

DIRECT POLYMERIZATION OF SULFONATED POLY(ARYLENE
ETHER) RANDOM COPOLYMERS AND POLY(IMIDE)
SULFONATED POLY (ARYLENE ETHER) SEGMENTED
COPOLYMERS: NEW CANDIDATES FOR PROTON EXCHANGE
MEMBRANE FUEL CELL MATERIAL SYSTEMS

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University in partial fulfillment of the requirements for the degree of

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Fuel Cell

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ABSTRACT

Commercially available 4,4'-dichlorodiphenylsulfone (DCDPS) was successfully disulfonated with fuming sulfuric acid to yield 3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone (SDCDPS). Subsequently, DCDPS and SDCDPS were systematically reacted with 4,4'-biphenol under nucleophilic step polymerization conditions to generate a series of high molecular weight, film-forming, ductile, ion conducting copolymers. These were converted to the acid form and investigated as proton exchange membranes for fuel cells. Hydrophilicity increased with the level of sulfonation. However, water sorption increased gradually until about 50 mole percent SDCDPS was incorporated, and thereafter showed a large increase to yield water soluble materials for the 100% SDCDPS system. Atomic force microscopy (AFM) confirmed that the morphology of the copolymers displayed continuity of the hydrophilic phase at 60 mole percent SDCDPS. Conductivity measurements in the 40-50 mole percent SDCDPS range, where excellent mechanical strength was maintained, produced values of 0.1 S/cm or higher which were comparable to the control, Nafion™. These compositions also show a high degree of compatibility with heteropolyacids such as phosphotungstic acid. These inorganic compounds provide a promising mechanism for obtaining

conductivity at temperatures well above the boiling point of water and membrane compositions containing them are being actively pursued.

The water soluble 100% SDCDPS system was further investigated by successfully functionalizing the endgroups to afford aromatic amines via appropriate endcapping with *m*-aminophenol. Oligomers and polymers from 5-30 kg/mole number average molecular weight were synthesized and well characterized by NMR spectroscopy, endgroup titrations and size exclusion chromatography. The diamino-telechelic sulfonated segment was reacted with several dianhydrides and diamines to produce multiblock, hydrophobic polyimide-hydrophilic sulfonated polyarylene ether copolymers. Both ester-acid and amic acid synthesis routes were utilized in combination with spin-casting and bulk imidization. A series of tough, film-forming segmented copolymers was prepared and characterized. AFM measurements demonstrated the generation of quite well defined, nanophase-separated morphologies which were dependent upon composition as well as aging in a humid environment. Characterizations of the segmented copolymers for conductivity, and water and methanol sorption were performed and comparisons to state-of-the-art perfluorinated Nafion™ systems were made. It is concluded that the segmented or block systems have the potential to enhance certain desirable PEM characteristics in fuel cells, particularly those related to swelling, retention of mechanical strength at elevated temperatures, and critical adhesion issues in membrane electrode assemblies.

To Sue and the Boys:

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Chapter I

Background, Overview and Objectives

Research in the area of polymer electrolyte membrane fuel cells has increased markedly over the last few years.¹ Polymer electrolyte, or proton exchange membrane (PEM) fuel cells are devices which generate electrical power via the direct employment or reformation of a fuel source, such as hydrogen, methanol, methane, gasoline, etc., into a source of protons. The conversion of fuel to protons liberates free electrons which can be used to do work, after they are reacted with a source of oxygen, usually air, to form water. Although this technology has been available for decades, recent commercial efforts have emphasized improving the efficiency and lifetime of the system, while academic research has been more focused on generating a better fundamental understanding of the chemistry and physics involved to enable system optimization.

There is a recognized need for the synthesis of new polymeric materials for use as high temperature ($> 80^{\circ}\text{C}$, the temperature limit of current state-of-the-art Nafion[®] fluoropolymer) PEMs, which also have lower methanol permeability. Nafion is the dominant membrane material for PEMs at this time. It is commercially available in various molecular weights and ionic concentrations but does have some limitations, such as a maximum use temperature of 80°C . Platinum or platinum/alloy catalysts are used to convert H_2 and O_2 to protons and elemental oxygen, respectively. These catalysts are very sensitive to carbon monoxide, CO, which is often present as an impurity in the fuel source. CO poisoning by chemisorption onto platinum cumulatively reduces the effectiveness of the catalysts and decreases fuel cell energy output. Increasing the operating temperature to over 100°C , preferably $120\text{-}150^{\circ}\text{C}$, would represent a major improvement. New polymers under study at Virginia Tech are being designed to have excellent thermal and chemical stability and to have the added advantage of a synthetic

¹ Appleby, A. J., Ed. *Fuel Cells: Trends in Research and Applications*; Hemisphere Publishing Corp.: New York, 1987; p.281
Dyer, C. K. *Sci. Amer.* **1999**, 72-93.

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

approach that is simplified compared to that of Nafion. The targeted new materials must be capable of performing for many thousands of hours at high temperatures under the rigorous acidic and free radical-rich environment of a proton exchange membrane fuel cell (PEMFC). For direct methanol fuel cells, they also must have a greatly reduced permeability to methanol, as compared to Nafion. Nafion is considered to be a two-phase system wherein the ion-conducting sites aggregate into a separate and distinct phase. New materials under investigation also feature this heterogeneous morphology.

New membrane materials have been synthesized in our labs via use of step growth polymerization techniques. This method allows ionic functionalization of the monomeric starting materials in controlled concentration, location and more thermally stable positions. In an effort to reduce the cost of the final PEM, commercial grade 4,4'-dichlorodiphenylsulfone (DCDPS) was utilized as the monomer that could be functionalized to serve as the ionic segment of the polymer backbone. This differs from the post sulfonation of polymers, e.g. SO₃ or concentrated sulfuric acid, which can cause side reactions. Although the ionic group in Nafion is a perfluorinated sulfonic acid, novel polymers described herein contain aromatic sulfonic acid groups. It is argued that the deactivated phenyl rings will be better locations to promote ion conductivity than the activated phenyl ring sulfonation that occurs via post sulfonation reactions. The deactivated rings are more stable against desulfonation since the anticipated intermediate carbocation required for desulfonation is more difficult to stabilize on a deactivated ring. Sulfonated DCDPS (SDCDPS) was polymerized with biphenol and with or without *m*-aminophenol monofunctional molecular weight endcapper, using traditional step growth polymerization conditions. This allows the generation of controlled molecular weight poly (arylene ether sulfones) having up to two sulfonated sites per repeat unit and with (optionally) primary amine endgroups. Analysis of these new materials showed that polydispersities (Mw/Mn) were about 2.0 and that a series of 10, 20 and 30,000 g/mol polymers could be synthesized.

The amine terminated poly (arylene ether sulfones) (PAEs) were then be used as telechelic oligomers in a segmented polymerization to form poly (imide) (PI)

copolymers. The procedure used a specific PAE that was dissolved along with a second diamine and a dianhydride in N-methylpyrrolidone to successfully prepare viscous copolymer solutions after 24 hours. The solutions could be cast onto a glass plate to form ductile transparent films, after drying under vacuum. Variation of the ratio of PAE to unsulfonated diamine, as well as variation of the nature of the dianhydride, generated several series of segmented PAE/PI copolymers. By controlling the degree of ionic character in the copolymers, several performance factors could be controlled. Phase separation, water uptake, ion exchange capacity and conductivity were all affected by the concentration of ionic groups in the copolymers.

Chapter II

Literature Review

A. Poly (arylene ether sulfones)

1. Introduction

Poly (arylene ether sulfones) are engineering thermoplastic materials that display a variety of desirable properties including high ductility and good hydrolytic, oxidative and thermal stability. These materials have been synthesized via a number of techniques with the most important commercial routes being nucleophilic aromatic substitution² and to some extent, electrophilic aromatic substitution.³ The nucleophilic aromatic substitution is the route used by BP-Amoco in the synthesis of their bisphenol-A based poly (arylene ether sulfone) UDEL[®] and the analogous biphenol based Radel^{®4}. The syntheses of poly (arylene ether sulfones) and their sulfonated analogs, conducted as part of this research effort, also utilize the nucleophilic aromatic substitution reaction and are discussed below.

² Hedrick, J. C.; Labadie, J. L.; Ueda, M. In *Step Growth Polymers for High Performance Materials; New Synthetic Methods*; Hedrick, J. C., Labadie, J. L., Eds.; American Chemical Society: Washington, D.C., 1996; Vol. 624, p 225.

Hedrick, J. L.; Mohanty, D. K.; Johnson, B. C.; Viswanathan, R.; Hinkley, J. A.; McGrath, J. E. *Journal of Polymer Science, Part A* **1986**, *23*, 287-300.

Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *Journal of Polymer Science, Part A-1* **1967**, *5*, 2375-2398.

Mecham, S. J.; Jayaraman, S.; Lee, Y. J.; Mecham, J. B.; Riley, D. J.; Glass, T. E.; McGrath, J. E. *Polymer Preprints* **1995**, *36*, 789-790.

Viswanathan, R.; Johnson, B. C.; McGrath, J. E. *Polymer* **1984**, *25*, 1827-1836.

Cotter, R. J. *Engineering Plastics: A Handbook of Polyarylethers*; Gordon and Breach, 1995.

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

Wang, S.; McGrath, J. E. In; Press, I., Ed., 2000.

³ Rose, J. B. *Polymer* **1974**, *15*, 456.

Rose, J. B. *Chem. Ind.* **1968**, 461.

Harris, J. E. and Johnson, R. N. In *Encycl. Poly. Sci. and Eng.*; Bikales, N. M., Ed.; John Wiley and Sons: New York, 1988; Vol. 13, p 196.

Jennings, B. E.; Jones, M. E. B.; Rose, J. B. *Journal of Polymer Science, Part C* **1967**, *16*, 715.

⁴ Roovers, F.; Ethier, R.; Toporowski, P. M. *High Perf. Poly.* **1990**, *2*, 151.

Roovers, F.; Toporowski, P. M.; Ethier, R. *High Perf. Poly.* **1990**, *2*, 165.

2. Nucleophilic Aromatic Substitution

The S_NAr mechanism is most important when poly (arylene ether sulfones) are considered. The general mechanism is shown in figure 2.1.⁵

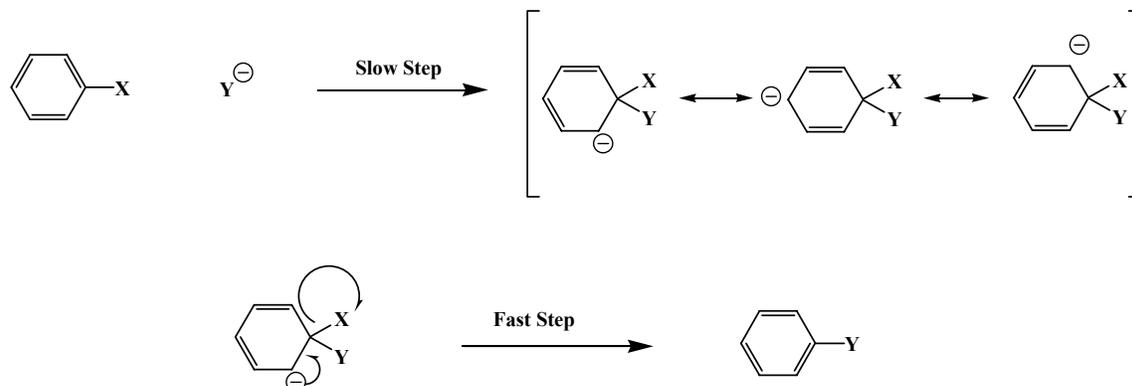


Figure 2.1: S_NAr Mechanism⁶

The initial step involves the attack of the nucleophile at the activated site to form a resonance stabilized arenium ion intermediate, which is generally accepted to be the rate determining step. The much faster second step involves the departure of the leaving group, which is driven by the reestablishment of aromaticity in the phenyl ring.

a. S_NAr : The Activating Group

For the S_NAr mechanism to function at a reasonable rate, electron withdrawing groups ortho and/or para in relation to the substitution position are needed, although steric hindrance can present a problem when considering ortho substitution.

An electron withdrawing group such as a nitro group can stabilize the Meissenheimer salt intermediate,⁷ shown in figure 2.2, which have been confirmed by NMR⁸ and X-ray crystallography.⁹

⁵ March, J. *Advanced Organic Chemistry*; 3rd ed.; John Wiley and Sons: New York, 1985.

Miller, J. A. *Aromatic Nucleophilic Substitution*; American Elsevier: New York, 1968.

⁶ March, J. *Advanced Organic Chemistry*; 3rd ed.; John Wiley and Sons: New York, 1985.

⁷ Meissenheimer, J. *Liebigs. Ann. Chem.* **1902**, 323, 205.

⁸ Fyfe, C. A.; Koll, A.; Damji, W. H.; Malkiewich, C. D.; Forte, P. A. *Can. J. Chem.* **1977**, 55, 1468.

⁹ Messmer, G. G.; Palenik, G. J. *Chem. Comm.* **1969**, 470.

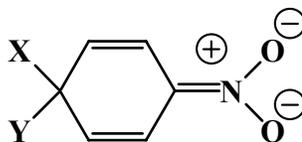


Figure 2.2: Meisenheimer intermediate salt⁷

The approximate order of the electron withdrawing group corresponds to the deactivating power of the substituent and has been observed to be: ¹⁰ NO > NO₂ > SO₂Me > CF₃ > CN > CHO > COR > COOH > Br > Cl > I > H > F > CMe₃ > Me > OMe > NMe₂ > OH > NH₂. Nitro, sulfone and ketone groups are common activating groups used in the synthesis of poly (arylene ethers).

b. S_NAr: The Leaving Group

The leaving group is an equally important variable in the S_NAr mechanism. Bunnett¹¹ reported that the influence on the rate of reaction, with a halogen as the leaving group, is F >> Cl ≥ Br ≥ I, in spite of the fact that the carbon-halogen bond strength decreases in the same order. This suggests that the breaking of the carbon-halogen bond is not part of the rate-determining step and that the leaving group has an electronic effect on the carbon to which it is attached. The greater electronegativity of the fluorine atom allows it to inductively withdraw electron density away from the activated carbon atom, further activating it to attack by a nucleophile, as well as stabilizing the Meisenheimer intermediate. Steric effects may also play a role (i.e. fluorine is the smallest atom of the series), allowing better access of the nucleophile to the activated carbon.

¹⁰: Miller, J. A. *Aromatic Nucleophilic Substitution*; American Elsevier: New York, 1968.

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.* **1976**, *41*, 1560.

¹¹ Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273-412.

c. S_NAr: The Nucleophile

The nucleophilicity of the nucleophile is a critical variable in the polymerization to form poly (arylene ether sulfones). From Bunnett,¹¹ an approximate order of nucleophilic strength is given as $\text{ArS}^- > \text{RO}^- > \text{R}_2\text{NH}^- > \text{ArO}^- > \text{OH}^- > \text{ArNH}_2 > \text{NH}_3 > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{H}_2\text{O} > \text{ROH}$. This order indicates that the phenoxide anion is the strongest nucleophile in the reaction, greater than the hydroxide ion, the halogens and water.

d. S_NAr: The Solvent

Choosing a solvent that is compatible with the S_NAr mechanism is crucial to the success of the reaction, for it must meet three major requirements:

- 1) The solvent must not react with any of the reactants; this would lead to side products
- 2) All the reactants and products have to be completely soluble to allow the reaction to proceed and to avoid unreacted chain ends
- 3) The solvent must aid in “loosening” the nucleophilic anion and its associated metal counter-ion

Nucleophilic substitution reactions are commonly conducted in polar aprotic solvents to avoid solvent/nucleophile interactions that alter the strength of the nucleophile.¹² Protic solvents highly solvate the nucleophile and reduce its ability to react at the targeted activated carbon site whereas the solvation effect is inoperable when polar aprotic solvents are used.¹³ Several common polar aprotic solvents are shown in figure 2.3. These not only reduce the solvation of the nucleophile but also solvate the metal cation associated with the nucleophile allowing it better access to the activated carbon.¹⁴

¹² Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; 3rd ed.; Plenum Press: New York, 1990.

¹³ Alexander, R.; Ko, E. C. F.; Parker, A. J.; Broxton, T. J. *J. Am. Chem. Soc.* **1968**, *90*, 5049.

Fuchs, R. L.; Cole, L. L. *J. Am. Chem. Soc.* **1973**, *95*, 3194.

¹⁴ Magnera, T. F.; Caldwell, G.; Sunner, J.; Iduta, J.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 6140.

e. S_NAr: Water

Water is a primary concern when considering possible contaminants present in the solvent. Water can act as a nucleophile, hydrolyze the activated halide, and alter the stoichiometry of the A-A/B-B step growth reaction which would limit the ultimate molecular weight of the polymer. Typically, the solvent is distilled from a suitable drying agent prior to use in a polymerization.

In the synthesis of poly (arylene ether sulfones) by nucleophilic aromatic substitution, the phenoxide nucleophile can be formed by use of a strong base, such as sodium hydroxide or by potassium carbonate. In either case, the reaction to form the phenoxide ion produces 2 moles of water per mole of bisphenol, which must be removed prior to the addition of the dihalide. Water removal can be accomplished by addition of an azeotroping agent such as o-dichlorobenzene, toluene, or xylene.

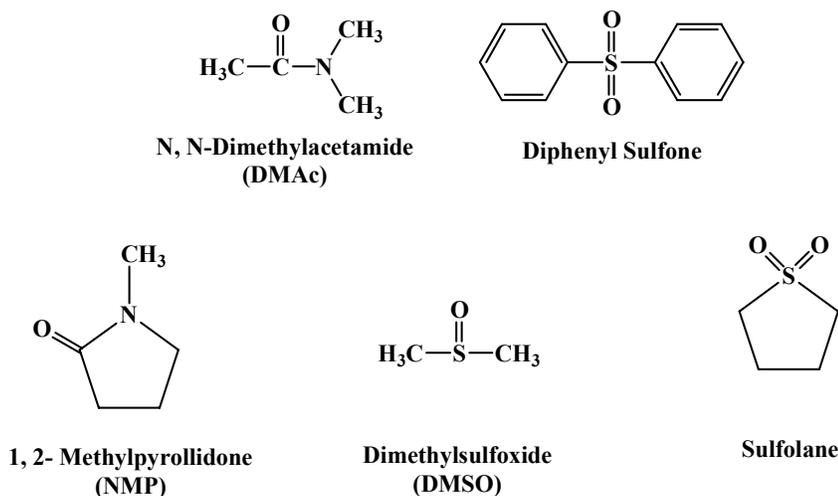
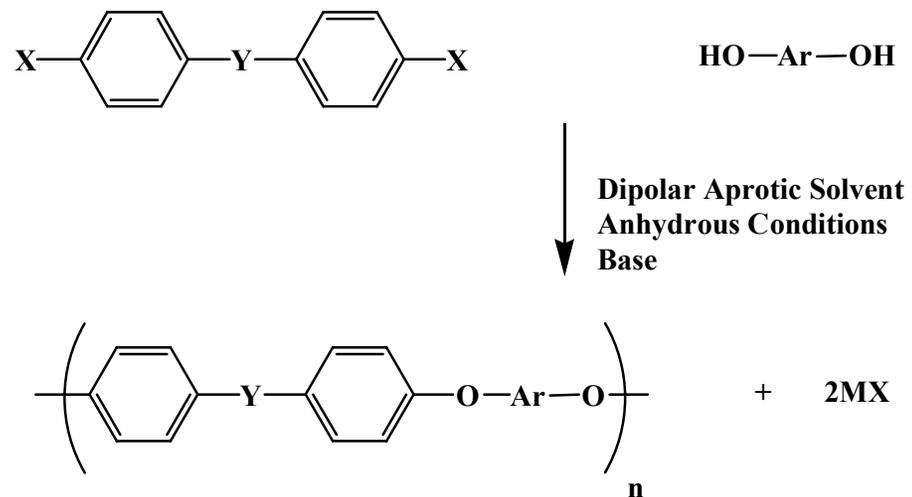


Figure 2.3: A few examples of polar aprotic solvents

f. Synthesis of Poly(arylene ethers) via Nucleophilic Aromatic Substitution

Poly (arylene ethers) can be prepared using nucleophilic aromatic substitution as shown in figure 2.4. There are two major approaches that utilize either a strong (e.g.



Where:

X = A halide; normally Cl or F

Y = An activating group, usually a sulfone, ketone or an aryl phosphine oxide

M = Metal counter-ion

Figure 2.4: General Nucleophilic Aromatic Substitution Step Growth Polymerization

sodium hydroxide) or a weak base (e.g. potassium carbonate). An aromatic bisphenol is reacted with a base to form either a phenolate anion with a weak base, or a diphenolate with a strong base. The phenolate then acts as the nucleophile and is reacted with an aromatic activated dihalide, displacing the halogen atom and forming a diaryl ether linkage.

**i) Synthesis of Poly (arylene ether sulfones):
Strong Base Method**

This is the initial nucleophilic aromatic route that was used to synthesize poly (arylene ethers) by Johnson and coworkers¹⁵ and is most likely the most prevalent commercial route in use today for bisphenol-A based systems.¹⁶ Johnson *et. al.* synthesized a large series of poly (arylene ethers) by this method using a variety of reaction conditions and monomers. The reaction using bisphenol-A is illustrated in figure 2.5.

Their research led to the conclusion that DMSO was the preferred solvent in almost all the polymerizations, with the exception of those in which weakly activated dichlorides or more acidic bisphenols were used. In those cases, it was found that sulfolane was a better solvent. Sulfolane was also found to be a better solvent when crystallization of the polymer occurred at low conversion in DMSO.

As was mentioned previously, the solvent is expected to solubilize both the reactants and the products, and in Johnson's work with poly (arylene ethers), the alkali diphenolate and the polymer were the most difficult to solubilize, requiring temperatures between 130-170°C. Monomers with lower reactivity were heated to higher reaction temperatures (near 230°) in sulfolane.

¹⁵ Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *Journal of Polymer Science, Part A-1* **1967**, *5*, 2375-2398.
Johnson, R. N.; Farnham, A. G.; U.S. 1979

¹⁶ Harris, J. E.; Johnson, R. N. In *Ency. Poly. Sci. and Eng.*; Bikales, N. M., Ed.; John Wiley and Sons: New York, 1988; Vol. 13, p 196.

Investigation also indicated the high sensitivity of the reaction to even small amounts of water due to hydrolysis of the metal phenolate, thereby producing hydroxide ion. The hydroxide ion could then react at the activated halide site creating an endgroup with low reactivity, offsetting stoichiometry and lowering the ultimate molecular weight of the polymer. Chain scission is another possibility when hydroxide ion is present in the solution for a time above room temperature.

It was also observed that the reactivity of the bisphenol was inversely related to its acidity. This is consistent with established principles that nucleophilicity generally increases with basicity. When DMSO was used as the reaction solvent, only sodium and potassium phenolates were sufficiently soluble.

The reactivity of the activated dihalide was affected by both the activating group and halide type. Fluorinated derivatives had faster reaction rates than chlorinated derivatives with identical activating groups. Stronger activating groups, such as sulfone, allowed a fast reaction with both fluorine and chlorine.

The main advantage of the strong base approach was the short reaction time needed to reach high molecular weight. Reaction times as short as an hour were used to synthesize commercially available bisphenol-A / 4,4'-dichlorodiphenylsulfone based UDEL, although some bisphenolates needed reaction times as long as 10 hours to reach completion. The disadvantage of the strong base method is the possibility of side reactions when water is present. To avoid problems, stoichiometry must be carefully controlled in the prepolymerization step and water must be quantitatively removed prior to addition of the activated dihalide.

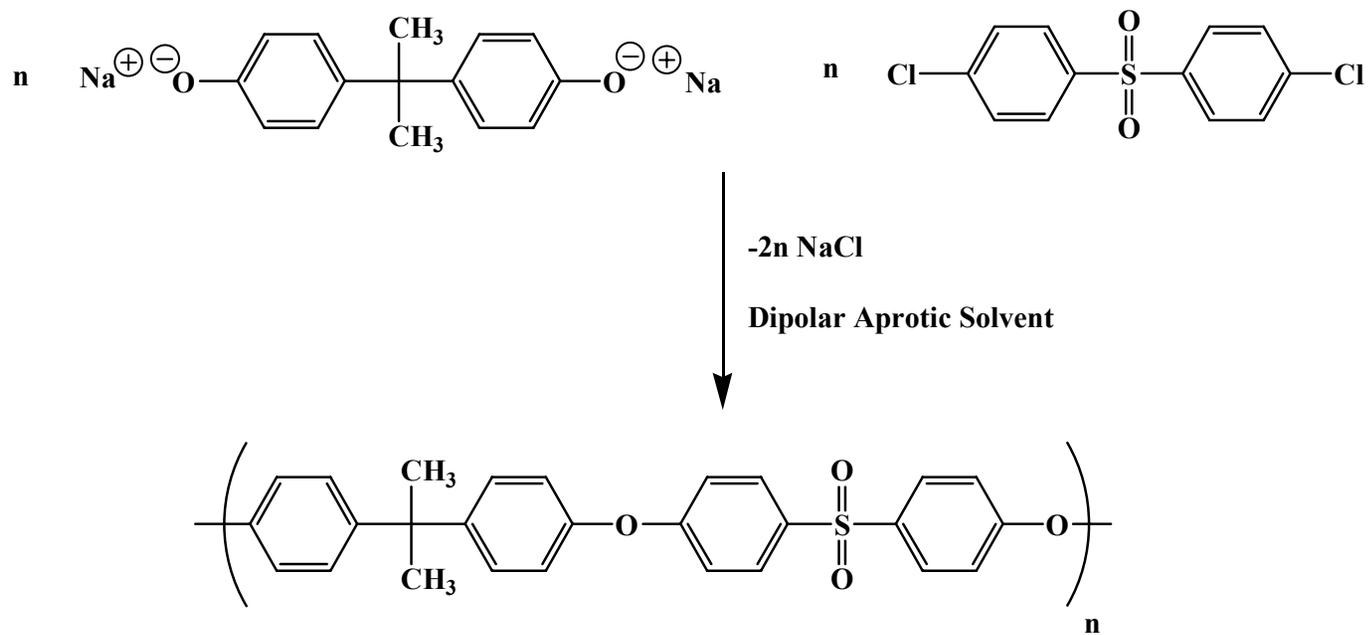


Figure 2.5: Nucleophilic Aromatic Substitution: Strong Base Bisphenolate¹⁶

ii) Synthesis of Poly (arylene ether sulfones):

Weak Base Method

Some of the first literature published on the weak base method was in the form of patents.¹⁷ In 1979, McGrath and coworkers¹⁸ investigated the weak base method in detail, using anhydrous potassium carbonate as base and N,N'-dimethylacetamide as the dipolar aprotic solvent. In 1984,¹⁹ they reported that this approach avoided the problems associated with the hydrolysis of monomer and polymer and the bisphenolate insolubility. The synthetic approach used by McGrath and coworkers is shown in figure 2.6, which illustrates the synthesis of a bisphenol-A poly (arylene ether sulfone). N, N'-dimethylacetamide (DMAc) was the dipolar aprotic solvent and toluene was used as the azeotroping agent to remove water that is in the system initially and that which is formed through the disproportionation of potassium bicarbonate. The potassium carbonate can react in a number of ways to produce phenolate and water, as illustrated in figure 2.7. High molecular weight was obtained and the molecular weight could be controlled by offsetting the stoichiometry slightly with an excess of bisphenol to generate phenolic endgroups.

To generate high molecular weight polymers, an excess of potassium carbonate was used (10-20%). Less than stoichiometric quantities of base lowered the molecular weight of the resulting polymer presumably because less than the targeted number of phenolate ions were formed. It was found that the moderate excess of potassium carbonate did not hydrolyze the dihalide monomer, 4,4'-dichlorodiphenylsulfone, nor the polymer chain under the chosen polymerization conditions. Base and phenolate concentrations were found to be dependent on reaction conditions. Base solubility was found to be dependent on the reaction temperature,

¹⁷ Berd, B.; Claus, C.; Ger. 2,749,645;

I. C. I. U.S.; Ger. 2,635,101; 1977

I. C. I. Ltd.; Jap. 7,812,991; 1978

Clendinning, R. A.; Farnham, A. G.; Zutty, N. L.; Priest, D. C.; Union Carbide Corporation; Canada 847,963; 1970

¹⁸ Viswanathan, R.; McGrath, J. E. *Polymer Preprints* **1979**, *20*, 365.

¹⁹ Viswanathan, R.; Johnson, B. C.; McGrath, J. E. *Polymer* **1984**, *25*, 1827-1836.

Viswanathan, R., Ph.D. Thesis; VPI&SU; Blacksburg; 1981

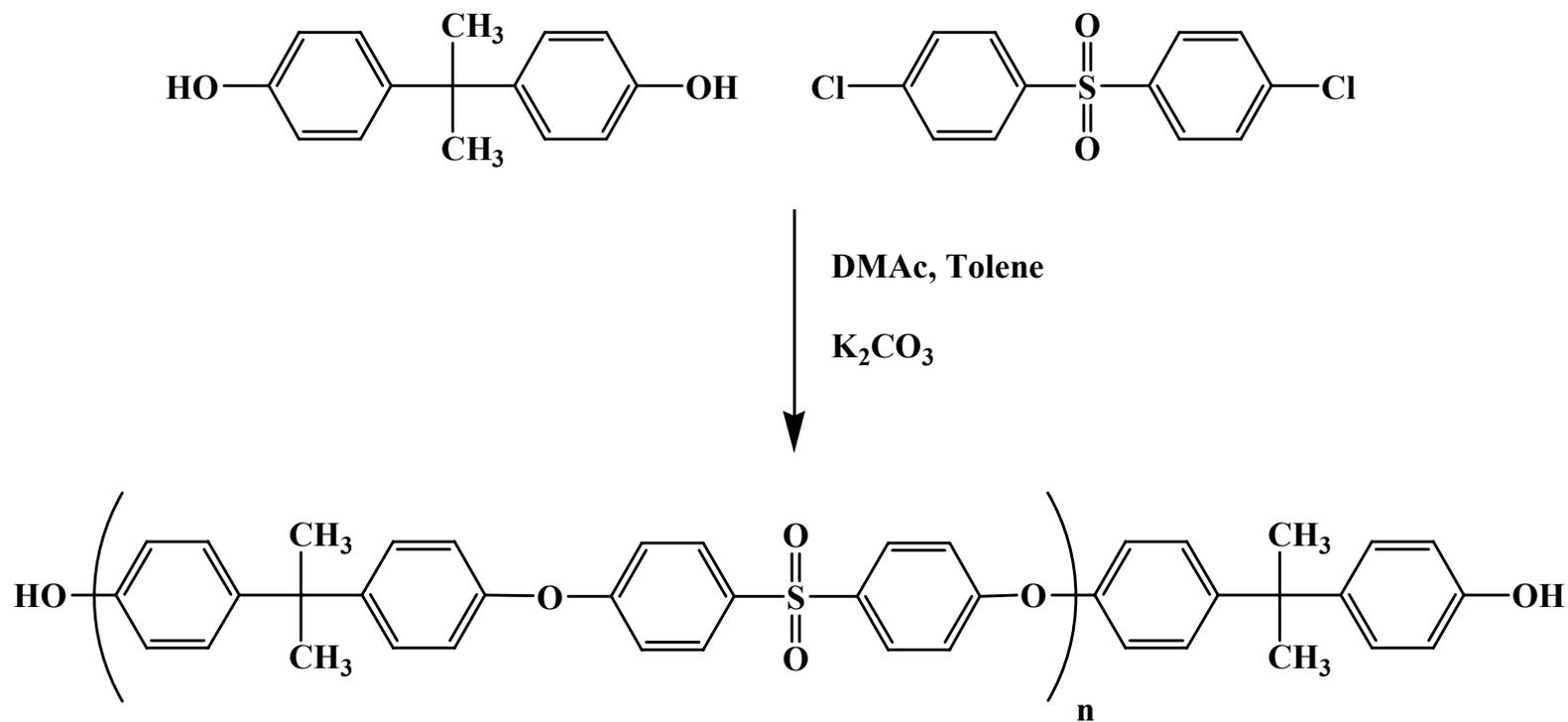


Figure 2.6: Weak Base Method for Synthesis of Poly (arylene ether sulfone) via Nucleophilic Aromatic Substitution

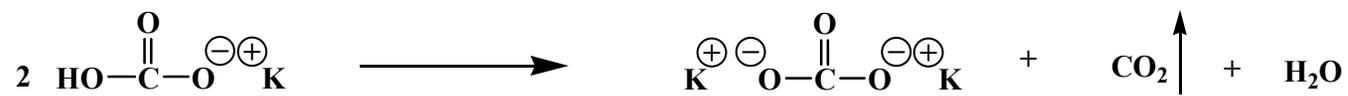


Figure 2.7: Reactions of Potassium Carbonate to Generate Phenolates and Water¹⁸

which was a function of the DMSO/NaOH strong base route, are needed for the weak base method, as discussed previously.

The reaction rate involved in the DMSO/NaOH route for the synthesis of bisphenol-A polysulfone was second order with respect to the concentration of functional groups.²⁰ The potassium carbonate/DMAc weak base route did not strictly follow the same second order kinetics, most likely due to base insolubility. The presence of both phenolate and unreacted bisphenol in solution increases the likelihood that the nucleophilicity of the phenolate will be reduced; due to hydrogen bonding with free phenolic functionality.

Both the solubility of the base and the time needed to achieve high molecular weight were temperature dependent. High molecular weight could be achieved in 10 hours at 157°C, while only low molecular weight species were found after 10 hours at 140°C.

Kinetic studies were conducted by McGrath and Priddy²¹ on model compounds derived from bisphenol A and 4-chlorodiphenylsulfone and it was discovered that potassium carbonate could not easily convert the bisphenol to a diphenolate prior to reaction with DCDPS. The study involved investigation of both the weak and strong base methods utilizing typical reaction conditions. In each case, samples were taken as time progressed and quenched with an excess of acetic acid to protonate any phenolates that were present. Either mono or disubstituted bisphenols were isolated by this method. The strong base method isolates indicated that both mono and disubstituted products were formed essentially immediately, whereas, 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

²⁰ Schultze, S. R.; Baron, A. L. *Advan. Chem. Ser.* **1969**, *96*, 692.

²¹ Priddy, D.; Smith, C. D.; McGrath, J. E. In *43rd Annual Southeastern Regional Meeting of the American Chemical Society*: Richmond, VA, 1991.

Priddy, D., Ph. D. Thesis, VPI & SU; Blacksburg, VA; 1994

formation of the monosubstituted product. After about 300 minutes of reaction, it was found that the amount of disubstituted product was increasing rapidly corresponding to a concentration decrease of monosubstituted product. It would seem reasonable to conclude from this evidence that the weak base has a limited ability to form diphenolate prior to reaction with the activated dihalide, and that it is more likely that the second phenolate is formed after the first has reacted to form an ether bond.

These data contributed to the understanding of why the weak base method does not follow strict second order kinetics. In the strong base reaction, the second order kinetics are dependent on the concentrations of the activated halide and the diphenolate. The weak base method has very little kinetic contribution from the diphenolate because of its low concentration initially, so it cannot be expected to follow the same kinetics. Additionally, the weak base method may start chains in one direction and link them subsequently. This phenomenon, along with base insolubility and hydrogen bonding of phenolate and unreacted phenolic groups, is likely to contribute to the relatively slow reaction rate of the weak base approach when compared to that of the strong base approach.

In industrial production, rapid reaction times are required to maintain low cost. This is the reason that the strong base method is used preferentially in industry, providing that the diphenolate is soluble (*e.g.* bisphenol A). Although the weak base method works well in wholly aromatic systems, the slow reaction rates are undesirable. The most important feature of the weak base method is the potential for better solubility of the monophenolate over that of the diphenolate. This allows a broader range of monomers (*e.g.* biphenol, hydroquinone, etc.) to be investigated as potential starting materials for poly (arylene ether) productions.

3. Physical Properties of Poly (arylene ether sulfones)

Poly (arylene ether sulfones) display many interesting physical characteristics. They are high modulus (stiff), usually amorphous transparent, tough thermoplastic materials that display relatively high glass transition temperatures in the range of 180 – 250°C depending on the structure of the backbone. Common backbone characteristics

include the rigid phenylene groups that are connected by flexible ether and sulfone linkages. The general rigidity associated with this class of polymers is usually associated with the inflexible phenyl groups, while the toughness is usually associated with the mobility of the ether linkages, which occurs even below T_g .²² These polymers are good candidates for high temperature molding and/or chemically aggressive applications due to their excellent thermal, chemical and oxidative stabilities. Poly (arylene ether sulfones) can be injection molded, blow molded and extruded using typical conditions required for other highly viscous amorphous polymers like polycarbonates. Although high temperatures of 300-400°C and high pressure are required to melt process these materials, they can be machined very easily due to their high T_g and inherent toughness, which minimize cracking and shattering.²³

Three examples of commercial poly (arylene ether sulfones) are illustrated in figure 2.8. These commercial polymers are all tough, rigid materials that have high impact strengths, which is likely to be derived principally from the second-order (β) transition at around -100°C. A number of dynamic mechanical studies have investigated the origin of this behavior. It is generally accepted that the low temperature transitions are due to more than one mechanism,²⁴ which include rotation of the backbone around the ether bond and may also involve the formation of a complex between the sulfone linkage and adsorbed water. Unfortunately, the mechanical loss peaks caused by these low temperature motions overlap, making them difficult to interpret in most cases. Poly (arylene ether sulfones) have very good hydrolytic stability compared to other thermoplastic polymers such as polycarbonates, polyesters and polyetherimides.²⁵ After hours of exposure to hot water and steam, little change in mechanical properties occurs. The low rate of polymer hydrolysis is nearly constant over a broad range of pH and these

²² Robeson, L. M.; Farnham, A. G.; McGrath, J. E., Eds. *Dynamic Mechanical Characteristics of Polysulfone and other Polyethers*; Gordon and Breach, 1978; Vol. 4, p.405-526

²³ Harris, J. E.; Johnson, R. N. In *Ency. Poly. Sci. and Eng.*; Bikales, N. M., Ed.; John Wiley and Sons: New York, 1988; Vol. 13, p 196.

²⁴ Dumias, J. J.; Cholli, A. L.; Jelinski, L. W.; Hedrick, J. L.; McGrath, J. E. *Macromolecules* **1986**, *19*, 1884.

Robeson, L. M.; Farnham, A. G.; McGrath, J. E. *Applied Poly. Symp.* **1975**, *26*, 373-385.

²⁵ Robeson, L. M.; Crisafulli, S. T. *J. Appl. Poly. Sci.* **1983**, *28*, 2925.

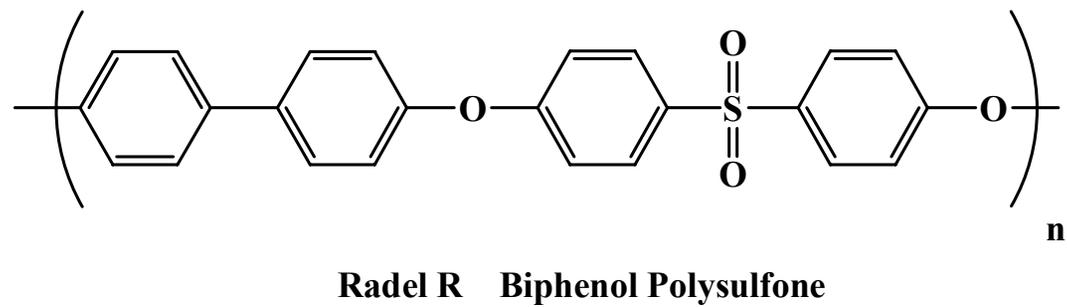
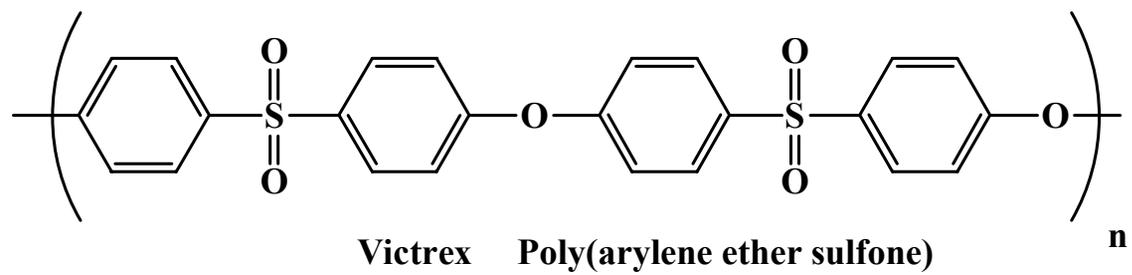
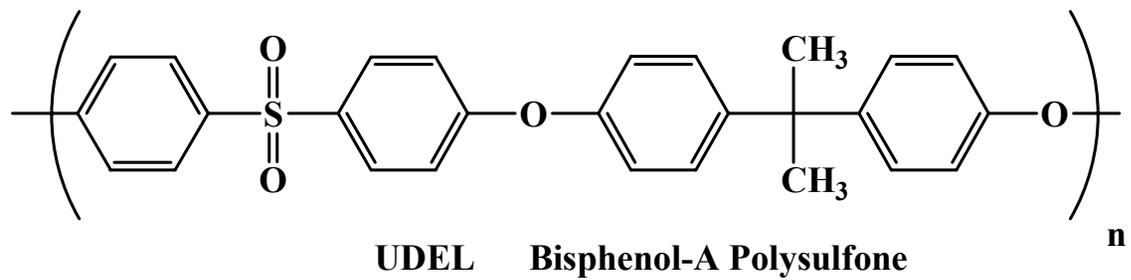


Figure 2.8: Commercial Poly (arylene ether sulfones)²⁷

materials are particularly resistant to aqueous mineral acid, alkali and salt solutions, although performance in the presence of organic solvents is not nearly as remarkable. The poly (arylene ether sulfones) crack, craze and swell in organic solvents even when dissolution does not occur. This is typical of many amorphous thermoplastic materials. In some cases, such as that of the commercial poly (arylene ether sulfone) Radel R, these materials crystallize in the presence of certain solvents, thereby forming unstable solutions.²⁶

The many highly desirable properties of poly (arylene ether sulfones), as well as the opportunity to tailor them by variation of the polymer backbone structure, molecular weight and endgroups, enables their use in a variety of applications. They are used in medical and food service applications that require repeated exposure to heat and steam for sterilization purposes, in electrical wire coatings due their low dielectric constant and in gas separation membrane support films. Bisphenol-A polysulfone is the most economical and is sold in the largest volume.²⁷

4. Sulfonated Poly (arylene ether sulfones)

A major thrust of this research involved the synthesis and characterization of sulfonated poly (arylene ether sulfones) for use as proton exchange membrane materials.

Although poly (arylene ether sulfones) have some excellent physical performance characteristics, the hydrophobicity of these materials has fueled work to modify this behavior. Some of the early work included investigation of sulfonated poly (arylene ether sulfones) by Noshay and Robeson²⁸ who used a relatively mild post-sulfonation procedure, a 2:1 ratio of SO₃/triethyl phosphate, to chemically modify a commercially available bisphenol-A based poly(ether sulfone). This same approach was used to generate sulfonated materials for desalinization membranes for reverse osmosis and other

²⁶ Roovers, F.; Ethier, R.; Toporowski, P. M. *High Perf. Poly.* **1990**, *2*, 151.

Roovers, F.; Toporowski, P. M.; Ethier, R. *High Perf. Poly.* **1990**, *2*, 165.

Attwood, T. E.; King, T.; Leslie, V. J.; Rose, J. B. *Polymer* **1977**, *18*, 369.

²⁷ Harris, J. E.; Johnson, R. N. In *Ency. Poly. Sci. and Eng.*; Bikales, N. M., Ed.; John Wiley and Sons: New York, 1988; Vol. 13, p 196.

²⁸ Noshay, A.; Robeson, L. M. *J. Of Appl. Poly. Sci.* **1976**, *20*, 1885.

water purification processes.²⁹ An interesting, but complex approach using gaseous sulfur dioxide followed by an oxidation step to sulfonate lithiated UDEL has also been developed by researchers in Germany.³⁰

Post-sulfonation reactions result in the placement of the sulfonic acid group ortho to the activated aromatic ether linkage. Moreover, only one sulfonic acid group per repeat unit can be achieved with bisphenol-A (figure 2.9). In contrast, sulfonation of the dihalide monomer 4,4'-dichlorodiphenylsulfone (DCDPS) results in sulfonic acid functionalization on both deactivated phenyl rings ortho to the chlorine moiety and allows for 2 sulfonic acids per repeat unit after polymerization (figure 2.10).

General conditions for sulfonation of DCDPS have been reported by Ueda *et al.*³¹ 4,4'-dichlorodiphenylsulfone was sulfonated utilizing conditions illustrated in figure 2.11.

This work by Ueda *et al.* showed that typical step-growth polymerization techniques could be used to generate high molecular weight poly (arylene ether sulfones) in DMAc utilizing SDCDPS to achieve sulfonation levels of up to 30 mole percent and inherent viscosities in NMP that approach values of 1.0 dL/g. A modified procedure to generate SDCDPS has been reported by Wang³² that decreases the reaction time. His paper details the synthesis and characterization of a series of sulfonated poly (arylene ether sulfones). Further work in this area resulted in poly (arylene ether sulfones) that were 100 percent sulfonated (i.e. each repeat unit contained an SDCDPS residue) while at the same time achieving high molecular weight or controlled molecular weight.³³

²⁹ McGrath, J. E., In *Poly (aryl ether) Membranes for Reverse Osmosis*; Turback, A. F., Ed., 1981; Vol. No. 153, pp 327-350. Johnson, B. C.; Yilgor, I.; Tran, C.; Iqbal, M.; Wightman, J.; Lloyd, D.; McGrath, J. E. *J. Polym. Sci. Polym. Chem. Ed.* **1984**, *22*.

³⁰ Kerres, J.; Zhang, Y.; W., C. *J. of Poly. Sci.: Part A.* **1997**, *36*, 1441.

³¹ Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J.; Yonetake, K.; Masuko, T.; Teramoto, T. *J. of Poly. Sci.: Part A.* **1993**, *31*, 853.

³² Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mecham, J. B.; Zawodzinski, T.; McGrath, J. E. *Macromolecular Symposia* **2000**, *under review*.

Wang, F.; Ji, Q.; Harrison, W.; Mecham, J. B.; Formato, R.; Kovar, R.; Osenar, P.; McGrath, J. E. *Polymer Preprints* **2000**, *41*, 237.

³³ Mecham, J. B.; Shobha, H. K.; Wang, F.; Harrison, W.; McGrath, J. E. *Polymer Preprints* **2000**, *41*, 183.

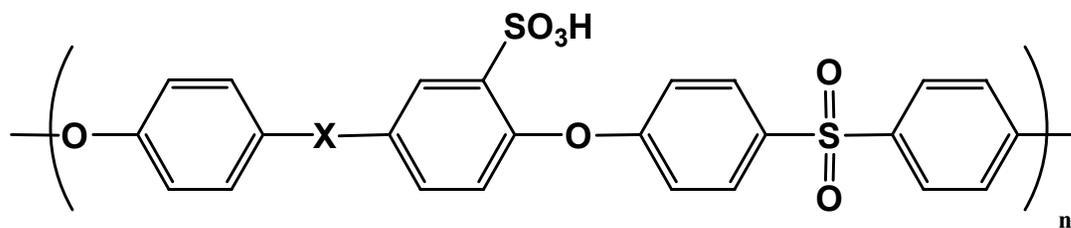


Figure 2.9: Post Sulfonation Repeat Unit

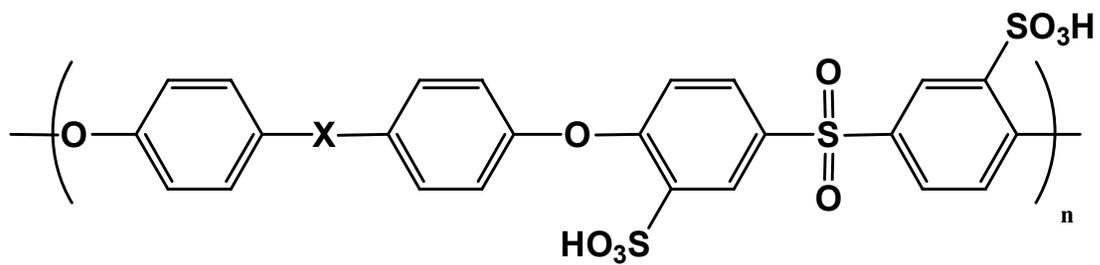


Figure 2.10: Direct Polymerization Repeat Unit

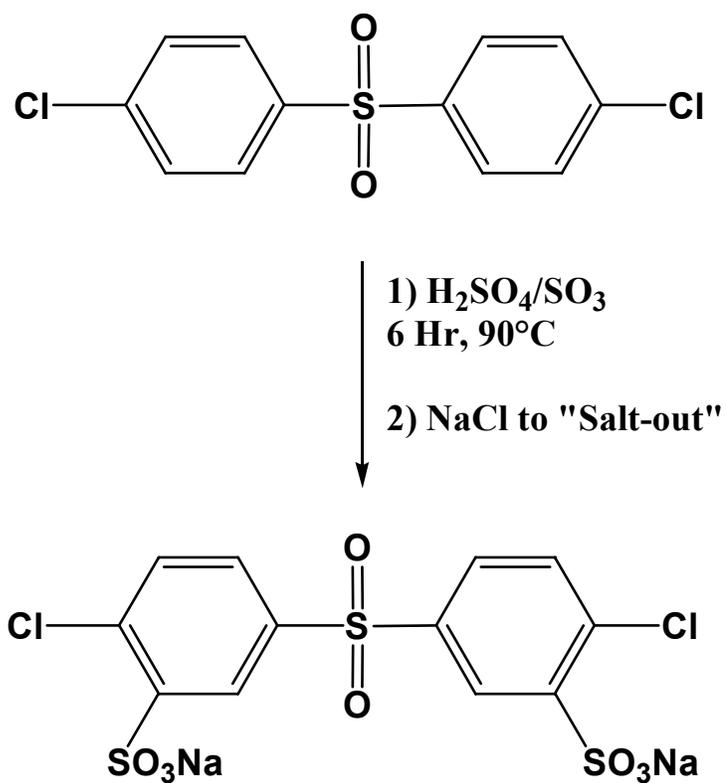


Figure 2.11: Reaction of DCDPS to form SDCDPS

B. Poly (imides)

1. Introduction

Since DuPont first commercialized Kapton over 30 years ago, a wide range of new polyimides with unique properties have been synthesized for a wide variety of applications. This class of polymers is characterized by their excellent thermal and mechanical properties which makes them a logical candidate for a broad range of high performance applications. A number of excellent books and reviews are available on these materials.³⁴

A number of synthetic routes to poly (imides) exist, but in this research, either the two-step or the ester-acid routes were utilized and will be discussed herein.

2. The Two – Step Approach to Polyimide Synthesis

Condensation poly (imides) were discovered almost 100 years ago by Bogert in 1908.³⁵ Almost 50 years later Edwards synthesized polyimides via a more practical approach using dianhydrides, or derivatives thereof, and diamines.³⁶ Although these were not true “high performance” materials, it was understood that fully aromatic poly (imides) would be suitable for high temperature applications. Successful synthesis of aromatic polyimides had to first solve problems with solubility and intractability that were initially experienced through the development of the most common and most documented method of poly (imide) synthesis, the two-step synthetic approach.³⁷

³⁴ Abadie, M. J.; Sillion, B. *Polyimides and other high temperature polymers*; Elsevier., 1991.

Feger, C.; Khoajsteh, M. M.; McGrath, J. E. *Polyimides: Chemistry, Materials and Characterization*; Elsevier., 1989.

Mittal, K. L., Ed. *Polyimides*; Plenum Press., 1984; Vol. 1 and 2.

³⁵ Bogert, T. M.; Renshaw, R. R. *J. Am. Chem. Soc.* **1908**, *30*, 1140.

³⁶ Edwards, W. M.; Robertson, M.; DuPont; U.S. 2,710,853; 1955

Edwards, W. M.; Robinson, I. M.; Squire, E. N.; DuPont; U.S. 3,867,609; 1959

³⁷ Scroog, C. E.; Endrey, A. L.; Abramo, S. V.; Berr, C. E.; Edwards, W. M.; Olivier, K. L. *J. Poly. Sci.: Part A.* **1965**, *3*, 1373.

Bower, G. M.; Frost, L. W. *J. Poly. Sci.: Part A.* **1963**, *1*, 3135.

Adrova, N. A.; Bessonov, M. I.; Laius, L. A.; Rudakov, A. P. *Polyimides*; Technomic: New York, 1970.

Dine-Hart, R. A.; Wright, W. W. *J. Appl. Poly. Sci.* **1967**, *11*, 609.

Jones, J. I.; Ochynski, F. W.; Rackley, F. A. *Chem. Ind.* **1962**, 1686.

In the first stage of a two-step polyimide synthesis, a dianhydride and a diamine are dissolved in a dipolar aprotic solvent. The resulting poly (amic acid) is then cyclodehydrated using either a thermal or a chemical process to form the final polyimide, illustrated in figure 2.12. The reaction to form a poly (amic acid) is thought to begin initially with the formation of a charge transfer complex between the anhydride and diamine as shown in figure 2.13³⁸. The amine attacks the carbonyl carbon, displacing the adjacent carboxyl group, which is stabilized by hydrogen bonding with the polar aprotic solvent³⁹, specifically N-methyl pyrrolidone or dimethyl acetamide, pushing the reaction toward completion of the polymerization. Using this approach, high molecular weight poly (amic acids) can be synthesized from a wide variety of dianhydrides and diamines. Given enough reaction time, even relatively unreactive monomers can be used to produce high molecular weight polyimides.

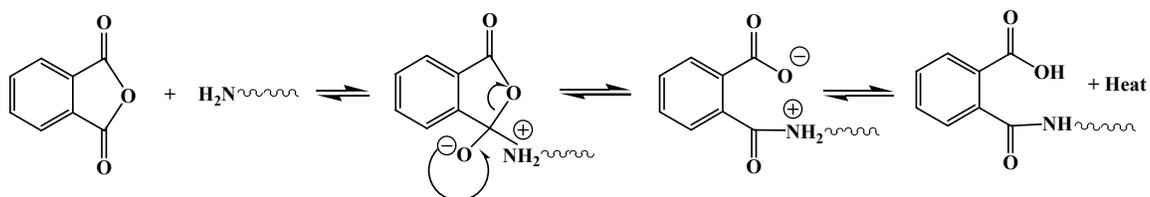


Figure 2.13: Charge Transfer Complex Between a dianhydride and Diamine³⁸

Frost, L. W.; Keese, J. J. *Appl. Poly. Sci.* **1964**, 8, 1039.

Edwards, W. M.; Endrey, A. L.; U.S. 803,347-803,349; 1959

(to E. I. DuPont de Nemours & Co.); France 1,239,491; 1960

(to E. I. DuPont de Nemours & Co.); Belgium 649,336 and 649,337; 1964

Edwards, W. M.; Endrey, A. L.; Britian 898,615 and 903,271; 1962

³⁸ Frost, L. W.; Keese, J. J. *Appl. Poly. Sci.* **1964**, 8, 1039.

³⁹ Brekner, M. J.; Feger, C. *J. Poly. Sci.: Part A.* **1987**, 25, 2005.

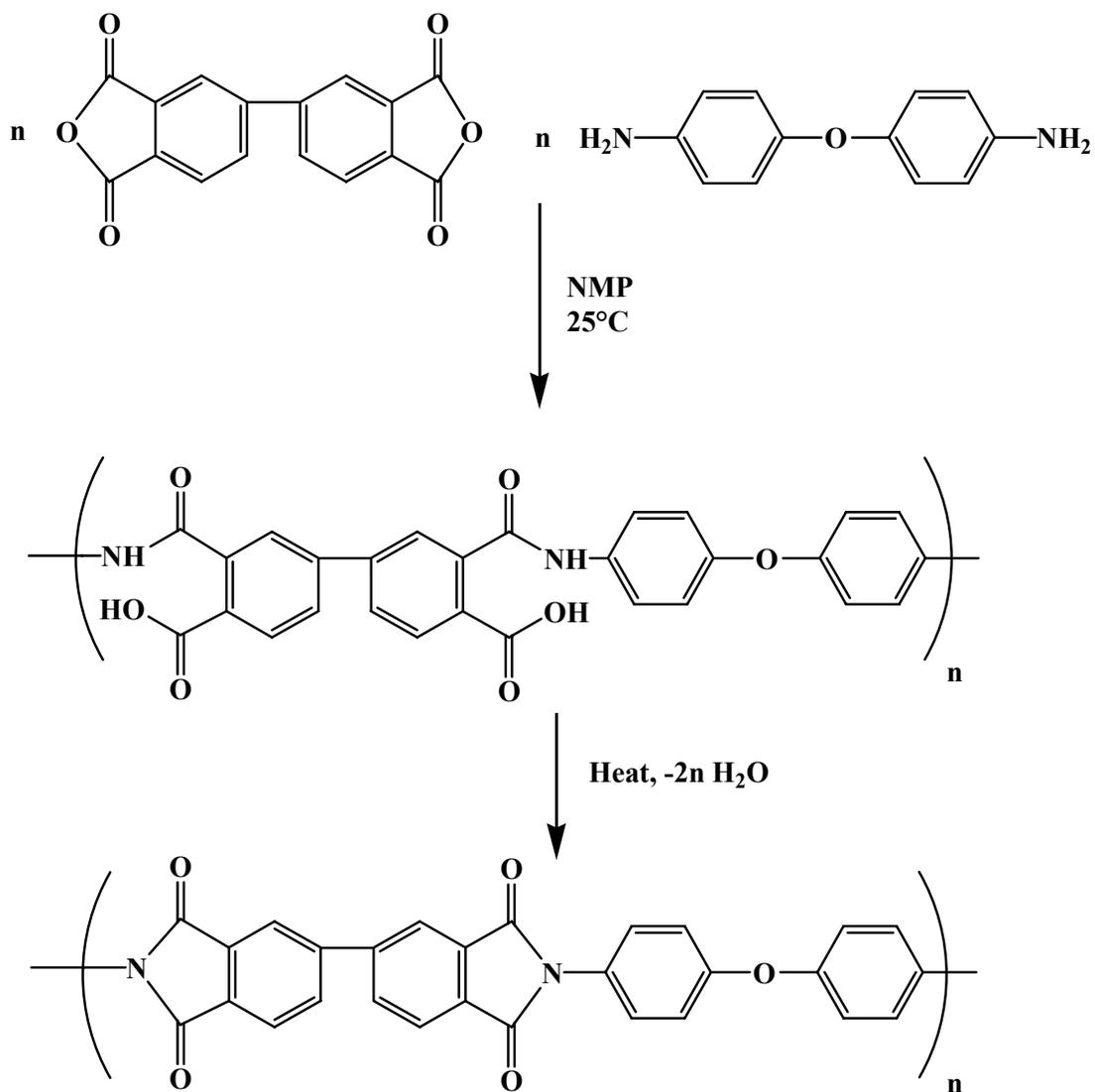


Figure 2.12: Two-Step Polyimide Synthetic Approach^{34, Mittal}

Since the propagation of the poly (amic acid) proceeds after a nucleophilic substitution reaction at the carbonyl carbon of the anhydride, anhydrides that are more electrophilic tend to react faster. The reactivity of an anhydride can be estimated by measuring its electron affinity, with higher values suggesting higher reactivity.⁴⁰

Reactivity of the diamines also follow a distinct trend and can be estimated using NMR. Rates of reaction towards poly (amic acid) formation tend to be higher when the ¹⁵N shifts are smaller. Additionally, diamines containing electron withdrawing bridging groups are more reactive than those with electron donating groups.⁴¹ Table 2.1 lists the ¹⁵N shifts for some of the more commonly used diamines.

The reaction temperature can greatly affect the extent of poly (amic acid) conversion. For this reason, the initial stage of the reaction is usually conducted below 50°C to prevent cyclization to the imide. If imidization occurs, it can release water, which can potentially hydrolyze any unreacted poly (amic acid), reducing its molecular weight. In some cases, the fully imidized product is insoluble, and premature cyclization can result in heterogeneity and low molecular weight due to a stoichiometric imbalance of reacting endgroups.

a. Bulk Imidization

The most common method used to convert the poly (amic acid) to polyimide is often bulk imidization and this is the best approach for insoluble polyimides.⁴² A film is usually cast onto a substrate, often a glass plate, and is heated in stages, typically in a vacuum oven or inert atmosphere, to induce cyclization and remove the solvent and water condensate that is produced during imidization. A typical heating ramp may start at room

⁴⁰ *Polyimides*; Chapman and Hall: New York, 1990.

⁴¹ Ando, S.; Matsuura, T.; Sasaki, S. *J. Poly. Sci.: Part A*. **1992**, *30*, 2285.

⁴² Snyder, R. W.; Thomson, B.; Bartges, B. *Macromolecules* **1989**, *22*, 4166.

Scroog, C. E. In *Encyclopedia of Polymer Science and Technology*; Bikales, N. M., Ed.; Interscience: New York, 1969; Vol. 11, p 247.

Cassidy, P. C.; Fawcett, N. C. In *Encyclopedia of Chemical Technology*; Wiley: New York, 1982; p 704.

temperature for an hour followed by a step-wise increase of the temperature: 80°C for 1 hour, 100°C for 1 hour, 200°C for 1 hour, 300°C for 1 hour. The polyimide is then slowly cooled to room temperature. The best results are obtained when the final reaction temperature is above the ultimate T_g of the system. This allows the chains enough freedom of motion to release nearly all the trapped water and solvent. Systems with stiffer backbones may not cyclize quantitatively, for instance, the PMDA/ODA system, shown in figure 2.14, for which ^{15}N NMR studies have indicated that almost 10 percent of the final product may be in the uncyclized form.⁴³ The major portion of the imidization of a PMDA/ODA poly (amic acid) has been shown to occur in the temperature range of 150-250°C as revealed by differential scanning calorimetry and thermogravimetric analysis experiments.⁴⁴

Side reactions, that can lead to crosslinking, can occur during the bulk imidization process.⁴⁵ A study employing Raman spectroscopy during the imidization of a PMDA/ODA poly (amic acid) revealed that imine bonds (C=N) were formed during the process,⁴⁶ however, several accounts of bulk imidization contradict many of the crosslinking theories.⁴⁷

b. Solution Imidization

Early efforts to design systems that could be imidized via solution techniques were developed in tandem with polyimide backbone structures that remained soluble

⁴³ Murphy, P. D.; Petro, R. A. D.; Lund, C. J.; Weber, W. D. *Macromolecules* **1994**, *27*, 279.

⁴⁴ Mittal, K. L., Ed. *Polyimides*; Plenum Press., 1984; Vol. 1 and 2,

⁴⁵ Snyder, R. W.; Thomson, B.; Bartges, B. *Macromolecules* **1989**, *22*, 4166.

Kim, Y. J.; Glass, T. E.; Lyle, G. D.; McGrath, J. E. *Macromolecules* **1993**, *26*, 1344.

⁴⁶ Saini, A. K.; Carlin, C. M.; Patterson, H. H. *J. Poly. Sci.: Part A*. **1992**, *30*, 419.

⁴⁷ Young, P. R.; Davis, P. R. J.; Chang, A. C.; Richardson, J. N. *J. Poly. Sci.: Part A*. **1990**, *28*, 3107.

Harris, F. W.; Lanier, L. H., Eds. *Structure-Solubility Relationships in Polymers*; Academic Press: New York, 1977; p.183

Vinogradova, S. V.; Korshak, V. V.; Vygodskii, Y. S. *Poly. Sci. USSR* **1966**, *8*, 888.

Vinogradova, S. V.; Vygodskii, Y. S.; Korshak, V. V.; Churochkina, N. A.; Tur, D. R. *Poly. Sci. USSR* **1971**, *13*, 1695.

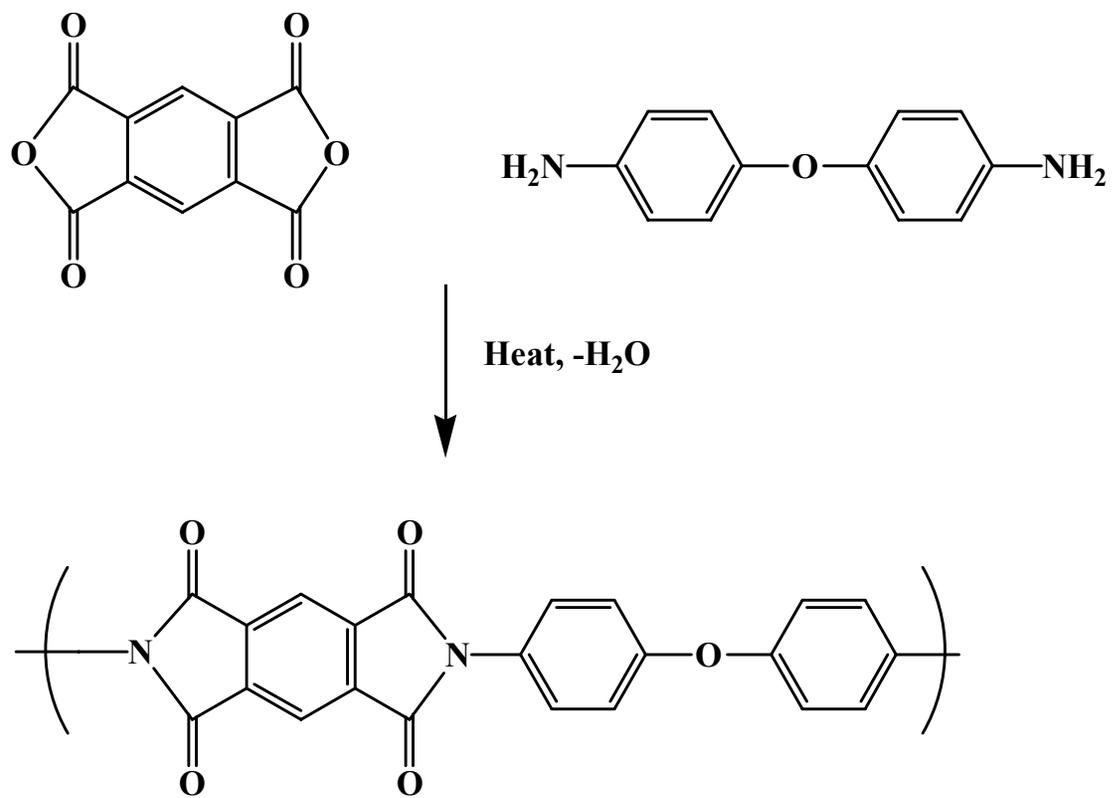
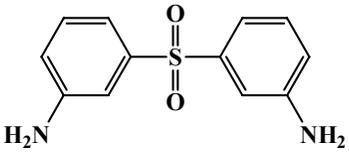
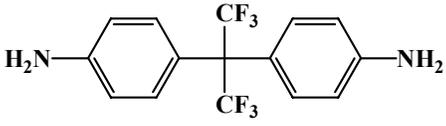
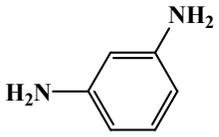
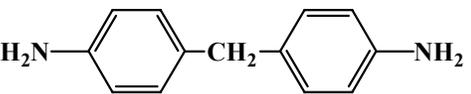
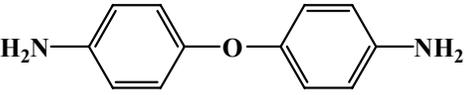


Figure 2.14: Pyromellitic Dianhydride/Oxydianiline Polyimide

Table 2.1: ^{15}N Chemical Shifts of several diamines⁴²

Diamine	Abbreviation (Name)	^{15}N Chemical Shift
	m-DDS Diaminodiphenylsulfone	65.7
	6F Diamine	64.0
	<i>m</i> -PDA <i>m</i> -phenylene diamine	60.8
	MDA 4,4'-methylenedianiline	59.4
	4,4'-ODA 4,4'-Oxydianiline	57.9
	<i>p</i> -PDA <i>p</i> -phenylene diamine	53.8

throughout the duration of the reaction.⁴⁸ This allowed the synthesis of high molecular weight, high T_g , fully aromatic polyimides using conditions that are significantly milder than traditional bulk imidization because of the increased chain mobility in the solution state that allows for more facile cyclodehydration.

Initial attempts to develop soluble polyimides met with mixed success, even when reactions were conducted at temperatures of 200°C in NMP. Most likely this was due to the presence of the water condensate in the NMP solution. It was not until the addition of an azeotropic solvent and removal of water by means of a Dean-Stark trap by McGrath *et al.* that consistent results could be generated.⁴⁹ The poly(amic acid) is heated to 150-180°C in the presence of an azeotropic agent, such as *o*-dichlorobenzene, xylene, or cyclohexyl pyrrolidone, which is added to remove the water that is formed as the poly(amic acid) cyclized to the corresponding polyimide structure.

The mechanisms involved in the solution imidization have been thoroughly investigated by Kim *et al.*⁵⁰ Initially, the intrinsic viscosity decreases, corresponding to a cleavage of the polymer chains, and reformation of amine and anhydride functionalities, in a manner similar to bulk imidization. As time progresses, the endgroups recombine and the viscosity increases as the poly(amic acid) is regenerated.⁵¹ This process can be followed by ¹H NMR by monitoring the concentration of free amine in solution. Kim determined that the solution imidization mechanism was an acid-catalyzed second order process shown in figure 2.15. The rate determining step (RDS) was defined as the nucleophilic attack of the carbonyl carbon by the amide nitrogen. The water evolved by this process is removed from the solution by the azeotropic solvent which drives the

⁴⁸ Vinogradova, S. V.; Vygodskii, Y. S.; Korshak, V. V. *Poly. Sci. USSR* **1970**, *12*, 2254.

⁴⁹ Johnson, B. C., PhD Dissertation; Virginia Tech; 1984

Summers, J. D., PhD Dissertation; Virginia Tech; 1988

McGrath, J. E.; Rogers, M. E.; Arnold, C. A.; Kim, Y. J.; Hedrick, J. C. *Makromol. Chem., Macromol. Symp.* **1991**, *51*, 103.

Waldbauer, R. O.; Rogers, M. E.; Arnold, C. A.; York, G. A.; Kim, Y. J.; McGrath, J. E. *Polymer Preprints* **1990**, *31*, 432.

⁵⁰ Kim, Y. J.; Glass, T. E.; Lyle, G. D.; McGrath, J. E. *Macromolecules* **1993**, *26*, 1344.

⁵¹ Young, P. R.; Davis, P. R. J.; Chang, A. C.; Richardson, J. N. *J. Poly. Sci.: Part A* **1990**, *28*, 3107.

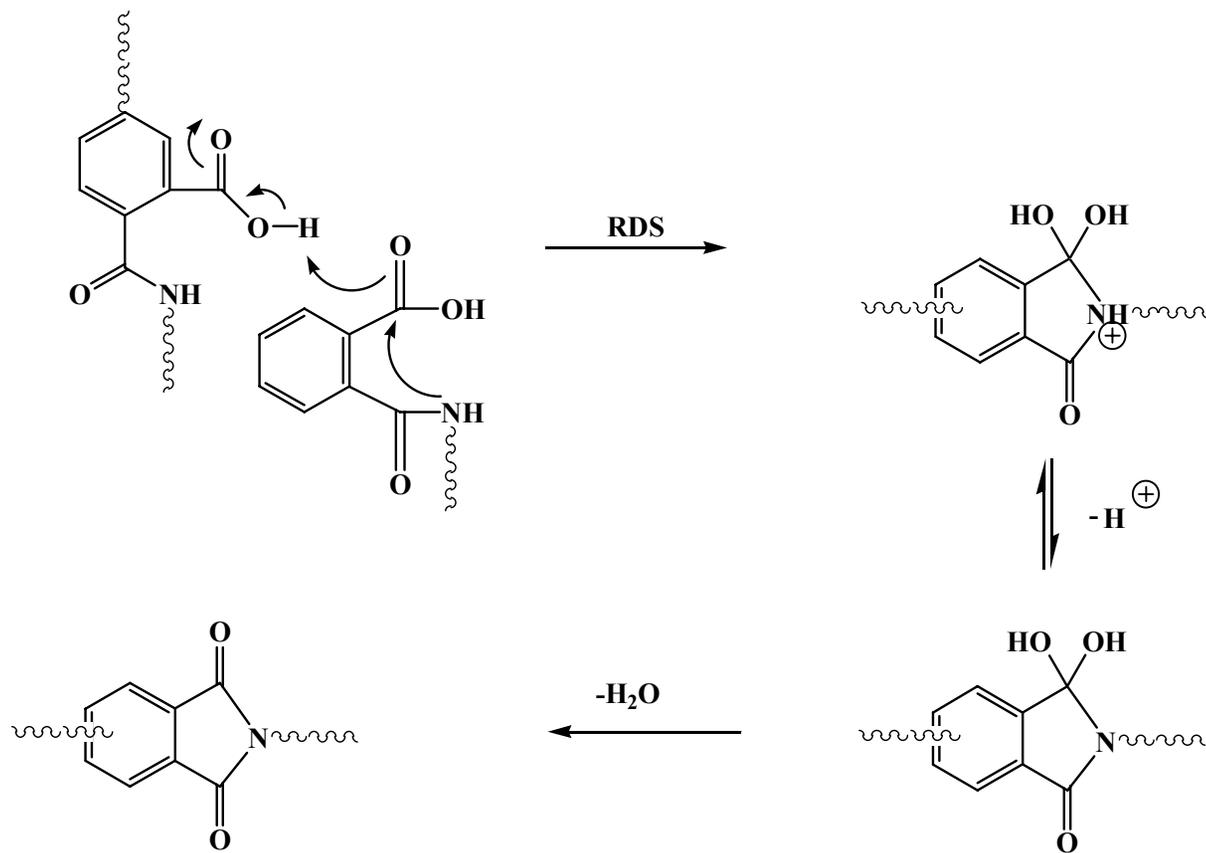


Figure 2.15: Acid catalyzed solution imidization⁵³

cyclization reaction to completion. This can be confirmed via analysis by proton NMR or FTIR.

Kim also investigated the possibility of crosslinking during cyclization when ketone-containing poly (amic acids) are utilized. The amine linkage can attack the ketone nucleophilically to generate an imine “crosslinked” insoluble polyimide network,⁵² in a similar fashion to imine formation in bulk imidization.⁵³ This result can be remedied by the addition of a small amount of aqueous hydrochloric acid.

c. Chemical Imidization

Imidization of poly (amic acids) can also be performed at room temperature using a chemical imidization method. Mixtures of acid anhydrides and tertiary amines can be used to affect imidization, but acetic anhydride and pyridine or triethylamine are most often utilized. The mechanism of chemical imidization is shown in figure 2.16.⁵⁴ The acid group of the polymer reacts with the acetic anhydride, forming an acetate group that allows cyclization to take place at lower temperatures, since it is a better leaving group than the proton it replaces. In the second step, N-acylation generates the imide heterocycle, while O-acylation gives the isoimide heterocycle. The efficiency of the reaction varies depending on the combination of reagents used. In some cases, especially when pyridine is substituted for triethylamine, the amic anhydride can tautomerize to form an iminol that can cyclize to form the kinetically favored isoimide. For the most part the amic acid condenses the acetic acid to yield the thermodynamically favored imide.⁵⁵ Any remaining acetate can reinforce attack on the isoimide to form the imide heterocycle, while thermal treatment can also yield the same result. If the poly (amic

⁵² Kim, Y. J.; Moy, T. M.; McGrath, J. E. In *Fourth International Conference on Polyimides*; Ellensville, N.Y., 1991.

⁵³ Saini, A. K.; Carlin, C. M.; Patterson, H. H. *J. Poly. Sci.: Part A*. **1992**, 30, 419.

⁵⁴ Angelo, R. J.; Golike, R. C.; Tatum, W. E.; Kreuz, J. A., Eds. *Recent Advances in Polyimide Science and Technology*; Society of Plastic Engineers: Poughkeepsie, New York, 1987; p.67

Roderich, W. R. *J. Org. Chem.* **1964**.

Cotts, P. M. In *Polyimides: Synthesis, Characterization and Applications*; Mittal, K. L., Ed.; Plenum: New York, 1984; Vol. 1, p 223.

⁵⁵ Angelo, R. J.; DuPont; U.S. 3,420,795; 1969

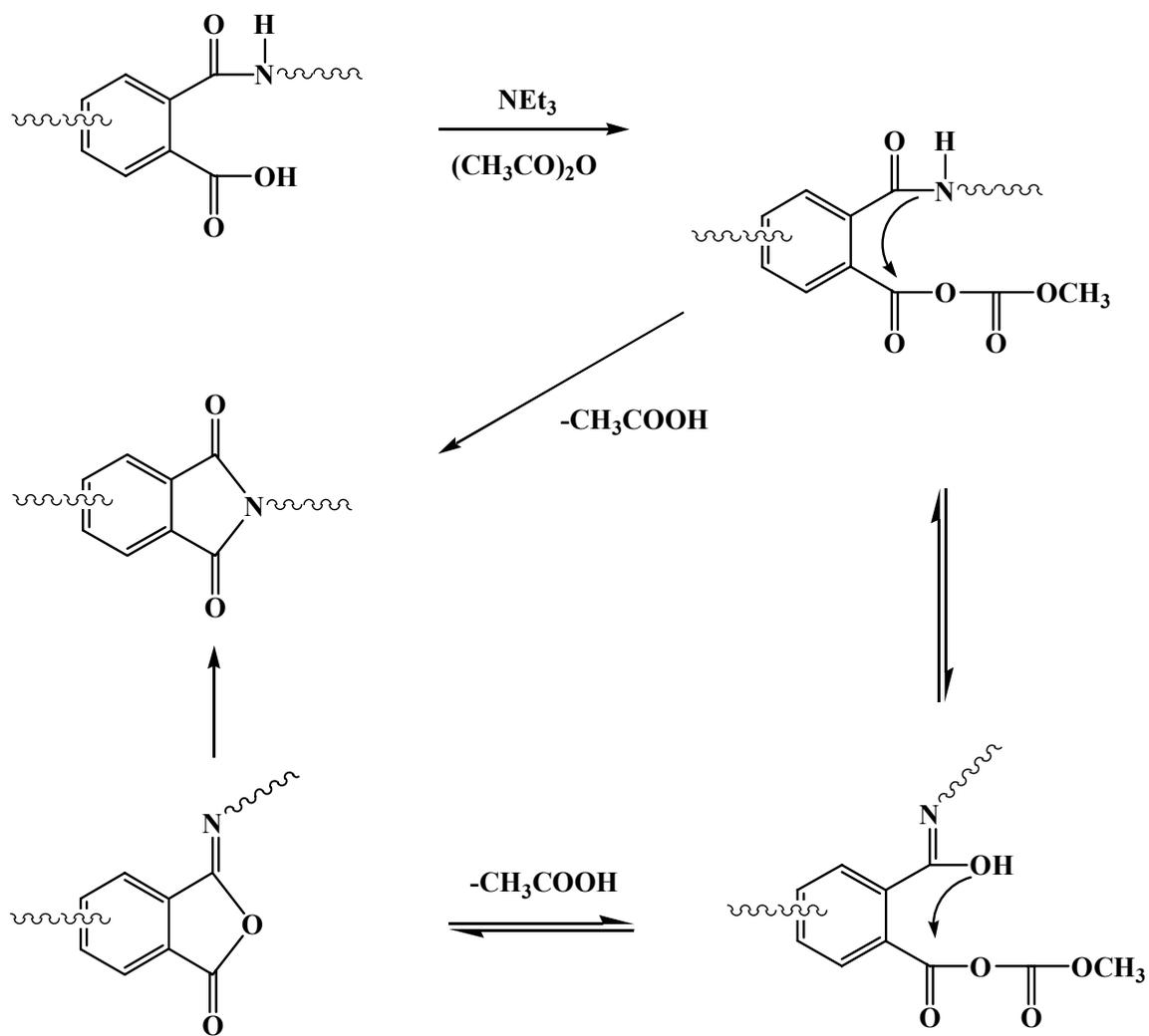


Figure 2.16: Proposed Mechanism for chemical imidization⁵⁷

acid) is chemically imidized with trifluoroacetic anhydride or dicyclohexyl carbodiimide, only the isoimide moiety is formed.⁵⁶

The resulting open chain amic acid and isoimide along the backbone of the chemically imidized polymer represent the major disadvantage of this technique. Although these “imidization defects” are unstable linkages that decrease the thermal stability and mechanical properties of the polymer, polyimides that utilize this imidization method have found commercial application, most likely because of their improved processability due to a lower T_g and increased solubility.⁵⁷

3. The Ester-Acid Approach to Polyimide Synthesis

Polyimides can also be synthesized by utilizing the hydrolysis products of dianhydride derivatives such tetracarboxylic acids or bis (ortho-ester-acids). Diester diacid dianhydride derivatives were used in conjunction with diamines in a bulk polymerization in the first successful attempt to use this approach,⁵⁸ which has the advantage of decreased moisture sensitivity as the diester-diacid is hydrolytically stable. Additionally, the diester-diacid is generally more soluble than the parent dianhydride.

Among the proposed polymerization mechanisms are: 1) the initial formation of a salt in a fashion similar to commercial nylon synthesis, followed by amidization and imidization; 2) attack of the amine on the esters, yielding an intermediate amic acid prior to imidization; and 3) in situ reformation of the dianhydride from the diester diacid followed by polymerization of dianhydride and diamine.

Although it is claimed in the patent literature that salt formation occurs when aliphatic diamines are used, it is doubtful that that this occurs with aromatic diamines due to their comparatively low basicity. Sillion and coworkers observed amic acid at

⁵⁶ [Angelo, 1967 #88; Angelo, 1963 #89]

⁵⁷ Landis, A. L.; Baselow, A. B. *National SAMPE Tech. Conf. Sr.* **1982**, *14*, 236.

⁵⁸ Edwards, W. M.; Robertson, M.; DuPont; U.S. 2,710,853; 1955

temperatures of up to 160° during the synthesis of polyamides from ester acids in NMP.⁵⁹ This observation has contributed to the view that the polymerization begins with the amine ester reaction and is followed by imidization of the amic acid intermediate, although there is evidence that contradicts this view.

Moy investigated the factors necessary for the consistent synthesis of soluble polyimides by the ester acid method, illustrated in figures 2.17 and 2.18.⁶⁰ Diester diacids are easily prepared by dissolving highly purified dianhydride in refluxing ethanol. The addition of a catalyst that can accept protons greatly accelerates the rate of formation. If the dianhydride is left in the solution for extended periods of time, undesirable tri- and tetra-esters can be produced which are incapable of reacting with the amine in the desired fashion.⁶¹ Moy's results indicated that at moderate temperatures the solution reaction of aromatic ester acids and aromatic amines begins with the conversion of the ester acid to anhydride and that by blocking anhydride formation, amide and imide formation are inhibited. These studies generated a set of reaction conditions that included solids contents of 15 to 20 weight percent (w/v) in NMP and temperatures of 170-180°C for a period of not more than 24 hours that allowed the synthesis of high molecular weight as well as controlled molecular weight polyimides.⁶²

⁵⁹ Quenneson, M. E.; Garapon, J.; Bartholin, M.; Sillion, B. In *Proceedings of the Second International Conference on Polyimides*: Ellenville, New York, 1985; p 74.

⁶⁰ Moy, T. M., PhD Dissertation; Virginia Tech; 1993

Moy, T. M.; DePorter, C. D.; McGrath, J. E. *Polymer (London)* **1993**, *34*, 819.

⁶¹ Smith, G. S.; Smith, R. L., Eds. *Advances in Polyimide Science and Technology* Lancaster PA, 1993; p.281

⁶² Moy, T. M., PhD Dissertation; Virginia Tech; 1993

Moy, T. M.; DePorter, C. D.; McGrath, J. E. *Polymer (London)* **1993**, *34*, 819.

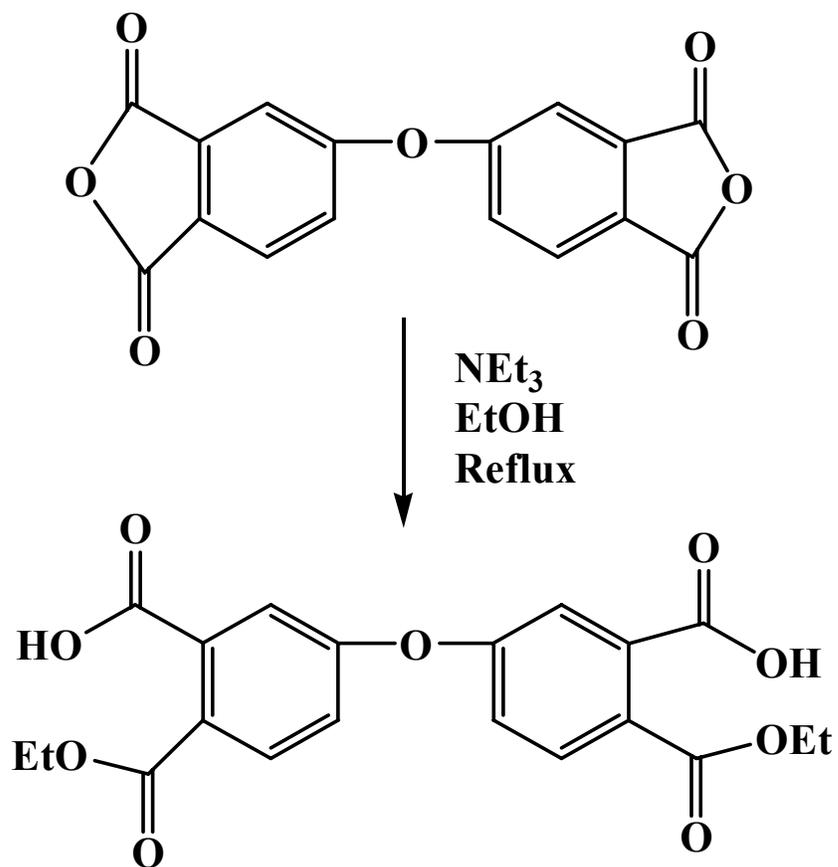


Figure 2.17: Synthesis of Diester Diacid from Anhydride Functionality

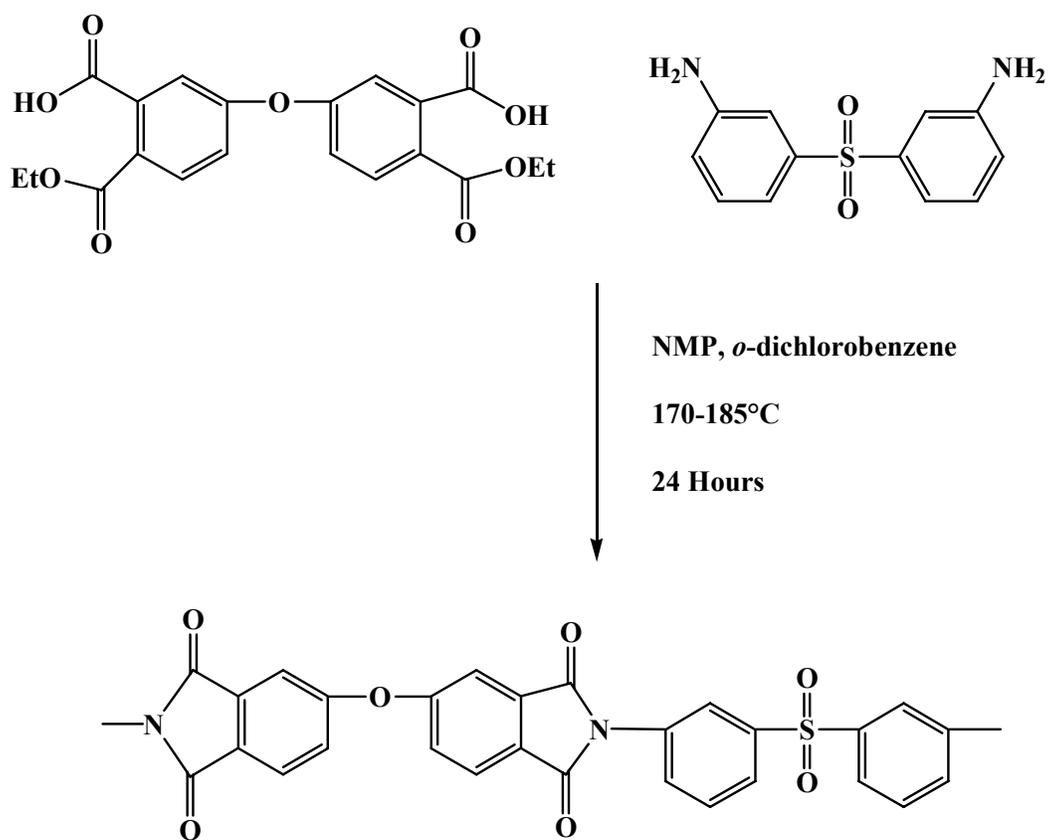


Figure 2.18: Polyimide Synthesis via the Ester-Acid Method⁶³

4. Physical Properties of Polyimides

a. Solubility

Aromatic polyimides can be characterized as high performance materials that are known for their high glass transition temperatures, and excellent thermooxidative and mechanical properties. These properties can be attributed to the strength of the primary aromatic main chain bonds and the rigidity that the imide heterocycle contributes to the polymer. Few other polymers approach the performance abilities of these materials and are mostly polymers containing other heterocycles: poly (benzimidazoles), polybenzoxazoles and poly (phenylquinoxalines).

If not designed carefully, aromatic polyimides are generally insoluble and infusible. Indeed, much of the earlier research on these materials has been in areas that increase solubility while retaining excellent thermal stability. This has been achieved in various ways. One of the simplest ways to achieve this was to incorporate monomers that contained a kink in their symmetry, such as *m*-phenylene diamine.⁶³ This tends to disrupt structural regularity thereby reducing rigidity and increasing solubility. Another approach is to incorporate flexible spacers into the polymer backbone, such as ether, sulfone, carbonyl, alkyl, and phosphine oxide moieties. Inserting these groups into the backbone imparts backbone rotations, bends and kinks which lower the rigidity of the system and can impart solubility, as long as crystalline regions are not present. Indeed, increasing the flexibility of the backbone can allow crystallization to occur from solution, over a period of time, as was the case with polymers synthesized with 3,3'-diaminodiphenylsulfone and biphenyltetracarboxylic dianhydride at NASA Langley.⁶⁴ The polyimides used in the current study were all amorphous materials that are soluble in NMP.

⁶³ Bell, V. L.; Stump, B. L.; Gager, H. *J. Poly. Sci.: Part A*. **1976**, *14*, 2275.

⁶⁴ Hergenrother, P. M.; Havens, S. J. *J. Poly. Sci.: Part A*. **1989**, *27*, 1161.

Havens, S. J.; Hergenrother, P. M. *J. Poly. Sci.: Part A*. **1988**, *24*, 13.

Havens, S. J.; Hergenrother, P. M. *J. Poly. Sci.: Part A*. **1992**, *30*, 1209.

The polyimides utilized in this study were synthesized in such a fashion that a segmented block polyimide-poly (arylene ether) copolymer resulted. As such, soluble polyimides were utilized such that films of the block copolymers could be cast that displayed a phase-separated morphology.

b. Morphology of Polyimides

Polyimides tend to be amorphous materials, but some important exceptions exist. As mentioned earlier, polyimides that exhibited semi-crystalline behavior were initially “stumbled upon” when flexible groups were added to the backbone to improve solubility. Kricheldorf has synthesized liquid crystalline aromatic polyester-imides by utilizing an imide-containing bisphenol and/or dicarboxylic acid monomer.⁶⁵

In addition to low melt viscosity, semi-crystalline polyimides have certain advantages over their amorphous counterparts, including increased upper use temperatures, reduced oxygen permeability, which may result in greater thermooxidative stability, and reduced water uptake. Srinivas⁶⁶ and Graham⁶⁷ synthesized and characterized semicrystalline polyimides with sufficient molecular order and mobility to allow rapid crystallization to occur upon cooling from the melt. The repeat unit of a 1,3-bis(4-aminophenoxy)benzene (TPER) / 3, 3', 4, 4' - biphenyltetracarboxylic dianhydride (BPDA) semicrystalline polymer is shown in figure 2.19.

⁶⁵ Kricheldorf, H. R.; Schwarz, G.; de Abajo, J.; de la Campa, J. G. *Polymer* **1991**, *32*, 942.

Kricheldorf, H. R.; Domschke, A.; Schwarz, G. *Macromolecules* **1991**, *24*, 1011.

Kricheldorf, H. R. *Polymer Preprints* **1992**, *33*, 447.

⁶⁶ Srinivas, S.; Graham, M. J.; Brink, M. H.; Gardner, S.; McGrath, J. E.; Davis, R. M.; Wilkes, G. L. *Polymer Eng. Sci.* **1996**, *36*, 1928.

Srinivas, S.; Caputo, F. E.; Graham, M. J.; Gardner, S.; Davis, R. M.; McGrath, J. E.; Wilkes, G. L. *Macromolecules* **1997**, *30*, 3012.

⁶⁷ Graham, M. J.; Srinivas, S.; Ayambem, A.; Ratta, V.; Wilkes, G. L.; McGrath, J. E. *Polymer Preprints* **1997**, *38*, 306.

Graham, M. J.; Srinivas, S.; Wilkes, G. L.; McGrath, J. E. *Polymer Preprints* **1996**, *37*, 485.

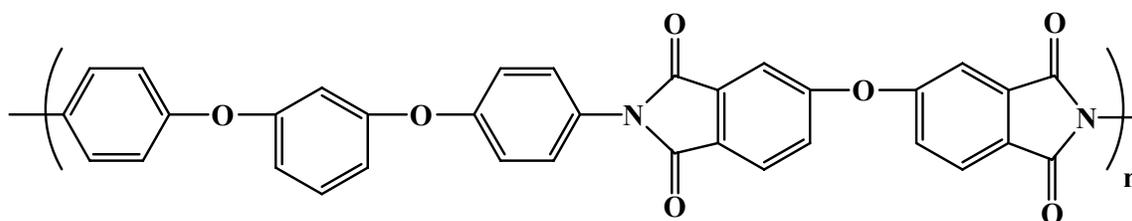


Figure 2.19 Repeat unit of a TPER/BPDA Semicrystalline Polyimide

c. Water Uptake and Hydrolytic Stability

Generally, polyimides are stable toward acid hydrolysis. In fact, Kapton, shown in figure 2.20, can be dissolved in concentrated sulfuric acid for nearly a week without any apparent degradation in molecular weight.⁶⁸ On the other hand, the imide

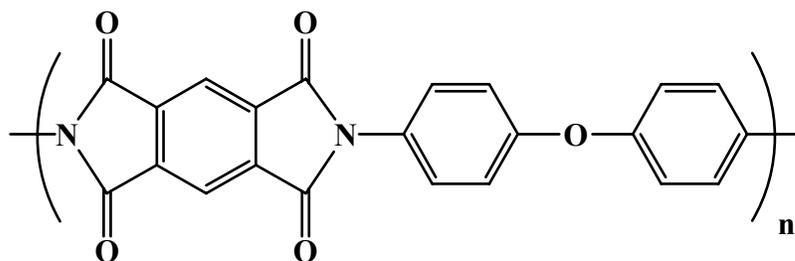


Figure 2.20: Kapton[®] Repeat Unit

heterocycle is easily hydrolyzed by strong aqueous bases and can be attacked by strong nucleophiles such as hydrazine and aliphatic diamines.⁶⁹ Generally, polyimides are hygroscopic materials. It has been shown that Kapton absorbs up to 4 percent water by weight⁷⁰ which can have an unfavorable effect mechanical properties.⁷¹

⁶⁸ Cotts, P. M. In *Polyimides: Synthesis, Characterization and Applications*; Mittal, K. L., Ed.; Plenum: New York, 1984; Vol. 1, p 223.

⁶⁹ Sillion, B., Ed. *Comprehensive Polymer Science* New York, 1989; Vol. Pergamon Press, p.519

⁷⁰ Hubbell Jr., W. H.; Brandt, H.; Munir, Z. A. *J. Poly. Sci.: Part A.* **1975**, *13*, 493.

Yang, D. K.; Koros, W. J.; Hopfenberg, H. B.; Stannett, V. T. *J. Appl. Poly. Sci.* **1985**, *30*, 1035.

⁷¹ Delasi, R.; Russell, J. *J. Appl. Poly. Sci.* **1971**, *15*, 2965.

C. Block Copolymers

1. Introduction

Block copolymers can be prepared by a variety of methods that include free radical, cationic and condensation. Over two thousand literature references were cited between the years of 1960 and 1976 in the block copolymer review by Noshay and McGrath.⁷² Other approaches that have been utilized are discussed in detail in several books and reviews.⁷³

From an economical and preparative point of view, the simplest method of generating a polymer hybrid is achieved by physically blending two or more components. The properties of the resulting blends are strongly dependent on the compatibility of the components, and as most polymers are immiscible, the lack of interfacial adhesion between the two components results in low strength materials.⁷⁴

Random and alternating copolymers are the most versatile and economical of all the classes of copolymers. Most random copolymers are synthesized from vinyl and/or conjugated diene starting materials and are characterized by a statistical or random ordering of the monomer units that is a result of the relative reaction rates of the individual components. The properties of random copolymers are a result of the weight fraction of the individual components and are intermediate to those of the corresponding homopolymers.

⁷² Noshay, A.; McGrath, J. E. *Block Copolymers: Overview and Critical Survey*; Academic Press: New York, 1977.

⁷³ Ceresa, R. J. *Block and Graft Copolymers*; Butterworths: London, 1962.

Aggarwal, S. L. *Block Copolymers*; Plenum: New York, 1970.

Burke, J. J.; Weiss, V., Eds. *Block and Graft Copolymers*; Syracuse University Press: Syracuse, New York, 1973;

Allport, D. C.; Janes, W. H., Eds. *Block Copolymers*; Applied Science Publisher Ltd.: Essex England, 1973;

Morton, M., Ed. *Encyclopedia of Polymer Science and Technology*; Wiley Interscience: New York, 1970; Vol. 15, p.508

⁷⁴ Paul, D. R.; Newman, S., Eds. *Polymer Blends*; Academic Press: New York, 1978;

Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic Press: New York, 1979.

Alternating copolymers are characterized by the alternate, as opposed to statistical, arrangement of comonomer units.⁷⁵ This type of copolymer is rather rare as pairs of monomers must be identified that have highly distinct reactivity ratios to generate an alternating structure. The properties are represented by a weighted average of the individual homopolymer properties.

Graft copolymers combine some of the features of both physical blends and random copolymers. In this case, the main chain repeat units have chemically dissimilar pendent units “hanging” from them, as shown in figure 2.21. The chemical linkage of A to B is responsible for the physical properties of these systems, which are characteristic of each of the individual components, rather than an average of the properties.

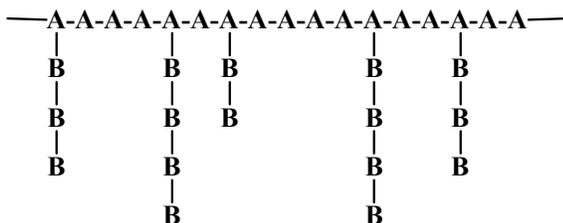
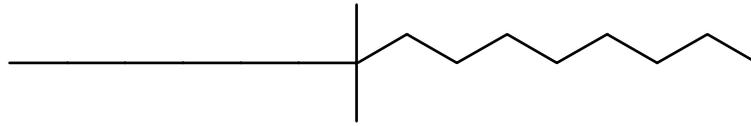


Figure 2.21: Schematic Representation of a Graft Copolymer

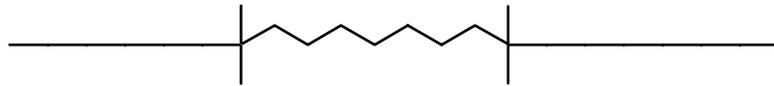
Linear block copolymers are comprised of chemically dissimilar segments much like grafts, but these are butted end to end with terminal connections. They can be arranged as a copolymer of two differing monomeric units, such as A-B, with only two distinct segments, in a triblock fashion, such as A-B-A, with three segments, or as multiblocks of the structure (A-B)_n, comprised of many segments, as shown in figure 2.22. Another, less common configuration, is the star block copolymer with arms that radiate from a central core of a chemical makeup that is dissimilar to that of the arms.

⁷⁵ Harwood, H. J. *Polymer Preprints* **1973**, *14*, 295.

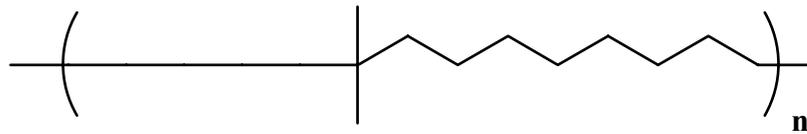
A-B Block Copolymer



A-B-A Block Copolymer



-(A-B)-_n **Block Copolymer**



Star Block Copolymer

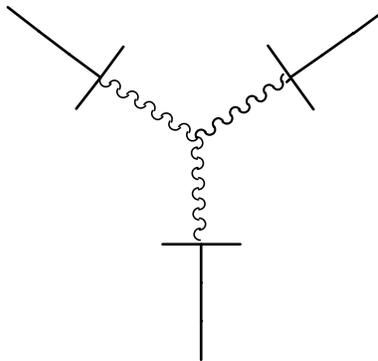


Figure 2.22: Block Copolymer Architecture

Block and graft copolymers have several distinct advantages over blends that include:

- 1) The covalent bond between segments eliminates the need for interfacial adhesion of the segments
- 2) New materials can be easily prepared simply by variation of their architecture
- 3) Block and graft copolymers can be used as compatibilizers in blends and function by strengthening the interfacial adhesion of the components.

Most of the properties that are uniquely associated with block copolymers are a result of phase separation. This phenomenon has been utilized commercially in the case of thermoplastic elastomers and impact modified thermoplastics.

2. Synthesis of Block Copolymers

A variety of polymerization techniques have been used to prepare block copolymers, including step-growth, living addition and to a lesser extent free radical synthesis procedures⁷⁶. While A-B diblock and A-B-A triblock architectures are synthesized via living anionic polymerization techniques, (A-B)_n are prepared by application of step growth⁷⁷ polymerization techniques. The statistical nature of step growth techniques generates segments with variable lengths, unlike the narrow polydispersities, predictable molecular weights and long block lengths that can be prepared by applying anionic methods. These features cannot be easily achieved with a

⁷⁶ Morton, M.; Fetters, L. J. *Macromol. Rev.* **1967**, *2*, 71.

Fetters, L. J. *J. Poly. Sci.: Part C.* **1969**, *2*, 71.

Fetters, L. J., Ed. *Chemical Reactions of Polymers*; Wiley: New York, 1964;

Hoffman, A. S.; Bacsikai, R. *Copolymerization*; Wiley: New York, 1964.

Szwarc, M. *Carbanions, Living Polymers, and Electron Transfer Processes*; Wiley: New York, 1968.

McGrath, J. E., Ed. *Anionic Polymerization: Kinetic, Mechanisms, and Synthesis*; American Chemical Society: Washington, D.C., 1980; Vol. 166, p.592

⁷⁷ Yilgor, E.; Tulpar, A.; Kara, S.; Yilgor, I. In *Silicones and Silicone Modified Materials*; ACS Symp. Ser., 2000; Vol. 729, pp 395-407.

McGrath, J. E.; Dunson, D. L.; Mechem, S. J.; Hedrick, J. C. *Adv. Polym. Sci.* **1999**, *140* (*Progress in Polyimide Chemistry*), 61-105.

Keifer, L. A.; Yoon, T. H.; Glass, T. E.; Jayaraman, S.; McGrath, J. E. *J. Poly. Sci.: Part A.* **1997**, *35*.

step growth approach, which does allow for a wider variety of chemical structures, including high performance structures and side chain liquid crystalline materials.⁷⁸

The available synthetic techniques are restricted considerably by the type of architecture that is desired. A wide range of chemical structures can be constructed by selecting one or more techniques.

3. Properties of Block Copolymers

The architecture of the block copolymer has a large influence on some of the properties of the block copolymers, but others are independent of the sequential arrangement. The properties that are most affected by the architecture of the copolymer include elastomeric behavior, melt rheology, and impact resistance in rigid materials. The properties that are independent of the architecture of the copolymer include those derived from the chemical nature of the segments, which include thermal behavior, electrical and transport properties, chemical resistance and thermal stability.

a. Morphology

Block copolymers can exhibit single-phase or two-phase behavior depending on the chemical makeup of the copolymer components. Single-phase block copolymers are advantageous when the individual components cannot be combined by application of random copolymerization techniques. More frequently, block copolymers are employed because of the unique properties that are displayed as a result of a two-phase morphology. Domain size, shape and continuity are the parameters that ultimately govern the macroscopic bulk properties of the material. It was not until the advent of styrene-butadiene (SB or SBS) block copolymers that were synthesized by anionic polymerization techniques that well controlled block length and narrow molecular weight distributions were possible. With this very precise control over block chemistry it was possible to systematically vary the volume fraction of each block over a full range of compositions. Depending on the relative volume fraction of the components, five general morphological arrangements are possible, as evidenced by Hashimoto's work with

⁷⁸ Nair, R.; Gregoiou, V.; Hammond, P. T. In *219th ACS National Meeting*; ACS: San Francisco, CA, 2000; Vol. PMSE-192.

polystyrene-polyisoprene (PS-PI) diblock copolymers, as well as similar work with other systems.⁷⁹ In Hashimoto's study, it was determined (Figure 2.23) that spherical PI domains were dispersed in a continuous matrix of PS when the volume fraction of PS, ϕ_{PS} , was > 0.76 , PI cylinders in PS matrices at $0.76 > \phi_{PS} > 0.67$, PI tetrapod networks in PS matrices at $0.66 > \phi_{PS} > 0.62$, PS-PI alternating lamella at $0.61 > \phi_{PS} > 0.32$, PS cylinders in PI matrices at $0.30 > \phi_{PS} > 0.18$, and PS spheres in PI matrices at $0.17 > \phi_{PS}$.

Both the domain arrangement, continuity, and border sharpness can be influenced by processing conditions.⁸⁰ In this case, processing conditions refer to the parameters surrounding the history of the formation of the solid state microstructure which usually involves the kinetic and thermodynamic aspects of the formation of the solid state. Lewis and Price⁸¹ performed TEM studies of the solid-state structure of styrene-butadiene-styrene (SBS) triblock copolymers cast from benzene at various rates of evaporation. The results indicated that similar morphological textures were formed at all but the fastest evaporation rates.

b. Thermal Properties

It is often the case that above a certain critical block length, microphase separation occurs; however, in some cases a two-component system may exist in a single phase indicating polymer-polymer miscibility. This can be induced by specific interactions or polar similarity between the two blocks. The comparison of the modulus/temperature behavior of single versus two-phase systems is shown in figure 2.24. The single-phase systems demonstrate a single T_g somewhere between the two

⁷⁹ Lewis, P. R.; Price, G. *Nature* **1969**, 223, 494.

Beecher, J. F.; Marker, L.; Bradford, R. D.; Aggarwal, S. L. *J. Poly. Sci.: Part C*. **1969**, 26, 117.

Inoue, T.; Soen, J.; Kwai, H.; Hashimoto, T. *J. Poly. Sci.: Part A*. **1969**, 7, 1283.

Matsuo, M.; Sagae, S.; Asai, H. *Polymer* **1969**, 10, 79.

Hashimoto, T.; Shibayama, M.; Fujimura, M.; Kawai, H. In *Block Copolymers, Science and Technology*; Meier, D. J., Ed.; Harwood Press: New York, 1983.

Aggarwal, S. L. *Polymer* **1976**, 17, 938.

⁸⁰ Aggarwal, S. L. *Polymer* **1976**, 17, 938.

⁸¹ Lewis, P. R.; Price, G. *Polymer* **1971**, 12, 258.

individual glass transitions of the components that is dependent on the relative volume fractions of each and that shifts horizontally with compositional variation.

In microphase-separated systems, each component exhibits a distinct glass transition, between which, a plateau of constant temperature occurs, as shown in figure 2.24. Flatter plateau regions indicate a greater degree of phase separation. Additionally, when the number average molecular weight reaches values above those that cause an increase in T_g , compositional changes cause a vertical shift in the modulus.

The above phenomena are usually probed via modulus temperature measurements, mechanical loss analysis, and or thermal analysis. The most sensitive technique for determining transitions in multiphase systems is via dynamic mechanical loss methods.

c. Mechanical Properties

Although not an important property in this research, it is well known that block copolymers can display rubbery properties while retaining thermoplastic processability. Generally, materials that exhibit this type of behavior have a larger volume fraction of a rubbery phase, or soft segment, with a T_g below room temperature, and a smaller volume fraction of hard segment. The soft block generates a material that has an overall flexible elastomeric character, while the hard block behaves as a physical crosslink site. The phase separation that occurs results in hard block association to produce small (100-300Å) dispersed domains that are chemically attached to the rubber matrix. The glassy or crystalline hard domains reinforce the rubber matrix to produce a high strength material. This is due to the discrete hard domains, their small size and uniformity, and the excellent interphase adhesion that is a result of the covalent link between the domains.⁸²

⁸² Noshay, A.; McGrath, J. E. *Block Copolymers: Overview and Critical Survey*; Academic Press: New York, 1977.

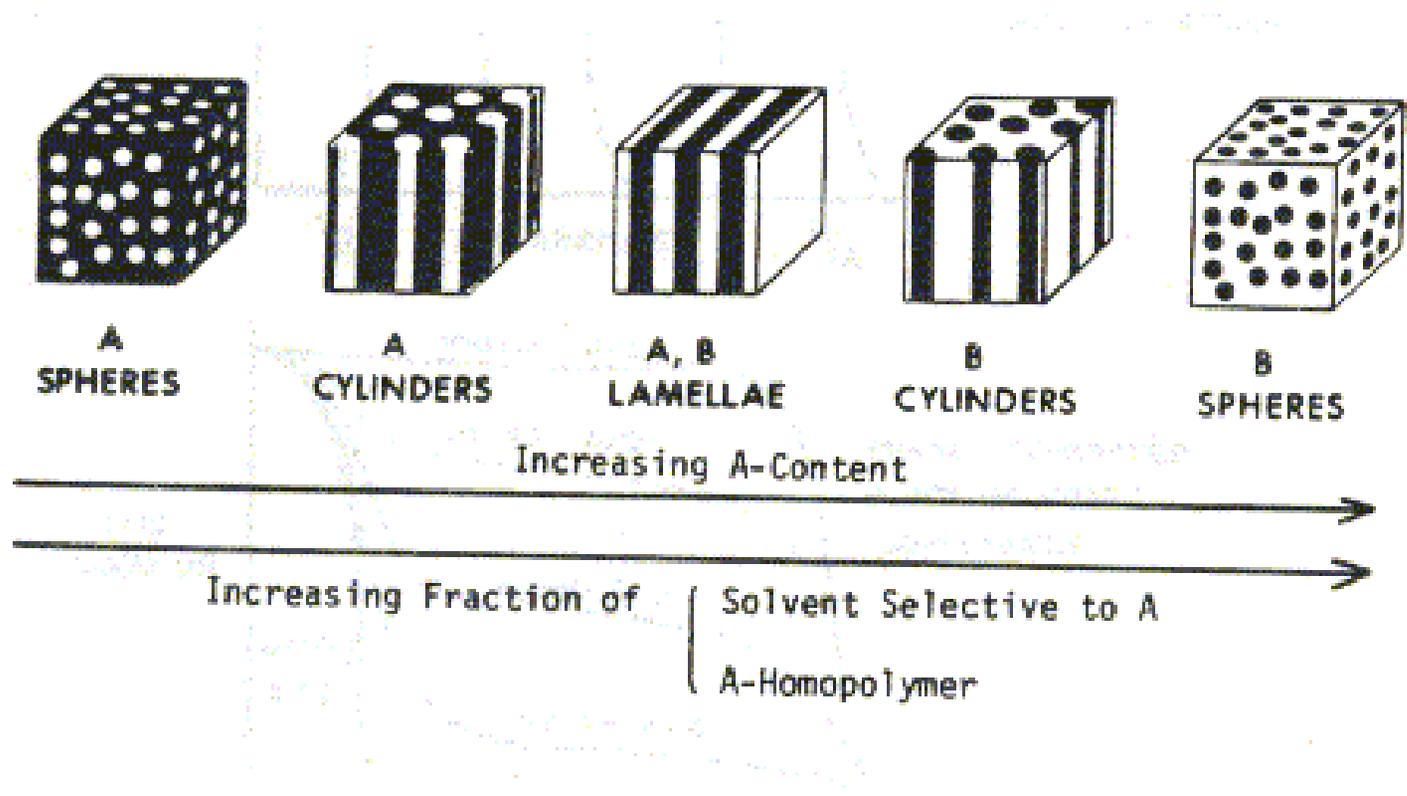


Figure 2.23: Block Copolymer Morphology^{80, Hashimoto}

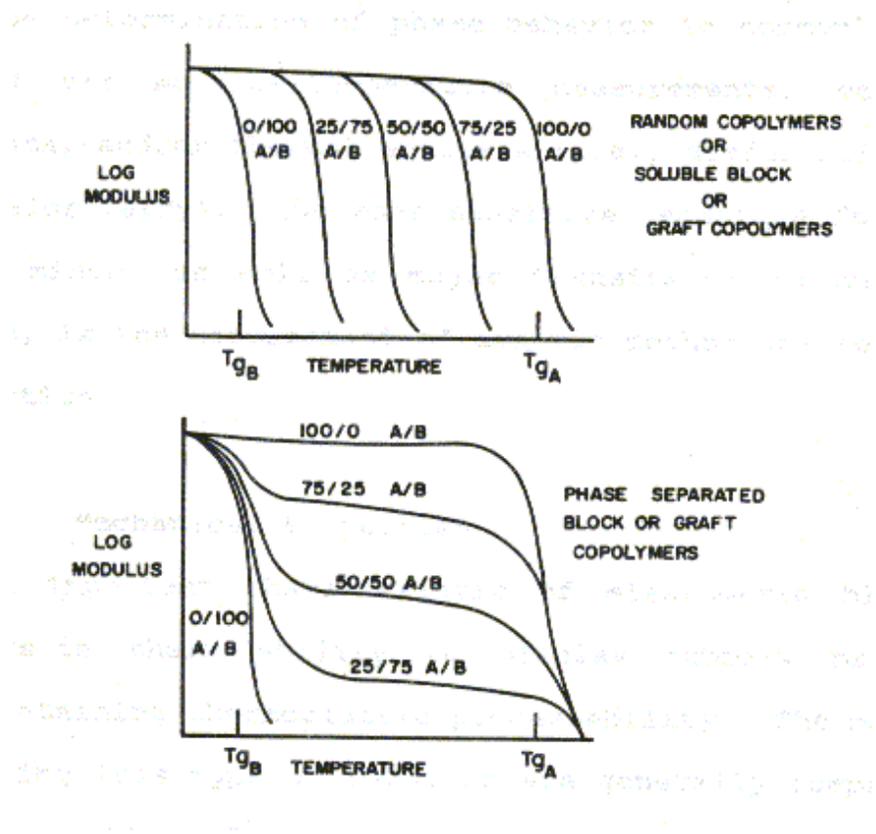


Figure 2.24: General Modulus Temperature Behavior of Homogeneous and Microheterogeneous Copolymers⁸³

⁸³ McGrath, J. E.; Matzner, M.; Robeson, L. M.; Barclay Jr., R. In *J. Poly. Sci.: Polym. Symp. No. 60*; Ambrose, R. J., Aggarwal, S. L., Eds.; Wiley: New York, 1977; p 31.

The properties of thermoplastic elastomers are a result of the relative volume fractions of each domain and their molecular weights. Block length must be long enough to generate a two-phase system, but not so long as to void thermoplastic behavior. The ratio of the hard to soft block affects the modulus, recovery characteristics and ultimate properties of the copolymer. The volume fraction of the hard segment must be large enough to generate an adequate level of physical crosslinking if good recovery characteristics and high tensile strength are desired. It is possible to have such a high volume fraction of hard segment that lamellae develop preferentially to a spherical geometry, which causes a loss in recovery properties.

Architecture plays a huge role in determining the resulting mechanical properties in elastomeric block copolymers. A-B systems are generally chemically crosslinked, whereas elastomeric A-B-A or (A-B)_n systems are usually capable of displaying the mechanical properties of a crosslinked rubber with the processability of a linear thermoplastic polymer.

D. Ion-containing Polymers

1. Introduction

Initial interest in polymers containing ionic sites stemmed from the development of organic ion exchange resins in the 1940s. A variety of properties and applications are a result of the interactions of the polymer bound ions. These interactions affect the physical and transport properties of the host material resulting in polymers that have found applications in a wide range of areas that include thermoplastic elastomers, permselective membranes, and microencapsulation membranes. The initial commercial interest was on ionomers: polymers composed of a hydrocarbon or fluorocarbon backbone containing a small fraction of pendant acid groups (usually less than ten mole percent) that were either partially or completely neutralized to the salt form. Some of the first commercial polymeric materials that contained ionic functionality were introduced in 1965 by Dupont under the trade name Surlyn[®] and were copolymers of ethylene and methacrylic acid. Several books and reviews have been written on the topic of these ion-containing materials.⁸⁴

2. Structure of Ionomers

Attempts to elucidate the spatial arrangement of the salt groups was initiated by Eisenberg in 1970.⁸⁵ His work showed that, on the basis of steric considerations, only a small number of ion pairs, called “multiplets”, could associate without the intervening presence of the polymer backbone and that there was also a tendency for the multiplets to associate into “clusters” that included parts of the polymer backbone. The association was favored by electrostatic interactions of the multiplets, but frustrated by the elastic nature of the polymer chains. Eisenberg’s first assumption was that the chains would not

⁸⁴ Wilkes, G. L.; Tant, M. R.; Mauritz, K. A., Eds. *Ionomers: Synthesis, Structure, Properties and Applications*; Blackie Academic and Professional: New York, 1997; p.514

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

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

In *Ions in Polymers*; Eisenberg, A., Ed.; American Chemical Society: Wash., D.C., 1980; Vol. Adv. Chem. Ser. 187.

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

⁸⁵ Eisenberg, A. *Macromolecules* **1970**, *3*, 147.

undergo dimensional changes as a result of ionic clustering, but later work by Forsman indicated a net increase in the chain dimensions as confirmed by neutron scattering experiments.⁸⁶

There is a large body of experimental and theoretical evidence that supports the existence of the salt groups in two distinct environments, i.e., multiplets and clusters. The multiplets exist in groups of 6 or 8 of ionic dipoles that associate to form higher order multipoles. These are dispersed throughout the polymer matrix and are not phase separated. This means that they can affect the physical properties of the polymer by acting as ionic crosslinks, potentially altering the glass transition temperature as well as water sorption and transport. Clusters are small (< 5nm) microphase separated regions that are rich in ion pairs, but also may contain small amounts of the polymer backbone. They comprise at least some of the properties of a separate phase and have a minimal effect on the properties of the polymer matrix.

The proportion of the salt groups that resides in either of the two environments in a particular ionic polymer is determined by the nature of the polymer backbone, the total concentration of salt groups, and their chemistry. Despite considerable research by various groups, the details of the local structure of these materials remains obscure as does the effect of water on their morphological structure.

3. Synthesis of Ion-Containing Polymer Systems

Until recently, two major approaches have been utilized to synthesize ion-containing polymer systems. The first approach involves a free radical copolymerization of a small amount of a monomer that could be chemically modified to an ionic moiety along with a monomer that is nonfunctional such as styrene or a diene. In the case of methacrylic acid, the metal carboxylate salt can be generated in a second step by neutralization with the appropriate metal hydroxide or acetate. The second major method involves the direct functionalization of a preformed polymer via a post-reaction. An example of this would be the sulfonation of commercially available poly (arylene ether

⁸⁶ Forsman, W. *Macromolecules* **1982**, *15*, 1032.

sulfone) by Noshay in 1976.⁸⁷ This same approach was used to generate materials for desalination membranes for reverse osmosis and other water purification processes.⁸⁸ Post-sulfonation reactions result in the placement of the sulfonic acid group ortho to the activated aromatic ether linkage. Since polymer chemical modification reactions typically result in limited yields, it is difficult to control the concentration of ionic sites on the polymer chain. The third and most recent method employed to introduce ionic sites into polymer chains is via direct polymerization. This method utilizes monomers that have already been synthesized in a fashion that yields an ionic moiety in the chemical structure. Polymerization to form polymers that have a controlled amount of a sulfonated monomer have been utilized in the synthesis of polyimides and poly (arylene ethers).⁸⁹ There are several advantages to this last approach which will be discussed in the following sections.

a. Functionalized Comonomer Approach

i. Addition Polymerization

Typical carboxylate ionomers are synthesized by direct copolymerization of a low level of acrylic and methacrylic acid with ethylene, styrene, alkyl acrylates, alkyl methacrylates, dienes and similar comonomers by employing free radical initiators.⁹⁰ The ethylene-based systems (Surlyns®) are commercially prepared by Dupont and are

⁸⁷ Noshay, A.; Robeson, L. M. *J. Of Appl. Poly. Sci.* **1976**, *20*, 1885.

⁸⁸ McGrath, J. E. In *Poly (aryl ether) Membranes for Reverse Osmosis*; Turback, A. F., Ed., 1981; Vol. No. 153, pp 327-350.
McGrath, J. E. *J. Poly. Sci.: Part A.* **1984**, *22*, 721.

⁸⁹ Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J.; Yonetake, K.; Masuko, T.; Teramoto, T. *J. of Poly. Sci.: Part A.* **1993**, *31*, 853.
Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mecham, J. B.; Zawodzinski, T.; McGrath, J. E. *Macromolecular Symposia* **2000**, under review.

Wang, F.; Ji, Q.; Harrison, W.; Mecham, J. B.; Formato, R.; Kovar, R.; Osenar, P.; McGrath, J. E. *Polymer Preprints* **2000**, *41*, 237.

Mecham, J. B.; Shobha, H. K.; Wang, F.; Harrison, W.; McGrath, J. E. *Polymer Preprints* **2000**, *41*, 183.

Shobha, H. K.; Smalley, G.; Sankarapandian, M.; McGrath, J. E. *Polymer Preprints* **2000**, *41*, 180.

Harrison, W.; Wang, F.; Mecham, J. B.; Glass, T. E.; Hickner, M.; McGrath, J. E. *Polymer Preprints* **2001**, *84* in press.

Gunduz, N.; McGrath, J. E. *Polymer Preprints* **2000**, *41*, 180.

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

⁹⁰ MacKnight, W. J.; Lundberg, R. D. *Rubber Chem. and Tech.* **1984**, *57*, 652.

Kihira, Y.; Yamamura, H.; Murakami, I. *J. Macromol. Sci., Phys.* **1987**, *B26*, 201.

King, M.; Eisenberg, A. *Ion-Containing Polymers: Physical Properties and Structure*; Academic Press: New York, 1977.

Brockman, N. L.; Eisenberg, A. *J. Poly. Sci.: Part B.* **1985**, *23*, 1145.

utilized in a variety of applications. Figure 2.25 shows the solution or bulk free radical polymerization of styrene and methacrylic acid. The carboxylate is easily generated by titration of the acid groups with various bases. Other examples include styrene-butadiene acrylic acid, butadiene-acrylonitrile-acrylic acid and butadiene-acrylic acid (Hycar, B. F. Goodrich) copolymers. In each case, less than 6 mole percent of the carboxylic monomer is utilized in order to preserve the elastomeric properties of the major component. A majority of these systems are prepared by emulsion polymerization.⁹¹ The free acid copolymerizes much easier than the salt form, so the polymerizations are conducted in acidic emulsion formulations. The salt form has limited solubility in the hydrocarbon phase, which can prevent monomer incorporation. In the late 1980s, workers investigated the polymerizability of sodium styrene sulfonate with styrene, dienes, and acrylates.⁹² In emulsion polymerizations, the sodium styrene sulfonate serves as both a comonomer and a surfactant. Thermal analyses for the acrylate and styrene based systems showed that the glass transition temperatures were independent of the concentration of sodium sulfonate. This result was unexpected, as post-sulfonated polystyrenes yielded T_g trends that varied with the level of sulfonation in the polymer, indicating that copolymerization utilizing an ionic monomer generates a different morphological structure than the post sulfonation approach.

ii) Step Growth Polycondensation

By using traditional step growth polymerization techniques, a wide range of monomers can be used to form an array of ion-containing polymers with various linking chemistries. Recently, researchers at Virginia Tech have studied poly (phenylene sulfide sulfones), polyimides, poly (arylene ether sulfones), and poly (arylene ether) polyimide segmented copolymers⁹³, while certain French researchers have concentrated on ion-

⁹¹ King, M.; Eisenberg, A. *Ion-Containing Polymers: Physical Properties and Structure*; Academic Press: New York, 1977.

⁹² Weiss, R. A.; Turner, S. R.; Lundberg, R. D. *J. Poly. Sci.: Part A*. **1985**, *23*, 525.

Weiss, R. A.; Lundberg, R. D. *J. Poly. Sci.: Part A*. **1980**, *18*, 3427.

Siadat, B.; Oster, B.; Lenz, R. W. *J. Appl. Poly. Sci.* **1981**, *26*, 1027.

Yilgor, I.; Packard, K. A.; Eberle, J.; Yilgor, E.; Lundberg, R. D.; McGrath, J. E. *Polymer Preprints* **1983**, *24*, 37.

⁹³ Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mecham, J. B.; Zawodzinski, T.; McGrath, J. E. *Macromolecular Symposia* **2000**, *under review*.

Wang, F.; Ji, Q.; Harrison, W.; Mecham, J. B.; Formato, R.; Kovar, R.; Osenar, P.; McGrath, J. E. *Polymer Preprints* **2000**, *41*, 237.

containing polyimides with six-membered ring imide linking groups.⁹⁴ In all cases, a difunctional monomer containing ionic functionalities has been incorporated into a step growth polymerization approach. By utilizing this method, the resulting polymer can be “tailored” to contain a predetermined level of ionic content. Both random and segmented topologies can be achieved with the proper approach, allowing precise control of important polymer parameters such as ion exchange capacity, water uptake and conductivity.

Research efforts by Mecham, Harrison and Wang have centered on poly (arylene ether) based systems.⁹³ The dihalide 4,4'-dichlorodiphenylsulfone (DCDPS) was sulfonated by using a slightly modified procedure, that was originally conceived by Ueda,⁹⁵ and is shown in figure 2.26. After isolation and purification, the sulfonated DCDPS (SDCDPS) was polymerized with biphenol, using several variations of a similar procedure, to generate random and segmented copolymers.

Random copolymers containing a controlled amount of SDCDPS were synthesized by Wang yielding creasable films across a wide range of compositions.⁹⁶ Characterization of the resulting high molecular weight polymers showed that conductivities approaching those of Nafion fluoropolymer could be achieved. This has important implications in the area of proton exchange membrane (PEM) fuel cells, where Nafion (figure 2.27) has been utilized as the PEM material since the Gemini space program in the late 1960s.

Mecham, J. B.; Shobha, H. K.; Wang, F.; Harrison, W.; McGrath, J. E. *Polymer Preprints* **2000**, *41*, 183.

Shobha, H. K.; Smalley, G.; Sankarapandian, M.; McGrath, J. E. *Polymer Preprints* **2000**, *41*, 180.

Harrison, W.; Wang, F.; Mecham, J. B.; Glass, T. E.; Hickner, M.; McGrath, J. E. *Polymer Preprints* **2001**, *84* in press.

Gunduz, N.; McGrath, J. E. *Polymer Preprints* **2000**, *41*, 180.

⁹⁴ Sillion, B., Ed. *Comprehensive Polymer Science* New York, 1989; Vol. Pergamon Press, p.519

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

Faure, S.; Cornet, N.; Gebel, G.; Mercier, R.; Pineri, M.; Sillion, B. In *Proceedings of Second International Symposium on New Materials for Fuel Cells and Modern Battery Systems*: Montreal, Canada, July 6-10, 1997; p 818.

Faure, S.; Mercier, R.; Aldebert, P.; Pineri, M.; Sillion, B.; France 9,605,707; 1996

⁹⁵ Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J.; Yonetake, K.; Masuko, T.; Teramoto, T. *J. of Poly. Sci.: Part A*. **1993**, *31*, 853.

⁹⁶ Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mecham, J. B.; Zawodzinski, T.; McGrath, J. E. *Macromolecular Symposia* **2000**, under review.

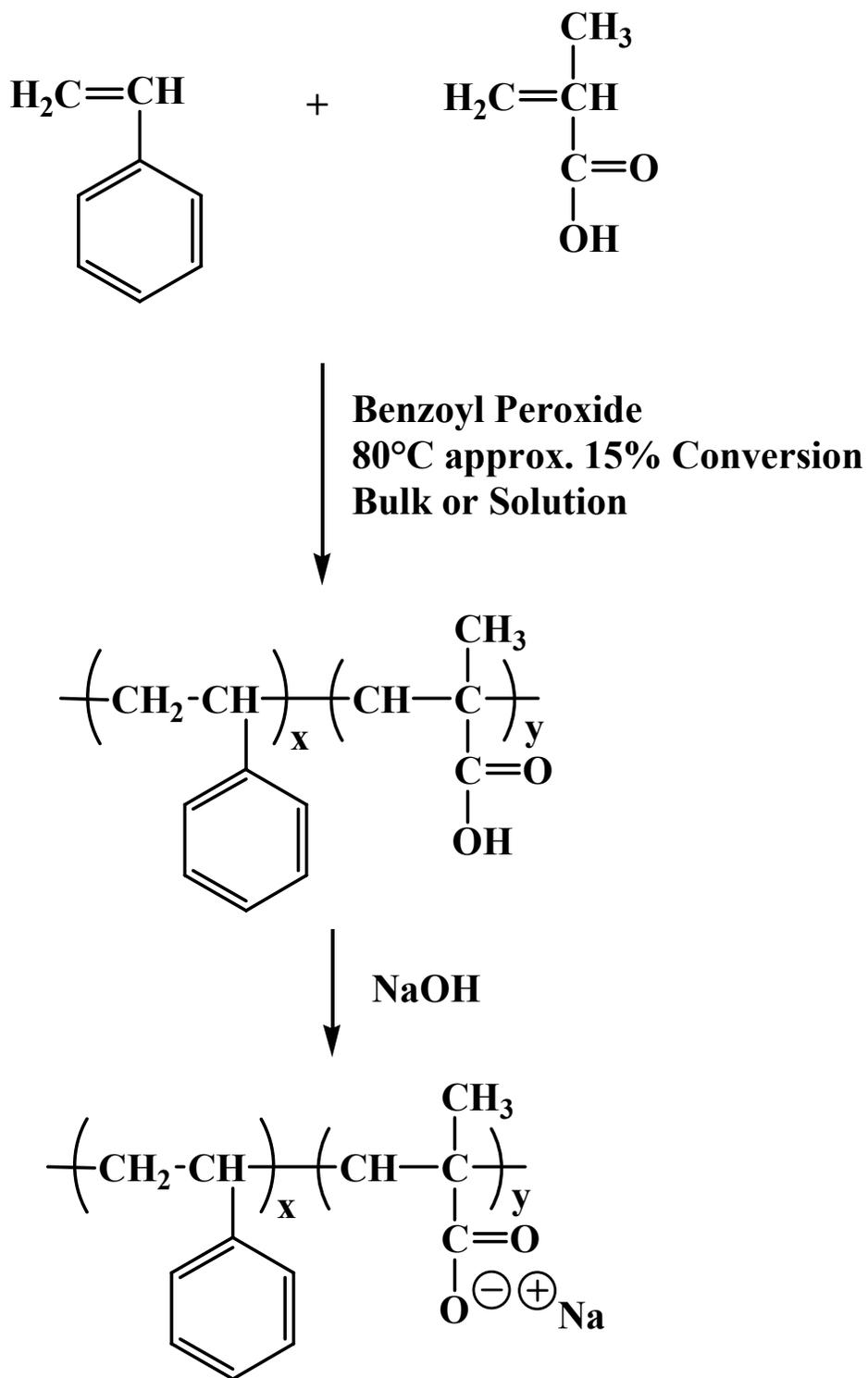


Figure 2.25: Synthesis of Styrene-Carboxylate Ionomers by Free Radical Polymerization

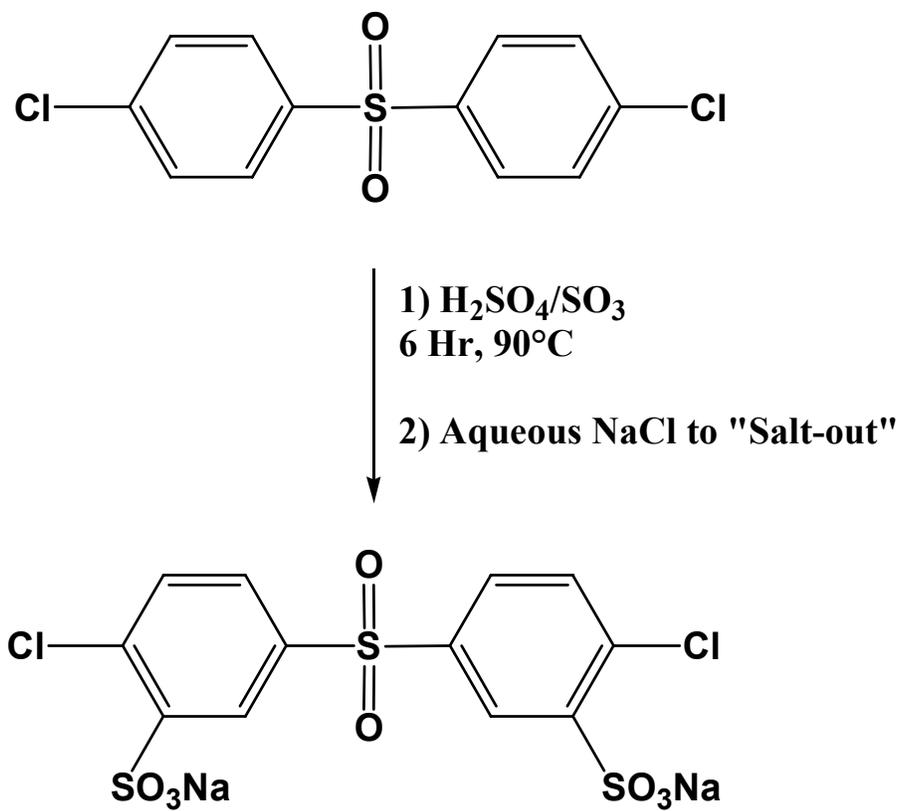


Figure 2.26: Sulfonation of 4,4'-dichlorodiphenylsulfone

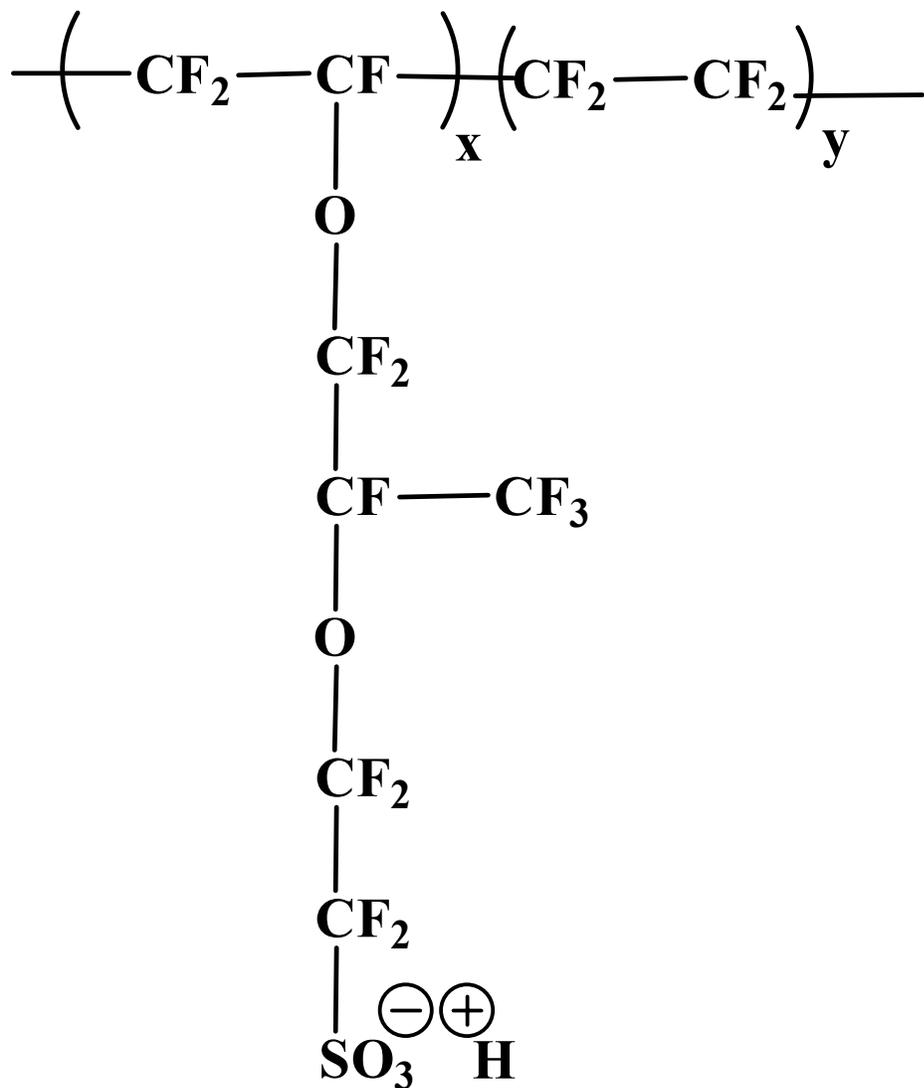


Figure 2.27: Chemical Structure of Nafion®

Platinum catalysts are used to liberate protons and electrons from the fuel source. These catalysts are susceptible to poisoning from carbon monoxide impurities that are often present in the hydrogen fuel stream, or as a reaction byproduct when methanol is used as a fuel. By raising the operating temperature to 100-120°C or higher, catalyst poisoning can be avoided. The chemical and thermal stability of poly (arylene ethers) (PAEs) is well noted, making these systems excellent candidates as new PEM materials, permitting needed higher operating temperatures at a substantially reduced cost.⁹⁷

Controlled molecular weight poly (arylene ethers) were produced by endcapping the polymers with *m*-aminophenol allowing for future incorporation of these polymers into segmented SPAE/polyimide copolymers and were investigated as a major focus in this dissertation. The polyimide is relatively hydrophobic compared to the hydrophilic SPAE, resulting in a microphase-separated copolymer. It is thought that phase separation can result in aggregation of ionic sites⁹⁸ to provide proton conductivities superior to a one-phase film.

Sillion *et al*⁹⁹ of the Organic Materials Labs in France, and others,¹⁰⁰ have investigated sulfonated polyimides containing 6-membered imide linkage groups that have sulfonate moieties on the biphenyl diamine residue as shown in figure 2.28. Ionic conductivities approached values achieved by Nafion.

Gunduz at Virginia Tech has also investigated polyimides as potential new PEM materials.¹⁰¹ Both 5 and 6-membered ring candidates (figures 2.29 and 2.30) have been investigated with the 6-membered ring materials showing better hydrolytic stability when cast films are converted from the salt to acid form in 1M sulfuric acid. The ability of the

⁹⁷ Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mechem, J. B.; Zawodzinski, T.; McGrath, J. E. *Macromolecular Symposia* **2000**, *under review*.

⁹⁸ Eisenberg, A. *Macromolecules* **1970**, *3*, 147.

⁹⁹ Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. *Polymer* **2001**, *42*, 359.

¹⁰⁰ Vallego, E.; Pourcelly, G.; Gavach, C.; Mercier, R.; Pineri, M. *J. Membrane Sci.* **1999**, *160*, 127.

Pineri, M.; Pourcelly, G.; Mercier, R.; Commissariat l'Energie Atomique; FR 2,789,912; 2000

¹⁰¹ Gunduz, N.; McGrath, J. E. *Polymer Preprints* **2000**, *41*, 180.

Gunduz, N., Ph. D. Dissertation, VPI & SU; Blacksburg VA; February 2001

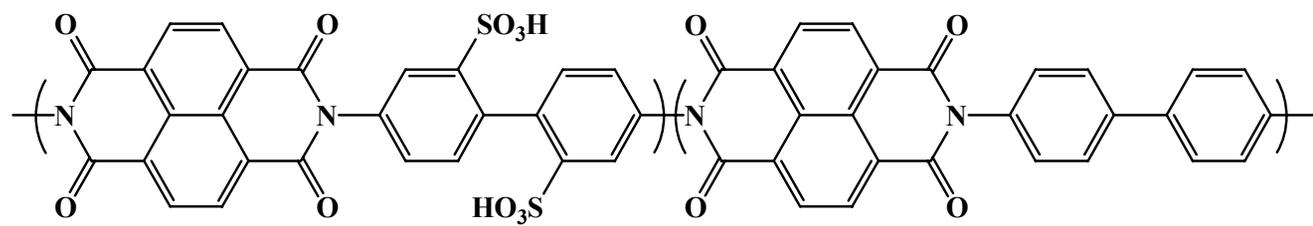


Figure 2.28: Sulfonated 6-membered Ring Polyimide utilized by Sillion¹⁰⁰

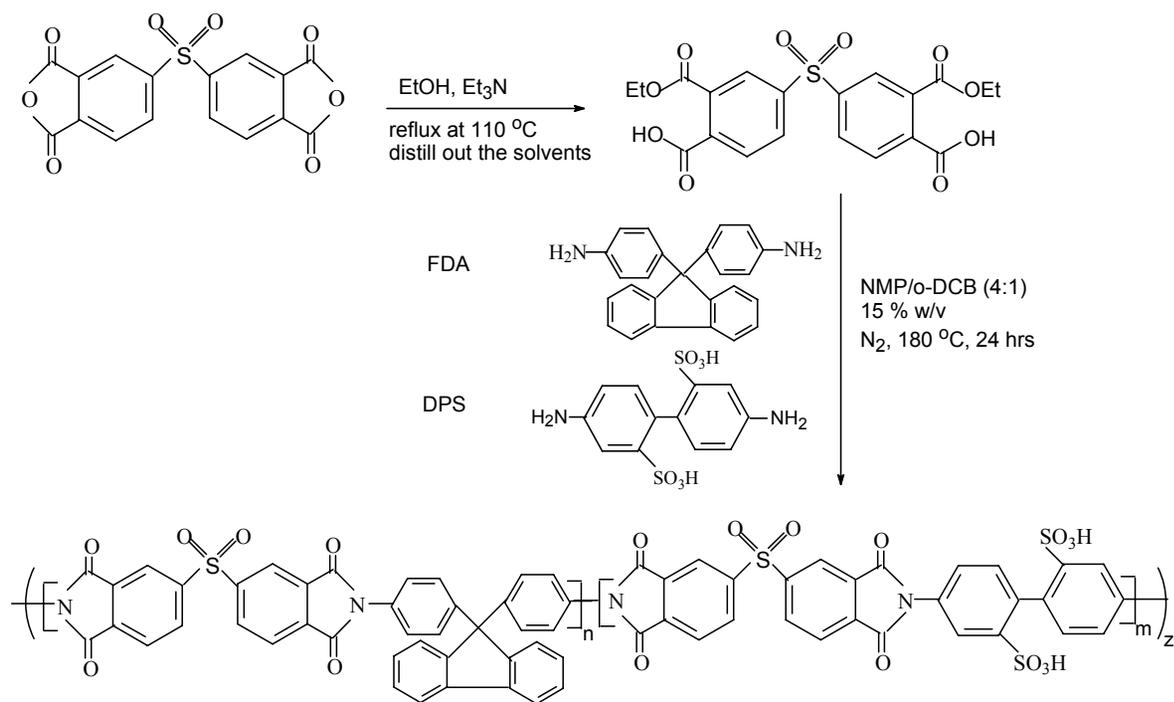


Figure 2.29: 5-membered Ring Polyimide containing Pendant Sulfonate Groups

films to remain stable during the chemical conversion from sulfonic sodium salt to sulfonic acid is crucial if the films are to be used as a PEM in a polymer electrolyte fuel cell. The triethyl ammonium salt form is needed to provide stability of the sulfonated monomers during polymerization, while the acid form is needed for proton conductivity when used as a PEM in a fuel cell. The polyimide containing 40 mole percent sulfonated diamine had an ion-exchange capacity very close to that of Nafion, while conductivity measurements yielded a value of 0.09 S/cm, which is near the value of Nafion at 0.1 S/cm.

b. Chemical Modification of Polymers

An alternate approach to introducing ionic functionalities into polymeric systems involves subsequent polymer modification reactions. This approach is especially suitable for the introduction of sulfonate groups via sulfonation of aromatic or unsaturated sites. The simplest example is the sulfonation of poly (styrene) by using either acetyl sulfate or sulfur trioxide/triethylsulfate, shown in figure 2.31.¹⁰² Acetyl sulfate is the reaction product of acetic anhydride and sulfuric acid. In the case of poly (styrene), a pendant sulfonate is formed, but main chain aromatic rings can also be functionalized with the sulfonic acid moiety.¹⁰³

The sulfonation of ethylene-propylene-diene (EPDM) monomer systems has generated considerable commercial interest.¹⁰⁴ By using Ziegler-Natta catalysis techniques, a random copolymerization of the three monomers can be achieved.¹⁰⁵ One of the preferred dienes is 5-ethylidene-2-norbornene which contains an endo- and exocyclic group. Polymerization proceeds through the endocyclic double bond and the exocyclic unsaturated site is available for subsequent sulfonation, as shown in figure

¹⁰² Makowski, H. S.; Lundberg, R. D.; Westerman, L.; Bock, J. In *Ions in Polymers*; Eisenberg, A., Ed.; Am. Chem. Soc.: Wash., D.C., 1980; Vol. 187.

Makowski, H. S.; Lundberg, R. D.; Singhal, G.; Exxon; U.S. 3,870,841; 1975

¹⁰³ Johnson, B. C.; Yilgor, I.; Tran, C.; Iqbal, M.; Wightman, J.; Lloyd, D.; McGrath, J. E. *J. Polym. Sci. Polym. Chem. Ed.* **1984**, *22*.

¹⁰⁴ Makowski, H. S.; Lundberg, R. D.; Westerman, L.; Bock, J. *Polymer Preprints* **1978**, *19*, 292.

¹⁰⁵ McGrath, J. E. In *Encyclopedia of Chemical Technology*; 3rd ed.; Wiley Interscience, 1979; Vol. 8.

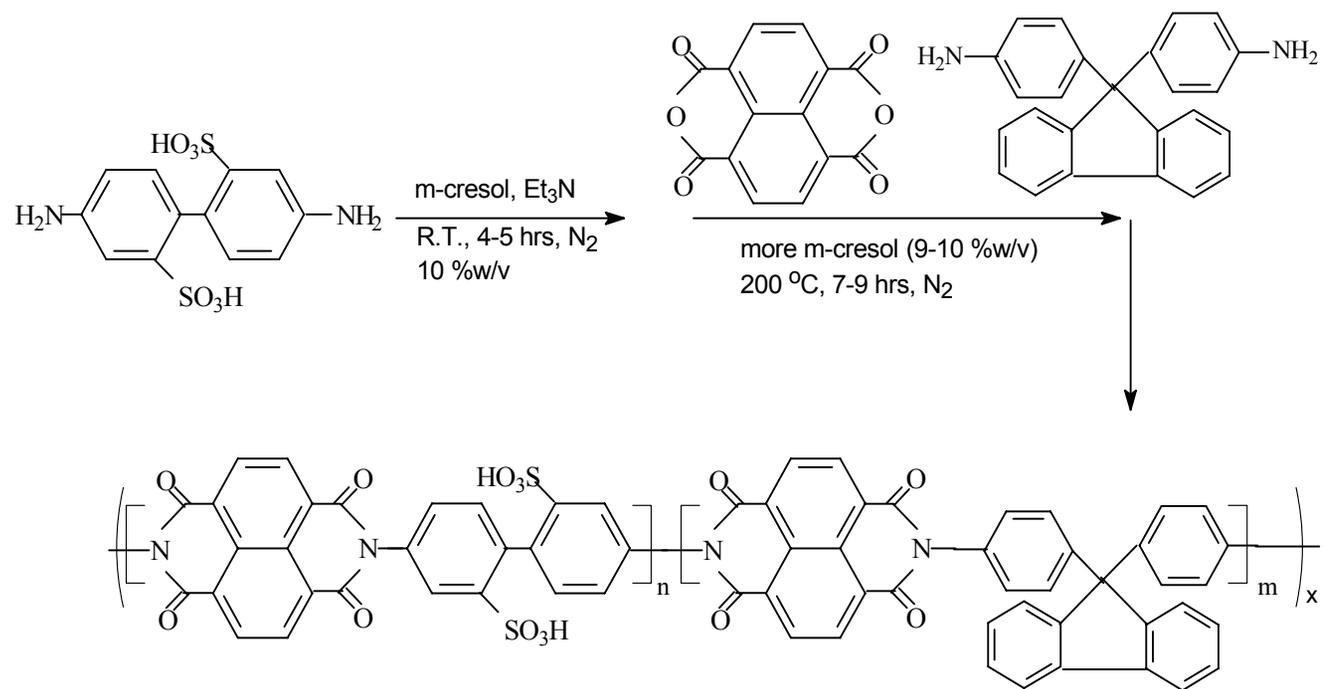


Figure 2.30: 6-membered Ring Polyimide containing Pendant Sulfonate Groups

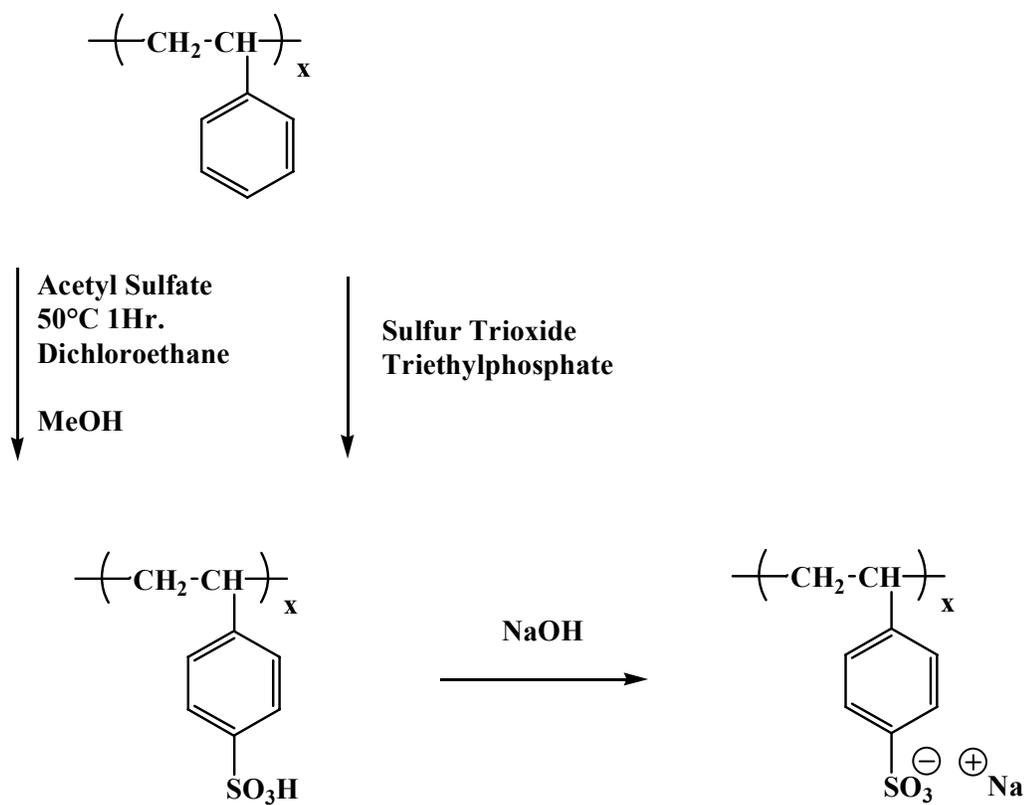


Figure 2.31: Sulfonation of Poly (styrene)

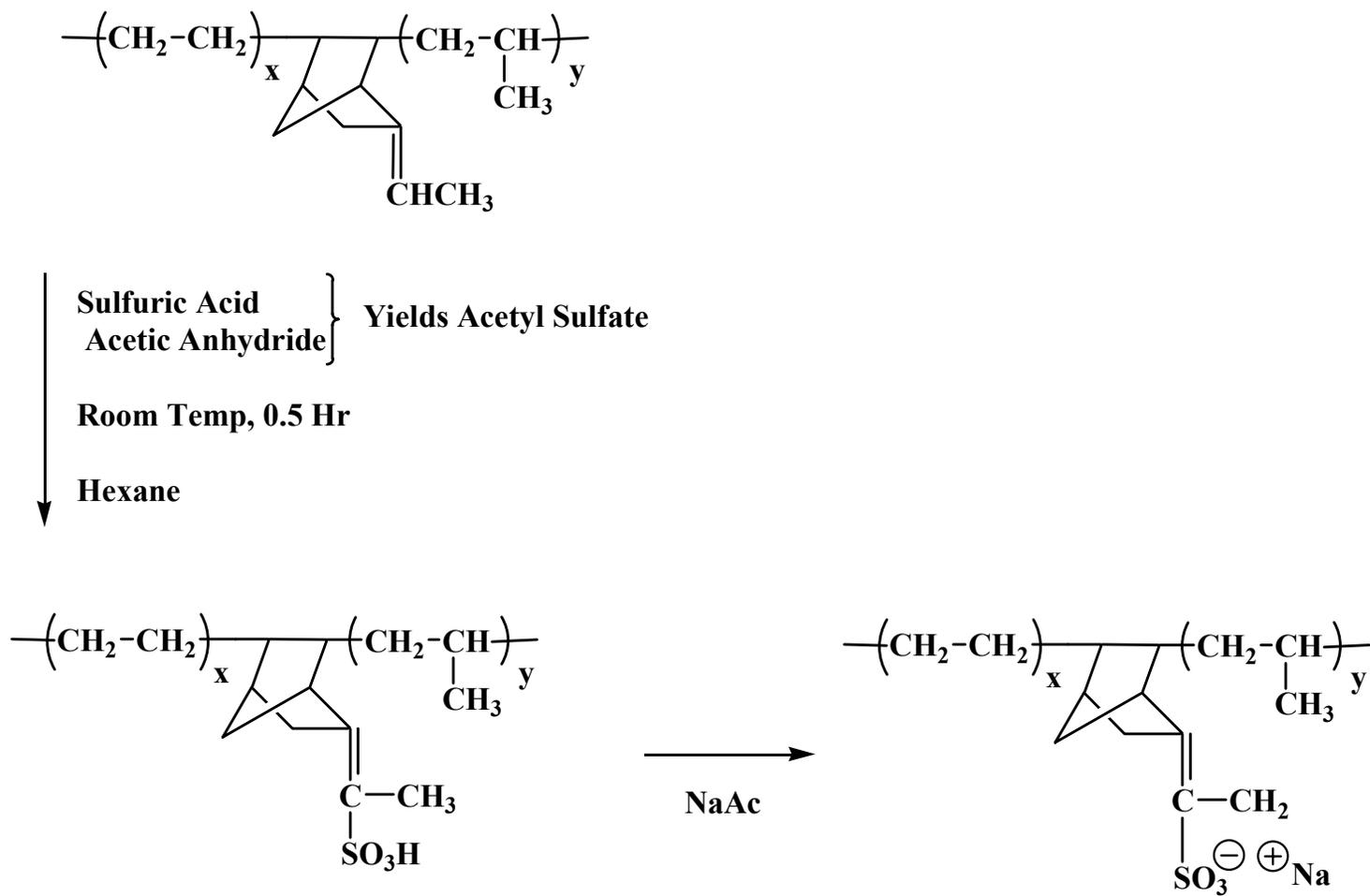


Figure 2.32: Sulfonation of EPDM¹⁰³

2.32. The sulfonation reactions generally reach a 95 percent conversion level of sulfuric acid to sulfonated polymer based on titration of the final product.¹⁰⁶

In a similar fashion, polypentamers (PP) can be sulfonated as illustrated in Scheme 2.33. The starting PP contains 82% trans and 17% cis double bonds with fewer than 1% vinyl side groups.¹⁰⁷ The PP ionomers have also been subsequently hydrogenated and the effect of backbone crystallinity on the ability of the ions to phase separate has been investigated.¹⁰⁸ This polymer provides an excellent model system which has contributed to the understanding of the effects of ionic domains on polymer morphology.

¹⁰⁶ MacKnight, W. J.; Lundberg, R. D. *Rubber Chem. and Tech.* **1984**, *57*, 652.

¹⁰⁷ Sanui, K.; Lenz, R. W.; MacKnight, W. J. *J. Poly. Sci.: Part A.* **1965**, *12*, 292.

¹⁰⁸ Sanui, K.; MacKnight, W. J.; Lenz, R. W. *J. Poly. Sci.: Part B.* **1973**, *11*, 427.

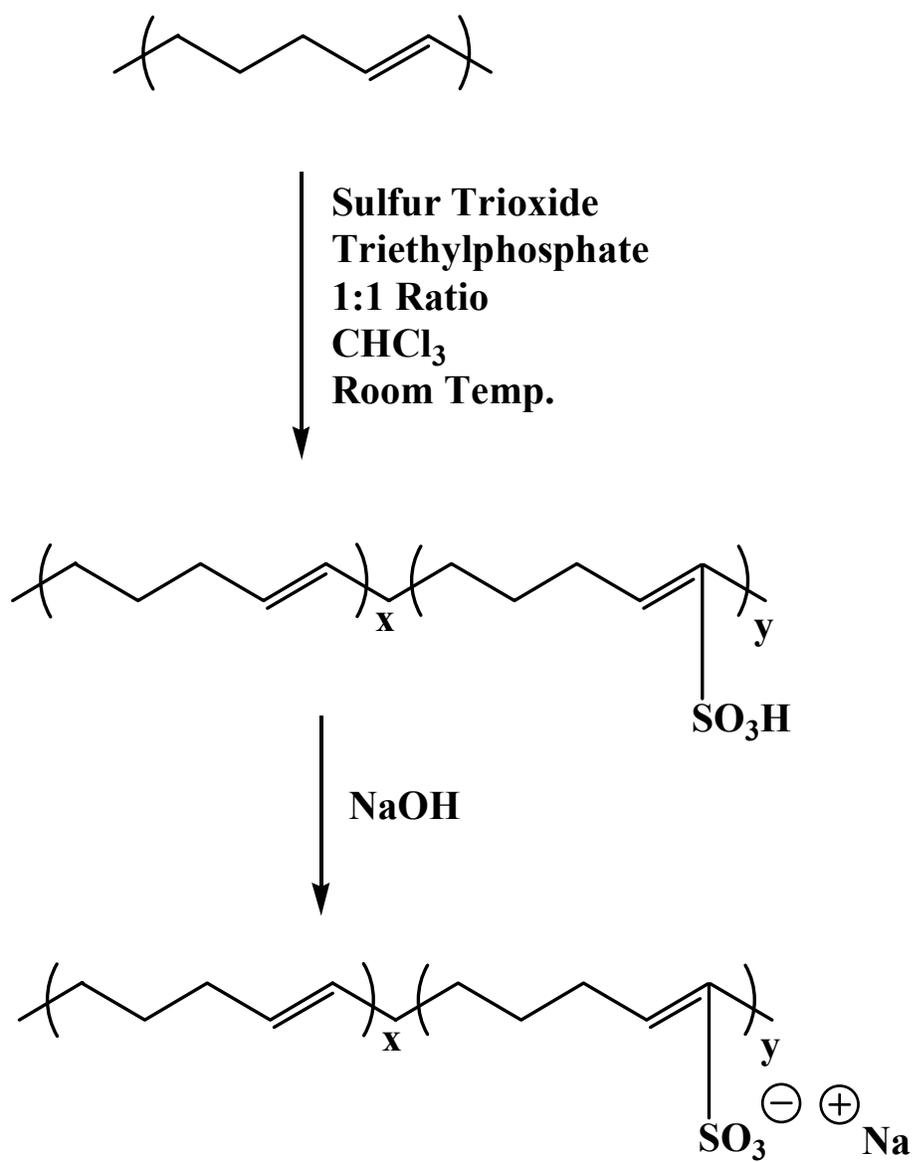


Figure 2.33: Sulfonation of Poly (pentamers)

E. Fuel Cells

1. Introduction

Global warming, tropical deforestation and the rapid increase in the worldwide population are just some of the issues that have received a great deal of media and public attention in the last two decades. In all of these issues, pollution is at the heart of the topic. The internal combustion engine that each of us uses in our everyday lives is a large contributor to air pollution worldwide. As a result, an international effort has been made to design alternative vehicular power sources, only one of which is the fuel cell.

Five major types of fuel cells are available and are defined by their electrolyte. These include molten carbonate, solid oxide, alkaline, phosphoric acid and solid polymer electrolyte. The latter, also referred to as proton exchange membrane fuel cells (PEMFC), are the most attractive candidates for alternative automotive and stationary power sources due to their smaller size and much lower operating temperatures,¹⁰⁹ compared to other fuel cell systems. This research has focused on fuel cells that utilize a solid polymer electrolyte as the functional proton conductor and this will be emphasized herein.

2. Polymer Electrolyte Membranes and the Hydrogen Fuel Cell

The most widely utilized polymer electrolyte membrane is Nafion, a tetrafluoroethylene copolymer containing pendent perfluorinated sulfonic acid groups. The membranes are commercially available and vary in thickness from 50 to 175 microns. When placed in an operating PEMFC, the membrane can be hydrated due to the presence of water and its interaction with the covalently attached sulfonic acid ions. These sites allow the free movement of positively charged hydrogen ions, or protons as they are commonly referred to, in one direction from anode to cathode. The movement of the protons through the

¹⁰⁹ Appleby, A. J., Ed. *Fuel Cells: Trends in Research and Applications*; Hemisphere Publishing Corp.: New York, 1987; p.281

FUEL CELLS

Methanol Fuel Cell

Hydrogen-Oxygen Fuel Cell

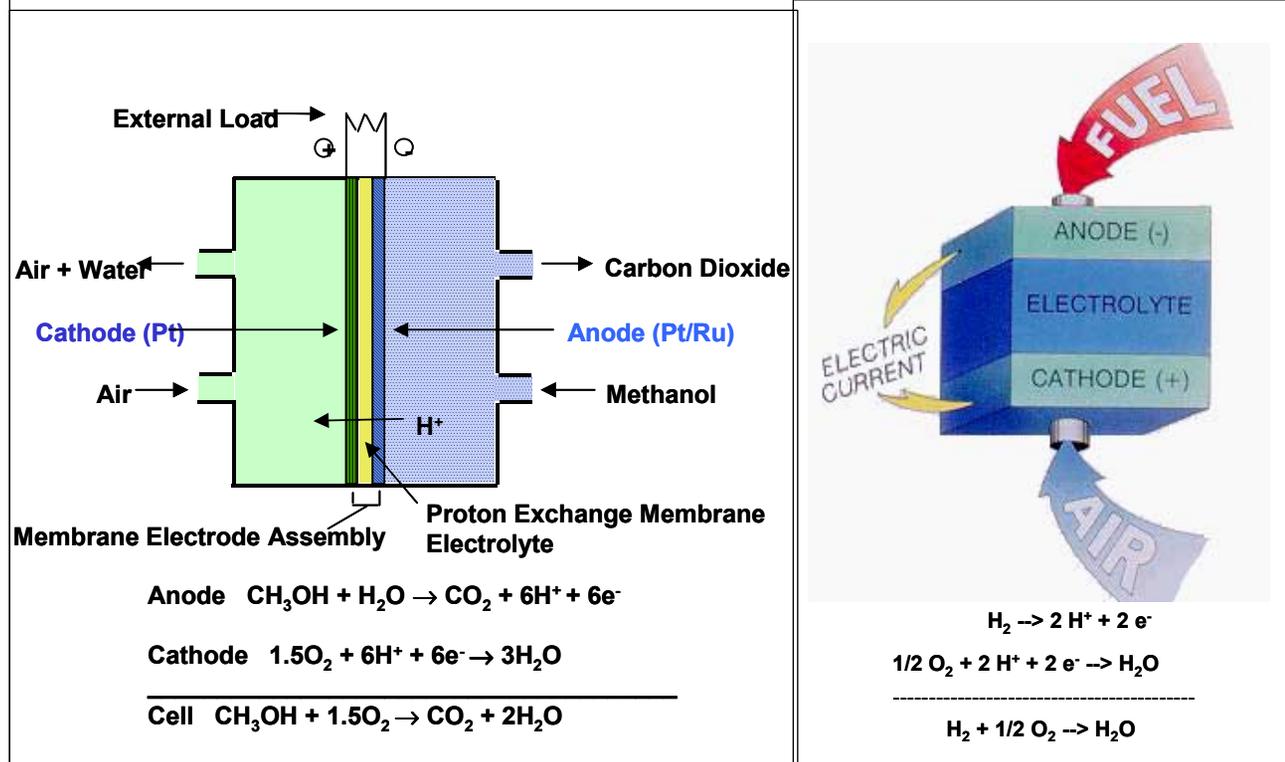


Figure 2.34: Methanol and Hydrogen Fuel Cell Schematic¹¹⁰

¹¹⁰ Zalowitz, M.; Thomas, S. "Fuel Cells: Green Power," Department of Energy, 1999 LA-UR-99-3231.

membrane allows generation of an electrical current as shown in the detailed schematic of both methanol and hydrogen fuel cells shown in figure 2.34.

PEMs made of Nafion® have good mechanical properties and excellent chemical stability at room temperature in the highly acidic oxidizing environment of a PEMFC. Nafion is also an effective gas separator and electrical insulator; both are key requirements of any PEM membrane material. The hydrogen fuel and the oxidant (air) must be kept physically separated to ensure efficient operation of the fuel cell. Without separation of the reactant gases, a direct electron transfer would occur and electrical output could not be utilized. The insulating properties of the membrane are particularly important. Because the electrons cannot be conducted through the membrane, they must move from the anode side of the cell through an external wire, connected to an electrical load, to the cathode side of the cell to complete the circuit.

If a methanol fuel cell is utilized, a liquid solution of methanol in water is supplied to the cathode side of the fuel cell in direct contact with the PEM, as opposed to a hydrogen gas stream. Current Nafion membranes are easily permeated by alcohols, which effectively cause a short circuit of the fuel cell system. New membranes being synthesized at Virginia Tech have been specifically designed to address the alcohol permeability problem in direct methanol fuel cells and are discussed in section 2.E.6 of this dissertation.

3. The Electrochemistry of Hydrogen and Methanol Fuel Cells

In the PEMFC, the electrochemical reactions consist of two distinct half reactions. On the anode side, where the hydrogen fuel is introduced, an oxidative half reaction takes place where molecular hydrogen yields two positively charged hydrogen ions that pass through the PEM to the cathode, while the resulting free electrons travel through an external circuit to the cathode side of the cell. Although platinum is an expensive catalyst, the surface area is maximized to reduce the level of loading needed to catalyze the reaction. Platinum particles with an average diameter of about 2nm are dispersed on

carbon black of about 0.7 microns in diameter to allow a large surface area and a corresponding large number of simultaneous reactions to produce sufficient current in the fuel cell. Generally, the ratio of carbon to platinum is 5:1 (i.e. 20 weight percent Pt on carbon) with a catalyst loading of $0.2\text{mg}/\text{cm}^2$ on both electrodes.¹¹¹ The reaction of the oxygen molecule with the platinum catalyst at the cathode side is a 4 electron reduction process that involves several steps that are summarized in the equation in figure 2.35. Currently, platinum catalysts, though expensive, seem to be the only

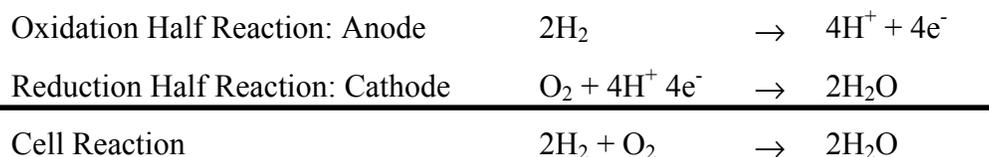


Figure 2.35: Electrochemistry of a Hydrogen Fuel Cell

catalysts capable of reducing molecular oxygen at high rates at temperatures below 80°C ; the maximum efficient operating temperature of a Nafion PEMFC. The mechanism of catalysis is not well understood, but the primary limiting factor is the relatively slow rate of oxygen reduction at the cathode. The oxygen half reaction is 100 times slower than the corresponding hydrogen half reaction.

In a methanol fuel cell, the electrochemistry is more complex. Typically, a 1M solution of methanol in water is exposed directly to the anode. To achieve a high current, a larger amount of platinum catalyst is used and is frequently mixed with ruthenium in a 67/33 ratio to increase efficiency, with loading levels on the anode side that are approximately 50 times higher than that on a hydrogen fuel cell at $10\text{ mg}/\text{cm}^2$. The cathode side of the methanol fuel cell has a catalyst loading of $5\text{mg}/\text{cm}^2$; approximately

¹¹¹ Hickner, M., Personal Communication, December, 2000

25 times greater than that on a hydrogen PEMFC.¹¹² The electrochemistry of the direct methanol fuel cell is summarized below in figure 2.36.

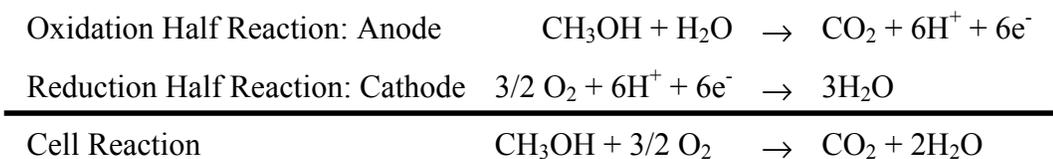


Figure 2.36: Electrochemistry of a Direct Methanol Fuel Cell

4. The Membrane Electrode Assembly

The platinum catalyst, dispersed on carbon, is mixed with a polymer solution and is either applied with a brush directly to the PEM or cast into a film and melt pressed onto the surface of the PEM. The combination of anode, membrane and cathode is referred to as the membrane electrode assembly, or MEA, shown in figure 2.37. The MEA has evolved over several generations, from early systems in the mid-1960s used in NASA's Gemini Space Program with catalyst loadings as high as $4\text{mg}/\text{cm}^2$ (for hydrogen fuel cells).¹¹³ As mentioned earlier, current catalyst loadings utilized at Los Alamos National Laboratories have decreased to about $0.2\text{ mg}/\text{cm}^2$ for hydrogen fuel cells, while current has risen to a level nearly 30 times greater than that in early systems to approximately 15 amp/mg of platinum. The thickness of the MEA is determined by the amount of platinum that is used in the electrodes. Catalyst loadings of $0.2\text{ mg}/\text{cm}^2$ generate layers that are approximately 10 microns thick, resulting in an MEA with a total thickness of about 0.2mm that is capable of producing greater than 1 amp/ cm^2 at 0.7 volts.

¹¹² Hickner, M., Personal Communication, December, 2000

¹¹³ Noyes, R. *Fuel Cells for Public Utility and Industrial Power*; Noyes Corp.: Park Ridge, NJ, 1977.

5. Fuel Cell Hardware

The remaining components of the fuel cell consist of various pieces of hardware that are designed to maximize the current through even application of the fuel and air supply over the entire electrode surfaces and efficient conduction of the resulting electrons. The backing layers are made of carbon and fashioned into a plate that is both porous and electrically conductive, ensuring even distribution of the gas from the flow field to the entire catalyst surface. The backing layer is also carefully designed to control water vapor concentration near the PEM, as an overabundance of water will effectively flood the cathode side of the cell, while underhydration of the PEM will limit the current. An exploded view of the fuel cell is shown in figure 2.38. The flow fields, commonly called plates, are located directly against the backing layers and serve to distribute the fuel over the entire surface of the MEA, as well as collect the electrical current. This is achieved by fabricating the plates out of metal or carbon, into which a serpentine channel is milled that carries the fuel from the point it enters the cell to the point it exits. The pattern, depth and width (usually less than a millimeter) of the milled channel control the effectiveness of fuel distribution and can also affect the water supply to the membrane and removal from the cathode side. The electrons are produced by the oxidation of the fuel and they must pass through the anode and backing plate before being conducted out of the cell, through an external circuit, and back into the cell on the cathode side. The flow fields make up the last pieces of fuel cell hardware. To generate currents greater than a volt, a fuel cell stack must be assembled.

By connecting a series of fuel cells, voltage can be increased above the 0.8 volts generated by a single cell. Individual fuel cells are connected in series to form a “stack” and are modified by combining the flow fields into a “bipolar plate” to decrease weight and volume. Since the bipolar plate separates the individual cells, it is important that it is gas impermeable to avoid direct fuel oxidation and current loss, while maintaining conductivity. The bipolar plate conducts electrons produced at the anode on one side of the plate to the cathode on the opposite side, while end plates are connected to an external circuit as shown in figure 2.39. A stack can consist of a few cells to more than one

hundred and can be connected in series or parallel combinations for large applications that require higher voltages.

Membrane/electrode assembly with backing layers

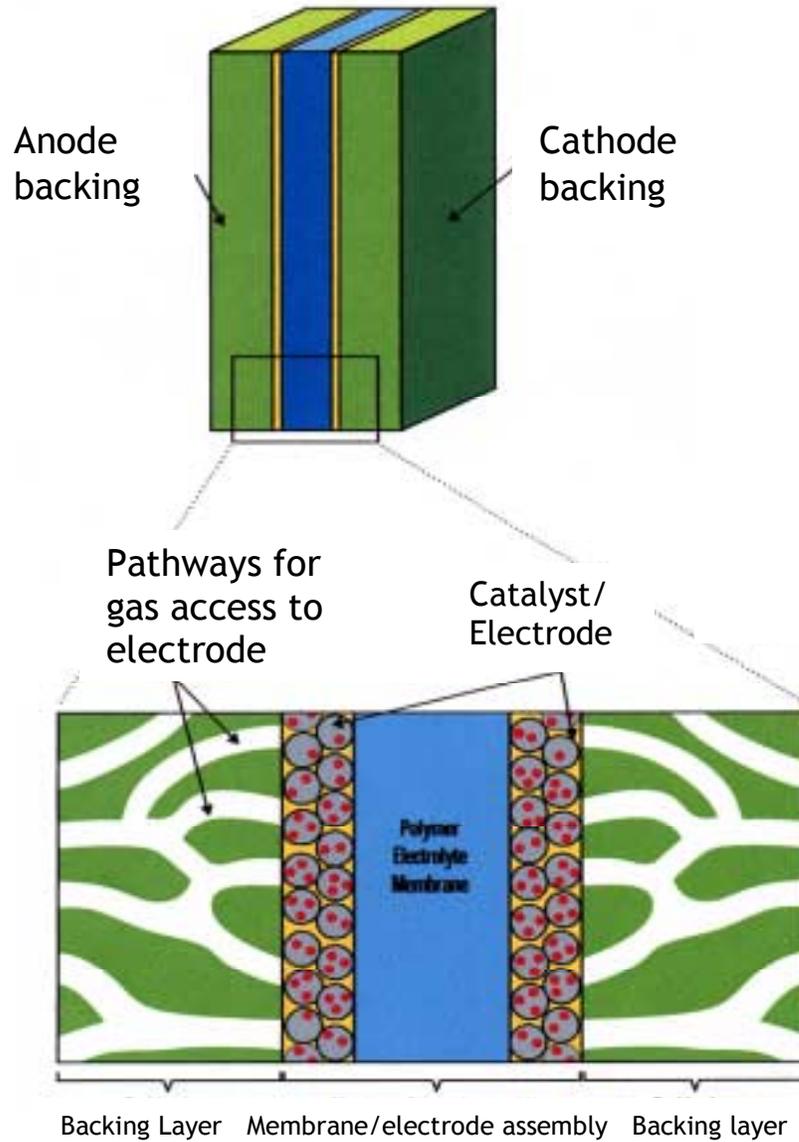


Figure 2.37: Membrane Electrode Assembly with Backing Layers¹¹⁴

¹¹⁴ Zalowitz, M.; Thomas, S. "Fuel Cells: Green Power," Department of Energy, 1999 LA-UR-99-3231.

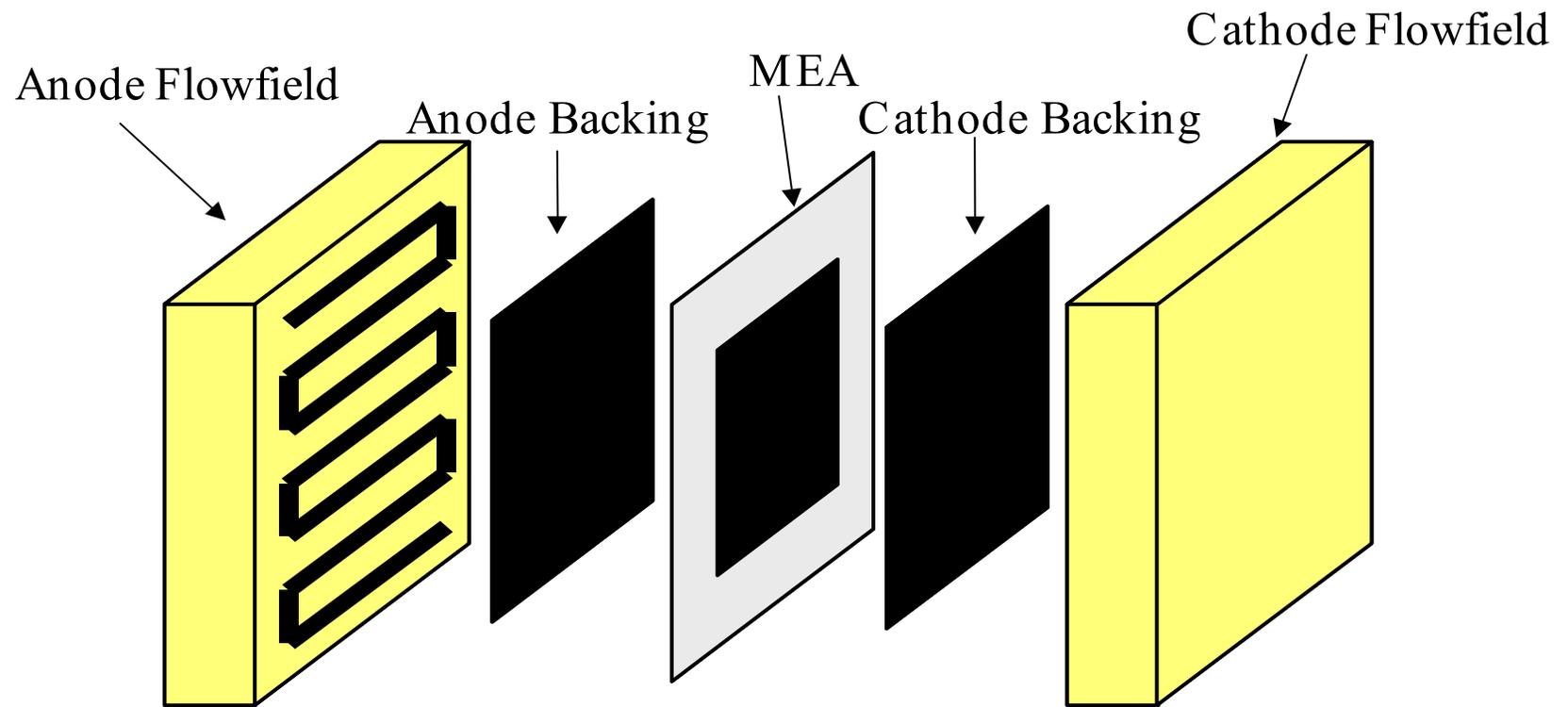


Figure 2.38: Exploded View of a Fuel Cell

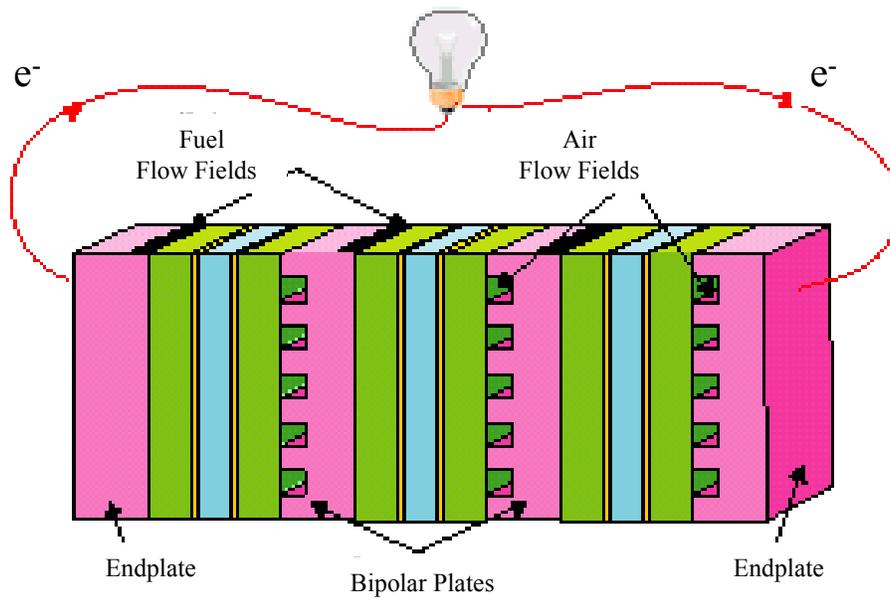


Figure 2.39: 3 Cell Stack illustrating Bipolar and Endplates

6. The Direct Methanol Fuel Cell

In a direct methanol fuel cell, oxygen from air is utilized as the oxidant, while liquid methanol is used as the fuel in the anode rather than hydrogen. Direct methanol fuel cell (DMFC) technology is relatively new compared to the hydrogen PEMFC systems, but optimization of DMFC is ongoing. Perhaps the greatest challenge involves the much higher amount of catalyst needed to achieve high levels of current. Additionally, when Nafion is used as the PEM, methanol fuel crosses through the membrane from anode to cathode (fuel crossover) decreasing current output and wasting fuel. A major thrust of the novel block copolymers discussed in this dissertation was to offer a low cost alternative to Nafion that was capable of performing at higher temperatures and efficiencies and decreased permeability to methanol.

DMFC has several advantages to hydrogen PEMFC systems, with delivery and consumer acceptance of liquid fuel distribution systems perhaps the most important. Methanol fuel distribution stations and pumps already exist and are much less complex and bulky than a hydrogen distribution system. The Chicago Transit Authority has been running a demonstration fleet of three PEMFC buses that operate on hydrogen gas stored in composite roof mounted high-pressure (3600 psi) tanks since late 1997. The fuel delivery station is an integral part of the demonstration fleet. Although inexpensive, hydrogen delivery is a slow process because of the high pressures involved and the need for temperature equilibration between the delivery system and the vessel being filled.¹¹⁵ Nearly two hours are needed to refill all three buses daily. Additionally, although current U.S. production of deliverable compressed hydrogen exceeds 2000 metric tons a day, this would only service 40,000 buses and about 3 million medium sized cars, underscoring the need for both increased hydrogen production levels and distribution locations.

Automakers and components manufacturers have already spent an estimated 2 billion dollars to develop methanol fuel cell vehicles, with Daimler-Chrysler, Toyota,

¹¹⁵ Raman, V. In *Fuel Cell Power for Transportation*; Seaba, J., Stobart, R., Eds.; Society of Automotive Engineers: Warrendale, PA, 1999; Vol. 1425, p 2.

General Motors, Volkswagen, Nissan, Honda and Volvo among the largest participants in research and development. It has been projected that the number of vehicles (worldwide) will increase from the current level of 600 million to 1 billion by 2015.¹¹⁶ The American Methanol Institute recently estimated that by the year 2010, automakers will have introduced at least 2 million methanol fuel cell vehicles worldwide, with the number surpassing 35 million by 2020. Fuel cell vehicle introduction will focus initially on the three states in the U.S. requiring the sale of zero emission vehicles by 2003 (California, New York and Massachusetts) as well as Germany and Japan. These are areas of high population that are candidates for early acceptance of alternative fuel vehicles because they tend to have higher levels of pollution and offer maximum scale efficiencies for the first wave of methanol fuel infrastructure.

The vast quantity of natural gas in the world ensures the availability of feedstock to produce the methanol needed for the future fleet of DMFC vehicles. In 1996, reserves stood at 49,912 trillion cubic feet (TCF) with annual consumption of 78 TCF. With a fleet of 35 million vehicles consuming 15.4 billion gallons of methanol annually (at 441 gal/yr each), this would create a demand for 1.4 TCF of natural gas per annum, which is only 2 % of current annual consumption.¹⁷⁶ It can be argued that the methanol supply and delivery infrastructure can be adjusted to meet future DMFC vehicle demands.

7. Water Uptake and Protonic Conductivity in Sulfonated Polymer Membranes

a. Water Uptake of Nafion Fluoropolymer

Proton transport in ionic polymer membranes, especially when in the acid form, is largely influenced by the water content of the membrane. Ionic membranes behave like insulators in the dry state, but become conductive as a function of the water content when hydrated. Various studies have been conducted as to the minimum water content threshold for measurable conductivity. Several researchers have shown that a minimum of 6 or 7 water molecules are needed per sulfonic acid site to generate sufficient

¹¹⁶ Lewis, R.; Dolan, G. In *Fuel Cell Power for Transportation*; Seaba, J., Stobart, R., Eds.; Society of Automotive Engineers: Warrendale, PA, 1999; Vol. 1425, p 22.

conductivity for use as a PEM.¹¹⁷ Among the ionic polymers with high protonic conductivity, the activation energy of proton conduction of Nafion perfluoropolymer is low in comparison to other polymers¹¹⁸ which may be due to the state of the water in the membrane. In a fuel cell using proton exchange membranes, the water content is controlled by humidification of the gas streams at each side of the membrane. Under these conditions, it has been shown¹¹⁹ that the proton conductivity reaches a maximum at temperatures between 55-70°C while water contents approach a minimum. This work established that at lower temperatures between 25-50°C, a variation in water content is less important than a temperature increase, which plays an important role in the kinetics of proton motion in the polymer membrane.

Work by Zawodzinski *et al.* also involved investigation of water uptake of Nafion 117 membranes.¹²⁰ Water uptake was studied by investigating membranes that were initially fully hydrated and were then exposed to a variety of drying conditions: 1) dried at room temperature under vacuum; 2) condition 1 followed by vacuum drying at 105°C for an hour; 3) drying at room temperature over P₂O₅; and 4) condition 3 followed by vacuum drying at 105°C. Earlier work by Bunce *et al.*¹²¹ has shown that the water content after drying under condition 1 resulted in $\lambda = 1$ (where λ = number of moles of water per mole of sulfonic acid group in polymer), whereas drying conditions 2, 3 and 4 resulted in total dehydration. The extent of rehydration of the membranes was dependent on the drying condition. Figure 2.40 illustrates the water uptake as a function of time and compares a film that was dried at room temperature under vacuum versus a film dried under vacuum at 105°C. The membrane that was dried at room temperature contained the

¹¹⁷ Yeo, R. S. *J. Electrochem. Soc.* **1983**, *130*, 533.

Pourcelly, G.; Oikonomou, A.; Hurwitz, H. D.; Gavach, C. *J. Electroanal. Soc.* **1990**, *287*, 43.

Randin, J. *J. Electrochem. Soc.* **1982**, *129*, 1215.

¹¹⁸ Yeo, R. S. *J. Electrochem. Soc.* **1983**, *130*, 533.

¹¹⁹ Reike, P. C.; Vanderborgh, N. E. *J. Membrane Sci.* **1987**, *32*, 313.

¹²⁰ Zawodzinski, T.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. *J. Electrochem. Soc.* **1993**, *140*, 1041.

¹²¹ Bunce, N.; Sondheimer, S.; Fyfe, C. A. *Macromolecules* **1986**, *19*, 333.

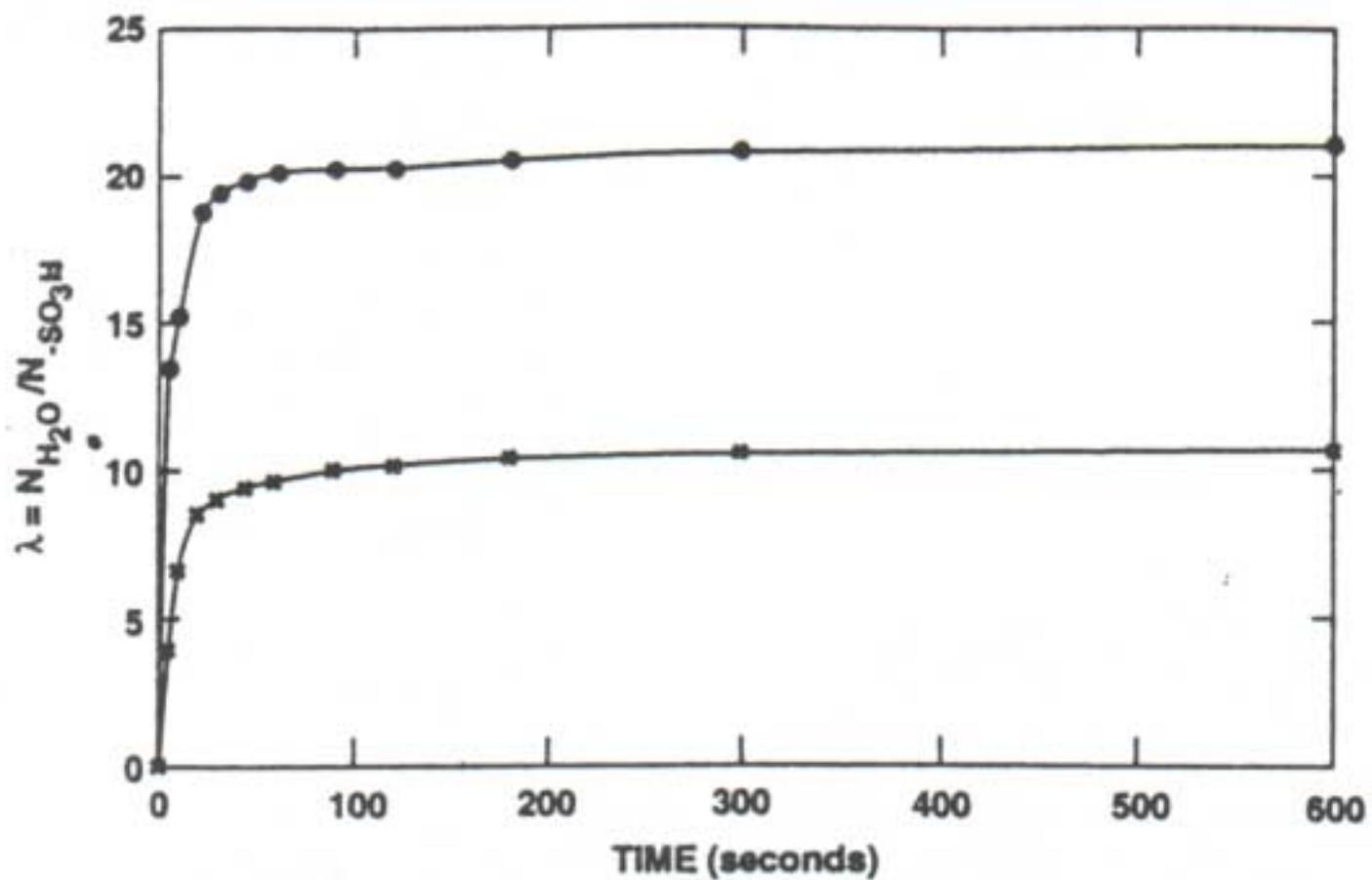


Figure 2.40: Water uptake as a function of time after drying at room (●) and elevated temperature¹²²

¹²²) Zawodzinski, T.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. *J. Electrochem. Soc.* **1993**, *140*, 1041.

Table 2.2: Water uptake of Nafion 117 using various methods¹²³

Water temperature ^e (°C)	Water uptake (H ₂ O/equivalent) Drying method			
	1 ^a	2 ^b	3 ^c	4 ^d
27	21.3	11.3	21.0	12
65	21.0	15.2	—	—
80	20.7	15.9	—	—

^a Dried under vacuum at room temperature.

^b Dried under vacuum at room temperature followed by 1 h at 105°C.

^c Dried over P₂O₅ at room temperature.

^d Dried over P₂O₅ at room temperature followed by 1 h at 105°C.

^e Temperature of membrane rehydration.

¹²³ Zawodzinski, T.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. *J. Electrochem. Soc.* **1993**, *140*, 1041.

same amount of water after rehydration as it did prior to drying ($\lambda = 22$), whereas the water uptake of the Nafion membrane dried at elevated temperature was only half of the initial value. Interestingly, the water uptake of the membrane dried at room temperature was independent of the water temperature, while the water content of the membrane dried at elevated temperature was a function of the water temperature. The results are summarized in table 2.2.

The most likely explanation for the above results involves the formation and dissociation of the ionic clusters as the membrane is dried. The pretreatment of the Nafion 117 membranes were boiled in 0.5M sulfuric acid for an hour, followed by an hour in boiling deionized water to remove any excess acid. The pretreatment should provide enough thermal energy to form hydrated ionic clusters, but reorientation of the polymer during the drying step is required for the clusters to be broken up, which requires enough energy for Nafion ionic side chains motion. As long as water is present, the sulfonic acid moiety remains ionized, but as the membrane becomes dehydrated, the ionic clusters shrink in size and remain aggregated. As the final traces of water are removed, the sulfonic acid group is no longer ionized, the coulombic barrier to reorientation is no longer present, and the clusters can be dissociated at temperatures near the glass transition of the polymer. This explanation applies the same principles suggested by Eisenberg, where cluster formation is a balance between the ionic dipole interactions that favor formation and elastic forces that disrupt their formation.¹²⁴

The dependence of membrane rehydration on drying conditions has important implications if they are used as an MEA in a fuel cell. One method of MEA fabrication requires hot-pressing a pair of gas diffusion electrodes that containing a Nafion dispersion onto the surface of the Nafion 117 membrane at 120°C. This process causes complete dehydration of the membrane causing a potential decrease in λ . This may have a negative effect on the maximum attainable conductivity of the membrane, since conductivity and water uptake have a roughly linear relationship.

¹²⁴ Eisenberg, A. *Macromolecules* **1970**, *3*, 147.

b. Protonic Conductivity of Nafion Fluoropolymer

Although many properties of Nafion fluoropolymer have been investigated¹²⁵, proton conductivity details are reported less frequently. Some of the pivotal work has been performed by Zawodzinski *et. al.*¹²⁶ and Kreuer *et. al.*¹²⁷

The conductivity of Nafion 117¹²⁸ has been reported by Zawodzinski *et. al.* as a function of water content (figure 2.41) and temperature (figure 2.42). At 30°C, the conductivity decreases in a generally linear fashion with decreasing water content. The value of the conductivity, 0.06 S/cm, where $\lambda = 14$ (where λ = number of moles of water per mole of sulfonic acid group in polymer), agrees with data reported by Rieke *et. al.*¹²⁹ An Arrhenius plot illustrating the temperature dependence over the range of 25-90°C is shown in figure 2.42. The observation that the plot is not linear illustrates the possibility that various mechanisms may be involved in protonic motion through the polymer membrane which can be calculated from the conductivity data. The diffusion coefficient of H⁺ can be calculated from the conductivity by using the Nernst-Einstein Equation¹³⁰, below. This equation was derived by W. Nernst in 1888¹³¹ and was originally used to calculate the diffusion coefficient of ions in dilute solutions.

¹²⁵ Pourcelly, G.; Gavach, C. In *Proton Conductors*; Colombari, P., Ed.; Cambridge University Press: London, 1992; p 295.

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

¹²⁶ Zawodzinski, T.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. *J. Electrochem. Soc.* **1993**, *140*, 1041.

Zawodzinski, T.; Neeman, M.; Sillerud, L. O.; Gottesfeld, S. *J. Phys. Chem.* **1991**, *95*, 6040.

¹²⁷ Kreuer, K. D.; Dippel, T.; Meyer, W.; Maier, J. In *Mat. Res. Soc. Symp. Proc.*, 1993; Vol. 293, p 273.

¹²⁸ Zawodzinski, T.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. *J. Electrochem. Soc.* **1993**, *140*, 1041.

¹²⁹ Reike, P. C.; Vanderborgh, N. E. *J. Membrane Sci.* **1987**, *32*, 313.

¹³⁰ Perry, R. H.; Chilton, C. H. *Chemical Engineer's Handbook*; 5th ed.; McGraw-Hill: New York, 1973.

¹³¹ Nernst, W. *Z. Phys. Chem* **1888**, *2*, 613.

$$D_0 = RT(l^+ * l^- / \Lambda_0)(z^+ + z^-)(z^+ * z^-)$$

Where:

D_0	Diffusivity of molecule at infinite dilution (ionic pair), in cm^2/sec
R	Gas constant, $8.931 * 10^{-10}$
T	Temperature, in Kelvin
l^+	Cationic conductance at infinite dilution, in S/equivalent
l^-	Anionic conductance at infinite dilution, in S/equivalent
Λ_0	Electrolyte conductance in infinite dilution, in S/equivalent
z^+	Valence of cation (absolute, no sign)
z^-	Valence of anion (absolute, no sign)

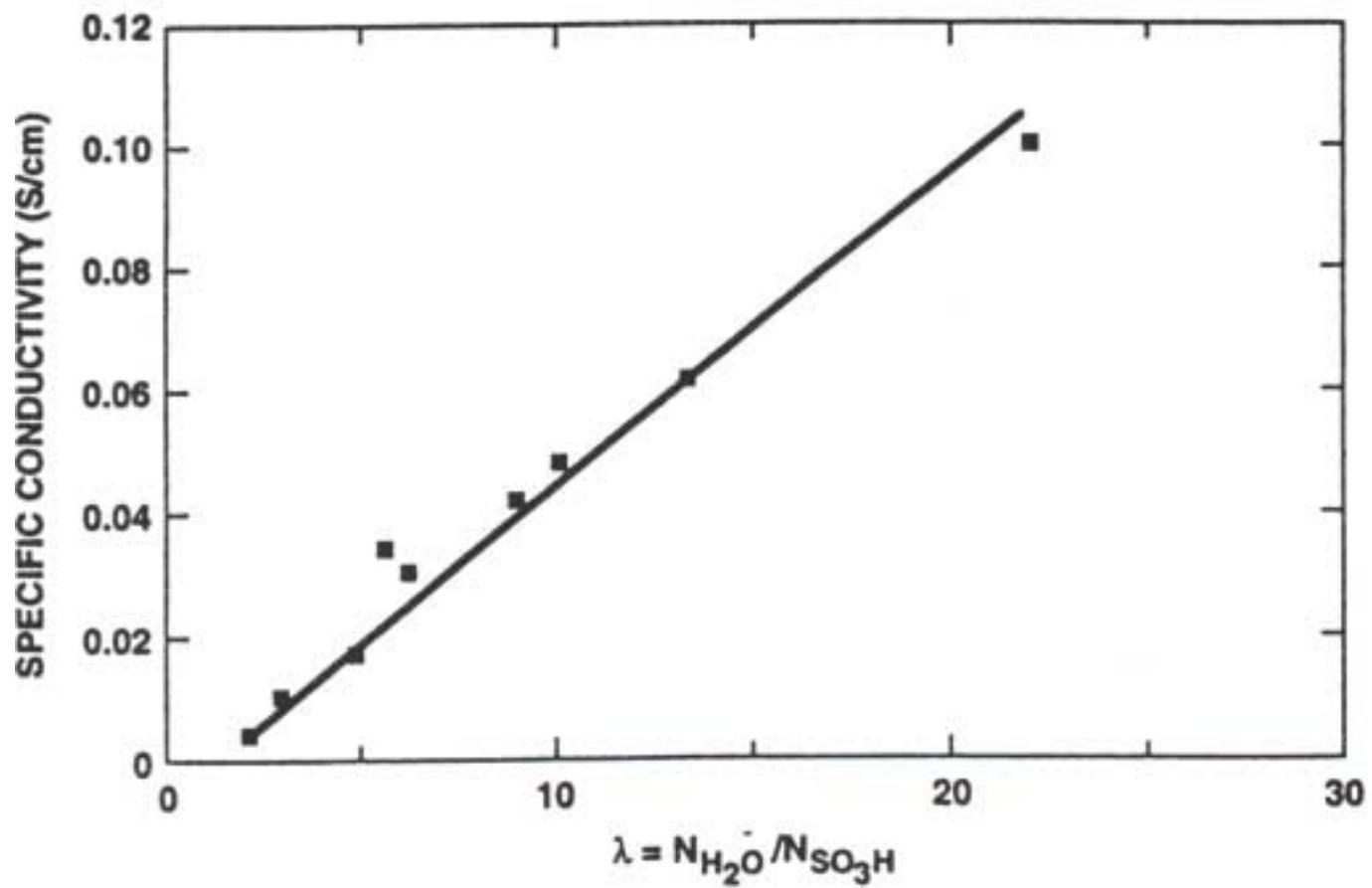


Figure 2.41: Nafion 117 Membrane Conductivity as a function of Water Content¹⁸¹

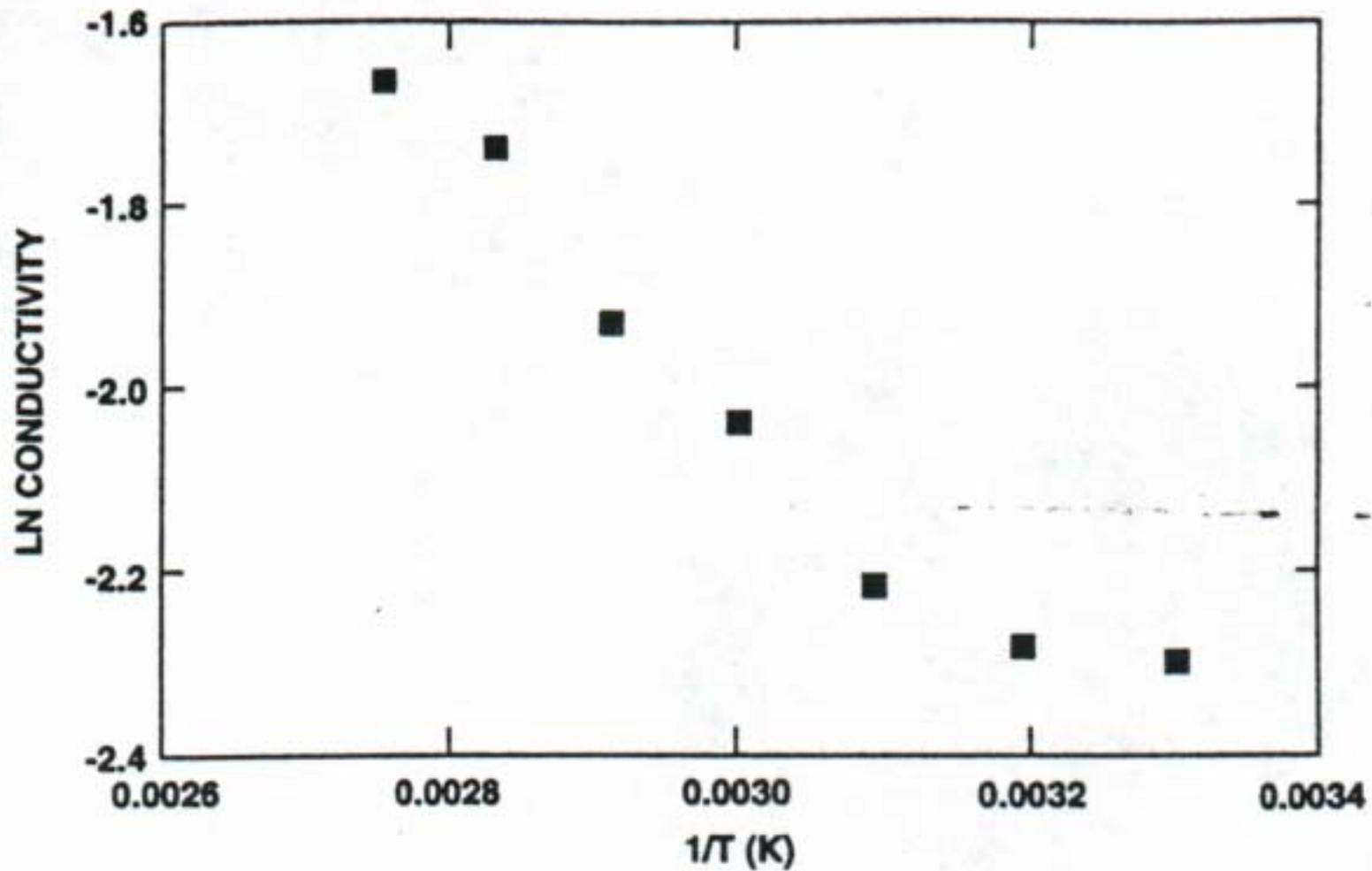


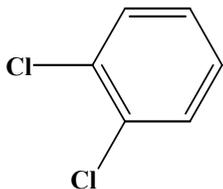
Figure 2.42: Arrhenius plot illustrating the temperature dependence of protonic conductivity in Nafion 117 between 25-90°C¹⁸¹

Chapter III

Experimental

A. Purification of Solvents and Reagents

1. 1,2-dichlorobenzene

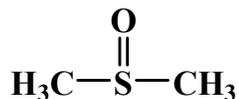


Molecular Weight: 147.00 g/mol

Boiling Point: 172-173°C

Purification: Reagent grade solvent was used as received from Aldrich Chemical

2. Dimethylsulfoxide



Molecular Weight: 78.13 g/mol

Boiling Point: 189°C

Purification: Reagent grade solvent was used as received from Aldrich Chemical

3. Ethanol

Molecular Formula: CH₃OH

Molecular Weight: 46.07 g/mol

Boiling Point: 78°C

Purification: Absolute (99%) . Used as received from Aldrich Chemical

4. Fuming Sulfuric Acid

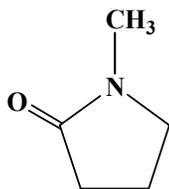
Molecular Formula: $\text{H}_2\text{SO}_4, 30\% \text{SO}_3$

Molecular Weight: 98.08 g/mol

Density: 1.925 g/ml

Purification: Used as received from Aldrich Chemical

5. 1-Methyl-2-pyrrolidinone



Molecular Weight: 99.13 g/mol

Boiling Point: 81-82°C/10mm

Purification: Purchased from Aldrich Chemical; Stirred over P_2O_5 overnight, distilled under vacuum and stored under nitrogen pressure

6. Potassium Carbonate

Molecular Formula: K_2CO_3

Molecular Weight: 138.21 g/mol

Melting Point: 891°C

Purification: Purchased from Aldrich Chemical; Dried under vacuum at 130°C prior to use in polymerization reactions

7. Sodium Hydrosulfide

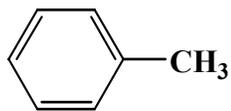
Molecular Formula: $\text{NaSH} \cdot x\text{H}_2\text{O}$

Molecular Weight: 56.06 g/mol (for NaSH)

Melting Point: 52-54°C

Purification: Used as received from Aldrich Chemical

8. Toluene

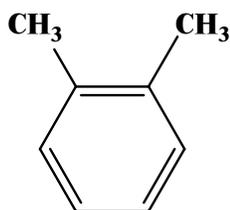


Molecular Weight: 92.14 g/mol

Boiling Point: 110°C

Purification: Purchased from Fisher Chemical Co. and used as received

9. *o*-Xylene



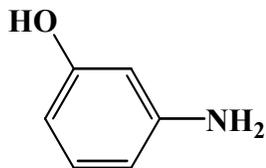
Molecular Weight: 106.17 g/mol

Boiling Point: 145-148°C

Purification: Purchased from Fisher Chemical Co. and used as received

B. Purification of Monomers

1. 3-Aminophenol

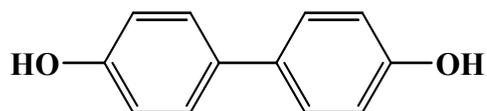


Molecular Weight: 109.13 g/mol

Boiling Point: 164°C/11mm

Purification: Purchased from Aldrich Chemical; Sublimed under high vacuum at 130°C. Light yellow starting material yielded white crystals.

2. 4,4'-Biphenol



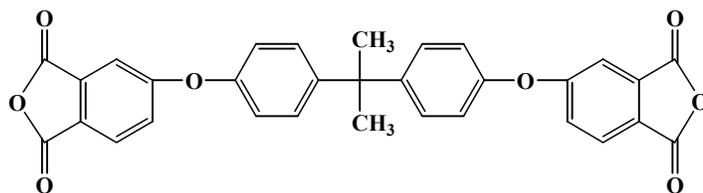
Molecular Weight: 186.21 g/mol

Melting Point: 282-284°C

Purification: Received as a monomer grade sample from Eastman Chemical Co..

Dried at 130°C prior to use in polymerization reactions.

3. 2,2'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane Dianhydride (Bisphenol A Dianhydride) (General Electric Co.)



Molecular Weight: 520.49 g/mol

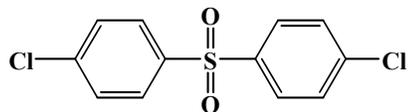
Melting Point: 193°C

Purification: In a three neck 1 liter flask equipped with an overhead stirrer, a nitrogen inlet and condenser, 100g of BPADA was dissolved in 580ml of toluene and 46ml of acetic anhydride and allowed to reflux for an hour before the heat was removed and the solution was allowed to cool. Crystallization took place overnight and the resulting solids were filtered off. This was repeated a total of three times to generate an overall yield of 93 percent.

In the synthesis of poly (imides) via the ester-acid route, half-ester derivatives were prepared in refluxing ethyl alcohol. The time to esterification was reduced by the addition of a stoichiometric amount of triethylamine. The

resulting bis(ester-triethylammonium carboxylate) could be used as a monomer directly without conversion to the parent ester-acid

4. 4,4'-Dichlorodiphenylsulfone

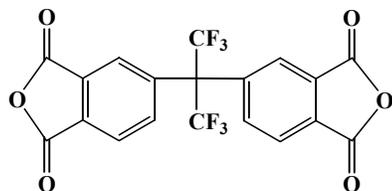


Molecular Weight: 287.16 g/mol

Melting Point (pure): 149°C

Purification: Received from Acros Chemical Co. Recrystallized from toluene to yield white needles

5. 5,5'-(2,2,2-Trifluoro-1-(trifluoromethyl) ethylidene) bis-1,3-isobenzofurandione) (Hexafluoroisopropylidene Dianhydride)

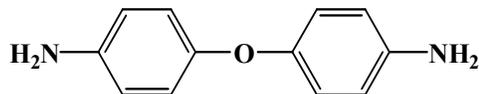


Molecular Weight: 444 g/mol

Melting Point (pure): 247°C

Purification: Ultra pure electronic grade 6FDA was obtained from Hoechst Celanese Corporation as a fine white powder which was dried overnight at 160°C prior to use in polymerization reactions.

6. 4,4'-Oxydianiline



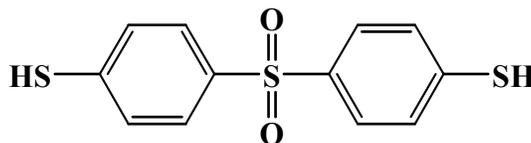
Molecular Weight: 200.24 g/mol

Melting Point: 192°C

Purification: Received from Aldrich Chemical. ODA was sublimed under vacuum at 170°C

C. Synthesis of Monomers

1. Synthesis of 4,4'-Dimercaptodiphenylsulfone



Synthesis of dimercaptodiphenylsulfone was achieved by nucleophilic aromatic substitution reaction of sodium hydrosulfide with 4,4'-dichlorodiphenylsulfone. This monomer was subsequently used in polymerizations to form poly (phenylene sulfide sulfones). A detailed description of the reaction (figure 3.1) follows.

In a two liter round bottom flask equipped with an overhead stirrer, a nitrogen inlet and a condenser, 43g (0.15 mol) of dichlorodiphenylsulfone (DCDPS) was dissolved in 100 mL of dimethylsulfoxide at 60°C. To the amber solution, 35.7g (0.45 mol) of sodium hydrosulfide (hydrate) was added along with 31.1g (0.225 mol) of potassium carbonate. The green solution changed to a rust color over a period of two hours at 60°C and was left to stir an additional 18 hours. The reaction was removed from the oil bath and allowed to cool to room temperature before the entire contents of the flask were added to a four liter beaker containing approximately 1 liter of ice water. Concentrated HCl was added dropwise until the pH reached three. The crude product

was filtered and redissolved in 2100 ml of a five percent solution of potassium carbonate at 70°C. Reprecipitation was performed a total of three times to generate a 68 percent yield (28g). The final product was vacuum filtered and dried under vacuum at 80°C for 12 hours.

2. Synthesis of 3,3'-Disodiumsulfonyl-4,4'-dichlorodiphenylsulfone

Synthesis of 3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone was achieved by electrophilic aromatic substitution reaction of fuming sulfuric acid with 4,4'-dichlorodiphenylsulfone. This monomer was subsequently used in polymerizations to form poly (phenylene sulfide sulfones), controlled molecular weight sulfonated (poly (arylene ethers) (SPAЕ) and segmented SPAЕ poly (imide) copolymers. A detailed description of the reaction to form 3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone follows.

To a 1 liter round bottom flask equipped with an overhead stirrer, nitrogen inlet and condenser, 60g (0.21 mol) of DCDPS was added along with a 2.2-fold molar excess of fuming sulfuric acid (0.46 mol, $d=1.925$, 26% SO_3 , 74ml). The temperature was raised to 120°C and a dark brown solution resulted. After approximately 3 hours, the reaction became heterogeneous, forming a thick white precipitate. The reaction mixture (figure 3.2) was allowed to cool to room temperature and was added to 1 liter of ice water to form a solution. 200g of sodium chloride was added with rapid stirring and the product was salted out of solution. This product was filtered, redissolved and reprecipitated from a 6:1 mixture of 2-propanol/water to isolate bright white crystals at 65 percent yield. Elemental analysis of the product is shown in the results and discussion section.

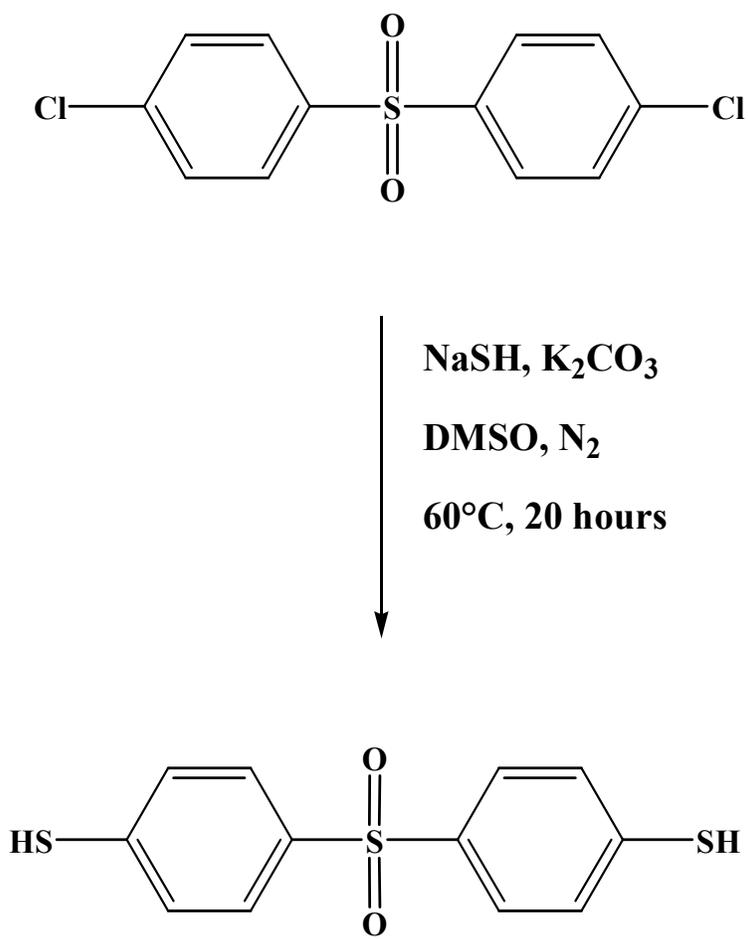


Figure 3.1: Synthesis of 4,4'-Dimercaptodiphenylsulfone

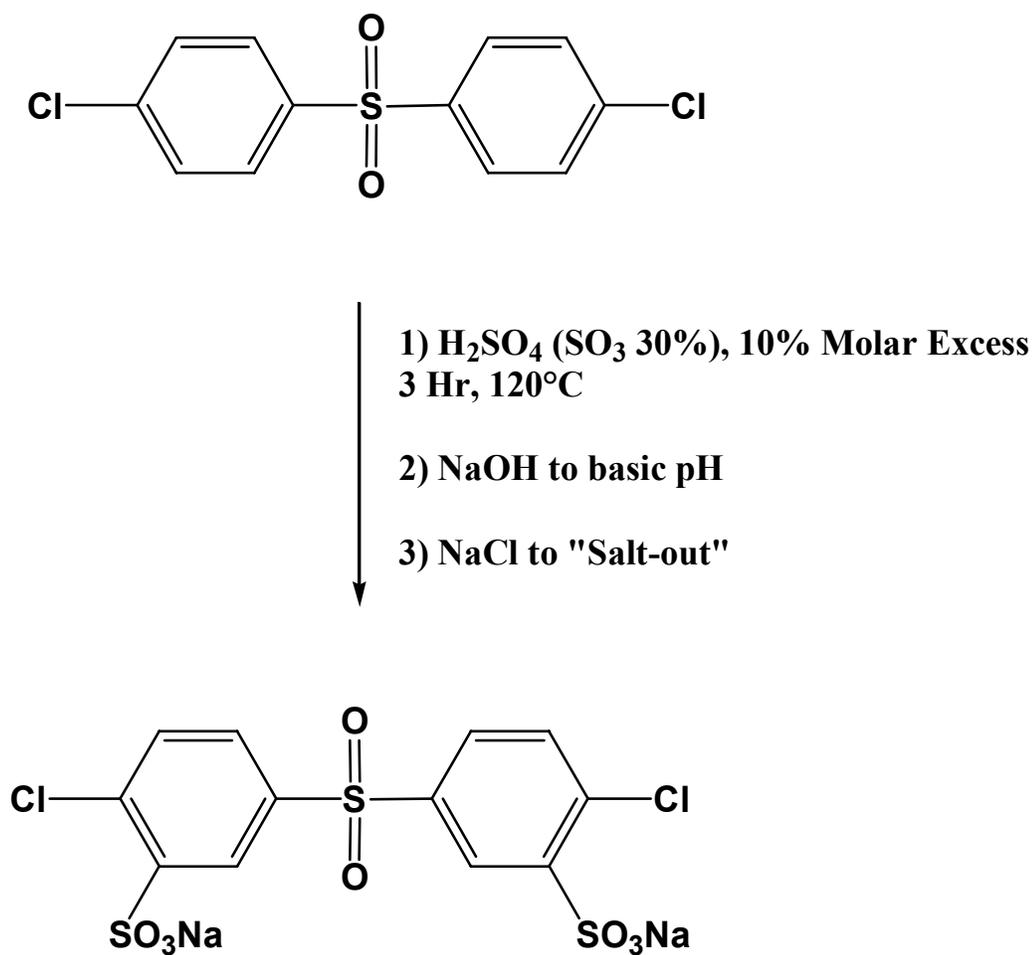


Figure 3.2: Synthesis of 3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone (SDCDPS)

D. Synthesis of Homopolymers and Copolymers

1. Synthesis of Sulfide Sulfone Homopolymers and Copolymers

a. Synthesis of Poly (phenylene sulfide sulfones)

A control polymerization using DCDPS and DMDPS in equimolar amounts was performed to establish the synthetic conditions needed to yield high molecular weight product. A 500mL round bottom flask equipped with an overhead stirrer, nitrogen inlet, Dean-Stark trap and condenser was charged with 12.96g (4.59×10^{-2} mol) dimercaptodiphenylsulfone (DMDPS), 13.279g DCDPS (4.59×10^{-2} mol) and 87ml of 1-Methyl-2-pyrrolidinone (NMP), heated to 100°C, and stirred to form a 30 weight percent solution. To the stirring solution 6.97g potassium carbonate (15 weight percent excess) was added along with 29mL of xylene as an azeotroping agent. The heat was increased to form a reflux at 155°C and the reaction was allowed to stir for 8 hours. The xylene was then stripped off, the heat was increased to 170°C and the reaction (figure 3.3) was left to stir overnight. Once finished, NMP was added to form a 15 weight percent solution, the flask contents were filtered to remove the salt (KCl) by-product and the polymer was precipitated in a water/methanol mixture (60:40) to yield a fibrous product that was dried at 160°C overnight under vacuum.

b. Synthesis of Sulfonated Poly (phenylene sulfide sulfones)

After the conditions to generate high molecular weight PPSS were established, efforts to synthesize a sulfonated analog began. The conditions needed to generate a high molecular weight PPSS that is 20 percent sulfonated (i.e., 20 mole percent of the DCDPS is in the sulfonated form (SDCDPS)) are described below. A 250mL round bottom flask equipped with an overhead stirrer, nitrogen inlet, Dean-Stark trap and condenser was charged with 5.0g (1.77×10^{-2} mol) dimercaptodiphenylsulfone (DMDPS), 4.076g DCDPS (1.416×10^{-2} mol), 1.73g (3.54×10^{-3} mol) SDCDPS and 36ml of 1-methyl-2-pyrrolidinone (NMP), heated to 100°C, and stirred to form a 30 weight percent solution. To the stirring solution, 3.18g potassium carbonate (15 weight percent excess) was added

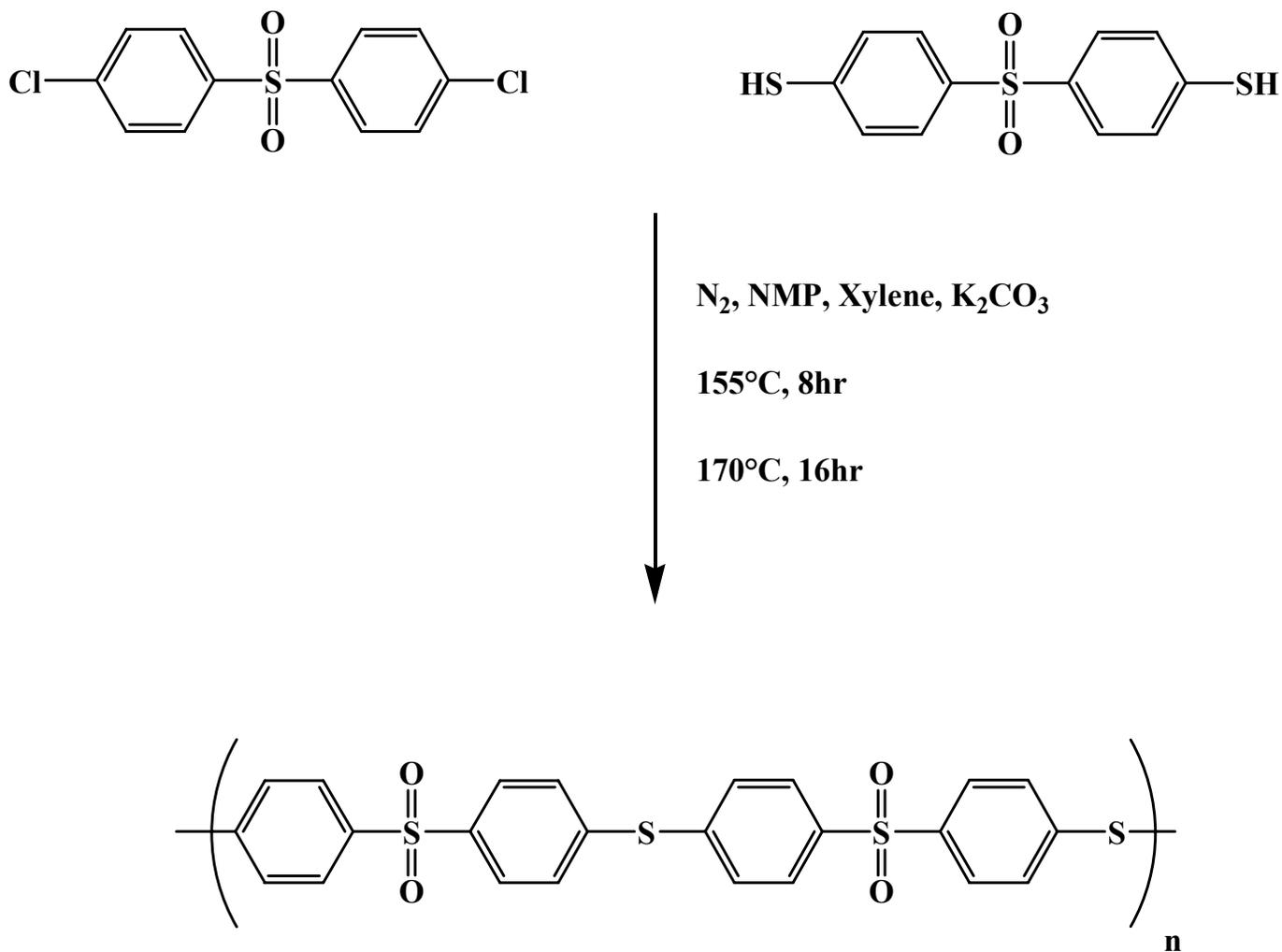


Figure 3.3: Synthesis of Poly (phenylene sulfide sulfones)

along with 12mL of xylene as an azeotroping agent. The heat was increased to form a reflux at 155°C and the reaction mixture (figure 3.4) was allowed to stir for 8 hours. The xylene was then stripped off, the heat was increased to 170°C and the reaction mixture was left to stir overnight. Once finished, NMP was added to form a 15 weight percent solution, the flask contents were filtered to remove the salt (KCl) by-product and the polymer was precipitated in 100 percent 2-propanol to yield a fibrous product that was dried in a 160°C vacuum oven overnight.

2. Synthesis of Biphenol-based Poly (arylene ether Homopolymers and Copolymers

a. Synthesis of a Biphenol / 4,4'-dichlorodiphenylsulfone Poly (arylene ether)

A control polymerization using DCDPS and biphenol in equimolar amounts was performed to establish the synthetic conditions needed to yield high molecular weight product. A 250mL round bottom flask equipped with an overhead stirrer, nitrogen inlet, Dean-Stark trap and condenser was charged with 1.8621g (1.0×10^{-2} mol) 4,4' biphenol(BP), 2.8716g DCDPS (4.59×10^{-2} mol) and 11mL of 1-methyl-2-pyrrolidinone (NMP), heated to 100°C, and stirred to form a 30 weight percent solution. To the stirring solution 1.5894g potassium carbonate (15 weight percent excess) was added along with 3ml of toluene as an azeotroping agent. The heat was increased to form a reflux at 155°C and the reaction was allowed to stir for 8 hours at which point the temperature was raised to 180°C and the reaction allowed to proceed overnight. The reaction mixture (figure 3.5) was then allowed to cool and sufficient NMP was added to generate a 15 percent solids solution which was filtered to remove KCl. The polymer was isolated in a 60/40 methanol water solution to yield fibrous polymer which was dried for 8 hours in a 200°C vacuum oven.

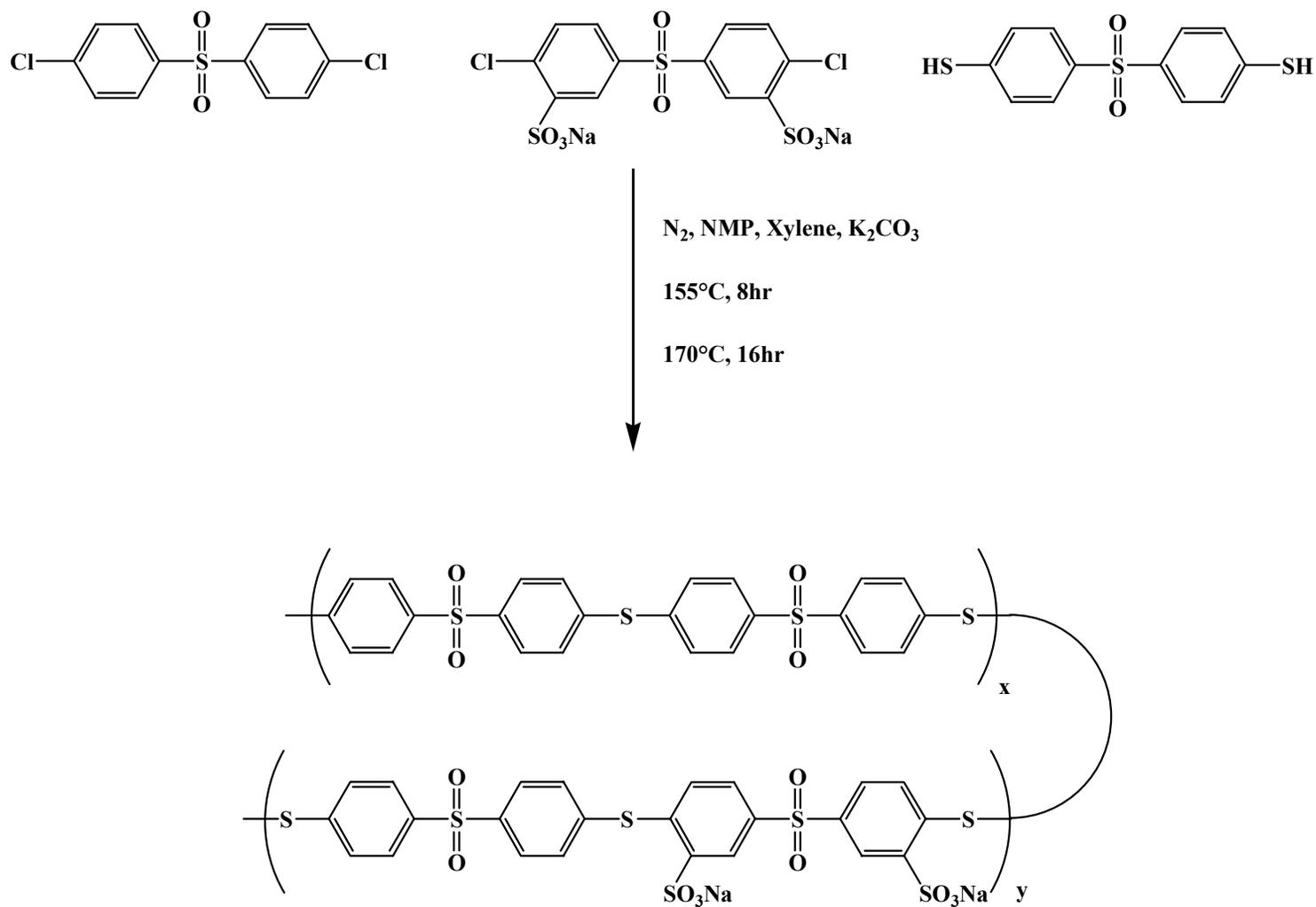


Figure 3.4: Synthesis of Sulfonated Poly(phenylene sulfide sulfones) (SPPSS)

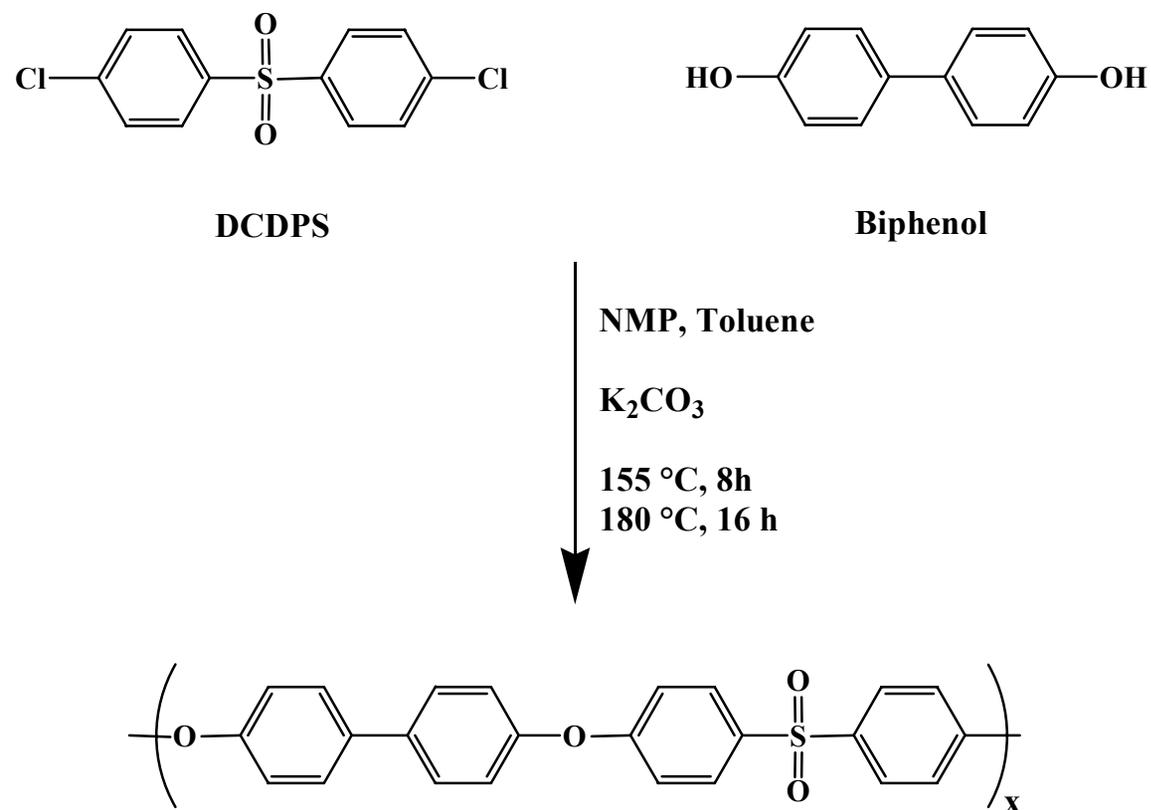


Figure 3.5: Synthesis of a biphenol / 4,4'-dichlorodiphenylsulfone poly(arylene ether)

**b. Synthesis of Biphenol/ 3,3-Disodiumsulfonyl-4,4'-
Dichlorodiphenylsulfone Poly (arylene ethers)**

A systematic series of sulfonated poly(arylene ethers) was synthesized by varying the ratio of SDCDPS to DCDPS. An equimolar amount of biphenol was added to yield high molecular weight polymers. A typical reaction to form a 60/40 SDCDPS/DCPDS polymer was conducted in a 250mL round bottom flask equipped with an overhead stirrer, nitrogen inlet, Dean-Stark trap and condenser was charged with 1.8621g (1.0×10^{-2} mol) 4,4' biphenol (BP), 1.1487g DCDPS (4.0×10^{-3} mol), 2.9476g SDCDPS (6.0×10^{-3}) and 15mL of 1-methyl-2-pyrrolidinone (NMP), heated to 100°C, and stirred to form a 30 weight percent solution. To the stirring solution 1.5894g potassium carbonate (15 weight percent excess) was added along with 4mL of toluene as an azeotroping agent. The heat was increased to form a reflux at 155°C and the reaction was allowed to stir for 2 hours at which point the temperature was raised to 200°C and the reaction was allowed to proceed overnight. The reaction mixture (figure 3.6) was then allowed to cool to room temperature and sufficient NMP was added to generate a 15 percent solids solution which was filtered to remove KCl. The polymer was isolated in isopropanol to yield fibrous polymer which was dried for 8 hours in a 200°C vacuum oven.

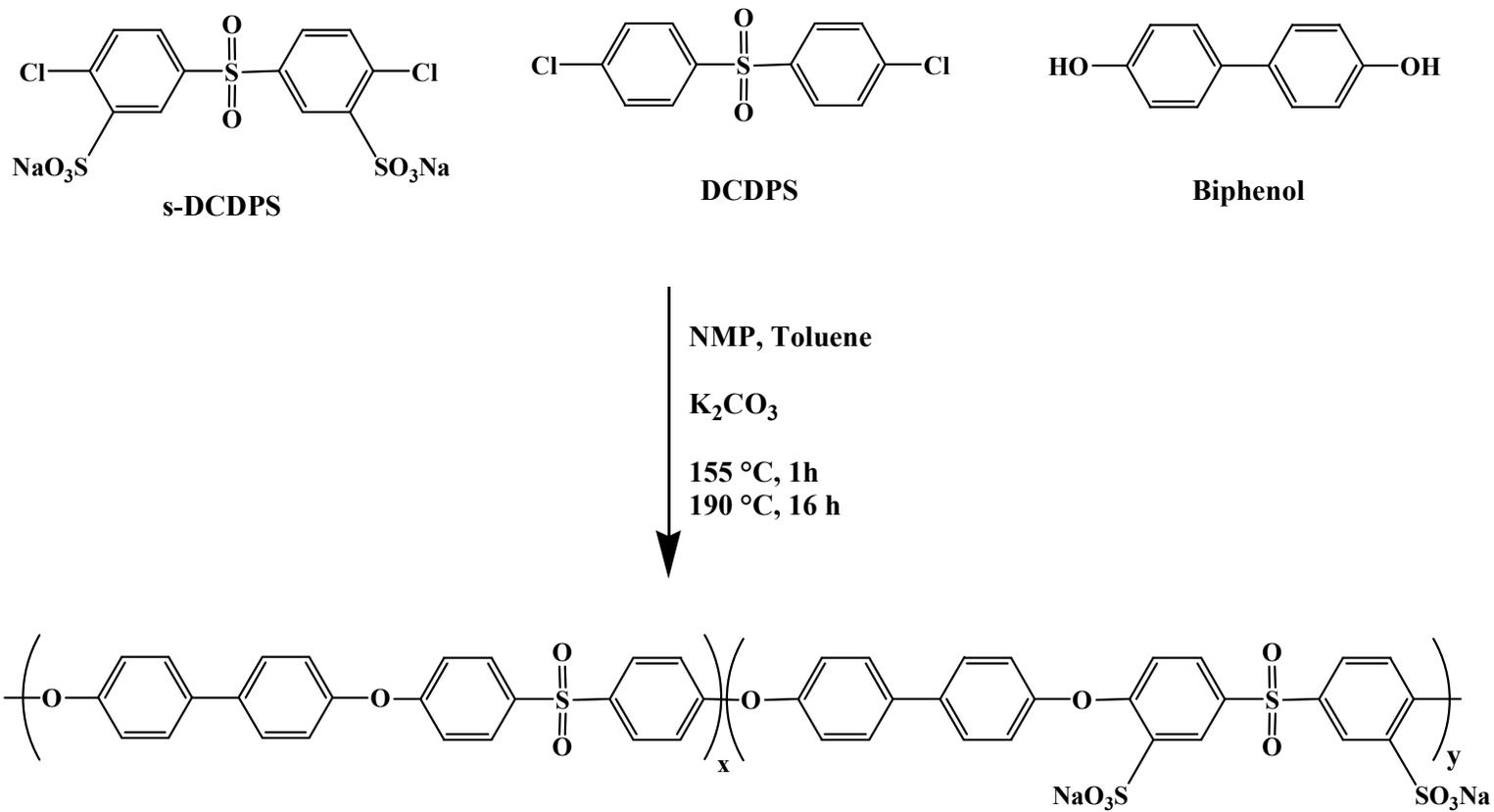


Figure 3.6: Synthesis of Biphenol/ 3,3'-Disodiumsulfonyl 4,4'-Dichlorodiphenylsulfone
Poly (arylene ethers)

E. Synthesis of Biphenol-based Poly (arylene ethers) of Controlled Molecular Weight

1. Synthesis of Controlled Molecular Weight Biphenol-based Poly (arylene ethers) With Telechelic Primary Amine Functionalization: Control of Molecular Weight (M_n) and Terminal Functionality

The polymerization described in this section was designed to yield polymers of controlled molecular weight rather than stoichiometrically balanced polymerizations described in previous sections. This was accomplished by applying a method that is described below and illustrated in Figure 3.7.

For the polymer shown in figure 3.7 with an M_n of 20000 g/mol, one notes that it has a repeat unit molecular weight of 400.45 g/mol and an endgroup molecular weight of 430.48 g/mol:

The target repeat unit chain molecular weight is: $20000 - 430.48 = 19569.52$

The numbers of repeat units are: $19569.52 / 400.45 = 48.68$

In each average polymer chain one has:

Biphenol: 48.68

DCDPS: 48.68, plus one unit from the endgroup = 49.68

m-aminophenol: 2

Dividing by 49.68 and normalizing affords a molar ratio of:

Biphenol: 0.979

DCDPS: 1

and

m-aminophenol: 4.0257×10^{-2}

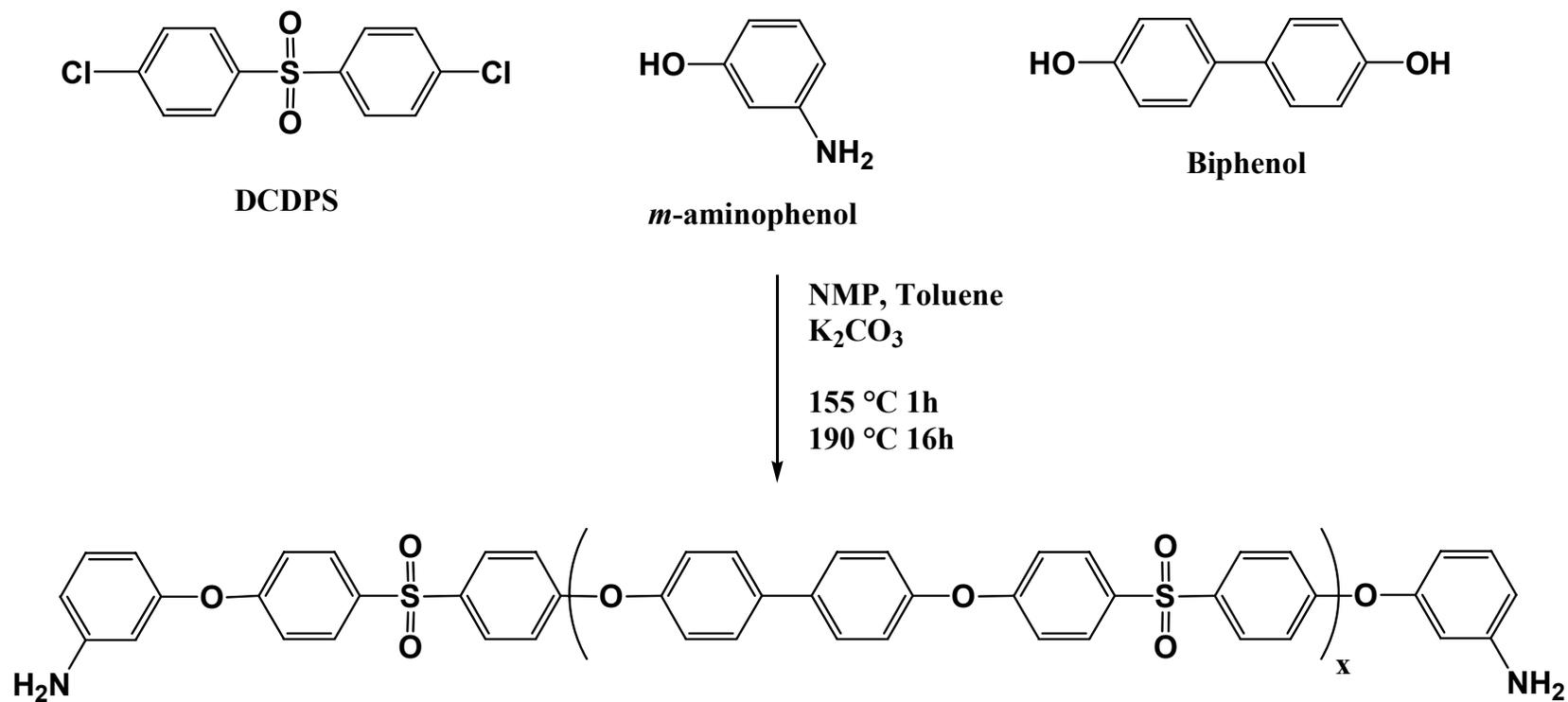


Figure 3.7: Synthesis of Controlled Molecular Weight Biphenol-based Poly (arylene ethers) With Telechelic Primary Amine Functionalization

One must choose a reaction size (*e.g.* approx. 20g) and estimate the weight of DCDPS to start with, followed by conversion to moles:

$$\textit{e.g.}, \text{DCDPS: } 10\text{g} \times 1\text{mol}/287.16\text{g} = 3.482 \times 10^{-2}\text{mol}$$

Using the moles of DCDPS, the molar ratios, and molecular weights for each monomer, the feed should contain:

$$\text{Biphenol: } 3.482 \times 10^{-2}\text{mol} \times 0.979 \times 186.21\text{g/mol} = 6.3478\text{g}$$

$$\textit{m}\text{-aminophenol: } 3.482 \times 10^{-2}\text{mol} \times 4.0257 \times 10^{-2} \times 109.13\text{g/mol} = 0.1618\text{g}$$

The last step is to add all components to the reaction flask quantitatively.

Using the above calculations, the procedure involved addition of the monomers, endcapper, and 38ml of NMP to a 250mL round bottom flask equipped with an overhead stirrer, nitrogen inlet, Dean-Stark trap and condenser to afford a 30 weight percent solids solution at 100°C. After dissolution, 13mL of toluene and 5.53g of potassium carbonate were added and the temperature was increased to 155°C for 8 hours at which point the temperature was raised to 180°C and the reaction allowed to proceed overnight. The reaction mixture was then allowed to cool and sufficient NMP was added to generate a 15 percent solids solution, which was filtered to remove KCl. The polymer was isolated in a 60/40 methanol water solution to yield fibrous polymer which was dried for 8 hours in a 200°C vacuum oven.

2. Synthesis of Controlled Molecular Weight Biphenol-based Sulfonated Poly (arylene ethers) with Telechelic Primary Amine Functionalization

Polymerization to form sulfonated analogs of the above polymer proceeded in a fashion very similar to that already described in section 3.E.1. Using the same approach to calculate the amount of each monomer needed to target the molecular weight of interest, these were added along with NMP to a 250mL round bottom flask equipped with an overhead stirrer, nitrogen inlet, Dean-Stark trap and condenser to give a 30 weight percent solids solution at 100°C. After dissolution, toluene and potassium carbonate were added and the temperature was increased to 155°C. Within an hour at this temperature a tan-colored precipitate began to form. At this point, the temperature was

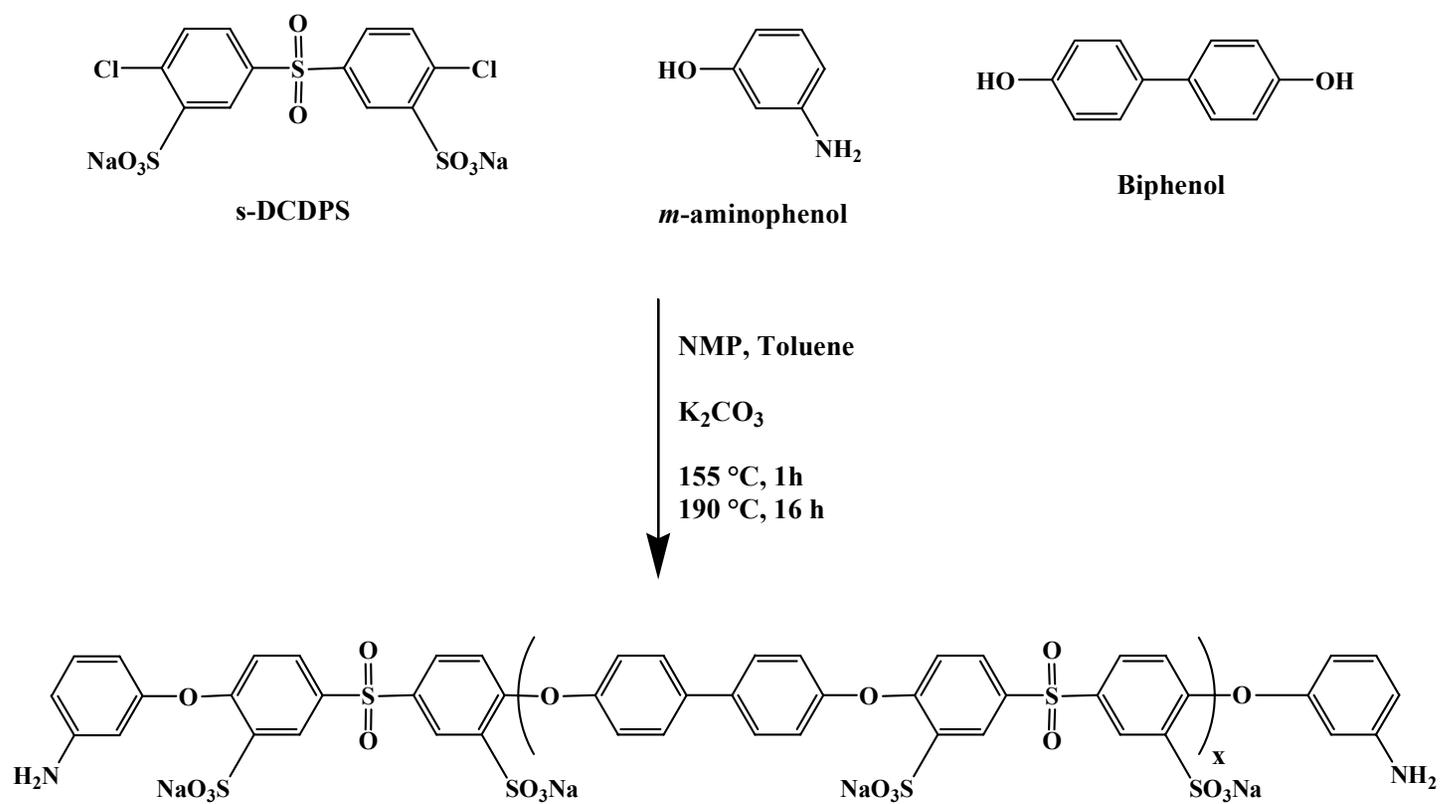


Figure 3.8: Synthesis of Controlled Molecular Weight Biphenol-based Sulfonated Poly (arylene ethers) with Telechelic Primary Amine Functionalization

raised to 190°C, the toluene was stripped and the reaction was allowed to proceed overnight. The reaction mixture (figure 3.8) was then allowed to cool and sufficient NMP was added to generate a 15 percent solids solution which was filtered to remove KCl. The polymer was isolated in 100 percent 2-propanol to yield a fibrous polymer which was dried for 8 hours in a 230°C vacuum oven.

F. Synthesis of Segmented Block Poly (imide) Poly (arylene ether) Copolymers

1. Synthesis of Bisphenol-A/Oxydianiline Poly (imide) Sulfonated Poly(arylene ether sulfone) / Poly (imide) Copolymers

The opportunity to synthesize a series of block copolymers was the rationale behind the synthesis of amine terminated sulfonated poly (arylene ethers sulfones) of controlled molecular weight as described in 3.E.2. Initial block copolymers utilized bisphenol-A dianhydride (BPADA) and 4,4'-oxydianiline (ODA) as starting materials due to their commercial availability and low cost. After conditions for synthesizing a control homopolymer based on BPADA/ODA were established, work began to generate a systematic series of sulfonated PAE/PI copolymers, as described below.

a. Ester-Acid Approach

Initial efforts to synthesis segmented block copolymers of sulfonated PAE/PI utilized the ester acid approach. This involves reflux of the dianhydride in anhydrous ethanol to form the bis(ester-triethylammonium carboxylate) derivative that can be used directly to form poly (imide) in subsequent steps. A typical reaction is illustrated in figure 3.9.

Synthesis of a 35 weight percent 18000g/mol PAE / 65 weight percent PI segmented copolymer is described below.

An 18,000g/mol 100% sulfonated (i.e. 2SO₃Na groups per repeat unit) PAE was synthesized as described previously in 3.E.2. . A 250mL round bottom flask equipped with an overhead stirrer, nitrogen inlet, reverse Dean-Stark trap and condenser was charged with 5.0g (9.6×10^{-3} mol) BPADA, 45ml ethanol and 11.25mL triethylamine and heated to 110°C to form a 10 weight percent solids solution. As soon as the BPADA

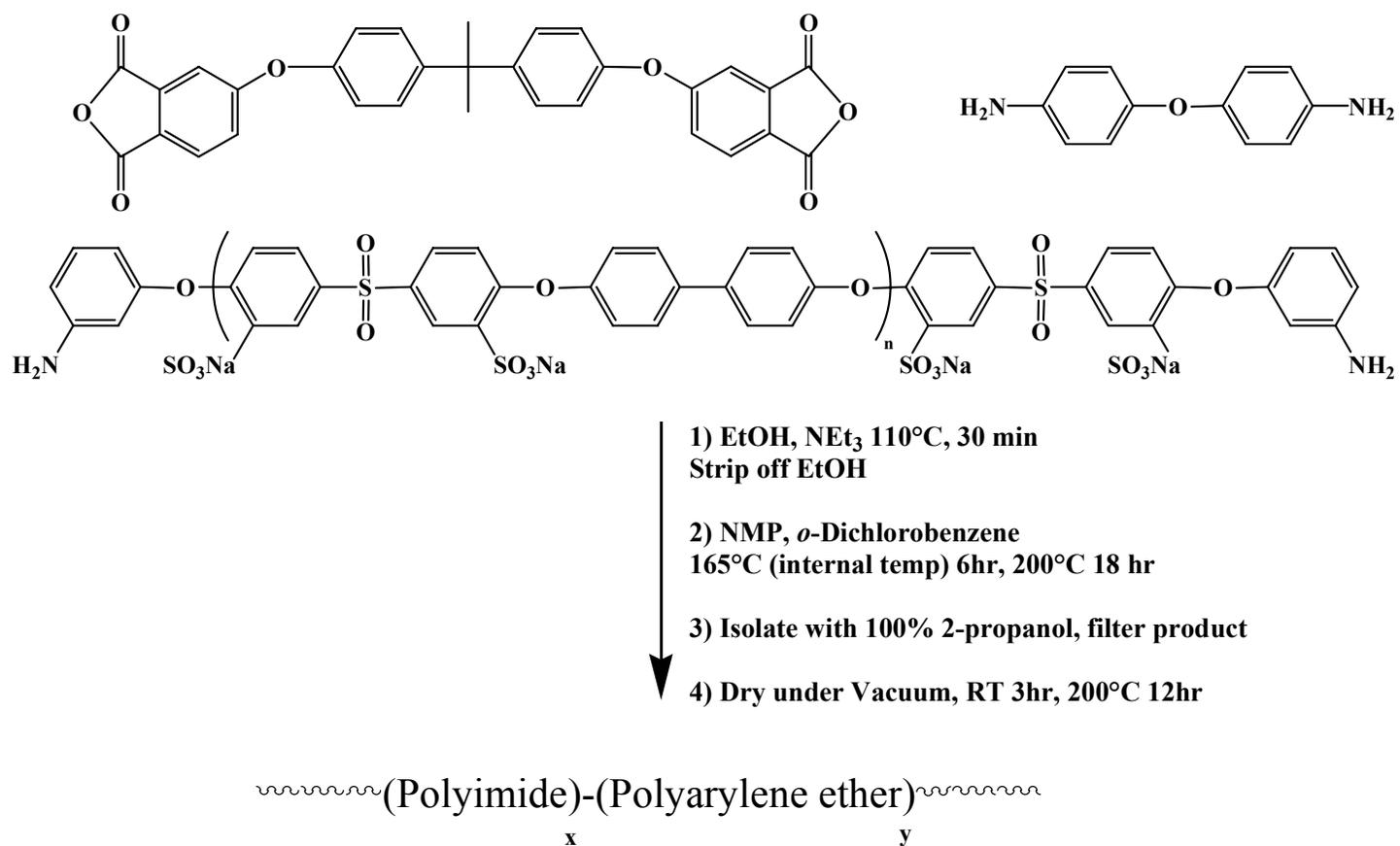


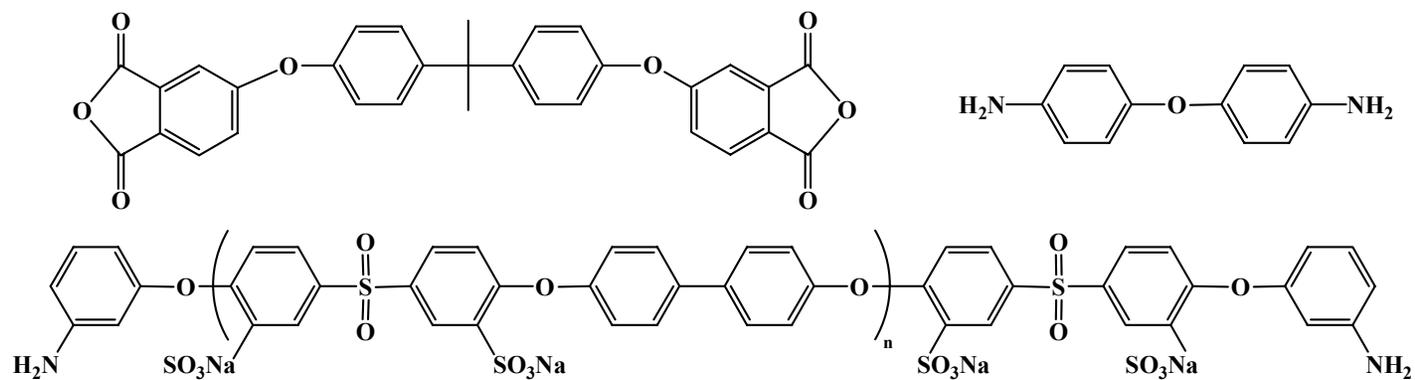
Figure 3.9: Synthesis of Bisphenol-A/Oxydianiline Poly (imide) Sulfonated Poly(arylene ether sulfone) Segmented Copolymers: Ester Acid Approach

went into solution, it was assumed that the bis(ester-triethylammonium carboxylate) derivative had been formed and the ethanol and triethylamine were stripped to yield a clear viscous fluid. The stirring was stopped and 1.8742g ODA (9.36×10^{-3} mol), 4.32g PAE (2.4×10^{-4} mol), 43.72mL NMP, and 11mL *o*-dichlorobenzene (azeotroping agent) were added to the flask to form a 20 weight percent solids reaction. The contents were heated to 165°C and the reaction was allowed to stir for 6 hours. The *o*-dichlorobenzene was then stripped and the temperature was increased to 200°C for an additional 18 hours. The viscous polymerization mixture was then allowed to cool to 100°C before precipitation into 100 percent 2-propanol, yielding a fibrous polymer.

b. Poly (amic acid) Approach

Initially, a systematic series of PAE/ (BPADA/ODA) PI copolymers was targeted for study with compositions in the range of 35, 50, 67 and 85 weight percent sulfonated poly (arylene ether sulfone). As progress was made, it became apparent that the use of *o*-dichlorobenzene as an azeotroping agent was causing phase separation during the polymerization. Presumably, the sulfonated PAE was unsolvated by the *o*-dichlorobenzene and as the composition was increased above 50 weight percent PAE, high molecular weight polymers could not be achieved. As an alternative, it was realized that the poly (amic acid) route to poly (imide) synthesis avoided the need for an azeotroping agent and that the PAEs would remain soluble throughout the polymerization. This approach also involves a thermal imidization step which necessitates casting a solution of the poly (amic acid) onto a substrate, generating a film as the final polymerization product. This eliminates a step in the processing of this series of polymers, for various forms of characterization involve study of the material in film form. The synthesis of a 50 weight percent, 18,000 g/mol sulfonated PAE / 50 weight percent (BPADA/ODA) poly (imide) is shown in figure 3.10 and described below.

A 18,000g/mol 100% sulfonated (i.e. 2SO₃Na groups per repeat unit) PAE was synthesized as described previously in 3.E.2. . A 250mL round bottom flask equipped with an overhead stirrer, nitrogen inlet and condenser was charged with 1g (4.37×10^{-5}



- 1) Add polyarylene ether; dissolve at 100°C in NMP
- 2) Cool to room temp
- 3) Add ODA/BPADA; stir for 24 hr at RT
- 4) Imidize under Vacuum; RT 12hr, 100°C 3hr, 200°C 2hr, 310°C 1hr



Figure 3.10: Synthesis of Bisphenol-A/Oxydianiline Poly (imide) Sulfonated Poly(arylene ether sulfone) Segmented Copolymers: Poly (amic acid) Approach

mol) sulfonated PAE, 7.5mL NMP and heated to 110°C to form a 15 weight percent solids solution. After about 1 hour at 110°C, the sulfonated PAE was in solution and the reaction was cooled to room temperature. The stirring was stopped and 0.2283g ODA (1.14×10^{-4} mol), 0.6153g BPADA (1.18×10^{-3} mol) and 3mL NMP were added to the flask to form a 20 weight percent solids reaction. The contents were left at room temperature and allowed to stir overnight. The following day, the viscous transparent amber poly (amic acid) solution was cast onto a silylated glass plate (to aid in film release from the glass surface) and placed in a vacuum oven. The oven was left at room temperature for 12 hours, then was heated to 100°C for 3 hours, 200°C for 2 hours and 310°C for an hour. After cooling the oven to room temperature, the films were removed from the oven and placed in plastic bags in an anhydrous nitrogen atmosphere and stored in a dessicator. This approach was used for 35, 59, 65 and 85 weight percent sulfonated PAE / (BPADA/ODA) poly (imide) copolymers and yielded tough creasable films in all cases.

c. Conversion to Sulfonic Acid from the Sulfonate Salt Form

All segmented block copolymers were synthesized with the sulfonated PAE in the salt, rather than sulfonic acid, form due to the higher stability of the salt during solution-based reactions. When these polymers are applied to fuel cell technology as proton exchange membranes, the protons exchange with the sulfonic acid sites to generate current. The films were easily converted using 1M sulfuric acid heated to the boiling point for an hour. The films were then boiled in deionized water for an hour twice to remove any excess sulfuric acid from the films. The films looked identical to the naked eye regardless of which counter-ion was present.

2. Synthesis of 6FDA/Oxydianiline Poly (imide) Sulfonated Poly(arylene ether) Copolymers

After a systematic series of PAE / PI copolymers was synthesized that utilized BPADA as the anhydride, it was realized that investigation of a series based upon 5, 5'-(2, 2, 2, Trifluoro -1- (trifluoromethyl) ethylidene] bis -1, 3 isobenzene-furandione) ((6FDA) needed to be explored. It was postulated that the 6F moiety was more stable than

the aliphatic isopropylidene group of BPADA in the harsh acidic oxidizing environment of a fuel cell, and that in identical compositions, a larger degree of phase separation may occur when fluorine was present. Initially, the ester-acid approach was used to synthesize sulfonated PAE / (6FDA/ODA) poly (imide) copolymers, but again better results were achieved when the poly (amic acid)/ thermal imidization approach was utilized.

a. Ester-Acid Approach

Initially, the ester-acid approach to poly (imide) synthesis was used because the anhydride could be “desensitized”, by conversion to the ester-acid form, to any water that may have been present in the system. It was nearly impossible to completely remove all water from the sulfonated PAE polymers; however, for the same reasons discussed in 3.F.1a, it was deemed that the presence of *o*-dichlorobenzene would limit the molecular weight of the resulting copolymers. Compositions of greater than 50 weight percent PAE resulted in lower molecular weight materials. Polymerizations utilized an approach identical to that described in section 3.F.1a and illustrated in figure 3.11.

b. Poly (amic acid) Approach

For reasons identical to those discussed in 3.F.1b, removal of *o*-dichlorobenzene from the polymerization scheme, all of the systematic series of 6FDA copolymers have been synthesized through use of the poly (amic acid) approach to poly (imide) synthesis. The polymerizations utilized an approach identical to that described in section 3.F.1b and illustrated in figure 3.12.

c. Conversion to Sulfonic Acid from the Sulfonate Salt Form

As mentioned previously in section 3.F.1c, segmented block copolymers were synthesized with the sulfonated PAE in the salt, rather than sulfonic acid, form due to the higher stability of the salt during solution-based reactions. When these polymers are applied to fuel cell technology as proton exchange membranes, the protons exchange with the sulfonic acid sites to generate current. The films were easily converted using

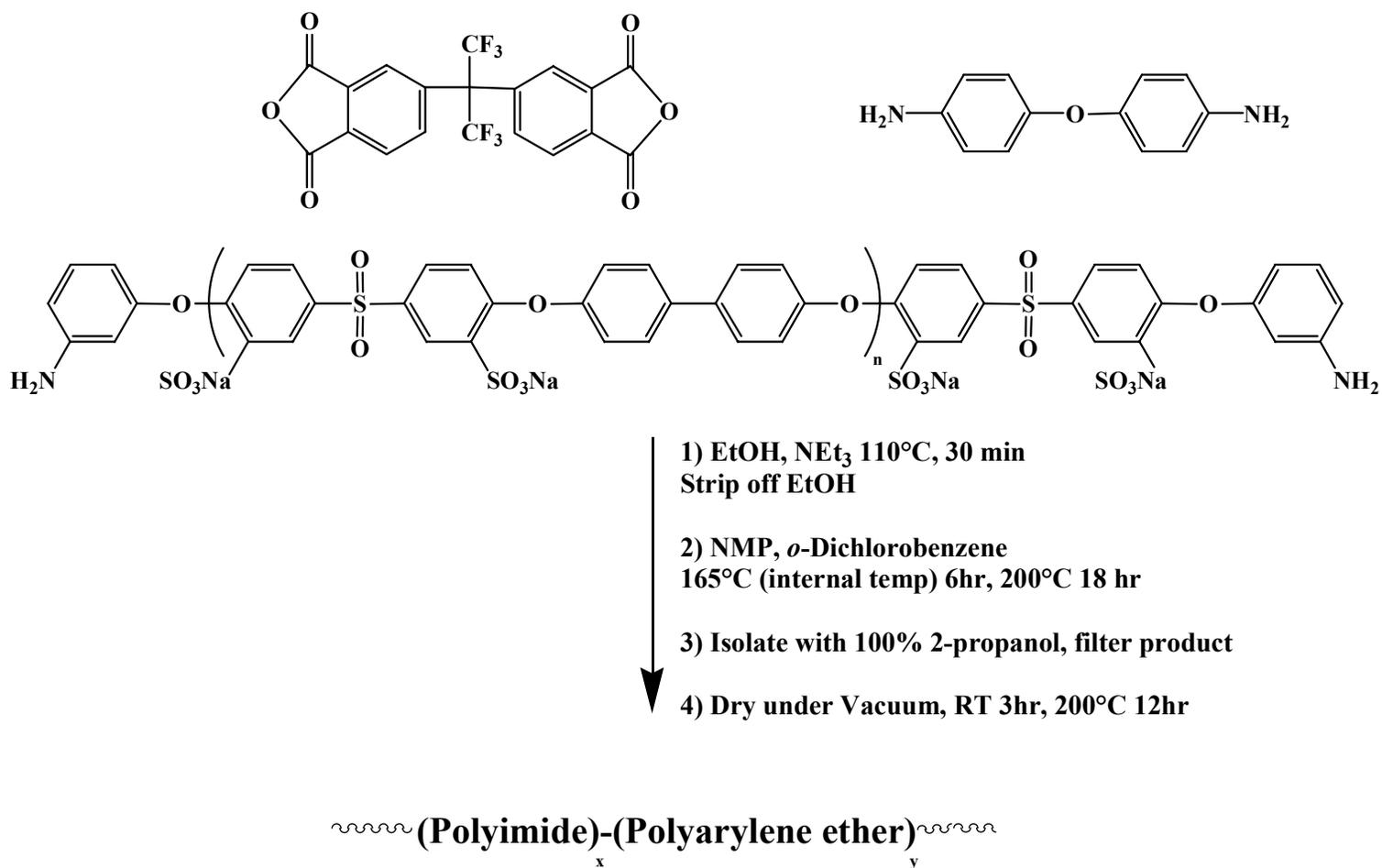
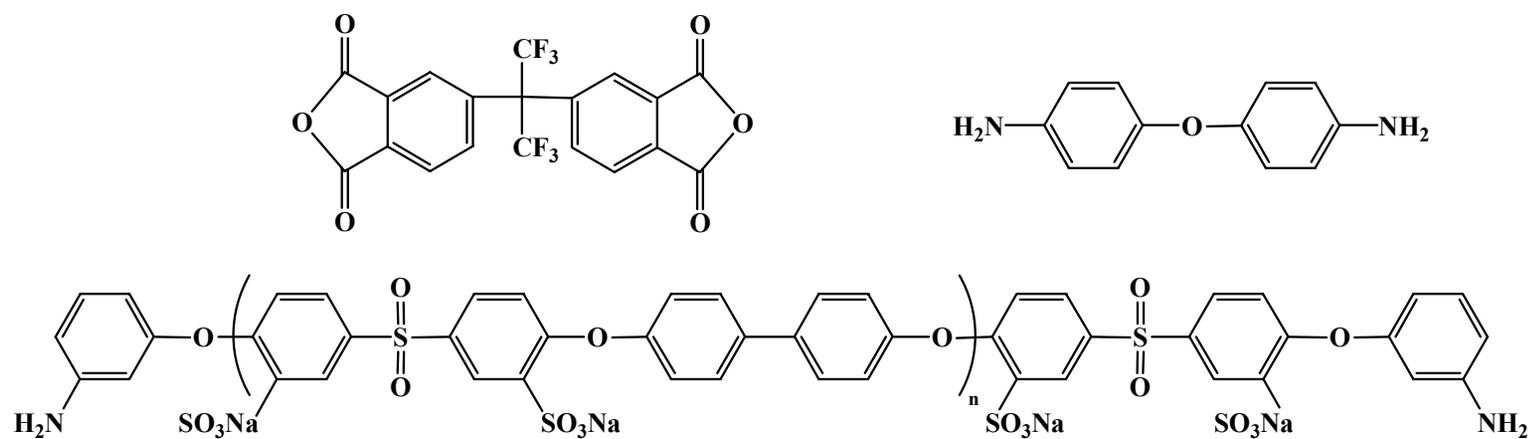


Figure 3.11: Synthesis of 6FDA/Oxydianiline Poly (imide) Sulfonated Poly(arylene ether sulfone) Segmented Copolymers: Ester-Acid Approach



- 1) Add polyarylene ether; dissolve at 100°C in NMP
- 2) Cool to room temp
- 3) Add ODA/6FDA; stir for 24 hr at RT
- 4) Imidize under Vacuum; RT 12hr, 100°C 3hr, 200°C 2hr, 310°C 1hr



Figure 3.12: Synthesis of 6FDA/Oxydianiline Poly (imide) Sulfonated Poly(arylene ether sulfone) Segmented Copolymers: Poly (amic acid) Approach

1M sulfuric acid heated to the boiling point for an hour. The films were then boiled in deionized water for an hour twice to remove any excess sulfuric acid from the films. The films looked identical to the naked eye regardless of which counter-ion was present.

G. Characterization of Monomers and Polymers

1. Elemental Analysis

Elemental analysis of 3,3'-disodium sulfonyl-4,4'-dichlorodiphenylsulfone was provided by Galbraith Laboratories. Relative percentages of carbon, hydrogen, oxygen, sulfur and sodium were obtained.

2. Nuclear Magnetic Resonance

NMR spectroscopy was measured on a Varian Unity 400 Mhz instrument. Dueterated dimethylsulfoxide was the only solvent employed.

a. ¹H NMR

This technique was used in various capacities. For monomer synthesis, it was used for structure elucidation, as well as for purity analysis. In the case of sulfonated poly (arylene ether sulfone) synthesis, proton NMR was mainly used for determination of copolymer composition and calculation of number average molecular weight (M_n), as gel permeation chromatography could not be used for molecular weight analysis for these systems. All samples were made at a concentration of 100mg/0.8mL of solvent and placed in a 5mm NMR tube after completely dissolved.

b. ¹³C NMR

Experiments to obtain quantitative integrations for ¹³C spectra were conducted with the assistance of Mr. Tom Glass of the analytical services department. The samples were prepared at a concentration of 300mg/3mL of solvent and were added to a 10mm NMR tube after completely solvated. After analysis of several samples, it became apparent that proton NMR experiments yielded results of greater sensitivity and accuracy.

3. Gel Permeation Chromatography

GPC measurements for the poly (arylene ether sulfone) control polymerization were obtained from Dr. Qing Ji. Sulfonated analogs were not investigated by GPC because of the increased interaction with the columns caused by the sulfonate groups. The instrument used was a Waters GPC/ALC 150°C chromatograph equipped with a differential refractive index detector and an online differential viscometric detector (Viscotec 150R) coupled in parallel. Waters μ Styragel HT3 + HT4 columns were used. The mobile phase was N-methylpyrrolidone containing 0.02M P₂O₅. The flow rate was 1.0 ml/min, the injection volume was 200 μ l, the experimental temperature was 60°C and the polymer concentration was approximately 4 mg/ml. TriSEC GPC Software V2.70e (Viscotek) was used to acquire and analyze the data. Absolute number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity (M_w/M_n) were calculated by universal calibration generated with a series of narrow molecular weight distribution polystyrene standards (Polymer Laboratories).¹³²

4. Intrinsic Viscosity

Intrinsic viscosity measurements of the homopolymers and segmented copolymers were made using a Cannon-Ubbelohde glass capillary viscometer. All measurements were taken in 1-methyl-2-pyrrolidinone (NMP) at 25°C. Four concentrations between 0.5 and 2 weight percent, with 3 replicate runs per concentration, were used to determine the intrinsic viscosity of the samples.

5. Fourier Transform Infrared Spectroscopy

FTIR spectra were obtained using a Nicolet Impact 400 Fourier Transform Infrared Spectrometer (resolution = 1.0 cm⁻¹) coupled to a Gateway 300 Mhz personal computer for data output and analysis. A background spectrum was obtained before the sample spectrum was collected. The software included with the FTIR automatically subtracted the background from the sample spectra. Sample spectra were collected at room temperature from 4000 cm⁻¹ to 600 cm⁻¹.

¹³² Konas, M.; Moy, T. M.; Rogers, M. E.; Shultz, A. R.; Ward, T. C.; McGrath, J. E. *J. Poly. Sci.: Part B, Polymer Phys.* **1995**, *33*, 1429.

6. Water Sorption

Water sorption data were obtained by drying sulfonic acid containing films at 80°C in a vacuum oven for 24 hours. The films were then weighed to obtain an initial dry weight. The films were then soaked in room temperature water for 24 hours. Data were obtained every ten minutes in the first hour, and once an hour for 5 hours and every 6 hours for a total of 24 hours. To obtain data, the films were removed from the water, blotted dry, and weighed. By subtracting the dry weight from the wet weight, and dividing by the dry weight the water uptake could be calculated

$$\text{Water sorption} = (w_{\text{wet}} - w_{\text{dry}}) / w_{\text{dry}}$$

7. Protonic Conductivity

Protonic conductivities of hydrated sulfonated copolymer films were obtained at 30°C using a Hewlett-Packard Model 4192A Impedance/Gain-Phase Analyzer. A scan from 1 Mhz to 1 Hz was performed utilizing the “window cell” geometry designed at Los Alamos National Laboratories¹³³ and shown in figure 3.13.

8. Thermogravimetric Analysis

Weight loss versus temperature was determined by thermogravimetric analysis using a Perkin-Elmer Series 7 instrument in an oxidizing (air) environment. The analysis was conducted using 7-10mg of sample and heating from 50-800°C at a heating rate of 10°C/minute. Data were collected and analyzed by a personal computer which plotted the data as residual weight percent against temperature. The 5 percent weight loss temperature values were recorded and these temperatures -50°C were used as a maximum to avoid degradation during dynamic mechanical (DMA) and dynamic scanning calorimetry (DSC) experiments.

9. Dynamic Mechanical Analysis

Dynamic mechanical analysis was performed on a Thermal Analysis (TA) Dynamic Mechanical Analyzer by Ms. Amy Eichstadt, a Ph.D. student in Chemistry (Professor Thomas C. Ward, advisor). Experiments were conducted in an oxidizing (air)

¹³³ Zawodzinski, T.; Neeman, M.; Sillerud, L. O.; Gottesfeld, S. *J. Phys. Chem.* **1991**, *95*, 6040.

atmosphere at a heating rate of 2°C/min and a frequency of 1 Hz in extension mode from 50 to 350°C.

10. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was performed on a Perkin-Elmer Series 7 instrument. TGA data were utilized to determine 5 percent weight loss values prior to any DSC analyses. The maximum temperature used for DSC was 50°C less than the 5 percent weight loss temperature. Samples were in film form, 5-10mg each, and were heated at a rate of 10°C/minute to yield information on the glass transition temperature of the material.

11. Atomic Force Microscopy

Tapping mode AFM performed with a Digital Instruments Dimension 3000, using micro-fabricated cantilevers with force constants of approximately 40 N/m. The ratio of amplitudes which are used in feedback control was adjusted to 0.6 of the free air amplitude for all the reported images. All samples were dehydrated at 80 °C for 24 hr under vacuum conditions. The samples were then imaged immediately in a relative humidity of about 35%.

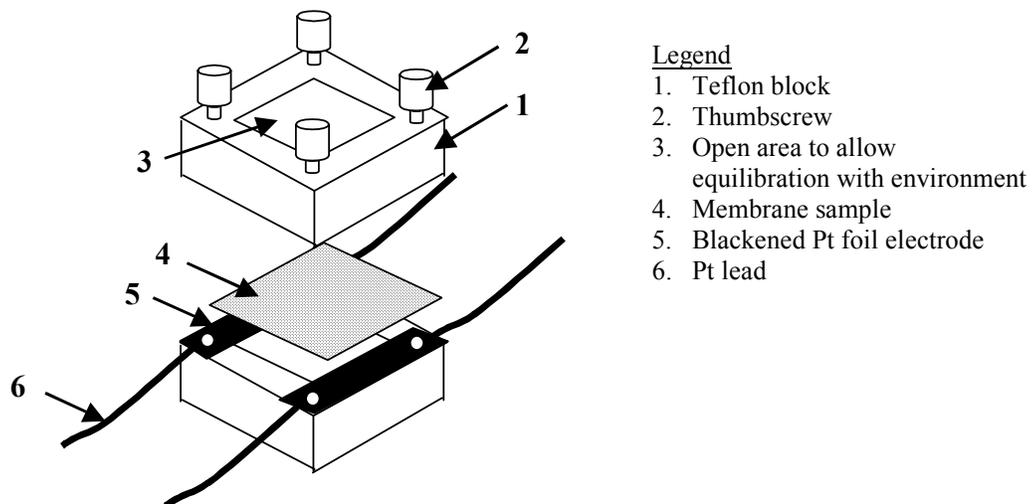


Figure 3.13: Conductivity Cell

Chapter IV

Results and Discussion

A. Introduction

This section presents and discusses the results obtained in this research on a new sulfonated monomer, 3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone (SDCDPS), and the homopolymer and copolymers that incorporated SDCDPS into their backbone structure. Both random and segmented block copolymers were synthesized that contained a controlled molar quantity of SDCDPS, to generate a set of systematic compositions. Sulfonated poly (phenylene sulfide sulfones) (PPSS) and poly (arylene ether sulfones) (PAE) were investigated as new materials for proton exchange membrane applications in hydrogen and methanol fuel cells. These two classes of polymers are noted for their excellent aqueous chemical resistance and thermo-oxidative stability making them suitable for the harsh acidic oxidizing environment of a proton exchange membrane fuel cell. Unsulfonated homopolymers were synthesized as control materials for the novel sulfonated copolymers. Characterization of the homopolymers and copolymers allowed identification of key performance capabilities in the areas of water sorption, phase separation and conductivity. These three metrics are of primary importance when polymers are utilized as proton exchange membranes in hydrogen or methanol fuel cells. A detailed discussion of the novel materials and their characterization is contained herein.

B. Monomer Synthesis

1. 4, 4' -Dimercaptodiphenylsulfone

Synthesis of 4,4'-dimercaptodiphenylsulfone (DMDPS) was achieved via a one step reaction shown in figure 4.1. Commercially available 4,4'-dichlorodiphenylsulfone was recrystallized from toluene and added to the reaction flask along with potassium carbonate and sodium hydrosulfide to facilitate a nucleophilic aromatic substitution reaction. The product was isolated by precipitation with HCl and redissolved in deionized water containing a slight stoichiometric excess of potassium carbonate. The last two steps were repeated three times to generate a yield of nearly 70 percent. The dried and purified product was dissolved in deuterated dimethylsulfoxide and analyzed by ^1H and ^{13}C NMR for structural confirmation as shown in figures 4.2 and 4.3.

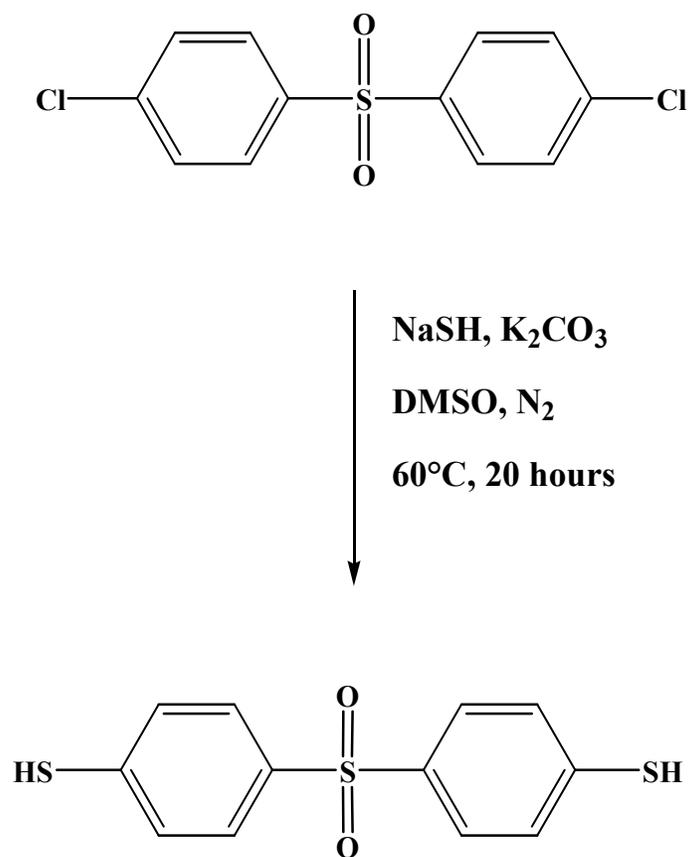


Figure 4.1: Synthesis of 4,4'-Dimercaptodiphenylsulfone

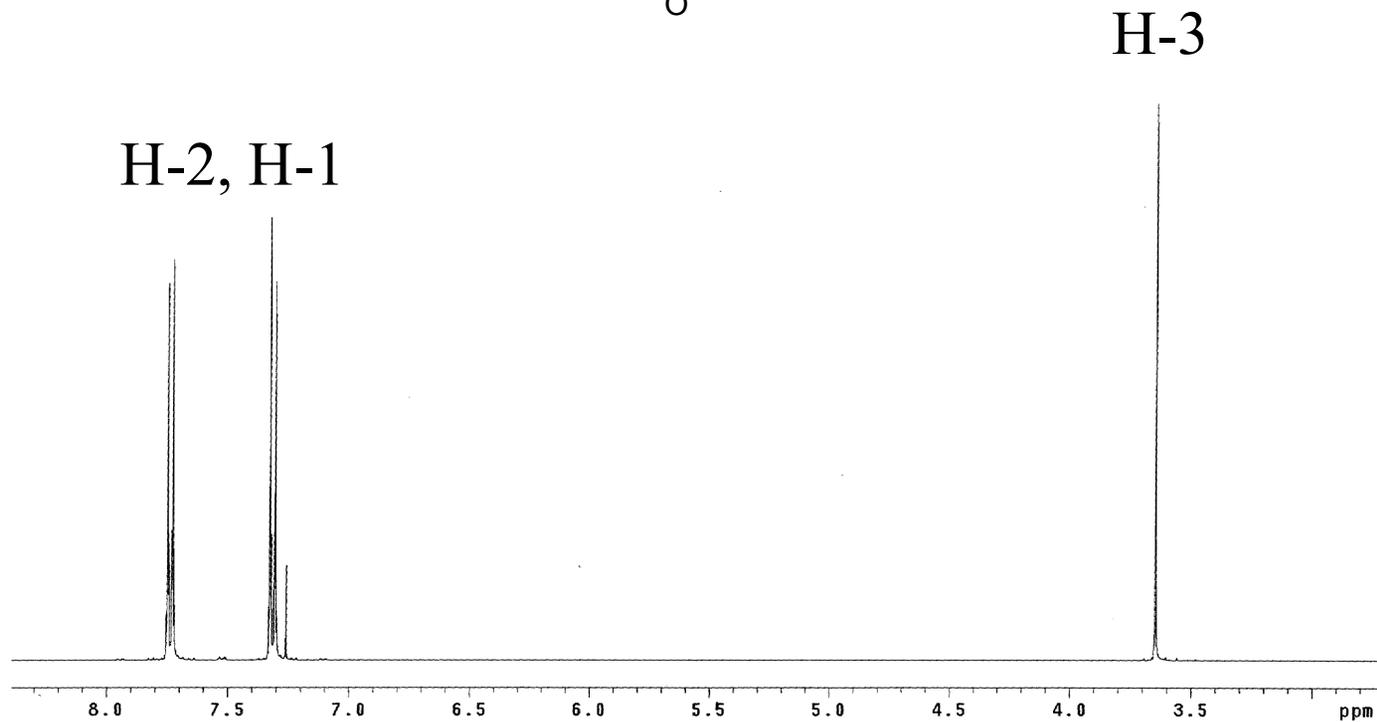
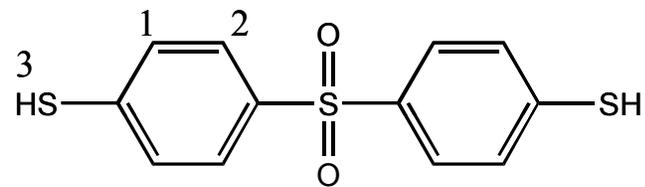


Figure 4.2: ¹H NMR of 4,4'-dimercaptodiphenylsulfone in CDCl₃

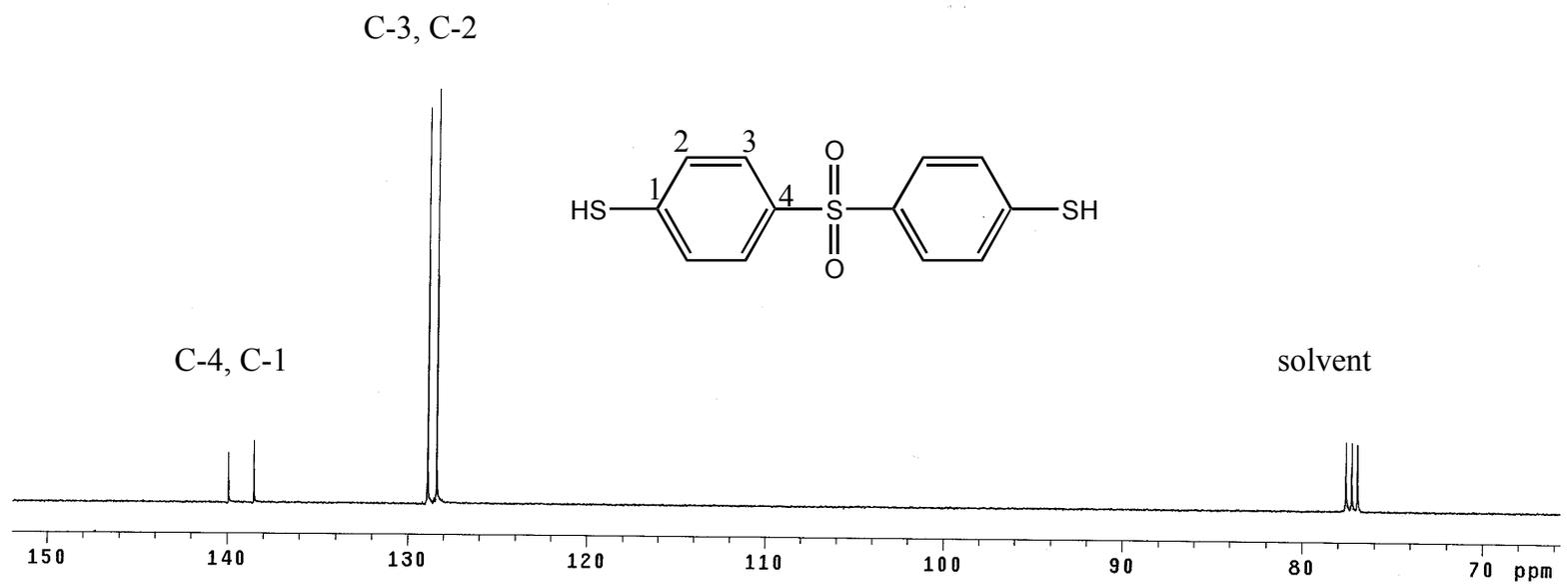


Figure 4.3: ^{13}C NMR of 4,4'-dimercaptodiphenylsulfone in CDCl_3

2. 3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone

Synthesis of 3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone (SDCDPS) was achieved in a one step electrophilic aromatic substitution reaction, shown in figure 4.4. First, 4,4'-dichlorodiphenylsulfone (recrystallized from toluene) was added to the reaction flask along with fuming sulfuric acid containing approximately 27 percent SO₃ to facilitate an electrophilic aromatic substitution reaction. The sulfonic acid functionalized product was isolated by “salting-out” with sodium chloride, titrated with sodium hydroxide to quantitatively form the sodium sulfonate and again salted out to isolate the product, SDCDPS. This procedure was developed after it was determined that isolation of the sulfonic acid functionalized product with sodium chloride resulted in less than quantitative formation of the sodium salt. The dried product was dissolved in deuterated dimethylsulfoxide and analyzed by ¹H NMR for structural confirmation, as shown in figure 4.5, which was achieved by comparison of integrations of the labeled proton signals. Elemental analysis was performed by Galbraith Labs and carbon, hydrogen, sulfur and sodium mass percentages were confirmed as shown in figure 4.6. Further characterization by fast atom bombardment mass spectrometry successfully identified the parent-ion at 467 Daltons (489.83-22.97 Na⁺).

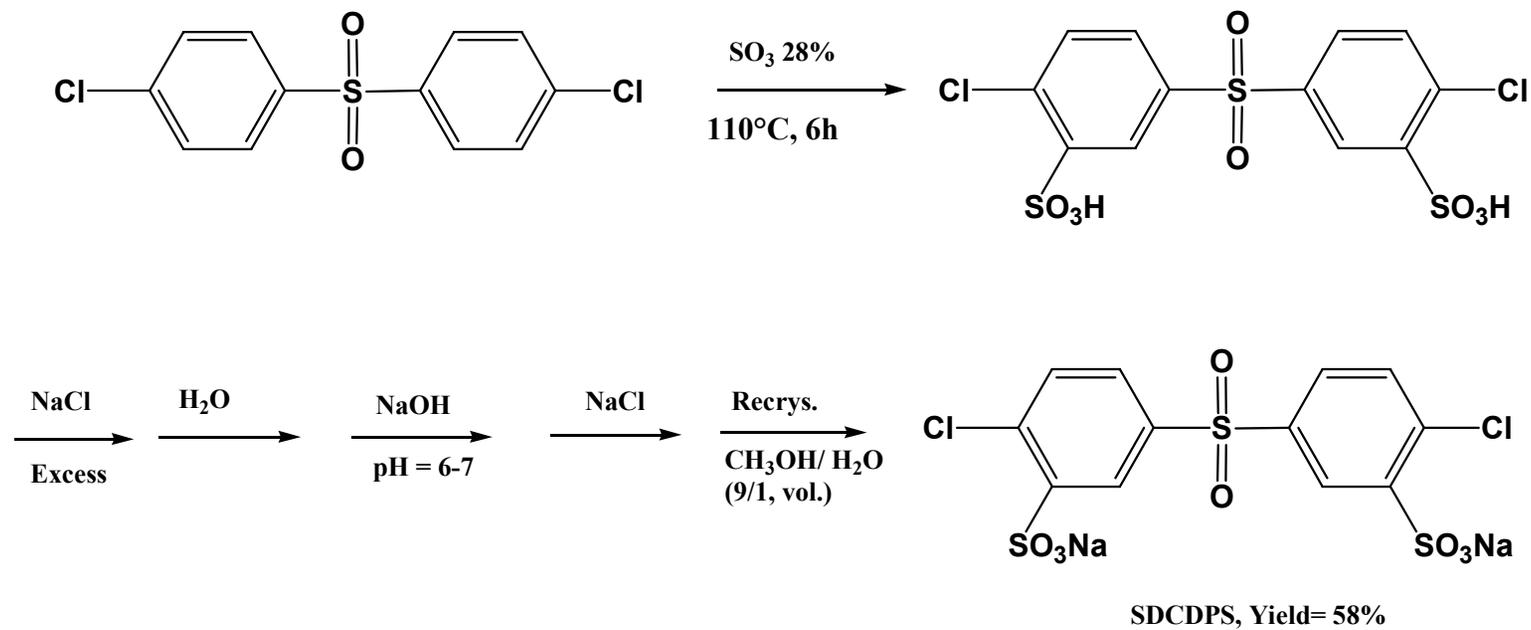


Figure 4.4.: 3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone

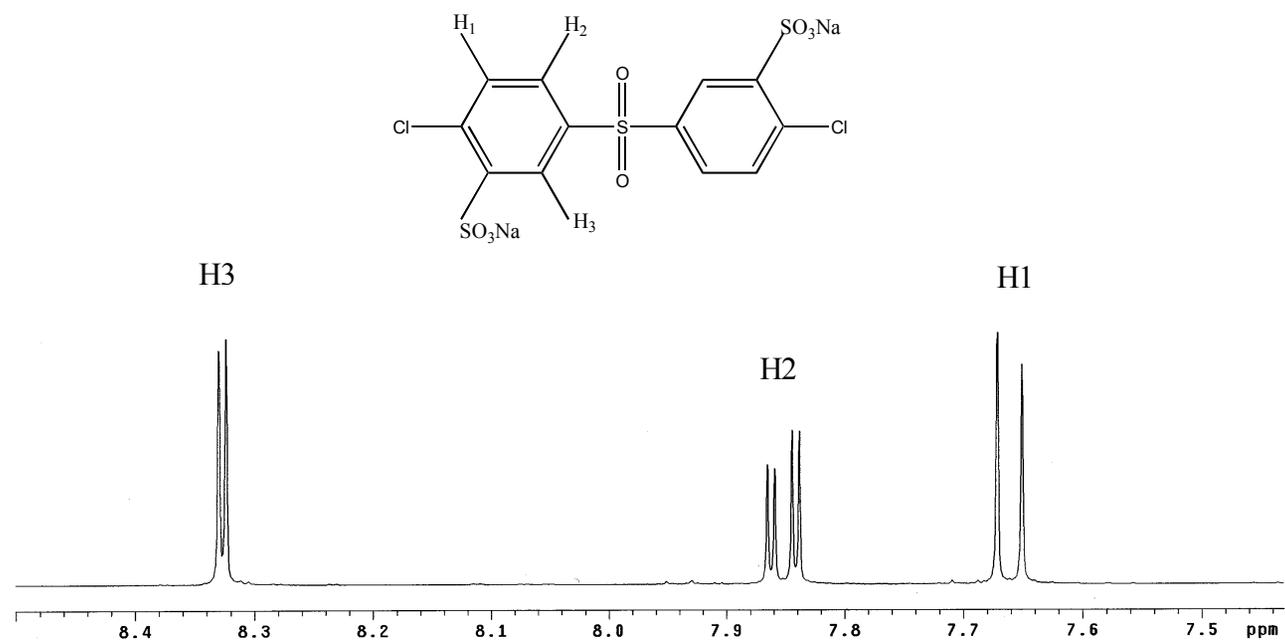


Figure 4.5: ^1H NMR of SDCDPS in d_6 -DMSO

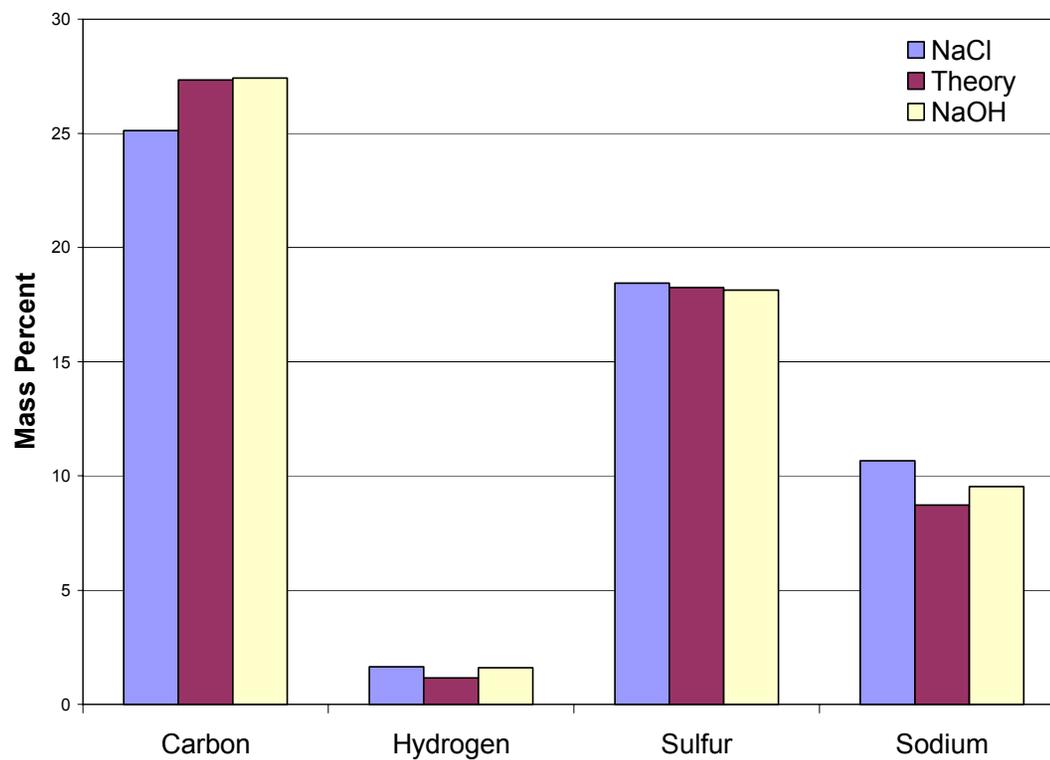


Figure 4.6: Elemental analysis results for SDCDPS showing results of product isolation with NaCl (left) versus titration with NaOH, followed by isolation with NaCl (right), as compared to theory (center)

C. Synthesis of Sulfide Sulfone Homopolymers and Copolymers

1. Synthesis of a Poly (phenylene sulfide sulfone) Homopolymer

As mentioned previously, poly (phenylene sulfide sulfones) (PPSS) are noted for their excellent chemical resistance and thermo-oxidative stability.¹³⁴ Early synthetic techniques on the related material, poly (phenylene sulfide) were complex and involved high temperatures and pressures.¹³⁵ A more facile synthetic method towards PPSS was recently developed at Virginia Tech, utilizing established step-growth polymerization techniques. This approach necessitated synthesis of a new monomer, DMDPS, described above. These new systems demonstrated thermo-oxidative stability similar to commercial PPSS systems; however, with careful control of endgroups, thermal stability increased.¹³⁶ This same approach was used in the synthesis of unsulfonated PPSS homopolymers (figure 4.7) to generate both a control material and a set of reaction conditions that could be applied to future sulfonated systems. DMDPS and DCDPS were added to a round bottom flask along with a 1.15 molar equivalents of potassium carbonate as compared to DMDPS. A sufficient amount of NMP was added to afford a reaction concentration of 30 weight percent solids. Xylene was added as an azeotroping agent at a 4:1 ratio of NMP to xylene and the reaction temperature was brought up to reflux at 155°C for 8 hours and then was raised to 170°C until completion. The product was filtered to remove salts, precipitated in a 40/60 mixture of water and methanol and vacuum dried at 160°C for several hours, redissolved in NMP at 15 weight percent and reprecipitated in methanol. The precipitate was filtered, vacuum dried at 180°C and submitted for GPC analysis which revealed an M_n of 53000g/mol.

¹³⁴ Campbell, R. W.; To Phillips Petroleum Co.; U. S. 4,016,145; 1997

¹³⁵ Hill Jr., H. W.; Brady, D. G. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Grayson, M., Ed.; Wiley: New York, 1982; Vol. 3, p 793.

Geibel, J. F.; Campbell, R. W. In *Comprehensive Polymer Science: Step Polymerization*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, 1989; Vol. 5, p 543.

¹³⁶ Liu, Y. N.; Bhatnagar, A.; Ji, Q.; Zhuang, H.; Geibel, J. F.; McGrath, J. E. *Polymer Preprints* **2000**, *38*, 109.

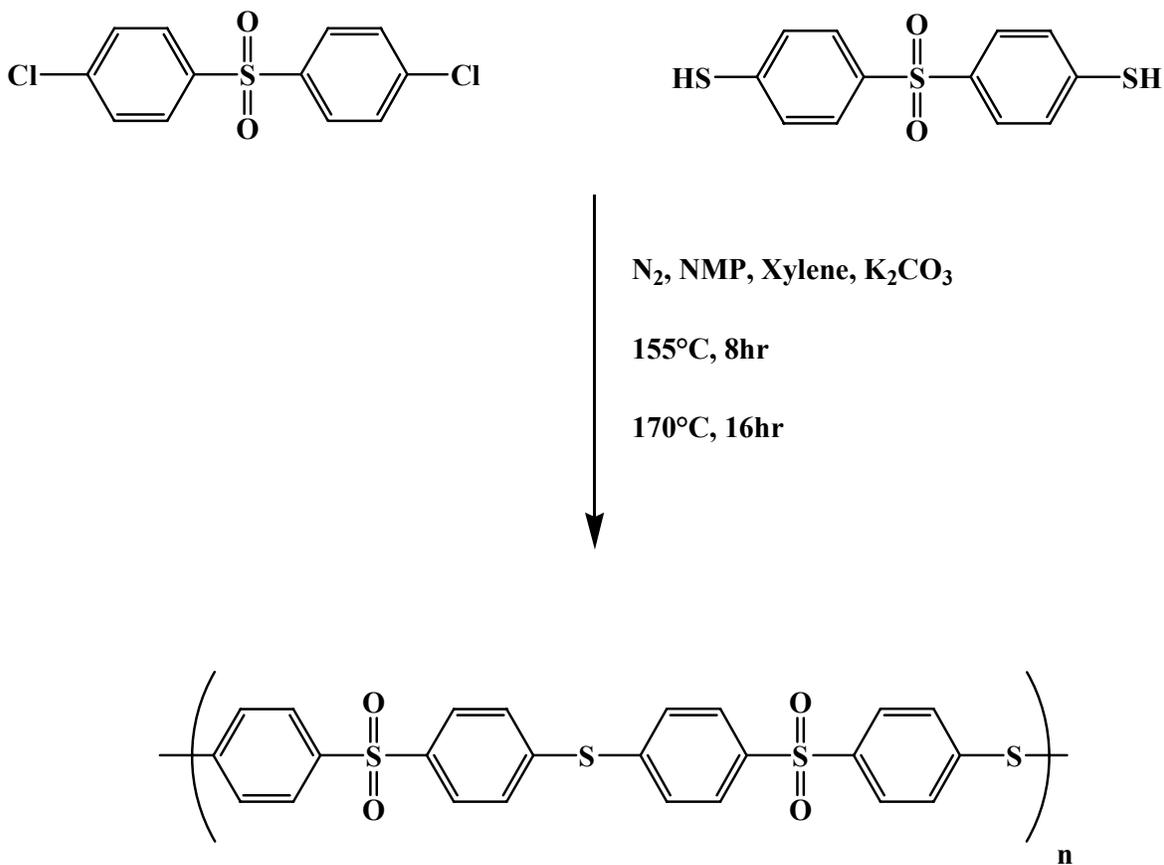


Figure 4.7: Synthesis of Poly (phenylene sulfide sulfones)

2. Synthesis of Sulfonated Poly (phenylene sulfide sulfone) Copolymers

Using the reaction conditions similar to those established for the unsulfonated control (section 4.C.1), a systematic series of sulfonated poly (phenylene sulfide sulfone) copolymers were synthesized with controlled degrees of sulfonation as shown in figure 4.8. Times, temperatures and concentration remained identical to those of the control, but certain aspects of the procedure were modified because of solubility difficulties with the sulfonated monomer. SDCDPS, DMDPS, DCDPS and potassium carbonate were added to the flask and dissolved in NMP at 100°C at a concentration of 30 percent solids. Once in solution, o-xylene was added as an azeotroping agent, the temperature was increased to the 155°C reflux temperature, and the reaction was allowed to proceed for 6 hours. The o-xylene was stripped from the reaction to allow the temperature to be increased to 180°C for an additional 16-22 hours. The polymers were filtered to remove salts and precipitated in a Waring blender containing isopropanol. Precipitation in methanol was attempted, but better results were achieved by using isopropanol, presumably due to its lower polarity. A series of three polymers was synthesized containing 10, 20 and 30 mole percent SDCDPS with the complimentary percentage of dihalide being comprised of DCDPS affording random sulfonated copolymers. Molecular weights capable of forming creasable films could not be achieved above 30 mole percent of SDCDPS presumably due to immiscibility that developed as the reaction proceeded beyond 8 hours. Even with the removal of the relatively non-polar azeotropic solvent xylene from the reaction, a heterogeneous solution could not be avoided.

Wang *et. al.* at Virginia Tech successfully synthesized sulfonated PPSS copolymers with higher degrees of sulfonation utilizing the more reactive¹³⁷ 4,4'-difluorodiphenylsulfone (DFDPS) and 3, 3', 4, 4'-disodiumsulfonyldifluorosulfone (SDFDPS) in place of the dichlorinated analogs, DCDPS and SDCDPS and synthesized a systematic series (0, 10, 20, 30, 40 and 60 mole

¹³⁷ Wang, F.; Mecham, J. B.; Harrison, W.; McGrath, J. E. *Polymer Preprints* **2000**, *40*, 180.

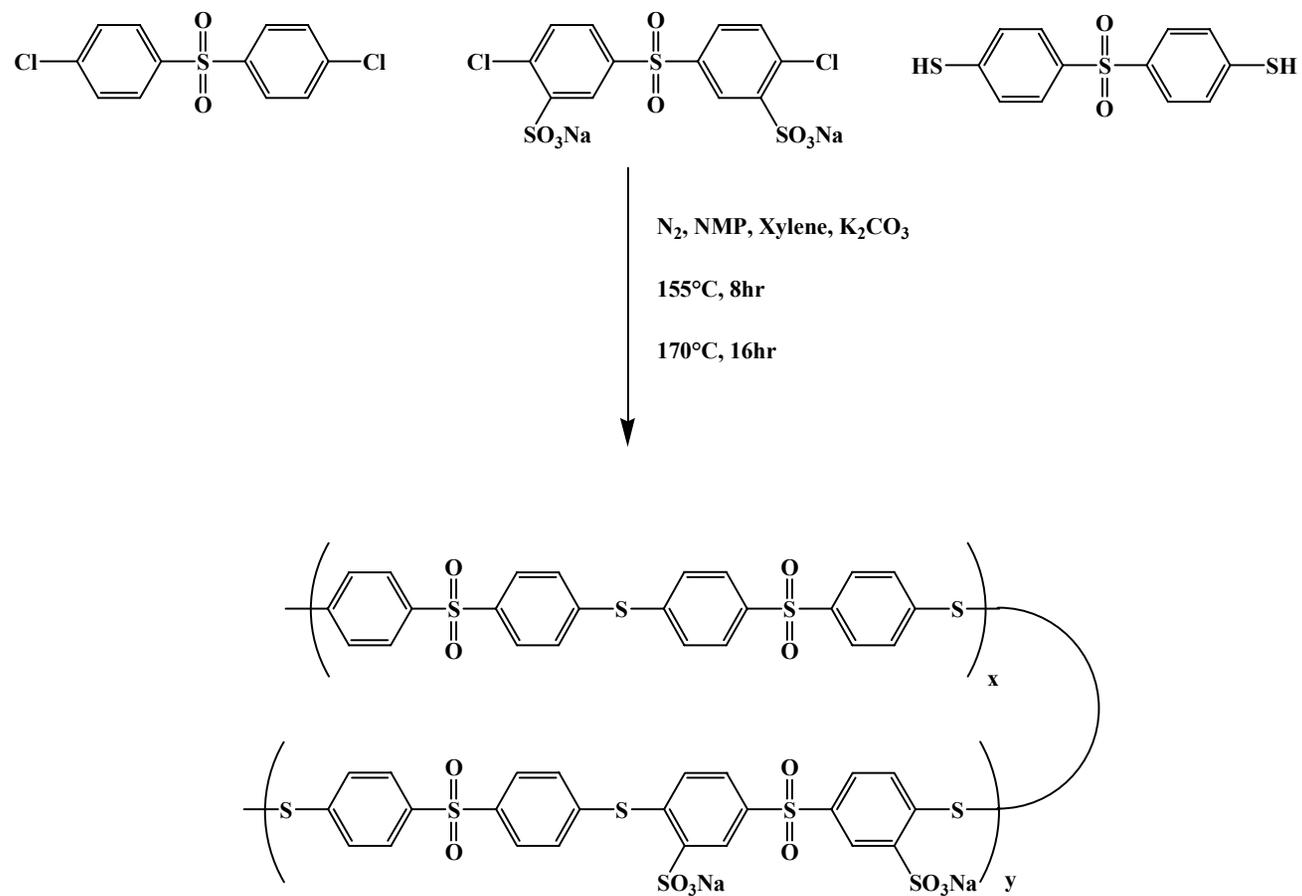


Figure 4.8: Synthesis of Sulfonated Poly (phenylene sulfide sulfones) (SPPSS)

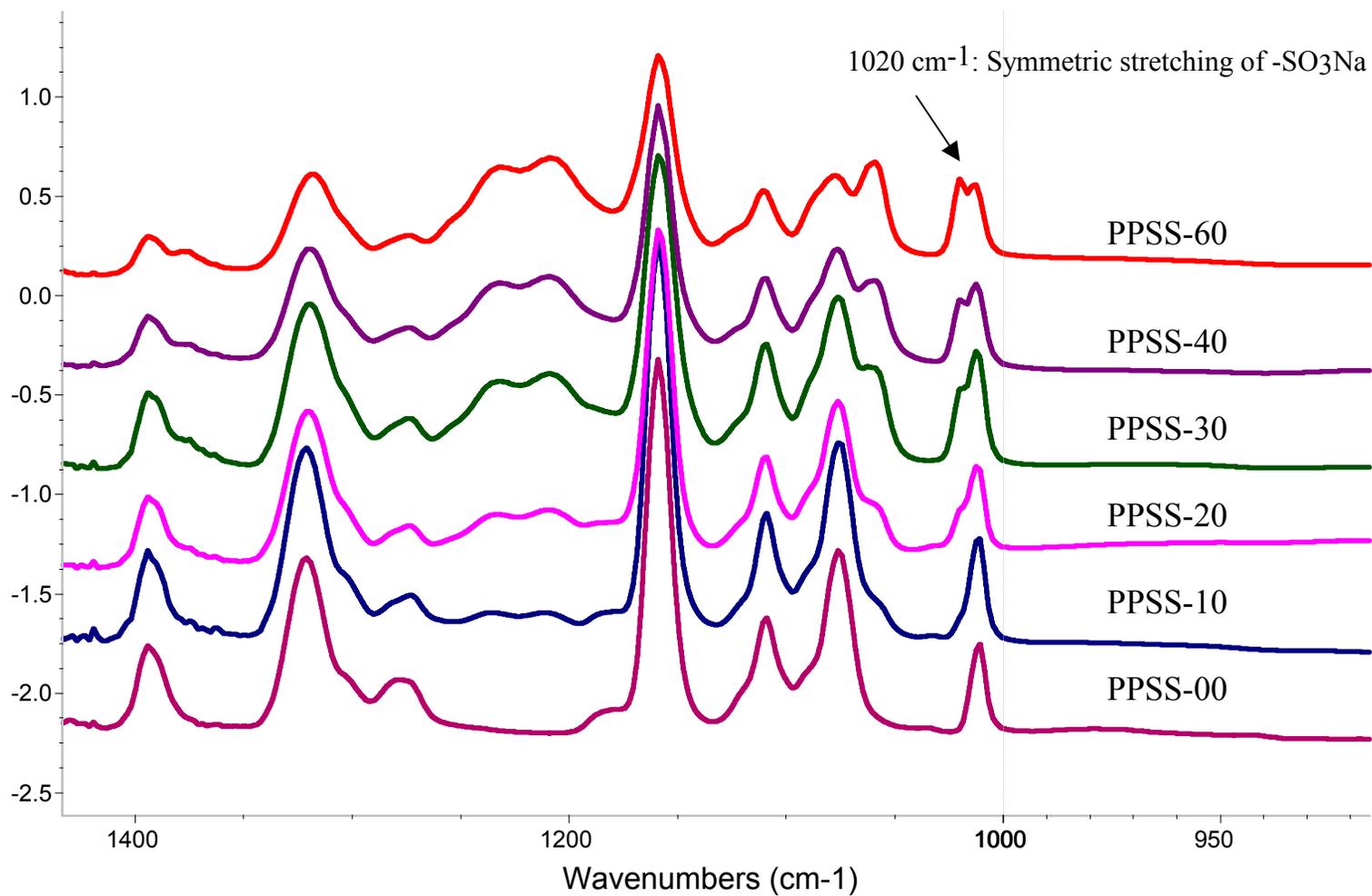


Figure 4.9: FTIR of Sulfonated PPSS synthesized from SDFDPS, DFDPS and Biphenol¹³⁸

percent SDFDPS) of sulfonated poly (phenylene sulfide sulfones), as shown in figure 4.9. FTIR measurements of this series revealed an increase in the size of the signal (at 1020 cm^{-1}) representing the SO_3Na vibration as shown in figure 4.9.

D. Biphenol-Based Homopolymers and Copolymers

1. Synthesis of Biphenol/4,4'-Dichlorodiphenylsulfone Poly (arylene ether)

A biphenol/DCPDS poly (arylene ether) homopolymer was synthesized as both a control and to establish reaction conditions for sulfonated random copolymer analogs. Biphenol, DCDPS and potassium carbonate were added to the reaction flask along with enough NMP to generate a concentration of 30 percent solids and toluene as the azeotroping agent. The reaction (figure 4.10) was heated to 155°C for 2 hours, after which a heterogeneous solution resulted. By raising the temperature to 190°C, a homogeneous solution was again formed and the reaction was allowed to proceed overnight, after which the salts were filtered off, and the solution was precipitated into a 50:50 mixture of methanol and water yielding fibrous polymer. After drying the product under vacuum for 8 hours at 200°C, GPC analysis revealed a number average molecular weight of 47,000 g/mol. Tough, creasable films were solution cast from dilute NMP concentrations of approximately 10 weight percent and vacuum dried at temperatures that ultimately reached 200°C.

The rationale behind applying biphenol-based poly (arylene ethers) (PAE) as novel proton exchange membrane materials is similar to that of the PPSS systems. As mentioned earlier, the excellent aqueous chemical resistance and thermo-oxidative stability that PAEs are known to possess make this system a natural choice as potential new PEM materials. Additionally, the relatively high glass transition temperature near 230°C, the lack of aliphatic hydrogens and lower methanol permeability than sulfonated perfluoro-based systems are all attractive characteristics when application as a PEM is considered. Typically, conditions inside the fuel cell include a pH that is near 1 and a high concentration of oxygen radicals. In cases where sulfonated perfluoro polymers are used in methanol fuel cells, they suffer from high methanol permeability, which can cause flooding of the cathode and reduce voltaic output, whereas PAEs have a much

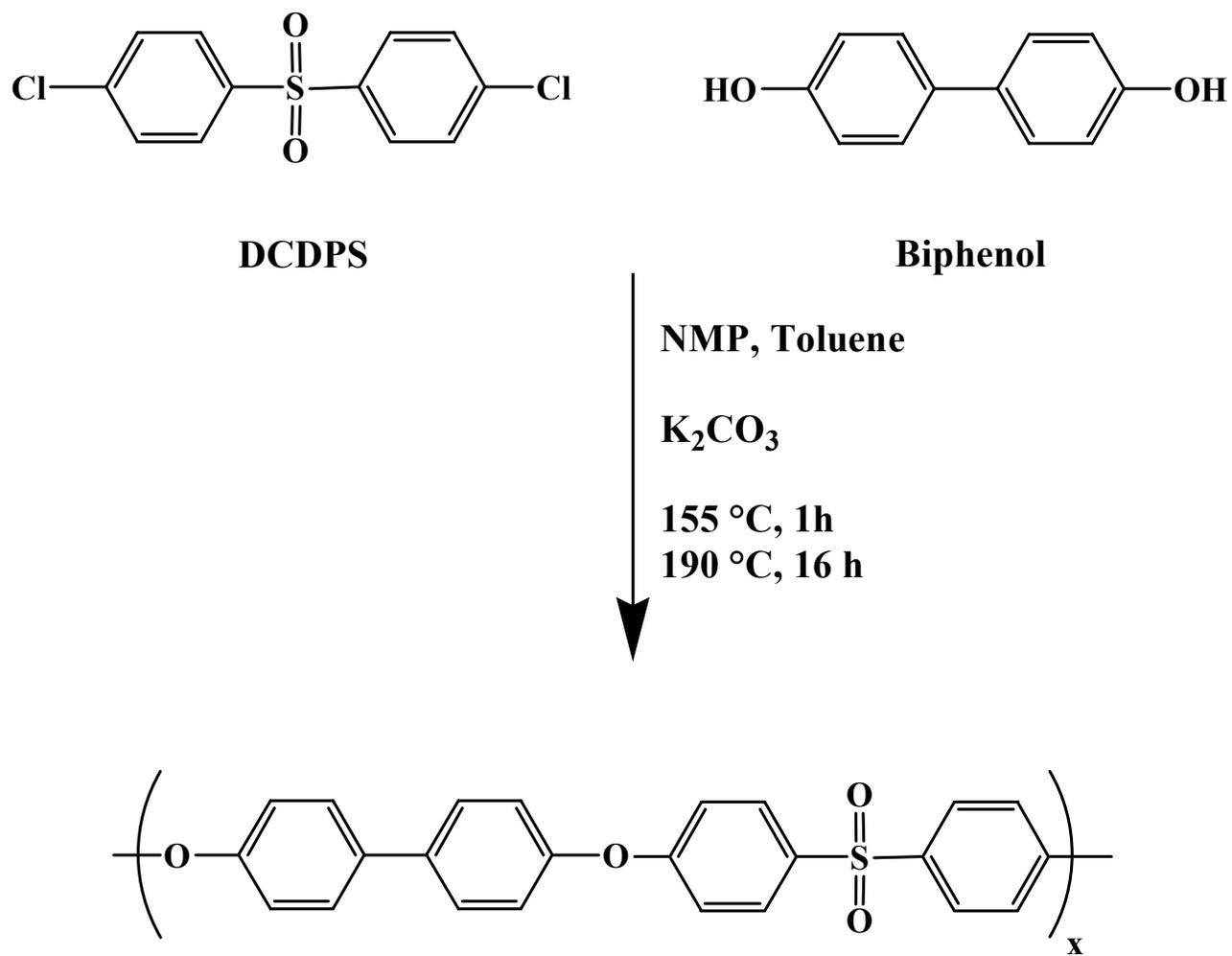


Figure 4.10: Synthesis of Biphenol/4,4'-Dichlorodiphenolsulfone

lower methanol permeability. The maximum service temperature of the sulfonated perfluoro- based PEMs is around 80°C which can cause problems as carbon monoxide is often present as an impurity in the fuel stream. By increasing the temperature to approximately 120°C, the reaction of carbon monoxide with the Pt anode, resulting in a drop in voltaic output, is minimized. This interaction can be reversed by increasing the cell temperature to nearly 150°C for a brief time, which would degrade the Nafion perfluorinated PEM, necessitating a costly, time-consuming rebuild of the fuel hardware and MEA.

2. Synthesis of Biphenol/3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone Poly (arylene ethers)

A systematic series of sulfonated biphenol/ SDCDPS PAEs containing degrees of sulfonation from 10 to 100 percent were synthesized using an approach analogous to the unsulfonated control material, as shown in figure 4.11 below. Unlike the similar sulfonated PPSS system, the reaction remained homogeneous once the ultimate temperature of 190°C was reached, regardless of the polymer's degree of sulfonation. Like the control polymerization, the reaction became heterogeneous after approximately an hour at 155°C, at which point the reaction temperature was increased to 190°C and a homogeneous solution was reestablished. When completed, the solution was filtered to remove salts, diluted to approximately 15 weight percent solids and precipitated in a Waring blender containing isopropanol. Initial attempts at identifying a suitable precipitation solvent revealed that methanol only worked well at degrees of sulfonation between zero and thirty mol percent. At degrees of sulfonation between thirty and fifty percent a stable latex dispersion resulted with methanol precipitation, while biphenol/SDCDPS PAEs higher degrees of sulfonation were actually methanol soluble, prompting the use of isopropanol. In fact, the 100 mole percent SDCDPS was so hydrophilic that it soluble in water.

The molecular weight of the sulfonated copolymers could not be characterized by GPC. Interaction of the ionic sites of the copolymers with the size exclusion columns

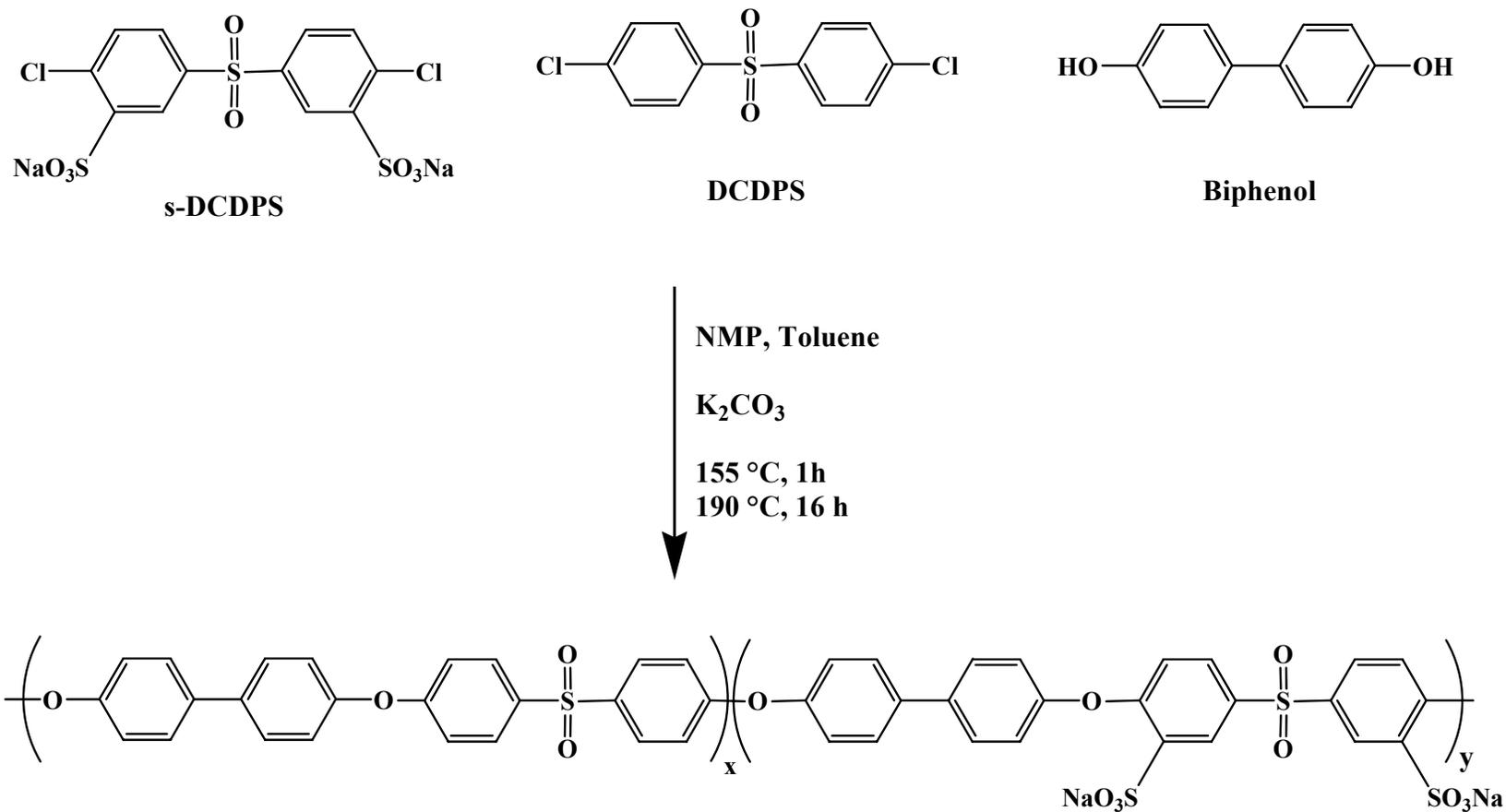


Figure 4.11: Synthesis of Biphenol/3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone Poly (arylene ethers)

Table 4.1: Intrinsic Viscosities and Percent Yield for
the Sulfonated Poly (phenylene sulfide sulfone) Copolymers

Samples	Monomers		Yield (%)	$[\eta]_{25^{\circ}\text{C}}^{\text{NMP}}$ (dl/g)
	SDCDPS	DCDPS		
PBPS-00	0	10	95	0.61
PBPS-10	1	9	93	0.73
PBPS-20	2	8	92	0.91
PBPS-30	3	7	90	1.1
PBPS-40	4	6	92	2.5
PBPS-60	6	4	93	3.2
PBPS-100	10	0	95	ND*

ND: Not Determined

resulted in extended retention times, which distorted the molecular weight calculations. Intrinsic viscosity was used to estimate the molecular weights of the copolymers. The intrinsic viscosity of copolymers increased with increasing ionic content as shown in table 4.1.

Water sorption experiments revealed the expected increase in grams of water uptake / gram of polymer as the mole percent of SDCDPS was increased and will be detailed in another section. This behavior has been observed with other random copolymers systems in the literature.¹³⁸ In random copolymer systems, as water sorption increases, swelling results in diminished mechanical properties. Although Nafion sulfonated perfluoro polymer does have certain performance limitations, it is very stable in terms of volume change with water uptake. This is illustrated in figure 4.12, where the water sorption behavior of poly (arylene ether sulfone), poly (arylene ether phosphine oxide) and poly (ether ether ketone) sulfonated polymers is compared and shown as a function of the degree of sulfonation. As this is currently the state of the art PEM material, it's likely that fuel cell systems that utilize Nafion will not be able to accommodate new PEM systems that swell in response to water uptake. In response to the dimensional instability of the random sulfonated PAE system, studies were initiated to synthesize a sulfonated segmented block copolymer system, which is detailed in a following section.

¹³⁸ Zaidi, M. J.; Mikhailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S. *J. Membrane Sci.* **2000**, *17*, 173.

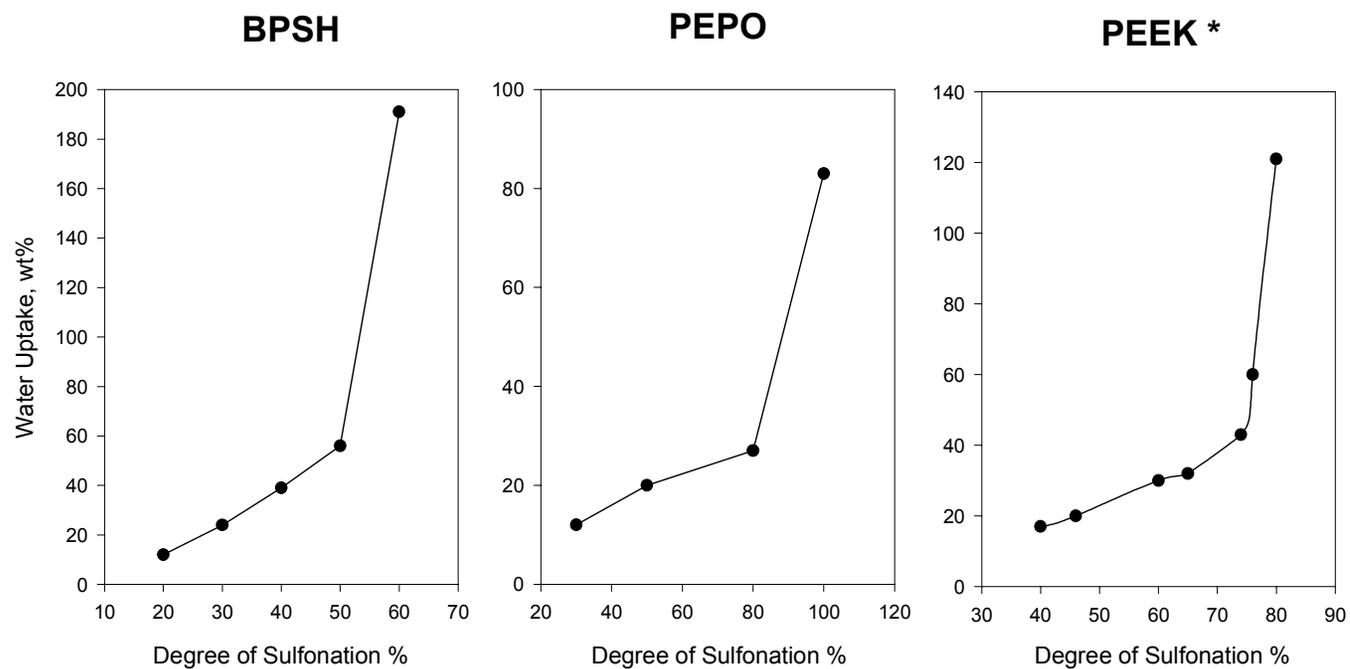


Figure 4.12: Influence of Degree of Sulfonation on Water Uptake of Polymer Membranes.

BPSH repeat unit contains two sulfonic acid groups, while PEPO contains one.

PEEK was post-sulfonated and the number of sulfonic acid groups per repeat unit was not reported

* see footnote 139

E. Biphenol-based Poly (arylene ethers) of Controlled Molecular Weight

1. Controlled Molecular Weight Biphenol-based Poly (arylene ethers) with Telechelic Primary Amine: Unsulfonated Control Polymer

Studies on the sulfonated random biphenol/DCDPS copolymers revealed that high molecular weight could be obtained at all compositions, including the 100 percent SDCDPS system. Although high molecular weight was attainable, the mechanical properties of the 100 percent SDCDPS system were poor and the material was water soluble, while lower ionic concentrations of 60 percent or greater underwent large volume changes. This led to the extension of this system as the hydrophilic ionic block in a hydrophilic/hydrophobic segmented block copolymer.

It has been reported that the Nafion systems form a two-phase membrane, with the majority of the polymer present in a separate phase from that of the ionic aggregates.¹³⁹ Small Angle X-ray Scattering (SAXS) studies by Heaney indicated that the size of the ionic aggregates was dependent upon the water content of the membrane, with the average size fluctuating approximately 20 percent from a dry state to full hydration. On average, the aggregates were 3 to 5 nm in diameter with a short-range order, or Bragg spacing, of 3 to 10 Angstroms. This result is supported by evidence for the same phenomenon by earlier SAXS studies conducted by Fujimara *et.al.*¹⁴⁰ In this study, a core-shell model was postulated, with the core consisting of the ionic aggregates, surrounded by a relatively pure fluorocarbon shell. The core-shell clusters are presumed to be distributed randomly throughout an intermediate phase containing fluorocarbon and isolated sulfonic acid sites.

Based on the experimental evidence that Nafion forms a two-phase membrane, a segmented block copolymer approach to segmented hydrophilic/hydrophobic segmented copolymers was initiated (figure 4.13). Prior to synthesis of a controlled molecular

¹³⁹ Heaney, M. D.; Pellegrino, J. *J. Membrane Sci.* **1989**, *47*, 143.

¹⁴⁰ Fujimara, M.; Hashimoto, T.; Kawai, H. *Macromolecules* **1982**, *15*, 136.

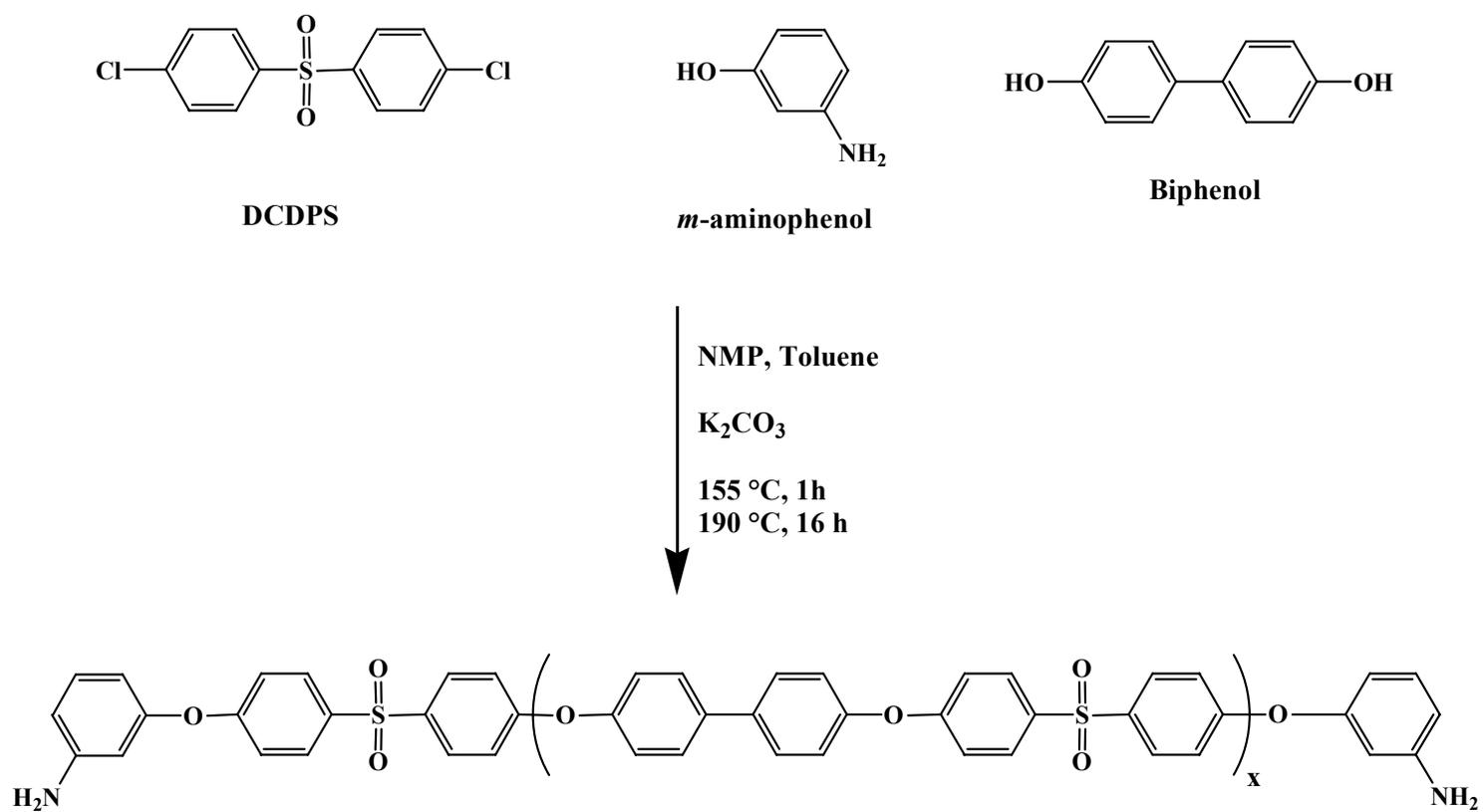


Figure 4.13: Controlled Molecular Weight Biphenol-based Poly (arylene ethers) with Telechelic Primary Amine

weight sulfonated poly (arylene ether), an unsulfonated control was synthesized. As previously mentioned, the chemical resistance and thermo-oxidative stability of the poly (arylene ethers) are well established making them excellent candidates for PEM in a fuel cell. These amine terminated ionic polymers could then be utilized as macromonomers in a second step with monomers that polymerize into a hydrophobic segment resulting in enhanced mechanical properties and decreased swelling in aqueous environments as compared to analogous random copolymers of the same backbone structure.

A control polymerization was conducted to assess the accuracy of ^1H NMR (figure 4.14) versus GPC for number average molecular weight determination (M_n). As was discussed earlier, our current GPC system cannot be used to determine the M_n of ion-containing polymers since the ionic functionalities interact with the separation columns, increasing retention times, which results in invalid data. The control poly (arylene ether) was targeted at 10,000 g/mol. The synthetic procedure is discussed in the experimental section of this dissertation and is similar to the approach used in earlier research at Virginia Tech.¹⁴¹ DCDPS was added to the reaction along with biphenol, potassium carbonate and freshly sublimed *m*-aminophenol. NMP was added to afford a concentration of 30 percent solids along with toluene and the reaction temperature was increased to 155°C. After approximately one hour, the reaction became heterogeneous, at which point the temperature was increased to 190°C and a homogenous solution was reestablished. Once finished, the polymer was precipitated into a 50:50 mixture of methanol/water. The polymer was dried for 8 hours in a vacuum oven at 200°C after which samples were prepared for ^1H NMR and GPC in deuterated DMSO and NMP respectively. These analyses revealed that the target molecular weight of 10,000 g/mol was successfully achieved.

¹⁴¹ Jurek, M.; McGrath, J. E. *Polymer* **1989**, *30*, 1559.

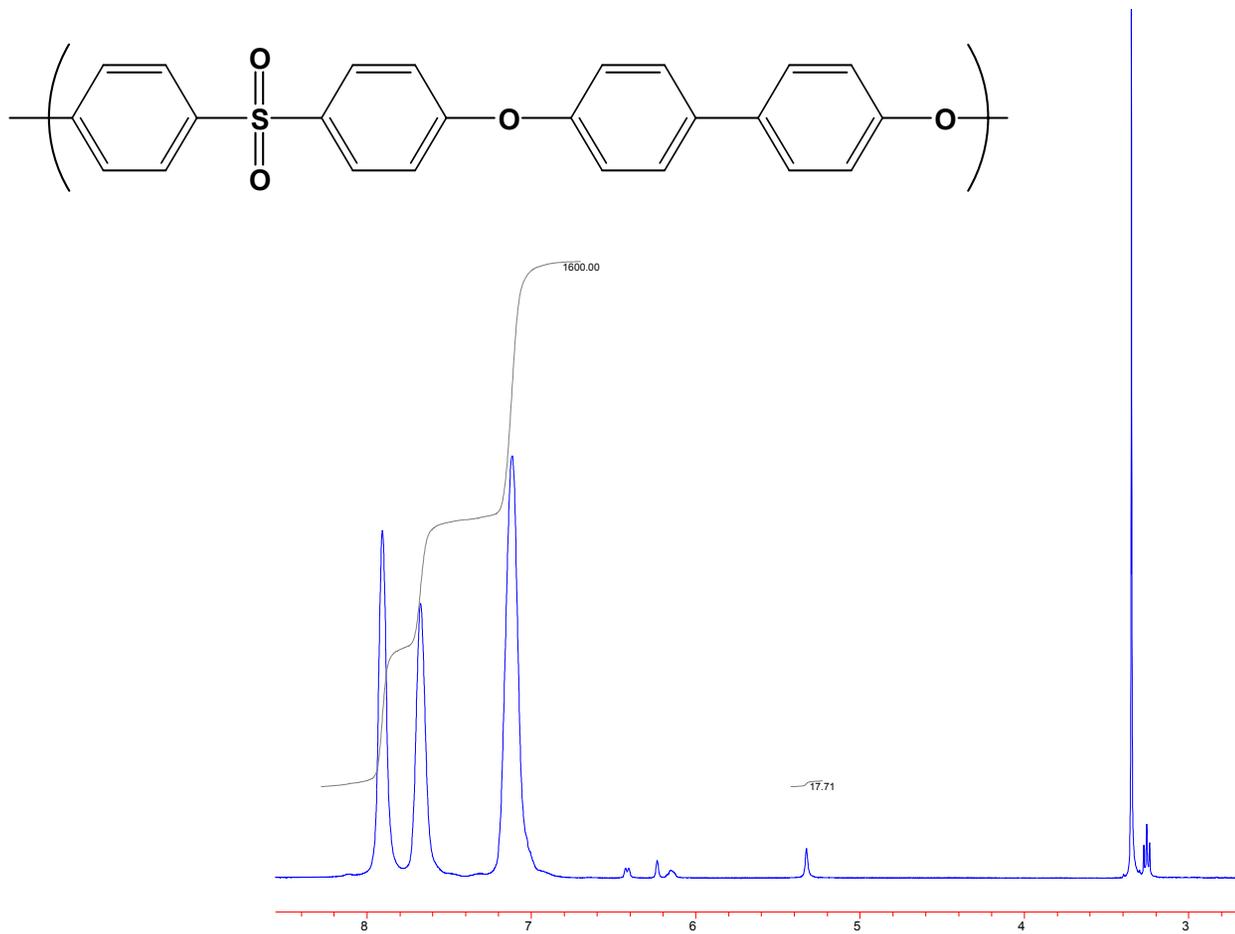


Figure 4.14: ¹H NMR of Biphenol/DCDPS control showing amine proton peak at 5.3ppm and phenyl ring protons at 7.1, 7.65 and 7.9ppm

2. Controlled Molecular Weight Biphenol-based Sulfonated Poly (arylene ethers) with Telechelic Primary Amine Functionalization

Using the synthetic approach that was established by the unsulfonated control polymerization, a series of controlled molecular weight poly (arylene ethers) containing 100 mole percent SDCDPS were synthesized as shown in figure 4.15. Number average molecular weights of 10,000, 20,000 and 30,000 grams per mole were targeted and successfully synthesized. Characterization of molecular weight was estimated by intrinsic viscosity measurements (table 4.2) at room temperature in NMP. A more quantitative evaluation of M_n was achieved by integration of selected peaks of proton NMR measurements performed in deuterated DMSO at room temperature as shown in figure 4.16. The telechelic primary amine functionality allowed the incorporation of these polymers as ionic blocks in segmented poly (imide) poly (arylene ether sulfone) block copolymers. The synthesis and characterization of these segmented block copolymers is discussed in the following sections.

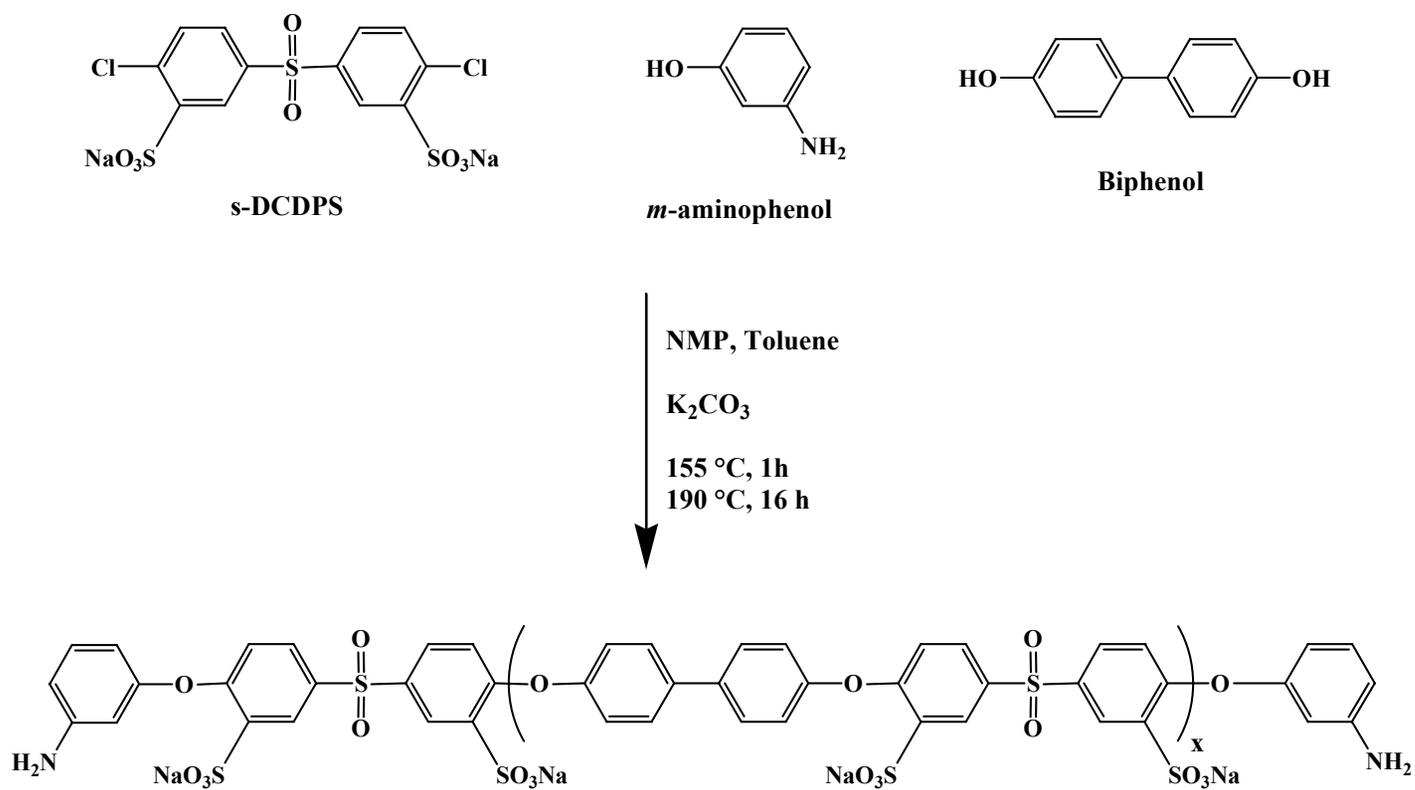


Figure 4.15: Controlled Molecular Weight Biphenol-based Sulfonated Poly (arylene ethers) with Telechelic Primary Amine Functionalization

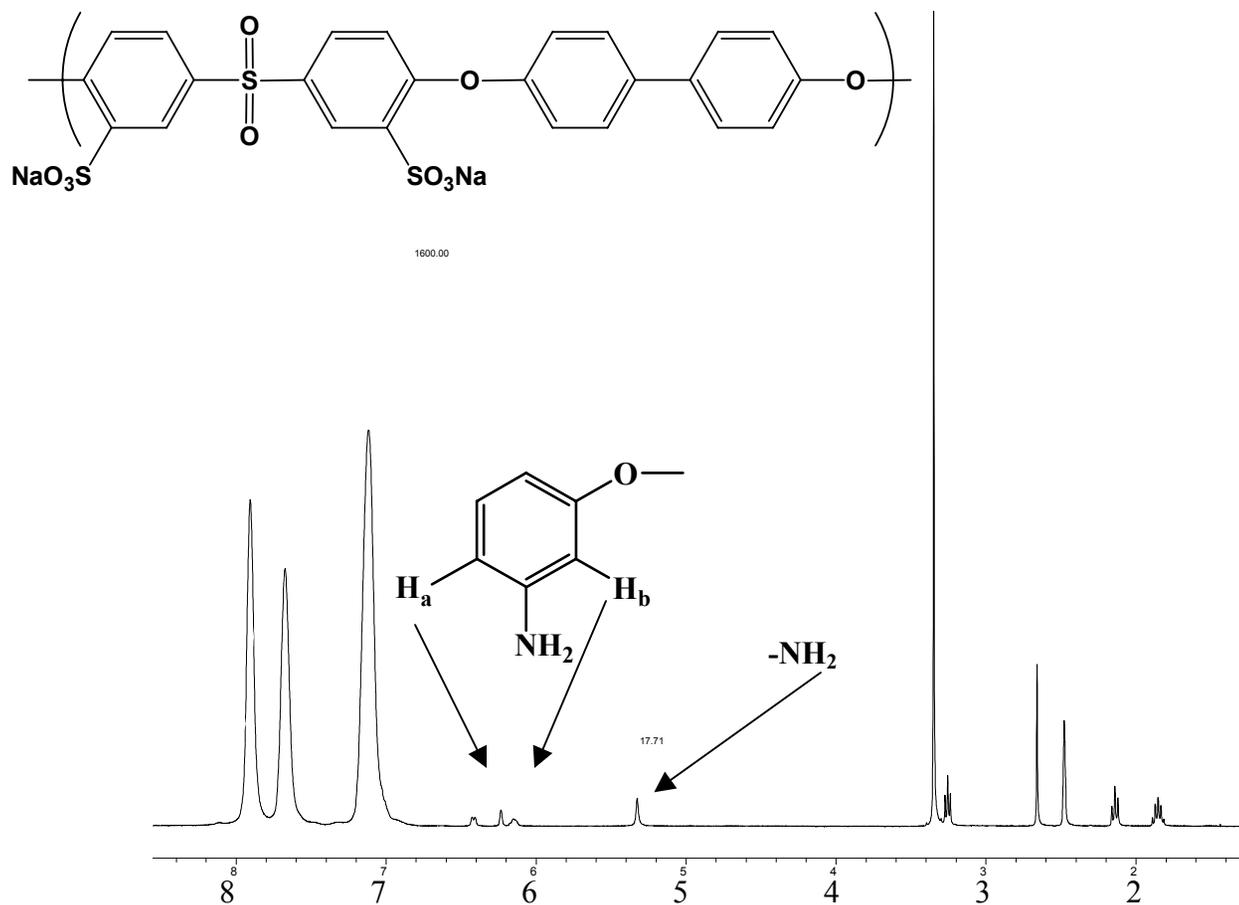


Figure 4.16: ¹H NMR of a 20,000 g/mol Primary Amine terminated Biphenol/SDCDPS Poly (arylene ether sulfone). Integrations of the amine protons at 5.3ppm or the aromatic protons ortho to the amine on the *m*-aminophenol moiety, at 6.15 and 6.2ppm, can be compared to integrations of the backbone protons at 7.1, 7.65 or 7.85ppm to provide and estimate of M_n .

Table 4.2:

^1H NMR M_n Values for Aminophenyl Functional
Controlled Molecular Weight BP/SDCDPS-Based Poly(arylene ether)s

Polymer, Theory	M_n by NMR Analysis
Control 10,000 g/mol	13500 g/mol
10,000 g/mol	8100 g/mol
20,000 g/mol	18000 g/mol
30,000 g/mol	29200 g/mol

F. Segmented Block Poly (imide) Poly (arylene ether) Copolymers

1. Bisphenol-A/Oxydianiline Poly (imide) Sulfonated Poly(arylene ether) Copolymers

Segmented polyimide/sulfonated poly (arylene ether) (PAE) copolymers were synthesized in an attempt to improve mechanical properties at high temperatures and high degrees of sulfonation. This approach also allows control of water sorption and swelling via variation of composition. The hydrophobic poly (imide) segments provide mechanical stability, while the sulfonated PAE segments provide the ion exchange sites needed for proton exchange membrane applications.

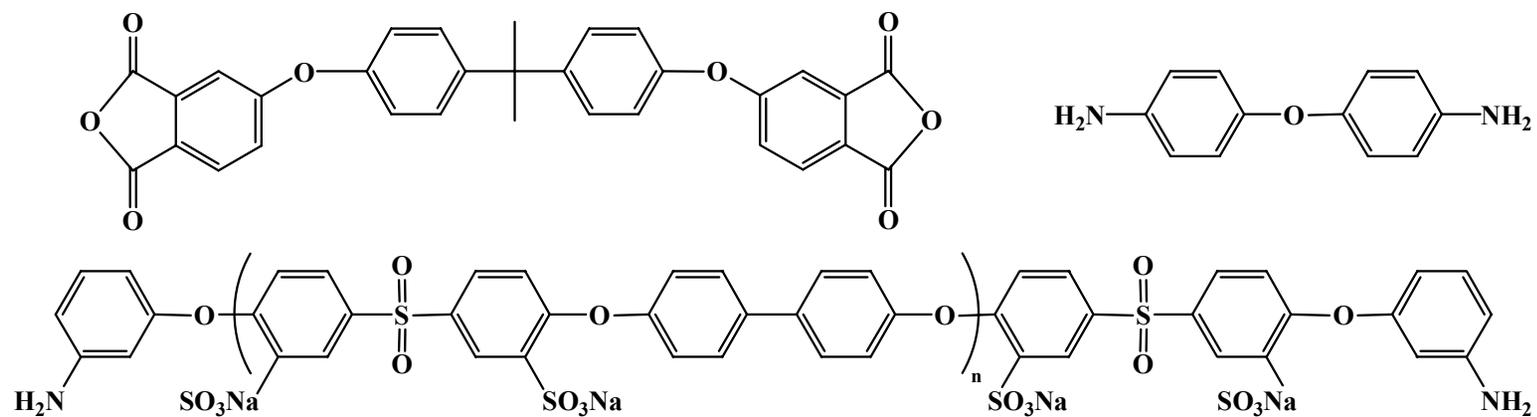
a. Ester-Acid Approach

This method involves ring opening of the dianhydride with refluxing anhydrous ethanol to yield the ester-acid derivative. In a second step, the monomeric diamine (e.g. 4,4'-oxydianiline) is added, along with the primary amine terminated poly (arylene ether) (SPAЕ) and NMP as illustrated in 4.17. Additionally, *o*-dichlorobenzene was added as an azeotropic agent to remove the water condensate that is formed as the amic acid cyclizes to form the imide linkage. As the concentration of the ionic segment was increased, the formerly homogeneous reaction mixture began to increase from a slightly hazy to an opaque heterogeneous reaction mixture. High molecular weight, film-forming polymers could not be achieved at degrees of sulfonation greater than 50 mole percent. For this reason, a different approach that involved the thermal imidization of the poly (amic acid) precursor was used to avoid the need for an azeotropic solvent.

b. Poly (amic acid) Approach

The thermal imidization of the poly (amic acid) precursor to the polyimide (figure 4.18) is conducted at room temperature in NMP. This method avoids the need for an azeotropic solvent as the condensation byproduct is removed at high temperature in a vacuum oven. In this particular case, the sulfonated poly (arylene ether) was dissolved in the reaction flask in NMP at 100°C to speed the process. The solution was then cooled to room temperature before the addition of 4,4'-oxydianiline (ODA) and bisphenol-A

tetracarboxylic dianhydride (BPADA). Once the reactant addition was completed, the amber solution was allowed to stir for 24 hours at room temperature. The viscous product was poured onto a glass plate and imidization was completed in a vacuum oven. Details of the thermal imidization process are described in section 3.F.1.b. Segmented copolymers synthesized using this method formed tough ductile films at degrees of sulfonation as high as 85 percent. Table 4.3 shows the results of intrinsic viscosity measurements for BPADA/ODA/SPAЕ segmented copolymers synthesized by either ester-acid or poly (amic acid) methods.



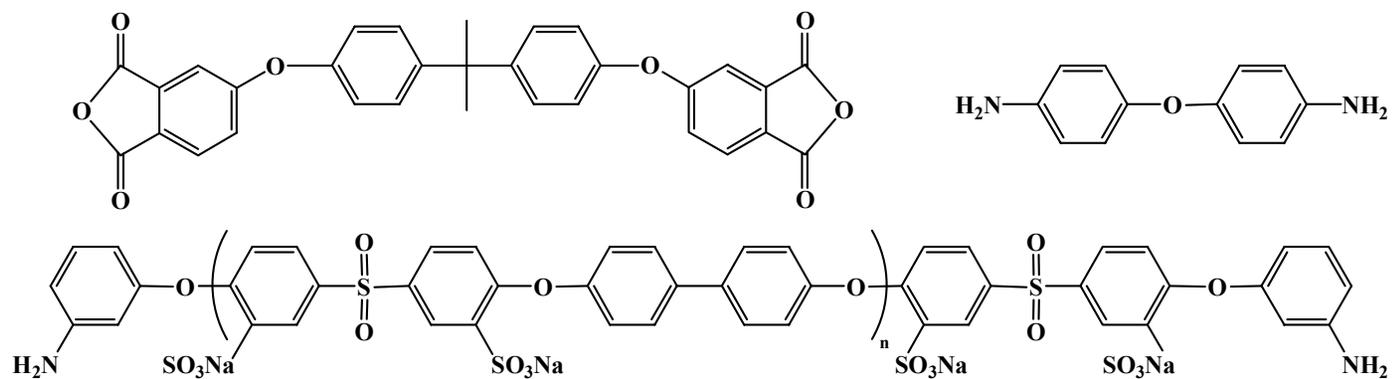
- 1) EtOH, NEt_3 110°C, 30 min
Strip off EtOH
- 2) NMP, *o*-Dichlorobenzene
165°C (internal temp) 6hr, 200°C 18 hr
- 3) Isolate with 100% 2-propanol, filter product
- 4) Dry under Vacuum, RT 3hr, 200°C 12hr



Figure 4.17: Synthesis of BPDA/ODA/SPAE Segmented Block Copolymer via Ester-Acid Approach

Table 4.3: Intrinsic Viscosity of Segmented BPADA/ODA Poly(imide)
Sulfonated Poly(arylene ether) Copolymers

<u>Mole Percent PAE</u>	<u>PAE</u> <u>M_n</u>	<u>Synthetic Route</u> Ester-Acid = EA Poly(amic acid) =PAA	<u>Intrinsic Viscosity</u> <u>(dL/g)</u> (NMP, 25 °C)
BPADA/ODA Control	0		1.0
35	10	EA	0.68
35	20	EA	0.83
50	10	EA	0.71
50	20	EA	0.79
65	10	PAA	1.15
65	20	EA	0.30
65	20	PAA	0.86
85	20	PAA	0.78



- 1) Add polyarylene ether; dissolve at 100°C in NMP
- 2) Cool to room temp
- 3) Add ODA/BPADA; stir for 24 hr at RT
- 4) Imidize under Vacuum; RT 12hr, 100°C 3hr, 200°C 2hr, 310°C 1hr



Figure 4.18: Synthesis of BPDA/ODA/SPAЕ Segmented Block Copolymer via Poly (Amic-Acid) Approach

2. 6FDA/Oxydianiline Poly (imide) Sulfonated Poly (arylene ether) Copolymers

a. Ester-Acid Approach

The ester acid approach was utilized initially with this system, using identical conditions to those illustrated in figure 4.17. This study was conducted in tandem with investigation of the BPADA/ODA system. It was realized that this synthetic approach was less than ideal, due to the heterogeneity that developed as the degree of sulfonation was increased above 50 mole percent, as described above.

b. Poly (amic acid) Approach

This method allowed the facile synthesis of a broader range of copolymer compositions while maintaining homogeneity throughout the course of the reaction. As discussed above and shown in figure 4.18, the poly (arylene ether) was dissolved in NMP at 100°C, after which the solution was allowed to cool before the addition of 4,4'-oxydianiline and 6FDA at room temperature. The reaction was stirred for 24 hours, resulting in a viscous solution, which was poured onto a glass plate and thermally imidized in a vacuum oven, the details of which are described in section 3.F.1.b. Table 4.4 shows the intrinsic viscosity results for the 6FDA/ODA/SPAE copolymers.

Table 4.4: Intrinsic Viscosity of Segmented 6FDA/ODA Poly(imide)
Sulfonated Poly(arylene ether) Copolymers

<u>Mole % PAE</u>	<u>PAE M_n</u>	<u>Synthetic Route</u> EA = Ester Acid Route PAA = Poly(amic acid) Route	<u>Intrinsic Viscosity</u> (<u>dL/g</u>) (NMP, 25°C)
6FDA/ODA Control	-	EA	1.5
35	10K	EA	0.56
35	20K	EA	0.71
50	10K	PAA	0.65
65	10K	PAA	0.69

G. Characterization of Copolymers

1. Thermal Analysis

a. Thermal Characterization of Poly (phenylene sulfide sulfone) Homopolymer and Sulfonated Random Copolymers

The introduction of sulfonate groups raises the glass transition temperature by increasing intermolecular interaction by pendant ions (i.e. an ionic effect) and by increasing chain unit bulkiness. Both effects hinder the rotational ability of the chains, thereby leading to the increased glass transition temperatures for the sulfonated polymers.

Sulfonated poly (phenylene sulfide sulfone) copolymers of various compositions, in both salt and sulfonic acid forms, were studied and compared for thermal weight loss behavior in a nitrogen atmosphere at a heating rate of 10° per minute as shown in figure 4.19 through 4.21. Copolymers containing lower degrees of sulfonation, and those that were in the salt form had better thermal stability. Additionally, a study of the stability of the 40 and 60 mole percent sulfonic acid functionalized PPSS copolymers revealed that the ionic moiety was stable in air at temperatures of up to 220°C for 30 minutes, as shown in figure 4.22.¹⁴² Differential scanning calorimetric studies only revealed a T_g in the homopolymer and 10 mole percent sulfonated PPSS of 216 and 235°C, respectively, with a heating rate of 10°C/min.

¹⁴² Wang, F.; Mechem, J. B.; Harrison, W.; McGrath, J. E. *Polymer Preprints* **2000**, *40*, 180.

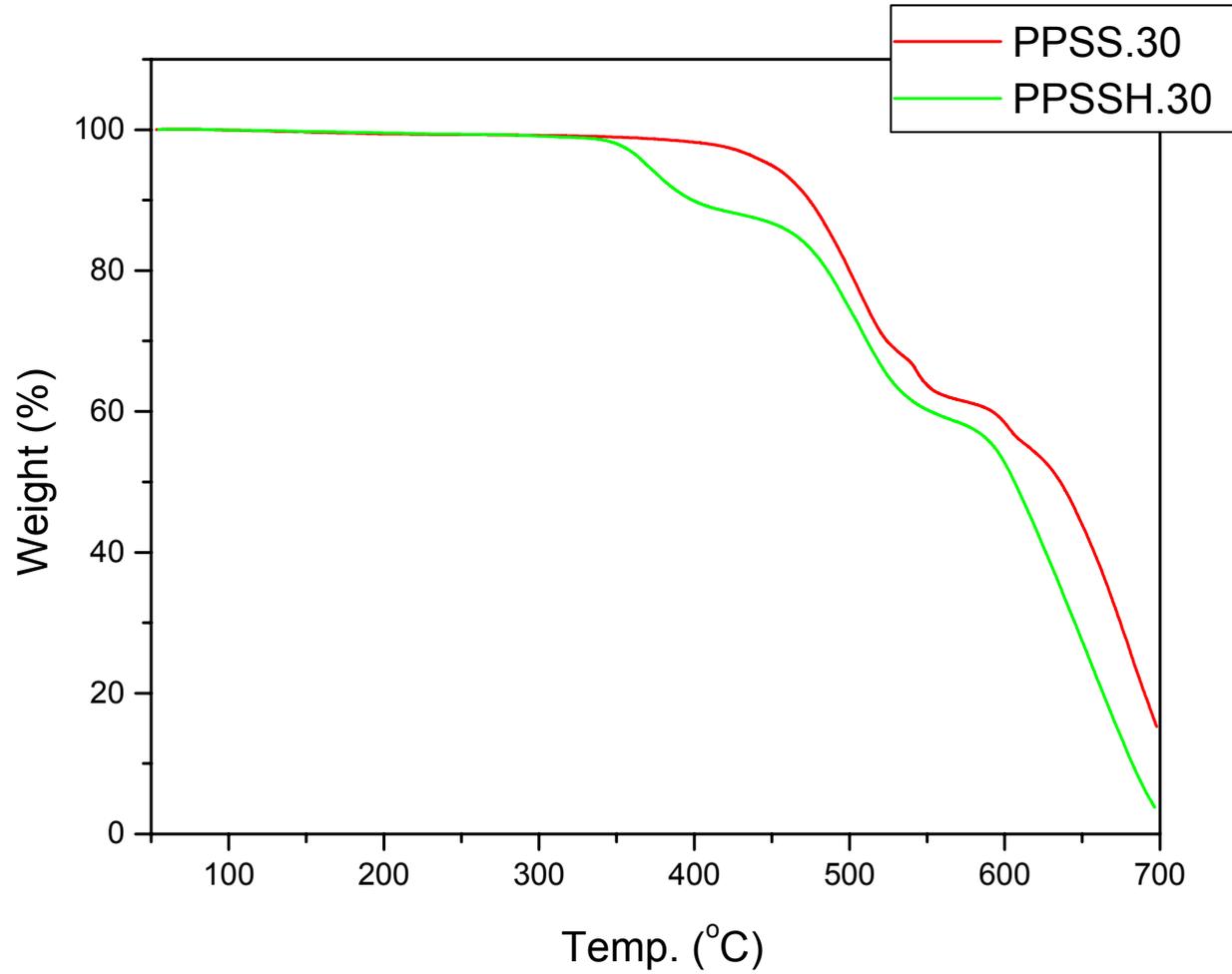


Figure 4.19: Thermal stability (N_2 / $10^\circ C/min$) of 30 mole percent sulfonated PPSS membranes in acid (PPSH) and salt (PPSS) form showing the expected higher thermal stability of salt. Samples were dried in the TGA furnace for 30 min. in N_2 at $150^\circ C$, prior to the heating scans.

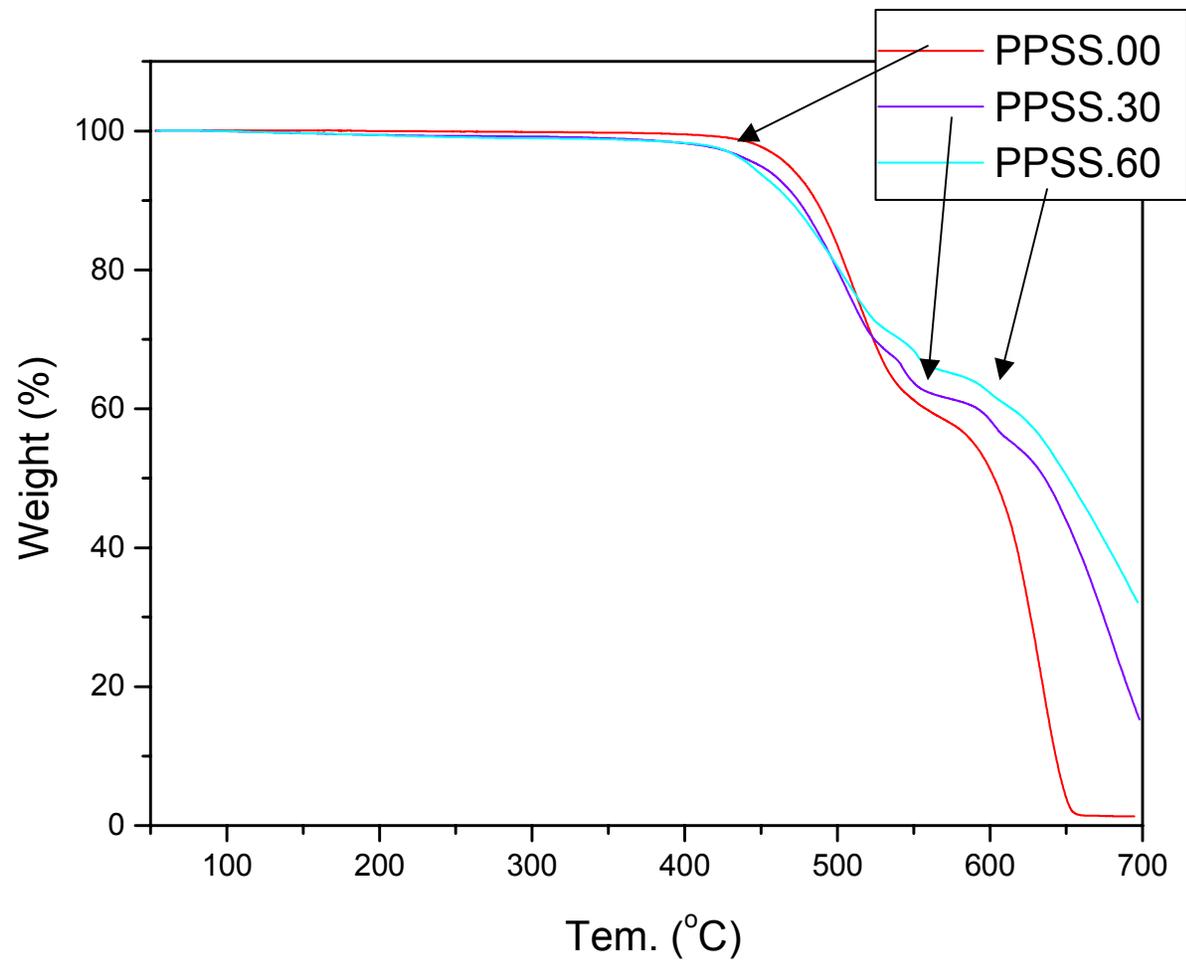


Figure 4.20: Thermal stability (N_2 / $10^\circ C/min$) of sulfonated PPSS membranes in the sodium salt form. Samples were dried in the TGA furnace for 30 min. in N_2 at $150^\circ C$ prior to the heating scans.

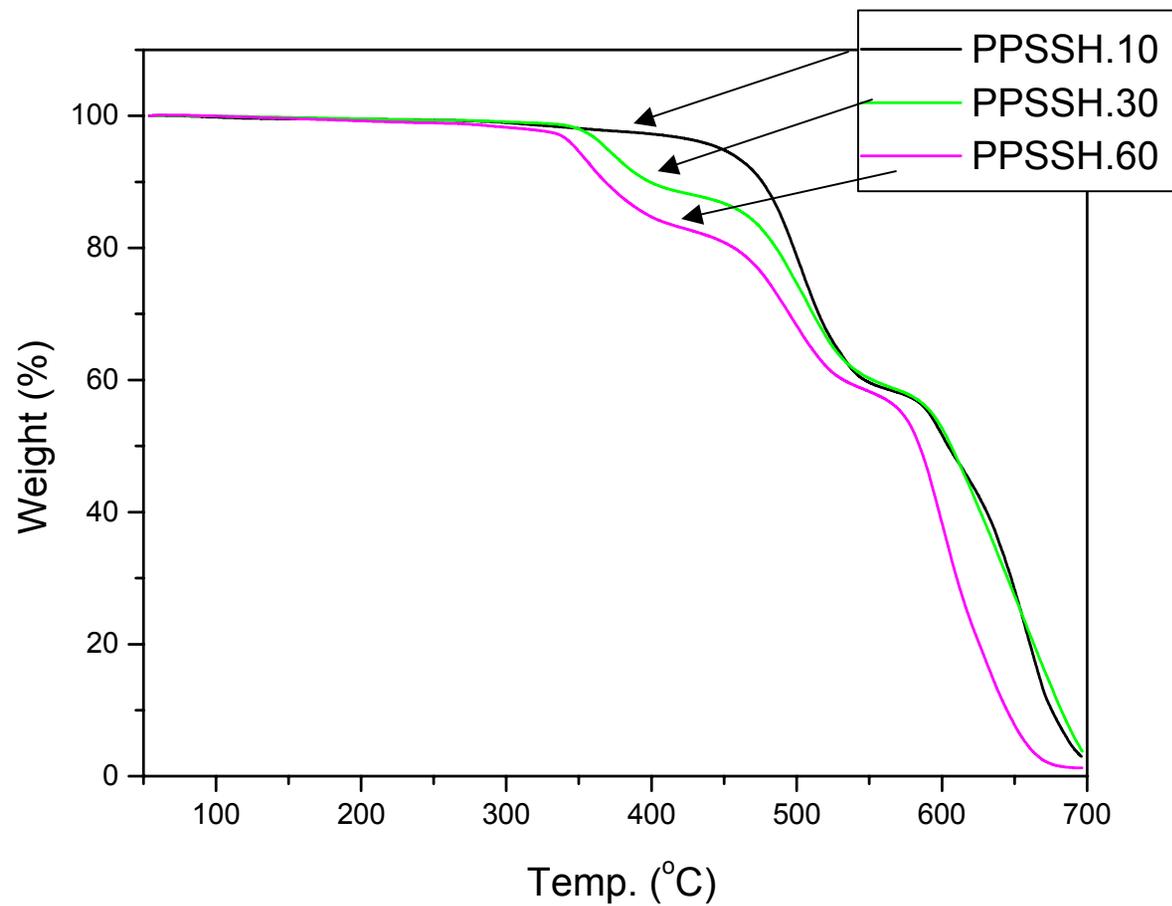
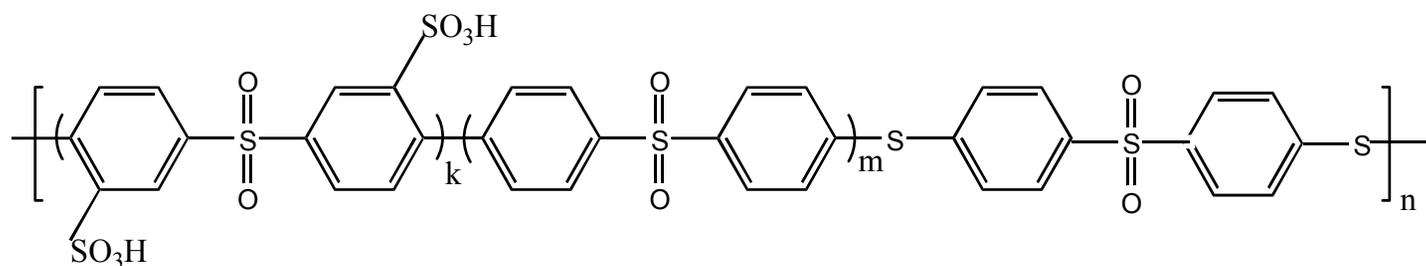


Figure 4.21: Thermal stability (N_2 / $10^\circ C/min$) of sulfonated PPSS membranes in sulfonic acid form. Samples were dried in the TGA furnace for 30 min. in N_2 at $150^\circ C$ prior to the heating scans.



k/m	Intrinsic Viscosity (dl/g) $[\eta]^{NMP}$				
	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 4.22: The solubility and stable intrinsic viscosity values up to 220°C reflect good thermal stability of $-SO_3H$ groups. The copolymers were heated in air at each temp. for 30 min. in air before IV determination

b. Biphenol-based Poly (arylene ethers)

The thermal stability of the control and sulfonated poly(arylene sulfone) copolymers (sodium form) were investigated by TGA. All the sulfonated samples were first pre-heated to 150°C for 30 minutes in the TGA furnace to remove any moisture and followed by dynamic TGA experiments which were run from 50 to 700°C, at a heating rate of 10°C/min under nitrogen. The influence of the degree of sulfonation on both 5% weight loss temperature and the residual char yield at 700°C are summarized in table 4.5. While the unsulfonated control had a 5% weight loss temperature of 456°C, the 5% weight loss temperatures for the copolymers with degrees of sulfonation between 10 and 60 mole percent decreased only slightly with the increase of sodium sulfonate in the polymer. However, the char yield at 700°C showed a reverse trend, confirming the objectives of Robeson and Matzner¹⁴³ to use SDCDPS as a flame retarding additive. The thermal stability of acid and sodium form membranes, (TGA curves for PBPS-60 and PBPSH-60) are compared in figure 4.23. There is only one weight loss step for salt PBPS-60 at around 500°C, which was assigned to the degradation of the polymer chain. PBPSH-60 shows an initial weight loss of about 17% of the original weight between 300 and 480°C, which is assigned to the loss of -SO₃H groups. The second thermal degradation above 500°C is attributed to the main chain polymer degradation. The theoretical weight percent of -SO₃H groups in PBPSH-60 is 19%, assuming that the elimination of a sulfonic acid group would release one SO₃ molecule, which is in a close agreement with the first weight loss in the TGA curve of PBPSH-60. This indicates that the degradation of acid form polymers initiates with the cleavage of the ionic groups, while the sodium sulfonate polymers possess better thermal stability than their sulfonic acid functionalized analogs. Initial results indicate that the post reacted groups on the activated phenyl rings appear to be less stable.

Figure 4.24 shows the DSC thermograms of the PBPSH system as a function of the degree of sulfonation. The DSC data indicated a linear increase of T_g in the range from 0% to 40% acid sulfonate group, followed by a larger base line shift at higher

¹⁴³ Robeson, L. M.; Matzner, M.; Union Carbide; U.S. 4,380,598; 1983

concentrations of ionic groups. The first derivative DSC traces shown in the inset of figure 4.24 clearly exhibit that a single T_g appeared in the 40% sulfonated sample, while the 50 and 60% sulfonated samples showed two glass transitions. The lower and upper transitions of these samples are attributed to the glass transitions of matrix and ionic clusters, respectively.

Table 4.5: Thermal characterization of Biphenol-based PAE copolymers by DSC and TGA

Polymers	T _g (°C) ^(a)	T _{5%} (°C) N ₂ , 10°C/min	Char Yield (%) at 700°C (N ₂)
PBPS-00	221	516	43
PBPS-10	232	507	62
PBPS-20	246	506	63
PBPS-30	260	506	65
PBPS-40	271	501	66
PBPS-60	283, 314	495	70

(a): Performed on control and acid form membranes

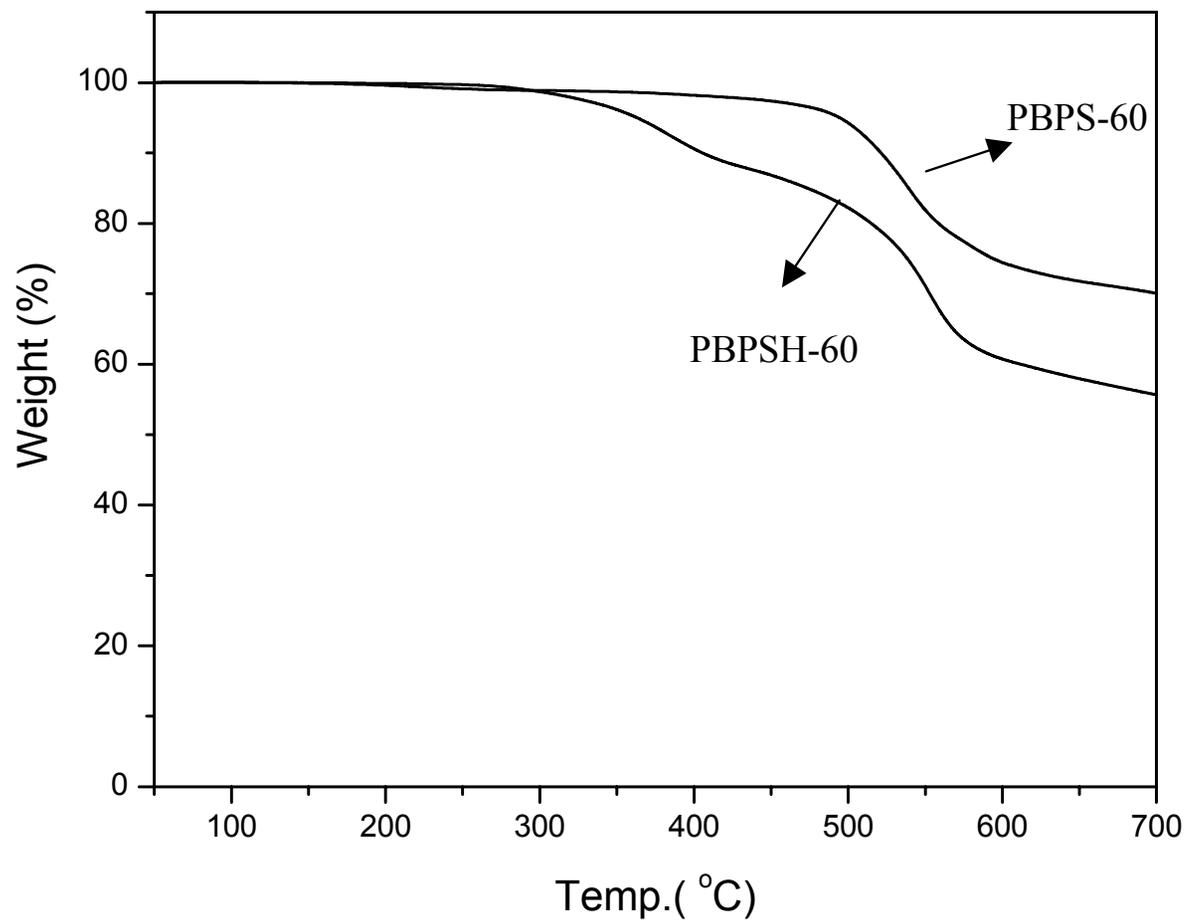


Figure 4.23: . The influence of the salt form or sulfonic acid form of the biphenol-based PAE on both 5% weight loss temperature and the residual char yield at 700°C in N₂ at a heating rate of 10°C/min

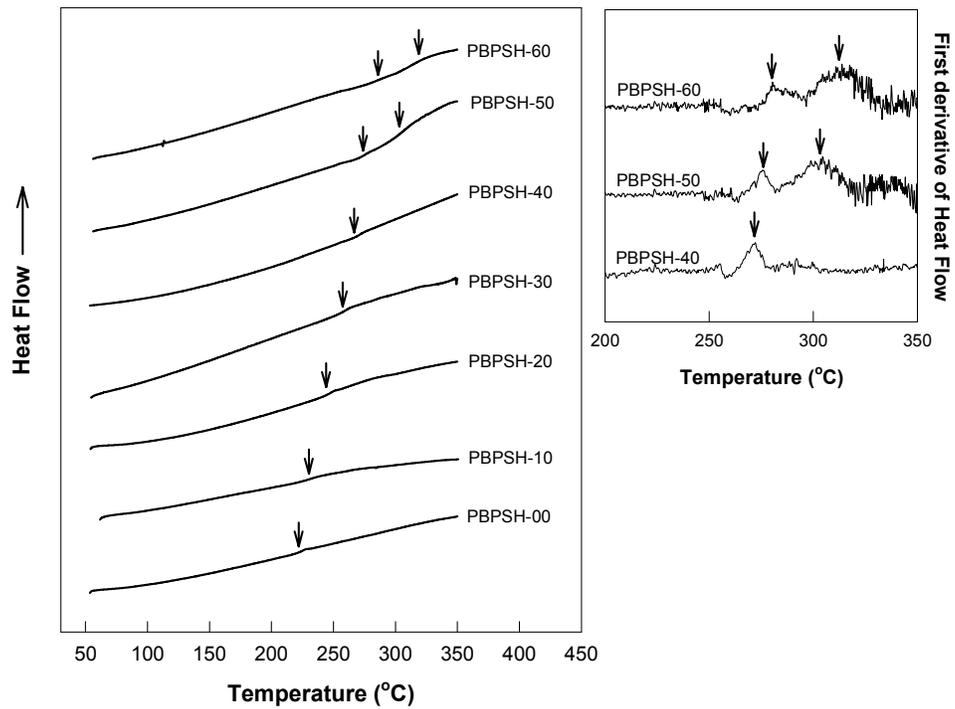


Figure 4.24: Influence of the Degree of Sulfonation on the Glass Transition Temperature of Sulfonated Poly(arylene ether sulfone) Copolymers

c. Segmented Block Poly (imide) Poly (arylene ether) Copolymers

i) Bisphenol-A/Oxydianiline Poly (imide) Sulfonated Poly (arylene ether) Copolymers

The thermal stability of the bisphenol-A poly (imide) (Ultem[®]) control and sulfonated poly(arylene sulfone) BPADA/ODA poly (imide) segmented block copolymers (sodium form; $M_n = 10,000$ g/mol) were investigated by TGA. All the sulfonated samples were first pre-heated to 200°C for 10 minutes in the TGA furnace to remove any moisture and followed by dynamic TGA experiments which were run from 50 to 700°C, at a heating rate of 10°C/min in air. The results are in shown in figure 4.25. The influence of the degree of sulfonation on both the 5% weight loss temperature and the residual char yield at 700°C are summarized in table 4.6. While the unsulfonated control had a 5% weight loss temperature of nearly 500°C, the 5% weight loss temperatures for the copolymers with degrees of sulfonation between 35 and 85 mole percent were lower. The char yield at 700°C for the copolymer containing 85 mole percent sulfonated poly (arylene ether) (SPAЕ) was nearly 21 percent. The 85 mole percent SPAЕ copolymer shows an initial weight loss of about 27 percent of the original weight between about 375 and 500°C, which is assigned to the loss of $-\text{SO}_3\text{H}$ groups. The second thermal degradation above 500°C is attributed to the main chain polymer degradation. Initial results indicate that the post reacted groups on the activated phenyl rings appear to be less stable.

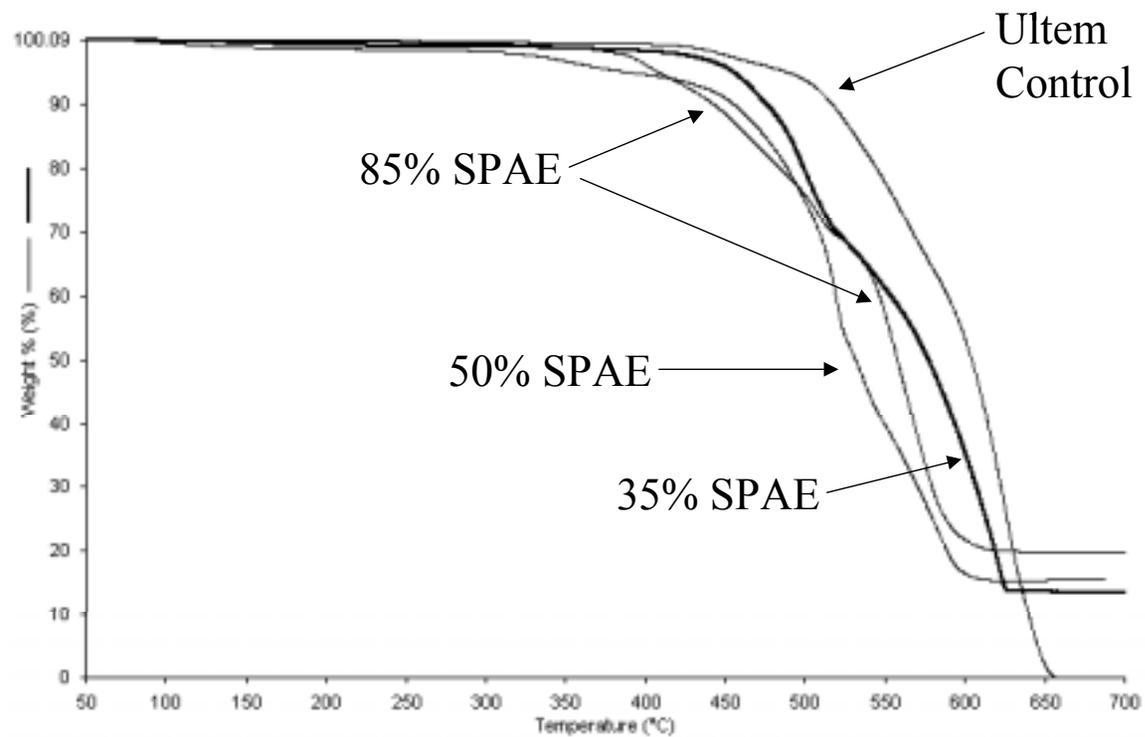


Figure 4.25: The influence of the degree of sulfonation (SPAE $M_n = 10,000$ g/mol) on both 5% weight loss temperature and the residual char yield at 700°C in air at a heating rate of 10°C/min

Table 4.6: Thermal characterization of BPADA/Oxydianiline Poly (imide)
Sulfonated Poly (arylene ether) Copolymers

<u>Mole %</u> <u>PAE</u>	<u>PAE</u> <u>M_n</u>	T _{5%} (°C) N ₂ , 10°C/min	Char Yield (%) at 700°C (Air)
Ultem Control	-	498	-
35	10K	368	4
50	10K	450	13
85	10K	455	27

ii) 6FDA/Oxydianiline Poly (imide) Sulfonated Poly (arylene ether) Copolymers

The thermal stability of the 6FDA poly (imide) control and sulfonated poly(arylene sulfone) 6FDA/ODA poly (imide) segmented block copolymers (sodium form, $M_n = 10,000$ g/mol) were investigated by TGA. All the sulfonated samples were first pre-heated to 200°C for 10 minutes in the TGA furnace to remove any moisture and followed by dynamic TGA experiments which were run from 50 to 800°C, at a heating rate of 10°C/min in air, as shown in figure 4.26. The influence of the degree of sulfonation on both the 5% weight loss temperature and the residual char yield at 700°C are summarized in table 4.7. While the unsulfonated control had a 5% weight loss temperature of 490°C, the 5% weight loss temperatures for the copolymers with degrees of sulfonation between 35 and 65 mole percent decreased with the increase of sodium sulfonate in polymer. The char yield at 800°C for the copolymer containing 65 mole percent sulfonated poly (arylene ether) (SPAЕ) was nearly 14 percent. The 65 mole percent SPAЕ copolymer shows an initial weight loss of about 8 percent of the original weight between 240 and 400°C, which is assigned to the loss of $-SO_3H$ groups. The second thermal degradation above 500°C is attributed to the main chain polymer degradation. Initial results indicate that the post reacted groups on the activated phenyl rings appear to be less stable.

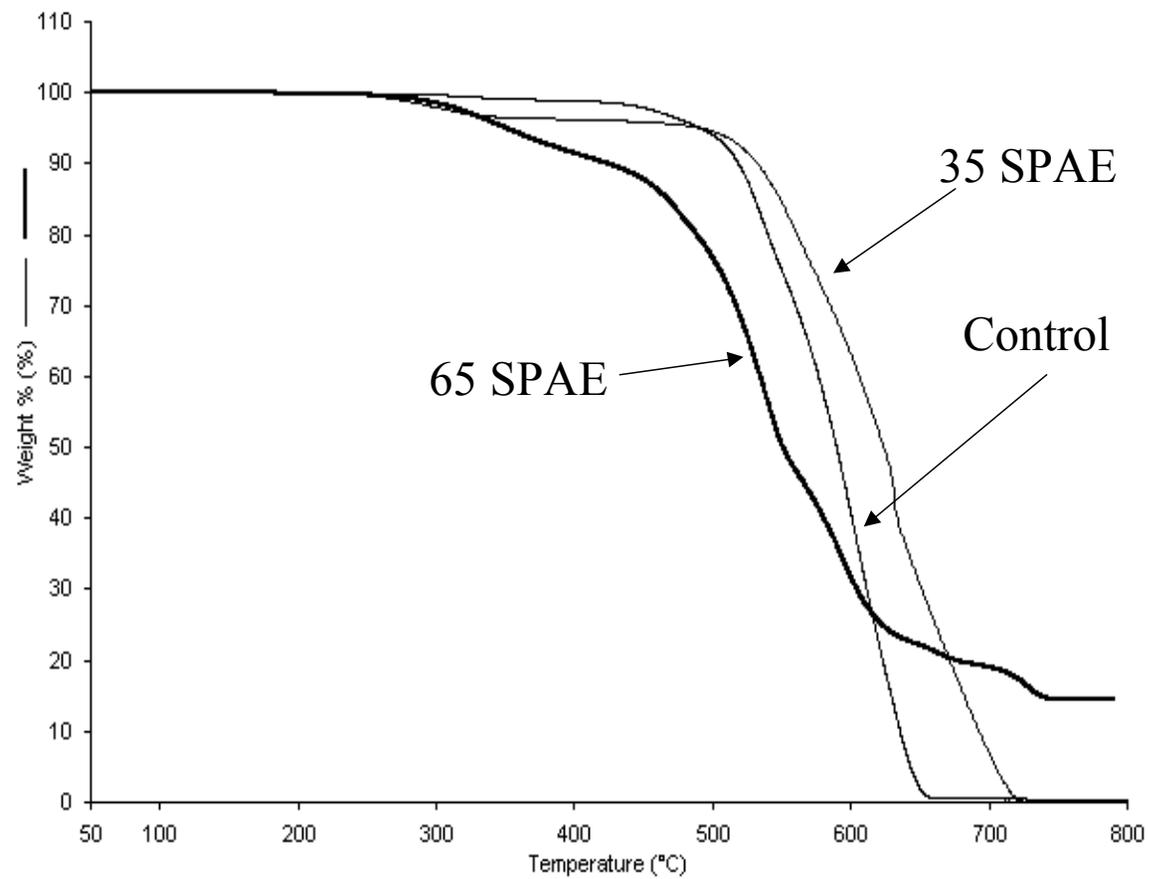


Figure 4.26: The influence of the degree of sulfonation (SPAE $M_n = 10,000$ g/mol) on both 5% weight loss temperature and the residual char yield at 700°C in air at a heating rate of 10°C/min

Table 4.7: Thermal characterization of 6FDA/Oxydianiline Poly (imide) Sulfonated Poly (arylene ether) Copolymers

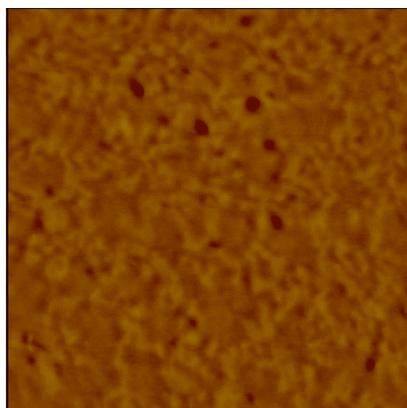
<u>Mole %</u> <u>PAE</u>	<u>PAE</u> <u>M_n</u>	T _{5%} (°C) N ₂ , 10°C/min	Char Yield (%) at 70°C (Air)
6FDA/ODA Control	-	490	-
35	10K	478	-
50	10K	390	6
65	10K	334	14

2. Atomic Force Microscopy (AFM)

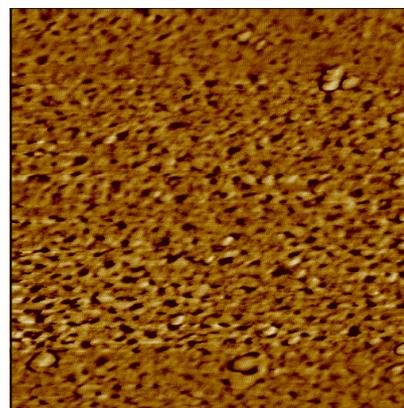
a. Biphenol-based Poly (arylene ether sulfones)

In order to investigate ionic clusters for random sulfonated poly(arylene ether sulfone) copolymers, AFM tapping mode phase images of the PBPSH system surface were recorded under ambient conditions on 750×750 nm size areas (Figure 4.27). For the unsulfonated control homopolymer, a relatively featureless phase morphology was obtained (photo a). In contrast, the sulfonated poly(arylene ether sulfone) revealed dark and cluster-like structures with a diameter of 10-25 nm that were clearly visible in the phase image. The dark structures were identified as the softer region, which represents the hydrophilic sulfonic acid group clusters which contain water. The domain size and its connectivity are varied depending on the degree of sulfonation. For 20 mole percent sulfonated copolymer(photo b), the isolated ionic cluster region had a diameter of 10 to 15 nm. With the 40 mole percent sulfonated copolymer(photo c), the phase contrast of the hydrophilic ionic domains increased and became more easily distinguished from the non-ionic matrix, but were still isolated (non-connected) with a diameter of about 25 nm. For the 60 percent sulfonated copolymer (photo d) the phase image revealed a significant change with the hydrophilic ionic domains becoming continuous to form plausible large channels making up the ionic cluster rich phase. Similar continuous ionic channel structures were also observed in ambient humidity conditioned Nafion 117 ionomer, in spite of the fact that the ionic domain size of the Nafion was smaller with a diameter of about 4-10 nm.¹⁴⁴ Based on the phase images of other compositions, this biphenol-based PAE system reaches its percolation limit at about 60 mole % of the disulfonated monomer. This explains not only the sudden increase of water uptake but also the existence of more than one T_g at sulfonation levels of 50 and 60 mole percent. The lack of two glass transitions at lower sulfonic acid concentrations is likely due to the small and isolated ionic domain structure at these concentrations.

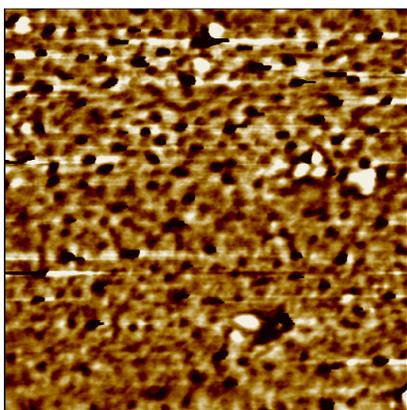
¹⁴⁴ McLean, R. S.; Doyle, M.; Sauer, B. B. *Macromolecules* **2000**, *33*, 6541.



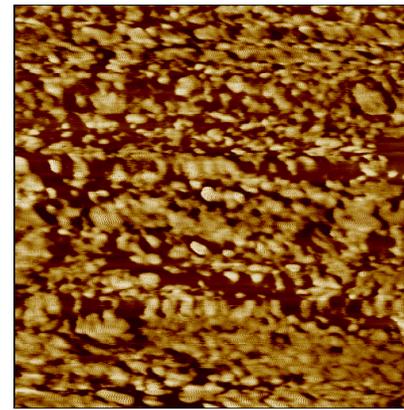
a



b



c



d

Figure 4.27: AFM tapping phase image for Sulfonated Poly(arylene ether sulfone) Copolymers(a) Unsulfonated Control(b) 20 mole percent $-\text{SO}_3\text{H}$ (c) 40 mole percent $-\text{SO}_3\text{H}$ (d) 60 mole percent $-\text{SO}_3\text{H}$; Scan boxes are 750×750 nm for each plot, Phase scale is $0\text{-}30^\circ$.

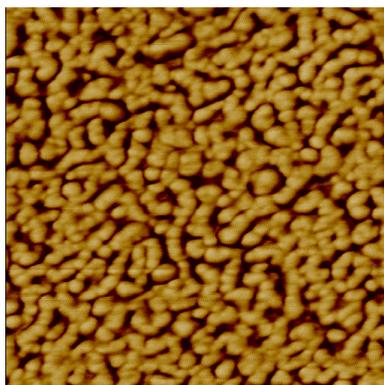
b. Segmented Block Poly (imide) Sulfonated Poly (arylene ether) Copolymers

The segmented block copolymers were investigated because of their natural tendency to phase separate when at least two incompatible polymer backbones are utilized. As with the random sulfonated copolymer systems, atomic force microscopy was used to produce tapping mode phase images of the sulfonated copolymer systems under ambient conditions on 750×750 nm areas.

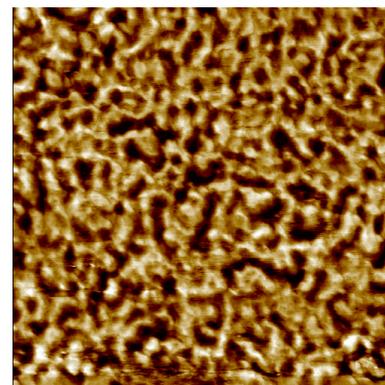
With either the partially aliphatic BPADA/ODA, or wholly aromatic fluorine-containing 6FDA/ODA poly (imide) hydrophobic segments, and sulfonated biphenol-based 10K PAE hydrophilic segments, continuous regions of each phase can be clearly seen in the AFM phase images shown in figure 4.28 with a diameter of the “bead-like” structures near 20 nm. When exposed to water the darker, softer sulfonated regions increase in size in figure 4.26-image b. This type of swelling behavior was not observed as clearly in the 6FDA copolymers and the phase contrast was not as evident as in the BPADA case; indeed little change was noted at this composition after exposure to water and the diameter of sulfonated regions was near 30nm.

As the molecular weight of the sulfonated poly (arylene ether) segment was increased from 10,000 to 30,000 g/mol and the mole percent in the copolymer was increased to 50 percent, the PAE sulfonated phase grew larger to about 60nm as seen in figure 4.26-image d.

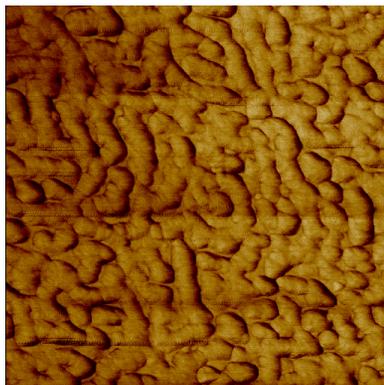
Because AFM is a surface characterization technique, the images that are generated from this type of analysis may not represent the bulk of the material.



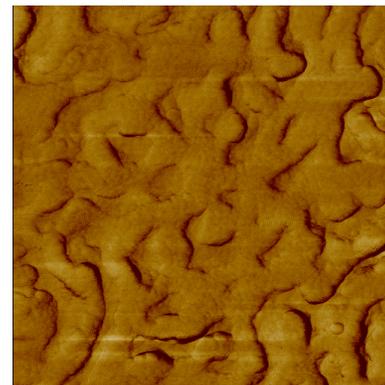
a) BPADA/ODA/ 35 mole % 10K PAE
Salt form, dry film



b) BPADA/ODA/ 35 mole % 10K PAE
Salt form, 3 days exposure to humid (35%
r.h.) air



c) 6FDA/ODA/ 35 mole % 10K PAE,
Salt form, dry film



d) BPADA/ODA/ 50 mole % 30K PAE
Salt form, dry film

Figure 4.28: AFM tapping phase image for Poly (imide) Sulfonated Poly(arylene ether sulfone) Segmented Copolymers. Scan boxes are 1000×1000 nm for each plot, Phase scale is $0-30^\circ$.

3. Membrane Studies

a. Water Sorption

Water sorption in proton exchange membranes is very important. The proton exchange reaction requires a significant amount of water to coordinate with the proton as it moves through the membrane. In general, good protonic conductivity cannot be achieved without water being present in the membrane.

i) Biphenol-based Sulfonated Poly (arylene ether sulfones)

Water uptake experiments were conducted on the random poly(arylene ether sulfones), the details of which are described in the experimental section. In general, it was found that water uptake increased as the molar ratio of sulfonated 4,4'-dichlorodiphenylsulfone (SDCDPS) was increased, as shown in table 4.8. Water uptake was very similar for both the acid and the sodium form membranes at less than 50 mole percent sulfonation. At 60 mole percent SDCDPS, the sulfonic acid membrane swelled approximately 20 percent more than the analogous salt form membrane.

ii) Segmented Block Poly (imide) Poly (arylene ether) Copolymers

Water uptake values for the segmented block copolymers were much lower than in the random poly (arylene ether) copolymers. The results are summarized in table 4.9. The low values were exhibited in all compositions with the exception of the 85 mole percent 30K sulfonated poly (arylene ether) / (BPADA/ODA) Poly (imide). This membrane showed a four-fold dimensional change after 24 hours of deionized water exposure and essentially formed a hydrogel, or highly hydrated film, having extremely poor mechanical properties.

Table 4.8: . Influence of sulfonate groups on water uptake of sulfonated poly (arylene ether) random copolymers

DCDPS/SDCDPS (molar ratio)	Water Uptake (%)	
	Na ⁺	H ⁺
9/1	4.5	4.4
8/2	9.8	12
7/3	18	20
6/4	28	31
4/6	55	78
0/10	Water Soluble	

Table 4.9: . Influence of sulfonate groups on water uptake of segmented sulfonated poly (arylene ether) poly (imide) copolymers

<u>Polyimide Dianhydride</u>	<u>Mole % PAE</u>	<u>PAE Segment M_n</u>	Water Uptake (Sodium Sulfonate) (%)
6FDA	35	10K	1
6FDA	50	10K	5
6FDA	65	10K	7
6FDA	65	20K	10
6FDA	85	20K	High
Bis-A	35	10K	4
Bis-A	65	10K	9
Bis-A	65	20K	12

b. Protonic Conductivity

i) Biphenol-based Sulfonated Poly(arylene ethers)

The protonic conductivities of the sulfonated poly(arylene ether) random copolymer acid form membranes were measured in the a conductivity cell shown in figure 3.13 at 30°C in liquid water. The membranes had proton conductivities of 0.11 and 0.17 S/cm for the BPSH-40 (IEC 1.72 meq/g) and BPSH-60 (IEC 2.42 meq/g), respectively, while the conductivity of Nafion 1135 (IEC 0.91 meq/g) was 0.12 S/cm under the same conditions. Figure 4.29 shows the conductivity of these samples as a function of temperature. Greater ion exchange capacities are needed with sulfonated poly(arylene ethers) to achieve similar conductivities to perfluorosulfonic acid Nafion polymers. This disparity is attributed to the strength of the acid group in each system. The acidity of perfluorosulfonic acid is much stronger than that of the aryl sulfonic acid, therefore, more acid moieties are needed in sulfonated poly(arylene ethers) to achieve the desired conductivity.

ii) Segmented Sulfonated Poly (arylene ether) Poly (imide) Copolymers

Conductivities of the block copolymers were not as high as those of the random sulfonated poly (arylene ether) copolymers. Across the entire range of compositions, the conductivity values were all near 0.03 ± 0.005 S/cm, regardless of poly (imide) type or sulfonated poly (arylene ether) block length. This result is most likely due to the surprisingly low level of water uptake that the copolymers exhibited. In the one case, in which the water uptake was above 20 weight percent [85 mole percent sulfonated poly (arylene ether) 6FDA Poly (imide)], the membrane was so soft and fragile that a conductivity measurement could not be conducted. In the cases in which the random sulfonated poly (arylene ether) copolymers showed conductivity values near or greater than Nafion, water uptake was greater than or equal to 28 weight percent.

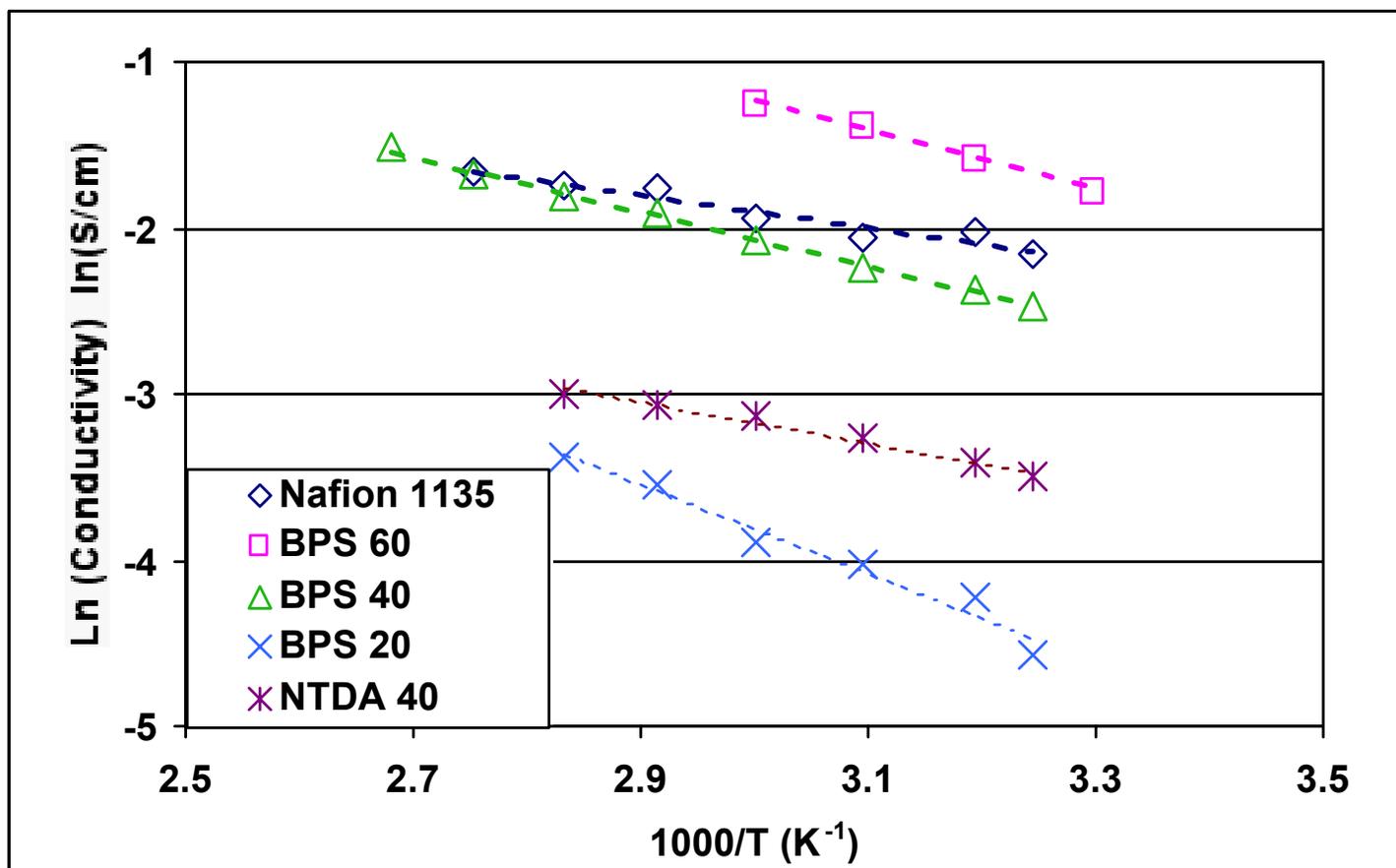


Figure 4.29: Protonic conductivity as measured from approximately 30 to 100°C. 40 mole percent sulfonated biphenol/SDCDPS PAE (BPS 40) nearly matches Nafion 1135 performance, which is exceeded by the 60 mole percent sulfonated polymer (BPS 60)

Chapter V

Conclusions

Utilizing fuming sulfuric acid (~ 27 % SO₃), 4,4'-dichlorodiphenylsulfone (DCDPS) was quantitatively sulfonated at the 3 and 3' positions to form SDCDPS. The sulfonic acid group was quantitatively titrated to the sodium sulfonate with sodium hydroxide.

Random sulfonated poly(phenylene sulfide sulfones) (PPSS) copolymers were synthesized from 4,4'-dimercaptodiphenylsulfone and 4,4'-difluorodiphenylsulfone (SDFDPS) using direct step growth polymerization techniques. High molecular weight polymers could be achieved with concentrations of up to 60 mole percent SDFDPS. Tough, ductile membranes were successfully cast from N-methylpyrrolidone solutions.

Sulfonic acid-form membranes based on PPSS were stable in air at 220°C for more than 30 minutes as determined by isothermal thermogravimetric analysis measurements, titrations of the sulfonic acid sites and intrinsic viscosity measurements. This suggests suitable stability for operating temperatures of 120-150°C as a proton exchange membrane. Initial thermogravimetric weight loss for the analogous sodium sulfonate salt-form membranes began at temperatures approximately 75°C higher than those of the sulfonic acid functionalized samples.

Random sulfonated biphenol-based poly (arylene ether) (BPSH) copolymers were successfully synthesized using sulfonated 4,4'-dichlorodiphenylsulfone (SDCDPS) and direct step growth polymerization techniques. High molecular weight polymers could be achieved with concentrations of up to 100 percent SDCDPS, but the 100 percent sulfonated polymer was soluble in deionized water.

Aging of 40 and 60 mole percent SDCDPS acid-form BPSH polymers in air at temperatures of up to 220°C were shown to be quite stable as determined by intrinsic viscosity (IV) measurements, which remained constant at temperatures of up to 220°C,

but increased when the temperatures approached 260°C. This may suggest branching of the polymers at higher temperatures.

Thermogravimetric analysis comparing dynamic weight loss of sodium sulfonate form to sulfonic acid functionalization of a 60 mole percent BPSH polymer was conducted. The experiment revealed initial weight loss for the salt form began at approximately 400°C, nearly 100 degrees greater than in the sulfonic acid case.

Conductivity measurements of the biphenol-based poly (arylene ethers) revealed that the novel polymers met or exceeded the performance of state-of-the-art Nafion perfluoropolymer under full hydration at 30°C. The 40 mole percent SDCDPS polymer had conductivity values nearly identical to Nafion 1135 (1100 meq/g; 3.5 mil thick membrane) over a broad temperature range (~ 30-100°C), while the 60 mole percent SDCDPS polymer exceeded Nafion 1135 conductivity values over the entire temperature range.

Wholly aromatic biphenol-based sulfonated poly (arylene ethers) of controlled molecular weight were successfully synthesized with telechelic amine functionality. Number average molecular weight was successfully controlled by using the monofunctional endcapper *m*-aminophenol. A systematic series of polymers with controlled degrees of sulfonation was synthesized and it was found that the polymer containing 100 mole percent SDCDPS was water soluble.

Sulfonated biphenol-based poly(arylene ethers) of controlled molecular weight with telechelic amine functionality were utilized to form poly (imide) segmented block copolymers. Both bisphenol-A/4,4'-oxydianiline (BPADA/ODA) and hexafluoroisopropylidene dianhydride/4,4'-oxydianiline (6FDA/ODA) segmented copolymers were synthesized in a range of compositions. Film-forming polymers could not be generated at poly (arylene ether) concentrations greater than 50 mole percent using the ester-acid route to poly (imides). It was hypothesized that the *o*- dichlorobenzene used in this approach was immiscible with the sulfonated poly(arylene ether) which

resulted in heterogeneity during the polymerization reaction. Thermal imidization of the analogous poly (amic acid) precursors resulted in ductile films across the whole range of compositions.

Thermal gravimetric analysis in air of the block copolymers revealed a decrease in thermal stability with increasing mole percent sulfonation, while char yields increased with increasing ionic content.

Atomic force microscopy was used to analyze the surface of thermally-imidized segmented copolymers. Phase separation of the copolymers was most prominent in compositions below 50 mole percent sulfonated poly (arylene ether). Higher concentrations resulted in poor phase definition. Membranes of both the BPADA/ODA and 6FDA/ODA segmented copolymers containing 35 mole percent of the sulfonated poly (arylene ether) revealed co-continuous sulfonated and unsulfonated regions. This supports the hypothesis that these multiblock copolymers would phase separate regardless of that fact that step growth polymerizations were utilized, which produces broader molecular weight distributions than living systems.

Water uptake and conductivity values were less than expected in both BPADA/ODA and 6FDA/ODA poly (imide) sulfonated poly(arylene ether) copolymer systems.

Vita

Jeffrey Brent Mecham, son of Randall and Jamie Mecham, was born on May 23, 1968 in La Mesa, California. He graduated from Skyline High School in June of 1986. In the fall of the same year, he began his undergraduate studies at San Diego State University. In the summer of 1987, he moved to Blacksburg, Virginia, and after establishing in-state residency, attended New River Community College, for the 1989-1990 school year. In the fall of 1990, he began his undergraduate studies at Virginia Polytechnic Institute and State University, where he also worked part-time as a laboratory technician and was responsible for GPC analysis of high performance polymers and adhesives under Dr. James E. McGrath. He obtained his B.S. in Biology, with a minor in Chemistry in the fall of 1993. He then worked full-time for Dr. McGrath as a laboratory technician before beginning graduate school in the spring of 1995 in pursuit of a Master's Degree in Chemistry under the direction of Dr. McGrath, which he completed in December of 1997. He continued his graduate studies at Virginia Tech with Dr. McGrath and, upon completion of his Doctor of Philosophy degree in the spring of 2001, will join NanoSonic, Inc., in Blacksburg, Virginia, as a Research Scientist.