MULTIBLOCK COPOLYMERS CONTAINING HYDROPHOBIC AND HYDROPHILIC SEGMENTS FOR ANION EXCHANGE MEMBRANES

by

Derek J. Strasser
ABSTRACT

Alkaline fuel cells have the potential to provide a cost effective conversion of energy compared to proton exchange membrane fuel cells that require more expensive noble metal catalysts. The anion exchange membrane (AEM) is an important component that separates electrodes and provides a conducting medium for anions. Proper design of hydrophobic-hydrophilic copolymer membranes that are highly hydroxide conductive yet remain chemically and physically stable under the highly basic conditions is required.

Polysulfone (PSf) is an attractive material owing to it excellent mechanical properties and film forming ability, thermal and chemical stability that it is readily modified to bear a variety of functional groups. Multiblock PSf copolymers have been investigated for several decades and for many applications. More recently, hydrophobic-hydrophilic PSf multiblock copolymers have been studied as AEMs and for application in electrochemical applications including alkaline fuel cells.

The research in this thesis was focused on the development of new multiblock PSf copolymer materials for AEMs that address current design challenges, but also provide additional insight to the structure-property relationships that will lead to improved AEM performance and base stability. Two main PSf multiblock copolymer systems were investigated.

Multiblock copolymers composed of bisphenol A PSf segments and tetramethylbisphenol A (TMBPA) polyformal (PF) segments were studied. The TMBPA PF segments provided compact repeat units of TMBPA with methylene linkages and the ability to bear up to four benzyltrimethylammonium cations. The solution processible PSf quaternary ammonium functionalized PF (PSf-QAPF) multiblock copolymers were shown to
form hydroxide conductive, well-connected phase separated membranes with excellent mechanical properties.

An alternative polymer system was investigated to prepare more alkaline stable materials. Cycopolymerization of \(N,N\)-diallylpiperidinium chloride was developed to prepare spirocyclic ammonium telechelic oligomers of poly(diallylpiperidinium) (PDApip). Copolymerization of the oligomers with PSf monomers was done followed by ion exchange to provide multiblock PSf-PDApip copolymers that were thermally stable up to 360 °C and highly conductive in the hydroxide form (up to 102 mS cm\(^{-1}\) at 80 °C). The PDApip homopolymer was exceptionally base stable over 1000 hrs. A series of PSf-PDApipOH multiblock copolymers with similar composition and ion exchange capacity with variation in PDApip block length were prepared and investigated to elucidate the impact of hydrophilic block length on membrane performance. The PSf-PDApip copolymer membranes displayed high hydroxide conductivity under humidified gas conditions, and the conductivity increased with increasing PDApip segment length, which was related to the morphology studied by tapping mode-atomic force microscopy.
## TABLE OF CONTENTS

ABSTRACT ............................................................................................................................. iii

LIST OF FIGURES ................................................................................................................. ix

LIST OF TABLES ................................................................................................................... xi

LIST OF SCHEMES .............................................................................................................. xii

ACKNOWLEDGMENT ........................................................................................................ xiv

CHAPTER 1 INTRODUCTION AND BACKGROUND ........................................................ 1

1.1 Introduction ..................................................................................................................... 1

1.2 High performance materials ........................................................................................ 2

1.2.1 High strength, reinforced multiblock copolymers .................................................... 2

1.2.2 Ductile multiblock copolymers ................................................................................. 6

1.3 Hydrophilic multiblock copolymers for biomedical application .................................. 12

1.4 Membrane technology ................................................................................................ 14

1.4.1 Gas Separation membranes ..................................................................................... 14

1.4.2 Multiblock ion exchange membranes ...................................................................... 17

1.4.2.1 Membranes for proton exchange membranes (PEM)s ..................................... 18

1.4.2.2 Membranes for anion exchange membranes (AEM)s ...................................... 32

1.5 Conclusions ................................................................................................................... 37

1.6 Thesis Statement ........................................................................................................... 38

1.7 References ..................................................................................................................... 41

CHAPTER 2 HIGHLY FUNCTIONALIZED POLYSULFONE-POLYFORMAL MULTIBLOCK COPOLYMERS FOR ANION EXCHANGE MEMBRANES .......................................................... 50

2.1 Introduction ................................................................................................................... 50

2.2 Experimental ............................................................................................................... 53

2.2.1 Materials ................................................................................................................. 53

2.2.2 Synthesis of phenol terminated polysulfone (PSf-OH) ........................................... 53
2.2.3 Synthesis of PSf-PF multiblock copolymers ......................................................... 54
2.2.4 Bromination of PSf-PF multiblock copolymers (PSf-BrPF) ................................. 54
2.2.5 Amination of PSf-BrPF (PSf-QAPF bromide) and membrane preparation .......... 55
2.2.6 Ion exchange to hydroxide .................................................................................. 55
2.2.7 Characterization .................................................................................................. 56

2.3 Results and Discussion ......................................................................................... 58
2.3.1 Synthesis of PSf-QAPF multiblock copolymers ................................................... 59
  2.3.1.1 Synthesis of PSf-OH ................................................................................ 59
  2.3.1.2 Synthesis of PSf-PF multiblock copolymers ............................................. 60
  2.3.1.3 Functionalization of PSf-PF multiblock copolymers and membrane fabrication ......................................................... 64
2.3.2 Characterization of PSf-QAPF multiblock copolymer membranes ..................... 69
  2.3.2.1 Water uptake and hydroxide conductivity .................................................. 69
  2.3.2.2 Surface morphology and mechanical properties ......................................... 71
  2.3.2.3 Membrane base stability .......................................................................... 73

2.4 Conclusions .......................................................................................................... 74

2.5 Acknowledgments ................................................................................................. 75

2.6 References ........................................................................................................... 75

CHAPTER 3 BASE STABLE POLY(DIALLYLPIPERIDINIUM HYDROXIDE) MULTIBLOCK COPOLYMERS FOR ANION EXCHANGE MEMBRANES .......................................................................................... 80

3.1 Introduction ......................................................................................................... 80

3.2 Experimental ....................................................................................................... 83
  3.2.1 Materials ........................................................................................................ 83
  3.2.2 Synthesis of N-allylpiperidine ...................................................................... 83
  3.2.3 Synthesis of N,N-diallylpiperidinium chloride (DApipCl) .............................. 84
  3.2.4 Synthesis of bis(4-fluorophenyl) disulfide ...................................................... 85
  3.2.5 Oxidation of 4-fluorothioanisole to 4-fluorophenylmethyl sulfone .............. 85
3.2.6 Synthesis of 4-fluorophenyl sulfide terminated poly(N,N-diallylpiperidinium chloride) (PDApipCl) .................................................................................................................. 86

3.2.7 Oxidation of 4-fluorophenyl sulfide terminated (PDApipCl) and ion metathesis to hexafluorophosphate ................................................................................................. 86

3.2.8 Synthesis of Polysulfone-PDApipPF$_6$ multiblock copolymers ........................................ 87

3.2.9 Membrane fabrication ................................................................................................... 88

3.2.10 Ion Exchange to hydroxide ................................................................................... 88

3.2.11 Characterization and Measurements ...................................................................... 88

3.3 Results and Discussion ................................................................................................. 92

3.3.1 Synthesis of PDApipPF$_6$ telechelics ....................................................................... 92

3.3.2 Synthesis of PSf-PDApipPF$_6$ multiblock copolymers ............................................ 96

3.3.3 Membrane fabrication and mechanical properties .................................................. 99

3.3.4 Morphology of the membranes ............................................................................. 101

3.3.5 Water uptake and hydroxide conductivity ............................................................ 103

3.3.6 Base stability ......................................................................................................... 106

3.4 Conclusions ................................................................................................................. 109

3.5 Acknowledgments ....................................................................................................... 110

3.6 References ................................................................................................................... 110

CHAPTER 4 EFFECT OF BLOCK LENGTH ON PROPERTIES OF MULTIBLOCK POLYSULFONE-POLY(DIALLYLPIPERIDINIUM HYDROXIDE) COPOLYMERS ......................................................... 117

4.1 Introduction .................................................................................................................. 117

4.2 Experimental ............................................................................................................... 119

4.2.1 Materials ................................................................................................................ 119

4.2.2 General Synthesis .................................................................................................. 120

4.2.2.1 Synthesis of multiblock PSf-PDApipPF$_6$ copolymers ........................................ 120

4.2.2.2 Membrane fabrication .................................................................................... 121

4.2.2.3 Ion exchange to hydroxide ............................................................................. 122

4.2.3 Characterization ...................................................................................................... 122
4.3 Results and Discussion .................................................................................................................................................. 125

4.3.1 Synthesis of 4-fluorophenyl sulfone terminated PDApipPF₆ oligomers ......................................................... 125

4.3.2 Summary of multiblock PSf-PDApipPF₆ copolymers synthesized ................................................................. 128

4.3.3 Membrane formation and ion exchange to hydroxide ......................................................................................... 130

4.3.4 Physical properties: IEC and water uptake ........................................................................................................... 130

4.3.5 Hydroxide conductivity .......................................................................................................................................... 132

4.3.6 Membrane phase separation ............................................................................................................................... 133

4.4 Conclusions ................................................................................................................................................................. 135

4.5 Acknowledgments .................................................................................................................................................... 136

4.6 References ................................................................................................................................................................. 136

CHAPTER 5 CONCLUSIONS AND FUTURE WORK ......................................................................................................................... 143

5.1 Conclusions ................................................................................................................................................................. 143

5.2 Future work ............................................................................................................................................................... 146

5.3 References ................................................................................................................................................................. 149

APPENDIX A CHARACTERIZATION OF ADDITIONAL PSF-QAPF MULTIBLOCK COPOLYMER MEMBRANES ........................................ 151

APPENDIX B ADDITIONAL CHARACTERIZATION POLY(DIALYLPIPERIDINIUM HYDROXIDE) MULTIBLOCK COPOLYMERS ................................................................................................................................. 152

B.1 Synthesis of 4-fluorothioanisole ............................................................................................................................... 154

B.2 Acknowledgments .................................................................................................................................................... 156

B.3 References ................................................................................................................................................................. 156
LIST OF FIGURES

Figure 1.1 Random PSf copolymer of BPA and DHTP ................................................................. 9
Figure 1.2 Structure of multiblock PSf-PB copolymer .............................................................. 16
Figure 1.3 Multiblock PSf copolymers containing the PPH moiety ........................................... 26
Figure 1.4 Multiblock PSf AEM materials containing benzyltrimethylammonium hydroxide functionalized TMBPA PSf hydrophilic segments ........................................... 34
Figure 1.5 PSf multiblock copolymers with bis-quaternary ammonium functionalized PPH-DMPA segments. ................................................................................................. 35
Figure 2.1 Multiblock PSf-QAPF copolymer ............................................................................... 52
Figure 2.2 GPC RI chromatograms of PSf-OH and PSf-PF multiblock copolymers ................. 62
Figure 2.3 $^1$H NMR spectrum of PSf-PF multiblock copolymer (PSf-PF4) ............................. 63
Figure 2.4 GPC chromatograms of PSf-PF multiblock copolymers before and after NBS/Zr(IV)Cl bromination ......................................................................................... 66
Figure 2.5 $^1$H NMR spectrum of PSf-BrPF multiblock copolymer (PSf-BrPF4) ....................... 67
Figure 2.6 $^1$H NMR spectrum of PSf-QAPF multiblock copolymers in DMSO-d$_6$ .......... 68
Figure 2.7 Hydroxide conductivity (A) and water uptake (B) vs. IEC for PSf-QAPF4-6. Closed symbols at 60 °C, open symbols at room temperature. .............................................. 70
Figure 2.8 TM-AFM 500 nm$^2$ phase images of PSF-QAPF4 (A), PSF-QAPF5 (B), PSF- QAPF6 (C). .................................................................................................................. 72
Figure 3.1 Polysulfone-PDApipOH multiblock copolymer .......................................................... 83
Figure 3.2 $^1$H NMR spectrum of PDApipCl in deuterium oxide .............................................. 94
Figure 3.3 $^1$H NMR spectrum of 4-fluorophenyl sulfone terminated PDApipPF$_6$ in acetonitrile-d$_3$ .................................................................................................................. 96
Figure 3.4 $^1$H NMR spectrum of PSf-PDApipPF$_6$ multiblock copolymer in DMSO-d$_6$ ...... 98
Figure 3.5 PSf-PDApip multiblock copolymer membrane ......................................................... 99
Figure 3.6 DSC traces for PDApipPF$_6$, homopolymer and PSf-PDApip1 copolymer. Third heating cycle at a rate of 10 °C per minute ................................................................. 102
Figure 3.7 Tapping mode-AFM phase images for PSf-PDApip1 (A), PSf-PDApip2 (B), PSf-PDApip3 (C), PSf-PDApip4 (D). ................................................................. 102
Figure 3.8  Hydroxide conductivity (closed symbols) and water uptake (open symbols) versus IEC ................................................................. 105

Figure 3.9  Arrhenius plot of hydroxide conductivity versus 1/T ................................................ 106

Figure 3.10  $^1$H NMR spectra with exposure to base for PDApipOH polymers .................. 107

Figure 3.11  A) Thermal decomposition data for PDApipPF$_6$ homopolymer and PSf-PDApip2 copolymer. B) Comparison of PF$_6^-$, Cl$^-$, and HO$^-$ counter ions. Samples were heated at a rate of 10 °C·per minute under nitrogen flow ...... 108

Figure 4.1  PSf-PDApipOH multiblock copolymer .................................................................. 119

Figure 4.2  $^1$H NMR spectrum of PDApipPF$_6$3 ................................................................ 128

Figure 4.3  $^1$H NMR spectrum of PSf-PDApip3 ............................................................... 129

Figure 4.4  Plot of hydroxide conductivity vs. PDApipOH segment molecular weight. ..... 133

Figure 4.5  SAXS profile for PSf-PDApipBr membranes at 60 °C and 0 % RH (A) and at 60 °C and 95 % RH (B). ................................................................. 134

Figure 4.6  AFM phase images for PSf-PDApip1 (A), PSf-PDApip2 (B), and PSf-PDApip3(C) taken under ambient temperature and humidity. .................. 135

Figure B.1  DQF-COSY NMR spectrum of PDApipPF$_6$ in acetonitrile-d$_3$ ......................... 152

Figure B.2  HMQC NMR spectrum of PDApipPF$_6$ in acetonitrile-d$_3$ ............................. 153

Figure B.3  UV/vis absorbance spectrum of 4-fluorophenylsulfide terminated PDApipCl ................................................................. 154

Figure B.4  Sample Nyquist (Top) and Bode (Bottom) plots ............................................. 155

Figure B.5  Polarization curves for PSf-PDApip membranes. Tokuyama A201 membrane is black, PSf-PDApip1 is yellow, PSf-PDApip2 is blue, PSf-PDApip3 is green. Closed symbols are measured at 60 °C and open symbols are measured at 80 °C ................................................................. 156
LIST OF TABLES

Table 1.1      Fluorine treatment influence on the selectivity of copolymer membranes........17
Table 1.2     Intrinsic viscosity data of PSf prepolymers and PSf-PPP multiblock
copolymers (a) molecular weight determined by SEC, (b) intrinsic viscosity
determined in NMP with 0.05 M LiBr at 25°C.................................................................29
Table 2.1      PSf-OH oligomer molecular weight characteristics ...........................................60
Table 2.2     Composition and molecular weight characterization of PSf-PF multiblock
copolymers.........................................................................................................................62
Table 2.3     Characterization of PSf-BrPF multiblock copolymers ........................................67
Table 2.4     Characterization of PSf-QAPF multiblock copolymer membranes. .................68
Table 2.5     Mechanical characteristics of PSf-QAPF membranes.......................................73
Table 3.1      Molecular weight characterization of PDApipCl ...............................................94
Table 3.2     Characterization of PSf-PDApip copolymer samples. .......................................98
Table 3.3     Water uptake for PSf-PDApipOH membranes between room temperature
and 80 °C .........................................................................................................................103
Table 3.4     Hydroxide conductivity of PSf-PDApipOH membranes.................................104
Table 4.1      Molecular weight characterization of PDApip oligomers..............................128
Table 4.2     Summary of PSf-PDApipOH multiblock copolymer compositions...............129
Table 4.3     Characterization of PSf-PDApip multiblock copolymer membranes...............131
Table A.1     Characterization of PSF-BrPF multiblock copolymers .................................151
Table A.2     Characterization of PSF-QAPF multiblock copolymer membranes...............151
Table B.1     PSf-PDApipOH device test data...............................................................156
<table>
<thead>
<tr>
<th>Scheme</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Synthesis of PSf-LCPE multiblock copolymers by acidolysis</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Synthesis of multiblock PSf-poly(oxy-1,4-phenylene-carbonyl-co-oxy-1,3-\nnapthaloyl) copolymers</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>Acidolysis synthesis of PSf-PET/HBA LC multiblock copolymers</td>
<td>5</td>
</tr>
<tr>
<td>1.4</td>
<td>Synthesis of PSf-PDSM under Mannich reaction conditions</td>
<td>7</td>
</tr>
<tr>
<td>1.5</td>
<td>Synthesis of PSf-PTMO multiblock copolymer</td>
<td>11</td>
</tr>
<tr>
<td>1.6</td>
<td>Synthesis of multiblock PSf-PEO Copolymers</td>
<td>13</td>
</tr>
<tr>
<td>1.7</td>
<td>Silylamine-hydroxyl reaction copolymerization of PSf and PDMS</td>
<td>15</td>
</tr>
<tr>
<td>1.8</td>
<td>Synthesis of sulfonated multiblock PSf PEM</td>
<td>19</td>
</tr>
<tr>
<td>1.9</td>
<td>Synthesis of sulfonated multiblock PSf-PAEB</td>
<td>22</td>
</tr>
<tr>
<td>1.10</td>
<td>Synthesis of highly sulfonated PAESK-PSF multiblock copolymers</td>
<td>23</td>
</tr>
<tr>
<td>1.11</td>
<td>Synthesis of multiblock copolymers of SEPOK-PSf</td>
<td>24</td>
</tr>
<tr>
<td>1.12</td>
<td>Synthesis of sulfonated multiblock PAESK-PSf</td>
<td>25</td>
</tr>
<tr>
<td>1.13</td>
<td>Synthesis of PSf-PPP multiblock copolymers</td>
<td>28</td>
</tr>
<tr>
<td>1.14</td>
<td>Two-step, one pot synthesis of PAEK-PAESK multiblock copolymers</td>
<td>30</td>
</tr>
<tr>
<td>1.15</td>
<td>Synthesis of dendritic, multiblock copolymers of PAESK</td>
<td>31</td>
</tr>
<tr>
<td>1.16</td>
<td>Functionalization of the BHF residues with benzyltrimethylammonium \nhydroxide groups in multiblock PSf-PAESK multiblock copolymers</td>
<td>33</td>
</tr>
<tr>
<td>1.17</td>
<td>Synthesis of multiblock PAESK-poly(phenylene) copolymers by Ullmann \ncoupling</td>
<td>37</td>
</tr>
<tr>
<td>2.1</td>
<td>Synthesis of PSf-PF multiblock copolymers. i) K\textsubscript{2}CO\textsubscript{3}, NMP, 170 °C, 20 \nhrs. ii) KOH, NMP, 10 min</td>
<td>60</td>
</tr>
<tr>
<td>2.2</td>
<td>Functionalization of PSf-PF multiblock copolymers i) DCM, NBS, \nZr(IV)Cl, RT. 6 hrs. ii) DMSO, TMA\textsubscript{(g)}, 48 hrs</td>
<td>66</td>
</tr>
<tr>
<td>3.1</td>
<td>Synthesis of PDApipPF\textsubscript{6} oligomers. i) MeOH/water, 60 °C, hv, 24 hrs.; ii) \nOxone, 60 °C, overnight; iii) Precipitation into saturated KPF\textsubscript{6}</td>
<td>93</td>
</tr>
<tr>
<td>3.2</td>
<td>Synthesis of PSf-PDApipPF\textsubscript{6} multiblock copolymers. i) DMAc/toluene, \npotassium carbonate, reflux temperature, ~3 hours</td>
<td>97</td>
</tr>
</tbody>
</table>
Scheme 4.1  UV initiated cyclopolymerization of \(N,N\)-diallylpiperdinium chloride in the presence of BFPDS disulfide photoiniferter ..............................................126

Scheme 5.1  Proposed functionalization of brominated PSf-PF multiblock copolymers with piperidinium iodide pendants........................................................................147

Scheme 5.2  Proposed synthesis of PPO-PDApipOH triblock copolymers ......................148

Scheme 5.3  Proposed scheme for the preparation of PSf-PDApipCl multiblock copolymer by the UV cyclopolymerization of \(N,N\)-diallylpiperdinium chloride in the presence of PSf-disulfide. .................................................................149
ACKNOWLEDGMENT

I extend my deepest thanks and gratitude to my Ph.D. advisor Dr. Daniel Knauss for his endless patience, invaluable support and guidance during my studies at the Colorado School of Mines. Without his innovative ideas, high standards, hard work, and motivation this Ph.D. thesis would not be possible. I also thank my thesis committee Dr. Stephen Boyes, Dr. James Ranville, and Dr. Andrew Herring for their ideas, assistance and support throughout my graduate education. I thank Dr. Yuan Yang for her constant willingness to help and her excellent support for the NMR laboratory. Thank you to Mr. Edward Dempsey for ensuring that all of the equipment and instruments were in working order and his help with maintenance and repairs. Thanks also goes to my current and past group members Dr. Nathaniel Rebeck, Dr. Yifan Li, Dr Yating Yang, and Dr. Feilong Liu for their help, support, and friendship which significantly contributed to my success. Special thanks to Dr. Chingching (Ami) Neyerlin for fostering our excellent collaborative relationship with the National Renewable Energy Laboratory and providing device test data.

My sincerest gratitude goes to Dr. Gaywyn Moore for her encouragement in my educational endeavors. Thanks to Dr. Douglas Dyckes and Dr. Mark Anderson for providing me the skills and knowledge to pursue my graduate career. Ultimately, the love and support from my parents who always believed in me, even when my faith was waning, has truly been the greatest gift and for that I am forever indebted.

Finally, I thank the U.S. Army Research Laboratory and the U.S. Army Research Office under the Multidisciplinary University Research Initiative (MURI grant number W11NR-10-1-0520) for their financial support of my research.
MY THESIS IS DEDICATED TO MY BELOVED PARENTS
CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1 Introduction

The investigation of block and multiblock copolymers that combine two or more incompatible materials with the goal of tuning or imparting new properties into the resultant copolymer has been of great interest for several decades. Multiblock copolymers have found utility in a myriad of applications including thermoplastic elastomers,\textsuperscript{1-3} engineering materials,\textsuperscript{4-5} shape memory plastics,\textsuperscript{6} and biomedical materials.\textsuperscript{7-9} The scope of application for multiblock copolymers is only exceeded by the plethora of polymers used to generate them. In the area of materials synthesized by step growth methods, multiblock copolymers have included poly(esters),\textsuperscript{10-12} poly(amides),\textsuperscript{13-14} poly(ethers),\textsuperscript{15} poly(urethanes),\textsuperscript{8,16} poly(ureas),\textsuperscript{17-18} poly(carbonates),\textsuperscript{19-20} poly(sulfones), and the combination thereof. Multiblock copolymers containing polysulfone segments have been used to modify existing homopolymers,\textsuperscript{21-22} as compatibilizers for polymer blends,\textsuperscript{23-25} biomedical devices,\textsuperscript{26} and significantly for polymer electrolyte membranes.\textsuperscript{27}

Much of the desired characteristics that are derived from multiblock copolymers arise from microphase separation. Phase separation allows the separated domains to have properties similar to their homopolymer analogues. Phase separated domains have a significant impact on the final material. Liquid crystal (LC) multiblock copolymers have enhanced mechanical properties, owing to the thermotropic behavior of LC polymers, when compared to the individual homopolymer.\textsuperscript{28} Furthermore, the ionic conductivity of multiblock copolymers has been significantly improved by the generation of continuous hydrophilic domains.\textsuperscript{29-30}
Poly(aryl ether sulfone), commonly referred to as polysulfone (PSf), is a class of polymers characterized as high glass transition ($T_g$) amorphous thermoplastic. The generic PSf repeat unit comprises bisphenyl sulfone and bisphenol residues. Incorporation of different bisphenol and sulfone structures into the polymer backbone has produced materials with a range of $T_g$’s (170-265 °C) and mechanical properties. The high thermal stability, film forming properties, mechanical strength, and chemical resistance characteristics have made PSf unique high performance engineering materials. These properties have contributed to the significant interest in incorporating PSf into multiblock copolymers with a broad span of applications.

The scope of this review is intended to cover the synthesis and applications of multiblock PSf copolymers.

1.2 High performance materials

Development of high performance polymers has been the aim of polymer research for many decades. Designing high performance plastics requires an intelligent balance of material properties such that the materials exhibit excellent toughness and thermal characteristics. One successful approach to designing new tailor-made high performance materials has been the development of multiblock copolymers in which covalently bound, immiscible polymers produce materials that exhibit synergistic characteristics.

1.2.1 High strength, reinforced multiblock copolymers

Research in the development of ultra-high strength, high modulus materials has indicated that polymers adopting a rigid-rod conformation have mechanical strengths at or near their theoretical limit. One class of materials exhibiting such behavior is liquid crystal polymers (LCP)s. LCPs typically have a rigid backbone structure resulting in extended polymer chains and crystalline domains. However, LCPs suffer from difficulty in processing
owing to their rigid structures, which significantly raise their melting point and lower their solubility. To counteract the processing difficulties of LCPs, flexible PSf segments have been introduced.

The introduction of flexible PSf segments into LCPs offers the attractive possibility of producing liquid crystal reinforced thermoplastics. In an early investigation, Auman and co-workers\(^{33}\) were able to synthesize multiblock PSf-liquid crystal polyester (PSf-LCPE) materials from acetoxy terminated PSf in the presence of the monomers chlorohydroxyhydroquinone diacetate and \textit{trans}-1,4-cyclohexane dicarboxylic acid via acidolysis (Scheme 1.1). The synthesis of the PSf-LCPE materials was only partially successful. The resulting polymeric materials obtained from 2,300 g·mol\(^{-1}\) PSf oligomers were shown to be largely a mixture of both PSf and LCPE homopolymers, as determined by fractionation. However, if the number average molecular weight of the PSf was decreased to 1,400 g·mol\(^{-1}\), multiblock materials were readily produced. Chromatograms obtained from size exclusion chromatography (SEC) of the PSf oligomer and the multiblock copolymer indicated a sizable shift to higher molecular weight.

Scheme 1.1 Synthesis of PSf-LCPE multiblock copolymers by acidolysis

The multiblock PSf-LCPE copolymers were thermally processible and were characterized by differential scanning calorimetry (DSC), post fractionation. Thermal
transitions associated with the crystal-crystal ($T_{kk}$) and crystal-nematic transitions ($T_{kn}$), were observed and confirmed the presence of the LCPE segments. Unfortunately, the glass transition ($T_g$) of the PSF segments was not observed due to overlap of the $T_{kk}$ transition and thus DSC could not establish a phase separated copolymer system.

The microphase separation of the PSf-LCPE multiblock copolymers was determined by optical microscopy with cross polarizers. Micrographs of the PSf-LCPE copolymers indicated that the schlieren nematic textures and birefringence observed with the LCPE homopolymer decreased with increasing PSf incorporation and the generation of a two-phase disordered material.

In another preliminary investigation, Chang designed a system of PSf-poly(oxy-1,4-phenylenecarbonyl-co-oxy-1,3-naphthaloyl) copolymers which were synthesized from hydroxyl terminated PSf, $p$-hydroxybenzoic acid and 2-hydroxy-6-naphtholic acid (Scheme 1.2). These PSf- poly(oxy-1,4-phenylenecarbonyl-co-oxy-1,3-naphthaloyl) copolymers were synthesized by transesterification with triphenylphosphine dichloride as a condensing agent. The resulting materials were fractionated into the THF and $p$-chlorophenol soluble fractions, and the $p$-chlorophenol insoluble fraction. The $p$-chlorophenol soluble fraction corresponded to the PSf- poly(oxy-1,4-phenylenecarbonyl-co-oxy-1,3-naphthaloyl) multiblock copolymer.

Scheme 1.2 Synthesis of multiblock PSf-poly(oxy-1,4-phenylenecarbonyl-co-oxy-1,3-naphthaloyl) copolymers
SEC, DSC, Fourier-transform infrared spectroscopy, optical microscopy and X-ray diffraction techniques were employed to characterize these materials. Successful copolymerizations were indicated by the increased molecular weight relative to the PSf starting material as determined by SEC. The DSC thermograms indicated two separate T_g’s, which corresponded to the individual component materials, and a T_m for the copolymer. Furthermore, the X-ray diffraction data indicated a 4.5-angstrom phase separation.

In similar work, Pospiech et al. synthesized a series of multiblock PSf-poly(ethylene terephthalate-co-1,4-oxybenzoate) (PET/HBA) copolymers by polymerization of acetoxy terminated PSf oligomers with carboxylic acid terminated PET/HBA oligomers by acidolysis shown below in Scheme 1.3. The acetoxy terminated PSf oligomers ranged in their M_n from 1,240 to 5,730 g mol^-1 and the carboxylic acid terminated PET/HBA oligomers ranged from 3,600 to 7,700 g mol^-1. The resulting materials obtained had molecular weights up to 71,900 g mol^-1, as determined by SEC. Further confirmation of high molecular weight materials was given by ^1H NMR analysis of the obtained copolymers. Residual acetoxy terminated bisphenol A (BPA) residues present in the materials were not observable indicating that their concentration was below the detection limit, thus high M_n was obtained.

Scheme 1.3 Acidolysis synthesis of PSf-PET/HBA LC multiblock copolymers.

Transmission electron microscopy (TEM) and DSC characterized the phase behavior of the multiblock copolymers. TEM images clearly indicated that as cast films show minimal phase separation, but when the films are annealed at temperatures below the T_g of the PSf
block to temperatures above it, the nematic structures typically observed with LCPs were present. DSC thermograms depicting the second heating cycle of high molecular weight PSf, PET/HBA LCP, and multiblock PSf-PET/HBA were compared. With respect to the multiblock copolymer, two separate glass transitions were detected with good correlation between the PET/HBA homopolymer and PET/HBA segments. The $T_g$ observed for the PSf segments were lower in comparison to the high molecular weight PSf, which was attributed to the low molecular weight of the segments and some phase mixing.

The mechanical properties for the PSf-PET/HBT multiblock copolymers were also evaluated. The multiblock PSf-PET/HBT copolymers were shown stiffer by the elastic modulus increasing from 2.5 GPa for the high molecular weight PSf to 6.6 GPa for the multiblock copolymer. Furthermore, the tensile strength and fracture strength increased from 72.4 and 48.3 MPa for the homopolymer to 78.7 to 77.6 MPa, respectively.

1.2.2 Ductile multiblock copolymers

Complementary to high strength reinforced thermoplastics are materials that show toughness by increasing the ductility. It has been determined that some thermoplastics and thermosets are somewhat brittle and prone to stress cracking.\textsuperscript{36-38} Efforts to develop high strength polymers with improved ductility have indicated incorporation of elastomers can produce materials with improved resistance to stress cracking and with a range of mechanical properties.

One such elastomer-toughened material that has been investigated is epoxy thermoset resins. Epoxy resins after curing are often very brittle due to their highly crosslinked architecture, so in an effort to improve the post curing mechanical properties, multiblock PSf-PDMS copolymers were synthesized with the premise that the PSf segments would be miscible with the epoxy resin and that phase separated PDMS segments would reduce the
brittleness. The segmented copolymers were synthesized from hydroxyl terminated PSf (Mₙ = 2.3 kg mol⁻¹), and propylamine terminated PDMS (Mₙ = 2.4 kg mol⁻¹) in the presence of formaldehyde, shown below in Scheme 1.4. Under the Mannich reaction conditions employed, the terminal amine was alkylated twice and formed an oxazine ring that connects the segments. Molecular weights in excess of 24.7 kg mol⁻¹ were obtained in this reaction system.

Scheme 1.4 Synthesis of PSf-PDMS under Mannich reaction conditions

Thermal analysis of the neat epoxy resin and epoxy containing multiblock copolymers were compared. The Tₑ of the neat epoxy resin was determined to be 177 °C, and the neat multiblock copolymer was determined to be 110 °C. When the PSf-PDMS multiblock copolymer was introduced at different weight percent, the single glass transition for the epoxy resin was depressed to 167 °C at 20 wt. %.

The surface structure of the films produced was investigated with atomic force microscopy (AFM). A well-connected network of PDMS domains was indicated by the AFM phase images. The significant difference in viscoelastic properties of the soft PDMS segments and hard PSf segments and epoxy matrix provided contrast and elucidated the phase separation. TEM analysis showed microspheres with an average diameter of 50 nm of multiblock copolymer present in the epoxy matrix.
Evaluation of the fracture resistance was also completed. It was shown that the fracture resistance was significantly increased by the presence of the multiblock copolymers. The critical stress intensity factor increasing almost three times with the addition of 5 wt.% PSf-PDMS multiblock copolymer.

In an effort to elucidate the impact on phase behavior and the corresponding mechanical properties of PSf-PDMS multiblock copolymers by introduction of fluorine into the PSf backbone, two series of multiblock PSf-PDMS copolymers were compared. One set of multiblock copolymers was produced from PSf derived from bisphenol AF (BPAF) and the other was produced from PSf derived from BPA. The phenoxide terminated PSf oligomers were copolymerized with silylamine terminated PDMS. The silylamine-hydroxyl reaction is accomplished by nucleophilic substitution with the evolution of dimethylamine. The PSf and PDMS oligomers were relatively low molecular weight, ranging between 5.4 and 6.8 kg mol$^{-1}$ for the PSf and between 4.1 and 10 kg mol$^{-1}$ for the PDMS.

Morphological characterization was completed by AFM, TEM and small angle x-ray scattering (SAXS). Surface morphology of as cast materials was shown to be strongly phase separated into interconnecting worm-like structures. Cross-sectional analysis by TEM indicated that for materials with approximately equal blocks, lamellae structures are obtained. Conversely, if the segments were significantly different in molecular weight or the PDMS segments were small relative to the PSf, no ordered morphology was observed. Corroboration of the observations from the microscopic characterizations was obtained by SAXS. Copolymers, which were observed to phase separate, showed a strong scattering peak from which the domain spacing was determined to be between 22 and 30 nm. The domain spacing was directly proportional to the segment lengths. Also, the introduction of fluorine in the backbone from the BPAF increased the scattering intensity by $\sim 40\%$ compared to copolymers of similar composition not containing fluorine. The increase in scattering
intensity was attributed to the higher electron density of the fluorine atoms and loosely to enhanced phase separation.

Each series of multiblock copolymers were characterized by their mechanical properties and were compared to their corresponding high molecular weight homopolysulfone. The weight percent of PDMS incorporated into the multiblock copolymer for each set was approximately 36, 47 and 65 wt.%. In all cases, the increase of PDMS into the multiblock copolymer corresponded to a decrease in the tensile strength and elastic modulus and a dramatic increase in the strain at break. The stress at break was reported to be reduced approximately by half, and the strain at break was increased approximately 400% for the fluorine containing multiblock copolymers at 65 wt.% PDMS. The multiblock copolymers without fluorine were reported to have the stress at break also reduced by half, however, the strain at break increased by approximately 600% at 65 wt.% PDMS.

In a similar investigation, the impact of rigid terphenyl groups introduced into the PSf segments of multiblock PSf-PDMS copolymers on mechanical and morphological behavior was also evaluated. The multiblock copolymers were synthesized by reacting a PSf random copolymer (Figure 1.1) derived from BPA and 4,4'-dihydroxyterphenyl (DHTP) with silylamine terminated PDMS. Molecular weights of the copolymers were related to their resulting intrinsic viscosities, which ranged from 0.135 to 0.441 dl g\(^{-1}\).

![Figure 1.1 Random PSf copolymer of BPA and DHTP](image)

Thermal characterization indicated that all but one of the copolymers showed two glass transitions. The first \(T_g\) at -122 °C corresponded to the PDMS segments and the \(T_g\) corresponding to the PSf segments was observed between 143 °C and 192 °C. The
determination of two distinct $T_g$s indicated that phase separation was achieved. The one copolymer, which displayed only a single $T_g$ at 189 °C, contained very short PDMS segments ($M_n = 1.3$ kg mol$^{-1}$), therefore phase mixing in this system was indicated. It was also shown that as the content of DHTP was increased from 20% to 25% in the PSf segments, the glass transition markedly increased from 161 °C to 189 °C for similar molecular weight segments. This result was attributed to the increased rigidity of the PSf segments. Surface phase separation of the copolymers was investigated with AFM. The micrographs clearly showed worm-like structures, which became more defined and interconnected as the PDMS content increased from 17% to 64%.

The mechanical properties of the DHTP containing PSf-PDMS multiblock copolymers were also investigated. The weight percent of PDMS in the multiblock copolymer was increased from 17 to 64 wt.%. High molecular weight PSf with 20 % DHTP and commercial UDEL® were used for comparison. The multiblock copolymers produced a range of mechanical properties. The PSf-PDMS multiblock copolymer containing 25 % DHTP and 17 wt. % PDMS had the highest tensile strength (yield stress = 66 MPa) compared to 37 MPa and 28 MPa for the PSf (20 % DHTP) and UDEL®, respectively. The most elastic material was the multiblock copolymer containing 65 wt. % PDMS which had a strain at break of 630 % compared to 5% and 6% for the PSf (20 % DHTP) and UDEL®, respectively.

Investigation of the impact that segment molecular weight in PSf-poly(tetramethylene oxide) (PSf-PTMO) has on phase separation in PSf/PSf-PTMO blends has also been completed. Carboxylic acid terminated PTMO oligomers were synthesized by the condensation of aminopropyl terminated PTMO with trimellitic anhydride (TMI) which was then followed by thermal imidazation. The carboxylic acid terminated PTMO ($M_n = 1.1$ or 2.5 kg mol$^{-1}$) oligomers were copolymerized with acetoxy terminated PSf by acidolysis (Scheme 1.5). The PSf oligomers had molecular weights ranging from 283 to 9000 g mol$^{-1}$. 


Multiblock copolymers with moderate molecular weights ($M_n$), ranging from 6.2 to 24.9 kg mol$^{-1}$ were produced in this reaction system. The lack of high molecular weight copolymers from this synthesis was determined to result from the side reaction of carboxylic acid, either from the TMI endcaps or the liberated acetic acid, attacking the ether linkages in the PTMO oligomers. Given the side reactions present, polymerization time was kept minimal and moderate molecular weights were obtained.

![Scheme 1.5 Synthesis of PSf-PTMO multiblock copolymer.](image)

The phase separation of these segmented copolymers was examined by thermal analysis. All of the copolymers synthesized from the 1.1 kg mol$^{-1}$ PTMO oligomer possessed only a single $T_g$, which increased from -10 °C to 144 °C with increasing PSf molecular weight. These results indicate a non-phase separated material. Conversely, some of the copolymers synthesized from the 2.5 k mol$^{-1}$ PTMO oligomer possessed a $T_g$ at -70 °C corresponding to the PTMO segments and a $T_g$ between 26 °C and 90 °C corresponding PSF segments. While two glass transitions were present, the $T_g$ associated with the PSf segments is severely depressed, which implies that there is a substantial amount of phase mixing in the system. In blending the PSf-PTMO segmented copolymers with 30 kg mol$^{-1}$ PSf, both phase separated and non-phase separated blends are attainable as indicated by DSC. The degree of phase separation was dependent on the PSf block length. Blends containing segmented copolymers in which the PSf blocks were smaller than 2.5 kg mol$^{-1}$ were phase separated as
indicated by the presence of a $T_g$ for the PSf-PTMO blend component (~30 °C) and the PSf rich phase approaching 170 °C. Blends containing PSf segments greater than 3.5 kg mol$^{-1}$ were partially miscible as indicated by a single $T_g$ for the PSf rich phase (approached 170 °C). Further comparison of the PSf-PTMO multiblock copolymer to the PSf/PSf-PTMO blend indicated that for the PSf-PTMO blended systems the molecular weight between entanglements ($M_e$) required for partial miscibility was 3 $M_e$ and for the PSF-PTMO was only 2 $M_e$ for partial miscibility.

Thus far in this review, it has been demonstrated that multiblock copolymers of PSf have shown utility in the development of high performance materials. PSf multiblock copolymers have been used in high strength reinforced materials as well as more elastic materials. While some of the studies did not explicitly investigate the mechanical properties, many of the materials produced have indicated the range of possible mechanical properties and therefore the ability to produce multiblock copolymers for specific properties and applications.

### 1.3 Hydrophilic multiblock copolymers for biomedical application

Development of hydrophobic-hydrophilic polymer materials for biomedical purposes is a research area with considerable interest. It has been shown that amphiphilic polymers are adept at providing drug delivery systems, owing to hydrophilic domains solvating therapeutics for controlled release. Consequently, polymeric biomedical materials have been developed with hydrophobic-hydrophilic compositions for a range of applications. The material properties for necessary for different biomedical applications range from the ability to organize into micelles to the formation of mechanically tough devices, with the capability of delivering therapeutics. In addition to drug delivery applications, hydrophobic-hydrophilic
polymers have also been shown to improve biocompatibility, which has been attributed to the hydrophilic character discouraging adverse immune system reactions.\textsuperscript{47}

Investigation of multiblock copolymers incorporating poly(ethylene oxide) (PEO) into the PSf derived from biphenol (BP) was completed for the purpose of creating a new drug delivery platform.\textsuperscript{26} The segmented copolymers generated in this study were prepared by copolymerizing chlorine terminated poly(ethylene oxide) with dichlorodiphenyl sulfone (DCDPS) and BP in a polysulfone synthesis (Scheme 1.6). The PEO oligomer had a molecular weight of 1.5 kg mol\(^{-1}\). The PEO content of the resultant materials could be accurately controlled via the stoichiometric ratio of chlorine terminated PEO and DCDPS. The resultant materials were shown to have molecular weights (\(M_n\)) ranging from 28 to 44 kg mol\(^{-1}\) and relatively narrow polydispersities, which were as low as 1.57. The composition of the PSf-PEO copolymers produced ranged from 20 to 39 wt.% in PEO.

\[
\begin{align*}
\text{Cl} & - \text{S} - \text{O} - \text{Cl} + \text{ClH}_2\text{CH}_2\text{C} -(\text{OCH}_2\text{CH}_2)_3\text{OCH}_2\text{CH}_2\text{Cl} + \text{HO} - \text{S} - \text{O} - \text{O} - \text{O} - \text{O} - \text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{K}_2\text{CO}_3 \\
& \xrightarrow{\text{DMAc, 160 °C}} \text{Cl}_x\text{H}_2\text{CH}_2\text{C} -(\text{OCH}_2\text{CH}_2)_3\text{OCH}_2\text{CH}_2\text{Cl} + \text{HO} - \text{S} - \text{O} - \text{O} - \text{O} - \text{O} - \text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}
\end{align*}
\]

\text{Scheme 1.6 Synthesis of multiblock PSf-PEO Copolymers}

The mechanical properties of the PSf-PEO multiblock copolymers were evaluated by their stress and elasticity. The stress at break ranged from 38 to 50 MPa, with the highest maximum stress produced by the multiblock copolymer containing 20 wt.% PEO. The percent strain at break was shown to be between 190 and 430\%, with the highest strain at break produced by the copolymer with 39 wt. \% PEO. Generally, the tensile strength was found to decrease with increasing PEO, and inversely, the percent strain increased with increasing wt. \% PEO.
The PSf-PEO multiblock copolymers were also evaluated for their drug release kinetics. It was shown that the therapeutics Sirolimus and Paclitaxel were released from films at a faster rate when the PEO content increased. It can be concluded that the drug release kinetics are tunable to the PEO wt. %.

1.4 Membrane technology

Developing new materials for membrane technology has been a vast research area with applications including gas separation, water treatment, electrolysis, and fuel cells to name a few. Microphase separation of multiblock copolymer materials has largely contributed to advancements in membrane function and material properties.

1.4.1 Gas Separation membranes

Membranes applied to gas separation are an important commercial technology. Due to the global push for reducing the environmental impact of greenhouse gases, the market share for gas separation membrane technology is projected to increase five times that of the year 2000 by the year 2020. Requirements for gas separation membranes include mechanical and thermal stability at elevated operating temperatures (75-100 °C), processibility into thin films or high surface area hollow fibers, and permeability and selectivity for separating a gas mixture. The permeability and selectivity of the membrane materials are influenced by the polymer structure, free volume, and polarity. PSf hollow fiber gas separation membranes have been in commercial use for many decades and were first developed by Permian. However, increased environmental regulation has driven demand for more selective and efficient systems.

Robeson and coworkers, investigated PSf-PDMS multiblock copolymers for gas separation membranes owing to PDMS being highly permeable to common gases in contrast to PSf. The study conducted involved the synthesis of the hydroxyl-terminated PSf
oligomers derived from BPA, which had weights ranging from 4.7 - 9.3 kg mol\(^{-1}\). The hydroxyl-terminated PSf oligomers were then copolymerized with silylamine terminated PDMS (\(M_n = 1.7 - 9.2\) kg mol\(^{-1}\)) thereby, generating multiblock copolymers (Scheme. 1.7).

Production of high molecular weight materials was shown to be most successful in chlorinated solvents, such as chlorobenzene, and with the slow addition of PDMS. Resulting weight average molecular weights (\(M_w\)) of the copolymers, determined by ultracentrifugation, were determined to be in excess of 238 kg mol\(^{-1}\). The composition of the PSf-PDMS copolymer ranged from 24 to 79 wt. % in PDMS.

![Scheme 1.7 Silylamine-hydroxyl reaction copolymerization of PSf and PDMS](image)

The phase separation of the copolymers was determined by analyzing their thermal transitions by DSC. For copolymers that contained PDMS segments where the molecular weight was between 4.9 and 9.2 kg mol\(^{-1}\), glass transitions at -120 and 160°C were observed for the PDMS and PSf segments, respectively. However, if the PDMS molecular weight was 1.7 kg mol\(^{-1}\), only a single glass transition at 140°C was observed and corresponded to the low molecular weight PSf segments and block mixing. All of the copolymer materials generated produced flexible transparent films, which depending on their PDMS content, had reduced tensile strength, reduced modulus and greater elongation.
The permeability characteristics of the membranes produced were also investigated. It was reported that the permeability was not significantly impacted by the wt. % PDMS, which was indicated by the permeability for the materials ranging from $1 \times 10^{-10}$ to $4 \times 10^{-8}$ cm$^2$ at standard temperature and pressure.

In a more recent study, thermoplastic elastomers containing PSf and poly(butadiene) (PB) segments were investigated for gas separation owing to their unique mechanical and morphological properties. Multiblock PSf-PB were synthesized by copolymerization of PSf oligomers ($M_n = 1.7$ kg mol$^{-1}$) and PB oligomers ($M_n = 2.2$ kg mol$^{-1}$) in the presence of 4,4’-diphenylmethane diisocyanate (MDI). The exact synthetic procedure and oligomer structure were not detailed however, the final structure of the multiblock copolymer is shown below in Figure 1.2. The molecular weight of the resultant copolymers was determined as high as 55 kg mol$^{-1}$. A series of segmented PSf-PB materials were generated wherein the weight % of PSf was varied from 20% to 70%. Each of the multiblock materials underwent treatment with gaseous fluorine following copolymerization.

\[
\left[\begin{array}{c}
\overset{\text{O}}{N} \overset{\text{O}}{N} \overset{\text{O}}{N} \\
\overset{\text{O}}{C} \overset{\text{O}}{C} \overset{\text{O}}{C}
\end{array}\right]_n \overset{\text{O}}{C}-\overset{\text{O}}{C}-\overset{\text{O}}{C}
\]

Figure 1.2 Structure of multiblock PSf-PB copolymer

The phase separation and percent weight gain from fluorination were characterized by SAXS. SAXS profiles were obtained for samples prior to and after fluorine treatment. All copolymers possessed a $q_{\text{max}}$ peak indicative of phase separation in the pre-and post-fluorination data sets. However, it was noted that post fluorination SAXS showed that the scattering intensity was markedly reduced, which was ascribed to the non-selective fluorination of both PSf and PB segments. When the PB segment density, which was calculated from the absolute scattering intensity, was plotted vs. percent weight gain from
fluorination, the trend indicated two linear regions. The first region corresponded to the addition of perfluorinated segments (% weight gain = 5-15%) and the other, the formation of continuous HF networks in the copolymer (% weight gain greater than 15%).

Ultimately, the separation factor for several gaseous mixtures was determined for the PSf-PB multiblock copolymer membranes (Table 1.1). With the exception of the H₂S/CO₂ mixture, the selectivity was improved by fluorination of the membranes.

Table 1.1 Fluorine treatment influence on the selectivity of copolymer membranes

<table>
<thead>
<tr>
<th>Gaseous Mixture</th>
<th>Separation factor of membrane</th>
<th>Initial membrane</th>
<th>Post fluorination membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂/CH₄</td>
<td>1.5</td>
<td>70-100</td>
<td></td>
</tr>
<tr>
<td>O₂/N₂</td>
<td>3.0</td>
<td>5.0-6.5</td>
<td></td>
</tr>
<tr>
<td>CO₂/CH₄</td>
<td>6.2</td>
<td>40-50</td>
<td></td>
</tr>
<tr>
<td>H₂S/CO₂</td>
<td>3.2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>H₂/H₂S</td>
<td>0.125</td>
<td>12-15</td>
<td></td>
</tr>
</tbody>
</table>

1.4.2 Multiblock ion exchange membranes

The development of new ion exchange membranes for application in electrochemical systems for lithium ion batteries, electrolysis, and fuel cells continues to be a research area of importance. Membranes designed for such applications have several basic requirements, which include mechanical strength, thermal and chemical stability, high ionic conductivity, and high electrical resistance. Efforts to meet these basic requirements have focused largely on microphase separated materials in which the ionic conducting portion of the copolymers aggregates in the membrane, thus producing conductive domains surrounded by a mechanically strong matrix. The proposed implications of the phase separated design are
that the conductive phase forms better-connected networks to conduct ions and the water management is improved, which leads to better mechanical properties.

1.4.2.1 Membranes for proton exchange membranes (PEMs)

PEMs for applications in fuel cells have been a prominent research topic given the increasing demand for clean energy. PEMs need to provide a selective barrier between the fuel cell electrodes. The requirements for a PEM include the ability to produce thin, mechanically and thermally robust films, which have a high ion exchange capacity and high conductivity. One strategy employed to a great extent in order to provide a solution to these requirements, is to use polymer materials that will phase separate into hydrophobic matrix and hydrophilic conductive domains. PEMs that are able to nano-phase separate can provide continuous ionic pathways for ion conduction. Owing to their excellent mechanical and thermal properties, PSFs provide a potentially suitable starting material. Multiblock PSFs that contain both a hydrophobic matrix and a hydrophilic conducting block are able to combine the mechanical and thermal stability of PSf with highly functionalized and conductive segments.

Multiblock copolymers designed for PEM application have been prolifically investigated. The basic design for the multiblock copolymers is the incorporation of sulfonated PSf into a non-sulfonated PSf material. The synthesis of multiblock PSf has been accomplished by either copolymerization of telechelic oligomers with complementary functionality or by the copolymerization of a telechelic oligomer with PSf monomers.

It has been shown that without the use of the relatively more reactive fluorinated sulfone monomers, transetherification occurs and leads to randomization of the blocks. Illustrating the point that block transetherification can be eliminated from multiblock PSf polymerization reactions was indicated through comparison of multiblock and random copolymers containing PSf derived from BPAF and sulfonated PSf derived from BP. The
fluorine terminated PSf oligomers of BPAF were produced by using a calculated excess of difluorodiphenyl sulfone (DFDPS). These oligomers were then copolymerized with the phenoxide terminated sulfonated PSf of BP (Scheme 1.8). In a similar copolymerization, the preformed oligomers were replaced by the corresponding monomers to produce the random copolymer.

Scheme 1.8 Synthesis of sulfonated multiblock PSf PEM

Analysis of $^{13}$C NMR spectra of the multiblock copolymer and the random copolymer clearly indicated that the carbons \textit{para} to the sulfone linkage in the multiblock copolymer appear as four well resolved sharp singlets. In contrast, the carbons in the random copolymer appear as six separate signals, which are subsequently split; therefore, any transesterification side reactions that occurred during synthesis of the multiblock copolymer were effectively below the detection limit of $^{13}$C NMR spectroscopy and were determined to be insignificant.

Characterization of the copolymer phase separation supported the minimization of transesterification. DSC measurements exhibited two distinct thermal transitions. One transition at 205 °C was determined to be the $T_g$ of the BPAF PSf segments and a broad transition from 250 to 300 °C was the relaxation of the sulfonated BP PSf segments. The phase separation indicated by thermal transitions was confirmed by TEM and SAXS. TEM images clearly indicated long-range ordered lamella, which consequently became more defined as the block lengths increased and furthermore, SAXS profiles indicated first-order
and second-order peaks associated with the $q_{\text{max}}$ and $2q_{\text{max}}$ signals associated with lamellar long-range order, and the domain spacing was between 21 and 36 nanometers. 

The synthesis of well-defined multiblock copolymers of PSf from fluorine-terminated oligomers has prompted the development of segmented materials from hexafluorobenzene (HFB) and or decafluorobiphenyl (DFBP) in the repeat units or as chain extenders. Incorporating HFB or DFPB in the copolymers has the advantage of adding hydrophobicity to the repeat units, due to the increased fluorine content, thus further enhancing phase separation of amphiphilic materials while maintaining the reactivity of the fluorine terminated oligomer starting materials. 

Synthesis of multiblock copolymers of PSf containing either the HFB or DFBP moiety require extra considerations with respect to reaction conditions. While providing unique and mild reaction systems, both the HFB and DFBP molecules have been shown to cause side reactions due to the extra fluorine content. In one study where multiblock PSf was produced from the disulfonated hydroxide-terminated PSf of BP and the fluorine terminated PSf of DFDP, the synthesis of the PSf of DFBP was shown to crosslink under certain conditions. Yu and coworkers presumed that the para fluoride was only slightly more reactive compared to those at the ortho positions. Consequently, it was shown that during the oligomer synthesis if the bisphenoxide is in stoichiometric excess, the reaction would go to gelation in approximately 1.5 hours. However, in conditions where the DFBP is in a stoichiometric excess of the bisphenoxide, high molecular weight materials were obtained within 2 hours. Therefore, it was concluded that the phenoxide species preferentially reacts at the para position first and any phenoxide remaining in the system will subsequently react at the ortho position.

In a separate study of amphiphilic PSf, multiblock materials were produced from oligomers of HFB-terminated poly(phenylene sulfone) (PPSf) and either hydroxyl-terminated
oligomers of the PSf of BP or the PSf of BPAF. The copolymerization stoichiometry between the two prepolymers was 1:1. Analysis of the $^{19}$F NMR spectra obtained for the multiblock materials clearly indicated that coupling reactions were occurring on HFB moieties adjacent to a sulfone linkage. Furthermore, coupling reactions were shown to occur at both ortho and para positions to the sulfone with coupling reactions at the ortho position being the major product. Therefore, the multiblock copolymer contained pendant HFB terminated bisphenol repeat units. While the coupling position in the course of the copolymerization was not detrimental to the final material, in that high molecular weight copolymers were still obtained that produced mechanically robust membranes, it was clearly unexpected. The branching phenomenon has also been reported in other works where the polydispersity was significantly larger (6-8) than for a typical linear step-growth polymerization.

The phase separation of the resultant branched multiblock PSf-PPSf membranes was investigated with AFM, TEM, and SAXS. Micrographs from AFM and TEM clearly indicated that the surface possessed an interconnected network of hydrophilic, conductive domains and the bulk morphologies, seen from TEM cross-sections, transitioned from small, disordered cylinders to well-ordered lamella as the block lengths increased. Finally, SAXS confirmed the visual observations from the obtained micrographs in that all of the segmented copolymers showed a strong scattering peak, which indicated a domain spacing of 16 nm.

Segmented PSf copolymers can also be synthesized by nucleophilic aromatic substitution of oligomers that contain fluorobenzonitrile endcaps. In the work completed by Rowlett et al, it was shown that the ortho nitrile group is sufficiently activating for nucleophilic aromatic substitution conditions, while furthermore it was indicated that block randomization is also avoided. Additionally, the pendant nitrile functionality has been shown to further enhance phase separation due to its ability to have strong diopole interactions. In
this study, fluorine terminated poly(arylene ether benzonitrile) (PAEB) oligomers were synthesized from BPAF and difluorobenzonitrile (Scheme 1.9). The PAEB telechelics were then copolymerized with either the sulfonated PSf of BP or the sulfonated PSf of hydroquinone (HQ), each of which was the same molecular weight as the PAEB oligomer.

![Scheme 1.9 Synthesis of sulfonated multiblock PSf-PAEB](image)

Similarly to the work of Chen, $^{61}$ $^{13}$C NMR was employed to determine the block character of the final material and it was determined that the arylene ether carbons were present as four well-resolved, sharp singlets.

The two series, BP based PSf and HQ based PSf, were generated to elucidate what effect the size of the repeat unit has on the phase separation, which was investigated via SAXS and TEM. Two separate trends in phase separation were observed in SAXS and were further confirmed by TEM. First, as the block length of the oligomers increased, so did the scattering intensity, which implied that the phase separation was enhanced. Second, segmented copolymers that contained HQ repeat units would show further enhanced phase separation with smaller block sizes, as seen by a stronger $2q_{\text{max}}$ scattering peak and was attributed to the higher ion exchange capacity (IEC) achieved with the smaller repeat unit.

The proton conductivity of the PSf-PAEB multiblock copolymers was evaluated for both the BP and HQ based membranes. It was reported that all of the membranes had
excellent proton conductivity with a maximum of 170 mS·cm⁻¹ obtained. It was also observed that in this polymer system, the impact of the block molecular weight was negligible. However, it was reported that the HQ based multiblock copolymers had higher conductivity compared to the BP based materials. This result was supported by the enhanced phase separation observed in the HQ based materials, which was determined from SAXS.

The design and synthesis of multiblock PSf PEMs is primarily focused on producing segmented materials that contain densely functionalized repeat units. Multiblock copolymers of the PSf synthesized from BP and the poly(arylene ether sulfone ketone) (PAESK) derived from 4,4’-dihydroxybenzophenone were synthesized. Fluorine terminated PAESK prepolymer were first sulfonated with fuming sulfuric acid and then were reacted with hydroxyl terminated PSf of BP oligomers (Scheme 1.10). The sulfonation of the PAESK prepolymer can install up to four sulfonic acid groups per repeat unit owing to the electron-donating character of the ether linkages, thus all four aromatic rings in the repeat unit can be functionalized. Molecular weights of the final segmented copolymer exceeded 140 kg mol⁻¹. Given that the PAESK and PSf oligomer molecular weights were determined to be 5 kg mol⁻¹ and from 6 to 24 kg mol⁻¹, respectively, it can be stated that a high number of segments were incorporated.

Scheme 1.10 Synthesis of highly sulfonated PAESK-PSF multiblock copolymers
The phase separation of the resulting copolymers was investigated with scanning transmission electron microscopy (STEM). The domains observed were poorly defined, but the domain sizes were observed to increase with increasing segment molecular weight.

Improved oxidative stability of PSf PEMs can be imparted by the inclusion of the triphenylphosphine oxide moiety into the polymer backbone. Miyake et al., synthesized a series of multiblock copolymers containing PSf and sulfonated poly(arylene ether phosphine oxide ketone) (SEPOK). The fluorine terminated hydrophilic SEPOK block was generated in two steps. First, bis(4-fluorophenyl) phenylphosphine oxide was reacted with dihydroxybenzophenone. A high degree of sulfonation was obtained with 30 wt% oleum, thus generating the SPEOK prepolymer. Lastly, the SPEOK oligomer was reacted with the phenoxide terminated PSf of BP to produce the final multiblock PSf-SPEOK material (Scheme 1.11).

Scheme 1.11 Synthesis of multiblock copolymers of SEPOK-PSf

The segmented copolymers were shown to have excellent phase separation as determined by STEM. The STEM images indicated that the copolymers had well-connected hydrophilic domains, which were on average 5 nm in width.

Ultimately, membranes of the PSf-SPEOK copolymers were tested for their oxidative stability with Fenton’s reagent for 1 hour and were determined to be stable. The stability was
determined to be a result of the phosphine oxide moiety to decompose hydrogen peroxide and the resulting radicals.

Efforts to enhance phase separation and improve ionic conductivity have resulted in several studies that have been conducted on multiblock PSf copolymers containing the fluorene moiety. Enhancement of phase separation with the fluorenyl group has several advantages including that it enhances the rigidity and increases the free volume of the polymer segments, and it provides a handle for up to four ionic species per repeat unit. Bae and coworkers synthesized high molecular weight multiblock copolymers from the oligomers of the PAESK of 4,4'-dihydroxybenzophenone and the PSf of 9,9-bis(4-hydroxyphenyl)fluorene (BHF), shown below in Scheme 1.12. The molecular weights of the resulting multiblock copolymer achieved were 122 kg mol\(^{-1}\) within 3 hours of reaction time.

![Scheme 1.12 Synthesis of sulfonated multiblock PAESK-PSf](image)

The sulfonated copolymers readily phase separated, which was evidenced by STEM and SAXS. The observed morphology in STEM micrographs indicated that as the block length increased so did the hydrophilic domain size. SAXS measurements indicated that the block length and IEC were independent of morphology under hydrated conditions.
The sulfonated PAESK-PSf segmented copolymers were tested under proton exchange membrane fuel cell conditions and proved to be inadequate due to oxidative degradation of the hydrophilic block. Furthermore, reactions of the aromatic rings and or the sulfonic acid groups with the platinum catalyst decreased performance at the cathode.

Another approach to imparting rigidity into the multiblock copolymer is the incorporation of phenolphthalein. Guo et al. synthesized hydroxyl terminated PSf oligomers from phenolphthalein (PPH) and sulfonated or non-sulfonated DCDPS (Figure 1.3). The PSf oligomers were then reacted with the sulfonated or unsulfonated PSf of BP, making use of the DFBP chain extender. All of the segmented copolymers exhibited high intrinsic viscosity (0.61 to 2.02 dL g\(^{-1}\)) thus, indicating that high molecular weight was obtained.

![Figure 1.3 Multiblock PSf copolymers containing the PPH moiety](image)

The morphological features of the films drop cast from N,N-dimethylacetamide (DMAc) were observed via tapping mode AFM (TM-AFM). Films that contained short (5 kg mol\(^{-1}\)) hydrophobic and hydrophilic segments displayed well-connected hydrophilic domains, however, when the block sizes increased to 10 kg mol\(^{-1}\) for both segments, the hydrophilic
domains were disrupted. The disruption was attributed to the bulky PPH repeat units. Ionic conductivities of 154 mS cm$^{-1}$ were obtained from materials composed of sulfonated PSf of BP and a matrix of the PSf of PPH, and were ultimately determined to be the best in the series.

The homopolymers of 2,5-benzophenones are very interesting materials in that they are easy to produce in high molecular weight via Ni(0) coupling polymerization and that they have excellent thermal and mechanical properties. Furthermore, the pendant phenyl groups can be functionalized post-polymerization. However, these materials suffer from an inability to form thin flexible films. To improve the film properties of poly(2,5-benzophenones) and impart ionic conductivity, Ghassemi et al. synthesized multiblock copolymers of poly(4’-phenyl-2,5-benzophenone) (PPP) and the PSf of biphenyl (BP).

Fluorine terminated PPP oligomers were synthesized from 2,5-dichlorobenzophenone in the presence of triphenylphosphine, 2,2’-bipyridyl, nickel(II) chloride and zinc metal, with 4-chloro-4’-fluorobenzophenone as an end capper. The synthetic approach was to copolymerize fluorine terminated PPP with hydroxyl terminated PSf oligomers (Scheme 1.13). The resulting multiblock copolymers were sulfonated on the pendant aromatic ring of the PPP segments. The resulting copolymer materials, while able to produce thin films, had quite low molecular weights. The molecular weights ranged from 11.6 – 17.3 kg mol$^{-1}$. Additionally, given that the molecular weight of the starting PPP segments was determined to be 5 kg mol$^{-1}$ and the PSf oligomers between 2.6 and 8.1 kg mol$^{-1}$, very few segments were actually incorporated into the final material. Furthermore, post-sulfonation thermal analysis indicated only a single $T_g$ and no other experiments were conducted to indicate phase separation.
In contrast to the sulfonated PPP-PSf materials, Wang et al. synthesized multiblock copolymers consisting of a PPP with the sulfonated PSf of BP. Adopting a similar synthetic strategy, fluorine terminated PPP oligomers were copolymerized with hydroxyl terminated PSf oligomers. The only deviations in the synthesis were that the PSf segments were to serve as the sulfonated conductive material and that the PSf oligomers were synthesized from sulfonated DCDPS. The multiblock copolymers produced had hydrophobic and hydrophilic segments of equal molecular weight. A series of three different materials was investigated in which the segment molecular weights were 3,000, 6,000, and 10,000 g·mol⁻¹. The final copolymer molecular weights were estimated by intrinsic viscosity, which exhibited a large increase (Table 1.2) compared to the PSf oligomers prior to copolymerization.

The final multiblock copolymer was determined to be microphase separated as indicated by glass transitions at 174°C and 224°C, which correspond to the PPP and sulfonated PSf blocks, respectively. The phase separation was further investigated with TM-AFM. The AFM images indicated the surface of the materials contained continuous hydrophilic domains surrounded by the PPP matrix.
Table 1.2 Intrinsic viscosity data of PSf prepolymers and PSf-PPP multiblock copolymers (a) molecular weight determined by SEC, (b) intrinsic viscosity determined in NMP with 0.05 M LiBr at 25°C.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ g/mol</th>
<th>$[\eta]$ (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSF 1</td>
<td>3,100</td>
<td>0.15</td>
</tr>
<tr>
<td>PSF 2</td>
<td>5,900</td>
<td>0.24</td>
</tr>
<tr>
<td>PSF 3</td>
<td>9,900</td>
<td>0.35</td>
</tr>
<tr>
<td>PSF-PBP 1</td>
<td>-</td>
<td>0.68</td>
</tr>
<tr>
<td>PSF-PBP 2</td>
<td>-</td>
<td>0.72</td>
</tr>
<tr>
<td>PSF-PBP 3</td>
<td>-</td>
<td>0.82</td>
</tr>
</tbody>
</table>

The proton conductivity of the PSf-PPP multiblock copolymers was also evaluated. It was shown that the conductivity increased from 30 to 60 mS·cm$^{-1}$ as the segment molecular weight increased from 3,000 to 10,000 g·mol$^{-1}$. It was concluded that the proton conductivity of the materials having the same IEC of 1.57 meq·g$^{-1}$, was concomitant with increasing segment length.

To this point in the review, the multiblock PSf copolymer membranes have been primarily designed to contain segments of multiply sulfonated relatively low molecular weight repeat units with phase separation driven by the sulfonated segments. An alternative method for increasing ionic clusters in PEMs was shown by Tian and coworkers, whereby poly(arylene ether ketone) (PAEK) segments containing the 2,2’,3,3’,5,5’-hexaphenyl-4,4’-dihydroxybiphenyl (HPBP) moiety was shown to have been sulfonated on all six pendent aromatic rings. The materials generated in this report were multiblock copolymers of hydrophobic PAESK segments and hydrophilic, sulfonated PAEK segments. A contrasting feature to the synthetic method employed was that unlike the previous PEM materials discussed where the final copolymers were generated from chain extension, these materials were made through the in situ method. A one-pot, two-step procedure whereby the fluorine
terminated HPBP PAEK was first synthesized from 4-fluorobenzophenone and HPBP, followed by the addition of 4-hydroxyphenyl sulfone and additional 4-fluorobenzophenone (Scheme 1.14). The resultant copolymer was then sulfonated by the slow addition of chlorosulfonic acid.

![Scheme 1.14 Two-step, one pot synthesis of PAEK-PAESK multiblock copolymers](image)

DSC and TEM elucidated the morphological features of the final sulfonated copolymer. Thermal analysis indicated a single $T_g$ at around 200 °C for both the unsulfonated and sulfonated materials, which ultimately was inconclusive with respect to phase separation. However, TEM micrographs indicated spherical phase domains for the sulfonated copolymer with spheres as large as 15 nm in diameter. The sphere diameter was determined to be directly proportional to the hydrophobic block length.

In a novel approach to improving both the phase separation and ionic conductivity, Matsumura and coworkers synthesized several multiblock PAESK copolymers with large dendritic repeat units based on hexaphenylbenzene.$^{84}$ The hexafuncational hexakis[4-(4-fluorophenylsulfonyl)phenyl] benzene monomer was synthesized via Friedel-Crafts reaction.
of hexaphenylbenzene and 4-fluorobenzenesulfonyl chloride. The dendritic, multiblock copolymer, shown below in Scheme 1.15, was synthesized from copolymerization of the PAESK oligomers in the presence of excess hexafunctional reagent. The optimal reaction conditions for producing high molecular weight copolymers were determined to be reaction of hydroxyl terminated prepolymer, where \( n = 26 \), with 2.6 equivalents of the hexafunctional chain extender. If too little of the hexafunctional agent was used, the reaction resulted in a cross linked gel, and if too much was used, only low molecular weights were obtained. Molecular weights obtained for copolymers of this system were as high as 19 kg mol\(^{-1}\). The copolymer was then functionalized with sulfonic acid groups in a three-step synthesis, where the terminal fluoride groups on the dendritic repeat units were reacted with 4-tritylbenzenethiol and then oxidized to form the sulfone linkage. The pendent phenyl groups were oxidized with chlorosulfonic acid producing the amphiphilic multiblock copolymers.

Scheme 1.15 Synthesis of dendritic, multiblock copolymers of PAESK
Unfortunately, the final resultant materials produced very brittle materials, which were not characterized further for their phase separation or ion conductivity. However, in a later work, using higher molecular weight PAESK prepolymers, where \( n = 50-80 \), the resulting films were mechanically viable. Furthermore, the synthesis was simplified; the hexafunctional chain extender was first functionalized with 1-(4-hydroxyphenyl)-2,3,4,5,6-pentaphenylbenzene, with an average degree of functionalization being four, thereby eliminating the oxidation of the thiol ether to sulfone. Morphological characterization of these materials was not directly measured, only implied by observing similar ionic conductivities with similar IECs seen in Nafion, which has been shown to display phase separation.

### 1.4.2.2 Membranes for anion exchange membranes (AEMs)

Over the past six years, increased attention has been given to PSf multiblock copolymer materials for AEMs. Similar to the body of work produced on PSf multiblock for PEM applications, PSf multiblock copolymers for AEMs are primarily focused on the production of membranes containing densely functionalized and hydroxide conductive phase separated domains.

Much of the PSf multiblock copolymer membrane research has investigated materials containing the BHF residue, due to it being readily incorporated into a PSf synthesis and functionalized by chloromethylation. Tanaka and coworkers produced PSf-PAESK multiblock copolymers in which phenoxide terminated PSf oligomers derived from the BHF bisphenol were copolymerized with fluorine terminated PAESK oligomers. The BHF PSf segments were then chloromethylated followed by amination with trimethylamine (Scheme 1.16).
Scheme 1.16 Functionalization of the BHF residues with benzyltrimethylammonium hydroxide groups in multiblock PSf-PAESK multiblock copolymers

The resulting AEMs were investigated for their phase separation by TEM. TEM images were collected for the multiblock and corresponding random copolymer. Phase separation was clearly observed in the multiblock copolymer and domain sizes of 4-5 nm were reported.

The hydroxide conductivity for the quaternary ammonium functionalized PSf-PAESK multiblock copolymers was also investigated. The hydroxide conductivity for the PSf-PAESK copolymer membranes was found to be a maximum of 126 mS·cm⁻¹ at 60 °C for a membrane having an IEC of 1.93 meq·g⁻¹. This result was significantly higher compared to the random copolymer (IEC = 1.88 meq·g⁻¹), which produced an ionic conductivity of 35 mS·cm⁻¹ at 60 °C. The superior performance of the PSf-PAESK multiblock copolymers was attributed to the hydrophilic conductive domains observed in the TEM images.

In a contrasting study to PAESK-PSf copolymers that contained multiply chloromethylated BHF residues for AEMs, segmented copolymers containing BHF PSf segments and tetramethylbisphenol A (TMBPA) PSf segments were studied. In this study, the fluorenlyl containing blocks were designed to serve as the matrix and the TMBPA...
containing blocks were functionalized via bromination and subsequent amination with either trimethylamine (TMA) or ethylimidazole. The resultant multiblock copolymer is shown in Figure 1.4. One significant synthetic advantage was that the functionalization was accomplished with N-bromosuccinimide and benzoyl peroxide, a much less toxic synthesis compared to chloromethylation with chloromethyl methyl ether. High molecular weight materials up to 108 kg mol\(^{-1}\) were obtained from the copolymerization. Amination of the two materials was accomplished by solution reactions for ethylimidazolium functionalization and by soaking precast films in aqueous TMA. The precast films were not completely aminated, as determined from the difference between the theoretical IEC and the titrated IEC, whereas the solution reaction with ethyl imidizole was closer to the theoretical value.

![Figure 1.4 Multiblock PSf AEM materials containing benzyltrimethylammonium hydroxide functionalized TMBPA PSf hydrophilic segments](image)

The microphase separation of the multiblock copolymer membranes was investigated with TM-AFM. Both the benzyltrimethylammonium and ethylimidazolium functionalized membranes were shown to be phase separated. The ethylimidazolium functionalized membranes were significantly more phase separated with well-defined hydrophilic pathways on the surface in contrast to the ill-defined less ordered TMA membrane.

Investigation of the hydroxide conductivity for the benzyltrimethylammonium and ethylimidazolium indicated that the ethylimidazolium functionalized multiblock copolymer had slightly higher hydroxide conductivities compared to the TMA functionalized multiblock

---

34
copolymers. However, it cannot be concluded whether this outcome was a function of the difference in IEC, phase separation, or the functional group.

Another approach to designing multiblock PSf copolymer materials containing multiply functionalized repeat units was reported in which bis-quaternary ammonium pendants were attached to the multiblock copolymer. Dong et al. synthesized multiblock PSf copolymers from fluorine-terminated BPA-PSf oligomers copolymerized with the PSf derived from 2-(3-(dimethylamino)propyl)-3,3’-bis(4-hydroxyphenyl)isoindolin-1-one (PPH-DMPA). The multiblock copolymers were subsequently reacted with (3-bromopropyl)trimethylammonium bromide resulting in the quaternary ammonium functionalized PSf materials (Figure 1.5).

\[
\begin{align*}
 &\left[\text{PSf}_{n} \mid \text{PPH-DMPA}_{y} \right] \\
 &\text{Figure 1.5 PSf multiblock copolymers with bis-quaternary ammonium functionalized PPH-DMPA segments.}
\end{align*}
\]

The phase separation of the multiblock PSf copolymer membranes was elucidated by SAXS. SAXS profiles for the multiblock copolymer and random copolymer control were obtained. The multiblock copolymer exhibited an ionomer scattering peak at \( q_{\text{max}} = 0.76 \text{ nm}^{-1} \) and the random copolymer showed a weak ionomer peak at \( q_{\text{max}} = 0.91 \text{ nm}^{-1} \). The stronger scattering intensity of the block copolymer was attributed to better phase separation and organization of ionic clusters.

The hydroxide conductivity of the multiblock copolymer was also evaluated and compared to the random copolymer of the same composition. It was shown that the hydroxide conductivity was higher for the multiblock copolymer with the maximum at 52
mS·cm⁻¹ at 80 °C while the random copolymer only achieved 40 mS·cm⁻¹ at the same temperature. The higher conductivity was determined to be a result of the improved phase separation of the multiblock copolymer.

In a recent effort to develop a PSf multiblock copolymer with high quaternary ammonium densities was accomplished by Ullmann coupling of dichloro-\(N,N\)-dimethylbenzylamine monomers with chlorine terminated PAESK oligomers. The unique approach still allows a high concentration of quaternary ammonium cations in the AEM owing to its very small repeat unit while forgoing chloromethylation or halogenation functionalization steps. Copolymerizations were completed from a set of PAESK oligomers with molecular weights of 1.4, 2.5 and 3.8 kg·mol⁻¹ and dichloro-\(N,N\)-dimethylbenzylamine monomers with the chlorine present at positions 1,4-, 2,4- and 1,3-. The polymerization reactions were carried out in DMAc with Ni(cod)₂ and 2,2’-bipyridine catalysts (Scheme 1.17). The copolymerizations produced multiblock copolymers with molecular weights ranging from 10.4 kg·mol⁻¹ to 29.4 kg·mol⁻¹. It was determined that the 2,4-dichloro-\(N,N\)-dimethylbenzylamine was the most reactive and was incorporated up to 80 % of the target, whereas the 1,3-dichloro and 1,4-dichloro monomers incorporated up to 60 %. The decreased reactivity of the 1,3-dichloro and 1,4-dichloro monomers was attributed to steric hindrance of the benzylamine. The multiblock PSf-poly(phenylene benzyl(dimethylamine) were then quaternized with iodomethane.

TEM was used to characterize the phase separation of the multiblock copolymers. Cross sectional TEM images obtained indicated that microphase separation was present in all materials. Multiblock copolymers produced from the 1,4-dichloro monomer developed larger domain sizes and better connectivity when compared to membranes of the same composition that were produced from the 2,4-dichloro and 1,3-dichloro monomers. Additionally, it was determined that the membrane IEC had negligible impact on the membrane morphology.
Scheme 1.17 Synthesis of multiblock PAESK-poly(phenylene) copolymers by Ullmann coupling.

The hydroxide conductivity was also evaluated for the PSf-poly(phenylene benzyltrimethylammonium). It was shown that the hydroxide conductivity increased with increasing membrane IEC. Furthermore, the hydroxide conductivity was found to reach a maximum of 130 mS cm\(^{-1}\) at 80 °C for the membrane with the highest IEC (2.47 meq g\(^{-1}\)).

Although the most significant amount of multiblock PSf copolymer membrane research has been conducted in the area of PEMs, it has been shown that PSf multiblock copolymers have been applied to other membrane technologies. It has also been shown that the microphase separation that is observed in the multiblock PSf copolymer membrane materials has enhanced the membrane performance for the given application.

1.5 Conclusions

This mini-review on the synthesis of polysulfone multiblock copolymers has shown many synthetic strategies for their development. The different synthetic methods have also indicated that different chemistries can be applied to produce multiblock PSf copolymers, which include nucleophilic substitution, reactions with carbonyl functionalities, and nucleophilic aromatic substitution. Also, the research involving ion exchange membranes has
provided much insight into strategies for functionalizing PSf copolymers. While this report includes predominantly linear architectures, there are examples of non-linear, dendritic, multiblock copolymers.

Material microphase separation was highlighted and the phase separation reported in many of the materials presented had impact on the material properties for each multiblock copolymer with respect to the application. Microphase separation was exploited for two main applications, the tuning and improvement of mechanical characteristics and the generation of functionalized domains in membrane applications. With respect to ion exchange membranes, phase separation was responsible for the improvement of membrane performance.

Clean energy systems are becoming increasingly economically viable and as a result the demand for research developing systems such as fuel cells is increasing. A significant portion of the research presented dealt with the synthesis and development of new polymer electrolyte membrane materials. Multiblock PSf copolymers that are able to phase separate into hydrophobic and hydrophilic domains have improved the ionic conductivity of the resulting membranes while providing mechanical properties for maintaining the membranes. In the specific area of AEMs, the conductive performance of the PSf multiblock copolymers have dramatically improved opening the possibility of the more cost effective alkaline fuel cell.

1.6 Thesis Statement

The goal of this thesis is to design different multiblock copolymer systems in order to gain understanding of the relationship between structure and performance with respect to anion exchange membrane applications, and to advance anion exchange membrane design such that mechanical strength, chemical stability and ionic conductivity are improved.
Research on multiblock anion exchange membranes has provided a general framework for the design of future materials such that the basic characteristics of hydrophobic-hydrophilic composition and ion exchange capacity have expected effects on the membrane properties and performance. However, the development of anion exchange membranes having improved ionic conductivity and chemical and thermal stability in combination with mechanical integrity continues. Answering the following questions will further elucidate the structure, architecture, and property relationships of amphiphilic copolymers for anion exchange membranes such that the improved understanding will help to further direct the design and preparation of new materials.

**Question 1:** Can the incorporation of polymer segments composed of compact densely functionalized repeat units into a multiblock copolymer system, improve the ionic conductivity of the resulting membrane by increasing the ion concentration in the hydrophilic domains?

Polyformal (PF) is an engineering thermoplastic that is readily produced and has compact repeat units composed of a bisphenol residue and methylene linkage. The design of multiblock PF copolymers with densely functionalized ion-conducting hydrophilic segments and their preparation into membranes will allow the study of membrane structure-property relationships. Chapter 2 describes the preparation of henol-terminated PSf oligomers that were then copolymerized with tetramethylbisphenol A in a PF synthesis followed by subsequent functionalization of the tetramethylbisphenol A units. A series of multiblock PSf-PF copolymers was synthesized in which the mole percentage of PF was varied to produce a range of IECs. A non-destructive post-polymerization bromination functionalization for PF segments was developed using zirconium(IV) chloride. Amination of the benzyl bromide units produced PSf-quaternary ammonium PF (PSf-QAPF). The water uptake and hydroxide conductivity of the PSf-QAPF membranes were evaluated and were related to the IEC and
the phase separation. The morphology of the PSf-QAPF membranes was examined by tapping mode atomic force microscopy. Mechanical properties were studied by tensile strength experiments. The base stability of the PSf-PF multiblock copolymer and the PSf-QAPF multiblock copolymer membranes were ultimately evaluated.

Question 2: Can incorporation of aliphatic spirocyclic ammonium derived polymer segments into a multiblock copolymer backbone exhibit improved chemical stability at high temperature while being highly conductive and mechanically robust when processed into an anion exchange membrane?

The development of base-stable cationic groups for anion exchange membranes is important for application in alkaline fuel cells. Spirocyclic ammonium groups have been shown to be particularly base stable, although few examples exist that incorporate them into polymer structures. A telechelic polymer with spirocyclic ammonium repeat units was designed by the cyclopolymerization of diallylpiperidinium chloride with a photoiniferter in Chapter 3. A series of hydrophobic-hydrophilic multiblock copolymers with varying ion exchange capacities were produced by copolymerizing the end-functionalized polydiallylpiperidinium (PDApip) oligomers with PSf monomers. The multiblock copolymers were solution cast in the hexafluorophosphate form from DMAc resulting in mechanically robust, colorless, transparent membranes. TM-AFM and DSC were used to investigate microphase separation in the copolymers. The hydroxide conductivity and water uptake for the membranes were evaluated. The stability at high temperatures and high pH conditions were also studied and related to the spirocyclic ammonium structure.

Question 3: Does varying the molecular weight of the hydrophilic segments in multiblock copolymer anion exchange membranes impact the microphase separation and affect the hydroxide conductivity, given similar composition and IEC?
Development of microphase separated AEMs in which hydroxide conductive, hydrophilic domains form within a hydrophobic and mechanically robust matrix has shown to be a successful strategy for improving AEM performance. Development of microphase separated AEMs in which hydroxide conductive, hydrophilic domains form within a hydrophobic and mechanically robust matrix has shown to be a successful strategy for improving AEM performance. In Chapter 4, a series of multiblock polysulfone-poly(diallylpiperidinium hydroxide) copolymers (PSf-PDApipOH) are described in which the molecular weight of the hydrophilic conducting poly(diallylpiperidinium hydroxide) (PDApipOH) segments was varied in order to assess the impact on AEM performance. The multiblock copolymers investigated in this study were prepared by condensation polymerization of preformed 4-fluorophenyl sulfone terminated poly(diallylpiperidinium hexafluorophosphate) (PDApipPF₆) oligomers with polysulfone monomers. The structure-property relationship between the hydroxide conductive PDApipOH segments and AEM performance was demonstrated by investigation of the microphase separation and hydroxide conductivity. The hydroxide conductivity and water uptake were studied and related to the phase separation, which was evaluated by SAXS and TM-AFM.

1.7 References


17. Sheth, J. P.; Aneja, A.; Wilkes, G. L.; Yilgor, E.; Atilla, G. E.; Yilgor, I.; Beyer, F. L., Influence of system variables on the morphological and dynamic mechanical behavior of


75. Miyatake, K.; Hirayama, D.; Bae, B.; Watanabe, M., Block poly(arylene ether sulfone ketone)s containing densely sulfonated linear hydrophilic segments as proton conductive membranes. *Polymer Chemistry* 2012, 3 (9), 2517-2522.


81. Ghassemi, H.; Ndip, G.; McGrath, J. E., New multiblock copolymers of sulfonated poly(4 '-phenyl-2,5-benzophenone) and poly(arylene ether sulfone) for proton exchange membranes. II. *Polymer* 2004, *45* (17), 5855-5862.


CHAPTER 2

HIGHLY FUNCTIONALIZED POLYSULFONE-POLYFORMAL MULTIBLOCK COPolYMERS FOR ANION EXCHANGE MEMBRANES

2.1 Introduction

Development of highly conductive anion exchange membranes (AEM)s for the burgeoning field of alkaline fuel cells has garnered significant interest. Maturation of alkaline fuel cell technology will bring about a more cost-effective alternative to the already commercialized proton exchange membrane fuel cell due to potential cost savings of replacing platinum with less expensive transition metal catalysts. Currently, one challenge hindering the implementation of alkaline fuel cells is the development of suitable anion exchange membranes. Significant research has been conducted to improve anion exchange membrane performance. Such research has produced materials with improved hydroxide conductivity, owing to significantly higher ion exchange capacities (IEC). However, high IEC has been shown to have deleterious effects on anion exchange membrane material properties by increasing the water uptake, which leads to decreased mechanical strength. Advancing anion exchange membranes to be both highly conductive and mechanically robust continues to be a challenge.

Designing AEMs with a polymer structure that will provide mechanical strength while also being alkaline stable is crucial. AEM research has been conducted with different types of materials including polysulfone, poly(phenylene), poly(phenylene oxide), polystyrene, and poly(olefin)s because they are promising in fulfilling the aforementioned properties. Furthermore, polysulfone, poly(phenylene), poly(phenylene oxide), and derivatives of polystyrene are readily modified through the aromatic ring or aromatic alkyl side chains to install cationic functional groups.
Another polymer material that is known to have good properties is the polyformal of bisphenol A. It has been shown to have good mechanical properties, and thermal stability in excess of 300 °C. In addition to the thermal and mechanical characteristics, polyformals have also been noted as alkaline resistant materials. The polyformal of bisphenol A is readily synthesized to produce high molecular weight materials by interfacial condensation polymerization with dibromomethane in the presence of potassium hydroxide. The resulting thermoplastic polyformal materials have a compact repeat unit structure consisting of the bisphenol residue connected with a methylene group. In addition to high molecular weight homopolymers, the synthesis of alternating multiblock copolymers containing polyformal segments have also been reported. To the best of the authors’ knowledge, polyformals have not been previously incorporated into AEM materials.

Designing ion exchange materials with multiply charged repeat units can generate hydrophilic domains with a high concentration of ionic functional groups. Ion exchange membranes containing multiply functionalized repeat units have emerged and show high conductivity for both proton and anion exchange membranes. The improved ionic conductivity has been ascribed to the high concentration of ionic groups in the hydrophilic domain. AEMs with densely charge-functionalized repeat units have been prepared from polysulfone materials and have incorporated several different bisphenol structures. The high degree of functionality notwithstanding, multiply functionalized polysulfone repeat units retain a large amount of unfunctionalized bulky material that increases the spacing between ionic groups and limits the concentration of cations in the resulting materials. AEMs that phase separate into a hydrophobic matrix and hydrophilic, hydroxide conductive domains have shown improved conductivity and dimensional stability. Furthermore, increasing the ion concentration within the hydrophilic, ion transporting domains of an AEM through the use of multiply functionalized repeat units has been shown
to be an effective strategy in improving conductivity.\textsuperscript{39-40} Utilizing a multiblock polysulfone architecture and multiply charged repeat units, hydroxide conductivity up to 126 mS·cm\textsuperscript{-1} in 60 °C water has been obtained.\textsuperscript{41} The high conductivity of the phase-separated multiblock polysulfone membranes was in stark contrast to the random copolymer of similar composition, in which the hydroxide conductivity reached a maximum of 35 mS·cm\textsuperscript{-1} under the same testing conditions.

We have designed multiblock polysulfone-polyformal copolymers that are densely functionalized with quaternary ammonium groups (Figure 2.1). The polysulfone (PSf) segments were designed to serve as the hydrophobic matrix, thus taking advantage of its beneficial properties as an engineering material, and the polyformal (PF) segments were designed to ultimately serve as the hydrophilic, ion conductive segments. The PF of tetramethylbisphenol A provided a convenient handle to selectively brominate the PF segments, and the quaternary ammonium functionalized polyformal (QAPF) was ultimately obtained by the Menshutkin reaction with trimethylamine. Controlling the mole fraction of PF segments in the multiblock copolymers enabled the production of a series of materials that ranged in IEC. The resulting PSf-QAPF multiblock copolymers could be processed into anion exchange membranes and were characterized to determine the hydroxide conductivity, water uptake, alkaline stability, surface morphology and mechanical properties.

![Figure 2.1 Multiblock PSf-QAPF copolymer](image)

Figure 2.1 Multiblock PSf-QAPF copolymer
2.2 Experimental

2.2.1 Materials

Bisphenol A (BPA) (97%) and tetramethylbisphenol A (TMBPA) (98%) were obtained from Sigma-Aldrich and recrystallized three times from toluene. N-bromosuccinimide (NBS) (Matheson Coleman and Bell) was recrystallized from water. N-methylpyrrolidone (NMP) (Sigma-Aldrich, HPLC grade) was distilled under reduced pressure from phosphorous pentoxide prior to use. Monomer grade 4,4’-dichlorodiphenyl sulfone (DCDPS) was obtained from Solvay Advanced Polymers. Zirconium(IV) chloride (99.95% sublimed grade) was purchased from Strem Chemicals. Trimethylamine (TMA) (99% anhydrous) and dibromomethane (98%) were purchased from Sigma-Aldrich. All other solvents and reagents were used as received.

2.2.2 Synthesis of phenol terminated polysulfone (PSf-OH)

Phenol terminated polysulfone oligomers (PSf-OH) with molecular weights of 2.5, 5.1, and 7.2 kg·mol⁻¹ were synthesized by nucleophilic aromatic substitution. The molecular weight of the polysulfone oligomers was controlled with a calculated excess of BPA, ensuring phenoxide termination. The synthesis of the 5.1 kg·mol⁻¹ PSf-OH is provided as an example. BPA (37.03 g, 0.1622 mol), DCDPS (39.01 g 0.1358 mol) and potassium carbonate (46.98 g, 0.3399 mol), followed by NMP (304 mL) and toluene (80 mL) were added to a 500 mL, two-piece, Morton style reactor that was fitted with an overhead stirring motor, Dean-Stark trap, condenser, nitrogen inlet, and thermocouple. The reactor was heated with a heating mantle controlled by a J-Kem 210 temperature controller. Water was removed from the reaction solution by azeotropically distillation at 150 °C for 3 hours. The temperature was then raised to 170 °C by distilling off the toluene, and the reaction mixture was stirred for 20 hours and then cooled to room temperature. The polysulfone was isolated by pouring the
room temperature reaction mixture into 3 L of acidic methanol (10% v/v) followed by vacuum filtration of the precipitate. The resulting off-white powder was boiled in water for 5 hours to remove any remaining salt, filtered and dried in a vacuum oven. The recovered mass was 54.8 g (91% yield).

2.2.3 **Synthesis of PSf-PF multiblock copolymers**

The synthesis of polysulfone-polyformal (PSf-PF) multiblock copolymers was accomplished by condensing PSf-OH oligomers and TMBPA with dibromomethane in the presence of potassium hydroxide. Provided is a procedure for the synthesis of a particular sample (PSf-PF4), following a general procedure adapted from the literature.  

```
PSf-OH (13.94 g, 2.733 mmol), TMBPA (2.68 g, 9.42 mmol), and potassium hydroxide (3.34 g, 5.95 mmol) were added to a 110 mL stainless steel, morton style Waring blender followed by 67 mL of NMP. The reaction mixture was stirred on high speed for two minutes and a noticeable rise in reaction temperature was observed. Dibromomethane (23 mL, 0.33 mol) was quickly added to the reaction mixture and stirring was continued for an additional 2 minutes, during which time the reaction temperature and solution viscosity quickly rose. The resulting polymer was isolated by precipitation of the reaction mixture into a 10-fold excess of methanol, filtered and dried in a vacuum oven. The recovered material was redissolved in chloroform (1 wt. %) and filtered through Celite. The resulting solution was concentrated to approximately 5 wt. % by rotary evaporation and precipitated into a 10-fold excess of methanol. The resulting beige-colored material was collected by filtration and dried to a constant mass under vacuum. The recovered mass was 15.4 g (93% yield).
```

2.2.4 **Bromination of PSf-PF multiblock copolymers (PSf-BrPF)**

Bromination of the benzylmethyl groups within the PF segments was effected by the use of NBS with zirconium(IV) chloride as a catalyst. The bromination procedure was
adapted from the literature and an example follows: in a 500 mL round bottom flask, multiblock copolymer PSf-PF4 (5.02 g, 0.114 mmol) was added to 250 mL dichloromethane and stirred at room temperature. Once a homogeneous solution was obtained, NBS (2.84 g, 1.59 mmol) and zirconium(IV) chloride (0.186 g, 0.798 mmol) were added. The reaction was stirred at room temperature for 6 hours and then precipitated into 2.5 L methanol. The obtained solid was filtered and dried at 60 °C under vacuum. The recovered mass was 4.88 g (84% yield). The percent conversion of benzylic methyl groups in the PF segments was determined from the integral values corresponding to the benzylbromide and benzylic methyl groups in the $^1$H NMR spectrum.

2.2.5 Amination of PSf-BrPF (PSf-QAPF bromide) and membrane preparation

PSf-BrPF copolymers were dissolved in DMSO (10 % w/v) and stirred at room temperature until completely dissolved. Once dissolved, TMA gas was bubbled through the solution for 10 minutes. The reaction flask was sealed and the resulting solution was stirred for a further 48 hours. The DMSO was removed by rotary evaporation to yield an amber-colored solid. Membranes were obtained by casting a 10 % (w/v) solution of the PSf-QAPF bromide copolymer in DMSO onto a glass substrate using a doctor blade (0.5 mm) to maximize uniformity. The membrane was dried at 90 °C under vacuum for 24 hours.

2.2.6 Ion exchange to hydroxide

Multiblock PSf-QAPF bromide membranes were soaked in 1M KOH for 48 hours to ion exchange to hydroxide. The membranes were then washed in successive deionized water solutions until a neutral pH was obtained.
2.2.7 Characterization

Polymer molecular weights were determined by gel-permeation chromatography (GPC) employing a Waters 600-MS HPLC pump with a Wyatt Technology Optilab RI and miniDawn multiangle light scattering detectors. Molecular weight separation was effected by two mixed-D columns from Polymer Laboratories with a THF flow rate of 1.0 mL/min at room temperature. The GPC system was calibrated with a series of polystyrene standards that were further used to determine molecular weights.

Proton nuclear magnetic resonance spectroscopy (\( ^1 \text{H} \) NMR) was performed on a JEOL ECA-500 FT-NMR instrument using either CDCl\(_3\) or DMSO-d\(_6\) as solvents. Chemical shift values (\( \delta \)) were referenced from the residual solvent signal. The solvent signals were subtracted from spectra by the processing software.

Tapping mode atomic force microscopy (AFM) was used to observe the surface morphology of the PSf-QAPF bromide membranes. Samples were spin coated onto silicon wafers from 1.5 % (w/v) polymer in DMSO solutions at a rate of 4000 rpm for 20 seconds. The spin coated wafers were then dried under vacuum at 80 °C overnight. Images were obtained from a Bruker Nanoscope III utilizing 48 N·m\(^{-1}\) silicon Pointprobe tip (purchased from Nanoworld). The amplitude set-point ratio (rsp) was set to 0.5 and the driving amplitude (\( A_0 \)) was set to 1.722V. Height and phase images of all samples were collected under ambient humidity and temperature.

The tensile properties of the membranes were measured on Mark-10 ESM1500 tensile tester with a 250 N load cell with a resolution of 0.1 N. The cross-head speed was 1 mm·min\(^{-1}\) and all samples were measured at ambient temperature and humidity. The membranes tested were cut into approximately 70 mm × 8 mm strips and dried under vacuum at 65 °C for 48 hours prior to testing. Each sample was approximately 25 µm in thickness. The ends of each
sample were tabbed with Scotch® 898 heavy duty filament tape to prevent slippage in the grips.

Base stability of the PSf-PF multiblock copolymer backbone was assessed by soaking the PSf-PF copolymer powder in both 1 M and 2 M aqueous KOH at 80 °C. The degradation study was completed over the course of 5 days. GPC was used to analyze changes in molecular weight.

The alkaline stability of the PSf-QAPF membranes was assessed by soaking the membrane in 1 M KOH 120 hours at 80 °C. The test was performed in a sealed Teflon reaction vessel. The stability was determined by $^1$H NMR spectroscopy in which changes in the benzyltrimethylammonium and formal linkage integrals were compared with samples prior to base exposure.

The ion exchange capacity (IEC) was determined by $^1$H NMR spectroscopy using the ratio of the benzyltrimethylammonium methyl and BPA methyl signals. PSf-QAPF bromide samples were prepared in DMSO-d$_6$ and filtered through a plug of magnesium sulfate to minimize the water signal. IEC values are reported using the mass calculated in the hydroxide form.

The percent water uptake (WU %) of the PSf-QAPF membranes was obtained by drying the membranes at 60 °C under vacuum for 24 hours and measuring the dry mass ($m_{\text{dry}}$). The membranes were then soaked in deionized water at either room temperature or 60 °C for 24 hours. The mass of the hydrated membranes was obtained by removing bulk water from the membrane surface and quickly weighing. Membranes were then soaked again and remeasured until a constant hydrated mass ($m_{\text{hydrated}}$) was obtained. The final water uptake of the membranes was determined by the equation:

$$WU(\%) = \frac{m_{\text{hydrated}} + m_{\text{dry}}}{m_{\text{hydrated}}} \times 100$$
Electrochemical impedance spectroscopy was used to measure the in-plane hydroxide conductivity of the PSf-QAPF membranes. The measurements were made on a BioLogic VMP3 Potentiostat using either a 4-probe Teflon or PEEK cell, with Pt electrodes, covering the frequency range of 1 Hz to 100 kHz. Conductivity measurements were made at room temperature and 60 °C with the test cells immersed in deionized 18 MΩ water purged with N₂. The hydroxide conductivity (σ) of the membranes was determined from the Nyquist plot and was calculated from the equation:

\[
\sigma = \frac{d}{T \times W \times R}
\]

Where d is the distance between the probes in cm, T and W are the hydrated thickness and width in cm and R is the ohmic resistance (Ω) at the corresponding temperature.

2.3 Results and Discussion

The objective of this work was to design a multiblock copolymer system in which the hydrophilic conducting phase would contain a highly functionalized and compact repeat unit structure. Given the demonstrated high ionic conductivity of multiblock copolymers containing multiply functionalized repeat units,⁴¹⁻⁴²,⁴⁶⁻⁴⁷ we hypothesized that incorporation of densely functionalized PF segments would provide a hydrophilic domain with enhanced hydroxide conductivity owing to the high concentration of quaternary ammonium cations as a result of the small repeat unit structure. The incorporation of PF materials for anion exchange membranes has not been previously investigated. Our synthetic strategy was to use TMBPA monomer for the PF and copolymerize with phenol-terminated PSf to produce multiblock copolymers in which the PF segments could be selectively functionalized. The TMBPA PF segments allow for as many as four quaternary ammonium cations per bisphenol residue, and
the resulting hydrophilic conducting PF segments should be phase-separated from a mechanically robust hydrophobic polysulfone.

2.3.1 Synthesis of PSf-QAPF multiblock copolymers

The preparation of PSf-QAPF multiblock copolymers comprises the synthesis of PSf-PF multiblock copolymers and the post-polymerization functionalization with quaternary ammonium cations. The initial investigation of PSf-PF multiblock copolymers was designed to elucidate effects of the PSf molecular weight on multiblock copolymer synthesis and structure. The post-polymerization functionalization and ultimate characterization of the PSf-PF multiblock copolymers was focused on a representative sample series resulting from the initial copolymer synthesis.

2.3.1.1 Synthesis of PSf-OH

Our design (Scheme 2.1) was to produce phenol-terminated PSf oligomers to be copolymerized with TMPBA in a PF synthesis. PSf-OH oligomers are readily obtained by using a calculated excess of BPA in the polymerization. Using a calculated excess of BPA not only ensures that the oligomers are phenol-terminated, it also produces oligomers of predictable molecular weight. Polymerizations of BPA with DCDPS were carried out such that three different molecular weight oligomers were produced. The targeted molecular weights of the PSf-OH oligomers were 2.5, 5.0, and 10.0 kg·mol⁻¹. The polymerizations were accomplished at 170 °C in NMP and were run for approximately 20 hours. The polymers were purified by precipitation in acidic methanol followed by boiling in water in
order to remove any trace amounts of starting materials and salt.

\[
\begin{align*}
\text{Cl-O-SO}_3\text{Br} + \text{HO-SO}_3\text{Cl} & \xrightarrow{\text{K}_2\text{CO}_3, \ NMP, 170 \degree C, 20 \text{ hrs.}} \text{HO-SO}_3\text{Br} \\
& \xrightarrow{\text{KOH, NMP, 10 min}} \text{PSf-PF}
\end{align*}
\]

Scheme 2.1 Synthesis of PSf-PF multiblock copolymers. i) K$_2$CO$_3$, NMP, 170 °C, 20 hrs. ii) KOH, NMP, 10 min

GPC was used to analyze the molecular weight of the PSf-OH oligomers. The absolute molecular weights for each oligomer were determined by multiangle light scattering using a dn/dc = 0.205 and the results reported in Table 2.1. The close agreements between the targeted and observed molecular weights indicate that molecular weight was predictable and supports phenol termination.

Table 2.1 PSf-OH oligomer molecular weight characteristics

<table>
<thead>
<tr>
<th>Sample</th>
<th>Target $M_n$ [g·mol$^{-1}$]</th>
<th>$M_n^a$ [g·mol$^{-1}$]</th>
<th>$M_w^a$ [g·mol$^{-1}$]</th>
<th>$D_m^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf-OH1</td>
<td>2,500</td>
<td>2,700</td>
<td>3,300</td>
<td>1.2</td>
</tr>
<tr>
<td>PSf-OH2</td>
<td>5,000</td>
<td>5,100</td>
<td>6,700</td>
<td>1.3</td>
</tr>
<tr>
<td>PSf-OH3</td>
<td>10,000</td>
<td>7,200</td>
<td>12,700</td>
<td>1.7</td>
</tr>
</tbody>
</table>

$^a$ Determined by GPC multiangle light scattering, dn/dc = 0.205

2.3.1.2 Synthesis of PSf-PF multiblock copolymers

A series of multiblock PSf-PF copolymers was synthesized from each PSf-OH oligomer in which the mole percentage of PF was varied such that a range of IECs could be
produced. The compositions for each series were targeted at 20, 30, and 40 mol % PF. Step-
growth polymerization of PSf-OH oligomers and TMBPA with dibromomethane was done to
produce high molecular weight copolymers with randomly distributed segments of PF. The
copolymerizations, adapted from a literature procedure, were performed in NMP with
potassium hydroxide and an excess of dibromomethane in a stainless-steel blender. The high
reactivity between dibromomethane and phenoxide monomers resulted in polymerization
reactions being completed in approximately 10 minutes, as evidenced by a large increase in
viscosity. After multiple precipitations in methanol and filtering through Celite, the final
multiblock copolymers were obtained in a greater than 90% yield.

GPC was used to characterized the molecular weight of the PSf-PF multiblock
copolymers. The molecular weight and dispersity ($D_m$) for the PSf-PF multiblock copolymers
were determined from a polystyrene standards calibration curve and results are listed in Table
2.2. The peaks observed in the GPC chromatograms of the PSf-PF multiblock copolymers
indicated a substantial increase in molecular weight (Figure 2.2) and support successful
copolymerization. A low molecular weight tail was observed in the chromatograms of the
copolymers, which could be attributed to small amounts of low molecular weight cyclic
materials as well as any residual unreacted PSf oligomers.

PSf-PF multiblock copolymer compositions were determined by $^1$H NMR
spectroscopy. $^1$H NMR spectra of the PSf-PF multiblock copolymers were obtained in CDCl$_3$
(Figure 2.3) and clearly indicate the presence of both PSf and PF segments. The mole
fraction of PF incorporated into the PSf-PF copolymer was calculated from the ratios of
integrals of the arylmethyl protons (G) and the isopropylidene methyl protons (E, I). The
mole fraction of PF incorporated was slightly lower than the targeted mole fraction in each of
the multiblock PSf- PF copolymers.
Table 2.2 Composition and molecular weight characterization of PSf-PF multiblock copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ PSf-OH [kg · mol$^{-1}$]</th>
<th>$M_n$ PSf-PF$^a$ [kg · mol$^{-1}$]</th>
<th>$M_w$ PSf-PF$^a$ [kg · mol$^{-1}$]</th>
<th>$D_m$</th>
<th>mole percent PF$^b$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf-PF1</td>
<td>34</td>
<td>70</td>
<td>2.1</td>
<td>19.3</td>
<td></td>
</tr>
<tr>
<td>PSf-PF2</td>
<td>2.5</td>
<td>21</td>
<td>46</td>
<td>2.2</td>
<td>26.9</td>
</tr>
<tr>
<td>PSf-PF3</td>
<td>52</td>
<td>100</td>
<td>2.0</td>
<td>33.3</td>
<td></td>
</tr>
<tr>
<td>PSf-PF4</td>
<td>44</td>
<td>89</td>
<td>2.0</td>
<td>15.2</td>
<td></td>
</tr>
<tr>
<td>PSf-PF5</td>
<td>5.1</td>
<td>40</td>
<td>91</td>
<td>2.3</td>
<td>24.5</td>
</tr>
<tr>
<td>PSf-PF6</td>
<td>70</td>
<td>142</td>
<td>2.0</td>
<td>30.8</td>
<td></td>
</tr>
<tr>
<td>PSf-PF7</td>
<td>40</td>
<td>82</td>
<td>2.1</td>
<td>18.4</td>
<td></td>
</tr>
<tr>
<td>PSf-PF8</td>
<td>7.2</td>
<td>51</td>
<td>116</td>
<td>2.2</td>
<td>26.3</td>
</tr>
<tr>
<td>PSf-PF9</td>
<td>46</td>
<td>107</td>
<td>2.3</td>
<td>33.0</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Molecular weights obtained from GPC were referenced to polystyrene standards. $^b$ The mole percent of PF was calculated from the $^1$H NMR spectrum.

Figure 2.2 GPC RI chromatograms of PSf-OH and PSf-PF multiblock copolymers
The block character of each of the PSf-PF materials was also determined by $^1$H NMR spectroscopy. Because there are two different types of bisphenols being connected by a formal linkage, there are three different combinations of linkages in the copolymers. The different formal linkage methylene protons in the $^1$H NMR spectra are present as three separate signals corresponding to the PF repeat units (linking two TMBPA units), PSf-PF linkages (linking a PSf-OH with TMBPA), and PSf-PSf linkages (inset in Figure 2.3). The two predominant formal methylene signals are the one corresponding to the PF repeat units ($\delta = 5.20$) and the one corresponding to a linkage between PSf and a TMBPA unit ($\delta = 5.48$). The furthest downfield signal, $\delta = 5.67$, is representative of two PSf-OH oligomers being linked with a formal group. The ratio of the methylene signal for the linkage of two PSf-OH oligomers varied depending on the molecular weight of the PSf-OH oligomer in the copolymerization. As the molecular weight of the PSf-OH oligomers increased, and therefore the concentration of PSf-OH groups in the polymerization mixture decreased, it was found
that the number of formal linkages connecting two PSf oligomers decreased. $^1$H NMR spectra of polymers PSf-PF7, PSf-PF8, and PSf-PF9 (from the highest molecular weight PSf-OH oligomer with $M_n = 7.2 \text{ kg} \cdot \text{mol}^{-1}$) indicated that the formal linkages between two PSf-OH oligomers becomes negligible.

Polymers for AEMs are required to be chemically stable and evaluating the PSf-PF multiblock copolymers prior to functionalization provided insight to the backbone stability at high temperature and high pH. The unfunctionalized PSf-PF4 multiblock copolymer powder was suspended in both 1 M and 2 M aqueous KOH and heated for 8 days. Gel permeation chromatography was used to determine any decrease in molecular weight as a result of hydroxide cleavage. Chromatograms of the PSf-PF4 copolymer clearly indicated that no cleavage of the PSf-PF backbone occurred; chromatograms prior to and after the measurement perfectly superimposed. The base stability of the PSf-PF multiblock copolymer produced is in agreement with reported stability of polyformal materials.$^{31,33}$

PSf-PF multiblock copolymers were successfully produced that ranged both in the molecular weight of the PSf segments and the mole fraction of PF incorporated. We chose as a representative series the copolymers derived from the PSf-OH2 oligomer (samples PSf-PF4, PSf-PF5, PSf-PF6) for complete characterization of anion exchange membrane properties.

### 2.3.1.3 Functionalization of PSf-PF multiblock copolymers and membrane fabrication

The synthetic strategy for post-polymerization modification (Scheme 2.2) was bromination of the TMBPA units in the PF segments followed by Menshutkin quaternization. The four arylmethyl groups of the TMBPA PF repeat units provided a convenient handle for such modification and the potential to incorporate up to four quaternary ammonium cations per repeat unit. Initially, bromination of the arylmethyl groups on the PF repeat unit were
attempted by Wohl-Ziegler reaction conditions. Reactions were completed with NBS and either benzoyl peroxide or UV light initiators in tetrachloroethane. Under both sets of reaction conditions (peroxide and UV light initiators) the recovered PSf-BrPF materials indicated severe reductions in molecular weight as evidenced by their inability to form films. We presumed the chains were primarily cleaved at the formal linkages due to their acid labile character. However, recent work also indicates that the polysulfone backbone can be unstable to NBS bromination. Bromination of arylmethyl groups on small molecules using NBS and zirconium(IV) chloride as catalyst in methylene chloride has been shown to be facile at or below room temperature, making the conditions comparatively mild. The bromination catalyzed by zirconium(IV) chloride has been determined to proceed through a similar radical reaction mechanism compared to the more standard Wohl-Ziegler method. We adapted the zirconium(IV) chloride catalyzed bromination conditions to selectively brominate the arylmethyl groups in the PF segments without cleavage of the backbone. The bromination reactions were completed in methylene chloride at room temperature over six hours. After two precipitations into methanol, the brominated PSf-BrPF multiblock copolymers were obtained as beige or light orange fibers. Characterization by GPC of the PSf-BrPF multiblock copolymers indicated some loss of molecular weight after bromination (Figure 2.4) however, the copolymers were still able to form tough, free standing films.

The average degree of bromination for the PSf-BrPF multiblock copolymers was obtained by comparing the integral values of the $^1$H NMR spectra (Figure 2.5) of the remaining arylmethyl peaks at 2.25 ppm (peak G) and the benzylbromide peaks at 4.5 ppm (peak G’) and are listed in Table 2.3. The mild reaction conditions were able to produce a high degree of functionalization (DF) with averages of more than 3.3 benzylbromides per PF repeat unit in each case and up to 3.9 benzylbromides for one sample.
Scheme 2.2 Functionalization of PSf-PF multiblock copolymers
i) DCM, NBS, Zr(IV)Cl, RT, 6 hrs. ii) DMSO, TMA(g), 48 hrs

Figure 2.4 GPC chromatograms of PSf-PF multiblock copolymers before and after NBS/Zr(IV)Cl bromination

Quaternization of the PSf-BrPF multiblock copolymers was completed in DMSO saturated with anhydrous trimethylamine. Membranes of the resulting PSf-QAPf multiblock copolymers were prepared by solution casting on glass slides. Membrane uniformity was controlled by running a doctor blade over the casting solution and uniform thicknesses of approximately 40 µm were obtained. The resulting membranes were light yellow to orange in color and transparent. Each of the membranes were flexible and creasable.
Table 2.3. Characterization of PSf-BrPF multiblock copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole Percent PF&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Percent of Bromination&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Average DF per repeat unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf-BrPF4</td>
<td>15.2</td>
<td>82</td>
<td>3.3</td>
</tr>
<tr>
<td>PSf-BrPF5</td>
<td>24.5</td>
<td>99</td>
<td>3.9</td>
</tr>
<tr>
<td>PSf-BrPF6</td>
<td>30.8</td>
<td>87</td>
<td>3.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from the <sup>1</sup>H NMR spectra

The IEC of the PSf-QAPF multiblock copolymers was determined by <sup>1</sup>H NMR spectroscopy. The <sup>1</sup>H NMR spectra (Figure 2.6) for the PSf-QAPF multiblock copolymers show a new signal (J) at 3.0 ppm corresponding to the methyl protons of the benzyltrimethylammonium functional groups. The IEC of each membrane was determined by comparison of the benzyltrimethylammonium methyl (J) and isopropylidene (E,I) integrals. The calculated IEC values were then compared to theoretical values, which assume quantitative conversion of benzylbromides to benzyltrimethylammonium (Table 2.4). The IEC calculation indicated that the actual IECs were about 15% lower than the theoretical values. The incomplete conversion of the benzylbromides to the benzyltrimethyl ammonium
indicates possible steric hindrance of the bulky BTMA cation preventing complete conversion. Incomplete conversion notwithstanding, PSf-QAPF membranes were generated and the IECs ranged from 1.1 to 1.9 meq \cdot g^{-1} for the three different samples.

![Figure 2.6 1H NMR spectrum of PSf-QAPF multiblock copolymers in DMSO-d6.](image)

**Table 2.4 Characterization of PSf-QAPF multiblock copolymer membranes.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>IEC\textsubscript{theory}\textsuperscript{a} [meq \cdot g^{-1}]</th>
<th>IEC\textsuperscript{b} [meq \cdot g^{-1}]</th>
<th>Water Uptake\textsuperscript{c} [%]</th>
<th>Hydroxide Conductivity\textsuperscript{d} [mS \cdot cm^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>RT</td>
<td>60 °C</td>
</tr>
<tr>
<td>PSf-QAPF4</td>
<td>1.1</td>
<td>1.1</td>
<td>6.7</td>
<td>15.6</td>
</tr>
<tr>
<td>PSf-QAPF5</td>
<td>2.0</td>
<td>1.6</td>
<td>10.6</td>
<td>18.3</td>
</tr>
<tr>
<td>PSf-QAPF6</td>
<td>2.2</td>
<td>1.9</td>
<td>16.4</td>
<td>43.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a)} Calculated from \textsuperscript{1}H NMR spectra. \textsuperscript{b)} Calculated based on 100% conversion of benzylbromides to BTMA cations. \textsuperscript{c)} The percent water uptake was measured in liquid water. \textsuperscript{d)} Hydroxide conductivity measured at room temperature and 60 °C in liquid water.
2.3.2 Characterization of PSf-QAPF multiblock copolymer membranes

2.3.2.1 Water uptake and hydroxide conductivity

The determination of water uptake for AEMs is important for characterizing the swelling behavior of the membrane and for the effect of water content on the hydroxide conductivity. The water uptake and hydroxide conductivities for the PSf-QAPF membranes were evaluated both at room temperature and at 60 °C (Table 2.4). The amount of water absorbed by each of the PSf-QAPF membranes was dependent on the IEC with the higher IEC membranes absorbing relatively more water. The water uptake measured for each of the multiblock membranes was modest and the highest water uptake (43.8%) corresponds to the PSf-QAPF6 membrane. The hydroxide conductivities were also observed to increase with increasing IEC as well as with the concomitant increase in water uptake of the membranes.

The conductivities at room temperature increased from 21 to 37 mS·cm⁻¹ on going from the lowest to highest IEC membranes. Further evaluation of the PSf-QAPF membranes at 60 °C showed further increases in conductivity with values of 49 to 78 mS·cm⁻¹ with increasing IEC (Figure 2.7). Both the water uptake and the hydroxide conductivity for the PSf-QAPF membranes demonstrate improvement over comparable densely functionalized multiblock and random polysulfone membranes described in the literature.¹⁵, ⁵⁰-⁵² PSf based multiblock copolymer AEMs containing hydrophobic segments of bisphenol AF PSf and segments of chloromethylated BPA PSf, which quaternized with trimethylamine, were reported to have hydroxide conductivity and water uptake values reaching 28 mS·cm⁻¹ and 47.5 wt.% respectively at an IEC of 2.28 meq·g⁻¹ at 60 °C.⁵² Bis(phenyltrimethylammonium) pendant functionalized multiblock PSf membranes exhibited hydroxide conductivity and water uptake values of 50 mS·cm⁻¹ and 20.8 wt. %, respectively for membranes with IEC of 2.05 meq·g⁻¹ at 60 °C.¹⁵ In a more recent study, random and multiblock cardo poly(aryl ether
sulfone) polysulfone copolymers containing cardo PSf repeat units/segments were functionalized with bis-quaternary ammonium pendants and were evaluated for their water uptake and hydroxide conductivity at 60 °C.\textsuperscript{50} The QRPES-60 membrane (IEC = 1.89 meq·g\textsuperscript{-1}) showed water uptake and hydroxide conductivity values of 52.9 wt.% and 30 mS·cm\textsuperscript{-1}. The QBPES-60 showed increased conductivity (40 mS·cm\textsuperscript{-1}) with slightly less water uptake (49.3 wt.%) at the similar IEC value of 1.86 meq·g\textsuperscript{-1}. PSf multiblock copolymer membranes containing segments of densely functionalized fluorenyl residues have also been produced.\textsuperscript{51} The benzyltrimethylammonium functionalized membrane (IEC = 1.84 meq·g\textsuperscript{-1}) exhibited water uptake of 56.2 wt.% and hydroxide conductivity up to 40.3 mS·cm\textsuperscript{-1} at 60 °C. The AEM characteristics of low water uptake and high hydroxide conductivity for the PSf-QAPF multiblock copolymer membranes are presumably related to microphase separation in the multiblock copolymers and the high density of functional groups in the functionalized polyformal blocks.

Figure 2.7 Hydroxide conductivity (A) and water uptake (B) vs. IEC for PSf-QAPF4-6. Closed symbols at 60 °C, open symbols at room temperature.
2.3.2.2 Surface morphology and mechanical properties

The multiblock copolymers were designed to segregate into separate domains of hydrophobic PSf and hydrophilic QAPF. Tapping-mode AFM was used to examine the surface morphology of the PSf-QAPF membranes. The membranes were spin-coated onto silicon wafers, dried and subsequently imaged (Figure 2.8). Dark and bright regions are observed in the phase images, and the conductive QAPF segments were determined to be the bright regions by analysis of histograms produced from the phase images. The phase images clearly indicate that as the mole percentage of QAPF increases in the membrane, the phase domains appear to become more connected. Furthermore, the hydrophilic domain size was found to decrease from 16.8 nm to 10.5 nm with increasing QAPF content. Decreases in the domain size has been previously investigated in unrelated multiblock copolymers.\textsuperscript{53} Influencing the chain mobility with either the segment size or number of segments was shown to lead to imperfections in the domains and in the phase separation at higher segment molecular weight or higher number of segments. The formation of a well-connected ion conductive domain in PSf-QAPF6 (C) can explain the sharp water uptake increase observed from PSf-QAPF5 (18.3 wt.%) to PSf-QAPF6 (43.5 wt%), and the corresponding increase in conductivity values from 62 meq·g\textsuperscript{-1} to 78 meq·g\textsuperscript{-1}. The improved conductivity and moderate increase in water uptake for the PSf-QAPF6 membrane (IEC = 1.9) indicate that the multiblock copolymer architecture with the largest mole fraction of QAPF was most effective in generating continuous conductive pathways.
Tensile testing was performed on the PSf-QAPF membranes under ambient temperature and humidity and the Young’s Modulus, yield stress, stress at break and the percent strain at break were measured (Table 2.5). Only small changes in the mechanical properties were observed for the membranes of different composition. The stiffness, as determined by the Young’s modulus, varied the most and increased with increasing QAPF content. The values were measured to be between 931 and 1273 MPa. The yield stress for each of the PSf-QAPF membranes was found to be consistent across all samples at approximately 50 MPa, while the stress at break was found to change slightly from 43 to 49 MPa, and the strain at break for the PSf-QAPF membranes was approximately 5 percent. The high tensile strength and high modulus indicate that the mechanical properties of the PSf-QAPF membranes are dominated by the PSf matrix and that the different volume fraction of the QAPF minor phase does not significantly impact the mechanical properties. The tensile properties of the PSf-QAPF materials are similar to those previously reported for PSf multiblock AEMs which have shown tensile strengths up to 45 MPa. The mechanical properties observed for the PSf-QAPF membranes are sufficient for anion exchange membrane applications.
Table 2.5 Mechanical characteristics of PSf-QAPF membranes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s Modulus [MPa]</th>
<th>Yield Stress [MPa]</th>
<th>Stress at Break [MPa]</th>
<th>Strain at Break [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSF-QAPF4</td>
<td>931 ± 99</td>
<td>50.2 ± 3.5</td>
<td>43.3 ± 1.0</td>
<td>5.5 ± 1.4</td>
</tr>
<tr>
<td>PSf-QAPF5</td>
<td>1109 ± 82</td>
<td>50.7 ± 1.3</td>
<td>48.5 ± 2.2</td>
<td>5.0 ± 1.4</td>
</tr>
<tr>
<td>PSf-QAPF6</td>
<td>1273 ± 47</td>
<td>49.0 ± 9.1</td>
<td>49.0 ± 9.1</td>
<td>4.0 ± 1.4</td>
</tr>
</tbody>
</table>

2.3.2.3 Membrane base stability

While the polyformal backbone was demonstrated to be base stable through evaluation of the unfunctionalized PSf-PF multiblock copolymer, the evaluation of the functionalized PSf-QAPF membranes was necessary to determine the stability as an AEM. The base stability of the PSf-QAPF4 multiblock copolymer membranes was evaluated by soaking the membrane in 1 M KOH for 5 days at both 60 and 80 °C followed by analysis of the $^1$H NMR spectra before and after treatment. Prior to immersion in base, the membranes were transparent, creasable, and light yellow in color. After immersion in base at 60 °C, the PSf-QAPF membrane remained transparent, while becoming more yellow in color. The membrane furthermore remained creasable. Analysis of the $^1$H NMR spectrum indicated some degradation with the number of formal linkages decreasing by 7 % and the BTMA cations reduce by 3 %. A more aggressive test of immersion in 1 M KOH at 80 °C over 5 days resulted in a membrane that was no longer creasable. The $^1$H NMR spectrum for the membrane after soaking at 80 °C indicated an 18% decrease in formal linkages and the BTMA cations had decreased by 35%. It is also of note that the degradation of formal linkages was predominantly occurring between QAPF repeat units with less degradation occurring between PSf and QAPF segments. Degradation of benzyltrimethylammonium in hydroxide above 60 °C is established in the literature. The degradation results indicate that
the hydrophilic character of the QAPF segments allowed hydroxide greater access to the formal linkages compared to the unfunctionalized PSf-PF4 copolymer and subsequent cleavage occurred more readily between hydrophilic QAPF repeat units. The decrease of formal linkages in the \(^1\)H NMR spectrum indicates a loss of molecular weight as evidenced by the increased brittleness of the membrane after soaking at 80 °C. The base stability tests show that the membrane may have adequate stability at 60 °C but that the membrane is significantly less stable at 80 °C.

2.4 Conclusions

This research has developed a synthetic method for the synthesis of PSf-QAPF multiblock copolymers and their potential application as anion exchange membranes. The synthesis is the first example of incorporating polyformal into multiblock anion exchange membranes. This work demonstrates the facile synthesis of high molecular weight PSf-PF multiblock copolymers from phenol-terminated polysulfone and the selective functionalization of the PF segments. The resulting PSf-QAPF multiblock copolymers were found to be solution processible and produced mechanically robust materials. The multiblock copolymers containing densely functionalized QAPF segments were shown to produce membranes that were highly conductive with low water uptake. The conductivity and water uptake for the PSf-QAPF multiblock copolymer membranes was facilitated by microphase separation in which well-connected domains were observed by tapping mode-AFM. PSf-PF multiblock copolymers prior to quaternary ammonium functionalization were shown to be base stable; however, when the PF segments were functionalized, degradation was observed at elevated temperatures. The promising results from this research encourage further development of PSf-PF multiblock copolymer materials for anion exchange membranes.
2.5 Acknowledgments

This material is based upon work supported by the U.S. Army Research Laboratory and the U.S. Army Research Office under MURI contract/grant number W11NR-10-0520. The authors thank Thomas Brenner and Prof. Reuben Collins for their assistance with AFM surface characterization and Blake Whitley and Prof. Kip Findley for their assistance with mechanical testing, and Solvay Advanced Polymers for their donation of 4,4’-dichlorodiphenylsulfone.

2.6 References


20. Ran, J.; Wu, L.; Ru, Y.; Hu, M.; Din, L.; Xu, T., Anion exchange membranes (AEMs) based on Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and its derivatives. *Polymer Chemistry* **2015**.


CHAPTER 3

BASE STABLE POLY(DIALLYLPIPERIDINIUM HYDROXIDE) MULTIBLOCK COPOLYMERS FOR ANION EXCHANGE MEMBRANES

Modified from a paper published in
Journal of Materials Chemistry A

Derek J. Strasser\textsuperscript{b}, Brendan J. Graziano\textsuperscript{c}, and Daniel M. Knauss\textsuperscript{d}

3.1 Introduction

The development of anion exchange membranes containing base-stable cations has received significant attention, particularly for application in alkaline fuel cells.\textsuperscript{1,2} The result of this research is a body of work in which tetraalkylammonium,\textsuperscript{3-6} imidazolium,\textsuperscript{7-9} and phosphonium\textsuperscript{10-12} cations have been modified and probed for their alkaline stability. In a recent study, some specific heterocyclic and spirocyclic ammonium small molecules were determined to have vastly improved base stability compared with the more typical tetraalkylammonium and imidazolium compounds.\textsuperscript{13} Heterocyclic \textit{N,N}-dimethylpiperidinium, \textit{N,N}-dimethylpyrrolidinium, and spirocyclic \textit{6-azonia-spiro}[5.5]undecane small molecules showed significant base stability, with the latter being the most stable. As a result of the determination of base stability for the small molecules, new polymeric materials containing pyrrolidinium\textsuperscript{14} and piperidinium\textsuperscript{15} type cations have been investigated as anion exchange membranes that can persist under highly alkaline conditions. Currently, only one example of AEM materials bearing spirocyclic ammonium
cations exists. Developing techniques to install stable spirocylic ammonium cationic groups onto a polymer backbone continues to be a challenge.

Cyclopolymerization of dialyl monomers is a chain growth polymerization technique that has been studied for several decades. The defining characteristic is the alternating intra- inter-molecular propagation mechanism in which 5 or 6 membered rings are typically formed. Cationic polymers derived from \( N,N \)-diallylammonium monomers are a well-established class of materials synthesized via cyclopolymerization with water soluble poly(diallyldimethylammonium chloride) (PDADMAC) produced commercially for many applications. PDADMAC is synthesized from diallyldimethylammonium chloride (DADMAC) by free radical cyclopolymerization, producing 5-membered heterocyclic repeat units. Free radical cyclopolymerization of DADMAC with comonomers has allowed the synthesis of numerous random copolymers for a range of applications. Controlled radical polymerization via reversible addition fragmentation transfer polymerization has also been studied for DADMAC. However, the formation of block copolymers is limited to only one example with water-soluble materials having been produced from the sequential polymerization of acrylamide and DADMAC. As an analogue of PDADMAC, the cyclopolymerization of \( N,N \)-diallylpiperidinium chloride (DApipCl) has been reported to yield poly(diallylpiperidinium chloride) (PDApipCl). The interesting structural difference between PDADMAC and PDApipCl is the spirocyclic quaternary ammonium repeat units that are obtained in the PDApipCl materials. To date, there is no literature indicating the synthesis of hydrophobic-hydrophilic block copolymers containing either PDADMAC or PDApipCl.

Disulfides have been shown to have high chain transfer constants thereby limiting the molecular weight in various radical polymerizations, and free radical polymerizations in the presence of disulfides have been shown to produce \( \alpha,\omega \)-functionalized telomers. Aryl
disulfides have also been used as initiator (initiator-transfer-terminator) for vinyl polymerizations, thereby eliminating the need for an additional source of radical initiators.\textsuperscript{37-40} Ultimately, the use of disulfides as initiator eliminates end groups resulting from any additional radical initiator and can cleanly produce difunctional telechelic oligomers.

Multiblock is a type of polymer architecture that can combine the properties of two different materials into one unique copolymer system. Alternating hydrophobic-hydrophilic multiblock architecture has been employed in designing both anion\textsuperscript{41,42} and proton exchange membranes.\textsuperscript{43,44} Multiblock copolymers can be derived from either the reaction between two different complementarily functionalized telechelic prepolymers or the presence of an appropriately functionalized telomer in a polymerization reaction with comonomers. The synthesis of multiblock copolymers is a facile technique to prepare materials capable of microphase separation, and the production of multiblock copolymer materials designed for anion exchange membranes have shown improved ionic conductivity and dimensional stability compared to random copolymer analogues.\textsuperscript{45,46}

We have designed a series of hydrophobic-hydrophilic multiblock copolymer membranes with the structure depicted in Figure 3.1, incorporating polysulfone (PSf) and poly(diallylpiperidinium hydroxide) (PDApipOH) segments. Employing 4-(fluorophenyl)disulfide as a photoiniferter, we were able to readily produce $\alpha,\omega$-4-fluorophenyl sulfide functionalized PDApipCl. Oxidation of the 4-fluorophenyl sulfide end groups to 4-fluorophenyl sulfone sufficiently activated the telomers for nucleophilic aromatic substitution. Ion exchange to hexafluorophosphate enabled solubility of the cationic prepolymer in DMAc, and multiblock copolymers were then produced by nucleophilic aromatic substitution under typical polysulfone synthesis conditions. Our design allowed for tuning of the ion exchange capacity by varying the weight percent of the poly(diallylpiperidinium hexafluorophosphate) (PDApipPF$_6$). The final multiblock
copolymers were fabricated into membranes, ion exchanged to hydroxide, and evaluated for
hydroxide conductivity, water uptake, phase separation, mechanical properties, and base and
thermal stability.

\[
\text{Figure 3.1 Polysulfone-PDApipOH multiblock copolymer}
\]

3.2 Experimental

3.2.1 Materials

Allyl chloride (98%) was purchased from Alfa Aesar and was distilled under nitrogen
prior to use. Bisphenol A (97%) and bis(4-fluorophenyl) sulfone (99%) were obtained from
Sigma-Aldrich and were twice crystallized from toluene. \(N,N\)-dimethylacetamide (DMAc)
(99.9%) was purchased from Sigma-Aldrich and distilled from phosphorous pentoxide prior
to use. Piperidine (99%), allyl bromide (99%), 4-fluorothiophenol (98%), \(N,N,N,N\)-
tetramethylethylenediamine (TMEDA) (99%), and potassium peroxymonosulfate (Oxone)
were obtained from Sigma-Aldrich and were used as received. Acetonitrile-\(d_3\), DMSO-\(d_6\),
and deuterium oxide were obtained from Sigma- Aldrich. CDCl\(_3\) was purchased from
Cambridge Isotope Laboratories. All other chemicals and solvents were used as received
from commercial sources.

3.2.2 Synthesis of \(N\)-allylpiperidine

\(N\)-allylpiperidine was obtained by condensing piperidine with allyl bromide. A 250
mL round bottom flask, equipped with a magnetic stir bar and an addition funnel, was
charged with sodium hydroxide (14.5 g, 0.36 mol) and water (20 mL). The mixture was stirred at 0 °C until all the sodium hydroxide was dissolved. Piperidine (30 mL, 0.30 mol) was then added to the aqueous solution and the addition funnel was charged with allyl bromide (26.3 mL, 0.30 mol). Allyl bromide was slowly added to the ice cold solution over a period of 30 minutes and then allowed to warm to room temperature for an additional 1.5 hours. The resulting oil layer was separated and the aqueous layer was extracted once with chloroform and combined with the oil. The chloroform was evaporated and the product distilled from sodium hydroxide at room temperature under 100 mtorr vacuum producing a colorless liquid (35.6 g, 93.7% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 5.89 (1H, ddt, 17.0 Hz, 10.3 Hz, 6.6 Hz), 5.16 (1H, d, 17.0 Hz), 5.12 (1H, d, 10.3 Hz), 2.96 (2H, d, 6.6 Hz), 2.37 (4H, bS), 1.59 (4H, quin, 5.3 Hz), 1.42 (2H, bt, 5.3 Hz).

3.2.3 Synthesis of N,N-diallylpiperidinium chloride (DApipCl)

The synthesis of N,N-diallylpiperidinium chloride was accomplished by the nucleophilic substitution of N-allylpiperidine with allyl chloride. A 250 mL round bottom flask equipped with a magnetic stir bar was charged with N-allylpiperidine (35.6 g, 0.284 mol), allyl chloride (29.0 mL, 0.356 mol), and water (55 mL). The flask was sealed with a rubber septum that was secured with copper wire. The two-phase reaction was stirred vigorously at 65 °C for 2 days. The resulting oil layer was separated and the aqueous phase washed once with diethyl ether, combined with the oil layer and concentrated by rotary evaporation. Acetone (200 mL) was added to the resulting viscous oil and a white precipitate formed. The white solid was collected by filtration and dried under vacuum at 200 mtorr (37.6 g, 66.5% yield). $^1$H NMR (500 MHz, D$_2$O): δ 5.85 (2H, m), 5.45 (4H, m), 3.76 (4H, d, 10 Hz), 3.18 (4H, m), 1.74 (4H, s), 1.51 (2H, s). $^{13}$C NMR (125 MHz, D$_2$O): δ 128.7, 124.1, 61.0, 58.4, 20.7, 19.3. HRMS (EI) for [C$_{11}$H$_{20}$ClN]$^+$: calculated 201.1284, found 201.1238.
3.2.4 Synthesis of bis(4-fluorophenyl) disulfide

Synthesis of bis(4-fluorophenyl) disulfide was accomplished by oxidation of 4-fluorothiophenol. A 25 mL round bottom flask was charged with 4-fluorothiophenol (2.39 g, 0.018 mol), Cu(II)Cl (28 mg, 0.16 mmol), TMEDA (54 µL, 0.36 mmol), and THF (5 mL). Oxygen was bubbled through the reaction mixture for 1 hour and the flask was subsequently sealed with a septum under an oxygen atmosphere. The reaction was stirred overnight at room temperature, and then filtered through a plug of activated alumina and the solvent removed by rotary evaporation. The resulting yellow oil was dissolved in chloroform, washed twice with aqueous KOH (10 wt.%), dried over MgSO₄ and the chloroform removed by rotary evaporation. The remaining material was crystallized from methanol (1.17 g, 51.3% yield).

^1^H NMR (500 MHz, CDCl₃): δ 7.44 (4H, dd, 8.60 Hz, 5.16 Hz) 7.01 (4H, t, 8.60 Hz).

^1^3^C NMR (125 MHz, CDCl₃): δ 163.7, 161.7, 132.3, 132.2, 131.4, 131.3, 116.5, 116.3.

3.2.5 Oxidation of 4-fluorothioanisole to 4-fluorophenylmethyl sulfone

Synthesis of 4-fluorophenylmethyl sulfone was adapted from a literature procedure. In a 15 mL round bottom flask containing a magnetic stir bar, 4-fluorothioanisole (0.210 g, 1.50 mmol) and Oxone (1.36 g, 2.21 mmol) were suspended in 3 mL water. The suspension was heated at 60 °C and stirred overnight. Upon cooling, a white solid precipitated and was collected by filtration. The recovered solid was then dissolved in a minimum of hot methanol. Water was carefully added until turbid and the mixture was cooled to effect crystallization. The obtained white solid was filtered and dried (0.203 g, 79% yield)

λ max(acetonitrile)/nm 216 (ε/dm³ mol⁻¹ cm⁻¹ 7800) ^1^H NMR (500 MHz, CDCl₃): δ 7.96 (2H, m), 7.24 (2H, m), 3.05(3H, s).
3.2.6 Synthesis of 4-fluorophenyl sulfide terminated poly(\(\text{N,N-diallylpiperidinium chloride}\)) (PDApipCl)

The synthesis of telechelic PDApipCl oligomers was designed to produce materials of relatively low molecular weight bearing 4-fluorophenyl sulfide end groups. A typical synthesis was as follows: DApipCl (12.6 g, 62.5 mmol) was taken up in a 1:1 solution of water and methanol and diluted to 25 mL in a volumetric flask, producing a 2.5 M stock monomer solution. A 10 mL test tube with a magnetic stir bar was charged with bis(4-fluorophenyl) disulfide (50.8 mg, 0.20 mmol) and DApipCl (4.03 g, 20 mmol, 8.0 mL of stock solution). The test tube was septum sealed and the suspension was purged with nitrogen in an ice bath for 30 min. The reaction tube was placed in a stainless-steel beaker containing silicon oil maintained at 60 °C on a hot plate. The lid for the beaker was designed such that a UV pen light (254 nm) would sit in the middle of the beaker with the reaction tubes approximately 2 cm away. The reaction was allowed to warm for 10 minutes and then the UV light was illuminated. The polymerization was carried out for 24 hours with constant UV radiation. The viscous solution was then precipitated into acetone and the resulting white solid was collected, dissolved in methanol and again precipitated into acetone. The final white powder was collected by vacuum filtration, washed with acetone, and dried at 80 °C under vacuum (1.91 g, 47% yield) \(^1\)H NMR (500 MHz, D\(_2\)O): \(\delta\) 7.44 (4H, m), 7.08 (4H, m), 3.84(2H, bs), 3.32(4H, m), 3.10(2H, bs), 2.53(2H, bs), 2.10(2H, bs), 1.79(4H, bs), 1.57(2H, bs), 1.47(2H, bs), 1.23(2H, bs). \(^13\)C NMR (125 MHz, D2O): \(\delta\) 68.3, 67.0, 63.9, 63.4, 60.3, 42.3, 37.8, 29.5, 26.2, 21.6, 21.2, 20.7.

3.2.7 Oxidation of 4-fluorophenyl sulfide terminated (PDApipCl) and ion metathesis to hexafluorophosphate

4-fluorophenyl sulfide terminated PDApipCl (2.43 g, 0.22 mmol sulfide end groups) was introduced into a 25 mL round bottom flask equipped with a magnetic stir bar and 5 mL
water and stirred until dissolved. Oxone (270 mg, 0.44 mmol) was added to the solution and stirred until homogenous. The reaction mixture was heated at 60 °C overnight. The reaction mixture was concentrated by rotary evaporation and then precipitated into acetone. The white solid was dissolved in 5 mL water and precipitated into a saturated solution of aqueous potassium hexafluorophosphate. The white solid was collected by filtration and washed with copious amounts of water and dried at 80 °C under vacuum (1.96 g recovered).

### 3.2.8 Synthesis of Polysulfone-PDApipPF$_6$ multiblock copolymers

The multiblock copolymers were synthesized to achieve a targeted weight percent incorporation of PDApip. The weight percent of PDApip incorporated was between 16 and 40%, calculated in the hydroxide form. A representative procedure (sample PSf-PDApip3) is as follows: A 25 mL 3-neck round bottom flask fitted with an overhead stir motor, Dean-Stark trap prefilled with toluene, condenser and a nitrogen inlet was charged with bisphenol A (0.653 g, 2.86 mmol), potassium carbonate (0.059 g, 4.30 mmol), DMAc (9.8 mL) and toluene (3 mL). The reaction flask was heated under nitrogen in a 150 °C oil bath to remove water to the Dean-Stark trap for 3 hours and then cooled to room temperature. Bis(4-fluorophenyl) sulfone (0.700 g, 2.75 mmol) and 4-fluorophenyl sulfone terminated PDApipPF$_6$ (1.10 g, 0.10 mmol end groups) were added. The reaction was then heated to reflux for 3 hours, during which time the viscosity of the reaction dramatically increased. The solution was diluted with an additional 9 mL DMAc, cooled to room temperature and precipitated into methanol. The resulting off-white fibers were collected by filtration and stirred in water overnight to remove any residual salts. The multiblock copolymer was collected by filtration, washed with methanol, and dried at 80 °C under vacuum (2.22 g, 95% yield).
3.2.9 Membrane fabrication

PSf-PDApipPF$_6$ membranes were fabricated by casting the multiblock copolymer solution onto a glass substrate. Polymer solutions were 15 % w/v of copolymer in DMAc and were filtered through a plug of glass wool prior to casting. The polymer solutions were deposited onto a glass sheet and were made uniform with a doctor blade set to 750 $\mu$m. The glass was heated to 75 °C on a hotplate to slowly evaporate solvent. PSf-PDApipPF$_6$ membranes were removed from the substrate by soaking in water. The free-standing membranes were then dried under vacuum.

3.2.10 Ion Exchange to hydroxide

Ion exchange to hydroxide was accomplished by first exchanging to chloride and then to hydroxide. The PSf-PDApipPF$_6$ membranes were immersed in a saturated solution of ammonium chloride and heated in a 100 °C oil bath for 48 hours. Following ion exchange to chloride, PSf-PDApipCl membranes were then immersed in 2 M potassium hydroxide for 48 hours to complete the ion exchange to hydroxide. The resulting membranes were washed with successive nitrogen-purged deionized water baths until a neutral pH was obtained.

3.2.11 Characterization and Measurements

Polymer structure and composition were determined by $^1$H NMR spectroscopy on a JEOL ECA-500 FT-NMR using CDCl$_3$, deuterium oxide, DMSO-d$_6$ or acetonitrile-d$_3$ as solvent. The NMR chemical shift values (δ) were referenced using residual solvent signals.

Ultraviolet-visible (UV-vis) spectroscopy was performed with a Thermo Electron Corporation Evolution 300 PC spectrophotometer and was used for end group analysis of the PDApip oligomers. All measurements were made in quartz cuvettes between 200 and 400 nm and were referenced against pure solvents. Samples were prepared with either methanol
Thermal transitions were measured by differential scanning calorimetry (DSC) on a TA Instruments Q20 DSC. Samples were prepared in T-zero aluminum pans and measured from 30-250 °C for 3 cycles. The heating rate was 10 °C per minute and the cooling rate was 40 °C per minute. The third heating was used to determine the glass transition temperature ($T_g$).

Tapping mode atomic force microscopy (TM-AFM) was used to observe the surface morphology of the PSf-PDApipPF₆ membranes. Images were obtained from an Oxford Instruments AFM 3D utilizing a 42 N·m⁻¹ silicon Pointprobe tip (purchased from Nanoworld). PSf-PDApipPF₆ multiblock copolymer solutions were made from DMAc at a 0.2 % w/v concentration and drop cast onto 1 cm² silicon wafers. The silicon wafers were then dried overnight on a 75 °C hot plate. Prior to AFM analysis, the PSf-PDApipPF₆ coated wafers were allowed to equilibrate to ambient temperature and humidity. The amplitude set-point ratio (rsp) was set to 0.6 and the driving amplitude ($A_0$) was set to 1 V. Height and phase images of all samples were collected under ambient humidity and temperature.

Tensile properties of PSf-PDApipCl multiblock copolymers were measured using a Mark-10 ESM1500 test stand equipped with a 250 N load cell, having a 0.1 N resolution. Each membrane was stretched at a rate of 10 mm·min⁻¹. Membrane samples were cut and the dimensions measured exactly (roughly 50 μm in thickness, 6 mm in width and 20 mm in length). Each membrane was allowed to equilibrate to ambient humidity for 24 hours. The relative humidity at the time of measurement was approximately 25 %.

The ion exchange capacity (IEC) of the PSf-PDApipCl multiblock copolymer membranes was determined using the Mohr titration method. Membrane samples, previously

or acetonitrile to approximately 0.1 wt% solutions. The presence of 4-fluorophenyl sulfide and 4-fluorophenyl sulfone was detected at wavelengths of 251 nm and 216 nm, respectively.
exchanged to the chloride form, were washed and dried at 80 °C for 24 hours to obtain the dry mass. An accurately weighed dried membrane was immersed in 40 mL of 1 M sodium nitrate and soaked for 24 hours. The solution was diluted to 50 mL in a volumetric flask and five 9 mL aliquots were titrated with a standardized 0.04955 M silver nitrate solution with potassium chromate as indicator. The ion exchange capacity was determined from the following formula:

\[
IEC = \frac{V_T \times C_T \times V_S}{M_D}
\]

where \(V_T\) and \(C_T\) are the volume and concentration of the silver nitrate titrant, \(V_A\) and \(V_S\) are the volume of the aliquot and initial solution, respectively, and \(M_D\) is the dry mass of the membrane.

Percentage of water uptake (WU%) for the membranes was determined gravimetrically in the hydroxide form. Membranes were converted to the hydroxide form, washed to neutral pH, and dried under vacuum (~200 mtorr) for 24 hours to obtain a dry mass (\(M_D\)). The membranes were then soaked in degassed 18 MΩ water under a nitrogen atmosphere at a given temperature. The hydrated membrane mass (\(M_W\)) was determined by quickly wiping off surface water, obtaining the mass and re-soaking. Each membrane was measured 4 times at each temperature and the percent water uptake was determined by the following equation:

\[
WU(\%) = \frac{M_W - M_D}{M_D} \times 100
\]

Electrochemical impedance spectroscopy (EIS) was used to determine the in-plane hydroxide conductivity. A Biologic VMP3 potentiostat using a 4-probe Teflon cell with platinum electrodes, immersed in nitrogen-purged 18 MΩ water and measuring in a frequency range of 300 KHz to 100 Hz was used. Membranes were measured against a Nafion 117 standard to validate the data. A Bode plot was used to validate the frequency
range with constant impedance. The intercept on the real resistance axis in the Nyquist plot was taken as the membrane resistance. The ionic conductivity of the membranes was determined by the following calculation:

\[ \sigma = \frac{d}{W \times T \times R} \]

where \( \sigma \) is the ionic conductivity in S\( \cdot \)cm\(^{-1}\), \( d \) is the distance between the reference electrodes in cm, \( W \) and \( T \) represent the width and thickness in cm for the membrane at room temperature under fully hydrated conditions and \( R \) is the measured resistance (\( \Omega \)) of the membrane.

The alkaline stability of the PDApipOH homopolymer was determined by adapting a previously established method. A 5 mL Teflon vial was charged with PDApipCl (0.101 g, 0.50 mmol), potassium hydroxide (0.115 g, 2.05 mmol) and nitrogen-purged methanol-d\(_4\) (2 mL), generating a 1 M solution in hydroxide and a 3-fold excess of base. The Teflon vial was further purged with nitrogen, sealed and placed in an 80 °C oil bath for 42 days. Samples were measured by \(^1\)H NMR spectroscopy at 0, 7, and 42 days and analyzed for the presence of degradation products.

Thermogravimetric analysis (TGA) of both the PDApip homopolymer and PSf-PDApip multiblock copolymers was accomplished with a Seiko TG/DTA 320 Thermal Analyzer with a RT Instruments software upgrade. Measurements were run under a nitrogen atmosphere with a heating rate of 10 °C per minute. Samples in the hexafluorophosphate form were heated to 150 °C to drive off residual water, then cooled and measured. Samples in either the chloride or hydroxide form were heated at 60 °C for an hour, cooled and measured.

The conductivity stability of the membranes at elevated temperature was also evaluated. PSf-PDApipOH membranes were immersed in a nitrogen-purged 1 M potassium
hydroxide solution at 80 °C for 5 days. After immersion, the membranes were washed with degassed, 18 MΩ water repeatedly until a neutral pH was obtained and their hydroxide conductivity at 80 °C was measured.

3.3 Results and Discussion

The objective of the research was to produce base-stable anion exchange membranes that are highly conductive and mechanically robust. We hypothesized that the spirocyclic ammonium structure of the PDApip repeat units would provide a hydrophilic ion conductive medium with enhanced base stability, given the demonstrated base stability of similar spirocyclic small molecules. The ammonium spirocyclic structure with combined 5-membered and 6-membered rings was not specifically studied in the prior research on base stability of small molecules, but our synthesis procedure using the designed diallylammonium monomer could readily allow for the preparation of such polymer incorporated structures for further study. Polysulfone (PSf), a common engineering thermoplastic, was chosen to serve as the hydrophobic matrix due its excellent thermal, mechanical and film forming properties.

3.3.1 Synthesis of PDApipPF₆ telechelics

Our design was to produce telechelic 4-fluorophenyl sulfone terminated PDApip oligomers (Scheme 3.1) to be further utilized in a polysulfone synthesis. The first step was the synthesis of α,ω-4-fluorophenyl sulfide terminated PDApipCl. The UV initiated radical cyclopolymerization of DApipCl monomer in the presence of the photoiniferter bis(4-fluorophenyl) disulfide was expected to produce 4-fluorophenyl sulfide terminated polymers containing the desired spirocyclic ammonium repeat units. Polymerizations were carried out with a monomer/initiator feed ratio of 100/1 in a 1:1 methanol:water solution in order to maintain solubility of the resultant polymer and aid in solubility of the disulfide. Using
bis(4-fluorophenyl) disulfide as a photoiniferter limits the initiating species to only 4-fluorophenyl thiyl radicals in the initiation and degenerative chain transfer processes. Termination in the polymerization of DADMAC, the dimethyl analogue, has been shown to terminate exclusively by combination of growing chains as a result of steric hindrance.\textsuperscript{51} By extension, we assumed that the PDApipCl oligomers would terminate similarly, resulting in only 4-fluorophenyl sulfide end groups as a result of initiation, chain transfer to disulfide, and any polymer chain termination by combination.

Scheme 3.1 Synthesis of PDApipPF\textsubscript{6} oligomers. i) MeOH/water, 60 °C, hv, 24 hrs.; ii) Oxone, 60 °C, overnight; iii) Precipitation into saturated KPF\textsubscript{6}

Nuclear magnetic resonance spectroscopy was used to elucidate the polymer structure and confirm the presence of 4-fluorophenyl sulfide end groups. The proton NMR spectrum (Figure 3.2) indicates that the cyclopolymerization forms 5-membered rings as evidenced by diastereotopic protons, C and E, resulting from chiral centers, D.\textsuperscript{52} The cis\textendash trans ratio, estimated from the D protons observed in the \textsuperscript{1}H NMR spectrum, was 6:1.\textsuperscript{52} The 4-fluorophenyl sulfide end groups were also observed downfield in the proton NMR spectrum. The peaks A and B arise from the protons ortho to the fluorine and sulfide groups, respectively. Assignments were further supported with DQF-COSY and HMQC NMR spectra (Appendix B, Figures A1 and A2). Due to the polymers being precipitated twice in
acetone, which is a good solvent for the bis(4-fluorophenyl) disulfide, the presence of the aromatic signals clearly indicates end group functionality rather than contribution from trace amounts of disulfide starting material. The number average molecular weights ($M_n$) were determined from the ratio of aromatic peaks (using the integral values of the A protons from the 4-fluorophenyl sulfide end groups) to PDApipCl repeat units (using the downfield peak at 3.84 ppm of the E protons adjacent to the nitrogen on the 5-membered ring). Three polymerizations were completed and the resulting $M_n$ for each polymerization is provided in Table 3.1.

![Figure 3.2 $^1$H NMR spectrum of PDApipCl in deuterium oxide.](image)

Table 3.1 Molecular weight characterization of PDApipCl

<table>
<thead>
<tr>
<th>Sample</th>
<th>[M] / [I]</th>
<th>NMR $M_n$ [g·mol$^{-1}$]</th>
<th>UV-vis $M_n$ [g·mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDApip1</td>
<td>100/1</td>
<td>14,800</td>
<td>10,200</td>
</tr>
<tr>
<td>PDApip2</td>
<td>100/1</td>
<td>12,300</td>
<td>11,600</td>
</tr>
<tr>
<td>PDApip3</td>
<td>100/1</td>
<td>11,000</td>
<td>12,300</td>
</tr>
</tbody>
</table>
End group analysis and molecular weight determination was further investigated by UV-vis spectroscopy (Appendix Figure A.3). The $M_n$ was determined from the end group concentration in the UV-vis spectra for each polymerization and agreed well with the values determined by NMR spectroscopy, Table 3.1. Additionally, the concentration of 4-fluorophenyl sulfide groups present in the recovered sample was determined from the UV-vis absorbance data and indicated the quantitative conversion of disulfide to sulfide end groups during the polymerization. The complete incorporation is a good indication of the successful degenerative transfer of the photoiniferter.

The 4-fluorophenyl sulfide end groups could be used directly in a nucleophilic aromatic substitution polymerization, as sulfide groups have been demonstrated to activate aryl fluorides for reaction,\textsuperscript{53, 54} however, oxidation of the sulfides to the more activating sulfones was expected to improve the reactivity in nucleophilic aromatic substitution. Oxidation of the 4-fluorophenyl sulfide to 4-fluorophenyl sulfone was accomplished using Oxone, adapting a procedure that has been demonstrated for simple aromatic sulfides.\textsuperscript{49} The oxidized oligomers were isolated as PDApipPF$_6$ by precipitation from a solution of potassium hexafluorophosphate. The hexafluorophosphate counterion enabled solubility in polar aprotic solvents including $N$-methylpyrrolidone (NMP), DMAc, dimethylsulfoxide (DMSO), 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone (DMPU), and acetonitrile. Furthermore, the PDApipPF$_6$ oligomers became insoluble in water and methanol. The conversion from sulfide to sulfone in the PDApipPF$_6$ oligomers was determined by NMR spectroscopy. The $^1$H NMR spectrum (Figure 3.3) indicated quantitative conversion with a clear downfield shift of the protons ortho to the sulfide at 7.44 ppm to 7.95 ppm for the sulfone product.
Figure 3.3 $^1$H NMR spectrum of 4-fluorophenyl sulfone terminated PDApipPF$_6$ in acetonitrile-d$_3$

3.3.2 Synthesis of PSf-PDApipPF$_6$ multiblock copolymers

A series of four PSf-PDApip (indicated as samples 1-4) multiblock copolymers, in which the weight percentage of PDApipPF$_6$ was varied, was designed to produce high molecular weight materials and a range of IECs. Step-growth polymerization of 4-fluorophenyl sulfone terminated PDApipPF$_6$ with bis(4-fluorophenyl) sulfone and bisphenol A (Scheme 3.2) was completed to produce multiblock copolymers containing randomly distributed segments of PDApipPF$_6$. The polymerization reactions were done in DMAc at reflux temperature until the solution viscosity dramatically increased. A highly viscous solution was observed, where the stirred reaction mixture was observed to pull away from the reaction flask, after approximately 3 hours of reaction time. After repeated precipitations and washing with water, the final yield from each polymerization was greater than 95% with the exception of PSf-PDApip1, in which the recovered yield was only 85%.
Scheme 3.2 Synthesis of PSf-PDApipPF₆ multiblock copolymers. i) DMAc/toluene, potassium carbonate, reflux temperature, ~3 hours

Multiblock copolymer compositions were determined by proton NMR spectroscopy. ¹H NMR spectra of the multiblock copolymers were obtained in DMSO-d₆ (Figure 3.4) and clearly indicate the presence of both PSf and PDApipPF₆. Peaks labeled I, J, K, and L indicate the presence of the polysulfone aromatic rings and peak M, overlapped with the PDApipPF₆ corresponds to the isopropylidene methyl groups on the bisphenol A portion of the polysulfone backbone. The compositions (Table 3.2) were determined by comparing the integration from peaks J and E, corresponding to the protons adjacent to the sulfone in the polysulfone backbone and protons adjacent to the nitrogen on the 5-membered ring in the PDApip backbone. The contribution of the PDApip end groups to the J peak was assumed to be negligible. The composition analysis was used to determine the IEC (for simplicity presented as values calculated in either the chloride form or hydroxide form). The IECs were found to range from 0.9-2.02 meq·g⁻¹ when calculated in the hydroxide form.
Figure 3.4 $^1$H NMR spectrum of PSf-PDApipPF$_6$ multiblock copolymer in DMSO-d$_6$

Table 3.2 Characterization of PSf-PDApip copolymer samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NMR wt%$^a$ PDApipOH</th>
<th>% Yield</th>
<th>IEC [Cl]$^a$ [meq·g$^{-1}$]</th>
<th>IEC [Cl]$^b$ [meq·g$^{-1}$]</th>
<th>IEC [HO]$^c$ [meq·g$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf-PDApip1</td>
<td>16.2</td>
<td>85</td>
<td>0.87</td>
<td>0.89 ± 0.01</td>
<td>0.90</td>
</tr>
<tr>
<td>PSf-PDApip2</td>
<td>22.3</td>
<td>91</td>
<td>1.19</td>
<td>1.25 ± 0.02</td>
<td>1.29</td>
</tr>
<tr>
<td>PSf-PDApip3</td>
<td>29.0</td>
<td>96</td>
<td>1.54</td>
<td>1.49 ± 0.03</td>
<td>1.53</td>
</tr>
<tr>
<td>PSf-PDApip4</td>
<td>40.2</td>
<td>93</td>
<td>2.10</td>
<td>1.95 ± 0.18</td>
<td>2.02</td>
</tr>
</tbody>
</table>

a) Determined from $^1$H NMR spectroscopy, b) determined by titration of chloride, c) calculated from the chloride titration values
3.3.3 Membrane fabrication and mechanical properties

Multiblock copolymer membranes in the hexafluorophosphate form were found to be soluble in a range of polar aprotic solvents including DMAc, NMP and DMPU. PSf-PDApipPF$_6$ multiblock copolymers were dissolved in DMAc and cast onto glass. The resulting membranes were found to be colorless and transparent (Figure 3.5).

Figure 3.5 PSf-PDApip multiblock copolymer membrane

The PSf-PDApipPF$_6$ multiblock copolymer membranes were ion-exchanged to chloride. The ion exchange to chloride was performed for two reasons: chloride is easily titrated, and ion exchange can occur under a range of temperatures and concentrations without side degradation reactions. To facilitate the ion exchange from hexafluorophosphate, ammonium chloride was used owing to its significant solubility in water compared to the potassium salt, which is only slightly soluble. Membranes were soaked in saturated ammonium chloride in a 100 °C oil bath for 48 hours, followed by repeated rinsing to remove excess salt. The conditions employed were presumed necessary to remove the large hexafluorophosphate counter ion, which also has comparatively less solubility compared to the chlorides in water. Once the membranes were ion exchanged and rinsed of excess salt, they were dried under vacuum.
PSf-PDApip membranes in the hexafluorophosphate form were somewhat stiff and susceptible to cracking; however, when the membranes were ion exchanged to chloride they were found to be tough and creaseable when dry. After ion exchange to chloride, the copolymers were rendered insoluble in all the above-mentioned polar aprotic solvents, as well as insoluble in water, alcohols, acetonitrile, tetrahydrofuran, and chloroform. Insolubility in THF and chloroform, which are good solvents for polysulfone, provided more evidence for the success of the copolymerization.

Mohr titrations of chloride were accomplished to further characterize each composition, ion exchange capacity, and also to determine quantitative removal of the hexafluorophosphate counter ion. Removal of the hexafluorophosphate counter ion is significant to regaining hydrophilicity in the PDApip segments and assisting in the exchange to hydroxide. Each material was titrated five times and the results show that the ion exchange capacities agreed well with the NMR spectroscopy determined values (Table 3.2).

Tensile testing of two samples, PSf-PDApip1 and PSf-PDApip4 membranes was completed in the chloride form to evaluate the mechanical characteristics for the synthesized membranes at the high and low end of the PDAPip incorporation. The Young’s modulus and the tensile stress at break were found to decrease from 92 MPa to 81 MPa and 27 MPa to 21 MPa, respectively as the IEC of the membranes increased from 0.9 to 2.02 meq·g⁻¹. The percent elongation at break was also found to decrease from 39 to 22 % as the IEC increased. It is clear that under ambient humidity and temperature, the PSf-PDApipCl membranes are relatively flexible as indicated by the Young’s modulus, and that a slight decrease in the tensile strength is observed when the IEC was increased to 2.02 meq·g⁻¹. The tensile strength for other polysulfone based alkaline exchange membranes have been reported with values between 10 and 40 MPa.55-57 Comparatively, polyethylene-
polyvinylbenzyltrimethylammonium block copolymer membranes were reported to have
tensile strength between 13.5 and 22.5 MPa for IECs between 1.17 and 1.92 meq g\(^{-1}\).

3.3.4 Morphology of the membranes

An important design feature of block and multiblock copolymers is that of
microphase separation. It has been reported that anion exchange membranes from block
copolymers have higher ionic conductivities and improved dimensional stability when
compared to their random copolymer analogues.\(^3\),\(^42\) Microphase separation was determined
by both DSC and AFM. Figure 3.6 shows the DSC trace for both the PDApipPF\(_6\)
homopolymer and the PSf-PDApipPF\(_6\) multiblock copolymer. The PDApipPF\(_6\)
homopolymer indicated a clear endotherm corresponding to a glass transition (T\(_g\)) at 210 °C.
Copolymer PSf-PDApip1 was analyzed by DSC and compared to the PDApipPF\(_6\)
homopolymer. The DSC trace for copolymer PSf-PDApip1 clearly indicated two
endotherms at 180 °C and 210 °C corresponding to the glass transitions of polysulfone and the
PDApipPF\(_6\) homopolymer, respectively. The weak endotherm observed at 210 °C is a result
of the low weight percentage of PDApip in the copolymer composition. Additionally, no
observable decrease in the T\(_g\) was observed for the PDApip segments in the copolymer,
indicating immiscibility of the blocks.

Tapping mode AFM was used to elucidate the surface morphology for each of the
PSf-PDApipPF\(_6\) multiblock copolymers. As indicated by the phase images in Figure 3.7,
microphase separation is observed in all of the copolymer compositions, as was suggested by
the above DSC analysis. The as-cast films were not annealed and do not show highly
ordered domains. It was determined that the dark portions of each image increase as the
weight percentage of PDApipPF\(_6\) increases in the copolymer composition, thereby
corresponding to the PDApipPF\(_6\) segments. Analysis of the phase profile for each copolymer
sample showed that the domain spacing between the dark segments was inversely proportional to the composition. The domain spacing decreased from 53 to 38 nm when the PDApip weight percentage increased from 16.2 to 40.2%. The lack of long-range order notwithstanding, the two higher composition copolymers, PSf-PDApip3 and PSf-PDApip4, indicated well-connected networks of PDApipPF$_6$. The implication of the observed microphase separation, as will be indicated below, is that the water uptake and ultimately the hydroxide conductivity were influenced.

Figure 3.6 DSC traces for PDApipPF$_6$ homopolymer and PSf-PDApip1 copolymer. Third heating cycle at a rate of 10 °C per minute

Figure 3.7 Tapping mode-AFM phase images for PSf-PDApip1 (A), PSf-PDApip2 (B), PSf-PDApip3 (C), PSf-PDApip4 (D).
3.3.5 Water uptake and hydroxide conductivity

The water uptake and hydroxide conductivity of the PSf-PDApipOH membranes were measured at room temperature and further evaluated in a range of temperatures up to 80 °C. As shown in Table 3.3, the water uptake of each of the synthesized membranes increased with IEC, ranging from 14 to 36 % at room temperature, with the most significant difference occurring between membranes PSf-PDApip1 and PSf-PDApip2. Presumably, the large increase of water uptake between membranes PSf-PDApip1 and PSf-PDApip2 (IECs 0.90 and 1.29 meq·g\(^{-1}\)) is an indication of a threshold increase in the connectivity of the hydrophilic domains. It is presumed that the phase separated nature of the PSf-PDApip membranes contributed to the relatively low water uptake.

Table 3.3 Water uptake for PSf-PDApipOH membranes between room temperature and 80 °C

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC (HO(^-)) [meq·g(^{-1})]</th>
<th>Water uptake [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RT 40 °C 60 °C 80 °C</td>
<td></td>
</tr>
<tr>
<td>PSf-PDApip1</td>
<td>0.90 14.6 ± 0.92 15.3 ± 0.70 19.0 ± 1.14 20.3 ± 2.75</td>
<td></td>
</tr>
<tr>
<td>PSf-PDApip2</td>
<td>1.29 33.1 ± 0.79 33.7 ± 0.95 35.0 ± 1.48 35.4 ± 1.21</td>
<td></td>
</tr>
<tr>
<td>PSf-PDApip3</td>
<td>1.53 34.6 ± 0.73 37.0 ± 0.44 38.5 ± 0.93 41.9 ± 3.10</td>
<td></td>
</tr>
<tr>
<td>PSf-PDApip4</td>
<td>2.02 36.0 ± 0.74 38.5 ± 0.74 41.7 ± 1.52 45.4 ± 3.55</td>
<td></td>
</tr>
</tbody>
</table>

The hydroxide conductivity for the PSf-PDApipOH membranes was evaluated in 18 MΩ water at room temperature and further from 40-80 °C (Appendix Figure A.4). As indicated in Table 3.4, the data shows that the hydroxide conductivity increases with increasing IEC. Figure 3.8 depicts the relationships of both hydroxide conductivity and water uptake with the IEC over a range of temperatures. Temperature was determined to have the most significant influence on conductivity performance. As an example, the PSf-
PDApip4 membrane, having an IEC of 2.02 meq·g⁻¹, doubled in hydroxide conductivity from room temperature to 80 °C while the water uptake only increased by 9 wt%.

Table 3.4 Hydroxide conductivity of PSf-PDApipOH membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC (HO⁻) [meq·g⁻¹]</th>
<th>Hydroxide Conductivity [mS·cm⁻¹]</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>Eₐ [kJ·mol⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>RT</td>
<td>40 °C</td>
<td>60 °C</td>
<td>80 °C</td>
<td>80 °C</td>
<td></td>
</tr>
<tr>
<td>PSf-PDApip1</td>
<td>0.90</td>
<td>14 ± 0.2</td>
<td>18 ± 0.2</td>
<td>23 ± 0.5</td>
<td>25 ± 0.5</td>
<td>22 ± 0.2</td>
<td>8.8</td>
</tr>
<tr>
<td>PSf-PDApip2</td>
<td>1.29</td>
<td>29 ± 0.3</td>
<td>38 ± 0.2</td>
<td>50 ± 0.2</td>
<td>60 ± 0.3</td>
<td>60 ± 0.8</td>
<td>11.1</td>
</tr>
<tr>
<td>PSf-PDApip3</td>
<td>1.53</td>
<td>35 ± 0.5</td>
<td>47 ± 0.3</td>
<td>63 ± 0.2</td>
<td>79 ± 0.7</td>
<td>74 ± 1.3</td>
<td>12.3</td>
</tr>
<tr>
<td>PSf-PDApip4</td>
<td>2.02</td>
<td>51 ± 0.6</td>
<td>64 ± 0.3</td>
<td>79 ± 0.6</td>
<td>102 ± 1.2</td>
<td>10.1</td>
<td></td>
</tr>
<tr>
<td>Nafion117</td>
<td>0.92</td>
<td>80 ± 0.6</td>
<td>105 ± 0.4</td>
<td>132 ± 0.5</td>
<td>158 ± 0.8</td>
<td>-</td>
<td>10.3</td>
</tr>
</tbody>
</table>

a) Hydroxide conductivity measured after soaking in 1 M KOH at 80 °C for 120 hours. b) Measurement was not completed

The high conductive performance of the PSf-PDApip materials is competitive to the conductivity values that have been reported for other PSf AEMs. Li and co-workers reported conductivity as high as 46 mS·cm⁻¹ at 60 °C for benzyltrimethylammonium (BTMA) functionalized PSf.⁵⁷ BTMA functionalized and crosslinked PSf interpenetrating networks developed by Gong, et al. indicated conductivity up to 25 mS·cm⁻¹ at 60 °C.⁵⁹ The benchmark BTMA functionalized PSf membranes are those developed by Tanaka, et al., which showed conductivity of 126 mS·cm⁻¹ at 60 °C.⁴⁵ Imidazolium functionialized PSf AEMs have also been extensively studied. PSf AEMs bearing random tethered imidazolium cations showed conductivity as high as 72 mS·cm⁻¹ at 60 °C.⁶⁰ Similar PSf membranes with imidazolium functionalized fluorenyl moieties were reported to display conductivity up to 112 mS·cm⁻¹ at 80 °C.⁶¹
The conductivity dependence on temperature can be rationalized by the activation energy for hydroxide anion transport. The activation energy was calculated from the Arrhenius plot (Figure 3.9) for the PSf-PDApip membranes (and compared with that measured for Nafion 117) and was found to range from 9-12 kJ\cdot mol^{-1}. The calculated activation energies of the PSf-PDApip membranes were similar to the activation energy determined for Nafion 117 (10 kJ\cdot mol^{-1}). Furthermore, the calculated activation energies for the PSf-PDApip membranes are similar to or lower than that for other AEMs reported. In a recent report by Li, et al., benzyltrialklylammonium and imidazolium functionalized PSf membranes were evaluated. The \( E_a \) values obtained were 11.36 kJ\cdot mol^{-1} for BTMA, 13.28 kJ\cdot mol^{-1} for benzyltriethylammonium, and 10.76 kJ\cdot mol^{-1} for methylimidazolium functionalized PSf. Slade and coworkers reported activation energies ranging from 12.3-12.9 kJ\cdot mol^{-1} for BTMA grafted fluorinated ethylene propylene membranes, and piperidinium functionalized PPO membranes developed by Dang, et. al were reported to have activation energies ranging from 12-14 kJ\cdot mol^{-1}. 
3.3.6 Base stability

Tolerance to a highly basic environment at elevated temperatures is key to the application of anion exchange membranes and was strongly considered in the design of the current polymer structures. Spirocyclic ammonium small molecule cations have been previously shown to be highly stable compared to the more typical tetraalkylammonium and imidazolium cations.\textsuperscript{13, 64} Currently, there exists one study of spirocyclic ammonium functionalized AEM, however the spirocyclic ammonium cations were not fully aliphatic and significantly degraded at 60 °C.\textsuperscript{16}

Initially, we investigated the base tolerance of the PDApipOH homopolymer at 80 °C in a 1 M KOH/methanol-d\textsubscript{4} solution using the conditions in an established procedure.\textsuperscript{7} The test was conducted for \(~1000\) hours with samples periodically examined by \textsuperscript{1}H NMR spectroscopy (Figure 3.10). It was determined that over the entirety of the experiment no observable Hoffman elimination took place, as evidenced by the lack of development of any vinyl signals in the \textsuperscript{1}H NMR spectra. Furthermore, the spectra for each of the samples taken at 0, 7, and 42 days do not indicate any new proton signals arising from any substitution
reactions and the integration areas of the peaks were maintained, further indicating that the PDApipOH homopolymer was highly stable under the testing conditions.

Figure 3.10 $^1$H NMR spectra with exposure to base for PDApipOH polymers

Base stability for the synthesized PSf-PDApipOH multiblock copolymers was also evaluated by thermogravimetric analysis (TGA) and measurements of conductivity loss. TGA was conducted on both the PDApip homopolymer and the PSf-PDApip2 multiblock copolymer membrane while in the hexafluorophosphate form (Figure 3.11A) to provide a baseline of their corresponding thermal stabilities. Analysis of the TGA data indicated that the 5 % weight loss for the PDApipPF$_6$ homopolymer and PSf-PDApip2 copolymer occurred at 354 °C and 352°C, respectively. An additional degradation step was observed at 480 °C in the PSf-PDApip2 copolymer, corresponding to the degradation of the polysulfone backbone. The 5 % weight loss for the PSf-PDApip2 copolymer was further evaluated in both the chloride and hydroxide forms (Figure 3.11B) and was found to be 346 °C and 360 °C respectively. The small weight loss occurring between 100 and 200 °C was presumed to be loss of residual water for the copolymers with the more hygroscopic chloride and hydroxide.
counterions. The exceptionally high degradation temperatures found for the PDApip homopolymer and PSf-PDApip copolymer, regardless of counterion, demonstrates the significant base stability of the particular spirocyclic group and are among the highest thermal stabilities reported for any ammonium functionalized polymers. Comparatively, the BTMA hydroxide small molecule, PSf based polymers and polyethylene based polymers functionalized with BTMA, dimethylbenzimidazolium hydroxide, imidazolium functionalized halloysite nanotubes, quaternized imidazolium spheres, N-methylpiperidinium hydroxide, and N-methylpyrrolidinium hydroxide have all been similarly examined by TGA, with the highest thermal stability reported at 260 °C. The PSf-PDApipOH materials show a dramatically greater thermal stability.

Figure 3.11 A) Thermal decomposition data for PDApipPF₆ homopolymer and PSf-PDApip2 copolymer. B) Comparison of PF₆⁻, Cl⁻, and HO⁻ counter ions. Samples were heated at a rate of 10 °C per minute under nitrogen flow

Conductive stability after prolonged exposure to high pH and elevated temperature conditions is the ultimate test of alkaline tolerance. PSf-PDApip membranes used for initial conductivity measurements were exposed to 1 M KOH at 80 °C, and their conductivity re-evaluated (Table 3.4). After 120 hours of exposure, the PSf-PDApip membranes did indicate a small loss of conductivity performance. PSf-PDApip1 and PSf-PDApip3 membranes
indicated an approximately 8% and 6% loss of hydroxide conductivity, respectively, while PSf-PDApip2 did not show any measurable loss of conductivity from exposure to base. While only a small loss of conductivity is observed for the samples, the materials were observed to show some embrittlement and PSf-PDApip4 cracked while placing it in the probe for analysis after hydroxide exposure. The slight decrease in hydroxide conductivity observed for the PSf-PDApipOH membranes is an improvement compared to similar PSf based materials. Many studies have investigated the conductivity stability and have shown significant decreases in hydroxide conductivity at 60 °C for both BTMA\textsuperscript{57, 70} and imidazolium\textsuperscript{59, 61} functionalities. The piperidinium functionalized PPO reported by Dang, et al., indicated significant stability at 90 °C with no significant changes in NMR spectra, but did indicate a similar slight decrease in hydroxide conductivity between 6 and 9%\textsuperscript{15}.

### 3.4 Conclusions

This research has developed a synthetic method for the preparation of PSf-PDApipOH muliblock copolymer membranes. The synthesis method produces the first examples of hydrophobic-hydrophilic block copolymers that incorporate spirocyclic, aliphatic ammonium repeat units. This work demonstrates degenerative chain transfer radical cyclopolymerization of diallylpiperidinium chloride to produce difunctional oligomers that were subsequently copolymerized by step-growth techniques. The resulting PSf-PDApipPF\textsubscript{6} multiblock copolymers were found to be solution processible and produced durable films. Tapping mode AFM indicated phase separation between the PSf and PDApipPF\textsubscript{6} segments with continuous PDApipPF\textsubscript{6} domains forming as the weight fraction increased. The polymer structure and phase-separated morphology resulted in materials with low water uptake, high hydroxide conductivity, and sufficient mechanical properties. The PDApipOH material was shown by \textsuperscript{1}H NMR spectroscopy to be highly alkaline stable with no observable degradation at 80 °C over 1000 hours. Furthermore, assessment of the alkaline stability of PSf-PDApip
multiblock copolymers indicated that these materials show remarkable tolerance to base at high temperature, indicated by thermogravimetric analysis in the hydroxide form. The promising results encourage further research on developing PDApipOH containing materials for their application in alkaline fuel cells.

3.5 Acknowledgments

This material is based upon work supported by the U.S. Army Research Laboratory and the U.S. Army Research Office under MURI contract/grant number W11NR-10-1-0520. The National Science Foundation is acknowledged for additional support through the REU program under grant number EEC 1631778.

3.6 References


70. Gao, L.; He, G.; Pan, Y.; Zhao, B.; Xu, X.; Liu, Y.; Deng, R.; Yan, X., Poly(2,6-dimethyl-1,4-phenylene oxide) containing imidazolium-terminated long side chains as
CHAPTER 4

EFFECT OF BLOCK LENGTH ON PROPERTIES OF MULTIBLOCK POLYSULFONE-POLY(DIALLYLPIPERIDINIUM HYDROXIDE) COPOLYMERS

4.1 Introduction

Research in the area of anion exchange membranes (AEMs) has gained interest due to the development of membrane materials with improved base stability.\textsuperscript{1-3} The advances made in cation stability are enabling new materials to be investigated as alternatives to commercialized proton exchange membranes. AEMs for use in electrochemical devices have significant advantages over proton exchange membranes because they have potential to utilize non-noble metal catalysts and oxidation-reduction reaction kinetics are faster at high pH conditions.\textsuperscript{4-5} However, device performance is strongly dependent on the ionic conductivity of the membrane material.

Development of microphase separated AEMs in which hydrophilic hydroxide conductive domains form within a hydrophobic and mechanically robust matrix has been shown to be a successful strategy for improving AEM performance.\textsuperscript{6} Research conducted on phase-separated materials for AEMs has produced hydrophobic-hydrophilic copolymers of different architectures including block,\textsuperscript{7-20} graft\textsuperscript{21-29}, and comb.\textsuperscript{30} The resulting AEMs display nanoscale morphological features ranging from spheres to lamellae. It has been shown that AEMs forming hydrophilic conductive domains have higher conductivity compared to random copolymers of similar structure and composition.\textsuperscript{31} Furthermore, microphase-separated AEMs have enhanced water management characteristics, resulting in improved swelling behavior.\textsuperscript{32-33}
Multiblock is another type of copolymer architecture that has been shown to produce phase-separated membranes.\textsuperscript{34-48} One advantage of designing multiblock hydrophilic-hydrophobic copolymers is that high molecular weight copolymers can be prepared from a broad range of molecular weights in the component materials. Manipulation of the multiblock composition and the molecular weight of the component segments can tune the microphase separation.\textsuperscript{6} Research conducted on multiblock polysulfone (PSf) materials has produced copolymers from a variety of bisphenol monomers.\textsuperscript{49-53} PSf multiblock copolymers have been produced with a large range in ion exchange capacities (IEC)s and composition of hydrophobic-hydrophilic segments. However, there are only a few investigations of the structure-property relationships relating to the component molecular weight at a constant IEC and the multiblock AEM performance.\textsuperscript{49-50, 54-55}

We have previously demonstrated that poly(diallylpiperidinium hydroxide) (PDApipOH) is an exceptionally base stable cationic polymer and that multiblock copolymers can be produced with PSf (PSf-PDApipOH).\textsuperscript{3} The counterion of the polydiallylpiperidinium (PDApip) block can be exchanged between hexafluorophosphate (PDApipPF\textsubscript{6}), chloride (PDApipCl) and hydroxide (PDApipOH) and the PSf-PDApipOH copolymers display properties of high ionic conductivity along with relatively low water uptake in addition to their base stability.

In the current work, we have designed a series of multiblock PSf-PDApipOH copolymers (Figure 4.1) in which the molecular weight of the hydrophilic conducting PDApipOH segments was varied in order to assess the impact on AEM performance. Employing the previously established synthetic methods,\textsuperscript{3} \(\alpha,\omega\)-4-fluorophenyl sulfone terminated PDApipPF\textsubscript{6} oligomers were generated and subsequently copolymerized with PSf monomers to generate PSf-PDApipPF\textsubscript{6} multiblock copolymers. Ion exchange of the PF\textsubscript{6} counterion was then performed to produce hydrophilic PSf-PDApipOH. The hydrophilic
PDApipOH segments were selected to serve as the conductive phase of the AEM materials owing to their previously established conductivity, chemical and thermal stability, and the regularity of their compact repeat unit structure. The synthetic design generated different samples of PSf-PDApipOH multiblock copolymers that were each similar in composition and IEC but varied in the molecular weight of the telechelic PDApip oligomers. Membranes were evaluated for the effect of PDApip block molecular weight on their morphological characteristics and water uptake and hydroxide conductivity.

![Figure 4.1 PSf-PDApipOH multiblock copolymer](image)

**Figure 4.1 PSf-PDApipOH multiblock copolymer**

### 4.2 Experimental

#### 4.2.1 Materials

Allyl chloride (98%) was purchased from Sigma-Aldrich and was distilled under nitrogen prior to use. *N,N*-dimethylacetamide (DMAc) (99.9%, HPLC grade) was purchased from Sigma-Aldrich and distilled from phosphorous pentoxide. Bisphenol A (97%) and bis(4-fluorophenyl) sulfone (99%) were purchased from Sigma-Aldrich and crystallized twice from toluene. Piperidine (99%), allyl bromide (99%), 4-fluorothiophenol (98%), and potassium peroxymonosulfate (Oxone) were obtained from Sigma-Aldrich and were used as received. Acetonitrile-d₃, DMSO-d₆, and deuterium oxide were purchased from Sigma-Aldrich. All other chemicals and solvents were used as received from commercial sources.
4.2.2 General Synthesis

Synthesis of the photoiniferter bis(4-fluorophenyl) disulfide (BFPDS), monomer \(N,N\)-diallylpiperidinium chloride, and \(\alpha,\omega\)-4-fluorophenyl sulfone terminated PDApipPF\(_6\) oligomers were prepared as previously reported.\(^3\) The variation in molecular weight of the \(\alpha,\omega\)-4-fluorophenyl sulfone terminated PDApipPF\(_6\) oligomers was accomplished by changing the ratio of BFPDS to \(N,N\)-diallylpiperidinium chloride as follows: A 25 mL stock solution of 2.5 M \(N,N\)-diallylpiperidinium chloride in water:methanol (3:1) was prepared in a volumetric flask. 10 mL test tubes containing a magnetic stir bar were charged with 40.7 mg (0.16 mmol), 50.8 mg (0.20 mmol) or 68.7 mg (0.27 mmol) BFPDS photoiniferter and 8 mL (20 mmol) of the stock \(N,N\)-diallylpiperidinium chloride solution. The ratio of BFPDS to \(N,N\)-diallylpiperidinium chloride for each polymerization was calculated to be 1:75, 1:100, and 1:125. The test tubes were sealed with a rubber septum, cooled in an ice bath and purged with \(N_2\) gas for 20 min. Once purged, the test tubes were placed into a 60 °C oil bath, stirred for 20 min and then exposed to constant UV light (254 nm) while stirring for 24 hours. The 4-fluorophenyl sulfide terminated PDApipCl oligomers were isolated by precipitation into acetone, re-dissolving the obtained solid mass in methanol (~10 % wt./vol.) and precipitating again into acetone. The 4-fluorophenyl sulfide terminated PDApipCl oligomers were collected by vacuum filtration and dried overnight at 80 °C under vacuum. The end group oxidation to 4-fluorophenyl sulfone, and ion exchange to hexafluorophosphate were completed as previously described.\(^3\)

4.2.2.1 Synthesis of multiblock PSf-PDApipPF\(_6\) copolymers

The synthesis of PSf-PDApipPF\(_6\) multiblock copolymers was designed to achieve maximum molecular weight while targeting an IEC of ~ 2.0 in the hydroxide form. To generate the desired multiblock copolymer composition from preformed PDApipPF\(_6\)
oligomers, the weight percent of PSf required was calculated in terms of equivalents of bis(4-fluorophenyl) sulfone with respect to the degree of polymerization of the PDApipPF₆ oligomers. The amount of bisphenol A was calculated to give a 1:1 feed ratio of 4-fluorophenyl and phenoxide reactive species. A representative procedure (PSf-PDApip1) is as follows: a 25 mL 3-neck round bottom flask fitted with an overhead stir motor, Dean-Stark trap prefilled with toluene, condenser, and a N₂ inlet was charged with bisphenol A (0.575 g, 2.52 mmol) and potassium carbonate (0.418 g, 3.02 mmol). The solids were dissolved in DMAc (10.8 mL) with toluene (3 mL) added to azeotropically remove water. The reaction mixture, under a N₂ atmosphere, was then heated in a 150 °C oil bath for 3 hours and then cooled to room temperature. 4-fluorophenyl sulfone terminated PDApip1 (1.50 g, 0.234 mmol) and bis(4-fluorophenyl) sulfone (0.624 g, 2.45 mmol), were then added to the reaction mixture. The solution was heated in a 160 °C oil bath overnight, after which time the solution viscosity increased significantly. The viscous solution was diluted with DMAc (10 mL), cooled to room temperature and precipitated into 200 mL of methanol. The off-white fibers were collected by filtration and boiled in water for 30 minutes to remove residual salts. The polymer fibers were then collected by filtration, and dried in a vacuum oven at 80 °C to a constant mass (2.35g, 93 % yield).

4.2.2.2 Membrane fabrication

PSf-PDApipPF₆ membranes were generated by solution casting the multiblock copolymers in the hexafluorophosphate form. Multiblock PSf-PDApipPF₆ copolymers were dissolved in DMAc to generate a 15 % w/v solution and were deposited onto a glass substrate. The glass was then heated to 75 °C and allowed to dry overnight. The PSf-PDApipPF₆ membrane was removed from the glass substrate by submersion in water. The final PSf-PDApipPF₆ membrane was then dried under vacuum overnight.
4.2.2.3 Ion exchange to hydroxide

The PSf-PDApipPF$_6$ membranes were first exchanged to the bromide form and then to hydroxide. Ion exchange from hexafluorophosphate to bromide was accomplished by submerging the PSf-PDApipPF$_6$ membranes in a saturated aqueous solution of ammonium bromide and soaking at room temperature for 72 hours. Following ion exchange to bromide, the polysulfone-poly(diallylpiperidinium bromide) (PSf-PDApipBr) membranes were then washed twice with deionized water to remove excess ammonium bromide. Soaking the PSf-PDApipBr multiblock copolymer membranes in 1 M KOH for 48 hours completed ion exchange to hydroxide. The final PSf-PDApipOH membranes were then washed with N$_2$ purged 18 MΩ water until the washings were neutral pH. Careful consideration for CO$_2$ contamination was given, as such the membranes were characterized immediately.

4.2.3 Characterization

$^1$H NMR spectroscopy was performed using a JEOL ECA-500 spectrometer. Chemical shift values ($\delta$) were referenced from residual solvent signals associated with acetonitrile-d$_4$ or DMSO-d$_6$.

Tapping mode atomic force microscopy (TM-AFM) was used to elucidate PSf-PDApipBr membrane surface morphology. The phase images were obtained with an Oxford Instruments AFM 3D utilizing a 42 N ⋅ m$^{-1}$ Pointprobe AFM tip from Nanoworld. PSf-PDApipBr membranes were cut into 1 cm$^2$ membranes and adhered to glass microscope slides with double sided tape. The membranes were then heated to 60 °C at 95 % RH for 1 hour and subsequently dried under vacuum at room temperature for 24 hours. The images were collected with a driving amplitude of 1 V and the amplitude set point ratio of 0.50 under ambient temperature and humidity.
Synchrotron small-angle X-ray scattering experiments were performed at the Advanced Photon Source, Argonne National Laboratories. Using a custom built environmental chamber and previously established measurement techniques, scattering experiments were conducted at 60 °C at both 0 % and 95 % relative humidity. The PSf-PDApipBr membranes were measured in the bromide form and 2D scattering patterns were obtained. The azimuthally integrated 2D scattering experiments were graphically analyzed by plotting the intensity as a function of the scattering vector magnitude, q, where

\[
q \text{ [Å}^{-1}\text{]} = \frac{4\pi \sin (\theta)}{\lambda}
\]

\( \lambda \) is 1.03 Å and \( \theta \) is the scattering angle. The Bragg domain spacing, d, was calculated from the equation \( d = \frac{2\pi}{q} \).

The ion exchange capacity of the PSf-PDApipOH membranes was determined from the back-titration method. PSf-PDApipBr membranes were ion exchanged from bromide to hydroxide in 1 M KOH. The PSf-PDApipOH membranes were then washed with N\(_2\) purged 18 M\(\Omega\) water until the washings were at neutral pH. The PSf-PDApipOH membranes were then neutralized in 20 mL of standardized HCl (0.02501 M) for 48 hours and subsequently vacuum dried at 80 °C for 48 hours. The dry mass of the membranes was approximately 0.04 g in the chloride form. The IEC for each membrane was determined, in triplicate, by titrating 3 mL samples of HCl solution with standardized NaOH (0.004690 M) to determine the amount of unreacted HCl. The IEC was calculated from the following equation:

\[
IEC \ [\text{mmol} \cdot \text{g}^{-1}] = \frac{HCl_i - HCl_f}{Mass_d}
\]

where HCl\(_i\) is the millimoles (mmol) of HCl per 3 mL sample, HCl\(_f\) is the determined mmol of unreacted HCl after 48 hours and Mass\(_d\) is the dry mass (g) of the membrane in the chloride form.
The percent water uptake (WU%) of each PSf-PDpipBr membrane was determined by dynamic vapor sorption (DVS) with a Surface Measurement Systems DVS Advantage at 60 °C and 95 % relative humidity (RH). The membranes were converted from the hexafluorophosphate form to the bromide form and dried under vacuum at 80 °C for 48 hour. The membranes were then placed in the DVS environmental chamber and were cycled between dry and hydrated conditions at 60 °C 3 times. The soaking time for each step in the measurement was 120 minutes. Following the measurements, the dry masses and the hydrated masses were averaged and water uptake percent (WU) was calculated from the following equation:

\[ WU \% = \frac{Mass_h - Mass_d}{Mass_d} \times 100 \]

where Mass\(_h\) and Mass\(_d\) are the hydrated and dry masses for the membrane.

The hydroxide conductivity for the PSf-PDApipOH membranes was determined by electrochemical impedance spectroscopy (EIS) using a Biologic VMP3 potentiostat. In-plane conductivity measurements were made using a Teflon 4-point probe cell with platinum electrodes in a TestEquity environmental chamber set to 60 °C and 95 % relative humidity. Membranes were prepared by cutting approximately 2 mm wide strips and ion exchanging from bromide to hydroxide. The PSf-PDApipOH membranes were then washed in N\(_2\) purged 18 MΩ water until the washings were neutral pH. The membranes were then quickly loaded into the test cell and placed in the environmental chamber. EIS measurements were made in the frequency range of 100 Hz to 300 kHz. A minimum of 15 loops were obtained for each membrane to allow for equilibration. Nyquist and Bode plots of the obtained data were analyzed to obtain the low frequency high resistance intercept which was taken as the membrane resistance. The hydroxide conductivity was then determined from the following calculation:
\[ \sigma \, [S \cdot cm^{-1}] = \frac{d}{W \times T \times R} \]

where \( d \) (cm) is the distance between the reference electrodes, \( W \) (cm) and \( T \) (cm) are the width and thickness of the membrane and \( R \) is the measured resistance (\( \Omega \)). The membrane dimensions were determined in the hydrated state.

4.3 Results and Discussion

The objective of this research was to investigate the influence of hydrophilic segments, composed of aliphatic spirocyclic repeat units of various molecular weights, on the performance of anion exchange membranes given similar composition. Reports have indicated that the hydroxide conductivity of AEMs is strongly affected by the phase separation and morphology.\(^{59-60}\) We hypothesized that the hydroxide conductivity of multiblock PSf-PDApipOH copolymers would vary depending on the molecular weight of the hydrophilic PDApipOH segments. In this investigation, we designed and synthesized a series of PSf-PDApipOH multiblock copolymer membranes of similar composition and IEC in which the molecular weight of the conductive PDApipOH segments are varied.

4.3.1 Synthesis of 4-fluorophenyl sulfone terminated PDApipPF\(_6\) oligomers

Disulfides have been employed in radical polymerizations to control the molecular weight of the resulting polymer by degradative chain transfer processes (Scheme 4.1).\(^{61-63}\) In the present work, our design was to produce a series of \( \alpha,\omega \)-4-fluorophenyl sulfone PDApipPF\(_6\) oligomers of varying molecular weight to be later incorporated in a polysulfone synthesis. Polymerization reactions were completed in a 3:1 methanol/water solvent system and used monomer:initiator ratios of 75:1, 100:1 and 125:1. Following polymerization, the \( \alpha,\omega \)-4-fluorophenyl sulfide oligomers were oxidized with Oxone to the 4-fluorophenyl sulfone derivatives and ion exchanged to the PF\(_6\) form. In previous work, 4-fluorophenyl
sulfone terminated PDApipPF₆ oligomers were produced from a single monomer:initiator ratio of 100:1 and the resultant polymers were confirmed to be di-functional by their ability to produce high molecular weight multiblock PSf-PDApipPF₆ copolymers. By extension, using the same polymerization conditions with different monomer:initiator feed ratios different α,ω-functionalized oligomers should be produced.

Scheme 4.1 UV initiated cycopolymerization of N,N-diallylpiperdinium chloride in the presence of BFPDS disulfide photoiniferter
$^1$H NMR spectroscopy was used to determine the polymer structure and evaluate the number average molecular weight ($M_n$) of the 4-fluorophenyl sulfone terminated PDApipPF$_6$ oligomers. The $^1$H NMR spectrum (Figure 4.2) confirmed the formation of 5-member rings, resulting in spirocyclic repeat units, and the presence of 4-fluorophenyl sulfone end groups. The polymer structure and peak assignment are supported by existing literature investigating the cyclopolymerization of diallylammonium monomers.$^{3, 64-65}$ Advantageous to determining molecular weight, the 4-fluorophenyl sulfone end groups have spectroscopically unique peaks in the $^1$H NMR spectra associated with the aromatic ring. The molecular weight of the 4-fluorophenyl sulfone terminated PDApipPF$_6$ oligomers was determined by calculating the degree of polymerization (DP). The DP was obtained by comparing integrals associated with the 4-fluorophenyl sulfone end groups (peak A, 4H) and the PDApipPF$_6$ repeat units (downfield E, 2H, at 3.8 ppm). The obtained molecular weights for the 4-fluorophenyl sulfone terminated PDApipPF$_6$ oligomers are reported in Table 4.1. Additionally, the concentration of 4-fluorophenyl sulfone end groups per known mass of polymer was determined from the $^1$H NMR spectra by comparing the integral values of the 4-fluorophenyl sulfone end groups to the solvent peak produced from a known mass of methylene bromide. Methylene bromide was selected as a standard owing to it spectroscopically unique signal. Determination of the concentration of 4-fluorophenyl sulfone end groups is important to obtaining high molecular weight copolymers.

PDApipPF$_6$ oligomers with increasing molecular weights were produced by the UV initiated cyclopolymerization of $N,N$-diallylpiperidinium chloride by increasing the monomer to initiator ratio. The molecular weights (Table 4.1) were determined to be 6,400, 13,300 and 17,200 g·mol$^{-1}$ for PDApipPF$_6$1, PDApipPF$_6$2, and PDApipPF$_6$3, respectively. For the given set of polymerization conditions, increasing the monomer to initiator ratio resulted in a
decrease of initiation and chain transfer reactions leading to a higher degree of polymerization and molecular weight.

![Figure 4.2 1H NMR spectrum of PDApipPF6](image)

Table 4.1 Molecular weight characterization of PDApip oligomers

<table>
<thead>
<tr>
<th>Sample</th>
<th>[BFPDS]: [DApip]</th>
<th>DP^a</th>
<th>M_n [g·mol⁻¹]^a</th>
<th>Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDApipPF₆₁</td>
<td>1:75</td>
<td>35</td>
<td>6,400</td>
<td>22</td>
</tr>
<tr>
<td>PDApipPF₆₂</td>
<td>1:100</td>
<td>73</td>
<td>13,300</td>
<td>37</td>
</tr>
<tr>
<td>PDApipPF₆₃</td>
<td>1:125</td>
<td>94</td>
<td>17,200</td>
<td>27</td>
</tr>
</tbody>
</table>

^a) Determined from 1H NMR spectra and calculated in the hydroxide form for continuity with later characterization.

4.3.2 Summary of multiblock PSf-PDApipPF₆ copolymers synthesized

The multiblock copolymers investigated in this study were produced by condensation of preformed 4-fluorophenyl sulfone PDApipPF₆ oligomers with polysulfone monomers and are listed in Table 4.2. The objective of the polymerizations was to produce a series of PSf-
PDApipPF₆ multiblock copolymers with consistent weight fraction of PDApip (~40 wt.%) from the different molecular weight PDApipPF₆ starting materials. The copolymerizations produced high molecular weight materials in yields greater than 90%. The molar and weight percent of PDApipPF₆ incorporated into the PSf-PDApipPF₆ copolymers was calculated from the ¹H NMR spectra. Compositions of the PSf-PDApipPF₆ multiblock copolymers were determined by comparing peak integrals associated with the PSf repeat unit (B, 4H) and the PDApipPF₆ repeat unit (downfield E, 2H at 3.8 ppm) (Figure 4.3). It was assumed that the contribution of the PDApipPF₆ end groups to the B peak associated with the PSf repeat units was negligible.

Table 4.2 Summary of PSf-PDApipOH multiblock copolymer compositions

<table>
<thead>
<tr>
<th>Sample</th>
<th>PDApipOH Mₐ [g·mol⁻¹]</th>
<th>PDApipOHᵃ mol.%</th>
<th>PDApipOHᵇ wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf-PDApip1</td>
<td>6,400</td>
<td>58.6</td>
<td>36.9</td>
</tr>
<tr>
<td>PSf-PDApip2</td>
<td>13,300</td>
<td>61.0</td>
<td>39.3</td>
</tr>
<tr>
<td>PSf-PDApip3</td>
<td>17,200</td>
<td>59.6</td>
<td>37.9</td>
</tr>
</tbody>
</table>

a) Determined from the ¹H NMR spectrum (based on the hydroxide form). b) Calculated from the mole fraction.

Figure 4.3 ¹H NMR spectrum of PSf-PDApip3
4.3.3 Membrane formation and ion exchange to hydroxide

PSf-PDApipPF₆ multiblock copolymers were fabricated into AEMs by solution processing. The multiblock copolymers were dissolved in DMAc, drop cast onto glass slides and dried. The resulting membranes were found to be colorless and transparent. The PSf-PDApipPF₆ multiblock copolymer membranes were ion exchanged to hydroxide following an ion exchange first to bromide. Ion exchange from PF₆ to chloride by heating PSf-PDApipPF₆ membranes in a saturated solution of ammonium chloride at 100 °C was reported in earlier work. In this study, ion exchange to bromide was found to be effective under milder conditions and was completed by soaking the membranes in saturated ammonium bromide at room temperature over 72 hours followed by repeated washings to remove the excess salt. Ion exchange to hydroxide was accomplished by soaking the PSF-PDApipBr membranes in 1 M KOH and rinsing the membranes with N₂ purged 18 MΩ water.

4.3.4 Physical properties: IEC and water uptake

Back-titration of hydroxide in the PSf-PDApipOH multiblock copolymer membranes was completed in order to determine the complete removal of PF₆ and to characterize the IEC of each membrane. Removal of PF₆ from the PSf-PDApipPF₆ membranes is important for the accurate characterization of the water uptake and hydroxide conductivity due to the increased hydrophobic character and bulk of the PF₆ counterion. The membranes were neutralized in a standardized HCl solution. Following neutralization, the remaining acid solutions were titrated five times to obtain the IEC for the membranes (Table 4.3). The IEC values determined by back-titration of hydroxide are shown to be in close agreement with the IEC values estimated from the composition for the PSf-PDApipOH multiblock copolymers determined by NMR spectroscopy.
Table 4.3 Characterization of PSf-PDApip multiblock copolymer membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC $^a$ [meq·g$^{-1}$]</th>
<th>IEC [HO]$^b$ [meq·g$^{-1}$]</th>
<th>Water Uptake$^c$ [wt.%]</th>
<th>$\sigma^c$ [mS·cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf-PDApip1</td>
<td>2.02</td>
<td>1.86 ± 0.04</td>
<td>17.0 ± 0.010</td>
<td>37.5 ± 0.3</td>
</tr>
<tr>
<td>PSf-PDApip2</td>
<td>2.14</td>
<td>1.99 ± 0.07</td>
<td>21.8 ± 0.015</td>
<td>47.4 ± 0.6</td>
</tr>
<tr>
<td>PSf-PDApip3</td>
<td>2.07</td>
<td>1.71 ± 0.07</td>
<td>19.4 ± 0.012</td>
<td>62.9 ± 1.9</td>
</tr>
</tbody>
</table>

a) Determined from the $^1$H NMR spectrum composition and calculated in the hydroxide form. b) Measured by back-titration of hydroxide. c) Water uptake by DVS in the bromide form measured at 60 °C and 95 % RH.

d) hydroxide conductivity measured at 60 °C and 95 % RH.

Water uptake is an important factor that affects ionic conductivity in AEMs. Evaluation of the water uptake using humidified gas rather than liquid water is important for a more accurate assessment of membrane performance. Water absorbed in AEMs is known to dissociate the cationic groups attached to the membrane material and facilitate hydroxide transport. Membranes that exhibit higher water uptake tend to have higher hydroxide conductivity compared to membranes with lower water uptake. However, excessive water uptake can also have the deleterious effects of diluting the cations in the membrane material and decreasing the mechanical strength. The water uptake for the PSf-PDApip membranes was evaluated at 60 °C and 95 % relative humidity in the bromide form by dynamic vapor sorption (DVS) (Table 4.3). The PSf-PDApipBr multiblock copolymer membranes showed low water uptake values of 17.0, 21.8, and 19.4 wt.% for PSf-PDApip1, PSf-PDApip2 and PSf-PDApip3 membranes, respectively. Evaluation of the water uptake was completed in the bromide form in order to eliminate the effects of carbonate and bicarbonate formation during the measurements. It is expected that the water uptake for the PSf-PDApipOH membranes is not significantly different. Minimal variability was observed in the water uptake measurements due to the membranes having similar IECs (from similar compositions).

However, the slight variation in the composition of the three multiblock copolymer samples did result in the highest water uptake observed for the PSf-PDApip2 membrane, which was
the membrane with the highest IEC (IEC = 1.99 meq g\(^{-1}\)) The modest water uptake values for the PSf-PDApipBr membranes were considered to be a result of the copolymer phase separation and membrane morphology. The low water uptake values determined by DVS for the hydrophobic-hydrophilic PSf-PDApipBr copolymer membranes are similar to the low water uptake values of other hydrophobic-hydrophilic block copolymer membranes produced in our group.\(^{67}\)

4.3.5 Hydroxide conductivity

For alkaline fuel cell application, the hydroxide conductivity is of particular interest. It has been previously reported that AEMs derived from diblock copolymers of similar compositions with varying hydrophilic block lengths (prepared by controlled-living radical polymerization techniques) show an increase in hydroxide conductivity with increasing hydrophilic block length. This finding was attributed to the membrane morphology.\(^{68-69}\) The PSf-PDApipOH multiblock copolymer membranes were evaluated for their hydroxide conductivity at 60 °C and 95 % RH. The results of the in-plane EIS experiments (Figure 4.4) indicate that the hydroxide conductivity was strongly dependent on the molecular weight of the PDApipOH hydrophilic conductive segments. While there was some variation in the IEC from the slight variation in composition among the samples and the variation in IEC did have an effect on the water uptake (Table 4.3), the IEC and concomitant water uptake had a minimal impact on the conductivity compared to the molecular weight of the PDApipOH segments. Illustrating this effect, the PSf-PDApip1 membrane (IEC = 1.86), which was synthesized from PDApipPF\(_6\) (M\(_n\) = 6,400 g·mol\(^{-1}\)) had a hydroxide conductivity of 37.5 mS·cm\(^{-1}\). In contrast, the PSf-PDApip3 membrane (IEC = 1.76), which was synthesized from PDApipPF\(_6\)\(_3\) (M\(_n\) = 17,200 g·mol\(^{-1}\)) had a hydroxide conductivity of 62.9 mS·cm\(^{-1}\). These results indicate that the nanoscale, conductive domains in the PSf-PDApip membranes are largely responsible for the membrane performance. With respect to multiblock PSf
copolymer AEMs, there are reports in which the composition of materials has been investigated and by extension, membranes with similar composition but different segment molecular weights.\textsuperscript{49-50, 54-55} Hu et al. produced a series of benzyltrimethyl ammonium functionalized membranes (IEC ~ 1.3) wherein the hydroxide conductivity at 60 °C increased from 15.4 to 29.4 mS cm\textsuperscript{-1}.\textsuperscript{54} However, the phase separation of the membranes was not investigated. In contrast, there are several studies of multiblock PSf copolymer AEMs wherein no discernable trend in the relationship between segment molecular weight and hydroxide conductivity was observed.\textsuperscript{49-50, 55}

![Figure 4.4 Plot of hydroxide conductivity vs. PDApipOH segment molecular weight.](image)

4.3.6 Membrane phase separation

Developing AEMs with hydrophobic-hydrophilic phase separated morphology is important for the formation of well-connected hydroxide conducting domains. SAXS characterization of anion exchange membranes has been employed to determine the Bragg spacing between formed ionic clusters and the phase separated morphology of the bulk material.\textsuperscript{35, 51} The multiblock copolymer PSf-PDApipBr membranes were investigated by SAXS in order to characterize the anticipated phase separation. The SAXS profiles for the PSf-PDApipBr membranes were obtained at 60 °C under dry and 95 % RH conditions.
Shown in Figure 4.5A, the PSf-PDApip2 and PSf-PDApip3 membranes exhibited strong scattering peaks corresponding to domain spacing of 24 and 25 nm, respectively. The PSf-PDApip1 membrane showed a weak scattering peak corresponding to a domain spacing of 18 nm, which was expected due to presumed lower molecular weight PSf segments occurring between the PDApipBr segments. The scattering peaks exhibited by the PSf-PDApipBr membranes was attributed to the aggregation of PDApipBr segments that result in hydrophilic domains. When the RH was increased to 95% the scattering intensity decreased for all of the PSf-PDApipBr membranes (Figure 4.5B). The decrease in the intensity of the scattering peaks with increased humidity indicated that the water uptake disrupted the PDApipBr domains. However, the domain spacing did not change appreciably with the increase of RH, which indicated that the swelling was minimal and that the membranes exhibit dimensional stability. Additionally, the absence of secondary scattering peaks in the SAXS profiles indicates that the PSf-PDApipBr membranes did not form well-ordered morphological features.

![Figure 4.5 SAXS profile for PSf-PDApipBr membranes at 60 °C and 0 % RH (A) and at 60 °C and 95 % RH (B).](image)

Although phase separation and the corresponding domain spacing for the PSf-PDApipBr membranes was indicated by SAXS, further investigation of the morphology is required to provide a more detailed characterization. TM-AFM was performed on the PSf-
PDApipBr membranes to elucidate the surface morphology. Phase images were generated from membranes treated at 60 °C and 95% RH prior to measurement such that membrane phase separation would correlate closely to the SAXS and hydroxide conductivity measurements. The phase images produced (Figure 4.6) clearly indicate hydrophobic-hydrophilic phase separation and the absence of well-ordered structures. The phase images also indicate that with increasing molecular weight in the PDApipBr segments connectivity in the phase separation is improved and is most obvious between PSf-PDApip1 (Figure 4.6A) and PSf-PDApip3 (Figure 4.6C). This result is due to increase in molecular weight of the PDApipBr segments and supports the position and intensity of the SAXS scattering peaks. The improved connectivity of hydrophilic conductive pathways observed in the AFM images support the increase of the hydroxide conductivity with increasing PDApipOH segment molecular weight.

![AFM phase images for PSf-PDApip1 (A), PSf-PDApip2 (B), and PSf-PDApip3 (C) taken under ambient temperature and humidity.](image)

**Figure 4.6** AFM phase images for PSf-PDApip1 (A), PSf-PDApip2 (B), and PSf-PDApip3 (C) taken under ambient temperature and humidity.

### 4.4 Conclusions

This study investigates the structure property relationships between conductive segment molecular weight, morphology and AEM performance for multiblock PSf-PDApipOH copolymer membranes. This work demonstrates the use of photoinitiated
degradative chain transfer cyclopolymerization to produce 4-fluorophenyl sulfone terminated PDApipPF$_6$ oligomers of several different molecular weights. Furthermore, it is shown that PSf-PDApipPF$_6$ multiblock copolymer membranes of similar composition and IEC are readily produced from polycondensation reactions in the presence of PSf monomers. The resulting multiblock PSf-PDApipPF$_6$ copolymers were fabricated into membranes and after ion exchange to the bromide form, exhibited low water uptake under conditions of 95% RH. SAXS and TM-AFM were employed to deduce the morphology of the copolymer membranes, and it is demonstrated that well-connected conductive domains are present. Furthermore, the hydroxide conductivity increased with increasing PDApipOH segment molecular weight, demonstrating the multiblock copolymer structure relationship with AEM performance. The promising results encourage further investigation into the structure property relationships of multiblock AEM materials and that block molecular weight of hydrophilic segments can have a significant impact on the properties.

4.5 Acknowledgments

This material is based upon work supported by the U.S. Army Research Laboratory and the U.S. Army Research Office under MURI contract/grant number W11NR-10-1-0520. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE), Office of Science, User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

4.6 References


CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

Anion exchange membranes developed from PSf materials have demonstrated utility as AEMs with potential for application in alkaline fuel cells. The application of phase separation design and incorporation of cationic functionalities with improved base stability have led to the next generation of membrane materials. As such, alkaline fuel cells employing solid polymer electrolyte separators are promising for providing clean energy conversion. However, the challenge of designing AEM materials which are highly conductive, mechanically sufficient and base stable in both the polymer backbone and cation functionality remains a challenge. Therefore, it is imperative that research continue and draw from recent discoveries so that AEMs and alkaline fuel cells reach commercial maturation.

PSf multiblock copolymers composed of hydrophobic and hydrophilic segments have created positive impacts on AEM performance. Multiblock PSf copolymer materials were readily produced from step-growth polymerization techniques with either oligomers of complementary functionality or a difunctional oligomer with PSf monomers.

Polysulfone-polyformal (PSf-PF) multiblock copolymers provided an interesting scaffold for facile and selective functionalization to investigate densely functionalized and phase separated AEMs. The objective of the work presented in Chapter 2 was to investigate the influence of densely functionalized hydrophilic segments on AEM performance. The facile preparation of phenoxide terminated PSf oligomers of predictable molecular weight, which produced high molecular weight TMBPA PF multiblock copolymers, indicates the utility of PSf in multiblock copolymer preparation. Furthermore, the copolymerization of phenoxide terminated PSf in a PF synthesis produced multiblock copolymers without
randomization of the PSf segments indicating that the PSf backbone was highly stable to the copolymerization conditions. The excellent mechanical properties of the high molecular weight quaternary ammonium functionalized PSf-QAPF copolymer membranes were the result of the PSf segments providing a robust matrix for the QAPF hydrophilic domains. Localized high concentration of quaternary ammonium cations and selective absorption of water in the QAPF segments led to improved hydroxide conductivity and swelling behavior due to the phase separation of the ion conductive domains produced in the PSf-QAPF membranes. The benzyltrimethylammonium functionalized multiblock PSf-QAPF copolymer membranes had a modest affinity for water, which increased with the IEC and resulted in hydroxide conductivity up to 78 mS cm\(^{-1}\) at 60 °C. Ultimately, incorporation of densely functionalized segments composed of compact repeat units into multiblock copolymer AEMs demonstrated improved hydroxide conductivity and low water uptake when compared to several materials with similar design. However, densely functionalized multiblock copolymers with higher hydroxide conductivity and significantly higher water uptake values exist. While it cannot be conclusively stated that incorporating compact densely functionalized segments within multiblock copolymer AEMs was an absolute improvement over all such membrane materials, it can be concluded that the design produced phase separated membranes with improved balance of properties.

In order to develop a more base stable AEM, multiblock PSf copolymers were designed to incorporate segments of poly(diallyl)piperidinium hydroxide (PDAppOH), which is an aliphatic polymer with spirocyclic ammonium repeat units. UV initiation of the free radical cyclopolymerization of \(N,N\)-diallylpiperidinium chloride with a photoiniferter and absent of additional radical sources proved to be a facile method for the preparation of difunctional poly(diallylpiperidinium chloride) oligomers. The development of a radical polymerization method with quantitative control of end groups leads to the possibility of
many different radically derived polymers that can be subsequently copolymerized by step-growth techniques. The polymerization method resulted in high molecular weight PSf-PDApipOH multiblock copolymers produced from 4-fluorophenyl sulfone terminated PDApipPF₆ oligomers and the materials produced are the first demonstration of block copolymer membranes from diallylammonium polymers. The spirocyclic quaternary ammonium cations in the PDApipOH oligomers were found to be exceptionally base stable, remaining unchanged after 1000 hours of testing. In addition to the base stability of the PDApipOH, the PSf-PDApipOH membrane was thermally stable up to 360 °C in the hydroxide form due to the combined thermal stability of the component materials. The design of phase separated copolymer membranes composed of PSf and PDApipOH led to enhanced AEM performance. Highly conductive PSf-PDApipOH membranes reached 102 mS·cm⁻¹ at 80 °C with a hydroxide conductivity activation energy as low as 8.8 kJ·mol⁻¹. The multiblock copolymer AEMs containing segments of the spirocyclic ammonium PDApipOH represent a considerable advance in AEM technology. Significant improvement of the base stability at high temperatures of AEMs containing PDApipOH which also demonstrate high hydroxide conductivity indicate the potential impact of such materials in the development of the next generation of AEMs.

In order to improve understanding of the structure property relationships of the PSf-PDApipOH multiblock copolymer membranes as they relate to AEM performance, specifically the impact of the hydrophilic segment molecular weight, a series of multiblock copolymers were produced with similar IEC, composition and increasing PDApipOH molecular weight. Control of the domain spacing and degree of phase separation in the nanoscale domains in phase separated AEMs was indicated in the results described in Chapter 4. Higher molecular weight hydrophilic segments were shown to enhance phase
separation and increase the domain spacing between ion conductive domains. Furthermore, hydroxide conductivity was improved with minimal change in the water uptake for membranes with higher molecular weight PDApipOH segments which, reached 63 mS·cm\(^{-1}\) at 60 °C and 95 % relative humidity. Ultimately, it was demonstrated that the molecular weight of the hydrophilic PDApipOH segments in multiblock AEMs impacted the performance. Multiblock AEM hydroxide conductivity was improved with increased PDApipOH molecular weight which was concomitant with improved phase separation and increase domain spacing and indicates the importance and control of phase separation in the design and fabrication of AEMs.

5.2 Future work

Two different multiblock PSf copolymer materials have been investigated in this thesis and have contributed to the knowledge base for the continuing development of AEMs for alkaline fuel cells. The discoveries made notwithstanding, further investigations into the design aspects of AEMs are required to improve understanding so that the potential of AEMs is realized.

In Chapter 2 the densely functionalized QAPF segments positively impacted phase separation, water uptake and hydroxide conductivity of the multiblock copolymer membranes. However, the degradation observed in the backbone and in the quaternary ammonium cations will result in decreased performance. Studies have indicated that using aliphatic spacer chains for tethering cationic functional groups to polymer backbones has improved the base stability.\(^1\) Modification of the PSf-PF multiblock copolymer to incorporate spacer chains can improve the stability of the cationic functional groups (Scheme 5.1). Furthermore, moving the electron deficient cations further from the backbone and the formal linkages will make the methylene carbon of the formal linkages less electropositive and less
prone to nucleophilic attack by hydroxide and result in a more base stable material while maintaining a density of functionality.

Poly(phenylene oxide) (PPO) is another thermoplastic which exhibits excellent mechanical properties and film forming abilities. PPO has also been shown to be more chemically stable in high temperature, high pH conditions compared to PSf. Existing literature has indicated that PPO is a promising material for use in AEMs. In this thesis, we have developed a method for the preparation of 4-fluorophenyl sulfone terminated poly(diallylpiperidinium hexafluorophosphate) and show that multiblock PSf copolymer can be produced from it by nucleophilic aromatic substitution. It follows that the preparation of triblock PPO-PDApipOH copolymers is possible (Scheme 5.2). Designing the hydrophobic PPO to end cap the PDApipOH is advantageous in that the expected nanoscale domains in resulting membranes will be connected via PPO blocks and will lead to excellent mechanical properties. The greater base stability of PPO is expected to contribute to the generation of AEMs capable of longer operating lifetimes and stable performance.

Scheme 5.1 Proposed functionalization of brominated PSf-PF multiblock copolymers with piperidinium iodide pendants
Due to the excellent membrane properties observed in the PSf-PDApipOH materials, numerous possibilities exist for incorporating base stable PDApipOH into copolymers and membranes. In Chapter 3, a lengthy and cost prohibitive procedure was developed for the preparation of PSf-PDApipOH multiblock copolymers. The synthesis can be simplified by investigating polysulfone disulfide as the photoiniferter. Reports exist detailing the preparation of thiophenol terminated PSf oligomers and their subsequent oxidation to higher molecular weight polymers containing disulfide linkages.\textsuperscript{9-11} It is also known that the monomer $N,N$-diallylpiperidinium chloride has solubility in some polar organic solvents compatible with PSf.\textsuperscript{12-13} Therefore, it is possible to directly prepare the multiblock PSf poly(diallylpiperidinium chloride) from the polysulfone disulfide and the $N,N$-diallylpiperidinium chloride monomer (Scheme 5.3). This proposed strategy eliminates the cost and time of preparing the bis(4-fluorophenyl) disulfide, oxidation of the 4-fluorophenyl sulfide end groups, and potentially the ion exchange to hexafluorophosphate.

![Scheme 5.2 Proposed synthesis of PPO-PDApipOH triblock copolymers](image-url)
Scheme 5.3 Proposed scheme for the preparation of PSf-PDApipCl multiblock copolymer by the UV cyclopolymerization of N,N-diallylpiperidinium chloride in the presence of PSf-disulfide.

5.3 References


Chemically Stable Anion Exchange Membrane, Poly(2,6 dimethyl 1,4 phenylene oxide)-b-Poly(vinyl benzyl trimethyl ammonium), for Electrochemical Applications. *Journal of the Electrochemical Society* 2016, 163 (7), H513-H520.


APPENDIX A

CHARACTERIZATION OF ADDITIONAL PSF-QAPF MULTIBLOCK COPOLYMER MEMBRANES

Table A.1 Characterization of PSF-BrPF multiblock copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole Percent PF&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Percent of Bromination&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Average DF per repeat unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf-BrPF1</td>
<td>19.3</td>
<td>89</td>
<td>3.6</td>
</tr>
<tr>
<td>PSf-BrPF2</td>
<td>26.9</td>
<td>81</td>
<td>3.3</td>
</tr>
<tr>
<td>PSf-BrPF3</td>
<td>33.3</td>
<td>65</td>
<td>2.6</td>
</tr>
<tr>
<td>PSf-BrPF7</td>
<td>18.4</td>
<td>81</td>
<td>3.2</td>
</tr>
<tr>
<td>PSf-BrPF8</td>
<td>26.3</td>
<td>66</td>
<td>2.6</td>
</tr>
<tr>
<td>PSf-BrPF9</td>
<td>33.0</td>
<td>76</td>
<td>3.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from the <sup>1</sup>H NMR spectra.

Table A.2 Characterization of PSF-QAPF multiblock copolymer membranes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole Percent PF&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>IEC&lt;sub&gt;theory&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (meq/g)</th>
<th>IEC&lt;sup&gt;a&lt;/sup&gt; (meq/g)</th>
<th>WU (%)</th>
<th>HO- Conductivity&lt;sup&gt;c&lt;/sup&gt; (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf-QAPF1</td>
<td>19.3</td>
<td>1.5</td>
<td>1.1</td>
<td>8.2</td>
<td>13 ± 0.5</td>
</tr>
<tr>
<td>PSf-QAPF2</td>
<td>26.9</td>
<td>1.9</td>
<td>1.5</td>
<td>12.1</td>
<td>25 ± 0.3</td>
</tr>
<tr>
<td>PSf-QAPF3</td>
<td>33.3</td>
<td>1.9</td>
<td>1.8</td>
<td>24.1</td>
<td>39 ± 0.6</td>
</tr>
<tr>
<td>PSf-QAPF7</td>
<td>18.4</td>
<td>1.3</td>
<td>1.1</td>
<td>7.8</td>
<td>21 ± 0.1</td>
</tr>
<tr>
<td>PSf-QAPF8</td>
<td>26.3</td>
<td>1.5</td>
<td>1.3</td>
<td>12.4</td>
<td>22 ± 0.3</td>
</tr>
<tr>
<td>PSf-QAPF9</td>
<td>33.0</td>
<td>1.9</td>
<td>1.6</td>
<td>19.2</td>
<td>29 ± 0.2</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from <sup>1</sup>H NMR spectra. <sup>b</sup> Calculated based on 100% conversion of benzylbromides to BTMA cations. <sup>c</sup> Measured in room temperature water.
Proton NMR signals were assigned from the DQF-COSY NMR Spectrum. Proton assignments for the PDApipPF₆ repeat unit are as follows: C protons δ = 1.24 & 1.48 ppm, D protons δ = 2.47 & 2.05 ppm, E protons δ = 3.76 & 3.07 ppm, F protons δ = 3.31 & 3.27
ppm, G protons δ = 1.83 ppm, H protons δ = 1.61 ppm. Correlations of the D protons with both the E and C protons and correlations of G protons with both F and H protons supports the assignment.

![Chemical structure of PDApipPF₆](image)

Figure B.32 HMQC NMR spectrum of PDApipPF₆ in acetonitrile-d₃

Proton and carbon assignments were made from the HMQC NMR spectrum. C protons were assigned to carbon signals at δ = 26.2 & 29.5 ppm for cis and trans. The trans carbon signal and correlation at 29.5 ppm was very weak. D protons were assigned to carbon signals at δ = 37.8 & 42.3 ppm for cis and trans. E protons were assigned to carbon signals at
\[ \delta = 67.0 \text{ and } 68.3 \text{ ppm. } \] The trans carbon signal and proton correlation at 68.3 ppm was very weak. The assignment for protons and carbons C, D & E support the formation of the 5-member ring.

**B.1 Synthesis of 4-fluorothioanisole**

Synthesis of 4-fluorothioanisole was completed using an established procedure.\(^1\)

\[ \lambda_{\text{max}}(\text{MeOH})/\text{nm} \ 251 \ (\varepsilon/\text{dm}^3 \ \text{mol}^{-1} \ \text{cm}^{-1} \ 7500) \] \(^1\)H NMR (500 MHz, CDCl\(_3\)): \[ \delta \ 7.42 \ (2\text{H, m}), \ 6.99 \ (2\text{H, m}), \ 2.46(3\text{H, s}). \]

![UV/vis absorbance spectrum of 4-fluorophenylsulfide terminated PDApipCl](image)

Figure B.3 UV/vis absorbance spectrum of 4-fluorophenylsulfide terminated PDApipCl

The concentration of 4-fluorophenyl sulfide end groups was determined from a Beer’s Law calibration curve of 4-fluorothioanisole as a model for the end groups. The UV-Vis absorbance spectrum of 4-fluorothioanisole indicated two strong absorbance maxima at 204 nm and 251 nm, S3. The calibration curve was built from the absorbance at 251 nm. The 4-fluorophenylsulfide terminated PDApipCl oligomers presented similar absorbance spectra.
Hydroxide conductivity for all membranes was measured in the frequency range of 100 Hz to 300 kHz. A Bode plot was used to validate the frequency range with constant impedance. The intercept on the real resistance axis in the Nyquist plot was taken as the membrane resistance $R$.

Figure B.4 Sample Nyquist (Top) and Bode (Bottom) plots
Table B.1 PSf-PDApipOH device test data

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC (mmol/g)</th>
<th>σ (mS/cm)</th>
<th>Loading: Anode (mgPtRu/cm²)</th>
<th>Loading: Cathode (mgPt/cm²)</th>
<th>Cell HFR (mΩ·cm²)</th>
<th>R_{OH}^{mem} (mΩ·cm²)</th>
<th>OCV (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A201</td>
<td>1.8</td>
<td>42</td>
<td>0.32</td>
<td>0.32</td>
<td>184</td>
<td>149</td>
<td>1.03</td>
</tr>
<tr>
<td>PSF-PDApip1</td>
<td>1.29</td>
<td>-</td>
<td>0.4</td>
<td>0.3</td>
<td>380</td>
<td>345</td>
<td>0.8</td>
</tr>
<tr>
<td>PSF-PDApip2</td>
<td>1.53</td>
<td>35</td>
<td>0.401</td>
<td>0.439</td>
<td>165</td>
<td>135</td>
<td>1.02</td>
</tr>
<tr>
<td>PSF-PDApip3</td>
<td>2.02</td>
<td>51</td>
<td>0.458</td>
<td>0.451</td>
<td>115</td>
<td>80</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Figure B.5 Polarization curves for PSf-PDApip membranes. Tokuyama A201 membrane is black, PSf-PDApip1 is yellow, PSf-PDApip2 is blue, PSf-PDApip3 is green. Closed symbols are measured at 60 °C and open symbols are measured at 80 °C.

B.2 Acknowledgments

The device performance data was kindly provided by Chingching (Ami) Neyerlin and Bryan Pivovar at the National Renewable Energy Lab.

B.3 References