[9,10]. The half-reactions for a PAFC are:

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[5] Hirschenhofer, J.H.; Stauffer, D.B.; Engleman, R.R., *Fuel Cells: A Handbook* for the Department of Energy; B/T Books: Orinda, CA, 1996; p.1-1.

[6] Liebhafsky, H.A.; Cairns, E..J., *Fuel Cells and Fuel Batteries*, John Wiley and Sons, Inc., New York1968; p.7

[7] Appleby, A. J., Ed. *Fuel Cells: Trends in Research and Applications*; Hemisphere Publishing Corp.: New York, 1987.

[8] Appleby, A.J.; Foulks, F.R., *Fuel Cell Handbook*, Van Nostrand Reinhold, New York, 1989.

[9] Beard, B.C.; Ross, P.N., *J. Electrochem. Soc.* 1986, 133, 1839.

[10] Glass, J.T.; Cahen, G.L.; Stoner, G.E.; Taylor, E.J., *J. Electrochem. Soc.* 1987, 134, 58.

Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Eqn 1

Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ Eqn 2

Overall: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ Eqn 3

PAFCs are being developed as stationary or utility power devices[5]. The apparent simplicity in the actual application of phosphoric acid fuel cells is hampered by the gradual leakage of phosphoric acid by currently available components[11]. A depiction of a phosphoric acid fuel cell is given in Figure 2a.

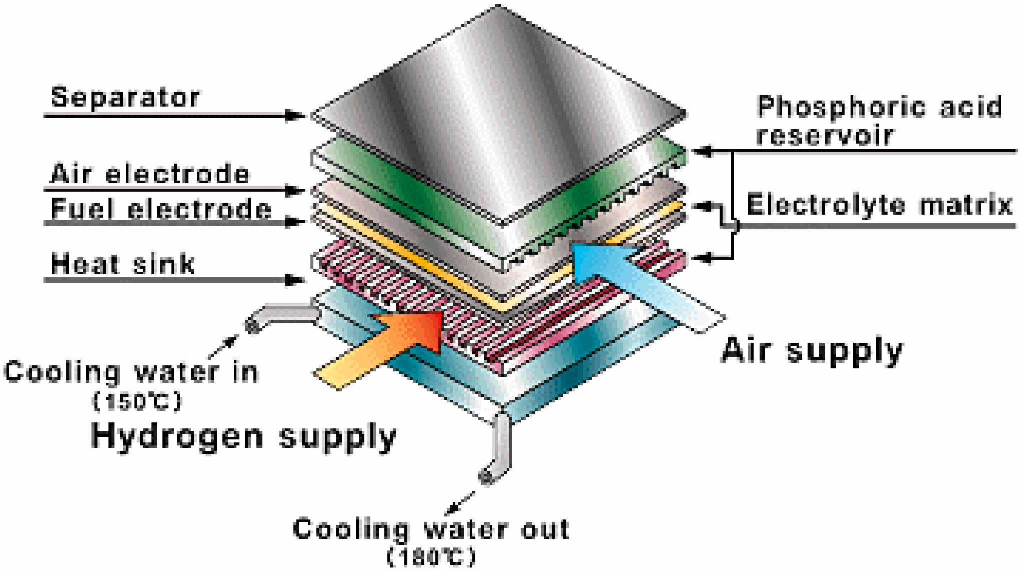

FIGURE 2A. Components of a single-cell phosphoric acid fuel cell.

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[11] Carrette, L.; Friedrich, K.A.; Stimming, U., *J. ChemPhysChem* 2000, 1, 162-193.

1.1.2 **Molten Carbonate Fuel Cells (MCFC)**

Molten carbonate fuel cells (MCFC) operate at high temperatures, typically 600 °C to 700 °C, and use highly conductive molten salts[12]. Molten carbonate fuel cells usually employ a combination of sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3) to provide carbonate ions (CO_3^{2-}) for conduction[13]. Alternative systems utilize lithium carbonate (Li_2CO_3) and potassium carbonate as the co-electrolyte[14]. A ceramic matrix of lithium aluminum oxide ($LiAlO_2$) retains the mixtures of carbonates[5]. The electrochemical reactions in a MCFC are:

Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ Eqn 4

Cathode: $\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$ Eqn 5

Overall: $H_2 + \frac{1}{2} O_2 + CO_2\text{(cathode)} \rightarrow H_2O + CO_2 \text{ (anode)}$ Eqn 6

The high operating temperature of MCFCs allows for less expensive nickel catalysts to be used[15]. Even at high temperatures, MCFCs display losses of efficiency due to contamination[6] from H_2S, HCl, H_2Se, and As. While cost is always an important entity in any developing technology, nickel-based anodes are reportedly structurally unstable and exhibit high nickel oxide dissolution (cathode) under some conditions in MCFC[16].

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[12] Minh, N, "High Temperature Fuel Cells", *Chemtech* 1991, 21 (1), 32-37.

[13] Selman, R.J, *Energy* 1986, 11, 153.

[14] Okada, O.; Yokoyama, K., "Development of Polymer Electrolyte Fuel Cell Cogeneration Systems for Residential Applications", *Fuel Cells* 2001, 1 (1) 72.

[15] Petri, R.J.; Benjamin, T.G., in *Proceedings of the 21st Intersociety Energy Conversion Engineering Conference*, Vol. 2, American Chemical Society, Washington, DC, p. 1156, 1986.

[16] Kinoshita, K.; McLarnon, F.; Cairns, E., *Fuel Cells, A Handbook*, prepared by Lawrence Berkeley Laboratory, May 1988.

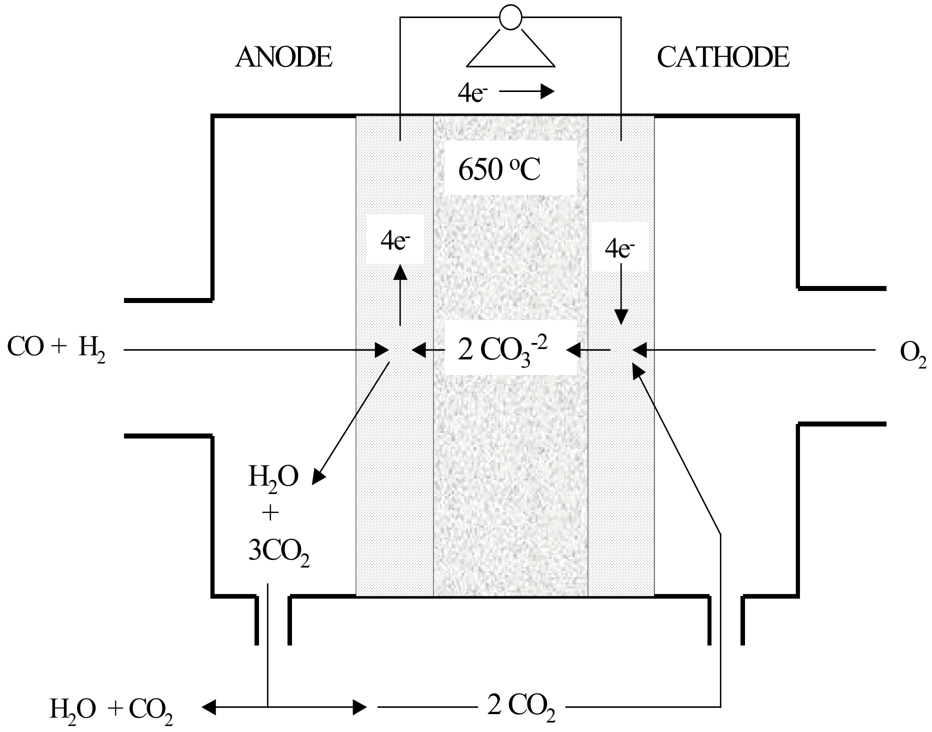

FIGURE 2B. Schematic of a molten carbonate fuel cell[12]

1.1.3 **Solid Oxide Fuel Cells (SOFC)**

Solid oxide fuel cells (SOFCs) utilize oxygen ions to conduct protons[11,17]. SOFCs operate at the highest temperature range of the five types of fuel cells, ~650 - 1000 ^{o}C. The electrolyte for this fuel cell is usually a yttrium oxide (Y_2O_3) with ZrO_2 (possibly for stabilization) alloy[6,12]. This electrolyte is a solid, nonporous metal oxide system. The anode is either Co-ZrO_2 or Ni-ZrO_2 cement, and the cathode is Sr-doped $LaMnO_3$[5]. The appropriate half-reactions are:

Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ Eqn 7

Cathode: $\frac{1}{2} O_2 + 2e- \rightarrow O^{2-}$ Eqn 8

Overall: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ Eqn 9

SOFCs do not use liquid electrolytes and hence don't have their associated problems (i.e., leaking, corrosion, etc.). The solid oxide fuel cell's high operation temperature promotes fast kinetics without the requirement of precious metals. It produces a *quality* heat byproduct for secondary or co-generation applications; however, the 650 – 1000 ^{o}C operating temperature range requires special ceramic materials that can withstand such temperatures[18]. SOFCs are for stationary power generation and are reported[5] to have been of interest to companies such as Westinghouse Electric Corporation and Allied-Signal Aerospace Company (now Honeywell, Inc.) since the 1950s.

Carbon monoxide (Equation 10) and steam reformation of hydrocarbons such as methane (Equation 11) can be used as fuels for solid oxide fuel cells[8]. For maximum efficiency, pores that can permit gas to cross the solid oxide electrolyte must be avoided.

$CO + H_2O \rightarrow H_2 + CO_2$ Eqn 10

$CH_4 + H_2O \rightarrow 3\ H_2 + CO$ Eqn 11

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[17] Carrette, L.; Friedrich, K.A.; Stimming, U., "Fuel Cells-Fundamentals and Applications", *Fuel Cells* 2001, 1(1), 5.

[18] Minh, "Ceramic Fuel Cells", *J. Am. Ceram. Soc.*1993, 76 (3) 563-588.

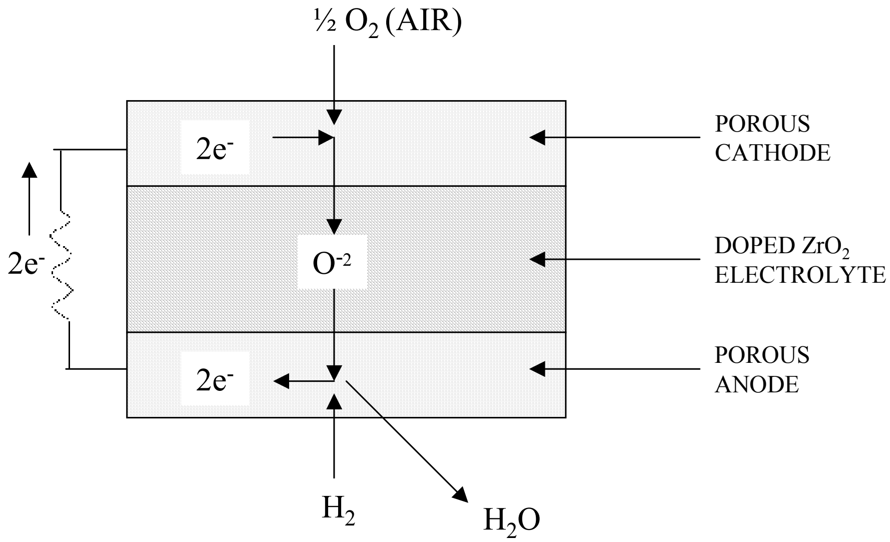

FIGURE 2C. Principle of operation: high-temperature solid oxide electrolyte fuel[18].

1.1.4 **Alkaline Fuel Cells (AFC)**

Potassium hydroxide (KOH) is the typical electrolyte in alkaline fuel cells[19]. Sodium hydroxide electrolyte alkaline fuel cells have also been investigated[20]. The high concentration of the potassium hydroxide, which was originally retained in an asbestos matrix, dictates the necessary operation temperature for an efficient cell[21]. A fuel cell at a KOH concentration of 35 to 50 weight percent can be operated at temperatures below 120 °C whereas a cell containing 85 weight percent KOH concentration requires higher temperature (~250 °C). The concentration of the potassium hydroxide and the necessary temperature are associated with the overall pressure requirements within the system[22].

Influenced by operating temperatures, precious (e.g., platinum) and non noble metals (e.g., nickel, silver, metal oxides, etc.) have been employed in alkaline fuel cells[23,24]. Alkaline fuel cells are extremely sensitive to carbon dioxide (CO_2) poisoning[25]. Interestingly, the carbon dioxide not only reduces the efficiency of the catalysts[26] but it is detrimental to the hydroxide concentration in the system[5]. Carbon dioxide reduces the concentration of hydroxide ions by the reaction:

$$CO_2 \quad + \quad 2OH^- \rightarrow \quad CO_3^{\ 2-} \; + \quad H_2O \qquad \text{Eqn 12}$$

The reduction in hydroxide ions reduces the electrolyte conductivity and causes other negative consequences[5,27]. These undesirable side effects necessitate the usage of pure hydrogen and oxygen, which in turn limits AFC to specialized applications[5].

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[19] Appleby, A.J., *Energy* 1986, 11, 13.

[20] Carrette, L.; Friedrich, K.A.; Stimming, U., “Fuel Cells: Principles, Types, Fuels, and Applications”, *Chemphyschem* 2000, 1,162.

[21] Sheibley, D.W.; Martin, R.A, *Prog. Batteries Solar Cells* 1987, 6, 155.

[22] Bockris, J. O’M.; Appleby, A.J., *Energy* 1986, 11, 95.

[23] Liebhafsky, H.A.; Cairns, E..J., *Fuel Cells and Fuel Batteries*, John Wiley and Sons, Inc., New York, 1968.

[24] Appleby, A.J.; Foulks, F.R., *Fuel Cell Handbook*, Van Nostrand Reinhold, New York, 1989.

[25] Taylor, E.J.; Srinivasan, S., in *Power Sources for Electric Vehichles*, B.D. McNicol and D.A. Rand, Eds., Elsevier Science Publisher, Amsterdam, The Netherlands, 1984, p. 839.

[26] K. Kordesch, K.; Gsellmann, J.; Kraetschmer, B., in *Power Sources 9*, J. Thompson, Ed., Academic Press, New York, 1983, p.381.

[27] Tomantschger, K.; McClusky, F.; Oporto, L.; Reid, A.; Kordesch, K., *J. Power Sources* 1986, 18, 317.

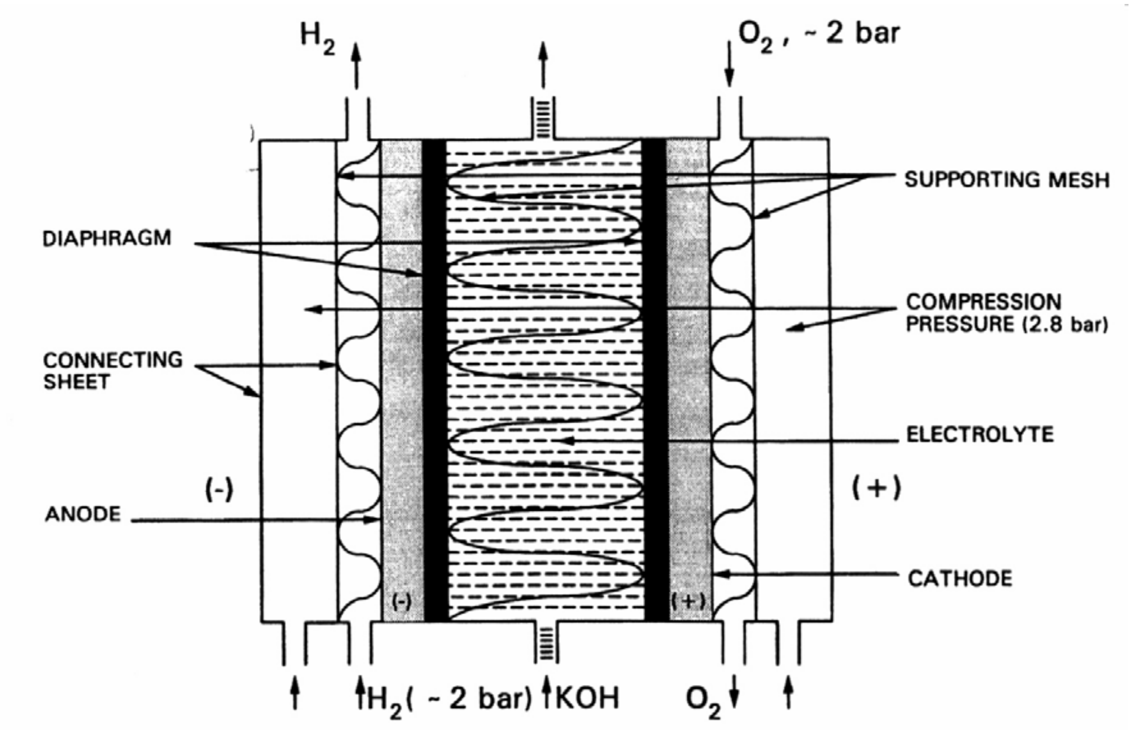

FIGURE 2D. Operation of an alkaline fuel cell.

1.1.5 **Proton Exchange Membrane Fuel Cells (PEMFC)**

Proton exchange membrane fuel cells (PEMFC) are referred to as polymer electrolyte fuel cells (PEFCs) as well as solid polymer electrolyte fuel cells (SPEFC) depending on the proposed application[28]. Proton exchange membrane fuel cells have gained international attention as candidates for alternative automotive and stationary power sources due to features such as their adaptable size and low operating temperatures[29,30,31]. The electrolyte of PEMFC, as the name suggests, is a polymeric membrane/film. Perfluorinated copolymers are the current state-of- the-art proton exchange membranes (PEM)[32,33]. The typical operation temperature of PEMFCs is in the range of 80 - 100°C[34]. This operating temperature range is currently limited by the perfluorinated proton exchange membrane[5,8,11] and the associated water loss. The area of proton exchange membranes development will be discussed in detail in a later section.

The electrochemical reactions of proton exchange membrane fuel cells using hydrogen and oxygen gas are the same as phosphoric acid fuel cells according to the following reactions:

Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Eqn 1

Cathode: $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$ Eqn 2

Overall: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$, Eqn 3

The direct methanol fuel cell (DMFC) is one type of PEMFC that uses an aqueous methyl alcohol (CH_3OH) solution as the fuel. There are several electrochemical reactions relating to the oxidation of methyl alcohol. The *major* half-reactions for a DMFC are:

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[28] Gottesfeld, S.; Zawodzinski, T.A., *Polymer Electrolyte Fuel Cells*, in Advances in Electrochem. Sci. and Eng., R. C. Alkire, H. Gerischer, D.M. Kolb, and C.W. Tobias, Eds., Vol.5, p. 187-297, 1993.

[29] Zalbowitz, M.; Thomas, S. "Fuel Cells: Green Power," Department of Energy, 1999 LA-UR-99-3231.

[30] Dhathathreyan, K.S.; Sridhr, P.; Sasikumar, G.; Ghosh, K.K.; Velayuthan, G.; Rajalakshmi, N.; Subramaniam, C.K.; Raja, M.; Ramya, K., *Int. J. Hydrogen Energy* 1999, 24, 1107.

[31] Korgesch, K.; Simader, G., *Fuel Cells and Their Applications*, Wiley-VCH, Weinheim, 1996.

[32] Zalbowitz, M.; Thomas, S. "Fuel Cells: Green Power," Department of Energy, 1999 LA-UR-99-3231.

[33] Savadogo, O., *J. New Mat. Electrochm. Sys.* 1998, 1, 47.

[34] Carrette, L.; Friedrich, K.A.; Stimming, U., “Fuel Cells-Fundamentals and Applications”, *Fuel Cells* 2001, 1(1), 5.

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ Eqn 13

Cathode: ${}^3/_2 O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ Eqn 14

Overall: $CH_3OH + H_2O + {}^3/_2 O_2 \rightarrow CO_2 + 3H_2O$ Eqn 15

Figure 3 is a pictorial representation of the intermittent steps involved in the oxidation of methanol[11].

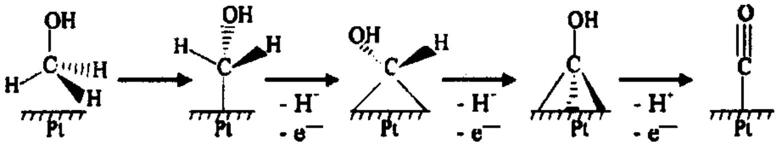

FIGURE 3. Methanol oxidation via platinum catalyst[11]

Efficient redox reactions in PEMFCs require a precious metal catalyst, usually platinum[7] and its alloys. The proficient oxidation of hydrogen using platinum has a reported[35] rate constant of 10^{-5} s^{-1}. The following are the proposed reactions for the hydrogen oxidation process:

$2\,Pt_{(s)} + H_2 \rightarrow 2\,Pt\text{-}H_{ads}$ Eqn 16

$Pt\text{-}H_{ads} \rightarrow H^+ + e^- + Pt_{(s)}$. Eqn 17

where $Pt_{(s)}$ is the solid platinum catalyst and H_{ads} is adsorbed hydrogen.

However, the platinum catalyst has a well known temperature-dependent intolerance towards carbon monoxide[36,37,38]. Carbon monoxide binds[39] to and blocks the active sites on platinum, thereby, reducing the available number sites for hydrogen gas to be oxidized to protons. These reductions of active catalyst sites reduce the overall efficiency of the fuel cell system. Alloys of platinum (e.g., platinum-ruthenium, platinum

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[35] Barber, J.; Morin, S.; Conway, B.E., *Electrochem. Soc. Proc.* 1997, 97, 101.

[36] Appleby, A. J., Ed. *Fuel Cells: Trends in Research and Applications*; Hemisphere Publishing Corp.: New York, 1987; p.281

[37] Oetjen, H.-F.; Schmidt, V.M.; Stimming, U.; Trila, F., *J. Elecrochem. Soc.* 1996, 143, 3838.

[38] Ianiello, R.; Schmidt, V.M.; Stimming, U.; Stumper, J.; Wallau, A., *Electrochim. Acta* 1994, 39, 1863.

[39] Grgur, B.N.; Markovic, N.M.; Ross, P.N., *Electrochim. Acta* 1998, 43, 3631.

molybdenum, and others) have been examined[40,41,42,43] and are proposed to be more tolerant towards carbon monoxide. The co-metals are proposed to expedite the oxidation of carbon monoxide to carbon dioxide (CO_2) which has a different adsorption energy[44]. Marovic *et al*. reported enhanced rates of oxygen reduction using platinum-nickel and platinum-cobalt catalyst[45]. Very recently, platinum-alumina catalysts were developed and were demonstrated to selectively oxidize carbon monoxide[46].

Many studies have been undertaken in attempts to understand the oxygen reduction reactions (ORR) at the cathode. It is, perhaps, beyond the scope of this literature review to cover the diverse details of these various investigations; however, some general features will be reviewed. It is well noted that the hydrogen oxidation reaction is much faster than the oxygen reduction reaction, under typical proton exchange membrane fuel cell conditions. Studies have shown that controlled change in gas pressure, concentration, and temperature can favorably influence the ORR kinetics[28]. The general equation for the oxygen reduction in an aqueous acid environment is[28]:

$$O_{2.ads} + 4H^+ + 4e^- \rightarrow 2\,H_2O \qquad \text{Eqn 18}$$

Alternatively, since the binding of carbon monoxide to platinum is a thermally reversible (exothermic) process, increasing the operating temperature of the PEMFC can reduce CO influences on cell performance[29]. At temperatures greater than 100 °C, desorption of carbon monoxide is faster than adsorption[47]. This reversibility has led to intense investigations[48] into alternative proton exchange membranes that can successfully operate at temperatures greater than 100 °C.

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[40] Ley, K.L.; Liu, R.; Pu, C.; Fan, Q.; Leyarovska, N.; Segre, C.; Smotkin, E.S., *J. Electrochem. Soc.*1997, 144, 1543.

[41] Morimoto, Y.; Yeager, E.B.; *J. Electroanal. Chem.* 1998, 444, 95.

[42] Watanabe, M.; Uchida, M.; Motoo, S., *J. Electroanal. Chem.* 1987. 229, 395.

[43] Wei, Z.; Guo, H.; Tang, Z., *J. Power Sources* 1996, 58, 239.

[44] Holleck, G.; Pasqariello, D.; Clauson, S., in the Second Int. Symp. Proton Conducting Membrane Fuel Cells II, S. Gottsfeld, and T.R. Fuller, Eds., Boston, MA, 1998, p150.

[45] Markovic, N. M.; Schmidt, T. J.; Stamenkovic, V.; Ross, P. N., *Fuel Cells* 2001, 1 (2), 105.

[46] Manailp, A.; Gulari, E., *Appl. Cataly. B: Environmental* 2002, 37 (1), 17.

[47] Carrette, L.; Friedrich, K.A.; Stimming, U., "Fuel Cells: Principles, Types, Fuels, and Applications", *ChemPhysChem* 2000, 1,162

[48] Kerres, J.A., *J. Membr. Sci*. 2001, 185 (1), 3.

1.2 **Proton Exchange Membrane Candidates**

One of the most important components in a proton exchange membrane fuel cell is the actual proton exchange membrane (PEM). The proton exchange membrane performs two basic, essential functions in PEMFCs: (1) a separator to prevent mixing of the fuel (i.e., hydrogen gas, methanol, etc.) and the oxidant (i.e., pure oxygen or air), and (2) an electrolyte for transporting protons from the anode to the cathode[49]. Desirable properties of the proton exchange membrane in fuel cells include[33]:

(a) chemical and electrochemical stability in the fuel cell operating conditions;
(b) good mechanical strength and stability in operating conditions;
(c) chemical properties of components compatible with the (interfacial) bonding requirements of the PEMFC;
(d) low permeability to reactant species;
(e) high electrolyte transport to maintain uniform electrolyte content and prevent localized drying;
(f) high proton conductivity with minimal resistance and zero electronic conductivity; and
(g) low production cost relative to the application.

Renewed interest in commercializible and economical alternative energy source has prompted intense and diverse investigations into improving various aspects of proton exchange membrane fuel cells during the last couple of decades. During this time, numerous groups have worked to develop alternative PEMs to replace expensive perfluorinated sulfonic acid copolymers. This section will review some of the past, current and proposed proton exchange membranes described in the literature.

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[49] Appleby, A.J.; Foulkes, R.L., *Fuel Cell Handbook*, Van Nostrand Reinhold, New York, 1989

1.2.1 **Styrene and Derivatized Styrene PEM**

The first employed proton exchange membrane fuel cell in the Gemini program was a crosslinked polystyrene sulfonic acid (PSSA),[6,14,23] somewhat similar to ion-exchange columns. The one-kilowatt (1 kW) fuel cell stack was used as both an auxiliary power source and as a source of water for the astronauts. However, the polystyrene sulfonic acid was not durable under the actual PEMFC operation conditions. The mediocre performance is suspected to have led NASA to depend on alkaline fuel cells for the subsequent missions[47]. The attack on the tertiary benzylic carbon by hydroxy radicals is likely the cause of PSSAs degradation. The hydroperoxide radicals may be formed by the reaction of a hydrogen atom with molecular oxygen. Still, some investigators[50] propose some applicability of sulfonated polystyrene for PEMFCs.

The initial poor performance of polystyrene has not deterred other researchers from continuing research on modified polystyrene materials. One *modern* method for innovating some novel copolymers has been to induce grafting and/or crosslinking[51,52]. Grafting sulfonate-containing moieties is rationalized to force phase separation of the sulfonic acids generating ion-conducting domains[53]. This phase separation and clustering within ion- containing polymers have been well studied[54,55,56,57,58,59] in the area called ionomers. Ionomers are generalized as copolymers containing ionizable groups. Ionomers are usually, yet arbitrarily, defined as copolymers that contain less than 15 mole percent of the ionic group[60,61].

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[50] Carretta, N.; Tricoli, V.; Picchioni, F., *J. Membr. Sci.* 2000, 166, 189.

[51] Buchi, F.N.; Gupta, B.; Haas, O.; Scherer, G.G., *Electrochim. Acta* 1995, 40, 345.

[52] Lehtinen, T.; Sundholm, G.; Holmberg, S.; Sundholm, F, Bjornbom, P.; Bursell, M., *Electrochim. Acta* 1998, 43, 1881.

[53] Ding, J.; Chuy, C.; Holdcroft, S., *Macromol* 2002, 35,1348.

[54] Eisenberg, A.; Hird, B.; Moore, R.B., *Macromol* 1990, 23, 4098.

[55] Wilkes, G. L.; Tant, M. R.; Mauritz, K. A., Eds. *Ionomers: Synthesis, Structure, Properties and Applications*; Blackie Acadamic and Professional: New York, 1997.

[56] Eisenberg, A.; King, M., Eds. *Ion-Containing Polymers*; Academic Press: New York, 1977.

[57] Eisenberg, A.; Kim, J. S. *Introduction to Ionomers*; John Wiley ans Sons, Inc.: New York, 1998.

[58] MacKnight, W.J.; Taggart, T.P.; Stein, R.S., *J. Polym. Sci., Polym. Symp.* 1974, 45,113.

[59] Lundberg, R.D.,; Makowski, H.S., in *Ions in Polymers*, Eisenberg, A., Ed., American Chemical Society: Wash., D.C., 1980, Chapter 2; Vol. Adv. Chem. Ser. 187

[60] In *Coulombic Interactions in Macromolecular Systems*; Eisenberg, A., Bailey, F. E., Eds.; American Chemical Society: Wash., D.C., ACS Symposium Series No. 302, 1986.

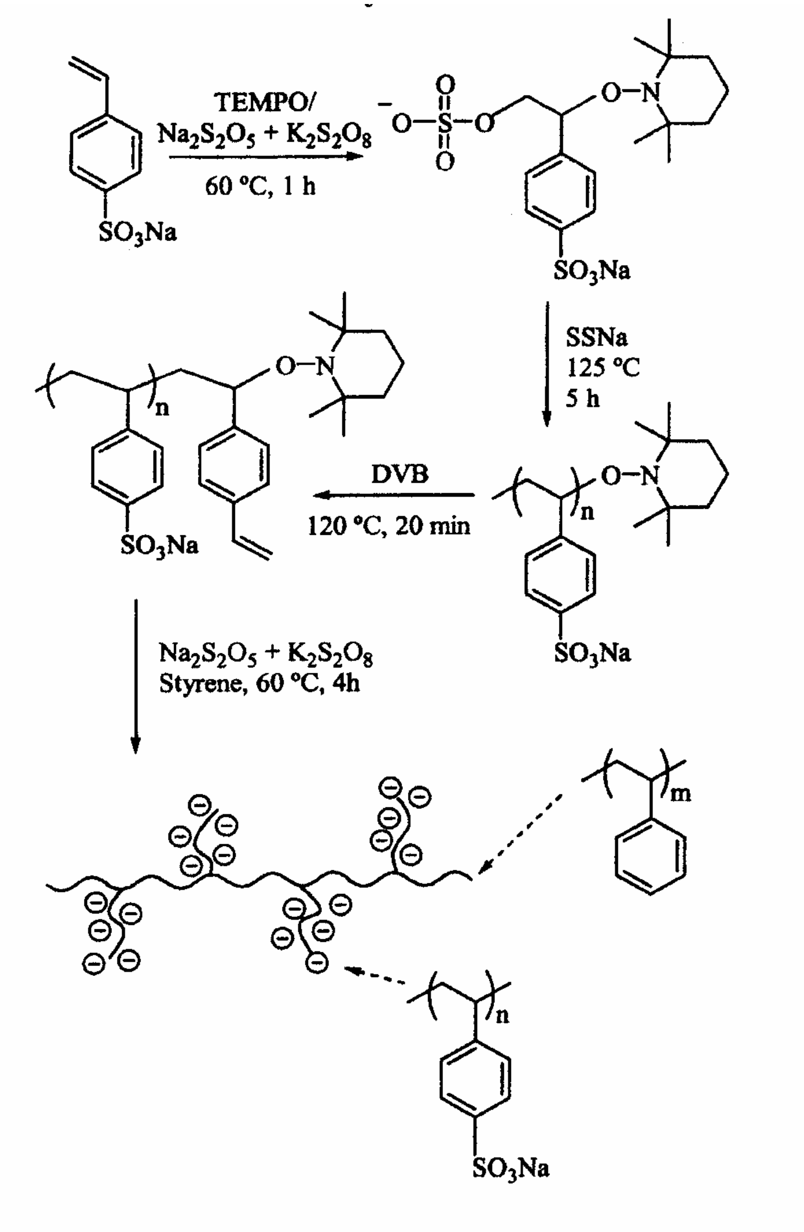

FIGURE 4. Preparation of polystyrene-g-poly (sodium styrenesulfonate)[53]

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[61] Tant, M.; Wilkes, G.L., *J. Macromol. Sci.Rev. Macromol. Chem. Phys.*1988, C28,1.

Holdcroft *et al.*[53] recently reported the synthesis of polystyrene with grafted poly (sodium styrenesulfonate) via stable free radical polymerization. These grafted copolymers reportedly displayed excellent proton conductivities (up to ~0.24 S/cm). The synthetic route is given in Figure 4. Other researchers have synthesized similar random[62,63,64] and block[65] copolymers. Tri-block copolymers produced by DAIS-Analytic Corporation (Figure 5), which may be based on sulfonated styrene-co-ethylene-co-butylene, have been described in the literature[66,67,]. These sulfonated Kraton®-type block copolymers are post-sulfonated. The stability of these aliphatic hydrocarbon copolymers is, in general, inferior to the current state-of-the-art perfluorinated copolymers[53]. For this reason, the DAIS membranes are being promoted for the low temperature (<60 °C), portable power markets[67,68].

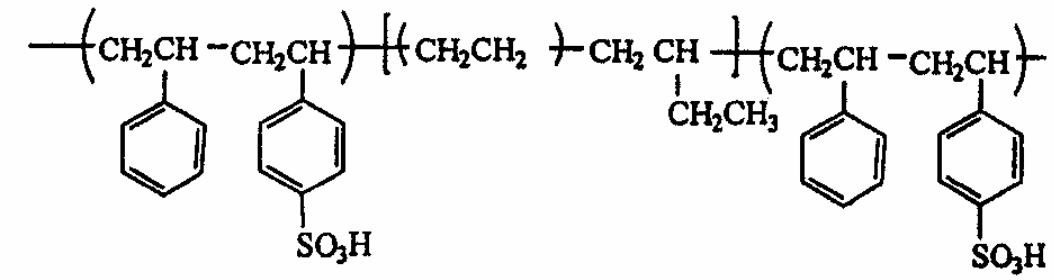

FIGURE 5. Reported structure of DAIS-Analytic Triblock PEM[73].

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[62] Ding, J.; Chuy, C.; Holdcroft, S., *Chem. Mater.* 2001, 13, 2231.

[63] Keoshkerian, B.; Georges, M.K.; Boils-Boissier, D., *Macromol* 1995, 28, 6381.

[64] Hawker, C.J., *Acc. Chem. Res.* 1997, 30, 373.

[65] Bouix, M.; Gouzi, J.; Charleux, B.; Vairon, J.P.; Guinot, P., *Macromol. Rapid Commun.* 1998, 19,209.

[66] Ehrenberg, S.G.; Serpico, J.M.; Sheikh, Ali, B.M.; Tangredi, T.N.; Zador, E.; Wnek, G.E., *Proceedings of the 2nd International Symposia on New Materials for Fuel Cell and Modern Battery Systems*, Montreal, Canada, 1997.

[67] Wnek, G.E.; Rider, J.N.; Serpico, J.M.; Einset, A.G., *Proceedings of the 1st International Symposium on Proton Conducting Membrane Fuel Cells*, Electrochem. Soc. Proceedings, p. 247, 1995.

[68] Basura, V.I.; Chuy, C.; Beattie, P.D.; Holdcroft, S., *J. Electroanal. Chem.* 2001, 501, 77.

Polystyrene with grafted fluoro-ethylene-propylene moieties has been investigated and shown to have to some improved performance[69]. Researchers in the UK (Lowell, Cranfield University) reportedly successfully grafted PSSA off ethylenetetrafluoroethylene copolymers. Chen *et al.*[70] has developed a latex of sulfonated polystyrene blended with polyvinylidene fluoride and polyvinylpyrrolidone with a reported conductivity of 10^{-2} S/cm.

It has been reported that the most stable polystyrene analogue is a vinyl perfluorosulfonic system developed by Ballard Power[71], shown below in Figure 5a. Using α,β,β-trifluorostyrene Ballard's third generation PEM[72], trade name BAM3G, has displayed long-term stability (over 100,000 hours[72]), and high proton conductivity (~0.08 S / cm)[73]. Unfortunately, the high cost of these membranes is comparable to that of other perfluorinated polymers. Little is reported on the mechanical or thermal transition

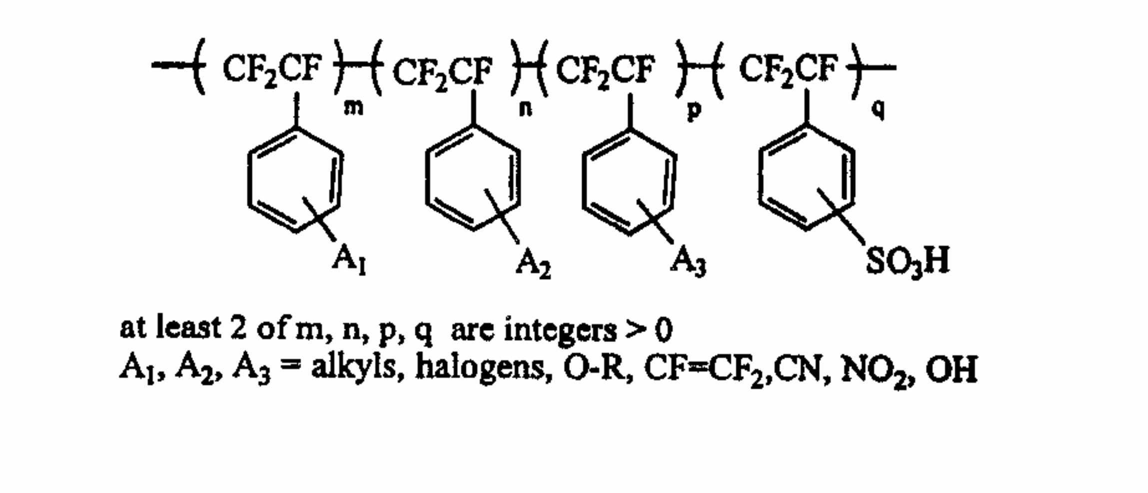

FIGURE 5A. Reported molecular structure of Ballard Advanced Materials Corp's BAM3G[73]

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[69] Buchi, F.N.; Gupta, B.; Rouilly, M.; Hauser, P.C.; Chapiro, A., Scherer, G.G., 27th Intersociety Energy Conversion Engineering Conference Proceedings, Vol.3, San Diego, CA, 1992.

[70] Chen, N.; Hong, L., *Solid State Ionics*2002, 146, 377.

[71] Steck, A., Proc. of the 1st Internat. Symp. on New Materials for Fuel Cell Systems, O. Savadago, P.R. Roberge, T.N. Vezioglu, Eds., Montreal, July 1995, p. 74.

[72] Wei, J.; Stone, C.; Steck, A.E., *US Patent 5,422,411* (1995).

[73] Basura, V.I.; Chuy, C.; Beattie, P.D.; Holdcroft, S., *J. Electroanaly. Chem.* 2001, 5011, 77.

behavior, but they would be expected to be rather brittle.

Researchers at General Electric laboratories proposed the use of phenol-formaldehydes and similar hydrocarbon-based polymers as proton exchange membrane candidates, over 60 years ago.[74]. The phenolformaldehyde polymers were obtained by the reaction of para- and unsubstituted phenol with formaldehyde. Linear and crosslinked phenolformalhyde[74,84] polymers were synthesized. Sulfonated phenol-

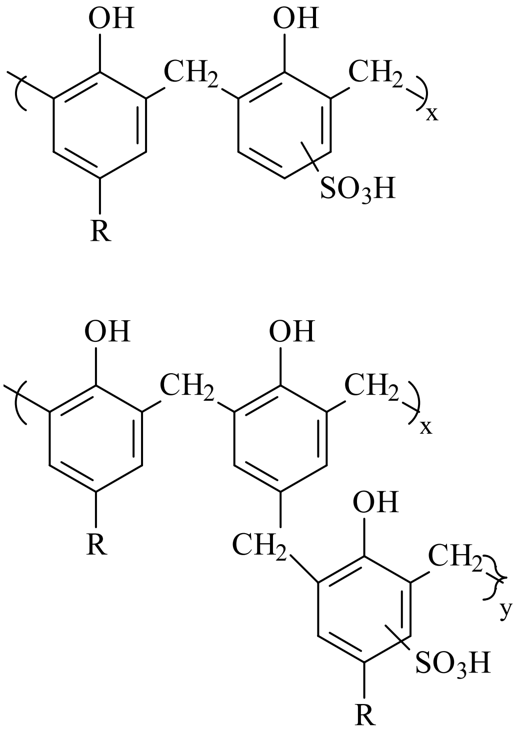

FIGURE 6. Idealized chemical structure of linear and cross-linked sulfonated phenolformaldehyde

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[74] Adams, B.; Holmes, E., *Brit. Patent No. 450,308*, 1935.

formaldehyde membranes (Figure 6) demonstrated comparably poor performance as polystyrene sulfonic acid [28]. Acid catalyzed (by the pendent sulfonic acid groups) hydrolysis was the suspected mode of degradation for the membranes, even though oxidation of the benzylic units might seem more likely.

1.2.2 **Perfluorinated Copolymers**

Perfluorinated sulfonic acid copolymers are easily the most widely studied and applied proton exchange membranes in proton exchange membrane fuel cell investigations. The *Teflon-like* perfluorinated copolymers have demonstrated the most superior properties of any aliphatic polymer examined[75,76]. Perfluorinated polymers are well known for their exceptionally high chemical and thermal stabilities. Several studies have confirmed the chemical stability of perfluorinated polymers in various conditions, including strong bases, strong oxidizing and reducing agents[5,8]. These copolymers are chemically stable against the oxidative conditions of a fuel cell due to the strong carbon-fluorine bonds[77], which are approximately 4 kcal stronger than aliphatic carbon-hydrogen bonds[78]. The development of perfluorinated polymers increased confidence in the application of proton exchange membrane fuel cells after the early failure using sulfonated polystyrene[11].

Nafion®, produced and marketed by E.I. DuPont de Nemours, was developed for space exploration applications[79]. These fully fluorinated electrolytes have been the focus of several books and reviews in PEMFC literature[80,81]. The proposed structure of Nafion® is shown in Figure 7. Dow, Asahi Chemical and Aciplex have developed similar fluoropolymers[82]. Dow marketed their perfluorinated copolymer under the name of Dow XUS®. Dow XUS® was manufactured at 2 mil thickness (verses the original

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[75] Kordesch, K.; Simader, G., *Fuel Cells and their Applications* 1996, Wiley-VCH, p.72

[76] Eisenberg, A.; Yeager, H. L. *Perfluorinated Ionomer Membranes*; ACS Symposium Series #180:, 1982.

[77] Liebhafsky, H.A.; Cairns, E..J., *Fuel Cells and Fuel Batteries*, John Wiley and Sons, Inc., New York, 1968

[78] Kerr, J.A., *Chem. Rev* 1966, 66, 465.

[79] Steck, A., *J. Power Sources*1990, 29, 239.

[80] Pourcelly, G.; Gavach, C. In *Proton Conductors*; Colomban, P., Ed.; Cambridge University Press: London, 1992; p 295.

[81] Kerres, J.A., *J. Membr. Sci*. 2001, 185 (1), 3.

[82] Wakizoe, M.; Velev, O.A.; Srinivasan, S. *Electrochim. Acta* 1995, 40, 335.

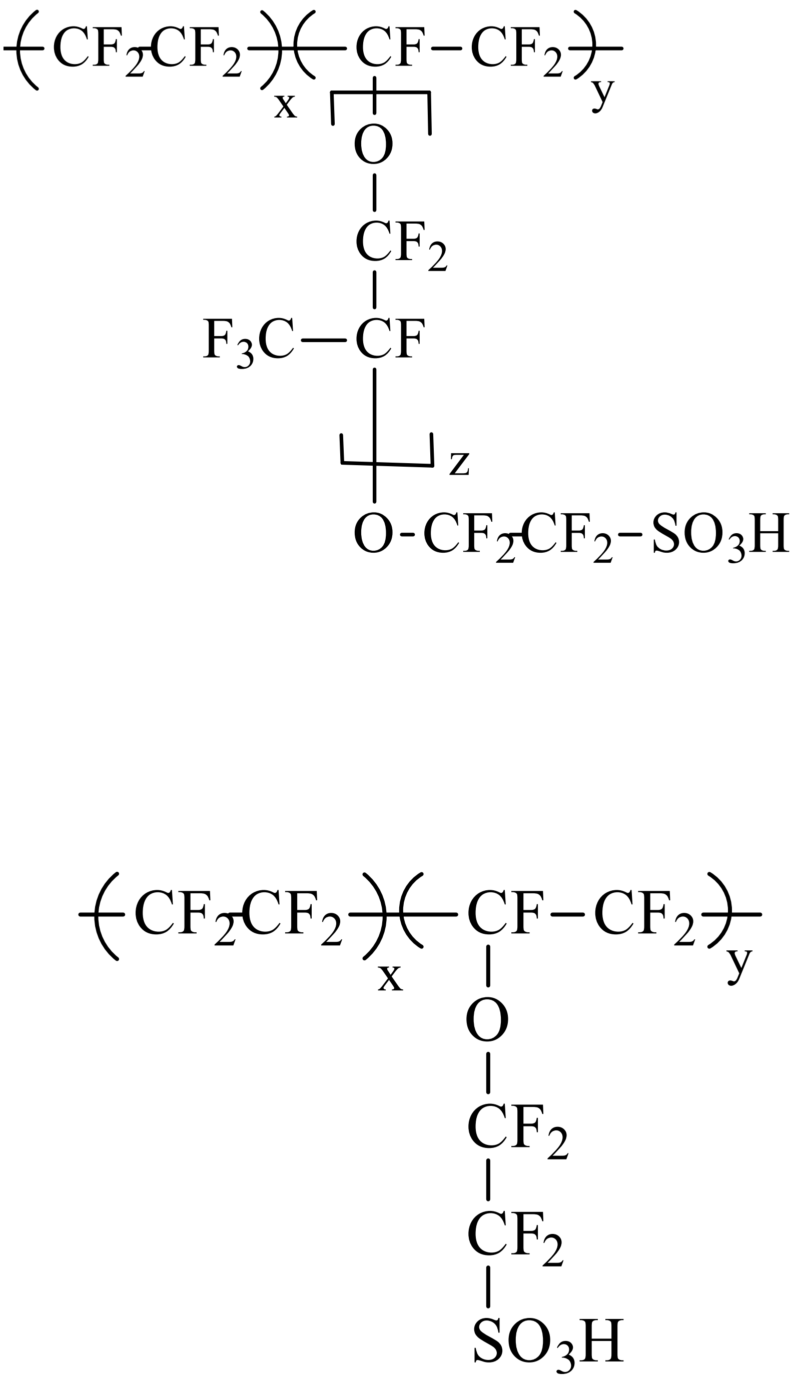

FIGURE 7. Proposed structure of Nafion® and Dow XUS® perfluorinated copolymers[20,85,86], respectively.

thickness of Nafion at 7 mils) and had a lower equivalent weight, i.e., more pendent sulfonic acid groups per -CF_2 unit[83]. Nafion films are now produced at various thicknesses, but mostly at about 1100 equivalent weights (~13 mole % comonomer). The proposed structures are given in Figure 7. The thinner membrane and higher concentration of proton exchange sites reportedly allowed Dow XUS® to display better performance in several aspects than Nafion®.

Control of the equivalent weight in these polymers is managed by varying the molar ratio of tetrafluoroethylene (**x**) and the specialty sulfonyl comonomer (**y**). By varying this ratio, a wide range of copolymers with different equivalent weights (800-1500) may be produced. Nafion 950 and Nafion 1100 are perhaps the most commonly investigated membranes. These perfluorinated copolymers are melt processible in the sulfonated fluoride form. Due to the associated high cost of the specialty co-monomers, Dow XUS was more expensive than Nafion. A general drawback with all perfluorinated proton exchange membranes is their cost[71]. The relatively high selling price is probably related to the economics of producing the specialty perfluorosulfonic fluoride monomers, and then converting to the sulfonic acid. Figure 7a displays the proposed synthesis of the specialty monomers used for Nafion and Dow XUS[84]. Patent literature suggests that the copolymerization synthesis of Nafion® and other perfluorinated copolymers is actually performed using the sulfonyl fluoride, which is then converted into its proton conductive acid form prior to use[85,86].

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[83] Srinivasan, S.; Velev, O.A.; Parthasarathy, A.; Manko, D.J.; Appleby, A.J., *J. Power Sources* 1991, 36, 299.

[84] Steck, A.E.; Stone, C., *in Proc. of 2nd Int. Symp. on New Mat. for Fuel Cell and Mod. Battery Sys.* O. Savadogo and P.R. Roberge, Eds., Montreal, Canada, 1997, 782.

[85] Ezzell, B.R.; Carl, W.P.; Mod, W.A., *US Patent 4,358,412*, 1982.

[86] Connollym, D.J.; Gresham, W.F., *US Patent 3,282, 875* 1966

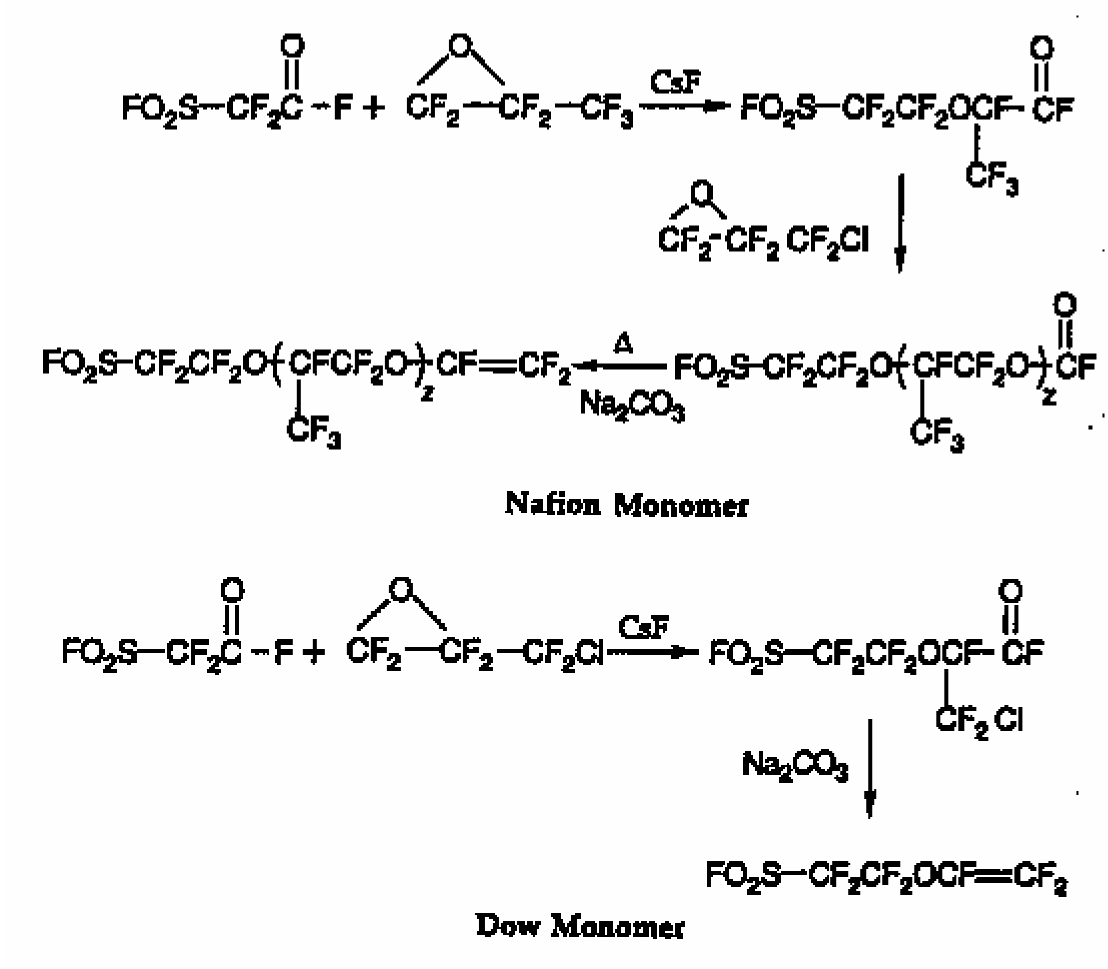

FIGURE 7A. Proposed synthesis of perfluorinated comonomers utilized for Nafion® and Dow XUS® copolymers[71,84,85,86].

Literally thousands of references, including several book reviews[87,88] are available on various aspects of perfluorinated membranes. Among these are the influence and importance of phase separation or ionic domain formation with the Nafion® and similar perfluorosulfonic acid copolymers, as described in the previous section. A number of techniques including NMR, IR, mechanical and dielectric relaxation, electron microscopy and X-ray studies have suggested ion clustering in Nafion®. These ionic aggregates have been proposed to contribute to Nafion-type membranes' advantages over many other synthesized materials, usually post-sulfonated polymers, which will be discussed in another section.

The flexible, hydrophobic fluorinated backbone of the polymer is believed to promote aggregation of the hydrophilic side chains containing the sulfonic acid groups during processing and / or conversion to its sulfonic acid. According to the Eisenberg-Hird-Moore Model, the ionic sites aggregate into multiplets[54,56,89]. The aggregates within Nafion have been credited[90,91] with enhancing the protonic conductivity. Gierke proposed the ionic clusters as being short ion channels or networks[92]. The calculated cluster diameter ranges between 3 and 5 nm for a 1200 equivalent weight polymer containing on average 70 ion exchange sites and 1000 water molecules[93]. Figure 7b depicts the arrangement. In this model, the counter-ions, the fixed sites and water phase separate from the hydrophobic fluorocarbon matrix into approximately spherical domains interconnected by short narrow channels. The sizes or diameters of the clusters are dependent on the water content of the membrane[94]. Furthermore, reorganization

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[87] Srinivasan, S.; Manko, D.J.; Koch, H.; Enayetullah, M.A.; Appleby, J.A., *J. Power Sources* 1990, 29 (3-4), 367.

[88] Zawodinski, T.; Springer, T.E.; Uribe, F.; Gottesfield, S., *Solid State Ionics* 1993, 60, 199.

[89] Kim, J.-S.; Eisenberg, A., In *Ionomers: Characterization, Theory and Applications* 1996, S. Schlick, Ed., CRC Press, New York.

[90] Gierke, T.D.; Munn, G.E.; Wilson, F.C., *J. Polym. Sci., Polym. Phys. Ed.* 1981, 19, 1687

[91] Porat, Z.; Fryer, J.R.; Huxham, M.; Rubinstein, I., *J. Phys. Chem.* 1995, 99, 4667.

[92] Hsu, W.Y.; Geirke, T.D., *Macromol.* 1982, 15, 101.

[93] Hsu, W.Y. and Gierke, T.D., *J. Membrane Sci.* 1983, 13, 307.

[94] Gierke, T.D., Munn, G.E. and Wilson, F.C. *J. Polym. Sci. Polym. Phys. Ed*. 1981, 19, 1687.

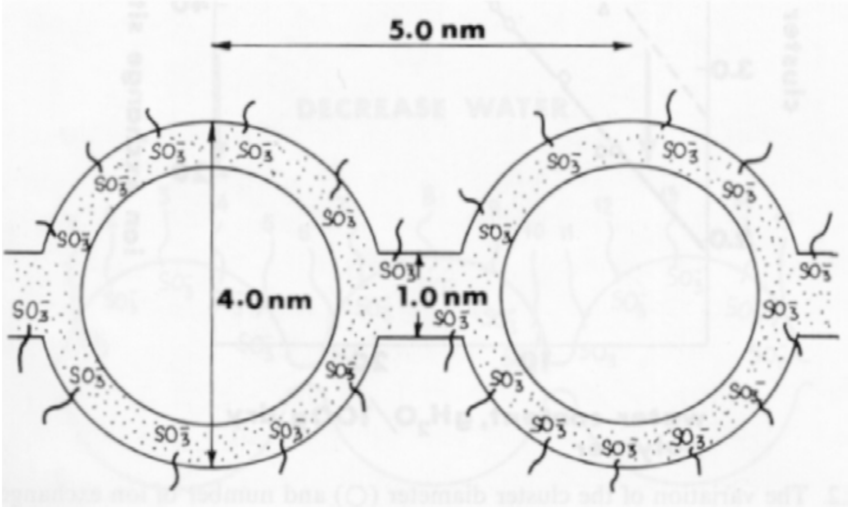

FIGURE 7B. IONIC CLUSTER NETWORK MODEL FOR PERFLUOROSULFONIC ACID COPOLYMER[93].

occurred during hydration/dehydration cycles as suggested by a change in the number of sulfonic acid groups as well as the number of clusters after the cycle (Figure 7c). More recent publications[95,96,97] suggest a more lamellar-like structure for the aggregates, but still agree with their importance for the high proton conductivity in perfluorosulfonic acid copolymers.

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[95] Kreuer, K.D., *J. Membr. Sci.* 2001, 185, 29.

[96] Litt, M.H., *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1997, 38, 80.

[97] Young ,S.K.; Trevino, S.F.; Beck-Tan, N.C., *J. Polym. Sci. Part B: Polym. Phys* 2002,40, 387.

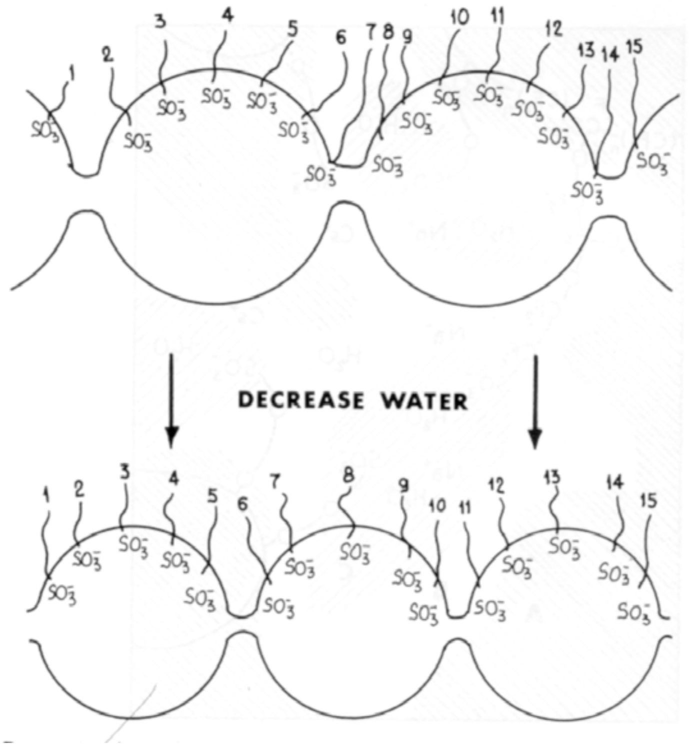

FIGURE 7C. Redistribution of ionic sites/cluster during dehydration cycles[94].

An additional important feature of Nafion-like membranes is the presence of semi-crystallinity. The Nafion with equivalent weights of greater than 1000 possess some crystalline domains originating from long tetrafluoroethylene sequences[98]. The amount of crystallinity depended on the amount of specialty sulfonated comonomer incorporated and decreased nearly completely at low (<1000) equivalent weights. Semi-crystalline domains in these presumed random copolymers are associated with the good water insolubility and relatively modest water swelling.

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[98] Starkweather Jr, H. W. *Macromolecules* 1982, 15, 320.

1.2.3 Post-Sulfonated Aromatic Engineering Thermoplastics

Generally, *engineering thermoplastics* are a broad class of polymeric materials that produce tough, ductile films and are characterized by good thermal and mechanical properties[99]. Their properties allow for diverse applications in the adhesive, films and coatings, automotive, and electronic industries[100]. Engineering thermoplastics encompass polymers such as polyarylates, poly (arylene ethers), polyimides, polyetherimides, and others. The aromatic rings of these polymers make them easily modified for various applications. One successfully demonstrated modification is sulfonation, via a variety of sulfonating agents.

1.2.3.1 Poly (arylene ethers)

Poly (arylene ethers) are a class of high performance engineering thermoplastics with high glass transition temperatures, high thermal stability, good mechanical properties, and exceptional resistance to hydrolysis and oxidation[101,102,103,104,105,106]. While there are many variations of poly(arylene ethers), the major branches of these important materials are poly(ether sulfones) and poly(ether ketones). The general structure of poly(arylene ethers) is given in Figure 8. The synthetic routes to these materials will be discussed later.

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[99] Clagett, D.C. in *Encyclopedia of Polymer Science and Engineering,* H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges, Eds., Vol. 6, John Wiley and Sons, New York, 1986.

[100] Odian., G., *Principles of Polymerization*, 3rd Edition, John Wiley and Sons, New York, 1991.

[101] Cotter, R.J. *Engineering Plastics: Handbook of Polyarylethers*, Gordan and Breach Publishers: Basel, Switzerland, 1995.

[102] Hedrick, J.L.; Labadie, J.W., *Step-Growth Polymers for High Performance Materials: New Synthetic Methods*, ACS Symp. Ser. 624, 1996.

[103] Johnson, R.N. in *Encyclopedia of Polymer Science and Technology*, N.M. Bikales, Ed., John Wiley & Sons: New York, 1969.

[104] Riley, D.J.; Gungor, A.; Srinivasan, S.; Sankarapandian, M.; Tchatchoua, C.; Muggli, M.W.; Ward, T.C.; McGrath, J.E.; Kashiwagi, T., *Polym. Eng. Sci* 1997, 37, 1501.

[105] Johnson, R.N.; Farnham, A.G., *US Patent 4,175,175* 1979.

[106] Wang, S.; McGrath, J. E., in T. E. Long and M. Rogers Eds., Wiley and Sons, 2002, in press.

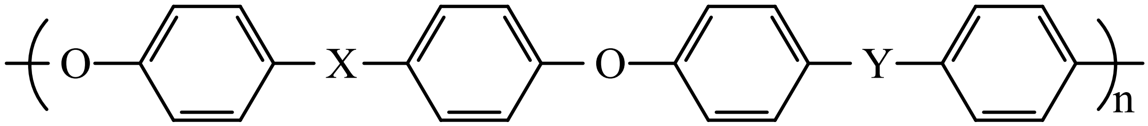

FIGURE 8. Generic representation of poly (arylene ethers)

(1) **Poly(Arylene Ether Sulfones)**

Perhaps the first sulfonation of a poly(arylene ether sulfone) was reported in the patent literature by Quentin[107]. Chlorosulfonic acid was employed in an electrophilic substitution reaction to introduce ionic groups along the commercially available polymer known as Udel®, marketed by Solvay Advanced Polymers(Figure 9). The room temperature sulfonation reactions were conducted for different time intervals to yield polymers with different levels of sulfonation.

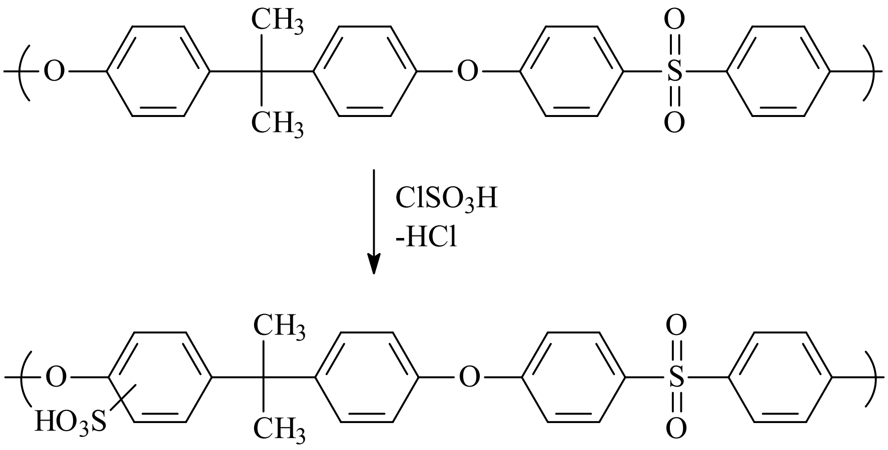

FIGURE 9. Sulfonation of Udel® Polysulfone[112]

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[107] (a) J.P. Quentin, Sulfonated Polyarylether Sulfones, *US Patent 3,709,841,* 1973.; (b) Brousse, C.L.; Cheapurlet, R.; Quentin, J.P., *Desalinaton* 1976, 18, 137.

Many other researchers[108,109,110,111] have tried to repeat this pioneering work. However, chlorosulfonic acid causes undesirable and detrimental side reactions, such as chain scission, branching and / or cross-linking at the isopropylidene group of the bisphenol A-based polymers. Recently, several researchers used trimethylsilyl chlorosulfonate to sulfonate Udel[108,109]. The silyl-protected reagent reportedly minimized chain scission, etc., as determined by viscosity experiments.

Organosulfur reactions have been well studied for small molecules[112]. This knowledge has translated into useful reactions on polymers. One such example of this exchange of science is the use of sulfur trioxide (SO_3) and sulfur trioxide complexes to *mildly* sulfonate polymers. Sulfur trioxide is commonly used for the sulfonation of molecules that decompose in strongly acidic media.[112,113] Sulfur trioxide, due to three oxygen atoms double-bonded to the sulfur, is a stronger sulfonation agent than concentrated sulfuric acid and is reactive enough to sulfonate benzene directly, even at temperatures as low as 0-10 °C[112,114].

Noshay and Robeson[115] utilized a sulfur trioxide and triethyl phosphate complex (SO_3-TEP) to sulfonate commercially available Udel, the industrially important bisphenol A-based polysulfone. Coplan and Gotz demonstrated sulfonation of deactivated poly(ether sulfone) using SO_3[116]. Johnson *et al.* performed a comprehensive study on functional membranes in the area of water desalination using SO_3-TEP [117]. They were able to introduce different amounts of sulfonic acid groups along the polymer chain. Moreover, Johnson found no evidence of a crosslinking side reaction using sulfur trioxide

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[108] R. Nolte, K. Ledjeff, M. Bauer, and R. Mulhaupt, *J. Membr. Sci.*, 1993, 83, 211.

[109] H.S. Chao and D.R. Kelsey, *US Patent 4,625,000*, 1986.

[110] F. Lufrano, I.Gatto, P. Staiti, V. Antonucci, E. Passalacqua, *Solid State Ionics*, 2001, 145, 47.

[111] Genova-Dimitrova, P.; Baradie, B.; Foscallo, D.; Poinsignon, C.; Sanchez, J.Y., *J. Membr. Sci.* 2001, 185, 59.

[112] Cremlyn, R.J., *An Introduction to Organosulfur Chemistry*, John Wiley & Sons: New York, 1996.

[113] Cerfontain, H., *Mechanistic Aspects in Aromatic Sulfonation and Desulfonation, Part 1: Electrophilic Aromatic Sulfonation and Related Reactions*, Interscience, New York, 1967.

[114] Cremlyn, R.J.; Bassin, P., *Phosphorus, Sulfur, and Silicon*, 1991, 56, 245.

[115] Noshay, A.; Robeson, L. M. *J. Of Appl. Poly. Sci.* 1976, *20*, 1885.

[116] Coplan, M.J.; Gotz, G., *US Patent 4,413,106*, 1983.

[117] Johnson, B. C.; Yilgor, I.; Tran, C.; Iqbal, M.; Wightman, J.; Lloyd, D.; McGrath, J. E. *J. Polym. Sci. Polym. Chem. Ed.* 1984, 22, 721.

as demonstrated by easy re-dissolution of the modified polymers. O'Gara *et al.*[118] also employed SO_3-TEP for sulfonation of PES while exploring multiplet / cluster formations using small angle x-ray spectroscopy (SAXS). Nolte and colleagues were likewise able to generate similar sulfonated membranes, as well as water-soluble polymers, using sulfur trioxide in chloroform ($CHCl_3$)[119]. Furthermore, these researchers sacrificed some of the sulfonic acid groups to introduce cross-links, after derivatization and reacting with a diamine, to influence the swelling behavior of the hydrated films.

In a recent publication, Morley and Roberts adapted molecular modeling and the related calculations to study the complex electrophilic substitution mechanism(s) by sulfur trioxide[120]. Others[113,121,122,123] have proposed various possible mechanisms or intermediate species involved in the sulfonation of aromatic compounds via sulfur trioxide, but it was experimentally not possible to properly characterize the intermediates[120] which are difficult to isolate. Figure 10 displays these suggested routes. Experimental data have suggested the possible Wheland intermediates (5) and (6)[121,122]. Rearrangement of (6) allows for the postulation of a toluene pyrosulfonic acid, intermediate (7). The molecular modeling calculations favor (6). The toluenesulfonic anhydride (9) is the main byproduct of the otherwise efficient substitution reaction.

A new sulfonation process for generating polysulfone ionomers has been described by Kerres et al[124,125,126]. The procedure includes the cryogenic deprotonation of the Udel poly(ether sulfone) using n-butyllitium, then reacting the lithiated polymer with sulfur dioxide (SO_2), and finally performing an oxidation/hydrolysis to yield the sulfonic acid. The scheme is given in Figure 11. As shown, this procedure introduced the

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[118] O'Gara, J.F.; Williams, D.J.; MacKnight, W.J.; Karasz, F.E., *J. Polym. Sci.Part B: Polym. Phys.* 1987, 25, 1519,

[119] Nolte, R.; Ledjeff, Bauer, M.; Mulhaupt, R., *J Membr. Sci.* 1993, 33, 211.

[120] Morley, J.O.; Roberts, D.W., *J. Org. Chem.* 1997, 63, 7358.

[121] Bosscher, J.K.; Cerfontain, H., *Tetrahedron* 1968, 24, 6543.

[122] Lammertsma, K.; Cerfontain, H., *J. Chem. Soc., Perkin Trans. 2*, 1980, 2, 28.

[123] Bosscher, J.K.; Cerfontain, H., *J. Chem. Soc. Part B.* 1968, 1524.

[124] Kerres, J. ; Cui, W.; Reichle, S., *J. Polym. Sci. Part A: Polym. Chem*. 1996, 34, 2421.

[125] Kerres, J.; Cui, W.; Eigenberger, G.; Bevers, D.; Schnumberger, W.; Fischer, A, Wendt, H., *in Proc. of the 11th Hydrogen Conf.*, T.N. Veziroglu, C.J. Winter, J.P. Basalt, G. Kreysa, Eds., Stuttgart, Germany, 1996, p. 1951.

[126] Kerres, J.; Zhang, W.; Cui, W., *J. Polym. Sci. Part A: Polym. Chem.* 1998, 36, 1441.

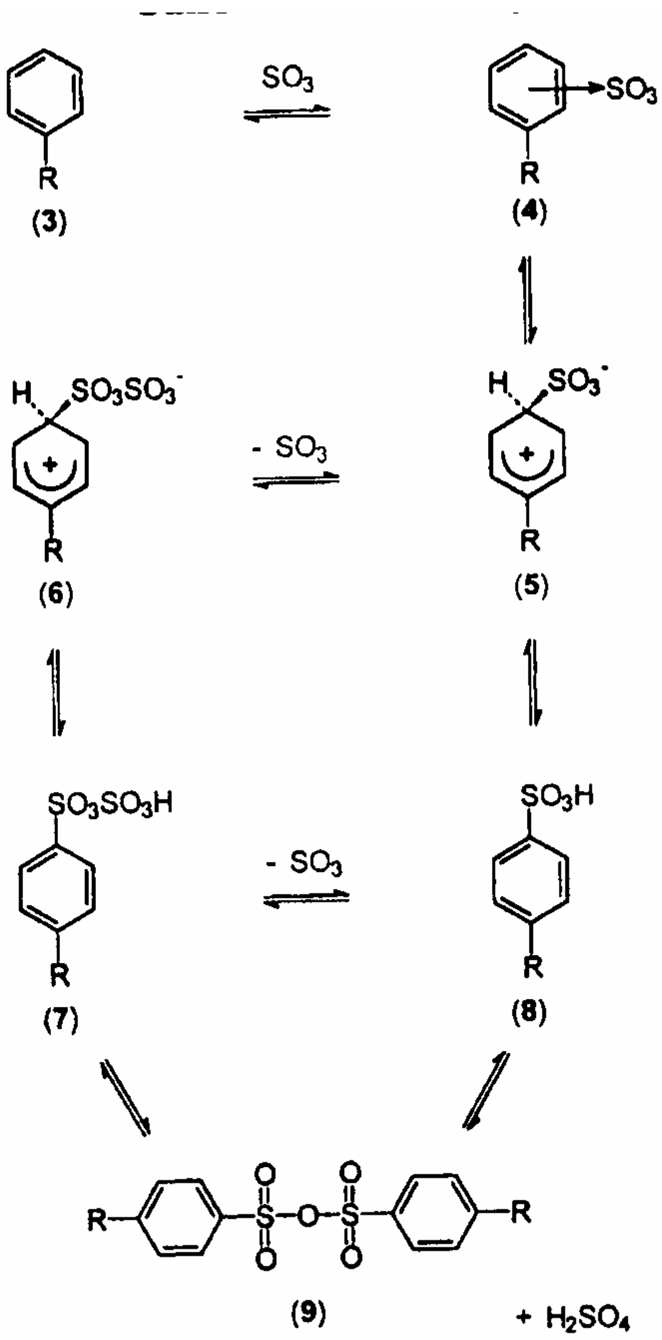

FIGURE 10. Postulated Mechanism and Intermediates of Toluene Sulfonation via Sulfur Trioxide[120].

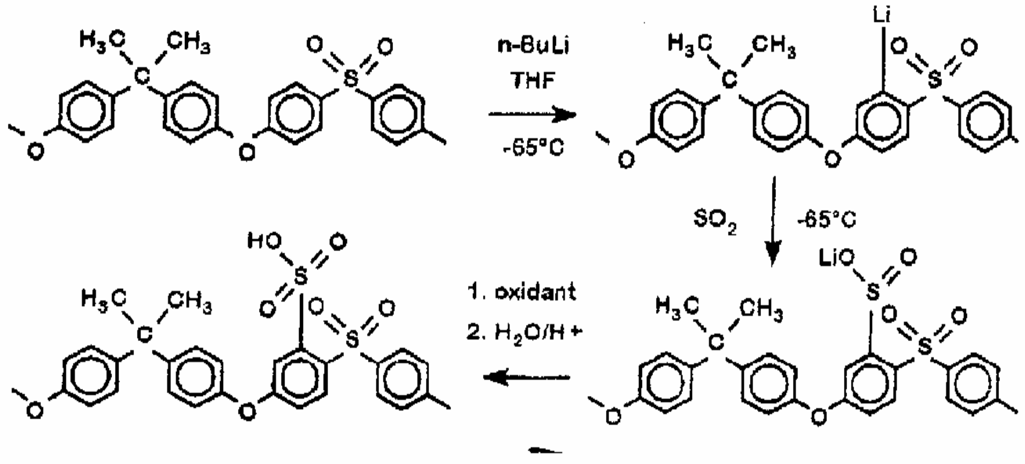

FIGURE 11. Synthetic route to sulfonated poly (ether sulfones) via metalation[124, 113]

sulfonate group on the ring adjacent to the sulfone bridge, different from the other sulfonating agents/routes. While academically interesting, the procedure may still be, like other post modifications, difficult to control and reproduce, especially on a larger scale under cryogenic conditions.

Nolte *et al.*[108] prepared and described crosslinked sulfonated poly(arylene ether sulfone)s. Nolte and colleagues developed an in-situ crosslinking technique, during membrane processing, by reacting some of the polymer's pendent sulfonic acids with 1,1'-carbonyl diimidazole. The *activated* moieties (N-sulfonyl-imidazoles), after neutralization of the polymer mixture, were reacted with aliphatic diamines (Figure 12). The crosslinked polymers reportedly displayed at least a 50 % reduction in swelling by water than the uncrosslinked sulfonated poly(arylene ether sulfone)s.

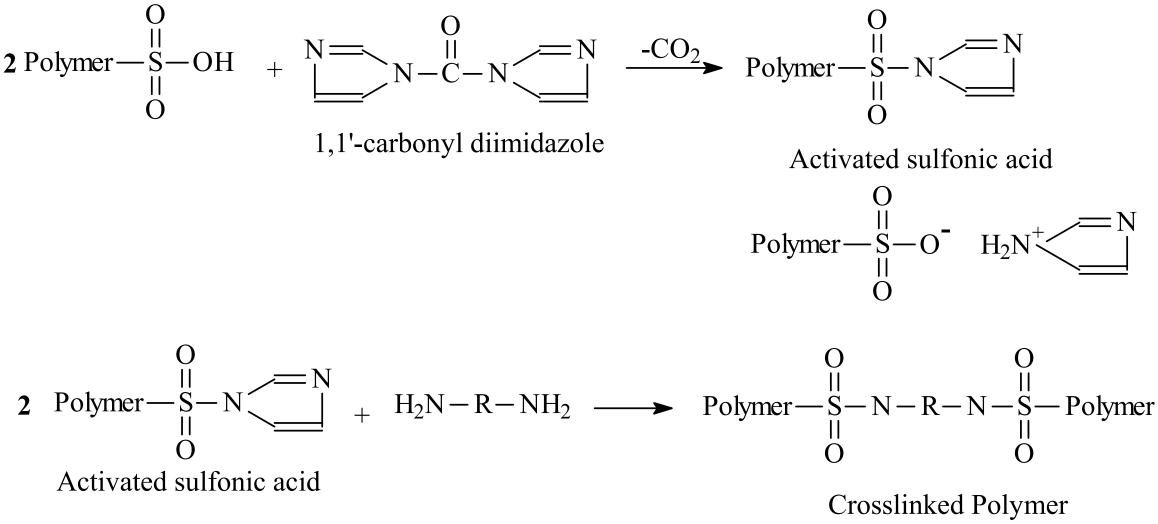

FIGURE 12. Crosslinking of sulfonated PAES using 1,1'-carbonyl diimidazole.[108]

(2) **Poly(Arylene Ether Ketones)**

Poly (arylene ether ketones) have been modified using various sulfonation agents. Due to the semi-crystalline nature of certain poly (ether ketone)s and their corresponding poor solubility in many solvents, sulfonations were first achieved in concentrated sulfuric acid. The first investigation of sulfonated poly(ketone)s[127] utilized this route. Other researchers have increased the literature base for sulfonated poly(ether ketones)[128,129,130,131,132,133,134]. Schneller *et al.* [132] proposed using SPEEK for proton

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[127] Lee, J.; Marvel, C.S., *J. Polym. Sci.: Polym. Chem. Ed.* 1984, 22, 295.

[128] Bishop, M.T.; Karasz, F.E., Russo, P.S., *Macromolecules* 1985, 18, 86.

[129] Bailly, C.; Williams, D.J.; Karasz, F.E.; MacKnight, W.J., *Polymer* 1987, 28, 1009.

[130] Jin, X.; Bishop, M.T.; Ellis, T.S.; Karasz, F.E., *Brit. Poly. J.* 1985, 17, 4.

[131] Devaux, J.; Delimov, D.; Daousti, D.; Legras, R.; Mercier, J.P.; Strazielle, C.; Nield, E., *Polymer* 1985, 26, 1994.

[132] Schneller, A.; Ritter, H.; Ledjeff, K.; Nolte, R.; Thorwirth, R., *EP 0574791 A2* 1993.

[133] Linkous, C.A.; Anderson, H.R.; Kopitzke, R.W.; Nelson, G.L., *in Proc. of the 11th Hydrogen Conf.*, T.N. Veziroglu, C.J. Winter, J.P. Basalt, G. Kreysa, Eds., Stuttgart, Germany, 1996, p. 559.

[134] Peer, M., *UK Patent Appl. GB 2217134 A* 1989.

exchange membranes. Using sulfuric acid, the influence of temperature, time, and water content (i.e., concentration of acid used) have been investigated and optimum conditions have been established[135]. However, one criticism of sulfonation using sulfuric acid to sulfonate polymers is that the rate of polymer dissolution strongly influences the rate of sulfonation. This dissolution while simultaneously sulfonating the polymer complicates the process and restricts any homogeneity of the procedure. This directly leads to difficulty in reproducibility in subsequent experiments or batches.

Chlorosulfonic acid has been successfully used to better control the degree of sulfonation by varying the molar amount of chlorosulfonic acid used[127,136]. Recently, Hamciuc *et al.*[137] reported the sulfonation and chlorosulfonation of poly (ether ketone)s containing hexafluoroisopropylidene groups ("6F"). Using 100% chlorosulfonic acid in two hours, the authors reported the formation of the repeat unit shown in Figure 13. The introduction of the 6F-moiety greatly decreased the chemical degradation experienced by the bisphenol A based polyketones.

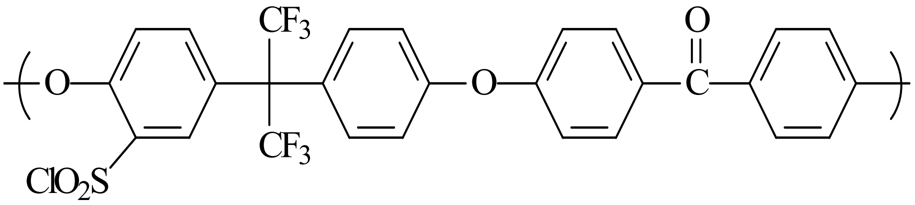

FIGURE 13. Chlorosulfonated hexafluoroisopropylidene containing poly (ether ketone)[137]

A series of papers by Belgium researchers has been published on the sulfonation of poly (ether ketone)s[138,139,140]. These scientists presented data consistent with first-

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[135] Bishop, M.T.; Karasz, F.E.; Ruso, P.S.; Langley, K.H., *Macromolecules* 1985, 18, 86.

[136] Litter, M.I.; Marvell, C.S., *J. Polym. Sci,: Polym. Chem. Ed*1985, 23, 2205.

[137] Hamciuc, C.; Bruma, M.; Klapper, M., *J. Macromol. Sci.: Pure Appl. Chem.* 2001, A38 (7), 659.

[138] Daoust, D.; Devaux, J.; Godard, P., *Polym Int.* 2001, 50(8), 917.

order kinetics with respect to the unsulfonated repeat units[138], using 96% and 97% concentrated sulfuric acid. Also, they noted a slowing effect on substitution of sulfonate groups. This is reasonable if one considers the fact that sulfonate groups are electron withdrawing. Interestingly, the researchers investigated the influence of the fluorine end-groups on the mechanism and kinetics of sulfonation with concentrated sulfuric acid. Noting that the sulfonation is a function of a number of variables (e.g., acid strength, concentration of the polymer, generation of water as a by-product, temperature, time, etc.)[139], the authors concluded that the halide of the fluorine-terminated polymers does have a surprisingly long-range (up to 3 repeat units) influence on the sulfonation.

1.2.4 **Poly (Benzyl Sulfonic Acid) Siloxanes (PBSS)**

A few researchers have proposed proton exchange membranes based on modified alkoxy silanes[141,142,143,144]. Synthesized by the hydrolysis and condensation of benzyl-triethoxyl silane precursors in a mixture of methanol, water, and triflic acid[143,144], high molecular weight polymers were reported. Figure 14 shows a representative structure.

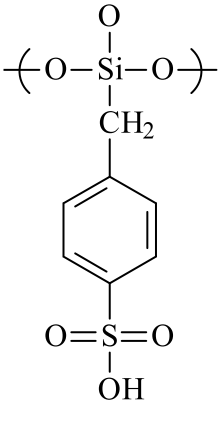

FIGURE 14. Proposed chemical structure of poly (benzyl sulfonic acid) siloxane[143].

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[139] Daoust, D.; Devaux, J.; Godard, P., *Polym Int.* 2001, 50(8), 925.

[140] Daoust, D.; Devaux, J.; Godard, P., *Polym Int.* 2001, 50(8), 932.

[141] Chanbouillet, Y.; Ravaine, D.; Armand, M.B.; Poinsignon, C., *J. Non-Cryst. Solids* 1988, 103, 325.

[142] Schmidt, H.; Papall, M.; Rousseau, F.; Poinsignon, C.; Armand, M.B.; Sanchez, Y., *Proceedings of 2nd Int. Symp. on Polymer Electrolytes*, B. Scrossati, Ed. , Elsevier, London, 1990, p. 325.

[143] Ganthier-Luneau, J.; Denoyelle, A.; Sanchez, J.Y.; Poinsignon, C., *Elecrochem. Acta* 1992, 37, 1615.

[144] Poinsignon, C., in *1st Int. Symp. on New Mat. for Fuel Cell Sys.*, Montreal, Canada, July 1995, poster No. 29.

Sulfonation was achieved via chlorosulfonic acid in dichloromethane. Copolymers were also prepared by incorporating n-hexyl trimethoxy silane and triethoxy silane[143]. Crosslinking of these novel polymers was accomplished by hydrosilylation of the silane groups with divinylbenzene in THF. High thermal stabilities (up to 250 °C) and room temperature proton conductivities of 1.6 x 10^{-2} S/cm were reported[143]. Interestingly, these materials have been proposed for direct methanol fuel cells, but no methanol crossover information was presented. It would be surprising if the polar siloxane bond was stable in the presence of the strong sulfonic acid.

1.2.5 **Poly(phenylquinoxalines) (PPQ)**

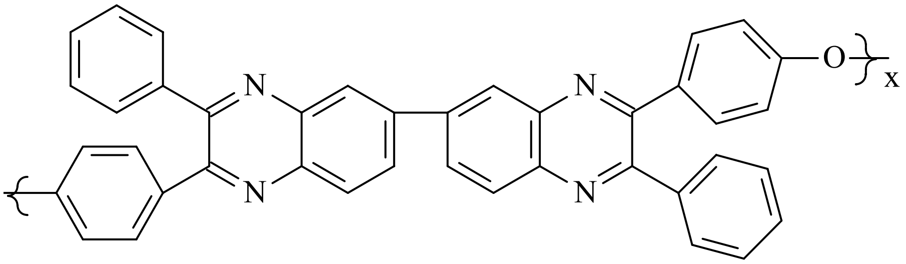

FIGURE 15. STRUCTURE OF POLY (PHENYLQUINOXALINES).

Poly (phenylquinoxalines) have been investigated as PEM candidates[71,145,146]. These polymers were investigated by Ballard Advanced Materials as one of their *first generation* ("BAM-1G") proton exchange membranes[33]. Poly(phenylquinoxalines) were sulfonated to various degrees using chlorosulfonic acid. Sulfonation was reportedly

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[145] Kopitzke, R.W.; Linkous, C.A.; Nelson, G.L., *Polymer Degradation and Stability* 2000, 67, 335.

[146] Steck, A.E.; Stone, C., *in Proc. of 2nd Int. Symp. on New Mat. for Fuel Cell and Mod. Battery Sys.* O. Savadogo and P.R. Roberge, Eds., Montreal, Canada, 1997, 782.

controllable from approximately 50 to well over 100 percent (i.e., greater than one sulfonate group per repeat unit)[146]. While the initial performance in single cell-fuel cell tests was good, sulfonated PPQ operated only 350 hours before failing[146]. Details on the mode of failure were not disclosed.

1.2.6 **Poly (Phenylene Oxide) (PPO)**

Ballard Advanced Materials also investigated the sulfonated polymer resulting from the polymerization of 2,6-diphenyl phenol (Figure 16)[33,146]. The acronym of P_3O is used to describe the unmodified polymer. The sulfonated P_3O (*P_3OSO_3H*) was accomplished by first brominating the polymer and then subsequently sulfonating it[147]. These membranes had a maximum continuous running lifetime of 500-600 hours[33,146] under Ballard's single cell-fuel cell test conditions.

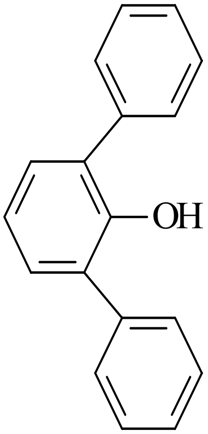

FIGURE 16. CHEMICAL STRUCTURE OF 2,6-DIPHENYL PHENOL

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[147] Hodgdon, R.B.; Hay, A.S., *U.S. Patent 3,528,858*, 1970.

1.3 Direct, Step-Growth Polymerization of Sulfonated Monomers

A novel approach has been developed by several research groups to obtain sulfonated aromatic copolymers-- the copolymerization of sulfonated monomers. The direct copolymerization of a modified monomer is an insightful and different approach than that of modification of a pre-formed polymer. Monomer modification allows *molecular-design* control, to some degree, of the resulting copolymer. Numerous, subtle sequence effects can be enhanced. Surprisingly, this synthetic route has only been applied to high performance, condensation-type polymer (i.e., non-addition or elastomeric polymers) systems within the last two decades. Primarily three distinct systems have received the most attention in the literature: (1) polyimides; (2) poly(arylene ethers), including sulfones, ketones, and phosphine oxides; and (3) poly(sulfide sulfones). The following sections will explore the development of these sulfonated copolymer membranes.

1.3.1 "Direct" Sulfonated Polyimides Copolymers

Polyimides, in general, are regarded as high performance materials possessing high thermal stability and excellent mechanical properties[148,149,150]. Polyimides are rigid, heterocyclic polymers that may be semi-crystalline, if flexible units or moieties are not incorporated. Pendant side groups have also been introduced in various polyimides to disrupt long-range packing order to minimize crystallinity[151]. Recently, several research groups[152,153,154] have incorporated sulfonic acid groups into polyimides, not for

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[148] Mittal, K.L. (ed) *Polyimides: Synthesis, Characterization and Applications*, *1&2*. Plenum, NY, 1984.

[149] Feger, C., Khojasteh, M.M., McGrath, J.E.(eds) *Polyimides: Materials, Chemistry and Characterization*. Elsevier, Amsterdam, 1989

[150] Wilson, D., Stenzenberger, H.D., Hergenrother, P.M. (eds) *Polyimide*s Blackie Glasgow, 1990;.

[151] Ghosh, M.K., Mittal, K.L. (eds.) *Polyimides: Fundamentals and Applications*; Marcel Dekker: 1996.

[152] Faure, S.; Cornet, G.; Mercier, R.; Pineri, M.; Sillion, B., *in Proc. 2nd Int. Symp. New Mat. for Fuel Cell and Mod Battery Syst.,* O. Savadogo and P.R. Roberge, Eds., Montreal, Canada, 1997, p.818.

[153] Gunduz, N.; McGrath, J. E. *Polymer Preprints* **2000**, 41(1), 180.

aforementioned crystallinity concerns, but for utility as proton exchange membranes for fuel cells.

Pineri and collaborative French researchers[152,155,156,157,158] described sulfonated polyimides synthesized using commercially available monomers, including 4,4'-diamino-2,2'-biphenyldisulfonic acid (BDSA), shown in Figure 17. These researchers copolymerized this BDSA with 4,4'-oxydianiline, and either of two dianhydrides, 4,4'-oxydiphthalic anhydride or 1,4,5,8-naphthalene tetracarboxylic dianhydride. The copolymerization was employed to encourage solubility and to generate distinct hydrophobic and hydrophilic segments along the copolymer.

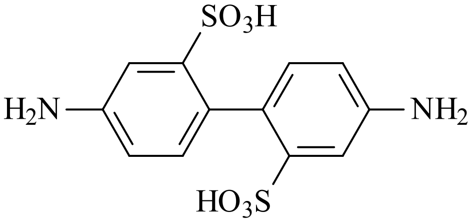

Figure 17. Chemical structure of 4,4'-diamino-2,2'-biphenyldisulfonic acid (BDSA**).**

The dianhydride structure proved to have important effects on the life-time of the polymers[33]. The 4,4'-oxydiphthalic anhydride yields traditional 5-membered heterocyclic rings, while the naphthalene tetracarboxylic dianhydride produces 6-membered heterocyclic rings. While the water uptake of both polymer series reportedly remained constant at increasing temperatures, unlike the Nafion control, the phthalic sulfonated polyimides failed before 100 hours of testing in a fuel cell. Failure of these membranes due to hydrolysis of the sulfonated sequence was proposed as the degradation site[156]. The sulfonated napthalic polyimides reportedly were stable for over 3000

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[154] Bernard, R. J.; Sherrington, D. C., in the 5th European Tech. Symp. Polyimides and High Performance Functional Polymers Proc., Montpellier, France, May 3-5, 1999.

[155] Faure, S.; Mercier, R.; Aldbert, P.; Pineri, M.; Sillion, B., *French Patent 96 05707*, 1996.

[156] Gebel, G.; Aldebert, P.; Pineri, M., *Polymer* 1993, 34, 333.

[157] Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M., *Polymer* 2001, 42, 359.

[158] Vallejo, E.; Pourcelly, G.; Gavach, C.; Mercier, R.; Pineri, M., *J. Membr. Sci.* 1999, 160, 127.

hours[159] at an unreported temperature. These results suggest that the six-membered heterocyclic rings are more stable than the five-membered ring analogue, as suggested by Rustanov and others[160].

Gunduz and McGrath[153,161,162] synthesized sulfonated polyimides using an impressive variety novel sulfonated monomers and comonomers. These soluble sulfonated copolymers were reportedly synthesized to high molecular weights, as based on measured high intrinsic viscosities and the ability to cast tough ductile films. The films were solution cast on glass substrates and the sulfonated polyimides were characterized as thermally stable materials. Figure 18 displays the sulfonated monomers these researchers investigated. Expected improved solubilities and membrane properties justified the variances in the structures. A sample copolymerization is depicted in Figure 19. The highest protonic conductivity reported is about 0.02 S/cm, which compares favorably to most of the aforementioned post-sulfonated polymers. Hong *et al*[163] investigated similar directly sulfonated polyimide copolymers and has been able to demonstrate high conductivities (e.g. 0.1 S/cm) in some cases. Hydrolytic stability at 80°C is still a major issue.

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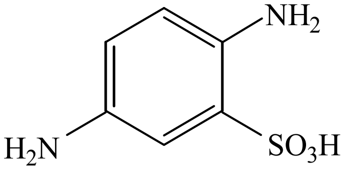
[159] Faure, S.; Cornet, N.; Gebel, G.; Mercier, R.; Aldbert, P.; Pineri, M.; Sillion, B. in *Proc. 2nd Int. Symp. on New Mater. for Fuel Cell and Modern Battery Syst*, Montreal Canada, 1997, p. 818.

[160] Rusanov, A.L. and Bulycheva, E.G. *Polyimides and Other High Temperature Polymers*, Abadie, M.J.M. and Sillion, B. (eds.), Elsevier, 1991, p. 125-149; (b) Mercier, R. *French Patent*; (c) Ponomarev, I.I., Nikol'skii, O.G., Volkova, Y.A., and Zakharov, A.V., *Polymer Science, Ser. A,* 1994, 36 (9), 1185.

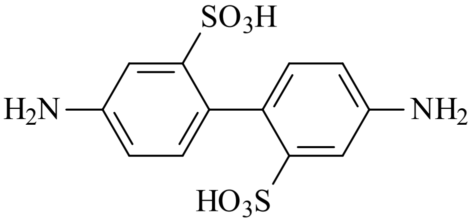
[161] Gunduz, N., *SYNTHESIS AND CHARACTERIZATION OF SULFONATED POLYIMIDES AS PROTON EXCHANGE MEMBRANES FOR FUEL CELLS* , Ph.D. Thesis, VPI&SU, 2001.

[162] Gunduz, N.; McGrath, J.E., *Polymer Preprints* 2000, 41(2), 1565.

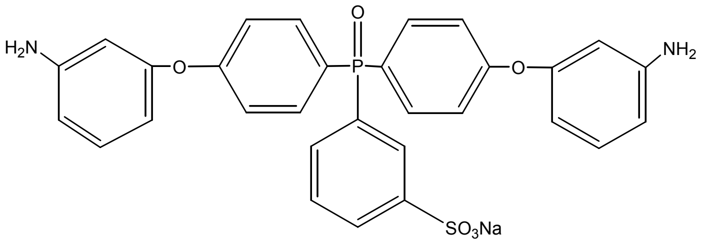
[163] Hong, Y. T.; Einsla, B.; Kim, Y.S.; McGrath, J. E., *Polymer Preprints* 2002, 43 (1), 666; (b) Hong, Y.T., et al. *J. Polym. Sci*., 2002, in press.

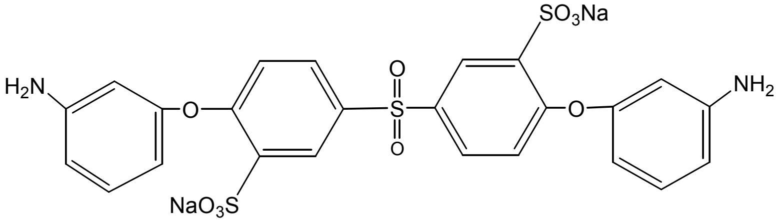


1,4-Diaminobenzene sulfonic acid (pPDA-SO_3H)



4,4’-diamino-2,2’-biphenyldisulfonic acid





3,3’-Disulfonated 4,4’-bis(3-aminophenoxy)phenyl sulfone (s-DADPS)[163]

FIGURE 18. Sulfonated diamines investigated by Gunduz, *et al*[161].

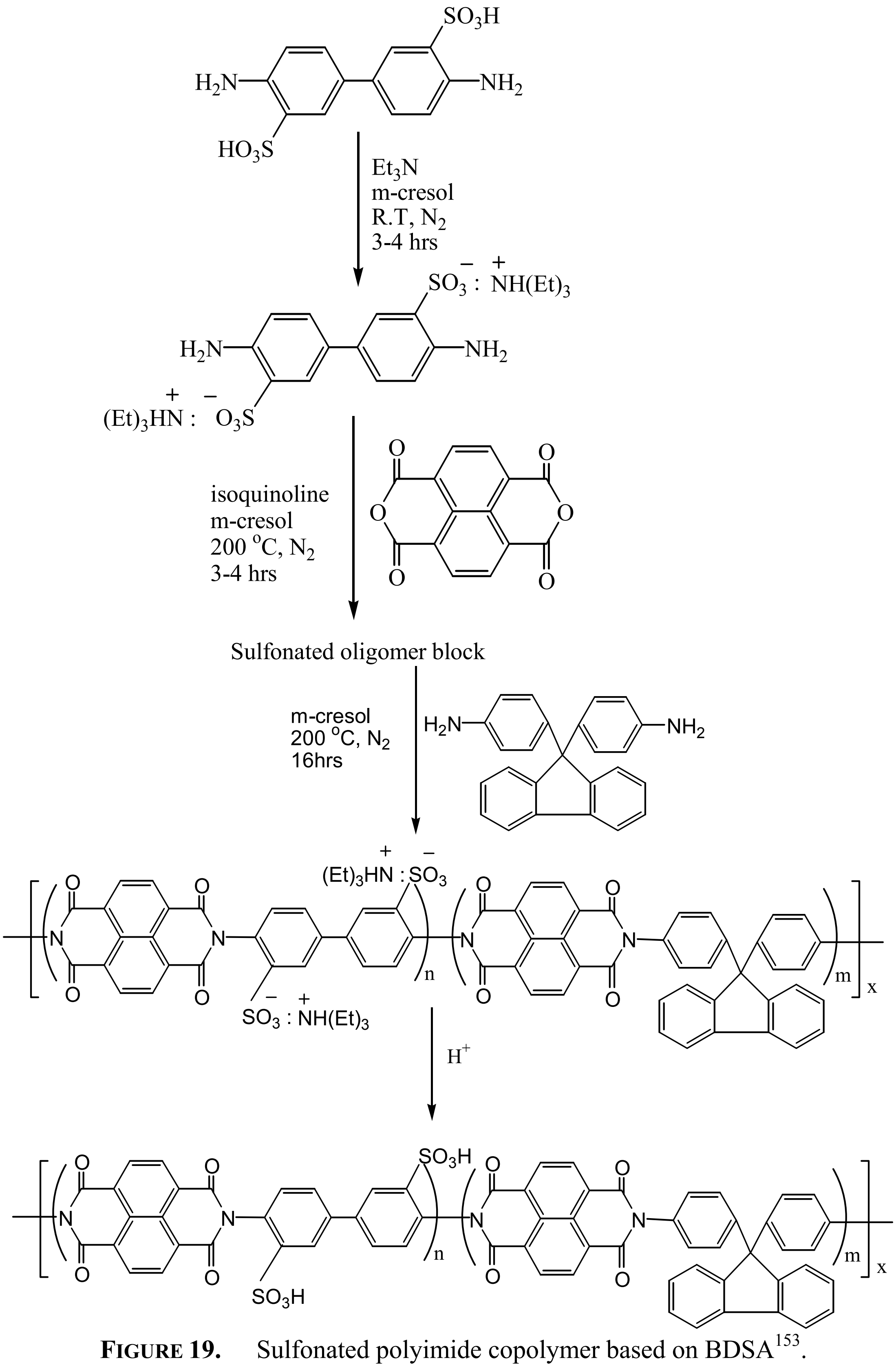


FIGURE 19. Sulfonated polyimide copolymer based on BDSA[153].

Shobha *et al*. (Virginia Tech, unpublished results) reported the synthesis and characterization of a new sulfonated monomer for application for proton exchange membranes (Figure 20). No copolymers have yet been reported using this monomer.

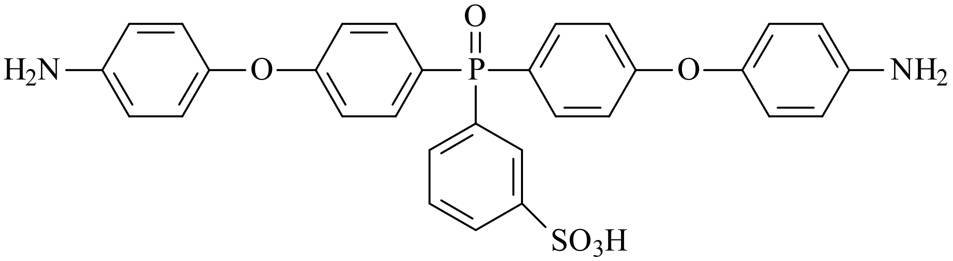


FIGURE 20. Structure of novel phosphine oxide based sulfonated diamine.

1.3.2 **“Direct” Sulfonated Poly (Arylene Ether) Copolymers**

Poly (arylene ethers) have been synthesized via a number of synthetic routes, which will be reviewed in a later section. Nevertheless, sulfonated poly(ether sulfones), poly(ether ketones), and poly(ether phosphine oxides) have been synthesized using sulfonated comonomers. The following sections will survey these novel copolymers.

(1) **Poly(arylene ether sulfones)**

Perhaps the first reported synthesis of sulfonated poly(arylene ether sulfones) via a pre-sulfonated monomer was reported by Ueda et al[164]. The disulfonated dihalide monomer, sodium 5,5’-sulfonylbis(2-chlorobenzenesulfonate), was generated by reacting 4,4’-dichlorodiphenyl sulfone (DCDPS) with fuming sulfuric acid. This monomer will herein be referred to as 3,3’-disulfonated 4,4’- dichlorodiphenyl sulfone (SDCDPS). Figure 21 displays the Ueda *et al*. reaction procedure. This monomer, after recrystallization, was copolymerized with bisphenol A and the unmodified 4,4’-dichlorodiphenyl sulfone. The molar concentration of the sulfonated dihalide monomer employed was reported up to 30 molar percent of any copolymer. Even though Ueda *et al.*[164] mention reverse osmosis hollow fibers in the introduction of their paper it is not clear whether they ever proposed an actual application for their sulfonated copolymers. It is noteworthy that Robeson and Matzner earlier synthesized SDCDPS and employed it as an additive to improve the flame retardancy of polyesters[165].

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[164] Ueda, M.; Toyota, H.; Ochi, T.; Sugiyama, J.; Yonetake, K.; Masuko, T.; Teramoto, T., *J. Polym. Sci., Polym. Chem. Ed.*,1993, 31, 85.

[165] Robeson, L. M.; Matzner, M., *US Pat. # 4380598 Flame Retardant Polyarylate Compositions* to Union Carbide, April 19, 1983.

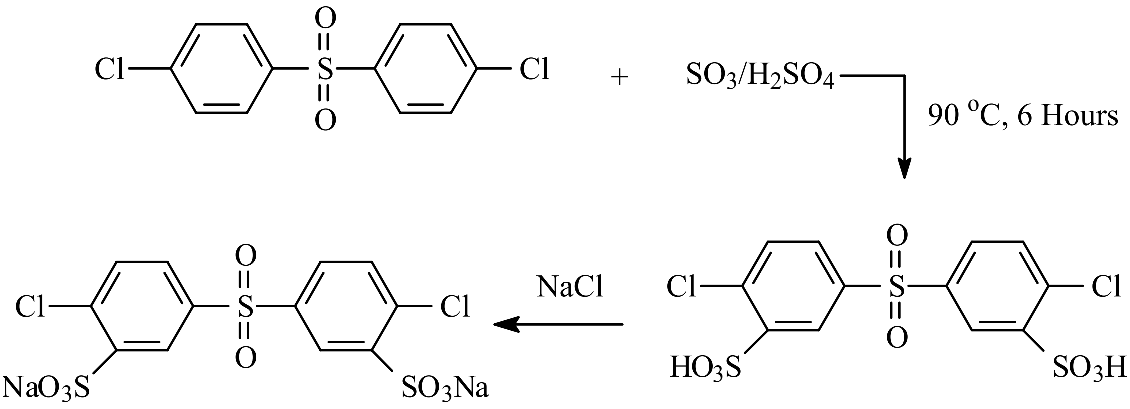

FIGURE 21. Synthesis of 3,3'-disulfonated 4,4'-dichlorodiphenyl sulfone[164]

However, Ueda's copolymerization research has been expanded and reinvigorated by McGrath *et al*[166] and colleagues[167] focusing on the development of proton exchange membrane candidates for fuel cells. Members of the McGrath research group at Virginia Tech have developed novel sulfonated poly(arylene ether sulfone) copolymers. First, the synthesis of sulfonated dichlorodiphenyl sulfone was modified, resulting in higher monomer yields[168]. Second, partially and wholly aromatic sulfonated poly (arylene sulfone) copolymers were synthesized using several different bisphenols[169,170]. Third, the copolymers employed higher molar concentrations (up to 100 mol percent) of SDCDPS. It was demonstrated that a higher reaction temperature (~190 °C) was needed to achieve very high molecular weight copolymers using the DCDPS/SDCDPS system. Nonetheless, further research using more reactive 4,4'-difluorodiphenyl sulfone (DFDPS)

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[166] McGrath, J.E.; Formato, R.; Kovar, R.; Harrison, W.; Mecham, J.B., *ACS Symposium* March 1999.

[167] Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mecham, J.B.; Zawodzinski, T.A.; McGrath, J.E., *Macromol. Symp* 2001, 175 (1), 387; (b) ibid, *J Membr. Sci.* **2002**. 197, 231.

[168] Wang, F.; Ji, Q.; Harrison, W.; Mecham, J.B.; Formato, R.; Dovar, R.; Osenar, P.; McGrath, J.E., *PolymerPreprints* 2000, 41 (1), 237.

[169] (a) Harrison, W.; Shobha, H.; Wang, F.; Mecham, J.; Glass, T.; O'Connor, K.; McGrath, J.E., *Polymer Preprints* 2000, 41 (1), 1239; (b) Harrison, W.; Wang, F.; Hickner, M.; Kim, Y.S.; McGrath, J.E., *Polymer Preprints*2002, 43(1).

[170] Harrison, W.; Wang, F.; Kim, Y-S.; Hickner, M.; McGrath, J.E., ACS *Polymer Preprints* 2002, 43 (1), 701; (b) ibid, *J. Polym* Sci., submitted 2002.

and the synthesized 3,3'-disulfonated 4,4'-difluorodiphenyl sulfone (SDFDPS) was shown to yield high molecular weight copolymers with a polymerization temperature of ~175 °C[171].

Interestingly, functionalized oligomers have been reported by Mecham *et al*[172,173,174] from this same Virginia Tech research group. Meta-amino phenol was used as a mono-functional endcapper with 4,4'-biphenol and SDCDPS. The synthesis of these wholly aromatic, 100% sulfonated oligomers is presented in Figure 22. The molecular weights of the amine-terminated sulfonated oligomers were controlled from 10,000 to 30,000 g/mol. Subsequent copolymerization of the functionalized oligomers with different diamines and dianhydrides was employed to synthesize novel multiblock polyimide-block-sulfonated poly(ether sulfone) copolymers[173]. This may have been the first reported synthesis of such membranes for any application. Similar to earlier described aliphatic triblock copolymer, like DAIS materials in Figure 4, these polymers were designed to have well defined morphology and influence on the phase separation of the hydrophilic [sulfonated poly(ether sulfone)] regions and the hydrophobic [polyimide] regions, (see Figure 23). These membranes displayed high thermal stabilities. Surprisingly, these membranes had very low water uptake (maximum 12% at any composition), and hence, measured proton conductivities (0.03 S/cm maximum measured value reported)[173] were believed to suffer. Further clarification of this phenomenon is required.

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[171] Wang, F.; Mecham, J.B.; Harrison, W.L.; McGrath, J.E., *PolymerPreprints* 2000, 41 (2), 1401.

[172] Mecham, J.B.; Shobha, H.K.; Wang, F.; Harrison, W.L.; McGrath, J.E., *ACS Polymer Preprints* 200, 41(2), 247.

[173] Mecham, J.B., *Ph.D. Thesis*, VPI & SU, December 2001.

[174] Mecham, J.B.; Wang, F.; Glass, T.E.; Xu, J.; Wilkes, G.L.; McGrath, J.E., *Polymeric Materials: Science and Engineering* 2001, 84, 105.

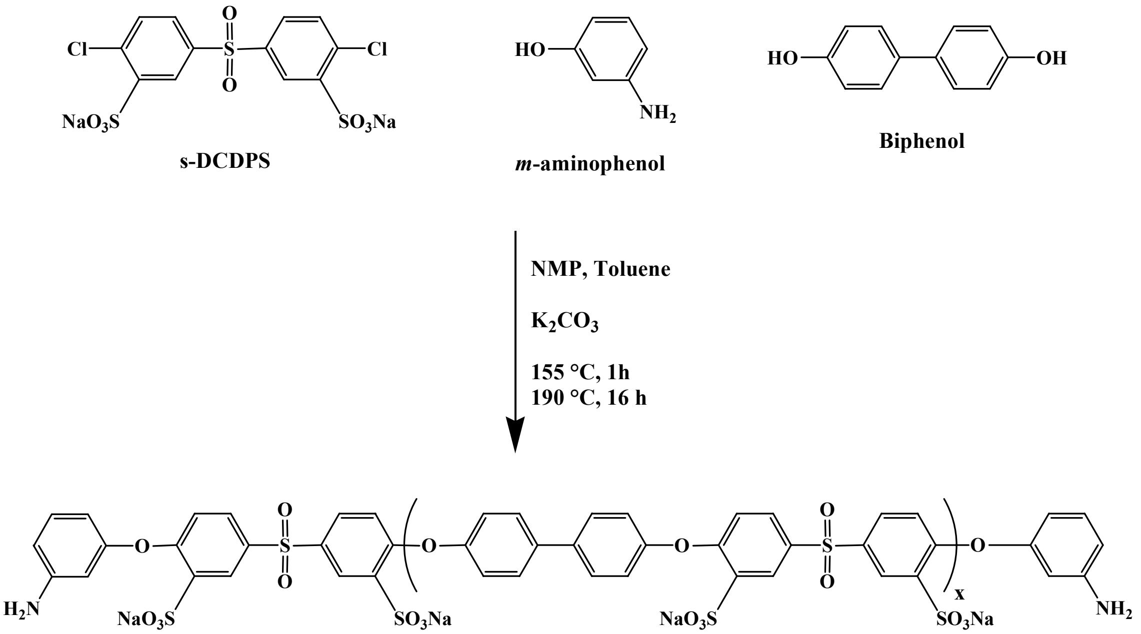
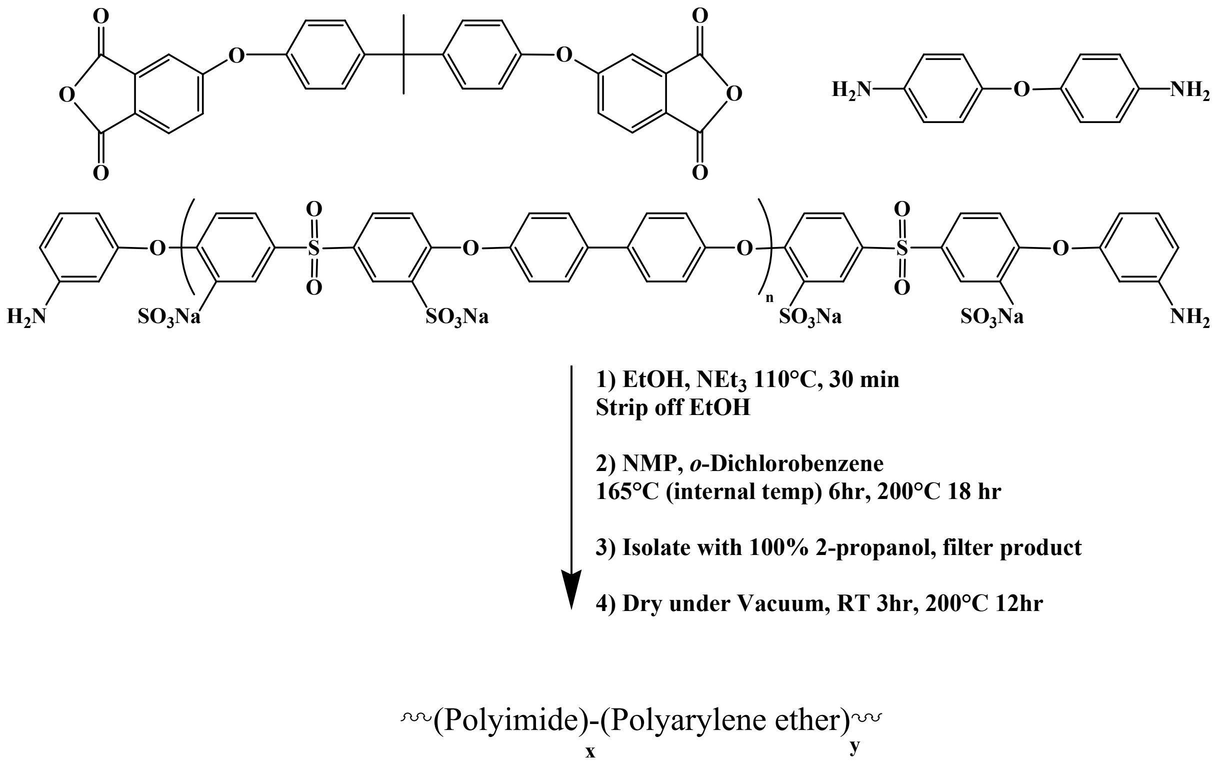


FIGURE 22. Synthesis of amine-terminated sulfonated poly (arylene ether sulfone) oligomers.[173]



1) EtOH, NEt_3 110°C, 30 min
Strip off EtOH

2) NMP, *o*-Dichlorobenzene
165°C (internal temp) 6hr, 200°C 18 hr

3) Isolate with 100% 2-propanol, filter product

4) Dry under Vacuum, RT 3hr, 200°C 12hr

$\sim(\text{Polyimide})_x\text{-}(\text{Polyarylene ether})_y\sim$

FIGURE 23. Synthesis of polyimide-block-sulfonated poly(arylene ether sulfone) [173]

(2) **Poly(arylene ether ketones)**

Similar direct copolymerization techniques for sulfonated poly(arylene ether sulfone) copolymers were demonstrated by other researchers to synthesize a series of sulfonated poly(arylene ether ketones)[175,176,177,178]. Using 3,3'-disulfonated 4,4'-difluorodiphenyl ketone (Figure24), Wang *et al*. produced high molecular weight copolymers with a bisphenol and the unsulfonated 4,4'-difluorodiphenyl ketone. Figure 25 gives a typical polymerization scheme[176].

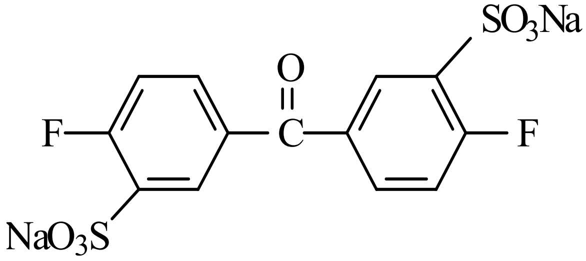


FIGURE 24. Structure of 3,3'-disulfonated 4,4'-difluorodiphenyl ketone[177].

Comparable to the sulfonated poly (arylene ether sulfone) copolymers, the sulfonated poly (arylene ether ketone) copolymers were synthesized in high yields using appropriate reaction conditions. The measured thermal stability was high for these polymers in air and nitrogen. However, no proton conductivity values were reported since only the salt form was examined and it was not the interest of the researchers. Interestingly, Gan *et al.* synthesized similar sulfonated poly(arylene ether ketones) via Friedel-Crafts acylation reactions of oligomers[178].

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[175] Wang,F.; Chen, T.; Xu, J., *Macromolecular Chem. and Phys*1998, 199, 1421.

[176] Wang,F.; Li, J.; Chen, T.; Xu, J., *Polymer*, 1999, 40, 795

[177] Wang, F.; Qi, Y.H..; Chen, T.L.; Xing, Y.; Lin, Y.H.; Xu,J.P., *Acta Crystallographica Section C-Crystal Structure Comm.*, 1999, 55, 871.

[178] Gan, D.; Lu, S.; Wang, Z., *Polym. Int.* 2001, 50, 812.

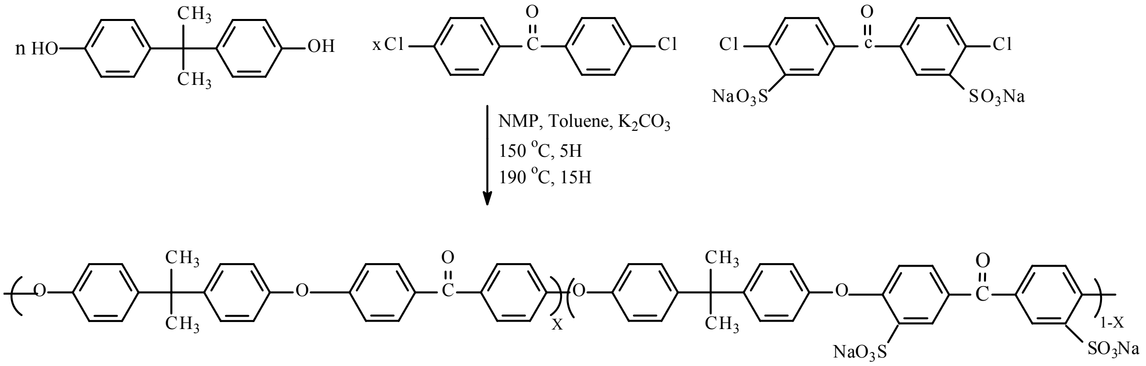

FIGURE 25. Sulfonated poly (arylene ether ketone) copolymers via direct polymerization.[176]

Hexafluoroisopropylidene bisphenol A (6F Bisphenol A) was recently used to polymerize more thermally stable amorphous sulfonated poly (ether ketone)s via direct copolymerization as competitive candidates for PEMFCs[179]. The representative repeat unit is given in Figure 23. High proton conductivities (up to 0.08 S/cm) were reported at 30 °C.

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[179] (a) Hopp, R.; Wang, F.; McGrath, F.E., 2001 Summer Undergraduate Research Program Reports, Virginia Tech, August 2001; (b) Wang, F. et al. *Electrochemical Society Proceedings*, Philadelphia, PA., 2 002 .

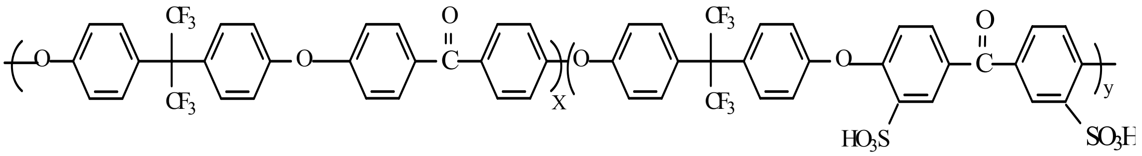

FIGURE 26. Structure of 6F-containing sulfonated poly (ether ketone) via direct copolymerization[179].

(3) **Poly(arylene ether phosphine oxide)**

Poly (arylene ether phosphine oxides) have been established as high performance polymers and effective flame retardant materials[180,181,182]. Recently, 4,4'-bis(fluorophenyl) phenyl phosphine oxide (BFPPO) was modified by fuming sulfuric acid and purified to yield a mono-substituted sulfonated monomer[183]. Sulfonated BFPPO (SBFPPO) was isolated from a mixture of starting material, and di- and tri-sulfonated compounds. The latter compounds were the minor products. Figure 27 displays the structure of SBFPPO.

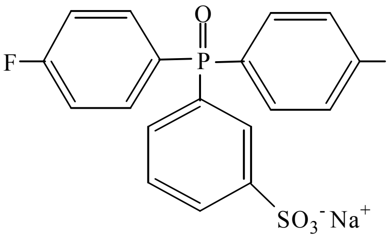

FIGURE 27. Structure of sulfonated 4,4'-bis(phenyl) phenyl phosphine oxide[183].

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[180] Hergenrother, P.M., *Angew Chem. Int. Ed. Engl.* 1990, 29, 34.

[181] Smith, C.D.; Grubbs, H.J.; Webster, H.F.; Gungor, A.; Wightman, J.P.; McGrath, J.E., *High Perfor. Polym.* 1991, 4, 211.

[182] Riley, D.J.; Gungor, A.; Srinivasan, S.A.; Sankarapandian, M.; Tchatchoua, C.; Muggli, M.W.; Ward, T.C.; McGrath, J.E., *Polym Eng. Sci.* 1997, 37(9), 1501.

[183] Shobha H.K., Smalley, G.R., Sankarapandian, M. and McGrath, J.E. *ACS Polymer Preprints* 2000, 41(1), 180

Sulfonated, wholly aromatic copolymers were synthesized using various molar ratios of SBFPPO and BFPPO, and 4,4'-biphenol. The polymers showed high thermal stabilities and glass transition temperatures (T_gs). The measured proton conductivities were lower than comparable directly polymerized poly(ether sulfone)s and poly(ether ketone)s. This may be due to the fact that there are two proton exchange (sulfonic acid) sites on the modified sulfone and ketone dihalide monomers verses only one on the sulfonated 4,4'-bis(phenyl) phenyl phosphine oxide monomer. Also, a high degree of hydrogen bonding between the pendent sulfonic acid and the phosphine oxide moiety was observed which was believed to decrease the conductivity at 30 ^{o}C.

1.3.3 **Poly(arylene sulfide sulfones) (PSS)**

Sulfonated poly(sulfide sulfones) or poly (thioethers sulfones) were achieved via direct polymerization of sulfonated difluorodiphenyl sulfone (SDFDPS) and a synthesized thiobisphenol[184]. 4,4'-Dimercaptodiphenylsulfone (DMDPS) was synthesized by the nucleophilic aromatic substitution reaction of sodium hydrosulfide with 4,4'-dichlorodiphenylsulfone[185]. This monomer synthesis is hampered by the impurities in the sodium hydrosulfide (available at a maximum purity of ~75%). The major impurity is water as the sodium hydrosulfide is a hydrate. Product yields as high as 60% were reported in the synthesis of the DMDPS monomer.

Sulfonated copolymers were produced using polymerization conditions similar to those used to produce the sulfonated poly(arylene ether) copolymers. The polymers showed high thermal stability, in both the acid and sodium-salt form. Figure 28 displays the repeat unit and the reported intrinsic viscosity after two sulfonated copolymers, in their free-acid forms, had been heated at various temperatures. Overall, no significant change in intrinsic viscosities was noted even after the sulfonated copolymers had been exposed to temperatures up to 220 ^{o}C.

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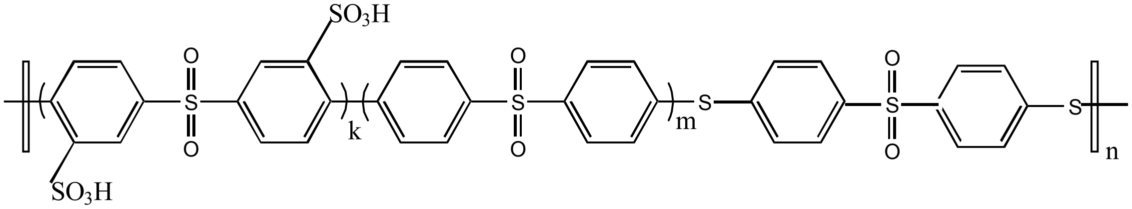
[184] Wang, F.; Mecham, J. B.; Harrison, W.; McGrath, J. E. *Polymer Preprints* **2000**, *40*, 180; Wiles, K., et al, Polymer Preprints, **2002**, 42.

[185] Liu, Y. *Ph.D. Thesis*, VPI & SU, 1999.



k/m	Intrinsic Viscosity (dl/g) $[\eta]^{NMP}_{25\,^{o}C}$				
	23°C	100°C	140°C	180°C	220°C
4/6	4.3	4.3	4.0	3.7	3.6
6/4	3.0	3.0	3.1	3.0	2.9

FIGURE 28. Influence of aging temperature exposure for 30 minutes on intrinsic viscosity of sulfonated PSS[184].

1.4 Miscellaneous Blends and Nanocomposites

Recently, several researchers have investigated additives for sulfonated copolymers to improve proton conductivity, as well as membrane properties. This section will highlight some of these developing proton exchange membrane composite candidates.

1.4.1 Polymer Blends

Physical polymer blending has been a long-standing, yet simple tool to modify the properties of polymeric materials[186,187]. Several book reviews describe various aspects of the preparation of polymer blends[188,189]. However, it is well known that many polymers do not blend well. Micro- and macroscopic phase separation has been observed in many polymer systems in the absence of polymer-polymer interaction or adhesion[190]. Nevertheless, physical blending can alter certain properties. In the field of proton exchange membranes, polymer blending, in general, has been investigated to improve or modify properties such as mechanical strength, water swelling behavior, methanol permeability, and proton conductivity.

Several research groups have investigated sulfonated poly(arylene ether) blends with different engineering plastics in many variations; sulfonated poly(ether sulfones) with poly(ether sulfones), sulfonated poly(ether sulfones) with poly(ether ketones)[191], sulfonated poly(ether ketones) with poly(ether sulfones),[192,193] and sulfonated poly

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[186] Paul, D. R.; Newman, S., Eds. *Polymer Blends*; Academic Press: New York, 1978.

[187] Noshay, A.; McGrath, J. E. *Block Copolymers: Overview and Critical Survey*; Academic Press: New York, 1977.

[188] Paul, D.R.; Bucknall, C., *Polymer Blends Vol.I. Formulation, Formulation, V. II, Performance* John Wiley & Sons: New York, 2000.

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[193] Bowen, W.R.; Doneva, T.A.; Yin, H.B., *J Membr. Sci.* 2001, 181, 253.

(arylene ethers) with *basic* polymers like poly(benzimidazoles)[194,195,196,197,198] is just a partial list of reported blends for PEMFC applications. The logic for these experiments lay in the reasonable belief that the unmodified polymer acts as a structural support and decreases the swelling of the blended sulfonated polymer, which primarily functions as the ion exchange material[199].

An important commercially available composite proton exchange membrane system was developed by W.L. Gore and Associates[33]. Marketed under the trade name of Gore-Select, sulfonated perfluorinated polymers are supported on woven polytetrafluorethylene (PTFE or Teflon). Similar supported membranes have been applied in other industries[200,201].

Several researchers[202,203,204,205] have investigated the *micro-reinforced* Gore-Select product. The films are characterized as translucent with good thermal, chemical and dimensional stability. However, preliminary results[202] showed the same water uptake and lower ionic conductivities than Nafion of the same equivalent weights. One advantage of the reinforced membranes is the fact that the thickness of the proton exchange membrane can be decreased and still possess sufficient mechanical strength[33] for fuel cell applications. Indeed, 12μm Gore Select PEM films with higher equivalent weight (900) were evaluated and demonstrated good proton conductances, but the reported values were still lower than the control material[202].

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[194] Jorissen, L.; Gogel, V.; Kerres, J.; Garche, J., *J. Power Sources* 2001, 2578, 1.

[195] Kerres, J.; Ullrich, A., Meier, F.; Haring, T., *Solid State Iionics* 1999, 125, 243.

[196] Kerres, J.; Ullrich, A., Meier, F.; Haring, T.; Baldauf, M.; Gebhardt, U.; Preidel, W., *J. New Mater. Eleclrochem. Soc.* 2000, 3, 229.

[197] Mikhailenko, S.D.; Zaidi, S.M.J.; Kaliaguine, S., *J. Polym. Sci.: Part B, Polym. Phys.*, 2000, 38(1), 1386.

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[199] Werbrugge, M.W.; Hill, R.F.; Schneider, E.W., *J. Am. Inst. Chem. Eng.* 1992, 38, 93.

[200] Taylor, E.J.; Paxienza, C.; Waterhouse, R.; Wilernski, G., in *The Electrochem. Soc. Ext. Abst.* , Oct. 1986, Vol. 86-2(590), p.883.

[201] Pletcher, D.; Walsh, F.C.,, Eds., in *Industrial Electrochemistry*, Chapman and Hall, New York, 1990, p.179.

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[205] Velev, O.; Tran, D., Srinivassan, S., Appleby, A.J.; Dhar, H.P., in *The Electrochem. Soc. Ext. Abst.* May 1996, Abst No. 29.

1.4.2 **Additives and Dopants**

As discussed in an earlier section, operation of proton exchange membrane fuel cells at temperatures above 100 ^{o}C is advantageous in several ways, including the generally expected improved fuel cell efficiency. However, perfluorinated polymers perform poorly at temperatures above 80 ^{o}C, due mainly to anticipated dehydration. Furthermore, the boiling of water at temperatures above 100 ^{o}C, except under pressure, compounds difficulties in the development of functioning *high temperature* PEMFC. Much research, within the last decade or so, has been undertaken to find components and/or systems that allow higher temperature operation. The field of nanocomposite proton exchange membranes has developed out of these efforts.

Heteropolyacids (HPAs) are highly conductive in the crystalline form[206]. Accordingly, HPAs have been blended into various polymers in the search for new PEMs[207,206,208,209,210]. Several heteropolyacids, including phosphotungstic acid, silicotungstic acid, zirconium phosphate, phosphomolybdic acid, etc., have been investigated. Higher proton conductivities were reported for these composite membranes. Kim *et al*[207] reported proton conductivity values of ~0.15 S/cm at 140 ^{o}C at 100% relative humidity, under pressure for developmental directly sulfonated poly(ether sulfone) copolymers containing 30 weight percent of very well dispersed phosphotungstic acid. The HPA is suggested to provide an alternative mechanism for proton conductivity in low water environments. Unpublished data for an unsulfonated, partially fluorinated poly(arylene ether nitrile) containing 50 weight percent phosphotungstic acid demonstrated a proton conductivity of 0.05 S/cm at room temperature,[211] which is expected to increase at elevated temperatures. The heteropolyacid was proposed to be well dispersed via an association with the polar nitrile group of the host polymer matrix

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[206] Zaidi, S.M.J.; Mikhailenko, S.D.; Robertson, G.P.; Guiver, M.D.; Kaliaguine, S.J., *J. Membr. Sci.* 2000, 173, 17.

[207] Kim, Y-.S.; Wang, F.; Hickner, M.; Zawodzinski, T.A.; McGrath, J.E., *ACS Polym Mat: Sci. Eng. Preprints* 2001, 85; *ibid* J. Membr. Sci., accepted Nov 2002.

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[210] Costamagna, P.; Yang, C.; Bocarsly, A.B.; Srinivasan, S., *Electrochim. Acta* 2002, 47, 1023.

[211] Harrison, W.; Sumner, M.; Kim, Y.-S.; Riffle, J.S; McGrath, J.E., Group Meeting Discussion, March 2002 .

since the films were transparent. This association was investigated by FTIR, which demonstrated shifts (in wave numbers) of the nitrile group and tungsten-oxygen bond of the HPA. Ductile composite membranes were observed, even with the high weight fraction of phosphotungstic acid, but further investigations, such as the long-term stability of these composites, are needed.

Composite membranes based on zirconium hydrogen phosphonates[210,212,213], zeolites[214], silica[215,216] and other components[217,218] have been investigated with improvements reported in many properties relative to their matrix materials. As one example of improved membrane behavior, Nafion filled with cesium ions displayed reduced methanol crossover[219]. Silica-Nafion composites allowed direct methanol fuel cell operation at 145 °C due to higher initial water uptake[215]. Recently, boron phosphate was reported to have increased the proton conductivity of post-sulfonated PEEK[220].

Liquid phosphoric acid-doped membranes have also been investigated for non-aqueous PEMFC systems[221,222,223,224,225]. Doped polybenzimidazoles have received the most attention. Doping levels of up to six molecules of H_3PO_4 per repeat unit were achieved[222], and depending on doping technique, film thickness, etc., proton conductivities of 0.01-0.04 S/cm were reported. Some basic concerns, such as acid leaching, will need to be addressed before there is widespread application of these systems is realized. It is also notable that Ballard Advanced Materials' first generation

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[212] Hamlen, R.P., *US Patent 5,849,428* , 1998.

[213] Yang, C.; Costamagna, P.; Srinivasan, S.; Benziger, J.; Bocarsly, A.B., *J. Power Sources* 2001, 103(1), 1.

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[216] Watanabe, M.; Uchida, H.; Seki, Y.; Emori, M.; Stonehart, P., *J. Electrochem. Soc.* 1996, 143, 3847.

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[225] Wainright, J.S.; Wang, J.T.; Weng, D.; Savinell, R.S.; Litt, M., *J. Electrochem. Soc.* 1995, 141, L121.

membranes (BAM1G) were based on somewhat related sulfonated polybenzimidazoles, which only lasted about 350 hours before failure[146].

A number of papers have focused on the doping of polyethylene oxides (PEO). For example, a PEO + NH_4ClO_4 system gave a reported conductivity up to 5 x 10^{-5} S/cm[226]. This same research group reported a similar system using PEO and NH_4I that gave a conductivity of about the same value[227]. The doping of an ethylene oxide-propylene oxide copolymer with an alkali metal salt has been described[228]. This system had a room temperature conductivity of 10^{-5}, but improved conductivity at 100 ^{o}C (10^{-3}). Compared to Nafion, these systems are too resistive (low proton conduction) to be useful for power generation.

As seen by this survey, inexhaustive amounts of literature available are covering different aspects of fuel cell development, other than membrane performance.

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[227] Maurya, K.K.; Srivastava, N.; Hashmi, S.A.; Chandra, S., *J Phys. D: Appl. Phys.,* 1992, 27, 6357.

[228] Florjanczyk, A.Z.; Kraweic, W.; Wieczorek, W.; Siekierski, M.. *J Polym. Sci. Polym. Phys. Ed.* 1995, 33, 629.

II. LITERATURE REVIEW: POLY (ARYLENE ETHER) SYNTHESIS

Since the main focus of this dissertation is on the synthesis of poly(arylene ether sulfone) copolymers, a discussion of the synthetic routes to poly(arylene ethers) will be presented here.

1.5 **The Ullman Reaction**

Poly (arylene ethers) have been synthesized from unactivated halides using the Ullman reaction[229,230,231232,233]. Ullman-type reactions have been well studied for small molecules. They involve the reaction of a phenol, in the presence of a copper catalyst, with an aromatic halide. This synthetic route to aromatic polyethers has been worked with non-activated aromatic halides; this reality allows for utility of monomers to produce poly(arylene ethers) not possible by usual activated nucleophilic aromatic substitution mechanisms[234]. The general synthetic approach is given in Figure 29. Dibromo-monomers were most reactive via this approach since breaking the aryl halide bond is the rate determining step. In fact, the halide reactivity was I > Br > Cl >> F.

Early research produced only low molecular weight products. Stamatoff[235,236] was possibly the first to report high molecular weight polymers using a modified Ullman procedure. He successfully condensed p-bromo-sodium phenolate using cuprous chloride and an organic base as cocatalyst. To yield high molecular weight polymers it was demonstrated that a dry, oxygen- free polymerization system must be maintained along with high temperatures, using nitrobenzene, benzophenone, etc. as solvents. Non-linear

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[229] Farnham, A.G.; Johnson, R.N., *US Patent 3,332, 909* , 1967.

[230] Jurek, M.J., McGrath, J.E., *ACS Polymer Preprints* 1987, 28(1), 180.

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[233] Jennings, B.E.; Jones, M.E.B.; Rose, J.B., *J. Polym. Sci.: Part C* 1967, 16, 715,

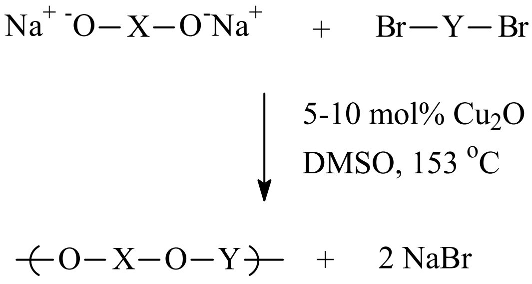
[234] S. Wang and J. E. McGrath, " Polyarylene Ethers": A Review, in M. Rogers and T.E. Long, eds., Step Polymerization, Wiley, 2002

[235] (a) Stamatoff, G.S., *French Patent 1,301,174* , 1962, (b) Stamatoff, G.S., *US Patent 3,228,910* , 1966.

[236] Stamatoff, G.S., *Chem Abstracts 66*, 56009q.

and/or crosslinked polymers were produced when even trace amounts of oxygen were present in the system. Oxygen promoted a free radical side reaction leading to the branched polymers[237].

Benzophenone solvent with a cuprous chloride-pyridine complex as the catalyst is a better polymerization system[238]. The resulting polymers demonstrated thermal stability ad low dielectric constants of interest to microelectronics. Unfortunately, the Ullman reaction approach has been characterized by poor reproducibility, the need for specialty brominated monomers, and the difficulty of removing copper salts.[234]



where X and Y = aromatic groups

FIGURE 29. Ullman synthesis of poly (arylene ethers)[229].

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[237] Pankova, E.S.; Martsenitsena, S.V.; Derlin, A.A., *Vysokomol Soyed A*, 1975, 17(7), 1415.

[238] Burgoyne, W.; Robeson, L. M. US Patent *5,658,994*, 1997.

1.6 Nickel Coupling Reaction

Perhaps, the newest approach for preparing poly(arylene ethers) is via nickel coupling reactions. Ni^0 is used in the formation of aromatic carbon-carbon bonds[239]. Also, nickel coupling reactions can utilize more commonly available chlorinated monomers, in contrast to brominated compounds needed for Ullman-type reactions. Aprotic solvents are used as the reaction media at the relatively low polymerization temperatures of 60 to 80 ^{o}C[240,241]. Interestingly, activated dihalide as well as nonactivated dihalide monomers may be polymerized. Ghassemi *et al.*[242] reported the synthesis of aromatic phosphine oxide containing polymers via nickel coupling reactions.

1.7 Friedel-Crafts Electrophilic Substitution

A third synthetic route to poly(arylene ethers), in particular poly(arylene ether sulfones), is via Friedel-Crafts electrophilic substitution[243,244]. The sulfone linkages are formed by the reaction of aryl sulfonyl chlorides with aromatic compounds. Using this mechanism, poly(arylene ether sulfones) can be synthesized in solvents such as dimethyl sulfone, chlorinated biphenyl and nitrobenzene, or in the melt. The primary byproduct for these polymerizations is HCl.

The sulfonylation mechanism has been reviewed[112,245] and involves two steps. The first step is the formation of the sulfonylium cation $ArSO_2^+$ resulting from the action of the Lewis-acid catalyst on the sulfonyl halide (Figure 30). The second step is the electrophilic cation attack on the aromatic carbon to generate an intermediate complex followed by the elimination of a proton yielding the new sulfone linkage. It is important that the aromatic ring being attacked not contain electron withdrawing groups, such as -

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[239] Colon, I.; Kwiatokowski, G.T., *J. Polym. Sci., Polym. Chem.* 1990, 28, 367.

[240] Colon, I.; Maresca, L. M.; Kwiatkowski, G. T. *U S Patent 4, 263 466* , 1991

[241] Havelka, P. A.; Shearea, V. V. *Macromolecules* 1999, *32*, 6418.

[242] Ghassemi, H.; McGrath, J.E., *Polymer* 1997, 38, 3139; (b) idid, *Polymer Preprints* **2003**, 43(1).

[243] Ivin, K.J.; Rose, J.B., *Advances in Macromolecular Chemistry*, W.M. Pasika, Ed., Academic Press, London, Vol. 1, 336, 1968.

[244] J.B. Rose, *Polymer* 1974, 15, 456.

SO_2- or –CO-, for facile reaction with the electron-deficient sulfonylium cation. Several catalysts, such as $AlCl_3$, $AlBr_3$, $FeCl_3$, $SbCl_5$, BF_3, etc., have been utilized in Friedel-Crafts reactions[114,112,251,246].

High catalyst concentrations were employed in the early electrophilic aromatic substitution syntheses of polysulfones. It was realized that if high temperatures (120 to 250 °C) were used, especially in melt reactions, lower concentrations (0.1 to 4 wt% $FeCl_3$) of Lewis acids could be used[247,248]. However, variations in polymer structure have been noted due to sulfonylation on various positions on the arylene-ring[249]. Furthermore, bulk polymerizations via Friedel-Craft mechanisms commonly resulted in branched or crosslinked material, as evident by polymer insolubility.

Polymers made via Friedel-Craft sulfonylation mechanism were made in solution at temperatures of ~120 °C[250]. The products were, in general, soluble high molecular weight poly(arylene sulfones). Not surprisingly, electron-donating groups enhance the sulfonylation process. Moreover, the polymerization of relatively deactivated monomers, like benzophenone (Figure 31), was slow and some branching was suspected[252].

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[245] Suter, C.M.; in *The Organic Chemistry of Sulfur*, New York, 1944, p.670.

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[250] Cudby, M. E. A.; Feasey, R. G.; Jennings, B. E.; Jones, M. E. B.; Rose, J. B. *Polymer* 1965, *6*, 589.

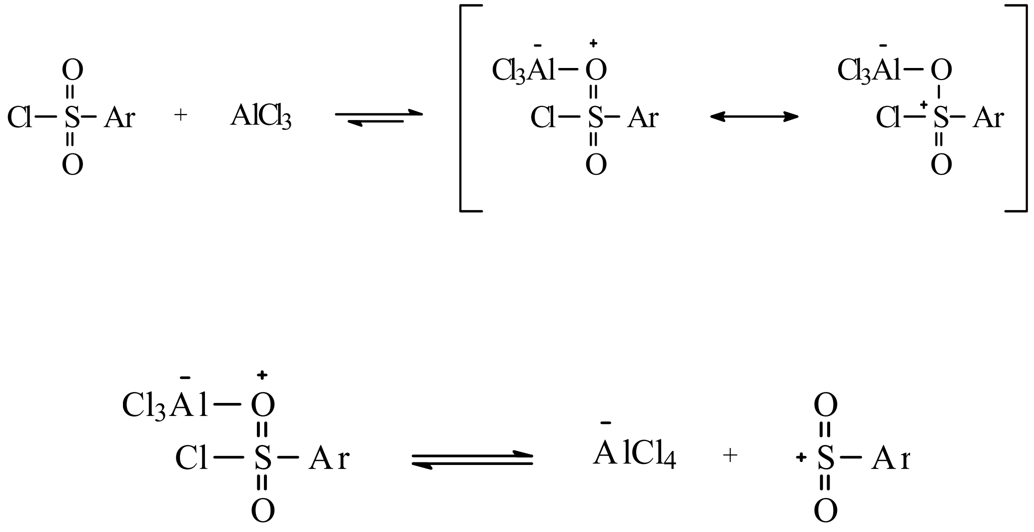

FIGURE 30. Generation of sulfonylium cation[251].

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[251] Olah, G.A., in *Friedel-Crafts Chemistry*, Wiley, New York, 1973, p. 488.

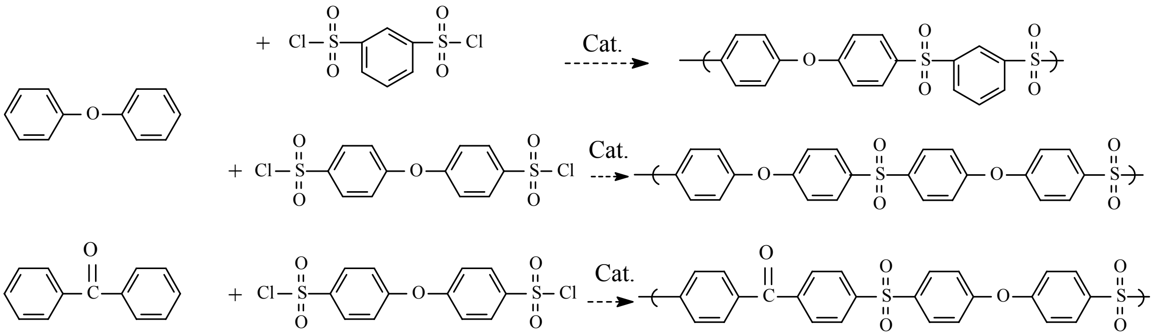

FIGURE 31. Synthesis of poly (arylene ether sulfones) via Electrophilic Substitution.[252]

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[252] Jennings, B.E.; Jones, M.E.B.; Rose, J.B., *J. Polym. Sci.: Part C* 1967, 16, 715.

1.8 Nucleophilic Aromatic Substitution

Poly (arylene ethers) are now most commonly synthesized via nucleophilic aromatic substitution mechanisms[101,253,254,255,256]. Nucleophilic aromatic substitution (S_NAr) reactions, in the synthesis of polymers, have been the focus of some good reviews[99,234, 257,258]. Many important polymers are synthesized via the S_NAr mechanism[259].

The important nucleophilic aromatic substitution mechanism utilized activated halide monomers. The need for activating groups has been well established. The nucleophilic aromatic substitutions on simple aromatic halides require high temperatures because they are not very reactive[260,261]. For example, the nucleophilic aromatic substitution of chlorobenzene with a hydroxide ion is given in Figure 32.

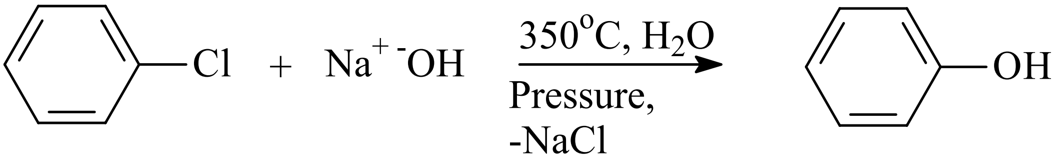

FIGURE 32. Nucleophilic aromatic substitution of chlorobenzene[262].

The low reactivity of chlorobenzene can be explained by resonance structures. Four different resonance structures can be drawn, including three of which that have a double bond between the positive chlorine and the negative ring. The implied double bond

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[253] Hedrick, J. C.; Labadie, J. W., Macromolecules 1990, 23, 1561.

[254] Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci., Part A-1* 1967, *5*, 2375-2398.

[255] Rose, J. B. In *Recent Advances in Mechanistic and Synthetic Aspects of Polymerization*; D. Riedel Publishing: Boston, 1987.

[256] (a) Hedrick, J. C., Labadie, J. L., Eds.; American Chemical Society: Washington, D.C., 1996; Vol. 624, p 225.; (b) Hedrick, J. L.; Mohanty, D. K.; Johnson, B. C.; Viswanathan, R.; Hinkley, J. A.; McGrath, J. E. *J. Poly Sci, Part A* 1986, *23*, 287-300.

[257] Johnson, R.N., in *Encyclopedia of Polymer Science and Engineering,* N.M. Bikales, Ed., John Wiley & Sons: New York, 1969.

[258] Stock, L.M., *Aromatic Substitution Reactions*, K.L. Rinehart, Jr., Ed., Prentice-Hall Inc.: Englewood Cliffs, NJ, 1968.

[259] (a) Roovers, F.; Ethier, R.; Toporowski, P. M. *High Perf. Poly.* 1990, *2*, 151; (b) Roovers, F.; Toporowski, P. M.; Ethier, R. *High Perf. Poly.* 1990, *2*, 165.

[260] Bunnett, J.F., Zahler, R.F., *Chem. Rev.* 1951, 49, 273.

[261] Schulze, S.R.; Baron, A.L., *Adv. Chem. Series* 1969, 91, 589.

[262] Morrison, R.T.; Boyd, R.N., *Organic Chemistry*, 3rd Ed., Allyn and Bacon, Inc.; Boston, 1973, p. 827.

character of the C-Cl bond would justify its stability as well as a calculated shorter bond length than those in alkyl halides[262].

When an activating-electron withdrawing group is ortho- or, preferably, para-, due to steric considerations, to the halogen milder reaction conditions can be used (Figure 33). Indeed, there is a kind of additive effect with the number of activating groups.

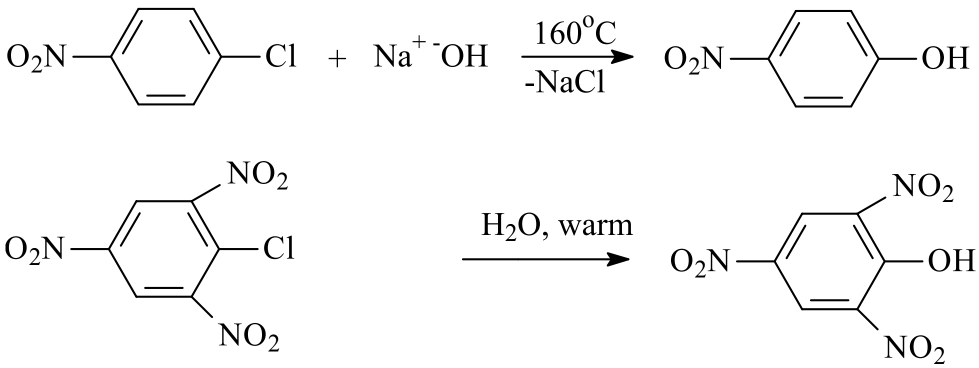

Figure 33. Influence of activating group(s) on nucleophilic aromatic substition[262].

There is an ordering of increasing activating power for electron withdrawing groups on aromatic nucleophilic substitution. The order of important electron withdrawing groups is[263]: $NO > NO_2 > SO_2Me > CF_3 > CN > CHO > COR > COOH > F > Cl > Br > I > H > Me > CMe_3 > OMe > NMe_2 > OH > NH_2$. Other factors are important to the overall rate of the S_NAr reactions. The nucleophile, the leaving group, and the solvent all influence the reaction rate.

The importance of the activating group lies in its ability to stabilize the intermediate *Meisenheimer complex*[264]. As shown in Figure 31, the ability of the activating group (Y) to accept the negative charge for the attacked rings serves to stabilize this intermediate complex. The Meisenheimer complex has been characterized

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[263] (a) Berliner, E.; Monack,LC., *J. Amer. Chem. Soc.* 1952, 74, 1574; (b) Kornblum, N.; Cheng, L.; Kerber, R.C.; Kestner, M.M.; Newton, B.N.; Pinnick, H.W.; Smith, R.G.; Wade, P.A., *J. Org. Chem.Soc.* 1976, 41, 1560.

[264] Meisenheimer, J. *Liebigs Ann. Chem.* 1902, *323*, 205.

by low temperature NMR[265], and identified by crystallography[266]. For nucleophilic aromatic substitution, the rate determinating step is the attack of the nucleophile on the carbon-halide bond and not the expulsion of the halide.

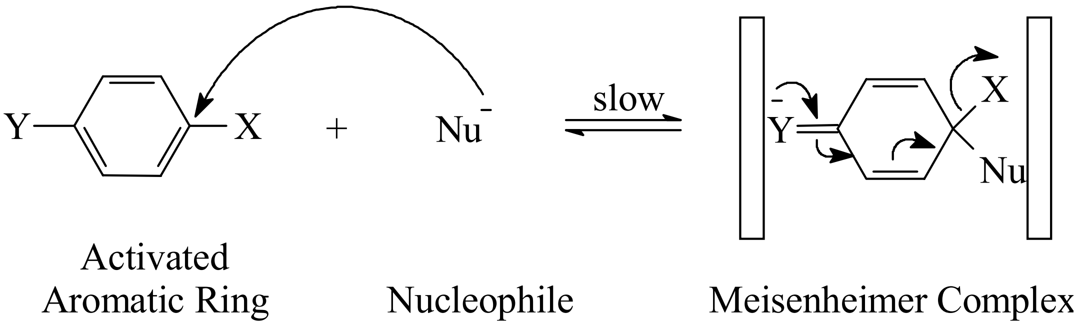

FIGURE 34. The rate determining step of nucleophilic aromatic substitution reaction.

The nucleophilicity of the attaching nucleophile is also important. The nucleophilicity has been approximately arranged in following order:

$ArS^- > RO^- > R_2NH^- > ArO^- > OH^- > ArNH_2 > NH_3 > I^- > Br^- > Cl^- > H_2O > ROH$[267].

It is recognized that there are a number of factors that influence the overall reaction. Besides the nucleophile and the activating group, the reaction conditions and the nature of the solvent are also important. Moreover, the orientation of the activating group to the leaving group is significant. Activating groups in the ortho- and para-positions of the leaving groups increase the nucleophilic substitution due to their ability to stabilize the intermediate by conjugation, as seen in Figure 34.

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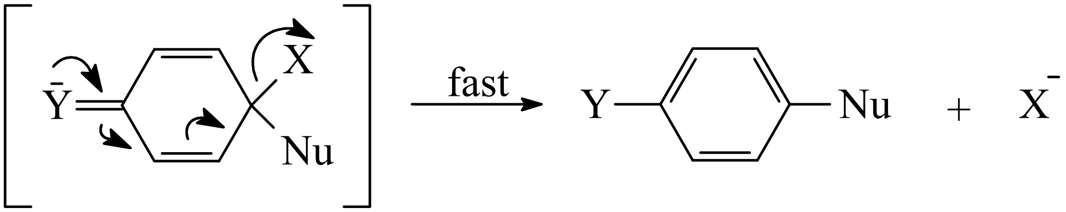
[265] Fyfe, C. A.; Koll, A.; Damji, W. H.; Malkiewich, C. D.; Forte, P. A. *Can. J. Chem.* **1977**, *55*, 1468.

[266] Messmer, G. G.; Palenik, G. J. *Chem. Comm.* **1969**, 470.

[267] Bunnett, J.F.; Zahler, R.E., *Chem Rev* 1951, 49, 273.

The second step in the nucleophilic aromatic substitution is the decomposition of the Meisenheimer intermediate by the release of the leaving group. This expulsion is not



the rate determining step. The order of:

F- > NO2- > -SOPh > Cl- > Br- ~ I- > -OAr > -OR > -SR

has been proposed for the leaving group in the nucleophilic aromatic substitution reaction[268].

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[268] (a) Miller, J.A., in *Aromatic Nucleophilic Substituion,* Elsevier, London, 1961, p. 61, and (b) Beck, J.R., *Tetrahedron* 1978, 34, 2057.

Two related yet different approaches to poly(arylene ether sulfones) have developed using nucleophilic aromatic substitution. They can be generally separated into categories based on the type of base employed for the synthesis of the polymer. While the overall mechanism is still similar there are some differences in processes of the strong base or weak based approaches.

1.4.1 **Strong Base Approach**

In the late 1960s, R. N. Johnson et al. published and patented probably the first successful syntheses of high molecular weight poly(arylene ethers) by nucleophilic aromatic substitution via step-growth or polycondensation reactions as depicted in Figure 35[269]. Prior to this pioneering research, poly (arylene ether sulfones) were primarily synthesized via Friedel-Craft mechanisms.

Johnson et al. investigated various aspects for the synthesis of the poly (arylene ethers). Different bisphenolate salts were investigated; bisphenates derived from potassium hydroxide reacted faster than those from sodium hydroxide. Insolubility in dimethyl sulfoxide (DMSO) prevented the lithium, calcium, and magnesium salts of bisphenol A from being polymerized. Also, bisphenols with electron withdrawing groups, such as the sulfone in bisphenol S, were more acidic and, therefore, less nucleophilic due to stabilization. A higher boiling solvent like sulfolane could be used when more stringent reaction conditions were required. But, in general, it was found that high molecular weight polymer could be recovered usually within five hours.

Strict stoichiometric control of the amount of sodium hydroxide is one requirement that has been noted as a disadvantage of the strong base method. Excess base will allow a reaction between the activated halide and hydroxide ions. Such an undesirable reaction would change the stoichiometry of the overall reaction (i.e., bisphenolate to halide), and will also generate a less reactive bisphenol and probably decrease the resulting degree of polymerization. Also, the excess base can react with

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[269] Johnson, R.N.; Farnham, A.G.; Clendinning, R.A.; Hale, W.F., Merriam, C.N., *J. Polym. Sci.: Part A-1*, 1967, 5, 2375.

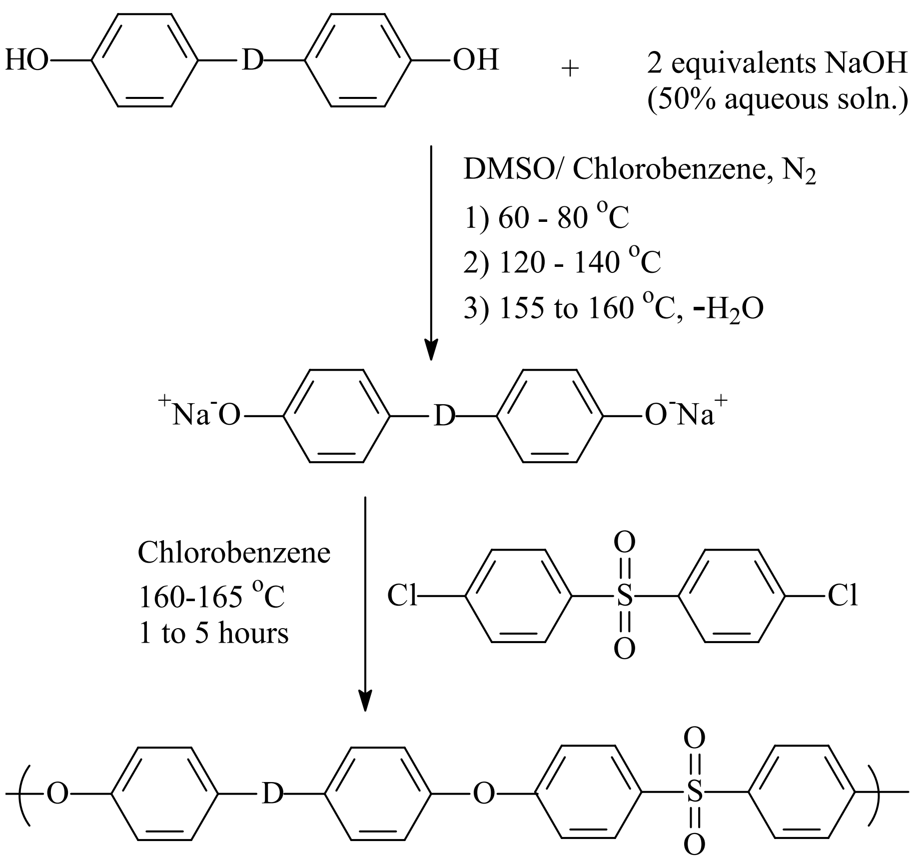

FIGURE 35. Strong base-nucleophilic aromatic substitution synthesis of poly (arylene ethers)[269].

and cleave the activated aromatic ether linkages of the polymer causing a reduction in the final molecular weight of the polymer.

The presence of an insufficient amount of base is also detrimental to the polymerization. Besides offsetting the one-to-one stoichiometry of reactive groups, the free bisphenols can hydrogen bond with other phenolates in the reaction mixture[270]. A depiction is given in Figure 35a. This interaction decreases the nucleophilicity of the phenolate.

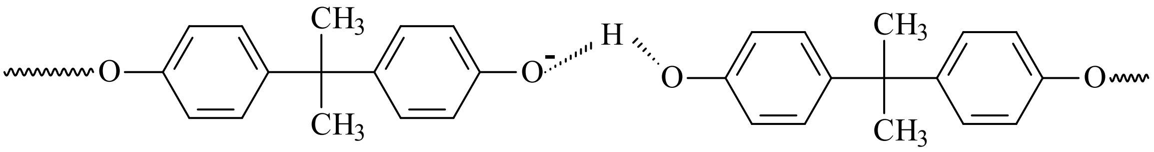

FIGURE 35A. Hydrogen bonding of a phenol and a phenolate[270].

The importance of the exclusion of moisture was also noted by Johnson et al., since water could hydrolyze the activated dihalide monomer, causing similar stoichiometric problems as excess base.

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[270] Storozhuk, I.P.; Bakhmotov, V.I.; Mikitaev, A.K.; Waletskii, P.M.; Yu, I.; Musaev, V.; Korshak, V.; Fedin, E.I, *Vysokomol. Soed., A* 1977, 19(8), 800.

1.4.2 **Weak Base Approach**

A Canadian patent to Clendenin *et al.*[271] disclosed the synthesis of poly(arylene ether sulfones) using potassium carbonate (K_2CO_3) and potassium bicarbonate ($KHCO_3$). Similar systems were published in later patents[272,273]. McGrath and colleagues at Virginia Tech have generated systematic studies utilizing the weak base, and dimethyl acetamide (DMAc) as the reaction solvent en route to fundamental understanding of the system, as well as some novel poly(ether sulfones)[274,275,276,277].

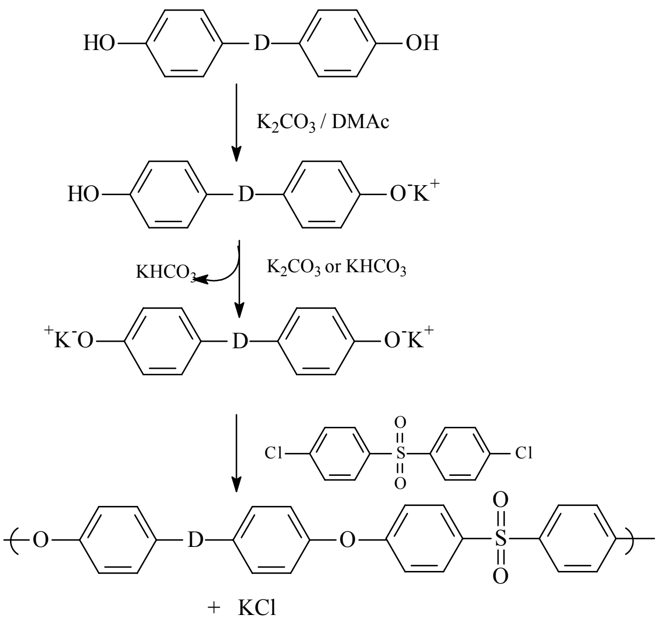

FIGURE 36. Bisphenate route to polysulfones via weak base process.

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[271] Clendinning, R.A.; Farnham, A.G.; Zutty, N. L.; Priest, D.C., *Canada Patent 847,963* , 1970.

[272] Berd, B.; Claus, C.; *German Patent. 2,749,645* , 1975.

[273] (a) I. C. I. U.S.; *German Patent 2,635,101*; 1977; (b) I. C. I. Ltd.; *Japan Patent 7,812,991* , 1978.

[274] Viswanathan, R.; Johnson, B.C.; McGrath, J.E., *Polymer* 1984, 12 (25), 1827.; (b) Viswanathan, R. et. al., *Polymer Prep*rints, 1979; (c) R. Viswanathan, *Ph.D. Thesis*, VPI&SU, 1981.

[275] (a) Mohanty, D.K., Ph.D. Thesis, VPI&SU, June 1983; and (b) B.C.Johnson, Ph.D. Thesis, VPI&SU, June 1984.

[276] Hedrick, J.L.; Mohanty, D.K.; Johnson, B.C.; Viswanathan, R.; Hinkley, J.A.; McGrath, J.E., *J. Polym. Sci., Polym. Chem.* 1986, 23, 287.

[277] Hedrick, J.L.; Dumais, J.J.; Jelinski, L.W.; Patsiga, R.A.; McGrath, J.E., *J. Polym. Sci., Polym. Chem.* 1987, 25, 2289.

Viswanathan *et al.*[274] proposed mechanisms for the synthesis of poly(arylene ether sulfone) via the potassium carbonate process. There are two possible mechanisms. Figure 36 displays the bisphenate route. Like the strong base route, the dimetal

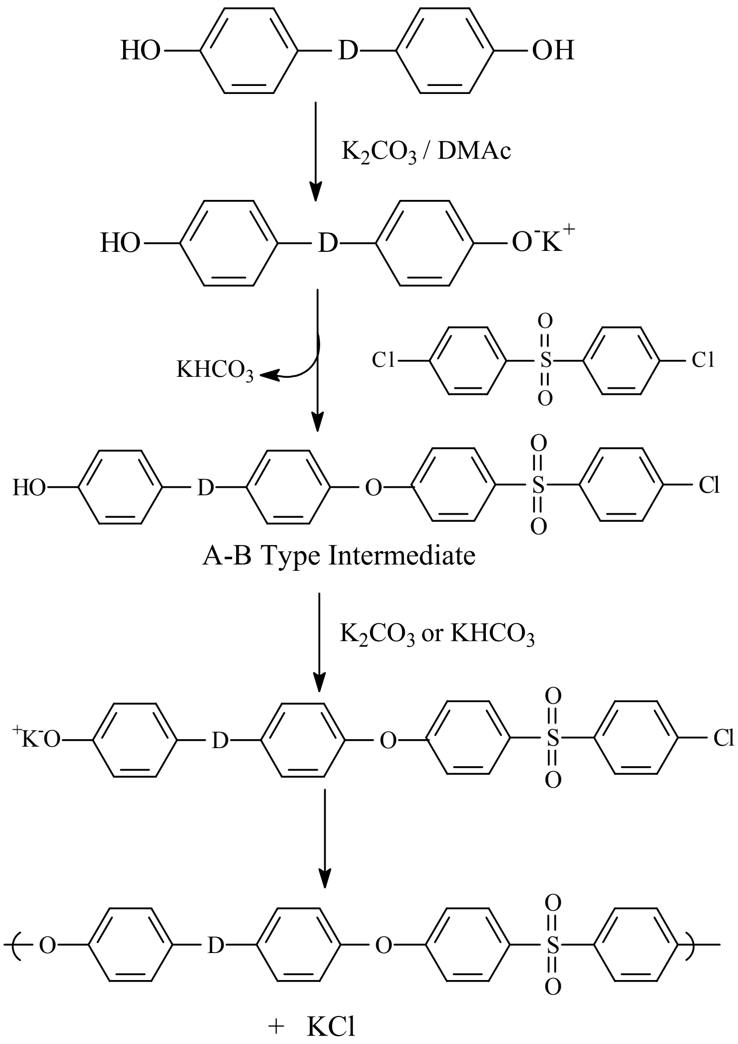

FIGURE 37. Monophenolate mechanism to polysulfone via weak base process[279].

---

bisphenate is formed, but *in situ*, followed by attack on two activated dihalides.

The alternative route is involves a monophenate species, shown below (Figure 37). The monophenolate mechanism was the preferred route[274,278].

Priddy *et al*. studied model reactions to explore the kinetics of the weak and strong base processes[278,279]. In the study, typical polymerization-type reactions were set up under both weak base and strong base conditions. The kinetics of the reactions were followed by taking samples from the reaction solutions as a function of time. After workup, the isolated compounds were examined and the end-groups analyzed. In the strong base reactions, both mono and disubstituted products were isolated essentially immediately. However, the weak base approach yielded only mono substituted products for the first 100 minutes of the reaction. The initial rate of formation of the disubstituted product with the weak base method was much lower than the rate of formation of the monosubstituted product. It was not until five hours of reaction time that the amount of disubstituted product approached the concentration of monosubstituted product.

In addition to proposing a mechanism for the potassium carbonate/DMAc process, this group of researchers was able to demonstrate that strict stoichiometry of the bases via this route was not required. The strong base amount had to be controlled for aforementioned reasons, however, high stoichiometric excesses (up to 50mol%) of potassium carbonate did not cause any hydrolysis of the halide[274]. In fact, the typical polymerization reactions employed up to 20 mol% excess potassium carbonate.

Notably, the need for a water azeotroping agent was established. During the reaction potassium carbonate can undergo the following decomposition:

$$K_2CO_3 \dashrightarrow KHCO_3 \dashrightarrow H_2CO_3 \dashrightarrow H_2O + CO_2$$

---

[278] Priddy, D.; Smith, C. D.; McGrath, J. E. In *43rd Annual Southeastern Regional Meeting of the American Chemical Society*: Richmond, VA, 1991.

[279] Priddy, D., *Ph. D. Thesis*, VPI & SU, 1994

The water formed can act as a nucleophile and, after reacting with the activated halide, produce an unreactive bisphenol; this can be avoided by using toluene or xylene as dehydrating agents.

While investigating semi-crystalline polymers, these researchers demonstrated the applicability of higher boiling solvents, like N-methyl-2-pyrrolidone (NMP)[275a], n-cyclohexyl-2-pyrrolidone (CHP)[275b], and sulfolane, to the weak base process. CHP is not miscible with water at elevated temperatures, so an azeotroping agent is not necessary. However, CHP is not as polar as NMP and co-solvent systems were necessary to keep the reagents, intermediates, and polymers solubilized. The potassium carbonate-weak base process has successfully been applied to many other polymer systems[280,281,282,283,284,285].

Kricheldorf and collaborators have developed a *bulk* or melt variation of nucleophilic aromatic substitution. Commonly referred to as the *Kricheldorf Method*, silylated bisphenols react with activated difluorides to yield various poly (arylene ethers)[286,287]. Other dihalides produce exclusively low molecular weight products. The polymerization by this type of reaction is an extension of small molecule reactions for trimethylsilyl ethers, esters, etc.[288]. The silylated compounds, such as bisphenols, diamines, etc., can be purified by distillation. A catalytic amount of cesium fluoride is used in the desilylation reaction[289]. The reaction is given in Figure 38. The polymer can be used directly after synthesis since fluorotrimethylsilane, the volatile by-product, can be vacuumed distilled from the reactor. The formation of the strong fluorine-silicon bond and the volatility of the by-products limit any equilibrium to be established for the polymer production.

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[280] Smith, C.D.; Grubbs, H.; Webster, H.F.; Gungor, A.; Wightman, J.P.; McGrath, J.E., *High Performance Polymer* 1991, 3(4), 211.

[281] Mohanty, D.K.; Lin, T.S.; Ward, T.C.; McGrath, J.E., *Sampe Symp.* 1986, 31, 945.

[282] Wang, S.; Ji, Q.; Tchatchoua, C.N.; Shultz, A.R.; McGrath, J.E., *J. Polym. Sci.: Polym. Phys. Ed.* 1999, 37, 1849.

[283] Miyatake, K.; Hay, A.S., *J. Polym. Sci., Part A: Polym. Chem.* 2001, 39, 3770.

[284] Srinivasan, S.A.; McGrath, J. E., *Polymer 1998, 39 (12), 2415.*

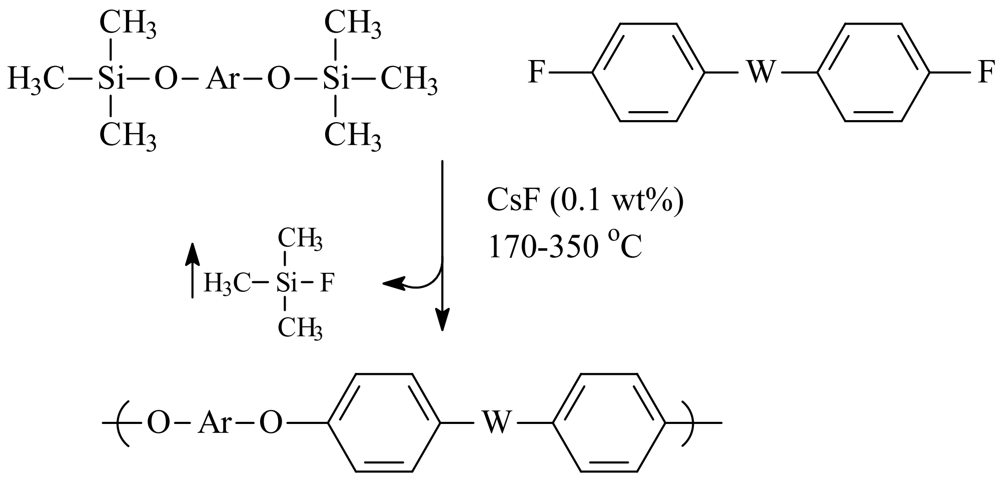
[285] Shobha, H.K.; Smalley, G.R.; Sankarapandian, M; McGrath, J.E., *ACS Polymer Preprints* 2000, 41, 180.

[286] Kricheldorf, H.R.; Bier, G., *J. Polym. Sci.Polym. Chem. Ed.* 1983, 21, 2283.

[287] Kricheldorf, H.R.;Jahnke, p, *Makromol. Chem.* 1990, 191, 2027.

[288] Fieser, M., *Reagents for Organic Synthesis,*Vol. 10, Wiley: New York, 1982.

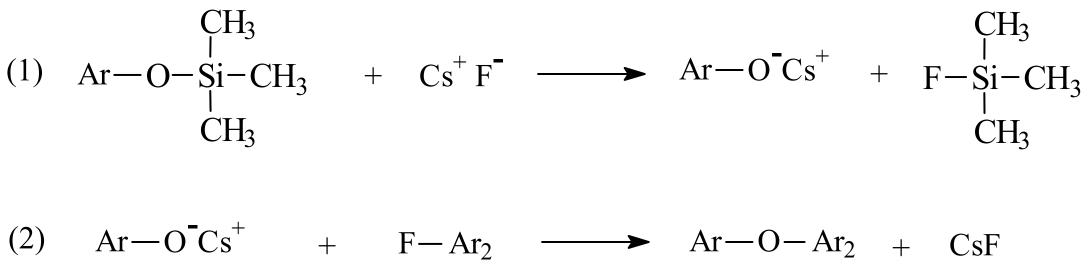
[289] Kricheldorf, H.R.; Delius, U.; Tonnes, K.U. *New Polym. Mater.* 1988, 1, 127.



Where Ar = Aryl Group, W = electron withdrawing group

FIGURE 38. Synthesis of poly (arylene ethers) via silyl ether displacement

The proposed silyl ether displacement mechanism is shown below. It involves, first, the conversion of the silyl ether into the cesium phenolate followed by attack of the phenolate on the activated halide monomer yielding a new ether linkage. Even though the catalyst, typically CsF, concentration is low (0.1-0.3 mol%), it is very important in this method for synthesizing high molecular weight poly (arylene ether sulfones).



$$(1)\quad Ar-O-Si(CH_3)_3 + Cs^+F^- \longrightarrow Ar-O^-Cs^+ + F-Si(CH_3)_3$$

$$(2)\quad Ar-O^-Cs^+ + F-Ar_2 \longrightarrow Ar-O-Ar_2 + CsF$$

FIGURE 38A. SILYL ETHER DISPLACEMENT REACTION MECHANISM

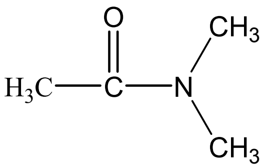
CHAPTER 2

EXPERIMENTAL

Condensation or step-growth polymerizations involve the stepwise, sequential condensation of functional monomers. To produce high molecular weight, linear polymers, several general requirements need to be satisfied. These critical requirements include (1) difunctionality, (2) one-to-one stoichiometry, (3) high monomer and reagent purity, and (4) very high (> 99%) conversions. The following sections describe the careful purification of solvents and monomers required for these polymerizations.

2.1 Solvent Purification

2.1.1 N,N-Dimethylacetamide (DMAc)

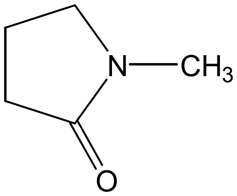


Source: Fisher Scientific

Molecular Weight: 89.13 g/mol

Purification: DMAc was dried over calcium hydride (CaH) or phosphorus pentoxide (P_2O_5) for at least 12 hours. DMAc was distilled under reduced pressure (~ 80 °C) and stored over molecular sieves under nitrogen.

2.1.2 **N-Methyl-2-Pyrrolidone (NMP)**

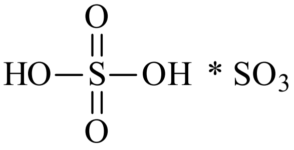


Source: Fisher Scientific

Molecular Weight: 99.13 g/mol

Purification: NMP was dried over P_2O_5 for at least 12 hours then distilled under reduced pressure (~ 120 °C) and stored over molecular sieves.

2.1.3 **Fuming Sulfuric Acid**



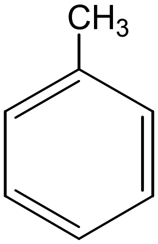
$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH \;*\; SO_3$$

Source: Aldrich Chemical

Molecular Weight: 98.08 g/mol , density: 1.925g/mL

Purification: Sulfuric acid containing oleum (27-30% SO_3) was used as received. Film was used to wrap and seal the bottle after each use.

2.1.4 **Toluene**

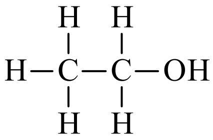


Source: Fisher

Molecular Weight: 92.14 g/mol

Purification: Toluene was transferred into 250 mL round-bottom flasks and stored over molecular sieves under nitrogen.

2.1.5 **Ethanol or Ethyl Alcohol**



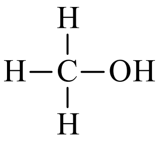
$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{OH} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

Source: Aldrich

Molecular Weight: 46.07 g/mol

Purification: Absolute (99%) ethanol was used as a coagulating and / or recrystallization solvent and used without any purification.

2.1.6 **Methanol or Methyl Alcohol**



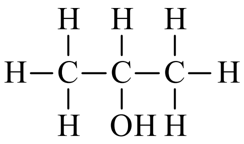
$$H-\overset{H}{\underset{H}{C}}-OH$$

Source: Fisher

Molecular Weight: 32.04 g/mol

Purification: Methanol was used as a coagulating and / or recrystallization solvent and was used without any purification.

2.1.7 **Isopropyl Alcohol or 2-Propanol or Isopropanol**



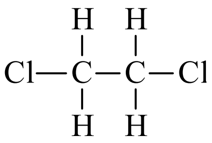
$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-H$$

Source: Fisher

Molecular Weight: 60.01 g/mol

Purification: Isopropanol was used as a coagulating and / or as a recrystallization solvent and used without any purification.

2.1.8 **1,2-Dichloroethane (DCE)**



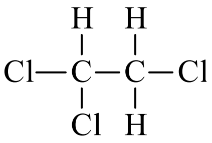
$$\mathrm{Cl{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}Cl}$$

Source: Aldrich

Molecular Weight: 98.96 g/mol

Purification: A.C.S. reagent grade 1,2-dichloroethane was stored over molecular sieves, otherwise used without any purification.

2.1.9 **1,1,2-Trichloroethane (TCE)**



$$\mathrm{Cl{-}\overset{H}{\underset{Cl}{C}}{-}\overset{H}{\underset{H}{C}}{-}Cl}$$

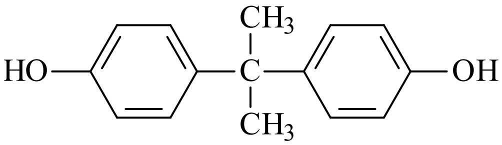
Source: Aldrich

Molecular Weight: 133.41 g/mol

Purification: 1,1,2-trichloroethane was supplied containing 2-propanol (~5%). Therefore, the 2-propanol was separated via distillation and discarded, while the 1,1,2-trichloroethane was distilled onto molecular sieves and stored under nitrogen.

2.2 Reagents and Purification of Monomers

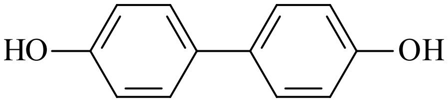
2.2.1 Bisphenol A (Bis A) or 2,2’-bis(4-hydroxyphenol)propane or 4,4'-isopropylidenediphenol



Source:	Dow Chemical
Molecular Weight:	228.29 g/mol
Melting Point:	152-153 °C

Purification: Bisphenol A was recrystallized from a 25% (w/v) solution of toluene. After refluxing for several hours, the solution was allowed to cool to room temperature. The milky white crystals were collected by filtration and dried in a vacuum for over 12 hours at 60 °C, then at least 12 hours at 90 °C.

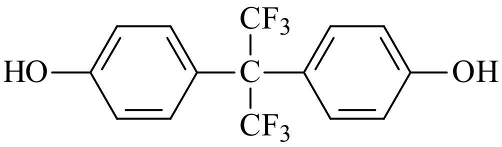
2.2.2 4,4’-Biphenol (BP)



Source:	BP-Amoco
Molecular Weight:	186.21 g/mol
Melting Point:	282-284 °C

Purification: Monomer grade biphenol was used as received. Prior to use, it was dried in a vacuum oven for at least 12 hours at 100 °C. Biphenol can be recrystallized from deoxygenated acetone or from toluene.

2.2.3 **6F-Bisphenol A (6F) or 4,4'-(hexafluoroisopropylidene) diphenol**



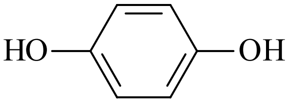
Source: Ciba

Molecular Weight: 336.33 g/mol

Melting Point: 160-162 °C

Purification: 6F bisphenol A (sometimes called bisphenol AF) was received as a slightly colored (pink) powder. It was first dissolved in warm acetic acid and precipitated with deionized water. The precipitated powder was then filtered and recrystallized from refluxing toluene yielding off-white crystals. The collected crystals were dried in a vacuum oven for at least 12 hours at 120 °C. 6F can also be purified by sublimation.

2.2.4 **Hydroquinone (HQ) or 1,4-benzene diol**



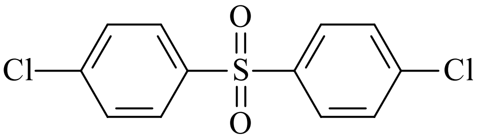
Source: Eastman Chemical

Molecular Weight: 110.10 g/mol

Melting Point: 172-173 °C

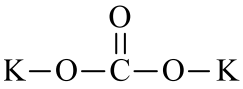
Purification: Hydroquinone was recrystallized from a 25% (wt/v) deoxygenated methanol solution in a crystallization dish. The mixture was heated slowly until a homogenous solution was attained. The solution was allowed to cool slowly to room temperature over night. The large crystals were crushed and dried under vacuum at 60 °C for at least 12 hours. Hydroquinone could also be recrystallized from water or sublimed under reduced pressure with heat.

2.2.5 4-4'-Dichlorodiphenyl sulfone (DCDPS) or Bis (4-chlorophenyl) sulfone



Source:	BP-Amoco (now Solvay)
Molecular Weight:	287.13 g/mol
Melting Point:	145-147 °C
Purification:	Monomer grade dichlorodiphenyl sulfone was used as received. Prior to use, it was dried in a vacuum oven for at least 12 hours at 100 °C. DCDPS can be recrystallized from toluene and yields large crystals that are pulverized prior to drying.

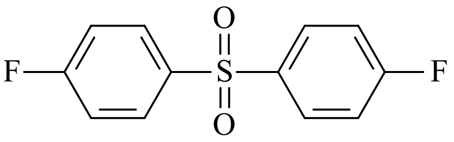
2.2.6 Potassium Carbonate (Anhydrous)



$$K-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-K$$

Source:	Aldrich
Molecular Weight:	138.21 g/mol
Melting Point:	Not determined.
Purification:	Potassium carbonate was dried under vacuum at 120 °C for at least 12 hours prior to use.

2.2.7 **4,4’-Difluorodiphenyl Sulfone (DFDPS) or Bis (4-fluorophenyl) sulfone**



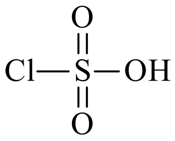
Source: Aldrich

Molecular Weight: 254.25 g/mol

Melting Point: 100-102 °C.

Purification: Difluorodiphenyl sulfone (99%) was dried under vacuum at 65 °C for at least 12 hours prior to use. DFDPS could be recrystallized from toluene and yield off-white crystals. Also, one attempt was made to synthesize difluorodiphenyl sulfone from dichlorodiphenyl sulfone, using a reported synthetic route[290], will be discussed under the *Monomer Synthesis* section.

2.2.8 **Chlorosulfonic acid**



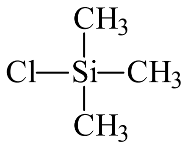
$$Cl-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH$$

Source: Aldrich

Molecular Weight: 116.52 g/mol

Purification: Chlorosulfonic acid was used as received. Film was used to wrap and seal moisture from the contents. The container was stored in a desiccator once opened.

2.2.9 **Chlorotrimethylsilane or Trimethylchlorosilane**



$$\mathrm{Cl-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-CH_3}$$

Source: Aldrich

Molecular Weight: 108.64 g/mol

Purification: Chlorotrimethylsilane (98%) was used as received. A positive pressure of nitrogen was used when syringing the reagent from the sealed container. Chlorotrimethylsilane was stored in a desiccator once opened.

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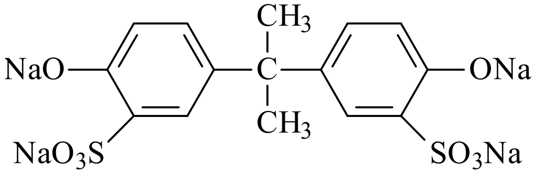
[290] Viswanathan, R., *Ph.D. Thesis* VPI & SU, 1981, p.83.

2.3 Monomer Synthesis

2.3.1 Sodium Salt of 3,3'-Disulfonated –4,4'-(bis-isopropylidene) diphenol or Sulfonated Bisphenol A

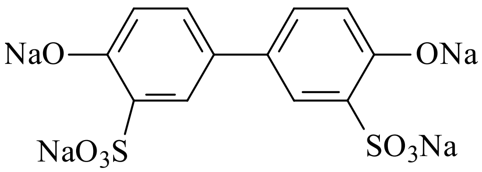


Source:	Synthesized in house
Molecular Weight:	476.33 g/mol
Melting Point:	Not observed below 350 °C.

Reagents: Sulfonated bisphenol A was synthesized using bisphenol A and 97% concentrated sulfuric acid (Fisher) via electrophilic aromatic substitution.

Procedure: To a 100-mL, 3 necked round bottom flask, fitted with a condenser, nitrogen inlet, and an overhead mechanical stirrer, 20 g (0.088 mol) bisphenol A and 40 mL sulfuric acid were added. The mixture was stirred vigorously at 30 °C for 18 hours. The mixture underwent several color changes during this time (a tan→ to an orange→ to a yellow). The final mixture was poured into a 200 mL ice bath stirred by a magnetic stir bar. Upon adding to water, insoluble solids precipitated to the bottom of the flask. The aqueous solution was filtered, neutralized with 2*M* NaOH to a final pH 8. Next, 100 g sodium chloride was added and the mixture was allowed to stand overnight. Finally, the solid precipitate was collected by filtration and recrystallized from isopropyl alcohol and water (10/1). Yield: 20%.

2.3.2 Sodium Salt of 3,3'-Disulfonated-4,4'- Biphenol or Sulfonated Biphenol



Source: Synthesized in house

Molecular Weight: 434.24 g/mol

Melting Point: Not observed below 350 °C.

Reagents: Disulfonated biphenol was synthesized using 4,4'-biphenol and 97% concentrated sulfuric acid via electrophilic aromatic substitution.

Procedure: To a 100- mL, 3 necked round bottom flask, fitted with a condenser, nitrogen inlet, and an overhead mechanical stirrer, 20 g (0.107 mol) biphenol and 40 mL sulfuric acid were added. The mixture was stirred vigorously at 30 °C for 18 hours. The mixture underwent several color changes during this time (off-white→ orange→ yellow). The final mixture was poured into a 200 mL ice bath stirred by a magnetic stir bar. The isolation steps were similar to those described above for sulfonated bisphenol A, except a methanol and water mixture (9/1, v/v) was used for recrystallization. Yield: 75%.

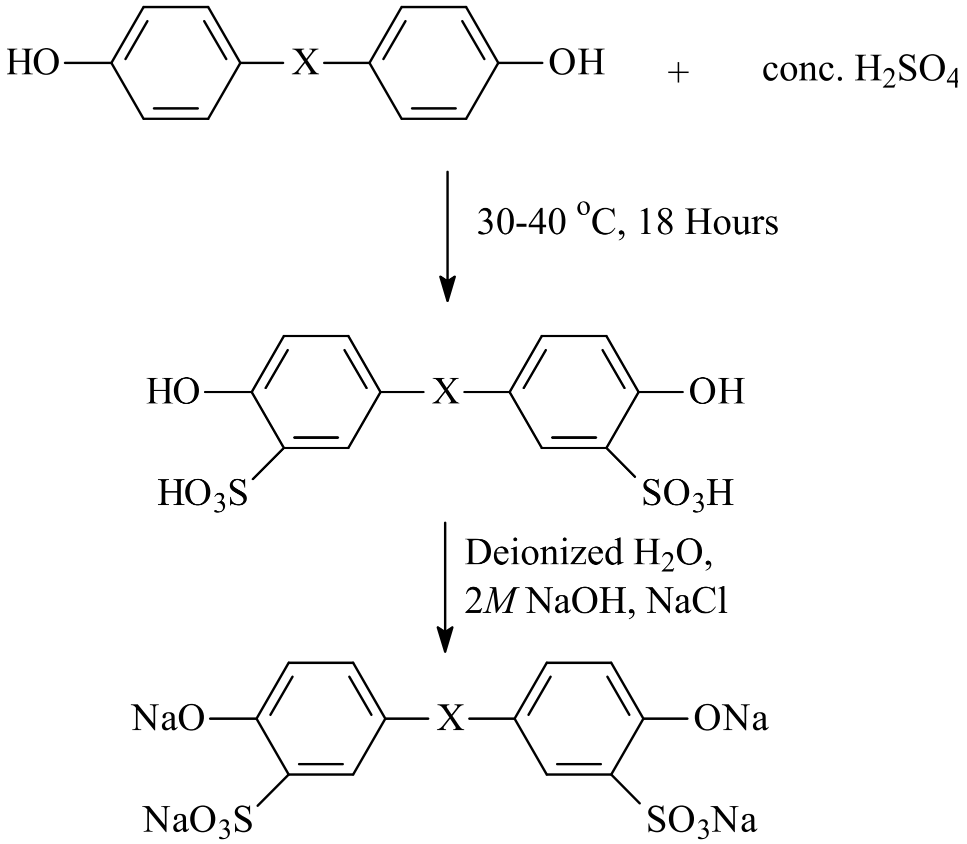
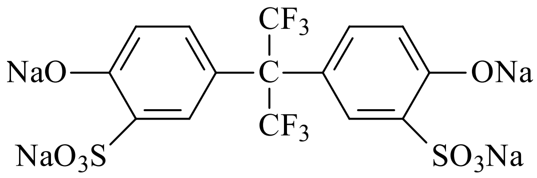


FIGURE 39. Synthesis of novel disulfonated bisphenols.

2.3.3 Sodium Salt of 3,3'-Disulfonated-4,4'-(bis-hexafluoroisopropylidene) diphenol or Sulfonated 6F-Bisphenol A



Source: Synthesized in house

Molecular Weight: 584.28 g/mol

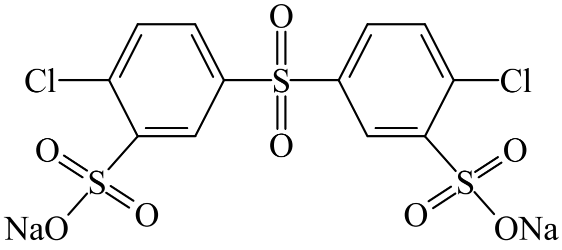
Melting Point: Not observed below 350 °C.

Reagents: Sulfonated 6F-bisphenol A was synthesized using 6F-bisphenol A and 97% concentrated sulfuric acid via electrophilic aromatic substitution.

Procedure: To a 100-mL, 3 necked round bottom flask, fitted with a condenser, nitrogen inlet, and an overhead mechanical stirrer, 20 g (0.059 mol) bisphenol A and 40 mL sulfuric acid were added. The mixture was stirred vigorously at 40 °C for 18 hours. The mixture under went several color changes during this time (pink → green → orange → yellow). The final mixture was poured into a 200 mL ice bath stirred by a magnetic stir bar. The isolation steps were similar to those described above for sulfonated bisphenol A, except a methanol and water mixture (9/1, v/v) was used for recrystallization. Yield: 80%.

2.3.4 **Sodium Salt of 3,3’-Disulfonated-4,4’-dichlorodiphenyl sulfone (SDCDPS)**

Source:	Synthesized in house
Molecular Weight:	491.24 g/mol



Melting Point: Not observed below 350 °C.

Reagents: Disulfonated dichlorodiphenyl sulfone was synthesized using 4,4’-dichlorodiphenyl sulfone and fuming sulfuric acid via electrophilic aromatic substitution.

Procedure: The procedure utilized was slightly modified from previously reported procedures[164,291]. To a 100-mL, three necked flask equipped with a mechanical stirrer and a nitrogen inlet/outlet was added 28.7 g of DCDPS dissolved in 60mL 30% fuming sulfuric acid. The solution was heated to 110 °C for 6 hours. The reaction mixture was allowed to cool to room temperature and added into 400ml of ice-water. Next, 180 g of NaCl was added and, subsequently, the disodium salt of disulfonated dichlorodiphenyl sulfone precipitated as a white powder. The latter was filtered and re-dissolved in 400 mL of cold deionized water, treated by 2N NaOH aqueous solution to a pH of 6~7, and finally an excess amount of NaCl was added again to *salt out* the sodium form of the sulfonated monomer. The crude product was filtered and recrystallized from a mixture of

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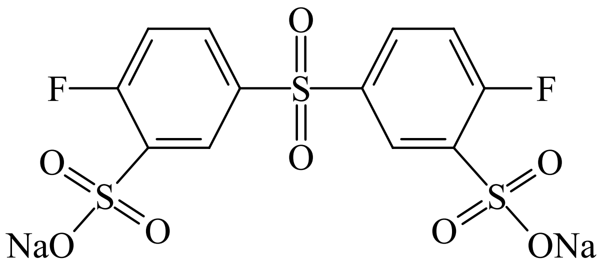
[291] L.M. Robeson, and M. Matzner, *US Patent 4,380,598*, 1983.

alcohol (methanol or isopropanol) and deionized water (9/1, v/v), producing white needle-like crystals. Yield: 87%.

2.3.5 Sodium Salt of 3,3'-Disulfonated-4,4'-difluorodiphenyl sulfone (SDFDPS)



Source: Synthesized in house

Molecular Weight: 458.33 g/mol

Melting Point: Not observed below 350 ^{o}C.

Reagents: Disulfonated difluorodiphenyl sulfone was synthesized using 4,4'-difluorodiphenyl sulfone and fuming sulfuric acid via electrophilic aromatic substitution.

Procedure: To a 250-mL, three necked flask equipped with a mechanical stirrer and a nitrogen inlet/outlet was added 25 g of DCDPS dissolved in 50mL 30% fuming sulfuric acid. The solution was heated to 110 ^{o}C for 6 hours with vigorous stirring. The reaction mixture was allowed to cool to room temperature and added into 400ml of ice-water. The remaining steps are the same as for the SDCDPS synthesis, except recrystallization was accomplished with ethyl alcohol and water (8/1). Yield: 70%

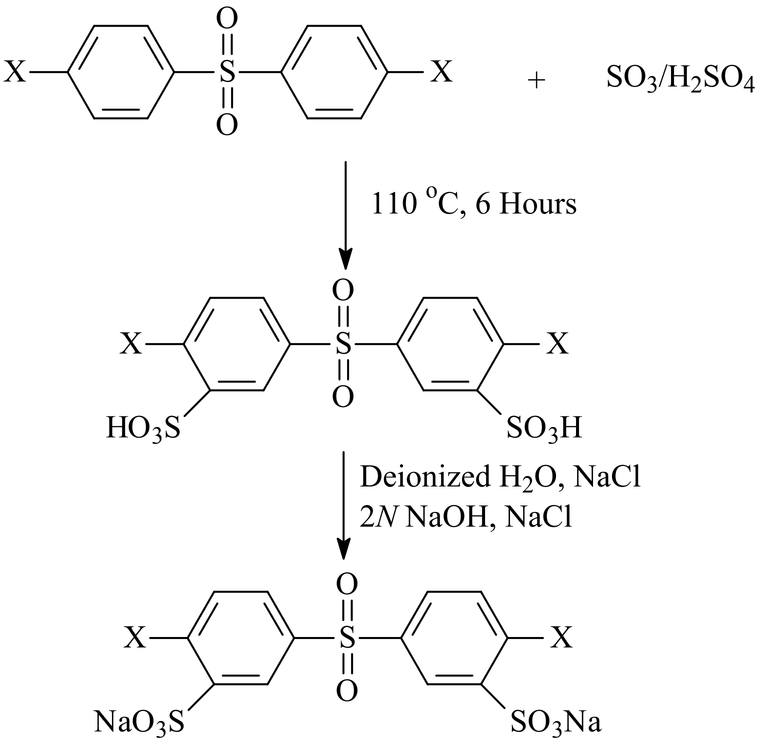


Figure 40. General synthesis of disodium salt of the disulfonated sulfone dihalide monomers

2.3.6 **Synthesis of 4,4'-Difluorodiphenyl Sulfone**

Source:	In house
Molecular Weight:	254.25 g/mol
Melting Point:	96 - 98 °C.
Reagents:	4,4'-dichlorodiphenyl sulfone (DCDPS), anhydrous potassium fluoride (KF), and sulfolane.

Procedure: 100 grams (1.75 mols) of dried KF (finely powdered) were added to 300 mL of sulfolane contained in a 1000-mL 3-necked round bottom flask equipped with an overhead mechanical stirrer, a nitrogen inlet, and a condenser. Vigorous stirring was used to produce fine dispersion, while heating at 100 °C under nitrogen. 25 grams (0.75 mols) DCDPS were added to the dispersion, then the mixture was heated to reflux overnight. After about 20 hours, the reaction mixture was cooled to room temperature and poured into 500 mL of deionized water under vigorous agitation. The precipitated powder was filtered and washed several times with water to remove any salts. After drying at 60 °C, the crude powder product was distilled under vacuum and the main fraction was collected. The difluorodiphenyl sulfone (DFDPS) was recrystallized from toluene. Yield: 65%. Note: All copolymerizations utilized commercial DFDPS.

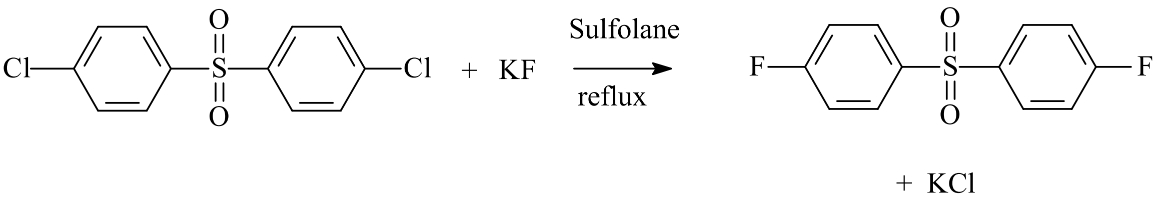


FIGURE 41. Synthesis of difluorodiphenyl sulfone from dichlorodiphenyl sulfone[290].

2.4 Copolymer Synthesis

The direct synthesis of sulfonated copolymers by polycondensation was achieved via nucleophilic aromatic substitution mechanisms. The fluorine containing sulfone monomers (DFDPS and SDFDPS) are more reactive than the corresponding chloro-dihalides (DCDPS and SDCDPS). Due to their inherent differences, two slightly different synthetic procedures were developed to obtain high molecular weight polymers that will successfully generate tough, ductile films. Strict stoichiometric control was necessary for both systems.

2.4.1 DCDPS/SDCDPS Copolymer Synthesis

Although the reactivities of the various bisphenols were different, the basic polymerization procedure was the same. A typical polymerization for all sulfonated copolymers will be described using the bisphenol A-40 system: Firstly, 1.2624g (5.5mmol) 4,4’-bisphenol A, 0.9621g (3.3mmol) DCDPS, and 1.0806g (2.2mmol) SDCDPS were added to a 3-neck flask equipped with overhead mechanical stirrer, nitrogen inlet and a Dean Stark trap. Next, 1.15 mole equivalent of potassium carbonate and NMP were introduced to afford a 20% solids concentration. Toluene (NMP/Toluene = 2/1, v/v) was used as an azeotropic agent. The reaction mixture was heated under reflux at 150ºC for 4 hours to dehydrate the system. The temperature was raised slowly to 190ºC by controlled removal of the toluene. The reaction mixture was reacted for 16-30 hours during which the solution became very viscous. The solution was cooled to room temperature and diluted with DMAc. The solution was filtered to remove most of the salts and isolated as swollen strings by addition to stirred deionized water. The precipitated copolymer was washed several times with deionized water to further remove salts, including soaking in deionized water at 60 ^{o}C overnight. Finally, the filtered copolymer was vacuum dried at 120ºC for 24 hours. Copolymers with other bisphenols and dihalide compositions were also prepared by this procedure. The homopolymers for each respective bisphenol was synthesized using DCDPS and a polymerization temperature of 175 ^{o}C. Each homopolymer was isolated by precipitation into methanol and water (11/1, v/v) stirred in a blender.

2.4.2 **DFDPS/SDFDPS Copolymer Synthesis**

The *DFDPS/SDFDPS system* was employed for only a few copolymers in which ductile films were not easily achieved using the DCDPS/SDCDPS synthesis procedure. These include the copolymerization of 6F bisphenol A with 50% and 60% SDFDPS, bisphenol A with 60% SDFDPS, biphenol with 50% and 60% SDFDPS, and hydroquinone with 50% and 60% SDFDPS. Copolymerizations utilizing DFDPS and SDFDPS required less thermal energy due to the enhanced comonomer reactivity. A typical reaction is presented for hydroquinone-50. First, 2.018g (18mmol) hydroquinone, 2.353g (9 mmol) DFDPS, and 4.201g (9 mmol) SDFDPS were added to a simple 3-neck flask equipped with mechanical stirrer, nitrogen inlet and a Dean Stark trap. Next, 1.15 mole equivalent of potassium carbonate and DMAc were introduced to afford a 20% solids concentration. Toluene was used as an azeotropic agent (DMAc/Toluene = 2/1, v/v). The reaction mixture was heated under reflux at 150ºC for 4 hours to dehydrate the system. Toluene was slowly removed to raise the temperature to 175ºC and held constant for at least 16 hours. The viscous solution was cooled and diluted with more DMAc. The copolymer isolation steps are as given above for DCDPS/SDCDPS polymerizations.

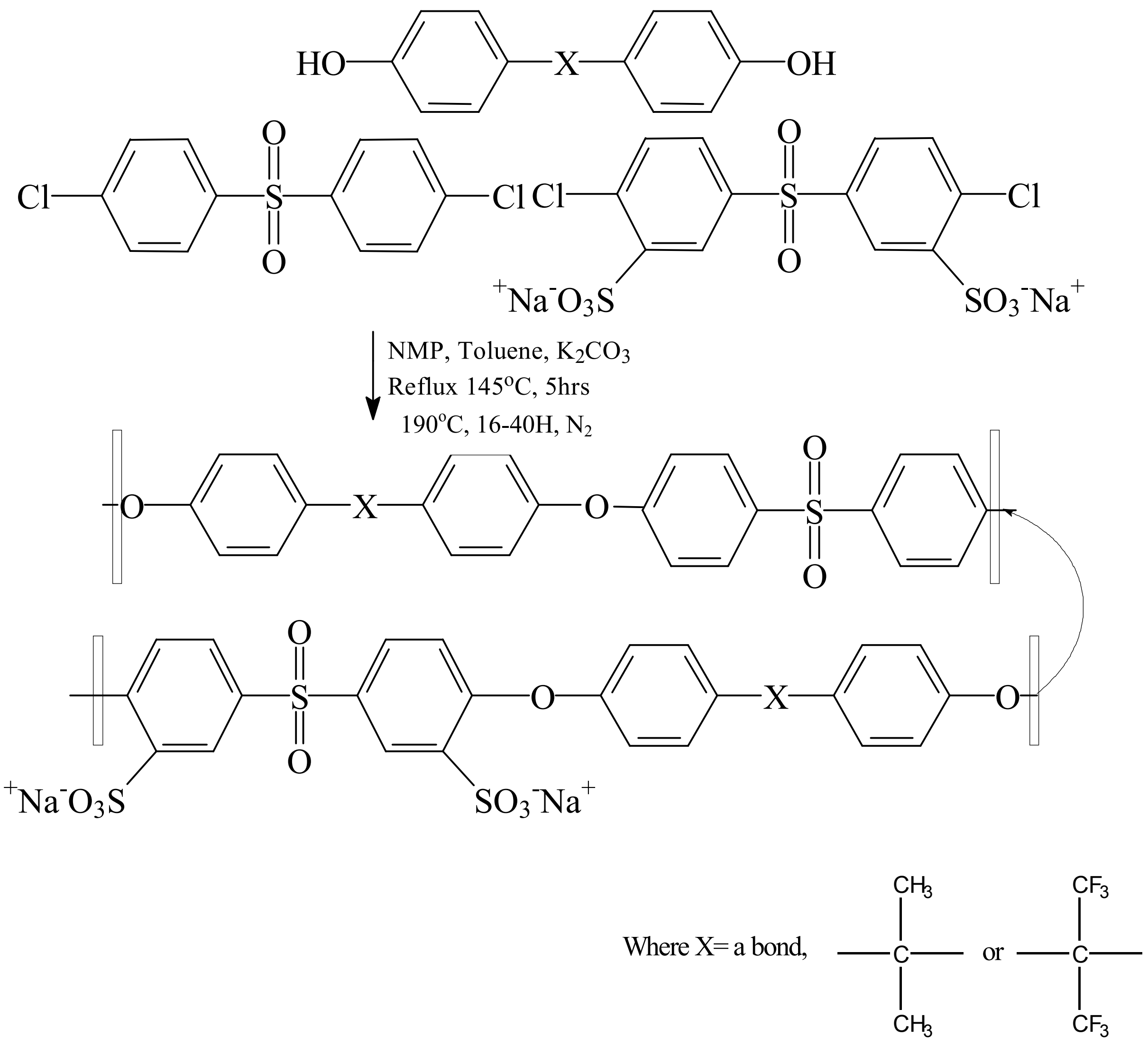


FIGURE 42. Synthesis of sulfonated poly (arylene ether sulfone) copolymers via direct polymerization.

2.5 **Polymer Post - Sulfonation**

The sulfonation of poly (arylene ethers) has been well studied, as surveyed in sections of the Literature Review (Chapter 1). Some investigation of the sulfonation of control (homopolymers) polymers based on bisphenol A, biphenol, and 6F bisphenol A were conducted to provide comparative materials to the directly sulfonated copolymers.

The sulfonation technique utilized in this study was generally similar to published procedures[108,109]. A typical polymer sulfonation will be described using bisphenol A based poly (arylene ether sulfone), chlorosulfonic acid (50 mol%), chlorotrimethylsilane, and 1,2-dichloroethane as follows:

To a 100 mL, 3-necked round bottom flask fitted with a mechanical stirrer, condenser, and an addition funnel with a nitrogen connection, 5 grams of dried Bisphenol A polysulfone (11.3mmol) were dissolved in 60 mL 1,2-dichloroethane (5-10 % wt/v solution was typical). Next, a mixture of chlorotrimethylsilane (1.228g, 12.5mmol) diluted in 10 mL 1,2-dichloroethane was added. Finally, a mixture of 0.658 grams (0.0056mmol) chlorosulfonic acid in 10 mL 1,2-dichloroethane was added dropwise over 30 minutes. The reaction solution was stirred at a high rate overnight (~24 hours) at a constant temperature of 30 ^{o}C. The reaction mixture generally remained homogeneous (i.e., in solution) during the entire reaction time. After the desired time, the reaction solution was added dropwise into stirred methanol, and washed with methanol and then cold water. The polymers were dried in a vacuum oven at ~90 ^{o}C for at least 24 hours. Note: The post-sulfonated polymers that were soluble in methanol were subsequently recovered by distillation via rotovap of the solvents, dissolved in DMAc and cast into films on glass substrates. All dried sulfonated polymers were stored in a desiccator.

Similar reaction conditions were used for other compositions (i.e., mol% chlorosulfonic acid), and homopolymers. Note: Biphenol based poly (ether sulfones) were not readily soluble in 1,2-dichloroethane and were alternatively dissolved in 1,1,2-trichloroethane for sulfonation.

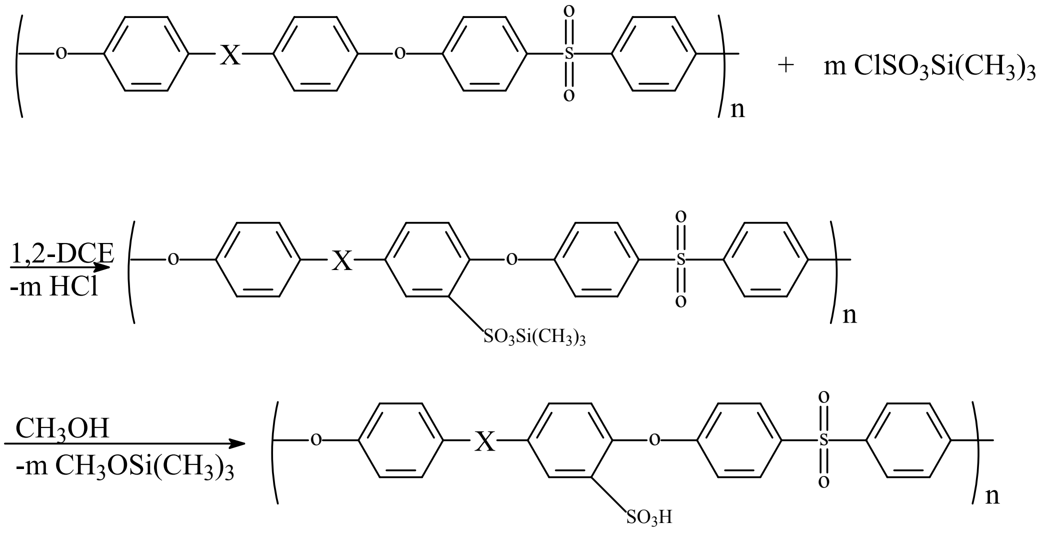


FIGURE 43 Synthesis of sulfonated poly(arylene ether sulfone)s via the silyl ester of chlorosulfonic acid.

2.6 Characterization

2.6.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton (^{1}H) and Carbon (^{13}C) Nuclear Magnetic Resonance were used to obtain the chemical composition of the monomers and polymers utilized, both commercial and synthesized, in this research. Samples were dissolved in appropriate deuterated solvents (DMSO-d_6, $CDCl_3$, or D_2O), at a typical concentration of 10% (0.1g / 1 mL). NMR spectra were obtained on a Varian Unity Spectrometer operating at 400 MHz. ^{1}H and ^{13}C spectra were referred to tetramethylsilane (TMS) at 0 ppm.

2.6.2 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR was utilized to confirm the functional groups of synthesized homo-and copolymers. Measurements were conducted on a Nicolet Impact 400 FTIR Spectrometer using thin solution-cast polymer films.

2.6.3 Gel Permeation Chromatography (GPC) or Size Exclusion Chromatography (SEC)

GPC measurements were used to determine molecular weight and molecular weight distributions of synthesized homopolymers. GPC was conducted with a Waters GPC/ALC 150C instrument equipped with a differential refractometer detector and an on-line differential viscometer (Viscotek 150R) coupled in parallel. TriSEC GPC Software V2.70e (Viscotek) was used to acquire and analyze the data. GPC measurements were performed using an NMP (HPLC grade) mobile phase, containing 0.02 M P2O5, at a flow rate of 1.0 ml/min and an injection volume of 200 μl with the polymer concentration of approximately 4 mg/ml. The stationary phase was crosslinked polystyrene gel (Waters μ styragel HT 103 Å, mean particle diameter 10 μm) packed in three (7.8 mm I.D. x 30 cm) stainless steel columns. The column- compartments, lines and detectors were maintained at a temperature of 60 ^{o}C during measurements. A series of polystyrene standards having narrow molecular weight distributions (Polymer Laboratory) were employed to generate a universal calibration curve[292,293]. Number average molecular weight (Mn), weight average molecular weight (Mw) and polydispersity (Mw/Mn) were determined by using the universal calibration mentioned above.

2.6.4 Intrinsic Viscosity Determinations ([η])

The measurements of intrinsic viscosity of homo- and sulfonated poly(arylene ether sulfones) were performed using a Cannon- Ubbelohde viscometer, thermostatically controlled in a water bath. Intrinsic viscosities were measured at 25 ^{o}C in NMP. Intrinsic viscosities provide information on the *size* of a polymer molecule in solution. Typically, the intrinsic viscosity provides a qualitative inference of molecular weight. Intrinsic viscosities were very important in this dissertation since GPC could not be effectively used for sulfonated copolymers.

2.6.5 Thermogravimetric Analysis (TGA)

Dynamic TGA was performed on a Perkin Elmer TGA7 instrument in either air or nitrogen to assess the thermal and thermo-oxidative stability of sulfonated poly(arylene ether sulfones). The samples were heated at a rate of 10 ^{o}C/min. Weight loss was measured and reported as a function of temperature. The thermal stability of the polymers was generally reported at the observed temperature of 5% weight loss.

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[292] Konas, M.; Moy, T.M.; Rogers, M.E.; Shultz, A.R.; Ward, T.C.; McGrath, J.E., *J. Polym. Sci., Part B: Polym. Phys.* 1995, 33, 1429.

[293] Konas, M.; Moy, T.M.; Rogers, M.E.; Shultz, A.R.; Ward, T.C.; McGrath, J.E., *J. Polym. Sci., Part B: Polym. Phys.* 1995, 33, 1441.

2.6.6 **Differential Scanning Calorimetry (DSC)**

Differential scanning calorimetry, a Perkin-Elmer DSC 7 instrument, was used to determine the thermal transition temperatures of the synthesized polymers. Films were usually stacked to provide a suitable sample size (~5 - 10mg). Programmed heating cycles were used to heat the samples at a heating rate of 10 ^{o}C/min under a nitrogen atmosphere. The midpoint of the specific heat increase in the transition region during the second heating is reported at the Tg (glass transition temperature).

2.6.7 **Mass Spectroscopy (MS)**

Fast-Atom Bombardment Mass Spectroscopy (FAB^{+}MS) analysis was conducted using a Fisons VG Quattro mass spectrometer to determine molecular weight of synthesized monomers.

2.6.8 **Elemental Analysis**

Galbraith Laboratories (TN) performed elemental analysis of all synthesized monomers. The atomic compositional percentages of carbon, hydrogen, oxygen, sulfur and sodium were obtained.

2.6.9 **Non-Aqueous Potentiometric Titration**

Non-aqueous potentiometric titrations were employed to determine the milliequivalent (meq) weight of sulfonic acid groups in sulfonated poly(arylene ether sulfones). This value was then used to experimentally determine the Ion-Exchange Capacity (IEC) of the sulfonated copolymers containing pendant sulfonic acid groups. The ion-exchange capacity is defined as the milliequivalents of reactive –SO_3H sites per gram of polymer and have units, therefore, of meq/g. The measured IEC values are compared to the theoretical or calculated IEC value based on the moles of sulfonated dihalide monomer charged to the reaction flask. Potentiometric titrations were performed using a MCI GTOS Automatic Titrator equipped with a standard calomel electrode and a reference electrode.

A typical sulfonated poly(arylene ether sulfone) titration is conducted as follows: Tetra methyl ammonium hydroxide (TMAH) was utilized as titrant (~ 0.02 N) for the titration of sulfonic acid groups in the polymer. The titrant was standardized against dry potassium hydrogen phthalate (KHP) immediately prior to titrating. Sulfonated polymers were dried at ~120 ^{o}C before being weighing and dissolving in dimethyl acetamide (DMAc). The end-point was detected as the maximum of the first derivative for the potential versus the used volume of titrant. The end point was then used to calculate the IEC (meq/g) of the sulfonated membrane. The reported experimentally calculated IECs were those of the average of at least three titrated samples.

2.6.10 **Film Preparation**

Films were prepared by casting solutions of homo- and sulfonated copolymers dissolved in DMAc on clean glass substrates. The concentration of the polymer solution was varied from 5 – 15% (w/v) which allowed some control over the thickness of the films. Polymer solutions were filtered to remove particulates using a disposable syringe and disc filters (0.45μm) prior to casting. Removal / evaporation of DMAc was accomplished via an infrared lamp in an inert (N_2) environment with gradual increasing lamp intensity over 24 hours. The films were then placed in a vacuum oven at 120 ^{o}C for approximately 20 hours and 150 ^{o}C for four hours. For thicker films, a stainless steel ring (3’’ diameter) was used on top of the glass substrate to function as a mold.

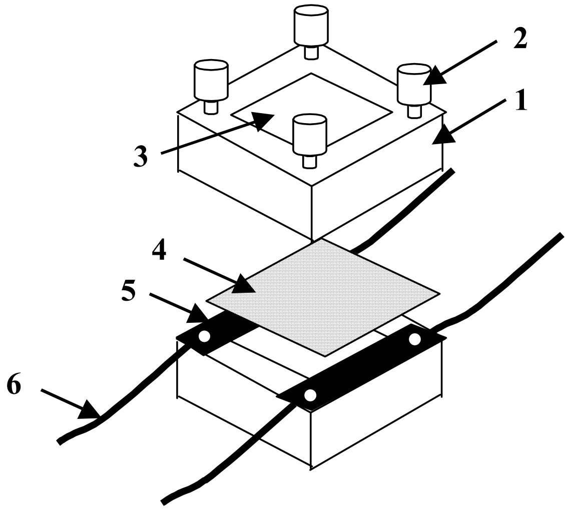
2.6.11 **Water Sorption/Uptake**

Water uptake was determined on films of all synthesized poly(arylene ether sulfones) in both their salt and acid forms. The acid-form films were dried at 120 °C and the salt-form films were thoroughly dried at 150 °C under vacuum to a constant weight which was recorded. The dried film was then immersed in water at 30 °C and periodically weighed on an analytical balance until constant water uptake weight was obtained. Typically, the equilibrium water sorption occurred within 72 hours. Some films were examined for water sorption at 80 °C and handled in a similar manner to study the effect of temperature on water sorption. The water uptake is reported as a percentage and determined by taking the equilibrium weight difference between the wet film (W_{wet}) and the dry film (W_{dry}) and dividing by the dry film (W_{dry}) weight. The equation is given below.

$$\text{Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

2.6.12 **Conductivity Measurements**

Conductivity measurements were performed on membranes using the cell shown in Figure 40. This cell geometry, developed by researchers at Los Alamos National Laboratory, was chosen to ensure that the membrane resistance dominated the response of the system. An impedance spectrum was recorded from 10MHz to 10Hz using a Solatron 1260 Impedance/Gain-Phase Analyzer. The resistance of the film was taken at the frequency which produced the minimum imaginary response. All impedance measurements were performed at room temperature under full hydration conditions. The proton conductivity is the reciprocal of the resistance and reported in units of Siemens per centimeter (S/cm).



Legend
1. Teflon block
2. Thumbscrew
3. Open area to allow equilibration with environment
4. Membrane sample
5. Blackened Pt foil electrode
6. Pt lead

FIGURE 44. Schematic of Conductivity Cell[294]

2.6.13 **Electron Spectroscopy for Chemical Analysis (ESCA)**

ESCA, also known as XPS, was used to determine the surface atomic concentration on thin films of 6F bisphenol A-based sulfonated poly(arylene ether sulfone) copolymers. Mr. Frank Cromer of the Virginia Tech Chemistry Department kindly conducted all ESCA experiments.

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[294] Zawodzinski, T. A.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. J., *J Electrochem Soc.* **1993**, 140, 1041.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Introduction

The present research focused on the relationships between the chemical structure of the bisphenol, the degree of sulfonation of the resulting sulfonated polymers, and a variety of chemical, physical, and electrical properties. The physical properties of the copolymers will be analyzed. Several different monomers were sulfonated in order to systematically synthesize different copolymers for proton exchange membrane fuel cells. The first section will describe monomer synthesis and characterization.

A systematic series of sulfonated copolymers derived from bisphenol A, biphenol, hydroquinone, or 6F-bisphenol A was investigated. Each of the bisphenols was reacted with 4,4'-dichlorodiphenyl sulfone (DCDPS) and the disodium salt of disulfonated dichlorodiphenyl sulfone (SDCDPS). These permitted copolymers to be prepared which were expected to vary in hydrolytic and oxidative stability as well as hydrophobicity. Given that the sulfonated dihalide monomers are less reactive than their non-sulfonated homologues, 4,4'-difluorodiphenyl sulfone (DFDPS) was also used. At higher molar concentrations of sulfonated dihalide, difluorodiphenyl sulfone and the synthesized disodium salt of disulfonated difluorodiphenyl sulfone (SDFDPS) were utilized to take advantage of their respective increased reactivity compared to the dichloro- analogue. Unsulfonated homopolymers were synthesized as control materials for direct comparison with the novel sulfonated copolymers. Characterization of the homopolymers and copolymers allowed identification of important properties for any useful applications. Polymer structure, molecular weight, thermal and thermo-oxidative stabilities are thought to be important parameters for fuel cell performance. In addition to these properties, proton exchange membranes require reasonable water sorption and high proton conductivity. Each of these parameters will be discussed and their unique importance to novel sulfonated copolymers will be emphasized.

3.1.1 **Sulfonated Bisphenols**

As shown earlier, monomer modification is a powerful tool for varying the properties of the resulting polymer. However, it is advantageous to use commercially available and inexpensive materials whenever possible. This research made use of commodity monomers and common solvents. Bisphenol A, biphenol, hydroquinone and 6F bisphenol A, shown in Figure 45, are well-known and readily available monomers. Bisphenol A is employed in many commercial polymers such as polycarbonates, polyesters, and Udel ®, a poly(ether sulfone). Biphenol is used in these polymer systems when more rigid materials are desired. An important commercial poly (ether sulfone), Radel® by BP-Amoco, takes advantage of properties imparted by biphenol. Hydroquinone is commonly utilized in various polymers, such as PEEK, when crystallinity is of interest. More of a specialty monomer, 6F bisphenol A has been employed for flexible, thermo-oxidativelystable polymers. The carbon-fluorine (C-F) bond on the hexafluoroisopropylidene unit in 6F bisphenol A is much more stable than the carbon-hydrogen (C-H) bond on the isopropylidene unit in bisphenol A, and has been investigated for improved flame retardancy.

Substituted bisphenols have been employed in the synthesis of poly (arylene ether sulfones). [295,296]. High molecular weight, film-forming polymers were reported when the substituted bisphenols were reacted with dichlorodiphenyl sulfone via modified potassium carbonate, weak base polymerization conditions[295]. Various compositional copolymers resulting from the reaction of hydroquinone, durohydroquinone, and dichlorodiphenyl sulfone were produced. A representative repeat unit is given in Figure 46.

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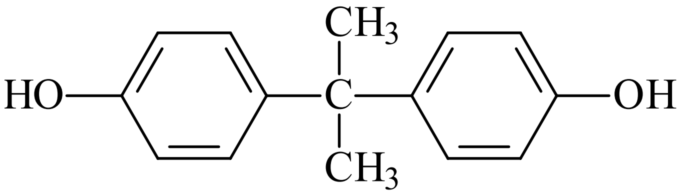
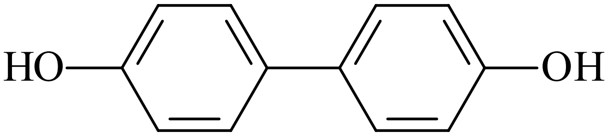
[295] Al-Omran, A.; Rose, J.B., *Polymer* 1996, 37(9), 1735.

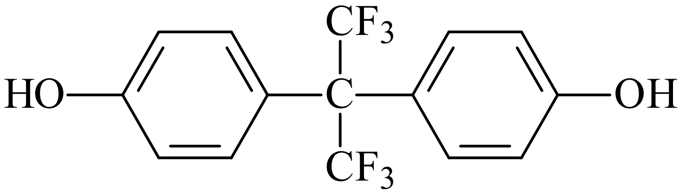
[296] Farnhan, A.G.; McGrath, J.E.; Robeson, L.M., *Polymerisation and Polycondensation Process, Applied Polymer Symposia 26, N.A.J. Platzer*, Ed., Wiley, New York, 1975, p. 373.



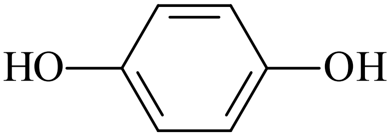
Bisphenol A (Bis A)



Biphenol (BP)



6F Bisphenol A (6F)



Hydroquinone (HQ)

FIGURE 45. Structures of bisphenols utilized in this research.

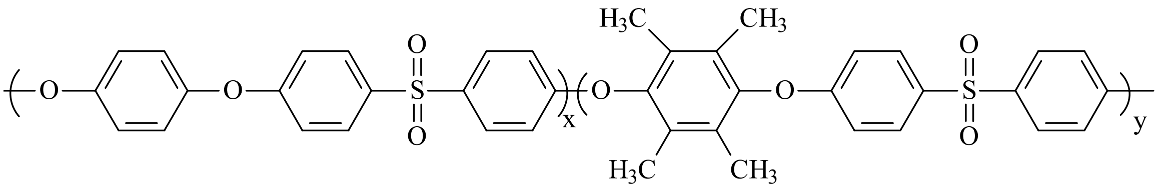


FIGURE 46. A poly (arylene ether sulfone) using a substituted bisphenol[295]

Miyatake *et al.* recently reported the synthesis of poly (arylene ethers) using 2,3,5,6-tetraphenylhydroquinone and decafluorobiphenyl.[297] In their work, they showed that high molecular weight polymers were produced. The success of this previous research using substituted bisphenols merited high expectations in using sulfonated bisphenols as comonomers in the direct synthesis of unique sulfonated poly (arylene ether sulfones).

The sulfonation of bisphenol A, biphenol, and 6F bisphenol A were investigated. All three monomers were sulfonated using concentrated sulfuric acid. Surprisingly, no literature information on the preparation of these sulfonated monomers was uncovered. However, the sulfonation of other aromatic compounds via electrophilic aromatic substitution reaction has been well documented[112,113] and has been applied to both small molecules and polymers. Figure 47 displays the mechanism of a benzene ring sulfonation using hot sulfuric acid as reagent. Because of their similarities, the syntheses of the three sulfonated bisphenols will be discussed together.

There are several potential synthetic routes and sulfonating agents available to sulfonate bisphenols. Sulfuric acid is arguably the simplest.

Purified bisphenol A was dissolved in concentrated sulfuric acid as described in the experimental section. The sulfonation reaction was investigated at 30 °C for 6 hours and for 18 hours. These time frames were arbitrarily selected. A homogeneous solution was observed within two hours. During both reaction time frames a chromatic change was easily noticed in the reaction solution. The reaction mixture, even before heating, displayed a brownish tan color. After about 4-6 hours a vivid orange mixture was

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[297] Miyatake, K.; Oyaizu, K.; Tsuchida, E.; Hay, A.S., *Macromolecules* 2001, 34, 2065.

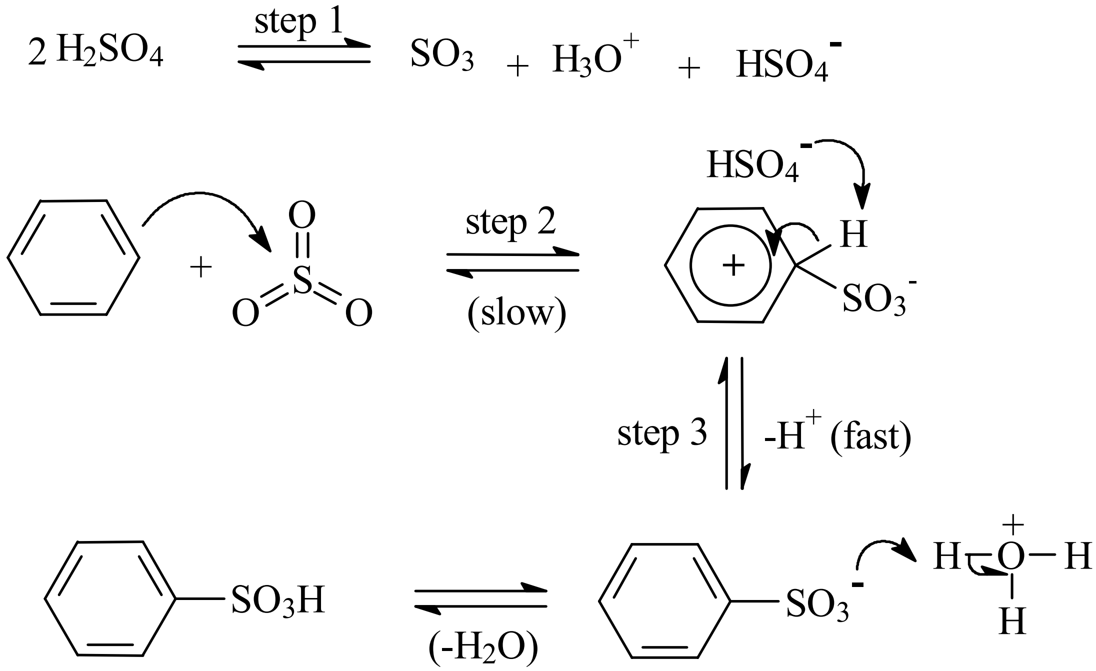

FIGURE 47. Electrophilic aromatic substitution of benzene in hot sulfuric acid.[112]

observed. During this stage, the mixture foamed, if vigorously agitated. The reaction mixture was poured into an ice bath. The aqueous solution became slightly cloudy and was filtered. After filtration and neutralization with sodium hydroxide solution to pH ~8, sodium chloride was added to generate a concentrated, saturated solution. After 24 hours the solid precipitate was filtered, dried under vacuum at 120 °C. The solid was only partially soluble in DMSO and only partially soluble in water. Deuterated solvents (DMSO-d_6 and D_2O) were used to obtain spectroscopic (^{1}H and ^{13}C NMR) information. Careful observation of the spectra suggested that the starting material, mono-substituted adduct, as well as the desired di-substituted products were present. The starting material and the mono-substituted compounds were in comparable amounts, with the disulfonated bisphenol A being recovered in the smallest relative amount (< 10%). The structures of these three species are shown below (Figure 48).

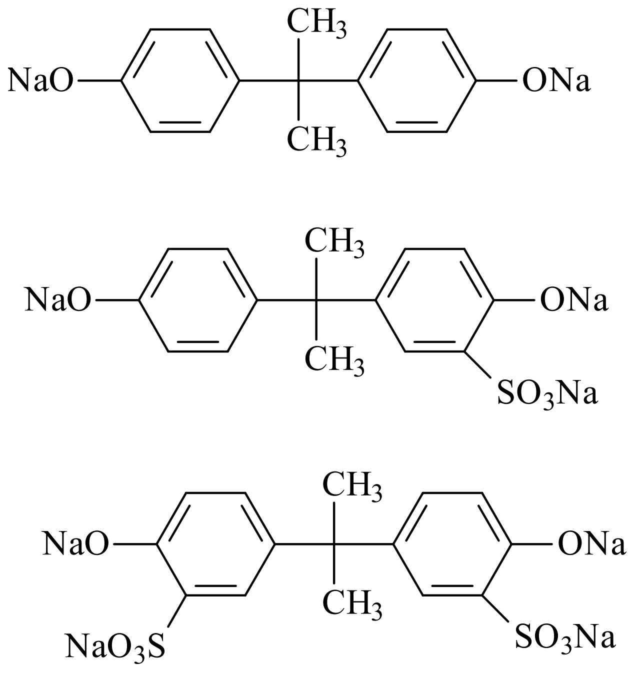

FIGURE 48. Proposed (basic form) products resulting from the sulfonation of bisphenol A, during the reaction progression (6 hours).

Given that the starting material and other intermediates were still present in the reaction mixture, the reaction was allowed to proceed for an additional 12 hours. TLC identified the presence of both mono-and di-sulfonated bisphenol A, but, unfortunately, a large percentage of insoluble material was recovered. The soluble products were treated as those of the 6-hour reaction mentioned above (i.e., water ⇒ filtration ⇒ sodium hydroxide neutralization ⇒ sodium chloride ⇒ filtration). The water-insoluble solid could not be dissolved in hot DMSO or NMP, and was assumed to be a resinous side product, thereby limiting any further analysis. The isopropylidene unit is prone to acid-catalyzed cleavage. One possible mechanism for that cleavage is depicted in Figure 49. It is likely this degradation process which ruled out heating for the attempted sulfonation reaction of bisphenol A.

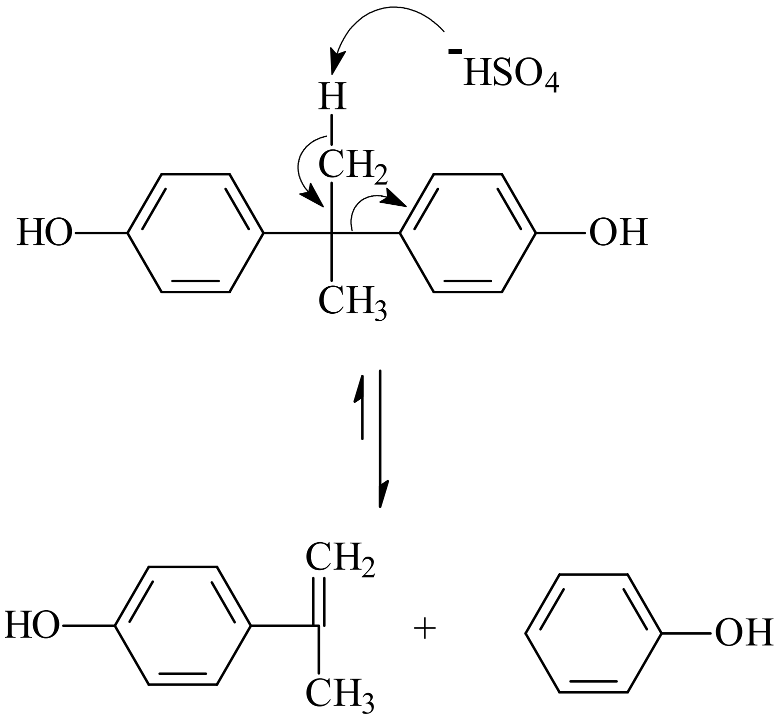

FIGURE 49. Possible acid catalyzed cleavage of the isopropylidene group in Bisphenol A.

The tetrasodium salt of disulfonated bisphenol A was isolated and, the yield after purification was low, approximately 10%. The synthesis of sulfonated bisphenol A is complicated by the possibility of acid catalyzed cleavage (Figure 49). Figure 50 displays the ^{1}H NMR of an isolated product recovered by extraction of the reaction mixture, precipitation into water, and neutralization. Chloroform and 1,2-dichloroethane were used to extract the crude mixture. As shown, the isolated compound as determined via ^{1}H NMR spectra is the disodium salt of monosulfonated sulfonated phenol.

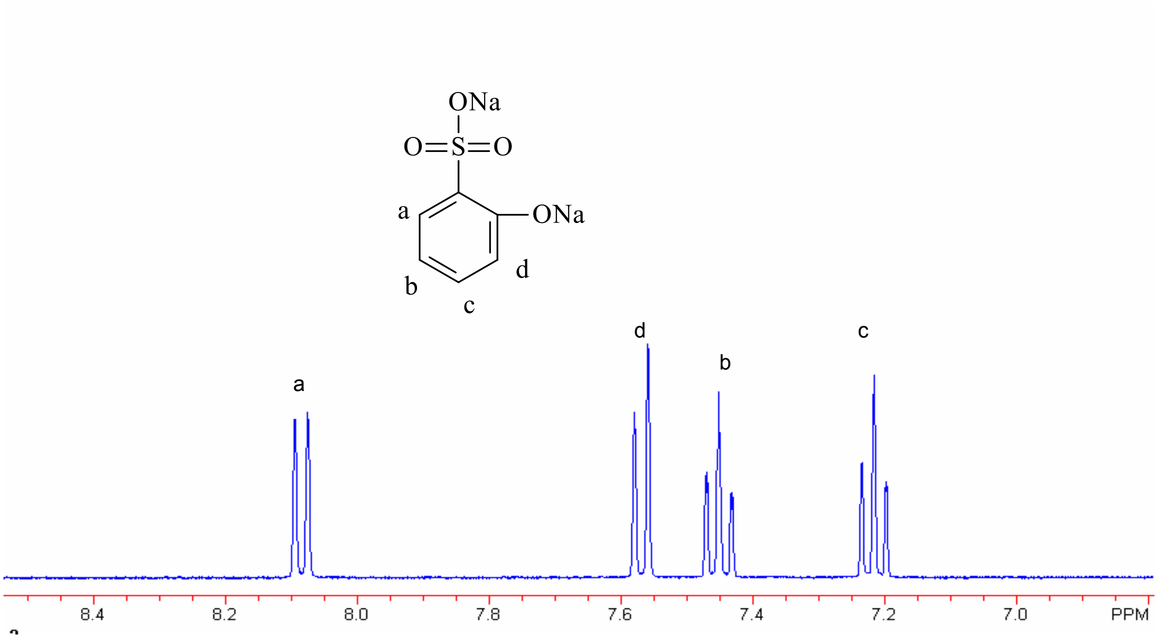

Figure 50. Proton NMR of basic-form product (disodium salt of monosulfonated phenolate) isolated from the sulfonation of bisphenol A in concentrated sulfuric acid. D_2O is the solvent.

Biphenol and 6F bisphenol A were also used to produce the corresponding sulfonated monomers. With both of these starting materials, the acid catalyzed cleavage (Figure 49) is not expected. Both biphenol and 6F bisphenol were, respectively, dissolved in concentrated sulfuric acid and allowed to react for 18 hours. Due to the electron withdrawing effect of the six fluorines of 6F bisphenol A, the reaction mixture was heated slightly at a temperature of 40 ^{o}C to enhance the reactivity.

In the sulfonation of monosubstituted benzenes, substituent effects have been well identified[112,298]. Electron-donating substituents expedite the electrophilic aromatic substitution reactions. When electron-donating groups such as alkoxy, hydroxy or alkyl groups are attached to the aromatic ring, mild sulfonating conditions (0-30 ^{o}C) have been reported to give high yields of ortho- and para- substituted sulfonated products. Not surprisingly the size of the substituent was shown to influence the product ratio (ortho- to para-) as bulky groups may hinder ortho- substitutions.

When electron-withdrawing groups, such as a nitro- or a carbonyl substituent, are attached to the aromatic compound more stringent reaction conditions (temperature greater than 100 ^{o}C) were required. Figure 51 displays various substituted benzenes and calculated electron density on each carbon. As depicted, the electron-withdrawing strength of the substituents dictates the electron-density on the carbons of the ring.

The 6F bisphenol A reaction mixture was treated as described for disulfonated bisphenol A. The yield for disulfonated 6F bisphenol A after purification was approximately 70%. The mass spectra of disulfonated 6F bisphenol A is shown in Figure 52. The aromatic region of the proton NMR for unmodified and sulfonated 6F bisphenol A is shown in Figure 53. From these spectra the disappearance of the hydroxyl- signal (~10 ppm) in *Spectra (b)* agrees with the formation of the tetrasodium salt- form of the monomer. Furthermore, the 3 distinct peaks with equal integration areas confirmed the new chemical structure with the resonances at ~7.7 ppm belonging to the protons adjacent to the attached sulfonate groups.

The fast-atom-bombardment (FAB) mass spectrum of sulfonated 6F bisphenol A showed the molecular ion peak for the tetrasodium salt at 585 Daltons. Also, quick

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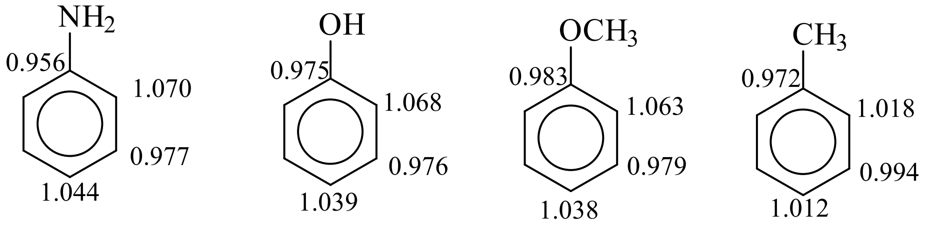
[298] Carey, F.A., Sundberg, R.J., *Advanced Organic Chemistry, 3rd Ed.*, Plenum Press, New York, 1990.

assignments can be made for the peak occurring at 563 Daltons which corresponded to the loss of one sodium atom and 541 Daltons for the loss of a second sodium atom.

Disulfonated biphenol was successfully synthesized in a greater than 75% yield. ^{1}H NMR (in D_2O) and fast-atom bombardment mass spectroscopy (411 Daltons, M – Na^+) was also utilized to confirm the structure. Unfortunately, the tetrasodium salts of disulfonated bisphenol A, disulfonated biphenol and disulfonated 6F bisphenol A are not soluble in DMAc or NMP and ^{1}H NMR was not be utilized further for this study.

Electron-releasing substituents



Electron-attracting substituents

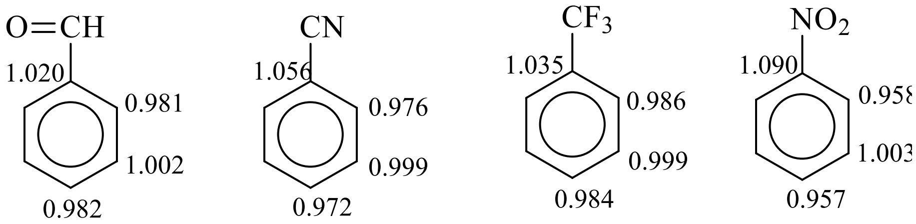


FIGURE 51. Pi-electron density for some substituted benzenes[298].

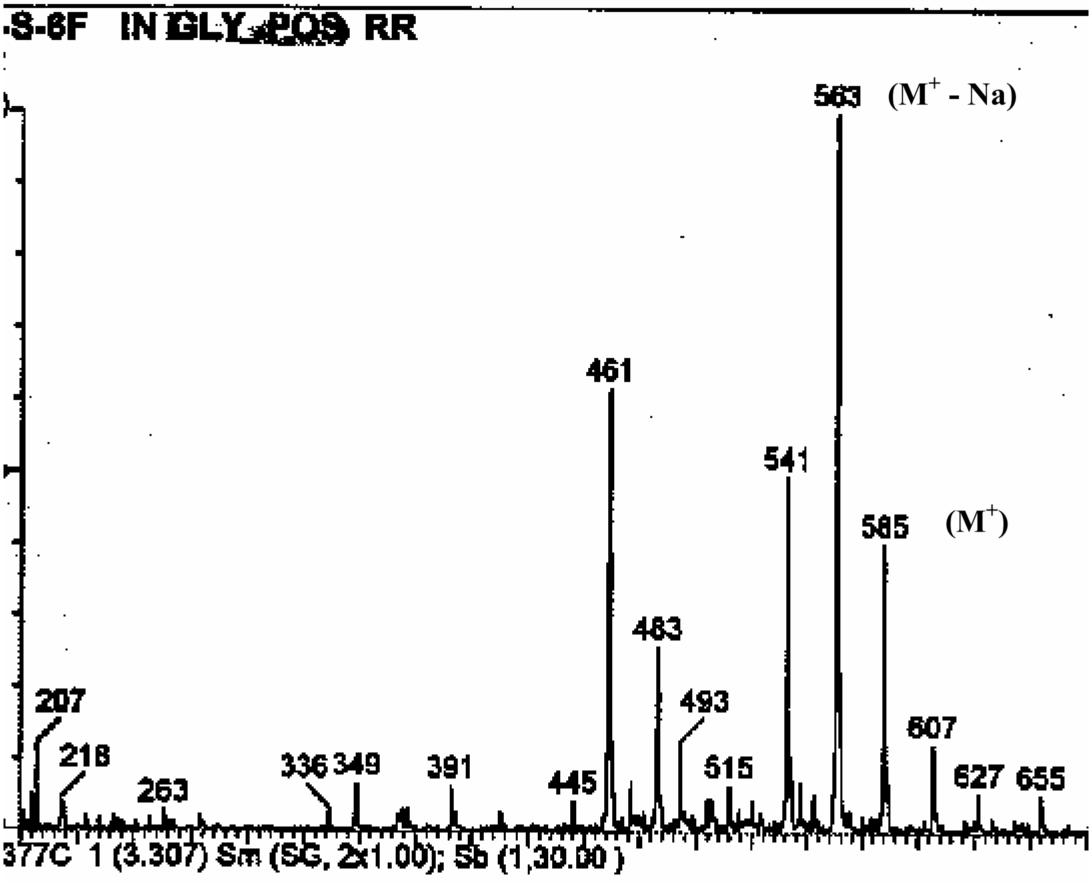


FIGURE 52. Mass Spectrum of sulfonated 6F bisphenol A.

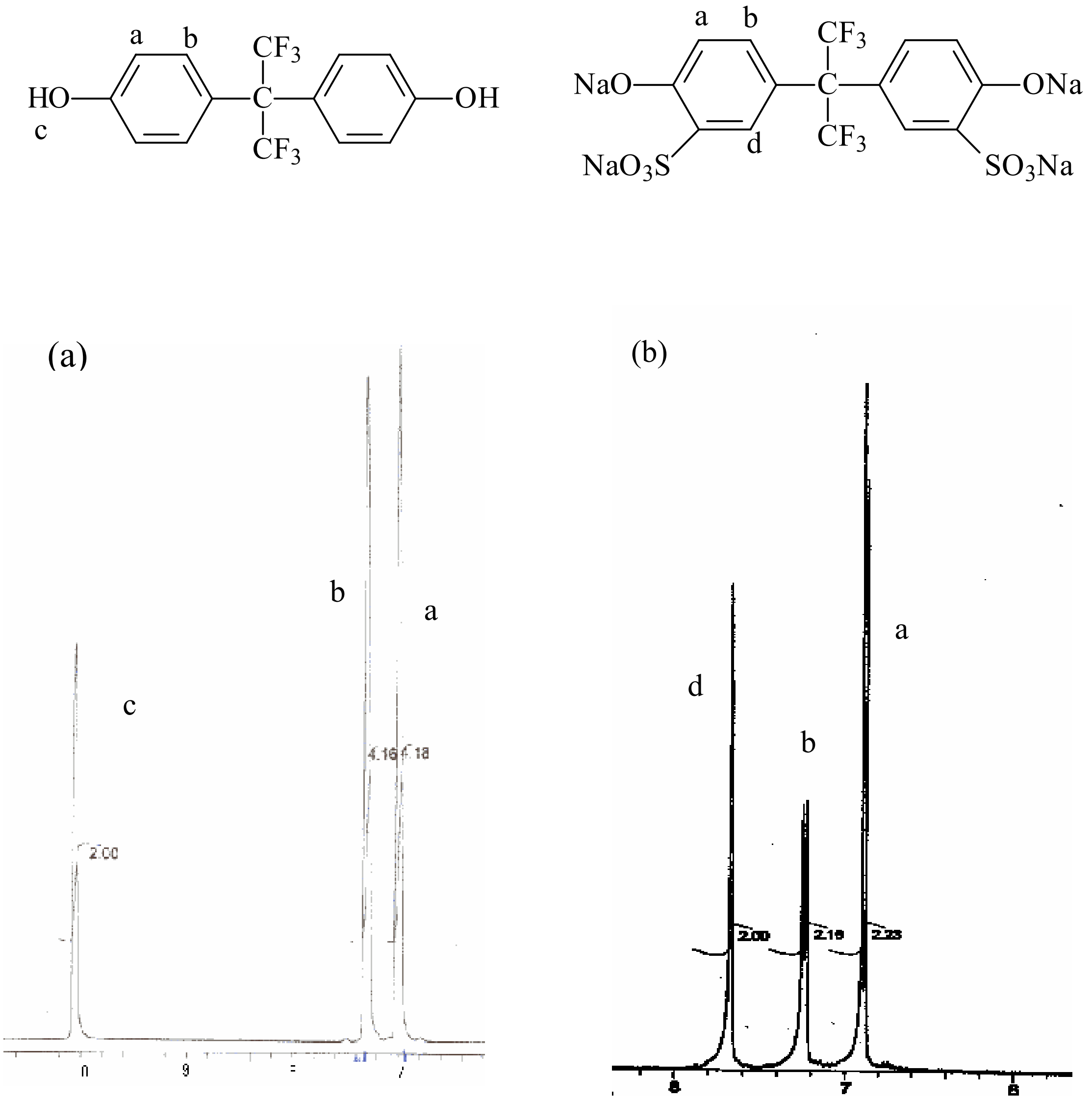
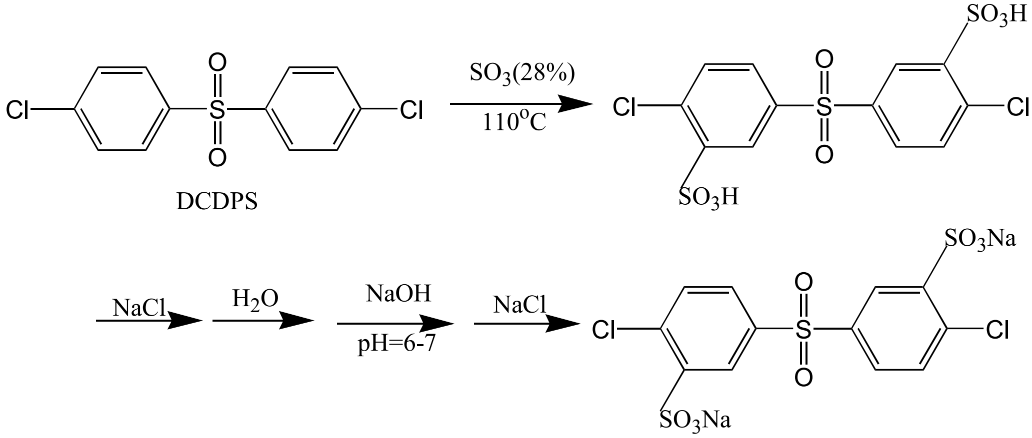


FIGURE 53. ^{1}H NMR of the aromatic region of (a) 6F bisphenol A and (b) sulfonated 6F bisphenol A salt.

3.1.2 **Sulfonated Dihalides**

The key monomer 4,4'-dichlorodiphenyl sulfone was sulfonated also by electrophilic aromatic substitution reaction via a modification of the procedure[166,167,170] reported by Ueda et al [164]. Ueda synthesized copolymers with bisphenol A using compositions of up to 30 mol % sulfonated dichlorodiphenyl sulfone and the unmodified dihalide. Robeson and Matzner also reported this compound in patent literature[299] for flame retardant aromatic polyesters, wherein sulfonated dichlorodiphenyl sulfone was simply blended into the polymer as an additive.



SDCDPS

Our procedure is outline in the above scheme. The monomer synthesis procedure reported by Ueda utilized fuming sulfuric acid in a six-hour reaction at a temperature of 90 °C. A yield of ~58%, after recrystallization from a methanol and water mixture, was reported. A detailed study for the synthesis of this disulfonated monomer was conducted and is, in fact, continuing during current scaling up efforts. Reaction temperatures of 90, 100, 110, and 120 °C were explored. The reaction temperature of 90 °C, which was reported by Ueda, produced a white precipitate after approximately 6 hours. The precipitate was the 3,3'-disulfonic acid-4,4'-dichlorodiphenyl sulfone. A similar precipitate was observed when the reaction was conducted at 100 °C. Dr. Jeff Mecham undertook the laborious task of isolating and purifying this compound using column

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[299] Robeson, L.M.; Matzner, M., *U.S. Patent 4,380,598*, 1983.

chromatography[300]. When the reaction temperature was maintained at 110 °C or greater, a homogeneous solution was sustained throughout the duration of reaction. If the reaction mixture was cooled in an ice-bath, a precipitated can then be observed. The homogenous nature of the reaction at 110 °C allowed higher yields (approaching 90%) of the desired disulfonated dichlorodiphenyl sulfone was attained. No doubt the reaction is also dependant on the concentration.

Further modifications of the reported procedure consisted of neutralizing the aqueous (after adding in to deionized water) reaction solution with sodium hydroxide. Caution was taken to keep the titrated solution cold in order to inhibit nucleophilic attack on the aromatic halide by hydroxide ion. The neutralization of the sulfonic acid units with sodium hydroxide was to confirm complete conversion of the sulfonic acid moiety to the more stable sodium sulfonate. Ueda *et al*. depended only on the exchange of the sodium cation by using a large molar excess of sodium chloride in a process termed "salting out". Figure 54 displays the elemental analysis results based on different work-up procedures.

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[300] Jeff Mecham, *Personal Conversation and Group Meeting,, October, 1999.*

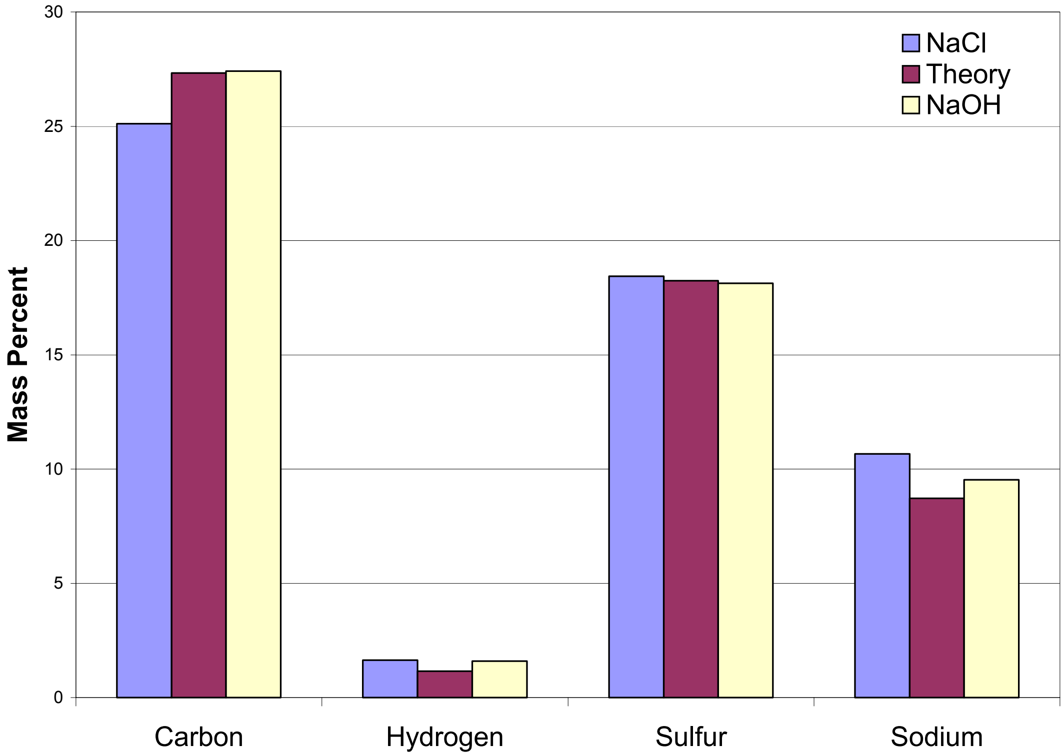


FIGURE 54. The SDCDPS elemental analysis: atomic composition as a function of monomer work-up. Excess NaCl only (left bar), titration with NaOH followed by isolation with NaCl (right bar), and the theoretically expected quantity (center bar).

Figure 54 suggest that the additional step of titration with sodium hydroxide prior to salting out with sodium chloride gave better elemental agreement with the expected values than merely exchanging with excess sodium chloride. The product using only sodium chloride appears to resulted in less than quantitative formation of the sodium salt.

Finally, the recrystallization solvent was investigated. Ueda *et al* used a methanol and water mixture to purify the monomer. However, the sulfonated dichlorodiphenyl sulfone is moderately soluble, at room temperature, in methanol and readily soluble in water. Both ethanol and isopropyl alcohol have proved to be desirable alternatives to methanol and provide pure, fine needle-like crystals. Water was still necessary to ensure removal of residual sodium chloride in the product since sodium chloride is not appreciably soluble in alcohols. Further optimization and single crystal analysis of the product is ongoing.

This modified electrophilic substitution reaction procedure gives only the expected disulfonated product identified after work-up and crystallization. The sulfonated dichlorodiphenyl sulfone monomer has the expected structure with the sulfonated groups meta- to the sulfonyl group and ortho- to the chlorine group. Recall that the lone pair of electrons on chlorine can help stabilize the ortho- substitution even though it may decrease the rate of electrophilic substitution due to an electron-withdrawing effect[298].

The electrophilic substitution reaction, under these conditions, gives only the di-substituted product. Since there are two rings it is conceivable that a mono sulfonated product could be isolated. However, the reaction was easily monitored using thin-layer chromatography (TLC). Approximately one hour after homogeneity was reached three different spots were observed when a mixture of ethyl acetate and methanol (7:1) was used as the mobile phase. The peaks were identified as starting material (DCDPS), followed by mono substituted DCDPS, then di-substituted DCDPS relative to the solvent front. In fact the disulfonated DCDPS product was typically unmoved from the original spotting location. At 110 ^{o}C, the reaction was complete (i.e., only disulfonated dichlorodiphenyl sulfone) in approximately 5 hours but, as reported, was continued for 6 hours. Performing the sulfonation reaction of dichlorodiphenyl sulfone at 120 ^{o}C also yielded the sulfonated monomer in good yields (~70%) after only 4.5 hours and crystallization from an alcohol and water mixture.

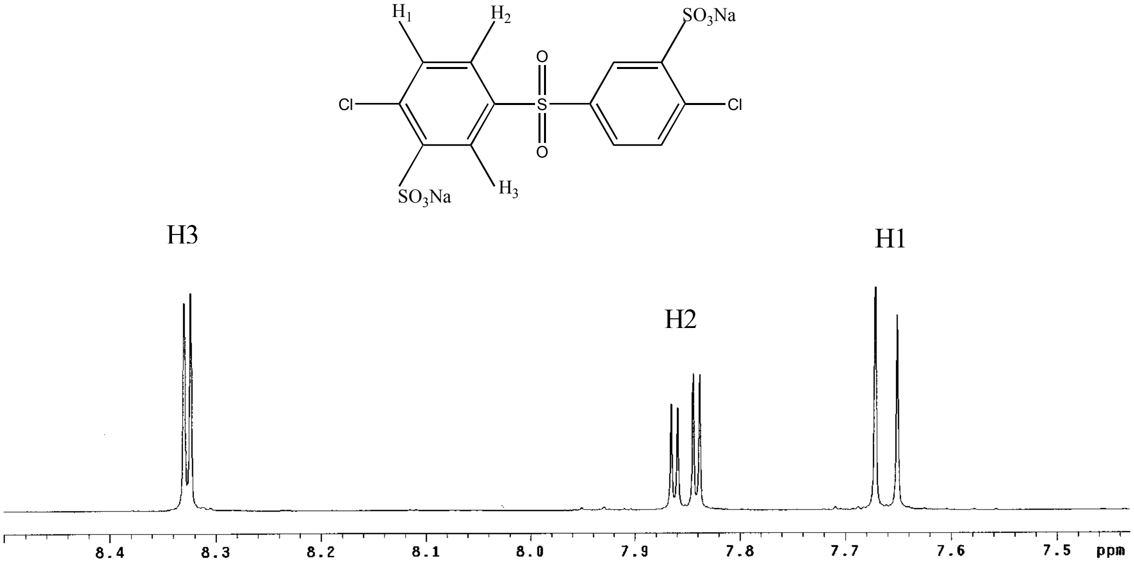


FIGURE 55. ^{1}H NMR of 3,3’-disodium-4,4’-disulfonated dichlorodiphenyl sulfone.

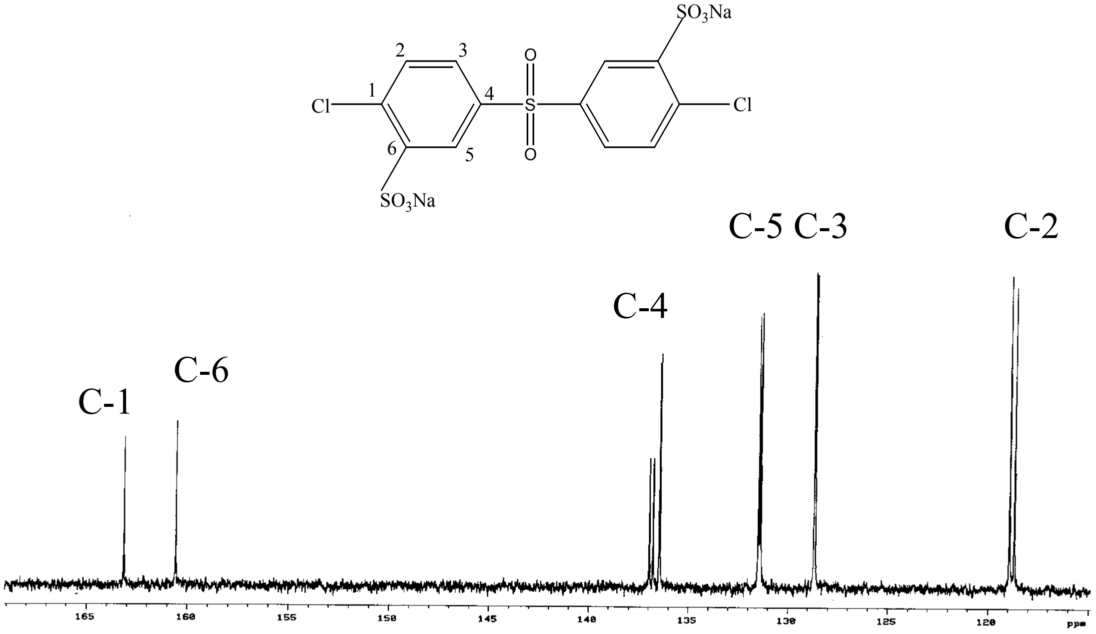


FIGURE 56. ^{13}C NMR of 3,3’-disodium-4,4’-disulfonated dichlorodiphenyl sulfone

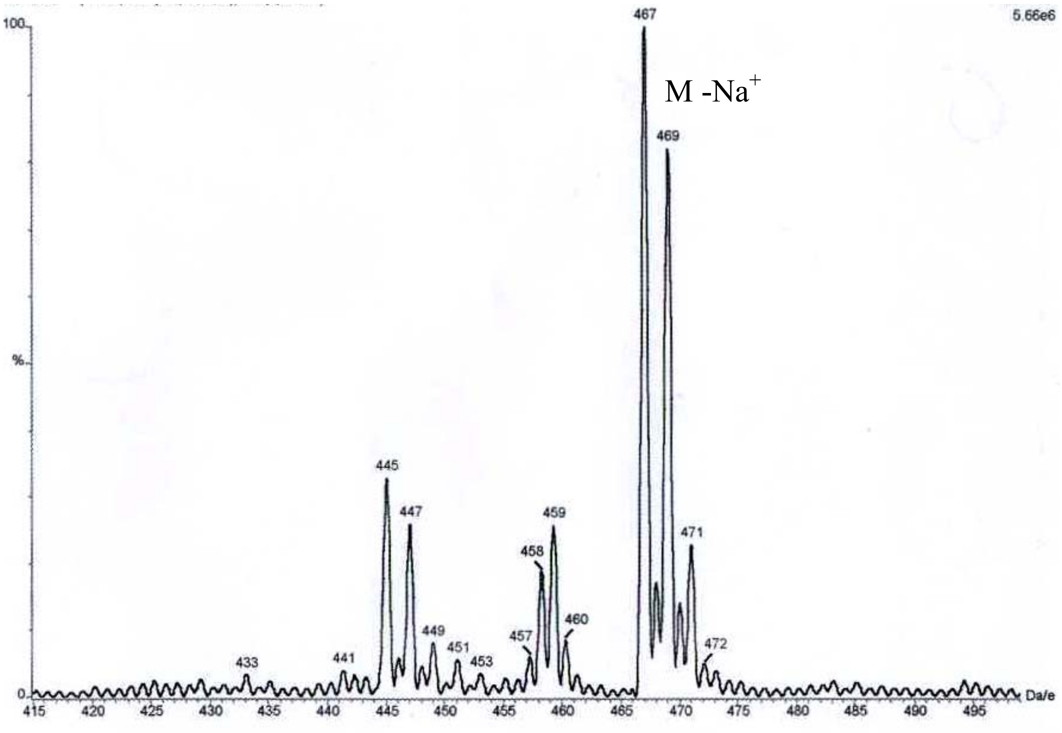


FIGURE 57. Mass spectrum of 3,3'-disodium sulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS).

After recrystallization, the dried product was dissolved in dimethylsulfoxide (DMSO-d_6) and analyzed by ^{1}H and ^{13}C NMR for structural confirmation (Figure 55 and 56). Figure 57 displays the fast atom bombardment mass spectrum. The successful identification of the parent ion at 467 Daltons (489.83-22.97 Na^+) further confirm the monomer structure.

Difluorodiphenyl sulfone was also sulfonated using fuming sulfuric acid at 110 °C. A homogeneous mixture was maintained during the six hours of reaction time. A less pronounced color change was visible as compared to the sulfonation of the various bisphenols. The sulfonations of dichlorodiphenyl sulfone and difluorodiphenyl sulfone produced a faint color ranging from light green to light brown thoughout the synthesis. The sulfonated difluorodiphenyl sulfone reaction solution was isolated by addition into ice-cold deionized water, titrated with sodium hydroxide and precipitated with sodium chloride as detailed for SDCDPS. Care was taken to maintain a low solution temperature to minimize or eliminate the formation of the unreactive bisphenol via nucleophilic attack on the activated halide by water or the –OH of the sodium hydroxide. Recrystallization was successfully performed in an ethanol and water (8:1) mixture to yield fine needles. No melting point was observed for either disodium salt of the sulfonated dihalide monomers at temperatures below 350 °C. Figure 58 displays the aromatic region of a proton NMR spectrum of sulfonated difluorodiphenyl sulfone. The coupling of the protons to the fluorine atoms is known to split the respective peaks. Mass spectroscopy and elemental analyses were completed and provided expected results. Elemental analysis results (calculated): carbon 31.45; sulfur 20.9; hydrogen 1.32; sodium 10.03. Found: carbon 31.44; sulfur 21.33; hydrogen 1.4; sodium 9.89.

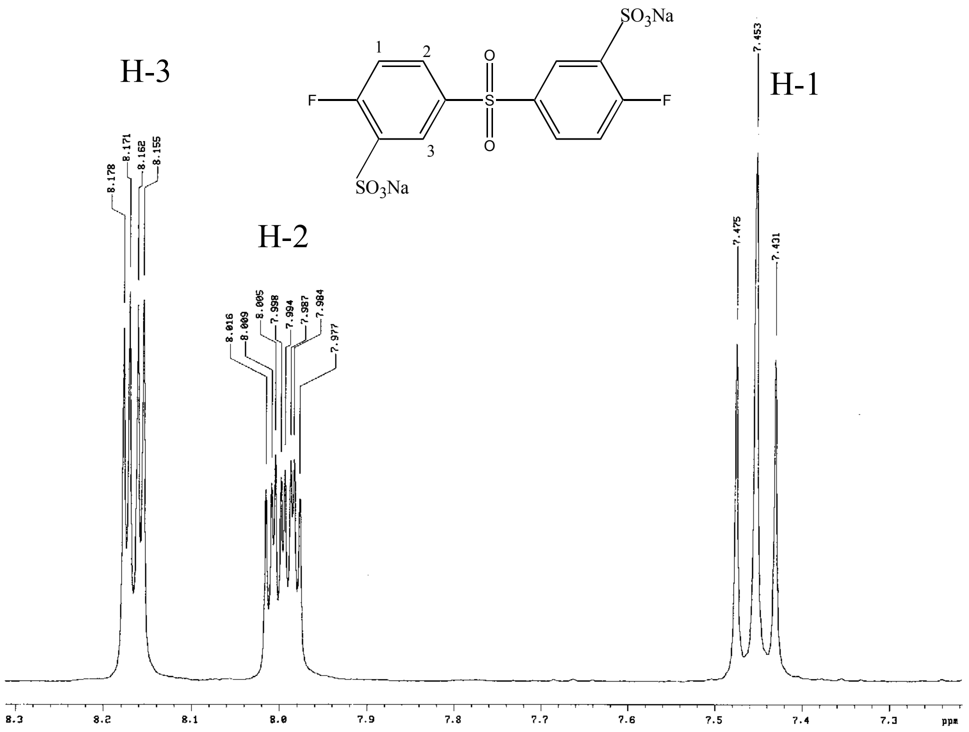


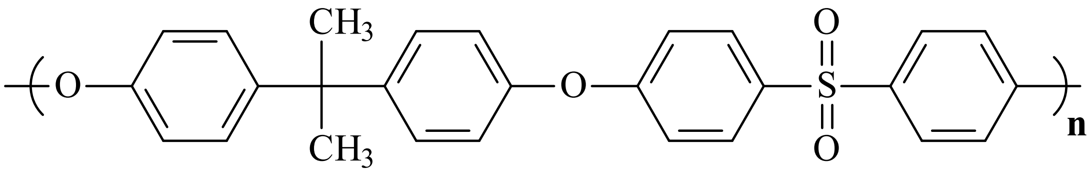
FIGURE 58. ^{1}H NMR of 3,3’-disodium sulfonated-4,4’-difluorodiphenyl sulfone.

3.2 Polymer Synthesis

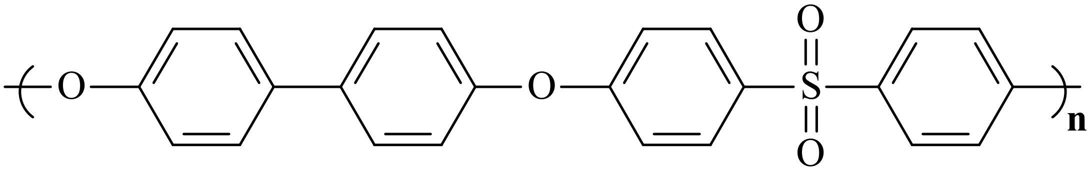
As described in the literature review section in Chapter 1, there are several synthetic routes to poly (arylene ether sulfones). Nucleophilic aromatic substitutions have several advantages for the generation of linear polymers over electrophilic approaches. Of the three noted nucleophilic aromatic substitution procedures, the weak base (potassium carbonate in an aprotic solvent) procedure is probably the preferable choice. The strong base, sodium hydroxide, approach is a two-pot procedure that requires careful stoichiometric control of the reactants. Krichildorf's method utilizes silylated bisphenols and is limited to fluorinated monomers. The weak base procedure is a one-pot process that does not require any additional preparation of monomers.

3.2.2 Synthesis of Homopolymers

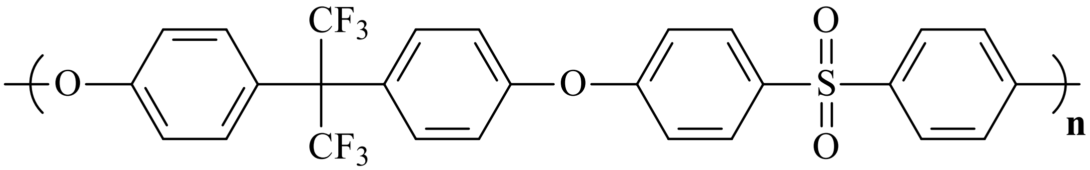
Model or control polymers were synthesized using bisphenol A, biphenol, hydroquinone, and 6F bisphenol A (also referred to as bisphenol AF), respectfully, with 4,4'-dichlorodiphenyl sulfone. Each bisphenol was polymerized with a stoichiometric amount of dichlorodiphenyl sulfone with typically a fifteen-mole percent (15 mol%) excess of potassium carbonate, based on the bisphenol. High molecular weight polymers were synthesized in DMAc and NMP at a typical polymerization temperature of 175 ^{o}C in 16 hours, after dehydrating the system with toluene at 145-155 ^{o}C for four hours. The viscous polymer solution was diluted with DMAc and filtered to remove most of the salts. The filtered polymer was isolated from solution by precipitation into a mixture of vigorously stirred methanol and water (10/1) in a blender, then collected by filteration. The fibrous strings were dried in a vacuum oven for 24 hours at temperatures of at least 160 ^{o}C. Figure 53 depicts the repeat units of the control poly (arylene ether sulfones). Table 1 displays the molecular weights (M_n) and intrinsic viscosity ($[\eta]$) of each control polymer via universal calibrated GPC in NMP.



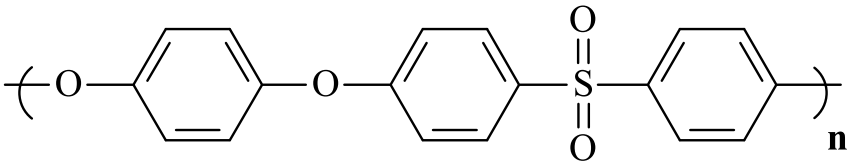
Bisphenol A based poly(ether sulfone) , **Bis A**



Biphenol based poly(ether sulfone), **BP**



6F bisphenol A based poly(ether sulfone), **6F**



Hydroquinone based poly(ether sulfone), **HQ**

FIGURE 59. Repeat unit of each control poly (arylene ether sulfone).

Table 1. Typical molecular weight (M_n) from Universal calibration GPC and Intrinsic Viscosity [η] of control poly (arylene ether sulfone)s using NMP as solvent.

Polymer	**M_n (g/mol)**	**[η] (dL/g)**, 25 °C
Bis A	46000	0.72
BP	42000	0.60
6F	39000	0.63
HQ	44000	0.59

The above facile polymerization conditions to yield high molecular weight control (unsulfonated) polymers suggested acceptable reaction conditions for their respective sulfonated copolymers. A series of novel sulfonated polymers was prepared by copolymerizing one of four bisphenols, dichlorodiphenyl sulfone and sulfonated dichlorodiphenyl sulfone at varying molar ratios of dihalide monomers. In addition, copolymers were also synthesized using the difluorodiphenyl sulfone / sulfonated difluorodiphenyl sulfone comonomer system when high percentages of sulfonated units (> 40 mol %) were desired.

3.2.2 Synthesis of Sulfonated Copolymers

A group of copolymers was synthesized using (always 4,4'-isomers) bisphenol A, biphenol, hydroquinone or 6F bisphenol A with various molar stoichiometric amounts of dichlorodiphenyl sulfone and sulfonated dichlorodiphenyl sulfone. The respective molar amount of the sodium salt of 3,3'-disulfonated 4,4'-dichlorodiphenyl sulfone (SDCDPS) was increased in increments of ten mole % while, in order to maintain stoichiometric balance, the dichlorodiphenyl sulfone (DCDPS) molar amount was correspondingly decreased. Series of sulfonated copolymerizations were attempted using 0 to 60 mol% sulfonated comonomer.

A typical reaction, using similar polymerization conditions as the control polymers, is given for hydroquinone containing 40 mol% sulfonated dichlorodiphenyl sulfone and 60 mol% unsulfonated sulfone monomer. First, 1.10 g (10 mmol) hydroquinone, 1.1487 g (4 mmol) 4,4'-dichlorodiphenyl sulfone (DCDPS), 2.9476 g (6 mmol) disodium-3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS) and 1.15 equivalents (1.6 g) of potassium carbonate were added to a 3-neck flask fitted with a mechanical stirrer, a nitrogen inlet and a Dean Stark trap. Dry N,N-dimethylacetamide (DMAc) (~30 mL) was introduced to afford a 20% solids concentration, and toluene (12 mL) was used as an azeotroping agent. The reaction mixture was refluxed at 150 ºC for 4 hours to remove most of the toluene and dehydrate the system. Next, the reaction temperature was raised slowly to 175 ºC for 20 hours. The viscous solution obtained was cooled and diluted

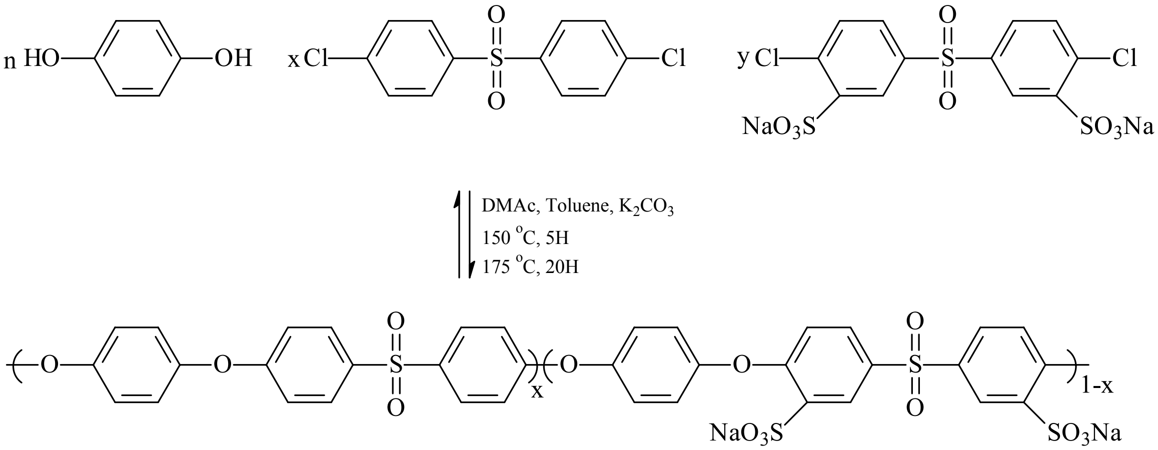


FIGURE 60. Synthesis of hydroquinone based sulfonated poly (arylene ether sulfone) copolymers via direct copolymerization.

with DMAc to allow easier filtering. The reaction product was filtered through filter paper to remove most of the salts, and isolated by addition to stirred deionized water. The disulfonated copolymers were dried under vacuum at 120 ºC for 24 hours after being washed several times with deionized water.

The sulfonated copolymers were isolated from deionized water as swollen fibers. The amount of swelling in the copolymers was a direct function of the degree of sulfonation, based on the amount of sulfonated dichlorodiphenyl sulfone utilized. For each sulfonated copolymer, films were cast on glass substrates using redissolved copolymers as described in the experimental section. It was quickly noticed that all copolymers with more than 40 mol% sulfonated dichlorodiphenyl sulfone typically did not produce coherent dry films. Table 2 displays the intrinsic viscosities of the copolymers. Even though high intrinsic viscosities, normally indicative of high molecular weight polymers, are determined in NMP when 40 and 50 mol% sulfonated dichlorodiphenyl sulfone, the cast dry films were somewhat brittle. Revisiting the paper by Ueda *et al.*[164], it was apparent that they encountered similar difficulties of producing high molecular weight polymers. These researchers reported poly (arylene ether sulfone) copolymers using up to 30 mol% SDCDPS with an obvious decreased inherent viscosity (η_{inh} ~ 0.85 and 0.68 dL/g) compared to their sulfonated copolymer using only 20 mol% SDCDPS (η_{inh} ~ 1.0). Film forming properties were not discussed in their paper.

Unfortunately, due to interaction with the size exclusion columns in the gel permeation chromatograph (GPC) the sulfonated copolymers, dissolved in NMP containing P_2O_5, were retained in the columns and gave meaningless molecular weight data. Intrinsic viscosity data were relied on heavily to gain some information of the size on the sulfonated polymeric materials. The relationship between viscosity and molecular weight in dilute solutions is given by the Mark-Houwink-Sakurada Equation (MHS)[100]. The MHS equation, used to determine or relate intrinsic viscosity to the viscosity average molecular weight (M_v) of a polymer, is:

$$[\eta] = kM_v^a$$

where [η] is the intrinsic viscosity, and k and a are constants dependent upon solvent, temperature, and the type of polymer. Unfortunately, quantitative characterization of polyelectrolytes is difficult.

Table 2. Intrinsic viscosity values of various Poly(arylene ether sulfone) Sulfonated Copolymers with copolymerization temperature of 175 ^{o}C.

Polymer Type	**$[\eta]^{NMP,25oC}$**
BisA-0	0.72
BisA-S10	0.80
BisA-S20	0.90
BisA-S30	0.99
BisA-S40	1.20
BP-0	0.60
BP-S10	0.74
BP-S20	0.92
BP-S30	1.00
BP-S40	1.20
6F-0	0.63
6F-S10	0.69
6F-S20	0.76
6F-S30	0.79
6F-S40	0.85
HQ-0	0.59
HQ-S10	0.65
HQ-S20	0.80
HQ-S30	0.89
HQ-S40	0.98

However, one must recall the intrinsic viscosity is a measure of the hydrodynamic volume/mass of the polymer in a solvent. The sulfonated poly (arylene ether sulfone) copolymers have an increasing number of pendent bulky sulfonic acid moieties as the molar amount of the sulfonated dihalide is increased. The bulky side groups make the copolymer appear larger and contribute to the observed high intrinsic viscosities. Similar trends of increased intrinsic viscosities with increased ionic content have been reported by several researchers for a number of polymer systems[54, 55,128,129,184,301].

The aforementioned copolymers synthesized employing hindered bisphenols were successful in producing high molecular weight polymers when slightly higher reaction temperatures and high boiling solvents like sulfolane were used. McGrath *et al*. used a temperatures up to 190 °C while investigating biphenol based sulfonated poly (ether sulfone) copolymers via direct polymerization[166]. By increasing the reaction temperature and using NMP, a higher boiling solvent than DMAc, film forming polymers were prepared using up to 60 mol% dichlorodiphenyl sulfone.

Accordingly, a series of sulfonated copolymers using bisphenol A, hydroquinone and 6F bisphenol was polymerized at higher temperatures and NMP. A typical polymerization is given using bisphenol A and 60 mol% sulfonated dichlorodiphenyl sulfone. First, 2.28 g (10mmol) bisphenol A, 1.1487g (4mmol) DCDPS, 2.9476g (6mmol) SDCDPS with 1.15 equivalent of potassium carbonate were added to a 3-neck flask equipped with mechanical stirrer, nitrogen inlet and a Dean Stark trap. NMP was introduced to afford a 20% solids concentration and toluene was used as an azeotropic agent. The reaction mixture was heated under reflux at 155ºC for 4 hours to remove most of the toluene and dehydrate the system. Next, the temperature was raised slowly to 190ºC for at least 16 hours. The viscous solution was cooled and diluted with N,N-dimethyl acetamide (DMAc). The reaction product was filtered to remove most of the salts, and isolated by addition to stirred deionized water. The sulfonated copolymer was washed with deionized water and dried under vacuum at 120 ºC for 24 hours. Copolymers with other compositions were also prepared by this procedure.

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[301] Lundberg, R.D.; Makowski, H.S., *J. Polym. Sci., Polym. Phys. Ed.,* 1980, 18, 1821.

Much effort has gone into the development and understanding of the conditions needed to achieve high molecular weight, film forming sulfonated copolymers. The use of pure monomers was necessary. Arguably of equal importance was the necessity for the gradual increase in the reaction temperature. Almost invariably, if the reaction temperature was quickly ramped from the reflux temperature to the final 190 °C polymerization produced only low molecular weight products. These oligomers

Table 3. Intrinsic viscosity values (dL/g)* of sulfonated poly (arylene ether sulfone) copolymers based on various bisphenols synthesized at 190 oC.

Mol% of Sulfonated Dichlorodiphenyl Sulfone →

Polymer Type/ [η]	10%	20%	30%	40%	50%
Bis A	0.78	0.82	1.20	1.56	1.70
6F	0.69	0.86	1.49	1.70	1.82
BP	0.80	0.91	1.51	1.82	1.97
HQ	0.81	1.07	1.80	2.01	2.10

* Intrinsic viscosity determined in NMP at 25 °C.

had typical intrinsic viscosities ranging from 0.1 to 0.4 dL/g. The dark color and low viscosity of the reaction solutions were characteristic of these unsuccessful copolymerizations. The dark color may reflect to some degradation of oligomers and possibly some solvent degradation. When the polymerization temperature was gradually increased by incremental distillation of toluene, transparent, wheat-colored viscous solutions could be observed after 20 hours. Table 3 shows the intrinsic viscosities of the sulfonated poly (arylene ether sulfone)s polymerized at a final temperature of 190 °C.

Table 3 shows the increase in intrinsic viscosity with increasing degree of sulfonation. The intrinsic viscosities of each sulfonated copolymer was increased using 190 °C compared to the corresponding copolymers polymerized at 175 °C. The transparent films of all the copolymers were all coherent and fairly ductile. Thin films for the 6F bisphenol copolymer with 40 mol% SDCDPS would form but were not creasible. Even thick 6F-40 films fell apart in boiling water within 15 minutes. The boiling water test was used as a screening method for all the sulfonated films.

Wang *et al*. reported the synthesis of the 3,3'-disulfonated 4,4'-difluorodiphenyl sulfone in research investigating sulfonated sulfide sulfone copolymers[184] (Figure 61). Poly(phenylene sulfide sulfones) are engineering polymers similar to poly (arylene ether sulfones) and are known for their excellent chemical resistance and thermo-oxidative stability.[302]

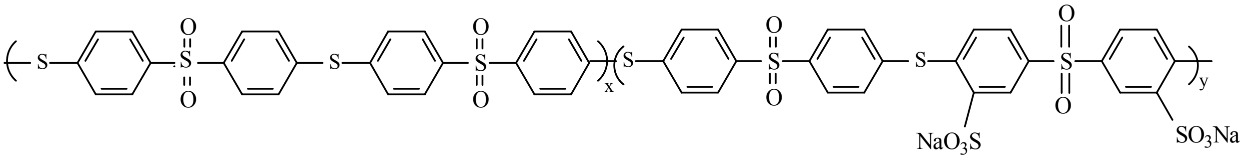

FIGURE 61. Sulfonated poly (sulfide sulfone) via direct copolymerization[184]

Sulfonated poly (arylene ether sulfone) copolymers were also synthesized using bisphenol A, biphenol, hydroquinone and 6F bisphenol A and difluorodiphenyl sulfone and sulfonated difluorodiphenyl sulfone. The sulfonated difluorodiphenyl sulfone monomer synthesis was discussed earlier (Section 3.1.2). Since good film forming polymers were achieved using up to 40 mol% sulfonated dichlorodiphenyl sulfone, the sulfonated difluorodiphenyl sulfone monomer (SDFDPS), copolymerized with difluorodiphenyl sulfone (DFDPS), was employed for 50 and 60 mol% sulfonated poly(arylene ether sulfones). A copolymer using 6F bisphenol A was also produced using 40 mol% SDFDPS.

Several polymerizations using the difluorosulfone copolymer system were attempted at 190 ^{o}C using conditions similar to those described for the DCDPS/SDCDPS copolymers. However, low viscosity solutions that produced discolored (brown) fibrous powder were obtained at this temperature. Suspecting some degradation of either the monomers and/or oligomers formed early in the reaction, the polymerization conditions were reverted to the procedure using the lower polymerization reaction condition temperatures. After dehydrating the reaction system with refluxing toluene at 150 ^{o}C, the reaction mixture was slowly heated to 175 ^{o}C and allowed to react for 16-30 hours. Following the removal of the salts by filtering the diluted polymer solution, swollen polymer fibers were collected from stirred deionized water. Successful copolymerizations for all four bisphenols occurred under these reaction conditions. The sulfonated poly (arylene ether sulfone) copolymer produced tough, ductile films by solution casting on glass substrates from DMAc. Table 4 displays the intrinsic viscosity values.

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[302] Campbell, R. W.; To Phillips Petroluem Co.; *U. S. 4,016,145*; 1997

Table 4. Influence of bisphenol and the degree of sulfonation on the intrinsic viscosity (dL/g) of disulfonated poly (arylene ether sulfone)copolymers via direct copolymerization using DFDPS and SDFDPS.

mol% SDFDPS →

Polymer Type/$[\eta]^{\mathrm{NMP},\ 25\ \mathrm{C}}$	50	60
Bis A	1.95	2.15
BP	2.19	2.34
HQ	2.21	2.38
6F	2.09	2.22

The same trend of increased intrinsic viscosity with increased degree of sulfonation was also exhibited for the copolymers using difluorodiphenyl sulfone and sulfonated difluorodiphenyl sulfone. Comparison of the intrinsic viscosities tabulated in Table 3 to Table 4 showed that for each copolymer higher viscosities were measured using the DFDPS/SDFPFS system. Even though the intrinsic viscosity values were not greatly different, their film ductilities and stabilities in boiling water were clearly greatly improved.

Acidification of Sulfonated Copolymer Films

In addition to the stability test in boiling water, the films were exposed to relatively high concentrations of sulfuric acid for testing as proton exchange membranes. The films of all the sulfonated copolymers were cast in their salt- forms, essentially from the polymerization flask. Surface analysis (ESCA) and phosphorescence spectroscopy showed that a large percentage of the sulfonate groups were converted from their sodium salt form, as introduced as the sulfonated comonomer, to the potassium salt. The potassium was obviously, and not surprisingly, exchanged from the potassium carbonate utilized as the base during the copolymerization.

To be used for proton conductivity, the films in proton exchange membranes in fuel cells must be in their free-acid form. To convert the films into their acid-form, they were typically soaked in 2 *N* sulfuric acid at room temperature for at least 24 hours (also termed **Method 1**). The high relative concentration and large molar excess (approximately 20 times) of the sulfuric acid to the sulfonated groups on the polymer backbone was the driving force for the exchange reaction. Poly(arylene ether sulfones) are very stable in aqueous acids, as noted earlier.

3.3 **Polymer Characterization**

Although there are many techniques used to characterize polymers. Spectroscopic and thermal characterization are two important techniques used to gather information. FTIR and ^{1}H NMR were employed to provide structural and compositional characterizations of the control and sulfonated copolymers synthesized from bisphenol A, biphenol, hydroquinone, and 6F bisphenol A. The somewhat specialized characterization technique of impedance spectroscopy was utilized to study the proton conductivities of each sulfonated copolymer.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to explore the thermal behavior of the polymers synthesized in this investigation. The important property of water uptake was determined by measuring the dry weight of the films and the equilibrium wet weight of the polymer.

Spectroscopic Analysis

3.3.1 **Fourier Transform Infrared Spectroscopy (FTIR)**

Fourier transform infrared spectroscopy is a powerful tool used to characterize the functional groups in a material. FTIR has been successfully utilized to characterize many sulfonated polymers. [161,175,176,303,304] Tran developed FTIR quantitative techniques to characterize post-sulfonated poly(arylene ether sulfones)[304]. By standardization of absorption for one or more functional groups that are not changing during the reaction, it was demonstrated that the absorption intensity of the sulfonic acid increased with increasing degree of sulfonation.

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[303] Sakurai, K.; Douglas, E.P.; MacKnight, W.J., *Macromolecules*, 1993, 26, 208.

[304] Tran, C., *M.S. Thesis*, VPI & SU, 1980

Accordingly, a series of FTIR spectra were compiled and standardized for the sulfonated poly(arylene ether sulfones) synthesized via direct copolymerization in this research. The quantitative series of FTIR spectra for the biphenol based sulfonated copolymers is depicted in Figure 62. The polymer spectra were normalized by using the absorption of the Ar-O-Ar linkage at 1006 cm^{-1} in the polymer backbone. The obvious increase in *intensity* of salt of the sulfonate group stretching frequency at 1030 cm^{-1} and 1098 cm^{-1} with increasing degree of sulfonation provides proof of the successful incorporation of the sulfonated activited dihalide (sulfonated dichlorodiphenyl sulfone or sulfonated difluorodiphenyl sulfone) in the copolymers. Similar FTIR series were produced for all four bisphenol copolymers.

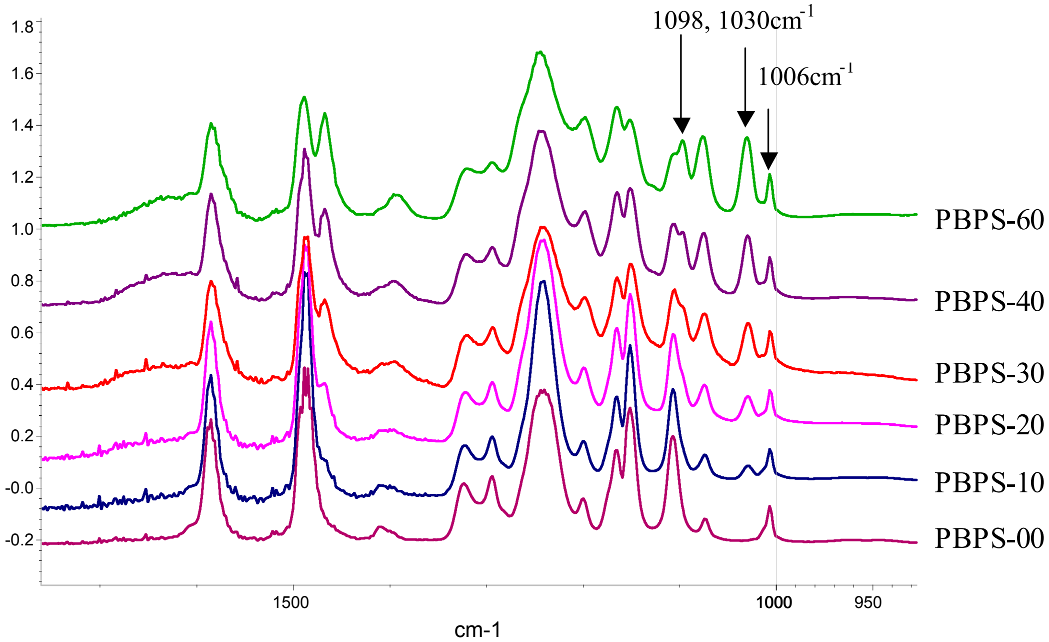
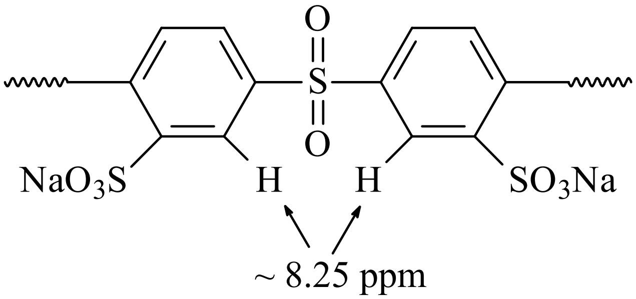


FIGURE 62. Influence of the degree of disulfonation on the FT-IR of sulfonated poly (arylene ether sulfone) copolymers

3.3.2 ^{1}H NMR Spectroscopy

Proton NMR spectroscopy has been repeatedly employed to provide structural confirmation of the synthesized poly (arylene ether sulfones). For this research, NMR has allowed for structural as well as compositional determinations for each copolymer. By integration and appropriate rationing of known reference protons of the polymer, the relative copolymer compositions of the various sulfonated polymers were determined.



The two protons ortho- to the sulfone and adjacent to the sulfonate group (~8.25 ppm) on the sulfonated dihalide monomer were well separated from the other aromatic protons of all the copolymers. The ^{1}H NMR spectrumfor the copolymer in 6F-30 Figure 63 is a representative ^{1}H NMR spectrum. The integration revealed that 27 mol% of sulfonated dichlorodiphenyl sulfone was incorporated into the polymer; this is well within experimental error for this method. Similar integrations and calculations for the other sulfonated poly (arylene ether sulfones) were performed and were typically within plus/minus ten percent (10%) of the expected values. The proton NMR integration calculations for a selected sulfonated poly (arylene ether sulfone), 6F-30, via direct copolymerization is shown in Table 5.

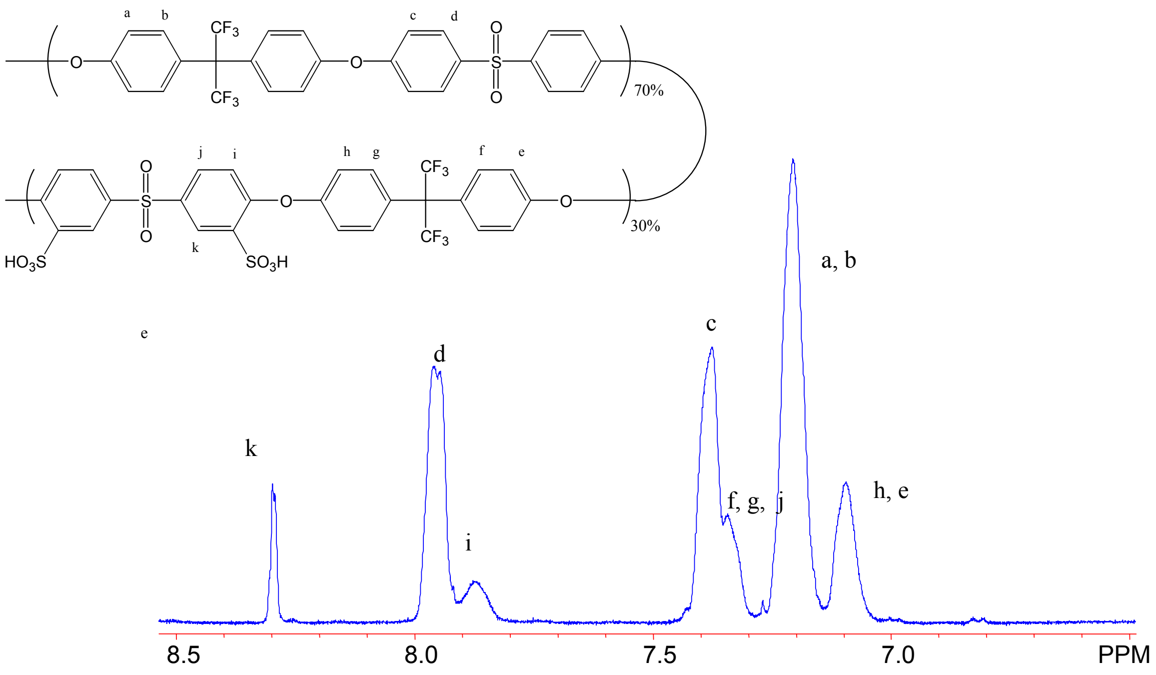


FIGURE 63. ^{1}H NMR and peak assignments of 6F-30 sulfonated copolymer.

Table 5. Degree of sulfonation based on ^{1}H NMR integration calculation for selected sulfonated poly(arylene ether sulfones) synthesized via direct copolymerization.

Copolymer	Degree of Disulfonation (%)
Bis A-30	33
Bis A-40	37
BisA-50	48
BP-30	32
BP-40	40
BP-50	49
HQ-30	34
HQ-40	42
HQ-50	53
6F-30	27
6F-40	41
6F-50	52

<u>Sample Calculation</u> using 6F-30 sulfonated copolymer:

Using the integration for the 2- ***k*** protons (I_k) and the integration for the 8-(***a*** + ***b***) protons ($I_{(a+b)}$), if $I_k = 3.6$ and $I_{(a+b)} = 52.8$,

then [I_k / 2 protons] ÷ [($I_{(a+b)}$) / 8 protons] =*Fraction of Sulfonated Repeat Units*

So, [3.6 / 2] ÷ [52.8 / 8] = 1.8 ÷ 6.6 = 0.273

0.273 x 100% = 27.3% *Sulfonated Repeat Units*

Wang *et al*. was able to use *endcapping* and ^{1}H NMR spectroscopy to determine the molecular weights of biphenol based sulfonated poly(arylene ether sulfones) synthesized via direct polymerization[305]. Figure 64 depicts the endcapping reaction.

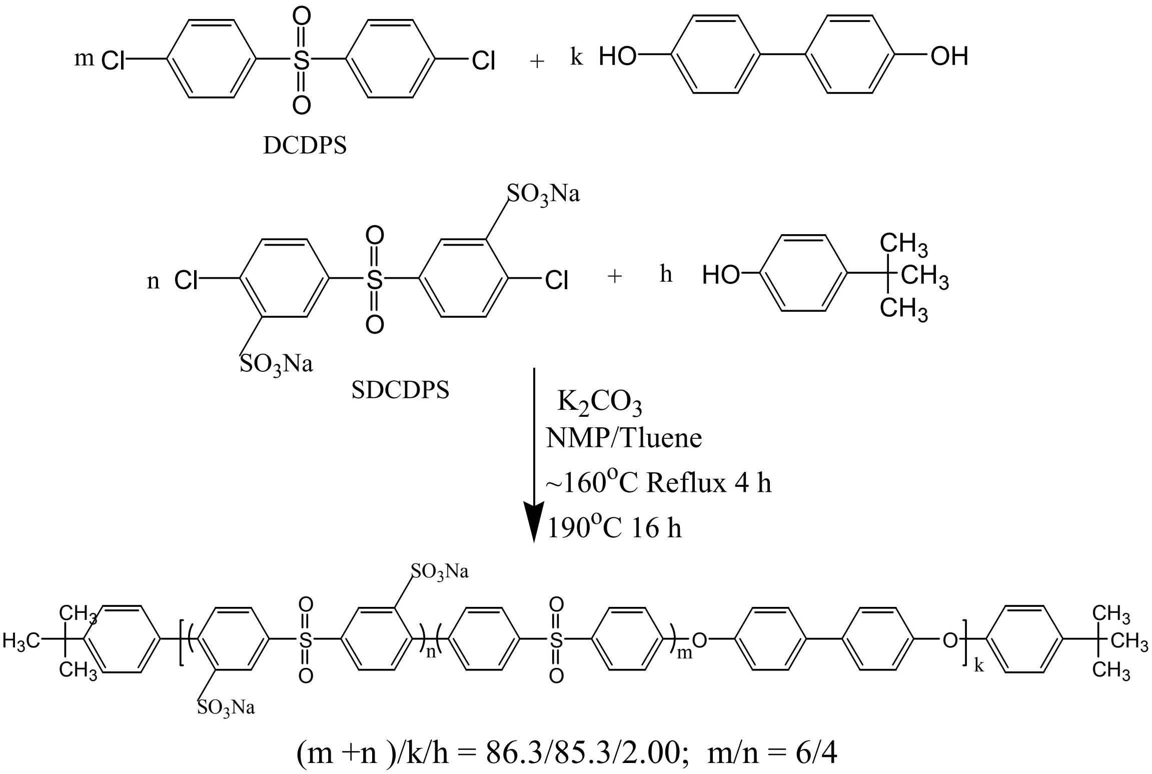


FIGURE 64. Synthesis of t-butyl phenyl terminated sulfonated poly (arylene ether sulfone) via direct copolymerization.

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[305] Wang, F.; Glass, T.; Li, X.; Harrison, W.; Hickner, M.; Kim, Y-S.; McGrath, J.E., *ACS Polymer Preprints* 2002, 43(1), 492.; (b) *ibid.*, Macromolecular Symposia, in press 2002.

As shown, t-butylphenol was added in controlled amounts, according to Carother's Equation, with biphenol, dichlorodiphenyl sulfone (60 mol%) and sulfonated dichlorodiphenyl sulfone (40 mol%). T-butylphenol has a functionality of one and, therefore, can only react once under the polymerization reaction conditions. The monofunctional t-butylphenol was demonstrated to be at the terminus of essentially all the sulfonated copolymer chains.

Using similar calculations used to determine the degree of sulfonation as described above, the nine (9) protons of the t-butylphenol were rationed to the integration to the aromatic protons of the polymer backbone. These researchers were able to successfully terminate the sulfonated copolymers with t-butylphenol at desired molecular weights of 20,000, 30,000, and 40,000 g/mol. As mentioned earlier, interaction of the sulfonated copolymers with the columns prevented successful GPC measurements.

Wang *et al*. also performed intrinsic viscosity measurements on the terminated sulfonated poly(arylene ether sulfones) and was able to, thereby, relate a calculated molecular weight to an intrinsic viscosity. The summary was: $M_n = 20{,}000$, $[\eta] = 0.54$; $M_n = 30{,}000$, $[\eta] = 0.61$; and $M_n = 40{,}000$, $[\eta] = 0.87$, for forty percent sulfonated, biphenol based poly (arylene ether sulfones) (i.e., BP-40). These results are valuable for comparison with the sulfonated copolymers synthesized in this research. The NMR spectra of the t-butylphenyl terminated BP-40 copolymers are shown in Figure 65.

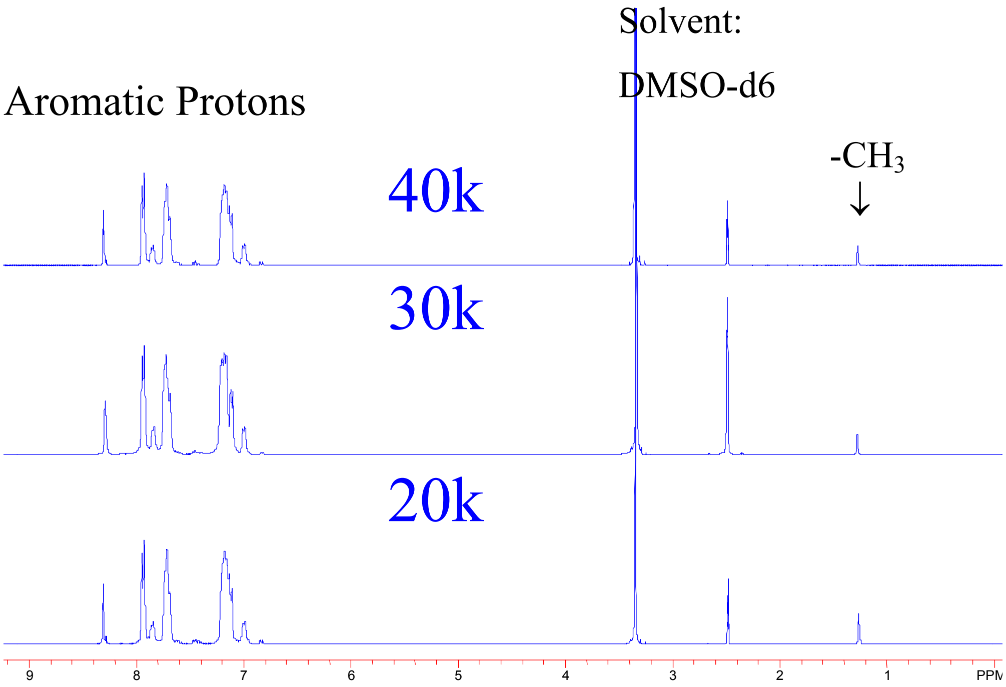

FIGURE 65. ^{1}H NMR of t-butylphenyl terminated biphenol-based sulfonated poly (arylene ether sulfone) copolymers with controlled molecular weight[305]

Thermal Characterization

3.3.3 Differential Scanning Calorimetry (DSC)

Polymers thermal that transitions are very important properties of the material, because they will dictate many of the possible applications for the polymer. Differential scanning calorimetry is one important characterization technique utilized for determining the glass transition temperature and the crystalline melting transition temperature for polymers. The crystalline-melting transition temperature (T_m) a polymer is the melting temperature of the semi-crystalline regions or domains within the polymer. The glass transition temperature (T_g) of a polymer is the temperature at which backbone segments in the amorphous domains of the polymer attain sufficient thermal energy to move in a coordinated manner. In the region of the glass transition temperature, the polymer will change from a glassy material to a rubbery material.

There are many factors that affect the glass transition of a polymer. Some of these factors include polymer structure, molecular symmetry, molecular weight, structural rigidity, and the presence of secondary forces[100]. The secondary forces may be due to the presence of polar groups introducing interaction such as hydrogen bonding. For sulfonated ionomer-type polymers, the addition of the sulfonic acid group, usually has an additional effect. The introduction of sulfonate groups raises the glass transition temperature by increasing bulkiness to the polymer chain unit, thereby increasing the barrier to rotation of the chains; this influences the ability of segmental motion within the polymers.

Characterization of the thermal transitions of ion-containing polymers has been of interest to many scientists[306.307,308]. The research has been predominately in flexible vinylidene-type copolymers. Generally, ion-containing copolymers will display substantially higher glass transition temperatures than their parent polymers. For some

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[306] Takamatsu, T.: Eisenberg, A., *J. Appl. Polym. Sci* 1979, 24, 2221.

[307] Ehramann, M.; Muller, R.; Galin, J.C.; Bazuin, C.G., *Macromolecules* 1993, 26, 4910.

[308] Eisenberg, A.; Kim, J., *Introduction to Ionomers*, Wiley-Interscience Pub., 1998.

polymer systems, two distinct glass transitions have been observed [55,56,309,310]. Increased T_gs can be seen with the incorporation of as little as 5% of the ionic moiety. One explanation for the presence of two T_gs is that the ionic moieties phase separate and *cluster* on the micron to submicron (nano-) scale forming ion-rich domains with different thermal transition behavior than the bulk polymer.

When the ion-containing polymer sample is heated the "polymer chain segments" not directly bound to an ionic moiety may undergo their own transition. The EHM model[306,308] is one representation based on these interactions and observations of restricted mobility in ion containing polymers. Figure 66 is a depiction of aggregation for the EHM model. Due to the aggregation and strong clustering of the ionic species the chain segments directly attached have a restricted mobility. A higher temperature must be applied to supply enough thermal energy to overcome the interactions of the ionic groups before these domains dissociate. Differences as large as 60 °C have been observed in the two transitions (T_gs)[311].

Differential scanning calorimetry (2nd Heat) analysis was used to characterize the thermal transition for the four series of sulfonated poly (arylene ether sulfones) synthesized in this research. A heating rate of 10 °C/min was used on polymer films of typical weights of 5-10 mg. The glass transition of the control copolymers as well as the ten-percent sulfonated copolymers was well defined and recorded as the midpoint of the transition. Sulfonated copolymers of 30 percent sulfonation demonstrated a very broad thermal transition making a definite Tg assignment difficult to discern. The glass transition temperature for sulfonated copolymers with higher degrees of sulfonation was determined by the first derivative of the thermoscan. The measured T_gs of the sulfonated copolymer, in their salt form, are given in Table 6. There was a linear, increasing trend in the glass transition temperatures with increasing degrees of sulfonation. Also, the more flexible bisphenols, i.e., bisphenol A and 6F bisphenol A, displayed lower glass transitions than the wholly aromatic sulfonated copolymers as expected. However, the presence of two T_gs was not observable.

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[309] Matsuura, H.; Eisenberg, A., *J. Polym. Sci,. Polym. Phys. Ed.* 1976, 14, 1201.

[310] Tong, X.; Bazuin, C.G., *Chem. Mater.* 1992, 4, 370.

[311] Kim, J.-S.; Jackman, R.J.; Eisenberg, A., *Macromolecules* 1994, 27, 2789.

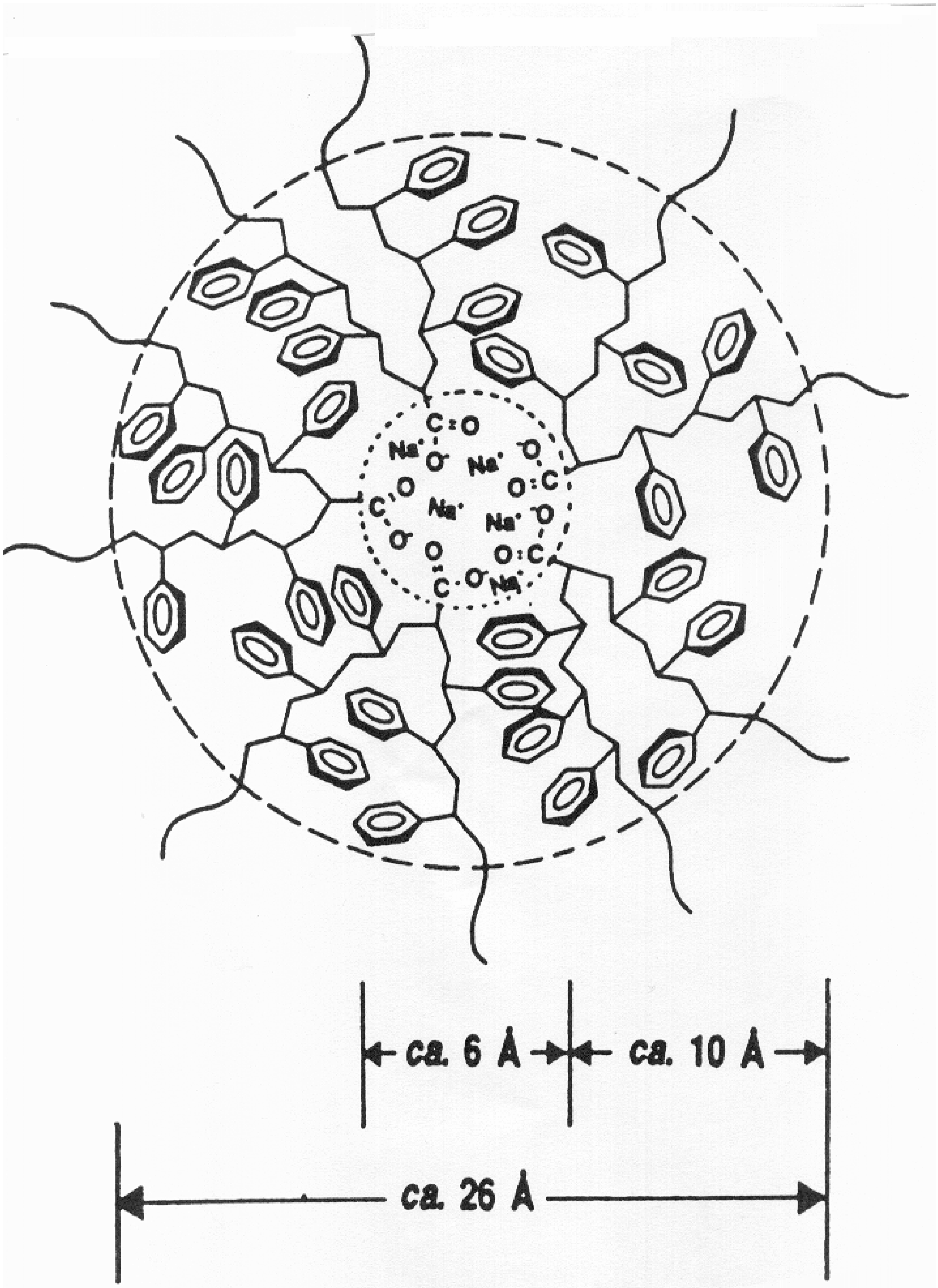

FIGURE 66. Aggregation of ionic species in the EMH model[306].

Table 6. Influence of bisphenol structure and degree of disulfonation on the glass transition temperature (sulfonate form), °C.

mol % SDCDPS →

Polymer	0	10	20	30	40	50	60
Bis A	180	188	200	215	230	242	255
BP	210	222	240	253	274	285	300
6F	193	205	220	233	243	250	265
HQ	200	212	225	240	255	279	305

The difficulty in discerning two thermal transitions in post- sulfonated poly (arylene ethers) has been investigated[312,313]. The small size and the questionable existence of the phase-separated aggregates in an already stiff (glassy) polymer are among the interpretations for broadened T_g intervals, which would make distrinct thermal transitions difficult. The phase separation phenomenon within the sulfonated poly(arylene ether sulfone) copolymers will be discussed in a later section.

The determinations of glass transition temperature of all directly sulfonated copolymers were also attempted in their acid form. Unfortunately using DSC, the T_gs were indistinguishable from the baseline for the bisphenol A, 6F bisphenol A, and hydroquinone based copolymers. Similar observations have been reported for sulfonated polymers such as sulfonated PEEK[129,175], and other sulfonated polymers[161,173,195]. The more rigid bisphenol-based series displayed detectable transitions. The thermoscans are given in Figure 67. Close examination of the thermoscans detected a second *transition* in the copolymers that contains greater than 40 mol percent sulfonic acid groups (ie., BPSH-50, and BPSH-60). It is also important to note that the expected T_gs of the dry, acid-form sulfonated poly (arylene ether sulfones) copolymers are expected to be close to the thermal degradation temperature of the copolymers. Thermal degradation will be discussed in the next section.

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[312] O'Gara, J.F.; Williams, D.J.; Macknight, W.J.; Karasz, F.E., *J. Polym. Sci.: Part B: Polym. Phys.*, 1987, 25, 1519.

[313] Johnson, B.C.; Yilgor, I.; Tran, C.; Iqbal, M.; Wightman, J.P.; Lloyd, D.R.; McGrath, J.E., *J. Polym. Sci.*, 1984, 22, 721.

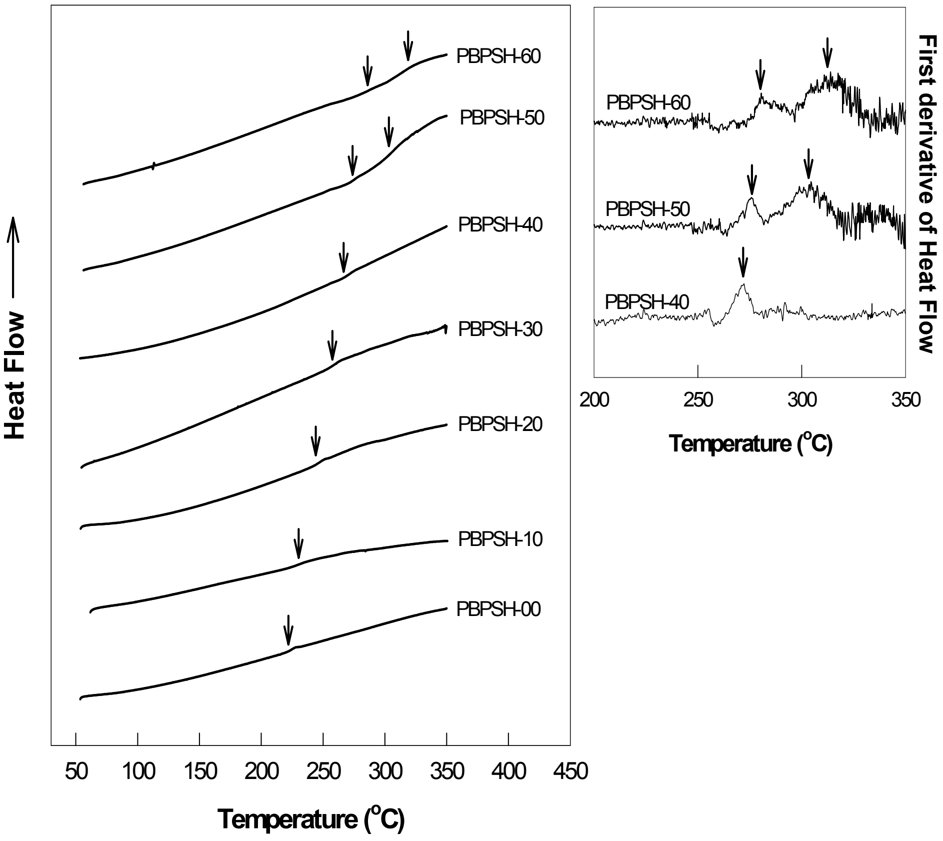

FIGURE 67. Influence of the degree of sulfonation on the glass transition temperature of biphenol-based sulfonated poly (arylene ether sulfone) copolymers.

3.3.4 **Thermogravimetric Analysis (TGA)**

The thermal and thermo-oxidative stability as a function of weight loss of the control and sulfonated poly(arylene sulfone) copolymers were investigated by thermogravimetric analysis. All four seriesof sulfonated copolymers were examined in both their salt and free-acid form. All the sulfonated samples were pre-heated at 150°C for 30 minutes in TGA furnace to remove trace solvent and moisture. Then, the dynamic TGA experiments were run from 50 to 700 °C, at a heating rate of 10°C/min under nitrogen. The influences of the bisphenol and the degree of sulfonation of the acid-form films on both 5% weight loss temperature and the residual char yield at 700 °C are summarized in Table 7. All four series of sulfonated poly (arylene ether sulfone) copolymers in the salt form did not show any thermal or thermo-oxidative degradation before 450 °C (~ 410 °C for bisphenol A-based copolymers).

The biphenol, hydroquinone, 6F biphenol A, and to some extent bisphenol A, afford highly thermally stable polymers. The aliphatic isopropylidene group in the bisphenol A residue is less oxidatively stable compared to its wholly aromatic counterparts. The 5% weight loss of the bisphenol A polymers was higher in nitrogen than in air. Not surprisingly, the differences in stability were typically at least 180 °C. The salt forms of each sulfonated copolymer was considerably more thermally stable than the comparable sulfonated polymer in its acid form. Figure 68 depicts the thermal stability (as a function of weight loss), in nitrogen, for BP-60 in both the acid and salt form. The observable trend that higher the degrees of sulfonation produce higher char yields was typical. The high char yields (up to 65 % in nitrogen for BP-60) of the sodium sulfonate containing copolymers correlate well with the findings of Robeson *et al.*[291] which demonstrated the utility of sulfonated dichlorodiphenyl sulfone in the sodium salt form as an additive in fire retardant polyarylate blends.

Table 7. Influence of bisphenol structure and degree of sulfonation on the TGA behavior in air and nitrogen of acid-form copolymers

Polymer	$T_{(5\%)}$, Air	$T_{(5\%)}$, N_2	Char Yield (%) 700 °C in Air
Bis A-00	410	475	5
Bis A-10	235	300	5
Bis A-20	230	290	8
Bis A-30	220	295	7
Bis A-40	225	295	8
Bis A-50	220	275	6
Bis A-60	225	275	8
BP-00	500	550	7
BP-10	220	310	6
BP-20	230	285	8
BP-30	225	275	5
BP-40	220	280	6
BP-50	220	275	5
BP-60	225	275	9
6F-00	485	520	10
6F-10	230	310	7
6F-20	230	300	8
6F-30	225	295	9
6F-50	220	290	9
6F-60	220	275	6
HQ-00	510	550	9
HQ-10	235	320	8
HQ-30	230	300	7
HQ-40	225	300	8
HQ-50	220	295	9
HQ-60	220	290	11

The 5% weight loss temperature of the acid-form-sulfonated copolymers was higher in nitrogen than in air on average of about 50 ^{o}C, as expected. All of the copolymers displayed a distinct two-step degradation. The first degradative weight loss temperature, in air, ranged from 250 to 300 ^{o}C for the acid-form polymers and was attributed to the loss of the sulfonate group. The second weight loss was attributed to the thermo-oxidative degradation of the polymer backbone, which occcurred above 420 ^{o}C for all four polymer series. The char yields from the acid-form of the copolymers were all in the range of 5-12 % as shown in Table 7. The chars at 700 ^{o}C were possibly more a function of the bisphenol than of the degree of sulfonation because of the early degradative loss of the sulfonic acid groups. The char yields for the comparable salt-form copolymers were consistently higher than their free-acid copolymers and also scaled with the degree of sulfonation.

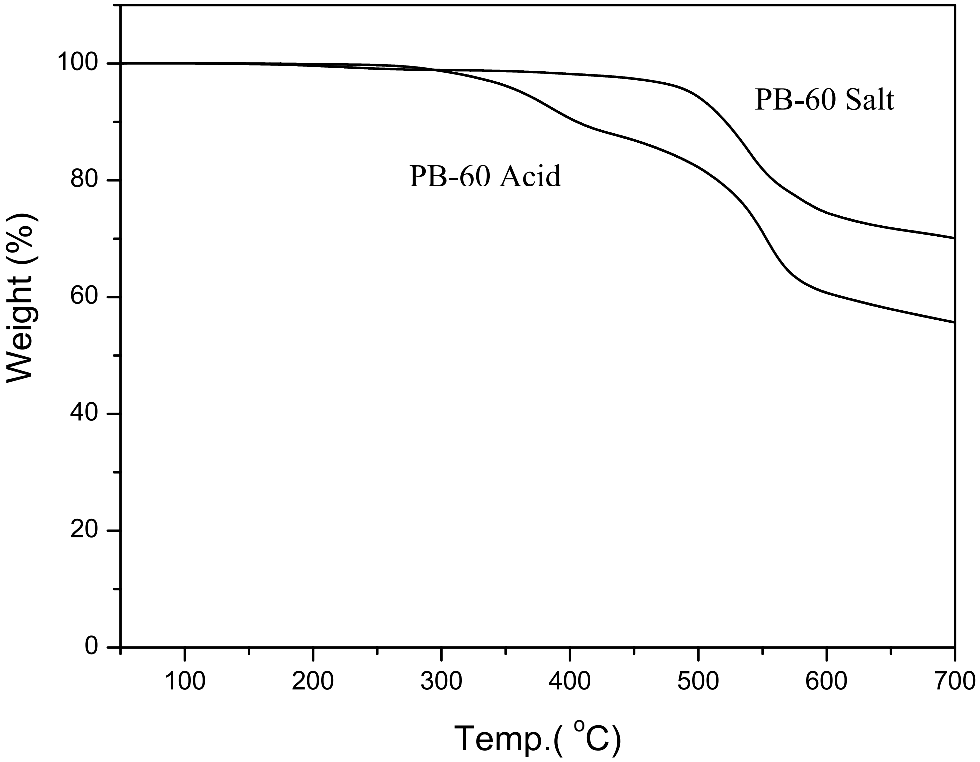

FIGURE 68. TGA thermogram of weight loss of acid-form and salt-form BP-60 in N_2.

Membrane Characterization

3.3.5 **Solution Properties**

Polymer solubility is an important property and is often related to several parameters, including the type of polymer, architecture, and, of course, the solvent. The sulfonated poly(arylene ether sulfone) copolymers were tested for solubility in several common solvents, include NMP, DMAc, DMSO, chloroform, and water. The copolymers were typically examined at 10% polymer solutions (weight/volume) in each solvent. The results are presented in Table 8.

All control and sulfonated copolymers were dissolved in NMP and DMAc when agitated with a magnetic stirrer to yield clear, homogeneous solutions. After four weeks the unsulfonated hydroquinone control polymer (HQ-00) solution became opaque and eventually crystallized from the DMAc solution. No precipitation/crystallization was observed at any other composition of the hydroquinone-based sulfonated copolymers. The bisphenol A-based sulfonated copolymers were soluble in chloroform up to 30 mol percent sulfonated dihalide compositions in the polymerization feed. At high degrees of sulfonation the polymers were swollen to a gel, but did not give a true solution at 10% concentrations.

The relatively high solubility of the sulfonated poly (arylene ether sulfone) copolymers in common solvents agrees with the absence of branching or cross-linking during polymerization.

Table 8. Influence of bisphenol structure and degree of sulfonation on sulfonated poly (arylene ether sulfone) copolymers solubility behavior in common solvents (10% wt/vol) at room temperature.

Polymer	NMP	DMAc	DMSO	Water	Chloroform
Bis A-30	Y	Y	Y	SW	Y
Bis A-40	Y	Y	Y	SW	SW
Bis A-50	Y	Y	Y	SW	SW
Bis A-60	Y	Y	Y	SW	SW
BP-30	Y	Y	Y	SW	N
BP-40	Y	Y	Y	SW	N
BP-50	Y	Y	Y	SW	N
BP-60	Y	Y	Y	SW	N
6F-30	Y	Y	Y	SW	SW
6F-40	Y	Y	Y	SW	N
6F-50	Y	Y	Y	SW	N
6F-60	Y	Y	Y	SW	N
HQ-30	Y	Y	Y	SW	N
HQ-40	Y	Y	Y	SW	N
HQ-50	Y	Y	Y	SW	N
HQ-60	Y	Y	Y	SW	N

Y ≡ solubale; SW ≡ swells; N ≡ insoluble, not swelling

3.3.6 **Water Uptake/Sorption**

Water is very important in proton exchange membrane fuel cells. The protonic conductivity of a polymer exchange membrane is strongly dependent on the membrane structure and the membrane water content[28]. Proton conductivity typically decreases as the film and/or system becomes dehydrated. Water molecules hydrate the protons produced at the anode producing a hydronium-like species, $H^+(H_2O)_n$.

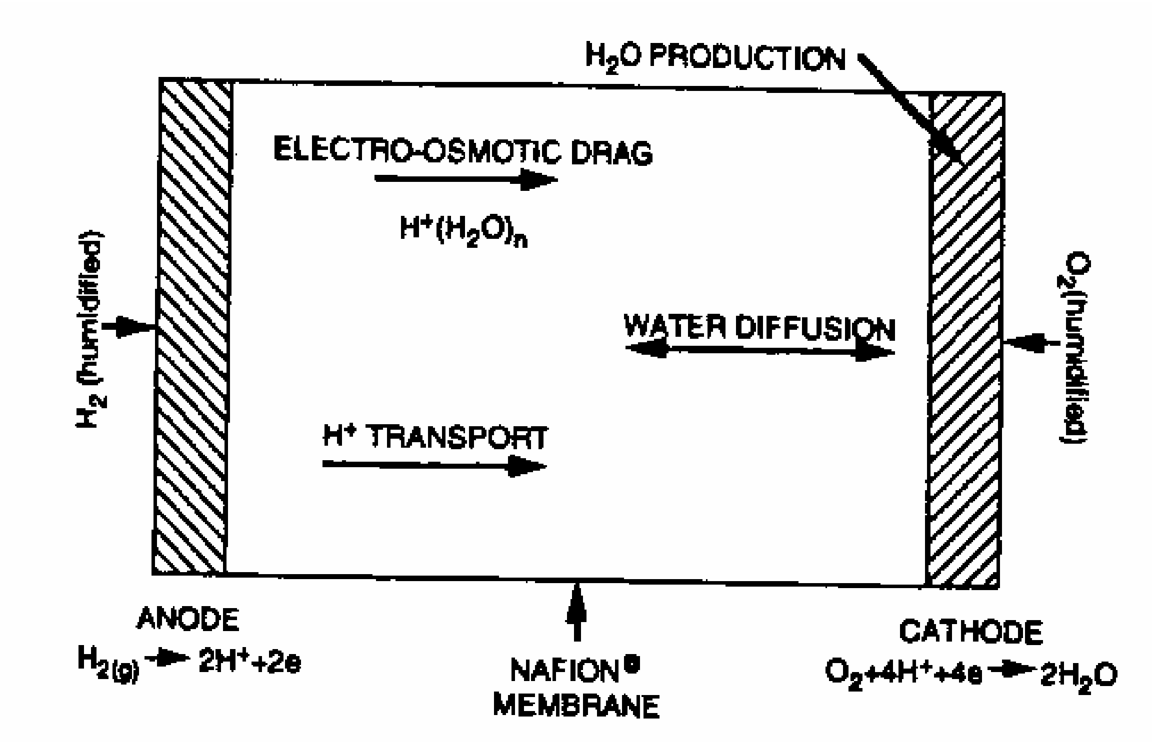

FIGURE 69. Schematic representation of water sources and movement in PEMFCs[28].

Proper water management is vital to proper operation and performance of PEMFCs. As depicted in Figure 69, there exists a complex system involving water management in proton exchange membrane fuel cells. Beyond the use of humidified gases[28], many researchers have proposed ways to keep the PEMFC system hydrated[314,315,316,317,318], especially at the anode. The electro-osmotic drag of water from the anode to the cathode tends to dry out the anode. Even though there will be some back-diffusion of water towards the anode, water accumulates at the cathode and may cause "flooding" and a loss of performance. One approach that has been described to re-introduce water at the anode is inserting a wet *wick* into the cell that allows water to drip onto the proton exchange membrane[315]. Alternatively, Cisar *et al*. introduced small, circular channels or "tubes" into the PEM into which water is pumped to the system[316].

The largest amount of water is introduced in the fuel cell during the *treatment* and hydration of the PEM. Preconditioning of the proton exchange membranes in purified water is a customary practice. The films are hydrated before being placed into the fuel cell. The importance of the polymer treatment and handling has been demonstrated[319,320]. Water uptake or the level of hydration may be a function of a number parameters. Among the possible parameters are the types of polymer, temperature, and time required to reach an equilibrium state within the film.

The water uptake for the sulfonated poly(arylene ether sulfone) copolymers synthesized in this research was determined, as weight percent, by the following equation:

$$\text{water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad \text{Eqn 17}$$

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[314] Wilson, M.S.;Zawodzinski, C.; Gottesfeld, S., *Proceedings Abstracts at The 1998 Fuel Cell Seminar*, Palm Springs, California, November 1998, p. 651.

[315] Watanabe, M.; Satoh, Y.; Shimura, C., *J. Electrochem. Soc.*, 1993, 140, 3190.

[316] Cisar, A.J.; Gonzalez-Martin, A.; Hitchens, G.D.; Murphy, O.J., *US Patent 5,635,039*, 1997.

[317] Wilson, M.S. ; Zawodzinski, C.; Gottesfeld, S., in *in Proton Conducting Membrane Fuel Cells: 2nd International Symposium,* 1998, Electrochem. Soc. Proceedings Series, 98, 27.

[318] Wood III, D.L.; Yi, J.S.; Nguyen, T.V., *Electrochim. Acta* 1998, 43 (24), 3795.

[319] Zawodzinski, T.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. *J. Electrochem. Soc.* 1993, *140*, 1041.

where W_{wet} and W_{dry} are the equilibrium weights of the wet and dry membranes, respectively. The equilibrium weight was taken as the weight at which no further change in weight was observed. The equilibrium dry weight was determined using an analytical balance after thoroughly drying the acid-form films at 120 ^{o}C and the salt-form of the films at 150 ^{o}C. The equilibrium sorption was typically achieved after 40 to 70 hours of soaking in deionized water.

The sulfonated poly (arylene ether sulfone) copolymers showed increasing water uptake with increasing degree of sulfonation. Other researchers obtained similar results[321,322]. The results are tabulated on Table 9. Beyond the increase in water sorption along any copolymer series as a function of the degree of sulfonation, a dependence on the bisphenol was observed. The water sorptions in the acid-form films of the sulfonated copolymers were tested and showed generally higher water uptake than the corresponding salt-form.

Table 9. Influence of the degree of sulfonation and the bisphenol structure on the water uptake of sulfonated poly(arylene ether sulfone) copolymers at 30oC acidified in 1.5 M sulfuric acid (24 hours, 30 ^{o}C) followed by soaking for 24 hours in deionized water.

Mol Percent of Disulfonated Halide Monomer →

Bisphenol	0	10	20	30	40	50	60
Bis A	3	7	13	25	37	48	68
BP	2	5	10	18	28	38	65
6F	2	5	9	13	25	34	42
HQ	2	7	23	31	50	68	>140

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[320] Bunce, N.; Sondheimer, S.; Fyfe, C. A. *Macromolecules* 1986, *19*, 333.

[321] Zaidi, S.M.J.; Mikhailenko, S.D.; Robertson, G.P.; Guiver, M.D.; Kaliaguine, S., *J. Membr. Sci.,* 2000, 173, 17.

[322] Leung, L.; Bailly, C..; O'Gara, J.F.; Williams, D.J.; Karasz, F.E.; MacKnight, W.G., *Polym. Commun*., 1987, 28, 20.

While copolymers formed from bisphenol A and biphenol displayed similar water uptakes, hydroquinone based copolymers sorbed higher amounts of water at comparable degrees of sulfonation. In contrast, 6F bisphenol A based sulfonated copolymers displayed lower levels of water uptake at corresponding degrees of sulfonation. The hydrophobic nature of the fluorines in the 6F bisphenol A structure apparently makes the copolymers less hydrophilic than other sulfonated copolymers. No analogous generalization can easily explain the higher water uptake of the hydroquinone copolymers, except it has the lowest molar mass. Hydroquinone is structurally very similar to biphenol and similar water sorption(s) were expected. One possible explanation for the differences in water uptake may be found in the microstructure of the membrane of the copolymers and will be discussed later.

An optimum degree of sulfonation needs to be established for producing the PEM with the "best" performance. While higher levels of sulfonation will provide higher proton conductivity, other membrane properties may suffer. A membrane that is too hydrophilic would swell greatly yielding a *hydrogel* and may be weak and not efficiently serve as a barrier for the fuel and oxidizer. Furthermore, undesirable stress by the swollen membrane may be placed on the fuel cell hardware. As shown in Table 9, at between the 50 and 60 percent disulfonation levels very high water uptake levels (>180 weight percent) for bisphenol A and biphenol based copolymers were observed. A similarly high increase in water uptake is observed for hydroquinone copolymers between 40 and 50 percent disulfonation. The change causes at least a two-fold increase in water sorption after short term (~24 hours) soaking. At these levels of hydration the copolymers are essentially hydrogels and have little structural (i.e., mechanical) stability. 6F bisphenol A copolymers sorb less water and still maintain a good structural / film behavior.

Similar nonlinear or abruptly large water sorptions have been observed in several post-sulfonated sulfonated copolymers, including polysulfones[108,323] and polyketones[129].

Not surprisingly, increased temperature increased the water uptake of the sulfonated poly (arylene ether sulfone) copolymers. Nolte *et al.*[108] and Kerres *et al.*[126]

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[323] Arnold, C.; Assink, R.A., *J. Membr. Sci.* 1988, 38, 71.

have shown that some of their post-sulfonated poly (arylene ether sulfones) were soluble in water at elevated temperatures (above 60 °C) unless some (controlled) degree of cross-linking reaction was performed. Films of the directly sulfonated copolymers synthesized in the present research were evaluated for their water uptake at 80 °C for 48 hours. The results, shown in Table 10, indicated a typically 30 wt% higher water uptake at 80 °C compared to 30 °C.

Table 10. Influence of the degree of sulfonation and the bisphenol structure on the water uptake of selected salt-form compositions of sulfonated poly (arylene ether sulfone) copolymers at 80 °C.

mol% SDCDPS →

Polymer	20	30	40	50
Bis A	27	45	75	>200
BP	25	40	64	>200
6F	18	30	55	100
HQ	35	80	>300	hydrogel

Several researchers have investigated the water uptake of perfluorinated sulfonic acid copolymers[324,325]. The correlation between water content and conductivity was reaffirmed. Interestingly, an interdependence between the *treatment* of Nafion and water content was observed by Bunce *et al.*[326]. It was shown that the water uptake after different drying conditions changed the amount of water Nafion films re-absorbed.

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[324] (a)Yeo, R. S. *J. Electrochem. Soc.* 1983, 130, 533; (b) Pourcelly, G.; Oikonomou, A.; Hurwitz, H. D.; Gavach, C. *J. Electroanal. Soc.* 1990, 287, 43; (c) Randin, J. *J. Electrochem. Soc.* 1982, 129, 1215.

[325] Zawodzinski, T.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. *J. Electrochem. Soc.* 1993, 140, 1041.

[326] Bunce, N.; Sondheimer, S.; Fyfe, C. A. *Macromolecules* 1986, *19*, 333.

Nafion films that were dried under vacuum at room temperature absorbed more water than films dried at temperatures over 100 °C in a vacuum oven.

Similar analysis for the biphenol-based sulfonated poly(arylene ether sulfone) copolymer series was conducted. For this experiment salt forms films were cast on glass substrates and dried using only infrared lamp heating (~70 °C) in a nitrogen purge. These films were weighed and submerged in deionized water at 30 °C for 48 hours. The results are tabulated in Table 11. In comparison to films dried in a vacuum oven (Table 8) the biphenol-based sulfonated copolymers sorbed up to 40 wt% more water.

Table 11. Influence of the infrared lamp-drying on water uptake in salt-form of biphenol-based sulfonated poly (arylene ether sulfone) copolymer membranes at 30 °C.

BP-20	BP-30	BP-40	BP-50	BP-60
18	27	38	56	130

One possible explanation for the different water uptakes may be the organization of the ionic clusters/aggregates. During normal 150 °C drying of the salt-form copolymer films trace solvent and/or water may allow some mobility of the polymer chains causing the production of different size aggregates. The drying temperature of the infrared lamp (~80 °C) is considerably less that the copolymers T_g and, therefore, may not allow the same chain mobility. Comparable discussions have been given by Eisenberg[57, 327] and others[55,60] on the formation of ionomer clusters. Among many elements, ionic interactions and polymer elasticity are important factors involved in cluster formation. The different sized clusters may sorb different quantities of water. A different acidification method (**Method 2**) was developed and its influence on several properties, including water uptake will be discussed in Section 3.3.9.

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[327] Eisenberg, A. *Macromolecules* **1970**, *3*, 147.

3.3.7 **Proton Conductivity**

From an application point-of-view, good protonic conductivity of a proton exchange membrane is clearly one of the most important properties. The magnitude of the specific conductivity is determined by a combination of *charge carrier density* and the *charge carrier mobility*[28]. The charge carrier is, of course, the proton and is dependent, to some extent, on the number of pendent sulfonic acid groups along the polymer chain.

There are other factors that influence the overall proton conductivity. As noted earlier, the film thickness was important as exemplified by Dow's thin (2 mils) perfluorosulfonic acid proton exchange membrane. The importance of water (and water uptake in the PEM) on proton conductivity has already been discussed.

Proton conductivity was measured on solution cast films of all the sulfonated poly (arylene ether sulfone) copolymers synthesized in this research. The conductivities were, of course, measured in the acidified form of the sulfonated copolymers. The conversion of the sodium salt membranes to their respective free acid membrane has been the subject of several studies. Kim *et al*.[328] have recently shown the influence on proton conductivity of the acidification treatment of biphenol-based sulfonated poly (arylene ether sulfone) copolymers. Higher proton conductivities were measured for fully submerged/hydrate membranes that were treated with boiling 0.5M sulfuric acid for 1 hour than for membranes that were converted in 0.5M sulfuric acid for 24 hours at room temperature. Titration and NMR experiments were conducted to verify that no additional sulfonation occurred during the boiling treatment. A change in morphology was proposed as the cause of the increase in proton conductivity. Further discussions on morphology will be presented in a later section.

An extremely important factor on proton conductivity was found to be the conditions under which the measurements were made. Proton conductivities have been reported on most of the PEM candidates outlined in Chapter I. The conductivities were determined for fully hydrated (immersed) films, films at different humidity levels, films

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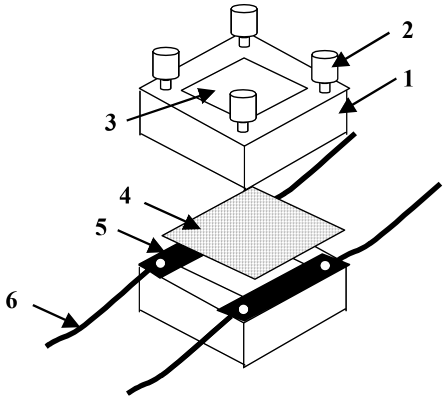
[328] Kim, Y.S; Wang, F.; Hickner, M.; McCartney, S.; Hong, Y. T.; Harrison, W.; Zawodzinski, T.A.; McGrath, J.E.,. *J.Poly Sci: Physics*, **2002**, in press (b) *ibid*., The Electrochemical Society 201st Meeting, Philadelphia, PA, May 12-17, 2002, Abstr.# 182.

at different temperatures, films with various additives / dopants, etc. It is well known the temperature influences the proton conductivity. Furthermore, the analyzing cell's configuration should also be noted. Most proton conductivities are measured using either a *2-point* or *4-point* probe. The advantage of one probe over the other is still debatable, but the 4-point probe is commonly used for anisotropic materials.

Proton conductivities of the fully hydrated acid-form sulfonated poly(arylene ether sulfone) copolymers were performed at 30 ^{o}C using a Solatron 1260 Impedance instrument. The 2-point analyzer is shown below. Actually, the resistance, **R**, (units of ohm) of each copolymer membrane was determined and then the reciprocal was taken to determine the proton conductance, ∂, (units of Siemens/cm). The equation employed for the conductivity determination is also given below. The proton conductivity results are given in Tables 12A-D. The ion exchange capacity of each polymer is displayed in the tables. Recall the ion exchange capacity is the average number of sulfonic acid groups per unit mass of polymer (milli-equivalents/gram).



Legend
1. Teflon block
2. Thumbscrew
3. Open area to allow equilibration with environment
4. Membrane sample
5. Blackened Pt foil electrode
6. Pt lead

$$\partial = \frac{1}{R} \quad \frac{I}{A} .$$

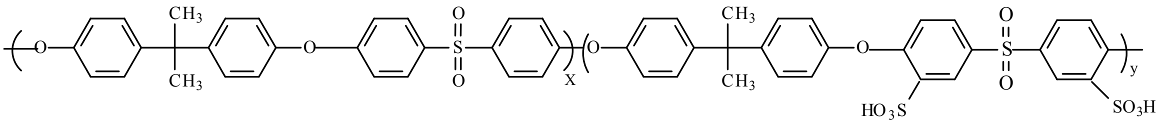
Where ∂ = conductivity (S/cm)
R = resistance (ohms)
I = length between electrodes (cm)
A = cross-sectional area of film (cm^{2})

As expected, the unsulfonated control polymer membranes, which have an ion exchange capacity of zero, showed no measurable proton conductivities. Along each copolymer series, the proton conductivity increased with increasing ion exchange capacity. For each comparable degree of disulfonation the hydroquinone based sulfonated copolymers had the highest exchange capacity. This was expected since the formula weight of the repeat unit for the hydroquinone copolymers is smaller than the repeat units of the other copolymers. The hydroquinone-based sulfonated copolymers also showed higher proton conductivity. Films of the hydroquinone copolymer that contained 60 mol% sulfonated dihalide sulfone comonomer (HQ-60) had excessive water uptake and, therefore, were not submitted for proton conductivity measurements.

The 6F bisphenol A based sulfonated copolymers (6F-XX) showed high proton conductivity even though their respective water uptakes were lower than those of the other sulfonated copolymers. The conductivities of the 6F sulfonated copolymers were lower than those of the other copolymers with comparable levels of sulfonation; this may be related to their lower water content. However, the measured values are still at least an order of magnitude higher than the conductivities typically reported for sulfonated polymers[206] prepared by some post-sulfonating reactions.

Closer examination of the data across the different bisphenol structures revealed that at similar ion exchange capacities the proton conductivity is essentially the same. For example, an IEC value of approximately 2 meq/g corresponded to a proton conductivity of all the various sulfonated copolymers of approximately 0.10 S/cm. **This revelation should be expected but has not been highlighted or reported by others, which is probably due to difficulties in the control of polymer post-sulfonation reactions and the lack of a systematic study.**

Table 12A. Influence of Degree of Sulfonation on Several Features of Bisphenol A based Copolymers

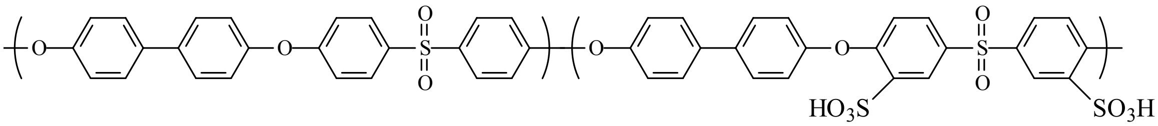


XX, mol% SDCDPS	**Degree of Sulfonation by ^{1}H NMR**	**$[\eta]^{NMP}$**	**IEC$^{\#}$, meq/g**	**Conductivity (S/cm),** 30°C, *Method 1* acidification
0	-	0.70	0	-
10	12	0.78	0.41	0.01
20	18	0.82	0.79	0.03
30	31	1.20	1.12	0.06
40	37	1.86	1.58	0.08
50	48	2.48 2.75*	1.78	0.11
60	56	2.80 3.08*	2.13	0.17

* Copolymerization using DFDPS/SDFDPS system.

#Determined from non-aqueous potentiometric titration.

Table 12B. Influence of Degree of Sulfonation on Several Features of Biphenol based Copolymers

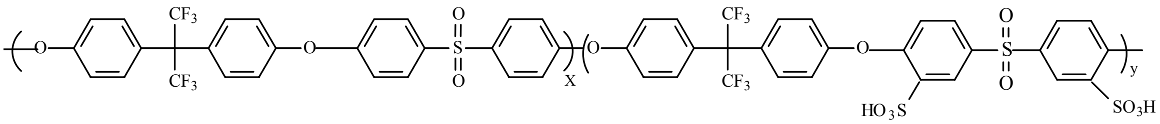


XX, mol% SDCDPS	**Degree of Sulfonation by ^{1}H NMR**	$[\eta]^{\mathbf{NMP}}$	**IEC, meq/g**	**Conductivity (S/cm),** 30°C, *Method 1* acidification
0	-	0.65	0	-
10	8	0.70	0.41	0.009
20	23	0.93	0.89	0.03
30	31	1.51	1.31	0.05
40	40	1.82	1.51	0.09
50	49	2.09 2.52*	1.98	0.11
60	58	2.69 2.94*	2.22	0.16

* Copolymerization using DFDPS/SDFDPS system.

#Determined from non-aqueous potentiometric titration

Table 12C. Influence of Degree of Sulfonation on Several Features of 6F Bisphenol A based Copolymers

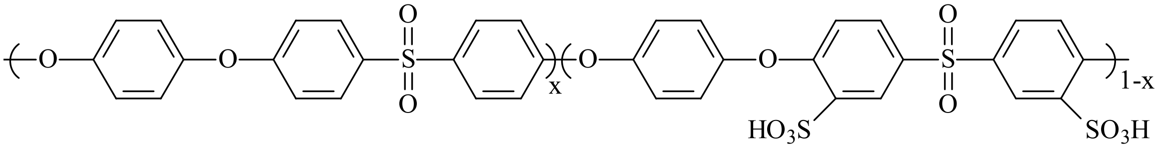


XX, mol% SDCDPS	**Degree of Sulfonation by ^{1}H NMR**	$[\eta]^{NMP}$	**IEC$^{\#,}$ meq/g**	**Conductivity (S/cm),** 30°C, *Method 1* acidification
0	-	0.59	0	-
10	9	0.69	0.32	0.005
20	19	0.86	0.59	0.008
30	27	1.49	0.87	0.02
40	41	1.70	1.16	0.06
50	52	2.01 2.42*	1.50	0.08
60	58	2.07 2.53*	1.77	0.10

* Copolymerization using DFDPS/SDFDPS system.

#Determined from non-aqueous potentiometric titration.

Table 12D. Influence of Degree of Sulfonation on Several Features of Hydroquinone based Copolymers



XX, mol% SDCDPS	**Degree of Sulfonation by ^{1}H NMR**	$[\eta]^{NMP}$	**IEC$^{\#}$, meq/g**	**Conductivity (S/cm),** 30^{o}C, *Method 1* acidification
0	-	0.89	0	-
10	13	0.86	0.60	0.03
20	18	1.20	1.00	0.06
30	32	1.82	1.58	0.08
40	38	2.29	1.94	0.11
50	46	2.37 2.65*	2.48	0.13
60	55	2.41 2.88*	2.77	N/D

* Copolymerization using DFDPS/SDFDPS system.

#Determined from non-aqueous potentiometric titration

3.3.8 **Morphology**

The solid state organization that develops within various copolymers may give rise to distinct regions that define that copolymer's morphology. Block and semi-crystalline polymers are often studied for their morphology and the properties invoked by morphology variations[329]. Many elastomeric-type ionomers have also shown distinct morphologies. Phase separation and clustering of the ionic moieties from the bulk polymer present a different type of morphology. The size of the new ionic domains is typically reported in the sub-micron (nanometer) scale. The sizes of the clusters are influenced by a number of factors[93,94,95,328, 330,331], including the number of ion groups, semicrystallinity, amount of hydration, and the treatment (i.e., drying, acidification, solvent, etc.) to the polymer.

The influence of the bisphenol structure on the morphology and on thee clustering of the sulfonate groups was investigated. Bisphenol A and 6F bisphenol A are structurally similar but the 6F bisphenol is much more hydrophobic. Biphenol and hydroquinone add more rigidity to the polymer system. Tapping-mode atomic force microscopy (TM-AFM) was employed to explore the morphological characteristics of the four series of sulfonated copolymers. Tapping mode phase imaging is a comparatively new atomic force microscopy technique[332]. TM-AFM is powerful because it can distinguish areas with different properties (eg. hardness, etc.) regardless of their topographical nature [330,333,334].

Phase images of the directly sulfonated poly(arylene ether sulfone) copolymers were recorded to investigate the ionic clustering under ambient conditions. The sulfonated copolymers were thoroughly dried under vacuum to remove water, etc. from the thin film samples. All four control (unsulfonated) polymers showed no

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[329] (a) Noshay, A.; McGrath, J. E. *Block Copolymers: Overview and Critical Survey*; Academic Press: New York, 1977; (b) Aggarwal, S. L. *Block Copolymers*; Plenum: New York, 1970.

[330] Zawodzinski, T.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. *J. Electrochem. Soc.* **1993**, 140, 1041.

[331] James, P.J.; McMaster, T. J.; Newton, J. M.; Miles, M. J., *Polymer* **2000**, 41, 4223.

[332] Binnig, G.; Quate, C. F.; Gerber, C., *Phys Rev Lett* **1986**, 56, 930.

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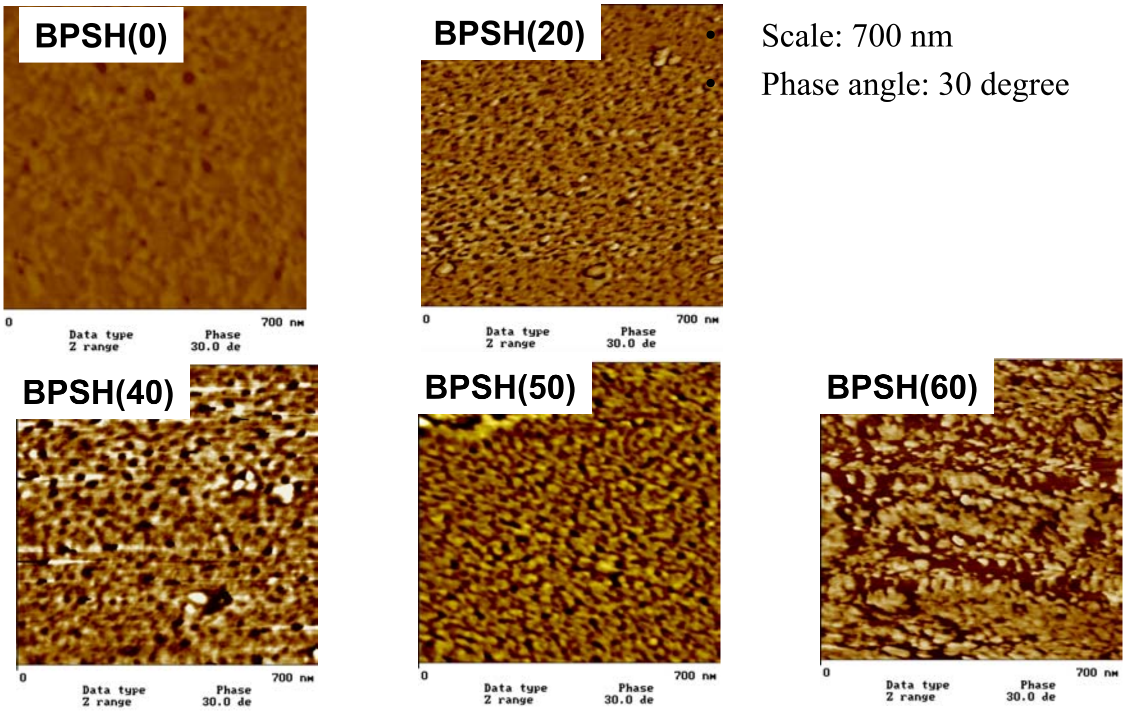
[334] Howard, A. J.; Rye, R. R.; Houston, J. E., *J Appl Phys* **1996**, 79, 1885.

distinguishable features. Distinct dark phases/regions are observed for the sulfonated copolymers. These dark regions are attributed to the clustering of the softer pendant sulfonic acid groups (which contain some water) and are organized on the size scale of ~7-25 nm. The dampening effects in the hydrated ionic groups are presented as dark domains in phase contrast mode. Sample micrographs on the 4,4'-biphenol based series from TM-AFM are shown in Figure 70.



- Scale: 700 nm
- Phase angle: 30 degree

FIGURE 70. TAPPING MODE-AFM MICROGRAPH OF ACID-FORM BIPHENOL-BASED SULFONATED POLY (ARYLENE ETHER SULFONE) COPOLYMERS[167]. SCAN BOXES ARE 700 X 700 NM FOR EACH PLOT.

The aggregate size and connectivity ("co-continuous phase") was shown within a copolymer series to be dependent upon the degree of disulfonation. For example BP-20 has an aggregate domain size of ~10 to 15 nm in diameter, while BP-40 aggregates were ~20-25 nm in diameter. The BP-40 clusters were elongated, yet defined and separated. However, BP-60 demonstrated connected aggregates representing a new morphology. Many of these connected domains were greater than 100 nm in length. The continuous domains may parallel the "channels" (4-10 nm) observed[97,335] in Nafion 117 under ambient conditions. The channel formation is likely the source of the very high water uptakes observed in the hydrogel-like, hydrophilic continuous BPSH-60 reported earlier in Table 11 and depicted in the above AFM micrographs.

An influence was also attributed to the bisphenol structure. The aggregates of hydroquinone based sulfonated copolymer were consistently larger than those of other sulfonated copolymers of comparable degrees of sulfonation. On the other hand, the 6F-based sulfonated copolymers showed smaller aggregated domains (Figure 71). The 6F-60 displayed separated ionic domains, similar to those observed in BP-40 AFM micrographs. These differences in domain sizes and connectivity may have an influence of the observed contrast in water uptake behavior of the copolymers within and across the four copolymer series.

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[335] R.S. McLean, M.Doyle, B.B. Sauer, *Macromolecules* **2000,** 33, 6541.

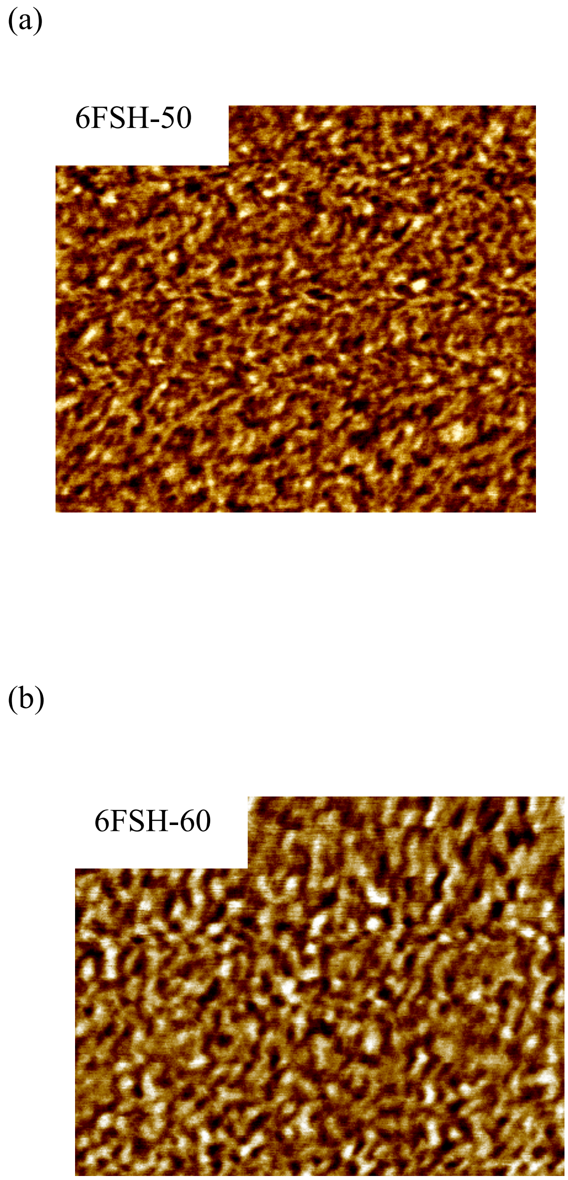

FIGURE 71. Tapping mode –AFM phase image of 6F sulfonated copolymers (a) 6FSH-50 and (b) 6FSH-60. The micrographs are 700 x 700 nm windows with phase angle scales of 0-30 °.

Copolymer *post-treatment* has also shown an influence on a number of properties. Here, the term post-treatment encompasses how the sulfonated copolymer films were converted from their salt forms into their respective acid forms. The influence of drying conditions on water uptake of biphenol-based copolymers was demonstrated in Section 3.3.6 (see Tables 9 and 11). An alternative film- acidification procedure to the 30 °C in 1.5 M sulfuric acid ("Method 1") is immersion in 0.5 M boiling (~ 100 °C) sulfuric acid solution for 2 hours followed by immersion in boiling deionized water for 2 hours ("Method 2"). Method 2 is obviously a more aggressive acidification procedure and has been shown to influence several properties. Table 13A-C tabulates water uptake and conductivity values of Method 1 and Method 2 post-treatments for selected copolymers.

Table 13A Influence of acidification method on water uptake and conductivity of select bisphenolA-based sulfonated poly (arylene ether sulfone) copolymers

	Water Uptake (wt%)		**Conductivity (S/cm)**	
Dihalide mol%	**Method 1**	**Method 2**	**Method 1**	**Method 2**
Bis A-20	13	20	0.03	0.04
Bis A-30	25	40	0.06	0.08
Bis A-40	37	68	0.08	0.10

Table 13B Influence of acidification method on water uptake and conductivity of select biphenol-based sulfonated poly (arylene ether sulfone) copolymers

	Water Uptake (wt%)		**Conductivity (S/cm)**	
Dihalide mol%	**Method 1**	**Method 2**	**Method 1**	**Method 2**
BP-20	10	17	0.03	0.04
BP-30	18	31	0.05	0.06
BP-40	28	58	0.09	0.10

Table 13C Influence of acidification method on water uptake and conductivity of select 6F bisphenol A-based sulfonated poly (arylene ether sulfone) copolymers

	Water Uptake (wt%)		**Conductivity (S/cm)**	
Dihalide mol%	**Method 1**	**Method 2**	**Method 1**	**Method 2**
6F-20	9	15	0.008	0.01
6F-30	13	23	0.02	0.03
6F-40	25	54	0.06	0.08

Each sulfonated copolymer displayed higher water uptake and proton conductivity after Method 2 acidification compared to Method 1 acidification. The boiling conditions in Method 2 caused a morphological change within the copolymers, as observed by subsequent TM-AFM microscopy[328]. The higher proton conductivity with increased water uptake of Method 2 films agrees with earlier noted[326] trends.

3.3.9 **Surface Analysis (ESCA) of Directly Sulfonated 6F Copolymers**

Films of 6F bisphenol A based sulfonated poly (arylene ether sulfone) copolymers were analyzed by ESCA to determine the surface atomic composition / concentration. Researchers at DuPont used contact angle measurement to conclude that perfluorinated sulfonic acid polymers, namely Nafion, have a fluorine-rich surface. The fluorine (C-F) bonding has been suggested to be influential in the chemical stability of these materials. More recently Gottesfeld and Zawodzinski[28] used contact angle experiments to explore their observed differences in water absorption level of Nafion in the presence of water vapor verses liquid water. These authors proposed Figure 72 (shown below) as an explanation.

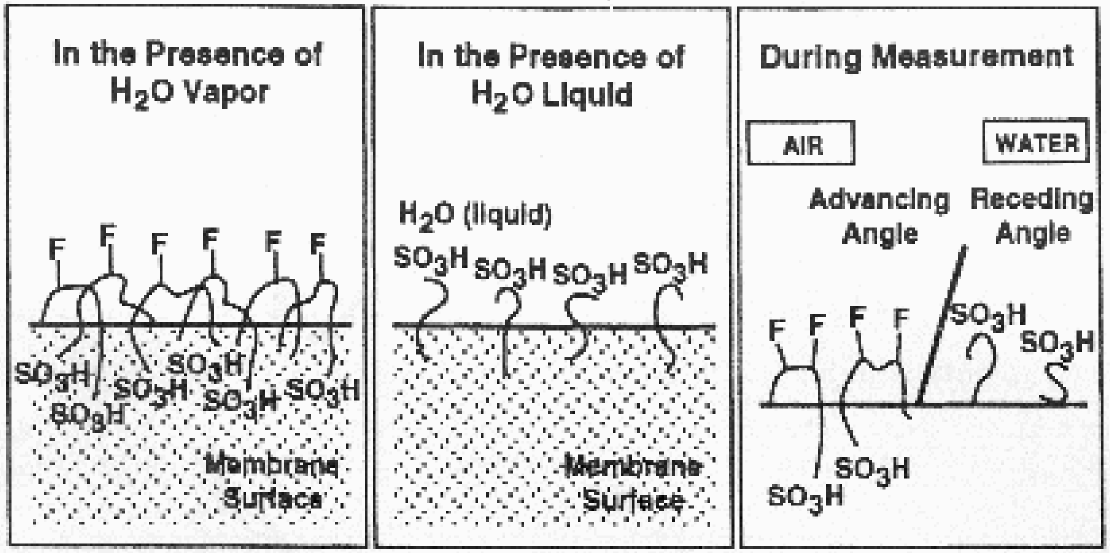

FIGURE 72. Depiction of perfluorosulfonic acid membrane surface composition in contact with water vapor and with liquid water (based on contact angle measurements)[28].

As shown a fluorine-rich surface covers the film in the high humidity / water vapor environment. However when the Nafion film was submerged in liquid water sulfonic acid groups dominated the surface, after some elapsed time. This surface change, from hydrophobic fluorine to hydrophilic sulfonic acid, appeared to be a natural adjustment for the elastomeric polymer since no additional treatment was applied on the film.

The 6F-based poly(arylene ether sulfone) copolymers showed a relatively high surface fluorine content. Electron Spectroscopy for Chemical Analysis (ESCA) data are shown in Table 14. The films were evaluated in both the salt and acidified forms. Furthermore, the influence of Method 1 and Method 2 was explored.

Table 14 Influence of the degree of disulfonation in 6F-based poly(arylene ether sulfone) copolymers and acidification treatment on the fluorine surface content* as determined by ESCA. (%Fluorine).

Degree of Sulfonation ⟶

Treatment↓	0	40	50	60
Theoretical	21	18.3	18.0	17.6
Salt	0.6	0.8	0.9	4.3
Method 1	N/A	6.5	8.0	9.2
Method 2	N/A	12	12.5	13.4

* Only the *air side* of the films was evaluated.

N/A means not available (i.e., not analyzed)

The surface fluorine contents of the sulfonated copolymer films increased with increasing degree of sulfonation, but were all lower than the theoretical values based on structural formula / composition. Furthermore, post-treatment does influence the films' surface composition. Interestingly, the acidified films regardless of post-treatment had significantly higher fluorine concentration on the film surface than did the comparable salt-form film, suggesting higher *self-assembly*. It must be noted that the high vacuum ESCA analysis required well dried films and therefore only indirect comparisons can be inferred between Nafion and the 6F sulfonated copolymers. Further experimentation, such as surface contact angles, is suggested so that wet films may be examined and direct comparisons can be made accordingly. Nevertheless, these results do suggest some self-assembly of the film surface as a function of both the degrees of sulfonation and film post-treatment, which may be important in the oxidative stability of the membrane in a fuel cell.

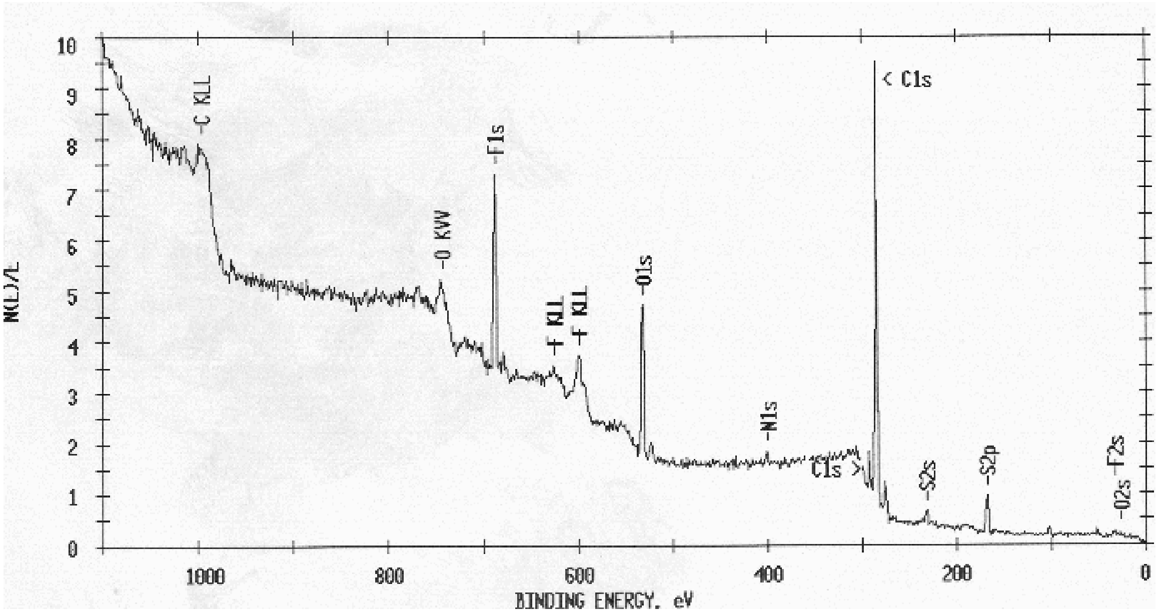

Figure 73. **ESCA Survey scan of the surface atomic composition of 6F-50 acidified film.**

CHAPTER 4

Journal of Polymer Science Publication

Influence of Bisphenol Structure on the Direct Synthesis of Sulfonated Poly(arylene ether) Copolymers. I

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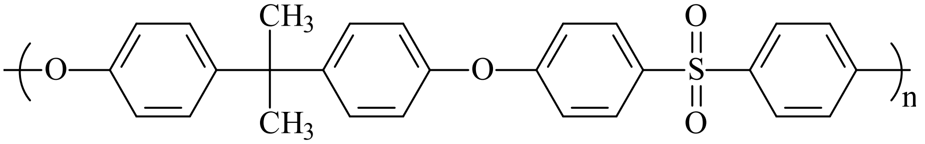
ABSTRACT: New sulfonated poly(arylene ether sulfone) copolymers have been successfully synthesized in high molecular weight with controlled degrees of disulfonation up to 70 mol% via direct copolymerization of sulfonated aromatic dihalides, aromatic dihalides, and one of four structurally distinct bisphenols. The wholly aromatic acid form proton conducting copolymers are of interest as proton exchange membranes (PEM) for fuel cells. The disodium salts of 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone and 3,3'-disulfonated-4,4'-difluorodiphenyl sulfone comonomers were synthesized via sulfonation of 4,4'-dichlorodiphenyl sulfone or 4,4'-difluorodiphenyl sulfone with 30% fuming sulfuric acid at 110 ^{o}C. Four bisphenols (4,4'-bisphenol A, 4,4'-bisphenol AF, 4,4'-biphenol, and hydroquinone) were investigated for the syntheses of novel copolymers with controlled degrees of sulfonation. The composition and incorporation of the sulfonated repeat unit into the copolymer were confirmed by ^{1}H NMR and Fourier transform infrared spectroscopy (FTIR). Solubility tests on the sulfonated copolymers confirm that no cross-linking and probably no branching occurred during the copolymerizations. Tough, ductile films could be solvent cast and exhibited increased water absorption with increasing degrees of sulfonation. These copolymers are promising candidates for high temperature proton exchange membranes in fuel cells which will be reported separately in a forthcoming paper.

Key Words: sulfonated activated halide monomers, direct copolymerizations, proton exchange membranes, fuel cells, polyether sulfones, bisphenol structures.

Introduction

Poly(arylene ether sulfones) are engineering thermoplastics which are well-known since the pioneering studies of R. N. Johnson and A. G. Farnham *et. al* to have excellent mechanical and chemical properties [1-3]. They are utilized as films, coatings, membranes in ultrafiltration systems, gas separators, and other high performance molded and/or extruded applications[4]. Chemical modifications of polymers can be employed to tailor properties of many materials. Post-sulfonations of aromatic rings[5,6] is one example of an electrophilic aromatic substitution reactions which can be exploited for increasing the hydrophilicity of poly(arylene ether sulfone)s.

Post- sulfonation of poly (arylene ether sulfone)s has been accomplished with various sulfonating agents. Chlorosulfonic acid was perhaps the earliest reported sulfonation agent for poly(arylene ether sulfone)s[7]. Many researchers have further investigated this methodology for poly(arylene ether sulfone)s[8-10] as well as for other aryl containing polymers[11,12]. However, undesirable chain scission, particularly with isopropylidene units (Bisphenol A), branching and/or cross-linking can occur using chlorosulfonic acid[6]. There are reports of decreased intrinsic viscosity and insolubility (partial gelation), and the inability to produce coherent films after modification. Sulfonation with sulfuric acid has also been demonstrated for many aromatic



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polymers[13-15]. Noshay and Robeson[5] introduced a mild sulfonation procedure in which a complex of sulfur trioxide and triethyl phosphate was used to sulfonate commercially bisphenol A based poly(arylene ether sulfone), Udel® **(1)**, as shown in Scheme 1 B. C. Johnson *et al.*[6] utilized this route to prepare materials intended for applications as desalination membranes. While the milder sulfur trioxide-triethyl phosphate complex produces materials devoid of side reactions, the procedure requires careful handling and preparation and generally is limited to only one sulfonate per activated unit. An interesting, but somewhat lengthy sulfonation process involving lithiating Udel® with n-butyllithium at low temperatures, sulfinating the metallated aromatic ring using sulfur dioxide, and finally oxidizing to afford the modified sulfonated poly(arylene ether sulfone) was demonstrated by Kerres[16].

In our experience, only modest control and reproducibility over the sequence lengths of sulfonated units is afforded by post-sulfonation procedures. Accordingly, several groups[17,18], including our own[19-22] have explored monomer sulfonations and subsequent controlled copolymerization. Matzner and Robeson demonstrated the sulfonation of 4,4'-dichlorodiphenyl sulfone (DCDPS) [23] for the purposes of producing more fire resistant polyarylates . Ueda *et al.*[24] copolymerized 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone, 4,4'-dichlorodiphenyl sulfone, and bisphenol A to generate copolymers utilizing up to 30 mole percent of the disulfonated monomer, although relatively little characterization was provided. One may argue that this approach allows for much better control of the position and degree of sulfonation of poly(arylene ether sulfones).

Current interest involves the synthesis of potentially economical, commercially viable and highly thermo-oxidatively stable engineering polymers as candidates for proton exchange membranes in fuel cells (PEMFCs). Fuel cells are attractive alternative energy devices that convert chemical energy directly into electrical energy by a series of platinum catalyzed reactions[25]. The proton exchange membrane (PEM) should minimize mixing of the reactant gases and also serve as an electrolyte, permitting proton conduction from the anode to the cathode. Perfluorinated copolymers, such as Nafion® (DuPont), are the current fuel cell PEM materials of choice. These are good proton conductors and are very stable chemically. Conversely, perfluorinated copolymers have several limitations, some of which include (a) low moduli as well as modest Tg values; (b) reduced conductivity at temperatures above 80 °C; and (c) relatively high methanol permeability, which limits efficient application for direct methanol fuel cells. They are also recognized to be currently quite expensive.

Systematic results derived by copolymerizing four different bisphenols with 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS) or 3,3'-disulfonated-4,4'-difluorodiphenyl sulfone(SDFDPS) and their respective parent compounds are presented in this paper. The chemical structures of the bisphenols were selected to investigate anticipated differences in thermo-oxidative and hydrolytic stability, as well as hydrophilicity in the resultant copolymers. The isopropylidene link in the bisphenol A unit could be unstable at elevated temperatures under the strongly acidic PEM fuel cell conditions and the oxidative stability may also be an issue. Bisphenol A (BA) and 6F-bisphenol A (6FBA) produced flexible film forming materials, but have distinct differences in hydrophilicity as judged by water swelling and subsequent photoelectron spectroscopy (XPS) measurements. Biphenol (BP) and hydroquinone (HQ) afforded more rigid (i.e., higher Tg), wholly aromatic copolymers. The results may be compared with our earlier reports which were primarily focused on 4,4'-biphenol systems[22,26]. Moreover, the influences of the varying reactivities of the bisphenols on the conditions required for syntheses of high molecular weight sulfonated poly(arylene ether sulfone) copolymers with controlled degrees of sulfonation have also been explored.

Experimental

Reagents: 4,4'-Isopropylidenediphenol (Bisphenol A, Bis A), obtained from Dow Chemical, was recrystallized from toluene and dried under vacuum. 4,4'-Hexafluoroisopropylidenediphenol (Bisphenol AF or 6F Bisphenol A), received from Ciba, was purified by sublimation and dried under vacuum. Eastman Chemical provided high purity 4,4'-biphenol (BP) and the hydroquinone (HQ) which were dried, but otherwise used as received. Highly purified 4,4'-dichlorodiphenyl sulfone (DCDPS) was dried and used as received (Solvay Advanced Polymers). The specialty monomer 4,4'-difluorodiphenyl sulfone (DFDPS) was purchased from Aldrich and recrystallized from toluene. N-methyl-2-pyrrolidinone (NMP) (Fisher) was vacuum distilled from calcium hydride onto molecular sieves under vacuum, then stored under nitrogen. N,N-Dimethylacetamide (DMAc) (Fisher) was distilled under vacuum from phosphorous pentoxide and stored over molecular sieves under nitrogen. Potassium carbonate was vacuum-dried prior to polymerization. Toluene and sodium chloride were obtained from Aldrich and used as received.

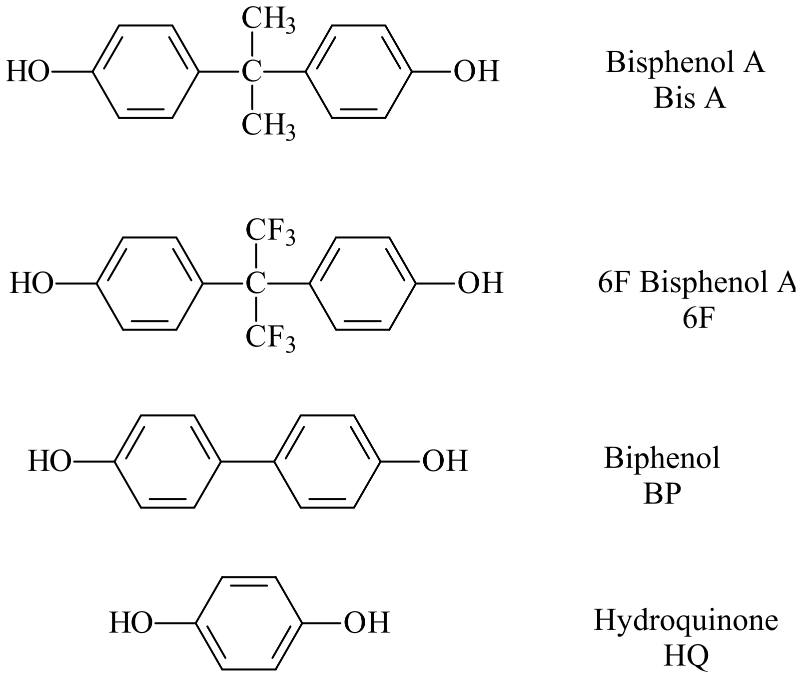

Figure 1. Bisphenol structures investigated.

Synthesis of disodium salt of 3,3'-Disulfonated-4,4'-Dichlorodiphenyl Sulfone (SDCDPS)

An optimized procedure from previously reported approaches[19,20] was developed and utilized for the synthesis of SDCDPS from 4,4'-dichlorodiphenyl sulfone (DCDPS). A typical procedure is as follows: DCDPS (28.7 g, 99 mmol) was dissolved in 60 mL of 30% fuming sulfuric acid (approximately a two-equivalent excess) in a 100-mL, three necked flask equipped with a mechanical stirrer and a nitrogen inlet/outlet. The solution was heated to 110 °C for 6 hours to produce a homogenous solution. Then it was cooled to room temperature and dissolved into 400 mL of icewater. Next, 180 grams of sodium chloride were added, which produced a white precipitate identified as the disodium salt of 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone. The powder was filtered, re-dissolved in 400 mL of deionized water and then the pH was reduced to 6~7 by adding aqueous 2N sodium hydroxide. An excess of NaCl (~180 grams) was added to salt out the sodium form of the disulfonated monomer. The crude product was filtered and recrystallized from a heated mixture of alcohol (methanol or isopropanol) and deionized water (7/3, v/v), producing fine white needle-like crystals upon cooling over night. Proton (^{1}H) NMR, carbon (^{13}C) NMR, as well as fast atom bombardment mass spectroscopy were used to confirm structure and purity of the monomer. Elemental analysis was satisfactory assuming a dihydrate was formed as suggested earlier[22]: Calcd.: C, 27.3; H, 1.15; S, 18.2; Na, 8.72. Found: C, 27.4; H, 1.23; S, 19.6; Na, 9.36.; Mass spectrum: 467 Daltons (SDCDPS - Na+). No melting point was observed for this ionic compound below 300 °C. The yield after recrystallization was 88%, based on DCDPS.

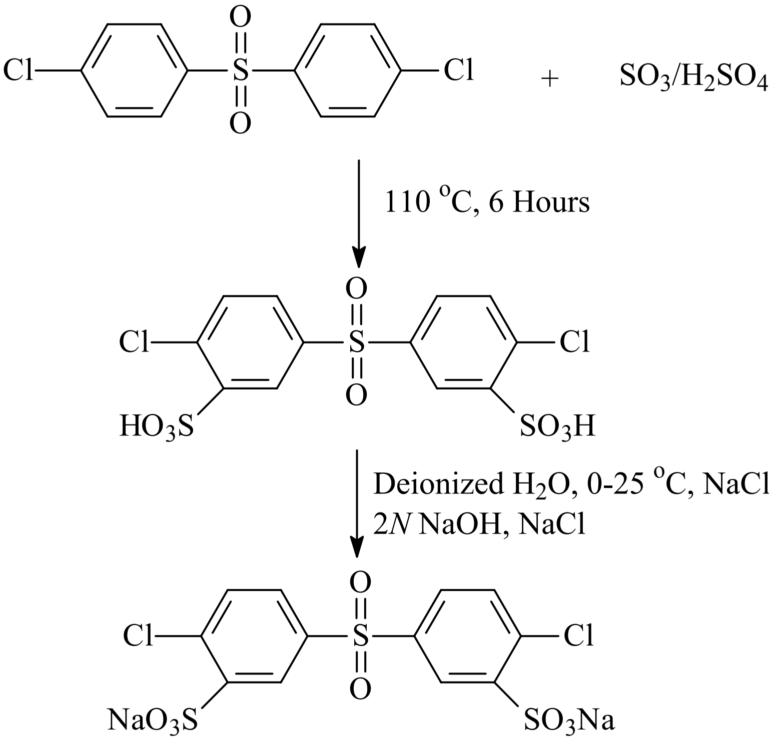

Figure 2. Synthesis of disodium salt of3,3’-disulfonated-4,4’-dichlorodiphenyl sulfone (SDCDPS).

Synthesis of disodium-3,3'-disulfonated-4,4'-difluorodiphenyl sulfone (SDFDPS)

The synthesis of SDFDPS was successfully produced from 4,4’-difluorodiphenyl sulfone using a similar procedure to that described for SDCDPS synthesis and recrystallized from isopropanol and deionized water (5/1, v/v). SDFDPS was also characterized using ^1H and ^{13}C NMR spectroscopy and the atomic composition was confirmed with elemental analysis. Recrystallized yield: 70%.

Note: prior to copolymerization, SDCDPS and SDFDPS were dried at temperatures up to 130 °C under vacuum for at least 24 hours before use to remove water.

Care must be taken when weighing this hydroscopic monomer, to achieve desired stoichiometries.

A practical nomenclature for the copolymers described in this manuscript will be as follows. Four different bisphenols and various ratios of disulfonated dihalide to non-sulfonated dihalide were employed, we will herein use X-YY symbolism, where X refers to the bisphenol and YY is the mole percent of the disulfonated dihalide. For example, Bis A-20 describes the bisphenol A based disulfonated copolymer that utilized 20 mol% 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS) with 80 mol% 4,4'-dichlorodiphenyl sulfone (DCDPS).

Synthesis of Sulfonated Poly(arylene ether sulfone) Copolymers using SDCDPS via Nucleophilic Step-Growth Copolymerization

The copolymerization procedures for the well dried monomers were similar for all bisphenols, even though the reactivities were different. A typical copolymerization for all sulfonated copolymers will be described using the bisphenol A-40 system. Firstly, 1.2624 g (5.5 mmol) bisphenol A, 0.9621 g (3.3 mmol) DCDPS, and 1.0806 g (2.2 mmol) SDCDPS (rapidly weighed) were added to a 3-neck flask equipped with an overhead mechanical stirrer, nitrogen inlet and a Dean Stark trap. Potassium carbonate (6.3 mmol, 0.88 g), and sufficient NMP (18 mL) were introduced to afford a 20% (w/v) solids concentration. Toluene (9 mL) (usually NMP/Toluene = 2/1, v/v) was used as an azeotroping agent. The reaction mixture was refluxed at 150 ºC for 4 hours to dehydrate the system. The temperature was raised slowly to 190 ºC by controlled removal of the toluene. The reaction was allowed to proceed for 16-35 hours, during which the solution became very viscous. The solution was cooled to room temperature and diluted with enough DMAc to allow easier filtering. After filtering through filter paper to remove most of the salts, the copolymer was isolated by coagulation in stirred deionized water. The precipitated copolymer was also washed several times with deionized water to attempt to completely remove salts, then extracted in deionized water at 60 ^{o}C overnight. Finally, it was vacuum dried at 120 ºC for 24 hours. Copolymers with other bisphenols and compositions were also prepared via similar procedures. The homopolymer control from each respective bisphenol and DCDPS were similarly recovered by simple dilution filtration, and then precipitation in a methanol and water mixture (8/1, v/v) in Waring blender.

Synthesis of Sulfonated Poly(arylene ether sulfone)s using SDFDPS via Nucleophilic Step-Growth Copolymerization

Copolymerizations utilizing 4,4'-difluorodiphenyl sulfone (DFDPS) and 3,3'-disulfonated-4,4'-difluorodiphenyl sulfone (SDFDPS) could be conducted at lower reaction temperatures due to the well known enhanced comonomer reactivity. A typical reaction is presented for hydroquinone-50. Hydroquinone (2.018 g, 18 mmol), DFDPS (2.353 g, 9 mmol) and SDFDPS (4.201 g, 9 mmol) were added to a 3-neck flask equipped with a mechanical stirrer, nitrogen inlet and Dean Stark trap. Next, 2.9 g of dried potassium carbonate, and DMAc (43 mL) were introduced into the reaction flask. Toluene (22 mL) was used to azeotrope water. The reaction mixture was refluxed at 150 ºC for 4 hours to dehydrate the system. Toluene was slowly removed to increase the reaction temperature to 175 ºC and held constant for at least 16 hours. The viscous reaction solution was cooled and diluted with DMAc. The disulfonated copolymer isolation steps were similar to those previously described for DCDPS/SDCDPS copolymerizations.

Membrane preparation

Membranes in the sodium sulfonate form were prepared by first redissolving the copolymer in DMAc to afford 5-10% transparent solutions followed by casting onto clean glass substrates. The films were carefully dried with infrared heat at gradually increasing temperatures (up to ~ 60 ^{o}C) under a nitrogen atmosphere, and then vacuum-dried at temperatures up to 150 ^{o}C for two days.

Acidification of Sulfonated Copolymers Membranes

The sulfonated poly(arylene ether sulfone) copolymer films were converted to their acid- form by boiling the cast membranes in 0.5 M sulfuric acid for 1.5 hours, followed by 1 hour extraction in boiling deionized water, which has been referred to as Method 2[27]. An alternative acidification procedure, entailing immersion of membranes for 24 hours in 1.5 M sulfuric acid at 30 ^{o}C followed soaking for 24 hours in deionized water, was investigated; the effect of the acidification treatment on conductivity and hydrophilicity is significant and will be discussed in a separate paper[27]. The acidified membranes were either dried under vacuum at 90 ^{o}C in 48 hours or stored in deionized water at 30 ^{o}C.

Characterization Methods

Fourier Transform Infrared (FTIR) Spectroscopy

Thin films of the copolymers were solvent cast from DMAc (~5%, w/v) and spectra were recorded for both the disodium-salt and diacid forms using a Nicolet Impact 400 FT-IR spectrometer to confirm the functional groups concentration of the copolymers.

Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H and ^{13}C NMR analyses were conducted on a Varian UNITY 400 spectrometer. All spectra were obtained from a 10% solution (w/v) in dimethylsulfoxide-d_6 solution at room temperature. Monomer purity as well as copolymer compositions were analyzed via NMR spectroscopy.

Intrinsic Viscosity, Solution Properties and Water Uptake

Homo- and sulfonated copolymer solubilities were determined at 10% concentration (w/v) in a number of solvents, including NMP, DMAc, DMSO, and chloroform. Intrinsic viscosities were determined in NMP at 25 ºC using an Ubbelohde viscometer.

Water uptake was determined on films for all of the poly(arylene ether sulfone) copolymers in both the sulfonate and acidified forms. The films were first thoroughly dried at 150 ^{o}C under vacuum to a constant weight, which was recorded. The dried film was then immersed in water at 30 ^{o}C and periodically weighed on an analytical balance until constant water uptake weight was obtained. Typically, the apparent equilibrium water sorption occurred within 48 hours. The water uptake is reported as a percentage and determined by taking the weight difference between the wet film and the dry film and dividing by the dry film weight**.**

$$\text{Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

Where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively.

Non-Aqueous Potentiometric Titration

Non-aqueous potentiometric titrations were conducted using a MCI Automatic Titrator Model GT-05. The acidified membrane dissolved solutions in DMAc were titrated by standard tetramethyl ammonium hydroxide in isopropyl alcohol solution (TMAH). Quantitative determination of pendent sulfonic acid groups along the copolymer chain via titration confirmed the spectroscopic values and also allowed for the direct measurement of the ion exchange capacity (IEC, meq/g).

Thermogravimetric Analysis (TGA)

The thermo-oxidative behavior of both the salt-form (sulfonate) and the acid-form copolymers was performed on a TA Instruments TGA Q 500. Samples were pieces of thin films and totaled a weight of 10 to 15 mg. The films were dried under vacuum for at least 12 hours prior to analysis to remove absorbed water. The samples were evaluated over the range of 30 to 800 ^{o}C at a heating rate of 10 ^{o}C/min in air.

RESULTS AND DISCUSSION

Monomer Synthesis

High yields of 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS) and 3,3'-disulfonated-4,4'-difluorodiphenyl sulfone (SDFDPS) monomers was prepared via electrophilic aromatic substitution on 4,4'-dichlorodiphenyl sulfone (DCDPS) and 4.4'-difluorodiphenyl sulfone (DFDPS), respectively, in fuming sulfuric acid using the reaction conditions depicted in Figure 2. A higher reaction temperature of 110 ^{o}C afforded a homogeneous reaction solution, whereas a precipitant was observed at high concentrations (e.g., 50%) when the monomer was synthesized at 90 ^{o}C, as reported earlier[24]. The higher yields may be associated with the homogeneous nature of the higher temperature synthesis and the absolute values are likely to be concentration dependent. The higher reactivity and possible hydrolysis of the aryl C-F bond in 4,4'-difluorodiphenyl sulfone required that ice-cold water be employed during the precipitation and, especially, during the sodium hydroxide neutralization steps. Hydroxide ions and, under some conditions water, may attack the activated halide to possibly produce an undesired phenolic impurity. High purity SDCDPS and SDFDPS were obtained in good yields (88% and 70%, respectively) after recrystallizing from 400 mL methyl or isopropyl alcohol / water mixtures. Clearly there is a difference in polarity, etc. from the use of methanol verses isopropanol and this may have some influence in the final yield, yet both alcohols afforded pure product. The ^{1}H and ^{13}NMR spectra are shown for SDCDPS in Figure 3a and 3b and ^{1}H NMR spectrum of SDFDPS in Figure 4. One may note that fluorine couples with hydrogen, which produces splitting in the signals as shown.

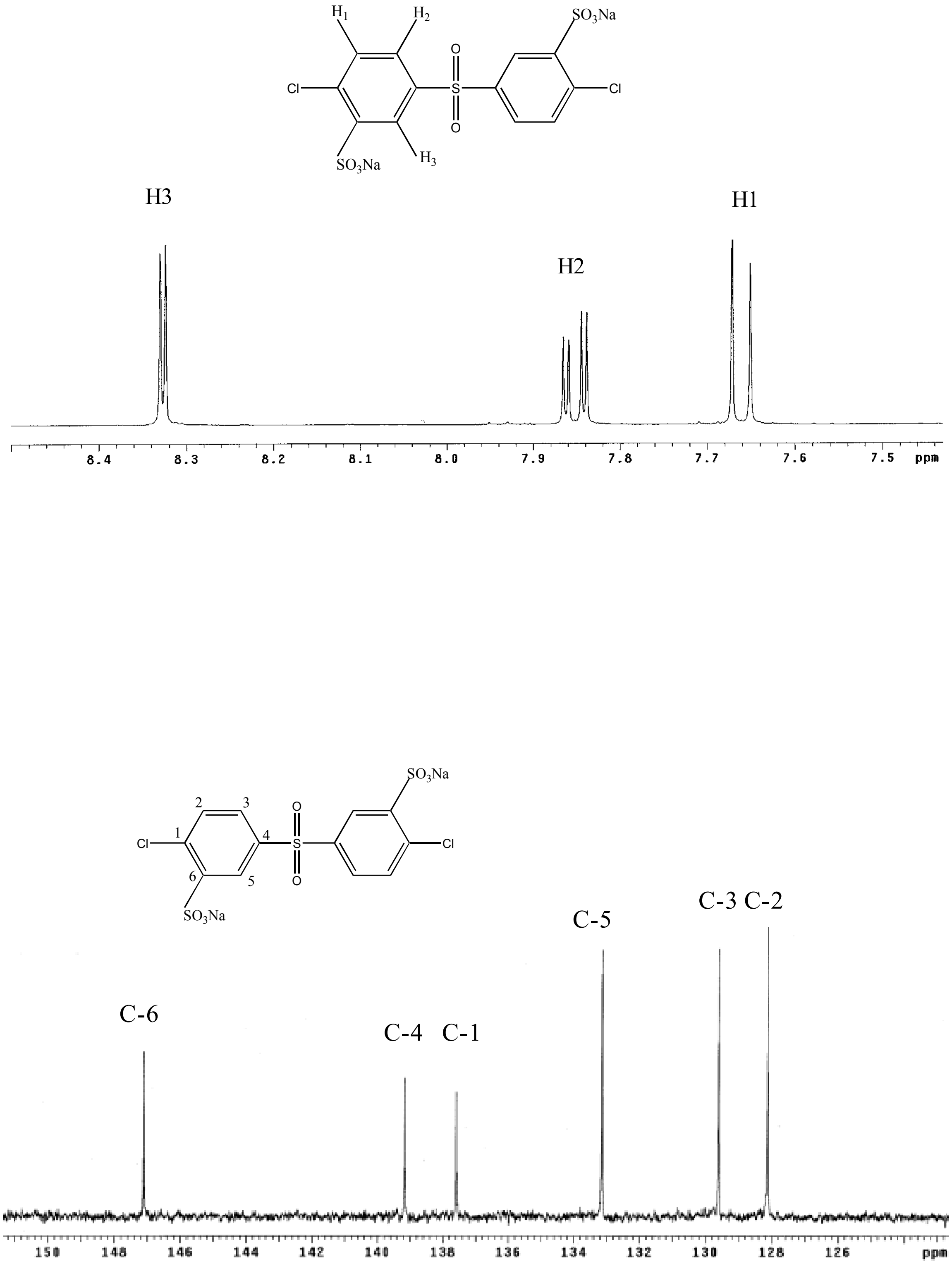

Figure 3a and 3b. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of SDCDPS. Deuterated dimethylsulfoxide is the solvent.

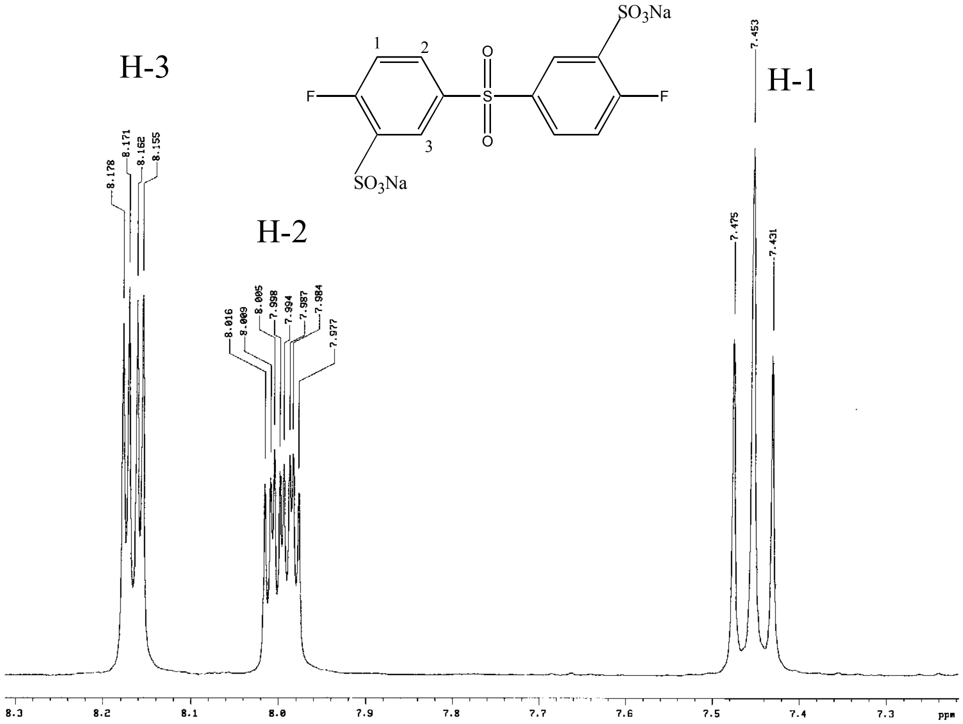

Figure 4. ^{1}H NMR spectrum of 3,3'-disulfonated-4,4'-difluorodiphenyl sulfone (SDFDPS). Deuterated dimethylsulfoxide is the solvent.

Extensive spectroscopic (FTIR, ^{1}H NMR, ^{13}C NMR, and MS) analysis of 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone and 3,3'-disulfonated-4,4'-difluorodiphenyl sulfone verified the expected synthesis of the monomers and allowed structural designation that agreed with the earlier reported syntheses^{24}. The strong acid-base exchange of the sodium hydroxide with the acidic proton of the sulfonate group was expected to be more effective and quantitative than the exchange reaction with even excess sodium chloride, which is only a modest base. Moreover, elemental analysis consistently showed better agreement with the theoretical formula composition with the additional step of sodium hydroxide neutralization (Figure 5).

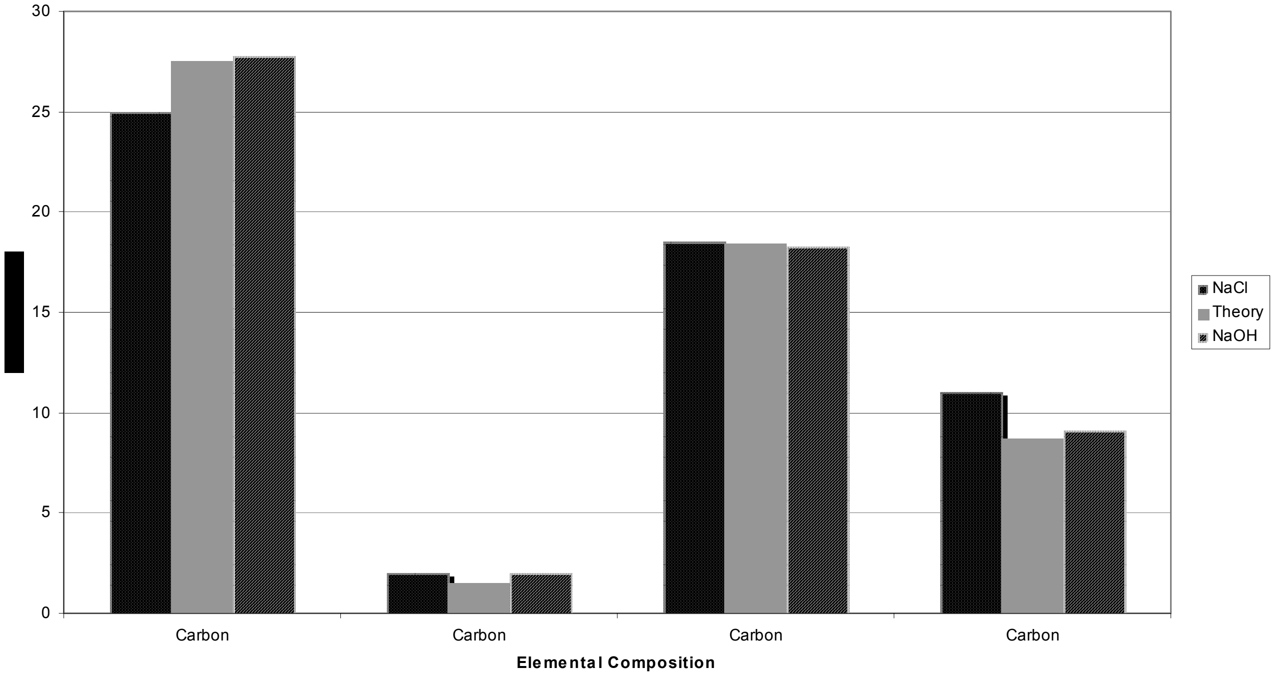

Figure 5. Elemental analysis atomic composition as a function of experimental work-up.

Copolymer Synthesis and Characterization

Nucleophilic aromatic substitution step (condensation) polymerization long been successfully employed to synthesize high molecular weight poly (arylene ether sulfones)[1-3]. Using typical polymerization conditions one may dehydrate the aprotic dipolar reaction system with toluene until a final polymerization temperature of 175 -

190°C is reached. Careful dehydration is required to obtain very high molecular weight. The higher temperatures are required with the less reactive, sterically hindered comonomer, SDCDPS. These reaction conditions were successful and were also used with bisphenol A, 4,4'-biphenol, hydroquinone and 6F bisphenol A. The reaction sequence is depicted in Figure 6. The high molecular weight sulfonated copolymers were isolated as swollen "strings" by precipitating in stirred deionized water after first diluting the viscous reaction solutions from 20 percent solids to ~10 percent solids with DMAc and filtering through filter paper to remove the salts.

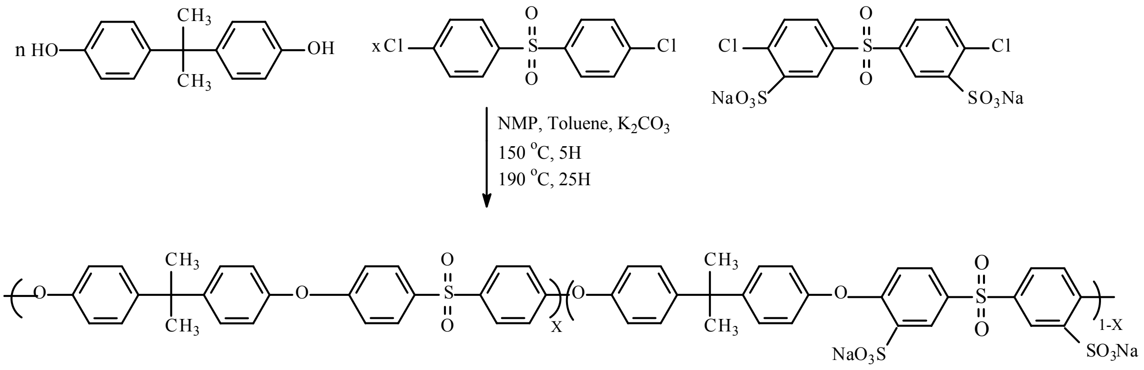

Figure 6. Synthesis of random bisphenol A-based disulfonated poly (arylene ether sulfone) copolymers.

The intrinsic viscosities of the sulfonated poly(arylene ether sulfone) copolymers and their experimental ion exchange capacities (meq/g) are compiled in Table 1A-1D. The intrinsic viscosity in NMP at 25 °C is a function of both bisphenol structure, the degree of disulfonation, and molecular weight, as expected. The intrinsic viscosity increased, but not necessarily molecular weight, as higher molar concentrations of the 3,3'-sulfonated-4,4'-dichlorodiphenyl sulfone was charged to the reaction flask, as observed for other ionomers[28]. Redissolving the isolated copolymers in DMAc produced homogeneous solutions, which were cast onto glass substrates to form coherent films. Even though apparently high intrinsic viscosities (~ 1.5 dL/g) were determined, somewhat brittle dry film behavior could be noted when greater than 40 mol% SDCDPS was used, especially for the 6F bisphenol A copolymer, if the reaction was stopped after only 20 hours. The lower reactivity of the deactivated 6F bisphenol A phenolate may have produced lower molecular weight copolymers which caused the films to be less ductile in the dry state. Difficulties were apparently encountered by earlier workers[24] as evident by lower inherent viscosities, under their reaction condition, when 30 mol% SDCDPS was used. Simply increasing copolymerization time for these second order reactions (up to 40 hours) at 190 °C was successful in yielding ductile films, which correlated with solution intrinsic viscosities values in NMP greater than 2.0 dL/g.

The synthesis of 3,3'-disulfonated-4,4'-difluorodiphenyl sulfone has been reported from our laboratory earlier, and was employed to investigate related sulfonated poly(sulfide sulfones) [29]. Accordingly, the higher reactivity of SDFDPS was exploited to produce higher molecular weight sulfonated copolymers, as suggested by the intrinsic viscosities and film ductility. Bisphenol A, biphenol, hydroquinone, and 6F bisphenol A were reacted with 4,4'-difluorodiphenyl sulfone (DFDPS) and 3,3'-sulfonated-4,4'-difluorodiphenyl sulfone (SDFDPS), respectively. The lower (175 °C) polymerization temperature proved to be significant; some degradation process (possibly only involving the reaction solvent) occurs at elevated temperatures using DFDPS/SDFDPS system as observable by a darker reaction mixture, which can afford brittle films. The successful results are also tabulated in the tables (Table 1A – 1D). Creasible films of all the sulfonated copolymers (up to 60 mol% disulfonated dihalide) were obtained.

FTIR and ^{1}H NMR were powerful tools used to identify and characterize the four series of sulfonated copolymers. NMR allowed for compositional and structural determinations for each copolymer. Integration and appropriate analysis of known reference protons of the copolymer allowed the relative composition of the various copolymers to be determined. The protons adjacent to the sulfonate group derived from the disulfonated dihalide monomer in the copolymer were well separated from the other aromatic protons (~8.25 ppm). The ^{1}H NMR for the copolymer 6F-30 in Figure 7 is a representative spectrum. The calculation is provided for 6F-30[30]. The integration concluded that 27 mol% of 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone was incorporated into the polymer. This may be within reasonable experimental error for this method. Alternatively, proper weighing of the hydroscopic monomer is challenging. Similar calculations done for all four sulfonated copolymer series are tabulated on Tables 1A-1D.

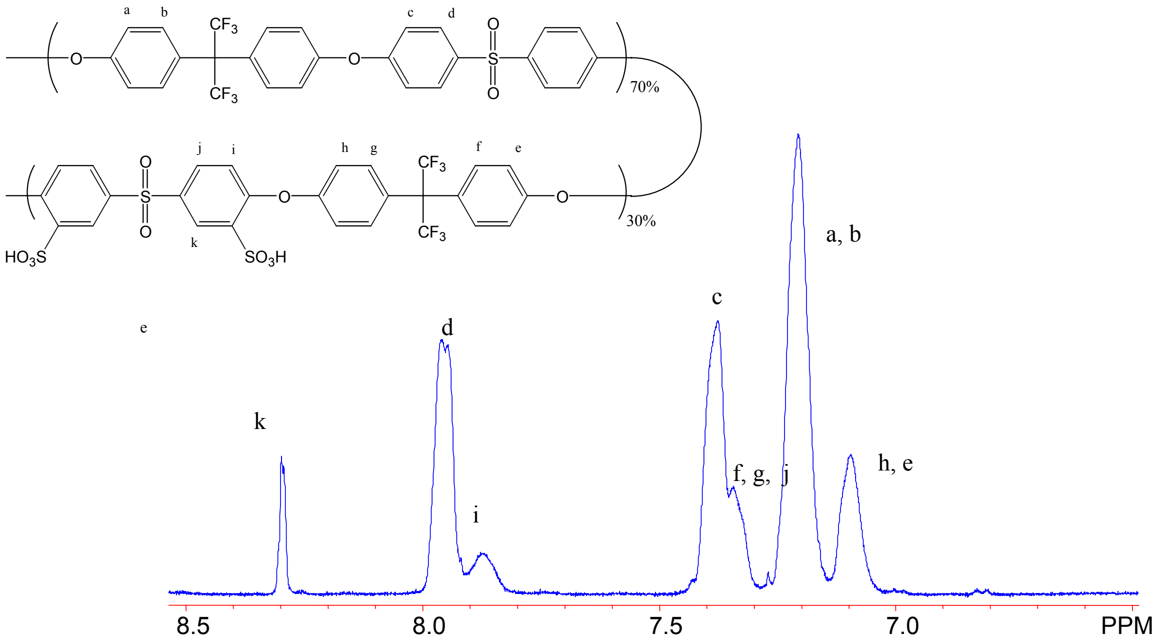

Figure 7. ^{1}HNMR of 6F-30 sulfonated poly(arylene ether sulfone) copolymer, in DMSO-d_6.

Standardized FTIR spectra allowed for qualitative and quantitative determination of the functional groups of the synthesized copolymers. Figure 8 shows the FTIR series for 4,4'-biphenol based sulfonated copolymer series as a function of degree of sulfonation. The IR peak at 1008 cm^{-1} is characteristic of the Ar-O-Ar linkage, which was selected for normalizing each of the sulfonated copolymers. Peaks at 1030 cm^{-1} corresponded to a vibrational stretching for the salt of the sulfonic acid group. The intensity increased with the amount of the incorporated sulfonated dihalide, which was observed for all sulfonated copolymer series.

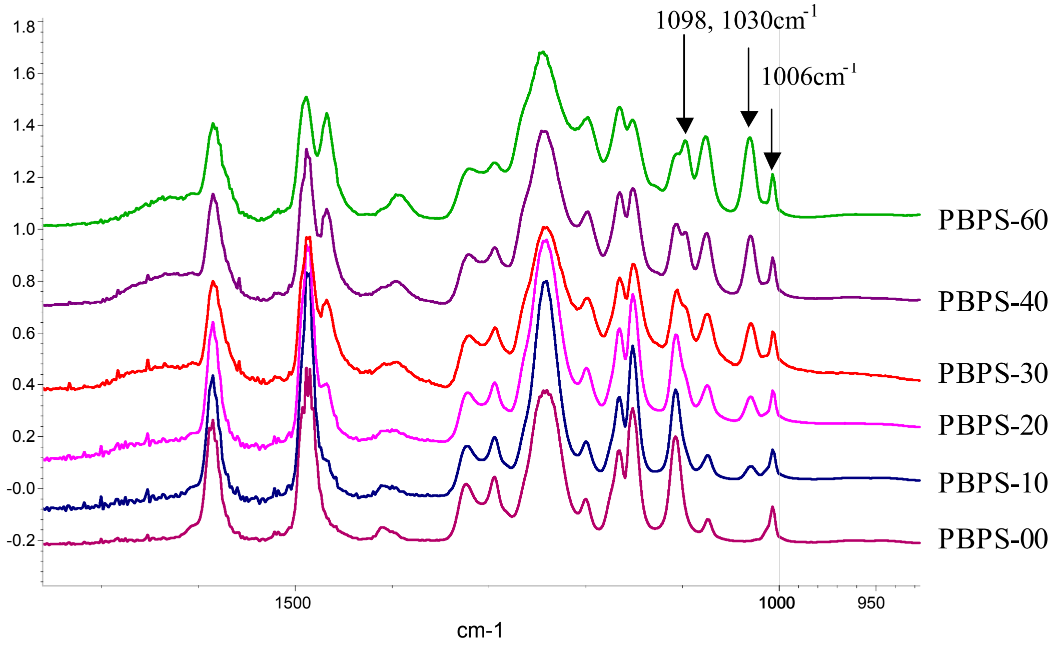

Figure 8. Influence of the degree of sulfonation on the FT-IR of biphenol-based sulfonated poly (arylene ether sulfone) copolymers.

Thermo-oxidative behavior of all unsulfonated (control) and sulfonated copolymers were investigated by thermogravimetry programmed from 30 to 800 ^{o}C at a heating rate of 10 ^{o}C/min under in air. All salt-form sulfonated copolymers displayed very high stabilities comparable to their respective control polymers. The partially aliphatic bisphenol A based copolymers, in general, displayed the lowest thermo-oxidative stabilities (5% weight loss of ~490 ^{o}C) regardless of sulfonation level. This may be attributed to the aliphatic C-H bonds of the isopropylidene group. The biphenol and hydroquinone based copolymers displayed similar thermal behavior with initial 5% weight losses of ~520 ^{o}C. An increase in the degree of disulfonation within the copolymers increased the resulting char yields and this trend was typical for all four copolymer series.

The dried, acid-form copolymer samples were examined under the same drying and heating conditions. A two-step degradation profile was observed for all copolymers in their acid-form, Figure 9. The first weight loss is typically assigned to desulfonation processes while the second weight loss peak is due to main chain polymer degradation[7,8]. At copolymer compositions of less than 40 percent the first weight loss observed is over 350 °C. These temperatures are much higher than was anticipated. However, at higher degrees of sulfonation the initial 5% weight loss was significantly lower, ~230 °C. This may be due to difficulty in water removal, or that more than one origin of weight loss. Zaidi *et al*. observed higher than theoretical desulfonation weight loss while investigating post- sulfonated PEEK samples[31]. Moreover, Samms *et al*. utilized TGA coupled to mass spectrometry (TGA-MS) to show that only partial polymer desulfonation occurs over the temperature range of 200 – 300 °C[32]. Tightly bound water associated with the sulfonic acid groups[33] may be present, even after the applied drying conditions, which may be related to mobility issues, eg. glass transition temperature.

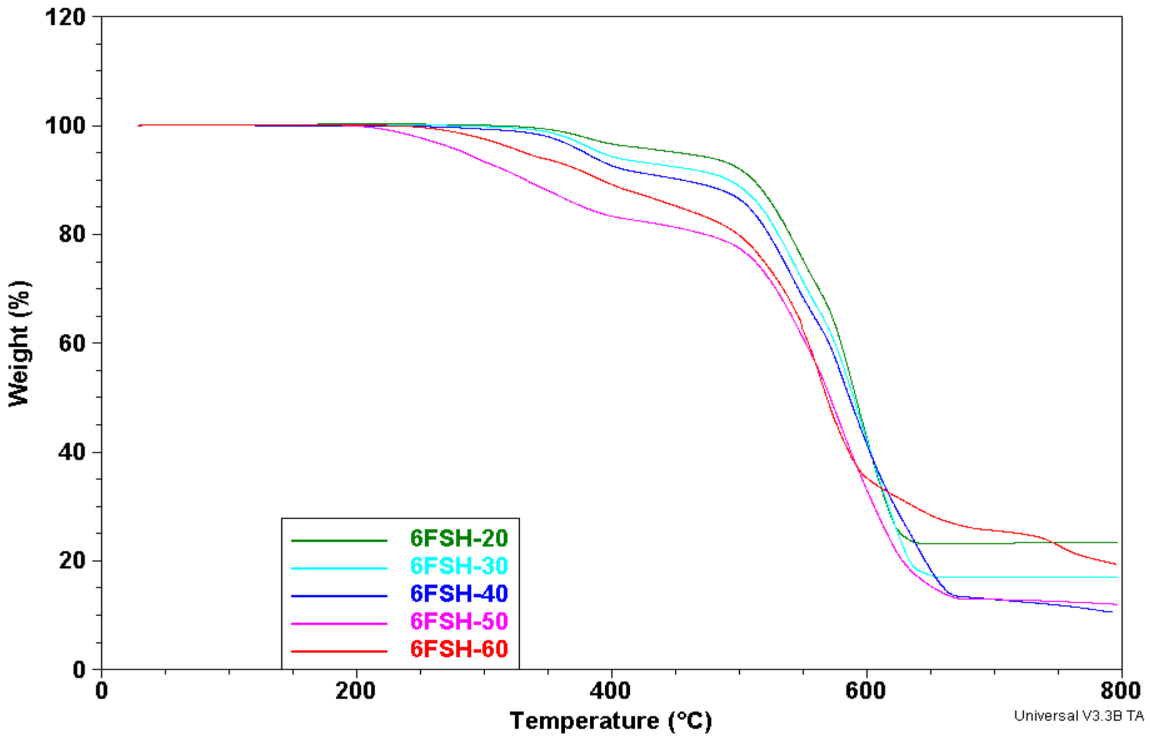

Figure 9. Influence of the copolymer composition on the TGA thermograms of acid-form 6F-based sulfonated copolymers, in air at 10 ^{o}C/min.

To further explore desulfonation temperatures (i.e., thermal oxidative stability of the pendent sulfonic acid group) a modified heating cell was connected to the FTIR. A ceramic heating cell allowed for copolymer films to be examined after exposure to a programmed temperature. Figure 10 displays the FTIR spectra series of 6FSH-30 after treatment at 140–260 ^{o}C in the heating cell for 30 minutes. Monitoring the sulfonic acid peak at 1030 cm^{-1} one can see a discernible change in the selected scans. The FTIR spectra at 180 and 220 ^{o}C show very similar profiles. When the film is exposed to 260 ^{o}C for 30 minutes there is an apparent decrease in peak intensity. This decrease can be due to at least two possible factors, desulfonation, branching via electrophilic substitution, and/or dehydration. Further experiments are underway to gain insight on this phenomenon.

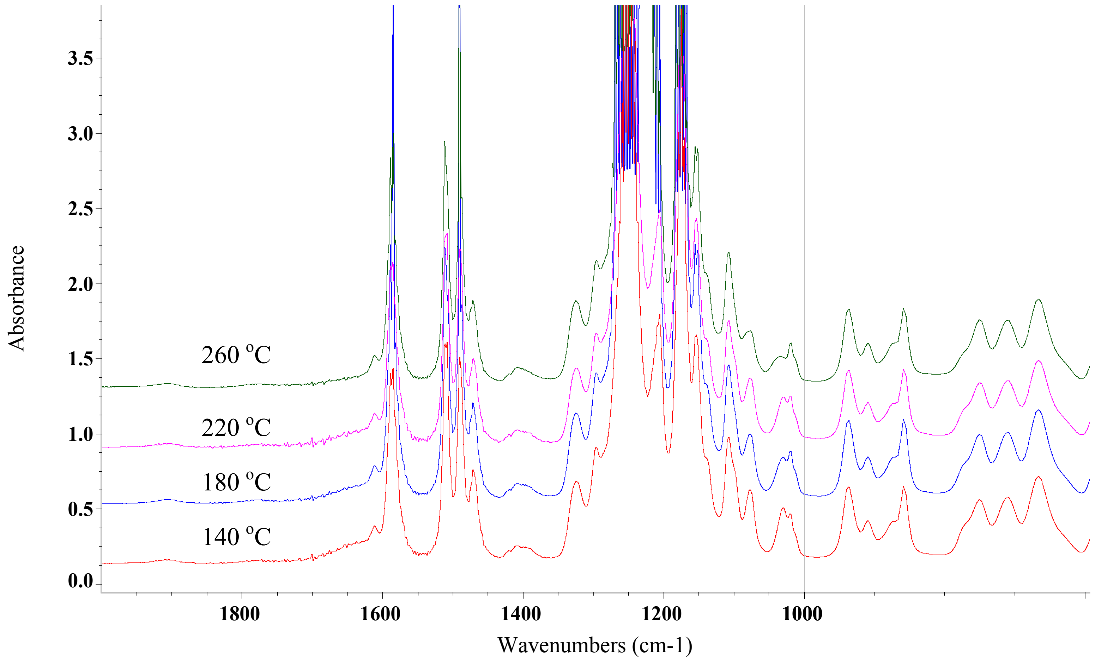

Figure 10. FT-IR spectra of 6FSH-30 after heat treatment at selected temperatures.

Solution Behavior and Water Uptake

The sulfonated poly(arylene ether sulfone) copolymers were tested for solubility in several common solvents, include NMP, DMAc, chloroform, and water. The copolymers were examined at typically 10% solutions (w/v) in each potential solvent. All control and sulfonated copolymers were soluble in NMP and DMAc and when agitated with a magnetic stir bar yielded clear, homogeneous solutions. After four weeks the unsulfonated hydroquinone control polymer (HQ-00) solution became opaque and eventually crystallized from the DMAc solution. No precipitation/crystallization was observed at any composition of the hydroquinone-based sulfonated copolymers. The bisphenol A-based copolymers were soluble in chloroform at compositions of up to 30 mol percent sulfonated dihalide, while higher sulfonated membranes formed apparent gels.

Poly(arylene ether sulfone)s are, in general, hydrophobic polymers. The hydrophilic nature of the sulfonated poly(arylene ether sulfone)s have been examined by water sorption/uptake measurements. All the sulfonated copolymers were swollen by deionized water at 30 ^{o}C but were not soluble. Ueda *et al*. reported lower water contact angles as a function of sulfonation compared to the unsulfonated control polymer[24]. The water sorption of modified membranes was a function of both the degree of sulfonation and the molecular structure. Water uptakes, at 30 ^{o}C, as a function of the degree of sulfonation and bisphenol are summarized in Table 3. The formula used for water uptake was,

$$\text{Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively. The W_{dry} for each film was the stable (equilibrium) weight of the polymer after drying under vacuum at 120 °C for at least 24 hours. W_{wet} was determined after submersion in deionized water at 30 °C for 48 hours and the excess water removed by blotting with a paper towel. This was sufficient time to reach equilibrium at this temperature. The results are tabulated on Table 3.

The water uptake for each copolymer increased with increasing sulfonation, but the bisphenol also had a marked influence on the water sorption. While bisphenol A and biphenol displayed similar water sorption, hydroquinone at equivalent mole percents was higher than comparably sulfonated copolymers. Conversely, 6F bisphenol A systems had the lowest water sorption. This result was anticipated due to the hydrophobic nature of hexafluoroisopropylidene connecting units.

One can hypothesize that an optimal degree of sulfonation could exist depending on the various proposed application. For the bisphenol A, biphenol, and hydroquinone sulfonated copolymer series a drastic increase in water uptake is observed at different composition, over an approximately 10 mol% sulfonation increment, depending on the bisphenol. Thus, a water sorption of 140 weight percent was exhibited by HQ-60, which was almost twice the water uptake of the HQ-50 copolymer. Water uptakes of more than 70 weight percent were determined for Bis A-60 and BP-60. However, over the examined range of sulfonation, similar suddenly high water uptakes for 6F bisphenol A-based sulfonated copolymers require higher sulfonated comonomer concentrations.

Using tapping mode-atomic force microscopy (TM-AFM), an extension of our earlier studies[22,26] show there appears to be a morphological phase change within the sulfonated copolymers, corresponding to the observed abrupt increase in water uptake, and these points will be further amplified elsewhere[27]. While the sulfonated poly(arylene ether sulfone) copolymers with the excessively high water uptake may have applicability to other technologies, they are probably not useful PEMs. As expected, the mechanical properties of the highly water swollen copolymers are low compared to the other moderately hydrophilic sulfonated copolymers.

CONCLUSIONS

An improved method was developed for preparing 3,3’-disulfonated 4,4’-dichlorodiphenyl sulfone and the analogous 3,3’-disulfonated-4,4’-difluorodiphenyl sulfone monomers in high yields. A series of novel sulfonated poly (arylene ether sulfone)s were synthesized via direct copolymerization of the disulfonated dihalide sulfone monomers with 4,4’-dichlorodiphenyl sulfone and any of four different bisphenols. This method resulted in the random incorporation of the sulfonated monomer throughout the copolymers, probably through the well-known ether-ether interchange process. Varying the stoichiometric ratio of the disulfonated activated aryl dihalide comonomer to the unmodified dihalide comonomer easily controlled the degree of disulfonation in the copolymers. Moreover, the direct copolymerization strategy positioned the sulfonic acid groups on the more stable, and more acidic deactivated sulfone unit as opposed to polymer (post) sulfonation of the electron rich bisphenol moieties.

The bisphenol structure and degree of disulfonation influenced the properties of the sulfonated copolymers, including solubility, ion exchange capacity, and water uptake. All sulfonated copolymers were soluble in polar, aprotic solvents at room temperature. The ion exchange capacities of the sulfonated copolymers were easily controlled by changing the molar ratio of the DCDPS to sulfonated DCDPS. Water uptake increased linearly with increasing degrees of sulfonation up to 50 mol% of the disulfonated repeat unit. However, at compositions higher than 50 mol% of the disulfonated unit, dramatic increases in water uptake and related membrane swelling were observed. The copolymers containing hydroquinone exhibited the highest water uptake, while the 6F bisphenol A sorbed the lowest values. The proton conductivity and other critical PEM features for fuel cells will be reported in Part II in this journal.

ACKNOWLEDGEMENTS

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30. **Determination of Degree of Sulfonation in 6F-30 copolymer via 1H NMR**
Using the integration for the 2- k protons (Ik) and
the integration for the 8-(a + b) protons (I(a+b)),
if Ik = 3.6 and I(a+b) = 52.8, respectively,
then [Ik / 2 protons] ÷ [(I(a+b)) / 8 protons] = Percent Sulfonated Repeat Unit
So, [3.6 / 2] ÷ [52.8 / 8] = 1.8 ÷ 6.6 =
0.273 x 100% = 27.3% Sulfonated Repeat Units

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Table 1A. Influence of Degree of Disulfonation on Several Features of Bisphenol A based Copolymers

Bisphenol	**XX, mol% SDCDPS**	**Degree of Sulfonation by ^{1}H NMR**	$[\eta]^{NMP}_{25^\circ C}$	**IEC#, meq/g**	**Water Uptake, weight %**
Bis A	0	-	0.70	0	3
Bis A	10	12	0.78	0.41	7
Bis A	20	18	0.82	0.79	13
Bis A	30	31	1.20	1.12	27
Bis A	40	37	1.86	1.58	37
Bis A	50	48	2.48 2.75*	1.78	48
Bis A	60	56	2.80 3.08*	2.13	68

* Copolymerization using DFDPS/SDFDPS system.
#Determined from non-aqueous potentiometric titration.

Table 1B. Influence of Degree of Disulfonation on Several Features of Biphenol based Copolymers

Bisphenol	**XX, mol% SDCDPS**	**Degree of Sulfonation by ^{1}H NMR**	$[\eta]^{NMP}_{25^{\circ}C}$	**IEC, meq/g**	**Water Uptake, weight %**
Biphenol	0	-	0.65	0	2
Biphenol	10	8	0.70	0.41	5
Biphenol	20	23	0.93	0.89	10
Biphenol	30	31	1.51	1.31	18
Biphenol	40	40	1.82	1.51	28
Biphenol	50	49	2.09 2.52*	1.98	38
Biphenol	60	58	2.69 2.94*	2.22	55

* Copolymerization using DFDPS/SDFDPS system.
#Determined from non-aqueous potentiometric titration

Table 1C. Influence of Degree of Disulfonation on Several Features of 6F Bisphenol A based Copolymers

Bisphenol	XX, mol% SDCDPS	Degree of Sulfonation by ^{1}H NMR	$[\eta]^{NMP}_{25^{\circ}C}$	IEC$^{\#,}$ meq/g	Water Uptake, weight %
6F	0	-	0.59	0	2
6F	10	9	0.69	0.32	5
6F	20	19	0.86	0.59	9
6F	30	27	1.49	0.87	13
6F	40	41	1.70	1.16	25
6F	50	52	2.01 2.42*	1.50	34
6F	60	58	2.07 2.53*	1.77	42

* Copolymerization using DFDPS/SDFDPS system.
#Determined from non-aqueous potentiometric titration.

Table 1D. Influence of Degree of Disulfonation on Several Features of Hydroquinone based Copolymers

Bisphenol	**XX, mol% SDCDPS**	**Calc'd. Degree of Sulfonation by ^{1}H NMR**	$[\eta]_{25^\circ C}^{NMP}$	**IEC$^{\#}$, meq/g**	**Water Uptake, weight %**
HQ	0	-	0.89	0	2
HQ	10	13	0.86	0.60	7
HQ	20	18	1.20	1.00	23
HQ	30	32	1.82	1.58	31
HQ	40	38	2.29	1.94	50
HQ	50	46	2.37 2.65*	2.48	68
HQ	60	55	2.41 2.88*	2.77	>140

* Copolymerization using DFDPS/SDFDPS system.
#Determined from non-aqueous potentiometric titration

CHAPTER 5

SUMMARY AND CONCLUSIONS

This research involved the synthesis and characterization of poly (arylene ether sulfone) copolymers as candidates for proton exchange membranes in fuel cells. The principal objective of this research was to systematically synthesize four series of sulfonated poly (arylene ether sulfone) copolymers containing controlled amounts of sulfonic acid groups via the direct copolymerization of sulfonated comonomers. As important to fuel cell operation conditions, the four novel sulfonated copolymers were evaluated for their film- forming characteristics, water uptake, morphology, ion-exchange capacity, and proton conductivity. The thermal stabilities of the copolymers were also evaluated.

Five sulfonated monomers were synthesized by electrophilic aromatic substitution of commercially available compounds 4,4’-bisphenol A, 4,4’-biphenol, 6F bisphenol A, 4,4’-dichlorodiphenyl sulfone, and 4,4’-difluorodiphenyl sulfone in fuming sulfuric acid and isolated as their respective sodium salts. Due to insolubility of the three sulfonated bisphenols they could not be copolymerized under the conditions employed in this work, but they are recommended for use in future research. However, 3,3’-disulfonated 4,4’-dichlorodiphenyl sulfone (SDCDPS) and 3,3’-disulfonated 4,4’-difluorodiphenyl sulfone (SDFDPS) were synthesized with high purity in very good yields.

Four bisphenols, bisphenol A, biphenol, 6F bisphenol A, and hydroquinone, were utilized in the direct copolymerization with either dichlorodiphenyl sulfone and sulfonated dichlorodiphenyl sulfone or difluorodiphenyl sulfone and sulfonated difluorodiphenyl sulfone to yield high molecular weight, film-forming polymers. The copolymerizations produced random sulfonated poly (arylene ether sulfone) copolymers with up to 60 mol% sulfonated dihalide comonomer. Essentially quantitative incorporation of the 3,3-sulfonated-4,4’-dichlorodiphenyl sulfone or 3,3’-sulfonated-4,4’-difluorodiphenyl sulfone into the copolymers was achieved based on potentiometric titration, ^{1}H NMR and FTIR spectroscopic methods, and the copolymers compositions were easily controlled by varying the comonomers' stoichiometric feed ratios. The influence of the bisphenol structure, as well as the degree of sulfonation, on the properties of each sulfonated poly (arylene ether sulfone) copolymers was of particular interest.

All four copolymer series demonstrated high thermo- oxidative stability in their acid-form with no significant weight loss until ~300 ^{o}C in TGA at 10 ^{o}C /min. The salt form of each sulfonated copolymer was also evaluated and showed comparable stabilities to its respective control polymer. The sulfonated copolymers demonstrated a two-step degradation. The first weight loss between 300 - 400 ^{o}C was attributed to desulfonation and the loss of absorbed or bound water. The second weight loss, typically at 450 ^{o}C, was due to the decomposition of the polymer backbone. The polymer backbone thermo-oxidative degradation was dependent upon the bisphenol structure, with bisphenol A-based copolymers being the least stable. The acid-form 5% weight loss temperatures for all four copolymer series decreased with increasing sulfonation, but these temperatures are considerably above the proposed operation temperature (120 -150^{o}C) of proton exchange membrane fuel cells.

Water uptake and proton conductivities were determined for each sulfonated poly (arylene ether sulfone) copolymer. The water uptake increased as a function of disulfonation. Also, the bisphenol structure influenced the amount of water absorbed by the copolymers. Hydroquinone-based sulfonated copolymers showed the highest water uptake at comparable degrees of sulfonation while 6F bisphenol A-based copolymers showed the lowest. It was shown that the acidification method as well as the drying conditions also played prominent roles in water uptake. The very high levels of water uptake of many of the highly sulfonated copolymers may limit their applicability in PEMFCs due to excessive swelling.

The proton conductivities of each sulfonated copolymer also increased with increasing degrees of sulfonation. This agrees well with expectations due to the related increase in the ion exchange capacity, i.e., the increasing number of pendant sulfonic acid groups. The conductivity measurements for optimized copolymers established values that matched or surpassed those of commercial control Nafion® under similar test conditions (0.1 S/cm at 30 ^{o}C). The water content and closely related acidification method influenced the measured conductivities. Importantly, under similar conditions it was determined that across the four copolymer series the proton conductivities were the same at similar ion exchange capacities. This conclusion should be expected but has not been highlighted or reported by others. This is probably due to difficulties in the control of polymer post-sulfonation reactions and the lack of a previous systematic study.

CHAPTER 6

SUGGESTED FUTURE WORK

Results outlined in previous chapters demonstrated the vast opportunities of synthesizing novel polymeric materials and the exciting ability to influence several important properties. There is still a great deal of information that needs to be ascertained in order to completely understand the structure-property relationships of the copolymers and their effects on the membrane properties. The incorporation of bis (4-hydroxyphenyl) phenyl phosphine oxide (BOHPPO) or other monomers containing polar groups may provide polymers with interesting properties. These polar groups may be able to interact with the pendent sulfonic acid groups. Xiao *et al*.[336] recently reported lower water uptake by incorporating carbonyl groups, which the authors demonstrated via FTIR studies to be due to the presence of hydrogen bonding. These results are consistent with unpublished data on sulfonated poly (arylene ether) copolymers that contain polar nitrile groups[337].

It is also recommended that work continue on a procedure to copolymerize the sulfonated bisphenols described in this research--in particular disulfonated biphenol and disulfonated 6F bisphenol A. Such a study may be in order to provide a comprehensive comparison on the impact of the location (*activated* vs. *deactivated* ring) of the pendent sulfonic acid on stability, acidity, etc. The isolation of a different salt, perhaps the potassium or lithium salt, may lead to improved solubility. The use of co-solvents may be necessary to obtain the desired solution. Due to the high water solubility of the sulfonated bisphenol salts, the use of a small amount of water as part of the co-solvent system may be possible. The water will be removed azeotropically during the reaction.

The investigation on the synthesis of sulfonated block copolymers for direct comparison to the random copolymers synthesized in this research may provide interesting microstructures and properties. Poly (arylene ether ketone)-block- sulfonated

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[336] Xiao, G.; Sun, G.; Yan, D.; Zhu, P.; Tao, P., *Polymer* **2002**, 43, 5335.

[337] Mike Sumner, Ph.D Candidate, VPI & SU, Personal Conversation, July 2002.

poly (arylene ether sulfone) copolymers are only one possibility. The unsulfonated polyketone block will be hydrophobic and may modify or restrict the water sorption of the sulfonated block domains. The success of this reaction will depend on the careful control of the molecular weight of the blocks, the minimization of ether-ether interchange reactions, and the separation of the two blocks. The selection of the poly (ether ketone) block may be important –especially considering the possibility of this segment being semi-crystalline.

As mentioned in Chapter 1, considerable work has been initiated using additives such as various heteropolyacids (HPA). Some work has already been done by my colleague Dr. Kim in our group using the biphenol-based poly (arylene ether sulfone) copolymers and has shown improved conductivity and modification in water uptake with the incorporation of different weight percents of tungsten or zirconium- based HPAs. More extensive work should be done using the various copolymer systems using the data and knowledge gained in this research.

APPENDIX

SYNTHESIS OF SULFONATED POLY (ARYLENE ETHER SULFONES) VIA CHLOROSULFONIC ACID

As detailed in Chapter 1 the sulfonation of polymers has been investigated for over four decades. While many sulfonating agents have been employed chlorosulfonic acid was selected in this research due to its simplicity and adaptability. For instance, sulfuric acid has been criticized for its heterogeneous nature in generating sulfonated polymers while sulfur trioxide and sulfur trioxide complexes require special handling and / or preparation. The sulfonation of pre-dissolved polymers via chlorosulfonic acid allows for a statistically equivalent opportunity for each repeat unit to undergo electrophilic substitution. Furthermore, no additional preparation is required for chlorosulfonic acid use.

In this study sulfonated poly (arylene ether sulfones) were successfully produced using chlorosulfonic acid or its trimethyl silylated derivative. The degree of sulfonation was controlled, to some extent, by varying the molar equivalents of polymer to chlorosulfonic acid. The reaction scheme is given below.

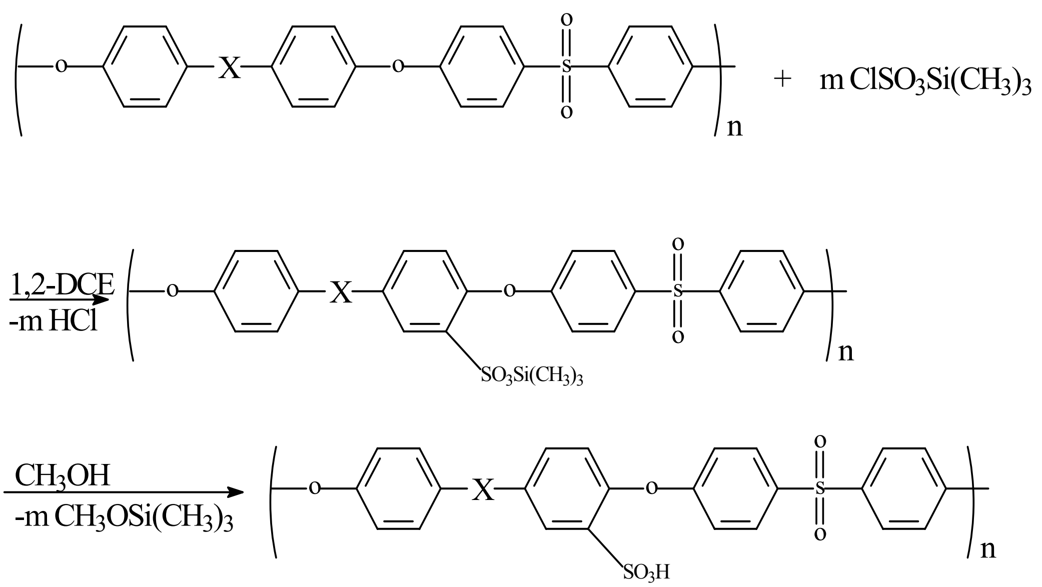

FIGURE A. SYNTHESIS OF SULFONATED POLY (ARYLENE ETHER SULFONES) VIA TRIMETHYL SILYL-DERIVATIVE OF CHLOROSULFONIC ACID.

Experimental

Reagents: 4,4'-Isopropylidenediphenol (Bisphenol A, Bis A), obtained from Dow Chemical, was recrystallized from toluene and dried under vacuum. Hexafluoroisopropylidenediphenol (Bisphenol AF or 6F Bisphenol A, 6F), received from Ciba, was purified by sublimation and dried under vacuum. Eastman Chemical provided high purity 4,4'-biphenol (BP) which was dried under vacuum prior to use. Highly purified 4,4'-dichlorodiphenyl sulfone (DCDPS) was dried and used as received (Solvay Advanced Polymers). N-methyl-2-pyrrolidinone (NMP) (Fisher) was vacuum distilled from calcium hydride onto molecular sieves under vacuum, then stored under nitrogen. Potassium carbonate was vacuum-dried prior to polymerization. The solvent 1,1,2-trichloroethane (TCE), received from Aldrich containing 2-propanol (~5%), was purified by distillation and stored under nitrogen in the presence of molecular sieves and. Chlorosulfonic acid, chlorotrimethylsilane, 1,2 –dichloroethane (DCE), and toluene were obtained from Aldrich and used as received.

Synthesis of Poly(arylene ether sulfone) via Nucleophilic Step-Growth

A typical polymerization for all poly (arylene ether sulfones) will be exemplified by the synthesis of 4,4’-bisphenol A and 4,4’-dichlorodiphenyl sulfone. Bisphenol A (3.98 g, 17.4 mmol) and DCDPS (5.00g, 17.4 mmol) were added to a 100mL, 3-neck flask equipped with an overhead mechanical stirrer, nitrogen inlet and a Dean Stark trap. Potassium carbonate (2.65g, 19.1 mmol) and NMP (50 mL) were introduced to afford a 20% (w/v) solids concentration. Toluene (25 mL) (usually NMP/Toluene = 2/1, v/v) was used as an azeotroping agent. The reaction mixture was refluxed at 150 ºC for 4 hours to dehydrate the system. The temperature was raised to 175 ºC by removal of the toluene. The reaction was allowed to proceed for approximately 24 hours, during which the solution became very viscous. The solution was cooled to room temperature and diluted with 40 mL DMAc to allow easier filtering. After filtering through filter paper to remove most of the salts, the polymer was isolated by coagulation in a methanol and water mixture (8/1, v/v) in a Waring blender. The polymers were then dried in a vacuum oven for at least 24 hours at 150 ºC.

Homogeneous Sulfonation of Poly(arylene ether sulfones) via Timethylsilyl Chlorosulfonate

Three different poly(arylene ether sulfones) were sulfonated using chlorosulfonic acid in an inert halogenated solvent. A sample sulfonation will be given using high molecular weight 6F bisphenol A based poly(arylene ether sulfone) as follows: To a flame-dried, 100-mL 3-necked round bottom flask fitted with a condenser, an overhead mechanical stirrer, and a modified addition funnel with a nitrogen inlet 5.5 g (9.9mmol) of dried polymer was dissolved in 60 mL 1,2-dichloroethane. Next, 11 mmol chlorotrimethylsilane (~10% molar excess) was added to the solution, followed drop-wise by 9.9 mmol chlorosulfonic acid diluted in 10 mL dichloroethane over 30 minutes. The reaction solution was stirred vigorously overnight. The final polymer mixture was precipitated into stirred cold methanol or isopropanol. The sulfonated polymers were vacuum dried at 100 ^{o}C overnight. The other polymers were sulfonated and isolated via similar procedures. Biphenol based poly(arylene ether sulfone) was alternatively dissolved in 1,1,2-trichloroethane due to low solubility in dichloroethane.. Polymers that were alcohol soluble were isolated via roto-evaporation of the low boiling solvents. All experiments were done in duplicate or triplicate.

Characterization

Intrinsic viscosities were measured in NMP at 25 °C using an Ubbelohde viscometer. Gel Permeation Chromatography (GPC) measurements were performed to characterize the molecular weights and molecular weight distributions of the polymers. The elution solvent for GPC characterization was NMP that contained ~0.02M phosphorus pentoxide at 60 °C. A Waters 150C instrument, having both a differential refractive index detector and a Viscotek differential viscometer in parallel, permitted absolute molecular weight determinations using universal calibration techniques.

FTIR measurements were obtained using a Nicolet Impact 400 instrument. The FTIR measurements were conducted using thin films of the control, unsulfonated polymers and the sulfonated polymers. Proton (^{1}H) NMR spectra of all polymers were obtained in deuterated DMSO (d_6-DMSO) at typical concentrations of 7-10% polymer solution (w/v). Galbrieth Analytical (Tennessee) performed elemental analyses.

Glass transition temperatures (Tg) of the control and modified polymers were measured with a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 10 °C/min. All the reported results were obtained during the second heat and are the midpoint temperature of the specific heat transition. Thermogravimetric analysis (TGA) was obtained on a Perkin-Elmer TGA-7 instrument. Samples of 5-10 mg were heated at 10 °C/min from 25 to 800 °C in an air atmosphere.

Results and Discussion

Three high molecular weight poly(arylene ether sulfones) were successfully synthesized via nucleophilic aromatic substitution reactions between bisphenol A, biphenol, and 6F bisphenol A, respectively, and 4,4'-dichlorodiphenyl sulfone in the presence of potassium carbonate in NMP. The mixture was first heated at 150 °C for 4 hours and finally allowed to react at 175 °C after the removal of toluene. The reaction was allowed to proceed overnight (~20 hours). After the desired time had elapsed, the viscous mixture was diluted to yield approximately a 10 % solids solution, filtered through filter paper, then finally precipitated in methanol and water mixture. The molecular weights and intrinsic viscosities for the three different poly (arylene ether sulfones) are given in Table A.

The post-sulfonation reaction is presented in Figure A. The reactions for the bisphenol A and 6F bisphenol A polymers were conducted in 1,2-dichloroethane by using chlorosulfonic acid and trimethylchlorosilane under nitrogen.. The bisphenol based poly (arylene ether sulfone0s displayed better solubility in 1,1,2-trichloroethane, which alternatively used. The initial concentrations of the polymer solution were kept at approximately 10 (w/v) percent. As described in the Experimental section, trimethylchlorosilane was diluted with the appropriate halogenated solvent and slowly added to the solution. The desired amount of chlorosulfonic acid was determined, weighed

Table A. GPC and Intrinsic Viscosity Characterization of Bisphenol A (Bis A), 6F-Bisphenol A (6F) and Biphenol (BP) based Poly (arylene ether sulfone) Homopolymers

Polymer	M_n x 10^{-3} *	M_w x 10^{-3} *	Mw / Mn	$[\eta]^{NMP, 25C}$,(dl/g)
Bis A	36.4	72.6	2.0	0.52
6F	33.2	69	2.1	0.50
BP	40	85	2.1	0.60

* GPC data collected using NMP as solvent at 60 °C.

into a dry vial, and dissolved in ~10 mL solvent. The trimethylchlorosilane was always used in excess relative to the chlorosulfonic acid.

Three series of sulfonated poly(arylene ether sulfones) with different degrees of sulfonation were synthesized. In this research chlorotrimethylsilane was employed as a protecting agent. Trimethylsilyl chlorosulfonate was generated *in situ*[338], as shown in Figure B. Trimethylsilyl chlorosulfonate is the adduct of chlorotrimethylsilane and chlorosulfonic acid. It's purpose is to minimize side reactions with the polymer. The desired sulfonic acid will be regenerated during the modified sulfonated polymers' precipitation / isolation steps in alcohol.

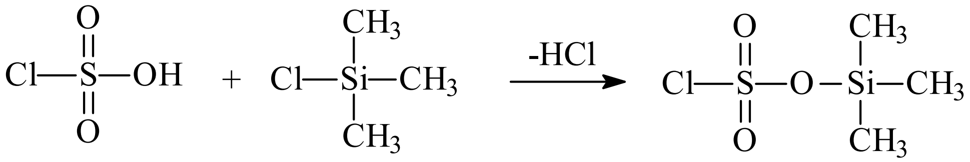

FIGURE B. *IN SITU* **GENERATION OF TRIMETHYLSILYL CHLOROSULFONATE.**

Several researchers have investigated the use of chlorosulfonic acid as a sulfonating agent for several aromatic polymers[339,340,341,342]. As discussed earlier, undesirable side reactions, including branching and chain-scission, have been observed during various post-sulfonation reactions of polymers. Polymer chain branching is possible via protonation of the –OH of a sulfonic acid group followed by the loss of water generating an active sulfonyl ($-SO_2+$) which can undergo electrophilic substitution on an

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[338] Nolte, R.; Ledjeff, K.; Bauer, M.; Mulhaupt, R., *J. Membr. Sci.* **1993**, 83, 211.

[339] Hamciuc, C.; Bruma, M.; Klapper, M., *J. Macromol. Sci.: Pure Appl. Chem.* **2001**, A 38 (7), 659.

[340] Lee, J.; Marvel, C.S., *J. Polym. Sci.: Polym. Chem. Ed.* **1984**, 22, 295.

[341] Litter, M.I.; Marvell, C.S., *J. Polym. Sci.: Polym. Chem. Ed.* **1985**, 23, 2205.

[342] Genova-Dimitrova, P.; Baradie, B.; Foscallo, D.; Poinsignon, C.; Sanchez, J.Y., *J. Membr. Sci.* **2001**, 185, 59.

adjacent aryl ring. Chao and Kelsey[343] recognized that a silyl ester will not have the acidic proton to catalyze this side reaction. Chain scission most likely occurs at the isopropylidene group in bisphenol A based polymers, but in the absence of the pendant acidic group the proposed mechanism is doubtful.

Viscometric measurements were conducted to detect possible chain scission during the electrophilic substitution. As shown in Table B, the intrinsic viscosities of each sulfonated polymer series increased with increasing degree of sulfonation. Each sulfonation reaction (i.e., at a given mol percent chlorosulfonic acid) was done at least twice; however, the data in Table B is for one experiment. Sulfonated polymers with comparable degrees of sulfonation had similar intrinsic viscosities, and the average values are presented in the Tables C1-3. No obvious signs of chain scission or high extents of branching were observed using this protected sulfonation agent, consistent with increasing intrinsic viscosity with increasing degrees of sulfonation. This is further evident by the readily soluble products. The increase in intrinsic viscosity is attributed to the increase in hydrodynamic size of the sulfonated polymer chain relative to the unmodified polymer chain. The increase in intrinsic viscosity is consistent with the trends observed in other polyelectrolytes, including the poly (arylene ether sulfone) copolymers described in the thesis.

Table B. Averaged intrinsic viscosity data of poly (arylene ether sulfones) and sulfonated poly (arylene ether sulfones) via chlorotrimethylsilane and chlorosulfonic acid with different degrees of sulfonation

Actual Degree of Sulfonation→

Bisphenol type	0	<15%	~25	~35	~60
Bis A	0.52	0.59	0.76	0.81	0.93
BP	0.60	0.63	0.70	0.77	0.91
6F	0.50	0.55	0.62	0.70	0.88

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[343] Chao, H. S., and Kelsey, D. R., *US Patent 4,625,000*, 1986.

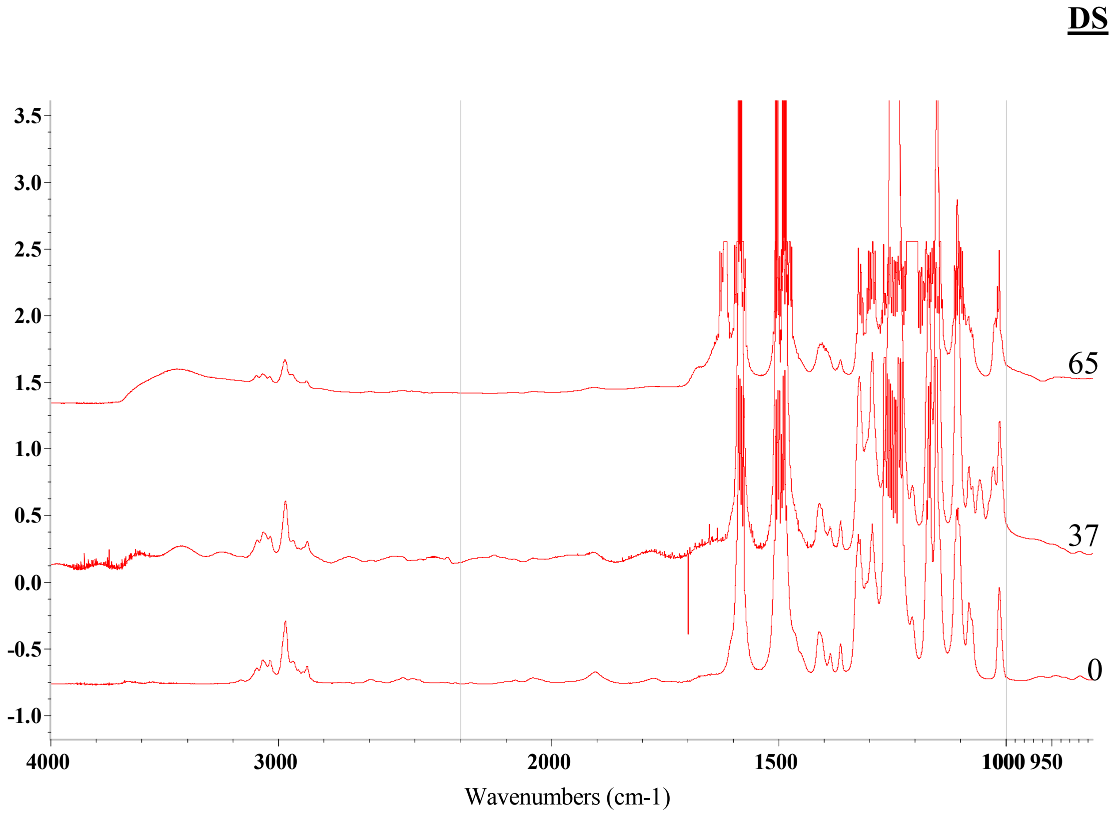


FIGURE C1. Infrared spectra of bisphenol A based poly (arylene ether sulfones) with various degrees of sulfonation.

FTIR and NMR confirmed the successful electrophilic substitution of trimethylsilyl chlorosulfonate onto the three poly (arylene ether sulfones) synthesized in the research. Figures C1-3 are the FTIR spectra series of representative sulfonated poly (arylene ether sulfones). The 1025 cm^{-1} peak corresponds to the new sulfonic acid group. This signal increases with increasing sulfonation.

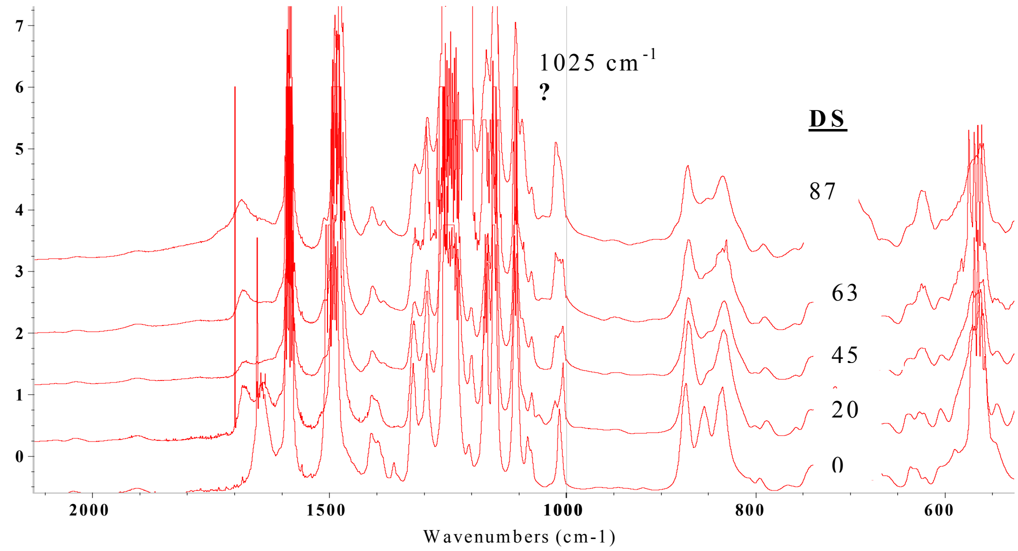


FIGURE C2. FTIR spectra of post-sulfonated biphenol based poly (arylene ether sulfone) with different degrees of sulfonation

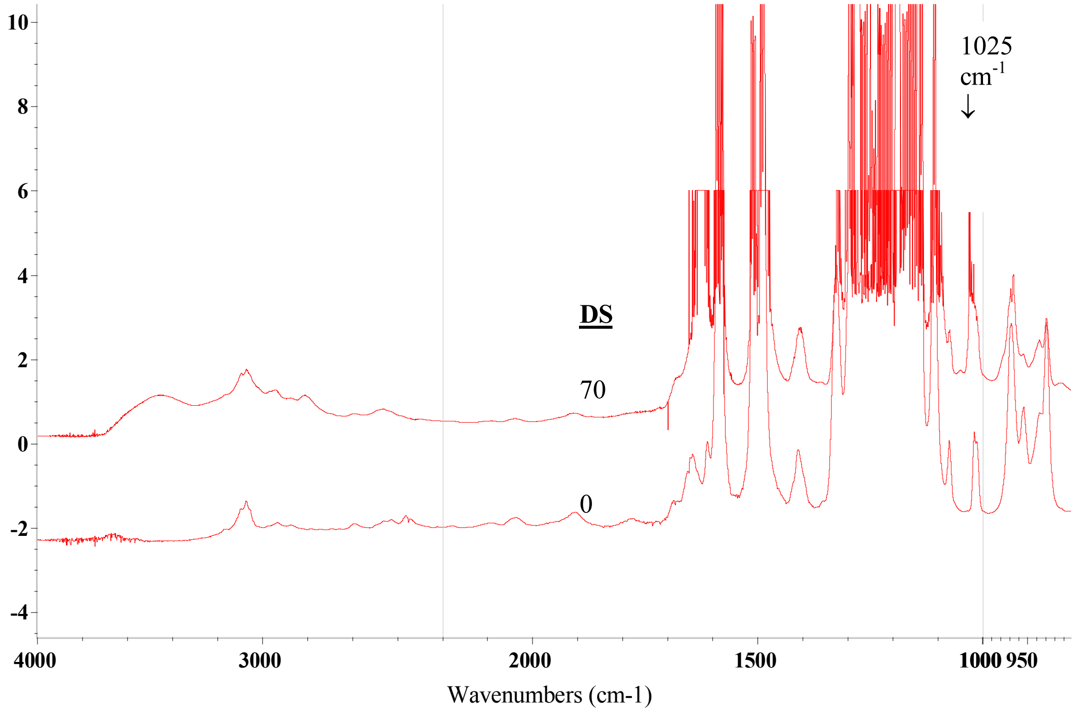


FIGURE C3. Infrared spectra of 6Fbisphenol A-based poly (arylene ether sulfones) with various degrees of sulfonation

The infrared spectra of all three poly (arylene ether sulfone) polymers and of the various sulfonated derivatives were normalized using the characteristic absorption band at ~1010 cm^{-1}. This band is due to the stretching of the carbon-oxygen-carbon linkages present in all the polymers and is expected to be unaffected during the electrophilic substitution reaction. Few changes in the spectra are observed at low degrees of sulfonation; a shoulder or slight broadening of the ether linkage may be the only noticeable difference. However, as the amount of chlorosulfonic acid is increased in the reaction, causing a corresponding increase in the degree of sulfonation, the distinct appearance of an absorption at ~1025 cm^{-1} was observed. The intensities of the bands characteristic of the sulfonic acid groups increased with increasing levels of sulfonation, as expected.

The broad absorption band appearing at ~3400 – 3500 cm^{-1} may be due to the O-H vibration from the sulfonic acid group and/or the absorbed water. The polymer films were all dried prior to taking the spectra under vacuum at 80 °C for at least 12 hours. For the hydrophilic or water-soluble sulfonated polymers it was noticed that the intensity of this peak was very high relative to polymers of low to modest levels of sulfonation.

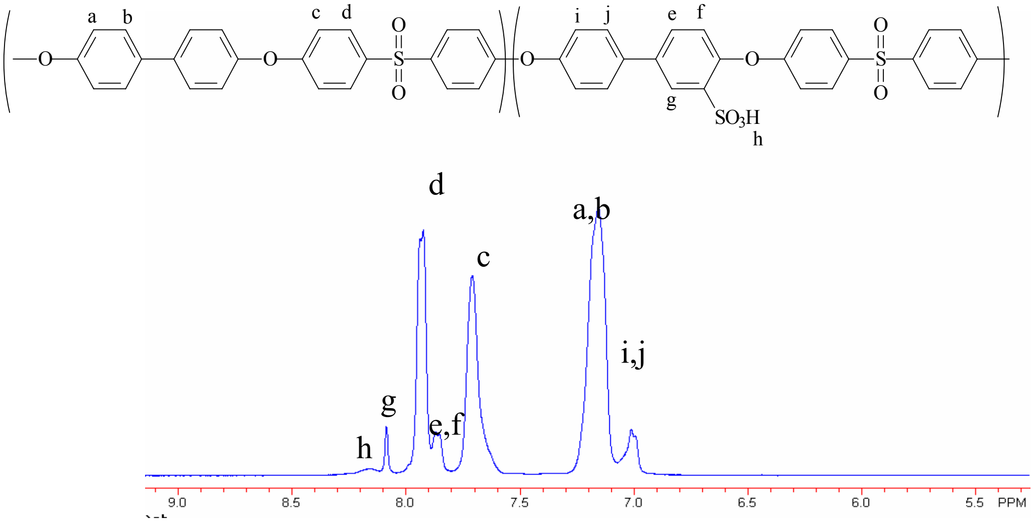


FIGURE D. ^{1}H NMR of sulfonated biphenol based-poly (arylene ether sulfone).

Figure D is a representative ^{1}H NMR spectrum of a post-sulfonated biphenol based-poly (arylene ether sulfone). The proton resonance at ~8.2 ppm is assigned to the proton adjacent to the new pendent sulfonic acid. Using the integration of this proton and a known proton, one is able to determine the actual degree of sulfonation. The spectral assignments were determined using the unmodified (control) polymers (not shown). The degree of sulfonation of the sulfonated polymer in shown in Figure D is approximately 25%.

While the trimethylsilyl chlorosulfonate proved to be sufficient in sulfonating the three different homopolymers (i.e., bisphenol A, biphenol, and 6F bisphenol A based poly (arylene ether sulfones)), the precise control of the degree of substitution was ambiguous. The target degrees of sulfonation were sequentially changed by varying the molar concentration ratios of polymer to sulfonating agent, as outlined in Section 2.5. A sample calculation is given below for 100 % sulfonated (i.e., 1 sulfonic acid per repeat unit) 6F poly(arylene ether sulfone).

$$\frac{\text{5.50 gram 6F polysulfone}}{\text{550.47 gram/mol 6F polysulfone}} = \text{9.99 mmol 6Fpolymer}$$

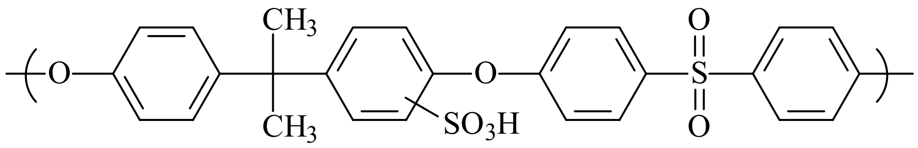
9.99 mmol chlorosulfonic acid ($ClSO_3H$) x 116.52 g/mol $ClSO_3H$ = 1.164g $ClSO_3H$

Equation 1. Sample calculation for equimolar (1 : 1) sulfonation of 6F bisphenol A poly(arylene ether sulfone)

Precise weighing, transferring and handling of polymer, chlorotrimethylsilane and chlorosulfonic acid were performed during the reaction preparations. All glassware, syringes, etc. were rigorously dried in a drying oven and / or via a Bunsen burner prior to use. Additionally, all polymers were dried overnight in a vacuum oven at approximately 150 °C prior to dissolution.

Despite these efforts the final degree of sulfonation (DS) was never equal to the target level. Tables C1-3 summaries the results. The reported 'actual degree of sulfonation' was determined via ^{1}H NMR calculations and is an average of comparable experiments. The degree of sulfonation was also determined by elemental analysis of selected polymers. By comparison of the ratio of sulfur to carbon in the control polymers to the sulfur to carbon ratio in a sulfonated polymer any change can be attributed to the structural modification (i.e. sulfonation). The calculated degree of sulfonation was always less than the expected (targeted) degree of sulfonation. Elemental analysis and NMR calculated degree of sulfonation were comparable (± 15%). The results of the elemental analyses are shown in Table D.

Table C1. Characterization of sulfonated bisphenol A-based poly(arylene ether sulfone) using chlorosulfonic acid



Molar Ratio*	Actual DS♦	[η] $^{\text{NMP, 25 C}}$	Water Uptake (weight %)	Tg (°C) ♠
1 : 0	-	0.52	0.5	180
1 : 0.3	8	0.55	2	182
1 : 0.5	12	0.59	5	183
1 : 0.75	28	0.76	19	193
1 : 1	39	0.87	42	200
1 : 2	57∞	0.90∞	WS∞	ND

* Polymer to Chlorosulfonic acid

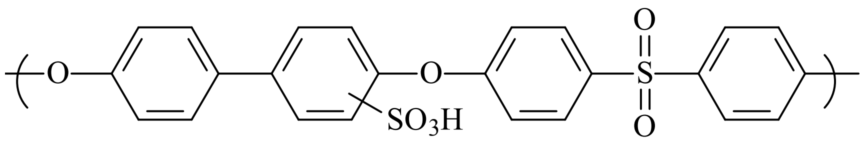
♦ DS = Degree of Sulfonation; determined by ^{1}H NMR

♠ Determined via DSC in air @ 10 °C/min

∞ Values in parenthesis are for water-soluble polymer(s).

ND = Not detected

Table C2. Characterization of sulfonated biphenol-based poly(arylene ether sulfone) using chlorosulfonic acid



Molar Ratio*	Actual DS♦	$[\eta]^{\text{NMP, 25 C}}$	Water Uptake (weight %)	Tg (°C) ♠
1 : 0	-	0.60	0.3	215
1 : 0.3	10	0.66	5	220
1 : 0.5	15	0.70	8	224
1 : 0.75	25	0.73	23	230
1 : 1	37	0.80	40	230
1 : 2	48 (65) ∞	0.85 (ND) ∞	500 (ND) ∞	ND

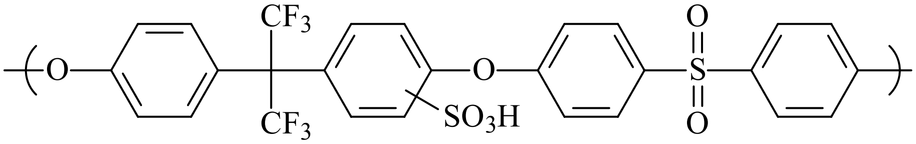
* Polymer to Chlorosulfonic acid

♦ DS = Degree of Sulfonation; determined by ^{1}H NMR

♠ Determined via DSC in air @ 10 °C/min

∞ Values in parenthesis are for water soluble polymer(s).

Table C3. Characterization of sulfonated 6F bisphenol A-based poly(arylene ether sulfone) using chlorosulfonic acid



Molar Ratio*	Actual DS♦	$[\eta]^{\text{NMP, 25 C}}$	Water Uptake (weight %)	Tg (^{o}C) ♠
1 : 0	-	0.52	0.5	192
1 : 0.3	8	0.55	2	198
1 : 0.5	12	0.60	5	200
1 : 0.75	22	0.67	9	212
1 : 1	35	0.74	43	ND
1 : 2	47 (76$^{\infty}$)	0.83 (0.95$^{\infty}$)	>200 (ND$^{\infty}$)	ND

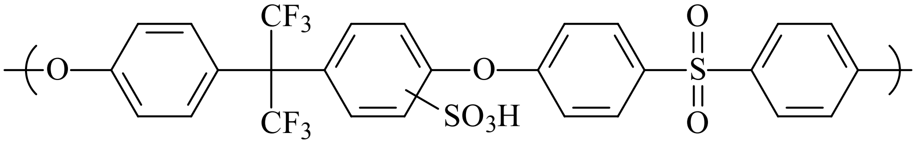
* Polymer to Chlorosulfonic acid

♦ DS = Degree of Sulfonation; determined by ^{1}H NMR

♠ Determined via DSC in air @ 10 ^{o}C/min

∞ Values for water soluble polymers.

Table D. Determination of Degree of Sulfonation via Elemental Analysis



Sample	Carbon	Sulfur	DS♦	DS$^{\alpha}$
6F control	60.8	5.5	--	--
6F-1	47.4	27.4	30	34
6F-2	53.8	23.1	27	32

♦ Degree of sulfonation via ^{1}H NMR

$^{\alpha}$ Degree of sulfonation determination by elemental analysis: (DS) = $S/C_{\text{sample}} - S/C_{\text{control}}$

A plot of the actual degree of sulfonation verses the theoretical (expected) degree of sulfonation based on chlorosulfonic acid concentration is shown in Figure E. This study was performed only on 6F bisphenol A polymers. An efficiency value of sulfonation was determined to be approximately 30% for chlorosulfonic acid based on this plot. To investigate the influence, if any, chlorotrimethylsilane had on the efficiency of sulfonation several reactions were performed in the absence of the protecting agent. As seen in Figure E there is no distinguishable influence on the final degree of sulfonation.

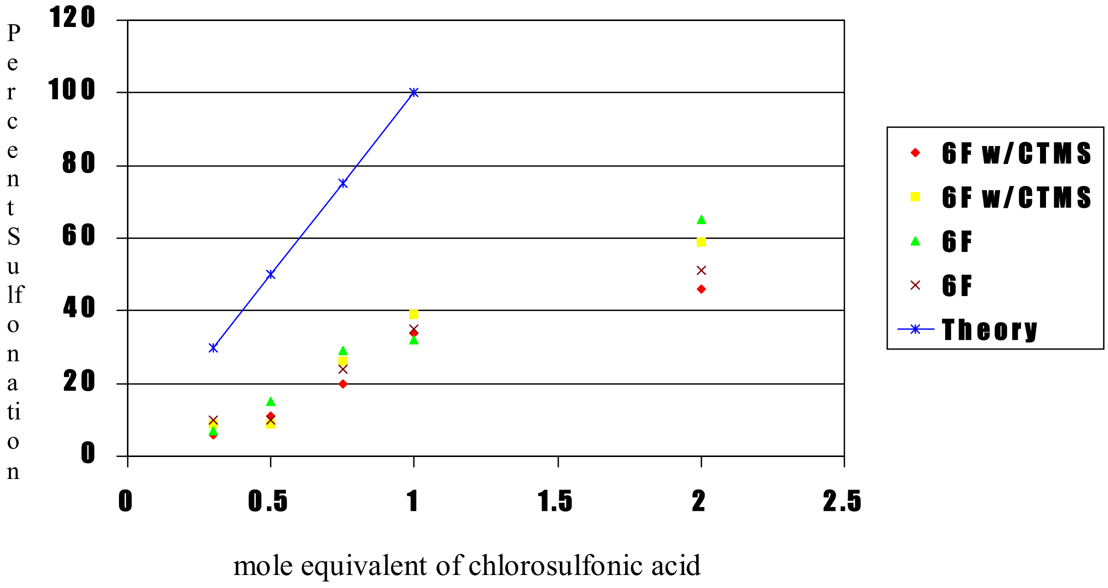


FIGURE E. Graph of sulfonation efficiency (actual degree of sulfonation) as a function of chlorosulfonic acid concentration.

Genova-Dimitrova *et al.*[342] and Hamciuc *et al.*[339] investigated other factors, such as the influence of the sulfonating solvent, temperature, time and concentration while sulfonating poly (arylene ethers) via chlorosulfonic acid. All of these variables were determined to be significant on the final degree of sulfonation of the polymers. Hamciuc *et al.*[339] also investigated the sulfonation efficiency of chlorosulfonic acid as a function of temperature and time. These researchers report a high of 60% efficiency when sulfonating a poly (arylene ether sulfone) for 24 hours at 35 °C, but it is noted that high temperature for shorter times did not match this value.

The process of generating the all sulfonated polymers involved several influential factors with the dominate three being concentration, addition rate, and agitation rate. The concentration of the polymer solution (i.e., poly(aryl ether sulfone) in the halogenated solvent) had to be less than ten percent weight to volume(10% w/v). At higher concentrations the solution quickly became opaque upon adding the chlorosulfonic acid mixture. The opaqueness is attributed to the precipitation of the polymer. Another controlling factor was the addition rate of the sulfonating agent. The chlorosulfonic acid was always diluted with 10 mL dry solvent. Adding the chlorosulfonic acid solution quickly (e.g. ~10ml of sulfonating solution within 10 minutes) or slowly (10ml within 60 minutes) results in precipitation of the polymer. The drop-wise addition of chlorosulfonic acid within 25-30 minutes repeatedly provided the best (fairly homogeneous) solutions. Fast agitation rates were also very important in maintaining the polymer solutions. The difficulty in sustaining homogeneous solutions during sulfonation may be a competing issue involving the changing solution polarity, etc. during the addition of chlorosulfonic acid and also the changes to the polymer due to the sulfonation.

The thermal stability of the three poly (arylene ether sulfones) was studied by thermogravimetric analysis. The sulfonated polymers with low degrees of sulfonation (i.e., less than 15%) exhibited comparable decomposition temperatures and similar behaviors as those of their respective parent (control) polymers. These polymers showed very high thermo-oxidative stabilities of over 500 °C for the 6F bisphenol A and biphenol –based polymers; polymers containing bisphenol A showed stabilities up to ~ 480 °C. At moderate degrees of sulfonation –between 25 – 50%, a two step degradation behavior

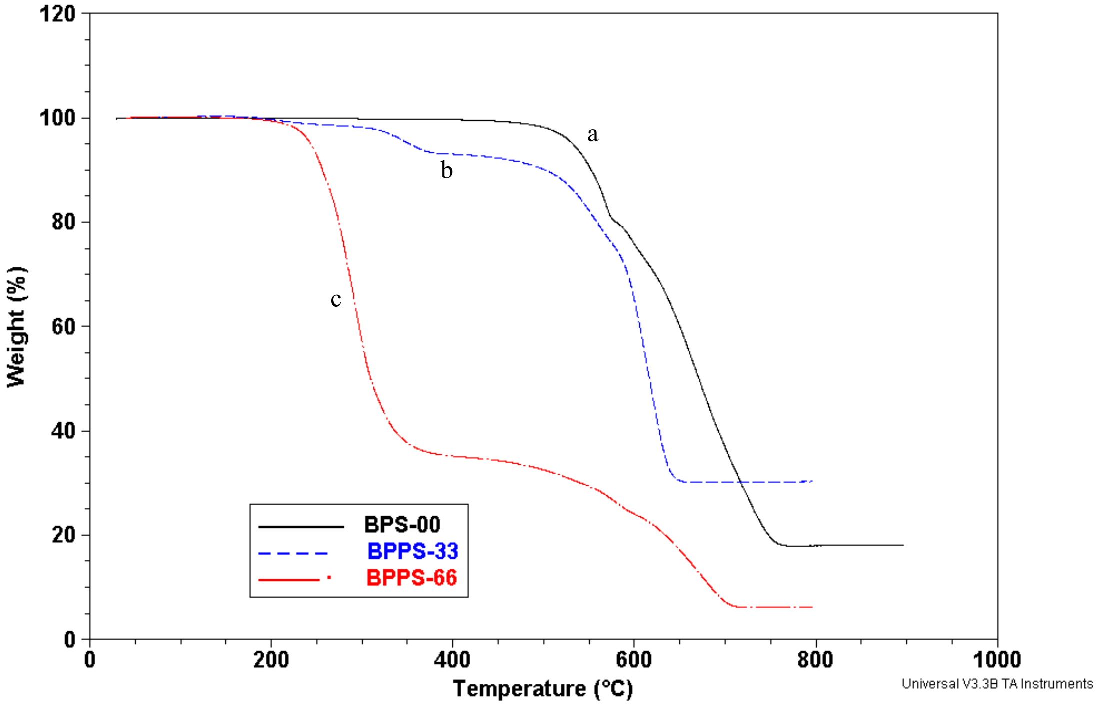


FIGURE F. Thermogravimetric analysis (TGA) of biphenol based sulfonated poly(arylene ether sulfone). (a) Control (b) DS ~ 33 % (c) Water soluble polymer with DS ~ 66 %

was observed. The first step occurs about 325 ^{o}C and is credited to the desulfonation degradation. The second step parallels the parent polymer degradation. Plot b in Figure F is a good example. The degradative weight loss began considerably earlier at high levels of sulfonation (i.e., greater than 50%). Plot c in Figure F showed a dramatic weight loss starting at 200 ^{o}C. In this thermogram, the degradation surpassed 60 % weight loss. This would correlate to significantly more than 66 mol% of pendent sulfonic acid groups. This sulfonated biphenol – based polymer was water soluble and apparently absorbed water during the sample preparation. The presence of absorbed and/or bound water has been discussed earlier in the thesis.

Conclusions

Three poly (arylene ether sulfones) based on bisphenol A, biphenol, and 6F bisphenol A were prepared using dichlorodiphenyl sulfone in NMP via nucleophilic aromatic substitution. These high molecular weight polymers were sulfonated with chlorosulfonic acid derivatized by chlorotrimethylsilane in halogenated solvents at ambient temperatures. This procedure did not show any evidence of chain cleavage or branching during the mild electrophilic aromatic substitution reactions. The degree of sulfonation was determined via ^1H NMR spectroscopy and elemental analysis, and was qualitatively monitored using FTIR. The degree of sulfonation was controlled by varying the molar ratio of sulfonating agent to polymer, and an efficiency of sulfonation value of about 30% was determined. Properties, such as solubility-- particularly methanol and water solubility, and thermal stability, were influenced by the degree of sulfonation. Sulfonated polymers with degrees of sulfonation up to 90% were achieved. The modified polymers could produce flexible films from common solvents. However, precise composition by post reaction methodologies were difficult, to impossible. The random post-sulfonated materials were very different than the directly copolymerized systems.

Vita

William Lamont Harrison, son of Willie and Lugretta Harrison, was born on March 12, 1973 in Laurinburg, NC. William has two sisters, Vonda and Tiffany. Before graduating Scotland High School in June 1991, William met Dionne Ellerbe, who would eventually become his wife. In August of the same year, he went to Winston-Salem State University, and completed requirements for a B.S. in Chemistry in 1995, earning Magna Cum Laude honors, with the assistance of an US Environmental Protection Agency fellowship. During his matriculation at WSSU, he worked with many special scientists, especially his department chair Professor Astor Herrell, who encouraged him to continue his education. William entered Hampton University (VA) in the fall of 1995 with an assistantship through the National Science Foundation. Professor Godson C. Nwokogu advised him through his Master's research project entitled "Synthesis and Characterization of Polyarylate Copolymers based on Bisphenol A and Iso/Terephthalic Acids via Melt Acidolysis". William entered Virginia Polytechnic Institute and State University in the fall of 1997 under the advisement of Professor James E. McGrath. While at Virginia Tech, he enjoyed learning from many talented researchers and had the opportunity to present at numerous national meetings. William enjoyed the happiness received from his two children, Lamonte' and Leah, and the time he took to volunteer and work with many students in the surrounding communities. William research efforts at Virginia Tech focused primarily the syntheses and characterization of poly (arylene ethers), and earned him his Doctoral degree in Organic/Polymer Chemistry in December 2002. He is currently a post doctoral research associate in the department of chemistry at Virginia Tech.